



RADIOANALYTICAL CHEMISTRY EXPERIMENTS

MOSES ATTREP

BERND KAHN

1																	18									
1	H																2	He								
3	Li	B												5	B	6	C	7	N	8	O	9	F	10	Ne	
11	Na	Mg	Al	Si	P	S	Cl	Ar	13	Al	14	Si	15	P	16	S	17	Cl	18	Ar						
19	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	32	Ge	33	As	34	Se	35	Br	36	Kr				
37	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	48	Cd	50	Sn	51	Sb	52	Te	53	I	54	Xe		
55	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	80	Tl	82	Pb	83	Bi	84	Po	85	At	86	Rn		
87	Fr	Ra	Ac	Rf	Db (105)	Sg	Bh	Hs	Mt	110	D	111	112	Cn	113	Nh	114	Fl	115	Mc	116	Lv	117	Ts	118	Og
(118)	(120)	(121)	(122)	(123)	(124)	(125)	(126)	(127)	(128)	(129)	(130)	(131)	(132)	(133)	(134)	(135)	(136)	(137)	(138)	(139)	(140)	(141)	(142)	(143)	(144)	(145)
LANTHANIDES			58	59	60	61	62	63	64																	
			Ce	Pr	Nd	Pm	Sm	Eu	Gd																	
ACTINIDES			90	91	92	93	94	95	96	97	98	99	100	101	102	103										
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr										
SUPERACTINIDES			(122)	(123)	(124)	(125)	(126)	(127)	(128)	(129)	(130)	(131)	(132)	(133)	(134)	(135)	(136)	(137)	(138)	(139)	(140)	(141)	(142)	(143)	(144)	(145)

Radioanalytical Chemistry Experiments

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 Springer

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ISBN: 978-0-387-46914-0

e-ISBN: 978-0-387-46925-6

Library of Congress Control Number: 2007938040

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Printed on acid-free paper.

9 8 7 6 5 4 3 2 1

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Acknowledgments

The authors thank the National Nuclear Security Administration, U.S. Department of Energy, for providing financial support for writing and testing these experiments under Grant DE-FG07-01ID14224, and in particular, Dan Griggs and Stephen Chase, who provided encouragement as project officers. We also thank the Georgia Institute of Technology, where this work was performed.

The authors thank their associates in the Environmental Radiation Center, EOSL, GTRI, especially Robert Rosson and Liz Thompson for their extensive and valuable editorial support; and Jeff Lahr, Ramon Garcia, and David Crowe for assistance in the laboratory. Our sympathy goes to the family of Ramon Garcia, who died while work on the Radioanalytical Chemistry text and experiments was in progress.

The authors thank the graduate students Ryan Cantor, Amir Saheb, and Christina Hampton, in the School of Chemistry and Biochemistry at the Georgia Institute of Technology, for performing most of these experiments. Moreover, Ryan Cantor helped in developing some of the experiments and selecting illustrations. We also thank Dr. Jiri Janata for reviewing early drafts of the experiments.

The Editorial Advisory Board members who worked on the Radioanalytical Chemistry Text also reviewed this manual and advised the authors. We thank:

Darleane Hoffman, Lawrence Berkeley Laboratory
Kenneth Inn, National Institute of Standards and Technology
John Keller, Oak Ridge National Laboratory
Harry Miley, Pacific Northwest National Laboratory
Stan Morton, General Engineering Laboratory
Glenn Murphy, University of Georgia
Richard Perkins, Pacific Northwest National Laboratory
Charles Porter, US Environmental Protection Agency, retired
John Wacker, Pacific Northwest National Laboratory

B.K. thanks his wife Gail for her support and encouragement. M.A. thanks his wife Katherine for her support, comments, help, patience, and encouragement during the preparation of these experiments.

Introduction to the Course

The experiments in this manual were selected to accompany the textbook *Radioanalytical Chemistry*. The manual is intended to acquaint the senior or graduate student with the practices of radioanalytical chemistry and develop some familiarity with the various techniques and methods commonly used in the radioanalytical laboratory and the counting room. The authors believe that only hands-on experience can translate the guidance provided by a textbook to an understanding of the applications that form the basis of this aspect of radiochemistry.

These experiments are based on methods actually applied or developed for instruction by the two authors during their careers in the radiochemistry laboratory. Each experiment has been tested by students in an academic laboratory setting. The experiments were practice-taught for one semester to a group of graduate chemistry students. The students' responses were then used to modify the presentation of the experiments for inclusion in this manual.

The focus of the experiments is on the work in the radioanalytical chemistry laboratory – initial sample processing, radioanalyte purification, and preparation of the sample for counting. Certain aspects of radiation detection, such as counting efficiency and self-absorption for the various radiations, are addressed in these experiments. We expect that the student learns about the principles and applications of radiation detection instruments in a separate radiation detection course, which can be presented before, after, or in parallel with this course.

More experiments were included than can be assigned in the typical 15-week semester, to allow the instructor to select experiments that most appropriately fit the selected instructional program or available resources. Most experiments are intended for two 3-hour laboratories and one 1-hour pre- or post-laboratory session per week. A few more elaborate experiments are divided into several parts so that some parts may be dropped, or additional laboratory time may be assigned to the entire experiment.

Two experiments (#11 and #17) require extensive reading of the radiochemical literature, design of a proposed experiment, discussions with the instructor, and presentation to fellow students before the student begins to perform laboratory work. If selected, these experiments should be assigned near the beginning of the semester and evaluated near the end.

Selection of experiments undoubtedly will be guided by the availability (or rather, unavailability) of specific radiation detection instruments, radionuclide solutions, or chemicals required by certain experiments. Within the limits of what is available, the instructor will wish to select those experiments that provide the best learning experience for the students and are consistent with the overall objectives of the teaching program. From personal experience, the

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authors also expect the instructor to modify some experiments and substitute others that have been found instructive and stimulating.

The specific practices and laboratory skills associated with individual experiments are briefly identified below to provide the instructor with an overview and assist in selecting experiments. A discussion of the principles to be presented and emphasized is discussed in the following section of this Introduction. The subsequent section emphasizes the safety precautions to be maintained in the radioanalytical chemistry laboratory.

Practices addressed by individual experiments

- Pipetting and weighing: #1
- Precipitation separation: #7, 8, 10, 13, and 16
- Ion exchange separation: #7, 13, 14, and 15
- Solvent extraction separation: #7 and 16
- Distillation separation: #9
- Electrodeposition: #15
- Mass spectrometry: #19
- Carrier preparation: #5, 8, 10, 13, and 14
- Tracer preparation and use: #6, 8, 15 and 16
- Methods development: #11 and 17
- Sample processing: #12
- Reagent blank use: #8, 9, 14 and 19
- Effect of radiation self-absorption: #2, 3 and 10
- Choice of methods: #7, 11, 13/14, 15/16; 17

Use of specific radionuclides

- Cesium-137: #2
- Cobalt 60: #2
- Iodine-131: #10 and 11
- Potassium-40: #3 and 4
- Plutonium-242 and -239: #6, 15, 16 and 17
- Radium-226 and -228: #8
- Strontium-90: #13 and 14
- Strontium-89: #2
- Thallium-204: #2
- Thorium-234 (from uranium): #7
- Tritium (H-3): #9
- Uranium: #7 and 19
- Mixed gamma-ray standard solution (europium-154 and -155, antimony-125): # 2
- Mixed fission product solution (about 1-week old): #18

Use of specific radiation detectors

- Alpha-particle spectrometer: #6, 7, 15 and 16
- Gas-flow proportional counter (beta and alpha particles): #2, 4, 6, 13 and 14
- Liquid scintillation counter (low-energy beta particles): #9
- Gamma-ray spectrometer: #2, 3, 8 and 18
- Radiation detector calibration: #2, 3, 4, 6, 8, 10, and 18

Before the students begin their laboratory work, the instructor is advised to emphasize the importance of the following considerations:

- Laboratory safety, as discussed below. Consult the Material Data Safety Sheets (MDSS) for information regarding hazards – carcinogens, flammability, corrosiveness, etc. – associated with chemicals used in the experiments.
- Knowledge of pertinent radioanalytical chemistry principles, including the appropriate vocabulary.
- Good laboratory practices, in particular, preparation for performing the experiment. This includes, but is not limited to, reading and comprehending the assigned experiment prior to the laboratory period and having at hand all required equipment and reagents.

Principles of Radioanalytical Chemistry

The primary function of the radioanalytical chemistry laboratory is to prepare samples for radioactivity measurement. The radioactive species are identified by detecting the radiation that they emit. The goal of the analysis is to produce a sample for counting that has no interference from other radioactive species and to quantify the recovery of the radioactive species in the analysis.

The method selected to prepare a radionuclide for counting depends on the skills and preferences of the analyst, available detectors, and conditions associated with the radioactive analyte, accompanying radionuclides, and the sample matrix. All aspects have to be considered to obtain a measurement that meets reliability and sensitivity specifications for radionuclide identification and detection. In some cases, the analyst has many options; in others, choice is restricted by circumstances such as small samples, low radionuclide concentration, half-life considerations, or unavailability of certain detector types.

The more the analyst knows concerning the numerous nuclear and radiochemical properties and characteristics of the analyzed radionuclide, the easier it is to select the most appropriate analysis and to resolve problems in ascertaining the quality and validity of the results. Especially for non-routine sample analysis, the nuclear properties of the radionuclide of interest must guide selection of the method of analysis and detection. The appropriate passages of the accompanying text *Radioanalytical Chemistry* are referenced when more detailed discussions are needed.

Overall, radiochemical analysis for the measurement of a radioactive species requires three basic steps:

- 1) preparation of the radionuclide in the sample by chemical separation and purification,
- 2) detection of the emitted radiation by an instrumental method, and
- 3) collection, analysis and treatment of data.

The execution of each step requires a range of activities, each of which are covered thoroughly in the appropriate chapters of the *Radioanalytical Chemistry* textbook. Sample separation and purification are of particular concern, in the sense that no reasonable counting data can be obtained and

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analyzed from improperly prepared samples. In brief, the following chemical preparation steps are part of any radiochemical analysis and should be performed with care and attention to detail to obtain good laboratory results.

Chemical Preparation of the Sample

Initial Sample Preparation. When received, the sample must be handled according to the proper protocol to maintain its chemical and legal integrity. Some pretreatment to preserve the sample usually is performed at collection time and should be properly described in “chain of custody” documentation that accompanies the sample, as described in the *Radioanalytical Chemistry* text.

In the laboratory, a solid sample must be dissolved or leached to release the analytes. The analysis will be conducted with the resultant solution if chemical purification is needed.

Carrier or Tracer Addition. To quantify the purified final sample that will be measured by a radiation detection instrument (as compared to a mass spectrometer), a carrier or tracer is added to the sample. The carrier usually is the same element as the radioanalyte (“isotopic carrier”) and is standardized, typically at 5–20 mg/mL concentration. The carrier serves two purposes: to provide macro quantities so that certain chemical steps (such as precipitation) may be performed on the sample, and to determine the chemical yield, usually by weight. A tracer serves only to determine the chemical yield of the process; its nanogram quantities or less, comparable to the radioanalyte in the sample, prevent use as carrier. The tracer is measured by its characteristic radiation at the same time as the radioanalyte. An advantage in alpha-particle spectral analysis is that the activity of the analyte can be calculated from the activity of the tracer without knowledge of the detector counting efficiency, as discussed below.

Isotopic Exchange/Equilibrium. Chemical steps are required at the outset of the procedure to insure isotopic exchange between the radionuclide to be analyzed (the radioanalyte) and the tracer or carrier that has been added. The carrier or tracer and the radioanalyte must be in the same oxidation state and chemical species in solution. This effort is not required for radionuclides that exist in only a single form, such as Group 1A (Li, Na, K, Rb) elements that are consistently in their +1 state in solution. Other elements (such as I or Ru) that have multiple oxidation states, and also can form stable complexes, will require steps to insure that the added carrier or tracer and the radioanalyte exchange before the analysis is started.

To illustrate this concept, assume that a sample is to be analyzed for radio-lanthanum. The lanthanum in the sample is complexed with some organic ligand (L^-) that forms an anionic complex, LaL_5^{2-} . Lanthanum carrier as La^{+3} is added to the sample but no exchange steps are performed. If the first step for the separation and purification of lanthanum is to adsorb it on a cation-exchange resin, the carrier lanthanum cation may adsorb on the column while the radio-lanthanum as a complex anion will pass through the column. When the analysis is completed, an adequate carrier yield but no lanthanum radionuclide may be observed in the sample to give an erroneously low radioanalytical result. This problem could have been avoided if the complex had been destroyed in the first step or sufficient reagent had been added to

complex the carrier and allow the radio-lanthanum and carrier lanthanum to be in the same state.

The case is different if, for instance, radio-sodium is being analyzed in a sample. The sodium ion does not form complexes, nor does it have multiple oxidation states. When mixed, the carrier ions and the radio-sodium ions are immediately rendered indistinguishable in terms of the chemical separation and purification steps. In this case, only mixing and no exchange step is required.

Chemical Separation Steps. The radioanalytical or radiochemical procedure is a series of chemical steps performed on the sample to insure that the suitably exchanged radioanalyte plus carrier are separated from substances, both radioactive and non-radioactive, that will interfere with the analysis. The final sample must be free of radionuclides that could be mistaken as the radioanalyte when counted. It also must be free of non-radioactive elements that would falsely elevate the chemical yield (recovery), excessively attenuate the emitted radiation, or otherwise interfere in the identification and quantification of the radioanalyte.

The first step after exchange often concentrates the radionuclide and carrier to perform subsequent steps more easily in a smaller volume. Further steps by precipitation, solvent extraction cycles, ion exchange, or distillation improve sample purification. In these processes, the analyte is separated from various known impurities. One type of separation step is adjusting the oxidation states of analyte or impurity. A special step may be inserted to enhance separation of an impurity that is difficult to remove.

As an example of concentration from a large volume, a silver radioanalyte can be precipitated as AgCl in an early step. This process combines purification with concentration because only palladium follows silver under specified conditions.

An example of removing multiple interfering elements is strontium purification in the presence of fission products. Ferric ion is added as a “holdback” carrier for the rare earths (and other radionuclides) and then precipitated as Fe(OH)₃, the “scavenger” that carries these radioactive impurities. This or any other step can be repeated for enhanced removal of impurities.

Preparation of the Purified Sample for Counting. The last chemical step is preparing a source for measuring the radiation emitted by the radioanalyte. Traditionally, the sample is prepared as a stoichiometric compound that is easily and reliably weighed to determine yield. The counting forms may be metals such as silver or ruthenium, complex salt such as Cs₂IrCl₆ for measuring iridium, or – more commonly – a non-hydrated insoluble simple salt or oxide. An unstable chemical form, such as one that is hygroscopic or light sensitive, would not be chosen for yield determination and counting.

When the analyte and added tracer both emit alpha particles, the samples typically are electrodeposited. Analyte and tracer are counted simultaneously, and the analyte activity is determined from the tracer activity and the ratio of the net count rate for the analyte relative to the tracer.

The sample in the final counting form must be handled with care and skill. When radionuclides that emit alpha particles are poorly electrodeposited, the quality of the counting data – the alpha-particle spectrum – may be degraded due to extraneous material deposited over the active surface. The energy peak

and the count rate beneath the peak may not be as well-defined as they should be, and one peak may interfere with another.

For samples that emit beta particles, the sample must be evenly distributed, with defined and uniform thickness. Quantifying geometry and self-absorption of beta particles is unreliable for an unevenly deposited source.

Characteristics of Successful Sample Preparation

The following characteristics should be examined to indicate whether a radioanalytical separation is successful:

- *Good Chemical Yield.* If the yield is too low, the loss suggests a sample processing problem, and measurement reliability is decreased. Many radioanalytical laboratories impose a cutoff at a minimum chemical yield value such as 50% for an analysis to be acceptable.
- *Reliable Sample for Radiation Detection.* The sample must be prepared for counting by an effective method. Many such methods have been published, each appropriate for its element. For example, strontium may be prepared for counting as strontium oxalate or carbonate, and iodine as silver or palladium iodide. Samples submitted for mass spectrometric analysis must be in a form that is suitably volatilized and processed by the instrument.
- *Low Count Rates in Blanks.* Radioactive contamination in a “blank” should be zero, or constant and extremely small. A procedure blank is a deionized water sample that is processed through the complete analysis. Carrier is added, every step is performed to the end of the analysis, and the final form is counted. Blanks are processed as part of each sample batch to check the quality of the analysis with regard to laboratory contamination for this batch.

The blank shows whether the reagents, glassware, and work environment contribute any radioactivity to samples. A blank will have a zero net count rate – that is, the measured or gross count rate minus the detector background count rate – if no radioactivity is observed. If the net count rate is above zero, it should be low compared to the net count rate of the analyte. Efforts should be made to find and reduce the source of contamination.

- *Radiochemical Purity.* A sample is radiochemically pure at the time of counting if no other radionuclide is detected in it. As a general rule, the radiochemical procedure is chosen to separate from the radioanalyte all other radionuclides that are in the sample. Purification steps must be added to the usual procedure if the level of contaminant radionuclides is very high relative to the concentration of the radioanalyte.

Re-analysis with better purification should be considered if the count rate is unexpectedly high or the observed half life and radiation energies are not those of the radioanalyte. Contaminant radionuclides may be tolerated if they do not interfere with counting the radioanalyte, or can be subtracted from the count rate with only a minor increase in detection uncertainty. In spectral analysis of alpha particles and gamma rays, for example, contaminant radionuclides are tolerated in the sample if they do not interfere with counting the characteristic spectral peaks of the analyte.

- *Chemical Yield versus Radiochemical Purity.* The conditions for acceptance or rejection on the basis of chemical yield may have to be revised when a sample contains major contaminants. The needed additional purification steps invariably decrease the chemical yield, hence a chemical yield below 50 percent may be acceptable. A skilled radiochemist is capable of minimizing those losses while producing a high-purity sample. This ability to balance purity and yield comes with practice, knowledge of radioanalytical techniques, and familiarity with the chemistry of the elements involved.

Additional Considerations: Radionuclide Source and Category

Because more than 1,000 radionuclides have been observed, laboratories generally specialize by categories such as source, half-life, type of emitted radiation, sampling location, and amount. Overlap in categories is inevitable. For example, the products of fission may be accompanied by activation products; they may be short-lived at high levels in the process stream and long-lived at low levels in the environment.

Analyte half-lives need to be considered to arrange for rapid collection, transfer to the laboratory, and radioanalytical chemistry processing before they decay to poorly-detectable low amounts. Types of emitted radiation control the detector that must be purchased, calibrated, and operated. Radiochemists and radiation-detector operators who commonly handle a specific category of radionuclides become skilled in purifying and counting these radionuclides.

Among common radionuclide sources are the natural environment, fallout from nuclear weapon tests, effluents from nuclear research laboratories, the nuclear power fuel cycle, radiopharmaceutical development, manufacturing, and various application, teaching and research uses. Decontamination and decommissioning activities at former nuclear facilities and the potential of terrorist radionuclide uses are current topics of interest for radioanalytical chemistry laboratories. Simplified information on the numerous radionuclides is conveniently found in *Charts of the Nuclides* such as *Nuclides and Isotopes* (revised by J. R. Parrington, H. D. Knox, S. L. Breneman, E. M. Baum, and F. Feiner, 15th Edition, 1996, distributed by GE Nuclear Energy).

The sources of the radionuclide samples sent to the laboratory include the environment, nuclear facilities (for process control and bioassay monitoring), and nuclear research laboratories. Each contributes its own set of radionuclides. In environmental samples, for example, one may find the naturally-occurring radionuclides $^{226+228}\text{Ra}$ and isotopes of U and Th, and man-made ^3H (tritium), ^{90}Sr , ^{99}Tc , $^{131+129}\text{I}$, ^{137}Cs , isotopes of Pu, and ^{241}Am . Appendix 1 has a list of commonly analyzed radionuclides in environmental samples, and Appendices 2, 3, and 4 show the natural decay series for ^{238}U , ^{235}U , and ^{232}Th , respectively.

Laboratories specialize in analyzing radionuclides at either high or low levels. Personnel-protection installations and practices are required for high levels of radiation from high levels of radionuclides. Low-level radioanalytical chemistry requires separation from high levels because results are easily undermined by contamination.

Working with Radioactivity: Rules, Practices and Safety Precautions

Any chemistry laboratory is a place that has many sources of hazards, including explosive, toxic or flammable chemicals, noxious vapors, broken glass, and hot liquids and solids. In addition to the rules given below, good practice requires that the instructor and student review each experiment for all potential hazards and discuss steps to avoid or mitigate such hazards. The review should include considerations of dangerous chemicals and conditions in each experiment.

Radioanalytical chemistry laboratories generally are divided into three separate areas: (1) a sample-receiving facility, (2) a wet laboratory for initial sample processing, radionuclide separations, and counting-source preparations, and (3) counting rooms where radiation detection and measurement equipment is housed. The counting room is separated to maintain the detectors and their electronic systems in a clean and stable environment. The student is required to follow all procedures, rules, and protocols established for the laboratory and counting room. Failure to do so may result in radioactive contamination and the considerable expense and effort to restore the working facilities to their original utility and cleanliness. The institution where this course is being taught undoubtedly has training requirements that must be met before the student embarks on any work with radioactive materials. The instructor will inform the students of these requirements.

Safe handling of chemicals and radionuclides in these experiments requires practice and the exercise of attention and care. This is true for all levels of radioactivity, including levels in the becquerel range.

For the purposes of these experiments, the following practices are strongly encouraged. The instructor may insist on additional practices and recommend reading a designated safety manual. In addition, Chapter 14 of the textbook *Radioanalytical Chemistry* covers the topic of laboratory safety. The student's responsibility is to follow all rules presented here, by the instructor, and in the safety manual.

- Wear personal protective equipment when chemical and radioactive materials are handled. This includes eye protection gear, a laboratory coat, and gloves (rubber or plastic).
- Always treat laboratory equipment in a radioanalytical chemistry laboratory as if it contained or had contained radioactive material. Glassware that has been used with radioactive material should be segregated and properly labeled.
- Always handle radioactive solids, solutions, and gases in a work area that can be easily cleaned and checked for radioactivity.
- Never pipette by mouth.
- Do not perform any laboratory work in the counting room area.
- Do not eat, drink, smoke or chew in a radiological area.
- Perform experiments with volatile materials or radioactive gases in a well-ventilated fume hood rated for that class of work. Good practice for safety purposes is to conduct most work with radioactive materials in a fume hood.
- After a radioactive spill or other contamination of persons or environment, immediately notify the laboratory instructor so that he/she can inform the

Radiological Safety staff and instruct you about the proper method and protocol for cleaning up the spill, not spreading the contaminant, and monitoring persons and areas.

- At the conclusion of the laboratory period or an experiment, and when leaving the laboratory area for any reason, monitor hands, feet, head, body, and clothing with a hand-held radiation counter before exiting, as specified by your instructor. Your laboratory instructor will demonstrate the proper technique and show you the proper instruments for the type of radiation you that you will use.
- Dispose of all wastes in accord with instructions.
- Return all radioactive and chemical materials to their place of storage. This may simply mean returning the radioactive materials to the laboratory instructor and the chemicals to their storage cabinets.
- Keep all laboratory equipment and materials in the radiological work areas. They should not be transported to non-radiological work areas unless given permission by the laboratory instructor.
- Maintain good housekeeping in the laboratory. Keep hoods, bench tops, and floor unobstructed. When carrying over an experiment from one period to the next, store materials that you are using neatly and place them so they do not interfere with activities by others or are in danger of being spilled or overturned. At the conclusion of an experiment, clean up so no residue of the work remains.
- Ask the instructor if you are uncertain regarding any practice or step. In case of doubt, do not proceed on your own.

Experiment 1

Practice in Pipetting and Weighing Samples for Radioactivity Counting

Objective

To practice pipetting small volumes and weighing small quantities that are encountered in a radioanalytical chemistry laboratory.

Introduction

The radioanalytical chemist must be skilled in handling samples for making radioactivity measurements. While weighing and pipetting are two skills that chemists should already have mastered, it is possible that the small quantities of material normally required for radioanalytical work might present some difficulty. This experiment is designed to hone the student's ability to perform small-scale mass and volume measurements. These exercises focus on using an analytical balance that is capable of measuring mass to within 0.01 mg, and pipettes in the range of 10 μL ($1 \mu\text{L} = 0.001 \text{ mL}$) to 1.0 mL in capacity.

Any functional set of pipettes can be used. However, the student should be familiar with the two main types of pipettes: glass μL pipettes and automatic pipettes.

As a reminder, pipettes are classified either TD (to deliver) or TC (to contain). The TD pipettes are the more common of the two. With a TC-type pipette, the residual contents in the pipette must be extracted by repeated washing. Always read the label of a glass pipette to determine if it is TD or TC.

Automatic plastic pipettes have become a common feature in the laboratory, and are gradually replacing glass μL pipettes in everyday use. These pipettes are controlled by a specified-volume button or dial-volume controls commonly, and are used to deliver small volumes with accuracy.

In this experiment, three or four types of pipettes are selected to deliver water to a clean container. By weighing the delivered volumes, the accuracy of the different delivery methods is compared. The experiment also allows for the precision of pipette delivery to be observed.

Safety Reminders

- Follow the usual safety procedures when working in a radiological laboratory.
- Caution should be exercised when preparing and working with corrosive mineral acids.
- All liquids/solids are to be properly disposed of according to laboratory rules and protocol.

Equipment and Supplies

If your laboratory no longer employs glass pipettes, use only the automatic plastic type in this experiment.

- 1-mL volumetric pipette designated TD (to deliver)
- 1-mL pipette, graduated in 0.1 mL units (Mohr type)
- 0.01 mL (10 λ) automatic pipette designated TD (to deliver)
- 0.1 mL (100 λ) automatic pipette designated TD (to deliver)
- 0.1 mL (100 λ) glass micro-pipette designated TC (to contain) (optional)
- planchets with 0.5-cm-high lip (sides), stainless steel (or other suitable container)
- analytical balance capable of weighing to 0.1 mg
- forceps

Reagents

- Deionized water

Procedure

- Step 1. Mark and weigh six clean, dry planchets. Record weights to the nearest 0.1 mg. *Use forceps. Do not handle the planchets with your hands because residue from fingers will compromise weight.*
- Step 2. Deliver the following quantities of water to the planchet and immediately weigh after each delivery. *If the liquid is not weighed immediately, sample loss by evaporation can cause error.* Perform each measurement twice.

A	1 mL of water with the 1-mL volumetric pipette designated TD
B	1 mL with the 1-mL pipette, graduated in 0.1 mL units
C	0.1 mL with the 1-mL pipette, graduated in 0.1 mL units
D	0.1 mL with the 100-lambda glass micro-pipette designated TC
E	0.1 mL with the 100 lambda automatic pipette designated TD
F	0.01 mL with the 10 lambda automatic pipette designated TD

Record these measurements in Data Table [1.1](#).

Data Table 1.1 Measurements Collected in Step 2

Measurement	Planchet Weight	Planchet + Water Weight 1	Planchet + Water Weight 2
A			
B			
C			
D			
E			
F			

Data Table 1.2 Measurements Collected in Step 3

Measurement	Planchet Weight	Planchet + Water Weight
1A		
2A		
3A		
4A		
1F		
2F		
3F		
4F		

Step 3. Prepare and weigh eight clean, dry planchets as in Step 1. Deliver 1 mL of water with a 1 mL volumetric pipette designated **TD** to each of 4 planchets and 0.010 mL of water with a 10- λ pipette (**TD**) to each of the other 4 planchets and weigh them again. Record the measurements in Data Table [1.2](#).

Treatment of Data

Subtract the tare weights to obtain net weights of water delivered. Using a density value of 0.998 g/mL at room temperature (22 °C), calculate the volume from the average mass. Distinguish **TD** and **TC** results.

Prepare Data Table [1.3](#). Calculate the percent deviation (+/-) of the experimental volume recorded from the volume value marked on the pipette. See the *Radioanalytical Chemistry* textbook, Section 10.3 “Measurement Uncertainty,” for guidance on calculating standard deviation.

Data Table 1.3 Treatment of Data Collected in Step 2

Measurement	Average Water Weight	Experimental Volume
A		
B		
C		
D		
E		
F		

Data Table 1.4 Treatment of Data Collected in Step 3

Measurement	Average Water Weight	Standard Deviation
1A-4A		
1F-4F		

Standard Deviation = _____

Prepare Data Table 1.4. Calculate the average of each set of four measurements and the standard deviation of the mean. Compare the average of measurements 1A-4A and 1F-4F in Step 3 to the average measurement of (A) and (F) in Step 2.

Questions

1. Which delivery system is, in your opinion, the most reliable to deliver 0.1 mL of solution? Explain.
2. In Step 2, each planchet sample was weighed twice. In Step 3, four different planchets samples were prepared identically and weighed. Explain the different purposes of the replicate measurements made in these steps.
3. List sources of error in making weighing measurements to determine volume in this manner.
4. In many laboratories, the liquid measurements are performed by mass rather than by volume. List the pros and cons of making the measurement by volume and by weight. Which would you select? Why?
5. Devise an experiment to compare measuring by mass and by volume for minimizing uncertainty due to evaporation.

Experiment 2

Radiation Detection Instrument Calibration and Quality Assurance

Objective

This Experiment is split into two parts. The objective in each is to calibrate a detector.

In Part 2A, the student will calibrate a gas-flow, end-window, anti-coincidence proportional counter for beta-particle counting efficiency as function of energy with certified standard solutions, and perform quality assurance (QA) counting tests.

In Part 2B, the student will calibrate a germanium (Ge) gamma-ray spectrometer with certified standard solutions for counting efficiency as function of energy and sample volume, and perform quality assurance (QA) counting tests.

Calibration of alpha-particle detectors is addressed in Experiment 6.

Calibration of a liquid scintillation detector for beta-particle counting is discussed in Experiment 9.

Overview

With minor exceptions, the samples handled in a radiochemical laboratory are eventually measured with radiation detection instruments. The types of counting equipment in the counting room depend primarily on the scope and purpose of the radioanalytical chemistry laboratory mission. Common detectors of this type are listed in Table [2.1](#).

The extent of accompanying electronic and computer support depends on the mission and work load of the laboratory.

The detection systems first must be calibrated for counting efficiency to permit conversion of the sample count rate to the disintegration rate. These systems are monitored periodically for their stability and performance by measuring the count rates of reliable radionuclide sources and the radiation background. Records are maintained for each instrument to comply with quality assurance specifications. Graphs of count rates recorded at frequent intervals for periods of months or years provide a visual record of detector and background stability and indicate deviations from the norm.

Table 2.1 Common Detectors

Detector Type	Examples
Alpha-particle detector	proportional counters; silicon (Si) diode with spectrometer
Beta-particle detector	proportional counters; Geiger-Muller counters; liquid scintillation (LS) counters
Gamma-ray detector	thallium-activated sodium iodide (NaI(Tl) detector with spectrometer; germanium (Ge) detector with spectrometer

Part 2A: Introduction

The counting efficiency of most beta-particle and gamma-ray detectors depends on radiation energy. In the proportional counter system shown in Fig. 2A.1, some beta particles are stopped before they enter the sensitive detection volume by the sample itself, any sample covering, the air between the sample and the detector, and the detector window. The beta particles that are stopped before they enter the detector in the shown system have energies below ~ 40 keV. This fraction of beta particles removed from the flux directed toward the detector window is relatively large for beta-particle groups with low maximum energies, and relatively small for beta-particle groups with high maximum energies. The fraction of low-energy beta particles also is affected by the shape of the beta-particle spectrum, which varies among radionuclides.

The counting efficiency for the shown system approaches 52% for radionuclides with high maximum beta-particle energies (see Fig. 2A.2). This value exceeds the 39.6% based on the geometry of a 2.2-cm-dia. sample on a filter relative to the detector window. The counting efficiency exceeds the

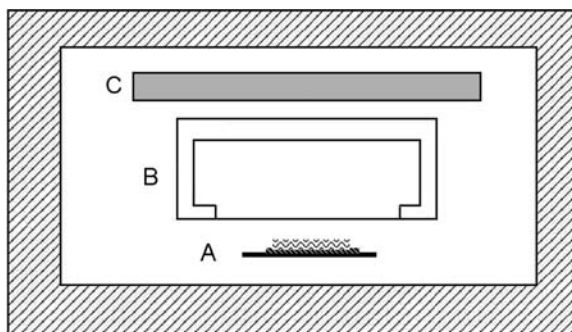


Figure 2A.1 Cross-sectional view of a low-level anti-coincidence beta-particle counter. A. Sample on a planchet. B. Thin window detector. C. Guard detector. Lead shielding surrounds the entire detector system. Typical background count rates are about 1 count per minute for beta particles and 0.1 count per minute for alpha particles. A sample mounted on a planchet (A) is placed below the thin window. When the guard detector (C) is triggered by an extraneous radiation that penetrates the lead shield, the sample detector (B) is inactivated. Immediately following, the detector (B) responds to beta particles from the sample. For low-activity samples, the probability is low that a particle from the sample registers a pulse at the same time that the counter is inactivated.

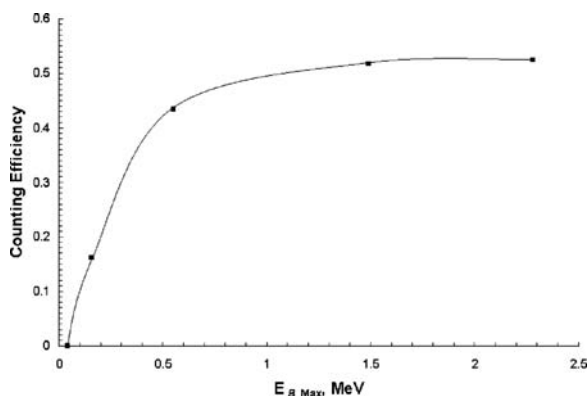


Figure 2A.2 Typical curve of beta-particle counting efficiency vs. energy for a thin-window proportional counter.

geometric arrangement because of scattering from the sample support and nearby solids. Back-scattering adds about 0.25 of the direct radiation, and other scattering, about 0.02.

Beta particle calibration sources span energies from about 100 to 3,000 keV for proportional counters, and down to a few keV for liquid scintillation counters. In this experiment, a low-background, gas-flow, end-window proportional counter with automatic sample changer for alpha- and beta-particle counting is calibrated. Beta-particles sources are counted with pulse-height discrimination to eliminate interference from alpha particles; the discriminator may be turned off when no alpha particles are present.

The samples in this experiment are prepared for beta-particle counting by pipetting a selected small volume of a radionuclide standard solution onto the center of a planchet and then evaporating the solution to dryness. The planchet is then placed to face the end-window of the detector for counting. For the usual low-level samples, the planchet is placed as close to the window as possible without damaging or contaminating the window, and is counted for an extended period, typically for several thousand seconds. Blank planchets also are counted – usually for even longer periods – to measure the radiation background of the system. Considerable time is needed to count all samples, hence the completion of this experiment will be delayed until all data are accumulated and processed.

The counting efficiency (ϵ) of the proportional detector is calculated as the ratio of the net count rate, in s^{-1} , to the activity (A), in Bq, of this standard radionuclide solution. The net count rate is the standard's gross count rate (R_G) minus the detector's background count rate (R_B). The reported disintegration rate (A) is the product of the radionuclide concentration, in Bq L^{-1} , and the amount of counted sample, in L, adjusted for the radioactive decay of the radionuclide between standardization and measurement. Equation 2A.1 is the general form of this equation.

$$\epsilon = \frac{R_G - R_B}{A} \quad (2A.1)$$

An alternative unit to the Bq, or disintegration per second, is the curie (Ci), which is 3.7×10^{10} dps (the activity of 1.0 gram of radium). Appendix 5 has

definitions for the two major units of radioactivity and the multiple units in the international system (SI).

The counting efficiency is used to calculate the disintegration rates of samples of known radionuclide identity but of unknown activity (to the student) from their count rate and volume or mass. The counting efficiency of radionuclides other than those used for calibration may be estimated by interpolating efficiencies as a function of maximum beta-particle energy, and adjusting for the decay fraction when multiple beta-particle groups are emitted by a single radionuclide.

The beta-particle counting efficiency for a specific detector and radionuclide depends on numerous factors, notably intrinsic detector efficiency, the source dimensions, distance from the detector, thickness and electron density, support (backing) characteristics, scattering and attenuation environment, and beta-particle energy distribution. Hence, the counting efficiency for other radionuclides may differ somewhat from the interpolated estimate, and to a greater degree for samples that are precipitated with different amounts and types of carrier, or placed in different sample holders. The effect of sample thickness is shown in Experiment 4. More discussion of counting efficiency can be found in your *Radioanalytical Chemistry* textbook, Section 8.2.1.

Safety Reminders

- Follow the usual safety procedures when working in a radiological laboratory.
- Caution should be exercised when preparing and working with corrosive mineral acids.
- Liquids and solids are to be properly disposed of according to laboratory rules and protocol.
- Standards must be returned to the designated place of storage.

Equipment and Supplies

- Low background gas-flow, end window proportional counter with automatic sample changer for alpha and beta counting (or equivalent counting system)
- Steel planchets, 5-cm-dia., with 0.5-cm-high sides
- Pipettes, 100 μ

Reagents

- Three certified standard low-level beta-particle solutions such as ^{60}Co ($E_{\text{beta max}}$ 0.32 MeV, 99.9%), ^{204}Tl (0.76 MeV, 97.1%), and ^{89}Sr (1.50 MeV, 100%), each about 100 Bq/L
- Beta-particle solution of activity unknown to the student

Procedure

Step 1. Place 10 blank planchets in the proportional counter system and count each for 50,000 s at settings (a) and (b) to determine the beta-particle background count rate.

- a) beta particle, no alpha/beta pulse-height discrimination
- b) beta particle with alpha/beta pulse-height discrimination

Record your measurements in Data Table [2A.1](#)

Step 2. Prepare sources in duplicate for the proportional counter by pipetting the appropriate volume – typically 100λ – specified by the instructor of each of 3 standard solutions and the unknown solution onto the center of a separate planchet. You will have a total of 8 planchets: 2 each for the beta-particle standards and the unknown beta-particle sample. Dry under heat lamps placed at sufficient distance over the planchets for slow drying.

Step 3. Place in the counter sample changing system the planchets with the the beta-particle standard sources and the unknown beta-particle sample. Add two background planchets. Set the time control to count each sample for a time period specified by the instructor so that each accumulated count is at least 1,000 counts (typically, 500 s per sample, 50,000 s per background). Count each of the samples at settings (a) and (b). Repeat the count. Record your measurements in Data Table [2A.2](#)

Step 4. Count one of the beta-particle standard sources 10 times, using setting (a). Record your measurements in Data Table [2A.3](#)

Data Table 2A.1 Background Data for Step 1

Planchet #	Beta Count Rate under Setting (a)	Beta Count Rate under Setting (b)
1		
2		
3		
4		
5		
6		
7		
8		
9		
10		

Data Table 2A.2 Sample Counting Data for Step 3

Planchet ID	Beta Count Rate under Setting (a)	Beta Count Rate under Setting (b)
β Std 1		
β Std 1		
β Std 2		
β Std 2		
β Std 3		
β Std 3		
β Unk 1		
β Unk 2		
Bkg 1		
Bkg 2		

Data Table 2A.3 Replicate Beta-particle Counts for Step 4

Planchet ID	Beta Count Rate under Setting (a)
β Std Count 1	
β Std Count 2	
β Std Count 3	
β Std Count 4	
β Std Count 5	
β Std Count 6	
β Std Count 7	
β Std Count 8	
β Std Count 9	
β Std Count 10	

Treatment of Data

See Appendix 6 and the *Radioanalytical Chemistry* textbook for definitions and formulae for calculating count rate and standard deviation (σ) with error propagation.

Blank Planchet Background Counts

When all the samples have been counted, collect the counting data and perform the following calculations.

- Compute the mean value (m) in counts per s and the standard deviation (σ) for the results of the background counts at each setting.
- Determine the values of $(m + 2 \sigma)$ and $(m - 2 \sigma)$, and also for the 3σ range. These ranges will serve as the warning and control limits for the beta-particle background.

Standard Solutions and Unknown Solutions Counting Data and Calculations

Use the data from the measurements of the solutions of standards and unknown to calculate the following for each, with standard deviation. The instructor will provide the beta-particle values in disintegration per minute values for the standard sources.

