

H. R. Verma



Atomic and Nuclear Analytical Methods

XRF, Mössbauer, XPS, NAA and
Ion-Beam Spectroscopic Techniques



Springer

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With 128 Figures and 24 Tables

 Springer

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Dedicated
to
the fond memory of
my dear daughter
GAGANDEEP
who was keen to see this book
in print but lost her life
in a road accident
on Aug. 9, 1997
at the young age of
15 years & 10 months

Preface

Generally speaking, the Nuclear Science Laboratories of the universities and other research institutes support infrastructure for the application of atomic and nuclear measurement techniques to a variety of fields. These laboratories have state-of-the-art equipment for detecting and measuring all sources of α -, β -, and γ -radiation and are equipped with a broad range of detection systems for measuring and analyzing nuclear radiation. Semiconductor, scintillation and gas-filled detectors including Ge(Li), Si(Li), and NaI(Tl) are available with the necessary supporting electronics. A variety of standard α -, β -, X -, and γ -radiation sources are available for calibrating (energy and efficiency) these detectors and performing other studies with radiation detectors. To perform data acquisition and analysis, a network of personal computers complete with multichannel analyzer software, is interfaced to computer-controlled nuclear electronics components. These computers are equipped with commercial software for statistical analysis, spectral unfolding and other data analysis. For undertaking the research activities in these laboratories, the Master level and research students are trained in experimental methods in the field of radiation physics.

The term “Research” describes innovation, which means development with existing technology and for the development of existing technology. While basic research is motivated by curiosity, the applied research is designed to be useful for specific needs. The main research activities in the field of low-energy physics are oriented towards atomic and nuclear physics. Applied research in the field is devoted to the development and implementation of Atomic and Nuclear Analytical Methods such as *X-ray fluorescence spectrometry*, *Mössbauer spectrometry*, *X-ray photoelectron spectroscopy*, *Neutron Activation Analysis* and *accelerator-based Ion beam analysis (IBA) spectroscopy* in various interdisciplinary studies for qualitative and quantitative analysis of various elements in industrial/biological/metallurgical/geological samples. XRF, Mössbauer spectroscopy, and X-ray photoelectron spectroscopy are the table-top techniques, which make use of the radioactive sources while the ion-beam measurements involve the particle accelerators. By accelerating particles to

different energies and smashing them into targets, different phenomena at both the atomic and the nuclear level have been observed. The ion beam analysis is based on the interaction between accelerated charged particles and the bombarded material leading to the emission of particles or radiation whose energy is characteristic of the elements, which constitute the sample material. The spectrometric analysis of this secondary emission may lead to the detection of specific elements as well as the determination of the concentration of these elements and the determination of the nature, thickness, position, or concentration gradient of several layers of elements or compounds.

It is the proud privilege of the author to be primarily associated in teaching and research relating to many of the analytical techniques. It was a long felt desire to provide the material in a unified and comparative form for the students to fulfill the requirement of the course material for extensive studies as well as for researchers engaged in these fields. Keeping this in mind, a comprehensive write-up of X-ray fluorescence (XRF), Mössbauer spectroscopy (MS), X-ray photoelectron spectroscopy (XPS), neutron activation analysis (NAA), particle-induced X-ray emission analysis (PIXE), Rutherford backscattering analysis (RBS), elastic recoil detection (ERD), nuclear reaction analysis (NRA), particle-induced γ -ray emission analysis (PIGE) and Accelerator Mass Spectrometry (AMS) has been presented in this book. I hope that this attempt will yield fruitful results to its readers.

Acknowledgement

I am thankful to my wife Mrs. Baljit K. Verma for her endurance during the time I was awfully busy in not only writing this book but also throughout my research career. Thanks are also due to my sons Nitinder and Deepinder who gave me the moral support and had to bear the loss of my full company during their pleasurable young days.

I am grateful to all the honorable authors and publishers of various books and journals, the works/publications of whom have been consulted during the preparation of this book and referred therein.

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Contents

1	X-ray Fluorescence (XRF) and Particle-Induced X-ray Emission (PIXE)	1
1.1	Introduction	1
1.2	Principle of XRF and PIXE Techniques	2
1.3	Theory and Concept	5
1.3.1	Spectral Series, The Moseley Law	7
1.3.2	Line Intensities and Fluorescence Yield	8
1.3.3	Critical Excitation Energies of the Exciting Radiation/Particles	9
1.4	Instrumentation/Experimentation	12
1.4.1	Modes of Excitation for XRF Analysis	12
1.4.2	X-ray Detection and Analysis in XRF	19
1.4.3	Source of Excitation and X-ray Detection in PIXE Analysis	31
1.4.4	Some Other Aspects Connected with PIXE Analysis	39
1.5	Qualitative and Quantitative Analysis	48
1.6	Thick vs. Thin Samples	50
1.6.1	Formalism for Thin-Target XRF	52
1.6.2	Formalism for Thick-Target XRF	54
1.6.3	Formalism for Thin-Target PIXE	56
1.6.4	Formalism for Thick-Target PIXE	58
1.7	Counting Statistics and Minimum Detection Limit	62
1.8	Sources of Background	64
1.8.1	Contribution of Exciter Source to Signal Background	66
1.8.2	Contribution of Scattering Geometry to Signal Background	67
1.8.3	Contribution of Detection System to Signal Background	67
1.9	Methods for Improving Detection Limits	68
1.10	Computer Analysis of X-Ray Spectra	70

1.11	Some Other Topics Related to PIXE Analysis	71
1.11.1	Depth Profiling of Materials by PIXE	71
1.11.2	Proton Microprobes	72
1.11.3	Theories of X-Ray Emission by Charged Particles	73
1.12	Applications of XRF and PIXE Techniques	76
1.12.1	In Biological Sciences	76
1.12.2	In Criminology	78
1.12.3	In Material Science	78
1.12.4	Pollution Analysis	80
1.12.5	For Archaeological Samples	82
1.12.6	For Chemical Analysis of Samples	85
1.12.7	For Analysis of Mineral Samples	85
1.13	Comparison Between EDXRF and WDXRF Techniques	86
1.13.1	Resolution	86
1.13.2	Simultaneity	86
1.13.3	Spectral Overlaps	86
1.13.4	Background	86
1.13.5	Excitation Efficiency	87
1.14	Comparison Between XRF and PIXE Techniques	87
1.15	Conclusion	90
2	Rutherford Backscattering Spectroscopy	91
2.1	Introduction	91
2.2	Scattering Fundamentals	92
2.2.1	Impact Parameter, Scattering Angle, and Distance of Closest Approach	92
2.2.2	Kinematic Factor	93
2.2.3	Stopping Power, Energy Loss, Range, and Straggling...	95
2.2.4	Energy of Particles Backscattered from Thin and Thick Targets	97
2.2.5	Stopping Cross-Section	99
2.2.6	Rutherford Scattering Cross-Section	99
2.3	Principle of Rutherford Backscattering Spectroscopy	104
2.4	Fundamentals of the RBS Technique and its Characteristics	107
2.5	Deviations from Rutherford Formula	110
2.5.1	Non-Rutherford Cross-Sections	111
2.5.2	Shielded Rutherford Cross-Sections	112
2.6	Instrumentation/Experimental	113
2.6.1	Accelerator, Beam Transport System, and Scattering Chamber	113
2.6.2	Particle Detectors	114
2.7	RBS Spectra from Thin and Thick Layers	119
2.7.1	RBS Spectrum from a Thin Layers	119
2.7.2	RBS Spectrum from Thick Layers	121

2.8	Spectrum Analysis/Simulation	126
2.9	Heavy Ion Backscattering Spectrometry	129
2.10	High-Resolution RBS	131
2.11	Medium Energy Ion Scattering	133
2.12	Channeling	135
2.13	Rutherford Scattering Using Forward Angles	137
2.14	Applications of RBS	139
2.15	Limitation of the RBS Technique	140
3	Elastic Recoil Detection	143
3.1	Introduction	143
3.2	Fundamentals of the ERDA Technique	145
3.2.1	Kinematic Factor	145
3.2.2	Scattering Cross-Sections and Depth Resolution in ERD	147
3.2.3	Stopping Power and Straggling	149
3.3	Principle and Characteristics of ERDA	149
3.4	Experimental	150
3.4.1	ERDA Using E-Detection (Conventional Set-Up)	151
3.4.2	ERDA with Particle Identification and Depth Resolution	155
3.5	Heavy Ion ERDA	170
3.6	Data Analysis	173
3.7	Advantages and Limitations of ERDA	175
4	Mössbauer Spectroscopy (MS)	177
4.1	Introduction	177
4.2	Concept and Theory	178
4.2.1	Nuclear Resonance Fluorescence	178
4.2.2	Nuclear Physics of ^{57}Fe	182
4.2.3	Lamb-Mössbauer Factor (Recoil-Free Fraction)	184
4.2.4	Some Other Mössbauer Isotopes and their γ -Transitions	186
4.2.5	Characteristic Parameters Obtainable Through Mössbauer Spectroscopy	187
4.3	Experimental Set-Up	192
4.3.1	A Basic Mössbauer Spectrometer Set-Up	193
4.3.2	Advances in Experimental Set-Up/Method of Analysis	199
4.4	Evaluation of Mössbauer Spectra	200
4.5	Conversion Electron Mössbauer Spectroscopy	201
4.6	Applications	205
4.6.1	Chemical Analysis	205
4.6.2	Nondestructive Testing and Surface Studies	206
4.6.3	Investigation of New Materials for Industrial Applications	207

XII Contents

4.6.4	Characterization of Nanostructured Materials	209
4.6.5	Testing of Reactor Steel	209
4.6.6	In Mars Exploration	210
4.6.7	Study of Actinides	210
4.6.8	Study of Biological Materials	211
4.6.9	Investigation of Lattice Dynamics Using the Rayleigh Scattering of Mössbauer γ -rays	212
5	X-Ray Photoelectron Spectroscopy	213
5.1	Introduction	213
5.2	Principle and Characteristics of XPS	214
5.3	Instrumentation/Experimental	219
5.3.1	Commonly Used X-ray Sources for XPS Analysis	220
5.3.2	Photoelectron Analyzers/Detectors	224
5.3.3	Experimental Workstation	229
5.3.4	Data Acquisition and Analysis	230
5.4	Principle Photoelectron Lines for a Few Elements	232
5.5	Salient Features of XPS and a Few Practical Examples	232
5.6	Applications of XPS	237
5.6.1	Microanalysis of the Surfaces of Metals and Alloys	237
5.6.2	Study of Mineral Surfaces	238
5.6.3	Study of Polymers	238
5.6.4	Study of Material Used for Medical Purpose	239
5.6.5	For Surface Characterization of Coal Ash	240
5.6.6	Surface Study of Cements and Concretes	240
5.6.7	Study of High Energy Resolution Soft X-rays Core Level Photoemission in the Study of Basic Atomic Physics	240
5.7	Advantages and Limitations of XPS	241
6	Neutron Activation Analysis	243
6.1	Introduction	243
6.2	Principle	244
6.2.1	Prompt vs. Delayed NAA	246
6.2.2	Epithermal and Fast Neutron Activation Analysis	247
6.3	Experimental	247
6.3.1	Neutron Sources	249
6.3.2	A Few Radioisotopes Formed Through (n, γ) Reaction (Used for Elemental Identification) and their Half-Lives	253
6.3.3	Scintillation and Semiconductor γ -Ray Detectors	253
6.3.4	γ -Ray Spectrometer	256
6.4	Quantitative Analysis Using NAA	258
6.4.1	Absolute Method for a Single Element	259
6.4.2	Comparison Method	260
6.4.3	Simulation: MCNP Code	260

6.5	Sensitivities Available by NAA	261
6.6	Applications of NAA	262
6.6.1	In Archaeology	262
6.6.2	In Biochemistry	262
6.6.3	In Ecological Monitoring of Environment	263
6.6.4	In Microanalysis of Biological Materials	263
6.6.5	In Forensic Investigations	264
6.6.6	In Geological Science	264
6.6.7	In Material Science (Detection of Components of Metals, Semiconductors, and Alloys)	265
6.6.8	In Soil Science, Agriculture, and Building Materials ...	266
6.6.9	For Analysis of Food Items and Ayurvedic Medicinal Materials	266
6.6.10	Detection of Explosives, Fissile Materials, and Drugs ...	266
6.7	Advantages and Limitations of NAA	267
6.7.1	Advantages of NAA	267
6.7.2	Limitations of NAA	268
7	Nuclear Reaction Analysis and Particle-Induced Gamma-Ray Emission	269
7.1	Introduction	269
7.2	Principle of NRA	271
7.2.1	Reaction Kinematics for NRA	272
7.2.2	Examples of Some Important Reactions	274
7.3	Particle-Induced γ -Emission Analysis	277
7.4	Experimental Methods	278
7.5	Detection Limit/Sensitivity	282
7.6	Applications of NRA	284
7.6.1	For Material Analysis	284
7.6.2	For Depth Profiling Studies	286
7.6.3	For Tracer Studies and for the Study of Medical Samples	286
7.6.4	For the Study of Archaeological Samples	287
7.7	Applications of PIGE	287
7.7.1	For Material Analysis	287
7.7.2	For the Study of Medical Samples	287
7.7.3	For the Study of Archaeological Sample	288
7.7.4	For the Study of Aerosol Samples	289
7.7.5	For the Study of Soil, Concrete, Rocks, and Geochemical Samples	290
7.8	Common Particle-Particle Nuclear Reactions	291
7.8.1	Proton-Induced Reactions	291
7.8.2	Deuteron-Induced Reactions	292
7.8.3	^3He -, ^4He -Induced Reactions	292
7.8.4	Some Important Reactions Used for NRA Analysis ...	293
7.9	Some Important Reactions Used for PIGE Analysis	293

8	Accelerator Mass Spectrometry (AMS)	295
8.1	Introduction	295
8.2	Principle	297
8.3	Experimental	298
8.4	AMS Using Low-Energy Accelerators	303
8.5	Sample Preparation for AMS	305
8.6	Time-of-Flight Mass Spectrometry (TOF-MS)	306
8.7	Detection Limits of Particles Analyzed by AMS	308
8.8	Applications of AMS	309
8.8.1	In the Field of Archeology	309
8.8.2	In the Field of Earth Science	309
8.8.3	For Study of Pollution	310
8.8.4	In the Field of Biomedicine	311
8.8.5	In the Field of Hydrology	313
8.8.6	In Material Analysis	313
8.8.7	In the Field of Food Chemistry	314
8.8.8	For Study of Nutrients	314
8.8.9	In the Field of Geological Science	315
8.8.10	For Study of Ice-Cores	316
8.9	Use of Various Isotopes for Important AMS Studies	316
8.9.1	Use of ^{10}Be	316
8.9.2	Use of ^{14}C	317
8.9.3	Use of ^{26}Al	317
8.9.4	Use of ^{36}Cl	317
8.9.5	Use of ^{41}Ca	318
8.9.6	Use of ^{59}Ni	318
8.10	AMS of Molecular Ions	318
8.11	Advantages and Limitations of AMS	319
A	Appendix	323
A.1	Some Useful Data Tables	323
B	Appendix	333
B.1	Relation of Energies, Scattering Angles, and Rutherford Scattering Cross-Sections in the Center-of-Mass System and Laboratory System	333
C	Appendix	339
	References	341
	Index	365

X-ray Fluorescence (XRF) and Particle-Induced X-ray Emission (PIXE)

1.1 Introduction

X-ray Fluorescence (XRF) and Particle-Induced X-ray Emission (PIXE) are the two well-established nondestructive analytical techniques of X-ray emission spectroscopy. These techniques are powerful tools for rapid multielement nondestructive analyses and enable simultaneous detection of many elements in a solid or liquid with high-detection sensitivities, even in those cases where only small sample amounts are available. The fluoresced X-rays from the sample are collected and displayed with either energy dispersive or wavelength dispersive detector systems. The elements are identified by the wavelengths (qualitative) of the emitted X-rays while the concentrations of the elements present in the sample are determined by the intensity of those X-rays (quantitative). XRF and PIXE have emerged as efficient and powerful analytical tools for major, minor, and trace elemental analysis in a variety of fields like biology, environment, medicine, archaeology, and forensic science. These techniques can be used for analyzing rocks, metals, ceramics, and other materials. Handling of samples is greatly simplified by the open-air nature of the instrument used for XRF studies. However, operation outside a vacuum chamber has the disadvantage of decreased sensitivity to light elements.

XRF and PIXE techniques are similar in their fundamental approach and are based on the common fact that when an electron is ejected from an inner shell of an atom, an electron from a higher shell drops into this lower shell to fill the hole left behind. This results in the emission of an X-ray photon equal in energy to the energy difference between the two shells. However, the difference between the two techniques is the mechanism by which the inner-shell electron is emitted. The major difference between XRF and PIXE lies in the mode of excitation. In the XRF technique, high-energy X-ray photons are directed at the sample and this ejects the inner shell electrons while in the PIXE technique, the inner-shell electrons are ejected when protons or other charged particles, like He-ions, are made to impinge on the sample. The first Born approximation predicts in general that the excitation produced by different

charged particles should depend only on their charge and velocity, provided that the velocity is large compared to that of the electrons of interest in the target atom. If the velocity is high enough, not only should electrons and protons produce the same excitation but it is also the same as that produced by photons. The other differences between XRF and PIXE, such as excitation characteristics (mechanism of inner-shell excitation, effect of heavier projectiles/charge state effect, production of nondiagram lines, etc.), background distribution, analytical volume, lower limits of detection, and types of samples analyzed are also of importance and will also be discussed in this chapter.

The field of XRF is not only active at the international level but the IAEA is interested to extend the applicability range of the XRF technique, is apparent from the latest research paper by Markowicz et al. (2006) who have elaborated the specific philosophy behind the functioning of the IAEA XRF Laboratory at Seibersdorf Austria and its role in the XRF community including the methodological development and construction of XRF instruments in order to extend the applicability range of the XRF technique, particularly in support of applications of the analytical technique in developing IAEA member states.

1.2 Principle of XRF and PIXE Techniques

The principle of both of these techniques is to excite the atoms of the substance to be analyzed by bombarding the sample with sufficiently energetic X-rays/ γ -rays or charged particles. The ionization (photoionization for XRF and ionization caused due to Coulomb-interaction in case of PIXE) of inner-shell electrons is produced by the photons and charged particles, respectively. When this interaction removes an electron from a specimen's atom, frequently an electron from an outer shell (or orbital) occupies the vacancy. The distribution of electrons in the ionized atom is then out of equilibrium and within an extremely short time ($\sim 10^{-15}$ s) returns to the normal state, by transitions of electrons from outer to inner shells. When an outer-shell electron occupies a vacancy, it must lose a specific amount of energy to occupy the closer shell of more binding energy. This amount is readily predicted by the laws of Quantum Mechanics and usually much of the energy is emitted in the form of X-rays. Each of such electron transfer, for example from the L-shell to the K-shell, represents a loss in the potential energy of the atom. When released as an X-ray photon, the process is X-ray emission. This energy appears as a photon (in this case a $K\alpha$ photon) whose energy is the difference between the binding energies of the filled outer shell and the vacant inner-shell. In the normal process of emission, an inner-shell electron is ejected producing the photoelectron. Similarly, in the ion-atom collisions one or more of the atomic electrons can get free (single or multiple ionization), one or several electrons can be transferred from one collision partner to the other, one or both of the collision partners can become excited, and a combination of these

elementary processes can also take place. The excess energy is taken away by either photons (characteristic X-rays) – when an electron from a higher level falls into the inner-shell vacancy or Auger (higher-shell) electrons – when the energy released during the process of hole being filled by the outer shell electron, is transferred to another higher-shell electron. These emissions have characteristic energies determined fundamentally by the binding energy of the levels. The fraction of radiative (X-ray) decays is called the fluorescence yield, and is high for deep inner-shells. The de-excitation process leading to the emission of characteristic X-rays and Auger electrons is shown in Fig. 1.1. The Auger effect is most common with low-Z elements.

We have seen earlier that an electron from the K shell (or higher shell, if the energy of the impinging radiation (X-rays/ γ -rays) or charged particles is less than the binding energy of the K-shell) is ejected from the atom creating a vacancy in that shell as the projectile pass through the target atom. This vacancy is filled by an electron from the L or M shell. In the process, it emits a characteristic K X-ray unique to this element and in turn, produces a vacancy in the L or M shell. For instance, when exciting the K-shell ($1s_{1/2}$), the hole can be filled from $L_{III}(2p_{3/2})$ or $L_{II}(2p_{1/2})$ subshells, leading to $K\alpha_1$

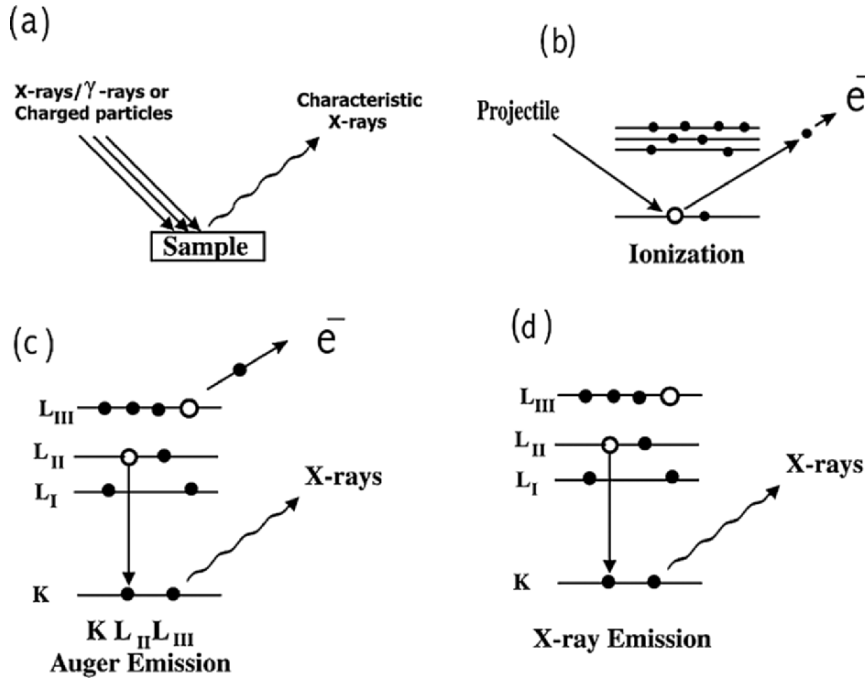


Fig. 1.1. (a) Schematic of the phenomenon of X-ray emission (b) Vacancy creation in the inner shell by X-rays or charged particles (c) process of Auger electron emission comprising of de-excitation and emission of higher-shell electron (d) process of X-ray emission

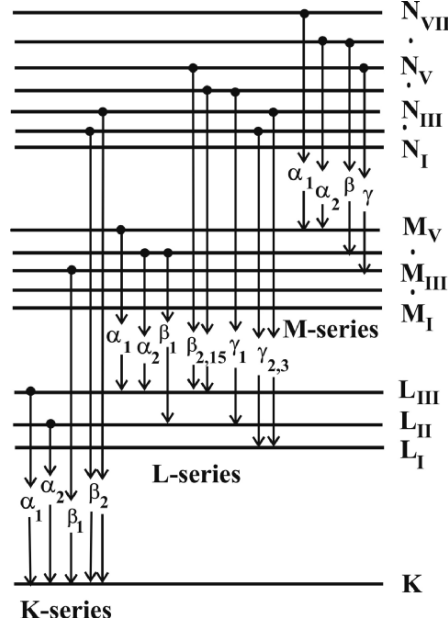


Fig. 1.2. Energy level diagram showing the origin of some of the K, L, and M X-rays

Table 1.1. Designation of various K and L X-ray transitions to denote transitions of electrons

K X-ray Lines	L X-ray Lines	
$K\alpha_1(K-L_{III})$	$L\gamma_1(L_{II}-N_{IV})$	
$K\alpha_2(K-L_{II})$	$L\gamma_2(L_I-N_{II})$	
$K\beta_1(K-M_{III})$	$L\gamma_3(L_I-N_{III})$	
$K\beta_2(K-N_{II,III})$	$L\gamma_4(L_I-O_{III})$	
$K\beta_3(K-M_{II})$	$L\gamma_6(L_{II}-O_{IV})$	

and $K\alpha_2$ lines. Electrons cannot come from the L_1 (i.e. $2s_{1/2}$) sub-shell, because a change in angular momentum is required in the quantum transition. The next shell with electrons is the valence band ($n = 3$) that gives rise to the widely separated and weak $K\beta$ lines. The energy level diagram showing the origin of some of the K, L, and M X-rays is presented in Fig. 1.2.

X-Ray Notation (Siegbahn)

The designation of various K and L X-ray transitions to denote transitions of electrons is given in Table 1.1.

As mentioned earlier, the spectroscopic notation for X-rays will be as:

$$\begin{aligned} L\alpha_1 &\rightarrow 2p_{3/2} - 3d_{5/2} \\ L\beta_1 &\rightarrow 2p_{1/2} - 3d_{3/2} \end{aligned}$$

because the spectroscopic notation for L_I , L_{II} , L_{III} , subshells are $2s_{1/2}$, $2p_{1/2}$, $2p_{3/2}$, respectively, and those for M_I , M_{II} , M_{III} , M_{IV} , and M_V are $3s_{1/2}$, $3p_{1/2}$, $3p_{3/2}$, $3d_{3/2}$, and $3d_{5/2}$, respectively, as explained in Sect. 1.3.

Apart from the characteristic X-ray lines called the diagram lines, non-diagram lines (satellite, hypersatellite and RAE) also appear in the complex K X-ray spectrum. The X-ray lines arising out of the multiply ionized atoms are termed K satellite (KL^n) and K-hypersatellite lines (K^2L^n), where K^mL^n denotes the vacancy from the de-excitation of the double K vacancies and were observed in ion-atom collisions for the first time by Richard et al. (1972). The K satellite lines arise from the group of lines corresponding to the transitions from initial states having one hole in the K-shell and n -holes in the L-shell i.e., $(1s)^{-1}(2p)^{-n} \rightarrow (2p)^{-n-1}$ and represented by $K\alpha L^n$. On the other hand, the hypersatellite X-ray will be due to the $(1s)^{-2} \rightarrow (1s)^{-1}(2p)^{-1}$. The double K vacancies are usually filled by the independent transitions of two electrons accompanied by the emission of two photons or Auger electrons. The $K\alpha$ satellite lines will be represented as $K\alpha(2p)^5$, $K\alpha(2p)^4$, $K\alpha(2p)^3$, ... meaning that 5, 4, 3, ... electrons remain intact in the 2p shell while $K\alpha(2p)^6$ will represent the $K\alpha$ principle line with all the six 2p electrons intact. Similar terminology is also used for $K\beta$ satellite lines. Another category in which electron and photon are simultaneously emitted (known as the Radiative Auger effect RAE lines), comprises of single-photon two electron rearrangement transitions (Verma 2000). In the RAE process, the decay of a K-shell vacancy proceeds as a normal K Auger process except that there is emission of a photon along with an electron in addition to an electron filling the K-shell vacancy. Instead of the initial hole being filled with emission of either a full energy $K\alpha$ photon or a full energy Auger electron, there is simultaneous emission of a lower-energy photon $h\nu$ and excitation of an L-shell/M-shell electron, i.e., $h\nu + E_{\text{kin}}(Y_j) = E(KY_iY_j)$, where Y denotes an L- or M-shell and i and j denote the concerned subshells. Thus $E_{\text{kin}}(Y_j)$ is the kinetic energy of the ejected L_j/M_j -electron and $E(KY_iY_j)$ is the full Auger electron energy. The RAE process competes with the characteristic $K\alpha$ or $K\beta$ X-ray emission processes and produces a broad structure in the X-ray spectra, with energy less than $K\alpha_{1,2}/K\beta_{1,3}$ diagram line.

If the de-excitation takes place during the collision i.e., while the projectile and target electron clouds overlap, “noncharacteristic” molecular orbital (MO) X-ray can be emitted. However, the “characteristic” or separated atom X-rays will be seen if the vacancy de-excites after the collision.

1.3 Theory and Concept

According to the quantum theory, every electron in a given atom moves on in an orbital that is characterized by four quantum numbers:

- *Principal (shell) quantum number (n)* is associated with successive orbitals. The binding energy between the electron and the nucleus is

proportional to $1/n^2$; where n is a positive integer 1, 2, 3, 4, ... that designates the K, L, M, N, ... shells, respectively.

- *Azimuthal (subshell) quantum number (l)* is a measure of the orbital angular momentum which, according to Sommerfeld, accounts for the existence of elliptic and circular electron orbitals; l can take all integral values between 0 and $(n - 1)$; $l = 0$ corresponds to a spherical orbital while $l = 1$ corresponds to a polar orbital. A value of $l = 0$ corresponds to s , $l = 1$ is p , $l = 2$ is d , and so forth.
- *Magnetic quantum number (m)* is responsible for determining the shape of an electron's probability cloud (but does not effect the electron's energy) and can take all the integer values between $-l$ to $+l$, including zero. The magnetic quantum number describes the orbitals within a sublevel. Thus for a given value of l , " m " has $(2l + 1)$ different values.
- *Spin quantum number (s)* can only take two possible values $+1/2$ and $-1/2$. The spin quantum number, allows two electrons of opposite spin (or symmetry) into each orbital.

The number of orbitals in a shell is the square of the principal quantum number (n) i.e., $1^2 = 1$, $2^2 = 4$, and $3^2 = 9$. Furthermore, there is one orbital in an s subshell ($l = 0$), three orbitals in a p subshell ($l = 1$), and five orbitals in a d subshell ($l = 2$). The number of orbitals in a subshell is given by $(2l + 1)$. Since each orbital can accommodate two electrons (one with spin up ($s = +1/2$) and one with spin down ($s = -1/2$) and thus each electron is existing in one of those strange probability clouds, which have widely varying shapes and sizes). The number of electrons in a subshell is given by $2(2l + 1)$. Electronic configuration in an energy state is usually designated by symbols containing a number and a letter containing an index, for example $3d^6$. The number "3" represents the principal quantum number while the letters s, p, d, f, g represent the l values 0, 1, 2, 3, 4, respectively. The index number indicates that there are six electrons in this quantum state. This is because of the reason that there are five different shapes for " d " and hence there is room for ten electrons i.e., $2(2l + 1)$. The numbers of electrons in any given state are controlled by Pauli's exclusion principle according to which no two electrons can have the identical combination of all the four quantum numbers. The electron configuration (say) for ^{17}Cl is $1s^2 2s^2 2p^6 3s^2 3p^5$. The first number represent the energy level, the letters represent the sublevel while the superscripts indicate the number of electrons in the sublevel. The total of the superscripts in an electron configuration equals the atomic number of the element.

The energy levels of different subshells are represented by notation such as $1s_{1/2}$, $2p_{1/2}$, $2p_{3/2}$, ... as shown in Fig. 1.3. States such as $1s_{1/2}$ means $n = 1$, $l = 0$, $j = 1/2$, $2p_{1/2}$ means $n = 2$, $l = 1$ and $j = 1/2$ and $2p_{3/2}$ means $n = 2$, $l = 1$, and $j = 3/2$, where $j = (l \pm s)$. Since the maximum number of electrons in any subshell is given by $(2j + 1)$, therefore the number of electrons in $2p_{1/2}$, $2p_{3/2}$ will be 2 and 4, respectively, making a total of 6 electrons in $2p$ state.

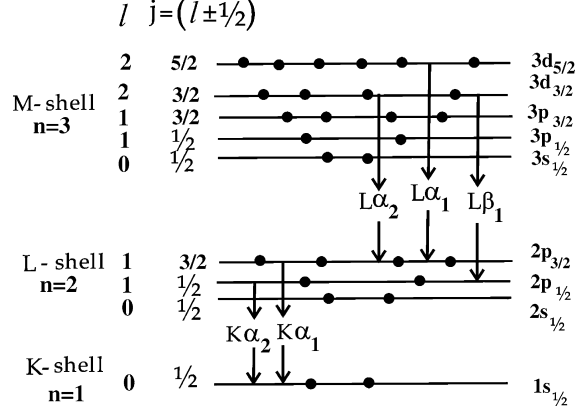


Fig. 1.3. Energy levels of different subshells of an atom along with their quantum numbers and occupancy of electrons

The XRF and PIXE spectra are primarily from transitions that occur after the loss of a $1s$ or $2s$ electron. Transitions that fill in the “ $1s$ ” i.e., K level are of the highest energy, and are called K-lines. $K\alpha_1$ and $K\alpha_2$ lines are from the $n = 2$ level to $n = 1$ level i.e., $K\alpha_1$ originate from $2p_{1/2}$ and $K\alpha_2$ from $2p_{3/2}$ and leave a hole in $2p$ -subshells while $K\beta$ lines leave a hole in the $3p$ shell. In spectroscopic notation:

$$\begin{aligned} K\alpha_1 &\rightarrow 1s_{1/2} - 2p_{3/2} \\ K\alpha_2 &\rightarrow 1s_{1/2} - 2p_{1/2} \end{aligned}$$

The emission of X-rays is governed by the following selection rules for allowed electric dipole (E1) transitions:

$$\Delta n \geq 1, \Delta l = \pm 1, \Delta j = 0, \pm 1 \quad (1.1)$$

Since the spectroscopic notation for L_I, L_{II} , and L_{III} are $2s_{1/2}$, $2p_{1/2}$, and $2p_{3/2}$, respectively, while those for M_I, M_{II} , M_{III} , M_{IV} , and M_V are $3s_{1/2}$, $3p_{1/2}$, $3p_{3/2}$, $3d_{3/2}$, and $3d_{5/2}$, respectively; the spectroscopic notation for some L X-rays lines is given by

$$\begin{aligned} L\alpha_1 &\rightarrow 2p_{3/2} - 3d_{5/2} \\ L\beta_1 &\rightarrow 2p_{1/2} - 3d_{3/2} \end{aligned}$$

The most important of the forbidden transitions are the magnetic dipole (M1) transitions for which $\Delta l = 0$; $\Delta j = 0$ or ± 1 and the electric quadrupole (E2) transitions for which $\Delta l = 0, \pm 2$; $\Delta j = 0, \pm 1$, or ± 2 .

1.3.1 Spectral Series, The Moseley Law

By definition, a spectral series is a group of homologous lines, e.g., the $K\alpha_1$ lines or $L\alpha_1$ lines, etc. of all the elements. In 1913, Moseley established an

experimental relation between the frequency (ν) of X-rays for each spectral series and the atomic number Z of the element from which it was emitted and expressed it as:

$$\nu = Q(Z - \sigma)^2$$

where Q is the proportionality constant and σ is so-called screening constant. The value of Q is $(3R/4) \times c$ for $K\alpha$ and $(5R/36) \times c$ for $L\alpha$ transition. Here c is the velocity of light ($= 3 \times 10^8 \text{ ms}^{-1}$) and R is the Rydberg constant ($= 2\pi^2 me^4/h^3$) which is numerically equal to $1.09737316 \times 10^7 \text{ m}^{-1}$. The energy of different classical circular orbitals is calculated using $E_n = RZ^2h/n^2$ (since $E_n = 2\pi^2 me^4 Z^2/n^2 h^2$), where h ($= 4.136 \times 10^{-15} \text{ eVs}^{-1}$) is the Planck's constant. The energies of $K\alpha$ and $L\alpha$ X-ray lines can be derived from Bohr's theory will thus be given by:

$$E_{K\alpha} = (3/4)(Z - \sigma)^2 E_f; \quad E_{L\alpha} = (5/36)(Z - \sigma)^2 E_f \quad (1.2)$$

where E_f is the ionization energy of hydrogen atom i.e., 13.6 eV.

The X-ray energies of various $K\alpha$ and $L\alpha$ lines increase as a smooth function of the atomic number Z according to the Moseley law $E_x = Z_{\text{eff}}^2 \left(\frac{1}{n^2} - \frac{1}{m^2} \right)$. Here n indicates the lower energy level e.g., 1 for K X-rays, 2 for L X-rays, and so on, while m is the energy level of the higher state e.g., $m = 2, 3, \dots$. These transitions are energetic enough not to get varied much with oxidation state or chemical bonding of the element. These are therefore used as the fingerprints of various elements to which they belong.

1.3.2 Line Intensities and Fluorescence Yield

The intensity of emission of a particular line (say $L\alpha_1$ which is $L_{\text{III}}-M_V$ transition) will depend upon various factors, e.g., (a) the probability that the incident radiation will ionize an atom on the L_{III} level; (b) the probability that the vacant site created on L_{III} will be filled by an M_V electron; and (c) the probability that the $L\alpha_1$ photon will leave the atom without being absorbed within the atom itself (Auger effect).

To calculate the relative intensities of allowed and emitted X-ray lines, we make use of the "sum rule" which states that the total intensity of all lines proceeding from a common initial level or to common final level is proportional to the statistical weight $(2j + 1)$ of that level. For example, the $K\alpha_2 : K\alpha_1 = 1 : 2$ (if these are the only electronic transitions proceeding from the L_{II} i.e., $2p_{1/2}$ and L_{III} i.e., $2p_{3/2}$ subshells) because these transitions are $K \rightarrow L_{\text{II}}$ and $K \rightarrow L_{\text{III}}$, respectively, and the ratio of the line intensities will be the statistical weights of the levels from which the electrons originate i.e., $L_{\text{II}} : L_{\text{III}}$ for which $(2j + 1) = 2 : 4$ i.e., $1 : 2$. The intensity ratio $I(K\alpha_2)/I(K\alpha_1)$ varies from 0.503 to 0.533 for elements from $_{20}\text{Ca}$ to $_{50}\text{Sn}$ while $I(K\beta)/I(K\alpha)$ increases from 0.128 to 0.220 for the above range of elements. The variation in the relative intensities within the L-spectra is more noticeable as given in Table 1.2.

Table 1.2. The variation in the relative intensities of L X-ray transitions

Line →	L α_1	L α_2	L β_1	L β_2	L γ_1	L l
Relative Intensity	100	10	50–100	10–20	5–10	3–6

Fluorescence yield is one of the major factors that determine the intensities of X-ray spectra. For each excited state of an isolated atom, the fluorescence yield is defined as $\omega_x = \Gamma_x / \Gamma_{\text{tot}}$ in terms of the radiative and total transition probabilities “ Γ ” for the particular state (the transition probabilities further depend on the angular momentum quantum number, the number of electrons available for transition as well as the excitation energy). The average fluorescence yield is also determined from $\omega_x^{\text{av}} = \frac{\sigma_x}{\sigma_x + \sigma_A}$ where σ_x and σ_A represent the X-ray and Auger electron cross-sections, respectively.

Thus the fluorescence yield (ω_K) is related to the number of photons emitted in unit time divided by the number of vacancies formed at that time i.e.,

$$\omega_K = \frac{n K\alpha_1 + n K\alpha_2 + n K\beta + \dots}{N_K} \quad (1.3)$$

For L- and M-shells comprising of three and five subshells, respectively, if N excited states are produced with population distribution n_i each having fluorescence yield ω_x^i , then the average fluorescence yield for the distribution is given by $\omega_x^{\text{av}} = N^{-1} \sum_i n_i \omega_x^i$.

Fluorescence yield values increase with atomic number and also differ significantly from one electron shell to another: ω_K is much larger than ω_L and ω_L is much larger than ω_M . The values of ω_K are known with a higher degree of accuracy than the ω_L values (Bambynek et al. 1972) because the former relate to a one-level shell while the latter are weighted averages for the L_I, L_{II}, and L_{III} shells. Experimental results indicate that ω_K increases from 0.0025 to 0.901 for elements ${}_6\text{C}$ to ${}_{56}\text{Ba}$.

1.3.3 Critical Excitation Energies of the Exciting Radiation/Particles

For analysis by XRF technique, the energy of the exciting radiation should be more than the binding energy of the particular shell/subshell (from which the electron has to be knocked out) so that the electron ejection takes place. For example the energy of the incident photon ($h\nu$) should be greater than the binding energy of the K-shell (E_K), called K absorption edge for K α and K β X-ray emission and should be greater than L_I, L_{II}, or L_{III} for L β_3 (L_I-M_{III}), L β_1 (L_{II}-M_{IV}), and L $\alpha_{1,2}$ (L_{III}-M_V, M_{IV}) X-ray emission, respectively.

For analysis by PIXE technique, if the incident projectile of charge “ Z_1 ” and mass “ M_1 ” is moving with velocity “ V_1 ” (and hence energy $E_0 = M_1 V_1^2 / 2$) to eject an inner-shell electron from the target having mass M_2 , the energy transferred in a head-on collision is

$$T_m = \frac{4M_1M_2E_0}{(M_1 + M_2)^2} \approx \frac{4M_1E_0}{M_2} \quad (1.4)$$

Considering that the ejection of the inner-shell electron occurs because of the energy transfer in the collision, the threshold for causing the vacancy due to electron ejection will occur when $T_m = E_K$ (K-shell B.E). Hence $E_0 = (M_2/4M_1) \times E_K = U \times E_K$ where $U = M_2/4M_1$. The experimental results indicate that X-rays are produced at values of U considerably less than this, which indicates that the ionization occurs not by collision with a free electron but by collision with the atom as a whole. Under these circumstances, considerably greater amount of energy can be transferred since the projectile energy is required to be more than the energy of the emitted X-ray for reasons of energy conservation. Since the beam energy is always higher than the limiting value of ~ 100 keV, one can safely say that there is no threshold for X-ray production exists in PIXE analysis. There is a threshold of course, which is related to the molecular overlap of orbitals between the individual atoms (target and incident particle) and the compound atom (target plus incident particle). Merzbacher and Lewis (1958) have set a lower limit of 100 keV for incident particle energy, which allows the inequality $\frac{1}{4\pi\epsilon_0} \times \frac{ze^2}{hv} \ll 1$ to apply.

In the process of X-ray production by electron bombardment however, the electron energy (product of electron charge e and accelerating potential V) must be greater than the binding energy of the shell (i.e., E_K for K X-rays).

The basic concepts regarding ion-energy, ion-current, relative ion velocity, atomic sizes and orbital electron velocities, energy transferred to electrons is discussed in the subsequent sections.

Ion-Energy and Ion-Current

The ion energy depends on the type of accelerator, whether it is single ended or tandem-type. For a single-ended accelerator, $E = qV$ i.e., for 3 MV acceleration voltage, protons will have energy of 3 MeV while Cl^{10+} ions will have energy of 30 MeV. For the Tandem accelerator with accelerating potential of “ V ” MV where we start with the singly charged negative ions from the source, the energy of the ion beam $E = (q + 1)V$.

Since the ion current $I = qe/t$, therefore the ion currents (number of ions/s) $N/t = I/qe$ will be 6×10^6 for 1 pA and 6×10^4 for 100 pA of proton and deuteron beam having $q = 1$. For still heavier ions, the q value will be equal to the charge state of the ions produced in the ion-source due to stripping in the C-foil or Ar-gas. For example for ${}^4\text{He}^{1+}$ and α -particle (${}^4\text{He}^{2+}$), the charge state (q) values are 1 and 2, respectively. Similarly for ${}^{12}\text{C}^{q+}$, the charge state can have any value between 1 and 6 depending on the number of electrons present on the C-ion. In this case, since the atomic number (Z) of carbon atom is equal to 6, the q -value will be equal to 1, 2, 3, ..., 6 if number of intact electrons on the C-ion are 5, 4, 3, ..., 0 and so on.

Relative Ion Velocities

Since the ion velocity $V_1 = 1.384 \times 10^9 \sqrt{(E_0/M_1)} \text{ cm s}^{-1}$

Therefore $(V_1/c) = 0.046 \times \sqrt{(E_0/M_1)}$, where E_0 is in MeV and M_1 is in amu

Thus Relative velocity of 1 MeV protons = 4.6% of velocity of light

Relative velocity of 4 MeV protons = 9.2% of velocity of light

Similarly

Relative velocity of 2 MeV deuterons = 4.6% of velocity of light

Relative velocity of 8 MeV deuterons = 9.2% of velocity of light and

Relative velocity of 4 MeV α -particles = 4.6% of velocity of light

Relative velocity of 16 MeV α -particles = 9.2% of velocity of light

Atomic Sizes and Orbital Electron Velocities

Shell radius $(a_n) = 0.53(n^2/Z)$

Relative velocities of atomic electrons $(v_e/c) = Z/(137n)$, where n is the principal quantum number.

For $_{13}\text{Al}$ K shell $(v_e/c) = 9.5\%$, for $_{20}\text{Ca}$ K shell $(v_e/c) = 14.6\%$

and for $_{30}\text{Zn}$ K-shell electrons $(v_e/c) = 21.9\%$

For $_{82}\text{Pb}$ K shell $(v_e/c) = 59.8\%$, Pb L shell $(v_e/c) = 29.9\%$ and

Pb M shell $(v_e/c) = 20\%$

Maximum cross-sections corresponding to velocity matching demands that the ion velocities from accelerators be comparable with bound electron velocities.

Energy Transferred to Electrons

Since the proton energy $E_p = 0.5 m_p v_p^2$, therefore for protons energy of 1 MeV, energy transferred to electrons $T = 0.5 m_e v_e^2$ comes out to be just 11 keV due to ratios of masses of electrons and the velocities of electrons and protons.

Why Particle Energy in the Range of 1–4 MeV u^{-1} ?

For Protons

We know that E_p should be less than the Coulomb barrier (E_C) is given by:

$$E_C = \frac{Z_1 Z_2}{\left(M_1^{1/3} + M_2^{1/3}\right)} \text{ MeV} \quad (1.5)$$

The velocity matching consideration demand that the maximum ionization cross-sections occur around ion energy (MeV u^{-1}) given by:

$$E_p = 134 U^2 n^4 / Z_2^2 \quad (1.6)$$

For K-shell ionization of $_{15}\text{P}$ ($U = 2.1 \text{ keV}$) $\Rightarrow E_p = 2.4 \text{ MeV u}^{-1}$

For K-shell ionization of $_{20}\text{Ca}$ ($U = 3.7 \text{ keV}$) $\Rightarrow E_p = 4.6 \text{ MeV u}^{-1}$

For Deuterons and α -Particles

With heavy ions, the value of ionization cross-section σ_K, σ_{Li} can be calculated from the corresponding proton values using the Z_1^2 scaling law, e.g.,

$$\sigma_{Li}^{ion}(E) = Z_1^2 R \sigma_{Li}^{ion}(E_1/M_1)$$

Thus

$$\begin{aligned}\sigma_D(E) &= \sigma_p(E/2) \text{ i.e. } 2 \text{ MeV protons} \Rightarrow 4 \text{ MeV deuterons} \\ \sigma_{He}(E) &= 4\sigma_p(E/4) \text{ i.e. } 2 \text{ MeV protons} \Rightarrow 8 \text{ MeV } \alpha\text{-particles}\end{aligned}$$

1.4 Instrumentation/Experimentation

1.4.1 Modes of Excitation for XRF Analysis

X-ray fluorescence spectroscopy can be accomplished using (a) radioactive sources as exciters or (b) X-ray tube as exciter.

Radioactive Sources as Exciters

A radioactive source (preferably monochromatic) can be used as an exciter. The sources of ^{55}Fe , ^{109}Cd and ^{241}Am of a few milliCurie (mCi) activity are used as primary sources. The half-life, X-ray/ γ -ray energies and analysis range of elements are listed in Table 1.3. For more energies however, the secondary exciters using Cu (8.14 keV), Se (11.37 keV), Y (15.2 keV), Mo (17.8 keV), Sn (25.8 keV), Sm (41.0 keV), and Dy (46.9 keV) can be used with Am^{241} as a primary source. X-rays from the primary source are directed at a selectable secondary exciter target, usually Tin (Sn). The

Table 1.3. Various radioisotopes used as excitation sources

Isotope	Half-life	Energy (keV)	Analysis Range
$^{55}\text{Fe}^a$	2.7 yr.	5.9, 6.4	Al to Cr for K X-rays
$^{109}\text{Cd}^b$	470 days	22.16, 24.94 88.03 (γ)	Ti to Ru K X-rays Ta to U for L X-rays
^{241}Am	433 yr.	59.6	Fe to Tm for K X-rays Ta to U for L X-rays

^a ^{55}Fe decays through EC (100%) to the ground state of ^{55}Mn . The excitation X-rays are the lines from ^{55}Mn .

^b ^{109}Cd decays to the 88 keV excited state of ^{109}Ag through EC(100%) which further decays to the ground state of ^{109}Ag through γ -ray emission. Thus, the excitation line is the 88.03 keV γ -transition from ^{109}Ag . Using 88 keV γ -transition of ^{109}Cd , one can excite K X-rays of elements from Ru to Pb. (The 22.16 and 24.94 keV are the $K\alpha$ and $K\beta$ lines from ^{109}Ag .)

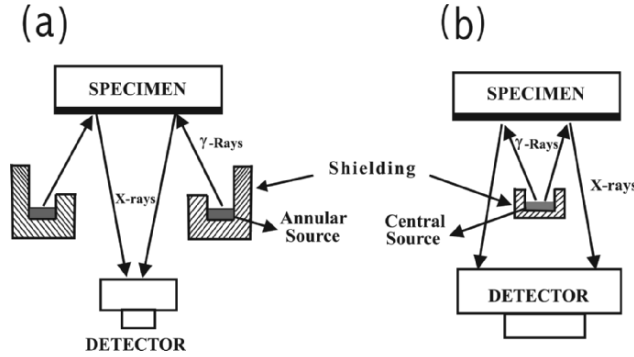


Fig. 1.4. Geometries applied in radioisotope-induced XRF analysis using (a) annular source and (b) central source

characteristic X-rays from that exciter target are aimed at the unknown sample. This causes emission (fluorescence) of characteristic X-rays from the sample. These X-rays from the sample are captured in a Si(Li) detector and analyzed by computer. The energy spectrum of these X-rays can be used to identify the elements found in the sample.

Typical geometries applied in radioisotope-induced XRF analysis (Lal 1998, Bandhu et al. 2000) using annular and central source are shown in Fig. 1.4a, b. A graded shield of copper and aluminum suppresses low-energy photons in the source. Tungsten alloy collimator with Al lining collimates the photon beam from the secondary X-ray exciters of different metals. A tungsten shield covers the source to avoid direct radiation exposure of the detector. There is a tungsten spacer, which defines the secondary fluorescence target cavity when used in secondary excitation mode and acts as a spacer in the direct excitation mode.

Table 1.3 lists various radioisotopes used as excitation sources for XRF analysis. To perform the qualitative and quantitative XRF analysis based on a radioisotope excitation, one should know the relative intensities and the precise energies of the X- or γ -rays emitted by the source. Verma and Pal (1987) have calculated the K and L X-ray emission intensities for some radio nuclides (^{141}Ce , ^{143}Ce , ^{152}Eu , ^{159}Dy , ^{160}Tb , ^{169}Yb , ^{237}U , and ^{239}Np) using the latest data for γ -ray intensities, electron capture, and internal conversion coefficients for the parent nuclides, fluorescence yield values and Coster-Kronig transition probabilities.

The influence of the photons emitted by a ^{241}Am XRF excitation source below 59.6 keV on sample fluorescence production has been analyzed and general method for evaluating the contribution of the various lines from the source in specific equipment configurations is presented by Delgado et al. (1987). A typical L X-ray spectrum of Pb by ^{241}Am source (Kumar et al. 1999) is presented in Fig. 1.5, which also shows the peaks due to elastically- and inelastically-scattered photons from the ^{241}Am source.

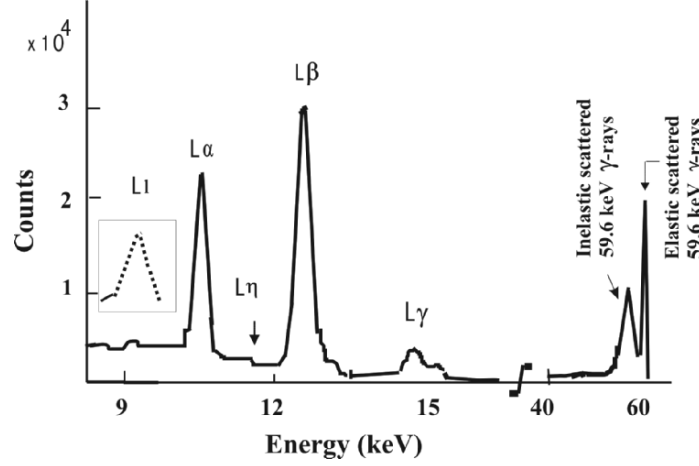


Fig. 1.5. Typical L X-ray spectrum and scattered photons from Pb target by ^{241}Am source

The excitation by X-ray sources requires the knowledge about the values of critical excitation energies of different sources to enable the excitation of inner-shell electrons of various elements present/expected to be present in the sample. Two basic processes i.e., the attenuation and the scattering of X-rays are involved when the intensity is reduced to I_x after the photon beam of intensity I_o passes through the material of thickness x . The reduced intensity is given by Lambert law $I_x = I_o \exp(-\mu x)$, where μ is called the linear attenuation coefficient. The mass attenuation coefficient is further related to the linear attenuation coefficient by $\mu_m = \mu/\rho$ and is the sum of mass photoelectric absorption coefficient (τ) and mass scattering coefficient (σ) expressed in $\text{cm}^2 \text{g}^{-1}$. It means that the fraction of intensity ($I_o - I_x$) that is not transmitted in the same direction as the incident photons is lost mainly as a result of absorption due to photoelectric effect (giving rise to ionization of the atom and emission of X-rays) and the scattering (incoherent/inelastic scattering increasing the wavelength of the incident radiation called Compton scattering or coherent/elastic scattering of unmodified wavelength called Rayleigh scattering). In the low-energy range of photons ($<100 \text{ keV}$), the photoelectric absorption coefficient is almost 95% of the attenuation coefficient μ_m . The significant property of the photoelectric absorption coefficient, for any element, is that it increases rapidly with decreases in energy of the photon, falls off vertically at particular value (called the absorption edge) and then again starts increasing again as shown in Fig. 1.6.

