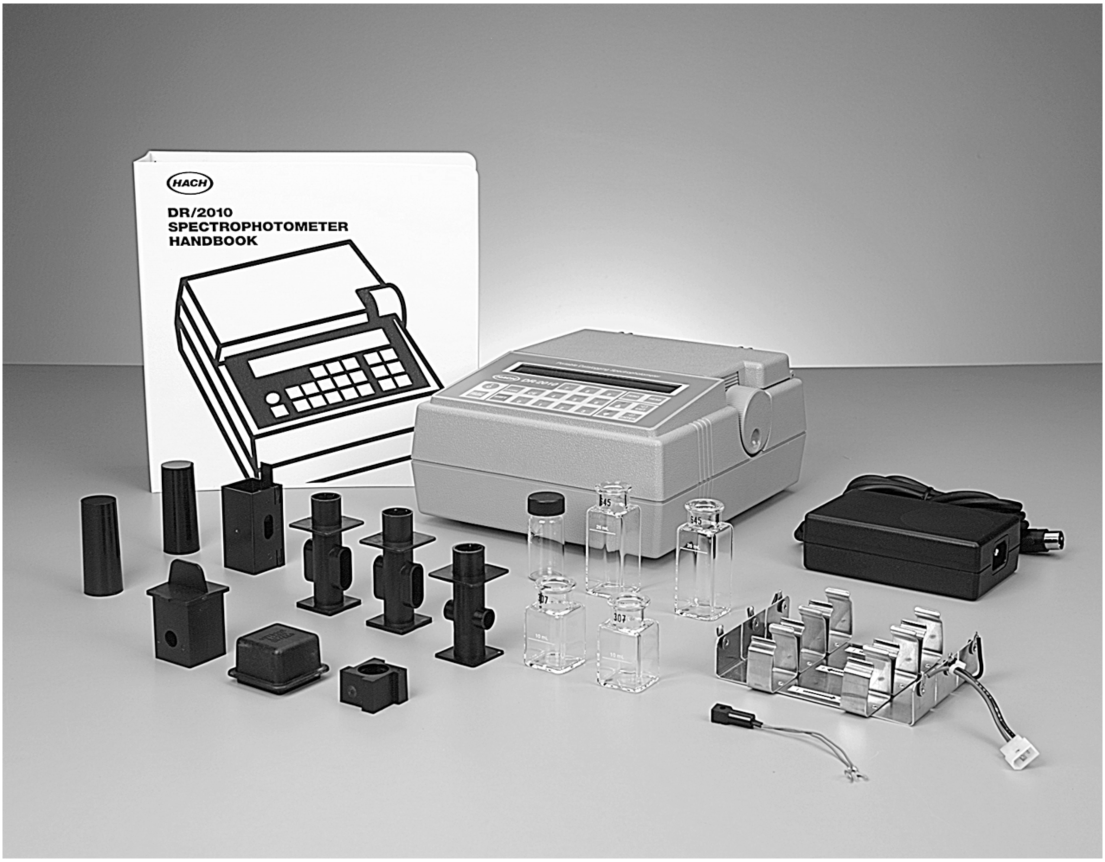
49300-22

DR/2010
SPECTROPHOTOMETER

PROCEDURES MANUAL



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INTRODUCTION

This manual is divided into five sections:

Section I Chemical Analysis Information
This section applies to all the procedures. It provides background information and reference/review material for the technician or chemist. Commonly used techniques are explained in detail.

Section II Sample Pretreatment
This section provides a brief overview of sample pretreatment and three digestion procedures. Two are USEPA digestions. The Hach Digesdahl method is also included.

Section III Waste Management and Safety
Section 3 includes information an waste management, regulations, waste disposal and resources on waste management. The Safety portion covers reading an MSDS and general safety guidelines.

Section IV Procedures
Section 4 contains step-by-step illustrated instructions for measuring over 120 parameters. The steps also include helpful notes. Each procedure contains information on sample collection, storage and preservation, accuracy checks, possible interferences, summary of method and a list of the reagents and apparatus necessary to run the test.

Section V Ordering Information
This section provides information needed for ordering, shipping, return of items and Hach trademarks.

Before attempting the analysis procedures the analyst should read the instrument manual to learn about the spectrophotometer’s features and operation.

Hach Company Trademarks

AccuGrow®
AccuVac®
AccuVer™
AccuVial™
Add-A-Test™
AgriTrak™
AluVer®
AmVer™
APA 6000™
AquaChek™
AquaTrend®
BariVer®
BODTrak™
BoroTrace™
BoroVer®
C. Moore Green™
CA 610™
CalVer®
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CyaniVer®
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DithiVer®
Dr. F. Fluent™
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DR/Check™
EC 310™
FerroMo®
FerroVer®
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FilterTrak™ 660
Formula 2533™
Formula 2589™
Gelex®
H_2O University™
H_2OU™
Hach Logo®
Hach One®
Hach Oval®
Hach.com™
HachLink™
Hawkeye The Hach Guy™
HexaVer®
HgEx™
HydraVer®
ICE-PIC™
IncuTrol®
Just Add Water™
LeadTrak®
M-ColiBlue24®
ManVer®
MolyVer®
Mug-O-Meter®
NetSketcher™
NitraVer®
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Results You Can Trust℠
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PbEx®
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Pocket Colorimeter™
Pocket Pal™
Pocket Turbidimeter™
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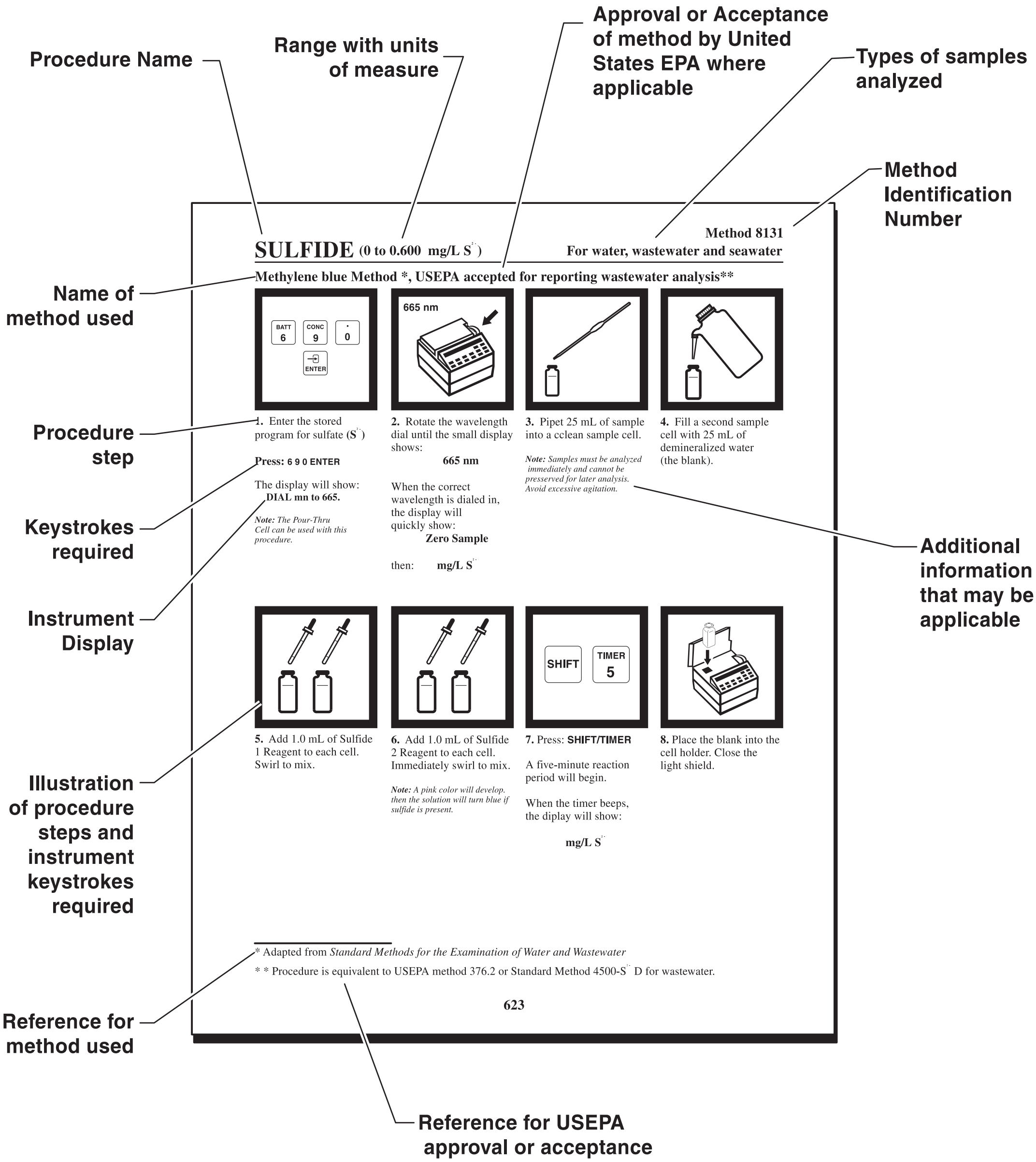
PrepTab™
ProNetic™
Pump Colorimeter™
QuanTab®
Rapid Liquid™
RapidSilver™
Ratio™
RoVer®
*sens***ion**™
Simply Accurate℠
SINGLET™
SofChek™
SoilSYS™
SP 510™
Spec√™
StablCal®
StannaVer®
SteriChek™
StillVer®
SulfaVer®
Surface Scatter®
TanniVer®
TenSette®
Test ‘N Tube™
TestYES!℠
TitraStir®
TitraVer®
ToxTrak™
UniVer®
VIScreen™
Voluette®
WasteAway™
ZincoVer®

Sample Procedure Explained



Method 8131

SULFIDE **(0 to 0.600 mg/L S^{2-})**

For water, wastewater and seawater

Methylene blue Method *, USEPA accepted for reporting wastewater analysis**

1. Enter the stored program for sulfate (**S^{2-}**)

Press: **6 9 0 ENTER**

The display will show:
DIAL mn to 665.

Note: *The Pour-Thru Cell can be used with this procedure.*

2. Rotate the wavelength dial until the small display shows:
665 nm

When the correct wavelength is dialed in, the display will quickly show:
Zero Sample

then: **mg/L S^{2-}**

3. Pipet 25 mL of sample into a cclean sample cell.

Note: *Samples must be analyzed immediately and cannot be presserved for later analysis. Avoid excessive agitation.*

4. Fill a second sample cell with 25 mL of demineralized water (the blank).

5. Add 1.0 mL of Sulfide 1 Reagent to each cell. Swirl to mix.

6. Add 1.0 mL of Sulfide 2 Reagent to each cell. Immediately swirl to mix.

Note: *A pink color will develop. then the solution will turn blue if sulfide is present.*

7. Press: **SHIFT/TIMER**

A five-minute reaction period will begin.

When the timer beeps, the diplay will show:

mg/L S^{2-}

8. Place the blank into the cell holder. Close the light shield.

---

* Adapted from *Standard Methods for the Examination of Water and Wastewater*

* * Procedure is equivalent to USEPA method 376.2 or Standard Method 4500-S^{2-} D for wastewater.

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Procedure Name

Range with units of measure

Approval or Acceptance of method by United States EPA where applicable

Types of samples analyzed

Method Identification Number

Name of method used

Procedure step

Keystrokes required

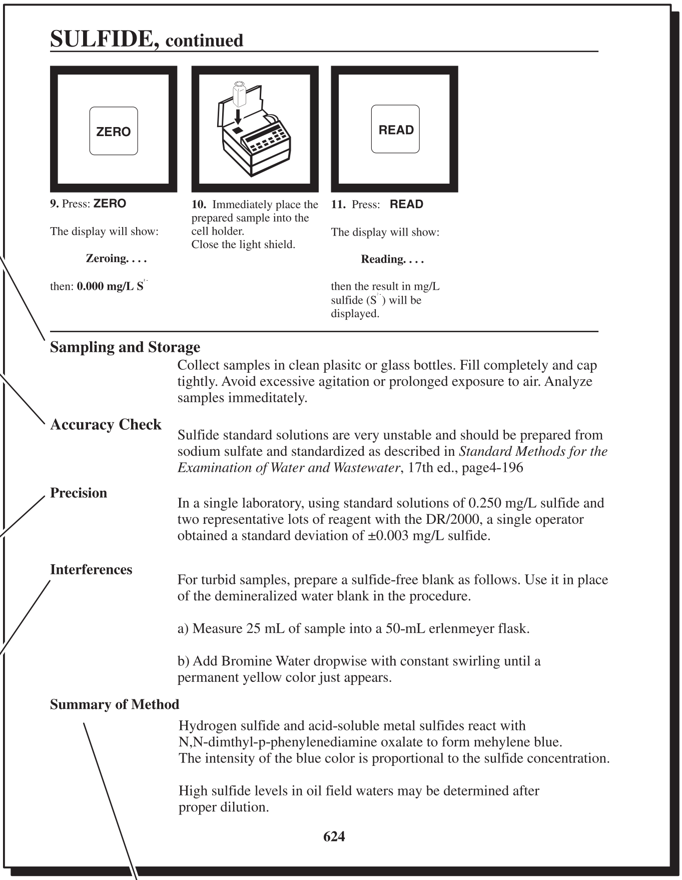
Instrument Display

Additional information that may be applicable

Illustration of procedure steps and instrument keystrokes required

Reference for method used

Reference for USEPA approval or acceptance



SULFIDE, continued

9. Press: **ZERO**

The display will show:

Zeroing. . . .

then: **0.000 mg/L S^{--}**

10. Immediately place the prepared sample into the cell holder.
Close the light shield.

11. Press: **READ**

The display will show:

Reading. . . .

then the result in mg/L sulfide (S^{--}) will be displayed.

Sampling and Storage

Collect samples in clean plasitc or glass bottles. Fill completely and cap tightly. Avoid excessive agitation or prolonged exposure to air. Analyze samples immeditately.

Accuracy Check

Sulfide standard solutions are very unstable and should be prepared from sodium sulfate and standardized as described in *Standard Methods for the Examination of Water and Wastewater*, 17th ed., page4-196

Precision

In a single laboratory, using standard solutions of 0.250 mg/L sulfide and two representative lots of reagent with the DR/2000, a single operator obtained a standard deviation of ±0.003 mg/L sulfide.

Interferences

For turbid samples, prepare a sulfide-free blank as follows. Use it in place of the demineralized water blank in the procedure.

a) Measure 25 mL of sample into a 50-mL erlenmeyer flask.

b) Add Bromine Water dropwise with constant swirling until a permanent yellow color just appears.

Summary of Method

Hydrogen sulfide and acid-soluble metal sulfides react with N,N-dimthyl-p-phenylenediamine oxalate to form mehylene blue.
The intensity of the blue color is proportional to the sulfide concentration.

High sulfide levels in oil field waters may be determined after proper dilution.

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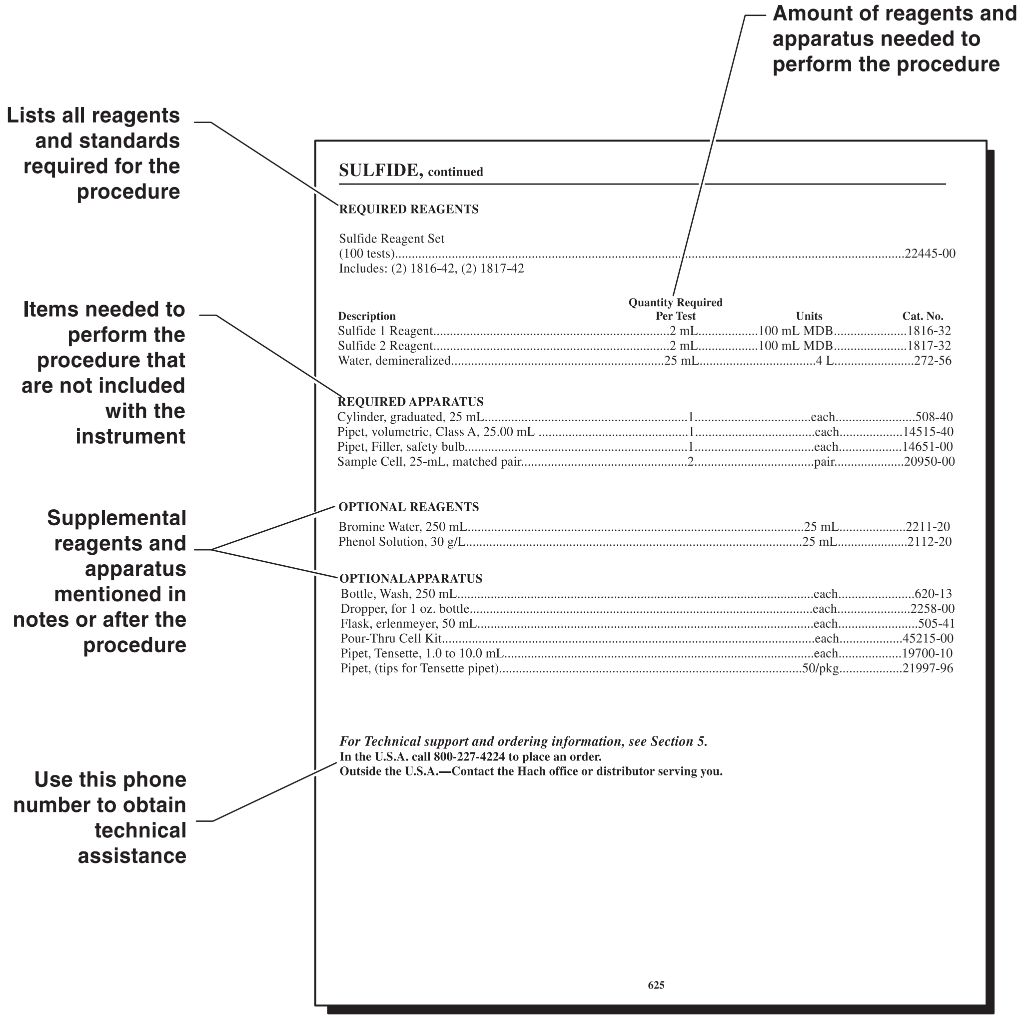
Specific sampling and storage information for this test

Confirm accuracy with these steps (in addition, may also be used to troubleshoot a test, improve technique, check reagents and to assure cleanliness of glassware)

Expected repeatability of the procedure

Levels of common sample substances or conditions that will cause inaccurate results

Concise explanation of method



Amount of reagents and apparatus needed to perform the procedure

Lists all reagents and standards required for the procedure

Items needed to perform the procedure that are not included with the instrument

Supplemental reagents and apparatus mentioned in notes or after the procedure

Use this phone number to obtain technical assistance

SULFIDE, continued

REQUIRED REAGENTS

Sulfide Reagent Set
(100 tests)...22445-00
Includes: (2) 1816-42, (2) 1817-42

Description	Quantity Required Per Test	Units	Cat. No.
Sulfide 1 Reagent	2 mL	100 mL MDB	1816-32
Sulfide 2 Reagent	2 mL	100 mL MDB	1817-32
Water, demineralized	25 mL	4 L	272-56

REQUIRED APPARATUS

Cylinder, graduated, 25 mL	1	each	508-40
Pipet, volumetric, Class A, 25.00 mL	1	each	14515-40
Pipet, Filler, safety bulb	1	each	14651-00
Sample Cell, 25-mL, matched pair	2	pair	20950-00

OPTIONAL REAGENTS

Bromine Water, 250 mL	25 mL	2211-20
Phenol Solution, 30 g/L	25 mL	2112-20

OPTIONALAPPARATUS

Bottle, Wash, 250 mL	each	620-13
Dropper, for 1 oz. bottle	each	2258-00
Flask, erlenmeyer, 50 mL	each	505-41
Pour-Thru Cell Kit	each	45215-00
Pipet, Tensette, 1.0 to 10.0 mL	each	19700-10
Pipet, (tips for Tensette pipet)	50/pkg	21997-96

For Technical support and ordering information, see Section 5.
In the U.S.A. call 800-227-4224 to place an order.
Outside the U.S.A.—Contact the Hach office or distributor serving you.

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SECTION I CHEMICAL ANALYSIS INFORMATION

Abbreviations

The following abbreviations are used throughout the text of the procedure section:

Abbreviation	Definition	Abbreviation	Definition
°C	degree(s) Celsius (Centigrade)	**HR**	high range
°F	degree(s) Fahrenheit	**kg/ha**	kilograms per hectare
ACS	American Chemical Society reagent grade purity	**l or L**	Liter. Volume equal to one cubic decimeter (dm^3)
APHA Standard Methods	*Standard Methods for the Examination of Water and Wastewater,* published jointly by the American Public Health Association (APHA), the American Water Works Association (AWWA), and the Water Environment Federation (WEF). Order from Hach requesting Cat. No. 22708-00 or from the Publication Office of the American Public Health Association. This book is the standard reference work for water analysis. Many procedures contained in this manual are based on *Standard Methods.*	**lbs/Ac**	pounds per acre
		LR	low range
		MDL	Method detection limit
		MDB	marked dropping bottle
		mg/L	milligrams per liter (ppm)
		µg/L	micrograms per liter (ppb)
		ml or mL	(milliliter)-approximately the same as a cubic centimeter (cc) or 1/1000 of a liter. Also known as a “cc”.
AV	AccuVac	**MR**	medium range
Bicn	bicinchoninate	**NIPDWR**	National Interim Primary Drinking Water Regulations
CFR	Code of Federal Regulations	**NPDES**	National Pollutant Discharge Elimination System
conc	concentrated	**P**	phosphorus
DB	dropping bottle	**PCB**	Poly chlorinated biphenyl
EDL	Estimated detection limit	**PV**	PhosVer®
F&T	free and total	**RL**	Rapid Liquid™
FAU	Formazin Attenuation Units. Turbidity unit of measure based on a Formazin stock suspension.	**SCDB**	self-contained dropping bottle
FM	FerroMo®	**TNT**	Test ‘N Tube™
FV	FerroVer®	**TPH**	Total petroleum hydrocarbons
FZ	FerroZine®	**TPTZ**	(2,4,6-Tri-(2-Pyridyl)-1,3,5-Triazine)
g	grams	**ULR**	Ultra low range
gr/gal	grains per gallon (1 gr/gal = 17.12 mg/L)	**USEPA**	United States Environmental Protection Agency

Converting Chemical Species

Species conversion factors for many commonly used substances are preprogrammed into the DR/2010 (see *Table 1*). Conversions are method specific and are viewable after taking the reading by pressing **CONC**.

Table 1 Conversion Factors

To Convert From...	To...	Multiply By...	Conversion used in program #
mg/L Al	mg/L Al_2O_3	1.8895	9, 10
mg/L B	mg/L H_3BO_3	5.7	45
mg/L Ca-$CaCO_3$	mg/L Ca	0.4004	220
mg/L $CaCO_3$	mg/L Ca	0.4004	227
mg/L $CaCO_3$	mg/L Mg	0.2428	227
µg/L Carbo.	µg/L Hydro.	1.92	182
µg/L Carbo.	µg/L ISA	2.69	182
µg/L Carbo.	µg/L MEKO	3.15	182
mg/L Cr^{6+}	mg/L CrO_4^{2-}	2.231	90, 95
mg/L Cr^{6+}	mg/L Na_2CrO_4	3.115	90, 95
mg/L Mg-$CaCO_3$	mg/L Mg	0.2428	225
mg/L Mn	mg/L $KMnO_4$	2.876	290, 295
mg/L Mn	mg/L MnO_4^-	2.165	290, 295
mg/L Mo^{6+}	mg/L MoO_4^{2-}	1.667	315, 320, 322
mg/L Mo^{6+}	mg/L Na_2MoO_4	2.146	315, 320, 322
mg/L N	mg/L NH_3	1.216	342, 343, 346, 347, 348
mg/L N	mg/L NO_3^-	4.427	346, 347, 348
mg/L Na_2CrO_4	mg/L Cr^{6+}	0.321	670
mg/L Na_2CrO_4	mg/L CrO_4^{2-}	0.72	670
mg/L NH_2Cl-N	mg/L Cl_2	5.0623	386
mg/L NH_2Cl-N	mg/L NH_2Cl	3.6750	386
mg/L NH_3-N	mg/L NH_3	1.216	380, 385, 387
mg/L NH_3-N	mg/L NH_4^+	1.288	380, 385, 387
mg/L NO_2^-	mg/L $NaNO_2$	1.5	373
mg/L NO_2^-	mg/L NO_2^--N	0.3045	373
mg/L NO_2^--N	mg/L $NaNO_2$	4.926	345, 371, 375
µg/L NO_2^--N	µg/L $NaNO_2$	4.926	376
mg/L NO_2^--N	mg/L NO_2^-	3.284	345, 371, 375
µg/L NO_2^--N	µg/L NO_2^-	3.284	376
mg/L NO_3^--N	mg/L NO_3^-	4.427	344, 351, 353, 355, 359, 361
mg/L PO_4^{3-}	mg/L P	0.3261	480, 482, 485, 490, 492, 535
µg/L PO_4^{3-}	µg/L P	0.3261	488
mg/L PO_4^{3-}	mg/L P_2O_5	0.7473	480, 482, 485, 490, 492, 535
µg/L PO_4^{3-}	µg/L P_2O_5	0.7473	488
mg/L SiO_2	mg/L Si	0.4674	651, 656
µg/L SiO_2	µg/L Si	0.4674	645

Hardness Conversion

Table 2 lists the factors for converting one unit of measure for hardness to another unit of measure. For example, to convert mg/L $CaCO_3$ to German parts/100,000 CaO, multiply the value in mg/L x 0.056.

Table 2 Hardness Conversion Factors

Units of Measure	mg/L $CaCO_3$	British gr/gal (Imperial) $CaCO_3$	American gr/gal (US) $CaCO_3$	French parts/ 100,000 $CaCO_3$	German Parts/ 100,000 CaO	meq/L[1]	g/L CaO	lbs./cu ft $CaCO_3$
mg/L $CaCO_3$	1.0	0.07	0.058	0.1	0.056	0.02	5.6x10^{-4}	6.23x10^{-5}
English gr/gal $CaCO_3$	14.3	1.0	0.83	1.43	0.83	0.286	8.0x10^{-3}	8.9x10^{-4}
US gr/gal $CaCO_3$	17.1	1.2	1.0	1.72	0.96	0.343	9.66x10^{-3}	1.07x10^{-3}
Fr. p/ 100,000 $CaCO_3$	10.0	0.7	0.58	1.0	0.56	0.2	5.6x10^{-3}	6.23x10^{-4}
Ger. p/ 100,000 CaO	17.9	1.25	1.04	1.79	1.0	0.358	1x10^{-2}	1.12x10^{-3}
meq/L	50.0	3.5	2.9	5.0	2.8	1.0	2.8x10^{-2}	3.11x10^{-2}
g/L CaO	1790.0	125.0	104.2	179.0	100.0	35.8	1.0	0.112
lbs./cu ft $CaCO_3$	16,100.0	1,123.0	935.0	1,610.0	900.0	321.0	9.0	1.0

[1] ‘epm/L, or ‘mval/L’
Note: 1 meq/L = 1N/1000

Dissolved Oxygen

Table 3 lists the mg/L dissolved oxygen in water at saturation for various temperatures and atmospheric pressures. The table was formulated in a laboratory using pure water. The values given are only approximations for estimating the oxygen content of a particular body of surface water.

Table 3 Dissolved Oxygen Saturation in Water

		Pressure in Millimeters and Inches Hg							
		mm							
		775	760	750	725	700	675	650	625
Temp		inches							
°F	°C	30.51	29.92	29.53	28.45	27.56	26.57	25.59	24.61
32.0	0	14.9	14.6	14.4	13.9	13.5	12.9	12.5	12.0
33.8	1	14.5	14.2	14.1	13.6	13.1	12.6	12.2	11.7
35.6	2	14.1	13.9	13.7	13.2	12.9	12.3	11.8	11.4
37.4	3	13.8	13.5	13.3	12.9	12.4	12.0	11.5	11.1
39.2	4	13.4	13.2	13.0	12.5	12.1	11.7	11.2	10.8
41.0	5	13.1	12.8	12.6	12.2	11.8	11.4	10.9	10.5
42.8	6	12.7	12.5	12.3	11.9	11.5	11.1	10.7	10.3
44.6	7	12.4	12.2	12.0	11.6	11.2	10.8	10.4	10.0
46.4	8	12.1	11.9	11.7	11.3	10.9	10.5	10.1	9.8
48.2	9	11.8	11.6	11.5	11.1	10.7	10.3	9.9	9.5
50.0	10	11.6	11.3	11.2	10.8	10.4	10.1	9.7	9.3
51.8	11	11.3	11.1	10.9	10.6	10.2	9.8	9.5	9.1
53.6	12	11.1	10.8	10.7	10.3	10.0	9.6	9.2	8.9
55.4	13	10.8	10.6	10.5	10.1	9.8	9.4	9.1	8.7
57.2	14	10.6	10.4	10.2	9.9	9.5	9.2	8.9	8.5
59.0	15	10.4	10.2	10.0	9.7	9.3	9.0	8.7	8.3
60.8	16	10.1	9.9	9.8	9.5	9.1	8.8	8.5	8.1
62.6	17	9.9	9.7	9.6	9.3	9.0	8.6	8.3	8.0
64.4	18	9.7	9.5	9.4	9.1	8.8	8.4	8.1	7.8
66.2	19	9.5	9.3	9.2	8.9	8.6	8.3	8.0	7.6
68.0	20	9.3	9.2	9.1	8.7	8.4	8.1	7.8	7.5
69.8	21	9.2	9.0	8.9	8.6	8.3	8.0	7.7	7.4
71.6	22	9.0	8.8	8.7	8.4	8.1	7.8	7.5	7.2
73.4	23	8.8	8.7	8.5	8.2	8.0	7.7	7.4	7.1
75.2	24	8.7	8.5	8.4	8.1	7.8	7.5	7.2	7.0
77.0	25	8.5	8.4	8.3	8.0	7.7	7.4	7.1	6.8
78.8	26	8.4	8.2	8.1	7.8	7.6	7.3	7.0	6.7
80.6	27	8.2	8.1	8.0	7.7	7.4	7.1	6.9	6.6

Table 3 Dissolved Oxygen Saturation in Water (continued)

		Pressure in Millimeters and Inches Hg							
		mm							
		775	760	750	725	700	675	650	625
Temp		inches							
°F	°C	30.51	29.92	29.53	28.45	27.56	26.57	25.59	24.61
82.4	28	8.1	7.9	7.8	7.6	7.3	7.0	6.7	6.5
84.2	29	7.9	7.8	7.7	7.4	7.2	6.9	6.6	6.4
86.0	30	7.8	7.7	7.6	7.3	7.0	6.8	6.5	6.2
87.8	31	7.7	7.5	7.4	7.2	6.9	6.7	6.4	6.1
89.6	32	7.6	7.4	7.3	7.0	6.8	6.6	6.3	6.0
91.4	33	7.4	7.3	7.2	6.9	6.7	6.4	6.2	5.9
93.2	34	7.3	7.2	7.1	6.8	6.6	6.3	6.1	5.8
95.0	35	7.2	7.1	7.0	6.7	6.5	6.2	6.0	5.7
96.8	36	7.1	7.0	6.9	6.6	6.4	6.1	5.9	5.6
98.6	37	7.0	6.8	6.7	6.5	6.3	6.0	5.8	5.6
100.4	38	6.9	6.7	6.6	6.4	6.2	5.9	5.7	5.5
102.2	39	6.8	6.6	6.5	6.3	6.1	5.8	5.6	5.4
104.0	40	6.7	6.5	6.4	6.2	6.0	5.7	5.5	5.3
105.8	41	6.6	6.4	6.3	6.1	5.9	5.6	5.4	5.2
107.6	42	6.5	6.3	6.2	6.0	5.8	5.6	5.3	5.1
109.4	43	6.4	6.2	6.1	5.9	5.7	5.5	5.2	5.0
111.2	44	6.3	6.1	6.0	5.8	5.6	5.4	5.2	4.9
113.0	45	6.2	6.0	5.9	5.7	5.5	5.3	5.1	4.8
114.8	46	6.1	5.9	5.9	5.6	5.4	5.2	5.4	4.8
116.6	47	6.0	5.9	5.8	5.6	5.3	5.1	4.8	4.7
118.4	48	5.9	5.8	5.7	5.5	5.3	5.0	4.8	4.6
120.2	49	5.8	5.7	5.6	5.4	5.2	5.0	4.7	4.5
122.0	50	5.7	5.6	5.5	5.3	5.1	4.9	4.7	4.4

Sample Collection, Preservation and Storage

Correct sampling and storage are critical for accurate testing. For greatest accuracy, thoroughly clean sampling devices and containers to prevent carryover from previous samples. Preserve the sample properly; each procedure has information about sample preservation.

- The least expensive containers are polypropylene or polyethylene.
- The best and most expensive containers are quartz or PTFE (polytetrafluoroethylene, Teflon).
- Avoid soft glass containers for metals in the microgram-per-liter range.
- Store samples for silver determination in light absorbing containers, such as amber bottles.

Avoid contaminating the sample with metals from containers, distilled water or membrane filters. Thoroughly clean sample containers as described under Acid Washing Bottles.

Preservation slows the chemical and biological changes that continue after collection. These changes may change the amount of a chemical species available for analysis. Normally, analyze the samples as soon as possible after collection, especially when the analyte concentration is expected to be low. This also reduces the chance for error and minimizes labor.

Preservation methods include pH control, chemical addition, refrigeration and freezing. *Table 4* gives the recommended preservation for various substances. It also includes suggested types of containers and the maximum recommended holding times for properly preserved samples.

Preserve aluminum, cadmium, chromium, cobalt, copper, iron, lead, nickel, potassium, silver and zinc samples for at least 24 hours by adding one Nitric Acid Solution Pillow 1:1 (Cat. No. 2540-98) per liter of sample. Check the pH with pH indicator paper or a pH meter to assure the pH is 2 or less. Add additional pillows if necessary. Adjust the sample pH prior to analysis by adding an equal number of Sodium Carbonate Anhydrous Powder Pillows (Cat. No. 179-98). Or raise the pH to 4.5 with Sodium Hydroxide Standard Solution, 1 N or 5 N.

Table 4 Required Containers, Preservation Techniques and Holding Times[1]

Parameter No./Name	Container[2]	Preservation[3,4]	Maximum Holding Time[5]
Table 1A - Bacterial Tests			
1-4. Coliform, fecal and total	P,G	Cool, 4°C, 0.008%, $Na_2S_2O_3$[6]	6 hours
5. Fecal streptococci	P,G	Cool, 4°C, 0.008%, $Na_2S_2O_3$[6]	6 hours
Table 1B - Inorganic Tests			
1. Acidity	P, G	Cool, 4°C	14 days
2. Alkalinity	P, G	Cool, 4°C	14 days
4. Ammonia	P, G	Cool, 4°C, H_2SO_4 to pH<2	28 days
9. Biochemical oxygen demand (BOD)	P, G	Cool, 4°C	48 hours
10. Boron	P, PFTE or quartz	HNO_3 to pH<2	6 months
11. Bromide	P, G	None required	28 days
14. Biochemical oxygen demand, carbonaceous	P, G	Cool, 4°C	48 hours
15. Chemical oxygen demand	P, G	Cool, 4°C, H_2SO_4 to pH<2	28 days
16. Chloride	P, G	None required	28 days
17. Chlorine, total residual	P, G	None required	Analyze immediately
21. Color	P, G	Cool, 4°C	48 hours
23-24. Cyanide, total and amenable to chlorination	P, G	Cool, 4°C, NaOH to pH>12, 0.6 g ascorbic acid[6]	14 days[7]
25. Fluoride	P	None required	28 days
27. Hardness	P, G	HNO_3 to pH<2, H_2SO_4 to pH<2	6 months
28. Hydrogen ion (pH)	P, G	None required	Analyze immediately
31, 43. Kjeldahl and organic nitrogen	P, G	Cool 4°C, H_2SO_4 to pH<2	28 days
Metals[8]			
18. Chromium VI	P, G	Cool, 4°C	24 hours
35. Mercury	P, G	HNO_3 to pH<2	28 days
Metals, except boron, chromium VI and mercury: 3, 5-8, 12, 13, 19, 20, 22, 26, 29, 30, 32-34, 36, 37, 45, 47, 51, 52, 58-60, 62, 63, 70-72, 74, 75[9].	P, G	HNO_3 to pH<2	6 months
38. Nitrate	P, G	Cool, 4°C	48 hours
39. Nitrate-nitrite	P, G	Cool 4°C, H_2SO_4 to pH<2	28 days
40. Nitrite	P, G	Cool, 4°C	48 hours
41. Oil and grease	G	Cool, 4°C, HCl or H_2SO_4 to pH<2	28 days
42. Organic Carbon	P, G	Cool, 4°C, HCl or H_2SO4 or H_3PO_4 to pH<2	28 days
44. Orthophosphate	P, G	Filter immediately; Cool, 4°C	48 hours
46a. Oxygen, dissolved probe	G Bottle and top	None required	Analyze immediately
46b. Oxygen, dissolved, Winkler	Do	Fix on site and store in dark	8 hours
48. Phenols	G only	Cool 4°C, H_2SO_4 to pH<2	28 days

Table 4 Required Containers, Preservation Techniques and Holding Times[1] (continued)

Parameter No./Name	Container[2]	Preservation[3,4]	Maximum Holding Time[5]
49. Phosphorus, elemental	G	Cool, 4°C	48 hours
50. Phosphorus, total	P, G	Cool, 4°C, H_2SO_4 to pH<2	28 days
53. Residue, total	P, G	Cool, 4°C	7 days
54. Residue, filterable	P, G	Cool, 4°C	7 days
55. Residue, Nonfilterable (TSS)	P, G	Cool, 4°C	7 days
56. Residue, Settleable	P, G	Cool, 4°C	48 hours
57. Residue, volatile	P, G	Cool, 4°C	7 days
61. Silica	P, PFTE or quartz	Cool, 4°C	28 days
64. Specific conductance	P, G	Cool, 4°C	28 days
65. Sulfate	P, G	Cool, 4°C	28 days
66. Sulfide	P, G	Cool 4°C, add zinc acetate plus sodium hydroxide to pH>9	7 days
67. Sulfite	P, G	none required	Analyze immediately
68. Surfactants	P, G	Cool, 4°C	48 hours
69. Temperature	P, G	None required	Analyze immediately
73. Turbidity	P, G	Cool, 4°C	48 hours

1 This table was adapted from Table II published in the Federal Register, July 1, 1997, 40 CFR, Part 136.3, pages 26-27. Organic tests are not included.

2 Polyethylene (P) or glass (G).

3 Sample preservation should be performed immediately upon sample collection. For composite chemical samples each aliquot should be preserved at the time of collection. When use of an automated sampler makes it impossible to preserve each aliquot, then chemical samples may be preserved by maintaining at 4°C until compositing and sample splitting is completed.

4 When any sample is to be shipped by common carrier or sent through United States Mails, it must comply with the Department of Transportation Hazardous Material Regulations (49 CFR Part 172). The person offering such material for transportation is responsible for ensuring such compliance. For the preservation requirements of Table II, the Office of Hazardous Materials, Materials Transportation Bureau, Department of Transportation has determined that the Hazardous Materials Regulations do not apply to the following materials: Hydrochloric acid (HCl) in water solutions at concentrations of 0.04% by weight or less (pH about 1.96 or greater); Nitric acid (HNO_3) in water solutions at concentrations of 0.15% by weight or less (pH about 1.62 or greater); Sulfuric acid (H_2SO_4) in water solutions at concentrations of 0.35% by weight or less (pH about 1.15 or greater); and Sodium hydroxide (NaOH) in water solutions at concentrations of 0.080% by weight or less (pH about 12.30 or less).

5 Samples should be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before analysis and still be considered valid. Samples may be held for longer periods only if the permitee, or monitoring laboratory, has data on file to show that the specific types of samples under study are stable for the longer time, and has received a variance from the Regional Administer under §136.3(e). Some samples may not be stable for the maximum time period given in the table. A permitee, or monitoring laboratory, is obligated to hold the sample for a shorter time if knowledge exists to show that this is necessary to maintain sample stability. See §136.3(e) for details. The term “analyze immediately” usually means within 15 minutes or less after sample collection.

6 Should only be used in the presence of residual chlorine.

7 Maximum holding time is 24 hours when sulfide is present. Optionally all samples may be tested with lead acetate paper before pH adjustments in order to determine if sulfide is present. If sulfide is present, it can be removed by the addition of cadmium nitrate powder until a negative spot test is obtained. The sample is filtered and then NaOH is added to pH 12.

8 Samples should be filtered immediately on-site before adding preservative for dissolved metals.

9 Numbers refer to parameter number in 40 CFR, Part 136.3, Table 1B.

Collecting Water Samples

Obtain the best sample by careful collection. In general, collect samples near the center of the vessel or duct and below the surface. Use only clean containers (bottles, beakers). Rinse the container several times first with the water to be sampled.

Take samples as close as possible to the source of the supply. This lessens the influence the distribution system has on the sample. Let the water run long enough to flush the system. Fill sample containers slowly with a gentle stream to avoid turbulence and air bubbles. Collect water samples from wells after the pump has run long enough to deliver water representative of the ground water feeding the well.

It is hard to obtain a truly representative sample when collecting surface water samples. Obtain best results by testing several samples. Use samples taken at different times from several locations and depths. The results can be used to establish patterns for that particular body of water.

Generally, as little time as possible should elapse between collecting the sample and analyzing it.

Depending on the test, special precautions in handling the sample may be necessary. This prevents natural interferences such as organic growth or loss or gain of dissolved gases. Each procedure describes sample preservatives and storage techniques for samples that are held for testing.

Acid Washing Bottles

If a procedure suggests acid-washing, use the following procedure:

a) Clean the glassware or plasticware with laboratory detergent (phosphate-free detergent is recommended).

b) Rinse well with tap water.

c) Rinse with a 1:1 Hydrochloric Acid Solution or 1:1 Nitric Acid Solution. The nitric acid rinse is important for testing for lead.

d) Rinse well with deionized water. Up to 12-15 rinses may be necessary if chromium is being determined.

e) Air dry.

Use chromic acid or chromium-free substitutes to remove organic deposits from glass containers. Rinse containers thoroughly with water to remove traces of chromium.

Wash glassware for phosphate determinations with phosphate-free detergents and acid-wash with 1:1 HCl. Thoroughly rinse the glassware with deionized water. For ammonia and Kjeldahl nitrogen, rinse with ammonia-free water.

Correcting for Volume Additions

If you use a large volume of preservative, correct for the volume of preservative added. This accounts for dilution due to the acid added to preserve the sample and the base used to adjust the pH to the range of the procedure. This correction is made as follows:

1. Determine the volume of initial sample, the volume of acid and base added, and the total final volume of the sample.
2. Divide the total volume by the initial volume.
3. Multiply the test result by this factor.

Example:
A one-liter sample was preserved with 2 mL of nitric acid. It was neutralized with 5 mL of 5 N sodium hydroxide. The result of the analysis procedure was 10.00 mg/L. What is the volume correction factor and correct result?

1. $\text{Total Volume} = 1000\text{ mL} + 2\text{ mL} + 5\text{ mL} = 1007\text{ mL}$
2. $\frac{1007}{1000} = 1.007 = \text{volume correction factor}$
3. $10.0\text{ mg/L} \times 1.007 = 10.07\text{ mg/L} = \text{correct result}$

Hach 1:1 Nitric Acid Pillows contain 2.5 mL of acid: correct for this volume. The addition of a Sodium Carbonate Power Pillow neutralizes the 1:1 Nitric Acid Pillow does not need to be corrected for.

Boiling Aids

Boiling is necessary in some procedures. Using a boiling aid such as boiling chips (Cat. no. 14835-31) reduces bumping. Bumping is caused by the sudden, almost explosive conversion of water to steam as it is heated. Avoid bumping; it may cause sample loss or injury.

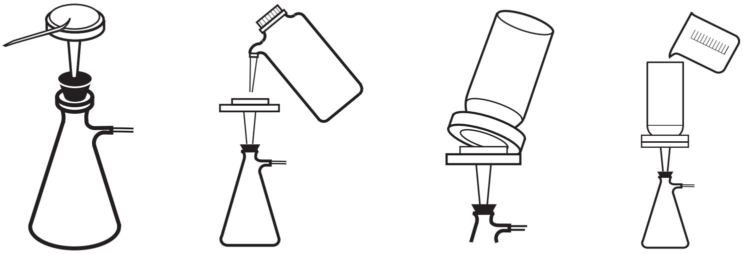
Make sure the boiling aids will not contaminate the sample. Do not use boiling aids (except glass beads) more than once. Loosely covering the sample during boiling will prevent splashing, reduce the chances of contamination and minimize sample loss.

Sample Filtration

Filtering separates particles from the aqueous sample. Filtration uses a medium, usually filter paper, to retain particles but pass solution. This is especially helpful when sample turbidity interferes with analysis. Two general methods of filtration are gravity and vacuum. Gravity filtration uses gravity to pull the sample though the filter paper. Vacuum filtration uses suction and gravity to move the sample through the filter. An aspirator or vacuum pump creates the suction. Vacuum filtration is faster than gravity filtration. Vacuum filter (see *Figure 1*) as follows:

1. Using tweezers, place a filter paper into the filter holder.
2. Place the filter holder assembly in the filtering flask. Wet the filter with deionized water to ensure adhesion to the holder.
3. Position the funnel housing on the filter holder assembly.
4. While applying a vacuum to the filtering flask, transfer the sample to the filtering apparatus.
5. Slowly release the vacuum from the filtering flask and transfer the solution from the filter flask to another container.

Figure 1 Vacuum Filtration



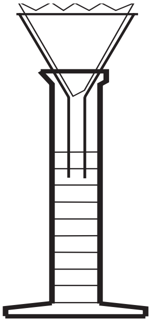
REQUIRED APPARATUS FOR VACUUM FILTRATION

Description	Unit	Cat. No.
Filter Discs, glass 47 mm	100/pkg	2530-00
Filter Holder, membrane	each	13529-00
Flask, filter, 500 mL	each	546-49
Pump, vacuum, hand operated	each	14283-00
OR		
Pump, vacuum, portable, 115 V	each	14697-00
Pump, vacuum, portable, 230 V	each	14697-02

Many of the procedures in this manual use gravity filtration. The only labware required is filter paper, a conical funnel and a receiving flask. This labware is included under Optional Equipment and Supplies at the end of a procedure. Gravity filtration is better for retaining fine particles. For faster filtering, add solution until the filter paper cone is three-fourths filled. Never fill the cone completely. Gravity filter (see *Figure 2*) as follows:

1. Place a filter paper into the funnel.
2. Wet the filter with deionized water to ensure adhesion to the funnel.
3. Place the funnel into an erlenmeyer flask or graduated cylinder.
4. Pour the sample into the funnel.

Figure 2 Gravity Filtration



REQUIRED APPARATUS FOR GRAVITY FILTRATION

Description	Unit	Cat No.
Cylinder, graduated, 100 mL	each	508-42
Funnel, poly, 65 mm	each	1083-67
Filter Paper, 12.5 cm	each	1894-57
Flask, erlenmeyer, 125 mL	each	505-43

Testing for metals requires acid and heat to pretreat the sample. Since these conditions destroy filter paper, vacuum filtration with glass fiber filter discs is recommended. Also, glass filter discs, unlike paper, do not retain colored species.

Temperature Considerations

For best results, most tests in this manual should be performed with sample temperatures between 20 °C (68 °F) and 25 °C (77 °F). If a test requires closer temperature control, notes in the procedure will indicate this.

Sample Dilution Techniques

Ten and 25 mL are the volumes used for most colorimetric tests. However, in some tests, the color developed in the sample may be too intense to be measured. Unexpected colors may develop in other tests. In both cases, dilute the sample to determine if interfering substances are present.

To dilute the sample easily, pipet the chosen sample portion into a clean graduated cylinder (or volumetric flask for more accurate work). Fill the cylinder (or flask) to the desired volume with deionized water. Mix well. Use the diluted sample when running the test.

To help with dilutions, *Table 5* shows the amount of sample used, the amount of deionized water used to bring the volume up to 25 mL and the multiplication factor.

The concentration of the sample is equal to the diluted sample reading multiplied by the multiplication factor.

More accurate dilutions can be done with a pipet and a 100-mL volumetric flask (see *Table 6* for more information). Pipet the sample and dilute to volume with deionized water. Swirl to mix.

Table 5 Sample Dilution Volumes

Sample Volume (mL)	mL deionized Water Used to Bring the Volume to 25 mL	Multiplication Factor
25.0	0.0	1
12.5	12.5	2
10.0[1]	15.0	2.5
5.0[1]	20.0	5
2.5[1]	22.5	10
1.0[1]	24.0	25
0.250[1]	24.75	100

[1] For sample sizes of 10 mL or less, use a pipet to measure the sample into the graduated cylinder or volumetric flask.

Table 6 Multiplication Factors for Diluting to 100 mL

Sample Volume (mL)	Multiplication Factor
1	100
2	50
5	20
10	10
25	4
50	2

Sample Dilution and Interfering Substances

Sample dilution may influence the level at which a substance may interfere. The effect of the interferences decreases as the dilution increases. In other words, higher levels of an interfering substance can be present in the original sample if it is diluted before analysis.

An Example:

Copper does not interfere at or below 100 mg/L for a 25.00 mL sample in a procedure. If the sample volume is diluted with an equal volume of water, what is the level at which copper will not interfere?

$$\frac{\text{Total volume}}{\text{Sample volume}} = \text{Dilution factor}$$

$$\frac{25}{12.5} = 2$$

$$\text{Interference Level} \times \text{Dilution Factor} = \text{Interference level in sample}$$

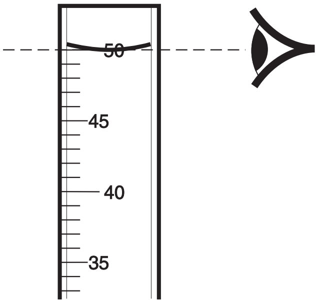
$$100 \times 2 = 200$$

The level at which copper will not interfere in the undiluted sample is at or below 200 mg/L.

Using Pipets and Graduated Cylinders

When small sample quantities are used, the accuracy of measurements is important. *Figure 3* illustrates the proper way of reading the sample level or the meniscus formed when the liquid wets the cylinder or pipet walls.

Figure 3 Reading the Meniscus



Rinse the pipet or cylinder two or three times with the sample to be tested before filling. Use a pipet filler or pipet bulb to draw the sample into the pipet. Never pipet chemical reagent solutions or samples by mouth. When filling a pipet, keep the tip of the pipet below the surface of the sample as the sample is drawn into the pipet.

Serological pipets have marks that indicate the volume of liquid delivered by the pipet. The marks may extend to the tip of the pipet or may be only on the straight portion of the tube. If the marks are only on the straight part of the tube, fill serological pipets to the zero mark and discharge the sample by draining the sample until the meniscus is level with the desired mark. If the serological pipet has marks extended to the tip of the pipet, fill the pipet to the desired volume and drain all the sample from the pipet. Then blow the sample out of the pipet tip for accurate measurements.

Volumetric (transfer) pipets have a bulb in the middle and a single ring above the bulb to indicate the volume of liquid when it is filled to the mark . To discharge a volumetric pipet, hold the tip of the pipet at a slight angle against the container wall and drain. Do not attempt to discharge the solution remaining in the tip of the pipet after draining. Volumetric pipets are designed to retain a small amount of sample in the pipet tip.

If sample drops stay on the walls of the pipet, the pipet is dirty and is not delivering the correct amount of sample. Wash the pipet thoroughly with a laboratory detergent or cleaning solution and rinse several times with deionized water.

Using the TenSette Pipet

For best results use a new tip each time you pipet. After several uses, the pipet tip may retain some liquid, causing inaccurate delivery. Each pipet is supplied with 100 tips; order Hach replacement tips for best results.

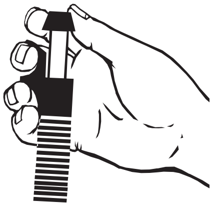
Always use careful, even hand movements for best reproducibility. If the pipet does not operate smoothly, disassemble and coat the piston and retainer with high-quality stopcock grease. Also coat the metering turret lightly with grease. Refer to the TenSette Pipet manual.

For best pipetting accuracy, the solution and the room temperature should be between 20-25 °C.

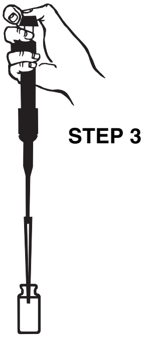
Never lay the pipet down with the liquid in the tip. Solution could leak into the pipet and cause corrosion.

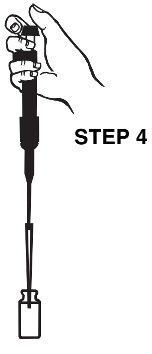
Operating the TenSette Pipet

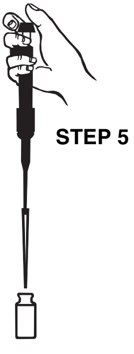
1. Attach a clean tip by holding the pipet body in one hand and gently pressing the large end of the pipet tip onto the tapered end of the pipet. Be sure a good seal is obtained.



2. Turn the turret cap to align the desired volume with the mark on the pipet body.
3. Using a smooth motion, press down on the turret cap until it reaches the stop. Immerse the tip about 5 mm (1/4 inch) below the solution surface to avoid drawing air into the pipet. Do not insert the tip any deeper or the delivery volume may be affected.
4. While maintaining a constant pressure, allow the turret to return slowly to the extended position. A rapid return may affect the delivery volume.
5. With the turret up, take the tip out of the solution and move it to the receiving vessel. Do not press on the turret cap while moving the pipet.

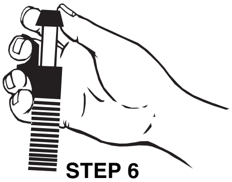






6. Use the thumb and forefinger to twist the turret cap to the next higher volume position to ensure quantitative transfer of the sample.
   The “F” position provides full blowout.

7. With the tip in contact with the side of the receiving vessel, slowly and smoothly press down on the turret cap until it reaches the stop and the solution is completely discharged.



STEP 6

STEP 7

Mixing Water Samples

The following two methods may be helpful in tests that require mixing sample with chemicals (usually indicated by “swirl to mix” instructions).

1. When mixing sample in a square sample cell, swirl with a simple twisting motion; see *Figure 4*. Grasp the neck of the cell with the thumb and index finger of one hand. Rest the concave bottom of the cell on the tip of the index finger of other hand. Mix by rotating the cell quickly one way and then in the reverse direction.

2. Swirling is recommended when mixing samples in a graduated cylinder or a titration flask. Grip the cylinder (or flask) firmly with the tips of three fingers; see *Figure 5*. Hold the cylinder at a 45-degree angle and twist the wrist. This should move the cylinder in an approximately 12-inch circle, creating enough rotation to complete the mixing in a few turns.

This swirling procedure is the most gentle and offers the least interference from the atmosphere when testing for carbon dioxide and other gases. Both methods are simple but take a bit of practice in order to obtain the best results.

Figure 4 Swirling a Sample Cell

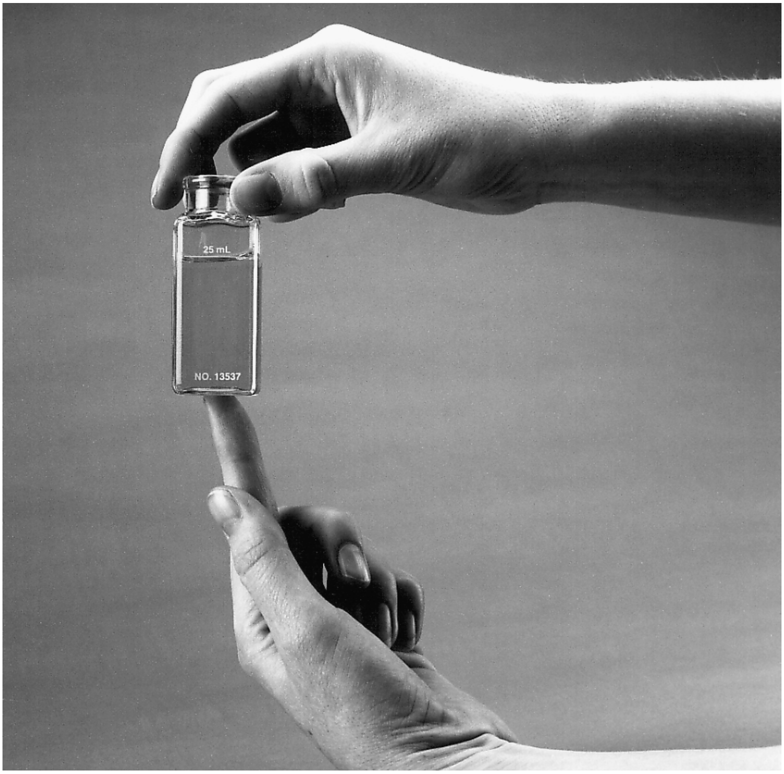
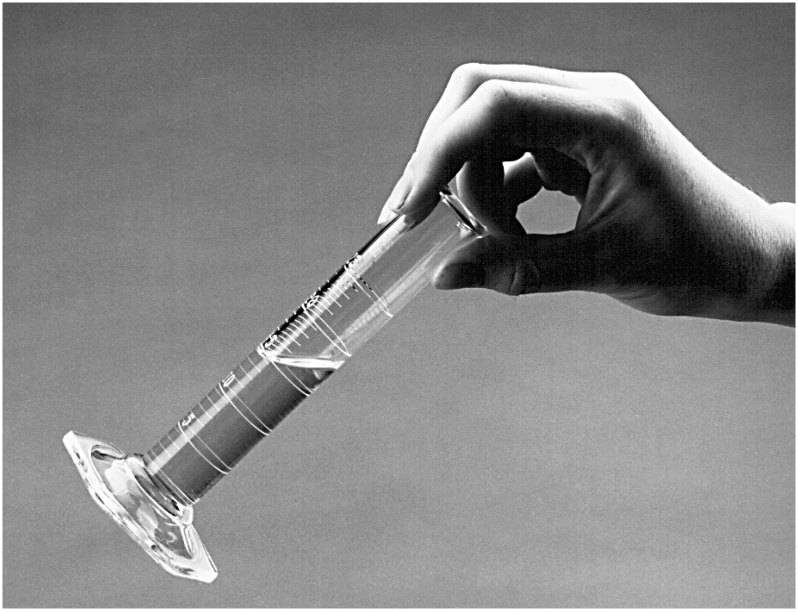


Figure 5 Swirling a Graduated Cylinder



Using Sample Cells

Orientation of Sample Cells

Two types of matched sample cells are shipped with the DR/2010; a matched pair of taller 25 mL sample cells and a shorter matched pair of 10 mL sample cells. Both types are matched with the spectrophotometer light beam passing through the side with the fill mark and the opposite side. Matched pairs have been tested and paired so that significant error will not be introduced because of variations in the glass. A solution in both cells should give the same absorbance (±0.002 Abs). For more information, see *Sample Cell Matching*, below.

To minimize variability of measurements using a particular cell, always place the cell into the cell holder with the same orientation. The cells are placed in the instrument with the fill marks facing left (viewer's left).

In addition to proper orientation, the sides of the cells should be free of smudges, fingerprints, etc. to ensure accurate readings. Wipe the sides of the cells with a soft cloth to clean the surface before taking measurements.

Care of Hach 1-inch Sample Cells

Store sample cells in their boxes when not in use to protect them from scratching and breaking. It is good laboratory practice to empty and clean sample cells after analyses are complete--avoid leaving colored solutions in the cells for extended periods of time. Finish the cleaning procedure with a few rinses of deionized water and allow to dry. Individual procedures often recommend specific cleaning methods for special circumstances.

Cleaning Sample Cells

Most laboratory detergents can be used at recommended concentrations. Neutral detergents such as Neutracon are safer if regular cleaning is required, as in the case of protein residues.

If using a detergent, you can speed cleaning by increasing the temperature or using an ultrasonic bath.

Rinsing is more efficient when using distilled water.

Sample Cell Matching

Sample cells shipped with the DR/2010 are matched and distortion-free. Nicks and scratches from normal use can cause an optical mismatch between two sample cells and introduce error in the test results. This type of error can sometimes be avoided by optically re-matching the sample cells as follows:

1. Turn the instrument on and select the constant-on mode. Wait 5 minutes for the lamp to warm up.
2. Enter the stored program for absorbance. Press **0 ENTER**. The display will show: **Abs**.
3. Rotate the wavelength dial until the small display shows 510 nm or the wavelength commonly used.
4. Pour at least 25 mL (10 mL for 10-mL cells) of deionized water into each of two sample cells.
5. Place one sample cell into the cell holder. Orient the fill mark to the left. Close the light shield.
6. Press: **ZERO**. The display will show: **0.000 Abs**.
7. Place the other sample cell into the cell holder using the same orientation as in step 5. Close the light shield.
8. Wait about 3 seconds for the reading to stabilize. Record the result.

Two sample cells are matched when their absorbance readings are within 0.002 Abs of each other. If the cells do not match, there are two alternative options to purchasing a new set.

If more than two sample cells are on hand, repeat steps 7-8 for with these cells to determine if any match the original cell. If two cells match, mark them appropriately and keep them as a set.

As a last option, change the orientation of the cells to find a matched configuration. Repeat the steps above for two sample cells, placing both cells in the cell compartment with the fill marks facing forward. If the absorbance reading of the second cell is within +/- 0.002, the cells can be used as a matched set in that particular orientation. All future work with this particular set would require the same orientation. If necessary, repeat matching process with different orientations as needed.

If the sample cells cannot be matched within ±0.002 Abs, they may still be used by compensating for the difference. For example, if the second cell reads 0.003 absorbance units higher than the first cell, correct future readings (when using these two cells) by subtracting 0.003 absorbance units (or the equivalent concentration) from the reading. Likewise, if the second cell reads -0.003 absorbance units, add that value to the reading.

Volume Measurement Accuracy

The 10-and 25-mL sample cells supplied with the spectrophotometer have fill marks to indicate either 10 mL or 25 mL. The fill marks are intended to measure the volume to be analyzed. Do not use these fill marks to perform sample dilutions.

If a sample must be diluted, use a pipet, graduated mixing cylinder and/or a volumetric flask for accurate measurement. When diluting, accuracy is important because a slight mistake in measuring a small sample will cause a substantial error in the result. For instance, a 0.1-mL mistake in the dilution of a 1.0-mL final volume produces a 10% error in the test result.

Volumes for standard additions can be measured in the 25-mL cells, but it is not recommended for the 10-mL cells due to a potentially excessive relative error. An error of 0.5 mL in 25 mL is only 2%, while a 0.5 mL error in 10 mL is 5%.

For 10 mL standard additions, follow this procedure:

1. Pipet 10.0 mL of sample into a clean, dry 10 mL cell (the unspiked sample).
2. Add the standard (spike) to a 25 mL portion of sample in a 25-mL mixing cylinder. Stopper and mix thoroughly.
3. Transfer 10 mL to another 10-mL cell (use fill mark) for analysis.

Using AccuVac Ampuls

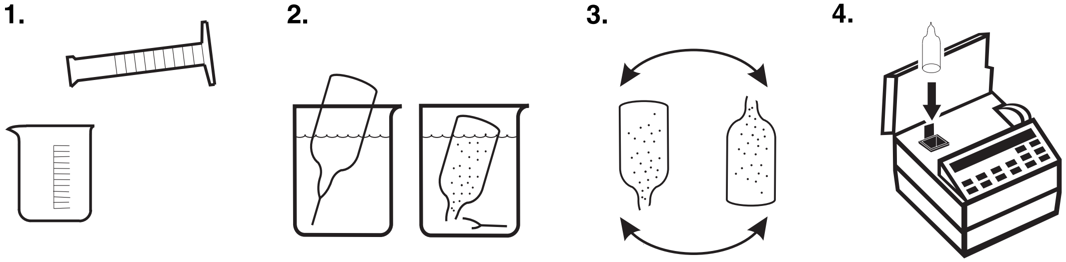
AccuVac ampuls contain pre-measured powder or liquid in optical-quality glass ampuls.

1. Collect the sample in a beaker or other open container.
2. Place the ampul tip well below the sample surface and break the tip off (see *Figure 6*) against the beaker wall. The break must be far enough below the surface to prevent air from being drawn in as the level of the sample lowers (the AccuVac Breaker may be used instead of breaking the ampul against the beaker side).

3. Invert the ampul several times to dissolve the reagent. Do not place your finger over the broken end; the liquid will stay in the ampul when inverted. Wipe the ampul with a towel to remove fingerprints, and other marks.

4. Insert the ampul into the AccuVac adapter in the DR/2010 and read the results directly.

Figure 6 Using AccuVac Ampuls



Using Reagent Powder Pillows

Hach uses dry powdered reagents when possible. This minimizes leakage and deterioration problems. Some powders are packaged in individual, pre-measured, polyethylene “powder pillows” or foil pillows called PermaChem® pillows. Each pillow contains enough reagent for one test. Open the powder pillows with nail clippers or scissors; see *Figure 7*.

Figure 7 Opening Powder Pillows

Using PermaChem Pillows

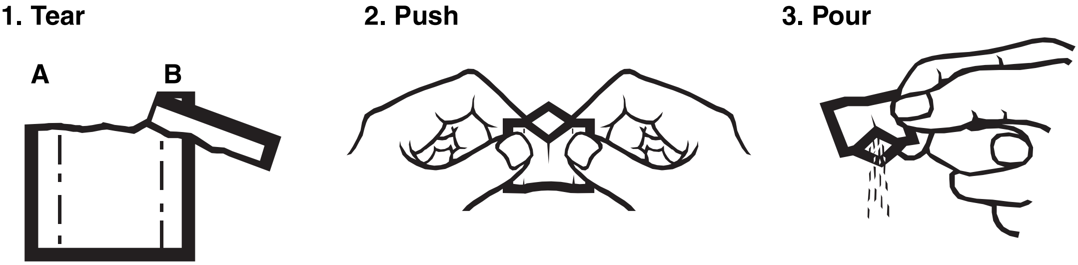
1. Tap the pillow on a hard surface to collect the powdered reagent in the bottom.

2. Tear (or cut) across, from A to B, holding the pillow away from your face.

3. Using two hands, push both sides toward each other to form a spout.

4. Pour the pillow contents into the sample cell and continue the procedure according to the instructions.

Figure 8 Opening PermaChem Pillows


1. Tear
2. Push
3. Pour

Using the Pour-Thru Cell

The Pour-Thru Cell is an optional accessory that improves accuracy and makes measuring more convenient. It gives better results when measuring at very low levels because it avoids any error that may result between optical differences from single sample cells. Installation instructions for the Pour-Thru Cell are given in the Instrument Manual. Each procedure notes if the Pour-Thru Cell can be used; some procedures will not allow the use of a Pour-Thru cell.

The DR/2010 offers many methods that use 10-mL sample sizes. The Pour-Thru Cell **cannot** be used for procedures that use 10-mL sample sizes and reagents. This volume does not flush the cell well enough to avoid sample carryover errors. When possible, 25-mL reagents are listed for those who prefer to use the Pour-Thru Cell.

When the procedure instructs you to place a 25-mL sample cell into the cell holder, pour the solution into the funnel of the installed Pour-Thru Cell Assembly (unless noted in the procedure).

Avoid spilling solution onto the instrument. The funnel height and orientation may be adjusted for easier pouring.

The funnel height also determines the speed of sample flow through the cell. The higher the funnel, the faster the flow. When properly adjusted, the funnel drains completely with the final level of liquid in the tube about 5 cm (2 inches) below the tip of the funnel. This adjustment minimizes air bubbles in the cell.

Measurement or instrument commands should only be made after the solution has stopped flowing through the cell.

Occasionally, remove the Pour-Thru Cell to check for accumulation of film on the windows. If the windows appear hazy, soak the cell in a detergent bath and rinse thoroughly with deionized water. The cell may be dissembled for cleaning. Do not over-tighten the screws during re-assembly as the threads are easily stripped.

Always rinse thoroughly with deionized water after each series of tests, or more often if specified in the procedure.

Caution:
Do not use or clean the Pour-Thru Cell with organic solvents such as acetone, chloroform, toluene or cyclohexanone.

Reagent and Standard Stability

Hach always strives to make stable formulations and package them to provide maximum protection. Most chemicals and prepared reagents do not deteriorate after manufacture. However, the way they are stored and the packaging can affect how long the reagents are stable. Light, bacterial action, and absorption of moisture and gases from the atmosphere can affect shelf life. Some chemicals may react with the storage container or they may react with other chemicals.

Chemicals supplied with the DR/2010 Spectrophotometer have an indefinite shelf life when stored under average room conditions, unless the packaging says something different. Product labels state any special storage conditions required. Otherwise, store reagents in a cool, dry, dark place for maximum life. It is always good practice to date chemicals when you receive them. Use older supplies first. If in doubt about the reagent shelf life, run a standard to check its effectiveness.

Interferences

Substances in the sample may interfere with a measurement. Hach mentions common interferences in the test procedures. The reagent formulations eliminate many interferences. You can remove others with sample pretreatments described in the procedure.

If you get an unusual answer, a color that you don't expect, or you notice an unusual odor or turbidity, the result may be wrong. Repeat the test on a sample diluted with deionized water; see *Sample Dilution Techniques*. Compare the result (corrected for the dilution) with the result of the original test. If these two are not close, the original result may be wrong and you should make an additional dilution to check the second test (first dilution). Repeat this process until you get the same corrected result twice in a row.

More information about interferences and methods to overcome them is contained in *Standard Additions* and the *General Introduction* section of APHA Standard Methods. Hach urges the analyst to obtain this book and refer to it when problems are encountered.

pH Interference

Many of the procedures in this manual only work within a certain pH range. Hach reagents contain buffers to adjust the pH of the typical sample to the correct pH range. However, the reagent buffer may not be strong enough for some samples. This occurs most often with highly buffered samples or samples with extreme sample pH.

The *Sampling and Storage* section of each procedure gives the proper pH range for the sample.

Adjust the sample to the proper pH range before testing. If this information is not given, follow these steps:

1. Measure the pH of your analyzed sample with a pH meter. For measuring K^+ or Cl^- , use pH paper.
2. Prepare a reagent blank using deionized water as the sample. Add all reagents called for in the procedure. Timer sequences, etc., may be ignored. Mix well.
3. Measure the pH of the reagent blank with a pH meter.
4. Compare the pH values of your analyzed sample with the reagent blank.

5. If there is little difference in the values of your analyzed sample and the reagent blank, then pH interference is not the problem. Follow the *Accuracy Check* given in the procedure to more clearly identify the problem.

6. If there is a large difference between the value of your analyzed sample and the reagent blank, adjust the sample pH to the value of the reagent blank. Adjust the sample pH to this same pH for all future samples before analysis. Use the appropriate acid, usually nitric acid, to lower the pH. Use the appropriate base, usually sodium hydroxide, to raise the pH. Adjust the final result for any dilution caused by adding acid or base; see *Correcting for Volume Additions*.

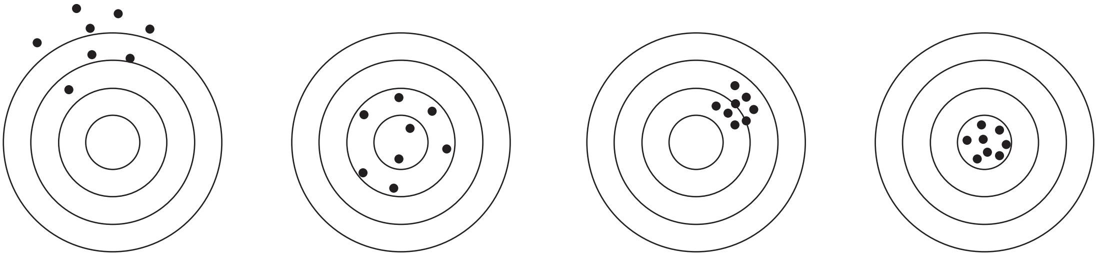
7. Analyze the sample as before.

8. Some purchased standards may be very acidic and will not work directly with Hach procedures. Adjust the pH of these standards as described above. Adjust the final concentration of the standard for the dilution. The Hach standard solutions suggested in the procedures are formulated so that no pH adjustment is necessary.

Accuracy and Precision

Accuracy is the nearness of a test result to the true value. Precision is how closely repeated measurements agree with each other. Although good precision suggests good accuracy, precise results can be inaccurate. The following paragraphs describe how to improve accuracy and precision of analyses by using Standard Additions.

Figure 9 Precision and Accuracy Illustrated



Not accurate, not precise

Accurate, not precise

Precise, not accurate

Accurate and precise

One of the greatest aids is knowing what is in the sample. You don't need to know exactly what is in each sample, but be aware of substances that are likely to interfere in the analysis method you use. When using a method, it may be helpful to determine if those interferences are present.

Standard Additions

Standard Additions is a common technique for checking test results. Other names are “spiking” and “known additions.” The technique can test for interferences, bad reagents, faulty instruments, and incorrect procedures.

Perform Standard Additions by adding a small amount of a standard solution to your sample and repeating the test. Use the same reagents, equipment, and technique. You should get about 100% recovery. If not, you have an identifiable problem.

If Standard Additions works for your test, a Standard Additions Method section will be in the procedure under *Accuracy Check*. Follow the detailed instructions given.

If you get about 100% recovery for each addition, everything is working right and your results are correct.

If you don’t get about 100% recovery for each addition, a problem exists. You can tell if you have an interference. Repeat the Standard Additions using deionized water as your sample. If you get about 100% recovery for each addition, you have an interference. If you didn’t get good recoveries with the deionized water, the following checklist may help to find the problem quickly:

1. Check to see that you are following the procedure exactly:

  a) Are you using the proper reagents in the proper order? Are you using 10-mL reagents with a 10-mL sample or 25-mL reagents with a 25-mL sample?

  b) Are you waiting the necessary time for color to develop?

  c) Are you using the correct glassware?

  d) Is the glassware clean?

  e) Does the test need a specific sample temperature?

  f) Is the sample’s pH in the correct range?

Hach’s written procedure should help you to answer these questions.

2. Check your reagents. Repeat the Standard Additions using new, fresh reagents. If your results are good, the original reagents were bad.

3. Check the performance of your instrument. Follow the instructions in the *Maintenance* section of the *DR/2010 Instrument Manual*.

4. If nothing else is wrong, the standard is almost certainly bad. Repeat the Standard Additions with a new standard.

If the check list does not determine the problem, use the decision tree (*Figure 10*) and explanation of each branch, below, to identify the problem.

Branch A
Suppose a single standard addition to the sample did not give the correct concentration increase. A possible cause could be interferences. Other causes include defective reagents, incorrect technique, a defective instrument/apparatus or defective standard used for the standard addition.

If interferences are known or assumed to be absent, proceed to Branch B. If interferences are known to be present, proceed to Branch C.

Branch B
Perform multiple standard additions on a sample of deionized water as in the following example using iron as the analyte of interest:

1. Pour 25 mL of deionized water into a 25-mL sample cell.

2. Add 0.1 mL of a 50-mg/L iron standard solution to a second 25 mL sample of deionized water.

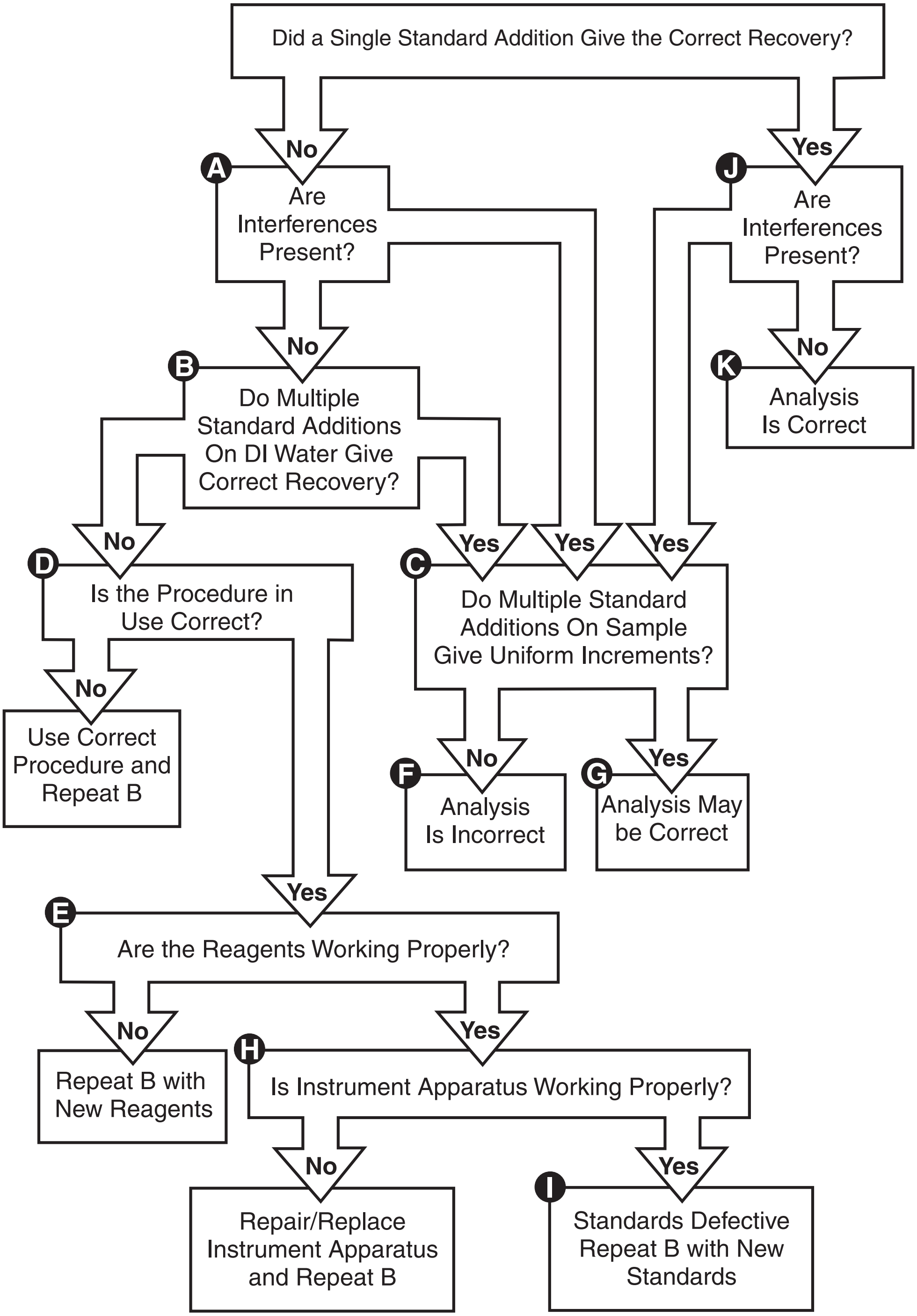
3. Add 0.2 mL of the same standard to a third 25 mL sample of deionized water.

4. Add 0.3 mL of the same standard to a fourth 25 mL sample of deionized water. Analyze all these samples for iron.

5. Tabulate the data as shown below:

mL of standard Added	mg/L of Standard Added	mg/L of Iron Found
0	0	0
0.1	0.2	0.2
0.2	0.4	0.4
0.3	0.6	0.6

Figure 10 Standard Additions Decision Tree



The data show several points:

- The chemicals, instrument, procedure/technique and standards are working correctly because the iron added to the water sample was completely recovered in the same uniform steps that match the standard addition increments.
- Because iron added to the deionized water was recovered, but iron added to an actual sample was not recovered (Branch A), the sample contains an interference which prevents the test reagents from working properly.
- An iron analysis previously done on the actual sample using this method gave an inaccurate result.

If the results of multiple standard additions give the correct increment for each addition, proceed to Branch C.

If the results of multiple standard additions do not give the correct increment for each addition, go to Branch D.

Branch C
If interfering substances are present, the analysis may be incorrect. However, with multiple standard additions, it may be possible to arrive at an approximate result if the increases are uniform.

Suppose the sample result for iron was 1.0 mg/L. Because interferences may be present, a standard addition of 0.1 mL of a 50 mg/L iron standard to a 25 mL sample is made. The expected increase in the iron concentration is 0.2 mg/L, but the actual increase is 0.1 mg/L. Then 0.2 and 0.3 mL of the same standard are added to two more 25 mL samples and analyzed for iron.

If there is a uniform increase in concentration between each addition (i.e., 0.1 mg/L difference between each addition), use Branch G. If the increase in concentration is not uniform (i.e., 0.1, 0.08, 0.05), go to Branch F.

Branch D
Carefully check the instructions for the test. Make sure to use the correct reagents in the correct order. Be sure the colorimeter is adjusted to the correct wavelength and the glassware in use is what is required. Be sure time for color development and the sample temperature are as specified. If the procedure technique was incorrect, repeat Branch B. If the procedure was correctly followed, proceed to Branch E.

Branch E

Check the reagent performance. This may be done by obtaining a fresh lot of reagent or by using a known standard solution to run the test. Make sure the color development time given in the procedure is equal to the time required for the reagent in question. If the reagent(s) is defective, repeat Branch B with new reagents. If the reagents are good, proceed with Branch H.

Branch F

Examples of non-uniform increments between standard additions are shown below.

Example A

mL of Standard Added	mg/L Standard Added	mg/L Found
0	0	1.0
0.1	0.2	1.10
0.2	0.4	1.18
0.3	0.6	1.23

Example B

mL of Standard Added	mg/L Standard Added	mg/L Found
0	0	0
0.1	0.2	0
0.2	0.4	0.2
0.3	0.6	0.4

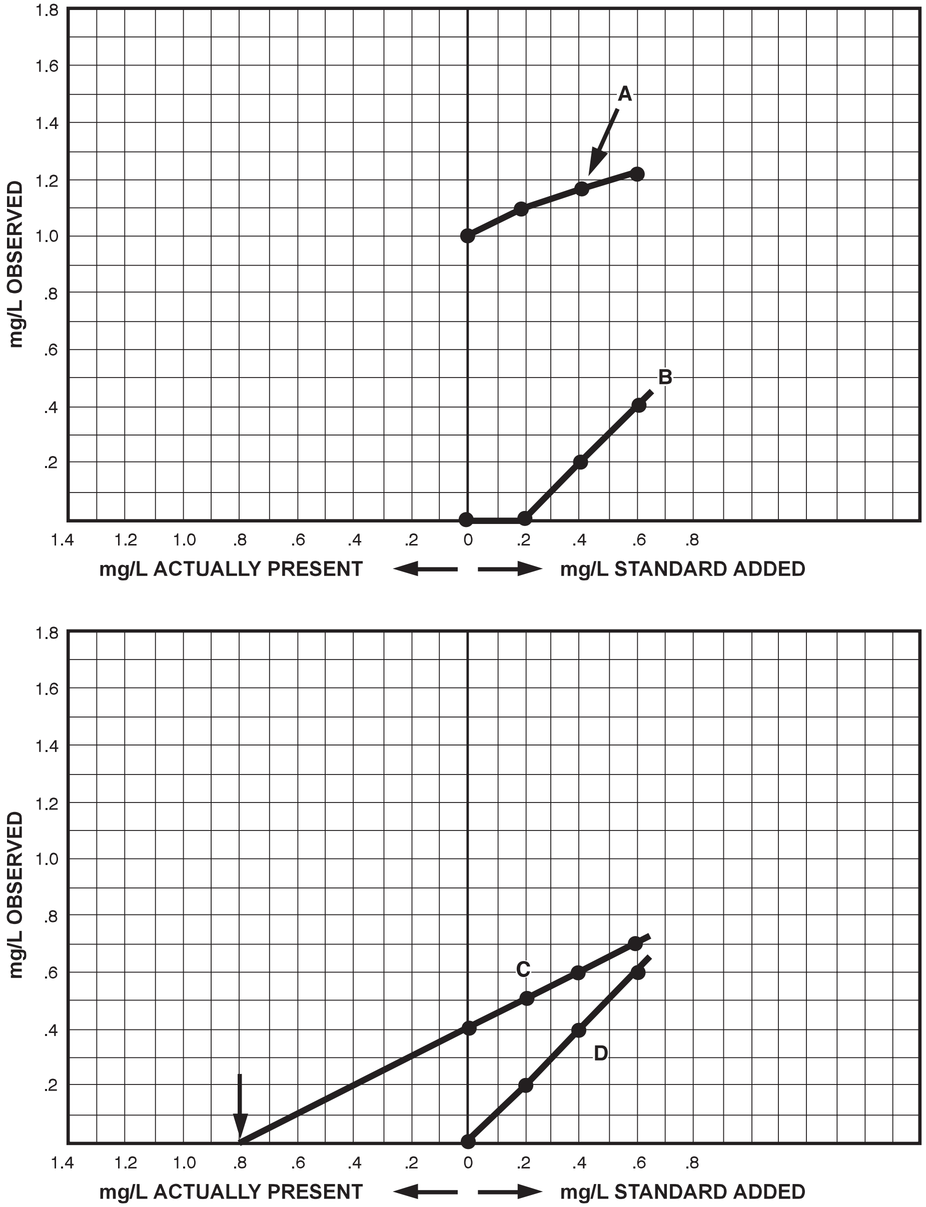
These examples show the effect of interferences on the standard addition. Data plotted on the graph in Figure 10 for samples A and B show that the four data points do not lie on a straight line.

The plot for sample A illustrates an interference that becomes progressively worse as the concentration of the standard increases. This type of interference is uncommon and may be caused by an error or malfunction of the procedure, reagents or instrument. It is recommended Branch B be performed to verify the supposed interference.

The plot for sample B shows a common chemical interference which becomes less or even zero as the concentration of standard increases. The graph shows the first addition was consumed by the interference and the remaining additions gave the correct increment of 0.2 mg/L.

The apparent interference in Example B could be the result of an error made in the standard addition. Repeat the analysis to see if an error was made during standard addition. If not, the method is not appropriate for the sample matrix. When these two types of interferences occur, try to analyze the sample with another method which uses a different type of chemistry.

Figure 11 Multiple Standard Additions Graph



Branch G

Examples of uniform increments between standard additions are given below.

Example C

mL of Standard Added	mg/L Standard Added	mg/L Found
0	0	0.4
0.1	0.2	0.5
0.2	0.4	0.6
0.3	0.6	0.7

The plot for sample C illustrates a common interference with a uniform effect on the standard and the substances in the sample. The four data points form a straight line which may be extended back through the horizontal axis. The point where the line meets the axis can be used to determine the concentration of the substance you are measuring.

In this example, the first analysis gave 0.4 mg/L. After extrapolating the line to the horizontal axis, the graph shows the result should be much closer to the correct result: 0.8 mg/L.

Apparent interferences may also be caused by a defect in the instrument or standards. Before assuming the interference is chemical, check Branch B.

Example D

mL of Standard Added	mg/L Standard Added	mg/L Found
0	0	0
0.1	0.2	0.2
0.2	0.4	0.4
0.3	0.6	0.6

The plot for sample D illustrates a problem for the analyst. The increments are uniform and the recovery of the standard was complete. The result of the first analysis was 0 mg/L and the line extrapolates back through 0 mg/L. If interferences are known to be present, the interferences may be present in an amount equal to the substance in question, preventing the analyst from finding the substance. This would be an uncommon situation.

Branch H
Check operation of the instrument and/or apparatus used to perform the test. Perform the wavelength and linearity checks in the instrument manual. Check glassware used in the procedure and make sure it is extremely clean. Dirty pipets and graduated cylinders can cause contamination and will not deliver the correct volume.

If a defect is found in the instrument and/or apparatus, repeat Branch B after repair or replacement. If the instrument and apparatus are working, proceed with Branch I.

Branch I
After determining the procedure, reagents, instrument and/or apparatus are correct and working properly, you may conclude the only possible cause for standard additions not functioning correctly in deionized water is the standard used for performing standard additions. Obtain a new standard and repeat Branch B.

Branch J
If the standard additions gives the correct result, the analyst must then determine if an interfering substance(s) is present. If interfering substances are present, proceed to Branch C. If they are not present, the analysis is correct.

If you still cannot identify the problem, extra help is available. Please call our Technical Support Group at 800-227-4224 (U.S.A.) or 970-669-3050. A representative will be happy to help you.

Method Performance

Estimated Detection Limit

Ranges for chemical measurements have limits. The lower limit is important because it determines whether a measurement is different from zero. Many experts disagree about the definition of this detection limit, and determining it can be difficult. The Code of Federal Regulations (40 CFR, Part 136, Appendix B) provides a procedure to determine the "Method Detection Limit" or MDL. The MDL is the lowest concentration that is different from zero with a 99% level of confidence. A measurement below this MDL may be useful, but there is a greater chance that it is actually zero.

The MDL is not fixed; it varies for each reagent lot, instrument, analyst, sample type, etc. Therefore, a published MDL may be a useful guide, but is only accurate for a specific set of circumstances. Each analyst should determine a more accurate MDL for each specific sample matrix using the same equipment, reagents and standards that will routinely be used for measurements.

Hach provides a value called the Estimated Detection Limit (EDL) for USEPA accepted and approved programs. It is the calculated lowest average concentration in a deionized water matrix that is different from zero with a 99% level of confidence. Specifically, it is the upper 99% confidence limit for zero concentration based on the calibration data used to prepare the pre-programmed calibration curve. **Do not use the EDL as a MDL**. The conditions for MDL determination must be exactly the same as the conditions used for analysis. The EDL may be useful to the analyst as a starting point in determining a MDL or as a way to compare methods. Measurements below the EDL may also be valuable because they can show a trend, indicate the presence of analyte and/or provide statistical data. However, these values have a large uncertainty.

Method Detection Limit (MDL)

This method is in accordance with the USEPA definition in 40 CFR, Part 136, Appendix B in the 7-1-94 edition.

The USEPA defines the method detection limit (MDL) as the minimum concentration that can be determined with 99% confidence that the true concentration is greater than zero. Since the MDL will vary from analyst to analyst, it is important that analysts determine the MDL based on their unique operating conditions.

The procedure for determining MDL is based on replicate analyses at a concentration 1 to 5 times the estimated detection limit. The MDL value is calculated from the standard deviation of the replicate study results multiplied by the appropriate Student's t value for a 99% confidence interval. For this definition, the MDL does not account for variation in sample composition and can only be achieved under ideal conditions.

1. Estimate the detection limit. Use the Hach estimated detection limit (EDL) value stated in the *Method Performance* section of the analysis procedure.

2. Prepare a laboratory standard of the analyte in deionized water which is free of the analyte that is 1 to 5 times the estimated detection limit.

3. Analyze at least 7 portions of the laboratory standard and record each result.

4. Calculate the average and standard deviation (s) of the results.

5. Compute the MDL using the appropriate Student's *t* value (see table below) and the standard deviation value:

MDL = Student's *t x s*

Number of Test Portions	Student's *t* Value
7	3.143
8	2.998
9	2.896
10	2.821

For example:
The EDL for measuring iron using the FerroZine method is 0.003 mg/L. An analyst accurately prepared 1 liter of a 0.010 mg/L (about 3x the EDL) laboratory standard by diluting a 10-mg/L iron standard in iron-free deionized water.

Eight portions of the standard were tested according to the FerroZine method with the following results:

Sample #	Result (mg/L)
1	0.009
2	0.010
3	0.009
4	0.010
5	0.008
6	0.011
7	0.010
8	0.009

Using a calculator program, the average concentration = 0.010 mg/L and the standard deviation (*s*) = 0.0009 mg/L

Based on the USEPA's definition, calculate the MDL as follows:

MDL for FerroZine method = 2.998 (Student's *t*) x 0.0009 (*s*)

MDL = 0.003 mg/L (agrees with initial estimate)

***Note:** Occasionally, the calculated MDL may be very different than Hach's estimate of the detection limit. To test how reasonable the calculated MDL is, repeat the procedure using a standard near the calculated MDL. The average result calculated for the second MDL derivation should agree with the initial* *calculated MDL. Refer to 40 CFR, Part 136, Appendix B (7-1-94), pages 635-637 for detailed procedures to verify the MDL determination.*

Note: *Run a laboratory blank, containing deionized water without analyte, through the test procedure to confirm that the blank measurement is less than the calculated MDL. If the blank measurement is near the calculated MDL, repeat the MDL procedure using a separate blank for analysis for each standard solution portion analyzed. Subtract the average blank measurement from each standard and use the corrected standard values to calculate the average and standard deviation used in the MDL.*

Precision

Every measurement has a degree of uncertainty. Just as a ruler with 0.1-mm markings leaves some doubt as to the exact length of a measurement, chemical measurements also have some degree of uncertainty. The quality of the entire calibration curve determines the precision.

Uncertainty in chemical measurements may be due to systematic errors and/or random errors. A systematic error is a mistake that is always the same for every measurement made. For example, a blank can add to each measurement for a specific compound, giving consistently high results (a positive bias). Random errors are different for every test and add either positive or negative bias. Random errors may be caused by variation in analytical technique and cause response variation. Hach chemists work hard to eliminate systematic errors in Hach procedures using Hach reagents, but response variation occurs in all chemical measurements.

Estimating Precision

The method performance section in each procedure provides an estimate of the procedure's precision. Two types of estimates are used throughout this manual. Most of the procedures use a "replicate analysis" estimate, based on real data. Some newer procedures use a 95% or 99% confidence interval, which is based on the calibration generated data for that particular chemistry.

In replicate analysis, a Hach chemist prepares a specific concentration of the analyte in a deionized water matrix. The standard is then analyzed seven individual times with the two reagent lots used in the calibration (14 total samples). A standard deviation of the two sets of seven values is calculated. The larger value is reported in the method. The reported value provides an estimate of the "scatter" of results at a particular point in the calibration curve.

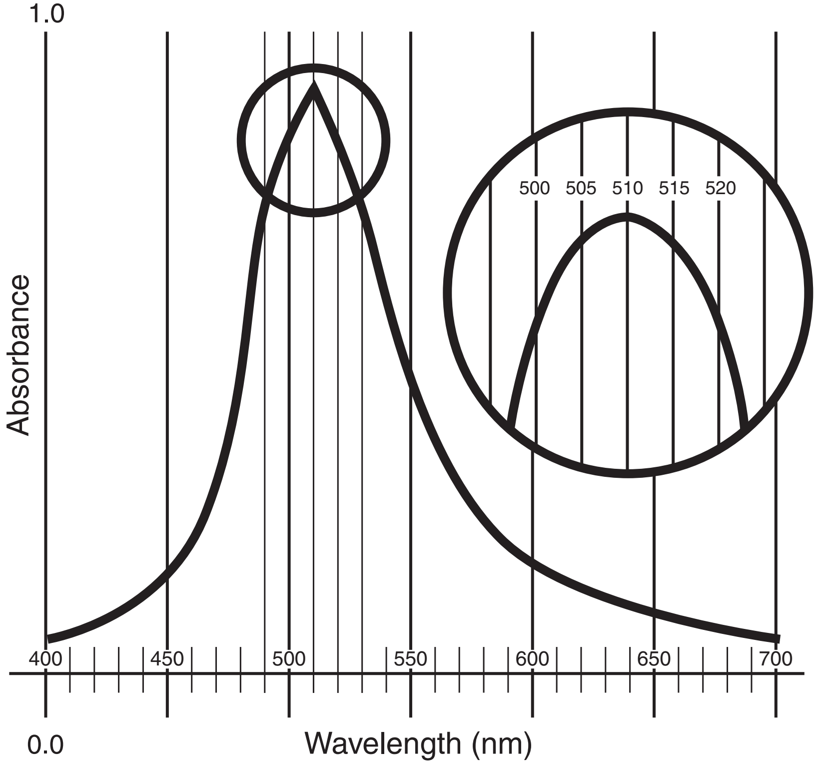
In the confidence interval technique, an estimate is obtained from the calibration data itself, with no additional replicate analyses. In this case, the precision is the 95 or 99% confidence interval for the stated concentrations. The precision range is an estimate of the average response variation and is based on multiple reagent lots and instruments used in the calibration. Therefore, it will not exactly predict the true precision range for each reagent lot, but does provide a useful estimate.

In either case, it is important to stress that the estimates are based on the deionized water matrix. Precision on real samples with varying matrices can be quite different than these estimates.

Selecting the Best Wavelength

When developing a new procedure or using procedures that are sensitive to wavelength, it is normal to select the wavelength where the instrument gives the greatest absorbance (see *Figure 12*). Because Hach chemists have selected the best wavelength for the procedures in this manual, selecting the wavelength is not necessary for most procedures.

Figure 12 Selecting the Best Wavelength



To select the best wavelength on the DR/2010:

1. Turn the instrument ON. Select the constant-on mode. Wait 5 minutes for the instrument to warm up.

2. Enter the stored program for absorbance. Press: **0 ENTER.**
   The display will show: **Abs**

3. Rotate the wavelength dial until the small display shows the approximate wavelength of interest.

   Note: *Sample color provides a good indication of what wavelength region to use. A yellow solution absorbs light in the 400-500 nm region. A red solution absorbs light between 500-600 nm. A blue solution absorbs light in the 600-700 nm range.*

4. Prepare the sample and blank for analysis. FIll the appropriate sample cells with the blank and the sample solutions (cells can be 10- or 25-mL cells, COD vial, 1-cm vials, etc.).

5. Place the blank in the cell holder. Orient the fill mark to your right. Close the light shield.

6. Press: **ZERO.** The display should read: **0.000 Abs**

7. Place the prepared sample into the cell holder. Close the light shield. Read the absorbance.

8. Increase the wavelength so it is at least 100 nm greater than the range of interest. Re-zero as in Steps 5-6. Measure and record the absorbance of the sample.

9. Repeat, decreasing the wavelength by 50 nm. Re-zero, then measure and record the absorbance at each increment. Continue this process through the wavelength range of interest. Note the wavelength of greatest absorbance (see *Table 7* as an example).

Table 7 Example of Initial Wavelength Search[1]

Wavelength	Absorbance
550 nm	0.477
500 nm	0.762
450 nm	0.355
400	0.134

[1] This indicates 500 nm as the region to search for the best wavelength.

10. Adjust the wavelength to 50 nm more than the highest absorbance point on the initial search (step 9). Re-zero as in Steps 5 and 6.

11. Measure and record the absorbance. Repeat, decreasing the absorbance in 5-nm steps. Re-zero, then measure and record the absorbance at each increment. Continue until the entire range of interest is measured (see *Table 8* as an example).

Table 8 Example of Intermediate Wavelength Search[1]

Wavelength	Absorbance
520	0.748
515	0.759
510	0.780
505	0.771
500	0.771
495	0.651
490	0.590

[1] This indicates the best wavelength to use is around 510 nm.

12. Increase the wavelength to 10 nm above the highest absorbance in Step 11. Re-zero as in Steps 5 and 6. Measure and record the absorbance. Repeat the measuring process (re-zeroing is not necessary at each increment), decreasing the wavelength by 1 nm each time.

Table 9 Example of Detailed Wavelength Search[1]

Wavelength	Absorbance
512	0.769
511	0.773
510	0.780
509	0.787
508	0.781
597	0.764

[1] The optimum wavelength is 509 nm.

13. Check to be sure there is enough difference in absorbance between samples with low and high analyte concentrations by measuring two sample solutions that contain the expected low and high concentrations of analyte at the optimum wavelength. The change in absorbance caused by increases/decreases in concentration depends on the sensitivity of the procedure and chemistry. Chemistries with

small absorbance changes are less sensitive, but tend to have larger ranges. Chemistries with large absorbance changes are more sensitive, but tend to have smaller ranges.

Adapting HACH Procedures to Other Spectrophotometers

Hach procedures may be used with other spectrophotometers if calibration curves that convert absorbance or %T to concentration are made. Regardless of the spectrophotometer used, prepare the sample and calibration standards following the Hach procedure and use the optimum wavelength used in the Hach procedure.

The example below describes a calibration for iron in the 0-2.4 mg/L range. A series of iron standards are prepared and measured to establish the calibration curve. The absorbance vs. concentration is plotted on linear graph paper (as in *Figure 11, Multiple Standard Additions Graph*) or %T vs. concentration is plotted on semi-logartihmic paper. Points on the graph are connected with a smooth line (curved or straight). If necessary, use the curve to make a calibration table.

Preparing a Calibration Curve

1. Prepare five or more standards of known concentration that cover the expected range of the test. Run tests as described in the procedure on each prepared standard. Then pour the customary volume of each known solution into a separate clean sample cell of the type specified for your instrument.

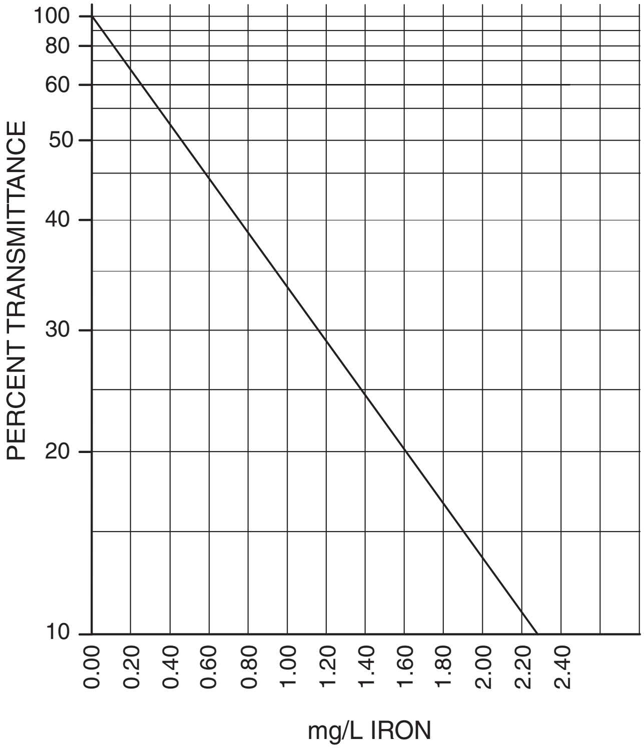
2. Select the proper wavelength. Standardize (zero) the instrument using an untreated water sample or a reagent blank, whichever the procedure instructs you to use.

3. Measure and record the %T or absorbance of the known solutions. To use %T vs. concentration see section *%T Versus Concentration Calibration*. To use absorbance vs. concentration, see section *Absorbance Versus Concentration Calibration*.

%T Versus Concentration Calibration

If measuring %T, use semilogarithmic graph paper and plot %T (vertical scale) versus concentration (horizontal scale). For *Figure 13*, iron standard solutions of 0.1, 0.2, 0.4, 0.8, 1.2, 1.6 and 2.0 mg/L were measured on a Spectronic 20 at 500 nm using half-inch test tubes. Results were plotted and the calibration table values were extrapolated from the curve (*Table 10*).

Figure 13 Logarithmic Calibration Curve



To convert %T readings to concentration, prepare a table such as *Table 10* and select the appropriate line from the "%T Tens" column and the appropriate column from the %T Units columns. The %T Ten value is the first number of the %T reading and the %T Units value is the second number of the %T reading. For example, if the instrument reading was 46%, the 40 line in the %T Tens column and the 6 column in the %T Units would be selected. The cell where these two intersect (0.78 mg/L) is the iron concentration of the sample.

Table 10 Calibration Table

%T Tens	% Units									
	0	1	2	3	4	5	6	7	8	9
0										
10	2.30	2.21	2.12	2.04	1.97	1.90	1.83	1.77	1.72	1.66
20	1.61	1.56	1.51	1.47	1.43	1.39	1.35	1.31	1.27	1.24
30	1.20	1.17	1.14	1.11	1.08	1.04	1.02	0.99	0.97	0.94
40	0.92	0.89	0.87	0.84	0.82	0.80	0.78	0.76	0.73	0.71
50	0.69	0.67	0.65	0.64	0.62	0.60	0.58	0.56	0.55	0.53
60	0.51	0.49	0.48	0.46	0.45	0.43	0.42	0.40	0.39	0.37
70	0.36	0.34	0.33	0.32	0.30	0.29	0.28	0.26	0.25	0.24
80	0.22	0.21	0.20	0.19	0.17	0.16	0.15	0.14	0.13	0.12
90	0.11	0.09	0.08	0.07	0.06	0.05	0.04	0.03	0.02	0.01

Absorbance Versus Concentration Calibration

If absorbance values are measured, plot the results on linear graph paper. Plot the absorbance value on the vertical axis and the concentration on the horizontal axis.

Plot increasing absorbance values from bottom to top. Plot increasing concentration values from left to right. Values of 0.000 absorbance units and 0 concentration will begin at the bottom left corner of the graph. A calibration table can be extrapolated from the curve or the concentration values can be read directly from the graph. Or determine an equation for the line using the slope and y-intercept.

USEPA Approved and Accepted Definitions

The United States Environmental Protection Agency (USEPA) establishes limits for maximum contamination levels of certain constituents in water. It also requires that specific methodology be used to analyze for these constituents. These methods originate from several sources. The USEPA has developed some of these methods. In other cases, the USEPA has evaluated and approved methods developed by manufacturers, professional groups and public agencies such as:

- American Public Health Association
- American Water Works Association
- Water Environmental Federation
- American Society for Testing and Materials
- United States Geological Survey
- Associates of Official Analytical Chemists

All USEPA-approved methods are cited in the *Federal Register* and compiled in the Code of Federal Regulations (CFR). USEPA approved methods may be used for reporting results to the USEPA and other regulatory agencies.

USEPA Accepted

Hach has developed several procedures that are equivalent to USEPA approved methods. Even though minor modifications exist, the USEPA has reviewed and accepted certain procedures for reporting purposes. These methods are not published in the *Federal Register,* but are referenced to the equivalent USEPA method in the procedure.

Digestion

Several procedures require sample digestion. Digestion uses chemicals and heat to break down a substance into components that can be analyzed. This section has three different digestion procedures.

The Hach Digesdahl system is a process that yields a digest suitable for the determination of metals, total phosphorus and total kjeldahl nitrogen (TKN). It is rapid, convenient and the method of choice.

For USEPA reporting purposes, USEPA-approved digestions are required. USEPA presents two digestions (mild and vigorous) for metals analysis. These are much more inconvenient and time consuming compared to the Hach Digesdahl system. Other digestion procedures are required for mercury, arsenic, phosphorus and TKN.

EPA Mild Digestion with Hot Plate for Metals Analysis Only

1. Acidify the entire sample at the time of collection with concentrated nitric acid by adding 5 mL of acid per liter (or quart) of sample.

2. Transfer 100 mL of well-mixed sample to a beaker or flask. Add 5 mL of distilled 1:1 hydrochloric acid (HCl).

3. Heat using a steam bath or hot plate until the volume has been reduced to 15-20 mL. Make certain the sample does not boil.

4. After this treatment, the sample may be filtered to remove any insoluble material.

5. Adjust the digested sample to pH 4 by drop-wise addition of 5.0 N Sodium Hydroxide Standard Solution. Mix thoroughly and check the pH after each addition.

6. Quantitatively transfer the sample with deionized water to a 100-mL volumetric flask and dilute to volume with deionized water. Continue with the procedure. This mild digestion may not suffice for all sample types. A reagent blank also should be carried through the digestion and measurement procedures.

EPA Vigorous Digestion with Hot Plate for Metals Analysis Only

A vigorous digestion can be followed to ensure all organo-metallic bonds are broken.

1. Acidify the entire sample with redistilled 1:1 Nitric Acid Solution to a pH of less than two. Do not filter the sample before digestion.
2. Transfer an appropriate sample volume (see *Table 11*) into a beaker and add 3 mL of concentrated redistilled nitric acid.
3. Place the beaker on a hot plate and evaporate to near dryness, making certain the sample does not boil.
4. Cool the beaker and add another 3 mL of the concentrated redistilled nitric acid.
5. Cover the beaker with a watch glass and return it to the hot plate. Increase the temperature of the hot plate so that a gentle reflux occurs. Add additional acid, if necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change color or appearance with continued refluxing).
6. Again, evaporate to near dryness (do not bake) and cool the beaker. If any residue or precipitate results from the evaporation, add redistilled 1:1 hydrochloric acid (5 mL per 100 mL of final volume). See *Table 11*.
7. Warm the beaker. Add 5 mL of 5.0 N sodium hydroxide and quantitatively transfer the sample with deionized water to a volumetric flask. See *Table 11* below for the suggested final volume.
8. Adjust the sample to pH 4 by drop-wise addition of 5.0 N Sodium Hydroxide Standard Solution; mix thoroughly and check the pH after each addition. Dilute to volume with deionized water. Multiply the result by the correction factor in *Table 11*. A reagent blank also should be carried through the digestion and measurement procedures.

Table 11 Vigorous Digestion Volumes

Expected Metal Concentration	Suggested Sample Vol. for Digestion	Suggested Volume of 1:1 HCl	Suggested Final Volume After Digestion	Correction Factor
1 mg/L	50 mL	10 mL	200 mL	4
10 mg/L	5 mL	10 mL	200 mL	40
100 mg/L	1 mL	25 mL	500 mL	500

General Digesdahl Digestion (Not USEPA accepted)

Many samples may be digested using the Digesdahl Digestion Apparatus (Cat. No. 23130). It is designed to digest many types of samples such as oils, wastewater, sludges, feeds, grains, plating baths, food, and soils. In this procedure the sample is oxidized by a mixture of sulfuric acid and hydrogen peroxide. Digestion of a dry sample requires less than ten minutes, while liquid samples require about 1 minute/mL. The digestion is done in a special flat-bottomed 100-mL volumetric flask. Aliquots (sample portions) are taken for analysis using colorimetric methods.

Procedures for digestion and using the Digesdahl Digestion Apparatus are based on the type and form of the sample, and are found in the Digesdahl Digestion Apparatus Instruction Manual, which is included with each Digesdahl Digestion Apparatus.

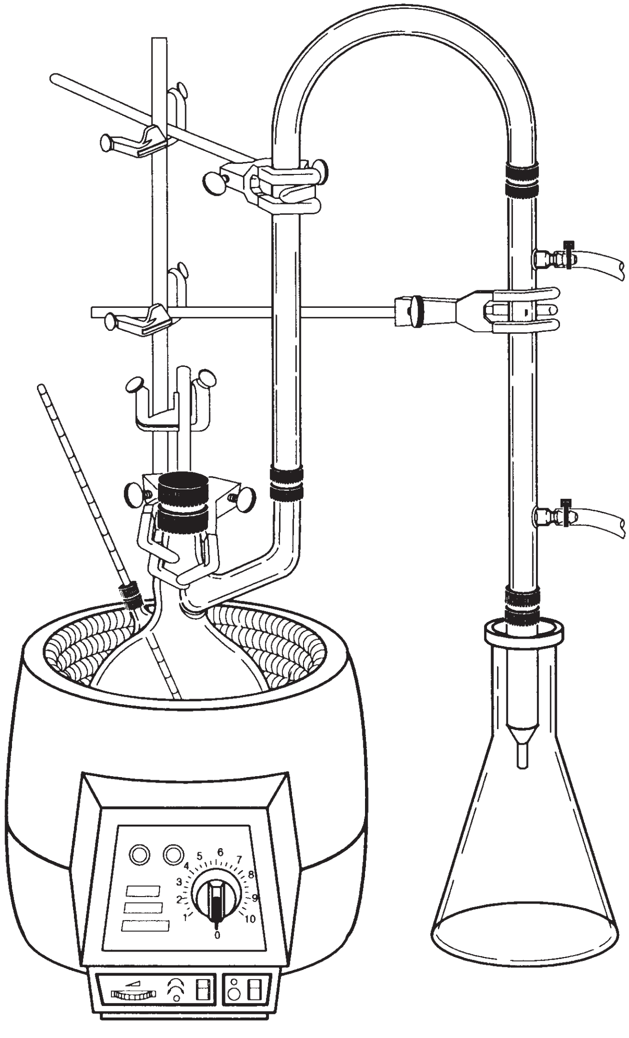
Distillation

Distallation Applications for the General Purpose Distillation Apparatus include:

- fluoride
- albuminoid nitrogen
- ammonia nitrogen
- phenols
- selenium
- volatile acids

Arsenic and cyanide require specialty glassware sets in addition to the General Purpose Set (the Arsenic Distillation Apparatus and the Cyanide Distillation Apparatus). All connecting glassware is manufactured with threaded connectors for ease and safety. The General Purpose Heater provides efficient heating and the Support Apparatus anchors the glassware.

Figure 14 General Purpose Distillation Apparatus with Heater and Support Apparatus



SECTION III WASTE MANAGEMENT AND SAFETY

Waste Management

This section provides guidelines for laboratory waste management. It should assist you in complying with USEPA regulations governing waste management. It summarizes basic requirements, but does not contain all USEPA regulations. It does not relieve people from complying with all regulations contained in the Code of Federal Regulations. Regulations change regularly and additional state and local laws may apply to you. Each waste generator is responsible for knowing and obeying these laws.

Waste Minimization

Waste minimization is the foundation of good waste management. Minimizing waste greatly reduces the disposal problems and expense. If possible, try to generate less waste rather than recycle or re-use it. For laboratories, ways to reduce waste include:

- Use the smallest sample size possible.
- Choose methods that use non-hazardous or “less” hazardous reagents when possible.
- Buy chemicals in small quantities which will be used before they expire. This eliminates disposal of out-dated materials.
- Clean glassware and laboratory apparatus with non-hazardous soaps when possible, rather than solvents or acids which may be hazardous.

Regulatory Overview

Federal waste disposal regulations were issued in accordance with the Resource Conservation and Recovery Act (RCRA). They are given in Title 40 Code of Federal Regulations (CFR) part 260. The Act controls all forms of solid waste disposal and encourages recycling and alternative energy sources. The major emphasis is controlling hazardous waste disposal. The regulations create a system to identify wastes and track waste generation, transport, and ultimate disposal. Each facility involved in managing hazardous waste must be registered with the USEPA. This includes the generator, transporters, and treatment, storage, and disposal facilities (TSDF).

Under federal regulations, there are three categories of generators with increasingly more strict regulation for larger quantity generators. The categories are based on the amount of hazardous waste generated in any given month.

The categories are as follows:

- Conditionally Exempt Small Quantity Generator - less than 100 kg (220 lb.) per month
- Small Quantity Generator - between 100 kg (220 lb.) and 1,000 kg (2,200 lb.) per month
- Large Quantity Generator - greater than 1,000 kg (2,200 lb.) per month

Note: *If a laboratory generates acutely hazardous waste (as defined on 40 CFR 261) or accumulates more than a certain amount of waste, the facility may be moved into a larger generator status. Check with your environmental compliance manager or state and local officials to determine which category your facility is in.*

Hazardous Waste Definition

For regulatory purposes, a “hazardous waste” is a material which is subject to special laws by the USEPA under 40 CFR 261. In addition, many states or local authorities regulate additional materials as hazardous waste. Be aware that many very toxic compounds are not regulated by this definition of hazardous waste. However, improper management or disposal of these compounds may lead to legal problems under other laws such as CERCLA (Superfund) or common law tortes.

The 40 CFR 261 defines a hazardous waste as a solid waste which is not excluded from regulation and meets any of the following criteria:

- It is a discarded commercial chemical product, off-specification species, container residue, or spill residue of materials specifically listed in 40 CFR 261.33;
- It is a waste from a specific source listed in 40 CFR 261.32;
- It is a waste from a non-specific source listed in 40 CFR 261.31; or
- It displays any of the following characteristics of hazardous waste defined in 40 CFR 261.20-24:
    - ignitability
    - corrosivity
    - reactivity
    - toxicity

There are many exceptions to these regulations, and each generator should review the regulations and determine if they are excluded from the regulations.

Characteristic Hazardous Waste Codes

Hazardous wastes are managed by specific codes assigned in 40 CFR 261.20-261.33. These codes are provided to help you identify hazardous waste. The generator is responsible for making the actual waste code determination.

Selected characteristic waste codes for chemicals which may be generated using Hach methods for water analysis are given in the following table. A complete list of waste codes is found in 40 CFR 261.24.

USEPA Code	Characteristic	CAS No.	Regulatory Level (mg/L)
D001	Ignitability	na	na
D002	Corrosivity	na	na
D003	Reactivity	na	na
D004	Arsenic	6440-38-2	5.0
D005	Barium	6440-39-3	100.0
D018	Benzene	71-43-2	0.5
D006	Cadmium	7440-43-9	1.0
D022	Chloroform	67-66-3	6.0
D007	Chromium	7440-47-3	5.0
D008	Lead	7439-92-1	5.0
D009	Mercury	7439-97-6	0.2
D010	Selenium	7782-49-2	1.0
D011	Silver	7440-22-4	5.0

How to Determine if Waste is Hazardous

Federal laws do not require you to test a material to decide if it is a hazardous waste. You may apply product knowledge to decide if a material is hazardous. Often, information on a material safety data sheet (MSDS) is enough to decide. If the product is specifically listed in the regulation, it is a hazardous waste.

You also need to decide if it has any characteristics of a hazardous waste. Physical information on the MSDS may help you decide. If the flash point is below 60 °F (15 °C) or is classified by DOT as an oxidizer, the material may be ignitable. If the pH of the material is ≤2 or ≥12.5, the material may be corrosive. If the material is unstable, reacts violently with water, or may generate toxic gases, vapors, or fumes when mixed with water, it may be reactive.

Use the chemical composition data to decide if a material is toxic. This decision is based on the concentration of certain contaminants (heavy metals and a number of organic compounds). If the waste is a liquid, compare the concentration of the contaminants in the liquid to the concentrations listed in 40 CFR 261.24. If the waste is a solid, analyze the sample by the Toxicity Characteristic Leachability Procedure (TCLP) and compare the results to the concentration listed in the 40 CFR 261.24. Levels above the threshold amount listed in the table are considered hazardous.

See the description of an MSDS (page 71) for help in finding information for making hazardous waste determinations.

Examples of Hazardous Waste

A number of chemicals used in and final solutions created from Hach procedures are hazardous wastes when they are disposed. In addition, substances in the sample matrix may be a hazardous waste. Sometimes, reagents which would be hazardous are neutralized or changed during the analytical procedure. In that case, the final solutions are not regulated. Finally, many reagents and final solutions may be non-regulated. The generator must either use their knowledge of the materials used or conduct analytical tests to determine if the final material is a hazardous waste.

Examples of tests using Hach reagents that generate hazardous waste include those containing mercury or mercury compounds such as COD tests or Nessler's reagent. Conversely, a test using Hach reagents such as ManVer 2 Hardness Indicator Powder Pillows and EDTA Titration Cartridges does not produce a hazardous waste.

Hazardous Waste Disposal

Hazardous waste must be managed and disposed of according to federal, state, and local regulations. The waste generator is responsible for making hazardous waste determinations. Analysts should check with the facility's environmental compliance people for specific instructions.

Hazardous wastes should be handled by treatment, storage, and disposal facilities (TSDF) that have USEPA permits. In some cases, the generator may treat the hazardous waste. In most cases, a permit from the USEPA is required to treat hazardous waste. Laboratories are not exempt from these regulations. If your facility is a "Conditionally Exempt Small Quantity Generator," special rules may apply. Check 40 CFR 261 to determine if you have to comply with all the laws.

The most common allowed treatment is elementary neutralization. This refers to neutralizing wastes that are hazardous only because they are corrosive or are listed only for that reason. Neutralize acidic solutions by adding a base such as sodium hydroxide; neutralize basic solutions by adding an acid such as hydrochloric acid. Slowly add the neutralizing agent while stirring. Monitor the pH. When it is at or near 7, the material is neutralized and may be flushed down the drain. Many wastes generated from Hach procedures may be treated in this manner.

Other chemical or physical treatments such as cyanide destruction or evaporation may require a permit. Check with your environmental department or local regulators to determine which rules apply to your facility.

Laboratory chemicals may be mixed and disposed of with other hazardous wastes generated at your facility. They may also be accumulated in accordance with 40 CFR 262.34 satellite accumulation rules. After collection they may be disposed of in a “labpack.” A number of environmental and hazardous waste companies offer labpacking services. They will inventory, sort, pack, and arrange proper disposal for hazardous waste. Find companies offering these services in the Yellow Pages under "Waste Disposal - Hazardous" or contact state and local regulators for assistance.

Management of Specific Wastes

Hach has several documents to assist customers in managing waste generated from our products. You can obtain the following documents by calling 1-800-227-4224 or 970-669-3050 and requesting the literature codes given:

Literature Code	Title
1321	Waste Reduction: A Primer
9323	Mercury Waste Disposal Firms
9325	COD Waste Management
9326	COD Heavy Metal Total Concentrations

Special Considerations for Cyanide Containing Materials

Several procedures in this manual use reagents that contain cyanide compounds. These materials are regulated as reactive (D003) waste by the Federal RCRA. Waste disposal instructions provided with each procedure tell you how to collect these materials for proper disposal. It is imperative that these materials be handled safely to prevent the release of hydrogen cyanide gas (an extremely toxic material with the smell of bitter almonds). Most cyanide compounds are stable and can be safely stored for disposal in highly alkaline solutions (pH >11) such as 2 N sodium hydroxide. Never mix these wastes with other laboratory wastes that may contain lower pH materials such as acids or even water.

If a cyanide-containing compound is spilled, you must be careful not to be exposed to hydrogen cyanide gas. Take the following steps to destroy the cyanide compounds in an emergency:

a) Use a fume hood, supplied air or self-contained breathing apparatus.

b) While stirring, add the waste to a beaker containing a strong solution of sodium hydroxide and either calcium hypochlorite or sodium hypochlorite (household bleach).

c) Add a lot of hydroxide and hypochlorite. Let the solution stand for 24 hours.

d) Neutralize the solution and flush it down the drain with a large amount of water. If the solution contains other regulated materials such as chloroform or heavy metals, it may still need to be collected for hazardous waste disposal. Never flush hazardous wastes down the drain.

Resources

Many sources of information on proper waste management are available. The USEPA has a hotline number for questions about the Resource Conservation and Recovery Act (RCRA). The RCRA Hotline number is 1-800-424-9346. You may also get a copy of the appropriate regulations. Federal hazardous waste regulations are found in 40 CFR 260- 99. Obtain this book from the U.S. Government Printing Office or a number of other vendors. Other documents which may be helpful to the laboratory hazardous waste manager include:

1. Task Force on Laboratory Waste Management. *Laboratory Waste Management, A Guidebook*; American Chemical Society, Department of Government Relations and Science Policy: Washington, DC 1994.

2. Task Force on Laboratory Waste Management. *Waste Management Manual for Laboratory Personnel*; American Chemical Society, Department of Government Relations and Science Policy: Washington, DC 1990.

3. Task Force on Laboratory Waste Management. *Less is Better*; 2nd ed.; American Chemical Society, Department of Government Relations and Science Policy: Washington, DC 1993.

4. Committee on Chemical Safety. *Safety in Academic Chemistry Laboratories*, 5th ed.; American Chemical Society: Washington, DC, 1990.

5. Armour, Margaret-Ann. *Hazardous Laboratory Chemicals Disposal Guide*; CRC Press: Boca Raton, FL, 1991.

6. *Environmental Health and Safety Manager's Handbook*; Government Institutes, Inc.: Rockville, MD, 1988.

7. Lunn, G.; Sansone, E.B. *Destruction of Hazardous Chemicals in the Laboratory*; John Wiley and Sons: New York, 1990.

8. National Research Council. *Prudent Practices for Disposal of Chemicals from Laboratories*; National Academy Press: Washington, DC, 1983.

9. National Research Council. *Prudent Practices for Handling Hazardous Chemicals in Laboratories*; National Academy Press: Washington, DC, 1981.

10. Environmental Protection Agency, Office of Solid Waste and Emergency Response. *The RCRA Orientation Manual*; U.S. Government Printing Office: Washington, DC, 1991.

11. Environmental Protection Agency, Office of Solid Waste and Emergency Response. *Understanding the Small Quantity Generator Hazardous Waste Rules: A Handbook for Small Business*; U.S. Government Printing Office: Washington, DC, 1986.

Material Safety Data Sheets

Material safety data sheets (MSDS) describe the hazards of chemical products. This section describes the information provided on a Hach MSDS and how to locate important information for safety and waste disposal. The information provided on the MSDS applies to the product as sold by Hach. The properties of any mixtures obtained by using this product will be different.

How to Obtain an MSDS

Hach ships a MSDS to each customer with the first order of any chemical product. A new MSDS may be sent when the information on the data sheet is updated. Please review all new MSDSs for new information. If you need another copy of an MSDS, simply call 1-800-227-4227.

Sections of an MSDS

Each MSDS has ten sections. The sections and the information found in them are described below.

Header Information

The Hach catalog number, MSDS date, change number, company address and telephone number, and emergency telephone numbers are listed at the top of the MSDS.

1 Product Identification

This section contains:

- Hach product name
- Chemical Abstract Services (CAS) number
- Chemical name
- Chemical formula, if appropriate
- Chemical family to which the material belongs

2 Ingredients

This section lists each component in the product. It contains the following information for each component:·

- PCT: Percent by weight of this component
- CAS NO.: Chemical Abstract Services (CAS) registry number for this component
- SARA: Superfund Amendments and Reauthorization Act, better known as the “Community Right to Know Law.” Says if the component is listed in SARA 313. If the component is listed and you use more than the amount listed, you must report this to the USEPA every year.
- TLV: Threshold Limit Value. The maximum airborne concentration for an 8 hour exposure that is recommended by the American Conference of Governmental Industrial Hygienists (ACGIH).
- PEL: Permissible Exposure Limit. The maximum airborne concentration for an 8 hour exposure that is regulated by the Occupational Safety and Health Administration (OSHA).
- HAZARD: Physical and health hazards of the component are explained.

3 Physical Data

The physical properties of the product are given in this section. They include the physical state, color, odor, solubility, boiling point, melting point, specific gravity, pH, vapor density, evaporation rate, corrosivity, stability, and storage precautions.

4 Fire, Explosion Hazard And Reactivity Data

This section contains the flash point and flammable limits of the material. It also includes how to fight fires if the material catches on fire. Key terms in this section include:

- Flashpoint: The temperature at which a liquid will give off enough flammable vapor to ignite.
- Flammability and ignitability are usually defined by the flash point.
- Lower Flammable Limit (LFL or LEL): The lowest concentration that will produce a fire or flash when an ignition source is present.
- Upper Flammable Limit (UFL or UEL): The vapor concentration in air above which the concentration is too rich to burn.
- NFPA Codes: The National Fire Protection Association (NFPA) has a system to rate the degree of hazards presented by a chemical. These codes are usually placed in a colored diamond. The codes range from 0 for minimal hazard to 4 for extreme hazard. They are grouped into the following hazards: health (blue), flammability (red), reactivity (yellow), and special hazards (white).

5 Health Hazard Data

This section describes different ways the chemical can enter your body (ingestion, inhalation, skin contact). It also gives acute (immediate) and chronic (long-term) health effects. If the material causes cancer or genetic damage, it is identified in this section.

6 Precautionary Measures

This section contains special precautions for the material. These may include special storage instructions, handling instructions, conditions to avoid, and protective equipment required to use this material safely.

7 First Aid

First aid instructions for exposures to the chemical are given in this section. Be sure to read this section before inducing vomiting in a victim. Some chemicals are better treated by not inducing vomiting. Seek prompt medical attention for all chemical exposures.

8 Spill And Disposal Procedures

This section tells about safe work practices for cleaning up and disposing of spilled material. Please refer to the Waste Management section of this manual. Final determination of proper and legal disposal options is the responsibility of the waste generator. Be sure you know the federal, state, and local laws that apply to your facility.

9 Transportation Data

Domestic and International shipping information is provided in this section. It gives shipping name, hazard class, and ID number of the product.

10 References

This section lists the reference materials used to write the MSDS.

Following the Reference section, the product is listed as having SARA 313 chemicals or California Proposition 65 List Chemicals, if applicable. Also found here is any special information about the product.

Safety

Safety is the responsibility of each person performing analytical procedures. Because many of the procedures in this methods manual use potentially hazardous chemicals and equipment, it is important to prevent accidents by practicing good laboratory techniques. The following guidelines apply to water analysis. These guidelines do not cover every aspect of safety, but they are important for preventing injuries.

Material Safety Data Sheet

A material safety data sheet (MSDS) comes with the first shipment of all products. The MSDS provides environmental and safety information about the products. Always read the MSDS before using a new product.

Reading Labels Carefully

Read each reagent label carefully. Pay particular attention to the precautions given. Never remove or block the label on a reagent container while it contains reagent. Do not put a different reagent into a labeled container without changing the label. When preparing a reagent or standard solution, label the container clearly. If a label is hard to read, re-label promptly according to your facility’s hazard communication program.

Warning labels also appear on some of the apparatus used with the test procedures. The protective shields with the COD Reactor and the Digesdahl Digestion Apparatus point out potential hazards. Be sure these shields are in place during use and observe the precautions on the label.

Protective Equipment

Use the right protective equipment for the chemicals and procedures. The MSDS contains this information. Protective equipment may include:

- Eye protection such as safety glasses or goggles to protect from flying objects or chemical splashes.
- Gloves to protect skin from toxic or corrosive materials, sharp objects, very hot or very cold materials, or broken glass. Use tongs or finger cots when transferring hot apparatus.
- Laboratory coats or splash aprons to protect skin and clothing from splashes.
- Footwear to protect feet from spills. Open toed shoes should not be worn in chemistry settings.
- Respirators may be needed to protect you from breathing toxic vapors if adequate ventilation, such as fume hoods, are not available.
- Use fume hoods as directed by the procedure or as recommended in the MSDS.
- For many procedures, adequate ventilation is enough. Be sure there is enough fresh air and air exhaust to protect against unnecessary exposure to chemicals.

First Aid Equipment and Supplies

Most first aid instructions for chemical splashes in eyes or on skin call for thorough flushing with water. Laboratories should have eyewash and shower stations. For field work, carry a portable eyewash unit. Laboratories should also have appropriate fire extinguishers and fume hoods.

General Safety Rules

Follow these rules to make work with toxic and hazardous chemicals safer:

1. **Never** pipet by mouth. Always use a mechanical pipet or pipet bulb to avoid ingesting chemicals.
2. Follow test procedures carefully and observe all precautionary measures. Read the entire procedure carefully before beginning.

3. Wipe up all spills promptly. Get proper training and have the right response equipment to clean up spills. See your safety director for more information.

4. **Do not** smoke, eat, or drink in an area where toxic or irritating chemicals are used.

5. Use reagents and equipment only as directed in the test procedure.

6. **Do not** use damaged labware and broken equipment.

7. Minimize all chemical exposures. **Do not** breathe vapors or let chemicals touch your skin. Wash your hands after using chemicals.

8. Keep work areas **neat** and **clean**.

9. **Do not** block exits or emergency equipment.

OSHA Chemical Hygiene Plan

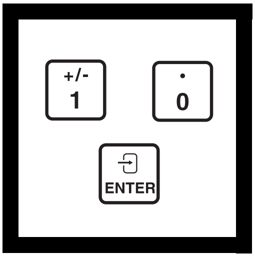
The Occupational Safety and Health Administration (OSHA) enforces laws about the control exposure to hazardous chemicals in laboratories. These regulations are in Title 29 CFR 1910.1450. They apply to all employers who use hazardous chemicals. They require employers to develop and use a written Chemical Hygiene Plan and appoint a qualified person as the Chemical Hygiene Officer.

Method 8012

ALUMINUM (0 to 0.80 mg/L)

For water and wastewater

Aluminon Method*



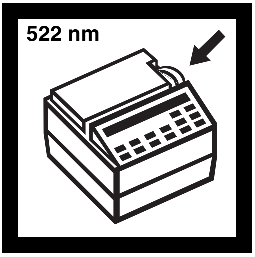
1. Enter the stored program number for aluminum (Al).

Press: **1 0 ENTER**

The display will show:

Dial nm to 522

Note: *The Pour-Thru Cell can be used if rinsed well with deionized water between the blank and prepared sample.*



2. Rotate the wavelength dial until the small display shows:

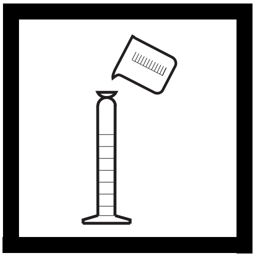
522 nm

When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

then: **mg/L Al^{3+}**

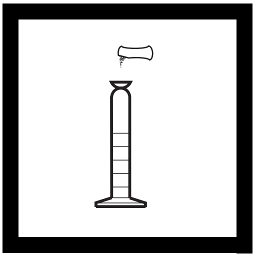
Note: *Total aluminum determination needs a prior digestion; use any of the three procedures given in Digestion (Section II).*



3. Fill a 50-mL graduated mixing cylinder to the 50-mL mark with sample.

Note: *Rinse cylinder with 1:1 Hydrochloric Acid and deionized water before use to avoid errors due to contaminants absorbed on the glass.*

Note: *The sample temperature must be between 20-25 °C (68-77 °F) for accurate results.*



4. Add the contents of one Ascorbic Acid Powder Pillow. Stopper. Invert several times to dissolve powder.

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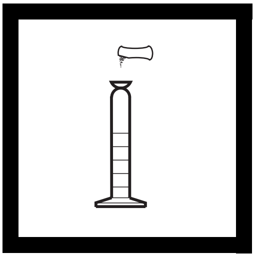
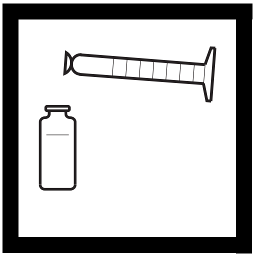
* Adapted from *Standard Methods for the Examination of Water and Wastewater.*



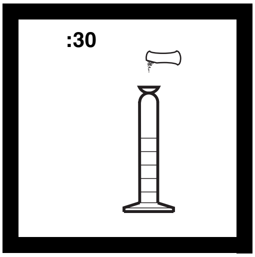
5. Add the contents of one AluVer 3 Aluminum Reagent Powder Pillow. Stopper. Invert repeatedly for one minute to dissolve.

Note: *A red-orange color develops if aluminum is present.*

Note: *Inconsistent results will be obtained if any powder is undissolved.*

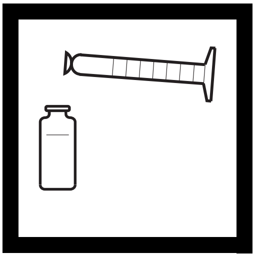


6. Pour 25 mL of mixture into a 25-mL sample cell (the prepared sample).

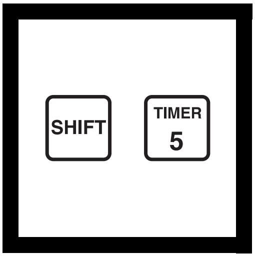


7. Add contents of one Bleaching 3 Reagent Powder Pillow to the remaining 25 mL in the mixing graduated cylinder. Stopper. Vigorously shake for 30 seconds.

Note: *This solution should turn a light to medium orange upon bleaching. It will not become colorless.*



8. Pour the remaining 25 mL of mixture in the cylinder into a second 25-mL sample cell (the blank).



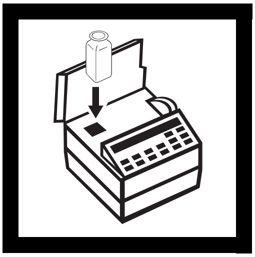
9. Press:

SHIFT TIMER

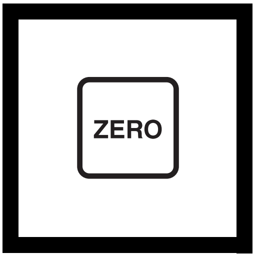
A 15-minute reaction period will begin.

When the timer beeps, the display will show:

mg/L Al^{3+}



10. Within five minutes after the timer beeps, place the blank into the cell holder. Close the light shield.

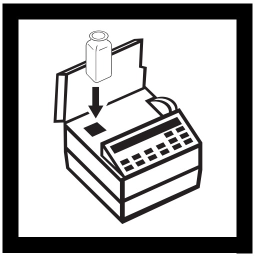


11. Press: **ZERO**

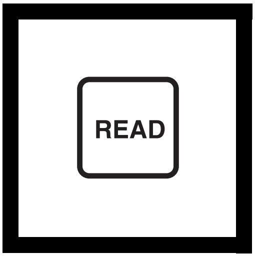
The display will show:

Zeroing. . . .

then: **0.00 mg/L Al^{3+}**



12. Immediately place the prepared sample into the cell holder. Close the light shield.



13. Press: **READ**

The display will show:

Reading. . . .

then the result in mg/L aluminum will be displayed.

Note: *Clean the graduated cylinder and sample cells with soap and brush immediately following the test.*

Note: *For most accurate results, analyze a reagent blank (deionized water) and subtract the amount determined on each lot of reagents from the sample reading.*

Forms ▲▼ Al_2O_3 Al^{3+}

Sampling and Storage

Collect samples in a clean glass or plastic container. Preserve the sample by adjusting the pH to 2 or less with nitric acid (about 1.5 mL per liter). Preserved samples can be stored up to six months at room temperature. Before analysis, adjust the pH to 3.5–4.5 with 5.0 N Sodium Hydroxide. Correct the test result for volume additions; see Correcting for Volume Additions in Section I for more information.

Accuracy Check

Standard Additions Method

a) Snap the neck off an Aluminum Voluette Ampule Standard Solution, 50 mg/L as Al.

b) Use the TenSette Pipet to add 0.1 mL, 0.2 mL, and 0.3 mLof standard, respectively, to three fresh 50-mL samples. Mix each thoroughly.

c) Analyze each sample as described above. The aluminum concentration should increase 0.1 mg/L for each 0.1 mL of standard added.

d) If these increases do not occur, see Standard Additions (Section I) for more information.

Standard Solution Method

Prepare a 0.4-mg/L aluminum standard solution by pipetting 1.00 mL of Aluminum Standard Solution, 100 mg/L as Al^{3+}, into a 250-mL volumetric flask. Dilute to the mark with deionized water. Prepare this solution immediately before use. Perform the aluminum procedure as described above. The mg/L Al reading in Step 13 should be 0.4 mg/L Al.

Or, using the TenSette Pipet, add 0.8 mL of solution from an Aluminum Voluette Ampule Standard Solution (50 mg/L as Al) into a 100-mL volumetric flask. Dilute to volume with deionized water. Prepare this standard immediately before use.

Precision

In a single laboratory, using a standard solution of 0.2 mg/L Al and two representative lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±0.016 mg/L Al^{3+}.

Interferences

The following do not interfere up to the indicated concentrations.

Alkalinity	1000 mg/L as $CaCO_3$
Iron	20 mg/L
Phosphate	50 mg/L

Interferences from higher alkalinity concentrations can be eliminated by the following pretreatment:

a) Add one drop of m-Nitrophenol Indicator Solution to the sample taken in Step 3. A yellow color indicates excessive alkalinity.

b) Add one drop of 5.25 N Sulfuric Acid Standard Solution. Stopper the cylinder. Invert to mix. If the yellow color persists, repeat until the sample changes to colorless. Continue with the test.

Polyphosphate causes a negative interference at all levels and must be absent. Before testing, polyphosphate must be converted to orthophosphate by acid hydrolysis as described under the phosphorus procedures.

Acidity interferes at greater than 300 mg/L as $CaCO_3$. Samples with greater than 300 mg/L acidity as $CaCO_3$ must be treated as follows:

a) Add one drop of m-Nitrophenol Indicator Solution to the sample taken in Step 3.

b) Add one drop of 5.0 N Sodium Hydroxide Standard Solution. Stopper the cylinder. Invert to mix. Repeat as often as necessary until the color changes from colorless to yellow.

c) Add one drop of Sulfuric Acid Standard Solution, 5.25 N, to change the solution from yellow back to colorless. Continue with the test.

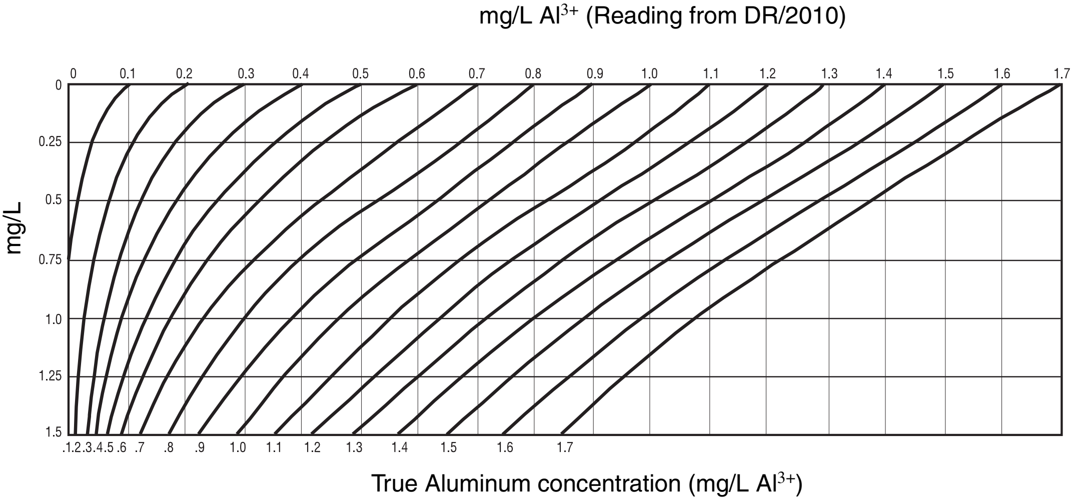
Calcium does not interfere.

Fluoride interferes at all levels by complexing with aluminum. The actual aluminum concentration can be determined using the Fluoride Interference Graph when the fluoride concentration is known. To use the fluoride interference graph:

1. Select the vertical grid line along the top of the graph that represents the aluminum reading obtained in Step 13.
2. Locate the point of the vertical line (DR/2010 reading) where it intersects with the horizontal grid line that indicates how much fluoride is present in the sample.
3. Extrapolate the true aluminum concentration by following the curved lines on either side of the intersect point down to the true aluminum concentration.

For example, if the aluminum test result was 0.7 mg/L Al^{3+} and the fluoride present in the sample was 1.0 mg/L F^-, the point where the 0.7 grid line intersects with the 1.0 mg/L F^- grid line falls between the 1.2 and 1.3 mg/L Al curves. In this case, the true aluminum content would be 1.27 mg/L.

Fluoride Interference Graph



Summary of Method

Aluminon indicator combines with aluminum in the sample to form a red-orange color. The intensity of color is proportional to the aluminum concentration. Ascorbic acid is added to remove iron interference. The AluVer 3 Aluminum Reagent, packaged in powder form shows exceptional stability and is applicable for fresh water samples.

REQUIRED REAGENTS

	Cat. No.
Aluminum Reagent Set (100 Tests)	22420-00

Includes: (4) 14290-99, (1) 14577-99, (1) 14294-49

Description	Quantity Required Per Test	Unit	Cat. No.
AluVer 3 Aluminum Reagent Powder Pillow	1 pillow	100/pkg	14290-99
Ascorbic Acid Powder Pillow	1 pillow	100/pkg	14577-99
Bleaching 3 Reagent Powder Pillow	1 pillow	100/pkg	14294-49

REQUIRED APPARATUS

Cylinders, graduated mixing, 50 mL	1	each	1896-41
Sample Cell, 25 mL, matched pair	2	pair	20950-00

OPTIONAL REAGENTS

Aluminum Standard Solution, 100 mg/L	100 mL	14174-42
Aluminum Standard Solution, Voluette ampule, 50 mg/L as Al, 10 mL	16/pkg	14792-10
Hydrochloric Acid Solution, 6N (1:1)	500 mL	884-49
m-Nitrophenol Indicator Solution, 10 g/L	100 mL	2476-32
Nitric Acid, ACS	500 mL	152-49
Nitric Acid Solution, 1:1	500 mL	2540-49
Sodium Hydroxide Standard Solution, 5.0 N	100 mL MDB	2450-32
Sodium Hydroxide Standard Solution, 5.0 N	50 mL MDB	2450-26
Sulfuric Acid Standard Solution, 5.25 N	100 mL MDB	2449-32
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Ampule Breaker Kit	each	21968-00
Brush	each	690-00
Flask, volumetric, 100 mL	each	547-42
Flask, volumetric, 250 mL	each	547-46
Fluoride Combination Electrode	each	50265-00
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
pH Meter, *sension*™*1*, portable	each	51700-10
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pour-Thru Cell Assembly Kit	each	45215-00
Thermometer, -20 to 105 °C	each	1877-01

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

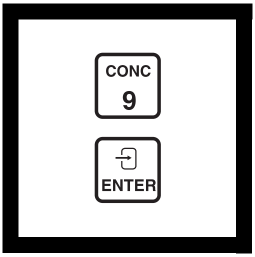
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8326

ALUMINUM (0 to 0.220 mg/L)

For water

Eriochrome Cyanine R Method*



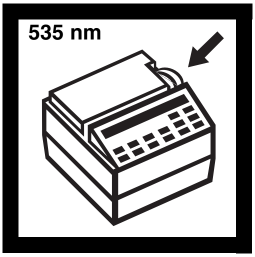
1. Enter the stored program number for aluminum (Al), Eriochrome Cyanine R (ECR) method.

Press: **9 ENTER**

The display will show:

Dial nm to 535

Note: *The Pour-Thru Cell cannot be used.*



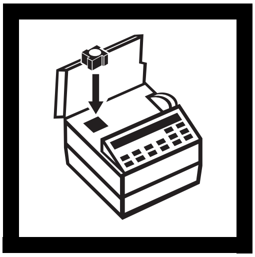
2. Rotate the wavelength dial until the small display shows:

535 nm

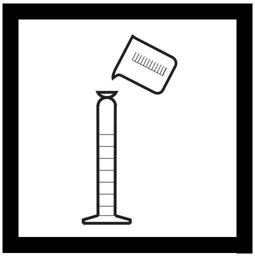
When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

then: **mg/L Al ECR**



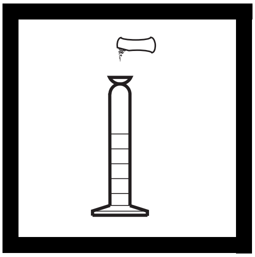
3. Insert the 10-mL Cell Riser into the cell compartment



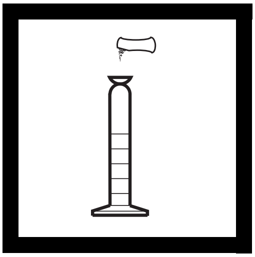
4. Fill a 25-mL graduated mixing cylinder to the 20-mL mark with sample.

Note: *Rinse cylinder with 1:1 hydrochloric acid and deionized water before use to avoid errors.*

Note: *The sample temperature must be 20-25 °C (68-77 °F).*

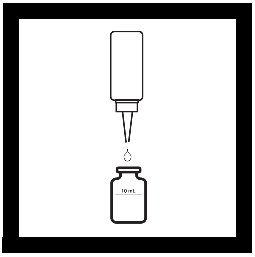


5. Add the contents of one ECR Reagent Powder Pillow. Stopper. Invert several times to dissolve powder, then wait 30 seconds.

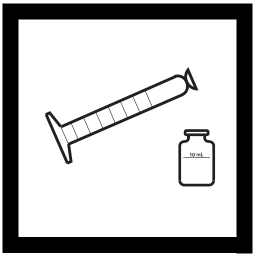


6. Add the contents of one Hexamethylenetetramine Buffer Reagent Powder Pillow. Stopper. Invert several times to dissolve powder.

Note: *An orange to purple color develops if aluminum is present.*



7. Put 1 drop of ECR Masking Reagent Solution into a 10-mL sample cell.

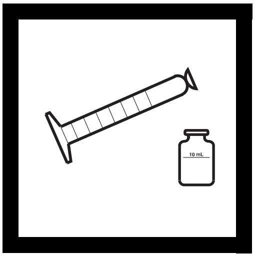


8. Pour 10 mL from the mixing graduated cylinder into the 10-mL sample cell. Swirl to mix (the blank.)

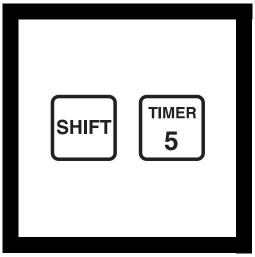
Note: *The solution will start to turn yellow.*

---

* Adapted from *Standard Methods for the Examination of Water and Wastewater.*



9. Pour the remaining 10 mL of mixture into a second 10-mL sample cell to make the prepared sample.



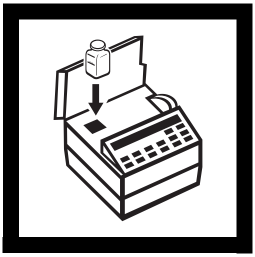
10. Press:

SHIFT TIMER

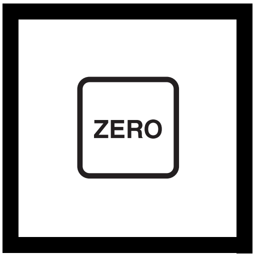
A 5-minute reaction period will begin.

When the timer beeps, the display will show:

mg/L Al ECR



11. Within five minutes after the timer beeps, place the blank into the cell holder. Close the light shield.



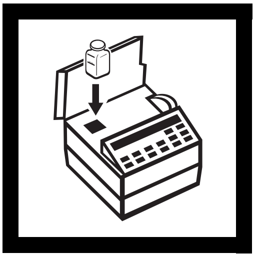
12. Press: **ZERO**

The display will show:

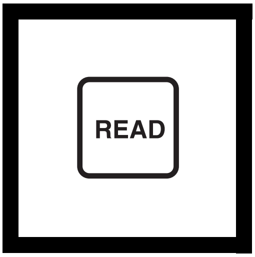
Zeroing. . . .

then:

0.000 mg/L Al ECR



13. Immediately place the prepared sample into the cell holder. Close the light shield.



14. Press: **READ**

The display will show:

Reading. . . .

then the result in mg/L aluminum will be displayed.

Forms ▼ Al
Al_2O_3

Note: *If fluoride (F^-) is present, it needs to be measured and the actual value determined (see Table 2).*

Sampling and Storage

Collect samples in a clean glass or plastic container. Preserve samples by adjusting the pH to 2 or less with nitric acid (about 1.5 mL per liter). Preserved samples can be stored up to six months at room temperature. Before analysis, adjust the pH to 2.9 to 4.9 with 12.0 N Potassium Hydroxide Standard Solution and/or 1 N Potassium Hydroxide Solution. Correct the test result for volume additions; see Corrections for Volume Additions in Section I.

Accuracy Check

Standard Solution Method

Prepare a 0.100 mg/L aluminum standard solution by pipetting 1.00 mL of Aluminum Standard Solution, 100 mg/L as Al^{3+}, into a 1000-mL volumetric flask. Dilute to the mark with deionized water. Prepare this solution daily. Perform the aluminum procedure as described above. The mg/L Al should be 0.10 mg/L Al.

Or, using the TenSette pipet, add 0.2 mL of solution from an Aluminum Voluette Ampule Standard Solution (50 mg/L as Al) into a 100-mL volumetric flask. Dilute to volume with deionized water. Perform the aluminum procedure as described above. The mg/L Al reading should be 0.10 mg/L.

Method Performance

Precision

In a single laboratory, using a standard solution of 0.100 mg/L Al and two representative lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±0.004 mg/L Al.

Interferences

Table 1 lists common interferences and the amount of interference that can be expected.

A sample pH between about 4.9 and 7.5 causes dissolved aluminum to partially convert to colloidal and insoluble forms. This method measures much of that hard-to-detect aluminum without any pH adjustment as is necessary in some other methods.

Polyphosphate interference can be reduced by converting polyphosphate to orthophosphate by the following steps:

a) Rinse a 50-mL mixing graduated cylinder and a 125-mL erlenmeyer flask containing a magnetic stir bar with 6 N

Hydrochloric Acid. Rinse again with deionized water. These rinses will remove any aluminum present.

Table 1 Interferences

Substance	Concentration	Error
Acidity	0-62 mg/L as $CaCO_3$	0%
Alkalinity	0-750 mg/L as $CaCO_3$	0%
Ca^{2+}	0-1000 mg/L as $CaCO_3$	0%
Cl^-	0-1000 mg/L	0%
Cr^{6+}	0.2 mg/L	-5% of reading
Cu^{2+}	2 mg/L	-5% of reading
Fe^{2+}	0-4 mg/L	+ mg/L Fe^{2+} X 0.0075
Fe^{3+}	0-4 mg/L	+ mg/L Fe^{3+} X 0.0075
F^-	see Table 2	
Hexametaphosphate	0.1 mg/L as PO_4^{3-}	-5% of reading
Mg^{2+}	0-1000 mg/L as $CaCO_3$	0%
Mn^{2+}	0-10 mg/L	0%
NO^{2-}	0-5 mg/L	0%
NO^{3-}	0-20 mg/L	0%
pH	2.9-4.9	0%
	7.5-11.5	0%
PO_4^{3-} (ortho)	4 mg/L	-5% of reading
SO_4^{2-}	0-1000 mg/L	0%
Zn^{2+}	0-10 mg/L	0%

***Note:** Rinse two erlenmeyer flasks if a reagent blank is used; see Step b below.*

b) Measure 50 mL of deionized water into the 125-mL erlenmeyer flask using the graduated cylinder. This is the reagent blank. Because of the test sensitivity, this step must be done only when any of the reagents used in the following pretreatment are replaced even if the new reagent has a matching lot number. When the pretreated sample has been analyzed, subtract the aluminum concentration of the reagent blank from the sample results.

c) Measure 50 mL of sample into the 125-mL erlenmeyer flask using the graduated cylinder. Use a small amount of deionized water to rinse the cylinder contents into the flask.

d) Add 4.0 mL of 5.25 N Sulfuric Acid Solution.

e) Use a combination hot plate/stirrer to stir and boil the sample for at least 30 minutes. Add deionized water as needed to maintain a sample volume of 20-40 mL. Do not boil dry.

f) Cool the solution to near room temperature.

g) Add 2 drops of Bromphenol Blue Indicator Solution.

h) Add 1.5 mL of 12.0 N Potassium Hydroxide Standard Solution using the calibrated, plastic dropper provided. Swirl to mix. The solution color should be yellow or green but not purple. If the color is purple, begin with Step a again using an additional 1 mL of Sulfuric Acid Solution in Step d.

i) While swirling the flask, add 1.0 N Potassium Hydroxide Solution, a drop at a time, until the solution turns a dirty green color.

j) Pour the solution into the 50-mL graduated cylinder. Rinse the flask contents into the graduated cylinder with deionized water to bring the total volume to 50 mL.

k) Use 20 mL this solution in Step 3 of the ECR method.

Fluoride interference can be corrected by using Table 2.

An Example: If the fluoride concentration is known to be 1.00 mg/L F^- and the ECR method gives a DR/2010 reading of 0.060 mg/L aluminum, what is the true mg/L aluminum concentration?

Answer: 0.183 mg/L

Intermediate values can be found by interpolation. Do not use correction graphs or charts found in other publications.

Summary of Method

Eriochrome cyanine R combines with aluminum in a sample to produce an orange-red color. The intensity of color is proportional to the aluminum concentration.

Table 2 True aluminum concentration (mg/L) vs. DR/2010 reading (mg/L) and fluoride concentration (mg/L) when the Eriochrome cyanine R method is used.

	Fluoride Concentration (mg/L)										
DR/2010 Reading (mg/L)	0.00	0.20	0.40	0.60	0.80	1.00	1.20	1.40	1.60	1.80	2.00
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.010	0.010	0.019	0.030	0.040	0.052	0.068	0.081	0.094	0.105	0.117	0.131
0.020	0.020	0.032	0.046	0.061	0.077	0.099	0.117	0.137	0.152	0.173	0.193
0.030	0.030	0.045	0.061	0.077	0.098	0.124	0.146	0.166	0.188	0.214	0.243
0.040	0.040	0.058	0.076	0.093	0.120	0.147	0.174	0.192	0.222		
0.050	0.050	0.068	0.087	0.109	0.135	0.165	0.188	0.217			
0.060	0.060	0.079	0.100	0.123	0.153	0.183	0.210	0.241			
0.070	0.070	0.090	0.113	0.137	0.168	0.201	0.230				
0.080	0.080	0.102	0.125	0.152	0.184	0.219					
0.090	0.090	0.113	0.138	0.166	0.200	0.237					
0.100	0.100	0.124	0.150	0.180	0.215						
0.120	0.120	0.146	0.176	0.209	0.246						
0.140	0.140	0.169	0.201	0.238							
0.160	0.160	0.191	0.226								
0.180	0.180	0.213									
0.200	0.200	0.235									
0.220	0.220										
0.240	0.240										

True Aluminum Concentration (mg/L) Al

REQUIRED REAGENTS

	Cat No.
Aluminum Reagent Set (100 tests)	26037-00

Includes: (1) 26038-49, (2) 26039-46, (1) 23801-23

Description	Quantity Required Per Test	Unit	Cat. No.
ECR Reagent Powder	1 pillow	100/pkg	26038-49
Hexamethylenetetramine Buffer Reagent	1 pillow	100/pkg	26039-99
ECR Masking Reagent Solution	1 drop	25 mL	23801-23

REQUIRED APPARATUS

Cell Riser, 10 mL sample cell	1	each	45282-00
Cylinder, 25 mL, mixing graduated	1	each	20886-40
Sample Cell, with 10-mL mark, matched pair	2	pair	24954-02

OPTIONAL REAGENTS

Description	Unit	Cat. No.
Aluminum Standard Solution, 100 mg/L	100 mL	14174-42
Aluminum Standard Solution, Voluette ampule, 50 mg/L as Al, 10 mL	16/pkg	14792-10
Bromphenol Blue Indicator Solution	100 mL MDB	14552-32
Hydrochloric Acid Solution, 6 N (1:1)	500 mL	884-49
Nitric Acid, ACS	500 mL	152-49
Nitric Acid Solution, 1:1	500 mL	2540-49
Potassium Hydroxide Solution, 1 N	50 mL SCDB	23144-26
Potassium Hydroxide Standard Solution, 12.0 N	100 mL	230-32
Potassium Hydroxide Standard Solution, 12.0 N	500 mL	230-49
SPADNS Fluoride Reagent AccuVac Ampules	25/pkg	25060-25
Sulfuric Acid Standard Solution, 5.25 N	100 mL MDB	2449-32
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Ampule Breaker Kit	each	21968-00
Brush	each	690-00
Cylinder, graduated, mixing, 50 mL	each	1896-41
Flask, erlenmeyer, glass, 125 mL	each	505-43
Flask, volumetric, 100 mL	each	14574-42
Flask, volumetric, 1000 mL	each	14574-53
Fluoride Combination Electrode	each	50265-00
Hot Plate, Stirrer, 120 V	each	23442-00
Hot Plate, Stirrer, 240 V	each	23442-02
Pad, cooling, 4" x 4"	each	18376-00
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
pH Meter, *sension*™*1*, portable	each	51700-10
Pipet Filler, safety bulb	each	14651-00
Pipet, serological, 2 mL	each	532-36
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 1.00 mL	each	14515-35
Pipet, volumetric, Class A, 4.00 mL	each	14515-04
Stir Bar, Octagonal, 25.4 x 7.9 mm	each	20953-52
Thermometer, -20 to 105 °C	each	1877-01

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8013

ARSENIC (0 to 0.200 mg/L)

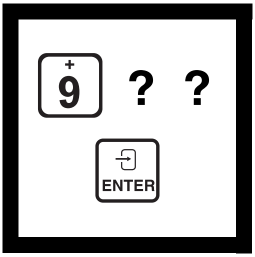
For water, wastewater, and seawater

Silver Diethyldithiocarbamate Method*

USEPA accepted for reporting (distillation required)**

User
Calibration

1. This procedure requires a user-entered calibration before sample measurement. See the steps in the User Calibration section to set up and calibrate a program for arsenic.



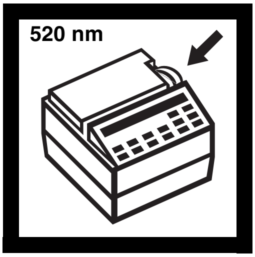
2. Enter the user stored program number for arsenic (As).

Press: **9 ? ? ENTER**

The display will show:

Dial to 520 nm

Note: *The Pour-Thru Cell cannot be used.*

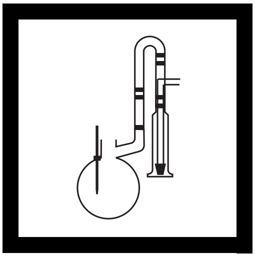


3. Rotate the wavelength dial until the small display shows:

520 nm

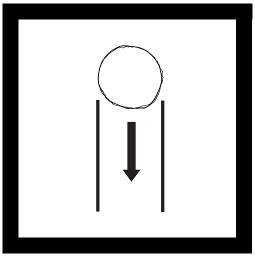
When the correct wavelength is dialed in the display will quickly show: **Zero Sample**

then: **mg/L As**

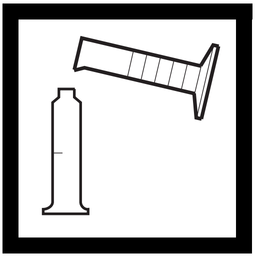


4. Prepare the Hach distillation apparatus for arsenic recovery. Place it under a fume hood to vent toxic fumes.

Note: *See the Hach Distillation Manual for assembly instructions.*

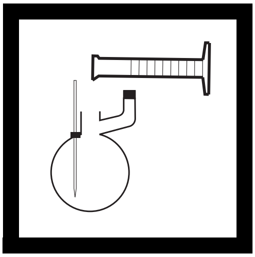


5. Dampen a cotton ball with 10% Lead Acetate Solution. Place it in the gas scrubber. Be certain the cotton seals against the glass.

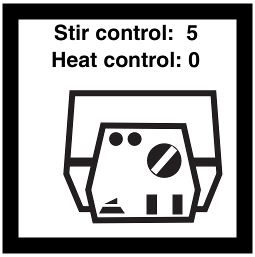


6. Measure 25 mL of prepared arsenic absorber solution into the cylinder/gas bubbler assembly with a graduated cylinder. Attach it to the distillation apparatus.

Note: *Prepare the arsenic absorber solution as directed under Reagent Preparation below.*



7. Measure 250 mL of sample into the distillation flask using a graduated cylinder.

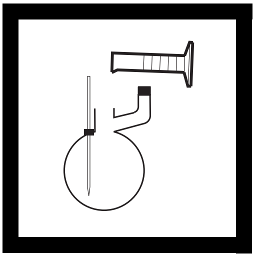


8. Turn on the power switch. Set the stir control to 5. Set the heat control to 0.

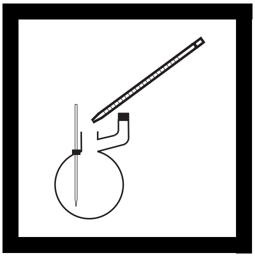
---

* Adapted from *Standard Methods for the Examination of Water and Wastewater.*

** Equivalent to USEPA method 206.4 for wastewater and Standard Method 3500-As for drinking water.

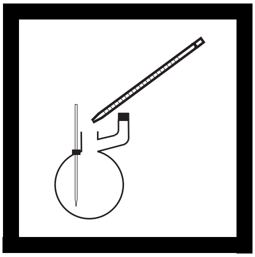


9. Measure 25 mL of hydrochloric acid, ACS, into the flask using a graduated cylinder.



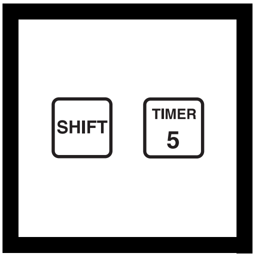
10. Measure 1 mL of Stannous Chloride Solution into the flask.

Note: *Use a serological pipet to measure the solution.*



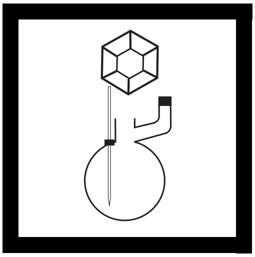
11. Add 3 mL of Potassium Iodide Solution to the flask. Cap.

Note: *Use a serological pipet to measure the solution.*

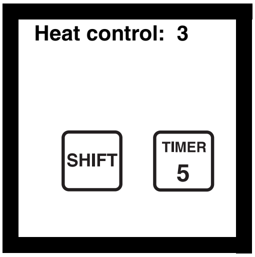


12. Press: **SHIFT TIMER**

A 15-minute reaction period will begin.



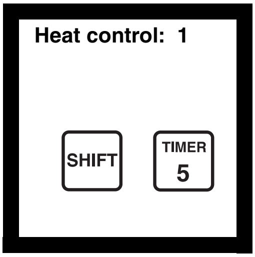
13. When the timer beeps, add 6.0 g of 20-mesh zinc to the flask. Cap immediately.



14. Set the heat control to 3.

Press: **SHIFT TIMER**

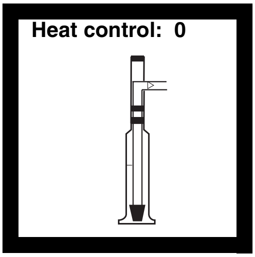
A second 15-minute reaction period will begin.



15. When the timer beeps, set the heat control to 1.

Press: **SHIFT TIMER**

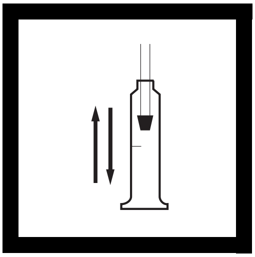
A third 15-minute reaction period will begin.



16. When the timer beeps, the display will show: **mg/L As**

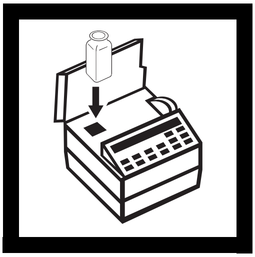
Turn off the heater.

Remove the cylinder/gas bubbler assembly as a unit.

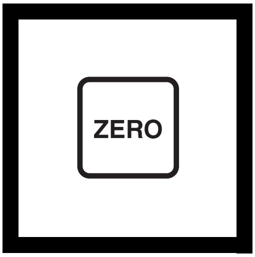


17. Rinse the gas bubbler by moving it up and down in the arsenic absorber solution.

18. Fill a dry sample cell with unreacted arsenic absorber solution (the blank). Stopper. Place it into the cell holder.



19. Place the blank into the cell holder. Close the light shield.

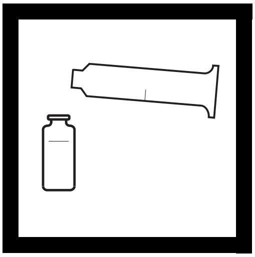


20. Press: **ZERO**

The display will show:

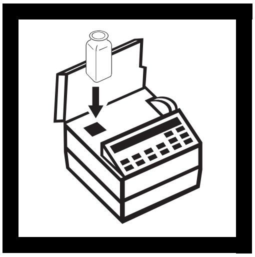
Zeroing. . .

then: **0.000 mg/L As**

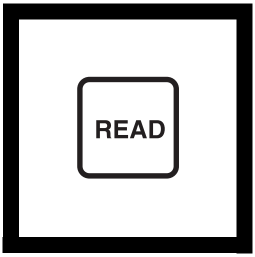


21. Pour the reacted arsenic absorber solution into a sample cell (the prepared sample). Stopper.

Note: *If the solution volume is less than 25 mL, add pyridine to bring the volume to exactly the 25-mL mark. Swirl to mix.*



22. Place the prepared sample into the cell holder. Close the light shield.



23. Press: **READ**

The display will show:

Reading. . .

then the result in mg/L arsenic (As) will be displayed.

Sampling and Storage

Collect samples in acid washed glass or plastic bottles. Adjust the pH to 2 or less with sulfuric acid (about 2 mL per liter). Preserved samples may be stored up to six months at room temperature. Correct the test result for volume additions; see Correction for Volume Additions in Section I.

Reagent Preparation

Prepare the arsenic absorber solution as follows:

1. Weigh 1.00 g of silver diethyldithiocarbamate on an analytical balance.
2. Transfer the powder to a 200-mL volumetric flask. Dilute to volume with pyridine. (Use pyridine only in a fume hood.)
3. Mix well to dissolve. Store the reagent, tightly sealed, in an amber bottle. The reagent is stable for one month if stored in this manner. Larger volumes of reagent can be prepared if the reagent is used within one month.

User Calibration

Standard Preparation

a) Prepare a 10.0-mg/L arsenic working standard by pipetting 1.00 mL of Arsenic Standard Solution, 1000 mg/L As, into a 100-mL volumetric flask. Dilute to volume with deionized water.

b) Prepare standards of 0.04, 0.08, 0.12, and 0.16 mg/L arsenic by diluting 1.0, 2.0, 3.0, and 4.0 mL, respectively, of the working standard into four 250-mL volumetric flasks. Dilute to volume with deionized water.

Initial Setup of Arsenic Program

A one-time setup of a program for arsenic is required. An arsenic program template is pre-programmed into memory to make the process easier. After the setup is complete, the calibration can be entered for each new lot of reagents used or as necessary.

Note: *The templates within User Program cannot be run directly. They must be copied into a usable program number (greater than 950) as in ste c and d. Then, calibrate the program.*

a) Press **SHIFT USER PRGM**. Use the **UP** arrow key to scroll to **Copy Program**. Press **ENTER**.

b) Scroll to or enter the template number for arsenic (900). Press **ENTER**.

c) Scroll to or enter the desired user program number for arsenic (>950). Press **ENTER**. Record the program number for reference.

d) The display will show: **Program Copied.**

e) Press **EXIT**. The program is now ready to be calibrated.

User Calibration of Arsenic Program

a) Use the test procedure to develop color in the standards just before recording the absorbance values for the calibration.

b) Press **SHIFT USER PRGM**. Use the **UP** arrow to scroll to **Edit Program**. Press **ENTER**.

c) Scroll to or enter the program number for arsenic (from step c in Setup). Press **ENTER**.

d) Use the **DOWN** arrow to scroll down to **Calib Table:X** (X= denotes a number which indicates the number of data points in the table). Press **ENTER**.

e) The instrument will prompt **Zero Sample**. Place the blank solution (unreacted arsenic absorber) in the cell holder. Close the light shield. Press **ZERO**. The instrument will prompt you to adjust to the proper wavelength if necessary.

f) The first concentration point will be displayed. Press **ENTER** to display the stored absorbance value of the first concentration point.

g) Place the first developed standard solution (same concentration as the value displayed) in the cell holder. Close the light shield. Press **READ** to display the measured absorbance of the standard. Press **ENTER** to accept the displayed absorbance value.

h) The second concentration point will be displayed. Press **ENTER** to display the stored absorbance value of the second concentration point. Place the second developed standard solution in the cell holder. Close the light shield. Press **READ** to display the measured absorbance value of the standard.

i) Press **ENTER** to accept the absorbance reading. The next concentration point will then be displayed.

j) Repeat steps h and i as necessary for the remaining standards.

k) When you are finished reading the absorbance values of the standards, press **EXIT**. Scroll down to **Force Zero**. Press **ENTER** to change the setting. Change to **ON** by pressing the arrow key, then press **ENTER.**

l) Scroll down to **Calib Formula**. Press **ENTER** twice or until only the **0** in **F(0)** is flashing. Press **DOWN** arrow to select **F1** (linear calibration). Press **ENTER** to select **F1**.

Note: *Other calibration fits may be used if appropriate.*

m) Press **EXIT** twice. The display will show **Store Changes?** Press **ENTER** to confirm.

n) Press **EXIT**. The program is now calibrated and ready for use. Start on step 2 of the iconed procedure.

Interferences

Antimony salts may interfere with color development.

Summary of Method

Arsenic is reduced to arsine gas by a mixture of zinc, stannous chloride, potassium iodide and hydrochloric acid in a specially equipped distillation apparatus. The arsine is passed through a scrubber containing cotton saturated with lead acetate and then into an absorber tube containing silver diethyldithiocarbamate in pyridine. The arsenic reacts to form a red complex which is read colorimetrically. This procedure requires a manual calibration.

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
Arsenic Standard Solution, 1000 mg/L As	varies	100 mL	14571-42
Hydrochloric Acid, ACS	25 mL	500 mL	134-49
Lead Acetate Solution, 10%	1 mL	100 mL	14580-42
Potassium Iodide Solution, 20%	3 mL	100 mL	14568-42
Pyridine	50 mL	500 mL	14469-49
Silver Diethyldithiocarbamate	1 g	25 g	14476-24
Stannous Chloride Solution	1 mL	100 mL	14569-42
Zinc, 20-mesh, ACS	6 g	454 g	795-01

REQUIRED APPARATUS

Balance, analytical	1	each	26103-00
Balls, cotton	1	100/pkg	2572-01
Boat, weighing	2	500/pkg	21790-00
Bottle, amber, 237 mL	1	6/pkg	7144-41
Cap, polypropylene	1	6/pkg	21667-06
Cylinder, graduated, 25 mL	2	each	508-40
Cylinder, graduated, 250 mL	1	each	508-46
Distillation Apparatus Arsenic Accessories	1	set	22654-00
Distillation Apparatus General Purpose Accessories	1	set	22653-00
Flask, volumetric, 100 mL	1	each	14574-42
Flask, volumetric, 200 mL	1	each	14574-45
Flask, volumetric, 250 mL	4	each	14574-46
Pipet Filler, safety bulb	1	each	14651-00
Pipet, serological, 5 mL	2	each	532-37
Pipet, volumetric, 1 mL	2	each	14515-35
Pipet, volumetric, 2 mL	1	each	14515-36
Pipet, volumetric, 3 mL	1	each	14515-03
Pipet, volumetric, 4 mL	1	each	14515-04
Sample Cells, 1-inch, matched	2	pair	20950-00
Stopper, hollow, poly, No. 0	2	6/pkg	14480-00

Select one based on available voltage:

Distillation Apparatus Heater, 115 Vac, 60 Hz	each	22744-00
Distillation Apparatus Heater, 230 Vac, 50 Hz	each	22744-02

OPTIONAL REAGENTS

Description	Unit	Cat. No.
Hydrochloric Acid, ACS	2.8 kg	134-06
Sulfuric Acid, conc.	100 mL MDB	1270-32
Pyridine, ACS	4 L	14469-17
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

pH Meter, *sension™1*, portable	each	51700-10
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
Pipet, serological, 2 mL	each	532-36
Pipet, TenSette, 1.0 to 10.0 mL	each	19700-10
Pipet Tips, for 19700-01	50/pkg	21997-96
Pipet Tips, for 19700-01	1000/pkg	21997-28

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order..
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8014

BARIUM (0 to 100 mg/L)

For water, wastewater, oil-field water, and seawater

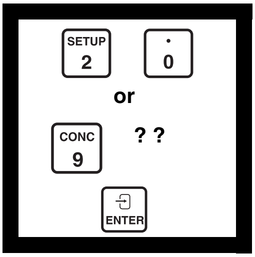
Turbidimetric Method* (Powder Pillows or AccuVac Ampuls)

Using Powder Pillows

Choose Desired Program Accuracy

1. Perform a User-Entered Calibration to obtain the most accurate results. See User Calibration Section following this procedure. Programs 20 and 25 can be used directly for process control or applications where a high degree of accuracy is not needed.

Note: *Reagent lot variation and the nature of turbidity testing require user calibration for best results.*



2. Enter the stored program number for barium (Ba).

Press: **2 0 ENTER**

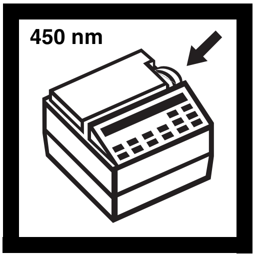
or

9 ? ? ENTER

The display will show:

Dial nm to 450

Note: *The Pour-Thru Cell cannot be used with this procedure.*

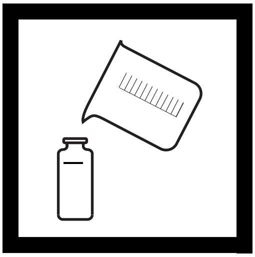


3. Rotate the wavelength dial until the small display shows:

450 nm

When the correct wavelength is dialed in the display will quickly show: **Zero Sample**

then: **mg/L Ba**



4. Fill a sample cell with 25 mL of sample.

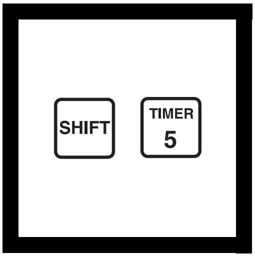
Note: *Filter highly colored or turbid samples. Large amounts of color or turbidity will cause high readings. Use the filtered sample in Steps 4 and 7.*

---

* Adapted from Snell and Snell, Colorimetric Methods of Analysis, Vol. II, 769 (1959).

5. Add the contents of one BariVer 4 Barium Reagent Powder Pillow to the cell (the prepared sample). Swirl to mix.

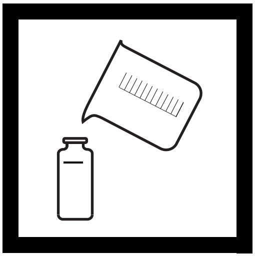
Note: *A white turbidity will develop if barium is present.*



6. Press: **SHIFT TIMER**

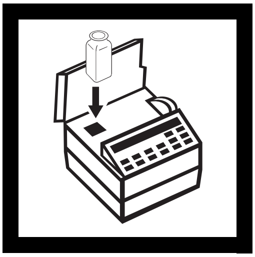
A five-minute reaction period will begin.

Note: *Do not disturb the sample during this period. If the BariVer 4 Barium Reagent does not dissolve, mix the reagent and sample in a 25-mL graduated cylinder before pouring it into the sample cell.*



7. Fill another sample cell (the blank) with 25-mL of sample.

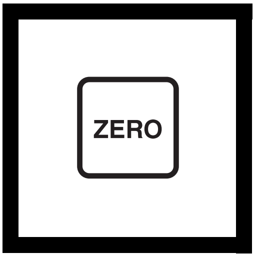
Note: *Determine a reagent blank for each new lot of reagent by repeating steps 4 through 11 using deionized water as the sample.*



8. When the timer beeps, the display will show:

mg/L Ba

Place the blank into the cell holder. Close the light shield.

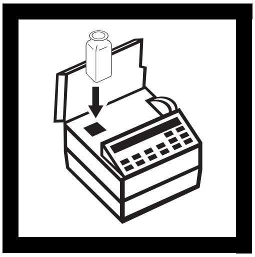


9. Press: **ZERO**

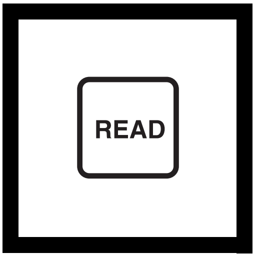
The display will show:

Zeroing. . .

then: **0. mg/L Ba**



10. Within 5 minutes after the timer beeps, place the prepared sample into the cell holder. Close the light shield.



11. Press: **READ**

The display will show:

Reading. . .

then the result, in mg/L barium will be displayed.

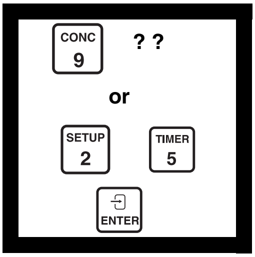
Note: *Clean the sample cell immediately after each test with soap, water, and a brush to prevent a film of barium sulfate from developing on the inside of the sample cell.*

Using Accuvac Ampuls

Choose Desired Program Accuracy

1. Perform a User-Entered Calibration to obtain the most accurate results. See User Calibration Section following this procedure. Programs 20 and 25 can be used directly for process control or applications where a high degree of accuracy is not needed.

Note: *Regent lot variation and the nature of turbidity testing require user calibration for best results.*



2. Enter the stored program number for barium using AccuVac ampuls.

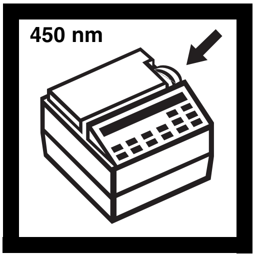
Press: **9 ? ? ENTER**

or

2 5 ENTER

The display will show:

Dial nm to 450



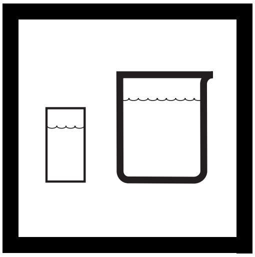
3. Rotate the wavelength dial until the small display shows:

450 nm

When the correct wavelength is dialed in the display will quickly show**:**

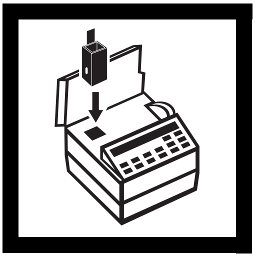
Zero Sample

then: **mg/L Ba AV**



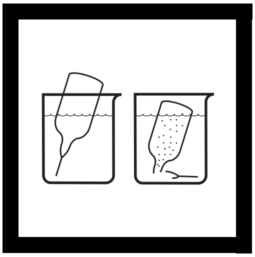
4. Fill a zeroing vial with at least 10 mL of sample (the blank). Collect at least 40 mL of sample in a 50-mL beaker.

Note: *Filter highly colored or turbid samples.*



5. Place the AccuVac Vial Adapter into the cell holder of the instrument.

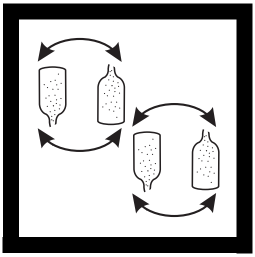
Note: *Place the grip tab at the rear of the cell holder.*



6. Fill a Barium Accu-Vac Ampul with sample (the prepared sample).

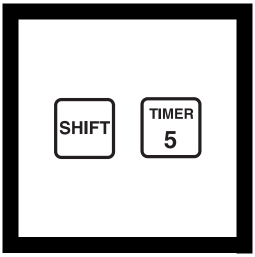
Note: *Keep the tip immersed while the ampul fills completely.*

Note: *Determine a reagent blank for each new lot of ampuls by repeating Steps 4 through 12 using deionized water as the sample.*



7. Quickly invert the ampul several times to mix, then wipe off any liquid or fingerprints.

Note: *A white turbidity will develop if barium is present.*

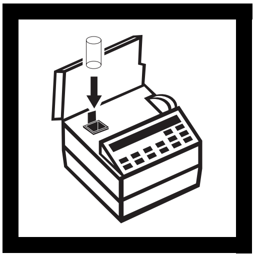


8. Press:

SHIFT TIMER

A five-minute reaction period will begin.

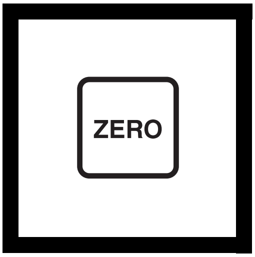
Note: *Do not disturb the sample during the five-minute period.*



9. When the timer beeps, the display will show:

mg/L Ba AV

Place the blank into the cell holder. Close the light shield.

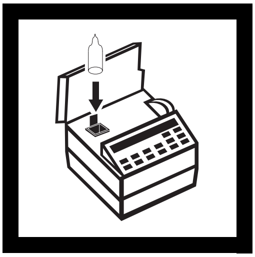


10. Press: **ZERO**

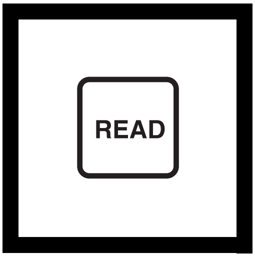
The display will show:

Zeroing. . .

then: **0. mg/L Ba AV**



11. Within 5 minutes after the timer beeps, place the prepared sample into the cell holder. Close the light shield.



12. Press: **READ**

The display will show:

Reading. . .

then the result in mg/L barium will be displayed.

Sampling and Storage

Collect samples in an acid cleaned glass or plastic container. Adjust the pH to 2 or less with nitric acid (about 2 mL per liter). Preserved samples can be stored up to six months at room temperature. Adjust the pH to 5 with 5.0 N sodium hydroxide before analysis. Correct the test result for volume additions; see Corrections for Volume Additions in Section I.

Accuracy Check

Standard Additions Method

a) Fill three graduated mixing cylinders with 25 mL of sample.

b) Use the TenSette Pipet to add 0.1 mL, 0.2 mL and 0.3 mL of Barium Standard Solution, 1000 mg/L, respectively, to the three mixing cylinders and mix each thoroughly (for AccuVac ampuls, transfer to clean, dry 50-mL beakers).

c) Analyze each sample as described above. The barium concentration should increase 4 mg/L for each 0.1 mL of standard added.

d) If these increases do not occur, see Standard Additions in Section I for more information.

Standard Solution Method

Prepare a 100.0-mg/L barium standard solution by pipetting 10.00 mL of Barium Standard Solution, 1000 mg/L, into a 100-mL volumetric flask and diluting to the mark with deionized water. Prepare this solution daily. Perform the barium procedure as described above. The resulting barium reading should be 100 mg/L.

User Calibration

For most accurate results, the use of a user-calibrated program is highly recommended. The Hach stored programs 20 and 25 are intended for process control samples or other applications where a high degree of accuracy is not necessary.

A one-time setup of a user program for barium is required. A barium program template is pre-programmed into memory to make the process easier. After the setup is complete, the calibration can be entered for each new lot of reagents used or as necessary.

Standard Preparation

A new calibration should be performed for each new lot of BariVer 4 Barium Reagent as follows:

a) Prepare calibration standards containing 10, 20, 30, 50, 80, 90, and 100 mg/L Ba by pipetting 1, 2, 3, 5, 8, 9, and 10 mL of the 1000-mg/L Barium Standard Solution into 100-mL volumetric flasks.

b) Dilute to the mark with deionized water. Mix thoroughly.

c) Use the stored program number in the powder pillow or AccuVac Ampul procedure above. Prepare a new calibration for each new lot of reagent, using the same stored program number.

Initial Setup of Barium Program

Note: *The templates within User Program cannot be run directly. They must be copied into a usable program number (greater than 950) as in steps c and d. The program must then be calibrated.*

a) Press **SHIFT USER-PROGRAM**. Use the **UP** arrow to scroll to **Copy Program**. Press **ENTER**.

b) Scroll to or enter the template number for barium [901, 902 (AV)]. Press **ENTER**.

c) Scroll or enter the desired user program number for barium (>950). Press **ENTER**. Record the program number for reference.

d) The display will show **Program Copied**. Press **EXIT**. The program is now ready to be calibrated.

User Calibration of Barium Program

a) Use the test procedure to develop the turbidity in the standards just before recording the absorbance values for the calibration.

b) Press **SHIFT USER PRGM**. Use the **UP** arrow to scroll to **Edit Program**. Press **ENTER**.

c) Scroll to or enter the program number for barium (from step c in Setup). Press **ENTER**.

d) Use the **DOWN** arrow to scroll down to **Calib Table:X** (X= denotes a number which indicates the number of data points in the table). Press **ENTER**.

e) The instrument will prompt **Zero Sample**. Place the blank solution in the cell holder. Close the light shield. Press **ZERO**. The instrument will prompt you to adjust to the proper wavelength if necessary.

f) The first concentration point will be displayed. Press **ENTER** to display the stored absorbance value of the first concentration point.

g) Place the first developed standard solution (same concentration as the value displayed) in the cell holder. Close the light shield. Press **READ** to display the measured absorbance of the standard. Press **ENTER** to accept the displayed absorbance value.

h) The second concentration point will be displayed. Press **ENTER** to display the stored absorbance value of the second concentration. Place the second developed standard solution in the cell holder. Close the light shield. Press **READ** to display the measured absorbance value of the standard.

i) Press **ENTER** to accept the absorbance reading. The next concentration point will then be displayed.

j) Repeat steps h and i as necessary for the remaining standards.

k) When you are finished reading the absorbance values of the standards, press **EXIT**. Scroll down to **Force Zero**. Press **ENTER** to change the setting. Change to **ON** by pressing the arrow key, then press **ENTER.**

l) Scroll down to **Calib Formula**. Press **ENTER** twice or until only the **0** in **F(0)** is flashing. Press **DOWN** arrow to select **F3** (cubic calibration). Press **ENTER** to select **F3**.

***Note:** Other calibration fits may be used if appropriate.*

m) Press **EXIT** twice. The display will show **Store Changes?** Press **ENTER** to confirm.

n) Press **EXIT**. The program is now calibrated and ready for use. Start on step 2 of the iconed procedure.

Precision

In a single laboratory using a standard solution of 100 mg/L barium and two representative lots of reagents with the DR/2010, a single operator obtained a standard deviation of ±1 mg/L barium.

In a single laboratory using a standard solution of 100 mg/L barium and two representative lots of AccuVac ampuls with the DR/2010, a single operator obtained a standard deviation of ±1.5 mg/L barium.

Interferences

The following may interfere when present in concentrations exceeding those listed below:

Silica	500 mg/L
Sodium Chloride	130,000 mg/L as NaCl
Magnesium	100,000 mg/L as $CaCO_3$
Calcium	10,000 mg/L as $CaCO_3$
Strontium	Interferes at any level

If strontium is known to be present, the total concentration between barium and strontium may be expressed as a PS (Precipitated by Sulfate). While this does not distinguish between barium and strontium, it gives an accurate indication of scaling tendency.

Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment; see pH Interferences in Section I.

Summary of Method

The BariVer 4 Barium Reagent Powder combines with barium to form a barium sulfate precipitate, which is held in suspension by a protective colloid. The amount of turbidity present caused by the fine white dispersion of particles is directly proportional to the amount of barium present.

REQUIRED REAGENTS (USING POWDER PILLOWS)

Description	Quantity Required Per Test	Unit	Cat. No.
BariVer 4 Barium Reagent Powder Pillows	1 pillow	100/pkg	12064-99

REQUIRED APPARATUS (USING POWDER PILLOWS)

Sample cell, with 25-mark, matched pair	2	pair	20950-00

REQUIRED REAGENTS (USING ACCUVAC AMPULS)

BariVer 4 Barium Reagent AccuVac Ampuls	1 ampul	25/pkg	25130-25

REQUIRED APPARATUS (USING ACCUVAC AMPULS)

Adapter, AccuVac Vial	1	each	43784-00
Beaker, 50 mL	1	each	500-41
Zeroing vial	1	each	21228-00

OPTIONAL REAGENTS

Barium Standard Solution, 1000 mg/L Ba	100 mL	14611-42
Barium Standard Solution, 50 mg/L Ba	500 mL	1951-49
Nitric Acid, ACS	500 mL	152-49
Nitric Acid Solution, 1:1	500 mL	2540-49
Sodium Hydroxide Standard Solution, 5.0 N	1 L	2450-53
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Brush	each	690-00
Cylinder, Graduated, Mixing, 25 mL	each	20886-40
Filter Paper, folded, 12.5 cm	100/pkg	1894-57
Funnel, poly, 65 mm	each	1083-67
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
pH Meter, *sension*™*1*, portable	each	51700-10
Pipet, serological, 2 mL	each	532-36
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet Filler, safety bulb	each	14651-00
Pipet, Volumetric, 1.00 mL, Class A	each	14515-35
Pipet, Volumetric, 2.00 mL, Class A	each	14515-36
Pipet, Volumetric, 3.00 mL, Class A	each	14515-03
Pipet, Volumetric, 5.00 mL, Class A	each	14515-37
Pipet, Volumetric, 8.00 mL, Class A	each	14515-08
Pipet, Volumetric, 9.00 mL, Class A	each	14515-09
Pipet, Volumetric, 10.00 mL, Class A	each	14515-38
Sample Cell, 1-inch, polystyrene, disposable	12/pkg	24102-12

For technical support and ordering information, see Section V.

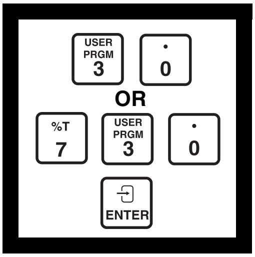
In the U.S.A. call 800-227-4224 to place an order.
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8079

BENZOTRIAZOLE (0 to 16.0 mg/L) or TOLYLTRIAZOLE (0 to 20.0 mg/L)

UV Photolysis Method*

For cooling or boiler water



1. Enter the stored program number for benzotriazole.

Press: **3 0 ENTER**

or

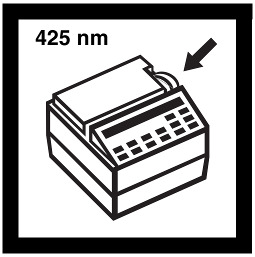
Enter the stored program number for tolyltriazole.

Press: **7 3 0 ENTER**

The display will show:

Dial nm to 425

Note: *The Pour-Thru Cell can be used.*



2. Rotate the wavelength dial until the small display shows:

425 nm

When the correct wavelength is dialed the display will quickly show:

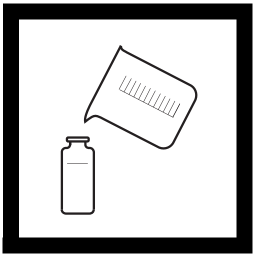
Zero Sample

then:

mg/L BENZOTRIAZ.

or

mg/L TOLYLTRIAZ.



3. Fill a sample cell with 25 mL of sample.

Note: *Sample temperature should be between 20-25 °C (68-78 °F).*

Note: *If sample contains nitrite or borax (sodium borate), adjust the pH to between 4 to 6 with 1 N sulfuric acid.*

4. Add the contents of one Triazole Reagent Powder Pillow. Swirl to dissolve completely.

Note: *If the sample contains more than 500 mg/L hardness (as $CaCO_3$), add 10 drops of Rochelle Salt Solution.*

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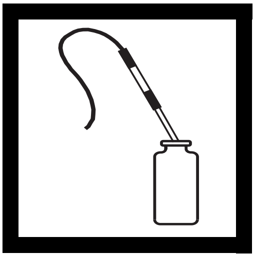
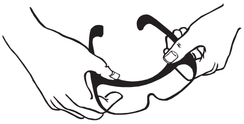
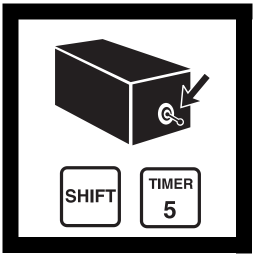
* Adapted from Harp, D., Proceedings 45th International Water Conference, 299 (October 22-24, 1984).



5. Insert the ultra-violet lamp into the sample cell.

Note: UV safety goggles should be worn while the lamp is on.



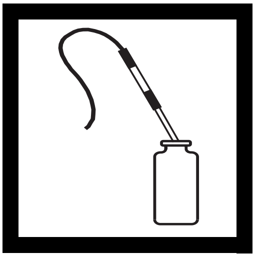


6. Turn the UV lamp ON and press:

SHIFT TIMER

A five-minute reaction period will begin.

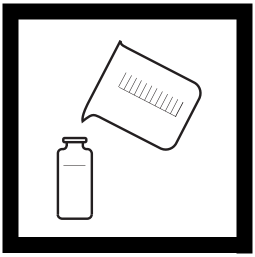
Note: *A yellow color will form if triazole is present.*



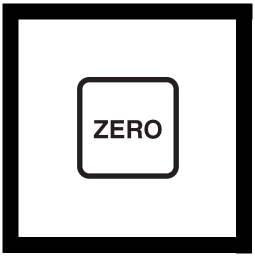
7. When the timer beeps, turn the lamp off and remove it from the cell (the prepared sample). Swirl the cell to mix thoroughly.

Note: *Low results will occur if photolysis (lamp ON) takes place for more or less than five minutes.*

Note: *Avoid handling the quartz surface of the lamp. Rinse the lamp and wipe with a soft, clean tissue between tests.*



8. Fill another sample cell with 25 mL of sample (the blank). Place the blank into the cell holder. Close the light shield.



9. Press: **ZERO**

The display will show:

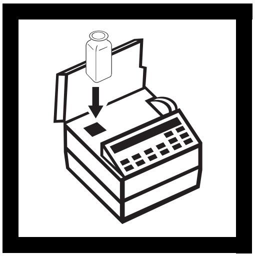
Zeroing. . .

then:

0.0 mg/L
BENZOTRIAZ.

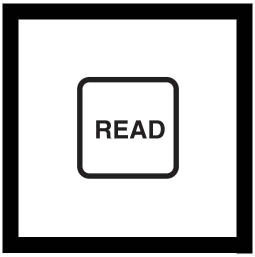
or

0.0 mg/L
TOLYLTRIAZ.



10. Place the prepared sample into the cell holder.

Close the light shield.



11. Press: **READ**

The display will show

Reading. . .

then the result in mg/L benzotriazole or mg/L tolyltriazole will be displayed.

Sampling And Storage

The most reliable results are obtained when samples are analyzed as soon as possible after collection.

Accuracy Check

Standard Additions Method

a) Use the TenSette pipet to add 0.1, 0.2 and 0.3 mL of standard solution, 500 mg/L benzotriazole, to three 25-mL samples. Perform the test according to the above procedure.

Note: *The test will not distinguish between benzotriazole and tolyltriazole.*

b) Each addition of 0.1 mL of standard solution should increase the benzotriazole reading by 2 mg/L over the reading of an unspiked sample when using program 30.

c) If these increases are not obtained see Standard Additions in Section I for more information.

UV Lamp Check

To verify the ultraviolet lamp (normal life equals 5000 hours) is working properly, perform the following test:

a) Prepare a 5.0 mg/L benzotriazole standard solution by pipetting 10.0 mL of benzotriazole standard solution, 500 mg/L benzotriazole, into a 1-L volumetric flask. Dilute to volume.

b) Analyze according to the above procedure. If the result is significantly below 5.0 mg/L, replace the lamp.

Precision

In a single laboratory using a standard solution of 10.0 mg/L benzotriazole and two representative lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±0.15 mg/L.

In a single laboratory using a standard solution of 10.0 mg/L tolyltriazole and two representative lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±0.15 mg/L.

Interferences

The following may interfere when present in concentrations exceeding those listed below:

Strong oxidizing or reducing agents present in the sample will interfere directly.

Table 1

Acrylates (as methyl acrylate)	50 mg/L
Alum	400 mg/L
Borate (as sodium tetraborate)	4000 mg/L
Chlorine (as Cl_2)	20 mg/L
Chromium (as chromate)	12 mg/L
Copper	10 mg/L
Hardness	500 mg/L as $CaCO_3$
Iron	20 mg/L
Lignosulfonates	40 mg/L
Magnesium	300 mg/L as $CaCO_3$
Molybdenum (as molybdate)	200 mg/L
Nitrite	4000 mg/L
Phosphonates (AMP or HEDP)	100 mg/L
Sulfate	200 mg/L
Zinc	80 mg/L

Summary of Method

Benzotriazole or tolyltriazole, used in many applications as corrosion inhibitors for copper and copper alloys, are determined by a proprietary catalytic ultraviolet (UV) photolysis procedure requiring less than 10 minutes to perform.

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
Triazole Reagent Powder Pillows	1 pillow	100/pkg	21412-99

REQUIRED APPARATUS

UV Safety Goggles	1	each	21134-00
Select one based on available voltage:			
Lamp, UV, with power supply, 115 Vac, 60 Hz	1	each	20828-00
Lamp, UV, with power supply, 230 Vac, 50 Hz	1	each	20828-02
Sample Cell, 25 mL, matched pair	2	pair	20950-00

OPTIONAL REAGENTS

Benzotriazole Standard Solution, 500 mg/L	100 mL	21413-42
Rochelle Salt Solution	25 mL* DB	1725-33
Sulfuric Acid Standard Solution, 1.0 N	100 mL MDB	1270-32

OPTIONAL APPARATUS

Flask, volumetric, 1000 mL	each	14574-53
Lamp, UV, (lamp only)	each	20823-00
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
pH Meter, *sension™1*, portable	each	51700-10
Pipet Filler, safety bulb	each	14651-00
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet Tips, for 19700-01 TenSette Pipet	1000/pkg	21856-28
Pipet, volumetric, Class B, 10 mL	each	515-38
Pour-Thru Cell Assembly Kit	each	45215-00
Single to dual UV lamp cord adapter	each	19485-00
Stopwatch	each	14645-00
Thermometer, mercury-filled, -20 to 110 °C	each	566-01
Timer, interval, 1 second to ten hours	each	23480-00

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

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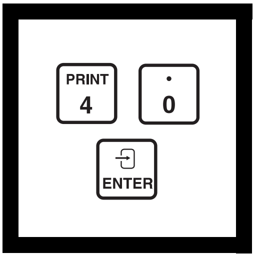
* Contact Hach for larger sizes.

Method 8015

For water and wastewater

BORON (0 to 14.0 mg/L)

Carmine Method*



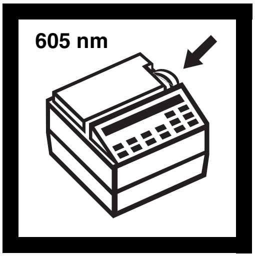
1. Enter the stored program number for boron (B).

Press: **4 0 ENTER**

The display will show:

Dial nm to 605

Note: *The Pour-Thru cell cannot be used with this procedure.*



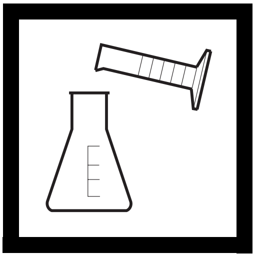
2. Rotate the wavelength dial until the small display shows:

605 nm

When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

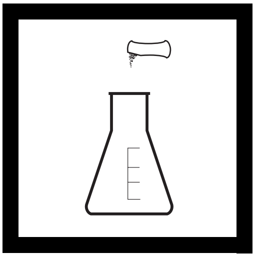
then: **mg/L B**



3. Measure 75.0 mL of sulfuric acid, ACS, using a 100-mL graduated cylinder, into a 300-mL erlenmeyer flask.

Note: *All glassware must be completely dry. Excess water will cause low results.*

Warning: Do not use a stoppered or capped vessel to complete Steps 3 and 4.

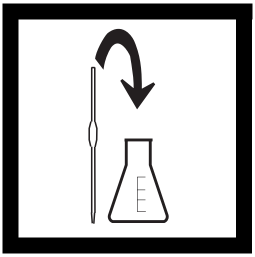


4. Add the contents of one BoroVer 3 Reagent Powder Pillow to the 300-mL flask.

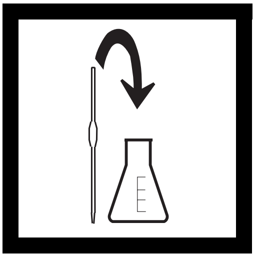
Swirl to mix.