- Calculate the beta-particle counting efficiency observed for the standard solutions in both detector settings, using the following Equation 2A.2:

$$\varepsilon = \frac{R}{VADF} \quad (2A.2)$$

where:

- ε = counting efficiency
- R = net count rate, cps
- V = sample volume (or mass), L (or kg)
- A = activity, Bq L⁻¹
- F = fraction of total activity assigned to measured radiation
- D = decay correction for interval between time for which activity is determined and sample is measured

- b. Calculate the average net count rates of the unknown solution with the standard deviation in count per second
- c. For each beta-particle standard source, calculate the efficiency at both settings (with and without discrimination) and record in Data Table 2A.4. Determine the standard deviation for each setting. Calculate the fraction of the beta activity that is removed by alpha/beta pulse-height discrimination for the sample and the standard source.
- d. Prepare a graph of counting efficiency vs. maximum beta-particle energy for the three beta-particle standards.
- e. Estimate the beta-particle activity in Bq L⁻¹ of the unknown solution, based on the maximum beta-particle energy of the radionuclide identified by the instructor and the above-constructed curve.
- f. Calculate the standard deviation of the mean count rate for the standard source that was measured repeatedly.

Data Table 2A.4 Calculated Counting Efficiencies

Planchet ID	Efficiency under Setting (a) and σ	Efficiency under Setting (b) and σ	Fraction of Count Removed under Setting (b)
β Std 1			
β Std 2			
β Std 3			
β Unk			

Questions

1. Compare the standard deviation of the set (mean) to the standard deviation of a single count.
2. What is the difference between the beta particle count rate with and without pulse-height discrimination?
3. What is the significance of 1σ , 2σ , and 3σ deviations reported with a numerical value? For the beta-particle standard solution counted repeatedly, what percentage of the values is in the range of $+1\sigma$ to -1σ ?
4. How does the beta-particle-efficiency value (ε), calculated from your data, compare to that used by the count room for the same counters? If it is more than 5% higher or lower, give a reasonable explanation.

Part 2B: Introduction

One of the three major systems in the radioanalytical chemistry counting room is the gamma-ray spectrometer. This detection system generally has the particular advantage of requiring little or no sample processing. Large samples can be counted because gamma rays are relatively penetrating, and purification is not needed if a specific radionuclide can be measured by its characteristic gamma rays in the presence of other radionuclides. The high-purity germanium (Ge) detector has the advantage, relative to the thallium-activated sodium iodide [NaI(Tl)] detector, of about 40-fold better resolution, defined as the full width of a peak at half its maximum height (FWHM). That is, the spectrometer for a Ge detector has the potential for showing many more peaks, fully separated from each other, than does a NaI(Tl) detector. The spectrometer for a Ge detector usually has 1,024 or 4,096 channels to display this good resolution.

Passage of a gamma ray into a detector results in a full-energy peak by the photoelectric effect, as well as two other primary interactions that result in an energy continuum by Compton scattering and peaks by the pair production interaction at 0.51 MeV and at the full energy minus twice 0.51 MeV (see Chapter 2 of the text *Radioanalytical Chemistry*). Secondary interactions add to the full-energy peak, can cause peak summing for two or more simultaneously detected gamma rays, add to the energy continuum due to external gamma-ray scattering, and may show an “escape peak” just below the full-energy peak.

A full-energy peak associated with a characteristic gamma ray that is emitted by the radionuclide of interest usually is selected for identifying the radionuclide. Further, the count rate beneath this peak is integrated for use as the gross count rate, R_G , related to the activity of the radionuclide, as shown in Equation 2A.1. The background count rate, R_B , is estimated from the 2 or 3 channels to each side of the peak, by summing their count rates and multiplying by the ratio of the number of channels that represent the peak divided by the number of channels used on the sides of the peak.

The counting efficiency for full-energy peaks detected with a Ge spectrometer system initially increases with energy and then decreases, as shown in Fig. 2B.1. The initial increase is due to decreasing attenuation of gamma rays with increasing energy in the metal container of the Ge detector. The curve of efficiency with energy decreases from the maximum value due to decreasing fraction of energy deposition in the detector as the gamma-ray energy increases. The shown values were obtained both by measuring radionuclide standards and by Monte Carlo simulation. The decreasing values have been found to resemble a straight line in logarithmic coordinates over the indicated range.

In this experiment, the Ge detector with spectrometer is calibrated for its efficiency, ϵ , with a standard that emits a set of gamma rays at energies that span the range of interest, usually from a few keV to 1.5 MeV. The counting efficiency is calculated from the ratio of the net count rate to the reported disintegration rate at each full-energy peak in the spectrum. A correction for radioactive decay is needed.

These counting efficiencies are determined for a series of sample volumes. Curves of counting efficiency as functions of gamma-ray energy are drawn

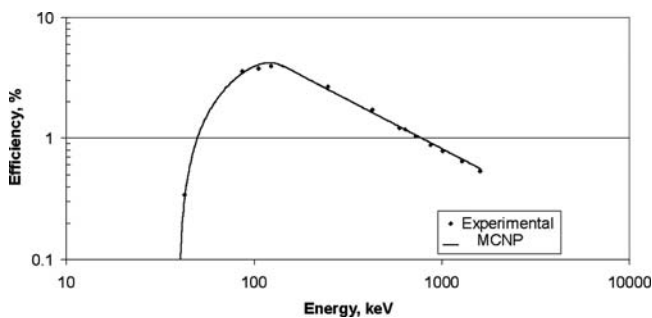


Figure 2B.1 Typical curve of gamma-ray counting efficiency vs. energy for Ge detector

for the various sample volumes. Differences as a function of volume can occur because of changes in the amount of radionuclide in the source, the geometrical relation of source to detector, and gamma-ray self-absorption (see Experiment 3).

Quality assurance (QA) measurements also are performed with a set of QA gamma-ray sources to confirm that the radiation detection instrument is functioning normally. The measurements are performed at regular intervals and the results are plotted to show the mean value and random deviations by 1 and 2 standard deviations (σ and 2σ). The factors that are considered include the count rate at characteristic control source peaks, the resolution of these peaks, and the background radiation shown by the detector. Any significant deviations beyond the 2-sigma values on the control charts require a repeated measurement and – if confirmed – corrective actions before further measurements are performed.

Safety Reminders

- Follow the usual safety procedures when working in a radiological laboratory.
- Caution should be exercised when preparing and working with corrosive mineral acids.
- Liquids and solids are to be properly disposed of according to laboratory rules and protocol.
- Standards must be returned to the designated place of storage.

Equipment and Supplies

- Ge gamma-ray spectral analysis counting system
- 500-mL cylindrical container with lid
- Marinelli (reentrant) 500-mL beaker with lid
- 1-mL pipette (to deliver) or calibrated automatic 1-mL pipetter
- 10-mL graduated cylinder
- 100-mL graduated cylinder
- 1-L volumetric flask

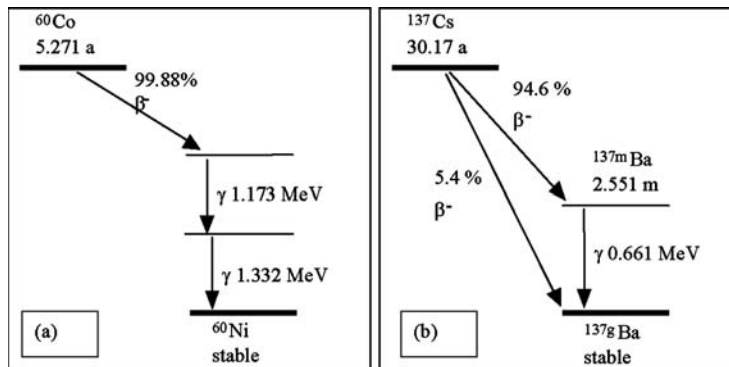


Figure 2B.2 Cobalt-60 (a) and cesium-137 (b) decay schemes.

Reagents

Quality control point source (e.g., ^{60}Co and ^{137}Cs ; see Fig. 2B.2 for decay schemes)

- NIST gamma-ray certified standard solution with multiple gamma rays from 30 keV to 1,500 keV (e.g., ^{154}Eu , ^{155}Eu , and ^{125}Sb)
- 4 M HCl: Pour 333 mL of concentrated HCl into 500 mL deionized water and dilute to 1L. See Appendix 7 for concentrations of common acids and bases.
- Ethanol (absolute or 95%)

Checking QA acceptability for Ge detector calibration

Procedure

Step 1. Count the quality control source under specified conditions for a brief period (e.g., 500 s) to obtain count rates in the channels beneath the full-energy peaks. Count the radiation background for a long period (e.g., 200,000 s).

Step 2. Measure the control source count rate of each peak and compare it to the routinely recorded counting room QA information on these source-peak count rates.

Step 3. Calculate the full width at half maximum (FWHM) for each peak and compare these values to those reported in the count room QA data.

Step 4. Compare the background count rate values at specified energy regions to those reported in the count room QA data.

Step 5. If these results are within the limits of existing QA limits, continue with the experiment. If not, report the discrepancy to the instructor and await guidance.

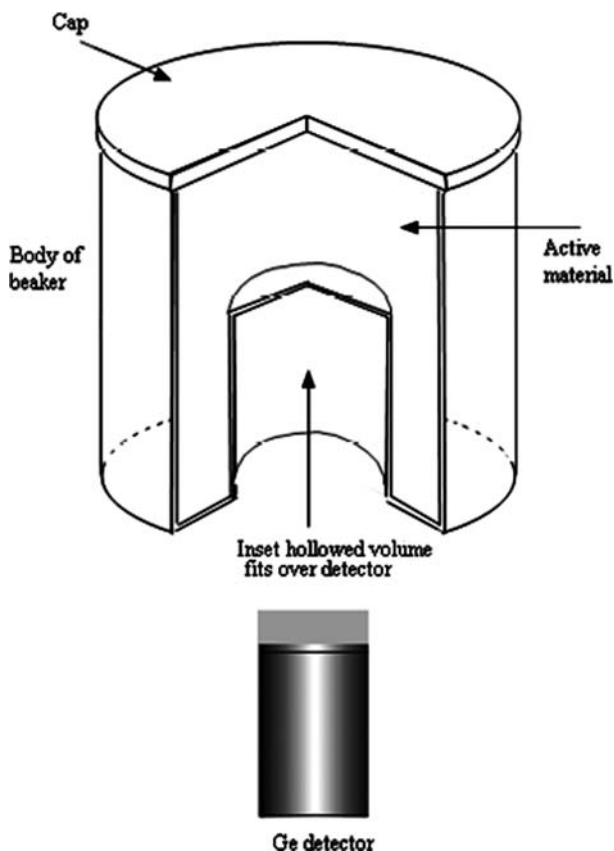


Figure 2B.3 Marinelli beaker positioned over detector.

Germanium detector calibration as function of sample volume and gamma-ray energy

Solutions of increasing volume are prepared in a cylindrical container by successive dilutions of a 1-mL gamma-ray standard solution pipetted into a 500-mL cylinder. Each sample is counted with the Ge detector with spectrometer to observe the change in counting efficiency with increasing sample volume.

Just before the end, transfer the sample to a Marinelli beaker for counting to observe the effect of improved geometry. Figure 2B.3 shows a schematic drawing of the Marinelli beaker with the design feature that allows it to fit over the Ge detector. The counting results with the same sample for the re-entrant beaker and the cylinder are compared.

Procedure

Step 1. Into the 500-mL cylindrical container, pipette the following:

- 1 mL of ethanol (to decrease the surface tension)
- 3 mL of 4 M HCl
- 1 mL of NIST standard radionuclide solution.

Carefully swirl to mix. Be certain to cover the bottom evenly, but do not swirl the solution up onto the container walls. *The total initial volume is 5.0 mL.* Screw the lid on the container and carefully place in position in the germanium gamma-ray detector counting chamber; it should be centered and level. Count twice for a sufficient time period to accumulate 2000 counts (typically 100 s). Check to confirm that at least 2,000 counts have been accumulated at each of the peaks used for calibration. Collect the gross gamma-ray count rates for the full-energy peaks in Data Table [2B.1](#).

Step 2. Remove the cylinder from the detector. Remove the lid, add 5 mL of 4 M HCl and swirl to mix, taking the same precautions as before. *The total volume is now 10.0 mL.* Screw the lid on the container and carefully place in position in the germanium gamma-ray detector counting chamber; it should be centered and level. Count twice for at least 100 s. Collect the data and place in Data Table [2B.1](#).

Step 3. Remove the cylinder from the detector. Remove the lid, add 15 mL of 4 M HCl and swirl to mix, taking the same precautions as before. *The total volume is now 25.0 mL.* Screw the lid on the container and carefully place in position in the germanium gamma-ray detector counting chamber; it should be centered and level. Count twice for at least 100 s. Collect the data and place in Data Table [2B.1](#).

Step 4. Remove the cylinder from the detector. Remove the lid, add 25 mL of 4 M HCl and swirl to mix, taking the same precautions as before. *The total volume is now 50.0 mL.* Screw the lid on the container and carefully place in position in the germanium gamma-ray detector counting chamber; it should be centered and level. Count twice for at least 100 s. Collect the data and place in Data Table [2B.1](#).

Step 5. Remove the cylinder from the detector. Remove the lid, add 50 mL of 4 M HCl and swirl to mix, taking the same precautions as before. *The total volume is now 100 mL.* Screw the lid on the container and carefully place in position in the germanium gamma-ray detector counting chamber; it should be centered and level. Count twice for at least 100 s. Collect the data and place in Data Table [2B.1](#).

Step 6. Remove the cylinder from the detector. Remove the lid, add 100 mL of 4 M HCl and swirl to mix, taking the same precautions as before. *The total volume is now 200 mL.* Screw the lid on the container and carefully place in position in the germanium gamma-ray detector counting chamber; it should be centered and level. Count twice for 200 s. Collect the data and place in Data Table [2B.1](#).

Step 7. Remove the cylinder from the detector. Remove the lid, add 200 mL of 4 M HCl and swirl to mix, taking the same precautions as before. *The total volume is now 400 mL.* Screw the lid on the container and carefully place in position in the germanium gamma-ray detector counting chamber; it should be centered and level. Count twice for 200 s. Collect the data and place in Data Table [2B.1](#).

Step 8. Remove the cylinder from the detector. Remove the lid, add 80 mL of 4 M HCl and swirl to mix, taking the same precautions as before. *The total volume is now 480 mL.* Screw the lid on the container and carefully place in position in the germanium gamma-ray detector counting chamber; it should be centered and level. Count twice for 200 s. Collect the data and place in Data Table [2B.1](#).

Step 9. Carefully transfer the 480 mL of solution to the Marinelli reentrant beaker. Wash cylindrical container with 20 mL of 4 M HCl and pour into Marinelli beaker. Carefully stir. Close lid. *The total volume is now 500 mL.* Carefully place in position in the germanium gamma-ray detector counting chamber; it should be centered and level. Count twice for 200 s. Collect the data and place in Data Table [2B.1](#).

Treatment of Data

You will be given each gamma-ray energy and the associated activity (radionuclide concentration) in the standard solution. Enter these values at the top and bottom, respectively of Data Tables [2B.1](#) and [2B.2](#). If the software program reports the integrated values for the gamma peaks in the standard sample, simply record the reported count rate on the data sheet and skip steps a – d below. *Note that the gamma-ray spectrum usually includes peaks that the instructor will specify as being unsuitable for efficiency calibration.*

Determine the counting efficiencies vs energy for each volume:

- Sum the counts in all channels of each full-energy peak and note the number of channels the peak occupies.
- Sum the counts in 2 or 3 channels at each side of the peak channels; divide this value by the number of channels to obtain the count per channel; and multiply this value by the number of channels in the peak region to obtain the detector background plus Compton distribution.
- Subtract the detector background and Compton distribution from the sum of the peak counts. Divide by the counting period in seconds to obtain the net count rate (except for possible background peaks beneath the source peak).
- Refer to the background spectrum and search for any background peaks in the regions of interest for the peaks. If some are found, calculate for each its net count rate and subtract it from the net count rate in Step c. Record net count rates in Data Table [2B.1](#).
- Assign each measured gamma-ray peak to the appropriate radionuclide in the Standard Certificate. Compute for each measurement the counting efficiency for each gamma ray, based on the gamma-ray emission rates given in the standard certificate. Note the date of the certificate and correct for radioactive decay to the time of measurement, based on the half-lives listed in the Certificate.
- From Data Table [2B.2](#) gamma-ray energies and counting efficiencies for all counting configurations, plot a curve of the counting efficiency versus energy on a log-log scale between 30 keV and 1,500 keV for each system. *Note: Any peak for a gamma ray that is emitted in coincidence*

(simultaneously) with a second gamma ray, has a falsely low counting efficiency because the coincident gamma ray appears as a peak that represents the sum of the two gamma-ray energies.

Comparison of counting efficiencies

Calculate the ratios of the counting efficiencies for the various energies at each sample volume relative to those for the 480-mL volume in the cylindrical container to observe the effect of sample volume on efficiency.

Average these ratios for energies above 150 keV energy to examine whether they are consistent for each volume. Examine the inconsistencies. Plot average ratios as a function of the volume to provide a means for interpolating.

Compare the counting efficiencies for the 500 mL volume in the Marinelli beaker with those in the cylindrical container.

Questions: Part 2B

1. Try to explain the shape of the counting efficiency vs. energy curve for the germanium detector. Refer to your *Radioanalytical Chemistry* textbook, Chapters 2 and 8.
2. Discuss the possible problem with results obtained for a water sample counted in a Marinelli beaker when sediment later was observed at the bottom of the beaker.
3. What is the advantage in using the Marinelli beaker?
4. Make a list of ways you might be able to improve or reduce the uncertainty in preparing a calibration curve for varying volumes.

Source

Experiment 2 was adapted from experiments used at Environmental Radiation Center, EOSL, GTRI, Georgia Institute of Technology.

Experiment 3

Determination of Gamma Ray Self-absorption in a KCl Sample

Objective

To measure with a Ge detector and spectrometer the gamma-ray self-absorption of ^{40}K in a KCl sample, contained in a calibrated 500-mL cylindrical container.

Introduction

Generally, gamma rays are so energetic that the effect of self-absorption by the sample itself is not a serious problem. Because gamma rays may be scattered, absorbed, or undergo positron-electron pair formation, as described in *Radio-analytical Chemistry* (see, for instance, Section 2.4.4 of that text), when the sample size is large, one must correct for self-absorption. Sample volumes of 0.5 – 3.0 L require such self-absorption corrections unless efficiency calibration was performed for samples in the same configuration and with similar density and gamma-ray attenuation coefficient. The self-absorption factor, f , can be calculated with Equation 3.1:

$$f = \frac{1 - e^{-\mu x}}{\mu x} \quad (3.1)$$

where

f = self-absorption factor,

μ = gamma-ray mass attenuation coefficient; in this experiment, it applies to the 1.461-MeV gamma ray, with a value of $0.051 \text{ cm}^2/\text{g}$ in KCl. It is $0.058 \text{ cm}^2/\text{g}$ in water,

x = sample thickness (area mass) in g/cm^2

Full-energy peaks usually are measured – as in this experiment – with a Ge detector and spectrometer system to identify the energy at the peak maximum and determine the intensity given by the integrated area beneath the peak.

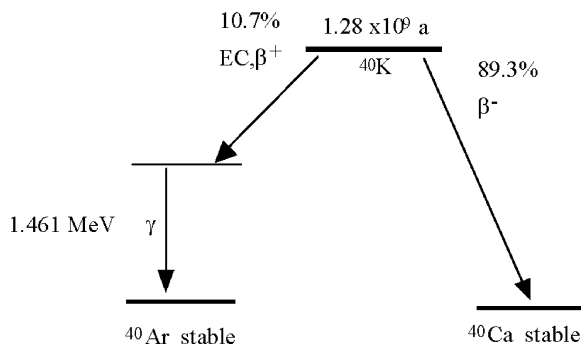


Figure 3.1 Decay scheme for ^{40}K .

The salt used in this experiment is potassium chloride (KCl). Potassium-40 is a naturally-occurring isotope of potassium (abundance = 0.0117%) whose half life is 1.28×10^9 years. It emits a gamma ray at 1.461 MeV with a decay fraction of 10.7%, in addition to beta particles with a decay fraction of 89.3%. The decay scheme for ^{40}K is given in Fig. 3.1. A tared container (see Experiment 2) is filled with solid KCl, closed, weighed, and counted.

The net count rate at a given mass, R_m , is related to the self-absorption factor at that mass, f_m , in terms of the activity, A , gamma-ray decay fraction, d , and counting efficiency at zero self-absorption, ϵ_0 , by Equation 3.2:

$$\frac{R_m}{A} = f_m \epsilon_0 d \quad (3.2)$$

Equation 3.1 is used to calculate f_m . The activity times d is 1.7 gamma rays per second per gram of KCl. R_m is the average of the two net count rates measured in this experiment.

Safety Reminder

- Follow the usual safety procedures when working in a chemical and radiological laboratory.

Equipment and Supplies

- Plastic sample counting container (500 mL capacity)
- Spatula
- Ruler marked in cm
- Balance capable of weighing up to 1 kg to nearest gram
- Germanium detector and spectrometer calibrated for a sample container of the size used in this experiment (see Experiment 2B) placed at the specified distance to the detector

Reagents

- Potassium chloride (KCl) reagent grade

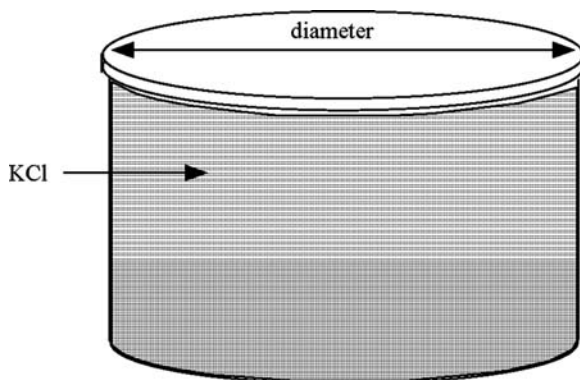


Figure 3.2 Container filled with KCl.

Procedure

Step 1. Measure the inside diameter and height of a tared 500 mL plastic cylinder container. Fill it to the top with KCl. Record the mass of the KCl. Close the top. Calculate the sample cross-sectional area and divide the KCl mass by the area to obtain the sample thickness (area mass) in g/cm^2 . Record your measurements in Data Table [3.1](#).

Step 2. Count the sample twice with the germanium detector for 1,000 seconds.

Treatment of Data

1. If the software for calculating gamma ray activity subtracts the background count rate and divides by the energy-dependent counting efficiency for the specified container and the recorded sample mass, you will receive the gamma rays disintegration rate per unit time and mass for the sample. This result is based on the counting efficiency measured for a water sample (i.e., for the self-absorption factor of water, not KCl), and for the mass entered at the time of counting (presumably, for potassium chloride).

If computation is by hand, calculate the net counts per second (c/s) of the ^{40}K gamma-ray peak at 1.461 MeV. Examine the background count rate and subtract the background contribution from the 1.461 MeV peak count rate. Note that the background count rate includes a peak at that energy (due to potassium salt in the environment). Enter data into Data Table [3.2](#).

Data Table 3.1 Sample dimensions

Diameter of container in cm	_____
Area of container (top) $\pi(d/2)^2 =$	_____ cm^2
Mass of container + KCl	_____ g
Mass of container	_____ g
Mass of KCl	_____ g
Area mass of KCl	_____ g/cm^2

Data Table 3.2 Hand computation of peak count rate

Net background count rate calculated for K-40 channels from water solution _____ c/s
Net sample count rate of K-40 peak (1 st) _____ c/s
Net sample count rate of K-40 peak (2 nd) _____ c/s
Net sample count rate of K-40 peak (average) _____ c/s

Data Table 3.3 Calculated K-40 counting efficiency

Activity of K-40 gamma ray, based on mass _____ d/s-g
Self-absorption factor for KCl (f_{KCl}) _____
Calculated ϵ_0 for K-40 gamma ray _____

- Calculate the ratio of the net count rate to the disintegration rate of ^{40}K gamma rays in the sample, based on the half life, gamma-ray decay fraction, ratio of ^{40}K to potassium mass, and K/KCl ratio of 39.1/74.6. Calculate the self-absorption factor with Eq. 3.1. Calculate the counting efficiency at zero self-absorption with Eq. 3.2 and record in Data Table **3.3**
- The ratio f_{KCl}/f_{water} , calculated for KCl and water, respectively, by Eq. 3.1, is the correction factor for multiplying the counting efficiency obtained from a graph such as prepared in Experiment 2B with a water solution, for a sample with different density and material, such as soil or vegetation. Compare this ratio with the ratio of the measured count rate for KCl in this experiment to the count rate inferred from the graph of counting efficiency vs. gamma-ray energy in Experiment 2B. Note that some extrapolation is needed to apply the Experiment 2B graph, both because the volume is 480 mL compared to 500 mL in this experiment, and because the ^{40}K energy of 1.461 MeV does not correspond to any of the energies of the gamma rays emitted by the standard.

Questions

- Show by calculation that there are 104 gamma-rays per 1.00 g of KCl.
- What is the error contributed to the calculation when the counting efficiency obtained for water is applied to the counting efficiency for KCl measurement?
- Look up the density (note that the density x container height = area mass) and the gamma-ray mass attenuation factor of commonly counted materials to compare the influence on the self-absorption factor of density and atomic number (i.e., electrons per atom).

Source

This experiment was adapted from an experiment in the Radiation Technology laboratory course, GIT Nuclear and Radiological Engineering program.

Experiment 4

Preparation of a Beta-particle Self-absorption Curve for ^{40}K

Objective

To quantify beta-particle self-absorption in KCl samples of varying thicknesses.

Introduction

Essential to reporting amounts of radioactivity in samples is the ability of the radiochemist to convert observed quantities of radioactivity (e.g., count per second) to an absolute scale (e.g., disintegration per second). When the sample radioactivity is measured with a radiation counter, the factor that converts the observed count rate to the absolute scale is the *counting efficiency*. The counting efficiency is defined as the ratio of the net count rate to the disintegration rate.

The efficiency of the detection system is based on both detector and sample parameters. Detector parameters include the intrinsic detector efficiency, the geometric relation of detector to sample, scattering by the sample support and nearby material, and attenuation between the sample and the detector. Sample parameters include material stopping power based on composition, mass, diameter and thickness; type and amount of sample cover and backing; and radiation type, energy, decay fraction, and decay rate.

This experiment examines the count rate as a function of sample thickness. All other variables are held constant (except for a small change in source-detector distance). As the sample becomes thicker, more of the beta particles are absorbed in the sample itself. This is called *self-absorption*, and is shown in Figure 4.1. In thin samples, self-absorption is relatively small or negligible, but in thick samples it is measurable and must be considered when calculating the counting efficiency.

This experiment examines the self-absorption of the beta particles emitted by ^{40}K ($t_{1/2} = 1.28 \times 10^9$ a, $E_{\text{max}} = 1.311$ MeV, 89.3%), a naturally-occurring isotope of potassium (abundance = 0.0117%), in potassium chloride (KCl) salt. The degree of beta-particle self-absorption (including self-scattering) depends on the energy of the beta particles, the sample matrix elemental

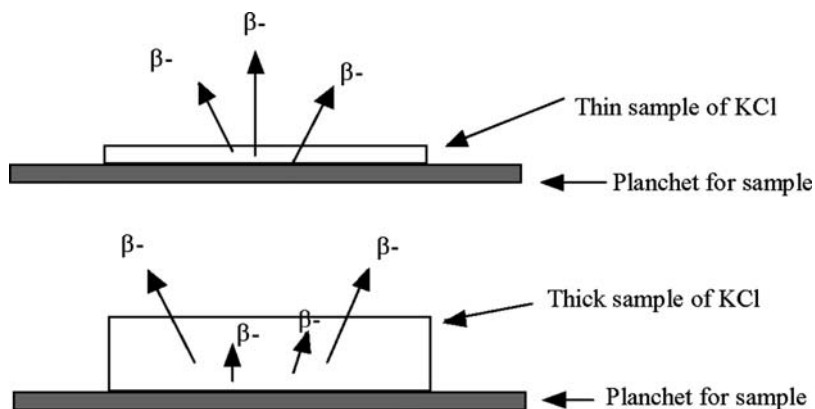


Figure 4.1 Beta particle emission from “thin” and “thick” radioactive samples.

composition and density, and the sample thickness. A convenient way of expressing thickness is as mg/cm^2 (the area mass).

Beta particle self-absorption can be approximated as in Equation 4.1:

$$f = \frac{1 - e^{-\mu'x}}{\mu'x} \quad (4.1)$$

where f = self-absorption factor,

μ' = equivalent mass attenuation coefficient for beta-particle group in cm^2/mg ,

x = sample thickness in mg/cm^2 .

Curves for this equation have been obtained by measuring various beta-particle emitters in several geometric arrangements of source and detector. One of the empirical relations found between μ' and the maximum beta-particle energy, E , in MeV, is shown by Equation 4.2:

$$\mu' = 0.017E^{-1.43} \quad (4.2)$$

For ^{40}K beta-particles with $E = 1.311$ MeV, μ' is 0.0115 cm^2/mg .

The formula for the self-absorption factor is exact for gamma rays (see Experiment 3) but approximate for beta particles. That it is applicable at all is due to the near-linear decrease of the logarithm of the count rate with absorber thickness of a beta-particle group (see Figure 2.6 in the *Radioanalytical Chemistry* textbook). The obvious deviation is that this relation ends at the range of the maximum-energy beta particle, whereas it continues indefinitely for gamma rays.

The simplest and most direct reliable way to characterize the self-absorption of beta particles in a sample is to obtain a self-absorption curve by counting the same radionuclide in aliquots of a solid sample over a range of sample thickness. Aliquots can be prepared with the same specific activity (activity per unit mass) but with different masses, in identical planchets. The sample aliquots are counted and the results are presented in graphic form for interpolating the self-absorption factor for the sample mass of interest.

If the activity of the radionuclide is known, as for ^{40}K , its counting efficiency for the particular counter, can be calculated by averaging ε_0 from a set of net count rates for aliquots of different thickness, each with the value of f calculated by Eqs. 4.1 and 4.2. Equation 4.3 may be used at each measurement.

$$R_m = A_m \varepsilon_0 f \quad (4.3)$$

where

R_m = measured net count rate per unit mass of KCl, in c/s-g

A_m = activity in beta particle per mass d/s-g, calculated from the known value for potassium, multiplied by 39.1/74.6 to adjust for the presence of KCl

ε_0 = counting efficiency without self-absorption, and

f = self-absorption factor described above, i.e., R_{m0}/R_m

R_{m0} = count rate per mass at zero self-absorption, in c/s-g

Because Eq. 4.2 is empirical and based on measurements under counting conditions that may have been different from this experiment, it is wiser to obtain your own value of μ' from the measurements. This is done by plotting values of R_m as function of x , drawing a line of best fit through the measurement points and extrapolating the line to $x = 0$. Values of μ' and R_0 that best describe the line then are obtained by trial and error, beginning with the value of μ' suggested by Eq. 4.2, or with a curve-fitting program.

The appropriateness of the value of ε_0 can be checked by comparison with the counting efficiency values obtained for very thin samples – where f approaches 1.0 – in Experiment 2. Interpolation is needed for the ^{40}K maximum beta-particle energy of 1.311 MeV, and the lesser value of ε_0 at the larger sample diameter in the present experiment must be taken into account. An estimate based on calculating the detector-sample geometry underestimates the counting efficiency because additional beta particles are back-scattered into the detector from the planchet and its support.

Safety Reminders

- Follow the usual safety procedures when working in a radiological laboratory.
- Caution should be exercised when preparing and working with mineral acids that are extremely corrosive.
- All liquids/solids are to be properly disposed of according to laboratory rules and protocol.

Equipment and Supplies

- Analytical balance (0.1 mg accuracy)
- Beta particle counting system, preferably an end-window proportional detector with gas flow and anti-coincidence shielding
- Spatula

Data Table 4.1 KCl weight

Planchet	Planchet Weight	Approx. KCl Weight	Exact KCl Weight	KCl in mg/cm ²
1		0.5 g		
2		0.7 g		
3		1.0 g		
4		1.5 g		
5		2.0 g		
6		3.0 g		

- Planchets, 5-cm diameter with 0.5-cm-high sides, stainless steel (other planchets can be used)
- Delivery pipette, plastic

Reagents

- Potassium chloride, reagent grade
- Glue solution: 1 g rubber cement per 100 mL of toluene
- Toluene

Procedure

Note: This procedure uses the planchets described above. With other size planchets, the KCl mass should be adjusted to produce samples of similar thickness in mg/cm².

- Step 1. Weigh each planchet to the nearest 0.1 mg.
- Step 2. Weigh an amount of KCl into each tared planchet that approximates the quantities listed in Data Table 4.1. Record the weight to the nearest 1 mg.
- Step 3. Shake planchet gently to distribute uniformly over the surface area.
- Step 4. Place several drops of glue solution on each planchet and gently tap to distribute the KCl uniformly. Dry in air or under heat lamp.
- Step 5. Count samples as indicated below.

Counting

Count the samples with the low level-beta particle counting system. Count each planchet for 5,000 s at the operating voltage for beta particles. Obtain the background count rate with a blank planchet. Calculate the net cps with Eq. 4.4. and record in Data Table 4.2

$$R_{net} = \frac{N_{total}}{t_s} - \frac{N_{bkgd}}{t_{bkgd}} \quad (4.4)$$

where

R_{net} = net count rate, in c/s

N_{total} = total sample counts recorded for the counting period counted,

Data Table 4.2 KCl count rate

Planchet #	N _{bkg}	N _{total}	R _{net}
1			
2			
3			
4			
5			
6			

t_s = total time sample was counted (5,000 s), in s

N_{bkg} = total background counts recorded for the background counting period, and

t_{bkg} = total time background was counted (5,000 s or longer), in s.

Calculate the standard deviation. See Appendix 6.

Standard deviation of $R_{\text{net}} = \frac{N_{\text{bkg}}}{t_{\text{bkg}}}$

Report each value as the count rate $\pm \sigma$ (for example, 56.8 ± 0.7 cps).

Treatment of Data

- Look up the pertinent information to calculate the beta particle emission rate per gram of KCl. Compare your value to the estimated rate of 14 beta particles/s-g of KCl.
- From Data Tables 4.1 and 4.2, prepare Data Table 4.3 that contains the following information:
 - the thickness of each sample in mg/cm^2 (assume that the 2-inch-diameter planchet has an area of 20 cm^2),
 - the calculated net count rate per mass KCl for each sample, with standard deviations,
 - the counting efficiency (R_{net}/A) for each sample, with standard deviations,
 - the self-absorption factor calculated by Eq. 4.1 for each sample,
 - the calculated counting efficiency at zero self-absorption for each sample by Eq. 4.3.
- On a graph plot:
 - Net count rate per calculated disintegration rate (R_{net}/A) vs. the sample thickness (x);
 - self-absorption factor (f) vs. the sample thickness (x).

Data Table 4.3 Self-absorption factor and counting efficiency

Planchet	Thickness	$R_{\text{net}} (+/-\sigma)$	$R_{\text{net}} / A (+/-\sigma)$	f	ϵ_0
1					
2					
3					
4					
5					
6					

4. For each point calculate the counter efficiency for each sample. This is the factor that provides a value of the curves at $x = 0$ and $f = 1.0$. What is the average of all the counting efficiency values? How does this value compare to measured counting efficiency values for beta particles of this energy in this type of detector?
5. Attempt to fit a better curve of the self-absorption factor f through the measured values. Record the best values of R_0 , μ' , and ϵ_0 :
_____.

Questions

1. A laboratory reports activity values for a set of samples but make no corrections for varying sample thickness. What would you suggest in order to obtain better activity values? The radionuclide that is being analyzed has a very long half-life.
2. If ^{40}K is counted as potassium hexachloroplatinate (K_2PtCl_6) rather than KCl , would you expect beta self-absorption to be greater or less per mg/cm^2 of precipitate? Explain.
3. You are preparing to count beta particles from samples that contains low levels of ^{99}Mo . The final counting form is MoO_3 . Outline an experiment to prepare a ^{99}Mo beta self-absorption curve. How would the self-absorption be used to correct the observed counting activity in actual measurements (consider Tc-99m ingrowth)?

Source

This experiment was adapted from an experiment in the Radiation Technology laboratory course, GIT Nuclear and Radiological Engineering program.

Experiment 5

Preparation and Standardization of Carriers

Objective

To prepare and standardize carriers for radioanalytical chemistry procedures.

Introduction

A carrier usually consists of milligram quantities (10–30 mg) of a non-radioactive element. It is added to a sample for which the radioactive isotope of that element is being analyzed radioanalytically. The carrier is in solution so that it may be conveniently delivered by volume with a pipette. Prepared carrier solutions should be re-standardized periodically, usually every 6 to 12 months, in case of problems such as evaporation loss, colloid formation, container instability, or carrier decomposition.

This experiment demonstrates three variants of a method for preparation and standardization of carriers. *Two of these carriers – strontium and yttrium – are used in Experiment 12 of this manual.*

An alternative to preparing standardized carriers is to purchase certified standards for other analytical methods. For example, standards for atomic absorption procedures have a concentration of 1,000 ppm (mg/L) and could be pipetted in 10-ml aliquots. This choice is suitable if the laboratory analyzes a large number of samples and a certificate is required for the standard solution.

All standardization should be performed at least in triplicate. If the results do not agree within ~0.5 %, the standardization should be repeated.

All carrier solutions should be properly labeled to indicate the carrier element (e.g., Sr, Y). Also on the label should be the concentration of the carrier with its standard deviation, the concentration and the chemical form of the solution (e.g., 0.01M HNO₃), the date of preparation and the initials of the analyst. An example is given in Fig. [5.1](#).

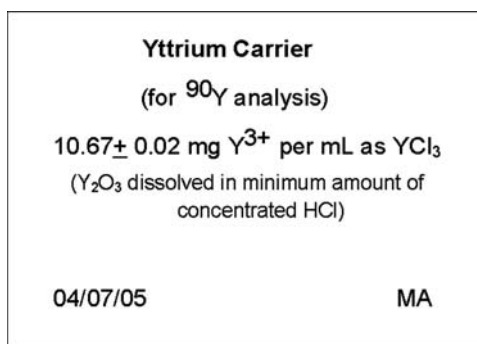


Figure 5.1 Example of label for carrier solution.

Safety Reminder

- Follow the usual safety procedures when working in a radiological laboratory.
- Caution should be exercised when preparing and working with corrosive mineral acids.
- All liquids/solids are to be properly disposed of according to laboratory rules and protocol.

Equipment and Supplies

- Analytical balance
- Drying oven
- 1-L volumetric flask
- Paper filters, medium porosity
- Dark glass reagent bottle
- Standard glass reagent bottles
- Beaker, 50 mL
- Crucible
- Sintered-glass crucible
- Pipette, 5-mL

Reagents

- Primary-standard grade AgNO_3
- standard-grade Y_2O_3
- standard-grade $\text{Sr}(\text{NO}_3)_2$
- concentrated HNO_3 (see Appendix 7)
- concentrated HCl (see Appendix 7)
- saturated $(\text{NH}_4)_2\text{C}_2\text{O}_4$
- concentrated NH_4OH
- 95% ethanol
- Deionized water

A. Preparation of Silver Carrier (10 mg Ag⁺/mL): Primary Standard Method

Step 1. Oven-dry approximately 16 to 17 g of primary-standard grade AgNO₃ in a clean crucible at 110 °C for one hour. Remove from the oven and cool in a desiccator.

Step 2. Weigh exactly 15.75 g of this dried AgNO₃. Place in 50 mL beaker and dissolve in a minimum amount of deionized water. Add 3 drops of concentrated nitric acid. Transfer to a 1 L volumetric flask. Use some dilution water to wash beaker and dilute solution in flask to the mark with deionized water.

Step 3. Thoroughly mix. Transfer with filtering into a dark glass bottle. Calculate the amount of Ag⁺ per mL of solution. Prepare a label that indicates the mg Ag⁺/mL, date, and preparer initials. Affix to bottle. Store in a dark place. (*Note: Silver solutions are protected from direct light because the silver ions will be reduced photochemically to black silver metal.*)

B. Preparation and Standardization of Yttrium Carrier (10 mg Y³⁺/mL): Direct Ignition to the Oxide or precipitation as the Oxalate

Step 1a. Dissolve 12.67 g of Y₂O₃ in a 50 mL beaker with a minimum of concentrated HCl. Transfer the solution to a 1 L volumetric flask. Use some dilution water to wash beaker and make up solution to 1 L with deionized water. Transfer with filtering to a glass reagent bottle.

Step 2a. In at least triplicate, pipette exactly 5.0 mL of the carrier solution to a clean weighed porcelain crucible. Evaporate the solution carefully to dryness and ignite the residue in a muffle furnace at 1000 °C for 1 hour.

Step 3a. Let cool and weigh as Y₂O₃. Take the average of the replicate results. Label the carrier bottle as mg Y³⁺/mL or as mg Y₂O₃ /mL, date, and initial.

Alternative for Experiment 12 in selecting steps 15a or 15b:

Step 1b: Dissolve 6.46 g of Y₂O₃ and continue with Step 1a.