The sharp discontinuities in the absorption curve are related to the critical excitation energies (and their corresponding wavelengths) of the element for the K-shell/ L_I , L_{II} , and L_{III} subshells of the L-shell/ M_I , M_{II} , M_{III} , M_{IV} , and M_V subshells of the M-shell, etc. The K- and L-shell absorption edges for a few elements given in wavelength ($\text{\AA}$) by Bearden (1967), converted in keV,

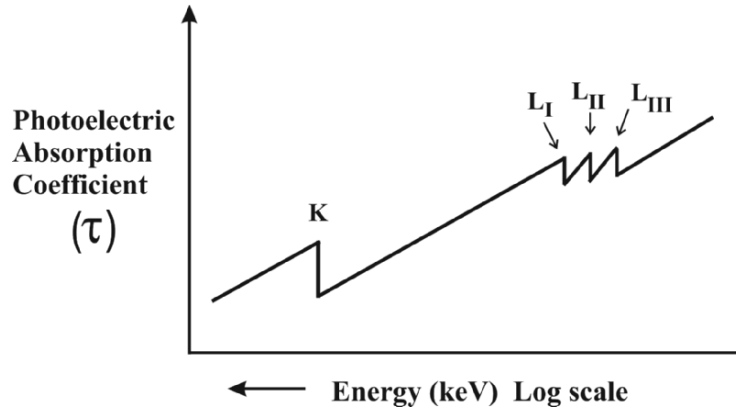


Fig. 1.6. Schematic diagram showing the variation of the photoelectric absorption coefficient as a function of energy for a typical target element

Table 1.4. The K- and L-shell absorption edges for a few elements

Element	Absorption Edge (in keV)			
	K	L _I	L _{II}	L _{III}
¹¹ Na	1.072			
¹³ Al	1.560			
²⁰ Ca	4.040			
²⁹ Cu	8.980		0.953	0.933
³⁴ Se	12.653	1.653	1.475	1.434
³⁹ Y	17.033	2.377	2.154	2.080
⁴⁹ In	27.928	4.238	3.940	3.730
⁶³ Eu	48.627	8.062	7.621	6.982
⁷³ Ta	67.391	11.687	11.131	9.880
⁷⁹ Au	80.519	14.352	13.732	11.923

are presented in Table 1.4. For example, for ⁷³Ta, the K absorption edge is at 67.391 keV while the L_{III}, L_{II}, and L_I absorption edges are at 9.880, 11.131, and 11.687 keV, respectively, which means that at 9.880 keV, the critical value for excitation of the L_{III} energy level is reached and ionization at this level is now possible, the sharp increase in absorption that results is called the L_{III} absorption edge. The K absorption edge at 67.391 keV indicates that at energies higher than this, the absorption decreases to very low values.

To detect the X-rays emerging from the sample, a solid state Si(Li) detector, cooled to liquid nitrogen temperature, is used to detect the characteristic X-rays. The detector has a resolution of about 160 eV at 5.9 keV. The pulses from the detector are processed by a shaping amplifier and converted into pulse height by the analog-to-digital converter (ADC) of the multichannel analyzer (MCA).

X-ray Tube as Exciter

X-ray tubes offer greater analytical flexibility at a cost of more complexity. Main features of X-ray tube are as given in Table 1.5.

The considerations for the applied Voltage are as follows:

1. At 50 kV, all K-lines up to $Z = 63$ (Eu) are excited.
2. At 100 kV, all K-lines up to $Z = 87$ (Fr) are excited.
3. 100 kV will excite all K-lines more efficiently than 50 kV, but there are no dispersive crystals available to diffract the lines at a reasonable angle and the background increases so that the line/background remains essentially the same.
4. The intensity of the characteristic X-ray lines of the target of the X-ray tube (overriding the background continuum) are given by $I = A C(V - V_K)^n$, where A is constant, C is the current, V is the applied voltage which must be equal to the critical voltage V_K (in the case of K-lines) and the exponent is a constant that has a value between 1.5 and 2 depending on the emission line. The rapid increase in intensity predicted by the earlier equation does not materialize when V exceeds three or four times the critical voltage V_K or V_L .
5. The short wavelength limit is given by λ_0 i.e., the spectrum starts abruptly at a wavelength that does not depend on the target material but follows the relation.

$$\lambda_0(\text{in } \text{\AA}) = \frac{12.39813}{V(\text{in kV})} \quad (1.7)$$

Further, the shorter wavelength limit λ_0 varies as the reciprocal of the applied voltage.

Excitation by the characteristic tube lines may be accomplished by having several different target tubes (^{24}Cr , ^{29}Cu , ^{42}Mo , ^{45}Rh , ^{74}W , ^{78}Pt or the dual target W/Cr) in any of the desired energy ranges. Mo has advantage for K-lines of ^{32}Ge to ^{41}Nb and L-lines from ^{76}Os and up while Cr is best target for K-lines from ^{23}V down and L-lines from ^{58}Ce down. By anode selection, the operator is able to enhance the K lines of Molybdenum (~ 17 keV), the L lines of tungsten (~ 8 and 10 keV) or the L lines of Molybdenum (~ 2.3 keV). By using these lines, especially with a proper filter in between tube and sample, the operator is able to excite fluorescence. Characteristic tube excitation can be used in conjunction with a filter of the target material to reduce the

Table 1.5. Main features of an X-ray Tube

Tube voltage	10–100 kV in steps of 5 kV
Tube current	0–100 mA in steps of 1 mA
Vacuum Pump	Diffusion-Rotary pump
Operating pressure	$\approx 10^{-6}$ Torr
Water flow rate	≈ 4 litre/min

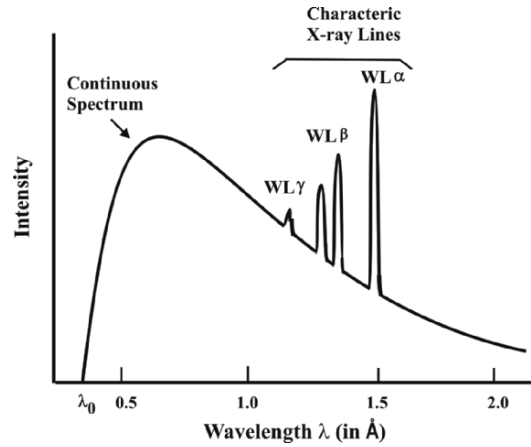


Fig. 1.7. Typical emission spectrum from a $_{74}\text{W}$ target X-ray tube

background. A typical emission spectrum from a $_{74}\text{W}$ target X-ray tube is shown in Fig. 1.7.

The continuum or Bremsstrahlung radiation from high atomic number target elements of the tube, which extends to the highest energy of the electron beam, may also be used for excitation. For example the elements up to curium ($\text{K}\alpha \sim 40 \text{ keV}$) may be fluoresced using the Bremsstrahlung spectrum and W-target. Both of these give high background. One can find the shortest wavelength λ_0 (highest energy) photon that can be emitted, which corresponds to the incident electron losing all of its kinetic energy in a single collision. For a 35 kV accelerating voltage, the shortest wavelength X-ray that can be emitted is about 0.035 nm. Thus, the continuous part of the X-ray spectrum spans the range from λ_0 to infinitely long wavelengths. The continuous spectrum is used for X-ray diffraction experiments (where X-rays are diffracted by cubic crystals to determine their orientation in space). By changing the target material of the X-ray tube, the effect caused on the continuous X-ray spectrum can be elaborated with reference to Fig. 1.7. The continuous part of the X-ray spectrum varies in intensity with wavelength (equivalent with photon energy $E = hc/\lambda$). There is a broad intensity peak for wavelength near 0.4 Å (0.04 nm), which is somewhat smaller than the spacing of atoms in crystalline solids. The photons with longer wavelengths (lower photon energy) are emitted, although the intensity is not as great as that produced at shorter wavelengths.

Characteristic X-rays are usually used in diffraction experiments where the sample has many different crystal orientations, such as in a polycrystalline or powder sample, as well as for single crystal structure determination. The $\text{K}\alpha$ characteristic line is preferred for use in such experiments since it has the highest intensity. To filter the output of an X-ray tube with the purpose of selecting the prominent line of the target X-ray of the tube, the filter is

chosen with an absorption edge between the two peaks to cause preferential absorption of the peak with shorter wavelength. For example, one mil (0.001") thick brass foil plus a 1 mil nickel foil can be used over the window of the tungsten X-ray tube. The copper and zinc content in the brass causes high absorption of $L\beta$ and $L\gamma$ tungsten lines, while nickel causes high absorption of the $L\alpha$ tungsten lines.

Wide ranges of X-ray tubes are available with side or end windows. Latest developments in tube technology are the introduction of the dual-anode tubes. In a dual anode tube, a layer of chromium is deposited on a gold substrate or scandium on a molybdenum substrate. At low power the tube behaves like a conventional chromium or scandium tube, but at higher voltages, the radiation from the underlying anode materials is produced to give more excitation of the heavy elements. This enables a single X-ray source to be used over a broad atomic range or in other words excitation can be optimized for general purpose working or for more specialized tasks. The direct optical position sensor (DOPS) goniometer provides remarkable accuracy and reads the θ and 2θ positions from finely etched grating disks which are fitted onto the goniometer axes.

An alternative geometrical set-up known as triaxial geometry (Bandhu et al. 2000) consists of an X-ray tube to fluoresce a selectable secondary target such as Ti, Ag, Ba and to reduce the backscattered radiation is as shown in Fig. 1.8.

The energy of the characteristic X-ray lines produced will be less than the energy of the exciter X-rays. Hence the selection of the target for the X-ray tube is very important. The choice of exciter will depend on the absorption edges of the elements (Table 1.4) present in the sample. Characteristic X-ray production is most efficient when the excitation energy is just above the absorption edge of the particular element of interest. There is a possibility for the variation of voltage (kV) and current (mA) applied to the X-ray tube. The kV and mA settings determine the efficiency with which the X-ray lines are excited in the tube and thus in the sample. The X-ray intensity increases

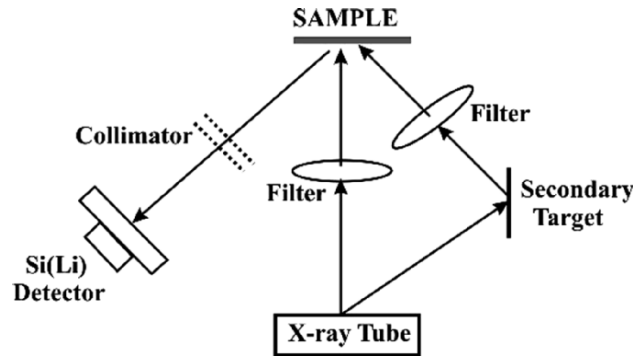


Fig. 1.8. The energy dispersive X-ray fluorescence set-up with triaxial geometry

when either the anode voltage or the emission current is increased. However, the characteristic X-ray lines get broadened as the anode voltage is increased.

If the absorption of characteristic radiation in target material itself is accounted, then the intensity of characteristic radiation depends on the anode voltage as $I \propto (V - V_K)^{1.65}$ where V is the applied high voltage and V_K is the K absorption edge expressed in volts (8.98 kV for Cu). As the anode voltage is increased, the Bremsstrahlung radiation spreads toward high energy side and its intensity follows the quadratic relationship of high voltage so that it goes on increasing as anode voltage increases. Besides this, the intensity of characteristic radiation gets saturated after some value of anode voltage. This behavior is manifestation of self-absorption effect in target material. It is known that for $V > V_K$, the electron penetration depth in the target becomes large compared to the maximum depth from which the characteristic X-rays can come out.

X-ray tubes usually have a power output of 3 kW and may be either a side window or end-window type. The low-power X-ray tube could be used for EDXRF while power of the tube for WDXRF is 3–4 kW. Direct excitation using a high-power X-ray tube and EDXRF allow to reach detection limits in the parts per billion or picogram range.

1.4.2 X-ray Detection and Analysis in XRF

The X-rays detection and analysis is usually carried out in two modes:

- *Wavelength dispersive X-ray spectroscopy (WDS)* uses the reflection of X-rays off of a crystal at a characteristic angle to detect X-rays of specific wavelength.
- *Energy dispersive X-ray spectroscopy (EDS)* works on the principle of separating and detecting X-rays of specific *energy* and displays them as histograms. Imaging of elements is also possible using this capability.

Wavelength Dispersive (WD) X-ray Spectrometry

Wavelength dispersive X-ray fluorescence relies on a diffractive device such as a crystal, to isolate the peak corresponding to an analytical line since the diffracted wavelength is much more intense than other wavelengths that scatter of the device. The excitation in WDXRF is carried by X-ray tube. The detection and measurement of intensity is based on the principle of X-ray diffraction i.e., the characteristic X-rays of each element have a distinct wavelength, and by adjusting the tilt of the crystal (which will select and diffract only a small fraction of the incoming X-rays at each angle θ) in the spectrometer, at a specific angle it will diffract the wavelength of specific element's X-rays. Diffraction obeys the Bragg equation

$$n\lambda = 2d \sin \theta \quad (1.8)$$

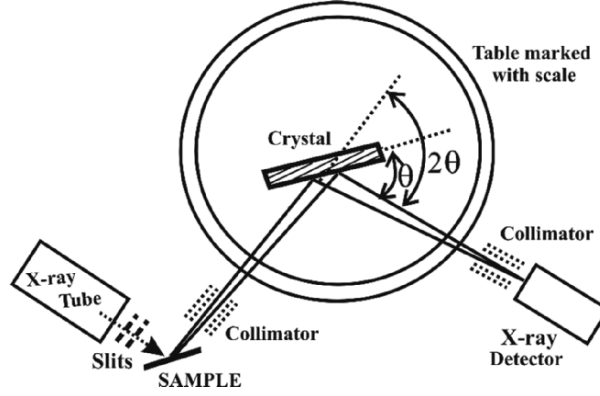


Fig. 1.9. Principle and Schematic of WDXRF spectrometry

where λ is the wavelength of the X-ray line, $2d$ is the lattice spacing, and θ is the angle of diffraction. The wavelength λ may be converted to energy using the formula:

$$E(\text{in keV}) = \frac{12.398}{\lambda}(\text{in } \text{\AA}) \quad (1.9)$$

The system used in conventional wavelength dispersive spectrometry generally consists of an X-ray tube, an analyzing crystal, and detector (scintillation or gas flow proportional counter) as shown in Fig. 1.9.

The diffracted beam will pass through a 0.02° receiving slit and then into a scintillation detector (for medium to high-energy X-rays) or gas flow proportional detector with a specially prepared thin polyester film window (for medium to low-energy X-rays). The gas-flow proportional counting tube has a tin wire running down its middle, at 1–2 kV potential. The X-rays are absorbed by gas molecules (e.g., P10: 90% Ar, 10% CH₄) in the tube, with photoelectrons ejected; which in turn produce a secondary cascade of interactions, yielding an amplification of the signal ($\times 10^3$ – 10^5) so that it can be handled by the electronics. This signal is sent simultaneously to a rate meter and a strip chart recorder. The output on the strip chart is given in “Intensity vs. 2θ ”, where θ is the angle of diffraction. Improvement in the whole electronic counting chain, including the pulse height selector have increased the count rate capability $\sim 10^6$ cps with accuracy and linearity of better than 1%. The angle corresponding to any wavelength can be calculated using the relation $\theta = \sin^{-1}(n\lambda/2d)$ where n is the order of diffraction. Corresponding to the wavelength of X-ray lines, $2d$ value of the crystal and the order of diffraction, the detection range (θ -values) can be calculated. Different diffracting crystals, with $2d$ (lattice spacing) varying from 2.5 to 100 Å, are used to be able to “reach” the different wavelengths of various elements. In recent years, the development of “layered synthetic crystals” of large $2d$ has lead to the ability to analyze the lower Z elements (Be, B, C, N, O), although inherent limitations in the physics of the process (e.g., large loss of signal by absorption

Table 1.6. Common dispersing crystals and their characteristics

Crystal ^a /Plane	$2d$ (Å)	Detection Range/Lowest- Z Detection	
		for K X-rays	for L X-rays
LiF (220)	2.848	^{23}V	^{58}Ce
LiF (200)	4.028	^{19}K	^{49}In
NaCl (200)	5.639		
Calcite (103)	6.071		
Si (111)	6.276	^{15}P	^{40}Zr
Ge (111)	6.533	^{15}P	^{40}Zr
Quartz (1011)	6.686		
ADP (1011)	7.498		
EDDT (020)	8.742	^{13}Al	^{35}Br
PET (022)	8.808	^{13}Al	^{35}Br
ADP (101)	10.648		
Mica (002)	19.949		
TAP (1011)	25.763	^8O	^{23}V
RAP (010)	26.115		
KAP (1010)	26.632		

^aADP $\Rightarrow$ Ammonium di-hydrogen Phosphate, KAP $\Rightarrow$ Potassium Acid Phthalate, TAP $\Rightarrow$ Thallium Acid Phosphate, EDDT $\Rightarrow$ Ethyl di-amide D-Tartrate ($\text{C}_6\text{H}_{14}\text{N}_2\text{O}_6$), PET $\Rightarrow$ Penta Erythritol, RAP $\Rightarrow$ Rubidium Acid Phthalate.

in the sample) limit the applications. Table 1.6 later lists the names of a few analyzing crystals along with their $2d$ values and detection range.

A collimator is positioned at sample changer port between the crystal and detector to restrict the angles that are allowed to strike the diffraction device. Sollar slit and similar types of collimators are thus used to prevent beam divergence. It intercepts divergent secondary radiation from sample so that a parallel beam arrives at crystal and at detector window. The effect of increased collimation improves effective resolution and decreases background. However, it also decreases the line intensity. The path of X-rays could be either through air or vacuum. Air is suitable for K-lines of ^{26}Fe and above and L-lines of ^{72}Hf and above while vacuum can help to detect elements even for low- Z elements like ^{12}Mg .

As an example, let the specimen at the center of the goniometer be a single crystal of LiF with (200) planes parallel to the large face. The crystal is bombarded by all X-rays, continuous and characteristic, which are emitted from the X-ray tube. However, it passes on, or diffracts, only that wavelength which satisfies Bragg's law. Thus, at $2\theta = 40^\circ$ for example (i.e. $\sin\theta = 0.342$) and with $2d = 4.028 \text{ Å} = 0.4028 \text{ nm}$, those X-rays diffracted to the counter have a wavelength $\lambda(2\theta = 40^\circ) = 0.1378 \text{ nm}$.

The wavelength dispersive spectrometry has an overall low efficiency owing to several intensity losses through the restriction on solid angles and the low "reflectivity" of the analyzing crystal. Furthermore, the qualitative method of

unknown materials by WDXRF is often a slow process, implying a series of scans with several analyzing crystals to cover the whole X-ray spectrum and their interpretations.

Soft X-rays ($E < 1 \text{ keV}$) are rapidly absorbed by matter and have escape depths from a solid surface only a few μm corresponding to approximately the top thousand atomic layers of a sample. Therefore changes in peak profile, satellite peaks, etc., which are informative of chemical effects, can be used to infer chemical changes in sample surfaces. Since the air attenuation of X-ray becomes quite significant at low energies, the entire sample chamber is placed in vacuum.

The flat crystal spectrometer consists of a crystal mount located at the center of a turntable on which the detector rides. A precision stepping motor drives gear train, which causes the rotation of the crystal mount through the Bragg angle θ° ($\sim 0.01^\circ/\text{step}$) while at the same time the turntable rotates through angle $2\theta^\circ$. In this way when the crystal reflects at angle θ° , the detector is maintained in the correct position (at angle $2\theta^\circ$) to observe X-ray, which satisfies the Bragg equation (1.7). The energy resolution of the spectrometer can be estimated from the relation

$$\Delta E = (dE/d\theta) \Delta\theta = E \cot \theta \Delta\theta \quad (1.10)$$

where E is the X-ray energy and $\Delta\theta$ is the angular divergence of the X-rays incident on the Bragg crystal. The best energy resolution is obtained with a crystal having a $2d$ -spacing only slightly greater than the wavelength of interest. For a flat crystal spectrometer the angular divergence is primarily determined by a set of entrance parallel plate collimators (sollar slits). Similar set of soller slits in front of the detector can be used to reduce background due to scattered X-rays and electrons.

Detection of the reflected X-rays is accompanied by means of either a gas flow proportional counter or a NaI (Tl) scintillation detector. Since the energy resolution of the crystal spectrometer $\approx 1\text{--}2 \text{ eV}$, it not only distinguishes the $K\alpha_1$, $K\alpha_2$, $K\beta_1$, and $K\beta_2$ diagram lines clearly but is also able to yield information about the nondiagram lines (satellite and hypersatellite lines) in the complex K X-ray spectrum. The $K\alpha$ satellite lines will be represented as $K\alpha(2p)^5$, $K\alpha(2p)^4$, $K\alpha(2p)^3, \dots$ meaning that 5, 4, 3, $\dots$ electrons remain intact in the 2p shell while $K\alpha(2p)^6$ will represent the $K\alpha$ principle line with all the six 2p electrons intact. Similar terminology is also used for $K\beta$ satellite lines. The K hypersatellite lines result from the de-excitation of the double K vacancies. Another category comprises of single-photon two-electron rearrangement transitions, known as the Radiative Auger Effect (RAE) lines.

Figure 1.10 shows the photon-induced K X-ray spectrum of Zn recorded with a crystal spectrometer, which clearly shows the satellite, hypersatellite, and the RAE (Radiative Auger Effect – A broad weak X-ray emission structure with several maxima on the low-energy side of the characteristic X-ray lines which has been interpreted as a radiative $K \rightarrow L^2$ transition resulting in the simultaneous emission of a photon and an L-shell electron. Radiative

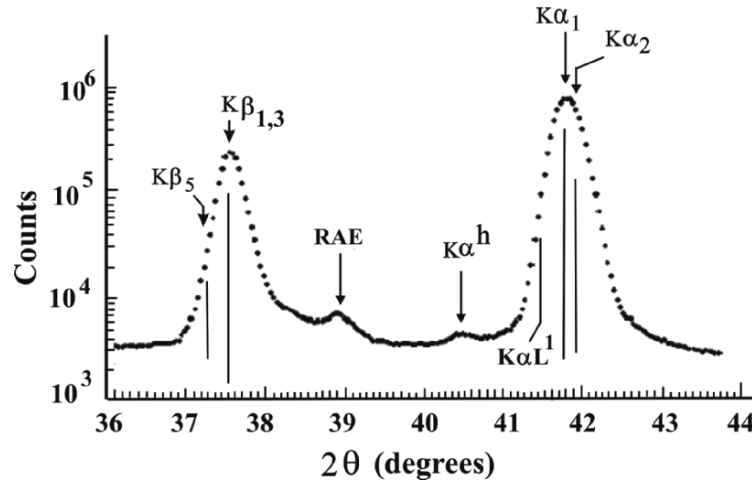


Fig. 1.10. Zn K X-ray spectrum excited by X-ray tube and recorded by a flat crystal spectrometer

Auger process is an intrinsic energy-loss process in an atom when a characteristic X-ray photon is emitted due to an atomic many-body effects) apart from the diagram lines $K\alpha_1$, $K\alpha_2$, $K\beta_1$, and $K\beta_2$ (Verma 2000).

Wavelength dispersive X-ray spectroscopy (WDS) may extend the threshold of detection by at least an order of magnitude as compared to the energy dispersive X-ray spectroscopy. Since the L X-ray spectra produced by heavier ions displays more complicated structure due to multiple vacancy production (Kageyama et al. 1996), WDS is must for analysis of such complex spectra. However, WDS requires optically flat, stable specimens and is limited to bulk analysis modes, limiting spatial resolution to more than $0.5\mu\text{m}$.

Energy Dispersive X-Ray Fluorescence

Figure 1.11 shows a schematic view of an energy dispersive XRF spectrometer. The basic components of an EDXRF spectrometer are X-ray source, sample, and the detector. Several devices such as source filters, secondary targets, collimators, and focussing optics are used to modify the shape or intensity of the source spectrum or the X-ray beam shape. Collimators (usually circular or a slit whose sizes range from approximately 10 microns to several millimeters) are used between the excitation source (X-ray tube or radioactive source) and the sample to restrict the size or shape of the source beam for exciting small areas. Filters (between the X-ray source and the sample or between sample and the detector) perform one of two functions: background reduction and improved fluorescence. The filter absorbs the low-energy X-rays (below the absorption edge energy of the filter element) while higher energy X-rays are transmitted. The advances in instrumentation/geometry for EDXRF has been

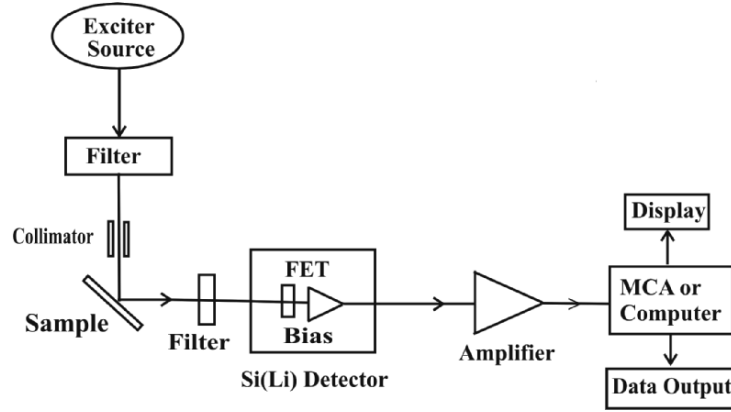


Fig. 1.11. Schematic view of a Si(Li) EDXRF spectrometer

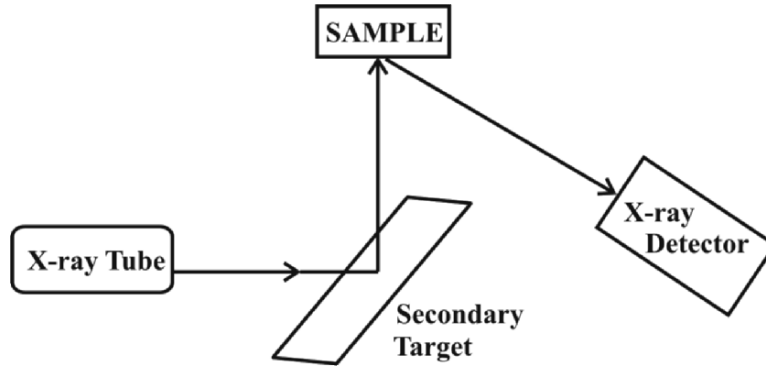


Fig. 1.12. Secondary source for X-ray fluorescence

discussed by a number of workers (Bisgård et al. 1981, Lal et al. 1987, Krishnan 1998, Bandhu et al. 2000, Romano et al. 2005).

To obtain a more monochromatic source peak with lower background than with filters, secondary sources are used. A secondary source can be produced by placing a target element between the X-ray tube and the sample, as shown in Fig. 1.12. The X-ray tube excites the secondary target and the Secondary target fluoresces and excites the sample. The detector as usual detects the X-rays from the sample. Because simple collimation blocks unwanted X-rays, it happens to be a highly inefficient method. Focusing optics like polycapillary devices (used in microbeam XRF) have been developed so that the beam could be redirected and focused on a small spot (less than 100 μm spot size).

The single crystal semiconductor Si(Li) X-ray detector known as semiconductor X-ray detector sorts the X-rays directly on the basis of their energy. X-rays enters the detector and ionize the silicon atoms producing electron-hole pairs in the deep intrinsic layer. An applied voltage ($\approx 750\text{ V}$) across the

crystal collects these electron-hole pairs. Since each ionization takes 3.81 eV of energy from the X-ray, the total (e-h) pair collected is:

$$Q = (E/3.81) \times 1.6 \times 10^{-10} \text{ Coulomb} \quad (1.11)$$

which is linearly proportional to E , the energy of the incident X-rays. This charge is integrated into a current pulse by a field effect transistor (FET) preamplifier and is subsequently amplified and converted to a voltage pulse. The original problem in fabricating semiconductor detectors was the insufficient thickness of the depletion zone. To obtain thickness greater than a few millimeters required very high resistivity, which could only be obtained with intrinsic materials. This problem of fabricating semiconductor detectors with depletion zone greater than a few millimeters was overcome by compensating the semiconductor material. The Si(Li) detector is basically a small crystal of silicon (Si), especially processed by lithium (Li) ions through the lattice to compensate for electrical impurities (p-type silicon is the starting material). When the Li-drifted crystal is provided with evaporated electrodes and cooled to liquid nitrogen temperature, it forms a low-leakage sensitive volume, which can be ionized by incident radiation. The high mobility and the low ionization energy (0.33 eV in Si) of *Li* impurity is primarily responsible for its choice as a compensator for p-type material in the preparation of NIP diode. Since *Li* is ionized at room temperature and has a small ionic radius (0.6 Å) compared to the lattice dimension of Si (5.42 Å), it is easily drifted through the lattice as an interstitial ion by the application of electric field.

The Si(Li) detector is enclosed in its own vacuum, isolated from the specimen chamber with a detector window, and maintained at liquid nitrogen temperatures with a cold finger and liquid nitrogen dewar (in order to decrease the number of electrons in the conduction band produced by thermal agitation, and thereby reduce “electronic noise”; decrease the noise from the FET-preamplifier; and prevent the diffusion of Li^+ which would be rapid at room temperature under the influence of the high potential across the crystal). The crystal itself is quite small – typically a wafer with an area of approximately 10 mm^2 and a thickness of 1 mm, since the X-rays have to pass through three layers before given the opportunity to generate its pulse within the intrinsic region of the detector. If the X-ray is not absorbed by the specimen, it may be absorbed by the detector window, which is typically 5–10 μm of beryllium or aluminum coated polypropylene. It might also be absorbed by the 200 Å gold conductive layer or the 1,000 Å dead layer on the detector surface. The gold is a component of the HV sandwich, and the *dead layer* is an inactive layer within the crystal, the thickness of which is attributable to the manufacturing procedure used to make the detector intrinsic and, to some degree, also attributable to the given detector and its age.

The overall efficiency of this system is much better than the WDXRF because of less restrictive solid angle losses and the diffraction losses. Although there is only a little absorption of low energy X-rays (since Z is so low for Be), the performance of the Si(Li) detector is limited at the low energy end

by absorption due to Beryllium window. Beryllium (Be) window is used since Be thin windows can be fabricated to be vacuum tight. This imposes a limit to $_{11}\text{Na}$ or $_9\text{F}$ as the lightest analyzable element with Be-window of 1 or 0.3 mil (1 mil = 0.001"). Windowless Si(Li) detector have been used to measure spectral peaks down to carbon but because the detector must be kept free from contamination, the use of windowless detectors can not be allowed under all conditions. The typical energy resolution for Si(Li) detector is ~ 160 eV for 5.9 keV X-rays. When a Si(Li) detector is used to collect X-ray photons with energies below 2 keV, the characteristic peaks in the spectrum show significant spectral distortion i.e., deviation from the ideal Gaussian shape observed for higher energy photons. This effect is due to incomplete collection of the charge deposited by the incident photon in the diode and can be as high as 30% for a line such as $\text{N K}\alpha$ at 400 eV.

The efficiency calibration of a Si(Li) detector at very low X-ray energies (below 3.3 keV) presents serious problems owing to a lack of practical radioactive standards in this energy region and to the discontinuity in the efficiency response caused by the K-absorption edge of silicon (at 1.84 keV). The solution lies in making theoretical efficiency calculations based on the detector parameters or measuring the efficiency by alternate experiment using secondary excitations from low- Z elements (Mg, Al, Si, etc.) taking the primary exciter as proton beam or radioactive source of known activity. While the secondary fluorescence method, for calculation of the efficiency of the detector, requires the precise X-ray production cross-section values for different target elements at the energy of bombardment, the theoretical calculations for efficiency values of the detector, at various energies, can be done according to the relation

$$\varepsilon(E) = \frac{\Omega}{4\pi} T(E) \times A(E) (1 - P_{\text{esc}}(E)) \quad (1.12)$$

where Ω is the solid angle subtended by the source on the detector and can be calculated using A/r^2 , where A is the active surface area of the Si(Li) detector and r is the distance of the detector from the X-ray source. In (1.12), P_{esc} is the escape probability while $T(E)$ and $A(E)$ are transmission factor and absorption factors, respectively, given by:

$$\begin{aligned} T(E) &= \exp(-\mu_{\text{Be}}(E) \times x_{\text{Be}} - \mu_{\text{Au}}(E) \times x_{\text{Au}} - \mu_{\text{Si}}(E) \times x_{\text{Si}}^d) \\ A(E) &= 1 - \exp(-\mu_{\text{Si}}(E) \times x_{\text{Si}}^s) \end{aligned} \quad (1.13)$$

The transmission factor $T(E)$ includes the transmission of photons through the Be-window of thickness x_{Be} , gold contact layer of thickness x_{Au} , Si dead-layer of thickness x_{Si}^d , and Si detector sensitive volume of thickness x_{Si}^s , respectively, while $A(E)$ is the absorption factor in the detector sensitive volume. The absorption coefficients are obtained from XCOM computer code (Berger and Hubbel 1987). The experimental efficiency curve for a Si(Li) detector using different radioactive sources along with one based on the theoretical calculations is shown in Fig. 1.13. Inset in the figure shows the efficiency below 3 keV

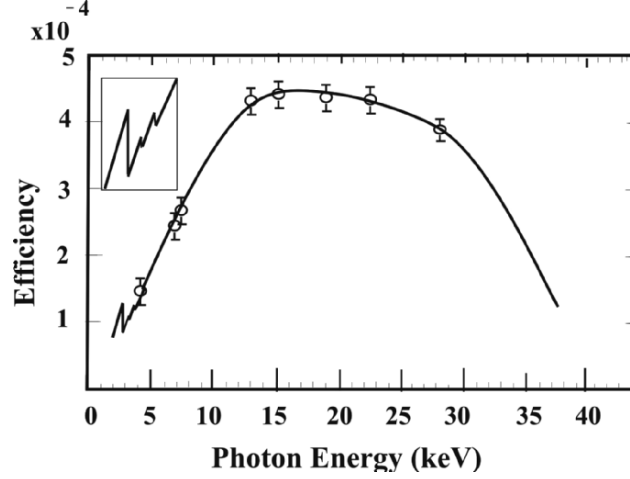


Fig. 1.13. Plot of the experimental (absolute) efficiency curve as a function of photon energy (keV) using ^{55}Fe , ^{57}Co , and ^{241}Am radioactive sources along with one based on the theoretical calculations. Inset shows the efficiency below 3 keV energy (on log energy scale)

energy (on log energy scale for better viewing). A sharp drop at 1.836 keV is due to the K-absorption edge of Si-dead layer and the jumps at the location of the Au M X-ray energies are due to the thin Au contact layer on the front of the diode. The efficiency drops at lower and higher energies are mainly due to the Be-window and Si-sensitive volume of the detector causing absorption of low-energy and high-energy X-rays, respectively, since the absorption and transmission processes are a function of energy due to dependence of absorption coefficient $\mu(E)$ on energy E of the incident X-rays. This relationship determines both how deep a detector needs to be to stop the incident X-rays and the reduction in efficiency due to the window thickness and crystal dead layer thickness.

The efficiency calibration of a Si(Li) detector in the energy range of 5–60 keV using radioactive sources has been reported by Verma (1985). A modified theoretical model for calculating the efficiency of a Si(Li) detector has been presented by Garg et al. (1987) while the comparison of experimental efficiencies for different Si(Li) detectors in the energy range, 4.5–17.5 keV has been made by Yap et al. (1987). Table 1.7 lists the radioactive sources for efficiency calibration of the Si(Li) detector.

The Si(Li) detector has an intrinsic resolution i.e., FWHM (full width at half-maximum) given by the relation

$$\text{FWHM} = 2.35(\varepsilon F E_{\gamma})^{1/2} \quad (1.14)$$

where $\varepsilon = 3.81 \text{ eV/pair}$; F (Fano factor i.e., ratio of statistical variance to the yield) = 0.12, and E_{γ} = photon energy. Thus at 1 keV, the intrinsic resolution is approximately 52 eV and at 10 keV, it is about 162 eV.

Table 1.7. The radioactive sources for energy and efficiency calibration of the Si(Li) detector (Ref. IAEA chart of the Nuclides)

Source	Half-life	Transition Energy (KeV)		Transition Intensity (%)
Mn ⁵⁴	312.1 days	5.406	(K α_2 of Cr)	7.43
		5.415	(K α_1 of Cr)	14.70
		5.95	(K β of Cr)	2.95
Fe ⁵⁵	2.73 yr.	5.888	(K α_2 of Mn)	8.24
		5.899	(K α_1 of Mn)	16.28
		6.49	(K β of Mn)	3.29
Co ⁵⁷	270.5 days	6.391	(K α_2 of Fe)	16.8
		6.404	(K α_1 of Mn)	33.11
		7.06	(K β of Fe)	6.68
		14.4	(γ)	9.16
Zn ⁶⁵	244.3 days	8.028	(K α_2 of Cu)	11.51
		8.048	(K α_1 of Cu)	22.60
		8.91	(K β of Cu)	4.61
Sr ⁸⁵	64.8 days	13.336	(K α_2 of Rb)	17.11
		13.395	(K α_1 of Rb)	33.01
		15.0	(K β of Rb)	8.70
Y ⁸⁸	106.6 days	14.098	(K α_2 of Sr)	17.46
		14.165	(K α_1 of Sr)	33.69
		15.80	(K β of Sr)	9.05
Am ²⁴¹	432.2 yr.	3.35	(Np M)	6.35
		11.89	(Np L1)	0.85
		13.94	(Np L α)	13.0
		17.8	(Np L β)	19.3
		20.8	(Np L γ)	4.93
		26.345	(γ)	2.4
		33.119	(γ)	0.103
		43.463	(γ)	0.057
		59.537	(γ)	35.7

There is a statistical probability that some of the X-rays, generated in the sample and impacting the Si(Li) detector will “inadvertently” knock out Si K-shell electrons in the detector, reducing that X-ray’s energy measured in the detector by the Si absorption edge energy (1.84 keV). Let us consider that we have a sample with lots of Fe (K α of 6.40 keV); the Si-escape peak of FeK α will appear at 4.56 keV. This escape peak is only seen for the major elements present in the sample. The ratio of escape peak and exciting primary radiation (parent + escape) intensity in a Si(Li) detector is given by

$$\begin{aligned}
 \eta &= I_{\text{esc}} / (I_{\text{parent}} + I_{\text{esc}}) \\
 &= \frac{\omega_k}{2} \times \frac{\tau_K}{2} \frac{\tau_K}{\mu_p} \left[1 - \frac{\mu_s}{\mu_p} \ln \left(1 + \frac{\mu_p}{\mu_s} \right) \right] \quad (1.15)
 \end{aligned}$$

where μ_p and μ_s are the mass attenuation coefficients for the primary (p) and secondary (s) radiation. Each primary X-ray line comprises a Lorentzian energy distribution that is convoluted with overall detector response function which comprises a Gaussian line shape, an exponential tail, a flat shelf (including a step at 1.75 keV) and an enhanced shelf region between a peak and its escape peak.

In an energy dispersive spectrometer, the interference from the X-ray lines of the trace element with the analyte element significantly degrades the detection limits particularly when the interfering peak is from an element of major consideration. Even though the intense peak may not overlap the trace element peak, it can increase the background for the small peak if the major peak has a higher energy.

Since Si(Li) detectors require liquid nitrogen cooling to provide acceptable resolution, further refinements in detector technology have led to the introduction of alternative detector (Sokolov et al. 2004) types including Si(PIN) detectors (which do not require cryogenic cooling – the thermoelectric cooler cools both the silicon detector and the input FET transistor to the charge sensitive preamplifier), Si-drift detectors (expansive, but with a very high count rate capability), and various semiconductor materials of higher atomic number (Ge, CdZnTe, HgI₂) that can extend the detector efficiency beyond the 20 keV limit typical of Si(Li) detectors. The use of HgI₂ crystal is advantageous because of the high atomic number of the elemental components and the large band gap (2.1 eV) associated with electronic transitions. However, while the ionization efficiency for the Si(Li) detector is 3.8 eV per electron-hole pair formed, it is 4.2 eV for HgI₂ resulting in a lower charge collection and a poorer energy resolution for the HgI₂ detector. The tentative value of 175 eV (FWHM) for the MnK α photopeak has been obtained with the preamplifier input FET cooled by liquid nitrogen and HgI₂ at room temperature. The difficulties in reliably producing detector crystal, dramatical decrease of the energy resolution with increasing count rate and relatively fast degradation of their performance, are the hampering factors in the commercial availability of these detectors. HPGe, the high-purity Ge-detectors (Low energy photon spectrometers) can be used in the X-ray region and in energy extended to about 1 MeV, but Ge has a more pronounced efficiency change about its K-absorption edge (at ~ 11 keV) than does Si (at 1.75 keV). So Silicon makes a better-behaved detector. Since ^{32}Ge has a higher atomic number than ^{14}Si , therefore the problem with entrance window and dead layers are more severe with Ge-detectors than with Silicon detectors.

The Si(Li) begins to lose efficiency at higher X-ray energies. Practically a millimeter thick detector has only about 15% efficiency at 50 keV, and efficiency falls rapidly above that energy. Thus Si(Li) detector covers energies in the range of ~ 40 keV. The lower energies are limited by the beryllium entrance window (~ 0.5 mil thickness). However, the intrinsic Ge detector with less than 0.1 μm Ge of dead layer and 5 mil of thin Be-window gives good efficiency at higher energies up to 100 keV. In GAMMA-X detectors

manufactured by ORTEC, the 0.3 μm boron ion-implanted contact and thin beryllium front window allows photons of energy down to 3 keV to enter the active volume of the detector. Except for the anomaly at the 11-keV germanium absorption edge, virtually all photons up to 200 keV are detected. Above that energy, the efficiency falls off with the total absorption cross-section of Ge, which is dominated by the fall-off in the photoelectric cross-section.

A gas (usually 90%Ar + 10%CH₄) filled proportional counter is an alternative ED detector (except at short wavelengths where a Xe sealed proportional counter is preferred) particularly in industrial applications. This detector provides resistance to vibrations, mechanical reliability, and minimal temperature dependency. A proper choice of the filling gas of proportional counter is of great importance in minimizing the background caused by the wall effect. Although the resolution of this detector is relatively very poor, the detection limit in the ppm range can be obtained.

Whenever the wavelength of the characteristic X-ray used for analysis (region of interest) is near to or coincides with the characteristic X-ray lines of one or more matrix elements, spectral interferences (also called peak overlaps) occur, which can be a serious source of error in quantitative microanalysis. For example, K-lines of adjacent elements like ¹³Al and ¹⁴Si, ¹⁶S and ¹⁷Cl, ¹⁹K and ²⁰Ca, etc. overlap. Similarly K-line of ¹⁶S overlap with L-line of ⁴²Mo, K line of ¹⁷Cl overlap with L-line of ⁴⁵Rh, K-line of ³³As overlap with L-line of ⁸²Pb. The extent of overlap is determined by the resolution of the detector. To tackle such a problem, Schreiner and Jenkins (1979) have given an off-line nonlinear least squares fitting procedure as part of "RUNFIT" software which supports most of the intensity/correction algorithms currently employed in X-ray fluorescence spectrometry. Donovan et al. (1993) have given an improved algorithm for the quantitative treatment of interference corrections in wavelength-dispersive X-ray spectrometry analysis.

With energy-dispersive X-ray analysis data, *Imaging of different elements* can be done to locate the distribution of elements since the composition varies with position across an image area. In mapping, it would be ideal if the entire EDS spectrum could be saved at every picture element so that the same full spectrum procedures could be followed (Myklebust et al. 1989; Ingram et al. 1998). Mapping control software usually allows placing windows across each characteristic peak of interest and defining two or more background windows. Representative methods of analysis include (1) line scans of relative element concentrations along a scanned line passing through a selected object, (2) presence/absence analysis (dot mapping) at a specific X-ray energy level to detect a specific element, or (3) cumulative computer maps that can image up to 15 low resolution maps of different elements at the same time and can recursively collect data until the required resolution is obtained. The mapping collection software of Newbury and Bright (1999) allows definition of windows for several characteristic peaks of interest and five background windows. The latter are placed above and below each characteristic peak window. First-order background corrections are then made by simple linear interpolation with the

background windows closest in energy to, and to either side of the peak of interest. When minor or trace peaks are to be mapped, background windows are assigned as close as possible to the characteristic peak location. For X-ray imaging simulation in the field of biomedicine, Lazos et al. (2003) has described a software simulation package of the entire X-ray projection radiography process including beam generation, absorber structure and composition, irradiation set-up, radiation transport through the absorbing medium, image formation, and dose calculation.

Some manufacturers of EDXRF spectrometers (e.g., Horiba, Jorden Valley, Rigaku, Shimadzu Scientific Instruments, Oxford Instruments, etc.) have developed X-ray analytical microscopes for imaging which include CCD camera, focused X-Ray system, and a vacuum Fluorescent X-Ray probe. These spectrometers allow measurements on spot sizes as small as 10 microns on samples as small as 512 microns square or up to 100 mm square. These spectrometers are being used in fields as diverse as electronics, medicine, food, cosmetics, life science, plastics and alloy analysis, provide elemental mapping of a number of elements simultaneously in a wide variety of sample types.

Longoni et al. (2004) have designed an X-ray fluorescence spectrometer (for elemental mapping applications) based on a ring-shaped monolithic array of silicon drift detectors (SDDs) with a hole in the center. The coaxial X-ray excitation beam, focused by a polycapillary X-ray lens, reaches the sample after passing through the central hole. This geometry optimizes the useful solid angle for collecting the fluorescence from the sample, while the optics maximizes the photon density in the excitation spot. These features, together with the very high detection rate of SDDs, allow a high scanning rate in elemental mapping to be achieved. Moreover, the spectroscopic resolution of SDDs (cooled by thermoelectric Peltier elements) is comparable to that of the classical Si(Li) liquid nitrogen-cooled detectors. The authors have given several examples of applications of the novel spectrometer in various fields from archeology to biology.

1.4.3 Source of Excitation and X-ray Detection in PIXE Analysis

The PIXE technique is similar to EDXRF (described in “Energy Dispersive X-ray Fluorescence (EDXRF)”) except that the exciter source in this case is beam of proton, α -particles, or heavy ions of $1\text{--}3\text{ MeV amu}^{-1}$. Although the ions of energy less or greater than the range specified earlier can also be used but the yield of X-rays will relatively decrease as the X-ray yield (cross-section) depends on the energy of the projectile. The energy of the proton beam in PIXE is $\approx 3\text{ MeV}$ because the X-ray production has maximum cross-section at $\approx 3\text{ MeV}$. The charged particles obtainable from particle accelerator (Pelletron, cyclotron, Van de Graaff accelerator), lose energy while traversing through sample material. In the energy range under consideration, the energy loss is mainly due to the interaction of those particles with the electrons in the material causing excitation and ionization. Thus the principle of PIXE

technique consists of ionizing the atomic levels using the charged particles. This ionization is followed by a rearrangement of the electronic architecture with emission of characteristic X-rays. The detection of this radiation is realized by Si(Li) or intrinsic Ge semiconductor detectors. The characteristics of the PIXE technique are (1) nondestructiveness (2) rapidity (± 15 min) (3) easy preparation of the sample, and (4) determination of most of elements with $Z > 13$ with a good sensibility (ppm or sub ppm) and with a good confidence.

In the early 1970s, applied nuclear physicists quickly appreciated the beautiful match of particle-induced X-ray emission (PIXE) analysis to air particulate pollution sampling. Because X-rays from elements $Z \leq 13$ are strongly absorbed in typical target and any layers intervening between the target and the depleted region of the detector, it is practically impossible to analyze elements with $Z \leq 13$. For analysis of light elements below $Z = 13$, the other accelerator-based techniques like Rutherford Backscattering (RBS) – discussed in Chap. 2, Elastic Recoil detection Analysis (ERDA) – discussed in Chap. 3, Nuclear Reaction Analysis (NRA) – discussed in Chap. 7, are used as complementary techniques to PIXE analysis.

Significant changes have occurred in the past two decades especially in the use of focused ion beams in PIXE microprobes, milliprobes, and external beam systems. An important advantage of the external beam (i.e., beam brought into the atmosphere through a thin exit foil) is the possibility of analyzing volatile materials. An additional advantage of an external beam is that heat dissipation from the surface of the sample is effective and samples may be cooled easily.

The beam of charged particles can be obtained from single ended Van de Graaff or Tandem accelerator (Pelletron) or cyclotron. Figure 1.14 shows the typical diagram of a 3 MV Van de Graaff Tandem accelerator (Pelletron) to procure the beam of charged particles.

The Pelletron accelerator is basically a charged particle accelerator very similar to the Van de Graaff. In a Pelletron accelerator the charging belt used in a conventional Van de Graaff, has been replaced by a more stable and dependable rugged chain, consisting of metal cylinders, called pellets, joined by links of solid insulating plastic. The gap between the metal cylinders, serve as a spark gap providing excellent protection to the insulating links. Pelletron is essentially a two stage (tandem) electrostatic accelerator, in which the singly charged negative ions of the required projectile element, produced in the ion source, are directed to the low energy “accelerator tube” in which the metal electrodes, uniformly graded in electric potential and electrically insulated from each other, are suitably spaced. The charged particles are then accelerated toward an electrode called “terminal,” maintained at a very high positive DC potential. In the terminal, the accelerated negative ions obtained from the ion source are stripped off by one or more electrons, during the collision of the negative ions with the atoms of the gaseous or solid targets (usually carbon foils are used as strippers). These multiply charged positive

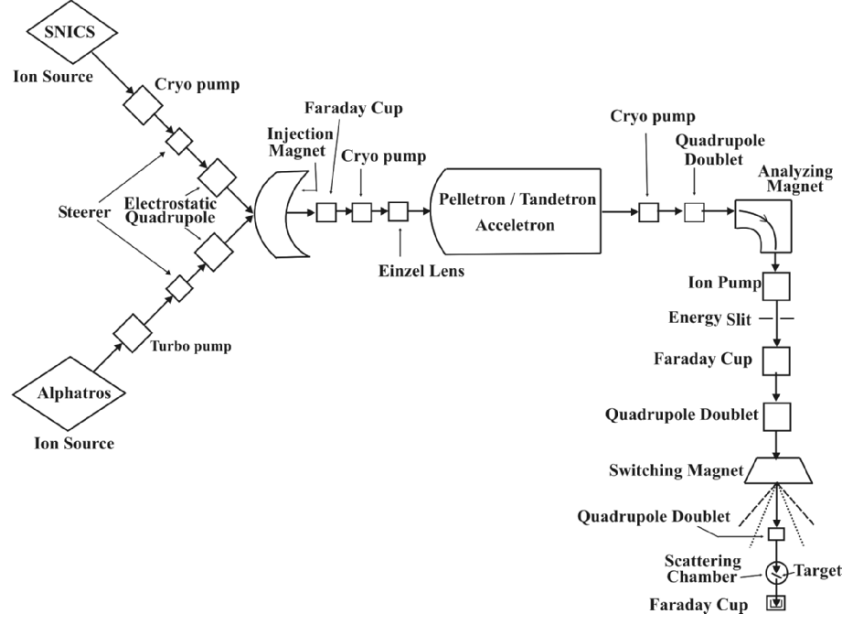


Fig. 1.14. A Pelletron accelerator to procure the beam of charged particles

ions (charge state q^+) are then accelerated again as they pass through the high-energy accelerator tube. The kinetic energy attained by the ions emerging from the tandem pelletron accelerator is thus given by:

$$E = V(1 + q) \text{ MeV} + \text{Injection energy}$$

where V is the terminal voltage in MV.