Note: *The powder will dissolve within five minutes.*

Note: *Use adequate ventilation; see Reagent Preparation below.*



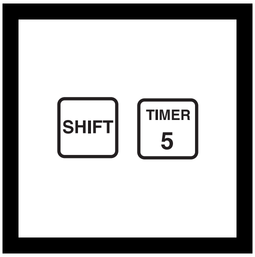
5. Accurately pipet 2.00 mL of deionized water into a 125-mL erlenmeyer flask (the blank).



6. Accurately pipet 2.00 mL of sample into another 125-mL erlenmeyer flask (the prepared sample).

7. Add 35 mL of the BoroVer 3/sulfuric acid reagent solution to each erlenmeyer flask using a 50-mL graduated cylinder.

Swirl to mix completely.



8. Press:

SHIFT TIMER

A 25-minute reaction period will begin.

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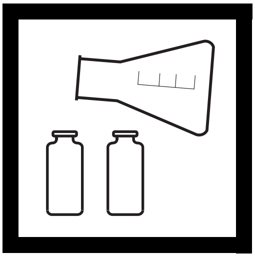
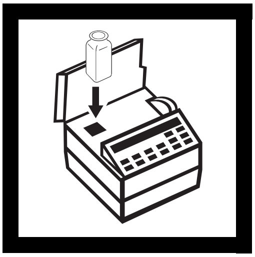
* Adapted from Standard Methods for the Examination of Water and Wastewater.



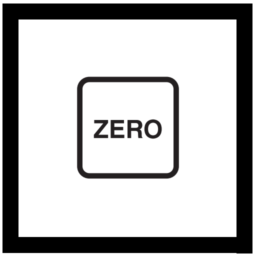
9. When the timer beeps, the display will show:

mg/L B

Pour 25 mL from each flask into two sample cells (the blank and the prepared sample).



10. Place the blank into the cell holder. Close the light shield.

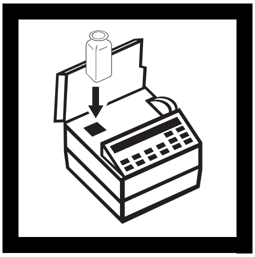


11. Press: **ZERO**

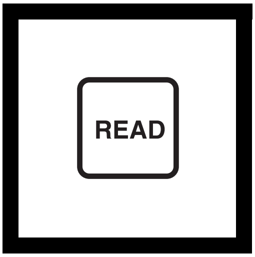
The display will show:

Zeroing. . .

then: **0.0 mg/L B**



12. Place the prepared sample into the cell holder. Close the light shield.



13. Press: **READ**

The display will show:

Reading. . .

then the result in mg/L boron will be displayed.

Forms ▲▼ H_3BO_3 B

Sampling and Storage

Collect samples in polyethylene bottles or alkali-resistant boron-free glass.

Reagent Preparation

Prepare additional BoroVer 3/sulfuric acid solution by mixing one BoroVer 3 Reagent Powder Pillow per 75 mL of sulfuric acid, ACS, adding the powder pillows individually with stirring. Preparation of this solution generates gaseous HCl when the indicator pillow is added to the concentrated sulfuric acid. Use of a fume hood or other well-ventilated lab area is strongly advised. This solution will be stable for up to 48 hours if stored in plastic containers. It should not be stored in Pyrex or Kimax (borosilicate) vessels for longer than one hour because the solution will leach boron from these containers. Use soft glass or polyethylene containers for storage.

Accuracy Check

Standard Additions Method

a) Snap the neck off a Boron Voluette Ampule Standard, 250 mg/L B.

b) Use the TenSette Pipet to add 0.1, 0.2 and 0.3 mL of standard to three 25-mL portions of sample.

c) Perform the above procedure. The boron concentration reading should increase 1 mg/L for each 0.1 mL of standard solution added.

d) If these increases do not occur, see Standard Additions in Section I for more information.

Standard Solution Method

Check the accuracy of the test using Boron Standard Solution, 4 mg/L as B. Or, prepare this solution as follows:

a) Pipet 4.00 mL of the Boron Voluette Ampule Standard, 250 mg/L B, into a 250-mL volumetric flask.

b) Dilute to volume with deionized water. Swirl to mix.

Analyze according to the above procedure using either of these solutions as the sample. Results should be between 3.6 and 4.4 mg/L Boron.

Precision

In a single laboratory using a standard solution of 10 mg/L boron and one representative lot of reagent with the DR/2010, a single operator obtained a standard deviation of ±0.20 mg/L boron.

Interferences

The ions commonly found in water and wastewater do not interfere.

Summary of Method

Boron is determined by its reaction with carminic acid in the presence of sulfuric acid to produce a reddish to bluish color. The amount of color is directly proportional to the boron concentration.

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
BoroVer 3 Boron Reagent Powder Pillows	1 pillow	100/pkg	14170-99
Sulfuric Acid, ACS	75 mL	4 Kg	979-09
Water, deionized	2.0 mL	4 L	272-56

REQUIRED APPARATUS

Description	Quantity Required Per Test	Unit	Cat. No.
Cylinder, graduated, 50 mL	1	each	508-41
Cylinder, graduated, 100 mL	1	each	508-42
Flask, erlenmeyer, 125 mL	2	each	505-43
Flask, erlenmeyer, 300 mL	1	each	505-47
Pipet, volumetric, Class A, 2.00 mL	2	each	14515-36
Sample Cell, 25 mL, matched pair	2	pair	20950-00

OPTIONAL REAGENTS

Description	Unit	Cat. No.
Boron Standard Solution, 4 mg/L as B	500 mL	1963-49
Boron Standard Solution, Voluette ampule, 250 mg/L B, 10 mL	16/pkg	14249-10

OPTIONAL APPARATUS

Description	Unit	Cat. No.
Ampule Breaker Kit	each	21968-00
Cylinder, graduated, 500 mL	each	20885-49
Flask, erlenmeyer, 1000 mL	each	505-53
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 4.00 mL	each	14515-04
Pipet Filler, safety bulb	each	14651-00
Sample cell, with 25-mL mark	pair	13537-02

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

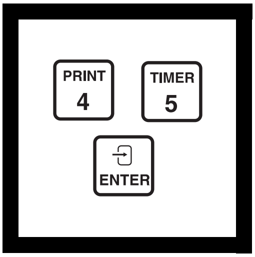
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 10061

BORON, Low Range (0 to 1.50 mg/L as B)

For water and wastewater

Azomethine-H Method* **

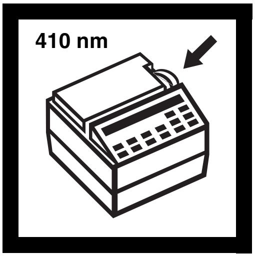


1. Enter the stored program number for boron (B) LR method.

Press: **4 5 ENTER**

The display will show:
Dial nm to 410

Note: *The Pour-Thru cell may be used with this procedure.*



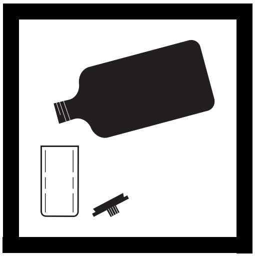
2. Rotate the wavelength dial until the small display shows:

410 nm

When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

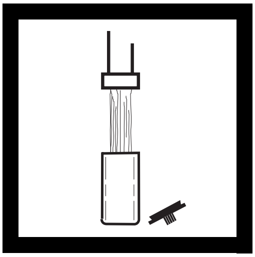
then: **mg/L B LR**



3. Fill a clean plastic sample cell to the 25-mL mark with Ultra-Pure water. Label this cell as the “blank”.

Note: *For most accurate work, perform a blank analysis with each sample analysis.*

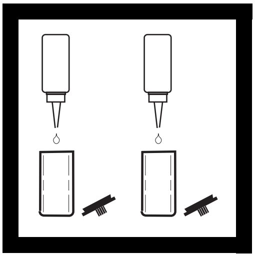
Note: *For most accurate work, the sample cell pair should be matched. See* ***Cell Matching Procedure*** *following these steps.*



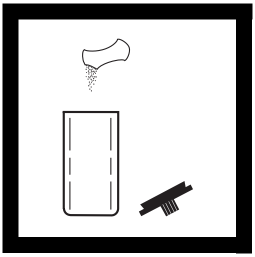
4. Fill a second clean plastic sample cell to the 25-mL mark with the sample.

Note: *If the sample is highly colored, turbid, or contains interferences, see* ***Interferences*** *section for sample pre-treatment.*

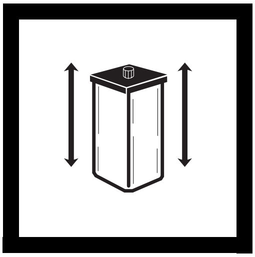
Note: *For most accurate work, sample temperature should be between 22-24 °C (71.5-75.2 °F). If outside this range, measure and record the sample temperature; see* ***Temp. Compensation Section****.*



5. Add 10 drops of 1 M EDTA Solution to each cell. Cap and invert each cell twice to mix.

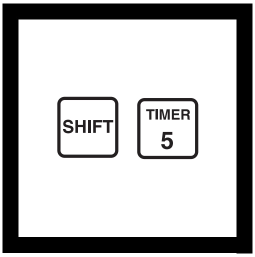


6. Open one pillow of BoroTrace #2 Reagent. and add the contents of the pillow to the cell containing the sample.



7. Cap and begin to shake to dissolve the powder.

Note: *Proceed immediately with Steps 8 and 9.*



8. Press:

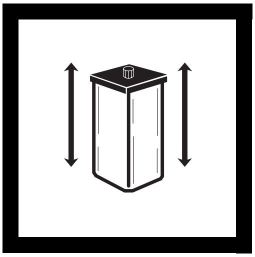
SHIFT TIMER

A 10-minute reaction period will begin.

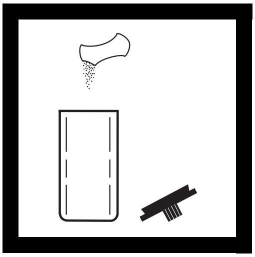
---

* Adapted from ISO Method 9390

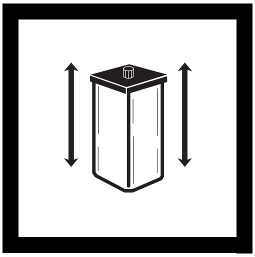
** Patent pending



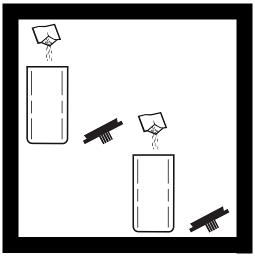
9. Continue shaking vigorously for 30 seconds. Let the cell sit capped for the duration of the timed reaction.



10. During the timed period, add the contents of a second BoroTrace #2 Reagent pillow to the cell containing the blank.



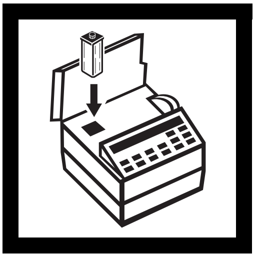
11. Cap the cell containing the blank and shake vigorously until the powder is dissolved.



12. After the timer beeps, add the contents of one BoroTrace #3 Reagent to each cell. Cap and shake to dissolve.
The display will show:

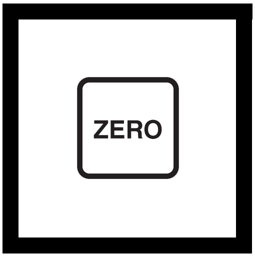
mg/L B LR

Note: *The addition of BoroTrace #3 Reagent "stops" the reaction.*



13. Place the blank cell into the cell holder. Close the light shield.

Note: *Clean the cell walls with a soft tissue or cloth to remove fingerprints before placing the cell into the cell holder.*



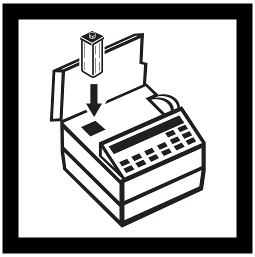
14. Press: **ZERO**

The display will show:

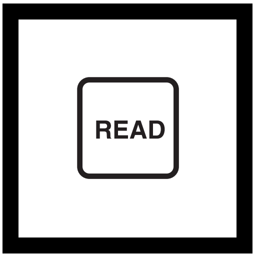
Zeroing...

then:

0.00 mg/L B LR



15. Place the prepared sample into the cell holder. Close the light shield.



16. Press: **READ**

The display will show:

Reading. . .

then the result in mg/L boron will be displayed.

Note: *Correct the result for sample temperature. If outside 22-24 °C (71.5-75.2 °F); see Sample Temperature Compensation Section.*

Forms ▲ H_3BO_3
▼ B

Sample Collection, Preservation and Storage

Collect samples in clean polyethylene bottles. Do not use borate-based detergents or soaps to clean sample containers or labware used for this method. After use, rinse all plastic containers with large amounts of deionized water, allow to air dry, and keep covered.

Cell Matching Procedure

1. Rinse and fill two plastic cells with deionized water.
2. Wipe the sides of the cells with a soft cloth or tissue.
3. Set the instrument to zero absorbance at 410 nm with one of the cells.
4. Read the absorbance of the other cell.
5. Cells which read within 0.002 absorbance are considered matched.

Interferences

The following have been tested for interference and found *not* to interfere up to the indicated levels (in mg/L):

Table 1 Non-interfering Substances/Maximum Level Tested

Substance	Maximum Level Tested (mg/L)
Aluminum (3^+)	10
Benzotriazole	20
Biocides:	
Carbamate-type	120
Isothiazolin-type	120
Quat-type	90
Thiocyanate-type	60
Bromide	120
Calcium	1000 (as $CaCO_3$)
Chloride	2500
Copper (2^+)	20
Fluoride	25
Magnesium	1000 (as $CaCO_3$)
Manganese (7^+)	5
Molybdate (Mo^{6+})	60
Nitrate	1000
Phosphonates, AMP	20
Phosphonates, HEDP	20

Table 1 Non-interfering Substances/Maximum Level Tested (Continued)

Substance	Maximum Level Tested (mg/L)
Polyacrylates	20 (as Acumer 1000, 1100)
Polymaleic Acid	40 (as Belcene 200)
Silica	120
Sulfate	1800
Sulfite	40
Tolyltriazole	20
Zinc (2^+)	10

Table 2 Interfering Substances and Suggested Treatments

Interfering Substance, Interference Level, (positive or negative interference)	Recommended Treatment
Alkalinity >500 mg/L(+ or -)	1. Adjust the pH of the sample to between 5 - 7 using 1.0 N Sulfuric Acid Solution. 2. Continue with step 5 of the test procedure.
Biocides, polyimino-type, all levels (+ or -)	Certain long-chain polymer biocides containing nitrogen compounds may form a turbidity after the addition of BoroTrace #2 Reagent. Remove the polymer from the sample by the following procedure: 1. Connect a SCX cartridge to a 30-cc syringe, without plunger. 2. Add 5 mL Eluant Solution to the syringe, insert plunger, and force Eluant Solution through the cartridge. Remove cartridge from syringe. 3. Add 1 mL pH 7.2 Phosphate Buffer solution to 30 mL sample and mix. 4. Reconnect the SCX cartridge to the syringe, without the plunger. 5. Transfer the buffered sample to the syringe, insert plunger, and slowly force sample through the cartridge, using a clean plastic cell as the receiver. 6. Discard the first 5 mL of treated sample. 7. Slowly force the sample through the SCX cartridge at a rate of about one drop per second into the plastic cell. 8. Continue until the cell is filled to the 25-mL mark. 9. Continue with Step 5 of the test procedure.
Color (+)	1. Zero the instrument (0.00 mg/L B) using Ultra-Pure water. 2. Adjust the sample pH to between 3-4, using 1.0 N Sulfuric Acid Solution. 3. Measure the apparent concentration, in mg/L B, of the acidified sample. 4. Subtract the apparent concentration of the acidified sample from the result obtained in Step 16 of the test procedure.
Halogens (Bromine or Chlorine all levels (+)	Halogen disinfectants in the sample can produce a red-color after the addition of BoroTrace #2 Reagent. To eliminate this interference: 1. Add 1 pillow Dechlorinating Reagent to 25-mL each of Ultra-Pure Water and sample. 2. Cap and shake to dissolve. 3. Continue with Step 5 of the test procedure.

Table 2 Interfering Substances and Suggested Treatments (Continued)

Interfering Substance, Interference Level, (positive or negative interference)	Recommended Treatment
Iron (Fe^{3+} or Fe^{2+}), above 8 mg/L (+)	High levels of iron in the sample can produce a red-color after the addition of BoroTrace #2 Reagent. To compensate, increase the amount of EDTA that is added to each cell (Step 6) from 10 drops to 15 drops. Alternatively, dilute the sample with Ultra-Pure water and continue with Step 5. Correct the results in Step 16 using the appropriate dilution factor.
Nitrites, all levels (+)	1. Add 0.1 gram scoop Sulfamic Acid to 25-mL each Ultra-Pure water and sample in plastic cells. 2. Cap and shake to dissolve. 3. Uncap and wait 5 minutes. 4. Add 5N Sodium Hydroxide Reagent solution to each cell to adjust pH between 5-8 (using pH paper). 5. Continue with Step 5 of the test procedure.
Turbidity (+)	Filter the sample through a 3 µm membrane prior to testing. Do not use a glass fiber filter.

Sample Temperature Compensation

The reaction chemistry is very much dependent on the sample temperature. Hach calibrations are performed at 23 °C (73.4 °F). If the sample temperature is outside the range of 22-24 °C (71.5-75.2 °F), multiply the results, in mg/L (Step 16) by the appropriate multiplier.

Sample Temp.		Multiplier
°C	°F	
5	41	0.70
7	44.5	0.73
10	50	0.78
12	53.5	0.81
14	57	0.84
16	61	0.87
18	64	0.91
20	68	0.94
25	77	1.04
26	79	1.06
27	80.5	1.08
28	82.5	1.10
29	84	1.12
30	86	1.15

Method Performance

Precision

at mg/L B	99% Confidence Limits
0.30	±0.03 mg/L B
1.00	±0.03 mg/L B
1.50	±0.07 mg/L B

For more information regarding Hach's precision estimates, see Section I.

Estimated Detection Limit

The estimated detection limit for program 45 is 0.02 mg/L B. The EDL is the calculated lowest average concentration in deionized water matrix that is different from zero with a 99% level of confidence. For more information on derivation and use of Hach's estimated detection limit, see Section I.

Sensitivity

Portion of Curve	∆Abs	∆Concentration
0.10 mg/L B	0.010	0.012 mg/L
0.60	0.010	0.011
1.20	0.010	0.014

Accuracy Check

Preparing a 1.0 mg/L Standard

Using plastic pipet, transfer 4.0 mL of Boron Standard Solution, 250 mg/L as B, into a 1000 mL plastic volumetric flask. Dilute to volume with deionized water, stopper and mix thoroughly.

Standard Additions Method

1. Prepare a 50.0 mg/L boron standard by pipeting 5.0 mL of a 1000 mg/L Boron Standard Solution into a 100 mL plastic volumetric flask. Dilute with deionized water, stopper and mix thoroughly.
2. Use the TenSette Pipet to add 0.1, 0.2, and 0.3 mL of the 50.0 mg/L boron standard to three 25-mL water samples, respectively.
3. Analyze each sample as described above.
4. The boron concentration should increase 0.20 mg/L for each 0.1 mL increment.

Summary of Method

Azomethine-H, a Schiff base, is formed by the condensation of an aminonaphthol with an aldehyde by the catalytic action of boron. The boron concentration in the sample is proportional to the developed color.

REQUIRED REAGENTS

Description	Cat. No.
BoroTrace Reagent Set	26669-00

Includes: (1) 26666-69, (1) 26667-99, (1) 22419-26, (1) 25946-49

Description	Quantity Required Per Test	Unit	Cat. No.
BoroTrace #2 Reagent Pillows	2	100/pkg	26666-69
BoroTrace #3 Reagent Pillows	2	100/pkg	26667-99
EDTA Solution, 1M	20 drops	50 mL SCDB	22419-26
Ultra-Pure Aldehyde-Free Reagent Water	25 mL	500 mL	25946-49

REQUIRED EQUIPMENT AND SUPPLIES

Cells, Sample, 1-inch, polystyrene	2	2/pkg	24102-22

OPTIONAL REAGENTS AND STANDARDS

Boron Standard Solution, 250 mg/L as B, 10-mL Voluette	16/pkg	14249-10
Boron Standard Solution, 1000 mg/L as B	100 mL	1914-42
Dechlorinating Reagent Powder Pillows	100/pkg	14363-69
Eluant Solution	1 L	22256-53
Phosphate Buffer, pH 7.2	1 L	431-53
Sodium Hydroxide Standard Solution, 5.0 N	50 mL SCDB	2450-26
Sulfamic Acid, ACS	113 g	2344-14

OPTIONAL EQUIPMENT AND SUPPLIES

Cells, Sample, 1-inch, polystyrene	12/pkg	24102-12
Filter Holder Assembly	each	2468-00
Flask, Volumetric, polypropylene, 100 mL	each	14060-42
Flask, Volumetric, polypropylene, 1000 mL	each	14060-53
Membrane Filters, 3-micron	25/pkg	25940-25
pH Paper, pH 1-11	each	3931-33
Pipet, Mohr-Type, Polypropylene, 5 mL	each	2106-37
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	each	21856-96
Pour-Thru Cell Assembly Kit	each	45215-00
SCX Cartridge	each	26730-00
Spoon, measuring, 0.1 g	each	511-00
Syringe, 30-cc	each	22258-00
Thermometer, -20 to 105 °C	each	1877-01

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

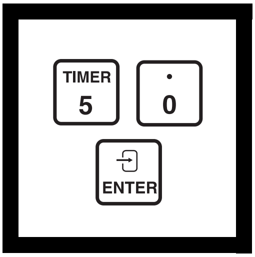
Method 8016

BROMINE (0 to 4.50 mg/L)

For water, wastewater, and seawater

DPD Method* (Powder Pillows or AccuVac Ampuls

Using Powder Pillows



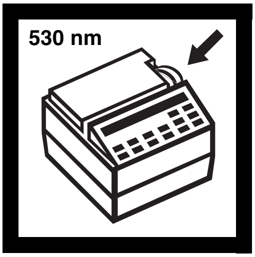
1. Enter the stored program number for bromine (Br_2) powder pillows.

Press: **5 0 ENTER**

The display will show:

Dial nm to 530

Note: *The Pour-Thru Cell can be used with 25-mL reagents only.*

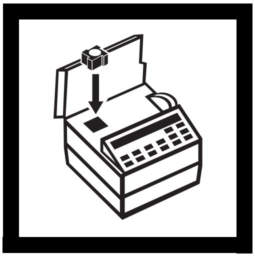


2. Rotate the wavelength dial until the small display shows:

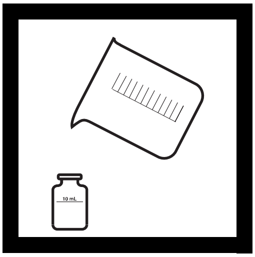
530 nm

When the correct wavelength is dialed in the display will quickly show: **Zero Sample**

then: **mg/L Br_2**



3. Insert the 10-mL Cell Riser into the cell compartment.



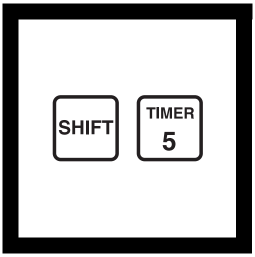
4. Fill a sample cell with 10 mL of sample.

Note: *Samples must be analyzed immediately.*

5. Add the contents of one DPD Total Chlorine Powder Pillow to the sample cell (the prepared sample).

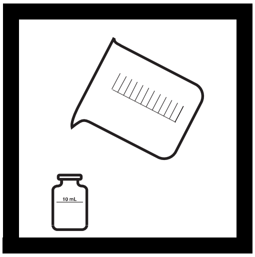
Swirl to mix.

Note: *A pink color will develop if bromine is present.*



6. Press: **SHIFT TIMER**

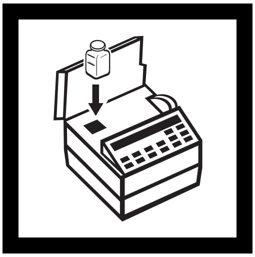
A three-minute reaction period will begin.



7. When the timer beeps, the display will show:

mg/L Br_2

Fill a second sample cell (the blank) with 10 mL of sample.



8. Place the blank into the cell holder. Close the light shield.

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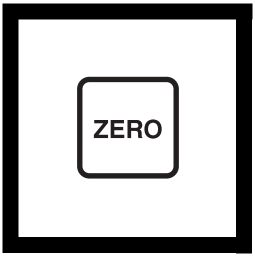
* Adapted from *Standard Methods for the Examination of Water and Wastewater*

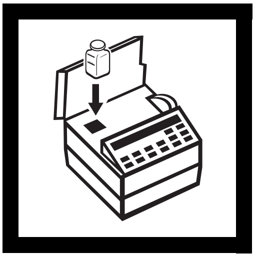


9. Press: **ZERO**

The display will show:

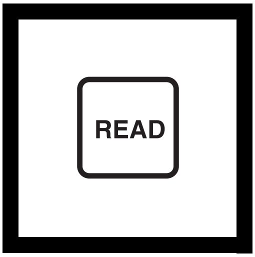
Zeroing. . .

then: **0.00 mg/L Br_2**



10. Within three minutes after the timer beeps, place the prepared sample into the cell holder.

Close the light shield.



11. Press: **READ**

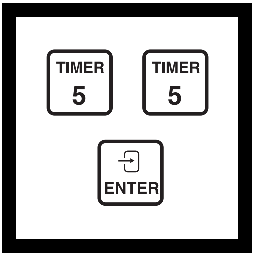
The display will show:

Reading. . .

then the result in mg/L Br_2 will be displayed.

Note: *If the sample temporarily turns yellow after reagent addition, or shows* ***OVER-RANGE****, dilute a fresh sample and repeat the test. A slight loss of bromine may occur during dilution. Multiply the result by the appropriate dilution factor; see Sample Dilution Techniques in Section I.*

Using AccuVac Ampuls

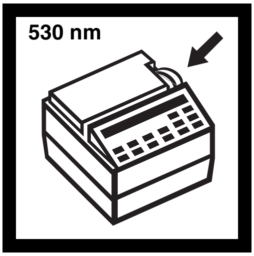


1. Enter the stored program number for bromine (Br_2) AccuVac ampuls.

Press: **5 5 ENTER**

The display will show:

Dial nm to 530



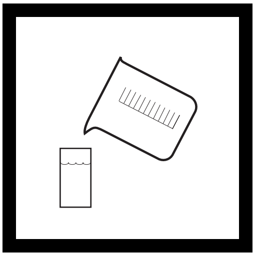
2. Rotate the wavelength dial until the small display shows:

530 nm

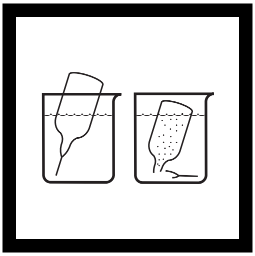
When the correct wavelength is dialed in the display will quickly show: **Zero Sample**

then: **mg/L Br_2 AV**

Note: *Samples must be analyzed immediately.*

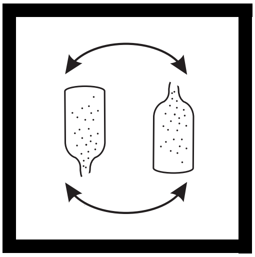


3. Fill a zeroing vial (the blank) with at least 10 mL of sample. Collect at least 40 mL of sample in a 50-mL beaker.



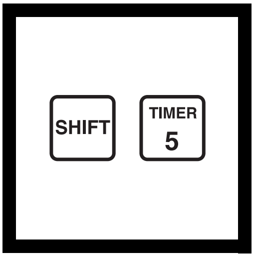
4. Fill DPD Total Chlorine Reagent AccuVac Ampule with sample.

Note: *Keep the tip immersed while the ampul fills completely.*



5. Quickly invert the ampul several times to mix. Wipe off any liquid or fingerprints.

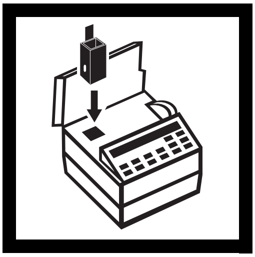
Note: *A pink color will form if bromine is present.*



6. Press:

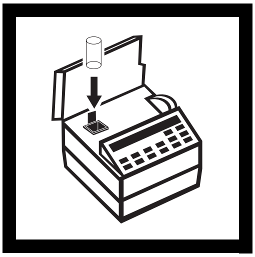
SHIFT TIMER

A three-minute reaction period will begin.



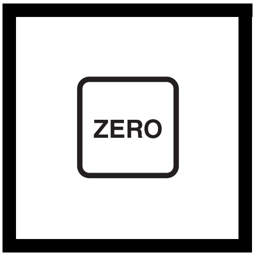
7. Place the AccuVac Vial Adapter into the cell holder.

Note: *Place the grip tab at the rear of the cell holder.*



8. When the timer beeps, the display will show: **mg/L Br_2 AV**

Place the blank into the cell holder. Close the light shield.

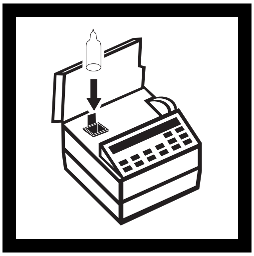


9. Press: **ZERO**

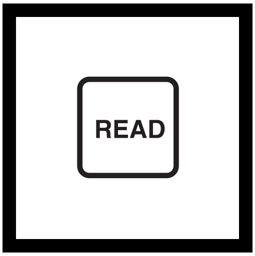
The display will show:

Zeroing. . . .

then: **0.00 mg/l Br_2 AV**



10. Within three minutes after the timer beeps, place the AccuVac Ampul into the cell holder. Close the light shield.



11. Press: **READ**

The display will show:

Reading. . . .

then the result in mg/L Br_2 will be displayed.

Note: *If the sample temporarily turns yellow after sample addition, or shows* ***OVER-RANGE****, dilute a fresh sample and repeat the test. A slight loss of bromine may occur during dilution. Multiply the result by the appropriate dilution factor; see Sample Dilution Techniques in Section I.*

Sampling and Storage

Analyze samples for bromine **immediately** after collection. Bromine is a strong oxidizing agent, and it is unstable in natural waters. It reacts rapidly with various inorganic compounds and more slowly oxidizes organic compounds. Many factors, including reactant concentrations, sunlight, pH, temperature, and salinity influence decomposition of bromine in water.

Avoid plastic containers since these may have a large bromine demand. **Pretreat glass** sample containers to remove any bromine demand by soaking in a dilute bleach solution (1 mL commercial bleach to l liter of deionized water) for at least 1 hour. Rinse thoroughly with deionized or distilled water. If sample containers are rinsed thoroughly with deionized or distilled water after use, only occasional pre-treatment is necessary.

A common error in testing for bromine is introduced when a representative sample is not obtained. If sampling from a tap, let the water flow for at least 5 minutes to ensure a representative sample. Let the container overflow with the sample several times, then cap the sample container so there is no headspace (air) above the sample. If sampling with a sample cell, rinse the cell several times with the sample, then carefully fill to the 10-mL mark. Analyze immediately.

Accuracy Check

Standard Additions Method (using powder pillows)

a) Perform a sample analysis and record the result.

b) Snap the top off a LR Chlorine PourRite Ampule Standard Solution, 25-30 mg/L Cl_2.

c) Use a TenSette Pipet to add 0.1 mL of the standard to the reacted sample (this is the spiked sample). Swirl to mix.

d) Place the spiked sample into the DR/2010 and read the spiked sample result.

e) Calculate the equivalent concentration of mg/L bromine added to the sample:

$$\text{mg/L Bromine} = \frac{0.1\ (\text{vol. standard added}) \times \text{Label value (mg/L Chlorine)} \times 2.25}{10.1\ (\text{sample + standard volume})}$$

f) The spiked sample result (step d) should reflect the analyzed sample result (step a) + the added, calculated mg/L Br_2 (step e).

g) If this increase does not occur, see Standard Additions in Section I for more information.

Standard Additions Method (using AccuVac Ampuls)

a) Snap the top off a LR Chlorine PourRite Ampule Standard Solution, 25-30 mg/L Cl_2.

b) Use a graduated cylinder to measure 25 mL of sample into each of two beakers.

c) Use a TenSette Pipet to add 0.2 mL of the standard to one of the beakers (this is the spiked sample). Swirl to mix.

d) Fill a DPD Total Chlorine AccuVac Ampul completely from each beaker.

e) Analyze the spiked and unspiked sample as described in the procedure.

f) Calculate the equivalent concentration of mg/L bromine added to the sample:

$$\text{mg/L Bromine} = \frac{0.2\ (\text{vol. standard added}) \times \text{Label value (mg/L Chlorine)} \times 2.25}{25.2\ (\text{sample + standard volume})}$$

g) The spiked sample result should reflect the analyzed sample result + the added, calculated mg/L Br_2 (step f).

h) If these increases do not occur, see *Standard Additions* in *Section I* for more information.

Precision

In a single laboratory using standard solutions of 1.00 mg/L chlorine (equivalent to 2.25 mg/L bromine) and two representative lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±0.012 mg/L chlorine. This is equivalent to ±0.027 mg/L bromine.

In a single laboratory using a standard solution of 1.10 mg/L chlorine (equivalent to 2.48 mg/L bromine) and two representative lots of AccuVac ampuls with the DR/2010, a single operator obtained a standard deviation of ±0.009 mg/L chlorine. This is equivalent to ±0.019 mg/L bromine.

Interferences

Samples containing more than 300 mg/L alkalinity or 150 mg/L acidity as $CaCO_3$ may not develop the full amount of color, or it may instantly fade. Neutralize these samples to a pH of 6 to 7 with 1 N sulfuric acid or 1 N sodium hydroxide. Determine the amount required on a separate 10 mL sample. Add the same amount to the sample to be tested. Correct the test result for volume additions; see *Correction for Volume Additions* in *Section I* for more information.

Chlorine, iodine, ozone, chloramines, and oxidized forms of manganese and chromium also may react and show as bromine. Compensate for the effects of oxidized manganese or chromium by adjusting the pH to 6 to 7 as described above. Add 3 drops of 30 g/L potassium iodide to 25 mL of sample, mix, and wait one minute. Add 3 drops of 5 g/L Sodium Arsenite and mix. Analyze 10 mL of this sample as described above. (If chromium is present, allow exactly the same reaction period with DPD for both analyses.) Subtract the result of this test from the original analysis to obtain the correct bromine result.

DPD Total Chlorine Reagent Powder Pillows and AccuVac Ampuls contain a buffer formulation which will withstand high (>1000 mg/L) levels of hardness without interference.

Summary of Method

Bromine reacts with DPD (N,N-diethyl-p-phenylenediamine) to form a magenta color which is proportional to the total bromine concentration.

REQUIRED REAGENTS (USING POWDER PILLOWS)

Description	Quantity Required Per Test	Unit	Cat. No.
DPD Total Chlorine Reagent Powder Pillows	1 pillow	100/pkg	21056-69

REQUIRED REAGENTS (USING ACCUVAC AMPULS)

DPD Total Chlorine Reagent AccuVac Ampuls	1 ampul	25/pkg	25030-25

REQUIRED APPARATUS (USING POWDER PILLOWS)

Cell Riser, 10-mL sample cell		each	45282-00
Sample Cells, 10-mL, matched pair		pair	24954-02

REQUIRED APPARATUS (USING ACCUVAC AMPULS)

Adapter, AccuVac vial	1	each	43784-00
Beaker, 50 mL	1	each	500-41
Vial, zeroing	1	each	21228-00

OPTIONAL REAGENTS

Chlorine Standard Solution, PourRite ampule, 25-30 mg/L, 10 mL		20/pkg	26300-20
Potassium Iodide Solution, 30 g/L		100 mL* MDB	343-32
Sodium Arsenite, 5 g/L		100 mL* MDB	1047-32
Sodium Hydroxide Standard Solution, 1 N		100 mL* MDB	1045-32
Sulfuric Acid Standard Solution, 1 N		100 mL* MDB	1270-32
Water, deionized		4 L	272-56

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* Contact Hach for larger sizes

OPTIONAL APPARATUS

Description	Unit	Cat. No.
AccuVac Snapper Kit	each	24052-00
Ampule Breaker Kit	each	24846-00
Cylinder, graduated, 25 mL	each	508-40
pH Meter, *sension*™*1*, portable	each	51700-10
pH Indicator Paper, 1 to 11 pH units	5 rolls/pkg	391-33
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96

OPTIONAL 25 mL ANALYSIS ITEMS

DPD Total Chlorine Reagent Powder Pillows	100/pkg	14064-99
Pour-Thru Cell Assembly	each	45215-00
Sample Cell, 25 mL, matched pair	pair	20950-00

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

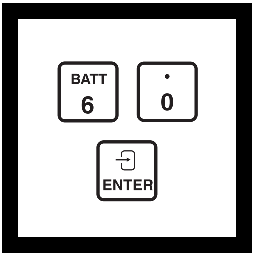
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8017

CADMIUM (0 to 80 µg/L)

For water and wastewater

Dithizone Method*



1. Enter the stored program number for cadmium (Cd).

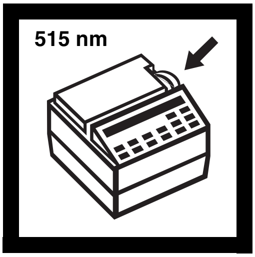
Press: **6 0 ENTER**

The display will show:

Dial nm to 515

Note: The Cell cannot be used.

Note: Clean all glassware with Nitric Acid Solution, 1:1. Rinse with deionized water.



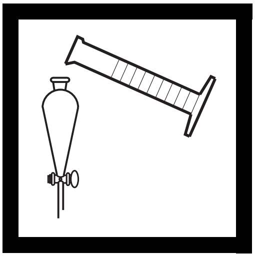
2. Rotate the wavelength dial until the small display shows:

515 nm

When the correct wavelength is dialed in the display will quickly show: **Zero Sample**

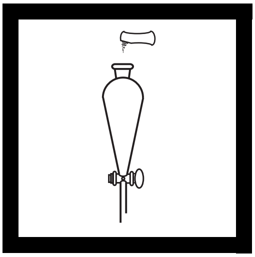
then: **µg/L Cd**

Note: Total cadmium determination requires a digestion (see Section II).



3. Fill a 250-mL graduated cylinder to the 250-mL mark with sample. Pour the sample into a 500-mL separatory funnel.

Note: Cloudy and turbid samples may require filtering with a glass membrane filter before running test. Report results as µg/L soluble cadmium.



4. Add the contents of one Buffer Powder Pillow, citrate type for heavy metals. Stopper the funnel. Shake to dissolve.

Note: For best results, determine a reagent blank. Use deionized water in place of the sample. Subtract the reagent blank value from each sample reading. Repeat for each new lot of reagent.

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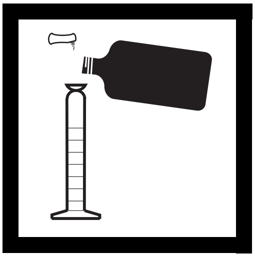
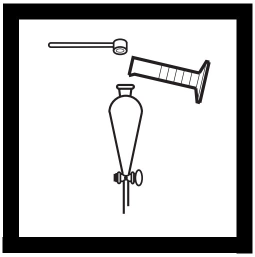
* Adapted from *Standard Methods for the Examination of Water and Wastewater.*



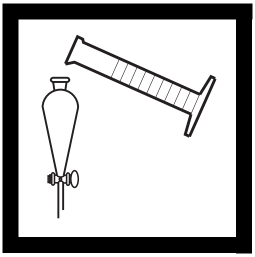
5. Add 30 mL of chloroform to a 50-mL mixing graduated cylinder. Add the contents of one DithiVer Metals Reagent Powder Pillow. Stopper. Invert repeatedly to mix (DithiVer solution).

Note: *Use adequate ventilation. The DithiVer powder will not all dissolve. See DithiVer Solution Preparation and Storage.*

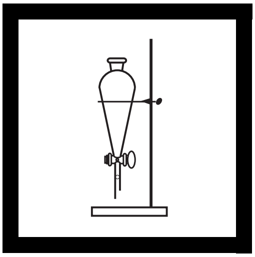


6. Add 20 mL of 50% Sodium Hydroxide Solution and then a 0.1-g scoop of potassium cyanide to the funnel. Shake vigorously for 15 seconds. Remove the stopper and let stand for one minute.

Note: *Spilled reagent will affect test accuracy and is hazardous.*

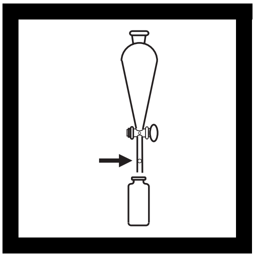


7. Add 30 mL of the DithiVer solution to the 500-mL separatory funnel. Stopper, invert, and open stopcock to vent. Close the stopcock and shake funnel once or twice; vent again. Close the stopcock and shake the funnel vigorously for 60 seconds.



8. Let the funnel stand undisturbed for roughly one minute.

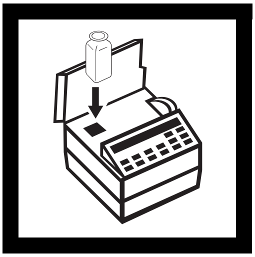
Note: *The bottom (chloroform) layer will be pink if cadmium is present.*



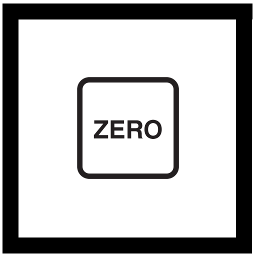
9. Insert a cotton plug the size of a pea into the delivery tube of the funnel and slowly drain the bottom (chloroform) layer into a dry 25-mL sample cell (the prepared sample). Cap.

Note: *The cadmium-dithizone complex is stable for hours if the sample cell is kept tightly capped and out of direct sunlight.*

10. Fill a dry 25-mL sample cell with chloroform (the blank). Cap.



11. Place the blank into the cell holder. Close the light shield.

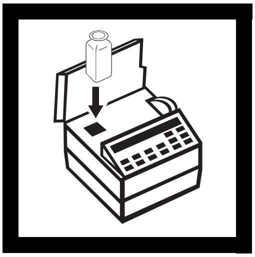


12. Press: **ZERO**

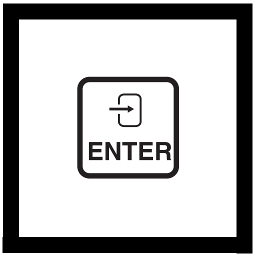
The display will show:

Zeroing. . .

then: **0. µg/L Cd**



13. Place the prepared sample into the cell holder. Close the light shield.



14. Press: **READ**

The display will show:

Reading. . .

then the result in
µg/L cadmium
will be displayed.

Safety Precautions

Perform the entire procedure in a fume hood if possible. Using gloves that are resistant to chloroform solutions (i.e. VITON) and safety goggles is recommended.

Sampling and Storage

Collect samples in an acid-cleaned glass or plastic container. Adjust the pH to 2 or less with nitric acid (about 2 mL per liter). Store preserved samples up to six months at room temperature. Adjust the pH to 2.5 with 5.0 N sodium hydroxide before analysis. Correct the test result for volume additions; see Correction for Volume Additions in Section I.

Dithiver Solution Preparation and Storage

Store DithiVer powder pillows away from light and heat. A convenient way to prepare this solution is to add the contents of 16 DithiVer Metals Reagent Powder Pillows to a pint bottle of chloroform and invert several times until well mixed (carrier powder may not dissolve). Store dithizone solution in an amber glass bottle. This solution is stable for 24 hours.

Accuracy Check

Standard Additions Method

a) Snap the neck off a Cadmium Voluette Ampule Standard Solution, 25 mg/L Cd.

b) Use the TenSette Pipet to add 0.1 mL, 0.2 mL, and 0.3 mL of standard, respectively, to three 250-mL samples. Mix each thoroughly.

c) Analyze each sample as described above. The cadmium concentration should increase 10 µg/L for each 0.1 mL of standard added.

d) If these increases do not occur, see Standard Additions in Section I for more information.

Standard Solution Method

Prepare a 5.0-mg/L cadmium standard solution by pipetting 5.00 mL of Cadmium Standard Solution, 100-mg/L Cd, into a 100-mL volumetric flask. Dilute to the mark with deionized water and mix thoroughly. Prepare a fresh solution daily.

Pipet 2.00 mL of the 5.0-mg/L cadmium standard solution into 248 mL of deionized water in a 500-mL separatory funnel. This is a 40 µg/L cadmium solution. Perform the cadmium test as described in the procedure.

Precision

In a single laboratory using a standard solution of 61 µg/L cadmium and two representative lots of reagents with the DR/2010, a single operator obtained a standard deviation of ±0.9 µg/L cadmium.

Interferences

The following do not interfere:

Aluminum	Cobalt	Manganese
Antimony	Iron	Nickel
Arsenic	Lead	Tin
Calcium	Magnesium	Zinc
Chromium		

The following interfere causing high results when present in concentrations exceeding those listed below:

Copper	2 mg/L
Bismuth	80 mg/L
Mercury	all levels
Silver	2 mg/L

Eliminate interference from these metals by the following treatment, beginning after Step 5.

a) Measure about 5 mL of the DithiVer solution into the separatory funnel. Stopper the funnel, invert and open the stopcock to vent. Close the stopcock and shake the solution vigorously for 15 seconds. Allow the funnel to stand undisturbed until the layers separate (about 30 seconds). A yellow, red, or bronze color in the bottom (chloroform) layer confirms the presence of interfering metals. Draw off and discard the bottom (chloroform) layer.

b) Repeat extraction with fresh 5 mL portions of the DithiVer solution (discarding the bottom layer each time) until the bottom layer shows a pure dark green color for three successive extracts. Extractions can be repeated several times without appreciably affecting the amount of cadmium in the sample.

c) Extract the solution with several 2 or 3 mL portions of pure chloroform to remove any remaining DithiVer, again discarding the bottom layer each time.

d) Continue with Step 6.

e) In Step 7, substitute 28.5 mL of DithiVer solution for the 30 mL.

f) Continue with Step 8.

Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment; see pH Interferences in Section I.

Pollution Prevention and Waste Management

Both chloroform (D002) and cyanide (D003) solutions are regulated as hazardous wastes by the Federal RCRA. Do **not** pour these solutions down the drain. Collect chloroform solutions and the cotton plugs used in the delivery tube of the separatory funnel for disposal with laboratory solvent waste. Be sure cyanide solutions are stored in a caustic solution with a pH >11 to prevent release of hydrogen cyanide gas.

Summary of Method

The dithizone method determines cadmium in water and wastewater. The DithiVer metals reagent is a stable powder form of dithizone. Cadmium ions in basic solution react with dithizone to form a pink to red cadmium-dithizonate complex, which is extracted with chloroform.

REQUIRED REAGENTS

	Cat No.
Cadmium Reagent Set (68 Tests)	22422-00

Includes: (1) 14202-99, (1) 14458-17, (4) 12616-68, (1) 767-14, (4) 2180-49

Description	Quantity Required Per Test	Unit	Cat. No.
Buffer Powder Pillows, citrate for heavy metals	1 pillow	100/pkg	14202-99
Chloroform, ACS	30 mL	500 mL	14458-49
DithiVer Metals Reagent Powder Pillows	1 pillow	25/pkg	12616-68
Potassium Cyanide, ACS	0.1 g	113 g	767-14
Sodium Hydroxide Solution, 50%	20 mL	500 mL	2180-49
Cotton Balls, absorbent	1	100/pkg	2572-01

REQUIRED APPARATUS

Clippers, for opening pillows	1	each	968-00
Cylinder, graduated, 25 mL	1	each	508-40
Cylinder, graduated, 250 mL	1	each	508-46
Cylinder, mixing, graduated, 50 mL	1	each	1896-41
Funnel, separatory, 500 mL	1	each	520-49
Sample Cells, 25 mL, matched pair	2	pair	20950-00
Spoon, measuring, 0.1 g	1	each	511-00
Support Ring, 4"	1	each	580-01
Support Stand, 5 x 8"	1	each	563-00

OPTIONAL REAGENTS

Description	Unit	Cat. No.
Cadmium Standard Solution, 100 mg/L as Cd	100 mL	14024-42
Cadmium Standard Solution, Voluette ampule, 25 mg/L Cd, 10 mL	16/pkg	14261-10
Nitric Acid, ACS	500 mL	152-49
Nitric Acid Solution, 1:1	500 mL	2540-49
Sodium Hydroxide Standard Solution, 5.0 N	100 mL MDB	2450-32
Sodium Hydroxide Standard Solution, 5.0 N	50 mL SCDB	2450-26
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Ampule Breaker Kit	each	21968-00
Cylinder, graduated, 5 mL	each	508-37
Filter Discs, glass, 47 mm	100/pkg	2530-00
Flask, erlenmeyer, 500 mL	each	505-49
Flask, filtering, 500 mL	each	546-49
Flask, volumetric, 100 mL	each	547-42
Hot Plate, 3 1/2" diameter, 120 Vac	each	12067-01
Hot Plate, 3 1/2" diameter, 240 Vac	each	12067-02
Membrane Filter Holder, graduated, 500 mL, for 47 mm filter	each	2340-00
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
pH Meter, *sension*™*1*, portable	each	51700-10
Pipet, serological, 2 mL	each	532-36
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet, volumetric, 2.00 mL	each	515-36
Pipet Filler, safety bulb	each	14651-00
Stopper, hollow, poly, Size No. 2	6/pkg	14480-00
Tongs, crucible	each	569-00

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

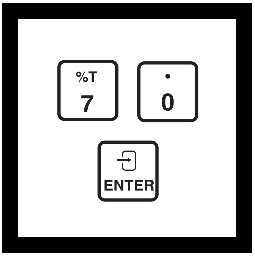
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8113

For water and wastewater

CHLORIDE (0 to 20.0 mg/L Cl^-)

Mercuric Thiocyanate Method*



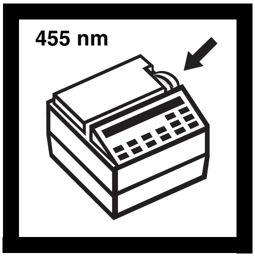
1. Enter the stored program number for Chloride (Cl^-).

Press: **7 0 ENTER**

The display will show:

Dial nm to 455

Note: *The Pour-Thru cell can be used with this procedure. Collect the waste solution for proper disposal.*



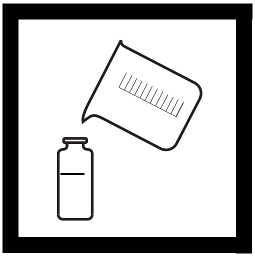
2. Rotate the wavelength dial until the small display shows:

455 nm

When the correct wavelength is dialed in the display will quickly show:

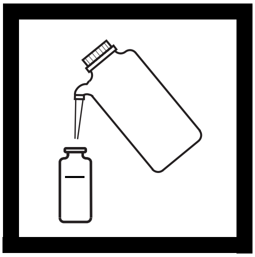
Zero Sample

then: **mg/L Cl^-**

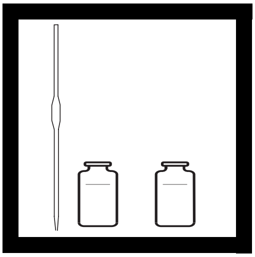


3. Fill a sample cell with 25 mL of sample.

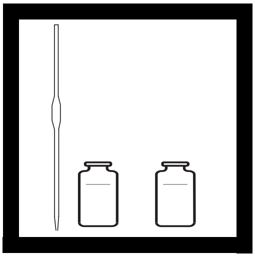
Note: *Filter turbid samples.*



4. Fill another cell with 25 mL of deionized water (the blank).



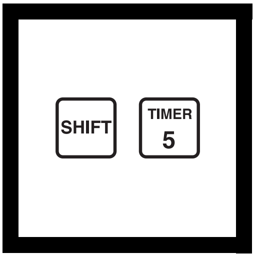
5. Pipet 2.0 mL of Mercuric Thiocyanate Solution into each cell. Swirl to mix.



6. Pipet 1.0 mL of Ferric Ion Solution into each sample cell.

Swirl to mix.

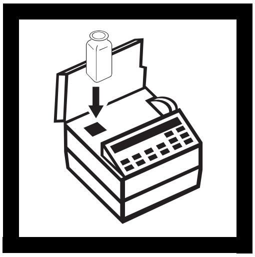
Note: *An orange color will develop if chloride is present.*



7. Press:

SHIFT TIMER

A two-minute reaction period will begin.



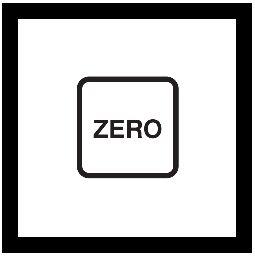
8. When the timer beeps, the display will show:

mg/L Cl^-

Place the blank into the cell holder. Close the light shield.

---

* Adapted from Zall, et. al., Analytical Chemistry, 28 (11) 1665 (1956).

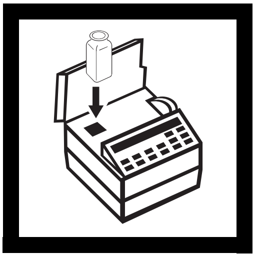


9. Press: **ZERO**

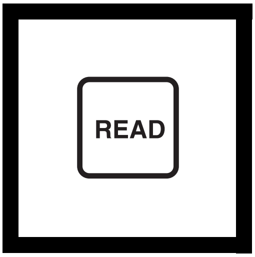
The display will show:

Zeroing. . .

then: **0.0 mg/L Cl^-**



10. Place the prepared sample into the cell holder. Close the light shield.



11. Press: **READ**

The display will show:

Reading. . .

then the result in mg/L chloride (Cl^-) will be displayed.

Note: *The prepared sample and blank contain mercury and must be disposed of according to current Federal, State, and local hazardous waste regulations.*

Sampling and Storage

Samples can be stored for at least 28 days at room temperature in glass or plastic bottles.

Accuracy Check

Standard Additions Method

a) Use the TenSette Pipet to add 0.1 mL, 0.2 mL and 0.3 mL of Chloride Standard Solution, 1000 mg/L as Cl^-, to each of three 25-mL water samples. Mix each thoroughly.

b) Analyze each sample as described above.

c) The chloride concentration should increase 4.0 mg/L for each 0.1 mL of standard added.

d) If these increases do not occur, see *Standard Additions in Section I* for more information.

Standard Solution Method

Prepare a 10.0 mg/L chloride standard solution by diluting 5.00 mL of Chloride Standard Solution, 1000 mg/L to 500 mL with deionized water. Run the test using the 10.0 mg/L chloride standard in place of the sample. The results should be between 9.0 and 11.0 mg/L chloride.

Precision

In a single laboratory using a standard solution of 10 mg/L chloride and two lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±0.3 mg/L chloride.

Interferences

The pH of the sample after addition of reagents should be about 2. If the sample is strongly acid or alkaline, adjust a portion of sample before testing to a pH of about 7. Use either 5.0 N Sodium Hydroxide Standard Solution or a 1:5 dilution of perchloric acid. Use pH paper, as most pH electrodes will contaminate the sample with chloride.

Summary of Method

Chloride in the sample reacts with mercuric thiocyanate to form mercuric chloride and liberate thiocyanate ion. Thiocyanate ions react with the ferric ions to form an orange ferric thiocyanate complex. The amount of this complex is proportional to the chloride concentration. Chloride at these levels also can be determined directly using the Chloride Ion Selective Electrode (Cat. No. 50255-00).

REQUIRED REAGENTS

	Cat. No.
Chloride Reagent Set (50 Tests*)	23198-00

Description	Quantity Required Per Test	Unit	Cat. No.
Ferric Ion Solution	2 mL	100 mL	22122-42
Mercuric Thiocyanate Solution	4 mL	200 mL	22121-29
Water, deionized	25 mL	4 L	272-56

REQUIRED APPARATUS

Pipet, volumetric, 1.0 mL, Class A	1	each	14515-35
Pipet, volumetric, 2.0 mL, Class A	1	each	14515-36
Pipet Filler, safety bulb	1	each	14651-00
OR			
Pipet, TenSette, 0.1 to 1.0 mL	1	each	19700-01
Pipet Tips, for 19700-01 TenSette pipet	1	50/pkg	21856-96
Sample Cell, 25 mL, matched pair	2	pair	20950-00

OPTIONAL REAGENTS

Chloride Standard Solution, 1000 mg/L as Cl	500 mL	183-49
Perchloric Acid, ACS, 70%	680 g	757-65
Sodium Hydroxide Standard Solution, 5.0 N	50 mL SCDB	2450-26

OPTIONAL APPARATUS

Chloride Analysis Package (electrochemical)	each	23484-00
Filter Paper, folded, mod. rapid, 12.5 cm	100/box	692-57
Flask, erlenmeyer, 125 mL	each	505-43
Flask, volumetric, 500 mL	each	547-49
Funnel, filtering, polypropylene, 75 mm	each	1083-68
pH/ISE Meter, *sension*™**2**, Portable	each	51725-10
pH Paper, 1 to 11 pH	5 rolls/pkg	391-33
Pipet, volumetric, Class A, 5.00 mL	each	14515-37
Pour-Thru Cell Assembly Kit	each	45215-00

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

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* 50 tests equals 25 samples and 25 blanks.

Method 8021

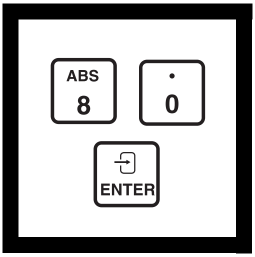
CHLORINE, FREE (0 to 2.00 mg/L)

For water, wastewater, and seawater

DPD Method* (Powder Pillows or AccuVac Ampuls)

USEPA accepted for reporting wastewater and drinking water analyses.**

Using Powder Pillows



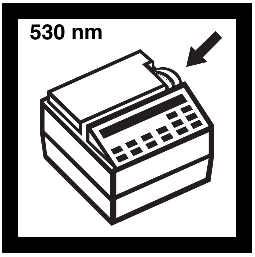
1. Enter the stored program number for free and total chlorine (Cl_2) powder pillows.

Press: **8 0 ENTER**

The display will show:

Dial nm to 530

Note: *The Pour-Thru Cell can be used with 25-mL reagents only.*

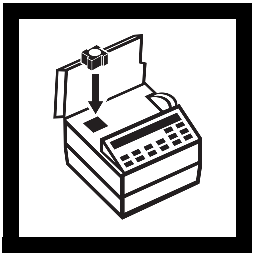


2. Rotate the wavelength dial until the small display shows:

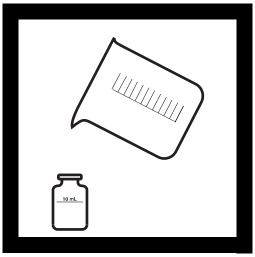
530 nm

When the correct wavelength is dialed in the display will quickly show: **Zero Sample**

then: **mg/L Cl_2**



3. Insert the 10-mL Cell Riser into the sample compartment.



4. Fill a sample cell with 10 mL of sample (the blank). Place it into the cell holder. Close the light shield.

Note: *Samples must be analyzed immediately and cannot be preserved for later analysis.*

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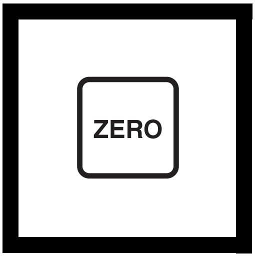
* Adapted from *Standard Methods for the Examination of Water and Wastewater.*

** Procedure is equivalent to USEPA method 330.5 for wastewater and Standard Method 4500-Cl G for drinking water.

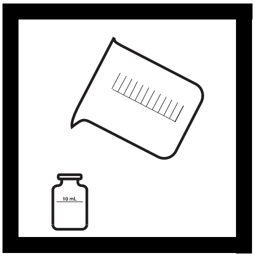


5. Press: **ZERO**

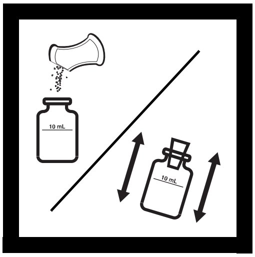
The display will show:

Zeroing. . .

then: **0.00 mg/L Cl_2**



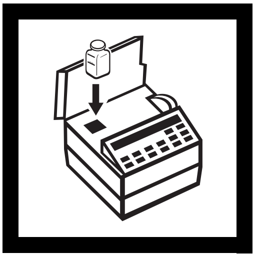
6. Fill another cell with 10 mL of sample.



7. Add the contents of one DPD Free Chlorine Powder Pillow to the sample cell (the prepared sample). Stopper the cell and shake for 20 seconds.

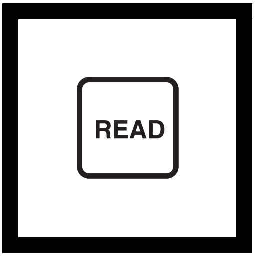
Note: *A pink color will develop if free chlorine is present.*

Note: *Shaking dissipates bubbles which may form in samples containing dissolved gases.*



8. Immediately (within one minute of reagent addition) remove stopper and place the prepared sample into the cell holder. Close the light shield.

Note: *Proceed immediately to Step 9.*



9. Press: **READ**

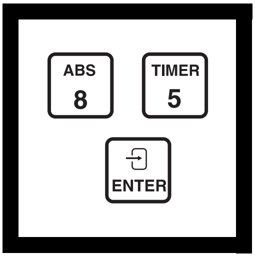
The display will show:

Reading. . .

then the result in mg/L chlorine (Cl_2) will be displayed.

Note: *If the sample temporarily turns yellow after reagent addition, or shows* ***OVER-RANGE****, dilute a fresh sample and repeat the test. A slight loss of chlorine may occur during dilution. Multiply the result by the appropriate dilution factor; see Sample Dilution Techniques (Section I).*

Using AccuVac Ampuls

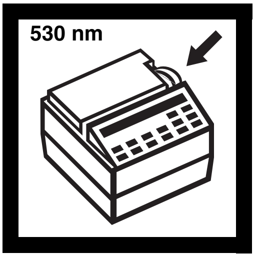


1. Enter the stored program number for free and total chlorine (Cl_2) AccuVac ampuls.

Press: **8 5 ENTER**

The display will show:

Dial nm to 530

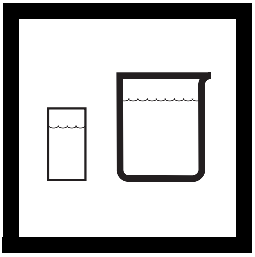


2. Rotate the wavelength dial until the small display shows

530 nm

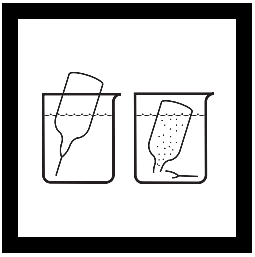
When the correct wavelength is dialed in the display will quickly show: **Zero Sample**

then: **mg/L Cl_2 AV**



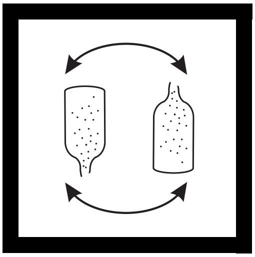
3. Fill a zeroing vial (the blank) with at least 10 mL of sample. Collect at least 40 mL of sample in a 50-mL beaker.

Note: *Samples must be analyzed immediately and cannot be preserved for later analysis.*



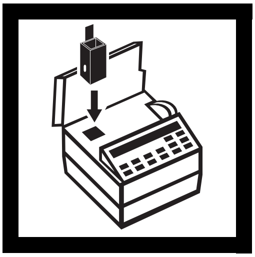
4. Fill a DPD Free Chlorine Reagent AccuVac Ampul with sample.

Note: *Keep the tip immersed while the ampul fills completely.*



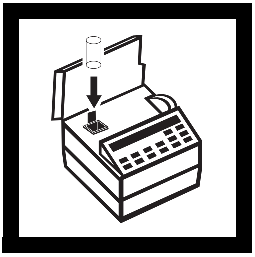
5. Quickly invert the ampul several times to mix. Wipe off any liquid or fingerprints.

Note: *A pink color will form if chlorine is present.*

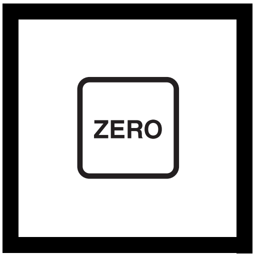


6. Place the AccuVac Vial Adapter into the cell holder of the instrument.

Note: *Place the grip tab at the rear of the cell holder.*



7. Place the blank into the cell holder. Close the light shield.

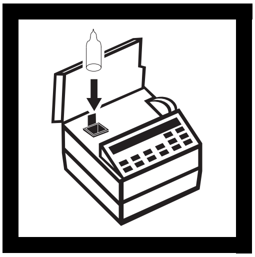


8. Press: **ZERO**

The display will show:

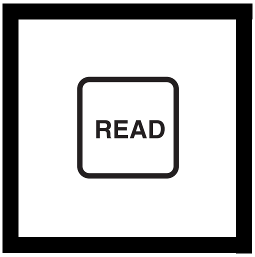
Zeroing. . .

then: **0.00 mg/L Cl_2 AV**



9. Immediately (within one minute of sample addition) place the AccuVac ampul into the cell holder. Close the light shield.

Note: *Proceed immediately to Step 10.*



10. Press: **READ**

The display will show:

Reading. . .

then the result in mg/L Cl_2 will be displayed.

Note: *If the sample temporarily turns yellow after sample addition, or shows* ***OVER-RANGE****, dilute a fresh sample and repeat the test. A slight loss of chlorine may occur during dilution. Multiply the result by the appropriate dilution factor; see Sample Dilution Techniques (Section I).*

Sampling and Storage

Analyze samples for chlorine **immediately** after collection. Free chlorine is a strong oxidizing agent, and it is unstable in natural waters. It reacts rapidly with various inorganic compounds and more slowly oxidizes organic compounds. Many factors, including reactant concentrations, sunlight, pH, temperature, and salinity influence decomposition of free chlorine in water.

Avoid plastic containers since these may have a large chlorine demand. **Pretreat glass** sample containers to remove any chlorine demand by soaking in a dilute bleach solution (1 mL commercial bleach to l liter of deionized water) for at least 1 hour. Rinse thoroughly with deionized or distilled water. If sample containers are rinsed thoroughly with deionized or distilled water after use, only occasional pre-treatment is necessary.

A common error in testing for chlorine is introduced when a representative sample is not obtained. If sampling from a tap, let the water flow for at least 5 minutes to ensure a representative sample. Let the container overflow with the sample several times, then cap the sample container so there is no headspace (air) above the sample. If sampling with a sample cell, rinse the cell several times with the sample, then carefully fill to the 10-mL mark. Analyze immediately.

Accuracy Check

Standard Additions Method (using powder pillows)

a) Perform a sample analysis and record the result.

b) Snap the top off a LR Chlorine PourRite Ampule Standard Solution, 25-30 mg/L Cl_2.

c) Use a TenSette Pipet to add 0.1 mL of the standard to the reacted sample (this is the spiked sample). Swirl to mix.

d) Place the spiked sample into the DR/2010 and read the spiked sample result.

e) Calculate the equivalent concentration of mg/L chlorine added to the sample:

$$\text{mg/L Chlorine} = \frac{0.1\ (\text{vol. standard added}) \times \text{Label value (mg/ (L chlorine))}}{10.1\ (\text{sample + standard volume})}$$

f) The spiked sample result (step d) should reflect the analyzed sample result (step a) + the added, calculated mg/L Cl_2 (step e).

g) If these increases do not occur, see Standard Additions in Section I for more information.

Standard Additions Method (using AccuVac Ampuls)

a) Snap the top off a LR Chlorine PourRite Ampule Standard Solution, 25-30 mg/L Cl_2.

b) Use a graduated cylinder to measure 25 mL of sample into each of two beakers.

c) Use a TenSette Pipet to add 0.2 mL of the standard to one of the beakers (this is the spiked sample). Swirl to mix.

d) Fill a DPD Free Chlorine AccuVac Ampul completely from each beaker.

e) Analyzed the spiked and unspiked sample as described in the procedure.

f) Calculate the equivalent concentration of mg/L chlorine added to the sample:

$$\text{mg/L Chlorine} = \frac{0.2(\text{vol. standard added}) \times \text{Label value}(\text{mg/ L Cl}_2)}{25.2(\text{sample} + \text{standard volume})}$$

g) The spiked sample result should reflect the analyzed sample result + the added, calculated mg/L Cl_2 (step f).

h) If this increase does not occur, see *Standard Additions* in *Section I* for more information.

Precision

In a single laboratory using a standard solution of 1.00 mg/L chlorine and two representative lots of reagents with the DR/2010, a single operator obtained standard deviations of ±0.012 mg/L chlorine.

In a single laboratory using a standard solution of 1.10 mg/L chlorine and two representative lots of AccuVac ampuls with the DR/2010, a single operator obtained a standard deviation of ±0.009 mg/L chlorine.

Estimated Detection Limit (EDL)

The EDL for program 80 and program 85 is 0.01 mg/L CL_2. The EDL is the calculated lowest average concentration in a deionized water matrix that is different from zero with a 99% level of confidence. For more information on derivation and use of Hach's estimated detection limit, see *Section I*.

Interferences

Samples containing more than 250 mg/L alkalinity or 150 mg/L acidity as $CaCO_3$ may not develop the full amount of color, or the color may instantly fade. Neutralize these samples to a pH of 6 to 7 with 1 N sulfuric acid, or 1 N sodium hydroxide. Determine the amount required on a separate 25-mL sample; then add the same amount to the sample to be tested.

Samples containing monochloramine will cause a gradual drift to higher chlorine readings. When read within one minute of reagent addition, 3.0 mg/L monochloramine will cause an increase of less than 0.1 mg/L in the free chlorine reading.

Bromine, iodine, ozone, oxidized manganese, and chromium also may react and show as chlorine. To compensate for the effects of oxidized manganese or chromium adjust pH to 6 to 7 as described above, then add 3 drops of potassium iodide, 30 g/L, to 25 mL of sample, mix and wait 1 minute. Add 3 drops of sodium arsenite, 5 g/L, and mix. Analyze 10 mL of this sample as described above. (If chromium is present, allow exactly the same reaction period with the DPD for both analyses.) Subtract the result of this test from the original analysis to obtain the correct chlorine result.

Do not use the same sample cells for free and total chlorine. If trace iodide from the total chlorine reagent is carried over into the free chlorine determination, monochloramine will interfere. It is best to use separate, dedicated sample cells for free and total chlorine determinations.

DPD Free Chlorine Reagent Powder Pillows and AccuVac Ampuls contain a buffer formulation which will withstand high (at least 1000 mg/L) levels of hardness without interference.

Summary of Method

Chlorine in the sample as hypochlorous acid or hypochlorite ion (free chlorine or free available chlorine) immediately reacts with DPD (N,N-diethyl-p-phenylenediamine) indicator to form a magenta color which is proportional to the chlorine concentration.

REQUIRED REAGENTS (USING POWDER PILLOWS)

Description	Quantity Required Per Test	Unit	Cat. No.
DPD Free Chlorine Reagent Powder Pillows, 10 mL	1 pillow	100/pkg	21055-69

REQUIRED REAGENTS (USING ACCUVAC AMPULS)

DPD Free Chlorine Reagent AccuVac Ampuls	1 ampul	25/pkg	25020-25

REQUIRED APPARATUS (USING POWDER PILLOWS)

Cell Riser, 10-mL sample cell		each	45282-00
Sample Cell, 10-mL, matched pair		pair	24954-02
Stopper, hollow, No 2, LDPE, fits 10 & 25-mL cells	1	6/pkg	14480-00

REQUIRED APPARATUS (USING ACCUVAC AMPULS)

Adapter, AccuVac vial	1	each	43784-00
Beaker, 50 mL	1	each	500-41
Vial, zeroing	1	each	21228-00

OPTIONAL REAGENTS

Description	Unit	Cat. No.
Chlorine Standard Solution, PourRite ampule, 25-30 mg/L, 10 mL	20/pkg	26300-20
DPD Free Chlorine Reagent w/dispensing cap	250 tests	21055-29
Potassium Iodide Solution, 30 g/L	100 mL* MDB	343-32
Sodium Arsenite, 5 g/L	100 mL* MDB	1047-32
Sodium Hydroxide Standard Solution, 1.000 N	100 mL* MDB	1045-32
Sulfuric Acid Standard Solution, 1.000 N	100 mL* MDB	1270-32
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

AccuVac Snapper Kit	each	24052-00
Ampule Breaker Kit	each	24846-00
Cylinder, graduated, 25 mL	each	508-40
pH Meter, *sension™1*, portable	each	51700-10
pH Paper, 1 to 11 pH units	5 rolls/pkg	391-33
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96

OPTIONAL 25 ML ANALYSIS ITEMS

DPD Free Chlorine Reagent Powder Pillows, 25 mL	100/pkg	14070-99
Pour-Thru Cell Assembly Kit	each	45215-00
Sample Cell, 25-mL, matched pair	pair	20950-00

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

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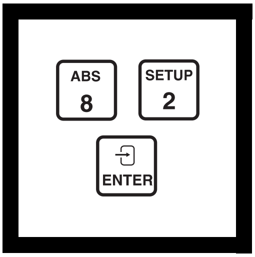
* Marked Dropper Bottle - contact Hach for larger sizes.

Method 10059

CHLORINE, FREE (0 to 2.00 mg/L)

DPD Rapid Liquid Method *

For treated water



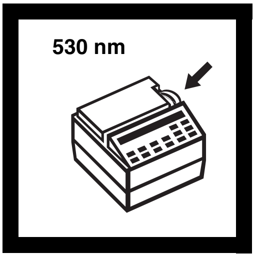
1. Enter the stored program number for free and total chlorine (Cl_2).

Press: **8 2 ENTER**

The display will show:

Dial nm to 530

Note: *Samples must be analyzed immediately and cannot be preserved for later analysis.*

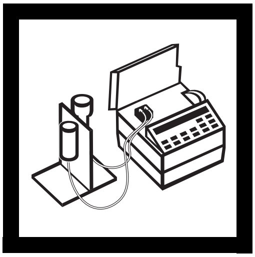


2. Rotate the wavelength dial until the small display shows:

530 nm

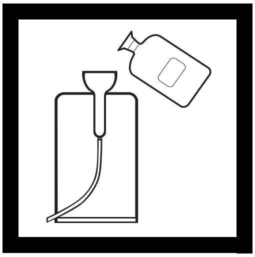
When the correct wavelength is dialed in, the display will quickly show: **Zero Sample**

then: **mg/L Cl_2 RL**

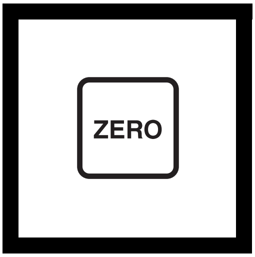


3. Install the Pour-Thru Cell and flush with 50 mL of deionized water.

Note: *Clean the Pour-Thru Cell and all labware as specified in Treating Analysis Labware.*



4. Pour approximately 50 mL of sample into the Pour-Thru Cell.

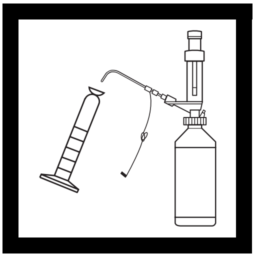


5. When the flow has stopped, press: **ZERO**

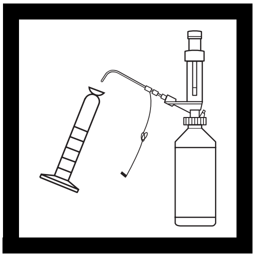
The display will show:

Zeroing. . . .

then: **0.00 mg/L Cl_2 RL**

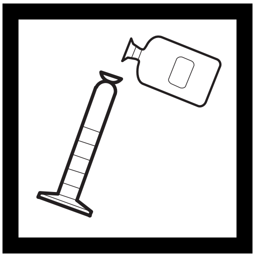


6. Add 1.0 mL of Free Chlorine Buffer Solution to a clean, dry 100-mL glass mixing cylinder using the Repipet dispenser.



7. Add 1.0 mL of prepared Free Chlorine Indicator Solution to the same mixing cylinder. Swirl to mix the reagents. Proceed to step 8 immediately.

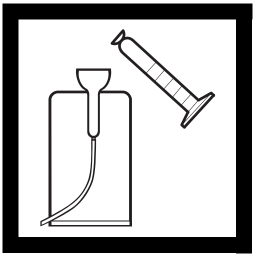
Note: *See Reagent Preparation for instructions on preparing the indicator solution.*



8. Carefully fill the mixing cylinder to the 80-mL mark with sample. Stopper the cylinder and gently invert it twice to mix. Proceed to step 9 immediately.

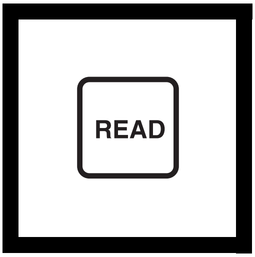
---

* Adapted from *Standard Methods for the Examination of Water and Wastewater.*



9. Fill the funnel of the Pour-Thru Cell with the reacted sample from the mixing cylinder.

Note: *It is not necessary to pour the entire sample into the Pour-Thru Cell; approximately half of the sample may be discarded.*



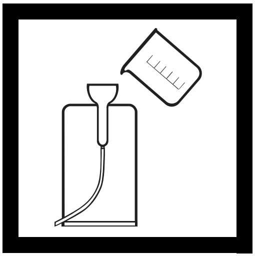
10. After the flow has stopped, press: **READ**

The display will show:

Reading. . . .

then the result in mg/L chlorine (Cl_2) will be displayed.

Note: *If the display shows* ***OVERRANGE****, dilute a fresh sample and repeat the test. A slight loss of chlorine may occur during the dilution. Multiply the result by the appropriate dilution factor; see Section I.*



11. Flush the Pour-Thru Cell with at least 50 mL of deionized water immediately after use.

Note: *Protect the Pour-Thru Cell from contamination by inverting a small beaker over the top of the glass funnel when not in use.*

Sampling and Storage

Samples must be analyzed immediately and cannot be preserved for later analysis. A common testing error is introduced if the analyst does not obtain a representative sample. If sampling from a tap, let the water flow for at least five minutes to ensure a representative sample. Let the container overflow with the sample several times, then cap the sample container so there is no headspace (air) above the sample. Perform the chlorine analysis immediately.

Avoid plastic containers since these may have a chlorine demand. Pretreat glass sample containers to remove any chlorine demand by soaking in a dilute bleach solution (1 mL commercial bleach to l liter of deionized water) for at least 1 hour. Rinse thoroughly with deionized water.

If sample containers are rinsed thoroughly with deionized water after use, only occasional pretreatment is necessary. A pre-treated BOD bottle with a ground-glass stopper makes an ideal sample container for chlorine analysis.

Treating Analysis Labware

Glassware used in this test must be chlorine demand-free. Fill the 100 mL mixing cylinder and sample container with a dilute solution of chlorine bleach prepared by adding 1 mL of commercial bleach to 1 liter of water. Soak in this solution at least one hour. After soaking, rinse with copious amounts of deionized water and allow to dry before use. If the mixing cylinder is thoroughly rinsed with deionized water and allowed to dry after each use, only occasional pretreatment is necessary. Do not use the same mixing cylinder for Free and Total Chlorine analysis.

Treat the Pour-Thru Cell similarly with dilute bleach and let stand for several minutes. Rinse several times with deionized water.

Cleaning the Pour-Thru Cell

The Pour-Thru Cell may accumulate a buildup of colored reaction products, especially if the reacted solutions are allowed to remain in the cell for long periods after measurement. Remove the buildup by rinsing the cell with 5.25 N Sulfuric Acid followed by several rinsings with deionized water.

Reagent Preparation

The Free Chlorine Indicator Solution must be prepared before use. Using a powder funnel, add the contents of one 24 g bottle of DPD Powder (Cat. No. 22972-55) to one 473-mL bottle of Free Chlorine Indicator Solution (Cat. No. 23140-11). Invert several times and swirl until the powder is completely dissolved. A pink color may develop, but should not affect results.

This solution will give accurate results for at least one month after mixing when stored at 20-25 °C (68-77 °C). Write the date of preparation on the Indicator Solution Bottle. Discard any remaining solution after one month. Use of this reagent after one month may result in high reagent blanks and low values at high concentration. Do not combine fresh reagent with previously mixed reagent.

Accuracy Check

Standard Additions Method

a) Snap the top off a Chlorine Voluette Ampule Standard Solution, 50 to 75 mg/L Cl_2.

b) Use the TenSette Pipet to add 0.3, 0.6 and 0.9 mL of standard to three 80-mL samples, respectively. Swirl gently to mix.

c) Analyze each sample as described above. Each 0.3 mL of standard will cause an incremental increase in chlorine, the exact value of which depends on the concentration in the ampule. Check the label enclosed with the ampules for this value.

d) Calculate the concentration of chlorine added to each sample as follows:

$$\frac{\text{mL of standard addition}}{\text{mL of standard addition} + \text{mL of sample}} \times \text{chlorine concentration in ampule}$$
$$= \text{concentration of chlorine added to the sample}$$

Example: $\frac{0.3 \text{ mL}}{80.3 \text{ mL}} \times 72.3 \text{ mg/L} = 0.27 \text{ mg/L chlorine added to the sample}$

e) If the concentration of each sample does not increase by the calculated amount, refer to *Standard Additions* in *Section I.*

Precision

In a single laboratory using 8 concentrations of chlorine standards and two lots of reagents with a DR/2010, a single operator obtained a calibration curve that showed a 99% confidence interval at 1.00 mg/L of ±0.004 mg/L chlorine.

Interferences

Samples containing more than 400 mg/L alkalinity may not develop the full amount of color, or it may instantly fade. Neutralize these samples to a pH of 6 to 7 with 1 N Sulfuric Acid. Determine the amount required on a separate 80-mL sample, then add the same amount to the sample to be tested.

***Note:** If sodium arsenite is used, collect the spent sample for proper disposal according to the hazardous waste regulations for arsenic. Refer to the Instrument Manual for information on modifying the Pour-Thru Cell for collecting the sample after analysis.*

Samples containing monochloramine will cause a gradual drift to higher chlorine readings. When read within one minute of reagent addition, 3.0 mg/L monochloramine will cause an increase of less than 0.1 mg/L in the free chlorine reading.

Bromine, iodine, ozone and oxidized forms of manganese also may react and show as chlorine. Hexavalent chromium at levels >1 mg/L will cause a positive interference.

To compensate for the effects of manganese (Mn^{4+}) or chromium (Cr^{6+}), adjust pH to 6 to 7 as described above, then add 9 drops of potassium iodide, 30 g/L, to 80 mL of sample, mix and wait 1 minute. Add 9 drops of sodium arsenite, 5 g/L, and mix. Analyze this sample as described above. (If chromium is present, allow exactly the same reaction period with the DPD for both analyses.) Subtract the result of this test from the original analysis to obtain the accurate chlorine result.

Hardness at levels below 1000 mg/L as $CaCO_3$ will not interfere.

Summary of Method

Chlorine in the sample as hypochlorous acid or hypochlorite ion (free chlorine or free available chlorine) immediately reacts with DPD (N,N-diethyl-p-phenylenediamine) indicator to form a red color which is proportional to the chlorine concentration.

REQUIRED REAGENTS

	Cat. No.
Reagent Set	25569-00
Includes: (1) 22972-55, (1) 23140-11, (1) 23141-11	

Description	Quantity Required Per Test	Unit	Cat. No.
DPD Indicator Powder		24 g	22972-55
Free Chlorine Indicator Solution	1 mL	473 mL	23140-11
Free Chlorine Buffer Solution	1 mL	473 mL	23141-11

REQUIRED APPARATUS

Cylinder, mixing, glass, 100 mL	1	each	1896-42
Dispenser, fixed volume, 1.0 mL Repipet Jr.	2	each	21113-01
Pour-Thru Cell Assembly Kit	1	each	45215-00

OPTIONAL REAGENTS

Description	Unit	Cat. No.
Chlorine Standard Solution, Voluette Ampule, 50-75 mg/L, 10 mL	16/pkg	14268-10
Chlorine Standard Solution, Voluette Ampule, 50-75 mg/L, 2 mL	20/pkg	14268-20
Potassium Iodide Solution, 30 g/L	100 mL* MDB	343-32
Sodium Arsenite, 5 g/L	100 mL* MDB	1047-32
Sodium Hydroxide Standard Solution, 1.000 N	100 mL* MDB	1045-32
Sulfuric Acid Standard Solution, 1.000 N	100 mL* MDB	1270-32
Sulfuric Acid Standard Solution, 5.25 N	1 L	2449-53
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Ampule Breaker Kit	each	24846-00
Beaker, poly, 50 mL	each	1080-41
Bottle, wash, 125 mL	each	21901-43
Bottle, BOD, w/stopper, 300 mL	each	621-00
Funnel, powder	each	22644-67
pH Meter, *sension*™*1*, portable	each	51700-10
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

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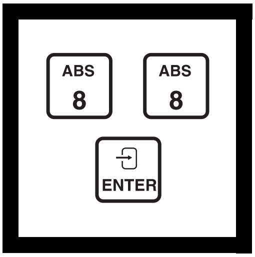
* Contact Hach for larger sizes.

Method 10069

CHLORINE, FREE, HIGH RANGE (0 to 5.00 mg/L as Cl_2)

DPD Method*

For water and wastewater



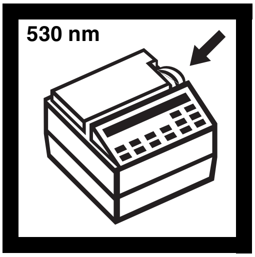
1. Enter the stored program for free chlorine, HR method.

Press: **88 ENTER**

The display will show:

DIAL nm TO 530

Note: *The Pour-Thru Cell can be used with this procedure.*



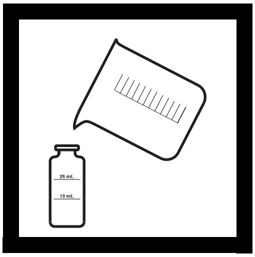
2. Rotate the wavelength dial until the small display shows:

530 nm

When the correct wavelength is dialed in the display will quickly show:

Zero Sample

then: **mg/L Cl_2 HR**



3. Fill two clean dual-screened sample cells each to the 10-mL mark with sample.

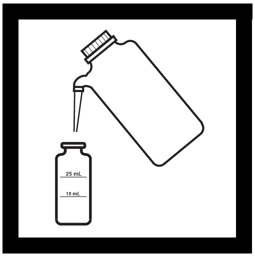
Note: *For most accurate work, use two clean 25-mL mixing graduated cylinders.*

Note: *Samples must be analyzed immediately.*

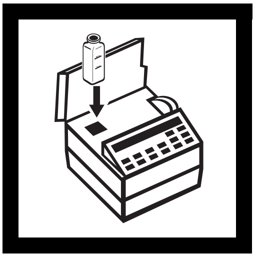
Note: *If using Cat. No. 26294 sample cells, use Cat. No. 14480 stoppers.*

4. Add the contents of one DPD Free Chlorine Powder Pillow for 25 mL samples to one cell. Stopper the cell and invert several times to dissolve the powder. Remove the stopper from the sample cell.

Note: *A magenta color will develop if chlorine is present.*



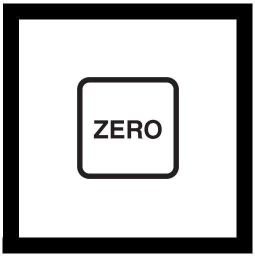
5. Within one minute of reagent addition, add deionized Water to each cell to the 25-mL mark. Cap and invert each cell twice to mix.



6. Place the diluted sample (without reagent) into the cell holder. Close the light shield.

Note: *Place the cell so that the graduations are facing forward.*

Note: *Remove the cell stoppers to fully close the light shield.*

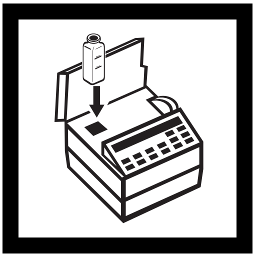


7. Press: **ZERO**

The display will show:

Zeroing...

then: **0.00 mg/L Cl_2 HR**



8. Place the prepared, reacted sample into the cell holder. Close the light shield.

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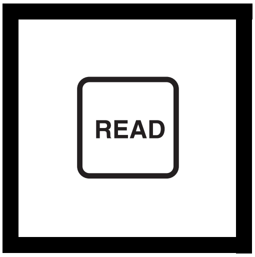
* Adapted from *Standard Methods for the Examination of Water and Wastewater*



9. Press: **READ**

The display will show:

Reading. . . .

then the result in mg/L Cl_2 will be displayed.

Sampling and Storage

Analyze samples for chlorine immediately after collection. Free chlorine is a strong oxidizing agent and reacts rapidly with various compounds. Many factors such as sunlight, pH, temperature and sample composition will influence decomposition of free chlorine in water.

Avoid plastic containers since these may have a large chlorine demand. Pretreat glass sample containers to remove any chlorine demand by soaking in a dilute bleach solution (1 mL commercial bleach to 1 liter of deionized water) for at least 1 hour. Rinse thoroughly with deionized or distilled water. If sample containers are rinsed thoroughly with deionized or distilled water after use, only occasional pre-treatment is necessary.

A common error in testing for chlorine is obtaining a representative sample. If sampling from a tap, let the water flow for at least 5 minutes to ensure a representative sample. Let the container overflow with the sample several times, then cap the sample container so there is no headspace (air) above the sample. If sampling with a sample cell, rinse the cell several times with the sample, then carefully fill to the 10-mL mark. Proceed with the chlorine test immediately.

Interferences

Do not use the same sample cells for free and total chlorine. If trace iodide from the total chlorine reagent is carried over to the free chlorine test, monochloramine could interfere. It is best to use separate, dedicated sample cells for free and total chlorine determinations.

Table 1 Interfering Substances and Suggested Treatments

<table>
<tr><th>Interfering Substance</th><th>Interference Level and Treatment</th></tr>
<tr><td>Bromine, Br_2</td><td>Interferes at all levels</td></tr>
<tr><td>Chlorine Dioxide, ClO_2</td><td>Interferes at all levels</td></tr>
<tr><td>Chloramines, organic</td><td>May interfere</td></tr>
<tr><td>Iodine, I_2</td><td>Interferes at all levels</td></tr>
<tr><td>Manganese, oxidized (Mn^{4+}, Mn^{7+})
or
Chromium, oxidized (Cr^{6+})</td><td>Adjust sample pH to 6-7.
Add 3 drops potassium iodide (30 g/L) to a 10-mL sample.
Mix and wait 1 minute.
Add 3 drops sodium arsenite (5 g/L) and mix.
Analyze the treated sample as described in the procedure.
Subtract the result from this test from the original analysis to obtain the correct chlorine concentration.</td></tr>
<tr><td>Monochloramine</td><td>For conventional free chlorine (beyond the “breakpoint”) typical monochloramine concentrations are very low. If monochloramine is present in the sample, its interference in the free chlorine test depends on sample temperature, relative concentration or monochloramine to free chlorine, and the time required to perform the analysis.
Typical interference levels of monochloramine on the free chlorine test with a 1-minute test time are listed below (interference as mg/L Cl_2).
<table>
<tr><td></td><td colspan="4">Sample Temp. °C(°F):</td></tr>
<tr><td>NH_2Cl Level</td><td>5(40)</td><td>10(50)</td><td>20(68)</td><td>30(83)</td></tr>
<tr><td>1.2 mg/L</td><td>+0.15</td><td>0.19</td><td>0.30</td><td>0.29</td></tr>
<tr><td>2.5 mg/L</td><td>+0.35</td><td>0.38</td><td>0.55</td><td>0.61</td></tr>
<tr><td>3.5 mg/L</td><td>+0.38</td><td>0.56</td><td>0.69</td><td>0.73</td></tr>
<tr><td>5.0 mg/L</td><td>+0.68</td><td>0.75</td><td>0.93</td><td>1.05</td></tr>
</table></td></tr>
<tr><td>Ozone</td><td>Interferes at all levels</td></tr>
<tr><td>Peroxides</td><td>May interfere</td></tr>
<tr><td>Extreme sample pH
or
Highly buffered samples</td><td>Adjust to pH 6-7 using acid or base.</td></tr>
</table>

Method Performance

Precision

at mg/L Cl_2	99% Confidence Limits
0.10	±0.02 mg/L
2.50	±0.02 mg/L
3.40	±0.02 mg/L

Sensitivity

Portion of Curve	ΔAbs	ΔConcentration
at 0.10 mg/L Cl_2	0.010	0.040 mg/L
at 2.50 mg/L Cl_2	0.010	0.046 mg/L
at 3.40 mg/L Cl_2	0.010	0.049 mg/L

Accuracy Check

Standard Additions Method

a) Snap the neck off a HR Chlorine Ampule Standard Solution.

b) Use the TenSette Pipet to add 0.1 mL of the standard to 10-mL of sample (this is the spiked sample). Swirl to mix.

c) Analyze the spiked sample, beginning at Step 4 of the procedure.

d) Calculate the concentration of mg/L chlorine added to the sample:

$$\frac{0.1 \text{ mL (volume of sample added)} \times \text{Label Value (mg/L chlorine)}}{10.1 \text{ (sample + standard volume)}}$$

e) The spiked sample result (Step c) should reflect the analyzed sample result + the calculated mg/L Cl_2 added (Step d).

f) If this increase does not occur, see *Standard Additions* in *Section I* for more information.

Summary of Method

The range of analysis using the DPD method for free chlorine can be extended by adding more indicator in proportion to sample volume. Thus, a larger fill powder pillow of DPD Free Chlorine Reagent is added to a 10-mL sample portion. After color development, the sample volume is adjusted to 25 mL using deionized water. This allows color measurement to be made directly in the 1-inch sample cell, eliminating the need to transfer to a smaller pathlength cell.

Dilution of the reacted sample avoids potential loss of chlorine when the sample is diluted prior to testing. In addition, chlorine demand-free water is not required. Some loss of accuracy and precision will occur from dilution. The DPD procedure for free chlorine (program 80) is recommended for concentrations less than 2 mg/L.

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
DPD Free Chlorine Reagent Powder Pillows	1 pillow	100/pkg	14070-99
deionized Water	30 mL	500 mL	272-49

REQUIRED EQUIPMENT AND SUPPLIES

Cells, Sample, 1-inch, matched pair w/stopper	2	each	26126-02
or			
Cells, Sample, 1-inch, dual graduated	2	each	26294-02
Stopper, Hollow	2	6/pkg	14480-00

OPTIONAL REAGENTS AND STANDARDS

Chlorine Standard Solution, PourRite ampules, 50-75 mg/L	20/pkg	14268-20
Potassium Iodide Solution, 30 g/L	100 mL MDB	343-32
Sodium Arsenite, 5 g/L	100 mL MDB	1047-32
Sodium Hydroxide Standard Solution, 1N	100 mL MDB	1045-32
Sulfuric Acid Standard Solution, 1N	100 mL MDB	1270-32

OPTIONAL EQUIPMENT AND SUPPLIES

Ampule Breaker Kit	each	24846-00
Cylinder, graduated, mixing 25-mL	2	20886-40
pH Paper, pH 1-11	each	391-33
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	each	21856-96
Pour-Thru Cell Assembly Kit	each	45215-00

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

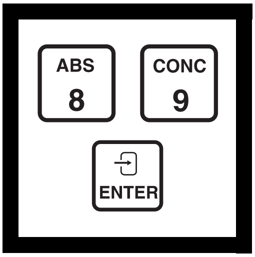
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 10102

CHLORINE, FREE (0.00 to 5.00 mg/L)

For water, wastewater and seawater

DPD Test ‘N Tube™ Method*

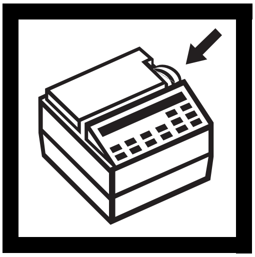


1. Enter the stored program number for Test ‘N Tube Free Chlorine (Cl_2).

Press: **8 9 ENTER**

The display will read:

Dial nm to 530

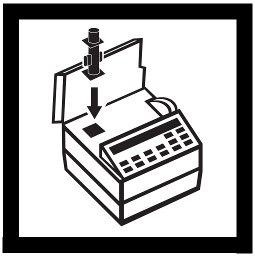


2. Rotate the wavelength dial until the small display reads:

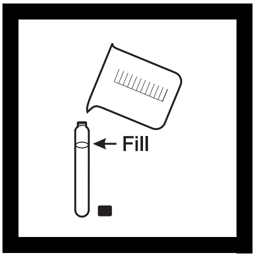
530 nm

When the correct wavelength is dialed in the display will quickly show: **Zero Sample**

then: **mg/L Cl_2**



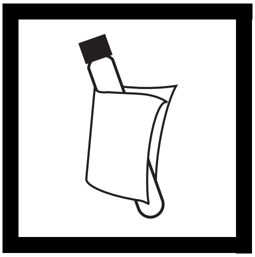
3. Insert the COD Vial Adapter into the cell holder with the marker to the right.



4. Fill an empty Test ‘N Tube vial with sample. This is the sample blank.

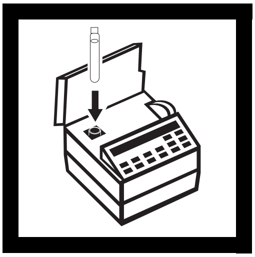
Note: *Fill to the top of the Hach logo “oval” mark.*

Note: *Samples must be analyzed immediately and cannot be preserved for later analysis.*

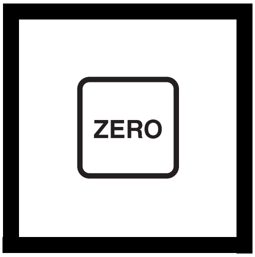


5. Clean the outside of the sample blank vial with a towel.

Note: *Wiping with a damp cloth followed by a dry one removes fingerprints and other marks.*



6. Place the blank into the adapter with the Hach logo facing the front of the instrument. Place the cover on the adapter.



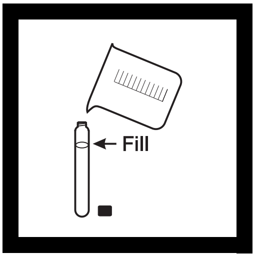
7. Press: **ZERO**

The display will show:

Zeroing...

then:

0.00 mg/L Cl_2 TNT



8. Remove the cap from a Free Chlorine DPD-TNT vial. Add 10 mL of sample.

Note: *Fill to the top of the Hach logo “oval” mark.*

Note: *A pink color will develop if chlorine is present.*

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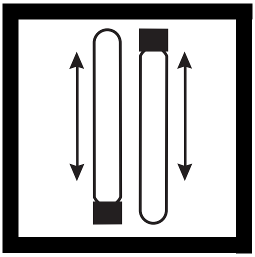
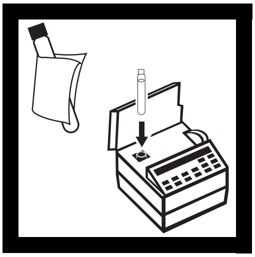
* Adapted from *Standard Methods for the Examination of Water and Wastewater.*

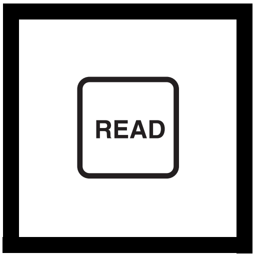


9. Cap and invert at least 10 times to dissolved the powder. This is the prepared sample.

Note: *Use slow, deliberate inversion for complete recovery. Ten inversions should take at least 30 seconds. One inversion equals turning the vial upside down, then returning it to an upright position.*



10. Within 30 seconds after mixing, wipe the prepared sample vial with a towel, then place it in the vial adapter with the Hach logo facing the front of the instrument. Place the cover on the adapter.



11. Press: **READ**

The display will show:

Reading...

then the result in mg/L chlorine will be displayed.

Sampling and Storage

Analyze samples for chlorine **immediately** after collection. Free chlorine is a strong oxidizing agent, and is unstable in natural waters. It reacts rapidly with various inorganic compounds and more slowly oxidizes organic compounds. Many factors, including reactant concentrations, sunlight, pH, temperature and salinity influence decomposition of chlorine in water.

Avoid plastic containers since these may have a large chlorine demand. **Pretreat glass** sample containers to remove any chlorine demand by soaking in a dilute bleach solution (1 mL commercial bleach to l liter of deionized water) for at least 1 hour. Rinse thoroughly with deionized or distilled water. If sample containers are rinsed thoroughly with deionized or distilled water after use, only occasional pre-treatment is necessary.

A common error in testing for chlorine is obtaining a unrepresentative sample. If sampling from a tap, let the water flow for at least five minutes to ensure a representative sample. Let the container overflow with the sample several times, then cap the sample containers so there is no headspace (air) above the sample. Perform the analysis immediately.

Accuracy Check

Standard Additions Method

a) Snap the top off a High Range Chlorine PourRite™ Ampule Standard Solution.

b) Use a TenSette® Pipet to add 0.1 mL of the standard to the 10-mL sample in a beaker (this is the spiked sample). Swirl to mix.

c) Anaylze the spiked sample according to the procedure.

Calculate the concentration of mg/L chlorine added to the sample:

$$\text{mg/L chlorine added} = \frac{0.1\ (\text{vol. standard added}) \times \text{l Label value (mg/L Cl}_2)}{10.1\ (\text{sample + standard volume}}$$

d) The spiked sample result (step c) should reflect the analyzed sample result + the calculated mg/L Cl_2 added (step d).

e) If these increases do not occur, see *Standard Additions* in *Section 1* for more information.

Method Performance

Precision

In a single laboratory, using a standard solution of 2.80 mg/L chlorine and two representative lots of reagent with a DR/2010, a single operator a standard deviation of ±0.02 mg/L chlorine.

Estimated Detection Limit (EDL)

The EDL for program 89 is 0.07 mg/L. The EDL is the calculated lowest average concentration in a deionized water matrix that is different from zero with a 99% level of confidence. For more information on derivation and use of Hach's estimated detection limit, see *Section 1.*

Interferences

<table>
<tr><th>Interfering Substance</th><th>Interference Level and Treatment</th></tr>
<tr><td>Acidity</td><td>Greater than 150 mg/L $CaCO_3$. May not develop full color or color may fade instantly. Neutralize to pH 6-7 with 1 N sodium hydroxide. Determine amount to be added on separate sample aliquot, then add the same amount to the sample being tested. Correct for volume addition (See <i>Correcting for Volume Additions</i> in <i>Section 1</i>.</td></tr>
<tr><td>Alkalinity</td><td>Greater than 250 mg/L $CaCO_3$. May not develop full color or color may fade instantly. Neutralize to pH 6-7 with 1 N sulfuric acid. Determine amount to be added on separate sample aliquot, then add the same amount to the sample being tested. Correct for volume addition (See <i>Correcting for Volume Additions</i> in <i>Section 1.</i></td></tr>
<tr><td>Bromine</td><td>Interferes at all levels</td></tr>
<tr><td>Chlorine Dioxide</td><td>Interferes at all levels</td></tr>
<tr><td>Chloramines, organic</td><td>May interfere</td></tr>
<tr><td>Hardness</td><td>No effect at less than 1,000 mg/L as $CaCO_3$</td></tr>
<tr><td>Iodine</td><td>Interferes at all levels</td></tr>
<tr><td>Manganese, oxidized (Mn^{4+}, Mn^{7+})
or
Chromium, oxidized (Cr^{6+})</td><td>1. Adjust sample pH to 6-7.
2. Add 3 drops potassium iodide (30 g/L) to a 25-mL sample.
3. Mix and wait one minute.
4. Add 3 drops sodium arsenite (5 g/L) and mix.
5. Analyze 10 mL of the treated sample as described in the procedure.
6. Subtract the result from this test from the original analysis to obtain the correct chlorine concentration.</td></tr>
<tr><td>Monochloramine</td><td>For conventional free chlorine disinfection (beyond the breakpoint), typical monochloramine concentrations are very low. If monochloramine is present in the sample, its interference in the free chlorine test depends on the sample temperature, relative amount of monochloramine to free chlorine, and the time required to do the analysis. Typical interference level of monochloramine in the free chlorine test are listed below (as mg/L Cl_2).
<table>
<tr><th>NH_2Cl</th><th colspan="4">Sample Temp. °C (°F)</th></tr>
<tr><th>(as Cl_2)</th><th>5 (40)</th><th>10 (50)</th><th>20 (68)</th><th>30 (83)</th></tr>
<tr><td>1.2 mg/L</td><td>+0.15</td><td>+0.19</td><td>+0.30</td><td>+0.29</td></tr>
<tr><td>2.5 mg/L</td><td>0.35</td><td>0.38</td><td>0.55</td><td>0.61</td></tr>
<tr><td>3.5 mg/L</td><td>0.38</td><td>0.56</td><td>0.69</td><td>0.73</td></tr>
</table>
</td></tr>
<tr><td>Ozone</td><td>Interferes at all levels</td></tr>
<tr><td>Peroxides</td><td>May interfere</td></tr>
<tr><td>Extreme sample pH and highly buffered samples</td><td>Adjust to pH 6-7. See <i>Interferences</i> in <i>Section 1</i>.</td></tr>
</table>

Summary of Method

Chlorine in the sample as as hypochlorous acid or hypochlorite ion (free chlorine or free available chlorine) immediately reacts with DPD (N, N-diethyl-p-phenylenediamine) to form a magenta color which is proportional to the chlorine concentration.

Pollution Prevention and Waste Management

Samples treated with sodium arsenite for manganese or chromium interferences will be hazardous wastes as regulated by Federal RCRA for arsenic (D004). See *Section 3* for more information on proper disposal of these materials.

REQUIRED REAGENTS & APPARATUS

Description	Quantity Required Per Test	Unit	Cat. No.
Test 'N Tube DPD Free Chlorine Reagent	1 vial	50/pkg	21055-45
Test 'N Tube Vials (for blank)	1 vial	25/pkg	25831-25

REQUIRED APPARATUS

COD/TNT Adapter	1	each	44799-00

OPTIONAL REAGENTS

Chlorine Standard Solution, PourRite ampule, 2 mL, 50-75 mg/L Cl_2		20/pkg	14268-20
Potassium Iodide Solution, 30 g/L		100 mL* MDB	343-32
Sodium Arsenite Solution, 5 g/L		100 mL* MDB	1047-32
Sodium Hydroxide Standard Solution, 1.00 N		100 mL* MDB	1045-32
Sulfuric Acid Standard Solution, 1.000 N		100 mL* MDB	1270-32

OPTIONAL APPARATUS

Beaker, 50 mL		each	500-41
pH Indicator Paper, 1 to 11 pH units		5 rolls/pkg	391-33
pH Meter, *sens***ion**™***1***, portable		each	51770-10
Pipet, TenSette, 0.1 to 1.0 mL		each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet		50/pkg	21856-96
PourRite Ampule Breaker		each	24846-00
Test Tube Rack		each	18641-00

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

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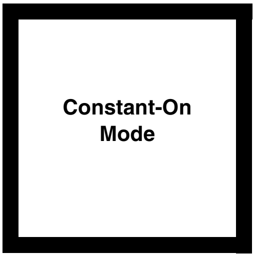
* Marked Dropper Bottle - contact Hach for larger sizes.

Method 8370
For water

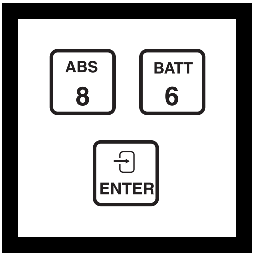
CHLORINE, TOTAL, Ultra Low Range (0-500 µg/L)

DPD Method* ; USEPA accepted for reporting drinking water analysis**; Patent No. 5,362,650



1. Configure the DR/2010 to be used in the constant-on mode (see Instrument Manual). Allow the instrument to warm up 5-10 minutes.

Note: *The Pour-Thru Cell must be used.*

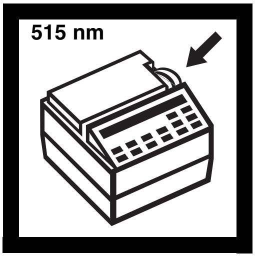


2. Enter the stored program number for Ultra Low Range Chlorine.

Press: **8 6 ENTER**

The display will show:

Dial nm to 515



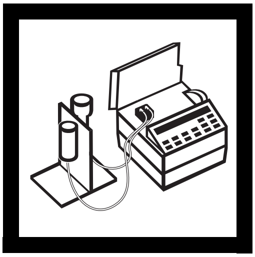
3. Rotate the wavelength dial until the small display shows:

515 nm

When the correct wavelength is dialed in the display will quickly show:

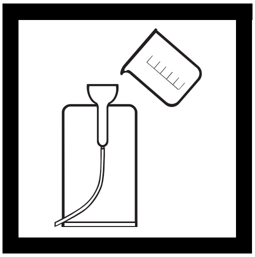
Zero Sample

then: **µg/L Cl_2 ULR**

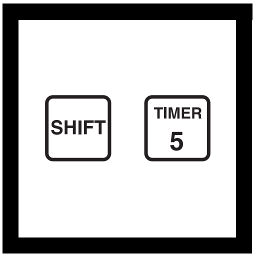


4. Install the Pour-Thru Cell and flush with 50 mL of deionized water.

Note: *See Treating Analysis Labware section.*

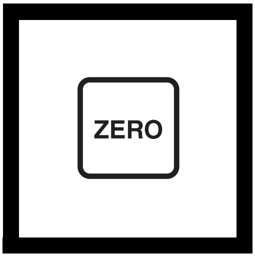


5. Pour at least 50 mL of sample into the Pour-Thru Cell.



6. After the flow stops, begin a 3-minute period by pressing:

SHIFT TIMER



7. When the timer beeps, the display will show:

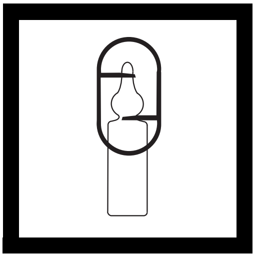
µg/L Cl_2

Press: **ZERO**

The display will show:

Zeroing. . .

then: **0 µg/L Cl_2 ULR**



8. Break open one ampule of ULR Chlorine Buffer Solution.

Note: *The Ampule Breaker is a convenient way to open ampules.*

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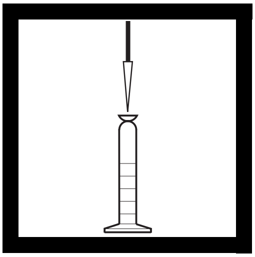
* Adapted from *Standard Methods for the Examination of Water and Wastewater.*

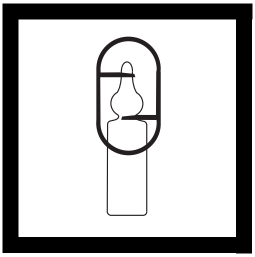
** Method is equivalent to 4500-Cl G.



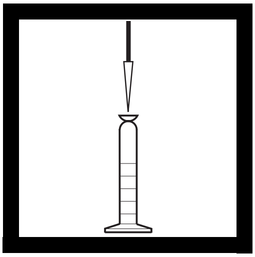
9. Using a TenSette Pipet with a clean tip, transfer 1.0 mL of buffer to a clean, treated 50-mL graduated mixing cylinder.

Note: *See* Treating Analysis Labware *section.*

Note: *The ampules contain more than 1.0 mL for ease of reagent transfer. Discard excess reagent.*

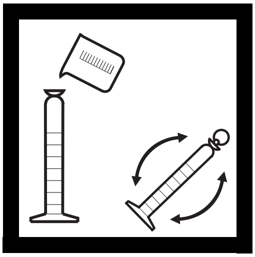


10. Break open one ampule of DPD Indicator Solution for Ultra Low Range Chlorine.



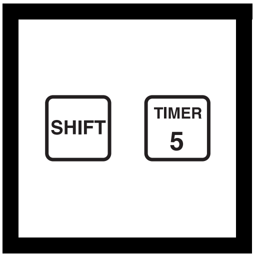
11. Using a TenSette Pipet with a clean tip, transfer 1.0 mL of indicator from the ampule to the cylinder. Swirl to mix the reagents.

Proceed with Step 12 within 1 minute.



12. Avoiding extra agitation, carefully fill the cylinder to the 50-mL mark with sample. Stopper. Gently invert it twice to mix (the prepared sample).

Note: *Analyze samples immediately after collection.*

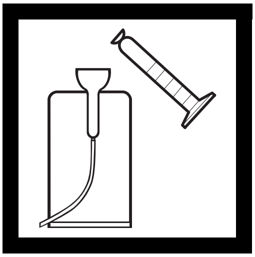


13. Press:

SHIFT TIMER

A three-minute reaction period will begin.

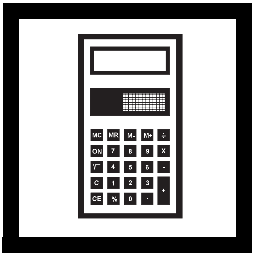
Note: *Measure the sample 3-4 minutes after mixing the sample and reagents. If less than 3 minutes elapses, reaction with chloramines may be incomplete. A reading after 4 minutes may result in higher reagent blank values.*



14. When the timer beeps, pour the contents of the graduated mixing cylinder into the Pour-Thru Cell.

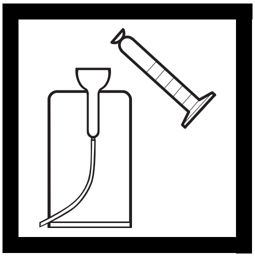
Read the Display.

15. After the flow stops, the result in μg/L Cl_2 will be displayed.



16. Determine the reagent blank using the procedure on page 177. Subtract the reagent blank value (in μg/L) from the value obtained in Step 15.

Note: *Determine the reagent blank value for a combined lot of Indicator/ Buffer at least once a day. If sample color or turbidity varies, determine a reagent blank for each sample.*

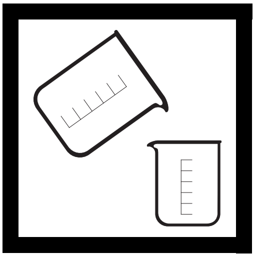


17. Flush the Pour-Thru Cell with at least 50 mL of deionized water immediately after use.

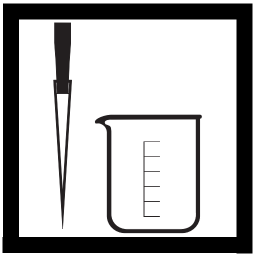
Determining the Reagent Blank Value

Repeat Steps 1-4.

1. Set up the DR/2010 as described in Steps 1-4 of the procedure.

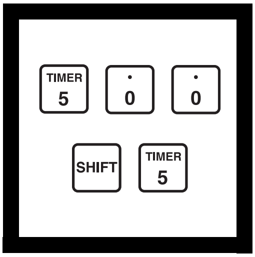


2. Collect about 100 mL of deionized or tap water in a clean 250-mL beaker.



3. Using a TenSette Pipet, add 1.0 mL of Blanking Reagent to the beaker. Swirl several times to mix.

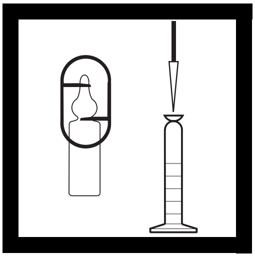
Note: The Blanking Reagent removes chlorine from the sample.



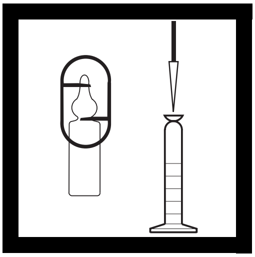
4. Press:

5 0 0 SHIFT TIMER

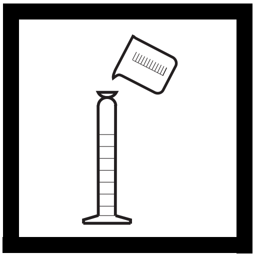
A five-minute reaction period will begin.



5. After the timer beeps, break open one ampule of ULR Chlorine Buffer Solution. Using a TenSette Pipet with a clean tip, transfer 1.0 mL of buffer from the ampule to a clean 50-mL graduated mixing cylinder.



6. Break open one ampule of ULR DPD Indicator Solution. Using a TenSette Pipet with a clean tip, transfer 1.0 mL of indicator from the ampule to the cylinder. Swirl to mix the reagents. Proceed with Step 7 within 1 minute.



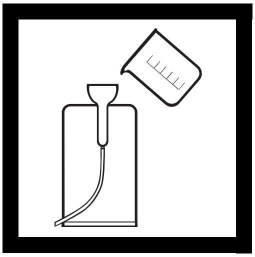
7. Fill the cylinder to the 50-mL mark with the dechlorinated water from Step 3. Cap and invert twice to mix. Save the remaining water for Step 9.

SHIFT TIMER 5

8. Press:

SHIFT TIMER

A three-minute reaction period will begin.



9. During the reaction period, flush the Pour-Thru Cell with the remainder of the original dechlorinated water from Step 7.

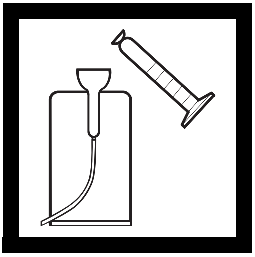
ZERO

10. When the flow stops, press: **ZERO**

The display will show:

Zeroing. . .

then: **0 µg/L Cl_2 ULR**

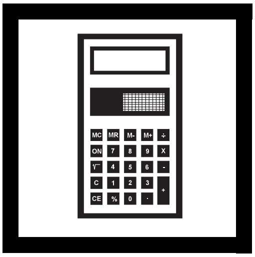


11. When the timer beeps, pour the contents of the cylinder into the Pour-Thru Cell.

Read the Display.

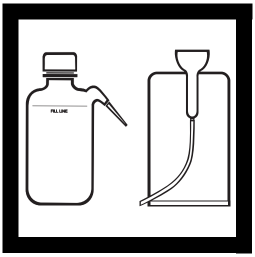
12. After the flow stops, the reagent blank value will be displayed in µg/L Cl_2.

Record this value.



13. Use this value to correct the sample result obtained in the procedure.

Note: *The reagent blank value is normally less than 5 μg/L. If the value is greater than 5 μg/L, an interfering substance may be present in the blanking water or the DPD Indicator may be developing some color. Blanks of up to 5 μg/L may be used.*



14. Flush the Pour-Thru Cell with at least 50 mL of deionized water immediately after use.

Sampling and Storage

Analyze samples for chlorine **immediately** after collection. Free chlorine is a strong oxidizing agent, and it is unstable in natural waters. It reacts rapidly with various inorganic compounds and more slowly oxidizes organic compounds. Many factors, including reactant concentrations, sunlight, pH, temperature and salinity influence decomposition of chlorine in water.

Avoid plastic containers since these may have a large chlorine demand. **Pretreat glass** sample containers to remove any chlorine demand by soaking in a dilute bleach solution (1 mL commercial bleach to l liter of deionized water) for at least 1 hour. Rinse thoroughly with deionized or distilled water. If sample containers are rinsed thoroughly with deionized or distilled water after use, only occasional pre-treatment is necessary.

A common error in testing for chlorine is introduced when a representative sample is not obtained. If sampling from a tap, let the water flow for at least 5 minutes to ensure a representative sample. Let the container overflow with the sample several times, then cap the sample containers so there is no headspace (air) above the sample. If sampling with a sample cell, rinse the cell several times with the sample, the carefully fill to the 10-mL mark. Perform the chlorine analysis immediately.

Treating Analysis Labware

Glassware used in the test must be chlorine demand-free. Treat all glassware with a dilute solution of chlorine bleach prepared by adding 0.5 mL of commercial bleach to 1 liter of water. Soak glassware in this solution at least one hour. After soaking, rinse the glassware with copious amounts of deionized water and allow to dry before use.

Treat the Pour-Thru Cell similarly with dilute bleach and let stand for several minutes and then rinse several times with deionized water.

Cleaning the Pour-thru Cell

The Pour-Thru Cell may accumulate a buildup of colored reaction products, especially if the reacted solutions are allowed to remain in the cell for long periods after measurement. Remove the buildup by rinsing the cell with 5.25 N sulfuric acid followed by several rinsings with deionized water.

Precision

In a single laboratory, using a standard solution of 9 µg/L chlorine, and one lot of reagents, and a DR/2010, a single operator obtained a standard deviation of ±0.4 µg/L.

Minimum Detection Level

Based on the USEPA's procedure for estimating the method detection limit (40 CFR, Pt. 136, App. B, 7-1-95), the estimated detection limit, using the procedure as written, is less than 2 µg/L chlorine.

Interferences

Do not use the same sample cells for free and total chlorine. If trace iodide from the total chlorine reagent is carried over into the free chlorine determination, monochloramine will interfere. It is best to use separate, dedicated sample cells for free and total chlorine determinations.

Oxidized manganese reacts directly with DPD. The apparent chlorine result is about 3 µg/L per every µg/L Mn^{7+}. Mn^{2+} does not interfere up to 5000 µg/L.

Copper (Cu^{2+}) and iron (Fe^{3+}) do not interfere up to 1000 µg/L each.

Bromine, iodine, ozone, and other strong oxidizing agents may also interfere.

Nitrite interference will vary according to the following table:

mg/L Nitrite	Apparent µg/L Chlorine
2.0	3
5.0	5
10.0	7
15.0	16
20.0	18

Summary of Method

This method is designed for clean water, low in color and turbidity. The main applications include monitoring for trace chlorine breakthrough of activated carbon beds and feedwater to reverse osmosis membranes or ion-exchange resins.

Several modifications to the normal DPD chlorine method are necessary to measure trace levels of chlorine. The 1-inch Pour-Thru Cell **must** be used in the spectrophotometer. Liquid reagents are also **required**.

The reproducible optics of the Pour-Thru Cell give more stable readings than is possible with sample cells, resulting in more stable measurements.

The reagents are packaged in ampules and sealed under argon gas to ensure stability. Use of liquid reagents eliminates any slight turbidity that might be caused by using powdered reagents. Due to the possible oxidation of the reagents (which could give a positive chlorine reading in the blank), a reagent blank must be determined at least once a day for each lot of reagent used. This reagent blank value is subtracted from the sample result and the corrected value is the actual chlorine concentration.

REQUIRED REAGENTS

	Cat. No.
ULR Chlorine Reagent Set (about 20 tests) Includes: (1) 24930-23, (1) 24931-20, (1) 24932-20	25630-00

Description	Quantity Required Per Test	Unit	Cat. No
ULR Chlorine Buffer Solution	1 mL	20/pkg	24931-20
DPD Indicator Solution for ULR Chlorine	1 mL	20/pkg	24932-20
Blanking Reagent for ULR Chlorine	1 mL	29 mL	24930-23

REQUIRED APPARATUS

Beaker, 250 mL	1	each	500-46
Cylinder, mixing, graduated, 50 mL	1	each	1896-41
Pipet Tips, for 19700-01 TenSette Pipet	2	50/pkg	21856-96
Pour-Thru Cell Assembly Kit	1	each	45215-00
TenSette Pipet, 0.1 to 1.0 mL	1	each	19700-01

OPTIONAL REAGENTS

Sodium Hydroxide, 50% w/w	500 mL	2180-49
Sulfuric Acid Solution, 5.25 N	1 L	2449-53
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Ampule Breaker Kit	each	24846-00
Bottle, Wash, 250 mL	each	620-31

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 10014

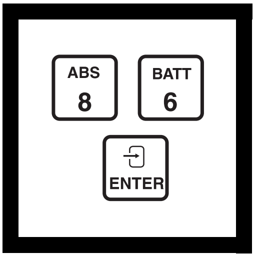
CHLORINE, TOTAL, Ultra Low Range (0-500 µg/L) For Treated Wastewater

DPD Method[1] [2] USEPA Accepted for reporting wastewater analysis[3]

Constant-On
Mode

1. Configure the DR/2010 to be used in the constant-on mode (see Instrument Manual). Allow the instrument to warm up 5-10 minutes.

Note: The Pour-Thru cell must be used.

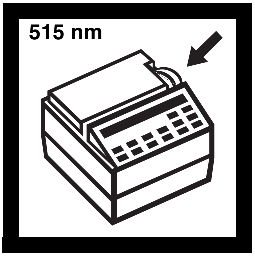


2. Enter the stored program number for Ultra Low Range Chlorine.

Press: **8 6 ENTER**

The display will show:

Dial nm to 515

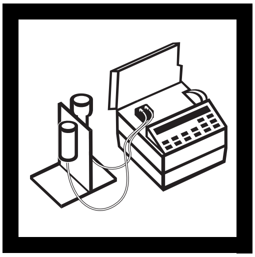


3. Rotate the wavelength dial until the small display shows:

515 nm

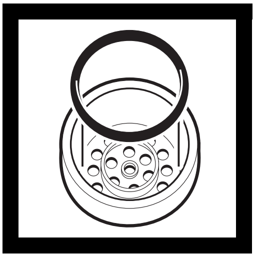
When the correct wavelength is dialed in the display will quickly show: **Zero Sample**

then: **µg/L $C1_2$ ULR**

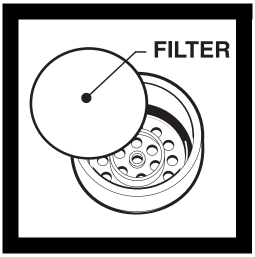


4. Install the Pour-Thru Cell and flush with 50 mL of deionized water.

Note: See Treating Analysis Labware section.

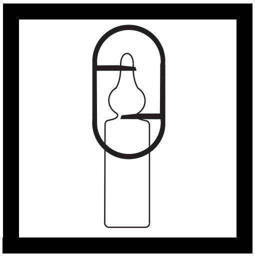


5. Unscrew the cap from the Quick Filter[2] plunger assembly. Be sure the O-ring is properly seated in the cap.



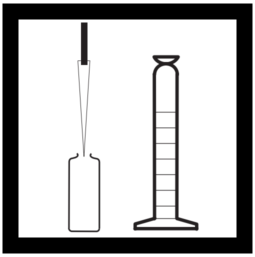
6. Install a new 3-micron filter into the cap well. Wet the filter with a few drops of deionized water. Re-assemble and hand-tighten the cap onto the plunger.

Note: To obtain accurate results, use a new 3-micron filter (specified) for each test.



7. Break open one ampule of ULR Chlorine Buffer Solution.

Note: The Ampule Breaker is a convenient, safe way to open ampules.



8. Using a TenSette Pipet with a clean tip, transfer 1.0 mL of buffer to a clean, treated 50-mL graduated mixing cylinder.

Note: See Treating Analysis Labware section.

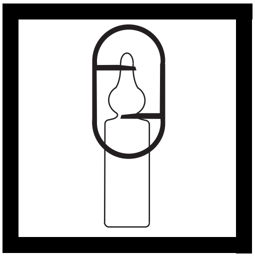
Note: The ampules contain more than 1.0 mL for ease of reagent transfer. Discard excess reagent.

---

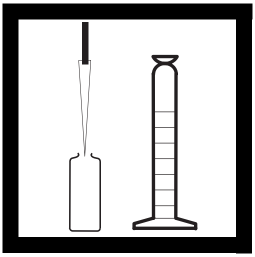
[1] U.S. Patent 5,362,650

[2] U.S. Patent 5,549,816

[3] Procedure is equivalent to Standard Method 4500-Cl D for wastewater

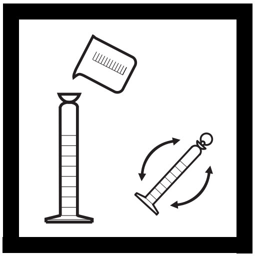


9. Break open one ampule of DPD Indicator Solution for Ultra Low Range Chlorine.

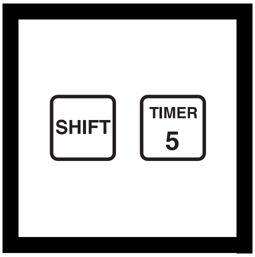


10. Using a TenSette Pipet with a clean tip, transfer 1.0 mL of indicator from the ampule to the cylinder. Swirl to mix reagents.

Proceed with Step 12 within one minute.



11. Avoiding extra agitation, carefully fill the cylinder to the 50-mL mark with sample. Stopper. Gently invert twice to mix (the prepared sample).



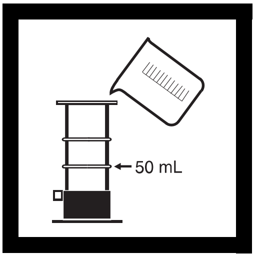
12. Press:

SHIFT TIMER

A three-minute reaction period will begin.

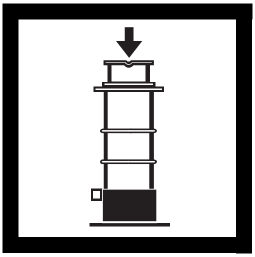
Note: *Measure the sample absorbance 3-6 minutes after mixing the sample and reagents. If less than three minutes elapses, reaction with chloramines may be incomplete. A reading after 6 minutes may result in higher blank values*

Note: *Perform steps 13-18 during the reaction period.*

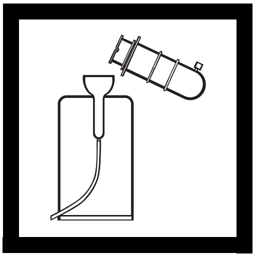


13. During the three-minute period, push the valve button on the Quick Filter's barrel assembly to the "closed" position. Place the barrel assembly into its stand. Pour about 50 mL of the original sample into the barrel.

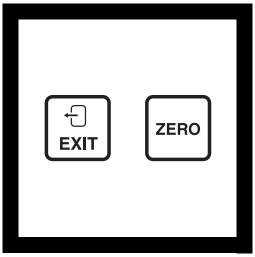
Note: *The lower ring on the barrel assembly represents about 50 mL.*



14. Insert the plunger into the barrel and slowly push the plunger down with even pressure until the plunger is fully seated.



15. Pour the filtered sample from the plunger reservoir into the Pour-Thru Cell.

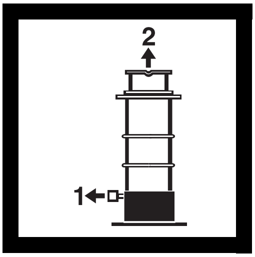


16. After the flow stops, press: **EXIT**, then **ZERO**

The display will show:

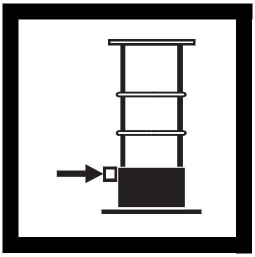
Zeroing. . .

then: **0 µg/L Cl_2 ULR**

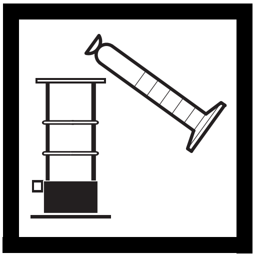


17. Pull the barrel's valve button to the open position (1). Pull the plunger up to separate it from the barrel assembly (2). Discard the remaining unfiltered sample.

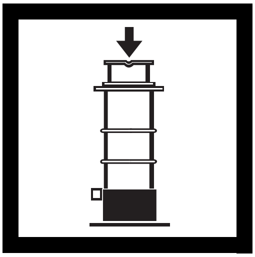
Note: *For very turbid samples, install a new membrane. Alternatively, use a second Quick Filter unit with a new membrane filter installed.*



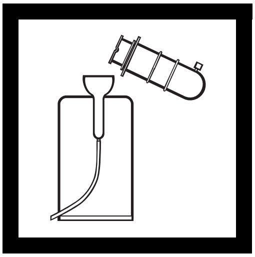
18. Push the barrel's valve button to the closed position. Place the barrel assembly into its stand.



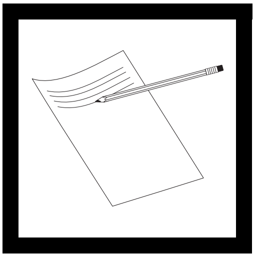
19. When the timer beeps, pour the contents of the graduated mixing cylinder into the barrel.



20. Insert the plunger into the barrel and slowly push the plunger down with even pressure, until the plunger is fully seated.

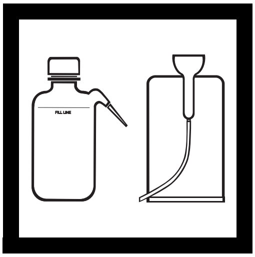


21. Pour the filtered, reacted sample from the plunger reservoir into the Pour-Thru Cell.

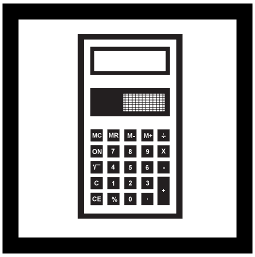


22. After the flow stops and the reading stabilizes, the result in µg/L Cl2 will be displayed. Record the result.

Note: *If a dechlorination agent such as sulfite or sulfur dioxide is present in the sample, the sample result, corrected for the reagent blank, will read "0" or a slightly negative value.*



23. Flush the Pour-Thru Cell with at least 50 mL of deionized water immediately after use.



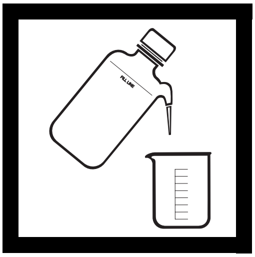
24. Determine the reagent blank using the procedure on page 186. Subtract the reagent blank value (in µg/L) from the value obtained in Step 22.

Note: *Determine the reagent blank value for a combined lot of Indicator/ Buffer at least once a day.*

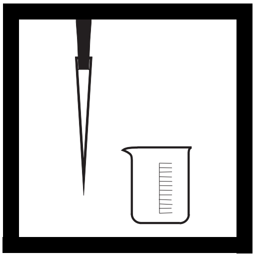
Determination of the Reagent Blank Value

Repeat Steps 1-4

1. Set up the DR/2010 as described in Steps 1-4 of the procedure.

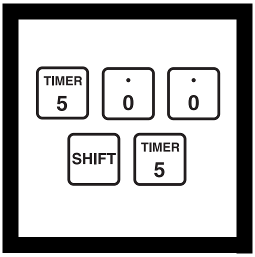


2. Collect about 100 mL deionized or tap water in a clean 250-mL beaker.



3. Using a TenSette Pipet, add 1.0 mL Blanking Reagent to the beaker. Swirl several times to mix.

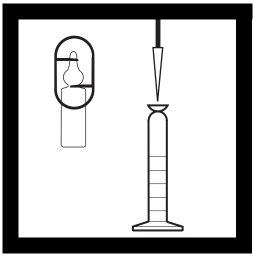
Note: *The Blanking Reagent removes chlorine from the sample.*



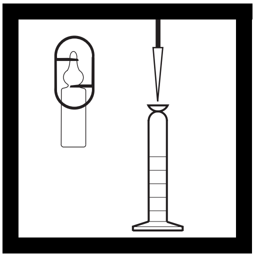
4. Press:

5 0 0 SHIFT TIMER

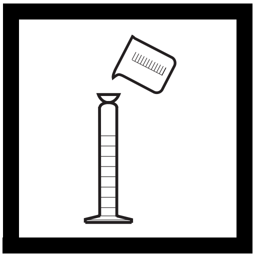
A five-minute reaction period will begin.



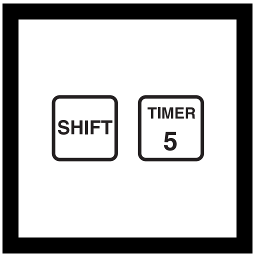
5. After the timer beeps, break open one ampule of ULR Chlorine Buffer Solution. Using a TenSette Pipet with a clean tip, transfer 1.0 mL of buffer from the ampul to a clean 50-mL graduated mixing cylinder.



6. Break open one ampule of ULR DPD Indicator Solution. Using a TenSette Pipet with a clean tip, transfer 1.0 mL of indicator from the ampule to the cylinder. Swirl to mix the reagents. Proceed with Step 7 within 1 minute.



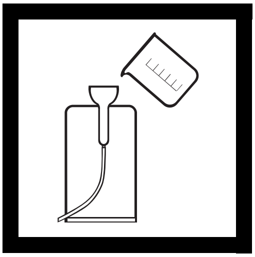
7. Fill the cylinder to the 50-mL mark with the dechlorinated water from Step 3. Cap and invert twice to mix. Save the remaining water for Step 9.



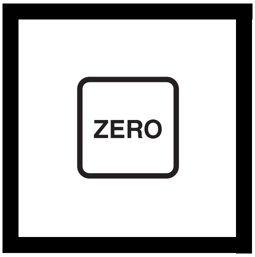
8. Press:

SHIFT TIMER

A three-minute reaction period will begin.



9. During the reaction period, flush the Pour-Thru Cell with the remainder of the original dechlorinated water from Step 7.

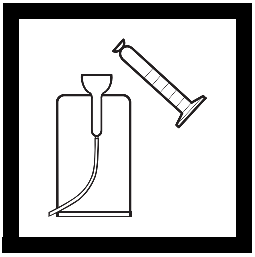


10. When the flow stops, press **ZERO**

The display will show:

Zeroing. . .

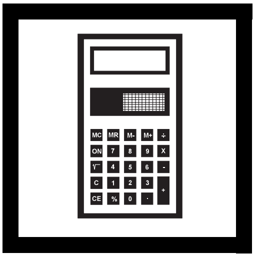
then: **0 µg/L Cl_2 ULR**



11. When the timer beeps, pour the contents of the cylinder into the Pour-Thru Cell.

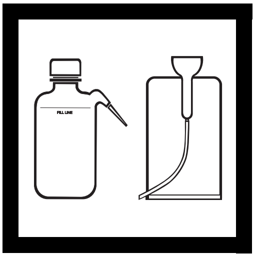
Read the Display.

12. After the flow stops, the reagent blank value will be displayed in µg/L Cl2. Record this value.



13. Use this value to correct the sample result obtained in the procedure.

Note: *The reagent blank value is normally less than 5 µg/L. If the value is greater than 5 µg/L, an interfering substance may be present in the blanking water or the DPD Indicator may be developing some reagent color. Blanks of up to 5µg/L may be used successfully.*



14. Flush the Pour-Thru Cell with at least 50 mL deionized water immediately after use.

Sample Collection and Storage

Analyze samples for chlorine **immediately** after collection. Free chlorine is a strong oxidizing agent, and it is unstable in natural waters. It reacts rapidly with various inorganic compounds and more slowly oxidizes organic compounds. Many factors, including reactant concentrations, sunlight, pH, temperature, and salinity influence decomposition of chlorine in water.

Avoid plastic containers since these may have a large chlorine demand. **Pretreat glass** sample containers to remove any chlorine demand by soaking in a dilute bleach solution (1 mL commercial bleach to l liter of deionized water) for at least 1 hour. Rinse thoroughly with deionized or distilled water. If sample containers are rinsed thoroughly with deionized or distilled water after use, only occasional pre-treatment is necessary.

A common error in testing for chlorine is introduced when a representative sample is not obtained. If sampling from a tap, let the water flow for at least 5 minutes to ensure a representative sample. Let the container overflow with the sample several times, then cap the sample containers so there is no headspace (air) above the sample. If sampling with a sample cell, rinse the cell several times with the sample, the carefully fill to the 10-mL mark. Analyze immediately.

Treating Analysis Labware

Glassware used in the test must be chlorine demand-free. Treat all glassware with a dilute solution of chlorine bleach prepared by adding 0.5 mL of commercial bleach to 1 liter of water. Soak glassware in this solution at least one hour. After soaking, rinse the glassware with large amounts of deionized water and allow to dry before use.

Treat the Pour-Thru Cell similarly with dilute bleach and let stand for several minutes and then rinse several times with deionized water.

Cleaning The Pour-thru Cell

The Pour-Thru Cell may accumulate a buildup of colored reaction products, especially if the reacted solutions are allowed to stand in the cell for long periods after measurements. Remove the buildup by rinsing with 5.25 N sulfuric acid followed by several rinsings with deionized water.

Precision

In a single laboratory using a standard solution of 9 µg/L chlorine, one lot of reagents, and a DR/2010, a single operator obtained a standard deviation of ±0.44 µg/L.

Estimated Detection Limit (EDL)

The EDL for program 86 is 3 µg/L CL_2. The EDL is the calculated lowest average concentration in a deionized water matrix that is different from zero with a 99% level of confidence. For more information on derivation and use of Hach's estimated detection limit, see Section I.

Interferences

Do not use the same sample cells for free and total chlorine. If trace iodide from the total chlorine reagent is carried over into the free chlorine determination, monochloramine will interfere. It is best to use separate, dedicated sample cells for free and total chlorine determinations.

Oxidized manganese reacts directly with DPD. The apparent chlorine result is about 3 µg/L per µg/L Mn^{7+}. Mn^{2+} does not interfere up to 5000 µg/L.

Bromine, iodine, ozone, and other strong oxidizing agents may also interfere.

Copper and iron do not interfere up to 1000 µg/L each.

Nitrite interference will vary according to the following table:

mg/L Nitrite	Apparent µg/L Chlorine
2.0	3
5.0	5
10.0	7
15.0	16
20.0	18

Summary of Method

Several modifications to the normal DPD chlorine method are necessary to measure trace levels of chlorine in treated wastewaters. The 1-inch Pour-Thru Cell **must** be used in the spectrophotometer. Liquid reagents are also **required**. The reproducible optics of the Pour-Thru Cell give more consistent readings than is possible with movable sample cells, resulting in more stable readings.

The reagents are packaged in ampules and sealed under argon gas to ensure stability. Use of liquid reagents eliminates any slight turbidity that might be caused by using powdered reagents. Due to the possible oxidation of the reagents (which could give a positive chlorine reading in the blank), a reagent blank must be determined at least once per day for each lot of reagents used. This reagent blank is subtracted from the sample result and the corrected value is the actual chlorine concentration.

It is essential that interfering sample turbidity be removed using a 3-micron membrane filter. To avoid loss of chlorine, the filtration is performed **after** reaction of DPD with chlorine in the sample. The filter used in the test has been specifically selected as to not retain the colored reaction product. Sample color is compensated by zeroing the spectrophotometer on a filtered sample.

REQUIRED REAGENTS

	Cat. No.
ULR Chlorine Reagent Set (about 20 tests) Includes: (1) 24930-23, (1) 24931-20, (1) 24932-20	25630-00
ULR Chlorine Filter Apparatus Set	25956-00

Description	Quantity Required per test	Unit	Cat. No.
ULR Chlorine Buffer	1 mL	20/pkg	24931-20
DPD Indicator Solution	1 mL	20/pkg	24932-20
Blanking Reagent Solution	1 mL	29 mL	24930-23

REQUIRED APPARATUS

Description	Quantity Required per test	Unit	Cat. No.
Beaker, 250 mL	1	each	500-46
Cylinder, mixing, grad., 50 mL	1	each	1896-41
Pipet Tips, for TenSette Pipet	2	50/pkg	21856-96
Pour-Thru Cell Assembly Kit	1	each	45215-00
TenSette Pipet, 0.1 to 1.0 mL	1	each	19700-01

OPTIONAL REAGENTS

Description	Unit	Cat. No.
Sulfuric Acid Solution, 5.25N	1L	2449-53
Water, deionized	4L	272-56

OPTIONAL APPARATUS

Description	Unit	Cat. No.
Ampule Breaker	1	24846-00
Bottle, wash, 250 mL	each	620-31
Membrane Filters, 3-micron	100/pkg	25940-00

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8167

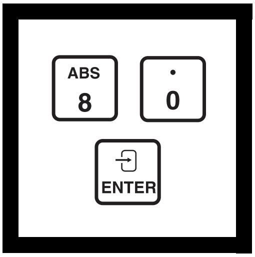
CHLORINE, TOTAL (0 to 2.00 mg/L)

For water, wastewater and seawater

DPD Method* (Powder Pillows or AccuVac Ampuls)

USEPA accepted for reporting water and wastewater**

Using Powder Pillows



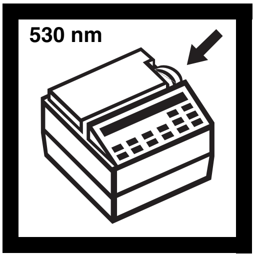
1. Enter the stored program number for free and total chlorine (Cl_2) powder pillows.

Press: **8 0 ENTER**

The display will show:

Dial nm to 530

__Note:__ The Pour-Thru Cell can be used with 25-mL reagents only.

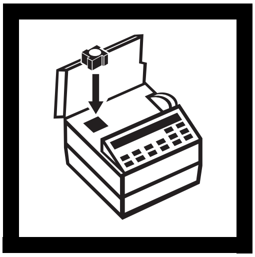


2. Rotate the wavelength dial until the small display shows:

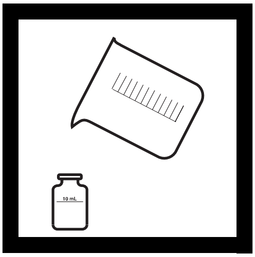
530 nm

When the correct wavelength is dialed in the display will quickly show: **Zero Sample**

then: **mg/L Cl_2**



3. Insert the 10-mL Cell Riser into the sample compartment.



4. Fill a 10-mL sample cell with 10 mL of sample.

__Note:__ Samples must be analyzed immediately and cannot be preserved for later analysis.

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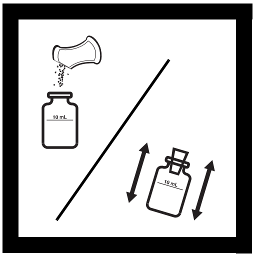
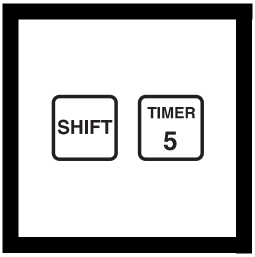
* Adapted from *Standard Methods for the Examination of Water and Wastewater.*

** Procedure is equivalent to USEPA method 330.5 for wastewater and Standard Method 4500-Cl G for drinking water.



5. Add the contents of one DPD Total Chlorine Powder Pillow to the sample cell (the prepared sample). Stopper the sample cell and shake for 20 seconds. Remove the stopper.

Note: *Shaking dissipates bubbles which may form.*



6. Press:

SHIFT TIMER

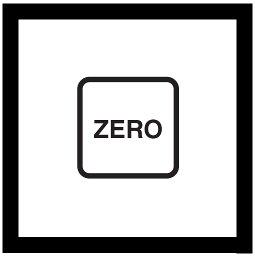
A three-minute reaction period will begin.

Note: *A pink color will develop if chlorine is present.*

7. When the timer beeps, the display will show:

mg/L Cl_2

Fill another sample cell (the blank) with 10 mL of sample. Place it into the cell holder. Close the light shield.

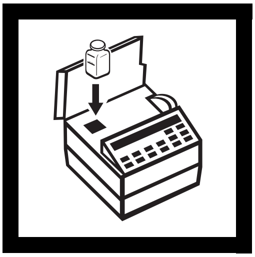


8. Press: **ZERO**

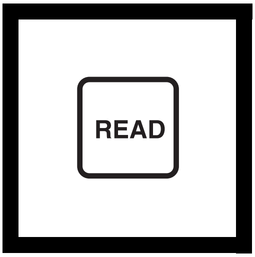
The display will show:

Zeroing. . .

then: **0.00 mg/L Cl_2**



9. Within three minutes after the timer beeps, place the prepared sample into the cell holder. Close the light shield.



10. Press: **READ**

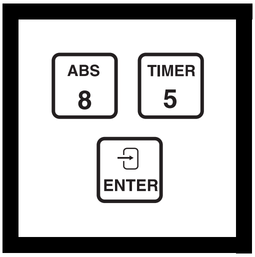
The display will show:

Reading. . .

then the result in mg/L chlorine (Cl_2) will be displayed.

Note: *It the sample temporarily turns yellow after sample addition, or shows* ***OVER-RANGE,*** *dilute a fresh sample and repeat the test. A slight loss of chlorine may occur during dilution. Multiply the result by the appropriate dilution factor; see Sample Dilution Techniques (Section I).*

Using AccuVac Ampuls

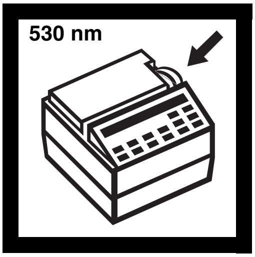


1. Enter the stored program number for free and total chlorine (Cl_2) AccuVac ampuls.

Press: **8 5 ENTER**

The display will show:

DIAL nm TO 530



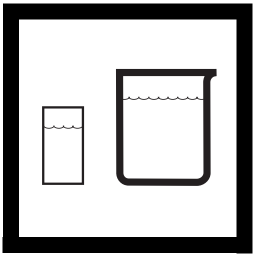
2. Rotate the wavelength dial until the small display shows:

530 nm

When the correct wavelength is dialed in the display will quickly show:

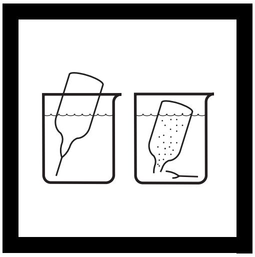
Zero Sample

then: **mg/L Cl_2 AV**



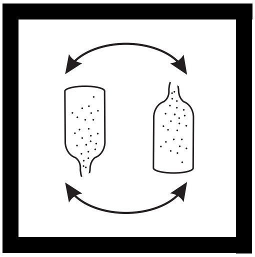
3. Fill a zeroing vial (the blank) with at least 10 mL of sample. Collect at least 40 mL of sample in a 50-mL beaker.

Note: *Samples must be analyzed immediately and cannot be preserved for later analysis.*



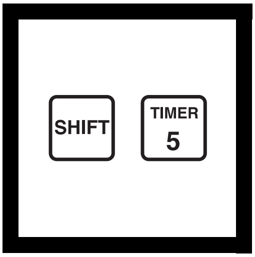
4. Fill a DPD Total Chlorine Reagent AccuVac Ampul with sample.

Note: *Keep the tip immersed while the ampul fills completely.*



5. Quickly invert the ampul several times to mix. Wipe off any liquid or fingerprints.

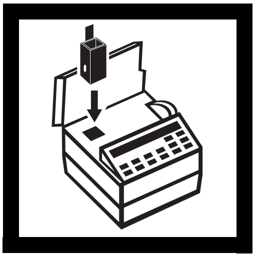
Note: *A pink color will form if chlorine is present.*



6. Press:

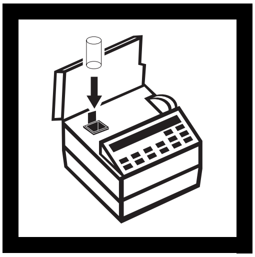
SHIFT TIMER

A three-minute reaction period will begin.



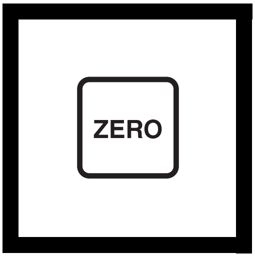
7. Place the AccuVac Vial Adapter in the cell holder of the instrument.

Note: *Place the grip tab at the rear of the cell holder.*



8. When the timer beeps, the display will show: **mg/L Cl_2 AV**

Place the blank into the cell holder. Close the light shield.

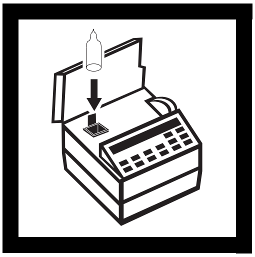


9. Press: **ZERO**

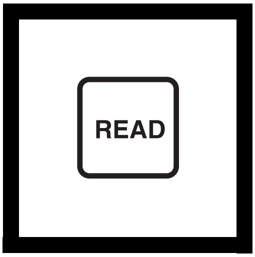
The display will show:

Zeroing. . .

then: **0.00 mg/L Cl_2 AV**



10. Within three minutes after the timer beeps, place the AccuVac ampul into the cell holder. Close the light shield.



11. Press: **READ**

The display will show:

Reading. . .

then the result in mg/L chlorine (Cl_2) will be displayed.

Note: *If the sample temporarily turns yellow after sample addition, or shows* ***OVER-RANGE****, dilute a fresh sample and repeat the test. A slight loss of chlorine may occur during dilution. Multiply the result by the appropriate dilution factor; see Sample Dilution Techniques (Section I).*

Sampling and Storage

Analyze samples for chlorine **immediately** after collection. Free chlorine is a strong oxidizing agent, and it is unstable in natural waters. It reacts rapidly with various inorganic compounds and more slowly oxidizes organic compounds. Many factors, including reactant concentrations, sunlight, pH, temperature and salinity influence decomposition of chlorine in water.

Avoid plastic containers since these may have a large chlorine demand. **Pretreat glass** sample containers to remove any chlorine demand by soaking in a dilute bleach solution (1 mL commercial bleach to l liter of deionized water) for at least 1 hour. Rinse thoroughly with deionized or distilled water. If sample containers are rinsed thoroughly with deionized or distilled water after use, only occasional pre-treatment is necessary.

A common error in testing for chlorine is introduced when a representative sample is not obtained. If sampling from a tap, let the water flow for at least 5 minutes to ensure a representative sample. Let the container overflow with the sample several times, then cap the sample containers so there is no headspace (air) above the sample. If sampling with a sample cell, rinse the cell several times with the sample, then carefully fill to the 10-mL mark. Perform the chlorine analysis immediately.

Accuracy Check

Standard Additions Method (using powder pillows)

a) Perform a sample analysis and record the result.

b) Snap the top off a LR Chlorine PourRite Ampule Standard Solution, 25-30 mg/L Cl_2.

c) Use a TenSette Pipet to add 0.1 mL of the standard to the reacted sample (this is the spiked sample). Swirl to mix.

d) Place the spiked sample into the DR/2010 and read the spiked sample result.

e) Calculate the equivalent concentration of mg/L chlorine added to the sample:

$$\text{mg/ L Chlorine} = \frac{0.1\,(\text{vol. standard added}) \times \text{Label value}(\text{mg/ L } Cl_2}{10.1\,(\text{sample} + \text{standard volume})}$$

f) The spiked sample result (step d) should reflect the analyzed sample result (step a) + the added, calculated mg/L Cl_2 (step e).

g) If this increase does not occur, see Standard Additions in Section I for more information.

Standard Additions Method (using AccuVac Ampuls)

a) Snap the top off a LR Chlorine PourRite Ampule Standard Solution, 25-30 mg/L Cl_2.

b) Use a graduated cylinder to measure 25 mL of sample into each of two beakers.

c) Use a TenSette Pipet to add 0.2 mL of the standard to one of the beakers (this is the spiked sample). Swirl to mix.

d) Fill a DPD Total Chlorine AccuVac completely from each beaker.

e) Analyze the spiked and unspiked sample as described in the procedure.

f) Calculate the equivalent concentration of mg/L chlorine added to the sample:

$$\text{mg/ L Chlorine} = \frac{0.2(\text{vol. standard added}) \times \text{Label value(mg/ L Cl}_2}{25.2(\text{sample} + \text{standard volume})}$$

g) The spiked sample result should reflect the analyzed sample result + the added, calculated mg/L Cl_2 (step f).

h) If this increase does not occur, see *Standard Additions* in *Section I* for more information.

Precision

In a single laboratory, using a standard solution of 1.00 mg/L chlorine and two lots of reagents with the DR/2010, a single operator obtained standard deviations of ±0.012 mg/L chlorine.

In a single laboratory, using a standard solution of 1.10 mg/L chlorine and two representative lots of AccuVac Ampuls with the DR/2010, a single operator obtained a standard deviation of ±0.009 mg/L chlorine.

Estimated Detection Limit (EDL)

The EDL for programs 80 and 85 is 0.01 mg/L CL_2. The EDL is the calculated lowest average concentration in a deionized water matrix that is different from zero with a 99% level of confidence. For more information on derivation and use of Hach's estimated detection limit, see *Section I.*

Interferences

Do not use the same sample cells for free and total chlorine. If trace iodide from the total chlorine reagent is carried over into the free chlorine determination, monochloramine will interfere. It is best to use separate, dedicated sample cells for free and total chlorine determinations.

Samples containing more than 300 mg/L alkalinity or 150 mg/L acidity as $CaCO_3$ may not develop the full amount of color, or it may instantly fade. Neutralize these samples to a pH of 6 to 7 with 1 N sulfuric acid, or 1 N sodium hydroxide. Determine the amount required on a separate 10 mL sample. Add the same amount to the sample to be tested. Correct for volume additions; see *Corrections for Volume Additions* in *Section I.*

Bromine, iodine, ozone, oxidized manganese, and chromium also may react and read as chlorine. To compensate for the effects of oxidized manganese or chromium, adjust the pH to between 6 and 7 as described above; then add 3 drops of potassium iodide, 30 g/L, to 25 mL of sample, mix, and wait one minute. Add 3 drops of sodium arsenite, 5 g/L, and mix. Analyze 10 mL of this sample as described above. (If chromium is present, allow exactly the same reaction period with the DPD for both analyses.) Subtract the result of this test from the original analysis to obtain the correct chlorine result.

DPD Total Chlorine Reagent Powder Pillows and AccuVac Ampuls contain a buffer formulation which will withstand high levels of hardness (at least 1000 mg/L) without interference.

Summary of Method

Chlorine can be present in water as free available chlorine and as combined available chlorine. Both forms can exist in the same water and be determined together as the total available chlorine. Free chlorine is present as hypochlorous acid and/or hypochlorite ion. Combined chlorine exists as monochloramine, dichloramine, nitrogen trichloride and other chloro derivatives.

The combined chlorine oxidizes iodide in the reagent to iodine. The iodine reacts with DPD (N, N-diethyl-p-phenylenediamine) along with free chlorine present in the sample to form a red color which is proportional to the total chlorine concentration. To determine the concentration of combined chlorine, run water free chlorine and total chlorine tests. Subtract the results of the free chlorine test from the results of the total chlorine test to obtain combined chlorine.

REQUIRED REAGENTS (USING POWDER PILLOWS)

Description	Quantity Required Per Test	Unit	Cat. No.
DPD Total Chlorine Reagent Powder Pillows	1 pillow	100/pkg	21056-69

REQUIRED REAGENTS (USING ACCUVAC AMPULS)

DPD Total Chlorine Reagent AccuVac Ampuls	1 ampul	25/pkg	25030-25

REQUIRED APPARATUS (USING POWDER PILLOWS)

Cell Riser, 10-mL sample cell	1	each	45282-00
Sample Cell, 10-mL, matched pair	2	pair	24954-02
Stopper, hollow, LDPE, No. 2 (fits 10 & 25-mL cells)	1	6/pkg	14480-01

REQUIRED APPARATUS (USING ACCUVAC AMPULS)

Description	Quantity Required Per Test	Unit	Cat. No.
Adapter, AccuVac vial	1	each	43784-00
Beaker, 50 mL	1	each	500-41
Vial, zeroing	1	each	21228-00

OPTIONAL REAGENTS

Chlorine Standard Solution, PourRite ampule, 25-30 mg/L	20/pkg	26300-20
DPD Total Chlorine Reagent w/dispensing cap	250 tests	21056-29
Potassium Iodide Solution, 30 g/L	100 mL* MDB	343-32
Sodium Arsenite, 5 g/L	100 mL* MDB	1047-32
Sodium Hydroxide Standard Solution, 1 N	100 mL* MDB	1045-32
Sulfuric Acid Standard Solution, 1 N	100 mL* MDB	1270-32
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

AccuVac Snapper Kit	each	24052-00
Ampule Breaker Kit	each	24846-00
Cylinder, graduated, 25 mL	each	508-40
pH Indicator Paper, 1 to 11 pH units	5 rolls/pkg	391-33
pH Meter, *sension*™*1*, portable	each	51700-10
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96

OPTIONAL 25 mL ANALYSIS ITEMS

DPD Total Chlorine Reagent Powder Pillows	100/pkg	14064-99
Pour-Thru Cell Assembly Kit	each	45215-00
Sample Cell, 25-mL, matched pair	pair	20950-00

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

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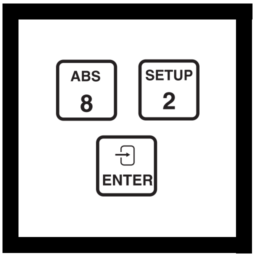
* Marked Dropper Bottle - contact Hach for larger sizes.

Method 10060

CHLORINE, TOTAL (0 to 2.00 mg/L)

DPD Rapid Liquid Method *

For treated water



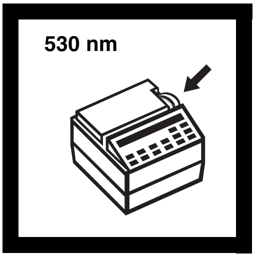
1. Enter the stored program number for free and total chlorine (Cl_2).

Press: **8 2 ENTER**

The display will show:

Dial nm to 530

Note: *Samples must be analyzed immediately and cannot be preserved for later analysis.*



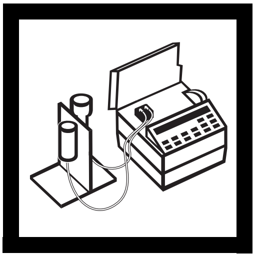
2. Rotate the wavelength dial until the small display shows:

530 nm

When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

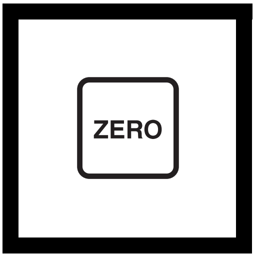
then: **mg/L Cl_2 RL**



3. Install the Pour-Thru Cell and flush with 50 mL of deionized water.

Note: *Clean the Pour-Thru Cell and all labware as specified in Treating Analysis Labware.*

4. Pour approximately 50 mL of sample into the Pour-Thru Cell.

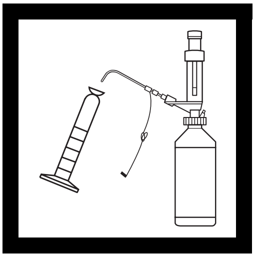


5. When the flow has stopped, press: **ZERO**

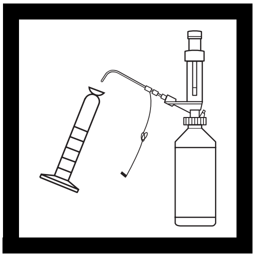
The display will show:

Zeroing. . . .

then: **0.00 mg/L Cl_2 RL**

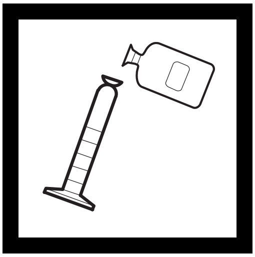


6. Add 1.0 mL of Total Chlorine Buffer Solution to a clean, dry, glass 100-mL mixing cylinder using the Repipet dispenser.



7. Add 1.0 mL of prepared Total Chlorine Indicator Solution to the same mixing cylinder. Swirl to mix the reagents. Proceed to step 8 immediately.

Note: *See Reagent Preparation for instructions on preparing the indicator solution.*



8. Carefully fill the mixing cylinder to the 80-mL mark with sample. Stopper the cylinder and gently invert it twice to mix.

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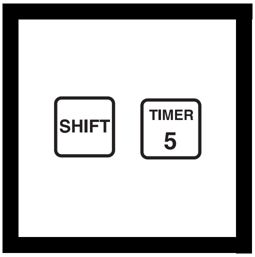
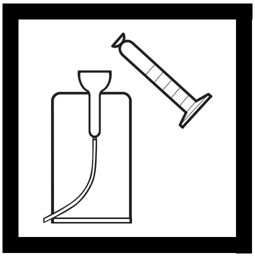
* Adapted from *Standard Methods for the Examination of Water and Wastewater.*



9. Press:

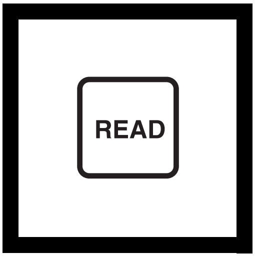
SHIFT TIMER

A one-minute reaction period will begin.



10. When the timer beeps, fill the funnel of the Pour-Thru Cell with the reacted sample from the mixing cylinder.

Note: *It is not necessary to pour the entire sample into the Pour-Thru Cell; approximately half of the sample can be discarded.*



11. After the flow has stopped, press: **READ**

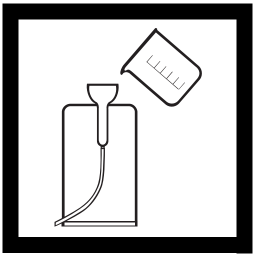
The display will show:

Reading. . . . .

then the result in mg/L chlorine (Cl_2) will be displayed.

Note: *Complete this step within two minutes after the timer beeps.*

Note: *If the display shows OVERRANGE, dilute a fresh sample and repeat the test. A slight loss of chlorine may occur during the dilution. Multiply the result by the appropriate dilution factor; see Sample Dilution Techniques in Section I.*



12. Flush the Pour-Thru Cell with at least 50 mL of deionized water immediately after use.

Note: *Protect the Pour-Thru Cell from contamination by inverting a small beaker over the top of the glass funnel when not in use.*

Sampling and Storage

Samples must be analyzed immediately and cannot be preserved for later analysis. A common testing error is introduced if the analyst does not obtain a representative sample. If sampling from a tap, let the water flow for at least five minutes to ensure a representative sample. Let the container overflow with the sample several times, then cap the sample container so there is no headspace (air) above the sample. Perform the chlorine analysis immediately.

Avoid plastic containers since these may have a chlorine demand. Pre-treat glass sample containers to remove any chlorine demand by soaking in a dilute bleach solution (1 mL commercial bleach to l liter of deionized water) for at least 1 hour. Rinse thoroughly with deionized water. If sample containers are rinsed thoroughly with deionized water after use, only occasional pretreatment is necessary. A pre-treated BOD bottle with a ground-glass stopper is an ideal sample container for chlorine analysis.

Treating Analysis Labware

Glassware used in this test must be chlorine demand-free. Fill the 100 mL mixing cylinder and sample container with a dilute solution of chlorine bleach prepared by adding 1 mL of commercial bleach to 1 liter of water. Soak in this solution at least one hour. After soaking, rinse with copious amounts of deionized water and allow to dry before use. If the mixing cylinder is rinsed thoroughly with deionized water and allowed to dry after use, only occasional pretreatment is necessary. Do not use the same mixing cylinder for Free and Total Chlorine analysis.

Treat the Pour-Thru Cell similarly with dilute bleach and let stand for several minutes. Rinse several times with deionized water.

Cleaning the Pour-Thru Cell

The Pour-Thru Cell may accumulate a buildup of colored reaction products, especially if the reacted solutions are allowed to remain in the cell for long periods. Remove the buildup by rinsing the cell with 5.25 N sulfuric acid followed by several rinsings with deionized water.

Reagent Preparation

The Total Chlorine Indicator Solution must be prepared before use. Using a powder funnel, add the contents of one 24 g bottle of DPD Powder (Cat. No. 22972-55) to one 473-mL bottle of Total Chlorine Indicator Solution (Cat. No. 22634-11). Invert several times and swirl until the powder completely dissolves. A pink color may develop, but this should not affect test results.

This solution will give accurate results for at least one month after mixing when stored at 20-25 °C (68-77 °C). Write the date of preparation on the Indicator Solution Bottle. Discard any remaining solution after one month. Use of this reagent after one month may result in high reagent blanks and low values at high concentration. Do not combine fresh reagent with previously mixed reagent.

Accuracy Check

Standard Additions Method

a) Snap the top off a Chlorine Voluette Ampule Standard Solution, 50-75 mg/L Cl_2.

b) Use the TenSette Pipet to add 0.3, 0.6 and 0.9 mL of standard to three 80-mL samples, respectively. Swirl gently to mix.

c) Analyze each sample as described above. Each 0.3 mL of standard will cause an incremental increase in chlorine, the exact value of which depends on the concentration in the ampule. Check the label on the ampules for this value.

d) Calculate the concentration of chlorine added to each sample as follows:

$$\frac{\text{mL of standard addition}}{\text{mL of standard addition } + \text{ mL of sample}} \times \text{chlorine concentration in ampule}$$
$$= \text{concentration of chlorine added to the sample}$$

Example:

$$\frac{0.3\text{ mL}}{80.3\text{ mL}} \times 72.3\text{ mg/L} = 0.27\text{ mg/L chlorine added to the sample}$$

e) If the concentration of each sample does not increase by the calculated amount, refer to Standard Additions in Section I.

Precision

In a single laboratory using 9 concentrations of chlorine standards and two lots of reagents with a DR/2010, a single operator obtained a calibration curve that showed a 99% confidence interval at 1.00 mg/L of ±0.005 mg/L chlorine.

Interferences

***Note:** If sodium arsenite is used, collect the spent sample for proper disposal according to the hazardous waste regulations for arsenic. Refer to the DR/2010 Instrument Manual for information on modifying the Pour-Thru Cell for collecting samples after analysis.*

Samples containing more than 700 mg/L alkalinity may not develop the full amount of color, or it may instantly fade. Neutralize these samples to a pH of 6-7 with 1 N sulfuric acid. Determine the amount of acid required on a separate 80-mL sample; then add the same amount of acid to the sample to be tested.

Bromine, iodine, ozone and oxidized forms of manganese also may react and show as chlorine. Hexavalent chromium a levels >1 mg/L will cause a positive interference.

To compensate for the effects of manganese (Mn^{4+}) or chromium (Cr^{6+}), adjust pH to 6 to 7 as described above, then add 9 drops of potassium iodide, 30 g/L, to 80 mL of sample, mix and wait 1 minute. Add 9 drops of sodium arsenite, 5 g/L, and mix. Analyze this sample as described above. (If chromium is present, allow exactly the same reaction period with the DPD for both analyses.) Subtract the result of this test from the original analysis to obtain the accurate chlorine result.

Hardness at levels below 1000 mg/L as $CaCO_3$ will not interfere.

Summary of Method

Chlorine can be present in water as free available chlorine and as combined available chlorine. Both forms can exist in the same water and can be determined together as the total available chlorine. Free chlorine is available as hypochlorous acid or hypochlorite ion. Combined chlorine exists as monochloramine, dichloramine, nitrogen trichloride and other chloro derivatives.

The combined chlorine oxidizes iodide in the reagent to iodine. The iodine reacts with DPD (N,N-diethyl-p-phenylenediamine) indicator along with free chlorine present in the sample to form a red color which is proportional to the total chlorine concentration. To determine the concentration of combined chlorine, run a free chlorine test. Subtract the results from the results of the total chlorine test to obtain combined chlorine.

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
Rapid Liquid Total Chlorine Reagent Set Includes: (1)22972-55, (1) 22634-11, (1) 22635-11			25570-00
DPD Indicator Powder,		24 g	22972-55
Total Chlorine Indicator Solution	1 mL	473 mL	22634-11
Total Chlorine Buffer Solution	1 mL	473 mL	22635-11

REQUIRED APPARATUS

Description	Quantity Required Per Test	Unit	Cat. No.
Cylinder, mixing, glass, 100 mL	1	each	1896-42
Dispenser, fixed volume, 1.0 mL RePipet Jr.	2	each	21113-01
Pour-Thru Cell Assembly Kit	1	each	45215-00

OPTIONAL REAGENTS

Description	Unit	Cat. No.
Chlorine Standard Solution, Voluette Ampule, 50-75 mg/L, 10 mL	16/pkg	14268-10
Chlorine Standard Solution, Voluette Ampule, 50-75 mg/L, 10 mL	20/pkg	14268-20
Potassium Iodide Solution, 30 g/L	100 mL* MDB	343-32
Sodium Arsenite, 5 g/L	100 mL* MDB	1047-32
Sodium Hydroxide Standard Solution, 1.000 N	100 mL* MDB	1045-32
Sulfuric Acid Standard Solution, 1.000 N	100 mL* MDB	1270-32
Sulfuric Acid Standard Solution, 5.25 N	1 L	2449-53
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Description	Unit	Cat. No.
Ampule Breaker Kit	each	21968-00
Beaker, poly	50 mL	1080-41
Bottle, Wash, 125 mL	each	21901-43
Bottle, BOD, w/stopper	300 mL	621-00
Funnel, powder	each	22644-67
pH Meter, EC10, portable	each	50050-00
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
PourRite Ampule Breaker	each	24846-00

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

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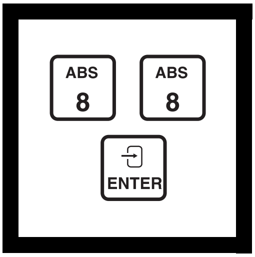
* Contact Hach for larger sizes.

Method 10070

CHLORINE, TOTAL, HIGH RANGE (0 - 5.00 mg/L as Cl_2)

DPD Method *

For water and wastewater



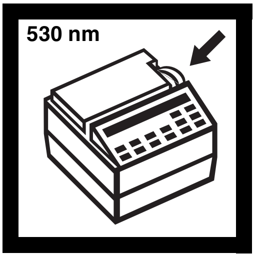
1. Enter the stored program for total chlorine, HR method.

Press: **8 8 ENTER**

The display will show :

DIAL nm TO 530

Note: *The Pour-Thru Cell can be used with this procedure.*

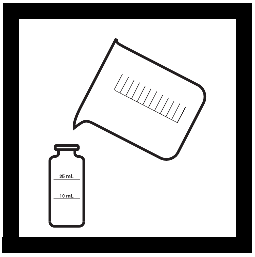


2. Rotate the wavelength dial until the small display shows:

530 nm

When the correct wavelength is dialed in the display will quickly show: **Zero Sample**

then: **mg/L Cl_2 HR**

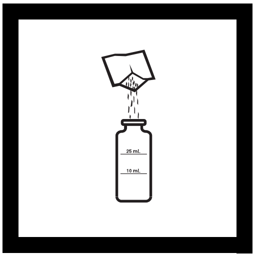


3. Fill two clean dual-screened sample cells each to the 10-mL mark with sample.

Note: *For most accurate work, use two clean 25-mL mixing graduated cylinders.*

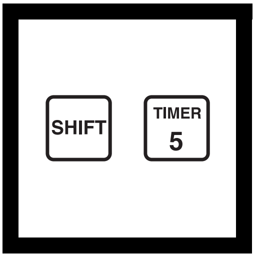
Note: *Samples must be analyzed immediately.*

Note: *If using Cat. No. 26294 sample cells, use Cat. No. 14480 stoppers.*



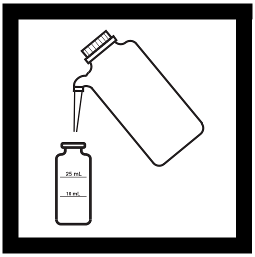
4. Add the contents of one DPD Total Chlorine Powder Pillow for 25-mL sample to one cell. Stopper the cell and invert several times to dissolve the powder. Un-stopper the cell.

Note: *A magenta color will develop if chlorine is present.*



5. Press: **SHIFT TIMER**

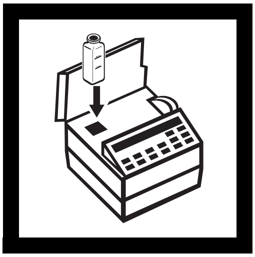
A two minute reaction period will begin.



6. When the timer beeps, the display will show:

mg/L Cl_2 HR

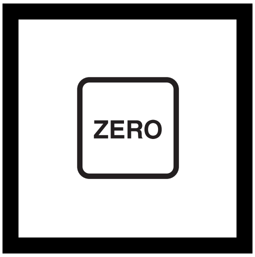
Within three minutes after the timer beeps, add Deionized Water to each cell to the 25-mL mark. Cap and invert each cell twice to mix.



7. Place the diluted sample (without reagent) into the cell holder. Close the light shield.

Note: *Place the cell so that the graduations are facing forward (perpendicular to the light beam).*

Note: *Remove the cell stoppers so the light shield will close tightly.*



8. Press: **ZERO**

The display will show:

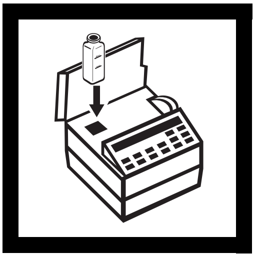
Zeroing . . .

then:

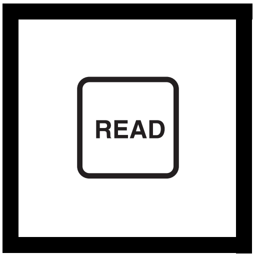
0.00 mg/L Cl_2 HR

---

* Adapted from *Standard Methods for the Examination of Water and Wastewater.*



9. Place the prepared, reacted sample into the cell holder. Close the light shield.



10. Press: **READ**

The display will show:

Reading. . . .

then the result in mg/L Cl_2 will be displayed.

Sampling and Storage

Analyze samples for chlorine immediately after collection. Free and combined chlorine are strong oxidizing agents and will react rapidly with various compounds. Many factors such as sunlight, pH, temperature and sample composition will influence decomposition of chlorine in water.

Avoid plastic containers since these may have a large chlorine demand. Pretreat glass sample containers to remove any chlorine demand by soaking in a dilute bleach solution (1 mL commercial bleach to 1 liter of deionized water) for at least 1 hour. Rinse thoroughly with deionized or distilled water. If sample containers are rinsed thoroughly with deionized or distilled water after use, only occasional pre-treatment is necessary.

A common error in testing for chlorine is introduced when a representative sample is not obtained. If sampling from a tap, let the water flow for at least 5 minutes to ensure a representative sample. Let the container overflow with the sample several times, then cap the sample container so there is no headspace (air) above the sample. If sampling with a sample cell, rinse the cell several times with the sample, then carefully fill to the 10-mL mark. Proceed with the chlorine test immediately.

Interferences

Do not use the same sample cells for free and total chlorine. If trace iodide from the total chlorine reagent is carried over to the free chlorine test, monochloramine could interfere. It is best to use separate, dedicated sample cells for free and total chlorine determinations.

Interfering Substance	Interference Level and Treatment
Bromine, Br_2	Interferes at all levels
Chlorine Dioxide, ClO_2	Interferes at all levels
Chloramines, organic	May interfere
Iodine, I_2	Interferes at all levels
Manganese, oxidized (Mn^{4+}, Mn^{7+}) or Chromium, oxidized (Cr^{6+})	Adjust sample pH to 6-7. Add 3 drops potassium iodide (30 g/L) to a 10-mL sample. Mix and wait 1 minute. Add 3 drops sodium arsenite (5 g/L) and mix. Analyze the treated sample as described in the procedure. Subtract the result from this test from the original analysis to obtain the correct chlorine concentration.
Ozone	Interferes at all levels
Peroxides	May interfere
Extreme sample pH or Highly buffered samples	Adjust to pH 6-7 using acid or base.

Method Performance

Precision

at mg/L Cl_2	99% Confidence Limits
0.10	±0.02 mg/L
2.50	±0.02 mg/L
3.40	±0.02 mg/L

Sensitivity

Portion of Curve	∆Abs	∆Concentration
at 0.10 mg/L Cl_2	0.010	0.040 mg/L
at 2.50 mg/L Cl_2	0.010	0.046 mg/L
at 3.40 mg/L Cl_2	0.010	0.049 mg/L

Accuracy Check

Standard Additions Method

a) Snap the neck off a HR Chlorine Ampule Standard Solution.

b) Use the TenSette Pipet to add 0.1 mL of the standard to 10-mL of sample (this is the spiked sample). Swirl to mix.

c) Analyze the spiked sample, beginning at Step 4 of the procedure.

d) Calculate the concentration of mg/L chlorine added to the sample:

$$\frac{0.1\text{ mL (volume of standard added)} \times \text{Label Value (mg/L chlorine)}}{10.1\text{ (sample + standard volume)}}$$

e) The spiked sample result (Step c) should reflect the analyzed sample result + the calculated mg/L Cl_2 added (Step d).

f) If this increase does not occur, see Standard Additions in Section I for more information.

Summary of Method

The range of analysis using this method for total chlorine can be extended by adding more indicator in proportion to sample volume. A larger fill powder pillow of DPD Total Chlorine Reagent is added to a 10-mL sample portion. After color development, the sample volume is adjusted to 25 mL using deionized water. Color measurement is made directly in the 1-inch cell, eliminating the need to transfer to a smaller pathlength cell.

Dilution of the reacted sample avoids potential loss of chlorine when the sample is diluted prior to testing. In addition, chlorine demand-free water is not required. Some loss of accuracy and precision will occur during dilution. The DPD procedure (program 80) is recommended for concentrations less than 2 mg/L and the ULR Chlorine DPD procedure (program 86) is recommended for concentrations less than 500 µg/L.

Combined chlorine is the difference between total and free chlorine results.

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
DPD Total Chlorine Reagent Powder Pillows	1 pillow	100/pkg	14064-99
deionized Water	30 mL	500 mL	272-49

REQUIRED EQUIPMENT AND SUPPLIES

Cells, Sample, 1-inch, matched pair w/stopper	2	each	26126-02
or			
Cells, Sample, 1-inch, dual graduated	2	each	26294-02
Stopper, Hollow (for use with 26294-02 cells)	2	6/pkg	14480-00

OPTIONAL REAGENTS AND STANDARDS

Chlorine Standard Solution, PourRite ampules, 50-75 mg/L		20/pkg	14268-20
Potassium Iodide Solution, 30 g/L		100 mL MDB	343-32
Sodium Arsenite, 5 g/L		100 mL MDB	1047-32
Sodium Hydroxide Standard Solution, 1N		100 mL MDB	1045-32
Sulfuric Acid Standard Solution, 1N		100 mL MDB	1270-32

OPTIONAL EQUIPMENT AND SUPPLIES

Ampule Breaker Kit		each	24846-00
Cylinder, graduated, mixing 25-mL		2	20886-40
pH Paper, pH 1-11		each	391-33
Pipet, TenSette, 0.1 to 1.0 mL		each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet		each	21856-96
Pour-Thru Cell Assembly Kit		each	45215-00

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

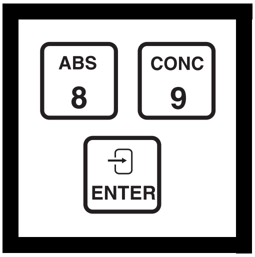
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 10101

CHLORINE, TOTAL (0.00 to 5.00 mg/L)

DPD Test 'N Tube™ Method*

For water, wastewater and seawater

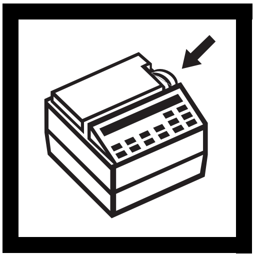


1. Enter the stored program number for Test 'N Tube Total Chlorine (Cl_2).

Press: **8 9 ENTER**

The display will read:

Dial nm to 530

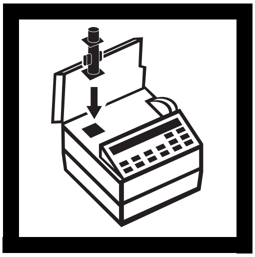


2. Rotate the wavelength dial until the small display reads:

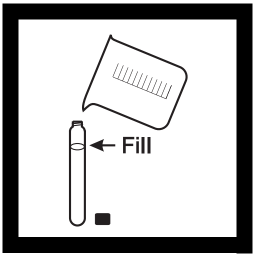
530 nm

When the correct wavelength is dialed in the display will quickly show: **Zero Sample**

then: **mg/L Cl_2**



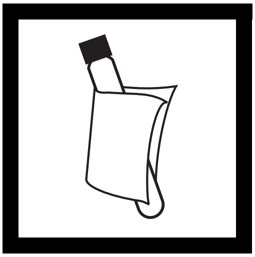
3. Insert the COD Vial Adapter into the cell holder with the marker to the right.



4. Fill an empty Test 'N Tube vial with sample. This is the sample blank.

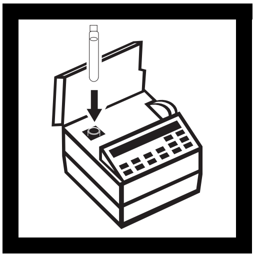
Note: *Fill to the top of the Hach logo "oval" mark.*

Note: *Samples must be analyzed immediately and cannot be preserved for later analysis.*

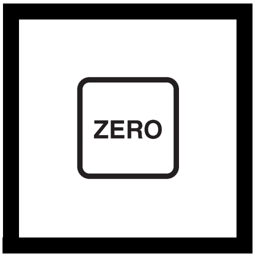


5. Clean the outside of the sample blank vial with a towel.

Note: *Wiping with a damp cloth followed by a dry one removes fingerprints and other marks.*



6. Place the blank into the adapter with the Hach logo facing the front of the instrument. Place the cover on the adapter.



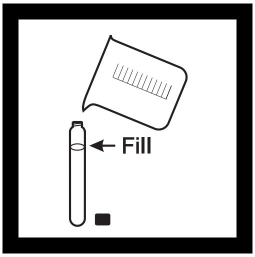
7. Press: **ZERO**

The display will show:

Zeroing...

then:

0.00 mg/L Cl_2 TNT



8. Remove the cap from a Total Chlorine DPD-TNT vial. Add 10 mL of sample.

Note: *Fill to the top of the Hach logo "oval" mark.*

Note: *A pink color will develop if chlorine is present.*

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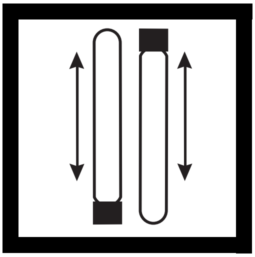
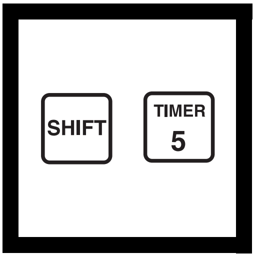
* Adapted from *Standard Methods for the Examination of Water and Wastewater.*



9. Cap and invert at least 10 times to dissolved the powder. This is the prepared sample.

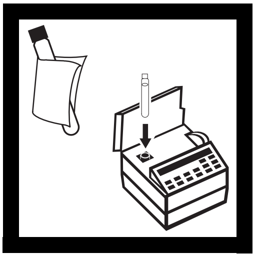
***Note:** Use slow, deliberate inversion for complete recovery. Ten inversions should take at least 30 seconds. One inversion equals turning the vial upside down, then returning it to an upright position.*



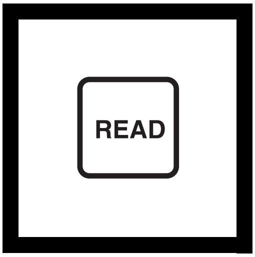
10. Press:

SHIFT TIMER

A three-minute reaction period will begin.



11. When the timer beeps, wipe the prepared sample vial with a towel, then place it in the vial adapter with the Hach logo facing the front of the instrument. Place the cover on the adapter.



12. Press: **READ**

The display will show:

Reading...

then the result in mg/L chlorine will be displayed.

Sampling and Storage

Analyze samples for chlorine **immediately** after collection. Free and combined chlorine are strong oxidizing agents, and are unstable in natural waters. They react rapidly with various inorganic compounds and more slowly oxidizes organic compounds. Many factors, including reactant concentrations, sunlight, pH, temperature and salinity influence decomposition of chlorine in water.

Avoid plastic containers since these may have a large chlorine demand. **Pretreat glass** sample containers to remove any chlorine demand by soaking in a dilute bleach solution (1 mL commercial bleach to l liter of deionized water) for at least 1 hour. Rinse thoroughly with deionized or distilled water. If sample containers are rinsed thoroughly with deionized or distilled water after use, only occasional pre-treatment is necessary.

A common error in testing for chlorine is obtaining an unrepresentative sample. If sampling from a tap, let the water flow for at least five minutes to ensure a representative sample.

Let the container overflow with the sample several times, then cap the sample containers so there is no headspace (air) above the sample. Perform the analysis immediately.

Accuracy Check

Standard Additions Method

a) Snap the top off a HR Chlorine PourRite™ Ampule Standard Solution.

b) Use a TenSette™ Pipet to add 0.1 mL of the standard to the 10-mL sample in a beaker (this is the spiked sample). Swirl to mix.

c) Anaylze the spiked sample according to the procedure.

d) Calculate the concentration of mg/L chlorine added to the sample:

$$\text{mg/L chlorine added} = \frac{0.1\ \text{(vol. standard added)} \times \text{Label value (mg/L chlorine)}}{10.1\ \text{(sample + standard volume)}}$$

e) The spiked sample result (step c) should reflect the analyzed sample result + the calculated mg/L Cl_2 added (step d).

f) If these increases do not occur, see *Standard Additions* in *Section 1* for more information.

Method Performance

Precision

In a single laboratory, using a standard solution of 2.80 mg/L chlorine and two representative lots of reagent with a DR/2010, a single operator obtained a standard deviation of ±0.02 mg/L chlorine.

Estimated Detection Limit (EDL)

The EDL for program 89 is 0.07 mg/L. The EDL is the calculated lowest average concentration in a deionized water matrix that is different from zero with a 99% level of confidence. For more information on derivation and use of Hach’s estimated detection limit, see *Section 1.*

Interferences

Interfering Substance	Interference Level and Treatment
Acidity	Greater than 150 mg/L $CaCO_3$. May not develop full color or color may fade instantly. Neutralize to pH 6-7 with 1 N sodium hydroxide. Determine amount to be added on separate sample aliquot, then add the same amount to the sample being tested. Correct for volume addition (see *Correcting for Volume Additions* in *Section 1)*.
Alkalinity	Greater than 250 mg/L $CaCO_3$. May not develop full color or color may fade instantly. Neutralize to pH 6-7 with 1 N sulfuric acid. Determine amount to be added on separate sample aliquot, then add the same amount to the sample being tested. Correct for volume addition (see *Correcting for Volume Additions* in *Section 1)*.
Bromine	Interferes at all levels
Chlorine Dioxide	Interferes at all levels
Chloramines, organic	May interfere
Hardness	No effect at less than 1,000 mg/L as $CaCO_3$
Iodine	Interferes at all levels
Manganese, oxidized (Mn^{4+}, Mn^{7+}) or Chromium, oxidized (Cr^{6+})	**1.** Adjust sample pH to 6-7. **2.** Add 3 drops potassium iodide (30 g/L) to a 25-mL sample. **3.** Mix and wait one minute. **4.** Add 3 drops sodium arsenite (5 g/L) and mix. **5.** Analyze 10 mL of the treated sample as described in the procedure. **6.** Subtract the result from this test from the original analysis to obtain the correct chlorine concentration.
Ozone	Interferes at all levels
Peroxides	May interfere
Extreme sample pH and highly buffered samples	Adjust to pH 6-7 (see *Interferences* in *Section 1)*.

Summary of Method

Chlorine can be present in water as free available chlorine and as combined available chlorine. Both forms can exist in the same water and be determined together as the total available chlorine. Free chlorine is present as hypochlorous acid and/or hypochlorite ion. Combined chlorine exists as monochloramine, dichloramine, nitrogen trichloride and other chloro derivatives.

The combined chlorine oxidizes iodide in the reagent to iodine. The iodine reacts with DPD (N, N-diethyl-p-phenylenediamine) along with free chlorine present in the sample to form a red color which is proportional to the total chlorine concentration. To determine the concentration of combined chlorine, run free chlorine and total chlorine tests. Subtract the results of the free chlorine test from the results of the total chlorine test to obtain combined chlorine.

Pollution Prevention and Waste Management

Samples treated with sodium arsenite for manganese or chromium interferences will be hazardous wastes as regulated by Federal RCRA for arsenic (D004). See *Section 3* for more information on proper disposal of these materials.

REQUIRED REAGENTS & APPARATUS

Description	Quantity Required Per Test	Unit	Cat. No.
Test ‘N Tube DPD Total Chlorine Reagent	1 vial	25/pkg	21056-25
Test ‘N Tube Vials	1 vial	25/pkg	25831-25

REQUIRED APPARATUS

COD/TNT Adapter	1	each	44799-00

OPTIONAL REAGENTS

Chlorine Standard Solution, PourRite Ampule, 2 mL, 50-75 mg/L Cl_2	20/pkg	14268-20
Potassium Iodide Solution, 30 g/L	100 mL* MDB	343-32
Sodium Arsenite Solution, 5 g/L	100 mL* MDB	1047-32
Sodium Hydroxide Standard Solution, 1.00 N	100 mL* MDB	1045-32
Sulfuric Acid Standard Solution, 1.000 N	100 mL* MDB	1270-32

OPTIONAL APPARATUS

Beaker, 50 mL	each	500-41
pH Indicator Paper, 1 to 11 pH units	5 rolls/pkg	391-33
pH Meter, *sension*™*1*, portable	each	51700-10
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
PourRite Ampule Breaker	each	24846-00
Test Tube Rack	each	18641-00

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

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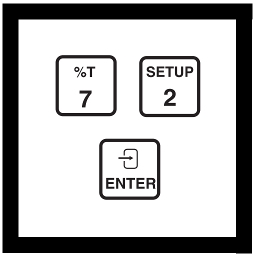
* Marked Dropper Bottle - contact Hach for larger sizes.

Method 8065

CHLORINE DIOXIDE, LR (0 to 1.00 mg/L)

For water and wastewater

Chlorophenol Red Method*



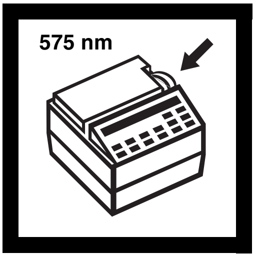
1. Enter the stored program number for chlorine dioxide (ClO_2), low range.

Press: **7 2 ENTER**

The display will show:

Dial nm to 575

Note: *The Pour-Thru Cell can be used with this procedure. Rinse with deionized water after each analysis.*

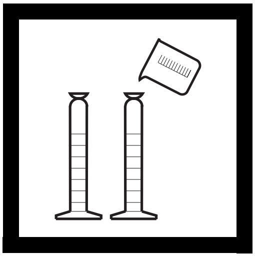


2. Rotate the wavelength dial until the small display shows:

575 nm

When the correct wavelength is dialed in the display will quickly show: **Zero Sample**

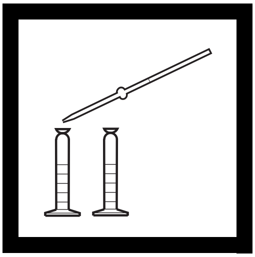
then: **mg/L ClO_2 LR**



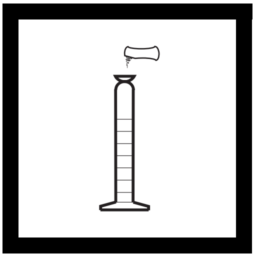
3. Fill two 50-mL graduated mixing cylinders with sample to the 50-mL mark.

Note: *Analyze samples immediately after collection.*

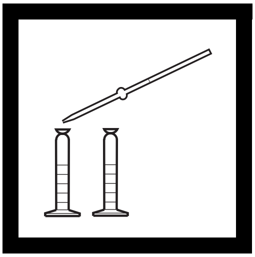
Note: *For most accurate results, analyze each portion at the same sample temperature.*



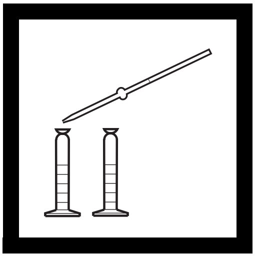
4. Using a TenSette Pipet or Class A pipet, add 1.00 mL of Chlorine Dioxide Reagent 1 to each cylinder. Stopper. Invert several times to mix.



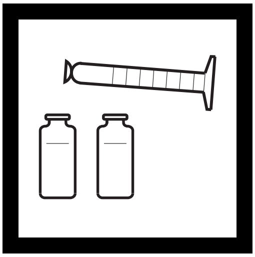
5. Add the contents of one Dechlorinating Reagent Powder Pillow to one cylinder. Invert several times until dissolved. This solution is the blank. The other solution is the prepared sample.



6. Using a Class A pipet, add exactly 1.00 mL Chlorine Dioxide Reagent 2 to each cylinder. Stopper. Invert several times to mix.



7. Using a Class A or TenSette pipet, add 1.00 mL of Chlorine Dioxide Reagent 3 to each cylinder. Stopper. Invert several times to mix.



8. Pour 25 mL from each cylinder into respective sample cells.

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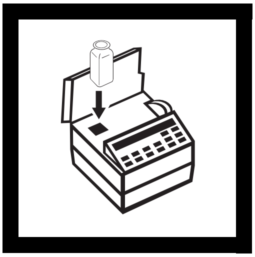
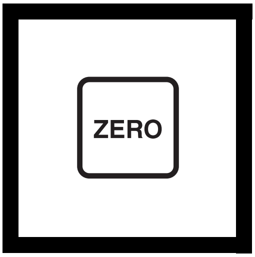
* Adapted from Harp, Klein, and Schoonover, *Jour. Amer. Water Works Assn.*, 73 387-388 (1981)



9. Place the blank into the cell holder. Close the light shield.



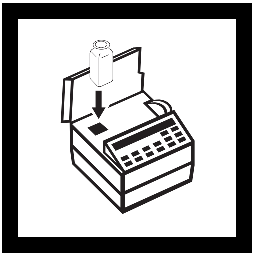
10. Press: **ZERO**

The display will show:

Zeroing. . .

then:

0.00 mg/L ClO_2 LR



11. Place the prepared sample into the cell holder.

Press: **READ**

The display will show:

Reading. . .

then the result in mg/L ClO_2 will be displayed.

Sampling and Storage

Collect samples in clean plastic or glass bottles. Fill completely and cap tightly. Avoid excessive agitation and exposure to light, especially sunlight. Samples must be analyzed immediately upon collection and cannot be preserved or stored for later analysis.

Precision

In a single laboratory using a standard solution of 0.45 mg/L ClO_2 and two representative lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±0.014 mg/L ClO_2.

Interferences

For highly acidic or alkaline water, 2.0 mL each of Chlorine Dioxide Reagent 1 and Chlorine Dioxide Reagent 3 may be required instead of 1.0 mL.

Ozone interferes at 0.5 mg/L.

The following do not interfere at or below these concentrations:

ClO^-	5.5 mg/L	Fe^{3+}	5 mg/L
ClO_2^-	6 mg/L	Hardness	1000 mg/L
ClO_3^-	6 mg/L	Turbidity	1000 NTU
CrO_4^{2-}	3.6 mg/L		

Summary of Method

Chlorine Dioxide (ClO_2) is determined by its combination with chlorophenol red at pH 5.2 to form a colorless complex. The net effect is bleaching of the color in an amount proportional to the chlorine dioxide concentration. The method is specific for ClO_2 and is unreactive to other active chlorine or moderate oxidizing compounds.

REQUIRED REAGENTS

	Cat. No.
Chlorine Dioxide Reagent Set (100 Tests)	22423-00

Includes: (2) 20700-42, (2) 20701-42, (2) 20702-42, (1) 14363-69

Description	Quantity Required Per Test	Unit	Cat. No.
Chlorine Dioxide Reagent 1	2 mL	100 mL	20700-42
Chlorine Dioxide Reagent 2	2 mL	100 mL	20701-42
Chlorine Dioxide Reagent 3	2 mL	100 mL	20702-42
Dechlorinating Reagent Powder Pillows	1 pillow	100/pkg	14363-69

REQUIRED APPARATUS

Cylinder, mixing, graduated, 50 mL	2	each	1896-41
Pipet, volumetric, Class A, 1.00 mL	3	each	14515-35
Pipet Filler, safety bulb	1	each	14651-00
Sample Cell, 25 mL, matched pair	2	each	20950-00

OPTIONAL APPARATUS

Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet Tips, for 19700-01 TenSette Pipet	1000/pkg	21856-28
Pour-Thru Cell Assembly Kit	each	45215-00

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

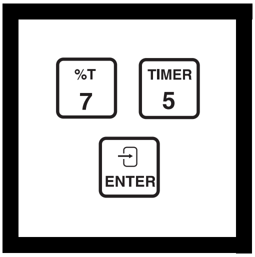
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8138

CHLORINE DIOXIDE, HR (0 to 700 mg/L)

For water and wastewater

Direct Reading Method



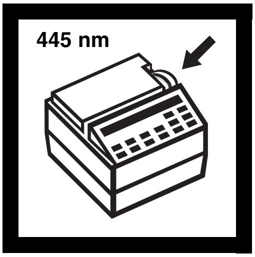
1. Enter the stored program number for chlorine dioxide (ClO_2), high range.

Press: **7 5 ENTER**

The display will show:

Dial nm to 445

Note: *The Pour-Thru Cell can be used with this procedure.*



2. Rotate the wavelength dial until the small display shows:

445 nm

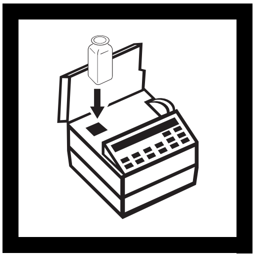
When the correct wavelength is dialed in the display will quickly show:

Zero Sample

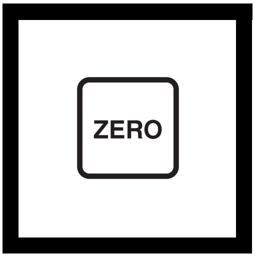
then: **mg/L ClO_2 HR**

3. Fill a sample cell (the blank) with 25 mL of deionized water.

Note: *Analyze samples immediately after collection.*



4. Place the blank into the cell holder. Close the light shield.



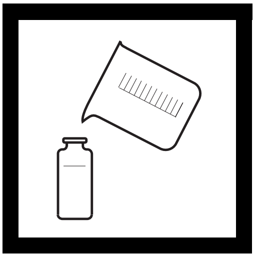
5. Press: **ZERO**

The display will show:

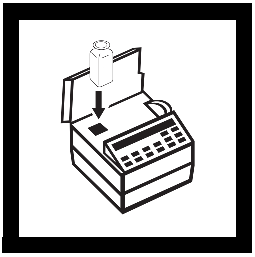
Zeroing. . .

then:

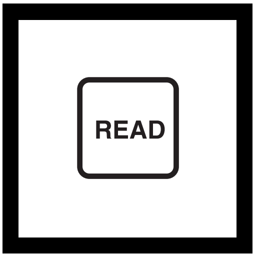
0. mg/L ClO_2 HR



6. Fill another sample cell with sample (the prepared sample).



7. Place the prepared sample into the cell holder. Close the light shield.



8. Press: **READ**

The display will show:

Reading. . .

then the result in mg/L chlorine dioxide (ClO_2) will be displayed.