Step 2b. In at least triplicate, pipette exactly 5 mL of the carrier solution to a 50-mL glass beaker. Add 25 mL of saturated (NH₄)₂C₂O₄ solution to precipitate Y₂(C₂O₄)₃·xH₂O. Add a few drops concentrated NH₄OH, if necessary to complete the precipitation. Digest in hot-water bath for 10 minutes. Filter through a tared sintered-glass crucible to collect the precipitate. Wash out the beaker with two portions of 5 mL water and add to the precipitate in the crucible. Dry precipitate by washing with two portions of 95% ethanol. Dry crucible with precipitate in oven at 110° C for 30 minutes.

Step. 3b. Remove from oven, let cool, and weigh as yttrium oxalate. Take the average of replicate results. Label the carrier bottle as mg Y^{3+} or yttrium oxalate per mL, date, and initial. Note that the yttrium oxalate includes waters of hydration.

C. Preparation and Standardization of Strontium Carrier (10 mg Sr^{2+} /mL): Preparation of a Salt

Step 1. Dissolve 24.15 g of $Sr(NO_3)_2$ in a 50 mL beaker with deionized water and add 10 mL of concentrated HNO_3 . Transfer to a 1 L volumetric flask, use some dilution water to wash out the beaker, and dilute to 1 L with deionized water. Mix, and transfer with filtering to a glass reagent bottle.

Step 2. In triplicate, pipette exactly 5.0 mL carrier solution into a 50-mL beaker. Add 25 mL of saturated $(NH_4)_2C_2O_4$ solution. Stir and let stand for at least 15 minutes.

Step 3. Filter the SrC_2O_4 precipitate through a weighed 15-mL sintered glass crucible of fine porosity. Wash the beaker with two portions of 5 mL of water and add to the precipitate in the crucible. Wash the precipitate twice with 5 mL of 95% ethanol. Dry crucible with precipitate in the oven at $110^\circ C$ for 30 minutes.

Step 4. Remove from the oven, let cool, and weigh. Calculate the Sr^{2+} amount based on the amount of strontium oxalate weighed for each sample. Take the average of the replicate results. Label the bottle by indicating the concentration of the strontium as mg Sr^{2+} or strontium oxalate per mL, date, and initial. Note that the strontium oxalate includes waters of hydration.

Questions

1. After you prepared the silver carrier from a primary standard reagent of silver nitrate in Section A, you read on the label of the reagent container that the silver nitrate is 98.56% pure. How do you correct the carrier solution information on that basis?
2. After you prepared the strontium carrier in Section C, you realized that you had used tap water instead of deionized water. Speculate how this error would affect the results of yield measurement.

Sources

Section B was adapted from the Radiochemical Procedure, YTTRIUM II, R. J. Prestwood, in *Collected Radiochemical and Geochemical Procedures*, Compiled and Edited by Jacob Kleinberg, LA-1721 5th Edition, Los Alamos National Laboratory (May 1990).

Section C was adapted from the Radiochemical Procedure, STRONTIUM-90, B.P. Bayhurst, in *Collected Radiochemical and Geochemical Procedures*, Compiled and Edited by Jacob Kleinberg, LA-1721 5th Edition, Los Alamos National Laboratory (May 1990).

Experiment 6

Preparation and Counting of ^{242}Pu Tracer Solution

Objective

To prepare a standardized plutonium tracer for use and compare its activity in 2 detector systems calibrated for alpha-particle counting efficiency.

Introduction

A tracer usually is a solution of a standardized radionuclide that is an isotope of the analyte radionuclide. With the identical chemical behavior of tracer and analyte, the yield of the tracer, determined radiometrically, represents the yield of the analyte. In this respect, the radioactive tracer has the same function as the stable carrier. Furthermore, for alpha particles of the usual 4–10 MeV energy in a thin source, the ratio of net count rate to activity is the same for the tracer and the analyte, so that the analyte activity is directly calculated from the activity of the tracer and ratio of the net count rates at the peaks of the analyte relative to the tracer, measured with an alpha-particle spectrometer.

An isotopic radioactive tracer commonly is used for radionuclides that have no stable isotopes, notably for high-Z radionuclides that emit alpha particles. They also may be applied if a carrier is available as a more convenient way of determining the yield. A non-isotopic radionuclide can function as tracer for procedural steps in which it and the analyte react identically.

In this experiment, a known activity of ^{242}Pu is diluted for use as tracer and its activity is checked with a detector that was previously calibrated for alpha-particle counting. *This tracer will be used in Experiments 14 and 15 for the analysis of ^{239}Pu*

For application as a tracer, a radioisotope is selected on the basis of availability, emitted radiation that can be distinguished from that of the analyte, an appropriately long half-life, and minimal radioactive impurities, including radioactive progeny. As discussed below, the tracer may either be purchased from a supplier as a standard or calibrated in the laboratory. An even safer procedure is to purchase a standard and check its reliability with a calibrated detector.

Direct Dilution of a Certified Solution. When standard tracer solutions are purchased from commercial sources, detailed certificates must accompany them (see Section 11.2.6 in *Radioanalytical Chemistry*). Because the activity of the certified tracer solution usually is greater than needed for tracing individual samples, one or several sequential dilutions must be performed meticulously to produce the solution from which an aliquot will be pipetted into the samples. Dilutions should be prepared in a chemical form identical to the original solution with regard to type and concentration of acids and reagents to assure tracer solubility and stability. The analyst should perform dilutions by weight rather than by volume for precise work. The final dilution is usually planned to obtain a solution from which about 0.05 Bq is pipetted into a sample that contains that amount or less of plutonium analyte.

Dissolution of a Primary Metal. This method is not likely to be used by many radioanalytical laboratories because of special facility requirements. Dedicated hoods and glove box facilities are used to handle the usual types and quantities of special nuclear materials. Samples of metallic plutonium, uranium, or neptunium can be purchased with certification of both purity and mass for use of the metal as the “primary” standard material. The metal is dissolved in acid and then diluted to prepare the solution of desired concentration.

Standardization by Counting. For this method, a detector initially is calibrated for detection efficiency pertinent to the utilized tracer with a standard radionuclide in quantity and radioactivity form that is known and traceable to NIST. The tracer solution is then prepared for counting, counted, and labeled for radionuclide concentration on the basis of the net count rate and the detection efficiency. Its activity is calculated together with the counting error, adjusted for radioactive decay and dilution. All of these measurements should be performed in replicate to provide average values and their measurement uncertainty.

This experiment illustrates use of ^{242}Pu , but other suitable isotopes of plutonium (see Fig. 14.1 of this manual) that emit alpha particles may be calibrated. Suitability of tracer is based on the knowledge that the tracer radionuclide is not in the sample, or at a concentration so low – no more than 1% of the tracer – that it will not interfere with yield determination.

Although the counting efficiency generally is the same for thin samples of all commonly measured alpha-particle radionuclides, irrespective of energy, it is best to check this calibration with a standard solution of the selected tracer radionuclide. The alpha-particle energies for ^{242}Pu are shown in the decay scheme in Fig. 6.1. *The energies of the two alpha-particle groups are so similar that the spectrum commonly shows only a single major peak with slight but observable asymmetry due to the lower-energy, lower-intensity, alpha-particle group. This combined peak is considered to represent 100% of the ^{242}Pu alpha-particle emission.*

At best, samples are prepared for counting the tracer solution in the same manner as the samples that subsequently will be analyzed. In this experiment, however, the sample is prepared for counting by evaporation, whereas in Experiments 14 and 15, the sample is prepared, respectively, by electrodeposition or by precipitation of a milligram amount of carrier. Although these differences should not affect the counting efficiency of extremely

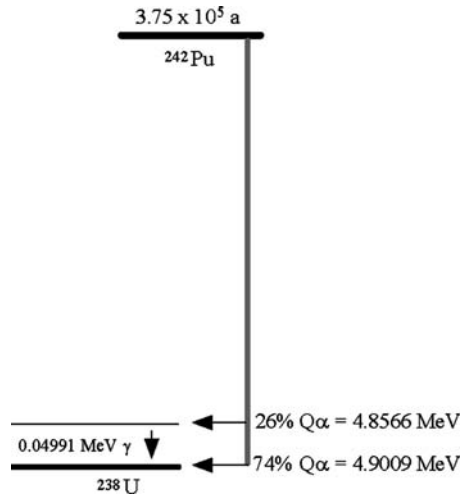


Figure 6.1 Decay scheme for ^{242}Pu .

thin samples, it will be desirable to compare the alpha-particle spectra for resolution and peak symmetry to assure that the impact of sample thickness is minimal. Unduly thick samples cause tailing at the low-energy side of the peak with resultant decrease in peak resolution, i.e., peak widening and asymmetry. Moreover, the evaporated sample should be on the same type of disk as is used for electrodeposition, and in the same central portion of about 1 square centimeter.

Safety Reminders

- Follow the usual safety procedures when working in a radiological laboratory.
- Caution should be exercised when preparing and working with corrosive mineral acids.
- All liquids/solids are to be properly disposed of according to laboratory rules and protocol.

Equipment and Supplies

- Si detector with spectrometer system
- Gas-flow anti-coincidence, end-window proportional counter
- Meeker burner or equivalent
- Stainless steel disks, 2-cm dia.
- Planchets, 5-cm dia. for holding disks
- Pipettes, preferably with automatic pipetter of desired delivery capacity
- Heat lamp
- Forceps
- Mylar film

Reagents

- Plutonium Tracer Solution: Plutonium-242 or other suitable plutonium isotope tracer of known activity per unit volume or per unit mass. Prepare 100 mL of a diluted solution of the same chemical composition and acid strength as the original. The ^{242}Pu concentration should be in the range of 0.4 – 1.2 Bq/mL for delivery with a 100- λ pipette, or ten times less for delivery with a 1-mL pipette. Shake well and keep tightly sealed with fritted glass stopper and a cover of mylar film to prevent leakage.

Activity of standard tracer per unit volume,(dpm/mL): _____

- Acid for dilution, identical to ^{242}Pu standard solution

Procedure

This calibration is to be performed with 3 or more replicate samples. The volume of the solution delivered to the planchets should be between 1 mL and 100 λ . (The volume used should allow the solution to remain within the location of the usual sample deposit, a radius of about 0.5 cm from the center of the planchet. If the volume used is too large, it will encourage excessive spreading on the planchet.) These samples are dried under a heat lamp. Then, the dried residue is fixed on the surface of the disk by gently flaming the disk over a Meeker burner flame. (*Note: A Meeker burner is different from a Bunsen burner in that it burns hotter and has a metal grid over the flame that causes the flame and heat from the burner to vibrate as the fuel burns.*)

Step 1. Clean and dry 4 disks for checking the tracer activity and determining the counter background.

Step 2. Carefully pipette 100 λ the designated quantity (0.04 – 0.1 Bq) of tracer solution onto the center of each of 3 disks for calibrating the counter. Record in Data Table 6.1 the volume or mass delivered, and calculate the activity in dps.

Data Table 6.1 Tracer activity of sample of diluted solution

Disk ID	Volume/Mass Delivered	Activity (dps)
Std. #1		
Std. #2		
Std. #3		

Average activity, A_{Std} (dps) = _____

Step 3. Dry each disk under a heat lamp. Evaporate slowly to encourage evenness in the dried sample and prevent loss of solution by splattering.

Step 4. When the solution has completely dried, hold the disk with a pair of tongs or forceps and gently flame over the Meeker burner. Allow disk to cool on a clean surface.

Step 5. Fasten disk to center of planchet with double-sided tape at the back of the disk. Count sample. Repeat with 2 other samples and blank with proportional counter.

Step 6. Place disk on slide and insert into vacuum chamber used for spectral analysis. Close counting chamber and start vacuum pump. Count sample. Repeat with 2 other samples and blank.

Counting

Standard disks and background disk are counted with a proportional counter and then sequentially in each of three spectral analysis vacuum chambers.

Count the alpha particles in each tracer sample for a time period sufficient to accumulate at least 1000 counts. An initial estimate of the sample counting period is based on the activity of the tracer and the known counting efficiency. Count all disks for the same period of time. The samples may be counted more than once. Count the spectral analysis background for approximately 200,000 s and the proportional-counter alpha-particle background at least 30,000 s. Record data in Data Table [6.2](#).

Treatment of Data

Definitions and equations for statistical calculations are given in the Appendix 6 on statistics.

For Data Table [6.2](#), calculate the count rate, R , in counts per second (cps) and the respective standard deviation (σ) for each count in each type

Data Table 6.2 Count rate

Disk ID	Count period, s	Counts	Count Rate, cps	Net Rate, cps
Spectrometer				
Std #1				
Std #2				
Std. #3				
Bkgd				
Prop. Counter				
Std. #1				
Std. #2				
Std #3				
Bkgd				

Data Table 6.3 Calculated activity

Group ID	R (cps) $\pm \sigma$	A (dps)	A (dps/mL) $\pm \sigma$
Spectrometer			
Std.#1			
Std.#2			
Std #3			
Bkgd.			
Proportional Counter			
Std.#1			
Std.#2			
Std.#3			
Bkgd.			

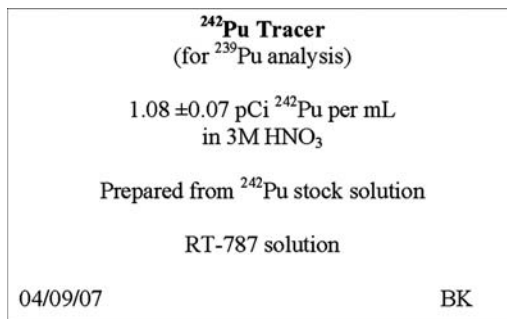


Figure 6.2 Example of label for standardized ²⁴²Pu tracer solution.

of detector. Calculate the activity in Data Table [6.3](#). Equation 2A.2 relates net count rate to activity in the sample on the basis of counting efficiency previously obtained by others for these detectors.. Report the average Bq/mL value and the average standard deviation for each set of counts in each detector. Record the counting efficiency value used for each detector:

Si detector counting efficiency (___ shelf): ___ %
Proportional counter alpha-particle efficiency: ___ %

Compare the activity reported for the tracer solution with the activity obtained with the proportional counter and the alpha-particle spectrometer based on their respective counting efficiency (ϵ) values, adjusted for sample volume and radioactive decay. Discuss whether the differences in activity are significant and decide which values are more reliable and should be associated with the tracer solution for subsequent measurements of plutonium.

Prepare a label for the standardized tracer solution as shown in Fig. [6.2](#).

Questions

1. What are the assumptions in using the alpha-particle counting technique with regards to the different energies associated with different radionuclides?
2. Why can you assume negligible self-absorption of the alpha particles in the samples prepared for counting?
3. How well does the measured activity compare with the reported certified activity? Make a list of ways you could improve the calibration of the tracer. How would you implement them?

Source

Developed by the authors from commonly-used procedures.

Experiment 7

Basic Radiochemical Techniques Applied to Uranium-Thorium Separation: Precipitation, Solvent Extraction, and Ion Exchange

Objective

To illustrate three common radiochemical separation techniques – precipitation, solvent extraction, and cation exchange – in parts 7A, 7B, and 7C. These methods separate thorium from its uranium parent. Radionuclide recovery is measured by comparing count rates to the original sample, not by carrier yield determination.

Introduction

The starting material is a solution of a known amount of natural or depleted uranium. Thorium-234 ($t_{1/2} = 24.20$ d), a beta-particle emitter, is a progeny of ^{238}U ($t_{1/2} = 4.47 \times 10^9$ a), an alpha-particle emitter. It is in secular radioactive equilibrium with the parent (see Sections 2.2.4 and 9.3.1 of *Radioanalytical Chemistry*). Thorium-234 decays to $^{234\text{m}}\text{Pa}$ ($t_{1/2} = 1.17$ min, 99.9%), followed by ^{234}Pa ($t_{1/2} = 6.75$ h, 0.13%). The decay sequence is given in Figure 7.1. The $^{234\text{m}}\text{Pa}$ daughter will reach radioactive equilibrium with ^{234}Th in 10 minutes. With an end-window beta-particle detector, the energetic beta particles (2.29 MeV max) from $^{234\text{m}}\text{Pa}$ usually are counted more efficiently than the low-energy beta particles (0.198 MeV max) from ^{234}Th , but both are counted.

To compare the measured separated ^{234}Th , including its $^{234\text{m}}\text{Pa}$ ingrown daughter and any carried uranium impurity, to the initial amounts of radionuclides, an aliquot of the initial solution is evaporated on the same type of planchet and counted with the same proportional detector in its alpha-particle and beta-particle detection modes. In addition, alpha-particle spectral analysis is performed to identify ^{238}U , ^{235}U , and ^{234}U and any of the progeny shown in Appendix 2 that emit alpha particles, such as ^{230}Th .

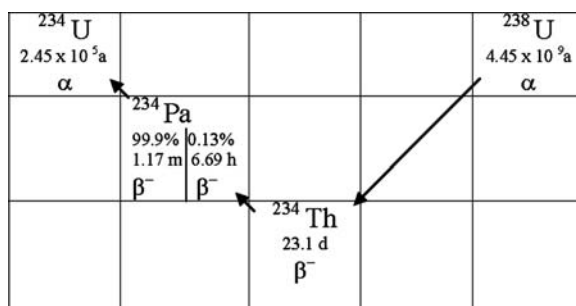


Figure 7.1 Radioactive decay of ^{238}U and ^{234}Th .

In the first separation procedure, thorium co-precipitates as a fluoride with neodymium fluoride, NdF_3 . The filter with NdF_3 is mounted in a planchet and counted for the beta particles from ^{234}Th and $^{234\text{m}}\text{Pa}$, and alpha particles from any remaining uranium. (See Appendix 8 for a brief description of the filter circles commonly used in preparation of samples for counting, and Appendix 9 for some general rules regarding the solubility of ions commonly encountered in radioanalytical separations).

In the second separation, uranium is extracted from thorium. Ethyl acetate is the extractant for uranium, which is bound in a nitrate complex. Thorium remains in the aqueous phase. Thorium is then co-precipitated with $\text{Nd}(\text{OH})_3$ to avoid absorption of the beta particles emitted by ^{234}Th and $^{234\text{m}}\text{Pa}$ by the large amount of NH_4NO_3 if the solution were simply evaporated and counted. The filter with $\text{Nd}(\text{OH})_3$ is mounted on a planchet for counting beta and alpha particles.

In third separation, thorium is retained on a cation-exchange resin while uranium is eluted from the resin column. Thorium is then eluted as an oxalate complex and evaporated on a planchet for counting. The planchet is flamed to volatilize the oxalic acid and then counted.

Flow diagrams for each of the separation steps are given in Figs. [7.4](#), [7.6](#), and [7.8](#). They provide a visual overview of the separation designs.

Preliminary Calculations

Calculate the total disintegration rate of alpha particles, in disintegration per minute, from the three isotopes of uranium in 1 mL of 0.02 M UO_2^{2+} solution of natural uranium. Calculate also the beta-particle disintegration rate of the ^{234}Th and its short-lived $^{234\text{m}}\text{Pa}$ progeny that are in radioactive equilibrium with the ^{238}U .

Safety Reminders

- Follow the usual safety procedures when working in a radiological laboratory. Additional care should be taken when working with the uranium solution to avoid contaminating the work area, particularly if low-level radiological analyses are being conducted in the area. Glassware and other laboratory equipment used in this experiment that has come in contact with

the uranium solution should be segregated from laboratory ware designated for low-level radioanalytical analyses.

- Caution should be exercised when preparing and working with corrosive mineral acids. Concentrated HF should be handled with gloves in a hood when preparing the solution and handling the HF solution. Hydrofluoric acid can cause painful burns to the skin and eyes, and should not be inhaled.
- All liquids and solids are to be properly disposed according to laboratory rules and protocol.

7A. Separation of Thorium from Uranium by Co-precipitation with NdF_3

Principle of Separation. Thorium co-precipitates with NdF_3 while UO_2^{2+} remains in solution. Filter paper with the neodymium fluoride precipitate and associated thorium is mounted on a planchet and counted for alpha and beta particles. The presence of alpha particles in the NdF_3 precipitate indicates the amount of uranium that accompanies the precipitate unless ^{230}Th is present. The ratio of the beta-particle count rate in the precipitate to the count rate in the initial sample of uranium with ^{234}Th and $^{234\text{m}}\text{Pa}$ indicates the fractional yield of the co-precipitation process.

Equipment and Supplies

- Proportional counter to detect alpha particles and beta particles
- Spectrometer with Si detector for alpha particles
- Centrifuge tubes, 50-mL plastic
- Volumetric flasks, 1 L, 250 mL, 100 mL
- Bottle, plastic, 1 L
- Pipet: 1 mL and 2 mL capacity, automatic, disposable tip
- Filtering apparatus for preparing precipitates for counting. See Figures 7.2 and 7.3 below.
- Filters, Millipore^R
- Forceps
- Planchets, 5 cm dia., lip around edge, stainless steel

Reagents

- Uranium solution: Uranyl nitrate solution, 0.02 M UO_2^{2+} : Dissolve 10.0 g $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in water and dilute in a volumetric flask to 1 L.
- Neodymium carrier: 10 mg Nd^{3+} /mL. Dissolve 6.38 g of Nd_2O_3 in a beaker with 10 mL of concentrated nitric acid; heat if necessary. Transfer solution to flask and dilute to 250 mL with de-ionized water. If neodymium nitrate or neodymium chloride is available, the carrier may be prepared from one of these salts, with the weight of salt recalculated to match the chemical formula.
- Neodymium carrier, 1 mg Nd^{3+} /mL. Pipette 10 mL of the 10 mg/mL Nd^{3+} carrier into a 100-mL volumetric flask, dilute to 100 mL with 0.1 N HNO_3 . Mix well.

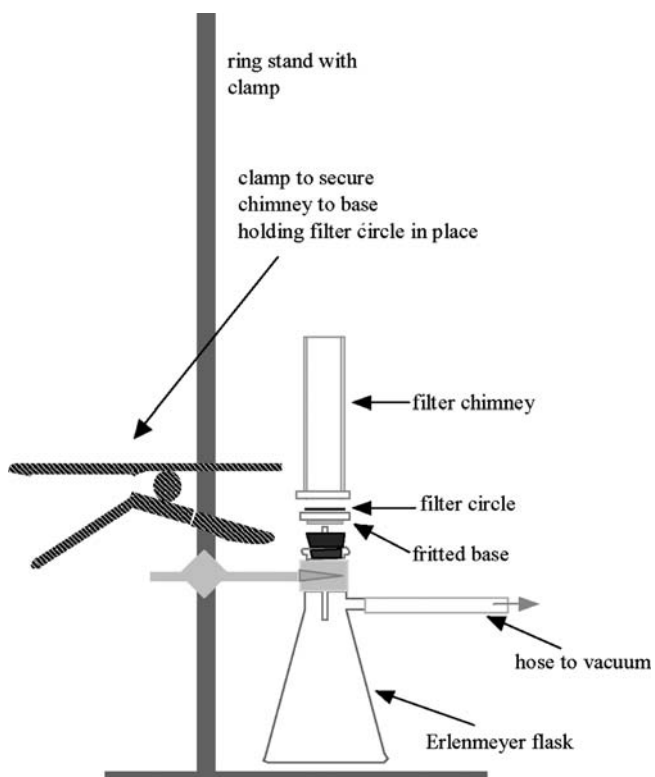


Figure 7.2 Schematic filtering apparatus.



Figure 7.3 Laboratory filtering apparatus.

- 1 M HCl: Add 83 mL of concentrated HCl to 800 mL of deionized water and dilute to 1 L.
- 1.5 N HF: Add 104 mL of 29 N (48%) reagent grade HF to 800 ml of deionized water and dilute to 1 L. Store in a plastic bottle.
- Ethanol, 95%

Procedure

See Figure 7.4 for the flow diagram of this procedure.

Step 1. Pipet 1.0 mL of the uranyl solution into a 50 mL plastic centrifuge tube. Add 10 mL of 1 M HCl and 1 mL of Nd^{3+} carrier (1 mg/mL). Mix by swirling.

Step 2. Add 5 mL of 1.5 M HF, stir with plastic stirrer, and let stand for 30 minutes to precipitate NdF_3 that carries ThF_4 .

Step 3. Assemble the filtering apparatus with the filter. Pour the solution through the filter. Rinse the centrifuge tube twice with 5 mL of water and pour rinse water through filter. Record the time of separation of thorium from uranium. Wash and dry the precipitate with three 5-mL portions of ethanol.

Date and time of NdF_3 (with thorium) separation: _____

Step 4. Disassemble the filtering apparatus and remove the filter with forceps. Fix the filter to a planchet with 2-sided tape. Count the sample three times with a proportional counter for alpha particles and beta particles for 3,000 s. Record mid-point of counting time. Record counting data in Data Table 7.1. Also measure detector background data for at least the same period and record in Data Table 7.1.

Step 5. Pipette 100 λ of the uranium solution each onto the centers of two planchets and dry under a heat lamp. Count one with the proportional counter and then with the alpha-particle spectrometer. Save the second planchet for Part 7C, Step 8.

Date and mid-time of ^{234}Th counting: _____

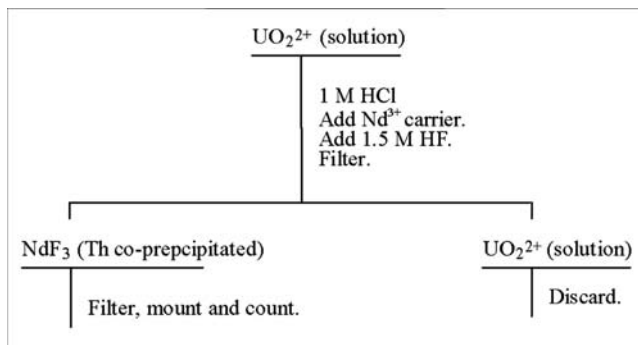


Figure 7.4 Flow diagram for the U-Th separation by co-precipitation of ThF_4 with NdF_3 .

Counting

Determine counting efficiency of the proportional detector in Step 5 for three 3,000-s periods to measure alpha particles and beta particles. Record in Data Table 7.2. Also perform overnight count (50,000 s) for alpha-particle spectral analysis of the planchet to identify the uranium isotopes and any other radionuclides and to determine their relative amounts from their alpha-particle energy spectra and record results in Data Table 7.2. Count alpha- and beta-particle background in proportional counter and alpha-particle spectral background in spectrometer for at least the same periods.

If you wish to confirm the presence of ^{234}Th by measuring its half life, count the sample twice weekly for 4 weeks.

Data Table 7.1 Thorium precipitate count rates

	Count 1 Alpha Beta	Count 2 Alpha Beta	Count 3 Alpha Beta
Gross count rate (cps)			
Background count rate (cps)			
Net count rate (cps)			

Average count rate (R): (alpha) _____ cps; (beta) _____ cps
 Average net beta-particle count rate corrected for ^{234}Th decay between separation from uranium and counting: _____

Data Table 7.2 Uranium solution count rate

	Count 1 Alpha Beta	Count 2 Alpha Beta	Count 3 Alpha Beta
Proportional counter.			
Gross count rate (cps)			
Background count rate (cps)			
Net count rate (cps)			
Spectrometer:	^{238}U Peaks	^{234}U Peaks	Other peaks
Energy, keV			
Gross peak count rate (cps)			
Background peak rate (cps)			
Net peak count rate (cps)			

Average proportional counter net α -particle and beta-particle rate (R) of three counts (alpha) _____cps; (beta) _____cps
 Ratio, adjusted for uranium amounts in sample, of net alpha and decay-corrected net beta-particle counting rate in Table 7.1 to Table 7.2 (alpha) _____(beta) _____

Treatment of Data

See Appendix 6 on statistics for calculations of uncertainties.

For each alpha-particle and beta-particle count rate, subtract the respective background count rate and report the net count rate with its uncertainty.

Correct the beta-particle count rate for radioactive decay by dividing by $e^{-0.693t/t_{0.5}}$ where t is the time of decay between separation and counting for ^{234}Th and $t_{0.5}$ is the half life of ^{234}Th .

Estimate the fraction of uranium that remained in the sample from the alpha-particle count rate compared to the count rate in the initial sample, adjusted for the amount of uranium in the solution. Do the same for thorium based on the comparison of beta-particle count rates. Estimate the efficiency of separating ^{234}Th from ^{238}U .

Questions

1. If the sample were counted over a period of hours or days, would the count rate change with time? Explain.
2. How effective was this method of separation of thorium from the uranium? How could it be improved?
3. Would this be an effective method to produce carrier-free ^{234}Th based on the calculated fraction that was separated? Explain.

7B. Separation of Uranium from Thorium by Solvent Extraction of Uranium

Principle of Separation. Uranium forms a nitrate complex that is extractable into ethyl acetate (as well as other organic extractants). Thorium does not readily form an extractable nitrate complex. When ethyl acetate is contacted with an aqueous solution, the uranium-nitrate complex is partitioned favorably into the ethyl acetate whereas thorium nitrate is not. The distribution of the metal ion between the two phases is expressed as $D = C_{\text{organic}}/C_{\text{aqueous}}$ where C is the concentration in moles or dps per unit volume in the respective phases. The thorium remains in the aqueous phase and is precipitated as the hydroxide for counting.

Equipment and Supplies

- Proportional counter to detect alpha particles and beta particles
- 30-mL or 100-mL separatory funnel, ring, and stand: see Fig. 7.5
- Beaker, 50 mL
- Pipette, 1-mL, with disposable tip
- Transfer pipettes
- Volumetric flask, 1 L
- Bottle, glass, 200 mL
- Planchets, 5-cm dia., lip around edge, stainless steel.
- Centrifuge tubes, 50-mL plastic or glass
- Pipette, 1-mL automatic disposable tip
- Filter apparatus
- Filters, Millipore^R
- Forceps
- Heat lamp

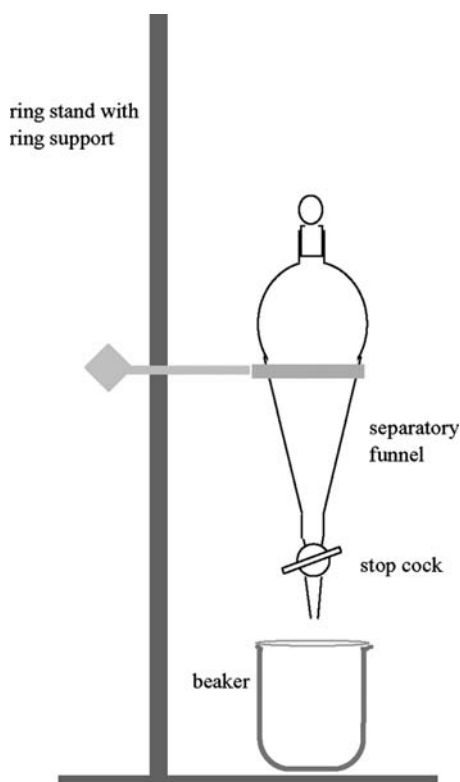


Figure 7.5 Schematic separatory funnel and stand.

Reagents

- Uranium solution: *See 7A.*
- Neodymium carrier, 1 mg Nd^{3+} /mL. *See 7A.*
- Ethyl acetate, reagent grade.
- NH_4NO_3 , saturated: Add about 190 g solid NH_4NO_3 to 100 mL deionized water and stir until it no longer dissolves; a small quantity of undissolved NH_4NO_3 should remain.
- 6 M NH_4OH : Add 400 mL of concentrated NH_4OH to 400 mL deionized water and dilute to 1 L.
- Ethanol, 95%

Procedure

See Figure [7.6](#) for the flow diagram of this procedure.

Step 1. Pipette 1.0 mL of the uranyl nitrate solution into a clean 50 mL beaker. Place under a heat lamp or on a hot plate at low setting and evaporate to near dryness. Remove from heat and cool. Add 5 mL of saturated ammonium nitrate solution. Carefully swirl to dissolve any dried uranium salt.

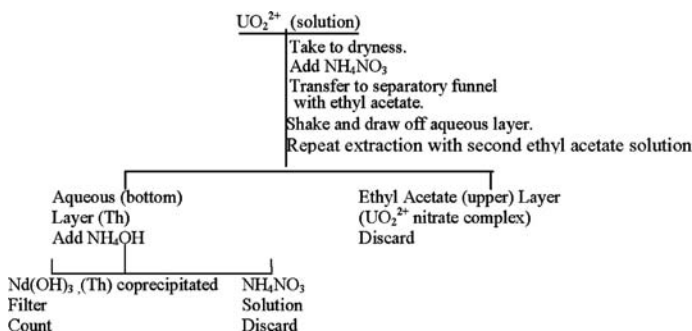


Figure 7.6 Flow diagram for U-Th separation by solvent extraction of U.

Step 2. Transfer the uranyl nitrate in saturated ammonium nitrate solution to a 30-mL separatory funnel. Rinse the beaker with 5 mL of saturated ammonium nitrate and add the rinse to the separatory funnel. Add 20 mL of ethyl acetate to the separatory funnel. Cap the separatory funnel.

Step 3. Shake the separatory funnel vigorously for at least one minute. Invert the funnel, open the stopcock to relieve the pressure, then close the stopcock. Place the separatory funnel on the stand to allow the two phases to separate. Remove the cap and draw down the aqueous (lower) layer into a clean centrifuge tube. Draw down the ethyl acetate layer into a container for disposal.

Step 4. Return the aqueous layer to the separatory funnel and add 20 mL of fresh ethyl acetate. Repeat the extraction and separation in Step 3. Record the time. Collect the aqueous lower layer in a clean centrifuge tube. Discard the organic layer.

Date and time of uranium separation: _____.

Step 5. Pipette 1 mL Nd carrier (1 mg/mL) into the aqueous solution in the centrifuge tube and mix. Add 1 mL 6 M NH_4OH with stirring to precipitate $\text{Nd}(\text{OH})_3$ and co-precipitate thorium.

Step 6. Assemble the filtering apparatus and pour the solution through the filter. Rinse the centrifuge tube twice with 5 mL of water and pour the rinse through the filter. Rinse and dry with three 5-mL portions of ethanol.

Step 7. Disassemble the filtering apparatus and remove the filter with forceps. Fix filter to planchet with double-sided tape. Count the sample with a proportional counter for alpha particles and beta particles. Record mid-point of counting time. Record counting data as described in the counting section below.

Date and mid-time of ^{234}Th counting: _____

Counting

Count the sample for both alpha particles and beta particles for 3,000 s. Count background for 3,000-s intervals before and after the samples. Record in Data Table 7.3.

Data Table 7.3 Thorium precipitate count rates

	Count 1 Alpha Beta	Count 2 Alpha Beta	Count 3 Alpha Beta
Gross count rate (cps)			
Background count rate (cps)			
Net count rate (cps)			
Average net count rate (R) of three counts: (alpha)____ cps; (beta)____ cps			
Ratio adjusted for uranium amount of net alpha-particle and decay-corrected beta-particle counting rates in Table 7.3 to Table 7.2 (alpha)____; (beta)____			

Treatment of Data

See Appendix 6 on statistics for calculation of uncertainty.

For each alpha-particle count and beta-particle count, subtract the respective background to obtain the net count rate with its uncertainty.

Correct the net beta-particle count rate for radioactive decay by dividing by $e^{-0.693t/t_{0.5}}$, where t is the time of decay between separation and counting for ^{234}Th , and $t_{0.5}$ is the half life of ^{234}Th . Report in Data Table 7.3. *If any ^{238}U remains in solution, that fraction maintains ^{234}Th and ^{234m}Pa without decay by the ^{234}Th half life, so that only the fraction of ^{234}Th not supported by ^{238}U will decay with a short half life.*

Estimate the fraction of uranium that remained in the sample from the alpha-particle count rate compared to the count rate in the initial sample, adjusted for the amount of uranium in the solution. Do the same for thorium, based on the comparison of beta-particle count rates. Estimate the efficiency of separating ^{234}Th from ^{238}U .

Questions

1. Conduct a literature survey to find other extraction systems for separating uranium from thorium. Select one or two of these and compare the benefits and disadvantages of each compared to the ethyl acetate system.
2. How could you extract a larger fraction of uranium into ethyl acetate in a single extraction pass?
3. Show mathematically how the fraction of extracted uranium can be increased by multiple consecutive extraction passes.

7C. Separation of Thorium from Uranium by Ion Exchange Chromatography

Principle of Separation. Uranium as the UO_2^{2+} ion in strong chloride solutions forms an anionic chloride species such as UO_2Cl_3^- ; thorium does not. If a solution in which the chloride ion has been adjusted to form the uranyl chloride complex is passed through a cation exchange column, the uranium passes through the column and cationic Th^{+4} is absorbed. After the column is washed to insure that no uranium remains, the absorbed thorium is complexed with oxalate ions to form an anion and is released from the column. Although thorium generally is precipitated with oxalate ions, with excess quantities of oxalate it forms a soluble anionic species. The mass of thorium in this experiment is extremely low relative to that of oxalate and will not form a precipitate.

Equipment and Supplies

- Proportional counter to detect alpha particles and beta particles
- 10-cm-long x 0.8-cm-dia. ion exchange column; see Figure 7.7
- Beakers, 50 mL
- Volumetric flasks, 1 L
- Pipette, 1.0 mL automatic with disposable tips
- Transfer pipet, plastic
- Planchets, 5-cm dia., lip around edge, stainless steel
- Heat Lamp
- Forceps

Reagents

- Uranyl solution *See 7A*
- Cation Exchange Resin: AG 50W-x 4 or x 8 cation exchange resin, 100–200 mesh, H⁺ form
- HCl, concentrated
- 1 M HCl: Add 83 mL of concentrated HCl to 800 mL of deionized water in a 1 L flask and dilute to 1 L.
- 3 M HCl: Add 250 mL of concentrated HCl to 500 mL deionized water and dilute to 1 L.
- 6 M HCl: Add 500 mL of concentrated HCl to 400 mL deionized water and dilute to 1 L.
- 0.5 M $\text{H}_2\text{C}_2\text{O}_4$: Dissolve 45 g oxalic acid in 500 mL deionized water and dilute to 1 L.

Procedure

See Figure 7.8 for the flow diagram for this procedure.

Step 1. Pipette 1.0 mL of the uranyl nitrate solution into a clean 50-mL beaker. Heat the beaker under a heat lamp and carefully evaporate to near

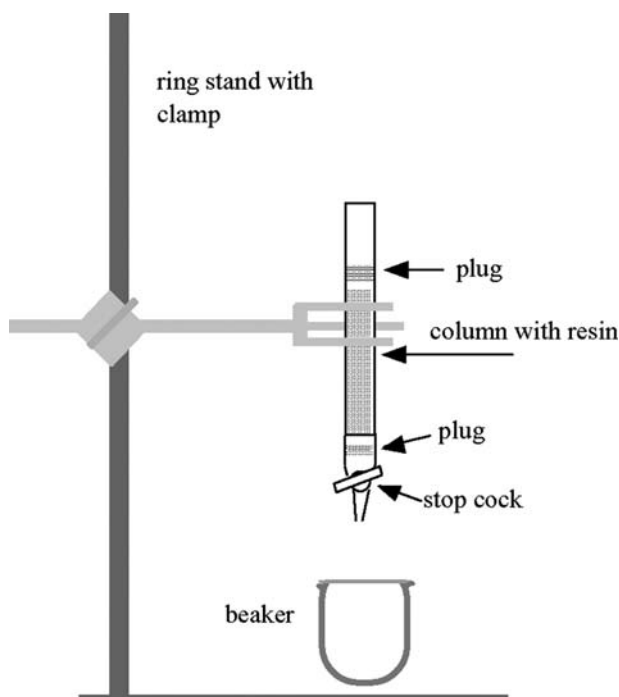


Figure 7.7 Arrangement for ion exchange column separation.

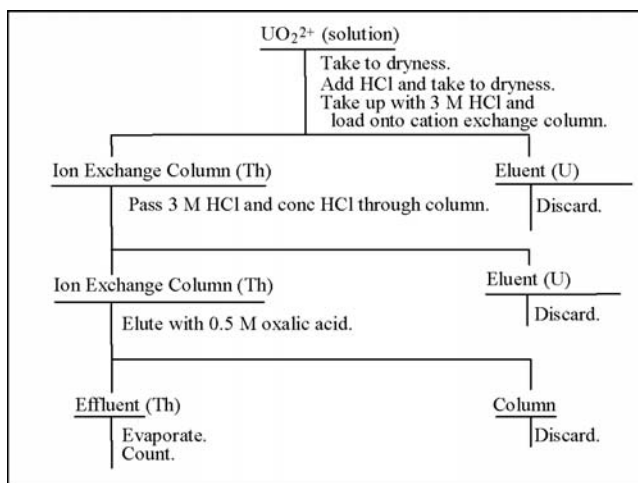


Figure 7.8 Flow diagram for the separation of uranium from thorium by ion exchange chromatography.

dryness. Cool the beaker. Add 2–3 mL of concentrated HCl. Evaporate to near dryness. Cool the beaker and take up uranium in 3 mL of 3 M HCl. Mix well to dissolve any dried uranium salt.