The high DC voltage on the terminal is produced by transferring to it a steady current of positive ions. The main parts of the accelerator are:

Ion Sources

The negative ion beams from the ion source are injected into the pelletron accelerator at an energy of about 100 keV by the injector system. The two negative ion-sources are as given below:

Duoplasmatron

Duoplasmatron is a two stage gaseous arc discharge source. The first stage is maintained at relatively high pressure (3×10^{-2} Torr) and low voltage (typically 20 V) between a thermionic cathode and an intermediate electrode, acting as primary anode. The plasma produced in the first stage is guided by a strong axial magnetic field through an aperture within the intermediate electrode to the second discharge chamber maintained at lower pressure

(2×10^{-3} Torr) and higher voltage (typically 80 V). The plasma created in the second stage flows out through a small aperture in the anode and expands into the third chamber called “expansion cup.” In a duoplasmatron, the plasma is compressed by a nonuniform magnetic field. The magnetic field confines the electrons so as to limit intense ionization to a small region around the anode aperture. The power in this intense discharge is dissipated as heat by anode structure fabricated from a high melting point and low vapor pressure material like molybdenum. The outer anode and the intermediate electrode are made from magnetic material. The ion beam current density of the order of 10^{-2} – 1 A cm^{-2} can be attained with a duoplasmatron.

SNICS (Source of Negative Ions by Cesium Sputtering)

In this ion source the cesium atoms used to cause sputtering, are ionized in an inert-gas discharge. The cathode containing a small amount of the material whose beam is to be produced, is inserted in the chamber through the air lock. The ionized cesium then sputters the solid cathode material to produce negative ions. This ion-source is used to produce the negative ions of almost all the solid materials.

Injection of Negative Ions in the Main Accelerator

The negative ions from the ion sources are first preaccelerated and then guided to the accelerator entrance by “injector magnet”. The Einzel lens assembly preaccelerates the negative ions from the ion source and focuses the beam on to the image slit through the injector magnet.

The injector magnet is 90° dipole magnet. It separates the particular ion from flux of ions coming from the ion-source. The injector magnet focuses the ion beam on to the slit through the beam profile monitor. A slit and a Faraday cup are provided just behind the injector magnet to separate the unwanted ions and to measure the beam flux to be injected into the accelerator.

A beam profile monitor (BPM) is provided before the slit. It provides the continuous display of the shape and position of the beam in both the X - and Y -coordinates. In BPM, a helical wire on a rotatory drive crosses the beam vertically and then horizontally during each revolution. A cylindrical collector around the grounded wire collects beam-induced secondary electrons from the wire to provide a signal proportional to the intercepted beam at that instant.

Main Accelerator Tube

The main accelerator consists of a number of accelerating columns on each side of the terminal. Each column consist of a pair of hollow circular aluminum casting supported by ceramic insulators.

The central part of the tube is the high-voltage terminal. It is spherical in shape and charged by motor driven chains consisting of metallic pellets

insulated by nylon studs. The charge is induced onto the chain by induction electrodes at the base of the tank. This charge is then deposited on the terminal, thereby raising its potential. The high potential terminal is supported by insulating columns consisting of two insulating plates. Hoops are used along the insulating plates to maintain equipotential planes. The ions passing through the terminal are made to pass through the stripper (gas or a thin carbon foil) which changes the negative ions into positive ions. The positive ions are further accelerated in the accelerator column raising the energy of the beam to $(1 + q)$ V. When the accelerator is to be used to produce low-energy beam, shorting rod system is used. Shorting rod system consists of stainless steel and/or nylon rods provided at either end of the tank to be introduced into the column to electrically short the selected columns as and when required. This system is very useful during tube conditioning, operation at low voltage or trouble shooting in the column.

For the stabilization of beam energy, the terminal voltage is stabilized by a feedback system. The feed back signal taken from the capacitive pickoff plate, on the control slit, after the analyzing switching magnet, is combined with the absolute voltage signal. The signals are used to control the biased corona needles pointing at the high-voltage terminal.

The beam coming out of the stripper foil with different charge states passes through a quadrupole lens to select a particular charge state. The entire accelerator column, including the charging system and accelerator tube, is enclosed within a pressure vessel filled with SF_6 gas at a pressure of ~ 100 psi. The SF_6 is chosen because of its excellent dielectric strength.

Analyzing Magnet

The accelerated beam coming out of the accelerator is focused on to the analyzing magnet. The quadrupole lens, provided at the outlet of the accelerator, focuses the accelerated ion beam on the analyzing magnet through the beam profile monitor, slit, and Faraday cup. The analyzing magnet analyzes the ions of particular mass and energy. In vertical type of accelerators, the analyzing magnet also bends the vertical beam into horizontal plane.

Switching Magnet and Beam Steerers

Since it is not possible to perform all the accelerator related experiments at a single port, a number of ports have to be provided to the accelerated ion-beam obtained from the accelerator. This task is accomplished by the switching magnet which is a quadrupole magnet. It not only directs the beam to different ports maintained at $\pm 15^\circ$, $\pm 30^\circ$, and $\pm 45^\circ$ to the main beam line, but also analyzes the ion-beam for its mass and energy.

Although the switching magnet directs the beam into a particular port, yet it may need minor adjustment in the horizontal and vertical direction.

This minor adjustment of the beam in the horizontal and vertical direction is done with the help of electrostatic beam steerers.

To minimize the transmission losses of the ion beam and its proper focusing, a number of beam steerers, quadrupole lenses, Faraday cups, and beam profile monitors are used throughout the low and high energy beam transportation system. Since in a heavy ion accelerator, charge exchange or scattering collisions can cause energy loss and spread of the ion beam, a number of vacuum pumps are used to provide clean and ultrahigh vacuum conditions for the passage of ion beams.

The beam current on the target ranges from 1 to 100 nA. Smaller beam currents are required due to the consideration of count rate, spectra energy resolution as well as to avoid the target destruction due to excessive heating/burning. The intensity of the proton beam may be measured directly on the target when the electrical conductivity of the sample is sufficient. For insulators (that can not be reduced to a powder in which a conducting ligand is added) regularly rotating index shutting off part of the incident proton beam is used as a monitor.

Scattering Chamber, Target Holder, and Samples

Scattering chamber encloses the evacuated ($<10^{-6}$ Torr) area where the ion beam strikes the target. It is made up of steel provided with windows/ports and is connected to the beam line by means of a gate valve so that the vacuum in the beam line and the scattering chamber could be maintained separately. The base of the chamber is calibrated to measure the angle between the target and the ion beam. The targets are usually placed at 45° to the beam direction. A Faraday cup is housed behind the target at the end of the chamber window. The thin targets are mounted on the target ladder placed at the centre of the chamber. The target ladder can be maneuvered vertically and about its axis externally. The surface barrier detectors, needed to yield information about the scattered charged particles are also arranged inside the chamber in the forward or in the backward direction. The Si(Li) detector is placed at 90° to the beam direction to collect the characteristic X-rays of the target. Since the X-rays are detected by the Si(Li) detector, the chamber is so designed that by using a flange, the neck of the detector can be inserted the flange so that the distance from the target is decreased. Angular positions are provided at the base of the chamber for accurate positioning of the SBD detector, which is used for charged particle detection (for normalization). Figure 1.15 shows the target chamber for PIXE analysis.

Since the target chamber in PIXE analysis is highly evacuated ($\sim 10^{-6}$ Torr), it is preferable to prepare a rotating target holder on which many different samples can be loaded at any time and one must be in a position to place a particular target facing the beam by maneuvering the target holder from outside manually or through remote control. It is necessary so that it may not be required to vent the vacuum chamber after each sample

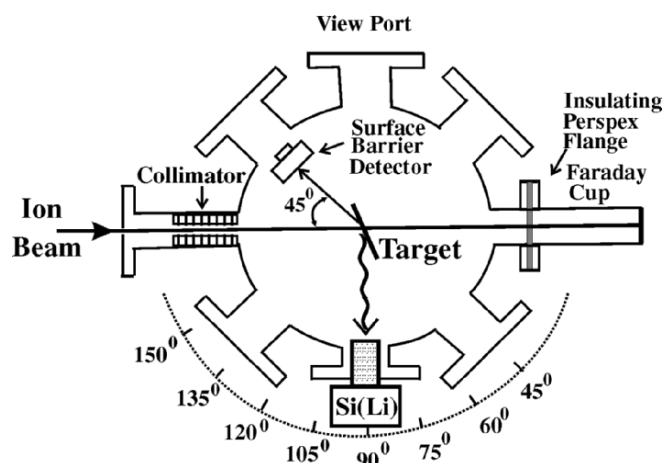


Fig. 1.15. Target chamber for PIXE analysis

run. The target holder assembly usually is a ladder type made of stainless steel with equidistant holes in it. The position of the target can be well determined from the position of a pointer attached to the target holder shaft from outside which slides over a vertically fixed scale. The ladder could also be manually rotated from outside in order to orient the targets at the desired angle with respect to the beam direction.

The samples in PIXE analyses are usually self-supporting or are sputtered or coated on a thin-foil or on a thick backing containing no detectable amount of the element of interest. Most samples are analyzed in their original state; aerosol filter, archaeological samples, soil, biological samples, etc. However, as PIXE technique is probing only top 10–50 μm of the sample (depending on the material, energy of incident beam and most importantly on the energy of characteristic X-rays), it is very important that the area/volume irradiated by the beam (usually a circular area with the diameter of 1–10 mm) is representative of the whole sample. Therefore, if the sample is obviously not homogeneous, like for example some pottery and geological samples, the sample should be grinded to a fine powder (preferably with particle size smaller than 1–2 μm), thoroughly mix it with 20% analytical grade carbon powder and consequently press into pellets.

Detection System

In PIXE analysis, the X-rays are detected by a Si(Li) energy dispersive system that includes a pre-amplifier (to optimize the coupling of the detector output to the amplifier) and an amplifier (to amplify the signal after shaping the pulses). The analog signal from the amplifier is fed into an analog to digital converter (ADC), which is then transferred into the memory of the on-line

computer via a CAMAC interface. The X-ray spectrum can be viewed on multichannel analyzer (MCA) terminal and the analysis can be carried out using the computer.

The $K\alpha$, $K\beta$ (or/and their components) lines of various elements as seen from the spectrum are compared with the standard X-ray fluorescence lines from the table. The net counts in different regions of interests (ROIs) including different peaks are calculated after subtracting the background. In other words, the linear or quadratic background can be fitted to an MCA spectrum which needs to be subtracted to calculate the net area under the peak. The background counts are calculated by averaging the counts on rather flat portion of the peak, taking the same number of channels on both side of the peak.

For analysis of a complex spectrum (containing many overlapping peaks) using multichannel analyzer, the three parameters i.e., energy (E), resolution i.e., full-width at half maximum (FWHM) and the area, have to be adjusted with certain constraints. It may not be possible to adjust all the three adjustable parameters simultaneously during the fit. For example, in spectrum analysis the energy of the known peaks should not be optimized as the peaks may appear at slightly different energy due to multiple ionization (explained in Sect. 1.4.4). However, the overall energy calibration coefficients for the entire spectrum, which relate channel number to energy, might well be optimized during the fit. Similarly, the FWHM of the detected X-ray peaks are not independent, but rather typically follow a predictable detector response function:

$$\text{FWHM} = A + B^* \sqrt{E}$$

Finally, even the amplitude of an XRF peak might not be a free parameter, since, for example one might want to constrain the $K\beta$ peak to be a fixed fraction of the $K\alpha$. Such constraints allow one to fit overlapping $K\alpha/K\beta$ peaks with much better accuracy.

The analysis can also be carried out using the standard computer code. However, the procedure for analysis is the same as described earlier. PIXEF (for PIXE-fit): the Livermore PIXE spectrum analysis package has been developed by Antolak and Bench (1994). This software initially computes an approximation to the background continuum, subtracts from the raw spectral data and the resulting X-ray peaks are then fitted to either Gaussian or Hypermet distributions. The energy dependent ionization cross-sections for each element's K-shell or L-subshell are procured from the analytical functional fit, while the subshell and total photoelectric cross-sections are determined directly from the Dirac-Hartree-Slater calculations of Scofield. Schematic of a typical PIXE spectrum is as shown in Fig. 1.16.

The main trend in PIXE analysis had also been on the development and extensive application of proton microprobe (beam diameter $\cong$ micrometer) as it offers better spatial resolution, generates a far lower background resulting in better detection ability.

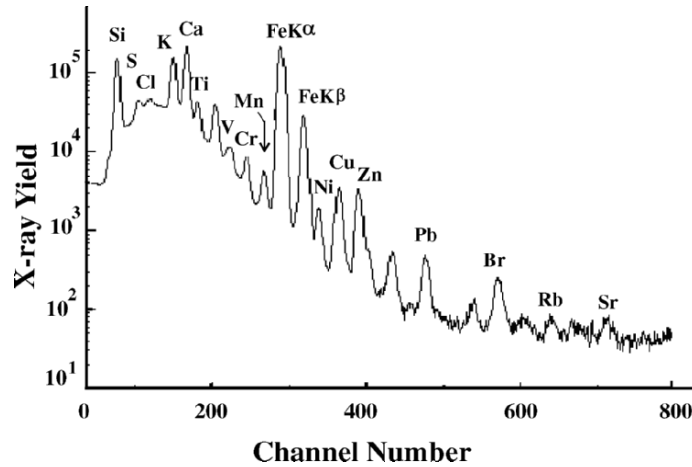


Fig. 1.16. A typical PIXE spectrum. The names of the elements over the peaks in the spectrum refer to the X-ray lines of those elements

1.4.4 Some Other Aspects Connected with PIXE Analysis

Choice of Beam/PIXE Using Heavy Ion Beams

PIXE work is normally carried out with protons of 2–3 MeV. Two aspects are important for consideration i.e., (a) PIXE using low energy protons (<1 MeV) and (b) PIXE using heavy charged particles/ ions like deuterons, α -particles and heavy ions like $^3\text{He}^+$, $^3\text{He}^{2+}$, C^+ , N^+ , O^+ , Ne^+ , etc.

Since the PIXE analysis is based on two fundamental quantities i.e., the interaction of the charged particles with the sample material (stopping) and the X-ray production cross-sections, the electronic stopping cross-sections reach their maximum value and the X-ray production cross-sections are subject to steep variation in the low energy range of the projectile. The energy dependence of the X-ray production cross-section must be accurately known to achieve reliable results during the analysis. A few workers like Paul and Muhr (1986), Paul and Sacher (1989), Paul and Bolik (1993), Orlic (1989), and Cohen (1990) have given the values for K and L X-ray production cross-sections with protons and α -particles.

The advantage of low energy PIXE are as follows (1) the minimum detectable limits are shifted toward lighter elements, (2) the ratio of secondary to primary radiation decreases, and (3) the small ranges and low X-ray yields of protons below 1 MeV restrict the analyzed layer to a few μm (or mg cm^{-2}) on the surface of the target. The limitation of low energy PIXE is the decrease of sensitivity (by one or two orders of magnitude) due to low X-ray production. This is reflected in longer counting times and the possibility of target damage because of higher amount of accumulated charge (Miranda 1996).

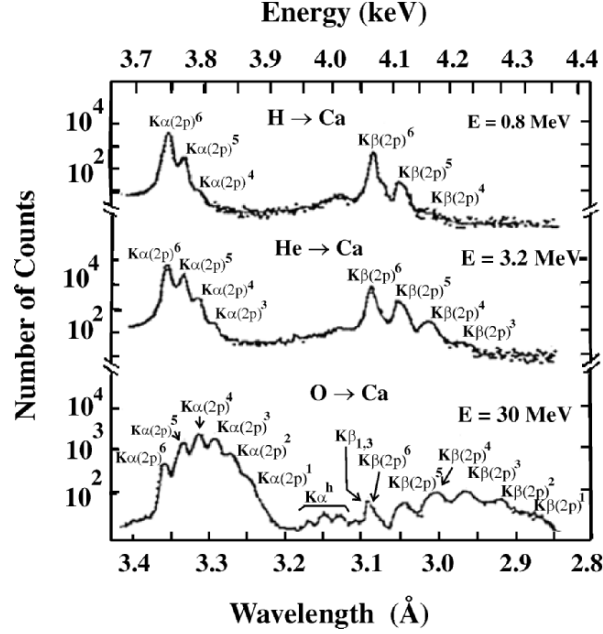


Fig. 1.17. Multiple ionization caused due to the bombardment of heavy ions (spectrum of satellite lines along with the diagram lines)

If heavy ions are used for bombardment in PIXE studies, a more complex spectrum (Fig. 1.17) is caused because of the following two reasons – first, the projectile has a greater mass and charge and would therefore be expected to exert a more disruptive effect on the target atom; and secondly, the projectile has an electronic level structure of its own, causing multiple ionization i.e., that one or more L electrons are ejected simultaneously with a K shell electron or double K ionization takes place. Due to appearance of the new set of lines (satellite and hyper-satellite), the principle X-ray lines get broadened and shifted to the higher energy side when observed by a Si(Li) detector. However, the complexity of the spectrum is very much visible when observed through a crystal spectrometer (energy resolution $\approx 1\text{--}2\text{ eV}$). The $K\alpha$ satellite lines will be represented as $K\alpha(2p)^5$, $K\alpha(2p)^4$, $K\alpha(2p)^3$, ... meaning that 5, 4, 3, ... electrons remain intact in the 2p shell while $K\alpha(2p)^6$ will represent the $K\alpha$ principle line with all the six 2p electrons intact. Similar terminology is also used for $K\beta$ satellite lines.

The PIXE method using 30 MeV α -particles, has been applied for the elemental analysis of metal targets by Bauer et al. (1978) who have reported the advantage of better accuracy and deep penetration ($\sim 100\text{ }\mu\text{m}$) of α -particles into the sample. The $K\alpha$ X-ray yield of thick targets for alpha particles ranging from 1 to 100 MeV was reported by Castiglioni et al. (1992). The heavy ions such as C^+ , N^+ , O^+ , and Ne^+ are not very suitable for PIXE studies mainly because the cross-sections for X-ray production are too small (not

proportional to Z_1^2) to produce appreciable yields. Moreover, the PIXE work using heavy ions is not yet well established as only a few measurements on the K and L X-ray production cross-sections, in different selected elements, with various selected projectiles, are available (Mokler et al. 1970, Datz et al. 1971, Mukoyama et al. 1980, O'Kelley et al. 1984, Andrews et al. 1985, Tanis et al. 1985, Mehta et al. 1993, Wang et al. 1993, Tribedi et al. 1993, 1994, Goyal et al. 1995, Semaniak et al. 1995, Padhi et al. 1996, Baraich et al. 1997, Bogdanovic et al. 1997). The experimental values for K X-ray cross-sections indicate that the cross-sections increase more than predicted by the ECPSSR theory of Brandt and Lapicki (1979, 1981). Due to variation in the ion-beam energy of heavy-ions, the X-ray lines shift to higher energies (and Auger lines to lower energies) as more energetic projectiles produce more vacancies in the valence shell in addition to the inner-shell vacancy, called the multiple ionization. Since the observation of broad and poorly resolved peaks consisting of many satellite lines with little of the diagram lines (Fig. 1.17) indicates that it has been caused by multiple ionization. Based on the energy shift of the diagram lines and change in the intensity of the transitions, the modified values of the fluorescence yields (ω_K) have been derived. The modified values happen to be as much as 40% larger than the single-vacancy fluorescence yield values. Reasonable agreement with the ECPSSR theory is obtained for $^{17}\text{Cl} + ^{35}\text{Br}$ where $Z_1/Z_2 \sim 0.5$ (regime of MO theory) with the agreement becoming progressively worse, for $Z_1/Z_2 \rightarrow 1$ (Tanis et al. 1985). Thus the precise values for X-ray cross-sections for various projectiles, based on any theoretical approach, are not available.

A few important formulae relating to heavy-ion induced PIXE are given later:

1. The cross-section for ionization of the n th shell

$$\sigma_n = 8\pi a_0^2 \frac{Z_1^2 f_n}{Z_2^4 \eta_n} \quad (1.16)$$

where Z_1 is the incident particle charge, Z_2 the effective target nuclear charge, a_0 is the Bohr radius, η_n depends on the incident energy, and f_n is a quantity related to the electronic wave function.

2. Charged particle Bremsstrahlung is proportional to $(Z_1/M_1)^2$, is small for heavy projectiles.
3. Maximum of the cross-section ($\propto Z_1^2$) occurs at an energy proportional to square of the projectile charge.

Although the X-ray production cross-sections are function of the incident beam energy and increase with increase of energy (σ_x depends only on the projectile velocity and not its mass) yet the beam energy of 2 to 3 MeV u^{-1} is preferred. The limiting value on the higher energy side is important due to the reason that the energy of the beam should be less than the Coulomb barrier so that the nuclear reaction are not caused to produce γ -radiations and increase the background. The target atomic number (Z_2)-value for which

Table 1.8. The Atomic number of the target element for which the Coulomb barrier equals the Centre of Mass (CM) beam energy

Energy (MeV u ⁻¹)	Target Atomic Number (Z_2) – Values For				
	Protons	Deuterons	α	${}^3\text{He}^+$	${}^3\text{He}^{2+}$
2	6	18	18	34	13
3	11	33	33	60	22
4	23	70	70		76

the Coulomb barrier equals the CM beam energy is given in Table 1.8, which has been calculated using (1.5).

This means that for a target material with a Z_2 -value lower than those given in Table 1.8, the projectile is able to penetrate into the nucleus and produce γ -rays through nuclear reactions. Thus with protons of 3 MeV, we cannot detect trace elements having $Z < 11$. Although it is theoretically possible to detect elements with $Z > 6$ using protons of 2 MeV yet we can not detect the elements like C, N, etc. due to the limitation caused by the Si(Li) detector (The low energy X-rays of elements with $Z < 11$ are absorbed in the window of the detector). The choice of protons of 3 MeV energy is thus appropriate.

The choice between protons, deuterons, and α -particles depends on the following factors:

- Variation of cross-sections for these heavy atomic ions vis-à-vis protons

$$\sigma_{Z_1, M_1}(E_1) = Z_1^2 \times \sigma_{1,1} \left(\frac{E_1}{M} \right) \exp \left[\sum_{i=0}^4 a_i Z_1^i \right] \quad (1.17)$$

The cross-sections for K-shell ionization do exhibit some reasonable regularities specifically, for protons and α -particles of the same *velocity*, the cross-sections scale approximately with Z_1^2 , i.e., $\sigma_K({}^4\text{He}) \approx 4 \times \sigma_K({}^1\text{H})$. Roughly speaking, relative to the cross-sections for 2 MeV protons, the energy of deuterons and α -particle beam and the magnitude of cross-section will vary as follows:

$$\sigma_{1,1}(2 \text{ MeV}) = \sigma_{1,2}(4 \text{ MeV}) \text{ and } \sigma_{1,1}(2 \text{ MeV}) = \sigma_{2,4}(8 \text{ MeV})/4$$

This trend is reminiscent of the stopping powers (discussed in Chap. 2). While proton and α -particle-induced X-ray emission have received wide attention (Johansson et al. (1970), Campbell et al. 1975), the high-energy heavy ion bombardment (HEHIX) provides improved prospects for simultaneous multi-element trace analysis over proton or X-ray bombardment. This observation is based on the following expression for predicting K X-ray production cross-sections σ_K which can be derived using the equation

$$\sigma_K = f(Z_1^2(E_1/M_1)^4 Z_2^{-12}) \quad (1.18)$$

Here Z_1 and Z_2 are atomic number of projectile and target, respectively, and E_1/M_1 is the velocity of projectile. Thus with heavy ion beam ($Z_1 > 5$) of velocity from $0.2\text{--}10\text{ MeV u}^{-1}$, σ_K , becomes very large ($10^3\text{--}10^5$ barn) for a broad range of elements and so the analytical capability (detection of trace elements ($10^{-10}\text{--}10^{-1}$ g) in microsamples ($10^{-4}\text{--}10^{-5}$ g) is improved.

Both the plane wave Born approximation (PWBA) (Merzbacher and Lewis 1958) and the binary encounter approximation (BEA) (Garcia (1970)) predict a “universal curve” in the variables σI_K^2 and E_1/I_K to describe the K-shell ionization cross-section of any atomic number target bombarded with a determine ion projectile at any energy. The cross-section being σ , I_K the binding energy of the target electron in the K-shell and E_1 the projectile energy, the fitted fifth order polynomial (Romo-Kröger (2000)) is:

$$\ln(\sigma I_K^2) = \sum_{i=1}^5 b_i \left(\frac{E_1}{I_K} \right)^i, \quad (1.19)$$

where $\{b_i\} = \{11.122, 0.6564, 0.5981, 0.0091, 0.0285, 0.006\}$.

The ionization cross-sections reach a maximum when the velocity of the incident ion matches that of the electron being ejected. A $\log_{10} - \log_{10}$ plot with the abscissa labeled by [dimensionless] and ordinate by $U_K^2 \times \sigma_K / Z_1^2 [\text{keV}^2 \text{ cm}^2]$, (where λ is the ratio M_1/m_e , E is the projectile energy, and U_K is the K-shell binding energy) is called the universal plot. The reasonably reliable values for PIXE cross-sections are available on Website www.exphys.unilinz.ac.at/Frameset/Staff.htm maintained by Prof. H. Paul at the University of Linz, Austria.

Before studying the ionization with heavy ions, we must evaluate the universal curve obtained with protons. This curve indicates that there is a marked difference of direct dependence on Z_2 , the atomic number of the target and the best fit is obtained by changing I_K by $I_K^{0.95}$, in both the abscissa and the ordinate, rather than a fixed effective charge Z_2 by $(Z_2 - 0.3)$. For cases with higher Z_2 or when $Z_1 \sim Z_2$, in which case there are other mechanisms during the ion-atom interaction, a new scaling has been made to get the proton-equivalent cross-sections, consisting in dividing the cross-sections by $Z_1^{0.8}$ rather than Z_1^2 as in the normal scaling. This corresponds to a screened nuclear charge instead of simply the projectile charge Z_1 (Romo-Kröger 2000).

The experiments conducted with protons (1.65 MeV), $^{16}\text{O}^{n+}$ (8 and 16 MeV), $^{40}\text{Ar}^{4+}$ (39 MeV), $^{63}\text{Cu}^{n+}$ (33 and 65 MeV), $^{82}\text{Kr}^{5+}$ (40.5 MeV), $^{82}\text{Kr}^{7+}$ (84 MeV), and ^{129}Xe (56 MeV) using beam current (on target) ranging from 0.03 to 100 nA, indicate that the X-ray yields are maximized when the binding energies of electrons being excited in the collision partners are approximately matched. It has been found that (1) the peak X-ray yields are obtained with a projectile $Z = Z_2 + (1 \text{ to } 5)$ (2) the enhancement effects decrease and hence the yield improves with increasing energy. Further background between the Bremsstrahlung drops off and the projectile K_α X-ray was found to be uniformly low.

For the high- Z elements ($60 < Z < 92$), the PIXE analyses can be done by detecting the L and M X-rays. The yields of K X-rays for low- Z and L X-rays of high- Z , of similar energies, are of the same order of magnitude i.e., the K X-ray cross-sections for high- Z elements decrease while the L X-ray cross-sections increase. Secondly, the K X-ray energies of these high- Z elements (being large) are not detected by the Si(Li) detector as the efficiency of the detector decreases significantly. Clearly, the analytical usefulness of heavy ion beams extends beyond X-ray emitters of atomic number lower than that of the projectile.

Heavy-ion induced X-ray emission applied to thick samples features several advantages, which are related to the small sample size assayed. As an example, with a $1\text{ MeV u}^{-1}\text{ Kr}^{7+}$ beam of $\sim 3\text{ mm}$ diameter, the weight of graphite subjected to analysis would be less than $15\text{ }\mu\text{g}$. Consequently problems associated with their target analysis (absorption of X-rays interference due to the substrate in the case of thin layer analysis) using X-ray methods are avoided.

Limitations of Heavy-Ions for PIXE Analysis

Use of heavy ions like ^{12}C , ^{16}O , ^{28}Si and still more heavy ions have the following limitation for PIXE analysis:

1. The interaction of heavy charged particles tend to destroy target by sputtering
2. The projectile X-rays are also produced, which may interfere/overlap with target (sample) X-rays
3. Molecular Orbital (MO) formation for $Z_1 \sim Z_2$

The interplay between the energy levels of the projectile and the target atoms will move the energy levels to levels appropriate to the “quasimolecule.” At sufficiently close distance of approach, the levels become those of an atom of atomic number $Z_1 + Z_2$. At intermediate separation, new X-rays seen from neither atom individually may appear. In general, the energy levels change adiabatically as the two atoms approach, but some electrons may be promoted to higher levels, leaving vacancies in the inner-shells as the atoms recede. The theory of X-ray production involving quasimolecular orbitals, has been explained in Sect. 1.11.3 under subtitle “Electron Promotion”.

Enhancement Effects

In PIXE analysis, one may come across a situation where the proton-induced characteristic X-rays of major and minor elements cause secondary fluorescence of the X-rays of other elements, enhancing its signal. Secondary fluorescence can be particularly important when the specimen matrix (different base material causing different absorption of X-rays) is composed of elements of similar atomic number; steels and other alloys are example. Neglect of

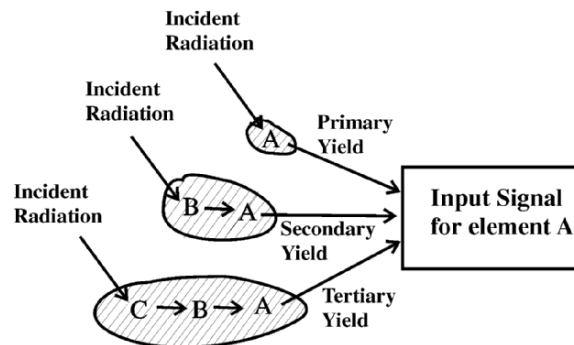


Fig. 1.18. Primary X-ray production, secondary, and tertiary fluorescence

secondary fluorescence in processing the spectral data will lead to erroneous matrix elements concentrations and these in turn will generate errors in concentrations of trace elements (Campbell et al. 1989). Similarly, any element can absorb or scatter the fluorescence of the element of interest. For example if a sample contains ^{26}Fe and ^{20}Ca , the incoming source X-ray fluoresces ^{26}Fe and the ^{26}Fe fluorescence is sufficient in energy to fluoresce ^{20}Ca . During analysis, ^{20}Ca is detected while Fe is not detected.

Figure 1.18 illustrates the situation where the PIXE yield of an element A is enhanced through the fluorescence of A by proton-induced X-rays of an element B. This can occur if the K X-ray energy of B is slightly higher than the K absorption edge of A. The examples are: Iron (B) $\rightarrow$ Chromium (A); Nickel (B) $\rightarrow$ Iron (A).

The lines formed by the overlap of many narrow (discrete) contributions and some continuous ones including one primary intensity plus several enhancement terms produce complicated spectrum. Fernández and Tartari (1995) have suggested the way to overcome the difficulties that such spectral complexity introduces in the process of extracting the primary fluorescence intensity from the experimental spectrum by using a theoretical spectrum.

Charging/Sparking/Heating in PIXE

The main difficulty in PIXE analysis is the collection of beam charges from insulating targets. For this purpose, the targets can be sprayed with electrons from electron gun integrated with the faraday cup. Charging effects might be responsible for local electrical potential producing the acceleration of secondary electrons resulting in intense Bremsstrahlung spectra. This effect can also be reduced by carbon shadowing or by covering the sample with a metal grid. A potential problem in PIXE analysis of thick nonconducting samples is one of the charge build-up and subsequent sparking which can cause large spikes in the spectrum and/or may deflect the proton beam resulting in poor precision. Spikes have the effect of irreproducibly increasing the background

over a large but random portion of the spectrum. Techniques such as spraying the sample with electrons from an electron gun or increasing the pressure in the target chamber can solve the problem.

The X-ray yield is strongly dependent on charge factors such as (a) imperfect charge accumulation (due to sample imperfect or beam sputtering) and (b) charge leakage (by carbon deposits or poor vacuum). Heavy ions tend to cause sputtering leaving behind minute cracks *and craters* on the large surface. This possibly leads to shorter discharge routes and a lower X-ray yield. The carbon build-up due to target burning at the beam spot from traces of oil vapors in the system conduct charge and gives low X-ray yield. With insulating materials, often poor vacuum is used. The gases in the neighborhood of the target surface are ionized by the ion beam creating a conducting path and eliminating charge build-up. Pressure exceeding 3×10^{-4} Torr was found to be adequate to centralize charge build-up and eliminating the charge-induced X-ray effect.

A few papers have discussed the problem of charge build-up on insulating samples in PIXE analysis (Gocłowski et al. 1983, Pillay and Peisach 1994). Pillay and Peisach (1994) and their other works with low energy (600–1500 keV) ions like $^3\text{He}^+$, $^3\text{He}^{2+}$, $^{14}\text{N}^+$, $^{16}\text{O}^+$, and $^{20}\text{Ne}^+$ have shown an abnormal X-ray yields, which originate from a discharge of high potential resulting from a charge build up on the surface of an insulating target with the production of a flux of electrons. These energetic electrons would have sufficient energy to excite X-rays even in situations where PIXE yields are negligible.

The very high-energy ion beam can also cause heat-up of the sample unless the current is kept low. These temperatures can cause damage to the sample and/or loss of volatiles, which may change the sample composition.

In order to reduce the high-energy Bremsstrahlung component due to the target charge-up, the use of electron gun, the foil technique, the poor vacuum, and helium filled chamber can be made. In the electron gun method, an electron gun with a commercial tungsten filament from glow lamps is used. A voltage of 6.0 V and 0.3 A gives a glow current sufficient to neutralize the charge produced by the ion beam on thick samples. Similarly placing a carbon foil (few $\mu\text{g cm}^{-2}$) about 2 cm before the target helps to eliminate the charge accumulation and the weaker X-ray lines, which were completely masked due to charging, become clearly visible.

Charge State Effect

In the description of the ion–atom collision, the electron–electron interactions play a special role due to which the electrons of the colliding partners can be excited or ionized additionally (dynamic screening) or they can undergo elastic scattering among each other (static screening). This indicates that the ionization cross-sections for the direct Coulomb ionization must be governed by the charge state (electron configuration) of the projectile (Hock et al. 1985).

The charge state fractions for heavy ions after passing through a thin foil depend upon the foil thickness. This dependence is due to the K-shell vacancies resulting from the ion–solid interaction. Hence each charge state fraction can contribute to the K-to-K electron transfer process while the ion is moving through the target thus modifying the electron configuration.

Heavy projectiles are in general highly ionized by stripping during the acceleration process before they hit the target atom. Due to the Bohr-Lamb criterion, for the average charge state, projectile electrons with projectile velocity $v_1 \leq$ orbital velocity of the electron v_2 , are ionized during penetration through a stripper foil (i.e., roughly up to $\eta = 1$). Hence the heavy projectile may only have the inner-shell electrons without any outer-shell electrons. Thus only direct excitation process in the projectile may be possible. On the other hand, capture to empty projectile states – which is normally not possible for the “neutral” target atom may also yield X-ray emission.

According to Frey et al. (1996), the effective charge of a swift heavy ion depends on its charge state and the way the charge state is screened. The incomplete screening of the charge of the ion by its remaining electrons increases the effective charge. The second screening effect is caused by target electrons due to long range of Coulomb interaction (becomes important for the energy loss process), reduces the potential of the ion due to a dynamic enhancement of the electron density at the position of the ion and reduces the effective charge compared to the real charge of the ion. According to Hock et al. (1985), the effective charge in the collision should approach the ionic charge of the projectile at high velocity limits.

The experiments relating to equilibrium charge state distribution of ions, passing through C-foils, have been done by Shima et al. (1986, 1992). The effective nuclear charges Z_1^{eff} for charge equilibrated projectiles have been calculated by Banas et al. (1999) by weighting effective charges for a given projectile charge state $Z_1^{\text{eff}}(q)$ by equilibrium charge state fractions $F(q)$ following the procedure described by Toburan et al. (1981). O’Kelley et al. (1987) have given the formulae to calculate the effective charge on the basis of the Bohr stripping criterion, for a Thomas-Fermi atom. Schiewitz and Grande (2001) have presented two fit formulae for mean equilibrium charge state of projectiles ranging from protons to uranium in gas and in solid targets.

Based on the effective charge, the theoretical cross-section values can be calculated using the first-order theories. Theoretically, the PWBA is not accurate to reproduce the experimental inner-shell ionization cross-sections for collision systems with $Z_1/Z_2 > 0.1$ in the v_1 (velocity of projectile) $< v_2$ (orbital velocity of the electron) region. For comparison, velocity v_1 in atomic units can be calculated using $6.35[E(\text{MeV})/M]^{1/2}$ while velocity v_2 in atomic units is calculated using $[\text{BE}(\text{eV})/13.6]^{1/2}$.

In one of our papers (Baraich et al. 1997), we have found a rather nice agreement between experimental and ECPSSR theory for Ni+Pb, Bi collisions using the equilibrium charge state for the projectile. The scaled projectile velocity is in the range of 1.2–1.6 in agreement with Hock et al. (1985) and the

ionic charge is the relevant effective charge in this region. Thus the experimental data can be reproduced with the best perturbative theory ECPSSR effective charge calculations.

No firm theoretical mechanism representing projectile charge structure in effective charge parameterization has yet been discovered.

1.5 Qualitative and Quantitative Analysis

For qualitative analysis, one has to look at the energy of the X-ray peaks and identify the elements from which these characteristic lines have originated. The X-ray energies of interest lie below 20 keV, where the X-rays of element with $Z < 45$ and L X-rays of the heavy elements are observed. Table 1.9 indicates the energies of K and L X-rays of a few elements:

For a sample having many elements, the L X-ray peak of a heavy element may coincide with the K X-ray peak of a light element causing confusion in analysis. Many elements, present in relatively very small quantity cause difficulty in their detection. The presence of two strong L-lines can be used to remove interference, for instance the determination of $_{82}\text{Pb}$ can be made in the presence of $_{33}\text{As}$ by using the $\text{L}\beta$ component.

When a given sample contains many elements, the X-ray lines for different elements are depicted from the energies of various X-ray lines. The energy resolution i.e., full-width at half-maximum (FWHM) is the limiting parameter for many X-ray measurements. This is so because if the energy resolution is poor, there will be overlap of component X-ray lines of one element with that of the other due to the small energy difference between the X-ray lines of

Table 1.9. Energies of K and L X-rays of a few elements

Z	Elements	K α (keV)	K β (keV)	L α (keV)	L β (keV)	L γ (keV)
13	Al	1.49	1.55			
20	Ca	3.69	4.01			
25	Mn	5.90	6.49			
30	Zn	8.63	9.62			
35	Br	11.89	13.37			
40	Zr	15.73	17.83	2.05	2.13	
45	Rh			2.70	2.83	
50	Sn			3.45	3.66	4.15
55	Cs			4.29	4.78	5.28
60	Nd			5.22	5.92	6.59
65	Tb			6.26	7.18	8.10
70	Yb			7.41	8.59	9.78
74	W			8.36	9.82	11.29
79	Au			9.66	11.53	13.99
83	Bi			10.77	13.00	15.25

adjacent elements. In the case of overlap of X-ray peaks of different elements, the elements are recognized from the nonoverlapping lines and the possibility of the existence of the corresponding line in the overlap. The peak overlaps occur because the spectral resolution of EDS (~ 150 eV) is much poor as compared to WDS (~ 5 eV). Since the energy resolution for a Si(Li) detector is of ~ 150 eV for Mn $K\alpha$ X-ray line, the separation of some peaks can therefore be poor and the interference between adjacent lines will make detection limits considerably worse. Examples include the case where small amounts of Fe are being investigated in the presence of large amounts of Mn (Mn $K\beta$ is very close to Fe $K\alpha$), and the case where Cu, Zn, and Na are present together, the L lines of Cu and Zn are close to the K lines of Na. In an energy dispersive spectrometer, even though the intense peak may not overlap the weak peak of trace element, it can increase the background for the weak peak if the intense peak has a higher energy.

When both overlapping peaks are weak and approximately equal in intensity, simple mathematical expressions for peak shapes and background can be used in a least square fitting procedure to extract the individual intensities using the Gaussian peak shapes. When the interfering peak has a very high intensity, then its shape must be known very accurately in the region where the trace element peak occurs. With an incorrect peak shape, the least square fitting method will produce a large error in the trace peak intensity. The best solution to such problem is to record the reference spectra of the two interfering elements using single element standards. This reference spectrum method can be used to subtract the background. A blank standard composed of the matrix with no trace elements is analyzed to establish the background spectrum, which is subtracted from the unknown to yield the trace element peaks without background.

The quantitative analysis with XRF and PIXE techniques generally requires calibration of the system against known reference standards (NBS, IAEA, Micromatter). These reference standards can be thin or thick ones. Yet, an absolute quantitative analytical method without external standards has been developed for thick sample analysis by XRF and PIXE and has been applied to bronze and brass alloys by Gil et al. (1989). For light ion PIXE using protons, the theoretical cross-sections and ion stopping powers are generally accepted to around $\pm 5\%$. Hence if the system is calibrated against thin targets of known composition, thick target yields can be calculated generally with a precision approaching $\pm 5 - \pm 15\%$. For absolute quantification, the knowledge regarding formalism for both thin and thick samples is required and the same is being discussed in Sect. 1.6. The spectrum of a material will contain additional peaks called escape peaks (discussed in “Energy Dispersive X-ray Fluorescence” and sum peaks due to the pitfalls in quantitative analysis using EDXRF and PIXE techniques.

The Sum peaks in the spectrum occur when the count rates are so high that when the two X-rays impinge on the detector virtually instantaneously, the pulse created and measured is the sum of the two X-ray energies. For

example, for a sample with lots of Si ($K\alpha$ of 1.74 keV) and Al ($K\alpha$ of 1.487); a peak at 3.23 keV is the sum peak, not to be assumed to be a K peak ($K\alpha$ of 3.31 keV).

If the X-ray detector in EDXRF analysis is very close to the sample or there is high beam currents in PIXE analysis, there may be “pulse pileup” where the electronics cannot keep up with the X-rays impacting the detector. The electronics/software therefore has to try to adjust for the X-rays not counted, by calculating a “dead time” correction; the larger the correction, the greater the margin of error. Generally the dead time should be kept below 20–30% (usually indicated on the monitor), either by lowering the beam current, inserting apertures in front of the detector nosepiece, or retracting the detector (if adjustable). Excessive dead time can also cause a shift of the peak position.

1.6 Thick vs. Thin Samples

Two terms relating to sample thickness are important in X-ray emission analysis: one is the linear thickness of a specimen, below which the absorption effect vanishes; the other is the critical thickness of a specimen above which the specimen becomes infinitely thick. Thick samples infer that the incident or exciting radiation is either absorbed in the sample or backscattered from it. On the other hand a thin target is a sample that is so thin that the energy loss of the particle beam in the target is very negligibly small and the intensity loss of the lowest energy photon of interest emerging from the sample material is negligible. The thickness of the sample can be related to the range of the charged particle (impinging the sample), which in turn is defined as the linear distance of the matter within which the charged particle is completely absorbed. The range of the charged particle in matter depends upon the substance as well as on the nature and energy of the charged particle. The details about stopping power and ranges is given in Sect. 2.2.3 of Chap. 2. The stopping power and ranges for various projectile-target systems can be evaluated using the computer program TRIM 91 by Ziegler et al. (1985).

The study of complex materials (nonhomogeneous matrices containing medium and/or heavy atoms as major elements) by PIXE requires the tailoring of the experimental set up to take into account the high X-ray intensity produced by these main elements present at the surface, as well as the expected low intensity from other elements “buried” in the substrate. The determination of traces is therefore limited and the minimum detection limit is generally lower by at least two orders of magnitude in comparison with those achievable for low Z matrices ($Z \leq 20$). Additionally, those high Z matrices having a high absorption capability, are not always homogeneous. The nonhomogeneity may be, on the one hand, a layered structure or on the other hand, inclusions which are to be localized. PIXE measurements at various incident energies (and with various projectiles (p, d, He^3 , He^4)) are then an alternative

method to overcome those difficulties. The use of special filters to selectively decrease the intensity of the most intense X-ray lines, the accurate calculation of the characteristic X-ray intensity ratios ($K\alpha/K\beta$, $L\alpha/L\beta$) of individual elements, the computation of the secondary X-ray fluorescence induced in thick targets are amongst the most important parameters to be investigated in order to solve these difficult analytical problems. Examples include Cr, Fe, Ni, Cu, Ag, and Au based alloys with various coatings as encountered in industrial and archaeological materials. RBS (Chap. 2), NRA and PIGE (Chap. 7) are sometimes simultaneously necessary as complementary (or basic) approaches to identify corroded surface layers (Demortier 1999).

In a more general case, the major considerations attributable to the thickness of the sample are self absorption of the characteristic X-rays (absorption by the specimen) and scatter mass thickness (property for scattering of X-rays – product of density and thickness of the specimen since the intensity of scattered X-rays is proportional to the mass thickness of the specimen) that may occur when the excitation energy passes through the material in the specimen chamber. If the photons are incident on the material, the attenuation coefficient can be calculated using XCOM computer software by Berger and Hubbel (1987). The program provides total cross-sections and attenuation coefficients as well as partial cross-sections for the following processes: incoherent scattering, coherent scattering, photoelectric absorption, and pair production in the field of the atomic nucleus and in the field of the atomic electrons. For compounds, the quantities tabulated are partial and total mass interaction coefficients, which are equal to the product of the corresponding cross-sections times the number of target molecules per unit mass of the material. The reciprocals of these interaction coefficients are the mean free paths between scatterings, between photoelectric absorption events, or between pair production events. The sum of the interaction coefficients for the individual processes is equal to the total attenuation coefficient. Total attenuation coefficients without the contribution from coherent scattering are also given, because they are often used in γ -ray transport calculations. For the purpose of interpolation with respect to photon energy, the coherent and incoherent scattering cross-sections and the total attenuation coefficients are approximated by log–log cubic-spline fits as functions of energy.

For a thin target, the atomic abundance of the trace element present is obtained by dividing the yield of X-rays per incident charged particle (in PIXE) or photon (in XRF) and the detection efficiency. However if one uses a target of moderate thickness, as is necessary to achieve a good counting rate, the correction due to self absorption (in XRF) and also the correction for the loss of energy of the charged particle (in PIXE) is to be applied since the charged particle of varying energy produces vacancies in inner atomic shells at various depths of the target, the cross-section for vacancy production goes on varying, normally decreasing at low energies.

In many problems of trace analysis, the scatter mass limits the performance of the X-ray energy spectrometer in thick samples. Since the backscatter

contribution to the spectrum increases with decreasing atomic number matrices, it has been found that the inelastic or Compton contribution to the backscatter dominates the spectrum. At increasing higher excitation energies (using secondary targets) the spread between the Compton peak and the elastic peak becomes increasingly greater. Since the measured X-ray intensity of element is considered as directly proportional to the mass (m_i), the increased thickness gives better sensibility.

The advantage of thin sample analysis is that self absorption of radiation can be neglected and the cross-section being constant, can be used in calculating the concentration. Other advantages of thin foil technique are low background in the measurement and absence of charge effects present in thick insulating sample.

1.6.1 Formalism for Thin-Target XRF

To convert the peak intensities into the elemental mass concentrations, a fundamental parameter approach is used. According to this approach, the intensity N_{ij} of the fluorescent X-ray line i of the j th element, is related to the mass m_j of the element present in the sample

$$N_{ij} = I_0 G \varepsilon_{ij} \beta m_j \sigma_{ij}(E) \quad (1.20)$$

where N_{ij} are the number of counts s^{-1} for the i th X-ray ($K\alpha, K\beta, L\alpha, \dots$) photopeak of the j th element, I_0 is the intensity of the photon emitted by the source, G is the geometry factor. ε_{ij} represents the relative efficiency to excite and detect the fluorescent X-rays from j th element, m_j is the elements concentration ($g\text{ cm}^{-2}$) which is to be determined and $\sigma_{ij}(E)$ is the XRF cross-section.

The absorption correction term β , for intermediate thick sample, is given by

$$\beta = \frac{1 - \exp[-(\mu_i \csc \phi - \mu_f \csc \psi)]M}{(\mu_i \csc \phi - \mu_f \csc \psi)M} \quad (1.21)$$

Here M is the total mass of the sample, $\mu_i(\mu_f)$ is the mass absorption coefficient at incident (fluorescent) energy and $\phi(\psi)$ is the grazing angle of incidence (fluorescence).

The self-absorption effects become negligible if the targets are very thin and of uniform thickness, The elemental concentration $m_j(g\text{ cm}^{-2})$ in various samples can be determined using the expression:

$$m_j = \frac{N_{ij}}{I_0 \times G \times \varepsilon_{ij} \times \sigma_{ij}} \quad (1.22)$$

The XRF cross-section $\sigma_{ij}(E)$ is defined as:

$$\sigma_{ij}(E) = \sigma_{\text{photo}}^i(E) \left(1 - \frac{1}{J_{K,L}}\right) \times \omega_x \times F_{ij} \quad (1.23)$$

where $\sigma_{\text{photo}}^j(E)$ is the photoelectric cross-section of the element j at the excitation energy E and $J_{K,L}$ is the jump ratio, ω_x is the fluorescence yield for subshell “x” from which the i th X-ray originates and F_{ij} is the fractional emission rate. An indirect way to calculate the photoelectric or photoionization cross-section, $\sigma_j(E)$ or $\sigma_{\text{photo}}(E)$ involves the subtraction of $\sigma_{\text{incoherent}}(E)$, $\sigma_{\text{coherent}}(E)$ and $\sigma_{\text{pair prod.}}(E)$ cross-section from the total measured cross-section of the incident photons with the matter. The values of $\sigma_{\text{photo}}(E)$ have been given by Storm and Israel (1970).

The variation of total attenuation cross-section $\sigma_{\text{tot}}(E)$ as a function of incident photon energy, displays the characteristic saw-tooth structure in which sharp discontinuities arise whenever the incident energy coincides with the ionization energy of the electrons in the K, L, M, ... shells as shown in Fig. 1.6. The sharp discontinuities, also known as absorption jumps in cross-sections at photon energies corresponding to the shell binding energies (Table 1.4), are due to the photoelectric interaction becoming energetic in that shell. The K-jump ratio is defined as the ratio of the upper to the lower edge photoionization cross-section at the K-shell binding energy. In other words, the absorption jump factor (J_K) is associated with the photoelectric absorption coefficient τ for different shells/subshells (i.e. $\tau_K, \tau_{L_I}, \tau_{L_{II}}, \dots$) and is defined as the fraction of the total absorption that is associated with a given level for a given interval of energy. For example, the jump factor J_K at energy E_A is:

$$J_K = \frac{\tau_K}{\tau_K + \tau_{L_I} + \tau_{L_{II}} + \tau_{L_{III}} + \dots} \quad (1.24)$$

Veigle (1973) has given an empirical relation between K-jump ratio and the atomic number of the element

$$J_K = \left(\frac{125}{Z} \right) + 3.5 \quad (1.25)$$

From K-jump ratio, one can obtain K-shell to total photoionization cross-section ratio. Again there is an empirical relation, given by Hubbel (1969) between K-shell to total photoionization cross-section ratio and atomic number of the element

$$\sigma_{\text{photo}}(E)/\sigma_K(E) = 1 + 0.01481 (\ln Z)^2 - 0.00078 (\ln Z)^3 \quad (1.26)$$

Further, K-jump ratio and K-shell-to-total photoionization cross-section ratios are connected by the relation:

$$\frac{\sigma_{\text{photo}}(E)}{\sigma_K(E)} = \left(\frac{J_K - 1}{J_K} \right) = \left(1 - \frac{1}{J_K} \right) \quad (1.27)$$

Fluorescence yield (ω_x) of an atomic shell/subshell is defined as the probability that a vacancy in that shell/subshell is filled through radiative transitions. Since the vacancy can also be filled by nonradiative processes (Auger electrons and Coster-Kronig transitions), the fluorescence yield (ω_K or ω_L) = Radiative yield/Total yield. The fluorescence yield values have been given by Bambynek et al. (1972) and Krause (1979).

Since the rate of decay of a vacancy state is the sum of radiative and non-radiative transition rates, the ratios of the intensities of individual X-ray lines are proportional to the ratio of the rates for the corresponding transitions. The fractional emission rates F_{ij} (where i is the number of subshell and j is the transition e.g., For L_α we take $F_{3\alpha}$) is defined as:

$$F_{ij} = \frac{j\text{th X-ray emission rate}}{\text{Total X-ray emission rate for all transition from } i\text{th subshell}} \quad (1.28)$$

Scofield (1974) has calculated atomic X-ray emission rates for the elements $5 \leq Z \leq 104$ while the experimental values of the relative K and L X-ray emission rates have been given by Salem et al. (1974).