Sampling and Storage

Chlorine dioxide is very volatile and unstable; analyze samples immediately upon collection.

Summary of Method

Chlorine dioxide, a yellow gas, can be measured directly in a water solution. This method uses a wavelength of 445 nm to increase the range of the test.

REQUIRED REAGENT

Description	Quantity Required Per Test	Unit	Cat. No.
Water, deionized	25 mL	4 L	272-56

REQUIRED APPARATUS

Sample Cell, 25 mL, matched pair	2	pair	20950-00

OPTIONAL APPARATUS

Pour-Thru Cell Assembly Kit		each	45215-00

For technical support and ordering information, see Section V.

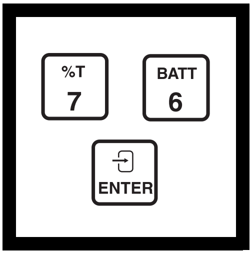
In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 10126

CHLORINE DIOXIDE (0.00 to 5.00 mg/L)

DPD Method* **For water**

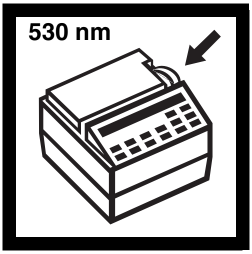


1. Enter the stored program number for the DPD chlorine dioxide method.

Press: **76 ENTER**

The display will show:

Dial nm to 530

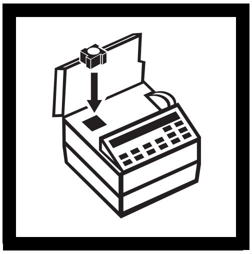


2. Rotate the wavelength dial until the small display shows:

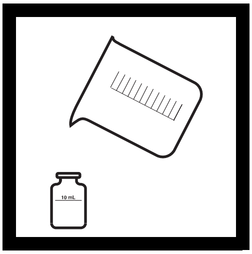
530 nm

When the correct wavelength is dialed in the display will quickly show: **Zero Sample**

then: **mg/L ClO_2**



3. Insert the 10-mL Cell Riser into the sample compartment.



4. Fill a sample cell with 10 mL of sample (the blank). Place it into the cell holder. Close the light shield.

Note: *Samples must be analyzed immediately after collection because chlorine dioxide is unstable in solutions. See Sampling and Storage following these steps.*

Note: *For best results, run a reagent blank using deionized water as the sample. Subtract the blank value from the sample reading to obtain the final result.*

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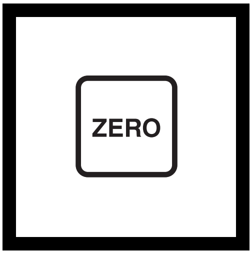
* Adapted from *Standard Methods for the Examination of Water and Wastewater.*

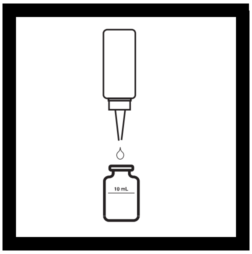


5. Press: **ZERO**

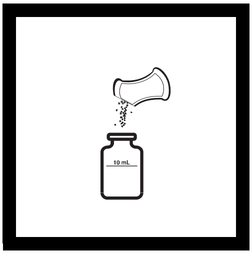
The display will show:

Zeroing. . .

then: **0.00 mg/L ClO_2**



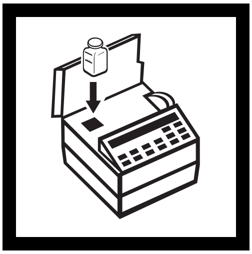
6. Add four drops of Glycine Reagent to the sample. Swirl to mix.



7. Add the contents of one DPD Free Chlorine Powder Pillow to the sample cell (the prepared sample). Swirl to mix.

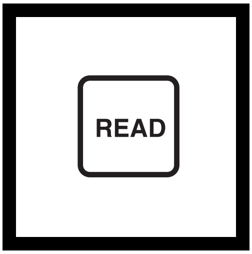
Note: *A pink color will develop if chlorine dioxide is present.*

Note: *Perform step 9 within one minute after reagent addition.*



8. Let the cell sit for 30 seconds to allow the undissolved powder to settle. Within one minute of reagent addition, place the prepared sample into the cell holder. Close the light shield.

Note: *Proceed immediately to step 9.*



9. Press: **READ**

The display will show:

Reading. . .

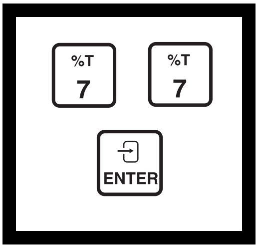
then the result in mg/L chlorine dioxide (ClO_2) will be displayed.

Forms ▲▼ **Cl_2**

Note: *If the sample temporarily turns yellow after reagent addition, or shows* **OVER-RANGE***, dilute a fresh sample and repeat the test. A slight loss of chlorine dioxide may occur during dilution. Multiply the result by the appropriate dilution factor; see Sample Dilution Techniques (Section I).*

Note: *Use chlorine dioxide-free water to dilute samples that are over range.*

Using AccuVac® Ampuls

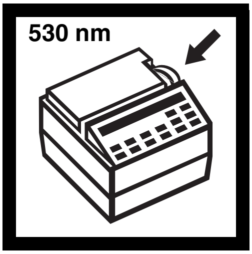


1. Enter the stored program number for the DPD chlorine dioxide (ClO_2) AccuVac ampul method.

Press: **77 ENTER**

The display will show:

Dial nm to 530

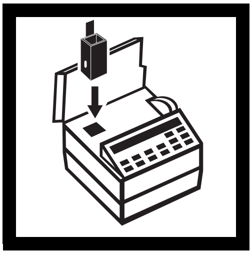


2. Rotate the wavelength dial until the small display shows

530 nm

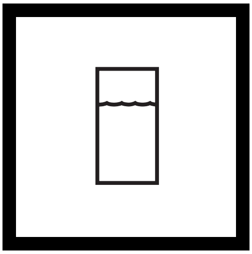
When the correct wavelength is dialed in the display will quickly show: **Zero Sample**

then: **mg/L ClO_2 AV**



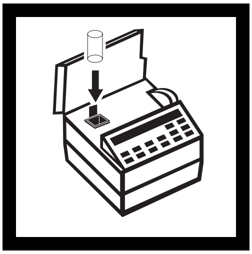
3. Place the AccuVac Vial Adapter into the cell holder of the instrument.

Note: *Place the grip tab at the rear of the cell holder.*

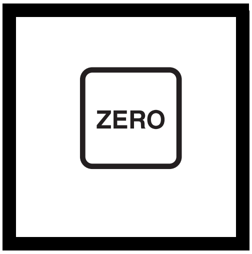


4. Fill a zeroing vial (the blank) with at least 10 mL of sample.

Note: *For best results, run a reagent blank using deionized water as the sample. Subtract the blank value from the sample reading to obtain the final result.*



5. Place the blank into the cell holder. Close the light shield.

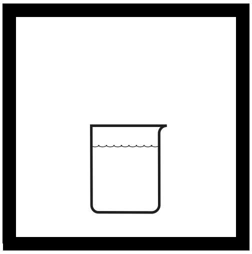


6. Press: **ZERO**

The display will show:

Zeroing. . .

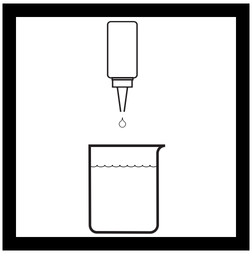
then:
0.00 mg/L ClO_2 AV



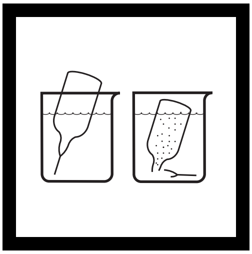
7. Fill a 50-mL beaker with 40 mL of sample.

Note: *The volume of sample used is important; use 40 mL.*

Note: *Samples must be analyzed immediately after collection because chlorine dioxide is unstable in solutions. See Sampling and Storage following these steps.*



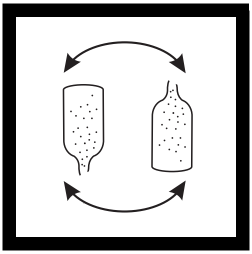
8. Add 16 drops of Glycine Reagent to the sample in the beaker. Swirl to mix.



9. Fill a DPD Free Chlorine Reagent AccuVac Ampul with sample.

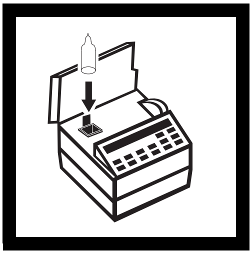
Note: *Keep the tip immersed while the Ampul fills completely.*

Note: *Perform steps 10 and 11 within one minute of filling the Ampul with sample.*



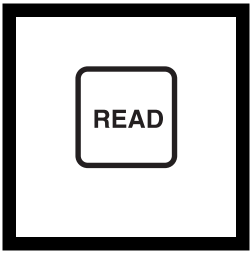
10. Quickly invert the Ampul several times to mix. Wipe off any liquid or fingerprints. Let the Ampul sit for 30 seconds to let any undissolved reagent settle.

Note: *A pink color will form if chlorine dioxide is present.*



11. Within one minute of sample addition, place the AccuVac Ampul into the cell holder. Close the light shield.

Note: *Proceed immediately to Step 12.*



12. Press: **READ**

The display will show:

Reading. . .

then the result in mg/L ClO_2 will be displayed.

Forms ▲▼ **Cl_2**

Note: *If the sample temporarily turns yellow after sample addition, or shows* **OVER-RANGE,** *dilute a fresh sample and repeat the test. A slight loss of chlorine dioxide may occur during dilution. Multiply the result by the appropriate dilution factor; see Sample Dilution Techniques (Section 1).*

Note: *Use chlorine dioxide-free water to dilute samples.*

Sampling and Storage

Analyze samples for chlorine dioxide **immediately** after collection. Chlorine dioxide is a strong oxidizing agent, and is unstable in natural waters. It reacts rapidly with various inorganic compounds, but oxidizes organic compounds more slowly. Many factors, including reactant concentrations, sunlight, pH, temperature, and salinity influence decomposition of chlorine dioxide in water.

Avoid plastic containers since these may have a large chlorine dioxide demand. **Pretreat glass** sample containers to remove any demand by soaking in a dilute bleach solution (1 mL commercial bleach to l liter of deionized water) for at least 1 hour. Rinse thoroughly with deionized or distilled water. If sample containers are rinsed thoroughly with deionized or distilled water after use, only occasional pre-treatment is necessary.

A common error in testing for chlorine dioxide is introduced when a representative sample is not obtained. If sampling from a tap, let the water flow for at least five minutes to ensure a representative sample. Let the container overflow with the sample several times, then cap the sample container so there is no headspace (air) above the sample. If sampling with a sample cell, rinse the cell several times with the sample, then carefully fill to the 10-mL mark. Analyze immediately.

Accuracy Check

Because chlorine dioxide is difficult and hazardous to produce, check the DPD and glycine reagents by using chlorine standards. Proceed as follows:

1. Prepare a 1-mg/L free chlorine standard.

Method 1

a. Obtain Free Chlorine Standards, Hach Cat. No. 14268-10.

b. Determine the concentration of the standard from the certificate of analysis shipped with the standard (50-75 mg/L). Calculate the volume of standard needed:

mL standard needed = 100 ÷ standard concentration

c. Pipet the volume of standard needed into a 100-mL volumetric flask. Dilute to the line with chlorine dioxide demand-free deionized water. Invert to mix.

Method 2

Dilute 1 drop of 5% chlorine bleach in 1 liter of chlorine dioxide demand-free deionized water. This as the standard.

2. Verify the standard's concentration using the Hach Free Chlorine Method, #8021.

3. Perform the chlorine dioxide test on the standard without adding glycine (*step 7* or *step 8*)

4. The chlorine dioxide reading should be about 2.3 times greater than the chlorine result. If so, this verifies the DPD and the instrument are functioning properly.

5. Repeat the chlorine dioxide test on the chlorine standard, including the glycine addition (*step 6* or *8*). The reading should be less than 0.10 mg/L. This verifies that the glycine is eliminating free chlorine interference.

Method Performance

Precision

Program	Standard	95% Confidence Limits
76	0.24 mg/L	0.22–0.26 mg/L ClO_2
76	4.79 mg/L	4.74–4.84 mg/L ClO_2
77	0.26 mg/L	0.24–0.28 mg/L ClO_2
77	4.83 mg/L	4.77–4.89 mg/L ClO_2

For more information on determining precision data and method detection limits, see *Section 1*.

Estimated Detection Limit

Program	EDL
76	0.04 mg/L ClO_2
77	0.04 mg/L ClO_2

For more information on derivation and use of Hach's estimated detection limit, see *Section 1*.

Sensitivity
Program Number: 76

Portion of Curve:	∆Abs	∆Concentration
0.40	0.010	0.042 mg/L
2.50	0.010	0.045 mg/L
4.00	0.010	0.047 mg/L

Program Number: 77

Portion of Curve:	∆Abs	∆Concentration
0.40	0.010	0.047 mg/L
2.50	0.010	0.051 mg/L
4.00	0.010	0.053 mg/L

See Section 1 for more information about the derivation and use of Hach’s sensitivity statement.

Interferences

A substance interferes if it changes the final reading by 0.1 mg/L ClO_2 or more.

Interfering Substance	Interference Levels and Treatments
Acidity	Greater than 150 mg/L $CaCO_3$. May not develop full color or color may fade instantly. Neutralize to pH 6–7 with 1 N sodium hydroxide. Determine amount to be added on separate sample aliquot, then add the same amount to the sample being tested. Correct for volume addition (see *Section 1, Correction For Volume Additions).*
Alkalinity	Greater than 250 mg/L $CaCO_3$. May not develop full color or color may fade instantly. Neutralize to pH 6–7 with 1 N sulfuric acid. Determine amount to be added on separate sample aliquot, then add the same amount to the sample being tested. Correct for volume addition (see Section 1, *Correction For Volume Additions)*.
Bromine, Br_2	Interferes at all levels.
Chlorine, Cl_2	May interfere at levels greater than 6 mg/L. Additional glycine may be able to compensate for this interference.
Chloramines, organic	May interfere.

Interfering Substance	Interference Levels and Treatments
Flocculating agents	High levels of most flocculating agents can be tolerated. This tolerance is decreased if chlorine is present. See the information about metals in this table. In the presence of 0.6 mg/L Cl_2, $Al(SO_4)_3$ (< 500 mg/L) and $FeCl_2$ (<200 mg/L) may be tolerated.
Hardness	No effect at less than 1,000 mg/L as $CaCO_3$.
Iodine, I_2	Interferes at all levels.
Manganese, oxidized (Mn^{4+}, Mn^{7+}) or Chromium, oxidized (Cr^{6+})	Oxidized manganese interferes at all levels. Oxidized chromium interferes at levels greater than 2 mg/L. To remove the interferences: **1.** Adjust sample pH to 6–7. **2.** Add 3 drops potassium iodide (30 g/L) to a 25-mL sample. **3.** Mix and wait one minute. **4.** Add 3 drops sodium arsenite (5 g/L) and mix. **5.** Analyze 10 mL of the treated sample as described in the procedure. **6.** Subtract the result of this test from the original analysis to obtain the correct chlorine dioxide concentration.
Metals	Various metals may interfere by combining with the glycine needed to remove the chlorine interference. Metal interference is limited except when chlorine is present. In the presence of 0.6 mg/L Cl_2, both copper (>10 mg/L) and nickel (>50 mg/L) interfere. Other metals may also interfere, depending on their ability to prevent glycine from reacting with any Cl_2 in the sample. It may be necessary to add more glycine to overcome this interference.
Monochloramine	Causes a gradual drift to higher readings. When read within 1 minute after reagent addition, 3 mg/L monochloramine causes less than a 0.1 mg/L ClO_2 increase in the reading.
Ozone	Interferes at levels greater than 1.5 mg/L.
Peroxides	May interfere.
Extreme sample pH	Adjust to pH 6–7. See Section *1, pH Interferences.*
Highly buffered samples	Adjust to pH 6–7. See Section *1, pH Interferences.*

Summary of Method

Chlorine dioxide reacts with DPD (N,N-diethyl-p-phenylenediamine) Indicator Reagent (to the extent of one-fifth of its total available chlorine content corresponding to reduction of chlorine dixide to chlorite) to form a pink color. The color intensity is proportional to the ClO_2 in the sample. Chlorine interference is eliminated by adding glycine, which converts free chlorine to chloroaminoacetic acid, but has no effect on chlorine dioxide at the test pH.

CHLORINE DIOXIDE, continued

REQUIRED REAGENTS (Using Powder Pillows)

Description			Cat. No.
Chlorine Dioxide DPD/Glycine Reagent Set (100 tests)			27709-00
Includes one of each:			
DPD Free Chlorine Reagent Powder Pillows, 10 mL	1	100/pkg	21055-69
Glycine Reagent	4 dropds	29 mL	27621-33

REQUIRED REAGENTS (Using AccuVac Ampuls)

Description	Quantity Required per test	Unit	Cat. No.
Chlorine Dioxide DPD/Glycine AccuVac® Ampul Reagent Set (25 tests)			27710-00
Includes one of each:			
DPD Free Chlorine Reagent AccuVac® Ampuls	1 ampul	25/pkg	25020-25
Glycine Reagent	16 drops	29 mL	27621-33

REQUIRED APPARATUS (Using Powder Pillows)

Cell Riser, 10-mL sample cell	1	each	45282-00
Sample Cell, 10-mL, matched pair	2	pair	24954-02
Stopper, hollow, No 2, LDPE, fits 10 & 25-mL cells	1	6/pkg	14480-00

REQUIRED APPARATUS (Using AccuVac® Ampuls)

Adapter, AccuVac® vial	1	each	43784-00
Beaker, 50 mL	1	each	500-41
Vial, zeroing	1	each	21228-00

OPTIONAL REAGENTS

Chlorine Standard Solution, Voluette™ ampule, 50–75 mg/L, 10 mL	16/pkg	14268-10
DPD Free Chlorine Reagent w/dispensing cap	250 tests	21055-29
Potassium Iodide Solution, 30 g/L	100 mL* MDB	343-32
Sodium Arsenite, 5 g/L	100 mL* MDB	1047-32
Sodium Hydroxide Standard Solution, 1.000 N	100 mL* MDB	1045-32
Sulfuric Acid Standard Solution, 1.000 N	100 mL* MDB	1270-32
Water, deionized	4 L	272-56
Water, sterile, chlorine-dioxide demand free	500 mL	26415-49

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* Marked Dropper Bottle - contact Hach for larger sizes.

OPTIONAL APPARATUS

Description	Unit	Cat. No.
AccuVac® Ampul Snapper Kit	each	24052-00
Ampule Breaker Kit	each	24846-00
Cylinder, graduated, 25 mL	each	508-40
pH Meter, *sension*™*1*, portable	each	51700-10
pH Paper, 1 to 11 pH units	5 rolls/pkg	391-33
Pipet, TenSette®, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette® Pipet	50/pkg	21856-96

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

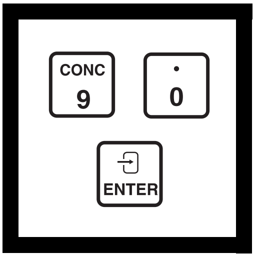
Method 8023

CHROMIUM, HEXAVALENT (0 to 0.60 mg/L Cr^{6+}) For water and wastewater

1,5-Diphenylcarbohydrazide Method* (Powder Pillows or AccuVac Ampuls)

USEPA accepted for wastewater analyses**

Using Powder Pillows



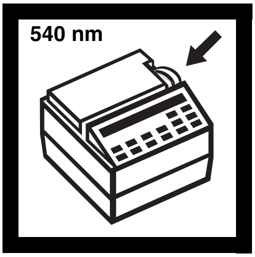
1. Enter the stored program number for hexavalent chromium (Cr^{6+}).

Press: **90 ENTER**

The display will show:

Dial nm to 540

Note: *The Pour-Thru Cell can be used with 25-mL reagents only.*



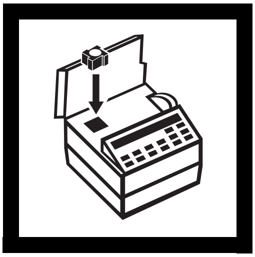
2. Rotate the wavelength dial until the small display shows:

540 nm

When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

then: **mg/L Cr^{6+}**



3. Insert the 10-mL Cell Riser into the cell compartment.

4. Fill a sample cell with 10 mL of sample.

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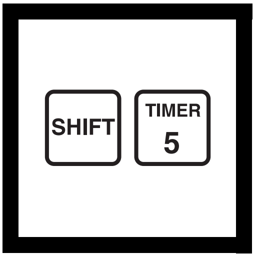
* Adapted from *Standard Methods for the Examination of Water and Wastewater.*

** Procedure is equivalent to USGS method I-1230-85 for wastewater.

5. Add the contents of one ChromaVer 3 Reagent Powder Pillow to the cell (the prepared sample). Swirl to mix.

Note: *A purple color will form if Cr^{6+} is present.*

Note: *At high chromium levels a precipitate will form. Dilute sample according to Sample Dilution Techniques (Section I).*

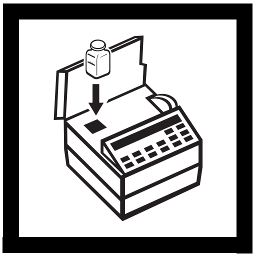


6. Press: **SHIFT TIMER**

A five-minute reaction period will begin.

7. Fill another sample cell with 10 mL of sample (the blank).

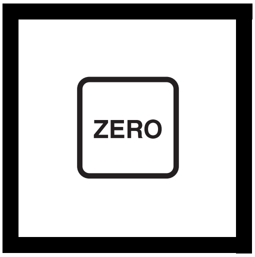
Note: *For turbid samples, add the contents of one Acid Reagent Powder Pillow. This ensures turbidity dissolved by the acid in the ChromaVer 3 Chromium Reagent is also dissolved in the blank.*



8. When the timer beeps, the display will show:

mg/L Cr^{6+}

Place the blank into the cell holder. Close the light shield.

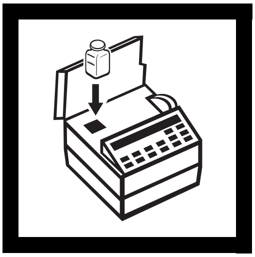


9. Press: **ZERO**

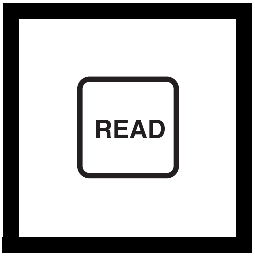
The display will show:

Zeroing. . .

then: **0.00 mg/L Cr^{6+}**



10. Place the prepared sample into the cell holder. Close the light shield.



11. Press: **READ**

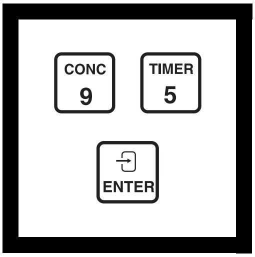
The display will show:

Reading. . .

then the results in mg/L hexavalent chromium will be displayed.

Forms ▲▼ Na_2CrO_4
Cr^{6+}
CrO_4^{2-}

Using AccuVac Ampuls

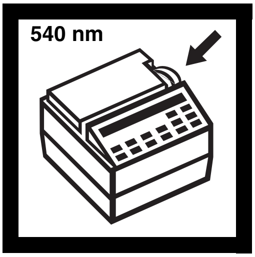


1. Enter the stored program number for hexavalent chromium.

Press: **9 5 ENTER**

The display will show:

Dial nm to 540

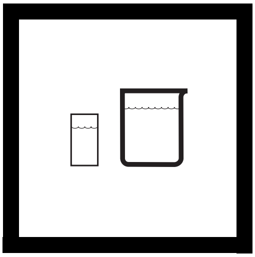


2. Rotate the wavelength dial until the small display shows:

540 nm

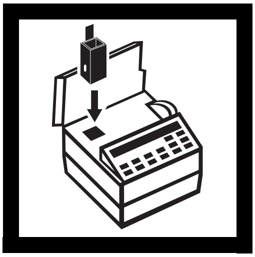
When the correct wavelength is dialed in the display will quickly show: **Zero Sample**

then: **mg/L Cr^{6+} AV**



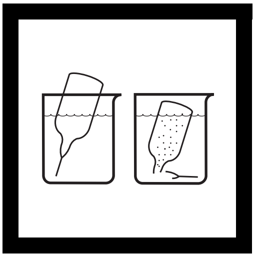
3. Fill the zeroing vial with at least 10 mL of sample (the blank). Collect at least 40 mL of sample in a 50-mL beaker.

Note: *For turbid samples, add the contents of one Acid Reagent Powder Pillow to 10 mL of the blank. This ensures turbidity dissolved by the acid in the ChromaVer 3 Chromium Reagent is also dissolved in the blank.*



4. Place the AccuVac Vial Adapter into the cell holder.

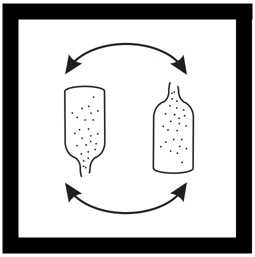
Note: *Place the grip tab at the rear of the cell holder.*



5. Fill a ChromaVer 3 Reagent AccuVac Ampul (the prepared sample) with sample.

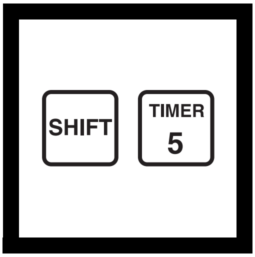
Note: *Keep the tip immersed while the ampul fills completely.*

Note: *ChromaVer 3 should be white to tan in color. Replace if it is brown or green.*



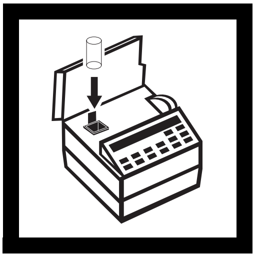
6. Quickly invert the ampul several times to mix. Wipe off any liquid or fingerprints.

Note: *A purple color will form if hexavalent chromium is present.*



7. Press: **SHIFT TIMER**

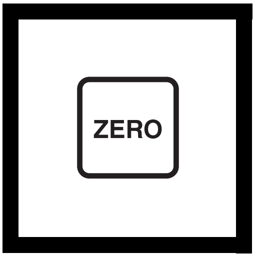
A five-minute reaction period will begin.



8. When the timer beeps the display will show:

mg/L Cr^{6+} AV

Place the blank into the cell holder. Close the light shield.



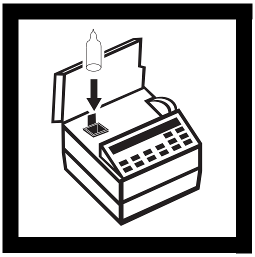
9. Press: **ZERO**

The display will show:

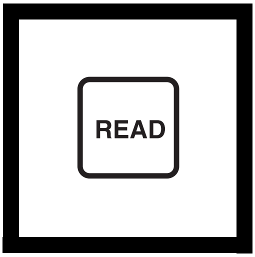
Zeroing. . .

then:

0.00 mg/L Cr^{6+} AV



10. Place the prepared sample into the cell holder. Close the light shield.



11. Press: **READ**

The display will show:

Reading. . .

then the result in mg/L hexavalent chromium will be displayed.

Forms ▲▼
Na_2CrO_4
CrO_4^{2-}
Cr^{6+}

Sampling and Storage

Collect samples in a cleaned glass or plastic container. Store at 4 °C (39 °F) up to 24 hours. Samples must be analyzed within 24 hours.

Accuracy Check

Standard Additions Method

a) Snap the neck off a Chromium Voluette Ampule Standard, 12.5 mg/L Cr^{6+}.

b) Use the TenSette Pipet to add 0.1 mL, 0.2 mL and 0.3 mL of standard, respectively, to three 25-mL samples contained in 25-mL mixing cylinders. Mix each thoroughly.

c) Transfer 10 mL of each solution into a 10-mL sample cell.

d) Analyze each sample as described above. The chromium concentration should increase 0.05 mg/L for each 0.1 mL of standard added.

e) If these increases do not occur, see Standard Additions in Section I for more information.

Standard Solution Method

Prepare a 0.25-mg/L Cr^{6+} solution by pipetting 5.00 mL of hexavalent chromium standard solution, 50.0 mg/L Cr^{6+}, into a 1000-mL volumetric flask and diluting to the mark with deionized water. Prepare this solution daily. Perform the chromium procedure as described above. The mg/L Cr^{6+} reading should be 0.25 mg/L Cr^{6+}.

Method Performance

Precision

In a single laboratory using a standard solution of 0.4 mg/L Cr^{6+} and two representative lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±0.003 mg/L Cr^{6+}.

In a single laboratory using a standard solution of 0.4 mg/L Cr^{6+} and two representative lots of AccuVac ampuls with the DR/2010, a single operator obtained a standard deviation of ±0.001 mg/L Cr^{6+}.

Estimated Detection Limit (EDL)

The EDL for program 90 (powder pillows) and program 95 (AccuVac Ampuls) is 0.01 mg/L Cr^{6+}.

The EDL is the calculated lowest average concentration in a deionized water matrix that is different from zero with a 99% level of confidence. For more information on derivation and use of Hach's estimated detection limit, see Section I.

Interferences

The following substances do not interfere in the test, up to the following concentration:

Substance	Concentration
Mercurous & Mercuric Ions	Interferes Slightly
Iron	1 mg/L
Vanadium	1 mg/L

Vanadium interference can be overcome by waiting ten minutes before reading.

Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment; see pH Interference in Section I.

Summary of Method

Hexavalent chromium is determined by the 1,5-diphenylcarbohydrazide method using a single dry powder formulation called ChromaVer 3 Chromium Reagent. This reagent contains an acidic buffer combined with 1,5-diphenylcarbohydrazide, which reacts to give a purple color which is proportional to the amount of hexavalent chromium present.

REQUIRED REAGENTS AND APPARATUS (USING POWDER PILLOWS)

Description	Quantity Required Per Test	Unit	Cat. No.
Cell Riser, 10 mL sample cell	1	each	45282-00
ChromaVer 3 Chromium Reagent	1 pillow	100/pkg	12710-99
Sample cell, with 10-mL mark, matched pair	2	pair	24954-02

REQUIRED REAGENTS AND APPARATUS (USING ACCUVAC AMPULS)

Description	Quantity Required Per Test	Unit	Cat. No.
ChromaVer 3 AccuVac ampuls	1 ampul	25/pkg	25050-25
Adapter, AccuVac Vial	1	each	43784-00
Beaker, 50 mL	1	each	500-41
Sample Cell, 25 x 54 mm, 10 mL, with cap	1	each	21228-00

OPTIONAL REAGENTS

Description	Unit	Cat. No.
Acid Reagent Powder Pillows	50/pkg	2126-66
Chromium, Hexavalent, Standard Solution, 50 mg/L Cr^{6+}	100 mL	810-42
Chromium, Hexavalent, Standard Solution, Voluette ampule, 12.5 mg/L Cr^{6+}, 10 mL	16/pkg	14256-10
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Description	Unit	Cat. No.
AccuVac Snapper Kit	each	24052-00
Ampule Breaker Kit	each	21968-00
Cylinder, graduated, mixing, 25 mL	each	20886-40
Flask, volumetric, Class A, 1000 mL	each	14574-53
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
pH Meter, *sension*™*1*, portable	each	51700-10
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet, volumetric, 5.00 mL, Class A	each	14515-37
Pipet Filler, safety bulb	each	14651-00

OPTIONAL 25 mL ANALYSIS ITEMS

Description	Unit	Cat. No
ChromaVer 3 Chromium Reagent (for 25 mL samples)	50/pkg	12066-66
Clippers, for opening pillows	each	968-00
Pour-Thru Cell Assembly Kit (for 25-mL samples/reagents only)	each	45215-00
Sample cell, with 25-mL mark, matched pair	pair	20950-00

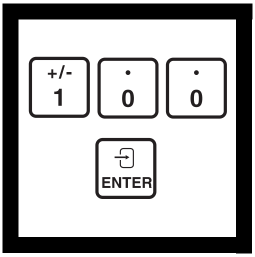
For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

CHROMIUM, TOTAL (0 to 0.60 mg/L)

Alkaline Hypobromite Oxidation Method* **



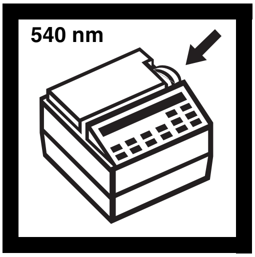
1. Enter the stored program number for total chromium (Cr).

Press: **1 0 0 ENTER**

The display will show:

Dial nm to 540

Note: *The Pour-Thru Cell can be used.*



2. Rotate the wavelength dial until the small display shows:

540 nm

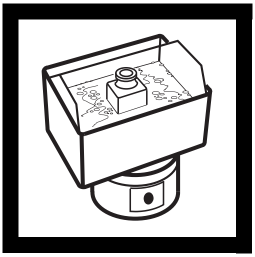
When the correct wavelength is dialed in the display will quickly show:

Zero Sample

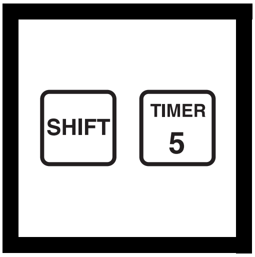
then: **mg/L Cr**

3. Fill a clean sample cell with 25 mL of sample.

4. Add the contents of one Chromium 1 Reagent Powder Pillow (the prepared sample). Swirl to mix.



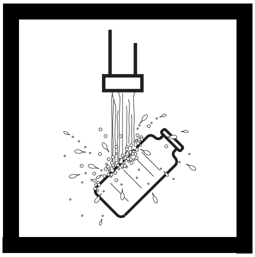
5. Place the prepared sample into a boiling water bath.



6. Press:

SHIFT TIMER

A five-minute reaction period will begin.



7. When the beeper sounds, remove the prepared sample. Using running tap water, cool the cell to 25 °C.

Note: *Use finger cots to handle the hot sample cell.*

8. Add the contents of one Chromium 2 Reagent Powder Pillow. Swirl to mix.

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* Adapted from *Standard Methods for the Examination of Water and Wastewater.*

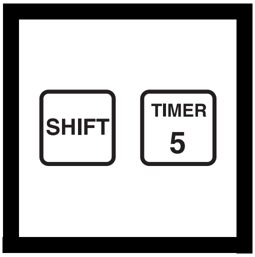
** Procedure is equivalent to Standard Method 3500-Cr D for wastewater.

9. Add the contents of one Acid Reagent Powder Pillow.
Swirl to mix.

10. Add the contents of one ChromaVer 3 Chromium Reagent Powder Pillow.
Swirl to mix.

Note: *A purple color will form if chromium is present.*

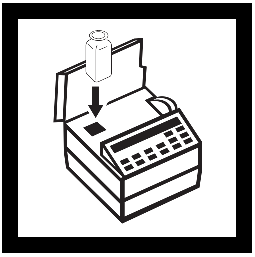
Note: *ChromaVer 3 is white to tan in color. Replace brown or green powder. Undissolved powder does not affect accuracy.*



11. Press:

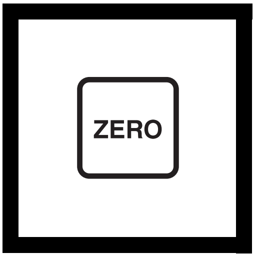
SHIFT TIMER

A five-minute reaction period will begin.



12. When the timer beeps, fill another sample cell with 25 mL of sample (the blank). Place it into the cell holder. Close the light shield.

Note: *For turbid samples, treat the blank as described in Steps 4 through 9.*

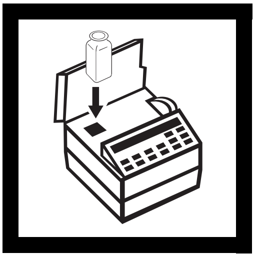


13. Press: **ZERO**

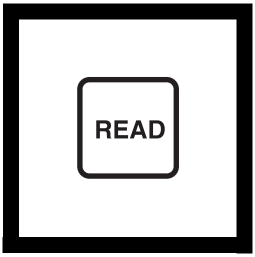
The display will show:

Zeroing. . .

then: **0.00 mg/L Cr**



14. Place the prepared sample into the cell holder. Close the light shield.



15. Press: **READ**

The display will show:

Reading. . .

then the result in mg/L chromium will be displayed.

Note: *Determine a reagent blank for each new lot of ChromaVer 3 using deionized water as the sample. Subtract this value from each result obtained.*

Forms ▲▼ Na_2CrO_4
Cr
CrO_4^{2-}

Sampling and Storage

Collect samples in acid-washed glass or plastic containers. To preserve samples, adjust the pH to 2 or lower with nitric acid (about 2 mL per liter). Store preserved samples at room temperature up to six months. Adjust the pH to about 4 with 5.0 N Sodium Hydroxide before analysis. Correct the test results for volume additions.

Accuracy Check

Standard Additions Method

a) Fill three 25-mL graduated mixing cylinders with 25 mL of sample.

b) Snap the top off a Trivalent Chromium Voluette Ampule Standard, 12.5 mg/L as Cr^{3+}.

c) Use the TenSette pipet to add 0.1, 0.2, and 0.3 mL of standard to the three 25-mL mixing cylinders. Mix each thoroughly.

d) Transfer 10 mL of solution to 10-mL sample cells.

e) Analyze each sample as described above. The chromium concentration should increase 0.05 mg/L for each 0.1 mL of standard added.

f) If these increases do not occur see Standard Additions (Section I).

Standard Solution Method

Prepare a 0.25 mg/L trivalent chromium standard by diluting 5.00 mL of chromium standard solution, 50 mg/L as Cr^{3+}, to 1000 mL with deionized water. Prepare this solution daily. Perform the chromium procedure as described above. The mg/L Cr reading should be 0.25 mg/L.

Precision

In a single laboratory using a standard solution of 0.4 mg/L chromium and two representative lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±0.025 mg/L chromium.

Interferences

Large amounts of organic material may inhibit complete oxidation of trivalent chromium. If high levels of organic material are present, see Digestion in Section II for instruction on sample digestion. Perform the analysis as described on the digested sample.

Iron does not interfere.

Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment; see pH Interferences in Section I.

Summary of Method

Trivalent chromium in the sample is oxidized to the hexavalent form by hypobromite ion under alkaline conditions. The sample is acidified. Total chromium content is determined by the 1,5-diphenylcarbohydrazide method. Determine trivalent chromium by subtracting the result of a separate hexavalent chromium test from the total chromium result.

REQUIRED REAGENTS

	Cat. No.
Total Chromium Reagent Set (100 Tests)	22425-00
Includes: (1) 2126-99, (1) 12066-99, (1) 2043-99, (1) 2044-99	

Description	Quantity Required Per Test	Unit	Cat. No.
Acid Reagent Powder Pillows	1 pillow	100/pkg	2126-99
ChromaVer 3 Chromium Reagent Powder Pillows	1 pillow	100/pkg	12066-99
Chromium 1 Reagent Powder Pillows	1 pillow	100/pkg	2043-99
Chromium 2 Reagent Powder Pillows	1 pillow	100/pkg	2044-99

REQUIRED APPARATUS

Clippers, for opening pillows	1	each	968-00
Water bath and rack	1	each	1955-55
Hot plate, 3 1/2" diameter, 120 Vac	1	each	12067-01
Hot plate, 3 1/2" diameter, 240 Vac	1	each	12067-02
Sample Cell, with 25-mL mark, matched pair		pair	20950-00

OPTIONAL REAGENTS

Description	Unit	Cat. No.
Chromium, trivalent, standard solution, 50 mg/L Cr^{3+}	100 mL	14151-42
Chromium, trivalent, standard solution, Voluette ampule, 12.5 mg/L Cr^{3+}, 10 mL	16/pkg	14257-10
Nitric Acid, ACS	500 mL	152-49
Nitric Acid Solution 1:1	500 mL	2540-49
Sodium Hydroxide Solution 5.0 N	50 mL* SCDB	2450-26
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Description	Unit	Cat. No.
Ampule Breaker Kit	each	21968-00
Cylinder, graduated, polypropylene, 25 mL	each	1081-40
Cylinder, graduated, mixing, 25 mL	each	20886-40
Finger Cots	2/pkg	14647-02
Flask, volumetric, 1000 mL	each	547-53
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
pH Meter, *sension*™*1*, portable	each	51700-10
Pipet, serological, 2 mL	each	532-36
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 5.00 mL	each	14515-37
Pipet Filler, safety bulb	each	14651-00
Pour-Thru Cell Assembly Kit	each	45215-00

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

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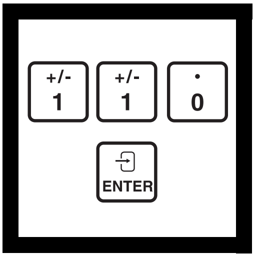
* Contact Hach for larger sizes.

Method 8078

COBALT (0 to 2.00 mg/L)

For water and wastewater

1-(2-Pyridylazo)-2-Naphthol (PAN) Method*



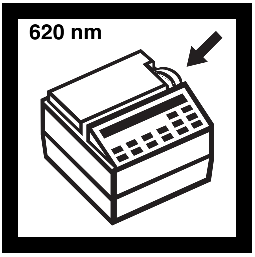
1. Enter the stored program number for cobalt (Co).

Press: **1 1 0 ENTER**

The display will show:
Dial nm to 620

Note: *Adjust the pH of stored samples before analysis.*

Note: *The Pour-Thru cell can be used with 25-mL reagents only. Rinse well with water after use.*



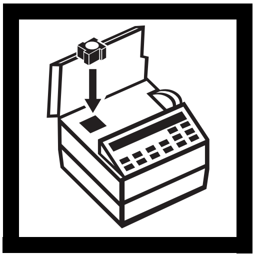
2. Rotate the wavelength dial until display shows:

620 nm

When the correct wavelength is dialed in, the display will quickly show:

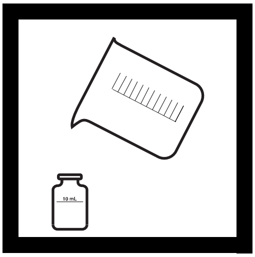
Zero Sample

then: **mg/L Co**



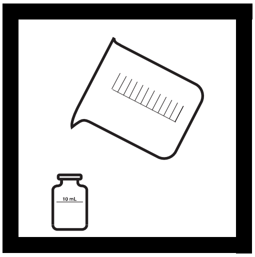
3. Insert the 10-mL Cell Riser into the sample compartment.

Note: *Total recoverable cobalt needs a prior digestion; use one of the three procedures given in Digestion (Section II). If EDTA is present, use the vigorous digestion.*



4. Fill a 10-mL sample cell with 10 mL of sample (the prepared sample).

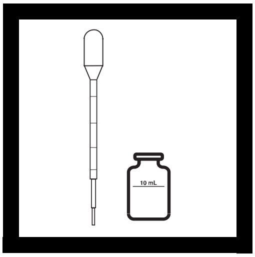
Note: *If sample is less than 10 °C (50 °F), warm to room temperature prior to analysis.*



5. Fill a second 10-mL sample cell with 10 mL of deionized water (the blank).

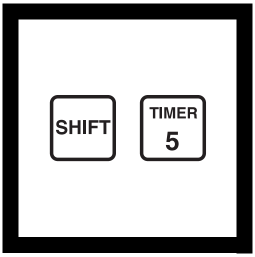
6. Add the contents of one Phthalate-Phosphate Reagent Powder Pillow to each sample cell. Stopper each cell. Immediately shake to dissolve.

Note: *If sample contains iron (Fe^{3+}), all of the powder must dissolve completely before continuing with Step 7.*



7. Add 0.5 mL of 0.3% PAN Indicator Solution to each sample cell. Stopper. Invert several times to mix.

Note: *Use plastic dropper provided.*



8. Press:

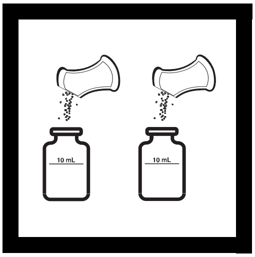
SHIFT TIMER

A three-minute reaction period will begin.

Note: *During color development, the sample solution color may vary from green to dark red, depending on the chemical makeup of the sample. The deionized water blank should be yellow.*

---

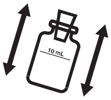
* Adapted from Watanbe, H., *Talanta*, 21 295 (1974).

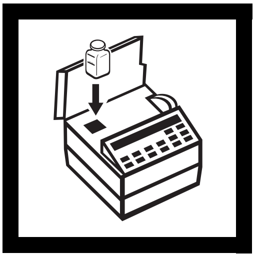


9. When the timer beeps, the display will show:

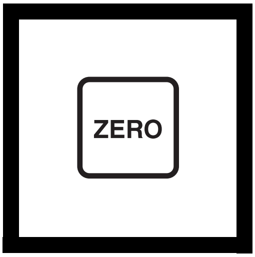
mg/L Co

Add the contents of one EDTA Reagent Powder Pillow to each sample cell. Stopper. Shake to dissolve.





10. Remove both stoppers. Place the blank into the cell holder. Close the light shield.

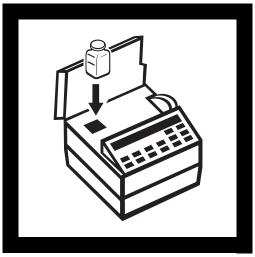


11. Press: **ZERO**

The display will show:

Zeroing. . . .

then: **0.00 mg/L Co**



12. Place the prepared sample into the cell holder. Close the light shield.

Press: **READ**

The display will show:

Reading. . . .

then the result in mg/L Co will be displayed.

Note: *If the sample contains nickel refer to the Nickel (PAN) procedure, program 340.*

Sampling and Storage

Collect samples in acid-washed plastic bottles. Adjust the sample pH to 2 or less with nitric acid (about 5 mL per liter). Preserved samples can be stored up to six months at room temperature. Adjust the sample pH between 3 and 8 with 5.0 N Sodium Hydroxide Standard Solution just before analysis. Do not exceed pH 8 as this may cause some loss of cobalt as a precipitate. Correct test results for volume additions; see *Correction for Volume Additions* in *Section I.*

Accuracy Check

Standard Solution Method

Prepare a 1.0 mg/L cobalt standard solution by diluting 10.0 mL of a 10 mg/L working stock solution to 100 mL in a volumetric flask. Prepare the working stock solution daily by diluting 10.00 mL of cobalt Standard Solution, 1000 mg/L as Co, to 1000 mL with deionized water. This is a 10 mg/L cobalt standard solution.

Precision

In a single laboratory using standard solutions of 0.75 mg/L cobalt and two representative lots of reagents with the DR/2010, a single operator obtained a standard deviation of ±0.001 mg/L cobalt.

Interferences

The following may interfere in concentrations exceeding those listed below.

Al^{3+}	32 mg/L
Ca^{2+}	1000 mg/L as ($CaCO_3$)
Cd^{2+}	20 mg/L
Cl^-	8000 mg/L
Cr^{3+}	20 mg/L
Cr^{6+}	40 mg/L
Cu^{2+}	15 mg/L
F^-	20 mg/L
Fe^{2+}	interferes directly; must not be present
Fe^{3+}	10 mg/L
K^+	500 mg/L
Mg^{2+}	400 mg/L
Mn^{2+}	25 mg/L
Mo^{6+}	60 mg/L
Na^+	5000 mg/L
Pb^{2+}	20 mg/L
Zn^{2+}	30 mg/L

Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment; see *pH Interferences* in *Section I.*

Summary of Method

After buffering the sample and masking any Fe^{3+} with pyrophosphate, the cobalt is reacted with 1-(2-Pyridylazo)-2-Naphthol indicator. The indicator forms complexes with most metals present. After color development, EDTA is added to destroy all metal-PAN complexes except nickel and cobalt. Both nickel and cobalt can be determined on the same sample.

REQUIRED REAGENTS

Cobalt Reagent Set, 10 mL size (100 Tests)	26516-00
Includes: (2) 7005-99, (1) 21502-32, (2) 26151-49	

Description	Quantity Required Per Test	Unit	Cat. No.
EDTA Reagent Powder Pillows	2 pillows	100/pkg	7005-99
Phthalate-Phosphate Reagent Powder Pillows, 10-mL size	2 pillows	100/pkg	26151-99
PAN Indicator Solution, 0.3%	1.0 mL	100 mL	21502-32
Water, deionized	10 mL	4 L	272-56

REQUIRED APPARATUS

Cell Riser, 10 mL	1	each	45282-00
Cylinder, mixing, graduated, 25 mL	1	each	20886-40
Sample Cell, 10 mL, matched pair	2	pair	24954-02
Stopper, HDPE, #16	2	6/pkg	20955-16

OPTIONAL REAGENTS

Cobalt Standard Solution, 1000 mg/L Co	100 mL	21503-42
Nitric Acid, ACS	500 mL	152-49
Nitric Acid Solution, 1:1	500 mL	2540-49
Sodium Hydroxide Standard Solution, 5.0 N	100 mL MDB	2450-32
Sodium Hydroxide Standard Solution, 5.0 N	1 L	2450-53

OPTIONAL APPARATUS

Dropper, 0.5 and 1.0 mL mark	5/pkg	14197-05
Flask, volumetric, Class A, 100 mL	each	14574-42
Flask, volumetric, Class A, 1000 mL	each	14574-53
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
pH Meter, *sension*™*1*, portable	each	51700-10
Pipet, serological, 1 mL	each	532-35
Pipet, serological, 5 mL	each	532-37
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 10.0 mL	each	14515-38
Pipet Filler, safety bulb	each	14651-00
Thermometer, -20 to 105 °C	each	1877-01

OPTIONAL 25 mL ANALYSIS ITEMS

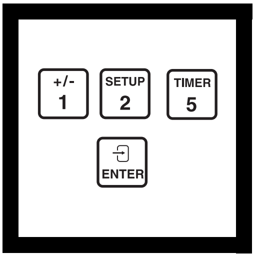
Cobalt Reagent Set, 25 mL size (100 Tests)		22426-00
Includes: (2) 7005-99, (4) 21501-66, (2) 21502-32		
Clippers, for opening pillows	each	968-00
Pour-Thru Cell Assembly Kit (for 25 mL reagents only)	each	45215-00
Sample Cell, 25 mL, matched pair	pair	20950-00

Method 10068

COLOR, NCASI 253 (0 to 500 units)

Platinum-Cobalt Method*

For pulp and paper industry water



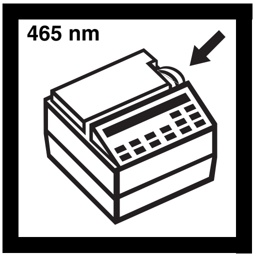
1. Enter the stored program number for NCASI color.

Press: **1 2 5 ENTER**

The display will show:

Dial nm to 465

Note: *The Pour-Thru Cell can be used with this procedure.*



2. Rotate the wavelength dial until the small display shows:

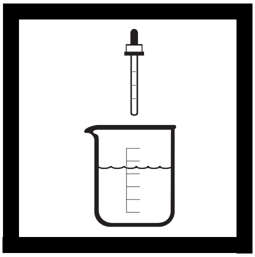
465 nm

When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

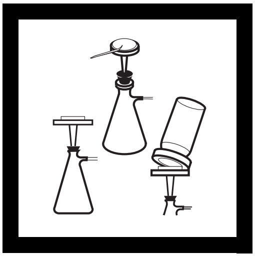
then:

UNITS PtCo NCASI

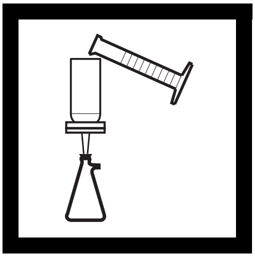


3. Collect 200 mL of sample in a 400-mL beaker. Adjust the pH to 7.6 with 1.0 N HCl or 1.0 N NaOH. If overall additions exceed 2.0 mL, start over using a stronger acid or base.

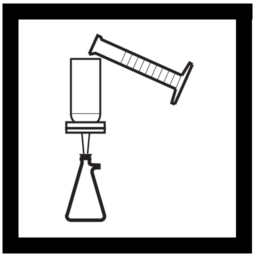
Note: *For sample dilution, use the phosphate buffer described under Sampling and Storage so pH adjustment is easier.*



4. Assemble the filtering apparatus (membrane filter, filter holder, filter flask, and aspirator)

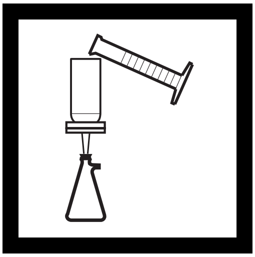


5. Rinse the filter by pouring about 50 mL of deionized water through the filter. Discard the rinse water.



6. Pour another 50 mL of deionized water through the filter. Keep this for Step 7.

7. Fill a sample cell (the blank) with 25 mL of filtered deionized water. Discard the excess.



8. Pour about 50 mL of sample through the filter.

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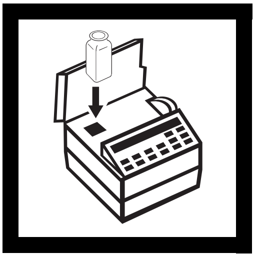
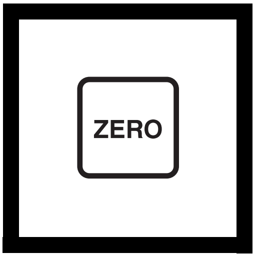
* Adapted from *NCASI Method 253,* June 1978.

9. Fill a second sample cell (the prepared sample) with 25 mL of filtered sample.



10. Place the blank into the cell holder. Close the light shield.



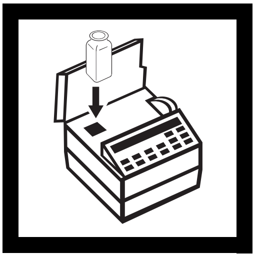
11. Press: **ZERO**

The display will show:

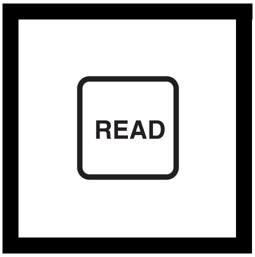
Zeroing. . . .

then:

0. UNITS PtCo NCASI



12. Place the prepared sample into the cell holder. Close the light shield.



13. Press: **READ**

The display will show:

Reading. . . .

and then the result in platinum-cobalt units will be displayed.

Sampling and Storage

Collect samples in clean glass bottles. Use phosphate buffer for sample dilution when necessary. The buffer simplifies sample pH adjustment.

Preparation of Phosphate Buffer for Dilutions

In a 1000-mL volumetric flask, dissolve 13.61 g of potassium phosphate, monobasic, in about 300 mL of deionized water. Dilute to volume, stopper and mix thoroughly. This is a 0.1 M potassium phosphate buffer.

Place a 2000-mL beaker on a magnetic stirrer. Add a stir bar to the beaker. Stirring gently, add 500 mL of 0.1 M potassium phosphate buffer and approximately 424 mL of 0.1 N NaOH. Dilute to 1000 mL with deionized water. Using a pH meter, adjust the final pH to 7.6 (±0.05) using 0.1 N HCl or 0.1 N NaOH.

Dilute samples with color values greater than 500 units with the buffer solution above. Correct final results for sample dilution by multiplying the final result by the total volume (original volume + dilution volume) and dividing by the original volume (see Section I).

Accuracy Check

Standard Solution Method

A 500 platinum-cobalt units color standard solution is available for checking test accuracy. A 250 platinum-cobalt units standard can be made by pipetting 50.0 mL of the 500 platinum-cobalt units standard into a 100-mL volumetric flask and diluting to volume with deionized water.

Method Performance

Precision

Concentration	99% Confidence Limit
50 units PtCo Color	46-54 units PtCO Color
250	247-253
500	495-505

For more information on determination of precision estimates, see Section I.

Estimated Detection Limit (EDL)

The EDL for program 125 is 5 units PtCO Color. The EDL is the calculated lowest average concentration in a deionized water matrix that is different from zero with a 99% level of confidence. For more information on derivation and use of Hach's estimated detection limit, see Section I.

Interferences

The color value of a water sample depends on the pH. Proper pH control to 7.6 is important as higher pH values cause an increase in color values. Turbidity in the sample gives false high readings on true color analysis and should be removed by filtration.

Summary of Method

The sample is filtered and pH adjusted to 7.6. By filtering out suspended particles, a sample's true color can be measured. The stored program is calibrated in color units based on the APHA-recommended standard of 1 color unit being equal to 1 mg/L platinum as the chloroplatinate ion.

REQUIRED REAGENTS

Description	Quantity Required Per Test	Units	Cat. No.
Hydrochloric Acid Standard Solution, 1.0 N	varies	1 L	23213-53
Sodium Hydroxide Standard Solution, 1.0 N	varies	900 mL	1045-53
Water, deionized	varies	4 L	272-56

REQUIRED APPARATUS

Aspirator, vacuum	1	each	2131-00
Beaker, 400 mL	1	each	500-48
Cylinder, graduated, 50 mL	1	each	508-41
Filter Holder, 47 mm, 300 mL graduated	1	each	13529-00
FIlter, membrane, 47mm, 0.8 microns	1	100/pkg	26408-00
Flask, filtering, 500 mL	1	each	546-49
Stopper, No 7, one hole	1	6/pkg	2119-07
Tubing, rubber	1	12 ft	560-19
Sample Cell, 25-mL, matching pair	2	pair	20950-00

OPTIONAL REAGENTS

Color Standard Solution, 500 platinum-cobalt units	1 L	1414-53
Hydrochloric Acid Standard Solution, 0.1 N	1 L	14812-53
Hydrochloric Acid Standard Solution, 6.0 N	500 mL	884-49
Potassium Phosphate, monobasic, ACS grade	454 g	170-01
Sodium Hydroxide Standard Solution, 0.1 N	1 L	191-53
Sodium Hydroxide Standard Solution, 5.0 N	1 L	2450-53

OPTIONAL APPARATUS

Beaker, 2000 mL, glass	each	500-54
Flask, volumetric, Class A, 100 mL	each	14574-42
Flask, volumetric, Class A, 1000 mL	each	14574-53
pH Indicator Paper, 1 to 11 pH units	5 rolls/pkg	391-33
pH Meter, EC10, portable	each	50050-00
Pipet, volumetric, Class A, 50 mL	each	14515-41
Pour-Thru Cell Assembly Kit	each	45215-00
Stir Bar, octagonal, 28x7.9 mm	each	20953-52
Stirrer, magnetic, 120 V, 7x7 inches	each	23444-00
Stirrer, magnetic, 240 V, 7x7 inches	each	23444-02

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

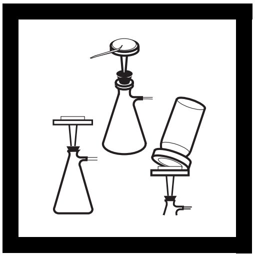
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8025

COLOR, TRUE AND APPARENT (0 to 500 units)

APHA Platinum-Cobalt Standard Method* **

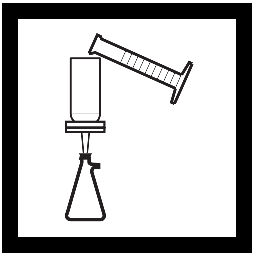
For water, wastewater, seawater



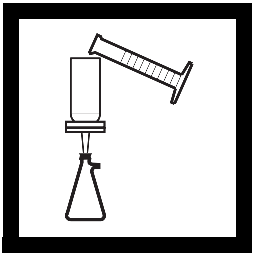
1. Assemble the filtering apparatus (membrane filter, filter holder, filter flask, and aspirator).

Note: *To test for apparent color, do not filter; begin at Step 4 and skip Step 7.*

Note: *The Pour-Thru Cell can be used with this procedure.*



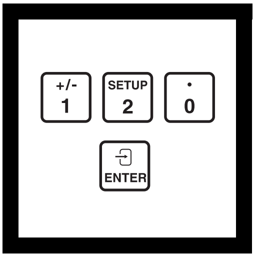
2. Rinse the filter by pouring about 50 mL of deionized water through the filter. Discard the rinse water.



3. Pour another 50 mL of deionized water through the filter. Keep this for Step 4.

4. Fill a sample cell (the blank) with 25 mL of filtered deionized water. Discard the excess.

Note: *For apparent color use unfiltered deionized water.*

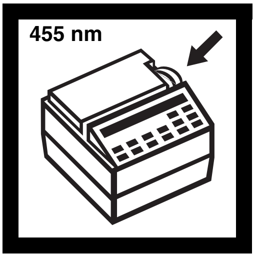


5. Enter the stored program number for true color.

Press: **1 2 0 ENTER**

The display will show:

Dial nm to 455



6. Rotate the wavelength dial until the small display shows:

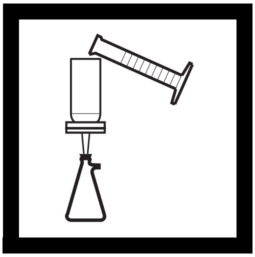
455 nm

When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

then:

UNITS PtCo APHA



7. Pour about 50 mL of sample through the filter.

8. Fill a second sample cell (the prepared sample) with 25 mL of the filtered sample.

Note: *For apparent color, use unfiltered sample.*

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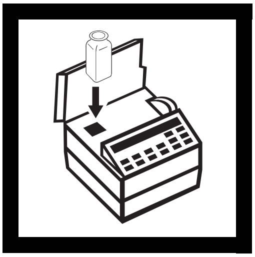
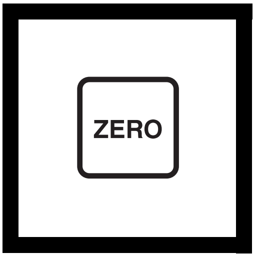
* Adapted from *Standard Methods for the Examination of Water and Wastewater.*

** *Wat. Res*. Vol. 30, No 11, pp. 2771-2775, 1996.



9. Place the blank into the cell holder. Close the light shield.



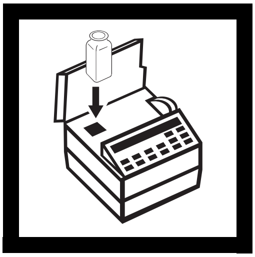
10. Press: **ZERO**

The display will show:

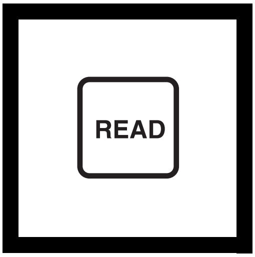
Zeroing. . . .

then:

0. UNITS PtCo APHA



11. Place the prepared sample into the cell holder. Close the light shield.



12. Press: **READ**

The display will show:

Reading. . . .

and then the result in platinum-cobalt units will be displayed.

Sampling and Storage

Collect samples in clean plastic or glass bottles. Analyze the sample as soon as possible after collection for best results. If prompt analysis is impossible, fill bottles completely and cap tightly. Avoid excessive agitation or prolonged contact with air. Samples can be stored for 48 hours by cooling to 4 °C (39 °F). Warm to room temperature before running the test.

Accuracy Check

Standard Solution Method

A 500 Platinum-Cobalt Units Color Standard solution is available for checking test accuracy. A 250 Platinum-Cobalt Units Standard can be made by pipetting 50.0 mL of the 500 Platinum-Cobalt Units Standard into a 100-mL volumetric flask and diluting to volume with deionized water. A ready-to-use 15 Platinum-Cobalt Units Standard is also available. The Pour-Thru Cell is recommended when using the 15 Platinum-Cobalt Units Standard.

Summary of Method

Color may be expressed as “apparent” or “true” color. The apparent color includes color from dissolved materials plus that from suspended matter. By filtering or centrifuging out the suspended materials, the true color can be determined. The procedure describes true color analysis. If apparent color is desired, it can be determined by measuring an unfiltered water sample. The stored program is used for both forms of color.

For low-level color measurements, the Pour-Thru Cell is recommended.

The stored program is calibrated in color at 455 nm units based on the APHA-recommended standard of 1 color unit being equal to 1 mg/L platinum as chloroplatinate ion.

REQUIRED REAGENTS

Description	Quantity Required Per Test	Units	Cat. No.
Water, deionized	50 mL	4 L	272-56

REQUIRED APPARATUS

Aspirator, vacuum	1	each	2131-00
Filter Holder, 47 mm, 300 mL graduated	1	each	13529-00
Filter, membrane, 47 mm, 0.45 microns	1	100/pkg	13530-00
Flask, filtering, 500 mL	1	each	546-49
Sample Cell, 25 mL, matched pair	2	pair	20950-00
Stopper, No 7, one hole	1	6/pkg	2119-07
Tubing, Rubber	1	12 ft	560-19

OPTIONAL REAGENTS

Color Standard Solution, 500 platinum-cobalt units	1 L	1414-53
Color Standard Solution, 15 platinum-cobalt units	1 L	26028-53

OPTIONAL APPARATUS

Cylinder, graduated, 50-mL, glass	each	508-41
Flask, volumetric, Class A, 100 mL	each	14574-42
Pipet, volumetric, Class A, 50 mL	each	14515-41
Pour-Thru Cell Assembly Kit	each	45215-00
Thermometer, -20 to 105 °C	each	1877-01

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

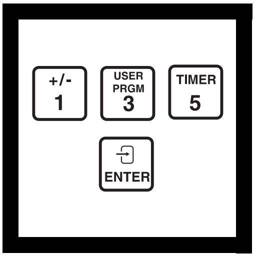
Method 8506

COPPER (0 to 5.00 mg/L)

For water, wastewater and seawater*

Bicinchoninate Method** (Powder Pillows or AccuVac Ampuls);
USEPA approved for reporting wastewater analysis (digestion needed; See Section II)***

Using Powder Pillows



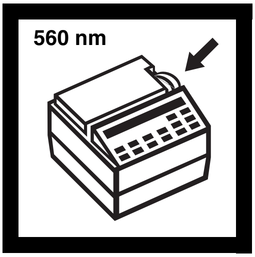
1. Enter the stored program number for copper (Cu), bicinchoninate powder pillows.

Press: **1 3 5 ENTER**

The display will show:

Dial nm to 560

Note: *The Pour-Thru Cell can be used for 25 mL reagents only.*



2. Rotate the wavelength dial until the small display shows:

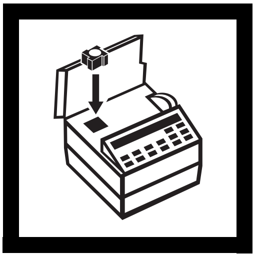
560 nm

When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

then: **mg/L Cu Bicn**

Note: *Determination of total copper needs a prior digestion (see Digestion, Section II).*



3. Insert the 10-mL Cell Riser into the cell compartment.

4. Fill a 10-mL sample cell with 10 mL of sample.

Note: *Determine a reagent blank for each new lot of reagent. Use deionized water in place of the sample in the procedure. Subtract this value from each result obtained.*

Note: *Adjust pH of stored samples before analysis.*

---

* Pretreatment required; see Interferences (Using Powder Pillows)

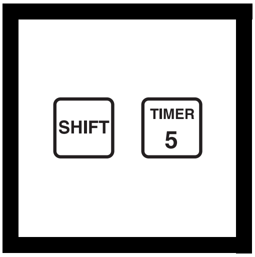
** Adapted from Nakano, S., *Yakugaku Zasshi*, 82 486-491 (1962) [*Chemical Abstracts*, 58 3390e (1963)]

*** Powder Pillows only: *Federal Register*, 45 (105) 36166 (May 29, 1980)

5. Add the contents of one CuVer 1 Copper Reagent Powder Pillow to the sample cell (the prepared sample).

Swirl to mix.

Note: *A purple color will develop if copper is present.*



6. Press:

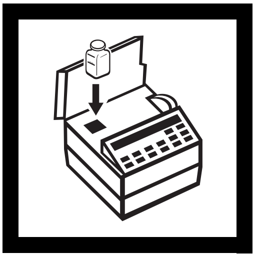
SHIFT TIMER

A two-minute reaction period will begin.

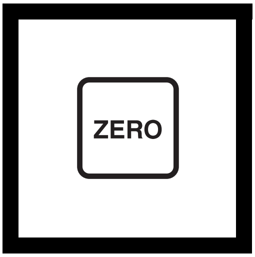
Note: *Accuracy is not affected by undissolved powder.*

7. When the timer beeps, the display will show: **mg/L Cu Bicn**

Fill a second 10-mL sample cell (the blank) with 10 mL of sample.



8. Place the blank into the cell holder. Close the light shield.



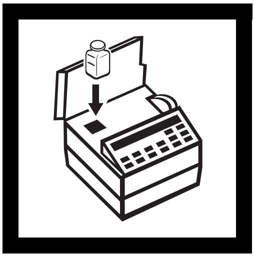
9. Press: **ZERO**

The display will show:

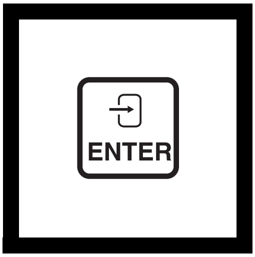
Zeroing. . .

then:

0.00 mg/L Cu Bicn



10. Within thirty minutes after the timer beeps, place the prepared sample into the cell holder. Close the light shield.



11. Press: **READ**

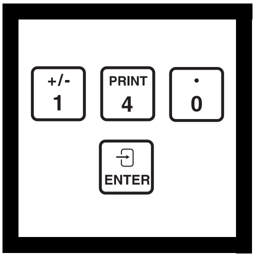
The display will show:

Reading. . .

then the result in mg/L copper will be displayed.

Using AccuVac Ampuls

Method 8026



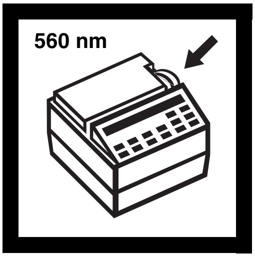
1. Enter the stored program number for copper (Cu), bicinchoninate AccuVac ampuls.

Press: **1 4 0 ENTER**

The display will show:

Dial nm to 560

Note: *Adjust pH of stored samples before analysis.*

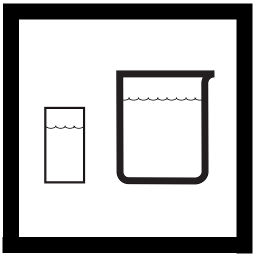


2. Rotate the wavelength dial until the small display shows:

560 nm

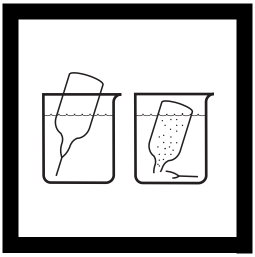
When the correct wavelength is dialed in, the display will quickly show: **Zero Sample**

then: **mg/L Cu Bicn AV**



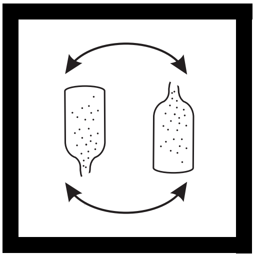
3. Fill a zeroing vial (the blank) with at least 10 mL of sample. Collect at least 40 mL of sample in a 50-mL beaker.

Note: *Determine a reagent blank for each new lot of reagent. Repeat procedure using deionized water in place of the sample. Subtract this value from each result obtained with this lot of reagent.*



4. Fill a CuVer 2 AccuVac Ampul with sample.

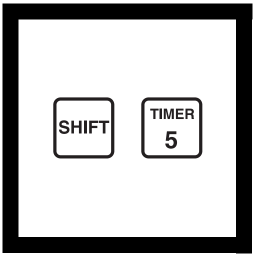
Note: *Keep the tip immersed while the ampul fills completely.*



5. Quickly invert the ampul several times to mix. Wipe off any liquid or fingerprints.

Note: *A purple color will form if copper is present.*

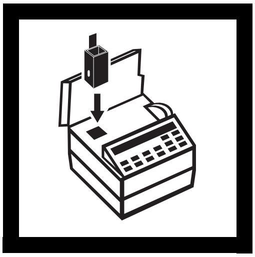
Note: *Accuracy is not affected by undissolved powder.*



6. Press:

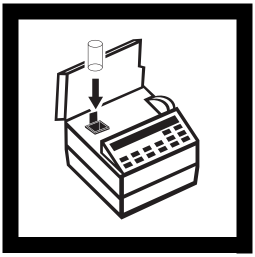
SHIFT TIMER

A two-minute reaction period will begin.



7. Place the AccuVac Vial Adapter into the cell holder.

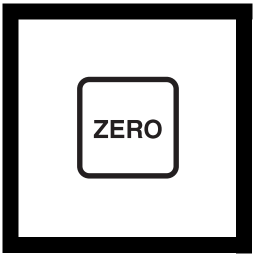
Note: *Place the grip tab at the rear of the cell holder.*



8. When the timer beeps, the display will show:

mg/L Cu Bicn AV

Place the blank into the cell holder. Close the light shield.



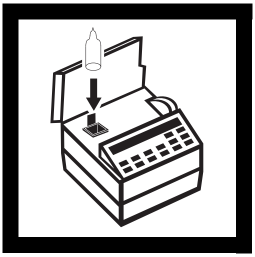
9. Press: **ZERO**

The display will show:

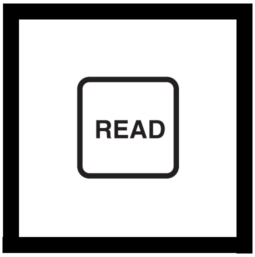
Zeroing. . .

then:

0.00 mg/L Cu Bicn AV



10. Within thirty minutes after the timer beeps, place the AccuVac ampul in the cell holder. Close the light shield.



11. Press: **READ**

The display will show:

Reading. . .

then the result in mg/L copper will be displayed.

Sampling and Storage

Collect samples in acid-cleaned glass or plastic containers. Adjust the pH to 2 or less with nitric acid (about 2 mL per liter). Store preserved samples up to six months at room temperature. Before analysis, adjust the pH to 4 to 6 with 8 N potassium hydroxide. Do not exceed pH 6, as copper may precipitate. Correct the test result for volume additions; see *Correction for Volume Additions* in *Section I* for more information. If only dissolved copper is to be determined, filter the sample before acid addition using the labware listed under *Optional Apparatus*.

Accuracy Check

Standard Additions Method

a) Fill three 25-mL graduated mixing cylinders with 25 mL of sample.

b) Snap the neck off a Copper PourRite Standard Ampule, 75 mg/L as Cu.

c) Use the TenSette Pipet to add 0.1, 0.2, and 0.3 mL of standard, respectively, to the mixing cylinders.
Stopper and mix thoroughly.

d) For analysis with AccuVacs, transfer the solutions to dry, clean 50-mL beakers to fill the ampules. For analysis with powder pillows, transfer only 10 mL of the solution to 10-mL sample cells.

e) Analyze each sample as described in the procedure. The copper concentration should increase about 0.3 mg/L for each 0.1 mL of standard added.

f) If these increases do not occur, see *Standard Additions* in *Section I* for more information.

Standard Solution Method

Prepare a 3.00 mg/L copper standard by pipetting 3.00 mL of Copper Standard Solution, 100 mg/L as Cu, into 100-mL volumetric flask. Dilute to volume with deionized water and mix well. Prepare this solution daily.

Precision

In a single laboratory, using a standard solution of 2.00 mg/L Cu and two representative lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±0.007 mg/L Cu.

In a single laboratory, using a standard solution of 2.00 mg/L Cu and two representative lots of AccuVac ampuls with the DR/2010, a single operator obtained a standard deviation of ±0.007 mg/L Cu.

Estimated Detection Limit (EDL)

The EDL for program 135 (Powder Pillows) and program 140 (AccuVac Ampuls) is 0.02 mg/L Cu. The EDL is the calculated lowest average concentration in a deionized water matrix that is different from zero with a 99% level of confidence. For more information on derivation and use of Hach's estimated detection limit, see *Section I.*

Interferences

Using Powder Pillows

If the sample is extremely acidic (pH 2 or less) a precipitate may form. Add 8 N Potassium Hydroxide Standard Solution drop-wise while swirling to dissolve the turbidity. Read the mg/L Cu. If the turbidity remains and turns black, silver interference is likely. Eliminate silver interference by adding 10 drops of saturated Potassium Chloride Solution to 75 mL of sample, followed by filtering through a fine or highly retentive filter. Use the filtered sample in the procedure.

Cyanide interferences prevent sufficient color development but can be overcome by adding 0.2 mL of formaldehyde to the 10 mL sample. Wait four minutes before taking the reading. Multiply the test results by 1.02 to correct for sample dilution by the formaldehyde.

To test samples such as seawater containing high levels of hardness, iron, or aluminum, analyze a 25 mL sample volume with a CuVer 2 Copper Reagent Powder Pillow instead of a CuVer 1 Pillow and the 10 mL sample volume (the taller 25 mL sample cells are required). Results obtained will include total dissolved copper (free and complexed).

To differentiate free copper from that complexed to EDTA or other complexing agents, analyze a 25 mL sample volume with a Free Copper Reagent Powder Pillow instead of the CuVer 1 pillow and the 10 mL sample volume (the taller 25 mL sample cells are required). Final results will be free copper only. Add a Hydrosulfite Reagent Powder Pillow to the developed sample and re-read the result. This result will include the total dissolved copper (free and complexed).

Using AccuVac Ampuls

The CuVer 2 Reagent contained in the AccuVac Ampuls is formulated to withstand high levels of calcium, iron and aluminum without interference.

Unlike CuVer 1 Reagent, CuVer 2 reacts directly with copper which is complexed by chelants such as EDTA. If free copper is to be determined separately from complexed copper, see the Powder Pillow Interference section above.

If the sample is very acidic it should be adjusted to a pH greater than 4 before analysis. If a turbidity forms and turns black, silver interference is likely. This can be eliminated by adding 10 drops of saturated Potassium Chloride Solution to 75 mL of sample, followed by filtration through a fine filter using the labware listed under Optional Apparatus. Use the filtered sample in the procedure.

Cyanide interferences prevent sufficient color development but can be overcome by adding 0.5 mL of formaldehyde to 25 mL of sample. Wait four minutes before taking the reading. Multiply final results by 1.02 to correct for sample dilution.

Summary of Method

Copper in the sample reacts with a salt of bicinchoninic acid contained in CuVer 1 or 2 Copper Reagent to form a purple colored complex in proportion to the copper concentration. This method includes procedures for both powder pillow and AccuVac reagents.

REQUIRED REAGENTS (USING POWDER PILLOWS)

Description	Quantity Required Per Test	Unit	Cat. No.
CuVer 1 Copper Reagent Powder Pillows, 10 mL sample	1 pillow	100/pkg	21058-69

REQUIRED REAGENTS (USING ACCUVAC AMPULS)

CuVer 2 Copper Reagent AccuVac Ampuls	1 ampul	25/pkg	25040-25

REQUIRED APPARATUS

Cell Riser, 10 mL	1	each	45282-00
Sample Cell, 10 mL, matched pair	2	pair	24954-02

REQUIRED APPARATUS (USING ACCUVAC AMPULS)

Adapter, AccuVac vial	1	each	43784-00
Beaker, 50 mL	1	each	500-41
Vial, zeroing	1	each	21228-00

OPTIONAL REAGENTS

Copper Standard Solution, 100 mg/L		100 mL	128-42
Copper PourRite Standard Ampule, 75 mg/L Cu, 2 mL		20/pkg	14247-20
CuVer 2 Reagent Powder Pillows		100/pkg	21882-99
Formaldehyde, 37%		100 mL* MDB	2059-99
Free Copper Reagent Powder Pillows		100/pkg	21186-69
Hydrochloric Acid Solution, 6 N		500 mL	884-49
Hydrosulfite Reagent Powder Pillows		100/pkg	21188-69
Nitric Acid, ACS		500 mL	152-49
Nitric Acid Solution, 1:1		500 mL	2540-49
Potassium Chloride Solution, saturated		59 mL SCDB	765-26
Potassium Hydroxide Standard Solution, 8.0 N		100 mL* MDB	282-32
Sodium Hydroxide Solution, 5.0 N		100 mL* MDB	2450-32
Water, deionized		4 L	272-56

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* Contact Hach for larger sizes.

OPTIONAL APPARATUS

Description	Unit	Cat. No.
AccuVac Snapper Kit	each	24052-00
Ampule Breaker Kit	each	24846-00
Cylinder, graduated, mixing, 25 mL	each	20886-40
Cylinder, graduated, polypropylene, 25 mL	each	1081-40
Cylinder, graduated, 100 mL	each	508-42
Filter Paper, folded, 12.5 cm	100/pkg	1894-57
Flask, volumetric, 100 mL	each	547-42
Funnel, polypropylene, 65 mm	each	1083-67
Hot Plate, 3 1/2" diameter, 120 Vac	each	12067-01
Hot Plate, 3 1/2" diameter, 240 Vac	each	12067-02
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
pH Meter, *sension*™*1*, portable	each	51700-10
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 3.00 mL	each	14515-03
Pipet Filler, safety bulb	each	14651-00

OPTIONAL 25 ML ANALYSIS ITEMS

CuVer 1 Copper Reagent Powder Pillows	100/pkg	14188-99
Clippers, for opening pillows	each	968-00
Pour-Thru Cell Assembly Kit (for 25 mL reagents only)	each	45215-00
Sample Cell, 25 mL, matched pair	pair	20950-00

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

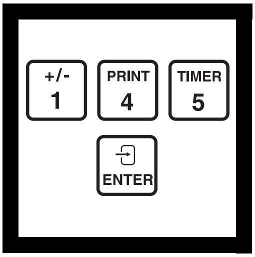
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8143

COPPER (0 to 210.0 µg/L)

For water, wastewater, and seawater

Porphyrin Method*



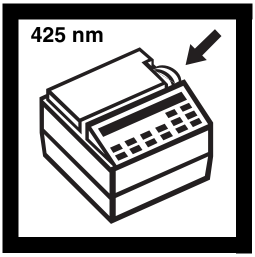
1. Enter the stored program number for copper (Cu), porphyrin method.

Press: **1 4 5 ENTER**

The display will show:

Dial nm to 425

Note: *The Pour-Thru Cell can be used with 25-mL reagents only. Rinse well with deionized water between the blank and prepared sample.*



2. Rotate the wavelength dial until the small display shows:

425 nm

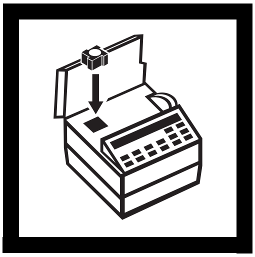
When the correct wavelength is dialed in the display will quickly show:

Zero Sample

then: **µg/L Cu Porph**

Note: *Total copper determination needs a prior digestion; use either the Digesdahl or vigorous digestion (Section II).*

Note: *This test is sensitive to the wavelength setting. The 425 nm wavelength should always be set by approaching from high to low values.*



3. Insert the 10-mL Cell Riser into the cell compartment.

4. Fill two sample cells with 10 mL of sample.

Note: *Wash all glassware with detergent. Rinse with tap water. Rinse again with Nitric Acid Solution, 1:1. Rinse a third time with copper-free, deionized water.*

Note: *For most accurate results, run a blank using copper-free deionized water. Subtract the blank value from each result. Repeat for each new lot of reagents.*

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* Adapted from Ishii and Koh, *Bunseki Kagaku,* 28 473 (1979).

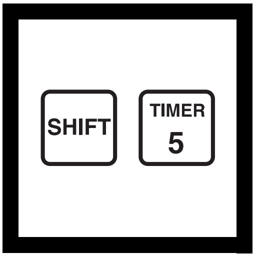
5. Add the contents of one Copper Masking Reagent Powder Pillow to one of the sample cells (the blank). Swirl to dissolve.

Note: *The other sample cell is the prepared sample.*

6. Add the contents of one Porphyrin 1 Reagent Powder Pillow to each sample cell. Swirl to dissolve.

7. Add the contents of one Porphyrin 2 Reagent Powder Pillow to each sample cell. Swirl to dissolve.

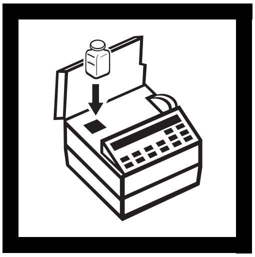
Note: *The yellow color will turn blue momentarily. If any copper is present, the sample will return to yellow.*



8. Press:

SHIFT TIMER

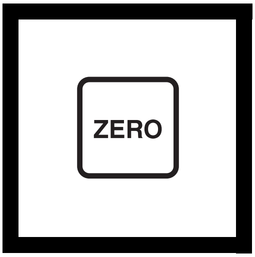
A three-minute reaction period will begin.



9. When the timer beeps, the display will show:

µg/L Cu Porph

Place the blank into the cell holder. Close the light shield.



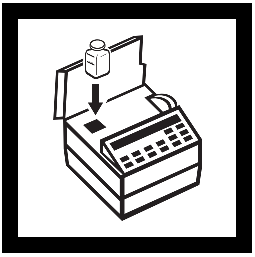
10. Press: **ZERO**

The display will show:

Zeroing. . . .

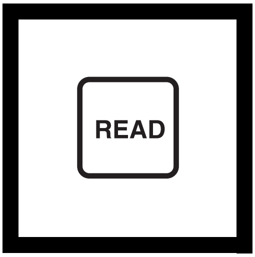
then:

0.0 µg/L Cu Porph



11. Place the prepared sample into the cell holder. Close the light shield.

Note: *If samples with high levels of metal are analyzed, a slight metallic deposit or yellow buildup may appear on the sample cell wall. Remove by rinsing with nitric acid.*



12. Press: **READ**

The display will show:

Reading. . . .

then the result in µg/L copper will be displayed.

Sampling and Storage

Collect samples in acid-washed plastic bottles. To preserve, adjust the pH to 2 or less with nitric acid (about 5 mL per liter). Store preserved samples up to six months at room temperature.

Before testing, adjust the pH of the sample to between 2 and 6. If the sample is too acidic, adjust the pH with 5.0 N Sodium Hydroxide Standard Solution. Correct test results for volume additions; see *Correction for Volume Additions* in *Section I* for more information.

Accuracy Check

Standard Additions Method

a) Fill six 25-mL graduated mixing cylinders with 25 mL of sample. Properly mark each pair of cylinders as “sample” and “blank”.

b) Using a TenSette Pipet, add 0.1 mL of Copper Standard Solution, and 10.0 mg/L Cu, to two of the cylinders. Add 0.2 mL of standard to two more of the cylinders. Add 0.3 mL of standard to the other two cylinders, making a total of six samples (2 at each volume of standard).

c) Analyze the samples as described above. The copper concentration reading should increase by 40 µg/L for each 0.1 mL of standard added.

d) If these increases do not occur, see Standard Additions in Section I for more information.

Standard Solution Method

To assure the accuracy of the test, prepare a 100 µg/L copper standard:

a) Pipet 1.00 mL of copper standard solution, 10.0 mg/L Cu, into a 100-mL volumetric flask.

b) Dilute to volume with copper-free, reagent-grade water.

c) Use this standard in place of the sample in the procedure. The reading should be 100 µg/L Cu.

d) Prepare this solution daily.

Precision

In a single laboratory, using standard solutions of 100 µg/L copper and two representative lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±0.31 µg/L copper.

Interferences

The following may interfere when present in concentrations exceeding those listed below:

Substance	Concentration	Substance	Concentration
Aluminum	60 mg/L	Magnesium	10,000 mg/L
Cadmium	10 mg/L	Manganese	140 mg/L
Calcium	15,000 mg/L	Mercury	3 mg/L
Chloride	90,000 mg/L	Molybdenum	11 mg/L
Chromium (Cr^{6+})	110 mg/L	Nickel	60 mg/L
Cobalt	100 mg/L	Potassium	60,000 mg/L
Fluoride	30,000 mg/L	Sodium	90,000 mg/L
Iron (Fe^{2+})	6 mg/L	Zinc	9 mg/L
Lead	3 mg/L		

Chelating agents, such as EDTA, interfere at all levels unless either the Digesdahl or vigorous digestion (Section II) is performed.

Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment: see *pH Interferences* in *Section I.*

Summary of Method

The porphyrin method is very sensitive to trace amounts of free copper. Due to the sensitivity of the method, a masking agent is used to prepare a "blank" for each sample. The method is free from most interferences and does not require any sample extraction or preconcentration. Interferences from other metals are eliminated by the copper masking reagent. The porphyrin indicator forms an intense, yellow-colored complex proportional to any free copper present in the sample. Total copper may be determined if a digestion is performed prior to analysis.

REQUIRED REAGENTS

	Cat. No.
Copper Reagent Set, 10-mL samples (100 Tests)	26033-00

Includes: (1) 26034-49, (2) 26035-49, (2) 26036-49

Description	Quantity Required Per Test	Unit	Cat. No.
Copper Masking Reagent Powder Pillows	1 pillow	100/pkg	26034-49
Porphyrin 1 Reagent Powder Pillows	2 pillows	100/pkg	26035-49
Porphyrin 2 Reagent Powder Pillows	2 pillows	100/pkg	26036-49

REQUIRED APPARATUS

Description	Unit	Cat. No.
Cell Riser, 10-mL sample cell	each	45282-00
Sample Cell, with 10-mL mark, matched pair	pair	24954-02

OPTIONAL REAGENTS

Copper Standard Solution, 10 mg/L Cu	100 mL MDB	129-32
Hydrochloric Acid Solution, 1:1 (6 N)	500 mL	884-49
Nitric Acid, ACS	500 mL	152-49
Nitric Acid Solution, 1:1	500 mL	2540-49
Sodium Hydroxide Standard Solution, 5 N	1 L	2450-53
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Cylinder, graduated, mixing, 25-mL	each	20886-40
Flask, volumetric, Class A, 100 mL	each	14574-42
Hot Plate, 7" x 7", 120 Vac	each	23441-00
Hot Plate, 7" x 7", 240 Vac	each	23441-02
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
pH Meter, *sension*™*1*, portable	each	51700-10
Pipet, Mohr, 5 mL	each	20934-37
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01	50/pkg	21856-96
Pipet, volumetric, Class A, 1 mL	each	14515-35
Pipet Filler, safety bulb	each	14651-00
Watch Glass	each	578-70

OPTIONAL 25-ML ANALYSIS ITEMS

Description	Quantity Required Per Test	Unit	Cat. No.
Copper Reagent Set, 25-mL samples		(100 Tests)	22427-00
Copper Masking Reagent Powder Pillows	1 pillow	100/pkg	21873-99
Porphyrin 1 Reagent Powder Pillows	2 pillows	100/pkg	21874-69
Porphyrin 2 Reagent Powder Pillows	2 pillows	100/pkg	21875-69
Pour-Thru Cell Assembly Kit (for 25-mL samples/reagents only)		each	45215-00
Sample Cell, 25-mL, matched pair		pair	20950-00

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8117

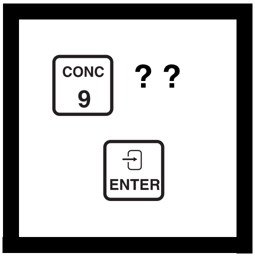
For finishing baths

COPPER, AUTOCATALYTIC (0 to 3.00 g/L)

Colorimetric Method

User Calibration

1. This procedure requires a user-entered calibration prior to sample measurement. See the User Calibration Section following this test to set up and calibrate a program for copper.



2. Enter the user stored program number for autocatalytic copper.

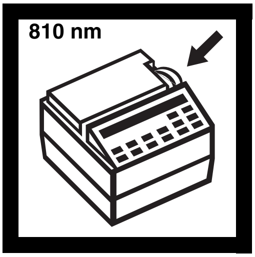
Press: **9 ? ? ENTER**

The display will show:

Dial nm to 810

Note: *Because of variations between plating bath formulations, make a new calibration for each formulation. Prepare and store the calibration as directed under User Calibration below.*

Note: *Analyze samples immediately for best results.*



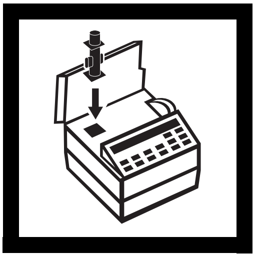
3. Rotate the wavelength dial until the small display shows:

810 nm

When the correct wavelength is dialed in, the display will show:

Zero Sample

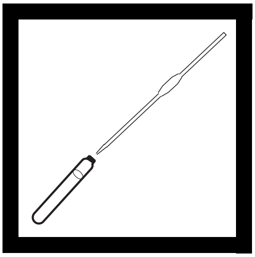
then: **g/L Cu**



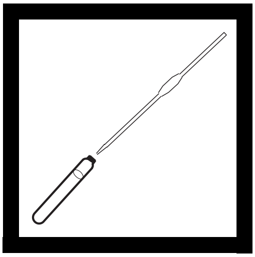
4. Insert the COD Vial Adapter into the cell holder.

Note: *Place the marker to the right.*

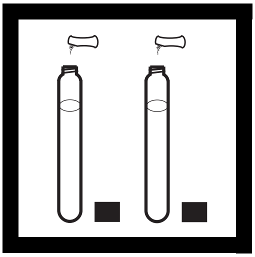
Note: *The Pour-Thru Cell cannot be used with this procedure.*



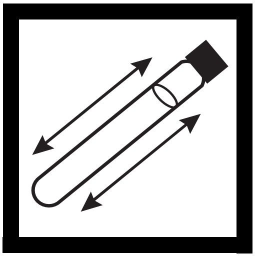
5. Pipet 3.0 mL of bath sample and 2.0 mL of deionized water into a 16-mm screw-capped tube (the prepared sample).



6. Pipet 5.0 mL of deionized water into a second culture tube (the blank).

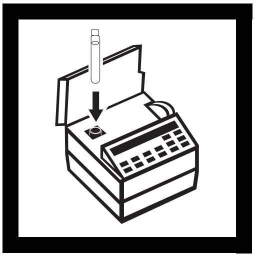


7. Add the contents of one Acid Reagent Powder Pillow to each tube. Mix gently.

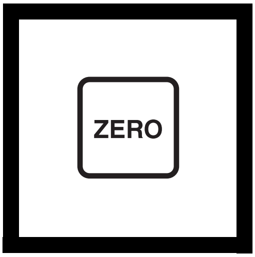


8. Wait until any foaming (effervescence) stops. Cap the tubes. Shake to dissolve all the powder.

Note: *Save the blank for future determinations.*



9. Place the blank into the vial adapter. Place the cover on the adapter.

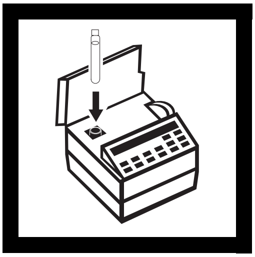


10. Press: **ZERO**

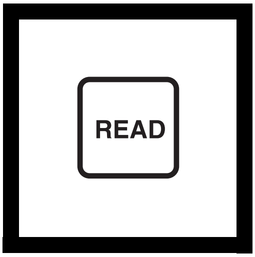
The display will show:

Zeroing. . .

then: **0.00 g/L Cu**



11. Place the prepared sample into the vial adapter. Place the cover on the adapter.



12. Press:**READ**

The display will show:

Reading. . .

then the result in g/L copper will be displayed.

Accuracy Check

Check for accuracy by titrating a sample of the bath in use to assure that the calibration is correct.

User Calibration

A one-time setup of a program for copper is required. A copper program template is pre-programmed into memory to make the process easier. After the setup is complete, the calibration can be entered for each new lot of reagents used or as necessary.

Standard Preparation

Perform a new calibration for each bath formulation used.

a) Prepare a sample of the plating bath which is known to be of correct strength (100%). Or, titrate a sample of the bath to determine its exact strength. This is the full strength standard.

b) Dilute 3 mL of this full strength bath sample with 3 mL of deionized water to make a half-strength standard.

c) Pipet 3.0 mL of the full strength and half strength bath sample into two 16-mm screw-capped vials. Add 2.0 mL of deionized water to each vial (5 mL total volume in each vial).

d) Pipet 5.0 mL of deionized water into a third vial.

Initial Setup of Copper Program

a) Press **SHIFT USER PRGM**. Use the **UP** arrow key to scroll to **Copy Program**. Press **ENTER**.

b) Scroll to or enter the template number for copper (903). Press **ENTER**.

c) Scroll to or enter the desired user program number for copper (>950). Press **ENTER**. Record the program number for reference.

d) The display will show: **Program Copied.**

e) Press **EXIT**. The program is now ready to be calibrated.

The templates within User Program cannot be run directly. They must be copied into a usable program number (greater than 950) as in step c and d. Then, calibrate the program.

User Calibration of Copper Program

a) Press **SHIFT USER PRGM**. Use the **UP** arrow to scroll to **Edit Program**. Press **ENTER**.

b) Scroll to or enter the program number for autocatalytic copper (from step c in Setup). Press **ENTER**.

c) Use the **DOWN** arrow to scroll down to **Calib Table:X** (X= denotes a number which indicates the number of data points in the table). Press **ENTER**.

d) The instrument will prompt **Zero Sample**. Place the blank solution in the cell holder. Close the light shield. Press **ZERO**. The instrument will prompt you to adjust to the proper wavelength if necessary.

e) The first concentration point (1.50 g/L) will be displayed. If necessary, change the value of the standard using the numeric key pad. Press **ENTER** to display the stored absorbance value of the first concentration point.

f) Place the first developed standard solution (50% strength solution) in the cell holder. Close the light shield. Press **READ** to display the measured absorbance of the standard. Press **ENTER** to accept the displayed absorbance value.

g) The second concentration point (3.00 g/L)will be displayed. If necessary, change the value of the standard using the numeric key pad. Press **ENTER** to display the stored absorbance value of the second concentration. Place the second developed standard solution (full strength solution) in the cell holder. Close the light shield. Press **READ** to display the measured absorbance value of the standard.

h) Press **ENTER** to accept the absorbance reading. The next concentration point will then be displayed.

i) Repeat steps h and i as necessary for the remaining standards.

j) Press **EXIT**. Scroll down to **Force Zero**. Press **ENTER** to change the setting. Change to **ON** by pressing the arrow key, then press **ENTER.**

k) Scroll down to **Calib Formula**. Press **ENTER** twice or until only the **0** in **F(0)** is flashing. Press **DOWN** arrow to select **F1** (linear calibration). Press **ENTER** to select **F1**.

Note: *Other calibration fits may be used if appropriate.*

l) Press **EXIT** twice. The display will show **Store Changes?**. Press **ENTER** to confirm.

m) Press **EXIT**. The program is now calibrated and ready for use. Start with step 2 of the iconed procedure.

Interferences

Other blue-colored bath components will interfere to cause high results.

Summary of Method

Bath samples are acidified to destroy the color of the alkaline copper complexes. The color of the acidic copper solution is then measured directly. Different bath formulations cause slight response variations, so a calibration must be performed for each bath formulation in use.

REQUIRED REAGENTS

Descriptions	Quantity Required Per Test	Unit	Cat. No.
Acid Reagent Powder Pillows	2 pillows	100/pkg	1042-99
Water, deionized	varies	4 L	272-56

REQUIRED APPARATUS

Cap, tube, for 22758-00	3	25/pkg	14238-25
COD Vial Adapter	1	each	44799-00
Pipet, serological, 5 mL	1	each	532-37
Pipet Filler, safety bulb	1	each	14651-00
Tube, culture, 16 x 100 mm	3	each	22758-00

OPTIONAL APPARATUS

Digital Titrator with plastic case, manual and 5 straight delivery tubes	each	16900-01
Pipet, TenSette, 1 to 10 mL	each	19700-10
Pipet Tips, for 19700-10 TenSette Pipet	50/pkg	21997-96

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

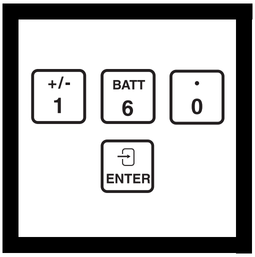
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8027

CYANIDE (0 to 0.200 mg/L)

For water, wastewater, and seawater

Pyridine-Pyrazalone Method*



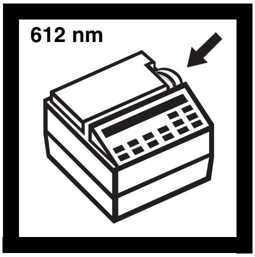
1. Enter the stored program number for cyanide (CN^-).

Press: **1 6 0 ENTER**

The display will show:

Dial nm to 612

__Note:__ The Pour-Thru Cell can be used with 25-mL reagents only.

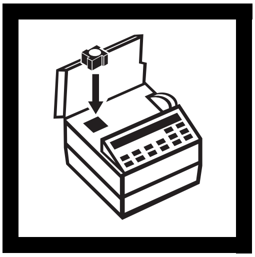


2. Rotate the wavelength dial until the small display shows:

612 nm

When the correct wavelength is dialed in, the display will quickly show: **Zero Sample**

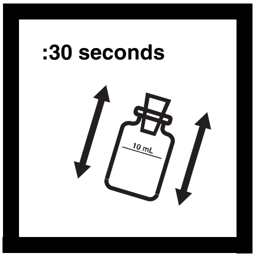
then: **mg/L CN^-**



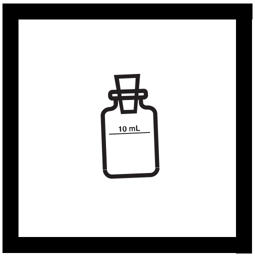
3. Insert a 10-mL Cell Riser into the cell compartment.

4. Using a graduated cylinder, pour 10 mL of sample into a 10-mL sample cell.

5. Add the contents of one CyaniVer 3 Cyanide Reagent Powder Pillow. Stopper the sample cell.



6. Shake the sample cell for 30 seconds.



7. Wait an additional 30 seconds while the sample cell is undisturbed.

8. Add the contents of one CyaniVer 4 Cyanide Reagent Powder Pillow. Stopper the sample cell.

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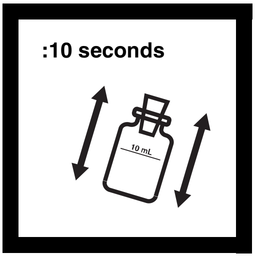
* Adapted from Epstein, Joseph, *Anal. Chem.* 19 (4), 272 (1947)

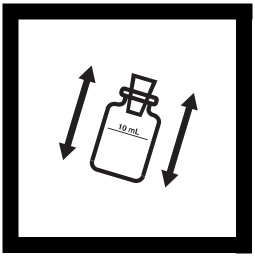


9. Shake the sample cell for ten seconds. Immediately proceed with Step 10.

Note: *Accuracy is not affected by undissolved CyaniVer 4 Cyanide Reagent Powder.*

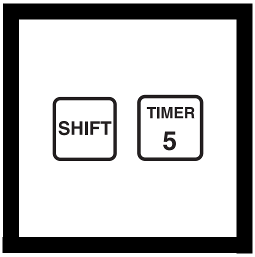
10. Add the contents of one CyaniVer 5 Cyanide Reagent Powder Pillow. Stopper the cell.

Note: *Delaying the addition of the CyaniVer 5 Cyanide Reagent Powder for more than 30 seconds after the addition of the CyaniVer 4 Cyanide Reagent Powder will give lower test results.*



11. Shake vigorously to completely dissolve the CyaniVer 5 Cyanide Reagent Powder (the prepared sample).

Note: *If cyanide is present, a pink color will develop which then turns blue after a few minutes.*

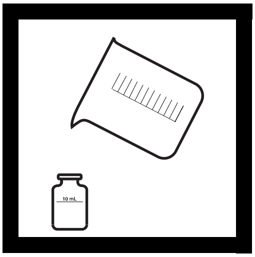


12. Press:

SHIFT TIMER

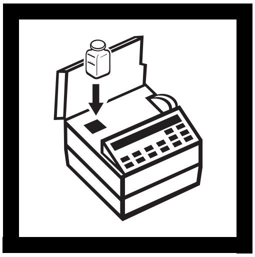
A 30-minute reaction period will begin.

Note: *Samples at less than 25 °C require longer reaction time and samples at greater than 25 °C give low test results.*

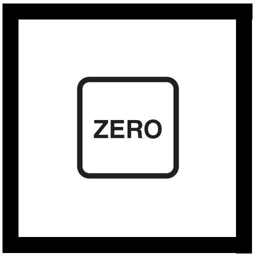


13. When the timer beeps, the display will show: **mg/L CN$^-$**

Fill another 10-mL sample cell (the blank) with 10 mL of sample.



14. Place the blank into the cell holder. Close the light shield.

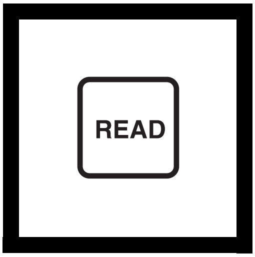


15. Press: **ZERO**

The display will show:

Zeroing. . .

then: **0.000 mg/L CN$^-$**



16. Remove the stopper. Place the prepared sample into the cell holder. Close the light shield.

Press: **READ**

The display will show:

Reading. . .

then the result in mg/L cyanide will be displayed.

Sampling and Storage

Samples collected in glass or plastic bottles should by analyzed as quickly as possible.

The presence of oxidizing agents, sulfides and fatty acids can cause cyanide loss during sample storage. Samples containing these substances must be pretreated as described in the following procedures before preservation with sodium hydroxide. If the sample contains sulfide and is not pretreated, it must be analyzed within 24 hours.

Preserve the sample by adding 4.0 mL of 5.0 N Sodium Hydroxide Standard Solution to each liter (or quart) of sample, using a glass serological pipet and pipet filler. Check the sample pH. Four mL of sodium hydroxide are usually enough to raise the pH of most water and wastewater samples to 12. Add more 5.0 N sodium hydroxide if necessary. Store the samples at 4 °C (39 °F) or less. Samples preserved in this manner can be stored for 14 days.

Before testing, samples preserved with 5.0 N sodium hydroxide or samples that are highly alkaline due to chlorination treatment processes or sample distillation procedures should be adjusted to approximately pH 7 with 2.5 N Hydrochloric Acid Standard Solution. Where significant amounts of preservative are used, a volume correction should be made; see *Correction for Volume Additions* in *Section I* for more information.

Oxidizing Agents

Oxidizing agents such as chlorine decompose cyanides during storage. To test for their presence and eliminate their effect, pretreat samples as follows:

a) Take a 25-mL portion of the sample and add one drop of m-Nitrophenol Indicator Solution, 10 g/L. Swirl to mix.

b) Add 2.5 N Hydrochloric Acid Standard Solution drop-wise until the color changes from yellow to colorless. Swirl the sample thoroughly after the addition of each drop.

c) Add two drops of Potassium Iodide Solution, 30 g/L, and two drops of Starch Indicator Solution, to the sample. Swirl to mix. The solution will turn blue if oxidizing agents are present.

d) If Step c suggests the presence of oxidizing agents, add two level 1-g measuring spoonfuls of ascorbic acid per liter of sample.

e) Withdraw a 25-mL portion of sample treated with ascorbic acid and repeat Steps a to c. If the sample turns blue, repeat Steps d and e.

f) If the 25-mL sample remains colorless, adjust the remaining sample to pH 12 for storage with 5 N Sodium Hydroxide Standard Solution (usually 4 mL/L).

g) Perform the procedure given under Interferences, Reducing Agents, to eliminate the effect of excess ascorbic acid, before following the cyanide procedure.

Sulfides

Sulfides will quickly convert cyanide to thiocyanate (SCN). To test for the presence of sulfide and eliminate its effect, pretreat samples as follows:

a) Place a drop of sample on a disc of hydrogen sulfide test paper that has been wetted with pH 4 Buffer Solution.

b) If the test paper darkens, add a 1-g measuring spoon of lead acetate to the sample. Repeat Step a.

c) If the test paper continues to turn dark, keep adding lead acetate until the sample tests negative for sulfide.

d) Filter the lead sulfide precipitate through filter paper and a funnel. Preserve the sample for storage with 5 N Sodium Hydroxide Standard Solution or neutralize to a pH of 7 for analysis.

Fatty Acids

Caution: Perform this operation in a hood as quickly as possible.

When distilled, fatty acids will pass over with cyanide and form soaps under the alkaline conditions of the absorber. If the presence of fatty acid is suspected, do not preserve samples with sodium hydroxide until the following pretreatment is performed. The effect of fatty acids can be minimized as follows:

a) Acidify 500 mL of sample to pH 6 or 7 with Acetic Acid Solution.

b) Pour the sample into a 1000-mL separatory funnel and add 50 mL of hexane.

c) Stopper the funnel and shake for one minute. Allow the layers to separate.

d) Drain off the sample (lower) layer into a 600-mL beaker. If the sample is to be stored, add 5 N Sodium Hydroxide Standard Solution to raise the pH to above 12.

Accuracy Check

Standard Additions Method

Caution: Cyanides and their solutions, and the hydrogen cyanide liberated by acids, are very poisonous. Both the solutions and the gas can be absorbed through the skin.

a) Prepare a 100 mg/L cyanide stock solution weekly by dissolving 0.1884 grams of sodium cyanide in deionized water and diluting to 1000 mL.

b) Pipet 5.0 mL of the 100 mg/L cyanide stock solution into a 100-mL volumetric flask to prepare a 5 mg/L cyanide working solution. Mix thoroughly.

c) Use a TenSette Pipet to add 0.1, 0.2, and 0.3 mL of the 5 mg/L solution to three 10-mL samples, respectively.

d) Swirl each sample and analyze according to the procedure. Each 0.1 mL of standard added should increase the cyanide concentration determined in Step 16 by 0.05 mg/L.

Standard Solution Method

Prepare a 100 mg/L cyanide stock solution weekly by dissolving 0.1884 grams of sodium cyanide in deionized water and diluting to 1000 mL.

Immediately before use, prepare a 0.10 mg/L cyanide working solution by diluting 1.00 mL of the 100 mg/L stock solution to 1000 mL using deionized water. Use this prepared standard in place of sample in Step 4. Results should be 0.10 mg/L CN^-.

Precision

In a single laboratory, using a standard solution of 0.095 mg/L CN^- and two representative lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±0.0043 mg/L CN^-.

Interferences

Turbidity

Large amounts of turbidity will interfere and cause high readings. If the water sample is highly turbid, it should first be filtered before use in Steps 4 and 13. Filter using the labware listed under Optional Apparatus. The test results should then be recorded as soluble cyanide.

Oxidizing and Reducing Agents

Large amounts of chlorine in the sample will cause a milky white precipitate after the addition of the CyaniVer 5 Reagent. If chlorine or other oxidizing agents are known to be present, or if reducing agents (such as sulfide or sulfur dioxide) are known to be present, pretreat the sample before testing as follows using adequate ventilation:

Oxidizing Agents

a) Adjust a 25-mL portion of the alkaline sample to between pH 7 and 9 with 2.5 N Hydrochloric Acid Standard Solution. Count the number of drops of acid added.

b) Add two drops of Potassium Iodide Solution and two drops of Starch Indicator Solution to the sample. Swirl to mix. The sample will turn blue if oxidizing agents are present.

c) Add Sodium Arsenite Solution drop-wise until the sample turns colorless. Swirl the sample thoroughly after each drop. Count the number of drops.

d) Take another 25-mL sample and add the total number of drops of Hydrochloric Acid Standard Solution counted in Step a.

e) Subtract one drop from the amount of Sodium Arsenite Solution added in Step c. Add this amount to the sample. Mix thoroughly.

f) Using 10 mL of this sample, continue with Step 4 of the cyanide procedure.

Reducing Agents

a) Adjust a 25-mL portion of the alkaline sample to between pH 7 and 9 with 2.5 N Hydrochloric Acid Standard Solution. Count the number of drops added.

b) Add four drops of Potassium Iodide Solution and four drops of Starch Indicator Solution to the sample. Swirl to mix. The sample should be colorless.

c) Add Bromine Water drop-wise until a blue color appears. Count the number of drops, and swirl the sample after the addition of each drop.

d) Take another 25 mL sample and add the total number of drops of Hydrochloric Acid Standard Solution counted in Step a.

e) Add the total number of drops of Bromine Water counted in Step c to the sample and mix thoroughly.

f) Using 10 mL of this sample, continue with Step 4 of the cyanide procedure.

Metals

Nickel or cobalt in concentrations up to 1 mg/L do not interfere. Eliminate the interference from up to 20 mg/L copper and 5 mg/L iron by adding the contents of one HexaVer Chelating Reagent Powder Pillow to the sample and then mixing before adding the CyaniVer 3 Cyanide Reagent Powder Pillow in Step 5. Prepare a reagent blank of deionized water and reagents to zero the instrument in Step 15.

Acid Distillation

For USEPA reporting purposes, samples must be distilled.

All samples to be analyzed for cyanide should be treated by acid distillation except when experience has shown that there is no difference in results obtained with or without distillation. With most compounds, a one-hour reflux is adequate.

If thiocyanate is present in the original sample, a distillation step is absolutely necessary as thiocyanate causes a positive interference. High concentrations of thiocyanate can yield a substantial quantity of sulfide in the distillate. The “rotten egg” smell of hydrogen sulfide will accompany the distillate when sulfide is present. The sulfide must be removed from the distillate prior to testing.

If cyanide is not present, the amount of thiocyanate can be determined. The sample is not distilled and the final reading is multiplied by 2.2. The result is mg/L thiocyanate.

The distillate can be tested and treated for sulfide after the last step of the distillation procedure by using the following lead acetate treatment procedure.

a) Place a drop of the distillate (already diluted to 250 mL) on a disc of hydrogen sulfide test paper that has been wetted with pH 4.0 Buffer Solution.

b) If the test paper darkens, add 2.5 N Hydrochloric Acid Standard Solution drop-wise to the distillate until a neutral pH is obtained.

c) Add a 1-g measuring spoon of lead acetate to the distillate and mix. Repeat Step a.

d) If the test paper continues to turn dark, keep adding lead acetate until the distillate tests negative for sulfide.

e) Filter the black lead sulfide precipitate through filter paper and funnel. This sample should now be neutralized to pH 7 and analyzed for cyanide without delay.

Distillation Procedures

A detailed procedure for the distillation of cyanide samples is included with the Hach Distillation Apparatus. Three detailed procedures, Free Cyanides, Cyanides Amenable to Chlorination, and Total Cyanides, are included with the four- and ten-port Midi-Distillation Apparatus. See the *Optional Apparatus* listing.

Summary of Method

The pyridine-pyrazolone method used for measuring cyanide gives an intense blue color with free cyanide. A sample distillation is required to determine cyanide from transition and heavy metal cyanide complexes.

REQUIRED REAGENTS

	Cat. No.
Cyanide Reagent Set (100 Tests), 10-mL sample	24302-00

Includes: (1) 21068-69, (1) 21069-69, (1) 21070-69

Description	Quantity Required Per Test	Unit	Cat. No.
CyaniVer 3 Cyanide Reagent Powder Pillows	1 pillow	100/pkg	21068-69
CyaniVer 4 Cyanide Reagent Powder Pillows	1 pillow	100/pkg	21069-69
CyaniVer 5 Cyanide Reagent Powder Pillows	1 pillow	100/pkg	21070-69

REQUIRED APPARATUS

Cell Riser, 10 mL sample cell	1	each	45282-00
Cylinder, graduated, 25 mL	1	each	508-40
Sample Cell, 10 mL, matched pair	2	2/pkg	24954-02
Stoppers, rubber	1	12/pkg	2118-01

OPTIONAL REAGENTS

Acetic Acid Solution, 10%	500 mL	14816-49
Ascorbic Acid	100 g	6138-26
Bromine Water	25 mL	2211-20
Buffer Solution, pH 4.0	500 mL	12223-49
Hexanes, ACS	4 L	14478-17
HexaVer Chelating Reagent Powder Pillows	100/pkg	243-99
Hydrochloric Acid Standard Solution, 2.5 N	100 mL MDB	1418-32
Lead Acetate, trihydrate, ACS	500 g	7071-34
Magnesium Chloride Solution	1000 mL	14762-53
m-Nitrophenol Indicator	100 mL MDB	2476-32
Potassium Iodide Solution, 30 g/L	100 mL MDB	343-32
Sodium Arsenite Solution, APHA	100 mL MDB	1047-32
Sodium Cyanide, ACS	28 g	184-20
Sodium Hydroxide Standard Solution, 0.25 N	1000 mL	14763-53
Sodium Hydroxide Standard Solution, 5.0 N	1 L	2450-53
Starch Indicator Solution	100 mL MDB	349-32
Sulfuric Acid Standard Solution, 19.2 N	500 mL	2038-49
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Description	Unit	Cat. No.
Beaker, glass, 600 mL	each	500-52
Bottle, wash, 500 mL	each	620-11
Cylinder, graduated, 50 mL	each	508-41
Cylinder, graduated, 250 mL	each	508-46
Distillation Apparatus, cyanide accessories	each	22658-00
Distillation Apparatus, general purpose accessories	each	22653-00
Distillation Apparatus Heater and Support Apparatus, 115 Vac, 60 Hz	each	22744-00
Distillation Apparatus Heater and Support Apparatus, 230 Vac, 50 Hz	each	22744-02
Dropper, plastic	each	6080-00
Filter Paper, folded, 12.5 cm	100/pkg	1894-57
Flask, volumetric, 1000 mL	each	547-53
Flask, volumetric, Class A, 250 mL	each	14574-46
Funnel, poly, 65 mm	each	1083-67
Funnel, separatory, 500 mL	each	520-49
Hydrogen Sulfide Test Papers	100/pkg	25377-33
Midi-Distillation Apparatus, 4-port	each	26384-00
Midi-Distillation Apparatus, 10-port	each	26385-00
pH Meter, *sension*™*1*, portable	each	51700-10
Pipet, volumetric, Class A, 1.00 mL	each	14515-35
Pipet, volumetric, Class A, 2.00 mL	each	14515-36
Pipet, volumetric, Class A, 5.00 mL	each	14515-37
Pipet Filler, safety bulb	each	14651-00
Scoop, double ended	each	12257-00
Spoon, measuring, 1.0 g	each	510-00
Support Ring, 4"	each	580-01
Support Stand	each	563-00
Thermometer, -20 to 105 °C	each	1877-01

OPTIONAL 25 ML ANALYSIS ITEMS

Cyanide Reagent Set, 25 mL (100 tests)	each	22428-00
Pour-Thru Cell Assembly Kit (for 25 mL analysis)	each	45215-00
Sample Cell, 25 mL, matched pair	each	20950-00

For technical support and ordering information, see Section V.

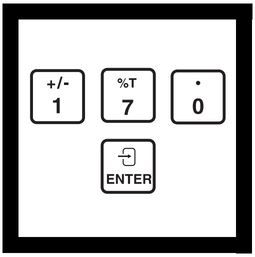
In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8139
For water

CYANURIC ACID (0 to 50 mg/L)

Turbidimetric Method



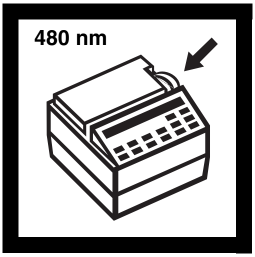
1. Enter the stored program number for cyanuric acid.

Press: **1 7 0 ENTER**

The display will show:

Dial nm to 480

Note: *The Pour-Thru Cell cannot be used with this procedure.*



2. Rotate the wavelength dial until the small display shows:

480 nm

When the correct wavelength is dialed in the display will quickly show: **Zero Sample**

then:

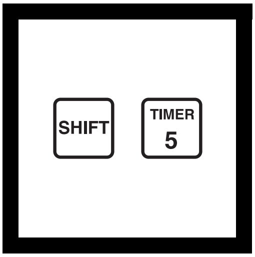
mg/L CYAN. ACID

3. Fill the sample cell with 25 mL of sample.

Note: *Filtering is required for highly turbid samples.*

4. Add the contents of one Cyanuric Acid 2 Reagent Powder Pillow (the prepared sample). Swirl to mix.

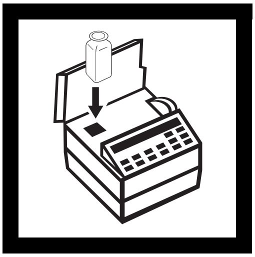
Note: *A white turbidity will form if cyanuric acid is present.*



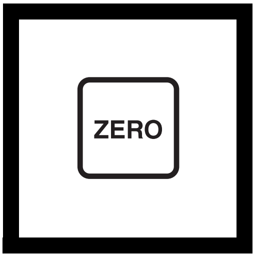
5. Press:

SHIFT TIMER

A three-minute reaction period will begin.



6. Fill a second sample cell with 25 mL of sample (the blank) and place it into the cell holder.



7. When the timer beeps, the display will show:

mg/L CYAN. ACID

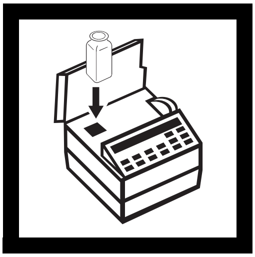
Press: **ZERO**

The display will show:

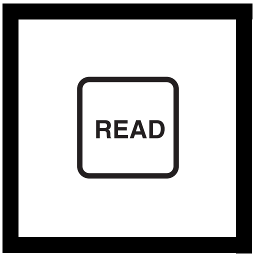
Zeroing. . .

then:

0.mg/L CYAN. ACID



8. Within 7 minutes after the timer beeps, place the prepared sample into the cell holder.



9. Press: **READ**

The display will show:

Reading. . .

then the results in mg/L cyanuric acid will displayed.

Note: *Clean sample cells with soap, water and a brush soon after each test to avoid a white film forming.*

Sampling and Storage

Collect samples in clean plastic or glass bottles. Samples must be analyzed within 24 hours.

Accuracy Check

Standard Solution Method

a) Dissolve 1.000 gram of cyanuric acid in l liter of deionized water to make a 1000 mg/L solution. Cyanuric acid is difficult to dissolve; it may take several hours to completely dissolve. This solution is stable for several weeks.

b) Dilute 2.00 mL of the 1000 mg/L solution to 100 mL with deionized water to make a 20 mg/L solution. Prepare fresh daily.

c) Testing the 20 mg/L solution should give test results of about 20 mg/L cyanuric acid.

Precision

In a single laboratory, using a standard solution of 25 mg/L cyanuric acid and two lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±1 mg/L cyanuric acid.

Summary of Method

The test for cyanuric acid uses the turbidimetric method. Cyanuric Acid 2 Reagent precipitates any cyanuric acid present and holds it in suspension. The amount of turbidity caused by the suspended particles is directly proportional to the amount of cyanuric acid present.

REQUIRED REAGENTS AND APPARATUS

Description	Quantity Required Per Test	Unit	Cat. No.
Cyanuric Acid 2 Reagent Powder Pillow	1 pillow	50/pkg	2460-66
Clippers, for opening powder pillows	1	each	968-00
Sample Cell, 25 mL, matched pair	2	pair	20950-00

OPTIONAL REAGENTS

Cyanuric Acid	25 g	7129-24
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Balance, Analytical, 115 V, Scientech, Model SA 120	each	26103-00
Balance, Analytical, 230 V, Scientech, Model SA 120	each	26103-02
Filter Paper, folded 12.5 cm	100/pkg	1894-57
Flask, volumetric, 100 mL	each	547-42
Flask, volumetric, 1000 mL	each	547-53
Funnel, poly, 65 mm	each	1083-67
Pipet, volumetric, Class A, 2.00 mL	each	14515-36

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

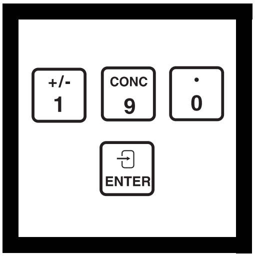
Method 8029

FLUORIDE (0 to 2.00 mg/L F^-)

For water, wastewater and seawater

SPADNS Method* (Reagent Solution or AccuVac Ampuls); USEPA accepted for reporting wastewater and drinking water analysis (distillation required; see Section II)**

Using SPADNS Reagent Solution



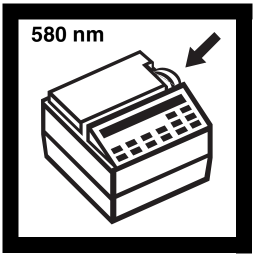
1. Enter the stored program number for fluoride (F^-).

Press: **1 9 0 ENTER**

The display will show:

Dial nm to 580

Note: *The Pour-Thru Cell cannot be used with this procedure.*



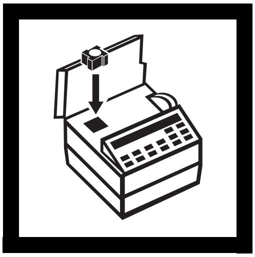
2. Rotate the wavelength dial until the small display shows:

580 nm

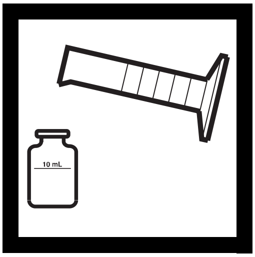
When the correct wavelength is dialed in, the display will quickly show: **Zero Sample**

then: **mg/L F^-**

Note: *Approach the wavelength setting from higher to lower values.*



3. Insert the 10-mL Cell Riser into the cell compartment.



4. Measure 10.0 mL of sample into a dry 10-mL sample cell (the prepared sample).

Note: *Use a graduated cylinder or pipet.*

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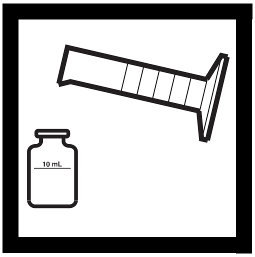
* Adapted from *Standard Methods for the Examination of Water and Wastewater*

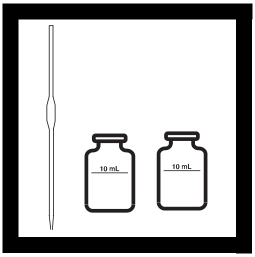
** Procedure is equivalent to Standard Methods 4500F-B,D for drinking water and wastewater.



5. Measure 10.0 mL of deionized water into a second dry sample cell (the blank).

Note: *Use a graduated cylinder or pipet.*

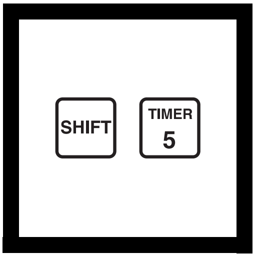
Note: *The sample and blank should be at the same temperature (±1 °C). Temperature adjustments may be made before or after reagent addition.*



6. Pipet 2.00 mL of SPADNS Reagent into each cell. Swirl to mix.

Note: *SPADNS Reagent is toxic and corrosive; use care while measuring.*

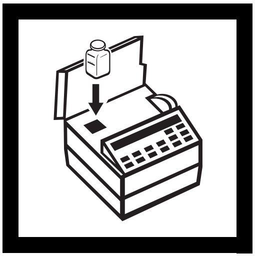
Note: *The SPADNS Reagent must be measured accurately.*



7. Press:

SHIFT TIMER

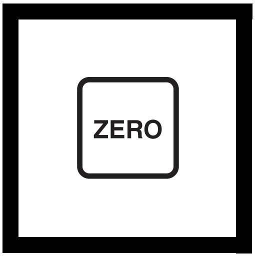
A one minute reaction period will begin.



8. When the timer beeps, the display will show:

mg/L F^-

Place the blank into the cell holder. Close the light shield.

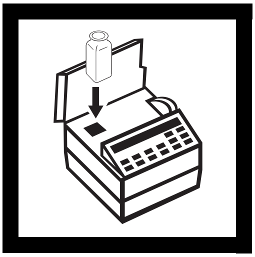


9. Press: **ZERO**

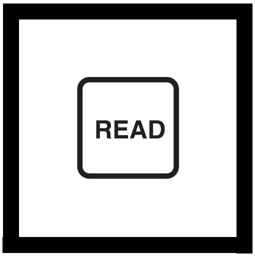
The display will show:

Zeroing. . .

then: **0.00 mg/L F^-**



10. Place the prepared sample into the cell holder. Close the light shield.



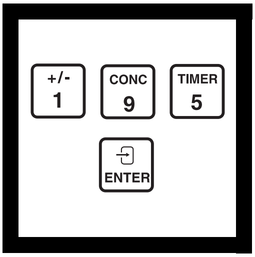
11. Press: **READ**

The display will show:

Reading. . .

then the result in mg/L F^- will be displayed.

Using AccuVac Ampuls

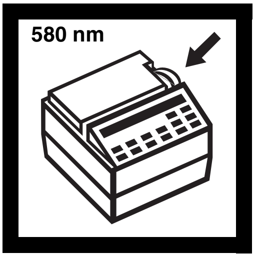


1. Enter the stored program number for fluoride (F^-) AccuVac ampuls.

Press: **1 9 5 ENTER**

The display will show:

Dial nm to 580



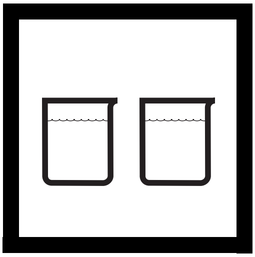
2. Rotate the wavelength dial until the small display shows:

580 nm

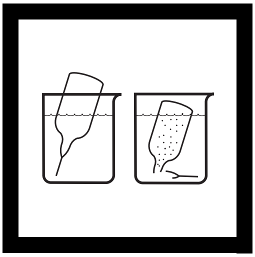
When the correct wavelength is dialed in, the display will quickly show: **Zero Sample**

then: **mg/L F^- AV**

Note: *Approach the wavelength setting from higher to lower values.*

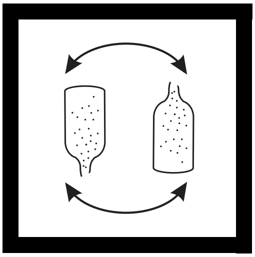


3. Collect at least 40 mL of sample in a 50-mL beaker. Pour at least 40 mL of deionized water into a second beaker.

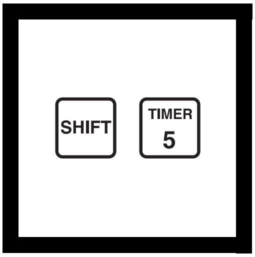


4. Fill a SPADNS Fluoride Reagent AccuVac Ampul with sample by breaking the tip on the bottom of the beaker. Fill a second AccuVac Ampul with deionized water (the blank) in the same manner.

Note: *Keep the tip immersed while the ampul fills completely.*



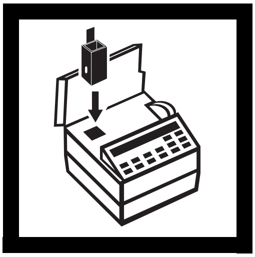
5. Quickly invert the ampuls several times to mix. Wipe off any liquid or fingerprints.



6. Press:

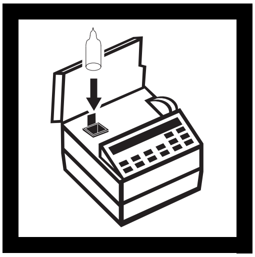
SHIFT TIMER

A one-minute reaction period will begin.



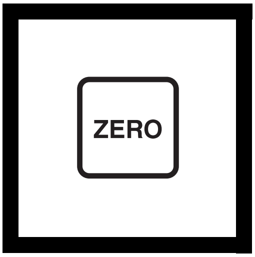
7. Place the AccuVac Vial Adapter into the cell holder of the instrument.

Note: *Place the grip tab at the rear of the cell holder.*



8. When the timer beeps, the display will show: **mg/L F^- AV**

Place the blank into the cell holder. Close the light shield.



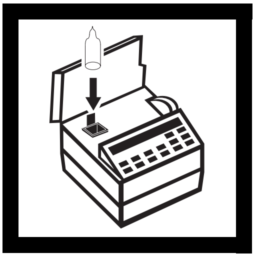
9. Press: **ZERO**

The display will show:

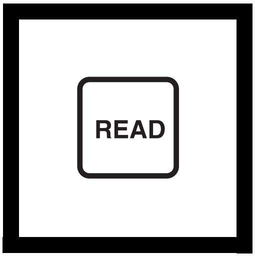
Zeroing. . .

then:

0.00 mg/L F^- AV



10. Place the AccuVac ampul containing the sample into the instrument. Close the light shield.



11. Press: **READ**

The display will show:

Reading. . .

then the result in mg/L fluoride will be displayed.

Sampling and Storage

Collect samples in plastic bottles. Samples may be stored up to 28 days.

Accuracy Check

Standard Solution Method

A variety of standard solutions covering the entire range of the test is available from Hach. Use these in place of sample to verify technique. Minor variations between lots of reagent become measurable above 1.5 mg/L. While results in this region are usable for most purposes, better accuracy may be obtained by diluting a fresh sample 1:1 with deionized water and retesting. Multiply the result by 2.

Precision

In a single laboratory, using standard solutions of 1.00 mg/L fluoride and two lots of SPADNS Reagent with the DR/2010, a single operator obtained standard deviations of ±0.02 mg/L fluoride.

Estimated Detection Limit (EDL)

The EDL for program 190 is 0.02 mg/L F^-. The EDL is the calculated lowest average concentration in a deionized water matrix that is different from zero with a 99% level of confidence. For more information on derivation and use of Hach's estimated detection limit, see *Section I.*

The EDL for program 195 is 0.02 mg/L F^-. The EDL is the calculated lowest average concentration in a deionized water matrix that is different from zero with a 99% level of confidence. For more information on derivation and use of Hach's estimated detection limit, see *Section I*.

Interferences

This test is sensitive to small amounts of interference. Glassware must be very clean. Repeating the test with the same glassware is recommended to ensure that results are accurate.

The following substances interfere to the extent shown:

Substance	Concentration	Error
Alkalinity (as $CaCO_3$)	5000 mg/L	-0.1 mg/L F^-
Aluminum	0.1 mg/L	-0.1 mg/L F^-
Chloride	7000 mg/L	+0.1 mg/L F^-
Iron, ferric	10 mg/L	-0.1 mg/L F^-
Phosphate, ortho	16 mg/L	+0.1 mg/L F^-
Sodium Hexametaphosphate	1.0 mg/L	+0.1 mg/L F^-
Sulfate	200 mg/L	+0.1 mg/L F^-

SPADNS Reagent contains enough arsenite to eliminate interference up to 5 mg/L chlorine. For higher chlorine levels, add one drop of Sodium Arsenite Solution to 25 mL of sample for each 2 mg/L of chlorine.

To check for interferences from aluminum, read the concentration one minute after reagent addition, then again after 15 minutes. An appreciable increase in concentration suggests aluminum interference. Waiting two hours before making the final reading will eliminate the effect of up to 3.0 mg/L aluminum.

Most interferences can be eliminated by distilling the sample from an acid solution as described below:

a) Set up the distillation apparatus for the general purpose distillation. See the Hach Distillation Apparatus Manual. Turn on the water and make certain it is flowing through the condenser.

b) Measure 100 mL of sample into the distillation flask. Add a magnetic stirring bar and turn on the heater power switch. Turn the stir control to 5.

c) Cautiously measure 150 mL of StillVer Distillation Solution (2:1 Sulfuric Acid) into the flask. If high levels of chloride are present, add 5 mg silver sulfate for each mg/L chloride present.

d) Turn the heat control to setting 10, with the thermometer in place. The yellow pilot lamp shows when the heater is on.

e) When the temperature reaches 180 °C (about one hour), turn the still off.

f) Dilute the collected distillate to 100 mL, if mecessary. Analyze the distallate by the above method.

Summary of Method

The SPADNS Method for fluoride determination involves the reaction of fluoride with a red zirconium-dye solution. The fluoride combines with part of the zirconium to form a colorless complex, thus bleaching the red color in an amount proportional to the fluoride concentration. This method is approved by the EPA for NPDES and NPDWR reporting purposes when the samples have been distilled. Seawater and wastewater samples require distillation. See Optional Apparatus for distillation Apparatus listing.

REQUIRED REAGENTS (USING SOLUTION)

Description	Quantity Required Per Test	Unit	Cat. No.
SPADNS Reagent for Fluoride	4 mL	500 mL	444-49
Water, deionized	10 mL	4 L	272-56

REQUIRED APPARATUS (USING SOLUTION)

Cell Riser, 10 mL	1	each	45282-00
Cylinder, graduated, 10 mL	1	each	508-38
Pipet Filler safety bulb	1	each	14651-00
Pipet, volumetric, Class A, 10.00 mL	1	each	14515-38
Pipet, volumetric, Class A, 2.00 mL	1	each	14515-37
Sample Cell, 10 mL, matched pair	2	pair	24954-02
Thermometer, -20 to 105°C	1	each	1877-01

REQUIRED REAGENTS (USING ACCUVAC AMPULS)

SPADNS Fluoride Reagent AccuVac Ampuls	2 ampuls	25/pkg	25060-25
Water, deionized	varies	4 L	272-56

REQUIRED APPARATUS (USING ACCUVAC AMPULS)

Adapter, AccuVac vial	1	each	43784-00
Beaker, 50 mL	2	each	500-41

OPTIONAL REAGENTS

Description	Unit	Cat. No.
Fluoride Standard Solution, 0.2 mg/L F^-	473 mL	405-02
Fluoride Standard Solution, 0.4 mg/L F^-	473 mL	405-04
Fluoride Standard Solution, 0.5 mg/L F^-	473 mL	405-05
Fluoride Standard Solution, 0.6 mg/L F^-	473 mL	405-06
Fluoride Standard Solution, 0.8 mg/L F^-	473 mL	405-08
Fluoride Standard Solution, 1.0 mg/L F^-	946 mL	291-16
Fluoride Standard Solution, 1.0 mg/L F^-	473 mL	291-11
Fluoride Standard Solution, 1.2 mg/L F^-	473 mL	405-12
Fluoride Standard Solution, 1.4 mg/L F^-	473 mL	405-14
Fluoride Standard Solution, 1.5 mg/L F^-	473 mL	405-15
Fluoride Standard Solution, 1.6 mg/L F^-	473 mL	405-16
Fluoride Standard Solution, 1.8 mg/L F^-	473 mL	405-18
Fluoride Standard Solution, 2.0 mg/L F^-	473 mL	405-20
Silver Sulfate, ACS	113 g	334-14
Sodium Arsenite Solution	100 mL MDB	1047-32
StillVer Distillation Solution	500 mL	446-49

OPTIONAL APPARATUS

AccuVac Snapper Kit	each	24052-00
Cylinder, graduated, 100 mL	each	508-42
Cylinder, graduated, 250 mL	each	508-46
Distillation Heater and Support Apparatus Set, 115 V, 50/60 Hz	each	22744-00
Distillation Heater and Support Apparatus Set, 230 V, 50/60 Hz	each	22744-02
Distillation Apparatus General Purpose Accessories	each	22653-00
pH Meter, *sension*™*1*, portable	each	51700-10
pH/ISE Meter, *sension*™*2*, portable	each	51725-10
Pipet, TenSette, 1.0 to 10.0 mL	each	19700-10
Pipet Tips, for 19700-10 TenSette Pipet	50/pkg	21997-96

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

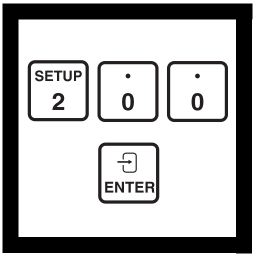
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8110

For water

FORMALDEHYDE (0 to 350 µg/L)

MBTH Method*



1. Enter the stored program number for formaldehyde (CH_2O).

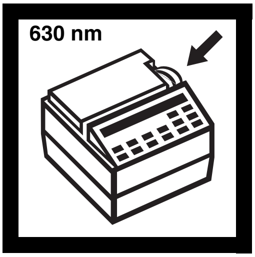
Press: **2 0 0 ENTER**

The display will show:

Dial nm to 630

Note: *Samples should be analyzed immediately after collection.*

Note: *The Pour-Thru Cell cannot be used.*



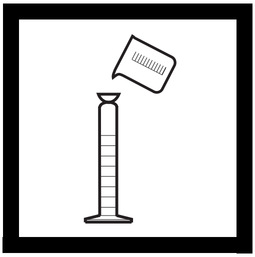
2. Rotate the wavelength dial until the small display shows:

630 nm

When the correct wavelength is dialed in the display will quickly show:

Zero Sample

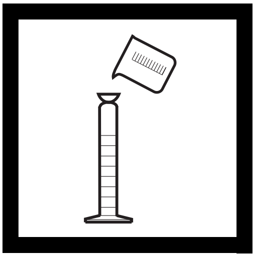
then: **µg/L CH_2O**



3. Accurately measure 25 mL of sample in a 50HmL mixing cylinder (the prepared sample).

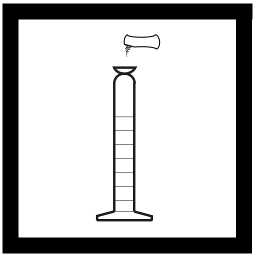
Note: *Wash glassware with chromic acid cleaning solution to remove trace contaminants.*

Note: *The sample should be at 25 ±1 °C, and the timing must be followed precisely. A temperature controlled water bath is recommended.*

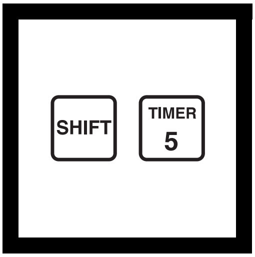


4. Accurately measure 25 mL of formaldehyde-free water in a second 50-mL mixing cylinder (the blank).

Note: *Obtain formaldehyde-free water by distilling water from alkaline permanganate (4 g sodium hydroxide, 2 g potassium permanganate per 500 mL water). Discard the first 50 to 100 mL of distillate.*



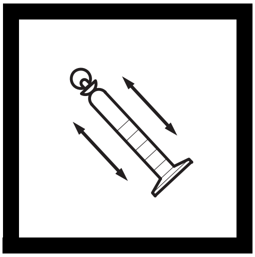
5. Add the contents of one MBTH Powder Pillow to the blank. Stopper the cylinder.



6. Immediately press:

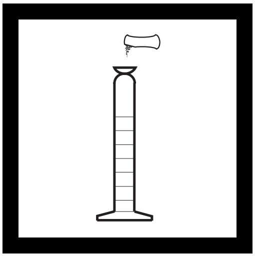
SHIFT TIMER

A 17-minute reaction period will begin.



7. Immediately after the reaction period starts, shake the cylinder vigorously for 20 seconds.

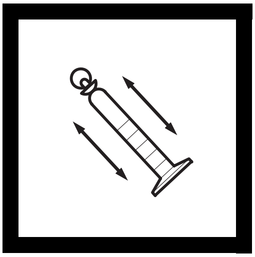
Note: *Do not wait for the timer to beep.*



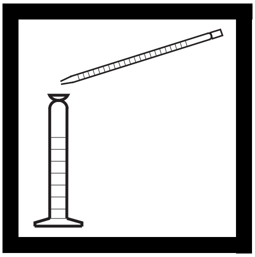
8. Add the contents of one MBTH Powder Pillow to the prepared sample when the timer shows 15:00. Stopper the cylinder.

---

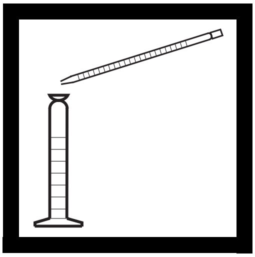
* Adapted from Matthews, T.G. and Howell, T.C., Journal of the Air Pollution Control Association, 31 (11), 1181-1184 (1981).



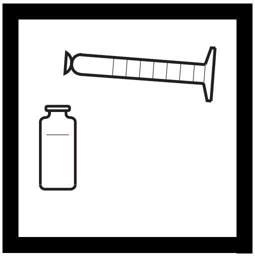
9. Shake the cylinder vigorously for 20 seconds.



10. Add 2.5 mL of Developing Solution For Low Range Formaldehyde to the blank when the timer shows 12:00. Stopper. Invert to mix.

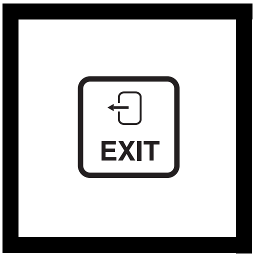


11. Add 2.5 mL of Developing Solution For Low Range Formaldehyde to the prepared sample when the timer shows 10:00. Stopper. Invert to mix.

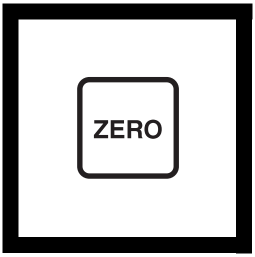


12. Slowly pour the blank into the sample cell just before the timer shows 2:00. Place the blank into the cell holder. Close the light shield.

***Note:** If bubbles form on the cell walls, swirl the cell to dislodge them.*



13. When the timer shows 2:00, press **EXIT** once.



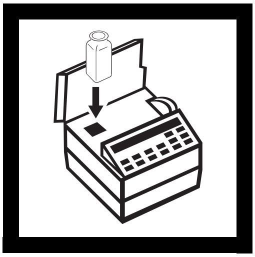
14. Press **ZERO**

The display will show:

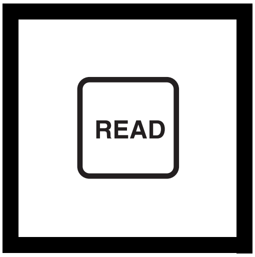
Zeroing. . .

then: **0. µg/L CH_2O**

***Note:** If desired, return the display to the timer mode by pressing* **SHIFT TIMER.**



15. Pour the prepared sample into a sample cell. Place it into the cell holder. Close the light shield.



16. When the timer beeps, the display will show: **µg/L CH_2O**

Immediately press:

READ

The display will show:

Reading. . .

then the result in µg/L formaldehyde (CH_2O) will be displayed.

Accuracy Check

Standard Additions Method

a) Snap the neck off a Formaldehyde Voluette Ampule Standard Solution, 4000 mg/L.

b) Pipet 2.00 mL of standard into a 1000-mL volumetric flask. Dilute to volume with formaldehyde-free water. Mix well. Prepare daily. This is an 8-mg/L formaldehyde standard solution.

c) Use the TenSette Pipet to add 0.1 mL, 0.2 mL, and 0.3 mL of diluted standard (8 mg/L) to three 25-mL water samples. Mix each sample thoroughly.

d) Analyze each sample as described above in the procedure. The formaldehyde concentration should increase 32 µg/L for each 0.1 mL of standard added.

e) If these increases do not occur, see *Standard Additions* in *Section I* for more information.

Standard Solution Method

Prepare a 320 µg/L formaldehyde standard by pipetting 1.0 mL of the 8-mg/L solution from the Accuracy Check into a 50-mL mixing cylinder. Dilute to 25.0 mL with formaldehyde-free water. Run the test directly on this sample.

Interferences

The following may interfere when present in concentrations exceeding levels listed below.

Acetate	1000 mg/L	Iron (Fe^{3+})	12 mg/L
Ammonium (as N)	10 mg/L	Lead	100 mg/L
Aniline	10 mg/L	Manganese	500 mg/L
Bicarbonate	1000 mg/L	Mercury	70 mg/L
Calcium	3500 mg/L	Morpholine	0.36 mg/L
Carbonate	500 mg/L	Nitrate	1000 mg/L
Chloride	5000 mg/L	Nitrite	8 mg/L
Copper	1.6 mg/L	Phenol	1050 mg/L
Cyclohexylamine	250 mg/L	Phosphate	200 mg/L
Ethanolamine	33 mg/L	Silica	40 mg/L
Ethylenediamine	1.5 mg/L	Sulfate	10000 mg/L
Glucose	1000 mg/L	Urea	1000 mg/L
Glycine	1000 mg/L	Zinc	1000 mg/L

Other aldehydes give a positive interference.

Precision

In a single laboratory using standards of 146 µg/L formaldehyde and two lots of reagent with the DR/2010, a single operator obtained a standard deviation of ± 3.1 µg/L formaldehyde.

Summary of Method

Formaldehyde reacts with MBTH (3-methyl-2-benzothiazoline hydrazone) and a developing solution to form a blue color in proportion to the formaldehyde concentration.

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
Formaldehyde Reagent Set (100 Tests)			22577-00
Includes: (2) 22571-69, (1) 22572-49			
Developing Solution for LR Formaldehyde	5 mL	500 mL	22572-49
MBTH Powder Pillows	2 pillows	100/pkg	22571-69
REQUIRED APPARATUS			
Clippers, for opening powder pillow	1	each	968-00
Cylinder, mixing, graduated, 50 mL	2	each	1896-41
Pipet, serological, 5 mL	1	each	532-37
Pipet Filler, safety bulb	1	each	14651-00
OPTIONAL REAGENTS			
Chromic Acid Cleaning Solution		500 mL	1233-49
Formaldehyde Standard Solution, Voluette ampule, 4000 mg/L, 10 mL		16-pkg	22573-10
Potassium Permanganate, ACS		454 g	168-01
Sodium Hydroxide, pellets, ACS		500 g	187-34
OPTIONAL APPARATUS			
Ampule Breaker Kit		each	21968-00
Beaker, 50 mL		each	500-41
Flask, volumetric, Class A, 1000 mL		each	14574-53
Pipet, TenSette, 0.1 to 1.0 mL		each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet		50/pkg	21856-96
Pipet, volumetric, Class A, 2.00 mL		each	14515-36
Pipet, volumetric, Class A, 1.00 mL		each	14515-35
Thermometer, -20 to 105 °C		each	1877-01
Water bath, 120 Vac, 60 Hz, 5 gal (19 L)		each	24638-00
Water bath, 240 Vac, 50 Hz, 5 gal (19 L)		each	24638-02

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

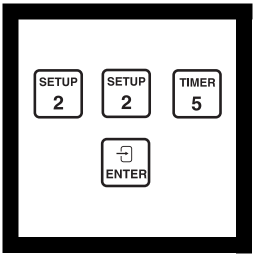
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8030

HARDNESS (0 to 4.00 mg/L Ca and Mg as $CaCO_3$)

For water, wastewater, seawater

Calcium and Magnesium; Calmagite Colorimetric Method



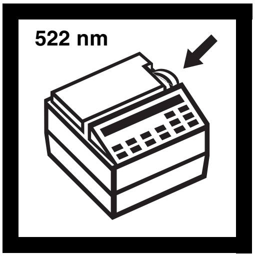
1. Enter the stored program number for magnesium.

Press: **2 2 5 ENTER**

The display will show:

Dial nm to 522

Note: *The Pour-Thru Cell can be used if rinsed well with deionized water between the blank and prepared sample.*



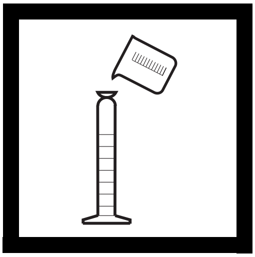
2. Rotate the wavelength dial until the small display shows:

522 nm

When the correct wavelength is dialed in, the display will quickly show:

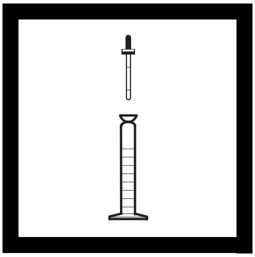
Zero Sample

then: **mg/L Mg-$CaCO_3$**

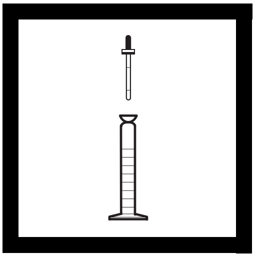


3. Pour 100 mL of sample into a 100-mL mixing cylinder.

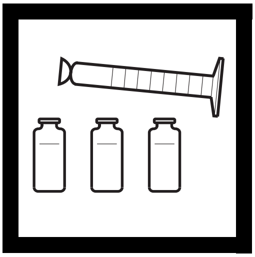
Note: *For the most accurate magnesium test results the sample temperature should be between 21-29 °C (70-84 °F).*



4. Add 1.0 mL of Calcium and Magnesium Indicator Solution using a 1.0-mL measuring dropper. Stopper. Invert several times to mix.

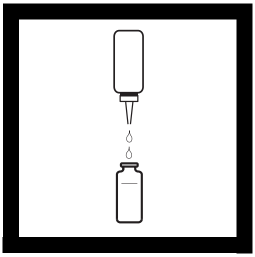


5. Add 1.0 mL of Alkali Solution for Calcium and Magnesium Test using a 1.0-mL measuring dropper. Stopper. Invert several times to mix.

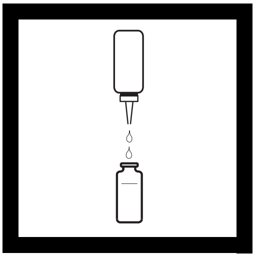


6. Pour 25 mL of the solution into each of three sample cells.

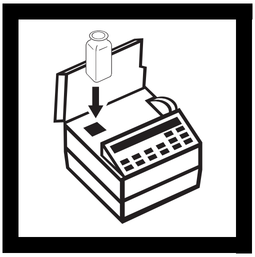
Note: *The test will detect any calcium or magnesium contamination in the mixing cylinder, measuring droppers or sample cells. To test cleanliness, repeat the test multiple times until you obtain consistent results.*



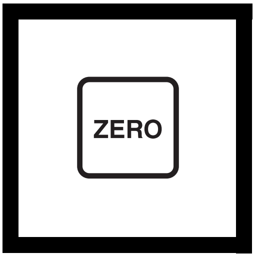
7. Add one drop of 1 M EDTA Solution to one cell (the blank). Swirl to mix.



8. Add one drop of EGTA Solution to another cell (the prepared sample). Swirl to mix.



9. Place the blank into the cell holder. Close the light shield.



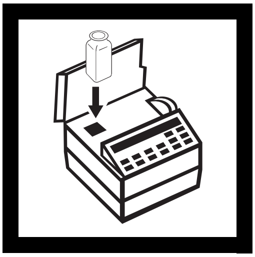
10. Press: **ZERO**

The display will show:

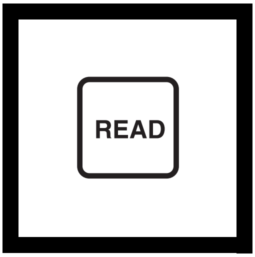
Zeroing. . .

then:

0.00 mg/L Mg-CaCO$_3$



11. Place the prepared sample into the cell holder. Close the light shield.



12. Press: **READ**

The display will show:

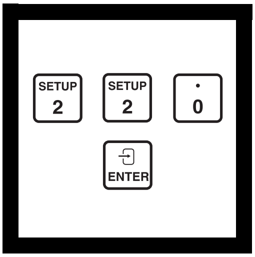
Reading. . .

then the result in mg/L Mg as CaCO$_3$ will be displayed.

Forms ▲ Mg-CaCO$_3$
▼ Mg

13. Press:

SELECT PRGM



14. Enter the stored program number for calcium.

Press: **2 2 0 ENTER**

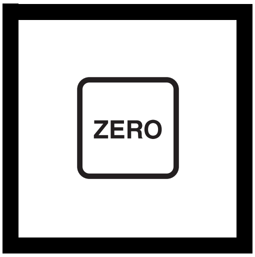
The display will show:

Zero Sample

then:

mg/L Ca-CaCO$_3$

Note: *Do not remove sample cell.*



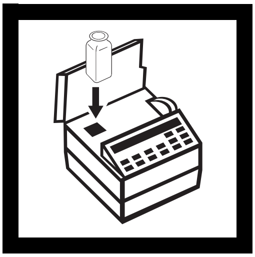
15. Press: **ZERO**

The display will show:

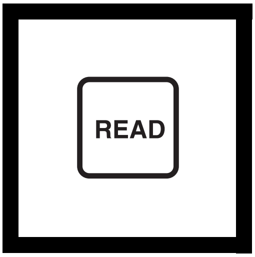
Zeroing. . .

then:

0.00 mg/L Ca-CaCO$_3$



16. Place the third sample cell into the cell holder.



17. Press: **READ**

The display will show:

Reading. . .

then the result in mg/L Ca as $CaCO_3$ will be displayed.

Forms ▲ Ca-$CaCO_3$
▼ Ca

Note: *mg/L total hardness equals mg/L Ca as* $CaCO_3$ *plus mg/L Mg as* $CaCO_3$

To convert from	To	Multiply by
mg/L Ca as $CaCO_3$	mg/L Ca	0.400
mg/L Mg as $CaCO_3$	mg/L $MgCO_3$	0.842
mg/L $MgCO_3$	mg/L Mg	0.29

Sampling and Storage

Collect samples in acid-washed plastic bottles. Adjust the sample pH to 2 or less with nitric acid (about 5 mL per liter). Cool samples to 4 °C. Preserved samples can be stored up to six months. Adjust the sample pH to between 3 and 8 with 5.0 N Sodium Hydroxide Standard Solution just before analysis. Correct the test results for volume additions; see *Correction for Volume Additions* in *Section I* for more information.

Precision

In a single laboratory using a standard solution of 1.5 mg/L Mg as $CaCO_3$ and 3 mg/L Ca as $CaCO_3$ with the DR/2010, a single operator obtained a standard deviation of ± 0.006 mg/L Mg as $CaCO_3$ and ± 0.02 mg/L Ca as $CaCO_3$.

Interferences

For the most accurate calcium test result, the test should be rerun on a diluted sample if the calcium is over 1.0 and the magnesium is over 0.25 mg/L as $CaCO_3$. No retesting is needed if either is below those respective concentrations.

The following cause a detectable error in test results.

Cr^{3+}	0.25 mg/L
Cu^{2+}	0.75 mg/L
EDTA, chelated	0.2 mg/L as $CaCO_3$
Fe^{2+}	1.4 mg/L
Fe^{3+}	2.0 mg/L
Mn^{2+}	0.20 mg/L
Zn^{2+}	0.050 mg/L

Traces of EDTA or EGTA remaining in sample cells from previous tests will give erroneous results. Rinse cells thoroughly before using.

Summary of Method

The colorimetric method for measuring hardness supplements the conventional titrimetric method because it can measure very low levels of calcium and magnesium. Also some interfering metals (those listed above) in the titrimetric method are inconsequential in the colorimetric method when diluting the sample to bring it within the range of this test.

The indicator dye is calmagite which forms a purplish-blue color in a strongly alkaline solution and changes to red when it reacts with free calcium or magnesium. Calcium and magnesium determinations are made by chelating calcium with EGTA to destroy any red color due to calcium and then chelating the calcium and magnesium with EDTA to destroy the red color due to both calcium and magnesium. By measuring the red color in the different states, calcium and magnesium levels are determined.

REQUIRED REAGENTS

	Cat. No.
Hardness Reagent Set (100 Tests)	23199-00
Includes: (1) 22417-32, (1) 22418-32, (1) 22419-26, (1) 22297-26	

Description	Quantity Required Per Test	Unit	Cat. No.
Alkali Solution for Calcium and Magnesium Test	1 mL	100 mL MDB	22417-32
Calcium and Magnesium Indicator Solution	1 mL	100 mL MDB	22418-32
EDTA Solution, 1 M	1 drop	50 mL SCDB	22419-26
EGTA Solution	1 drop	50 mL SCDB	22297-26

REQUIRED APPARATUS

Description	Quantity Required Per Test	Unit	Cat. No.
Cylinder, 100-mL mixing	1	each	1896-42
Dropper, measuring, 0.5 and 1.0 mL	2	20/pkg	21247-20
Sample Cell, 25 mL, matched pair	3	2	20950-00

OPTIONAL REAGENTS

Description	Unit	Cat. No.
Nitric Acid, ACS	500 mL	152-49
Sodium Hydroxide Standard Solution 5.0 N	100 mL MDB	2450-32

OPTIONAL APPARATUS

Description	Unit	Cat. No.
pH Meter, *sension*™*1*, portable	each	51700-10
Pipet, serological, 5 mL	each	532-37
Pour-Thru Cell Assembly Kit	each	45215-00
Thermometer, -20 to 105 °C	each	1877-01

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

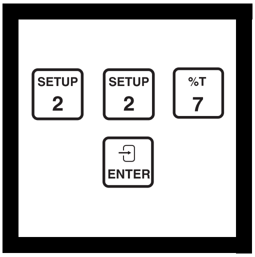
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8374

HARDNESS, TOTAL, Ultra Low Range (0 to 1,000 µg/L Ca & Mg as $CaCO_3$)

For Ultra Pure water

Calcium and Magnesium Chlorophosphonazo Colorimetric Method

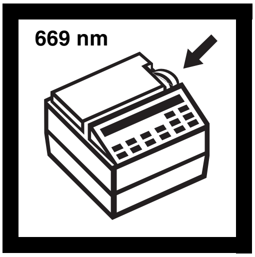


1. Enter the stored program number for Ultra Low Range Hardness.

Press: **2 2 7 ENTER**

The display will show:

Dial nm to 669



2. Rotate the wavelength dial until the small display shows:

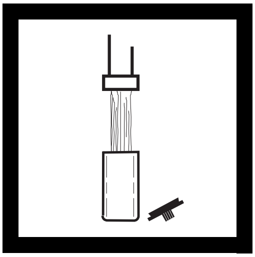
669 nm

When the correct wavelength is dialed in the display will quickly show:

Zero Sample

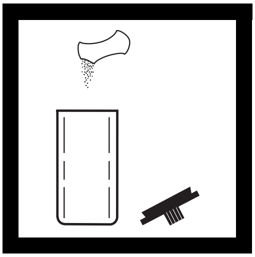
then: **µg/L $CaCO_3$**

3. Rinse a plastic sample cell and the cap three times with the water to be tested. Do not allow the underside of the cap to come in contact with surfaces that may contaminate it.



4. Fill the plastic sample cell to the 25-mL mark with sample.

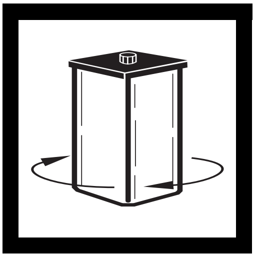
Note: *Plastic sample cells must be used; glass will contaminate the sample.*



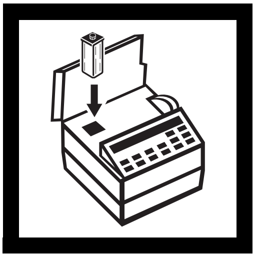
5. Add the contents of one Chlorophosphonazo Solution Pillow to the sample cell.

Note: *A small amount of solution may remain in the pillow. This will not affect results.*

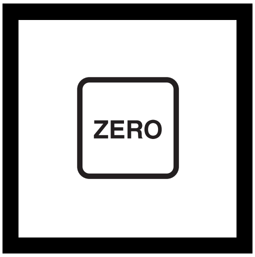
Note: *One mL of Chlorophosphonazo Indicator Solution (Cat. No. 25895-49) may be used instead of the solution pillow.*



6. Cap the cell and swirl to mix.



7. Place the sample cell into the cell holder. Close the light shield.

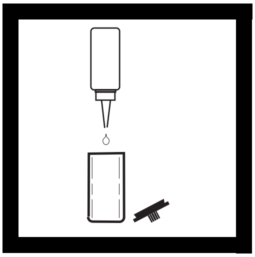


8. Press: **ZERO**

The display will show:

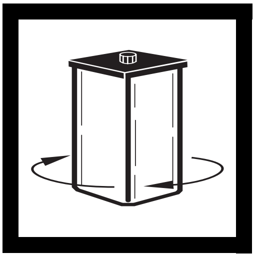
Zeroing. . .

then: **0 µg/L $CaCO_3$**

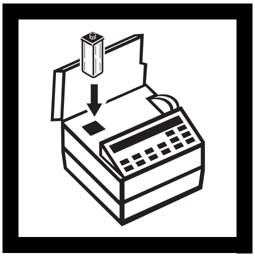


9. Remove the cell from the instrument. Add one drop of CDTA Reagent for Ultra Low Range Hardness.

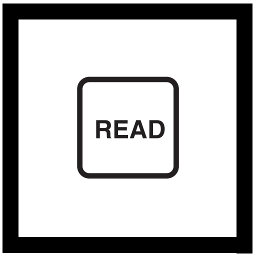
Note: *Complete Steps 10-12 within 1-2 minutes.*



10. Cap the cell and swirl to mix



11. Place the sample cell into the cell holder. Close the light shield.



12. Press: **READ**

The display will show:

Reading. . .

then the result in µg/L as $CaCO_3$ will be displayed.

Forms ▲▼ Mg
$CaCO_3$
Ca

Note: *Alternate forms should only be used when the sample is known to contain only Mg or Ca. This method does not distinguish between the two forms.*

Sampling and Storage

Do not use glass containers. Collect samples in clean plastic containers, preferably with screw-type closures. Rinse containers several times with water to be analyzed before capturing final sample. Seal to avoid contamination during transport. Analyze as soon as possible.

Accuracy Check

Standard Additions Method

a) Use a TenSette Pipet to add 0.1 mL, 0.2 mL, and 0.3 mL, of a 20 mg/L (as $CaCO_3$) Calcium Chloride standard to three 25-mL samples, respectively.

b) Perform the hardness test on each sample as described above.

c) Each 0.1 mL addition of standard should cause an increase of 80 µg/L hardness as $CaCO_3$.

d) If these increases do not occur, see Standard Additions in Section I for more information.

Standard Solution Method

Use the 0.50 mg/L (as $CaCO_3$) Calcium Chloride Standard Solution listed under Optional Reagents. Analyze this solution according to the above procedure. The result should be between 460 µg/L as $CaCO_3$ and 540 µg/L as $CaCO_3$.

Precision

In a single laboratory using a standard solution of 600 µg/L as $CaCO_3$, two representative lots of reagents and a DR/2010, a single operator obtained a standard deviation of 3 µg/L.

Interferences

Interference studies were conducted at various hardness levels between 0 and 500 µg/L as $CaCO_3$. Various cations and anions were evaluated at levels in the range appropriate to ultra pure water applications.

An ion is said to interfere when the concentration is changed by ±10%.

Table 1 Negative Interference

Ion	Level above which it interferes (µg/L)
Aluminum	150
Sodium	79,000

Table 2 Positive Interference

Ion	Level above which it interferes (µg/L)
Copper	250
Silicon	1,000

Table 3 No Interference

Ion	Highest ConcentrationTested (µg/L)
Potassium	1,000
Ammonium	1,000
Formaldehyde	47,000

Disposal Information

To dispose of sample cell contents, turn the cold tap water on, and pour the material carefully down the drain. Let the water run one minute to flush the system.

Summary of Method

Calcium and magnesium combine equivalently with the chlorophosphonazo III indicator to form a colored complex which absorbs light very strongly at 669 nm. One drop of the CDTA reagent breaks up this complex, and the resultant decrease in color is proportional to the amount of calcium and magnesium in the sample (as $CaCO_3$).

REQUIRED REAGENTS

Ultra Low Range Hardness Reagent Set 26031-00

Includes: (1) 24102-12, (1) 25895-99, (1) 25896-36

Description	Quantity Required Per Test	Unit	Cat. No.
Chlorophosphonazo Indicator Solution Pillows for Ultra Low Range Hardness	1 pillow	100/pkg	25895-99
CDTA Reagent for Ultra Low Range Hardness	1 drop	10 mL	25896-36
REQUIRED APPARATUS			
Clippers (Shears) for opening Solution Pillows	1	each	23694-00
Sample Cell, 1-inch, disposable, polystyrene w/ cap	1	12/pkg	24102-12
OPTIONAL REAGENTS			
Calcium Standard Solution, 20 mg/L as $CaCO_3$		946 mL	21246-16
Calcium Standard Solution, 0.50 mg/L as $CaCO_3$		946 mL	20580-16
Chlorophosphonazo Indicator Solution	1 mL	500 mL	25895-49
OPTIONAL APPARATUS			
Dispenser, 1.0 mL fixed volume, Repipet Jr.		each	21113-01
Pipet, TenSette, 0.1 to 1.0 mL		each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet		50/pkg	21856-96

For technical support and ordering information, see Section V.

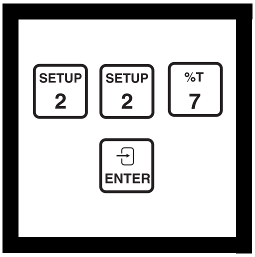
In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

HARDNESS, TOTAL, Ultra Low Range (0 to 1,000 µg/L Ca & Mg as $CaCO_3$)

For boiler, cooling, and ultra-pure waters

Calcium and Magnesium; Chlorophosphonazo Rapid Liquid Method

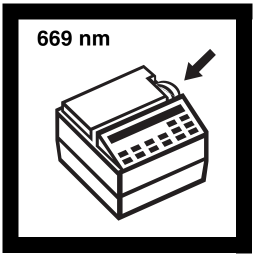


1. Enter the stored program number for ultra low range hardness.

Press: **2 2 7 ENTER**

The display will show:

Dial nm to 669



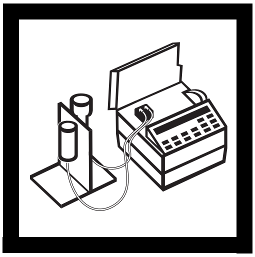
2. Rotate the wavelength dial until the small display shows:

669 nm

When the correct wavelength is dialed in, the display will quickly show:

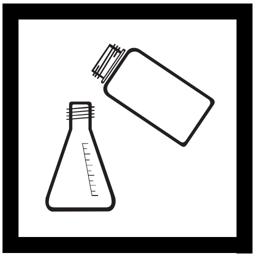
Zero Sample

then: **µg/L $CaCO_3$**

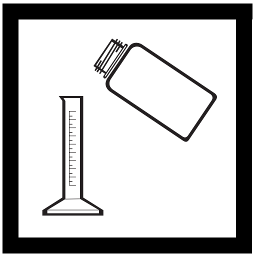


3. Install the Pour-Thru Cell and flush with 50 mL of ultra-pure water.

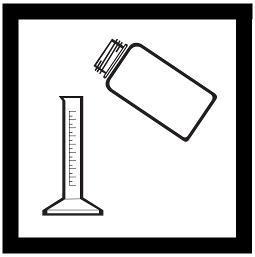
Note: *Pre-clean the Pour-Thru Cell and all labware as specified in Treating Analysis Labware.*



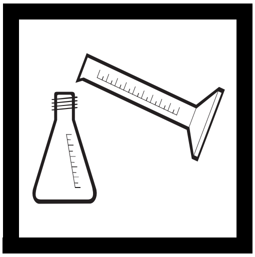
4. Rinse a clean 125-mL plastic Erlenmeyer flask three times with the sample.



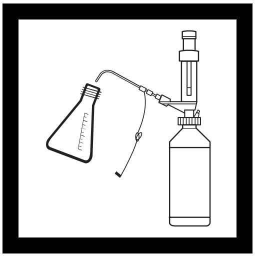
5. Rinse a clean 50-mL plastic graduated cylinder three times with the sample.



6. Fill this rinsed cylinder to the 50-mL mark with sample.



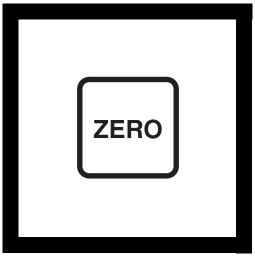
7. Pour the contents of the 50-mL cylinder into the flask.



8. Add 2.0 mL of Chlorophosphonazo Reagent to the sample using the Repipet Dispenser. Swirl to mix.

9. Pour approximately half (25 mL) of the sample into the Pour-Thru Cell.

Note: *A clean, dry, plastic 25-mL graduated cylinder may be used for measuring half of the sample.*

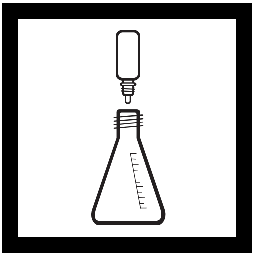


10. After the flow has stopped, press: **ZERO**

The display will show:

Zeroing. . . .

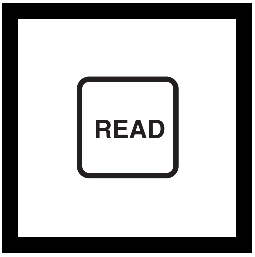
then: **0 µg/L** $\mathbf{CaCO_3}$



11. Add one drop of CDTA Reagent for Ultra Low Range Hardness to the remaining sample in the flask. Swirl to mix.

Note: *Complete steps 12-13 within 1-2 minutes.*

12. Pour the remaining sample into the Pour-Thru Cell.



13. After the flow has stopped, press: **READ**

The display will show:

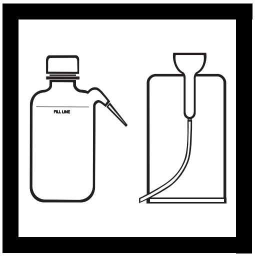
Reading. . . .

then the result in µg/L as $CaCO_3$ will be displayed.

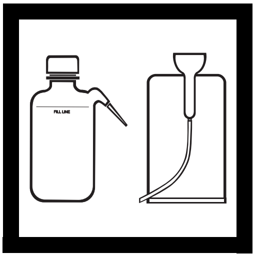
Forms ▲▼ Mg
$CaCO_3$
Ca

Note: *If the sample concentration is greater than 750 µg/L, a 1:1 dilution of the sample is recommended for greatest accuracy. Use ultra-pure (aldehyde-free) water for the dilution. Repeat the analysis on the diluted sample and multiply the resulting concentration by 2.*

Note: *Alternate forms should only be used when the sample is known to contain only Mg or Ca. This method does not distinguish between the two forms.*



14. Rinse the Pour-Thru cell with ultra-pure water using a wash bottle immediately after use.



15. Flush the Pour-Thru cell with an additional 50 mL of ultra-pure water.

Note: *Protect the Pour-Thru cell from contamination by inverting a small beaker over the top of the glass funnel when not in use.*

Treating Analysis Labware

Clean all containers used in this test thoroughly to remove any traces of calcium or magnesium. If possible, use plastic containers for all analysis and storage. Clean containers by normal means, then rinse with ultra-pure (aldehyde-free) water. Fill and soak for 10 minutes with a 1:25 dilution of Chlorophosphonazo Reagent in ultra-pure water. Rinse well with ultra-pure water. Keep containers tightly closed and dedicate them for ULR Hardness only. If containers are rinsed and capped after each use, only occasional soaking is necessary. Fill the Pour-Thru cell with this same mixture of chlorophosphonazo and water and let stand for several minutes. Rinse with ultra-pure water.

Avoid contamination of the Chlorophosphonazo Reagent bottle when placing the Repipet dispenser on the bottle. Rinse the inlet tubing and inside of the dispenser cap with copious amounts of ultra-pure water using a wash bottle. Place the inlet tubing into a beaker of ultra-pure water and depress the plunger 10-15 times to rinse the inside of the dispenser. (For best results, pour a small amount of reagent into the beaker of rinse water.) Remove the dispenser from the water and depress the plunger until all of the water has been expelled. Shake off any excess water on the dispenser, place the dispenser on the bottle, and tighten.

Sampling and Storage

Do not use glass containers. Collect samples in clean plastic containers, preferably with screw-type closures. Rinse containers several times with the water to be analyzed before capturing the final sample. Seal to avoid contamination during transport. Analyze as soon as possible.

Accuracy Check
Standard Additions Method

a) Use a TenSette Pipet to add 0.2 mL, 0.4 mL, and 0.6 mL, of a 20 mg/L (as $CaCO_3$) Calcium Chloride standard to three 50-mL samples, respectively.

b) Perform the hardness test on each sample as described above.

c) Each 0.2 mL addition of standard should cause an increase of 80 µg/L hardness as $CaCO_3$.

d) If these increases do not occur, see *Standard Additions* in *Section I.*

Standard Solution Method

Using the 0.50 mg/L (as $CaCO_3$) Calcium Chloride Standard Solution, perform the procedure using the standard in place of the sample.

The result should be between 460 µg/L and 540 µg/L as $CaCO_3$.

Precision

In a single laboratory using a standard solution of 600 µg/L as $CaCO_3$ and two representative lots of reagents with a DR/2010, a single operator obtained a standard deviation of 3 µg/L.

Interferences

Interference studies were conducted at various hardness levels between 0 and 500 µg/L as $CaCO_3$. Various cations and anions were evaluated at levels in the range appropriate to ultra pure water applications. An ion is said to interfere when the resulting concentration is changed by ±10%.

Table 1 Negative Interference

Ion	Level above which ion interferes (µg/L)
Aluminum	150
Sodium	79,000

Table 2 Positive Interference

Ion	Level above which ion interferes (µg/L)
Copper	250
Silicon	1,000

Table 3 No Interference

Ion	Highest Concentration Tested (µg/L)
Potassium	1,000
Ammonium	1,000
Formaldehyde	47,000

Summary of Method

Calcium and magnesium combine equivalently with the Chlorophosphonazo Indicator to form a colored complex which absorbs light very strongly at 669 nm. One drop of the CDTA reagent breaks up this complex, and the resultant decrease in color is proportional to the amount of calcium and magnesium (as $CaCO_3$) in the sample.

REQUIRED REAGENTS

ULR Hardness Reagent Set (100 tests)			26031-01

Includes: (1) 25895-49, (1) 25896-36

Description	Quantity Required Per Test	Unit	Cat. No.
Chlorophosphonazo Indicator Solution	2 mL	500 mL	25895-49
CDTA Reagent for Ultra Low Range Hardness	1 drop	10 mL SCDB	25896-36

REQUIRED APPARATUS

Cylinder, graduated, 50 mL, poly	1	each	1081-41
Dispenser, Fixed-volume, 2.0 mL, Repipet Jr.	1	each	22307-01
Flask, Erlenmeyer, PMP w/cap, 125 mL	1	each	20898-43
Pour-Thru Cell Assembly Kit	1	each	45215-00

OPTIONAL REAGENTS

Calcium Standard Solution, 20 mg/L as $CaCO_3$	946 mL	21246-16
Calcium Standard Solution, 0.50 mg/L as $CaCO_3$	946 mL	20580-16
Water, Ultra-pure (aldehyde-free)	500 mL	25946-49

OPTIONAL APPARATUS

Beaker, poly 50 mL	each	1080-41
Bottle, wash, 125 mL	each	21901-43
Cylinder, graduated, 25 mL, poly	each	1081-40
Flask, Erlenmeyer, PMP w/cap, 125 mL	6/pkg	20898-73
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

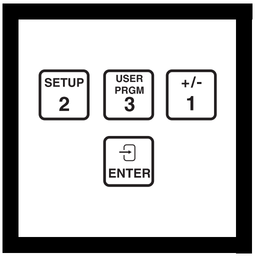
Method 8141

HYDRAZINE (0 to 500 µg/L)

For boiler water/feedwater, water, and seawater

p-Dimethylaminobenzaldehyde Method*

Using Reagent Solution



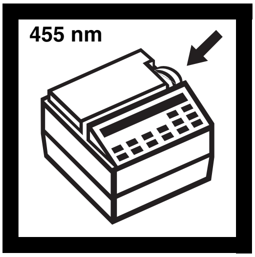
1. Enter the stored program number for hydrazine (N_2H_4).

Press: **2 3 1 ENTER**

The display will show:

Dial nm to 455

Note: *The Pour-Thru Cell can be used with 25-mL reagents only.*



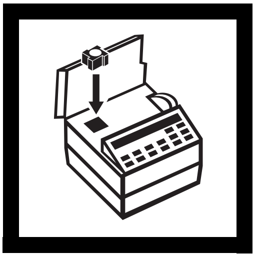
2. Rotate the wavelength dial until the small display shows:

455 nm

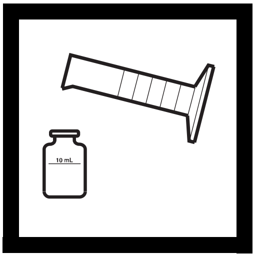
When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

then: **µg/L N_2H_4**



3. Insert the 10-mL Cell Riser into the cell compartment.



4. Pour 10.0 mL of deionized water into a sample cell (the blank) using a graduated cylinder.

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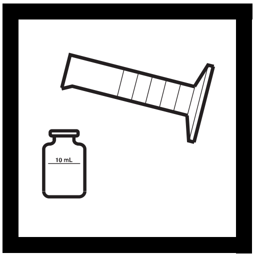
* Adapted from ASTM Manual of Industrial Water, D1385-78, 376 (1979).



5. Pour 10.0 mL of sample into a second sample cell (the sample) using a graduated cylinder.

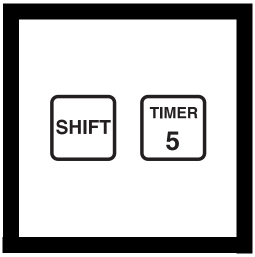
Note: *Sample temperature should be 21 ± 4 °C (70 ± 7 °F).*

Note: *For turbid samples, see* Interferences *section.*

6. Add 0.5 mL of HydraVer 2 Hydrazine Reagent to each sample cell. Swirl to mix.

Note: *A yellow color will develop if Hydrazine is present.*

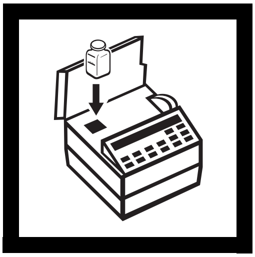
Note: *HydraVer 2 Hydrazine Reagent will cause a faint yellow color to appear in the blank.*



7. Press:

SHIFT TIMER

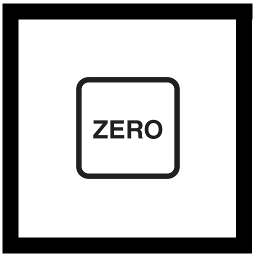
A 12-minute reaction period will begin.



8. When the timer beeps, the display will show:

µg/L N_2H_4

Immediately after the timer beeps, insert the blank into the cell holder. Close the light shield.

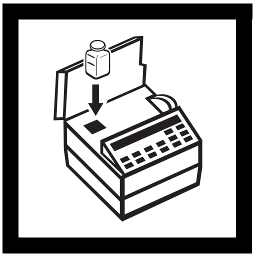


9. Press: **ZERO**

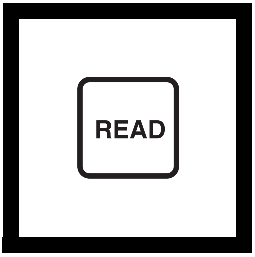
The display will show:

Zeroing. . . .

then: **0. µg/L N_2H_4**



10. Place the prepared sample into the cell holder. Close the light shield.



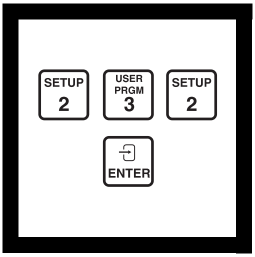
11. Press: **READ**

The display will show:

Reading. . . .

then the result in µg/L hydrazine will be displayed.

Using AccuVac Ampuls



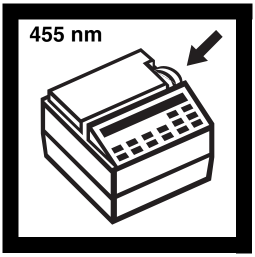
1. Enter the stored program number for hydrazine (N_2H_4).

Press: **2 3 2 ENTER**

The display will show:

Dial nm to 455

__Note:__ Samples must be analyzed immediately and cannot be preserved for later analysis.



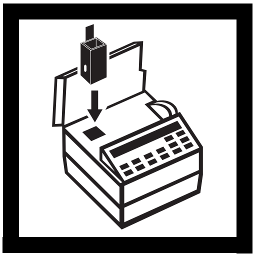
2. Rotate the wavelength dial until the small display shows:

455 nm

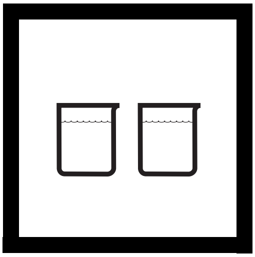
When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

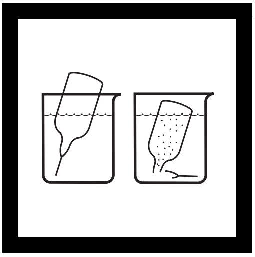
then: **µg/L N_2H_4 AV**



3. Place the AccuVac Vial Adapter into the cell holder.



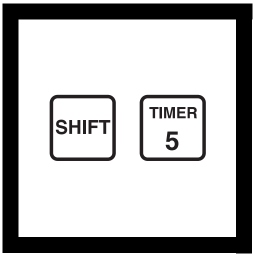
4. Collect at least 40 mL of sample in a 50-mL beaker. Pour at least 40 mL of deionized water into a second 50-mL beaker.



5. Fill a Hydrazine AccuVac Ampul with sample by breaking the AccuVac tip on the beaker bottom. Fill a second AccuVac Ampul with deionized water (the blank).

__Note:__ Keep the tip immersed while the ampul fills completely.

__Note:__ Sample temperature should be 21 ±4 °C (70 ±7 °F).



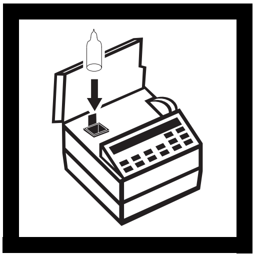
6. Press:

SHIFT TIMER

A 12-minute reaction period will begin.

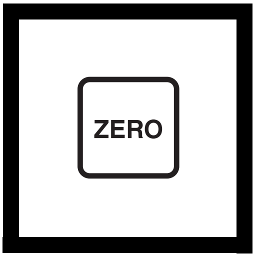
__Note:__ A yellow color will develop if Hydrazine is present.

__Note:__ HydraVer 2 Hydrazine Reagent will cause a faint yellow color to appear in the blank.



7. When the timer beeps, the display will show: **µg/L N_2H_4 AV**

Immediately after the timer beeps, insert the blank into the cell holder. Close the light shield.

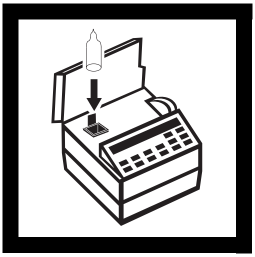


8. Press: **ZERO**

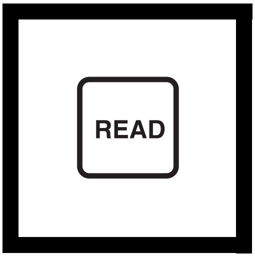
The display will show:

Zeroing. . . .

then: **0. µg/L N_2H_4 AV**



9. Place the prepared sample into the cell holder. Close the light shield.



10. Press: **READ**

The display will show:

Reading. . . .

then the result in µg/L hydrazine will be displayed.

Sampling and Storage

Collect samples in glass or plastic containers. Fill the containers completely and cap them tightly. Avoid excessive agitation or exposure to air. Samples must be analyzed immediately after collection and cannot be preserved for later analysis.

Accuracy Check

Standard Solution Method

To assure the accuracy of the test, prepare the following solutions:

a) Prepare a 25 mg/L stock solution by dissolving 0.1016 g of hydrazine sulfate in deionized water then diluting to 1000 mL. Prepare stock solution daily.

b) Prepare a 0.1 mg/L (100 µg/L) hydrazine working solution by diluting 0.4 mL of the 25 mg/L stock solution to 100 mL with deionized water. Prepare just before analysis.

c) Use the working solution in place of the sample in Step 5. The result should be 100 µg/L hydrazine.

Precision

In a single laboratory using standard solutions of 225 µg/L hydrazine (N_2H_4) and 2 representative lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±2.3 µg/L hydrazine.

In a single laboratory using standard solutions of 253 µg/L hydrazine (N_2H_4) and 1 lot of AccuVac Ampuls with the DR/2010, a single operator obtained a standard deviation of ±1.67 µg/L hydrazine.

Interferences

For highly colored or turbid samples, prepare a blank by oxidizing the hydrazine in a portion of the sample. This can be accomplished with a 1:1 mixture of deionized water and household bleach. Add two drops of the mixture to 40 mL of sample in a graduated mixing cylinder and invert to mix. Use this solution in Step 4, in place of deionized water, to prepare the blank.

Ammonia does not interfere up to 10 mg/L; at 20 mg/L it causes a postivie error of up to 20%. Morpholine does not interfere up to 10 mg/L.

Summary of Method

Hydrazine reacts with the p-dimethylaminobenzaldehyde from the HydraVer 2 Reagent to form a yellow color which is proportional to the hydrazine concentration.

REQUIRED REAGENTS (FOR REAGENT SOLUTION)

Description	Quantity Required Per Test	Unit	Cat. No.
HydraVer 2 Hydrazine Reagent	1 mL	100 mL* MDB	1790-32
Water, deionized	10 mL	4 L	272-56

REQUIRED APPARATUS (FOR REAGENT SOLUTION)

Cell Riser, 10 mL	1	each	45282-00
Cylinder, graduated, 25 mL	1	each	508-40
Sample Cell, 10-mL, matched pair	2	pair	24954-02

REQUIRED REAGENTS (USING ACCUVAC AMPULS)

Hydrazine Reagent AccuVac Ampul	2	25/pkg	25240-25
Water, deionized	40 mL	4 L	272-56

REQUIRED APPARATUS (USING ACCUVAC AMPULS)

Adapter, AccuVac Vial	1	each	43784-00
AccuVac Snapper Kit	1	each	24052-00
Beaker, 50 mL	1	each	500-41

OPTIONAL REAGENTS

Hydrazine sulfate	100 g	742-26

OPTIONAL APPARATUS

Balance, AccuLab PocketPro, portable	each	25568-00
Cylinder, graduated, mixing, 25 mL	each	1896-40
Flask, volumetric, 100 mL	each	547-42
Flask, volumetric, 1000 mL	each	547-53
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Thermometer, -20 to 105 °C	each	1877-01
Weighing Boat, 67/46 mm	500/pkg	21790-00

OPTIONAL 25-ML ANALYSIS ITEMS

HydraVer 2 Hydrazine Reagent	100 mL MDB*	1790-32
Pour-Thru Cell Assembly Kit (for 25 mL reagents only)	each	45215-00
Sample Cell, 25-mL, matched pair	pair	20950-00

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

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* Contact Hach for larger sizes.

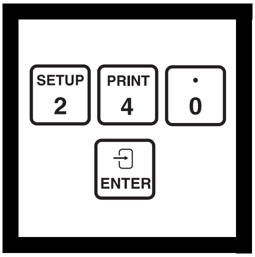
Method 8031

IODINE (0 to 7.00 mg/L)

For water, wastewater and seawater

DPD Method* (Powder Pillows or AccuVac Ampuls)

Using Powder Pillows



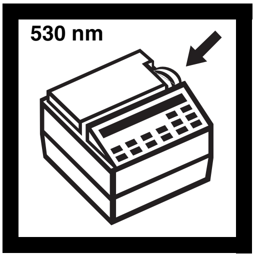
1. Enter the stored program number for iodine (I_2) powder pillows.

Press: **2 4 0 ENTER**

The display will show:

Dial nm to 530

Note: *The Pour-Thru Cell can be used with 25-mL reagents only.*



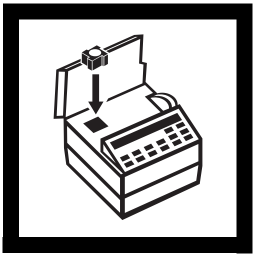
2. Rotate the wavelength dial until the small display shows:

530 nm

When the correct wavelength is dialed in, the display will quickly show

Zero Sample

then: **mg/L I_2**



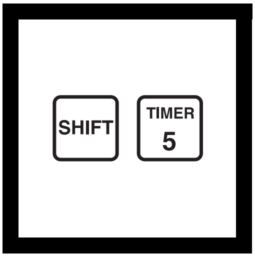
3. Insert the 10-mL Cell Riser into the cell compartment.

4. Fill a cell with 10 mL of sample.

Note: *Samples must be analyzed immediately and cannot be preserved for later analysis.*

5. Add the contents of one DPD Total Chlorine Powder Pillow to the sample cell (the prepared sample). Swirl to mix.

Note: *A pink color will develop if iodine is present.*



6. Press:

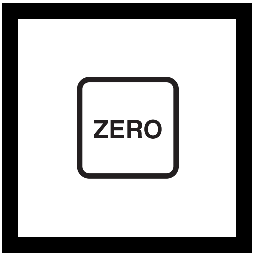
SHIFT TIMER

A three-minute reaction period will begin.

7. When the timer beeps the display will show:

mg/L I_2

Fill a second sample cell with 10 mL of sample (the blank). Place it into the cell holder.



8. Press: **ZERO**

The display will show:

Zeroing. . . .

then: **0.00 mg/L I_2**

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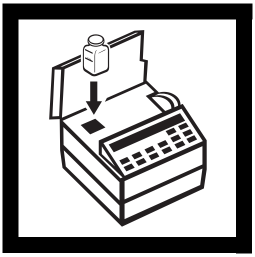
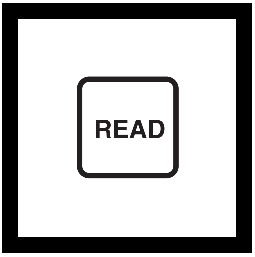
* Adapted from Palin, A.T., *Inst. Water Eng.*, 21 (6) 537-547 (1967)



9. Within three minutes after the timer beeps, place the prepared sample into the cell holder. Close the light shield.



10. Press: **READ**

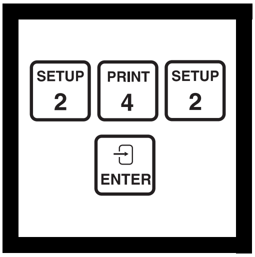
The display will show:

Reading. . . .

then the result in mg/L I_2 will be displayed.

Note: *If the sample temporarily turns yellow after reagent addition, or reads* ***OVER-RANGE,*** *dilute a fresh sample. Repeat the test. A slight loss of iodine may occur during dilution. Apply the appropriate dilution factor; see Sample Dilution Techniques (Section I).*

Using AccuVac Ampuls

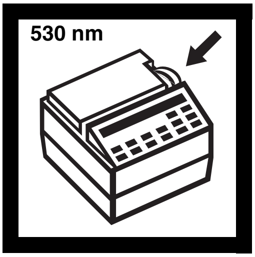


1. Enter the stored program number for iodine (I_2) AccuVac ampuls.

Press: **2 4 2 ENTER**

The display will show:

Dial nm to 530



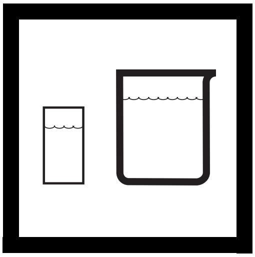
2. Rotate the wavelength dial until the small display shows:

530 nm

When the correct wavelength is dialed in, the display will quickly show:

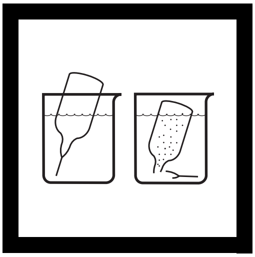
Zero Sample

then: **mg/L I_2 AV**



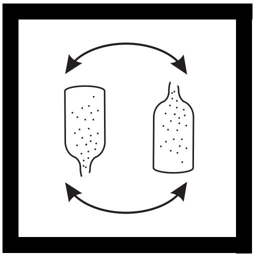
3. Fill a zeroing vial (the blank) with at least 10 mL of sample. Collect at least 40 mL of sample in a 50-mL beaker.

Note: *Samples must be analyzed immediately and cannot be preserved for later analysis.*



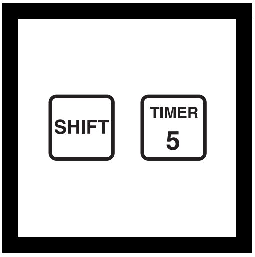
4. Fill a DPD Total Chlorine Reagent AccuVac Ampul with sample.

Note: *Keep the tip immersed while the ampul fills completely.*



5. Quickly invert the ampul several times to mix. Wipe off any liquid or fingerprints.

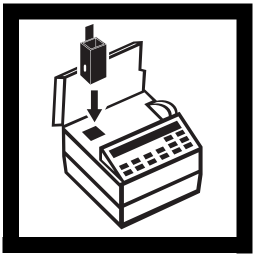
Note: *A pink color will form if iodine is present.*



6. Press:

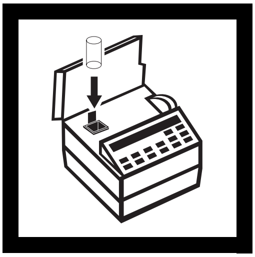
SHIFT TIMER

A three-minute reaction period will begin.



7. Place the AccuVac Vial Adapter into the cell holder.

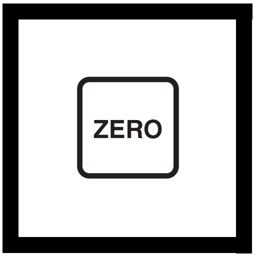
Note: *Place the grip tab at the rear of the cell holder.*



8. When the timer beeps the display will show:

mg/L I_2 AV

Place the blank into the cell holder. Close the light shield.

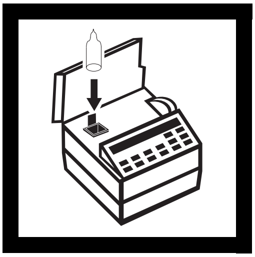


9. Press: **ZERO**

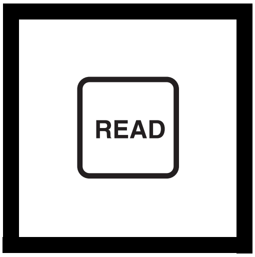
The display will show:

Zeroing. . . .

then: **0.00 mg/L I_2 AV**



10. Within three minutes after the timer beeps, place the AccuVac ampul into cell holder. Close the light shield.



11. Press: **READ**

The display will show:

Reading. . . .

then the result in mg/L I_2 will be displayed.

***Note:** If the sample temporarily turns yellow after sample addition, or shows **OVER-RANGE**, dilute a fresh sample. Repeat the test. A slight loss of iodine may occur during dilution. Apply the appropriate dilution factor; see Sample Dilution Techniques (Section I).*

Sampling and Storage

Analyze samples for iodine **immediately** after collection. Free iodine is a strong oxidizing agent, and it is unstable in natural waters. It reacts rapidly with various inorganic compounds and more slowly oxidizes organic compounds. Many factors, including reactant concentrations, sunlight, pH, temperature and salinity influence decomposition of iodine in water.

Avoid plastic containers since these may have a large iodine demand. **Pretreat glass** sample containers to remove any iodine demand by soaking in a dilute bleach solution (1 mL commercial bleach to l liter of deionized water) for at least 1 hour. Rinse thoroughly with deionized or distilled water. If sample containers are rinsed thoroughly with deionized or distilled water after use, only occasional pre-treatment is necessary.

A common error in testing for iodine is introduced when a representative sample is not obtained. If sampling from a tap, let the water flow for at least 5 minutes to ensure a representative sample. Let the container overflow with the sample several times, then cap the sample containers so there is no headspace (air) above the sample. If sampling with a sample cell, rinse the cell several times with the sample, then carefully fill to the 10-mL mark. Perform the analysis immediately.

Standard Additions Method (using powder pillows)

a) Perform a sample analysis and record the result.

b) Snap the top off a LR Chlorine PourRite Ampule Standard Solution, 25-30 mg/L Cl_2.

c) Use a TenSette Pipet to add 0.1 mL of the standard to the reacted sample (this is the spiked sample). Swirl to mix.

d) Place the spiked sample into the DR/2010 and read the spiked sample result.

e) Calculate the equivalent concentration of mg/L iodine added to the sample:

$$\text{mg/L Iodine} = \frac{0.1\ (\text{vol. standard added}) \times \text{Certificate value}\ (\text{mg/L Chlorine}) \times 3.6}{10.1\ (\text{sample + standard volume})}$$

f) The spiked sample result (step d) should reflect the analyzed sample result (step a) + the added, calculated mg/L I_2 (step e).

g) If this increase does not occur, see *Standard Additions* in *Section I* for more information.

Standard Additions Method (using AccuVac Ampuls)

a) Snap the top off a LR Chlorine PourRite Ampule Standard Solution, 25-30 mg/L Cl_2.

b) Use a graduated cylinder to measure 25 mL of sample into each of two beakers.

c) Use a TenSette Pipet to add 0.2 mL of the standard to one of the beakers (this is the spiked sample). Swirl to mix.

d) Fill a DPD Total Chlorine AccuVac completely from each beaker.

e) Analyze the spiked and unspiked sample as described in the procedure.

f) Calculate the equivalent concentration of mg/L chlorine added to the sample:

$$\text{mg/L Iodine} = \frac{0.2\ \text{(vol. standard added)} \times \text{Certificate value (mg/L Chlorine)} \times 3.6}{25.2\ \text{(sample + standard volume)}}$$

g) The spiked sample result should reflect the analyzed sample result + the added, calculated mg/L I_2 (step f).

h) If this increase does not occur, see *Standard Additions* in *Section I* for more information.

Precision

In a single laboratory using a standard solution of 1.00 mg/L chlorine and two representative lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±0.012 chlorine. This is equivalent to ±0.04 mg/L iodine.

In a single laboratory using a standard solution of 1.10 mg/L chlorine and two representative lots of AccuVac ampuls with the DR/2010, a single operator obtained a standard deviation of ±0.009 mg/L chlorine. This is equivalent to ±0.03 mg/L iodine.

Interferences

Samples containing more than 300 mg/L alkalinity or 150 mg/L acidity as $CaCO_3$ may not develop the full amount of color, or it may instantly fade. Neutralize these samples to a pH of 6 to 7 with 1 N sulfuric acid or 1 N sodium hydroxide. Determine the amount required on a separate 25-mL sample. Add the same amount to the sample to be tested. Correct for volume additions.