Step 2. During the evaporation in Step 1, prepare the ion-exchange column by placing a glass wool plug inside the column above the stopcock. Close the

stopcock and pour a slurry of 2 cc AG 50W cation- exchange resin (100-200 mesh, H+ form) in water into the column. Let some water flow from column, but keep water level above the resin. Tap the column to assist uniform settling and remove any air bubbles. Condition the column by passing 10 mL of 3 M HCl through the column. Control stopcock to keep liquid level above top of resin.

Step 3. Place a 50-mL beaker under the column to collect the eluent fractions. Add the uranium sample in 3 M HCl from Step 1 to the top of the column with a transfer pipette. Open the stopcock to let the solution flow at a rate of about 1 mL/minute. Record the time of uranium separation. Rinse the beaker that contained the uranium sample twice with 5 mL of 3 M HCl and pour it through the column. Pass an additional 10 mL of 3 M HCl through the column. Then wash the column with 4 mL of concentrated HCl. Close the stopcock when the liquid just covers the resin.

Date and time of uranium separation: _____

Step 4. Remove the uranium-eluent collection beaker and place a clean 50-mL beaker beneath the column to collect the thorium eluent. Elute the thorium with 10 mL of 0.5 M $\text{H}_2\text{C}_2\text{O}_4$ at the rate of about 1 ml per minute.

Step 5. Heat the eluted oxalic acid with thorium on a hot plate to reduce the volume to about 2 mL. Let cool.

Step 6. Transfer the oxalate eluent to a planchet and evaporate under a heat lamp. Let dried planchet cool. Wash out the beaker with 2 mL water and add wash water to planchet. Evaporate under heat lamp. Repeat washing and evaporation. Flame the planchet with a Meeker burner to burn off the remaining oxalic acid. Let the planchet cool.

Step 7. Count the sample three times for 3,000 s each with a proportional counter for alpha and beta particles and record in Data Table [7.4](#). Record the time.

Date and mid-time of ^{234}Th counting: _____

Step 8. Evaporate 10 ml 0.5 M oxalic acid to about 2 mL and pour onto the second planchet with dried 100- λ sample of the initial uranium solution (see Part 7A, Step 5). Evaporate to dryness under the heat lamp. Flame the planchet as in Step 6. Count three times for 3,000 s each with proportional counter for alpha and beta particles. Record in Data Table [7.5](#)

Counting

Count the sample planchet with the thorium eluent in Step 7, for both alpha particles and beta particles.

Count the second dried aliquot of the initial uranium solution in Step 8 for both alpha particles and beta particles.

Count background for 3,000-s intervals before and after the samples. Record results in Data Tables [7.4](#) and [7.5](#).

Data Table 7.4 Count rate of thorium deposit

	Count 1 Alpha Beta	Count 2 Alpha Beta	Count 3 Alpha Beta
Gross count rate (cps)			
Background count rate (cps)			
Net count rate (cps)			

Average net count rate (R) of three counts: (alpha)___ cps; (beta)___cps

Data Table 7.5 Count rate of uranium solution with oxalic acid

	Count 1 Alpha Beta	Count 2 Alpha Beta	Count 3 Alpha Beta
Gross count rate (cps)			
Background count rate (cps)			
Net count rate (cps)			

Average net count rate (R): (alpha)___ cps; (beta)___cps

Average net beta-particle count rate corrected for decay between separation from uranium and counting: _____

Ratio of alpha particle and decay-corrected beta particle net count rates in Table 7.4 to Table 7.5 (alpha)___; (beta)___cps

Ratio of net count rates in Table 7.5 to Table 7.2 (alpha)___; (beta)___

Treatment of Data

See Appendix 6 on statistics for calculations of uncertainties.

For each alpha particle count and beta particle count, subtract the respective background and report the net count rate with its uncertainty.

Correct the beta-particle count rate for radioactive decay by dividing by $e^{-0.693t/t_{0.5}}$, where t is the time of decay between separation and counting for ^{234}Th and $t_{0.5}$ is the half life of ^{234}Th .

Estimate the fraction of uranium that remained in the sample from the alpha particle count rate compared to the count rate in the initial sample, adjusted for the amount of uranium in solution. Do the same for thorium based on the comparison of beta-particle count rates. Estimate the efficiency of separating ^{234}Th from ^{238}U .

4. Evaluate the effect of beta-particle absorption in residual oxalic acid on the count rates of the initial uranium solution.

Questions

1. The ion exchange column separates not only uranium from thorium but a number of other elements. What advantage(s) do you see in the ion exchange procedure relative to the precipitation or the extraction procedure? If you were designing a separation scheme, which of the method would you use? Why?

2. Of all the methods used, which is the most effective in the separation of uranium from thorium? Which do you prefer and why?

References

- Experiments in Nuclear Science, G.D. Chase, S. Ripuper, and J.W. Sulcoski, pp. 119-120, Burgess Publishing Co., Minneapolis, MN (1964) for Section B.
- C. J. Orth and W. R. Daniels, "A Rapid Procedure for the Separation of Carrier-Free Thorium from Uranium and Fission Products" pp I-154-155, in Collected Radiochemical and Geochemical Procedures, 5th Edition, compiled and edited by Jacob Kleinberg, DOE Report LA-1721 (May, 1990) for Section C.
- The experiment in Section A was developed by the authors from commonly-used procedures.

Experiment 8*

Determination of Radium-226 and Radium-228 in Drinking Water

Objective

To measure the naturally-occurring radium isotopes ^{226}Ra and ^{228}Ra in drinking water.

Introduction

One important parameter in determining the quality of drinking water is the measurement of its radioactivity level. The two main radium isotopes of concern are ^{226}Ra , a progeny of naturally-occurring ^{238}U , and ^{228}Ra , a progeny of naturally-occurring ^{232}Th . The decay series for these natural radionuclides, as well as ^{235}U , are given in Appendices 2–4.

Earlier methods used in the analysis of radium isotopes in water required labor-intensive radiochemical separations and subsequent measurement of alpha particles for ^{226}Ra and beta particles for ^{228}Ra . The method used in this experiment applies simpler gamma-ray spectral analysis of the progeny of both ^{226}Ra and ^{228}Ra .

The analysis, described in Part 8A, begins with the co-precipitation of ^{226}Ra and ^{228}Ra on barium sulfate ($K_{\text{sp}} = 1.0 \times 10^{-10}$). The precipitate is collected on filter paper and stored, to await the ingrowth of radioactive progeny. The ^{222}Rn daughter of ^{226}Ra is strongly retained in the barium sulfate precipitate, together with its short-lived progeny that emit gamma rays. The ^{228}Ac daughter of ^{228}Ra that emits gamma rays co-precipitates together with its parent. By counting a major gamma ray from ^{214}Pb (351.9 keV) and one from ^{214}Bi (609.3 keV), the activity of ^{226}Ra is determined. By counting two major gamma rays emitted by ^{228}Ac (338.3 and 911.2 keV), the activity of ^{228}Ra is determined. Measurement of two gamma rays per radium parent is recommended to balance the lesser detection efficiency with use of only one gamma ray each, and the greater potential for interferences with the additional (more than 2) gamma rays that are emitted.

* Prepared by Robert Rosson, Environmental Radiation Center, EOSL, GTRI, Georgia Institute of Technology, Atlanta GA 30332-0841

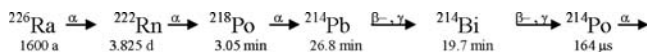


Figure 8.1 Radium-226 and direct progeny.

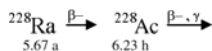


Figure 8.2 Radium-228 and direct progeny.

Figures 8.1 and 8.2 show the short-lived radioactive decay chains for ${}^{226}\text{Ra}$ and ${}^{228}\text{Ra}$, respectively, to illustrate the relationship of the progeny to the two radium isotopes. Long-lived radionuclides continue both the chains.

For ${}^{226}\text{Ra}$, 26 days are needed (based on 7 half lives of the longest-lived progeny in the chain, ${}^{222}\text{Rn}$) to reach 99% of radioactive equilibrium of the progeny. If less time is to be allowed for the ingrowth of ${}^{222}\text{Rn}$, then the fractional ingrowth must be calculated to obtain the amount of ${}^{226}\text{Ra}$ in the sample. For this calculation, the ingrowth factor is $(1 - e^{-\lambda t})$ where λ is the decay constant ($\lambda = 0.693/t_{1/2}$) for ${}^{222}\text{Rn}$. The ingrowth calculation is illustrated in Example 1.

Example 1

Problem: A purified radium sample is counted for gamma rays, 5.2 days after the chemical separation of barium sulfate from a water sample. (5.2 days is the interval from the separation time to the mid-time of the counting period). What fraction of the activity of ${}^{226}\text{Ra}$ is observed in the gamma ray count?

Solution: The half life of ${}^{222}\text{Rn}$ is $t_{1/2} = 3.825$ days. The equation for the fraction of equilibrium activity is:

$$1 - e^{-\lambda_{226}t}$$

Insert the appropriate values:

$$\lambda_{226} = \frac{0.693}{3.825} = 0.181 \text{ days}^{-1}$$

$$t = 5.2 \text{ days}$$

$$1 - e^{-\lambda_{226}t} = 1 - e^{-0.9421} = 1 - 0.39 = 0.61$$

The activity observed at 5.2 days is 61% of saturation activity. The value observed at the 5.2 day count time is divided by 0.61 to obtain value of the saturation activity.

The case of ${}^{228}\text{Ra}$ is simpler than that in Example 1. Although the half life of ${}^{228}\text{Ac}$ requires a 2-day interval to exceed 99% of equilibrium, no delay is needed because ${}^{228}\text{Ac}$ also is co-precipitated with barium sulfate, so that initial radioactive equilibrium within the precipitate remains undisturbed.

Hence, the sample can be counted immediately for its ${}^{228}\text{Ra}$ content with the Ge detector and gamma-ray spectrometer system. The count must be delayed only for ingrowth of the ${}^{226}\text{Ra}$ progeny. A screening measurement of gross alpha activity prescribed by EPA in its drinking-water regulations specifies

that a gross alpha-particle activity of 5 pCi/L (0.2 Bq/L) or less eliminates the need for ^{226}Ra analysis, and thus, the need for delayed counting.

Some water samples also contain 3.66-d ^{224}Ra , a progeny of ^{228}Ac and ^{228}Th . If the sample is measured within about one week of collection by gamma-ray spectrometer, the characteristic gamma rays of ^{224}Ra (at low intensity) and of its progeny ^{212}Pb and ^{208}Tl (at higher intensity) can be detected. Storing the water sample for several weeks before processing will remove ^{224}Ra by radioactive decay.

A reagent blank is processed in Part 8B of this experiment to resolve the problem of contamination due to airborne ^{222}Rn and its progeny. The special background problem encountered with measuring progeny of ^{226}Ra is that one of them – ^{222}Rn – is a gas that emanates from the ground and building materials such as concrete and brick, accompanies the air in the laboratory and the counting room, and can be retained in the barium sulfate precipitate and its filter paper. The concentration of ^{222}Rn and its short-lived progeny in air fluctuates with meteorological conditions and room ventilation, so that the background count rate in the spectral analysis regions of interest also can vary. To resolve this problem, either the contamination due to ^{222}Rn progeny must be maintained sufficiently low that its fluctuation does not measurably affect the count rate, or the background must be monitored for each batch of samples.

In Part 8C, the barium carrier is prepared and a standard source of ^{226}Ra and ^{228}Ra is prepared and counted to calibrate the Ge detector for this radium analysis. The counting efficiency for three of the four characteristic gamma rays that are used to determine the activity of the two radium isotopes can be derived from a curve of efficiency vs. energy of the type prepared in Experiment 2. The efficiency for the 0.6093-MeV gamma ray, however, lies below this curve because of a complication associated with two gamma rays that are emitted simultaneously with good efficiency, in this case, numerous more energetic gamma rays of ^{214}Bi . The counting efficiency of this gamma ray must be determined for the specific Ge detector dimensions and sample location.

Safety Reminder

- Follow the usual safety procedures when working in a radiological laboratory.
- Caution should be exercised when preparing and working with corrosive mineral acids.
- All liquids and solids are to be properly disposed according to laboratory rules and protocol.

Equipment

- 10-mL and 1,000 mL graduated cylinders
- Borosilicate beaker, 1- 2-, or 4-L
- Beakers, 100 mL
- Stirring rods, glass
- Pipette, 5 mL

- Pipetter capable of measuring tenths of mL
- Heated magnetic stirrer and stir bar
- Analytical balance (capable of weighing to nearest 0.01 mg)
- Filtering apparatus
- Filter circles (Whatman 42, 2.5 cm diameter or suitable size for filtering apparatus)
- Ring and Disk mount
- Mylar film cover
- Vacuum pump
- Reagent bottles
- Sintered-glass crucible, fine porosity
- Drying oven
- Plastic squirt bottle for deionized water

Note: All glassware for the experiment should be acid-washed and rinsed with deionized water before use.

Reagents

- ^{226}Ra standard solution, diluted to concentration of about 40 Bq per mL, in 0.01 N HNO_3
- ^{228}Ra standard solution, diluted to concentration of about 40 Bq per mL, in 0.01 N HNO_3
- Concentrated HNO_3
- Concentrated HCl
- Concentrated H_2SO_4
- Barium chloride: Reagent grade $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$
- Barium carrier, standardized, 9 mg Ba^{2+} /mL: Dissolve 16.01 g of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ in deionized water, add 5 mL of concentrated nitric acid, and dilute to 1 L with deionized water. (See **Barium Carrier Standardization** at end of Part 8C.)
- Sulfuric acid, 18 N: Cautiously add 500 mL of concentrated sulfuric acid to 400 mL of deionized water and dilute to 1 L with deionized water.
Note: The reaction of concentrated sulfuric acid with water is an extremely exothermic one. Add concentrated sulfuric acid to water in small quantities, with stirring.
- Sulfuric acid, 0.01 N: Add 0.55 mL of 18 N H_2SO_4 to 100 mL deionized water and dilute to 1 L.
- Ethanol, 95%
- Diethyl ether

8A. Determination of Radium in Drinking Water

Procedure

Step 1. Measure the volume of preserved drinking water in a large graduated cylinder and record the volume to the nearest 1 mL. The sample should have been preserved with 4 mL of concentrated HNO_3 per gallon (3.7 L) of drinking water or enough concentrated HNO_3 to make the pH of the water < 2.

Transfer to a beaker. *The instructor will specify the quantity of water in the sample.*

Step 2. Add 10 mL of concentrated HCl for every liter of water used and mix thoroughly.

Step 3. Accurately pipette 5.0 mL of barium carrier (9 mg/mL) into the sample. Stir and heat to boiling.

Step 4. Precipitate barium sulfate by adding 10 mL of 18 N H₂SO₄ in a fine stream while stirring. Record the date and time of precipitation. Cool 30 minutes in an ice bath or allow overnight settling in covered beaker.

Date and time of BaSO₄ precipitation: _____

Note: The following steps describe a specific method of filtering, weighing and mounting the sample. The instructor may provide alternate instructions for preparing the barium sulfate source appropriate for the available counting facilities.

Step 5. Filter the solution that contains the BaSO₄ through a tared filter. One approach is to let the precipitate settle and then decant carefully approximately 800 mL of a 1-L sample; slurry the precipitate in the remaining water, pour it through the filter; and wash any remaining precipitate from the beaker to the filter with a jet of deionized water. *Avoid pulling excess air through the filter because airborne radon progeny will add to the sample counting results (see Part 8B).*

Step 6. Wash and dry the precipitate on the filter with 10 mL of ethanol, followed by 10 mL of diethyl ether. Turn off the suction as the last of the diethyl ether passes through the filter.

Step 7. Remove the dried filter with the precipitate. Weigh the tared filter on a tared planchet to the nearest 0.1 mg. Record the weight in Data Table [8.1](#)

Step 8. Mount the precipitate in a holder such as a ring and disk with Mylar cover. Label the sample according to counting room protocol.

Step 9. Count immediately for 60,000 s with a Ge detector plus gamma-ray spectrometer to observe the gamma rays emitted by the ²²⁸Ra daughter in the sample if these results are needed promptly. Count after 2 – 4 weeks to permit ingrowth of the ²²⁶Ra progeny and determine the levels of both ²²⁶Ra and ²²⁸Ra. Record mid-time of counting. Record net count rates in energy regions of interest in Data Table [8.2](#) and [8.3](#).

Dates and mid-times of counting: _____

Chemical Yield Calculation

Subtract the tared filter paper plus planchet weight from the combined weight of the filter, planchet, and precipitate to determine the net weight of the BaSO₄ precipitate. Enter result in Data Table [8.1](#). Divide this net weight of the precipitate by the theoretical weight of the precipitate based on the amount of

standardized barium carrier that is used in the precipitate. This is the chemical yield (Y_s) for the sample precipitate.

Data Table 8.1 Chemical yield

	Mass
Filter Paper + Precipitate + planchet	
Filter Paper + planchet	
Barium Carrier (as BaSO ₄)	

$$\frac{\text{Final mass of barium sulfate}}{\text{Initial mass of barium sulfate}} = \text{chemical yield} \quad (8.1)$$

Chemical Yield = _____

Counting

After the selected ingrowth period, record the time and count the sample according to the counting procedures. The count time may be adjusted if the radium concentration is higher than usual or the detector counting efficiency is unusually high or low.

Ingrowth interval: _____

Treatment of Gamma-Ray Counting Data

Radium-226 Concentration Calculation

Determine the amount of ²²⁶Ra according to the following equation for the 351.9 keV gamma-ray of the progeny ²¹⁴Pb and the 609.3 keV gamma-ray of the progeny ²¹⁴Bi, respectively.

$$A_s = \left[\frac{1}{(0.037) V Y_s D_s \varepsilon} \right] \left(\frac{R}{F_i} \right) \quad (8.2)$$

Where

A_s = the concentration of ²²⁶Ra in pCi/L,

0.037 = conversion factor from disintegrations per second to picocuries (pCi) [0.037 dps = 1 pCi],

Y_s = chemical yield determined for the sample,

D_s = ingrowth factor ($1 - e^{-\lambda t}$), where $\lambda = 0.693/t_{1/2}$; t = time interval in d between the separation of the radium from the water and the midpoint of the counting time, and $t_{1/2}$ = half life of ²²²Rn of 3.82 d,

R = net counts per s for the gamma-ray under consideration (background and Compton contributions have been subtracted; the uncertainty or error reported for that gamma ray should be noted),

F_i = branching ratio for gamma-ray under consideration; see Data Table 8.2 for value,

ϵ = counting efficiency of specific gamma ray; see Part 8.C for measurement, and

V = sample volume, L.

Record all information in Data Table 8.2 Based on the values calculated for each gamma-ray and their respective uncertainties, calculate a weighted average for the two. See section on **Weighted Average Calculations** in Appendix 6. Report the value as pCi or Bq ²²⁶Ra per L water with its uncertainty.

Data Table 8.2 Activity of ²²⁶Ra

²²⁶ Ra	351.9 keV γ	609.3 keV γ
Sample volume (V)		
Chemical Yield Fraction (Y)		
Ingrowth factor (D)		
Net gamma ray count rate (R)		
Branching ratio (F _i)	0.358	0.448
Counting efficiency (ϵ)		
Activity ²²⁶ Ra (pCi/L \pm σ)		

Activity ²²⁶Ra in pCi/L (weighted average)_____

Radium-228 Concentration Calculation

Determine the amount of ²²⁸Ra according to the above equation, but for the 338.3 keV and 911.2 keV gamma-rays of the progeny ²²⁸Ac. The following items are different from the above equation for ²²⁶Ra:

D_s refers to the ²²⁸Ac half-life of 6.15 h, but parent and daughter are in equilibrium (D_s = 1.00) immediately because both are co-precipitated with barium sulfate.

F_i refers to the branching ratios of the two characteristic gamma rays of ²²⁸Ac that are shown in Data Table 8.3

Record the data for this set of calculations in Data Table 8.3 Based on the values calculated for each gamma-ray and their respective uncertainties, calculate a weighted average for the two. See section on **Weighted Average Calculations** in Appendix 6. Report the value as pCi or Bq ²²⁸Ra per L water with its uncertainty.

Data Table 8.3 Activity of ²²⁸Ra

²²⁸ Ra	338.3 keV γ	911.2 keV γ
Sample volume (V)		
Chemical Yield Fraction (Y)		
Ingrowth factor (D)		
Net gamma ray count rate (R)		
Branching ratio (F _i)	0.113	0.266
Counting efficiency (ϵ)		
Activity ²²⁸ Ra (pCi/L \pm σ)		

Activity ²²⁸Ra in pCi/L (weighted average)_____

8B. Preparation of a Reagent Blank and Testing for Airborne Radon and Progeny

Procedure

Note: If both the reagent blank and testing for airborne radon progeny are to be done, perform the two samples in parallel. Make certain that glassware could not have accumulated radon progeny from air while standing in the open.

Step 1. *Reagent blank.* Measure a 1-liter volume of deionized water. Add 1 mL of concentrated HNO_3 to the sample. Pour the measured volume into a clean borosilicate beaker large enough to contain it without spilling, e.g., 2-L volume.

Step 2. Add 10 mL of concentrated HCl to the deionized water and mix thoroughly.

Step 3. Accurately pipette 5.0 mL of barium carrier (9 mg/mL) into the sample. Stir and heat to boiling.

Step 5. Precipitate barium sulfate by adding slowly 10 mL of 18 N H_2SO_4 in a fine stream with stirring. Record date and time of separation of radon daughter plus progeny from radium parent. Cool 30 minutes in an ice bath or allow to digest overnight covered..

Note: The following steps describe a specific method of filtering, weighing and mounting the sample. The instructor may provide alternate instructions for preparing the barium sulfate source appropriate for the available counting facilities.

Date and time of radium separation: _____

Step 6. Place a tared filter of the type and dimensions used in Procedure 8A in the filter funnel apparatus that is attached to a vacuum source.

Step 7a. *For reagent blank.* Filter the BaSO_4 solution on the tared filter paper. Keep filtration time to a minimum and measure the total time that the air is drawn through the filter. Wash the precipitate that remains in the beaker to the filter by rinsing the beaker with a jet of deionized water. Wash and dry the precipitate on the filter with 10 mL of ethanol, followed by 10 mL of diethyl ether. Turn off the suction when the final amount of diethyl ether has passed through the filter.

OR

Step 7b. *For detection of airborne radon progeny.* Filter a reagent blank solution that contains the BaSO_4 on the tared filter paper. Wash the precipitate that remains in the beaker to the filter by rinsing the beaker with a jet of deionized water. Wash and dry the precipitate on the filter with 10 mL of ethanol, followed by 10 mL of diethyl ether. Draw air through the sample for a measured time of 30 minutes to 1 hour to collect airborne radon and

Data Table 8.4 Chemical yield of blank and airborne sample

	Blank	Airborne Sample
Filter Paper + Precipitate, mg		
Filter Paper, mg		
Barium Carrier (as precip. BaSO ₄), mg		
Chemical Yield		

daughters. Record date, time of collection of radon progeny from air, and collection period.

Date, time, and period of collection of radon progeny from air: _____

Step 8. Remove the filter with the precipitate. Weigh the tared filter on a tared planchet the nearest 0.1 mg. Record the weight in Table [8.4](#)

Step 9. Mount the precipitate on a holder such as a ring and disk, and cover with Mylar film. Label the sample according to counting room protocol.

Step 10. Count the gamma rays emitted by the sample with a Ge detector plus spectrometer after the same time interval as in Procedure 8A. The airborne radioactivity sample should be counted as soon as possible after sample collection, with data recorded in Data Table [8.5](#) Repeat counting after selected intervals and record in Data Table [8.6](#) as indicated below. Determine the chemical yield as described in Procedure 8A, based on the information recorded in Data Table [8.4](#)

Counting

Reagent Blank. Inspect the gamma-ray spectrum carefully to determine if any of the gamma-rays from radium-226 are present. If so, record results in Data Table [8.5](#) Determine the amount according to the process described in Part 8A.

Activity ²²⁶Ra in pCi/L (weighted averages): _____

Airborne Radon Progeny. Scheme 1. Count the sample immediately on the germanium detector, recording the time interval from separation to filtration Record in Data Table [8.5](#) Then count again in one week, followed by a third

Data Table 8.5 Activity of ²²⁶Ra in blank and airborne sample

	351.9 keV	609.3 keV	351.9 keV	609.3 keV
Sample volume (V)	Blank		Airborne Sample	
Chemical Yield Fraction (Y)				
Ingrowth factor (D)				
Net gamma ray count rate (R)				
Branching ratio (F _i)	0.358	0.448	0.358	0.448
Counting efficiency (ε)				
Activity ²²⁶ Ra (pCi/L ± σ)				

Data Table 8.6 Gamma-ray decay study of radionuclides on filters

Gamma-ray energy and net count rate interval, d	Count 1		Count 2		Count 3	
		351.9	609.3	351.9	609.3	351.9

Data Table 8.7 Alpha- and beta-particle decay study

Interval, d	Gross	Bkgd.	Net	Gross	Bkgd.	Net
	α (cps)	α (cps)	α (cps)	β (cps)	β (cps)	β (cps)

count in two weeks after sample collection. Be sure to compare the spectrum of the sample to a detector background spectrum counted the same length of time. Record results in Data Table 8.6. Identify the radionuclides by gamma ray spectrometry.

Scheme 2. Count the sample immediately with an α and β counter (e.g., the proportional counter) for 200 minutes. Repeat the count each day for 14 days or until the count rate equals or nearly equals the background. Obtain background counts for both alpha-particle and beta-particle counting modes. Subtract respective backgrounds for each count period and record in Data Table 8.7

Plot data of alpha-particle and beta-particle net count rates (on log scale) on the same graph versus time (linear scale) in days.

8C. Preparation of ^{226}Ra and ^{228}Ra Standard and Barium Carrier

Procedure

Preparation and counting of ^{226}Ra and ^{228}Ra standards for calibration of Ring and Disk source (*in triplicate*)

Step 1. Pipette exactly 5 mL of barium carrier into 100-mL beaker that contains 20 ml of deionized water. Add 5 drops of concentrated HCl. Pipette 1 ml of ^{226}Ra standard solution and also pipette 1 mL of ^{228}Ra standard solution into the beaker. Stir well.

Data Table 8.8 Radium count rate

	²²⁶ Ra		²²⁸ Ra	
Energy (keV)	351.9 γ	609.3 γ	338.3 γ	911.2 γ
Decay fraction	0.358	0.448	0.113	0.266
Yield (fraction)				
Activity (dps)				
Gross count rate (cps)				
Net count rate (cps)				
Count rate, ingrowth corrected (cps)				
Counting efficiency				

Step 2. Heat the solution to boiling and add 20 ml of 18 N H₂SO₄ in a steady stream with stirring to precipitate BaSO₄ with radium standards. Digest while boiling for 10 minutes. Let solution cool.

Date and time of precipitation: _____

Step 3. Pour slurry through tared filter circle in filtering apparatus. Rinse beaker with four 5-mL portions of 0.01 N H₂SO₄ onto filter. Wash and dry filter and precipitate with 10 mL of ethanol and then with 10 ml of diethyl ether.

Step 4. Transfer filter to tared planchet and weigh. Subtract tared weights to calculate weight of BaSO₄ and the yield of BaSO₄ relative to the pipetted amount. Record yield in Data Table 8.8. Prepare filter on a holder such as a ring and disk with Mylar film cover. Store for counting.

Step 5. After interval of about 4 weeks since BaSO₄ precipitation, count filter in holder with Ge detector and spectrometer for at least 3,000 s. Make certain that location of holder relative to the detector is identical for this calibration measurement and all sample measurements.

Step 6. Record the gross count rates of all four characteristic peaks in Data Table 8.8. Calculate the net count rate for each peak. Use equation 8.2 (given in Procedure 8A) to calculate the counting efficiency, ϵ , for each of the four gamma rays; this is based on the activity, A_s , of each of the two standard solutions in the pipetted solution volume, V (i.e., 1 mL). The ingrowth factor, D_s , is 1.00 for ²²⁸Ra and 0.99 for ²²⁶Ra when the interval between radium precipitation and counting is 26 days. Calculate the average counting efficiency and standard deviation.

Barium carrier standardization (*in triplicate*)

Step 1. Pipette exactly 5.0 mL of carrier into a clean 100-mL beaker that contains 20 mL of deionized water. Add 5 drops of concentrated HCl. Heat the solution to boiling and add 20 mL of 18 N H₂SO₄ in a steady stream with stirring. Digest the sample on the hot plate for 10 minutes. Remove the beaker from the hot plate and let the solution cool to room temperature.

Step 2. Slurry the precipitate and filter into a clean, tared sintered-glass crucible of fine porosity. Rinse beaker with four 5-mL portions of 0.01 N H_2SO_4 and add to filter to ensure quantitative transfer of all of the precipitate to the crucible. Wash the precipitate twice with 20 mL of 0.01 N H_2SO_4 .

Step 3. Remove the crucible from the filtering funnel and dry in the oven at 110°C for 2 hours.

Step 4. Place the crucible in a desiccator to cool. Weigh to constant weight. Record the weight for calculating the barium mass per mL. Report the average standardized barium in $\text{mg Ba}^{2+}/\text{mL}$ and as BaSO_4/mL (to the nearest 0.1 mg) and label bottle (see Experiment 5). The spread in the values should be less than 1%.

Net weight of BaSO_4 : (1)_____ ; (2)_____ ; (3)_____ ; (average)_____

Questions

1. If a sample contains 0.56 pCi ^{226}Ra per L, (a) calculate the mg/L of ^{226}Ra in the water. (b) Calculate the mg/L of natural uranium that would be in the water if the ^{226}Ra is in radioactive equilibrium with its parent ^{238}U .
2. List the assumption(s) associated with the reported chemical yield for the recovery of radium by its co-precipitation on BaSO_4 . Design an experiment to test assumptions.
3. If the chemical yield for several samples is in excess of 100%, offer plausible explanations that would give rise to this observation. How would you correct or compensate for this observation?
4. Three different laboratories conduct an experiment to determine the amount of airborne radioactivity on BaSO_4 . Laboratory A finds no activity; B observes both alpha and beta activity that decay with a half life of several days; C observes alpha and beta activity that increase with time. Explain their disparate findings.
5. If airborne activity is a serious and troublesome problem for a laboratory, suggest ways to eliminate or minimize it.
6. Calculate the amount of barium carrier that will remain in a 4-L sample, as described here. What percent barium is lost due to its solubility? Design an experiment to check this result. See the introduction for the solubility product value.

Source

Adapted from “Method for the Determination of Radium-228 and Radium-226 in Drinking Water by Gamma-ray Spectrometry Using HPGE or Ge(Li) Detectors”, ERC, GTRI, Georgia Institute for Technology, Atlanta, GA, an Approved Test Procedure of the US EPA (see Federal Register, March 12, 2007, pp. 11,200–11,249).

Experiment 9

Radiochemical Determination of Tritium in Water

Objective

To determine the concentration of tritium (^3H) in water by liquid scintillation counting.

Introduction

Tritium (^3H or T) is a radioactive isotope of hydrogen with a half life of 12.3 years that emits only low-energy beta-particles ($E_{\text{beta max}} = 0.0186 \text{ MeV}$). Its decay scheme is shown in Fig. 9.1. Tritium is naturally produced in the stratosphere by cosmic rays. It also has entered the environment in large quantities from nuclear weapons production and testing, and from the nuclear power fuel cycle. It is primarily associated with water as HTO, but also exists in the environment as the gases HT, DT, or T_2 , and in organically-bound forms such as CH_3T .

In this experiment, tritiated water is purified by simple distillation, and the tritium beta particles in the condensate are measured with a liquid scintillation (LS) counter. Such distillation also can collect tritiated water samples from solids. Tritium in other forms must be processed before it can be counted like tritium in water; for example, tritiated hydrogen gas and tritiated organic substances can be oxidized to form water. Additional separations may be needed if the liquid or solid sample contains radioactive gases or volatile substances other than tritium that may be collected with the distilled tritiated water. Such radioactive impurities can be identified in the data output from the LS counter of an energy spectrum that differs from that of pure tritium, or of counts in energy regions where tritium counts are not found.

An aliquot of the distilled and condensed tritium-containing water sample is prepared for LS counting by adding it to an LS cocktail in a counting vial. Also counted in the same batch are two other vials with scintillation cocktail, one with a standard tritium solution, and the other with a blank water solution.

To calculate the tritium activity in an analyzed sample, the count rate in the blank sample – the “background” – first is subtracted from the gross

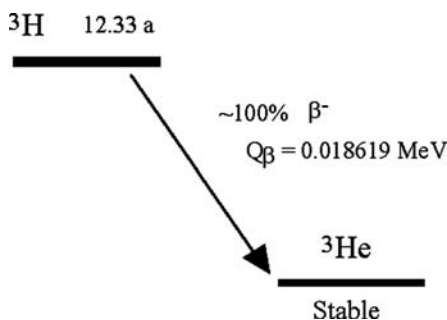


Figure 9.1 Decay scheme for tritium (${}^3\text{H}$).

count rate of the sample and the standard solution to obtain their net count rates. The sample net count rate is then multiplied by the ratio of the standard solution activity to its net count rate to obtain the sample activity. The results of sample analysis may be reported in Bq, pCi, or disintegrations per second per unit mass or volume of water. Sometimes the concentration is reported in a “Tritium Unit,” TU, which is 1 tritium atom per 10^{18} hydrogen atoms, or 7.17 disintegrations per minute per kg of water.

Modern LS counter systems include energy spectral analysis that permits distinguishing tritium from radionuclides that emit beta-particle groups with a significantly different energy range. Because beta particles are emitted over an energy range, emissions by two or more radionuclides partially overlap in spectral analysis, unlike the clearly separated peaks observed for alpha particles and gamma rays. Tritium with its very low beta-particle energies can be distinguished from many other radionuclides that emit more energetic beta particles, but a small fraction of these more energetic beta-particle groups is counted in the tritium region of interest (ROI).

Conventionally, tritium is measured by selecting an energy ROI that is sufficiently wide to include most counts due to tritium but relatively few due to other radionuclides and the instrument background. Data from other ROI’s – typically at higher energies – should be recorded at the same time to assure that the instrument background is stable and that no other radionuclides are in the purified sample. Counts due to more energetic radionuclides can be subtracted from the tritium ROI if the energy spectrum of beta particles from these radionuclides is known.

The sample is purified by distillation to separate the tritium-containing water from both non-radioactive and radioactive impurities. Various substances can cause scintillations by means other than radionuclide emission – by chemical fluorescence or luminescence – or interfere with (“quench”) detection of scintillations due to radionuclides. Even after purification, both processes are inevitable, but to a limited extent. Luminescence due to visible light will decay when the sample is stored in a darkened region of the LS system before the sample is counted. The degree of quenching, notably due to water in the sample, is determined instrumentally by reference to comparison sources and recorded, so that any deviation from the quenching observed for the tritium standard can be taken into account.

Safety Reminders

- Follow the usual safety procedures when working in a radiological laboratory.
- Caution should be exercised when preparing and working with corrosive mineral acids.
- All liquids/solids are to be properly disposed of according to laboratory rules and protocol. Ask instructor how to dispose of samples that contain scintillation cocktail.

Equipment and Supplies

- Distillation apparatus: Flask (125-ml or 250-mL), condenser, heater, rheostat, and azeotropic collection vessel. See distillation apparatus in Figures 9.2 and 9.3 (*Note on the azeotropic collection vessel: it is used to collect tritiated water from solids by addition of a selected organic liquid that is distilled with a fixed fraction of water at a common boiling point and then separates into two phases when cooling in the collection vessel. In the exercise described here, it is simply used as a convenient collector.*)
- Pipette, 10-mL capacity
- Liquid scintillation counting vials, 20-mL capacity, glass or plastic depending upon the type with which the counting system is calibrated
- Liquid scintillation counting system, low-background, with spectrometer

Reagents

- Scintillation cocktail such as Ultima Gold™
- Tritium standard solution, diluted to a concentration of about 1 Bq per mL
- Blank water, deionized water with tritium content negligible relative to analyzed samples.

Procedure

Step 1. Transfer an appropriate amount of the water sample (usually about 20 mL) to the distillation flask. Connect the condenser and collection vessel and clamp to stand.

Step 2. Set the rheostat to boil the water gently. Distill the water sample and collect 11 mL or more of the distilled water in the condensate collection vessel.

Step 3. Cool the sample to room temperature. Transfer an aliquot with a 10-mL pipette to a clean scintillation counting vial.

Step 4. Add 10-mL of scintillation cocktail, place cap on vial and tighten. Shake sample and place in the LS counting chain.

Step 5. Prepare background sample vial with blank water. Combine 10 mL of this distilled water sample and 10 mL of the scintillation cocktail, tighten cap, shake well, and add to the LS counting chain.

Step 6. Prepare a tritium comparison solution from a tritium standard solution of known tritium activity. Pipette 10 mL of the diluted solution into a 20-mL

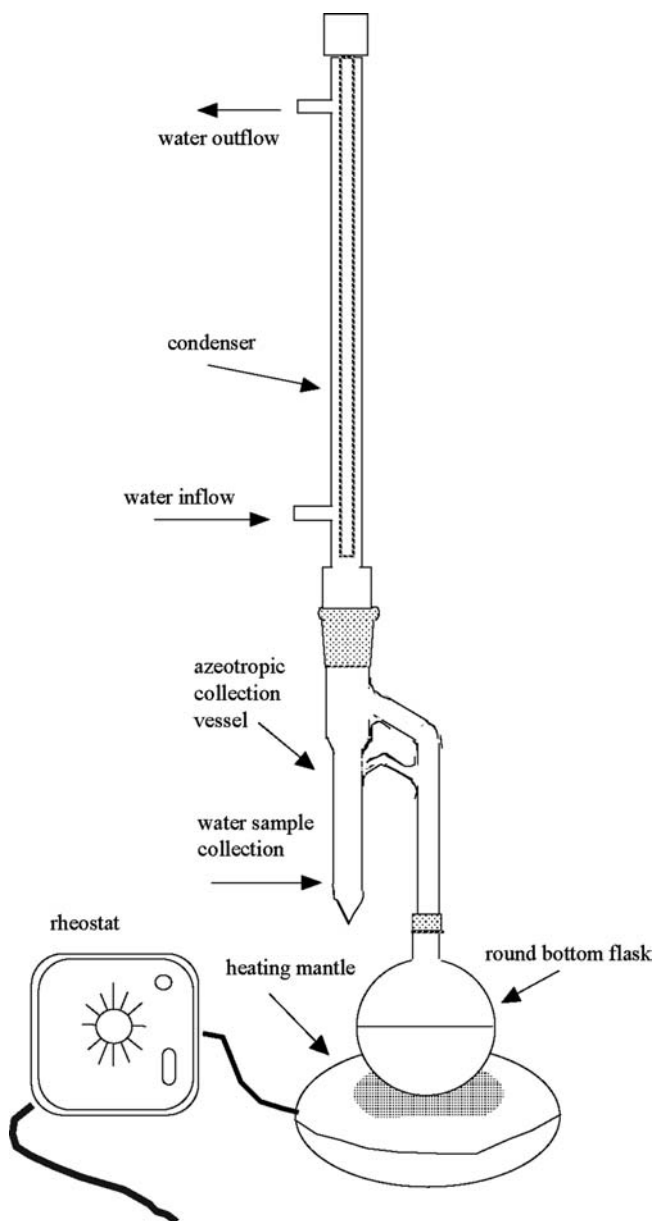


Figure 9.2 Distillation apparatus schematic.

vial, add 10 mL of scintillation cocktail, tighten cap, and shake well. Add to the LS counting chain.

Counting

The vials that contain the sample, blank, and the diluted standard solution are counted according to the protocol for operating the liquid scintillation counter for tritium measurement. The vials are placed in holders in a chain that moves first to a darkened holding area for decay of luminescence and



Figure 9.3 Distillation apparatus.

then to an elevator that places each vial individually between two photomultiplier tubes for counting. The signal pulses that are counted result from interaction by the tritium beta particles in the cocktail-water mixture that generates light detected by the photomultiplier tubes. The protocol specifies the energy-window setting, controls related to quenching and luminescence, the counting period, and desired counting repetition. It may also specify calculations performed by the program, such as subtraction of background count rate, and conversion of count rate to activity

The results of the counts are recorded in Data Table [9.1](#). The samples are counted for an established time period, typically 3,000 to 12,000 s, to achieve an appropriate detection sensitivity. Samples often are counted twice or more to indicate the precision of measurement.

Determination of the Counting Efficiency for Tritium

The counting efficiency of the liquid scintillation counting system is determined according to the following relationship:

$$\varepsilon_T = \frac{(R_{gross} - R_{bkg})}{A^0} \quad (9.1)$$

where

ε_T = counting efficiency for tritium,

R_{gross} = gross count rate of the standard (cps),

Data Table 9.1 Tritium count rates

	Gross count rate	Net count rate
Standard		
Blank		
Sample		

R_{bkg} = average blank (background) count rate (cps), and
 A° = disintegration rate (“activity”) of tritium in the standard sample (d/s or Bq).