The accuracy of numerical calculations of the X-ray production cross-sections depends upon accuracy of various terms which are involved in the expression (1.23) and comes out to be 4–6%.

1.6.2 Formalism for Thick-Target XRF

If the target is appreciably thick, a fraction of the incident photons gets absorbed by the target as they penetrate deep in the target material. Similarly a fraction of fluorescent X-rays emitted by the target are absorbed as they reach the surface of the target. Correction has thus to be applied to take care of these absorption effects.

Figure 1.19 shows the schematic diagram for the arrangement of source, thick target, and detector in reflection geometry.

Let t be the actual thickness of the target (g cm^{-2}). To make correction t is replaced by t_{eff} an effective thickness given by:

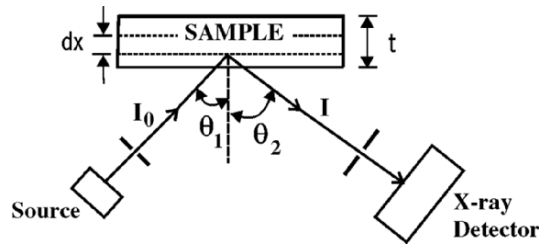


Fig. 1.19. Schematic diagram showing the arrangement of source, thick target, and detector in reflection geometry

$$t_{\text{eff}} = \beta \times t = \frac{1 - \exp(-) \left(\frac{\mu_{\gamma}}{\cos \theta_1} + \frac{\mu_x}{\cos \theta_2} \right) \times t}{\left(\frac{\mu_{\gamma}}{\cos \theta_1} + \frac{\mu_x}{\cos \theta_2} \right)} \quad (1.29)$$

Here μ_{γ} and μ_x (in $\text{cm}^2 \text{g}^{-1}$) are the mass absorption coefficients of the target material for incident photons and characteristic X-rays produced in the target with the impact of incident photons. Thus (1.22) gets modified to:

$$m_j = \frac{N_{ij}}{I_0 \times G \times \varepsilon_{ij} \times \sigma_{ij} \times \beta_{ij}} \quad (1.30)$$

where β_{ij} is the correction factor for the i th X-ray ($K\alpha, K\beta, L\alpha, L\beta, \dots$) photopeak of the j th element.

The mass absorption coefficients listed in the literature are at particular energies, say $E_1, E_2, E_3, \dots$. The interpolated value at a specified energy E in between E_1 and E_2 is calculated using the following formulae:

$$\mu(E) = \mu(E_2) \times (E/E_2)^{\eta} \quad (1.31)$$

where

$$\eta = \frac{\log(\mu(E_1)) - \log(\mu(E_2))}{\log(E_1) - \log(E_2)} \quad (1.32)$$

Trace analysis permits some simplification of the quantitative models used to calculate concentrations from measured intensities. There are usually two methods for accurate measurement i.e., internal standard method and fundamental parameter method.

In the internal standard method, the sample can be homogenized and split into three or more identical samples. The first sample is analyzed qualitatively and a rough estimate of the concentration of each element is made. The second sample is spiked with known amounts of one or two element to bring the concentration to approximately 10 times the estimated concentration in the unknown. From the known standards, one can draw the calibration curve and from the differences in the intensities one can calculate the concentration of each element in the unknown.

A more ideal situation is the availability of a number of samples having constant composition of the matrix but only trace elemental concentration varying from specimen to specimen. Here the most desirable method for generating the calibration curves is by making up standards of known composition. The set of standards can include the range of concentrations for all the elements, as several standards are required for each element.

In the fundamental parameter calculation, the calculations of different parameters of (1.30) is made especially for low-atomic number specimens containing only trace elements as these considerably simplify the theoretical calculations. Fundamental methods are particularly simple if monochromatic excitation is used.

1.6.3 Formalism for Thin-Target PIXE

The X-ray yield for each energy interval E to $(E - dE)$ of the ion is given by the product of the number of incident particles hitting the target and the number of target atoms in the region corresponding to the energy interval per unit area, the vacancy production cross-section in the atomic shell, the fluorescence yield of the atomic shell, the freedom of X-rays being detected (e.g., $K\alpha, K\beta, \dots$), the attenuation of these X-rays in traversing a distance x (where x is determined from the distance traversed by the ion in the bulk material of the target in getting slowed down from the incident energy to the energy $E - \Delta E$) and the efficiency of detection of the X-rays including the solid angle of the detector.

The solid targets are considered to be thin, if only a fraction of the energy is lost by the projectile while traversing through the target. If the target is thicker than the range of the ion in the target, the thickness traversed by the ion would be the range itself and the final energy of the ion would be zero (see formalism for thick targets in that case). In the case of thin targets, when N_p protons of energy E_0 pass through a thin, uniform and homogenous target of effective thickness t (in cm) of atomic number Z and atomic mass A , the i th ($K\alpha, L\alpha, \dots$) X-ray yield is:

$$Y_{x_i}(Z, E_0) = \sigma_{x_i}(Z, E_0) \times (nt') \times N_p \times \varepsilon_{x_i} \quad (1.33)$$

where $\sigma_{x_i}(Z, E_0)$ is the production cross-section (in cm^2 per atom) of the i th X-ray of element Z at energy E_0 , which can be calculated by incorporating the correction factors as:

$$\sigma_{x_i} = \frac{Y_{x_i}}{(nt') \times \varepsilon_{x_i} \times N_p} \times \frac{\Gamma_x}{\Gamma_R} \times C_i \quad (1.34)$$

Here ε_{x_i} is the detection efficiency of the X-ray detector that accounts for the absorption by the chamber window, solid angle subtended by the Si(Li) detector at the target; nt' is target areal density i.e., number of target atoms per unit area; n is target number density; t is target thickness; C_i is Correction factor due to the energy loss of the charged particle and self-absorption of the X-rays due to finite thickness of the target, and Γ_x and Γ_R are the Dead-time correction for the X-ray and charged particle detectors.

The effective target thickness (t') is calculated from the actual thickness (t) using the relation

$$t' = t \exp \left[- \left(\frac{\mu}{\rho} \right) \times \frac{t \sec \theta_0}{2} \right] \quad (1.35)$$

where μ/ρ is the mass attenuation coefficient (in $\text{cm}^2 \text{g}^{-1}$) and θ_0 is the direction of detected X-rays to the target surface normal.

The particle flux incident on the target N_p is calculated by applying Rutherford scattering formula (see Chap. 2)

$$N_p = \frac{N_{Sc}(E, \theta)}{\left[\frac{d\sigma}{d\Omega}(E, \theta) \right]} \frac{1}{(nt') d\Omega} \quad (1.36)$$

Combining these two equations we get

$$\sigma_{x_i} = \frac{Y_{x_i}}{N_{Sc}} \frac{d\Omega}{\varepsilon_{x_i}} \left[\frac{d\sigma}{d\Omega}(E, \theta) \right] \frac{\Gamma_x}{\Gamma_R} C_i \quad (1.37)$$

From this formula for thin target, we find that the target density factor cancels out and thus the error due to uncertainty in the measurement of target thickness gets eliminated. However, the target thickness is used in the determination of the correction factor C_i . Depending upon the target thickness, the correction factor C_i can be calculated by either of the two methods.

The method of O'Kelley (1984) is applied when the energy loss by the projectile in the target is large (about 20% of the incident projectile) i.e., when the target thickness is of the order of 1 mg cm^{-2} . In this method

$$C_i = C_x \times C_R \quad (1.38)$$

where C_x and C_R are the correction factors due to self absorption of the X-rays by the target and slowing down of the projectile in the target, respectively.

$$C_x = \mu' t' / (1 - \exp(-\mu' t')) \quad (1.39)$$

where $\mu' = \mu \cos \theta / \cos \phi$; μ is the self attenuation mass coefficient for the X-ray energy.

$$C_R = \frac{1}{(1 - \overline{\Delta E_R}/E_1)^2} \quad (1.40)$$

$$\overline{\Delta E_R} = S(E_1) t' / 2$$

where $S(E_1)$ is the stopping power of the target for the incident projectile of energy E_1 .

The energy lost by the projectile in the target is given by:

$$\overline{\Delta E} = \frac{2 \left[1 - (1 + \mu' t') e^{-\mu' t'} \right]}{\mu' t' (1 - e^{-\mu' t'})} \times \overline{\Delta E_R} \quad (1.41)$$

When the target thickness is such that the energy loss of the projectile in target is negligible i.e., target thickness is of the order of $\mu\text{g cm}^{-2}$

$$C_i = \frac{1 + \frac{\beta + 2}{2} \times \frac{\Delta E}{E_1}}{1 - \frac{1}{2} \left[\alpha - \beta + \frac{\mu(E_1)}{S(E_1)} \right] \frac{\Delta E}{E_1}} \quad (1.42)$$

Here α and β are the parameters which are determined from the X-ray production cross-section and stopping power of the target

$$\begin{aligned}\sigma^X &\propto E_1^\alpha \\ S(E_1) &\propto E_1^\beta\end{aligned}\tag{1.43}$$

The ionization cross-sections values ($\sigma_K^I, \sigma_{L_1}^I, \sigma_{L_2}^I, \sigma_{L_3}^I, \dots$), available in the literature (Orlic et al. 1989, Cohen 1990) can be converted to the production cross-sections using the following relations:

$$\begin{aligned}\sigma_{K\alpha}^X &= \sigma_K^I \times \omega_K \times \Gamma_{K\alpha} / (\Gamma_{K\alpha} + \Gamma_{K\beta}) \\ \sigma_{K\beta}^X &= \sigma_K^I \times \omega_K \times \Gamma_{K\beta} / (\Gamma_{K\alpha} + \Gamma_{K\beta}) \\ \sigma_{L\alpha}^X &= (\sigma_{L_1}^I f_{12} f_{23} + \sigma_{L_1}^I f_{23} + \sigma_{L_2}^I f_{23} + \sigma_{L_3}^I) \omega_3 F_{3\alpha} \\ \sigma_{L\beta}^X &= \sigma_{L_1}^I \omega_1 F_{1\beta} + (\sigma_{L_2}^I + \sigma_{L_1}^I f_{12}) \omega_2 F_{2\beta} \\ &\quad + (\sigma_{L_1}^I f_{13} + \sigma_{L_1}^I f_{12} f_{23} + \sigma_{L_2}^I f_{23} + \sigma_{L_2}^I) \omega_3 F_{3\beta} \\ \sigma_{L\gamma}^X &= \sigma_{L_1}^I \omega_1 F_{1\gamma} + (\sigma_{L_2}^I + \sigma_{L_1}^I f_{12}) \omega_2 F_{2\gamma}\end{aligned}\tag{1.44}$$

The fluorescence yield values (ω_i) of the L-subshell and the Coster-Kronig transition probabilities (f_{ij}) are listed by Krause (1979). The relative radiative transition probabilities (F_{ij}) of the i th subshell contributing to the j th peak can be taken from Cohen (1990). The ionization cross-sections can be theoretically calculated using the ECPSSR theory (see Sect. 1.11.3 for different theories on ion-atom collision).

For $Z_1/Z_2 > 0.3$ and for projectiles having either one vacancy or bare-projectiles, the electron capture contribution to the inner-shell target vacancy production rates become significant and must be added to direct ionization contribution.

If the experiment is conducted with heavy ions like deuteron and α -particles, the value of ionization cross-section σ_K, σ_{L_i} can be calculated from the corresponding proton values using the Z_1^2 scaling law e.g.,

$$\sigma_D(E) = \sigma_P(E/2) \text{ and } \sigma_{He}(E) = 4\sigma_P(E/4)$$

The scaling law is extended for still heavier ions like ${}_6\text{C}^{n+}, {}_8\text{O}^{n+}, \dots$, using term R which takes care of the effective charge due to charge exchange between the projectile and the target. Thus

$$\sigma_{L_i}^{\text{ion}}(E) = Z_1^2 R \sigma_{L_i}^{\text{proton}}(E_1/M_1)\tag{1.45}$$

1.6.4 Formalism for Thick-Target PIXE

The solid targets are considered to be thick if the projectile lose whole of its energy while passing through the target. In PIXE analysis of thick samples, the following points have to be considered: the slowing down of protons (or

other charged particles) and the decrease of ionization cross-section $\sigma_{x_i}(E)$ in deeper layers, the attenuation of characteristic X-rays in deeper layers by the photoelectric effect and scattering and the enhancement of X-rays with those elements with absorption edges just below the emission energies of dominant elements. Neglecting the enhancement effect, the number of X-rays of an element $Y(Z)$ is proportional to the mass concentration $W(Z)$ of this element in the homogenous sample i.e.

$$Y(Z) = N_p \times \left(\frac{N_{av}}{M} \right) \times \varepsilon_{x_i} \times W(Z) \int_{E_0}^0 \frac{\sigma_{x_i}(E) \times T(E)}{S(E)} dE \quad (1.46)$$

where E_0 is the incident proton energy (MeV), N_{av} is the Avogadro number, M is the atomic weight of the trace element of atomic number Z , and σ_{x_i} is the X-ray production cross-section (cm^2 per atom). The X-ray production cross-sections of an X-ray transition at projectile energy E_1 are related to the measured values by the Merzbacher–Lewis (ML) formula

$$\sigma_{x_i}(E_1) = \frac{1}{n\varepsilon_{x_i}} \left[S(E_1) \left(\frac{dY_{x_i}}{dE_1} \right)_{E_1} + \mu_{x_i} \frac{\cos \theta}{\cos \phi} (Y_{x_i})_{E_1} \right] \quad (1.47)$$

where n is the target number density; ε_{x_i} is efficiency of the Si(Li) detector corrected for solid angle at X-ray peak energy; $S(E_1)$ is Stopping power of the projectile in the target element (use TRIM); $(dY/dE_1)_E$ is Slope of the curve between X-ray yield per particle at the incident particle energy, μ_{x_i} is mass absorption coefficient of the target element at the energy of i th X-ray peak (use XCOM); $(N_{L_{x_i}})_{E_1}$ is Yield of the i th X-ray peak per incident particle at the projectile energy E_1 ; and θ and ϕ are the angles which the normal to the target makes with the beam direction and Si(Li) detector.

In the thick target analysis the main error is caused due to the determination of dY/dE_1 and uncertainty in the stopping power. The particle flux N_p incident on the target is calculated from the yield of scattered particles (N_{sc}), using the Rutherford scattering formula (1.36).

In (1.47), the efficiency of the detector (ε_{x_i}) also includes the effect of solid angle subtended by the detector on the target and the attenuation of the X-rays between the target and the front face of the detector; The stopping power $S(E_1)$ values at different energies for different elements of the given compound can be calculated from analytical relationship, for finding the interpolated values, by using the multiple parameter least square fitting to the available data (Andersen and Ziegler 1977). The total value of the stopping power for the compound $X_n Y_m$ at a particular energy can be calculated by using Bragg's additivity rule (Bragg and Kleeman 1905)

$$S(X_n Y_m) = n S(X) + m S(Y) \quad (1.48)$$

where $S(X)$ and $S(Y)$ are the stopping powers ($\text{MeV cm}^2 \text{g}^{-1}$) of the elements X and Y , respectively. Bragg's rule does not take into account effects of chemical bonding, physical state, or lattice structure.

As the thickness of the target becomes appreciable, the fraction of fluorescent X-rays emitted by the target gets attenuated as they reach the surface of the target. Thus correction to the values of absorption coefficient has to be applied to take care of this absorption effect. The values for self absorption coefficient can be calculated from the values given by Hubbel (1982) who has presented the absorption coefficients for photon energies 1 keV–20 MeV for elements with atomic number $Z = 1$ –92. The values for self absorption coefficient can be calculated using the X-COM program of Berger and Hubbel (1987). In practice it is not possible to obtain the absorption coefficients from the tabulated values since the absorption coefficients are often needed at photon energies other than those included in the tables. Photon cross-sections for compounds can of course be obtained rather accurately (except at energies close to absorption edges) as weighted sums of the cross-sections for the atomic constituents. However, the required numerical work is tedious, and the task is further complicated by the fact that photoabsorption cross-sections and total attenuation coefficients are discontinuous at absorption edges. The presence of these discontinuities makes it desirable that cross-section tables for compounds include photon energies immediately above and below all the absorption edges for all the atomic constituents, and this requires much additional interpolation. Since the cross-sections in the vicinity of absorption edges have simple sawtooth shapes, the values at the edge can be obtained by extrapolation of the near-edge subshell cross-sections to the threshold edge energies according to the procedure employed by Berger and Hubbel (1987) using XCOM program.

The photon attenuation $T(E_1)$ is expressed by the relation

$$T(E_1) = \exp \left[-\mu \int_{E_0}^{E_1} \frac{dE_1}{S(E_1)} \times \frac{\cos \theta_i}{\cos \theta_0} \right] \quad (1.49)$$

where $\mu = \sum \mu_j \times C_j$ is the composite mass attenuation coefficient of the matrix ($\text{cm}^2 \text{g}^{-1}$); μ_j is the coefficient of the j th matrix element; C_j is the relative concentration of the j th matrix element; θ_i is the angle of the incident beam with respect to the matrix normal, and θ_0 is the angle of the detector with respect to the matrix normal. To calculate the matrix corrections, the integration is replaced by a summation of sample slices of equal proton energy loss and some approximations are introduced. The absorption coefficients $\mu(E_x)$ at X-ray energy E_x is calculated using (1.31). A critical survey of the mathematical matrix correction procedures for X-ray fluorescence analysis has been made by Tertian (1986).

If the sample is reduced to a fine powder, the analysis of the nonmajor elements (less than a few percent) may be obtained by the internal standard

technique. The Internal Standard method rests on the principle of adding a known concentration of a reference element. Introducing one percent of the element to be analyzed in the powdered sample gives rise to a very slight difference in the attenuation factors. The use of selective absorbers is often necessary for the separation of peaks of neighboring elements with vast difference in the intensities.

If we compare the X-ray yield of the sample with a standard in the same geometrical conditions, the weight (W_Z) of an element of atomic number Z can be estimated using the relation

$$W_Z = \frac{M_Z}{M_{st}} \times \frac{\sigma_{st}^x}{\sigma_Z^x} \times \frac{\varepsilon_{st}}{\varepsilon_Z} \times \frac{Y_Z}{Y_{st}} \times W_{st} \quad (1.50)$$

where M is the atomic mass, σ^x is the X-ray production cross-section, ε is the detector efficiency of the Si(Li) detector, and Y is the number of counts for X-ray peaks corrected for the absorption in the target, the vacuum chamber window and the air path. The suffices “st” and Z refer to the standard element and element of atomic number Z . For the analysis of trace element in a known matrix is the derivation of $f(\alpha, E_1, \theta, \phi)$ values from measurements on thin single element standards. This permits determination of the concentration $W(Z)$ from the measured X-ray yields $Y(Z)$.

For specimen such as alloys there is no distinction between trace and matrix elements and we simply have a specimen of unknown elemental composition. In this case (1.50) transforms to

$$W(Z) = \frac{I_{st}(Z)}{I(Z)} \frac{Y(Z)}{Y_{st}(Z)} \quad (1.51)$$

where $I(Z)$ and $I_{st}(Z)$ are the integrals of the (1.46) for the specimen and the standard, respectively. Since the parameters $S(E_1)$, $T(E_1)$ of integral are not known, an iterative solution of the set of equations (1.51) is found. This starts with a “guessed” set of concentration values from which $S(E_1)$, $T(E_1)$ and the integral may be evaluated and a new set of $W(Z)$ values obtained by comparing calculated and measured values $Y(Z)$; the new $W(Z)$ values used to recalculate $S(E_1)$, $T(E_1)$ and the integral for another round and so on. The iteration is terminated when self-consistency is achieved for either the $W(Z)$ values or the calculated X-ray yields $Y(Z)$.

The computing treatment of a PIXE spectrum can give the elementary concentration of more than 20 elements with a detection limit near the ppm. The reality or the confidence in these absolute values given by the PIXE method depends on many factors such as the counting statistics, the background under the particular peak and the spectrum interpretation (refer to Fig. 1.20 for spectrum background).

When analyzing a spectrum, various factors such as the secondary fluorescence, autoabsorption of X-rays by the target and filters, escape peaks, and electronic pile-up have to be taken into account. With all these possible errors, the confidence in the results is near 5% in the case of thick targets for which

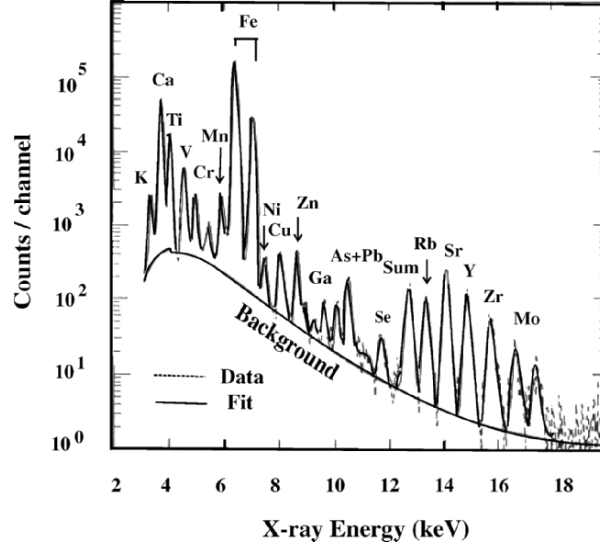


Fig. 1.20. The background and the elements in a PIXE spectrum of Perspex

the slowdown of incident particles, when they penetrate the target, is another source of error. Indeed, the probability of X-ray production depends on the incident particle energy and it is not always evident to precisely know the energy lost per unit of charged particle penetration in the analyzed matter.

1.7 Counting Statistics and Minimum Detection Limit

The measurement of peak intensity from an X-ray peak is illustrated through Fig. 1.21, where the counts/channel are plotted on log-scale. The peak is generally described by the Gaussian distribution, which is represented as:

$$P(x) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(x - \mu)^2}{2\sigma^2}\right) \quad (1.52)$$

The two parameters μ and σ^2 correspond to the mean and variance (square of the standard deviation) of the distribution. The resolution (FWHM) is interpreted in terms of σ as:

$$\text{FWHM} = 2\sigma\sqrt{2 \ln 2} = 2.35\sigma \quad (1.53)$$

The error in the measurement of the area (counts under the peak) depends on the limits. For example area lying between $(\mu - 0.68\sigma)$ and $(\mu + 0.68\sigma)$ has 50% probability or measured with 50% confidence, area lying between $(\mu - \sigma)$ and $(\mu + \sigma)$ has 68% probability or measured with 68.3% confidence, area lying between $(\mu - 1.65\sigma)$ and $(\mu + 1.65\sigma)$ has 90% probability or measured with 90% confidence while area lying between $(\mu - 2\sigma)$ and $(\mu + 2\sigma)$ has 95.5% probability and area lying between $(\mu - 3\sigma)$ and $(\mu + 3\sigma)$ has 99.7% probability.

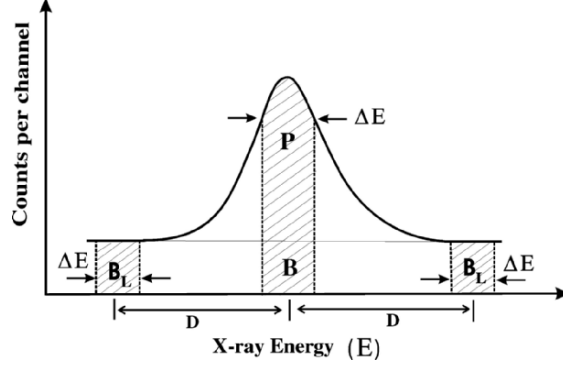


Fig. 1.21. Peak and background measurements from the spectrum of a typical X-ray line

The integral of the counts under the peak (say for n_p channels)

$$N_t = p + B$$

where p is the net area of the peak above the background and B is the contribution due to background. Therefore,

$$p = N_t - B$$

The expected standard deviation for p is,

$$\sigma_p = \sqrt{(\sigma_{N_t}^2 + \sigma_B^2)} \quad (1.54)$$

The background (under the peak) is estimated by integrating $n_B/2$ channels symmetrically on either side of the peak. If N_B are the background counts ($= B \cdot n_B/n_p$);

$$\sigma_p = (N_t + N_B)^{1/2}$$

The figure of merit $F_m = (\sigma_p/p)^{-1}$. A high value of F_m corresponds to a small statistical error.

The line to background intensity ratio (L/B) is the ratio of the net peak height above background to the background height. The plot of figure of merit as a function the integration limits show that ΔE should be set at 1.2 times the FWHM of the characteristic peak, when the minimum detection limit is reached. At high L/B ratio, the width of the peak integration region should be approximately twice the FWHM.

If the data is accumulated for the present livetime t_l , the intensities or number of counts per sec. under the peak are given by,

$$I_{p-b} = p/t_l = (N_t - B)/t_l$$

and the percent standard deviation is I_{p-b}

$$\sigma = (\sigma_p/p) \times 100\% \quad (1.55)$$

To detect the presence of the peak, the difference $\delta = (N_t - B)$ is examined. If δ is larger than the detection threshold δ_{MDL} , the element is claimed to be present. If a 95% confidence threshold is desired, then;

$$\begin{aligned}\delta_{\text{MDL}} &= 1.645\sigma_\delta \\ (I_{\text{p-b}})_{\text{MDL}} &= 1.645(I_b/t_l)^{1/2}\end{aligned}$$

If m is the sensitivity, the concentration is related to intensity by:

$$I_p = mC + I_b$$

or

$$mC = I_{\text{p-b}} = I_p - I_b$$

then

$$C_{\text{MDL}} = (1.645/m) \sqrt{(I_b/t_l)} \quad (1.56)$$

The minimum detection limit is based on the criterion that peak-to-background ratio be equal to or larger than 1 and defines the concentration level above which it is possible to say with confidence that the element is present. For the simple standard method, earlier equation can be written as:

$$C_{\text{MDL}} = \frac{1.645 C_{\text{std}}}{\left[\left(\frac{I_{\text{p-b}}}{I_b}\right) \times (I_{\text{p-b}}) \times t_l\right]^{1/2}} = \frac{1.645 C_{\text{std}}}{\left[\left(\frac{P}{B}\right) \times \left(\frac{P}{t_l}\right) \times t_l\right]^{1/2}} \quad (1.57)$$

where the intensities or counts are measured on the standard of concentration C_{std} .

Based on the analysis made for thousands of thick obsidian and pottery samples analyzed over a six-year period, the accuracy and precision of PIXE measurements for thin and thick sample analyses have been found to be as low as $\pm 1.6\%$ for major elements with precision ranging from $\pm 5\%$ to $\pm 10\%$ depending on the elemental concentration (Cohen 2002).

1.8 Sources of Background

Figure 1.22 shows a typical background intensity distribution curves for XRFS and PIXE in the energy range of 0–30 keV. The background intensity distribution follows those of the excitation cross-section. In PIXE, the ionization cross-section of the elements decrease with increasing atomic number, while in X-ray photoexcitation the cross-section increase with increasing atomic number; thus the background curves are opposed.

In PIXE, the background level at higher energy is mainly due to the Compton scattering of X-rays from the decay of excited nuclear states e.g., 3 MeV protons on Al produce γ -transitions of 170, 843, and 1,013 keV due to ^{27}Al . Protons of 5 MeV bombarded on V produce γ -transitions 320 keV due to ^{51}V , 48 MeV ^{16}O on C produce γ -transitions of 440 keV due to ^{23}Na ; the 440 keV level in ^{23}Na is populated through the $^{12}\text{C}(^{16}\text{O}, \alpha p)^{23}\text{Na}$ reaction.

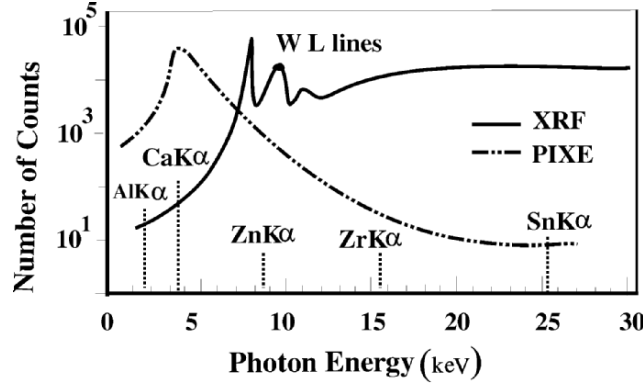


Fig. 1.22. Typical background intensity distribution curves for XRF and PIXE analyses in the 0–30 keV energy range

The γ -peaks are transitions from states in the target nucleus populated by inelastic scattering. The Compton scattering of these γ -rays is responsible for the observed background level. As this is very critical for the sensitivity, it is worthwhile to consider the nuclear reaction cross-sections. Since the Compton scattering of the γ -rays is much more important than the projectile Bremsstrahlung for the 3 and 5 MeV/u bombardment energies, from the point of view of $1/Z_1^2$ scaled background, it appears that it is not advantageous to employ projectile heavier than protons. At lower bombarding energies however the X-rays will be of less importance and it will be left to the projectile Bremsstrahlung to determine background at high radiation energies.

The $(1/Z_1^2)(d\sigma/dE_r)$ (in barns/keV) plot against E_r (radiation energy in keV) by Folkmann et al. (1974) gives the background radiation energies upto 100 keV for 3–5 MeV/amu projectiles of protons, α -particles and ^{16}O bombarded on plastic foil. For radiation energy up to ~ 20 keV, the secondary electron Bremsstrahlung falls very steeply roughly as E_r^{-10} to -12 . At about 20 keV, the curves become flat and in case of the proton, they come down to the vicinity of the projectile Bremsstrahlung. For lower proton energies 0.5–3 MeV, it gives a quantitative description of the high-energy proton background because of the $(Z_1/M_1 - Z_2/M_2)^2$ term in the cross-section formula for electric dipole radiation. The projectile Bremsstrahlung becomes negligible for α and ^{16}O bombardment on light nuclei.

One reason that the observed background is higher than the proton Bremsstrahlung (and for α and ^{16}O it is even much higher) lies in the high energy of these projectiles and their consistently higher probability of producing X-rays by nuclear reactions.

Since the minimum detection limit is controlled by the sensitivity for the element and the background contribution, it is important to understand the sources of background in order to reduce their contribution for the trace element analysis. The sources of background are described in the following sections.

1.8.1 Contribution of Exciter Source to Signal Background

When X-ray tube is used as a source *in the XRF analysis*, the most significant contribution to background is due to the X-ray tube spectrum scattered by the specimen especially when an unfiltered, or broadband, excitation spectrum is used on thick, low atomic-number specimens. Scattering of the Bremsstrahlung continuum (due to electron beam hitting the anode in the X-ray tube) leads to a high background level at all energies. Scattering of the characteristic anode lines from the specimen is also an important source of interference.

Since both coherent and incoherent scattering are involved, there is broadening of the characteristic lines, depending on the line energies and the spectrometer resolution. Frequently the X-ray tube spectrum contains unwanted characteristic lines from materials used in the anode and window construction. These lines become interfering peaks as they scatter from the specimen just like the major characteristic anode lines.

In the PIXE analysis, secondary electron bremsstrahlung (SEB) is the main cause of background. SEB is produced by the secondary electrons ejected from the target atoms due to the inelastic collision of the charged particle with the target nuclei and give rise to the continuous X-rays. The Bremsstrahlung produced is a continuous spectrum with intensity upward toward a high energy limit. The lower end of the spectrum is dominated by a Bremsstrahlung process giving rise to much greater intensities and results from electrons which are knocked on by the protons as they slow down in the target material. However the continuous spectrum produced by the inner-shell electrons is the dominant feature of the continuous nature of photon Bremsstrahlung energies of a few keV which is normally inseparable from the characteristic radiation.

The maximum energy of free electrons knocked on in this way is given by $T_{\max} = 4m M_1 E_1 / (m + M_1)^2$ where m is the mass of the electron; E_1, M_1 are the projectile energy and mass, respectively.

For $m \ll M_1, T_{\max}(\text{keV}) \cong 2E_1(\text{MeV})/M_1(\text{amu})$

The intensity of secondary Bremsstrahlung is proportional to Z_1^2 (projectile atomic number) and that it extends up to photon energies well above $T_{\max}$. To calculate SEB effect some knowledge of the energy distribution of knocked on electrons is needed. The number of secondary electrons with energies in excess of T_m falls off very rapidly with increasing electron energy. Above a few keV, the Bremsstrahlung produced by these secondary electrons is undetectable and only the projectile bremsstrahlung remains.

The cause of projectile Bremsstrahlung is the radiation of energy due to accelerated charged particles and the intensity of Bremsstrahlung is proportional to $(Z_1/M_1)^2$ which is considerably weaker than electron Bremsstrahlung. The background in the projectile target collision spectra due to Bremsstrahlung is classified into four categories:

1. *Secondary Electron Bremsstrahlung* (SEB) – cause of low energy background and is produced by the secondary electrons ejected from the target atoms during irradiations.
2. *Projectile Bremsstrahlung* (PB) of the bombarding particles slowed down in close collisions with the matrix nuclei.
The SEB is often six orders of magnitude larger than other sources of background while the PB is orders of magnitude less intense than electron Bremsstrahlung for X-ray energies below $T_{\max}$.
3. *Compton scattering*: In case of higher bombarding energies, the Compton scattering of X-rays from nuclear reactions between projectiles and matrix nuclei contributes to the background radiation. As an example, F and Na have very high cross-sections for (projectile, γ) reactions and the γ -rays produced by these reactions Compton (incoherently) scatter in the X-ray detector leaving only a small fraction of their energy with the recoiling Compton electron in the detector producing large high energy X-ray background, usually much stronger than the projectile Bremsstrahlung background. The energy at which the Compton edge (the maximum energy imparted to the recoil electron due to Compton interaction) occurs, is given by $E_c = 2\alpha E_0(1 + 2\alpha)^{-1}$, where E_0 is the energy of the X/ γ -rays incident on the detector and $\alpha = E_0/2m_0c^2$ where m_0c^2 ($= 511$ keV) is the energy equivalent to the rest mass of the electron.
4. *Background due to the insulating targets*: Insulating targets pose special difficulties because localized high voltages on the target surface accelerate free electrons, producing high background up to tens of keV X-ray energy.

1.8.2 Contribution of Scattering Geometry to Signal Background

1. In specimen having a high degree of crystal structure, interfering diffraction peaks become possible.
2. Background and contaminant lines can also be produced by the specimen chamber and the specimen holder, especially when very thin specimens are analyzed. This is because of the fact that the intensity contribution from the specimen itself will be very low.
3. Fluorescence of the chamber walls can provide contaminant lines which pass back through the thin specimen to the X-ray spectrometer. Radiation scattered from the chamber walls and the specimen holder can also increase the level of background.

The X-ray spectrometer itself contributes to the background. With the wavelength spectrometer, the most important contribution is due to the second and higher order diffraction.

1.8.3 Contribution of Detection System to Signal Background

With energy dispersive spectrometers, the detector system provides the limiting background contribution when monochromatic excitation is used for trace

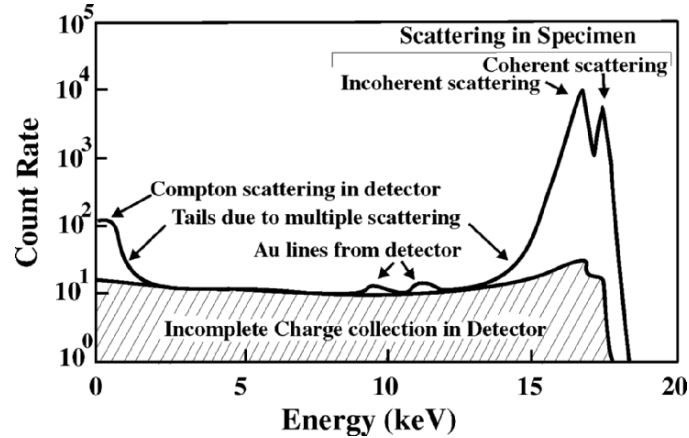


Fig. 1.23. Background contribution in the EDXRF spectrometer with monochromatic excitation at 17.4 keV

analysis. Figure 1.23 illustrates the effect on a pure-water specimen excited by monochromatic excitation i.e., 17.4 keV Molybdenum $K\alpha$ line from a graphite monochromator on a Molybdenum anode X-ray tube. The excitation X-rays are coherently and incoherently scattered from the water specimen to produce the intense peaks at 17.4 and 16.8 keV, respectively. The incoherent peak is much broader due to the range of scattering angles included about the nominal 90° scattering angle. The low-energy tail on the incoherent peak extending down to about 10 keV is primarily due to multiple Compton scattering in the specimen. The major background is due to incomplete charge collection in the Si(Li) detector which occurs because the holes and electrons produced in the detector by 16.8 and 17.4 keV X-rays combine before these are collected. The result is a pulse of abnormally low-amplitude recorded at a lower than normal energy. Some improvements can be gained by collimating the detector and using only the central 50% of its sensitive area.

Since the gold contact layer in front of the Si(Li) detector are fluoresced by the incoming X-rays, these cause the Au L and Au M X-rays lines in the EDXRF spectrum. The intensity of these lines is a function of the thickness of the gold contact layer and it may vary significantly from detector to detector. The gold L lines are often broadened on the high-energy side due to the ejected photoelectrons recoiling from the gold layer into the detectors' sensitive volume. The silicon escape peaks and the presence of sum peaks also cause hindrance to the analysis of X-rays spectra.

1.9 Methods for Improving Detection Limits

The minimum detectable amount is that concentration of the element that gives a net intensity (I_L) equal to three times the square root of the

background intensity $(I_B)^{1/2}$. In the case of X-ray tube exciter, the sensitivity can be greater if constant potential generator is used, kV and mA are as high as possible (but not to decrease I_L/I_B), target lines lie close to short-side of the absorption edge of its analytical line (usually a target just higher in Z number) and thin X-ray tube window is used.

Since the major background source limiting trace element analysis is the scattered X-ray tube continuum in XRF, a simple and effective means of removing this limitation is the use of a primary beam filter. If a thin aluminum filter is employed, the filtered X-ray tube spectrum of the chromium K-lines will strongly attenuate the chromium lines and all longer wavelengths allow the short-wavelength radiations. Thus a low background region is created for trace elements with longer wavelength. These elements will be excited by the shorter wavelength continuum passing through the filter. It is important to note that the sensitivity (m) for the trace elements will be reduced unless the tube current can be reduced to compensate. However the detection limit will be improved if the ratio $\sqrt{I_B}/m$ is reduced, which is possible depending on the choice of filter thickness.

In XRF, monochromatic excitation provides good trace sensitivity only over a restricted range of elements close to the selected excitation energy. This occurs because the cross-section for ionizing the appropriate shell in the atom decreases rapidly as the excitation energy is increased above the absorption energy of the analyte element.

Figure 1.24 illustrates the sensitive range for simultaneous trace element analysis as a function of monochromatic excitation energy. The bands are defined, one for the analysis of the $K\alpha$ line and the other for analysis of the $L\alpha$ line. The high atomic number boundary on each band is controlled by interferences with the incoherent scattered peak. The starting point is to assume that the highest energy line, which can be analyzed, is of the excitation energy and the absorption edge for this line must also be below the excitation

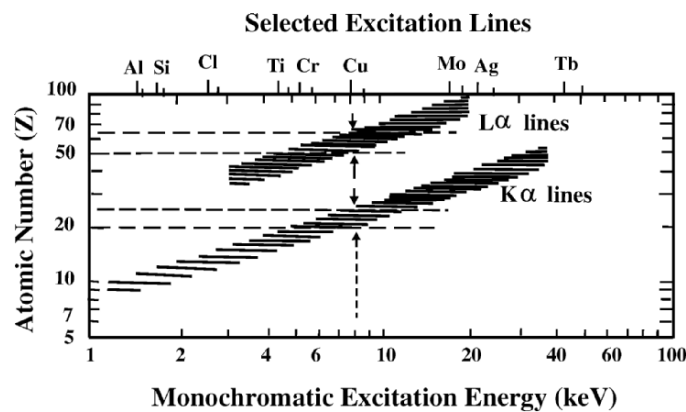


Fig. 1.24. Sensitive range for trace analysis with monochromatic excitation

energy. Thus the analysis of a wide range of elements will require several analyses with different excitation energies.

The thickness of the specimen is another important parameter. Although the detected intensity of the scattered excitation radiation is high with thick specimens yet it causes two problems. First, the maximum excitation intensity, which can be used, is limited by the counting rate of the scattered (coherent/incoherent) radiation rather than the analyte line, which limits the achievable sensitivity for the analyte line. Second, the intense high-energy scattered radiation produces a significant background under the analyte line due to incomplete charge collection in the Si(Li) detector, which increase the background. Both these effects combine to degrade the minimum detection limits. The thickness effect can be understood by maximizing the ratio of fluoresced intensity (I_i) to the scattered intensity (I_{sc}). An ideal situation is achieved by keeping the thickness (t) = 10% of infinite thickness t_∞ (t_∞ means $I_i = 99\%$); where an increase of tube current by only a factor of 7.3 over the thick-specimen case causes an improvement in detection limit by a factor of 3.4.

1.10 Computer Analysis of X-Ray Spectra

The X-ray full energy peaks from semiconductor detectors are generally described by Gaussian distribution, modified to allow for tailing. The peak fit to an element J is given by:

$$\text{PEAK}_j(x, H_j, \sigma, \mu) = H_j \exp[-1/2\{(x - \mu)/\sigma\}^2] \quad (1.58)$$

Here, x is the channel location at which the function is evaluated. H_j is the amplitude computed for the reference line of the element j . The symbols μ and σ represent the centroid and width, calculated at the X-ray energy of the line being fitted. The background points are chosen in selected channel regions by determining the local minimum for each region. The background fit at channel x is calculated (by second or third-order polynomial) as:

$$\text{BKGD}(x, P_y) = \exp(P_0 + P_1 \times x + P_2 \times x^2 + P_3 \times x^3) \quad (1.59)$$

The peak centroid (μ) and peak width (σ) are calculated according to the following linear calibration

$$\text{Peak centroid} = P_4 + P_5 \times E$$

and

$$\text{Peak width} = (P_6 + P_7 \times E)^{1/2} \quad (1.60)$$

Here E represents the appropriate energy corresponding to channel x , and P 's are the fitting parameters. The second of the equation gives the dependence

of resolution on noise and on the statistical nature of the charge formation. P_7 is related to P_5 by:

$$P_7 = P_5 \times F \times \varepsilon$$

where F is the Fano factor and ε is the energy to create one electron-hole pair in silicon.

The background fit BKGD (x, P_y) and the collection of peak fits $\sum_j \text{PEAK}_j(x, H_j, \sigma, \mu)$ are summed at each channel x to yield the total fitting function FIT (x, P, H_j), as:

$$\text{FIT}(x, P, H_j) = \text{BKGD}(x, P_y) + \sum_j \text{PEAK}_j(x, H_j, \sigma, \mu) \quad (1.61)$$

The least square fitting can be performed by the method of Marquardt which combines a gradient-type search for minimum χ^2 with linearization of the fitting function.

The exit from the iterative fitting loop is made automatic or manual when “ χ ” is less than 10^{-4} . For those elements which are not detected, the program can also provide the limit of detection (ppm) calculated as $3\sqrt{B/S}$, where B is the integrated background (i.e., nonpeak) count in a region centered at the computed centroid and having a width of one FWHM while S is the number of counts of elemental X-rays in the line.

From the estimates of the amplitudes H_j and width “ σ ” of the fitted peaks, the peak areas are computed as:

$$\text{AREA}_j = \sqrt{2\pi} \times \sigma \times H_j \quad (1.62)$$

which are converted to elemental abundances.

1.11 Some Other Topics Related to PIXE Analysis

1.11.1 Depth Profiling of Materials by PIXE

The most commonly used accelerator-based techniques for depth profiling are Rutherford Backscattering (RBS) which will be discussed in Chap. 2, Elastic Recoil Detection (ERD) which will be discussed in Chap. 3, and Nuclear Reaction Analysis (NRA) which will be discussed in Chap. 7. PIXE analysis has the advantage of a very good sensitivity and possible simultaneous detection of all heavier elements.

The X-ray yield from an infinitesimal volume at depth x , of the elements with $n(x)$ atoms per unit volume is given by:

$$dY = \frac{Q}{e} \times n(x) \times \sigma \left[E \left(E_1, \frac{x}{\cos \theta} \right) \right] dx \quad (1.63)$$

where E_1 is the energy of protons of energy E , bombarded under an angle θ , Q/e represents the proton flux and $\sigma[E(E_1, x/\cos\theta)]$ is the cross-section for proton energy $E(E_1, x/\cos\theta)$ at the depth $x/\cos\theta$. The fraction of X-rays emitted into the angle ϕ at which the detector with efficiency (ε) and solid angle (Ω) is positioned, is then given by:

$$dY = \frac{Q\varepsilon\Omega}{4\pi e} \times n(x) \times \sigma\left[E\left(E_1, \frac{x}{\cos\theta}\right)\right] \exp\left(-\frac{\mu x}{\cos\phi}\right) dx \quad (1.64)$$

where μ is the absorption coefficient of the considered X-rays. If we integrate (1.64) over the whole proton range, R , the expression for the total yield is obtained:

$$Y = K \int_0^{R\cos\theta} C(x) \times \sigma\left[E\left(E_1, \frac{x}{\cos\theta}\right)\right] \exp\left(-\frac{\mu x}{\cos\phi}\right) dx \quad (1.65)$$

where $C(x) = n(x)W/N_0$, W is the atomic weight of the element. N_0 is the Avogadro number and $K = Q\varepsilon\Omega N_0/4\pi\varepsilon\Omega$. For $C(x) = 1$, (1.65) presents the efficiency (α) of the PIXE for the thick-target measurements. From this equation, it can be seen that $C(x)$ profile can be obtained by varying the absorption or cross-section term. This can be done, for example by varying the proton energy or tilting the target.

For deconvolution of an unknown profile, we consider $C(x)$ as

$$C(x) = \Sigma C_j f_j(x) \quad (1.66)$$

where C_j are the components of the f -basis (step-like functions with edges determined by the proton ranges used).

If A_{ij} is the contribution of the X-ray yield of each slab with unit concentration of the element of interest and i corresponds to the i th energy used, then

$$i = \Sigma A_{ij} C_j \quad (1.67)$$

where

$$A_{ij} = K \int_{x_{j-1}}^{x_j} \sigma\left[E\left(E_1, \frac{x}{\cos\theta}\right)\right] \exp\left(-\frac{\mu x}{\cos\phi}\right) dx \quad (1.68)$$

For imaging of different elements in PIXE analysis (which is needed to locate the distribution of elements since the composition varies with position across an image area), there will be variation in the X-ray yields i.e., counts ppm⁻¹. This effect can be corrected using a method based on combining the yields calculated for end-member components in order to make dynamic analysis for quantitative PIXE (Ryan 2001).

1.11.2 Proton Microprobes

Proton microprobes represent a natural evolution of the PIXE analysis work which seek smaller area beams for lowered minimum detectable mass levels and allows an expansion of such analyses to encompass even the spatial

distribution of elements in specimens. Beams of MeV ions, with diameters below $100\text{ }\mu\text{m}$, can be prepared by either collimation or ion focusing. Using quadrupole lens with cylindrical form of pole tips, the beam size of $2 \times 2\text{ }\mu\text{m}^2$ and stability of better than $1\text{ }\mu\text{m}$ has been attained. The focusing arrangement (four magnetic quadruples) allows equal magnification in both places from an object slit. The current density ranges from $5\text{--}20\text{ pA }\mu\text{m}^{-2}$ at initial beam currents between 1 and $3\text{ }\mu\text{A}$. It has been used for surface analysis of lunar samples, monazite crystals, mica foils and meteorites. In general the proton microbeam arrangement can be used to study distribution of elements in surfaces in one of the following ways:

- Charged particles activation analysis for light elements e.g., oxygen, carbon, nitrogen, and fluorine.
- Proton-induced X-ray technique (PIXE) for elements heavier than ^{11}Na .
- Rutherford – scattering from heavy elements in light matrices.
- Determination of foil thickness through activation methods.

The sensitivity of 10–100 ppm has been obtained for a current of 1–100 nA by using the microbeam.

1.11.3 Theories of X-Ray Emission by Charged Particles

The ionization mechanism of X-rays induced by charged particles is of three kinds (1) Coulomb ionization (2) electron capture, and (3) electron Promotion.

Coulomb Ionization

According to direct Coulomb ionization models (valid for $Z_1 \ll Z_2$ and $v_1 \geq v_2$), the ionization cross-section for a certain shell becomes maximum when the reduced energy $E/(\lambda U)$ is equal to unity. Here λ is the mass of projectile in electron mass unit and U is the average binding energy of the shell. The direct Coulomb ionization phenomenon is described by the following approximations:

Binary Encounter Approximation (BEA)

This theory (Garcia 1970) is based on the classical energy transfer process wherein a projectile interacts with an inner-shell electron having a velocity distribution representative of its binding energy.

Semiclassical Approximation (SCA)

Bang and Hansteen (1959) and later Hansteen and Mosebekk (1973) treated the ion–atom collision process in a semiclassical approximation, considering the projectile motion classically and the transition of the inner-shell electron to the continuum quantum mechanically.

Plane Wave Born Approximation (PWBA)

In this approximation, the incident charged particles are treated as plane waves whereas the target electrons are described by hydrogenic wave function. The interaction between the projectile and the electron is treated to first order (Merzbacher and Lewis 1958).

Perturbed Stationary State Theory with Energy loss, Coulomb deflection, and relativistic effects (ECPSSR)

The PWBA theory has the validity for highly asymmetric collisions ($Z_1 \ll Z_2$). For nearly symmetric collisions, where PWBA theory is no longer valid, the perturbation of the target electronic states by the presence of the projectiles, disturbances to the projectile motion by the Coulomb deflection caused by the target nucleus and the relativistic motion of the target electrons are some of the corrections which have been introduced (Brandt and Lapicki 1979, 1981).

Electron Capture

The ionization of a target atom by a moving ion proceeds not only through direct ionization to the continuum but also through the electron capture by the projectile. Electron capture is the process in which one or more nonradiative electrons are captured while a fast highly stripped projectile passes through the electron cloud of the target. It is dominant for the systems with $Z_1 = Z_2$ and $v_1 \approx v_{2s}$. The Theory for electron capture is known as Oppenheimer, Brinkman and Kramer formalism followed by modification by Nikolaev (OBKN approximation).

Electron Promotion

In electron promotion, the electron is ejected through the quasimolecular orbital formed during ion-atom collision (Fano & Lichten 1965). This mechanism becomes dominant when $Z_1 \approx Z_2$ and $v_1 \ll v_2$, where v_1 and v_2 are velocities of the projectile and the bound electron in the target atom, the observed cross-sections for inner-shell ionization become many order of magnitude larger than predicted by any theory. The reason ascribed is the electron promotion via crossing molecular orbitals (MO). In this MO model (Fano and Lichten 1965, Kessel (1971), Saris (1971), Taulberg et al. 1975, Mokler and Folkmann 1978, Anholt 1979), as the nuclei approach, all shells of both atoms are involved and the energy levels move over to levels appropriate to the “quasimolecule” formed by the two atoms. In other words, the colliding atoms are treated as diatomic molecule whose interatomic separation varies during the collision. At sufficiently close distances of approach, the levels become those of an atomic number $Z_1 + Z_2$. At intermediate separation

new X-rays seen from neither atom individually, may appear. The molecular quantum numbers, having little importance for the widely separated atoms, become dominating factors as the collision brings the nuclei close together. In general, the energy levels change adiabatically as the two atoms approach, but some electrons from lower orbitals may be promoted to higher levels (electron promotion), leaving vacancies in the inner-shells as the atoms recede. This will happen only if there is a matching of an inner-shell energy level of the projectile with any inner-shell of the target atom.

Earlier the MO model was applied to the symmetric systems like Ar–Ar, Ne–Ne, etc. which was latter extended to the asymmetric systems like Cu–Ar, Al–Ar, etc. with the condition that an MO must have the same values of the $(n-l)$ in both the united atom (UA) and separated atoms (SA) limits. This is due to the reason that swapping takes place when two SA energy levels with the same values of m and $n-l$ change their relative order on an energy level diagram (Barat and Lichten 1972). To substantiate the theoretical model, the experimental measurements relating to molecular orbital formation in different asymmetric systems have been done by Mokler (1972), Anholt (1979), Montenegro and Sigaud (1985), Anholt et al. (1986).