Bromine, chlorine, ozone and oxidized forms of manganese and chromium also may react and read as iodine. To compensate for the effects of oxidized manganese or chromium adjust pH to 6 to 7 as described above. Add three drops of potassium iodide, 30 g/L, to 10 mL of sample, mix and wait one minute. Add three drops of sodium arsenite, 5 g/L, and mix. Analyze 10 mL of this sample as described above. (If chromium, is present, allow the same reaction period with the DPD for both analyses). Subtract the result of this test from the original analysis to obtain the correct iodine result.

DPD Reagent Powder Pillows and AccuVac ampuls are formulated with a buffer which will withstand high levels (1000 mg/L) of hardness without interference.

Summary of Method

Iodine reacts with DPD (N, N-diethyl-p-phenylenediamine) to form a magenta color which is proportional to the total iodine concentration.

REQUIRED REAGENTS (USING POWDER PILLOWS)

Description	Quantity Required Per Test	Unit	Cat. No.
DPD Total Chlorine Reagent Powder Pillow, 10 mL	1 pillow	100/pkg	21056-69

REQUIRED APPARATUS (USING POWDER PILLOWS)

Cell Riser, 10-mL	1	each	45282-00
Sample Cell, 10 mL, matched pair	2	pair	24954-02

REQUIRED REAGENTS (USING ACCUVAC AMPULS)

DPD Total Chlorine Reagent AccuVac Ampuls	1 ampul	25/pkg	25030-25

REQUIRED APPARATUS (USING ACCUVAC AMPULS)

Adapter, AccuVac vial	1	each	43784-00
Beaker, 50 mL	1	each	500-41
Vial, zeroing	1	each	21228-00

OPTIONAL REAGENTS

Chlorine Standard Solution PourRite Ampule, 25 to 30 mg/L Cl_2	20/pkg	26300-20
Potassium Iodide Solution, 30 g/L	100 mL* MDB	343-32
Sodium Arsenite Solution, 5 g/L	100 mL* MDB	1047-32
Sodium Hydroxide Standard Solution, 1 N	100 mL* MDB	1045-32
Sulfuric Acid Standard Solution, 1 N	100 mL* MDB	1270-32
Water, deionized	4 L	272-56

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* Contact Hach for larger sizes.

OPTIONAL APPARATUS

Description	Unit	Cat. No.
AccuVac Snapper Kit	each	24052-00
Ampule Breaker Kit	each	21968-00
Cylinder, graduated, 25 mL	each	508-40
pH Meter, *sension*™*1*, portable	each	51700-10
pH Paper, 1 to 11 pH units	5 rolls/pkg	391-33
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96

OPTIONAL 25-ML ANALYSIS ITEMS

Description	Unit	Cat. No.
DPD Total Chlorine Reagent Powder Pillows	100/pkg	14064-99
Pour-Thru Cell Assembly Kit	each	45215-00
Sample Cell, 25-mL, matched pair	pair	20950-00

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

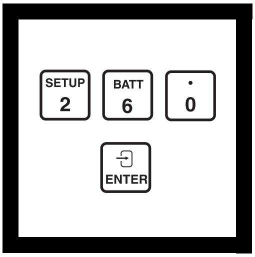
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8147

IRON (0 to 1.300 mg/L)

For water and seawater

FerroZine Method*



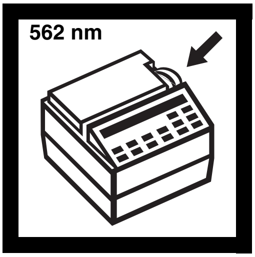
1. Enter the stored program number for total iron (Fe), FerroZine method.

Press: **2 6 0 ENTER**

The display will show:

Dial nm to 562

Note: *The Pour-Thru Cell can be used with this procedure.*



2. Rotate the wavelength dial until the small display shows:

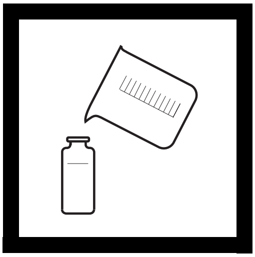
562 nm

When the correct wavelength is dialed in the display will quickly show:

Zero Sample

then: **mg/L Fe FZ**

Note: *Total iron determinations need a prior digestion; use any of the three procedures given in Digestion (Section II).*



3. Fill a sample cell to the 25-mL mark with sample.

Note: *Rinse glassware with a 1:1 hydrochloric acid and deionized water before use to avoid errors due to iron deposits on the glass.*

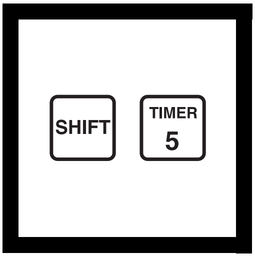
Note: *For proof of accuracy, a 0.4 mg/L iron standard solution (preparation given in the Accuracy Check) can be used in place of the sample.*

4. Add the contents of one FerroZine Iron Reagent Solution Pillow to the cell (the prepared sample). Swirl to mix.

Note: *Do not allow the clippers to come into contact with the contents of the pillow.*

Note: *0.5 mL of FerroZine Iron Reagent Solution can be used in place of the solution pillow if preferred.*

Note: *If the sample contains rust, see Interferences below.*



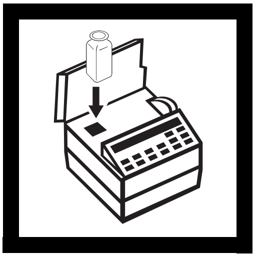
5. Press:

SHIFT TIMER

A five-minute reaction period will begin.

Note: *A violet color will develop if iron is present.*

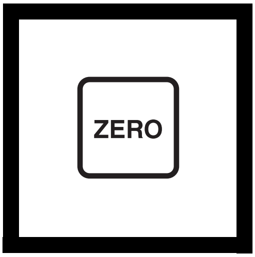
6. Fill another sample cell (the blank) with 25 mL of sample.



7. When the timer beeps, the display will show:

mg/L Fe FZ

Insert the blank into the cell holder. Close the light shield.



8. Press: **ZERO**

The display will show:

Zeroing. . .

then: **0.000 mg/L Fe FZ**

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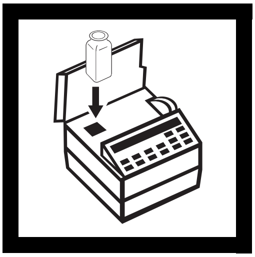
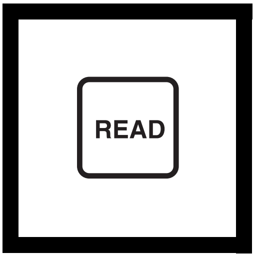
* Adapted from Stookey, L.L., Anal. Chem., 42 (7) 779 (1970).



9. Place the prepared sample into the cell holder. Close the light shield.



10. Press: **READ**

The display will show:

Reading. . .

then the result in mg/L iron will be displayed.

Sampling and Storage

Collect samples in acid-washed glass or plastic bottles. To preserve samples, adjust the sample pH to 2 or less with nitric acid (about 2 mL per liter). Samples preserved in this manner can be stored up to six months at room temperature. If only dissolved iron is to be reported, filter sample immediately after collection and before addition of nitric acid.

Before testing, adjust the sample pH to 3–5 with ammonium hydroxide, ACS. Do not exceed pH 5 as iron may precipitate. Correct test results for volume additions; see *Correction for Volume Additions* in *Section I* for more detailed information.

Accuracy Check

Standard Additions Method

a) Snap the neck off an Iron Voluette Ampule Standard, 25 mg/L Fe.

b) Use the TenSette pipet to add 0.1 mL of standard to the prepared sample measured in Step 10.

c) Swirl to mix and allow another five-minute reaction period, then measure the iron concentration as in Step 10.

d) Add two additional 0.1 mL standard increments, taking a concentration reading after allowing the five-minute reaction period for each increment.

e) Each additional 0.1 mL increment of standard added should cause a 0.1 mg/L increase in the concentration reading.

f) If these increases do not occur, see *Standard Additions* in *Section I* for more information.

Standard Solution Method

Prepare a 0.4 mg/L iron working solution as follows:

a) Pipet 1.00 mL of iron standard solution, 100 mg/L Fe, into a 250 mL volumetric flask.

b) Dilute to volume with deionized water. This solution should be prepared daily. Analyze the working solution according to the above procedure.

Precision

In a single laboratory, using a standard solution of 0.80 mg/L iron and two representative lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±0.0027 mg/L iron.

Interferences

Copper and cobalt may interfere to give slightly high results.

Strong chelates such as EDTA will interfere in the FerroZine method for determining iron. The FerroVer or TPTZ methods should be used for these samples. The TPTZ method is suggested for low concentrations.

Any of the three digestions given in *Digestion* (**Section I**) used in place of the treatments below will eliminate the following interferences.

If rust or hydroxides are present, boil the sample, with the FerroZine Iron Reagent added in Step 4, for one minute in a boiling water bath then cool to 24 °C (75 °F) before proceeding with Step 5. The reduced sample volume should be returned to 25 mL with deionized water.

If the sample contains magnetite (black iron oxide) or ferrites, perform the following procedure.

a) Fill a 25-mL graduated cylinder with 25 mL of sample.

b) Transfer the sample water into a 125-mL erlenmeyer flask.

Note: *Do not allow to boil dry.*

c) Add the contents of one FerroZine Iron Reagent Solution Pillow and swirl to mix.

d) Place the flask on a hot plate or over a flame and bring to a boil.

e) Continue boiling gently for 20 to 30 minutes.

Note: *A purple color will develop if iron is present.*

f) Return the boiled sample to the graduated cylinder. Rinse the erlenmeyer flask with small amounts of deionized water and empty into the graduated cylinder.

g) Return the sample volume to the 25-mL mark with deionized water.

h) Pour the solution into a sample cell and swirl to mix.

i) Proceed with Steps 5 through 10.

Summary of Method

The FerroZine Iron Reagent forms a purple colored complex with trace amounts of iron in samples that are buffered to a pH of 3.5. This method is applicable for determining trace levels of iron in chemical reagents and glycols and can be used to analyze samples containing magnetite (black iron oxide) or ferrites after treatment as described in Interferences.

REQUIRED REAGENTS AND APPARATUS

Description	Quantity Required Per Test	Unit	Cat. No.
FerroZine Iron Reagent Solution Pillows	1 pillow	50/pkg	2301-66
Clippers, for opening pillows	1	each	968-00
Sample Cell, 25-mL, matched pair		pair	20950-00

OPTIONAL REAGENTS

Ammonium Hydroxide, ACS	500 mL	106-49
Hydrochloric Acid Solution, 1:1 (6N)	500 mL	884-49
FerroZine Iron Reagent Solution	1000 mL	2301-53
Iron Standard Solution, 100 mg/L Fe	100 mL	14175-42
Iron Standard Solution, Voluette ampule, 25 mg/L Fe, 10 mL	16/pkg	14253-10
Nitric Acid, ACS	500 mL	152-49
Nitric Acid Solution, 1:1	500 mL	2540-49
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Description	Unit	Cat. No.
Ampule Breaker Kit	each	21968-00
Cylinder, graduated, 25 mL	each	508-40
Dropper, calibrated, 0.5-mL & 1.0-mL mark	6/pkg	23185-06
Flask, erlenmeyer, 125 mL	each	505-43
Flask, volumetric, 250 mL, Class B	each	547-46
Hot plate, 3 1/2" diameter, 120 Vac	each	12067-01
Hot plate, 3 1/2" diameter, 240 Vac	each	12067-02
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
pH Meter, *sens**ion***™***1***, portable	each	51700-10
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pour-Thru Cell Assembly Kit	each	45215-00
Thermometer, -20 to 105 °C	each	1877-01
Water Bath, with sample cell rack	each	1955-55

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

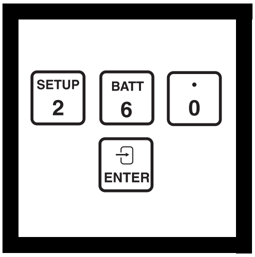
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8147

IRON (0 to 1.300 mg/L)

FerroZine Rapid Liquid Method*

For boiler, cooling, and natural waters



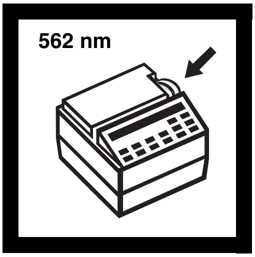
1. Enter the stored program number for total iron (Fe), FerroZine method.

Press: **2 6 0 ENTER**

The display will show:

Dial nm to 562

Note: *Adjust pH of stored samples before analysis.*

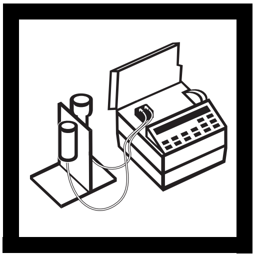


2. Rotate the wavelength dial until the small display shows:

562 nm

When the correct wavelength is dialed in, the display will quickly show: **Zero Sample**

then: **mg/L Fe FZ**

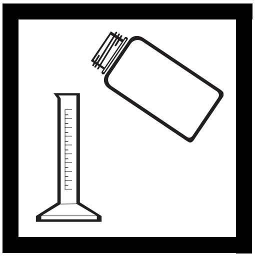


3. Install the Pour-Thru Cell and flush with 50 mL of deionized water.

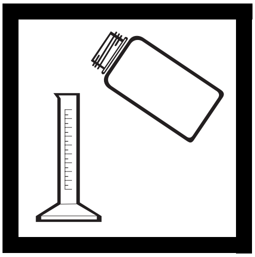
Note: *Clean the Pour-Thru Cell and all labware as specified in Treating Analysis Labware.*

4. Rinse two clean 125-mL plastic Erlenmeyer flasks three times with the sample.

Note: *Total iron determinations need a prior digestion; use any of the three digestion procedures given in Section I.*



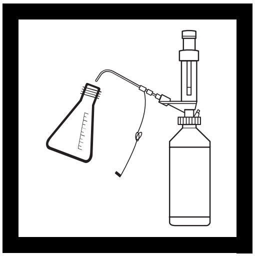
5. Rinse a clean 50-mL plastic graduated cylinder three times with the sample.



6. Fill this rinsed cylinder to the 50-mL mark with sample.

Note: *If the sample contains rust, see Interferences below.*

7. Pour the contents of the 50-mL cylinder into one of the flasks. Measure a second 50-mL portion of sample into the graduated cylinder and pour the contents into the second flask.



8. Add 1.0 mL of FerroZine Iron Reagent Solution to one of the flasks using the Repipet Dispenser. Swirl to mix. The other flask will be the blank.

Note: *Crystals may form in the FerroZine Reagent when stored at cold temperatures. Place the bottle in warm water to dissolve the crystals.*

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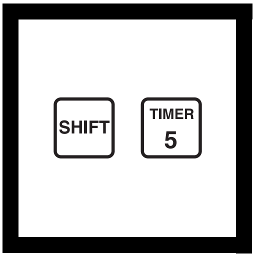
* Adapted from Stookey, L.L., Anal. Chem., 42 (7) 779 (1970).



9. Press:

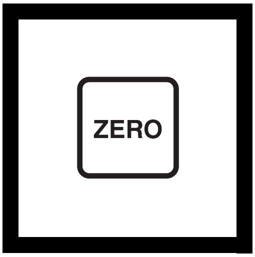
SHIFT TIMER

A five-minute reaction period will begin.

__Note:__ A violet color will develop if iron is present.

10. When the timer beeps, the display will show: **mg/L Fe FZ**

Pour the contents of the flask containing the blank into the Pour-Thru Cell.



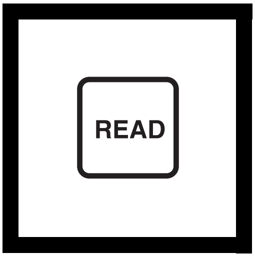
11. After the flow has stopped, press: **ZERO**

The display will show:

Zeroing. . . .

then: **0.000 mg/L Fe FZ**

12. Pour the contents of the flask containing the prepared sample into the Pour-Thru Cell.

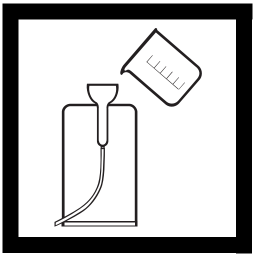


13. After the flow has stopped, press: **READ**

The display will show:

Reading. . . .

then the result in mg/L iron will be displayed.



14. Flush the Pour-Thru Cell with 50 mL of deionized water.

__Note:__ Protect the Pour-Thru Cell from contamination by inverting a small beaker over the top of the glass funnel when not in use.

Treating Analysis Labware

All containers used in this test must be cleaned thoroughly to remove any traces of iron. Rinse labware and the Pour-Thru Cell with a 1:1 HCl solution or with a 1:25 dilution of FerroZine Reagent. Rinse several times with deionized water.

Keep flasks tightly closed when not in use. Dedicate these containers for iron analysis only. If containers are rinsed and capped after each use, only occasional treatment with HCl or FerroZine is necessary.

Cleaning the Pour-Thru Cell

The Pour-Thru Cell may accumulate a buildup of colored products, especially if the reacted solutions are allowed to stand in the cell for long periods after measurement. Remove the color by rinsing with a 1:1 dilution of HCl, followed by several deionized water rinses. Cover the glass funnel when it is not in use.

Sampling and Storage

Collect samples in acid-washed glass or plastic bottles. To preserve samples, adjust the sample pH to 2 or less with nitric acid (about 2 mL per liter). Samples preserved in this manner can be stored up to six months at room temperature. If only dissolved iron is to be reported, filter sample immediately after collection and before addition of nitric acid.

Before testing, adjust the sample pH to 3 to 5 with ammonium hydroxide, ACS. Do not exceed pH 5 as iron may precipitate. Correct test results for volume additions; see *Correction for Volume Additions* in *Section I.*

Accuracy Check

Standard Additions Method

a) Snap the neck off an Iron Voluette Ampule Standard, 25 mg/L Fe.

b) Use the TenSette pipet to add 0.2, 0.4, and 0.6 mL of standard to three 50 mL samples, respectively.

c) Analyze each sample as described above. The iron concentration should increase 0.1 mg/L for each 0.2 mL of 25 mg/L standard added.

d) If these increases do not occur, see *Standard Additions* in *Section I.*

Standard Solution Method

Prepare a 0.4 mg/L iron working solution as follows:

a) Pipet 1.00 mL of iron standard solution, 100 mg/L Fe, into a 250 mL volumetric flask.

b) Dilute to volume with deionized water. Prepare this solution daily. Analyze the working solution according to the above procedure. Results should be between 0.360 and 0.440 mg/L Fe.

Precision

In a single laboratory, using standard solutions of 0.500 mg/L Fe and two representative lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±0.0027 mg/L iron.

Interferences

Copper and cobalt may interfere to give slightly high results.

Strong chelates such as EDTA will interfere in the FerroZine method for determining iron. The FerroVer or TPTZ methods should be used for these samples. The TPTZ method is suggested for low concentrations.

Any of the three digestions given in *Digestion*, (*Section I*) can be used in place of the treatments given below to eliminate the following interferences.

If rust or hydroxides are present, the sample, with the FerroZine Iron Reagent from Step 8, should be boiled for one minute in a boiling water bath, then cooled to 24 °C (75 °F) before proceeding with Step 9. The reduced sample volume should be returned to 50 mL with deionized water.

If the sample contains magnetite (black iron oxide) or ferrites, perform the following procedure.

a) Fill a 50-mL graduated cylinder with 50 mL of sample.

b) Transfer the sample into a clean glass 125-mL Erlenmeyer flask.

c) Add 1.0-mL of FerroZine Iron Reagent Solution and swirl to mix.

d) Place the flask on a hot plate or over a flame and bring to a boil.

e) Continue boiling gently for 20 to 30 minutes.

Note: *Do not allow to boil dry.*

f) Return the boiled sample to the graduated cylinder. Rinse the Erlenmeyer flask with small amounts of deionized water and empty into the graduated cylinder.

Note: *A purple color will develop if iron is present.*

g) Return the sample volume to the 50-mL mark with deionized water.

h) Pour the solution into a 125-mL Erlenmeyer flask and swirl to mix.

i) Proceed with Steps 9 through 13.

Summary of Method

The FerroZine Iron Reagent forms a purple colored complex with trace amounts of iron in samples that are buffered to a pH of 3.5. This method is applicable for determining trace levels of iron in chemical reagents and glycols and can be used to analyze samples containing magnetite (black iron oxide) or ferrites.

REQUIRED REAGENTS AND APPARATUS

Description	Quantity Required Per Test	Unit	Cat. No.
FerroZine Iron Reagent Solution	1 mL	500 mL	2301-49
Cylinder, graduated, 50 mL, poly	1	each	1081-41
Dispenser, Fixed Volume, 1.0 mL, Repipet Jr.	1	each	21113-01
Flask, Erlenmeyer, PMP w/cap, 125 mL	2	each	20898-43
Pour-Thru Cell Assembly Kit	1	each	45215-00

OPTIONAL REAGENTS

Ammonium Hydroxide, ACS	500 mL	106-49
Hydrochloric Acid Solution, 1:1 (6N)	500 mL	884-49
FerroZine Iron Reagent Solution	1000 mL	2301-53
Iron Standard Solution, 100 mg/L Fe	100 mL	14175-42
Iron Standard Solution, Voluette ampule, 25 mg/L Fe, 10 mL	16/pkg	14253-10
Nitric Acid, ACS	500 mL	152-49
Nitric Acid Solution, 1:1	500 mL	2540-49
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Description	Unit	Cat. No.
Ampule Breaker Kit,	each	21968-00
Beaker, poly, 50 mL	each	1080-41
Bottle, wash, 125 mL	each	21901-43
Dropper, calibrated, 0.5-mL & 1.0-mL mark	6/pkg	23185-06
Flask, Erlenmeyer, 125 mL, PMP w/cap	6/pkg	20898-73
Flask, Erlenmeyer, 125 mL	each	505-43
Flask, Erlenmeyer, 50 mL	each	505-41
Flask, volumetric, 250 mL, Class A	each	14574-46
Hot plate, 3 1/2 inch diameter, 120 Vac	each	12067-01
Hot plate, 3 1/2 inch diameter, 240 Vac	each	12067-02
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
pH Meter, *sension*™*1*, portable	each	51700-10
Pipet, serological, 2 mL	each	532-36
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 1.00 mL	each	14515-35
Pipet Filler, safety bulb	each	14651-00
Thermometer, -20 to 105 °C	each	1877-01

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

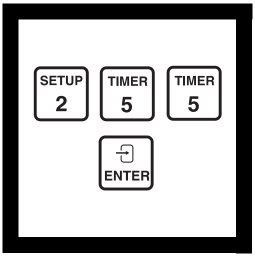
Method 8146

IRON, FERROUS (0 to 3.00 mg/L)

For water, wastewater, and seawater

1,10 Phenanthroline Method* (Powder Pillows or AccuVac Ampuls)

USING POWDER PILLOWS



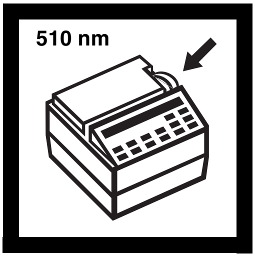
1. Enter the stored program number for ferrous iron, (Fe^{2+})- powder pillows.

Press: **2 5 5 ENTER**

The display will show:

Dial nm to 510

Note: *The Pour-Thru Cell can be used with this procedure.*



2. Rotate the wavelength dial until the small display shows:

510 nm

When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

then: **mg/L Fe^{2+}**

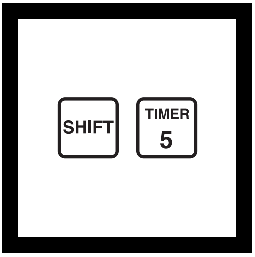
3. Fill a sample cell with 25 mL of sample.

Note: *Analyze samples as soon as possible to prevent oxidation of ferrous iron to ferric, which is not determined.*

4. Add the contents of one Ferrous Iron Reagent Powder Pillow to the sample cell (the prepared sample). Swirl to mix.

Note: *An orange color will form if ferrous iron is present.*

Note: *Undissolved powder does not affect accuracy.*



5. Press:

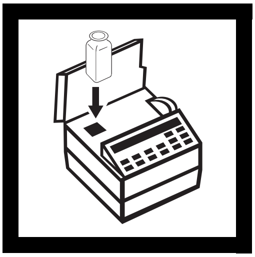
SHIFT TIMER

A three-minute reaction period will begin.

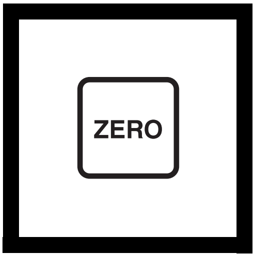
6. When the timer beeps, the display will show:

mg/L Fe^{2+}

Fill a second sample cell with 25 mL of sample (the blank).



7. Place the blank into the cell holder. Close the light shield.



8. Press: **ZERO**

The display will show:

Zeroing. . .

then: **0.00 mg/L Fe^{2+}**

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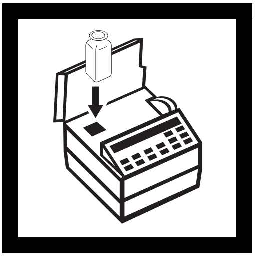
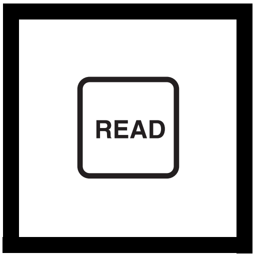
* Adapted from *Standard Methods for the Examination of Water and Wastewater.*



9. Place the prepared sample into the cell holder. Close the light shield.



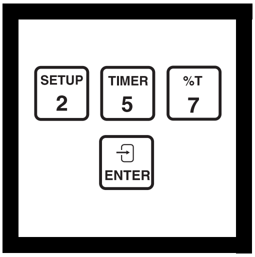
10. Press: **READ**

The display will show:

Reading. . .

then the result in mg/L Fe^{2+} will be displayed.

Using AccuVac Ampuls



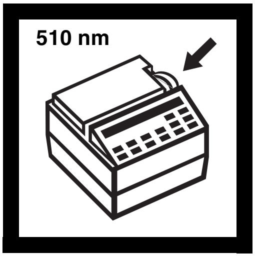
1. Enter the stored program number for ferrous iron (Fe^{2+})-AccuVac ampuls.

Press: **2 5 7 ENTER**

The display will show:

Dial nm to 510

Note: *Analyze samples as soon as possible to prevent air oxidation of ferrous iron to ferric, which is not determined.*



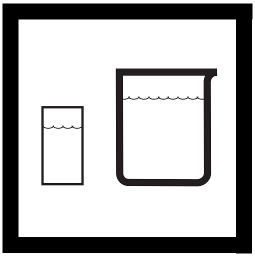
2. Rotate the wavelength dial until the small display shows:

510 nm

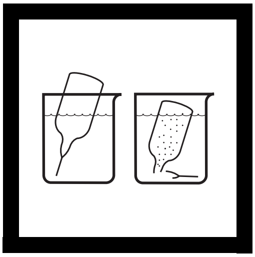
When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

then: **mg/L Fe^{2+} AV**

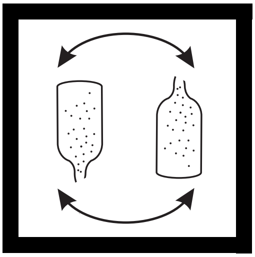


3. Fill a zeroing vial with at least 10 mL of sample (the blank). Collect at least 40 mL of sample in a 50-mL beaker.



4. Fill a Ferrous Iron AccuVac Ampul with sample.

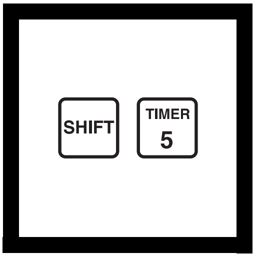
Note: *Keep the tip immersed while the ampul fills completely.*



5. Quickly invert the ampul several times to mix. Wipe off any liquid or fingerprints.

Note: *An orange color will form if ferrous iron is present.*

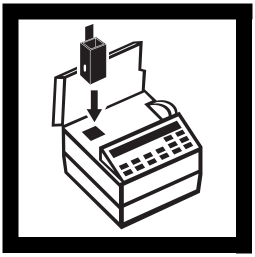
Note: *Undissolved powder does not affect accuracy.*



6. Press:

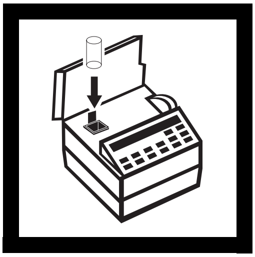
SHIFT TIMER

A three-minute reaction period will begin.



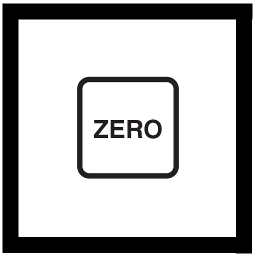
7. Place the AccuVac Vial Adapter into the cell holder.

Note: *Place the grip tab at the rear of the cell holder.*



8. When the timer beeps, the display will show: **mg/L Fe^{2+} AV**

Place the blank into the cell holder. Close the light shield.

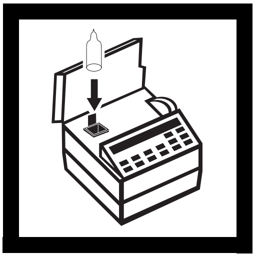


9. Press: **ZERO**

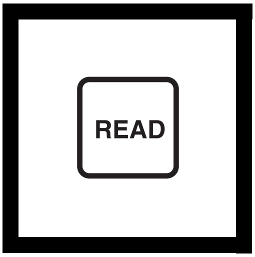
The display will show:

Zeroing. . .

then: **0.00 mg/L Fe^{2+} AV**



10. Place the AccuVac ampul into the cell holder. Close the light shield.



11. Press: **READ**

The display will show:

Reading. . .

then the result in mg/L Fe^{2+} will be displayed.

Accuracy Check

Standard Solution Method

Prepare a ferrous iron stock solution (100 mg/L Fe^{2+}) by dissolving 0.7022 grams of ferrous ammonium sulfate, hexahydrate, in deionized water. Dilute to 1 liter. Prepare immediately before use. Dilute 1.00 mL of this solution to 100 mL with deionized water to make a 1.00 mg/L standard solution. Prepare immediately before use.

Run the test using the 1.00 mg/L Fe^{2+} Standard Solution by following either the powder pillow or AccuVac procedure. Results should be between 0.90 mg/L and 1.10 mg/L Fe^{2+}.

Precision

In a single laboratory using an iron standard solution of 1.000 mg/L Fe^{2+} and two representative lots of powder pillow reagents with the DR/2010, a single operator obtained a standard deviation of ±0.006 mg/L Fe^{2+}.
In a single laboratory using a standard solution of 1.000 mg/L Fe^{2+} and two representative lots of AccuVac ampuls with the DR/2010, a single operator obtained a standard deviation of ±0.009 mg/L Fe^{2+}.

Summary of Method

The 1,10-phenanthroline indicator in Ferrous Iron Reagent reacts with ferrous iron in the sample to form an orange color in proportion to the iron concentration. Ferric iron does not react. The ferric iron (Fe^{3+}) concentration can be determined by subtracting the ferrous iron concentration from the results of a total iron test.

REQUIRED REAGENTS (USING POWDER PILLOWS)

Description	Quantity Required Per Test	Units	Cat. No.
Ferrous Iron Reagent Powder Pillows	1 pillow	100/pkg	1037-69

REQUIRED REAGENTS (USING ACCUVAC AMPULS)

Ferrous Iron Reagent AccuVac Ampuls	1 ampul	25/pkg	25140-25

REQUIRED APPARATUS (USING POWDER PILLOWS)

Sample Cell, 25 mL, matched pair		pair	20950-00

REQUIRED APPARATUS (USING ACCUVAC AMPULS)

Adapter, AccuVac Vial	1	each	43784-00
Beaker, 50 mL	1	each	500-41
Vial, Zeroing		each	21228-00

OPTIONAL REAGENTS

Ferrous Ammonium Sulfate, hexahydrate, ACS		113g	11256-14
Water, deionized		4 L	272-56

OPTIONAL APPARATUS

AccuVac Snapper Kit		each	24052-00
Flask, volumetric, 100 mL, Class B		each	547-42
Flask, volumetric, 1000 mL, Class B		each	547-53
Pipet, volumetric, Class A, 1.00 mL		each	14515-35
Pipet Filler, safety bulb		each	14651-00
Pour-Thru Cell Assembly Kit		each	45215-00

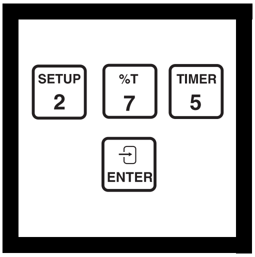
For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order. Outside the U.S.A.—Contact the Hach office or distributor serving you.
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8365

IRON, TOTAL (0 to 1.80 mg/L) For cooling water with molybdenum-based treatment

FerroMo™ Method*



1. Enter the program for iron (Fe) FerroMo method.

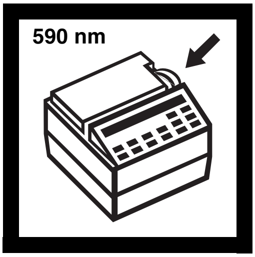
Press: **2 7 5 ENTER**

The display will show:

Dial nm to 590

Note: *Adjust the pH of preserved samples before analysis.*

Note: *The Pour-Thru Cell may be used.*



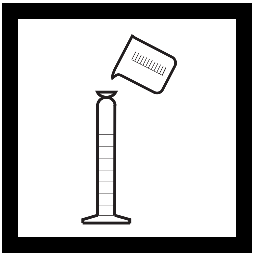
2. Rotate the wavelength dial until the small display shows:

590 nm

When the correct wavelength is dialed in, the display will quickly show: **Zero Sample**

then: **mg/L Fe FM**

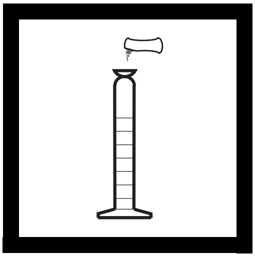
Note: *Determination of total iron requires digestion; See Section II .*



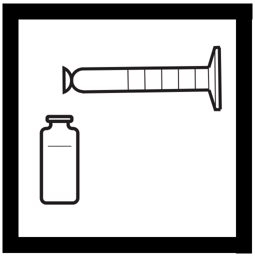
3. Fill a 50-mL graduated mixing cylinder with 50 mL of sample.

Note: *Sample pH is important in the test; see pH Interferences in Section I.*

Note: *Rinse glassware with 1:1 Hydrochloric Acid Solution. Rinse again with deionized water. This removes iron deposits which can cause slightly high results.*

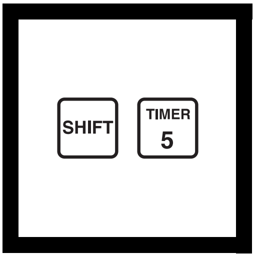


4. Add the contents of one FerroMo Iron Reagent 1 Powder Pillow to the graduated cylinder. Stopper. Invert several times to mix. Remove the stopper. This is the blank.



5. Transfer 25 mL of the blank to a 25-mL matched sample cell.

6. Add the contents of one FerroMo Iron Reagent 2 Powder Pillow to the sample cell. Swirl to dissolve. This is the prepared sample.

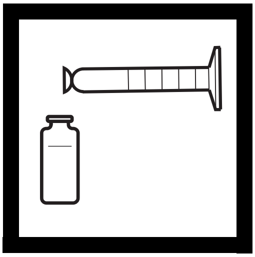


7. Press:

SHIFT TIMER

A three-minute reaction period will begin.

Note: *A blue color will develop if iron is present.*



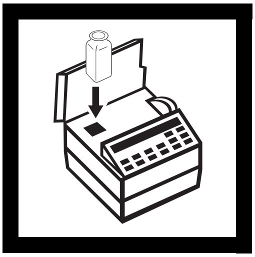
8. When the timer beeps, the display will show:

mg/L Fe FM

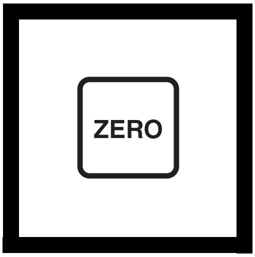
Fill a second sample cell with 25 mL of the blank from Step 4.

---

* Adapted from G. Frederic Smith Chemical Company, *The Iron Reagents*, 3rd ed. (1980).



9. Insert the blank in the cell holder. Close the light shield.

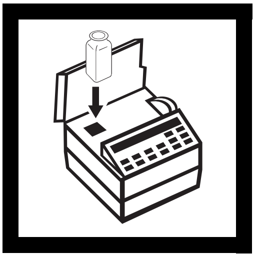


10. Press: **ZERO**

The display will show:

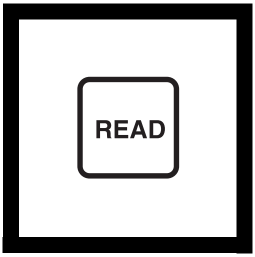
Zeroing. . .

then: **0.00 mg/L Fe FM**



11. Place the prepared sample in the cell holder. Close the light shield.

Note: *For samples containing high levels of molybdate (≥100 mg/L), read the sample immediately after zeroing the blank.*



12. Press: **READ**

The display will show:

Reading. . .

then the result in mg/L iron will be displayed.

Note: *For best results, run the procedure using iron-free distilled water instead of sample in Step 3. Subtract the value obtained in Step 12 from all later tests. Repeat this procedure for each new lot of FerroMo reagent.*

Sampling and Storage

Collect samples in acid-cleaned plastic or glass bottles. If prompt analysis is impossible, preserve the sample by adjusting to pH 2 or less with hydrochloric acid (about 2 mL per liter). Preserved samples may be stored up to six months at room temperature. If reporting only dissolved iron, filter the sample immediately after collection and before adding the acid.

Before analysis, adjust the sample pH to between 3 and 4 with 5.0 N Sodium Hydroxide Standard Solution. Do not exceed pH 5 as iron may precipitate. Correct the test result for volume; see *Correction for Volume Additions* in *Section I.*

Accuracy Check

Standard Solution Method

Prepare a 0.4 mg/L iron working solution as follows:

a) Pipet 1.00 mL of Iron Standard Solution, 100 mg/L Fe, into a 250-mL volumetric flask.

b) Dilute to volume with deionized water. Prepare this solution daily. Analyze this working solution according to the above procedure. Results should be between 0.36 and 0.44 mg/L Fe.

Standard Additions Method

a) Snap the neck off an Iron Voluette Ampule Standard Solution, 25 mg/L.

b) Use a TenSette® Pipet to add 0.1 mL of standard to the prepared sample measured in Step 12. Swirl to mix.

c) Measure the sample as in Step 11-12. Take this measurement immediately without the 3-minute reaction period in Step 7.

d) Add two additional 0.1 mL aliquots of standard, taking a concentration reading after each 0.1 mL addition. The iron concentration should increase by 0.1 mg/L for each 0.1 mL of standard added.

e) If these increases do not occur, see *Standard Additions* in *Section I.*

Precision

In a single laboratory, using a standard solution of 1.00 mg/L Fe and two representative lots of reagents with the DR/2010, a single operator obtained a standard deviation of ±0.007 Fe.

Interferences

A sample pH of less than 3 or greater than 4 after reagent addition may inhibit color formation, cause the developed color to fade or result in turbidity. Adjust the sample pH before reagent addition to between 3 and 8 using a pH meter or pH paper. Drop by drop, add an appropriate amount of acid (1.0 N Sulfuric Acid Solution) or base (1.0 N Sodium Hydroxide Standard Solution). Make volume corrections if significant amounts of acid or base are used (see *Correction for Volume Additions* in *Section I*).

Summary of Method

FerroMo Iron 1 Reagent contains a reducing agent combined with a masking agent. The masking agent eliminates interference from high levels of molybdate. The reducing agent converts precipitated or suspended iron (rust) to the ferrous state. FerroMo Iron Reagent 2 contains the indicator combined with a buffering agent. The indicator reacts with the ferrous iron in the sample, buffered between pH 3-4, resulting in a deep blue-purple color.

REQUIRED REAGENTS

	Cat. No.
FerroMo Reagent Set (100 tests)	25448-00

Includes: (4) 25437-68, (2) 25438-66

Description	Quantity Required Per Test	Unit	Cat. No
FerroMo Iron Reagent 1 Powder Pillows	1 pillow	25/pkg	25437-68
FerroMo Iron Reagent 2 Powder Pillows	1 pillow	50/pkg	25438-66

REQUIRED APPARATUS

Clippers, for opening powder pillows	1	each	968-00
Cylinder, graduated, mixing, 50 mL	1	each	1896-41

OPTIONAL REAGENTS

Hydrochloric Acid Solution, 6.0 N (1:1)	500 mL	884-49
Hydrochloric Acid, ACS	500 mL	134-49
Iron Standard Solution, 100 mg/L Fe	100 mL	14175-42
Iron Standard Solution, Voluette Ampule, 25 mg/L Fe, 10 mL	16/pkg	14253-10
Sodium Hydroxide Standard Solution, 1.0 N	100 mL MDB	1045-32
Sodium Hydroxide Standard Solution, 5.0 N	100 mL MDB	2450-32
Sulfuric Acid Standard Solution, 1.0 N	100 mL MDB	1270-32
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Ampule Breaker Kit	each	21968-00
Cylinder, graduated, mixing, 25 mL	each	20886-40
Flask, volumetric, Class A, 250 mL	each	14574-46
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
pH Meter, *sension*™*1*, portable	each	51700-10
Pipet Filler, safety bulb	each	14651-00
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 1.00 mL	each	14515-35
Pour-Thru Cell Assembly Kit	each	45215-00
Sample Cell, disposable, polystyrene	12/pkg	24102-12

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

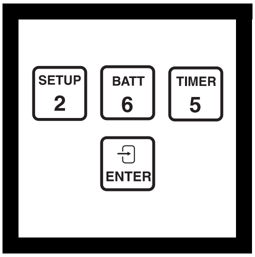
Method 8008

IRON, TOTAL (0 to 3.00 mg/L)

For Water, Wastewater, and Seawater

FerroVer Method* (Powder Pillows or AccuVac Ampuls)

USEPA approved for reporting wastewater analysis (digestion is required; see Section II)**



1. Enter the stored program number for iron (Fe) FerroVer, powder pillows.

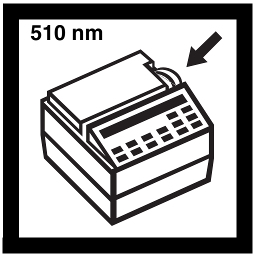
Press: **2 6 5 ENTER**

The display will show:

Dial nm to 510

Note: *Adjust pH of stored samples before analysis.*

Note: *The Pour-Thru cell may be used with 25-mL reagents only.*

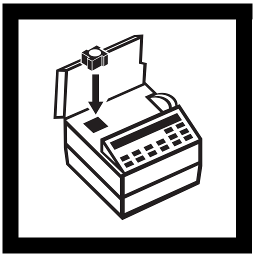


2. Rotate the wavelength dial until the small display shows:

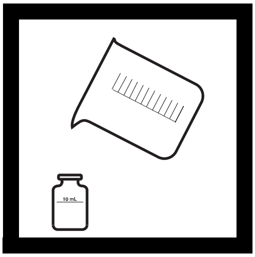
510 nm

When the correct wavelength is dialed in, the display will quickly show: **Zero Sample**

then: **mg/L Fe FV**



3. Insert the Cell Riser for 10-mL sample cells.



4. Fill a clean sample cell with 10 mL of sample.

Note: *Determination of total iron needs a prior digestion; use the mild, vigorous or Digesdahl digestion (Section II).*

---

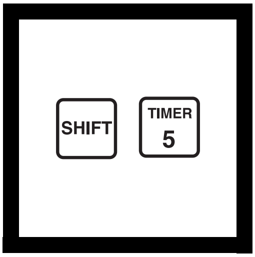
* Adapted from Standard Methods for the *Examination of Water and Wastewater.*

** *Federal Register*, 45 (126) 43459 (June 27, 1980).

5. Add the contents of one FerroVer Iron Reagent Powder Pillow to the sample cell (the prepared sample). Swirl to mix.

Note: *An orange color will form if iron is present.*

Note: *Accuracy is not affected by undissolved powder.*

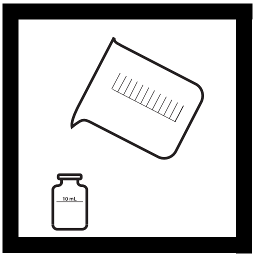


6. Press:

SHIFT TIMER

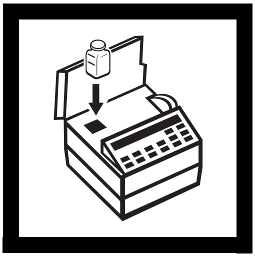
A three minute reaction period will begin.

Note: *Samples containing visible rust should be allowed to react at least five minutes.*



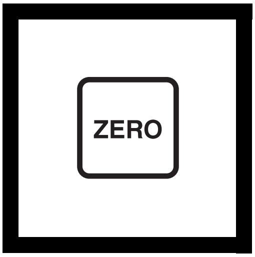
7. When the timer beeps, the display will show: **mg/L Fe FV**

Fill another sample cell with 10 mL of sample (the blank).



8. Place the blank into the cell holder. Close the light shield.

Note: *For turbid samples, treat the blank with one 0.1-gram scoop of RoVer Rust Remover (use 0.2-g for 25-mL samples). Swirl to mix.*



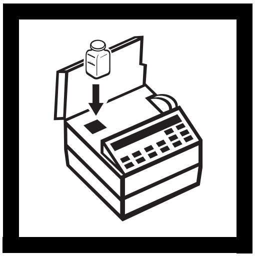
9. Press: **ZERO**

The display will show:

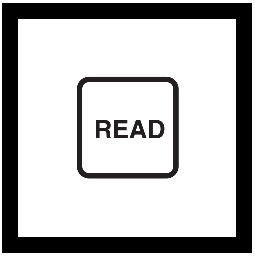
Zeroing . . .

then:

0.00 mg/L Fe FV



10. Within thirty minutes after the timer beeps, place the prepared sample into the cell holder. Close the light shield.



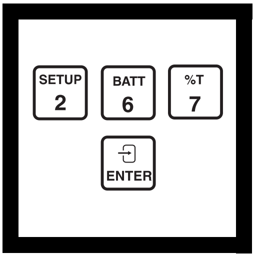
11. Press: **READ**

The display will show:

Reading . . .

then the result in mg/L iron will be displayed.

Using AccuVac Ampuls



1. Enter the stored program number for iron (Fe), AccuVac ampuls.

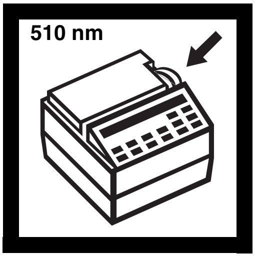
Press: **2 6 7 ENTER**

The display will show:

Dial nm to 510

Note: *Adjust pH of stored samples before analysis.*

Note: *Determination of total iron needs a prior digestion; use the mild, vigorous or Digesdahl digestion (Section II).*



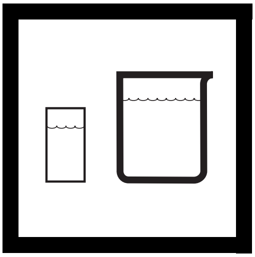
2. Rotate the wavelength dial until the small display shows:

510 nm

When the correct wavelength is dialed in, the display will quickly show:

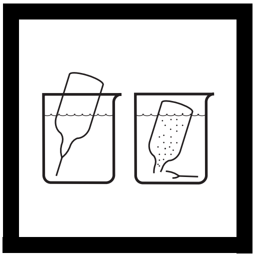
Zero Sample

then: **mg/L Fe FV AV**



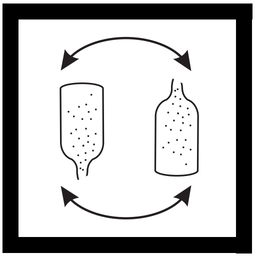
3. Fill a zeroing vial (the blank) with at least 10 mL of sample. Collect at least 40 mL of sample in a 50-mL beaker.

Note: *For turbid samples, treat the blank with one 0.1 g scoop of RoVer Rust Remover. Swirl to mix.*



4. Fill a FerroVer AccuVac Ampul with sample.

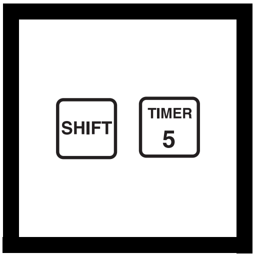
Note: *Keep the tip immersed while the ampul fills completely.*



5. Quickly invert the ampul several times to mix. Wipe off any liquid or fingerprints.

Note: *An orange color will form if iron is present.*

Note: *Accuracy is not affected by undissolved powder.*

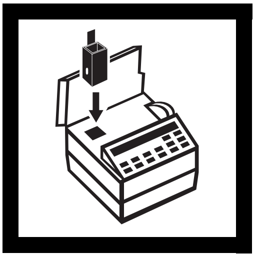


6. Press:

SHIFT TIMER

A three-minute reaction period will begin.

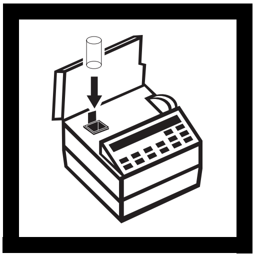
Note: *Samples containing visible rust should be allowed to react at least five minutes.*



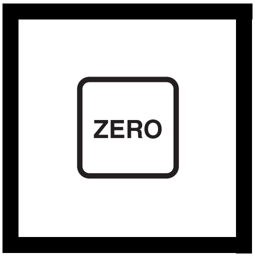
7. When the timer beeps, the display will show: **mg/L Fe FV AV**

Place the AccuVac Vial Adapter into the cell compartment.

Note: *Place the grip tab at the rear of the cell holder.*



8. Place the blank into the cell holder. Close the light shield.



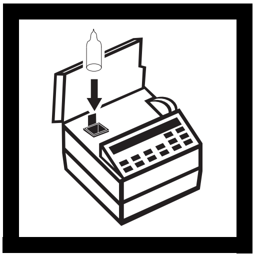
9. Press: **ZERO**

The display will show:

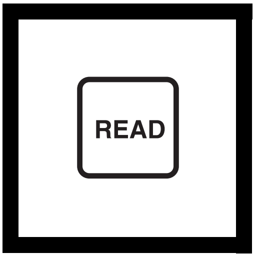
Zeroing . . .

then:

0.00 mg/L Fe FV AV



10. Within 30 minutes after the timer beeps, place the AccuVac ampul into the cell holder. Close the light shield.



11. Press: **READ**

The display will show:

Reading . . .

then the result in mg/L iron will be displayed.

Sampling and Storage

Collect samples in acid-cleaned glass or plastic containers. No acid addition is necessary if analyzing the sample immediately. To preserve samples, adjust the pH to 2 or less with nitric acid (about 2 mL per liter). Preserved samples may be stored up to six months at room temperature. Adjust the pH to between 3 and 5 with 5.0 N sodium hydroxide Standard Solution before analysis. Correct the test result for volume additions; see *Correcting for Volume Additions* in *Section I* for more information.

If only dissolved iron is to be determined, filter the sample before acid addition using the labware listed under *Optional Apparatus*.

Accuracy Check

Standard Additions Method

a) Fill three 25-mL graduated mixing cylinders with 25 mL of sample.

b) Snap the neck off a 50 mg/L Iron Voluette Ampule Standard Solution.

c) Use the TenSette Pipet to add 0.1, 0.2, and 0.3 mL of standard, respectively, to the three mixing cylinders and mix thoroughly.

d) For analysis using AccuVac Ampuls, transfer solutions to dry, clean 50-mL beakers to facilitate filling of the ampuls. For analysis with powder pillows, transfer only 10 mL of solution to the 10-mL sample cells.

e) Analyze each standard addition sample as described above. The iron concentration should increase 0.2 mg/L for each 0.1 mL of standard added.

f) If these increases do not occur, see *Standard Additions* in *Section I* for troubleshooting information.

Standard Solution Method

Prepare a 1.00 mg/L iron standard by diluting 1.00 mL of Iron Standard Solution, 100 mg/L Fe, to 100 mL with deionized water. Or dilute 1.00 mL of an Iron Voluette Ampule Standard Solution (50 mg/L) to 50 mL in a volumetric flask. Prepare this solution daily. Run the test, following the procedure for powder pillows or AccuVacs, using the 1.00 mg/L Iron Standard Solution. Results should be between 0.90 mg/L and 1.10 mg/L Fe.

Precision

In a single laboratory, using a standard solution of 1.000 mg/L Fe and two representative lots of powder pillow reagents with the DR/2010, a single operator obtained a standard deviation of ±0.006 mg/L.

In a single laboratory, using a standard solution of 1.000 mg/L Fe and two representative lots of AccuVac ampuls with the DR/2010, a single operator obtained a standard deviation of ±0.009 mg/L Fe.

Estimated Detection Limit (EDL)

The EDL for program 265 (Powder Pillows) and program 267 (AccuVac Ampuls) is 0.02 mg/L Fe. The EDL is the calculated lowest average concentration in a deionized water matrix that is different from zero with a 99% level of confidence. For more information on derivation and use of Hach's estimated detection limit, see *Section I*.

Interferences

The following will not interfere below the levels shown:

Chloride	185,000 mg/L
Calcium	10,000 mg/L as $CaCO_3$
Magnesium	100,000 mg/L as $CaCO_3$
Molybdate Molybdenum	50 mg/L as Mo

A large excess of iron will inhibit color development. A diluted sample should be tested if there is any doubt about the validity of a result.

FerroVer Iron Reagent Powder Pillows and AccuVac Ampuls contain a masking agent which eliminates potential interferences from copper.

Samples containing some forms of iron oxide require the mild, vigorous or Digesdahl digestion (see *Section II*). After digestion adjust the pH to between 2.5 and 5 with ammonium hydroxide.

Samples containing large amounts of sulfide should be treated as follows in a fume hood or well ventilated area: Add 5 mL of hydrochloric acid to 100 mL of sample and boil for 20 minutes. Adjust the pH to between 2.5 and 5 with 5 N sodium hydroxide and readjust the volume to 100 mL with deionized water. Analyze as described above.

Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment; see *pH Interferences* in *Section I.*

Summary of Method

FerroVer Iron Reagent reacts with all soluble iron and most insoluble forms of iron in the sample, to produce soluble ferrous iron. This reacts with the 1,10-phenanthroline indicator in the reagent to form an orange color in proportion to the iron concentration.

REQUIRED REAGENTS (Using Powder Pillows)

Description	Quantity Required Per Test	Unit	Cat No.
FerroVer Iron Reagent Powder Pillows, 10 mL samples	1 pillow	100/pkg	21057-69

REQUIRED REAGENTS (Using AccuVac Ampuls)

Description	Quantity Required Per Test	Unit	Cat No.
FerroVer Iron Reagent AccuVac Ampuls	1 ampul	25/pkg	25070-25

REQUIRED APPARATUS (Using Powder Pillows)

Description	Quantity Required Per Test	Unit	Cat No.
Cell Riser, 10 mL sample cell	1	each	45282-00
Sample Cell, 10 mL, matched pair		each	24954-02

REQUIRED APPARATUS (Using AccuVac Ampuls)

Description	Quantity Required Per Test	Unit	Cat No.
Adapter, AccuVac vial	1	each	43784-00
Beaker, 50 mL	1	each	500-41
Vial, Zeroing		each	21228-00

OPTIONAL REAGENTS

Description	Unit	Cat. No.
Ammonium Hydroxide, ACS	500 mL	106-49
Hydrochloric Acid Standard Solution, 6 N	500 mL	884-49
Hydrochloric Acid, ACS	500 mL	134-49
Iron Standard Solution, 100 mg/L	100 mL	14175-42
Iron Voluette Ampule Standard, 50 mg/L	16/pkg	14254-10
Nitric Acid, ACS	500 mL	152-49
Nitric Acid Solution, 1:1	500 mL	2540-49
RoVer Rust Remover	454 g	300-11
Rust Suspension	15 mL SCDB	1279-36
Sodium Hydroxide Standard Solution, 5.0 N	100 mL MDB	2450-32
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

AccuVac Snapper Kit	each	24052-00
Ampule Breaker Kit	each	21968-00
Clippers, Shears 7 1/4 "	each	23694-00
Cylinder, graduated, glass, 25 mL	each	508-40
Cylinder, graduated, poly, 25 mL	each	1081-40
Cylinder, graduated, poly, 100 mL	each	1081-42
Cylinder, Mixing, 25 mL	each	20886-40
Digesdahl Digestion Apparatus, 115 V	each	23130-20
Digesdahl Digestion Apparatus, 230 V	each	23130-21
Filter Discs, glass, 47 mm	each	2530-00
Filter Holder, membrane	each	2340-00
Filter Pump	each	2131-00
Flask, erlenmeyer, 250 mL	each	505-46
Flask, filtering, 500 mL	each	546-49
Flask, volumetric, Class A, 50 mL	each	14574-41
Flask, volumetric, Class A, 100 mL	each	14574-42
Hot Plate, 3 1/2" diameter, 120 Vac	each	12067-01
Hot Plate, 3 1/2" diameter, 240 Vac	each	12067-02
pH Meter, *sension*™*1*, portable	each	51700-10
pH Indicator Paper, 1 to 11 pH	each	391-33
Pipet Filler, safety bulb	each	14651-00
Pipet, serological, 2 mL	each	532-36
Pipet, serological, 5 mL	each	532-37
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 1.00 mL	each	14515-35
Spoon, measuring, 0.1 g	each	511-00

OPTIONAL 25 mL ANALYSIS ITEMS

Description	Unit	Cat. No.
FerroVer Reagent Powder Pillows, 25 mL	100/pkg	854-99
Pour-Thru Cell Assembly Kit (for 25-mL reagents only)	each	45215-00
Sample Cell, 25 mL, matched pair	pair	20950-00
Spoon, measuring, 0.2 g	each	638-00

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

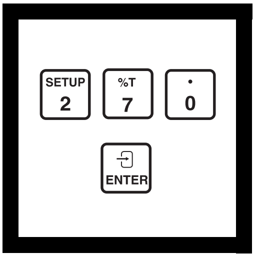
Method 8112

IRON, TOTAL (0 to 1.80 mg/L)

For water, wastewater, and seawater

TPTZ Method* (Powder Pillows or AccuVac Ampuls)

Using Powder Pillows



1. Enter the stored program number for iron (Fe) TPTZ powder pillow method.

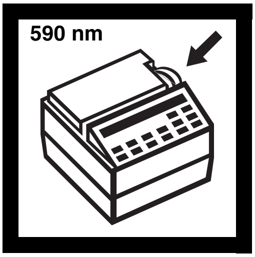
Press: **2 7 0 ENTER**

The display will show:

Dial nm to 590

__Note:__ Adjust pH of stored samples before analysis.

__Note:__ The Pour-Thru Cell can be used with 25-mL reagents only.



2. Rotate the wavelength dial until the small display shows:

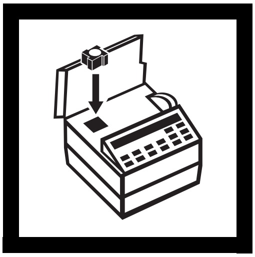
590 nm

When the correct wavelength is dialed in, the display will quickly show:

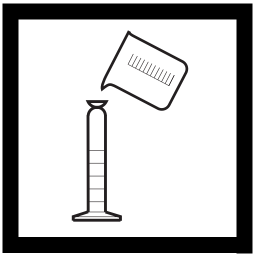
Zero Sample

then: **mg/L Fe TPTZ**

__Note:__ Total iron determination needs a prior digestion. Use any of the three procedures in Digestion (Section II).



3. Insert the 10-mL Cell Riser into the cell compartment.



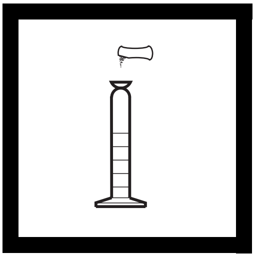
4. Fill a 10-mL graduated mixing cylinder with 10 mL of sample.

__Note:__ Sample pH is important in this test; see pH discussion in Interferences.

__Note:__ Rinse glassware with a 1:1 hydrochloric acid and deionized water before use to avoid errors due to iron deposits on the glass.

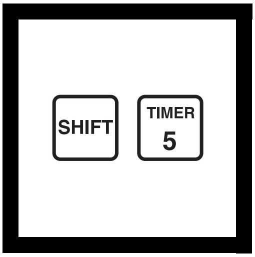
---

* Adapted from G. Frederic Smith Chemical Co., *The Iron Reagents*, 3rd ed. (1980).



5. Add the contents of one TPTZ Iron Reagent Powder Pillow (the prepared sample). Stopper and shake the cylinder for 30 seconds. Remove the stopper.

Note: A blue color will develop if iron is present.

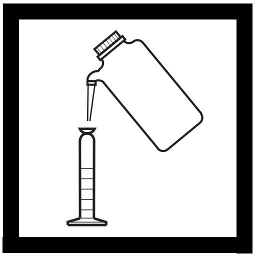


6. Press:

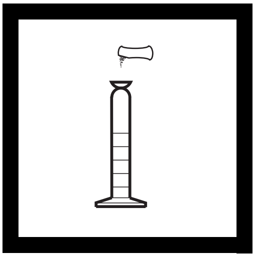
SHIFT TIMER

A three-minute reaction period will begin.

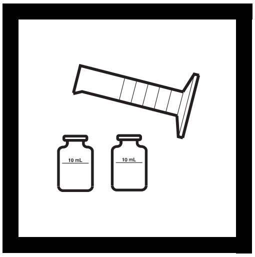
Note: Continue with Steps 7 to 9 while the timer is running.



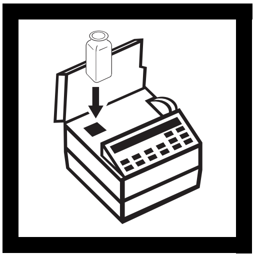
7. Fill a second 10-mL graduated mixing cylinder with 10 mL of deionized water.



8. Add the contents of a TPTZ Iron Reagent Powder Pillow to the deionized water (the blank). Stopper. Shake the cylinder for 30 seconds. Remove the stopper.

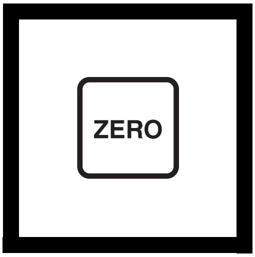


9. Transfer the prepared sample and the blank into two matched 10-mL sample cells.



10. When the timer beeps, the display will show: **mg/L Fe TPTZ**

Insert the blank into the cell holder. Close the light shield.



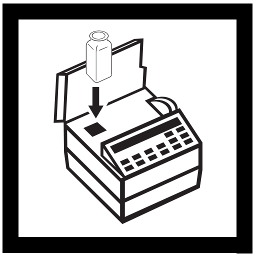
11. Press: **ZERO**

The display will show:

Zeroing. . . .

then:

0.00 mg/L Fe TPTZ



12. Place the prepared sample into the cell holder. Close the light shield.

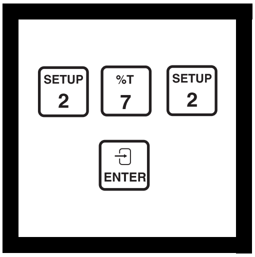
Press: **READ**

The display will show:

Reading. . . .

then the result in mg/L iron will be displayed.

Using AccuVac Ampuls



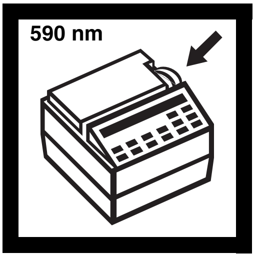
1. Enter the stored program number for iron (Fe) TPTZ AccuVac method.

Press: **2 7 2 ENTER**

The display will show:

Dial nm to 590

Note: *Adjust pH of stored samples before analysis.*



2. Rotate the wavelength dial until the small display shows:

590 nm

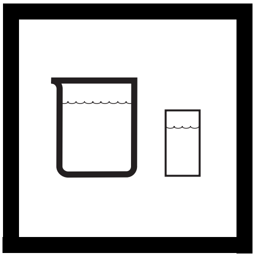
When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

then:

mg/L Fe TPTZ AV

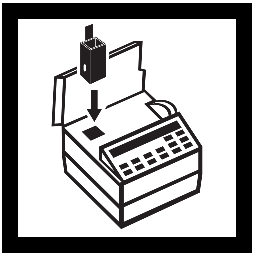
Note: *Total iron determination needs a prior digestion. Use any of the three procedures in Digestion (Section I).*



3. Collect at least 40 mL of sample in a 50-mL beaker. Fill a zeroing vial with at least 10 mL of sample. Cap the Zeroing Vial.

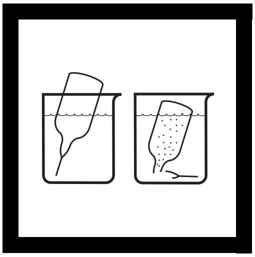
Note: *Sample pH is important in this test; see pH discussion in Interferences.*

Note: *Rinse glassware with a 1:1 hydrochloric acid and deionized water before use to avoid errors due to iron deposits on the glass.*



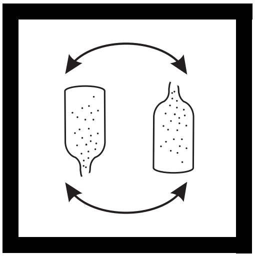
4. Insert the AccuVac Vial Adapter into the cell holder.

Note: *Insert the vial adapter so the grip tab is at the rear of the instrument.*



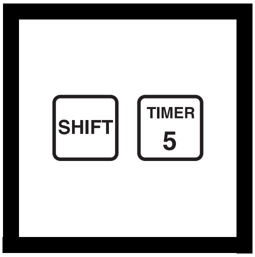
5. Fill a TPTZ Iron AccuVac Ampul with sample.

Note: *Keep the tip immersed while the ampul fills completely.*



6. Invert the ampul (the prepared sample) repeatedly to mix. Wipe off any liquid or fingerprints.

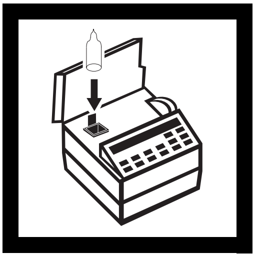
Note: *A blue color will develop if iron is present.*



7. Press:

SHIFT TIMER

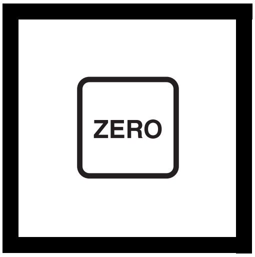
A three-minute reaction period will begin.



8. When the timer beeps the display will show:

mg/L Fe TPTZ AV

Place the zeroing vial into the adapter. Close the light shield.



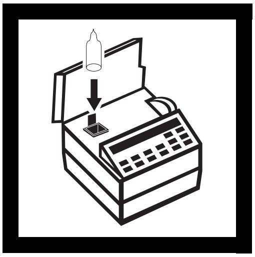
9. Press: **ZERO**

The display will show:

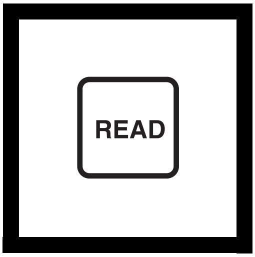
Zeroing. . . .

then:

0.00 mg/L Fe TPTZ AV



10. Place the prepared sample into the adapter. Close the light shield.



11. Press: **READ**

The display will show:

Reading. . . .

then the result in mg/L iron will be displayed.

Note: *For the most accurate results, run the procedure using iron-free deionized water instead of sample. Subtract the value obtained in Step 11 from all later tests. Repeat for each new lot of AccuVac reagent.*

Sampling and Storage

Collect samples in acid-washed glass or plastic bottles. Adjust the sample pH to 2 or less with nitric acid (about 2 mL per liter). Store samples preserved in this manner up to six months at room temperature. If reporting only dissolved iron, filter sample immediately after collection and before addition of nitric acid.

Before testing, adjust the pH of the stored sample to between 3 and 4 with 5.0 N Sodium Hydroxide Standard Solution. Do not exceed pH 5 as iron may precipitate. Correct the test result for volume additions; see *Correction for Volume Additions* in *Section I.*

Accuracy Check

Standard Additions Method

a) Fill three 25-mL graduated mixing cylinders with 25 mL of sample.

b) Snap the neck off an Iron PourRite Ampule, 50 mg/L (NIST) as Fe.

c) Use the TenSette Pipet to add 0.1, 0.2 and 0.3 mL of standard, respectively, to the three mixing cylinders. Stopper and swirl to mix thoroughly.

d) For analysis with AccuVacs, transfer solutions to dry, clean 50-mL beakers to fill the ampules. For analysis with powder pillows, transfer only 10 mL of solution to the 10-mL graduated cylinders.

e) Analyze each standard addition sample as described in the procedure. The iron concentration reading should increase by 0.2 mg/L for each 0.1 mL addition of standard.

f) If these increases do not occur, see *Standard Additions* in *Section I* for more information.

Standard Solution Method

Prepare a 1.0 mg/L iron working solution as follows:

a) Using Class A glassware, pipet 1.00 mL of Iron Standard Solution, 100 mg/L Fe, into a 100-mL volumetric flask.

b) Dilute to volume with deionized water. Stopper and invert repeatedly to mix.

Precision

In a single laboratory using a standard solution of 1.00 mg/L Fe and two representative lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±0.009 mg/L Fe.

In a single laboratory using a standard solution of 1.00 mg/L Fe and one representative lot of AccuVac Ampuls with the DR/2010, a single operator obtained a standard deviation of ±0.007 mg/L Fe.

Interferences

In the powder pillow procedure if the sample, without a TPTZ Iron Reagent Powder Pillow, has a color or turbidity greater than the blank in Step 8 (deionized water plus TPTZ Iron Reagent), then use the sample as the blank.

A sample pH of less than 3 or greater than 4 after the addition of reagent may inhibit color formation, cause the developed color to fade quickly or result in turbidity. Adjust the sample pH in the sample cell before the addition of reagent to 3-4 by using a pH meter or pH paper and adding dropwise an appropriate amount of iron-free acid or base such as 1.0 N Sulfuric Acid Standard Solution or 1.0 N Sodium Hydroxide Standard Solution. Make a volume correction if significant volumes of acid or base are used; see *Correction for Volume Additions (Section I).*

Interference tests were performed using an iron concentration of 0.5 mg/L. When interferences occurred, the color formation was inhibited or a precipitate formed. The following do not interfere with the test when present up to the levels listed:

Cadmium	4.0 mg/L
Chromium (3+)	0.25 mg/L
Chromium (6+)	1.2 mg/L
Cobalt	0.05 mg/L
Copper	0.6 mg/L
Cyanide	2.8 mg/L
Manganese	50.0 mg/L
Mercury	0.4 mg/L
Molybdenum	4.0 mg/L
Nickel	1.0 mg/L
Nitrite Ion	0.8 mg/L

Summary of Method

The TPTZ Iron Reagent forms a deep blue-purple color with ferrous iron. The indicator is combined with a reducing agent which converts precipitated or suspended iron, such as rust, to the ferrous state. The amount of ferric iron present can be determined as the difference between the results of a ferrous iron test and the concentration of total iron.

REQUIRED REAGENTS (USING POWDER PILLOWS)

Description	Quantity Required Per Test	Unit	Cat. No.
TPTZ Iron Reagent Powder Pillows, 10 mL sample	2 pillows	100/pkg	26087-99

REQUIRED REAGENTS (USING ACCUVAC AMPULS)

Description	Quantity Required Per Test	Unit	Cat. No.
TPTZ Low Range Iron Reagent AccuVac Ampuls	1 ampul	25/pkg	25100-25

REQUIRED APPARATUS (USING POWDER PILLOWS)

Description	Quantity Required Per Test	Unit	Cat. No.
Cell Riser, 10-mL	1	each	45282-00
Cylinder, graduated, mixing, 10 mL	varies	each	20886-38
Sample Cell, 10-mL, matched pair	2	pair	24954-02

REQUIRED APPARATUS (USING ACCUVAC AMPULS)

Description	Quantity Required Per Test	Unit	Cat. No.
Adapter, AccuVac Vial	1	each	43784-00
Beaker, 50 mL	1	each	500-41
Zeroing Vial	1	each	21228-00

OPTIONAL REAGENTS

Description	Unit	Cat. No.
Hydrochloric Acid Solution, 1:1, 6.0 N	500 mL	884-49
Iron Standard Solution	100 mL	14175-42
Iron Standard Solution, PourRite Ampule, 50 mg/L Fe (NIST), 2 mL	20/pkg	14254-20
Nitric Acid, ACS	500 mL	152-49
Nitric Acid Solution, 1:1	500 mL	2540-49
Sodium Hydroxide Standard Solution, 1.0 N	100 mL MDB	1045-32
Sodium Hydroxide Standard Solution, 5.0 N	100 mL MDB	2450-32
Sulfuric Acid Standard Solution	100 mL MDB	1270-32
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Description	Unit	Cat. No.
AccuVac Snapper Kit	each	24052-00
Ampule Breaker Kit	each	24846-00
Cylinder, graduated, mixing, 25 mL, tall	each	21190-40
Flask, volumetric, Class A, 100 mL	each	14575-42
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
pH Meter, *sension*™*1*, portable	each	51700-10
Pipet Filler, safety bulb	each	14651-00
Pipet, serological, 2 mL	each	532-36
Pipet TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 1.00 mL	each	14515-35

OPTIONAL 25-ML ANALYSIS ITEMS

Description	Unit	Cat. No.
Pour-Thru Cell Assembly Kit (for 25 mL reagents only)	each	45215-00
Sample Cell, 25- mL, matched pair	pair	20950-00
TPTZ Iron Reagent Powder Pillows, 25 mL sample	100/pkg	22756-99

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

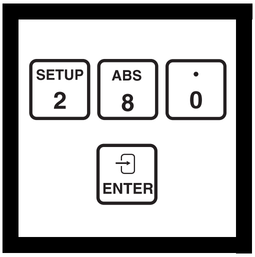
Method 8033

LEAD (0 to 160 µg/L)

For water and wastewater

Dithizone Method*

USEPA accepted for reporting wastewater analysis (digestion is required; see Section II)**



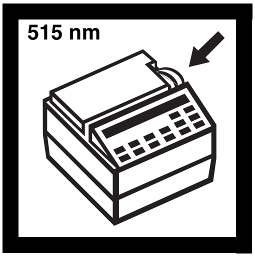
1. Enter the stored program number for lead (Pb).

Press: **2 8 0 ENTER**

The display will show:

Dial nm to 515

Note: *The Pour-Thru Cell cannot be used with this procedure*



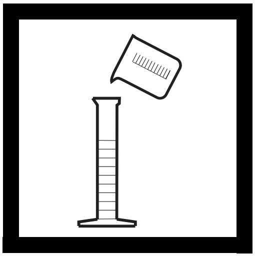
2. Rotate the wavelength dial until the small display shows:

515 nm

When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

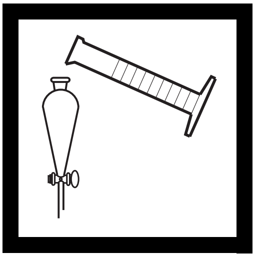
then: **µg/L Pb**



3. Fill a 250-mL graduated cylinder to the 250-mL mark with sample.

Note: *Clean all glassware with a 1:1 Nitric Acid Solution. Rinse with deionized water.*

Note: *Cloudy and turbid samples may require filtering. Report results as µg/L soluble lead. Use a glass membrane filter to avoid loss of lead by adsorption on filter paper.*



4. Transfer the sample into 500-mL separatory funnel.

Note: *Perform the procedure with proper ventilation or in a fume hood.*

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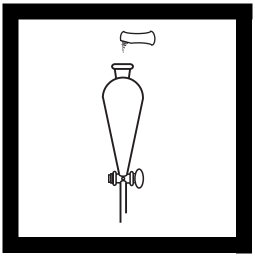
* Adapted from Snyder, L.J., *Analytical Chemistry*, 19 684 (1947).

** Procedure is equivalent to Standard Method 3500-Pb D for wastewater.

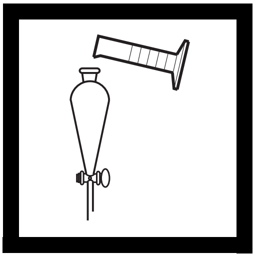


5. Add the contents of one Buffer Powder Pillow, citrate type for heavy metals. Stopper the funnel. Shake to dissolve.

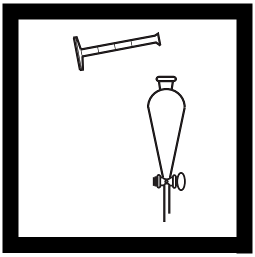
Note: *Spilled reagent will affect test accuracy and is hazardous.*

6. Add 50 mL of chloroform to a 50-mL graduated cylinder. Add the contents of one DithiVer Metals Reagent Powder Pillow. Stopper. Invert repeatedly to mix (Dithiver solution). Pour 30 mL of the DithiVer solution into a second 50-mL graduated cylinder.

Note: *Use adequate ventilation. The DithiVer Powder will not all dissolve. See DithiVer Solution Preparation.*

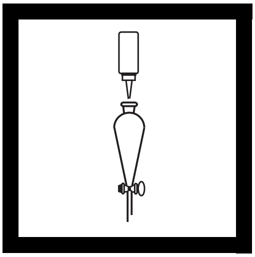


7. Add the 30 mL of DithiVer solution from the cylinder to the separatory funnel. Stopper. Invert. Open stopcock to vent.



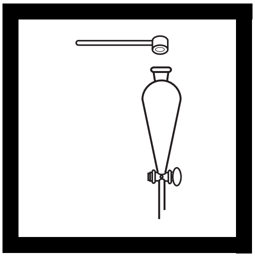
8. Add 5 mL of 5.0 N Sodium Hydroxide Standard Solution. Stopper. Invert. Open stopcock to vent. Shake the funnel once or twice and vent again.

Note: *Add a few drops of 5.25 N Sulfuric Acid Standard Solution if the solution turns orange on shaking. The blue-green color will reappear. To avoid high blanks, repeat procedure on new sample and use less sodium hydroxide.*



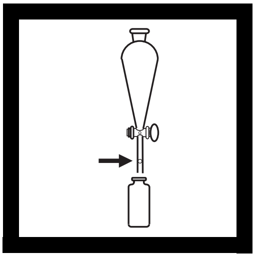
9. Continue adding 5.0 N Sodium Hydroxide Standard Solution dropwise until the color of the solution being shaken changes from blue-green to orange. Then add 5 more drops of 5.0 N Sodium Hydroxide Standard Solution.

Note: *For most accurate results, adjust the sample to pH 11.0 to 11.5 using a pH meter, omitting the five additional drops of Sodium Hydroxide Standard Solution.*



10. Add two heaping 1.0 g scoops of potassium cyanide to the funnel. Stopper. Shake vigorously until the potassium cyanide is all dissolved (about 15 seconds).

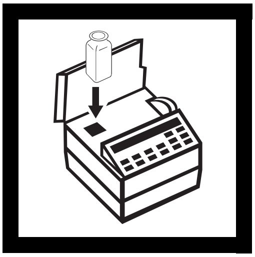
Note: *Wait one minute for the layers to separate. The bottom (chloroform) layer will be pink if lead is present.*



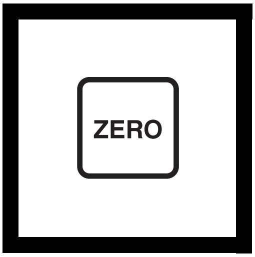
11. Insert a cotton plug the size of a pea into the delivery tube of the funnel and slowly drain the bottom (chloroform) layer into a dry 25-mL sample cell. Stopper. This is the prepared sample.

Note: *The lead-dithizone complex is stable for hours if the sample cell is kept tightly capped and out of direct sunlight.*

12. Fill a 25-mL sample cell (the blank) with chloroform. Stopper.



13. Place the blank into the cell holder. Close the light shield.

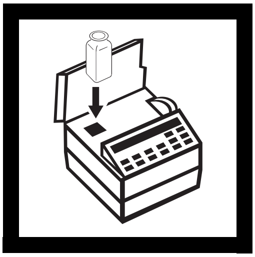


14. Press:**ZERO**

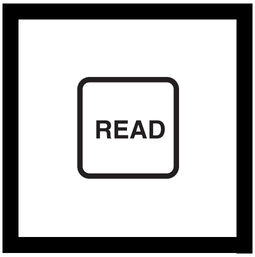
The display will show:

Zeroing. . . .

then: **0. µg/L Pb**



15. Place the prepared sample into the cell holder. Close the light shield.



16. Press: **READ**

The display will show:

Reading. . . .

then the result in µg/L lead will be displayed.

Dithiver Solution Preparation, Storage And Blank

Store DithiVer Powder Pillows away from light and heat. A convenient way to prepare this solution is to add the contents of 10 DithiVer Metals Reagent Powder Pillows to a 500-mL bottle of chloroform. Invert several times until well mixed (carrier powder may not dissolve). Store dithizone solution in an amber glass bottle. This solution is stable for 24 hours.

A reagent blank on deionized water should be carried out through the entire method to obtain the most accurate results. The amount of reagent blank determined on each lot of DithiVer Metals Reagent Powder Pillow is then subtracted from each reading obtained in Step 16.

Sampling and Storage

Collect samples in acid cleaned glass or plastic containers. Adjust the pH to 2 or less with nitric acid (about 2 mL per liter). Preserved samples can be stored up to six months at room temperature. Adjust the pH to 2.5 to 4.5 with 5.0 N sodium hydroxide before analysis. Correct the test result for volume additions; see *Correction for Volume Additions* in *Section I.*

Accuracy Check

Standard Additions Method

a) Snap the neck off a Lead Voluette Ampule Standard Solution, 50 mg/L as Pb.

b) Use the TenSette Pipet to add 0.1 mL, 0.2 mL, and 0.3 mL of standard to each of three 250-mL samples and mix each thoroughly.

c) Analyze each sample as described above. The lead concentration should increase 20 µg/L for each 0.1 mL of standard added.

d) If these increases do not occur, see *Standard Additions* in *Section I* for more information.

Standard Solution Method

Prepare a 10 mg/L lead standard solution by pipetting 10.00 mL of Lead Standard Solution, 100 mg/L, into a 100-mL volumetric flask. Add 0.2 mL of concentrated nitric acid with a TenSette pipet to prevent adsorption of lead on the flask walls. Dilute to mark with deionized water and mix well. To make a 120 µg/L Pb standard, pipet 3.00 mL of the 10.0-mg/L standard into 247 mL of deionized water in a 500-mL separatory funnel. Perform the lead procedure as described above.

Precision

In a single laboratory using a standard solution of 40 µg/L Pb and two representative lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±1.3 µg/L Pb.

Estimated Detection Limit (EDL)

The EDL for program 280 is 3 µg/L Pb. The EDL is the calculated lowest average concentration in a deionized water matrix that is different from zero with a 99% level of confidence. For more information on derivation and use of Hach's estimated detection limit, *see Section I.*

Interferences

The following do not interfere:

Aluminum	Calcium	Magnesium
Antimony	Chromium	Manganese
Arsenic	Cobalt	Nickel
Cadmium	Iron	Zinc

The following interfere:

Bismuth	Mercury	Tin
Copper	Silver	

Eliminate interference from these metals by the following treatment, beginning after procedure Step 6.

a) Measure about 5 mL of the prepared dithizone solution into the separatory funnel. Stopper the funnel, invert and open the stopcock to vent. Close the stopcock and shake the solution vigorously for 15 seconds.

b) Allow the funnel to stand undisturbed until the layers separate (about 30 seconds). A yellow, red, or bronze color in the bottom (chloroform) layer confirms the presence of interfering metals.

c) Draw off and discard the bottom (chloroform) layer.

d) Repeat extraction with fresh 5 mL portions of prepared dithizone solution (discarding the bottom layer each time) until the bottom layer shows a pure dark green color for three successive extracts. Extractions can be repeated a number of times without appreciably affecting the amount of lead in the sample.

e) Extract the solution with several 2 or 3 mL portions of pure chloroform to remove any remaining dithizone, again discarding the bottom layer each time.

f) Continue the procedure, substituting 28.5 mL of prepared dithizone solution for the 30 mL in Step 7.

Large amounts of zinc cause an indistinct color transition at the end point.

Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment; see *pH Interferences* in *Section I.*

Waste Disposal

Both chloroform (D002) and cyanide (D003) solutions are regulated as hazardous wastes by the Federal RCRA. Do not pour these solutions down the drain. Collect chloroform solutions and the cotton plug used in the delivery tubes of the separatory funnel for disposal with laboratory solvent waste. Be sure to store cyanide solutions in a caustic solution with a pH >11 to prevent potential release of hydrogen cyanide gas.

Summary of Method

The DithiVer Metals Reagent is a stable powder form of dithizone. Lead ions in basic solution react with dithizone to form a pink to red lead-dithizonate complex, which is extracted with chloroform.

REQUIRED REAGENTS

	Cat. No.
Lead Reagent Set (100 Tests)	22431-00

Includes: (1) 14202-99, (2) 14458-17, (4) 12616-68, (1) 767-14, (1) 2450-53, (2) 2450-26

Description	Quantity Required Per Test	Units	Cat. No.
Buffer Powder Pillows, Citrate for heavy metals	1 pillow	100/pkg	14202-99
Chloroform, ACS	50 mL	500 mL	14458-49
DithiVer Metals Reagent Powder Pillows	1 pillow	25/pkg	12616-68
Potassium Cyanide, ACS	2 g	113 g	767-14
Sodium Hydroxide Solution, 5.0 N	5 mL	1000 mL	2450-53
Sodium Hydroxide, 5.0 N	drops	50 mL DB	2450-26

REQUIRED APPARATUS

Description	Quantity Required Per Test	Units	Cat. No.
Clippers, for opening powder pillows	1	each	968-00
Cotton balls, absorbent	1	100/pkg	2572-01
Cylinder, mixing graduated, 50 mL	1	each	1896-41
Cylinder, graduated, 5 mL	1	each	508-37
Cylinder, graduated, 250 mL	1	each	508-46
Funnel, separatory, 500 mL	1	each	520-49
Ring, support, 4 in.	1	each	580-01
Sample Cell, 25 mL, matched pair	2	pair	20950-00
Spoon, measuring, 1.0 g	1	each	510-00
Stand, support, 5 x 8 in.	1	each	563-00
Stopper, hollow, No. 1	2	6/pkg	14480-01

OPTIONAL REAGENTS

Chloroform, ACS	4 L	14458-17
Lead Standard Solution, 100 mg/L Pb	100 mL	12617-42
Lead Standard Solution, Voluette ampuls, 50 mg/L Pb, 10 mL	16/pkg	14262-10
Nitric Acid Solution, 1:1	500 mL	2540-49
Nitric Acid, ACS	500 mL	152-49
Sodium Hydroxide Standard Solution, 5.0 N	50 mL SCDB	2450-26
Sodium Hydroxide Standard Solution, 5.0 N	100 mL SCDB	2450-32
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Ampule Breaker Kit	each	21968-00
Filter Discs, glass membrane, 47 mm	100/pkg	2530-00
Filter Holder, graduated, 47 mm	each	2340-00
Flask, erlenmeyer, 500 mL	each	505-49
Flask, filtering, 500 mL	each	546-49
Flask, volumetric, Class B, 100 mL	each	547-42
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
pH Meter, *sension*™*1*, portable	each	51700-10
Pipet Filler, safety bulb	each	14651-00
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet, serological, 2 mL	each	532-36
Pipet, transfer, 2.00 mL	each	515-36

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

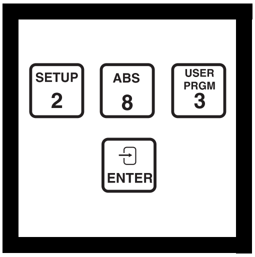
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8317

For drinking water

LEAD (0 to 150 µg/L)

LeadTrak™* Fast Column Extraction Method

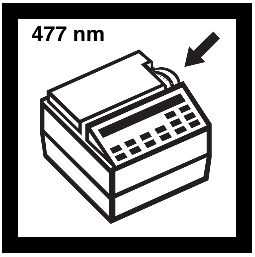


1. Enter the stored program number for lead (Pb), column extraction method.

Press: **2 8 3 ENTER**

The display will read:

Dial nm to 477



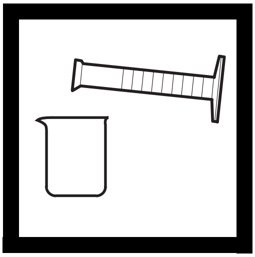
2. Rotate the wavelength dial until the small display reads:

477 nm

When the correct wavelength is dialed in the display will quickly show:

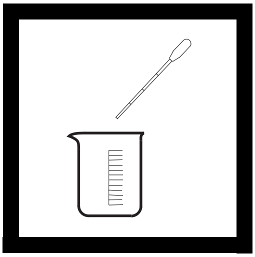
Zero Sample

then: **µg/L Pb FC**



3. Fill a 100-mL plastic graduated cylinder with 100 mL of sample. Pour the measured sample into a 250-mL plastic beaker.

Note: *The sampling requirements for "first-draw" analysis are detailed in the Sampling and Storage section.*



4. Using a plastic 1-mL dropper, add 1.0 mL of pPb-1 Acid Preservative Solution to the sample and swirl to mix.

Note: *If the sample is already preserved with pPb-l Acid Preservative (1.0 mL per 100 mL sample) omit Steps 4 and 5.*

Note: *Samples preserved with Nitric Acid require Steps 4 and 5.*

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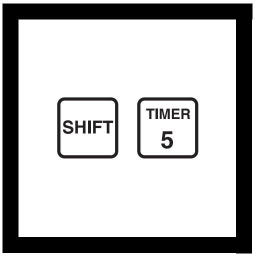
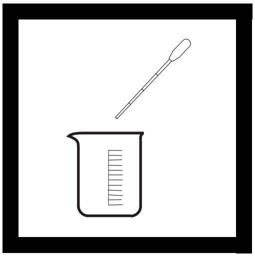
* Patent number 5,019,516



5. Press:

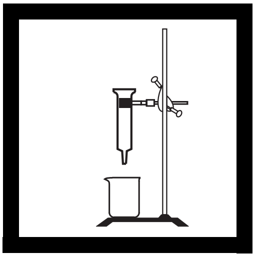
SHIFT TIMER

A two-minute reaction period will begin.



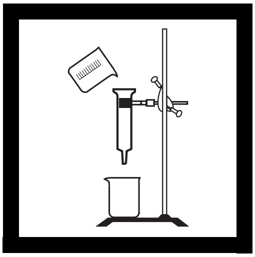
6. When the timer beeps, use a second 1-mL plastic dropper to add 2.0 mL of pPb-2 Fixer Solution. Swirl to mix.

Note: *Samples preserved with nitric acid or digested samples may exceed the buffer capacity of the Fixer Solution. After Step 6 adjust with 5 N sodium hydroxide to a pH of 6.7-7.1 before proceeding with Step 7.*

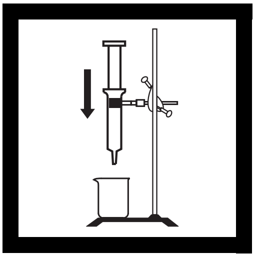


7. Mount a new Fast Column Extractor in a ring stand with a clamp. Place a 150-mL plastic beaker under the Extractor.

Note: *Fast Column Extractor is included in the LeadTrak Reagent Set. A new extractor is required for each test.*

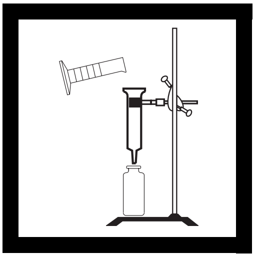


8. Pour the prepared sample slowly into the Column Extractor. Wait for the sample to flow through.

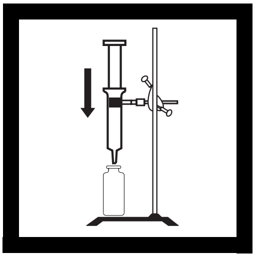


9. After the flow has stopped, fully compress the absorbent pad in the Extractor with the plunger. Discard the contents of the beaker. Withdraw the plunger slowly from the Extractor.

Note: *The absorbent pad should remain at the bottom of the Extractor when the plunger is removed. Recompress with the plunger if the pad has retracted with the plunger.*



10. Place a 25-mL sample cell under the Extractor. Using a 25-mL plastic graduated cylinder, add 25 mL of pPb-3 Eluant Solution to the Extractor.



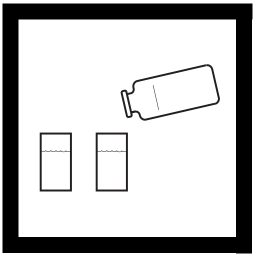
11. After the Eluant Solution has started to drip from the Extractor, insert the plunger and slowly force the remaining Eluant Solution through the Extractor. Fully compress the absorbent pad. The volume in the sample cell should be 25 mL.

12. Using a 1-mL plastic dropper, add 1.0 mL of pPb-4 Neutralizer Solution to the cell.

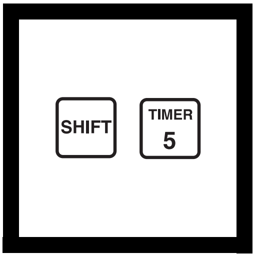
Swirl thoroughly to mix and proceed immediately to Step 13.

13. Add the contents of one pPb-5 Indicator Powder Pillow to the sample and swirl thoroughly to mix.

Note: *The solution color will turn brown.*



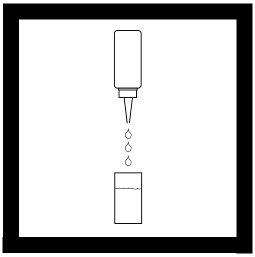
14. Split the sample by filling two 10-mL vials to the 10-mL lines with the prepared sample.



15. Press:

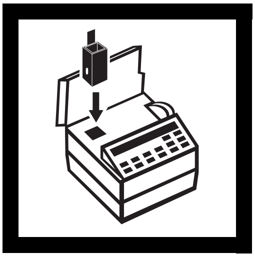
SHIFT TIMER

A second two-minute reaction period will begin.



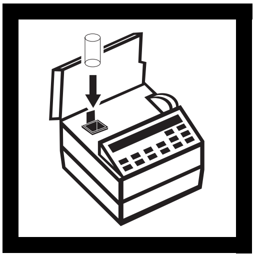
16. When the timer beeps, add three drops of pPb-6 Decolorizer Solution to one of the vials. Cap and invert to mix. Mark this vial as the reagent blank.

Note: *There will be little visual difference between the reagent blank and the sample. Both vials will be colored.*

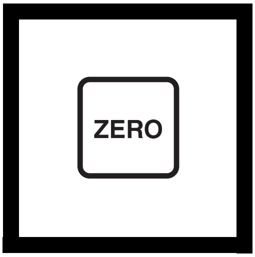


17. Place the AccuVac Vial Adapter into the cell holder.

Note: *Place the grip tab at the rear of the cell holder.*



18. Place the vial containing the blank into the cell holder. Close the light shield.

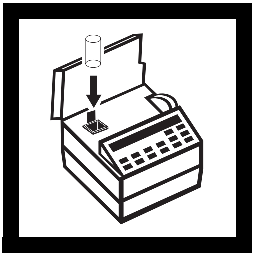


19. Press: **ZERO**

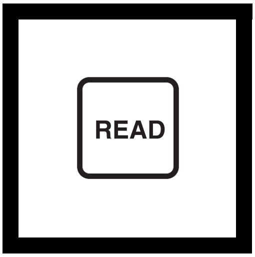
The display will show:

Zeroing. . .

then: **0 µg/L Pb FC**



20. Place the vial with the sample into the cell holder. Close the light shield.



21. Press: **READ**

The display will read:

Reading. . .

then the results in µg/L lead (Pb) will be displayed.

Note: *USEPA reporting requires running a reagent blank with lead-free, reagent-grade water. Determine a reagent blank for each new lot of reagents. Subtract the reagent blank value from each test result.*

Apparatus/Sample Preparation

Because lead is very common to our environment, care must be taken to prevent sample contamination. Follow these steps for greatest test accuracy:

a) Lead-free water is necessary to minimize sample contamination when rinsing apparatus or diluting sample. The water may be either distilled or deionized. If the water is obtained from a grocery store, verify the lead concentration is zero from the label. If the lead concentration is uncertain, determine the lead concentration with the LeadTrak test.

b) Plastic or glass sample containers and lids may be checked for contamination by rinsing with 1 mL of pPb-1 Acid Preservative. Add 100 mL of lead-free water. After 24 hours, analyze this solution using the LeadTrak test to confirm the absence of lead.

c) Rinse glassware used in this test with a small amount of dilute lead-free nitric acid or pPb-1 Acid Preservative followed by rinsing with lead-free water.

d) pPb-5 Indicator may be rinsed from the glass sample cells with a few drops of pPb-1 Acid Preservative or a small amount of dilute lead-free nitric acid.

e) Acidify solutions containing lead with nitric acid or pPB-1 to below pH 2 to prevent adsorption of lead onto the container walls.

Sampling

Samples may be collected either from household pipes (point-of-use) or from water sources. Samples may be stored up to six months.

Sampling for lead contamination in household pipes for point-of-use drinking water

a) Collect the sample after the water has been in pipes with no flow for 8 to 18 hours.

b) To a one-liter bottle add 10 mL of pPb-1 Acid Preservative.

c) Turn on tap and collect exactly the first liter of water in the bottle containing acid preservative. This is the first draw sample.

d) Cap and invert several times to mix.

e) After two minutes the sample is ready for analysis. Skip steps 4 and 5 in the analysis procedure. Use 100 mL of this preserved sample directly in Step 6.

Sampling for lead contamination from drinking water sources such as well water or water from main supply lines

a) Add 10 mL of pPb-1 Acid Preservative to a 1-liter bottle.

b) Turn the tap on for 3-5 minutes or until the water temperature has been stable for 3 minutes.

c) Collect exactly one liter of water in the bottle containing the acid preservative.

d) Cap and invert several times to mix.

e) After 2 minutes the sample is ready for analysis. Skip steps 4 and 5 in the analysis procedure. Use 100 mL of this preserved sample directly in Step 6.

Note: *Collect at least one liter of sample to obtain a representative sample. If less than one liter is collected, use 1 mL of pPb-1 Acid Preservative per 100 mL of sample.*

Note: *If nitric acid is to be substituted for pPb-1 as a preservative or the sample is digested, the buffering capacity of the pPb-2 Fixer Solution may be exceeded. Adjust the sample pH to 6.7 to 7.1 pH with 5 N sodium hydroxide after Step 6.*

Note: *Each sample type typically requires different sampling procedures. Consult with the appropriate regulatory agency in your area for more information about your specific sampling requirements.*

Accuracy Check

Standard Additions Method

The standard additions method for checking the validity of the test results can be performed as follows:

a) Use a TenSette Pipet to add 0.1 mL of a 10 mg/L Lead Standard Solution (included in the reagent set) to a second 100-mL portion of the sample.

b) Swirl the sample to mix. Then test the sample as described in the procedure. Each 0.1-mL of standard added should increase the lead concentration determined in Step 21 by 10 µg/L.

Standard Solution Method

a) Prepare a 50-µg/L lead standard solution by first pipetting 1.00 mL of Lead Standard Solution, 1000 mg/L as Pb, into a 100-mL plastic volumetric flask and diluting to the mark with lead-free water to make a 10 mg/L lead working solution. A 10 mg/L prepared standard is also included with each reagent set.

b) Pipet 5.00 mL of this working solution into a 1-liter plastic volumetric flask. Dilute to the mark with lead-free water. This 50-µg/L standard solution should be prepared immediately before use. Use this prepared standard in place of sample in step 3.

Alternatively, a 50-µg/L lead standard solution can be prepared by using a TenSette Pipet and pipetting 0.1 mL from a Lead Voluette Ampule, Standard Solution, 50 mg/L as Pb, into a 100-mL, plastic volumetric flask and diluting to volume with deionized water. This solution should be prepared immediately before use.

Interferences

Interference studies were conducted by preparing a known lead solution of approximately 25 µg/L as well as the potential interfering ion. The ion was said to interfere when the resulting concentration changed by ±10%.

Samples containing levels exceeding these concentration values may be diluted 1:1 and re-analyzed. Multiply the value obtained by the factor of 2 to determine the lead present in the original sample.

Ion	Interference Level
Aluminum, Al^{3+}	0.5 mg/L
Barium, Ba^{2+}	6 mg/L
Calcium, Ca^{2+}	500 mg/L
Chloride, Cl^-	1000 mg/L
Copper, Cu^{2+}	2 mg/L
Fluoride, F^-	10 mg/L
Iron, Fe^{2+}	2 mg/L
Magnesium, Mg^{2+}	500 mg/L
Manganese, Mn^{2+}	0.5 mg/L
Nitrogen, Ammonium, NH_4^+	500 mg/L
Nitrogen, Nitrate, NO_3^-	1000 mg/L
Sulfate, SO_4^{2-}	1000 mg/L
Zinc, Zn^{2+}	1 mg/L

Every effort has been made to prevent contamination in packaging the reagents. Use of black rubber stoppers, black dropper bulbs and droppers with inked graduations may contaminate the sample and should be avoided. Use the plastic droppers provided in the reagent set.

Glassware and plasticware should be rinsed with a dilute nitric acid solution such as 0.1 N Nitric Acid Standard Solution or a few drops of pPb-1 Acid Preservative Reagent to prevent sample contamination especially if the previous sample had a high lead level content. The sample cell walls will become colored from the pPb-5 Indicator and should be rinsed. The Extractor plunger is intended to be used for more than one test and should be rinsed as well.

Summary of Method

Acid soluble lead, as Pb^{2+}, in a potable water sample is first concentrated on a Fast Column Extractor. The lead is then eluted from the Extractor and determined colorimetrically with an indicator.

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
LeadTrak reagent set	1	20 tests/pkg	23750-00
(Reagent set includes the required reagents listed below)			

REQUIRED REAGENTS

pPb-1 Acid Preservative	1 mL	236 mL	23685-31
pPb-2 Fixer Solution	2 mL	43 mL	23686-55
pPb-3 Eluant	25 mL	500 mL	23687-49
pPb-4 Neutralizer	1 mL	22 mL	23688-55
pPb-5 Indicator Reagent Powder Pillows	1 pillow	20/pkg	23689-64
pPb-6 Decolorizer	3 drops	10 mL SCDB	23748-20

REQUIRED APPARATUS

Adapter, AccuVac	1	each	43784-00
Beaker, polypropylene, 250 mL	1	each	1080-46
Beaker, polypropylene, 150 mL	1	each	1080-44
Clamp, two-prong extension	1	each	21145-00
Clamp, holder	1	each	326-00
Clippers, small	1	each	936-00
Cylinder, graduated, polypropylene, 100 mL	1	each	1081-42
Cylinder, graduated, polypropylene, 25 mL	1	each	1081-40
Dropper, DPDE, 0.5 & 1.0-mL marks	3	10/pkg	21247-10
Pipet Tip, for 100 µl Pipetter	varies	10/pkg	22754-10
pPb Fast Column Extractor	1	each	23749-00
Sample Cell, 10-mL, with cap	2	each	21228-00
Support, ring stand	1	each	563-00
Syringe Plunger	1	each	23764-00

OPTIONAL REAGENTS

Description	Unit	Cat. No.
Lead Standard Solution, 1000 mg/L	100 mL	12796-42
Lead Standard Solution, Voluette ampule, 50 mg/L as Pb^{2+}, 10 mL	16/pkg	14262-10
Lead Standard Solution, 10 mg/L	25 mL	23748-20
Nitric Acid, ACS	500 mL	152-49
Nitric Acid Standard Solution, 0.1 N	100 mL	23328-42
pPb-1 Acid Preservative Reagent	237 mL	23685-31
Sodium Hydroxide Standard Solution, 5.0 N	1 L	2450-53
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Ampule Breaker Kit	each	21968-00
Bottle, sampling, 125 mL	each	23240-43
Bottle, sampling, 125 mL	48/pkg	23240-73
Bottle, sampling, 1000 mL	each	23242-53
Bottle, sampling, 1000 mL	24/pkg	23242-83
Dropper, 0.5 & 1.0 mL	10/pkg	21247-10
Flask, volumetric, plastic, 100 mL	each	20995-42
Flask, volumetric, plastic, 1000 mL	each	20995-53
pH Meter, *sension™1*, portable	each	51700-10
Pipet, serological, 5 mL	each	532-37
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet.	50/pkg	21856-96
Pipet, volumetric, Class A, 1.0 mL	each	14515-35
Pipet, volumetric, Class A, 5.0 mL	each	14515-37
Pipet Filler, 3-valve	each	12189-00
Pipetter, 100 µL	each	22753-00
Stopper, hollow	6/pkg	14480-00

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

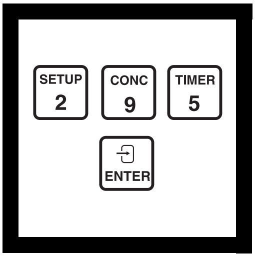
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8034

MANGANESE, HR (0 to 20.0 mg/L)

For water and wastewater

Periodate Oxidation Method* ;USEPA approved for reporting wastewater analysis (digestion is required; see Section II)**



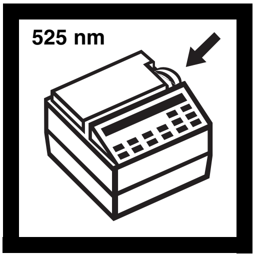
1. Enter the stored program number for manganese (Mn) periodate oxidation.

Press: **2 9 5 ENTER**

The display will show:

Dial nm to 525

Note: *The Pour-Thru Cell can be used with 25-mL reagents only.*



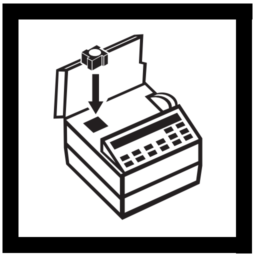
2. Rotate the wavelength dial until the small display shows:

525 nm

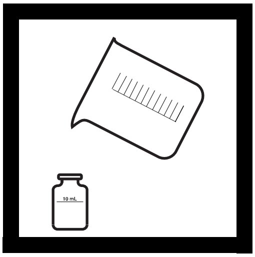
When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

then: **mg/L Mn HR**



3. Place the 10-mL cell riser into the cell compartment.



4. Fill a sample cell with 10 mL of sample.

Note: *Total manganese determination needs a prior digestion; use the mild digestion (Section II).*

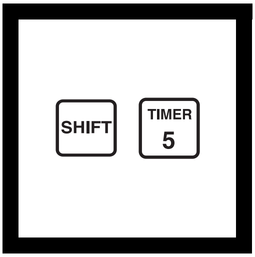
Note: *Adjust pH of stored samples before analysis.*

5. Add the contents of one Buffer Powder Pillow, citrate type. Swirl to mix.

6. Add the contents of one Sodium Periodate Powder Pillow to the sample cell (the prepared sample). Swirl to mix.

Note: *A violet color will form if manganese is present.*

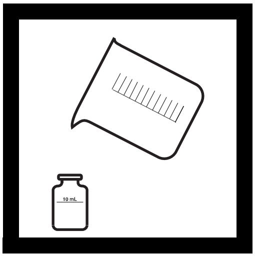
Note: *Accuracy is not affected by undissolved powder.*



7. Press:

SHIFT TIMER

A two-minute reaction period will begin.



8. When the timer beeps, the display will show:

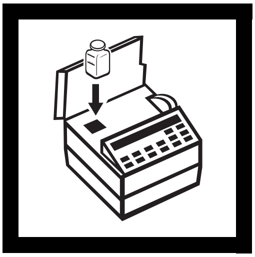
mg/L Mn HR

Fill another sample cell with 10 mL of sample (the blank).

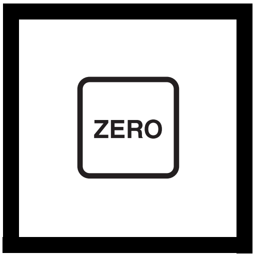
---

* Adapted from *Standard Methods for the Examination of Water and Wastewater.*

** *Federal Register*, 44 (116) 34193 (June 14, 1979).



9. Place the blank into the cell holder. Close the light shield.

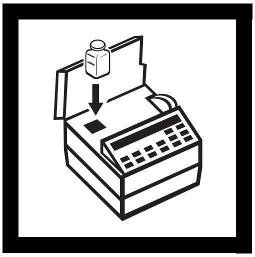


10. Press: **ZERO**

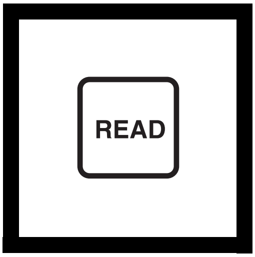
This display will show:

Zeroing. . .

then: **0.0 mg/L Mn HR**



11. Within eight minutes after the timer beeps, place the prepared sample into the cell holder. Close the light shield.



12. Press: **READ**

The display will show:

Reading. . .

then the result in mg/L Mn will be displayed.

Forms ▲▼ $KMnO_4$ Mn MnO_4^-

Sampling and Storage

Collect samples in acid-washed plastic bottles. Manganese may be lost by adsorption to glass container walls. Adjust the pH to less than 2 with nitric acid (about 2 mL per liter). Preserved samples may be stored up to six months at room temperature. Adjust the pH to 4 to 5 with 5.0 N sodium hydroxide before analysis. Do not exceed pH 5, as manganese may be lost as a precipitate. Correct the test result for volume additions; see *Correction for Volume Additions* in *Section I* for more information. If only dissolved Mn is to be determined, filter before acid addition.

Accuracy Check

Standard Additions Method

a) Fill three 25-mL graduated mixing cylinders with 25-mL of sample.

b) Snap the neck off a Manganese Voluette Ampule Standard Solution, 250 mg/L Mn.

c) Use the TenSette Pipet to add 0.1, 0.2 and 0.3 mL of standard, respectively, to the three mixing cylinders. Stopper each and mix thoroughly.

d) Transfer only 10 mL of each solution to the 10-mL sample cells.

e) Analyze each standard addition sample as described in the procedure. The manganese concentration should increase 1.0 mg/L for each 0.1 mL of standard added.

f) If these increases do not occur, see *Standard Additions* in *Section I* for troubleshooting information.

Standard Solution Method

Prepare a 10.0 mg/L manganese standard solution by pipetting 5.00 mL of Manganese Standard Solution, 1000 mg/L Mn, into a 500-mL volumetric flask. Dilute to the mark with deionized water. Or, prepare this standard by diluting 4.00 mL of a High Range Manganese Standard Voluette Ampule, 250 mg/L, to 100 mL. Prepare these solutions daily. Run the test using the 10.0 mg/L Manganese Standard Solution. Results should be between 9.0 and 11.0 mg/L Mn.

Interferences

The following may interfere when present in concentrations exceeding those listed below:

Calcium	700 mg/L
Chloride	70,000 mg/L
Iron	5 mg/L
Magnesium	100,000 mg/L

Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment; see *pH Interferences* in *Section I.*

Precision

In a single laboratory using a standard solution of 10.00 mg/L manganese and two representative lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±0.06 mg/L manganese.

Estimated Detection Limit (EDL)

The EDL for program 295 is 0.6 mg/L Mn. The EDL is the calculated lowest average concentration in deionized water matrix that is different from zero with a 99% level of confidence. For more information on derivation and use of Hach's estimated detection limit, see *Section I.*

Summary of Method

Manganese in the sample is oxidized to the purple permanganate state by sodium periodate, after buffering the sample with citrate. The purple color is directly proportional to the manganese concentration.

REQUIRED REAGENTS

	Cat. No.
High Range Manganese Reagent Set (100 tests) 10 mL	24300-00

Description	Quantity Required Per Test	Unit	Cat. No.
Buffer Powder Pillows, citrate type for manganese	1 pillow	100/pkg	21076-69
Sodium Periodate Powder Pillows for manganese	1 pillow	100/pkg	21077-69

REQUIRED APPARATUS

Description	Quantity Required Per Test	Unit	Cat. No.
Sample Cell, 10 mL, matched pair	2	2/pkg	24954-02
Cell Riser, 10 mL sample cell	1	each	45282-00

OPTIONAL REAGENTS

Description	Unit	Cat. No.
Hydrochloric Acid, 6 N	500 mL	884-49
Manganese Standard Solution, 1000 mg/L Mn	100 mL	12791-42
Manganese Standard Solution, Voluette ampule, High Range, 250 mg/L Mn, 10 mL	16/pkg	14258-10
Nitric Acid, ACS	500 mL	152-49
Nitric Acid Solution 1:1	500 mL	2540-49
Sodium Hydroxide Solution, 5.0 N	100 mL MDB	2450-32
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Description	Unit	Cat. No.
Ampule Breaker Kit	each	21968-00
Mixing Cylinder, 25 mL	each	20886-40
Dropper, plastic, 0.5 and 1.0 mL marks	10/pkg	21247-10
Flask, erlenmeyer, 250 mL	each	505-46
Flask, volumetric, Class A, 500 mL	each	26366-49
Flask, volumetric, Class A, 100 mL	each	14574-42
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
pH Meter, *sens*ion™*1*, portable	each	51700-10
Pipet, 4.0 mL, Class A	each	14515-04
Pipet, serological, 5 mL	each	532-37
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 5.00 mL	each	14515-37
Pipet Filler, safety bulb	each	14651-00

OPTIONAL 25 ML ANALYSIS ITEMS

Description	Unit	Cat. No.
High Range Manganese Reagent Set (100 tests) 25 mL	100/pkg	22432-00
Pour-Thru Cell Assembly Kit (for 25-mL reagents only)	each	45215-00
Sample Cell, 25 mL matched pair	pair	20950-00

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

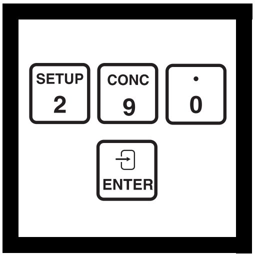
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8149

MANGANESE, LR (0 to 0.700 mg/L)

For water and wastewater

PAN Method*



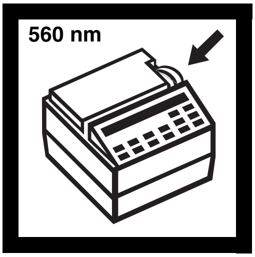
1. Enter the stored program number for manganese (Mn).

Press: **2 9 0 ENTER**

The display will show:

Dial nm to 560

Note: *The Pour-Thru Cell can be used with 25 mL reagents only.*



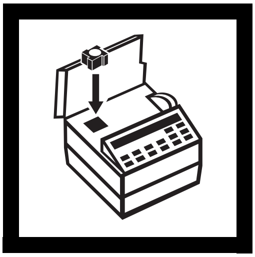
2. Rotate the wavelength dial until the small display shows:

560 nm

When the correct wavelength is dialed in, the display will quickly show:

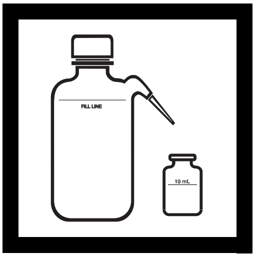
Zero Sample

then: **mg/L Mn LR**



3. Insert the 10-mL Cell Riser into the cell compartment.

Note: *Total manganese determination requires a prior digestion; see Digestion (Section II).*



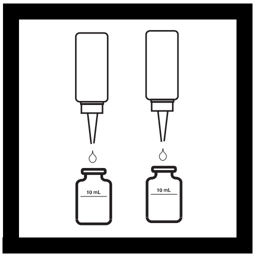
4. Fill a 10-mL sample cell with 10 mL of deionized water (this will be the blank).

Note: *Rinse all glassware with 1:1 Nitric Acid Solution. Rinse again with deionized water.*

5. Fill another 10 mL sample cell with 10 mL of sample (this will be the prepared sample).

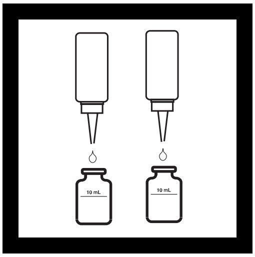
6. Add the contents of one Ascorbic Acid Powder Pillow to each cell. Swirl to mix.

Note: *For samples containing hardness greater than 300 mg/L $CaCO_3$, add four drops of Rochelle Salt Solution to the sample after addition of the Ascorbic Acid Powder Pillow.*



7. Add 15 drops of Alkaline-Cyanide Reagent Solution to each cell. Swirl to mix.

Note: *A cloudy or turbid solution may form in some samples after addition of the Alkaline-Cyanide Reagent Solution. The turbidity should dissipate after Step 8.*



8. Add 21 drops of PAN Indicator Solution, 0.1%, to each sample cell. Swirl to mix.

Note: *An orange color will develop in the sample if manganese is present.*

Note: *For 25-mL reagents, use 1 mL of each liquid reagent in Steps 7 and 8.*

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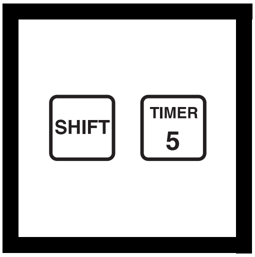
* Adapted from Goto, K., et al., Talanta, 24, 752-3 (1977).

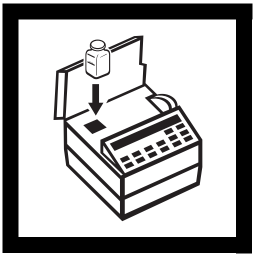


9. Press:

SHIFT TIMER

A two-minute reaction period will begin.

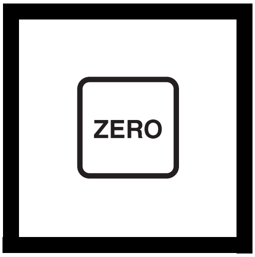
Note: *If the sample contains more than 5 mg/L iron, allow ten minutes for complete color development. To set the timer for ten minutes, press* **1000 SHIFT TIMER.**



10. When the timer beeps, the display will show:

mg/L Mn LR

Place the blank into the cell holder. Close the light shield.



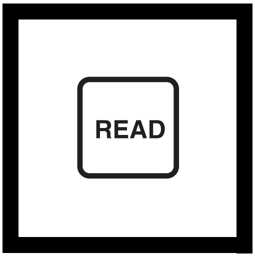
11. Press: **ZERO**

The display will show:

Zeroing. . . .

then:

0.000 mg/L Mn LR



12. Place the prepared sample into the cell holder. Close the light shield.

Press: **READ**

The display will show:

Reading. . . .

then the result in mg/L manganese will be displayed.

Forms ▲▼ $KMnO_4$, Mn, MnO_4^-

Note: *See Waste Disposal below for proper disposal of cyanide containing wastes.*

Sampling and Storage

Collect samples in a clean glass or plastic container. Adjust the pH to 2 or less with nitric acid (about 2 mL per liter). Preserved samples can be stored up to six months at room temperature. Adjust the pH to 4.0 to 5.0 with 5.0 N sodium hydroxide before analysis. Correct the test result for volume additions; see *Correction for Volume Additions* in *Section I.*

Accuracy Check

Standard Additions Method

Note: *Volume accuracy is very important when performing standard additions with 10-mL volumes. The fill mark on the 10-mL sample cell is not intended to measure standard addition volumes.*

a) Fill three 10-mL graduated mixing cylinders with 10.0 mL of sample.

b) Snap the neck off a Manganese Voluette Ampule Standard, 10 mg/L Mn.

c) Use the TenSette Pipet to add 0.1 mL, 0.2 mL and 0.3 mL of standard, respectively, to the three mixing cylinders. Stopper and mix each thoroughly.

d) Analyze each sample as described in the procedure. The manganese concentration should increase 0.1 mg/L for each 0.1 mL of standard added.

e) If these increases do not occur, see *Standard Additions* in *Section I* for more information.

Note: *An alternative to the above procedure is to measure 10.0 mL of sample into dry sample cells before performing standard additions. A volumetric pipet or a TenSette Pipet can be used to deliver the sample volume.*

Standard Solution Method

Prepare a 0.5 mg/L manganese standard solution as follows:

a) Pipet 5.00 mL of Manganese Standard Solution, 1000 mg/L Mn, into a 1000-mL volumetric flask.

b) Dilute to the mark with deionized water. Prepare this solution daily.

c) Pipet 10.00 mL of the above dilution into a 100-mL volumetric flask.

d) Dilute to the mark with deionized water. This second dilution is equivalent to 0.5 mg/L Mn.

Precision

In a single laboratory using a standard solution of 0.5 mg/L Mn and two representative lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±0.0049 mg/L Mn.

Interferences

The following do not interfere up to the indicated concentrations:

Aluminum	20 mg/L
Cadmium	10 mg/L
Calcium	1000 mg/L as $CaCO_3$
Cobalt	20 mg/L
Copper	50 mg/L
Iron	25 mg/L
Lead	0.5 mg/L
Magnesium	300 mg/L as $CaCO_3$
Nickel	40 mg/L
Zinc	15 mg/L

Waste Management

The alkaline cyanide solution contains cyanide. Cyanide solutions should be collected for disposal as reactive (D003) waste. Be sure cyanide solutions are stored in a caustic solution with pH > 11 to prevent release of hydrogen cyanide gas.

Summary of Method

The PAN method is a highly sensitive and rapid procedure for detecting low levels of manganese. An ascorbic acid reagent is used initially to reduce all oxidized forms of manganese to Mn^{2+}. An alkaline-cyanide reagent is added to mask any potential interferences. PAN Indicator is then added to combine with the Mn^{2+} to form an orange-colored complex.

REQUIRED REAGENTS

	Cat. No.
Manganese Reagent Set (50 Tests)	26517-00

Includes: (1) 14577-99, (1) 21223-26, (1) 21224-26, (1) 26058-02, (1) 12263-01

Description	Quantity Required Per Test	Unit	Cat. No.
Alkaline-Cyanide Reagent	30 drops	50 mL SCDB	21223-26
Ascorbic Acid Powder Pillows	2 pillows	100/pkg	14577-99
PAN Indicator Solution, 0.1%	42 drops	50 mL SCDB	21224-26
Water, deionized	10 mL	4 L	272-56

REQUIRED APPARATUS

Cell Riser, 10 mL	1	each	45282-00
Sample Cell, 10 mL, matched pair	2	pair	24954-02

OPTIONAL REAGENTS

Hydrochloric Acid Solution, 1:1 (6 N)	500 mL	884-49
Manganese Standard Solution, 1000 mg/L Mn	100 mL	12791-42
Manganese Standard Sol'n, PourRite Ampule, 10 mg/L Mn, 2 mL	20/pkg	26058-20
Nitric Acid Solution, 1:1	500 mL	2540-49
Rochelle Salt Solution.	29 mL	1725-33
Sodium Hydroxide Solution, 50%	500 mL	2180-49
Nitric Acid, ACS	500 mL	152-49

OPTIONAL APPARATUS

Ampule Breaker Kit	each	24846-00
Beaker, glass, 1000 mL	each	500-53
Cylinder, mixing, 10 mL	each	20886-38
Dropper, plastic calibrated, 1.0 mL	10/pkg	21247-10
Flask, volumetric, Class A, 1000 mL	each	14574-53
Flask, volumetric, Class A, 100 mL	each	14574-42
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 10.0 mL	each	14515-38
Pipet, volumetric, Class A, 5.0 mL	each	14515-37
Pipet Filler, safety bulb	each	14651-00

OPTIONAL 25 ML ANALYSIS ITEMS

Manganese Reagent Set (25 mL samples)	each	22433-00
Clippers, for opening powder pillows	each	968-00
Pour-Thru Cell Assembly Kit (for 25 mL reagents only)	each	45215-00
Sample Cell, 25 mL, matched pair	pair	20950-00

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 10065

MERCURY (0.1 to 2.5 µg/L)

For water and wastewater

Cold Vapor Mercury Concentration Method*

Phase 1: Sample Digestion- must be done in a fume hood! Toxic gases may be produced.

1. Transfer one liter of the sample to a 2000-mL erlenmeyer flask. Add a 50- mm magnetic stir bar to the sample. Place the flask on a magnetic stirring hot plate and begin stirring.

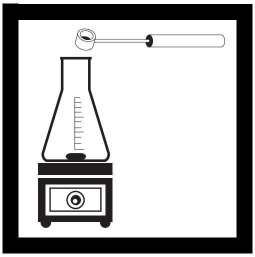
Note: *This procedure must be done in a fume hood. Toxic chlorine or other gases may be produced!*

Note: *Hach recommends using dedicated digestion glassware and sample cells for this procedure.*

2. Add 50 mL concentrated sulfuric acid to the sample.

Note: *Determine a reagent blank for each new lot of reagent by running the entire procedure, including the digestion, using one liter of deionized water instead of sample. Add the same amount of potassium permanganate as required by the sample. Subtract the reagent blank from each test result.*

3. Add 25 mL concentrated nitric acid to the sample.



4. Add 4.0 g of potassium persulfate to the sample. Stir until dissolved

Note: *Alternatively, add one 5-gram measuring scoop of potassium persulfate to the sample.*

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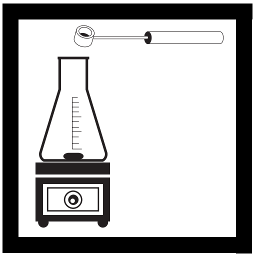
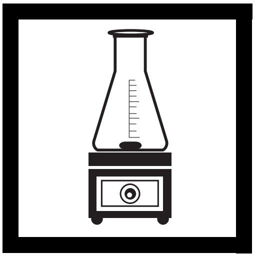
* U.S. Patent 573,378



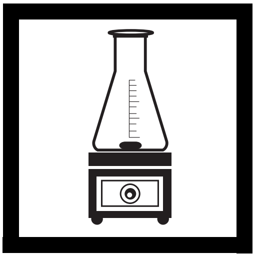
5. Add 7.5 g of potassium permanganate to the sample. Stir until dissolved.

Note: *Alternatively, add a 10-gram measuring scoop of potassium permanganate to the sample.*



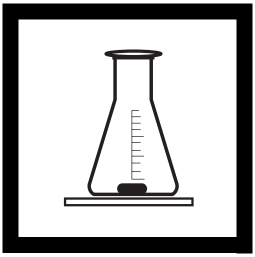
6. Cover the flask with a watch glass. Begin heating the sample to a temperature of 90 °C after the reagents have dissolved. **AVOID BOILING**.

Note: *For a mercury standard or reagent blank in distilled water the heat step is not necessary.*

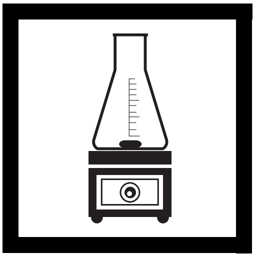


7. Continue to stir and heat the sample at 90 °C for two hours.

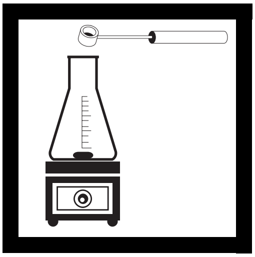
Note: *A dark purple color must persist throughout the two hour digestion. Some samples (sea waters, industrial effluents or samples high in organic matter or chloride concentration) require additional permanganate. It may be difficult to see a dark purple color if the sample contains a black/ brown manganese dioxide precipitate. You may add more potassium permanganate if the solution is not dark purple.*



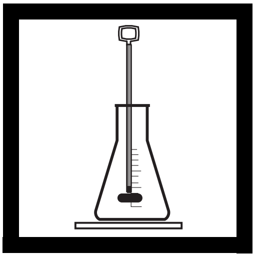
8. Cool the digested sample to room temperature. A brown/ black precipitate of manganese dioxide may settle during cooling. If the digested sample does not have a purple color, the digestion may be incomplete. Add more potassium permanganate.Return the sample to the magnetic stirring hot plate and continue digestion until a purple color persists.



9. Return the cool, digested sample to the cool, magnetic stirring hot plate. Turn the stirrer on.



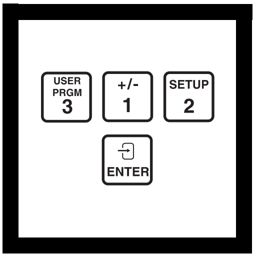
10. Using a 0.5-gram measuring spoon, add 0.5 g-additions of hydroxylamine-hydrochloride until the purple color disappears. Wait 30 seconds after each addition to see if the purple disappears. Add hydroxylamine-hydrochloride until all the manganese dioxide is dissolved.



11. Remove the stir bar.

12. The digested sample is now ready for processing by cold vapor separation and preconcentration. Proceed to Phase 2.

Phase 2: Cold Vapor Separation and Preconcentration of Mercury



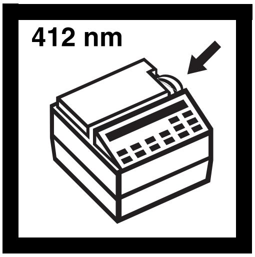
1. Enter the stored user program number for Cold Vapor Mercury.

Press: **312 ENTER**

The display will show:

Dial nm to 412

Note: *For a DR/2010 without this stored program, see Instrument Setup following these steps.*



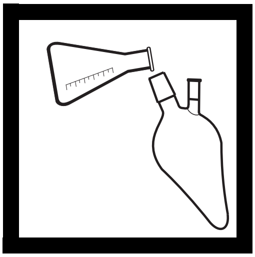
2. Rotate the wavelength dial until the small display shows:

412 nm

When the correct wavelength is dialed in, the display will quickly show:

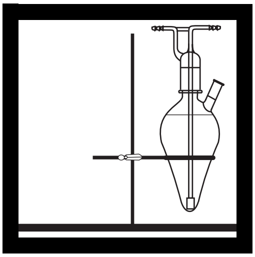
Zero Sample

then: **µg/L Hg CV**

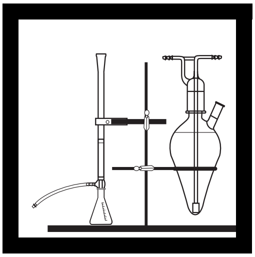


3. Transfer the digested sample to the Cold Vapor Gas Washing Bottle.

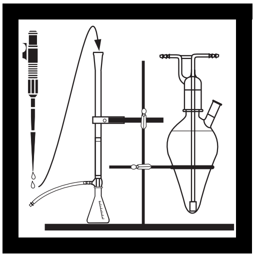
Note: *The volume of digested sample should contain 0.1 to 2.5 µg Hg.*



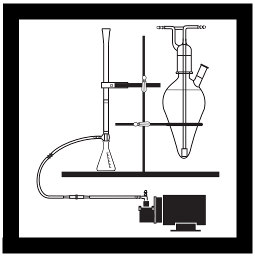
4. Set the Gas Washing Bottle in the support ring. Place the top on the Gas Washing Bottle. Wait until Step 11 to connect the mercury absorber column to the Gas Washing Bottle.



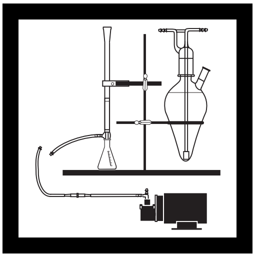
5. Connect the 100-mL erlenmeyer flask to the Mercury Absorber column.



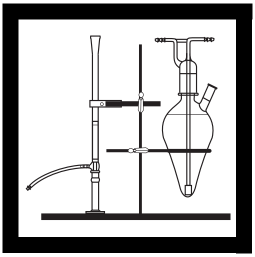
6. Pipet 8 mL of HgEX Reagent B into the Mercury Absorber column.



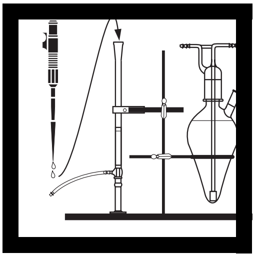
7. Connect the power to the vacuum pump and apply vacuum to the Mercury Absorber Column. Draw most of the HgEX Reagent B into the 100-mL erlenmeyer flask.



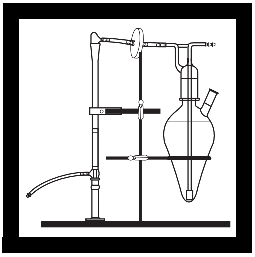
8. Disconnect the vacuum using the quick disconnect when HgEX Reagent B begins to drip from the inner delivery tube on the Mercury Absorber Column (about 10 seconds after starting the vacuum). Do not draw enough air through the column to begin drying the packing.



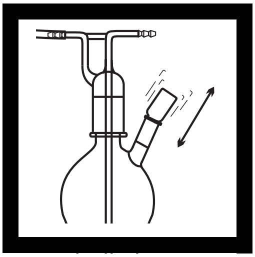
9. Remove the 100-mL erlenmeyer flask from the Mercury Absorber Column. Replace it with the 10-mL Distilling Receiver.



10. Pipet 2 mL of HgEX Reagent C into the Mercury Absorber Column.

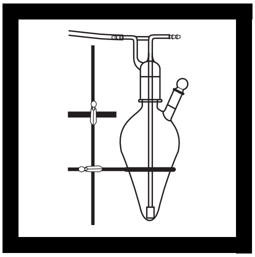


11. Connect the Mercury Absorber Column to the Gas Washing Bottle using the glass elbow.

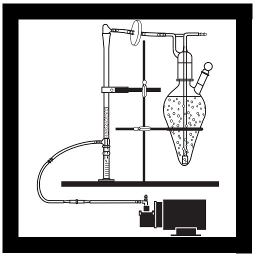


12. Shake an ampule of HgEX Reagent A to suspend the undissolved reagent. Open the ampule and gently shake the contents into the Gas Washing Bottle through the side neck.

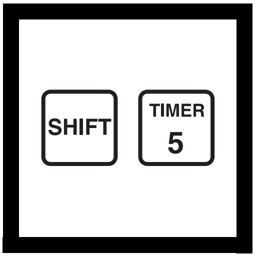
Note: *Shaking the ampule is not necessary if there is no undissolved reagent in the ampule.*



13. Stopper the side neck on the Gas Washing Bottle.



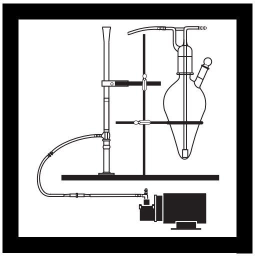
14. Reconnect the vacuum to the Mercury Absorber Column using the quick disconnect. The vacuum will pull HgEX Reagent C through the Mercury Absorber Column packing into the 10-mL receiver. Air bubbles should be produced at the gas dispersion tube in the Gas Washing Bottle.



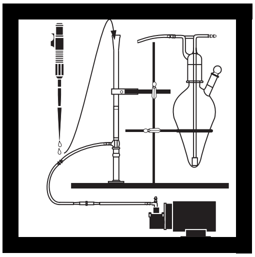
15. Press:
SHIFT TIMER

A five-minute reaction period will begin. Let the solution bubble for this period.

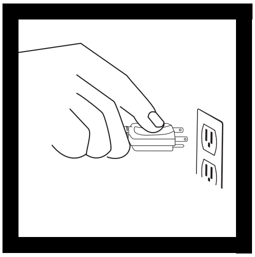
Note: *Air flow rate through the Gas Washing Bottle should be 1-5 liters per minute. Allow more time for lower air flow rates (i.e., if air flow rate is 1 liter/ minute, let the solution bubble for 10 minutes).*



16. After the timer beeps, remove the glass elbow from the top of the Mercury Absorber Column. Keep the vacuum pump on.

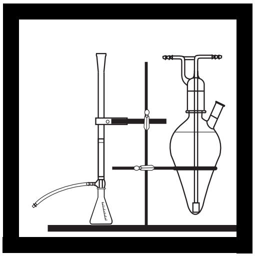


17. Pipet 8 mL of HgEX Reagent B into the Mercury Absorber Column to elute the captured mercury. Continue to apply vacuum to pull the HgEX Reagent B into the Distilling Receiver.

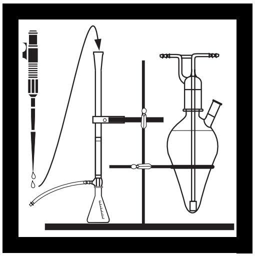


18. Turn off or disconnect power to the vacuum pump when the volume in the Distilling Receiver reaches the 10-mL mark.

Note: *If necessary, bring the volume in the Distilling Receiver up to 10 mL with HgEX Reagent B. To avoid low volumes, disconnect the vacuum a little sooner in Step 6. This leaves more HgEX Reagent B in the packing of the Mercury Absorber Column.*



19. Remove the Distilling Receiver from the Mercury Absorber Column. Reconnect the 100-mL erlenmeyer flask to the column.

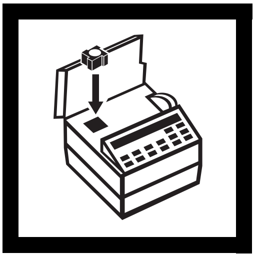


20. Pipet 3 mL of HgEX Reagent B into the Mercury Absorber Column (do not apply vacuum). This keeps the absorber packing wet between tests.

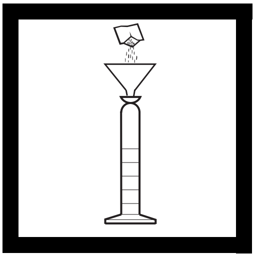
The Mercury Absorber Column eluate in the Distilling Receiver is ready for analysis.

Proceed to Phase 3.

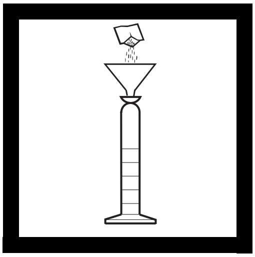
Phase 3: Colorimetric Analysis



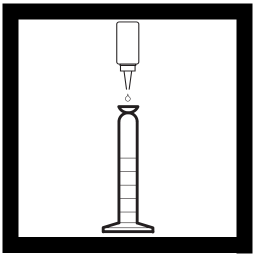
1. Insert the 10-mL Cell Riser into the sample cell compartment.



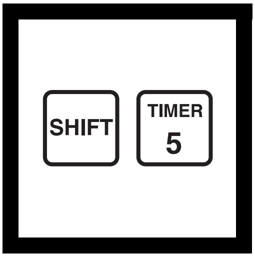
2. Using the funnel provided, add the contents of one HgEX Reagent 3 foil pillow to the eluate in the Distilling Receiver. Stopper the receiver. Invert the receiver to dissolve the reagent.



3. Add the contents of one HgEX Reagent 4 foil pillow to the Distilling Receiver using the funnel provided. Stopper the receiver. Invert the receiver to dissolve the reagent.

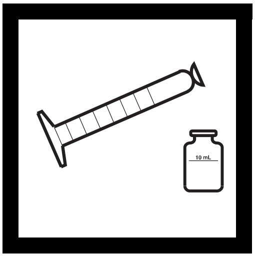


4. Add 8 drops of HgEX Reagent 5 to the Distilling Receiver. Stopper the Receiver. Invert to mix.



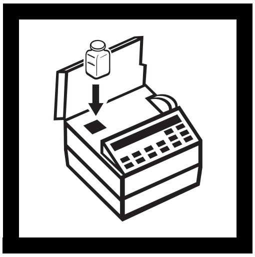
5. Press: **SHIFT TIMER**

A 2-minute reaction period will begin.

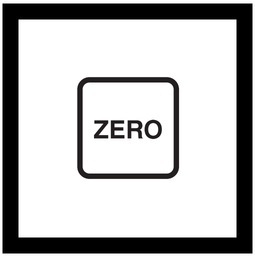


6. During the reaction period, transfer the solution to a 10-mL sample cell. Wipe the sample cell sides with a clean tissue.

Note: *The Pour-Thru Cell cannot be used with this procedure.*



7. After the timer beeps, place the prepared sample into the cell holder and close the light shield.



8. Press: **ZERO**

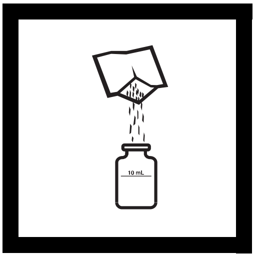
The display will show:

Zeroing. . .

then:

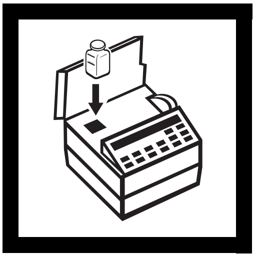
0.1 µg/L Hg CV

Note: *This program uses a non-zero intercept.*



9. Remove the cell from the cell holder. Add the contents of one HgEX Reagent 6 foil pillow to the solution. Swirl the cell until the reagent is completely dissolved. Immediately go to Step 10.

Note: *Do not use the funnel to add HgEX Reagent 6 to the sample cell. Any HgEX Reagent 6 in the funnel will make mercury undetectable in subsequent tests.*



10. Return the sample cell to the cell holder. Close the light shield.

Press: **READ**

The display will show

Reading...

Then the results in µg/L mercury will be displayed. This is the concentration of mercury in the original sample.

Sampling and Storage

Collect 1000 mL of sample in an analytically clean, glass or polyethylene terephthalate (PET) container. Add 10 mL of concentrated hydrochloric acid to preserve the sample before sample collection. Fill the container completely full to minimize air space when closed. Close a glass container with a ground glass stopper. Close a PET container with a PET cap or a polypropylene cap (no liner).

Store aqueous samples at 2-6 °C. Acid-preserved samples are stable for at least 6 months.

Accuracy Check

Standard Additions Method

a) Use a TenSette® pipet to add 0.10 mL of a 12.5 mg/L Mercury Standard Solution to the purged solution in the Gas Washing Bottle after an analysis has been performed. Immediately stopper the Gas Washing Bottle.

b) Begin at Step 5 of Phase 2. Follow the procedure steps.

c) Test the eluate as described in Phase 3. The displayed concentration should be between 1.1-1.4 µg/L Hg.

Standard Solution Method

a) Transfer 800 mL of deionized water into the Gas Washing Bottle.

b) Add 50 mL of concentrated sulfuric acid and 25 mL of concentrated nitric acid to the water. Swirl to mix.

c) Prepare a 0.1-mg/L mercury standard solution by serially diluting a 1000-mg/L Mercury Standard Solution:

- To make a 10.0-mg/L standard, add 1.0 mL of concentrated nitric acid to a 500-mL volumetric flask. Dilute 5.00 mL of a 1000 mg/L standard to 500 mL with deionized water. Mix well.
- To make a 1.0-mg/L standard solution, add 0.2 mL of concentrated nitric acid to a 100-mL volumetric flask. Dilute 10.00 mL of the 10.0-mg/L standard to 100 mL with deionized water. Mix well.
- To make a 0.1-mg/L standard solution, add 0.2 mL of concentrated nitric acid to a 100-mL volumetric flask. Dilute 10.00 mL of the 1.0-mg/L standard to 100 mL with deionized water. Mix well.

d) Pipet 10.0 mL of the 0.1-mg/L mercury standard solution into the Gas Washing Bottle. Swirl to mix.

e) Begin at Step 4 of Phase 2. Follow the procedure steps.

f) Test the eluate as described in Phase 3. The displayed concentration should be between 0.9-1.1 µg/L Hg.

System Start Up

Hach recommends that the analyst perform a few analyses on mercury standards and blanks for system equilibration before beginning sample testing. This allows the system to stabilize before processing samples.

Startup Standard

Test a mercury standard solution by following the procedure under Accuracy Check using the Standard Solution Method. Continue with step g (below) if the value is not within specified limits.

g) Pipet 10.0 mL of the 0.1-mg/L mercury standard solution into the purged solution in the Gas Washing Bottle. Immediately stopper the Gas Washing Bottle.

h) Begin at Step 5 of Phase 2. Follow the procedure steps.

i) Test the eluate as described in Phase 3. The displayed concentration should be between 0.9-1.1 µg/L Hg. Repeat steps g-i if the value is not within these limits.

Startup Blank

Run a system blank by using the purged solution in the Gas Washing Bottle after a satisfactory test of the Startup Standard has been completed.

j) Leave the purged solution in the Gas Washing Bottle. Do not add an aliquot of mercury standard.

k) Begin at Step 5 of Phase 2. Follow the procedure steps.

l) Test the eluate as described in Phase 3. The displayed concentration should be ≤0.2 µg/L Hg. Repeat the Startup Blank procedure until a reproducible value is obtained.

Method Performance

Precision

In a single laboratory using a standard solution of 1.00 µg/L Hg and two representative lots of reagent with a DR/2010, a single operator obtained a mean value of 0.95 µg/L Hg and a standard deviation of ±0.05 µg/L Hg for nine replicates.

Estimated Detection Limit

The estimated detection limit for the Cold Vapor Mercury method is 0.1 µg/L Hg.

Interferences

Standards were used to prepare a single test solution with the following matrix. A second test solution containing only mercury at the same concentration was prepared as the control. The two solutions were digested then analyzed concurrently. There was no interference from the matrix of the test solution at the concentrations listed:

Ion or Substance	Concentration	Ion or Substance	Concentration
Ag^+	7 mg/L Ag^+	Fe^{+2}	100 mg/L Fe^{+2}
Al^{+3}	10 mg/L Al^{+3}	Hg^{+2}	1 µg/L Hg^{+2}
Au^{+3}	500 µg/L Au^{+3}	Mo^{+6}	10 mg/L Mo^{+6}
Cd^{+2}	10 mg/ L Cd^{+2}	Ni^{+2}	10 mg/L Ni^{+2}
Co^{+2}	10 mg/L Co^{+2}	NO_3^--N	50 mg/L NO_3^--N
Cr^{+6}	10 mg/L Cr^{+6}	Pb^{2+}	10 mg/L Pb^{2+}
Cu^{+2}	10 mg/L Cu^{+2}	SiO_2	100 mg/L SiO_2
F^-	1.0 mg/L F^-	Zn^{+2}	10 mg/L Zn^{+2}

In addition, no interference occurred with a test solution containing 1000 mg/L Na^+, 1000 mg/L K^+, 1000 mg/L Mg^{2+}, and 400 mg/L Ca^{2+}.

Storage and Maintenance of the Cold Vapor Mercury Apparatus

Storage

Store the apparatus as follows for fastest system stabilization and greatest sensitivity:

- Store the Gas Washing Bottle filled with deionized water containing 15 mL of concentrated sulfuric acid. Seal the bottle with the Gas Washing Bottle stopper and top.
- Store the Mercury Absorber Column with the packing wetted with HgEX Reagent B. The erlenmeyer flask should be kept attached underneath the column. The top of the Mercury Absorber column should be attached to the Gas Washing Bottle with the glass elbow as in the procedure.

Glassware Care

Hach recommends using dedicated glassware and sample cells because of the sensitivity of this procedure. Thoroughly clean the glassware and sample cells between tests. After washing, rinse with 1:1 hydrochloric acid solution, then rinse several times with deionized water.

Maintaining the System

- With proper care and storage, the Mercury Absorber Column may be used an unlimited number of times.
- Replace the Mercury Scrubber in the air trap housing at least once for every reagent set used.
- Moisture build up on the Gas Washing Bottle side of the Acro® 50 Vent Filter will reduce the purging air flow rate. If this occurs replace the filter or dry it in an oven at 110 °C.

Summary of Method

The sample is digested to convert all forms of mercury in the sample to mercuric (Hg^{2+}) ions. The mercuric ions in the digested sample are converted to mercury vapor in a semi-closed system. The vapor is carried into a chemically activated absorber column by ambient air where the mercury vapor is converted to mercuric chloride.

The mercuric chloride is eluted off the column and a sensitive indicator is added. The instrument is zeroed using the absorbance peak of the unreacted indicator. A complexing agent is added to break the mercury:indicator complex. The increase in unreacted indicator causes an increase in absorbance which is proportional to the amount of mercury in the original sample.

Safety

Wear personal protective equipment such as safety glasses with side shields, or a face shield to protect your eyes. Use other protective equipment as necessary (such as a fume hood) to avoid chemical exposure. Perform all steps exactly as prescribed in the procedure.

Waste Disposal

Proper management and disposal of waste is the responsibility of the waste generator. Hach Company provides waste disposal information as a guideline only. It is up to the generator to arrange for proper disposal and comply with applicable local, state, and federal regulations governing waste disposal. Hach Company makes no guarantees or warranties, express or implied, for the waste disposal information represented in this procedure.

1. Dispose of the solution in the Gas Washing Bottle by neutralizing the solution to a pH of 6-9 and flushing to the sanitary sewer with water for several minutes.

2. The mercury contained in one liter of sample is concentrated by a factor of 100 by the Mercury Absorber Column. Mercury analysis within the range of the test may produce a solution in the sample cell that is above the RCRA Toxicity Characteristic limit of 0.20 mg/L Hg. The sample cell will contain 0.25 mg/L mercury if the original sample was at 2.5 µg/L mercury (the upper limit of the test range). Dispose of the solution in the sample cell as a hazardous waste if the test result was greater than 2 µg/L mercury in the original sample. Otherwise, pour the solution into the sanitary sewer and flush with water for several minutes.

3. The mercury scrubber will capture mercury vapor if the Mercury Absorber Column is not properly activated using HgEX Reagent B and HgEx Reagent C. In addition, mercury is also captured if the capacity of the Absorber Column is exceeded. If the Mercury Scrubber has captured mercury vapor, it must be disposed of according to applicable regulations.

REQUIRED REAGENTS

Description	Cat. No.
Cold Vapor Mercury Reagent Set (25 tests)	26583-00

Description	Quantity Required Per Test	Unit	Cat. No.
HgEX Reagent A, Stannous Sulfate Sol’n Ampules	1	25/pkg	26588-25
HgEX Reagent B, Sulfuric Acid Solution	19 mL	500 mL	26589-49
HgEX Reagent C, Sodium Hypochlorite Solution	2 mL	55 mL	26590-59
HgEX Reagent 3, Alkaline Reagent Powder Pillows	1 pillow	25/pkg	26584-48
HgEx Reagent 4, Indicator Powder Pillows	1 pillow	25/pkg	26585-48
HgEx Reagent 5, Hydroxide Solution	8 drops	10 mL SCDB	26586-36
HgEx Reagent 6, Complexing Reagent Pillows	1 pillow	25/pkg	26587-48
Mercury Scrubber	2/reagent set	2/pkg	26558-00

DIGESTION REAGENTS

Hydroxylamine Hydrochloride, ACS	varies	113 g	246-14
Nitric Acid, ACS	25 mL	500 mL	152-49
Potassium Permanganate, ACS	varies	454 g	168-01
Potassium Persulfate, ACS	4.0 g	454 g	26175-01
Sulfuric Acid, ACS	50 mL	4 kg	979-09

REQUIRED APPARATUS

Description	Quantity Required Per Test	Unit	Cat. No.
Cold Vapor Mercury Apparatus Set			26744-00
Acro® 50 Vent Filter	1	18/pkg	26833-18
Air Trap Housing	1	each	26639-00
Ampule Breaker	1	each	25640-00
Breaker/Capper Tool for Mercury Scrubber	1	each	26640-00
C-flex Tubing, 0.25” ID, white	4 ft	25 ft	23273-67
Cell Riser, DR/2010	1	each	45282-00
Clamp for Mercury Absorber Column	1	each	26562-00
Cylinder, 50 mL	1	each	508-41
Distilling Receiver, 10 mL	1	each	26554-38
Erlenmeyer Flask, 100 mL	1	each	26553-42
Funnel	1	each	25843-35
Gas Washing Bottle, 1200 mL	1	each	26622-00
Glass Elbow, with hose adapter	1	each	26552-00
Mercury Absorber Column	1	each	26555-10
Pump, vacuum, 115 V	1	each	14697-00
Pump, vacuum, 220 V	1	each	14697-02
Rod Clamp	2	each	326-00
Support Ring for Gas Washing Bottle	1	each	26563-00
Stopper, for Distilling Receiver	1	each	26559-00
Stopper, for Gas Washing Bottle	1	each	26623-00
Support Base and Rod	1	each	329-00
TenSette Pipet, 0.1-1.0 mL	1	each	19700-01
TenSette Pipet, 1.0-10.0 mL	1	each	19700-10
TenSette Pipet tips, for 19700-01	varies	50/pkg	21856-96
TenSette Pipet tips, for 19700-10	varies	50/pkg	21997-96
Tubing Quick Disconnect, HDPE	1	12/pkg	14810-00

DIGESTION APPARATUS

Description	Quantity Required Per Test	Unit	Cat. No.
Flask, Erlenmeyer, 2000 mL	1	each	24894-54
Hot Plate/Stirrer, 120 V	1	each	23442-00
Hot Plate/Stirrer, 240 V	1	each	23442-02
Spoon, measuring, 0.5 g	1	each	907-00
Stir Bar	1	each	20953-55
Thermometer, -20 to 110 °C	1	each	566-01
Watch Glass	1	each	578-67

OPTIONAL REAGENTS

Description	Unit	Cat. No.
Hydrochloric Acid, ACS	500mL	134-49
Mercury Standard Solution, 12.5 mg/L Hg (NIST)	100 mL	2389-42
Mercury Standard Solution, 1000 mg/L Hg (NIST)	100 mL	14195-42
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Description	Unit	Cat. No.
Analytical Balance, 115 V	each	26103-00
Analytical Balance, 230 V	each	26103-02
Cylinder, graduated, 1000 mL, with handle	each	26129-53
Flask, volumetric, Class A, 500 mL	each	14574-49
Flask, volumetric, Class A, 100 mL	each	14574-42
Incoming Air Filtration Apparatus	each	26846-00
Pipet, volumetric, Class A, 10.00 mL	each	14515-38
Pipet, volumetric, Class A, 5.00 mL	each	14515-37
Pipet, volumetric, Class A, 1.00 mL	each	14515-35
Pipet Filler	each	14651-00
Spoon, measuring, 5 g	each	26572-05
Spoon, measuring, 10 g	each	26572-10
Stir Bar Retriever	each	15232-00

For technical support and ordering information, see Section V.

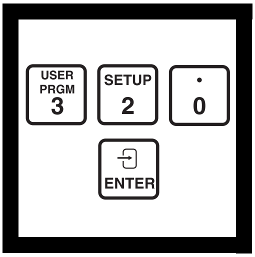
In the U.S.A. call 800-227-4224 to place an order.
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8036

MOLYBDENUM, MOLYBDATE, HR (0 to 35.0 mg/L)

Mercaptoacetic Acid Method*

For water and wastewater



1. Enter the stored program number for high range molybdenum (Mo^{6+}).

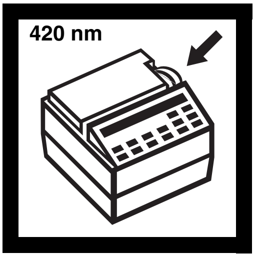
Press: **3 2 0 ENTER**

The display will show:

Dial nm to 420

Note: *Collect samples in glass or plastic bottles.*

Note: *The Pour-Thru cell can be used with 25-mL reagents only.*



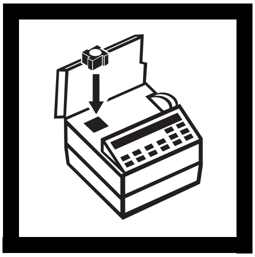
2. Rotate the wavelength dial until the small display shows:

420 nm

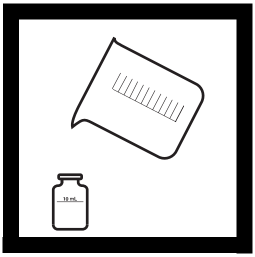
When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

then: **mg/L Mo^{6+} HR**



3. Place the 10-mL cell riser into the cell compartment.



4. Fill a sample cell with 10 mL of sample.

Note: *Filter turbid samples.*

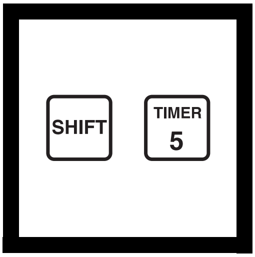
Note: *Adjust pH of stored samples before analysis.*

5. Add the contents of one MolyVer 1 Reagent Powder Pillow. Swirl to mix.

6. Add the contents of one MolyVer 2 Reagent Powder Pillow. Swirl to mix.

7. Add the contents of one MolyVer 3 Reagent Powder Pillow. Swirl to mix. This is the prepared sample.

Note: *Molybdenum will cause a yellow color to form.*



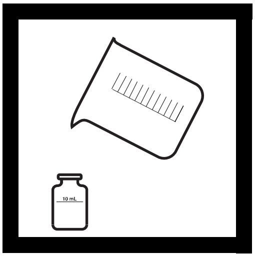
8. Press:

SHIFT TIMER

A five-minute reaction period will begin.

---

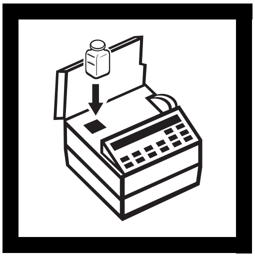
* Adapted from Analytical Chemistry, 25(9) 1363 (1953).



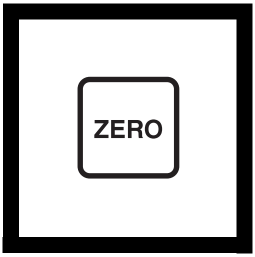
9. When the timer beeps, the display will show:

mg/L Mo^{6+} HR

Fill a second sample cell with 10 mL of sample (the blank).



10. Insert the blank into the cell holder. Close the light shield.



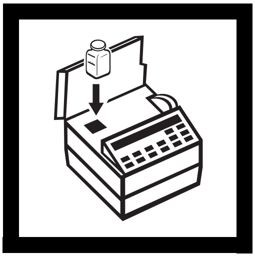
11. Press: **ZERO**

The display will show:

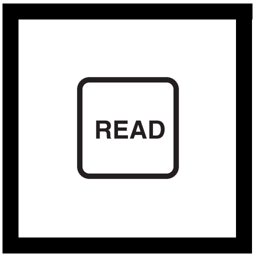
Zeroing. . . .

then:

0.0 mg/L Mo^{6+} HR



12. Place the prepared sample into the cell holder. Close the light shield.



13. Press: **READ**

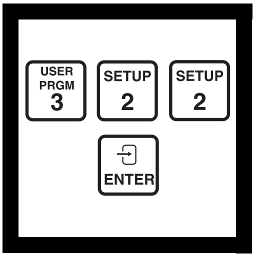
The display will read:

Reading. . . .

then the results in mg/L molybdenum will be displayed.

Forms ▲▼
Na_2MoO_4
Mo^{6+}
MoO_4^{2-}

Using AccuVac Ampuls

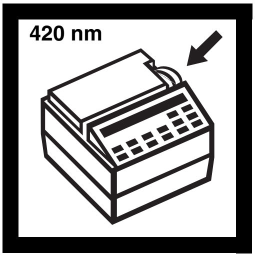


1. Enter the stored program number for high range molybdenum (Mo^{6+}) using AccuVac Ampuls.

Press: **3 2 2 ENTER**

The display will show:

Dial nm to 420



2. Rotate the wavelength dial until the small display reads:

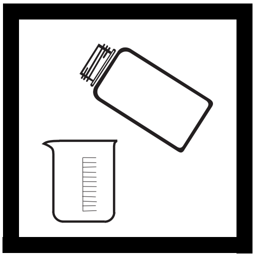
420 nm

When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

then:

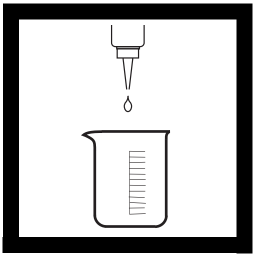
mg/L Mo^{6+} HR AV



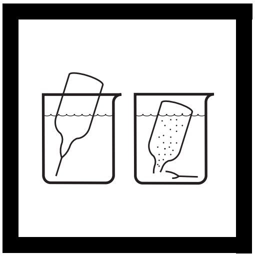
3. Collect at least 40 mL of sample in a 50-mL beaker.

Note: *Filter turbid samples.*

Note: *Adjust the pH of stored samples before analysis.*

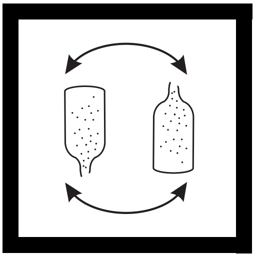


4. Add 4 drops of 0.4 M CDTA Solution to the beaker. Swirl to mix.



5. Fill a MolyVer 6 AccuVac Ampul with sample.

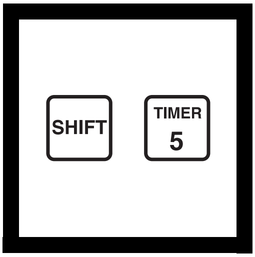
Note: *Keep the tip immersed while the ampul fills.*



6. Invert the ampul repeatedly to mix.

Note: *If molybdenum is present a yellow color will develop.*

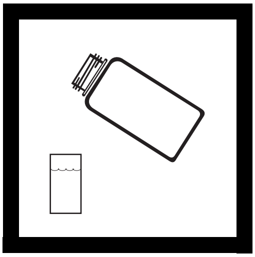
Note: *Undissolved reagent will not affect the result.*



7. Press:

SHIFT TIMER

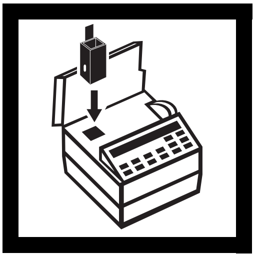
A five-minute reaction period will begin.



8. When the timer beeps, the display will show:

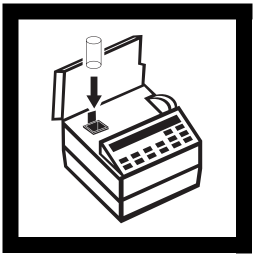
mg/L Mo^{6+} HR AV

Fill a Zeroing Vial with at least 10 mL of the original sample (the blank).

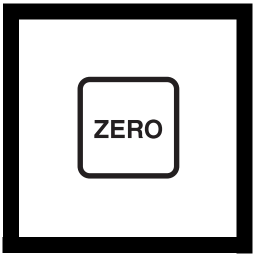


9. Place the AccuVac Vial Adapter into the cell holder of the instrument.

Note: *Place the grip tab toward the back of the instrument.*



10. Insert the blank into the cell holder. Close the light shield.



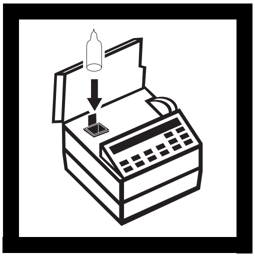
11. Press: **ZERO**

The display will show:

Zeroing. . . .

then:

0.0 mg/L Mo^{6+} HR AV



12. Place the prepared sample into the cell holder. Close the light shield.

Press: **READ**

The display will show:

Reading. . . .

then the result in mg/L molybdenum will be displayed.

Forms ▲▼ Na_2MoO_4 Mo^{6+} MoO_4^{2-}

Sampling and Storage

Collect samples in clean glass or plastic bottles. Adjust the pH to 2 or less with nitric acid (about 2 mL per liter). Preserved samples can be stored up to 6 months at room temperature. Adjust the pH to 7 with 5.0 N sodium hydroxide before analysis. Correct the test result for volume additions; see *Volume Additions* (*Section I*) for more information.

Accuracy Check

Standard Additions Method

a) Fill three 25-mL graduated mixing cylinders with 25 mL of sample.

b) Snap the neck off a Molybdenum Voluette Ampule Standard Solution, 500 mg/L Mo^{6+}.

c) Use the TenSette Pipet to add 0.1, 0.2 and 0.3 mL of standard, respectively, to the three mixing cylinders. Stopper each and mix thoroughly.

d) For analysis with AccuVacs, transfer solutions to dry, clean 50-mL beakers. For analysis with powder pillows, transfer only 10 mL of solution to the 10-mL sample cells.

e) Analyze each standard addition sample as described in the procedure. The molybdenum concentration reading should increase 2.0 mg/L for each 0.1 mL of standard added.

f) If these increases do not occur, see *Standard Additions* in *Section I* for troubleshooting information.

Standard Solution Method

To assure the accuracy of the test, use a Molybdenum Standard Solution, 10.0 mg/L Mo^{6+}. Follow the procedure for powder pillows or AccuVacs. Results should be between 9.0 and 11.0 mg/L Mo^{6+}.

Precision

In a single laboratory using standard solutions of 10.0 mg/L Mo^{6+} and two representative lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±0.07 mg/L Mo^{6+}.

In a single laboratory using standard concentrations of 20.0 mg/L Mo^{6+} and two representative lots of AccuVac reagents with the DR/2010, a single operator obtained a calibration curve with a 99% confidence interval of ±0.07 mg/L Mo^{6+}.

Interferences

Samples containing 10 mg/L copper or more will exhibit an increasing positive interference upon standing. Read these samples as soon as possible after the five-minute reaction period.

Aluminum, iron and nickel do not interfere at concentrations up to 50 mg/L. Chromium does not interfere at concentrations up to 1000 mg/L.

Interference from nitrite up to 2000 mg/L as NO_2^- can be eliminated by adding one Sulfamic Acid Powder Pillow per 25 mL of sample before beginning the procedure for either powder pillows or AccuVacs.

Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment; see *pH Interferences* in *Section I.*

Summary of Method

MolyVer 1 and 2 Reagents are added to buffer and condition the sample. MolyVer 1 contains a buffer to control the pH in addition to a chelating agent to mask interferences. MolyVer 3 provides the mercaptoacetic acid which reacts with molybdate molybdenum to form a yellow color proportional to the molybdenum concentration.

REQUIRED REAGENTS (FOR POWDER PILLOWS)

	Cat. No.
Molybdenum Reagent Set, 10 mL (100 Tests)	26041-00

Includes (1) 26042-99, (1) 26043-99, (1) 26044-99

Description	Quantity Required Per Test	Unit	Cat. No.
MolyVer 1 Reagent, Powder Pillows	1 pillow	100/pkg	26042-99
MolyVer 2 Reagent, Powder Pillows	1 pillow	100/pkg	26043-99
MolyVer 3 Reagent, Powder Pillows	1 pillow	100/pkg	26044-99

REQUIRED REAGENTS (FOR ACCUVAC)

CDTA Solution 0.4M		15 mL	26154-36
MolyVer 6, AccuVac Ampules		25/pkg	25220-25

REQUIRED APPARATUS (FOR POWDER PILLOWS)

Sample cell, 10 mL, matched pair		2/pkg	24954-02
Cell Riser, for 10-mL sample cell		each	45282-00

REQUIRED APPARATUS (FOR ACCUVAC)

Adapter, AccuVac Vial	1	each	43784-00
Beaker, 50 mL	2	each	500-41
Vial, Zeroing	1	each	21228-00

OPTIONAL REAGENTS

Molybdenum Standard Solution, 10 mg/L Mo^{6+}		100 mL.	14187-42
Molybdenum Standard Solution, Voluette ampule, 500 mg/L Mo^{6+}, 10 mL		16/pkg	14265-10
Nitric Acid, ACS		500 mL	152-49
Sodium Hydroxide, 5.0 N		100 mL MDB	2450-32
Sulfamic Acid Powder Pillows		100/pkg	1055-99
Water, deionized		4 L	272-56

OPTIONAL APPARATUS

Description	Unit	Cat. No.
Ampule Breaker Kit	each	21968-00
Cylinder, mixing, graduated, 25 mL	each	20886-40
Filter Paper, folded, 12.5 cm	100/pkg	1894-57
Flask, erlenmeyer, 250 mL	each	505-46
Funnel, poly, 65 mm	each	1083-67
Pipet, serological, 5 mL	each	532-37
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Snapper Kit, AccuVac	each	24052-00

OPTIONAL ANALYSIS 25 ML ITEMS

Molybdenum Reagent Set (100 tests) 25 mL	each	22434-00
Pour-Thru Cell Assembly kit (for 25 mL reagents only)	each	45215-00
Sample Cell, 25 mL, matched pair	pair	20950-00

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

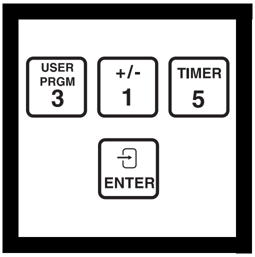
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8169

MOLYBDENUM, MOLYBDATE, LR (0 to 3.00 mg/L)

Ternary Complex Method

For boiler and cooling tower waters



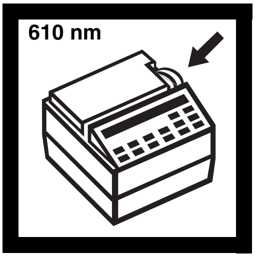
1. Enter the stored program number for molybdate molybdenum (Mo^{6+}), low range.

Press: **3 1 5 ENTER**

The display will read:

Dial nm to 610

Note: *The Pour-Thru Cell can not be used.*



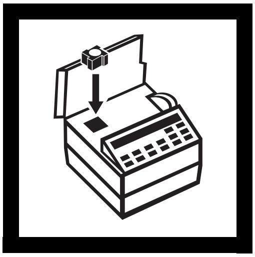
2. Rotate the wavelength dial until the small display reads:

610 nm

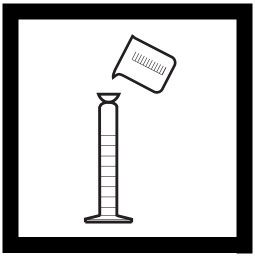
When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

then: **mg/L Mo^{6+} LR**

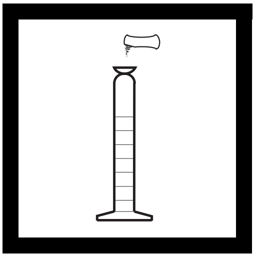


3. Insert the 10-mL Cell Riser into the sample cell compartment.

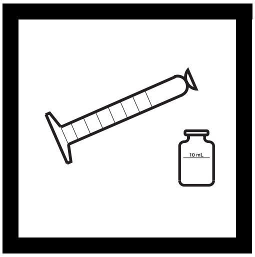


4. Fill a 25-mL mixing graduated cylinder with 20 mL of the water to be tested.

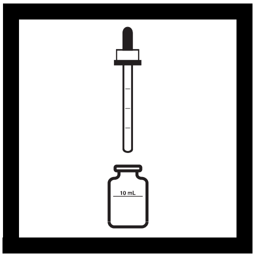
Note: *Filter turbid samples using the labware listed under Optional Apparatus.*



5. Add the contents of one Molybdenum 1 Reagent Powder Pillow to the graduated cylinder. Stopper, and shake the graduated cylinder to dissolve the reagents. This is the prepared sample.

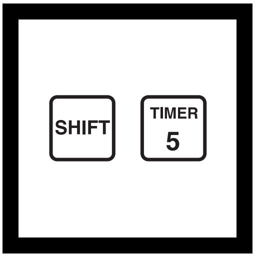


6. Pour 10 mL of the prepared sample into 10-mL sample cell.



7. Add 0.5 mL of Molybdenum 2 Reagent to the sample cell. Swirl to mix. This is the developed sample.

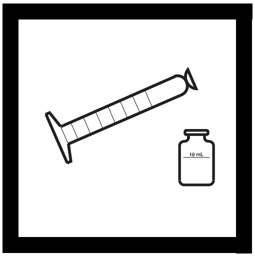
Note: *Molybdenum will cause a green color to form.*



8. Press:

SHIFT TIMER

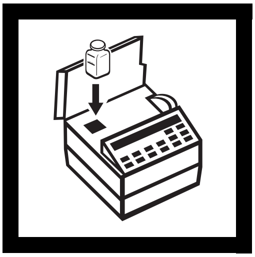
A two-minute reaction period will begin.



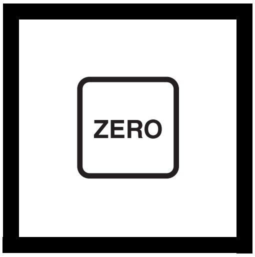
9. When the timer beeps, the display will show:

mg/L Mo^{6+} LR

Fill a second 10-mL sample cell with 10 mL of solution from the graduated cylinder (the blank).



10. Insert the blank into the cell holder. Close the light shield.



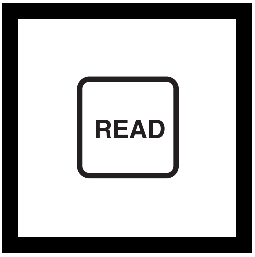
11. Press: **ZERO**

The display will show:

Zeroing. . . .

then:

0.00 mg/L Mo^{6+} LR



12. Place the developed sample into the cell holder. Close the light shield.

Press: **READ**

The display will show:

Reading. . . .

then the results in mg/L molybdenum (Mo^{6+}) will be displayed.

Forms ▲▼
MoO_4^-
Mo^{6+}
Na_2MoO_4

Sampling and Storage

Collect samples in glass or plastic bottles.

Accuracy Check

Standard Addition Method

a) Fill three 25-mL graduated mixing cylinders with 25 mL of sample.

b) Snap the neck off a Molybdenum Standard Solution, 75 mg/L Mo (NIST).

c) Use the TenSette Pipet to add 0.1, 0.2 and 0.3 mL of standard, respectively, to the three mixing cylinders. Stopper and mix thoroughly.

d) Discard enough solution from each cylinder to leave 20 mL of solution for analysis.

e) Analyze each standard as described in the procedure. The molybdenum concentration reading should increase by 0.3 mg/L for each 0.1 mL addition of standard.

f) If these increases do not occur, see *Standard Additions* in *Section I* for more information.

Standard Solution Method

Snap the neck off a 10-mL Voluette Standard Ampule, 250 mg/L as Mo. Using Class A volumetric glassware, pipet 8.0 mL of standard into a 1000-mL flask. Dilute to volume with deionized water, stopper and invert to mix. The final concentration is 2.0 mg/L as Mo.

Precision

In a single laboratory using standard solutions of 2.0 mg/L Mo^{6+} and two representative lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±0.015 mg/L Mo^{6+}.

Interferences

Interference studies were conducted by preparing a molybdenum standard solution (2 mg/L Mo^{6+}) as well as a solution of the potential interfering ion. When the standard solution concentration changed by ±5% with a given ion concentration, the ion was considered an interference:

Table 1 Negative Interference

Ion	Level above which it interferes (mg/L)
Iron	200
Copper	98
Chromium (Cr^{6+})	4.5*
Chloride	1,400
AMP (Phosphonate)	15
Phosphonohydroxyacetic Acid	32
Bisulfate	3,300
Nitrite	350
Aluminum	2
Acrylates	790
Alum	7
Lignin Sulfonate	105
Orthophosphate	4,500
Bicarbonate	5,650
EDTA	1,500
Borate	5,250
Ethylene Glycol	2% (by volume)
Sulfite	6,500
Diethanoldithiocarbamate	32

* Read molybdenum concentration immediately after the completion of the two-minute reaction period.

Table 2 Positive Interference

Ion	Level above which it interferes (mg/L)
Carbonate	1,325
Silica	600
Benzotriazole	210
Morpholine	6

Table 3 No Interference

Ion	Highest Concentration Tested (mg/L)
Zinc	400
Calcium	720
Magnesium	8,000
Manganese	1,600
Chlorine	7.5
PBTC (phosphonate)	500
Sulfate	12,800
Bisulfite	9,600
Nickel	250

Phosphonate HEDP at concentrations up to 30 mg/L will increase the apparent molybdenum concentration reading by approximately 10% (positive interference). For these samples, multiply the value obtained in step 12 by 0.9 to obtain the actual molybdenum concentration. As the concentration of HEDP increases above 30 mg/L, a decrease in the molybdenum concentration reading occurs (negative interference).

Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagent and require pretreatment. Adjust the sample pH to 3-5 (use a pH meter or pH paper) by adding drops of an of acid or base such as 1.0 N Sulfuric Acid Standard Solution, or 1.0 N Sodium Hydroxide Standard Solution. If a significant volume of acid or base is used, correct the result by dividing the total volume (sample + acid + base) by the original volume and multiplying the test result by this factor.

Large interferences are caused by some biocides used in cooling tower samples. Hach recommends testing the ternary complex procedure on molybdenum standards containing the specific biocides in use to determine if the ternary complex method will work with these samples.

After many samples have been analyzed, the sample cells may show a slight blue color. Rinse with Hydrochloric Acid Solution, 1:1, to eliminate the build-up.

Summary of Method

The ternary complex method for molybdenum determination is a method in which molybdate molybdenum reacts with an indicator and sensitizing agent to give a stable blue complex.

REQUIRED REAGENTS

Molybdenum Reagent Set, 20 mL sample (100 tests) 24494-00
Includes: (1) 23524-49, (1) 23525-12, (1) 25575-02

Description	Quantity Required Per Test	Unit	Cat. No.
Molybdenum 1 Reagent for 20 mL sample size	1 pillow	100/pkg	23524-49
Molybdenum 2 Reagent	0.5 mL	50 mL MDB	23525-12

REQUIRED APPARATUS

Cell Riser, 10 mL	1	each	45282-00
Cylinder, mixing, graduated, 25 mL	1	each	20886-40
Sample Cells, 10 mL, matched pair	2	pair	24954-02

OPTIONAL REAGENTS

Hydrochloric Acid Solution, 1:1, 6.0 N	500 mL	884-49
Molybdenum Standard Solution, Voluette Ampule 250 mg/L as Mo (NIST), 10 mL	16/pkg	25574-10
Molybdenum Standard Solution, PourRite Ampules, 75 mg/L, 2 mL	20/pkg	25575-20
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Description	Unit	Cat. No.
Ampule Breaker Kit	each	24846-00
Filter Paper, folded, 12.5 cm	100/pkg	1894-57
Flask, volumetric, 1000 mL, Class A	each	14574-53
Funnel, poly, 65 mm	each	1083-67
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet, volumetric, 8.00 mL, Class A	each	14515-08
Pipet Filler, safety bulb	each	14651-00

For technical support and ordering information, see Section V.

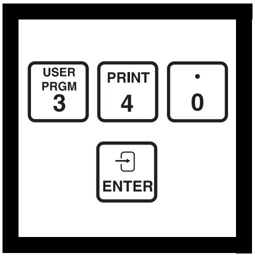
In the U.S.A. call 800-227-4224 to place an order.
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8150

NICKEL (0 to 1.000 mg/L)

For water and wastewater

1-(2 Pyridylazo)-2-Naphthol (PAN) Method*



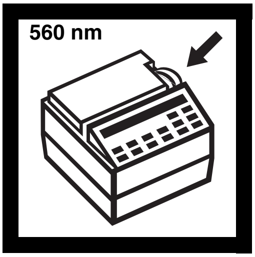
1. Enter the stored program number for nickel (Ni), PAN .

Press: **3 4 0 ENTER**

The display will show:

Dial nm to 560

Note: The Pour-Thru cannot be used.



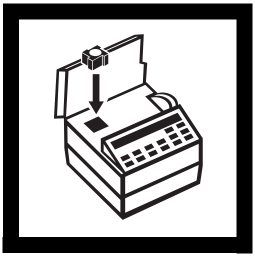
2. Rotate the wavelength dial until the small display shows:

560 nm

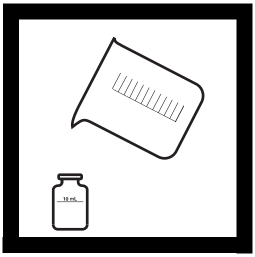
When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

then: **mg/L Ni PAN**

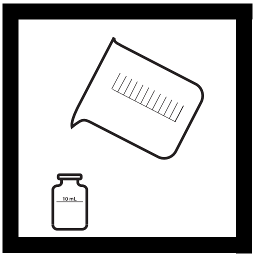


3. Insert the 10-mL Cell Riser into the cell compartment.

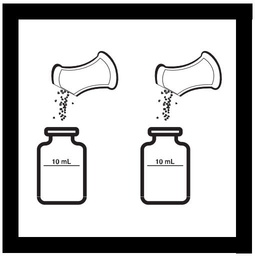


4. Fill a 10-mL sample cell with 10 mL of sample (the prepared sample).

***Note:** If sample is less than 10 °C (50 °F), warm to room temperature before analysis. Adjust the pH of stored samples.*



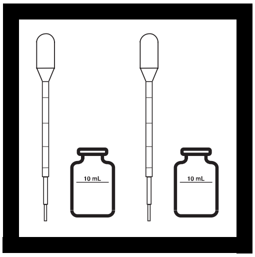
5. Fill a second 10-mL sample cell with 10 mL of deionized water (the blank).



6. Add the contents of one Phthalate-Phosphate Reagent Powder Pillow to each cell. Stopper. Shake immediately to dissolve.

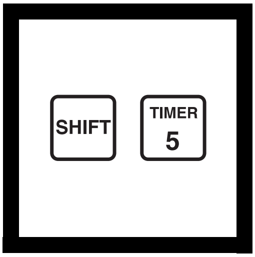
***Note:** If sample contains iron (Fe^{3+}), all the powder must be dissolved completely before continuing with Step 7.*

***Note:** Two #16 HDPE stoppers are required.*



7. Add 0.5 mL of 0.3% PAN Indicator Solution to each cell. Stopper. Invert several times to mix.

***Note:** Use the plastic dropper provided.*



8. Press:

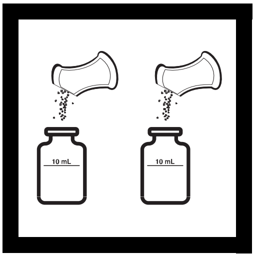
SHIFT TIMER

A 15-minute reaction period will begin.

***Note:** During color development, the sample solution color may vary from yellowish-orange to dark red . The blank should be yellow.*

---

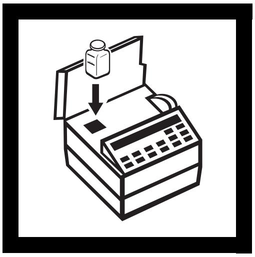
* Adapted from Watanabe, H., Talanta, 21 295 (1974)



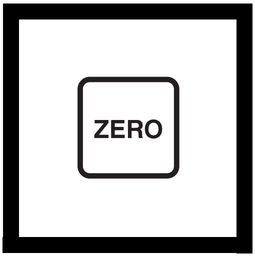
9. When the timer beeps, the display will show:

mg/L Ni PAN

Add the contents of one EDTA Reagent Powder Pillow to each cylinder. Stopper. Shake to dissolve.



10. Place the blank into the cell holder. Close the light shield.



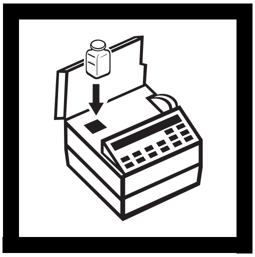
11. Press: **ZERO**

The display will show:

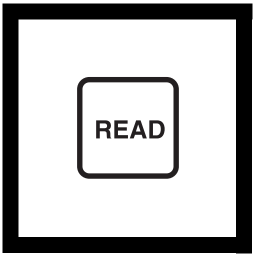
Zeroing. . . .

then:

0.000 mg/L Ni PAN



12. Place the prepared sample into the cell holder. Close the light shield.



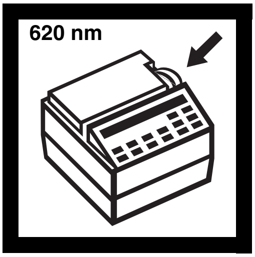
13. Press: **READ**

The display will show:

Reading. . . .

then the result in mg/L nickel will be displayed.

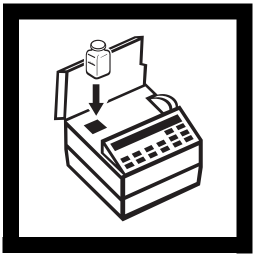
Note: *If the sample contains cobalt, continue with Steps 14 to 19.*



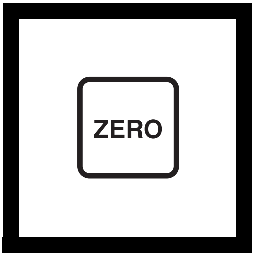
14. To correct for the presence of cobalt, rotate the wavelength dial to change the wavelength display to show:

620 nm

Press: **ENTER**



15. Place the blank into the cell holder. Close the light shield.



16. Press: **ZERO**

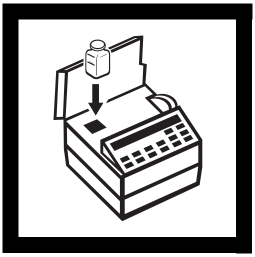
The display will show:

Zeroing. . . .

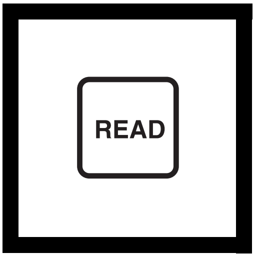
then:

0.000 mg/L Ni PAN

Note: *The wavelength setting will continue to flash.*



17. Place the prepared sample into the cell holder. Close the light shield.

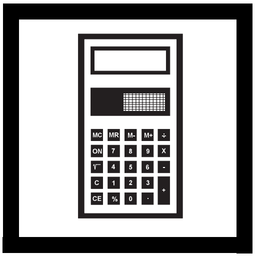


18. Press: **READ**

The display will show:

Reading. . . .

then the apparent nickel concentration in mg/L nickel due to the cobalt present will be displayed.



19. Use the equation below to correct for cobalt interference.

mg/L Ni (step 13) – (0.89) x mg/L Ni (step 18) = mg/L Ni

Note: *You may measure the cobalt concentration with the same prepared sample by using the Cobalt Stored Program No. 110.*

Sampling and Storage

Collect samples in acid-washed plastic bottles. Adjust the sample pH to 2 or less with nitric acid (about 5 mL per liter). Preserved samples can be stored up to six months at room temperature. Adjust the sample pH to between 3 and 8 with 5.0 N Sodium Hydroxide Standard Solution just before analysis. Do not exceed pH 8 as this may cause some loss of nickel as a precipitate. Correct test results for volume additions, see *Correcting for Volume Additions*, (*Section I*) for more information.

Accuracy Check

Standard Solution Method

Prepare a 0.5 mg/L nickel standard solution by diluting 10.0 mL of a 5 mg/L working stock solution to 100 mL in a 100-mL volumetric flask. Prepare the working stock solution daily by diluting 5.00 mL of Nickel Standard Solution, 1000 mg/L as Ni, to 1000 mL with deionized water.

Or, using the TenSette Pipet, add 0.2 mL of a Voluette Ampule Standard Solution for Nickel, 300 mg/L Ni, into a 100-mL volumetric flask. Dilute to volume with deionized water. This is a 0.6 mg/L standard solution.

Precision

In a single laboratory using standard solutions of 0.500 mg/L nickel and two representative lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±0.0037 mg/L nickel.

Interferences

The following may interfere when present in concentrations exceeding those listed below:

Al^{3+}	32 mg/L
Ca^{2+}	1000 mg/L as ($CaCO_3$)
Cd^{2+}	20 mg/L
Cl^-	8000 mg/L
Cr^{3+}	20 mg/L
Cr^{6+}	40 mg/L
Cu^{2+}	15 mg/L
F^-	20 mg/L
Fe^{3+}	10 mg/L
Fe^{2+}	interferes directly and must not be present.
K^+	500 mg/L
Mg^{2+}	400 mg/L
Mn^{2+}	25 mg/L
Mo^{6+}	60 mg/L
Na^+	5000 mg/L
Pb^{2+}	20 mg/L
Zn^{2+}	30 mg/L

Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and required sample pretreatment; see *pH Interferences (Section I).*

Chelating agents, such as EDTA, interfere. Use either the Digesdahl or vigorous digestion (Section I) to eliminate this interference.

Summary of Method

After buffering the sample and masking any Fe^{3+} with pyrophosphate, the nickel is reacted with 1-(2-Pyridylazo)-2-Naphthol indicator. The indicator forms complexes with most metals present. After color development, EDTA is added to destroy all metal-PAN complexes except nickel and cobalt. This method is unique because both nickel and cobalt can be determined on the same sample.

REQUIRED REAGENTS

	Cat. No.
Nickel Reagent Set, 10 mL sample (100 Tests) Includes: (2) 7005-99, (1) 21502-32, (2) 26151-99	26516-00

Description	Quantity Required Per Test	Unit	Cat. No.
EDTA Reagent Powder Pillows	2 pillows	100/pkg	7005-99
Phthalate-Phosphate Reagent Powder Pillows, 10-mL samples	2 pillows	100/pkg	26151-99
P.A.N. Indicator Solution, 0.3%	1 mL	100 mL	21502-32
Water, deionized	10 mL	4 L	272-56

REQUIRED APPARATUS

Cell Riser, 10-mL sample cell	1	each	45282-00
Sample Cell, 10-mL, matched pair	2	pair	24954-02
Stopper, HDPE, #16	2	6/pkg	20955-16

OPTIONAL REAGENTS

Nickel Standard Solution, 1000 mg/L Ni	100 mL	14176-42
Nickel Standard Solution, Voluette ampule, 300 mg/L Ni, 10 mL	16/pkg	14266-10
Nitric Acid, ACS	500 mL	152-49
Nitric Acid Solution, 1:1	500 mL	2540-49
Sodium Hydroxide Standard Solution, 5.0 N	100 mL MDB	2450-32

OPTIONAL APPARATUS

Flask, volumetric, Class A, 100 mL	each	14574-42
Flask, volumetric, Class A, 1000 mL	each	14574-53
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
pH Meter, *sension*™*1*, portable	each	51700-10
Pipet, serological, 1 mL	each	532-35
Pipet, serological, 5 mL	each	532-37
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 5.0 mL	each	14515-37
Pipet, volumetric, Class A,10.0 mL	each	14515-38
Pipet Filler, safety bulb	each	14651-00
Thermometer, -20 to 105 °C	each	1877-01

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

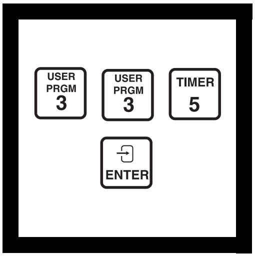
Method 8037

NICKEL (0 to 1.80 mg/L Ni)

For water, wastewater and seawater

Heptoxime Method*

USEPA accepted for reporting wastewater analysis (digestion required- see Section II)**



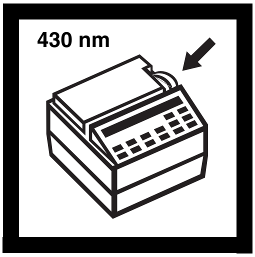
1. Enter the stored program number for nickel (Ni)-heptoxime method.

Press: **3 3 5 ENTER**

The display will show:

Dial nm to 430

Note: *The Pour-Thru cell can not be used.*



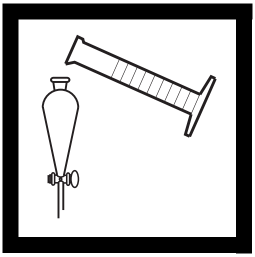
2. Rotate the wavelength dial until the small display shows:

430 nm

When the correct wavelength is dialed in, the display will quickly show:

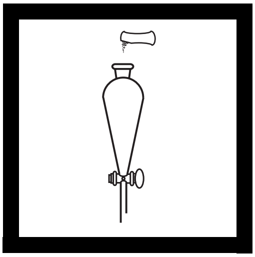
Zero Sample

then: **mg/L Ni Hept**

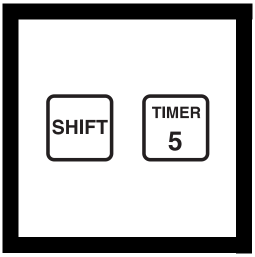


3. Measure 300 mL of sample in a 500-mL graduated cylinder. Pour into a 500-mL separatory funnel.

Note: *Adjust the pH of stored samples before analysis.*



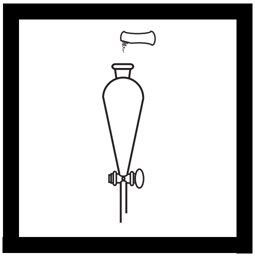
4. Add the contents of one Nickel 1 Reagent Powder Pillow to the funnel. Stopper. Shake to mix.



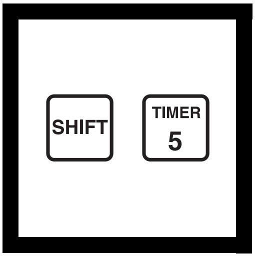
5. Press:

SHIFT TIMER

A five-minute reaction period will begin.



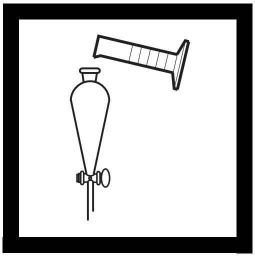
6. When the timer beeps, add the contents of one Nickel 2 Reagent Powder Pillow to the funnel. Stopper. Shake to mix.



7. Press:

SHIFT TIMER

A second five-minute reaction period will begin.

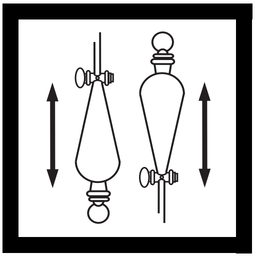


8. When the timer beeps, add 10 mL of chloroform. Stopper. Shake gently. Invert. Open the stopcock to vent.

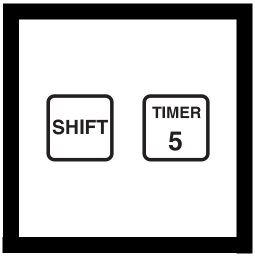
---

* Adapted from *Chemie Analytique*, 36 43 (1954).

** Procedure is equivalent to Standard Method 3500-Ni D for wastewater.



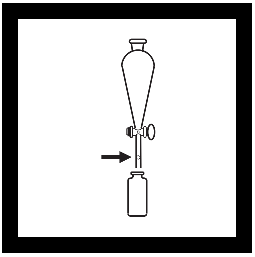
9. Close the stopcock. Shake for 30 seconds.



10. Press:

SHIFT TIMER

A third five-minute reaction period will begin. Shake the funnel several times over the five minute period.



11. When the timer beeps, the display will show:

mg/L Ni Hept

Wait for the layers to separate. Insert a small cotton plug into the delivery tube of the funnel. Drain the chloroform layer into a 25-mL sample cell (the prepared sample). Stopper.

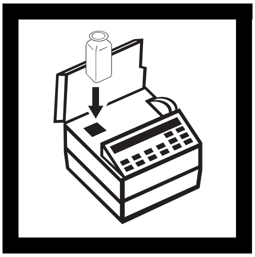
Note: *Use a plug about the size of a pea.*

12. Repeat Steps 8 to 11 two additional times with 10-mL portions of chloroform.

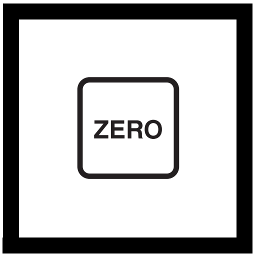
Note: *The five-minute reaction period is not necessary. Shake with chloroform to separate; then continue. Wait for layers to separate, then continue.*

Note: *The final volume of extract will be about 25 mL due to the slight solubility of chloroform in water.*

Note: *Swirl sample cell to mix extracts.*



13. Fill a second cell (the blank) with 25 mL of chloroform. Stopper. Place the blank into the cell holder. Close the light shield.



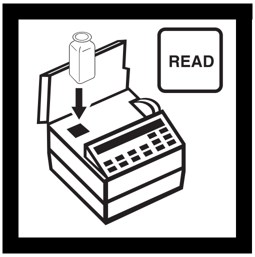
14. Press: **ZERO**

The display will show:

Zeroing. . .

then:

0.00 mg/L Ni Hept



15. Place the prepared sample into the cell holder. Close the light shield.

Press: **READ**

The display will show:

Reading. . .

then the result in mg/L nickel will be displayed.

Sampling and Storage

Collect samples in acid-washed plastic bottles. Adjust the sample pH to 2 or less with nitric acid (about 5 mL per liter). Preserved samples can be stored up to six months at room temperature. Adjust the sample pH to between 3 and 8 with 5.0 N Sodium Hydroxide Standard Solution just before analysis. Do not exceed pH 8 as this may cause some loss of nickel as a precipitate. Correct the test results for volume additions; see *Correcting for Volume Additions (Section I)* for more information.

Accuracy Check

Standard Additions Method

a) Snap the neck off a Nickel Voluette Ampule Standard Solution, 300 mg/L Ni.

b) Use the TenSette Pipet to add 0.1, 0.2 and 0.3 mL of standard to three 300-mL samples.

c) Analyze each sample as described above. The nickel concentration should increase 0.10 mg/L for each 0.1 mL of standard added.

d) If these increases do not occur, see *Standard Additions* (*Section I*) for more information.

Standard Solution Method

Prepare a 1.0 mg/L nickel standard solution by diluting 50.0 mL of a 10 mg/L working standard solution to 500 mL in a volumetric flask. The working stock solution should be prepared daily by diluting 10.00 mL of Nickel Standard Solution, 1000 mg/L as Ni, to 1000 mL with deionized water. For proof of accuracy, use this prepared standard in place of sample in step 3.

Or, use the TenSette® Pipet to add 1.0 mL of a Nickel Voluette Ampule Standard Solution, 300 mg/L Ni, into a 500-mL volumetric flask and dilute to volume with deionized water. This solution is 0.6 mg/L nickel. For proof of accuracy, use this prepared standard in place of sample in step 3.

Precision

In a single laboratory using standard solutions of 0.83 mg/L nickel and two representative lots of reagent with the DR/2010, a single operator obtained a standard deviation ±0.022 mg/L nickel.

Estimated Detection Limit (EDL)

The EDL for program 335 is 0.021 mg/L Ni. The EDL is calculated lowest average concentration in a deionized water matrix that is different from zero with a 99% level of confidence. For more information on derivation and use of Hach's estimated detection limit, see *Section I*.

Interferences

Cobalt, copper and iron interferences can be overcome by adding one or more additional Nickel 1 Reagent Powder Pillows in Step 4. The tolerance limits of these interferences are shown in the following table:

Pillows of Nickel Reagent	Tolerance Limit (mg/L)		
	Cobalt	Copper	Iron
1	1	10	20
2	7	16	65
3	13	22	110
4	18	28	155
5	25	35	200

A preliminary acid digestion is required to determine any suspended or precipitated nickel and to eliminate interference by organic matter. To eliminate this interference or to determine total recoverable nickel perform the EPA approved digestion in *Digestion (Section II)*.

Summary of Method

Nickel ion reacts with heptoxime to form a yellow-colored complex which is then extracted into chloroform to concentrate the color and enable a more sensitive determination. Chelating agents are added to the sample to overcome the interferences caused by cobalt, copper and iron.

REQUIRED REAGENTS

	Cat. No.
Nickel Reagent Set (50 Tests)	22435-00

Includes: (3) 14458-49, (2) 2123-68, (2) 2124-68

Description	Quantity Required Per Test	Unit	Cat. No.
Chloroform, ACS	55 mL	500 mL	14458-49
Nickel 1 Reagent Powder Pillows	1 pillow	25/pkg	2123-68
Nickel 2 Reagent Powder Pillows	1 pillow	25/pkg	2124-68

REQUIRED APPARATUS

Description	Quantity Required Per Test	Unit	Cat. No.
Clippers, for opening powder pillows	1	each	968-00
Cotton balls, absorbent	1	100/pkg	2575-01
Cylinder, graduated, 10 mL	1	each	508-38
Cylinder, graduated, 500 mL	1	each	508-49
Funnel, separatory, 500 mL	1	each	520-49
Ring, support, 4-inch	1	each	580-01
Sample Cell, 25 mL, matched pair		pair	20950-00
Stand, support, 127x203 mm	1	each	563-00
Stopper, hollow, poly, Size zero	2	6/pkg	14480-00

OPTIONAL REAGENTS

Nickel Standard Solution, 1000 mg/L Ni	100 mL	14176-42
Nickel Standard Solution, Voluette ampule, 300 mg/L Ni, 10 mL	16/pkg	14266-10
Nitric Acid, ACS	500 mL	152-49
Nitric Acid Solution, 1:1	500 mL	2540-49
Sodium Hydroxide Standard Solution, 5.0 N	1 L	2450-53
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Ampule Breaker Kit	each	21968-00
Flask, Erlenmeyer, 500 mL	each	505-49
Flask, volumetric, Class A, 500 mL	each	14574-49
Flask, volumetric, Class A, 1000 mL	each	14574-53
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
pH Meter, *sension*™*1*, portable	each	51700-10
Pipet, serological, 1 mL	each	532-35
Pipet, serological, 5 mL	each	532-37
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	pkg/50	21856-96
Pipet, volumetric, Class A, 10.00 mL	each	14515-38
Pipet Filler, safety bulb	each	14651-00
Pipet, volumetric, Class A, 50.00 mL	each	14515-41

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

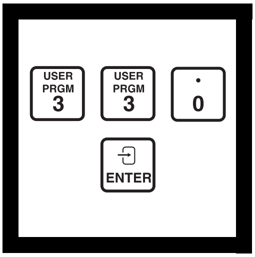
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8118

NICKEL, AUTOCATALYTIC (0 to 8.00 g/L)

For finishing baths

Photometric Method

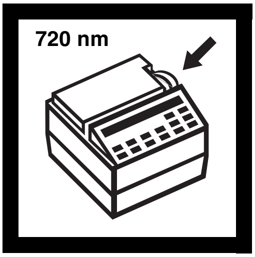


1. Enter the stored program number for autocatalytic nickel (Ni).

Press: **3 3 0 ENTER**

The display will show:

Dial nm to 720



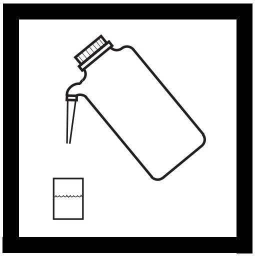
2. Rotate the wavelength dial until display shows:

720 nm

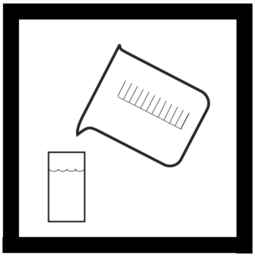
When the correct wavelength is dialed in the display will quickly show:

Zero Sample

then: **g/L Ni Acat**

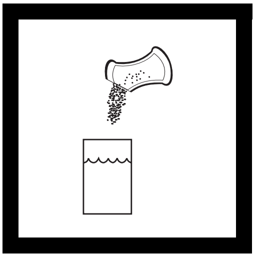


3. Fill a zeroing vial (the blank) with 10 mL of deionized water.



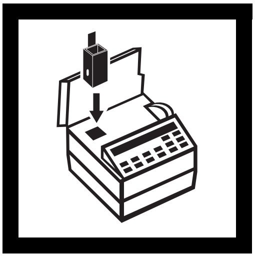
4. Fill a second zeroing vial with 10 mL bath sample.