Treatment of Data

The activity of each sample is determined using the following equation:

$$A_{\text{sample}} = \frac{(R_{\text{gross}} - R_{\text{bkg}})}{\epsilon_T} \quad (9.2)$$

where

A_{sample} = activity of tritium in the sample (Bq),
 R_{gross} = gross count rate of the sample (cps),
 A_{bkg} = average blank (background) count rate (cps), and
 ϵ_T = counting efficiency for tritium.

Data Reporting

Report the concentration of tritium in Bq/L for the analyzed sample. Report the uncertainty of each result from the counting data. Consult Appendix 6 on counting statistics.

Questions

1. Calculate the minimum detection limit of tritium for the counting system in this experiment. (See Section 10.4.2 of your *Radioanalytical Chemistry* textbook for guidance on calculating the MDA).
2. Knowing the origin of the sample, prepare a list of possible sources of the tritium in the sample you analyzed.
3. Prepare a list of possible non-tritium radionuclides that may contaminate the sample. Explain how the counted sample may be contaminated with this source. How may such contamination be identified with the LS counter system?
4. A water sample is brought into a laboratory for tritium analysis. Three separate fractions of 250 mL each are removed from the 1-gallon container, distilled separately. A 10 mL portion is taken for counting as was done in this experiment. The results were 130 Bq/L, 52 Bq/L and 110 Bq/L. Calculate the average and standard deviation of the mean. What might contribute to the spread in the results? Explain.
5. A nuclear device was accidentally dropped into a marsh region but there was no nuclear explosion, only a conventional explosion that spread bomb material. Is there any reason to look for tritium at the explosion site? Explain.

Source

This experiment describes routine measurements performed in the Environmental Radiation Center, GTRI, GIT.

Experiment 10

Determination of ^{131}I in Water

Objective

To determine the concentration of ^{131}I in drinking water by purification sequentially as silver iodide and palladium iodide, followed by counting beta particles.

Introduction

Radioactive iodine-131 ($t_{1/2} = 8.02$ d) emits beta particles and gamma rays (see the decay scheme in Figure 10.1). It is a major fission product; its fission yield varies somewhat with the particular fissile material, but is about 5%. Detection of ^{131}I is an important component of fresh fission products 1 – 4 weeks after fission. Once this isotope is introduced into the environment, it readily moves through the ecological system and into the food chain. Notably, it accumulates in the milk of animals and should be measured in cows' and goats' milk when fission products have entered the environment during the past month (see Experiment 11 on the determination of ^{131}I in milk). Iodine is biologically active in mammals as a vital component of thyroid hormones, hence accumulation of high levels of radio-iodine in human thyroid glands can be a concern.

The first step of the analysis ensures isotopic exchange of the stable carrier and the radio-iodine in the sample. In this experiment, iodate carrier is added and then reduced to iodide with sodium sulfite to cause exchange among iodate, iodine, and iodide species. (Read the discussion in the Introduction to the Course on isotopic exchange.) The resulting iodide is purified by precipitation, first as silver iodide (AgI) and then, after dissolution, as palladium iodide (PdI_2).

Iodine-131 is measured by counting beta particles (major beta-particle group maximum energy = 0.606 MeV, 89.4%) and/or gamma rays (major gamma ray energy = 0.364 MeV, 81.2%). When the option is available, gamma-ray measurement by spectral analysis with a Ge detector generally is more simple and convenient than beta-particle measurement because little or no chemical purification is needed. The ^{131}I half-life of only 8 days permits confirmation of its detection by decay measurements performed during a 2-week period. The relatively short half life also indicates that analysis must take place within a few weeks after sample collection.

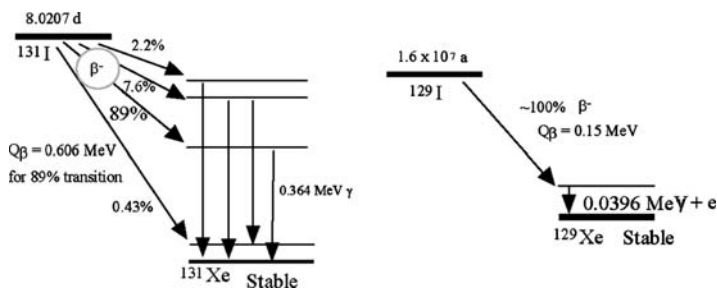


Figure 10.1 Simplified decay schemes for ^{131}I and ^{129}I

In this experiment, a standard ^{131}I solution also is precipitated as PdI_2 to calibrate the beta-particle detector. Two different weights of PdI_2 are precipitated so that interpolation of counting efficiency as a function of sample weight (i.e., source thickness) is possible, as discussed in Experiment 4.

This method also is suitable for separating and purifying other iodine radioisotopes in water samples, notably the fission products ^{129}I , ^{132}I , ^{133}I , and ^{135}I . The latter three are short-lived and only found in fresh fission products. Iodine-129 has the extremely long half-life of 1.57×10^7 a. It emits comparatively low-energy beta particles (maximum beta-particle energy = 152 keV), gamma rays (39.6 keV), characteristic xenon X rays, and conversion electrons. The decay scheme for ^{129}I is given in Figure 10.1. It is measured by counting the low-energy beta particles with a liquid scintillation detector, counting the 39.6-keV gamma ray and X rays (29 – 34 keV) with an X-ray detector, or neutron activation of ^{129}I and then counting the produced ^{130}I .

Safety Reminders

- Follow the usual safety procedures when working in a radiological laboratory.
- Caution should be exercised when preparing and working with corrosive mineral acids
- All liquids and solids are to be properly disposed of according to laboratory rules and protocol.

Equipment and Supplies

- Beakers, 1-, 2-, or 4-L
- Volumetric flasks, 100 mL, 1 L
- Magnetic stirrer and stir bar
- Centrifuge tubes, 50 mL
- Filtering apparatus
- Filters
- Pipettes, 500 λ and 1 mL
- Materials for mounting sample for counting, such as ring and disk with mylar cover
- Low-level beta-particle counting system, such as anti-coincidence proportional counter

Reagents

- 6 M ammonium hydroxide: Add 400 mL of concentrated ammonium hydroxide to 500 mL of water and dilute to 1 L.
- Ethanol: 95%
- 6 M hydrochloric acid: Add 500 mL of concentrated HCl to 400 mL of water and dilute to 1 L.
- Iodate carrier, 10 mg I/mL: Dissolve 1.685 g of KIO_3 in 50 mL of water and dilute to 100 mL in volumetric flask. (Standardization procedure is given at end of experiment.)
- ^{131}I standard solution as iodide: dilute standard solution to about 4 Bq per mL
- Nitric acid: concentrated, reagent grade
- 0.1N nitric acid: add 6.2 ml concentrated HNO_3 to 900 ml deionized water and dilute to 1.0 L
- 0.2 M palladium chloride, PdCl_2 : Dissolve 3.55 g of PdCl_2 in 80 mL of water and dilute to 100 mL.
- 0.1 M silver nitrate: Dissolve 17.0 g AgNO_3 in 100 mL of water and dilute to 1 L. Store in dark bottle.
- 1M sodium sulfite, Na_2SO_3 : freshly prepare by dissolving 12.6 g Na_2SO_3 in 80 mL of water and diluting to 100 mL.
- 2 N sulfuric acid: Carefully add 55.6 mL of concentrated sulfuric acid to 500 mL of water, mix, and dilute to 1 L with water.
- Zinc powder: reagent grade

Procedure

Note: Steps 1 and 2 insure that isotopic exchange occurs between the carrier and the radioiodine in the sample by interchange during reduction. Steps 3-10 purify iodine from other fission products.

Step 1. To a 1-L sample of water not previously acidified (*to avoid iodine loss by volatilization*), add 1 mL of iodate carrier (10 mg I) and 7.5 mL of concentrated nitric acid. Stir for 1 hour to achieve iodide-iodate interchange.

Step 2. Add 10 mL of freshly prepared 1 M sodium sulfite and stir for 30 min to reduce iodate to iodide.

Step 3. Add 20 mL of 0.1 M silver nitrate to precipitate AgI and stir for 1 hour. Wait 4 hours or until all the precipitate has settled. (*The precipitate will vary in color from a pale yellow to black.*)

Step 4. Carefully aspirate or decant all except about 40 mL of the supernatant liquid (supernate) without disturbing the precipitate.

Step 5. Transfer the residual solution with precipitate to a 50-mL centrifuge tube. Centrifuge. Discard the supernate. Wash the beaker with 40 mL of 0.1N nitric acid, add the wash to the centrifuge tube with the precipitate, and centrifuge. Discard the supernate.

Step 6. To the precipitate in the centrifuge tube, add 10 mL of deionized water and stir. Add 1 g of zinc powder and 2 mL of 2 N sulfuric acid to dissolve

silver iodide. Stir frequently until the zinc stops reacting (no more bubbling). This may take an hour.

Step 7. Centrifuge and pour the supernate into a clean centrifuge tube. Discard solid zinc residue.

Step 8. To the supernatant solution free of residue, add 2 mL of 6 M HCl and heat in a water bath. Add 1 mL of 0.2 M PdCl₂ and digest for 5 min. Centrifuge and discard the supernate.

Step 9. Dissolve the PdI₂ in 5 mL of 6 M NH₄OH and heat in a boiling water bath for about 5 minutes. If any residue remains, centrifuge and decant the supernatant into a clean centrifuge tube. Wash the residue with 5 ml water, centrifuge, and add wash to the supernatant solution in the other centrifuge tube.

Step 10. Neutralize the supernate with 6 M HCl (about 5 mL) and add an additional 2 mL of 6 M HCl. Heat in a water bath for 5 minutes. Add 1 mL of 0.2 M PdCl₂ solution to re-precipitate the PdI₂ and digest for 10 minutes in the hot water bath. Remove from the water bath and cool.

Step 11. Filter on a tared membrane filter. Wash the centrifuge tube with 5 mL of water and pour through the filter. Wash and dry filter twice with 5 mL portions of ethanol.

Step 12. Weigh the filter with the PdI₂ and compute the chemical yield. Mount for counting.

Chemical Yield: _____

Step 13. Count the sample for beta particles with proportional counter for 6,000 s and record results in Data Table 10.1 Measure the background count rate for 6,000 s immediately before or after the sample measurement. To check radioactive decay rate, repeat counting under identical conditions every second or third day for at least two weeks.

Data Table 10.1 Count rate

Date	Time	Gross Count Rate	Net Count Rate
1			
2			
3			
4			
5			
6			
7			

Measurement of Counting Efficiency

Note: Glassware and filtering apparatus for use with radioactive solutions should be kept separate from glassware and apparatus for measuring low-activity samples.

Step 1. Into four 50-mL centrifuge tubes that each contains 20 mL of deionized water, pipette iodate carrier: 1 mL into each of two tubes and 500 λ into each of the two other tubes. . Into each centrifuge tube, pipette 1.0 mL of ^{131}I standard solution, stir well, add 1 mL of 1M freshly prepared Na_2SO_3 , and add 5 drops of concentrated HNO_3 to reduce iodate to iodide. Stir well.

Step 2. To each centrifuge tube, add 2 mL of 0.2 M PdCl_2 . Heat, stir, and digest for 5 min to precipitate PdI_2 .

Step 3. Transfer slurry to tared paper filter in filtration apparatus. Wash out each centrifuge tube with 3 portions of 5 mL of water and pour through filter. Wash and dry with 3 portions of 5 mL ethanol. Place each filter on tared planchet and heat in oven at 100°C for 2 hours. Cool. Weigh. Calculate PdI_2 carrier weight and yield and record in Data Table 10.2 Mount filters for counting.

Data Table 10.2 Counting efficiency of calibration samples

Sample	Weight of Filter	Weight of Planchet	Weight of Filter + Planchet + Sample	Carrier Weight	Carrier Yield
500 λ A					
500 λ B					
1 mL A					
1 mL B					

Diluted Standard Solution activity: _____ Bq

Step 4. Count each mounted filter with the same beta-particle detector as the samples in this experiment, Step 13, for 6,000 s. Calculate the counting efficiency, ϵ , for ^{131}I in PdI_2 by equation (10.1). Decay correction is for the interval between the time recorded on standard certificate and the time of counting. Record information in Data Table 10.3

Data Table 10.3 Counting efficiency of calibration measurements (cont.)

Sample	Time of Counting	Decay Correction Factor	Measured Count Rate	Net Count Rate, decay corrected	Efficiency +/- Uncertainty
500 λ A					
500 λ B					
1 mL A					
1 mL B					

Counting

Count the sample every two or three days for 2 weeks to confirm the 8.02-day half-life. Record sequential measurements, as in Data Table 10.1. Plot a decay curve of \ln net count rate vs. time. Checking the decay curve also serves as a means of determining if there are any radioactive contaminants in the sample.

Treatment of Data

Calculate the net count rate from the gross count rate and the background.

Calculate the ^{131}I activity in the sample by the following equation. The activity units may be converted to units of pC or Bq.

$$A_{131} = \frac{R_{131}}{V\epsilon Y e^{-\lambda\Delta t}} \quad (10.1)$$

A_{131} = activity concentration of ^{131}I in disintegrations per s per L water;

R_{131} = net beta particle counts per s of ^{131}I at the time the sample was counted
(note that the decay fraction for beta particles is 1.00)

V = volume of the sample in liters;

ϵ = counting efficiency for ^{131}I mounted as PdI_2 in the mass range of the recovered carrier, see Data Table 10.3

Y = chemical yield (recovery of carrier);

$e^{-\lambda\Delta t}$ = decay correction factor for the radioactive decay of ^{131}I standard solution;

Δt = time interval from the midpoint of the count time to the reporting time, usually the sample collection time, in d.

λ = decay constant (for ^{131}I , 0.0864 d^{-1})

Calculate the counting efficiency at the two sets of precipitate weights and plot on a graph of efficiency vs. sample weight. Either fit a curve through the points as in Experiment 4 or approximate the curve by a straight line to estimate the counting efficiency as a function of sample weight for the counted samples.

Plot the net count rates in Data Table 10.1 on a semilog graph for \ln net count rate vs. time (linear) in days. Draw a straight line of best fit through the points. If the last few points curve upward, try to fit 2 straight lines to the points, one for the last few points and the other to the initial points minus the count rate attributed to the lower line. Calculate the negative slope (i.e., the decay constant) for the line (or both lines). Does the line confirm the half life of ^{131}I ? Estimate the uncertainty of the slope.

Questions

1. Create a flow diagram for this separation scheme, as in Experiment 7. Identify the iodine species after the reduction step.
2. One gallon of an environmental sample was brought in for ^{131}I analysis on Monday. A 1-L sample was analyzed. The chemical yield was only 21% because of a spill during the analysis. The measurement showed only about 0.5 pCi ^{131}I in the sample on Friday. Your supervisor is not satisfied with the results. What are your options? Justify your answer with calculations and your assumptions.
3. Another one-gallon sample was brought for ^{131}I analysis. According to careful analysis, it contains 3.45 dpm of ^{131}I per L. The sample appears to be contaminated with some long-lived radionuclide that exhibits a count rate of about 0.25 dpm per L. Design an experimental approach to (a) determine the amount of the long lived component and (b) identify the radionuclide.

4. Do the counting efficiency measurements show that the self-absorption of the beta particles of ^{131}I is significant or insignificant in the range of the counting precipitate of PdI_2 between 7 to 14 mg deposited on the filtered sample area?

Standardization of the Iodate (IO_3^-) Carrier

Perform the standardization in replicate (3 or more samples). Pipet 5.0 mL of the KIO_3 carrier into a 50-mL centrifuge tube. Add 5 drops of concentrated HNO_3 and stir. Then add 1 mL of freshly prepared 1 M Na_2SO_3 to reduce iodate to iodide. Place centrifuge tube with the sample in a hot water bath for 5 minutes. Stir occasionally. Add 5 mL of 0.2 M PdCl_2 solution to precipitate PdI_2 . Cool and filter through a tared sintered glass funnel. Wash the centrifuge tube with 5 mL of water and add wash to the filtering funnel. Wash and dry the filter with 5 mL of ethanol. Dry in oven at 70°C overnight. Remove samples from the oven, cool and weigh. Prepare a label to show the results; date and initial.

Source

This procedure was adapted from the procedure used at the Environmental Radiation Center, GTRI, Georgia Institute of Technology, Atlanta, GA and from the Prescribed Procedures for the Measurement of Radioactivity in Drinking Water: EPA-600/4-80-032, August, 1980.

Experiment 11

Modification of a Published Procedure for the Determination of Picocurie Concentrations of Iodine-131 in Milk

Objective

To select another eluent to replace perchlorate solution for the displacement of radio-iodine sorbed from milk on an anion exchange resin column in a method that is described in a published article.

Introduction

The procedure by B. Kahn, Determination of Picocurie Concentrations of Iodine-131 in Milk, *Agricultural and Food Chemistry* 13:2–24 (1965) describes the sorption of iodine in milk directly onto a strong anion-exchange resin column, washing the column, and then eluting radioiodine with 2 M NaClO₄. In today's environmentally sensitive and safety conscious atmosphere, certain laboratories may not wish to use perchlorate ions. The goal of this experiment is to substitute a more "friendly" eluting agent.

The student should find the article in the library or on-line, read it to understand the principle of the method, and then outline an approach for finding a replacement for the perchlorate ion. Once an anion such as I⁻ is sorbed on an anion-exchange resin, one of three approaches commonly is applied to remove it. Review the literature to find (1) an anion with much greater affinity for the ion-exchange medium than iodide; (2) an anion that can be added to the column at high molarity to displace the iodide, or (3) a reagent that can change iodide on the anion-exchange sites to a form that is bound more weakly, or not at all. Some of these approaches may be combined; other, more clever, methods may occur to the student.

The guiding principle in this exercise is for the student to collect enough published information to make an informed choice, discuss this choice and the underlying informational support with the instructor and fellow students, and develop a hypothesis that can be tested. With the instructor's guidance, the student will prepare a series of anion-exchange resin columns, load them with tracer ¹³¹I, and test the selected approach to remove effectively the tracer from the anion-exchange medium.

Safety Reminder

- Follow the usual safety procedures when working in a radiological laboratory.
- Special attention should be given to the toxicity and safety of any eluent that can replace perchlorate.
- All liquids/solids are to be properly disposed of according to laboratory rules and protocol.

Equipment and Supplies

- Radiation detector; typically, Ge detector and spectrometer for measuring ^{131}I
- 2-L beakers
- 20-mL vials (such as liquid scintillation vials) for collecting sequential eluent samples and counting them
- ion-exchange resin column with stopcock and reservoir (see Fig. 7.7)
- 1-mL pipette for radio-iodine tracerend

Reagents

- Radioiodine tracer solution of ^{131}I at a concentration of about 50 Bq per mL. (*Note: Your instructor will provide suitable tracer quantities of ^{131}I .*)
- Selected reagents for elution of radio-iodine from anion-exchange resin
- Iodide carrier, 10 mg per mL: dissolve 11.8 g NaI in 500 ml deionized water, filter, and dilute to 1 L in a volumetric flask
- Anion-exchange resin (*see article*)
- Deionized water
- Tap water

Procedure

Step 1. Read the article carefully.

Step 2. Write a procedure for testing other eluting agents in the style of the experiments in this laboratory manual to delineate each step in sufficient detail.

Step 3. Read about the radiochemistry of iodine to improve your understanding of the radioanalytical chemistry of iodine. An old but helpful monograph is *Radiochemistry of Iodine, NAS-NS-3062*, by Milton Kahn and Jacob Kleinberg, Office of Scientific and Technical Information, US DOE, 103 pp (1977). A copy may be obtained from the instructor, the library, or internet search. Also read about ion-exchange theory and practice, and in particular, the relative affinity of anions for strong-base ion-exchange material.

Step 4. Select one or more candidate substitutes for NaClO_4 based on your reading and explain to the instructor and fellow students your selection in

terms of, for example, the affinity of your selected anion and its molarity *vs.* iodide on the anion-exchange resin.

Step 5. Develop a set of experiments to test your candidate(s).

Step 6. Ask your laboratory instructor to approve your experiment before performing the tests.

Step 7. Test your selected eluent in an aqueous system. Prepare a set of identical anion-exchange resin columns according to the article. Prepare a set of identical 1-L samples of tap water. Pipette into each sample 1 mL iodide carrier and 5 mL radio-iodine tracer and mix. Let samples flow through column at flow rate of no more than 5 mL per minute. Prepare 200 mL solutions of the selected eluting agents.

Step 8. Pass each eluting agent through the resin column at flow of 5 mL per minute. Collect sequential 5-ml fractions of each eluent and measure the radio-iodine net count rate in each eluent fraction. Draw curve of net radio-iodine count rate *vs.* eluted volume. Select the eluting solution that removes radio-iodine from the resin column most effectively, *i.e.*, in the smallest volume.

Step 9. Obtain a 1-L milk sample and pipette into it 1 mL iodide carrier and 5 mL ^{131}I tracer. Mix well. Pass milk through same type of resin column as prepared in Step 7. Prepare 200 mL of eluting solution selected in Step 8 as being most effective.

Step 10. Repeat Step 8 with the selected most effective eluting solution for the column that retained radio-iodine from milk.

Counting

Pipette 5 mL ^{131}I tracer into the same type of vial used to collect the eluted samples and count for a sufficient time period to accumulate at least 5,000 net counts. Calculate the net count rate by dividing the gross count by the counting time and subtracting the background count rate. Compare all other results to this net count rate.

Count each vial with 5 mL of the eluted solutions for 600 s. Calculate the fraction of the total added activity in each vial. For each experiment, add these fractions for the number of elution samples to determine the total fraction of the input that was eluted.

Data Treatment and Report

Report results in a Data Table with all the pertinent information and measurements. List reagents and their concentrations used for elution tests.

Report the volume required for 99% elution of radio-iodine, or the percent eluted with 200 mL if 99% elution was not attained. Prepare curve of radio-iodine count rate as function of eluent fraction for each type of eluent to compare effectiveness.

Write your report, discussing the advantages and disadvantages of your new eluting agent. Suggest additional eluting agents for testing based on your results or reading.

Questions

1. Why is perchlorate a problem?
2. Discuss the relevance of knowing the amount of iodine that is bound by protein in milk in measuring the ^{131}I in milk samples by chemical processing. Make suggestions that could overcome this issue.
3. If the sample contained large quantities of radio-caesium, radio-strontium, and radio-silver would this have an effect on determining ^{131}I in the final product? Discuss.
4. Is the elution curve for milk different from that for tap water? Why?
5. Consider the possibility of other approaches for iodine elution and indicate the possible benefits.

Experiment 12

Vegetation Sample Preparation for Radiochemical Analysis of Radio-strontium

Objective

To prepare a vegetation sample for radiochemical analysis.

Introduction

This laboratory experiment describes the preparation of a vegetation sample (e.g., grass) for radiochemical analysis. The sample is dried and ashed. In Part 12A, the ash is fused with sodium hydroxide and sodium carbonate to bring it into solution. An alternative method in Part 12B uses a microwave-assisted digestion technique with nitric and hydrofluoric acid. The prepared sample is suitable for radionuclide analysis, notably for radio-strontium or plutonium.

Proper preparation of biological solids for radiochemical analysis is essential for obtaining valid radioanalytical chemistry results. The samples often must be large because the radioactivity levels are low. Gamma-ray spectral analysis is the preferred method of radiation measurement because it requires little preparation. If gamma-ray spectral analysis of the untreated sample is not feasible because few or no gamma rays are emitted, the sample must be dissolved. Dissolution is almost always required for alpha- and beta-particle analysis. The first step usually reduces the mass of the solid sample and prepares it for dissolution.

Some types of collection provide a concentrated or reduced-volume sample directly. Examples include filtration to collect airborne or waterborne particles, and sorption of airborne gases on charcoal and of aqueous ions on ion exchange resins. Water samples are reduced in volume by evaporation, and organic solids, by ashing. Certain radionuclides in water are concentrated by precipitation.

Biota samples usually are processed by dissolution in strong oxidizing acids or by dry combustion. In combustion, carbonaceous matter is removed at elevated temperatures as carbon dioxide and water in the presence of oxygen (air). Alternatively, some materials may be macerated with enzymes or in basic solution. Whatever process is used, the most important point in selecting

a procedure is that the radionuclides of interest are quantitatively recovered in a soluble form.

The process for converting the vegetation sample to a soluble form is selected for convenience, familiarity, safety, and optimal removal of interfering substances. A problem in dissolving salts of heavier Group IIA elements with mineral acids is that they may be insoluble sulfates. The most common method for bringing insoluble sulfates into solution is to subject the sample to hydroxide-carbonate fusion (fusion is discussed in Section 4.6.2 of your *Radioanalytical Chemistry* text). The fusion is performed in a metal crucible that is relatively insoluble under the fusion conditions. The temperature must be sufficiently high to melt the sulfates and convert them into carbonates. The carbonates are then dissolved to prepare the sample for analysis.

Preparation of a vegetation sample for radiochemical analysis in this procedure requires three steps. In the first, the sample is dried at 105°C. In the second, the dry material is ashed at 550°C to remove the carbonaceous material. In the third step, either fusion or microwave-oven dissolution brings the salts into solution.

Safety Reminders

- Follow the usual safety procedures when working in a radiological laboratory.
- Carefully handle very hot containers, fusion mixtures and samples from muffle furnaces.
- Caution should be exercised when preparing and working with corrosive mineral acids.
- All liquids/solids are to be properly disposed of according to laboratory rules and protocol.
- Perchloric acid is effective in dissolving certain solids but is not used here because it poses an explosion hazard, notably with carbon. The acid should only be used to dissolve carbon-containing materials where perchloric acid hoods are available and the chemist is fully trained and certified to work with perchloric acid for this purpose.

Equipment and Supplies

- Scales
- Nickel crucible, 125-mL or 250-mL size
- Nickel stirring rod
- Tongs
- Ice bath
- 50-mL centrifuge tubes
- Fine-porosity filter paper and filtering funnel
- Reagent bottles
- Drying pans, large, but suitable for oven volume
- Porcelain ashing dishes, large, but suitable for muffle furnace volume
- Pipettes, 1 and 4 mL

Reagents (for fusion of ash)

- Vegetation sample: grass or other suitable plant material, at least 250 g
- Strontium carrier, standardized, 10 mg Sr^{+2} /mL: see Experiment 5

- Barium carrier, ~ 10 mg Ba^{+2}/mL : Dissolve 9.5 g of $\text{Ba}(\text{NO}_3)_2$ in 200 mL of deionized water and dilute to 500 mL.
- 2 M calcium nitrate: Dissolve 236 g of reagent grade $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in 200 mL of deionized water and dilute to 500 mL.
- Sodium hydroxide pellets, reagent grade
- Sodium carbonate, solid, reagent grade
- Concentrated HNO_3
- 6 M HCl (Pour 500 mL of concentrated HCl carefully into ~ 400 mL deionized water, stir and dilute to 1 L with deionized water.
- Deionized water

12A. Drying, Ashing, and Fusion

Procedure

Sample ashing

Step 1. Weigh approximately 250 g of a fresh vegetation sample, such as grass. Record its moist weight in Data Table [12.1](#)

Step 2. Transfer the vegetation to a flat drying dish or pan. Dry overnight in an oven at 105°C . Remove the sample from the oven and let it cool to room temperature. Record the dried weight to nearest 0.1 g in Data Table [12.1](#). If the sample weighs more than 120 g, record the weight and calculate the dry-to-moist weight ratio. Then remove the vegetation in excess of 120 g, weigh the remaining sample, and record its weight in Data Table [12.1](#) for comparison with its ash weight.

Step 3. Place vegetation sample in several large porcelain dishes, one of which is tared. Gradually heat sample in open muffle furnace while dish is covered (with small opening to admit air) to char sample. Close furnace, increase the temperature to 550°C and ash overnight. Remove the porcelain dishes from the furnace. Remove the cover and mix ash with stirring rod. If black particles remain in the ash, return the porcelain dishes, partially covered with lid to admit air, to furnace, and close door. Ash the sample overnight again at 550°C . Remove the sample from furnace and let it cool to room temperature. Combine all ash samples in the tared porcelain dish. Weigh the porcelain with its contents. Record the ash weight in Data Table [12.1](#) and calculate the ratio of ash-to-dried weight relative to the near-120-g sample.

Sample fusion method

Step 4. Place 5.00 g of ash in a 125-mL or 250-mL nickel crucible. *Note: the type of crucible is selected that is relatively stable for the fusion temperature and mixture. Platinum crucibles are more stable but also more costly. See*

Data Table 12.1 Sample weight

1.	Weight of Fresh Vegetation
2.	Dried Weight
3.	Dry-to-Moist Ratio (Steps 2./1.)
4.	Weight of Dried Sample Used
5.	Ashed Weight
6.	Ash-to-Dried Ratio (Steps 5/4)

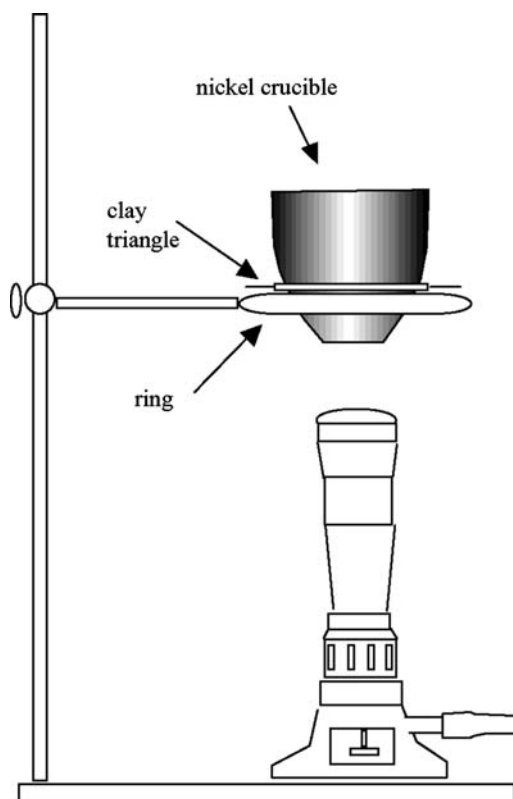


Figure 12.1 Arrangement for nickel crucible fusion.

Figures [12.1](#) and [12.2](#) for the fusion arrangement. Pipette 4 mL of strontium carrier and 1 mL of barium carrier onto the sample. Add 1 mL of 2 M $\text{Ca}(\text{NO}_3)_2$ solution. Add 25 g of NaOH pellets. Carefully heat over Meeker burner for 30 minutes. Remove from heat and slowly add 2.5 g of Na_2CO_3 to the hot melt, stir with nickel stirring rod, and continue heating the clear melt for 30 minutes to convert calcium, strontium, barium, and radium salts to carbonates.

Step 5. Transfer the crucible from the flame directly to a cold-water bath to crack the melt. (*Caution: the hot crucible in contact with water produces steam and possible splattering.*) Add 100 mL deionized water to the melt in the crucible. Boil gently over the flame to disintegrate the fused mixture.

Step 6. Cool the crucible in the ice bath. Slurry most of the solid and solution into two 50 mL glass centrifuge tubes. Balance the tubes and centrifuge them at full speed for approximately 1 minute. If the supernate is cloudy after centrifugation, centrifuge again until it is clear. Discard the supernatant solution by carefully pouring the supernatant into a beaker. Add the remaining contents of the crucible to the centrifuge tubes. Balance the tubes. Repeat the centrifugation. Discard the supernate as before. Use 80 mL of deionized water in several fractions to rinse the crucible and add the wash water to the two centrifuge tubes that contain the solids. Stir the solids vigorously in water. Repeat the centrifugation. Discard the supernate.



Figure 12.2 Fusion apparatus.

Step 7. Dissolve the solid carbonates in 20 mL of 6 M HCl (10 mL per tube) by boiling gently with constant stirring. (Use caution: the sample can be lost if the analyst has not practiced boiling in centrifuge tubes). Add 30 mL deionized water to each tube. Pour the contents of both tubes through a funnel fitted with a filter paper into a clean 500-mL bottle that is fitted with a cap. Wash the tubes and the filter paper with 240 mL of deionized water in several portions; add the wash water to the filtrate in the bottle. Discard the filter paper with any insoluble silicates.

Step 8. Mix the dissolved sample. Measure its volume and record it. Relate the initial dried sample weight to this volume. Close the bottle, label its content, and save the solution for the determination of radio-strontium (Experiment 13).

Sample volume: _____

Ratio of dried sample weight to volume: _____

12B. Drying, Ashing, and Acid Dissolution Procedure

Steps. 1 – 3. Follow Steps 1 – 3 from Part 12A (above).

In this alternative, a 1- or 3-g sample aliquot is treated by microwave-assisted dissolution according to the method by Garcia and Kahn cited following this procedure.

Step 4a. For *microwave-assisted digestion*, follow the procedure developed for the microwave system in the laboratory. Note that total dissolution of the solid is required for radioanalytical chemistry, whereas partial dissolution is acceptable for other analytical processes if the method has been tested for fractional recovery. Several references are given below that may be helpful in developing or using this method.

Step 4b. For *leaching* a vegetation ash sample, strong mineral acids such as HNO_3 can be used. *Note: A leach recovery fraction must be determined that applies specifically to the matrix, radioanalyte, leaching solution, and leaching program (temperature, relative volumes, time) under consideration.*

Questions

1. Why is it important to record the weights of the vegetation both as a wet weight and a dry weight?
2. If part of the sample were lost during the dissolution of the melt cake in Step 7, how would this affect your final results? Explain.
3. If the sample had an unusually high amount of silicates, what could you do to remedy the excess silicate problem?
4. What happens when strong sodium hydroxide solutions come in contact with glass?
5. Look up a procedure that uses only a wet ash method. Which do you think is better? Why?
6. Why is it not necessary to standardize the barium carrier and the calcium solution?

Source for Part 12A

Adapted from a procedure used at the Environmental Radiation Branch, GTRI, Georgia Institute of Technology, Atlanta, GA.

Sources for Part 12B

H.M. Kingston, ed., and S.J. Haswell, ed., *Microwave-Enhanced Chemistry*, 772 p, American Chemical Society, Washington, DC (1997).

David Barclay, "Microwave Digestion Moves into the 21st Century," *Today's Chemist at Work*, pp 28–32 March 2004; www.tcawonline.org

R. Garcia and B. Kahn, "Total Dissolution of Environmental and Biological Samples by Closed-Vessel Microwave Digestion for Radiometric Analysis," *J. Radioanalytical and Nuclear Chemistry* **250**, 85–91 (2001).

J.S. Alvarado, T.J. Neal, L.L. Smith and M.D. Erickson, "Microwave Dissolution of Plant Tissue and the Subsequent Determination of Trace Lanthanide and Actinide Elements by Inductively Coupled Plasma-Mass Spectrometry," *Analytica Chimica Acta* **322**, 11–20 (1996).

Experiment 13

Determination of Radio-strontium Isotopes in Environmental Samples

Objective

To determine radio-strontium isotopes in ash or water samples by conventional radiochemical separation method and counting beta particles.

Introduction

The two fission-produced radio-strontium isotopes of interest in environmental samples are ^{90}Sr and ^{89}Sr . Sr-90 has a fission yield of $\sim 5.8\%$, a half-life is 28.78 a, and the radioactive daughter ^{90}Y with a half life of 2.67 d, to which it decays by beta-particle emission. Sr-89 has a fission yield of $\sim 4.7\%$, a half life of 50.52 d, and decays to the stable daughter ^{89}Y . The decay schemes given in Figure 13.1 show that these two radio-strontium isotopes for practical purposes can only be measured by beta-particle counting.

The beta particles from ^{89}Sr are readily detectable in relatively recently-formed fission products. In fission-produced material that is two or more years old, beta particles from radio-strontium consist only of those emitted by ^{90}Sr . During the first day after fission, ^{91}Sr (half life, 9.63 h) and ^{92}Sr (half life, 2.71 h) can be measured by gamma-ray spectral analysis. Radioactive ^{85}Sr (half life, 64.84 d) is produced by $^{84}\text{Sr}(n,\gamma)$ or $^{85}\text{Rb}(p,n)$ reactions and is used as tracer for radio-strontium analysis by measuring its gamma ray.

In this procedure, strontium is concentrated from the sample with a cation exchange resin. Further steps for radio-strontium purification include precipitation of strontium nitrate in fuming nitric acid and scavenge steps with ferric hydroxide to remove insoluble hydroxides and with barium chromate to remove insoluble barium and radium. Strontium is then precipitated as SrC_2O_4 . The ^{90}Y is allowed to grow into radioactive equilibrium and is then “milked” from the strontium by precipitating the hydroxide. The yttrium precipitate is dissolved and $\text{Y}_2(\text{C}_2\text{O}_4)_3$ is then precipitated, weighed, mounted and counted. The amount of ^{90}Sr is determined by measuring the beta particles of 2.67-d ^{90}Y .

If ^{89}Sr is present, the ^{89}Sr and $^{90}\text{Sr} + ^{90}\text{Y}$ beta-particle counts will have to be resolved. This is done by counting the strontium oxalate precipitate at least

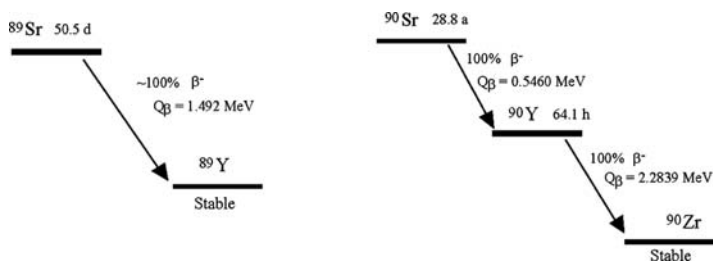


Figure 13.1 Decay schemes of ^{89}Sr and ^{90}Sr

twice. An interval of 3 weeks allows the ingrowth of ^{90}Y to equilibrium with ^{90}Sr and an observable decay of ^{89}Sr .

The counting efficiencies of ^{89}Sr , ^{90}Sr , and ^{90}Y are determined by adding standard solutions of ^{89}Sr and ^{90}Sr to different $\text{Sr}(\text{NO}_3)_2$ solutions and precipitating SrC_2O_4 . The precipitate with ^{90}Sr is counted twice – immediately after precipitation and then after about 18 days to recount ^{90}Sr also to count the ingrown ^{90}Y . The two efficiency values are calculated by solving simultaneous equations. The precipitate with ^{89}Sr must be counted only once to determine its counting efficiency, but can be counted a second time to confirm its half life.

Safety Reminders

- Follow the usual safety procedures when working in a radiological laboratory.
- Caution should be exercised when preparing and working with corrosive mineral acids.
- All liquids and solids are to be properly disposed of according to laboratory rules and protocol.
- This experiment uses corrosive glacial acetic acid and fuming nitric acid. Take special precautions and wear protective gloves when using these acids. A face shield is recommended when working with fuming nitric acid.

Equipment

- Low-level beta-particle counting system, such as an anti-coincidence proportional counter
- Analytical balance to measure within 0.1 mg
- Pipettes, 1 mL and 2 mL
- Beakers, 1 L, 150 mL
- Ion exchange column, for 10 mL resin (0.8-cm dia. x >20 cm long), with stopcock and glass-fiber plug at bottom (for similar system, see Fig. 15.4)
- Hot plate
- Ice bath
- Graduated cylinder, 10-mL and 500-mL

- Stirring rods
- Centrifuge tubes, 50-mL
- Filter and filtration apparatus

Reagents

- Strontium carrier, 10 mg Sr^{2+} /mL, see preparation and standardization in Experiment 5.
- Yttrium carrier, 10 mg Y^{3+} /mL, see preparation and standardization in Experiment 5
- Barium carrier: 10 mg Ba^{2+} /mL, dissolve 19.0 g $\text{Ba}(\text{NO}_3)_2$ in water and dilute to 1 L
- ^{90}Sr – ^{90}Y standard solution, diluted in 0.01 N nitric acid to a concentration of about 5 Bq per mL
- ^{89}Sr standard solution, diluted in 0.01 nitric acid to a concentration of about 5 Bq per mL
- Cation exchange resin, strong base, 8% cross linked, 100–200 mesh, analytical grade
- Fuming (yellow) nitric acid, reagent grade
- 8 M HNO_3 : Add 500 mL reagent grade concentrated nitric acid to 400 mL deionized water, mix, and dilute to 1.0 L
- 0.1 M HNO_3 : Add 6.25 mL of concentrated nitric acid to 400 mL deionized water, mix, and dilute to 1 L
- HCl: concentrated, reagent grade.
- 1 M HCl: Add 83 mL of concentrated HCl to 800 mL deionized water, mix, and dilute to 1 L.
- Iron carrier: 10 mg Fe^{3+} /mL, dissolve 48 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 100 mL of 1 M HCl and dilute with water to 1 L.
- NH_4OH , concentrated ammonium hydroxide
- $\text{HC}_2\text{H}_3\text{O}_2$, glacial acetic acid
- Na_2CrO_4 : 10%, dissolve 10 g Na_2CrO_4 in 100 mL of water
- $(\text{NH}_4)_2\text{C}_2\text{O}_4$: saturated aqueous solution of ammonium oxalate
- Ethanol, 95%
- Deionized water

Procedure

Step 1. Measure the dissolved sample ash with added strontium carrier from Experiment 12 with a graduated cylinder and pour into a 1-L beaker, OR pour 1 L (or less, as specified by the instructor) of a water sample into the 1-L beaker, pipette 2 mL strontium carrier into the water sample, and stir. Add 1 mL of 8 M HNO_3 per 100 mL of sample and mix. Bring to a boil and then cool.