Introducing two general parameters, the asymmetry parameter $\alpha = Z_1/Z_2$ and the adiabaticity parameter $\eta = (v_1/v_2)^2$ (where v_1 is the collision velocity and v_2 is the orbital velocity of the electron in the inner-shell of concern), the inner-shell vacancy production mechanism has been divided into two general categories by Madison and Merzbacher (1975) – the region for “direct coulomb ionization” $\alpha \ll 1$ and the regime for “quasimolecular excitation” $\alpha \approx 1$ and $\eta \ll 1$ as shown in Fig. 1.25. The third region with $\alpha \gg 1$ is the region for the production of multiply charged target recoil ions, a direct Coulomb ionization mechanism. This is due to the fact that the projectile

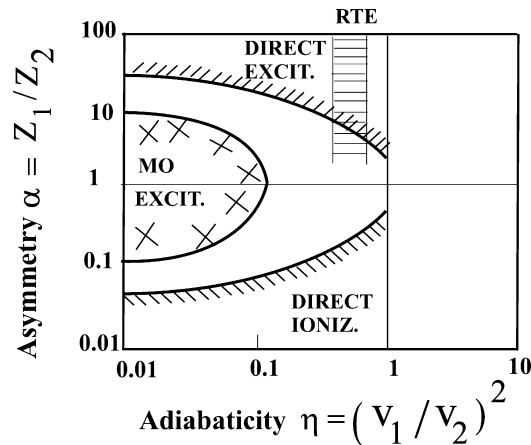


Fig. 1.25. Schematic representation of the main inner-shell processes for heavy ion-atom collisions and their applicability regions

ions will be having only the inner-shell electrons (and no outer-shell electrons as the heavy projectiles are highly ionized up to $\eta = 1$ due to stripping during the acceleration process) and one may detect excitation processes in the projectile and not an ionization or loss process. On the other hand, capture to empty projectile states – which is normally not possible for the neutral target atom – may also yield X-ray emission. Among these, the important capture processes are the (1) collision electron capture (CEC) to excited projectile states which can decay to by X-ray emission to the ground state; (2) radiative electron capture (REC) into ground or excited projectile states; the excited states decay additionally by X-ray emission; and (3) resonant electron capture (transfer) and excitation (RTE).

1.12 Applications of XRF and PIXE Techniques

Energy dispersive X-ray fluorescence (EDXRF) and particle-induced X-ray emission (PIXE) systems are particular appropriate for the analysis of geological, environmental, metallurgical, ceramic, and a wide range of other inorganic materials. Both techniques offer rapid, nondestructive analysis of test materials presented as solids, powders, particular collected on filter substrates and liquids. Since the X-ray fluorescence yield and detector efficiency are lower for light elements, EDXRF and PIXE are most often used for the analysis of elements in the range $11 < Z < 92$. PIXE is a very sensitive analytical technique (for the most of elements and samples limits of detection are of the order of 1 ppm) because of very high X-ray yields. PIXE method has been used in collaboration with scientist working in biology, and archaeology and other disciplines to obtain concentrations of micro and macroelements of the given sample. Several artifacts have been measured using PIXE method with different instruments. If a small part of the sample had to be investigated, the nuclear microprobe (with which the ion beam can be focused down to $1 \times 1 \mu\text{m}$) is applied. In case of large objects which can not be placed into vacuum chambers, the ion beam are extracted out through a thin foil and the samples are studied in helium atmosphere.

A survey of PIXE programs-1991 by Cahill et al. (1991) indicate that PIXE has been used in three major types of programs biological-medical (23%), material (21%) and aerosols (17%). Archaeological, mineralogy and others including Forensic sum to 22% of all programs.

1.12.1 In Biological Sciences

Both XRF and PIXE techniques are extensively used in biological and medical sciences for elemental analysis because of their ability in ultratrace analysis of K, Ca, Mn, Fe, Cu, Zn, Se, etc. in organic material. The bulk of living matter consists of the 11 major elements H, C, N, O, Na, Mg, P, S, Cl, K, and Ca.

Trace elements are heavy atoms linked to organic compounds by coordination or covalent bonds; these are Fe, I, Cu, Mn, Zn, Co, Mo, Se, Cr, Sn, V, F, and Si. Except for F, all these elements can be detected by XRF/PIXE. Trace elements in living matrices are not often coincidental contaminants but fulfill important functions. The presence of heavy metals in lumps, cryptogram, mosses, and lichens has been recognized and they are used as bio-indicators. Many of these elements can be detected by atomic absorption (AA) or by specific electrodes but using XRF/PIXE, no chemical separation is necessary. Using PIXE techniques, it may not be possible to identify light elements like C, N, O, F, Na but it is certainly possible by the other accelerator-based techniques like nuclear reactions.

The biological samples are either solid (bones, finger nails, teeth, hair, etc.). In such cases, no preceding preparation is required. In case of soft tissues and liquids (blood, urine, etc.), preceding preparation like freeze-drying or wet-ashing (with addition of internal standards) is required before doing the analysis. A restriction in the analysis of biological samples is sometimes the dimensions where the investigations are performed at the cellular level (size of the cell $\sim 10\ \mu\text{m}$). In this case microbeams $\sim 5\ \mu\text{m}$ in diameter or less can be used. Due to the biodiversity of organic samples, high number of samples is required to make statistical analysis. Walter et al. (1974) has described the analysis of biological, clinical, and environmental samples using proton-induced X-ray emission. Hall and Navon (1986) used 4.1 MeV external proton beam to simultaneously induce X-ray emission (PIXE) and γ -ray emission (PIGE) in biological samples that included human colostrum, spermatozoa, teeth, tree-rings, and follicular fluids. The analytical method was developed to simultaneously determine the elements lithium ($Z = 3$) through uranium ($Z = 92$) in the samples.

The use of PIXE for the analysis of botanical samples, determination of proteins and amino acids, Hair analysis, detection of trace elements in liquids (blood, serum, etc.) and in tissues (muscles, fibers, bones, teeth, etc.) has been described by Deconninck (1981). Hair is either individually analyzed by placing it on aluminum frame or a given mass of quantity of strontium nitrate can be added to it as internal standard. From this solution, the sample on nucleopore filter is prepared using a micropipette. The frozen samples of liver and spleen of about $\sim 10\ \mu\text{m}$ thickness, deposited on a thin Formvar film of less than $\sim 10\ \mu\text{g cm}^{-2}$ covering the glass plate, have also been studied. A typical PIXE spectrum of human teeth is as shown in Fig. 1.26. Among other biological samples, fish, mice, leaves and algae have been studied. Lowe et al. (1993) used PIXE for tissue analysis in a toxicity-disposition study of renal slices exposed to HgCl_2 , CdCl_2 , $\text{K}_2\text{Cr}_2\text{O}_7$, or NaAsO_2 alone or in a mixture. Characterization of Fe, Cu, and Zn has been reported in a recent study by Zhang et al. (2006) in organs of PDAPP transgenic mice, which express the familial Alzheimer's disease (AD) gene using XRF spectrometry.

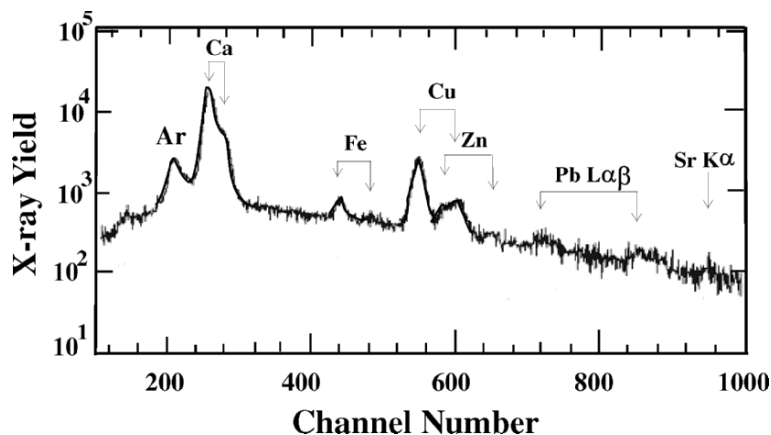


Fig. 1.26. Typical PIXE spectrum of human teeth

1.12.2 In Criminology

PIXE has been successfully applied to the problem of residues from gun firing. Certain elements including S, Ba, Fe, and Pb have been detected in significantly larger amounts on firing hands, than on nonfiring hands. Other elements such as K, Ca, Sb, Cr, Mn, Ni, and Cu have also been detected in the residue from firing arms. The technique used is to rinse hands with dilute nitric acid, to concentrate by evaporation and to place drops of liquid on a piece of Kapton foil which is bombarded with proton beam. Rožic et al. (2005) have determined the concentrations of the elements Pb, Rb, Sr, Y, Zr, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, and Co in the ash-samples of writing, copying and computer printing papers by EDXRF. Ashes of copying papers printed with black toner and black ink by laser and ink-jet printers were also analyzed. Most of the elements measured in papers showed the lowest concentrations in the ashes of Copier papers contains significantly higher amount of lead, strontium and zirconium compared to the papers of other manufactures. The concentrations of the elements Co, Mn, Fe, Cr, and Ti in the paper printed by laser printers are significantly higher compared to the nonprinted papers.

1.12.3 In Material Science

PIXE analysis method has been applied primarily for the nondestructive elemental analysis of ancient copper coins. However, the high yields of the copper X-rays and the high background which is created, cause serious difficulties in the accurate determination of zinc, nickel, iron, and in general for the elements with medium and low atomic numbers (Katsanos et al. 1986). For this reason, the complementary methods of proton-induced prompt γ -ray emission and proton activation methods have been explored. PIXE has been used in

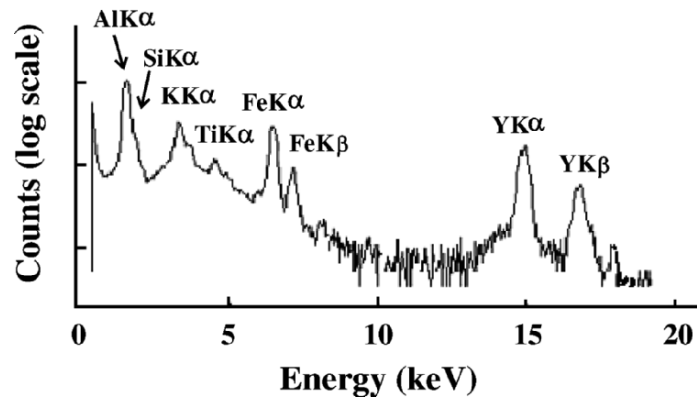


Fig. 1.27. A typical PIXE spectrum of Sialon, a type of ceramic containing Si, Al, O, and N

some of the key areas like study of corrosion and erosion and the study of high-temperature semiconductors based on ceramics with oxides of rare earth elements. Figure 1.27 shows the typical PIXE spectrum of Sialon (general sample composition: Si, Al, O, and N – Sialon is a type of ceramic used for high temperature applications) indicating the presence of the major as well as the minor elements.

The use of nondispersive X-ray fluorescence spectroscopy has been well established as an analytical technique for many problems in alloy analysis and coating thickness measurements in basic metal industry, but the highest excitation efficiency is achieved when the entry of the exciting radiation is restricted to an energy, which is just above the absorption edge of the “wanted” elements. A characteristic line of the substrate material is chosen and its attenuation by the overlaying material helps to determine the thickness. For example, in a tin plated steel, it is possible to measure the ratio of FeKα from a coated and uncoated specimen in order to determine the thickness of tin.

The problem of interelement effects in complex materials (ferrous and non-ferrous metals) is particularly significant. Several hundred alloy compositions exist and the most important alloying elements include Ti, V, Cr, Mn, Fe, Ni, Cu, and Zn which are virtually adjacent in atomic number and several of these elements may occur together in a single alloy. The greatest advantage is obtained when measuring the concentration of a single element at low concentration in a matrix of higher atomic number e.g., Cr in steel. The analyses of steels (Mn, Cr, and V in carbon and low alloy steels), brasses (Mn, Ni, and Fe in brasses) and aluminium alloys (Si, Cr, Mn, Fe, Ni, Cu, Zn) have been successfully carried out and reported by Clayton et al. (1973). Figure 1.28 shows the EDXRF analysis of a sample containing ^{26}Fe , ^{27}Co , ^{28}Ni , and ^{29}Cu (transition elements) from their Kα X-ray peaks.

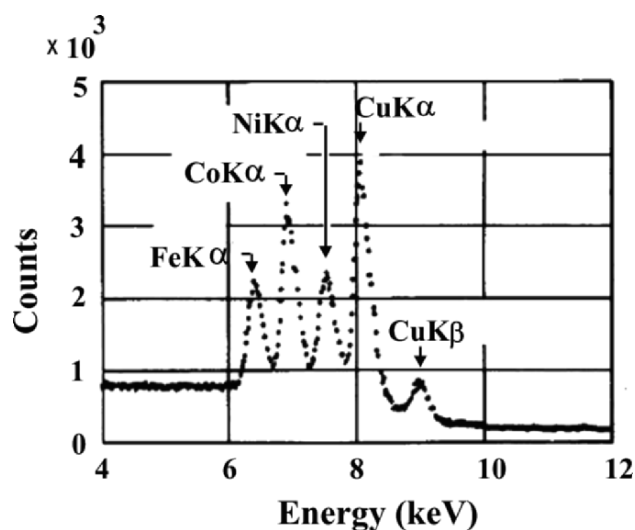


Fig. 1.28. EDXRF analysis of a sample containing Fe, Co, Ni, and Cu K α X-ray peaks

The comparison of results obtained from measurements on nickel-base alloys using the laboratory-based WD-XRF vs. portable ED-XRF spectrometer has been made by Zwicky and Lienemann (2004). Their comparison shows that the semiquantitative analyses using the WD-XRF spectrometer can be accepted as quantitative determinations. Although the portable EDXRF spectrometers are good enough for field investigations, the results obtained using these do not meet the quality requirements of laboratory analysis. For determining the composition of two- and three-component alloys of some technological materials, Mukhamedshina and Mirsagatova (2005) employed various X-ray fluorescence techniques. It has been found experimentally and confirmed theoretically that in some alloys, the composition can be determined without taking into account the absorption and secondary excitation of analytical characteristic lines, indicating that the contributions of these effects are opposite.

1.12.4 Pollution Analysis

The energy dispersive X-ray fluorescence (EDXRF) and particle-induced X-ray emission (PIXE) are the most widely used techniques for quantification of various elements present in aerosol samples. The population living in proximity to the industries and increased vehicular traffic are exposed to relatively high levels of air and water pollution. Numerous workers have studied the air and water samples by XRF and PIXE techniques for pollution monitoring, since the assessment of pollutant elemental levels and identification of their sources is prerequisite for understanding their effect on human health.

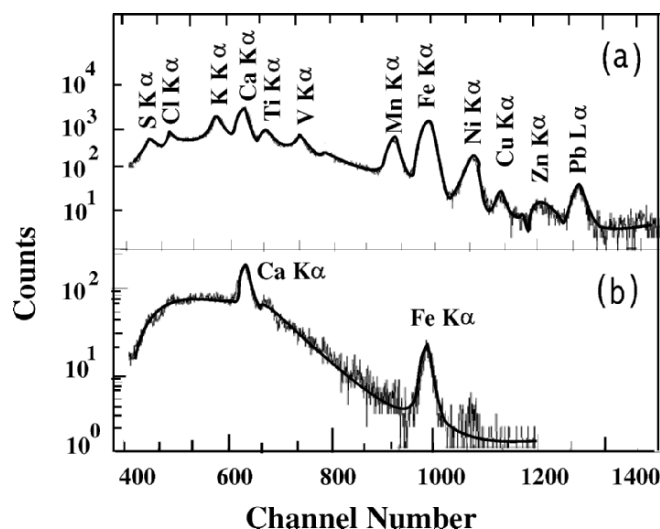


Fig. 1.29. (a) A typical PIXE spectrum of an aerosol sample and (b) the background spectrum from blank filter

In a study conducted at Chandigarh by Bandhu et al. (2000), Aerosol samples were collected on $0.8\ \mu\text{m}$ pore size using cellulose nitrate filter, were mounted on Millipore aerosol standard filter holder. The air through the filter paper sucked with the help of Millipore diaphragmatic vacuum pump. Sixteen elements namely S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Rb, Sr, and Pb have been detected. The air around Chandigarh is found to contain relatively more concentration of Fe, Ca, and Ti and very small amount of Ni and Cu. The typical spectra from aerosol sample along with the spectrum from blank filter measured by the PIXE and EDXRF are as shown in Figs. 1.29 and 1.30.

For PIXE analysis, carbon foil of $\sim 10\ \mu\text{g cm}^{-2}$ can be chosen as a matrix to make a self supporting target for water samples. The floating of the carbon foils is done in the water sample (which is to be analyzed) to assure the homogeneity in distribution of the trace elements. The water samples can also be prepared by depositing a few microliters on aluminized mylar or by filtering a pre-concentrated sample on nucleopore filter. Preconcentration is performed by taking 50 ml of each sample and adding $100\ \mu\text{l}$ of Pd ($1000\ \mu\text{g ml}^{-1}$) for internal standard. The solution is kept at pH 9 by adding NH_4OH . The metals are then precipitated as carbonates adding 1 ml diethyldithio carbonate (NaDDTC) solution. Pd diethyldithio carbonate is also formed in this reaction which is a stable complex and acts as a good co-precipitating agent. The precipitates thus obtained are collected by filtering on Nucleopore polycarbonate filter (pore size $0.4\ \mu\text{m}$, thickness $10\ \mu\text{m}$).

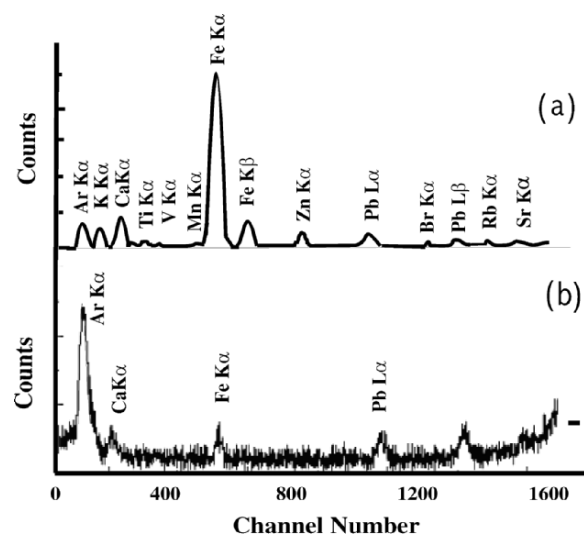


Fig. 1.30. (a) A typical EDXRF spectrum of aerosol sample and (b) the background spectrum from blank filter

Energy dispersive X-ray fluorescence (EDXRF) technique has been employed by Joshi et al. (2006) to determine the concentrations of different elements in water samples collected from different locations of famous Nainital Lake including tap water and spring water sample from Nainital (Uttaranchal). Lake Nainital is a constant source of drinking water for local people as well as tourists. A chelating agent (NaDDTC) was used for the preconcentration of the trace elements. Seventeen elements were detected. The concentrations of Na, Si, K, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Ag, Pb, and Bi were found to be within BIS/WHO limits.

1.12.5 For Archaeological Samples

A reliable knowledge of the composition of archaeological objects for major and trace elements is of primary interest for the archaeologists. The composition of the metal artifacts gives information on the ancient technological knowledge and helps to distinguish between prehistoric cultural traditions. Analytical work on gold jewellery of archaeological interest has been performed by Demortier (1996) with an emphasis to solders on the artifacts and to gold plating or copper depletion gilding using PIXE along with other ion-beam analytical techniques like RBS, NRA, and PIGE. On the basis of elemental analysis, these authors have identified typical workmanship of ancient goldsmiths in various regions of the world: finely decorated Mesopotamian items, Hellenistic and Byzantine craftsmanship, cloisonne of the Merovingian period, depletion gilding on Pre-Colombian tumbaga. Pieces of bronzes from two preroman sites in Spain with different cultural traits have been analyzed

by PIXE along with other ion beam analytical techniques like PIGE and RBS) and Auger electron Spectroscopy (AES) by Clement-Font et al. (1998) to extract complementary information on elemental composition and chemical state.

Motivated by the spread of Italian glass-working technology into central Europe, Šmit et al. (2000) conducted systematic investigation of the 16th century glasses of Ljubljana by using EDXRF and external beam PIXE methods due to their nondestructiveness. The manufacturing procedures were indicated by the Rb/Sr content in the glass i.e., the investigated glasses were mainly produced with the ash (not potash) of halophytic plants. PIXE analysis has been carried out by Río et al. (2006) on several mural paintings containing Maya blue from different Prehispanic archaeological sites (Cacaxtla, El Tajín, Tamuin, Santa Cecilia Acatitlán) and from several colonial convents in the Mexican plateau (Jiutepec, Totimehuacán, Tezontepec and Cuauhtinchán). The analysis of the concentration of several elements permitted to extract valuable information on the technique used for painting the mural, usually fresco. The trace element and Sr isotopic compositions of stoneware bodies made in Yaozhou and Jizhou were measured by Li et al. (2005) to characterize the Chinese archaeological ceramics and examine the potential of Sr isotopes in provenance studies. In contrast, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in Yaozhou samples have a very small variation and are all significantly lower than those of Jizhou samples, which show a large variation and cannot be well characterized with Sr isotopes. Geochemical interpretation reveals that $^{87}\text{Sr}/^{86}\text{Sr}$ ratios will have greater potential to characterize ceramics made of low Rb/Sr materials such as kaolin clay, yet will show larger variations in ceramics made of high Rb/Sr materials such as porcelain stone.

From the analysis of several archaeological samples by micro-PIXE, Neff and Dillmann (2001) have shown that ores containing important amount of phosphorus were used in ancient Europe to obtain iron by two different processes called the direct one and the indirect one. Phosphorus content was quantified as the heterogeneous phosphorus distribution was observed in the samples. The results confirm the fact that refining of phosphorus pig iron was possible with ancient refining processes. Moreover it seems that the phosphorus distribution ratio could be a discriminating factor to identify the iron making process.

Kumar (2002) has analyzed the pottery samples of Harrapan period collected from Sanghol (Dist. Ludhiana, Punjab, India). The absolute elemental concentration measurements were made by EDXRF measurements using Montanosoil and Brick clay as standards. The typical spectrum of pottery samples is shown in Fig. 1.31.

On the other hand, a typical PIXE spectrum of 13th century Iranian bowl taken in air using external beam is presented in Fig. 1.32. The two peaks each corresponding to Fe and Cu are their $K\alpha$ and $K\beta$ peaks, while the three peaks corresponding to Pb are its $L\alpha$, $L\beta$, and $L\gamma$ peaks. The presence of Argon peak in the spectrum is noteworthy.

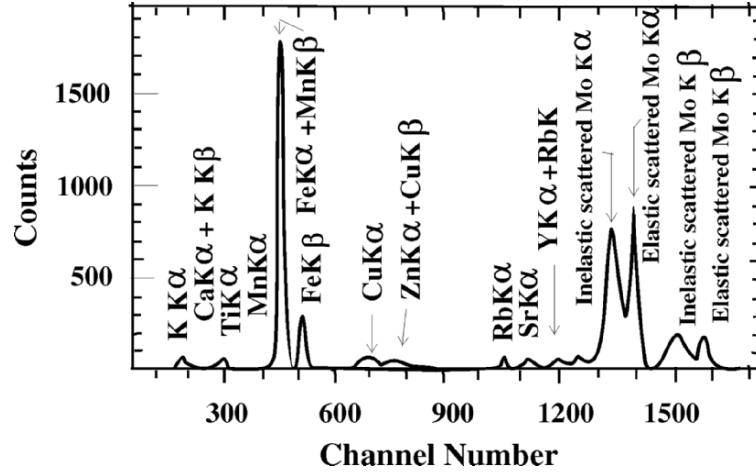


Fig. 1.31. Typical spectrum of pottery samples of Harrapan period collected from Sanghol (Kumar 2002)

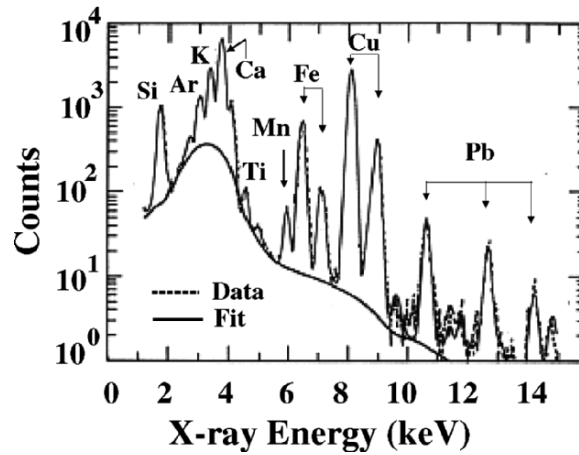


Fig. 1.32. A typical external beam PIXE spectrum of 13th century Iranian bowl taken in air. Note the presence of Argon (Ar) peak

Using a portable beam stability-controlled XRF spectrometer, Romano et al. (2005) have determined the concentrations of Rb, Sr, Y, Zr, and Nb in 50 fine potsherds from the votive deposit of San Francesco in Catania (Italy) by using a multilinear regression method in their bid for quantitative nondestructive determination of trace elements in archaeological pottery. A small portion of a few potsherds was even powdered in order to test the homogeneity of the material composing the fine pottery samples and the XRF data were compared with those obtained by chemical analysis of the powdered samples.

1.12.6 For Chemical Analysis of Samples

The X-rays emitted from valence band exhibit intensity, wavelength and line-shape changes as a function of the chemical composition. Thus XRF is a probe to examine the chemical state of the atoms (hence the electronic structure) on the surface. For example, XRF can help to determine the coordination number of Si-atoms in complex silicates by measuring the wavelength shift of the SiK α . X-ray fluorescence has been used to find the chemical composition of pigments and to analyze corrosion layers in-situ. Kawatsura et al. (2001) have used a wavelength-dispersive X-ray spectrometer system for particle-induced X-ray emission for chemical state analysis for various compound materials. High-resolution CuL $\alpha_{1,2}$ and L β_1 X-ray spectra from Cu, Cu₂O, and CuO targets are measured using this spectrometer system. The incident microbeam is focused 2.0 MeV protons with a beam size of $100 \times 30 \mu\text{m}^2$. The Cu L X-ray spectrum shows two main peaks and their satellites clearly. The main peaks are the L $\alpha_{1,2}$ and the L β_1 diagram lines, respectively. Due to a high detection efficiency of this spectrometer equipped with a position sensitive detector for soft X-rays, the intensity ratio L β_1 /L $\alpha_{1,2}$ is observable, which is the lowest for pure Cu metal, and the largest for CuO. Moreover, the L $\alpha_{1,2}$ X-ray spectrum for CuO shows a large shoulder at the high energy side of the main peak, which is considered to be due to the chemical bonding between Cu and O atoms.

Maeda et al. (2002) have developed a crystal spectrometer system for rapid chemical state analysis by external beam particle-induced X-ray emission. The system consists of a flat single crystal and a five-stacked position sensitive proportional counter assembly. Chemical state analysis in atmospheric air within several seconds to several minutes is possible. A mechanism for time-resolved measurements is installed in the system. Performance of the system is demonstrated by measuring the time-dependence of chemical shifts of sulfur K $\alpha_{1,2}$ line from marine sediment and aerosol samples. Earlier, Maeda et al. (1999) used a flat analyzing crystal and a position sensitive proportional counter to measure line shifts (with the precision of 0.1 eV) of Si K α and P K α X-rays from various samples for chemical state analysis of minor elements.

1.12.7 For Analysis of Mineral Samples

Proton-induced X-ray emission (PIXE) technique has been used to determine the distribution of minor and trace elements in magmatic Ni–Cu ores, volcanogenic massive sulphide Cu–Pb–Zn–(Ag–Au) ores and lode Au–(Ag) deposits. Minor elements of importance include possible by-products or co-products of metal refining, as well as deleterious impurities in mill-feed, e.g., Cd, In, Sn, As, Se, Te, Tl, and Hg. Weathering products of primary sulphide mineralization, including tropical laterites and other oxidized assemblages, were analyzed by Wilson et al. (2002) and found to contain a wide range of minor elements which reflect the bedrock style of mineralization. The iron

oxyhydroxide goethite, α -FeO(OH), contains trace levels of many elements, and in some cases 1 wt.% or more of base metals and arsenic, elements which are invisible in reflected-light microscopy. Other metals such as Ag are of sporadic occurrence in oxidized ores: they may be found as discrete mineral species, not incorporated into the dominant oxyhydroxides. The analysis of rare-earth bearing minerals has been done by Choi et al. (1996) using PIXE technique.

1.13 Comparison Between EDXRF and WDXRF Techniques

1.13.1 Resolution

Resolution is a very important parameter which describes the width (FWHM) of a spectral peak. The lower the resolution, the more easily an elemental line is distinguished from other nearby X-ray line. The resolution of the WDXRF system, which is dependant on the crystal and optics design, particularly collimation, spacing and positional reproducibility, varies from 2 to 10 eV at 5.9 keV. While the resolution in WDXRF depends on the diffracting crystal, the resolution of the EDX system is dependent on the resolution of the detector. This can vary from 150–200 eV for Si(Li) and HpGe and about 600 eV or more for gas filled proportional counter at 5.9 keV.

1.13.2 Simultaneity

EDXRF has the capability to detect a group of elements all at once while it is not possible with the WDXRF system.

1.13.3 Spectral Overlaps

Since the resolution of a WDXRF spectrometer is relatively high, spectral overlap corrections are not required. However, with the EDXRF analyzer, some type of deconvolution method must be used to correct for spectral overlaps as it has poor resolution. The spectral deconvolution routines however, introduce error due to counting statistics for every overlap correction onto every other element being corrected for. This can double or triple the error.

1.13.4 Background

The background radiation is one limiting factor for determining detection limits, repeatability, and reproducibility. Since a WDXRF system usually uses direct radiation flux, the background in the region of interest is directly

related to the amount of continuum radiation. However, the EDXRF system uses filters and/or targets to reduce the amount of continuum radiation in the region of interest, which is also resolution dependant, while producing a higher intensity X-ray peak to excite the element of interest. Thus although the WDXRF has an advantage due to resolution yet it suffers due to large background i.e., if a peak is one tenth as wide, it has one tenth the background. However, EDXRF counters with filters and targets can reduce the background intensities by a factor of ten or more.

1.13.5 Excitation Efficiency

Excitation efficiency is the main factor for determining detection limits, repeatability, and reproducibility. The relative excitation efficiency is improved by having more source X-rays closer to but above the absorption edge energy for the element of interest. WDXRF generally uses direct unaltered X-ray excitation, which contains a continuum of energies with most of them not optimal for exciting the element of interest. However, EDXRF analyzers may use filter to reduce the continuum energies at the elemental lines, and effectively increase the percentage of X-rays above the element absorption edge.

1.14 Comparison Between XRF and PIXE Techniques

Penetration Depths and Analytical Volume

The penetration depths and irradiation areas are totally different in PIXE and XRF. In XRF penetration depths are relatively large, of the order of a few millimeters while in PIXE analysis, the analytical depths are $\approx 10\text{--}50\text{ }\mu\text{m}$ because of the limited penetration of particles into the sample. Therefore PIXE analysis is essentially a surface technique even when applied to “thick” samples.

Excitation and Background Intensity

The background intensity distribution in XRF and PIXE spectra are opposite to each other (see Fig. 1.22) due to its dependence on the excitation cross-section. The PIXE excitation and ionization cross-sections of various elements decrease with increasing atomic number, while in X-ray photon excitation, the cross-section increase with increase atomic number. Since detection limits are largely controlled by the background intensity, EDXRF is a better technique for the determination of elements with low energy X-ray lines which fall especially in the range of 1–4 keV (Na through Ca), while PIXE is better for elements with relatively higher characteristic X-ray energies. For elements with atomic number greater than ≈ 50 , both techniques are forced to use L X-ray lines in place of K X-ray lines.

Energy Resolution

At energies lower than 20 keV, better energy resolution (FWHM) is achieved with wavelength dispersive X-ray fluorescence (WDXRF) as compared to proton-induced X-ray emission (PIXE) and energy dispersive X-ray fluorescence (EDXRF). While the FWHM using Si(Li) detector is ~ 160 eV, it is < 10 eV for WDXRF at 5.9 keV. Depending on the collimator (fine/extra-fine) and order of diffraction (first/second), the FWHM varies from 10 eV to 50 eV for LiF(220) crystal and from 10 eV to 70 eV for LiF(200) crystal at about 12 keV. However, the energy resolution with LiF(200) crystal is approximately equal to that of a Si(Li) detector system at energies around 20 keV.

Lower Limits of Detection

Since XRF and PIXE spectra have their low background regions at opposite parts of the spectrum, this condition raises the minimum detectable concentration for the lower- Z regions of each excitation group in XRF, whereas in PIXE the limits are raised for the heavier elements within each group detected by the various proton energies. These trends make XRF more favorable for elements having their absorption edges close to the exciting energies. They provide a great advantage, e.g., in the analysis of Ba and Ti, employing a fluoresce plate of rare-earth element heavier than Ce would yield a rather high sensitivity for $K\alpha$ (Ba).

In PIXE analysis, using proton beam of 1-3 MeV for most favored elements in low- Z matrices and thin targets, the best sensitivities down to 0.1 ppm have been obtained. These levels are achieved for elements near $Z = 40$ using K lines and $Z = 80$ using L lines. For elements with Z values different from 40 and 80 the LLDs increase rapidly to ~ 100 ppm and are > 100 ppm for $Z < 20$. For thick targets and $Z < 20$ most matrices yield LLDs that are generally lower than 100 ppm and can be as low as 1 ppm under favorable conditions (absolute detection limits down to 10^{-12} g and relative detection limit down to $0.1 \mu\text{g g}^{-1}$). Compared to XRF, the detection limit offered by PIXE is better by one order of magnitude.

Similar LLDs are found in XRFs although LLDs for $Z < 20$ are very much lower than those attainable by PIXE. Using WDXRF it is now possible to obtain LLDs in the range of 50–200 ppm for elements F through B.

Flexibility

Since the equipment used in XRF technique including radioisotope source is portable, the energy dispersive XRF spectrometers are used in various divergent fields like that in the metal industry, in gold mines, in oilfields for oil analysis (to determine sulfur in petroleum products and residual catalysts, monitor additives in lubricating oils, analyze regular wear metal in lubricants

and analyze wear debris) and for field testing for Lead and heavy metals in soil, etc. Although they have the potential to detect the full spectrum of XRF energies, the analytical performance is optimized by modifying the excitation efficiency so that specific group of elements in particular energy range of the fluorescence spectrum, can be preferentially excited and detected. These modifications include the use of primary beam metal foil filters (which modify the source spectrum reach in the sample to optimize the detection characteristics) and a number of developments in excitation geometry. Furthermore, it is possible to use the selective excitation method i.e., choosing the excitation energy less than the undesired X-rays of the particular element but more than the desired X-ray line energies. This helps to avoid the unnecessary X-ray lines in the spectrum thus simplifying the analysis. Thus, the person working with the analysis of samples by X-ray fluorescence (XRF) technique, has to adopt considerable flexibility of instrumental variables such as excitation voltage, X-ray tubes, collimators, crystals and detectors, pulse height selection but he has no flexibility as regards geometry of the spectrometer.

The PIXE analyst has less flexibility as regards detectors and excitation source but there is flexibility in choice of ion type, beam energy, sample support, and considerable flexibility in changing the geometry of the system. The sample is normally placed in a chamber inside the accelerator vacuum for direct excitation. However, the proton beam may be allowed to pass out of the beam tube through a thin window with negligible energy loss to produce a so-called external beam. (Beam have been extracted into air through Ni-foils, Be-foils, Al-foils, Kapton-foils, and through W-foils). The sample can then be placed directly in the external beam under normal pressure which although having certain disadvantages provided a very useful method for analyzing large, unusually shaped sample for which normal sample preparation techniques are unacceptable. The external beam PIXE method has been employed by Räsänen (1986) for typically thick organic, biomedical, bone and geological samples. The external beam PIXE makes it a very flexible technique for experimentation.

Applications

XRFs has been applied in a wide variety of fields for both qualitative and quantitative analysis e.g., exploration, mining and processing of minerals and materials, forensic and metallurgical fields. Most PIXE applications have been in the analysis of thin samples in which matrix effects are minimal or non-existent e.g., in the fields of biology, mineralogy, medicine, geochemistry, materials science, archaeological, environment, and geology.

Some specific problems undertaken include location of heavy metals in soil specimens due to application of sewage sludge, trace element profiling in electrical insulators, analysis of air particulate collected at urban locations, multilayer thin film analysis of solar cells.

1.15 Conclusion

Both XRF and PIXE techniques are capable of providing accurate and precise data when correctly applied to a suitable type of sample. Because X-rays are more penetrating than protons, the XRF technique samples a greater depth in a thick sample. However, the greater sampling depth requires more extensive corrections for interelement and matrix effects. One of the major problems facing PIXE analysis of thick samples is the extremely small analytical volume. Although PIXE is superior to XRF because the entire range of elements in a sample can be excited by high-energy protons without contributing a high background to the spectrum yet both have limitation of analyzing elements with $Z < 11$ due to Si(Li) detector. WDXRF can, however, be employed for the detection of ^{99}F . In XRF, the X-ray source must be filtered to remove bremsstrahlung in the region of the spectrum where the analytical X-ray lines occur. Therefore, the use of several excitation conditions is required for the XRF analysis of elements in different ranges of atomic number. Also, the high background found in XRF spectra raises the detection limit. The best obtainable detection limits vary between 10 and 100 ppm for solid samples. The WDXRF, however, is the better technique for the detection of elements with low energy lines, especially in the range 1–4 keV (Na through Ca) and when bulk or thick samples must be analyzed. WDXRF with its superior spectral resolution at medium to low energies can provide information on the chemical state in a sample of a number of elements e.g., Br, Se, As, Cr, S, and Al. PIXE is best applied to the analysis of thin samples when limited amounts of sample are available and/or when the analytic elements are present in very low concentration (less than 1–10 ppm), when analysis of only the surface layers is required and when low detection limits are necessary for elements with atomic numbers close to 40 and 80. Portable EDXRF systems provide the ability to take the spectrometer to the sample, thereby providing a powerful tool for field survey investigations.

Rutherford Backscattering Spectroscopy

2.1 Introduction

Rutherford backscattering spectroscopy technique is also one of the analytical techniques, which makes use of the accelerators. It is an important tool for material analysis and provides a powerful method to give depth distribution of the impurity element in ppm contained in the thin surface region of a sample. It is based on the phenomenon of Rutherford scattering. It is also called RBS, for Rutherford backscattering spectrometry (RBS). This method of analysis is based on the detection of the charged particles elastically scattered by the nuclei of the analyzed sample and can be indicated by $Y(a, a)Y$. RBS measures the energy of charged (usually alpha) particles that are backscattered (180° scattering geometry) off a sample. The amount of energy loss in the collision with the atomic nuclei depends on atomic number Z of each element present in the target material.

Although the RBS measurements can be termed as more accurate and realistic only in the backward direction yet the practical measurements usually include the scattering in the backward as well as in the forward direction and also the scattering with non-Rutherford cross-sections (cross-sections become non-Rutherford if nuclear forces become important – it happens at high-incident energies, high-scattering angles, and low-atomic number of the target). Thus the name RBS in such cases is badly selected name and RBS is sometimes called Particle Elastic Scattering (PES).

The RBS technique is widely used for near-surface layer analysis of solids and is useful to determine the profile of concentration vs. depth for heavy elements in a light material as a function of the detected energy. RBS using deuteron beam has been found to be a useful compromise between proton and α -particle RBS for the thicker layers often encountered in art and archaeology (Barfoot 1986).

While using PIXE, the multielement analysis is possible over a wide range of elements in a depth region, the RBS technique has an edge over PIXE technique in those cases where the depth distribution of one or more elements

is of interest (analyzed depth $2\text{ }\mu\text{m}$ for Helium ions and $20\text{ }\mu\text{m}$ for protons). The other method of profiling impurities is the use of nuclear reactions (NRA), which is limited to certain light elements.

2.2 Scattering Fundamentals

2.2.1 Impact Parameter, Scattering Angle, and Distance of Closest Approach

When a collimated beam of intensity I_0 particles $\text{cm}^{-2}\text{s}^{-1}$ (called the *flux*) falls on a target in the form of a thin foil, the incident particles get scattered from the scattering centers and the target atoms get recoiled as shown in Fig. 2.1. Since the force (Coulomb) between the target nucleus and the impinging α -particles is repulsive and follows inverse square law, it causes the path of a scattered α -particle to be a hyperbola. The angle between the asymptotes of the hyperbola is the angle of scattering θ . The scattering angle depends on a quantity called impact parameter b . The impact parameter is the perpendicular distance from the nucleus to the line that the incident α -particle would have followed if it had not been scattered.

Consider that a projectile having charge Z_1 and mass M_1 , moving with velocity v_1 (having kinetic energy E_0) is scattered from target nucleus of charge Z_2 and mass M_2 (at rest). It has been well established from the laws of conservation of energy and momentum, that the impact parameter (b) is given by

$$b = \frac{(Z_1 e)(Z_2 e) \cot(\theta/2)}{4\pi\epsilon_0 M_1 v_1^2} \quad (2.1)$$

The distance of closest approach or collision diameter d of the incoming particle, for head-on collision with the target nucleus is given by

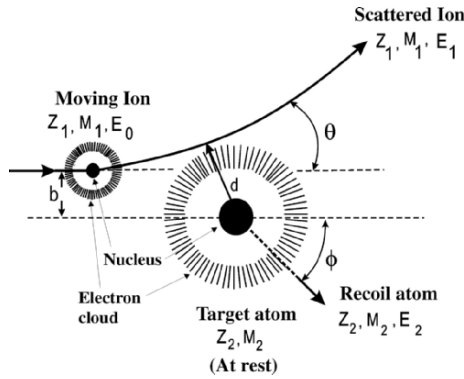


Fig. 2.1. Scattering of moving ion (Z_1, M_1) of energy E_0 by the target atom (Z_2, M_2)

$$d = \frac{Z_1 Z_2 e^2}{4\pi\epsilon_0} \frac{1}{E_0} \quad (2.2)$$

For backscattering to occur, the projectile and target must get close enough together such that the distance of closest approach is within the K-shell radius, and that is why we can ignore the electrons.

From (2.1) and (2.2), we get

$$b = \frac{d}{2} \cot(\theta/2) \quad (2.3)$$

where b is the impact parameter and d is the distance of closest approach.

Since there is a finite probability of scattering in different directions, the impinging particles can go anywhere after scattering. This is also because of the reason that it is not possible to aim impinging particles at a target nucleus to get a given value of impact parameter b , the problem of scattering can be handled statistically by drawing a ring of radius b and width (db) around each nucleus as discussed in Section “Differential scattering cross-section.”

2.2.2 Kinematic Factor

For scattering at the sample surface, the only energy loss mechanism is momentum transfer to the target atom. The ratio of the projectile energy after a collision to the projectile energy before a collision is defined as the kinematic factor. In other words, the energy fraction (E_1/E_0) transferred from primary to scattered particles, governed by the laws of conservation of energy and momentum, is given by the kinematic factor K . There is much greater separation between the energies of particles backscattered from light elements than from heavy elements because a significant amount of momentum is transferred from the incident particle to a light target atom. As the mass of the target atom increases, less momentum is transferred to the target atom and the energy of the backscattered particle asymptotically approaches the incident particle energy. This means that RBS is far more useful for distinguishing between two light elements than it is for distinguishing between two heavy elements. RBS has good mass resolution for light elements but poor mass resolution for heavy elements. However, the lighter elements than the incident particle cannot be detected as these elements will scatter at forward trajectories with significant energy.

To derive the relation for the kinematic factor, it is assumed that the interaction is elastic, projectile energy E_0 is much larger than the binding energy of the atom in the target and the nuclear reactions and resonance must be absent. The Kinematic factor $K(\theta, M_1, M_2)$ is given by the relation

$$K(\theta, M_1, M_2) = \frac{E_1}{E_0} = \left(\frac{(M_2^2 - M_1^2 \sin^2 \theta)^{1/2} + M_1 \cos \theta}{M_1 + M_2} \right)^2 \quad (2.4)$$

Note that the relationship for elastic scattering involving the ratio of scattered particle energy E_1 to the incident particle energy E_0 , is independent of incident energy. So K is a function of the mass ratio, $x = M_1/M_2$, and of the scattering angle θ . Kinematic factor K increases as ratio R decreases for a fixed scattering angle.

Special cases: The kinematic factors for $\theta = 180^\circ$ and $\theta = 90^\circ$ are given by the following relations:

$$K(\theta = 180^\circ) = \left(\frac{M_2 - M_1}{M_2 + M_1} \right)^2 = \left(\frac{1 - x}{1 + x} \right)^2 \quad (2.5)$$

$$K(\theta = 90^\circ) = \left(\frac{M_2 - M_1}{M_2 + M_1} \right) = \left(\frac{1 - x}{1 + x} \right) \quad (2.6)$$

The Kinematic factor for a few target elements (M_2) due to ^4He projectile are given in Table 2.1.

The variation of kinematic factor with mass M_2 and scattering angle is as shown in Fig. 2.2. Since the identification of a particular element in the sample

Table 2.1. Kinematic factors K_{M_2} for ^4He projectile and a few target masses M_2

Atomic mass M_2 (amu)	Scattering angle				
	180°	170°	150°	120°	90°
10	0.1834	0.1857	0.2044	0.2777	0.4283
30	0.5846	0.5869	0.6059	0.6683	0.7646
50	0.7255	0.7273	0.7412	0.7860	0.8518
70	0.7954	0.7967	0.8076	0.8422	0.8918
90	0.8369	0.8381	0.8470	0.8750	0.9148

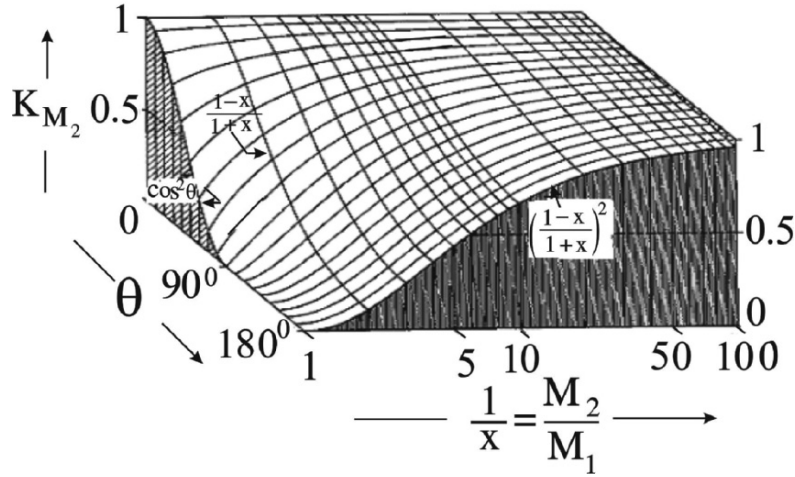


Fig. 2.2. Variation of kinematic factor with target mass M_2 and scattering angle θ

is made on the basis of the kinematic factor (and hence the backscattered energy), the backscattered energy is thus equivalent to a mass scale.

2.2.3 Stopping Power, Energy Loss, Range, and Straggling

When an incident particle penetrates a material, it loses its energy interacting with sample atoms. The interactions are usually divided into two separate processes, namely energy loss in elastic collisions with sample atom nuclei (nuclear stopping power) and inelastic collisions with electrons (electronic stopping power). The nuclear energy loss dominates in the low-velocity (energy) region but electronic energy loss is much larger at high velocities. In the energy range of 1–3 MeV/u, the energy loss is mainly due to interaction of the ions with the electrons in the material, causing excitation and ionization of the target atoms. A particle, which backscatters from an element at some depth in a sample, will have measurably less energy than a particle that backscatters from an element on the sample surface. If the atomic density (atoms cm^{-3}) of a target material is known, an energy loss in units of keV nm^{-1} can be used in ion beam analysis. The energy loss per unit path length is commonly called stopping power of the target material for a penetrating ion, despite the fact that it really is a resistive force instead of power. If the density of a material is not known, the density independent stopping cross-sections in unit eV per (10^{15} atoms cm^{-2}) are used in the analysis.

The amount of energy a projectile loses per distance traversed in a sample depends on the projectile, its velocity, the elements in the sample, and the density of the sample material. Typical energy losses for 2 MeV Helium range between 100 and 800 eV nm^{-1} . The observed energy loss divided by the average path length in the target ($\Delta E/\Delta x$) corresponds to a good approximation to the stopping power ($-dE/dx$) at the “average energy” defined by $E = E_0 - \Delta E/2$, where E_0 is the incident energy. The Bethe–Bloch formula for the stopping power is written as

$$-\frac{dE}{dx} = \frac{4\pi e^4 Z_1^2}{mv_1^2} \cdot \frac{N_0 Z_2}{A} \left(\ln \frac{2mv_1^2}{I} + \ln \frac{1}{1-\beta^2} - \beta^2 - \frac{C}{Z_2} + Z_1 L_1 + \Phi \right) \quad (2.7)$$

where e is the elementary charge, m is the electron mass, Z_1 and v_1 are the atomic number and the velocity of the projectile, Z_2 and A are the atomic number and the atomic weight of the target, N_0 is the Avogadro number, β is equal to v/c . The symbol I is the mean excitation energy, C/Z_2 is the shell correction, Φ is the Bloch correction, and $Z_1 L_1$ is the Barkas correction. Since the projectile mass is not included in the theoretical formula, the stopping power of matter is expected to be precisely equal for protons, deuterons, and other particles of the same $E \times M_p/M$ values (where E is the projectile energy, M_p is the proton mass and M is the projectile mass).

Fitting of the data with the analytical formulas (Verelas and Biersack 1970) can be written as

$$\begin{aligned} S_{\text{Low}} &= A_1 E^{1/2} \quad \text{and} \\ S_{\text{High}} &= \frac{A_2}{E} \ln \left(1 + \frac{A_3}{E} + A_4 E \right) \end{aligned} \quad (2.8)$$

where A_1 , A_2 , A_3 , and A_4 are fitting constants. The stopping power (S) from these low energy (S_{Low}) and high energy (S_{High}) stopping is calculated as

$$S = \frac{S_{\text{Low}} \times S_{\text{High}}}{S_{\text{Low}} + S_{\text{High}}} \quad (2.9)$$

By evaluating the stopping powers on inward and outward paths, one can determine the correlation between depth and energy which indicates that a good depth resolution requires not only a good detector energy resolution but also a well-defined energy of impinging particles. The depth resolution is also limited by the spread in energy loss on both paths in the target – which is termed as energy straggling and is caused by statistical fluctuations in the number and kind of encounters that an energetic particle undergoes when traveling in matter. For thin layers, the amount of energy straggling is considered to be proportional to the square of the energy loss, hence the depth resolution will deteriorate with increasing depth.

The range R of a charged particle in matter can be calculated using the relation

$$R = \int_0^{E_1} \frac{dE}{S(E)} \quad (2.10)$$

where $S(E)$ is the stopping power and E_1 is the initial energy of the charged particles. The ranges of a particle in two different materials of densities ρ_1 and ρ_2 and atomic masses M_1 and M_2 respectively, are related to each other by the semiempirical relation

$$\frac{R_1}{R_2} = \frac{\rho_2}{\rho_1} \sqrt{\frac{M_1}{M_2}} \quad (2.11)$$

The ranges of different particles (same initial velocity) for the same material can be compared by using the relation

$$\frac{R_1}{R_2} = \frac{M_1}{M_2} \frac{Z_2^2}{Z_1^2} \quad (2.12)$$

where Z and M are the atomic numbers and masses of the particles.

The first unified approach to the theory of stopping and ranges was made by Lindhard et al. (1963) and is known as LSS theory and is based on statistical models of atom–atom collisions. The primary advances were made by applying numerical methods. Rousseau et al. (1970) incorporated the more realistic Hartree–Fock atoms into the theory. The stopping and ranges of ions

in solids, calculated with an average accuracy of better than 10% for medium energy heavy ions and to better than 2% for high-velocity light ions have been presented by Ziegler et al. (1985). The functional shape of this most widely used parameterizations is based on the extensively studied experimental stopping powers reported for H^+ -ions. When the velocity of a heavy ion is increased, it loses its electrons and becomes more and more positively charged. At high velocities the ions become totally stripped from electrons. On the basis of the theory by Brandt and Kitagawa (1982), Ziegler et al. (1985) have given a semiempirical parameterizations (ZBL parameterization) for the calculation of the electronic stopping powers for every ion in every material. In solids, one observes an increased charge of fast ions due to the high-collision frequency (which exceeds the frequency of Auger and radiative decays). The electrons in the excited states are stripped off before they may decay to the ground state. A comparison of the calculations of effective charges in ion-atom collisions has been made by Hock et al. (1985). Schiweietz and Grande (2001) have given the improved charge state formulas in gaseous and solid targets. For helium ions the stopping power is the equivalent hydrogen stopping at the same velocity multiplied by the effective charge of He ions at the velocity in question. The stopping powers are always scaled to velocities, not to energies. The effective charge is calculated with a parameterization, which is obtained by fitting all the available experimental H and He stopping power data to a constructed function.