***Note:** Filter highly turbid samples.*



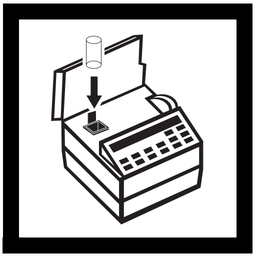
5. Add contents of one Potassium 1 Reagent Powder Pillow to the sample in the zeroing vial (the prepared sample). Cap. Shake to dissolve.

***Note:** If a visible turbidity forms upon addition of Potassium 1 Reagent, dilute sample 1:1 with deionized water and repeat Step 5. Multiply results obtained in Step 10 by 2.*

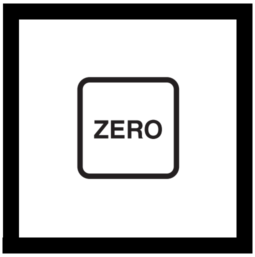


6. Place the AccuVac Vial Adapter into the cell holder.

***Note:** Place the grip tab at the rear of the cell holder.*



7. Place the blank into the cell holder. Close the light shield.

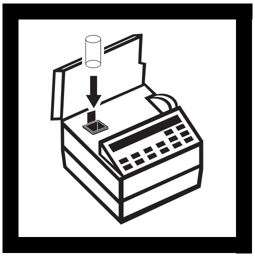


8. Press: **ZERO**

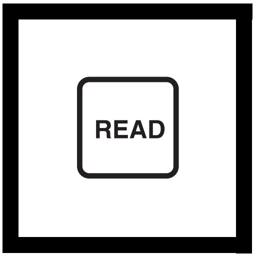
The display will show:

Zeroing. . .

then: **0.00 g/L Ni Acat**



9. Place the prepared sample into the cell holder. Close the light shield.



10. Press: **READ**

The display will show:

Reading. . .

then the result in g/L nickel (Ni) will be displayed.

Note: *This method gives accurate results on nearly all bath formulations. If the bath formulation in use responds differently, a new manual calibration should be done on this bath formulation. See User Stored Programs (Section I). Follow the procedure in the Operation Section of the instrument manual.*

Sampling and Storage

Collect samples in clean plastic or glass bottles. Store at 4 °C (39 °F) or lower.

Accuracy Check

Standard Solution Method

Check accuracy with a Nickel Standard Solution, 1000 mg/L (1.00 g/L), listed under Optional Reagents. This is used in place of sample in Step 4.

Precision

In a single laboratory using bath samples of 6.26 g/L nickel and two representative lots of powder pillow reagent with the DR/2010, a single operator obtained a standard deviation of ±0.024 g/L nickel.

Interferences

Copper will interfere by giving a similar blue color.

Summary of Method

A strong complexing agent chelates the nickel ions present in an "electroless" nickel bath to form a blue colored chelate. The blue color is then measured directly to give the g/L nickel present in the bath.

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
Potassium 1 Reagent Powder Pillows	1 pillow	25/pkg	14321-98
Water, deionized	10 mL	4 L	272-56

REQUIRED APPARATUS

Description	Quantity Required Per Test	Unit	Cat. No.
Adapter, AccuVac	1	each	43784-00
Clippers, for opening powder pillows	1	each	968-00
Vial, zeroing	2	each	21228-00

OPTIONAL REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
Nickel Standard Solution, 1000 mg/L		100 mL	14176-42
Nickel Standard Solution, 1000 mg/L		500 mL	14176-49

OPTIONAL APPARATUS

Description	Quantity Required Per Test	Unit	Cat. No.
Filter Paper, folded, 12.5 cm		100/pkg	1894-57
Funnel, poly, 65 mm		each	1083-67

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

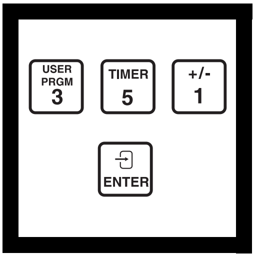
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8192

NITRATE, LR (0 to 0.40 mg/L NO_3^--N)

For water, wastewater, and seawater*

Cadmium Reduction Method



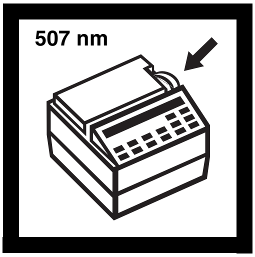
1. Enter the stored program number for low range nitrate nitrogen (NO_3^--N).

Press: **3 5 1 ENTER**

The display will show:

Dial nm to 507

Note: *The Pour-Thru Cell can be used with this procedure.*

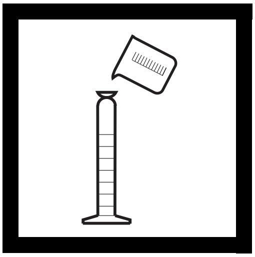


2. Rotate the wavelength dial until the small display shows:

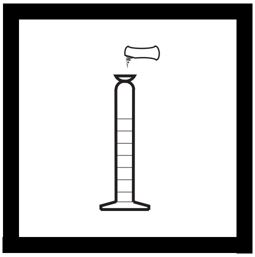
507 nm

When the correct wavelength is dialed in, the display will quickly show: **Zero Sample**

then: **mg/L NO_3^--N LR**



3. Fill a 50-mL mixing graduated cylinder to the 30-mL mark with sample.



4. Add the contents of one NitraVer 6 Nitrate Reagent Powder Pillow to the cylinder. Stopper.

Note: *Determine a reagent blank for each new lot of powder pillows. Repeat Steps 3 to 13, using deionized water as the sample. Subtract this value from each result obtained with this lot of reagent.*

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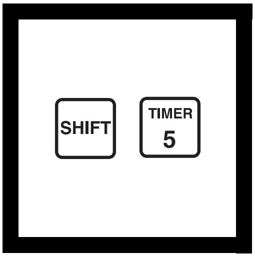
* Seawater requires a manual calibration; see *Interferences*.

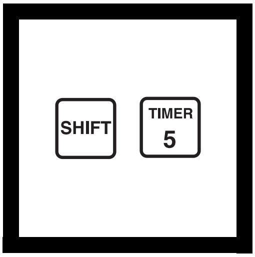


5. Press:

SHIFT TIMER

A 3-minute reaction period will begin. Shake the cylinder continuously during this period.

Note: *Shaking time and technique influence color development. For most accurate results, analyze a standard solution several times and adjust the shaking time to obtain the correct result.*



6. When the timer beeps, press:

SHIFT TIMER

A 2-minute period allows the cadmium to settle.

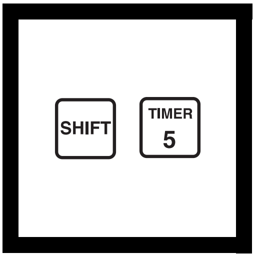
Note: *A cadmium deposit will remain after the NitraVer 6 Reagent powder dissolves and will not affect results.*

7. When the timer beeps, pour 25 mL of sample from the cylinder into a sample cell.

Note: *Do not transfer any cadmium particles.*

8. Add the contents of one NitriVer 3 Nitrite Reagent Powder Pillow to the sample cell (the prepared sample). Stopper.

Shake to dissolve.



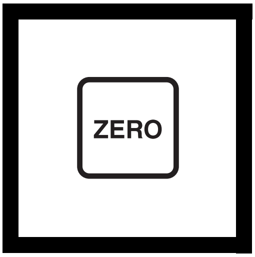
9. Press:

SHIFT TIMER

A 10-minute reaction period will begin.

10. When the timer beeps, the display will show: **mg/L N NO$_3^-$ LR**

Fill another sample cell with 25 mL of sample (the blank). Place the blank into the cell holder. Close the light shield.



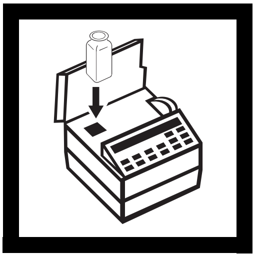
11. Press: **ZERO**

The display will show:

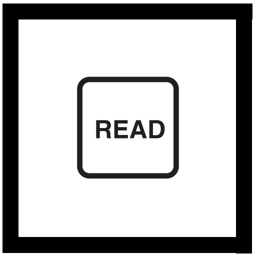
Zeroing. . .

then:

0.00 mg/L NO$_3^-$ -N LR



12. Within ten minutes after the timer beeps, remove the stopper from the prepared sample. Place the prepared sample into the cell holder. Close the light shield.



13. Press: **READ**

The display will show:

Reading. . .

then the result in mg/L nitrate expressed as nitrogen (NO_3^--N) will be displayed.

Note: *Rinse the sample cell and cylinders immediately after use to remove all cadmium particles.*

Forms ▲ NO_3^--N
▼ NO_3^-

Sampling and Storage

Collect samples in clean plastic or glass bottles. Store at 4 °C (39 °F) or lower if the sample is to be analyzed within 24 to 48 hours. Warm to room temperature before running the test. For longer storage periods, adjust sample pH to 2 or less with sulfuric acid, ACS (about 2 mL per liter). Sample refrigeration is still required.

Before testing the stored sample, warm to room temperature and neutralize with 5.0 N Sodium Hydroxide Standard Solution. Do not use mercury compounds as preservatives. Correct the test result for volume additions; see *Correction for Volume Additions*, (*Section I*) for more information.

Accuracy Check

Standard additions Method

a) Measure 30 mL of sample into three cylinders.

b) Using the TenSette Pipet, add 0.1, 0.2, and 0.3 mL of Nitrate Nitrogen, Voluette Ampule Standard Solution, 12 mg/L as (NO_3^--N), to the three samples. Mix well.

c) Analyze each sample as described above. The nitrate nitrogen concentration should increase 0.04 mg/L for each 0.1 mL of standard added.

d) If these increases do not occur, see *Standard Additions* (*Section I*) for more information.

Standard Solution Method

Prepare a 0.20 mg/L nitrate nitrogen standard by diluting 2.00 mL of the 10 mg/L Nitrate Nitrogen Standard Solution to 100 mL with deionized water. Or, using the TenSette Pipet, a 0.12 mg/L nitrate nitrogen standard can be prepared by diluting 1.0 mL of a Nitrate Nitrogen Voluette Ampule Standard Solution, 12 mg/L, to 100 mL with deionized water. Use these prepared standards in place of sample in Step 3.

Precision

In a single laboratory using standard solutions of 0.25 mg/L nitrate nitrogen (NO_3^--N) and two representative lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±0.010 mg/L nitrate nitrogen.

Interferences

This method registers both the nitrate and nitrite nitrogen present in the sample. If nitrite is present, the nitrite nitrogen test using program number 371 should be done on the sample.

The amount of nitrite nitrogen found should be subtracted from the results of the nitrate nitrogen test when the following pretreatment is used:

a) Add Bromine Water drop-wise to 30-mL of sample until a yellow color persists. Mix after adding each drop.

b) Add one drop of Phenol Solution. Swirl to destroy the yellow color.

c) Continue with Step 3 of the nitrate procedure.

Calcium interferes in amounts over 100 mg/L as $CaCO_3$.

Chlorides in amounts over 100 mg/L cause low results. To determine nitrate in high chloride samples or seawater a manual calibration must be performed. Prepare nitrate standard solutions with the approximate chloride concentration of the samples to be tested. See User Stored Programs in the DR/2010 Instrument Manual for more information.

Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment; see *pH Interferences* (*Section I*).

Summary of Method

Cadmium metal reduces nitrates present in the sample to nitrite. The nitrite ion reacts in an acidic medium with sulfanilic acid to form an intermediate diazonium salt which couples to chromotropic acid to form a pink-colored product.

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
Low Range Nitrate Reagent Set (100 tests) Includes: (1) 14065-99, (1) 14119-99			22451-00
NitriVer 3 Nitrite Reagent Powder Pillows	1 pillow	100/pkg	14065-99
NitraVer 6 Nitrate Reagent Powder Pillows	1 pillow	100/pkg	14119-99

REQUIRED APPARATUS

Description	Quantity Required Per Test	Unit	Cat. No.
Cylinder, graduated, mixing, 50 mL	1	each	1896-41
Sample Cell, 25 mL, matched pair		pair	20950-00
Stopper, hollow, No. 1	1	6/pkg	14480-01

OPTIONAL REAGENTS

Description	Unit	Cat. No.
Bromine Water	25 mL*	2211-20
Nitrate Nitrogen Standard Solution, 1 mg/L as NO_3^--N	500 mL	2046-49
Nitrate Nitrogen Standard Solution, 10 mg/L as NO_3^--N	500 mL	307-49
Nitrate Nitrogen Standard Solution, Voluette ampule, 12 mg/L as NO_3^--N, 10 mL	16/pkg	14333-10
Phenol Solution, 30 g/L	29 mL	2112-20
Pretreatment Kit, contains: (1) 2112-20, (1) 2211-20	each	2268-00
Sodium Hydroxide Standard Solution, 5.0 N	50 mL* SCDB	2450-26
Sulfuric Acid, ACS	500 mL*	979-49
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Nitrate at these levels can be determined directly using the Nitrate Ion Selective Electrode (Cat. No. 50235-00)

Ampule Breaker Kit	each	21968-00
Dropper, for 1-oz bottle	each	2258-00
Flask, volumetric, Class A, 100 mL	each	14574-42
pH Indicator Paper, 1 to 11 pH	5-roll/pkg	391-33
pH Meter, *sension*™*1*, portable	each	51700-10
Pipet, serological, 2 mL	each	532-36
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 2.00 mL	each	14515-36
Pipet Filler, safety bulb	each	14651-00
Pour-Thru Cell Assembly Kit	each	45215-00
Thermometer, -10 to 110 °C	each	1877-01

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

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* Contact Hach for larger sizes.

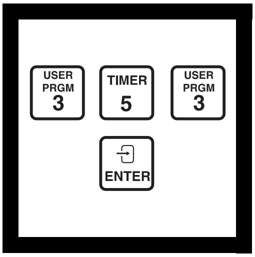
Method 8171

NITRATE, MR (0 to 4.5 mg/L NO_3^--N)

For water, wastewater, and seawater*

Cadmium Reduction Method (Using Powder Pillows or AccuVac Ampuls)

Using Powder Pillows



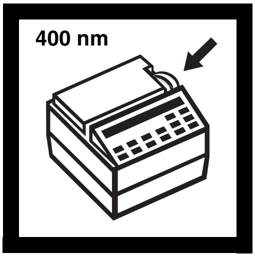
1. Enter the stored program number for medium range nitrate nitrogen (NO_3^--N).

Press: **3 5 3 ENTER**

The display will show:

Dial nm to 400

Note: *The Pour-Thru Cell can be used if rinsed well with deionized water after use.*

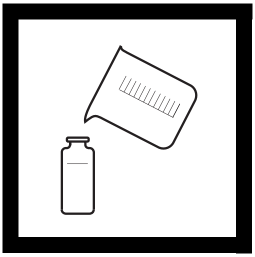


2. Rotate the wavelength dial until the small display shows:

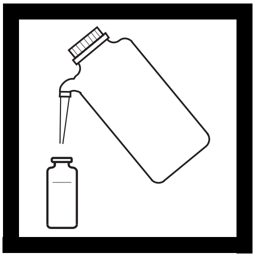
400 nm

When the correct wavelength is dialed in, the display will quickly show: **Zero Sample**

then: **mg/L NO_3^--N MR**



3. Fill a sample cell with 25 mL of sample (the prepared sample).



4. Fill another cell with 25 mL of deionized water (the blank).

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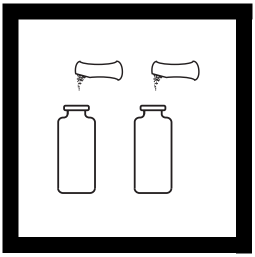
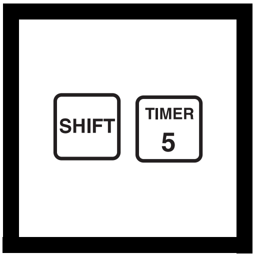
* Seawater requires a manual calibration; see *Interferences*.



5. Add the contents of one NitraVer 5 Nitrate Reagent Powder Pillow to each cell. Stopper.

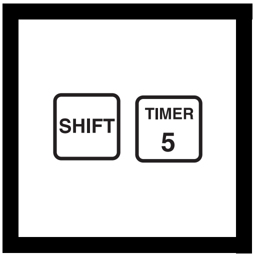


6. Press:

SHIFT TIMER

A one-minute reaction period will begin. Shake until the timer beeps.

***Note:** Shaking time and technique influence color development. For most accurate results, do successive tests on a standard solution and adjust the shaking time to obtain the correct result.*



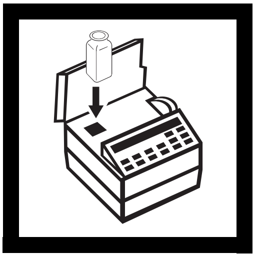
7. When the timer beeps, press:

SHIFT TIMER

A five-minute reaction period will begin.

***Note:** A cadmium deposit will remain after the NitraVer 5 Nitrate Reagent Powder dissolves and will not affect test results.*

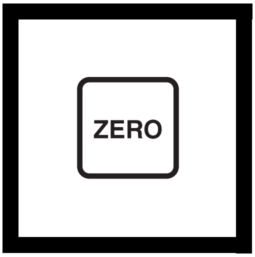
***Note:** An amber color will develop if nitrate nitrogen is present.*



8. When the timer beeps, the display will show:

mg/L NO_3^--N MR

Remove the stopper. Place the blank into the cell holder. Close the light shield.



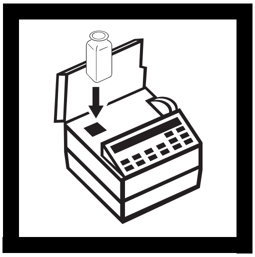
9. Press **ZERO**

The display will show:

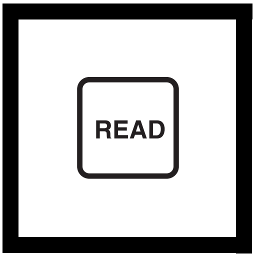
Zeroing. . .

then:

0.0 mg/L N NO_3^--N MR



10. Place the prepared sample into the cell holder. Close the light shield.



11. Press: **READ**

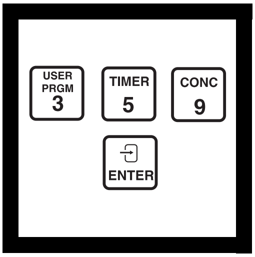
The display will show:

Reading. . .

then the result in mg/L nitrate expressed as nitrogen (NO_3^--N) will be displayed.4

Forms ▲ NO_3^- -N
▼ NO_3^-

Using AccuVac Ampuls

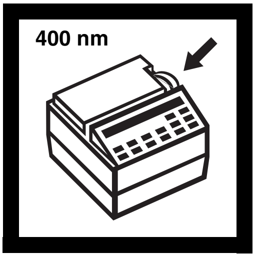


1. Enter the stored program number for medium range nitrate nitrogen (NO_3^--N) AccuVac ampuls.

Press: **3 5 9 ENTER**

The display will show:

Dial nm to 400



2. Rotate the wavelength dial until the small display shows:

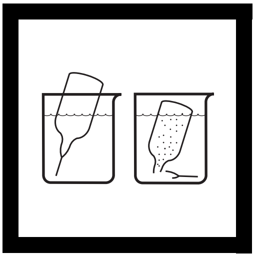
400 nm

When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

then:

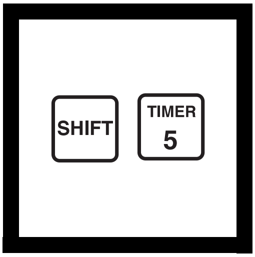
mg/L NO_3^--N M AV



3. Collect at least 40 mL of sample in a 50-mL beaker. Fill a NitraVer 5 Nitrate AccuVac Ampul with sample.

Note: *Keep the tip immersed while the ampul fills.*

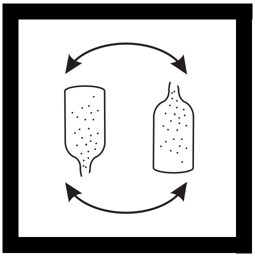
Note: *A reagent blank must be determined for each lot of NitraVer 5. Perform Steps 3 to 11 using deionized water as the sample. Subtract this value from each result obtained with this reagent lot.*



4. Press:

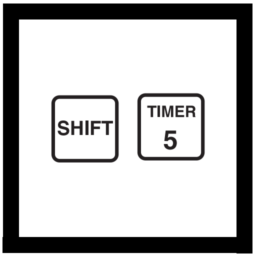
SHIFT TIMER

A one-minute shaking period will begin.



5. Invert the ampul repeatedly back and forth until the timer beeps. Wipe off any liquid or fingerprints.

Note: *Shaking time and technique influence color development. For most accurate results, do successive tests on a standard solution and adjust the shaking time to obtain the correct result.*



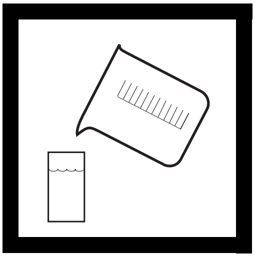
6. When the timer beeps, press:

SHIFT TIMER

A five-minute reaction period will begin.

Note: *A cadmium deposit will remain after the NitraVer 5 Nitrate Reagent Powder dissolves and will not affect results.*

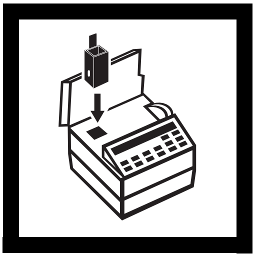
Note: *An amber color will develop if nitrate nitrogen is present.*



7. When the timer beeps, the display will show:

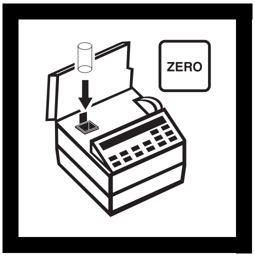
mg/L NO_3^--N M AV

Fill a zeroing vial with at least 10 mL of sample (the blank).



8. Place the AccuVac Vial Adapter into the cell holder of the instrument.

Note: *Place the grip tab at the rear of the cell holder.*



9. Place the blank into the cell holder. Close the light shield.

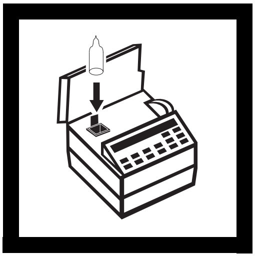
Press: **ZERO**

The display will show:

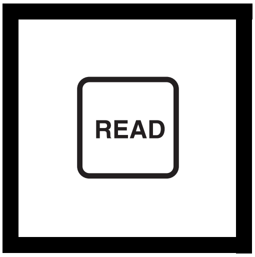
Zeroing . . .

then:

0.0 mg/L NO_3^--N M AV



10. Place the AccuVac ampul into the cell holder. Close the light shield.



11. Press: **READ**

The display will show:

Reading. . .

then the result in mg/L nitrate expressed as nitrogen (NO_3^--N) will be displayed.

Forms ▲ NO_3^- N
▼ NO_3^-

Sampling and Storage

Collect samples in clean plastic or glass bottles. Store at 4 °C (39 °F) or lower if the sample is to be analyzed within 24 to 48 hours. Warm to room temperature before running the test. For longer storage periods, adjust sample pH to 2 or less with sulfuric acid, ACS (about 2 mL per liter). Sample refrigeration is still required.

Before testing the stored sample, warm to room temperature and neutralize with 5.0 N Sodium Hydroxide Standard Solution.

Do not use mercury compounds as preservatives.

Correct the test result for volume additions; see *Correction for Volume Additions*, (*Section I)* for more information.

Accuracy Check

Standard Additions Method

a) Measure 25 mL of sample into three cells or 50-mL beakers.

b) Use the TenSette Pipet to add 0.1, 0.2, and 0.3 mL of Nitrate Nitrogen Standard Solution, 100 mg/L as NO_3^--N, to the three samples. Mix well.

c) Analyze each sample as described above. The nitrate nitrogen (NO_3^--N) concentration should increase 0.4 mg/L for each 0.1 mL of standard added.

d) If these increases do not occur, see *Standard Additions* (*Section I*) for more information. Use this standard in place of sample in Step 3.

Standard Solution Method

A 1.0 mg/L Nitrate Nitrogen Standard Solution is available from Hach. Or, dilute 1.00 mL of Nitrate Nitrogen Standard Solution, 100 mg/L as NO_3^--N, to 100.0 mL with deionized water. Use these standards in place of sample in Step 3.

Precision

In a single laboratory using standard solutions of 2.0 mg/L nitrate nitrogen (NO_3^--N) and two representative lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±0.10 mg/L nitrate nitrogen.

In a single laboratory using a standard solution of 1.5 mg/L (NO_3^--N) and two representative lots of AccuVac ampuls with the DR/2010, a single operator obtained a standard deviation of ±0.03 mg/L nitrate nitrogen.

Interferences

Compensate for nitrite interference as follows:

a) Add Bromine Water dropwise to the sample in Step 3 until a yellow color remains.

b) Add one drop of Phenol Solution to destroy the color.

c) Proceed with Step 3. Report results as total nitrate and nitrite.

Strong oxidizing and reducing substances will interfere.

Ferric iron causes high results and must be absent.

Chloride concentrations above 100 mg/L will cause low results. The test may be used at high chloride levels and in seawater, but you must perform a calibration using standards spiked to the same chloride concentration. See *User Entered Methods* in the *DR/2010 Spectrophotometer Instrument Manual* for more information.

Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment; see *pH Interferences* in *Section I.*

Summary of Method

Cadmium metal reduces nitrates present in the sample to nitrite. The nitrite ion reacts in an acidic medium with sulfanilic acid to form an intermediate diazonium salt which couples to gentisic acid to form an amber-colored product.

REQUIRED REAGENTS (Using Powder Pillows)

Description	Quantity Required Per Test	Unit	Cat. No.
NitraVer 5 Nitrate Reagent Powder Pillows	1 pillow	100/pkg	14034-99

REQUIRED REAGENTS (USING ACCUVAC AMPULS)

Description	Quantity Required Per Test	Unit	Cat. No.
NitraVer 5 Nitrate Reagent AccuVac Ampul	1 ampul	25/pkg	25110-25

REQUIRED APPARATUS (Using Powder Pillows)

Description	Quantity Required Per Test	Unit	Cat. No.
Sample Cells, 25 mL, matched pair	2	pair	20950-00
Stopper, rubber, size 2	2	12/pkg	2118-02

REQUIRED APPARATUS (Using AccuVac Ampuls)

Description	Quantity Required Per Test	Unit	Cat. No.
Adapter, AccuVac	1	each	43784-00
Beaker, 50 mL	1	each	500-41
Vial, zeroing	1	each	21228-00

OPTIONAL REAGENTS

Bromine Water 30 g/L	29 mL*	2211-20
Nitrate Nitrogen Standard Solution, 1 mg/L as (NO_3^--N)	500 mL	2046-49
Nitrate Nitrogen Standard Solution, 100 mg/L as (NO_3^--N)	500 mL	1947-49
Phenol Solution	29 mL	2112-20
Sodium Hydroxide Standard Solution, 5.0 N	59 mL*	2450-26
Sulfuric Acid, ACS	500 mL*	979-49
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

AccuVac Snapper Kit	each	24052-00
Cylinder, graduated, 25 mL	each	1081-40
Flask, volumetric, 100 mL	each	14574-42
Dropper, for 1-oz bottle	each	2258-00
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
pH Meter, *sens**ion***™***1***, portable	each	51700-10
Pipet Filler, safety bulb	each	14651-00
Pipet, serological, 2 mL	each	532-36
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 1.00 mL	each	14515-35
Pour-Thru Cell Assembly Kit	each	45215-00
Sample Cells, 1-inch, polystyrene, disposable	12/pkg	24102-12
Thermomter, -10 to 110 °C	each	1877-01

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

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* Contact Hach for larger sizes.

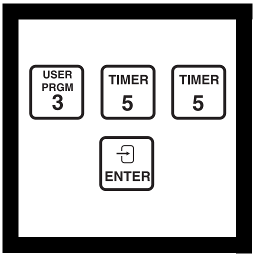
Method 8039

NITRATE, HR (0 to 30.0 mg/L NO_3^--N)

For water, wastewater, and seawater*

Cadmium Reduction Method (Powder Pillows or AccuVac Ampuls)

Using Powder Pillows



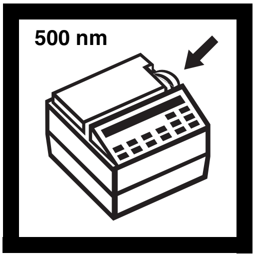
1. Enter the stored program number for high range nitrate nitrogen (NO_3^--N).

Press: **3 5 5 ENTER**

The display will show:

Dial nm to 500

Note: *The Pour-Thru Cell can be used if rinsed well with deionized water after use. Avoid pouring any cadmium particles into the cell.*



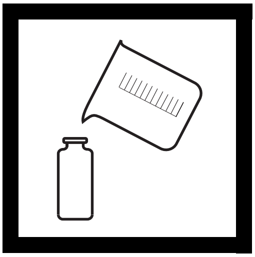
2. Rotate the wavelength dial until the small display shows:

500 nm

When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

then: **mg/L NO_3^--N HR**



3. Fill a sample cell with 25 mL of sample.

Note: *A reagent blank must be determined on each new lot of NitraVer 5. Perform Steps 3 to 11 using deionized water as the sample. Subtract this value from each result obtained with this lot of reagent.*

4. Add the contents of one NitraVer 5 Nitrate Reagent Powder Pillow to the cell (the prepared sample). Stopper.

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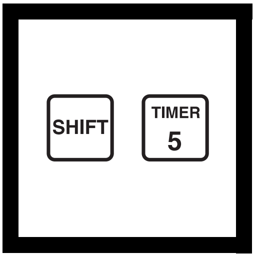
* For seawater, a manual calibration is required; see *Interferences*.

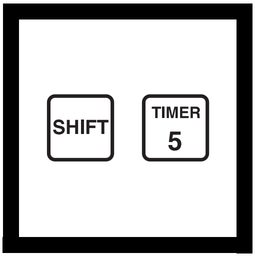


5. Press:

SHIFT TIMER

Shake the cell vigorously until the timer beeps in one minute.

Note: *Shaking time and technique influence color development. For most accurate results, make successive tests on a standard solution. Adjust the shaking time to obtain the correct result.*

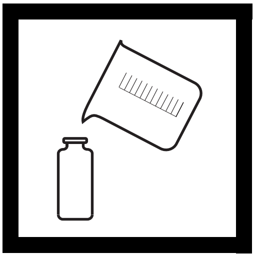


6. When the timer beeps, press:

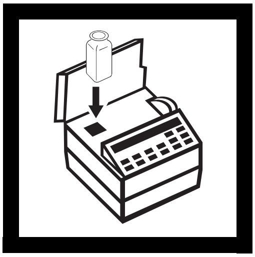
SHIFT TIMER

A five-minute reaction period will begin.

Note: *An amber color will develop if nitrate nitrogen is present.*



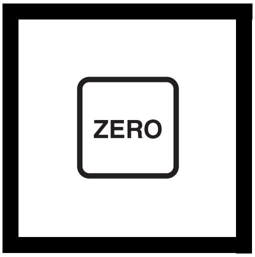
7. Fill another sample cell with 25 mL of sample (the blank).



8. When the timer beeps, the display will show:

mg/L NO_3^--N HR

Place the blank into the cell holder. Close the light shield.



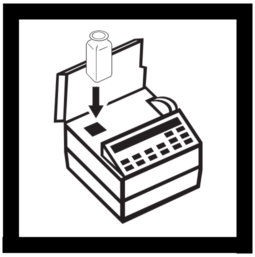
9. Press: **ZERO**

The display will show:

Zeroing. . .

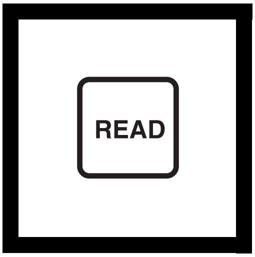
then:

0.0 mg/L NO_3^--N HR



10. Remove the stopper. Place the prepared sample into the cell holder. Close the light shield.

Note: *A cadmium deposit will remain after the NitraVer 5 Nitrate Reagent Powder dissolves and will not affect results.*



11. Press: **READ**

The display will show:

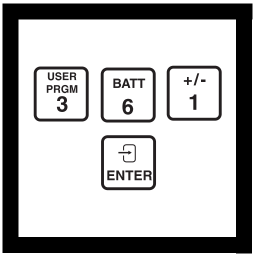
Reading. . .

then the result in mg/L nitrate nitrogen (NO_3^--N) will be displayed.

Note: *Rinse the sample cell immediately after use to remove all cadmium particles.*

Forms ▲ NO_3^- N
▼ NO_3^-

Using AccuVac Ampuls

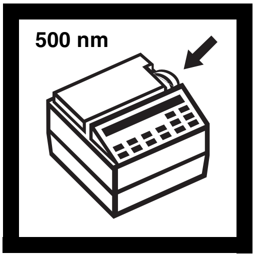


1. Enter the stored program number for high range nitrate nitrogen (NO_3^--N)-AccuVac ampuls.

Press: **3 6 1 ENTER**

The display will show:

Dial nm to 500



2. Rotate the wavelength dial until the small display shows:

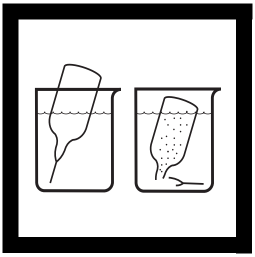
500 nm

When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

then:

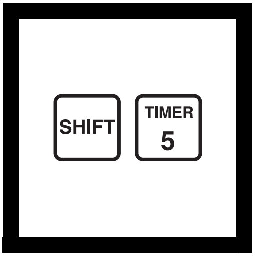
mg/L NO_3^--N H AV



3. Collect at least 40 mL of sample in a 50-mL beaker. Fill a NitraVer 5 Nitrate AccuVac Ampul with sample.

Note: *Keep the tip immersed while the ampul fills completely.*

Note: *A reagent blank must be determined on each new lot of NitraVer 5. Repeat Steps 3 to 11 using deionized water as the sample. Subtract this value from each result obtained with this lot of reagent.*

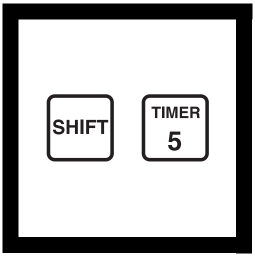


4. Press:

SHIFT TIMER

A one-minute mixing period will begin. Invert the ampul repeatedly until the timer beeps. Wipe off any liquid or fingerprints.

Note: *Shaking time and technique influence color development. For most accurate results, make successive tests on a 10 mg/L Nitrate Nitrogen Standard Solution. Adjust the shaking time to obtain the correct result.*



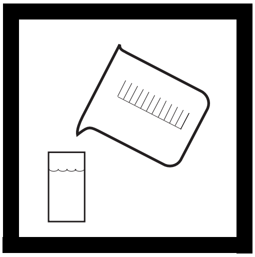
5. When the timer beeps, press:

SHIFT TIMER

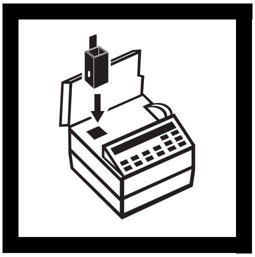
A five-minute reaction period will begin.

Note: *A cadmium deposit will remain after the NitraVer 5 Nitrate Reagent Powder dissolves and will not affect results.*

Note: *An amber color will develop if nitrate nitrogen is present.*

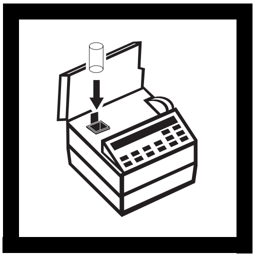


6. Fill a zeroing vial with at least 10 mL of sample (the blank).



7. Place the AccuVac Vial Adapter into the cell holder.

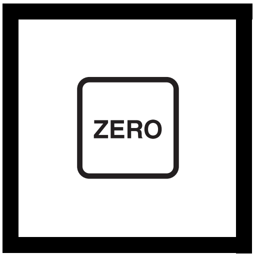
Note: *Place the grip tab at the rear of the cell holder.*



8. When the timer beeps, the display will show:

mg/L NO_3^--N H AV

Place the blank into the cell holder. Close the light shield.



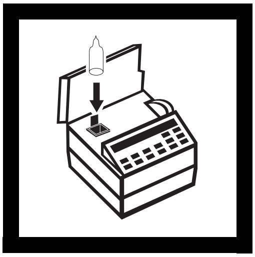
9. Press: **ZERO**

The display will show:

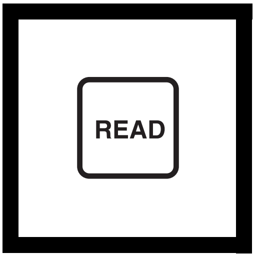
Zeroing. . .

then:

0.0 mg/L NO_3^--N H AV



10. Place the AccuVac ampul into the cell holder. Close the light shield.



11. Press: **READ**

The display will show:

Reading. . .

then the nitrate result in mg/L nitrogen (NO_3^--N) will be displayed.

Forms ▲ NO_3^- -N
▼ NO_3^-

Sampling and Storage

Collect samples in clean plastic or glass bottles. Store at 4 °C (39 °F) or lower if the sample is to be analyzed within 24 to 48 hours. Warm to room temperature before running the test. For storage periods up to 14 days, adjust sample pH to 2 or less with sulfuric acid, ACS, (about 2 mL per liter). Sample refrigeration is still required.

Before testing the stored sample, warm to room temperature. Neutralize the sample with 5.0 N Sodium Hydroxide Standard Solution.

Do not use mercury compounds as preservatives.

Correct test results for volume additions; see *Correction for Volume Additions*, (*Section I*) for more information.

Accuracy Check

Standard Additions Method

a) Snap the neck off a fresh High Range Nitrate Nitrogen Voluette Ampule Standard, 500 mg/L NO_3^--N.

b) Use the TenSette Pipet to add 0.1, 0.2, and 0.3 mL of standard to three 25-mL samples. Mix each thoroughly. (For AccuVac ampuls, use 50-mL beakers.)

c) Analyze each sample as described above. The nitrogen concentration should increase 2.0 mg/L for each 0.1 mL of standard added.

d) If these increases do not occur, see *Standard Additions (Section I)* for more information.

Standard Solution Method

Use a 10.0 mg/L Nitrate Nitrogen Standard Solution listed under Optional reagents to check test accuracy. Or, this can be prepared by diluting 1.00 mL of solution from a High Range Nitrate Nitrogen Voluette Ampule Standard Solution, 500 mg/L NO_3^--N, to 50.0 mL with deionized water. Use this standard in place of sample in Step 3 of the procedures.

Precision

In a single laboratory using standard solutions of 20.0 mg/L nitrate nitrogen (NO_3^--N) and two representative lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±0.8 mg/L nitrate nitrogen.

Using standard solutions of 30.0 mg/L (NO_3^--N) and one representative lot of AccuVac ampuls with the DR/2010, a single operator obtained a standard deviation of ±2.3 mg/L nitrate nitrogen.

Interferences

Compensate for nitrite interference as follows:

a) Add Bromine Water, 30 g/L, drop-wise to the sample in Step 3 until a yellow color remains.

b) Add one drop of Phenol Solution, 30 g/L, to destroy the color.

c) Proceed with Step 3. Report results as total nitrate and nitrite.

Strong oxidizing and reducing substances will interfere. Ferric iron causes high results and must be absent. Chloride concentrations above 100 mg/L will cause low results. The test may be used at high chloride levels (i.e., seawater), but a calibration must be performed using standards spiked to the same chloride concentration. See User Stored Programs in the DR/2010 Instrument Manual for more information.

Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment; see *pH Interferences (Section I).*

Summary of Method

Cadmium metal reduces nitrates present in the sample to nitrite. The nitrite ion reacts in an acidic medium with sulfanilic acid to form an intermediate diazonium salt. This salt couples to gentisic acid to form an amber-colored product.

REQUIRED REAGENTS (USING POWDER PILLOWS)

Description	Quantity Required Per Test	Unit	Cat. No.
NitraVer 5 Nitrate Reagent Pwd. Pillows, 25 mL	1 pillow	100/pkg	14034-99

REQUIRED REAGENTS (USING ACCUVAC AMPULS)

Description	Quantity Required Per Test	Unit	Cat. No.
NitraVer 5 Nitrate Reagent AccuVac Ampul	1 ampul	25/pkg	25110-25

REQUIRED APPARATUS (Using Powder Pillows)

Description	Quantity Required Per Test	Unit	Cat. No.
Stopper, rubber, size 2	1	12/pkg	2118-02
Sample Cell, 25 mL, matched pair		pair	20950-00

REQUIRED APPARATUS (USING ACCUVAC AMPULS)

Description	Quantity Required Per Test	Unit	Cat. No.
Adapter, AccuVac Vial	1	each	43784-00
Beaker, 50 mL	1	each	500-41
Zeroing Vial	1	each	21228-00

OPTIONAL REAGENTS

Bromine Water, 30 g/L	25 mL*	2211-20
Nitrate Nitrogen standard Solution, 10 mg/L NO_3^--N	500 mL	307-49
Nitrate Nitrogen Standard Solution, Voluette Ampule, 500 mg/L (NO_3^--N), 10 mL	16/pkg	14260-10
Phenol Solution, 30 g/L	25 mL	2112-20
Sodium Hydroxide Standard Solution, 5.0 N	50 mL* SCDB	2450-26
Sulfuric Acid, ACS	500 mL*	979-49
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Description	Unit	Cat. No.
AccuVac Snapper Kit	each	24052-00
Ampule Breaker Kit	each	21968-00
Cylinder, graduated, 25 mL	each	1081-40
Dropper, for 1-oz bottle	each	2258-00
Flask, volumetric, Class A, 50 mL	each	14574-41
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
pH Meter, *sens***ion**™***1***, portable	each	51700-10
Pipet, serological, 2 mL	each	532-36
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 1.00 mL	each	14515-35
Pipet Filler, safety bulb	each	14651-00
Pour-Thru Cell Assembly Kit	each	45215-00
Sample Cells, 1-inch, polystyrene, disposable	12/pkg	24102-12
Thermometer, -20 to 105 °C	each	1877-01

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

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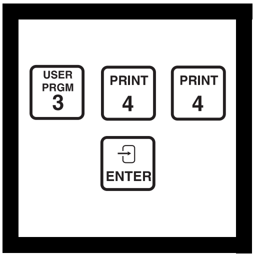
* Contact Hach for larger sizes.

Method 10020

For water and wastewater

NITRATE, HR (0 to 30.0 mg/L NO_3^- -N)

Chromotropic Acid Method, Test ‘N Tube™

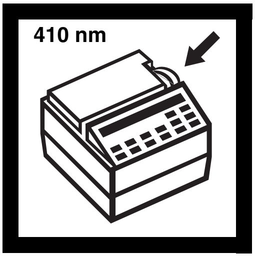


1. Enter the stored program number for Test 'N Tube nitrate nitrogen (NO_3^--N).

Press: **344 ENTER**

The display will show:

Dial nm to 410



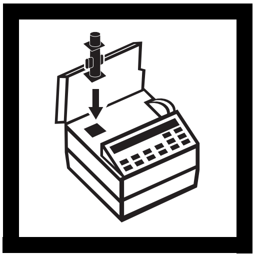
2. Rotate the wavelength dial until the small display shows:

410 nm

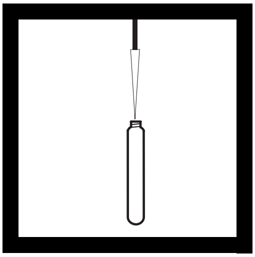
When the correct wavelength is dialed in, the display will quickly show: **Zero Sample**

then:

mg/L NO_3^--N TNT



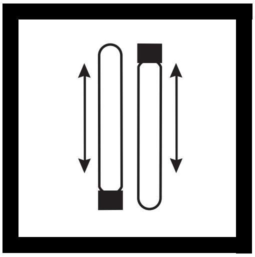
3. Place the COD Vial Adapter into the cell holder with the marker to the right.



4. Remove the cap from a NitraVer X Reagent A vial and add 1 mL of sample (this will be the sample blank).

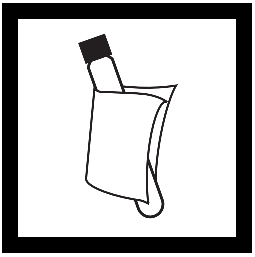
Note: *Run a reagent blank for this test. Use Nitrate-free water in place of the sample. Subtract this result from all tests run with this lot of NitraVer X Reagent B. Run a new reagent blank for each new lot.*

Note: *For proof of accuracy, use a 15 mg/L Nitrate Nitrogen Standard Solution in place of the sample.*



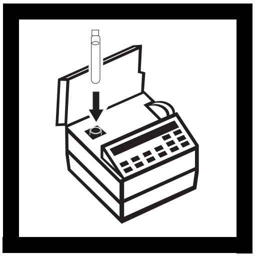
5. Cap the tube and invert 10 times to mix.

Note: *This test is technique sensitive. Low results may occur if these instructions are not followed. Hold the tube vertical with the cap pointing up. Invert the vial so the cap points down. Wait for all of the solution to flow to the cap end. Pause. Return the vial to the original position. Wait for all the solution to flow to the vial bottom. This process equals one inversion. Do this 10 times.*

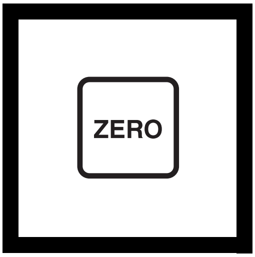


6. Clean the outside of the vial with a towel.

Note: *Wiping with a damp towel, followed by a dry one, will remove fingerprints and other marks.*



7. Place the sample blank into the vial adapter with the Hach logo facing the front of the instrument. Place the cover on the adapter.



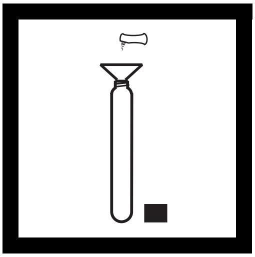
8. Press: **ZERO**

The display will show:

Zeroing. . .

then:

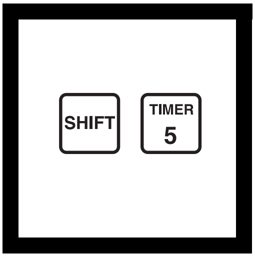
0.0 mg/L NO_3^--N TNT



9. Using a funnel, add the contents of one NitraVer X Reagent B Powder Pillow to the vial. Cap. Invert to mix (this is the prepared sample).

Note: *See step 5 for inversion instructions*

Note: *Some solid matter will not dissolve.*



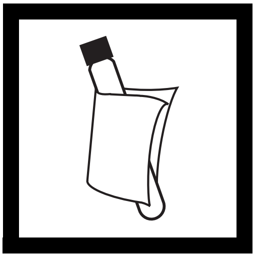
10. Press:

SHIFT TIMER

A five-minute reaction period will begin. Do not invert the vial again.

Note: *A yellow color will develop if nitrate nitrogen is present.*

Note: *Complete steps 12-14 within 5 minutes after the timer beeps.*

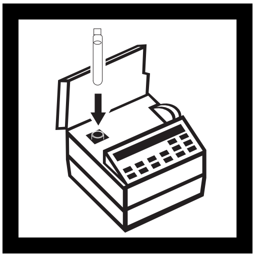


11. When the timer beeps, the display will show:

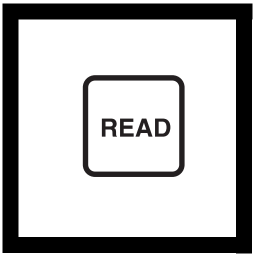
0.0 mg/L NO_3^--N TNT

Clean the outside of the vial with a damp towel.

Note: *Wiping with a damp towel, followed by a dry one, will remove fingerprints and other marks.*



12. Place the prepared sample into the vial adapter with the Hach logo facing the front of the instrument. Place the cover on the adapter.



13. Press: **READ**

The display will show:

Reading. . .

then the result in mg/L nitrate expressed as nitrogen (NO_3^--N) will be displayed.

Sampling and Storage

Collect samples in clean plastic or glass bottles. Store at 4 °C (39 °F) or lower if the sample is to be analyzed within 24 to 48 hours. Warm to room temperature before running the test. For longer storage periods (up to 14 days), adjust sample pH to 2 or less with concentrated sulfuric acid, ACS (about 2 mL per liter). Sample refrigeration is still required.

Before testing the stored sample, warm to room temperature and neutralize with 5.0 N Sodium Hydroxide Standard Solution.

Do not use mercury compounds as preservatives.

Correct the test result for volume additions; see *Correction for Volume Additions* in *Section I* for more information.

Accuracy Check

Standard Additions Method

a) Fill three 25-mL graduated mixing cylinders with 25 mL of sample.

b) Snap the neck off a fresh High Range Nitrate Nitrogen Voluette Ampule Standard, 500 mg/L NO_3^--N.

c) Use the TenSette Pipet to add 0.1, 0.2, and 0.3 mL of standard to the three mixing cylinders, respectively. Mix each thoroughly.

d) Analyze each sample as described in the procedure; use a 1-mL aliquot of a spiked sample prepared in Step C in each test. The nitrogen concentration should increase 2.0 mg/L for each 0.1 mL of standard added.

e) If these increases do not occur, see *Standard Additions* (*Section I*) for more information.

Standard Solution Method

Use a 15.0 mg/L Nitrate Nitrogen Standard Solution listed under Optional Reagents to check test accuracy. Or, this can be prepared by pipetting 3.00 mL of solution from a High Range Nitrate Nitrogen Voluette Ampule Standard Solution, 500 mg/L NO_3^--N into a Class A 100-mL volumetric flask. Dilute to the line with deionized water. Substitute this standard for the sample and perform the test as described in the procedure. The mg/L NO_3^--N reading should be 15 mg/L.

Precision

In a single laboratory, using a standard solution of 20.0 mg/L nitrate nitrogen (NO_3^--N) and two representative lots of reagent with the DR/2010, a single operator obtained a standard deviation of $\pm$0.2 mg/L N.

Interferences

Interfering Substance	Interference Level
Barium	A negative interference at more than 1 mg/L.
Chloride	Does not interfere below 1000 mg/L.
Hardness	Does not interfere.
Nitrite	A positive interference at concentrations greater than 12 mg/L. Remove nitrite interference up to 100 mg/L by adding 400 mg of urea (one full 0.5 g Hach measuring spoon) to 10 mL of sample. Swirl to dissolve. Proceed with the nitrate test as usual.

Summary of Method

Nitrate reacts with chromotropic acid under strongly acidic conditions to yield a yellow product with a maximum absorbance at 410 nm.

REQUIRED REAGENTS

	Cat. No.
NitraVer X Test 'N Tube Nitrate Reagent Set (50 vials)	26053-00

Includes: (4) 26055-46, (1) 272-42, (50) Nitrate Pretreatment Solution Vials*

Description	Quantity Required Per Test	Unit	Cat. No.
Nitrate Pretreatment Solution Vials	1	50/pkg	*
NitraVer® X Reagent B Powder Pillows	1	50/pkg	26055-46
Water, deionized	varies	100 mL	272-42

REQUIRED APPARATUS

COD Vial Adapter, DR/2010	1	each	44799-00
Funnel, micro	1	each	25843-35
Pipet, TenSette, 0.1 to 1.0 mL	1	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	varies	50/pkg	21856-96
Test Tube Rack	1-3	each	18641-00

OPTIONAL REAGENTS

Nitrate-Nitrogen Standard Solution, 15 mg/L NO_3^--N	100 mL MDB	24151-32
Nitrate-Nitrogen Standard Solution, Voluette ampule, 500 mg/L N	16/pkg	14260-10
Sodium Hydroxide Standard Solution, 5.0 N	50 mL DB	2450-26
Sulfuric Acid, ACS	500 mL	979-49
Urea, ACS	100 g	11237-26
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Ampule Breaker Kit	each	24846-00
Cylinder, graduated, mixing, 25-mL	each	26363-40
Flask, volumetric, Class A, 100 mL	each	14574-42
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
Pipet, serological, 2 mL	each	532-36
Pipet, volumetric, Class A, 3.00 mL	each	14575-03
Spoon, measuring, 0.5 g	each	907-00

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

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* Not available separately. Please order the complete set (Cat. No. 26053-45) as a replacement.

Method 8507

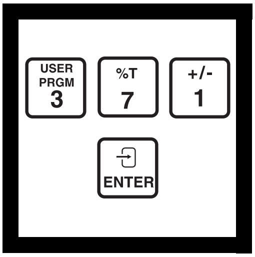
NITRITE, LR (0 to 0.300 mg/L NO_2^--N)

For water, wastewater, and seawater

Diazotization Method (Powder Pillows or AccuVac Ampuls),

USEPA Approved for reporting wastewater analysis*

Using Powder Pillows



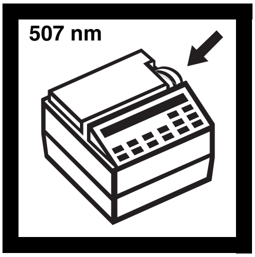
1. Enter the stored program number for low range nitrite nitrogen (NO_2^--N) powder pillows.

Press: **3 7 1 ENTER**

The display will show:

Dial nm to 507

Note: *The Pour-Thru Cell can be used with 25 mL reagents only.*



2. Rotate the wavelength dial until the small display shows:

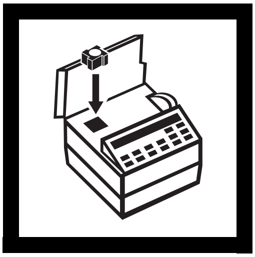
507 nm

When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

then:

mg/L NO_2^--N LR

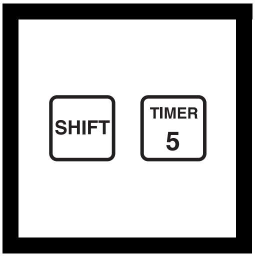


3. Insert the 10-mL Cell Riser into the cell compartment

4. Fill a 10-mL sample cell with 10 mL of sample.

5. Add the contents of one NitriVer 3 Nitrite Reagent Powder Pillow (the prepared sample). Stopper. Shake the cell to dissolve the powder.

Note: *A pink color will develop if nitrite nitrogen is present.*



6. Press:

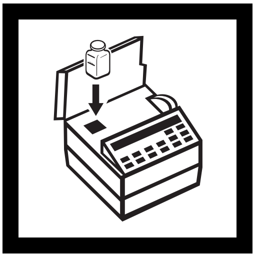
SHIFT TIMER

A 20-minute reaction period will begin.

7. When the timer beeps, the display will show:

mg/L NO_2^--N LR

Fill a second 10-mL sample cell with 10 mL of sample (the blank).



8. Place the blank into the cell holder. Close the light shield.

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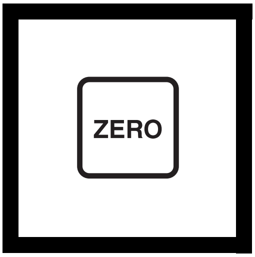
* *Federal Register*, 44(85) 25505 (May 1, 1979).



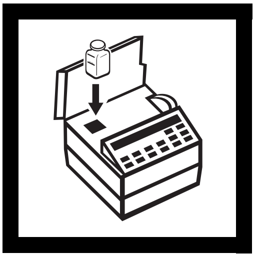
9. Press: **ZERO**

The display will show:

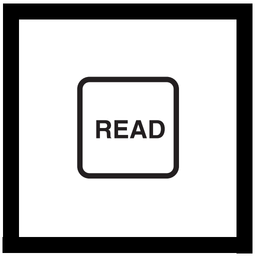
Zeroing. . . .

then:

0.000 mg/L NO_2^--N LR



10. Remove the stopper from the prepared sample. Place the cell into the cell holder. Close the light shield.



11. Press: **READ**

The display will show:

Reading. . . .

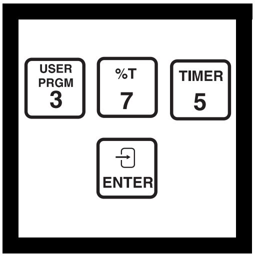
then the result in mg/L nitrite expressed as nitrogen (NO_2^--N) will be displayed.

Forms ▲▼ $NaNO_2$

NO_2^--N

NO_2^-

Using AccuVac Ampuls

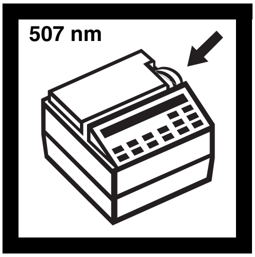


1. Enter the stored program number for low range nitrite AccuVac ampuls.

Press: **3 7 5 ENTER**

The display will show:

Dial nm to 507



2. Rotate the wavelength dial until the small display shows:

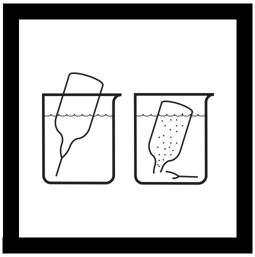
507 nm

When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

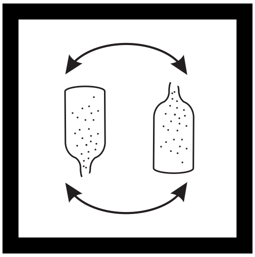
then:

mg/L NO_2^--N LR AV



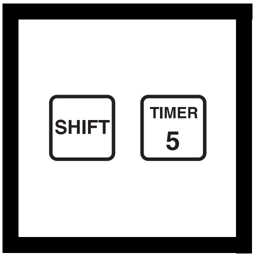
3. Collect at least 40 mL of sample in a 50-mL beaker. Fill a NitriVer 3 Nitrite AccuVac Ampul with sample.

Note: *Keep the tip immersed while the ampul fills.*



4. Invert the ampul several times to mix. Wipe off any liquid or fingerprints.

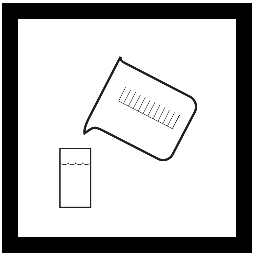
Note: *A pink color will develop if nitrite nitrogen is present.*



5. Press:

SHIFT TIMER

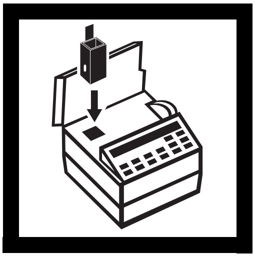
A 15-minute reaction period will begin.



6. When the timer beeps, the display will show:

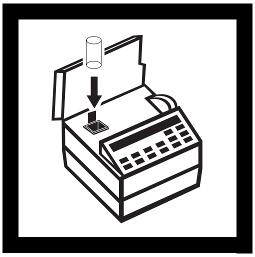
mg/L NO_2^--N LR AV

Fill a zeroing vial (the blank) with at least 10 mL of sample.



7. Place the AccuVac Vial Adapter into the cell holder.

Note: *Place the grip tab at the rear of the cell holder.*



8. Place the blank into the cell holder. Close the light shield.

Press: **ZERO**

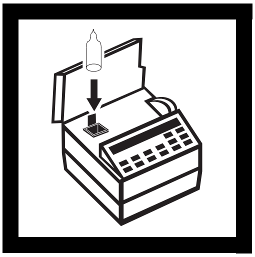
The display will show:

Zeroing. . .

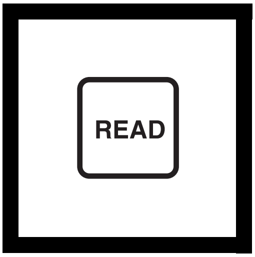
then:

0.000 mg/L

NO_2^--N LR AV



9. Place the AccuVac ampul into the cell holder. Close the light shield.



10. Press: **READ**

The display will show:

Reading. . . .

then the result in mg/L nitrite expressed as nitrogen (NO_2^--N) will be displayed.

Forms ▲▼ $NaNO_2$
NO_2^--N
NO_2^-

Sampling and Storage

Collect samples in clean plastic or glass bottles. Store at 4 °C (39 °F) or lower if the sample is to be analyzed within 48 hours. Warm to room temperature before running the test.

Accuracy Check

Standard Solution Method

Preparing accurate nitrite standards is difficult. Reagent-grade sodium nitrite usually assays less than 100% pure, so standardization of final solutions is necessary. Hach recommends using the standard preparation instructions in *Standards Methods for the Examination of Water and Wastewater*, Method 4500-NO_2^- B (p. 4-86 of 18th edition; p. 4-83 of 19th edition).

Hach offers the Nitrite Stock Solution, 250 µg/mL (250 mg/L) used in the Standard Methods standardization procedure (see *Optional Reagents*).

An approximate standard solution can be prepared from the stock solution without titrating the stock standard solution. For most accurate performance checks, standardize the stock standard with titration.

Preparing An Approximate 0.25 mg/L Nitrite Nitrogen Standard Solution

Pipet 1.00 mL of the 250-mg/L stock standard solution (APHA) into a 1000-mL volumetric flask. Dilute to volume with nitrite-free deionized water. Stopper and mix thoroughly.

Precision

In a single laboratory using a standard solution of 0.100 mg/L NO_3^--N and two representative lots of powder pillow reagent with the DR/2010, a single operator obtained a standard deviation of $\pm$0.0011 mg/L nitrite nitrogen.

In a single laboratory using a standard solution of 0.100 mg/LNO_3^--N and two representative lots of AccuVac ampuls with the DR/2010, a single operator obtained a standard deviation of $\pm$0.0007 mg/L nitrite nitrogen.

Estimated Detection Limit (EDL)

The EDL for program 371 (Powder Pillows) and program 375 (AccuVac Ampuls) is 0.001 mg/L NO_2^--N. The EDL is the calculated lowest average concentration in a deionized water matrix that is different from zero with a 99% level of confidence. For more information on derivation and use of Hach's estimated detection limit, see Section I.

Interferences

Strong oxidizing and reducing substances interfere.

Cupric and ferrous ions cause low results.

Ferric, mercurous, silver, bismuth, antimonous, lead, auric, chloroplatinate and metavanadate ions interfere by causing precipitation.

Very high levels of nitrate (100 mg/L nitrate as N or more) appear to undergo a slight amount of reduction to nitrite, either spontaneously or during the course of the test. A small amount of nitrite will be found at these levels.

Summary of Method

Nitrite in the sample reacts with sulfanilic acid to form an intermediate diazonium salt. This couples with chromotropic acid to produce a pink colored complex directly proportional to the amount of nitrite present.

REQUIRED REAGENTS (Using Powder Pillows)

Description	Quantity Required Per Test	Unit	Cat. No.
NitriVer 3 Nitrite Reagent Powder Pillows, 10 mL sample	1 pillow	100/pkg	21071-69

REQUIRED REAGENTS (Using AccuVac Ampuls)

NitriVer 3 Nitrite Reagent AccuVac Ampul	1 ampule	25/pkg	25120-25

REQUIRED APPARATUS (Using Powder Pillows)

Cell Riser, 10-mL	1	each	45282-00
Sample Cell, 10 mL, matched pair	2	pair	24954-02
Stopper, hollow, polyethylene, No. 1	1	6/pkg	14480-01

REQUIRED APPARATUS (Using AccuVac Ampuls)

Adapter, AccuVac Vial	1	each	43784-00
Beaker, 50 mL	1	each	500-41
Vial, zeroing	1	each	21228-00

OPTIONAL REAGENTS

Nitrite Stock Solution, 250 µg/mL as N	500 mL	23402-49
Sodium Nitrite, ACS	454 g	2452-01
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

AccuVac Snapper Kit	each	24052-00
Balance, analytical	each	22310-00
Flask, volumetric, 1000 mL, Class A	each	14574-53
Pipet, volumetric, 1.00 mL, Class A	each	14515-35
Pipet Filler, safety bulb	each	14651-00

OPTIONAL 25 ML ANALYSIS ITEMS

Clippers, for opening pillows	each	968-00
NitriVer 3 Nitrite Reagent Powder Pillows (25 mL sample)	100/pkg	14065-99
Pour-Thru Cell Assembly Kit	each	45215-00
Sample Cell, 25-mL, matched pair	pair	20950-00

For technical support and ordering information, see Section V.

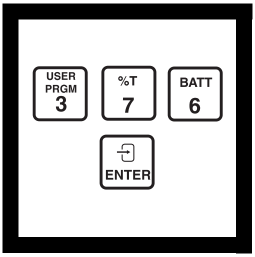
In the U.S.A. call 800-227-4224 to place an order.
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 10057

NITRITE, LR 0 to 250 µg/L NO_2^--N

For aquaculture, treated, and natural waters

Diazotization, NED Rapid Liquid Method*

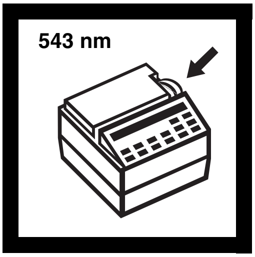


1. Enter the stored program number for low range nitrite nitrogen (NO_2^--N).

Press: **3 7 6 ENTER**

The display will show:

Dial nm to 543



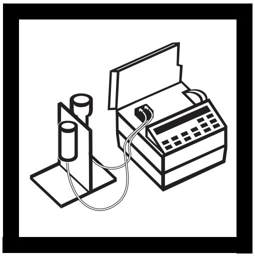
2. Rotate the wavelength dial until the display shows: **543 nm**

When the correct wavelength is dialed in, the display will quickly show

Zero Sample

then:

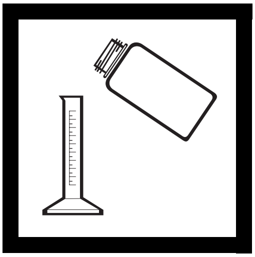
µg/L NO_2^--N LRRL



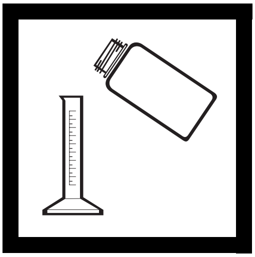
3. Install the Pour-Thru Cell and flush with 50 mL of deionized water.

***Note:** Clean the Pour-Thru Cell and all labware as specified in Treating Analysis Labware.*

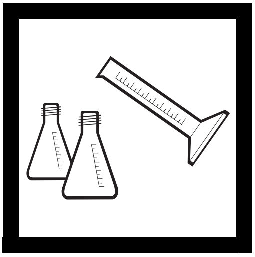
4. Rinse two clean 125-mL plastic Erlenmeyer flasks three times with the sample to be tested.



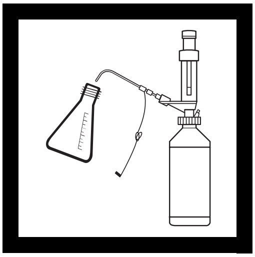
5. Rinse a clean 25-mL plastic graduated cylinder three times with sample.



6. Fill this rinsed cylinder to the 25-mL mark with sample.



7. Pour the contents of the 25-mL cylinder into one of the flasks. Measure a second 25-mL portion of sample into the graduated cylinder and pour the contents into the second flask.

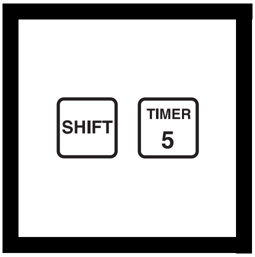


8. Add 1.0 mL of prepared Nitrite Reagent Solution to one of the flasks using the Repipet Dispenser. Swirl to mix. (The other flask will be used as the blank.)

***Note:** See Reagent Preparation for instructions on preparing the Nitrite Reagent.*

---

* Adapted from *Standard Methods for the Examination of Water and Wastewater.*



9. Press:

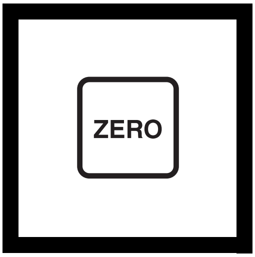
SHIFT TIMER

A ten-minute reaction period will begin.

10. When the timer beeps, the display will show:

µg/L NO_2^--N LRRL

Pour the contents of the flask containing the blank into the Pour-Thru Cell.



11. After the flow has stopped, press: **ZERO**

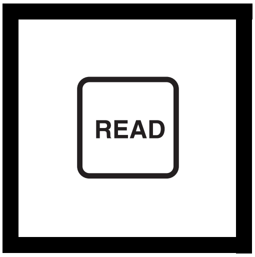
The display will show:

Zeroing. . . .

then:

0 µg/L NO_2^--N LRRL

12. Pour the contents of the flask containing the prepared sample into the Pour-Thru Cell.



13. Press: **READ**

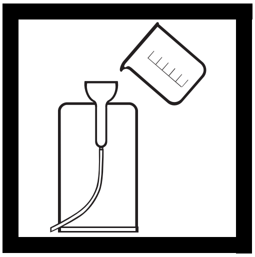
The display will show:

Reading. . . .

then the result in µg/L nitrite expressed as nitrogen (NO_2^--N) will be displayed.

Forms ▲▼
$NaNO_2$
NO_2^--N
NO_2^-

***Note:** Prepare a reagent blank when the nitrite concentration is less than 60 µg/L. Use deionized water in place of the sample in steps 4-13. Subtract this value from the sample result.*



14. Flush the Pour-Thru Cell with at least 50 mL of deionized water immediately after use.

***Note:** Protect the Pour-Thru Cell from contamination by inverting a small beaker over the top of the glass funnel when not in use.*

Reagent Preparation

The Nitrite Reagent Solution must be prepared by the user as follows:

Using a powder funnel, add the contents of one Nitrite Indicator Powder Pillow (Cat. No. 26209-64) to one 236-mL bottle of Nitrite Diluent Solution (Cat. No. 26208-31). The powder dissolves slowly, therefore the solution should be mixed by inverting the bottle continuously for 10-15 minutes. Alternatively, a magnetic stirrer may be used for mixing after adding a clean stir bar to the solution. If powder is still visible in the solution after this time, continue to mix until the powder is dissolved.

This solution will develop a brownish-purple color with time but will still give accurate results for two weeks after mixing if stored at 20-25 °C and away from direct sunlight. Record the date of preparation on the bottle and discard any remaining solution after two weeks. Do not add fresh reagent to previously mixed reagent. Use of this reagent after 2 weeks may result in high reagent blanks and low values at high concentrations.

Treating Analysis Labware

All containers used in this test must be cleaned thoroughly. Plastic flasks with screw-type closures work well for sampling and analysis. Clean containers by normal means, then rinse with deionized water. Soak labware for 10 minutes in a solution of 1 mL prepared reagent to 25 mL deionized water. Rinse well with deionized water. Pre-treat the Pour-Thru Cell with this same mixture of reagent and water followed by thorough rinsing with deionized water. Dedicate labware used for nitrite analysis only. If the labware is rinsed well after each use, only occasional pre-treatment is necessary.

Sampling and Storage

Collect samples in clean plastic or glass bottles. Analyze as soon as possible for best results.

If samples cannot be analyzed promptly, store for up to 48 hours at 4 °C (39 °F) or lower. Warm to room temperature before running the test.

Accuracy Check

Standard Solution Method

Prepare a nitrite nitrogen stock solution by dissolving 0.493 grams of sodium nitrite, ACS, in 1000 mL of nitrite-free deionized water to give a 100 mg/L nitrite nitrogen (NO_2^--N) stock solution. This solution is not stable and should be prepared daily. Use a Class A pipet to dilute 1.00 mL of the stock solution to 1000 mL with nitrite-free deionized water to give a 100 µg/L (NO_2^--N) nitrite nitrogen standard solution. Prepare this solution immediately before use.

This solution can also be prepared by diluting 5.00 mL of a 250 mg/L NO_2^--N stock solution to 250 mL to give a 5000 µg/L intermediate standard. Dilute 10.00 mL of the 5000 µg/L intermediate to 500 mL to give a 100 µg/L NO_2^--N standard.

Run the test using the 100 µg/L NO_2^--N standard in place of the sample. Results should be between 90 and 110 µg/L NO_2^--N.

Precision

In a single laboratory using seven concentrations of nitrite standards and two lots of reagent with the DR/2010, a single operator obtained a calibration curve that showed a 99% confidence interval at 100 µg/L of less than 1 µg/L.

Interferences

Strong oxidizing and reducing substances interfere. Ferrous ions cause low results. Mercuric, silver, bismuth, antimonous, lead, auric, chloroplatinate and metavanadate ions interfere by causing precipitation.

Very high levels of nitrate (100 mg/L nitrate as N or more) appear to undergo a slight amount of reduction to nitrite, either spontaneously or during the course of the test. A small amount of nitrite will be found at these levels. Ammonia below 50 mg/L as NH_3-N does not interfere.

The following ions do not interfere at concentrations lower than those given:

Al^{3+}	1 mg/L
Zn^{2+}	0.2 mg/L
Ca^{2+} as $CaCO_3$	1000 mg/L
Ni^{2+}	2.5 mg/L
Cu^{2+}	5 mg/L
Fe^{3+}	5 mg/L

Remove suspended solids by filtration.

Summary of Method

Nitrite in the sample reacts with sulfanilamide to form an intermediate diazonium salt. This couples with N-(1-napthyl)-ethylenediamine dihydrochloride to produce a red-colored complex directly proportional to the amount of nitrite present.

REQUIRED REAGENTS

Description		**Cat. No.**
Nitrite Reagent Package		26612-00
Includes:		
Nitrite Indicator Powder Pillows	4/pkg	26209-64
Nitrite Diluent Solution, 236 mL	4 each	26208-31

REQUIRED APPARATUS

Description	**Quantity Required Per Test**	**Unit**	**Cat. No.**
Clippers, for opening powder pillows	1	each	968-00
Cylinder, graduated, 25 mL, poly	1	each	1081-40
Dispenser, Fixed Volume, 1.0 mL Repipet Jr.	1	each	21113-01
Flask, Erlenmeyer, 125 mL PMP w/cap	2	each	20898-43
Flask, Erlenmeyer, 125 mL, PMP w/cap		6/pkg	20898-73
Pour-Thru Cell Assembly Kit	1	each	45215-00

OPTIONAL REAGENTS

Nitrite Standard Solution, 250 mg/L as NO_2^--N	500 mL	23402-49
Sodium Nitrite, ACS	454 g	2452-01
Water, deionized	500 mL	272-49
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Balance, analytical, 115V	each	26103-00
Balance, analytical, 230V	each	26103-02
Beaker, poly, 50 mL	each	1080-41
Flask, volumetric, Class A, 1000 mL	each	26366-53
Flask, volumetric, Class A, 500 mL	each	26366-49
Flask, volumetric, Class A, 250 mL	each	26366-46
Funnel, powder	each	22644-67
Pipet, serological, 10 mL	each	532-38
Pipet, volumetric, Class A 1.00 mL	each	14515-35
Pipet, volumetric, Class A, 5.00 mL	each	14515-37
Pipet, volumetric, Class A, 10.00 mL	each	14515-38
Pipet Filler, safety bulb	each	14651-00
Stir Bar, octagonal	each	20953-50
Stirrer, magnetic, battery-powered	each	21636-00
Stirrer, magnetic, 120 V	each	23436-00
Stirrer, magnetic, 240 V	each	23436-02
Thermometer, -20 to 105 °C	each	1877-01
Weighing Boat, 67/46 mm	500/pkg	21790-00

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

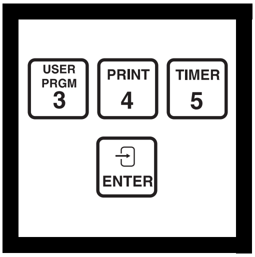
Method 8507

NITRITE, LR, Test ‘N Tube (0 to 0.500 mg/L NO_2^--N)

Diazotization (Chromotropic Acid) Method

For water, wastewater, and seawater

USEPA approved for water and wastewater analysis*

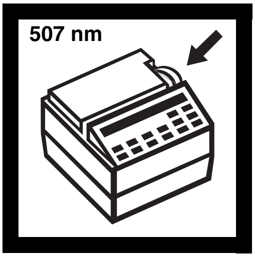


1. Enter the stored program number for Test 'N Tube nitrite nitrogen (NO_2^--N).

Press: **3 4 5 ENTER**

The display will show:

Dial nm to 507



2. Rotate the wavelength dial until the small display shows:

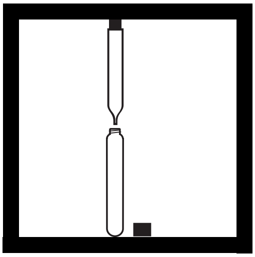
507 nm

When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

then:

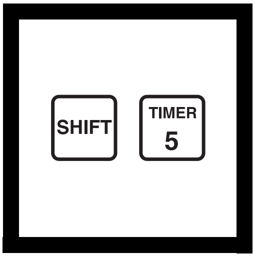
mg/L NO_2^--N TNT



3. Fill a Test 'N Tube NitriVer 3 Nitrite vial with 5 mL of sample. Cap and shake to dissolve powder. This is the prepared sample.

Note: *A pink color will develop if nitrite is present.*

Note: *For most accurate results, perform a reagent blank correction by using deionized water instead of sample. Subtract this result from all samples run with this lot of reagent.*



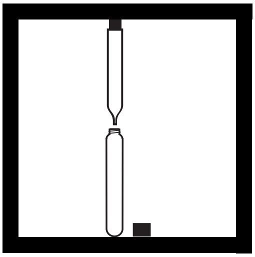
4. Press:

SHIFT TIMER

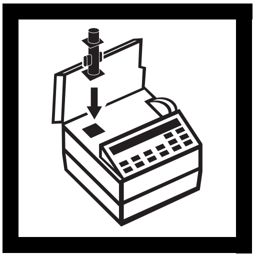
A 20-minute reaction period will begin.

When the timer beeps, the display will show:

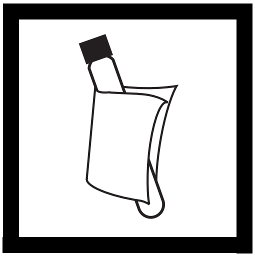
mg/L NO_2^--N TNT



5. Fill an empty Test 'N Tube vial with 5 mL of sample (the blank).

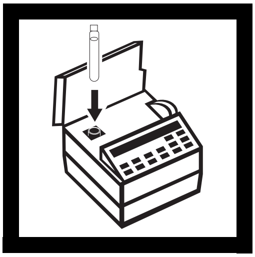


6. Place the COD Vial Adapter into the cell holder with the marker to the right.



7. Clean the outside of the vials with a towel.

Note: *Wiping with a damp towel, followed by a dry one, removes fingerprints and other marks.*



8. Place the blank into the vial adapter with the Hach logo facing the front of the instrument. Place the cover on the adapter.

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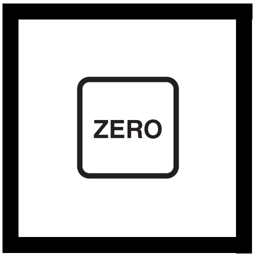
* *Federal Register* 44 (85) 35505 (May 1, 1979)



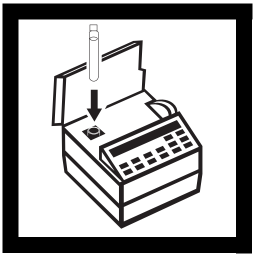
9. Press: **ZERO**

The display will show:

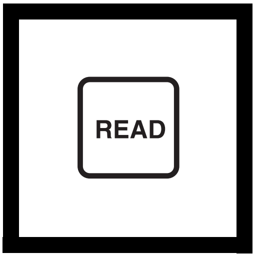
Zeroing. . . .

then:

0.000 mg/L
NO^-_2-N TNT



10. Place the prepared sample into the vial adapter. Place the cover on the adapter.



11. Press: **READ**

The display will show:

Reading. . . .

then the result in mg/L nitrite nitrogen will be displayed.

Forms ▲▼
$NaNO_2$
NO_2^--N
NO_2^-

Sampling and Storage

Collect samples in clean plastic or glass bottles.

Store at 4 °C (29 °F) or lower if the sample is to be analyzed within 48 hours. Warm to room temperature before running the test.

Accuracy Check

Standard Solution Method

Prepare a nitrite nitrogen standard solution by dissolving 0.493 grams of sodium nitrite, ACS, in 1000 mL of nitrite-free deionized water to give a 100 mg/L nitrite nitrogen (NO_2^--N) standard solution. This solution is not stable and should be prepared daily. Use a Class A pipet to dilute 1.00 mL of the stock solution to 1000 mL with nitrite-free deionized water to give a 0.10 mg/L (NO_2^--N) nitrite nitrogen standard solution. Prepare this solution immediately before use.

This solution can also be prepared by diluting 5.00 mL of a 250 mg/L NO_2^--N stock solution (Cat. No. 23402-49) to 250.0 mL to give a 5.00 mg/L intermediate standard.

Dilute 10.00 mL of the 5.0 mg/L intermediate to 500 mL to give a 0.100 mg/L NO_2^--N standard.

Run the test using the 0.100 mg/L NO_2^--N standard in place of the sample. Results should be between 0.090 and 0.110 mg/L NO_2^--N.

Precision

In a single laboratory, using a standard solution of 0.258 mg/L nitrite nitrogen and two representative lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±0.006 mg/L NO_2^--N.

Interferences

Interfering Substance	Interference Levels
Antimonous ions	Interfere by causing precipitation
Auric ions	Interfere by causing precipitation
Bismuth ions	Interfere by causing precipitation
Chloroplatinate ions	Interfere by causing precipitation
Cupric ions	Cause low results
Ferric ions	Interfere by causing precipitation
Ferrous ions	Cause low results
Lead ions	Interfere by causing precipitation
Mercurous ions	Interfere by causing precipitation
Metavanadate ions	Interfere by causing precipitation
Nitrate	Very high levels of nitrate (>100 mg/L nitrate as N) appear to undergo a slight amount of reduction to nitrite, either spontaneously or during the course of the test. A small amount of nitrite will be found at these levels.
Silver ions	Interfere by causing precipitation
Strong oxidizing and reducing substances	Interfere at all levels

Summary of Method

Nitrite in the sample reacts with sulfanilic acid to form an intermediate diazonium salt. This couples with chromotropic acid to produce a pink colored complex directly proportional to the amount of nitrite present.

REQUIRED REAGENTS

Description	Cat. No.
NitriVer® 3 Nitrite, Low Range Test ‘N Tube™ Reagent Set (50 vials)	26083-45

Includes: (50) NitriVer 3 Nitrite Vials*, (1) 22758-06, (1) 22411-06, (1) 272-42

Description	Quantity Required Per Test	Unit	Cat. No.
NitriVer® 3 Nitrite, Low Range TNT Vials	1	50/pkg	*
Tube, culture, 16 x 100 mm	1	6/pkg	22758-06
Cap, white	1	6/pkg	22411-06
Water, deionized	varies	100 mL	272-42

REQUIRED APPARATUS

Description	Quantity Required Per Test	Unit	Cat. No.
COD Vial Adapter	1	each	44799-00
Pipet, TenSette, 1 to 10 mL	1	each	19700-10
Pipet Tips for 19700-10 TenSette Pipet	1	50/pkg	21997-96
Test Tube Rack	1-3	each	18641-00

OPTIONAL REAGENTS

Description	Unit	Cat. No.
Nitrite Standard Solution, 250 mg/L as NO_2^--N	500 mL	23402-49
Sodium Nitrite, ACS	454 g	2452-01
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Description	Unit	Cat. No.
Balance, analytical	each	26103-00
Flask, volumetric, 250 mL	each	14574-46
Flask, volumetric, 500 mL	each	14574-49
Flask, volumetric, 1000 mL	each	547-53
Pipet, serological, 10 mL	each	532-38
Pipet, volumetric, Class A, 1.00 mL	each	14515-35
Pipet, volumetric, Class A, 5.00 mL	each	14515-37
Pipet, volumetric, Class A, 10.00 mL	each	14515-38

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

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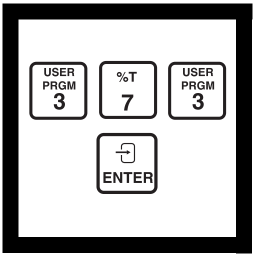
* Not available separately. Please order the complete set (Cat. No. 26083-45) as a replacement.

Method 8153

NITRITE, HR 0 to 150 mg/L NO_2^-)

For water and wastewater

Ferrous Sulfate Method*



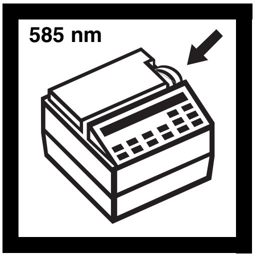
1. Enter the stored program number for high range nitrite (NO_2^-).

Press: **3 7 3 ENTER**

The display will show:

Dial nm to 585

Note: *The Pour-Thru Cell cannot be used.*



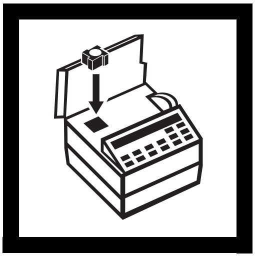
2. Rotate the wavelength dial until display shows:

585 nm

When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

then: **mg/L NO_2^- HR**

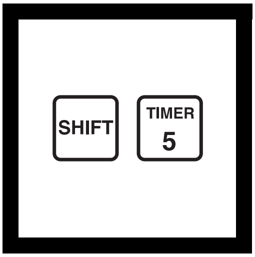


3. Insert the 10-mL Cell Riser into the cell compartment.

4. Fill a sample cell with 10 mL of sample.

5. Add the contents of one NitriVer 2 Nitrite Reagent Powder Pillow, stopper and shake to dissolve (the prepared sample).

Note: *A greenish-brown color will develop if nitrite is present.*

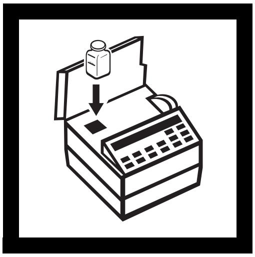


6. Press:

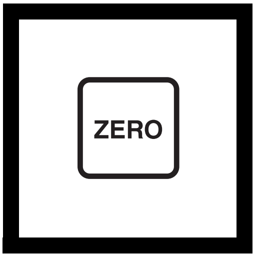
SHIFT TIMER

A ten-minute reaction period will begin.

It is critical to leave the sample undisturbed on a flat surface for the reaction period or low results may occur.



7. Fill another sample cell with 10 mL of sample (the blank). Place it into the cell holder.



8. When the timer beeps the display will show: **mg/L NO_2^- HR**

Press: **ZERO**

The display will show:

Zeroing. . . .

then: **0. mg/L NO_2^- HR**

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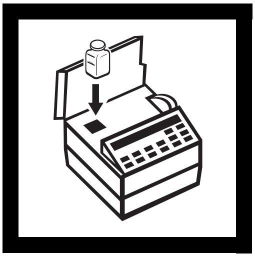
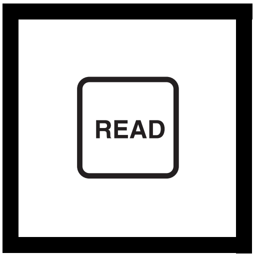
* Adpated from McAlpine, R. and Soule, B., *Qualitative Chemical Analysis,* New York, 476, 575 (1933).



9. Gently invert the prepared sample twice. Remove the stopper. Place the prepared sample into the cell holder. Close the light shield.

Note: Avoid excessive mixing or low results may occur.



10. Press: **READ**

The display will show:

Reading. . . . .

then the result in mg/L NO_2^- will be displayed.

Forms ▲▼ Na NO_2 / NO_2^- / NO_2^--N

Sampling and Storage

Collect samples in clean plastic or glass bottles.

The following storage instructions are necessary only when prompt analysis is impossible. Store at 4 °C (39 °F) or lower if the sample is to be analyzed within 48 hours. Warm to room temperature before analysis.

Accuracy Check

Standard Solution Method

Dissolve 0.150 grams of fresh sodium nitrite and dilute to 1000 mL with deionized water to prepare a 100 mg/L nitrite standard solution. Prepare this solution daily. The mg/L NO_2^- reading should me 100 mg/L.

Precision

In a single laboratory using standard solutions of 100 mg/L nitrite and two representative lots of reagents with the DR/2010, a single operator obtained a standard deviation of ±2.2 mg/L nitrite.

Interferences

This test does not measure nitrates nor is it applicable to glycol based samples. Dilute glycol based samples and follow the Nitrite, Low Range Procedure (Stored Program No. 371).

Summary of Method

The method uses ferrous sulfate in an acidic medium to reduce nitrite to nitrous oxide. Ferrous ions combine with the nitrous oxide to form a greenish-brown complex in direct proportion to the nitrite present.

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
NitriVer 2 Nitrite Reagent Powder Pillows, 10 mL sample	1 pillow	100/pkg	21075-69

REQUIRED APPARATUS

Stopper, hollow, polyethylene, No. 1	1	6/pkg	14480-01
Cell Riser, 10-mL sample cell		each	45282-00
Sample Cell, with 10-mL mark, matched pair		pair	24954-02

OPTIONAL REAGENTS

Sodium Nitrite, ACS	454 g	2452-01
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Balance, analytical	each	22310-00
Flask, volumetric, 1000 mL	each	547-53
Pipet, serological, 10 mL	each	532-38
Pipet Filler, safety bulb	each	14651-00
Scoop, spatula	each	12257-00
Weighing Boat, 67/46 mm diameter	500/pkg	21790-00

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

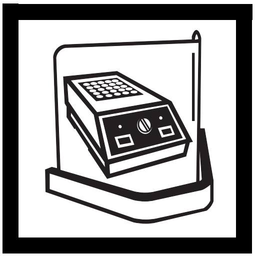
Method 10072

NITROGEN, TOTAL, HR, Test ’N Tube™ 10 to 150 mg/L N

TNT Persulfate Digestion Method

For water and wastewater

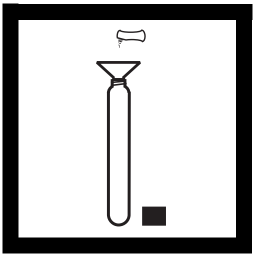
Note: *Digestion is required for determining total nitrogen. The digestion procedure is included in the method.*



1. Turn on the COD Reactor. Heat to 103-106 °C (optimum temperature is 105 °C). Place the plastic shield in front of the reactor.

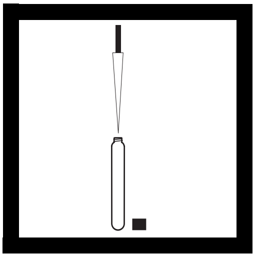
Note: *Ensure safety devices are in place to protect the analyst should splattering and leakage occur.*

Note: *For proof of accuracy, run a 125 mg/L NH_3-N standard through digestion and analysis.*



2. Prepare a reagent blank: Using a funnel, add the contents of one Total Nitrogen Persulfate Reagent Powder Pillow to one HR Total Nitrogen Hydroxide Digestion Vial.

Note: *Wipe off any reagent that gets on the lid or thetube threads.*



3. Add 0.5 mL of organic-free water to the vial. Cap the vial and shake vigorously for about 30 seconds.

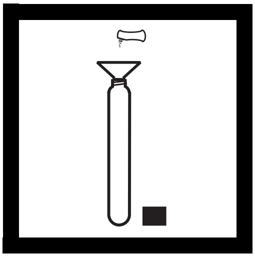
Process this reagent blank exactly the same as the sample, including digestion and color finish. Proceed to step *6*.

Note: *Alternate water must be free of all nitrogen-containing species.*

Note: *The persulfate reagent may not dissolve completely after shaking.*

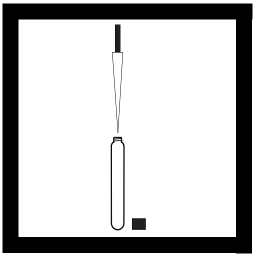
Note: *One reagent blank is sufficient for each set of samples using the same lots of reagents.*

Note: *The reagent blank is stable for as long as seven days when stored in the dark; see* Blanks for Colorimetric Measurement *following this procedure.*



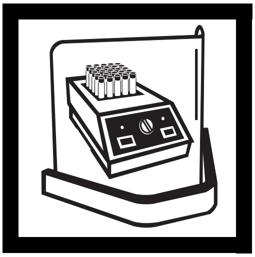
4. Prepare a sample: Using a funnel, add the contents of one Total Nitrogen Persulfate Reagent Powder Pillow to one HR Total Nitrogen Hydroxide Digestion Vial.

Note: *Wipe off any reagent that gets on the lid or thetube threads.*

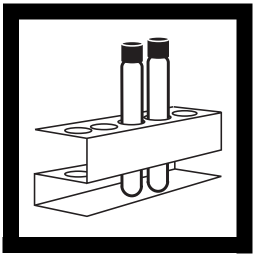


5. Add 0.5 mL of sample to the vial. Cap the vial and shake vigorously for about 30 seconds.

Note: *The persulfate reagent may not dissolve completely after shaking.*

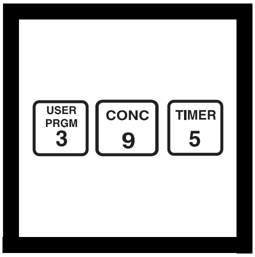


6. Place the vials in the COD Reactor. Heat for 30 minutes.



7. Using finger cots or gloves, remove the hot vials from the reactor and allow to cool to room temperature.

Note: *It is very important to remove the vials from the COD Reactor after exactly 30 minutes.*

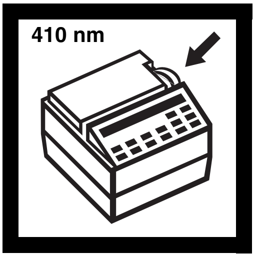


8. Enter the stored program number for Test 'N Tube HR Total Nitrogen.

Press: **3 9 5 ENTER**

The display will show:

Dial nm to 410



9. Rotate the wavelength dial until the small display shows:

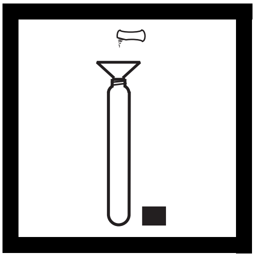
410 nm

When the correct wavelength is dialed in, the display will quickly show: **Zero Sample**

then:

mg/L N

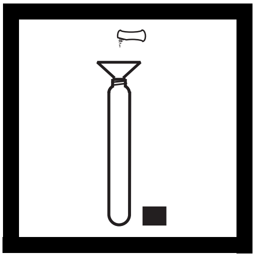
HR TN TNT



10. Add the contents of one Total Nitrogen Reagent A Powder Pillow to the vial containing the digested blank or sample. Cap the vial and shake for 15 seconds.

Press: **SHIFT TIMER** after shaking.

A three-minute reaction period will begin.

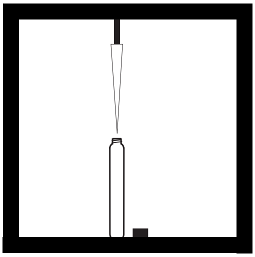


11. After the timer beeps, add one Total Nitrogen Reagent B Powder Pillow to the vial. Cap the vial and shake for 15 seconds.

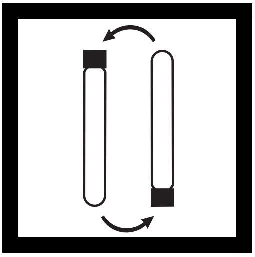
Press: **SHIFT TIMER** after shaking.

A two-minute reaction period will begin.

Note: *The reagent will not dissolve completely. The solution will begin to turn yellow.*

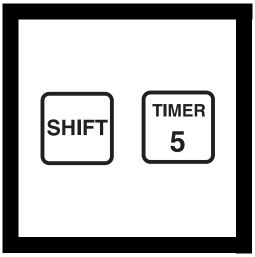


12. After the timer beeps, remove the cap from the Total Nitrogen Reagent C Vial. Add 2 mL of digested, treated sample (or reagent blank) to the vial. The vial will be warm.



13. Cap vial and invert slowly 10 times to mix. The vial will be warm.

Note: *Proper mixing is important for complete recovery. Hold the vial vertical with the cap up. Invert the vial and wait for all of the solution to flow to the cap end. Pause. Return the vial to the upright position and wait for all of the solution to flow to the vial bottom. This is one inversion (10 inversions = 30 seconds)*

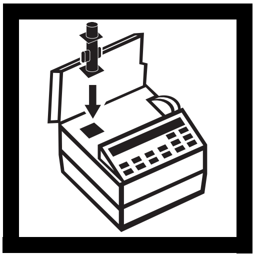


14. Press:

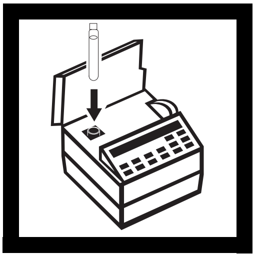
SHIFT TIMER

A five-minute reaction period will begin. Do not invert the vial again.

Note: *The yellow color will intensify.*

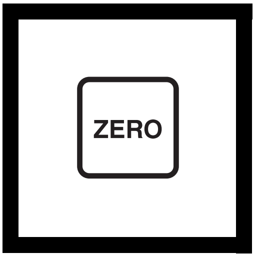


15. Insert the COD Vial Adapter into the cell holder with the marker to the right.



16. When the timer beeps, wipe the outside of the Total Nitrogen Reagent C vial containing the reagent blank. Place the vial into the adapter with the Hach logo facing the front of the instrument. Place the cover on the adapter.

Note: *Wipe with a damp towel, followed by a dry one, to remove fingerprints or other marks.*



17. Press: **ZERO**

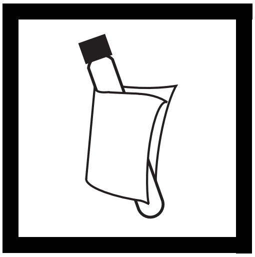
The display will show:

Zeroing. . .

then:

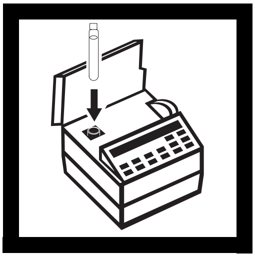
0 mg/L

N HR TN TNT



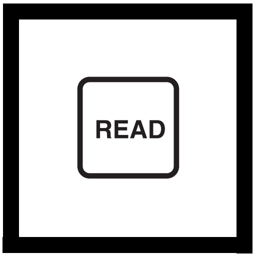
18. Wipe the Total Nitrogen Reagent C vial containing the sample.

Note: *Wipe with a damp towel, followed by a dry one, to remove fingerprints or other marks.*



19. Place the vial into the adapter with the Hach logo facing the front of the instrument. Place the cover on the adapter.

Note: *Multiple samples may be read after zeroing on one reagent blank.*



20. Press: **READ**

The display will show:

Reading. . .

then the result will be displayed in mg/L nitrogen.

Note: *If the test overranges, repeat the digestion and colorimetric finish with diluted sample. Digestion must be repeated for accurate results.*

Forms ▲▼ NH_3 N NO_3^-

Sampling and Storage

Collect samples in clean plastic or glass bottles. Best results are obtained with immediate analysis.

Preserve the sample by reducing the pH to 2 or less with concentrated sulfuric acid (at least 2 mL per liter). Store at 4 °C (39 °F) or less. Preserved samples may be stored up to 28 days. Warm the samples to room temperature and neutralize with 5 N sodium hydroxide before analysis. Correct the test result for volume additions; see *Correcting for Volume Additions* in *Section 1* of the *DR/2010 Procedures Manual*.

Accuracy Check

This method generally yields 95–100% recovery on organic nitrogen standards. For proof of accuracy, Hach offers a set of three Primary Standards for Kjeldahl Nitrogen.

1. Prepare one or more of the following solutions. Each preparation is for an equivalent 120 mg/L N standard. Use water that is free of all organic and nitrogen-containing species.

a) Weigh 1.6208 g of Ammonium p-Toluenesulfonate (PTSA). Dissolve in a Class A 1000-mL volumetric flask with deionized water. Add deionized water to the 1000-mL mark.

b) Weigh 2.1179 g of Glycine p-Toluenesulfonate. Dissolve in a Class A 1000-mL volumetric flask with deionized water. Add deionized water to the 1000-mL mark.

c) Weigh 2.5295 g of Nicotinic p-Toluenesulfonate. Dissolve in a Class A 1000-mL volumetric flask with deionized water. Add deionized water to the1000-mL mark.

2. Analyze each of these solutions using the test procedure. Calculate the percent recovery for each using this formula:

$$\%\ \text{recovery} = \frac{\text{measured concentration}}{120} \times 100$$

The percent recovery should be:

Compound	Lowest Expected % Recovery
Ammonia-PTSA	95%
Glycine-PTSA	95%
Nicotinic-PTSA	95%

Hach analysts have found Ammonia-PTSA to be the most difficult to digest. Other compounds may yield different percent recoveries.

Standard Solution Method

For proof of accuracy, substitute 0.5 mL of a 125 mg/L ammonia nitrogen standard solution for the sample in the procedure. To prepare a 125-mg/L N standard, use a 25-mL Class A pipet to transfer 25.00 mL of a 1000-mg/L Ammonia Nitrogen Standard (See “OPTIONAL REAGENTS” on page 498.) to a 200-mL Class A volumetric flask. Dilute to the line with organic-free water.

Standard Additions Method

a) Fill three 25-mL graduated mixing cylinders with 25 mL of sample.

b) Snap the neck off an Ammonia Nitrogen Voluette™ Ampule Standard Solution, 1000 mg/L as NH_3-N.

c) Use the TenSette® Pipet to add 0.1 mL, 0.2 mL, and 0.3 mL of standard, respectively, to the three mixing cylinders.

d) Stopper each cylinder and mix thoroughly.

e) Add 0.5 mL of each prepared solution, respectively, to three HR Total Nitrogen Hydroxide Digestion Vials.

f) Analyze each standard addition sample as described in the procedure. The nitrogen concentration should increase by approximately 4 mg/L N for each 0.1 mL of standard added.

g) If these increases do not occur, see *Standard Additions* in *Section I* of the *Procedures Manual* for troubleshooting information.

Blanks for Colorimetric Measurement

The reagent blank may be used repeatedly for measurements using the same lots of reagents. Store the reagent blank in the dark at room temperature (18–25 °C) for a maximum of seven days. If a small amount of white floc appears prior to the end of one week, discard the reagent blank and prepare a new one.

Precision

In a single laboratory, using a standard solution of125 mg/L NH_3-N and two lots of reagent with a DR/2010 Spectrophotometer, a single operator obtained a standard deviation of less than 3 mg/L N.

Interferences

The substances in the following table have been tested and found **not** to interfere up to the indicated levels:

Substance	Maximum Level Tested (mg/L)	Substance	Maximum Level Tested (mg/L)
Barium	10.4	Organic Carbon	600
Calcium	1200	pH	13 pH units
Chromium (3+)	2	Phosphorus	400
Iron	8	Silica	600
Lead	26.4 ppb	Silver	3.6
Magnesium	2000	Tin	6.0

Interfering substances that resulted in a concentration change of ±10%:

Substance	Level and Effect
Bromide	> 240 ppm; positive interference
Chloride	≥ 3000 ppm; positive interference

The large amounts of nitrogen-free organic compounds in some samples may decrease digestion efficiency by consuming some of the persulfate reagent. Samples known to contain high levels of organics should be diluted and re-run to verify digestion efficiency.

Summary of Method

An alkaline persulfate digestion converts all forms of nitrogen to nitrate. Sodium metabisulfite is added after the digestion to eliminate halogen oxide interferences. Nitrate then reacts with chromotropic acid under strongly acidic conditions to form a yellow complex with an absorbance mPress **ENTER** and then use the **DOWN ARROW** key to make the display read **Units: mg/L** and then press **ENTER** again.

3. Press **ENTER** and then use the number keys to make the display read **Factor3: 1.214** and then press **ENTER** again.

4. Press **EXIT**. The display should read **Alternate Form 3:**. Press the **DOWN ARROW** key. The display now should read **Alternate Form 4:**.

5. Press **ENTER**. The display should read **Decimal 4: 0.000**.

6. Press **ENTER** and then the **arrow** keys to make the display read **Decimal 4: 0000.** and then press **ENTER** again.

REQUIRED REAGENTS

Test ’N Tube HR Total Nitrogen Reagent Set (50 vials)			27141-00

Includes: (1) 26718-46, (1) 26719-46, (1) 26720-46, (50) Hydroxide Digestion Vials,* (50) Acid Solution Vials*

Description	Quantity Required Per Test	Unit	Cat. No.
HR Total Nitrogen Hydroxide Digestion Vials	1 vial	50/pkg	*
Total Nitrogen Persulfate Reagent Powder Pillows	1 pillow	50/pkg	26718-46
Total Nitrogen Reagent A, Bisulfite Powder Pillows	1 pillow	50/pkg	26719-46
Total Nitrogen Reagent B, Indicator Powder Pillows	1 pillow	50/pkg	26720-46
Total Nitrogen Reagent C Vials, Acid Solution	1 vial	50/pkg	*

REQUIRED APPARATUS

Description	Quantity Required Per Test	Unit	Cat. No.
COD Reactor, 115/230V, North American Plug	1	each	45600-00
COD Reactor, 230V, European Plug	1	each	45600-02
COD Vial Adapter, DR/2010	1	each	44799-00
Funnel, Micro	3	each	25843-35
Pipet, TenSette, 0.1–1.0 mL	1	each	19700-01
Pipet Tips for 19700-01	1	50/pkg	25589-96
Safety Shield	1	each	23810-00
Test Tube Cooling Rack	1-3	each	18641-00

OPTIONAL REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
Nitrogen, Ammonia, 1000 mg/L NH_3-N		1 L	23541-53
Nitrogen, Ammonia, Voluette Ampule, 1000 mg/L NH_3-N, 10 mL		16/pkg	23541-10
Primary Standards for Kjeldahl Nitrogen		set of 3	22778-00
Sodium Hydroxide Standard Solution, 5.0 N		59 mL MDB	2450-26
Sulfuric Acid, ACS		500 mL	979-49
Water, organic-free		500 mL	26415-49

OPTIONAL APPARATUS

Description	Quantity Required Per Test	Unit	Cat. No.
Ampule Breaker Kit,		each	21968-00
Balance, analytical, 115 Vac		each	26103-00
Balance, analytical, 230 Vac		each	26103-02
Cots, finger		2/pkg	14647-02
Cylinder, graduated, mixing, 25 mL	3	each	20886-40
Flask, Volumetric, Class A, 200 mL		each	14574-45
Flask, volumetric, Class A, 1000 mL	3	each	14574-53
pH Indicator Paper, 1 to 11 pH		5 rolls/pkg	391-33
Pipet, Volumetric, Class A, 25 mL	2	each	14515-40

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* These Items are not sold separately. Please order the complete set (Cat. No. 27141-00) as a replacement.

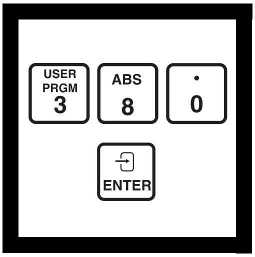
Method 8038

NITROGEN, AMMONIA (0 to 2.50 mg/L NH_3-N)

Nessler Method*

For water, wastewater, and seawater

USEPA Accepted for wastewater analysis. Distillation is required.



1. Enter the stored program number for ammonia nitrogen (NH_3-N).

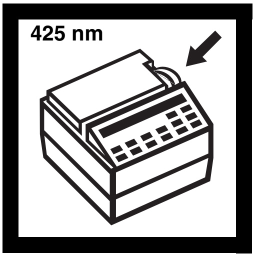
Press: **3 8 0 ENTER**

The display will show:

Dial nm to 425

Note: *Adjust the pH of stored samples before analysis.*

Note: *The Pour-Thru Cell can be used with this procedure. Clean the cell by pouring a few sodium thiosulfate pentahydrate crystals into the cell funnel. Flush it through the funnel and cell with enough deionized water to dissolve. Rinse out the crystals.*



2. Rotate the wavelength dial until the small display shows:

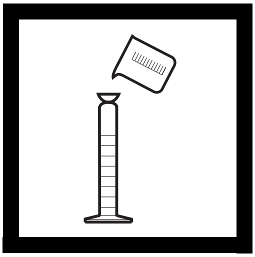
425 nm

When the correct wavelength is dialed in the display will quickly show:

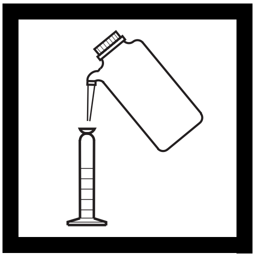
Zero Sample

then: **mg/L NH_3-N Ness**

Note: *This test is sensitive to the wavelength setting. To assure accuracy, run the test using a 1.0 mg/L standard solution and deionized water blank. Repeat Steps 10 to 12 at slightly different wavelengths, setting the dial from higher to lower values, until the correct result is obtained. The wavelength should be 425 ±2 nm. Always set this wavelength by approaching from high to low values.*



3. Fill a 25-mL mixing graduated cylinder (the prepared sample) to the 25-mL mark with sample.



4. Fill another 25-mL mixing graduated cylinder (the blank) with deionized water.

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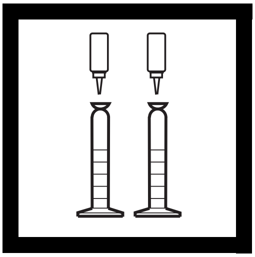
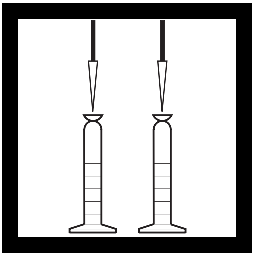
* Requires distillation; Adapted from *Standard Methods for the Examination of Water and Wastewater.*

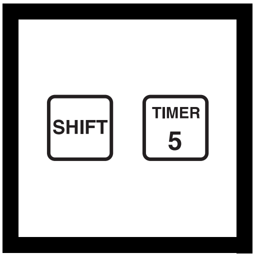


5. Add 3 drops of Mineral Stabilizer to each cylinder. Invert several times to mix. Add 3 drops of Polyvinyl Alcohol Dispersing Agent to each cylinder. Invert several times to mix.



6. Pipet 1.0 mL of Nessler Reagent into each cylinder. Stopper. Invert several times to mix.

***Note:** A yellow color will develop if ammonia is present. (The reagent will cause a faint yellow color in the blank.)*

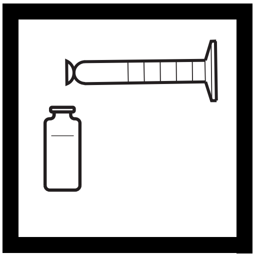


7. Press:

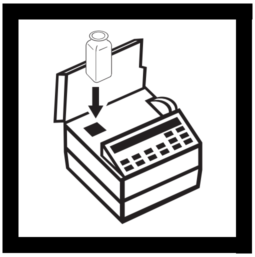
SHIFT TIMER

A one-minute reaction period will begin.

***Note:** Continue with Step 8 while timer is running.*



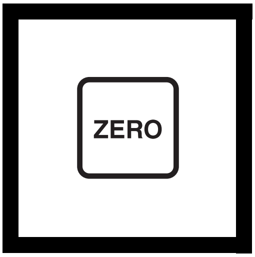
8. Pour each solution into a sample cell.



9. When the timer beeps, the display will show:

mg/L NH$_3^{-}$N Ness

Place the blank into the cell holder. Close the light shield.



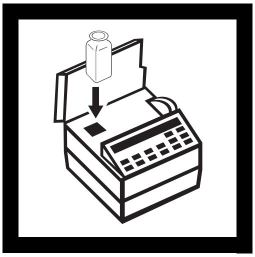
10. Press: **ZERO**

The display will show:

Zeroing. . . .

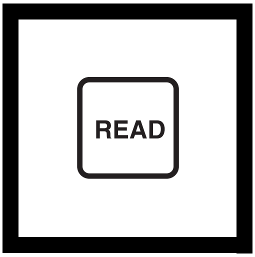
then:

0.00 mg/L NH$_3$-N Ness



11. Place the prepared sample into the cell holder. Close the light shield.

***Note:** Do not wait more than five minutes after reagent addition (Step 6) before performing Step 12.*



12. Press: **READ**

The display will show:

Reading. . . .

then the result in mg/L ammonia expressed as nitrogen (NH$_3^{-}$N) will be displayed.

Forms ▲▼ NH_4^+ NH_3-N NH_3

Sampling and Storage

Collect samples in clean glass or plastic bottles.

If chlorine is present, add one drop of 0.1 N sodium thiosulfate for each 0.3 mg/L Cl_2 in a 1-liter sample. Preserve the sample by reducing the pH to 2 or less with sulfuric acid (at least 2 mL). Store at 4 °C (39 °F) or less. Preserved samples may be stored up to 28 days. Before analysis, warm samples to room temperature and neutralize with 5 N sodium hydroxide. Correct the test result for volume additions: see *Correction for Volume Additions*, (*Section I*).

Accuracy Check

Standard Additions Method

a) Snap the neck off an Ammonium Nitrogen Voluette Ampule Standard Solution, 50 mg/L NH_3-N.

b) Use the TenSette Pipet to add 0.1, 0.2, and 0.3 mL of standard to three 25-mL samples. Mix each thoroughly.

c) Analyze each sample as described above. The nitrogen concentration should increase 0.20 mg/L for each 0.1 mL of standard added.

d) If these increases do not occur, see *Standard Additions (Section I)* for more information.

Standard Solution Method

To check accuracy, use a 1.0 mg/L Ammonium Nitrogen Standard Solution. Or, this can be prepared by diluting 1.00 mL of solution from a 50 mg/L NH_3-N Voluette Ampule Standard for Ammonium Nitrogen to 50.0 mL with deionized water.

Method Performance

Precision

In a single laboratory using standard solutions of 1.00 mg/L ammonia nitrogen (NH_3-N) and two representative lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±0.015 mg/L.

Estimated Detection Limit (EDL)

The EDL for program 380 is 0.06 mg/L NH_3-N.

The EDL is the calculated lowest average concentration in a deionized water matrix that is different from zero with a 99% level of confidence. For more information on derivation and use of Hach's estimated detection limit, see *Section I*.

Interferences

A solution containing a mixture of 500 mg/L $CaCO_3$ and 500 mg/L Mg as $CaCO_3$ does not interfere. If the hardness concentration exceeds these concentration, extra Mineral Stabilizer should be added.

Iron and sulfide interfere by causing a turbidity with Nessler Reagent.

Residual chlorine must be removed by addition of sodium arsenite solution. Use two drops to remove each mg/L Cl from a 250 mL sample. Sodium thiosulfate can be used in place of sodium arsenite. See *Sampling and Storage* section.

Less common interferences, such as glycine, various aliphatic and aromatic amines, organic chloramines, acetone, aldehydes and alcohols may cause greenish or other off colors or turbidity. It may be necessary to distill the sample if these compounds are present.

Seawater samples may be analyzed by addition of 1.0 mL (27 drops) of Mineral Stabilizer to the sample before analysis. This will complex the high magnesium concentrations found in sea water, but the sensitivity of the test will be reduced by 30 percent due to the high chloride concentration. For best results, perform a calibration, using standards spiked to the equivalent chloride concentration, or distill the sample as described below.

Distillation

a) Measure 250 mL of sample into a 250-mL graduated cylinder and pour into a 400-mL beaker. If necessary, destroy chlorine by adding 2 drops of Sodium Arsenite Solution per mg/L Cl_2.

b) Add 25 mL of Borate Buffer Solution and mix. Adjust the pH to about 9.5 with 1 N sodium hydroxide solution. Use a pH meter.

c) Set up the general purpose distillation apparatus as shown in the Hach Distillation Apparatus Manual. Pour the solution into the distillation flask. Add a stir bar.

d) Use a graduated cylinder to measure 25 mL of deionized water. Transfer the water to a 250-mL erlenmeyer flask. Add the contents of one Boric Acid Powder Pillow. Mix thoroughly. Place the flask under the still drip tube. Elevate so the end of the tube is immersed in the solution.

e) Turn on the heater power switch. Set the stir control to 5 and the heat control to 10. Turn on the water and adjust to maintain a constant flow through the condenser.

f) Turn off the heater after collecting 150 mL of distillate. Immediately remove the collection flask to avoid sucking solution into the still. Measure the distillate to ensure 150 mL was collected (total volume 175 mL).

g) Adjust the pH of the distillate to about 7 with 1 N sodium hydroxide. Pour the distillate into a 250-mL volumetric flask; rinse the erlenmeyer flask with deionized water. Add the rinsings to the volumetric flask. Dilute to the mark. Stopper. Mix thoroughly. Analyze as described above.

Summary of Method

The Mineral Stabilizer complexes hardness in the sample. The Polyvinyl Alcohol Dispersing Agent aids the color formation in the reaction of Nessler Reagent with ammonium ions. A yellow color is formed proportional to the ammonia concentration.

REQUIRED REAGENTS

Description	Cat. No.
Nitrogen Ammonia Reagent Set	24582-00

Includes: (1) 21194-49, (1) 23766-26, (1) 23765-26

Description	Quantity Required Per Test	Unit	Cat. No.
Nessler Reagent	2 mL	500 mL	21194-49
Mineral Stabilizer	6 drops	50 mL*SCDB	23766-26
Polyvinyl Alcohol Dispersing Agent	6 drops	50 mL*SCDB	23765-26
Water, deionized	25 mL	4 L	272-56

REQUIRED APPARATUS

Cylinder, graduated, mixing, tall form, 25 mL	2	each	21190-40
Pipet, serological, 1 mL	2	each	532-35
Pipet Filler, safety bulb	1	each	14651-00
Sample Cell, 25-mL, matched pair		pair	20950-00

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* Contact Hach for larger sizes.

OPTIONAL REAGENTS

Description	Unit	Cat. No.
Borate Buffer Solution	1000 mL	14709-53
Boric Acid Powder Pillows	50/pkg	14817-66
Nitrogen, Ammonia Standard Solution, 1 mg/L NH_3-N	500 mL	1891-49
Nitrogen, Ammonia Standard Solution, Voluette ampule, 50 mg/L NH_3-N	16/pkg	14791-10
Sodium Arsenite Solution, 5 g/L	100 mL MDB	1047-32
Sodium Hydroxide Standard Solution, 5.0 N	100 mL* MDB	2450-32
Sodium Hydroxide Standard Solution, 1.0 N	100 mL* MDB	1045-32
Sodium Thiosulfate Solution, 0.1 N	100 mL* MDB	323-32
Sodium Thiosulfate, pentahydrate	454 g	460-01
Sulfuric Acid, ACS	500 mL*	979-49

OPTIONAL APPARATUS

Ampule Breaker Kit	each	21968-00
Beaker, 400 mL	each	500-48
Cylinder, graduated, 25 mL	each	508-40
Cylinder, graduated, 250 mL	each	508-46
Distillation apparatus general purpose accessories	each	22653-00
Distillation heater and support apparatus set, 115 V	each	22744-00
Distillation heater and support apparatus set, 230 V	each	22744-02
Dropper, plastic, 0.5 and 1.0-mL marks	10/pkg	21247-10
Flask, erlenmeyer, 250-mL	each	505-46
Flask, volumetric, 50 mL	each	547-41
Flask, volumetric, 250 mL	each	547-46
pH Meter, *sension*™*1*, portable	each	51700-10
Pipet, serological, 2 mL	each	532-36
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 1.00 mL	each	14515-35
Pour-Thru Cell Assembly Kit	each	45215-00
Thermometer, -20 to 105 °C	each	1877-01

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

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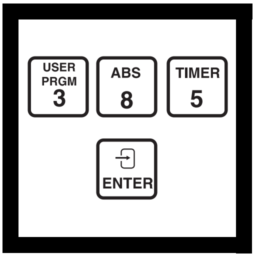
* Contact Hach for larger sizes.

Method 8155

NITROGEN, AMMONIA (0 to 0.50 mg/L NH_3-N) For water, wastewater, seawater

Salicylate Method*



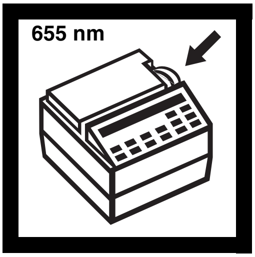
1. Enter the stored program number for ammonia nitrogen (NH_3-N), salicylate method.

Press: **3 8 5 ENTER**

The display will show:

Dial nm to 655

Note: *The Pour-Thru Cell can be used with 25-mL reagents only.*



2. Rotate the wavelength dial until display shows:

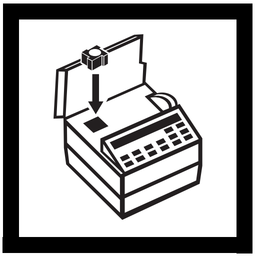
655 nm

When the correct wavelength is dialed in the display will quickly show:

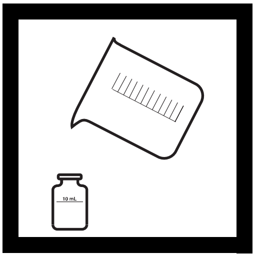
Zero Sample

then:

mg/L NH_3-N Salic

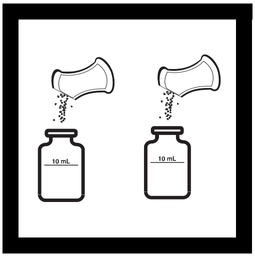


3. Insert the 10-mL Cell Riser into the cell compartment.

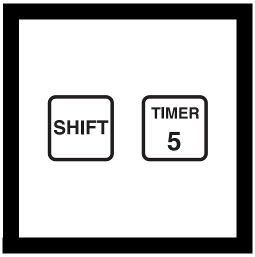


4. Pour 10 mL of sample into a 10-mL sample cell (the prepared sample).

5. Pour 10 mL of deionized water into a second 10-mL sample cell (the blank).



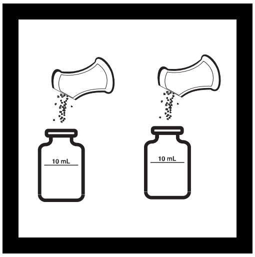
6. Add the contents of one Ammonia Salicylate Reagent Powder Pillow to each sample cell. Stopper. Shake to dissolve.



7. Press:

SHIFT TIMER

A three-minute reaction period will begin.



8. When the timer beeps add the contents of one Ammonia Cyanurate Reagent Powder Pillow to each sample cell. Stopper. Shake to dissolve.

Note: *A green color will develop if ammonia nitrogen is present.*

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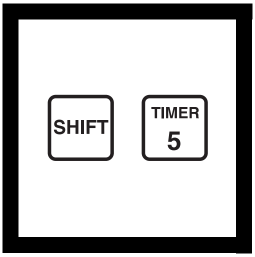
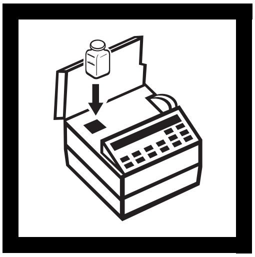
* Adapted from Clin. Chim. Acta., 14 403 (1966)



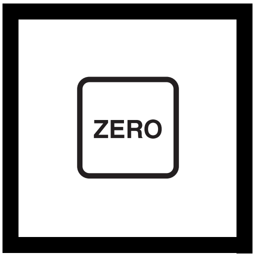
9. Press:

SHIFT TIMER

A 15-minute reaction period will begin.



10. When the timer beeps, place the blank into the cell holder. Close the light shield.



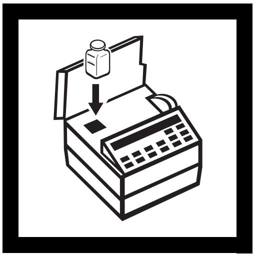
11. Press: **ZERO**

The display will show:

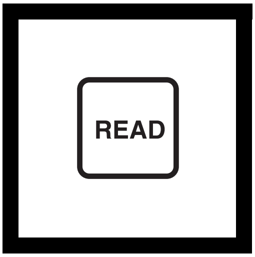
Zeroing. . .

then:

0.00 mg/L NH_3-N Salic



12. Place the prepared sample into the cell holder. Close the light shield.



13. Press: **READ**

The display will show:

Reading. . .

then the result in mg/L ammonia as nitrogen (NH_3-N) will be displayed.

Forms ▲▼ NH_4^+
NH_3-N
NH_3

Sampling and Storage

Collect samples in clean plastic or glass bottles. Most reliable results are obtained when samples are analyzed as soon as possible after collection.

If chlorine is known to be present, the sample must be treated immediately with sodium thiosulfate. Add one drop of Sodium Thiosulfate Standard Solution, 0.1 N, for each 0.3 mg of chlorine present in a one liter sample.

To preserve the sample, adjust the pH to 2 or less with concentrated sulfuric acid (about 2 mL per liter). Store samples at 4 °C or less. Samples preserved in this manner can be stored up to 28 days. Just before testing the stored sample, warm to room temperature and neutralize with 5.0 N Sodium Hydroxide Standard Solution. Correct the test result for volume additions; see *Correction for Volume Additions*, in *Section I* for more detailed information.

Accuracy Check

Standard Additions Method

a) Measure 25 mL of sample into three 25-mL mixing cylinders.

b) Use the TenSette Pipet to add 0.2, 0.4, and 0.6 mL of Ammonium Nitrogen Standard, 10 mg/L as NH_3-N to the three samples. Mix well.

c) Analyze a 10-mL portion of sample as described above. The ammonia nitrogen concentration should increase 0.08 mg/L for each 0.2 mL of standard added.

d) If these increases do not occur, see *Standard Additions (Section I)* for more information.

Standard Solution Method

Prepare a 0.20 mg/L ammonia nitrogen standard by diluting 2.00 mL of the Ammonia Nitrogen Standard Solution, 10 mg/L, to 100 mL with deionized water. Or, using the TenSette Pipet, prepare a 0.20 mg/L ammonia nitrogen standard by diluting 0.4 mL of a Ammonia Nitrogen Voluette Standard Solution, 50 mg/L as NH_3-N, to 100 mL with deionized water.

Precision

In a single laboratory using a standard solution of 0.20 mg/L ammonia nitrogen (NH_3-N) and two representative lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±0.015 mg/L ammonia nitrogen.

Interferences

The following ions may interfere when present in concentrations exceeding those listed below:

Calcium	1000 mg/L as $CaCO_3$
Magnesium	6000 mg/L as $CaCO_3$
Nitrite	12 mg/L as NO_2^--N
Nitrate	100 mg/L as NO_3^--N
Orthophosphate	100 mg/L as PO_4^{3-}-P
Sulfate	300 mg/L as SO_4^{2-}

Sulfide will intensify the color. Eliminate sulfide interference as follows:

a) Measure about 350 mL of sample in a 500-mL erlenmeyer flask.

b) Add the contents of one Sulfide Inhibitor Reagent Powder Pillow. Swirl to mix.

c) Filter the sample through a folded filter paper.

d) Use the filtered solution in Step 4.

Iron interferes with the test. Eliminate iron interference as follows:

a) Determine the amount of iron present in the sample following one of the Iron, Total procedures.

b) Add the same iron concentration to the deionized water sample in Step 5.

The interference from iron in the sample will then be successfully blanked out in Step 11.

Extremely acidic or alkaline samples should be adjusted to approximately pH 7. Use 1 N Sodium Hydroxide Standard Solution for acidic samples or 1 N Sulfuric Acid Standard Solution for basic samples.

Less common interferences such as hydrazine and glycine will cause intensified colors in the prepared sample.

Turbidity and sample color will give erroneous high values. Samples with severe interferences require distillation. Albuminoid nitrogen samples also require distillation. Hach recommends distillation using the Hach General Purpose Distillation Set. See optional apparatus listing. The distillation procedure is in the Nitrogen, Ammonia--Nessler Method.

Summary of Method

Ammonia compounds combine with chlorine to form monochloramine. Monochloramine reacts with salicylate to form 5-aminosalicylate. The 5-aminosalicylate is oxidized in the presence of a sodium nitroprusside catalyst to form a blue-colored compound. The blue color is masked by the yellow color from the excess reagent present to give a final green-colored solution.

REQUIRED REAGENTS AND APPARATUS

	Cat. No.
Ammonia Nitrogen Reagent Set For 10-mL Samples (100 Tests) Includes: (2) 26531-49, (2) 26532-99	26680-00

Description	Quantity Required Per Test	Unit	Cat. No.
Ammonia Cyanurate Reagent Powder Pillows	2 pillows	100/pkg	26531-99
Ammonia Salicylate Reagent Powder Pillows	2 pillows	100/pkg	26532-99
Cell Riser, 10 mL	1	each	45282-00
Sample Cell, 10 mL, 1-inch	2	2/pkg	24954-02
Stopper, hollow, polyethylene, #1	2	6/pkg	14480-01

OPTIONAL REAGENTS

Ammonia Nitrogen Standard Solution, 10 mg/L as (NH_3-N)	500 mL	153-49
Ammonia Nitrogen, Voluette Ampule, 50 mg/L as (NH_3-N), 10 mL	16/pkg	14791-10
Sodium Hydroxide Standard Solution, 1.0 N	100 mL MDB	1045-32
Sodium Hydroxide Standard Solution, 5.0 N	50 mL SCDB	2450-26
Sodium Thiosulfate Standard Solution, 0.1 N	100 mL MDB	323-32
Sulfide Inhibitor Reagent Powder Pillows	100/pkg	2418-99
Sulfuric Acid, concentrated, ACS	500 mL	979-49
Sulfuric Acid Standard Solution, 1.0 N	100 mL MDB	1270-32
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Description	Unit	Cat. No.
Cylinder, graduated, polypropylene, 500 mL	each	1081-49
Distillation Heater and Support Apparatus, 115 V	each	22744-00
Distillation Heater and Support Apparatus, 230 V	each	22744-02
Distillation Set, General Purpose	each	22653-00
Filter Paper, folded, 12.5 cm	100	1894-57
Flask, erlenmeyer, polypropylene, 500 mL	each	1082-49
Flask, volumetric, Class A, 100 mL	each	14574-42
Funnel, poly, 65 mm	each	1083-67
pH Meter, *sension™1*, portable	each	51700-10
Pipet Filler, safety bulb	each	14651-00
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 2.0 mL	each	14515-36
Thermometer, -20 to 105 °C	each	1877-01

OPTIONAL 25-ML ANALYSIS ITEMS

Ammonia Nitrogen Reagent Set, 25-mL test (100 Tests) Includes: (8) 23955-68, (8) 23953-68		22437-00
Ammonia Cyanurate Reagent Powder Pillows	25/pkg	23955-68
Ammonia Salicylate Reagent Powder Pillows	25/pkg	23953-68
Clippers, large	each	968-00
Pour-Thru Cell Assembly Kit	each	45215-00
Sample Cell, 25-mL, matched pair	pair	20950-00

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

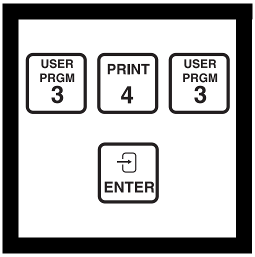
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 10031

NITROGEN, AMMONIA, High Range, Test 'N Tube

(0 to 50.0 mg/L NH_3-N) **For water, wastewater, and seawater**

Salicylate Method*



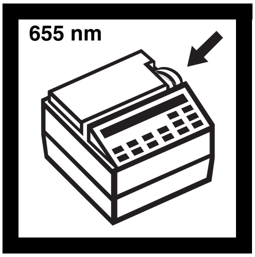
1. Enter the stored program number for High Range Test 'N Tube Ammonia Nitrogen (N).

Press: **3 4 3 ENTER**

The display will show:

Dial nm to 655

Note: *For proof of accuracy, run a 10 mg/L NH_3–N standard through the analysis.*



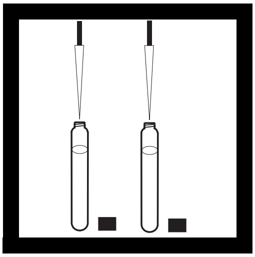
2. Rotate the wavelength dial until the small display shows:

655 nm

When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

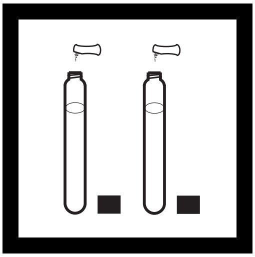
then: **mg/L N HR TNT**



3. Remove the caps from two High Range AmVer Diluent Reagent vials. Add 0.1 mL of sample to one vial (the sample). Add 0.1 mL of ammonia-free water to another (the blank).

Note: *For non-preserved samples with extreme pH, see Interferences on page 514.*

Note: *If sample cannot be analyzed immediately, see Sampling and Storage on page 513.*



4. Add the contents of one Ammonia Salicylate Reagent Powder Pillow for 5 mL sample to each vial.

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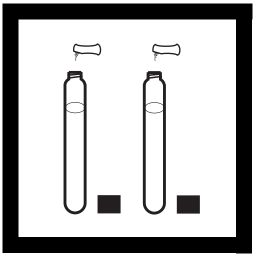
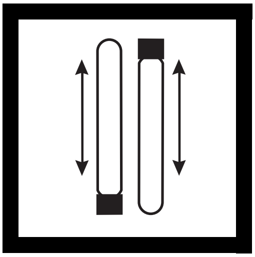
* Adapted from Clin. Chim. Acta., 14 403 (1966).

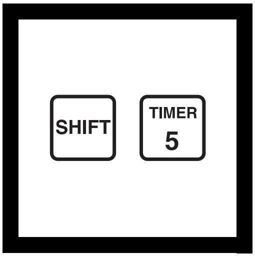


5. Add the contents of one Ammonia Cyanurate Reagent Powder Pillow for 5 mL sample to each vial.



6. Cap the vials tightly and shake thoroughly to dissolve the powder.

Note: *A green color will develop if ammonia is present.*



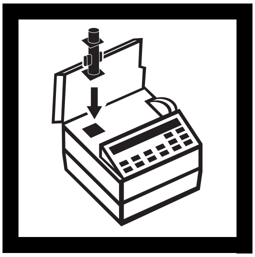
7. Press:

SHIFT TIMER

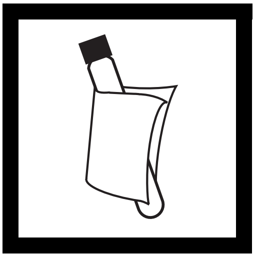
A 20-minute reaction period will begin.

When the timer beeps the display will show:

mg/L N HR TNT

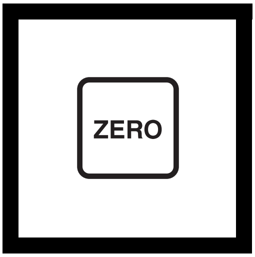


8. Place the COD vial adapter into the cell holder with the marker to the right.



9. After cleaning the outside of the vial with a towel, place the blank into the vial adapter with the Hach logo facing the front of the instrument. Place the cover on the adapter.

Note: *Wiping with a damp cloth, followed by a dry one, removes fingerprints and other marks.*



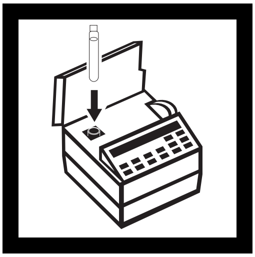
10. Press: **ZERO**

The display will show:

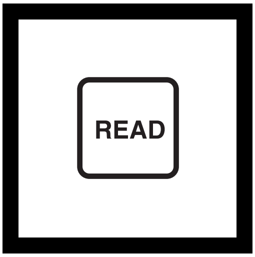
Zeroing…

then:

0.0 mg/L N HR TNT



11. Place the prepared sample into the vial adapter. Place the cover on the adapter.



12. Press: **READ**

The display will show:

Reading…

then the result in mg/L ammonia expressed as nitrogen (N) will be displayed.

Forms ▲ N
▼ NH_3

Sampling and Storage

Collect samples in clean plastic or glass bottles. Best results are obtained with immediate analysis. If chlorine is known to be present, add one drop of 0.1 N sodium thiosulfate for each 0.3 mg/L Cl_2 in a one liter sample. Preserve the sample by reducing the pH to 2 or less with hydrochloric acid (at least 2 mL). Store at 4 °C (39 °F) or less. Preserved samples may be stored up to 28 days. Before analysis, warm samples to room temperature and neutralize with 5 N sodium hydroxide. Correct the test result for volume additions.

Accuracy Check

Standard Solution Method

To check accuracy, use a 10 mg/L Ammonium Nitrogen Standard Solution or use an Ammonium Nitrogen Voluette Ampule Standard, 50 mg/L.

Precision

In a single laboratory, using a standard solution of 25 mg/L ammonia nitrogen (NH_3-N) and two representative lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±0.5 mg/L N.

Interferences

The following ions may interfere when present in concentrations exceeding those listed below.

Substance	Concentration and Suggested Treatments
Acidic or basic samples	Adjust to approximately pH 7. Use 1 N Sodium Hydroxide Standard Solution for acidic samples and 1 N Hydrochloric Acid Standard Solution for basic samples.
Calcium	50,000 mg/L as $CaCO_3$
Glycine, hydrazine	Will cause intensified colors in the prepared sample.
Magnesium	300,000 mg/L as $CaCO_3$
Iron	Eliminate iron interference as follows: 1. Determine the amount of iron present in the sample using one of the total iron procedures. 2. Add the same iron concentration to the deionized water in *step 9* in the procedure. 3. The interference will then be successfully blanked out.
Nitrite	600 mg/L as NO_2^-–N
Nitrate	5,000 mg/L as NO_3^-–N
Orthophosphate	5,000 mg/L as PO_4^{3-}–P
Sulfate	6,000 mg/L as SO_4^{2-}
Sulfide	Sulfide will intensify the color. Eliminate sulfide interference as follows: 1. Measure about 350 mL of sample in a 500-mL Erlenmeyer flask. 2. Add the contents of one Sulfide Inhibitor Reagent Powder Pillow. Swirl to mix. 3. Filter the sample through folded filter paper. Use the solution in *step 9*.
Turbidity and color	Give erroneous high values. Samples with severe interferences require distillation. Hach recommends the distillation procedure using the Hach General Purpose Distillation Set.

In some lab environments, airborne cross-contamination of the blank is possible. Prepare the blank before opening or handling any samples or standards; this avoids transferring ammonia. If the sample or standard containers have already been opened, prepare the blank in another location.

Summary of Method

Ammonia compounds combine with chlorine to form monochloramine. Monochloramine reacts with salicylate to form 5-aminosalicylate. The 5-aminosalicylate is oxidized in the presence of a sodium nitroprusside catalyst to form a blue colored compound. The blue color is masked by the yellow color from the excess reagent present to give a green solution.

REQUIRED REAGENTS

	Cat. No.
AmVer Reagent Set for Nitrogen-Ammonia Determination (50 tests)	26069-45

Includes: (1) 23952-66, (1) 23954-66, (1) 272-42, (50) AmVer™ HR Vials*

Description	Quantity Required Per Test	Unit	Cat. No.
AmVer HR Reagent, TNT vials	1 vial	50/pkg	*
Ammonia Salicylate Reagent Powder Pillows, 5 mL sample	1 pillow	50/pkg	23952-66
Ammonia Cyanurate Reagent Powder Pillows, 5 mL sample	1 pillow	50/pkg	23954-66
Water, deionized	varies	100 mL	272-42

REQUIRED APPARATUS

COD Vial Adapter, DR/2010	1	each	44799-00
Funnel, Micro	1	each	25843-35
Pipet, TenSette, 0-1 mL	1	each	19700-01
Pipet Tips for 19700-01 TenSette Pipet	varies	50/pkg	21856-96
Test Tube Rack	1-3	each	18641-00

OPTIONAL REAGENTS

Ammonium Nitrogen Standard Solution, 50 mg/L NH_3-N	500 mL	14791-10
Ammonia Nitrogen Standard Solution, 10 mg/L NH_3-N	500 mL	153-49
Hydrochloric Acid, ACS	500 mL	134-49
Sodium Hydroxide Standard Solution, 5.0 N	50 mL	2450-26
Sodium Thiosulfate Standard Solution, 0.1 N	100 mL MDB	323-32
Sulfide Inhibitor Powder Pillows	100/pkg	2418-99
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Distillation Apparatus Set, general purpose	each	22653-00
Filter Paper, folded	100/pkg	1894-57
Flask, erlenmeyer, 500 mL	each	505-49
Funnel, analytical	each	1083-68
Heater and Support Apparatus (for distillation), 115 V	each	22744-00
Heater and Support Apparatus (for distillation), 230 V	each	22744-02
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

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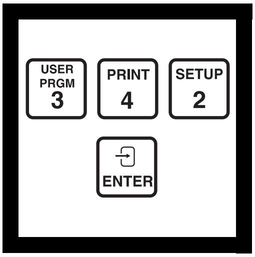
* Not available separately. Please order the complete set (Cat. No. 26069-45) as a replacement.

NITROGEN, AMMONIA, Low Range Test ‘N Tube

(0 to 2.50 mg/L NH_3-N) **For Water, Wastewater, and Seawater**

Salicylate Method*

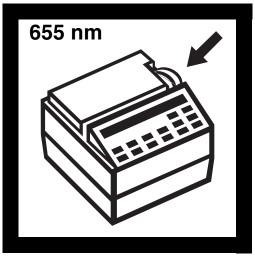


1. Enter the stored program number for Low Range Test 'N Tube Ammonia Nitrogen (N).

Press: **3 4 2 ENTER**

The display will show:

Dial nm to 655

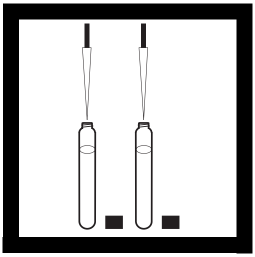


2. Rotate the wavelength dial until the small display shows:

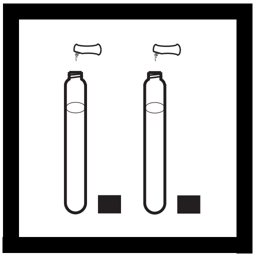
655 nm

When the correct wavelength is dialed in, the display will quickly show: **Zero Sample**

then: **mg/L N LR TNT**

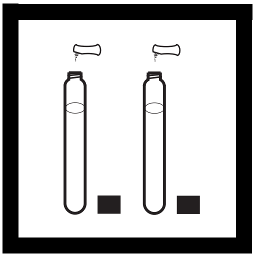


3. Remove the caps from two AmVer Diluent Reagent vials. Add 2 mL of sample to one vial (the sample). Add 2 mL of ammonia-free water to another (the blank).

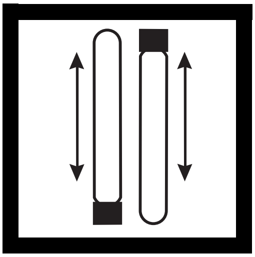


4. Add the contents of one Ammonia Salicylate Reagent Powder Pillow for 5 mL sample to each vial.

Note: *Adjust the pH of stored samples before analysis.*

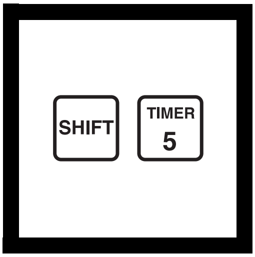


5. Add the contents of one Ammonia Cyanurate Reagent Powder Pillow for 5 mL sample to each vial.



6. Cap the vials tightly and shake thoroughly to dissolve the powder.

Note: *A green color will develop if ammonia is present.*



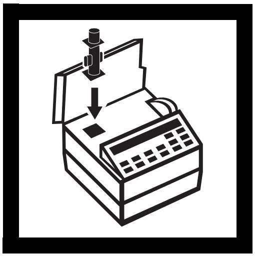
7. Press:

SHIFT TIMER

A 20-minute reaction period will begin.

When the timer beeps the display will show:

mg/L N LR TNT



8. Place the COD vial adapter into the cell holder with the marker to the right.

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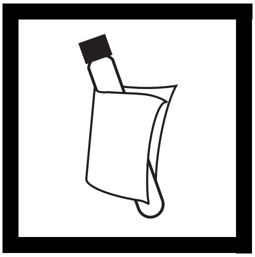
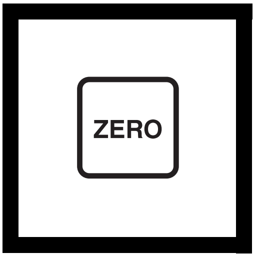
* Adapted from *Clin. Chim. Acta* 14:403 (1966)



9. After cleaning the outside of the vial with a towel, place the blank into the vial adapter. Place the cover on the adapter.

Note: *Wiping with a damp cloth followed by a dry one removes fingerprints and other marks.*



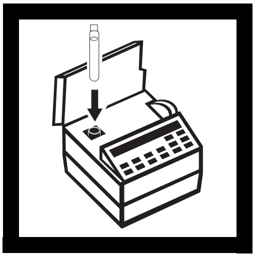
10. Press: **ZERO**

The display will show:

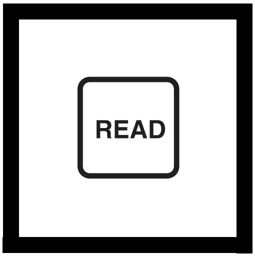
Zeroing. . . .

then:

0.00 mg/L N LR TNT



11. Place the prepared sample into the vial adapter. Place the cover on the adapter.



12. Press: **READ**

The display will show:

Reading

then the result in mg/L ammonia expressed as nitrogen (N) will be displayed.

Forms ▲▼ N
NH$_3$

Sampling and Storage

Collect samples in clean plastic or glass bottles. Best results are obtained with immediate analysis. If chlorine is known to be present, add one drop of 0.1 N sodium thiosulfate for each 0.3 mg/L Cl_2 in a one liter sample. Preserve the sample by reducing the pH to 2 or less with hydrochloric acid (at least 2 mL). Store at 4 °C (39 °F) or less. Preserved samples may be stored up to 28 days. Before analysis, warm samples to room temperature and neutralize with 5 N sodium hydroxide. Correct the test result for volume additions.

Accuracy Check

Standard Additions Method

a) Snap the neck off an Ammonium Nitrogen Voluette Ampule Standard Solution, 50 mg/L NH_3-N.

b) Use the TenSette Pipet to add 0.1, 0.2, and 0.3 mL of standard to three 25 mL samples. Mix thoroughly.

c) Analyze each sample as described above. The nitrogen concentration should increase 0.20 mg/L for each 0.1 mL of standard added.

d) If these increases do not occur, see *Standard Additions*, *Section I*, for more information.

Standard Solution Method

To check accuracy, use a 1.0 mg/L Ammonium Nitrogen Standard Solution listed under optional reagents. Or, dilute 1 mL of solution from a 50 mg/L Voluette Ampule Standard for Ammonium Nitrogen to 50 mL with deionized water using a 50-mL volumetric flask.

Precision

In a single laboratory, using a standard solution of 1.5 mg/L nitrate nitrogen (NO_3^--N) and two representative lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±0.03 mg/L N.

Interferences

Interfering Substance	**Interference Level and Treatment**
Calcium	2500 mg/L as $CaCO_3$
Iron	1. Determine the amount of iron present in the sample following one of the total iron procedures. 2. Add the same iron concentration to the deionized water in *step 9* of the procedure. The interference will then be successfully blanked out.
Magnesium	15,000 mg/L as $CaCO_3$
Nitrite	30 mg/L as NO_2^-–N
Nitrate	250 mg/L as NO_3^-–N
Orthophosphate	250 mg/L as PO_4^{3-}–P
pH	Acidic or basic samples should be adjusted to about pH 7. Use 1 N Sodium Hydroxide Standard Solution for acidic samples and 1 N Hydrochloric Acid Standard Solution for basic samples.
Sulfate	300 mg/L as SO_4^{2-}
Sulfide	Will intensify the color. 1. Measure about 350 mL of sample in a 500 mL Erlenmeyer flask. 2. Add the contents of one Sulfide Inhibitor Reagent Powder Pillow. Swirl to mix. 3. Filter the sample through a folded filter paper. 4. Use the filtered solution in *step 9*.
Other	Less common interferences such as **hydrazine** and **glycine** will cause intensified colors in the prepared sample. **Turbidity** and **color** will give erroneous high values. Samples with severe interferences require distillation. Hach recommends the distillation procedure using the Hach General Purpose Distillation Set. See *Optional Apparatus.*

Summary of Method

Ammonia compounds combine with chlorine to form monochloramine. Monochloramine reacts with salicylate to form 5-aminosalicylate. The 5-aminosalicylate is oxidized in the presence of a sodium nitroprusside catalyst to form a blue colored compound. The blue color is masked by the yellow color from the excess reagent present to give a final green colored solution.

REQUIRED REAGENTS

Description	Cat. No.
AmVer™ Reagent Set for Nitrogen, Ammonia, Low Range TNT (50 vials) Includes: (1) 23952-66, (1) 23954-66, (1) 272-42, (50) AmVer Diluent Low Range Vials*	26045-45

Description	Quantity Required Per Test	Unit	Cat. No.
AmVer™ Diluent Reagent, TNT Low Range Vials	1	50/pkg	*
Cyanurate Reagent Powder Pillows, 5 mL Sample	1	50/pkg	23954-66
Salicylate Reagent Powder Pillows, 5 mL Sample	1	50/pkg	23952-66
Water, deionized	varies	100 mL	272-42

REQUIRED APPARATUS

COD Vial Adapter, DR/2010	1	each	44799-00
Funnel, Micro	1	each	25843-35
Pipet, TenSette, 0-10 mL	1	each	19700-10
Pipet Tips for 19700-10	1	50/pkg	21997-96
Safety Bulb	1	each	14651-00
Test Tube Rack	1-3	each	18641-00

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* Not available separately. Please order the complete set (Cat. No. 26045-45) as a replacement.

OPTIONAL REAGENTS

Description	Unit	Cat. No.
Ammonium Nitrogen Standard Solution, 1.0 mg/L NH_3-N	500 mL	1891-49
Ammonium Nitrogen Standard Solution, 50 mg/L NH_3-N, 10 mL ampules	16/pkg	14791-10
Ammonium Nitrogen Standard Solution, 50 mg/L NH_3-N, 2 mL PourRite Ampules	20/pkg	14791-20
Hydrochloric Acid, ACS	500 mL	134-49
Sodium Hydroxide Standard Solution, 5.0 N	50 mL SCDB	2450-26
Sodium Hydroxide, 1.0 N	100 mL MDB	1045-32
Sodium Thiosulfate Standard Solution, 0.1 N	100 mL SCDB	323-32
Sulfide Inhibitor Reagent Powder Pillows	100/pkg	2418-99
Sulfuric Acid, 1.0 N	100 mL MDB	1270-32
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Ampule Breaker Kit	each	21968-00
Ampule Breaker Kit, PourRite	each	24846-00
Filter Paper, folded	100/box	1894-57
Flask, erlenmeyer, 500 mL	each	505-49
Flask, volumetric, 50 mL	each	547-41
Funnel, analytical	each	1083-68
Distillation Apparatus Set	each	22653-00
Heater and Support Apparatus (for distillation), 115 V	each	22744-00
Heater and Support Apparatus (for distillation), 230 V	each	22744-02
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
Thermometer, -20 to 110 °C	each	566-01
Thermometer, -10 to 260 °C	each	20959-26

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

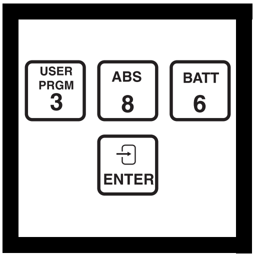
Method 10045

NITROGEN, MONOCHLORAMINE and FREE AMMONIA

Salicylate Method (0.00 to 0.50 mg/L NH_2Cl-N)

For drinking water

Using Powder Pillows

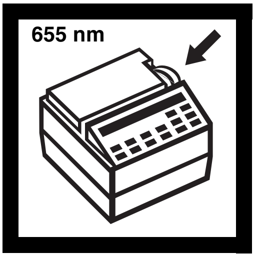


1. Enter the stored program number for monochloramine nitrogen (NH_2Cl-N), salicylate method.

Press: **3 8 6 ENTER**

The display will show:

Dial nm to 655

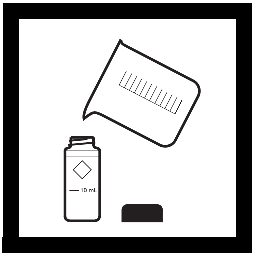


2. Rotate the wavelength dial until the display shows:

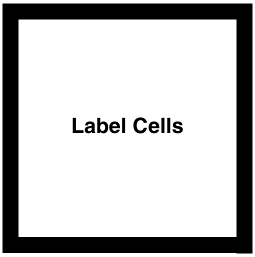
655 nm

When the correct wavelength is dialed in, the display will quickly show: **Zero Sample**

then: **mg/L NH_2Cl-N**

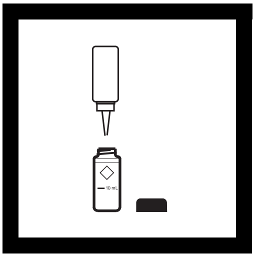


3. Fill three 10-mL round sample cells to the 10-mL line with sample.



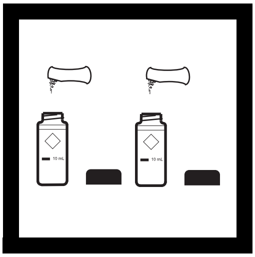
4. Label one cell “blank”, one cell “free ammonia” and one cell “monochloramine”.

5. Cap the cell labeled “blank”. Nothing will be added to it.



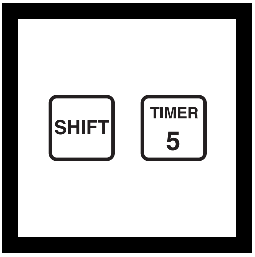
6. Add one drop of Hypochlorite Solution to the cell labeled “free ammonia”. Cap the cell and mix.

Note: Occasionally shake the Hypochlorite Solution bottle to ensure proper dispensation.



7. Promptly add the contents of one Monochloramine Reagent pillow to the cells labeled “free ammonia” and “monochloramine”. Cap and shake both cells to dissolve.

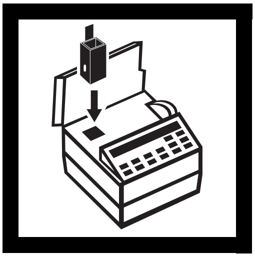
Note: Free ammonia is the ammonia (NH_3) and ammonium (NH_4^+) present in the sample, corrected for the monochloramine present.



8. Press:

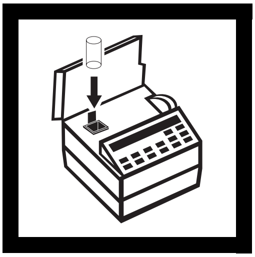
SHIFT TIMER

A 15-minute reaction period will begin. Wipe fingerprints, liquid, etc. off of the cells.

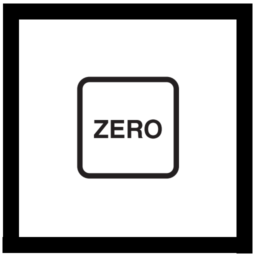


9. Place an AccuVac Vial Adapter into the cell holder.

Note: *Place the grip tab at the rear of the cell holder.*



10. When the timer beeps, place the blank into the cell holder. Close the light shield.



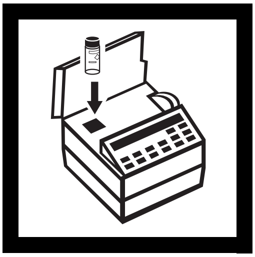
11. Press: **ZERO**

The display will show:

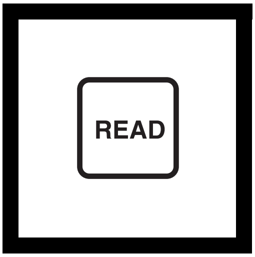
Zeroing. . . .

then:

0.00 mg/L NH_2Cl-N



12. Place the "monochloramine" cell into the cell holder. Close the light shield.



13. Press: **READ**

The display will show:

Reading. . . .

then the monochloramine result in mg/L as nitrogen will be displayed. Store or record this value.

Note: *Do not remove the sample cell.*

Forms ▲▼ NH_2Cl NH_2Cl-N Cl_2

14. Press:

SELECT PRGM

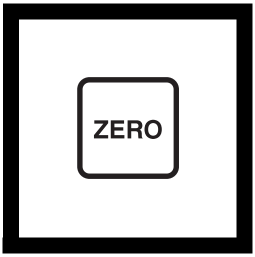
Enter the stored program number for free ammonia (NH_3-N).

Press: **3 8 7 ENTER**

The display will show:

Zero Sample

then: **mg/L NH_3-N Free**



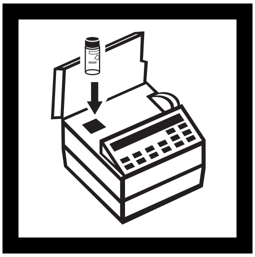
15. Press: **ZERO**

The display will show:

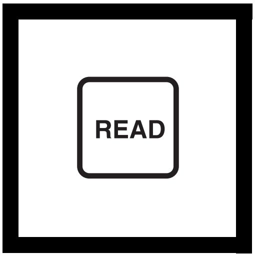
Zeroing. . . .

then:

0.00 mg/L NH_3-N Free



16. Place the "free ammonia" cell into the cell holder. Close the light shield.



17. Press: **READ**

The display will show:

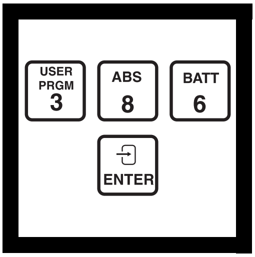
Reading. . . .

then the free ammonia result in mg/L as nitrogen will be displayed.

Note: *If the free ammonia and monochloramine results total over 0.5 mg/L as nitrogen, repeat the test with a diluted sample for best results. See Accuracy Check.*

Forms ▲▼ NH_4^+ NH_3-N NH_3

Using AccuVac Ampuls

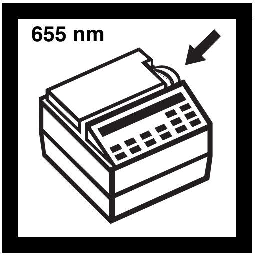


1. Enter the stored program number for monochloramine nitrogen (NH_2Cl-N), salicylate method.

Press: **3 8 6 ENTER**

The display will show:

Dial nm to 655



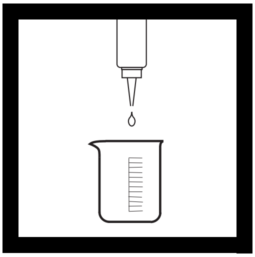
2. Rotate the wavelength dial until display shows: **655 nm**

When the correct wavelength is dialed in, the display will show:

Zero Sample

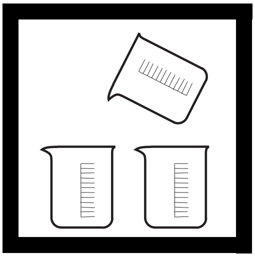
then: **mg/L NH_2Cl-N**

3. Label one 50-mL beaker “free ammonia” and one 50-mL beaker “monochloramine”.



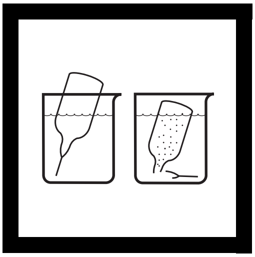
4. To test for free ammonia, dispense 5 drops of Hypochlorite Solution into the “free ammonia” beaker.

Note: *Occasionally shake the Hypochlorite Solution bottle to ensure proper dispensation.*



5. Mix by vigorously adding 40 to 50 mL of sample to each beaker.

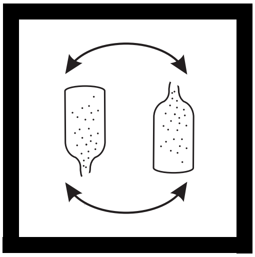
Note: ***Note:*** *Holding the pouring beaker 2 to 3 inches above the receiving beaker while pouring will create turbulence, causing the Hypochlorite Solution to mix into the sample.*



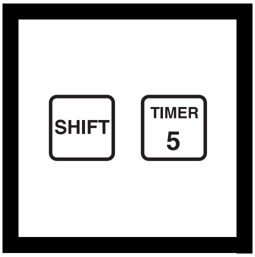
6. Promptly fill one Monochloramine AccuVac ampul from each beaker.

Note: *Keep the tips immersed while the ampuls fill.*

Note: *Mark the bottom of each ampule to correspond to the free ammonia or monochloramine beakers.*

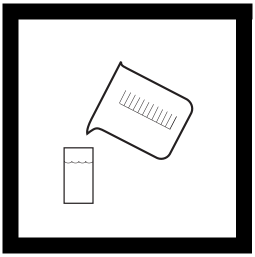


7. Invert the ampuls to dissolve the powder.

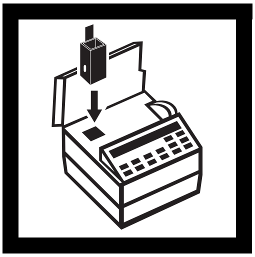


8. Press: **SHIFT TIMER**

A 15-minute reaction period will begin.

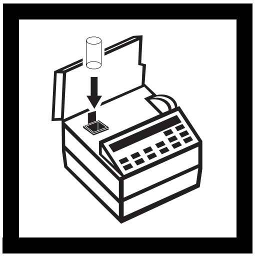


9. Fill a zeroing vial with sample. Wipe fingerprints, liquid, etc. from the ampuls and zeroing vial.

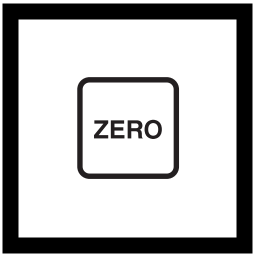


10. Place an AccuVac Vial Adapter into the cell holder.

Note: *Place the grip tab at the rear of the cell holder.*



11. When the timer beeps, place the zeroing vial into the cell holder. Close the light shield.



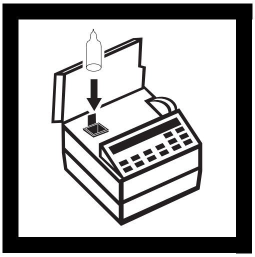
12. Press: **ZERO**

The display will show:

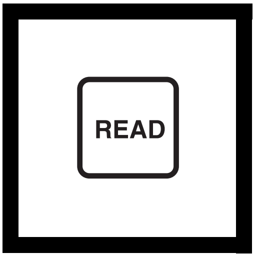
Zeroing. . . .

then:

0.00 mg/L NH_2Cl-N



13. Place the "monochloramine" ampul into the cell holder. Close the light shield.



14. Press: **READ**

The display will show:

Reading. . . .

then the monochloramine result in mg/L as nitrogen will be displayed.

Forms ▲▼ NH_2Cl NH_2Cl-N Cl_2

15. Press:

SELECT PRGM

Enter the stored program number for free ammonia (NH_3-N).

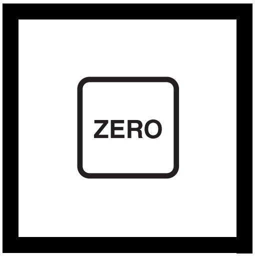
Press: **3 8 7 ENTER**

The display will show:

Zero Sample

then: **mg/L NH_3-N Free**

Do not remove the AccuVac.



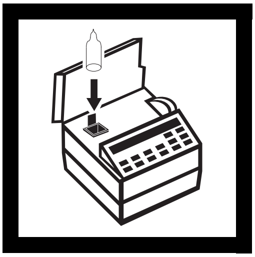
16. Press: **ZERO**

The display will show:

Zeroing. . . .

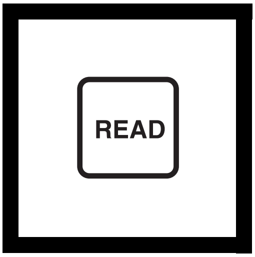
then:

0.00 mg/L NH_3-N Free



17. Place the ampul labeled "free ammonia" into the cell holder. Close the light shield.

Note:** If the display shows* **"LAMP OUT?", try testing a diluted sample.*



18. Press:**READ**

The display will show:

Zeroing. . . .

then the free ammonia result in mg/L as nitrogen will be displayed.

***Note:** If the free ammonia and monochloramine results total over 0.50 mg/L as nitrogen, for best results, repeat the test with a diluted sample. See Accuracy Check.*

Forms ▲▼ NH_4^+ NH_3-N NH_3

Sampling and Storage

Collect samples in clean glass bottles. Most reliable results are obtained when samples are analyzed as soon as possible after collection.

Accuracy Check

Dilution water is required when testing a diluted sample and preparing standard solutions. Dilution water must be free of ammonia, chlorine and chlorine demand. A convenient source is a recirculating, deionizer system with carbon filtration which produces 18 megaohm-cm water.

Standard Additions Method

a) Measure 50 mL of sample into three 50-mL mixing cylinders.

b) Use the TenSette Pipet to add 0.3, 0.6, and 1.0 mL of Ammonium Nitrogen Standard, 10 mg/L as NH_3-N to the three samples. Mix well.

c) Analyze each sample as described above. The ammonia nitrogen concentration should increase 0.02 mg/L for each 0.1 mL of standard added.

d) If these increases do not occur, see *Standard Additions (Section I)* for more information.

Standard Solution Method

Prepare a 0.50 mg/L ammonia nitrogen standard by diluting 5.00 mL of the Ammonia Nitrogen Standard Solution, 10 mg/L, to 100 mL with dilution water. Or, using the TenSette Pipet, prepare a 0.50 mg/L ammonia nitrogen standard by diluting 1.0 mL of an Ammonia Nitrogen Voluette Standard Solution, 50 mg/L as NH_3-N, to 100 mL with dilution water. Always use the newest lot of Hypochlorite Solution. Discard the old bottle when new lots of reagent are received.

Precision

In a single laboratory using a standard solution of 0.20 mg/L ammonia nitrogen (NH_3-N) and representative lots of reagent with the DR/2010, a single operator obtained a standard deviation of $\pm$0.009 mg/L ammonia nitrogen.

Interference

Ammonia contamination from air is a common cause of high test results. Beakers and other containers may require rinsing with excess sample just before use. Samples, solutions and deionized water will accumulate ammonia from the air.

The following ions may interfere when present at the concentrations listed in the table below:

Calcium	3000 mg/L as $CaCO_3$
Chlorine demand, non-ammonia	greater than 2 mg/L as Cl_2
Magnesium	1600 mg/L as $CaCO_3$
pH	less than 7
Sulfate	greater than 900 mg/L as SO_4^{2-}

Mixtures of small amounts of differing substances may produce test interference. To assess the influence of interferences in your sample, perform the Accuracy Check, Standard Addition Method.

Summary of Method

Monochloramine (NH_2Cl) and "free ammonia" (NH_3 and NH_{4+}) can exist in the same water sample. Added hypochlorite combines with free ammonia to form more monochloramine. Monochloramine reacts with salicylate to form 5-aminosalicylate. It reacts in the presence of a cyanoferrate catalyst to give a green solution. Free ammonia is determined by comparing the color intensities, with and without added hypochlorite.

REQUIRED REAGENTS (USING PILLOWS)

	Cat. No.
Monochloramine Reagent Set (50 tests)	26184-00

Includes: (4) 26183-68, (1)26072-36

Description	Quantity Required Per Test	Units	Cat. No.
Monochloramine Reagent Pillows	2 pillows	25/pkg	26183-68
Hypochlorite Solution	0.04 mL	15 mL	26072-36

REQUIRED REAGENTS (USING ACCUVAC AMPULS)

	Cat. No.
Monochloramine Reagent AccuVac Ampul Set (12 tests)	25210-98

Includes: (1) 25230-25, (1)26072-36

Hypochlorite Solution	0.2 mL	15 mL	26072-36
Monochloramine Reagent AccuVac Ampuls	2 ampuls	25/pkg	25230-25

REQUIRED APPARATUS (USING PILLOWS)

Clippers, large	1	each	968-00
Sample cell, 10-mL, with cap	3	6/pkg	24276-06

REQUIRED APPARATUS (USING ACCUVAC AMPULS)

Beaker, 50-mL	2	each	500-41
Vial, zeroing	1	each	21228-00

OPTIONAL REAGENTS

Nitrogen Ammonia Standard Solution, 10 mg/L as NH_3-N	500 mL	153-49
Nitrogen Ammonia Standard Ampule, 50 mg/L as NH_3-N, 10 mL	16/pkg	14791-10
Water, chlorine demand free	500 mL	27015-49

OPTIONAL APPARATUS

AccuVac Snapper Kit	each	24052-00
Ampule Breaker Kit	each	21968-00
Cylinder, 50 mL, mixing	each	20886-41
Flask, volumetric, Class A, 100 mL	each	14574-42
Pipet Filler, safety bulb	each	14651-00
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 5.0 mL	each	14515-36
Thermometer, -20 to 105 °C	each	1877-01
Wipers, disposable, Kimwipes, 30 x 30 cm, 280/box	box	20970-01

For technical support and ordering information, see Section V.

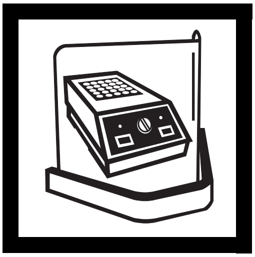
In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

NITROGEN, TOTAL, Test ’N Tube (0.0 to 25.0 mg/L N)

For water and wastewater

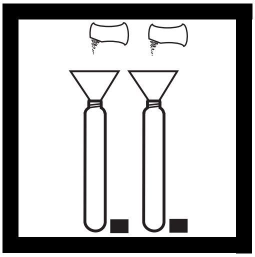
TNT Persulfate Digestion Method



1. Turn on the COD Reactor. Heat to 103-106 °C (optimum temperature is 105 °C). Place the plastic shield in front of the reactor.

Note: *Ensure safety devices are in place to protect the analyst from splattering should leakage occur.*

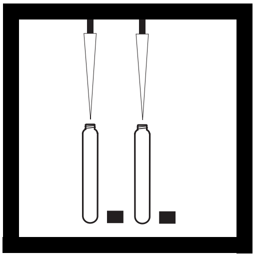
Note: *For proof of accuracy, run a 20 mg/L* NH_3*-N standard through digestion and analysis.*



2. Using a funnel, add the contents of one Total Nitrogen Persulfate Reagent Powder Pillow to each of two Total Nitrogen Hydroxide Reagent vials.

Note: *Wipe off any reagent that may get on the lid or the tube threads.*

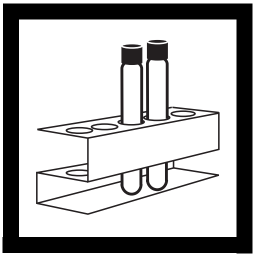
Note: *One reagent blank is sufficient for each set of samples.*



3. Add 2 mL of sample to one vial. Add 2 mL of organic-free water to another vial (the reagent blank). Cap both vials and shake vigorously (more than 30 seconds). Place the vials in the COD Reactor. Heat for 30 minutes.

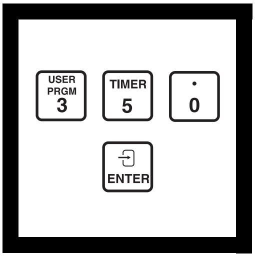
Note: *The persulfate reagent may not dissolve completely after mixing.*

Note: *Alternate water must be free of all nitrogen-containing species.*



4. Using finger cots or gloves, remove the hot vials from the reactor and allow to cool to room temperature.

Note: *It is very important to remove the vials from the COD Reactor after exactly 30 minutes.*

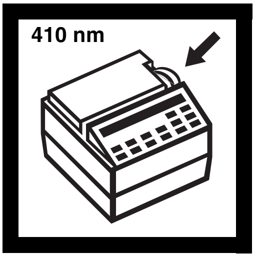


5. Enter the stored program number for Test 'N Tube Total Nitrogen.

Press: **350 ENTER**

The display will show:

Dial nm to 410



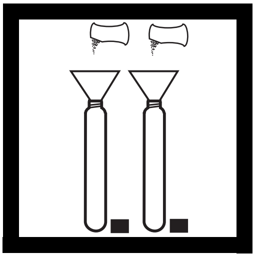
6. Rotate the wavelength dial until the small display shows:

410 nm

When the correct wavelength is dialed in, the display will quickly show: **Zero Sample**

then:

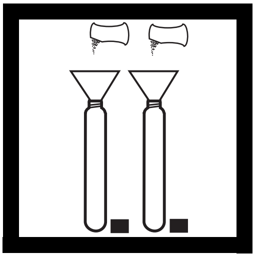
mg/L N TN TNT



7. Remove the caps from the cooled digested vials and add the contents of one TN Reagent A Powder Pillow to each vial. Cap vials and shake for 15 seconds.

Press: **SHIFT TIMER** after shaking.

A three-minute reaction period will begin.



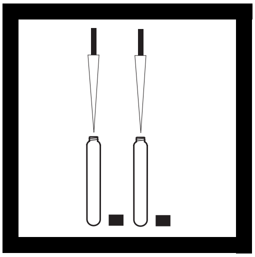
8. After the timer beeps, remove the caps from the cooled vials and add one TN Reagent B Powder Pillow to each vial. Cap vials and shake for 15 seconds.

Press: **SHIFT TIMER** after shaking.

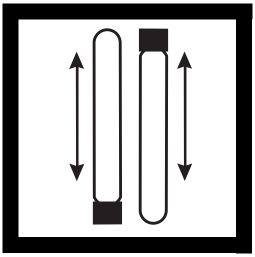
A two-minute reaction period will begin.

Note: *The reagent will not completely dissolve.*

Note: *The solution will begin to turn yellow.*

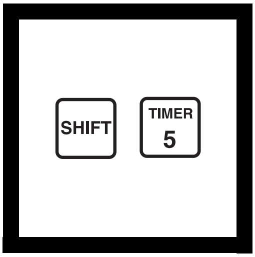


9. After the timer beeps, remove the caps from two TN Reagent C Vials and add 2 mL of digested, treated sample to one vial. Add 2 mL of the digested, treated reagent blank to the second TN Reagent C Vial.



10. Cap vials and invert 10 times to mix. Use slow, deliberate inversions for complete recovery. The vials will be warm.

Note: *Hold the vial vertical with the cap up. Invert the vial and wait for all of the solution to flow to the cap end. Return the vial to the upright position and wait for all of the solution to flow to the vial bottom. This is one inversion (10 inversions = 30 seconds)*

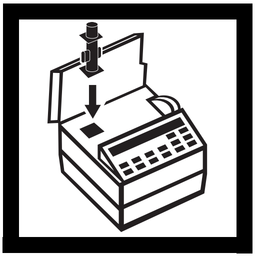


11. Press:

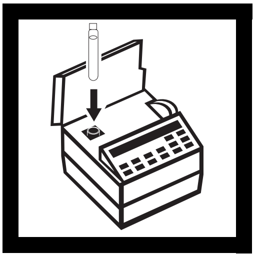
SHIFT TIMER

A five-minute reaction period will begin. Do not invert the vials again.

Note: *The yellow color will intensify.*



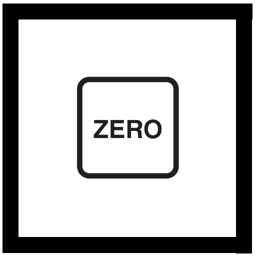
12. Place the COD Vial Adapter into the cell holder with the marker to the right.



13. When the timer beeps, wipe the reagent blank vial. Place the vial into the adapter with the Hach logo facing the front of the instrument. Place the adapter cover over the tube.

Note: *Wiping with a damp towel, followed by a dry one, will remove fingerprints or other marks.*

Note: *The reagent blank is stable when stored in the dark; see Blanks for Colorimetric Measurement following this procedure.*



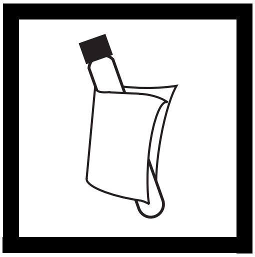
14. Press: **ZERO**

The display will show:

Zeroing. . .

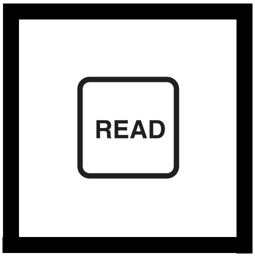
then:

0.0 mg/L N TN TNT



15. Wipe the TN Reagent C vial containing the prepared sample. Place the vial into the adapter with the Hach logo facing the front of the instrument. Place the adapter cover over the tube.

Note: *Multiple samples may be read after zeroing on one reagent blank.*



16. Press: **READ**

The display will show:

Reading. . .

then the result in mg/L nitrogen will be displayed.

Note: *If the test overranges, repeat the digestion and colorimetric finish with diluted sample. Digestion must be repeated for accurate results.*

Forms ▲▼ NH_3 N NO_3^-

Sampling and Storage

Collect samples in clean plastic or glass bottles. Best results are obtained with immediate analysis.

Preserve the sample by reducing the pH to 2 or less with concentrated sulfuric acid (at least 2 mL). Store at 4 °C (39 °F) or less. Preserved samples may be stored up to 28 days. Warm samples to room temperature and neutralize with 5 N sodium hydroxide before analysis. Correct the test result for volume additions; see *Correcting for Volume Additions* in *Section I.*

Accuracy Check

This method generally yields 95-100% recovery on organic nitrogen standards. For proof of accuracy Hach offers a set of 3 Primary Standards for Kjeldahl Nitrogen.

1. Prepare one or more the following 3 solutions. Each preparation is for an equivalent 25 mg/L N standard.

    a) Weigh 0.3379 g of Ammonium p-Toluenesulfonate (PTSA). Dissolve in a Class A 1000-mL volumetric flask with deionized water. Add deionized water to the 1000-mL mark.

    b) Weigh 0.4416 g of Glycine p-Toluenesulfonate. Dissolve in a Class A 1000-mL volumetric flask with deionized water. Add deionized water to the 1000-mL mark.

    c) Weigh 0.5274 g of Nicotinic p-Toluenesulfonate. Dissolve in a Class A 1000-mL volumetric flask with deionized water. Add deionized water to the 1000-mL mark.

2. Analyze each of these solutions using the test procedure. Calculate the percent recovery for each using this formula:

$$\%\ \text{recovery} = \frac{\text{measured concentration}}{25} \times 100$$

The percent recovery should be:

Compound	Lowest Expected % Recovery
Ammonia-PTSA	95%
Glycine-PTSA	95%
Nicotinic-PTSA	95%

Hach analysts have found Ammonia-PTSA to be the most difficult to digest.

Other compounds may yield different percent recoveries.

Standard Solution Method

For proof of accuracy, substitute 2 mL of a 20 mg/L ammonia nitrogen standard solution for the sample in the procedure. To prepare a 20-mg/L standard, use a 20-mL Class A pipet to transfer 20 mL of a 100-mg/L Ammonia Nitrogen Standard to a 100-mL Class A volumetric flask. Dilute to the line with organic-free water. A single analyst should obtain less than 5% variation on replicates.

Standard Additions Method

a) Fill three, 25-mL graduated mixing cylinders with 25 mL of sample.

b) Snap the neck off an Ammonia Nitrogen Voluette Ampule Standard Solution, 160 mg/L as NH_3-N

c) Use the TenSette Pipet to add 0.3 mL, 0.6 mL, and 0.9 mL of standard, respectively, to the three mixing cylinders.

d) Stopper each cylinder and mix thoroughly.

e) Add 2 mL of each prepared solution, respectively, to three Total Nitrogen Hydroxide Reagent Vials.

f) Analyze each standard addition sample as described in the procedure. The nitrogen concentration should increase by approximately 1.9, 3.8 and 5.6 mg/L N, respectively.

g) If these increases do not occur, see Standard Additions in Section I for troubleshooting information.

Blanks For Colorimetric Determination

The reagent blank may be used repeatedly for measurements using the same lots of reagents. Store the reagent blank in the dark at room temperature (18-25 °C) for a maximum of 7 days. If a smal amount of white floc appears prior to the end of 1 week, discard the reagent blank and prepare a new one.

Precision

A Hach chemist analyzed two independent nutrient standards. The lowest average percent recovery was 95% with a standard deviation of ±2%.

In a single laboratory, using a standard solution of 15 mg/L NH_3-N and two lots of reagent with a DR/2010 Spectrophotometer, a single operator obtained a standard deviation of less than 1 mg/L N.

Interferences

The substances in the following table have been tested and found **not** to interfere up to the indicated levels (in mg/L):

Substance	Maximum Level Tested (mg/L)	Substance	Maximum Level Tested (mg/L)
Barium	2.6	Organic Carbon	150
Calcium	300	pH	13 pH units
Chromium (3+)	0.5	Phosphorus	100
Iron	2	Silica	150
Lead	6.6 ppb	Silver	0.9
Magnesium	500	Tin	1.5

Interfering substances that resulted in a concentration change of ±10%:

Substance	Level and Effect
Bromide	>60ppm; positive interference
Chloride	>1000 ppm; positive interference

Hach chemists tested this chemistry on standard nitrogen solutions prepared from the following compounds and obtained 95% recovery:

- Ammonium chloride
- Ammonium sulfate
- Ammonium acetate
- Urea
- Glycine

Ammonium chloride or nicotinic-PTSA spikes in domestic influent, effluent and the ASTM standard specification for substitute wastewater (D 5905-96) also resulted in ≥95% recovery.

Summary of Method

An alkaline persulfate digestion converts all forms of nitrogen to nitrate. Sodium metabisulfite is added after the digestion to eliminate halide interferences. Nitrate then reacts with chromotropic acid under strongly acidic conditions to form a yellow complex with an absorbance maximum at 410 nm.

REQUIRED REAGENTS

Test 'N Tube Total Nitrogen Reagent Set (100 vials) 26722-00

Includes: (4) 26717-25, (4) 26721-25, (1) 26718-49, (1) 26719-49, (1) 26720-49

Description	Quantity Required Per Test	Unit	Cat. No.
Total Nitrogen Hydroxide Reagent Vials, 0.1 N	2 vials	25/pkg	26717-25
Total Nitrogen Persulfate Reagent Powder Pillows	2 pillows	100/pkg	26718-49
TN Reagent A Powder Pillows	2 pillows	100/pkg	26719-49
TN Reagent B Powder Pillows	2 pillows	100/pkg	26720-49
TN Reagent C Vials	2 vials	25/pkg	26721-25

REQUIRED APPARATUS

COD Reactor, 115/230V, North American Plug	1	each	45600-00
COD Reactor, 230V, European Plug	1	each	45600-02
COD Vial Adapter, DR/2010	1	each	44799-00
Funnel, Micro	3	each	25843-35
Safety Shield	1	each	23810-00
Test Tube Cooling Rack	1-3	each	18641-00

OPTIONAL REAGENTS

Nitrogen, Ammonia, 100 mg/L NH_3-N	500 mL	24065-49
Nitrogen, Ammonia, Voluette Ampule, 160 mg/L NH_3-N, 10 mL	16/pkg	21091-10
Sulfuric Acid, ACS	500 mL	979-49
Primary Standards for Kjeldahl Nitrogen	set of 3	22778-00
Sodium Hydroxide Standard Solution, 5.0 N	59 mL MDB	2450-26
Water, Organic-free	500 mL	26415-49

OPTIONAL APPARATUS

Balance, analytical, 110/220V	each	22310-00
Cylinder, graduated, mixing, 25 mL	each	20886-40
Flask, volumetric, Class A, 1000 mL (3 required)	each	14574-53
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
Pipet, TenSette, 0.1 to 1.0 mL (incl 50 tips)	each	19700-01
Pipet Tips for 19700-01	50/pkg	21856-96

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8075

NITROGEN, TOTAL KJELDAHL (0 to 150 mg/L)

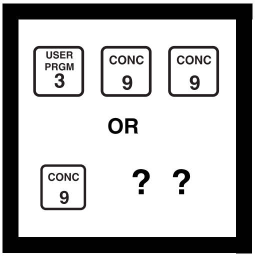
Nessler Method* digestion required

For water, wastewater, sludge

Choose Desired Program Accuracy

1. A User-Entered Calibration is necessary to obtain the most accurate results. See the User Calibration section at the back of this procedure. Program 399 can be used directly for process control or applications where a high degree of accuracy is not needed.

***Note:** Sensitivity to wavelength setting and regent lot variation necessitate user calibration for best results.*



2. Enter the stored program number for total Kjeldahl nitrogen.

Press: **3 9 9 ENTER**

for the factory stored program

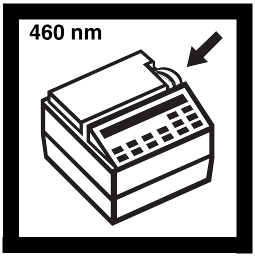
or **9 ? ? ENTER**

for the user stored program (see User Calibration).

The display will show:

Dial nm to 460

***Note:** The Pour-Thru Cell can be used. Periodically clean the cell by pouring a few sodium thiosulfate pentahydrate crystals into the cell funnel. Flush it through the funnel and cell with enough deionized water to dissolve. Rinse out the crystals.*



3. Rotate the wavelength dial until the small display shows:

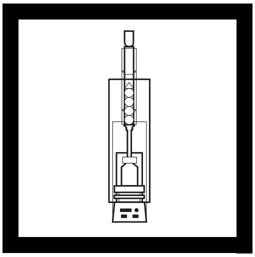
460 nm

When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

then: **mg/L TKN**

***Note:** Always set the wavelength by approaching from high to low values. For even greater accuracy, run the accuracy check and a deionized water blank. If the correct result is not obtained, repeat the accuracy check at slightly different wavelengths, again setting the dial from higher to lower values. The wavelength should be 460 ±2 nm.*

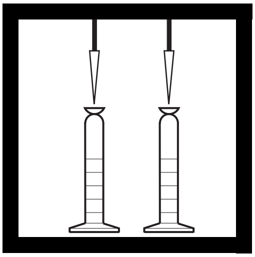


4. Digest the sample as described in *Section II,* or in the Digesdahl Digestion Apparatus Instruction manual.

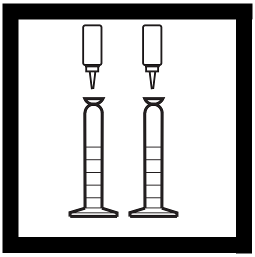
Digest an equal amount of deionized water as the blank.

---

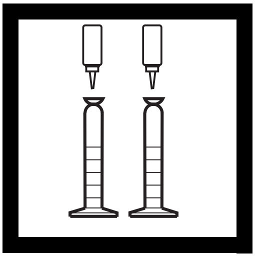
* Adapted from: Hach et al., *Journal of Association of Official Analytical Chemists*, 70 (5) 783-787 (1987); Hach et al., *Journal of Agricultural and Food Chemistry*, 33 (6) 1117-1123 (1985); *Standard Methods for the Examination of Water and Wastewater.*



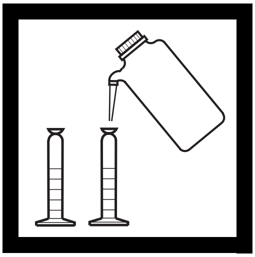
5. Select the appropriate analysis volume of the digested sample given in *Table 1*. Pipet the analysis volume from the sample and the digested blank into separate 25-mL graduated mixing cylinders.



6. Add one drop TKN Indicator to each cylinder. Add 8.0 N KOH dropwise to each cylinder, mixing after each addition. Continue until the first apparent blue color is visible.

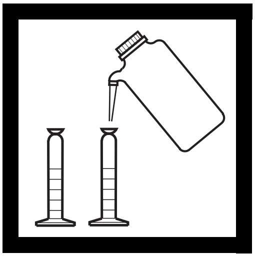


7. Add 1.0 N KOH one drop at a time, mixing after each addition, until the first permanent blue color appears.

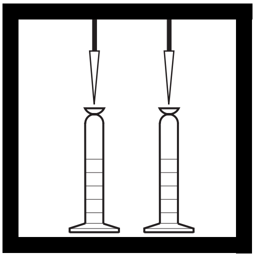


8. Fill both mixing cylinders to the 20-mL mark with deionized water. Add 3 drops of Mineral Stabilizer to each cylinder. Invert several times to mix. Add 3 drops of Polyvinyl Alcohol Dispersing Agent to each cylinder. Invert several times to mix.

Note: *Hold the dropping bottles upright while dispensing.*

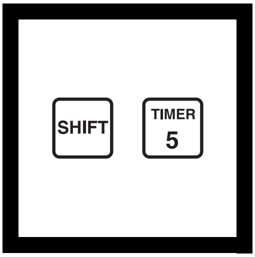


9. Fill both cylinders to the 25-mL mark with deionized water.



10. Pipet 1 mL of Nesslers Reagent to each cylinder. Stopper, invert repeatedly. The solution should not be hazy

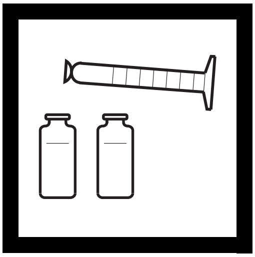
Note: *Any haze (or turbidity) will cause incorrect results.*



11. Press:

SHIFT TIMER

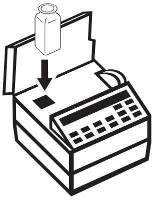
A two-minute reaction period will begin.



12. When the timer beeps, the display will show:

mg/L TKN

Pour the contents of each cylinder into a 25-mL sample cell.



13. Place the blank into the cell holder. Close the light shield.

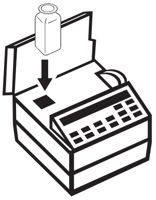
ZERO

14. Press: **ZERO**

The display will show:

Zeroing. . . .

then: **0. mg/L TKN**



15. Place the prepared sample into the cell holder. Close the light shield.

READ

16. Press: **READ**

The display will show:

Reading. . . .

then the result in mg/L total kjeldahl nitrogen as N will be displayed.

$$\text{ppm TKN} = \frac{75 \times A}{B \times C}$$

17. Use the formula shown to calculate the final TKN value.

Where:

A = mg/L read from the display

B = g (or mL of water) of sample taken for digest

C = mL analysis volume of digested sample (Step 5).

Note: *For water samples ppm TKN = mg/L TKN*

Table 1

AQUEOUS SAMPLES (Solutions of suspensions in water- less than 1% solids)	
Expected NItrogen Concentration (mg/L)	**Analysis Volume (mL)**
0.5-28	10.0
2-112	5.00
11-560	2.00
45-2250	1.00
425-22500	0.50
DRY SAMPLES	
Expected NItrogen Concentration (mg/L)	**Analysis Volume (mL)**
42-2200	10.0
106-5600	5.00
350-18000	2.00
1000-56000	1.00
4200-220000	0.50
OILS AND FATS	
Expected NItrogen Concentration (mg/L)	**Analysis Volume (mL)**
85-4500	10.0
210-11000	5.00
2100-110000	1.00

Sampling and Storage

Collect samples in a cleaned glass or plastic container. Adjust the pH to 2 or less with sulfuric acid (about 2 mL per liter) and cool to 4 °C. Preserved samples can be stored up to 28 days.

Accuracy Check

Standard Solution Method

Add one drop TKN indicator to each of two 25-mL mixing cylinders. Fill one cylinder with deionized water to the 20-mL mark. Fill the other 25-mL mixing graduated cylinder to the 20-mL mark with a 1.0 mg/L NH_3-N solution. Add 3 drops mineral stabilizer to each cylinder. Invert to mix. Add 3 drops Polyvinyl Alcohol Dispersing Agent to each cylinder. Invert to mix. Perform the Total Kjeldahl Nitrogen procedure starting with Step 9. This display should show 26-27 mg/L TKN in Step 15.

Kjeldahl Nitrogen Standard Method

This checks the efficiency of the digestion and colorimetric test. There are standards available for doing this test. For a complete procedure, see Digestion Accuracy Check in the Digesdahl Digestion Apparatus instruction manual.

User Calibration

For most accurate results, the use of a user-calibrated program is highly recommended. The Hach stored program 399 is intended for process control samples or other applications where a high degree of accuracy is not necessary.

A one-time setup of a program for TKN is recommended for each new lot of reagents. A new calibration may be performed for each lot of Nessler Reagent as follows.

Standard Preparation

Prepare standards representing concentrations of 20, 60, 80, 100, 140 and 160 mg/L NH_3-N as follows:

a) Using volumetric pipets, transfer 5.0, 15.0, 20.0, 25.0, 35.0, and 40.0 mL of 100 mg/L NH_3-N standard solution into six separate 100-mL volumetric flasks. Dilute to volume with deionized water, stopper, and invert to mix.

b) Begin at step 4 of the procedure using a 3-mL aliquot for the sample volume. Also prepare a blank solution by substituting a 3 mL aliquot of deionized water for sample in step 4.

Note: *Standard solutions are prepared as if a 25-mL volume was used for the digestion. Actual concentrations prepared in step a) are 5, 15, 20, 25, 35, and 40 mg/L NH_3-N. These represent original concentrations of 20, 60, 80, 100, 140, and 160 mg/L NH_3-N, based on the 25 to 100 mL dilution in the digestion.*

Initial Setup of TKN Program

a) Press **SHIFT USER PRGM**. Use the **UP** arrows to scroll to **Copy Program**. Press **ENTER**.

b) Scroll to or enter the template number for TKN (904). Press **ENTER.**

c) Scroll to or enter the desired user program number for TKN (>950). Press **ENTER**. Record the program number for reference.

d) The display will show **Program Copied**. Press **EXIT**. The program is now ready to be calibrated.

Note: *The templates within the User Program cannot be used directly. They must be copied into a usable program number (greater than 950) as in Steps c and d. For process control, the copied program can be used directly. For best results, however, the program should be calibrated with each new lot of reagents.*

User Calibration of TKN Program

a) Use the test procedure to develop color in the standards just before recording the absorbance values for the calibration.

b) Press **SHIFT USER PRGM**. Use the **UP** arrow key to scroll to **Edit Program**. Press **ENTER.**

c) Scroll or enter the program number for TKN (from step c in Initial Setup). Press **ENTER**.

d) Use the **DOWN** arrow to scroll down to **Calib Table:X** (X= denotes a number which indicates the number of data points in the table). Press **ENTER**.

e) The instrument will prompt **Zero Sample**. Place the blank solution in the cell holder. Close the light shield. Press **ZERO**. The instrument will prompt you to adjust to the proper wavelength if necessary.

f) The first concentration point will be displayed. Press **ENTER** to display the stored absorbance value of the first concentration point.

g) Place the first developed standard solution (same concentration as the value displayed) in the cell holder. Close the light shield. Press **READ** to display the measured absorbance of the standard. Press **ENTER** to accept the displayed absorbance value.

h) The second concentration point will be displayed. Press **ENTER** to display the stored absorbance value of the second concentration. Place the second developed standard solution in the cell holder. Close the light shield. Press **READ** to display the measured absorbance value of the standard.

i) Press **ENTER** to accept the absorbance reading. The next concentration point will then be displayed.

j) Repeat steps h and i as necessary for the remaining standards.

k) When finished reading absorbance values, press **EXIT**. Scroll down to **Force Zero.** Press **ENTER**. Change the Force Zero setting to ON by using an arrow key. Press **ENTER** again.

l) Scroll down to **Calib. Formula**. Press **ENTER** twice or until only the **0** in **F(0)** is flashing. Press the DOWN arrow to select **F1** (linear calibration). Press **ENTER** to select **F1**.

Note: *Other calibration fits may be used, if appropriate.*

m) Press **EXIT** twice. The display will show **Store Changes?.** Press **ENTER** to store the changes.

n) Press **EXIT**. The program is now calibrated and ready for use. Start on Step 2 of the procedure.

Precision

In a single laboratory using a standard solution of 64 mg/L TKN and two representative lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±0.8 mg/L TKN.

Summary of Method

“Total Kjeldahl Nitrogen” (also called crude protein) refers to the combination of ammonia nitrogen and organic nitrogen composed of trinegative nitrogen. These comounds are converted into ammonium salts by the action of sulfuric acid and hydrogen peroxide. The ammonia salts plus any ammonia present are then analyzed by a modified Nessler method test. The Mineral Stabilizer complexes calcium and magnesium. The Polyvinyl Alcohol Dispersing Agent aids the color formation in the reaction of Nessler Reagent with ammonium ions. A yellow color forms, proportional to the ammonia concentration.

REQUIRED REAGENTS

Description	Cat. No.
TKN Nitrogen Reagent Set	24953-00

Includes: (1) 282-32, (1) 979-49, (1)21194-49, (1) 21196-49, (1)22519-26, (1) 23144-26, (1) 23765-26, (1) 23766-26

Description	Quantity Required Per Test	Unit	Cat. No.
Hydrogen Peroxide, 50%	20 mL	500 mL	21196-49
Mineral Stabilizer	6 drops	50 mL SCDB	23766-26
Nesslers Reagent	2 mL	500 mL	21194-49
Polyvinyl Alcohol Dispersing Agent	6 drops	50 mL SCDB	23765-26
Potassium Hydroxide Standard Solution, 8.0 N	varies	100 mL MDB	282-32
Potassium Hydroxide Standard Solution, 1.0 N	varies	100 mL MDB	23144-26
Sulfuric Acid, ACS	6 mL	500 mL	979-49
TKN Indicator Solution	2 drops	50 mL SCDB	22519-26
Water, deionized	varies	4 L	272-56

REQUIRED APPARATUS

Boiling Chips, silicon carbide	2-3	500 g	20557-34
Cylinder, graduated, mixing, tall-form, 25 mL	2	each	21190-40
Pipet, TenSette, 0.1 to 1.0 mL	1	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	2	50/pkg	21856-96
Safety Shield, for Digesdahl	1	each	20974-00
Sample Cell, 25-mL, matched pair	2	pair	20950-00

Select one based on available voltage:

Digesdahl digestion apparatus, 115 Vac	1	each	23130-20
Digesdahl digestion apparatus, 230 Vac	1	each	23130-21

OPTIONAL REAGENTS

Description	Unit	Cat. No.
Nitrogen Standard Solution, 1 mg/L NH_3-N	500 mL	1891-49
Nitrogen Standard Solution, PourRite ampule, 150 mg/L NH_3-N, 10 mL	16/pkg	21284-10
Nitrogen Standard Solution, 100 mg/L NH_3-N	500 mL	24065-49
Sodium Thiosulfate, pentahydrate	454 g	460-01

OPTIONAL APPARATUS

Balance, AccuLab Pocket Pro	each	25568-00
Bottle, glass dispenser, 118 mL	each	591-00
Bottle, plastic wash, 32-oz (1000 mL)	each	620-16
Cylinder, graduated, 50 mL	each	508-41
Finger Cots	2/pkg	14647-02
Flask, volumetric, 100 mL	each	547-42
Mini Grinder, 120 Vac	each	20991-00
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
Pipet, volumetric, Class A, 0.50 mL	each	14515-34
Pipet, volumetric, Class A, 1.00 mL	each	14515-35
Pipet, volumetric, Class A, 2.00 mL	each	14515-36
Pipet, volumetric, Class A, 3.00 mL	each	14515-03
Pipet, volumetric, Class A, 4.00 mL	each	14515-04
Pipet, volumetric, Class A, 5.00 mL	each	14515-37
Pipet, volumetric, Class A, 10.00 mL	each	14515-38
Pipet, volumetric, Class A, 15.00 mL	each	14515-39
Pipet, volumetric, Class A, 20.00 mL	each	14515-20
Pipet, volumetric, Class A, 25.00 mL	each	14515-40
Pour-Thru Cell Assembly Kit	each	45215-00
Safety Glasses	each	18421-00

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

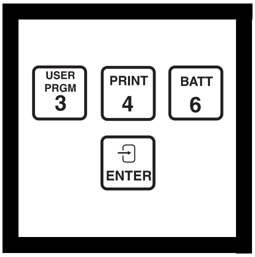
Method 10021

NITROGEN, TOTAL INORGANIC, Test 'N Tube (0 to 25.0 mg/L N)

Titanium Trichloride Reduction Method

For Water, Wastewater, and Seawater

Requires Centrifuge

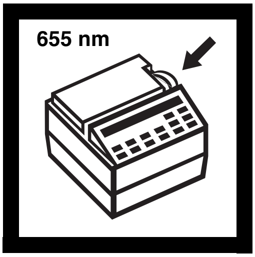


1. Enter the stored program number for Test 'N Tube Total Inorganic Nitrogen (TIN).

Press: **346 ENTER**

The display will show:

Dial nm to 655

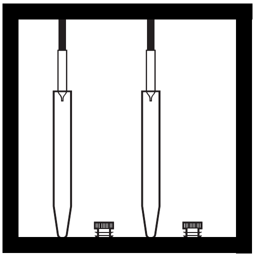


2. Rotate the wavelength dial until the display shows:

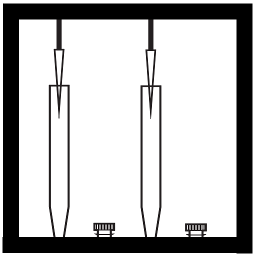
655 nm

When the correct wavelength is dialed in, the display will quickly show: **Zero Sample**

then: **mg/L N TIN TNT**

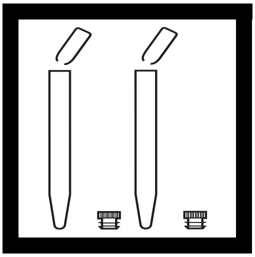


3. Pipet 8 mL of Total Inorganic Nitrogen Pretreatment Base Concentrate into each of two centrifuge tubes.



4. Pipet 1 mL of sample into one tube (the sample). Pipet 1 mL of deionized water into the other tube (the blank).

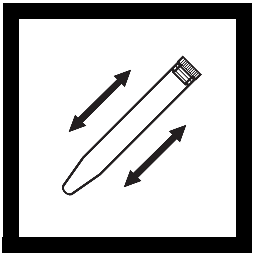
Cap the tubes and shake for 30 seconds to mix.