Step 2. Prepare a cation-exchange column that contains 10 mL of the cation exchange resin, has no bubbles or channels, and is covered with water. Condition the resin by passing ~50 mL of 0.1 M HNO_3 through the column. Discard the effluent.

Step 3. Pass the sample through the column. The flow rate should not exceed 5 mL/min. Discard the eluent. Wash the column with ~30 mL of 0.1 M HNO_3 . Discard the eluent.

Step 4. Elute the strontium fraction at a flow rate not to exceed 5 mL/min with 50 mL of 8 M HNO_3 . Collect the eluent in a clean 150 mL beaker.

Step 5. Evaporate the sample on a hot plate at low setting until only a small volume (~2 mL) remains. Transfer to a clean 50-ml centrifuge tube. Rinse beaker with two 3-mL portions of concentrated nitric acid and transfer each to the centrifuge tube.

Step 6. Add 30 mL of cold fuming nitric acid and stir. (*Cooling the fuming nitric acid reduces the time required for cooling in an ice bath.*) Place the centrifuge tube in an ice bath for approximately 10 minutes. Stir to precipitate white $\text{Sr}(\text{NO}_3)_2$. Centrifuge and discard the supernate. (*Note: if excess calcium salts were in the sample, it may be necessary to dissolve the precipitate in 5 mL water and reprecipitate it with 30 mL fuming nitric acid.*)

Step 7. Dissolve the $\text{Sr}(\text{NO}_3)_2$ precipitate in 20 mL of water and add 5 drops of iron carrier. Make the solution alkaline by adding concentrated NH_4OH dropwise to precipitate reddish-brown $\text{Fe}(\text{OH})_3$ scavenger. (*Note: a new bottle of NH_4OH should be used or fresh NH_4OH prepared by bubbling NH_3 in water to insure that no carbonates are in the NH_4OH .*) Add 10 drops more of NH_4OH solution. Stir and centrifuge. Decant the supernate into a clean centrifuge tube. Discard the $\text{Fe}(\text{OH})_3$ precipitate, which includes any ^{90}Y in the sample.

Date and time of ^{90}Y separation with $\text{Fe}(\text{OH})_3$ precipitate: _____

Step 8. Add 2 mL of glacial $\text{HC}_2\text{H}_3\text{O}_2$ to the supernate to bring the solution to pH 3.5 to 4.0 (check with pH paper). Add 2 mL of barium carrier and stir. Add, while stirring, 2 mL of 10% Na_2CrO_4 solution and digest for 10 to 15 minutes in a hot water bath with occasional stirring to precipitate yellow to orange colored BaCrO_4 . Centrifuge, then decant the supernate into a clean centrifuge tube and discard the precipitate (or save for analysis of radio-barium and radium).

Step 9. Add 5 mL of saturated $(\text{NH}_4)_2\text{C}_2\text{O}_4$ to the supernate, neutralize with ammonium hydroxide dropwise, and digest on a hot water bath for 5 to 10 minutes. A white precipitate of strontium oxalate forms. Centrifuge, and discard the supernate. Wash the precipitate by adding 2 mL of saturated $(\text{NH}_4)_2\text{C}_2\text{O}_4$ in 20 mL of water and stir. Centrifuge and discard the supernate

Note: If the sample is being measured for both ^{89}Sr and ^{90}Sr , mount the sample for counting as described in Step 10. If the sample is being measured only for ^{90}Sr , go to Step 10a.

Step 10. Slurry the precipitate from Step 9 with 10 mL of water and filter onto a tared filter circle held in a filtration apparatus. Wash the centrifuge tube twice with 5 mL of water and pour into filtration apparatus onto the precipitate. Wash and dry precipitate with two 5 mL portions of 95% ethanol.

Place on tared planchet and dry in an oven at 110°C for 30 minutes. Remove from oven, cool, and weigh the hydrate, $\text{SrC}_2\text{O}_4 \cdot x\text{H}_2\text{O}$. Mount the sample and count it twice for 3,000 s; also count the background twice. Record weighing and counting results in Data Table [13.1](#)

Dates and times of first and second counts: _____; _____

The count is repeated 3–9 weeks later (the longer the interval, the more precise the ^{89}Sr calculation). When counting for ^{89}Sr is completed, the sample may be processed for ^{90}Y to determine the amount of ^{90}Sr in the sample by transferring the filter to a centrifuge tube and following Step 11.

Date and time of count for ^{89}Sr calculation: _____

Step 10a. Store the $\text{Sr}_2\text{C}_2\text{O}_4$ precipitate in the centrifuge tube to permit the ^{90}Y to grow into radioactive equilibrium with the ^{90}Sr . This process requires ~18 days. This time period may be shortened if an ingrowth correction is made for the time interval between the iron scavenger of Step 7 and the $\text{Y}(\text{OH})_3$ precipitation that is described below.

Step 11. After the required time has lapsed, wash down the sides of the tube with 15 mL of 1 M HCl to dissolve the SrC_2O_4 . (If reprocessing the mounted $\text{Sr}_2\text{C}_2\text{O}_4$ precipitate, carefully transfer the filter circle into a centrifuge tube that contains 15 mL of 1 M HCl. To achieve quantitative transfer, remove the filter after the precipitate is dissolved, wash filter with 5 mL water and add the wash to the solution.)

Step 12. Pipette 2 mL of standardized yttrium carrier into the solution and stir, Add concentrated NH_4OH drop-wise until white $\text{Y}(\text{OH})_3$ precipitates and then add 5 mL in excess. Centrifuge, decant into a centrifuge tube, and save the supernate until the results of the analysis for yttrium have been checked. Record the time.

Date and time of yttrium separation: _____

Step 13. Dissolve the $\text{Y}(\text{OH})_3$ in a minimal amount of concentrated HCl added dropwise.. Add 15 mL of water. Add 3–5 drops of strontium nitrate solution as holdback carrier, stir, and again precipitate $\text{Y}(\text{OH})_3$ with 5 mL of concentrated NH_4OH . Centrifuge and discard the supernate. Wash the precipitate with 20 mL water. Centrifuge and discard the wash water.

Step 14. Dissolve the precipitate in the minimum amount of concentrated HCl added dropwise and add 15 mL of water. Adjust to pH 2–3 with ammonium hydroxide, if needed. Add 5 mL of saturated $(\text{NH}_4)_2\text{C}_2\text{O}_4$ solution and stir to precipitate $\text{Y}_2(\text{C}_2\text{O}_4)_3$. Digest in a hot water bath for 5 to 10 minutes.

Note: Step 15a describes the preparation of yttrium as the oxide for chemical yield determination and counting. As an alternative, Step 15b is the description for weighing and mounting yttrium as the oxalate.

Step 15a. Slurry the hydrated $\text{Y}_2(\text{C}_2\text{O}_4)_3$ onto an ash-less filter circle. Wash the centrifuge tube with 10 mL of water and pour through filter. Place the filter with precipitate in a clean porcelain crucible. In a muffle furnace, ignite

Data Table 13.1 Data ^{89}Sr , ^{90}Sr , and ^{90}Y count rates

^{89}Sr Yield		
^{90}Sr Yield		
^{90}Y Yield		
1 st Count Rate (Sr + Y)	Gross, cps	Net, cps
2 nd Count Rate (Sr + Y)		
Count Rate (Y)		
Background		
^{90}Y Ingrowth Time		
^{90}Y Ingrowth Fraction		

at 900°C for 1 hour. Remove from the furnace and cool. With a blunted or flattened tipped thick glass stirring rod, grind the Y_2O_3 into a powder. If necessary, add a few drops of ethanol and continue grinding to produce a fine precipitate. Take up in a few mL water and slurry the Y_2O_3 through a tared filter circle. Wash the precipitate with ethanol, dry in an oven at 110°C, cool, weigh, and mount for counting. Count twice for 3,000 s and record data in Data Table [13.1](#).

OR

Step 15b. Slurry the hydrated $\text{Y}_2(\text{C}_2\text{O}_4)_3$ onto a tared filter circle in a filtering apparatus. Wash the centrifuge tube with 10 mL of water and pour through filter. Wash and dry the $\text{Y}_2(\text{C}_2\text{O}_4)_3 \cdot x\text{H}_2\text{O}$ precipitate with two 5-mL portions of ethanol. Transfer to oven and dry at 110°C for 15 minutes. Cool, weigh, and mount for counting. Count twice for 3,000 s and record data in Data Table [13.1](#).

Date and time of counting: _____

Counting

Count the ^{90}Y sample with a low-background beta-particle detector. Repeat count-rate measurement for two to three 2.67-d half lives. Plot the net count rate as function of time on a semilog graph, draw straight line of best fit through measured points, and calculate slope of line, which equals $-\lambda$ or $-\ln 2/t_{1/2}$. A suggested counting frequency is twice daily for 8 d. When ^{89}Sr is present, count the strontium sample immediately after separation and then every 3 weeks for as much as 2 half lives of ^{89}Sr , if time is available.

Calculation of the ^{90}Sr concentration from yttrium precipitation and ^{90}Y counting data

Calculation of the amount of ^{90}Sr in the sample when no ^{89}Sr is present is by the following equation:

$$A_{\text{Sr}} = \frac{R_{\text{Y}}}{[V_a \epsilon_{\text{Y}} Y_{\text{Y}} Y_{\text{Sr}} (e^{-\lambda(t_3-t_2)})(1 - e^{-\lambda(t_2-t_1)})]} \quad (13.1)$$

A_{Sr} = ^{90}Sr concentration in Bq/L,
 R_{Y} = net count rate in cps of ^{90}Y

Table 13.1 Calculation for ^{89}Sr in a mixture of ^{89}Sr and ^{90}Sr

Description	Formula
Initial measurement	$R_1 = Y(A_{90\text{Sr}}\epsilon_{90\text{Sr}} + A_{90\text{Sr}}\epsilon_{90\text{Y}}D_{190\text{Y}} + A_{89\text{Sr}}\epsilon_{89\text{Sr}})$
Second measurement	$R_2 = Y(A_{90\text{Sr}}\epsilon_{90\text{Sr}} + A_{90\text{Sr}}\epsilon_{90\text{Y}}D_{290\text{Y}} + A_{89\text{Sr}}\epsilon_{89\text{Sr}}D_{289\text{Sr}})$
Solution for $A_{90\text{Sr}}$ at the initial count	$A_{90\text{Sr}} = \frac{(R_1 D_{289\text{Sr}} - R_2)}{Y[\epsilon_{90\text{Sr}}(D_{289\text{Sr}} - 1) + \epsilon_{90\text{Y}}(D_{289\text{Sr}} D_{190\text{Y}} - D_{290\text{Y}})]}$
Solution for $A_{89\text{Sr}}$ at the initial count	$A_{89\text{Sr}} = \frac{\left[\frac{R_1}{Y} - A_{90\text{Sr}}(\epsilon_{90\text{Sr}} + \epsilon_{90\text{Y}}D_{190\text{Y}})\right]}{\epsilon_{89\text{Sr}}}$

V_a = volume of the sample in L,

ϵ_Y = counting efficiency for ^{90}Y (see above),

Y_Y = chemical yield for the recovery of the yttrium carrier (mg Y recovered/mg Y added),

Y_{Sr} = chemical yield for the recovery of the strontium carrier (mg Sr recovered/ mg Sr added),

λ = the decay constant of ^{90}Y (0.260 d^{-1})

t_3 = time when ^{90}Y is counted in Step 15.

t_2 = time when yttrium is separated from strontium when radioactive equilibrium is being approached in Step 12

t_1 = time when ^{90}Sr is scavenged with ferric hydroxide that removes ^{90}Y , in Step 7

$(1 - e^{-\lambda(t_2 - t_1)})$ = saturation term for determining the degree of radioactive equilibrium the ^{90}Y has obtained from the time of separation for the strontium to the counting time (this term approaches the value of 0.99+ when $t_2 - t_1$ is equal to or greater than 18 days).

Calculation of ^{89}Sr and ^{90}Sr concentrations by counting the strontium precipitate immediately after preparation and then several weeks later

Table [13.1](#) describes the calculation for ^{89}Sr in a mixture of ^{89}Sr and ^{90}Sr .

The letter D represents the decay of ^{89}Sr or the ingrowth of ^{90}Y at the initial second measurement.

Measurement of Counting Efficiency

Step 1. *Prepare duplicate ^{90}Sr and ^{89}Sr solutions.* Into each of four centrifuge tubes with 20 mL of deionized water, add 1 mL of 0.1 M HNO_3 . Pipette 2 mL Sr carrier into each tube. Pipette 2 mL of yttrium carrier into each of the first 2 tubes. Into each of the first two tubes, pipette 1 mL of ^{90}Sr diluted standard solution; into each of the other two tubes, pipette 1 mL of ^{89}Sr diluted standard solution. Stir well.

Step 2. Add 1 ml iron carrier into each of the first 2 tubes and stir. Add fresh ammonium hydroxide drop-wise with stirring until a brown iron hydroxide precipitate forms. Centrifuge and thoroughly transfer both supernatant solutions to clean centrifuge tubes. Add 5 ml of water to each precipitate, stir, and centrifuge. Decant each wash solution into the corresponding supernatant solution. Discard precipitate.

Data Table 13.2 Yields of counting efficiency precipitates

	⁹⁰ Sr Sample #1	⁹⁰ Sr Sample #2	⁸⁹ Sr Sample #1	⁸⁹ Sr Sample #2
Date/Time of precipitation				
Gross weight, mg				
Tare weight, mg				
Net weight, mg				
Yield				

Data Table 13.3 Data Prompt count rates of each precipitate

	⁹⁰ Sr Sample #1	⁹⁰ Sr Sample #2	⁸⁹ Sr Sample #1	⁸⁹ Sr Sample #2
Date/Time of count.				
Ingrowth/decay interval, hr				
Gross count rate, cps				
Net count rate, cps				
Activity, dps				
Counting efficiency, ⁸⁹ Sr				
Counting efficiency, ⁹⁰ Sr				
Counting efficiency, ⁹⁰ Y				

Step 3. Neutralize each of first 2 solutions with a few drops 0.1 M HNO₃.

Step 4. To each of the 4 centrifuge tubes, promptly add 5 mL of saturated (NH₄)₂C₂O₄ and stir well. Record time of precipitation in Data Table [13.2](#).

Step 5. Slurry each solution with precipitate onto a tared filter disk in a filtering apparatus. Rinse each centrifuge tube with two portions of 5 mL water and pour through each filter. Wash and dry filter each with two portions of 5 mL ethanol. Dry in oven at 110°C for 2 hours. Let each filter cool and weigh it on tared planchet. Calculate weight of each precipitate and yield, and record in Data Table [13.2](#).

Step 6. Place each filter in a filter holder, identical to that used in the procedure. Count as soon as possible (within several hours) after the precipitation. Record gross count rates and background count rate in Data Table [13.3](#).

Step 7. Count four filters again after about 18 days. Count each filter twice for 3,000 s and also count the background. The two filters with ⁹⁰Sr standard solution are counted to calculate the counting efficiency of ⁹⁰Y and

Data Table 13.4 Count rates of each precipitate after time interval

	⁹⁰ Sr Sample #1	⁹⁰ Sr Sample #2	⁸⁹ Sr Sample #1	⁸⁹ Sr Sample #2
Date/Time of count.				
Ingrowth/decay interval, d				
Gross count rate, cps				
Net count rate, cps				
Counting efficiency				

^{90}Sr on the basis of the ^{90}Y ingrowth. Count the two filters with ^{89}Sr to calculate the counting efficiency and observe the radioactive decay of the radionuclide. Record the gross count rates and background count rate in Data Table [13.4](#).

Calculation of Counting Efficiencies

The following equations calculate the counting efficiencies for ^{90}Y , ^{90}Sr and ^{89}Sr . The ingrowth for ^{90}Y is included in Eq. 13.1 and Table [13.1](#). The decay of ^{90}Sr is taken to be negligible between measurements. The activity of ^{89}Sr and ^{90}Sr is at the time of the first count.

$$\varepsilon_{^{90}\text{Y}} = \frac{R_2 - R_1}{A_{^{90}\text{Sr}} Y (D_2 - D_1)^{^{90}\text{Y}}} \quad (13.2)$$

$$\varepsilon_{^{90}\text{Sr}} = \frac{R_1}{A_{^{90}\text{Sr}} Y} - D_1 Y^{^{90}\text{Y}} \varepsilon_{^{90}\text{Y}} \quad (13.3)$$

$$\varepsilon_{^{89}\text{Sr}} = \frac{R_1}{A_{^{89}\text{Sr}} Y D_{^{89}\text{Sr}}} \quad (13.4)$$

R_2 = net count rate in c/s after lengthy interval (typically, about, 18 days)

R_1 = net count rate in c/s promptly after strontium separation

A = activity of radio-strontium in Bq at time of measurement

D_2 = ingrowth fraction of ^{90}Y after lengthy interval (0.996 after 21 days);
decay fraction of ^{89}Sr (0.750 after 21 days)

D_1 = ingrowth fraction of ^{90}Y promptly after strontium separation (about
0.05 after 5 hours)

$D_{^{89}\text{Sr}}$ = Decay fraction of ^{89}Sr

Y = chemical yield of strontium

$\varepsilon_{\text{Sr}-90}$ = counting efficiency of ^{90}Sr

$\varepsilon_{\text{Y}-90}$ = counting efficiency of ^{90}Y

$\varepsilon_{\text{Sr}-89}$ = counting efficiency of ^{89}Sr

Questions

1. You are told that a sample contains “1-week-old” fission products in addition to the suspected radio-strontium isotopes. How would you modify the above procedure to respond to the presence of an excess amount of ^{140}Ba and rare earth fission products? Also, what other radiostrontium isotopes will be present, how does this presence affect the measurements, and what modifications are needed in the counting protocol? Be specific.
2. Calculate what the ratio of activity would be for $^{89}\text{Sr}/^{90}\text{Sr}$ if you are told the source of the fission products are from brief thermal neutron fission of ^{235}U and that the sample was 15.7 days old.

3. Why is it necessary to use “scavenge” techniques for the removal of barium (by barium chromate) and plutonium (by ferric hydroxide precipitation)?
4. Use calculations as shown in the beta-particle self-absorption experiment (#4) or a comparison of the two sets of efficiency values with and without added mass in Experiment #2 to suggest that the self-absorption of ^{90}Y beta particles is small for this experiment.
5. Construct a flow diagram for the strontium procedure.

Source

This procedure was developed in part from the procedure STRONTIUM-90 by B. P. Bayhurst in *Collected Radiochemical and Geochemical Procedures*, Compiled and Edited by Jacob Kleinberg, LA-1721 5th Edition, Los Alamos National Laboratory (May 1990).

Experiment 14

Determination of Radio-strontium in Water with a Strontium-specific Solid-phase Extraction Column

Objective

To determine ^{90}Sr with solid-phase extraction (SPE) column that is specific for the separation of radio-strontium.

Introduction

The SPE technique used in this procedure is analogous to ion exchange. The column consists of a crown ether sorbed on a solid matrix, and is available from a commercial supplier (Eichrome®). These columns typically hold a small amount of the SPE material, and thus require that the amount of strontium carrier (~ 5 mg) be less than that used in classical radiochemical separations (~ 20 mg).

This experiment demonstrates application of a batch process in which multiple samples are analyzed simultaneously with a quality control (QC) sample. For yield measurement, ^{90}Sr tracer is added to the QC sample; this is an alternative to the conventional carrier yield determination described in Experiment #13. This substitution of external for internal tracer yield measurement requires great care in processing as similarly as possible all samples in a batch. Any deviation of the individual yield from the QC-sample yield by more than 10% will be detected by measuring the recovered weight of the strontium carrier, and should stimulate examination of the procedure for irregular losses.

The measured recovery of added ^{90}Sr tracer in the QC sample is then taken to be the yield for all samples in a batch. If the ^{90}Sr tracer is from a standard solution, then the QC sample measurements provide the combined yield and counting efficiency. (*Note: This is described in the alpha-particle spectral analysis in Experiment 15.*) The ^{90}Sr activity in each sample is its net count rate multiplied by the ratio of the QC sample activity (in Bq or pCi) to the average QC sample count rate.

A reagent blank also is processed per batch as part of the QC program. The blank result represents the conventional background plus contaminants and

should be subtracted from the radio-strontium result. Any count rate of the blank in excess of the typical background count rate suggests that radioactive contaminants accompany radio-strontium in the procedure. This observation also should stimulate examination of the procedure to determine the need for improved control of reagents and laboratory cleanliness or a better purification process.

To measure ^{90}Sr , the time of separation of ^{90}Y from ^{90}Sr and the time of counting must be recorded. An additional measurement is performed later to check for the presence of ^{89}Sr , as discussed in Experiment #13. In relating the count rate for the quality control sample to that for any sample in the batch, the ingrowth of ^{90}Y must be considered. Alternatives are (1) assuring that the ingrowth times for the entire batch are similar (within a few hours); (2) adjusting for different ingrowth periods; and (3) inserting an 18-d period between separation and counting to ensure parent-daughter equilibrium.

Safety Reminder

- Follow the usual safety procedures when working in a radiological laboratory.
- Caution should be exercised when preparing and working with corrosive mineral acids.
- All liquids/ and solids are to be properly disposed of according to laboratory rules and protocol.

Equipment and Supplies

- Analytical balance capable of measuring to 0.1 mg
- Low-level beta-particle counting system, generally an anti-coincidence proportional counter
- Hot plate
- Beakers, 1 or 2 L, 150 mL
- Plastic containers, 20 mL or 50 mL
- Large stirring rod
- Ion-exchange column, 10 mL capacity (see Experiment #13 and Fig. 7.6)
- Planchets, stainless steel, suitable for the counting chamber of the counting system
- Filters and filtering apparatus
- Forceps
- Pipettes, 1 mL, 5mL volume

Reagents

- Cation exchange resin, strong base, 8% cross linked cation resin, 100-200 mesh, analytical grade
- Strontium SPE column: 2 mL resin bed, 4, 4'-(5')-bis(*t*-butyl-cyclohexano)-18-crown-6 on an inert polymeric support as supplied by Eichrome®. See Fig. [14.1](#)
- 8 M HNO_3 : Add 500 mL of concentrated nitric acid to 400 mL of deionized water and dilute to 1 L

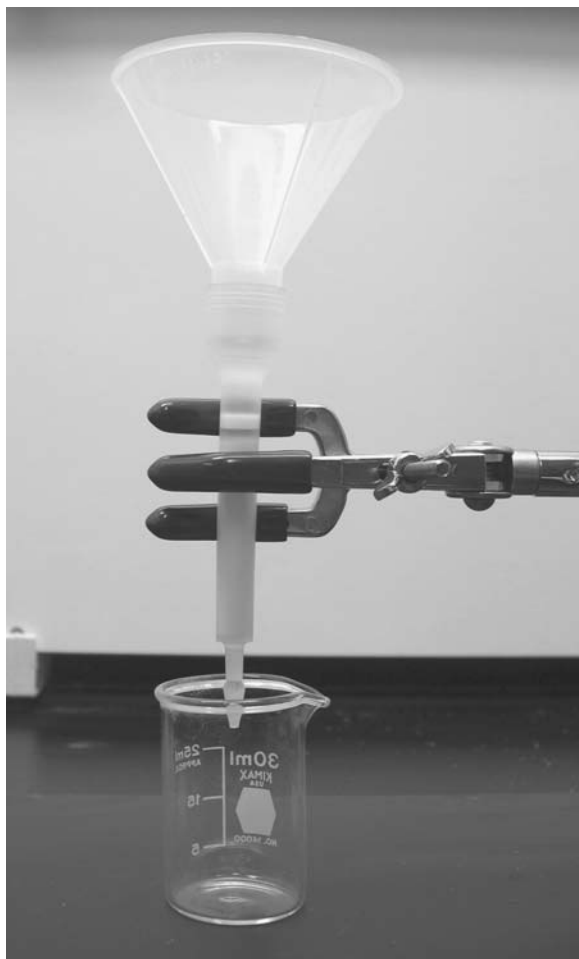


Figure 14.1 Eichrome column

- 0.1 M HNO_3 : Add 6.25 mL of concentrated nitric acid to 800 mL of deionized water and dilute to 1 L.
- Strontium carrier, 5 mg Sr^{2+} /mL: See *Preparation and Calibration of Sr Carrier at the end of this experiment*.
- Ethanol, 95%
- ^{90}Sr standard solution. Dilute with 0.05 M HNO_3 to prepare 50 mL of a ^{90}Sr solution at a concentration of about 1 Bq/mL.
- Deionized water

Procedure

Step 1. Pipette 1.0 mL of strontium carrier into a water sample (maximum volume 1 L). Add 1 mL of 8 M HNO_3 per 100 mL of sample and mix. Bring to a boil and then cool. *Note: Process a second, tracer standard, sample in parallel after pipetting 1.0 mL of ^{90}Sr standard solution into the acidified solution. Also process a third, blank, sample in parallel by the procedure below.*

Step 2. Precondition a cation-exchange column (see Fig. 7.6) that contains 10 mL of cation-exchange resin by passing ~50 mL of 0.1 M HNO_3 through the column. Then add the sample to the column, at a flow that does not exceed 5 mL/min. Discard the eluent.

Step 3. Wash the column with ~30 mL of 0.1 M HNO_3 . Discard the eluent wash solution.

Step 4. Elute the strontium fraction with 50 mL of 8 M HNO_3 at a flow that does not exceed 5 mL/min. Collect the eluent in a clean 150 mL beaker.

Step 5. Evaporate the eluent to *near* dryness (< 1 mL) on a hot plate. *Do not take to total dryness because a dried sample may be difficult to dissolve.*

Step 6. Take up the residue in 5 mL of 8 M HNO_3 . Carefully heat, if necessary, to dissolve any residue.

Step 7. Prepare a strontium SPE column according to the manufacturer's instruction. Condition the column by letting 5 mL of 8 M HNO_3 drain through it by gravity. Discard eluent.

Step 8. With a pipette, transfer about one-half of the sample from Step 6 to the SPE column and let the sample flow by gravity through the column. Add the second half of the sample after the first half has flowed through the column. Discard the eluent.

Step 9. Rinse the beaker that contained the sample with two 3 mL portions of 8 M HNO_3 and transfer with the original pipette, in turn, each rinse solution to the column.

Step 10. Wash the column with 10 mL of 8 M HNO_3 and discard eluent. Record the time of this wash as the ^{90}Y separation time.

Date and time of ^{90}Y separation _____

Step 11. Elute the strontium from the column with two 5-mL portions of 0.5 M HNO_3 . Collect the two eluents in a clean plastic container (a 20-mL liquid scintillation counting vial or a 50-mL centrifuge tube is suitable).

Note: The strontium carrier yield could be measured for each sample by adjusting the procedure after this Step to precipitate SrCO_3 . This change would require an increased analysis time and a lesser precision than usual because of the smaller carrier amount, required by the SPE column.

Step 12. Pipette a 3-5 mL portion of the strontium eluent onto a tared planchet beneath a turned-off heat lamp. Turn on the heat lamp and evaporate slowly. Repeat pipetting and continue the evaporation process until all of the eluent has been dried. Wash the plastic container with 3 mL 0.5 M HNO_3 and pipette on the dried eluent on the planchet. Dry with a heat lamp.

Data Table 14.1 Weight of strontium nitrate

Weight of Planchet(mg)	Weight of Planchet + Sr(NO ₃) ₂ (mg)	Weight of Sr(NO ₃) ₂ (mg)
Sample		
Standard		
Blank		

Step 13. Turn off the heat lamp, cool planchet to room temperature, and promptly weigh the planchet with strontium nitrate to the nearest 0.1 mg. Record the weight in Data Table [14.1](#). The weight of strontium nitrate is determined to identify any significant deviation in recovery among samples, relative to the QC sample. The weight can also indicate the extent of self-absorption.

Step 14 Count the sample planchet as soon as possible. Count the standard tracer planchet and the blank background planchet during the same time period. Count each sample a second time after an interval of 3–18 d.

Calculation of the ⁹⁰Sr Radioactivity in the Sample

$$C_{Sr} = \left(\frac{(R_{Sr} - R_b)}{V_{Sr}} \right) \left(\frac{(A_{std})}{(R_{std} - R_b)} \right) \quad (14.1)$$

Where

R_{Sr} = gross count rate of the sample, in cps

R_{Std} = gross count rate of the standard, in cps

R_b = background count rate, in cps

A_{Std} = activity of the standard added to the processed standard solution, in Bq

V_{Sr} = sample volume, in mL

C_{Sr} is the sample concentration in Bq/mL

This relation applies when the time interval between yttrium separation and counting is the same for the actual sample and the accompanying ⁹⁰Sr standard solution. If the time interval of the two differs by more than 15 min, then a correction must be made for the different ingrowth fractions of ⁹⁰Y and the different counting efficiencies of ⁹⁰Sr and ⁹⁰Y.

A calculation of activity based on separately determined counting efficiency and yield measurement is given in Experiment 13.

Preparation and Approximate Calibration of Strontium Carrier (5 mg Sr²⁺/mL) in terms of Sr(NO₃)₂

Dissolve 12.08 g of Sr(NO₃)₂ in deionized water, add 10 mL of concentrated HNO₃, and dilute to 1 L with deionized water. In triplicate, onto a tared planchet, pipette exactly 5.0 mL carrier solution and dry under a heat lamp. Let cool and weigh to nearest 0.1 mg. Calculate the weight of strontium nitrate, as processed by elution from the SPE column and evaporation. Record on label as mg/mL of evaporated nitrate, with initials and date.

Questions

1. For the crown ether strontium extractant, speculate how the active agent for separating strontium functions in this analysis.
2. This radiochemical method for ^{90}Sr assumes that ^{89}Sr is not in the sample. If a sample were presented to you that does contain both ^{89}Sr and ^{90}Sr , outline a method for determining the amount of ^{90}Sr within a period of 3-5 days.
3. Discuss the advantages and disadvantages of this type of column separation (specific crown ether extractant) for strontium. Why not use four times the column size to accommodate a “normal” amount of carrier (20 mg)?
4. For a batch of columns used to determine ^{90}Sr , the chemical yield for every sample was too low. Speculate about the causes of this observation. Devise a method to address this problem.
5. Sketch, in semilog coordinates, a net count rate vs. time curve (for a 3-week period) for a sample immediately after strontium separation in which only ^{90}Sr is present. Also prepare a curve for a sample with only ^{89}Sr . Finally, prepare a curve in which ^{89}Sr and ^{90}Sr are present in equal activity concentrations at the time of counting.

Sources

This procedure is modeled after *Standard Test for Strontium-90 in Water* (D 5811-00) from the Annual Book of ASTM Standards, 2003, Section II, Water and Environmental Technology, Volume 11.02 Water (II), pp 959–962, ASTM International, West Conshohocken, PA.

Preparation procedure for strontium carrier adopted from the Radiochemical Procedure, STRONTIUM-90, B.P. Bayhurst, in *Collected Radiochemical and Geochemical Procedures*, Compiled and Edited by Jacob Kleinberg, LA-1721 5th Edition, Los Alamos National Laboratory.

Experiment 15

Radiochemical Determination of Plutonium in Water by Ion Exchange Chromatographic Separation

Objective

To determine the amount of plutonium in a water sample after chemical purification by anion-exchange chromatographic separation and counting by alpha-particle spectrometer.

Introduction

Plutonium has been released into the environment primarily by atmospheric nuclear testing and at nuclear facilities that produce plutonium or store nuclear waste that contains plutonium. The plutonium isotopes of interest are shown in Fig. 15.1

The radioisotope ^{239}Pu is commonly measured in environmental samples around the world. Other plutonium isotopes, notably ^{238}Pu and ^{240}Pu , usually are present in some amounts. The method of detection is either alpha-particle spectrometry or mass spectrometry. Alpha-particle spectral analysis can distinguish ^{239}Pu from ^{238}Pu . Alpha-particle spectral analysis cannot distinguish ^{239}Pu from ^{240}Pu , because the main alpha particle groups emitted by the two isotopes have almost the same energy; these two isotopes are separated by mass spectrometric analysis. Plutonium isotopes generally also emit L X-rays at 13.6 keV and low-energy, low-intensity, gamma rays.

In this experiment, an alpha-particle spectrometer is used to determine the concentration of $^{239+240}\text{Pu}$. (*Although both isotopes will be represented in the final determination, for simplicity we will refer to this result as ^{239}Pu for the remainder of this experiment.*) An appropriate tracer of plutonium, usually ^{242}Pu , is added to the sample, as discussed in Experiment #6. The activity of the plutonium in the sample can be calculated from the measured ^{239}Pu count rate and the ratio of the plutonium tracer (e.g., ^{242}Pu) activity to its measured count rate. This plutonium concentration is reported in pCi or Bq per unit mass or volume of sample.

^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu	^{243}Pu	^{244}Pu
87.7 a	2.41×10^4 a	6.56×10^7 a	14.4 a	3.73×10^5 a	4.956 h	8.08×10^7
α	α	α	β^-	α	β^-	α
5.499, 5.456 .	5.156, 5.144, 5.105 . . .	5.168, 5.123 .	0.0208	4.901, 4.856 .	0.58, 0.49 . .	4.589, 4.546

Figure 15.1 Plutonium isotopes of interest.

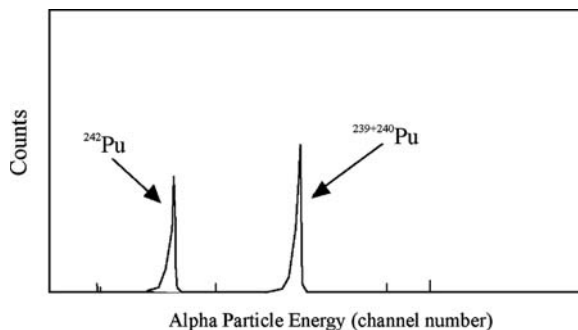


Figure 15.2 Alpha particle spectrum for a purified plutonium sample.

Figure 15.2 illustrates a simple alpha-particle spectrum. It contains $^{239-240}\text{Pu}$ ($E_{\alpha_{239}} = 5.156$ MeV, $E_{\alpha_{240}} = 5.168$ MeV) and the tracer ^{242}Pu ($E_{\alpha_{242}} = 4.901$ MeV). In addition to these main alpha-particle group, others with slightly lower energies cause the peaks to be asymmetric with a more gradual decrease at their low-energy side.

In the chemical procedure, the tracer and the sample plutonium first exchange with each other during nitric acid digestion. If the sample volume is large, plutonium is concentrated by co-precipitation and then dissolved. This step is unnecessary for processing a relatively small sample (< 50 mL), as shown below. Elements are then separated by anion-exchange chromatography. Plutonium is sorbed as a nitro-complex on an anion-exchange column. The column is washed to remove impurities. Plutonium then is stripped from the column by reducing it to destroy the anionic species.

Plutonium is electrodeposited onto a stainless steel disk to obtain a thin and uniform source for counting alpha particles. Counting is by spectral analysis to identify the plutonium alpha particles by peak energy and determine their activity by the integral of the count rate at the peak.

About the Separation and Options

For an experienced analyst who knows the techniques involved, the laboratory time to complete this experiment (excluding time for preparation) is 6–8 hours; it will take longer for those new to the procedure. The experiment can be interrupted conveniently before the ion-exchange process (Step 10), after the plutonium is stripped from the column (Step 12), and at the conclusion of the preparation for electrodeposition (Step 14). An alternative procedure is given for a 25-mL sample that skips the concentration Steps # 3–8.

An alternative method of plutonium purification by solvent extraction is given in Experiment 16. In that experiment, the counting source is prepared by co-precipitation with sub-milligram amounts of lanthanum fluoride.

Follow the column, disk, and electroplating preparation instructions that are given below the procedure. Follow the instructor's directions if the laboratory has a different electrodeposition system and procedure.

Safety Reminders

- Protective personal equipment must be worn when performing this experiment. This includes a laboratory coat, eye goggles, and plastic gloves. Proper closed shoes should be worn.
- Be careful while working with strong acids (HF, HNO₃, and H₂SO₄), a strong base (NH₄OH), flammable organic solvent, hot plates, high voltage, and low level radioactivity.
- All liquids are to be properly disposed according to laboratory rules and protocol.

Equipment for Chemical Separation and Counting

- Graduated cylinder, 1 L, 100 mL
- Glass beaker, 100 mL, 250 mL, 2 L or 4 L
- Watch glass to cover beaker
- Hot plate for stirring with magnet and magnetic stir bar
- Funnel, glass or plastic to accommodate 32 cm diameter filter paper
- Filter paper, 32 cm diameter, Whatman 41 or equivalent
- Centrifuge tubes, glass, 50 mL, as alternative to filter paper and funnel
- Ring stand or stand to hold filtration funnel
- Polyethylene squeeze bottle
- Large Millipore^R filtering apparatus.
- Membrane filter, 47 mm, 0.45 micron
- Filtering flask, 250 mL
- Serological pipet or plastic transfer pipette; 1-mL pipette or automatic pipetter capable of delivering 1 mL
- Glass chromatography column: 14.5 mm i.d., 250 mm active length, fritted glass disk support, and 250 mL reservoir, Teflon stopcock or similar setup
- Filtering apparatus, suction filter for 47 mm diameter
- Si alpha-particle detector with spectrometer system
- Volumetric flasks for reagent preparation
- Bottles for storing reagents, glass
- Labels for bottles

Equipment for Electrodeposition

- Electrodeposition apparatus (See Figure 15.3)
- DC power source, to supply, 25 A at 110 V for 12 parallel electrodeposition sites
- Platinum wire anode
- Electrodeposition disk: polished 2-cm (3/4 inch) diameter from 22 gauge stainless steel. Rinse in deionized water and store under deionized water until cell assembly.

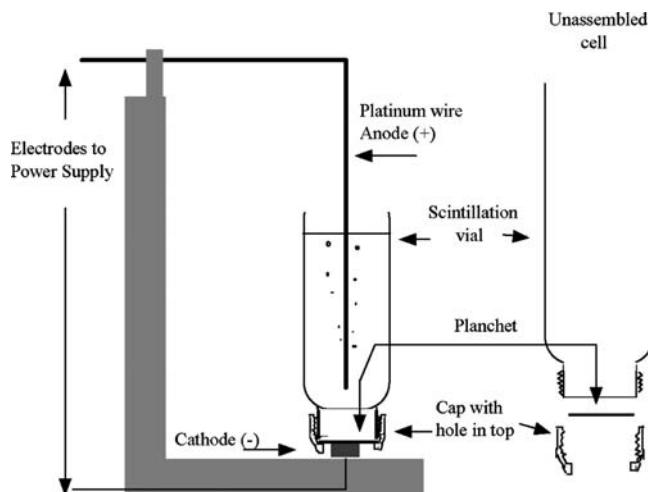


Figure 15.3 Electrodeposition cell.

- Planchet for holding disk, steel, 5-cm dia. with 0.5-cm-high sides
- Borosilicate Pasteur pipette (5-3/4 inch length disposable) or plastic delivery pipette (2 or 3 mL capacity)
- Engraving tool
- pH paper Hydrion^R, narrow range paper, pH 1.2 to 2.8
- Electroplating system
- Ammonia gas bubbler assembly: gas washing bottle, tubing and air pump

Disposable electrodeposition cells are constructed from 20 ml polyethylene liquid scintillation vials with the bottoms cut off. The cap is replaced with a black plastic cap with a 1.6-cm hole in the top. A polished stainless steel disk is inserted into the cap with the polished side toward the inside of the vial and the cap is tightly screwed into place. The splatter guard is made from plastic test tube cap that is slightly larger than the scintillation vial and has a hole bored into it approximately 0.6 cm from the edge to allow the platinum wire anode to pass through.

Reagents for Chemical Separation

The reagents for this experiment are reagent grade or higher. Smaller quantities may be prepared for the experiment than indicated. Most reagents preparation descriptions are for one liter volume. As always, when diluting acids and bases, add the concentrated reagent to water, then dilute to volume.

- Anion exchange resin: Dowex 1, 1 x 8-100, strongly basic anion exchanger, 50-100 mesh, chloride form
- Concentrated HCl (12 N, 37% HCl, reagent grade)
- 10 N HCl: Dilute 833 mL of concentrated HCl to 1 liter with deionized water.
- 6 N HCl: Dilute 500 mL of concentrated HCl to 1 liter with deionized water.