For heavy ions the stopping power curve can be divided into three different velocity regions (1) very low velocities, where the stopping powers are proportional to the ion's velocity, (2) high velocities, where the proton stopping powers can be scaled to obtain heavy ion stopping powers, and (3) a medium velocity region between the low-velocity and the high-velocity regions. The medium velocity region requires the most complex theory. Most of the detected light atoms lose their energy in the high-velocity region. Santry and Werner (1980, 1981) have measured stopping powers of a few elements for He-ions and deuterons. From a large collection of stopping power data, Paul and Schinner (2001) have given an empirical approach to the stopping power of solids and gases for ions from ${}^3\text{Li}$ to ${}^{18}\text{Ar}$.

2.2.4 Energy of Particles Backscattered from Thin and Thick Targets

Let M_1 and E_0 be the mass and energy of the incident particles, which are backscattered with energy E_1 and detected at an angle θ (obtuse angle), while the energy transferred to the target element of mass M_2 be E_2 (recoil at angle $180-\theta$). For general case, if θ_1 and θ_2 are the angles between the sample normal and the direction of the incident beam and of the scattered particle, respectively, and are always positive regardless of the side on which they lie w.r.t the normal of the sample, the formulas for various parameters (usable in the analysis) using Fig. 2.3, are given as follows.

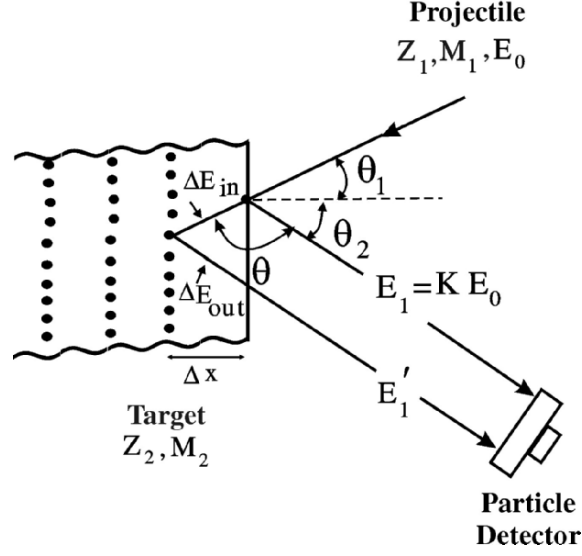


Fig. 2.3. Schematic diagram used for the derivation of formulas for energy loss of projectile ion in a target material

Backscattered (detected) energy from a thin target

$$E_1 = K E_0 \quad (2.13)$$

Backscattered (detected) energy from a thick target

$$\begin{aligned} E'_1 &= K (E_0 - \Delta E_{in}) - \Delta E_{out} = K E_0 - \Delta E_{in,out} \\ &= K \cdot E_0 - \left[\frac{K}{\cos \theta_1} \cdot \left(\frac{dE}{dx} \right)_{in} + \frac{K}{\cos \theta_2} \cdot \left(\frac{dE}{dx} \right)_{out} \right] \cdot x \end{aligned} \quad (2.14)$$

Energy loss (thick target)

$$\Delta E_{in,out} = K \Delta E_{in} + \Delta E_{out} \quad (2.15)$$

Energy loss factor

$$[S] = \frac{\Delta E}{\Delta x} = \frac{(K E_0 - E_1)}{dx} = \left[\left| \frac{K}{\cos \theta_1} \left(\frac{dE}{dx} \right) \right|_{in} + \left| \frac{1}{\cos \theta_2} \left(\frac{dE}{dx} \right) \right|_{out} \right] \quad (2.16)$$

For normal incidence θ_1 will be zero and hence (2.14) and (2.16) will change accordingly. In these equations, energy $K E_0$ is the edge of the backscattering and corresponds to the energy of particles scattered from atoms at the surface of the target. The energy E_1 is the measured value of a particle scattered from an atom at depth x . The subscripts “in” and “out” attached to ΔE refer to the energies at which dE/dx is evaluated.

2.2.5 Stopping Cross-Section

The energy loss dE/dx is considered to be an average over all possible energy-dissipative processes activated by the projectile on its way past a target atom. To interpret dE/dx as the result of independent contribution of every atom exposed to the beam i.e., equal to $S_A \cdot N \cdot \Delta x$, where S_A is the target area illuminated by the beam, N is the atom density of the target, and Δx is the target thickness. Considering the energy loss $\Delta E = (dE/dx)\Delta x$, we can set ΔE proportional to $N\Delta x$ and define the proportionality factor as the stopping cross-section ε , which is measured in the units of eV cm^2 . Thus

$$\varepsilon \equiv \frac{1}{N} \frac{dE}{dx} \quad (2.17)$$

Referring to Fig. 2.3, one can easily visualize that when the incident projectile gets scattered from an atom inside the target material (instead of the atom at the surface), the stopping cross-section factor is given by

$$[\varepsilon] = \left[\frac{K}{\cos\theta_1} \varepsilon_{\text{in}} + \frac{1}{\cos\theta_2} \varepsilon_{\text{out}} \right] \quad (2.18)$$

where the subscripts have their usual meaning.

The ^4He stopping cross-sections for a few elements at a few selected energies are given in Table 2.2.

2.2.6 Rutherford Scattering Cross-Section

Differential scattering cross-section

We have studied in Sect. 2.2.1 that there is a finite probability of scattering of α -particle from a target nucleus in a particular directions, the impinging particles can go anywhere after scattering i.e., it can get scattered in the forward direction ($\theta < 90^\circ$) and also in the backward direction ($\theta > 90^\circ$) as shown in Fig. 2.4. The probability value (called differential cross-section) depends on the angle of scattering.

Table 2.2. ^4He stopping cross-sections for a few elements at various energies (in 10^{-15} eV cm^2)

Element (Z)	Energy of ^4He (in MeV)				
	0.4	1.0	1.6	2.4	3.2
C (6)	33.32	36.19	29.72	23.1	19.0
Al (13)	55.39	52.43	47.5	40.38	34.96
Fe (26)	80.15	86.13	78.65	66.57	59.60
Ag (47)	88.03	116.2	100.0	86.66	78.52
Ta (73)	105.8	121.8	113.1	98.96	88.4
U (92)	150.7	166.6	150.3	129.5	115.2

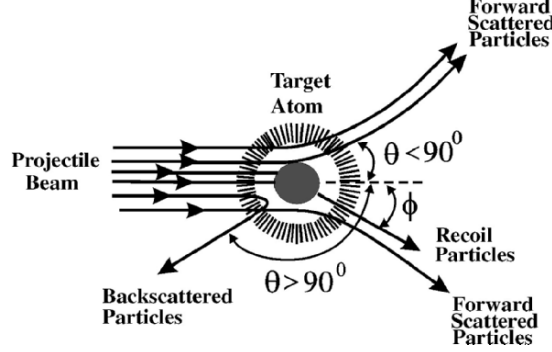


Fig. 2.4. Schematic diagram showing the forward and backward scattering of projectile from a target

The cross-section, as its name suggests, is the effective area for collision. The cross-section of a spherical target is $\sigma = \pi r^2$. In aiming a beam of particles at a target (which is much smaller than the beam), as in the Rutherford scattering experiment, the scattering process is treated statistically in terms of the cross-section for interaction with a nucleus.

To derive the formula for Rutherford scattering cross-section, only purely classical approach has been adopted and it is assumed that (1) the charges are point-like, (2) only the Coulomb force acts, (3) scattering is elastic and (4) target nucleus does not recoil (has infinite mass). The scattering cross-section which is the probability of being scattered through an angle, $\theta \pm d\theta$, is equal to the probability of having an impact parameter, $b \pm db$, which is further equal to the area around the target that has the impact parameter, $b \pm db$, times the number of scattering atoms (assuming no overlapping) divided by the total area of the target (or of the beam). The differential cross-section for Rutherford scattering is thus obtained by asking into what solid angle particles will be scattered if they are incident at impact parameters between b and $(b + db)$. The chance of having the impact parameter between b and $(b + db)$ is proportional to the cross-sectional area of the ring (annulus) of thickness db , which is $d\sigma = 2\pi b(db)$, as shown in Fig. 2.5.

For a simple unmovable nucleus placed on the path of the ion beam of intensity equal to N particles $\text{cm}^{-2} \text{s}^{-1}$, the number of the ions scattered in the angle interval from θ to $\theta + d\theta$ (or impact parameter between 'b' and 'b + db') is

$$dN = 2\pi b(db)N$$

By definition, the differential cross-section $d\sigma$ is equal to dN/N of the initial particle flux N scattered into the given solid angle $d\Omega$. Referring to the scattering geometry shown in Fig. 2.4, the Rutherford differential scattering cross-section will be the relative number of particles backscattered ($\theta > 90^\circ$) from a target atom into a given solid angle for a given number of incident particles per unit surface.

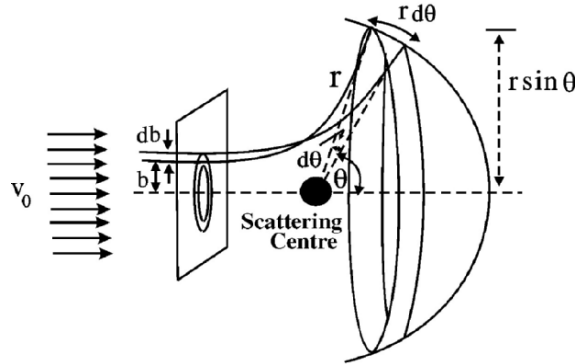


Fig. 2.5. Dependence of scattering on impact parameter b

$$\begin{aligned} \frac{d\sigma}{d\Omega} &= \frac{\text{Number of particles scattered per unit time into solid angle } d\Omega}{\text{Number of particles incident per unit time per unit area}} \\ \text{i.e., } \frac{d\sigma}{d\Omega} &= \frac{\text{Scattered flux/unit of solid angle}}{\text{Incident flux/unit of surface}} \end{aligned} \quad (2.19)$$

Thus, the value $d\sigma = dN/N = 2\pi b \, db$ is the differential cross-section.

The angle of scattering in Rutherford scattering depends upon the impact parameter, with larger deflection occurring for smaller impact parameters. The area of a circle of radius b ($=$ impact parameter) is then the cross-section for scattering above the angle associated with b , since any particle arriving with r less than b will scatter to a larger angle. Since $M_1 \ll M_2$, the center of mass frame *coincides* with the laboratory frame (see Appendix B). As a general case, if the incident energy is 'E', the dependence of scattering angle θ on the impact parameter b , can be expressed (as 2.1) by

$$b = \frac{Z_1 Z_2 e^2}{4\pi\epsilon_0 M_1 v_1^2} \cot(\theta/2) = \frac{Z_1 Z_2 e^2}{8\pi\epsilon_0 E} \cot(\theta/2) \quad (2.20)$$

Since the impact parameter has a one-to-one relation with the scattering angle, one can express $d\sigma$ *in terms of the scattering angle* as well. Putting the values of b from (2.20) and taking its derivative for db , we get

$$\begin{aligned} d\sigma &= 2\pi b(db) = 2\pi \left(\frac{Z_1 Z_2 e^2}{4\pi\epsilon_0 \cdot 2E} \right)^2 \cot(\theta/2) \operatorname{cosec}^2(\theta/2) d\theta \\ &= 2\pi \left(\frac{Z_1 Z_2 e^2}{8\pi\epsilon_0 E} \right)^2 \frac{1}{2} \frac{\cos(\theta/2)}{\sin^3(\theta/2)} d\theta \\ &= \left(\frac{Z_1 Z_2 e^2}{8\pi\epsilon_0 E} \right)^2 \frac{1}{4} \frac{2\pi 2\sin(\theta/2)\cos(\theta/2) d\theta}{\sin^4(\theta/2)} \\ d\sigma &= \left(\frac{Z_1 Z_2 e^2}{16\pi\epsilon_0 E} \right)^2 \frac{d\Omega}{\sin^4(\theta/2)} \end{aligned} \quad (2.21)$$

The $d\Omega = 2\pi \sin\theta d\theta$ is just the infinitesimal solid angle i.e., it is an infinitesimal fraction of the surface of the unit sphere, corresponding to a ring (annulus) of thickness $d\theta$ at an angle θ from the x -axis. This is exactly the area where the projectile will scatter if the impact parameter lies between b and $b + db$. Then $d\sigma$ can be interpreted as the area that is to be hit so that the α -particle would scatter into solid angle $d\Omega$. Such an area is called a *differential cross-section*. It is cross-section, because it plays the role of a cross-section of a ball that blocks the path of a projectile. It is called differential, because we specify a differential angle range for the scattered particle. The differential scattering cross-section has units of area per steradian, and specifies the effective target area for scattering into a given range of solid angle.

From (2.21), the differential scattering cross-section in the center of mass system can be written by denoting the energy as E_c and scattering angle as θ_c

$$\left(\frac{d\sigma}{d\Omega}\right)_c = \left(\frac{Z_1 Z_2 e^2}{16\pi\epsilon_0 E_c}\right)^2 \frac{1}{\sin^4(\theta_c/2)} \quad (2.22)$$

The differential scattering cross-section in the laboratory frame (see Appendix B for conversion from center-of-mass system to laboratory system) is given by

$$\left(\frac{d\sigma}{d\Omega}\right)_{lab} = \left(\frac{Z_1 Z_2 e^2}{8\pi\epsilon_0 E}\right)^2 \cdot \frac{1}{\sin^4 \theta} \cdot \frac{[M_2 \cos \theta + (M_2^2 - M_1^2 \sin^2 \theta)^{1/2}]^2}{M_2 \times (M_2^2 - M_1^2 \sin^2 \theta)^{1/2}}$$

For $M_2 \gg M_1$

$$\left(\frac{d\sigma}{d\Omega}\right)_{lab} = \left(\frac{Z_1 Z_2 e^2}{16\pi\epsilon_0 E}\right)^2 \frac{1}{\sin^4(\theta/2)} \quad (2.23)$$

Since the differential cross-section is the quantity an experimentalist would measure, it can be easily translated to numbers. Suppose a detector having surface area $A (= \pi r^2$ where r is its radius) is placed at a distance R away from the target. As mentioned earlier, $d\Omega$ is segment of the unit sphere at angle θ from the direction of the incoming beam. To get the solid angle corresponding to area A one has to consider the ratio $A/d\Omega = 4\pi R^2/4\pi = R^2$. In other words, $d\Omega = A/R^2$. Using $d\sigma = dN/N$, we can write

$$dN = \left(\frac{Z_1 Z_2 e^2}{16\pi\epsilon_0 E}\right)^2 \frac{ntAN/R^2}{\sin^4(\theta/2)} \quad (2.24)$$

where dN is the number of particles detected in area A per unit time (called yield i.e., detected counts per second) and N is the number of particles hitting the target on unit area in unit time. Equation (2.24) is a direct relation between measured quantities in which N was introduced because without N the formula would tell us the scattering probability for the case if there is only one target atom per unit area. Quantity “nt” in (2.24) is the number of atoms in the target atoms per unit area.

For small angles, (2.23) is remarkably good when laboratory angles and energies are used. Two important results (as shown in Fig. 2.6) are noteworthy

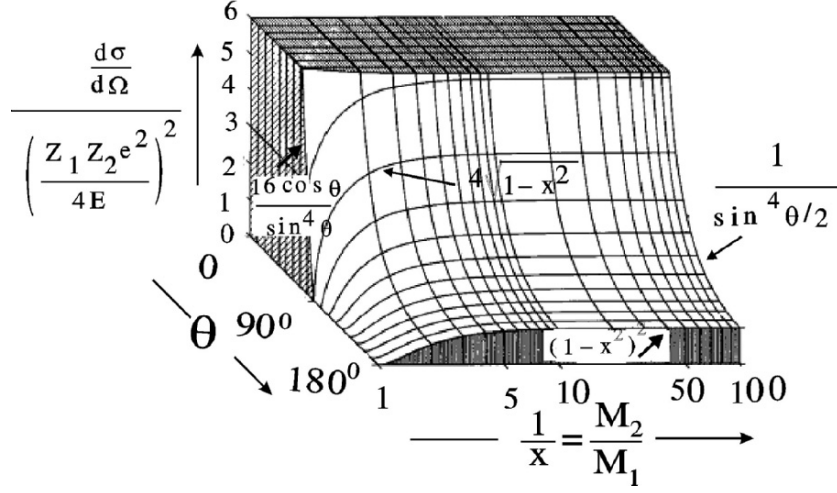


Fig. 2.6. Variation of $d\sigma/d\Omega$ with mass ratio (M_2/M_1) and $\sin^4(\theta/2)$

- (1) Rutherford scattering is very forward peaked, going as $1/\sin^4(\theta/2)$ at forward angles and (2) Rutherford scattering rises with decreasing energy as $1/E^2$.

The differential scattering cross-section allows calculating the absolute concentrations and is proportional to the square of the atomic number of the projectile (Z_1^2), square of the atomic number of the target (Z_2^2), and inversely proportional to the square of the incident energy (E^2).

Average differential scattering cross-section can be written as

$$\left(\frac{d\sigma}{d\Omega}\right)_{\text{av}} = \frac{1}{\Omega} \left(\int_{\Omega} \frac{d\sigma}{d\Omega} d\Omega \right) \quad (2.25)$$

Total scattering cross-section

The cross-section, which is a measure of the effective surface area seen by the impinging particles, expressed in units of area i.e., m^2 or barn ($1 \text{ barn} = 10^{-28} \text{ m}^2$), is the *integral cross-section* i.e., the integral of the differential cross-section on the whole sphere of observation (4π steradian). The total scattering cross-section is obtained if one integrates a differential cross-section over all angles then one obtains the *total scattering cross-section*. The *total scattering cross-section* is thus the integral of the differential cross-section over all solid angles, defined as

$$\sigma = \int \frac{d\sigma}{d\Omega} d\Omega = \frac{\text{Number scattered per unit time}}{\text{Number incident per unit time per unit area}} \quad (2.26)$$

and measures the effective target area for scattering in *any* direction.

The cross-section is a measure of the probability that an interaction occurs; the larger the cross-section, the greater the probability that an interaction will take place when a particle is incident on the target. In general, the cross-section depends on the initial and final states of both the target and the projectile (including energy, spin, angle of scatter, etc.). To calculate the cross-section, knowledge of the dynamics (nature of interaction) is required.

The Rutherford (scattering) cross-section can be calculated by integrating over the total solid angle and is given by

$$\sigma_R(E, \theta) = \left(\frac{Z_1 Z_2 e^2}{8\pi\epsilon_0 E} \right)^2 \frac{1}{\sin^4 \theta} \frac{\left[M_2 \cos \theta + (M_2^2 - M_1^2 \sin^2 \theta)^{1/2} \right]^2}{M_2 \times (M_2^2 - M_1^2 \sin^2 \theta)^{1/2}} \quad (2.27)$$

Note that since $\sigma_R \propto Z_1^2 Z_2^2 / E^2$, therefore the sensitivity increases with increasing Z_1 , increasing Z_2 , and decreasing E .

2.3 Principle of Rutherford Backscattering Spectroscopy

The principle of the RBS technique is that a beam of 1–3 MeV energy of low-mass ions (normally α -particles i.e., ${}^4\text{He}^{2+}$ or ${}^4\text{He}^+$ -ions) is made to impinge on the sample and a surface barrier semiconductor detector detects the scattered particles. It does not matter whether we use ${}^4\text{He}^+$ for ${}^4\text{He}^{2+}$ as the incident ion with regard to the spectra, since the “memory” of the incident charge state is lost as soon as the ion hits the target surface, because the electron binding energy is so small (It will only matter for charge integration purposes). The detector is placed such that particles, which scatter from the sample at close to 180° angle, will be collected. The RBS involves the measurement of the number and energy distribution of the energetic backscattered ions from atoms within the near-surface region of the solid target. The energy of these backscattered ions will depend on their incident energy and on the mass of the sample atom, which they hit, because the amount of energy transferred to the sample atom in the collision, depends on the ratio of masses between the ion and the sample atom. Thus, by measuring the energy of scattered ions one can infer the chemical composition of the sample. Additionally, in the case that the incident ion does not hit any of the atoms near the surface of the sample, but instead hits an atom deeper in, the incident ion loses energy gradually as it passes through the solid, and again as it leaves the solid. This means that RBS can be used as a means to perform a depth profile of the composition of a sample. This is especially useful in analysis of thin-film materials.

When a beam of particles passes through the target foil, the energy loss suffered by the particles exhibits a fluctuation around an average value. The energy loss suffered by the charged particle is represented as $-dE/dx$ (units of MeV cm^{-1}) or $-dE/\rho dx$ (in units of $\text{MeV g}^{-1} \text{cm}^{-2}$) or stopping cross-section $\epsilon = -dE/Ndx$ (i.e., energy loss on an atom to atom basis in units of

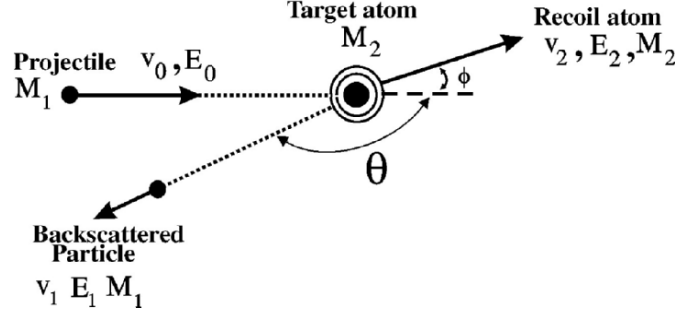


Fig. 2.7. Principle of the RBS technique: Beam of low-mass ions (normally α -particles (${}^4\text{He}^{2+}$) or ${}^4\text{He}^+$ -ions) of 1–3 MeV is made to impinge on the sample and the particles scattered through angle θ are detected by a particle detector

MeV cm^2). The technique is used to determine atomic mass and concentration of the constituents of an elemental target as a function of depth below the surface i.e., concentration profile of trace elements which are heavier than the major constituents of the substrate. The schematic diagram shown in Fig. 2.7 illustrates the principle of the RBS technique.

The energy E_1 of the scattered particle, given by (2.13), is written in terms of the scattering angle as

$$E_1 = KE_0 = \left[\frac{(M_2^2 - M_1^2 \sin^2 \theta)^{1/2} + M_1 \cos \theta}{M_1 + M_2} \right]^2 E_0 \quad (2.28)$$

where E_0 is the energy of the incident particle, K is the kinematic factor that depends on the mass of the incident particle M_1 , mass of the target atom M_2 and the scattering angle θ . Thus, for a given scattering angle θ and a given incident particle M_1 , the energy of the scattered particle E_1 mostly depends on the target atom M_2 , based on the condition that the distance of closest approach of the projectile nucleus is large enough so that the nuclear force is negligible i.e., the energy lost by the incident beam is negligible with regard of E_0 . When $M_1 \ll M_2$, the kinematic factor K increases with M_2 to attain unity, which allows the mass separation of target nuclei. A plot shown in Fig. 2.8 indicates the variation of kinematic factor (K) with target mass (M_2) at scattering angle of 170° for three projectiles ${}^1\text{H}^1$, ${}^2\text{He}^4$, and ${}^3\text{Li}^7$.

The relation between energy separation (ΔE_1) of any projectile energy and mass difference of target elements (ΔM_2) is given by

$$\Delta E_1 = E_0 \frac{dK}{dM_2} \Delta M_2 \Rightarrow \delta M_2 = \frac{\delta E}{E_0} \left(\frac{dK}{dM_2} \right)^{-1} \quad (2.29)$$

This relation indicates that the mass resolution δM_2 (1) decreases with increase of projectile energy E_0 (2) decreases for heavier elements M_2 and (3) light elements may overlap with thick layers of the substrate of heavier elements.

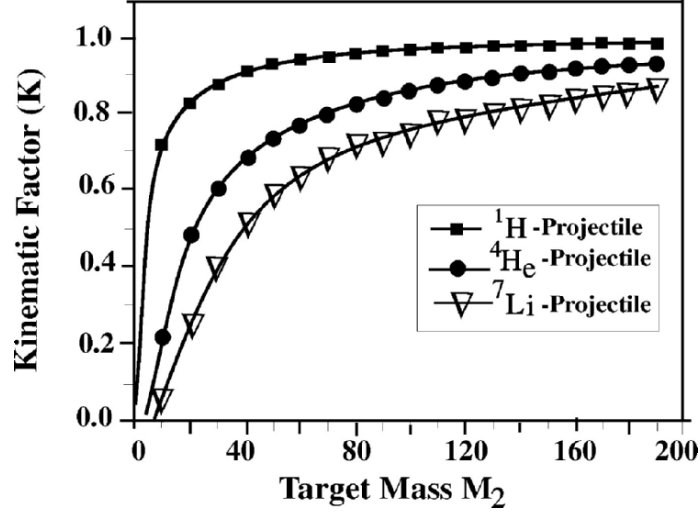


Fig. 2.8. Variation of kinematic factor K with mass of target nuclei M_2 for three projectiles $^1\text{H}^1$, $^2\text{He}^4$, and $^3\text{Li}^7$ at scattering angle of 170°

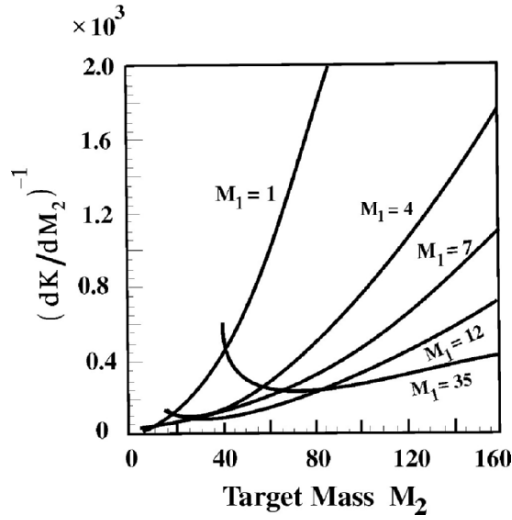


Fig. 2.9. Variation of $(dK/dM_2)^{-1}$ with mass of target nuclei M_2 for projectiles of mass number $M_1 = 1, 4, 7, 12$ and 35

Figure 2.9 depicting the variation of $(dK/dM_2)^{-1}$ with M_2 for different projectiles shows that there is an optimum mass resolution for projectiles with mass M_1 lying between 4 and 7. This is because of the reason that for surface barrier detectors, $dE = dE(M_1)$ and $dE(1) \sim 12\text{ keV}$, $dE(4) \sim 15\text{ keV}$, $dE(12) \sim 50\text{ keV}$. Since the mass resolution decreases due to poor

resolution of surface barrier detectors for heavier M_1 , therefore the heavier M_1 ions are useful only with magnetic analyzers and time-of-flight (TOF) detectors. The second limitation comes from the reason that the elements with mass $M_2 < M_1$ are not detectable at all. Hence, for the detection of light elements, for which RBS is used as a complementary technique to PIXE, it is useful to use lighter M_1 ions. With all these considerations, normally the alpha particles or He-ions with energy near 2 MeV are generally used for RBS analysis.

2.4 Fundamentals of the RBS Technique and its Characteristics

Rutherford backscattering occurs when 1–3 MeV ions are deflected through an obtuse angle (close to 180°) by the repulsive electrostatic field of an atomic nucleus. A beam of α -particles from a radioactive source strikes the foil and gets scattered. The number of flashes seen, as the α -particles hit a fluorescent screen, are then measured at different angles of scattering (θ). The profound observation of backscattering of α -particles by Ernest Rutherford in 1910 paved the way for discovery of the nucleus.

Since Rutherford scattering occurs outside the nucleus, the scattering probability is modified by a nuclear interaction if the incoming ion has sufficient kinetic energy to penetrate the nucleus. In the problem of scattering, we do not consider the case of high-energy incident particles, because, if the energy of the incident particles is more than the Coulomb barrier, the incident particles can cause a nuclear reaction to occur in the target, creating a radioactive isotope. An approximate empirical criterion for avoiding nuclear reaction is given by

$$E_0 < \frac{Z_1 Z_2}{\left(M_1^{1/3} + M_2^{1/3}\right)} \quad (2.30)$$

where E_0 is the kinetic energy of the incoming ion (in MeV), Z_1 , and Z_2 are the atomic numbers and M_1 and M_2 are the nucleon numbers of the incoming ion and the target atom, respectively. It is assumed here that the incoming ion energy is low enough that true Rutherford scattering occurs outside the nucleus, but high enough to avoid significant effects of screening by electrons, which, at large distances of approach, reduce the effective charge of the nucleus. These criteria are suitably met, for example, by He^+ ions with energy of around 1 MeV.

The probability of scattering of a positive ion by a positive nucleus is described by the Rutherford scattering cross-section as given by (2.8). The probability of scattering is proportional to the square of the atomic number of the target atom and inversely proportional to the square of the ion energy. Therefore scattering has higher probability for low-energy ions and heavy target atoms.

In RBS, light ions usually α -particle or He^+ -ion with energies from 1 to 3 MeV are made to impinge on a target while the number and energy of ions backscattered in the direction of the detector is measured. Since the collisions with the target nuclei are elastic, one can derive the mass of scattering centers from the measured energies using conservation laws. The excellent ability of this method, to extract quantitative data about abundances of elements, is due to the precise knowledge of Rutherford scattering cross-sections. Dealing with the technique of RBS, the following basic concepts are important:

1. Energy transfer from a projectile to a target nucleus in an elastic two-body collision – concept of kinematic factor ($K = E_1/E_0$ i.e., ratio of energy of the scattered particle to the energy of the incident particle).
2. Probability of occurrence of such a two-body collision – concept of scattering cross-section.
3. Average energy loss of an atom moving through a dense medium – concept of stopping cross-section and the capability of depth perception. The amount of energy a projectile loses per distance traversed in a sample depends on the projectile, its velocity, the elements in the sample, and the density of the sample material. Typical energy losses for 2 MeV He range between 100 and 800 eV nm⁻¹. The energy loss dependence on sample composition and density enables RBS measurements of layer thickness, a process called depth profiling. RBS is therefore used as a tool for surface analysis. In order to calculate the energy loss per unit of depth in a sample one can multiply stopping cross-section times the density of the sample material (atoms cm⁻²).
4. Statistical fluctuations in the energy loss of an atom moving through a dense medium – concept of energy straggling and to a limitation in the ultimate mass and depth resolution of RBS.

RBS has the following characteristics:

1. Multielement depth concentration profiles.
2. Fast, nondestructive and multielemental analysis technique for elements from Be to U. No light element can be detected on heavy substrates.
3. Matrix independent (unaffected by chemical bonding states).
4. Quantitative without standards.
5. High precision (typically $\pm 3\%$).
6. Bulk: % to 10^{-4} , depending on Z . Surface: $1\text{--}10^{-4}$. Increased sensitivity for heavier elements ($\propto Z_2^2$). It is best suited for analysis of heavier elements or layer on lighter substrates but less good for lighter elements on heavier substrates as it depends on Z and sample composition.
7. Depth range $\sim$ typically 2–20 μm .
8. Depth resolution : 5–50 nm.
9. Detection limit $\sim 10^{18} \text{ cm}^{-3}$.
10. Spatial definition: Beam spot size 0.5–2.0 mm.

Resolution for detecting adjacent elements can be improved, if (1) heavy particles are used (2) detection angles are chosen to be close to 180° , and (3) bombarding energy E_0 is sufficiently high. The detection resolution is, however reduced for heavier projectiles e.g., if $M = 180$ and $M = 190$ are to be distinguished under the same experimental conditions, the FWHM for α -particles should be $<0.5\%$, however with neon projectiles, the FWHM of about 2% is sufficient.

Experimentally the differential scattering cross-section is the probability that the incident particle will be scattered to a particular angle (not that it is just scattered) i.e., the scattering will result in signal at the detector at a particular angle i.e., each nucleus offers an area $d\sigma/d\Omega$ to the beam. Referring to Fig. 2.10, if S_A is the surface area of the target exposed, the total number of target atoms eligible for scattering collision $= S_A n t$

$$\frac{\text{Total cross-sectional area}}{\text{Area actually exposed}} = \frac{S_A n t \frac{d\sigma}{d\Omega}}{S_A} = \frac{1}{d\Omega} \frac{dQ}{Q}$$

or

$$\begin{aligned} \frac{d\sigma}{d\Omega} &= \frac{1}{n t} \frac{1}{d\Omega} \frac{dQ}{Q} \\ &= \frac{\text{Number of ions scattered per second into } d\Omega}{\text{Incident flux (s}^{-1}\text{cm}^{-2}) \times d\Omega} \end{aligned} \quad (2.31)$$

where Q = Number of particles that have hit the target (The value of Q is usually counted in terms of current and is of the order of microCoulombs (μC) such that $1 \mu\text{C} \equiv 6.2415 \times 10^{12}$ particles for $q = 1^+$),

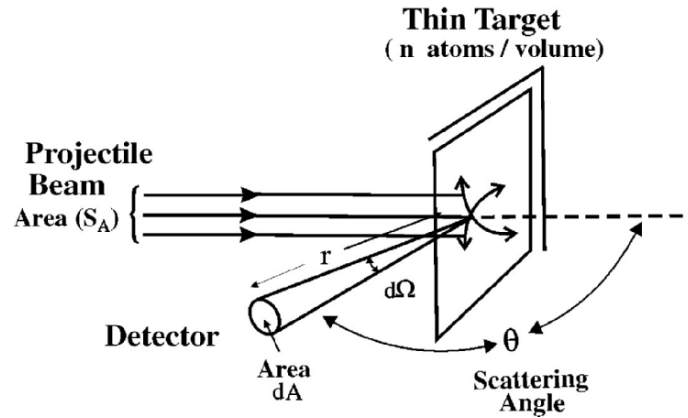


Fig. 2.10. Schematic diagram to show the scattering angle θ and solid angle $d\Omega (= dA/r^2)$ involved in the calculation of differential scattering cross-section

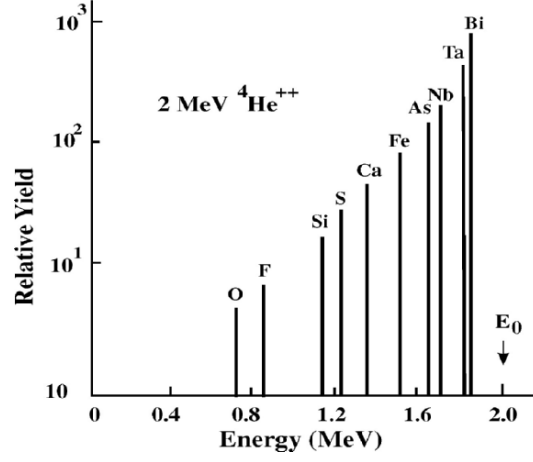


Fig. 2.11. Comparison of the scattering yields and scattered energy for various elements as a function of their atomic number

dQ = Number of particles recorded by the detector,

n = Volume density of the atoms in the detector, t = thickness,

nt = Number of target atoms per unit area (areal density in units of $\mu\text{g cm}^{-2}$ or atoms cm^{-2}). Here $n = N_A \rho t / M$ where N_A is the Avogadro number, M is molecular weight, ρt is the mass areal density, and ρ is the bulk density in units of g cm^{-3}],

and

$d\Omega$ = solid angle subtended by the target on the detector ($= dA/r^2$)

where r is the distance of the detector from the target and dA is the area of the detecting surface.

If the projectile energy is chosen properly (below Coulomb barrier and above electronic screening – see Sect. 2.5.2 for shielded Rutherford cross-sections), the scattering yield follows the Rutherford cross-section which is basically proportional to the square of the atomic number of the element and inversely proportional to the square of the projectile energy (Fig. 2.11). If the energy is higher than the upper value, the backscattering cross-section shows deviation from Rutherford formula as discussed in Sect. 2.5.

2.5 Deviations from Rutherford Formula

Huan-Sheng et al. (1991) measured Rutherford cross-sections for 165° backscattering of ^4He from sodium and aluminum for ^4He energy between 2.0 and 6.0 MeV. Their experimental results show that for sodium and aluminum, the upper energies are 3.0 and 3.5 MeV, respectively, at which the backscattering cross-section can still be predicted by the Rutherford scattering formula,

When the energy is higher than the upper value, the backscattering cross-section shows deviation from Rutherford formula.

2.5.1 Non-Rutherford Cross-Sections

The cross-sections become non-Rutherford if nuclear forces between the projectile and target nuclei become important. This happens at *high*-incident energies (E), *high*-scattering angles (θ), and for *low* Z_2 – values. For sufficiently high energies, the distance of closest approach between projectile and target nuclei reduces to the dimensions of nuclear size. The short-range nuclear forces then begin to influence the scattering process and deviation from Rutherford cross-sections appear. When the process is inelastic, the energy of the scattered particle differs from kE_0 as well. The value of the scattering cross-section is strongly dependent on energy, on the scattering angle and on the particular combination of projectile and target nuclei. The RBS measurements show that after certain energy, the resonant structure appears and that even in the resonance region, there may exist several energy regions where the cross-sections present an enhanced and smooth variation. The enhanced cross-sections, which do not obey the Rutherford law, are called *non-Rutherford cross-sections*. The enhanced cross-sections for lighter elements ($Z \leq 16$) relative to Rutherford values (σ_R) are from two-to-three times to several orders of magnitude greater than σ_R . In many instances this enhancement takes the form of a resonance feature accompanied by a low-energy “hole” where $\sigma < \sigma_R$ (Knox and Harmon 1989). The measured cross-sections, particularly for narrow resonance, often vary with the experimental conditions used, such as sample thickness, beam energy spread, and scattering angles. Evaluation of the non-Rutherford cross-sections have been done by Shen et al. (1994) using the R-matrix theory. Measurements for non-Rutherford cross-sections for 167° backscattering of ^4He from ^{14}N in the energy range from 4.5 to 9.0 MeV was measured by Foster et al. (1993) who found a large scattering resonance, approximately 80 times Rutherford and FWHM > 200 keV at 8.81 MeV. Measurements for non-Rutherford cross-sections at 165° backscattering of 2–9 MeV ^4He from carbon have been reported by Feng et al. (1994). Non-Rutherford cross-sections for carbon have been measured by Banks et al. (2006) at the 165° backscattering angle for 8.0–11.7 MeV α -particles.

The resonant cross-sections for light elements are increased significantly when proton beam is used for RBS measurements. High sensitivity for C, N, O, and Si is observed in case of 2.4 MeV proton beam and for O in case of 3.06 MeV α -particle beam (Fig. 2.12). The energy at which the cross-sections deviate significantly ($>5\%$) from Rutherford for scattering angle between 160° and 180° are given by

$$\text{For protons: } E_{\text{lab}}(\text{MeV}) = 0.12 Z_2 - 0.5$$

$$\text{For } \alpha\text{-particles: } E_{\text{lab}}(\text{MeV}) = 0.25 Z_2 + 0.4$$

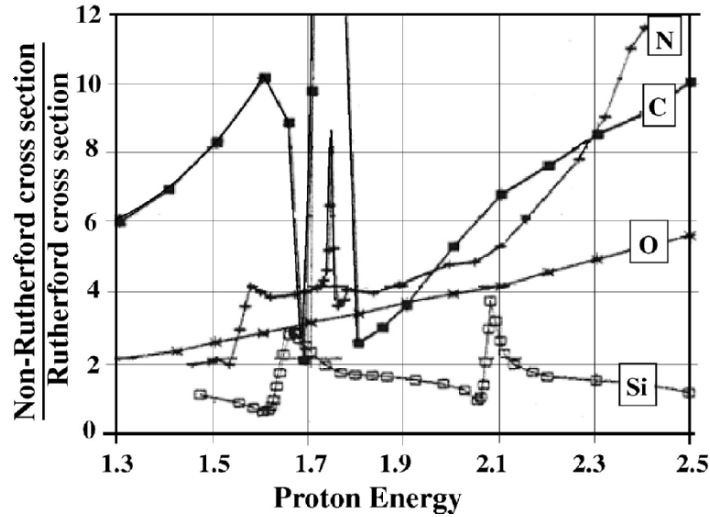


Fig. 2.12. Ratio of non-Rutherford to Rutherford cross-sections for C, N, O, and Si at different proton energies

A database of non-Rutherford scattering cross-sections of ^1H , ^4He , and several other light elements, is also included in the available computer simulation codes (listed at page 362) for RBS analysis.

Since non-Rutherford elastic scattering can be used for analysis of light elements in solids, Jiang et al. (2004) have measured the scattering cross-sections for $^{12}\text{C}(\text{p}, \text{p})^{12}\text{C}$, $^{12}\text{C}(\text{d}, \text{p})^{13}\text{C}$, and $^{12}\text{C}(\alpha, \alpha)^{12}\text{C}$ at an angle of 150° over relevant energy regions using thin films of carbon ($5.8 \mu\text{g cm}^{-2}$) on silicate glass with 4% uncertainty.

2.5.2 Shielded Rutherford Cross-Sections

Shielding by electron clouds of the projectile (ion) and the target atoms become important at *low* projectile energies (E), *low* scattering angles (θ) and for *high* Z_2 -values. For small scattering angles $\theta \rightarrow 0^\circ$, the Rutherford cross-sections tend to infinity, which violates the initial assumption that the cross-section of the target nuclei should be small enough not to allow overlap. Small scattering angles correspond to large flyby distances between the projectile and the target nuclei i.e., distances greater the radius of the innermost electron-shell of the target atom. At these distances the electrostatic interaction does not take place between bare nuclei as Rutherford formula assumes. A similar situation exists when a low-energy projectile collides with a heavy atom. In such instances one must use scattering cross-sections derived from a potential, which includes electron screening.

Shielding by electron cloud is taken into account by multiplying the scattering cross-section $\sigma_R(E, \theta)$ by a shielding factor $F(E, \theta)$. The shielding factor is obtained by solving the scattering equations for the shielded interatomic potential:

$$V(r) = \frac{Z_1 Z_2 e^2}{r} \phi(r/a) \quad (2.32)$$

where $\phi(r/a)$ is the screening function. Normally Thomas-Fermi or Lenz-Jenssen screening function is used. The screening radius a depends on the Bohr radius (a_0), Z_1 , and Z_2 and is given by

$$a = 0.885a_0 \left(Z_1^{2/3} + Z_2^{2/3} \right)^{-1/2} \quad (2.33)$$

The shielding for large (between 90° and 180°) scattering angles which comes out to be less than 15%, can be calculated by the formula given by L'Ecuyer et al. (1979) i.e.,

$$\frac{\sigma}{\sigma_R} = 1 - \frac{0.049 Z_1 Z_2^{4/3}}{E_{CM}} \quad (2.34)$$

Mass resolution using RBS can be improved in a number of ways:

- Use higher beam energy to effectively expand the energy spectrum
- Use heavier ions to provide better kinematic separation
- Select scattering geometry with $\theta \sim 180^\circ$
- Reduce the system energy resolution

2.6 Instrumentation/Experimental

2.6.1 Accelerator, Beam Transport System, and Scattering Chamber

The RBS measurements can be done using the equipment of IBA technique i.e., accelerator (which can give typically 1–4 MeV He^{2+} -ions), scattering chamber, and the particle detector.

The details about the Pelletron/Van de Graaff accelerator have been given in Chap. 1. However the α -particles can also be obtained from cyclotron. The beam is transported to the scattering chamber using *the analyzing and switching magnets* which select the mass of the radionuclide of interest selecting isotope of interest. In addition, they eliminate molecules completely by selecting only the highly charged ions that are produced in the terminal stripper of the Pelletron accelerator. *The electrostatic analyzer* which is a pair of metal plates at high voltage, deflects the beam by a duly selected angle of interest. This selects particles based on their energy and thus removes the ions that happen to receive the wrong energy from the accelerator.

The scattering chamber (as shown in Fig. 1.15 of Chap. 1) is a high vacuum cylindrical chamber made up of stainless steel of 15 to 20 cm radius and is provided with number of ports at various angle (for example $+45^\circ$, $+90^\circ$, -90° , -135° with respect to the beam axis) to make it general purpose. Viewing glass windows are provided for the various ports. The top and bottom plates are also provided with ports for cables, viewing, and for connecting to the vacuum pump. The chamber is provided with a triple-axis target manipulator (ladder) made of steel and capable of holding number of target ladders at a time. Each target ladder is about 10 cm long and 2.5 cm wide. The target manipulator is attached to a rectangular base plate which is clamped to an O-ring sliding seal on the top flange of the vacuum chamber. A screw fastened on the top flange moves the rectangular plate perpendicular to the beam axis to bring one ladder at a time to the beam line. Each ladder is capable of holding a number of target frames of approx. $2.5\text{ cm} \times 1.4\text{ cm}$, at a time including a quartz piece, a carbon foil, a blank, and a number of thin target foils. The movement of the target in the upward/downward direction can be monitored by a vertical scale attached to the clamping bars of the rectangular base plate. In a simple RBS set-up, the detector table is provided with two arms for mounting the detector holders (to hold the surface barrier detectors along with the collimators), one in the forward direction (which acts as a monitor detector) and another in the backward direction w.r.t the beam axis.

2.6.2 Particle Detectors

The scattered particles can be detected based on their characteristic parameters like energy loss dE/dx vs. E , production of electrons by heavy ions, momentum over charge ratio, etc. The stopping power and energy loss form the basis of particle detection by surface barrier detectors and $\Delta E - E$ spectrometry. Microchannel plates (MCPs) detect the electrons produced by heavy ions while the difference in the momentum over charge ratio of various particles is used in magnetic spectrometer (the detection of the ion is made after its traversal through a magnetic field). The description of these detector systems is given in the following sections.

Surface barrier detector

Semiconductor diodes are used in current mode to measure charged particles and are known as surface barrier detectors. They have very linear responses and are available with thin entrance windows. Surface barrier detectors are good beam monitors when used with low-noise current amplifiers. To understand the action of the particle detector, we will have to understand the basics of the semiconductor detectors.

The sensitive volume of a semiconductor detector is formed by the space-charge region (SCR) of a p-n diode. The SCR is often called depleted region,

because it is depleted of mobile charge carriers and the resulting electric field is not zero. The p–n diode is made of a low-doped silicon bulk which can be of n-type if it is doped with donor impurity atoms or of p-type if it is doped with acceptor impurity atoms. At the sides of the detector, highly doped implants of n^+ -type and p^+ -type are created and connected to the electrodes. In order to create the SCR, the p–n diode has to be depleted by applying a reverse biasing voltage, i.e., applying positive voltage to the n^+ -side and negative voltage to the p^+ side. The dopant atoms become ionized and they form the SCR. The depletion voltage is determined from the solution of the Poisson equation and is given by

$$V_{\text{dep}} = \frac{eNd^2}{2\epsilon} - V_{\text{bi}}$$

where d is the detector bulk thickness, N is the doping concentration in the silicon bulk, $V_{\text{bi}} \approx 0.5$ V is the built-in voltage in silicon, usually much smaller than the applied voltage and can be neglected, ϵ is the dielectric constant, e is the electron charge. If the applied bias voltage V_b is larger than V_{dep} the detector becomes overdepleted, and the electric field linearly increases from $(V_b - V_{\text{dep}})/d$ to $(V_b + V_{\text{dep}})/d$. If the applied bias voltage is smaller than V_{dep} the electric field is zero in the depth range from 0 to $d - \sqrt{2\epsilon V_b/(eN)}$ then it linearly increases up to $2V_b/d$. In the case of a not fully depleted (FD) detector, the SCR depth, usually called depletion depth, is

$$W_d = \sqrt{\frac{2\epsilon V_b}{eN}}$$

In case of a reverse-biased p–n junction formed by heavily doped n-type layer on the p-type Si-wafer, the depletion region extends in thickness primarily into the lightly doped p-region and very little into the strongly doped n^+ -region to keep the net charge zero. When the ionizing radiation is made to impinge on the detector through its thin window, the e–h pairs produced in the depletion region are collected to form a transient current in the external circuit. If the depletion depth (d) of the detector is less than its physical thickness (t), the detector is said to be partially depleted (PD). However, the detector can be made FD by choosing high-resistivity crystal material (low concentration of acceptor or donor impurities) or raising the applied voltage so that it penetrates through the entire detector thickness to the back of the metal contact and is referred as p–i–n diode. In the case of FD detectors, the electric field profile is uniform. The PD detectors are commonly used for the total energy measurements with the caution that their depletion depth is more than the range of the charged particles.

The surface barrier detectors are commonly made with n-type silicon and are characterized by very thin dead layer (an inactive layer within the crystal which is ~ 0.1 μm of silicon equivalent). This would correspond to an energy loss of about 4 keV for 1 MeV proton and 14 keV for 5 MeV α -particles.

The detector area is approximately 50 mm^2 , and the “sensitive depth” is approximately $100 \mu\text{m} = 0.1 \text{ mm}$. If bias voltage of $\sim 50 \text{ V}$ is applied, an electric field of $\sim 5,000 \text{ V cm}^{-1}$ is produced, which then sweeps out the charge carriers created by the passage of a charged particle as it slows down and stops in the detector. There is a thin gold window on the front for the electrical contact. As these detectors are sensitive to light, a high-leakage current (formed by the thermal generation of the electrons and holes) would result if care is not taken to operate them with proper shielding from light. To reduce the contribution of even the minority carriers to the leakage current, a heavily doped p^+ layer is used as a back contact in a detector with p -type material. However, for n -type surface barrier silicon detectors, aluminum is commonly used for the back contact.

The position sensitive semiconductor detectors, on the other hand, are useful not only for energy measurements but also for the position where the charged particle interacts with the detector. Such a detector consists of a strip of silicon with a standard SBD configuration on the front side but has a resistive layer along the length of the detector, on the back side. At the two ends of this resistive back side, two contacts are provided for taking out signals. The resistive contacts act as a charge divider, and the signals at the two ends depend not only on the radiation energy but also on the position of interaction. Totally depleted thin silicon detectors are frequently used as ΔE detectors in these $\Delta E - E$ telescopes (position sensitive detectors). These should preferably be in transmission mounts and the dead layers must be as small as possible at both the front and rear surfaces.

From different series (A, B, C... to indicate PD, totally depleted, annular PD, planar totally depleted, etc.), the specifications for ORTEC model number A-14-50-1000 mean that this detector is A-type (PD) with an active area of 50 mm^2 and depletion depth of $1,000 \mu\text{m}$, has maximum resolution of 14 keV for 5.486-MeV α -particles emitted by ^{241}Am source. Similarly, model number F-018-100-60 (for heavy ion PD silicon SBD) specifies that the detector has an active area of 100 mm^2 , depletion depth of $60 \mu\text{m}$ and resolution of 18 keV while model F-035-900-60 detector has an active area of 900 mm^2 , depletion depth of $60 \mu\text{m}$ and resolution of 35 keV . Heavy ion spectroscopy with silicon surface barrier detectors has been discussed in detail by ORTEC in its Application Note AN-40. The ORTEC brochure for its products indicates that the resolution of ruggedized (R-series) PD surface barrier detectors vary from about 15 to 80 keV for α -particles depending on the depletion depth varying from 100 to $500 \mu\text{m}$ and the active area varying 50 – $2,000 \text{ mm}^2$. The quoted value of resolution however, will deteriorate due to radiation damage.

ΔE vs. E telescope

A solid-state ΔE vs. E telescope works on the principle of dE/dx vs. E technique for charged particle identification. In this telescope, the particle is identified by the energy deposited in the various detectors (of known thicknesses) in

the “stack” as it comes to rest, and the incident direction (or trajectory) of the particle. The stacks consist of several thick silicon detectors placed one above the other. The knowledge of the angle of incidence of the particle (relative to the stack normal direction) is obtained through the use of a hodoscope, a device which is capable of determining a particle’s trajectory. The hodoscope is the scintillating optical fiber trajectory (SOFT) system, which uses a series of scintillating fibers in alternating directions to observe the trajectory of a particle. Each telescope stack contains two “matrix detectors,” which are thin detectors with charged-particle-sensitive strips on both sides; each side’s strips are aligned at 90° to those on the other side, providing event trajectories.