5. Snap the neck off two Total Inorganic Nitrogen Reductant ampules. Pour the contents of one ampule into one centrifuge tube. Repeat for each tube.

Note: *For safety, wear gloves while breaking the ampules.*

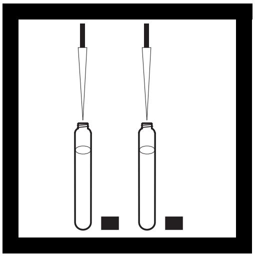
Note: *A black precipitate will form immediately and should remain black. Excessive shaking causes low results.*



6. Cap the tubes. Shake gently for 30 seconds to mix the reagents. Allow the tubes to sit for at least one minute. Centrifuge the tubes for 3 minutes, or until solids settle to bottom of tube.

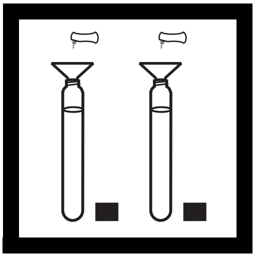
Press: **SHIFT TIMER** immediately after starting the centrifuge.

Note: *The solids will settle without use of centrifuge, but can take up to 30 minutes.*

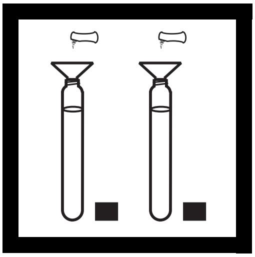


7. Remove the caps from two AmVer Diluent Reagent Test 'N Tubes for Low Range Ammonia Nitrogen. Pipet 2 mL of centrifuged sample to one vial. Add 2 mL of centrifuged blank to another vial. Label the tubes appropriately.

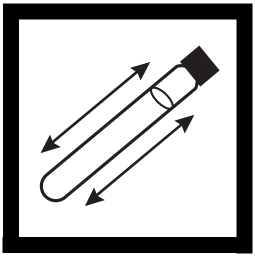
Note: *Pipet carefully to avoid disturbing the sediment.*



8. Add the contents of one Ammonia Salicylate Reagent Powder Pillow to each vial.

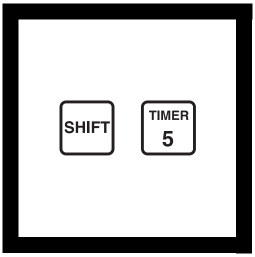


9. Using a funnel, add the contents of one Ammonia Cyanurate Reagent Powder Pillow to each vial.



10. Cap the vials tightly and shake thoroughly to dissolve the powder.

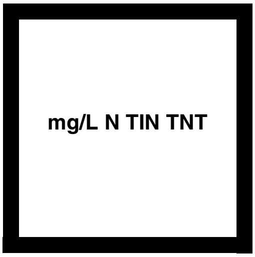
Note: *A green color will develop if inorganic nitrogen is present.*



11. Press:

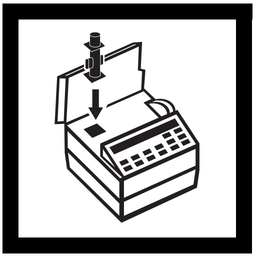
SHIFT TIMER

A 20-minute reaction period will begin.

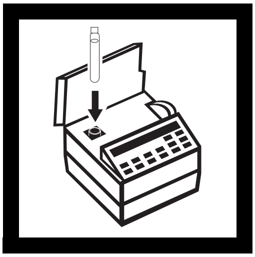


12. When the timer beeps the display will show:

mg/L N TIN TNT

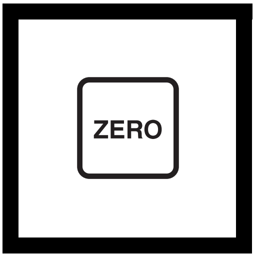


13. Place the COD vial adapter into the cell holder with the marker to the right.



14. After cleaning the outside of the vial with a towel, place the blank into the vial adapter. Place the cover on the adapter.

Note: *Wiping with a damp cloth followed by a dry one removes fingerprints and other marks.*



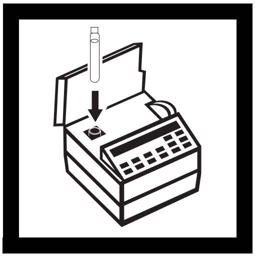
15. Press: **ZERO**

The display will show:

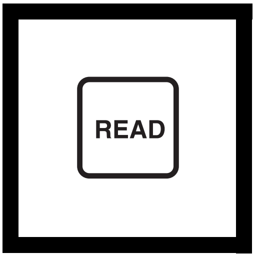
Zeroing. . .

then:

0.0 mg/L N TIN TNT



16. Place the prepared sample into the vial adapter. Place the cover on the adapter.



17. Press: **READ**

The display will show:

Reading. . .

then the result in mg/L Total Inorganic Nitrogen as nitrogen (N) will be displayed.

Forms ▲▼ NH_3 N NO_3^-

Sampling And Storage

Collect samples in clean plastic or glass bottles. Best results are obtained with immediate analysis. If chlorine is known to be present, add one drop of 0.1 N sodium thiosulfate for each 0.3 mg/L Cl_2 in a one liter sample.

Preserve samples by reducing the pH to 2 or less with concentrated hydrochloric acid (at least 2 mL). Store at 4 °C (39 °F) or less. Preserved samples may be stored up to 28 days. Warm samples to room temperature and neutralize with 5 N Sodium Hydroxide before analysis. Correct the test result for volume additions; see *Correcting for Volume Additions* in *Section I.*

Accuracy Check

Standard Additions Method

a) Fill three 25-mL graduated mixing cylinders with 25 mL of sample.

b) Snap the neck off a fresh High Range Nitrate Nitrogen Voluette Ampule Standard, 500 mg/L NO_3^--N.

c) Use the TenSette Pipet to add 0.1, 0.2, and 0.3 mL of standard, respectively, to the three 25-mL mixing cylinders. Mix thoroughly.

d) Analyze each sample as described in the procedure; use a 1-mL aliquot of the prepared sample in each test. The nitrogen concentration should increase 1.8 to 1.9 mg/L for each 0.1 mL of standard added.

e) If these increases do not occur, see *Standard Additions* in *Section I* for more information.

Standard Solution Method

To check accuracy, use a 10.0 mg/L Nitrate Nitrogen Standard Solution listed under Optional Reagents. Or, this can be prepared by diluting 1 mL of solution from a Voluette Ampule Standard for High Range Nitrate Nitrogen, 500 mg/L NO_3^--N, to 50 mL with deionized water. Substitute this standard for the sample and perform the test as described. Reccovery should be 95-100%.

Precision

Precision/Accuracy

The total inorganic nitrogen test provides an estimate of the total nitrite, nitrate, and ammonia nitrogen load in water or wastewater samples. This test is most applicable for monitoring an industrial process stream or a wastewater treatment stream where it is important to track the inorganic nitrogen load as it passes through the treatment process. The test exhibits different recoveries of each of the three nitrogen species, as summarized below. This test is not recommended for quantifying only one of the three species. In that case, use a specific procedure for each particular analyte.

Ammonia Nitrogen

In a single laboratory, using a standard solution of 20.0 mg/L NH_3^--N and two representative lots of reagent with the DR2010, a single operator obtained a mean recovery of 21.3 mg/L with a standard deviation of ±0.79 mg/L N (replicate number = 7 per reagent lot).

Nitrate Nitrogen

In a single laboratory, using a standard solution of 20.0 mg/L NO_3^--N and two representative lots of reagent with the DR/2010, a single operator obtained a mean recovery of 19.0 mg/L with a standard deviation of ±0.62 mg/L N (replicate number = 7 per reagent lot).

Nitrite Nitrogen

In a single laboratory, using a standard solution of 20.0 mg/L NO_2^--N and two representative lots of reagent with the DR/2010, a single operator obtained a mean recovery of 14.7 mg/L with a standard deviation of ±0.70 mg/L N (replicate number = 7 per reagent lot).

Interferences

The following ions may interfere when present in concentrations exceeding those listed below:

Table 1

Species	Level	Effect
Calcium	1000 mg/L as $CaCO_3$	Negative
Manganese (IV)	3 mg/L	Positive
Magnesium	1000 mg/L as $CaCO_3$	Positive
Sulfide	3 mg/L	Negative
Sulfate	250 mg/L	Negative

The following do not interfere below the levels listed:

Table 2

Species	Level
Al^{3+}	8 mg/L
Ba^{2+}	40 mg/L
Cu^{2+}	40 mg/L
Fe^{3+}	8 mg/L
Zn^{2+}	80 mg/L
F^-	40 mg/L
PO_4^{3-}-P	8 mg/L
SiO_2	80 mg/L
EDTA	80 mg/L

Summary of Method

Titanium (III) ions reduce nitrate and nitrite to ammonia in a basic environment. After centrifugation to remove solids, the ammonia is combined with chlorine to form monochloramine. Monochloramine reacts with salicylate to form 5-aminosalicylate. The 5-aminosalicylate is oxidized in the presence of a sodium nitroprusside catalyst to form a blue- colored compound. The blue color is masked by the yellow color from the excess reagent present to give a final green-colored solution.

REQUIRED REAGENTS

Description	Cat. No.
Total Inorganic Nitrogen Pretreatment Reagent Set ($TiCl_3$ Reduction)	26049-45
Includes: (1) 26051-20; (1) 2040-59, (50) TIN Pretreatment Diluent Vials*	
AmVer Reagent Set for Nitrogen-Ammonia Determination (50 tests)	26045-00
Includes: (1) 23952-66, (1) 23954-66, (1) 272-42, (50) AmVer Dilutent LR Vials*	

Description	Unit	Cat. No.
Total Inorganic Nitrogen Pretreatment Diluent Vials	1 L	*
Total Inorganic Nitrogen Reductant Ampule	50/pkg	26051-50
Total Inorganic Nitrogen Pretreatment Base Concentrate	50 mL	2040-59
AmVer Diluent Reagent, Low Range Test 'N Tube	50/pkg	*
Ammonia Salicylate Reagent Powder Pillows for 5-mL sample	50/pkg	23952-66
Ammonia Cyanurate Reagent Powder Pillows for 5-mL samples	50/pkg	23954-66
Water, deionized	100 mL	272-42

REQUIRED APPARATUS

Centrifuge, 115 V, 6 x 15 mL	1	each	26379-00
Centrifuge, 230 V, 6 x 15 mL	1	each	26379-02
COD Vial Adapter, DR/2010	1	each	44799-00
Funnel, micro	1	each	25843-35
Pipette, volumetric, Class A, 1.00 mL	1	each	14515-35
Pipet, TenSette, 0.1 to 1.0	1	each	19700-01
Pipet Tips for 19700-01	4	50/pkg	21856-96
Safety Bulb	1	each	14651-00
Test Tube Rack	1	each	18641-00

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* Not sold separately. Please order the complete set (Cat. No. 26049-25 or 26045-45) as a replacement.

OPTIONAL REAGENTS

Description	Unit	Cat. No.
Hydrochloric Acid, ACS	500 mL	134-49
Nitrate Nitrogen Standard Solution, 10 mg/L NO_3^--N	500 mL	307-49
Nitrate Nitrogen Standard Solution, Voluette Ampule, 500 mg/L NO_3^--N	16/pkg	14260-10
Sodium Hydroxide Standard Solution, 5.0 N	50 mL SCDB	2450-26
Sodium Thiosulfate Standard Solution, 0.1 N	100 mL MDB	323-32
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Ampule Breaker Kit	each	21968-00
Cylinder, graduated, mixing	each	20886-40
Flask, volumetric, Class A, 50.0 mL	each	14657-41
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

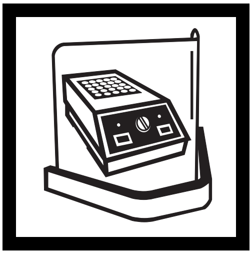
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 10129

ORGANIC CARBON, TOTAL, Low Range (0.0–20.0 mg/L C)

Direct Method*

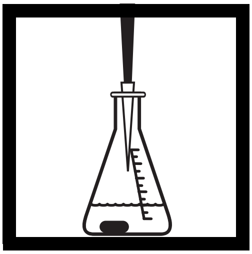
For water, drinking water, and wastewater



1. Turn on the COD reactor. Heat to 103-105 °C. Place the plastic shield in front of the reactor.

Note: *Ensure safety devices are in place to protect the analyst should leakage occur.*

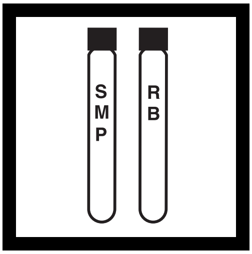
2. Use a graduated cylinder to add 10 mL of sample to a 50-mL Erlenmeyer flask containing a stir bar.



3. Add 0.4 mL of Buffer Solution, pH 2.0.

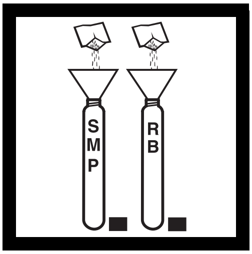
Note: *Use pH paper to make sure the sample pH is 2.*

4. Place the flask on a stir plate and stir at a moderate speed for 10 minutes.

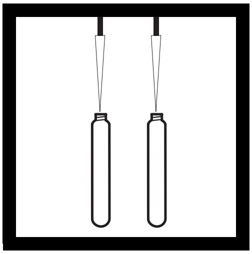


5. Label two Low Range Acid Digestion vials: **sample** and **reagent blank**.

Note: *A reagent blank is required for each series of samples.*



6. Using a funnel, add the contents of one TOC Persulfate Powder Pillow to each Acid Digestion vial (colorless liquid).



7. Use a TenSette Pipet to add 3.0 mL of **organic-free water** to the **reagent blank** vial and 3.0 mL of **prepared sample** to the **sample vial**. Swirl to mix.

8. Rinse two blue Indicator Ampules with deionized water and wipe them with a soft, lint-free wipe.

Note: Do not touch the ampules on the sides after wiping. Pick them up by the top.

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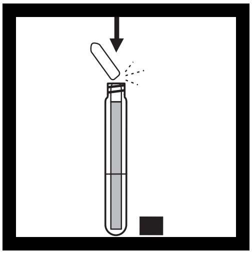
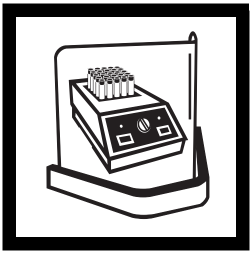
* Patent pending

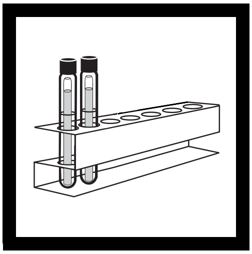


9. Lower one unopened ampule into each Acid Digestion vial. When the score mark on the ampule is level with the top of the Acid Digestion vial, snap the top off the ampule and allow it to drop into the Acid Digestion vial.

Note: Do not invert or tilt the vial after inserting the ampule to prevent the Indicator Reagent from mixing with the contents of the acid digestion vial.

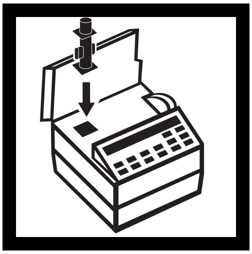


10. Cap the vial assemblies tightly and place them in the COD reactor for 2 hours at 103-105 °C.

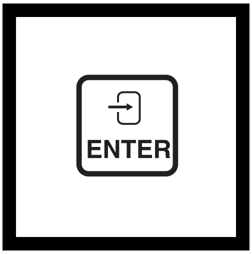


11. Carefully remove the vial assemblies from the reactor. Place them in a test tube rack.

Allow the vials to cool for **one hour** for accurate results.



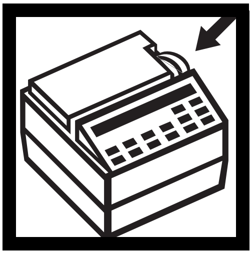
12. Place the COD Vial Adapter in the cell holder with the marker to the right.



13. Enter the stored program number for Low Range TOC.

Press: **ENTER 427**

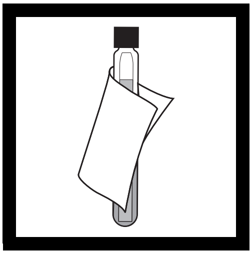
The display will show:
Dial nm to 600



14. Rotate the wavelength dial until the small display shows:
600 nm

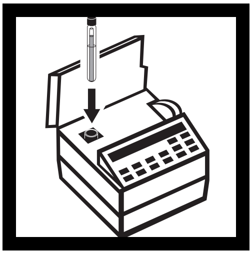
When the correct wavelength is dialed in, the display will quickly show:
Zero Sample

then: **mg/L C**

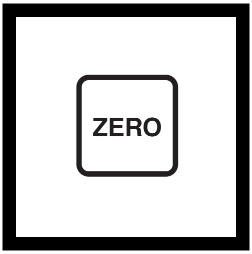


15. Wipe the reagent blank with a damp towel, followed by a dry one, to remove fingerprints or other marks.

***Note:** The liquid in the reagent blank vial should be dark blue.*



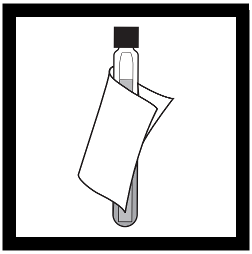
16. Place the **reagent blank** vial assembly in the adapter with the Hach logo facing the front of the instrument. Place the cover on the adapter.



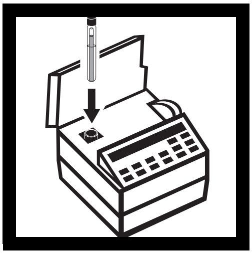
17. Press: **ZERO**

The display will show:
Zeroing...

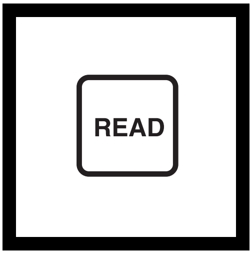
then: **0.0 mg/L C**



18. Wipe the sample vial assembly with a damp towel, followed by a dry one, to remove fingerprints or other marks.



19. Place the sample vial assembly in the adapter with the Hach logo facing the front of the instrument. Place the cover on the adapter.



20. Press: **READ**

The display will show:
Reading...

then the result in mg/L TOC as C will be displayed.

Sampling and Storage

Collect samples in clean glass bottles. Rinse the sample bottle several times with the sample to be collected. Fill the bottle with minimum headspace before capping. Test samples as soon as possible. Acid preservation is not recommended. Homogenize samples containing solids to assure representative samples.

Accuracy Check

Standard Solutions Method

a. Prepare a 1000 mg/L organic carbon stock standard by dissolving 2.1254 g dry primary standard Potassium Acid Phthalate in Organic-Free Reagent Water and dilute to 1000 mL. This stock standard is stable for about 1 month at room temperature. Alternatively, open one ampule of TOC Standard Solution (Cat. No. 27915-05).

b. Prepare a 10.0 mg/L C standard by transferring 10.00 mL of the stock standard to a 1000-mL Class A volumetric flask. Dilute to volume using Organic-Free Reagent Water. Stopper and mix thoroughly. Prepare this standard fresh daily.

Standard Additions Method

a. Prepare a 150 mg/L C standard by transferring 15.00 mL of 1000 mg/L C stock solution to a 100-mL Class A volumetric flask. Dilute to volume with organic-free water. Mix.

b. Use the TenSette Pipet to add 0.1, 0.2, and 0.3 mL of the 150 mg/L C standard to each of three Acid Digestion vials.

c. Add the contents of one TOC Persulfate powder pillow to each vial.

d. Add 3.0 mL of sample to each vial. Swirl to mix.

e. Proceed with the procedure starting at *step 8*.

f. The mg/L C concentration should increase by 5.0 mg/L for each 0.1 mL increment.

Method Performance

Precision

In a single laboratory, using a standard solution of 9.0 mg/L C and one lot of reagents, a single operator obtained a standard deviation of ±0.4 mg/L C.

Estimated Detection Limit

The estimated detection limit for Method 10129 is 0.3 mg/L C.

Sensitivity

At mid-range, the sensitivity, expressed as the concentration change per 0.010 absorbance change, is 0.2 mg/L C.

Interferences

The following have been tested for interference and found not to interfere up to the indicated levels:

Table 1 Non-interfering Substances

Substance	Maximum Level Tested
Aluminum	10 mg/L
Ammonia Nitrogen	1000 mg/L as N
ASTM Wastewater	No effect
Bromide	500 mg/L Br
Bromine	25 mg/L Br_2
Calcium	2000 mg/L as $CaCO_3$
Chloride	500 mg/L
Chlorine	10 mg/L Cl_2
Chlorine Dioxide	6 mg/L ClO_2
Copper	10 mg/L
Cyanide	10 mg/L CN
Iodide	50 mg/L
Iron (II)	10 mg/L
Iron (III)	10 mg/L
Magnesium	2000 mg/L as $CaCO_3$
Manganese (VII)	1 mg/L
Monochloramine	14 mg/L NH_2Cl as Cl_2
Nitrite	500 mg/L NO_2^-

Table 1 Non-interfering Substances<$paranumcontinued

Substance	Maximum Level Tested
Ozone	2 mg/L O_3
Phosphate	3390 mg/L PO_4^{2-}
Silica	100 mg/L SiO_2
Sulfate	5000 mg/L SO_4^{2-}
Sulfide	20 mg/L S^{2-}
Sulfite	50 mg/L SO_3^{2-}
Zinc	5 mg/L

If the sample contains greater than 600 mg/L $CaCO_3$ alkalinity, lower the sample pH to less than 7 before testing by adding sulfuric acid solution.

Most sample turbidity is either dissolved during the digestion stage or settled during the cooling period. Sample turbidities up to 50 NTU have been tested without interference.

Summary of Method

The total organic carbon (TOC) is determined by first sparging the sample under slightly acidic conditions to remove the inorganic carbon. In the outside vial, organic carbon in the sample is digested by persulfate and acid to form carbon dioxide. During digestion, the carbon dioxide diffuses into a pH indicator reagent in the inner ampule. The adsorption of carbon dioxide into the indicator forms carbonic acid. Carbonic acid changes the pH of the indicator solution which, in turn, changes the color. The amount of color change is related to the original amount of carbon present in the sample.

ZEQUIRED REAGENTS

Description	Unit	Cat. No.
Total Organic Carbon Direct Method Low Range Test ’N Tube Reagent Set	50 vials	27603-45

Includes:

Description	Quantity Required Per Test	Unit	Cat. No.
Acid Digestion Solution Vials, Low Range TOC	1	50/pkg	*
Buffer Solution, Sulfate	0.4 mL	25 mL	452-33
Indicator Ampules, Low Range TOC	1	10/pkg	*
TOC Persulfate Powder Pillows	1	50/pkg	*
Water, organic-free**	3.0 mL	500 mL	26415-49

REQUIRED APPARATUS

Description	Quantity Required Per Test	Unit	Cat. No.
COD Reactor, 115/230 V ac (U.S.A. and Canada)	1	each	45600-00
COD Reactor, 115/230 V ac (Europe)	1	each	45600-02
Cylinder, graduated, 10-mL	1	each	508-38
Flask, Erlenmeyer, 50-mL	1	each	505-41
Funnel, micro	1	each	25843-35
Magnetic Stirrer	1	each	23436-00
Safety Shield, laboratory bench	1	each	50030-00
Test Tube Rack	1-3	each	18641-00
Pipet, TenSette®, 0.1 to 1.0 mL	1	each	19700-01
Pipet, TenSette®, 1.0 to 10.0 mL	1	each	19700-10
Pipet Tips, for 19700-01 TenSette® Pipet	2	50/pkg	21856-96
Pipet Tips, for 19700-10 TenSette® Pipet	2	50/pkg	21997-96
Stir Bar, Magnetic	1	each	45315-00
Wipes, Disposable, Kimwipes	1	280/pkg	20970-00

OPTIONAL REAGENTS

Description	Unit	Cat. No.
TOC Standard Solution (KHP Standard, 1000 mg/L C)	5/pkg	27915-05
Potassium Acid Phthalate	500 g	315-34
Sulfuric Acid Reagent Solution, 5.25 N	100 mL MDB	2449-32

OPTIONAL APPARATUS

Description	Unit	Cat. No.
Analytical Balance	each	26103-00
Flask, volumetric, 1000-mL	each	14574-53
Flask, volumetric, 100-mL	each	14574-42
Pipet, Class A, 10.00-mL	each	14515-38
Pipet, Class A, 15.00-mL	each	14515-39

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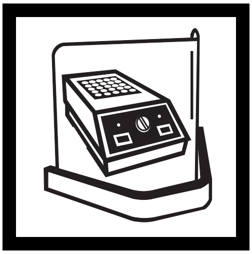
* These items are not sold separately.

** This item must be purchased separately.

Method 10128

ORGANIC CARBON, TOTAL, High Range (20–700 mg/L C)

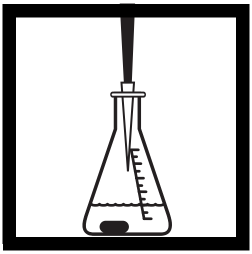
Direct Method* **For wastewater and industrial waters**



1. Turn on the COD reactor. Heat to 103-105 °C. Place the plastic shield in front of the reactor.

Note: *Ensure safety devices are in place to protect the analyst should leakage occur.*

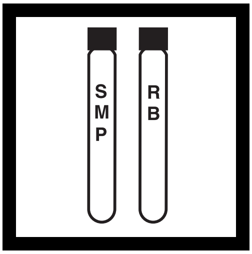
2. Use a graduated cylinder to add 10 mL of sample to a 50-mL Erlenmeyer flask containing a stir bar.



3. Add 0.4 mL of Buffer Solution, pH 2.0.

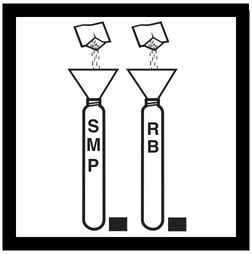
Note: *Use pH paper to make sure the sample pH is 2.*

4. Place the flask on a stir plate and stir at a moderate speed for 10 minutes.

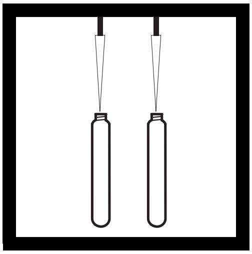


5. Label two High Range Acid Digestion vials: **sample** and **reagent blank**.

Note: *A reagent blank is required for each series of samples.*



6. Using a funnel, add the contents of one TOC Persulfate Powder Pillow to each Acid Digestion vial (colorless liquid).



7. Use a TenSette® Pipet to add 0.3 mL of **organic-free water** to the **reagent blank** vial and 0.3 mL of **prepared sample** to the **sample vial**. Swirl to mix.

8. Rinse two blue Indicator Ampules with deionized water and wipe them with a soft, lint-free wipe.

Note: Do not touch the ampules on the sides after wiping. Pick them up by the top.

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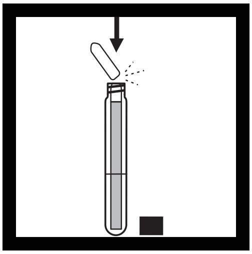
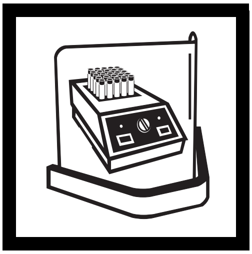
* Patent Pending.

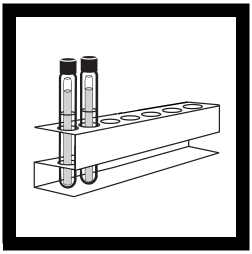


9. Lower one unopened ampule into each Acid Digestion vial. When the score mark on the ampule is level with the top of the Acid Digestion vial, snap the top off the ampule and allow it to drop into the Acid Digestion vial.

Note: Do not invert or tilt the vial after inserting the ampule. This prevents the Indicator Reagent from mixing with the contents of the Acid Digestion vial.

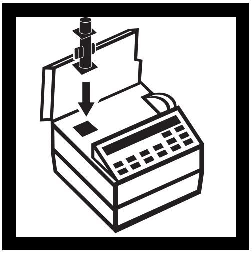


10. Cap the vial assemblies tightly and place them in the COD reactor for 2 hours at 103-105 °C.

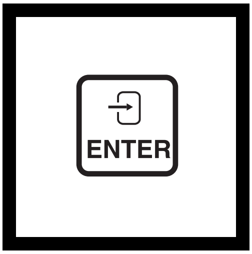


11. Carefully remove the vial assemblies from the reactor. Place them in a test tube rack.

Allow the vials to cool for **one hour** for accurate results.



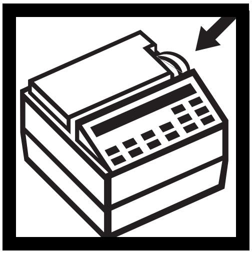
12. Place the COD Vial Adapter in the cell holder with the marker to the right.



13. Enter the stored program number for High Range TOC.

Press: **ENTER 426**

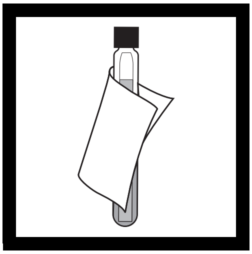
The display will show:
Dial nm to 600



14. Rotate the wavelength dial until the small display shows:
600 nm

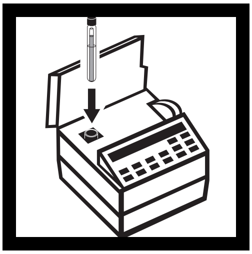
When the correct wavelength is dialed in, the display will quickly show:
Zero Sample

then: **mg/L C**

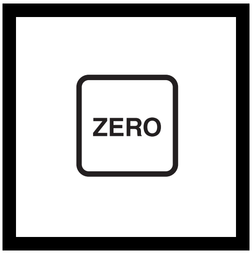


15. Wipe the reagent blank with a damp towel, followed by a dry one, to remove fingerprints or other marks.

Note: *The liquid in the reagent blank vial should be dark blue.*



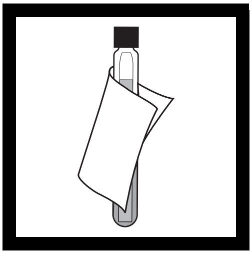
16. Place the **reagent blank** vial assembly in the adapter with the Hach logo facing the front of the instrument. Place the cover on the adapter.



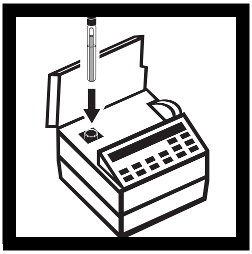
17. Press: **ZERO**

The display will show:
Zeroing...

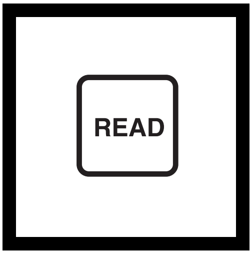
then: **0 mg/L C**



18. Wipe the sample vial assembly with a damp towel, followed by a dry one, to remove fingerprints or other marks.



19. Place the sample indicator vial assembly in the adapter with the Hach logo facing the front of the instrument. Place the cover on the adapter.



20. Press: **READ**

The display will show:
Reading...

then the result in mg/L TOC as C will be displayed.

Sampling and Storage

Collect samples in clean glass bottles. Rinse the sample bottle several times with the sample to be collected. Fill the bottle with minimum headspace before capping. Test samples as soon as possible. Acid preservation is not recommended. Homogenize samples containing solids to assure representative samples.

Accuracy Check

Standard Solutions Method

a. Prepare a 1000 mg/L organic carbon stock standard by dissolving 2.1254 g dry primary standard Potassium Acid Phthalate in Organic-Free Reagent Water and dilute to 1000 mL. This stock standard is stable for about 1 month at room temperature. Alternatively, open one ampule of TOC Standard Solution (Cat. No. 27945-05).

b. Prepare a 300 mg/L C standard by transferring 15.00 mL of the stock standard to a 50-mL Class A volumetric flask. Dilute to volume using Organic-Free Reagent Water. Stopper and mix thoroughly. Prepare this standard fresh weekly.

Standard Additions Method

a. Prepare a 300 mg/L C standard as described in *Standard Solutions Method*, below.

b. Use the TenSette Pipet to add 0.1, 0.2, and 0.3 mL of the 300 mg/L C standard to each of three Acid Digestion vials.

c. Add the contents of one TOC Persulfate powder pillow to each vial.

d. Add 0.3 mL sample to each vial. Swirl to mix.

e. Proceed with the procedure starting at *step 8*.

f. The mg/L C concentration should increase by 100 mg/L for each 0.1 mL increment.

Method Performance

Precision

In a single laboratory, using a standard solution of 360 mg/L C and one lot of reagents, a single operator obtained a standard deviation of ±11 mg/L C.

Estimated Detection Limit

The estimated detection limit for Method 10128 is 4 mg/L C.

Sensitivity

At mid-range, the sensitivity, expressed as the concentration change per 0.010 absorbance change, is 8 mg/L C.

Interferences

The following have been tested for interference and found not to interfere up to the indicated levels:

Table 1 Non-interfering Substances

Substance	Maximum Level Tested
Aluminum	10 mg/L
Ammonia Nitrogen	1000 mg/L as N
ASTM Wastewater	No effect
Bromide	500 mg/L Br
Bromine	25 mg/L Br_2
Calcium	2000 mg/L as $CaCO_3$
Chloride	5000 mg/L
Chlorine	10 mg/L Cl_2
Chlorine Dioxide	6 mg/L ClO_2
Copper	10 mg/L
Cyanide	10 mg/L CN
Iodide	50 mg/L
Iron (II)	10 mg/L
Iron (III)	10 mg/L
Magnesium	2000 mg/L as $CaCO_3$
Manganese (VII)	1 mg/L
Monochloramine	14 mg/L NH_2Cl as Cl_2
Nitrite	500 mg/L NO_2^-

Table 1 Non-interfering Substances<$paranumcontinued

Ozone	2 mg/L O_3
Phosphate	3390 mg/L PO_4^{2-}
Silica	100 mg/L SiO_2
Sulfate	5000 mg/L SO_4^{2-}
Sulfide	20 mg/L S^{2-}
Sulfite	50 mg/L SO_3^{2-}
Zinc	5 mg/L

If the sample contains greater than 1000 mg/L $CaCO_3$ alkalinity, lower the sample pH less to than 7 with sulfuric acid solution prior to testing.

Most sample turbidity is either dissolved during the digestion stage or settled during the cooling period. Sample turbidities up to 1000 NTU have been tested without interference.

Summary of Method

The total organic carbon (TOC) is determined by first sparging the sample under slightly acidic conditions to remove the inorganic carbon. In the outside vial, organic carbon in the sample is digested by persulfate and acid to form carbon dioxide. During digestion, the carbon dioxide diffuses into a pH indicator reagent in the inner ampule. The adsorption of carbon dioxide into the indicator forms carbonic acid. Carbonic acid changes the pH of the indicator solution which, in turn, changes the color. The amount of color change is related to the original amount of carbon present in the sample.

REQUIRED REAGENTS

Total Organic Carbon Direct Method High Range Test ’N Tube™ Reagent Set	50 vials	27604-45

Includes:

Description	Quantity Required Per Test	Unit	Cat. No.
Acid Digestion Solution Vials, High Range TOC	1	50/pkg	*
Buffer Solution, Sulfate	0.4 mL	25 mL	452-33
Indicator Ampules, High Range TOC	1	10/pkg	*
TOC Persulfate Powder Pillows	1	50/pkg	*
Water, organic-free**	0.3 mL	500 mL	26415-49

REQUIRED APPARATUS

COD Reactor, 115/230 V ac (U.S.A. and Canada)	1	each	45600-00
COD Reactor, 115/230 V ac (Europe)	1	each	45600-02
Cylinder, graduated, 10-mL	1	each	508-38
Flask, Erlenmeyer, 50-mL	1	each	505-41
Funnel, micro	1	each	25843-35
Magnetic Stirrer	1	each	23436-00
Safety Shield, laboratory bench	1	each	50030-00
Test Tube Rack	1-3	each	18641-00
Pipet, TenSette®, 0.1 to 1.0 mL	1	each	19700-01
Pipet, TenSette®, 1.0 to 10.0 mL	1	each	19700-10
Pipet Tips, for 19700-01 TenSette® Pipet	2	50/pkg	21856-96
Pipet Tips, for 19700-10 TenSette® Pipet	2	50/pkg	21997-96
Stir Bar, Magnetic	1	each	45315-00

OPTIONAL REAGENTS

TOC Standard Solution (KHP Standard, 1000 mg/L C)	5/pkg	27945-05
Potassium Acid Phthalate	500 g	315-34
Sulfuric Acid Reagent Solution, 5.25 N	100 mL MDB	2449-32

OPTIONAL APPARATUS

Analytical Balance	each	26103-00
Flask, volumetric, 1000-mL	each	14574-53
Flask, volumetric, 50-mL	each	14574-51
Pipet, Class A, 15.00-mL	each	14515-39

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* These items are not sold separately.

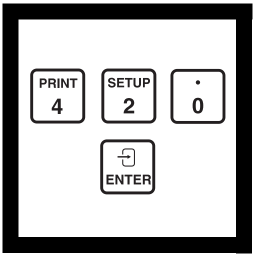
** This item must be ordered separately.

Method 8097

ORGANIC MATTER (0 to 5.00%)

For soil

Dichromate Method



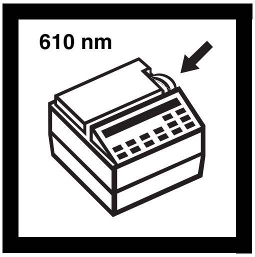
1. Enter the stored program number for organic matter in soil.

Press: **4 2 0 ENTER**

The display will show:

Dial nm to 610

Note: *The Pour-Thru Cell can be used with this procedure.*



2. Rotate the wavelength dial until the small display shows:

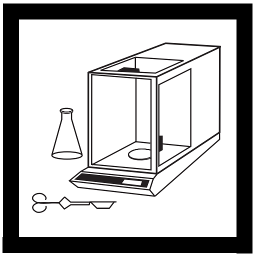
610 nm

When the correct wavelength is dialed in the display will quickly show:

Zero Sample

then:

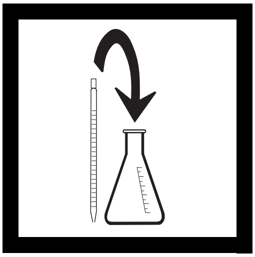
% ORGANICS S



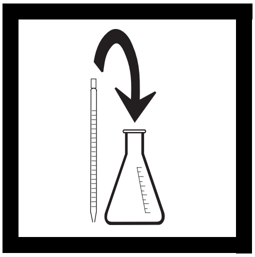
3. Weigh 1.00 g of soil and transfer to a 250-mL erlenmeyer flask.

Note: *If the soil contains more than 5% organic matter, use a smaller sample. For example, a 0.50-g sample will allow measurement of up to 10% organic matter. If a sample size other than 1.00 gram is used, multiply the results by the factor (F):*

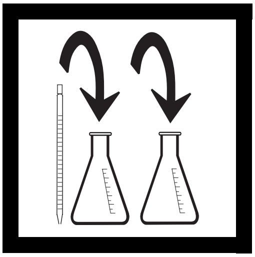
$$F = \frac{1.00\text{ g}}{\text{actual sample size used (g)}}$$



4. Pipet 10.0 mL of 1.000 N Potassium Dichromate Solution into the 250-mL erlenmeyer flask.

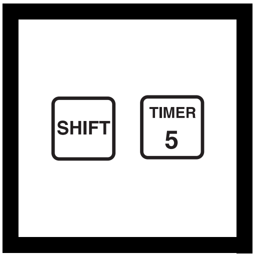


5. Prepare a blank by pipetting 10.0 mL of 1.000 N Potassium Dichromate Solution into an empty 250-mL erlenmeyer flask.



6. Pipet 20.0 mL of concentrated sulfuric acid into each flask.

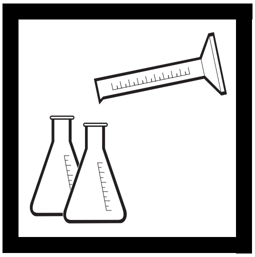
7. Cover each flask with an inverted 50-mL erlenmeyer flask. Swirl gently to mix. Place on cooling pads.



8. Press:

SHIFT TIMER

A 10-minute reaction period will begin.



9. When the timer beeps, the display will show:

% ORGANICS S

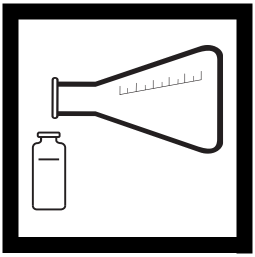
Immediately use a graduated cylinder to add 100 mL of deionized water to each flask. Swirl briskly to mix.

Note: *See Special Test Considerations below.*

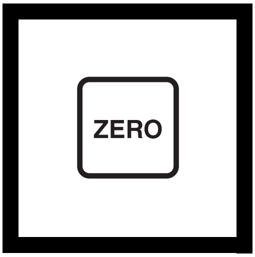
10. Filter at least 25 mL of the soil mixture into a 50-mL erlenmeyer flask. Do not filter the blank.

Note: *Do not use paper filters; use only glass fiber filters.*

Note: *As an alternative, let the sample sit undisturbed for 2 hours and decant sample from the top of the flask.*



11. Pour 25 mL of the blank into a sample cell (the blank). Place the blank into the cell holder. Close the light shield.



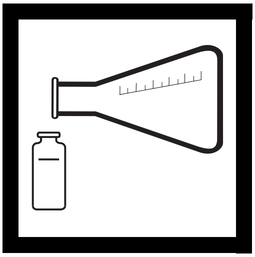
12. Press: **ZERO**

The display will show:

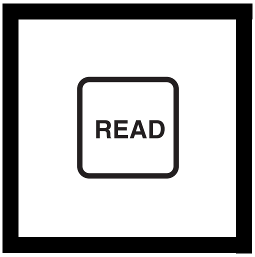
Zeroing. . .

then:

0.00% ORGANICS S



13. Pour 25 mL of the filtered soil solution into a sample cell (the prepared sample). Place the prepared sample into the cell holder. Close the light shield.



14. Press: **READ**

The display will show:

Reading. . .

then the result in % organics will be displayed.

Note: *If the sample size was not 1 gram, see note under Step 3.*

Note: *Colorimetric measurement of the filtrate is slightly temperature sensitive. The DR/2010 spectrophotometer was calibrated at room temperature (~ 25 °C).*

Accuracy Check

Standard Solution Method

Verify accuracy by using a CO_2 Standard Solution, 46.4 g/L potassium hydrogen phthalate (KHP), listed under Optional Reagents. Each mL of the standard is equivalent to a soil sample of 4.4% organic matter. In Step 3 add the 1.00 mL of standard instead of the soil sample and proceed with the test. The result should read 4.4% organic matter.

Precision

In a single laboratory using a potassium hydrogen phthalate standard equivalent to 2.50% organic matter and two representative lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±0.017% organic matter.

Interferences

Interferences include chlorides, ferrous iron, nitrate and the higher oxides of manganese. Chloride competes with organic carbon in reducing hexavalent chromium; one milli-equivalent of chloride is equal in reducing capacity to 3.5 mg of carbon. The chloride error is normally low enough to ignore, because 1% chloride in the soil would give an error of 0.1% (0.2% organic matter). In air-dried soil any ferrous iron will be oxidized to the ferric form, eliminating the interference from the ferrous form. Nitrate and manganese in soils are normally at such a low level that any interferences are negligible.

Special Test Considerations

When testing several samples, add the soil and potassium dichromate solution to all flasks (including the blank). Add the sulfuric acid to each flask in sequential order at uniform time intervals (such as 30 seconds), timing the 10-minute interval from the first flask. After 10 minutes, add deionized water to the flasks in the same order and the same interval. This will give the proper 10-minute reaction time for each sample. Because the reaction stops when the water is added, the time between filtering and measurement is not critical. If convenient, allow the flasks to stand overnight. The soil should settle out; pipet 25 mL of the clear solution for colorimetric measurement without filtering.

Use glass fiber filters to filter the soil residue. Fold the filter disc in half and then in half again. Open the filter disc to form a cone and press into the funnel. Pour the sample into the center of the filter, being careful not to overflow the filter. Fill the filter cone twice to obtain sufficient filtrate.

Cellulose filter papers of various grades have been tested for this method. All have shown a reaction with the reagents causing higher readings. Compensation for this effect may be possible by filtering the reagent blank through an identical piece of filter paper. However, best practice is to use the specified glass fiber filter disc.

Summary of Method

Unlike mineral nutrients in soil such as nitrogen, phosphorus and potassium, organic matter is a nondistinct component of soil. It is measured by an approximate relationship with organic carbon.

Organic carbon is oxidized to carbon dioxide in the dichromate method with a parallel reduction of hexavalent chromium (Cr^{6+}) to trivalent chromium (Cr^{3+}) and an accompanying color change from orange to green. The intensity of the green color is proportional to the trivalent chromium concentration which is related to the organic matter content in the soil.

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
Potassium Dichromate Solution, 1.000 N	20 mL	1 L	21971-53
Sulfuric Acid, ACS	40 mL	2.5 L	979-09

REQUIRED APPARATUS

Balance, Ohaus Model 505-10, 50 g	1	each	18475-00
Cylinder, graduated, 100 mL	1	each	508-42
Filter Disc, glass fiber filter, 9 cm	1	100/pkg	21987-55
Flask, erlenmeyer, 50-mL	2	each	505-41
Flask, erlenmeyer, 250-mL	2	each	505-46
Funnel, analytical, poly, 65 nm	1	each	1083-67
Pad, cooling, 4" x 4"	2	each	18376-00
Paper, weighing, 76 x 76 mm	1	500/pkg	14738-00
Pipet, serological, glass, 10 mL	1	each	532-38
Pipet, serological, glass, 25 mL	1	each	2066-40
Pipet Filler, safety bulb	1	each	14651-00
Sample Cells, 25 mL, matched pair		pair	20950-00

OPTIONAL REAGENTS

CO_2 Voluette Ampule, 10,000 mg/L as CO_2 (46.4 g/L Potassium hydrogen phthalate), 10 mL	16/pkg	14275-10
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Ampule Breaker Kit	each	21968-00
Pour-Thru Cell	each	45215-00
Thermometer	each	1877-01

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order. Outside the U.S.A.—Contact the Hach office or distributor serving you.

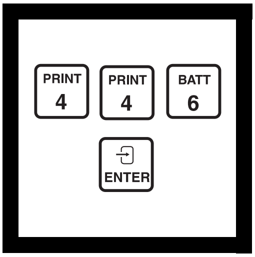
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8316

OXYGEN, DISSOLVED, LR (0 to 800 µg/L O_2)

For boiler feedwater

Indigo Carmine Method (Using AccuVac Ampuls)

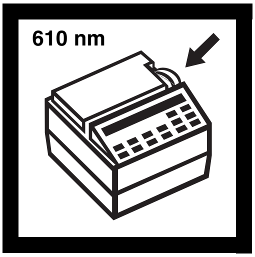


1. Enter the stored program number for low range dissolved oxygen.

Press: **4 4 6 ENTER**

The display will show:

Dial nm to 610



2. Rotate the wavelength dial until the small display shows:

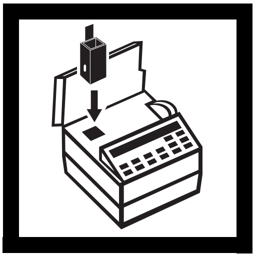
610 nm

When the correct wavelength is dialed in the display will quickly show:

Zero Sample

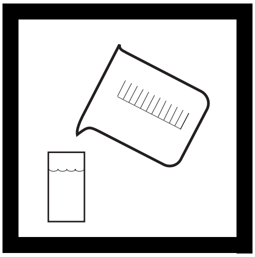
then:

µg/L O_2 LRDO AV



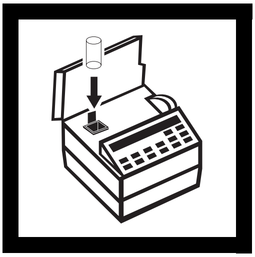
3. Place the AccuVac Vial Adapter into the cell holder.

Place the grip tab at the rear of the cell holder.

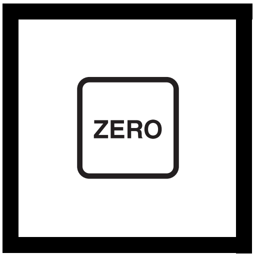


4. Fill a zeroing vial (the blank) with at least 10 mL of sample.

Samples must be analyzed on site and cannot be stored.



5. Place the blank into the cell holder. Close the light shield.



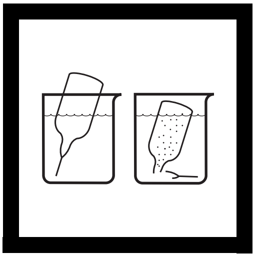
6. Press: **ZERO**

The display will show:

Zeroing. . .

then:

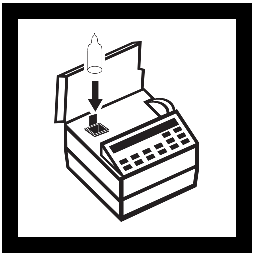
0. µg/L O_2 LRDO AV



7. Fill a Low Range Dissolved Oxygen AccuVac Ampul with sample.

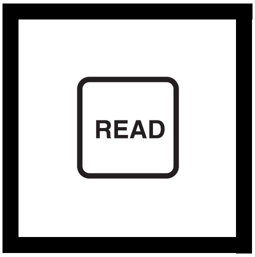
Note: *Keep the tip immersed while the ampul fills completely.*

Note: *The ampuls will contain a small piece of wire to maintain reagent quality. The solution color will be yellow.*



8. Immediately place the AccuVac ampul into the vial adapter. Close the light shield.

Note: *Use the initial reading. The reading is stable for 30 seconds. After 30 seconds, the ampul solution will absorb oxygen from the air.*



9. Press: **READ**

The display will show:

Reading. . .

then the result in µg/L dissolved oxygen will be displayed.

Sampling and Storage

The main consideration in this procedure is to prevent contaminating the sample with atmospheric oxygen. Sampling from a stream of water that is hard plumbed to the sample source is ideal. Use a funnel to maintain a continual flow of sample and yet collect enough sample to immerse the ampul. It is important not to introduce air in place of the sample. Rubber tubing, if used, will introduce unacceptable amounts of oxygen into the sample unless the length of tubing is minimized and the flow rate is maximized. Flush the sampling system with sample for at least 5 minutes.

Accuracy Check

The reagent blank for this test can be checked by following these steps:

a) Fill a 50-mL beaker with sample and add approximately 50 mg sodium hydrosulfite.

b) Immerse the tip of a Low Range Dissolved Oxygen AccuVac Ampul in the sample and break the tip. Keep the tip immersed while the ampul fills completely.

c) Determine the dissolved oxygen concentration according to the preceding procedure. The result should be 0 ±1 µg/L.

Interferences

Excess amounts of sodium thioglycolate, sodium ascorbate, sodium ascorbate + sodium sulfite, sodium ascorbate + cupric sulfate, sodium nitrite, sodium sulfite, sodium thiosulfate, and hydroquinone will not reduce the oxidized form of the indicator solution; therefore, they do not cause significant interference. A 100,000-fold excess of hydrazine will begin to reduce the oxidized form of the indicator solution.

Sodium hydrosulfite will reduce the oxidized form of the indicator solution and will cause a serious interference.

Summary of Method

The Low Range Dissolved Oxygen AccuVac Ampul contains reagent vacuum sealed in a 12-mL ampul. When the AccuVac ampul is broken open in a sample containing dissolved oxygen, the yellow solution will turn blue. The blue color development is proportional to the concentration of dissolved oxygen.

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
Low Range Dissolved Oxygen AccuVac Ampuls	1 ampul	25/pkg	25010-25

REQUIRED APPARATUS

Adapter, AccuVac Vial	1	each	43784-00
Beaker, 50 mL	1	each	500-41
Vial, zeroing	1	each	21228-00

OPTIONAL REAGENTS AND APPARATUS

AccuVac Snapper Kit	each	24052-00
Sodium Hydrosulfite, technical grade	500 g	294-34

For technical support and ordering information, see Section V.

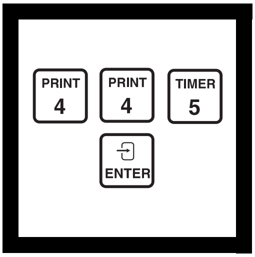
In the U.S.A. call 800-227-4224 to place an order.
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8166

OXYGEN, DISSOLVED, HR (0 to 13.0 mg/L O_2)

For water and wastewater

HRDO Method

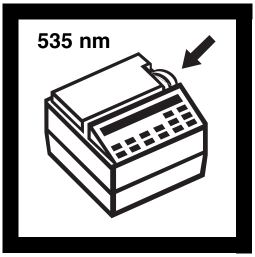


1. Enter the stored program number for dissolved oxygen.

Press: **4 4 5 ENTER**

The display will show:

Dial nm to 535



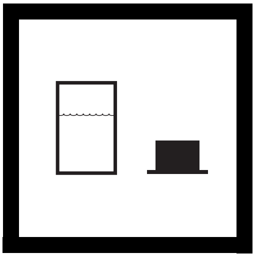
2. Rotate the wavelength dial until the small display shows:

535 nm

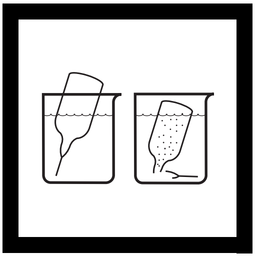
When the correct wavelength is dialed in the display will quickly show: **Zero Sample**

then:

mg/L O_2 HRDO AV

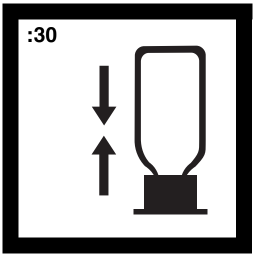


3. Fill a zeroing vial (the blank) with at least 10 mL of sample. Fill a blue ampul cap with sample.



4. Fill a High Range Dissolved Oxygen AccuVac Ampul with sample.

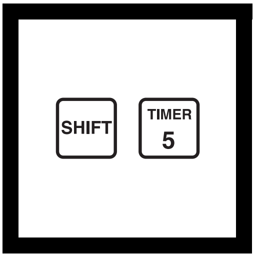
Note: *Keep the tip immersed while the ampul fills completely.*



5. Without inverting the ampul, immediately place the ampul cap that has been filled with sample securely over the tip of the ampul. Shake for about 30 seconds.

Note: *A small amount of the undissolved HRDO Reagent does not affect results.*

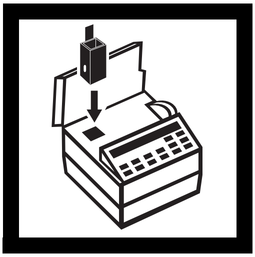
Note: *The cap prevents contamination with atmospheric oxygen.*



6. Press:

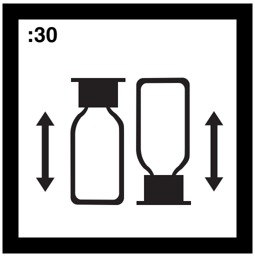
SHIFT TIMER

A 2-minute reaction period will begin.



7. Place the AccuVac Vial Adapter into the cell holder.

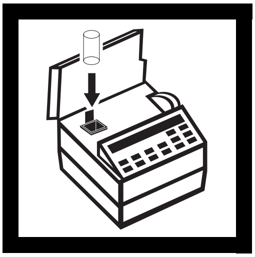
Note: *Place the grip tab at the rear of the cell holder.*



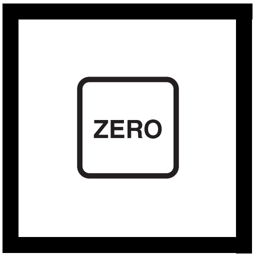
8. When the timer beeps, the display will show:

mg/L O_2 HRDO AV

Shake the ampul for 30 seconds.



9. Place the blank into the cell holder. Close the light shield.



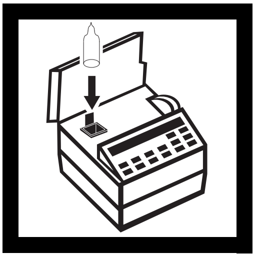
10. Press: **ZERO**

The display will show:

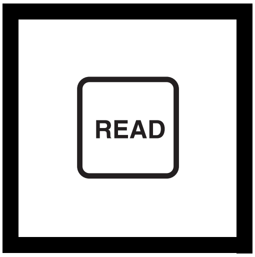
Zeroing. . .

then:

0.0 mg/L O_2 HRDO AV



11. Place the AccuVac ampul into the cell holder. Close the light shield. Wait approximately 30 seconds for the air bubbles to disperse from the light path.



12. Press: **READ**

The display will show:

Reading. . .

then the result in mg/L dissolved oxygen will be displayed.

Sampling and Storage

The main consideration in sampling with the High Range Dissolved Oxygen AccuVac Ampul is to prevent the sample from becoming contaminated with atmospheric oxygen. This is accomplished by capping the ampul with an ampul cap in the interval between breaking open the ampul and reading the absorbance. If the ampul is securely capped, it should be safe from contamination for several hours. The absorbance will decrease by approximately 3% during the first hour and will not change significantly afterwards.

Sampling and sample handling are important considerations in obtaining meaningful results. The dissolved oxygen content of the water being tested can be expected to change with depth, turbulence, temperature, sludge deposits, light, microbial action, mixing, travel time and other factors. A single dissolved oxygen test rarely reflects the accurate over-all condition of a body of water. Several samples taken at different times, locations and depths are recommended for most reliable results. Samples must be tested immediately upon collection although only a small error results if the absorbance reading is taken several hours later.

Accuracy Check

The results of this procedure may be compared with the results of a titrimetric procedure or dissolved oxygen meter.

Precision

In a single laboratory, using a standard solution of 7.22 mg/L O_2 determined by the Winkler method and two representative lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±0.20 mg/L O_2.

Interferences

The following do not interfere at a level of 10 mg/L which is in excess of naturally occurring levels of Cr^{3+}, Mn^{2+}, Fe^{2+}, Ni^{2+}, Cu^{2+} and NO_2^-.

Magnesium is commonly present in seawater and causes a negative interference. If the sample contains more than 50% seawater, the oxygen concentration obtained by this method will be 25% less than the true oxygen concentration. If the sample contains less than 50% seawater, the interference will be less than 5%.

Summary of Method

The High Range Dissolved Oxygen AccuVac Ampul contains reagent vacuum sealed in a 12-mL ampul. When the AccuVac ampul is broken open in a sample containing dissolved oxygen, it forms a yellow color which turns purple. The purple color development is proportional to the concentration of dissolved oxygen.

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
High Range Dissolved Oxygen AccuVac Ampuls, with 2 reusable ampul caps	1 ampul	25/pkg	25150-25

REQUIRED APPARATUS

AccuVac Dissolved Oxygen Sampler	1	each	24051-00
Adapter, AccuVac Vial	1	each	43784-00
Beaker, 50 mL	1	each	500-41
Caps, ampul, blue	varies	25/pkg	1731-25
Vial, zeroing	1	each	21228-00

OPTIONAL APPARATUS

AccuVac Snapper Kit	each	24052-00
BOD bottle and stopper, 300 mL	each	621-00

Dissolved oxygen may also be determined by titrimetric methods. Request Publication 8042 for additional information.

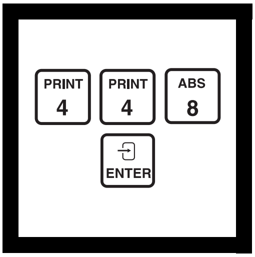
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8333

For aquaculture

OXYGEN, DISSOLVED, SHR (0 to 45.0 mg/L O_2)

Super High Range Method



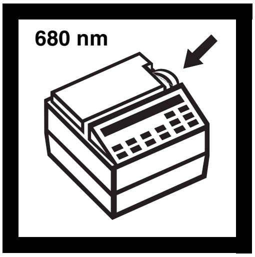
1. Enter the stored program number for dissolved oxygen.

Press: **4 4 8 ENTER**

The display will show:

Dial nm to 680

Note: *Samples must be analyzed on site and cannot be stored.*



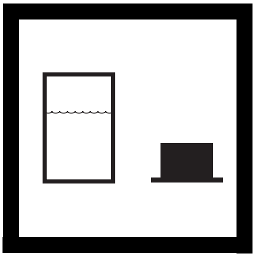
2. Rotate the wavelength dial until the small display shows:

680 nm

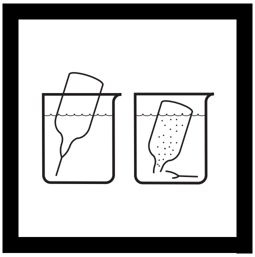
When the correct wavelength is dialed in the display will quickly show: **Zero Sample**

then:

mg/L O_2 SHRDO AV

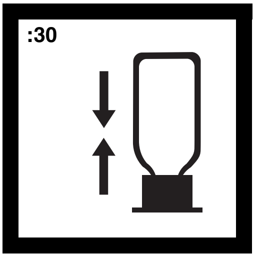


3. Fill a zeroing vial (the blank) with at least 10 mL of sample. Fill a blue ampul cap with sample.



4. Fill a High Range Dissolved Oxygen AccuVac Ampul with sample.

Note: *Keep the tip immersed while the ampul fills completely.*

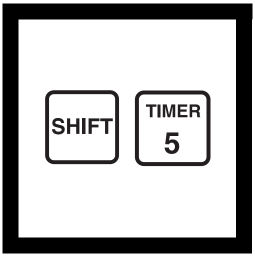


5. Without inverting the ampul, immediately place the ampul cap that has been filled with sample securely over the tip of the ampul.

Shake the ampul for approximately 30 seconds.

Note: *A small amount of the undissolved reagent does not affect results.*

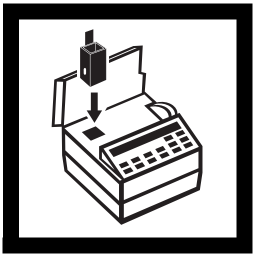
Note: *The cap prevents contamination with atmospheric oxygen.*



6. Press:

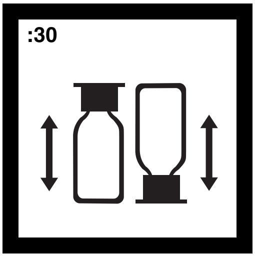
SHIFT TIMER

A 2-minute reaction period will begin.



7. Place the AccuVac Vial Adapter into the cell holder.

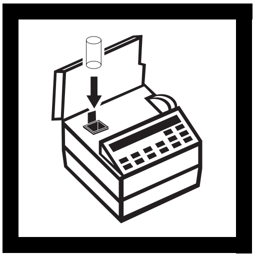
Note: *Place the grip tab at the rear of the cell holder.*



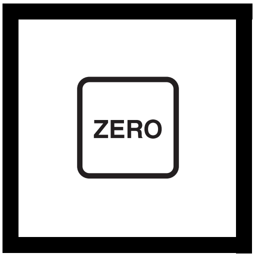
8. When the timer beeps, the display will show:

mg/L O_2 SHRDO AV

Shake the ampul for 30 seconds.



9. Place the blank into the cell holder. Close the light shield.



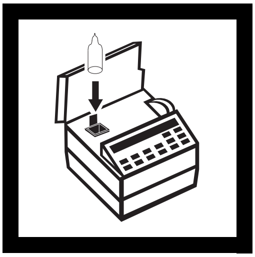
10. Press: **ZERO**

The display will show:

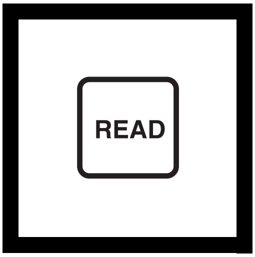
Zeroing. . .

then:

0.0 mg/L O_2 SHRDO AV



11. Place the AccuVac ampul into the cell holder. Close the light shield.



12. Press: **READ**

The display will show:

Reading. . .

then the result in mg/L dissolved oxygen will be displayed.

Sampling and Storage

The main consideration in sampling with the High Range Dissolved Oxygen AccuVac Ampul is to prevent the sample from becoming contaminated with atmospheric oxygen. This is accomplished by capping the ampul with an ampul cap in the interval between breaking open the ampul and reading the absorbance. If the ampul is securely capped, the ampul should be safe from contamination for several hours. The absorbance will decrease by approximately 3% during the first hour and will not change significantly afterwards.

Sampling and sample handling are important considerations in obtaining meaningful results. The dissolved oxygen content of the water being tested can be expected to change with depth, turbulence, temperature, sludge deposits, light, microbial action, mixing, travel time and other factors. A single dissolved oxygen test rarely reflects the accurate over-all condition of a body of water. Several samples taken at different times, locations and depths are recommended for most reliable results. Samples must be tested immediately upon collection although only a small error results if the absorbance reading is taken several hours later.

Accuracy Check

The results of this procedure may be compared with the results of a titrimetric procedure or dissolved oxygen meter.

Precision

In a single laboratory, using a standard solution of 33.0 mg/L O_2 determined by the Winkler method and three representative lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±1.3 mg/L O_2.

Interferences

The following do not interfere at a level of 10 mg/L which is in excess of naturally occurring levels of Cr^{3+}, Mn^{2+}, Fe^{2+}, Ni^{2+}, Cu^{2+} and NO_2^-.

Magnesium is commonly present in seawater and interferes. If the seawater contains more than 50% salt water, the true oxygen concentration will decrease by 25%. If the seawater contains less than 50% salt water, the interference will be less than 5%.

Summary of Method

The High Range Dissolved Oxygen AccuVac Ampul contains reagent vacuum sealed in a 12-mL ampul. When the AccuVac ampul is broken open in a sample containing dissolved oxygen, it forms a yellow color which turns purple. The purple color development is proportional to the concentration of dissolved oxygen.

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
High Range Dissolved Oxygen AccuVac Ampuls, with 2 reusable ampul caps	1 ampul	25/pkg	25150-25

REQUIRED APPARATUS

Adapter, AccuVac Vial	1	each	43784-00
Beaker, 50 mL	1	each	500-41
Caps, Ampul, Blue		6/pkg	1731-06
Vial, zeroing	1	each	21228-00

OPTIONAL APPARATUS

AccuVac Dissolved Oxygen Sampler	each	24051-00
AccuVac Snapper Kit	each	24052-00
BOD Bottle and Stopper, 300 mL	each	621-00
DO Sampler, w/60-mL bottle, samples to 3 m (10 ft.)	each	1962-00

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8000

OXYGEN DEMAND, CHEMICAL

For water, wastewater and seawater

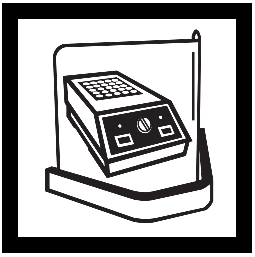
Reactor Digestion Method* ; USEPA approved for reporting wastewater analysis**

Digestion

1. Homogenize 100 mL of sample for 30 seconds in a blender.

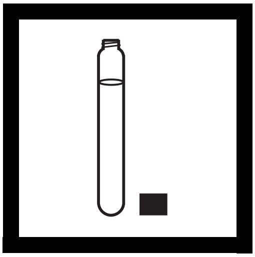
Note: *Mix the sample before homogenizing it. To improve accuracy and reproducibility, pour the homogenized sample into a 250-mL beaker and gently stir with a magnetic stir plate. For samples containing large amounts of solids, increase the homogenization time.*

Note: *Some of the chemicals and apparatus used in this procedure may be hazardous to the health and safety of the user if inappropriately handled or accidentally misused. Please read all warnings and the safety section of this manual. Wear appropriate eye protection and clothing for adequate user protection. If contact occurs, flush the affected area with running water. Follow instructions carefully.*



2. Turn on the COD Reactor. Preheat to it 150 °C. Place the plastic shield in front of the reactor.

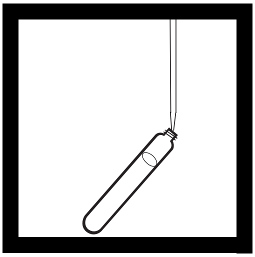
Note: *Ensure safety devices are in place to protect analyst from splattering should reagent leaking occur.*



3. Remove the cap of a COD Digestion Reagent Vial for the appropriate range:

Sample Conc. Range (mg/L)	COD Digestion Reagent Vial Type
0 to 150	Low Range
0 to 1500	High Range
0 to 15,000	High Range Plus

Note: *The reagent mixture is light-sensitive. Keep unused vials in the opaque shipping container, in a refrigerator if possible. The light striking the vials during the test will not affect results.*



4. Hold the vial at a 45-degree angle. Pipet 2.00 mL (0.2 mL for the 0 to 15,000 mg/L range) of sample into the vial.

Note: For the 0-15,000 mg/L range, *pipet only 0.20 mL of sample, not 2.00 mL of sample, using a TenSette Pipet. For greater accuracy a minimum of three replicates should be analyzed and the results averaged.*

Note: *Spilled reagent will affect test accuracy and is hazardous to skin and other materials. Do not run tests with vials which have been spilled. If spills occur, wash with running water.*

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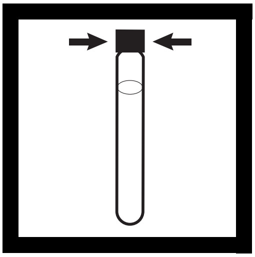
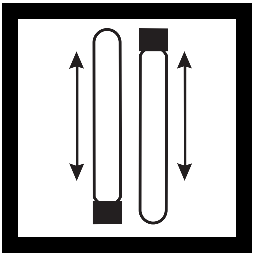
* Jirka, A.M.; Carter, M.J. *Analytical Chemistry*, 1975, 47(8). 1397.

** *Federal Register*, April 21, 1980, 45(78), 26811-26812. The 0-15,000 mg/L range is **not** USEPA approved.

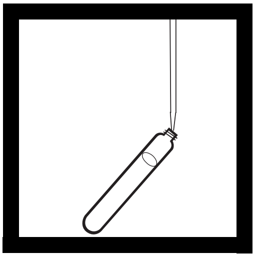


5. Replace the vial cap tightly. Rinse the outside of the COD vial with deionized water and wipe the vial clean with a paper towel.



6. Hold the vial by the cap and over a sink. Invert gently several times to mix the contents. Place the vial in the preheated COD Reactor.

Note: The vial will become very hot during mixing.

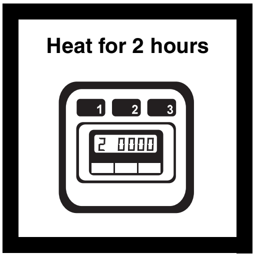


7. Prepare a blank by repeating Steps 3 to 6, substituting 2.00 mL (0.2 mL for the 0 to 15,000 mg/L range) deionized water for the sample.

Note: Be sure the pipet is clean.

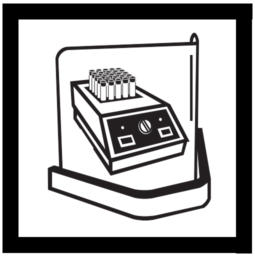
Note: One blank must be run with each set of samples. Run samples and blanks with the same lot of vials.

Heat for 2 hours

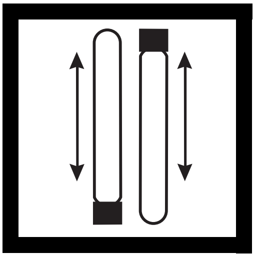


8. Heat the vials for 2 hours.

Note: Many samples are digested completely in less than two hours. If desired, measure the concentration (while still hot) at 15 minute intervals until the reading remains unchanged. Cool the vials to room temperature for final measurement.



9. Turn the reactor off. Wait about 20 minutes for the vials to cool to 120 °C or less.



10. Invert each vial several times while still warm. Place the vials into a rack. Wait until the vials have cooled to room temperature.

Note: If a pure green color appears in the reacted sample, measure the COD and, if necessary, repeat the test with a diluted sample.

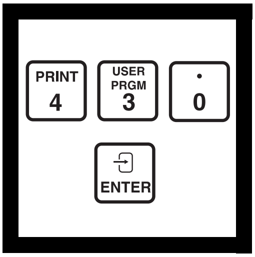
Choose a range

11. Use one of the following analytical techniques to measure the COD:

- Colorimetric method, 0-150 mg/L COD
- Colorimetric method, 0-1,500 mg/L COD
- Colorimetric method, 0-15,000 mg/L COD

Note: A titrimetric method is also available. Contact Hach Customer Service for details.

Colorimetric Determination, 0 to 150 mg/L COD

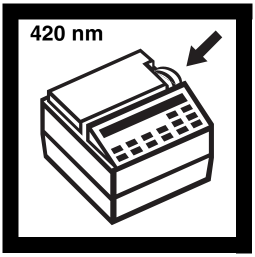


1. Enter the stored program number for chemical oxygen demand (COD), low range.

Press: **4 3 0 ENTER**

The display will show:

Dial nm to 420



2. Rotate the wavelength dial until the small display shows:

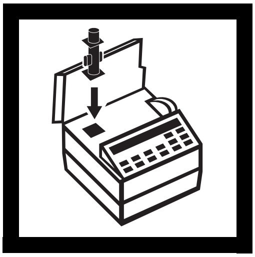
420 nm

When the correct wavelength is dialed in, the display will quickly show:

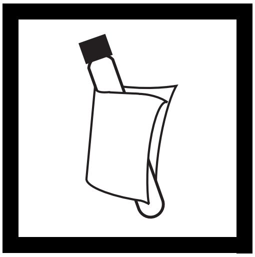
Zero Sample

then: **mg/L COD LR**

Note: *Approach the wavelength setting from the higher to lower values.*

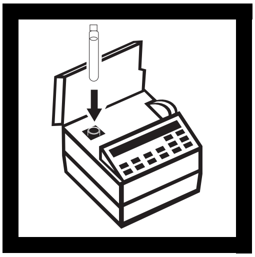


3. Place the COD Vial Adapter into the cell holder with the marker to the right.



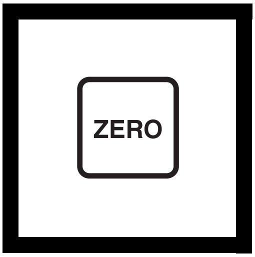
4. Clean the outside of the blank with a towel.

Note: *Wiping with a damp towel, followed by a dry one, will remove fingerprints or other marks.*



5. Place the blank into the adapter with the Hach logo facing the front of the instrument. Place the cover on the adapter.

Note: *The blank is stable when stored in the dark; see Blanks for Colorimetric Determination following these procedures.*

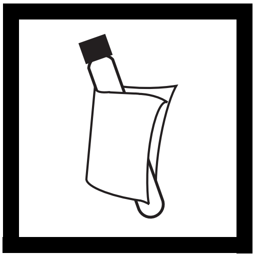


6. Press: **ZERO**

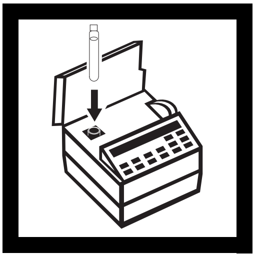
The display will show:

Zeroing. . . .

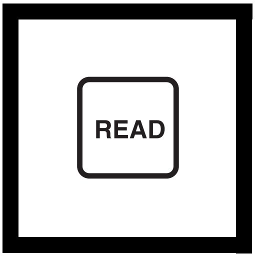
then: **0. mg/L COD LR**



7. Clean the outside of the sample vial with a towel.



8. Place the sample vial into the adapter with the Hach logo facing the front of the instrument. Place the cover on the adapter.



9. Press: **READ**

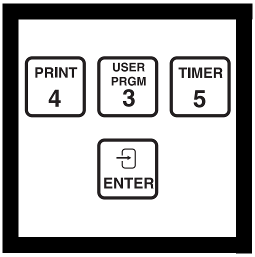
The display will show:

Reading. . . .

then the result in mg/L COD will be displayed.

Note: *For most accurate results with samples near 150 mg/L COD, repeat the analysis with a diluted sample.*

Colorimetric Determination, 0 to 1,500 and 0 to 15,000 mg/L COD

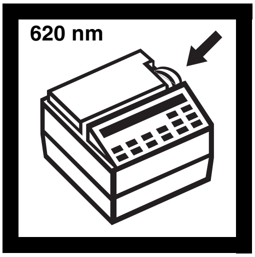


1. Enter the stored program number for chemical oxygen demand, high range.

Press: **4 3 5 ENTER**

The display will show:

Dial nm to 620



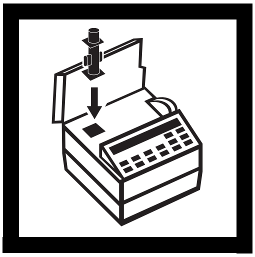
2. Rotate the wavelength dial until the small display shows:

620 nm

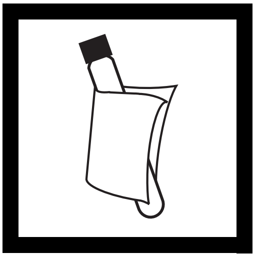
When the correct wavelength is dialed in, the display will show:

Zero Sample

then: **mg/L COD HR**

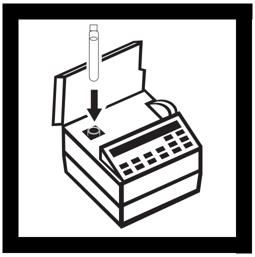


3. Place the COD Vial Adapter into the cell holder with the marker to the right.



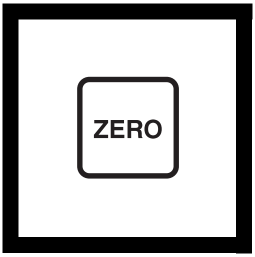
4. Clean the outside of the blank with a towel.

Note: *Wiping with a damp towel followed by a dry one will remove fingerprints or other marks.*



5. Place the blank into the adapter with the Hach logo facing the front of the instrument. Place the cover on the adapter.

Note: *The blank is stable when stored in the dark. See Blanks for Colorimetric Determination following these procedures.*

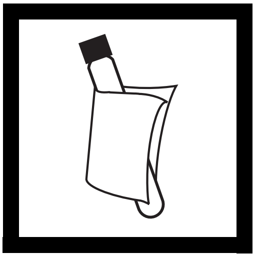


6. Press: **ZERO**

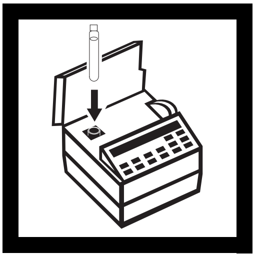
The display will show:

Zeroing. . . .

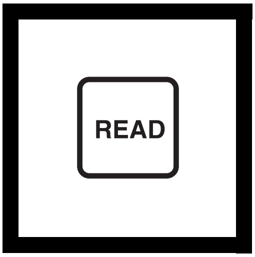
then: **0. mg/L COD HR**



7. Clean the outside of the sample vial with a towel.



8. Place the sample vial in the adapter with the Hach logo facing the front of the instrument. Place the cover on the adapter.



9. Press: **READ**

The display will show:

Reading. . . .

then the result in mg/L COD will be displayed.

Note: *When using High Range Plus COD Digestion Reagent Vials multiply the reading by 10.*

Note: *For most accurate results with samples near 1,500 or15,000 mg/L COD, repeat the analysis with a diluted sample.*

Sampling and Storage

Collect samples in glass bottles. Use plastic bottles only if they are known to be free of organic contamination. Test biologically active samples as soon as possible. Homogenize samples containing solids to assure representative samples. Samples treated with sulfuric acid to a pH of less than 2 (about 2 mL per liter) and refrigerated at 4 °C can be stored up to 28 days. Correct results for volume additions; see *Correction for Volume Additions*, (*Section I*) for more information.

Accuracy Check

Standard Solution Method

Check the accuracy of the 0 to 150 mg/L range with a 100 mg/L standard. Prepare by dissolving 85 mg of dried (120 °C, overnight) potassium acid phthalate (KHP) in 1 liter of deionized water. Use 2 mL as the sample volume. The result should be 100 mg/L COD. Or, dilute 10 mL of 1000-mg/L COD Standard Solution to 100 mL to produce a 100-mg/L standard.

Check the accuracy of the 0 to 1,500 mg/L range by using either a 300 mg/L or 1000 mg/L COD Standard Solution. Use 2 mL of one of these solutions as the sample volume; the expected result will be 300 or 1000 mg/L COD respectively.

Or, prepare a 500 mg/L standard by dissolving 425 mg of dried (120 °C, overnight) KHP. Dilute to 1 liter with deionized water.

Check the accuracy of the 0 to 15,000 mg/L range by using a 10,000 mg/L COD standard solution. Prepare the 10,000 mg/L solution by dissolving 8.500 g of dried (120 °C, overnight) KHP in 1 liter of deionized water. Use 0.2 mL of this solution as the sample volume; the expected result will be 10,000 mg/L COD.

Precision For Colorimetric Determination

In a single laboratory using standard solutions of 100 mg/L COD and 500 mg/L COD and two lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±2.7 mg/L COD, ±18 mg/L COD and ±100 mg/L COD for 0 to 150, 0 to 1,500 and 0 to 15,000 mg/L ranges, respectively.

Estimated Detection Limit (EDL)

The EDL for program 430 is 2 mg/L COD. The EDL is the calculated lowest average concentration in a deionized water matrix that is different from zero with a 99% level of confidence. For more information on derivation and use of Hach's estimated detection limit, see *Section I*.

The EDL for program 435 is 5 mg/L COD. The EDL is the calculated lowest average concentration in a deionized water matrix that is different from zero with a 99% level of confidence. For more information on derivation and use of Hach's estimated detection limit, see section I.

Interferences

Chloride is the primary interference when determining COD concentration. Each COD vial contains mercuric sulfate that will eliminate chloride interference up to the level specified in column 1 in the table below. Samples with higher chloride concentrations should be diluted. Dilute the sample enough to reduce the chloride concentration to the level given in column 2.

If sample dilution will cause the COD concentration to be too low for accurate determination, add 0.50 g of mercuric sulfate ($HgSO_4$) to each COD vial before the sample is added. The additional mercuric sulfate will raise the maximum chloride concentration allowable to the level given in column 3.

Vial Type Used	(1) Maximum Cl^- concentration in sample (mg/L)	(2) Suggested Cl^- concentration of diluted samples (mg/L)	(3) Maximum Cl^- concentration in sample when 0.50 $HgSO_4$ added
Low Range	2000	1000	8000
High Range	2000	1000	4000
High Range Plus	20,000	10,000	40,000

Blanks for Colorimetric Determination

The blank may be used repeatedly for measurements using the same lot of vials. Store it in the dark. Monitor decomposition by measuring the absorbance at the appropriate wavelength (420 or 620 nm). Zero the instrument in the absorbance mode, using a vial containing 5 mL of deionized water and measure the absorbance of the blank. Record the value. Prepare a new blank when the absorbance has changed by about 0.01 absorbance units.

Summary of Method

The mg/L COD results are defined as the mg of O_2 consumed per liter of sample under conditions of this procedure. In this procedure, the sample is heated for two hours with a strong oxidizing agent, potassium dichromate. Oxidizable organic compounds react, reducing the dichromate ion ($Cr_2O_7^{2-}$) to green chromic ion (Cr^{3+}). When the 0-150 mg/L colorimetric or titrimetric method is used, the amount of Cr^{6+} remaining is determined. When the 0-1,500 mg/L or 0-15,000 mg/L colorimetric method is used, the amount of Cr^{3+} produced is determined. The COD reagent also contains silver and mercury ions. Silver is a catalyst, and mercury is used to complex chloride interferences.

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
Select the appropriate COD Digestion Reagent Vial:			
Low Range, 0 to 150 mg/L COD	1 to 2 vials	25/pkg	21258-25
High Range, 0 to 1,500 mg/L COD	1 to 2 vials	25/pkg	21259-25
High Range Plus, 0 to 15,000 mg/L COD	1 to 2 vials	25/pkg	24159-25
Water, deionized	varies	4 L	272-56

REQUIRED APPARATUS

Blender, 2-speed, 120 V	1	each	26161-00
Blender, 2-speed, 240 V	1	each	26161-02
Cap Tool, COD	1	each	45587-00
COD Reactor, 120/240 Vac, North American fuses/plug	1	each	45600-00
COD Reactor, 120/240 Vac, European fuses and plug	1	each	45600-02
COD Vial Adapter, DR/2010	1	each	44799-00
Pipet, TenSette, 0.1 to 1.0 mL	1	each	19700-01
Pipet, volumetric, Class A, 2.00 mL	1	each	14515-36
Pipet Filler, safety bulb	1	each	14651-00
Test Tube Rack	1 to 2 racks	each	18641-00

OPTIONAL REAGENTS

COD Digestion Reagent Vials, 0 to 150 mg/L COD	150/pkg	21258-15
COD Digestion Reagent Vials, 0 to 1,500 mg/L COD	150/pkg	21259-15
COD Standard Solution, 300 mg/L	200 mL	12186-31
COD Standard Solution, 1000 mg/L	200 mL	22539-31
Potassium Acid Phthalate, ACS	500 g	315-34
Sulfuric Acid, ACS	500 mL*	979-49
Mercuric Sulfate	28.3 grams	1915-20

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* Contact Hach for larger sizes.

OPTIONAL APPARATUS

Description	Unit	Cat. No.
Balance, analytical, 115 V	each	26103-00
Balance, analytical, 230 V	each	26103-02
Beaker, 250 mL	each	500-46
Cylinder, graduated, 5 mL	each	508-37
Electromagnetic Stirrer, 120 V, with electrode stand	each	45300-01
Electromagnetic Stirrer, 230 V, with electrode stand	each	45300-02
Flask, volumetric, Class A, 1000 mL	each	14574-53
Flask, volumetric, Class A, 100 mL	each	14574-42
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
Pipet, serological, 5 mL	each	532-37
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg*	21856-96
Pipet, volumetric, Class A, 10 mL	each	14515-38
Safety shield, for COD Reactor	each	23810-00
Spoon, measuring, 0.5 g	each	907-00
Stir Bar, 22.2 x 4.76 mm (7/8" x 3/16")	each	45315-00
Stir Bar Retriever	each	15232-00

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

OXYGEN DEMAND, CHEMICAL (COD)

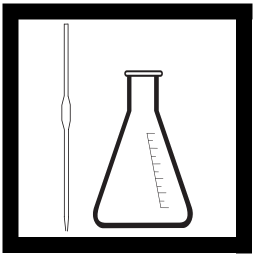
For water and wastewater

Dichromate Reflux Method* ; USEPA Accepted for reporting wastewater analysis**

Digestion

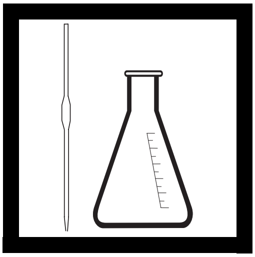
1. Homogenize 500 mL of sample for two minutes in a blender.

Note: *Blending ensures distribution of solids and improves accuracy and reproducibility.*

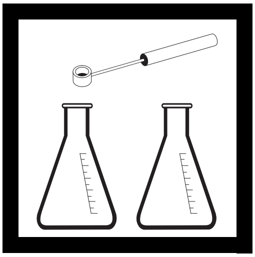


2. Pipet the appropriate sample volume and deionized water volume from into a digestion flask to make the prepared sample.

Note: *A reflux condenser and a 125-mL flask with 24/40 ground-glass joints are used for the reaction. Do not grease the glass joints, as this could contaminate the sample.*



3. Pipet 10.00 mL of deionized water into a second digestion flask to make the reagent blank.



4. Add one heaping 0.2-g spoonful of COD Catalyst Powder and a few glass beads to each flask. Swirl to mix.

COD Range (mg/L as O_2)	Sample Volume (mL)	deionized Water (mL)	Multiplier
0-800	10	0	1
800-1600	5	5	2
1600-4000	2	8	5
4000-8000	1	9	10

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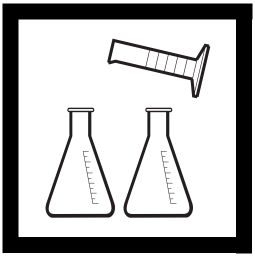
* Adapted from *J. Water Pollution Control Federation*, 36, 1479 (1964).

** Buret titration only; procedure is equivalent to USEPA method 410.1-.3 and Standard Method 5220C for wastewater.

5. Pipet 5.00 mL of 0.250 N Potassium Dichromate Standard Solution into each flask. Swirl to mix.

Note: *If the sample contains high levels of nitrite, add 1 mg of sulfamic acid to each 50 mL of Dichromate Standard Solution for each mg/L of nitrite nitrogen present. Use this solution for the prepared sample and the reagent blank.*



6. Measure 15.0 mL of sulfuric acid slowly into each flask. Swirl to mix thoroughly while adding.

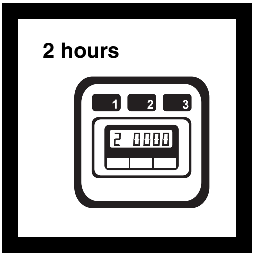
Note: *The flask will become hot when adding acid.*

Note: *Some of the chemicals and apparatus used in this procedure may be hazardous to the health and safety of the user. Please read all warnings, MSDS, and the safety section of this manual. Use appropriate eye protection and clothing. If contact occurs, flush the affected area with running water for 15 minutes.*

7. Attach a reflux condenser to each flask. Place each flask on a hot plate or over a flame.

Note: *Connect a hose from the bottom hose connection of the condenser to a water tap. Connect a second hose from the top hose connection to a drain. Run a slow to moderate stream of water through the condenser to condense the sample vapors.*

Note: *Be sure the flask contents are well mixed before heating to avoid sample boil-over.*



8. Gently boil the solution for two hours.

Note: *A pure green color in the sample shows the range may have been exceeded. Measure the COD and if necessary repeat the test with a diluted sample.*

9. Wait for the solutions to cool to room temperature with the reflux condensers attached.

***Note:** Upon cooling, some of the catalyst may precipitate. When doing colorimetric determinations, wait until the particles settle before measuring the color.*

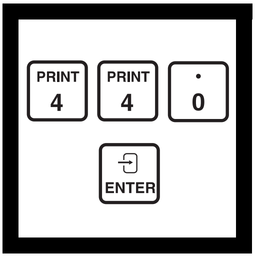
Colorimetric
or
Titrimetric

10. Use one of the following analytical techniques to determine the sample concentration:

- Colorimetric determination
- Buret titration

Method 8230

Colorimetric Determination



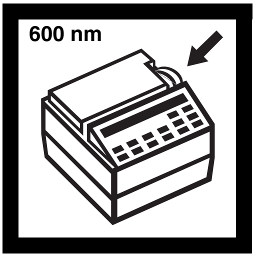
1. Enter the stored program number for chemical oxygen demand (COD)-reflux method.

Press: **4 4 0 ENTER**

The display will show:

Dial nm to 600

***Note:** The Pour-Thru Cell cannot be used.*



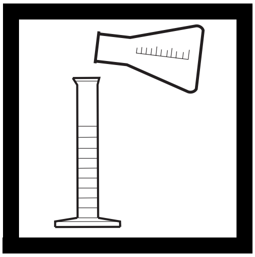
2. Rotate the wavelength dial until the small display shows:

600 nm

When the correct wavelength is dialed in the display will quickly show:

Zero Sample

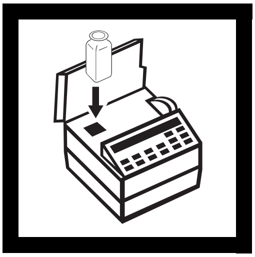
then: **mg/L COD Reflux**



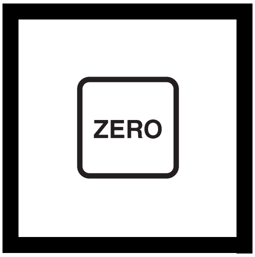
3. Pour the contents of each flask into a dry 50-mL graduated cylinder.

4. Adjust the volume to 29 mL, if necessary, with deionized water.

5. Pour the solutions into dry, labeled 25-mL sample cells.



6. Place the blank into the cell holder. Close the light shield.



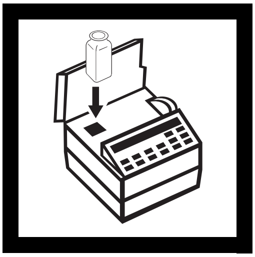
7. Press: **ZERO**

The display will show:

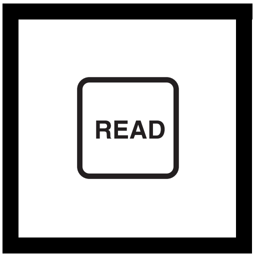
Zeroing. . . .

then:

0. mg/L COD Reflux



8. Place the prepared sample into the cell holder. Close the light shield.



9. Press: **READ**

The display will show:

Reading. . .

then the result in mg/L COD will be displayed.

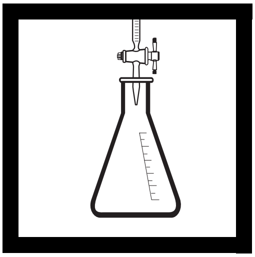
Note: *If the sample was diluted, multiply the final result by appropriate factor from Table 1.*

Method 8116

Buret Titration

1. When the flasks have cooled, rinse the inside of the condenser with a small amount of deionized water, remove the condenser from the flask. Add two drops of Ferroin Indicator to each flask.

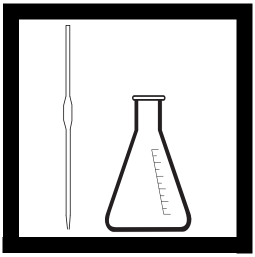
Note: *If the solution color changes from blue-green to orange-brown, the COD value is out of range. Repeat the digestion with a smaller sample volume plus the deionized water specified in Table 1.*



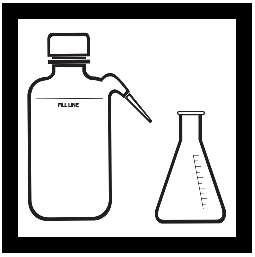
2. Titrate the solutions with 0.0625 N Ferrous Ammonium Sulfate Standard Solution (FAS) until the color changes sharply from blue-green to orange-brown. Record the number of mL of titrant required.

Note: *The mL required for the prepared sample is value B. The mL required for the reagent blank is value A.*

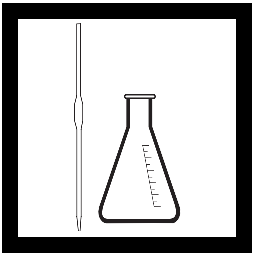
Note: *Steps 3 through 7 need only be done as required because the FAS deteriorates over time.*



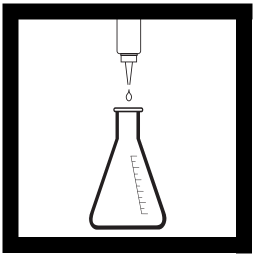
3. To make the required standard solution for titration in step 7, pipet 5.00 mL of 0.250 N Potassium Dichromate Standard Solution into a 125-mL erlenmeyer flask.



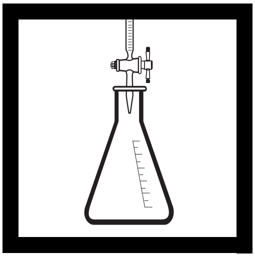
4. Add 30 to 50 mL of deionized water to standard solution in the flask.



5. Add 15 mL of concentrated sulfuric acid slowly to the flask, swirling continually.

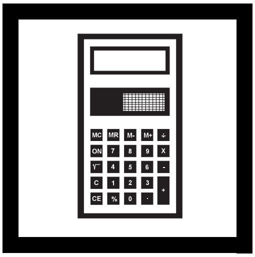


6. Add two drops of Ferroin Indicator Solution to the flask.



7. Titrate the standard solution with 0.0625 N Ferrous Ammonium Sulfate Standard Solution until the sample changes sharply from blue-green to orange-brown. Record the mL of titrant required.

Note: *This is value C in the following equation.*



8. Determine the mg/L COD according to the following equation:

$$(A - B) \times \frac{1000}{C} \times M$$

$$= \text{mg/L COD}$$

Where:

A = mL used in titration of reagent blank

B = mL used in titration of prepared sample

C = mL used in titration of standard solution in Step 7

M = Multiplier from Table 1

For example when using a 10-mL sample volume:

A = 19.75 mL

B = 10.00 mL

C = 20.00 mL

M = 1

COD as m/L O_2 =

$$19.75 - 10.00 \times \frac{1000}{20.00} \times 1$$

$$= 487.5$$

Sampling and Storage

Collect samples in glass bottles. Use plastic bottles only if they are known to be free of organic contamination. Test biologically active samples as soon as possible. Homogenize samples containing solids to assure representative samples. Add sulfuric acid to samples until the pH is less than 2 (at least 2 mL per liter) and refrigerate at 4 °C. Store up to 28 days. Correct results for volume additions; see Correction for Volume Additions, (Section I) for more information.

Accuracy Check

Standard Solution Method

Check accuracy by using 10.00 mL of 300 mg/L or 5.00 mL of 1000 mg/L COD Standard Solution as sample.

Or, prepare a 500 mg/L standard solution by dissolving 425 mg of dried (120 °C overnight) potassium acid phthalate and diluting to 1 liter with deionized water.

Precision for Colorimetric Determination

In a single laboratory using a standard solution of 500 mg/L COD and one representative lot of reagent with the DR/2010, a single operator obtained a standard deviation of ±6 mg/L COD.

Estimated Detection Limit (EDL)

The EDL for program 440 is 3 mg/L. The EDL is the calculated lowest average concentration in a deionized water matrix that is different from zero with a 99% level of confidence. For more information on derivation and use of Hach's estimated detection limit, see *Section I.*

Interferences

The COD Catalyst Powder contains mercuric sulfate to complex up to 1000 mg/L chloride. For higher chloride concentrations, dilute the sample so that the chloride concentration is less than 1000 mg/L.

If this is not feasible due to low COD values, add one 0.1-g spoonful of Mercuric Sulfate for each additional 2000 mg/L chloride. If a precipitate develops, use the buret titration and not the colorimetric determination.

Summary of Method

In the chemical oxygen demand test, the water sample is heated for two hours with a strong oxidizing agent, potassium dichromate. Oxidizable organic compounds react, reducing the dichromate ion ($Cr_2O_7^{2-}$) to green chromic (Cr^{3+}) ion.

REQUIRED REAGENTS (FOR COLORIMETRIC DETERMINATION)

Description	Quantity Required Per Test	Unit	Cat. No.
COD Catalyst Powder	0.4 g	12 g	14328-12
Potassium Dichromate Standard Solution, 0.250 N	10 mL	1000 mL	1809-53
Sulfuric Acid, ACS	30 mL	500 mL	979-49
Water, deionized	varies	4 L	272-56

REQUIRED REAGENTS (FOR BURET TITRATION)*

Description	Quantity Required Per Test	Unit	Cat. No.
COD Catalyst Powder	0.2 g	12 g	14328-12
Ferroin Indicator	0.1 mL	25 mL** DB	1812-33
Ferrous Ammonium Sulfate Standard Solution, 0.0625 N***	varies	500 mL	14095-49
Potassium Dichromate Standard Solution, 0.250 N	varies	1000 mL	1809-53
Sulfuric Acid, ACS	15 mL	500 mL**	979-49
Water, deionized	varies	4 L	272-56

REQUIRED APPARATUS (FOR COLORIMETRIC DETERMINATION)

Description	Quantity Required Per Test	Unit	Cat. No.
Blender, 120 V 50/60 Hz, 1.2 L	1	each	26161-00
Blender, 240V 50/60 Hz, 1.2 L	1	each	26161-02
Condenser, reflux	2	each	1806-00
Cylinder, graduated, 25 mL	1	each	508-40
Cylinder, graduated, poly, 50 mL	2	each	1081-41
Flask, erlenmeyer, 24/40 joint, 125 mL	2	each	1807-43
Glass Beads	varies	100/pkg	2596-00
Pipet, Mohr, 10 mL (for adding mineralized water)	1	each	20934-38
Pipet Filler, safety bulb	1	each	14651-00
Sample Cell, 25 mL, matched pair	2	pair	20950-00
Spoon, measuring, 0.2 g	1	each	638-00
Tubing, rubber, 7.9 mm (5/16") ID	1	3.6 m	559-19
Select one or more based on sample volume:			
Pipet, volumetric, Class A, 1.00 mL		each	14515-35
Pipet, volumetric, Class A, 2.00 mL		each	14515-36
Pipet, volumetric, Class A, 5.00 mL		each	14515-37
Pipet, volumetric, Class A, 10.00 mL		each	14515-38
Select one based on available voltage:			
Hot Plate, 7 x 7", 120 Vac		each	23441-00
Hot Plate, 7 x 7", 240 Vac		each	23441-02

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* Does not include reagent or apparatus for blanks or standardization.

** Contact Hach for larger sizes.

*** Ferrous Ammonium Sulfate Standard Solutions, as prepared by Hach, have a length of cadmium wire in each bottle. The cadmium wire will help preserve the standard solution. When titrating with these standards, do not return unused portions from the buret back to the bottle. Do not use an automatic buret.

REQUIRED APPARATUS (For Buret Titration)

Description	Quantity Required Per Test	Unit	Cat. No.
Blender, 120 V 50/60 Hz, 1.2 L	1	each	26161-00
Blender, 240V 50/60 Hz, 1.2 L	1	each	26161-02
Buret, 25 mL	1	each	14681-40
Buret Clamp, double	1	each	328-00
Condenser, reflux	1	each	1806-00
Cylinder, graduated, 10 mL	1	each	508-38
Cylinder, graduated, 25 mL	1	each	508-40
Flask, erlenmeyer, 24/40 joints, 125 mL	1	each	1807-43
Glass Beads	varies	100/pkg	2596-00
Measuring Spoon, 0.2 g	1	each	638-00
Pipet, Mohr, 10 mL (use for adding deionized water)	1	each	20934-38
Pipet Filler, safety bulb	1	each	14651-00
Spoon, measuring, 0.2 g	1	each	638-00
Support Base and Rod	1	each	329-00
Tubing, rubber	1	3.6 m	560-19
Select one or more based on sample volume:			
Pipet, volumetric, Class A, 1.00 mL		each	14515-35
Pipet, volumetric, Class A, 2.00 mL		each	14515-36
Pipet, volumetric, Class A, 5.00 mL		each	14515-37
Pipet, volumetric, Class A, 10.00 mL		each	14515-38
Select one based on available voltage:			
Hot Plate, 7 x 7", 120 Vac		each	23441-00
Hot Plate, 7 x 7", 240 Vac		each	23441-02

OPTIONAL REAGENTS

COD Standard Solution, 300 mg/L	200 mL	12186-29
COD Standard Solution, 1000 mg/L	200 mL	22539-29
Potassium Acid Phthalate, ACS	500 g	315-34
Sulfamic Acid, ACS	113 g	2344-14

OPTIONAL APPARATUS

Cylinder, graduated, poly, 50 mL	each	1081-41
Flask, erlenmeyer, 125 mL	each	505-43
Spoon, measuring, 0.1 g	each	511-00
pH Indicator Paper, 1 to 11	5 rolls/pkg	391-33
Pipet Filler	each	12189-00
Pipet, serological, 2 mL	each	532-36

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

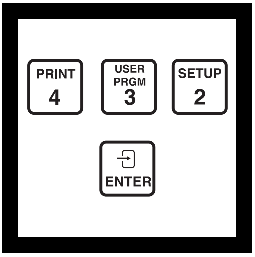
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 10067

OXYGEN DEMAND, CHEMICAL (20 to 1,000 mg/L)

Manganese III Digestion Method*
(without optional chloride removal)

For water and wastewater



1. Enter the stored user program number for Manganese III COD.

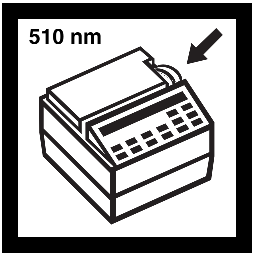
Press: **432 ENTER**

The display will show:

Dial nm to 510

Note: *If samples cannot be analyzed immediately, see Sampling and Storage following these steps.*

Note: *Preheat the COD Reactor to 150 °C for use later in the procedure.*



2. Rotate the wavelength dial until the small display shows:

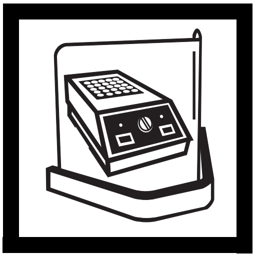
510 nm

When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

then: **mg/L COD Mn III**

Note: *Approach wavelength settings from higher to lower values.*



3. Turn the COD Reactor on and heat to 150 °C. Place the shield in front of the reactor.

Note: *To determine if the sample contains chloride, use Water Quality Test Strips for Low range Chloride. If the sample contains chloride, use the method that removes chloride from the sample (after this method).*

4. Homogenize 100 mL of sample for 30 seconds in a blender.

Note: *Blending promotes even distribution of solids and improves accuracy and reproducibility.*

Note: *Continue mixing the sample while pipetting if suspended solids are present.*

Caution: ***Some of the chemicals and apparatus used in this procedure may be hazardous to the health and safety of the user if inappropriately handled or accidentally misused. Please read all warnings and the safety section of this manual. Wear appropriate eye protection and appropriate clothing. If contact occurs, flush the affected area with running water. follow all instructions carefully.***

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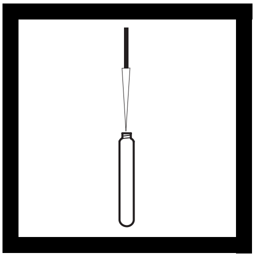
* U.S. Patent 5,556,787



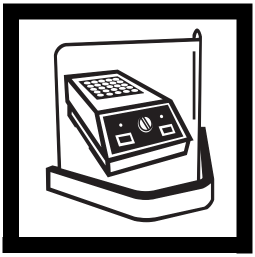
5. Pipet 0.50 mL of homogenized sample into a Mn III COD vial. Cap and invert several times to mix.

Note: *If the sample COD value is not between 20-1000 mg/L, dilute the sample with deionized water to obtain this range. Multiply the final result by the dilution factor.*

PREPARE BLANK

6. Prepare a blank (see note) by substituting 0.50 mL of deionized water for the sample.

Note: *The reagent blank is stable and can be reused. Verify reagent blank quality by measuring the absorbance of the blank vs. a clean COD vial filled with deionized water. The absorbance range should be about 1.4-1.5.*

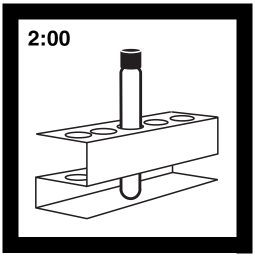


7. Place the vials in the COD Reactor that is preheated to 150 °C. Digest for one hour.

Note: *Boiling sample in the vials during digestion indicates the vial is not properly sealed; test results will be invalid.*

Note: *Samples can be digested up to four hours to oxidize more resistant organics. Treat the prepared blank in the same manner.*

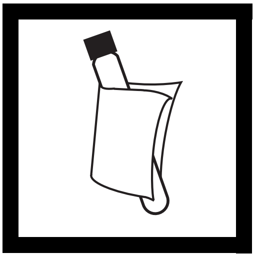
Note: *Ensure safety devices are in place to protect the analyst from splattering if leaks occur. Spilled reagent will affect test accuracy and is hazardous. Do not run tests with vials which have been spilled.*



8. Remove the vials and place them in a cooling rack for two minutes to air cool. Then cool the vials to room temperature in a cool water bath or running tap water. This usually takes about three minutes.

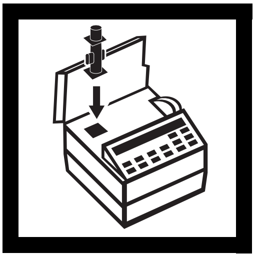
Note: *Occasionally a vial will develop a colorless upper layer and a purple lower layer. Invert the vial several times to mix and proceed.*

Note: *The Hach COD Vial Lifter allows the transfer of several vials at once.*

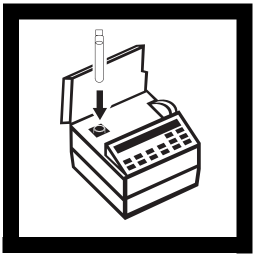


9. Remove the vials from the water and wipe with a clean, dry paper towel.

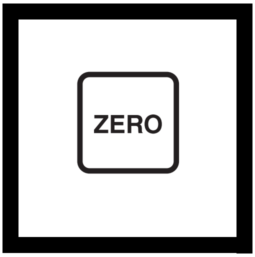
Invert the vials several times to mix.



10. Place the COD Vial Adapter into the cell holder.



11. Place the blank into the sample cell adapter. Place the cover on the adapter.



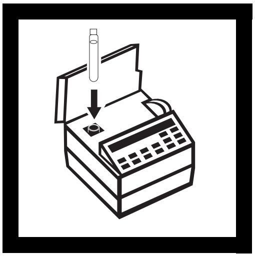
12. Press: **ZERO**

The display will show:

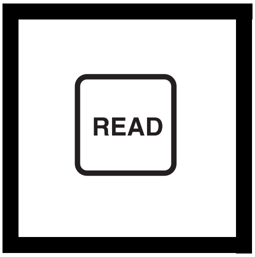
Zeroing. . .

then:

0 mg/L COD Mn III



13. Place the sample in the sample cell adapter. Place the cover on the adapter.



14. Press: **READ**

The display will show:

Reading. . .

then the results in mg/L COD will be displayed.

Note: *Adjust the result for any sample dilution in steps 4 or 6.*

Additional Information

For information about Sampling and Storage, Accuracy Checks, Interferences, Summary of Method, Reagents and Apparatus, see the following procedure.

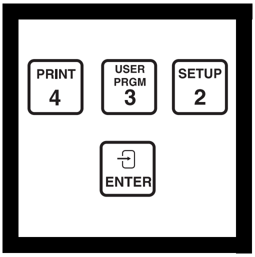
Method 10067

OXYGEN DEMAND, CHEMICAL (20 to 1,000 mg/L)

Manganese III Digestion Method*

(with optional chloride removal)

For water and wastewater



1. Enter the stored user program number for Manganese III COD.

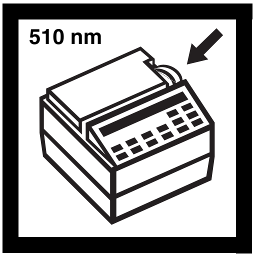
Press: **432 ENTER**

The display will show:

Dial nm to 510

Note: *If samples cannot be analyzed immediately, see Sampling and Storage following these steps.*

Note: *Preheat the COD Reactor to 150 °C for use later in the procedure.*



2. Rotate the wavelength dial until the small display shows:

510 nm

When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

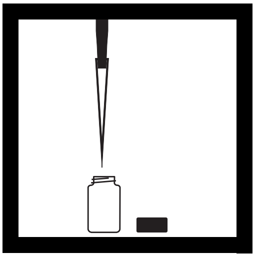
then: **mg/L COD Mn III**

Note: *Approach wavelength settings from higher to lower values.*

3. Homogenize 100 mL of sample for 30 seconds in a blender.

Note: *Blending promotes even distribution of solids and improves accuracy and reproducibility.*

Note: *Continue mixing the sample while pipetting if suspended solids are present.*



4. Using a TenSette Pipet or a pipet and safety bulb, pipet 9.0 mL of homogenized sample into an empty glass mixing cell. If the sample COD exceeds 1000 mg/L, dilute the sample as described in *Table 1*.

Note: *If suspended solids are present, continue mixing the sample while pipetting.*

Caution: ***Some of the chemicals and apparatus used in this procedure may be hazardous to the health and safety of the user if inappropriately handled or accidentally misused. Please read all warnings and the safety section of this manual. Wear appropriate eye protection and appropriate clothing. If contact occurs, flush the affected area with running water. follow all instructions carefully.***

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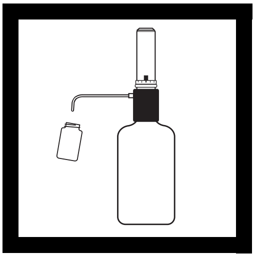
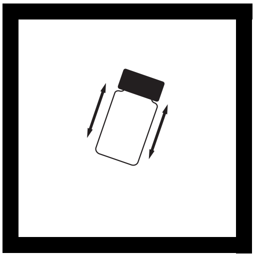
* U.S. Patent 5,556,787.



5. Using an automatic dispenser or TenSette Pipet, add 1.0 mL of concentrated sulfuric acid to the mixing cell.

Note: *Mixing concentrated sulfuric acid and water is not additive. Adding 1.0 mL of concentrated sulfuric acid to 9.0 mL of sample does not result in a final volume of 10.0 mL. This factor is built into the calibration curve.*



6. Cap the cell tightly and invert it several times. The solution will become hot. Cool to room temperature before proceeding.

Note: *Acidified samples are stable for several months when refrigerated at 4 °C.*

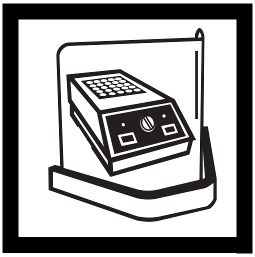
PREPARE BLANK

7. Prepare a blank (see note) by repeating *steps 4-6*, substituting 9.0 mL of deionized water for the sample.

Note: *The reagent blank is stable and can be reused. Verify reagent blank quality by measuring the absorbance of the blank vs. a clean COD vial filled with deionized water. The absorbance range, when using chloride removal, should be about 1.45-1.50.*

Note: *Use a clean pipet or rinse it thoroughly.*

Note: *One blank must be run with each lot of reagents. Run all samples and blanks with the same lot of vials (lot number is on the container label).*



8. If not already on, turn on the COD Reactor and heat to 150 °C. Place the shield in front of the reactor.

Note: *Ensure safety devices are in place to protect the analyst from splattering if leaks occur. Spilled reagent will affect test accuracy and is hazardous. Do not run tests with vials which have been spilled.*

Table 1 Dilution Table (for use with Chloride Removal Procedure Only)

Sample (mL)	Deionized Water (mL)	Range (mg/L COD)	Multiplication Factor
6.0	3.0	30-1500	1.5
3.0	6.0	60-3000	3
1.0	8.0	180-9000	9
0.5	8.5	360-18000	18

All dilutions require that the ratio of sample to sulfuric acid remain at 9:1. For other dilutions that are not listed in Table 1, simply add the sample volume + deionized water and divide by the sample volume to obtain the multiplication factor.

Example:

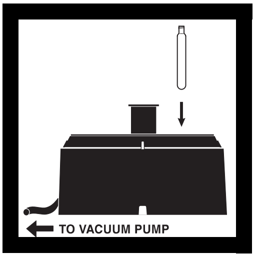
Dilute the sample to a range of 90-4500 mg/L COD

Sample Volume (2.0 mL) + Demineralized water (7.0 mL) = Total Volume (9.0 mL)

$$\text{Multiplication Factor} = \frac{\text{Total Volume}}{\text{Sample Volume}} = \frac{9.0\text{ mL}}{2.0\text{ mL}} = 4.5$$

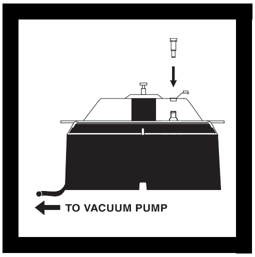
Standard test range is 20-1000 mg/L COD. Example Test Range = 4.5 (20) to 4.5 (1000) = 90-4500 mg/L COD

It is best to use 0.5 mL or more of sample for diluting. If sample values exceed 18,000 mg/L COD, use a separate sample dilution before the sample chloride removal procedure.

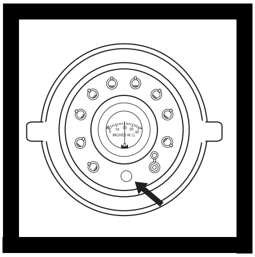


9. Label each Mn III COD vial and remove the cap. Place the vial in one of the numbered holes in the Vacuum Pretreatment Device (VPD)* base.

Note: *The VPD must be attached to a vacuum pump (not an aspirator-type vacuum) that can create a vacuum of 20 to 25 inches of mercury.*

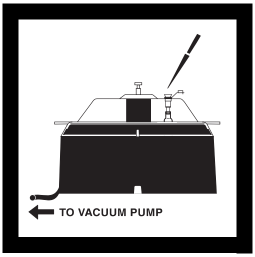


10. Place the VPD top on the base. Insert a fresh Chloride Removal Cartridge (CRC)** directly above each Mn III COD Reagent Vial. Plug any open holes in the VPD top using the stoppers provided.



11. Turn the vacuum pump on and adjust the vacuum regulator valve on top of the VPD until the internal gauge reads 20 inches of water.

Note: *The optimum setting allows the sample to flow through the CRC in about 30 to 45 seconds.*



12. Pipet 0.60 mL of acidified sample (made in Steps 6-8) into the CRC. Pipet 0.60 mL of acidified blank into another CRC.

Note: *If the sample does not flow through the CRC, increase the vacuum until flow starts, then reduce the vacuum to 20 inches of water. Proceed as usual.*

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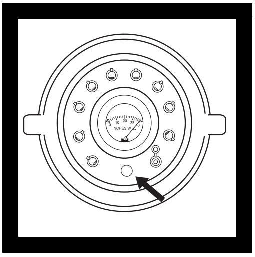
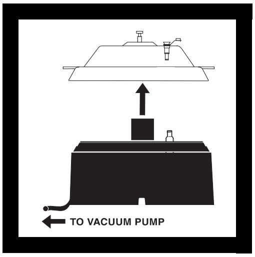
* Patent pending

** U.S. Patents 5,667,754; 5,683,914

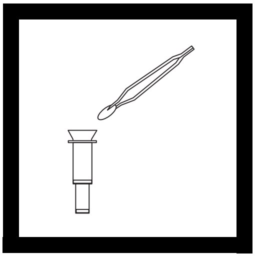


13. Close the vacuum regulator valve completely to achieve full vacuum. After one minute under full vacuum, open the VPD vacuum regulator valve to release the vacuum.

Note: *The maximum range of the vacuum gauge in the VPD is 40 inches of water; the gauge will not indicate the full vacuum level obtained. Full vacuum is 20-25 inches of mercury; this can be measured at the vacuum pump with a gauge that is calibrated in inches of mercury.*



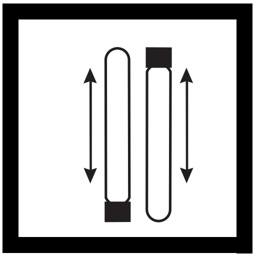
14. Turn the pump off. Remove the VPD top and set it beside the base.



15. Use forceps to remove the filter from the top of each CRC. Place each filter in the corresponding Mn III COD Vial (use the numbers on the VPD as a guide).

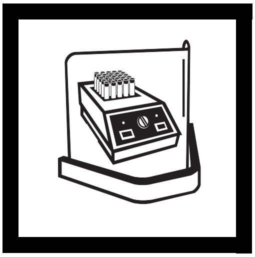
Note: *To avoid cross contamination, clean forcep tips between samples by wiping with a clean towel or rinsing with deionized water.*

Note: *If the sample does not contain suspended solids, it is not necessary to transfer the filter to the digestion vial.*



16. Remove the Mn III COD vial from the vacuum chamber and replace the original cap. Screw the cap on tightly. Invert several times to mix.

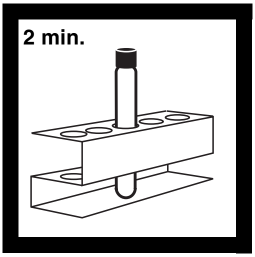
Note: *Dispose of the used Chloride Removal Cartridge. Do not reuse it.*



17. Place the vials in the COD Reactor that is preheated to 150 °C. **Place the safety shield in front of the reactor**. Digest for 1 hour.

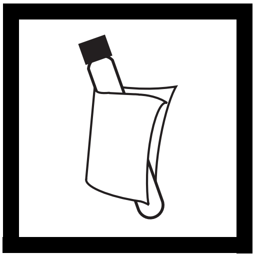
Note: *Boiling sample in the vials during digestion indicates the vial is not properly sealed; test results will be invalid.*

Note: *Samples can be digested up to 4 hours to oxidize more resistant organics. The prepared blank must be treated in the same manner.*



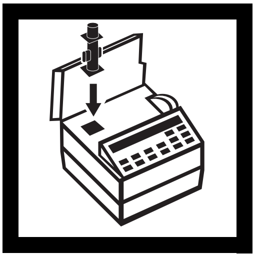
18. Remove the vials and place them in a cooling rack for two minutes to air cool. Then cool the vials to room temperature in a cool water bath or running tap water. This usually takes about 3 minutes.

Note: *Occasionally a vial will develop a colorless upper layer and a purple lower layer. Invert the vial several times to mix and proceed. This will not affect test results.*

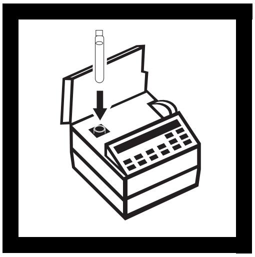


19. Remove the vials from the water and wipe with a clean, dry paper towel.

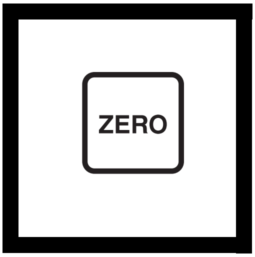
Invert the vials several times to mix.



20. Place the COD Vial Adapter into the cell holder.



21. Place the blank into the sample cell adapter. Place the cover on the adapter.



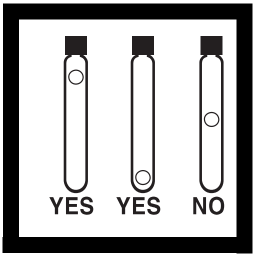
22. Press: **ZERO**

The display will show:

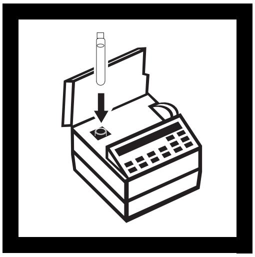
Zeroing. . .

then:

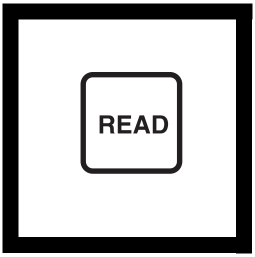
0 mg/L COD Mn III



23. If the chloride removal was done, make sure the filter disc is not suspended in the middle of the vial; it can interfere with the instrument reading. Move it with gentle swirling or by lightly tapping the vial on the table top.



24. Place the sample in the sample cell adapter. Place the cover on the adapter.



25. Press: **READ**

The display will show:

Reading. . .

then the results in mg/L COD will be displayed.

***Note:** Adjust the result for any sample dilution in Steps 4 or 6.*

Sampling and Storage

Collect samples in clean glass bottles. Use plastic bottles only if they are known to be free of organic contamination. Test biologically active samples as soon as possible. Homogenize samples containing solids to assure representative samples. Samples treated with concentrated sulfuric acid to a pH of less than 2 (about 2 mL per liter) and refrigerated at 4 °C may be stored up to 28 days. Correct results for volume additions; see *Correcting for Volume Additions* (*Section I*) for more information.

Accuracy Check

Standard Solution Method

Prepare an 800 mg/L COD standard solution by adding 0.6808 g of dried (103 °C, overnight) potassium acid phthalate (KHP) to 1 liter of deionized water. Use 0.50 mL of this solution (0.60 mL for the chloride removal procedure) as the sample volume. The result should be 800 ±26 mg/L COD. An 800 mg/L COD solution can also be purchased directly from Hach (see *Optional Reagents*).

Method Performance (for Manganese III COD without the chloride removal procedure)

Precision

In a single laboratory, using a standard solution of 800 mg/L COD and two representative lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±20 mg/L COD.

Estimated Detection Limit (EDL)

The EDL for program 432 is 4 mg/L COD. The EDL is the calculated lowest average concentration in a deionized water matrix that is different from zero with a 99% level of confidence. For more information on derivation and use of Hach's estimated detection limit, see *section I*.

Interferences

Inorganic materials may also be oxidized by trivalent manganese and constitute a positive interference when present in significant amounts. Chloride is the most common interference and is removed by sample pretreatment with the Chloride Removal Cartridge. If chloride is known to be absent or present in insignificant levels, the pretreatment can be omitted. A simple way to determine if chloride will affect test results is to run routine samples with and without the chloride removal, then compare results. Other inorganic interferences (i.e., nitrite, ferrous iron, sulfide) are not usually present in significant amounts. If necessary, these interferences can be corrected for after determining their concentrations with separate methods and adjusting the final COD test results accordingly.

Ammonia nitrogen is known to interfere in the presence of chloride; it does not interfere if chloride is absent.

Summary of Method

Chemical oxygen demand (COD) is defined as "... a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant" (APHA Standard Methods, 19th ed., 1995). Trivalent manganese is a strong, non-carcinogenic chemical oxidant that changes quantitatively from purple to colorless when it reacts with organic matter. It typically oxidizes about 80% of the organic compounds. Studies have shown that the reactions are highly reproducible and test results correlate closely to Biochemical Oxygen Demand (BOD) values and hexavalent chromium COD tests. None of the oxygen demand tests provide 100% oxidation of all organic compounds.

A calibration is provided which is based on the oxidation of Potassium Acid Phthalate (KHP). A different response may be seen in analyzing various wastewaters. The KHP calibration is adequate for most applications. The highest degree of accuracy is obtained when test results are correlated to a standard reference method such as BOD or one of the chromium COD methods. Special waste streams or classes will require a separate calibration to obtain a direct mg/L COD reading or to generate a correction factor for the precalibrated KHP response. The sample digestion time can be extended up to 4 hours for samples which are difficult to oxidize.

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
Chloride Removal Cartridges (CRC)	1	25/pkg	26618-25
Manganese III COD Reagent Vials	1	25/pkg	26234-25
Sulfuric Acid, concentrated, ACS	1 mL	4 Kg	979-09
Water, deionized	varies	4 L	272-56

REQUIRED APPARATUS

Adapter, COD, DR/2010	1	each	44799-00
Blender, Osterizer, 120 Vac, 14-speed	1	each	26747-00
Blender Container, 50-250 mL	1	2/pkg	26748-00
Cap, with inert Teflon liner, for mixing bottle	varies	12/pkg	24018-12
Chloride Removal Cartridge	1	25/pkg	26618-25
COD Reactor, 120 V	1	each	45600-00
COD Reactor, 240 V	1	each	45600-02
Forceps, extra fine point	1	each	26696-00
Mixing Bottle, glass, for sample + acid	1	each	24277-00
Pipet, TenSette, 1.0 to 10.0 mL	1	each	19700-10
Pipet Tips, for 19700-10 TenSette	2	50/pkg	21997-96
Pipet Tips, for 19700-10 TenSette	2	1000/pkg	21997-28
Pipet, TenSette, 0.1 to 1.0 mL	1	each	19700-01
Pipet Tips, for 19700-01 TenSette	2	50/pkg	21856-96
Pipet Tips, for 19700-01 TenSette	2	1000/pkg	21856-28
Safety Shield	1	each	23810-00
Test Tube Rack, stainless steel	1	each	18641-00
Vacuum Pretreatment Device (VPD)	1	each	49000-00
Vacuum Pump, 115 V	1	each	14697-00
Vacuum Pump, 230 V	1	each	14697-02

OPTIONAL REAGENTS AND APPARATUS

COD Standard Solution, 800 mg/L COD	200 mL	26726-29
Pipet Tips, for 19700-10	1000/pkg	21997-28
Potassium Acid Phthalate, ACS	500 g	315-34
Dispenser for sulfuric acid	each	25631-37

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

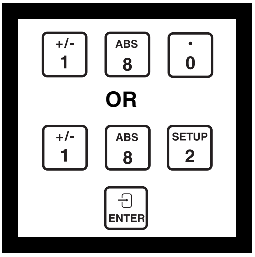
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8140

OXYGEN SCAVENGERS (Range varies according to compound*)

Iron Reduction Method for Oxygen Scavengers

For boiler water



1. Enter the stored program number for diethylhydroxylamine (DEHA).

Press: **1 8 0 ENTER**

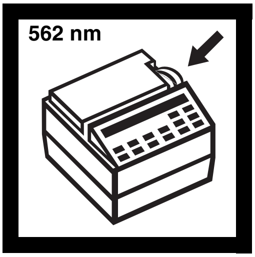
If testing other oxygen scavengers:

Press: **1 8 2 ENTER**

The display will show:

Dial nm to 562

Note: *The Pour-Thru Cell can be used with this procedure.*



2. Rotate the wavelength dial until the small display shows:

562 nm

When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

then: **µg/L DEHA**

for program 180

OR

µg/L Carbo

for program 182.

With program 182, press the **ARROW** keys to select the desired oxygen scavenger:

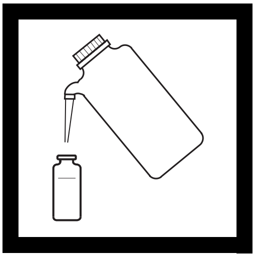
Forms ▲▼
µg/L Hydro
µg/L ISA
µg/L Carbo
µg/L MEKO

3. Fill a sample cell (the prepared sample) with 25 mL of sample.

Note: *The sample temperature should be 25 ±3 °C (77 ± 5 °F).*

Note: *Samples must be analyzed immediately and cannot be stored for later analysis.*

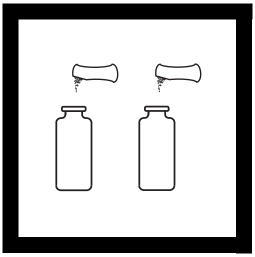
Note: *See Treating Analysis Labware section for information on cleaning labware.*



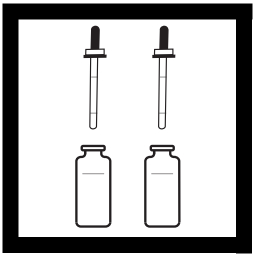
4. Fill a second sample cell (the blank) with 25 mL of deionized water.

---

* DEHA 0-450 µg/L; Carbohydrazide 0-600 µg/L; Hydroquinone 0-1000 µg/L; Iso-Ascorbic Acid (ISA) 0-1500 µg/L; Methylethyl Ketoxime (MEKO) 0-1000 µg/L

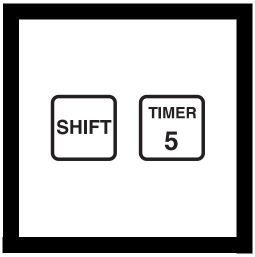


5. Add the contents of one DEHA Reagent 1 Powder Pillow to each sample cell. Swirl to mix.



6. Add 0.5 mL of DEHA Reagent 2 Solution to each sample cell. Mix. Place both sample cells in the dark.

__Note:__ A purple color will slowly develop if DEHA is present.



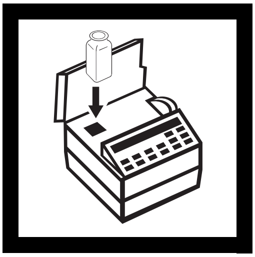
7. Immediately press:

SHIFT TIMER

A 10-minute reaction period will begin.

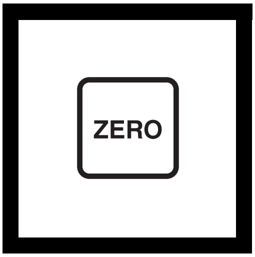
__Note:__ Both sample cells must remain in the dark for the 10-minute period.

__Note:__ Temperature and reaction time affect the results. Be sure these factors are controlled as described.



8. When the timer beeps, the display will show: **µg/L DEHA**

Place the blank into the cell holder. Close the light shield.

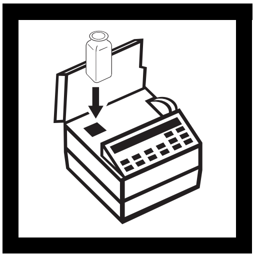


9. Press: **ZERO**

The display will show:

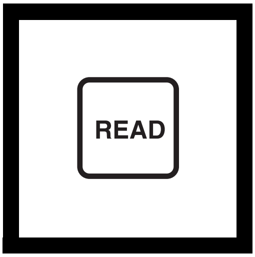
Zeroing. . . .

then: **0. µg/L DEHA**



10. Immediately place the prepared sample into the cell holder. Close the light shield.

__Note:__ To determine the ferrous iron content of the sample, repeat the above procedure, omitting Step 6. Subtract this result from those obtained in Step 11 to determine the actual DEHA concentration.



11. Press: **READ**

The display will show:

Reading. . . .

then the result in µg/L DEHA or µg/L default oxygen scavenger will be displayed.

▲ CARBOHYDRAZIDE
HYDROQUINONE
Forms DEHA
▼ ASCORBIC ACID
MEKO

Sampling and Storage

Most oxygen scavengers will react quickly with atmospheric oxygen. Collect samples in acid-rinsed plastic or glass containers, allowing the sample to over flow. Cap the container so air is excluded. Analyze the sample immediately.

Treating Analysis Labware

To prevent possible trace iron contamination, rinse sampling containers, sample cells, and the Pour-Thru Cell with 1:1 Hydrochloric Acid Solution. Follow with several rinsings of deionized water.

Precision

In a single laboratory, using standard solutions of 150 µg/L DEHA and two representative lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±2.3 µg/L DEHA.

Interferences

Substances which reduce ferric iron will interfere. Substances which complex iron strongly may also interfere. The following may interfere when present in concentrations exceeding those listed below:

Borate (as $Na_2B_4O_7$)	500 mg/L
Cobalt	0.025 mg/L
Copper	8.0 mg/L
Hardness (as $CaCO_3$)	1000 mg/L
Lignosulfonates	0.05 mg/L
Manganese	0.8 mg/L
Molybdenum	80 mg/L
Nickel	0.8 mg/L
Phosphate	10 mg/L
Phosphonates	10 mg/L
Sulfate	1000 mg/L
Zinc	50 mg/L

Light interferes with the color development.

Summary of Method

Diethylhydroxylamine (DEHA) or other oxygen scavengers present in the sample react with ferric iron in DEHA Reagent 2 Solution to produce ferrous ion in an amount equivalent to the DEHA concentration. This solution then reacts with DEHA 1 Reagent, which forms a purple color with ferrous iron, proportional to the concentration of oxygen scavenger.

REQUIRED REAGENTS

Oxygen Scavenger Reagent Set (50 tests)			24466-00

Includes: (2) 21679-69, (1) 21680-49

Description	Quantity Required Per Test	Unit	Cat. No.
DEHA Reagent 1 Powder Pillows	2 pillows	100/pkg	21679-69
DEHA Reagent 2 Solution	1 mL	473 mL	21680-49
Water, deionized	5 mL	4 L	272-56

REQUIRED APPARATUS

Dropper, 0.5 and 1.0-mL marks	1	10/pkg	21247-10
Sample Cell, 25 mL, matched pair		pair	20950-00

OPTIONAL REAGENTS

Hydrochloric Acid, 1:1 (6 N)	500 mL	884-49

OPTIONAL APPARATUS

Bottle, Wash, 250-mL	each	620-31
Cylinder, graduated, polypropylene, 25 mL	each	1081-40
Pour-Thru Cell Assembly Kit	each	45215-00
Stopper, hollow, poly, No. 0	6/pkg	14480-00
Thermometer, -20 to 105 °C	each	1877-01

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

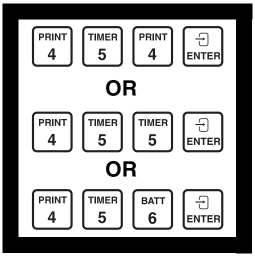
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8311

For water

OZONE (0 to 0.25 mg/L O_3, 0 to 0.75 mg/L O_3 or 0 to 1.50 mg/L O_3)

Indigo Method (Using AccuVac Ampuls)



1. Enter the stored program number for Ozone (O_3) AccuVac ampuls.

Press: **4 5 4 ENTER**

for low range (0-0.25 mg/L)

OR

Press: **4 5 5 ENTER**

for mid range (0-0.75 mg/L)

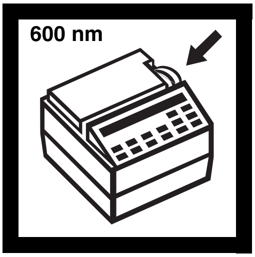
OR

Press: **4 5 6 ENTER**

for high range (0-1.50 mg/L)

The display will show:

Dial nm to 600



2. Rotate the wavelength dial until the small display shows:

600 nm

When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

then: **for #454:**

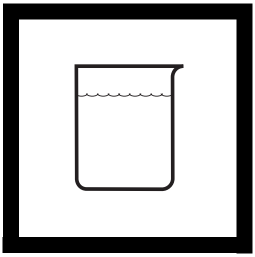
mg/L O_3 Indigo L

for #455:

mg/L O_3 Indigo M

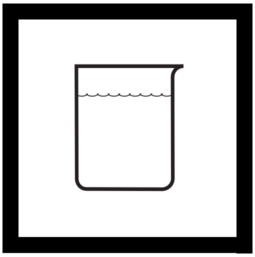
for #456:

mg/L O_3 Indigo H



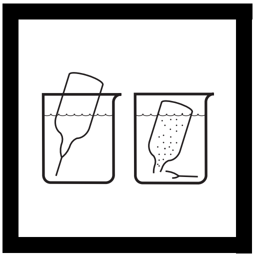
3. Gently collect at least 40 mL of sample in a 50-mL beaker.

Note: *Samples must be analyzed immediately and cannot be preserved for later analysis.*



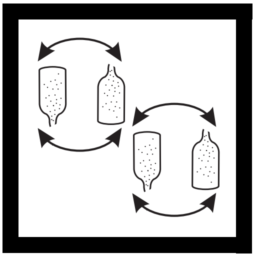
4. Collect at least 40 mL of ozone-free water (blank) in another 50-mL beaker.

Note: *Ozone-free water used for the blank may be deionized water or tap water.*



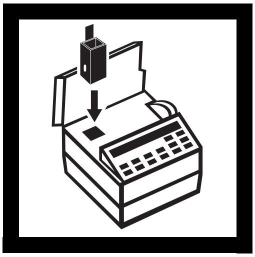
5. Fill one Indigo Ozone Reagent AccuVac Ampul with the sample and one ampul with the blank.

Note: *Keep the tip immersed while the ampul fills.*



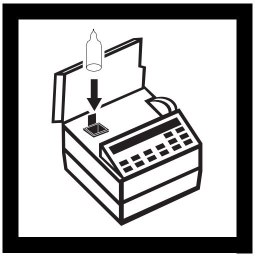
6. Quickly invert both ampuls several times to mix. Wipe off any liquid or fingerprints.

Note: *Part of the blue color will be bleached if ozone is present. (The sample will be lighter than the blank.)*



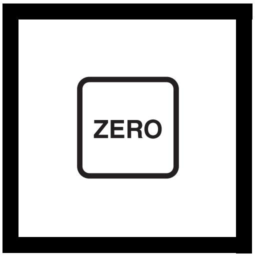
7. Place the AccuVac Vial Adapter into the cell holder.

Note: *Place the grip tab at the rear of the cell holder.*



8. Place the **sample** AccuVac ampul into the cell holder. Close the light shield.

Note: *Standardization for this procedure is intentionally reversed.*

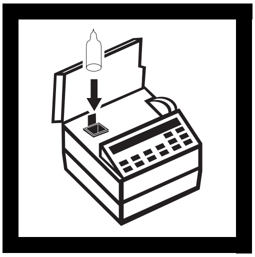


9. Press: **ZERO**

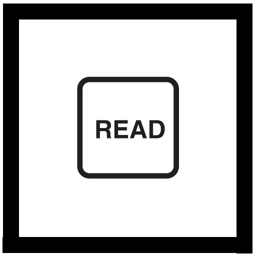
The display will show:

Zeroing. . . .

then: **0.00 mg/L O_3**



10. Place the AccuVac ampul containing the **blank** into the cell holder. Close the light shield.



11. Press: **READ**

The display will show:

Reading. . . .

then the result in mg/L ozone (O_3) will be displayed.

Sampling

The chief consideration when collecting a sample is to prevent the escape of ozone from the sample. The sample should be collected gently and analyzed immediately. Warming the sample, or disturbing the sample by stirring or shaking, will result in ozone loss. After collecting the sample, do not transfer it from one container to another unless absolutely necessary.

Stability of Indigo Reagent

Indigo is light-sensitive. Therefore, the AccuVac ampuls should be kept in the dark at all times.

However, the indigo solution decomposes slowly under room light after filling with sample. The blank ampul can be used for multiple measurements during the same day.

Summary of Method

The reagent formulation adjusts the sample pH to 2.5 after the ampul has filled. The indigo reagent reacts immediately and quantitatively with ozone. The blue color of indigo is bleached in proportion to the amount of ozone present in the sample. Other reagents in the formulation prevent chlorine interference. No transfer of sample is needed in the procedure. Therefore, ozone loss due to sampling is eliminated.

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
Ozone AccuVac Ampuls			
Select one or more based on range:			
0-0.25 mg/L	2 ampuls	25/pkg	25160-25
0-0.75 mg/L	2 ampuls	25/pkg	25170-25
0-1.50 mg/L	2 ampuls	25/pkg	25180-25

REQUIRED APPARATUS

Adapter, AccuVac	1	each	43784-00
Beaker, 50 mL	2	each	500-41

OPTIONAL APPARATUS

AccuVac Amul Samler, 12 feet (3.6 meters)	each	24051-00
AccuVac Snapper Kit	each	24052-00

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

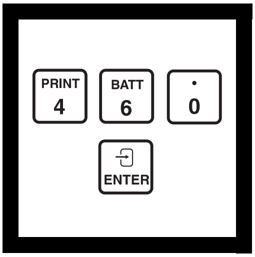
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8144

PALLADIUM (0 to 250 mg/L)

For palladium-tin activator baths

N,N'-Dimethyldithiooxamide Method



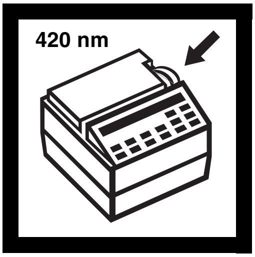
1. Enter the stored program number for palladium (Pd).

Press: **4 6 0 ENTER**

The display will show:

Dial nm to 420

Note: *The Pour-Thru Cell can be used if rinsed well with deionized water immediately after use.*



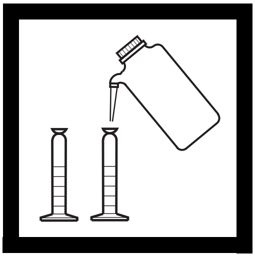
2. Rotate the wavelength dial until the small display shows:

420 nm

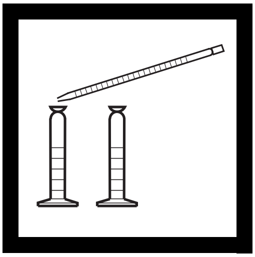
When the correct wavelength is dialed in the display will quickly show:

Zero Sample

then: **mg/L Pd**

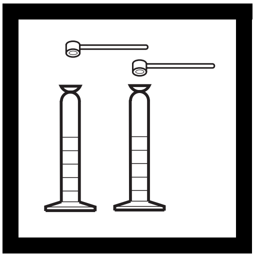


3. Fill two 25-mL mixing cylinders to the 20-mL mark with deionized water.



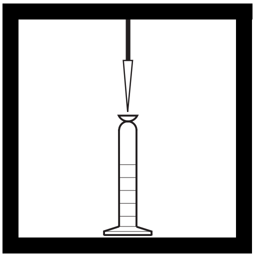
4. Add 5.0 mL of concentrated hydrochloric acid to each cylinder. Swirl to mix.

Note: *Use a Mohr pipet and pipet filler.*



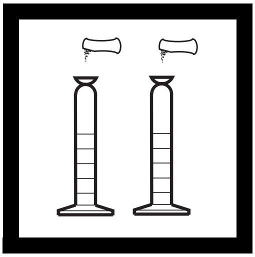
5. Add one 0.2-gram scoop of 2,2'bipyridine to each cylinder. Cap and invert to mix.

Note: *Because of the 2,2'bipyridine density, approximately 0.1 gram fills a 0.2-gram scoop.*

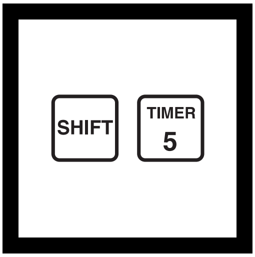


6. Add 0.5 mL of palladium activator sample to one of the mixing cylinders (the prepared sample). The other cylinder is the blank.

Note: *Use a TenSette Pipet or 0.5 mL volumetric pipet.*



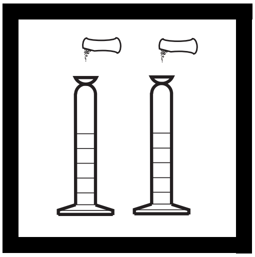
7. Add one Chromium 1 Reagent Powder Pillow to each cylinder. Stopper. Invert several times to mix.



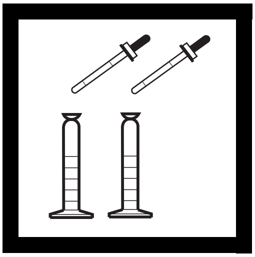
8. Press:

SHIFT TIMER

A five-minute reaction period will begin.

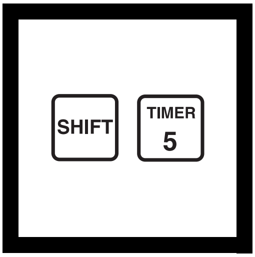


9. When the timer beeps, add one Sodium Meta Bisulfite Reagent Powder Pillow to each cylinder. Stopper. Invert several times to mix.



10. Add 1.0 mL of N,N'-Dimethyldithiooxamide Indicator Solution to each cylinder. Stopper. Invert several times to mix.

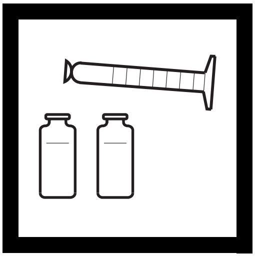
Note: *A pressure build up sometimes occurs when the indicator is added. Use a paper towel to remove to stopper if this occurs.*



11. Press:

SHIFT TIMER

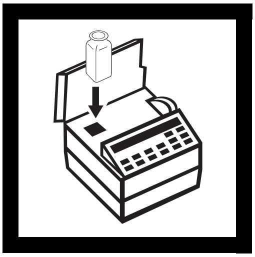
A two-minute reaction period will begin.



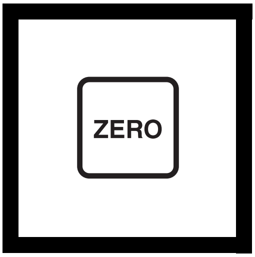
12. When the timer beeps, the display will show:

mg/L Pd

Pour the contents of each cylinder into a sample cell.



13. Place the blank in the cell holder. Close the light shield.

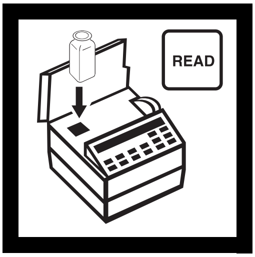


14. Press: **ZERO**

The display will show:

Zeroing. . .

then: **0. mg/L Pd**



15. Place the prepared sample into the cell holder. Close the light shield.

Press: **READ**

The display will show:

Reading. . .

then the result in mg/L Pd will be displayed.

Sampling and Storage

Collect samples in clean plastic or glass bottles. Analyze activator bath samples as soon as possible after collection. Mix the samples well before pipetting them into the graduated cylinders.

Precision

In a single laboratory using a standard solution of 162 mg/L palladium and two representative lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±1.4 mg/L palladium.

Interferences

Copper and nickel do not interfere under the reaction conditions of the test. Gold does not interfere in concentrations up to 50 mg/L.

Summary of Method

The test for palladium uses a hypobromite oxidation step which destroys the reducing agent present in palladium-tin activator solutions. The excess hypobromite is destroyed with sodium metabisulfite. The palladium then reacts under acid conditions with N,N'-dimethyldithio-oxamide to form a yellow color proportional to the palladium present. 2,2'Bipyridine is used to mask copper. This method is designed primarily for analyzing the palladium content of activator solutions used in the autocatalytic plating of printed circuit boards. Electrolytic and electroless palladium plating baths may also by analyzed by this method if the bath sample is first diluted to less than 250 mg/L palladium.

REQUIRED REAGENTS

	Cat. No.
Palladium Reagent Set (50 Tests)	23123-00

Includes: (2) 116-22, (1) 2043-99, (2) 134-49, (1) 23087-37, (2) 7095-49

Description	Quantity Required Per Test	Unit	Cat. No.
2,2'Bipyridine	0.2 g	5 g	116-22
Chromium 1 Reagent Powder Pillows	2 pillows	100/pkg	2043-99
Hydrochloric acid, ACS	10 mL	500 mL	134-49
N,N'-Dimethyldithiooxamide Indicator Solution	2 mL	100 mL MDB	23087-32
Sodium Metabisulfite Reagent Powder Pillows	2 pillows	100/pkg	7095-49
Water, deionized	40 mL	4 L	272-56

REQUIRED APPARATUS

Clippers, for opening powder pillows	1	each	968-00
Cylinder, mixing, tall-form, 25 mL	2	each	21190-40
Pipet, Mohr, 10 mL	1	each	20934-38
Pipet, TenSette, 0.1 to 1.0 mL	1	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	1	50/pkg	21856-96
Pipet Filler, safety bulb	1	each	14651-00
Sample Cells, 25 mL, matched pair		pair	20950-00
Spoon, measuring, 0.2 g	1	each	638-00

OPTIONAL APPARATUS AND REAGENTS

Palladium Standard Solution, 1000 mg/L	100 mL	23207-42
Pipet, volumetric, Class A, 0.5 mL	each	14515-34
Pour-Thru Cell Assembly Kit	each	45215-00

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

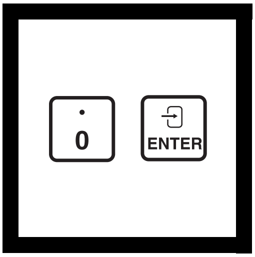
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 10053

For Soil

PCB IN SOIL (1 or 10 ppm Threshold)

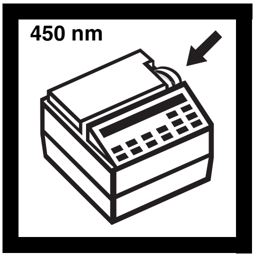
Immunoassay Method



1. Enter the stored program for absorbance.

Press: **0 ENTER**

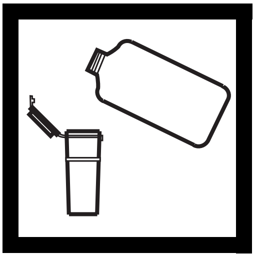
Note: *The Pour-Thru Cell cannot be used.*



2. Rotate the wavelength dial until the small display shows:

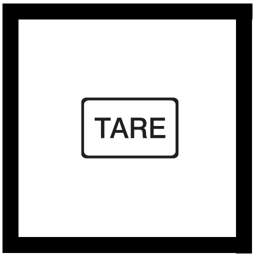
450 nm

PCB Phase 1: Soil Extraction



1. Fill the extraction vial to the 0.75-oz line with Soil Extractant Solution.

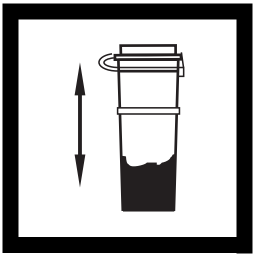
Note: *This is equivalent to adding 20 mL of Soil Extractant Solution.*



2. Place a plastic weighing boat on an analytical balance. Tare the balance.

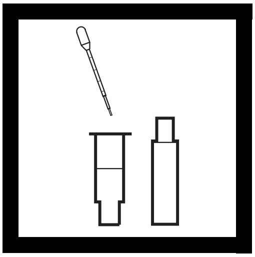
Note: *Use either the portable AccuLab Pocket Pro or a laboratory balance (see Optional Equipment and Supplies).*

3. Weigh out 10 ±0.1 g of soil in the plastic weighing boat. Carefully pour the soil from the weighing boat into the extraction vial.



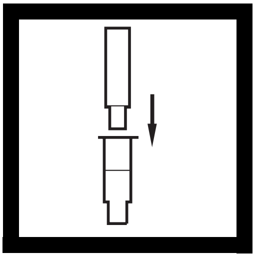
4. Cap the extraction vial tightly and shake vigorously for 1 minute.

5. Allow to settle for 1 minute. Gently open the extraction vial.



6. Using the disposable bulb pipet, withdraw 1.0-1.5 mL from the liquid (top) layer in the extraction vial. Transfer this aliquot into the filtration barrel (the <u>bottom</u> part of the filtering assembly; the plunger is inserted into it).

Note: *Do not transfer more than 1.5 mL into the barrel. The pipet is marked in 0.25-mL increments.*

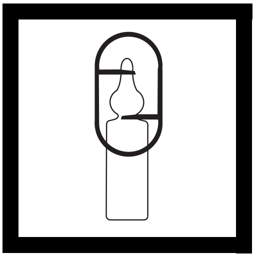


7. Insert the filtration plunger into the filtration barrel. Press firmly on the plunger until at least 0.5 mL of filtered sample is collected in the center of the plunger.

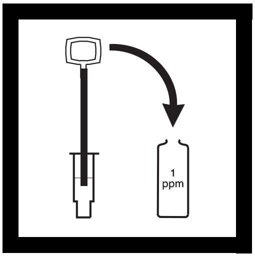
Note: *The liquid will be forced up through the filter. The liquid in the plunger is the filtered extract.*

Note: *It may be necessary to place the filtration assembly on a table and press down on the plunger.*

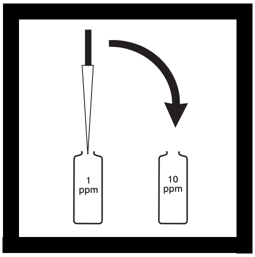
PCB Phase 2: Preparing Samples and Standards



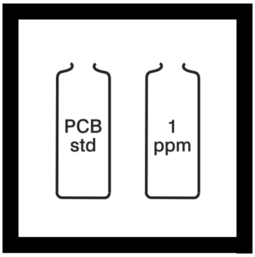
1. To prepare a 1-ppm threshold dilution, snap open a 1-ppm Dilution Ampule. Label the Dilution Ampule with appropriate information.



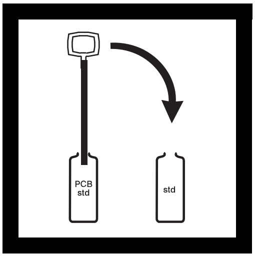
2. Using the WireTrol® pipet, withdraw 100 µL (0.1 mL) of sample extract from the filtration plunger and add it to the 1-ppm Dilution Ampule. Swirl to mix. Discard the capillary tube.



3. To prepare a 10-ppm threshold, snap open a 10-ppm Dilution Ampule. Label the Dilution Ampule. Using a TenSette Pipet, withdraw 1.0 mL from the 1-ppm Dilution Ampule (Step 2), and add it to the 10-ppm Dilution Ampule. Swirl to mix.



4. To prepare the standard, snap open a PCB Standard Ampule. Snap open a 1-ppm Dilution Ampule. Label the Dilution Ampule as "Standard."

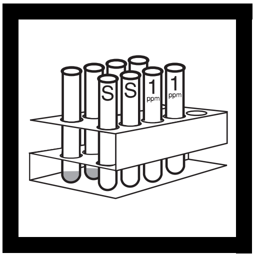


5. Using the WireTrol pipet withdraw 100 µl (0.1 mL) of the standard and add it to the 1-ppm Dilution Ampule. Swirl to mix thoroughly.

Note: *Dispense standard and sample below the level of the solution in the Dilution Ampules.*

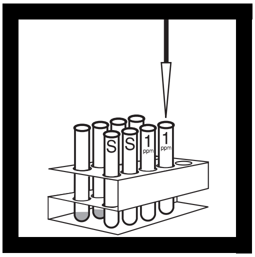
Note: *Use the standard dilution prepared above for both 1-ppm and 10-ppm thresholds. Do not further dilute the standard.*

PCB Phase 3: Immunoassay (Steps in this phase require exact timing)



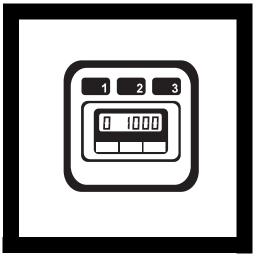
1. Label two PCB Antibody Tubes for each dilution ampule. Label two PCB Enzyme Conjugate tubes for each dilution ampule.

Note: *The PCB Conjugate and PCB Antibody tubes are matched lots. Mixing with other lots will cause erroneous results.*

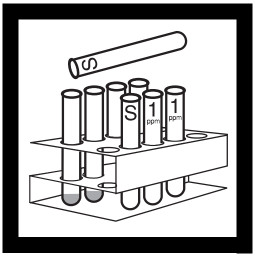


2. Use a TenSette Pipet to add a 1.0-mL aliquot from each dilution ampule prepared (1-ppm or 10-ppm) to the bottom of each appropriately labeled PCB Antibody Tube. Do this for each sample and standard. Use a new pipet tip for each solution.

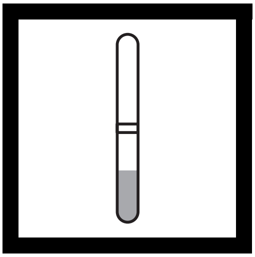
Note: *Do not touch the inside walls of the tubes.*



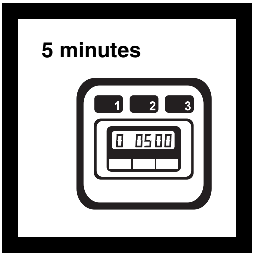
3. Begin a 10-minute reaction period.



4. At the end of the 10-minute reaction period, decant the solution from the Antibody Tubes into the respective Enzyme Conjugate Tubes.

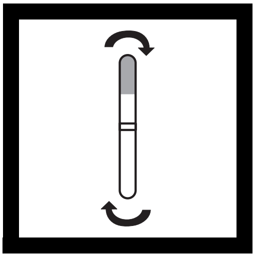


5. Invert and place the Antibody Tubes over the Enzyme Conjugate Tubes until they fit tightly onto the Enzyme Conjugate Tubes.

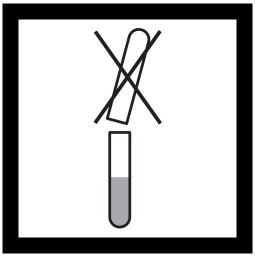


6. Begin a five-minute reaction period.

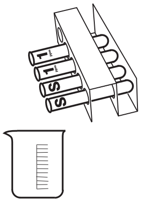
Note: *Immediately proceed with the next step.*



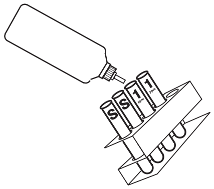
7. Immediately invert the solution repeatedly until the Antibody Tube has been filled four times and the Enzyme Conjugate has been dissolved. After the last inversion make sure that all of the solution is in the Antibody Tube and that it is upright.



8. Place the Antibody Tube in the rack and remove the Enzyme Conjugate Tube from the mouth of the Antibody Tube. Discard the used Enzyme Conjugate Tube.



9. After the five-minute period, discard the contents of the PCB Antibody Tubes into an appropriate waste container.



10. Wash each tube thoroughly and forcefully 4 times with Wash Solution. Empty the tubes into an appropriate waste container. Shake well to ensure most of the Wash Solution drains after each wash.

Note: *Wash Solution is a harmless detergent.*

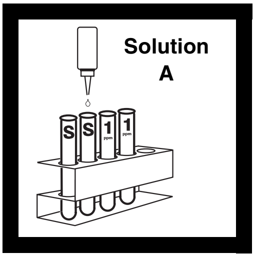
Continue to Phase 4

11. Continue to the next phase immediately.

Note: *Ensure most of the Wash Solution is drained form the tubes by turning the tubes upside down and gently tapping them on a paper towel to drain. Some foam may be left from the Wash Solution; this will not affect results.*

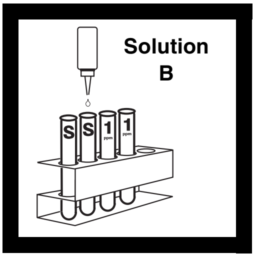
PCB Phase 4: Color Development

(Check reagent labels carefully. Reagents must be added in proper order!)



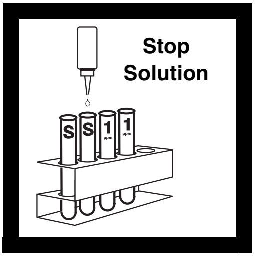
1. Add 5 drops of **Solution A** to each tube. Replace the bottle cap.

Note: *Hold all reagent bottles vertically for accurate delivery or erroneous results may occur.*



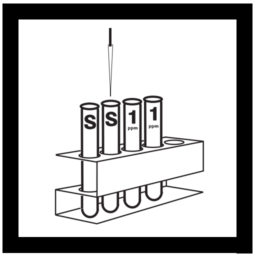
2. Begin a 2.5-minute period and immediately add 5 drops of **Solution B** to each tube. Swirl to mix. Replace the bottle cap.

Note: *Add drops to the tubes in the same order to ensure proper timing (i.e., left to right) Solution will turn blue in some or all of the tubes.*



3. Let each tube react for exactly 2.5 minutes. Then add 5 drops of **Immunoassay Stop Solution** to each tube. Replace the bottle cap.

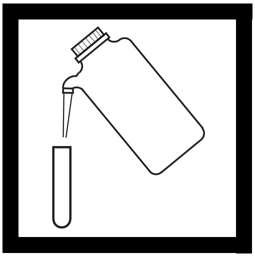
Note: *Blue solutions will turn yellow when Stop Solution is added. PCB concentration is inversely proportional to color development; a lighter color indicates higher levels of PCB.*



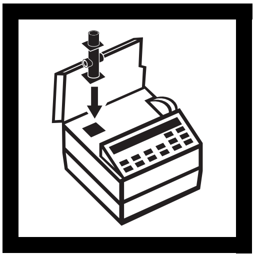
4. Using the TenSette Pipet and a new tip, add 0.5 mL of deionized water to each tube.

Swirl to mix.

PCB Phase 5: Measuring the Color

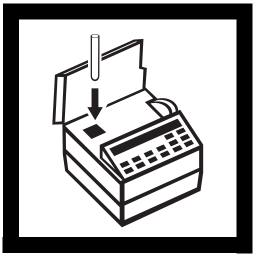


1. Fill a Zeroing Tube with deionized water (the blank). Wipe the outside of all the tubes with a tissue to remove smudges and fingerprints.

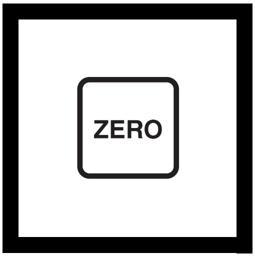


2. Insert the Immunoassay adapter into the sample cell compartment.

Note: *Align the adapter so the light beam openings face the sides of the DR/2010. Press firmly on the adapter to seat it.*



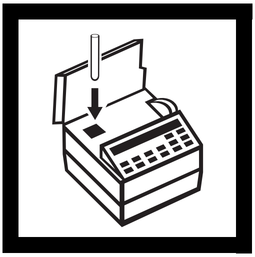
3. Place the blank in the cell holder. Place the cover on the adapter.



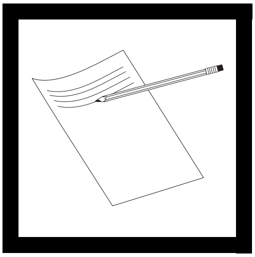
4. Press: **ZERO**

The display will show:

0.000 ABS



5. Insert Standard #1 Antibody Tube into the cell holder. Place the cover on the adapter.

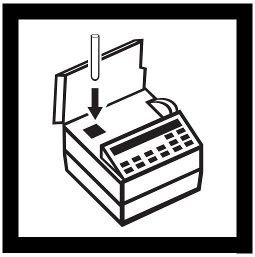


6. Record the absorbance reading.

Repeat
Steps 5 and 6
for
Standard #2

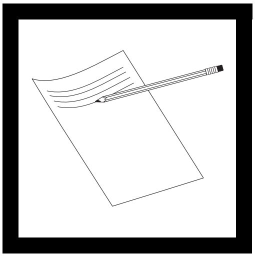
7. Repeat Steps 5 and 6 for the Standard #2 Antibody Tube.

Note: *If standard 1 and Standard 2 are more than 0.350 absorbance units apart, repeat the test beginning at Phase 2, Standard Preparation.*



8. Insert the Sample #1 Antibody Tube into the cell holder. Place the cover on the adapter.

Note: *PCB concentration is inversely proportional to the color intensity (or absorbance value). More color means less PCB in the sample.*



9. Record the absorbance reading.

Repeat
Steps 8 and 9
for
Standard #2

10. Repeat Steps 8 and 9 for the Sample #2 Antibody Tube. See Table 1 below to interpret results.

Interpreting the Results

Use Table 1 to interpret the results.

If sample absorbance is. . .	1 ppm Threshold	10 ppm Threshold
. . . less than the highest standard absorbance	Sample PCB is greater than 1 ppm	Sample PCB is greater than 10 ppm
. . . greater than the highest standard absorbance	Sample PCB is less than 1 ppm	Sample PCB is less than 10 ppm

Sensitivity

Compound		Concentration Required to Result in Positive Test at 1-ppm Threshold
PCBs		
	Arochlor 1260	0.4
	Arochlor 1254	0.4
	Arochlor 1248	1
	Arochlor 1242	2
	Arochlor 1016	4
	Arochlor 1232	4
Other Halogenated Compounds		
	2,4,6-trichloro-p-terphenyl	>10,000
	Halowax 1013	10,000
	Halowax 1051	1,000
	o,p-DDT	>10,000
	2,4-D	10,000
	Silvex	1,000
	bifenox	1,000
	tetradifon	100
	Dicofop, methyl	1,000
	dichlorofenthion	10,000
	trichloroethylene	>10,000
	1,2,4-trichlorobenzene	10,000
	2,4-dichloro-1-naphthol	50
	2,4-dichlorophenyl benzene sulfonate	1,000
	1-chloronaphthalene	>10,000
	pentachlorobenzene	>10,000
	hexachlorobenzene	>10,000
	2,5-dichloroaniline	>10,000
Miscellaneous Compounds		
	toluene	>10,000
	Naphthalene	>10,000
	DIALA(R) Oil AX	>10,000
	R-Temp fluid	>10,000
	Envirotemp 200 fluid	>10,000
	diesel fuel	>10,000
	gasoline	>10,000

Storing and Handling Reagents

- Wear protective gloves and eye wear.
- Store reagents at room temperature and out of direct sunlight (less than 80 °F or 27 °C).
- Keep aluminized pouch that contains antibody-coated tubes sealed when not in use.
- If Stop Solution or liquid from the extraction jar comes in contact with eyes, wash thoroughly with cold water and seek immediate medical help.
- Operational temperature of the reagents is 40-90 °F (5-32 °C).

Accuracy Check

To confirm results, use the standard method approved by the USEPA, Method 8015. This method is equivalent to SW-846 Method 4020 (USEPA letter, 1994).

Summary of Method

Samples, standard, and color-development reagents are added to test tubes coated with an antibody specific for PCB. The sample PCB concentration is determined by comparing the developed color intensity to that of a PCB standard. The PCB concentration is inversely proportional to the color development; a lighter color indicates a higher PCB concentration.

Pollution Prevention and Waste Management

The soil extractant (methanol) is an ignitable (D001) waste regulated by the Federal RCRA. Collect this material with laboratory solvents for disposal. If the soil samples being analyzed are contaminated with hazardous waste, the samples and resulting test waste may also need to be disposed of in accordance with RCRA.

REQUIRED REAGENTS AND STANDARDS

	Cat. No.
PCB Reagent Set (5 tests)	25859-00
Includes all consumable reagents and apparatus used in the test except PCB Standard Ampules)	
PCB Standard Ampules, U.S.A. orders, 350 µg/L, 1 mL	25851-05
(required reagent, must be ordered separately from the PCB Reagent Set. Not available for shipment outside the U.S.)	
PCB Standard Ampules, International orders, 350 µg/L, 1 mL	25851-05
(required reagent, must be ordered separately from the PCB Reagent Set)	

REQUIRED EQUIPMENT AND SUPPLIES

Description	Quantity Required Per Test	Unit	Cat. No.
Adapter, Immunoassay, DR/2010	1	each	46820-00
Cover, COD	1	each	19948-00
Clippers, large, for opening powder pillows	1	each	968-00
Gloves, poly, medium (large 25504-03)	1 pair	100/box	25504-02
Goggles, safety, vented	1	each	25507-00
Pen, laboratory, permanent, black	1	each	20920-00
TenSette Pipet, 0.1-1.0 mL	1	each	19700-01
TenSette Pipet Tips, for 19700-01	varies	50/pkg	21856-96
Timer	1	each	23480-00
WireTrol Pipet, 50/100 µL, with 250 capillary tubes	varies	each	25689-05
Zeroing Tube	1	each	26228-00
Rack, grip style	1	each	25873-00

OPTIONAL REAGENTS AND STANDARDS

Water, deionized, 4 liters	272-56
Water, deionized, 100 mL	272-42

OPTIONAL EQUIPMENT AND SUPPLIES

Ampul Breaker	each	21968-00
Balance, AccuLab	each	25568-00
Balance, Laboratory, Model SL 500	each	26105-00

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

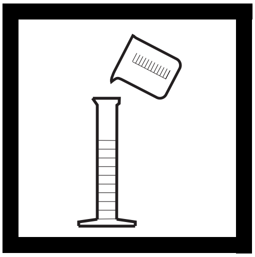
Method 8047

PHENOLS (0 to 0.200 mg/L)

For water, wastewater and seawater

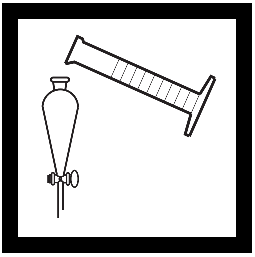
4-Aminoantipyrine Method*

USEPA accepted for reporting wastewater analysis (distillation is required; see Section II).**

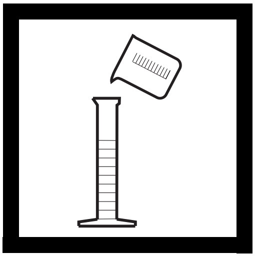


1. Measure 300 mL of deionized water in a 500-mL graduated cylinder.

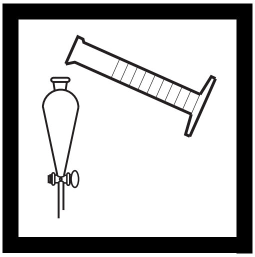
Note: *Analyze samples within four hours to avoid oxidation; see Sampling and Storage following these steps.*



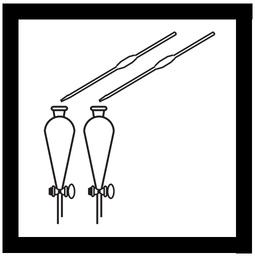
2. Pour the measured deionized water into a 500-mL separatory funnel (the blank).



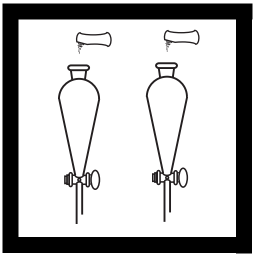
3. Measure 300 mL of sample in a 500-mL graduated cylinder.



4. Pour the measured sample into another 500-mL separatory funnel (the prepared sample).

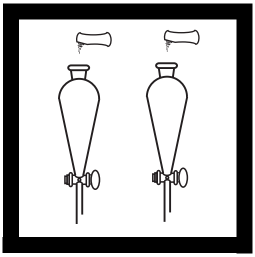


5. Add 5 mL of Hardness 1 Buffer to each separatory funnel. Stopper. Shake to mix.

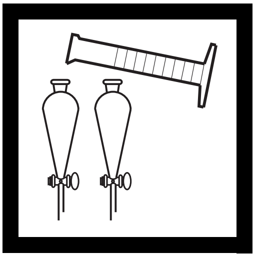


6. Add the contents of one Phenol Reagent Powder Pillow to each separatory funnel. Stopper. Shake to dissolve.

Note: *Spilled reagent will affect test accuracy and is hazardous to skin and other materials.*



7. Add the contents of one Phenol 2 Reagent Powder Pillow to each separatory funnel. Stopper. Shake to dissolve.



8. Add 30 mL of chloroform to each separatory funnel. Stopper each funnel.

Note: *Use chloroform only with proper ventilation. A fume hood is ideal.*

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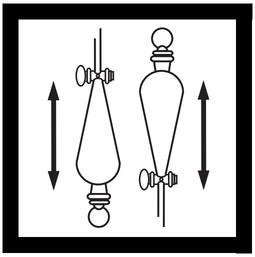
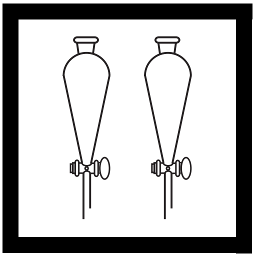
* Adapted from Standard Methods for the Examination of Water and Wastewater.

** Procedure is equivalent to USEPA method 420.1 for wastewater.

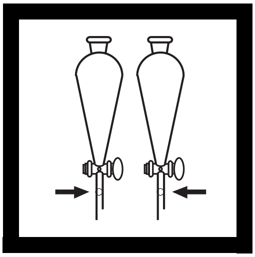


9. Invert each funnel and temporarily vent. Shake each funnel briefly and vent. Then vigorously shake each funnel for a total of 30 seconds.

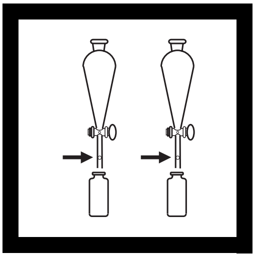


10. Remove the stoppers. Allow both funnels to stand until the chloroform settles to the bottom of the funnel.

***Note:** The chloroform will be yellow to amber if phenol is present.*



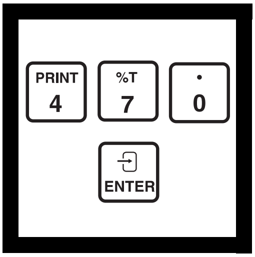
11. Insert a pea size cotton plug into the delivery tube of each funnel.



12. Drain the chloroform layer into separate 25-mL sample cells.

***Note:** The cotton removes any suspended water or particles from the chloroform.*

***Note:** Proceed promptly through the rest of the procedure; chloroform will evaporate, causing high readings.*



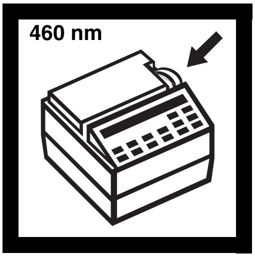
13. Enter the stored program number for phenols.

Press: **4 7 0 ENTER**

The display will show:

Dial nm to 460

***Note:** The Pour-Thru Cell cannot be used with this procedure.*



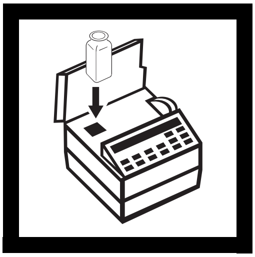
14. Rotate the wavelength dial until the small display shows:

460 nm

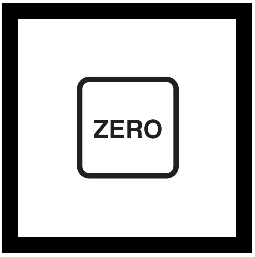
When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

then**:** **mg/L PHENOL**



15. Place the blank into the cell holder. Close the light shield.



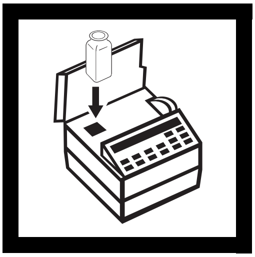
16. Press: **ZERO**

The display will show:

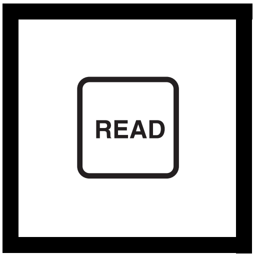
Zeroing. . . .

then:

0.000 mg/L PHENOL



17. Place the prepared sample into the cell holder. Close the light shield.



18. Press: **READ**

The display will show:

Reading. . . .

then the results in mg/L as phenol will be displayed.

Sampling and Storage

The most reliable results are obtained when samples are analyzed within four hours after collection. The following storage instructions are necessary only when prompt analysis is impossible. Collect 500 mL of sample in clean glass containers and add the contents of two Copper Sulfate Powder Pillows. Adjust the sample pH to 4 or below with 10% Phosphoric Acid Solution. Store at 4 °C (39 °F) or lower and analyze within 24 hours.

Accuracy Check

Standard Solution Method

Verify accuracy of the test by performing the analysis using known phenol standard solutions in place of the test sample. For greatest accuracy, standard solutions should be analyzed periodically to verify test accuracy and when new reagent lots are first used. Prepare standards as follows:

a) Weigh out 1.00 g of phenol, ACS. Transfer to a 1-liter volumetric flask. Dilute to the mark with freshly boiled and cooled deionized water. This is a 1-g/L stock solution.

b) Transfer 1 mL of the 1-g/L stock solution to a 100-mL volumetric flask. Dilute to the mark with deionized water. This is a 10-mg/L working solution.

c) Prepare 0.06, 0.12 and 0.18 mg/L standard solutions by using a pipet to add 3, 6, and 9 mL of the 10-mg/L working solution, respectively, to three separate 500-mL volumetric flasks. Dilute each to the mark with deionized water.

d) Perform the procedure with each of the three standard solutions and verify that the test results are correct.

Precision

In a single laboratory, using a standard solution of 0.08 mg/L phenol and two lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±0.0047 mg/L phenol.

Estimated Detection Limit (EDL)

The EDL for program 470 is 0.003 mg/L. The EDL is the calculated lowest average concentration in a deionized water matrix that is different from zero with a 99% level of confidence. For more information on derivation and use of Hach's estimated detection limit, see Section I.

Interferences

The sample pH must be between 3 and 11.5 for the best results. In the presence of sulfides or suspended matter, the following pretreatment will be necessary:

a) Fill a clean 500-mL graduated cylinder to the 350-mL mark with sample. Pour the sample into a clean 500-mL erlenmeyer flask.

b) Add the contents of one Sulfide Inhibitor Reagent Powder Pillow. Swirl to mix.

c) Filter 300 mL of the sample through a folded filter paper. Use this solution in Step 4.

Interference can be caused by reducing agents and oxidizing agents such as chlorine.

Sample distillation (below) will eliminate interferences.

a) Set up the distillation apparatus for the test by assembling the general purpose apparatus as shown in the Hach Distillation Apparatus Manual. Use the 500-mL erlenmeyer flask to collect the distillate. It may be necessary to elevate the flask with a laboratory jack. Place a stirring bar into the distillation flask.

b) Measure 300 mL of sample in a 500-mL graduated cylinder. Pour it into the distillation flask.

c) Using a serological pipet, add 1 mL of Methyl Orange Indicator Solution to the distillation flask. Turn on the heater power switch. Set the stir control to 5.

d) Add Phosphoric Acid Solution, 10%, drop-wise, until the indicator changes from yellow to orange.

e) Add the contents of one Copper Sulfate Powder Pillow and allow to dissolve (omit this step if copper sulfate was used to preserve the sample.)

f) Turn on the water and adjust so a constant flow of water is maintained through the condenser. Set the heat control to setting 10.

g) Turn off the still after collecting 275 mL of distillate.

h) Fill a 25-mL graduated cylinder to the 25-mL mark with deionized water. Turn the still back on. Add the water to the flask. Resume heating until another 25 mL of distillate is collected.

Summary of Method

The 4-aminoantipyrine method determines all ortho- and meta-substituted phenols or napthols but not para-substituted phenols. These phenols react with 4-aminoantipyrine in the presence of potassium ferricyanide to form a colored antipyrine dye. This dye is then extracted from aqueous solution with chloroform and the color is measured at 460 nm.

Sensitivity of the method varies with the type of phenolic compound. Because a water sample may contain various types of phenolic compounds, the results of the test are expressed as the equivalent concentration of phenol. Wastewater and seawater samples may require pretreatment.

REQUIRED REAGENTS

	Cat. No.
Phenols Reagent Set (100 Tests)	22439-00

Includes: (3) 424-49, (2) 14458-17, (4) 1836-66, (2) 872-99

Description	Quantity Required Per Test	Unit	Cat. No.
Buffer Solution, Hardness 1	10 mL	500 mL	424-49
Chloroform, ACS	60 mL	4 L	14458-17
Phenol 2 Reagent Powder Pillow	2 pillows	50/pkg	1836-66
Phenol Reagent Powder Pillow	2 pillows	100/pkg	872-99
Water, deionized	300 mL	4 L	272-56

REQUIRED APPARATUS

Description	Quantity Required Per Test	Unit	Cat. No.
Clippers, for opening powder pillows	1	each	968-00
Cotton Balls	2	100/pkg	2572-01
Cylinder, graduated, 50 mL	1	each	508-41
Cylinder, graduated, 500 mL	1	each	508-49
Funnel, separatory, 500 mL	2	each	520-49
Pipet, volumetric, Class A, 5.00 mL	1	each	14515-37
Ring, support, 4"	2	each	580-01
Sample Cell, 25 mL, matched pair	2	each	20950-00
Stand, support, 5" x 8" base	1	each	563-00

OPTIONAL REAGENTS

Copper Sulfate Powder Pillows	50/pkg	14818-66
Methyl Orange Indicator Solution	500 mL	148-49
Phenol, ACS	113 g	758-14
Phosphoric Acid Solution, 10%	100 mL	14769-32
Sulfide Inhibitor Reagent Powder Pillows	100/pkg	2418-99

OPTIONAL APPARATUS

Balance, AccuLab Pocket Pro 150B, handheld, 9V	each	25568-00
Cylinder, 25 mL, graduated	each	508-40
Distillation Apparatus General Purpose Accessories	each	22653-00
Distillation Apparatus Heater, 115 V	each	22744-00
Distillation Apparatus Heater, 230 V	each	22744-02
Filter Paper, 12.5 cm folded	100/pkg	1894-57
Flask, 500 mL erlenmeyer	each	505-49
Flask, volumetric, Class A, 100 mL	each	14574-42
Flask, volumetric, Class A, 500 mL	each	14574-49
Flask, volumetric, Class A, 1000 mL	each	14574-53
Funnel, 65 mm poly	each	1083-67
Jack, laboratory	each	22743-00
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
Pipet, serological, 1.0 mL	each	532-35
Pipet, volumetric, Class A, 1.00 mL	each	14515-35
Pipet, volumetric, Class A, 3.00 mL	each	14515-03
Pipet, volumetric, Class A, 6.00 mL	each	14515-06
Pipet, volumetric, Class A, 9.00 mL	each	14515-09
Pipet Filler, safety bulb	each	14651-00

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

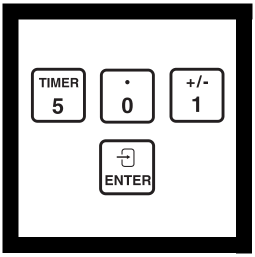
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8007

PHOSPHONATES (0-2.5 to 0-125 mg/L)

For water, wastewater, and seawater

Persulfate UV Oxidation Method*



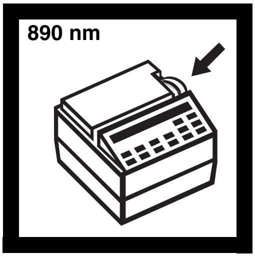
1. Enter the stored program number for phosphonates.

Press: **5 0 1 ENTER**

The display will show:

Dial nm to 890

Note: *The Pour-Thru Cell can be used with 25 mL reagents only.*



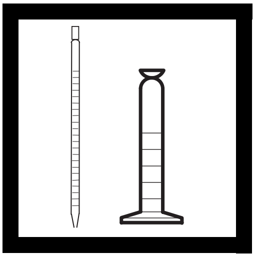
2. Rotate the wavelength dial until the small display shows:

890 nm

When the correct wavelength is dialed in the display will quickly show: **Zero Sample**

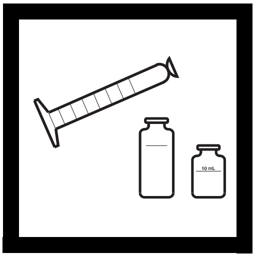
then:

mg/L PHOSPHONATE



3. Choose the appropriate sample size from Table 1 below. Pipet the chosen sample volume into a 50-mL graduated mixing cylinder. Dilute the sample to 50 mL with deionized water. Mix well.

Note: *Clean glassware with 1:1 hydrochloric acid, followed by a deionized water rinse. Do not use a commercial detergent.*



4. Fill a **10-mL** sample cell to the 10-mL mark with diluted sample from Step 3 (this is the blank).

Fill a **25-mL** sample cell to the 25-mL mark with diluted sample from Step 3.

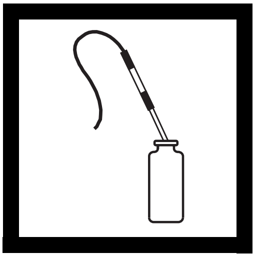
Table 1

Expected Range (mg/L phosphonate)	Sample Volume (mL)
0-2.5	50
0-5	25
0-12.5	10
0-25	5
0-125	1

---

* Adapted from Blystone, P.; Larson, P., A *Rapid Method for Analysis of Phosphonate Compounds*, International Water Conference, Pittsburgh, Pa. (Oct. 26-28, 1981).

5. Add the contents of one Potassium Persulfate for Phosphonate Powder Pillow to the 25-mL sample cell. Swirl to mix. This sample cell contains the prepared sample.

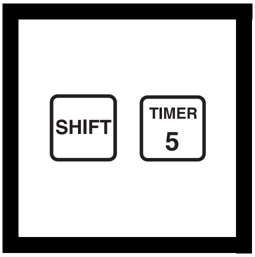


6. Insert the ultraviolet (UV) lamp into the prepared sample.

Note: *Wear UV safety goggles while the lamp is on.*

Note: *Do not handle the lamp surface. Fingerprints will etch the glass. Wipe lamp with a soft, clean tissue between samples. Do not use detergents with phosphates to wash glassware.*

Note: *A specially designed cord adapter is available for performing two digestions with a single power supply. A second UV Lamp is required.*



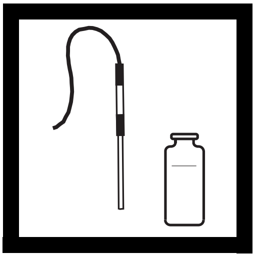
7. Turn on the UV lamp to digest the prepared sample.

Press: **SHIFT TIMER**

A 10-minute reaction period will begin.

Note: *Phosphonates are converted to orthophosphate in this step.*

Note: *The digestion step may take less time. Contaminated samples or a weak lamp could result in incomplete digestion. Check efficiency by running a longer digestion to see if readings increase.*

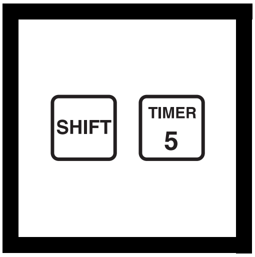


8. When the timer beeps, turn off the UV lamp. Remove it from the 25-mL sample cell.

9. Pour 10 mL of sample from the 25-mL sample cell into a second clean, dry 10-mL sample cell. This is the prepared sample.

10. Add the contents of one PhosVer 3 Phosphate Reagent Powder Pillow to each sample cell. Swirl immediately to mix.

Note: *A blue color will form if phosphate is present. Sample and blank cells may develop color.*

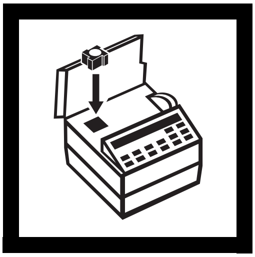


11. Press:

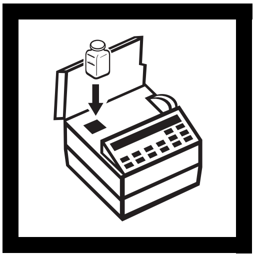
SHIFT TIMER

A two-minute reaction period will begin.

Note: *If sample is colder than 15 °C, 4 minutes are required for color development.*



12. Insert the 10-mL Cell Riser into the sample cell compartment.

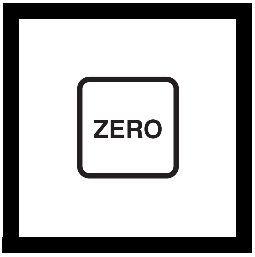


13. When the timer beeps, the display will show:

mg/L PHOSPHONATE

Place the blank into the cell holder. Close the light shield.

Note: *Perform Steps 15-16 within three minutes after the timer beeps.*



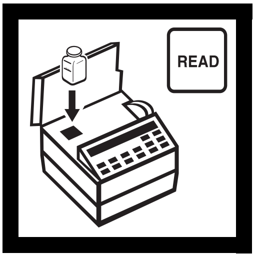
14. Press: **ZERO**

The display will show:

Zeroing. . .

then:

0.0 mg/L PHOSPHONATE



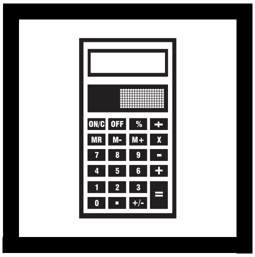
15. Place the prepared sample into the cell holder. Close the light shield.

Press: **READ**

The display will show:

Reading. . .

then a value in mg/L phosphonate will be displayed. Multiply this value by the appropriate multiplier from *Table 2* to obtain the actual concentration of phosphonates in the sample.



16. Results may be expressed in terms of active phosphonate by using the appropriate conversion factor and the equation found in *Table 3*.

Table 2

Sample Volume (mL)	Multiplier
50	0.1
25	0.2
10	0.5
5	1.0
1	5.0
Phosphonate concentration = Instrument Reading x Multiplier	

Table 3

Phosphonate Type	Conversion Factor
PBTC	2.84
NTP	1.050
HEDPA	1.085
EDTMPA	1.148
HMDTMPA	1.295
DETPMPA	1.207
HPA	1.49
Active Phosphonate (mg/L) = Phosphonate concentration from Step 15 x Conversion Factor	

Sampling and Storage

Collect samples in clean plastic or glass bottles that have been cleaned with 1:1 Hydrochloric Acid Solution and rinsed with deionized water. Do not use a commercial detergent. If prompt analysis is impossible, adjust the pH to 2 or less with about 2 mL of sulfuric acid, ACS, per liter of sample. Store at 4 °C (39 °F) or below. Preserved samples can be stored at least 24 hours. See *Section 1* for more information on dilution factors, cleaning instructions, etc.

Accuracy Check

Ideally, you should prepare a solution containing the phosphonate product being used. This checks UV conversion of phosphonate to orthophosphate.

Interferences

When testing a 5-mL sample volume, the following may interfere when present in concentrations exceeding those listed below:

The interference levels will decrease as the sample size increases. For example, copper does not interfere at or below 100 mg/L for a 5.00 mL sample. If the sample volume is increased to 10.00 mL, copper will begin to interfere above 50 mg/L.

Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment; see *pH Interferences* in *Section 1.*

Phosphites and organophosphorus compounds other than phosphonates react quantitatively. Meta and polyphosphates do not interfere.

Summary of Method

This method is directly applicable to boiler and cooling tower samples. The procedure is based on a UV catalyzed oxidation of phosphonate to orthophosphate. Range may be as low as 0 to 2.5 mg/L or as high as 0 to 125 mg/L.

Phosphonate is converted to orthophosphate during the UV digestion. Both the sample and the blank will develop color if orthophosphate is present in the sample. The increase in color in the sample is proportional to the phosphate produced in the digestion.

REQUIRED REAGENTS

Description	Cat. No
Phosphonate Reagent Set (100 tests, 10 mL sample) Includes: (2) 21060-69, (1) 20847-69	24297-00

Description	Quantity Required Per Test	Unit	Cat. No
PhosVer 3 Phosphate Reagent Powder Pillows, 10 mL	2 pillows	100/pkg	21060-69
Potassium Persulfate Powder Pillow for Phosphonate	1 pillow	100/pkg	20847-69
Water, deionized	varies	4 L	272-56

REQUIRED APPARATUS

Cell Riser, 10-mL, DR/2010	1	each	45282-00
Cell, sample, 1-inch, 10-mL	2	pair	24954-02
Cell, sample, 1-inch, 25-mL	2	pair	20950-00
Cylinder, mixing, graduated, 50 mL	1	each	1896-41
Goggles, UV safety	1	each	21134-00
Pipet, serological, 25 mL	1	each	2066-40
Pipet Filler, safety bulb	1	each	14651-00
UV Lamp with power supply, 115 Vac	1	each	20828-00
OR			
UV Lamp with power supply, 230 Vac	1	each	20828-02

OPTIONAL REAGENTS

Description	Unit	Cat. No
Hydrochloric Acid, 6.0 N (1:1)	500 mL	884-49
Sulfuric Acid, ACS	500 mL	979-49

OPTIONAL APPARATUS

Cord Adapter, single to dual UV lamp	each	19485-00
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
Pipet, serological, 2 mL	each	532-36
Pipet, TenSette, 1-10 mL	each	19700-10
Pipet Tips, for 19700-10 Tensette Pipet	50/pkg	21997-96
Pipet Tips, for 19700-10 Tensette Pipet	1000/pkg	21997-28
Thermometer, -20 to 105 °C	each	1877-01
UV Lamp, without power supply	each	20823-00

OPTIONAL 25 mL ANALYSIS ITEMS

Phosphonate Reagent Set for 25 mL samples (100 tests)	each	22440-00
Pour-Thru Cell Assembly Kit (for 25 mL reagents only)	each	45215-00

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

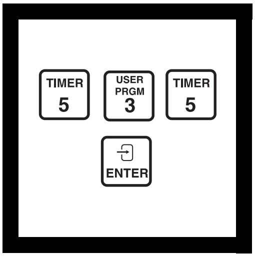
Method 8048

PHOSPHORUS, REACTIVE (0.00 to 5.00 mg/L PO_4^{3-})

PhosVer 3 Method, Test 'N Tube Procedure

For water, wastewater, and seawater

USEPA accepted for reporting wastewater analysis*

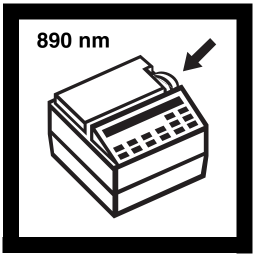


1. Enter the stored program number for reactive phosphorus Test 'N Tube.

Press: **5 3 5 ENTER**

The display will show:

Dial nm to 890

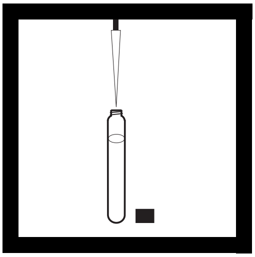


2. Rotate the wavelength dial until the small display shows:

890 nm

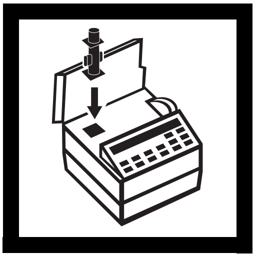
When the correct wavelength is dialed in, the display will quickly show: **Zero Sample**

then: **mg/L PO_4^{3-} TNT**



3. Use a TenSette Pipet to add 5.0 mL of sample to a Reactive Phosphorus Test 'N Tube Dilution Vial. Cap and mix.

Note: *Run a reagent blank for this test. Use deionized water in place of the sample. Subtract this result from all test results run with this lot of PhosVer 3 Reagent.*



4. Place the COD Vial Adapter into the cell holder with the marker to the right.

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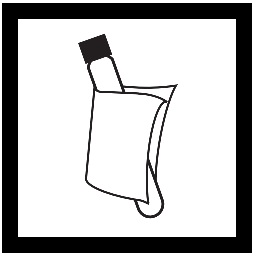
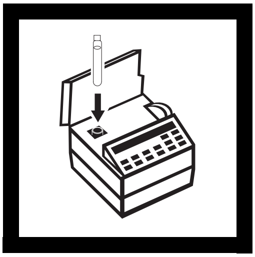
* Procedure is equivalent to USEPA Method 365.2 and Standard Method 4500-PE for wastewater.

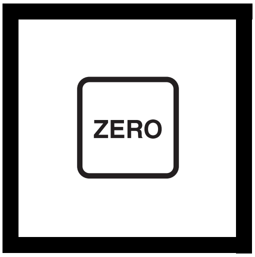


5. Clean the outside of the vial with a towel.

Note: *Wiping with a damp towel, followed by a dry one, will remove fingerprints or other marks.*



6. Place the vial into the adapter with the Hach logo facing the front of the instrument. Place the cover on the adapter.



7. Press: **ZERO**

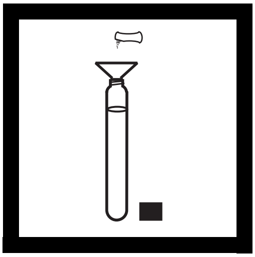
The display will show:

Zeroing. . .

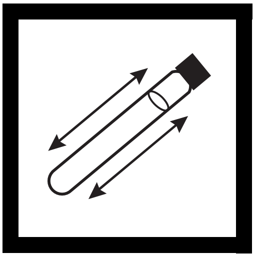
then:

0.00 mg/L PO_4^{3-} TNT

Note: *For multiple samples from the same source, zero only on the first sample. Read the remaining samples after adding the PhosVer 3 Reagent. Subtract the PhosVer 3 Reagent blank value from each reading.*

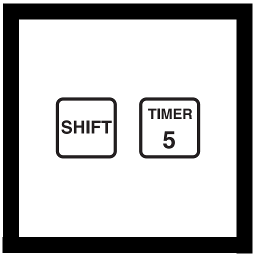


8. Using a funnel, add the contents of one PhosVer 3 Phosphate Powder Pillow to the vial.



9. Cap the vial tightly and shake for 10-15 seconds.

Note: *The powder will not completely dissolve.*

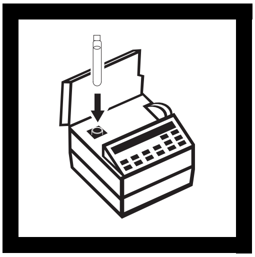


10. Press:

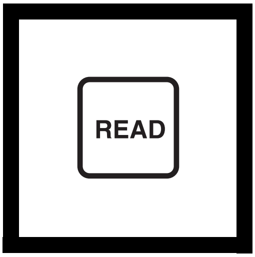
SHIFT TIMER

A 2-minute reaction time will begin.

Note: *Read samples between 2 and 8 minutes.*



11. When the timer beeps, place the vial in the adapter with the Hach logo facing the front of the instrument. Place the cover on the adapter.



12. Press: **READ**

The display will show:

Reading. . .

then the results in mg/L PO_4^{3-} will be displayed.

Forms ▲▼ P
PO_4^{3-}
P_2O_5

Sampling and Storage

Collect samples in plastic or glass bottles that have been acid cleaned with 1:1 Hydrochloric Acid Solution and rinsed with deionized water. Do not use commercial detergents containing phosphate for cleaning glassware used in this test. The sample should have a neutral pH (6-8 pH) and be at room temperature before adding reagents.

Analyze samples immediately after collection for best results. If prompt analysis is impossible, preserve samples for up to 48 hours by filtering immediately and storing at 4 °C. Warm to room temperature before analysis.

Accuracy Check

Standard Additions Method

***Note:** Clean glassware with 1:1 hydrochloric acid solution. Rinse again with deionized water. Do not use detergents containing phosphates to clean glassware.*

a) Fill three 25-mL graduated mixing cylinders with 25 mL of sample.

b) Snap the neck off a Phosphate Voluette Ampule Standard, 50 mg/L as PO_4^{3-}.

c) Use the TenSette Pipet to add 0.1 mL, 0.2 mL and 0.3 mL, respectively, to the three 25-mL aliquots of sample prepared in *step a*. Mix well.

d) Analyze each sample from Step C as described in the procedure. Use 5 mL of the prepared sample for each test. The concentration should increase as follows: 0.2 mg/L, 0.4 mg/L, 0.6 mg/L PO_4^{3}, respectively.

e) If these increases do not occur, see *Standard Additions* in *Section I* for more information.

Standard Solution Method

To check accuracy, use a 1.0 mg/L Phosphate Standard Solution listed under Optional Reagents. Or, prepare by pipetting 2.0 mL of solution from a Voluette Ampule Standard for Phosphate, 50 mg/L as PO_4^{3-}, into a 100-mL Class A volumetric flask. Fill to the line with deionized water. Substitute this standard for the sample and perform the procedure as described. The mg/L PO_4^{3-} reading should be 1.0 mg/L.

Interferences

Large amounts of turbidity may cause inconsistent test results because acid in the powder pillows may dissolve some of the suspended particles and because of variable desorption of orthophosphate from the particles.

The PhosVer 3 Phosphate Reagent Powder Pillows should be stored in a cool, dry environment.

The following may interfere when present in concentrations exceeding these listed below:

Aluminum	200 mg/L
Chromium	100 mg/L
Copper	10 mg/L
Iron	100 mg/L
Nickel	300 mg/L
Silica	50 mg/L
Silicate	10 mg/L
Sulfide	6 mg/L
Zinc	80 mg/L

Sulfide interference may be removed by oxidation with Bromine Water as follows:

a) Measure 25 mL of sample into a 50-mL beaker.

b) Swirling constantly, add Bromine Water drop-wise until a permanent yellow color develops.

c) Swirling constantly, add Phenol Solution dropwise until the yellow color just disappears. Proceed with *step 3*.