- 8 M HCl: Dilute 667 mL of concentrated HCl to 1 liter with deionized water.
- 1 N HCl: Dilute 83 mL of concentrated HCl to 1 liter with deionized water.
- Concentrated HNO₃ (16 N, 70%, reagent grade)
- 8 M HNO₃: Dilute 500 mL of concentrated HNO₃ to 1 liter with deionized water.
- 0.1 N HNO₃: Dilute 6 mL of concentrated HNO₃ to 1 liter with deionized water
- Sodium bisulfite (1%) NaHSO₃, in 6 M HCl: 1 g NaHSO₃ dissolved in 100 mL of 6 M HCl.
- 0.05 M NH₄I: 0.725 g of NH₄I dissolved in 100 mL of 10 M HCl; prepared fresh.
- 50% (w/w) NaNO₂: 50 g NaNO₂ dissolved in 50 mL deionized water.
- Concentrated H₂SO₄: 18 M, 95-98% sulfuric acid
- Concentrated NH₄OH: 15 M, 29.2 %
- 6 M NH₄OH: Dilute 400 mL concentrated NH₄OH to 1 L with deionized water.
- Ferric nitrate carrier: 20 mg Fe⁺³/mL: Dissolve 14.5 g Fe(NO₃)₃·9H₂O in 100 mL 0.1 M HNO₃.
- Ethanol, 95%
- Plutonium tracer solution, standardized. Concentration should be about 0.05 Bq/mL of ²⁴²Pu (²³⁸Pu tracer is used for some types of samples).
- Water, deionized

Reagents for Electroplating

- Thymol Blue solution (0.04%): Dissolve 0.04 g Thymol blue indicator in 100 mL 95% ethanol.
- Ethanol 95% adjusted to pH 8 with ammonium hydroxide
- Sulfuric acid, 1:99: Add 1 mL concentrated H₂SO₄ to 99 mL deionized water.
- 4 M Nitric acid: Dilute 250 mL concentrated HNO₃ to 1 L with deionized water.
- Ammonium hydroxide, 1:9: Add 10 mL concentrated NH₄OH to 90 mL deionized water.
- Ammonium nitrate, solid, reagent grade
- 1% Ammonium nitrate in 1:99 ammonium hydroxide: Dissolve 1 g NH₄NO₃ in 80 mL deionized water, add 1 mL concentrated ammonium hydroxide and dilute to 100 mL with deionized water.
- 2% Sodium dichromate in 4 M HNO₃. Dissolve 1 g of reagent grade sodium dichromate, Na₂Cr₂O₇·2H₂O, in 50 mL 4 M HNO₃.

Procedure for Chemical Separation

Step 1. Measure 1 to 4 L of a previously acidified water sample with a graduated cylinder and record the volume to the nearest 1 mL. (*The laboratory instructor will specify the volume to be used for the experiment.*) Filter the sample through a fluted filter paper and collect the sample in a clean beaker appropriate to the sample volume. [When analyzing a small sample volume,

measure 25 mL of a previously acidified water sample, filter, and collect the sample in a 100-mL beaker. Add 26 ml concentrated HNO_3 to adjust to nitric acid concentration suitable for Step #9.]

Step 2. Pipette 1 mL of the standardized Pu tracer into the sample and stir. [For the small sample, now go to Step #9.]

Step 3. Add 2 mL of ferric nitrate carrier to the large sample. Add a magnetic stirring bar. Stir the sample and cover with a watch glass. Place the beaker on a hot plate, bring to boil and boil gently for 30 minutes.

Step 4. While the sample is still boiling, carefully add 6 M NH_4OH to the sample from a polyethylene squeeze bottle with the spout inserted between the watch glass and the pouring lip of the beaker until the solution becomes turbid due to precipitation of brownish $\text{Fe}(\text{OH})_3$, which carries plutonium. While boiling continues, add an additional 10 mL of 6 M NH_4OH . Remove the stirring bar. Continue to boil for an additional 30 minutes.

Step 5. Remove the beaker from the hot plate and allow solution to cool and the flocculent precipitate to settle to the bottom of the beaker.

Follow either steps 6a-8a or 6b-8b as instructed.

Step 6a. Filter the supernate through a 47-mm, 0.45- micron, membrane filter in the larger Millipore filtering apparatus to collect the $\text{Fe}(\text{OH})_3$ with the co-precipitated plutonium. Slurry the precipitate remaining in the beaker with 10 mL deionized water and pour through the filter with the precipitate. Discard filtrate.

Step 7a. Place the filtering apparatus over a clean, 250 mL filtering flask. Gradually add 25 mL of warm 8 M HNO_3 to the filter to dissolve the precipitate and drain into flask.

Step 8a. Gradually add another 25 mL of 8 M HNO_3 to the filter to assure complete dissolution. Collect in the same 250 mL filter flask.

OR

Step 6b. Carefully decant most of the clear supernatant solution without carrying away the precipitate and discard the solution.

Step 7b. Stir precipitate into remaining supernatant solution and decant into 2 centrifuge tubes. Centrifuge and discard supernate. Wash out beaker with 20 ml water, transfer to centrifuge tubes that contain the precipitate, centrifuge, and discard supernate.

Step 8b. Dissolve precipitate in the 2 centrifuge tubes with 20 mL of 8 M HNO_3 each and transfer the 2 solutions to a 250 mL flask. Wash out each centrifuge tube with 5 mL of 8 M HNO_3 . Add wash water to flask and mix.

Step 9. Add 1 mL of 50% NaNO_2 solution to the dissolved sample in the flask [or to the small sample from Step #2] to adjust the Pu oxidation state to +4 and form the anionic nitrate complex of plutonium. Swirl to mix and let sample stand overnight, or at least two hours if the sample must be rushed. The sample is now approximately 50 mL of 8 M HNO_3 , and ready for the plutonium column.

Step 10. Transfer the sample solution to the reservoir of the conditioned column. (See Fig. 15.4 and **column preparation** procedure given below.) Rinse the sample beaker twice with 15 mL portions of 8 M HNO₃ and add both to the sample in the reservoir. Pass the sample through the column at a flow rate of approximately 2 mL per minute. *If the flow rate is too fast, the plutonium complex will not have time to absorb onto the resin and the recovery will be low.*

Step 11. Wash the column with 40 ml of 8 M HNO₃ at a flow rate of approximately 2 mL per minute to remove radionuclides other than plutonium. Discard effluent. Repeat wash.

Step 12. Elute the plutonium from the column into a clean 100-mL beaker with 50 mL of freshly prepared 0.05 N NH₄I solution in 10 M HCl at a flow rate of 2 mL per minute. *The column will turn dark brown due to the formation of I₂; this step destroys the anionic plutonium species complex that had been sorbed on the anion exchange resin.*

Step 13. Add 5 mL of concentrated HNO₃ to the 100 mL beaker, swirl to mix, and gently heat on the hot plate to evaporate to a small liquid residue to remove the iodine. Complete the conversion of the plutonium to the nitrate form by two additional treatments with 5 mL portions of concentrated HNO₃. Evaporate to near dryness each time, but do not dry.

Step 14. Take up the residue in 5 mL of concentrated HNO₃. Add 0.5 mL of concentrated H₂SO₄ and evaporate until the nitric acid has been volatilized and fumes of sulfuric acid appear. *Nitric acid fumes are fluffy white. Sulfuric acid fumes are dense white.* Remove from hot plate. Allow the sample to cool and add 3 mL of deionized water, swirling to mix.

Procedure for Electrodeposition

Step 15. Transfer the sample with a borosilicate glass Pasteur pipette or plastic transfer pipette to a prepared electroplating cell. *See diagram (Fig. 15.3) of electroplating cell and **cell preparation** procedure given below of electroplating planchet and cell.*

Step 16. Rinse the sample beaker with two portions of 3 mL of 1:99 sulfuric acid solution and add rinse to the cell. The total volume now should be near 10 mL.

Step 17. Add 2 drops of thymol blue indicator to the solution in the cell and swirl gently to mix.

Step 18. Adjust to pH 2.0-2.3 by bubbling gaseous ammonia into the solution. *The color change is from a red to a dirty yellow.* A gas washing bottle is used to bubble air through a concentrated ammonium hydroxide solution and then through a pipette immersed in the sample.

Step 19. Verify the sample pH with narrow range pH paper (1.4 to 2.8) or by comparing the indicator color to that of a solution of thymol blue at pH 2.0-2.3.

Step 20. Place cell on disk that is electroplating unit cathode and position platinum anode with splatter guard as shown in the Figure 15.3

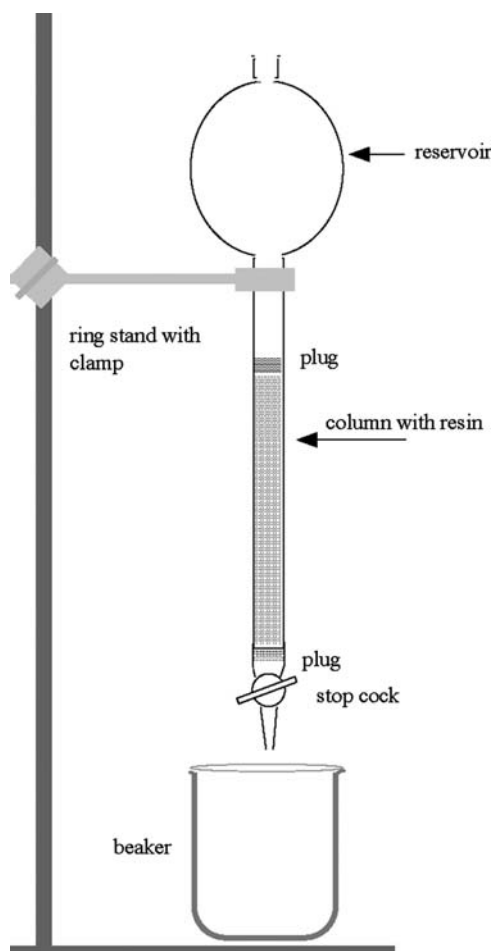


Figure 15.4 Schematic of an ion exchange column for plutonium separation.

Step 21. Turn power supply on and adjust current to 1.1 ampere. Monitor current for at least 20 minutes and readjust as necessary.

Step 22. Electroplate plutonium at 1.1 ampere for 1.0 hour.

Step 23. Add 10 mL of 1:9 ammonium hydroxide solution to the cell and wait one minute.

Step 24. Remove the electrode from the cell and turn off the power. Promptly use transfer pipette to discard the solution. Rinse the disk in the cell with 1% solution of ammonium nitrate in 1:99 ammonium hydroxide from a squirt bottle. Discard rinse.

Step 25. Disassemble the cell, remove the disk with forceps, and rinse the disk with ethanol adjusted to pH 8 with ammonium hydroxide.

Step 26. Hold the disk securely with tongs to flame the deposit over a Meeker burner for 15 seconds.

Step 27. When the disk is cool, affix it to the center of a labeled 5-cm-diameter planchet by two-sided tape.

Step 28. Count sample at specified distance from Si detector in vacuum chamber of alpha-particle spectrometer for 60,000 s.

Column Preparation

Wash the anion-exchange resin with deionized water in a beaker by repeatedly rinsing and decanting to remove fine particles that remain suspended. Transfer 8 mL of the washed resin as a slurry from a graduated cylinder to the column that is fitted with a frit or glass wool plug and has a stopcock at the bottom of the column. Let resin settle in the column while maintaining water cover, and tap to assure that no air bubbles or channels remain. Add a plug of glass wool on top of the settled resin to prevent resin from floating. Immediately prior to use, condition the column for the samples by passing through it 80 mL of 8 M HNO_3 at a flow rate of 2 mL/min. The apparatus is shown in Figures [15.4](#) and [15.5](#).

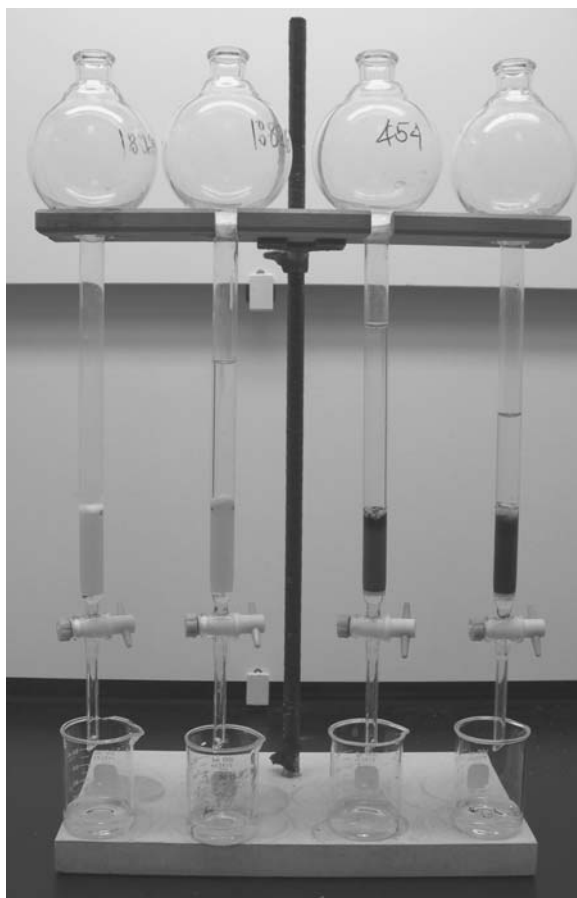


Figure 15.5 Ion exchange column for plutonium separation.

Column Regeneration

To regenerate the ion-exchange resin column for additional separations, immediately after use pass 50 mL of 1% NaHSO_3 in 6 M HCl through the column at a flow rate not to exceed 5 mL per minute. Assure absence of bubbles or channels in the column. Pass 50 mL of 6 M HCl through the column at the same flow rate. Wash the column with 80 mL of deionized water. Store the column with the resin covered with water until needed for the next sample. The resin should be discarded when no longer clean, and definitely after five applications. *For important samples, it is best to use fresh resin.*

Disk Preparation

Step 1. Engrave sample ID on the non-polished back surface.

Step 2. Degrease by washing disk with warm soapy water and rinsing with acetone.

Step 3. Immerse the cleaned disk in warm 2% sodium dichromate-4 M HNO_3 solution for 10 minutes.

Step 4. Rinse in deionized water and store under deionized water until time to assemble cell.

Cell Preparation

Step 1. Immerse polyethylene vial in 2% sodium dichromate- HNO_3 solution for 3-4 hours.

Step 2. Rinse with and immerse in 4 M HNO_3 for 1 hour to remove any residual chromate.

Step 3. Rinse in deionized water. Assemble cell as shown in Figure [15.3](#).

Step 4. Fill assembled cell with deionized water. Drain when ready to receive sample.

Treatment of Data

1. Calculation of the Activity of Plutonium in the Sample

At the end of the counting period, the counting data for the sample can be presented as a graphic spectrum, as counts-by-channel printout, and as integral count rates beneath each peak with calculated activity for specified radionuclides. The same information is needed for background measurements to permit background count rate subtraction from each peak. Most alpha-particle spectrometer systems have programs that integrate the peaks, subtract backgrounds, and calculate the plutonium isotope activity routinely. Follow

the instructor's directions for handling and reporting data. If the data are to be "hand" calculated, the following procedure may be used.

- Identify the alpha-particle energy peaks of the plutonium isotope analyte and tracer.
- Sum the number of counts in the channels for each peak and divide by the counting time to obtain gross count rate.
- Check spectrum for peaks not associated with plutonium isotopes. If any are found, identify the radionuclide by its alpha-particle energy. Scrutinize the decay schemes of such impurity radionuclides to determine whether they emit any alpha particles that are sufficiently near the energies of the plutonium alpha particles to interfere with plutonium identification and quantification, i.e., constitute part of the background.
- Subtract the background count rate in the summed channels for each peak.
- Calculate the analyte activity based on the ratio of the tracer activity to its count rate – which is the inverse of the chemical yield multiplied by the alpha-particle counting efficiency – and the decay fraction for the characteristic alpha particle, in Bq/L:

$$A \text{ of } {}^i\text{Pu (Bq/L)} = \frac{(R_i - B_{i\text{bkg}})(A_{tr})(f_{tr})}{(R_{tr} - B_{tr\text{bkg}})(V_{sa})(f_{sa})} \quad (15.1)$$

where,

R_i = gross c/s that appear in the ${}^i\text{Pu}$ alpha-particle energy region

$B_{i\text{bkg}}$ = background c/s in the same alpha-particle energy region as for the ${}^i\text{Pu}$

R_{tr} = gross c/s that appear in the ${}^{tr}\text{Pu}$ (tracer) alpha-particle energy region

$B_{tr\text{bkg}}$ = background c/s in the same alpha-particle energy as for the ${}^{tr}\text{Pu}$

A_{tr} = total activity of ${}^{tr}\text{Pu}$ tracer added to the samples in Bq

V_{sa} = volume of the samples in liter (L)

f_{sa} = decay fraction, alpha particle per sample radionuclide decay

f_{tr} = decay fraction, alpha particle per tracer radionuclide decay

A = Activity of plutonium analyte sample in Bq/L

2. Calculation of the Chemical Yield or Percent Chemical Recovery

Many laboratories have a criterion of performance based on the percent chemical yield. The recovery, for example, may have to exceed 50% to meet this criterion. The radiochemical yield is the fractional recovery of the amount of added tracer. Its measurement requires that the counter efficiency (ϵ) is known (see Experiment #6). The counting efficiency can have been determined in a previous experiment and recorded with the detector information.

The chemical yield or percent recovery of the sample is calculated by the following relationship:

$$\% \text{ Chemical Yield} = \left(\frac{\left[\frac{R_{tr} - B_{tr\text{bkg}}}{\epsilon} \right]}{A_{tr}} \right) \times 100 \quad (15.2)$$

where,

- R_{tr} = gross c/s that appear in the ^{239}Pu alpha-particle energy region,
 B_{trbkg} = background c/s in the same alpha-particle energy as for the ^{239}Pu ,
 A_{tr} = total activity of ^{239}Pu tracer added to the samples, multiplied by fraction of alpha particles of that energy per disintegration, in Bq,
 ε = counting efficiency

Calculate the uncertainty in your answers due to counting statistics alone. See Appendix 6 for discussion of counting statistics.

Questions

1. Write the chemical equations to show the oxidation state and species for plutonium in the steps leading to and through the column separation.
2. If one of the reagents in this experiment had been contaminated with detectable levels of fallout plutonium, how would this affect your results? Explain.
3. To produce the metal form of an actinide by electrodeposition is very difficult. What do you think the chemical species is on the surface of the disk when it is electroplated?
4. A sample of river water is found to contain the following plutonium isotopes: ^{239}Pu , ^{240}Pu , and ^{242}Pu . Speculate as to the origin/source of the plutonium in a sample of this type. How would you analyze for ^{242}Pu ?
5. How would you measure the ratio of $^{240}\text{Pu}/^{239}\text{Pu}$ in the sample from Question 4?

Source

This procedure was adapted from a procedure used at the Environmental Radiation Center, GTRI of the Georgia Institute of Technology, Atlanta, GA.

Experiment 16

Radiochemical Determination of Plutonium in Water by Solvent Extraction

Objective

To determine the amount of plutonium in a water sample after radioanalytical chemical purification by extraction into triisooctylamine solution and counting by alpha-particle spectrometer.

Introduction

Many radioanalytical methods are available for separating and purifying plutonium in environmental samples. For this experiment, the primary purification step for separating plutonium is by extraction with triisooctylamine (TIOA) in the organic solvent, *p*-xylene. Other common extraction agents are 2-thenoyltrifluoroacetone (TTA), cupferron in chloroform, tributyl phosphate, and trioctylphosphine dioxide. As in any extraction process, the analyte – plutonium in this case – must be distributed between the aqueous phase and the organic phase so that, at equilibrium, much more is in the organic phase than in the aqueous phase, while the undesirable interfering elements remain mostly in the aqueous phase.

The sample may be a large or a small volume of water, as determined by the instructor. A tracer is added to calculate the activity, as discussed below. The tracer and sample plutonium are prepared in the oxidation state Pu^{+4} by acid digestion with H_2O_2 . The plutonium is then purified by an extraction cycle from 9N HCl into TIOA. After extraction, the plutonium in TIOA is washed with HCl and then back-extracted into an aqueous solution.

An optional method for removing polonium follows, if ^{210}Po may be present, to prevent possible interference in spectral analysis by ^{210}Po alpha particles, whose energy is only 150 keV greater than that of ^{239}Pu . The ^{210}Po is a progeny of naturally-occurring ^{238}U . It is easily removed by spontaneous deposition on more readily oxidized metals such as nickel.

The sample then is prepared for alpha-particle counting by co-precipitation of plutonium with a small amount of lanthanum fluoride, which is collected

on a filter and mounted for counting. (An alternative preparation by electrodeposition of the plutonium onto a stainless steel disk is described in Experiment #15). The combined chemical recovery and counting efficiency of the analyte plutonium are determined by means of the added plutonium tracer of known concentration, as described in Experiment #15.

Safety Reminder

- Follow the usual safety procedures when working in a radiological laboratory.
- Caution should be exercised when preparing and working with corrosive mineral acids and a strong oxidant (30% hydrogen peroxide). In working with hydrofluoric acid, gloves must be worn. If HF comes in contact with the skin, severe and painful burns may occur.
- All liquids are to be properly disposed according to laboratory rules and protocol.

Equipment

- Graduated cylinder, 1 L, 100 mL (plastic and glass)
- Beaker, 4 L, 250 mL
- Funnel, glass or plastic to accommodate 32-cm diameter filter paper
- Filter paper, 32-cm diameter, Whatman 41 or equivalent
- Filter membrane, 25-mm diameter, 0.2 micrometer pore size
- Filtering apparatus, for 25-mm diameter filter
- Separatory funnels, 1-L, 500-mL
- Planchets, stainless steel, 5-cm diameter
- Volumetric flask 1 L
- Bottles, glass, for storing reagents; plastic bottle for HF solution
- Labels for bottles
- Hot plate

Reagents

The reagents required for this experiment are reagent grade or higher. Smaller quantities than indicated may be prepared for the experiment. Most reagents preparation descriptions are for one liter.

- Ethanol, 95%
- Concentrated HNO_3 (16 N, 70%, reagent grade)
- 0.1 N HNO_3 : Add 6 mL of concentrated HNO_3 to 900 ml of deionized water and dilute to 1 L.
- Concentrated HCl (12 N, 37% HCl, reagent grade)
- 9 N HCl: Add 750 mL of concentrated HCl to 200 mL of deionized water and dilute to 1 L.
- 6 N HCl: Add 500 mL of concentrated HCl to 400 mL deionized water and dilute to 1 L.
- 1 N HCl: Add 83 mL of concentrated HCl to 900 mL deionized water and dilute to 1 L.

- 1.5 N HF: Add 104 mL of 29 N (48%) reagent grade HF to 100 mL deionized water and dilute 1 L.
- Hydrogen peroxide, H₂O₂, 30% reagent grade
- Lanthanum carrier, 0.1 mg La⁺³/mL. Dissolve 0.0779 g high purity La(NO₃)₃·6H₂O in 200 mL of 1 N HCl and dilute to 250 mL with 1 N HCl.
- Nickel foil, 5 cm x 1 cm x 0.1 mm
- Plutonium-242 tracer solution, standardized. Concentration of about 0.05 Bq/mL
- Triisooctylamine (TIOA), [C₈H₁₇]₃N, reagent grade
- 10% TIOA solution in *p*-xylene: Dilute 100 mL of TIOA to 1 liter with *p*-xylene.
- *p*-xylene
- Water, deionized

Procedure

Step 1. Measure 1 to 4 L (or 25 mL, *as specified by instructor*) of water sample (which has been previously acidified) with a graduated cylinder and record the volume to the nearest 1 (or 0.1) mL. Filter the sample through a fluted filter paper and collect the filtrate in a clean beaker of appropriate size.

Step 2. Carefully add with stirring 100 mL of concentrated HCl. Pipette into the solution 1 mL of the standardized Pu tracer and mix the solution. (*Note: For the 25-mL sample, skip Step #3 and go to Step #4.*)

Step 3. Place the beaker on a hot plate at a low heat setting. Evaporate the solution to about 200 mL. Remove the beaker from the hot plate and let cool. Carefully add with stirring 200 mL of concentrated HCl.

Step 4. Add 2 mL of 30% H₂O₂ to the solution and mix to stabilize the +4 plutonium valence necessary for optimum extraction into TIOA. Return beaker to the hot place briefly and heat at a low setting for a few minutes. Remove beaker from the hot plate and set aside for 10 minutes.

Step 5. To prepare the organic phase, pour 100 mL of 10% TIOA in *p*-xylene into a clean 1-L separatory funnel (see Fig. 16.1). Add 50 mL of 9 N HCl, cap the separatory funnel, invert funnel and vent the funnel stopcock in a safe direction to release any vapors that build up in the funnel. *Perform venting operation after every subsequent shaking.* Close the stopcock and shake funnel for two minutes to equilibrate the HCl between the organic and aqueous phases. Place the separatory funnel on the stand and remove the cap. Allow phases to separate. Drain the lower, aqueous, phase and discard.

Step 6. Add the aqueous sample from Step #4 to the acid-equilibrated TIOA in the separatory funnel, cap, invert, and vent. Close stopcock. Shake the funnel vigorously for two minutes to equilibrate the plutonium between the phases.

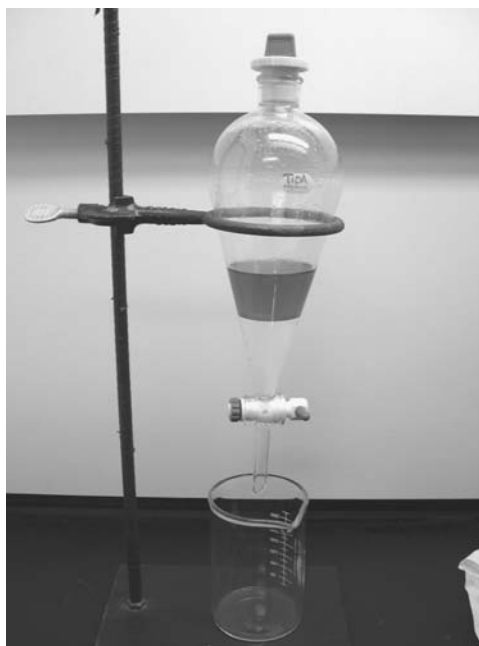


Figure 16.1 Separatory funnel.

Step 7. Place the separatory funnel on the stand, remove the cap and allow the phases to separate cleanly. Drain the lower, aqueous, phase and discard it.

Step 8. Add 50 mL of 9 N HCl wash solution to the TIOA solution in the separatory funnel and shake for two minutes to wash the organic phase.

Step 9. Remove cap and allow the phases to separate. Drain and discard the lower, aqueous, phase.

Step 10. Repeat washing (Steps 8 and 9) to insure removal of contaminants that were carried into the organic phase.

Step 11. Strip the plutonium from the TIOA solution by adding 100 mL of 0.1 N HNO_3 to the separatory funnel and shaking the funnel for two minutes.

Step 12. Place the funnel on the stand, remove cap, and allow the phases to separate. Drain and save the lower acid phase in a 250-mL beaker.

Step 13. Repeat Steps 11 and 12 to complete stripping the plutonium from the organic phase. Combine the aqueous strip solution with that collected in Step 12 in the 250-mL beaker. Discard the organic layer.

Step 14. Pour the combined 200 mL strip solutions into a clean 500-mL separatory funnel.

Step 15. Add 100 mL of *p*-xylene to the combined strip solutions and shake for two minutes to remove any TIOA carried into the aqueous acid phase. (*Residual TIOA makes the subsequent co-precipitation more difficult.*) Place the separatory funnel on the stand.

Step 16. Remove cap and allow the two phases to separate cleanly. Drain and save the lower aqueous layer in a clean 250-mL beaker. Discard the organic layer.

Step 17. Evaporate the aqueous solution from Step 16 almost to dryness (to about 1 mL) on a hot plate. Do not dry, over-heat, or bake. Remove the beaker and cool.

Step 18. Add 10 mL of concentrated HNO_3 to the residue. Swirl and evaporate almost to dryness. Cool. Repeat the HNO_3 evaporation to complete the destruction of the organic material. Remove beaker from the hot plate.

Step 19. Add 10 mL of concentrated HCl, swirl, and evaporate almost to dryness. Remove beaker from the hot plate and cool. Repeat the HCl evaporation.

(Note: Steps #20 through 22 are an optional procedure to remove ^{210}Po . To skip this demonstration, proceed to Step 23.)

Step 20. Take up the sample residue (*which may not be visible*) in 50 mL of 1 N HCl and warm gently to dissolve it. Continue heating with swirling until the solution begins to give off vapors at about 80°C . Do not overheat or boil.

Step 21. Suspend a clean nickel metal strip into the solution and stir for two hours to collect polonium by spontaneous deposition.

Step 22. Remove the nickel metal strip. Wash it with a few mL of deionized water from a wash bottle and add wash water to the solution. Discard or count the nickel metal strip. Evaporate the solution almost to dryness.

Step 23. Take up the residue from Steps #19 or 22 in 15 mL of 1 N HCl and warm to approximately 50°C to dissolve.

Step 24. Add 0.5 mL of 30% H_2O_2 . Pipette 1 mL of lanthanum (0.1 mg/mL) carrier into the solution and mix. Add 5 mL of 1.5 N HF. Mix well and set aside for 30 minutes to co-precipitate plutonium with the LaF_3 .

Step 25. Slurry precipitate onto membrane filter held in filtration apparatus.

Step 26. Rinse the sample beaker with 10 mL of deionized water and add to the filter funnel. Rinse the beaker with 10 mL of ethanol and add to the filter funnel to wash and dry precipitate.

Step 27. Disassemble the filter funnel. With tweezers or forceps, carefully remove the membrane filter and fix with double-sided tape at the center of a 5-cm planchet that has been etched with an identification number on its back.

Step 28. Count the sample for 60,000 s at an instructor-specified distance from the Si detector in the vacuum chamber of the alpha-particle spectrometer.

Treatment of Data

See Experiment #15 for data handling and calculations.

Questions

1. What is the effect on your result if high-purity deionized water were added to your sample in Step 3, instead of HCl?
2. If you accidentally lost about 1/3 of your sample during the extraction due to a leaky stopcock, how would this affect your answer?
3. If both this experiment and Experiment #15 are performed, compare the resolution (full width at half height, in keV) of the ^{242}Pu peaks.

Sources

1. Moore, F.L., Anal. Chem. 30, 908 (1958).
2. Harley, J.H., EML Procedures Manual, HASL-300. Environmental Measurement Laboratory, Department of Energy, New York, NY (1979).
3. Johns, F.B., et al., Radiochemical Analytical Procedures for Analysis of Environmental Samples, EMSL-LV-0529-17, USEPA, Las Vegas, NV (1979).
4. Coleman, G.A., The Radiochemistry of Plutonium, NAS-NS 3058, National Academy of Sciences, Washington DC

Experiment 17

Selection of a Method for the Radiochemical Determination of Plutonium in an Environmental Sample

Objective

To review the literature for a radioanalytical chemistry method to purify plutonium from other radionuclides, notably actinides, and from interfering stable substances in an environmental sample; and to compare the method selected by the student with the methods in Experiments # 15 and 16.

Introduction

This experiment is designed to allow the student to develop his/her skills in searching the literature for methods and materials applicable to a specific analysis. The following outline is a guide for the student to find such information, evaluate it critically, and put his/her ideas to the test by performing the analysis. For a fall-back position, commercially available SPE columns are in wide use (Horowitz et al. 1998). The SPE form applicable to strontium analysis is used in Experiment #14.

Procedure

Step 1. Search the literature/internet for methods, including commercially available materials, for the determination of plutonium. List the materials needed by the various methods. Investigate catalogs, internet sites, vendors, and the chemistry stock room for information on the availability and cost of materials. Consider and record the advantages and drawbacks of various methods.

Step 2. Propose a method that appears to be suitable with regard to your skills, the capabilities of the available laboratory, the cost of materials, and

the time available for performance. Submit a report of your findings for the instructor and present it to the class.

Step 3. Reach a decision on the method that you will test, based on advice from your instructor and fellow students. Your instructor will inform you about the availability of equipment and reagents in the laboratory.

Step 4. Review the selected method and, if necessary, rewrite it on the model of this manual, step by step. Be clear and straightforward in your presentation. Describe the counting procedure and show any equations needed to calculate activity.

Step 5. Make a list of all the equipment, supplies, reagents, and radionuclides, (including tracers) that you need for executing the experiment.

Step 6. Review the procedure for safety concerns. Make a list of warnings and guides, safety devices such as gloves, eyeshields, and clothing, and radiation protection actions.

Step 7. Submit the procedure to the instructor for review and approval.

Step 8. When the procedure is approved, collect equipment and reagents. Place instruments and equipment into operational form, test with calibration sources, and determine null or background values. Prepare needed solutions and dilutions. Calibrate tracer and carrier, if needed.

Step 9. Obtain a sample for the plutonium analysis and perform the experiment. Make careful notes in your notebook to describe successful and failed reactions and to recommend improvements.

Step 10. After the sample is counted, calculate the plutonium concentration in the sample. Show all calculations. Compare results obtained by all class members.

Questions

1. Compare and contrast the method you found and applied to the other plutonium methods in this manual. Make a list of advantages and disadvantages of each that addresses the following topics:
 - Time to perform the analysis
 - Ease/complexity of performing the analysis
 - Cost of analysis
 - Reliability and purity of the counted plutonium source.
2. If you were given the responsibility to analyze hundreds of environmental samples for plutonium on a limited budget, recommend the procedure that you would use.

Source

Horowitz, E.P., Chiaritzia, R., Dietz, M.L, Diamond, H., and Nelson, D.M. 1998. Separation and preconcentration of actinides from acidic media by extraction chromatography. *Anal Chim Acta* 281:361–372.

Experiment 18

Gamma-ray Spectral Analysis of a Solution of Mixed Fission Products

Objective

To analyze by gamma-ray spectrometer a sample that contains a mixture of fission products from neutron-irradiated fissile material. (*If a reactor is unavailable, the instructor may synthesize a mixture of radionuclides that emit gamma rays.*)

Introduction

Gamma-ray spectral analysis is a powerful tool for identifying and measuring radionuclides in an environmental sample. The sample usually is analyzed by a gamma-ray spectrometer with a germanium (Ge) detector as a first step because little sample processing is needed, the technique is simple to apply, and many radionuclides can be identified and quantified simultaneously. Analysis consists of determining the energy of each peak in a gamma-ray spectrum and the net count rate associated with each characteristic peak of the radionuclides.

The detection system is calibrated in terms of energy per channel in keV or MeV. It also is calibrated in terms of counting efficiency – counts per gamma ray – as a function of energy.

A radionuclide is identified by comparing observed gamma-ray characteristics – energy of characteristic peak and of other peaks, as well as their intensities – to published tabulations of radionuclides, listed by gamma-ray energies and half life, with additional information on gamma-ray fractions. The radionuclide identified by gamma-ray energy then is quantified by converting the net count rate in the region of interest (ROI) measured under a characteristic peak to a disintegration rate by applying its gamma-ray counting efficiency, gamma-ray decay fraction, and radioactive decay between the time of origin (or collection) and of counting. Reliability of radionuclide identification and quantification is improved when several gamma rays attributed to the same radionuclide yield consistent results, whereas inconsistent results suggest erroneous attribution.

As shown in Fig. 18.1, numerous gamma rays of different energies can be identified in the same spectrum. In the figure, each full-energy peak is characterized as the emitting radionuclide by its energy. Some peaks are too small to appear above the continuum from Compton interactions and the radiation background. In a few instances, peak resolution can be insufficient for identification, because two gamma rays with energies within a few keV of each other appear as a single peak. Erroneous identification and quantification are possible when a gamma ray does not represent a full-energy peak – for example, the 512-keV peak for ^{106}Ru in Fig. 18.1 also includes the 511-keV peak of annihilation radiation.

For half-life determination, sample counts are repeated after several time intervals. These intervals may be hours or days for relatively short-lived radionuclides, and increase to weeks or months for longer-lived ones. Decay calculations lead to error when a radioactive daughter of a radioactive parent is assumed to decay with the daughter half life, whereas ingrowth calculation is required. Major examples of this problem are the transient-equilibrium pairs ^{140}Ba - ^{140}La (which is no longer found in Fig. 18.1 after decay for a year) and ^{95}Zr - ^{95}Nb .

A sample such as the one with the gamma-ray spectrum shown in Fig. 18.1 that contains products from a fission event is analyzed to determine the concentrations of the constituent radionuclides. This information may be applied to infer the origin and age of the radionuclide mixture and any processes that it has undergone between formation and sampling. The fission yield curve in Fig. 18.2 is a generalized presentation of the fission yield, in atoms produced per fissioned atom, for isotopes from about 80 to 160 atomic mass units. The fission yield for ^{235}U has the shown two sharp peaks, but some heavy elements have only a single fission-yield peak. The products are “neutron rich” and consequently emit beta particles, followed in most instances by gamma rays. The half-lives of the radioactive fission fragments range from very short (<1 s) to very long (> 10^5 a); quite a few radionuclides decay with half lives in the commonly observed range of hours to years.

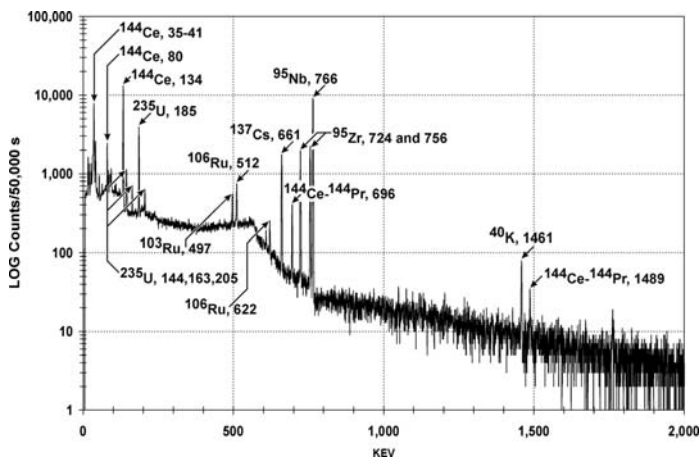


Figure 18.1 Gamma-ray spectrum of mixed fission products from ^{235}U after a 1 year decay.

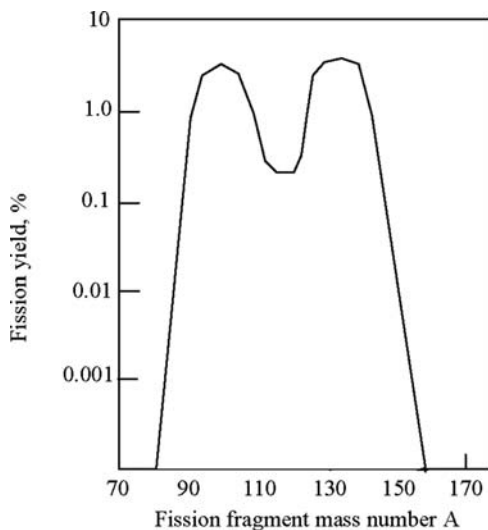


Figure 18.2 Generalized fission yield curve.

Many decay chains, each with about 5 isobars (isotopes with the same mass number), have been observed.

In theory, relating relative intensities of short- and long-lived fission products in a sample to their fission yields permits calculation of the time interval since fission, and a similar comparison at various atomic mass units can indicate the type of fission. In practice, physical and chemical differences among the measured radionuclides, and within the radionuclide decay chains that lead to these radionuclides, introduce fractionation during transport from source to sample by air, water, biological uptake, and during sample processing. Finding neutron-activation products such as ^{54}Mn and ^{60}Co in the sample indicates that neutron-irradiated material was both within the range of the fission neutrons and at least partially included in the fission product sample.

The sample being analyzed in this experiment contains fissionable material that had been sealed in a quartz tube and irradiated with neutrons. The material was dissolved in strong mineral acid to prepare it for radiochemical analysis of fission products. You will be informed of the date and time of the end of bombardment (EOB), the type of material, the amount of fissionable material in your sample, and the acid type and strength. You can assume that the person who prepared the sample based the amount of fissile material to be irradiated and the period of irradiation on the available neutron flux and the desired amounts of fission product radionuclides. You should estimate the activities of the major fission products that remain after the time interval between formation and analysis.

You will open the shipping container, transfer the solution to a volumetric flask, and dilute the original solution as needed for your purposes. This experiment must be planned and scheduled so that the time interval between the fission process and initial counting is sufficiently short to measure shorter-lived radionuclides before they can no longer be measured by you.

Transfer an aliquot of the sample into a container for which the detector has been calibrated in terms of gamma-ray counting efficiency (count per gamma-ray emission), as in Experiment 2B. After transferring the solution

from the shipping container, wash out the container, and add the wash to the sample solution.