As shown in the schematic diagram of Fig. 2.13, a particle entering at a known angle θ will deposit energy ΔE in the top detector of smaller thickness and energy E' in the bottom detector of large thickness. The derivative energy loss per unit path length (dE/dx) can be approximated by the quantity $\Delta E/(\Delta L \sec \alpha)$, where ΔL is the thickness of the top detector at the particle entry point. The total particle energy is approximated by E' , the energy deposited in the bottom detector. This is a reasonable assumption, as it has been found that charged particles tend to lose most of their energy near the end of their range. When the two quantities are multiplied together, the result is approximately equal to $Z^2 M$, where Z is the particle charge and M is its mass. As galactic cosmic rays are fully ionized, this is sufficient in principle to uniquely identify the particle, as $Z^2 M$ is unique for every nucleus we investigate. When a number of such events are collected, $\Delta E/(\Delta L \sec \alpha)$ vs. E' data will lie approximately along hyperbolas of constant $Z^2 M$. This

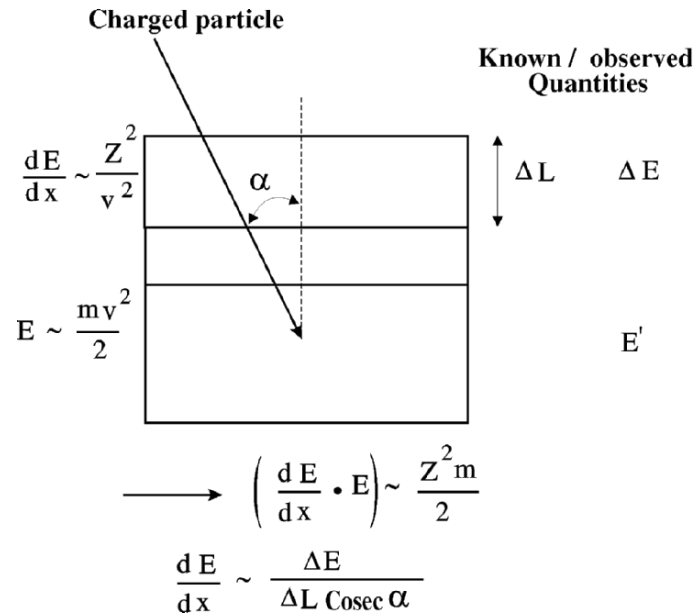


Fig. 2.13. Schematic of ΔE vs. E telescope

dependence has been verified during calibration runs using particle beams entering the telescope at constant angle.

Microchannel plate detector

A MCP is an array of hundreds of very thin, conductive glass capillaries (4–25 μm in diameter and having length to diameter ratios between 40 and 100) fused together, oriented parallel to one another and sliced into a thin plate. Each capillary or channel works as an independent secondary-electron multiplier to form a two-dimensional secondary-electron multiplier. The channel matrix is usually fabricated from a lead glass, treated in such a way as to optimize the secondary emission characteristics of each channel and to render the channel walls semiconducting so as to allow charge replenishment from an external voltage source. Each channel can thus be considered to be a continuous dynode structure which acts as its own dynode resistor chain. Parallel electrical contact to each channel is provided by the deposition of a metallic coating on the front and rear surfaces of the MCP, which then serve as input and output electrodes, respectively. The total resistance between electrodes is of the order of $10^9 \Omega$. Such MCPs, used singly or in a cascade, allow electron multiplication of the order of 10^4 – 10^7 coupled with ultrahigh-time resolution (<100 ps) and spatial resolution. The MCP shows a high-detection efficiency to electrons and ions. It is also sensitive to a wide range of other radiations including UV, VUV, soft X-ray photons, and neutrons. The MCP offers many advantages over conventional detectors, compact, light weight, good timing properties due to short length, high gain, excellent pulse height distribution, and two-dimensional imaging when used in conjunction with a phosphor screen.

When a heavy ion passes through the thin foil, electrons are ejected from the surface of the foil. An aluminized mylar foil of $\sim 1 \mu\text{m}$ thickness is mounted at 45° or 60° with respect to the beam. For slow moving heavy ions, many electrons are ejected. These electrons are accelerated by placing a negative high voltage (-300 V) on the foil and a large positive high voltage ($>1,600$ V) on the MCP detector which lies parallel to the foil. Two MCP plates are used to provide amplification and the resulting electrons are deposited on a resistive anode. The deposited charge is detected from the four corners of the anode and a position is derived from the charge division. In addition, the detectors use magnetic imaging to constrain the electrons from the foil and improve the position resolution as well as to compress the image so that larger foils than the MCP can be used. Currently, the $8 \times 10 \text{ cm}^2$ detector has been found to observe an image of about 15 cm in length.

Magnetic spectrometer

Separate identification for light elements is generally easy, but very difficult for very heavy atoms. Since the heavier elements crowd together at the upper end of the spectrum, their separation mostly depends on the energy resolution

of the particle detector. The ion beam laboratories normally use silicon particle detectors of about 10–12 keV resolutions. They are small, easy to use, and give rapid results. However, the depth and mass resolution of these methods is generally limited by the energy resolution of the detector. By switching to use of a magnetic mass spectrometer, the heavy ion RBS (HI-RBS) facility improves resolution by an order of magnitude better than the commonly used Si detector. This improved energy resolution translates into an order of magnitude improvement in the mass and depth resolution. This instrument works with a resolution better than ~ 4 keV.

Conventional mass spectrometer designs use a single particle detector, with data taken by stepping slowly through a range of magnetic field, pausing at each step to collect particles for a fixed amount of time. The result is very slow operation. In the HIRBS facility, the magnetic field remains fixed while data are taken simultaneously from detectors sensing from many different locations. Lanford et al. (1998) have developed compact broad range magnetic spectrometer for use in IBA. This spectrometer is seen to be capable of an energy resolution of $\Delta E/E \sim 1/2,000$ with a 1 msr solid angle. A typical magnetic spectrometer consists of two quadrupoles, one 60° dipole with a mean orbit radius of 1.5 m and one sextupole, providing a particle rigidity of 2.5 Tm. This QQDS configuration allows a variable dispersion by placing the focal plane detector at different positions behind the magnets. The maximum focal plane length of 0.5 m corresponds to relative energy ranges $E_{\min}/E_{\max}$ of 0.65 near the magnets and 0.81 at the most distant position. The calculated values of the energy resolution dE/E at these positions amount to 7×10^{-4} and 3.8×10^{-4} . The spectrometer can be rotated around the vertical axis of the UHV scattering chamber and connected to ports at fixed angles of 0° , 15° , 30° , 45° , and 60° , respectively. Channeling measurements can be accomplished in a wide temperature range from 25 K to about 2,000 K using different goniometers. A silicon multistrip PSD and a one-dimensional position sensitive ionization chamber telescope can be used as focal plane detectors.

RBS studies with high-depth resolution using small magnetic spectrometers has been undertaken by Grötzschel et al. (2004) who have employed the magnet with a mean radius of 0.65 m mounted vertically but can be positioned either at 35.5° or 144.5° . The backward position offers the advantage of a high-mass resolution, but the Rutherford cross-sections are a factor of about 100 lower than at the forward angle, which is the preferred position if kinematically possible.

2.7 RBS Spectra from Thin and Thick Layers

2.7.1 RBS Spectrum from a Thin Layers

A layer is termed as thin layer, if the energy loss in the layer is less than the experimental energy resolution. In this case, there is negligible change of cross-section in the layer. If Q particles are incident at an angle α to the

normal as shown in Fig. 2.14, the effective thickness will become $(\Delta t / \cos \alpha)$. If $d\Omega$ is detector solid angle, $d\sigma(E)/d\Omega$ is differential scattering cross-section, n is the number of atoms per unit volume ($= N_A \rho / M$) which can be obtained from Avogadro number N_A , density ρ , and atomic weight M of the target material, $n(\Delta t / \cos \alpha)$ = thickness of sublayer in atoms cm^{-2} , the number of counts (dQ) of backscattered particles or area under the peak is given by

$$dQ = Q \Delta \Omega \frac{d\sigma(E)}{d\Omega} \frac{n \Delta t}{\cos \alpha} \quad (2.35)$$

The convolution (Fig. 2.15) with experimental energy resolution can be done by assuming Gaussian energy resolution function $f(x)$ with standard deviation w

$$f(x) = \frac{1}{\sqrt{2\pi} w} e^{-\frac{(x-x_0)^2}{2w^2}} \quad (2.36)$$

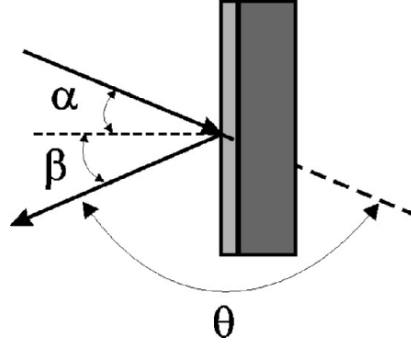


Fig. 2.14. Instead of normal incidence, the ion beam is incident at an angle α

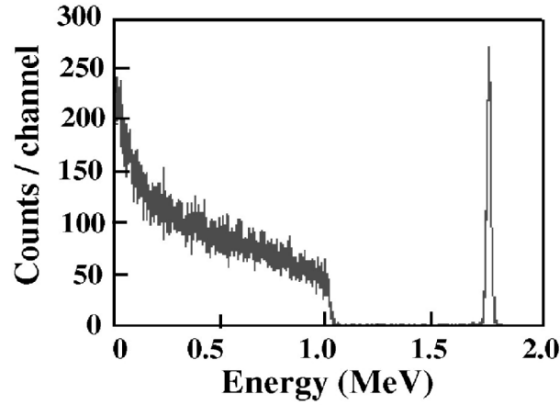


Fig. 2.15. Convolution of RBS spectrum

The count density function is represented by

$$n(E) = \frac{Q}{\sqrt{2\pi} w} e^{-\frac{(E - K E_0)^2}{2w^2}} \quad (2.37)$$

and

$$\text{Count } N_i \text{ in channel } i \quad N_i = \int_{E_i^{\text{Low}}}^{E_i^{\text{High}}} n(E) dE \quad (2.38)$$

The height of the peak (H) is represented by

$$H = \frac{\left(\frac{d\sigma}{d\Omega}\right) \Delta\Omega Q \Delta E}{\epsilon \sin \alpha} \quad (2.39)$$

The ratio of the spectrum heights for the two elements is given by

$$\frac{H_A}{H_B} = \frac{\left(\frac{Z_A}{E_A}\right)^2 \epsilon_B}{\left(\frac{Z_B}{E_B}\right)^2 \epsilon_A} \quad (2.40)$$

2.7.2 RBS Spectrum from Thick Layers

In the case of thick sample, the target is divided into thin sublayers (“slabs”) as shown in Fig. 2.16. The calculation for backscattering is done from front and back side of each sublayer taking energy loss into account.

$$\begin{array}{ll} \text{Energy at front side} & E_1 = E_0 - \Delta E_{\text{in}} \\ \text{Starting energy from front side} & E_1' = K E_1 \\ \text{Energy at surface} & E_1^{\text{out}} = E_1' - \Delta E_1^{\text{out}} \end{array}$$

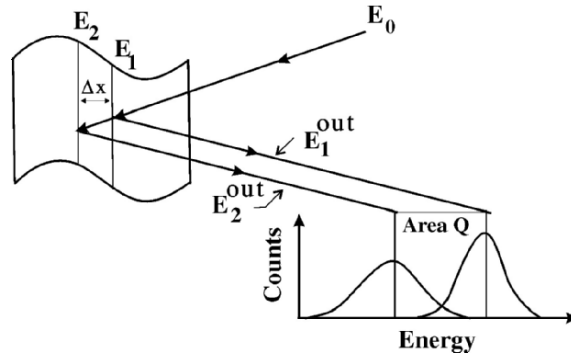


Fig. 2.16. RBS spectrum of a thick layer

$$\begin{array}{ll}
\text{Energy at back side} & E_2 = E_1 - \Delta E \\
\text{Starting energy from back side} & E_2' = K E_2 \\
\text{Energy at surface} & E_2^{\text{out}} = E_2' - \Delta E_2^{\text{out}}
\end{array}$$

Since each isotope of each element in sublayer is treated as a “brick”, the area (dQ) of the “brick” (as 2.31) is given by

$$dQ = Q d\Omega \frac{d\sigma(E)}{d\Omega} \frac{\Delta x}{\cos \alpha}$$

where dQ = Number of scattered counts, Q is number of incident particles, $d\Omega$ is detector solid angle, $d\sigma(E)/d\Omega$ is differential scattering cross-section Δx = thickness of sublayer in atoms cm^{-2} and α is angle of incidence.

Depth scale:

The signal from an atom at the sample surface will appear in the energy spectrum at position $E_1 = K E_0$. The signal from atoms of the same mass below the sample will be shifted by an amount of energy lost while the projectiles pass through the sample both before (ΔE_{in}) and after a collision (ΔE_{out}). Close to the surface, there exists a linear relation between the measured energy E_1 and the depth x at which the scattering took place. Therefore $E_1(x) = K E_0 - Sx$ where stopping power S , according to (2.14), is given by

$$S = \left[\frac{K}{\cos \theta_1} \left(\frac{dE}{dx} \right)_{\text{in}} + \frac{K}{\cos \theta_2} \left(\frac{dE}{dx} \right)_{\text{out}} \right]$$

Thus an RBS spectrum is an overlay of the depth profile of all individual atomic species present in the target material as shown in Fig. 2.17.

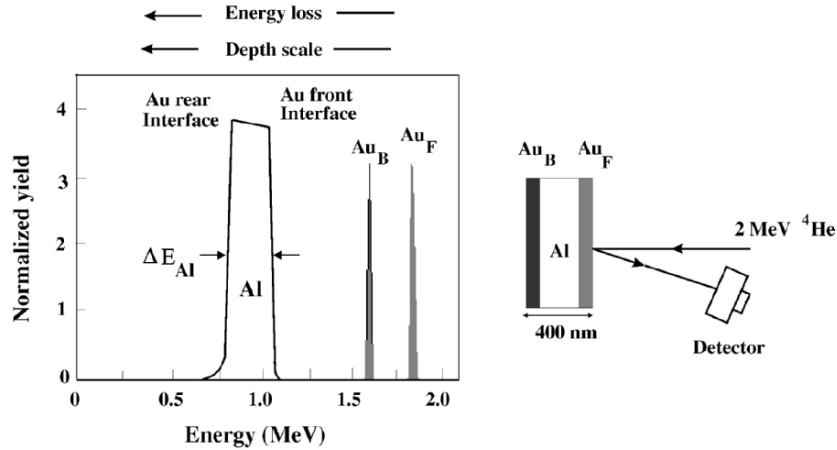


Fig. 2.17. Interpretation of the depth scale in RBS spectrum

To determine $\sigma(E)$, we use mean energy approximation i.e., use $\sigma(\langle E \rangle)$ with $\langle E \rangle = E_1 - \Delta E/2$ and mean cross-section is calculated using

$$\langle \sigma \rangle = \frac{\int_{E_2}^{E_1} \sigma(E) dE}{E_1 - E_2} \quad (2.41)$$

Shape of the Brick (Fig. 2.18) is governed by:

- (a) Height of high-energy side which is proportional to $\sigma(E_1)$
- (b) Height of low-energy side which is proportional to $\sigma(E_2)$

Normally, the use of linear interpolation is made. However, for *better approximation*, the heights of high-energy and low-energy side are considered proportional to $\sigma(E_1)/S_{\text{eff}}(E_1)$ and $\sigma(E_2)/S_{\text{eff}}(E_2)$, respectively. Here S_{eff} is the effective stopping power, taking stopping on incident and exit path into account. The quadratic interpolation with additional point $\langle E \rangle$ is another choice.

The *Convolution of brick with energy broadening* depends on the detector resolution, energy straggling and depth. The representation is shown in Figs. 2.18 and 2.19.

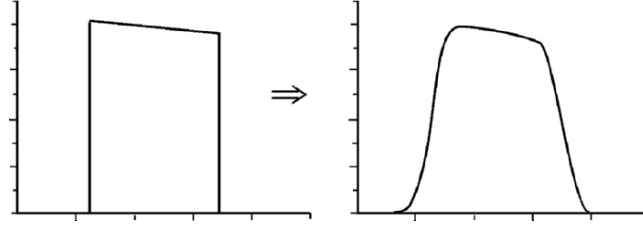


Fig. 2.18. Convolution of RBS spectrum with energy broadening

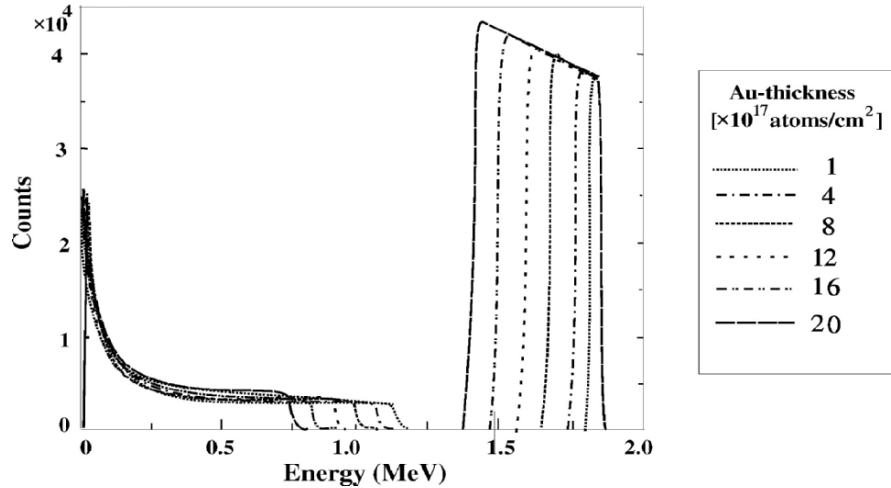


Fig. 2.19. A 2 MeV ^4He 165° backscattered from Au on Si-substrate

Matrix effects:

When a film contains say two elements A (of higher atomic mass number M_A) with certain thickness coated on substrate B (of lower atomic mass number M_B) with AB matrix, the scattered energy depends on the energy loss in substrate and matrix on the way going inside as well as during the way coming out of the matrix after scattering (Fig. 2.20a) and is given by equation

$$E_1 = E_0 - E_{\text{loss1}} - E_{\text{RBS}} - E_{\text{loss2}}$$

where E_1 is the backscattered energy measured, E_0 is the initial energy of M_1 , E_{loss1} is the energy loss in matrix, E_{RBS} is the backscattered energy loss, and E_{loss2} is the energy loss in matrix.

The scattered ion energy depends on the thickness of A on the substrate. Referring to Figs. 2.20b and 2.20c, when the thickness of A is increased, the peak height and width changes because the low-energy edge of the A-peak corresponds to scattering from A at the AB/B interface. The illustration shows that particles scattered from A at the AB/B interface of the lower thickness film (Fig. 2.20b) have more final energy while particles scattered from the same interface of the higher thickness film (Fig. 2.20c) have less final energy because they have passed through more AB. The entire A-peak spans a greater energy range, because of the increased thickness of the layer it represents.

As a practical case, let us take an example of two samples of the tantalum silicide (TaSi) films containing different Ta/Si compositions on Si substrates. One of the films is 230 nm thick, while the other film is 590 nm thick. The two RBS spectra, recorded using a 2.2 MeV He^{2+} ion beam, from two TaSi films of different Ta/Si compositions on Si substrates are shown in Fig. 2.21. In both spectra, the high-energy peak arises by scattering from tantalum in the TaSi film layer. The peak at lower energy is from silicon, which appears in both the

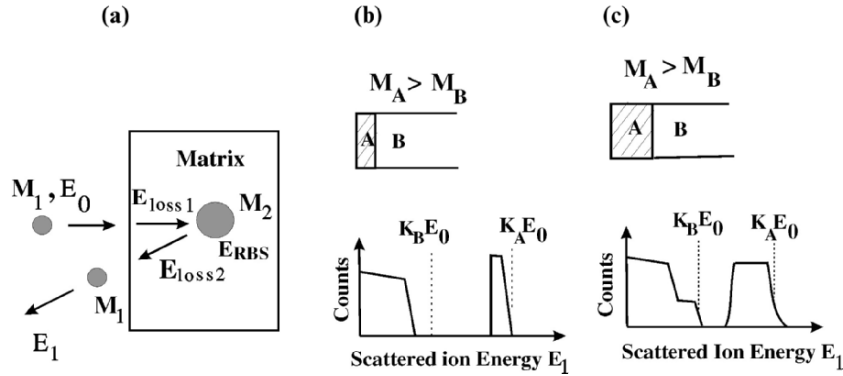


Fig. 2.20. Schematic diagram showing (a) losses in the matrix explained in the text (b) RBS spectrum of the sample with certain thickness of film A on the substrate B (c) RBS spectrum of the sample with increased thickness of film A

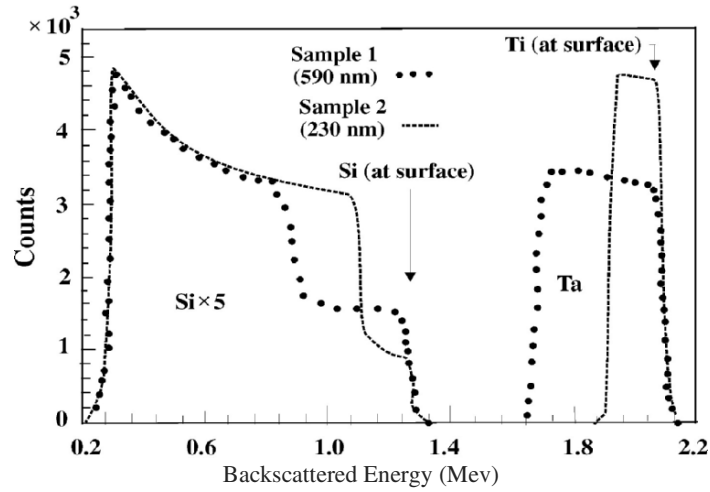


Fig. 2.21. RBS spectra of two films of TaSi of different Ta/Si compositions (thickness 230 nm and 590 nm, respectively) on Si substrates, recorded with a 2.2 MeV He^{2+} ion beam

TaSi films on the surface and in the Si substrate. Silicon is much less likely to cause scattering events than tantalum due to its smaller scattering cross-section. To make the features of the silicon signal in these two spectra easily distinguishable, the silicon peaks have been multiplied by five. For scattering at the sample surface, the only energy loss is due to momentum transfer to the target atom. The high-energy edge of the tantalum peaks near 2.1 MeV corresponds to backscattering from Ta at the surface while the high-energy edge of the silicon peaks near 1.3 MeV corresponds to backscattering from Si at the surface.

It is desired to find the ratio of Si to Ta and the thickness of the Ta and Si in the film. Both parameters can be easily determined by RBS. (1) The thickness of the TaSi layer can be calculated by measuring the energy width of the Ta peak or the Si step and dividing by the energy loss of He per unit depth in a TaSi matrix. For example, the low-energy edge of the Ta peak corresponds to scattering from Ta at the TaSi/Si interface. As shown in the figure, the particles scattered from tantalum at the TaSi/Si interface of the 230 nm film have a final energy of about 1.9 MeV, while particles scattered from the same interface of the 590 nm film have less final energy (about 1.7 MeV) because they have passed through more TaSi. The entire Ta peak spans a greater energy range, because of the increased thickness of the layer. (2) The ratio of Ta to Si at any given depth in the film can be obtained by measuring the height of the Ta and Si peaks and normalizing by the scattering cross-section for the respective element. The stopping cross-section for TaSi is significantly higher than for pure Si. This means that a backscattered particle will lose more energy per unit volume in TaSi than in pure Si. An implication of this

fact is that, for a given energy loss (ΔE), there are fewer atoms contained in a volume of TaSi than for the same volume of pure Si. This results in fewer backscattering events, and that means the peak for silicon will be lower in the TaSi than in the pure Si layer. In the spectrum, the silicon peak has a step at its high-energy end: the lower peak is the TaSi; the higher peak is the pure silicon. The height of a backscattering peak for a given layer is inversely proportional to the stopping cross-section for that layer. The stopping cross-section of TaSi is known to be only 1.37 times that of Si. This explains why the height of the peak corresponding to Si in the TaSi layer is less than one-half the height of the peak corresponding to Si in the substrate, even for a film with a Si:Ta ratio of 2:3.

2.8 Spectrum Analysis/Simulation

The RBS spectra are commonly analyzed to get relative concentrations of atoms within the sample and to get the depth distribution of these atoms. Simulation of RBS spectra is needed for the interpretation of experimental results since the sample compositions vs. depth cannot be directly retrieved from the experimental data. The films of a given sample can therefore be analyzed for composition, thickness, and uniformity with depth using a simulation program. In these simulations, one usually subdivides each layer of a multilayered multielemental target into thin strips of uniform density. Finally a spectrum is reconstructed, as it would appear in a multichannel analyzer in a true experimental situation. Since the projectile energy keeps changing both along the incident and outgoing paths and the energy loss ($-dE/dx$) is energy dependent, the areal density of each strip is eliminated by an equivalent energy interval which corresponds to the energy difference between the events scattered from the front and the back surfaces of the strip divided by the stopping cross-section evaluated at the front surface before scattering. Later, this energy difference is expressed in terms of the channel width of the multichannel analyzer.

Computer programs for interactive analysis have been developed allowing automatic or semiautomatic synthesis of sample parameters. Simulation programs for both channeling and random spectrum were presented by Kido and Oso (1985). The RUMP code initially presented by Doolittle in 1985 for the analysis and simulation of RBS data, has now been made workable on a PC and updated to include more functions. Gisa 3.95, developed by Saarilahti and Rauhala (1992) is another ion scattering analysis interactive code for the evaluation of RBS spectra workable on personal computer. This program can handle RBS spectra for most projectiles at all significant energies and all target materials. It includes basic features such as electronic screening, correction to Bohr straggling, nonlinear detector response, effect of the low-energy tail background, etc. It adopts the parameterization given by Ziegler and Biersack (1991) for calculation of stopping power values (Transport ions

in matter – TRIM 91 program). The experimental parameters to be provided for simulation are (a) BEAM for the projectile, its charge state, incident ion energy, and its calibration parameters (b) GEOM menu defines the scattering and target angles with respect to the beam direction, (c) DETECT menu requires the detector and solid angle, (d) METH menu enables the selection of the calculation method (RBS, non-RBS, stopping power, etc.), and (e) NORM (submenu of SIMUL) enables the normalization method to charge, to height, to a certain channel or ROI area and finally the TARGET (submenu of SIMUL) is meant for entering a new target structure for the simulation or editing an already existing target structure.

In the TRIM calculations (now called SRIM in modified version i.e., the stopping and range of ions in matter that includes quick calculations which produce tables of stopping powers, range, and straggling distributions for any ion at any energy in any elemental target or target with complex multilayer configurations), the calculations for a few parameters are made as follows:

- (a) The nuclear stopping in reduced energy is calculated using

$$S_n(\epsilon) = \frac{\ln(1 + 1.1383\epsilon)}{2[\epsilon + 0.01321\epsilon^{0.21226} + 0.19593\epsilon^{0.5}]} \text{ for } \epsilon \leq 30 \quad (2.42)$$

and

$$S_n(\epsilon) = \frac{\ln(\epsilon)}{2\epsilon} \text{ for } \epsilon > 30$$

where

$$\epsilon = \frac{32.53M_2E_0}{Z_1Z_2(M_1 + M_2)(Z_1^{0.23} + Z_2^{0.23})}$$

with E_0 expressed in keV.

- (b) The relative velocity of the ion v_r depends on the ion velocity v_i and the Fermi velocity according to the relation:

$$\begin{aligned} v_r &= v_i \left(1 + \frac{v_F^2}{5v_i^2} \right) \quad \text{for } v_i \geq v_F \\ v_r &= \frac{3v_F}{4} \left(1 + \frac{2v_i^2}{3v_F^2} - \frac{v_i^4}{15v_F^2} \right) \quad \text{for } v_i \leq v_F \end{aligned} \quad (2.43)$$

- (c) The fractional ionization (q) is calculated from the empirical relation:

$$q = 1 - \exp[0.803 y_r^{0.3} - 1.3167 y_r^{0.6} - 0.38157 y_r - 0.008983 y_r^2]$$

where

$$y_r = v_r / \left(v_0 Z_{\text{HI}}^{2/3} \right) \quad (2.44)$$

It is possible to deconvolute the spectrum of the particles scattered by a thick target composed of several layers of elements and to determine their nature and their thickness.

Figure 2.22 shows the energy spectrum of α -particles scattered from a double layer of hafnium and yttrium on a thick silicon substrate while Fig. 2.23 shows the RBS spectrum of a sample containing Si and Au in the C-substrate as function of atomic masses present in their successive layers and from surface atoms of a thin layer.

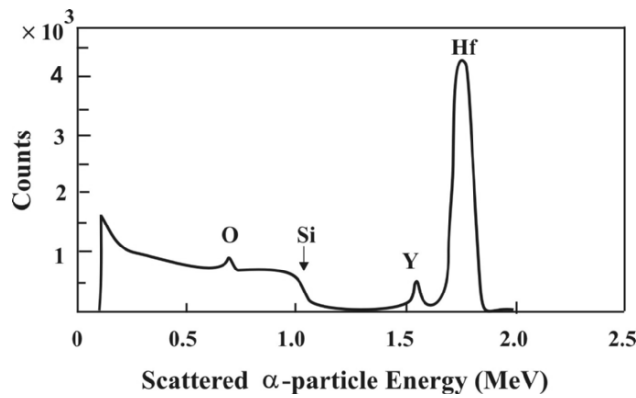


Fig. 2.22. Spectrum obtained after bombarding 2 MeV α -particles on a sample containing hafnium and yttrium on a thick silicon substrate

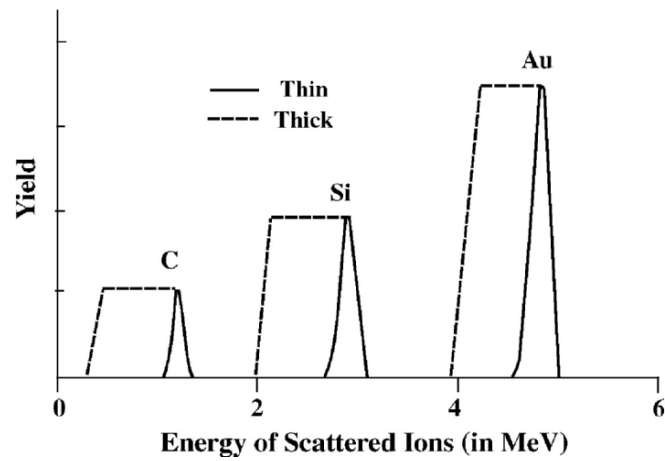


Fig. 2.23. Energy spectrum of ions scattered from surface atoms (*full curve*) and from atoms present in successive layers (*dashed curve*)

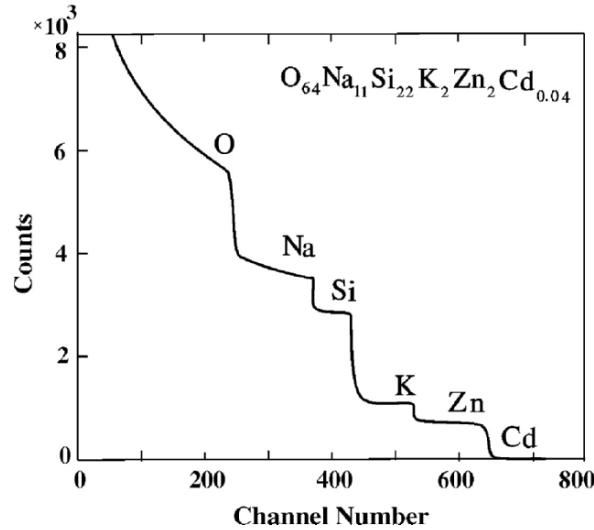


Fig. 2.24. RBS spectrum of ceramic glass $O_{64}Na_{11}Si_{22}K_2Zn_2Cd_{0.04}$ recorded by a beam of 1.9 MeV ^4He particles backscattered at 170°

Another example regarding shape of the RBS spectrum (Fig. 2.24) is that of ceramic glass — $O_{64}Na_{11}Si_{22}K_2Zn_2Cd_{0.04}$ recorded by a beam of 1.9 MeV ^4He particles backscattered at 170° .

2.9 Heavy Ion Backscattering Spectrometry

In RBS, only backscattered ions are detected, and backscattering can only occur if the target atom's mass is heavier than that of the incident ion. Conventional RBS is done with ^4He ions and the sensitivity of conventional RBS to low levels of impurities on a surface is limited to $\sim 10^{13}$ atoms cm^{-2} . If the impinged particle is heavier than $^4\text{He}^{2+}$, the technique is known as heavy ion backscattering spectrometry (HIBS). There are several advantages of using heavier ions such as ^{12}C , ^{16}O , ^{28}Si , or ^{35}Cl , where for example, better mass resolution is required for heavy elements or to eliminate large amounts of backscatters from oxygen when studying ceramic oxides. Moreover, collision cross-sections are higher for heavy primary ions, and there are no resonance effects at available energies. HIBS distinguishes itself from RBS through the use of TOF detectors (which have been optimized to provide a large scattering solid angle with minimal kinematic broadening) for improved mass sensitivity. To detect the surface contamination on wafers with greatly increased sensitivity relative to RBS, HIBS makes use of the fact that the differential scattering cross-section (or probability of backscattering into a detector) is proportional

to Z^2/E^2 . These heavy ion beams provide advantages in trace heavy element determinations of light element samples. The matrix elements are all scattered forward and cannot contribute interference signals. The principal advantage of HIBS over conventional RBS is the improved mass resolution for the analysis of high-atomic number samples. This property allows to measure the concentration diffusion profile induced by the diffusion of one element deep into the sample avoiding surface effects that could perturb the diffusion process. A detailed study of the use of MeV heavy ions ($2 \leq Z_1 \leq 10$) has been made by O'Connor and Chunyu (1989) to improve the limits of depth resolution in surface analysis.

A TOF ion detection system for HIBS has been described by Knapp et al. (1994) who have cited examples of the use of the TOF-HIBS system for measuring low-level contamination on Si wafers. This system has been quoted to have a sensitivity of $1 \times 10^9/\text{cm}^2$ for the heaviest of surface impurity atoms and a mass resolution capable of separating Fe from Cu. In a typical experiment, 50–200 keV C^+ ions backscattered from the sample surface pass through a thin C foil which ranges outmost of the ions backscattered from Si (and any lighter mass material) and simultaneously produce electrons which are detected by a microchannel plate (MCP) and give a timing start pulse. The C particle continues along its flight path until being stopped in a second MCP, giving a stop pulse. Three TOF detectors are used in parallel to give a large solid angle, increasing the efficiency and sensitivity of the system. This TOF detector technology allows higher mass resolution than surface barrier detectors. HIBS concentrations are calculated from first principles using integrated counts for the element of interest, just as in RBS.

Niwa et al. (1998) used an 8 MeV multicharged carbon or oxygen beam for RBS compositional analysis. The measured results on thin films of Co, Cu, Si, and Ni/Cr of a few nm thickness deposited on carbon substrates by vacuum evaporation or Ar sputtering, demonstrated that the mass resolution is much better for the heavy-ion RBS than for the He-RBS analysis. RBS measurements were also conducted by Mayor et al. (2002) on Nb/Co multilayers using helium as well as lithium ions as shown in Fig. 2.25. Theoretical calculations of the depth resolution are compared with experimental data for RBS yielded about the same or better depth resolution with Li^6 than with helium ions.

Weidhaas and Lang (2004) carried out the measurements on trace elements on surface by Rutherford backscattering using nitrogen ions. They found that the detection limit for heavy elements e.g., gold in silicon, a surface sensitivity of $10^{10} \text{ atoms cm}^{-2}$ is reached while for medium elements, e.g., As, Cr, and Fe, the detection limit is $\sim 10^{12} \text{ atoms cm}^{-2}$. HIBS has been used by Banks et al. (1998) for measuring extremely low levels of surface contamination on very pure substrates, such as Si wafers used in the manufacture of integrated circuits.

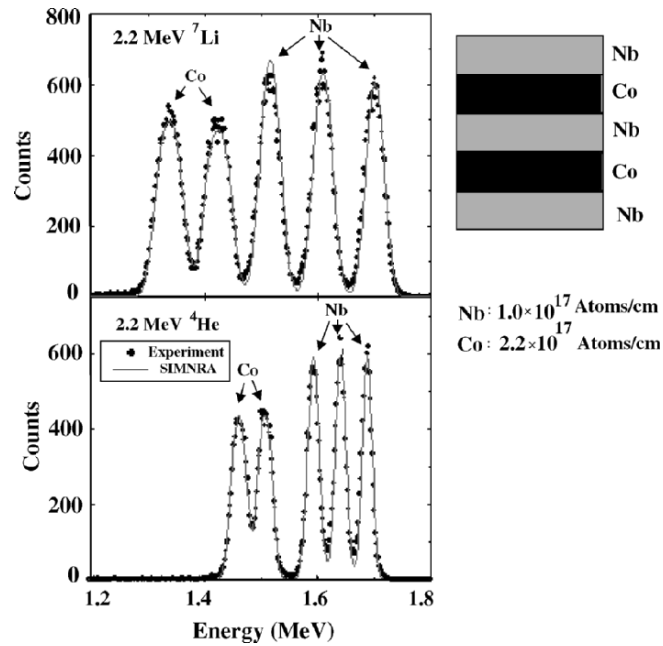


Fig. 2.25. Applications of heavy-ion RBS to compositional analysis of thin films

2.10 High-Resolution RBS

In normal RBS, the analysis of light elements in a heavier matrix is difficult because of the energy overlap of the beam ions scattered by light surface atoms and by heavier bulk atoms deeper in the sample. Although separate identification for light elements is generally easy but small amounts of the light elements are difficult to analyze because of the Z^2 dependence of the Rutherford cross-sections. Analysis of a sample containing C, O, Cr, Fe, Hg, and Au on Si substrate by RBS method using a beam of 2 MeV α -particles backscattered ($\theta = 165^\circ$) is as shown in Fig. 2.26. It is clear that the light elements overlap with thick layers of heavier elements. Furthermore, the identification is very difficult for very heavy atoms, since the heavier elements crowd together at the upper end of the spectrum and their separation mostly depends on the poor energy resolution of the particle detector.

As discussed in Sect. 2.6.2, the surface barrier detectors have energy resolution varying from about 15 to 80 keV for α -particles depending on the depletion depth (which varies from 100 to 500 μm) and the active area (which varies from 50 to 2,000 mm^2). The quoted value of resolution however, deteriorates due to radiation damage. The silicon particle detectors are small, easy to use, and give rapid results. However, by switching to use of a magnetic

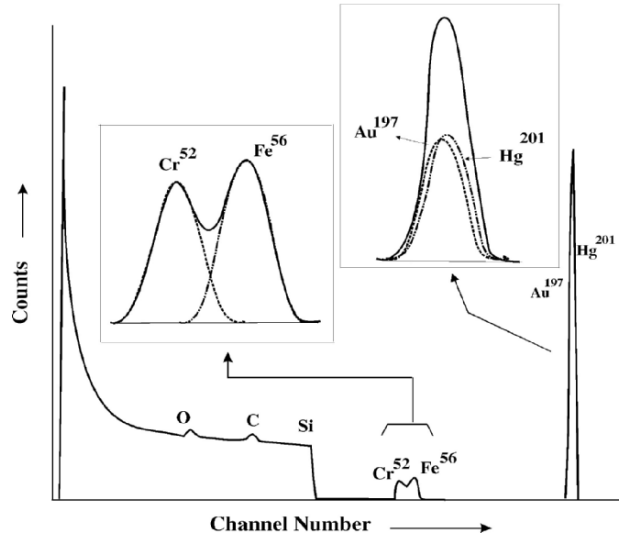


Fig. 2.26. Decreased mass resolution for heavier elements. The peaks shown in the inset due to ^{197}Au and ^{201}Hg overlap in the full spectrum

mass spectrometer, the facility called the high-resolution RBS (HIRRBS), improves resolution by more than a factor of 4. One can further make use of a mass spectrometer particle detector system instead of conventional single particle detector. While in the conventional mass spectrometer, the data is taken in steps by changing slowly through a range of magnetic field, pausing at each step to collect particles for a fixed amount of time, which results in very slow operation. In the HIRRBS facility with many detectors, the magnetic field remains fixed while data are taken simultaneously from detectors sensing from many different locations.

A HIRRBS system with a magnetic spectrometer ($\Delta E/E \sim 0.1\%$, including the energy spread of the incident beam) has been developed by Kimura et al. (1998) and the energy spectra of sub-MeV He^+ ions backscattered from single crystal surfaces have been measured with this HIRRBS system. The RBS spectra observed at grazing exit angles (several degrees) consist of several well-defined peaks that correspond to the ions scattered from successive atomic layers indicating the achievement of monolayer resolution. The same spectrometer is also used for ERD measurements as by installing an electrostatic deflector between the magnet and the ion detector; recoiled ions are distinguished from the scattered ions. Figure 2.27 shows the RBS spectrum (data presented as solid line and simulation presented as dashed line) HIRRBS study of a thin $\text{Ta}/\text{Ta}_x\text{N}_x$ bilayer.

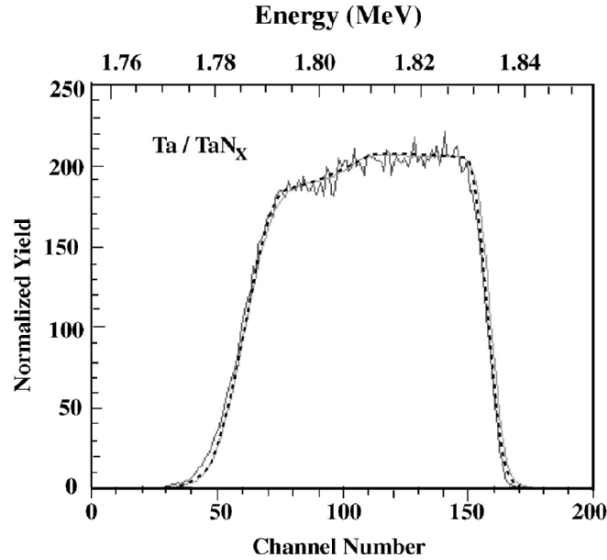


Fig. 2.27. RBS spectrum (data and simulation) HIRRBs study of a thin Ta/TaN_x bilayer

2.11 Medium Energy Ion Scattering

Medium Energy Ion Scattering (MEIS) is a refinement of RBS, but with greatly enhanced depth (energy) and angle resolution. The principle of this “nondestructive depth profiling” is exactly the same as that of Rutherford backscattering, but by using much lower energies than 1 MeV (since stopping power is maximum at about 100 keV for protons) and higher resolution detectors (based on the electrostatic deflection systems typically used in electron spectroscopy) much finer depth resolution ($\sim$ single atomic layer) can be achieved. MEIS is used for the determination of the composition and geometrical structure of crystalline surfaces and not deeply buried interfaces (Van der Veen 1985). For very high-depth resolution, we cannot use the Si charged particle detectors due to their limited (and fixed) energy resolution. Therefore, an (toroidal) electrostatic analyzer (TEA), to energy-analyze the scattered particles is used (Fig. 2.28). Here, we normally use elastic scattering of 100 keV protons to keep the voltages on the TEA reasonable, although this procedure limits the mass resolution. MEIS thus involves energy analysis of scattered primary ions, typically H^+ or He^+ at incident energies in the 100 keV range, as a function of incidence and emission direction.

In a MEIS experiment, a collimated beam of monoenergetic protons or He-ions impinges onto a crystalline target along a known crystallographic direction. The energy and angle of the scattered ions are analyzed simultaneously and allow MEIS to measure atomic mass, depth, and surface structure.

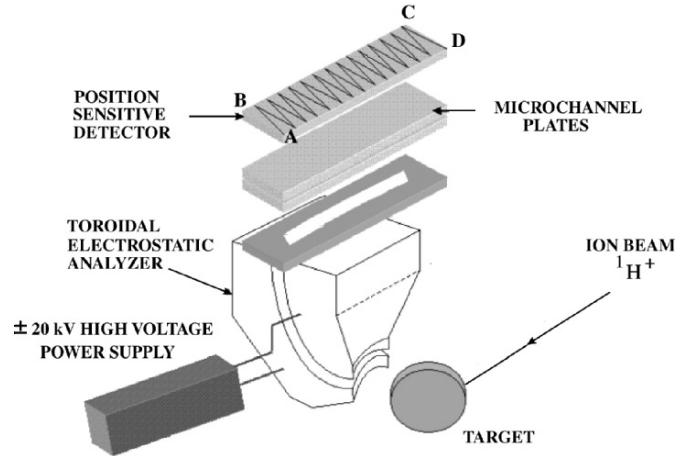


Fig. 2.28. Medium energy ion scattering spectrometer

This is because of the following (1) the scattered ion energy relates directly to the mass of the scattering atom (2) the energy loss relates directly to the depth of the scattering atom, and (3) the variation in scattered ion intensity with angle relates to the geometrical arrangement of surface atoms because the ion beam being aligned with a crystallographic axis, the surface atoms shadow deeper atoms from the ion beam.

Although a very powerful technique, there are less than ten machines worldwide because of the high-equipment cost. At the MEIS facility of the Daresbury laboratory, an ion source generates a positively charged beam of light mass ions, typically hydrogen or helium, which can be accelerated in the energy range 50 keV to a maximum of 400 keV. The experimental station facilities include interconnected ultrahigh vacuum (UHV) systems between which samples can be transferred under UHV (1) Scattering chamber, which houses the ion analyzer, sample goniometer, and two-dimensional (energy and angle) position sensitive detector and is where the ion scattering experiments are performed. (2) Preparation chamber, whose facilities include sputter cleaning, evaporation sources and gas dosing, is used for sample preparation and characterization prior to ion scattering experiments (3) Storage chamber, where a number of samples can be stored and which forms the junction of the sample transfer system, and (4) Loading chamber which is a fast pump down chamber used for introducing samples into the vacuum systems. A 6-axes goniometer is used to perform channeling in blocking out measurements, also done in UHV. The three orthogonal rotations are computer controlled while other three orthogonal translations are manually actuated.

The current at sample is 0.1–1.0 μA dependent on beam energy and ion species while the beam spot size at sample is 1 mm $\times$ 0.5 mm. The sample size is kept between 5 $\times$ 5 mm to a maximum of 15 mm diameter which can be kept in the temperature range of 300–1,300 K in UHV environment. The sample

has three rotational and three translational degrees of freedom whose loading time from air is typically 30 min. The two-dimensional (energy and angle) ion detector is chevron array anode with MCPs. The fractional resolution of the TEA ~ 150 eV for $E_0 = 100$ keV. The position sensitive detector yields a two-dimensional image (energy and angle) for each setting of the TEA voltage which is changed in steps to cover all the relevant masses. Also, in order to measure elements like C, N, and O lighter than the substrate (which is most often Si), not only a channeling IN configuration but also a blocking direction has been employed on the outward path so that the substrate yield is further reduced.

The geometrical structure information is derived through the use of elastic “shadow cones,” in both the incident and backscattering parts of the ion trajectory. This is because of the reason that for a particular crystal, certain ingoing directions can allow the ion beam to illuminate only the top one, two, or three layers according to choice. Ions scattered from the second layer will have their outward paths blocked at certain angles by first layer atoms. This alignment makes the technique surface specific. By appropriate choice of scattering geometry atomic displacements as small as 0.05 Å can be measured. Combined with this improved structural sensitivity is an ability to obtain sub-surface compositional information through the inelastic energy losses incurred as the ions penetrate further into the solid.

Broadly the proposed areas of application of MEIS fall into the following categories:

1. Adsorbate structures and reconstructions, particularly of metal surfaces. The high sensitivity of MEIS to movements of substrate atoms parallel to the surface makes the technique very useful in the study of such systems. MEIS allows one to quantify the number of displaced atoms and the number of reconstructed layers.
2. Alloy surfaces and epitaxial growth. This topic covers a range of subtopics; the formation and structure of surface alloy phases, even in immiscible systems; the depth variation of alloy components in the near-surface region (especially oscillatory compositional variations in surface segregation); the study of interfacial structure and film perfection in metal heteroepitaxy; the growth modes – i.e., island, layer-by-layer, etc. In several of these problem areas systems of potential interest for their magnetic properties are emphasized.
3. MEIS is also sensitive to perpendicular movements of atoms and is used to study oxide-on-metal and metal-on-oxide growth.

2.12 Channeling

A more interesting phenomenon occurs in RBS, if the sample is a crystal. In case of normal (random) scattering as shown in Fig. 2.29, the incident ions collide with atoms midway and are scattered because ions, not aligned with the

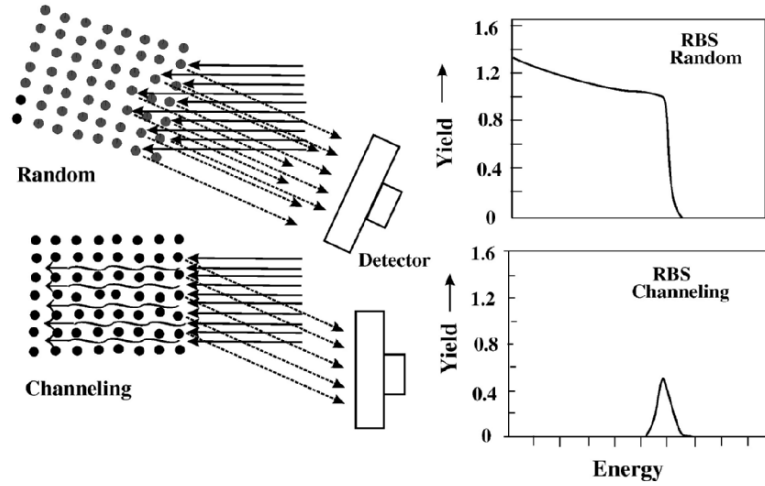


Fig. 2.29. RBS channeling vs. RBS random

array, impinging on the crystal scatter sooner without a channel to penetrate. However, when ions enter the sample in parallel with the crystal axis, they will wander through space among crystal atoms, go deep in the channel before scattering and only a few ions scatter from the surface. This phenomenon is called channeling. In case of channeling, the scattered ions have unique energy, which identifies the element.

In the channeling mode, extra atoms not aligned with the array will cause extra scattering. At this time, the number of backscattered ions decreases markedly. There is more than 95% reduction in the yield of small impact parameter interaction process of Rutherford scattering, when an ion beam is well aligned with a low-index crystallographic direction of a single crystal, say for example $\langle 100 \rangle$ of Si.

In channeling studies, the orientation of the crystal is made such that the particle beam arrives in alignment with the atomic structure. In this case, most of the particle beam will pass through the space between the planes of atoms and will penetrate deep within the crystal. Channeling studies take advantage of this phenomenon to find not only the structure of the crystal but is also useful for location of atoms in the lattice. RBS measurements in the channeling orientation are therefore, ideal for providing crystallographic information on radiation damages, crystal defects, impurity location in single crystals and strains in superlattice structures. The ion channeling process can be modeled in terms of ion scattering from atomic strings (axial channeling) or planes (planar channeling) with uniform continuum potentials. Using this continuum model, quantitative analysis is also possible.

2.13 Rutherford Scattering Using Forward Angles

RBS is widely used as a quantitative technique in IBA. For a thin film in which the energy loss is larger than the energy resolution of the detector, the stoichiometry can be obtained from the spectrum height, and the thickness of the film is determined by the energy loss in the film. For the films where the energy loss in the film is comparable to or smaller than the detector resolution, this is no longer possible and only the total number of atoms in the film can be extracted. As long as the areal density is accessible for all individual elements in the film (e.g., heavy elements on a light substrate), the film composition and thickness may still be obtained by combining the individual values. However, in most cases this is not possible because of contribution from other parts from the sample.

RBS is widely used since the scattering cross-sections hardly change with the scattering angles near 180° . As one can easily visualize from Fig. 2.6, the cross section drops rapidly with a steep slope at forward angles to comparatively very low values at backward angles. Even a change of 0.5° introduces a change of $\sim 15\text{--}20\%$ in the cross-section values at forward angles. However, the depth resolution can be improved significantly by using the glancing angles for the incident and/or backscattered ion, which increases the pathlength although the total accessible depth range will be reduced. Figure 2.30 shows the comparison of the geometry for RBS and Rutherford forward scattering (RFS). A comparison of the two geometries shows that the RBS geometry is with normal incidence ($\alpha = 0^\circ$) and grazing exit angle (with the detector at a backscattering angle close to 180°), while there is a tilted sample (with large tilt angle α) and small scattering angle θ in the RFS geometry. The advantage of the RFS geometry is that the large scattering cross-sections at

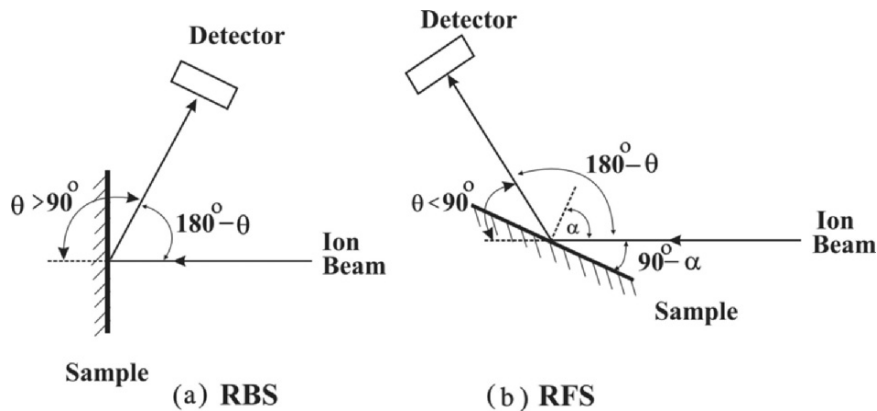


Fig. 2.30. Schematic illustration of the experimental geometry (a) standard RBS with normal beam incidence ($\alpha = 0$) and grazing exit angle (b) RFS scattering with large sample tilt angle α and small scattering angle θ

forward angles allows for the use of a small solid angle while maintaining good count rates and short acquisition times. The beam spot and solid angle of the detector are chosen to be very small to avoid geometrical energy broadening. The kinematic factor is almost close to 1 for almost all elements in this geometry. RFS can be used for channeling analysis and the size of the beamspot is not very crucial for obtaining good depth resolution.