Arsenate interferes at all levels.

Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment; see *pH Interferences* in *Section I.*

Precision

In a single laboratory, using a standard solution of 5.00 mg/L PO_4^{3-} and two lots of reagent with a DR/2010, a single operator obtained a standard deviation of ±0.06 mg/L PO_4^{3-}.

Estimated Detection Limit (EDL)

The EDL for program 535 is 0.01 mg/L PO_4^{3-}. The EDL is the calculated lowest average concentration in a deionized water matrix that is different from zero with a 99% level of confidence. For more information on derivation and use of Hach's estimated detection limit, see Section I.

Sample Disposal Information

Final samples will contain molybdenum. In addition, final samples will have a pH less than 2 and are considered corrosive (D002) by the Federal RCRA.

Summary of Method

Orthophosphate reacts with molybdate in an acid medium to produce a phosphomolybdate complex. Ascorbic acid then reduces the complex, giving an intense molybdenum blue color.

REQUIRED REAGENTS

Description	Unit	Cat. No.
Reactive Phosphorus Test ’N Tube Reagent Set	50 tests	27425-45
Includes: (1) 21060-46, (50) Ortho Phosphate Test ’N Tube Dilution Vials*		

Description	Quantity Required Per Test	Unit	Cat. No.
PhosVer 3 Phosphate Reagent Powder Pillows	1 Pillow	50/pkg	21060-46
50 Ortho Phosphate Test ’N Tube Dilution Vials		50/pkg	*

REQUIRED APPARATUS

Description	Quantity Required Per Test	Unit	Cat. No.
Test ’N Tube Vials	1	25/pkg	25831-25
COD Vial Adapter, DR/2010	1	each	44799-00
Funnel, micro	1	each	25843-35
Pipet, TenSette, 1 to 10 mL		each	19700-10
Pipet Tips, for 19700-10 TenSette Pipet		50/pkg	21997-96
Test Tube Rack	1-3	each	18641-00

OPTIONAL REAGENTS

Description	Unit	Cat. No.
Bromine Water, 30 g/L	29 mL	2211-20
Hydrochloric Acid Standard Solution, 6.0 N (1:1)	500 mL	884-49
Phenol Solution, 30 g/L	29 mL	2112-20
Phosphate Standard Solution, 1 mg/L as PO_4^{3-}	500 mL	2569-42
Phosphate Standard Solution, Voluette Ampule, 50 mg/L as PO_4^{3-}, 10 mL	16/pkg	171-10

OPTIONAL APPARATUS

Description	Unit	Cat. No.
Ampule Breaker Kit	each	21968-00
Aspirator, vacuum	each	2131-00
Cylinder, Graduated, Mixing, 25 mL	each	20886-40
Filter Holder, 47 mm, 300 mL, graduated	each	13529-00
Filter Membrane, 47 mm, 0.45 microns	100/pkg	13530-01
Flask, filtering, 500 mL	each	546-49
pH Indicator Paper, 1 to 11 pH units	5 rolls/pkg	391-33
pH Meter, EC10, portable	each	50050-00
Pipet Filler, Safety Bulb	each	14651-00
Pipet, TenSette, 0 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 5 mL	each	14515-37
Stopper, No. 7, one hole	6/pkg	2119-07
Tubing, rubber	12 feet	560-19

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

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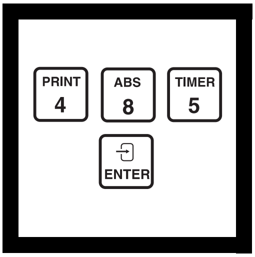
* These items are not sold separately.

Method 8178

PHOSPHORUS, REACTIVE (0 to 30.00 mg/L PO_4^{3-})

(Also called Orthophosphate) Amino Acid Method* For water, wastewater, seawater



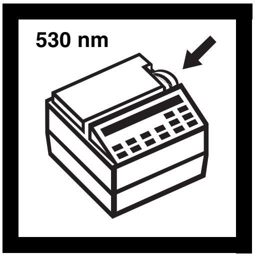
1. Enter the stored program number for the reactive phosphorus, amino acid method.

Press: **4 8 5 ENTER**

The display will show:

Dial nm to 530

Note: *The Pour-Thru Cell can be used with this procedure.*

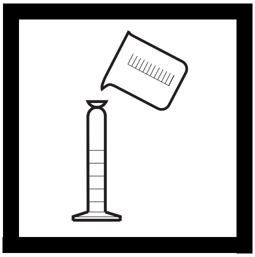


2. Rotate the wavelength dial until the small display shows:

530 nm

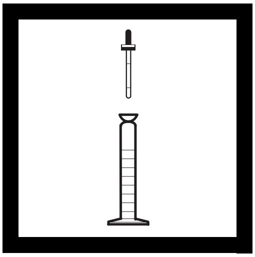
When the correct wavelength is dialed in, the display will quickly show: **Zero Sample**

then: **mg/L PO_4^{3-} AA**

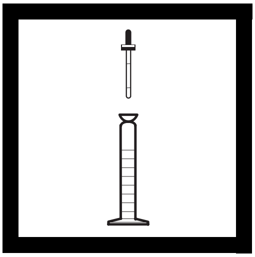


3. Fill a 25-mL graduated mixing cylinder with 25 mL of sample.

Note: *A reagent blank should be run with each lot of reagent. Repeat the test using deionized water as a sample. Subtract this value from each result obtained with this lot of reagent.*



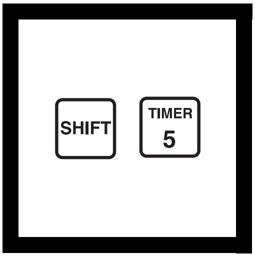
4. Add 1 mL of Molybdate Reagent using a 1-mL calibrated dropper.



5. Add 1 mL of Amino Acid Reagent Solution. Stopper and invert several times to mix (the prepared sample).

Note: *A blue color will form if phosphate is present.*

Note: *Substitute the contents of one Amino Acid Reagent Powder Pillow for 1 mL of amino acid reagent solution if desired.*

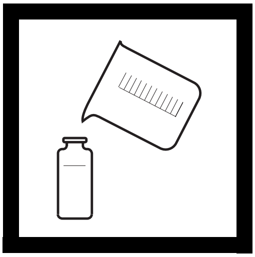


6. Press:

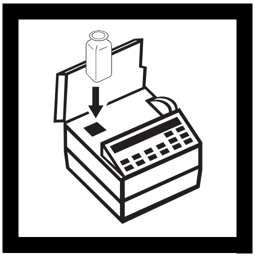
SHIFT TIMER

A 10-minute reaction period will begin.

Note: *Do step 7 while the timer is running.*



7. Pour 25 mL of sample (the blank) into a sample cell.



8. When the timer beeps, the display will show:

mg/L PO_4^{3-} AA

Place the blank into the cell holder. Close the light shield.

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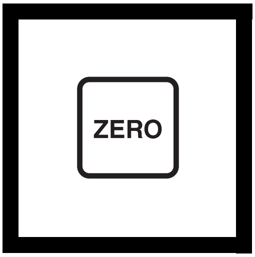
* Adapted from *Standard Methods for the Examination of Water and Wastewater.*



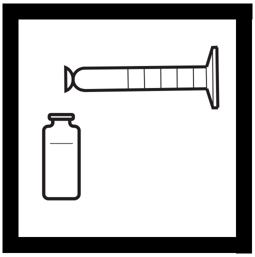
9. Press: **ZERO**

The display will show:

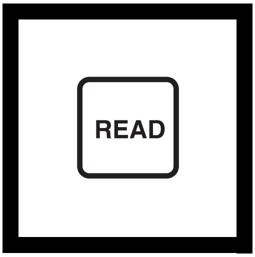
Zeroing. . .

then:

0.00 mg/L PO_4^{3-} AA



10. Pour the prepared sample into a sample cell. Place the prepared sample into the cell holder. Close the light shield.



11. Press: **READ**

The display will show:

Reading. . .

then the result in mg/L PO_4^{3-} will be displayed.

Forms ▲▼ P

PO_4^{3-}

P_2O_5

Sampling and Storage

Collect samples in clean plastic or glass bottles that have been cleaned with 1:1 Hydrochloric Acid Solution and rinsed with deionized water. Do not use a commercial detergent containing phosphate for cleaning glassware used in this test.

Analyze samples immediately for best results. If prompt analysis is not possible, preserve samples by filtering immediately and storing the sample at 4 °C (39 °F) for up to 48 hours.

Accuracy Check

Standard Additions Method

a) Fill three 25-mL graduated mixing cylinders with 25 mL of sample.

b) Snap the neck off a Phosphate Voluette Ampule Standard Solution, 500 mg/L as PO_4^{3-}.

c) Use the TenSette Pipet to add 0.1 mL, 0.2 mL and 0.3 mL of standard, respectively, to the three 25-mL mixing cylinders. Mix well.

d) Analyze each sample as described in the procedure and compare the results with that of the original test sample. Each 0.1-mL addition of standard should cause an increase of 2.0 mg/L orthophosphate (PO_4^{3-}).

e) If these increases do not occur, see Standard Additions (Section I) for more information.

Standard Solution Method

A 10.0 mg/L phosphate standard can be prepared by pipetting 10.0 mL of a Phosphate Standard Solution, 50 mg/L as PO_4^{3-}, into a 50-mL volumetric flask. Dilute to volume with deionized water.

Or, prepare a 10.0-mg/L PO_4^{3-} standard solution using the TenSette Pipet to add 1.00 mL of Phosphate Voluette Ampul Standard, 500 mg/L as PO_4^{3-}, into a 50-mL volumetric flask. Dilute to volume with deionized water.

For proof of accuracy, substitute this standard for the sample and perform the test as described. The mg/L PO_4^{3-} reading should be 10 mg/L.

Precision

In a single laboratory using a standard solution of 12.0 mg/L PO_4^{3-} and two lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±0.02 mg/L PO_4^{3-}.

Interferences

Samples with large amounts of turbidity may give inconsistent results. Some of the suspended particles may dissolve because of the acid used in the test. Also, results will vary because of variable desorption of orthophosphate from the particles. For highly turbid or colored samples, add 1 mL of 10 N Sulfuric Acid Standard Solution to another 25-mL sample. Use this in place of the sample to zero in Step 9. Use a pipet and pipet filler when measuring the sulfuric acid.

For best results the temperature of the sample should be 21 ±3 °C (70 ±5 °F).

Sulfide interferes. For samples with sulfide concentrations less than 5 mg/L use the following procedure to eliminate the interference:

a) Measure 50 mL of sample into a graduated cylinder. Pour the measured sample into a 125-mL erlenmeyer flask.

b) Add Bromine Water drop-wise with constant swirling until permanent yellow color develops.

c) Add Phenol Solution drop-wise until the yellow color just disappears. Use this solution in steps 3 and 7 of the procedure.

Nitrites bleach the blue color. Remove nitrite interference by adding 0.05 g of sulfamic acid to the sample. Swirl to mix. Continue with Step 4.

The following may interfere if present in concentrations exceeding those listed below:

Calcium	10,000 mg/L as $CaCO_3$
Chloride	150,000 mg/L as Cl^-
Magnesium	40,000 mg/L as $CaCO_3$

When phosphate is determined in water containing high salt levels, low results may occur. To eliminate this interference, dilute the sample until two successive dilutions yield approximately the same result.

As the concentration of phosphate increases, the color changes from blue to green, then to yellow and finally to brown. The brown color may suggest a concentration as high as 100,000 mg/L PO_4^{3-}. If a color other than blue is formed, dilute the sample and retest.

Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment; see *pH Interferences* in *Section I.*

Summary of Method

In a highly acidic solution, ammonium molybdate reacts with orthophosphate to form molybdophosphoric acid. This complex is then reduced by the amino acid reagent to yield an intensely colored molybdenum blue compound.

REQUIRED REAGENTS

	Cat. No.
High Range Reactive Phosphorus Reagent Set (100 Test)	22441-00

Includes: (1) 1934-32, (1) 2236-32

Description	Quantity Required Per Test	Units	Cat. No.
Amino Acid Reagent	1 mL	100 mL MDB*	1934-32
Molybdate Reagent	1 mL	100 mL MDB*	2236-32

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* Larger sizes available.

REQUIRED APPARATUS

Description	Quantity Required Per Test	Units	Cat. No.
Cylinder, 25 mL Graduated Mixing	1	each	1896-40
Sample Cells, 25 mL, matched pair	2	each	20950-00

OPTIONAL REAGENTS

Description	Units	Cat. No.
Amino Acid Reagent Powder Pillow	100/pkg	804-99
Bromine Water, 30 g/L	25 mL*	2211-20
Hydrochloric Acid Solution, 1:1 (6 N)	500 mL	884-49
Phenol Solution, 30 g/L	25 mL	2112-20
Phosphate Standard Solution, 50 mg/L PO_4^{3-}	500 mL	171-49
Phosphate Standard Solution, Voluette ampule, 500 mg/L PO_4^{3-}, 10 mL	16/pkg	14242-10
Sulfamic Acid, ACS	113 g	2344-14
Sulfuric Acid Standard Solution, 10 N	1 L	931-53
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Description	Units	Cat. No.
Ampule Breaker Kit	each	21968-00
Aspirator, vacuum	each	2131-00
Cylinder, graduated, 50 mL	each	508-41
Cylinder, graduated, mixing, 25 mL	each	20886-40
FIlter Holder, 47 mm, 300 mL, graduated	each	13529-00
Filter Membrane, 47 mm, 0.45 micron	100/pkg	13530-01
Flask, filtering, 500 mL	each	546-49
Flask, erlenmeyer, 125 mL	each	505-43
Flask, volumetric, Class A, 50 mL	each	14574-41
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
pH Meter, *sension*™*1*, portable	each	51700-10
Pipet, serological, 2.0 mL	each	532-36
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 10.00 mL	each	14515-38
Pipet Filler, safety bulb	each	12189-00
Pour-Thru Cell Assembly Kit	each	45215-00
Spoon, measuring, 0.05 g	each	492-00
Stopper, No. 7, one hole	6/pkg	2119-07
Thermometer, -20 to 105 °C	each	1877-00
Tubing, rubber,	12 feet	560-19

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

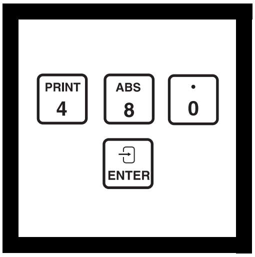
Method 8114

PHOSPHORUS, REACTIVE (0 to 45.0 mg/L PO_4^{3-})

(Also called Orthophosphate) Molybdovanadate Method For water and wastewater

(Reagent Solution or AccuVac Ampuls)*

Using Reagent Solution



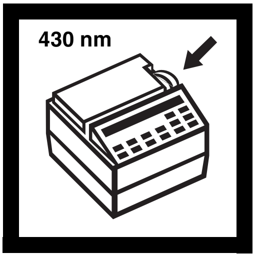
1. Enter the stored program number for reactive phosphorus, molybdovanadate method.

Press: **4 8 0 ENTER**

The display will show:

Dial nm to 430

Note: *The Pour-Thru Cell can be used with this procedure.*



2. Rotate the wavelength dial until the small display shows:

430 nm

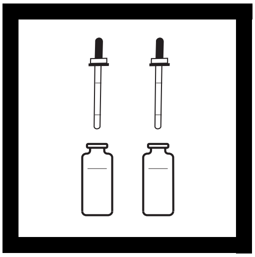
When the correct wavelength is dialed in, the display will quickly show: **Zero Sample**

then: **mg/L PO_4^{3-} MV**

3. Use a 25-mL graduated cylinder to fill a sample cell with 25 mL of deionized water (the blank).

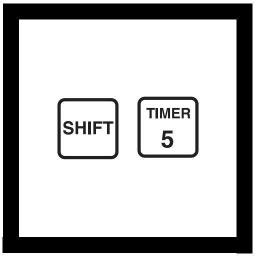
Note: *For best results, sample temperature should be 10-25 °C.*

4. Use another 25-mL graduated cylinder to fill a second sample cell with 25 mL of sample (the prepared sample).



5. Add 1.0 mL of Molybdovanadate Reagent to each sample cell. Swirl to mix.

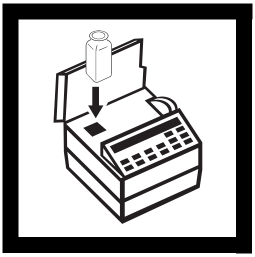
Note: *A yellow color will form if phosphate is present. A small amount of yellow will be present in the blank, because of the reagent.*



6. Press:

SHIFT TIMER

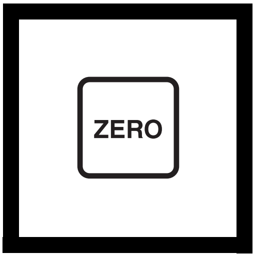
A three-minute reaction period will begin.



7. When the timer beeps, the display will show:

mg/L PO_4^{3-} MV

Place the blank into the cell holder. Close the light shield.



8. Press: **ZERO**

The display will show:

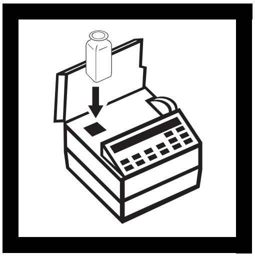
Zeroing. . .

then:

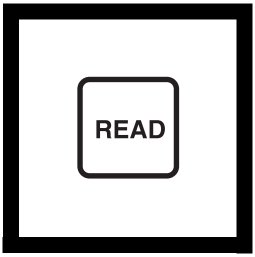
0.0 mg/L PO_4^{3-} MV

---

* Adapted from *Standard Methods for the Examination of Water and Wastewater.*



9. Place the prepared sample into the cell holder. Close the light shield.



10. Press: **READ**

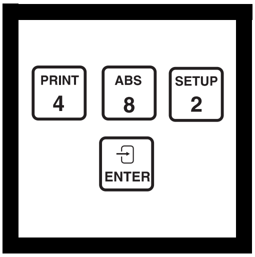
The display will show:

Reading. . .

then the result in mg/L PO_4^{3-} will be displayed.

Forms ▲▼ P, PO_4^{3-}, P_2O_5

Using Accuvac Ampuls

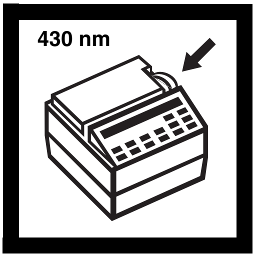


1. Enter the stored program number for reactive phosphorus, molybdovanadate method.

Press: **4 8 2 ENTER**

The display will show:

Dial nm to 430



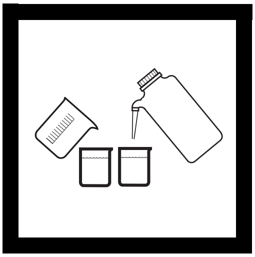
2. Rotate the wavelength dial until the small display shows:

430 nm

When the correct wavelength is dialed in, the display will quickly show: **Zero Sample**

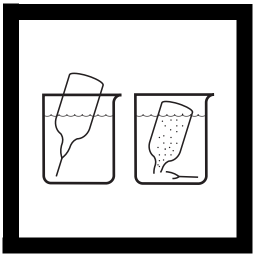
then:

mg/L PO_4^{3-} MV AV



3. Collect at least 40 mL of sample in a 50-mL beaker. Pour at least 40 mL of deionized water into a second beaker.

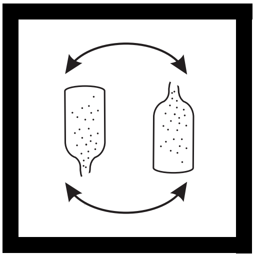
Note: *For best results, sample temperature should be 20-25 °C.*



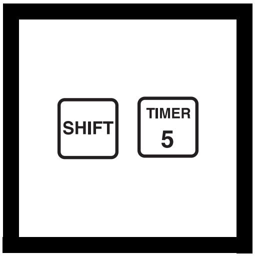
4. Fill a Molybdovanadate Reagent AccuVac Ampul with sample. Fill a second AccuVac Ampul with deionized water.

Note: *Keep the tip immersed while the ampul fills completely.*

Note: *A yellow color will form if phosphate is present. A small amount of yellow will be present because of the reagent.*



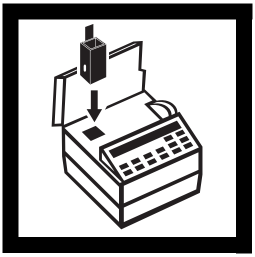
5. Invert the ampul several times to mix, then wipe off any liquid or fingerprints.



6. Press:

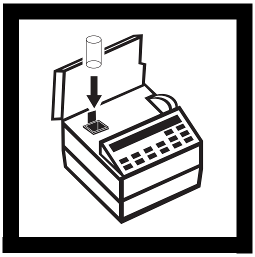
SHIFT TIMER

A five-minute reaction period will begin.



7. Place the AccuVac Vial Adapter into the cell holder of the instrument.

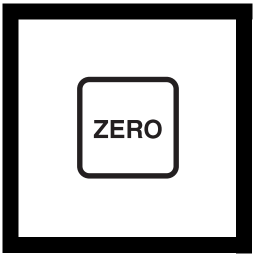
Note: *Place the grip tab at the rear of the cell holder.*



8. When the timer beeps, the display will show:

mg/L PO_4^{3-} MV AV

Place the blank into the cell holder. Close the light shield.



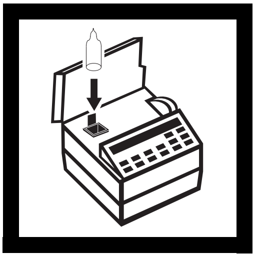
9. Press: **ZERO**

The display will show:

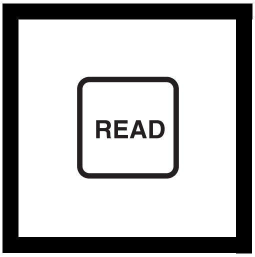
Zeroing. . .

then:

0.0 mg/L PO_4^{3-} MV AV



10. Place the prepared sample into the cell holder. Close the light shield.



11. Press: **READ**

The display will show:

Reading. . .

then the result in mg/L PO_4^{3-} will be displayed.

Forms ▲▼
P
PO_4^{3-}
P_2O_5

Sampling and Storage

Collect samples in clean plastic or glass bottles that have been cleaned with 1:1 Hydrochloric Acid Solution and rinsed with deionized water. Do not use a commercial detergent containing phosphate for cleaning glassware used in this test.

Analyze samples immediately for best results. If prompt analysis is impossible, preserve samples by filtering immediately and storing at 4 °C for up to 48 hours.

Accuracy Check

Standard Additions Method

a) Fill three 25-mL graduated mixing cylinders with 25 mL of sample.

b) Snap the neck off a Phosphate Voluette Ampule Standard Solution, 500 mg/L as PO_4^{3-}

c) Use the TenSette Pipet to add 0.1 mL, 0.2 mL and 0.3 mL of standard, respectively, to the three 25-mL water samples. Mix well.

d) Analyze each sample as described in the procedure and compare the results with that of the original test sample. Each 0.1-mL addition of standard should cause an increase of 2.0 mg/L PO_4^{3-}. For analysis with AccuVacs, transfer solutions to clean, dry 50-mL beakers to facilitate filling of the ampuls. For analysis with reagent solution, transfer 25 mL of solution to 25-mL sample cells.

e) If these increases do not occur, see *Standard Additions* (*Section I*) for more information.

Standard Solution Method

A 10.0 mg/L phosphate standard can be prepared by pipetting 10.0 mL of a Phosphate Standard Solution, 50 mg/L PO_4^{3-}, into a 50-mL volumetric flask. Dilute to volume with deionized water. Or, prepare a 10.0 mg/L PO_4^{3-} standard solution by pipetting 1 mL of Phosphate Voluette Ampule Standard, 500 mg/L as PO_4^{3-}, into a 50-mL volumetric flask. Dilute to volume with deionized water.

For proof of accuracy, substitute this standard for the sample and perform the test as described. The mg/L PO_4^{3-} reading should be 10 mg/L.

Wavelength Check

This test is sensitive to the wavelength setting. To ensure accuracy, the test should be run on a 10-mg/L standard solution and blank. Repeat Steps 7 to 10 (Steps 8-11 for AccuVacs) at slightly different wavelengths, setting the dial from higher to lower values until the correct result is obtained. The wavelength should be 430 ±2 nm. Always set this wavelength from high to low values.

Precision

In a single laboratory using standards of 20.0 mg/L PO_4^{3-}, two lots of reagent, and the DR/2010, a single operator obtained a standard deviation of ±0.09 mg/L PO_4^{3-}.

Interferences

Sulfide interference may be removed by oxidation with Bromine Water as follows:

a) Measure 25 mL of sample into a sample cell.

b) Add Bromine Water drop-wise with constant swirling until a permanent yellow color develops.

c) Add Phenol Solution drop-wise until the yellow color just disappears. Proceed with Step 4.

Positive interferences are caused by silica and arsenate only if the sample is heated.

Negative interferences are caused by arsenate, fluoride, thorium, bismuth, sulfide, thiosulfate, thiocyanate or excess molybdate.

Blue color is caused by ferrous iron but this does not affect results if ferrous iron concentration is less than 100 mg/L.

Ions that do not interfere in concentrations up to 1000 mg/L are pyrophosphate, molybdate, tetraborate, selenate, benzoate, citrate, oxalate, lactate, tartrate, formate, salicylate, Al^{3+}, Fe^{3+}, Mg^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+}, Li^{+}, Na^{+}, K^{+}, NH_4^{+}, Cd^{2+}, Mn^{2+}, NO_3^{-}, NO_2^{-}, SO_4^{2-}, SO_3^{2-}, Pb^{2+}, Hg^{+}, Hg^{2+}, Sn^{2+}, Cu^{2+}, Ni^{2+}, Ag^{+}, U^{4+}, Zr^{4+}, AsO_3^{-}, Br^{-}, CO_3^{2-}, ClO_4^{-}, CN^{-}, IO_3^{-}, SiO_4^{4-}.

Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment; see *pH Interferences* in *Section I.*

Summary of Method

In the molybdovanadate method, orthophosphate reacts with molybdate in an acid medium to produce a phosphomolybdate complex. In the presence of vanadium, yellow vanadomolybdophosphoric acid is formed. The intensity of the yellow color is proportional to the phosphate concentration.

REQUIRED REAGENTS (USING REAGENT SOLUTION)

Description	Quantity Required Per Test	Units	Cat. No.
Molybdovanadate Reagent	2.0 mL	100 mL* MDB	20760-32
Water, deionized	25 mL	4 L	272-56

REQUIRED REAGENTS (using AccuVac Ampuls)

Molybdovanadate Reagent AccuVac Ampuls	2	25/pkg	25250-25

REQUIRED APPARATUS (USING REAGENT SOLUTION)

Cell, sample, 1-inch, 25-mL	2	pair	20950-00
Cylinder, graduated, 25 mL	2	each	508-40

REQUIRED APPARATUS (using AccuVac Ampuls)

Adapter, AccuVac Vial	1	each	43784-00
Beaker, 50 mL	2	each	500-41

OPTIONAL REAGENTS

Bromine Water	29 mL*	2211-20
Hydrochloric Acid Solution, 1:1	500 mL	884-49
Phenol Solution, 30 g/L	29 mL	2112-20
Phosphate Standard Solution, 50 mg/L as PO_4^{3-}	500 mL	171-49
Phosphate Standard Solution, Voluette ampule, 500 mg/L as PO_4^{3-}, 10 mL	16/pkg	14242-10

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* Contact Hach for larger sizes.

OPTIONAL APPARATUS

Description	Units	Cat. No
Ampule Breaker Kit	each	21968-00
AccuVac Snapper Kit	each	24052-00
Aspirator, vacuum	each	2131-00
Cylinder, graduated, mixing, 25-mL	each	20886-40
Dispenser, fixed volume, 1.0 mL Repipet Jr.	each	21113-02
Filter Holder, 47 mm, 300 mL, graduated	each	13529-00
Filter membrane, 47 mm, 0.45 microns	100/pkg	13530-01
Flask, filtering, 500 mL	each	546-49
Flask, erlenmeyer, 50 mL	each	505-41
Flask, volumetric, Class A, 50 mL	each	14574-41
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
pH Meter, EC10, portable	each	50050-00
Pipet, serological, 2.0 mL	each	532-36
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 10.00 mL	each	14515-38
Pipet Filler, Safety Bulb	each	12189-00
Pour-Thru Cell Assembly Kit	each	45215-00
Stopper, No. 7, one hole	6/pkg	2119-07
Tubing, rubber	12 feet	560-19

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

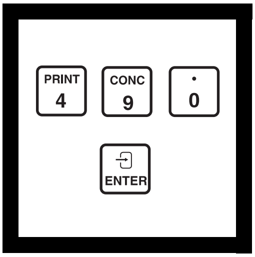
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8048

PHOSPHORUS, REACTIVE (0 to 2.50 mg/L PO_4^{3-})

(Also called Orthophosphate) PhosVer 3 (Ascorbic Acid) Method* **For water,**
(Powder Pillows or AccuVac Ampuls) **wastewater, seawater**
USEPA Accepted for wastewater analysis reporting**

Using Powder Pillows



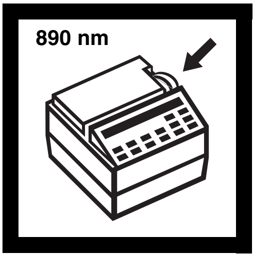
1. Enter the stored program number for reactive phosphorus, ascorbic acid method, powder pillows.

Press: **4 9 0 ENTER**

The display will show:

Dial nm to 890

Note: *The Pour-Thru Cell can be used with 25-mL reagents only.*

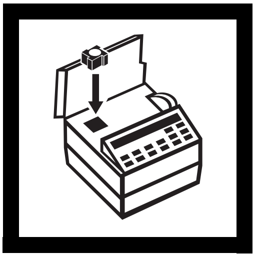


2. Rotate the wavelength dial until the small display shows:

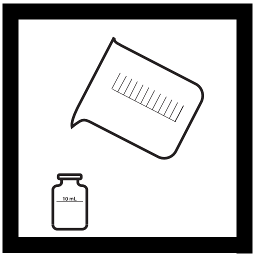
890 nm

When the correct wavelength is dialed in, the display will quickly show: **Zero Sample**

then: **mg/L PO_4^{3-} PV**



3. Insert a 10-mL Cell Riser into the cell compartment.



4. Fill a 10-mL sample cell with 10 mL of sample.

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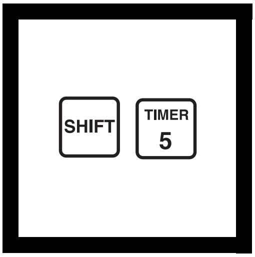
* Adapted from *Standard Methods for the Examination of Water and Wastewater.*

** Procedure is equivalent to USEPA method 365.2 and Standard Method 4500-P-E for wastewater.

5. Add the contents of one PhosVer 3 Phosphate Powder Pillow for 10-mL sample to the cell (the prepared sample). Swirl immediately to mix.

Note: *A blue color will form if phosphate is present.*

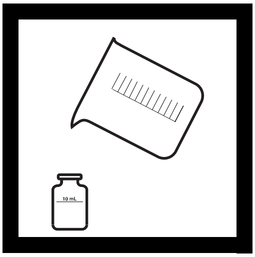


6. Press:

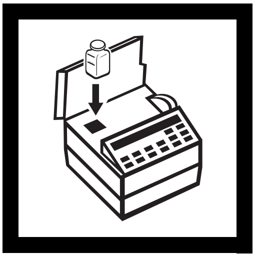
SHIFT TIMER

A two-minute reaction period will begin.

Note: *Use a 10 minute reaction period if determining total phosphorus following the acid-persulfate digestion.*

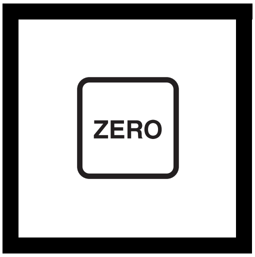


7. Fill a second 10-mL sample cell with 10 mL of sample (this is the blank).



8. When the timer beeps, the display will show: **mg/L PO_4^{3-} PV**

Place the blank into the cell holder. Close the light shield.



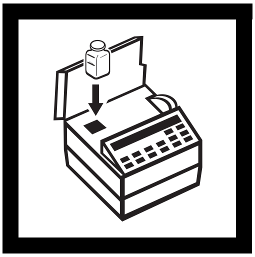
9. Press: **ZERO**

The display will show:

Zeroing. . .

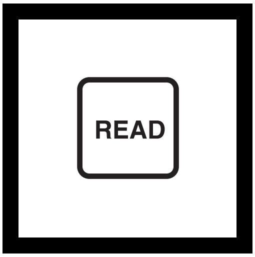
then:

0.00 mg/L PO_4^{3-} PV



10. Place the prepared sample into the cell holder. Close the light shield.

Note: *Run a reagent blank for this test. Use deionized water in place of the sample in Steps 4 and 7. Subtract this result from all test results run with this lot of PhosVer 3.*



11. Press: **READ**

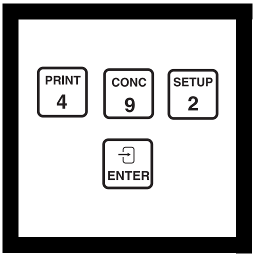
The display will show:

Reading. ..

then the results in mg/L PO_4^{3-} will be displayed.

Forms ▲▼ P
PO_4^{3-}
P_2O_5

Using AccuVac Ampuls

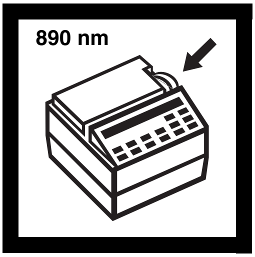


1. Enter the stored program number for reactive phosphorus, ascorbic acid method, AccuVac Ampuls.

Press: **4 9 2 ENTER**

The display will show:

Dial nm to 890



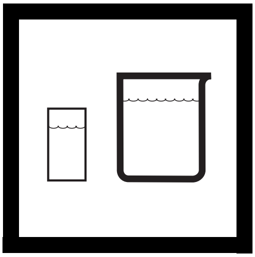
2. Rotate the wavelength dial until the small display shows:

890 nm

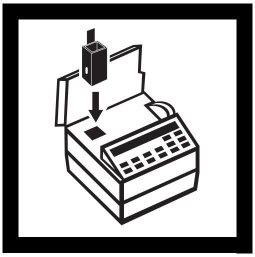
When the correct wavelength is dialed in, the display will quickly show: **Zero Sample**

then:

mg/L PO_4^{3-} PV AV

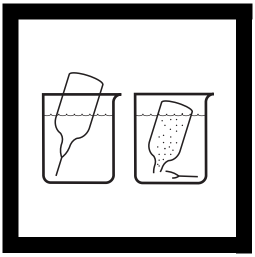


3. Fill a zeroing vial (the blank) with at least 10 mL of sample. Collect at least 40 mL of sample in a 50-mL beaker.



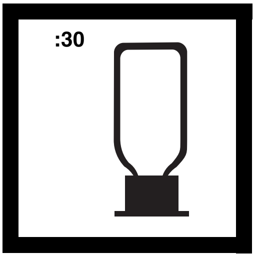
4. Place the AccuVac Vial Adapter into the cell holder.

Note: *Place the grip tab at the rear of the cell holder.*



5. Fill a PhosVer 3 Phosphate AccuVac Ampul with sample.

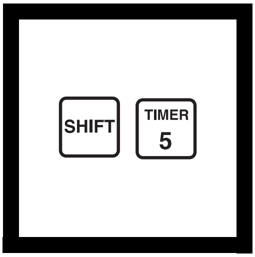
Note: *Keep the tip immersed while the ampul fills completely.*



6. Place an ampul cap securely over the tip of the ampul. Shake the ampul for approximately 30 seconds. Wipe off any liquid and fingerprints.

Note: *A blue color will form if phosphate is present.*

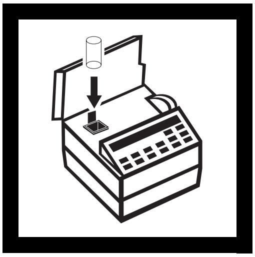
Note: *Accuracy is not affected by undissolved powder.*



7. Press:

SHIFT TIMER

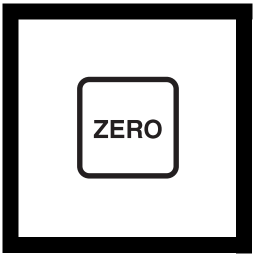
A two-minute reaction period will begin.



8. When the timer beeps, the display will show:

mg/L PO_4^{3-} PV AV

Place the zeroing vial into the cell holder.



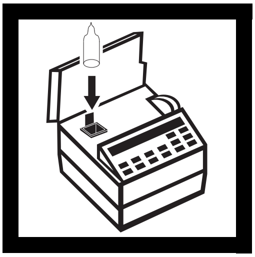
9. Press: **ZERO**

The display will show:

Zeroing. . .

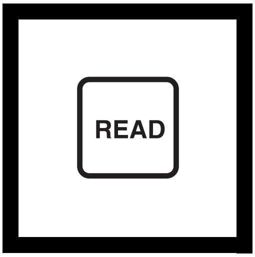
then:

0.00 mg/L PO_4^{3-} PV AV



10. Place the AccuVac ampul into the cell holder.

Note: *Run a reagent blank for the test. Use deionized water in place of the sample in Step 3. Subtract this result from all results with this lot of ampuls.*



11. Press: **READ**

The display will show:

Reading. . .

then the result in mg/L PO_4^{3-} will be displayed.

Forms ▲▼ P, PO_4^{3-}, P_2O_5

Sampling and Storage

Collect sample in plastic or glass bottles that have been cleaned with 1:1 Hydrochloric Acid Solution and rinsed with deionized water. Do not use commercial detergents containing phosphate for cleaning glassware used in phosphate analysis.

Analyze samples immediately after collection for best results. If prompt analysis is impossible, preserve samples for up to 48 hours by filtering immediately and storing samples at 4 °C.

Accuracy Check

Standard Additions Method

a) Fill three 25-mL graduated mixing cylinders with 25 mL of sample.

b) Snap the neck off a Phosphate Voluette Ampule Standard Solution, 50 mg/L PO_4^{3-}.

c) Use the TenSette Pipet to add 0.1 mL, 0.2 mL, and 0.3 mL of standard, respectively, to the three mixing cylinders. Stopper each and mix thoroughly.

d) For analysis with AccuVac Ampuls, transfer solutions to dry, clean 50 mL beakers to fill AccuVac ampuls. For analysis with powder pillows, transfer only 10 mL of solution to the 10 mL sample cells.

e) Analyze each standard addition sample as described in the procedure. The phosphate concentration should increase 0.2 mg/L for each 0.1 mL of standard added.

f) If these increases do not occur, see *Standard Additions* in *Section I* for more information.

Standard Solution Method

Prepare a 2.0 mg/L PO_4^{3-} standard solution by pipetting 4.0 mL of Phosphate Standard Solution, 50 mg/L as PO_4^{3-}, into a 100-mL volumetric flask. Dilute to volume with deionized water. Stopper and invert to mix. Use this solution in place of the sample in the procedure to insure the accuracy of the test. The mg/L PO_4^{3-} reading should be 2 mg/L.

Interferences

Large amounts of turbidity may cause inconsistent results in the phosphate tests because the acid present in the powder pillow may dissolve some of the suspended particles and because of variable desorption of orthophosphate from the particles. For highly turbid or colored samples, add the contents of one Phosphate Pretreatment Powder Pillow to 10 mL of sample. Mix well. Use this solution to zero the instrument.

The PhosVer 3 Phosphate reagent Powder Pillows should be stored in a cool, dry environment.

The following may interfere when present in concentrations exceeding these listed below:

Aluminum	200 mg/L
Chromium	100 mg/L
Copper	10 mg/L
Iron	100 mg/L
Nickel	300 mg/L
Silica	50 mg/L
Silicate	10 mg/L
Zinc	80 mg/L

Arsenate and hydrogen sulfide do interfere.

Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment; see *pH Interferences* in *Section 1*.

Precision

In a single laboratory using a standard solution of 1.00 mg/L PO_4^{3-} and two lots of reagents with the DR/2010, a single operator obtained a standard deviation of ±0.01 mg/L PO_4^{3-}.

In a single laboratory using a standard solution of 1.00 mg/L PO_4^{3-} and two representative lots of AccuVac ampuls with the DR/2010, a single operator obtained a standard deviation of ±0.02 mg/L PO_4^{3-}.

Estimated Detection Limit (EDL)

The EDL for program 490 is 0.01 mg/L PO_4. The EDL is the calculated lowest average concentration in a deionized water matrix that is different from zero with a 99% level of confidence. For more information on derivation and use of Hach's estimated detection limit, see Section I.

The EDL for program 492 is 0.01 mg/L PO_4. The EDL is the calculated lowest average concentration in a deionized water matrix that is different from zero with a 99% level of confidence. For more information on derivation and use of Hach's estimated detection limit, see *Section I*.

Summary of Method

Orthophosphate reacts with molybdate in an acid medium to produce a Phosphomolybdate complex. Ascorbic acid then reduces the complex, giving an intense molybdenum blue color.

REQUIRED REAGENTS (Using Powder Pillows)

Description	Quantity Required Per Test	Unit	Cat. No.
PhosVer 3 Phosphate Reagent Powder Pillows 10 mL sample size	1 Pillow	100/pkg	21060-69

REQUIRED APPARATUS (Using Powder Pillows)

Cell Riser, 10-mL	1	each	45282-00
Sample Cell, 10 mL, matched pair	2	pair	24954-02

REQUIRED REAGENTS (Using AccuVac Ampuls)

PhosVer 3 Phosphate Reagent AccuVac Ampuls	1 ampul	25/pkg	25080-25

REQUIRED APPARATUS (Using AccuVac Ampuls)

Description	Quantity Required Per Test	Unit	Cat. No.
Adapter, AccuVac Vial	1	each	43784-00
Beaker, 50 mL	1	each	500-41
Cap, ampul, blue	1	25/pkg	1731-25
Vial, zeroing	1	each	21228-00

OPTIONAL REAGENTS

Hydrochloric Acid Standard Solution, 6.0 N (1:1)	500 mL	884-49
Phosphate Pretreatment Powder Pillows	50/pkg	14501-66
Phosphate Standard Solution, Voluette ampul, 50 mg/L as PO_4^{3-}, 10 mL	16/pkg	171-10
Phosphate Standard Solution, 50 mg/L as PO_4^{3-}	500 mL	171-49
Phosphate Standard Solution, 1 mg/L as PO_4^{3-}	500 mL	2569-42
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

AccuVac Snapper Kit	each	24052-00
Aspirator, vacuum	each	2131-00
Cylinder, graduated, mixing, 25 mL, tall	each	20886-40
Filter Holder, 47 mm, 300 mL, graduated	each	13529-00
Filter, membrane, 47 mm, 0.45 microns	100/pkg	13530-01
Flask, filtering, 500 mL	each	546-49
Flask, volumetric, Class A, 100 mL	each	14574-42
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
pH Meter, *sension*™*1*, portable	each	51700-10
Pipet, 2 mL serological	each	532-36
Pipet, TenSette, 1.0 to 10.0 mL	each	19700-10
Pipet Tips, for 19700-10 TenSette Pipet	50/pkg	21997-96
Pipet Tips, for 19700-10 TenSette Pipet	1000/pkg	21997-28
Pipet, TenSette, 0.1 to 1.0 mL TenSette Pipet	each	19700-01
Pipet Tips, for 19700-01	50/pkg	21856-96
Stopper, No. 7, one hole	each	2119-07
Thermometer, -20 to 105 °C	each	1877-01
Tubing, rubber	12 feet	560-19

OPTIONAL 25 ML ANALYSIS ITEMS

PhosVer 3 Phosphate Reagent Set for 25 mL samples (100 tests)		2125-99
Pour-Thru Cell Assembly Kit (for 25 mL reagents only)	each	45215-00
Sample Cell, 25 ml matched pair	pair	20950-00

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

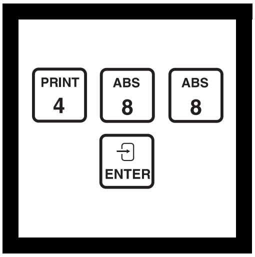
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 10055

PHOSPHORUS, REACTIVE, LOW RANGE (0 to 3,000 µg/L PO_4^{3-})

(also called orthophosphate) **For treated and natural waters**

Ascorbic Acid Rapid Liquid Method*

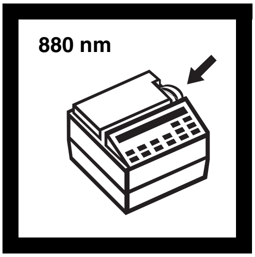


1. Enter the stored program for low range phosphate.

Press: **4 8 8 ENTER**

The display will show:

Dial nm to 880



2. Rotate the wavelength dial until the small display shows:

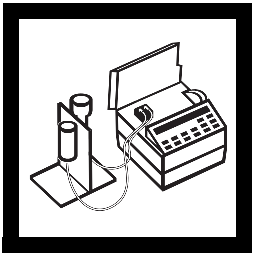
880 nm

When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

then:

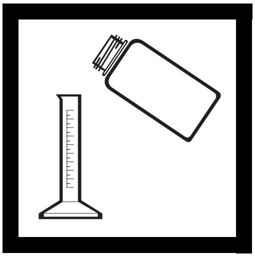
µg/L PO_4^{3-} LR RL



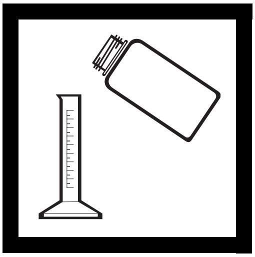
3. Install the Pour-Thru Cell and flush with 50 mL of deionized water.

Note: *Clean the Pour-Thru cell and all labware as specified in Treating Analysis Labware.*

4. Rinse two clean 125-mL plastic, screw-cap Erlenmeyer flasks three times with the sample.



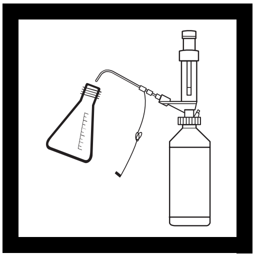
5. Rinse a clean 25-mL plastic graduated cylinder three times with the sample.



6. Fill this rinsed cylinder to the 25-mL mark with sample.

7. Pour the contents of the 25-mL cylinder into one of the flasks.

Measure a second 25-mL portion of sample into the graduated cylinder and pour the contents into the second flask.

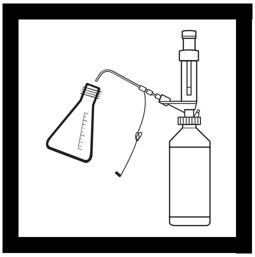


8. Add 1.0 mL of Molybdate reagent to each flask using a Repipet dispenser.

Swirl to mix.

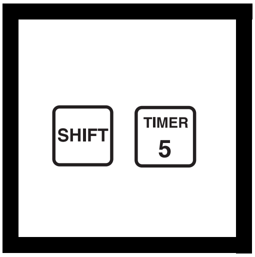
---

* Adapted from *Standard Methods for the Examination of Water and Wastewater.*



9. Add 1.0 mL of prepared Ascorbic Acid reagent to one of the flasks with a Repipet dispenser. Swirl to mix. The remaining flask will be the blank.

Note: *See Reagent Preparation for preparing the Ascorbic Acid reagent.*



10. Press:

SHIFT TIMER

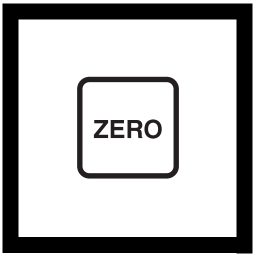
A 5-minute reaction period will begin.

Note: *Reaction time is dependent on sample temperature. For most accurate results, samples should be at room temperature (about 20 °C).*

11. When the timer beeps, the display will show:

$\mu g/L\ PO_4^{3-}$ LR RL

Pour the contents of the flask containing the blank into the Pour-Thru Cell.



12. After the flow has stopped, press: **ZERO**

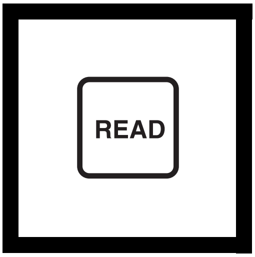
The display should show:

Zeroing. . . .

then:

0 $\mu g/L\ PO_4^{3-}$ LR RL

13. Pour the contents of the second flask into the Pour-Thru Cell.



14. After the flow has stopped, press: **READ**

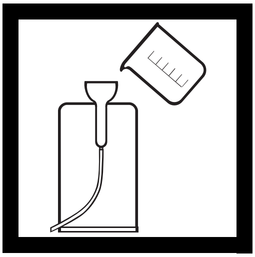
The display will show:

Reading. . . .

Then the result in µg/L PO_4^{3-} will be displayed.

Forms ▲▼ P_2O_5 PO_4^{3-} P

Note: *Obtain a reagent blank for each lot of reagents when the phosphate concentration is less than 750 µg/L. Use Zero Standard Water in place of the sample in Steps 4-14. Subtract the blank from the sample reading.*



15. Flush the Pour-Thru Cell with at least 50 mL of deionized water immediately after use.

Note: *Protect the Pour-Thru Cell from contamination by inverting a small beaker over the top of the glass funnel when not in use.*

Analysis Labware

All labware used in this test must be thoroughly cleaned to remove all traces of phosphate. Clean containers with a non-phosphate detergent followed by a rinse with deionized water. Fill and soak for 10 minutes with a 1:25 dilution of Molybdate Reagent in deionized water. Rinse well with Zero Standard water. Keep containers tightly closed when not in use. Treat the Pour-Thru Cell with this same mixture of molybdate and water followed by thorough rinsing with deionized water.

Dedicate these containers for low-level phosphate analysis. If these containers are rinsed and capped after use, only occasional pre-treatment is necessary.

Cleaning the Pour-Thru Cell

The Pour-Thru Cell may accumulate a buildup of colored products, especially if the reacted solutions are allowed to stand in the cell for long periods after measurement. Remove the color by rinsing with a 1:5 dilution of ammonium hydroxide, followed by several deionized water rinses. Invert a beaker over the glass funnel of the cell when not in use.

Reagent Preparation

The Ascorbic Acid reagent must be prepared before use. Using a powder funnel, add the contents of one 48g bottle of Ascorbic Acid Reagent Powder (Cat. No. 26512-55) to one 450 mL bottle of Ascorbic Acid Reagent Dilution Solution (Cat. No. 25999-49). Invert several times and swirl until the powder is completely dissolved.

This solution may develop a yellow color with time but will still give accurate results for up to one month after mixing if stored at 20-25 °C. Record the date of preparation on the bottle and discard any remaining solution after one month. Do not add fresh reagent to previously mixed reagent. Use of this reagent after one month may result in high reagent blanks and low values at high concentrations.

Sampling and Storage

Collect samples in clean plastic or glass bottles that have been cleaned with 1:1 Hydrochloric Acid Solution and rinsed with deionized water. Do not use detergenst that contains phosphate for cleaning labware.

Analyze samples as soon as possible for best results. If samples cannot be analyzed promptly, filter immediately and store the sample at 4 °C (39 °F) or below. Samples can be stored for 48 hours. Warm to room temperature before analysis.

Accuracy Check

Standard Additions Method

a) Snap the neck off a Phosphate Standard Solution Ampule, either 15 mg/L as PO_4^{3-} or 50 mg/L as PO_4^{3-} . Use the 15 mg/L standard when the phosphate concentration of samples is less than 1000 µg/L .

b) Use the TenSette Pipet to add 0.1 mL, 0.2 mL, and 0.3 mL of standard to three 25-mL samples. Mix well.

c) Analyze samples as described above. The phosphate concentration should increase 60 µg/L for each 0.1 mL of 15-mg/L standard added or 200 µg/L for each 0.1 mL of 500-mg/L standard added.

d) If these increases do not occur, see *Standard Additions* in *Section I* for more information.

Standard Solution Method

Run the test using a 1000 µg/L (1.000 mg/L) phosphate standard solution in place of the sample. Results should be 900 to 1100 µg/L phosphate.

Interferences

Samples with large amounts of turbidity may give inconsistent results because the acid present in the reagents may dissolve some of the suspended particles and variable desorption of orthophosphate from the particles may occur.

The following may interfere if present in concentrations exceeding those listed below:

Interfering Chemical	Concentration above which interference occurs
Aluminum	200 mg/L
Chromium	100 mg/L
Copper	10 mg/L
Iron	100 mg/L
Nickel	300 mg/L
Silica	50 mg/L
Silicate	10 mg/L
Zinc	80 mg/L

Arsenate and hydrogen sulfide interfere. Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment; see *Interferences* in *Section I*.

Precision

In a single laboratory, using nine concentrations of phosphate standards and two lots of reagent with a DR/2010, a single operator obtained a calibration curve that showed a 99% confidence interval at 1,000 µg/L of ±3 µg/L.

Summary of Method

Orthophosphate reacts with molybdate in an acid medium to produce a phosphomolybdate complex. Ascorbic acid then reduces the complex, giving an intense molybdenum blue color. Reactive phosphorus includes existing orthophosphate in the sample plus a small fraction of condensed phosphate that may be hydrolyzed to orthophosphate during the test.

REQUIRED REAGENTS

Rapid Liquid Low Range Phosphorus Reagent Set	26786-00

Includes: (1) 25998-49, (1) 25999-49, (1) 26512-55

Description	Quantity Required Per Test	Unit	Cat. No.
Molybdate Reagent Solution	2 mL	500 mL	25998-49
Ascorbic Acid Reagent Dilution Solution		450 mL	25999-49
Ascorbic Acid Reagent Powder		48 g	26512-55
Water, deionized		4 L	272-56

REQUIRED APPARATUS

Cylinder, graduated, 25 mL, poly	2	each	1081-40
Flask, erlenmeyer, 125 mL, PMP w/cap	2	each	20898-43
Pour-Thru Cell Assembly	1	each	45215-00
Dispenser, fixed volume, 1.0 mL Repipet Jr.	2	each	21113-01

OPTIONAL REAGENTS

Description	Unit	Cat. No.
Ammonium Hydroxide, ACS	500 ml	105-49
Hydrochloric Acid Solution, 1:1 (6 N)	500 mL	884-49
Molybdate Reagent Solution	1 L	25998-53
Phosphate Standard Solution, 1.00 mg/L as PO_4^{3-}	500 mL	2569-49
Phosphate Standard Solution, Voluette ampule, 50 mg/L PO_4^{3-}, 10 mL	16/pkg	171-10
Phosphate Standard Solution, 15 mg/L PO_4^{3-}	100 mL	14243-42
Water, zero standard solution	2.9 L	26001-03

OPTIONAL APPARATUS

Ampule Breaker Kit	each	21968-00
Aspirator, vacuum	each	2131-00
Beaker, poly, 50 mL	each	1080-41
Filter Holder, 47 mm, 300 mL, graduated	each	13529-00
Filter, membrane, 47 mm, 0.45 microns	100/pkg	13530-01
Flask, filtering, 500 mL	each	456-49
Flask, erlenmeyer, 125 mL, PMP w/cap	6/pkg	20898-73
Funnel, powder	each	22644-67
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
pH Meter, *sension*™*1*, portable	each	51700-10
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Stopper, No. 7, one hole	6/pkg	2119-07
Thermometer, -20 to 105 °C	each	1877-01
Tubing, rubber	12 feet	560-19

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

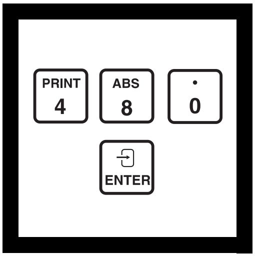
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8114

PHOSPHORUS, REACTIVE, HIGH RANGE (0 to 45.0 mg/L PO_4^{3-})

(also called orthophosphate) **For treated and natural waters**

Molybdovanadate Rapid Liquid Method*

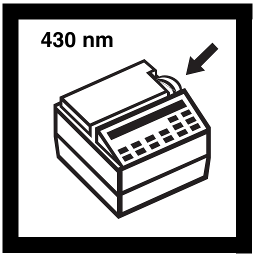


1. Enter the stored program number for reactive phosphorus, molybdovanadate method.

Press: **4 8 0 ENTER**

The display will show:

Dial nm to 430



2. Rotate the wavelength dial until the small display shows:

430 nm

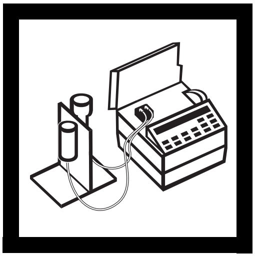
When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

then:

mg/L PO_4^{3-} MV

Note: *This procedure is sensitive to the wavelength setting. See Wavelength Check.*



3. Install the Pour-Thru Cell and flush with 50 mL of deionized water.

Note: *Pre-clean the Pour-Thru Cell and all labware as specified under Treating Analysis Labware.*

4. Rinse a clean plastic 125-mL Erlenmeyer flask and 25-mL graduated cylinder with deionized water. Measure 25 mL of deionized water into the flask. This is the blank.

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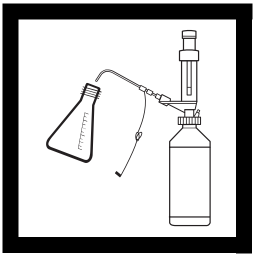
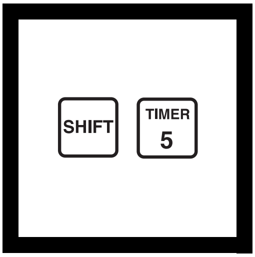
* Adapted from *Standard Methods for the Examination of Water and Wastewater.*

5. Rinse another clean flask and the graduated cylinder with the sample. Measure 25 mL of the sample into the flask.



6. Add 1.0 mL of Molybdovanadate Reagent to each flask using a Repipet dispenser. Swirl to mix.

***Note:** A yellow color will form if phosphate is present. A small amount of yellow will be present in the blank because of the reagent.*



7. Press:

SHIFT TIMER

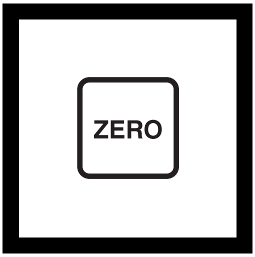
A three-minute reaction period will begin.

***Note:** If the sample concentration is greater than 24 mg/L* PO_4^{3-}*, read at exactly 3 minutes or make a 1:1 dilution of the sample.*

8. When the timer beeps, the display will show:

mg/L PO_4^{3-} MV

Pour the contents of the flask containing the blank into the Pour-Thru Cell.



9. After the flow has stopped, press: **ZERO**

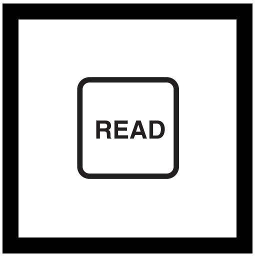
The display will show:

Zeroing. . . .

then:

0.0 mg/L PO_4^{3-} MV

10. Pour the contents of the flask containing the sample into the Pour-Thru Cell.

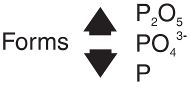


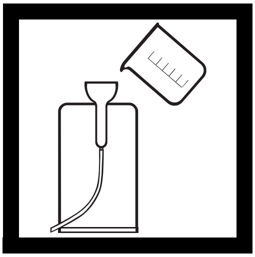
11. After the flow has stopped, press: **READ**

The display will show:

Reading. . . .

then the result in **mg/L PO_4^{3-}** will be displayed.





12. Flush the Pour-Thru Cell with 50 mL of deionized water.

***Note:** Protect the Pour-Thru Cell from contamination by inverting a small beaker over the glass funnel when not in use.*

Sampling and Storage

Collect samples in clean plastic or glass bottles that have been cleaned with 1:1 Hydrochloric Acid Solution and rinsed with deionized water. Do not use detergents that contains phosphate for cleaning labware.

Analyze samples as soon as possible for best results. If samples cannot be analyzed promptly, store the sample for up to 48 hours at 4 °C (39 °F) or below. Warm to room temperature before analyzing.

Treating Analysis Labware

Clean containers by normal means (do not use detergents containing phosphorus), then rinse with deionized water. Soak for several minutes in a 1:25 dilution of Molybdovanadate Reagent in deionized water. Rinse well with deionized water. Dedicate these containers for HR PO_4^{3-} analysis. Fill the Pour-Thru Cell with this same mixture of Molybdovanadate reagent and deionized water, and let stand for several minutes. Rinse with 50 mL of deionized water.

Cleaning The Pour-thru Cell

The Pour-Thru Cell may accumulate a buildup of colored products, especially if the reacted solutions are allowed to stand in the cell for long periods after measurement. Remove the color by rinsing with a 1:5 dilution of ammonium hydroxide, followed by several deionized water rinses. Invert a beaker over the glass funnel of the Pour-Thru Cell when not in use.

Accuracy Check

Standard Additions Method

a) Snap the neck off a Phosphate Voluette Ampule Standard Solution, 500 mg/L as PO_4^{3-}.

b) Use the TenSette Pipet to add 0.1 mL, 0.2 mL, and 0.3 mL of standard to three 25-mL samples. Mix well.

c) Analyze each sample as described in the procedure and compare the results with that of the original test sample. Each 0.1-mL addition of standard should cause an increase of 2.0 mg/L PO_4^{3-} or 0.67 mg/L P.

d) If these increases do not occur, see *Standard Additions* in *Section I* for more information.

Standard Solution Method

Use a 10.0 mg/L Phosphate Standard in place of the sample. Results should be between 9.0 and 11.0 mg/L phosphate.

Wavelength Check

This test is sensitive to the wavelength setting. To ensure accuracy, the test should be run on a 10-mg/L Phosphate Standard Solution and blank. Repeat Steps 8 to 11 at slightly different wavelengths, setting the dial from higher to lower values until the result reads 10.0 mg/L. Use square sample cells rather than the Pour-Thru Cell to facilitate the repeated zeroing and measurement of the standard. The wavelength should be 430 ±2 nm on the DR/2010. Record this wavelength and use it for future testing. Always set the wavelength from high to low values.

Precision

In a single laboratory using standards of 20.0 mg/L PO_4^{3-}, two lots of reagent and the DR/2010, a single operator obtained a standard deviation of ±0.09 mg/L PO_4^{3-}.

Interferences

Sulfide interference may be removed by oxidation with Bromine Water as follows:

a) Measure 25 mL of sample into a flask.

b) Add Bromine Water drop-wise with constant swirling until permanent yellow color develops.

c) Add Phenol Solution drop-wise until the yellow color just disappears. Proceed with *step 6*.

Positive interferences are caused by silica and arsenate only if the sample is heated.

Negative interferences are caused by arsenate, fluoride, thorium, bismuth, sulfide, thiosulfate, thiocyanate or excess molybdate.

Blue color is caused by ferrous iron but this does not affect results if the ferrous iron concentration is less than 100 mg/L.

Ions that do not interfere in concentrations up to 1000 mg/L are: pyrophosphate, molybdate, tetraborate, selenate, benzoate, citrate, oxalate, lactate, tartrate, formate, salicylate, Al^{3+}, Fe^{3+}, Mg^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+}, Li^{+}, Na^{+}, K^{+}, NH_4^{+}, Cd^{2+}, Mn^{2+}, NO_3^{-}, NO_2^{-}, SO_4^{2-}, SO_3^{2-}, Pb^{2+}, Hg^{+}, Hg^{2+}, Sn^{2+}, Cu^{2+}, Ni_2^{+}, Ag^{+}, U^{4+}, Zr^{4+}, AsO_3^{-}, Br^{-}, CO_3^{2-}, $Cl0_4^{-}$, CN^{-}, IO_3^{-}, SiO_4^{4-}.

Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment; see *pH Interferences* in *Section I.*

Summary of Method

In the molybdovanadate method, orthophosphate reacts with molybdate in an acid medium to produce a phosphomolybdate complex. In the presence of vanadium, yellow vanadomolybdophosphoric acid is formed. The intensity of the yellow color is proportional to the phosphate concentration.

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
Molybdovanadate Reagent,	2	500 mL	20760-49
Water, deionized	25	4 L	272-56

REQUIRED APPARATUS

Cylinder, graduated, 25 mL, poly	1	each	1081-40
Dispenser, fixed volume, 1.0 mL Repipet Jr.	1	each	21113-01
Flask, Erlenmeyer, 125 mL, PMP w/cap	2	each	20898-43
Pour-Thru Cell Assembly Kit	1	each	45215-00

OPTIONAL REAGENTS

Ammonium Hydroxide, ACS	500 mL	106-49
Bromine Water, 30 g/L	25 mL*	2211-20
Hydrochloric Acid Solution, 1:1	500 mL	884-49
Phenol Solution, 30 g/L	25 mL	2112-20
Phosphate Standard Solution, 10 mg/L as PO_4^{3-}	946 mL	14204-16
Phosphate Standard Solution, Voluette ampule, 500 mg/L as PO_4^{3-}, 10 mL	16/pkg	14242-10

OPTIONAL APPARATUS

Ampule Breaker Kit	each	21968-00
Beaker, poly, 50 mL	each	1080-41
Flask, erlenmeyer, 125 mL, PMP w/cap	6/pkg	20898-73
Flask, erlenmeyer, 50 mL	each	505-41
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
pH Meter, *sension*™*1*, portable	each	51700-10
Pipet, serological, 2.0 mL	each	532-36
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet Filler	each	12189-00
Sample Cell, 25 mL, matched pair	pair	20950-00
Thermometer, -20 to 105 °C	each	1877-01

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

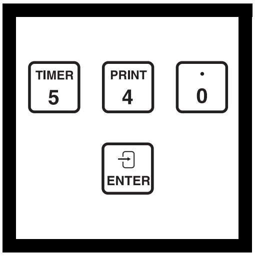
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8114

PHOSPHORUS, REACTIVE, HR (0.0 to 100.0 mg/L PO_4^{3-})

For water and wastewater

Molybdovanadate Method*, Test ’N Tube™ Procedure

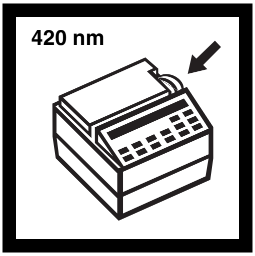


1. Enter the stored program number for phosphorus, reactive high range, Test ’N Tube.

Press: **540 ENTER**

The display will show:

Dial nm to 420



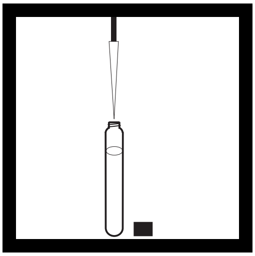
2. Rotate the wavelength dial until the small display shows:

420 nm

When the correct wavelength is dialed in, the display will quickly show: **Zero Sample**

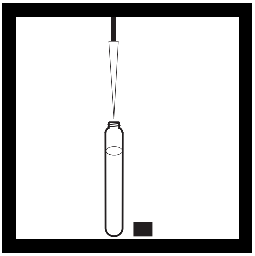
then:

mg/L PO_4^{3-} HR Rc



3. Use a TenSette® Pipet to add 5.0 mL of deionized water to a Reactive High Range Phosphorus Test ’N Tube Vial (the blank).

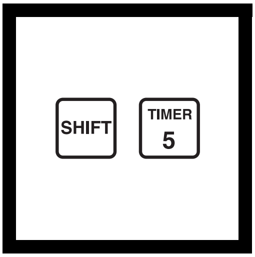
Cap and invert to mix.



4. Use a TenSette Pipet to add 5.0 mL of sample to a Reactive High Range Phosphorus Test ’N Tube Vial (the sample).

Cap and invert to mix.

Note: *For samples with extreme pH, see the Interference section.*

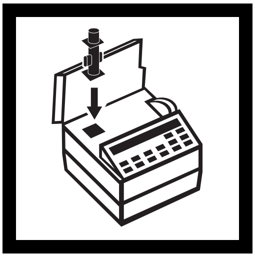


5. Press:

SHIFT TIMER

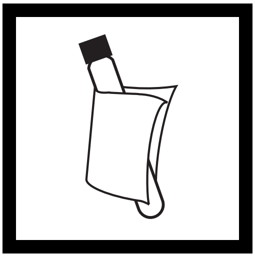
A 7-minute reaction time will begin.

Note: *Reaction time is for samples at 23 °C (73 °F). If the sample temperature is 13 °C (55 °F), wait 15 minutes. If the sample temperature is 33 °C (91 °F), wait two minutes.*



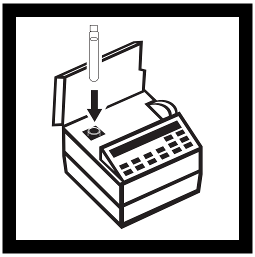
6. Place the COD Vial Adapter into the cell holder with the marker to the right.

Note: *Read the samples between 7–9 minutes.*



7. Clean the outside of the vials with a towel.

Note: *Wipe with a damp towel, followed by a dry one, to remove fingerprints or other marks.*



8. When the timer sounds, place the blank into the adapter with the Hach logo facing the front of the instrument. Place the cover on the adapter.

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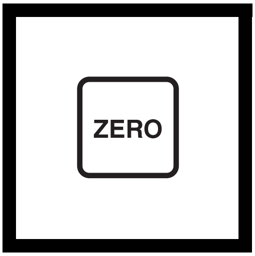
* Adapted from *Standard Methods for the Examination of Water and Wastewater.*



9. Press: **ZERO**

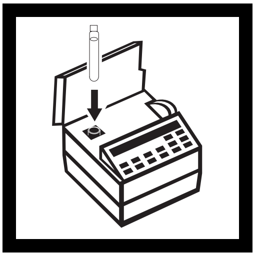
The display will show:

Zeroing. . .

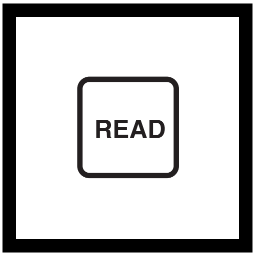
then:

0.0 mg/L PO_4^{3-} HR Rc

Note: *Reagent blanks for each lot of reagent may be used more than once. At room temperature, the reagent blank is stable for as long as three weeks; then prepare a new one.*



10. Place the sample vial in the adapter with the Hach logo facing the front of the instrument. Place the cover on the adapter.



11. Press: **READ**

The display will show:

Reading. . .

then the results in mg/L PO_4^{3-} will be displayed.

Forms ▲▼ **P**
PO_4^{3-}
P_2O_5

Note: *For best accuracy, do a wavelength check with each new lreagent ot (see* Accuracy Check).

Sampling and Storage

Collect samples in plastic or glass bottles that have been acid cleaned with 1:1 Hydrochloric Acid Solution and rinsed with deionized water. Do not use commercial detergents containing phosphate for cleaning glassware used in this test.

For best results, analyze the samples immediately after collection. If prompt analysis is impossible, preserve the samples for up to 48 hours by filtering immediately and storing at 4 °C. The sample should have a neutral (6–8) pH and be at room temperature before analysis.

Accuracy Check

***Note:** Clean glassware with 1:1 hydrochloric acid solution. Rinse again with deionized water. Do not use detergents containing phosphates to clean glassware.*

Standard Additions Method

a) Fill three 10-mL graduated mixing cylinders with 10 mL of sample.

b) Snap the neck off a Voluette™ ampule of Phosphate Standard Solution, 500 mg/L as PO_4^{3-}.

c) Use a TenSette Pipet to add 0.1 mL, 0.2 mL and 0.3 mL, respectively, to the three 10-mL aliquots of sample prepared in *step a*. Mix well.

d) Analyze each sample from *step c* as described in the procedure. Use 5.0 mL of the prepared sample for each test. The concentration should increase: 5 mg/L, 10 mg/L, and 15 mg/L PO_4^{3-}, respectively.

e) If these increases do not occur, see *Standard Additions in Section I* for more information.

Standard Solution Method

To check accuracy, prepare an 80 mg/L PO_4^{3-} standard by pipetting 8.0 mL of solution from a 10-mL Voluette Ampule of Phosphate Standard Solution, 500 mg/L as PO_4^{3-}, into an acid-cleaned 50-mL Class A volumetric flask. Fill to the line with deionized water. Substitute this standard for the sample and perform the procedure as described.

Wavelength Check

This test is sensitive to the wavelength setting. To ensure accuracy, using an 80 mg/L PO_4^{3-} standard solution and a blank follow *steps 8* through *11* several times at slightly different wavelengths until 80 ±2 mg/L as PO_4^{3-} is obtained. Always begin with the highest wavelength value to be tested and reset to a lower value for each successive test. The wavelength should be 420 ±2 nm.

Interferences

Large amounts of sample turbidity may cause inconsistent results in the test because the acid present in the reagents may dissolve some of the suspended particles and because of variable desorption of orthophosphate from the particles.

The following may interfere when present in concentrations exceeding these listed below:

Interfering Substance	Interference Level and Treatment
Arsenate	Only interferes if the sample is heated.*
Iron, ferrous	Blue color caused by ferrous iron does not interfere if iron concentration is less than 100 mg/L.
Molybdate	Causes negative interference above 1000 mg/L.
Silica	Only interferes if the sample is heated.*
Sulfide	Causes a negative interference. Remove interference as follows: **1.** Measure 25 mL of sample into a 50-mL beaker. **2.** Add Bromine Water drop-wise with constant swirling until a permanent yellow color develops. **3.** Add Phenol Solution drop-wise until the yellow color just disappears. Proceed with *step 1*.
Extreme pH or highly buffered samples	May exceed buffering capacity of the reagents. See *pH Interferences* in *Section 1.* Samples may require pretreatment. Sample pH should be about 7.
Fluoride, thorium, bismuth, thiosulfate or thiocyanate	Cause a negative interference.
Temperature, cold (less than 20 °C)	Cause a negative interference.
Temperature, hot (greater than 25 °C)	Cause a positive interference.
The following do not interfere in concentrations up to 1000 mg/L: Pyrophosphate, tetraborate, selenate, benzoate, citrate, oxalate, lactate, tartrate, formate, salicylate, Al^{3+}, Fe^{3+}, Mg^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+}, Li^{+}, Na^{+}, K^{+}, NH_4^{+}, Cd^{2+}, Mn^{2+}, NO_3^{-}, NO_2^{-}, SO_4^{2-}, SO_3^{2-}, Pb^{2+}, Hg^{+}, Hg^{2+}, Sn^{2+}, Cu^{2+}, Ni^{2+}, Ag^{+}, U^{4+}, Zr^{4+}, AsO_3^{-}, Br^{-}, CO_3^{2-}, ClO_4^{-}, CN^{-}, IO_3^{-}, SiO_4^{4-}.	

* Gentle warming of the sample to reach room temperature will not cause this substance to interfere.

Precision

In a single laboratory, using a standard solution of 80.0 mg/L PO_4^{3-} and two lots of reagent with a DR/2010, a single operator obtained a standard deviation of less than ±2.0 mg/L PO_4^{3-} .

Estimated Detection Limit (EDL)

The EDL for this test is 5.0 mg/L PO_4^{3-} . The EDL is the calculated lowest average concentration in a deionized water matrix that is different from zero with a 99% level of confidence. For more information on derivation and use of Hach's estimated detection limit, see *Section I*.

Sample Disposal Information

Final samples will contain molybdenum. In addition, final samples will have a pH less than 2 and are considered corrosive (D002) by the Federal RCRA. Consult the Material Data Safety Data Sheet for information specific to the reagents used.

Safety

Good safety habits and laboratory techniques should be used throughout the procedure. Consult the Material Safety Data Sheet for information specific to the reagents used.

Summary of Method

Orthophosphate reacts with molybdate in an acid medium to produce a phosphomolybdate complex. In the presence of vanadium, yellow vanadomolybdophosphoric acid forms. The intensity of the yellow color is proportional to the phosphate concentration.

REQUIRED REAGENTS

High Range Reactive Phosphorus Test 'N Tube™ Reagent Set	50 vials	27673-45

Includes: (50) Reactive High Range Phosphorus Test 'N Tube Reagent Vials*, (2) 272-42

Description	Quantity Required Per Test	Unit	Cat. No.
Reactive High Range Phosphorus Test 'N Tube Vials	1	50/pkg	*
Water, deionized		100 mL	272-42

REQUIRED APPARATUS

COD Vial Adapter, DR/2010	1	each	44799-00
Pipet, TenSette, 1 to 10 mL	1	each	19700-10
Pipet Tips, for 19700-10 TenSette Pipet	1	50/pkg	21997-96
Test Tube Rack	1–3	each	18641-00

OPTIONAL REAGENTS

Bromine Water, 30 g/L	29 mL**	2211-20
Hydrochloric Acid Standard Solution, 6.0 N (1:1)	500 mL	884-49
Phenol Solution, 30 g/L	29 mL	2112-20
Phosphate Standard Solution, PourRite ampule, 500 mg/L as PO_4^{3-}, 2 mL	20/pkg	14242-20
Phosphate Standard Solution, Voluette ampule, 500 mg/L as PO_4^{3-}, 10 mL	16/pkg	14242-10

OPTIONAL APPARATUS

Ampule Breaker Kit	each	21968-00
Aspirator, vacuum	each	2131-00
Cylinder, graduated, mixing, 10 mL, 3 required	each	20886-40
Filter Holder, 47 mm, 300 mL, graduated	each	13529-00
Filter, membrane, 47 mm, 0.45 microns	200/pkg	13530-00
Flask, filtering, 500 mL	each	546-49
Flask, volumetric, Class A, 50-mL	each	14574-41
pH Indicator Paper, 1 to 11 pH units	5 rolls/pkg	391-33
pH Meter, *sension*™*1*, portable	each	51700-10
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette® Pipet	50/pkg	21856-96
Pipet Tips, for 19700-10 TenSette® Pipet	250/pkg	21997-25
Pipet, volumetric, Class A, 5.00-mL	each	14515-37
Pipet, volumetric, Class A, 8.00-mL	each	14515-08
PourRite Ampule Breaker	each	24846-00

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* These items are not sold separately.

** Larger sizes available.

Method 8190

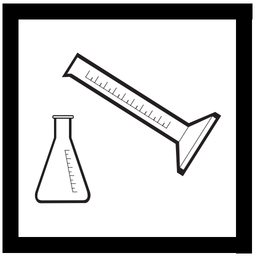
PHOSPHORUS, TOTAL

For water, wastewater, and seawater

(also called Organic and Acid Hydrolyzable)

Acid Persulfate Digestion Method*

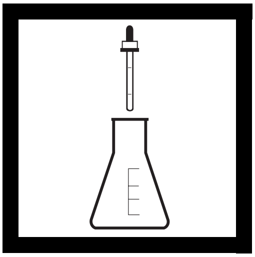
USEPA Accepted for reporting wastewater analysis**



1. Measure 25 mL of sample into a 50-mL (or larger) erlenmeyer flask using a graduated cylinder.

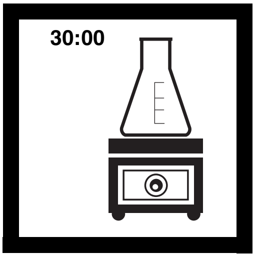
Note: *Rinse all glassware with 1:1 Hydrochloric Acid Solution. Rinse again with deionized water.*

2. Add the contents of one Potassium Persulfate Powder Pillow. Swirl to mix.



3. Add 2.0 mL of 5.25 N Sulfuric Acid Solution.

Note: *Use the 1-mL calibrated dropper provided.*



4. Place the flask on a hot plate. Boil gently for 30 minutes.

Note: *Samples should be concentrated to less than 20 mL for best recovery. After concentration maintain the volume near 20 mL by adding small amounts of deionized water. Do not exceed 20 mL.*

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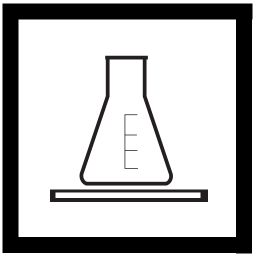
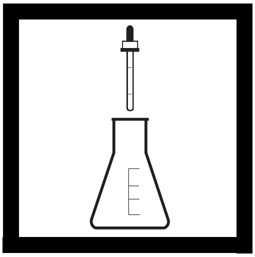
* Adapted from *Standard Methods for the Examination of Water and Wastewater.*

** Procedure is equivalent to USEPA Method 365.2 and Standard Method 4500-P B,5 & P E.



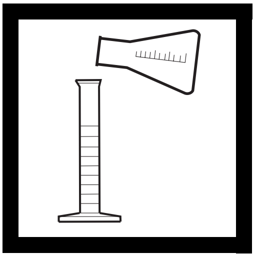
5. Cool the sample to room temperature.



6. Add 2.0 mL of 5.0 N Sodium Hydroxide Solution. Swirl to mix.

Note: *Use the 1-mL calibrated dropper provided.*

Note: *After adding sodium hydroxide, pH should be 8.2.*



7. Pour the sample into a 25-mL graduated cylinder. Return the volume to 25 mL.

Note: *Use deionized water rinsings from the flask to adjust the volume.*

Note: *Results of the reactive phosphorus test at this point will include the organic phosphate plus the orthophosphate and the acid-hydrolyzable (condensed) phosphate. The organic phosphate concentration is determined by subtracting results of an acid hydrolyzable phosphorus test from this result. Make sure that both results are in the same units before taking the difference.*

Choose reactive phosphorus test.

8. Proceed with a reactive phosphorus method that will cover the expected total phosphorus concentration range.

Sampling and Storage

Collect samples in plastic or glass bottles that have been acid cleaned with 1:1 Hydrochloric Acid Solution and rinsed with deionized water. Do not use commercial detergents containing phosphate for cleaning glassware used in this test.

Analyze samples immediately after collection for best results. If prompt impossible, preserve samples up to 28 days by adjusting the pH to 2 or less with sulfuric acid (about 2 mL per liter) and storing at 4 °C. Warm to room temperature before testing. Neutralize with sodium hydroxide.

Correct results for volume additions; see *Volume Additions* (*Section I*) for more information.

Interferences

For turbid samples, use 50 mL of sample and double the reagent quantities. Use 25 mL of the reacted sample to zero the instrument in the reactive phosphorus procedure. This compensates for any color or turbidity destroyed by this procedure. For alkaline or highly buffered samples it may be necessary to add additional acid in Step 3 to drop the pH of the solution below 1.

Summary of Method

Phosphates present in organic and condensed inorganic forms (meta-, pyro- or other polyphosphates) must be converted to reactive orthophosphate before analysis. Pretreatment of the sample with acid and heat provides the conditions for hydrolysis of the condensed inorganic forms. Organic phosphates are converted to orthophosphate by heating with acid and persulfate. Organically bound phosphates are thus determined indirectly by subtracting the result of an acid hydrolyzable phosphorus test from the total phosphorus result.

This procedure must be followed by one of the reactive phosphorus (orthophosphate) analysis methods for determination of the phosphorus content of the sample. If the ascorbic acid (PhosVer 3) method is used to measure the reactive phosphorus, this method is EPA approved for NPDES reporting.

The following reagents and apparatus are required besides those required for the reactive phosphorus test.

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
Potassium Persulfate Powder Pillows	1 pillow	100/pkg	2451-99
Sodium Hydroxide Solution, 5.0 N	2 mL	100 mL* MDB	2450-32
Sulfuric Acid Solution, 5.25 N	2 mL	100 mL* MDB	2449-32

REQUIRED APPARATUS

Cylinder, graduated, 25 mL	2	each	508-40
Flask, Erlenmeyer, 50 mL	1	each	505-41
Hot Plate, 4" diameter, 120 Vac		each	12067-01
Hot Plate, 4" diameter, 240 Vac		each	12067-02

OPTIONAL REAGENTS

Hydrochloric Acid, 6 N	500 mL	884-49
Sodium Hydroxide Solution, 5.0 N	1 L	2450-53
Sulfuric Acid, ACS	500 mL	979-49
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Cylinder, graduated, 50 mL	each	508-41
Flask, erlenmeyer, 125 mL	each	505-43
Pads, cooling, 4 X 4"	each	18376-00
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
pH Meter, *sension*™*1*, portable	each	51700-10

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

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* Contact Hach for larger sizes.

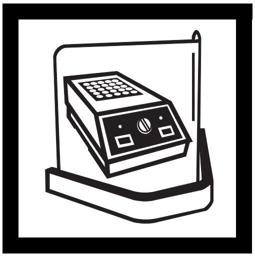
Method 8190

PHOSPHORUS, TOTAL (0.00 to 3.50 mg/L PO_4^{3-}) For water, wastewater and seawater

PhosVer 3 with Acid Persulfate Digestion* Test 'N Tube Method

USEPA Accepted for reporting wastewater analyses**

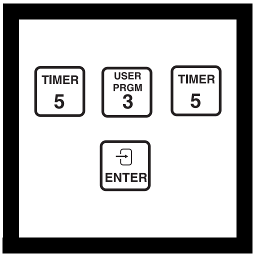
Test 'N Tube Procedure



1. Turn on the COD Reactor. Heat to 150 °C. Place the plastic shield in front of the reactor.

Note: *Ensure safety devices are in place to protect the analyst from splattering should leakage occur.*

Note: *See COD Reactor manual for temperature adjustment instructions.*

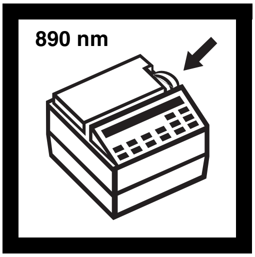


2. Enter the user-stored program number for reactive phosphorus, Test 'N Tube.

Press: **535 ENTER**

The display will show:

Dial nm to 890



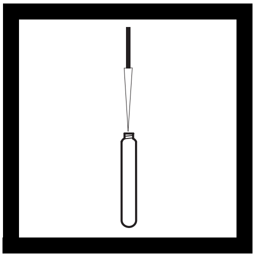
3. Rotate the wavelength dial until the small display shows:

890 nm

When the correct wavelength is dialed in, the display will quickly show:

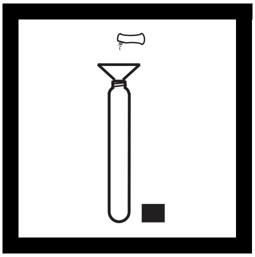
Zero Sample

then: **mg/L PO_4^{3-} TNT**

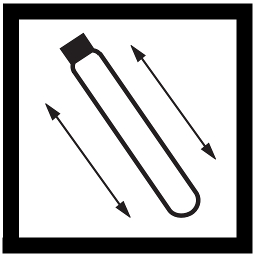


4. Use a TenSette Pipet to add 5.0 mL of sample to a Total and Acid Hydrolyzable Test Vial.

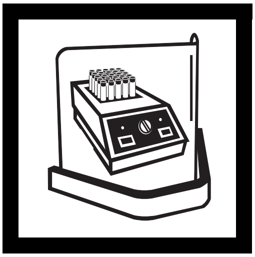
Note: *Run a reagent blank for this test. Use deionized water in place of the sample. Subtract this result from all test results run with this lot of PhosVer 3 reagent.*



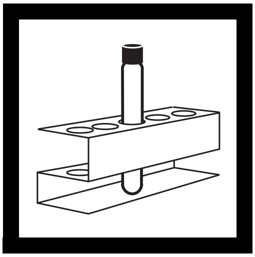
5. Using a funnel, add the contents of one Potassium Persulfate Powder Pillow for Phosphonate to the vial.



6. Cap tightly and shake to dissolve.



7. Heat the vial for 30 minutes at 150 °C.



8. Carefully remove the vial from the reactor. Place it in a test tube rack and allow to cool to room temperature.

Note: *Tubes will be hot.*

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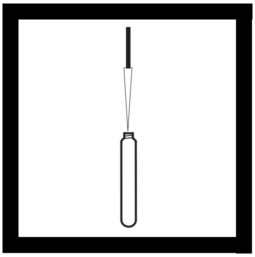
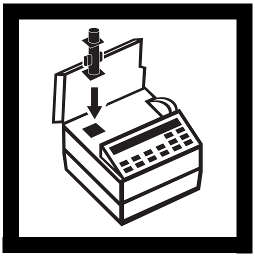
* Adapted from *Standard Methods for the Examination of Water and Wastewater.*

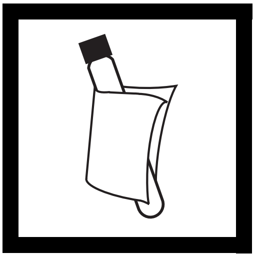
** Procedure is equivalent to USEPA Method 365.2 and Standard Method 4500-P B, 5 and P.E.



9. Use a TenSette Pipet to add 2 mL of 1.54 N sodium hydroxide to the vial. Cap and mix.

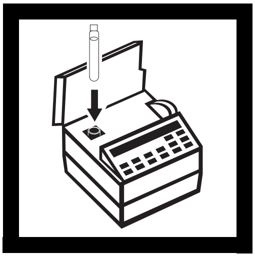


10. Place the COD Vial Adapter into the cell holder with the marker to the right.

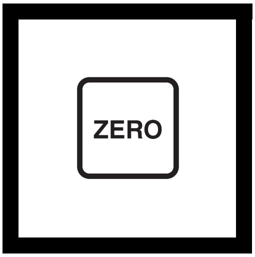


11. Clean the outside of the vial with a towel.

Note: *Wiping with a damp towel, followed by a dry one, will remove fingerprints or other marks.*



12. Place the sample vial in the adapter with the Hach logo facing the front of the instrument. Place the cover on the adapter.



13. Press: **ZERO**

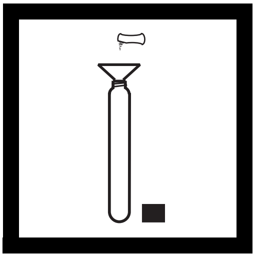
The display will show:

Zeroing. . .

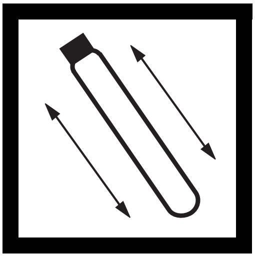
then

0.00 mg/L PO_4^{3-} TNT

Note: *For multiple samples from the same source, zero only on the first sample. Read the remaining samples after adding the PhosVer 3 reagent. Subtract the PhosVer 3 reagent blank value from each reading.*

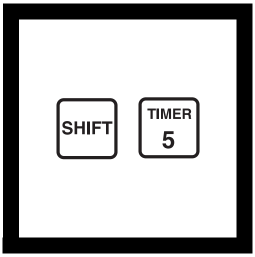


14. Using a funnel, add the contents of one PhosVer 3 Phosphate Reagent Powder Pillow to the vial.



15. Cap tightly and shake for 10-15 seconds.

Note: *The powder will not completely dissolve.*

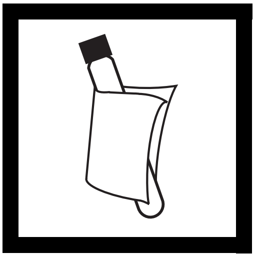


16. Press:

SHIFT TIMER

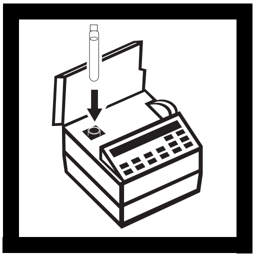
A 2-minute waiting period will begin.

Note: *Read samples between 2 and 8 minutes.*

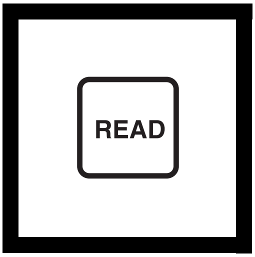


17. After the timer beeps, clean the outside of the sample vial with a towel.

Note: *Wiping with a damp towel, followed by a dry one, will remove fingerprints or other marks.*



18. Place the prepared sample vial into the adapter with the Hach logo facing the front of the instrument. Place the cover on the adapter.



19. Press: **READ**

The display will show:

Reading. . .

then the display will show the results in mg/L PO_4^{3-}.

Forms ▲▼ P
PO_4^{3-}
P_2O_5

IMPORTANT NOTE:

The test range for total phosphate is limited to 0 to 3.5 mg/L PO_4^{3-}. Values above 3.5 mg/L may be used to estimate dilution ratios, but should NOT be used for reporting purposes. If a test overranges, dilute the sample and repeat the digestion and colorimetric testing for accurate results.

Sampling and Storage

Collect samples in plastic or glass bottles that have been acid cleaned with 1:1 Hydrochloric Acid Solution and rinsed with deionized water. Do not use commercial detergents containing phosphate for cleaning glassware used in this test.

Analyze samples immediately after collection for best results. If prompt analysis is impossible, preserve the sample for up to 28 days by adjusting the pH to 2 or less with concentrated sulfuric acid (about 2 mL per liter) and refrigerating at 4 °C. Neutralize with sodium hydroxide and warm the sample to room temperature before analysis.

Correct results for volume additions (see *Volume Additions, Section I*).

Accuracy Check

Note: *Clean glassware with 1:1 hydrochloric acid solution. Rinse again with deionized water. Do not use detergents containing phosphates to clean glassware.*

Standard Additions Method

a) Fill three 25-mL graduated mixing cylinders with 25 mL of sample.

b) Snap the neck off a Phosphate Voluette Ampule Standard, 50 mg/L as PO_4^{3-}.

c) Use the TenSette Pipet to add 0.1 mL, 0.2 mL and 0.3 mL, respectively, to the three 25-mL aliquots of a water sample prepared in *step a*. Mix well.

d) Analyze samples from Step C as described in the procedure; use 5.0 mL of the prepared sample for each test. The concentration should increase as follows: 0.2 mg/L, 0.4 mg/L, 0.6 mg/L PO_4^{3-}, respectively.

e) If these increases do not occur, see *Standard Additions* (*Section I*) for more information.

Standard Solution Method

To check accuracy, use a 1.0 mg/L Phosphate Standard Solution listed under Optional Reagents. Or, this can be prepared by pipetting 2.0 mL of solution from a Voluette Ampule Standard for Phosphate, 50 mg/L as PO_4^{3-}, into a Class A 100-mL volumetric flask. Dilute to the mark with deionized water. Substitute this standard for the sample and perform the procedure as described. The mg/L PO_4^{3-} reading should be 1.0 mg/L.

Interferences

Large amounts of turbidity may cause inconsistent results in the test because the acid present in the powder pillows may dissolve some of the suspended particles and because of variable desorption of orthophosphate from the particles.

The PhosVer 3 Phosphate Reagent Powder Pillows should be stored in a cool, dry environment.

The following may interfere when present in concentrations exceeding these listed below:

Aluminum	200 mg/L
Chromium	100 mg/L
Copper	10 mg/L
Iron	100 mg/L
Nickel	300 mg/L
Silica	50 mg/L
Silicate	10 mg/L
Sulfide	90 mg/L
Zinc	80 mg/L

Arsenate interferes at all levels.

Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment. See *Section I* for more information.

Precision

In a single laboratory, using a standard solution of 3.00 mg/L PO_4^{3-} and two lots of reagent with a DR/2010, a single operator obtained a standard deviation of ±0.09 mg/L PO_4^{3-}.

Estimated Detection Limit

The Estimated Detection Limit (EDL) for this test is 0.04 mg/L PO_4^{3-}. The EDL is the calculated lowest average concentration in a deionized water matrix that is different from zero with a 99% level of confidence. For more information on derivation and use of Hach's estimated detection limit, see *Section I.*

Sample Disposal Information

Final samples will contain molybdenum. In addition, final samples will have a pH less than 2 and are considered corrosive (D002) by the Federal RCRA.

Summary of Method

Phosphates present in organic and condensed inorganic forms (meta-, pyro- or other polyphosphates) must be converted to reactive orthophosphate before analysis. Pretreatment of the sample with acid and heat provides the conditions for hydrolysis of the condensed inorganic forms. Organic phosphates are converted to orthophosphates by heating with acid and persulfate.

Orthophosphate reacts with molybdate in an acid medium to produce a phosphomolybdate complex. Ascorbic acid then reduces the complex, giving an intense molybdenum blue color.

REQUIRED REAGENTS

Description	Cat. No.
Total Phosphorus Test 'N Tube Reagent Set Includes: (1) 21060-46, (1) 20847-66, (1) 27430-42, (1) 272-56, (50) Test 'N Tube Dilution Vials*	27426-45

Description	Quantity Required Per Test	Unit	Cat. No.
PhosVer 3 Phosphate Reagent Powder Pillows	1 Pillow	50/pkg	21060-46
Potassium Persulfate Powder Pillows	1	50/pkg	20847-66
Sodium Hydroxide Standard Solution, 1.54 N	2 mL	100 mL	27430-42
Test 'N Tube Acid Dilution Vials	1	50/pkg	*
Water, deionized	100mL	4 L	272-56

REQUIRED APPARATUS

Description	Quantity Required Per Test	Unit	Cat. No.
COD Reactor, 115/230 Vac (U.S.A. and Canada)	1	each	45600-00
COD Reactor, 115/230 Vac (Europe)	1	each	45600-02
COD Vial Adapter, DR/2010	1	each	44799-00
Funnel, micro	1	each	25843-35
Safety Shield, laboratory bench	1	each	23810-00
Test Tube Rack	1-3	each	18641-00
Pipet, TenSette, 1 to 10 mL	1	each	19700-10
Pipet Tips, for 19700-10 TenSette Pipet	2	50/pkg	21997-96

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* These items are not sold separately.

OPTIONAL REAGENTS

Description	Unit	Cat. No.
Hydrochloric Acid Standard Solution, 6.0 N (1:1)	500 mL	884-49
Phosphate Standard Solution, 1 mg/L as PO_4^{3-}	500 mL	2569-49
Phosphate Standard Solution, Voluette Ampule, 50 mg/L as PO_4^{3-}, 10 mL	16/pkg	171-10
Sodium Hydroxide Standard Solution, 5.0 N	1 L	2450-53
Sulfuric Acid, ACS	500 mL	979-49
Total and Acid Hydrolyzable Test 'N Tube Reagent Set	50 tests	27427-45
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Ampule Breaker Kit	each	21968-00
Cylinder, graduated, mixing, 25 mL	each	20886-40
Flask, volumetric, Class A, 100 mL	each	14574-42
pH Indicator Paper, 1 to 11 pH units	5 rolls/pkg	391-33
pH Meter, *sension*™*1*, portable	each	51700-10
Pipet Filler, safety bulb	each	14651-00
Pipet, TenSette, 0 to 0.1 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

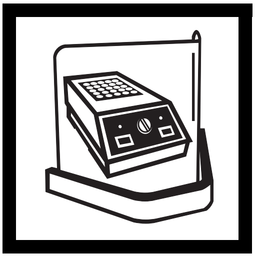
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 10127

PHOSPHORUS, TOTAL, HR (0.0 to 100.0 mg/L PO_4^{3-})

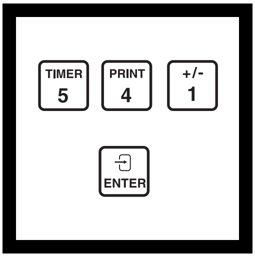
For water and wastewater

Molybdovanadate Method with Acid Persulfate Digestion, Test ’N Tube™ Procedure*



1. Turn on the COD Reactor. Heat to 150 °C. Place the plastic shield in front of the reactor.

Note: *Ensure safety devices are in place to protect the analyst if splattering or leakage occurs.*

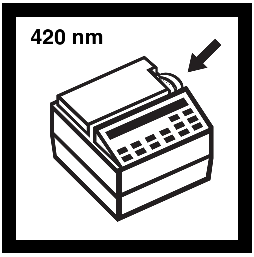


2. Enter the user-stored program number for phosphorus total high range, Test ’N Tube.

Press: **541 ENTER**

The display will show:

Dial nm to 420



3. Rotate the wavelength dial until the small display shows:

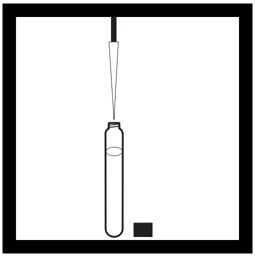
420 nm

When the correct wavelength is dialed in the display will quickly show:

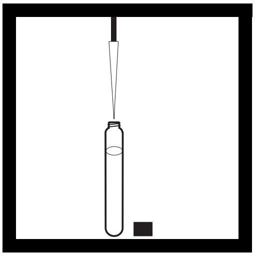
Zero Sample

then:

mg/L PO_4^{3-} HR Tl

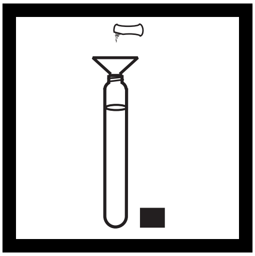


4. Use a TenSette Pipet to add 5.0 mL of deionized water to a Total Phosphorus Test ’N Tube Vial (the blank).

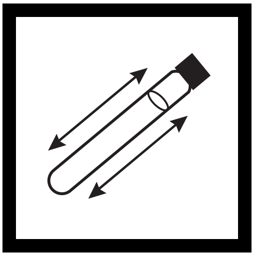


5. Use a TenSette Pipet to add 5.0 mL of sample to a Total Phosphorus Test ’N Tube Vial (the sample).

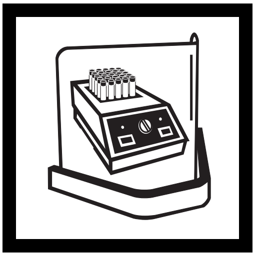
Note: *Adjust the pH of stored samples to 6–8 before analysis.*



6. Use a funnel to add the contents of one Potassium Persulfate Powder Pillow for Phosphonate to each vial.



7. Cap tightly and shake to dissolve.



8. Place the vials in the COD reactor. Heat for 30 minutes.

Press **SHIFT TIMER** to time the heating period.

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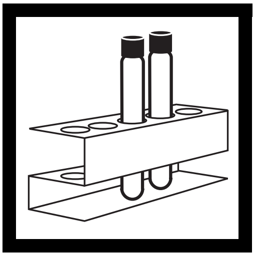
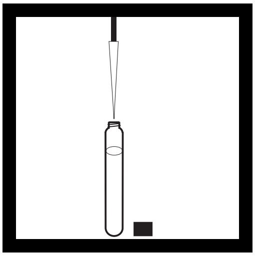
* Adapted from *Standard Methods for the Examination of Water and Wastewater.*



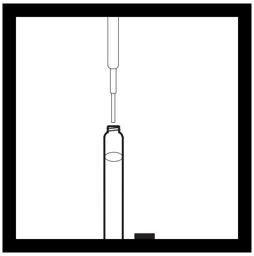
9. Carefully remove the vials from the reactor. Place them in a test tube rack and allow to cool to room temperature (18–25 °C).

Note: *Vials will be hot.*



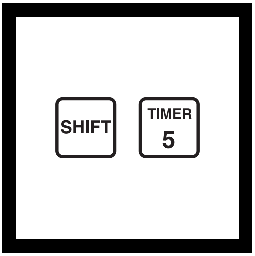
10. Use a TenSette Pipet to add 2.0 mL of 1.54 N sodium hydroxide to each vial.

Cap and invert to mix.



11. Use a polyethylene dropper to add 0.5 mL of Molybdovanadate Reagent to the vials.

Cap and invert to mix.

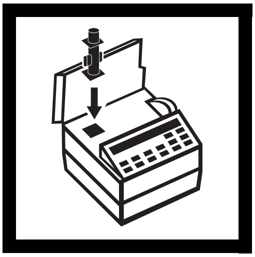


12. Press:

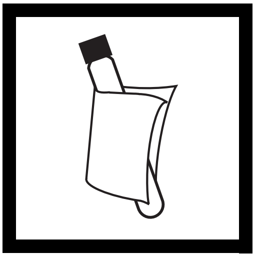
SHIFT TIMER

A 7-minute reaction period will begin.

Note: *Read the samples between 7 and 9 minutes.*

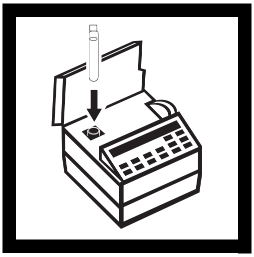


13. Place the COD Vial Adapter into the cell holder with the marker to the right.



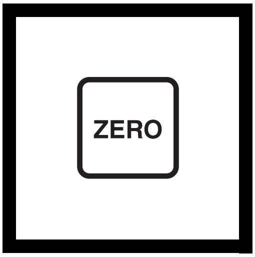
14. Clean the outside of the vials with a towel.

Note: *Wipe with a damp towel, followed by a dry one, to remove fingerprints or other marks.*



15. When the timer sounds, place the blank in the adapter with the Hach logo facing the front of the instrument. Place the cover on the adapter.

Note: *Reagent blanks for each lot of reagent may be used more than once, but should not be used for longer than one day.*



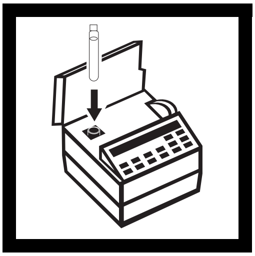
16. Press: **ZERO**.

The display will show:

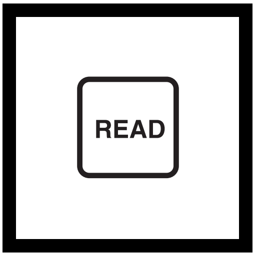
Zeroing. . .

then:

0.0 mg/L PO_4^{3-} HR Tl



17. Place the prepared sample vial into the adapter with the Hach logo facing the front of the instrument. Place the cover on the adapter.



18. Press: **READ**

The display will show:

Reading. . .

then the display will show the results in mg/L PO_4^{3-}.

Forms ▲▼ **P**
PO_4^{3-}
P_2O_5

Note: For maximum accuracy, perform a wavelength check with each new lot of reagent. See Accuracy Check.

Sampling and Storage

Collect samples in plastic or glass bottles that have been acid cleaned with 1:1 Hydrochloric Acid Solution and rinsed with deionized water. Do not use commercial detergents containing phosphates for cleaning glassware used in this test.

Analyze samples immediately after collection for best results. If prompt analysis is impossible, preserve the sample for up to 28 days by adjusting the pH to 2 or less with concentrated H_2SO_4 (about 2 mL per liter) and storing at 4 °C. Warm the sample to room temperature and neutralize with 5.0 N NaOH before analysis.

Correct results for volume additions (see *Volume Additions, Section I*).

Accuracy Check

Note: *Clean glassware with 1:1 hydrochloric acid solution. Rinse again with deionized water. Do not use detergents containing phosphates to clean glassware.*

Standard Additions Method

a) Fill each of three 10-mL graduated mixing cylinders with 10 mL of sample.

b) Snap the neck off a 10-mL Voluette Ampule of Phosphate Standard Solution, 500 mg/L as PO_4^{3-}.

c) Use a TenSette Pipet to add 0.1 mL, 0.2 mL and 0.3 mL, respectively, to the three 10-mL aliquots of the water sample prepared in *step a*. Mix well.

d) Analyze samples from *step c* as described in the procedure. Use 5.0 mL of the prepared sample for each test. The concentration should increase: 5 mg/L, 10 mg/L, and 15 mg/L PO_4^{3-}, respectively.

e) If these increases do not occur, see *Section I*.

Standard Solution Method

To check accuracy, prepare an 80-mg/L standard by pipetting 8.0 mL of solution from a Voluette Ampule of Phosphate Standard Solution, 500 mg/L as PO_4^{3-}, into an acid-cleaned, Class A, 50-mL volumetric flask. Dilute to the mark with deionized water. Substitute this standard for the sample and perform the procedure as described.

Wavelength Check

This test is sensitive to the wavelength setting. To ensure accuracy, using an 80 mg/L PO_4^{3-} standard solution and a blank follow *steps 15* through *18* several times at slightly different wavelengths until 80 ±2 mg/L as PO_4^{3-} is obtained. Always begin with the highest wavelength value to be tested and reset to a lower value for each successive test. The wavelength should be 420 ±2 nm.

Interferences

Large amounts of sample turbidity may cause inconsistent results in the test because the acid present in the reagents may dissolve some of the suspended particles and because of variable desorption of orthophosphate from the particles.

The following may interfere when present in concentrations exceeding these listed below:

Interfering Substance	Interference Level and Treatment
Arsenate	Causes positive interference if the sample is heated.*
Iron, ferrous	Blue color caused by ferrous iron does not interfere if iron concentration is less than 100 mg/L.
Molybdate	Causes negative interference above 1000 mg/L.
Silica	Causes positive interference if the sample is heated.*
Extreme pH or highly buffered samples	May exceed buffering capacity of the reagents. See *pH Interferences* in *Section I* . Samples may require pretreatment. Sample pH should be about 7.
Fluoride, thorium, bismuth, thiosulfate or thiocyanate	Cause a negative interference.
Temperature, Cold (less than 18 °C)	Causes a negative interference.
Temperature, Hot (greater than 25 °C)	Causes a positive interference. Post-digestion samples should be brought to room temperature (18–25 °C) before the addition of the Molybdovanadate Reagent or sodium hydroxide.
The following do not interfere in concentrations up to 1000 mg/L: Pyrophosphate, tetraborate, selenate, benzoate, citrate, oxalate, lactate, tartrate, formate, salicylate, Al^{3+}, Fe^{3+}, Mg^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+}, Li^{+}, Na^{+}, K^{+}, NH_4^{+}, Cd^{2+}, Mn^{2+}, NO_3^{-}, NO_2^{-}, SO_4^{2-}, SO_3^{2-}, Pb^{2+}, Hg^{+}, Hg^{2+}, Sn^{2+}, Cu^{2+}, Ni^{2+}, Ag^{+}, U^{4+}, Zr^{4+}, AsO_3^{-}, Br^{-}, CO_3^{2-}, ClO_4^{-}, CN^{-}, IO_3^{-}, SiO_4^{4-}.	

* Gentle warming of the sample to reach room temperature will not cause this substance to interfere.

Method Performance

Precision

In a single laboratory, using a standard solution of 80.0 mg/L PO_4^{3-} and two lots of reagent with a DR/2010, a single operator obtained a standard deviation of ±2.0 mg/L PO_4^{3-}.

Estimated Detection Limit

The Estimated Detection Limit (EDL) for this test is 5.0 mg/L PO_4^{3-}. The EDL is the calculated lowest average concentration in a deionized water matrix that is different from zero with a 99% level of confidence. For more information on derivation and use of Hach’s estimated detection limit, see *Section I.*

Safety

Good safety habits and laboratory techniques should be used throughout the procedure. Consult the Material Safety Data Sheet for information specific to the reagents used.

Sample Disposal Information

The final samples will contain molybdenum. In addition, the final samples will have a pH less than 2 and are considered corrosive (D002) by the Federal RCRA. Consult the Material Data Safety Data Sheet for information specific to the reagents used.

Summary of Method

Phosphates present in organic and condensed inorganic forms (meta-, pyro- or other polyphosphates) must be converted to reactive orthophosphate before analysis. Pretreatment of the sample with acid and heat provides the conditions for hydrolysis of the condensed inorganic forms. Organic phosphates are converted to orthophosphates by heating with acid and persulfate.

Orthophosphate reacts with molybdate in an acid medium to produce a phosphomolybdate complex. In the presence of vanadium, yellow vanadomolybdophosphoric acid forms. The intensity of the yellow color is proportional to the phosphate concentration.

REQUIRED REAGENTS

Total High Range Phosphorus Test ’N Tube™ Reagent Set50 vials27672-45
Includes: (50) Total Phosphorus Test ’N Tube Vials*, (2) 272-42, (1) 20847-66, (1) 20760-26, (1) 27430-42

Description	Quantity Required Per Test	Unit	Cat. No.
Molybdovanadate Reagent	0.5 mL	25 mL	20760-26
Potassium Persulfate Powder Pillows	1	50/pkg	20847-66
Sodium Hydroxide Solution, 1.54 N	2 mL	100 mL	27430-42
Total and Phosphorus Test ’N Tube Vials	1	50/pkg	*
Water, deionized		100 mL	272-42

REQUIRED APPARATUS

COD Reactor, 115/230 Vac (U.S.A. and Canada)	1	each	45600-00
COD Reactor, 115/230 Vac (Europe)	1	each	45600-02
COD Vial Adapter, DR/2010	1	each	44799-00
Dropper, LDPE, 0.5 to 1.0 mL	1	20/pkg	21247-20
Pipet, TenSette, 1 to 10 mL	1	each	19700-10
Pipet Tips, for 19700-10 TenSette Pipet	2	50/pkg	21997-96
Safety Shield, laboratory bench	1	each	50030-00
Test Tube Rack	1–3	each	18641-00

OPTIONAL REAGENTS

Hydrochloric Acid Standard Solution, 6.0 N (1:1)		500 mL	884-49
Phosphate Standard Solution, PourRite ampule, 500 mg/L as PO_4^{3-}, 2 mL		20/pkg	14242-20
Phosphate Standard Solution, Voluette Ampule, 500 mg/L as PO_4^{3-}, 10 mL		16/pkg	14242-10
Sodium Hydroxide Standard Solution, 5.0 N		1 L	2450-53
Sulfuric Acid, ACS, concentrated		500 mL	979-49

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* These items are not sold separately.

OPTIONAL APPARATUS

Description	Unit	Cat. No.
Ampule Breaker Kit	each	21968-00
Aspirator, vacuum	each	2131-00
Cylinder, graduated, mixing, 10-mL (3 required)	each	20886-38
Filter Holder, 47 mm, 300-mL, graduated	each	13529-00
Filter, membrane, 47 mm, 0.45 microns	200/pkg	13530-01
Flask, filtering, 500-mL	each	546-49
Flask, volumetric, Class A, 50-mL	each	14574-41
pH Indicator Paper, 1 to 11 pH units	5 rolls/pkg	391-33
pH Meter, *sension*™*1*, portable	each	51700-10
Pipet Filler, Safety Bulb	each	14651-00
Pipet, TenSette, 0.1- to 1.0-mL	each	19700-01
Pipet Tips, for 19700-01	50 pkg	21856-96
Pipet, volumetric, Class A, 8.00-mL	each	14515-08
Stopper, No. 7 one hole	6/pkg	2119-07
Tubing, rubber	12 feet	560-19

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

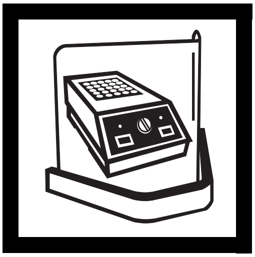
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8180

PHOSPHORUS, ACID HYDROLYZABLE (0.00 to 5.00 mg/L PO_4^{3-})

PhosVer3 with Acid Hydrolysis, Test 'N Tube Procedure

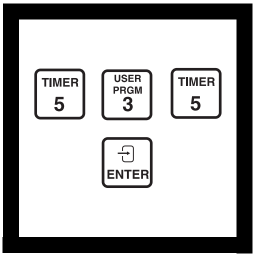
For water, wastewater, and seawater



1. Turn on the COD Reactor. Heat to 150 °C. Place the plastic shield in front of the reactor.

Note: *Ensure safety devices are in place to protect the analyst from splattering should leakage occur.*

Note: *See COD Reactor manual for temperature adjustment instructions.*

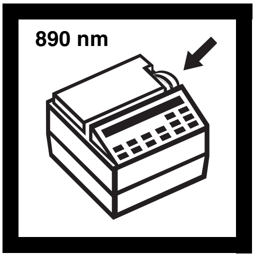


2. Enter the stored program number for reactive phosphorus Test 'N Tube.

Press: **5 3 5 ENTER**

The display will show:

Dial nm to 890

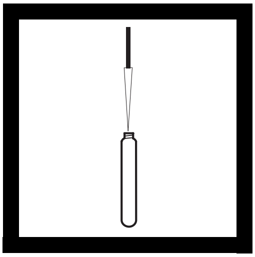


3. Rotate the wavelength dial until the small display shows:

890 nm

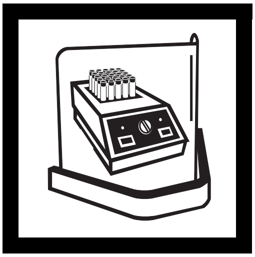
When the correct wavelength is dialed in, the display will quickly show: **Zero Sample**

then: **mg/L PO_4^{3-} TNT**

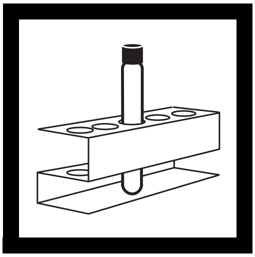


4. Use a TenSette Pipet to add 5.0 mL of sample to a Total and Acid Hydrolyzable Test Vial. Cap and mix.

Note: *Run a reagent blank for this test. Use deionized water in place of the sample. Subtract this result from all test results run with this lot of PhosVer 3 Reagent.*

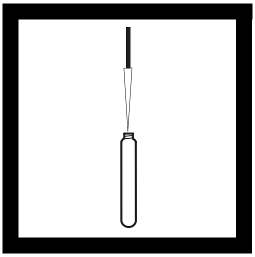


5. Heat the vial for 30 minutes at 150 °C.

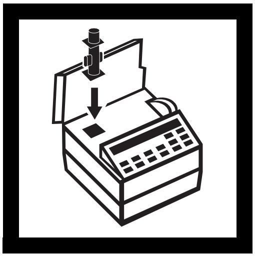


6. Carefully remove the vial from the reactor. Place it in a test tube rack and allow to cool to room temperature.

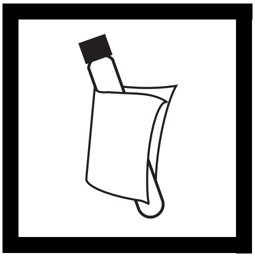
Note: *Tubes will be hot.*



7. Use a TenSette Pipet to add 2 mL of 1.00 N sodium hydroxide to the vial. Cap and mix.

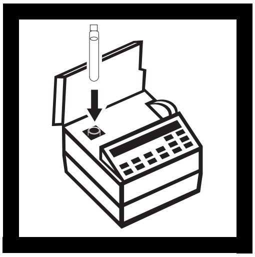


8. Insert a COD Vial Adapter into the cell holder with the marker to the right.

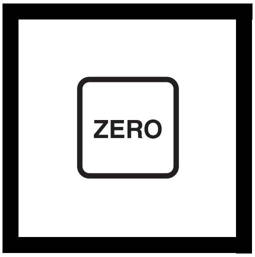


9. Clean the outside of the vial with a towel.

Note: *Wiping with a damp towel, followed by a dry one, will remove fingerprints or other marks.*



10. Place the sample vial in the adapter with the Hach logo facing the front of the instrument. Place the cover on the adapter.



11. Press: **ZERO**

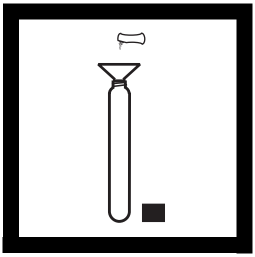
The display will show:

Zeroing. . .

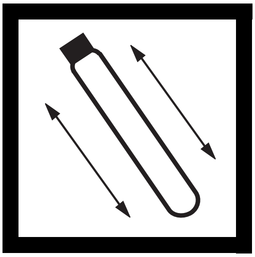
then:

0.00 mg/L PO_4^{3-} TNT

Note: *For multiple samples from the same source, zero on the first sample. Read the remaining samples after adding the PhosVer 3 reagent. Subtract the reagent blank value from each reading.*

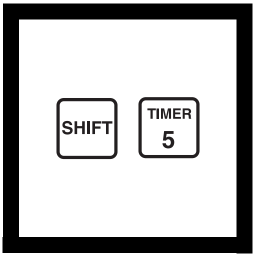


12. Using a funnel, add the contents of one PhosVer 3 Phosphate Reagent Powder Pillow to the vial.



13. Cap tightly and shake for 10-15 seconds.

Note: *The powder will not completely dissolve.*

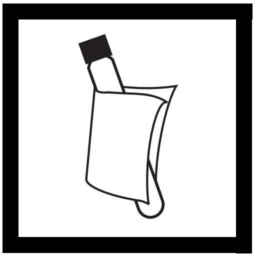


14. Press:

SHIFT TIMER

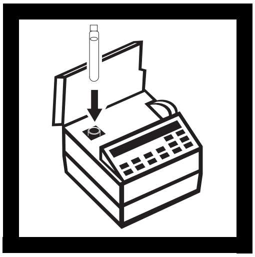
A 2-minute reaction period will begin.

Note: *Read samples between 2 and 8 minutes.*

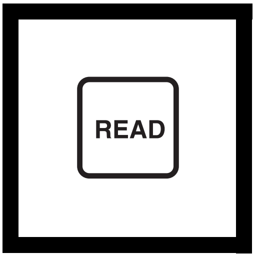


15. Clean the outside of the sample vial with a towel.

Note: *Wiping with a damp towel, followed by a dry one, will remove fingerprints or other marks.*



16. When the timer beeps, place the prepared sample into the adapter with the Hach logo facing the front of the instrument. Place the cover on the adapter.



17. Press: **READ**

The display will show:

Reading. . .

then the display will show the results in mg/L PO_4^{3-}.

Forms ▲▼ P
PO_4^{3-}
P_2O_5

Sampling and Storage

Collect samples in plastic or glass bottles that have been acid cleaned with 1:1 Hydrochloric Acid Solution and rinsed with deionized water. Do not use commercial detergents containing phosphate for cleaning glassware used in this test.

Analyze samples immediately after collection for best results. If prompt analysis is impossible, preserve samples for up to 24 hours by storing at 4 °C. Warm to room temperature before analysis.

Accuracy Check

Standard Additions Method

***Note:** Clean glassware with 1:1 hydrochloric acid solution. Rinse with deionized water. Do not use detergents containing phosphate.*

a) Fill three 25-mL graduated mixing cylinders with 25 mL of sample.

b) Snap the neck off a Phosphate Voluette Ampule Standard, 50 mg/L as PO_4^{3-}.

c) Use the TenSette Pipet to add 0.1 mL, 0.2 mL and 0.3 mL, respectively, to the three 25-mL aliquots of a water sample prepared in *step a*. Mix well.

d) Analyze each sample from Step c as described in the procedure. Use 5.0 mL of the prepared sample for each test. The concentration should increase as follows: 0.2 mg/L, 0.4 mg/L, 0.6 mg/L PO_4^{3-}, respectively.

e) If these increases do not occur, see *Standard Additions* in *Section I* for more information.

Standard Solution Method

To check accuracy, use the 1.0 mg/L Phosphate Standard Solution listed under Optional Reagents. Or, this can be prepared by pipetting 2 mL of solution from a Voluette Ampule Standard for Phosphate, 50 mg/L as PO_4^{3-}, into a 100-mL CLass A volumetric flask. Fill to the line with deionized water. Substitute this standard for the sample and perform the procedure as described. The mg/L PO_4^{3-} reading should be 1.0 mg/L.

Interferences

Large amounts of turbidity may cause inconsistent results in the test because the acid present in the powder pillows may dissolve some of the suspended particles and because of variable desorption of orthophosphate from the particles.

The PhosVer 3 Phosphate Reagent Powder Pillows should be stored in a cool, dry environment.

The following may interfere when present in concentrations exceeding those listed below:

Aluminum	200 mg/L
Chromium	100 mg/L
Copper	10 mg/L
Iron	100 mg/L
Nickel	300 mg/L
Silica	50 mg/L
Silicate	10 mg/L
Sulfide	9 mg/L
Zinc	80 mg/L

Arsenate interferes at all levels.

Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment; see *pH Interferences* (*Section I*).

Sulfide interference may be removed by oxidation with Bromine Water as follows:

a) Measure 25 mL of sample into a 50-mL beaker.

b) Swirling constantly, add Bromine Water drop-wise until a permanent yellow color develops.

c) Swirling constantly, add Phenol Solution dropwise until the yellow color just disappears. Proceed with *step 1*.

Precision

In a single laboratory, using a standard solution of 3.00 mg/L PO_4^{3-} and two lots of reagent with a DR/2010, a single operator obtained a standard deviation of ±0.04 mg/L PO_4^{3-}.

Estimated Detection Limit

The Estimated Detection Limit (EDL) for this test is 0.03 mg/L PO_4^{3-}. The EDL is the calculated lowest average concentration in a deionized water matrix that is different from zero with a 99% level of confidence. For more information on derivation and use of Hach's estimated detection limit, see *Section I.*

Sample Disposal Information

Final samples will contain molybdenum. In addition, final samples will have a pH less than 2 and are considered corrosive (D002) by the Federal RCRA.

Summary of Method

Phosphates present in condensed inorganic forms (meta-, pyro- or other polyphosphates) must be converted to reactive orthophosphate before analysis. Pretreatment of the sample with acid and heat provides the conditions for hydrolysis of the condensed inorganic forms. Orthophosphate reacts with molybdate in an acid medium to produce a phosphomolybdate complex. Ascorbic acid then reduces the complex, giving an intense molybdenum blue color.

REQUIRED REAGENTS

Total and Acid Hydrolyzable Test 'N Tube Reagent Set ....50 tests 27427-45
Includes: (1) 21060-46, (1) 20847-66, (1) 1045-42, (1) 272-56, Total and Acid Hydrolyzable Test Vials*

Description	Quantity Required Per Test	Unit	Cat. No.
PhosVer 3 Phosphate Reagent Powder Pillows	1 Pillow	50/pkg	21060-46
Potassium Persulfate Powder Pillows	1	50/pkg	20847-66
Sodium Hydroxide Standard Solution, 1.0 N	2 mL	100 mL	1045-32
Total and Acid Hydrolyzable Test Vials	1	50/pkg	*
Water, deionized	100 mL	4 liters	272-56

REQUIRED APPARATUS

COD Reactor, 115/230 Vac (U.S.A. and Canada)	1	each	45600-00
COD Reactor, 115/230 Vac (Europe)	1	each	45600-02
COD Vial Adapter, DR/2010	1	each	44799-00
Funnel, micro	1	each	25843-35
Pipet, TenSette, 1 to 10 mL	1	each	19700-10
Pipet Tips, for 19700-10 TenSette Pipet		50/pkg	21997-06
Safety Shield, laboratory bench	1	each	23810-00
Test Tube Rack	1-3	each	18641-00

OPTIONAL REAGENTS

Bromine Water, 30 g/L	29 mL	2211-20
Hydrochloric Acid Standard Solution, 6.0 N (1:1)	500 mL	884-49
Phenol Solution, 30 g/L	29 mL	2112-20
Phosphate Standard Solution, 1 mg/L as PO_4^{3-}	500 mL	2569-49
Phosphate Standard Solution, Voluette Ampule, 50 mg/L as PO_4^{3-}, 10 mL	16/pkg	171-10
Sodium Hydroxide Standard Solution, 5.000 N	1000 mL	2450-53
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Ampule Breaker Kit	each	21968-00
Cylinder, graduated, mixing, 25 mL	each	20886-40
Flask, volumetric, Class A, 100 mL	each	14574-42
pH Indicator Paper, 1 to 11 pH units	5 rolls/pkg	391-33
pH Meter, *sension*™*1*, portable	each	51700-10
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet, Tips for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 5.00 mL	each	14515-37
Pipet Filler, safety bulb	each	14651-00

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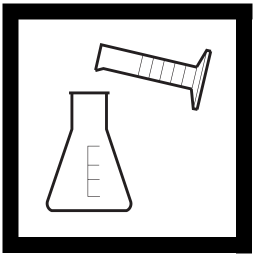
* These items are not sold separately.

Method 8180

PHOSPHORUS, ACID HYDROLYZABLE

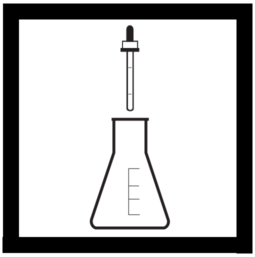
Hydrolysis to Orthophosphate Method*

For water, wastewater, seawater



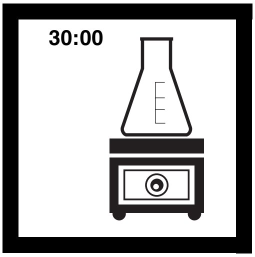
1. Measure 25 mL of sample into a 50-mL (or larger) Erlenmeyer flask using a graduated cylinder.

Note: *Wash all glassware with 6 N hydrochloric acid. Rinse with deionized water.*



2. Add 2.0 mL of 5.25 N Sulfuric Acid Solution.

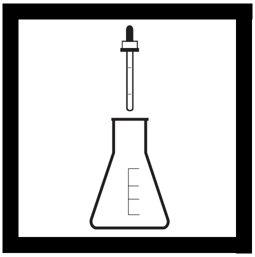
Note: *Use the 1-mL calibrated dropper provided.*



3. Place the flask (the prepared sample) on a hot plate. Boil gently for 30 minutes.

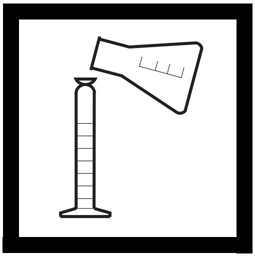
Note: *Sample should be concentrated to less than 20 mL for best recovery. After concentration, maintain the volume near 20 mL by adding small amounts of deionized water. Do not exceed 20 mL.*

4. Cool the prepared sample to room temperature.



5. Add 2.0 mL of 5.0 N Sodium Hydroxide Solution to the prepared sample. Swirl to mix.

Note: *Use the 1-mL calibrated dropper provided.*



6. Pour the prepared sample into a graduated cylinder. Add deionized water rinsings from the flask to return the volume to 25 mL. Proceed with the appropriate reactive phosphorus test.

Note: *Results of the reactive phosphorus test at this point will include the orthophosphate plus the acid-hydrolyzable (condensed) phosphate. The condensed phosphate concentration is determined by subtracting the results of a reactive phosphorus test on an untreated sample from this result. Make sure both results are in the same units.*

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* Adapted from *Standard Methods for the Examination of Water and Wastewater.*

Sampling and Storage

The most reliable results are obtained when samples are analyzed immediately. If prompt analysis is not possible, samples may be preserved up to 48 hours by cooling to 4 °C (39 °F). Warm to room temperature before testing.

Interferences

If the sample is turbid, use 50 mL of sample and double the reagent volumes. Use 25 mL of the hydrolyzed sample to zero the instrument in the reactive phosphorus procedure. This compensates for any turbidity dissolved by this procedure.

Summary of Method

This procedure lists the necessary steps to convert condensed phosphate forms (meta-, pyro- or other polyphosphates) to reactive orthophosphate before analysis. The procedure uses acid and heat to hydrolyze the sample. Organic phosphates are not converted to orthophosphate by this process, but a very small fraction may be unavoidably included in the result. Thus, the "acid hydrolyzable" phosphate results are primarily a measure of inorganic phosphorus. This procedure must be followed by one of the reactive phosphorus (orthophosphate) analysis methods for determination of the phosphorous content of the sample.

The following reagents and apparatus are required in addition to those required for the reactive phosphorus test.

REQUIRED REAGENTS

	Quantity Required		
Description	**Per Test**	**Unit**	**Cat. No.**
Sodium Hydroxide Solution, 5.0 N	2 mL	100 mL* MDB	2450-32
Sulfuric Acid Solution, 5.25 N	2 mL	100 mL* MDB	2449-32

REQUIRED APPARATUS

Cylinder, graduated, 25 mL	2	each	508-40
Flask, Erlenmeyer, 50 mL	1	each	505-71

OPTIONAL REAGENTS

Hydrochloric Acid, 6 N	500 mL	884-49
Water, deionized	4 L	272-17

OPTIONAL APPARATUS

Cylinder, graduated, 50 mL	each	508-41
Flask, erlenmeyer, 125 mL	each	505-43
Hot Plate, 4" diameter, 120 Vac	each	12067-01
Hot Plate, 4" diameter, 240 Vac	each	12067-02
Pad, cooling, 4" x 4"	each	18376-00
pH indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
pH Meter, *sension*™*1*, portable	each	51700-10

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

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* Contact Hach for larger sizes.

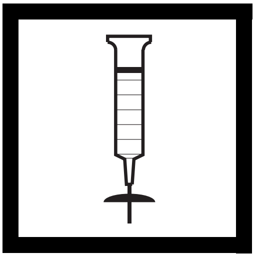
Method 8107

POLYACRYLIC ACID (0 to 20.0 mg/L as Acumer 1000 or 1100)

Absorption-Colorimetric Method*

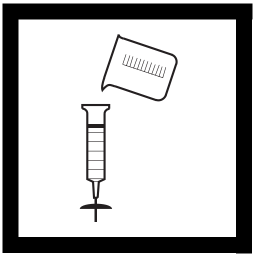
For water and brines

Sample Preparation



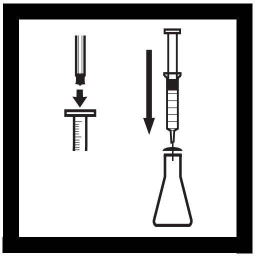
1. Remove the syringe plunger. Attach the prefilter to the syringe barrel. Twist to lock it on.

Note: *The Pour-Thru Cell cannot be used.*



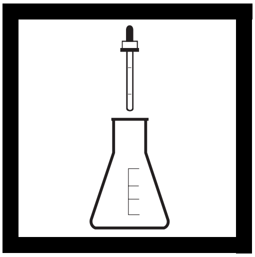
2. Rinse the syringe with the sample. Fill to the 30-cc mark.

Note: *The syringe markings may wear off with continued use. They can be made more permanent by scoring with a knife.*



3. Insert the plunger and force the sample through the filter into a 50 mL erlenmeyer flask labeled “sample.”

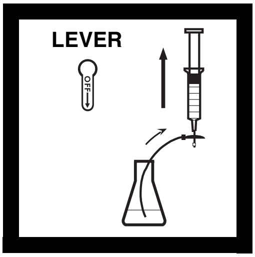
4. Fill another clean flask, labeled “reagent blank,” with approximately 30 mL of deionized water.



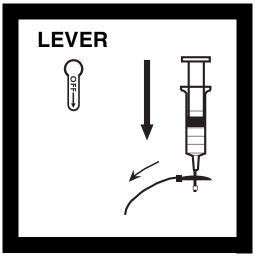
5. Add 0.5 mL of Buffer Solution, pH 2.5, to each flask. Swirl to mix.

Note: *Check the sample pH with pH indicator paper. If necessary, adjust to pH 2 or 3 with 1:1 Nitric Acid Solution.*

6. Fill a third flask, labeled “eluant,” with approximately 30 mL of Polyacrylic Acid Eluant Solution.



7. Assemble the syringe apparatus as shown (*see Figure 1*). Place the long end of the LC cartridge on the male tip of the three-way valve. Turn the valve to the aspirate (down) position. Draw about 5 cc of reagent blank through the tubing into the syringe. Draw in air to the 30-cc mark.



8. Rinse the syringe. Discard the solution through the tubing.

Note: *Move the plunger up and down several times to clear the tubing.*

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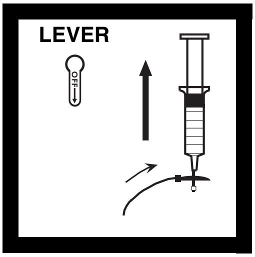
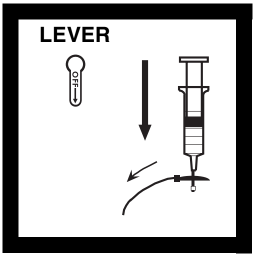
* Acumer is a trademark of Rohm and Haas Company.

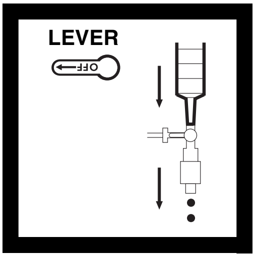


9. Draw the remaining reagent blank into the syringe through the tubing followed by a small volume of air, past the 30-cc mark.

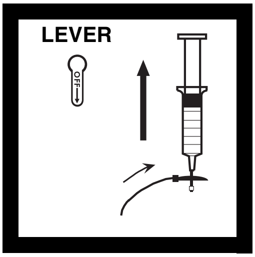
Note: *A small volume of air above the solution facilitates complete elution from the LC column.*



10. Push the plunger down to adjust the solution volume to exactly the 20-cc mark.



11. Rotate the valve lever to the pump (left) position and slowly force the solution through the LC column over a period of at least 15 seconds, discarding the solution. See *Figure 2*.



12. Again rotate the valve lever to the aspirate (down) position. Draw about 5 cc of eluant into the syringe through the tubing followed by air past the 25-cc mark.

Figure 1 Aspirate Setup

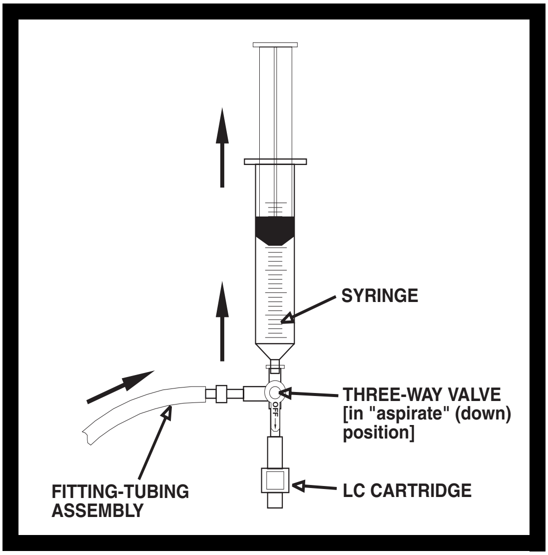
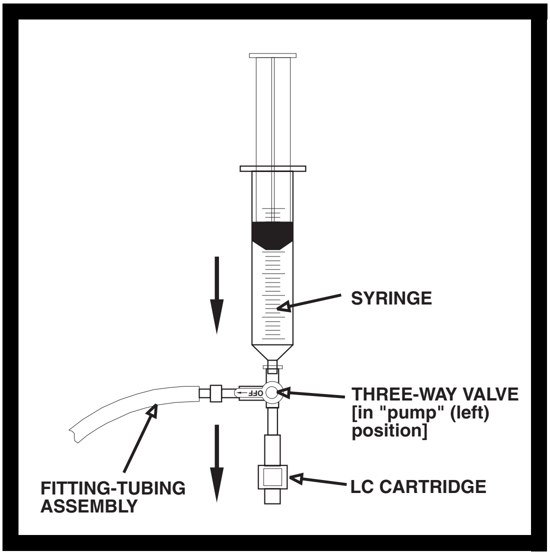
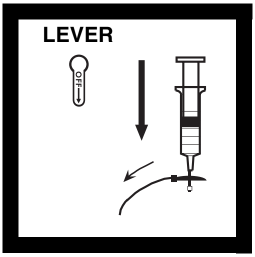


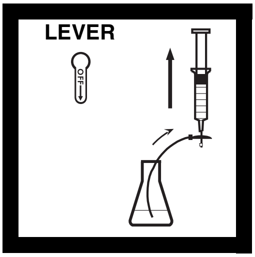
Figure 2 Pump Setup



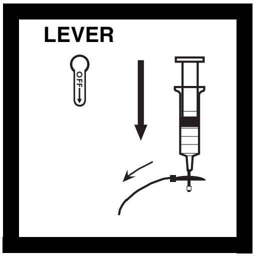


13. Rinse the syringe by shaking. Discard the eluant through the tubing.

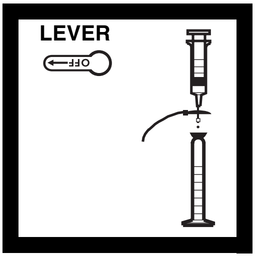
Note: *Move the plunger up and down several times to clear the tubing.*



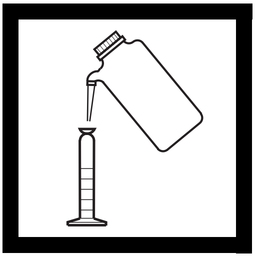
14. Draw at least 10 cc of eluant into the syringe through the tubing followed by air, past the 25-cc mark.



15. Push the plunger down to adjust the eluant volume to exactly the 10-cc mark.



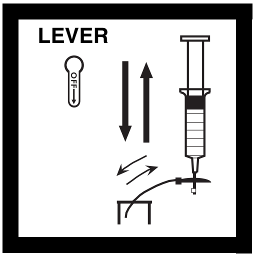
16. Rotate the valve lever to the pump (left) position. Over a period of 30 seconds force the eluant through the cartridge. Collect the eluant in a 25-mL tall-form graduated cylinder.



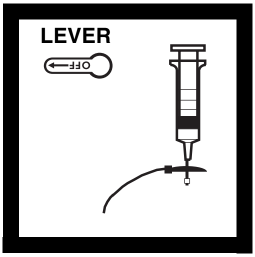
17. Fill the cylinder to exactly 25 mL with deionized water. Stopper. Invert to mix. Label this cylinder “reagent blank.”

Note: *Up to five samples can be run with one reagent blank.*

Note: *Volumes are critical at this point. The cylinders can be matched by pipetting 25.00 mL of deionized water into each and marking them, if necessary, at the correct volume. Tall-form cylinders must be used.*

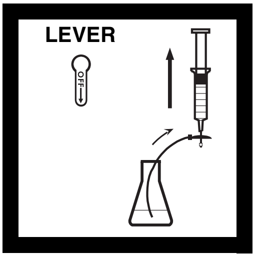


18. Clean the syringe and cartridge by drawing in 25 cc of deionized water with the valve lever in the aspirate (down) position. Discard the water back through the tubing.



19. Repeat, discarding the water through the cartridge with the valve lever in the pump (left) position.

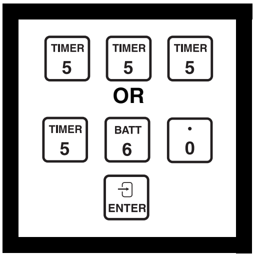
Note: *The cartridge must be rinsed to remove any traces of eluant, which would affect adsorption of pAA from the next sample.*



20. Return the valve to the aspirate (down) position and repeat Steps 8 through 20, using the buffered sample in place of reagent blank. Label the glassware “sample.”

Note: *After use, rinse the LC cartridge with 2 cc of eluant solution, then deionized water. Store the cartridge in the vial supplied, with a few drops of eluant solution.*

Colorimetric Analysis



1. Enter the stored program number for polyacrylic acid (pAA).

Press: **5 5 5 ENTER**

for units in Acumer 1000

OR

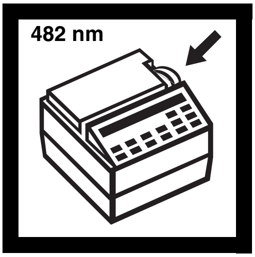
5 6 0 ENTER

for units in Acumer 1100.

The display will show:

Dial nm to 482

Note: *The Pour-Thru Cell cannot by used with this procedure.*



2. Rotate the wavelength dial until the small display shows:

482 nm

When the correct wavelength is dialed in, the display will show:

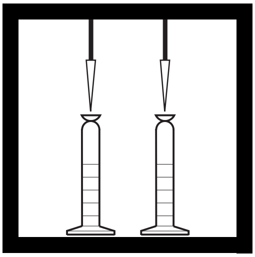
Zero Sample

then:

mg/L Acumer 1000

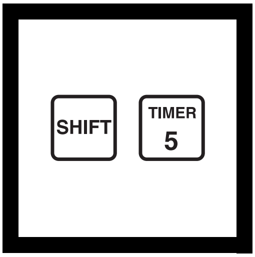
OR

mg/L Acumer 1100



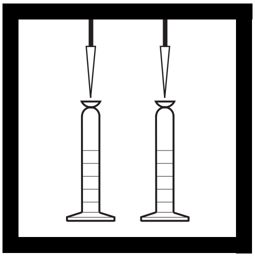
3. Pipet exactly 1.00 mL of Polyacrylic Acid 1 Reagent into each mixing cylinder. Stopper and mix. Proceed immediately to Step 4.

Note: *Use a volumetric pipet or TenSette Pipet to measure this volume.*



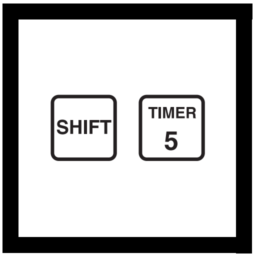
4. Press: **SHIFT TIMER**

A five-minute reaction period will begin. Place cylinders in the dark immediately.



5. When the timer beeps, add exactly 1.00 mL of Polyacrylic Acid 2 Reagent to each cylinder. Stopper and mix. Proceed rapidly through Steps 6 and 7.

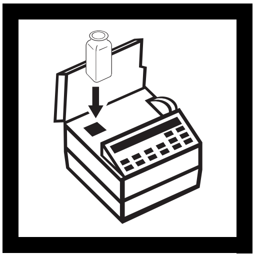
Note: *Use a volumetric pipet or TenSette Pipet to measure this volume.*



6. Press: **SHIFT TIMER**

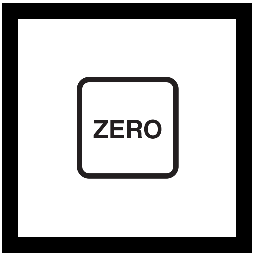
A second five-minute reaction period will begin. Do Step 7 immediately.

7. Transfer the solutions to two dry 25-mL sample cells, labeled “reagent blank” and “sample.” Immediately place the sample cells in the dark.



8. When the timer beeps, the display will show the appropriate units. Place the cell labeled “sample” into the cell holder.

Note: *The sample is used to zero the instrument.*



9. Press: **ZERO**

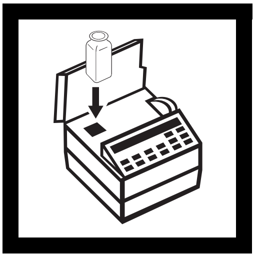
The display will show:

Zeroing. . . .

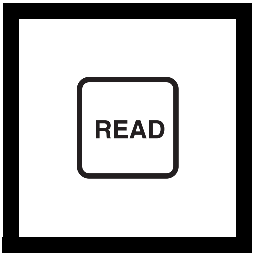
then: **0.0 mg/L**

in the appropriate polyacrylic acid units.

Note: *The reagent blankis stable in the dark for approximately fifteen minutes if needed for determining up to five samples.*



10. Immediately place the cell labeled “reagent blank” into the cell holder.



11. Press:**READ**

The display will show:

Reading. . . .

then result in mg/L polyacrylic acid as Acumer (total solids basis) will be displayed.

Note: *If concentrations of less then 1 mg/L are being determined, see the Interferences section.*

Note: *For concentrations above the range of the test, dilute the sample by an appropriate factor and repeat.*

Interferences

Filter turbid or oily samples through glass wool or a moderately rapid paper, such as S&S No. 560, before beginning the test.

The test works in brines having up to 75,000 mg/L total dissolved solids (TDS) and 20,000 mg/L chloride. Minimize the effect of most interferences by flushing the LC cartridge after the polyacrylic acid is adsorbed on the column. To flush, prepare 30 mL of deionized water buffered with 0.5 mL of Buffer Solution, pH 2.5. Repeat Steps 7 to 11 in the Sample Preparation section with this solution. Continue with Step 12.

Re-test samples with concentrations of less than 1 mg/L. Filter two 30-cc volumes of sample in Step 2. Use two 20-cc volumes (instead of one) of sample through the cartridge in Sample Preparations Steps 10 and 11. Continue with Step 12. Divide the resulting concentration by 2. Up to five 20-cc volumes of the sample can be run through the LC cartridge. It may be necessary to flush the LC cartridge as stated above.

Avoid use of facial tissue when drying glassware or apparatus, as it may contain interfering substances. Kimwipes or Kaydry wipers are recommended.

Summary of Method

Polyacrylic acids (pAA) in the sample are selectively adsorbed onto a liquid chromatographic column using a technique developed by Rohm and Haas Company. After separation from the sample, the pAA is eluted off the column and the concentration is determined colorimetrically.

Calibrations are based on Rohm and Haas Company Acumer (low molecular weight) polyacrylic acid products. Because commercially available polyacrylic acid can come in many strengths, preparation of the standards used for the calibrations was based on a 100% total solids basis and 100% active polymer. This method can be adapted for most other low molecular weight polyacrylic acids, polyacrylates or associated copolymers used as commercial scale inhibitors. For accurate work, diluted standards prepared from the product in use may be used to establish the calibration. If possible, the concentration of polymer in solution should be reported on a dry-weight basis.

REQUIRED REAGENTS

	Cat. No.
Polyacrylic Acid Reagent Set (30 Tests) Includes: (1) 22253-32, (1) 22762-42, (1) 22763-42, (1) 22256-53	22252-00

Description	Quantity Required Per test	Unit	Cat. No.
Buffer Solution, pH 2.5	1 mL	100 mL MDB	22253-32
Polyacrylic Acid 1 Reagent	2 mL	100 mL	22762-42
Polyacrylic Acid 2 Reagent	2 mL	100 mL	22763-42
Polyacrylic Acid Eluant Solution	30 mL	1000 mL	22256-53

REQUIRED APPARATUS

Cylinder, mixing, tall form, 25 mL	2	each	21190-40
Flask, erlenmeyer, 50 mL	3	each	505-41
Polyacrylic Acid Apparatus Set	1	each	22257-00
contains:			
Fitting-Tube Assembly		each	22266-00
LC Cartridge		each	22264-00
pH Paper		5 rolls/pkg	391-33
Prefilter, 5 µm 25 mm		each	22261-00
Syringe, 30 cc		each	22258-00
Three-Way valve		each	22259-00
Pipet, Volumetric, Class A, 1.00 mL	2	each	14515-35
Pipet Filler, safety bulb	1	each	14651-00
Sample Cell, 25-mL, matched pair	2	pair	20950-00

OPTIONAL REAGENTS

Nitric Acid Solution, 1:1	500 mL	2540-49
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Bottle, wash, 250 mL	each	620-31
Filter Paper, folded, S&S No. 560, 12.5 cm	100/pkg	692-57
Funnel, filtering, long stem, 75 mm	each	549-68
Funnel, separatory, 125 mL	each	520-43
Kaydry Wiper, 38 x 43 cm (15 x 17)	90/box	20969-00
Kimwipe Wiper, 11 x 22 cm (5 x 8)	280/box	20970-00
pH Indicator Paper, 1 to 11 pH units	5 rolls/pkg	391-33
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 25 mL	each	14515-40

Method 8049

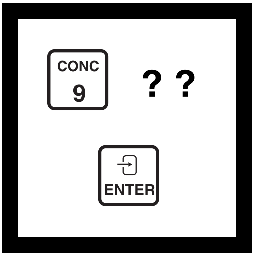
POTASSIUM (0 to 7.0 mg/L)

For water, wastewater, and seawater

Tetraphenylborate Method

User Calibration

1. This procedure requires a user-entered calibration prior to sample measurement. See the User Calibration section to set up and calibrate a program for potassium.



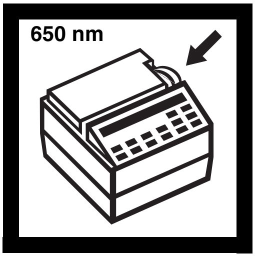
2. Enter the stored user program number for Potassium (K).

Press: **9 ? ? ENTER**

The display will show:

Dial to 650 nm

Note: *The Pour-Thru Cell cannot be used.*

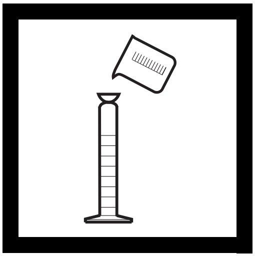


3. Rotate the wavelength dial until the small display shows:

650 nm

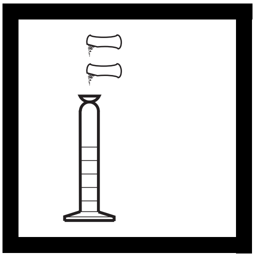
When the correct wavelength is dialed in, the display will quickly show: **Zero Sample**

then: **mg/L K**

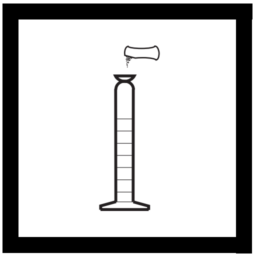


4. Fill a graduated mixing cylinder with 25 mL of sample.

Note: *Filter highly colored or turbid samples. Use filtered sample here and in Step 9.*

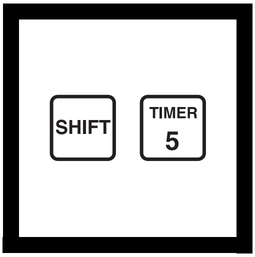


5. Add the contents of one Potassium 1 Reagent Pillow. Add the contents of one Potassium 2 Reagent Pillow. Stopper. Invert several times to mix.



6. Add the contents of one Potassium 3 Reagent Pillow after the solution clears. Stopper. Shake for 30 seconds.

Note: *A white turbidity will form if potassium is present.*

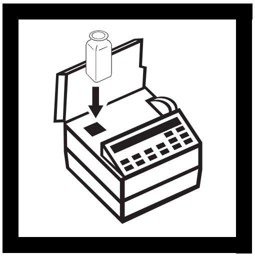


7. Press:

SHIFT TIMER

A three-minute reaction period will begin.

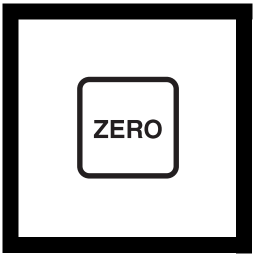
8. Pour the solution from the cylinder into a sample cell (the prepared sample).



9. When the timer beeps, the display will show:

mg/L K

Fill the second sample cell (the blank) with 25 mL of sample. Place it into the cell holder.

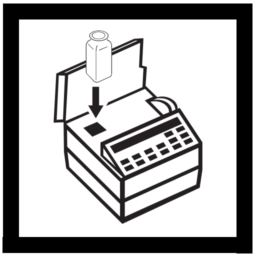


10. Press: **ZERO**

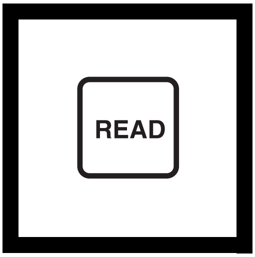
The display will show:

Zeroing. . . .

then: **0.0 mg/L K**



11. Within seven minutes after the timer beeps, place the prepared sample into the cell holder. Close the light shield.



12. Press: **READ**

The display will show:

Reading. . . .

then the result in mg/L potassium will be displayed.

Note: *Clean the cells with soap and a brush.*

Sampling and Storage

Collect samples in acid-washed plastic bottles. Adjust the pH to 2 or less with nitric acid (about 2 mL per liter). Preserved samples may be stored at least six months at room temperature. Adjust the pH to 4 to 5 with 5.0 N sodium hydroxide before analysis. Do not measure pH in the sample container with a pH electrode, as this will introduce potassium from the filling solution. Use pH paper or pour off sample and test pH in a separate beaker. Correct the test result for volume additions; see *Correction for Volume Additions* in *Section I*.

Accuracy Check

Standard Addition Method

a) Snap the neck off a Potassium Voluette Ampule Standard Solution, 250 mg/L.

b) Use the TenSette Pipet to add 0.1, 0.2, and 0.3 mL of standard to three 25-mL samples. Mix each thoroughly.

c) Analyze each sample as described above. The potassium concentration will increase 1.0 mg/L for each 0.1 mL of standard added.

d) If these increases do not occur, see *Standard Additions* (*Section I*) for more information.

Standard Solution Method

Check accuracy with a 5.0 mg/L Potassium Standard Solution (see *Optional Reagents*). Or, prepare this standard by diluting 5.00 mL of a 1000-mg/L Potassium Standard Solution to one liter with deionized water.

Calibration

A one-time setup of a program for potassium is required. A potassium program template is pre-programmed into memory to make the process easier. After the setup is complete, the calibration can be entered for each new lot of reagents used or as necessary.

Preparation of Standards

Prepare standards of 1, 2, 4, 6 and 8 mg/L potassium by diluting 0.1, 0.2, 0.4, 0.6 and 0.8 mL of the contents of the Potassium Voluette Ampule Standard, 250 mg/L, to 25.0 mL of deionized water in graduated mixing cylinders. Use a TenSette Pipet to measure the standard. Mix well. (Or, pipet 0.5, 1.0, 2.0, 3.0 and 4.0 mL from Potassium Voluette Ampule Standards, 500 mg/L, into 250-mL volumetric flasks. Dilute to volume. Mix well. Transfer 25 mL to each mixing cylinder.)

Initial Setup of Potassium Program

Perform a new calibration for each lot of Potassium 3 Reagent Powder Pillows as follows:

***Note:** The templates within User Program cannot be run directly. They must be copied into a usable program number (greater than 950) as in step c and d. Then, calibrate the program.*

a) Press **SHIFT USER PRGM**. Use the **UP** arrow key to scroll to **Copy Program**. Press **ENTER**.

b) Scroll to or enter the template number for potassium (905). Press **ENTER**.

c) Scroll to or enter the desired user program number for potassium (>950). Press **ENTER**. Record the program number for reference.

d) The display will show: **Program Copied.** Press **EXIT**. The program is now ready to be calibrated.

User Calibration of Potassium Program

a) Use the test procedure to develop color in the standards just before recording the absorbance values for the calibration.

b) Press **SHIFT USER PRGM**. Use the **UP** arrow to scroll to **Edit Program**. Press **ENTER**.

c) Scroll to or enter the program number for potassium (from step c in Setup). Press **ENTER**.

d) Use the **DOWN** arrow to scroll down to **Calib Table:X** (X= denotes a number which indicates the number of data points in the table). Press **ENTER**.

e) The instrument will prompt **Zero Sample**. Place the blank solution in the cell holder. Close the light shield. Press **ZERO**. The instrument will prompt you to adjust to the proper wavelength if necessary.

f) The first concentration point will be displayed. Press **ENTER** to display the stored absorbance value of the first concentration point.

g) Place the first developed standard solution (same concentration as the value displayed) in the cell holder. Close the light shield. Press **READ** to display the measured absorbance of the standard. Press **ENTER** to accept the displayed absorbance value.

h) The second concentration point will be displayed. Press **ENTER** to display the stored absorbance value of the second concentration. Place the second developed standard solution in the cell holder. Close the light shield. Press **READ** to display the measured absorbance value of the standard.

i) Press **ENTER** to accept the absorbance reading. The next concentration point will then be displayed.

j) Repeat steps h and i as necessary for the remaining standards.

k) When finished reading the absorbance values of the standards, press **EXIT**. Scroll down to **Force Zero**. Press **ENTER** to change the setting. Change to ON by pressing the arrow key, then press **ENTER.**

l) Scroll down to **Calib Formula**. Press **ENTER** twice or until only the **0** in **F(0)** is flashing. Press the **UP** arrow to select **F3** (cubic calibration). Press **ENTER** to select **F3**.

Note: *Other calibration fits may be used if appropriate.*

m) Press **EXIT** twice. The display will show **Store Changes?**. Press **ENTER** to confirm.

n) Press **EXIT**. The program is now calibrated and ready for use. Start with step 2 of the procedure.

Precision

In a single laboratory using a standard solution of 4 mg/L K and one representative lot of reagent with the DR/2010, a single operator obtained a standard deviation of ±0.13 mg/L K.

Interferences

The following ions do not interfere below the concentration shown:

Ammonium Nitrogen	15 mg/L as N
Calcium	7000 mg/L as $CaCO_3$
Chloride	15,000 mg/L
Magnesium	6000 mg/L as $CaCO_3$

Summary of Method

Potassium in the sample combines with sodium tetraphenylborate to form potassium tetraphenylborate, an insoluble white solid. The amount of turbidity produced is proportional to the potassium concentration.

REQUIRED REAGENTS

Description	Cat. No.
Potassium Reagent Set (100 tests) Includes: (4) 14321-98, (4) 14322-98, (1) 14323-99	24591-00

Description	Quantity Required Per Test	Unit	Cat. No.
Potassium 1 Reagent Pillows	1 pillow	25/pkg	14321-98
Potassium 2 Reagent Pillows	1 pillow	25/pkg	14322-98
Potassium 3 Reagent Pillows	1 pillow	100/pkg	14323-99
Potassium Standard Solution, Voluette Ampule, 250 mg/L,	10 mL	16/pkg	14790-10
Potassium Standard Solution, Voluette Ampule, 500 mg/L,	10 mL	16/pkg	21093-10

REQUIRED APPARATUS

Clippers, for opening powder pillows	1	each	968-00
Cylinder, mixing, graduated, 25 mL	1	each	1896-40
Sample Cell, 15 mL, matched pair	2	pair	20950-00

OPTIONAL REAGENTS

Potassium Standard Solution, 5 mg/L	500 mL	20583-49
Potassium Standard Solution, 1000 mg/L	100 mL	22404-42
Sodium Hydroxide Solution, 5.0 N	50 mL SCDB	2450-26
Water, deionized	4L	272-56

OPTIONAL APPARATUS

Ampule Breaker Kit	each	21968-00
Flask, volumetric, 250 mL, Class A	each	14574-46
Nitric Acid, ACS	500 mL	152-49
Nitric Acid, 1:1	500 mL	2540-49
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 1.00 mL	each	14515-35
Pipet, volumetric, Class A, 2.00 mL	each	14515-36
Pipet, volumetric, Class A, 3.00 mL	each	14515-03
Pipet, volumetric, Class A, 4.00 mL	each	14515-04

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

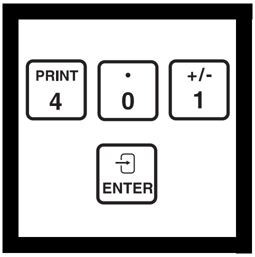
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8337

QUATERNARY AMMONIUM COMPOUNDS (0 to 5 mg/L as CTAB)

Direct Binary Complex Method

For cooling tower and pool/spa water



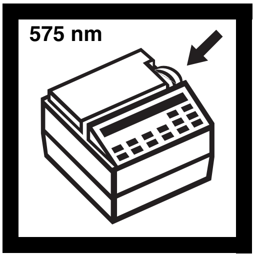
1. Enter the stored program number for quaternary ammonium compounds (QAC).

Press: **4 0 1 ENTER**

The display will show:

Dial nm to 575

Note: *The Pour-Thru Cell can be used with this procedure.*



2. Rotate the wavelength dial until the small display shows:

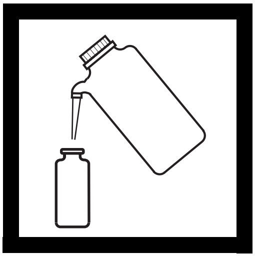
575 nm

When the correct wavelength is dialed in, the display will quickly show:

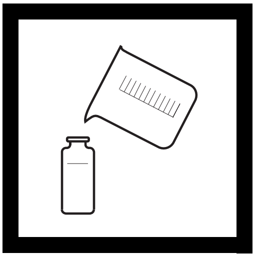
Zero Sample

then:

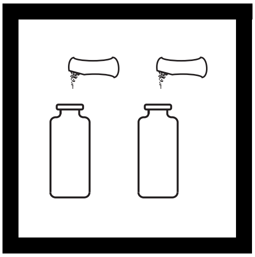
mg/L QAC as CTAB



3. Fill a sample cell (the blank) with 25 mL of deionized water.

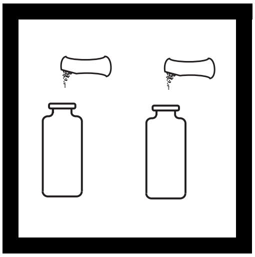


4. Fill another cell (the prepared sample) with 25 mL of sample.



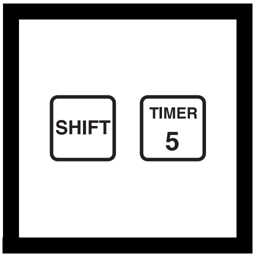
5. Add the contents of one Q.A.C. Reagent 1 Powder Pillow to each sample cell. Swirl (do not shake) the sample cells to dissolve the reagents.

Note: *Shaking the sample cell causes air bubble turbidity that dissipates slowly, interfering with the test results.*



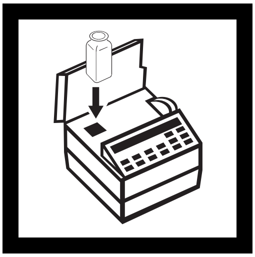
6. Add the contents of one Q.A.C. Reagent 2 Powder Pillow to each sample cell. Swirl (do not shake) the sample cells to dissolve the reagents.

Note: *A purple color will form if a quaternary ammonium compound is present.*



7. Press: **SHIFT TIMER**

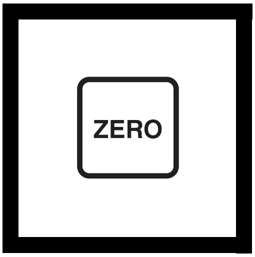
A two-minute reaction period will begin.



8. When the timer beeps, the display will show:

mg/L QAC as CTAB

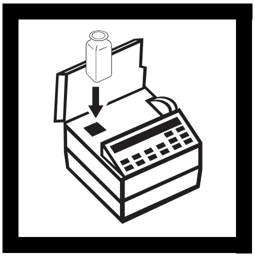
Place the blank into the cell holder. Close the light shield.



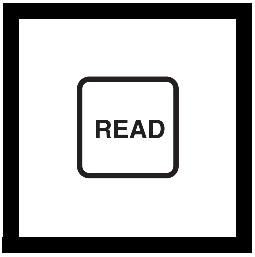
9. Press: **ZERO**

The display will show:

0.0 mg/L QAC as CTAB



10. Place the prepared sample into the cell holder. Close the light shield.



11. Press: **READ**

The display will show:

Reading. . . .

then the result in mg/L quaternary ammonium compounds as cetyltrimethylammonium bromide will be displayed.

Sampling and Storage

Collect samples in glass bottles that have been rinsed several times with sample before final sample filling. Do not use plastic containers as plastic adsorbs QACs.

Accuracy Check

Standard Solution Method

To assure the accuracy of the test, use a 5 mg/L CTAB Standard Solution prepared as follows:

a) Pipet 5 mL from the Q.A.C. Standard Solution, 100 mg/L as CTAB, into a 100-mL volumetric flask.

b) Dilute the solution to 100 mL with deionized water.
Mix thoroughly.

c) Analyze 25 mL of the 5 mg/L CTAB standard solution according to the preceding procedure. The result should be 5.0 ±0.1 mg/L.

Standard Additions Method

a) Use a TenSette Pipet to add 0.5, 1.0 and 1.5 mL of Q.A.C. Standard Solution, 100 mg/L as CTAB, to three 50-mL samples. Mix thoroughly.

b) Analyze 25 mL of each sample according to the above procedure. The QAC concentration should increase by 1.0 mg/L CTAB for each 0.5 mL addition of standard.

Interferences

Interference studies were conducted by preparing a CTAB standard solution of approximately 3 mg/L that also contained the potential interfering compound. The constituent was said to interfere when the resulting concentration changed by 10%.

Constituent	Level Above Which Constituent Interferes (mg/L)
Positive Interferences:	
Tribenzylamine	7
Urea	8
Liquimine 14-P, filming amine	1,825
Calcium (as $CaCO_3$)	1,350
Sodium polyphosphate	1,325
Magnesium, Mg^{2+}	1,350
Iron, Fe^{3+}	80
Chlorine, HOCl and OCl^-	7
Igepal nonionic surfactant	3
Triton X-100 nonionic surfactant	4
Iodine, I_3^-	3
Negative Interferences:	
Niaproof anionic surfactant	11
Sodium lauryl sulfate	8
Cyanuric acid	70
Polyacrylic acid	16
No Interferences: Highest Concentration Tested (mg/L)	
Silica, H_2SiO_2	400
Potassium alum, SiO_8	500
Sodium thiosulfate, $Na_2S_2O_3$	30

Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment. Adjust the sample pH to between 3 and 5 by using a pH meter or pH paper and adding dropwise an appropriate acid or base such as 1.0 N Sulfuric Acid Standard Solution or 1.0 N Sodium Hydroxide Standard Solution. If significant volumes of acid or base are used, a volume correction should be made by dividing the total volume (sample + acid + base) by the original sample volume and then multiplying the test result by this factor.

After several samples have been analyzed, the sample cells may exhibit a build-up of a pink or purple color. A rinse with 1.0 N Sodium Hydroxide Solution followed by a Alconox detergent wash and deionized water rinse will eliminate the build-up when it occurs.

Precision

In a single laboratory using standard solutions of 2.0 mg/L CTAB and two representative lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±0.07 mg/L CTAB.

Summary of Method

The test method makes use of a colorimetric chemistry in which a quaternary ammonium compound reacts with an indicator to produce a color change from pale pink to vivid purple. The test is conducted in a stabilized, acid-buffered solution containing a masking agent to eliminate potential interferences. This test is applicable to the monitoring of QAC's in swimming pools and cooling towers.

REQUIRED REAGENTS

Quaternary Ammonium Compounds Reagent Set (100 tests)	24592-00

Includes: (4) 24010-66, (8) 24012-68

Description	Quantity Required Per Test	Unit	Cat. No.
Q.A.C. Reagent 1	2 pillows	50/pkg	24010-66
Q.A.C. Reagent 2	2 pillows	25/pkg	24012-68

REQUIRED APPARATUS

Cylinder, graduated, 25 mL	1	each	508-40
Clippers, for opening powder pillows	1	each	968-00
Sample Cells, matched pair, 1-inch	2	pair	20950-00

OPTIONAL REAGENTS

Description	Unit	Cat. No.
Q.A.C. Standard Solution, 100 mg/L as CTAB	100 mL	24153-42
Sodium Hydroxide Standard Solution, 1.0 N	900 mL	1045-16
Sulfuric Acid Standard Solution, 1.0 N	50 mL SCDB	1270-26
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Filter Paper, folded, 12.5 cm	100/pkg	1894-57
Flask, volumetric, 100 mL, Class A	each	14574-42
Funnel, poly, 65 mm	each	1083-67
pH Meter, *sension*™*1*, portable	each	51700-10
Pipet, TenSette 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 5.00 mL	each	14515-37
Pipet Filler	each	12189-00
Pour-Thru Cell Assembly Kit	each	45215-00

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

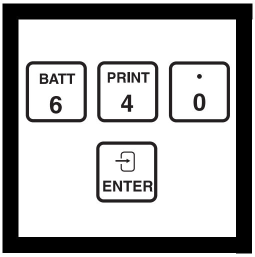
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8194

SELENIUM (0 to 1.00 mg/L)

For water and wastewater

Diaminobenzidine Method



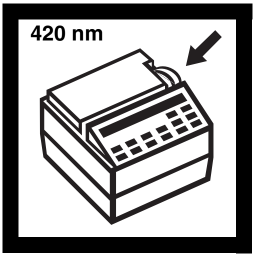
1. Enter the stored program for selenium (Se).

Press: **6 4 0 ENTER**

The display will show:

Dial nm to 420

Note: *The Pour-Thru Cell cannot be used.*



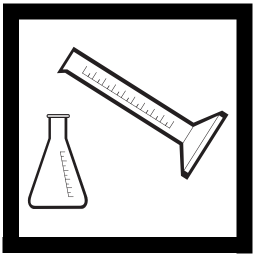
2. Rotate the wavelength dial until the small display shows:

420 nm

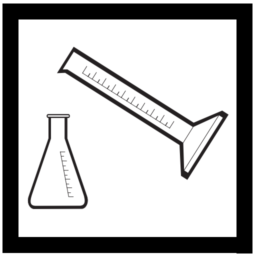
When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

then: **mg/L Se**

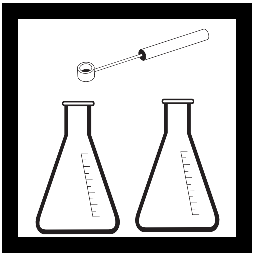


3. Measure 100 mL of deionized water into a 500-mL erlenmeyer flask (label the flask "blank").

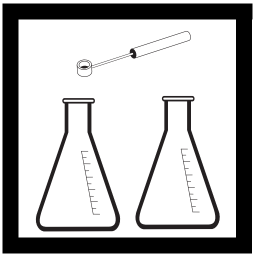


4. Measure 100 mL of sample into a second 500-mL erlenmeyer flask (label the flask "sample").

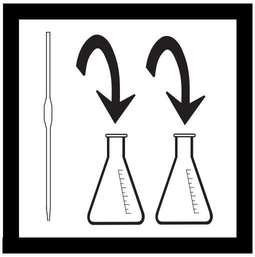
Note: *To determine total selenium, perform a distillation (see Distillation following these steps). Use the distillate in Step 4.*



5. Add a 0.2-g scoop of TitraVer Hardness Reagent to each flask. Swirl to mix.

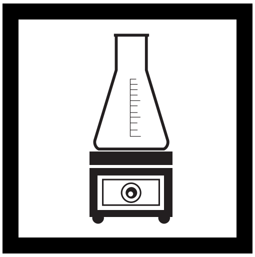


6. Add a 0.05-g scoop of diaminobenzidine tetrahydrochloride to each flask. Swirl to mix.

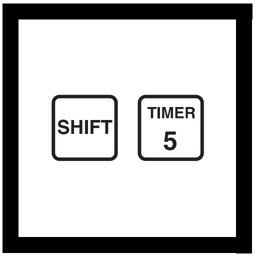


7. Add 5.0 mL of Buffer Solution, sulfate type, pH 2.0, to each flask. Swirl to mix.

Note: *If the sample has been distilled, omit the Buffer Solution. Adjust the pH of the sample distillate to 2.7 (±0.2 pH) using 5 N Sodium Hydroxide Standard Solution. Adjust the blank to the same pH value using 5.25 N Sulfuric Acid Standard Solution.*



8. Heat each flask on a hot plate or over a flame, bringing the contents to a gentle boil.

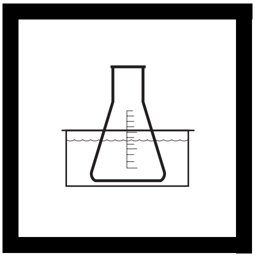


9. Press:

SHIFT TIMER

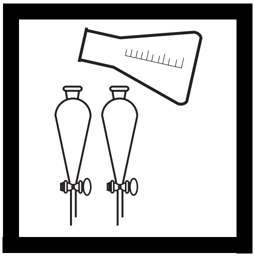
A five-minute reaction period will begin. Continue to boil the contents gently during this time period.

Note: *A yellow color will develop if selenium is present.*

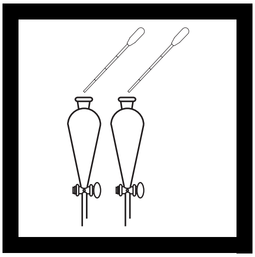


10. When the timer beeps, remove both flasks. Cool to room temperature using a water bath.

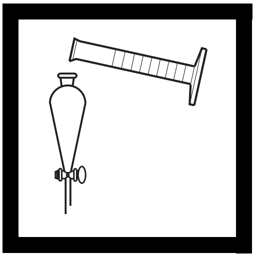
Note: *Do not boil more than one minute after the timer beeps.*



11. Transfer the contents of each flask to separate 250-mL separatory funnels. Label the funnels "blank" and "sample".

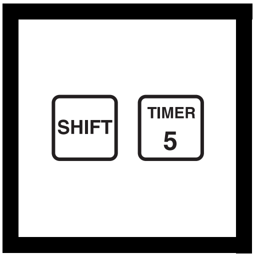


12. Add 2.0 mL of 12 N Potassium Hydroxide Standard Solution to each funnel using a calibrated 1.0-mL plastic dropper. Stopper. Shake each funnel to mix.



13. Add 30 mL of toluene to each funnel. Stopper. Shake each funnel vigorously for 30 seconds.

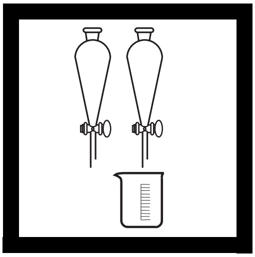
Note: *Use toluene only with adequate ventilation.*



14. Press:

SHIFT TIMER

A three-minute reaction period will begin.

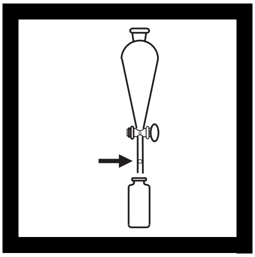


15. When the timer beeps, the display will show:

mg/L Se

Drain the lower water layer from each funnel and discard.

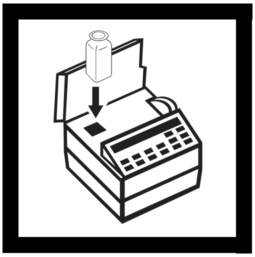
Note: *Do not wait more than 5 minutes after the timer beeps before completing Steps 16 through 20.*



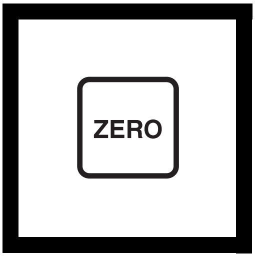
16. Insert a cotton plug into the delivery tube of each separatory funnel. Slowly drain the toluene into respective sample cells labeled "blank" and "sample". Stopper the sample cells.

Note: *Filtering the toluene through dry absorbent cotton will remove any water or suspended particles.*

Note: *The developed color is stable but should be measured as soon as possible.*



17. Place the blank into the cell holder. Close the light shield.

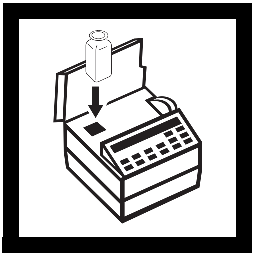


18. Press: **ZERO**

The display will show:

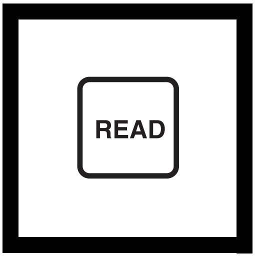
Zeroing. . . .

then: **0.00 mg/L Se**



19. Place the prepared sample in the cell holder. Close the light shield.

Note: *Acetone is a suitable solvent for removing toluene from glassware.*



20. Press: **READ**

The display will show:

Reading. . . .

then the results in mg/L selenium will be displayed.

Sampling and Storage

Collect samples in clean glass or plastic containers. Adjust the pH to 2 or less with nitric acid (about 1.5 mL per liter). Preserved samples can be stored for up to six months at room temperature. Correct the test result for volume additions (see *Section I*).

Distillation

Always perform this procedure under a fume hood! This distillation involves the use of a strong acid and oxidizer at high temperatures. To avoid personal injury, observe all laboratory safety precautions when operating the distillation apparatus.

a) Measure 500 mL of sample into a 1000-mL beaker.

b) Add 1 mL of Methyl Orange Indicator Solution to the beaker. Stir with a glass rod.

c) Using a dropper, add 0.1 N Hydrochloric Acid Standard Solution drop-wise until the solution turns pink. Add an additional 2 mL.

d) Pipet 5.0 mL Calcium Chloride Solution. Mix well.

e) Using a dropper, add 1-g/L Potassium Permanganate Standard Solution drop-wise until the solution is purple.

f) Place the beaker on a hot plate. Evaporate the solution to approximately 250 mL. Periodically add 1-g/L Potassium Permanganate Solution to keep the solution purple.

Note: *Any precipitate formed at this step is manganese dioxide and may be ignored.*

g) Cool the solution. While cooling, set up the distillation apparatus for the general purpose distillation as shown in the Hach Distillation Manual.

h) Pour the treated sample solution into the distillation flask. Add a stirring bar to the flask.

i) Pipet 5.0 mL of 0.1 N Sodium Hydroxide Standard Solution into the flask. Turn the stirrer power switch to ON. Set the stir control to 5.

j) Turn on the water and adjust so a constant flow is maintained through the condenser. Set the heat control to 10.

k) When only a few milliliters are left in the distillation flask, turn the power switch off. Discard the distillate in the erlenmeyer flask.

l) Perform this step under a hood. When the flask has cooled, add 50 mL of 19.2 N Sulfuric Acid Standard Solution to the flask. Add the contents of one Potassium Bromide Powder Pillow to the flask.

m) Fill a 250-mL beaker to the 75-mL mark with deionized water. Place it under the drip tube. Elevate the beaker with a laboratory jack so the tube extends below the level of the water.

n) Add 1.0 mL of 30% Hydrogen Peroxide Solution to the flask. Turn the stir control to 5 and the heat control to 10. Cap the distillation flask.

o) Heat the distillation flask until the yellow color is gone from the complete distillation apparatus, including the J-tube and condenser. Remove the beaker from under the drip tube.

p) Turn off the heater switch. When the J-tube and condenser have cooled, rinse them with deionized water. Add the washings to the 250-mL beaker. Total volume in the beaker should be approximately 100 mL.

q) Add the Phenol Solution drop-wise to the distilled sample to discharge the bromine color (a white precipitate of tribromophenol will form.)

r) Allow the precipitate to settle. Using a dropper, collect about 5 mL of the clear, colorless distillate and transfer to a test tube.

s) Test the solution for completeness of precipitation by adding 2 drops of Phenol Solution. If the solution becomes cloudy or white precipitate forms, residual bromine is still present (proceed to next step). If no cloudiness occurs, the sample is ready for analysis.

t) Transfer the 5-mL aliquot back to the beaker and continue to add Phenol Solution until no turbidity is formed in subsequent 5-mL aliquots.

u) Transfer the sample into a 500-mL volumetric flask. Rinse the beaker with deionized water and add to the flask.

v) Dilute to volume with deionized water, stopper and mix well. The distillate is now ready for analysis.

Accuracy Check

Standard Additions Method

a) Prepare a 100-mg/L Selenium Standard by adding 5.00 ml of a 1000-mg/L Selenium Stndard with a 5.00 ml Class A volumetric pipet to a 50 mL Class A volumetric flask. Dilute to the mark with deionized water..

b) Use a TenSette Pipet to add 0.1, 0.2, and 0.3 mL of the prepared Selenium Standard, 100 mg/L, to three 100-mL samples. Mix well.

c) Analyze as described above. Each 0.1 mL addition of standard should increase the selenium concentration by 0.1 mg/L.

d) If these increases do not occur, see Standard Additions in Section I for more information.

Standard Solution Method

Prepare a 0.50-mg/L selenium standard solution as follows:

a) Use a TenSette Pipet or 0.50-mL volumetric pipet to add 0.50 mL of 1000-mg/L Selenium Standard Solution to a 1000-mL volumetric flask.

b) Dilute to the mark with deionized water. Transfer 100 mL of the standard into a 500-mL erlenmeyer flask. Perform the test as described above.

Precision

In a single laboratory, using standard solutions of 0.6 mg/L selenium and two representative lots of reagent and a DR/2010, a single operator obtained a standard deviation of ±0.01 mg/L selenium.

Interferences

There are no positive inorganic interferences with this method.

Strong oxidizing agents such as iodine, bromine, or chlorine can react with the indicator to give low results.

Manganese and up to 2.5 mg/L ferric iron will not interfere.

Interferences will be eliminated by following the distillation procedure.

Summary of Method

An EDTA masking agent is added to the sample to remove interferences such as iron prior to the test. The addition of a sulfate buffer adjusts the sample to the optimum pH of 1 to 2. Under these conditions, diaminobenzidine reacts with all selenium present as selenite (Se^{4+}) to give a yellow-colored piazselenol complex which is extracted and the color intensity measured colorimetrically. Selenium present as Se^{2-} or Se^{6+} is not detected unless the sample is distilled.

REQUIRED REAGENTS

Description	Cat. No.
Selenium Reagent Set (45 Tests)	22442-00

Includes: (1) 452-49, (1) 7062-22, (2) 230-32, (1) 204-26, (1) 14470-17

Description	Quantity Required Per Test	Unit	Cat. No.
Buffer Solution, sulfate type, pH 2.0	10 mL	500 mL	452-49
Diaminobenzidine, tetrahydrochloride	0.1 g	5 g	7062-22
Potassium Hydroxide Standard Solution, 12 N	4 mL	100 mL MDB	230-32
TitraVer Hardness Reagent	0.4 g	100 g	204-26
Toluene, ACS	60 mL	4 liters	14470-17
Water, deionized	100 mL	4 liters	272-56

REQUIRED APPARATUS

Description	Quantity Required Per Test	Unit	Cat. No.
Cotton Balls, absorbent	1	100/pkg	2572-01
Cylinder, graduated, 100 mL	1	each	508-42
Cylinder, graduated, 50 mL	1	each	508-41
Dropper, 0.5 & 1.0 mL marks, glass	1	5/pkg	14197-05
Flask, erlenmeyer, 500 mL	2	each	505-49
Funnel, separatory, 250 mL	2	each	520-46
Pipet, volumetric, 5 mL	1	each	515-37
Pipet Filler, safety bulb	1	each	14651-00
Ring, support, 83 mm (3")	2	each	580-00
Sample Cells, matched pair, 1-inch	2	pair	20950-00
Spoon, measuring, 0.2 g	1	each	638-00
Spoon, measuring, 0.05 g	1	each	492-00
Squeezer, 0.025-1.00 mL plastic dropper	1	10/pkg	21247-10
Stand, support, 127 x 203 mm (5 x 8")	1	each	563-00

Select one based on available voltage:

Description	Quantity Required Per Test	Unit	Cat. No.
Hot Plate, 4" diameter, 120 Vac	1	each	12067-01
Hot Plate, 4" diameter, 240 Vac	1	each	12067-02

OPTIONAL REAGENTS

Acetone, ACS	500 mL	14429-49
Calcium Chloride Solution	1000 mL	428-53
Hydrochloric Acid Standard Solution, 0.1 N	1000 mL	14812-53
Hydrogen Peroxide, 30%	473 mL	144-11
Methyl Orange Indicator Solution, 0.1 N (0.05%)	500 mL	148-49
Nitric Acid, ACS	500 mL	152-49
Phenol Solution, 30 g/L	29 mL	2112-20
Potassium Bromide Powder Pillows	100/pkg	14819-99
Potassium Permanganate Standard Solution	100 mL	14164-42
Selenium Standard Solution, 1000 mg/L	100 mL	22407-42
Selenium Standard Solution, 100 mg/L, 2-mL ampules	20/pkg	12184-20
Sodium Hydroxide Standard Solution, 0.1 N	1000 mL	191-53
Sodium Hydroxide Standard Solution, 5.0 N	100 mL MDB	2450-32
Sulfuric Acid Standard Solution, 5.25 N	100 mL	2449-32
Sulfuric Acid Standard Solution, 19.2 N	500 mL	2038-49

OPTIONAL APPARATUS

Description	Unit	Cat. No.
Beaker, 250 mL	each	500-46
Beaker, 1000 mL	each	500-53
Bottle, wash, 500 mL	each	620-11
Clippers, for opening powder pillows	each	968-00
Cylinder, graduated, 500 mL	each	508-49
Distillation apparatus for general purpose	each	22653-00
Distillation apparatus heater, 115 V	each	22744-00
Distillation apparatus heater, 230 V	each	22744-02
Dropper, 0.5 and 1 mL marks	6/pkg	23185-06
Flask. volumetric, Class A, 50 mL	each	14574-41
Flask. volumetric, Class A, 200 mL	each	14574-45
Flask. volumetric, Class A, 500 mL	each	14574-49
Jack, laboratory	each	22743-00
pH Meter, *sension*™*1*, portable	each	51700-10
Pipet, serological, 10 mL	each	532-38
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 0.50 mL	each	14515-34
PourRite Ampule Breaker	each	24846-00
Rod, stirring, glass	3/pkg	1770-01
Stoppers, for cells, hollow No. 1	6/pkg	14480-01

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

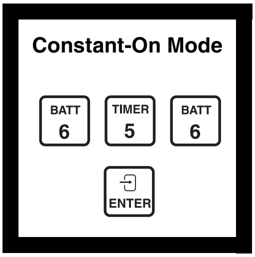
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8185

SILICA, HR (0 to 100.0 mg/L)

For water and seawater

Silicomolybdate Method



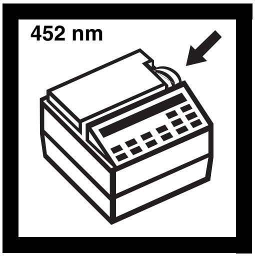
1. Make sure the instrument is in the constant-on mode. Enter the stored program for high range silica (SiO_2).

Press: **6 5 6 ENTER**

The display will show:

Dial nm to 452

Note: *The Pour-Thru Cell can be used with 25-mL reagents only.*



2. Rotate the wavelength dial until the small display shows:

452 nm

When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

then: **mg/L SiO_2 HR**

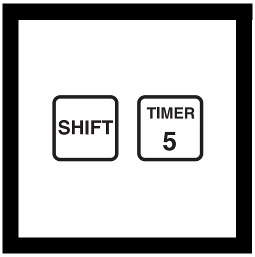
3. Fill a sample cell with 10 mL of sample.

Note: *Sample temperature should be 15 to 25 °C (59 to 77 °F).*

4. Add the contents of one Molybdate Reagent Powder Pillow for High Range Silica. Swirl to mix.

5. Add the contents of one Acid Reagent Powder Pillow for High Range Silica. Swirl to mix.

Note: *Silica or phosphate will cause a yellow color to develop.*

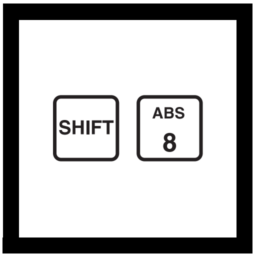


6. Press:

SHIFT TIMER

A 10-minute reaction period will begin.

Press **EXIT**. Continue with Steps 7-10 during the reaction period.



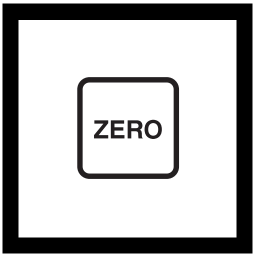
7. Press: **SHIFT ABS**

The display will show:

Abs

Rotate the wavelength dial to 460.

Press **ENTER**.

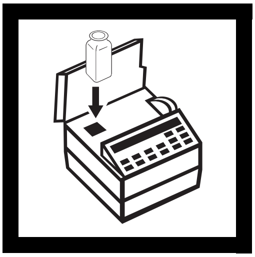


8. Press: **ZERO**

The display will show:

Zeroing. . . .

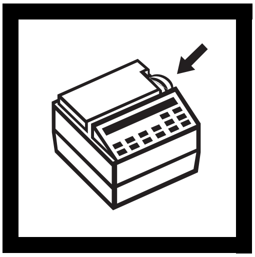
then: **0.000 ABS**



9. Prepare the Holmium Trichloride Solution (see note). Place the bottle with the holmium trichloride solution into the cell holder and close the light shield.

Note: *Add Holmium Trichloride Powder Pillow to 25 mL of deionized water in a square mixing bottle. Cap and mix to dissolve.*

Note: *This capped solution may be kept indefinitely.*



10. Starting at 460 nm, slowly turn the wavelength control dial to decrease the wavelength. Watch the display for the peak absorbance reading. This should occur between 450-454 nm.

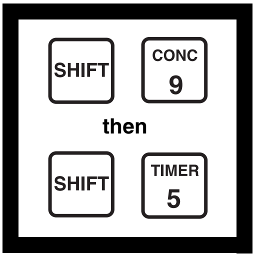
Press: **ZERO**

Without moving the wavelength dial, remove the holmium trichloride solution from the cell holder.

Note: *It is not necessary to reset the wavelength for more than one sample analysis or if the instrument is turned off. Resetting is necessary if the wavelength is changed. If the absorbance peak is outside the 452±1 nm range, the small display will flash "452 nm".*

11. When the timer beeps, add the contents of one Citric Acid Powder Pillow to the sample cell (the prepared sample). Swirl to mix.

Note: *The yellow color due to phosphate will disappear.*



12. Press: **SHIFT CONC**

then: **SHIFT TIMER**

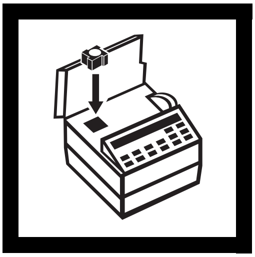
A 2-minute reaction period will begin.

13. When the timer beeps, the display will show:

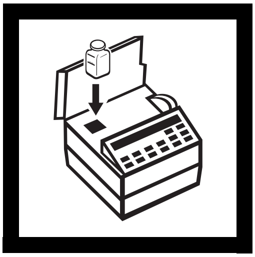
0.0 mg/L SiO_2 HR

Fill a second sample cell with 10 mL of sample (the blank).

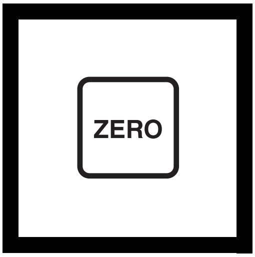
Note: *The display value may vary depending upon the wavelength setting determined in Step 10. The exact zero will be set in Step 16.*



14. Insert the 10-mL Cell Riser into the sample compartment



15. Place the blank in the cell holder. Close the light shield.



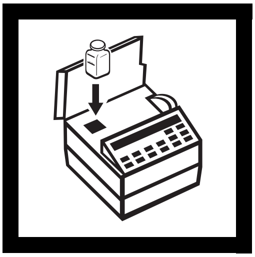
16. Press:**ZERO**

The display will show:

Zeroing. . . .

then:

0.0 mg/L SiO_2 HR



17. Within three minutes after the timer beeps, place the prepared sample in the cell holder. Close the light shield. The results in mg/L silica will be displayed.

▲ Si
Forms SiO_2

Sampling and Storage

Collect samples in clean plastic or glass bottles. Analyze samples as soon as possible after collection. Store samples up to 28 days at 4 °C (39 °F) or below. Warm samples to room temperature before analyzing.

Accuracy Check

Standard Additions Method

a) Open a High Range Silica Standard Solution, 1000 mg/L SiO_2.

b) Use the TenSette Pipet to add 0.1 mL, 0.3 mL, and 0.5 mL of the standard to three 10-mL samples. Mix each thoroughly.

c) Analyze each sample as described above. The silica concentration should increase 10.0 mg/L for each 0.1 mL of standard added.

d) If these increases do not occur, see Standard Additions in Section I for more information.

Standard Solution Method

To check the accuracy of the method, use the Silica Standard Solutions, 25 and 50 mg/L as SiO_2, listed under Optional Reagents. Analyze according to the above procedure using deionized water as the blank.

Precision

In a single laboratory, using a standard solution of 50.0 mg/L SiO_2 and two representative lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±0.45 mg/L silica.

Interferences

Color and turbidity interferences are eliminated by zeroing the instrument with the original water sample.

Sulfides and large amounts of iron interfere.

At levels of 50 mg/L phosphate (PO_4^{3-}), interference is not a problem. At 60 mg/L PO_4^{3-}, an interference of minus 2% is observed. At 75 mg/L, the PO_4^{3-} interference is minus 11%.

Occasionally a sample contains silica which reacts very slowly with molybdate. The nature of these “molybdate-unreactive” forms is not known. A pretreatment with sodium bicarbonate, then sulfuric acid will make these forms reactive to molybdate. The pretreatment is given in *Standard Methods for the Examination of Water and Wastewater* under Silica-Digestion with Sodium Bicarbonate. A longer reaction time with the sample and the molybdate and acid reagents (before adding citric acid) may help in lieu of the bicarbonate treatment.

Summary of Method

Silica and phosphate in the sample react with molybdate ion under acidic conditions to form yellow silicomolybdic acid complexes and phosphomolybdic acid complexes. Addition of citric acid destroys the phosphate complexes. Silica is then determined by measuring the remaining yellow color.

Due to wavelength sensitivity of the test, holmium trichloride is used to reproducibly set the wavelength required.

REQUIRED REAGENTS

	Cat. No.
High Range Silica Reagent Set, 10-mL sample (100 tests) Includes: (1) 21074-69, (1) 21062-69, (1) 21073-69	24296-00

Description	Quantity Required Per Test	Units	Cat. No.
Acid Reagent Powder Pillows for High Range Silica	1	100/pkg	21074-69
Citric Acid Powder Pillows	1	100/pkg	21062-69
Holmium Trichloride Powder Pillows	1	10/pkg	23432-67
Molybdate Reagent Powder Pillows for HR Silica	1	100/pkg	21073-69
Water, deionized	10 mL	4 L	272-56

REQUIRED APPARATUS

Bottle, square mixing, 25-mL mark	1	each	17042-00
Cap, bottle	1	6/pkg	21667-06
Cell Riser, 10-mL	1	each	45282-00
Sample Cell, 10-mL, matched pair	2	pair	24954-02

OPTIONAL REAGENTS

Silica Standard Solution, 10 mg/L	500 mL	1403-49
Silica Standard Solution, 25 mg/L	200 mL	21225-29
Silica Standard Solution, 50 mg/L	200 mL	1117-29
Silica Standard Solution, 1000 mg/L as SiO_2	500 mL	194-49
Sodium Bicarbonate, ACS	454 g	776-01
Sulfuric Acid Standard Solution, 1.000 N	100 mL MDB	1270-32

OPTIONAL APPARATUS

Description	Units	Cat. No.
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 Pipet	50/pkg	21856-96
Standard Methods for the Examination of Water and Wastewater	each	22708-00
Thermometer, - 20 to 105 °C	each	1877-01

OPTIONAL 25-ML ANALYSIS ITEMS

High Range Silica Reagent Set (100 tests) Includes: (1) 1042-99, (1) 14548-99, (2) 1041-66	22443-00

Description	Quantity Required Per Test	Units	Cat. No.
Acid Reagent Powder Pillows for High Range Silica	1	50/pkg	1042-99
Citric Acid Powder Pillows	1	100/pkg	14548-99
Holmium Trichloride Powder Pillows	1	10/pkg	23432-67
Molybdate ReagentPowder Pillows for High Range Silica	1	50/pkg	1041-66
Pour-Thru Cell Assembly		each	45215-00
Sample Cell, 25-mL, matched pair		pair	20950-00

For technical support and ordering information, see Section V.

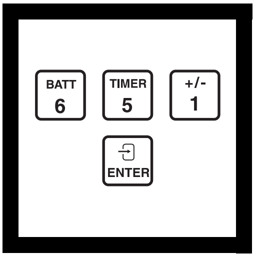
In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

SILICA, LR (0 to 1.600 mg/L)

For water and seawater

Heteropoly Blue Method*



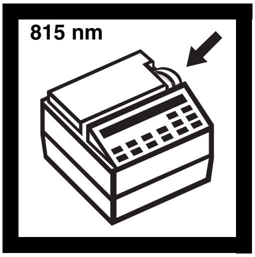
1. Enter the stored program number for low range silica (SiO_2).

Press: **6 5 1 ENTER**

The display will show:

Dial nm to 815

***Note:** The Pour-Thru cell can be used with 25-mL reagents only.*



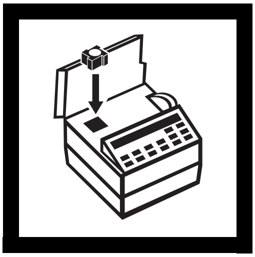
2. Rotate the wavelength dial until the small display shows:

815 nm

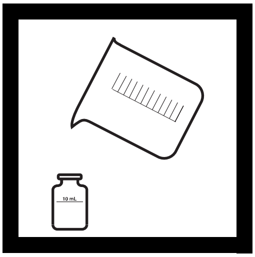
When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

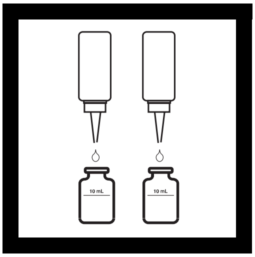
then: **mg/L SiO_2 LR**



3. Insert the 10-mL Cell Riser into the cell compartment.

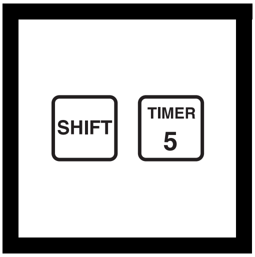


4. Fill two sample cells to the 10-mL line with sample.



5. Add 14 drops of Molybdate 3 Reagent to each sample cell. Swirl to mix.

***Note:** For greatest accuracy, hold dropping bottle vertical.*



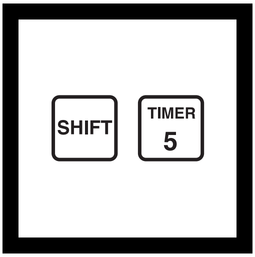
6. Press:

SHIFT TIMER

A 4-minute reaction period will begin.

***Note:** Reaction time given is for samples at 20 °C (68 °F). If the sample temperature is 10 °C (50 °F), wait 8 minutes. If the sample* **temperature is 30 °C (86 °F), wait 2 minutes.**

7. When the timer beeps, add the contents of one Citric Acid Reagent Powder Pillow to each sample cell. Swirl to mix.



8. Press:

SHIFT TIMER

A 1-minute reaction period will begin. Phosphate interference is eliminated during this period.

***Note:** The time given is for samples at 20 °C (68 °F). If the sample temperature is 10 °C (50 °F), wait 2 minutes. If the sample is 30 °C (86 °F), wait 30 seconds.*

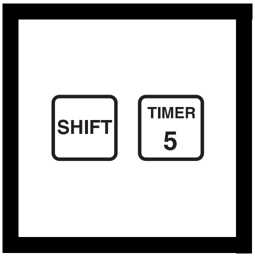
---

* Adapted from *Standard Methods for the Examination of Water and Wastewater.*

9. When the timer beeps, add the contents of one Amino Acid F Reagent Powder Pillow to one of the sample cells (the prepared sample). Swirl to mix.

Note: *The sample cell without the Amino Acid F Reagent is the blank.*

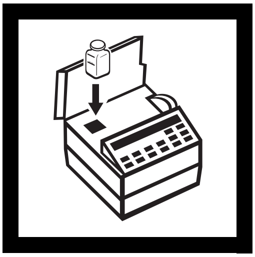
Note: *A blue color will develop if silica is present.*



10. Press:

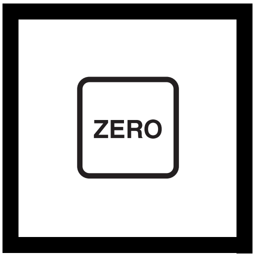
SHIFT TIMER

A 1-minute reaction period will begin.