Count the sample for a sufficient time period and frequency to collect reliable data for determining the gamma-ray energy, the count rate for characteristic gamma-ray energy peaks, and the rate of decay of that peak. Also count the empty container with the Ge detector and spectrometer to determine whether any radionuclides remain sorbed on container walls and to estimate the fractional loss by sorption for each radionuclide of interest. Note that the counting efficiency for radionuclides retained on the container must be estimated.

Because gamma-ray peaks from many radionuclides are observed in a single sample, select a counting time period during which a statistically reliable number of counts will accumulate for the lowest-intensity peak of interest. You will also have to decide the intervals at which measurements are repeated to observe radioactive decay of the individual peaks. Note that some gamma-ray peaks may be from radioactive daughters that initially grow into the sample rather than decay, and that later decay with the half life of the parent. Collect data as numerical tables of count rate per ROI energy channels and in graphical form of gamma-ray spectra (as in Fig. 18.1), and analyze the data for the energy, intensity, and half-lives of the components.

The experimental steps are designed for a specific type of mixed fission product solution. The instructor will specify the necessary changes to adapt to another type of sample and local rules for handling the sample.

Safety Reminder

- Follow the usual safety procedures when working in a radiological laboratory. This sample is more radioactive than most samples handled for other experiments. It also contains a wide variety of radionuclides, which makes cleanup more difficult if a spill occurs.
- Caution should be exercised when preparing and working with corrosive mineral acids.
- All liquids and solids are to be properly disposed of according to laboratory rules and protocol.

Equipment

- Germanium detector with supporting electronics, multi-channel analyzer (typically 1,000 – 4,000 channels) and computer software for data collection, analysis, and presentation, calibrated for energy and counting efficiency
- Sample container for holding the sample (instrument must be calibrated with respect to counting efficiency for the sample container and volume)
- Volumetric flasks
- Laboratory tissues
- Hypodermic syringe (when sample is in container with septum seal)
- Transfer pipettes

Reagents

- Sample of irradiated fissile material solution of known volume, chemical form, and approximate activity.

- Acid, identical in type and concentration to sample solution, for dilution
- 3 M HCl: Dilute 333 mL of concentrated HCl to 1 L with deionized water
- Commercial detergent, solution
- Ethanol, 95%
- Water, deionized

Procedure

Sample preparation and analysis

Step 1. Receive the sample according to the guidelines and protocol of the receiving institution. The persons who handle the sample must be properly trained and prepared. To receive and process the sample, the person must wear a laboratory coat, face protection, and gloves. The sample is unpacked and inspected in a hood behind a shield. (*Note: If the sample is packaged at an altitude different than that of the receiving location, there will be a pressure differential that must be taken into account when opening the sample.*) This process should be performed as promptly as possible after sample receipt to minimize decay of shorter-lived radionuclides.

Step 2. Survey the sample with a hand-held beta-gamma radiation monitor to verify that the radiation exposure level is acceptable in the laboratory. Use Equation 18.2 to estimate the radionuclide activity concentration from the exposure rate measurement. Swipe the container surface with a paper or cloth swipe. To verify the absence of radioactive surface contamination, count the swipe with detectors to measure alpha particles, beta particles, and gamma rays. The sample is unacceptable and must be returned to the originator if the external radiation or swipe radioactive contents exceed shipping regulations. If the sample is considered acceptable by the instructor, estimate the sample dilution required for counting the sample by gamma-ray spectral analysis under the usual geometric arrangement and with minor dead-time loss.

Step 3. Carefully open the sample vial in a hood, behind a shield. If the vial has a screw cap, inspect the vial to be sure no liquid is at the cap. If it has a septum-type cap, expect the possibility of a pressure differential and equalize the pressure in the sample vial to room (atmospheric) pressure with the hypodermic needle.

Step 4. Transfer the sample by pipette or syringe to a volumetric flask of the volume selected for sample analysis (usually 25–100 mL). Record the amount so transferred (by volume or mass), and compare to volume recorded in shipping papers. Quantitatively rinse the container several times with the same acid solution as that in which the sample was delivered. Transfer the rinse to the volumetric flask that contains the sample. Save the vial in which the sample was shipped (see Step 9). Dilute the sample in the volumetric flask to the mark with the same acid solution. (*Note: If the sample is to be measured by mass, make the appropriate balance measurements on the volumetric flask when empty, before adding wash and diluting liquid, and when full.*) Close the flask, label it, and thoroughly mix the sample by shaking.

Step 5. If further dilution is needed, pipette a suitable volume into a second volumetric flask and dilute to volume with the same acid solution. Close flask

and shake well. Label flasks in Steps 4 and 5 with identity, chemical form, extent of dilution, data, and analyst initials. Calculate dilution factor (final solution/initial solution as shipped).

Volume or mass of original sample: _____
Dilution factor for sample _____

Step 6. Transfer with a pipette a predetermined quantity of sample to a counting container calibrated for counting efficiency. Close and label it. Swipe the outside of the container and count swipe to check for radioactive contamination. If no radioactive contamination is detected, proceed to Step 7. If contamination is found, thoroughly clean container with a detergent solution and ethanol until no contamination remains. To assure cleanliness, seal the counting container in a plastic bag.

Step 7. Place counting container on Ge detector and immediately check that spectrometer live-time dial reads near 100% to assure that count rate is not excessive. If dead time is significant (live time <90%), remove sample and prepare a more dilute sample, as in Step 5. If live time is near 100%, set the count time to accumulate sufficient gamma ray data (typically 600 s) to obtain at least 1,000 counts in each of the characteristic gamma ray peaks of the shorter-lived radionuclides that are readily observable and of interest in the first count.

Step 8. Repeat measurement to obtain duplicate result; then repeat at selected intervals. The decrease in the count with time rate at a peak ROI is used to measure the half life with which it decays. Peaks of longer-lived radionuclides are measured as they become visible when gamma rays from shorter-lived radionuclides disappear from the spectrum. Increase the counting time in later measurements to compensate for radioactive decay and lower activity of longer-lived radionuclides. Increase the time interval between counts as the average half life of the sample increases. For example, count the sample daily for the first week, weekly for the next 4 weeks, and then monthly.

Shipping Vial

Step 9. Promptly place the emptied shipping container into a plastic bag and seal bag. Place bag into a plastic counting container and cap the counting container. Swipe counting container to check for surface contamination. If clean, seal counting container in plastic bag and place on Ge detector.

Step 10. Obtain a gamma-ray spectrum for 6,000 s. Analyze the data for the shipping container to calculate its residual radionuclide content and whether it represents a significant fraction of any fission product. Calculate the fraction of each radionuclide found in the solution that remained on container walls (see Treatment of Data, below).

Counting

Before counting the sample, perform detector system quality control measurements to assure that energy calibration, count-rate response, and background levels are within the acceptable range. Examine the energy calibration equation to confirm the relation of channel number to gamma-ray energy.

Examine the curve of counting efficiency vs energy to estimate the ratio of the net count rates to the disintegration rates at the energies of the expected peaks. Examine the background curve to identify peaks associated with the background.

Place the sample at a position and geometry relative to the detector whereby the gamma rays may be quantitatively analyzed. Count the sample for a period of time that will produce enough counts in the gamma-ray peak ROI to provide a low counting error, i.e., collect at least 1,000 counts per ROI. Promptly after each measurement, check that the expected energy peaks are observable, sufficient counts have been collected for statistical reliability, and that previously unidentified peaks are attributed to the radionuclides that emit them. For repeated counts, assure that the sample position on the detector is reproducibly identical.

Treatment of Data

Most spectral gamma-ray data programs analyze gamma rays according to their energy and intensity with software programs/routines that have capabilities for peak shaping, background subtraction, and counting statistics calculation (see Chapter 8 of your *Radioanalytical Chemistry* textbook). These programs also have the library capacity for radionuclides to match gamma-ray peaks for reporting radionuclide identity and activity adjusted for counting efficiency and gamma-ray decay fraction, and decay from EOB. (*Note: Adjust for different time zones.*) If “hand” calculation is needed, refer to the Treatment of Data section of Experiment #2, part B. Compile results as activity in Bq/mL of each radionuclide in the shipped solution. Convert Bq of each radionuclide that remained in the shipping container to Bq/mL of the solution in the shipping container, add to the activity measured in solution, and also calculate fraction that remained in the container.

Determine the number of atoms at the end of bombardment for any given radionuclide, i , from its gamma rays observed corrected for branching ratio values and the counting efficiency of that gamma ray by Eq. 18.1.

$$N_{EOB} = \frac{AD_i V}{\lambda_i e^{-\lambda_i t}} \quad (18.1)$$

where

N_{EOB} = number of atoms of radionuclide i at end of bombardment time

A_i = activity at count time of radionuclide i , in $\text{d s}^{-1}\text{mL}^{-1}$ or Bq mL^{-1}

Data Table 18.1 Measured radionuclides

Radionuclide	λ	A	t	N_{EOB}	Normalized yield
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Data Table 18.2 Radionuclides that remained in shipping vial

Radionuclide	Activity	Fraction of total observed
--------------	----------	----------------------------

- V = volume of sample measured for activity, in mL
 λ_i = the decay constant for radionuclide i in s^{-1} ($\ln 2/\text{half life}$)
 t = the time between the count time and the end of bombardment, in s.
 D_i = dilution factor

- 1) Prepare Data Table [18.1](#) listing each identified radionuclide, its decay constant, the value of the observed disintegration rate, the time interval since its production, the calculated number of atoms at EOB, and the reported fission yield, in atom fraction per fission. Note that the software program has automatically decay-corrected the count-time values back to EOB. It will give erroneous values for daughter radionuclides that grow instead of decay, such as ^{95}Nb and ^{140}La , for which a hand calculation for ingrowth is needed. If values are in curie units, convert to disintegrations per second (dps) and atoms.
- 2) Plot the atoms at EOB vs atomic number A for the data set.
- 3) Plot the atoms for the fission of ^{235}U (or other source) vs. atomic number A . for the same radionuclides after looking up the fission yield for each observed fission product.
- 4) Prepare a table of normalized data of the two graphs relative to ^{95}Zr (at 6.4% fission yield).
- 5) List all radionuclides that deviate from the experimental values as compared to the plot of item 3. Indicate if they are higher or lower. Consider which values compare well and which ones do not and whether some major fission products are missing from your sample.
- 6) Prepare Data Table [18.2](#) that lists the radionuclides observed to remain in the cleaned shipping vial and their activity. Estimate whether significant fractions of some radionuclides were absorbed on the wall of the container and propose explanations.
- 7) To estimate the total activity, A , in microcuries, in the sample, as received, in Step 2, use the following equation:

$$A = \frac{R}{6000E} \quad (18.2)$$

- E = gamma-ray energy, in MeV (use 1.0 MeV as an approximation)
 R = exposure rate reading of survey meter held at a distance of 1 foot from sample, in mR/h

This is an estimate that assumes emission of a single gamma ray of 1 MeV by each radioactive atom and that detector and sample both are points.

Questions

1. What is the expected ratio of $^{131}\text{I}/^{99}\text{Mo}$ for a thermal neutron fission of ^{235}U ? How does this value compare with what you determined?
2. If the $^{131}\text{I}/^{99}\text{Mo}$ ratio in a sample was found to be less than that determined in question number 1, what could you speculate is the reason for the difference?
3. A sample from an unknown origin comes into the laboratory. At the first gamma-ray count you observe a large amount of ^{239}Np . What qualitative conclusion could you make?
4. A sample from a suspected nuclear incident is processed by gamma-ray spectral analysis. The sample does not contain any ^{99}Mo , or at least none is observed. Also, the sample contains large amounts of ^{60}Co and ^{137}Cs but no other radionuclides detectable by gamma-ray emission. What do you conclude?

Experiment 19*

Measurement of Uranium Isotopes by Mass Spectrometer

Objective

To measure uranium isotopes in a water or urine sample with a mass spectrometer.

Introduction

Uranium Isotopes

Uranium in nature may be measured either radiometrically or chemically because the main isotope – ^{238}U – has a very long half life (i.e., relatively few of its radioactive atoms decay in a year). Its isotopes in water and urine samples usually are at low concentrations, for which popular analytical methods are: (1) radiochemical purification plus alpha-particle spectral analysis, (2) neutron activation analysis, (3) fluorimetry, and (4) mass spectrometry. The radiochemical analysis method is similar in principle to that of the measurement of plutonium isotopes in water samples (Experiments #15 and 16). Mass spectrometric measurement involves ionization of the individual atoms of the uranium analyte, separation of the ions by isotopic mass, and measurement of the number of separated isotopic ions (see Chapter 17 of *Radioanalytical Chemistry* text).

The uranium isotopes of interest for measurements are given in Fig. [19.1](#). Of these, only ^{237}U has a short half life and emits beta particles. The three naturally-occurring uranium isotopes – ^{234}U , ^{235}U , and ^{238}U – are shaded in the figure.

For the most part, the ratio of ^{235}U to ^{238}U is constant at an atom/atom ratio of 1/138 (0.72%), which corresponds to a radioactive decay ratio of 0.047. For the ratio of ^{234}U to ^{238}U , variations are observed due to geochemical processes, but – because uranium-234 is a progeny of ^{238}U – at radioactive equilibrium, the atom ratio is 5.4×10^{-5} , while the radioactive decay ratio is 1.00.

*Prepared by Robert Rosson, Environmental Radiation Center, EOSL, GTRI, Georgia Institute of Technology, Atlanta GA 30332-0841

^{233}U	^{234}U	^{235}U	^{236}U	^{237}U	^{238}U
$1.59 \times 10^{-5} \text{ a}$	0.0055	0.07	$2.34 \times 10^{-7} \text{ a}$	6.75 d	99.2745
$2.46 \times 10^{-5} \text{ a}$	$7.04 \times 10^8 \text{ a}$	$4.47 \times 10^9 \text{ a}$	α	β	α
α	α	α	α	β	α

Figure 19.1 Uranium isotopes of interest

With the advent of the nuclear era, other uranium isotopes have been introduced into the environment; on rare occasions, ^{233}U or ^{236}U can be detected in environmental samples. Some naturally occurring radionuclides are enriched or depleted anthropogenically; for example, the ratio of ^{235}U to ^{238}U is no longer constant due to enrichment of ^{235}U for nuclear reactors and weapons.

Mass Spectrometer

The analytical components of mass spectrometer (MS) analysis are

1. Sample preparation
2. Introduction into the mass spectrometer
3. Ionization of the sample
4. Measurement and readout

The actual method of analysis depends on the type of mass spectrometer system being employed and the concentration of uranium.

This experiment presents the measurement of uranium with an inductively coupled plasma mass spectrometer (ICP-MS). In this system, a nebulizer converts the aqueous sample to an aerosol carried with argon gas. A torch heats the aerosol to vaporize and atomize the contents in quartz tubes. The atoms are ionized with an efficiency of about 95% by an RF (radiofrequency) coil. The plasma expands at a differentially-pumped air-vacuum interface into a vacuum chamber. The positive ions are focused and injected into the MS while the rest of the gas is removed by the pump. The ions are then accelerated, collected, and measured as a function of their mass. Losses at various stages, notably the vacuum interface, result in a detection efficiency of about 0.1 %, which is still sufficient to provide great sensitivity. The amounts of uranium isotopes in the sample are determined by comparisons to standards. Because different laboratories have different instruments, the instructor will provide instrument operating instructions. Do not use the instrument until the instructor has checked the instrument and approved its use.

Safety Reminder

- Follow the established safety procedures for working in a radiological laboratory and instrument room.
- Caution should be exercised in preparing and working with corrosive mineral acids.
- If a biological sample such as the urine is considered a bio-hazard, take the necessary handling precautions associated with bio-hazardous materials.
- **ICP-MS safety:** This is a highly complex, delicate, and expensive instrument. Use the instrument only under direct professional supervision. Read manufacturer's safety instructions to avoid problems with high voltage, high temperature and glow from the plasma. Provide adequate

ventilation to remove plasma gases and cool electronic components of the instrument. Check that argon gas supply line and regulator are functioning properly. Insure absence of leaks in chilled water lines to protect high voltage components.

Apparatus and Equipment

- Inductively coupled plasma mass spectrometer (ICP-MS)
- Volumetric flasks, 50 mL
- Beakers, 50 mL

Reagents

- 2% nitric acid: Add 2 mL of concentrated ultra-pure nitric acid to 90 mL of deionized water and dilute to 100 mL. *Note: Use high-quality, ultra-pure nitric acid for this experiment. Reagent grade or analytical grade nitric acid and tap water probably have uranium at levels that will interfere with the analysis.*
- Uranium standard solution
- Multi-element standard solution for MS calibration
- Deionized water
- Argon carrier gas

Procedure

The procedure given below provides operating information for a specific instrument (the Finnegan Element 1). Follow guidance by the laboratory instructor to operate the instrument that is being used.

Step 1. Review MS instrument guidance for analyzing the isotopes of interest, i.e., ^{238}U , ^{235}U , and ^{234}U , to identify possible interference by other isotopes and dimers (combined atoms at the atomic masses of the uranium isotopes) and determine resolution setting. Match the resolution setting (low, medium, high) that determines the instrument ability to separate interfering isotopes from the desired isotope to your analytical sensitivity needs. Improving instrument resolution decreases the sensitivity; the decrease is by a factor of ten for each resolution change in this ICP-MS.

Step 2. Prepare the set of samples in dilute (2%) nitric acid for measurement. Also prepare duplicates, the uranium standards, and blanks of the nitric acid solution and deionized water. Note that a trial measurement of the uranium concentration is needed to select the appropriate isotopic uranium concentration ranges and prepare uranium standards in these ranges.

Step 3. Assure that all components of the ICP-MS instrument are at power. Turn on the operating components that are turned off between use, such as the argon gas flow, chiller and waste pump from nebulizer drain line.

Data Table 19.1 ICP-MS Instrument parameters

Element	Mass Range	Resolution	# of Readings	# of Passes
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Step 4. Turn on the computer that will prompt you to perform the steps to operate the instrument. The initial steps are: light the plasma, turn on the High Voltage to the detector, then allow the instrument to warm up.

Step 5. Calibrate the instrument for mass response by feeding a multi-element standard solution into the system. This is necessary to calibrate the mass response of the detector and introduction system (magnetic sector or quadrupole) to insure that the appropriate mass-window reading is being recorded. Record data in Data Table [19.1](#) and examine especially the region for masses 234, 235, and 238.

Step 6. Select parameters to process the samples of interest – in this case, uranium –within the sample concentration range. Parameters include the analyte element, its mass range, needed resolution to minimize interference, number of readings, and average number of passes and runs for each isotope. Select and optimize instrument settings so that ^{234}U , ^{235}U and ^{238}U isotopes will be measured. Record these settings in Data Table [19.1](#).

Step 7. Perform a brief trial run for ^{238}U , the most abundant isotope, in the samples to locate an appropriate instrument sensitivity range (see Step 2). If the uranium concentration is too high for reliable operation,, dilute the sample to obtain a suitable concentration range; if the concentration is very low, switch to more sensitive operation. Then calibrate at two more sensitive regions, first for ^{235}U and then for ^{234}U . *Note: Under usual conditions, the*

Data Table 19.2 Uranium standard calibration data

U Standard Concentration	Average Reading	Standard Deviation
^{238}U		
^{235}U		
^{234}U		

Data Table 19.3 Uranium sample data

Uranium Isotope	Average Concentration	Standard Deviation
^{238}U		
^{235}U		
^{234}U		

concentration of ^{235}U will be lower than ^{238}U by about 2 orders of magnitude, and that of ^{234}U , by about four orders of magnitude.

Step 8. Calibrate the instrument for analyte concentration response with uranium standards. If the response is near linear over the range of interest, use at least four uranium standard concentrations per sample concentration range, with one each at the upper and lower extreme. Repeat for the two other uranium isotopes in their own concentration ranges. Record the concentration calibration data in Data Table 19.2. Plot and examine calibration curves to assure their linearity.

Step 9. Perform measurements of samples, duplicates, and blanks. Collect data. Plot peaks to confirm resolution and absence of interference by nearby peaks. Follow computer program instructions to terminate analysis.

Step 10. Determine the concentration of the uranium isotopes in the uranium samples. Data collection, processing, and print-out usually are done by computer. Concentrations usually are reported in parts per billion (ppb, or $\mu\text{g/L}$). Some “hand” calculation is desirable to understand the process.

Treatment of Data

Record calibration data with standard deviation in Data Table 19.2. The software for the instrument directs multiple passes/runs on each sample and reports standard deviations for the measurements calculated from replicate results. Obtain a hard copy of the results. Then record the sample data in Data Table 19.3.

Calculate by Eq. 19.1 the alpha-particle activity (in s^{-1}), A , that is equivalent to the uranium isotope mass (in g), W , for ^{234}U , ^{235}U , and ^{238}U , where A_v is Avogadro’s number (in 6.02×10^{23} atom/g-mol), M is the atomic mass (in g/g-mol), and $t_{1/2}$ is the half life of the radioisotope (in s):

$$A = 0.693WA_v/Mt_{1/2} \quad (19.1)$$

Estimate the uncertainty of the results by considering not only the reported standard deviation of replicate measurements, but also the uncertainty of the standard, of the calibration curve, and due to any interference in the isotopic mass collection.

If a radiochemical measurement of uranium was performed on the same sample, compare the results of the two methods.

Questions

1. Uranium is considered to be “ubiquitous.” What are the implications of that property in analyzing uranium?
2. A water sample that you submitted for analysis is found to have a ^{235}U : ^{238}U atom/atom ratio of 1:146 by radiochemical analysis (alpha-particle spectrometry), but when measured by ICP-MS has a ^{235}U : ^{238}U atom/atom ratio of 1:62. What do you suspect happened regarding these analyses? Be specific.
3. In the 1970s, some uranium ore was mined in Gabon, Africa and sent to France for processing and enrichment in ^{235}U . The analyst found these samples to be depleted in ^{235}U . The uranium mine was inferred to have been the site of a self-sustaining natural reaction some 1.2 billion years ago. Outline a rapid analytical method to test if other uranium ores had undergone similar nuclear reactor conditions in the past, based on your experience with this experiment.

Source

US EPA. 1994. Trace elements by ICP/mass spectrometry, in *Methods for the determination of metals in environmental samples*, Supplement 1, Report EPA/600/R-94/111, Method 200.8 Rev. 5.4 (NTIS PB95-125472).

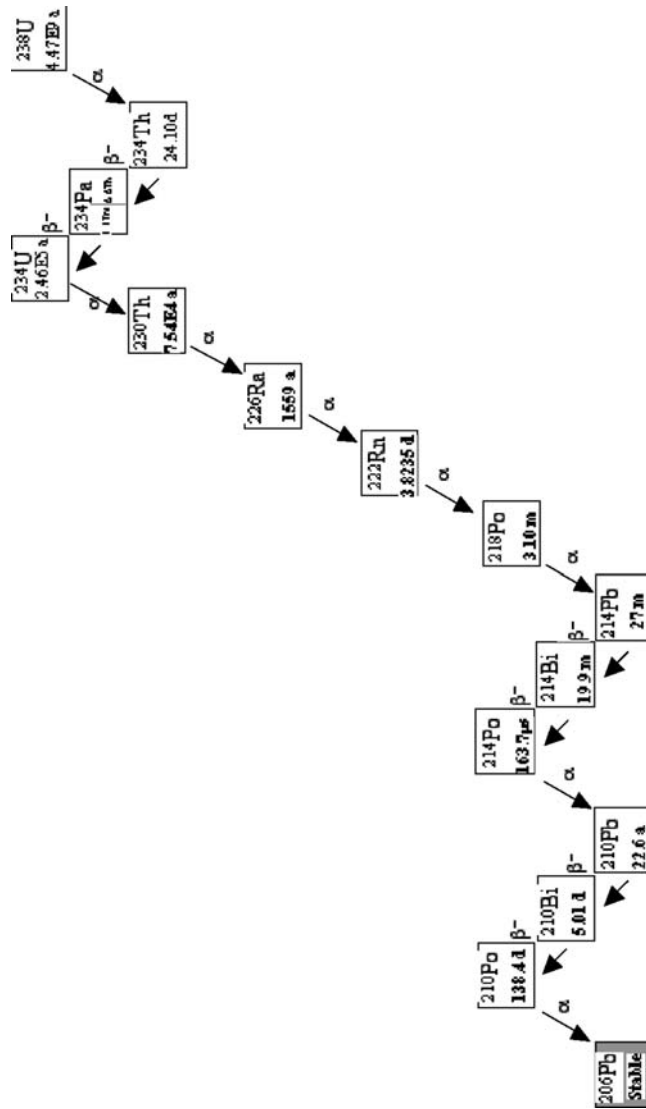
Appendices

Appendix 1. Table of Radionuclides Commonly Analyzed in Environmental Samples.

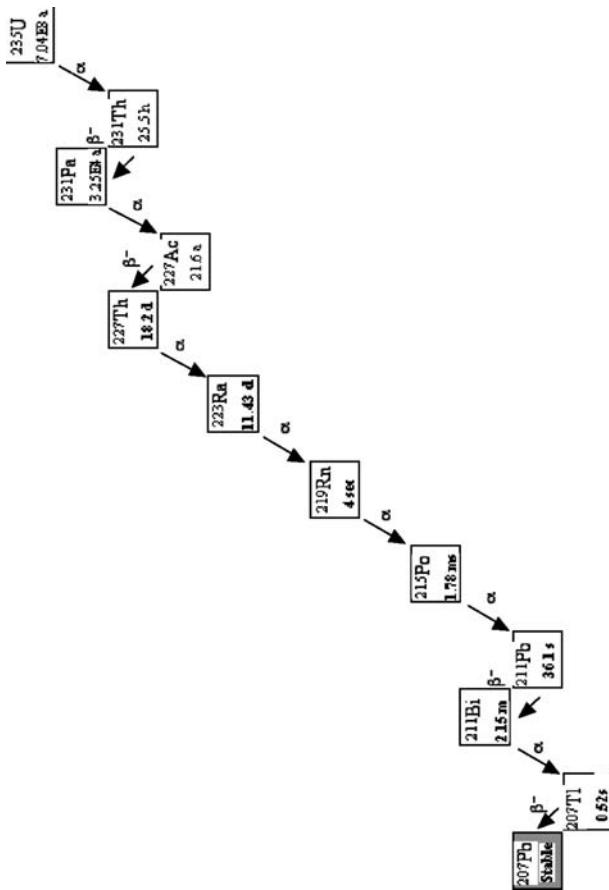
Radionuclide	Half Life	Main Mode(s) of Decay and Energy (MeV)
³ H	12.32 a	β ⁻ 0.0186
⁹⁰ Sr	28.78 a	β ⁻ 0.546
⁹⁹ Tc	2.13 x 10 ⁵ a	β ⁻ 0.294
¹²⁹ I	1.57 x 10 ⁷ a	β ⁻ 0.15; γ 0.0396, e ⁻
¹³¹ I	8.0207 d	β ⁻ 0.606; γ0.3645
¹³⁷ Cs	30.07 a	β ⁻ 0.514; γ 0.661
²²⁶ Ra	1599 a	α 4.7844, 4.602; γ 0.186
²²⁸ Ra	5.76 a	β ⁻ 0.039
²³⁴ U	2.46 x 10 ⁵ a	α 4.766, 4.725; γ 0.0532 (e ⁻)
²³⁵ U	7.04 x 10 ⁸ a	α 4.395, 4.3665; γ 0.1857, 0.1438
²³⁸ U	4.47 x 10 ⁹ a	α 4.197, 4.147; γ 0.0496 (e ⁻) weak
²³⁸ Pu	87.7 a	α 5.499, 5.456; α 0.0435 (e ⁻) weak
²³⁹ Pu	2.410 x 10 ⁴ a	α 5.156, 5.144; γ 0.0516 (e ⁻) weak
²⁴⁰ Pu	6.56 x 10 ³ a	α 5.168, 5.124; γ 0.0452
²⁴¹ Pu	14.4 a	β ⁻ 0.028
²⁴¹ Am	432.7 a	α 5.486, 5.443; γ 0.0596

Note: "a" is the notation for annum (years); "d" days. β is for beta (-) particle, α is for alpha particle, γ is for gamma ray and e⁻ indicates a conversion electron. The energies for beta particles are the maximum energy

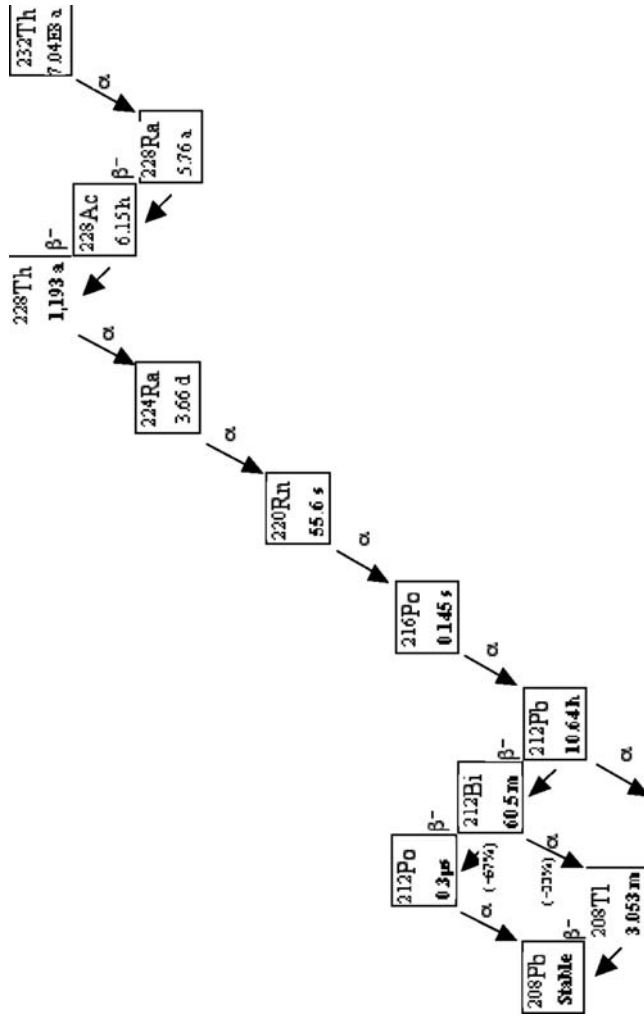
Appendix 2. ^{238}U Decay Series (major members)



Appendix 3. ^{235}U Decay Series (major members)



Appendix 4. ^{232}Th Thorium Decay Series (major members)



Appendix 5. Units of Radioactivity and Prefixes for Multiple Units in the International System

Symbol	Name	Definition of Unit
Bq	Becquerel	1 disintegration per second
Ci	Curie	3.700×10^{10} disintegrations per second

Name	Symbol	Multiple Unit
Exa	E	10^{18}
Peta	P	10^{15}
Tera	T	10^{12}
Giga	G	10^9
Mega	M	10^6
Kilo	k	10^3
Hecto	h	10^2
Deka	da	10^1
Deci	d	10^{-1}
Centi	c	10^{-2}
Milli	m	10^{-3}
Micro	μ	10^{-6}
Nano	n	10^{-9}
Pico	p	10^{-12}
Femto	f	10^{-15}
Atto	a	10^{-18}

Appendix 6. Equations for Count Rates, Standard Deviation, Propagation of Error, and Weighted Averages

A. Count Rate

The count rate (symbol R , in counts per unit time, such as minutes or seconds) is the data from a counter. “A” (activity) denotes the disintegration rate per unit time, such as dpm or dps (Becquerel). One Curie = 3.7×10^{10} Becquerel.

$$R = C/t$$

C = total counts accumulated in timer period t

For a single count of a radioactive sample we give the designation of “gross” count rate or $\text{cpm}_{\text{gross}}$. This indicates that the total counts observed in the sample are due to the sample plus the background activity during that same count period, t . When a background count is taken it is given the designation “background”, “b” or “bkg”.

The net count rate (R_{net}) is calculated as the gross count rate (R_g) less the background count rate (R_b):

$$R_{\text{net}} = R_{\text{gross}} - R_{\text{bkg}}$$

When the counting efficiency (ϵ) is known for a given detector and the net count rate, R_{net} is determined, the absolute activity is determined using the following relationship:

$$A = R_{\text{net}}/\epsilon$$

B. Standard Deviation (σ) for a Single Count

The standard deviation in counts, $\sigma = (C)^{1/2}$, where C is the total counts accumulated for the time period, t. The standard deviation for the net value is calculated as σ_{net} from the gross and background counts, the latter obtained for the background planchet:

$$\sigma_{\text{net}} = [(\sigma_{\text{gross}})^2 + (\sigma_{\text{bkg}})^2]^{1/2}$$

σ_{net} = standard deviation resulting from the subtraction of counting rate x time,

σ_{gross} = standard deviation of the sample before background is subtracted,

σ_{bkg} = standard deviation of the background count, and where

$$\sigma_{\text{gross}} = (C_{\text{total}})^{1/2} \text{ and } \sigma_{\text{bkg}} = (C_{\text{bkg}})^{1/2}$$

For the net count *rate*, R, its 1 σ for a sample counted for time, t, when the uncertainty of t is small compared to C, is

$$(R_{\text{gross}} t_{\text{gross}}^{-1} + R_{\text{bkg}} t_{\text{bkg}}^{-1})^{1/2} = \sigma_{R_{\text{net}}}$$

The standard deviation is the measure of the dispersion of results obtained in replicate measurements that are normally distributed, i.e., the extent to which such measured values are above or below the mean value for the set. Some sets of measured values are not normally distributed and are not described by a standard deviation. Other sets may be normally distributed on the whole, but have a few outlier values that are much higher or lower relative to the mean than inferred from the standard deviation. Such values may be set aside from calculating mean values by applying a specific rejection criterion (e.g. Chauvenet's); this may permit rejection of values that are twice or more the standard deviation larger or smaller than the mean for 10 values, and thrice or more for 100 values. Any rejection of values must be noted and justified when discussing results.

C. Propagation of Error

The propagation of error has been given for the subtraction of two numbers. In this section, the propagation of error for other mathematical operations is given.

When counting data with their associated uncertainty values are added, subtracted, multiplied, or divided with other counting data, or constants, the propagation of the error may be estimated in the final answer. Since both numbers will have associated uncertainties, it is necessary to use the correct relationships to establish the final error. The final error from that manipulation (when two data with their errors are used) will always have a final error larger than either of the errors of the two initial data. For more detailed treatment of counting errors, see *Radioanalytical Chemistry*, Chapter 10.

X and Y are symbols given to actual counting data with their respective counting uncertainties, σ_x and σ_y . The quantities would be expressed as $X \pm \sigma_x$ and $Y \pm \sigma_y$. An example is 163.4 ± 7.4 counts per minute. For each of the mathematical operations on two numbers the relations are given below:

Addition

$$(X \pm \sigma_x) + (Y \pm \sigma_y) = (X + Y) \pm [(\sigma_x)^2 + (\sigma_y)^2]^{1/2}$$

Subtraction

$$(X \pm \sigma_x) - (Y \pm \sigma_y) = (X - Y) \pm [(\sigma_x)^2 + (\sigma_y)^2]^{1/2}$$

Multiplication

$$(X \pm \sigma_x)(Y \pm \sigma_y) = XY \pm XY[(\sigma_x)^2/X^2 + (\sigma_y)^2/Y^2]^{1/2}$$

Division

$$(X \pm \sigma_x)/(Y \pm \sigma_y) = X/Y \pm X/Y[(\sigma_x)^2/X^2 + (\sigma_y)^2/Y^2]^{1/2}$$

The product or division of a constant with a number that has uncertainty is as follows where the number with the uncertainty is : $(X \pm \sigma_x)$ and the constant is K.

Multiplication

$$K(X \pm \sigma_x) = KX + K\sigma_x$$

Division

$$K/(X \pm \sigma_x) = K/X + K/\sigma_x \text{ or } (X \pm \sigma_x)/K = X/K + \sigma_x/K$$

D. Calculation of Weighted Average

The weighted average for several activity quantities having different levels of confidence can be estimated with the following equation.

$$A_w = [(A_1)(w_1) + (A_2)(w_2) + \dots(A_n)(w_n)]/w_T,$$

where

A_w = weighted average,

A_1, A_2, \dots, A_n = individual values,

w_1, w_2, \dots, w_n = respective individual weights, and

w_T = sum of the w_1, w_2, \dots, w_n

The individual weight factors (w_1, w_2, \dots, w_n) are calculated using $w_i = 1/(\sigma_i)^2$ where σ_i is the reported uncertainty for A_i .

The estimated error of A_w , the calculated weighted value is determined as follows

$$\sigma_{\text{weighted average}} = [\{ \sigma | A_w - A_i | \times (1/(\sigma_i)^2) / (n-1) \}]^{1/2}$$

Appendix 7. Concentration of Common Acids and Bases

Name and Formula	Specific Gravity	Percent	Molarity
Hydrofluoric Acid HF	1.17	48	28
Hydrochloric Acid HCl	1.18	37	12
Perchloric Acid HClO ₄	1.5–1.6	60	10
Nitric Acid HNO ₃	1.42	70	16
Nitric Acid (yellow fuming) HNO ₃	1.49	90	21
Sulfuric Acid H ₂ SO ₄	1.84	96	18
Phosphoric Acid H ₃ PO ₄	1.70	85	15
Acetic Acid HC ₂ H ₃ O ₂	1.05	99.5	17
Ammonium Hydroxide NH ₄ OH	0.90	27 as NH ₃	14

Appendix 8. Types of Filter Circles for Collecting Precipitates for Weighing and Mounting Samples for Radioactive Counting

Three types of filter circles usually are used for collecting precipitates in determining chemical yields and mounting for counting: paper fiber, glass-fiber, and plastic membrane. These come in a variety of diameters.

Because the filter circles are used to collect the precipitates for weighing and mounting the samples for counting, special attention must be given to handling them. Here are some general comments and rules regarding the filter circles.

- Do not handle the filter circles with your bare hands to avoid contamination with oil residue from your hand. Use a pair of forceps or tweezers for handling.
- Selection of the type of filter circle is based on the type of precipitate being collected. A gelatinous or clogging type of precipitate requires a fast-filtering paper.
- The most common pore size of a membrane filter is 45 micron.
- Plastic membranes generally do not require pre-conditioning such as washing with water or ethanol.
- Do not heat plastic membranes at elevated temperatures because the filter melts or becomes deformed.
- Glass or paper fiber circles should be pre-washed and dried prior to weighing to remove loose binders and fibers that will dislodge during filtration.
- Types of Whatman™ filters and the type of precipitates they can handle are as follows:

Whatman 41	coarse or gelatinous precipitates
Whatman 50	fine crystalline
Whatman 54	gelatinous or coarse
Whatman 541	fast filtration of gelatinous or coarse

For filter papers by other manufacturers, consult catalogues to find equivalents.

Appendix 9. Some General Rules Concerning Solubility of Common Inorganic Substances in Aqueous Media

1. Nearly all nitrates (NO_3^{1-}) are soluble with the exception of salts of Sr and Ba in fuming nitric acid.
2. All acetates ($\text{C}_3\text{H}_3\text{O}_3^{1-}$) are soluble.
3. All chlorides (Cl^{1-}) are soluble except AgCl , Hg_2Cl_2 , and PbCl_2 (Note: PbCl_2 is soluble in hot water.).
4. All sulfates (SO_4^{2-}) are soluble, except BaSO_4 , SrSO_4 , and PbSO_4 . CaSO_4 and Ag_2SO_4 are slightly soluble and CaSO_4 is more soluble in cold water than hot water.
5. Most of the alkali metals (Group IA: Li, Na, K, Cs, and Fr) salts and ammonium (NH_4^+) are soluble under most conditions. The alkali metals

- K and Cs form insoluble salts with anions such as phosphomolybdate, silicotungstate, and cobaltinitrite.
- All common acids such as HNO_3 are water soluble.
 - All oxides (O^{2-}) and hydroxides (OH^-) are insoluble except those of alkali metals and certain alkaline earth metals (Group IIA: Ca, Sr, Ba, Ra). $\text{Ca}(\text{OH})_2$ is moderately soluble.
 - All sulfides (S^{2-}) are insoluble except those of the alkali metals, alkaline earth metals, and ammonium sulfide.
 - All phosphates (PO_4^{3-}) and carbonates (CO_3^{2-}) are insoluble except those of alkali metals and ammonium salts.

Appendix 10. Periodic Table of the Elements

1																	18	
1 H											13	14	15	16	17	2 He		
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne	
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar	
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr	
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe	
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn	
87 Fr	88 Ra	89 Ac	104 Rf	105 Db (Hs)	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112	113	114	115	116	(117)	(118)	
(119)	(120)	(121)	(154)															
LANTHANIDES		58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu			
ACTINIDES		90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr			
SUPERACTINIDES		(122)	(123)	(124)	(125)	(126)	}									(153)		