11. When the timer beeps, the display will show: **mg/L SiO_2 LR**

Place the blank (solution without Amino Acid F Reagent) into the cell holder. Close the light shield.



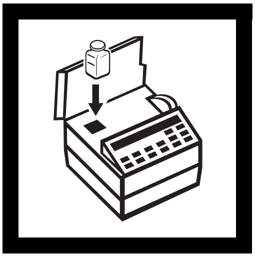
12. Press: **ZERO**

The display will show:

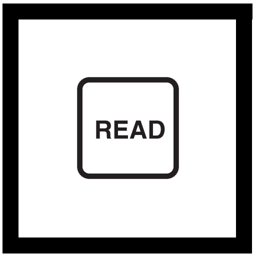
Zeroing. . . .

then:

0.000 mg/L SiO_2 LR



13. Place the prepared sample into the cell holder. Close the light shield.



14. Press: **READ**

The display will show:

Reading. . . .

then the result in mg/L silica will be displayed.

Forms ▲▼ SiO_2 LR
Si LR

Alternative Procedures

The DR/2010 may be calibrated to use the same reagents used in Hach's Silica Analyzers (651C, 1234D, Series 5000, and 31201 Trace pump). The Alternative Procedures Table lists the reagents and sample volumes to used, plus appropriate reaction periods for room-temperature samples.

Prepare an equivalent calibration as follows:

a) Store the calibration in the instrument memory using the procedure in the Operation section of the DR/2010 Instrument Manual. Store units as mg/l SiO_2, the decimal position as 0.000, the wavelength as 810 nm, and the appropriate timer intervals from the Alternative Procedures Table.

b) Prepare standards of 0.2, 0.4, 0.6, 0.8 and 1.0 mg/L SiO_2 by diluting 1.00, 2.00, 3.00, 4.00, and 5.00 mL of Silica Standard Solution, 50 mg/L SiO_2, to 250 mL with silica-free deionized water. Use Class A glassware to prepare these standards.

c) Choose the appropriate column from the Alternative Procedures Table to match your analyzer. Prepare the samples by following the sequence of steps listed in the table. First calibrate the DR/2010 at a silica concentration of zero. Prepare this sample using 50 mL of silica-free deionized water with the specified reagent volumes and corresponding reaction times. Now, using 25 mL of this prepared sample, measure and enter the sample absorbance as prompted by the instrument.

d) Next, prepare 50 mL of the first standard (0.2 mg/L) using the same procedure. Enter this concentration into the instrument. Again, using 25 mL of this standard, measure and enter the absorbance as prompted by the instrument. Analyze, measure and enter the remaining standards. For best results at low concentrations, use the Pour-Thru Cell.

e) To analyze samples using this calibration, enter the stored program number you selected at the **METHOD #** prompt. The calibration does not need to be re-entered for each new lot of reagent.

Alternative Procedure Table

Step	Series 5000 Analyzer	31201 (Trace Pump)	651C	1234D Analyzer
1. Your stored program number	9 ? ?	9 ? ?	9 ? ?	
2. Sample amount needed	50 mL	50 mL	50 mL	50 mL
3. Measurement wavelength	810 nm	810 nm	810 nm	810 nm

Alternative Procedure Table (Continued)

Step	Series 5000 Analyzer	31201 (Trace Pump)	651C	1234D Analyzer
4. Add Molybdate 3 (1995*)	1.0 mL	1.0 mL	0.5 mL	1.0 mL
5. Wait	5 min	5 min	5 min	5 min
6. Add Citric Acid (22542*) (23470**) or Sodium Citrate (14908*)	1.0 mL	1.0 mL	---------- ----------	---------- 1.0 mL
7. Wait	1 min	1 min	-----------	1 min
8. Add Amino Acid (1934*) or Amino Acid F (22541) (23531**)	--------- 1.0 mL	--------- 1.0 mL	1.0 mL --------	1.0 mL ---------
9. Wait	8 min	15 sec	8 min	8 min
10. Zero the DR/2010				
11. Measure Absorbance				

* Hach Catalog Number

**Hach Catalog number for Series 5000 reagent

Sampling and Storage

Collect samples in clean plastic bottles. Analyze samples as soon as possible after collection. If prompt analysis is not possible, store samples for up to 28 days by cooling to 4 °C (39 °F) or below. Warm samples to room temperature before analysis.

Accuracy Check

Standard Additions Method

a) Open a Low Range Silica Standard Solution Pillow, 20 mg/L SiO_2.

b) Using the TenSette Pipet, add 0.1, 0.2, and 0.3 mL of standard to three 10-mL samples. Mix thoroughly.

c) Analyze each sample as described above. The silica concentration should increase 0.2 mg/L for each 0.1 mL of standard added.

d) If these increases do not occur, see Standard Additions in Section I for more information.

Standard Solution Method

Silica Standard Solutions of 0.500 mg/L and 1.000 mg/L SiO_2 are listed under *Optional Reagents.* Use these in place of the sample and analyze according to the above procedure.

Precision

In a single laboratory, using standard solutions of 1.00 mg/L silica and two representative lots of reagent and a DR/2010, a single operator obtained a standard deviation of ±0.0067 mg/L silica.

Interferences

Color and turbidity interferences are eliminated by zeroing the instrument with the original sample.

Sulfides and large amounts of iron interfere.

Phosphate does not interfere at levels less than 50 mg/L PO_4. At 60 mg/L PO_4, an interference of -2% occurs. At 75 mg/L PO_4 the interference is -11%.

Occasionally a sample contains silica which reacts very slowly with molybdate. The nature of these “molybdate-unreactive” forms is not known. A pretreatment with sodium bicarbonate, then sulfuric acid will make these forms reactive to molybdate. The pretreatment is given in *Standard Methods for the Examination of Water and Wastewater* under Silica-Digestion with Sodium Bicarbonate. A longer reaction time with the sample and the molybdate and acid reagents (before adding citric acid) may help in lieu of the bicarbonate treatment.

Reagent Preparation

To prepare Amino Acid F Reagent Solution, dissolve 11.4 grams Amino Acid F Reagent Powder in 100 mL of 1.0 N Sodium Hydroxide Solution. The solution is stable for at least one month if stored in a plastic bottle.

Summary of Method

Silica and phosphate in the sample react with molybdate ion under acidic conditions to form yellow silicomolybdic acid complexes and phosphomolybdic acid complexes. Acid reduces the yellow silicomolybdic acid to an intense blue color, which is proportional to the silica concentration.

REQUIRED REAGENTS

	Cat. No.
Low Range Silica Reagent Set, 10 mL sample (100 tests)	24593-00

Includes: (1) 22540-49, (2) 21062-69 (1) 1995-26

Description	Quantity Required Per Test	Units	Cat. No.
Amino Acid F Reagent Powder Pillows	1 pillow	100/pkg	22540-69
Citric Acid Powder Pillows	2 pillows	100/pkg	21062-69
Molybdate 3 Reagent	28 drops	50 mL SCDB	1995-26

REQUIRED APPARATUS

Cell Riser, 10-mL	1	each	45282-00
Sample Cell, 10-mL, matched pair	2	pair	24954-02

OPTIONAL REAGENTS

Amino Acid F Reagent Powder (for Trace Pump Analyzer)	410 g	22833-55
Silica Standard Solution, 0.50 mg/L SiO_2	3.78 L	21008-17
Silica Standard Solution, 1.00 mg/L SiO_2	500 mL	1106-49
Silica Standard Solution, 50 mg/L SiO_2	200 mL	1117-29
Silica Standard Solution Pillows, 20 mg/L as SiO_2, 10 mL	16/pkg	14245-10
Sodium Bicarbonate, ACS	454 g	776-01
Sodium Hydroxide Standard Solution, 1.000 N	900 mL	1045-53
Sulfuric Acid Standard Solution, 1.0 N	1000 mL	1270-53

OPTIONAL APPARATUS

Bottle, 118 mL, polyethylene, oblong	6/pkg	23184-06
Dropper, 0.5- & 1.0-mL marks	6/pkg	23185-06
Flask, volumetric, Class A, 250 mL	each	14574-46
Pipet, serologic, 2 mL, poly	each	2106-36
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 1.00 mL	each	14515-35
Pipet, volumetric, Class A, 2.00 mL	each	14515-36
Pipet, volumetric, Class A, 3.00 mL	each	14515-03
Pipet, volumetric, Class A, 4.00 mL	each	14515-04
Pipet, volumetric, Class A, 5.00 mL	each	14515-37
Pipet Filler, safety bulb	each	14651-00
Standard Methods for the Examination of Water and Wastewater	each	22708-00
Thermometer, - 20 to 105 °C	each	1877-01

OPTIONAL 25-mL ANALYSIS ITEMS

Low Range Silica Reagent Set (100 tests)	23468-00

Includes: (1) 22538-69, (2) 14548-99 (1) 1995-32

Description	Quantity Required Per Test	Units	Cat. No.
Amino Acid F Reagent Powder Pillows	1 pillow	100/pkg	22538-69
Citric Acid Powder Pillows	2 pillows	100/pkg	14548-99
Molybdate 3 Reagent	1.0 mL	100 mL MDB	1995-32
Pour-Thru Cell Assembly	1	each	45215-00
Sample Cell, 25-mL, matched pair	2	pair	20950-00

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

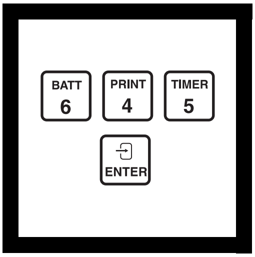
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8282

SILICA, ULTRA LOW RANGE (0 to 1000 µg/L)

For ultrapure water

Heteropoly Blue Method*



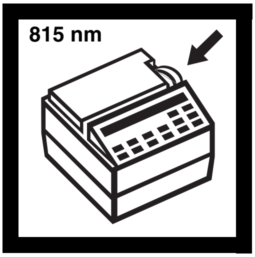
1. Enter the stored program for ultra low range silica.

Press: **6 4 5 ENTER**

The display will show:

Dial nm to 815

Note: *The Pour-Thru Cell must be used.*



2. Rotate the wavelength dial until the small display shows:

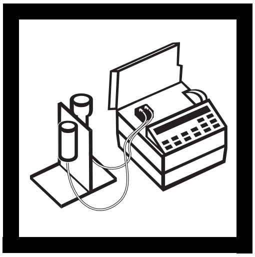
815 nm

When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

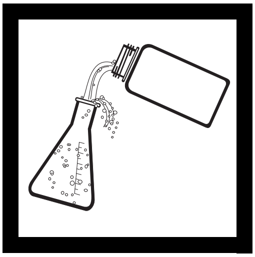
then:

μg/L SiO_2 ULR



3. Install the Pour-Thru Cell and flush with 50 mL of deionized water.

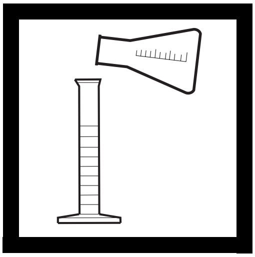
Note: *See Treating Analysis Labware for information on cleaning labware.*



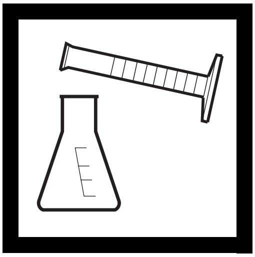
4. Fill two clean 250-mL erlenmeyer flasks to overflowing with the sample.

5. Fill a clean 50-mL plastic graduated cylinder with sample from one of the flasks and then discard the cylinder contents.

6. Repeat the rinsing of the cylinder three times from the same sample flask, discarding each rinse.



7. Fill the cylinder to the 50-mL mark with sample from the same flask, discarding any sample remaining in the flask.



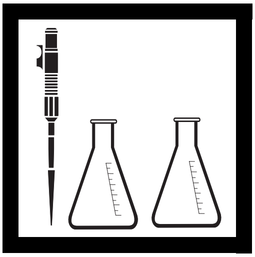
8. Pour the contents of the cylinder back into the original flask.

---

* Adapted from *Standard Methods for the Examination of Water and Wastewater.*

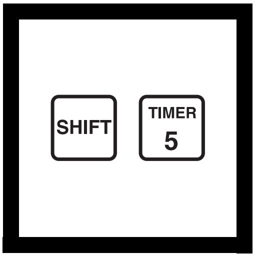
Repeat Steps 5-8
for second flask.

9. Repeat Steps 5-8 for the second flask containing sample, then continue with Step 10.



10. Using a TenSette Pipet, add 1.0 mL of Molybdate 3 Reagent to each flask. Swirl to mix.

Note: *An all-plastic 1.0-mL dropper is also available.*

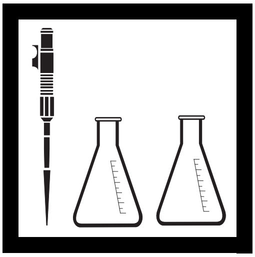


11. Press:

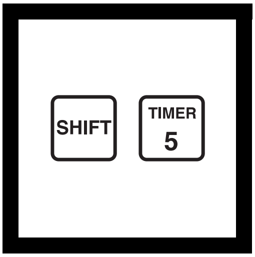
SHIFT TIMER

A 4-minute reaction period will begin.

Note: *The time given is for samples at 20 °C (68 °F). If the sample temperature is 10 °C (50 °F), wait 8 minutes. If the sample temperature is 30 °C (86 °F), wait 2 minutes.*



12. When the timer beeps, add 1.0 mL of Citric Acid F Reagent to each flask. Swirl to mix.



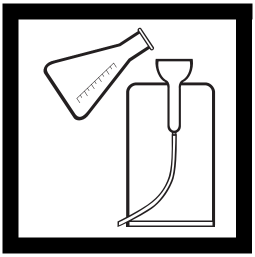
13. Press:

SHIFT TIMER

A 1-minute reaction period will begin.

Note: *The destruction of phosphate interference occurs during this period.*

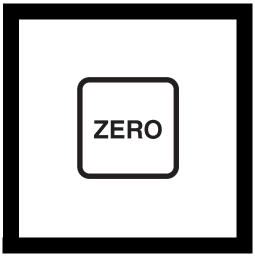
Note: *The time given is for samples at 20 °C (68 °F). If the sample temperature is 10 °C (50 °F), wait 2 minutes. If the sample temperature is 30 °C (86 °F), wait 30 seconds.*



14. When the timer beeps, the display will show:

µg/L SiO_2 ULR

Pour the contents of one flask through the Pour-Thru Cell.



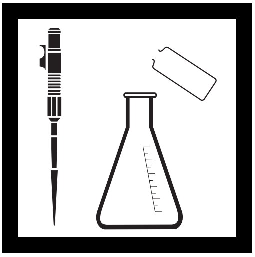
15. After the flow has stopped, press: **ZERO**

The display will show:

Zeroing. . . .

then:

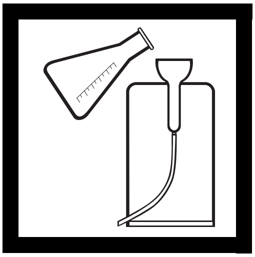
0 µg/L SiO_2 ULR



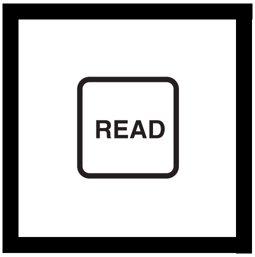
16. Add 1.0 mL of Amino Acid F Reagent Solution or pour the contents of one ampule of Amino Acid F Reagent into the second flask. Swirl to mix.

Note: *For greatest accuracy use a TenSette pipet to dispense 1.0 mL from the ampul.*

Note: *A faint blue color will develop if silica is present.*



17. Wait 15 seconds for color formation, then pour the contents of the second flask through the Pour-Thru Cell.



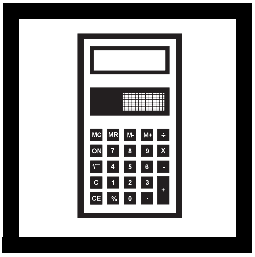
18. After the flow has stopped, press: **READ**

The display will show:

Reading. . . .

Then the result in µg/L of SiO_2 will be displayed.

Forms ▲ Si SiO_2



19. Subtract the reagent blank value found on the Molybdate 3 reagent container from the value obtained in Step 18.

Note: *See Reagent Blank section if analyzer reagents are used.*

20. Flush the Pour-Thru Cell with at least 50 mL of deionized water immediately after use.

Note: *Protect the Pour-Thru Cell from contamination by inverting a small beaker over the top of the glass funnel.*

Sampling and Storage

The sampling procedure in Steps 4-8 has proven effective in harsh and dirty testing environments. In this procedure it improves accuracy.

Use only plastic containers with tight-fitting closures. Glass containers can contaminate the sample with silica. Soak sampling containers with solution of one part Molybdate 3 Reagent to 50 parts low-level silica deionized water. Fill completely and let stand for several hours. Rinse thoroughly with low-level silica water, drain and close. Repeat this cleaning periodically.

Allow the sample stream to flow for 1 - 2 minutes before collection. Do not adjust the flow during the sampling period this may introduce particulates. Rinse the container well with sample before collecting the portion for analysis. Analyze as soon as possible.

Reagent Preparation

Amino Acid F Reagent Solution is available in either 100-mL bottles or a package of 20-unit dose ampules. The bottled reagent has a limited shelf life after opening due to air oxidation. The ampuled reagent is sealed under argon and is more stable (greater than 1 year). Instability is evidenced by reduced sensitivity at high silica concentrations. Check the bottled reagent on a routine basis by performing the test on a 1000 µg/L silica standard. If the concentration result is less than 950 µg/L, use a fresh bottle of Amino Acid F Reagent Solution.

Alternatively, prepare larger or smaller volumes of Amino Acid F Reagent solution by dissolving Amino Acid F Reagent Powder in Amino Acid F Reagent Solvent at a ratio of 11 grams per 100 mL. These reagents are available as the Amino Acid F Reagent Package listed under Optional Reagents. This prepared solution has limited stability; test routinely with the 1000 µg/L silica standard as above.

Users performing a large number of analyses may wish to use the Rapid Liquid Method for ULR Silica, program # 645.

Treating Analysis Labware

All containers used in this test must be cleaned thoroughly to remove any traces of silica. If possible, use plastic containers for all analysis and storage because glass can contaminate the sample with silica. Small bottles or flasks with screw-type closures work well. Clean containers by normal means (do not use phosphate detergents), then rinse with high quality deionized water with low-level silica concentration. Soak for 10 minutes with a 1:50 dilution of Molybdate 3 Reagent in low-level silica water. Rinse well with low-level silica water or the sample before use.

Keep containers for silica analysis only. Fill the Pour-Thru Cell with this same mixture of Molybdate 3 and water. Let stand for several minutes before use. Rinse with low-level silica water.

Reagent Blank

If analyzer reagents are used in the ULR Silica method, multiply the reagent blank value printed on the bottle label by the appropriate multiplier. Use this value in Step 19 of the procedure.

Analyzer	Reagent Used (Cat. No.)	Multiplier
1234D	Molybdate 3 (1995-17)	1.00
Series 5000	Molybdate 3 (1995-03)	1.09

Cleaning the Pour-thru Cell

The Pour-Thru Cell may accumulate a buildup of colored products, especially if the reacted solutions are allowed to stand in the cell for long periods after measurement. Remove the color by rinsing with a 1:5 dilution of ammonium hydroxide, followed by several deionized water rinses. Cover the glass funnel when it is not in use.

Accuracy Check

a) Use the TenSette Pipet to add 0.1, 0.2 and 0.3 mL of either 1-mg/L Silica Standard Solution or 10-mg/L Silica Standard Solution to three 50-mL samples, respectively.

b) Analyze each spiked sample as described above. The silica concentration should increase 2.0 µg/L for each 0.1 mL of 1-mg/L standard. The silica concentration should increase 20.0 µg/L for each 0.1 mL of 10-mg/L standard.

Precision

In a single laboratory, using blanks and standard additions of 5 µg/L Si, a single operator obtained a standard deviation of less than ±1 µg/L Si.

Interferences

Color and turbidty interferences are eliminated by zeroing the instrument with the original sample.

Phosphate does not interfere appreciably at levels less than 50 mg/L PO_4^{3-}. Sulfides and large amounts of iron interfere.

Summary of Method

A number of modifications are necessary to adapt the Low Range Silica method for analyzing trace levels in the Ultra Low Range Silica method. It is absolutely necessary to use the one-inch Pour-Thru Cell and liquid reagents. The Pour-Thru Cell increases the reproducibility of the optics and reduces the instability of the readings that result with moveable sample cells. Liquid reagents contribute to more reproducible readings and lower blanks by eliminating slight turbidity that may remain when using powdered reagents. In addition, the liquid reagents are used with Hach process analyzers for continuous silica measurement.

Silica and phosphate in the sample react with molybdate ion under acidic conditions to form yellow silicomolybdic acid complexes and phosphomolybdic acid complexes. Addition of citric acid destroys the phosphate complexes. An amino acid reagent is then added to reduce the yellow silicomolybdic acid to an intense blue color, which is proportional to the silica concentration.

REQUIRED REAGENTS

Description	Cat No
ULR Silica Reagent Set (using Amino Acid F solution; 100 tests) Includes: (2) 1995-32, (2) 22542-32, (1) 23864-42	25535-00
ULR Silica Reagent Set (using Amino Acid F ampules; 40 tests) Includes: (1) 1995-32, (1) 22542-32, (2) 23864-20	25814-00

Description	Quantity Required Per Test	Unit	Cat No
Amino Acid F Reagent Solution	1.0 mL	100 mL	23864-42
or			
Amino Acid F Reagent Ampuls	1 each	20/pkg	23864-20
Citric Acid F Reagent	2 mL	100 mL MDB	22542-32
Molybdate 3 Reagent	2.0 mL	100 mL MDB	1995-32

REQUIRED APPARATUS

Cylinder, graduated, 50 mL poly	1	each	1081-41
Flask, erlenmeyer, 250 mL PMP, w/ cap	2	each	20898-46
Pipet, TenSette, 0.1 to 1.0 mL	1	each	19700-01
Pipet Tips, for 19700-01 Pipet	3	50/pkg	21856-96
Pour-Thru Cell Assembly Kit	1	each	45215-00

OPTIONAL REAGENTS

Amino Acid F Reagent Package:		23531-03
Amino Acid F Reagent Powder		308 g
Amino Acid F Regent Solvent		2.7 L
Ammonium Hydroxide, ACS	500 mL	106-49
Molybdate 3 Reagent	2.9 L	1995-03
Molybdate 3 Reagent	3.78 L	1995-17
Silica Standard Solution, 1 mg/L SiO_2	500 mL	1106-49
Silica Standard Solution, 10 mg/L SiO_2	500 mL	1043-49
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Ampul Breaker	each	24846-00
Beaker, polypropylene, 100 mL	each	1080-42
Bottle, wash, 250 mL	each	620-31
Flask, erlenmeyer, 250 mL, PMP w/ cap	4/pkg	20898-76
Measuring Dropper, squeezer type, 1 mL	10/pkg	21247-10
Pipet Tips, for 19700-01 TenSette Pipet	1000/pkg	21856-28
Thermometer, -20 to 105 °C	each	1877-01

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

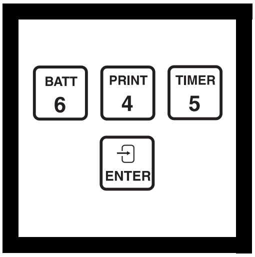
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8282

SILICA, ULR (0 to 1000 µg/L)

Heteropoly Blue Rapid Liquid Method*

For boiler, cooling, and ultra-pure waters

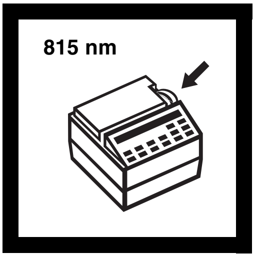


1. Enter the stored program for Ultra Low Range Silica.

Press: **6 4 5 ENTER**

The display will show:

Dial nm to 815

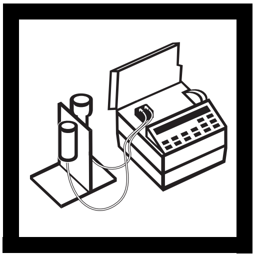


2. Rotate the wavelength dial until the small display shows:

815 nm

When the correct wavelength is dialed in, the display will quickly show: **Zero Sample**

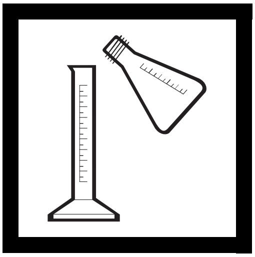
then: **µg/L SiO_2 ULR**



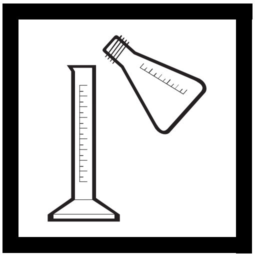
3. Install the Pour-Thru Cell and flush with 50 mL of deionized water.

Note: *Clean the Pour-Thru Cell and all labware as specified in Treating Analysis Labware.*

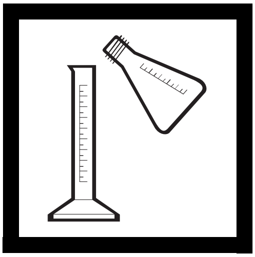
4. Fill two clean 250-mL plastic Erlenmeyer flasks to overflowing with the sample.



5. Fill a clean 50-mL plastic graduated cylinder with sample from one of the flasks and then discard the cylinder contents.



6. Repeat the rinsing of the cylinder three times from the same sample flask, discarding each rinse.



7. Fill this rinsed cylinder to the 50-mL mark with sample from the same flask, discarding any remaining sample in the flask.

8. Pour the contents of the 50-mL cylinder back into the original flask.

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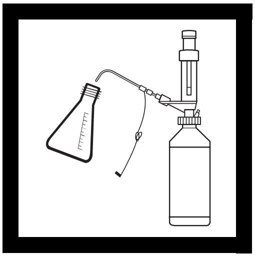
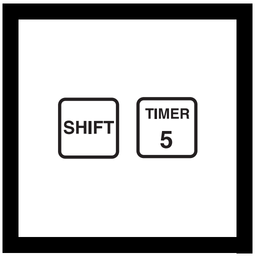
* Adapted from *Standard Methods for the Examination of Water and Wastewater.*

Repeat Steps 5-8

9. Repeat Steps 5-8 for the second flask containing sample, then continue with Step 10.



10. Using the Repipet dispenser, add 1.0 mL of Molybdate 3 Reagent to each flask. Swirl to mix.

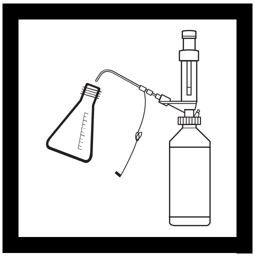


11. Press:

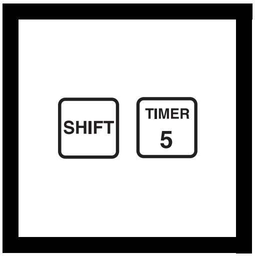
SHIFT TIMER

A 4-minute reaction period will begin.

Note: *Reaction time depends on sample temperature. The time given is for samples at 20 °C (68 °F). If the sample temperature is 10 °C (50 °F), wait 8 minutes. If the sample temperature is 30 °C (86 °F), wait 2 minutes.*



12. When the timer beeps, use the Repipet dispenser to add 1.0 mL of Citric Acid F Reagent to each flask. Swirl to mix.



13. Press:

SHIFT TIMER

A 1-minute reaction period will begin.

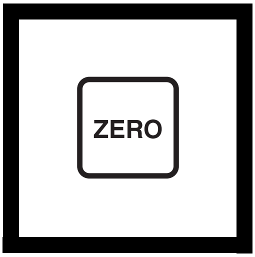
The destruction of possible phosphate interference occurs during this period.

Note: *Reaction time depends on sample temperature. The time given is for samples at 20 °C (68 °F). If the sample temperature is 10 °C (50 °F), wait 2 minutes. If the sample temperature is 30 °C (86 °F), wait 30 seconds.*

14. When the timer beeps, the display will show:

µg/L SiO_2 ULR

Pour the contents of one of the flasks through the Pour-Thru Cell.

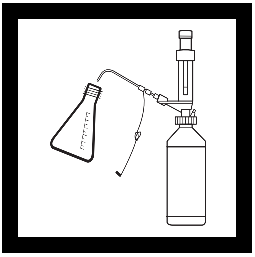


15. After the flow has stopped, press: **ZERO**

The display should show:

Zeroing. . . .

then: **0. µg/L SiO_2 ULR**

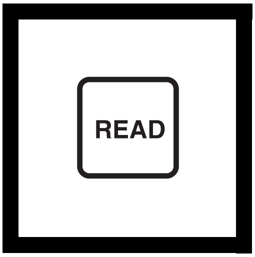


16. Add 1.0 mL of prepared Amino Acid F Reagent to the second flask using the Repipet dispenser. Swirl to mix.

Note: *A faint blue color will develop if silica is present.*

Note: *See Reagent Preparation section for instructions on preparing the Amino Acid F Reagent.*

17. Wait 15 seconds for color formation, then pour the contents of the second flask through the Pour-Thru Cell.



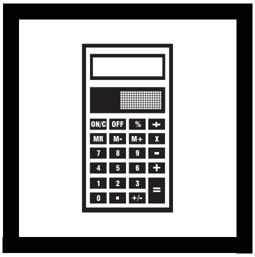
18. After the flow has stopped, press: **READ**

The display will show:

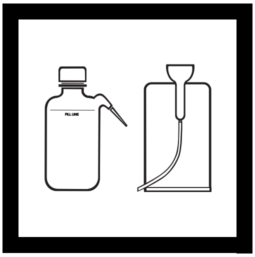
Reading. . . .

Then the result in µg/L of SiO_2 will be displayed.

Forms ▲ Si SiO_2



19. Subtract the reagent blank value found on the Molybdate 3 Reagent container from the value obtained in Step 18.



20. Flush the Pour-Thru Cell with at least 50 mL of deionized water immediately after use.

Note: *Protect the Pour-Thru Cell from contamination by inverting a small beaker over the top of the glass funnel when not in use.*

Reagent Preparation

The Amino Acid F Reagent Solution must be prepared before use. Using a powder funnel, add the contents of one 55 g bottle of Amino Acid F Reagent Powder (Cat. No. 26511-55) to one 475-mL bottle of Amino Acid Dilution Solution (Cat. No. 23530-11). Invert several times and swirl until the powder is completely dissolved.

This solution will give accurate results for at least one month after mixing if stored at 20-25 °C. Record the date of preparation on the Amino Acid F Solution bottle. Discard any remaining solution after one month. Use of this reagent after one month may result in high reagent blanks and low values at high concentrations. Do not combine fresh reagent with previously mixed reagent.

Treating Analysis Labware

All containers used in this test must be cleaned thoroughly to remove any traces of silica. If possible, use plastic containers for all analysis and storage because glass can contaminate the sample with silica. Small bottles or flasks with screw-type closures work well. Clean containers by normal means (do not use phosphate detergents), then rinse with high quality deionized water with a low-level silica concentration. Soak for 10 minutes with a 1:50 dilution of Molybdate 3 Reagent in low-level silica water. Rinse well with low-level silica water or the sample before use. Keep containers tightly closed and dedicate them for silica analysis only. Fill the Pour-Thru Cell with this same mixture of Molybdate 3 Reagent and water. Let stand for several minutes. Rinse with low-level silica water.

Cleaning the Pour-Thru Cell

The Pour-Thru Cell may accumulate a buildup of colored products, especially if the reacted solutions are allowed to stand in the cell for long periods after measurement. Remove the color by rinsing with a 1:5 dilution of ammonium hydroxide, followed by several deionized water rinses. Cover the glass funnel when it is not in use.

Sampling and Storage

The sampling procedure (Steps 4-9) has proven effective in harsh and dirty testing environments. It is used in this procedure to improve accuracy.

Use only plastic containers with tight-fitting closures. Glass containers can contaminate the sample with silica. Soak sampling containers with a solution of one part Molybdate 3 Reagent to 50 parts low-level silica deionized water. Fill completely and let stand for several hours. Rinse thoroughly with low-level silica water, drain and close. Repeat this cleaning periodically.

Allow the sample stream to flow for 1-2 minutes before collection. Do not adjust the flow during the sampling period; this may introduce particulates. Rinse the container well with sample before collecting the portion for analysis. Analyze as soon as possible.

Accuracy Check

Standard Additions Method

a) Use the TenSette Pipet to add 0.1, 0.2 and 0.3 mL of either 1-mg/L Silica Standard Solution or 10-mg/L Silica Standard Solution to three 50-mL samples, respectively.

b) Analyze each sample as described above. The silica concentration should increase 2 µg/L for each 0.1 mL of 1-mg/L standard. The silica concentration should increase 20 µg/L for each 0.1 mL of 10-mg/L standard.

c) If these increases do not occur, see Standard Additions in Section 1.

Precision

In a single laboratory, using blanks and standard additions of 5 µg/L silica on a DR/2010, a single operator obtained a standard deviation of less than 1 µg/L silica.

Interferences

Eliminate color and turbidity interferences by zeroing the instrument with the original sample. Phosphate does not interfere appreciably at levels less than 50 mg/L PO_4^{3-}. Sulfides and large amounts of iron interfere.

Summary of Method

A number of modifications are necessary to adapt the Low Range Silica method for analyzing trace levels in the Ultra Low Range Silica method. It is absolutely necessary to use the one-inch Pour-Thru Cell and liquid reagents. The Pour-Thru Cell increases the reproducibility of the optics and reduces the instability of the readings that result with moveable sample cells. Liquid reagents contribute to more reproducible readings and lower blanks by eliminating slight turbidity that may remain when using powdered reagents. In addition, the liquid reagents are used with Hach process analyzers for continuous silica measurement.

Silica and phosphate in the sample react with molybdate ion under acidic conditions to form yellow silicomolybdic acid complexes and phosphomolybdic acid complexes. Addition of citric acid destroys the phosphate complexes. An amino acid is then added to reduce the yellow silicomolybdic acid to an intense blue color, which is proportional to the silica concentration.

REQUIRED REAGENTS

Rapid Liquid ULR Silica Reagent Set 26785-00
Includes: (1) 26522-55, (1) 23530-11, (1) 22542-49, (1) 1995-49

Description	Quantity Required Per Test	Unit	Cat. No.
Amino Acid F Reagent Powder		55 g	26511-55
Amino Acid Reagent Dilution Solvent		475 mL	23530-11
Citric Acid F Reagent	1 mL	500 mL	22542-49
Molybdate 3 Reagent	1 mL	500 mL	1995-49

REQUIRED APPARATUS

Cylinder, graduated, 50 mL, poly	1	each	1081-41
Dispenser, fixed volume, 1.0 mL Repipet Jr.	3	each	21113-01
Flask, Erlenmeyer, 250 mL, PMP, w/ cap	2	each	20898-46
Pour-Thru Cell Assembly	1	each	45215-00

OPTIONAL REAGENTS

Ammonium Hydroxide, ACS	500 mL	106-49
Silica Standard Solution, 1 mg/L SiO_2	500 mL	1106-49
Silica Standard Solution, 10 mg/L SiO_2	500 mL	1403-49
Water, deionized	500 mL	272-49
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Beaker, polypropylene, 100 mL	each	1080-42
Beaker, poly, 50 mL	each	1080-41
Flask, Erlenmeyer, 250 mL, PMP w/ cap	4/pkg	20898-76
Funnel, powder	each	22644-67
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Thermometer, -20 to 105 °C	each	1877-01

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

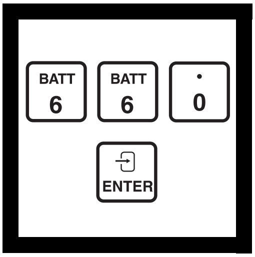
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8120

SILVER (0 to 0.60 mg/L)

For water and wastewater

Colorimetric Method



1. Enter the stored program for silver (Ag.)

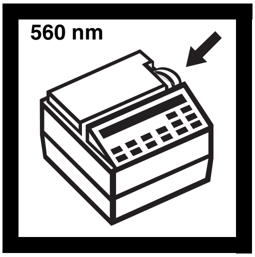
Press: **6 6 0 ENTER**

The display will show:

Dial nm to 560

Note: *If cyanide is present, digest the sample; see Digestion, below.*

Note: *The Pour-Thru cell cannot be used with this procedure.*



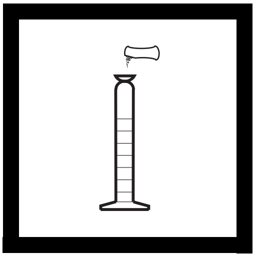
2. Rotate the wavelength dial until the small display shows:

560 nm

When the correct wavelength is dialed in, the display will quickly show:

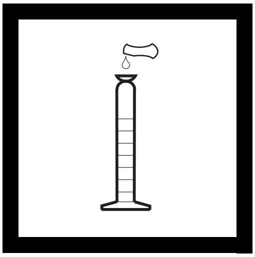
Zero Sample

then: **mg/L Ag**



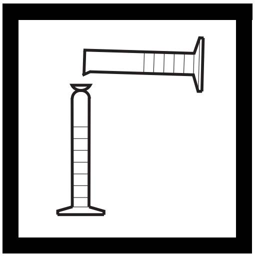
3. Add the contents of one Silver 1 Powder Pillow to a clean, dry 50-mL graduated mixing cylinder.

Note: *If the Silver 1 Powder becomes wet at this point, the powder will not dissolve completely, which will inhibit color development.*



4. Add the contents of one Silver 2 Reagent Solution Pillow to the cylinder. Swirl to completely wet the powder.

Note: *If clumps of dry powder are present when the sample is poured in, the powder will not dissolve completely. This will inhibit color formation.*

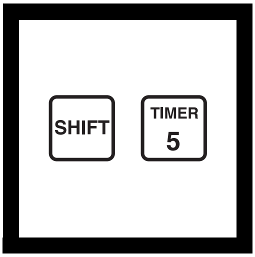


5. Using a 50-mL graduated cylinder, add 50 mL of sample to the cylinder. Stopper. Invert repeatedly for one minute.

Note: *Adjust the pH of stored samples before analysis.*

6. Pour 25 mL of the mixture into a sample cell (the blank). Add the contents of one Thiosulfate Powder Pillow to the sample cell. Swirl for 30 seconds to mix.

Note: *It is important to generate a blank for each sample.*

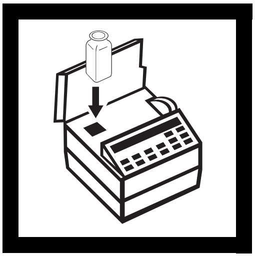


7. Press:

SHIFT TIMER

A 2-minute reaction period will begin.

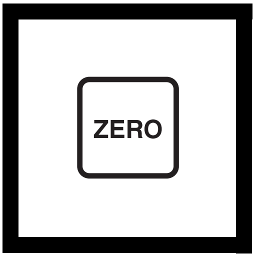
8. Pour the portion remaining in the cylinder into a second sample cell (the prepared sample).



9. When the timer beeps, the display will show:

mg/L Ag

Place the blank in the cell holder. Close the light shield.

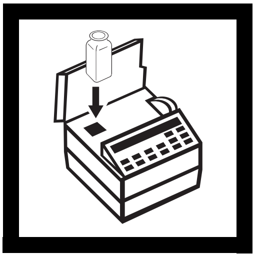


10. Press: **ZERO**

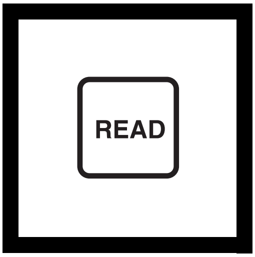
The display will show:

Zeroing. . . .

then: **0.00 mg/L Ag**



11. Place the prepared sample in the cell holder. Close the light shield.



12. Press: **READ**

The display will show:

Reading. . . .

then the results in mg/L silver will be displayed.

Note: *Rinse the cells carefully between samples to avoid development of a film on the cell walls.*

Sampling and Storage

Collect samples in acid-cleaned plastic or glass bottles. Using pH paper, adjust the pH to 2 or less with nitric acid (about 2 mL/liter). Store preserved samples at room temperature for up to 6 months. Before analysis, adjust the pH to 9-10 with 5.0 N sodium hydroxide. Do not use a pH meter because of silver contamination from the electrode. Correct for volume additions (see *SECTION 1*).

Accuracy Check

Standard Additions Method

a) Add 5.0 mL of 1000-mg/L Silver Solution to a 100-mL volumetric flask. Dilute to volume with deionized water. Mix well. This is a 50-mg/L silver standard solution.

b) Use a TenSette Pipet to add 0.1, 0.2 and 0.3 mL of this standard solution to three 50-mL samples (or sample portions diluted to 50 mL). Mix well.

c) Analyze as described above. Each 0.1 mL addition of standard should increase the silver concentration by 0.1 mg/L.

d) If these increases do not occur, see *Standard Additions* in *SECTION I* for more information.

Standard Solution Method

Prepare a 0.50-mg/L silver standard solution as follows:

a) Use a Class A 0.50-mL volumetric pipet to add 0.50 mL of 1000-mg/L Silver Standard Solution to a 1000-mL volumetric flask.

b) Dilute to the mark with deionized water and mix. Prepare this solution daily. Perform the silver test as described. Results should be between 0.45 and 0.55 mg/L Ag.

Precision

In a single laboratory, using standard solutions of 0.400 mg/L silver and two representative lots of reagent and a DR/2010, a single operator obtained a standard deviation of ±0.015 mg/L silver.

Interferences

Interference studies were conducted by preparing a known silver solution (about 0.4 mg/L) and the potential interfering ion. The ion was said to interfere when the silver concentration changed by ±10%.

Negative Interference:	
Aluminum	30 mg/L
Ammonia	750 mg/L
Cadmium	15 mg/L
Chloride	19 mg/L
Chromium^{6+}	90 mg/L
Copper	7 mg/L
Iron	30 mg/L
Lead	13 mg/L
Manganese	19 mg/L
Nickel	19 mg/L
Zinc	70 mg/L
Positive Interference:	
Calcium	600 mg/L
Magnesium	2000 mg/L
Mercury	2 mg/L

Digestion

Note: *Toxic hydrogen cyanide gas is generated during this digestion; use a fume hood.*

This digestion is for samples containing organic matter, thiosulfate or cyanide. Possible sources for these compounds are wastewater, silver electroplating baths and silver strike solutions. Digestion should be done with a Digesdahl Digestion Apparatus.

a) Add an appropriate size sample to the 100-mL volumetric flask of the Digesdahl. Add several boiling chips to prevent bumping.

Note: *Always wear safety glasses and use a safety shield, or operate the Digesdahl within a closed fume hood. Follow the additional safety precautions in the Digesdahl Apparatus Manual.*

Note: *Appropriate sample size is determined experimentally. The final sample concentration (after dilution to 100 mL) should be between 0-0.5 mg/L. Larger dilutions may be necessary for electroplating baths and silver strike solutions. Do not exceed the maximum sample volume of 25 mL. Several 25-mL aliquots may be digested in succession to concentrate a very dilute sample.*

b) Turn on the water aspirator and make sure there is suction in the fractionating head.

c) Add 3 mL of concentrated sulfuric acid to the sample in the volumetric flask. Immediately place the head on the volumetric flask. Never use less than 3 mL of acid.

d) Place the volumetric flask on the heater. Turn the temperature dial to 440 °C (825 °F).

e) After the sample begins to char or the sulfuric acid reflux line becomes visible, wait 3-5 minutes.

f) Visually confirm the presence of liquid in the flask before adding hydrogen peroxide.

g) Add 10 mL of 50% hydrogen peroxide to the sample via the capillary funnel in the fractionating head.

h) After the hydrogen peroxide has boiled off, heat the sample until heavy white sulfuric acid fumes are present. Continue heating and reduce the sample volume to near dryness. Do not let the sample go completely dry at any time.

Note: *If the sample goes to dryness, turn the Digesdahl off and cool completely. Add water to flask before handling. Repeat digestion from the beginning.*

Note: *If only thiosulfate is present in the sample, proceed to Step l.*

i) Add another 3 mL of sulfuric acid via the capillary funnel.

j) Add another 5 mL of hydrogen peroxide. Check the solution for digestion completion. If digestion is not complete, continue adding hydrogen peroxide in 5 to 10 mL portions. Several portions may be necessary.

Note: *Digestion is complete when the digestate is colorless or the color of the digestate does not change upon addition of hydrogen peroxide. Also, a completely digested sample will not foam.*

k) After digestion is complete and all the hydrogen peroxide is boiled off, reduce the volume of the digestate to near dryness. Do not allow the sample to become completely dry. Remove the flask from the heater. Cool to room temperature.

l) Slowly add about 25 mL of deionized water to the cooled flask. Add two drops of 1-g/L Phenolphthalein Indicator Solution.

m) Add 2 drops of 1-g/L Thymolphthalein Indicator Solution.

n) Using sodium hydroxide, adjust the pH of the solution to between 9-10. The solution will be pink in this pH range.

Note: *A purple color indicates a pH greater than 10. If this occurs, add a drop of sulfuric acid and 2 drops of each indicator; repeat pH adjustment. Initially, use 50% sodium hydroxide, then 1.0 N sodium hydroxide as the end point is approached.*

o) Filter turbid digestates; see *Filtering Samples* (*SECTION I*). Quantitatively transfer the filtrate (or unfiltered sample) to a clean 100-mL volumetric flask. Dilute to the mark with deionized water. The sample is ready for analysis.

Summary of Method

Silver ions in basic solution react with cadion 2B to form a green, brown or red-purple complex. Sodium thiosulfate acts as a decolorizing agent for the blank. The Silver 1 and Silver 2 reagents contain the buffer, indicator and masking agents. Organic extractions are not necessary and this method does not have as many interferences as the traditional dithizone method. It may also be used for electroplating and silver strike solutions.

REQUIRED REAGENTS

Description	Cat. No.
Silver Reagent Set (50 tests)	22966-00

Includes: (1) 22935-66, (1) 22936-66, (1) 22937-66

Description	Quantity Required Per Test	Units	Cat. No.
Silver 1 Powder Pillow	1 pillow	50/pkg	22935-66
Silver 2 Solution Pillow	1 pillow	50/pkg	22936-66
Sodium Thiosulfate Powder Pillow	1 pillow	50/pkg	22937-66

REQUIRED APPARATUS

Cylinder, graduated, 50 mL	1	each	21179-41
Cylinder, graduated, mixing, 50 mL	1	each	1896-41
Sample Cells, 25 mL, matched	2	pair	20950-00

OPTIONAL REAGENTS

Hydrogen Peroxide, 50%	490 mL	21196-49
Nitric Acid Solution, 1:1	500 mL	2540-49
Phenolphthalein Indicator Solution, 1 g/L	15 mL SCDB	1897-36
Silver Standard Solution, 1000 mg/L Ag	100 mL	14613-42
Sodium Hydroxide Solution, 1.0 N	100 mL MDB	1045-32
Sodium Hydroxide Solution, 5.0 N	100 mL MDB	2450-32
Sodium Hydroxide, 50%	500 mL	2180-49
Sulfuric Acid, ACS	4 kg	979-09
Thymolphthalein Indicator Solution, 1 g/L	15 mL SCDB	21853-36
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

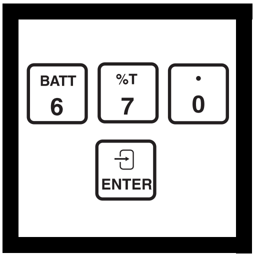
Boiling Chips, silicon carbide	500 g	20557-34
Digesdahl Digestion Apparatus, 115 Vac, 50/60 Hz	each	23130-20
Digesdahl Digestion Apparatus, 230 Vac, 50/60 Hz	each	23130-21
Flask, volumetric, Class A, 100 mL	each	14574-42
Flask, volumetric, Class A, 1000 mL	each	14574-53
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
Pipet, serological, 10.0 mL	each	532-38
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet, TenSette, 0.1 to 10.0 mL	each	19700-10
Pipet Tips, for 19700-01 Pipet	50/pkg	21856-96
Pipet Tips, for 19700-10 Pipet	50/pkg	21997-96
Pipet, volumetric, Class A, 0.50 mL	each	14515-34
Pipet Filler, safety bulb	each	14651-00
Safety Glasses	each	18421-00
Safety Shield, for Digesdahl	each	20974-00
Sample Cells, 1-inch, polystyrene, disposable	12/pkg	24102-12

Method 8022

For cooling water

SODIUM CHROMATE (0 to 1,100 mg/L)

Direct Colorimetric Method



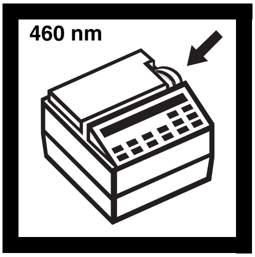
1. Enter the stored program for sodium chromate (Na_2CrO_4).

Press: **6 7 0 ENTER**

The display will show:

Dial nm to 460

Note: *The Pour-Thru Cell can be used for this procedure.*



2. Rotate the wavelength dial until the small display shows:

460 nm

When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

then: **mg/L Na_2CrO_4**

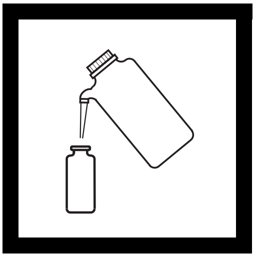
Note: *This test is sensitive to the wavelength setting. The 460 nm wavelength should always be approached from high to low values.*

3. Fill a clean sample cell to the 25-mL mark with sample.

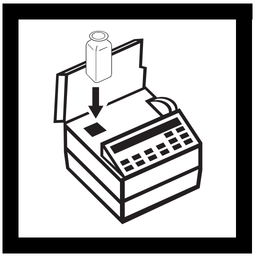
Note: *Filter turbid samples using the labware listed under Optional Apparatus.*

4. Add the contents of one Neutralizing Reagent Powder Pillow to the sample cell. Swirl to mix (the prepared sample).

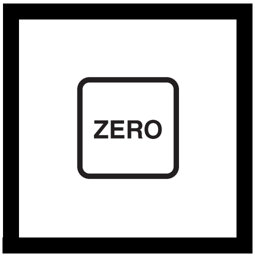
Note: *The neutralizing Reagent Powder Pillow is necessary only if the sample is orange or yellow-orange. If the color is in doubt, add the powder pillow.*



5. Fill a second cell with 25 mL of colorless water (the blank).



6. Place the blank in the cell holder. Close the light shield.

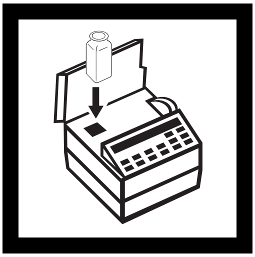


7. Press: **ZERO**

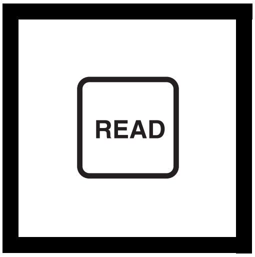
The display will show:

Zeroing. . . .

then: **0. mg/L Na_2CrO_4**



8. Place the prepared sample in the cell holder. Close the light shield.



9. Press: **READ**

The display will show:

Reading. . . .

then the results in mg/L sodium chromate (Na_2CrO_4) will be displayed.

Forms ▲▼ Cr^{6+} Na_2CrO_4 CrO_4^{2-}

Sampling and Storage

Collect samples in clean glass bottles.

Accuracy Check

For greater accuracy, a manual calibration may be stored as a user-stored program; see the *Operation* section of the DR/2010 Instrument Manual.

Standard Additions Method

a) Snap the neck off a Sodium Chromate Voluette Ampule Standard Solution, 25,000 mg/L Na_2CrO_4.

b) Use a TenSette Pipet to add 0.1, 0.2, and 0.3 mL of standard to three 25-mL samples, respectively. Swirl to mix.

c) Analyze the samples according to the above procedure. The sodium chromate concentration should increase by 100 mg/L for each 0.1 mL addition of standard.

d) If these increases do not occur, see *Standard Additions* in *Section I* for more information.

Standard Solution Method

Use a 1000 mg/L Sodium Chromate Standard Solution listed under Optional Reagents to check accuracy.

Interferences

Large amounts of turbidity will result in high readings. This test is not specific for chromate; any other compounds that absorb light at 460 nm will directly interfere.

Summary of Method

The test directly measures the intensity of the alkaline yellow color of the sodium chromate solution. In acid media, the solution is orange and must be treated. A neutralizing agent is added to raise the pH, giving the yellow color for the determination.

The test measures chromate in cooling waters when it is known to be present. The test will not differentiate other compounds also absorbing light at 460 nm.

REQUIRED REAGENTS

Description	Quantity Required Per Test	Units	Cat. No.
Neutralizing Reagent Powder Pillows	1 pillow	100/pkg	2127-99

REQUIRED APPARATUS

Sample Cell, 25 mL, matched pair	2	pair	20950-00

OPTIONAL REAGENTS

Sodium Chromate Standard Solution, 1000 mg/L Na_2CrO_4 (NIST)	500 mL	2503-49
Sodium Chromate Standard Solution, Voluette Ampule, 25,000 mg/L NNa_2CrO_4	16/pkg	14255-10

OPTIONAL APPARATUS

Ampule Breaker Kit	each	21968-00
Funnel, poly, 65 mm	each	1083-67
Filter Paper, folded, 12.5 cm	100/pkg	1894-57
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 Pipet	50/pkg	21856-96
Pour-Thru Cell Assembly	each	45215-00

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8051

SULFATE (0 to 70 mg/L)

For water, wastewater, and seawater

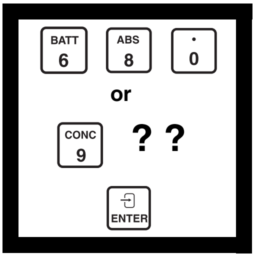
SulfaVer 4 Method* (Powder Pillows or AccuVac Ampuls), USEPA accepted for reporting wastewater analysis**

Using Powder Pillows

Choose Desired Program Accuracy

1. A User-Entered Calibration is necessary to obtain the most accurate results. See the *User Calibration* section at the back of this procedure. Program 680 can be used directly for process control or applications where a high degree of accuracy is not needed.

Note: *The nature of turbidimetric tests and reagent lot variation necessitate user calibration for best results.*



2. Enter the appropriate stored program number for sulfate (SO_4^{2-}) powder pillows.

Press: **6 8 0 ENTER**

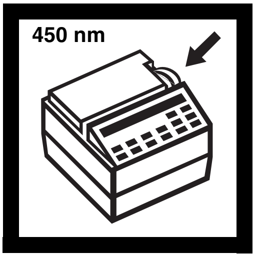
or

9 ? ? ENTER

The display will show:

Dial nm to 450

Note: *The Pour-Thru cell cannot be used with this procedure.*



3. Rotate the wavelength dial until the small display shows:

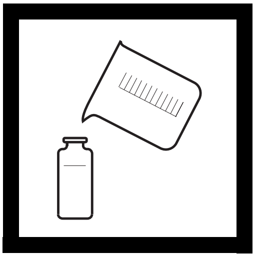
450 nm

When the correct wavelength is dialed in the display will quickly show:

Zero Sample

then: **mg/L SO_4^{2-}**

Note: *For greater accuracy, perform a user calibration for each new lot of SulfaVer 4 Sulfate Reagent Powder Pillows; see User Calibration following these steps.*



4. Fill a clean sample cell with 25 mL of sample.

Note: *Filter highly turbid or colored samples. Use filtered sample in this step and Step 7.*

---

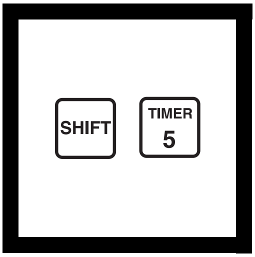
* Adapted from *Standard Methods for the Examination of Water and Wastewater.*

** Procedure is equivalent to USEPA method 375.4 for wastewater.

5. Add the contents of one SulfaVer 4 Sulfate Reagent Powder Pillow to the sample cell (the prepared sample). Swirl to dissolve.

A white turbidity will develop if sulfate is present.

Accuracy is not affected by undissolved powder.

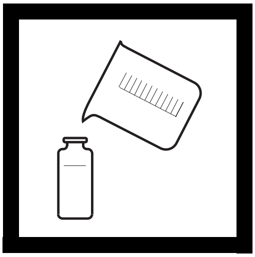


6. Press:

SHIFT TIMER

A 5-minute reaction period will begin.

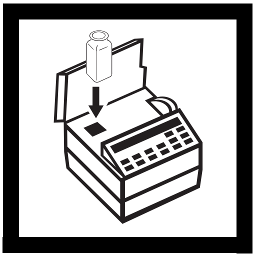
Allow the cell to stand undisturbed.



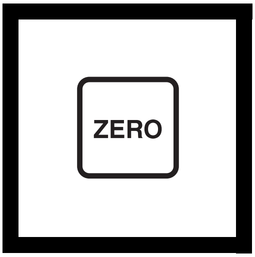
7. When the timer beeps, the display will show:

mg/L SO_4^{2-}

Fill a second sample cell with 25 mL of sample (the blank).



8. Place the blank into the cell holder. Close the light shield.

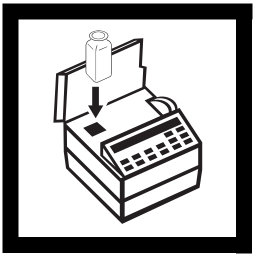


9. Press: **ZERO**

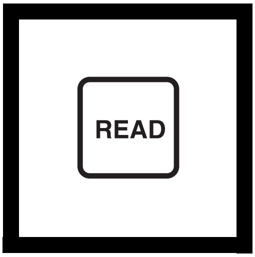
The display will show:

Zeroing. . .

then: **0. mg/L SO_4^{2-}**



10. Within five minutes after the timer beeps, place the prepared sample into the cell holder. Close the light shield.



11. Press: **READ**

The display will show:

Reading. . .

then the results in mg/L SO_4^{2-} will be displayed.

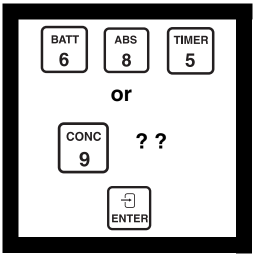
Note: *Clean the sample cells with soap and a brush.*

Using AccuVac Ampuls

Choose Desired Program Accuracy

1. A User-Entered Calibration is necessary to obtain the most accurate results. See User Calibration Section at the back of this procedure. Program 685 can be used directly for process control or applications where a high degree of accuracy is not needed.

Note: *The nature of turbidimetric tests and reagent lot variation necessitate user calibration for best results.*



2. Enter the stored program number for sulfate (SO_4^{2-}) AccuVac Ampuls.

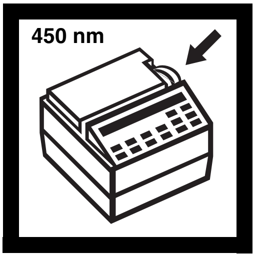
Press: **6 8 5 ENTER**

or

9 ? ? ENTER

The display will show:

Dial nm to 450



3. Rotate the wavelength dial until the small display shows:

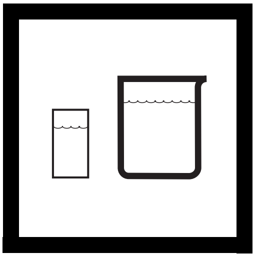
450 nm

When the correct wavelength is dialed in the display will quickly show:

Zero Sample

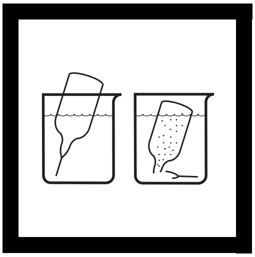
then:

mg/L SO_4^{2-} AV



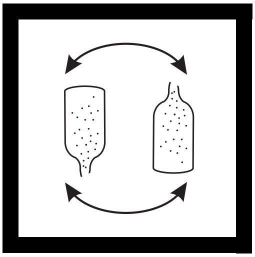
4. Fill a zeroing vial (the blank) with at least 10 mL of sample. Collect at least 40 mL of sample in a 50-mL beaker.

Note: *Filter highly turbid or colored samples. Use filtered sample in this step and Step 5.*



5. Fill a SulfaVer 4 Sulfate AccuVac ampul with sample.

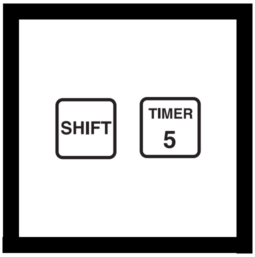
Note: *Keep tip immersed until the ampul fills completely.*



6. Quickly invert the ampul several times to mix. Wipe off any liquid or fingerprints.

Note: *A white turbidity will develop if sulfate is present.*

Note: *Accuracy is not affected by undissolved powder.*

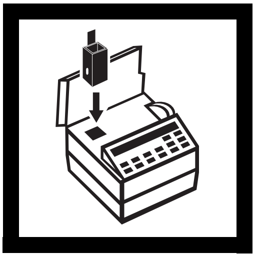


7. Press:

SHIFT TIMER

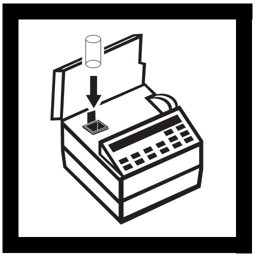
A 5-minute reaction period will begin.

Note: *Allow the ampul to stand undisturbed.*



8. Place the AccuVac Vial Adapter into the cell holder.

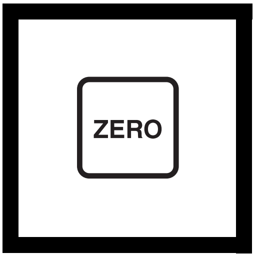
Note: *Place the grip tab at the rear of the cell holder.*



9. When the timer beeps, the display will show:

mg/L SO_4^{2-} AV

Place the blank into the cell holder. Close the light shield.



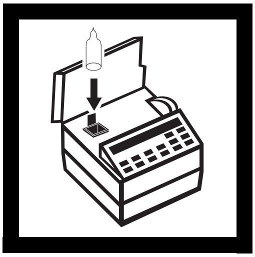
10. Press: **ZERO**

The display will show:

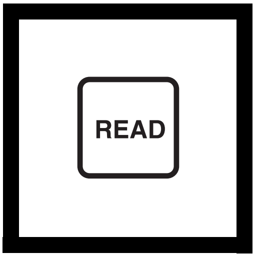
Zeroing. . .

then:

0. mg/L SO_4^{2-} AV



11. Within five minutes after the timer beeps, place the AccuVac ampul into the cell holder. Close the light shield.



12. Press: **READ**

The display will show:

Reading. . .

then the results in mg/L SO_4^{2-} will be displayed.

Sampling and Storage

Collect samples in clean plastic or glass bottles. Samples may be stored up to 28 days by cooling to 4 °C (39 °F) or lower. Warm to room temperature before analysis.

Accuracy Check

Standard Additions Method

a) Fill three 25-mL graduated mixing cylinders with 25 mL of sample.

b) Snap the neck off a Sulfate Voluette Ampule Standard Solution, 2500 mg/L SO_4^{2-}.

c) Use a TenSette Pipet to add 0.1, 0.2 and 0.3 mL of standard to the three 25-mL samples. Mix thoroughly. For AccuVac Ampuls, transfer to clean, dry 50-mL beakers.

d) Analyze each sample as described above. The sulfate concentration should increase 10 mg/L for each 0.1 mL of standard added.

e) If these increases do not occur, see Standard Additions in Section I for more information.

Standard Solution Method

Check the accuracy of the test by using the Sulfate Standard Solution, 50 mg/L, listed under Optional Reagents. Or, prepare this solution by pipetting 1.0 mL of the contents of a Voluette Ampule Standard for Sulfate (2500 mg/L) into a 50-mL volumetric flask. Dilute to volume with deionized water.

Substitute this standard for the sample and proceed with the test as described in the procedure. The mg/L SO_4^{2-} reading should be 50 mg/L.

User Calibration

For most accurate results, the use of a user-calibrated program is highly recommended. The Hach stored programs 680 and 685 are intended for process control samples or other applications where a high degree of accuracy is not necessary.

A one-time setup program for sulfate is required. A sulfate program template is pre-programmed into memory to make the process easier. After the setup is complete, the calibration can be entered for each new lot of reagents used or as necessary.

Standard Preparation

A new calibration should be performed for each new lot of SulfaVer 4 Sulfate Reagent as follows:

Prepare standards of 10, 20, 30, 40, 50, and 60 mg/L sulfate by pipetting 1, 2, 3, 4, 5, and 6 mL of a 1000-mg/L Sulfate Standard Solution into 100-mL volumetric flasks. Dilute to the mark with deionized water and mix well.

Initial Setup of Sulfate Program

The templates within User Program cannot be run directly. They must be copied into a usable program number (greater than 950) as in step c and d. Then, calibrate the program. The preprogrammed calibration (680 or 685) may be suitable for process control.

a) Press **SHIFT USER PRGM**. Use the **UP** arrow key to scroll to **Copy Program**. Press **ENTER**.

b) Scroll to or enter the template number for sulfate [906, 907 (AV)]. Press **ENTER**.

c) Scroll to or enter the desired user program number for sulfate (>950). Press **ENTER**. Record the program number for reference.

d) The display will show: **Program Copied.** Press **EXIT**. The program is now ready to be calibrated.

User Calibration of Sulfate Program

a) Use the test procedure to develop color in the standards just before recording the absorbance values for the calibration.

b) Press **SHIFT USER PRGM**. Use the **UP** arrow to scroll to **Edit Program**. Press **ENTER**.

c) Scroll to or enter the program number for sulfate (from step c in Setup). Press **ENTER**.

d) Use the **DOWN** arrow to scroll down to **Calib Table:X** (X= denotes a number which indicates the number of data points in the table). Press **ENTER**.

e) The instrument will prompt **Zero Sample**. Place the blank solution in the cell holder. Close the light shield. Press **ZERO**. The instrument will prompt you to adjust to the proper wavelength if necessary.

f) The first concentration point will be displayed. Press **ENTER** to display the stored absorbance value of the first concentration point.

g) Place the first developed standard solution (same concentration as the value displayed) in the cell holder. Close the light shield. Press **READ** to display the measured absorbance of the standard. Press **ENTER** to accept the displayed absorbance value.

h) The second concentration point will be displayed. Press **ENTER** to display the stored absorbance value of the second concentration. Place the second developed standard solution in the cell holder. Close the light shield. Press **READ** to display the measured absorbance value of the standard.

i) Press **ENTER** to accept the absorbance reading. The next concentration point will then be displayed.

j) Repeat steps h and i as necessary for the remaining standards.

k) When finished reading the absorbance values of the standards, press **EXIT**. Scroll down to **Force Zero**. Press **ENTER** to change the setting. Change to **ON** by pressing the arrow key, then press **ENTER.**

l) Scroll down to **Calib Formula**. Press **ENTER** twice or until only the **0** in **F(0)** is flashing. Press DOWN arrow to select **F3** (cubic calibration). Press **ENTER** to select **F3**.

Note: *Alternative calibration fits may also be used if appropriate.*

m) Press **EXIT** twice. The display will show **Store Changes?**. Press **ENTER** to confirm.

n) Press **EXIT**. The program is now calibrated and ready for use. Start with step 2 of the iconed test procedure.

Precision

In a single laboratory, using a standard solution of 50 mg/L sulfate and two representative lots of powder pillows with the DR/2010, a single operator obtained a standard deviation of ±0.9 mg/L sulfate.

In a single laboratory, using a standard solution of 50 mg/L sulfate and two representative lots of AccuVac ampuls with the DR/2010, a single operator obtained a standard deviation of ±2.2 mg/L sulfate.

Estimated Detection Limit (EDL)

The EDL for program 680 is 7 mg/L SO_4^{2-}. The EDL is the calculated lowest average concentration in a deionized water matrix that is different from zero with a 99% level of confidence. For more information on derivation and use of Hach's estimated detection limit, see Section I.

The EDL for program 685 is 7 mg/L SO_4^{2-}. The EDL is the calculated lowest average concentration in a deionized water matrix that is different from zero with a 99% level of confidence. For more information on derivation and use of Hach's estimated detection limit, see Section I.

Interferences

The following interfere at levels above those concentrations listed:

Calcium	20,000 mg/L as $CaCO_3$
Chloride	40,000 mg/L as Cl^-
Magnesium	10,000 mg/L as $CaCO_3$
Silica	500 mg/L as $CaCO_3$

Summary of Method

Sulfate ions in the sample react with barium in the SulfaVer 4 Sulfate Reagent and form insoluble barium sulfate turbidity. The amount of turbidity formed is proportional to the sulfate concentration.

REQUIRED REAGENTS (USING POWDER PILLOWS)

Description	Quantity Required Per Test	Units	Cat. No.
SulfaVer 4 Sulfate Reagent Powder Pillows	1 pillow	50/pkg	12065-99

REQUIRED REAGENTS (USING ACCUVAC AMPULS)

SulfaVer 4 Sulfate AccuVac Ampuls	1 ampul	25/pkg	25090-25

REQUIRED APPARATUS (USING POWDER PILLOWS)

Sample Cell, 25 mL, matched pair	2	each	20950-00
Brush	1	each	690-00

REQUIRED APPARATUS (USING ACCUVAC AMPULS)

Adapter, AccuVac Vial	1	each	43784-00
Beaker, 50-mL	1	each	500-41
Vial, zeroing	1	each	21228-00

OPTIONAL REAGENTS

Sulfate Standard Solution, 50 mg/L	500 mL	2578-49
Sulfate Standard Solution, 1000 mg/L	500 mL	21757-49
Sulfate Standard Solution, Voluette Ampule, 2500 mg/L, 10 mL	16/pkg	14252-10
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

AccuVac Snapper Kit	each	24052-00
Ampule Breaker Kit	each	21968-00
Cylinder, graduated, mixing, 25 mL	each	20886-40
Filter Paper, folded, 12.5 cm	100/pkg	1894-57
Flask, volumetric, 50 mL, Class A	each	14574-41
Flask, volumetric, 100 mL, Class A	each	14574-42
Funnel, poly, 65 mm	each	1083-67
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 Pipet	50/pkg	21856-96
Pipet, volumetric, 1.00 mL, Class A	each	14515-35
Pipet, volumetric, 2.00 mL, Class A	each	14515-36
Pipet, volumetric, 3.00 mL, Class A	each	14515-03
Pipet, volumetric, 4.00 mL, Class A	each	14515-04
Pipet, volumetric, 5.00 mL, Class A	each	14515-37
Pipet, volumetric, 6.00 mL, Class A	each	14515-06
Pipet Filler, safety bulb	each	14651-00

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

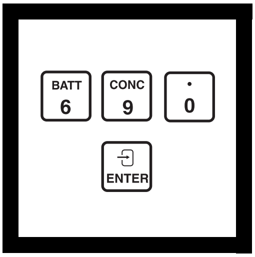
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8131

SULFIDE (0 to 0.600 mg/L S^{2-})

For water, wastewater and seawater

Methylene Blue Method* USEPA accepted for reporting wastewater analysis*



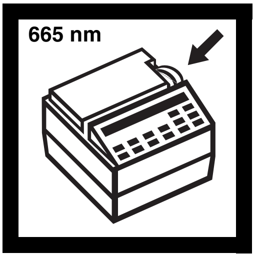
1. Enter the stored program for sulfide (S^{2-}).

Press: **6 9 0 ENTER**

The display will show:

Dial nm to 665

Note: *The Pour-Thru Cell can be used with this procedure.*



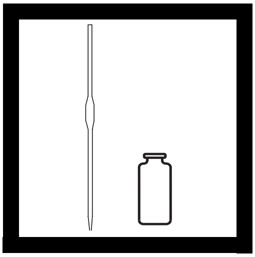
2. Rotate the wavelength dial until the small display shows:

665 nm

When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

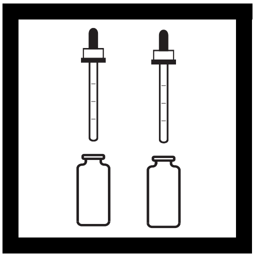
then: **mg/L S^{2-}**



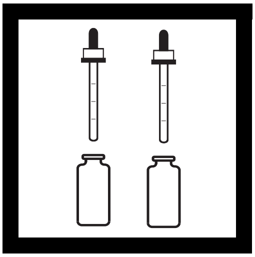
3. Pipet 25 mL of sample into a clean sample cell.

Note: *Samples must be analyzed immediately and cannot be preserved for later analysis. Avoid excessive agitation. Use a pipet to minimize loss of sulfide in the sample.*

4. Fill a second sample cell with 25 mL of deionized water (the blank).

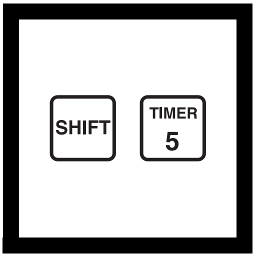


5. Add 1.0 mL of Sulfide 1 Reagent to each cell. Swirl to mix.



6. Add 1.0 mL of Sulfide 2 Reagent to each cell. Immediately swirl to mix.

Note: *A pink color will develop, then the solution will turn blue if sulfide is present.*



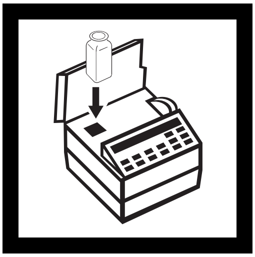
7. Press:

SHIFT TIMER

A 5-minute reaction period will begin.

When the timer beeps, the display will show:

mg/L S^{2-}



8. Place the blank into the cell holder. Close the light shield.

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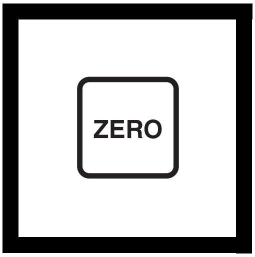
* Procedure is equivalent to USEPA method 376.2 or Standard Method 4500-S^{2-} D for wastewater.

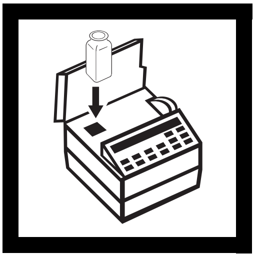


9. Press: **ZERO**

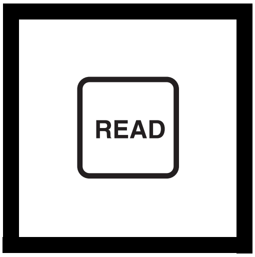
The display will show:

Zeroing. . . .

then: **0.000 mg/L S^{2-}**



10. Immediately place the prepared sample into the cell holder. Close the light shield.



11. Press: **READ**

The display will show:

Reading. . . .

then the result in mg/L sulfide (S^{2-}) will be displayed.

Note: *Some sulfide loss may occur if dilution is necessary.*

Sampling and Storage

Collect samples in clean plastic or glass bottles. Fill completely and cap tightly. Avoid excessive agitation or prolonged exposure to air. Analyze samples immediately.

Precision

In a single laboratory, using standard solutions of 0.250 mg/L sulfide and two representative lots of reagent with the DR/2010, a single operator obtained a standard deviation of ± 0.003 mg/L sulfide.

Estimated Detection Limit (EDL)

The EDL for program 690 is 0.01 mg/L S^{2-}.

The EDL is the calculated lowest average concentration in a deionized water matrix that is different from zero with a 99% level of confidence. For more information on derivation and use of Hach’s estimated detection limit, see *Section I.*

Interferences

For turbid samples, prepare a sulfide-free blank as follows. Use it in place of the deionized water blank in the procedure.

a) Measure 25 mL of sample into a 50-mL Erlenmeyer flask.

b) Add Bromine Water dropwise with constant swirling until a permanent yellow color just appears.

c) Add Phenol Solution dropwise until the yellow color just disappears. Use this solution in Step 5 in place of deionized water.

Strong reducing substances such as sulfite, thiosulfate and hydrosulfite interfere by reducing the blue color or preventing its development. High concentrations of sulfide may inhibit full color development and require sample dilution. Some sulfide loss may occur when the sample is diluted.

Soluble Sulfides

Determine soluble sulfides by centrifuging the sample in completely filled, capped tubes and analyzing the supernatant. Insoluble sulfides are then estimated by subtracting the soluble sulfide concentration from the total sulfide result.

Summary of Method

Hydrogen sulfide and acid-soluble metal sulfides react with N, N-dimethyl-p-phenylenediamine oxalate to form methylene blue. The intensity of the blue color is proportional to the sulfide concentration.

High sulfide levels in oil field waters may be determined by proper sample dilution.

REQUIRED REAGENTS

Description	Cat. No.
Sulfide Reagent Set (100 tests)	22445-00
Includes: (2) 1816-42, (2) 1817-42	

Description	Quantity Required Per Test	Units	Cat. No.
Sulfide 1 Reagent	2 mL	100 mL MDB	1816-32
Sulfide 2 Reagent	2 mL	100 mL MDB	1817-32
Water, deionized	25 mL	4 L	272-56

REQUIRED APPARATUS

Cylinder, graduated, 25 mL	1	each	508-40
Pipet, volumetric, 25.0 mL	1	each	14515-40
Pipet Filler, safety bulb	1	each	14651-00
Sample Cell, 25-mL, matched pair		pair	20950-00

OPTIONAL REAGENTS

Bromine Water, 30 g/L	29 mL	2211-20
Phenol Solution, 30 g/L	29 mL	2112-20

OPTIONAL APPARATUS

Bottle, Wash, 250 mL	each	620-31
Dropper, for 1 oz. bottle	each	2258-00
Flask, Erlenmeyer, 50 mL	each	505-41
Pour-Thru Cell Kit	each	45215-00
Pipet, TenSette 1.0 to 10.0 mL	each	19700-10
Pipet, tips for TenSette pipet 19700-10	50/pkg	21997-96

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

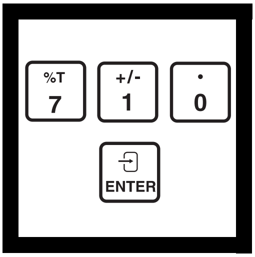
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8028

SURFACTANTS, ANIONIC (0 to 0.275 mg/L)

For water, wastewater, and seawater

(Also called: Detergents) Crystal Violet Method*



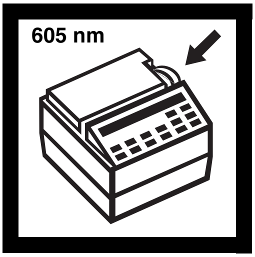
1. Enter the stored program number for anionic surfactants.

Press: **7 1 0 ENTER**

The display will show:

Dial nm to 605

Note: *The Pour-Thru cell cannot be used with this procedure.*



2. Rotate the wavelength dial until the small display shows:

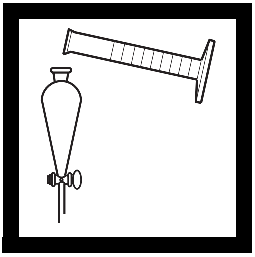
605 nm

When the correct wavelength is dialed in, the display will quickly show:

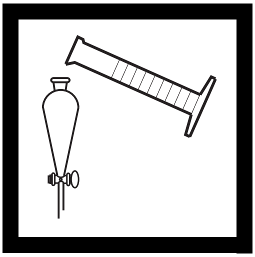
Zero Sample

then:

mg/L SURF. ANION



3. Fill a clean 500-mL graduated cylinder to the 300-mL mark with sample. Pour the sample into a clean 500-mL separatory funnel.



4. Add 10 mL of Sulfate Buffer Solution. Stopper the funnel. Shake the funnel for five seconds.

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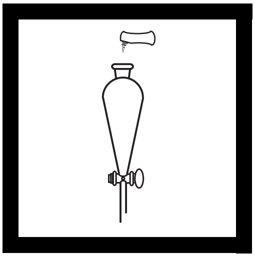
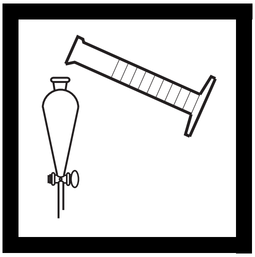
* *Analytical Chemistry*, 38, 791(1966).



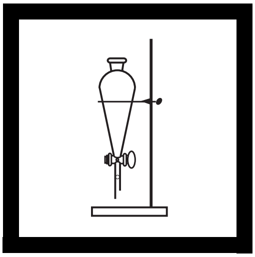
5. Add the contents of one Detergents Reagent Powder Pillow to the funnel. Stopper the funnel and shake to dissolve the powder.



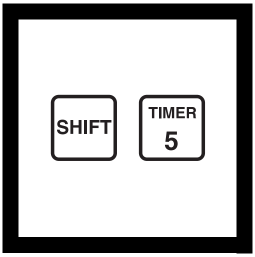
6. Add 30 mL of benzene to the funnel. Stopper the funnel and shake gently for one minute.

Note: *Spilled reagent will affect test accuracy and is hazardous to the skin and other materials.*

Note: *Use benzene only in a well-ventilated area.*



7. Place the separatory funnel in a support stand.

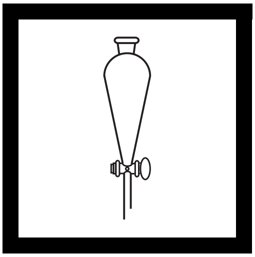


8. Press:

SHIFT TIMER

A 30-minute reaction period will begin.

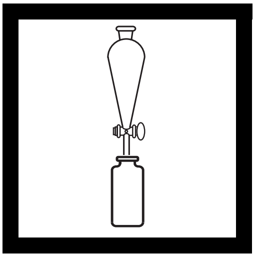
Note: *Excessive agitation may cause an emulsion to form, requiring a longer time for phase separation. For these samples, remove most of the water layer, then gently agitate the funnel with a clean inert object in the funnel such as a Teflon-coated magnetic stirring bar.*



9. After the timer beeps, the display will show:

mg/L SURF. ANION

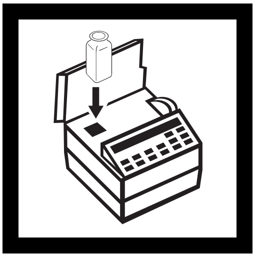
Remove the stopper and drain the bottom water layer. Discard this layer.



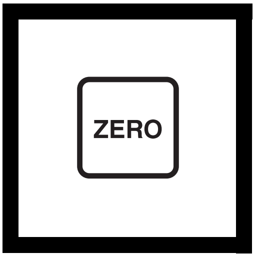
10. Drain the top benzene layer into a clean 25-mL sample cell (the prepared sample).

Note: *The benzene layer cannot be filtered before color measurement. Filtration removes the blue color.*

11. Fill another sample cell to the 25-mL mark with pure benzene (the blank).



12. Place the blank in the cell holder. Close the light shield.



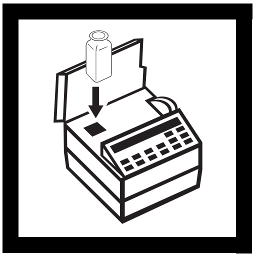
13. Press: **ZERO**

The display will show:

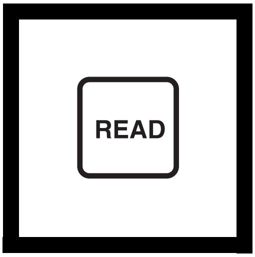
Zeroing. . . .

then:

0.000 mg/L
SURF. ANION



14. Place the prepared sample into the cell holder. Close the light shield.



15. Press: **READ**

The display will show:

Reading. . . .

then the result in mg/L anionic surfactants will be displayed.

Note: *Acetone may be used to clean benzene from glassware.*

Note: *The prepared sample and blank must be disposed of according to current Federal, State, and local regulations for benzene.*

Sampling and Storage

Collect samples in clean plastic or glass bottles. Analyze samples as soon as possible, but they may be stored at least 24 hours by cooling to 4 °C (39 °F). Warm to room temperature before testing.

Accuracy Check

Standard Additions Method

a) Snap the neck off a Detergent Voluette Ampule Standard solution, 60 mg/L as LAS.

b) Using the TenSette Pipet, add 0.1, 0.2, and 0.3 mL of standard to three 300-mL samples. Mix thoroughly.

c) Analyze each as described above. The anionic surfactants reading should increase 0.02 mg/L for each 0.1 mL of standard added.

d) If these increases do not occur, see *Standard Additions* (*Section I*) for more information.

Precision

In a single laboratory, using a standard solution of 0.1 mg/L LAS, two lots of reagent, and a DR/2010, a single operator obtained a standard deviation of ±0.0035 mg/L LAS as anionic surfactant.

Interferences

Perchlorate and periodate ions will interfere. High amounts of chloride, such as those levels found in brines and seawater, will cause low results.

Summary of Method

Detergents, ABS (alkyl benzene sulfonate) or LAS (linear alkylate sulfonate) are determined by association with crystal violet dye and extraction of the ion-pair complex into benzene.

REQUIRED REAGENTS

Description	Cat. No.
Detergent Reagent Set (25 tests)	24468-00

Description	Quantity Required Per Test	Unit	Cat. No.
Benzene, ACS	55 mL	500 mL	14440-49
Buffer Solution, sulfate type	10 mL	500 mL	452-49
Detergent Reagent Powder Pillow	1 pillow	25/pkg	1008-68
REQUIRED APPARATUS			
Clippers, for opening powder pillows	1	each	968-00
Cylinder, graduated, 25 mL	1	each	508-40
Cylinder, graduated, 50 mL	1	each	508-41
Cylinder, graduated, 500 mL	1	each	508-49
Funnel, separatory, 500 mL	1	each	520-49
Ring, support, 4 inch	1	each	580-01
Sample Cell, 25 mL, matched	2	pair	20950-00
Stand, support, 127 x 203 mm (5 x 8")	1	each	563-00
OPTIONAL REAGENTS			
Acetone, ACS		500 mL	14429-49
Detergent Standard Solution, Voluette ampule, 60 mg/L as LAS, 10 mL		16/pkg	14271-10
OPTIONAL APPARATUS			
Ampule Breaker Kit		each	21968-00
Pipet, TenSette, 0.1 to 1.0 mL		each	19700-01
Pipet Tips, for 19700-01 Pipet		50/pkg	21856-96
Stir Bar, 9 mm		each	20953-48
Thermometer, -20 to 105 °C		each	1877-01

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

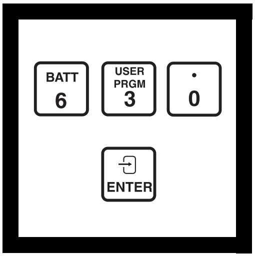
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8006

SUSPENDED SOLIDS (0 to 750 mg/L)

For water and wastewater

Photometric Method* (Also called Nonfilterable Residue)



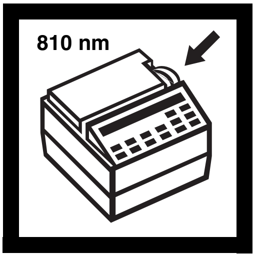
1. Enter the stored program number for suspended solids.

Press: **6 3 0 ENTER**

The display will show:

Dial nm to 810

Note: *The Pour-Thru Cell cannot be used with this procedure.*



2. Rotate the wavelength dial until the small display shows:

810 nm

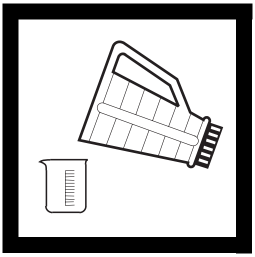
When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

then:

mg/L SUSP.SOLIDS

3. Blend 500 mL of sample in a blender at high speed for exactly 2 minutes.

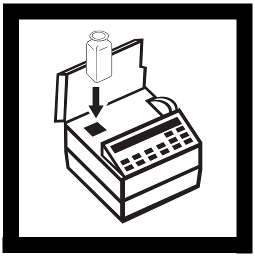


4. Pour the blended sample into a 600-mL beaker.

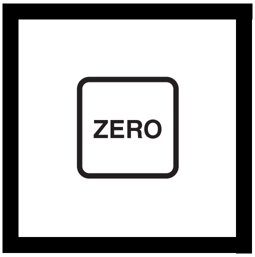
5. Stir the sample and immediately pour 25 mL of the blended sample into a sample cell (the prepared sample).

6. Fill a sample cell with 25 mL of tap water or deionized water (the blank).

Note: *Remove gas bubbles in the water by swirling or tapping the bottom of the cell on a table.*



7. Place the blank in the cell holder. Close the light shield.



8. Press: **ZERO**

The display will show:

Zeroing. . .

then:

0. mg/L SUSP.SOLIDS

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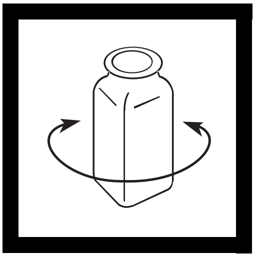
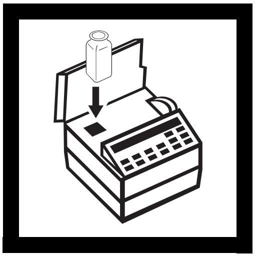
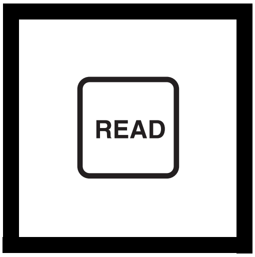
* Adapted from *Sewage and Industrial Wastes*, 31, 1159 (1959).



9. Swirl the prepared sample cell to remove any gas bubbles and uniformly suspend any residue.



10. Place the prepared sample into the cell holder. Close the light shield.



11. Press: **READ**

The display will show:

Reading. . .

then the result in mg/L suspended solids will be displayed.

Sampling and Storage

Collect samples in clean plastic or glass bottles. Analyze samples as soon as possible after collection. The sample may be stored seven days by cooling to 4 °C (39 °F).

Interferences

Calibration for this test is based on parallel samples using the gravimetric technique on sewage samples from a municipal sewage plant. For most samples, this calibration will provide satisfactory results. When higher accuracy is required, run parallel spectrophotometric and gravimetric determinations with portions of the same sample. The new calibration should be made on your particular sample using a gravimetric technique as a basis.

Summary of Method

This method of determining suspended solids is a simple, direct measurement which does not require the filtration or ignition and weighing steps that gravimetric procedures do. The USEPA specifies the gravimetric method for solids determinations, while this method is often used for checking in-plant processes.

REQUIRED APPARATUS

Description	Quantity Required Per Test	Unit	Cat. No.
Beaker, 600 mL, poly	1	each	1080-52
Blender, 1.2 L, 120V	1	each	26161-00
Blender, 1.2 L, 240 V	1	eacg	26161-02
Cylinder, graduated, 500 mL, poly	1	each	1081-49
Pipet, serologic, 25 mL	1	each	2066-40
Pipet, Filler, safety bulb	1	each	14651-00
Sample Cell, 25 mL, matched pair		pair	20950-00

OPTIONAL APPARATUS

Description	Unit	Cat. No.
Stirring Rod, glass	3/pkg	1770-01

For technical support and ordering information, see Section V.

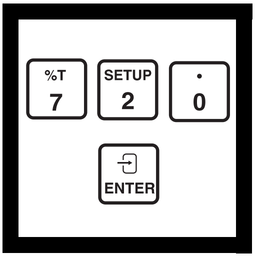
In the U.S.A. call 800-227-4224 to place an order.
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8193

TANNIN AND LIGNIN (0 to 9.0 mg/L)

For water, wastewater, boiler water

Tyrosine Method*



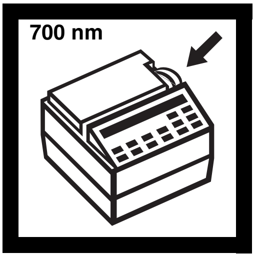
1. Enter the stored program number for tannin and lignin.

Press: **7 2 0 ENTER**

The display will show:

DIAL nm TO 700

Note: *The Pour-Thru Cell can be used for this procedure.*



2. Rotate the wavelength dial until the small display shows:

700 nm

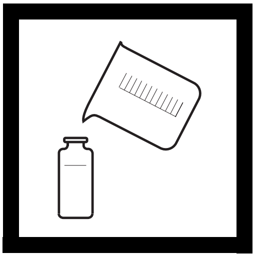
When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

then:

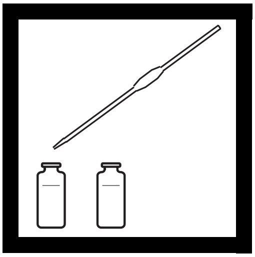
mg/L TANNIC ACID

3. Fill a clean sample cell to the 25-mL mark with deionized water (the blank).

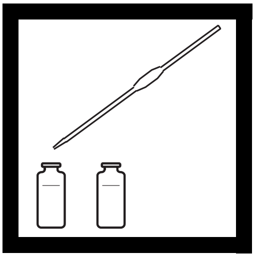


4. Fill a clean sample cell to the 25-mL mark with sample (the prepared sample).

Note: *Filter turbid samples and report results as mg/L soluble tannic acid.*

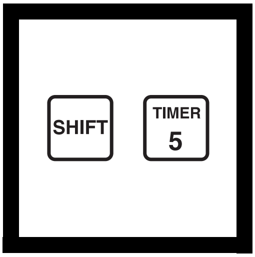


5. Pipet 0.5 mL of TanniVer 3 Tannin-Lignin Reagent into each cell. Swirl to mix.



6. Pipet 5.0 mL of Sodium Carbonate Solution into each cell. Swirl to mix.

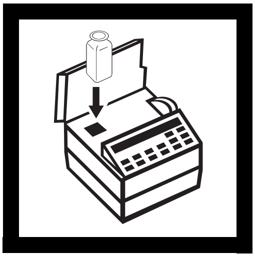
Note: *A blue color will develop if tannins and/or lignins are present.*



7. Press:

SHIFT TIMER

A 25-minute reaction period will begin.



8. When the timer beeps, the display will show:

mg/L TANNIC ACID

Place the blank in the cell holder. Close the light shield.

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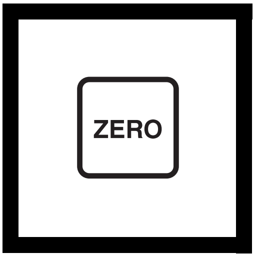
* Adapted from Kloster, M.B., *Journal American Water Works Association*, Vol. 66, No. 1, p. 44 (1974).



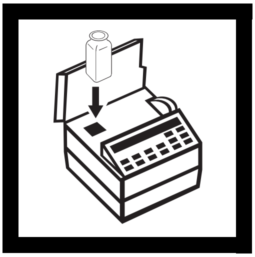
9. Press: **ZERO**

The display will show:

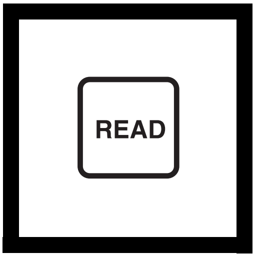
Zeroing. . . .

then:

0.0 mg/L TANNIC ACID



10. Place the prepared sample into the cell holder. Close the light shield.



11. Press: **READ**

The display will show:

Reading. . . .

then the result in mg/L tannic acid will be displayed.

Sampling and Storage

Collect samples in clean plastic or glass bottles.

Accuracy Check

Standard Solution Method

Prepare a 200-mg/L tannic acid standard solution by dissolving 0.200 grams of tannic acid in deionized water and diluting to 1000 mL. Prepare this solution monthly. A 2.0 mg/L tannic acid standard is prepared by diluting 10.00 mL of the stock solution to 1000 mL with deionized water. Prepare this standard daily.

Precision

In a single laboratory, using standard solutions of 5.0 mg/L tannic acid and two representative lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±0.08 mg/L tannic acid.

Interferences

Sulfite interference is eliminated by adding 1 mL of formaldehyde to the sample before testing the sample.

Ferrous iron causes a positive interference. Two mg/L of ferrous iron produces a color equivalent to about 1 mg/L of tannic acid. To eliminate interference of ferrous iron up to 20 mg/L, add one 0.2-g scoop of sodium pyrophosphate to the sample before testing.

Summary of Method

This test measures all hydroxylated aromatic compounds, included tannin, lignin, phenol and cresol. This method produces a blue color proportional to the amount of these compounds present in the sample. Report results as total tannin and lignin expressed as mg/L tannic acid.

REQUIRED REAGENTS

Tannin and Lignin Reagent Set (up to 100 tests) 22446-00
Includes: (2) 675-49, (1) 2560-42

Description	Quantity Required Per Test	Unit	Cat. No
Sodium Carbonate Solution	10 mL	500 mL	675-49
TanniVer 3 Tannin-Lignin Reagent	1 mL	100 mL	2560-42
Water, deionized	25 mL	4 liters	272-56

REQUIRED APPARATUS

Pipet, volumetric, Class A, 5.0 mL	1	each	14515-37
Pipet, volumetric, Class A, 0.5 mL	1	each	14515-34
Pipet, Filler, safety bulb		each	14651-00
Sample Cell, 25-mL, matched pair	2	pair	20950-00

OPTIONAL REAGENTS

Formaldehyde	100 mL	2059-32
Sodium Pyrophosphate, ACS	50 g	784-25
Tannic Acid	113 g	791-14

OPTIONAL APPARATUS

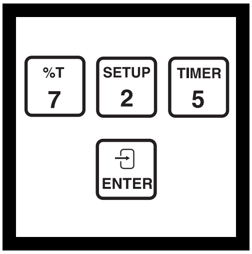
Balance, analytical	each	22310-00
Cylinder, graduated, 25 mL	each	508-40
Filter Paper, folded, 12.5 cm	100/pkg	1894-57
Flask, volumetric, 1000 mL	each	547-53
Funnel, poly, 65 mm	each	1083-67
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 10.00 mL	each	14515-38
Pour-Thru Cell Kit	each	45215-00
Spoon, measuring, 0.2 g	each	638-00
Weighing Boat, 67/47 mm	500/pkg	21790-00

For technical support and ordering information, see Section V.
In the U.S.A. call 800-227-4224 to place an order.
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 10132

THM Plus™: Trihalomethanes* 0–200 ppb as Chloroform

For screening THMs in drinking water



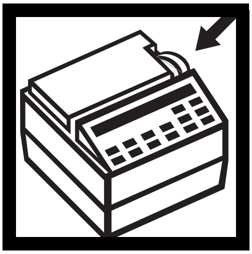
1. Enter the stored program number for Trihalomethane (THM) Plus.

Press: **725 ENTER**

The display will show:

Dial nm to 515

Note: *For the most precise results, use matched cells. See page 6.*



2. Rotate the wavelength dial until the small display shows:

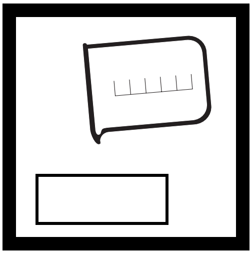
515 nm

When the correct wavelength is dialed in, the display will quickly show: **Zero Sample**

then: **ppb $CHCl_3$**

3. Prepare a hot water bath by adding 500 mL of water to an evaporating dish. Put the dish on a hot plate and turn heater on high.

Note: *If analyzing more than four samples, use 450 mL of water.*



4. Prepare a cooling bath by adding 500 mL of cold (18–25 °C) tap water to a second evaporating dish.

Note: *Maintain the water temperature between 18 and 25 °C.*

Note: *If analyzing more than four samples, use 450 mL of water.*

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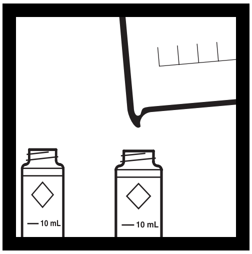
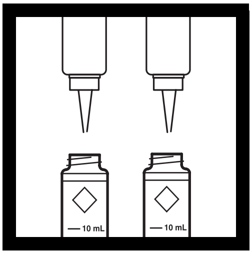
* Patent Pending



5. Fill two sample cells to the 10 mL mark with sample. Label one sample and the other blank.

Note: *Perform steps 5 through 9* ***rapidly*** *so as not to lose volatile THMs from the sample. If you are testing more than one sample, complete steps 5 through 9 for one sample before going on to the next.*

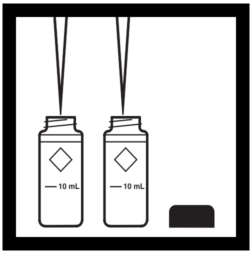
Note: *If dispensing sample with a pipette, the pipette must dispense quickly without causing aeration or back pressure.*



6. Add three drops of THM Plus Reagent 1 to each cell.

7. Cap tightly and mix gently by swirling each cell three times.

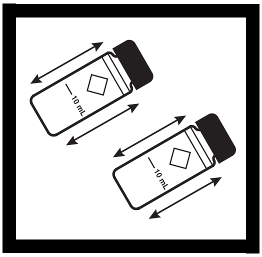
Note: *Vigorous shaking can cause loss of THMs.*



8. Use a TenSette® pipette to add 3 mL of THM Plus Reagent 2 to each cell.

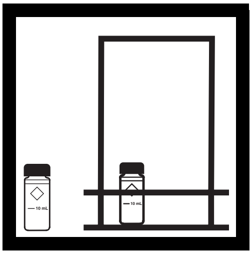
Note: *The liquid is viscous and a small amount may remain in the tip after dispensing. This will not affect the results.*

Note: *The THM Plus Reagent 2 must be at room temperature before use.*

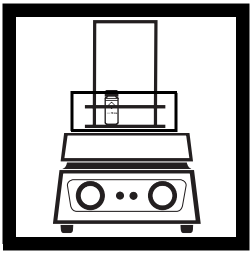


9. Cap tightly and mix by shaking ten times.

Note: *Thorough mixing ensures that all of the THM goes into the liquid and does not accumulate in the head space.*

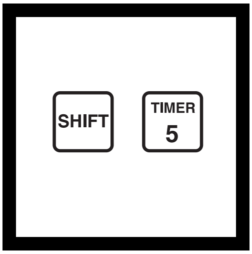


10. Place the sample cell in the cell holder assembly. Set the blank aside.

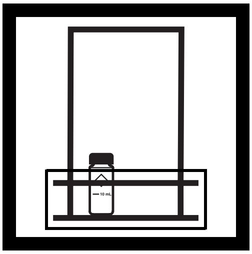


11. Place the assembly in the hot-water bath when the water is boiling rapidly.

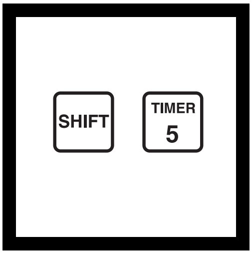
Note: *Do not allow water to rise above the white line near the top of the sample cells.*



12. Press **SHIFT TIMER** to begin a five-minute reaction period.



13. At the end of the reaction period, remove the assembly and sample cell from the hot-water bath and place in the cooling bath.



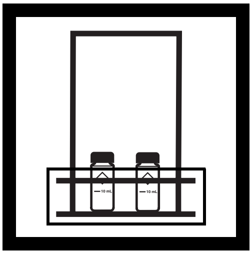
14. Press **SHIFT TIMER**. Cool for three minutes.

At the end of the cooling period, remove the cell from the cooling bath.

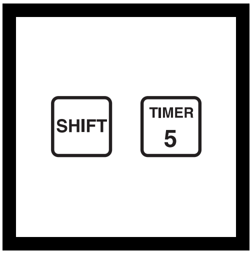
15. Use the Repipet Jr. to add 1 mL of THM Plus Reagent 3 to the sample cell and to the blank. Swirl to mix.

***Note:** The sample and blank will become warm.*

***Note:** The liquid is viscous and may not be entirely dispensed if measured using any other pipetting method.*



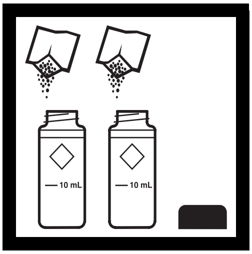
16. Replace the cooling water with fresh, cold tap water. Place the assembly containing the sample and blank cells into the cooling bath.



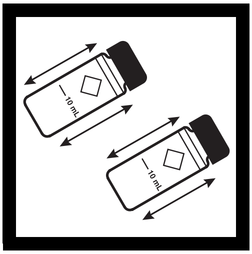
17. Press **SHIFT TIMER** to begin a three-minute cooling time.

At the end of the cooling period, remove the cells from the cooling bath.

***Note:** At the end of the cooling time, the temperature of the sample should be between 15 and 25 °C .*

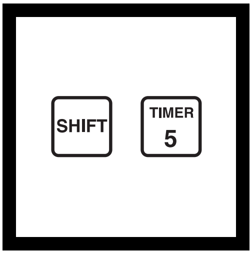


18. Add one THM Plus Reagent 4 Powder Pillow to the sample cell and one to the blank.

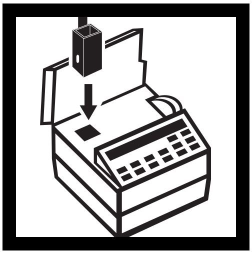


19. Cap each cell tightly and mix by shaking ten times.

***Note:** All the powder should dissolve.*

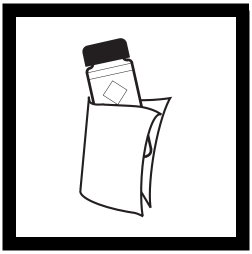


20. Press **SHIFT TIMER** to begin a 15-minute color development time.

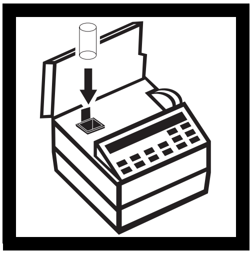


21. While the color is developing, insert the AccuVac® Ampul Adapter into instrument.

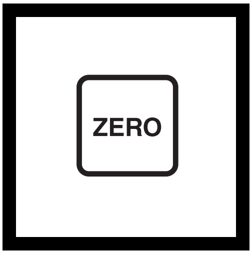
Note: *Place the grip tab at the rear of the cell holder.*



22. Wipe the reagent blank with a damp towel, followed by a dry one, to remove fingerprints or other marks.



23. When the timer beeps, place the blank into the adapter with the Hach logo facing the front of the instrument. Close the sample compartment lid.



24. Press: **ZERO**

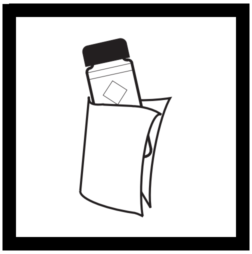
The display will show:

Zeroing. . .

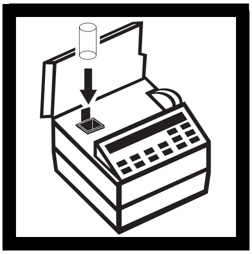
then:

ppb $CHCl_3$

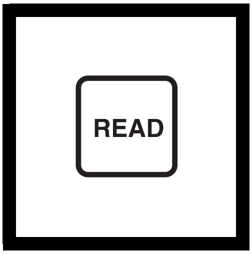
Note: *For multiple samples from the same source, zero only on the first sample.*



25. Wipe the sample cell with a damp towel, followed by a dry one, to remove fingerprints or other marks.



26. Place the prepared sample into the adapter with the Hach logo facing the front of the instrument. Close the sample compartment lid.



27. Press: **READ**

The display will show:

Reading. . .

then the display will show the results in ppb $CHCl_3$.

Note: *In the Constant-On mode, pressing* **READ/ENTER** *is not required.* **WAIT** *will not appear. When the display stabilizes, read the result.*

Sampling and Storage

Collect samples in 40-mL glass bottles sealed with Teflon®-lined septa caps. Use Cat. No. 27940-05 or equivalent for best results. Fill the bottles slowly to overflowing so that no air is included with the sample. Seal the bottles tightly and invert to check that no air has been trapped.

Because trihalomethane compounds (THMs) are extremely volatile, immediate analysis yields the greatest accuracy. If the samples cannot be analyzed immediately, add one drop of 1.0 N Sodium Thiosulfate to each sample bottle. This will prevent the formation of any additional THM compounds in chlorinated samples. Store the preserved samples at 4 °C in an atmosphere free of organic vapors. Samples should not be held more than 14 days. Allow the samples to equilibrate to room temperature before analyzing.

Ascorbic acid cannot be used as a preservative with the THM Plus method.

Accuracy Check

Standard Additions Method

Prepare the standard additions sample at the same time as the unspiked water sample.

1. Snap the neck off a THM Standard Ampule, 10 ppm as chloroform.
2. Using a Wiretrol™ Pipet (Cat. No. 25689-05), add 0.050 mL of the standard to 10 mL of water sample. Immerse the tip of the pipet below the surface of the water sample and dispense the aliquot of chloroform standard.
3. Cap the sample cell immediately and swirl three times to mix. Prepare the sample and the spiked sample according to the procedure *steps 6–27*.

See *Standard Additions* in *Section 1* for more information.

Chloroform is extremely volatile! Do not shake it when mixing.

Standard Solutions Method

Prepare a 99 ppb chloroform standard by pipetting 10.0 mL of organic-free water into a sample cell. Snap the neck off a THM Standard Ampule, 10 ppm as chloroform. Using a Wiretrol Pipette (Cat. No. 25689-05), transfer 0.100 mL of the chloroform standard into the organic-free water. Immerse the end of the pipet tip under the water to dispense the chloroform. Cap the sample cell immediately and swirl three times to mix. Immediately perform *steps 6–27* of the procedure. Do not make up the standard in advance. Use the standard immediately upon preparation.

Method Performance

Precision

In a single laboratory, using a standard solution of 60 ppb $CHCl_3$ and two representative lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±6 ppb $CHCl_3$.

Estimated Detection Limit

The EDL for program 725 is 6 ppb $CHCl_3$. For more information on derivation and use of Hach's estimated detection limit, see *Section 1*. To determine a method detection limit (MDL) as defined by the *40 CFR Part 136, Appendix B*, see *Section 1*.

Sample Cell Matching

The THM Plus method requires that the 1" sample cells be optically matched for best performance. Although sample cells supplied by Hach Company are distortion-free, nicks and scratches from handling, fingerprints, and other foreign material on the glass surfaces may cause an optical mismatch between two sample cells and introduce error into the test results. This type of error may be avoided by optically matching the sample cells and following the cell precaution statements listed in the procedure.

Procedure:

1. Turn on your instrument and set the wavelength to 515 nm.

2. Set the instrument to the Absorbance mode; Constant ON.

3. Pour at least 10 mL of deionized water into each of the samples cells to be matched.
4. Place one of the sample cells into the cell holder. Note and mark the orientation of the cell in the cell holder. Close the light shield. (Sample cells should be carefully wiped with a lint free cloth to remove any fingerprints or other foreign matter on the outside of the cell.)
5. Press: **ZERO**. The display will show: **0.000 Abs**
6. Place the next sample cell into the cell holder. Close the light shield.
7. Wait for the absorbance value to stabilize and record the value.
8. Turn the cell 180 degrees and repeat *steps 6–7*. Try to achieve an absorbance value within ±0.001 Abs of the first cell. Note the orientation of the sample cell in the cell holder. This will allow the cells to be oriented consistently in the cell holder .

Reagent Storage

Refrigerate THM Plus Reagent 2 for maximum stability. Long-term exposure to temperatures above 35 °C may cause reagent degradation.

Interferences

The substances in the following table have been tested and found not to interfere up to the indicated levels (in ppm):

Interference	Maximum Level tested
Chlorine	<10 ppm
Copper	<1000 ppm
Hardness, Ca	<1000 ppm as $CaCO_3$ May have some turbidity until Reagent 3 is added
Hardness, Mg	<4000 ppm as $CaCO_3$ May have some turbidity until Reagent 3 is added
Iron	<10 ppm
Lead	<2 ppm
Mercury	<10 ppm
Monochloramine	<20 ppm

Interference	Maximum Level tested
Nickel	<10ppm
Sodium Bisulfite	<100 ppm
EDTA	Interferes negatively at all levels

Additional disinfection by-products which react

Compound	Effect
1,1,1-trichloro-2-propanone	Interferes positively
1,1,1-tricholoacetonitrile	Interferes positively
Chloral hydrate	Interferes positively
Dibromochloroacetic acid	Interferes positively
Dichlorobromoacetic acid	Interferes positively
Tribromoacetic acid	Interferes positively
Trichloroacetic acid	Interferes positively

Summary of Method

The THM Plus method reacts with the trihalogenated disinfection by-products formed as the result of the disinfection of drinking water with chlorine in the presence of naturally occurring organic materials. These disinfection by-products (DBPs) may be produced in the treatment plant or the distribution system as long as the water is in contact with free chlorine residual. The formation of the DBPs is influenced by chlorine contact time, chlorine dose and residual, temperature, pH, precursor concentration, and bromide concentration.

The predominant DBPs formed by the chlorination of drinking water are the trihalomethanes or THMs. The four trihalogenated compounds that form are chloroform, bromoform, dichlorobromomethane, and dibromochloromethane. These four compounds comprise the Total Trihalomethanes (TTHMs) group which is regulated under the Safe Drinking Water Act. The combined concentration of the TTHMs, reported as chloroform, is regulated to be 100 ppb or less in drinking water samples. Other DBPs that may be present and react under the conditions of the THM Plus method are listed in Interferences.

In the THM Plus method, THM compounds present in the sample react with N, N,-diethylnicotinamide under heated alkaline conditions to form a dialdehyde intermediate. The sample is then cooled and acidified to pH 2.5. The dialdehyde intermediate formed is then reacted with 7-napthylamine-1,3 disulfonic acid to form a colored Schiff base which absorbs at 515 nm. The color formed is directly proportional to the total amount of THM compounds present in the sample. The results are reported as ppb chloroform.

Safety

Good safety habits and laboratory techniques should be used throughout the procedure. Consult the Material Safety Data Sheet for information specific to the reagents used.

REQUIRED REAGENTS

Description	Unit	Cat. No.
Reagent Set (50 tests)		27908-00

Includes: (1) 27539-29, (1) 27540-48, (1) 27541-42, (1) 27566-99

	Quantity Required		
Description	**Per Test**	**Unit**	**Cat. No.**
THM Plus Reagent 1	6 drops	15 mL	27539-29
THM Plus Reagent 2	6 mL	330 mL	27540-48
THM Plus Reagent 3	2 mL	110 mL	27541-42
THM Plus Reagent 4	2 pillows	100 pp	27566-99

REQUIRED APPARATUS

Beaker, 600-mL		each	500-52
Cell Holder Assembly, TTHM	1	each	47880-00
Evaporating Dish, 125 mm x 65 mm	2	each	27647-00
Hot Plate, 7 x 7 in., 120 Vac	1	each	23441-00
Hot Plate, 7 x 7 in., 240 Vac	1	each	23441-02
Repipetter, 1 mL	1	each	21113-02
Pipet, TenSette®, 1–10 mL	1	each	19700-10
Pipet tips, 1–10 mL (for 19700-10)		50/pkg	25589-96
Sample cells, 10 mL, w/caps.	2	6/box	24276-06
Wipers, Disposable, KimWipes		280/pkg	20970-00

OPTIONAL REAGENTS

Chloroform, 10 ppm, 2-mL ampoule		7/pkg	27567-07
Water, Reagent, Organic-free		500 mL	26415-49

OPTIONAL APPARATUS

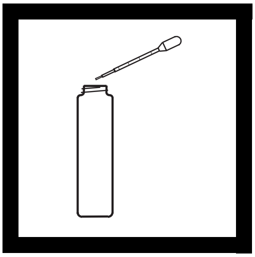
Flask, volumetric, 100 mL, class A		each	14574-42
Pipet, filler, safety bulb		each	14651-00
Pipet, volumetric, class A, 10 mL		each	14515-38
Pipettes, Wiretrol™, 50–100 µL		250/pkg	25689-05
Timer, 5-channel, 1 sec. to 100 hrs.		each	26304-00
Vials, glass, 40-mL, with Septa cap		5/pkg	27940-05

Method 10017
For wastewater

TOXTRAK TOXICITY TEST*

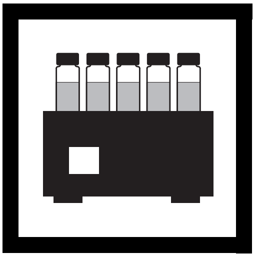
Colorimetric Method**

Inoculum Development

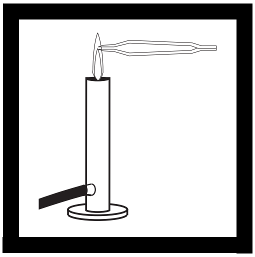


Using Indigenous Biomass

1. Using one of the dropper pipets provided, add 1.0 mL of source culture to a Tryptic Soy Broth Tube.

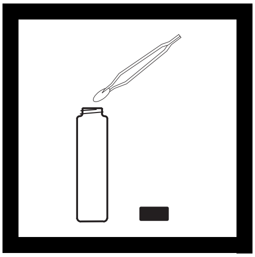


2. Incubate until the vial contents are visibly turbid (turbidity indicates bacterial growth).

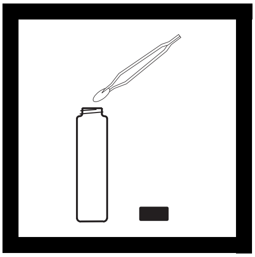


Using Bactrol Disks

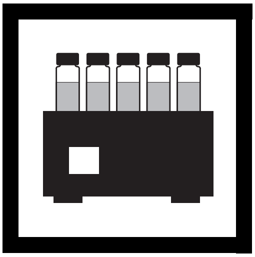
1. Flame sterilize forceps by dipping into alcohol and flame in an alcohol or Bunsen burner. Let the forceps cool.



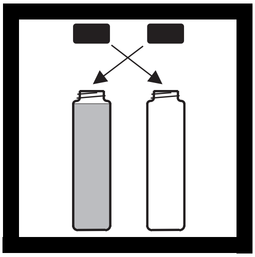
2. Remove the cap from the Bactrol inoculum bottle. Pick out one Bactrol Inoculum Disk with the sterilized forceps.



3. Remove the cap from a Lauryl Tryptose Broth Tube and drop in the Inoculum Disk. Shake to dissolve the disk.



4. Incubate the Lauryl Tryptose Broth Tube until the medium is visibly turbid. Turbidity will develop much faster if incubation is done at 35 °C instead of room temperature. At 35 °C, 10 hours is usually sufficient.



5. Inoculate a new Lauryl Tryptose Broth Tube by first inverting the tube in Step 4, and then switching the caps of the two tubes. Then invert the new tube. After incubation, use this new vial in subsequent tests.

Note: *In this way, several medium vials may be inoculated from one Bactrol Disk.*

Note: *If testing on consecutive days, keep inoculum several days in the incubator or at room temperature.*

Note: *Cultures 10 to 72 hours old give best results.*

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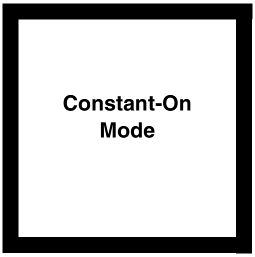
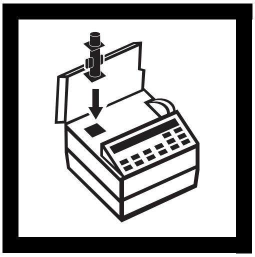
* U.S. Patent number 5,413,916.

** Liu, D., *Bull. Environ. Contam. Toxicol*. 26, 145-149 (1981).

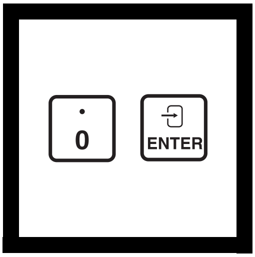
Colorimetric Reaction



1. Turn on the DR/2010 and put the instrument in constant-on mode. Allow the instrument to warm up for at least 15 minutes.



2. Place the 16-mm adapter into the cell holder with the marker to the right.

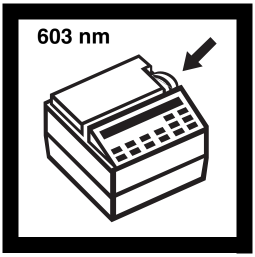


3. Enter the stored program number for absorbance.

Press: **0 ENTER**

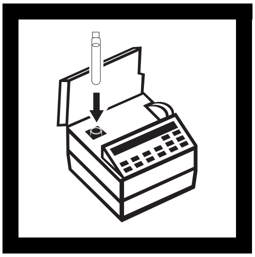
The display will show:

Abs

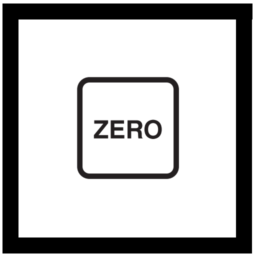


4. Rotate the wavelength dial until the small display shows:

603 nm



5. Fill a 16-mm reaction tube with deionized water. Label this tube as “blank.” Place the tube in the Test ‘N Tube adapter and place the lid on the adapter.

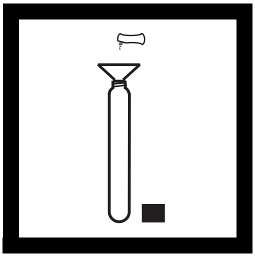


6. Press: **ZERO**

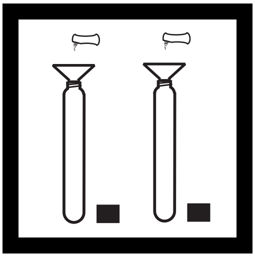
The display will show:

Zeroing. . .

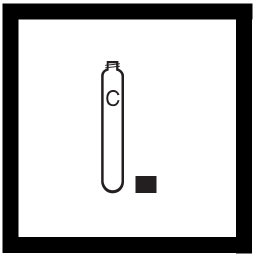
then: **0.000 Abs**



7. Label a tube “control.” Open one ToxTrak Reagent Powder Pillow and add the contents to the empty reaction tube.

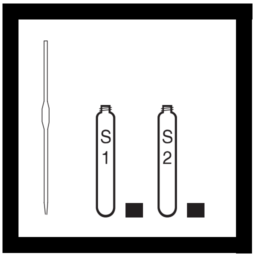


8. For each sample or dilution, repeat Step 7. Label each tube clearly.

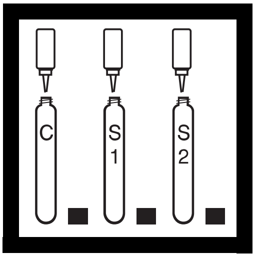


9. Add 5.0 mL of deionized water to the control tube.

Note: *For the control tube, use deionized water that is free of toxicity, or another water source that represents zero or baseline toxicity.*

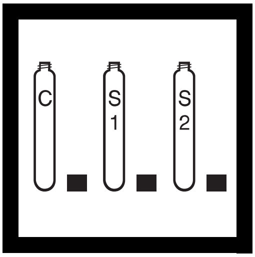


10. Add 5.0 mL of sample (or dilutions) to the sample tubes.

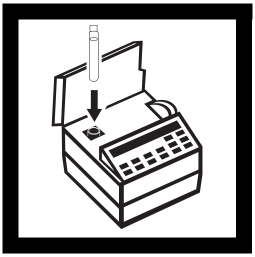


11. Add 2 drops of Accelerator Solution to each tube. Cap and shake to mix.

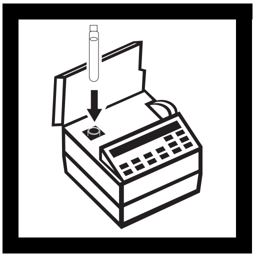
Note: *Shaking serves to fully oxygenate the samples, assuring that oxygen concentration is not a factor in determining respiration rate.*



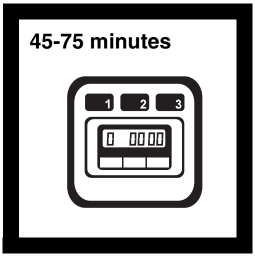
12. Add 0.5 mL of inoculum (previously prepared) to each tube. Cap and invert to mix.



13. Place the control tube in the cell holder. Place the lid on the adapter. Record the absorbance.

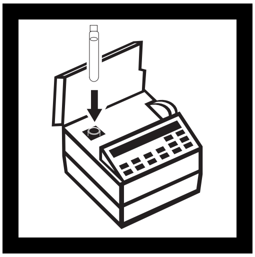


14. Repeat Step 13 for all samples and dilutions. Be sure to record each absorbance.

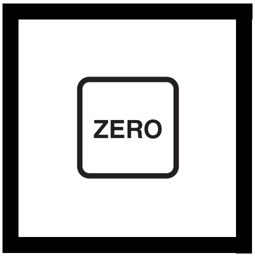


15. Allow the solutions in the tubes to react until the absorbance of the **control tube** decreases 0.60 ±0.10. This should take about 45-75 minutes.

Note: *Exact reaction time will vary depending upon a number of factors, including temperature, age of culture, number of bacteria, etc.*



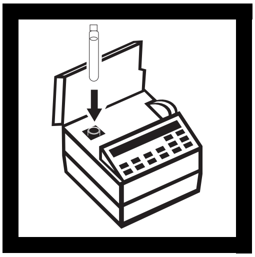
16. Place the blank tube prepared in Step 5 in the Test ‘N Tube adapter. Place the lid on the adapter.



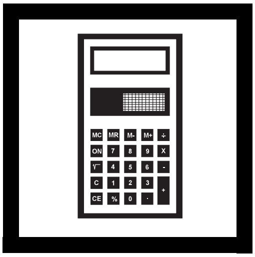
17. Press: **ZERO**

The display will show:

0.000



18. Place the control tube into the cell holder. Place the lid on the adapter. Record the absorbance value. Place each sample cell into the cell holder. Place the lid on the adapter. Record the absorbance value of each sample.



19. Calculate the % Inhibition as follows:

$$\%I = \left[I - \left(\frac{\Delta \text{Abs sample}}{\Delta \text{Abs control}} \right) \right] \times 100$$

See the example below.

Note: *Some toxins increase respiration and will give a negative % inhibition on all respiration-based toxicity tests. After repeated testing, samples which always give a % inhibition in Step 19 that is more negative than 10% should be considered toxic.*

Example:

The control tube (C) has an initial absorbance of 1.6 and decreases to 1.0 Abs. The sample tube has an initial absorbance of 1.7 and decreases to 1.3 Abs.

ΔAbs. Sample = 1.7 – 1.3 = 0.4

ΔAbs. Control = 1.6 – 1.0 = 0.6

$$\%I = \left(1 - \left(\frac{0.4}{0.6} \right) \right) \times 100$$

$\%I = 33.3$

Interpreting Results

The % Inhibition results obtained are only a relative measurement. They do not represent a true quantitative measurement of toxic concentration. The % Inhibition does not necessarily increase in direct proportion to the concentration of toxins. To determine the minimum inhibition concentration of a toxin, it is possible to make tenfold dilutions of the sample and determine the % Inhibition for the dilutions until the sample is diluted sufficiently so that no inhibition is observed. This is the No Observed Effect Concentration (NOEC).

Due to the many variables involved in the test, the limits of detection are on the order of 10% Inhibition. This would correlate to the Lowest Observed Effect Concentration (LOEC). If a sample shows less than 10% Inhibition, repeat the test. After several repetitions, look at the series of data to determine the likelihood of toxicity. Results below 10% are not reliable, but can be used to surmise some presence of toxicity if they are consistent.   See examples below:

Data Points: % Inhibition	Conclusion
7%, 9%, 5%, 8%, 5%	May be slightly toxic
7%, -4%, -5%, 5%, 1%	Most likely not toxic
-7%, -9%, -5%, -8%, -5%	May be slightly toxic

Some toxins will increase respiration and will give a negative % Inhibition on this and all other respiration-based toxicity tests. After repeated testing, samples that always give a % Inhibition that is more negative than -10% should be considered toxic.

Disposal of Test Cultures

Dispose of active bacterial cultures by using one of these methods:

1. Autoclave used test containers at 121 °C for 15 minutes at 15 pounds of pressure. Once the containers are sterile, pour the contents down the drain with running water. The reaction tubes may be washed and re-used.

2. Sterilize test containers by using a 1:10 dilution of commercial laundry bleach. Pour the test container contents and test containers into the bleach solution. Allow 10-15 minutes of contact time with the bleach solution. Then pour the liquid down the drain and wash the reaction tubes for re-use.

Summary of Method

This method is based on the reduction of resazurin, a redox-active dye, by bacterial respiration. When it is reduced, resazurin changes color from blue to pink. Toxic substances can inhibit the rate of resazurin reduction. A chemical accelerant has been added to shorten the reaction time.

REQUIRED REAGENTS

Description	Cat. No.
ToxTrak Reagent Set (25 tests)	25972-00

Includes: (1) 25607-66, (1) 25608-36, (1) 22336-15, (2) 21247-20, (2) 20962-08

Description	Quantity Required Per Test	Unit	Cat. No.
ToxTrak Reagent Powder Pillows	1 pillow	50/pkg	25607-66
ToxTrak Accelerator Solution	2 drops	15 mL SCDB	25608-36
Tryptic Soy Broth Tubes	1	15/pkg	22336-15

REQUIRED APPARATUS

Description	Quantity Required Per Test	Unit	Cat. No.
Clippers, to open powder pillows	1	each	936-00
Culture Tubes, 13 x 100	varies	10/pkg	20962-08
Dropper Pipet, 1 mL	varies	20/pkg	21247-20
Forceps, flat square tip	1	each	14537-00
Pipet, Volumetric, 5.0 mL, Class A		each	14515-37
Pipet Filler, Safety Bulb		each	14651-00
COD Adapter, 16 mm	1	each	44799-00

OPTIONAL REAGENTS

Description	Unit	Cat. No.
Culture Set (incl. Bactrol Discs and Lauryl Tryptose Broth Tubes)	25 cultures	25978-00
Bactrol Discs, *E. coli*	25/bottle	25809-25
Isopropanol	500 mL	14459-49
Lauryl Tryptose Broth Tubes	15/pkg	21623-15

OPTIONAL APPARATUS

Description	Unit	Cat. No.
Burner, Alcohol, 60 mL	each	20877-60
Burner, Bunsen	each	21627-00
Germicidal Cloth	50/pkg	24632-00
Incubator, Dri Bath, 25 well, 120 V	each	45900-00
Incubator, Dri Bath, 25 well, 240 V	each	45900-02
Test Tube Rack	each	24979-00

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.s

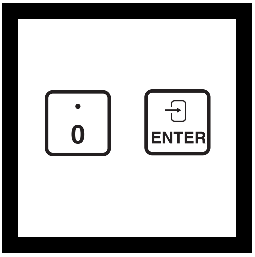
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 10050

For Soil

TPH IN SOIL (10 and/or 100 ppm TPH thresholds*)

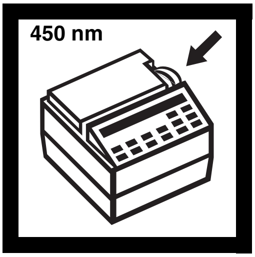
Immunoassay Method



1. Enter the stored program for absorbance.

Press: **0 ENTER**

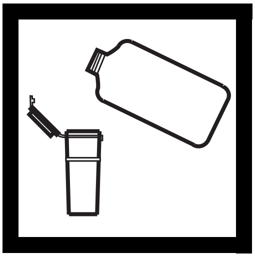
***Note:** The Pour-thru Cell cannot be used.*



2. Rotate the wavelength dial until the small display shows:

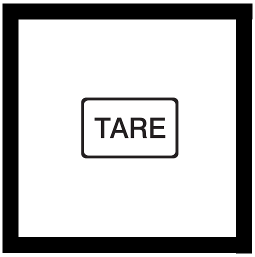
450 nm

TPH Phase 1: Soil Extraction



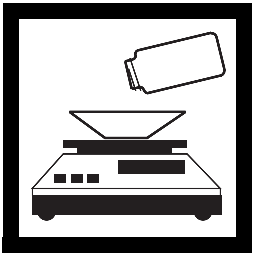
1. Fill the extraction vial to the 0.75 oz line with Soil Extractant Solution.

***Note:** This is equivalent to adding 20 mL of Soil Extractant Solution.*

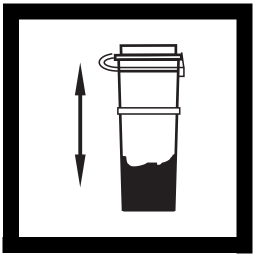


2. Place a plastic weighing boat on an analytical balance. Tare the balance.

***Note:** Use either a laboratory balance or the portable AccuLab Pocket Pro.*



3. Weigh out 10 ±0.1 g of soil in a plastic weighing boat. Carefully pour the soil into the extraction vial.

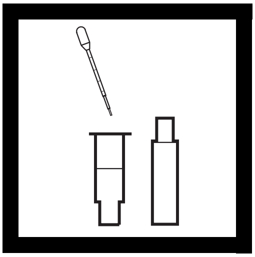


4. Cap the extraction vial tightly and shake vigorously for 1 minute.

---

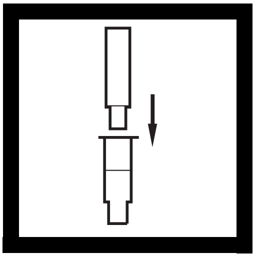
* Test is semi-quantitative. Results are expressed as greater or less than the threshold value used.

5. Allow to settle for 1 minute. Gently open the extraction vial.



6. Using the disposable bulb pipet, withdraw 1.0-1.5 mL from the liquid (top) layer in the extraction vial. Transfer this aliquot into the filtration barrel (the bottom part of the filtering assembly; the plunger is inserted into it).

Note: *Do not use more than 1.5 mL. The pipet has 0.25-mL increments on it.*

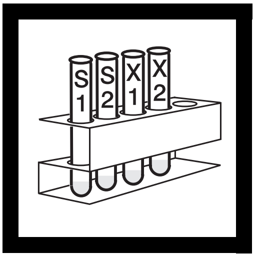


7. Insert the filtration plunger into the filtration barrel. Press firmly on the plunger until at least **0.5 mL** of filtered sample is collected in center of the plunger.

Note: *The liquid will be forced up through the filter. The liquid in the plunger is the filtered extract.*

Note: *It may be necessary to place the filtration assembly on a table and press down on the plunger.*

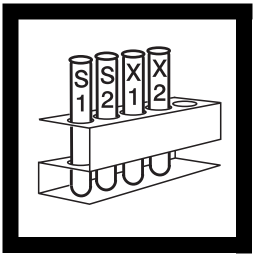
TPH Phase 2: Preparing Samples and Standards



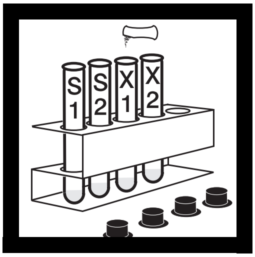
1. Label four TPH Enzyme Conjugate Tubes Standard 1, Standard 2, Sample 1 and Sample 2.

Note: In phase 2, choose the desired threshold level and perform Step 6 or Steps 7-9, but not both. Additional tubes are required to perform analyses at both threshold levels.

Note: The TPH Conjugate and Antibody tubes are matched lots. Mixing with other lots will cause erroneous results.

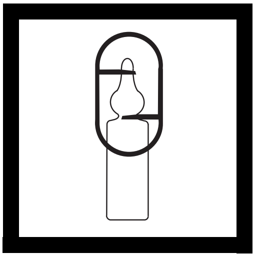


2. Label one TPH Antibody Tube for each sample and standard. Be sure to label the 10 and 100 ppm samples appropriately.



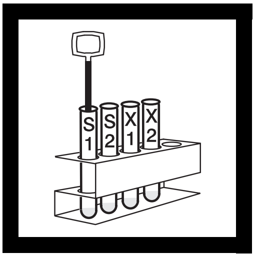
3. Pour the contents of one TPH Buffer Pillow into each Enzyme Conjugate tube.

Note: Squeezing the top portion of the pillow will help empty the pillow contents. If necessary, clip open the top corner of the pillow to release the liquid.



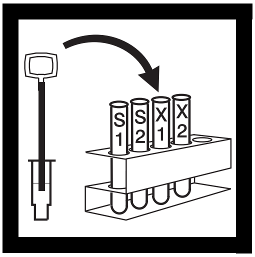
Preparing the TPH Standard

4. Snap open a TPH Standard Ampule.



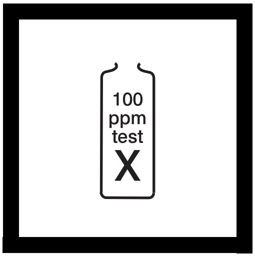
5. Using the WireTrol pipet, add 50 µL of TPH Standard to the Standard 1 and Standard 2 TPH Enzyme Conjugate tubes. Swirl to mix thoroughly.

Note: *Dispense standard below the level of the solution in the Enzyme Conjugate tubes.*



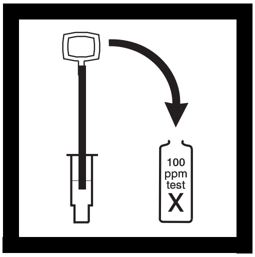
Preparing Samples for Measuring at 10-ppm Threshold

6. Using the WireTrol pipet, add 50 µL of the sample extract from the filter unit to the tubes labeled Sample 1 and Sample 2. Swirl each to mix.



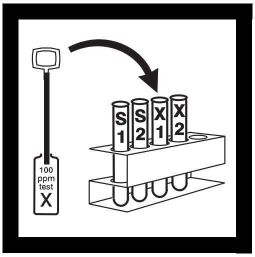
Preparing Samples for Measuring at the 100-ppm Threshold

7. Label a 100-ppm TPH Dilution Ampule for each sample. Snap open each Dilution Ampule.



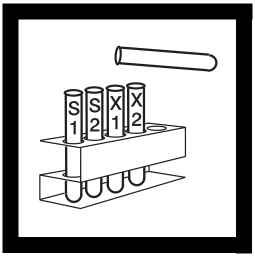
8. Using the WireTrol pipet, add 100 µL of the sample extract from the filtration plunger to the labeled 100 ppm Dilution Ampule. Mix by repeatedly drawing 100 µL into the pipet and dispensing back into the ampule.

Note: *The upper line on the WireTrol capillary tubes is equal to 100 µL.*



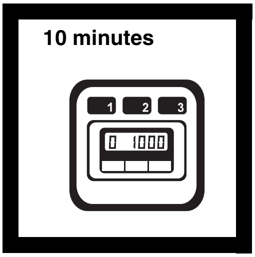
9. Using the WireTrol with a new pipet tip, add 50 µL of the diluted sample extract from the 100-ppm Dilution Ampule to the TPH Enzyme Conjugate tubes labeled Sample 1 and Sample 2. Swirl to mix.

TPH Phase 3: Immunoassay - steps in this phase require exact timing.



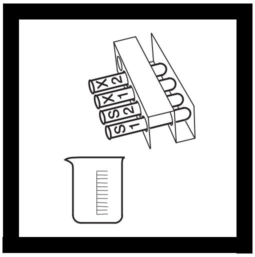
1. Pour the contents of the Enzyme Conjugate Tubes into the correct TPH Antibody Tubes. Swirl to mix.

Note: *The TPH Conjugate and Antibody tubes are matched lots. Mixing with other lots will cause erroneous results.*

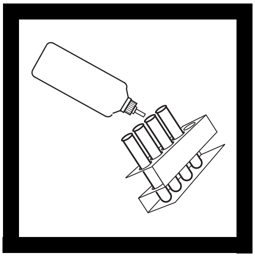


2. Begin a 10-minute reaction period.

Note: *During this phase analytes in the sample compete with the enzyme conjugate for a limited number of binding sites on the inside of the antibody tubes.*



3. After the 10-minute period, discard the contents of the TPH Antibody Tubes into an appropriate waste container.



4. Wash each tube thoroughly and forcefully 4 times with Wash Solution. Empty the tubes into an appropriate waste container. Shake well to ensure most of the Wash Solution drains after each wash.

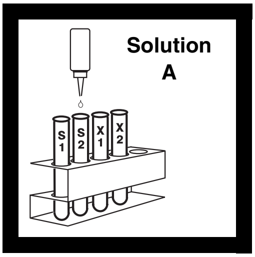
Note: *Wash Solution is a harmless detergent.*

Go To
next Phase
immediately!

5. Continue to the next phase immediately.

Note: *Ensure most of the Wash Solution is drained from the tubes. Turn the tubes upside down and gently tap on a paper towel to drain. Some foam may be left from the Wash Solution; this will not effect results.*

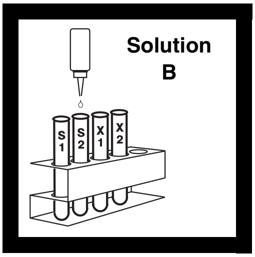
TPH Phase 4: Color Development



Check reagent labels carefully! Reagents must be added in proper order for valid test results.

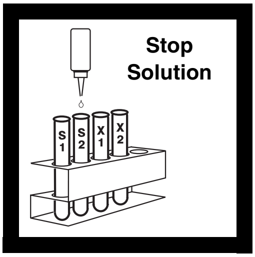
1. Add 5 drops of Solution A to each tube. Replace the bottle cap.

Note: *Hold reagent bottles vertically for accurate delivery or erroneous results may occur.*



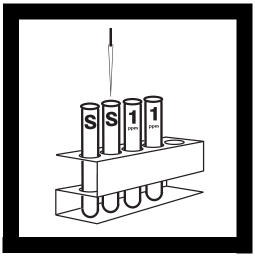
2. Begin a 2.5-minute period and immediately add 5 drops of Solution B to each tube. Swirl to mix. Replace the bottle cap.

Note: *Add drops to the tubes in the same order to ensure proper timing (i.e. left to right). Solution will turn blue in some or all of the tubes.*



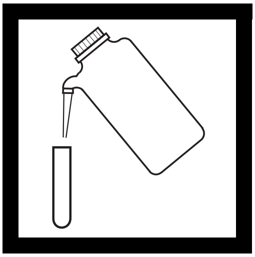
3. Let each tube react for exactly 2.5 minutes. Then add 5 drops of Immunoassay Stop Solution to each tube. Replace the bottle cap.

Note: *Blue solutions will turn yellow when Stop Solution is added. TPH concentration is inversely proportional to color development; a lighter color indicates higher levels of TPH.*

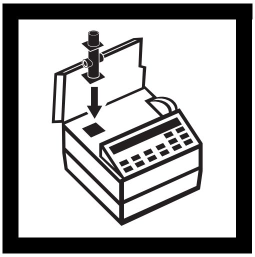


4. Using the TenSette Pipet with a new tip, add 0.5 mL of deionized water to each tube. Swirl to mix.

TPH Phase 5: Measuring the Color

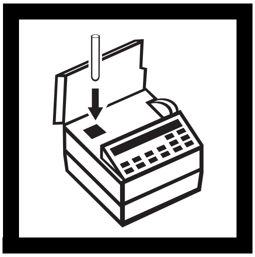


1. Fill a Zeroing Tube with deionized water (the blank).

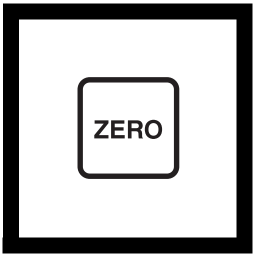


2. Insert the Immunoassay adapter into the sample cell compartment.

Note: *Align the adapter so the light beam openings face the sides of the DR/2010. Press firmly on the adapter to seat it.*



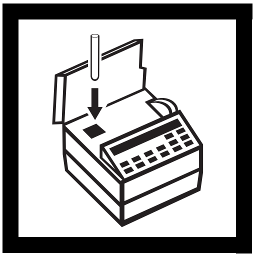
3. Place the blank in the cell holder. Place the cover on the adapter.



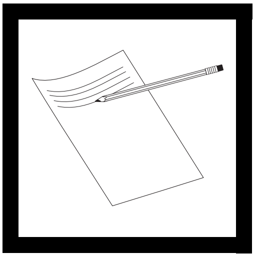
4. Press: **ZERO**

The display will show:

0.000 Abs



5. Insert Standard 1 sample cell into the cell holder. Close the light shield.

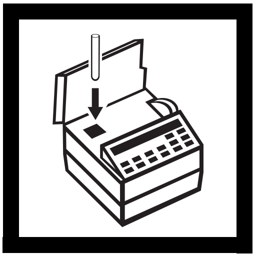


6. Record the absorbance reading.

Repeat
Steps 5 and 6
for
Standard #2

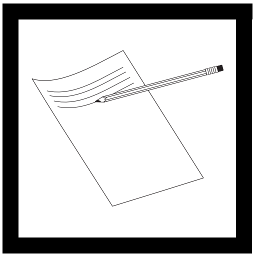
7. Repeat Steps 5 and 6 for the Standard 2 tube.

Note: *If Standard 1 and Standard 2 are more than 0.350 absorbance units apart, repeat the test beginning at Phase 2, Standard Preparation.*



8. Insert the Sample 1 tube into the cell holder. Place the cover on the adapter.

Note: *TPH concentration is inversely proportional to the color intensity (or absorbance value). More color means less TPH in the sample.*



9. Record the absorbance reading.

Repeat
Steps 8 and 9
for
Sample #2

10. Repeat Steps 9 and 10 for the Sample 2 tube. See *Table 1* below to interpret results.

Interpreting the Results

Use Table 1 to interpret the results.

Table 1

If sample absorbance is...	10 ppm Threshold	100 ppm Threshold
...less than the highest standard absorbance	Sample TPH is greater than 10 ppm	Sample TPH is greater than 100 ppm
...greater than the highest standard absorbance	Sample TPH is less than 10 ppm	Sample TPH is less than 100 ppm

Sensitivity

The TPH in Soil Test has sensitivities to the following chemicals at the stated levels.

Compound	Concentration required to give a Positive Result (ppm)*	Compound	Concentration required to give a Positive Result (ppm)**
Petroleum fuels		**Aromatic Compounds**	
Gasoline	10	Benzene	400
Diesel fuel	15	Toluene	40
#2 Fuel Oil	15	Ethylbenzene	7
Kerosene	15	o-Xylene	8.5
Jet Fuel A	15	m-Xylene	8
Jet Fuel JP-4	15	p-Xylene	45
#6 Fuel Oil	25	Styrene	7
Formulated Petroleum Products		1,2-Dicholorobenzene	2.5
Mineral spirits	40	Hexachlorobenzene	10
Machine Oil	> 1000	Naphthalene	0.8
Brake fluid	> 1000	Acenaphthene	0.5
Unused motor oil	> 1000	Biphenyl	10
Used Motor oil*	50	Creosote	1.5
Grease	> 1000	**Aliphatic Compounds**	
Mineral oil	> 1000	2-Methylpentane	35
Crude Oil* **		Hexanes, mixed	65
Ingram	60	Heptane	130
Vermilion	130	iso-Octane	8.5
Walker	100	Undecane	> 1000
Louisiana	100	Trichloroethylene	> 1000
Main Pass	100	MTBE	> 1000

* Samples with stated concentration will give positive result greater than 95% of the time when tested at stated concentration level.

** Samples with stated concentration will give positive result greater than 95% of the time when tested at stated concentration level.

*** Variable, depending on source

Storing and Handling Reagents

- Wear protective gloves and eye wear.
- Store reagents at room temperature and out of direct sunlight (less than 80 °F or 27 °C).
- Keep aluminized pouch that contains antibody-coated tubes sealed when not in use.
- If Stop Solution or liquid from the extraction jar comes in contact with eyes, wash thoroughly with cold water. Seek immediate medical help.
- Operational temperature of the reagents is 40-90 °F (5-32 °C).

Summary of Method

Samples, standard and color development reagents are added to test tubes coated with an antibody specific for petroleum fuels. The concentration of Total Petroleum Hydrocarbons (TPH) in a sample is determined by comparing the developed color intensity to that of a TPH standard. The TPH concentration is inversely proportional to the color development; a lighter color indicates a higher TPH concentration.

Safety

Good safety habits and laboratory techniques should be used throughout the procedure. Consult the Material Safety Data Sheet for information specific to the reagents used.

Measuring Hints

- Timing is critical; follow instructions carefully
- Handle the Antibody Tubes carefully. Scratching the inside or outside may cause erroneous results. Wipe tubes with a paper towel to remove smudges or fingerprints before measuring.
- Hold all dropper bottles vertically and direct drops to the bottom of the tube.
- Antibody Tubes and Enzyme Conjugate Tubes are made in matched lots. Do not mix with other reagent lots.

Pollution Prevention and Waste Management

The soil extractant (methanol) is an ignitable (D001) waste regulated by the Federal RCRA. Collect this material with laboratory solvents for disposal. If the soil samples being analyzed are contaminated with hazardous waste, the samples and resulting test waste may also need to be disposed in accordance with RCRA.

REQUIRED REAGENTS AND STANDARDS

Description	Cat. No.
TPH in Soil Reagent Set (5 tests)	26026-00

Includes all consumable reagents and apparatus used in the test

REQUIRED EQUIPMENT AND SUPPLIES

Description	Quantity Required Per Test	Unit	Cat. No.
Adapter, Immunoassay, DR/2010	1	each	46820-00
Clippers, large, for opening powder pillows	1	each	968-00
Gloves, poly, medium (large 25504-03)	2	100/box	25504-02
Goggles, safety, vented	1	each	25507-00
Pen, laboratory, permanent, black	1	each	20920-00
TenSette Pipet, 0.1-1.0 mL	1	each	19700-01
TenSette Pipet Tips, for 19700-01	1	50/pkg	21856-96
Timer	1	each	23480-00
WireTrol Pipet, 50 & 100 µL, w/ 250 capillary tubes	1	each	25689-05
Zeroing Tubes	1	each	26228-00

OPTIONAL EQUIPMENT AND SUPPLIES

Ampule Breaker (for PourRite ampules)	each	24846-00
Balance, AccuLab,	each	25568-00
Balance, Laboratory, model SL500	each	26105-00

OPTIONAL REAGENTS AND STANDARDS

Water, deionized	4 liters	272-56

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

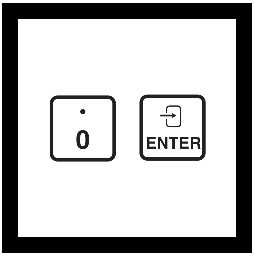
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 10052

For Water

TPH IN WATER (Thresholds vary according to analyte)*

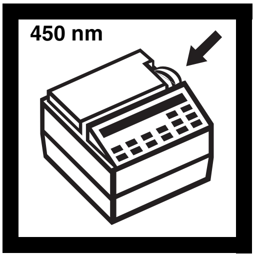
Immunoassay Method



1. Enter the stored program for absorbance.

Press: **0 ENTER**

Note: *The Pour-Thru Cell cannot be used.*



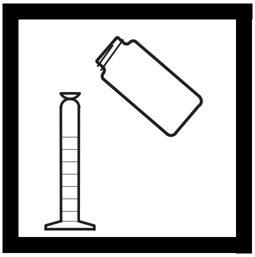
2. Rotate the wavelength dial until the small display shows:

450 nm

TPH Phase 1: Sample Preparation

1. Label a sample collection container. Collect at least 100 mL of sample. Before analysis, chill the samples.

Note: *Read Measuring Hints following these steps before testing.*



2. Choose the desired volume from *Table 1*, below. Measure the volume into a 50-mL graduated mixing cylinder. Add deionized water to the 50-mL mark. Stopper and mix.

3. Add the contents of one TPH Stabilizing Agent Powder Pillow to an empty sample bottle. Label the bottle.

Note: *Discard or recycle bottles after one use to prevent cross contamination.*

4. Pour the sample into the labeled sample bottle until the bottle is full. Cap. Mix until TPH Stabilizing Agent is dissolved. Proceed to Phase 2 promptly.

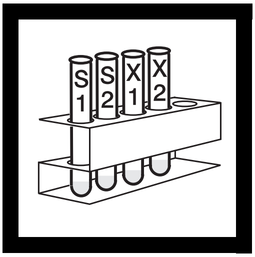
Table 1

Threshold	Sample Volume	Threshold	Sample Volume
220 ppb (m-xylene)	50 mL	5.5 ppm(m-xylene)	2 mL
550 ppb (m-xylene)	20 mL	11 ppm(m-xylene)	1 mL
1.1 ppm(m-xylene)	10 mL	22 ppm(m-xylene)	0.5 mL
2.2 ppm(m-xylene)	5 mL	55 ppm(m-xylene)	0.2 mL
Note: 1.1 ppm = 1100 ppb; 2.2 ppm = 2200 ppb			

---

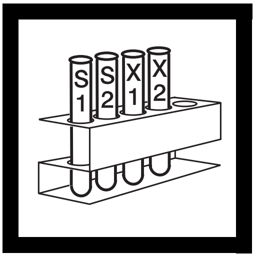
* Test is semi-quantitative; results are expressed as greater or less than the threshold value used.

TPH Phase 2: Immunoassay- Steps in this phase require exact timing.



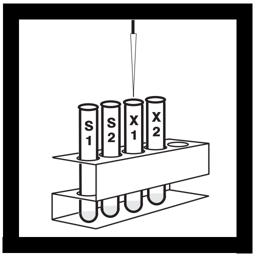
1. Label four TPH Enzyme Conjugate Tubes Standard 1, Standard 2, Sample 1 and Sample 2 for use in Step 7.

Note: *The TPH Conjugate and Antibody tubes are matched lots. Mixing with other lots will cause erroneous results.*

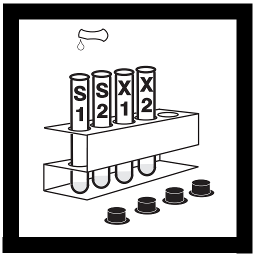


2. Label four TPH Antibody Tubes Standard 1, Standard 2, Sample 1 and Sample 2.

Note: *Sample 1 and Sample 2 tubes can be duplicate samples, different dilutions of the same sample, or 2 different samples.*

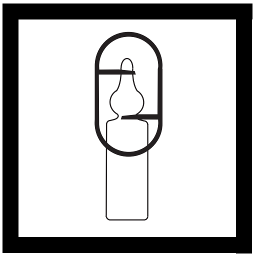


3. Using a TenSette Pipet, add 2.0 mL of prepared sample to each of the TPH Enzyme Conjugate Tubes labeled Sample 1 and Sample 2.

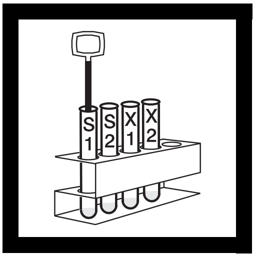


4. Add the contents of 2 TPH Standard Buffer Solution Pillows to each of the TPH Enzyme Conjugate Tubes labeled Standard 1 and Standard 2.

Note: *Squeeze the top of the inverted pillow to empty. If necessary, cut a top corner of the inverted pillow with clippers.*

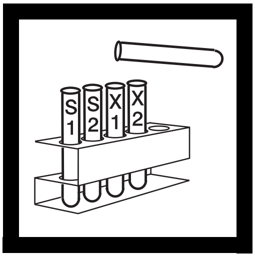


5. Snap open a TPH Standard ampule.

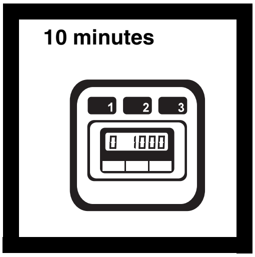


6. Using the WireTrol pipet, add 50 µL of TPH Standard to the Standard 1 and Standard 2 TPH Enzyme Conjugate. Swirl to mix thoroughly.

Note: *Dispense standard below the level of the solution in the Enzyme Conjugate tubes. Use a new tip for each tube.*

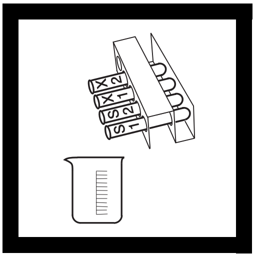


7. Pour the contents of the TPH Enzyme Conjugate Tubes into the correct TPH Antibody Tubes. Swirl to mix.

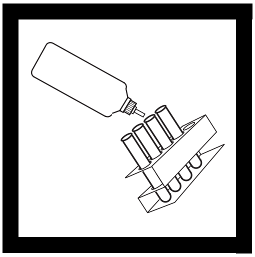


8. Begin a 10-minute reaction period.

Note: *During this phase, m-xylene and other substituted aromatics in the sample compete with the enzyme conjugate for a limited number of binding sites on the inside of the antibody tubes.*



9. After the 10-minute period, discard the contents of the TPH Antibody Tubes into an appropriate container.



10. Wash each tube thoroughly and forcefully 4 times with Wash Solution. Empty the tubes into an appropriate container. Shake well to ensure most of the Wash Solution drains after each wash.

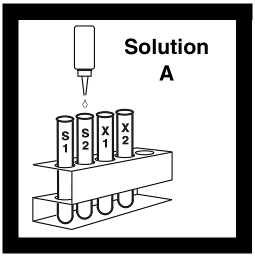
Note: *Wash Solution is a harmless dilute detergent.*

Go To
next Phase
immediately!

11. Continue to the next phase immediately

Note: *Ensure most of the Wash Solution is drained from the tubes. Turn the tubes upside down and gently tap on a paper towel to drain. Some foam may be left from the Wash Solution; this will not affect results.*

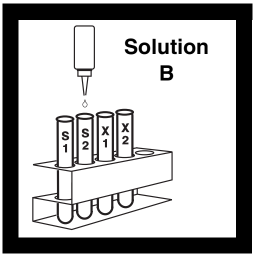
TPH Phase 3: Color Development



Check reagent labels carefully! Reagents must be added in proper order for valid test results.

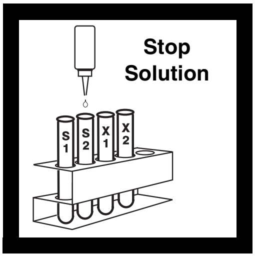
1. Add 5 drops of Solution A to each tube. Replace the bottle cap.

Note: *Hold reagent bottles vertically for accurate delivery or erroneous results may occur.*



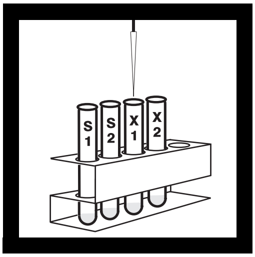
2. Begin a 2.5-minute period and immediately add 5 drops of Solution B to each tube. Swirl to mix. Replace the bottle cap.

Note: *Add drops to the tubes in the same order to ensure proper timing (i.e., left to right). Solution will turn blue in some or all of the tubes.*



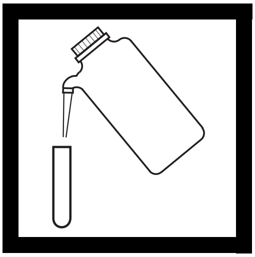
3. Let each tube react for exactly 2.5 minutes. Then add 5 drops of Immunoassay Stop Solution to each tube. Replace the bottle cap.

Note: *Blue solutions will turn yellow when Stop Solution is added. TPH concentration is inversely proportional to color development; a lighter color indicates higher levels of TPH.*

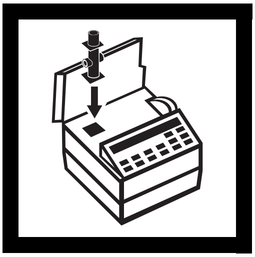


4. Using the TenSette Pipet and a new tip, add 0.5 mL of deionized water to each tube. Swirl to mix.

TPH Phase 4: Measuring the Color

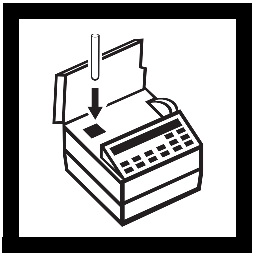


1. Fill a Zeroing Tube with deionized water (the blank). Wipe the outside of all tubes with a tissue to remove smudges and fingerprints.

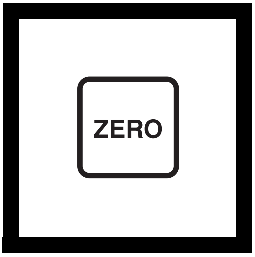


2. Insert the Immunoassay adapter into the sample cell compartment.

Note: *Align the adapter so the light beam openings face the sides of the DR/2010. Press firmly on the adapter to seat it.*



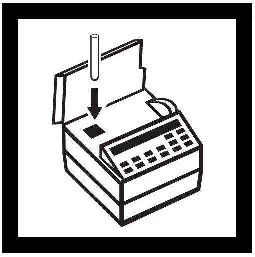
3. Place the blank in the cell holder. Place the cover on the adapter.



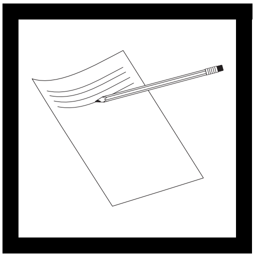
4. Press: **ZERO**

The display will show:

0.000 Abs



5. Insert Standard 1 tube into the cell holder. Place the cover on the adapter.

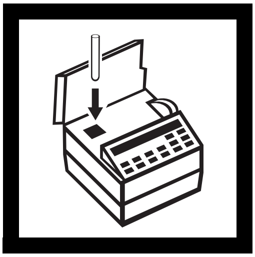


6. Record the absorbance reading.

Repeat
Steps 5 and 6
for
Standard #2

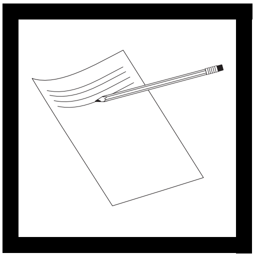
7. Repeat Steps 5 and 6 for the Standard 2 tube.

Note: *If Standard 1 and Standard 2 are more than 0.350 absorbance units apart, repeat the test beginning at Phase 2, Immunoassay.*



8. Insert the Sample 1 tube into the cell holder. Place the cover on the adapter.

Note: *TPH concentration is inversely proportional to the color intensity (or absorbance value). More color means less TPH in the sample.*



9. Record the absorbance reading.

Repeat
Steps 8 and 9
for
Sample #2

10. Repeat Steps 8 and 9 for the Sample 2 tube. See *Table 2* below to interpret results.

***Note:** Results are read as m-xylene. For other compounds, see Sensitivity section.*

Interpreting the Results

Use *Table 2* to interpret the results.

Table 2

If sample absorbance is...	Sample TPH Concentration is...
...less than the highest standard absorbance	... greater than the chosen threshold value
...greater than the highest standard absorbance	... less than the chosen threshold value

Sensitivity

The levels listed below are the concentrations in an undiluted water sample necessary to give a positive response.

Table 3

Compound	ppb	Uncertainty (90% CI)*
Gasoline	600	±100 ppb
Kerosene	920	±170 ppb
Diesel	940	±130 ppb
Jet Fuel A	490	±100 ppb
Mineral Spirits	1160	±320 ppb
Toluene	380	±50 ppb
Ethylbenzene	90	±25 ppb
m-Xylene	220	±40 ppb

* The CI, or Confidence Interval, at 90% is an expression of the uncertainty in the determined threshold value for each component listed above.

Threshold values may vary depending on the composition of the source contamination in real-world samples.

Surfactants in the sample may cause false positives.

To convert results to one of the compounds listed in *Table 3*, use the following equation:

Diluted Threshold Value for compound = (A/B) x C

where:

A = Undiluted threshold value for that compound (Table 3)

B = 220 (sensitivity to m-xylene)

C = Threshold chosen from Table 1

Example:

A water sample is tested for gasoline. The analyst uses a 20 mL sample for a 550 ppb as m-xylene threshold and a 2 mL sample for a 5.5 ppm as m-xylene threshold (from Table 1).

The absorbance readings for the standards are 0.728 and 0.780. The analyst uses the 0.780 absorbance tube as the standard value because it has the highest absorbance.

The sample absorbances are 0.206 for the 20-mL sample and 0.913 for the 2-mL sample.

When compared to the absorbance of the standard, the 20 mL aliquot indicates the sample contains more than 550 ppb as m-xylene because the sample absorbance is less than the standard absorbance. The 2- mL aliquot indicates the sample contains less than 5.5 ppm as m-xylene since the sample absorbance is greater than the standard absorbance.

Therefore, the original sample TPH concentration is between 550 ppb and 5 ppm as m-xylene.

To convert the results to read as gasoline, use the above equation.

For the 20-mL sample:

$$\frac{\text{600 ppb gasoline}}{\text{220 ppb m-xylene}} \times \text{550 ppb m-xylene} = \text{1500 ppb gasoline}$$

For the 2 mL sample:

$$\frac{\text{600 ppb gasoline}}{\text{220 ppb m-xylene}} \times \text{5.5 ppm m-xylene} = \text{15 ppm gasoline}$$

Sampling and Storage

If prompt analysis is not possible, chill the sample in an ice bath, refrigerator or cooler to limit the loss of volatile compounds. Analyze the sample as soon as possible after collection. Storing sample longer than 24 hours after collection may compromise the integrity of the sample. When collecting samples, fill containers completely (no headspace) and cover the container with a tightly sealed lid immediately after collection.

Measuring Hints

- Timing is critical; follow instructions carefully
- Handle the Antibody Tubes carefully. Scratching the inside or outside may cause erroneous results. Wipe tubes with a paper towel to remove smudges or fingerprints before measuring.
- Hold all dropper bottles vertically and direct drops to the bottom of the tube.
- Antibody Tubes and Enzyme Conjugate Tubes are made in matched lots. Do not mix with other reagent lots.
- Paper towels, liquid waste containers and laboratory tissue are required but not supplied.
- Chilling samples prior to analysis helps limit the loss of volatile compounds during Sample Preparation and Immunoassay Steps.

Storing and Handling Reagents

- Wear protective gloves and eye wear.
- Store reagents at room temperature and out of direct sunlight (less than 80 °F or 27 °C).
- Keep aluminized pouch that contains antibody-coated tubes sealed when not in use.
- If Stop Solution or liquid from the extraction jar comes in contact with eyes, wash thoroughly with cold water for 15 minutes. Seek immediate medical help.
- Operational temperature of the reagents is 40-90 °F (5-32 °C).

Summary of Method

The TPH Stabilizing Agent stabilizes the substituted aromatic organic compounds in samples. Sample, standard and color development reagents are added to test tubes that are coated with an antibody specific for petroleum fuels. The TPH concentration in samples is determined by comparing the developed color intensity to the color of a TPH standard. The TPH concentration is inversely proportional to the color development; a lighter color indicates a higher TPH concentration. Various thresholds are obtained by sample dilution. Specific compounds may be tested using the sensitivity values as described in the Sensitivity section.

REQUIRED REAGENTS AND APPARATUS

Description	Cat. No.
TPH in Water Reagent Set (5 tests)	26237-00

Includes all consumable reagents and apparatus used in the test

Description	Quantity Required PerTest	Unit	Cat. No.
Adapter, Immunoassay, DR/2010	1	each	46820-00
Ampule Breaker Kit	1	each	24846-00
Bottle, sampling, glass, square, 4 oz.	varies	3/pkg	21631-03
Clippers, large	1	each	968-00
Cover, COD	1	each	19948-00
Cylinder, graduated, mixing, 50 mL	varies	each	20886-41
Gloves, latex, medium (large: 25904-03)	pair	100/box	25904-02
Goggles, safety, vented,	1	each	25507-00
Pen, laboratory, permanent	1	each	20920-00
Pipet, WireTrol, 50/100 µL, w/ 250 capillary tubes	1	each	25689-05
Rack, grip style	1	each	25873-00
TenSette Pipet, 0.1-1.0 mL	1	each	19700-01
TenSette Pipet Tips, for 19700-01	varies	50/pkg	21856-96
Timer, 3 channel	1	each	23480-00
Zeroing Tube		each	26228-00

OPTIONAL REAGENTS AND SUPPLIES

Beaker, 100 mL	each	500-42
Water, deionized	4 L	272-56

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

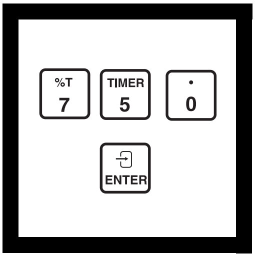
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8237

TURBIDITY (0 to 4400 FAU)

For water, wastewater, and seawater

Attenuated Radiation Method (direct reading)*



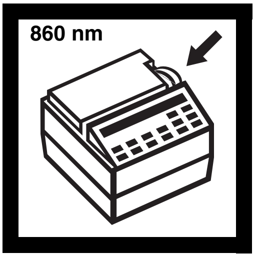
1. Enter the stored program number for turbidity.

Press: **7 5 0 ENTER**

The display will show:

Dial nm to 860

Note: *The Pour-Thru Cell cannot be used with this procedure.*



2. Rotate the wavelength dial until the small display shows:

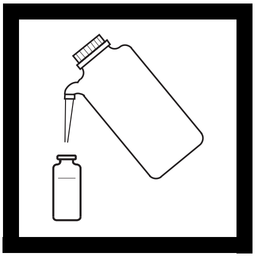
860 nm

When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

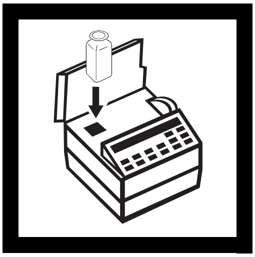
then:

FAU TURBIDITY

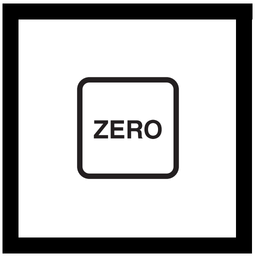


3. Pour 25 mL of deionized water (the blank) into a sample cell.

Note: *For highly colored samples, a filtered portion of the sample is used in place of the deionized water.*



4. Place the blank into the cell holder. Close the light shield.



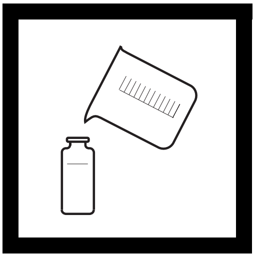
5. Press: **ZERO**

The display will show:

Zeroing. . . .

then:

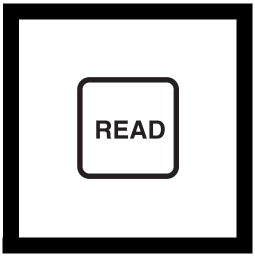
0. FAU TURBIDITY



6. Pour 25 mL of sample into another sample cell.

Immediately place this sample cell into the cell holder. Close the light shield.

Note: *The sample must be well mixed before transferring it to the sample cell.*



7. Press: **READ**

The display will show:

Reading. . . .

then the result in Formazin Attenuation Units (FAU) will be displayed.

---

* Adapted from ISO Method 7027.

Sampling and Storage

Collect samples in clean plastic or glass bottles. Analyze samples as soon as possible after collection but can be stored 48 hours by cooling to 4 °C (39 °F). Warm samples to room temperature before analyzing.

Accuracy Check

Standard Solution Method

Prepare a 200 FAU standard solution by pipetting 5.00 mL of a 4000 NTU Formazin stock solution into a 100-mL Class A Volumetric flask. Dilute to the mark with deionized water. Prepare this solution daily

Precision

In a single laboratory, using a standard solution of 1000 FAU with the DR/2010, a single operator obtained a standard deviation of ±49 FAU.

Summary of Method

This test measures turbidity, which is an optical property of the sample that results from scattering and absorption of light by particles in the sample. The amount of turbidity measured depends on the size, shape, color and refractive properties of the particles.

Formazin standards are used for calibration and readings are taken using Formazin Attenuation Units (FAU). A 4000 NTU Formazin stock standard is also defined as 4000 FAU. The optical measurement method for FAUs is very different than the NTU method. Color interference is minimized by taking measurements at 860 nm.

This test cannot be used for USEPA reporting purposes, but it may be used for daily in-plant monitoring and is best suited for measuring turbidity levels greater than 20 NTU. A turbidimeter should be used for accurately monitoring low levels of turbidity and for reporting purposes.

REQUIRED REAGENTS

Description	Quantity Required PerTest	Unit	Cat. No.
Water, deionized	25 mL	4 liters	272-56

REQUIRED APPARATUS

Description	Quantity Required PerTest	Unit	Cat. No.
Sample Cells, 25 mL, matched pair	2	pair	20950-00

OPTIONAL REAGENTS

Description	Unit	Cat. No.
Formazin Stock Solution, 4000 NTU	500 mL	2461-49
StablCal Solution, <0.1 NTU	500 mL	26597-49
StablCal Solution, 20 NTU	500 mL	26601-49
StablCal Solution, 200 NTU	500 mL	26604-49
StablCal Solution, 1000 NTU	500 mL	26606-49

OPTIONAL APPARATUS

Description	Unit	Cat. No.
Bottle, wash, 250 mL	each	620-31
Flask, volumetric, Class A, 100 mL	each	14574-42
Flask, filter, 500 mL	each	546-49
Filter Holder	each	13529-00
Filter Membrane, 47 mm, 0.45 microns	200/pkg	13530-01
Filter Pump, aspirator	each	2131-00
Pipet Filler, safety bulb	each	14651-00
Pipet, volumetric, Class A, 5.0 mL	each	14515-37
Stopper, rubber, one-hole, No. 7	6/pkg	2119-07
Tubing, rubber, 5/16” I.D.	12 feet	560-19
Tweezers, plastic	each	14282-00

Related Products

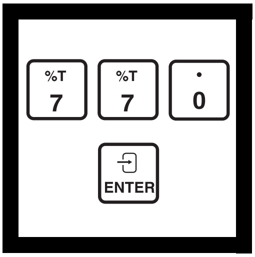
For the most precise turbidity measurements, the Hach Model 2100P Portable Turbidimeter, or Model 2100AN Turbidimeter are recommended. These instruments are true nephelometers that meet all the performance requirements for turbidity measurements described in APHA *Standard Methods,* the EPA *Methods of Chemical Analysis of Water and Wastes* and the *Federal Register.* For international use, Hach recommends the 2100 AN IS, a true nephelomter that meets ISO 7027 requirements.

Method 8196

VOLATILE ACIDS (0 to 2800 as mg/L HOAc)

For digestor sludges

Esterification Method*



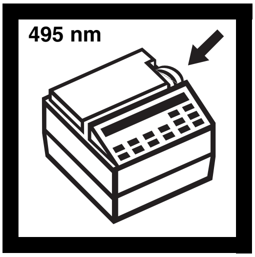
1. Enter the stored program number for volatile acids as acetic acid.

Press: **7 7 0 ENTER**

The display will show:

Dial nm to 495

Note: *If high levels of dissolved solids or mineral acids are present, see Hach's Water Analysis Handbook for alternate procedures.*



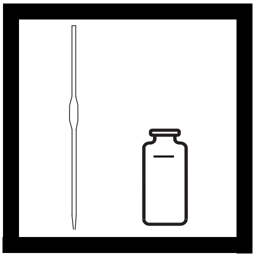
2. Rotate the wavelength dial until the small display shows:

495 nm

When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

then: **mg/L HOAc**

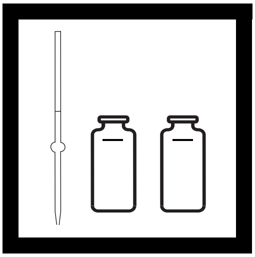


3. Pipet 0.5 mL of deionized water into a dry 25-mL sample cell (the blank).

Note: *The TenSette Pipet may be used for pipetting in this procedure.*

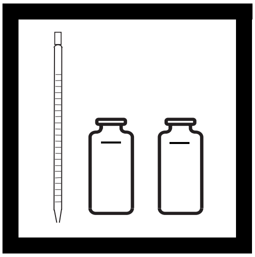
4. Filter or centrifuge 25 mL of the sample.

Note: *Centrifugation is faster than filtration.*

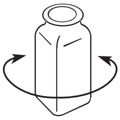


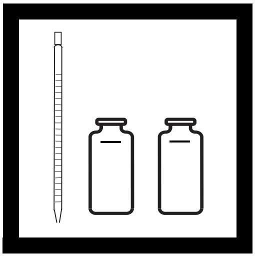
5. Pipet 0.5 mL of the filtrate or supernatant into another dry 25-mL sample cell (the prepared sample).

Note: *Use a Class A or TenSette Pipet.*

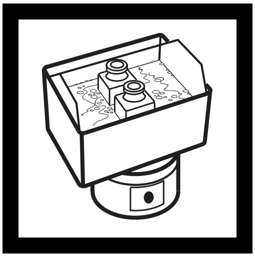


6. Pipet 1.5 mL of ethylene glycol into each sample cell. Swirl to mix.





7. Pipet 0.2 mL of 19.2 N Sulfuric Acid Standard Solution into each cell. Swirl to mix.



8. Place both cells into a boiling water bath.

Note: *Samples may be boiled in a 600-mL beaker.*

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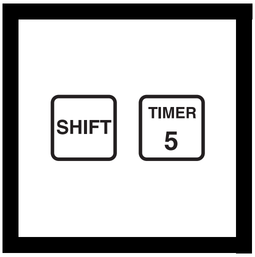
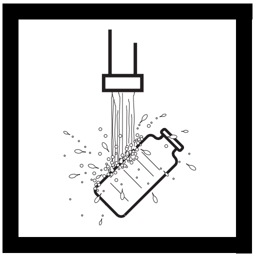
* Adapted from *The Analyst*, 87 949 (1962).



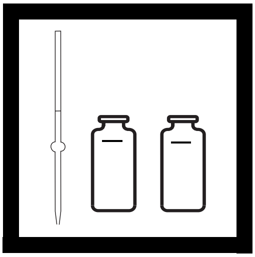
9. Press:

SHIFT TIMER

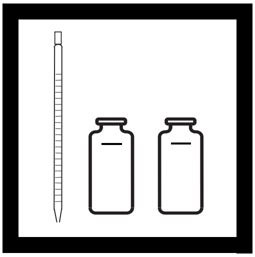
A 3-minute reaction period will begin.



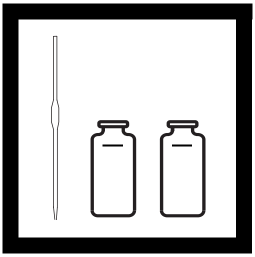
10. When the timer beeps, cool solutions to 25 °C (until cell feels cold) with running tap water.



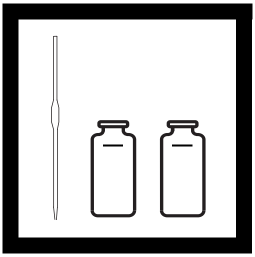
11. Pipet 0.5 mL of Hydroxylamine Hydrochloride Solution into each cell. Swirl to mix.



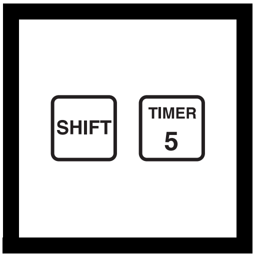
12. Pipet 2.0 mL of 4.5 N Sodium Hydroxide Standard Solution into each cell. Swirl to mix.



13. Add 10 mL of Ferric Chloride Sulfuric Acid Solution to each cell. Swirl to mix.



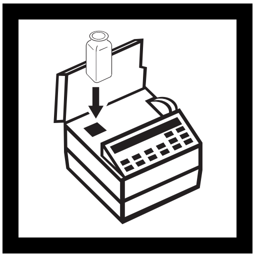
14. Add 10 mL of deionized water to each cell. Swirl to mix.



15. Press:

SHIFT TIMER

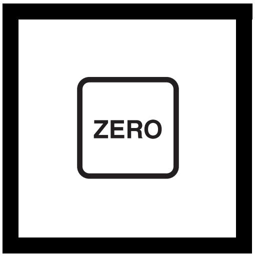
A 3-minute reaction period will begin.



16. When the timer beeps, the display will show:

mg/L HOAc

Immediately place the blank into the cell holder. Close the light shield.

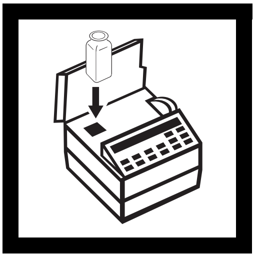


17. Press: **ZERO**

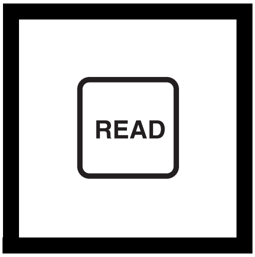
The display will show:

Zeroing. . . .

then: **0. mg/L HOAc**



18. Place the prepared sample into the cell holder. Close the light shield.



19. Press: **READ**

The display will show:

Reading. . . .

then the result in mg/L volatile acids as acetic acid will be displayed.

Sampling and Storage

Collect samples in plastic or glass bottles. Analyze samples as soon as possible after collection. Samples can be stored up to 24 hours by cooling to 4 °C (39 °F) or below. Warm to room temperature before running the test.

Accuracy Check

Standard Additions Method

a) Snap the neck off a Volatile Acids Voluette Ampule Standard Solution, 62,500 mg/L as acetic acid.

b) Use the TenSette Pipet to add 0.1, 0.2, and 0.3 mL of standard, respectively, to three 25-mL graduated mixing cylinders, each containing 25 mL of filtered sample. Stopper. Shake well to mix.

c) Remove a 0.5 mL aliquot of sample from each cylinder; add to three dry sample cells. Analyze all three samples along with the original test sample beginning with Step 6 of the procedure. The volatile acid concentration should increase 250 mg/L volatile acids as acetic acid for each 0.1 mL of standard added.

d) If these increases do not occur, see Standard Additions in Section I for more information.

Standard Solution Method

Prepare a 500 mg/L volatile acid standard by using the TenSette Pipet to add 0.8 mL of a Volatile Acids Voluette Ampule Standard Solution (62,500 mg/L as acetic acid) to a 100-mL volumetric flask. Dilute to volume with deionized water.

Precision

In a single laboratory, using a standard solution of 1550 mg/L volatile acids as acetic acid and two representative lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±34 mg/L.

Summary of Method

The volatile acids test is designed specifically for the determination of volatile acids in disgested sludges. The method is based on esterification of the carboxylic acids present and determination of the esters by the ferric hydroxamate reaction. All volatile organic acids present are reported as their equivalent mg/L acetic acid.

REQUIRED REAGENTS

Description	Cat. No.
Volatile Acids Reagent Set (90 tests)	22447-00

Includes: (1) 2039-53, (2) 2042-53, (1) 818-42, (1) 2040-53, (1) 2038-32

Description	Quantity Required Per Test	Units	Cat. No.
Ethylene, Glycol	3 mL	1000 mL	2039-53
Ferric Chloride-Sulfuric Acid Solution	20 mL	1000 mL	2042-53
Hydroxylamine Hydrochloride Solution, 100 g/L	1 mL	100 mL	818-42
Sodium Hydroxide Standard Solution, 4.5 N	4 mL	1000 mL	2040-53
Sulfuric Acid Standard Solution, 19.2 N	0.4 mL	100 mL MDB	2038-32
Water, deionized	20.5 mL	4 L	272-56

REQUIRED APPARATUS

Cots, finger	2	2/pkg	14647-02
Cylinder, graduated, 10 mL	1	each	508-38
Filter Paper, folded, 12.5 cm	1	100/pkg	1894-57
Flask, erlenmeyer, 50 mL	1	each	505-41
Funnel, poly, 65 mm	1	each	1083-67
Hot Plate, circular, 4-inch diam., 120 V	1	each	12067-01
Hot Plate, circular, 4-inch diam., 240 V	1	each	12067-02
Pipet Filler, safety bulb	1	each	14651-00
Pipet, serological, 2 mL	2	each	532-36
Pipet, volumetric, Class A, 0.5 mL	3	each	14515-34
Pipet, TenSette, 1.0 to 10.0 mL	1	each	19700-10
Pipet Tips, for 19700-10	varies	50/pkg	21997-96
Sample Cell, 25- mL, matched pair	2	pair	20950-00
Water Bath and Rack	1	each	1955-55

OPTIONAL REAGENTS

Volatile Acids Standard Solution, Voluette ampule, 62,500 mg/L as acetic acid, 10 mL	16/pkg	14270-10

OPTIONAL APPARATUS

Ampule Breaker Kit	each	21968-00
Beaker, 600 mL	each	500-52
Cylinder, graduated, mixing, 25 mL	each	1896-40
Cylinder, graduated, plastic, 250 mL	each	1081-46
Flask, volumetric, Class A, 100 mL	each	14574-42
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

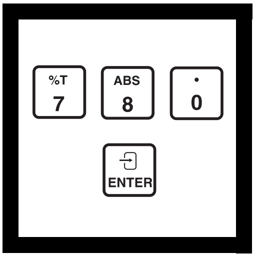
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Method 8009

ZINC (0 to 2.00 mg/L Zn)

For water and wastewater

Zincon Method* USEPA approved for wastewater analysis** (digestion needed; see Section II)



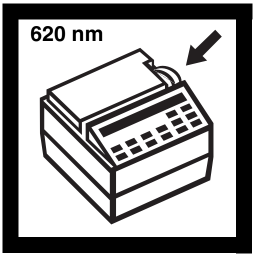
1. Enter the stored program number for zinc.

Press: **7 8 0 ENTER**

The display will show:

Dial nm to 620

Note: The Pour-Thru Cell cannot be used.



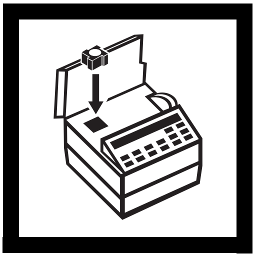
2. Rotate the wavelength dial until the small display shows:

620 nm

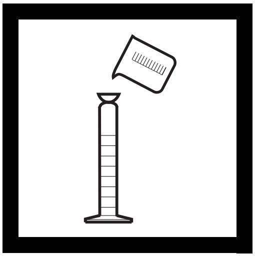
When the correct wavelength is dialed in, the display will quickly show:

Zero Sample

then: **mg/L Zn**

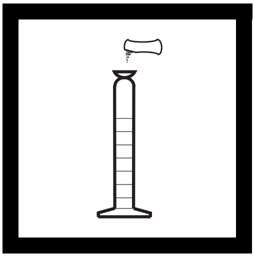


3. Insert the 10-mL Cell Riser into the cell compartment.



4. Fill a 25-mL graduated mixing cylinder with 20 mL of sample.

Note: Use only glass stoppered cylinders. Rinse with 1:1 hydrochloric acid and deionized water before use.

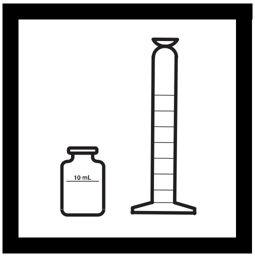


5. Add the contents of one ZincoVer 5 Reagent Powder Pillow. Stopper.

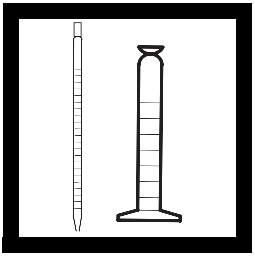
Invert several times to completely dissolve the powder.

Note: Powder must be completely dissolved.

Note: The sample should be orange. If it is brown or blue, dilute the sample and repeat the test.

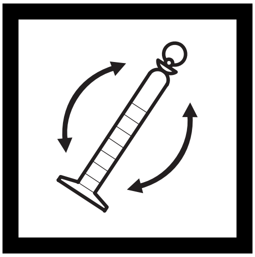


6. Measure 10 mL of the solution into a sample cell (the blank).



7. Add 0.5 mL of cyclohexanone to the remaining solution in the mixing cylinder.

Note: Use a plastic dropper as rubber bulbs may contaminate the cyclohexanone.



8. Stopper the cylinder. Shake vigorously for 30 seconds (the prepared sample).

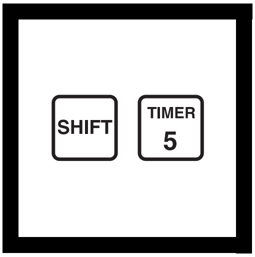
Note: The sample will be red-orange, brown or blue, depending on the zinc concentration.

***Caution:* ZincoVer 5 contains cyanide and is very poisonous if taken internally or inhaled. Do not add to an acidic sample. Store away from water and acids.**

---

* Adapted from *Standard Methods for the Examination of Water and Wastewater.*

** *Federal Register*, 45 (105) 36166 (May 29, 1980).

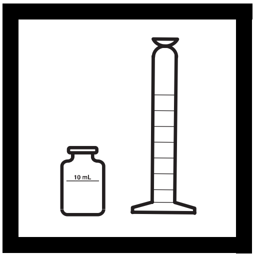


9. Press:

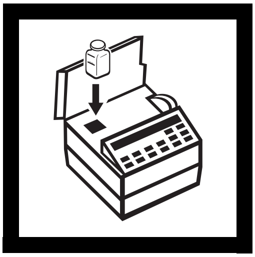
SHIFT TIMER

A 3-minute reaction period will begin.

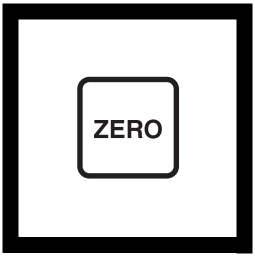
Note: *During this time period, complete Step 10.*



10. During the reaction period, pour the solution from the cylinder into a sample cell.



11. When the timer beeps, place the blank into the cell holder. Close the light shield



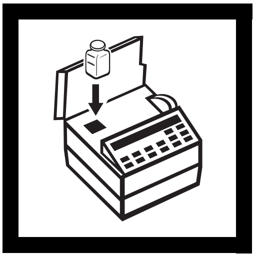
12. Press: **ZERO**

The display will show:

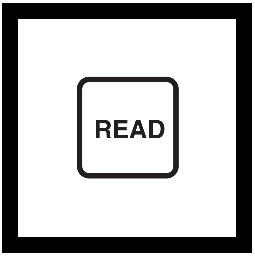
Zeroing. . . .

then:

0.00 mg/L Zn



13. Place the prepared sample into the cell holder. Close the light shield.



14. Press: **READ**

The display will show:

Reading. . . .

then the result in mg/L zinc will be displayed.

Sampling and Storage

Collect samples in acid-washed plastic bottles. For storage, adjust the pH to 2 or less with nitric acid (about 2 mL per liter). The preserved samples can be stored up to six months at room temperature.

Adjust the pH to 4-5 with 5.0 N sodium hydroxide before analysis. Do not exceed pH 5, as zinc may be lost as a precipitate. Correct the test result for volume additions; see Sampling and Storage, Volume Additions, in Section I for more information.

If only dissolved zinc is to be determined, filter the sample before adding the acid.

Accuracy Check

Standard Addition Method

a) Snap the neck off a Zinc Voluette Ampule Standard, 25 mg/L.

b) Use the TenSette Pipet to add 0.1, 0.2, and 0.3 mL of standard to three 25-mL samples. Mix each thoroughly.

c) Analyze each sample as described above. The zinc concentration should increase 0.1 mg/L for each 0.1 mL of standard added.

d) If these increases do not occur, see Standard Additions in Section I for more information.

Standard Solution Method

Prepare a 0.5 mg/L zinc standard solution by diluting 0.5 mL of Zinc Standard Solution, 100 mg/L as Zn, to 100 mL with deionized water. Prepare this solution daily.

Precision

In a single laboratory, using a standard solution of 1.00 mg/L Zn and two representative lots of reagent with the DR/2010, a single operator obtained a standard deviation of ±0.008 mg/L Zn.

Estimated Detection Limit (EDL)

The EDL for program 780 is 0.04 mg/L Zn. The EDL is the calculated lowest average concentration in deionized water matrix that is different from zero with a 99% level of confidence. For more information on derivation and use of Hach’s estimated detection limit, see Section I.

Interferences

The following may interfere when present in concentrations exceeding those listed below.

Substance	Concentration
Aluminum	6 mg/L
Cadmium	0.5 mg/L
Copper	5 mg/L
Iron (ferric)	7 mg/L
Manganese	5 mg/L
Nickel	5 mg/L

Large amounts of organic material may interfere. Perform the mild digestion (Section II) to eliminate this interference.

Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment (see pH Interference in Section I).

Pollution Prevention and Waste Management

ZincoVer 5 reagent contains potassium cyanide. Cyanide solutions are regulated as hazardous wastes by the Federal RCRA. Cyanide should be collected for disposal as reactive (D003) waste. Be sure that cyanide solutions are stored in a caustic solution with pH >11 to prevent the release of hydrogen cyanide gas.

In the event of a spill or release, clean up the area by using the following procedure:

a) Use a fume hood, supplied-air, or self-contained breathing apparatus.

b) While stirring, add the waste to a beaker containing a strong solution of sodium hydroxide and calcium hypochlorite or sodium hypochlorite (household bleach).

c) Maintain a strong excess of hydroxide and hypochlorite. Let the solution stand for 24 hours.

d) Neutralize and flush the solution down the drain with a large excess of water.

Summary of Method

Zinc and other metals in the sample are complexed with cyanide. Adding of cyclohexanone causes a selective release of zinc. Zinc then reacts with the 2-carboxy-2’-hydroxy-5’-sulfoforamazyl benzene (zincon) indicator. The zinc concentration is proportional to the resulting blue color.

REQUIRED REAGENTS

Zinc Reagent Set, 10-mL sample size (100 tests) 24293-00
Includes: (1) 14033-32, (1) 21066-69

Description	Quantity Required Per Test	Units	Cat. No.
Cyclohexanone	1 mL	100 mL MDB	14033-32
ZincoVer 5 Reagent Powder Pillows	1 pillow	100/pkg	21066-69

REQUIRED APPARATUS

Cell Riser, 10-mL	1	each	45282-00
Cylinder, graduated, mixing, 25mL	1	each	20886-40
Cylinder, graduated, 10-mL, Class A	1	each	26363-38
Sample Cell, 10-mL, matched pair	2	pair	24954-02

OPTIONAL REAGENTS

Bleach, household	1 gal	buy locally
Hydrochloric Acid Standard Solution, 6 N	500 mL	884-49
Nitric Acid, ACS	500 mL	152-49
Nitric Acid 1:1	500 mL	2540-49
Sodium Hydroxide Standard Solution, 5.0 N	50 mL SCDB	2450-26
Sodium hydroxide, 50% w/w	500 mL	2180-49
Water, deionized	4 L	272-56
Zinc Standard Solution, 100 mg/L Zn	100 mL	2378-42
Zinc Standard Solution, Voluette ampule, 25 mg/L as Zn, 10 mL	16/pkg	14246-10

OPTIONAL APPARATUS

Description	Units	Cat. No.
Ampule Breaker Kit	each	21968-00
Aspirator, vacuum	each	2131-00
Beaker, 600 mL	each	500-52
Cylinder, graduated, 100 mL	each	508-42
Dropper, plastic, 0.5 &1.0 mL marks	10/pkg	21247-10
Filter Discs, glass, 47 mm	100/pkg	2530-00
Filter Holder, glass, 47 mm, 300 mL, graduated	each	13529-00
Filter Membrane, 47 mm, 0.45 microns	100/pkg	13530-01
Flask, erlenmeyer, 250 mL	each	505-46
Flask, filtering, 500 mL	each	546-49
Flask, volumetric, Class A, 100 mL	each	14547-42
Hot plate, micro 115 V	each	12067-01
Hot plate, micro 230 V	each	12067-02
pH paper, 1 to 11 pH	5 rolls/pkg	391-33
pH Meter, *sension™1*, portable	each	51700-10
Pipet filler, safety bulb	each	14651-00
Pipet, serological, 2 mL	each	532-36
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet, TenSette, tips for 19700-01	50/pkg	21856-96
Pipet, TenSette, 1.0 to 10.0 mL	each	19700-10
Pipet, TenSette, tips for 19700-10	50/pkg	21997-96
Pipet, TenSette, tips for 19700-10	1000/pkg	21997-28
Pipet, volumetric, Class A, 5.00 mL	each	14515-37
Pipet, volumetric, Class A, 0.5 mL	each	14515-34
Sample Cell, 25-mL, matched pair	pair	20950-00
Stopper, No. 7, one hole	6/pkg	2119-07
Tubing, rubber	12 feet	560-19

For technical support and ordering information, see Section V.

In the U.S.A. call 800-227-4224 to place an order.

Outside the U.S.A.—Contact the Hach office or distributor serving you.

SECTION V GENERAL INFORMATION

HOW TO ORDER

By Telephone:	**By Mail:**
6:30 a.m. to 5:00 p.m. MST Monday through Friday (800) 227-HACH (800-227-4224) **By FAX:** (970) 669-2932	Hach Company P.O. Box 389 Loveland, CO 80539-0389 U.S.A.

Ordering information by E-mail: orders@hach.com

Information Required

- Hach account number (if available)
- Your name and phone number
- Purchase order number
- Brief description or model number
- Billing address
- Shipping address
- Catalog number
- Quantity

Technical and Customer Service (U.S.A. only)

Hach Technical and Customer Service Department personnel are eager to answer questions about our products and their use. Specialists in analytical methods, they are happy to put their talents to work for you.
Call **1-800-227-4224** or E-mail **techhelp@hach.com**.

International Customers

Hach maintains a worldwide network of dealers and distributors. To locate the representative nearest you, send E-mail to **intl@hach. com** or contact:

In Canada, Latin America, Africa, Asia, Pacific Rim:
Telephone: (970) 669-3050; FAX: (970) 669-2932

In Europe, the Middle East, or Mediterranean Africa:
HACH Company, c/o
Dr. Bruno Lange GmbH
Willstätterstr. 11
D-40549 Düsseldorf
Germany
Telephone: +49/[0]211.52.88.0
Fax: +49/[0]211.52.88.231

REPAIR SERVICE

Authorization must be obtained from Hach Company before sending any items for repair. Please contact the HACH Service Center serving your location.

In the United States:
Hach Company
100 Dayton Avenue
Ames, Iowa 50010
(800) 227-4224 (U.S.A. only)
Telephone: (515) 232-2533
FAX: (515) 232-1276

In Canada:
Hach Sales & Service Canada Ltd.
1313 Border Street, Unit 34
Winnipeg, Manitoba
R3H 0X4
(800) 665-7635 (Canada only)
Telephone: (204) 632-5598
FAX: (204) 694-5134
E-mail: canada@hach.com

In Latin America, the Caribbean, the Far East, the Indian Subcontinent, Africa, Europe, or the Middle East:
Hach Company World Headquarters
P.O. Box 389
Loveland, Colorado, 80539-0389
U.S.A.
Telephone: (970) 669-3050
FAX: (970) 669-2932
E-mail: intl@hach.com

WARRANTY

Hach warrants most products against defective materials or workmanship for at least one year from the date of shipment; longer warranties may apply to some items.

HACH WARRANTS TO THE ORIGINAL BUYER THAT HACH PRODUCTS WILL CONFORM TO ANY EXPRESS WRITTEN WARRANTY GIVEN BY HACH TO THE BUYER. EXCEPT AS EXPRESSLY SET FORTH IN THE PRECEDING SENTENCE, HACH MAKES NO WARRANTY OF ANY KIND WHATSOEVER WITH RESPECT TO ANY PRODUCTS. HACH EXPRESSLY DISCLAIMS ANY WARRANTIES IMPLIED BY LAW, INCLUDING BUT NOT BINDING TO ANY WARRANTY OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE.

LIMITATION OF REMEDIES: Hach shall, at its option, replace or repair nonconforming products or refund all amounts paid by the buyer. **THIS IS THE EXCLUSIVE REMEDY FOR ANY BREACH OF WARRANTY.**

LIMITATION OF DAMAGES: IN NO EVENT SHALL HACH BE LIABLE FOR ANY INCIDENTAL OR CONSEQUENTIAL DAMAGES OF ANY KIND FOR BREACH OF ANY WARRANTY, NEGLIGENCE, ON THE BASIS OF STRICT LIABILITY, OR OTHERWISE.

This warranty applies only to Hach products purchased and delivered in the United States.

Catalog descriptions, pictures and specification, although accurate to the best of our knowledge, are not a guarantee or warranty.

For a complete description of Hach Company’s warranty policy, request a copy of our Terms and Conditions of Sale for U.S. Sales from our Customer Service Department.

MAIL ORDER FORM

Send order to: HACH COMPANY, P.O. Box 608, Loveland, CO 80539-0608

Use this convenient form, your own purchase orders, or for PROMPT PHONE SERVICE CALL 1-800-227-4224. If ordering by phone, please have information related to items 1 - 4 (below) ready.

☐ Check box if “Ship To” information is identical to “Bill To”.

BILL TO

COMPANY

DIVISION OF

ADDRESS

CITY **STATE** **ZIP**

ATTENTION

PHONE NO. (___________) ________________________ EXTENSION ___________

SHIP TO

COMPANY

DIVISION OF

ADDRESS

CITY **STATE** **ZIP**

ATTENTION

HACH ACCOUNT NO. (If available) ❶

PAYMENT METHOD: ☐ **Check** ☐ **MasterCard** ☐ **Visa** ☐ **Purchase Order**

Card Account or Purchase Order No. ____________ Card Exp. Date ________ Signature ____________

❷ QUANTITY	❸ CAT. NO.	❹ DESCRIPTION	❺ UNIT SIZE	UNIT PRICE	TOTAL

❻ **Shipping Charge** ______

❼ **TAXABLE**? ☐ Yes ☐ No*

TOTAL ORDER ______

Prices are subject to change without notice

*If no, tax exempt document is: ☐ Enclosed ☐ On file at Hach

❶ If Hach account number is not known, leave the space blank.

❷ Most chemicals and apparatus are sold separately (“each”), but others are sold in units. Powder pillows, for example, are available in packages of 100. To purchase 100 powder pillows, order 1 unit, not 100 pillows. Be sure to order the number of units (packages) you need.

❸ Include all numbers given in the products listing.

❹ A one- or two-word description of the item.

❺ If more than one size of an item is offered, state the size you want.

❻ Unless otherwise instructed, Hach will choose the best and most efficient mode of transportation and calculate the amount.

❼ Check one box. Tax exempt status must be substantiated with documentation identifying your tax exempt number. If taxable, sales tax will be added.

TAPE HERE

FOLD HERE SECOND

NO POSTAGE
NECESSARY
IF MAILED
IN THE
UNITED STATES

BUSINESS REPLY MAIL

FIRST CLASS MAIL PERMIT NO. 100 LOVELAND, CO

POSTAGE WILL BE PAID BY ADDRESSE

HACH COMPANY—SALES DEPT.
P.O. Box 608
Loveland, CO 80539-0608

FOLD HERE FIRST