Rutherford scattering of MeV ^4He ions at forward angles has been used to determine the thickness and composition of single $\text{Si}_{1-x}\text{Ge}_x$ layers in Si. With scattering angles of about 20° the depth resolution comes out to be much greater than 25% better than the standard RBS at glancing backward angles (Endisch et al. 1995). The large scattering angles allow for the use of a small solid angle while maintaining good count rates and short acquisition times. Geometrical broadening of the energy spectra, due to the finite acceptance angle of the detector, is thus negligible. Since the kinematic factor is close to one for almost all elements in this geometry, the layers with different composition are therefore only distinguishable by the differences in spectrum height. However, the best accuracy for the stoichiometry is obtained by combining the measured energy loss in a layer with the areal density of the heavier element layer, which can be determined by standard RBS.

By using the forward scattering geometry, one has to be aware that the kinematic factor is close to 1 for almost all elements, which is quite different from normal RBS, where different elements can be distinguished through the rapid variation of kinematic factor with target mass. In case of Si and Ge, $K(\text{Si})$ is 0.566 and $K(\text{Ge})$ is 0.803 at a backscattering angle of 170° , while $K(\text{Si})$ is 0.983 and $K(\text{Ge})$ is 0.993 at a scattering angle of 20° . He-ions scattered in a SiGe layer will therefore appear at almost the same position in the energy spectrum, no matter if they have been scattered from Si or from Ge. Layers with different composition are identified by the spectrum height.

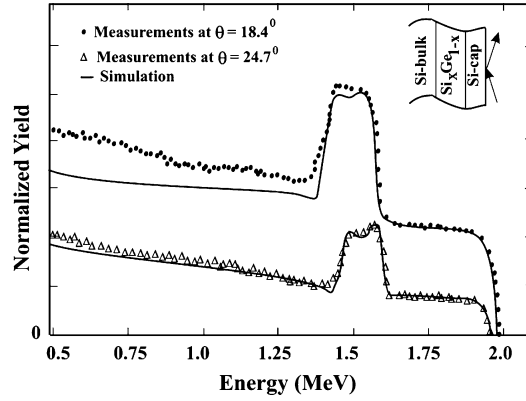


Fig. 2.31. RFS spectrum for SiGe sample at scattering angles of 18.4° (circle) and 24.7° (triangle) after subtracting the background. The solid lines indicate the simulation using the RUMP software

Because the spectrum height is proportional to Z^2 , the spectrum height is larger for a $\text{Si}_{1-x}\text{Ge}_x$ layer than for pure Si for all values of x . Figure 2.31 shows the measured RFS spectrum of SiGe sample with 2 MeV α -particles at two different detector angles after subtracting the background caused by multiple scattering after measuring a-Si sample. The measured yield is significantly more at lower energies as compared to simulated yield since the RUMP simulation does not take into account the multiple scattering effects. The spectrum shows that the depth scale for Si and Ge are superimposed because of almost identical kinematic factors. Thus, the Ge concentration can not be calculated by just using the Si-signal as background since the Ge signal is located almost on the top of the Si-dip. Therefore instead of using height and width of the signal from the SiGe layer measured by RFS, information from RFS and from RBS is used. The areal density of Ge is determined by RBS while the width of the signal from the SiGe layer is obtained by RFS.

The following errors affect the results of RFS analysis:

1. If the scattering angle is too small, an increased peak width due to multiple scattering is expected.
2. A source of possible background when using forward scattering can be caused by scattering from the slits or other beam defining parts directly into the detector. Because the slits are usually made from Ta and the scattering cross-section for small angles is extremely high, disturbing background can occur even at large distance if there is a direct line of sight from the slits to the detector.

For accurate results, the sample tilt angle and the scattering angle must be known very accurately. Assuming an uncertainty of 0.10° for sample and detector angles results in an error of 1% for the RFS measurement at 24° . For the RBS geometry, the effect is even larger, resulting in an error of 2% for the same angle uncertainties.

2.14 Applications of RBS

The RBS method has numerous applications. A few of these are listed as follows:

- (a) Absolute thickness of films, coatings and surface layers (in atoms cm^{-2})
- (b) Surface impurities and impurity distribution in depth (surface/interface contaminant detection in oxide layers, adsorbates, etc.)
- (c) Interdiffusion kinetics of thin films (metals, silicides, etc.)
- (d) Elemental composition of complex materials (phase identification, alloy films, oxides, ceramics, glassy carbon, etc.)
- (e) Quantitative dopant profiles in semiconductors
- (f) Process control monitoring – composition, contaminant control

2.15 Limitation of the RBS Technique

One of the main limitations of the RBS is its poor sensitivity for light elements present in a heavier matrix (Detection limit 1–10 atomic % for $Z < 20$, 0.01–1 atomic % for $20 < Z < 70$ and 0.01–0.001at.% $Z > 70$). This is because of the relatively low value of the backscattering cross-section for light elements (which is proportional to the square of the atomic number of the element $\sigma_{\text{RBS}} \propto Z^2$) and the fact that the energy of a particle will be low when it is backscattered from a light atom. The features corresponding to light elements in a heavy matrix therefore tend to drown in a background representing the presence of a matrix atom at a certain depth. Since backscattering from heavy matrix is not possible, this element cannot be detected at all by RBS.

Exercises

Exercise 1. Find the impact parameter and distance of closest approach for α -particle of 6.7 MeV energy impinging on gold target. What will be the distance of closest approach if scattering angle is 90° .

Solution. Using $d = (Z_1 Z_2 e^2 / 4\pi\epsilon_0)(1/E_0)$ and putting $Z_1 = 2$, $Z_2 = 79$, $e = 1.6 \times 10^{-19}$ C, $\epsilon_0 = 8.85 \times 10^{-12}$, $E_0 = 6.7 \text{ MeV} = 6.7 \times 10^6 \times 1.6 \times 10^{-19}$ J, we get

$$d = 3.39 \times 10^{-14} \text{ m}$$

As $\cot(90^\circ/2) = 1$ it follows that the impact parameter is by

$$b = d/2 = 1.695 \times 10^{-14} \text{ m}$$

For scattering at a particular angle the alpha particle comes closest to the nucleus when its momentum is perpendicular to the radius vector from the nucleus. By using the conservation of energy and the conservation of angular momentum it is fairly straightforward to show that for 90° scattering the distance of closest approach is

$$\frac{d}{(2(\sqrt{2}-1))} = 4.1 \times 10^{-14} \text{ m}$$

Exercise 2. Find the energy of the particles as well as the thickness of Au layer if the RBS spectrum contains 1,000 counts of α -particles backscattered from this Au layer? Given: Incident angle $\alpha = 0^\circ$, scattering angle $\theta = 170^\circ$, $E = 2 \text{ MeV}$, $\Delta\Omega = 10^{-3}$ steradian, $Q = 10 \mu\text{C}$.

Solution Hint.

- (a) For Energy of backscattered particles, use the formula $E_1 = KE_0$ where E_0 = energy of incident particle and K = kinematic factor given by the formula

$$K(\theta, M_1, M_2) = \left(\frac{(M_2^2 - M_1^2 \sin^2 \theta)^{1/2} + M_1 \cos \theta}{M_1 + M_2} \right)^2$$

(b) For thickness of the target

We know that

$$dQ = Q \left(\frac{d\sigma}{d\Omega} \right) \Delta\Omega N_x \cdot \left(\frac{\Delta x}{\cos \alpha} \right)$$

where dQ is the area under the peak, Q is number of incident particles i.e., incident charge divided by the charge of each particle or ion, N_x = atomic density of the element in atom cm^{-3} , is the solid angle, Δx = target thickness in cm which can be converted to $\mu\text{g cm}^{-2}$ by multiplying by density (ρ) of the element, $(d\sigma/d\Omega)$ is the scattering cross-section per unit solid angle in units of barns per steradian or cm^2 per steradian

Here $dQ = 1,000$, $Q = 10 \times 10^{-6} / (2 \times 1.6 \times 10^{-19}) = 3.125 \times 10^{13}$ particles, “2” in the denominator is because the charge state of α -particles is 2^+

Atomic density of Au (N_x) = 5.904×10^{22} atoms cm^{-3}

$d\sigma/d\Omega = 8.0634$ barn steradian $^{-1}$ (corresponding to $E = 2,000$ keV, $\theta = 170^\circ$ for incident α -particles on Au target calculated using formula for $d\sigma/d\Omega$)

Now calculate Δx which will be in the unit of cm and can be further converted to $\mu\text{g cm}^{-2}$ using the density of “Au” as 19.31 g cm^{-3} .

Exercise 3. The α -particles with kinetic energy 10 MeV are incident on a gold foil of thickness 0.1 mm at a rate of 10^7 particles per second. A detector of area 10^{-3} m^2 is placed at an angle of 30° to the direction of incident α -particles at a distance of 2 m from the foil. Calculate how many α -particles per second reach the detector? Given the density of gold is $1.93 \times 10^4 \text{ kg m}^{-3}$.

Solution Hint. Here $M_1 = 4$, $M_2 = 197$, $E_1 = 10 \text{ MeV}$, $A = 10^{-3} \text{ m}^2$, $R = 2 \text{ m}$, $t = 0.01 \times 19.3 \text{ g cm}^{-2}$.

Velocity of the particles $v_0 = \sqrt{(2qV \text{ m}^{-1})}$, where qV is the energy in joules. Flux of incident beam is nv_0 particles ($\text{cm}^{-2} \text{ s}^{-1}$), if density of particles in the beam is $n \text{ cm}^{-3}$

$$v_0 (\text{m s}^{-1}) = \sqrt{\frac{2 \times E_1 (\text{in MeV}) \times 10^6 \times 1.6 \times 10^{-19}}{M_1 \times 1.6724 \times 10^{-27}}}$$

Areal density of the target in atoms $\text{cm}^{-2} = (6.023 \times 10^{23} / M_2) \times t$.

Now use (2.23) to calculate Rutherford scattering cross-section.

$$\text{if } y = \sqrt{1 - \left(\frac{M_1 \sin \theta}{M_2} \right)^2}$$

$$d\sigma (\text{in barns}) = 4 \times \left(\frac{Z_1 Z_2}{4\pi} \frac{1.6 \times 10^{-19}}{8.854 \times 10^{-12}} \frac{1}{E_1} \right)^2 \times \frac{10^{28} \times (y + \cos \theta)^2}{y \times \sin^4 \theta}$$

$$N_{\text{sc}} = N_i \times d\sigma \times 10^{-24} \times (A/R^2) \times (6.023 \times 10^{23} / M_2) \times t (\text{in g cm}^{-2})$$

Elastic Recoil Detection

3.1 Introduction

The RBS technique for thin-film analysis described in Chap. 2, usually makes use of 2–3 MeV α -particles, and is based on the process of elastic scattering and the energy loss of the energetic primary and (back) scattered ions. RBS is a successful and often used simple and fast technique for depth profiling of elemental concentration. Since the collisions with the target nuclei are elastic, one can derive the mass of the scattering centers from the measured energies, making use of the laws of conservation of energy and momentum. The excellent ability of this method to extract quantitative data about abundances of elements is due to the precise knowledge of the Rutherford scattering cross-sections. However, the RBS has its limitations in terms of mass resolution for heavy elements and poor sensitivity for light elements present in the sample. The drawback of poor sensitivity for light target elements present in a heavier matrix is due to low values of the cross-sections ($\sigma_{\text{RBS}} \sim Z^2$) and the fact that the energy of a particle will be low when it is backscattered from a light atom (Chu et al. 1978). The features corresponding to light elements in a heavy matrix, therefore, tend to drown in a background representing the presence of matrix atoms at a certain depth. Since backscattering from hydrogen is not possible, this element cannot be detected at all by RBS. When the He^+ or He^{2+} beam strikes at a grazing angle, there is no backscattering of He^+ or He^{2+} from hydrogen, as helium is heavier than hydrogen. Instead, hydrogen is knocked in the forward direction with significant energy after being struck by He^+ or He^{2+} . Since carbon, mylar, and aluminium foils are commonly used, these foils cause significant energy loss and straggling in the forward scattered hydrogen.

In contrast to the RBS, the technique of detection of the recoiled (secondary) particles is called elastic recoil detection (ERD) which was first reported in 1976 by L'Ecuyer et al. The ERD provides depth as well as mass information regarding the target particle location and therefore allows simultaneous profiling of all elements within the substrate. ERD is

thus complementary technique to RBS which allows unambiguous particle identification saving the quantitative feature. It is used principally as a method for quantitative analysis of hydrogen content in thin layers (which has not been possible by any conventional method), and in the near-surface region of materials.

The ERD technique is a consequence of the conservation laws i.e., that the energy of the other participant in the collision, which is not detected in RBS (i.e., the target nuclei themselves), contains the same kind of information about the target. ERD is thus an accurate ion beam analysis technique specially suited for characterization (depth profiling) of light elements.

In ERD analysis, an energetic projectile is directed to impinge on a target at a grazing incidence and the atoms from the sample get recoiled in the forward direction as a result of the elastic scattering, and are detected by a suitable detector, viz. solid state and/or a gas filled telescope type detector. We thus identify the particles under investigation in a forward scattering geometry whereby both scattered and recoiled particles will move in the direction of the detector. In conventional ERD heavy primary ions (heavier than α -particles) are used. A thin filter, typically mylar, is placed in front of a silicon surface barrier detector (SBD) to stop and block out the elastically scattered incident ion beam, which would otherwise overload and quickly destroy the detector. The stopping power in the foil decreases substantially with decreasing mass of the moving particle. Therefore, the thickness of the foil can be chosen such that the light energetic recoils are allowed to reach the detector, while the heavy primary particles are completely stopped. The ERD is most suited for the situation for which RBS is inconvenient i.e., when the atom of interest in the target consist of light particles w.r.t the matrix or substrate atoms. In order to discriminate between forward scattered projectiles and different types of recoiling particles, absorber foils or mass discriminating detectors are used. The absorber foil stops both the primary and the heavy recoiled particles, if the primary ions of approximately the same mass as the matrix or substrate atoms are made to impinge on the target. In this way, the lighter particles are detected without any background. Using detector systems that are more sophisticated than this foil/detector combination, the recoiled particles can be identified allowing unambiguous interpretation of the data. The great advantage of ERDA with a mass (or nuclear charge) discriminating detector is that the depth profiles of all target elements can be obtained simultaneously well separated from each other.

In principle, conventional ERD can be carried out using the same instrumentation as RBS, apart from the stopper foil in front of the detector. Only the configuration i.e., the incidence and detector angle has to be altered. However in order to be able to benefit from the entire range of probe depths and element masses, the energy and mass of the primary ions, usually applied in RBS, are inadequate. Instead in ERD, primary particles ranging from C to Au with energies of the order of 1 MeV/u are usually applied. If one wishes to do ERD measurements on “RBS set-up” i.e., using beam of α -particles,

one is restricted to the detection of H and D (probe depth ~ 200 nm). The ready availability of low-energy helium beams from small accelerators has made ERDA a popular technique for the determination of hydrogen in solids, and studies of polymer interdiffusion.

Originally the ERD technique was developed for hydrogen detection and light element profiling with an absorber foil in front of the energy detector for beam suppression. Subsequently advanced versions of ERD analysis used various detection methods with particle identification capabilities to avoid the absorber foil and the connected difficulties. Time-of-flight (ToF) system, magnetic spectrometer, and different kinds of particle telescopes have been applied for the purpose. In most cases medium heavy ion beams, typically ^{36}Cl ions of about 30 MeV, have been used for ERD analysis.

Depending on the film thickness and the experimental conditions, ERD can provide areal concentration (atom cm^{-2}) and/or concentration ratio of elements present. A sensitivity in the ppm region with a depth resolution of some 10 nm and a depth range of 1 μm is obtained in standard ERD set-ups.

3.2 Fundamentals of the ERDA Technique

3.2.1 Kinematic Factor

We have studied in Chap. 2 that when a beam of alpha particles strikes the foil, these particles get scattered at an angle θ . During this process, the energy is transferred to the atoms of the target due to which these get recoiled through angle ϕ as shown in Fig. 3.1. Dealing with the technique of ERDA, the following basic concepts are important:

1. Energy transfer from a projectile to a target nucleus in an elastic two-body collision – concept of kinematic factor ($K = E_2/E_0$ i.e., ratio of energy of the recoiled particle to the energy of the incident particle)

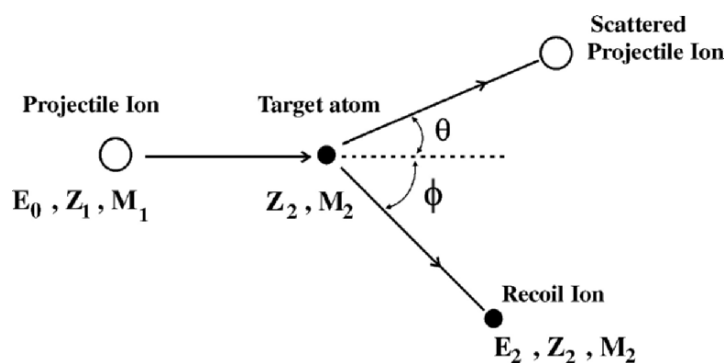


Fig. 3.1. Emission of recoil ions in the scattering process

2. Probability of occurrence of such a two body collision – concept of scattering cross-section
3. Average energy loss of an atom moving through a dense medium – concept of stopping power. Statistical fluctuations in the energy loss of an atom moving through a dense medium – concept of energy straggling

The collision can be described by simple expressions in terms of Coulomb repulsion between the projectile nucleus and the target nucleus. The energy E_2 transferred by projectile ions of mass M_1 and energy E_0 to target atoms of mass M_2 recoiling at an angle ϕ with respect to the incident direction, is given by:

$$E_2 = \frac{4M_1M_2}{(M_1 + M_2)^2} E_0 \cos^2 \phi \quad (3.1)$$

Equation (3.1) can be further written as

$$\frac{E_2}{M_2} = \frac{4 \cos^2 \phi}{(1 + M_2/M_1)^2} \left(\frac{E_0}{M_1} \right) \quad (3.2)$$

i.e., for ERDA with heavy ions, where $M_2/M_1 < 1$, all recoiling ions have similar velocities. Therefore the stopping powers, which depend on the particle velocity, are in the same regime for all recoils.

The energy fraction transferred from primary to recoil particles is given by the kinematic factor for recoiling:

$$K_r = \frac{4M_1M_2 \cos^2 \phi}{(M_1 + M_2)^2} \quad (3.3)$$

where ϕ is the recoil angle and the subscripts 1 and 2 denote the primary and recoil particles, respectively. The fraction of the primary energy K_s retained by the projectile particle when by the projectile particle is scattered over an angle θ , is given by

$$K_s = \left(\frac{(M_2^2 - M_1^2 \sin^2 \theta)^{1/2} + M_1 \cos \theta}{M_1 + M_2} \right)^2 \quad (3.4)$$

It is clear that both K_r and K_s are functions of the mass ratio M_2/M_1 and the angle ϕ and θ . Scattering of the primary particle and recoiling necessarily occur simultaneously. It is therefore interesting to compare the values for K_s and K_r at various detection angles as a function of the considered mass ratio (Fig. 3.2).

It is clear from the figure that the energy of the recoil particle is maximal when $M_1 = M_2$. Further, it is clear from (3.3) and (3.4) as well as Fig. 3.2 that for $M_2/M_1 > 1$, the kinematic factor for scattering (K_s) for the scattered incident particles is larger than the kinematic factor for recoiling (K_r) and increases with increasing mass ratio.

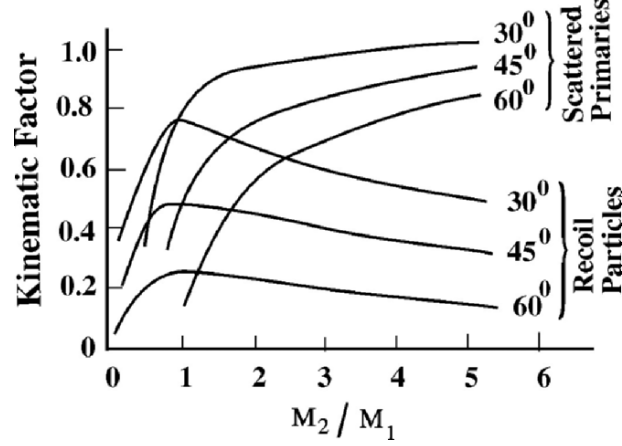


Fig. 3.2. Kinematic Factor K_r and K_s for elastic scattering as a function of the ratio of the target nucleus mass M_2 and the projectile nucleus mass number M_1 for various recoil and scattering angles

3.2.2 Scattering Cross-Sections and Depth Resolution in ERD

The chance that one particle from the beam ejects a recoil of element (Z_2, M_2) in such a way that it starts moving in the direction of the detector is proportional to the areal density (atom cm^{-2}) of this element and the detector solid angle of the detector. Treating the interaction as purely Rutherford scattering (since the energy available in the center of mass is at least five times below the Coulomb barrier) the elastic scattering cross-section is given by Rutherford differential cross-section for ERD i.e.,

$$\left(\frac{d\sigma}{d\Omega}\right)_{\text{ERD}} = \left(\frac{Z_1 Z_2 e^2}{2E_0}\right)^2 \cdot \frac{(1 + (M_1/M_2))^2}{\cos^3 \phi} \quad (3.5)$$

The $1/E_0^2$ dependence of the scattering cross-section shows that the yield of recoils, and hence the sensitivity of the technique, increases with depth due to the decreasing energy E_0 of the incident projectiles.

This differential cross-section can be used for collisions where the energy of the primaries is $\sim 1 \text{ MeV/u}$. On the low-energy side, the Rutherford scattering regime is limited because the presence of orbital electrons contributes significantly to the scattering potential at larger scattering distance. On the high-energy side, the scattering cross-section may deviate strongly from the Rutherford value when the distance of closest approach of the nuclei is within the range of the nuclear forces.

A new analysis technique using high-energy helium ions for the simultaneous ERD of all three hydrogen isotopes in metal hydride systems extending to depths of several micrometers has been presented by Browning et al. (2000). Their analysis shows that it is possible to separate each hydrogen

isotope in a heavy matrix (such as Erbium) to depths of $5\text{ }\mu\text{m}$ using incident 11.48 MeV ^4He ions with a detection system composed of a range foil and $\Delta E - E$ telescope detector. Newly measured cross-sections for the elastic recoil scattering of ^4He ions from protons and deuterons have also been presented by these authors in the energy range $10\text{--}11.75\text{ MeV}$ for the laboratory recoil angle of 30° . In another paper Browning et al. (2004) have reported the cross-section measurements for the elastic recoil of hydrogen isotopes, including tritium, with $^4\text{He}^{2+}$ ions in the energy range of $9.0\text{--}11.6\text{ MeV}$. The uncertainty in these cross-section values, which were measured by allowing a $^4\text{He}^{2+}$ beam to incident on solid targets of ErH_2 , ErD_2 , and ErT_2 , each of 500 nm nominal thickness and known areal densities of H, D, T, and Er, is estimated to be $\pm 3.2\%$.

In the surface approximation and assuming constant energy loss, the depth resolution δx can be written as

$$\delta x = \frac{\delta E_2}{E_2} (S_{\text{rel}})^{-1} \quad (3.6)$$

where S_{rel} is the relative energy loss factor, defined by

$$S_{\text{rel}} = \frac{dE_0/dx}{E_0} \frac{1}{\sin \alpha} + \frac{dE_2/dx}{E_2} \frac{1}{\sin \beta} \quad (3.7)$$

α and β are the incidence angle of the beam and the exit angle of the recoiling ion, respectively, as shown in Fig. 3.3. It is clear that the depth resolution depends on the relative energy resolution as well as the relative stopping power of incoming and outgoing ions.

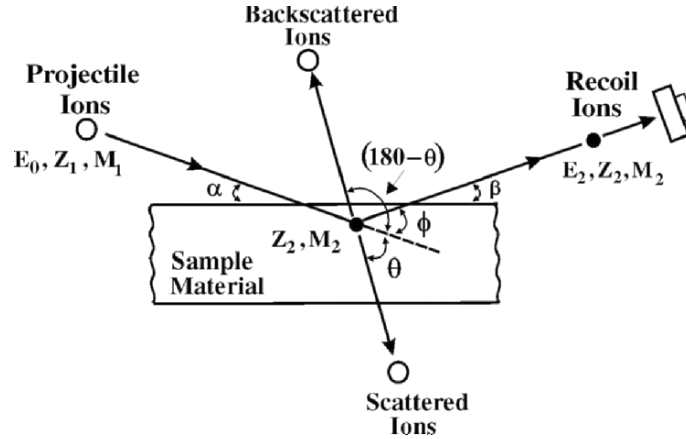


Fig. 3.3. Schematic diagram of the ERDA geometry for oblique incidence of the projectiles. β is the exit angle of the recoils with the surface and is related to recoil angle ϕ by $\phi = \alpha + \beta$, where ϕ is the angle of incidence with the surface

3.2.3 Stopping Power and Straggling

Ions lose energy while traversing through materials due to interaction of the ions with the electrons of the target material, causing excitation and ionization. The loss of energy due to small angle scattering on the nuclei in the material is about 1% of the total energy loss. Ziegler et al. (1985) have given an empirical parameterization for calculating the stopping cross-sections. One can determine the correlation between the depth and energy by evaluating the stopping powers on inward and outward paths. This implies that a good depth resolution requires not only well-defined energy of incident particles which are recoiled from a certain depth and detected under a preset detector angle but also a good detector energy resolution.

A spread in energy loss on both paths of the target (called energy straggling) is caused by the statistical fluctuations in the number and kind of encounters that an energetic particle undergoes while traveling in matter. For thin layers, the amount of energy straggling is considered to be proportional to the square of the energy loss. This causes deterioration of depth resolution with increasing depth.

3.3 Principle and Characteristics of ERDA

The physical basis which has given the method its name is elastic scattering of incident ions on a sample surface. The principle behind the ERD technique is that the sample to be analyzed is irradiated by a high-energy heavier projectile ion beam (the range of several MeVs) at grazing angle of incidence ' α '. Some of these primary ions push against the atoms of the specimen, ejecting some of target atoms elastically as shown in Fig. 3.3. The energy distributions of the different recoil atoms ejected from the target under a certain angle ϕ in the forward direction are recorded. The analysis of the number, mass, and energy of these particles by the use of a gas-filled ionization chamber allows the sensitive determination of the depth profiles of the light elements ($Z < 18$) of the specimen. A gas-filled ionization chamber allows, in contrast to commonly used surface barrier detectors, the determination of the atomic number and the emission angles of the ejected particles. Consequently, an enlargement of the solid angle (up to about 6 milliradian) does not worsen the remarkable depth resolution of the technique (< 10 nm), because the so-called kinematic errors are compensated mathematically by using the emission angles of the particles. The relatively large solid angle allows a fast measurement (1 spectrum per 30 s) without using too large beam intensities in order to minimize the ion beam-induced damage.

Since one can obtain the depth vs. concentration profiles of all the species (lighter than the projectile) present in the sample with a sensitivity of 0.1% and a depth resolution of 20 nm, this results in as many spectra as elements present in the sample, each one revealing the depth distribution

of the corresponding element, in an ideal situation. Two processes shape the spectrum: The transfer of energy from the primary particle during the collision and the loss of energy by the primary and recoil particles on the inward and outward paths, respectively. The first determines the energy of an atom recoiled from the surface, and the second determines the deviation from this energy with depth. ERD analysis mainly depends on four physical concepts (1) kinematic factor (2) differential scattering cross-section (3) stopping powers, and (4) energy straggling. By applying these four physical parameters, an ERDA spectrum can be transformed into a depth vs. concentration profile in order to obtain quantitative information.

ERD has the following characteristics:

Detection	Starting from hydrogen, detection of almost all elements possible
Standard Conditions	Depth profiling of elements is also possible ~20–100 MeV heavy ion beam (2 MeV ^4He for hydrogen detection) ToF, magnetic, gas detector ~10 min per sample
Precision	Stoichiometry: 1% relative thickness: <5%
Sensitivity:	Sensitivity: 10^{14} at/cm ² near the surface, 10^{18} at/cm ³ in the bulk
Depth Resolution	1 to 10 nm
General	Mainly applied for hydrogen, simultaneous profiles of all elements accessible depth range ~1 μm light elements detectable on heavy substrates

3.4 Experimental

In ERD analysis, heavy ions from an accelerator hit the sample at grazing incidence relative to the surface. The ERD set-up consists of an ultra high vacuum ($\sim 10^{-9}$ mbar) scattering chamber. An ion getter pump and a Ti sublimation unit achieve the ultra high vacuum in the chamber, which is needed to prevent build up of a hydrocarbon layer on the sample during ion bombardment. In the center of the scattering chamber, a target manipulator is placed in which a stepping motor can rotate with an accuracy of 0.1° . The detector is mounted at ~ 20 cm from the scattering center and can also be rotated with an accuracy of 0.1° . One of the various combinations of foil thickness and detector slit widths can be remotely selected at any scattering angle without breaking the vacuum. This is important since in some cases a large solid

angle detector is needed to limit the ion dose on the sample. Since ion dose accuracy contributes to the accuracy of the results, the same is measured by the ion scattering yield from carbon wings, covered with thin layer of gold, which periodically intersect the beam.

The ERD depth profiling of hydrogen (and deuterium and tritium) is a special case since this can be achieved in a straight forward manner using the conventional set-up (discussed in Sect. 3.4.1) and employing He beams in the energy range 2–3 MeV. However, the other elements like N and O cannot be examined simultaneously with hydrogen since the projectile mass needs to be more than the recoils. For this purpose, heavy ion beams are used and the ERD in this case is known as heavy ion ERDA (HI-ERDA) where the beams of ^{16}O , ^{28}Si , 30 MeV ^{35}Cl -ions, ^{48}Ti , 140 MeV ^{127}I -ions, and 200 MeV ^{197}Au -ions have been used. HI-ERDA will be discussed in Sect. 3.6.

In order to prevent the occurrence of an unnecessary large count rate of the scattered (unwanted) particles to go to the detector (for recoil ion measurements) placed at an angle $\phi(<90^\circ)$, we have to put a lower limit to the mass of the primary particles so that the maximum scattering angle (say θ_{max}) amounts to less than ϕ . From (B.10) in Appendix B, we can infer that when $M_1 > M_2$, there is a *maximum* possible value of the scattering angle θ in the laboratory frame which is always less than $\pi/2$. The maximum scattering angle θ_{max} (angle θ for scattered primaries and ϕ for recoils), deduced from the corresponding formula of the energy angle correlation of the scattered projectiles (Chu et al. 1978), is given by

$$\theta_{\text{max}} = \sin^{-1}(M_2/M_1) \quad (3.8)$$

This means that no primaries are scattered in the direction of the detector (located at angle ϕ) when $M_1 > (M_2/\sin \theta_{\text{max}})$. Here M_2 is the mass of the heaviest element in the film to be examined. Since the kinematic factors K_s and K_r (as given in (3.3) and (3.4)) are related to the energies of the scattered primaries and the recoils, respectively, it is clear from Fig. 3.2, that for $M_2/M_1 < 1$ the largest energy is carried by the heaviest recoils and for $M_2/M_1 > 1$, the scattered primaries have a larger energy when scattered at a heavier nucleus. The implication is that a simple measurement of the number and energy of particles at angles smaller than 90° does not result in an enhanced sensitivity for light elements when compared with RBS.

The particle identifying detection techniques are used to separate the forward scattered ions and recoils from the target with respect to their energy and atomic number/mass by one of the detection systems mentioned Sect. 3.4.1.

3.4.1 ERDA Using E-Detection (Conventional Set-Up)

In the earlier ERDA measurements, an SBD was used for particle detection. The method is known as ERD, carried in the simplest method or conventional set-up (in the reflection geometry). Since the heavy elements in the sample give rise to high-detected energies, and thus to a background continuum in the

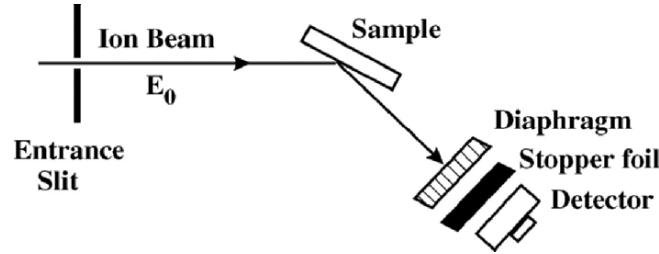


Fig. 3.4. Schematic view of ERD in the conventional set-up

case of a heavy element substrate, this method makes a distinction between the different particles moving in the direction of the detector. As the energy loss of light particles is much smaller than that of heavy particles, the light recoils can be separated from the scattered primaries and heavy recoils by simply eliminating the latter particles by a foil that is mounted in front of the detector (L'Ecuyer et al. 1976; Doyle and Peercy 1979) as shown in Fig. 3.4. Polymer or thin metallic films can be put in front of the detector both to protect it from scattered incident ions and to separate atoms of different recoil elements. If a beam of heavy ions is used, a combination of primary energy, detector angle, and foil thickness can be selected in such a way that the scattered particles are completely stopped in the foil and the lighter recoil particles are able to pass through the foil and reach the detector. The stopping is based on different stopping powers and kinematic factors for atoms of different elements. With a careful selection of the detector angle and absorber thickness, separation of 3–4 light elements or isotopes in a heavy element matrix is possible.

As an example based on the kinematic factor calculation, a plot is given in Fig. 3.5 where the calculated energies of recoiled particles before and after passing through the foil are given in a typical ERD experiment. The particles are recoiled from the surface of a 9 μm mylar film by a 30 MeV ^{28}Si ion beam at recoil angle of 30° , the recoiled particles are having energies of ^1H (3 MeV), ^2D (5 MeV), ^4He (7 MeV), ^7Li (12 MeV), ^9Be (14 MeV), ^{12}C (16 MeV), ^{14}N (17 MeV), ^{16}O (18 MeV), ^{19}F (19 MeV), and ^{28}Si (20 MeV). However, on passing through a 9 μm foil of mylar ($\text{C}_{10}\text{H}_8\text{O}_4$), the energies of ^1H (3 MeV), ^2D (5 MeV) remain unchanged while those for ^4He , ^7Li , ^9Be , ^{12}C , ^{14}N , ^{16}O , ^{19}F , and ^{28}Si change to 6 MeV, 10 MeV, 10.5 MeV, 10 MeV, 8.5 MeV, 7 MeV, 4 MeV, and 1 MeV, respectively. Thus the energy curve shows maxima for ^9Be , which means that the sequence of appearance in the spectrum is reversed for the elements between ^9Be and ^{28}Si , in this elemental range the lighter atoms will appear with the highest energy in the spectrum. The energy transfer is maximal when the recoil has the same mass as the projectile. However, the situation becomes different when the foil is used. The silicon particles as well as possible present heavier recoils, are completely stopped by the foil. The energy curve shows a maximum for ^9Be , which means that the sequence of appearance in the spectrum is reversed for the elements between ^9Be and ^{28}Si .

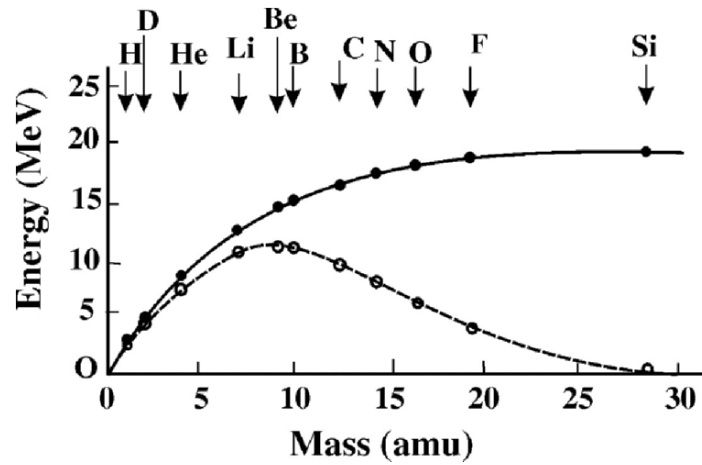


Fig. 3.5. Energy of different particles after being recoiled at an angle of 36° by a 30 MeV ^{28}Si -ions before (*full line – upper curve*) and after (*dashed line – lower curve*) passing a $9\text{ }\mu\text{m}$ mylar foil

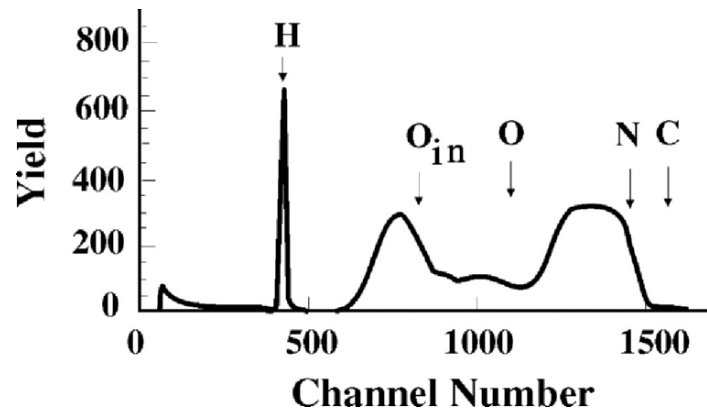


Fig. 3.6. Spectrum of a double-layered structure consisting of silicon oxynitride on top of silicon oxide, recorded in the conventional set-up

Figure 3.6 shows the ERD spectrum measured by bombarding 30 MeV ^{28}Si ions on 80 nm silicon oxynitride ($\text{SiO}_x\text{N}_y\text{H}_x$) film on top of 30 nm SiO_2 film. The substrate is a wafer of crystalline silicon, which does not contribute to the spectrum. The incident and detector angles amounted to 24° and 34° respectively. A $9\text{ }\mu\text{m}$ mylar foil was placed in front of the detector. The peaks corresponding to the recoil of light element H, N, O, and C present in the foil are marked. The H-peak represents the hydrogen contents of the silicon oxynitride layer while O_{in} – and O – peaks correspond to oxygen present at the interface and on the surface, respectively. Although contributions for the

H-peak originates from the same depth range as the contributions from the nitrogen feature yet it is very narrow and the scattering contribution from the interface and surface are not resolved, in contrast to the nitrogen peak. This effect is due to the differences in the stopping power and kinematic factor for different elements. The spectral energy width of an element, which is determined by the energy loss factor S (eV per 10^{15} atoms cm^{-2}), relates the energy of the recoils as they enter the detector to the depth of origin. Apparently the energy loss factor for hydrogen is much smaller than nitrogen.

The detected energy E_{det} of a particle recoiled from depth “ d ” is given by the following equation:

$$E_{\text{det}} = E_{\text{surf}} - \int_0^d S(x) dx \quad (3.9)$$

where d is expressed in units of areal density (i.e., atoms cm^{-2}). E_{surf} denotes the energy of the particular particle recoiled from the surface after passing the foil.

Referring to Fig. 3.7, if r_{in} and r_{out} are the inward and outward path lengths of the sample of the projectile and recoil, before and after a collision at depth x , and ϵ_{in} and ϵ_{out} are the stopping powers of the primary particle on the inward path and of the recoiled particle on the outward path, α is the angle of incidence i.e., the angle between the beam direction and target surface plane and ϕ is the recoil angle i.e., the angle between beam direction and recoil direction, and E_{foil} is the energy loss of the recoil particle in the foil, then E_2 and E_{det} are given by

$$\begin{aligned} E_2 &= K_r (E_0 - r_{\text{in}} \epsilon_{\text{in}}) - r_{\text{out}} \epsilon_{\text{out}} \\ &= K_r \left(E_0 - \frac{x \epsilon_{\text{in}}}{\sin \alpha} \right) - \frac{x \epsilon_{\text{out}}}{\sin(\phi - \alpha)} \end{aligned} \quad (3.10)$$

$$E_{\text{det}} = E_2 - \Delta E_{\text{foil}}(E_0) \quad (3.11)$$

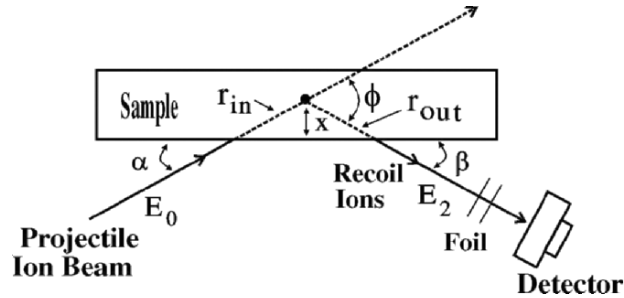


Fig. 3.7. Schematic diagram of the ERD configuration indicating the paths of projectile and recoil through the sample

where E_0 is the energy of the particle while E_2 and E_{det} are the energies of the recoil particle before and after passing through the foil, respectively, and ΔE_{foil} is the energy loss of the recoil particle in the foil.

3.4.2 ERDA with Particle Identification and Depth Resolution

In most of the cases, it is not possible to distinguish between different elements especially the shallow oxygen from nitrogen deeper in the silicon oxynitride films. This is because if the ratio of the concentration of the two elements is small, it will be difficult to determine the height of the oxygen signal as it will be superimposed on a background representing the nitrogen content of the film. Further, it will be impossible to determine the depth distribution of elements when they overlap in the ERD spectra. The necessity to identify the recoil particles or to distinguish them from scattered primaries and/or heavy recoils brings about loss of depth resolving power or loss of energy of MeV ions in the sample material. Therefore, there is a strong correspondence between the energy resolution of the detection device and the obtained depth resolution. Also, particles are detected with a mass larger than that of H or He. Therefore SBDs *are not* the most suitable devices for an optimum depth resolution, since their energy resolution degrades with increasing Z , giving rise to different energy scale for the distinct elements.

The identification of the recoiled particles can be achieved in several ways, commonly based on the characteristic parameter of the recoil in combination with its kinetic energy that is characteristic of the amplitude of the signal produced and its time information. *This parameter can be velocity in time-of-flight spectrometry* (ions of different mass have different flight times $= d/v$, where d is the flight path and v is the velocity of the ion), *momentum-over-charge ratio in magnetic spectrograph* (the detection of the ion is made after its traversal through a magnetic field) or *stopping power in $\Delta E - E$ spectrometry*. The new set-ups include solid state $\Delta E - E$ detectors (Bik et al. 1992; Bik and Habraken 1993) and gas $\Delta E - E$ detectors (Petrascu et al. 1984; Avasthi et al. 1994; Forster et al. 1996; Timmers et al. 2000; Elliman et al. 2004) with element separation and position sensitivity, magnetic spectrometers with charge-mass sensitive separation (Gossett 1986; Grötzschel et al. 2004) and ToF-E detectors with mass sensitive separation (Groleau et al. 1983).

Since the amount of energy ΔE lost by the ions with different Z in a given thickness dx is proportional to Mz^2 , it becomes a basis to separate the ions of different species by using a transmission type thin ΔE detector and a thick E -detector. The ion loses part of its energy in the first ΔE detector and the rest of energy E is deposited in the second detector. Transmission type ΔE detector provides information on Mz^2 and hence enables identification of the ion species. The sum of ΔE and E signals from two detectors provide total energy $E_t = E + \Delta E$.

ERD Using Transmission Telescope (with Gas Ionization Chamber)

A gas ionization chamber (GIC) plays the same role as a solid state detector for the detection of recoil ions/heavy particles (Petrascu et al. 1984; Stoquert et al. 1989; Assmann 1992). However, in contrast to solid-state detectors, gas ionization detectors are not affected by radiation damage due to heavy ion bombardment. They allow recoil ions with different atomic numbers Z to be distinguished and have an energy resolution of the order or better than 1%. In addition, large acceptance solid angles are possible, since position detection may be readily incorporated into the detector and kinematic energy broadening thus corrected. This is an advantage over *Time-of-flight spectrometry* systems where the acceptance solid angle is generally limited due to the requirement for a reasonable distance between start and stop detector. Even when large area position-sensitive detectors are employed in a ToF system the acceptance solid angle is typically only of the order of 1–2 milliradian. With gas ionization detectors, larger solid angles have been demonstrated.

Bragg detector (called Bragg Ionization Chamber (BIC)) works on the principle that the rate of energy loss is greatest at the very end of its trajectory – as evident from the famous Bragg curve (plot of $-dE/dx$ vs. x) where dE/dx is seen to rise sharply just as the particle is about to “range out.” This is due to the reason that energy loss dE/dx varies inversely as energy i.e., $dE/dx \sim (-)(1/E)$ meaning thereby that slower particles spend more time in the vicinity of atomic electrons and can ionize them more readily. As the particle is slowed by ionization losses, it loses energy faster and faster.

When an ion is stopped in detector material, the integrated ionization is proportional to the absorbed energy. The energy loss mechanism is mainly due to the Coulomb interaction (between the ion and electrons of detector material), which cause production of positive and negative charges. These charges are collected by electrodes to produce a signal which is amplified by low-noise electronics. The rate of energy loss of ion in a material is given by the well-known Bethe–Bloch equation:

$$-\frac{dE}{dx} = \frac{4\pi q_{\text{eff}}^2 e^4}{m_e v^2} nZ \left[\ln \left(\frac{2m_e v^2}{I} \right) - \ln(1 - \beta^2) - \beta^2 - \frac{C_K}{Z} \right] \quad (3.12)$$

where $\beta = v/c$ and the mean ionization (excitation) potential is given by $I \sim 11.5 Z$ or to a better approximation by $I \cong 9.1 Z(1 + 1.9 Z^{-2/3})$.

The correction term C_K in the stopping power formula is caused due to the non-participation of bound K electrons in the slowing down process. Qualitatively, this form of energy dependence follows from the fact that in the medium energy range ($I \ll E \ll Mc^2$ where M is the mass of the absorber atom) the first of the terms in the square brackets varies with energy and the others are negligibly small. Since logarithm term varies slowly with energy

and $q_{\text{eff}} = z$ for light ions, therefore Bethe–Bloch equation can be written in simplified form as

$$-\frac{dE}{dx} \propto \frac{Mz^2}{E} \quad (3.13)$$

At high energies the relativistic terms in conjunction with the initial term cause the numerical value of the stopping power to rise very gently so that a broad minimum is set-up in the neighborhood of $E \sim 3Mc^2$, whereas at low energies the initial term is dominant causing the term to drop rapidly back to the origin at energies below about $E \sim 500I$. In (3.12), the z^2 dependence, confirmed by experiments using protons and α -particles of the same velocity incident upon the same target material, shows that the ionizing power of the charged particles, increases quadratically with the charge state and assumes very high values for multiply charged heavy ions. However at low energies, incomplete stripping of ion violates the assumption of $q_{\text{eff}} = z$ and therefore causes the deviation of this equation from the actual case.

A BIC filled with isobutene and with about $1\text{ }\mu\text{m}$ entrance window (mylar) is placed at scattering angle $\sim 30^\circ$. Gas is introduced in the ionization chamber up to a pressure of 30–200 torr. The pressure of the gas is maintained constant by the gas handling system. BIC separates elements with energies $\geq 0.5\text{ MeV/u}$ according to their atomic number. The recoils enter the chamber through a thin gas tight window of a few micrometer thickness. When recoil particles penetrate the gas in the chamber, the electrons get liberated from the gas atoms leaving positively charged ions, as shown in Fig. 3.8.

The electric field present in the gas sweeps these electrons and ions out of the gas, the electrons going to the anode and the positive ions to the cathode. In the chamber, the current begins to flow as soon as the electrons and ions begin to separate under the influence of the applied electric field. The time it takes for the full current pulse to be observed depends on the drift velocity of the electrons and ions in the gas. Because the ions are thousands of times more massive than the electrons, the electrons always travel several orders

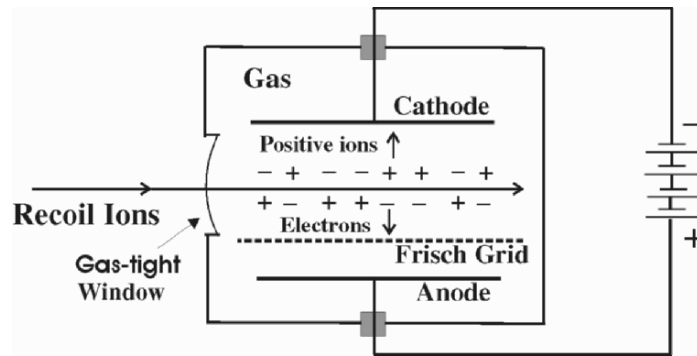


Fig. 3.8. Schematic diagram of a BIC

of magnitude faster than the ions. As a result, virtually all pulse ionization chambers make use of only the relatively fast electron signal.

The ionization chamber is used to measure the total energy of the recoil particle or, if the particle does not stop in the ionization chamber, the energy lost by the particle in the chamber. The energy loss of these recoils in the gas is measured through collection of the charge generated in the gas by the energetic particle. In addition to energy information, ionization chambers are now routinely built to give information about the position within the gas volume (hence called position sensitive detector) where the initial ionization event occurred.

Figure 3.9 shows the schematic diagram showing the scattering geometry along with the Bragg detector. Two parameters are measurable with the Ionization chamber: The Bragg peak height, which is proportional to the atomic number of the detected particle and the total energy of the particle. In a Bragg detector (also called Bragg Ionization Chamber i.e. BIC), different recoils are discriminated by the maximum of their energy loss (the maximum energy loss is proportional to the Bragg maximum, as long as the recoil energy is above the energy of the Bragg maximum), while in a dE/dx detector, the different recoils are discriminated by their initial energy loss (energy loss should be greater than the resolution of the detector to separate the recoils).

Performance of a BIC for depth profiling and surface analysis has been studied by Hentschel et al. (1989). Typical results are good selectivity of the atomic charge number Z up to 20 with a depth resolution of the order of 10 nm and submonolayer sensitivity. An important advantage is the possibility of combining in one measurement the spectroscopy of recoil ions and scattered projectiles. The method is limited by the condition that the energy of the detected particles should be within the operative region of a nearly constant Bragg-peak height. The low background in the operative region allows the analysis of profiles down to concentrations of about 0.01% of the stoichiometric ones. For different ions the energy calibrations has been found to differ by about 3%.

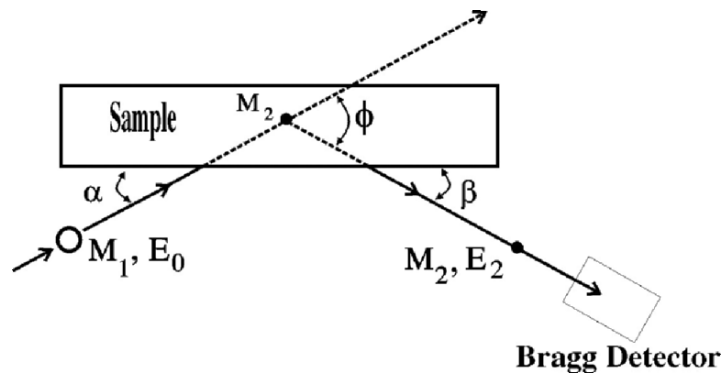


Fig. 3.9. Schematic diagram showing the scattering geometry and Bragg detector

ERD with Position-Sensitive Detectors

As explained earlier, there is a strong correspondence between the energy resolution of the detection device and the obtained depth resolution. The SBDs are not the most suitable devices for an optimum depth resolution, since their energy resolution degrades with increasing Z , giving rise to different energy scale for the distinct elements as the particles to be detected have mass larger than that of Hydrogen or Helium. The GICs are therefore, used as ΔE detectors in place of the semiconductor transmission detectors while semiconductor detectors are used as E -detector (stop detector) forming the $\Delta E - E$ telescope as shown in Fig. 3.10. The stop detector is positioned in the gas chamber. Since the gas ionization detector has to act as the ΔE detector, the recoil particle must have sufficient energy to pass through the detector gas. This can only be achieved using high energy (50–240 MeV) heavy (^{107}Ag or ^{127}I) primary particles, if it is required that the scattering process is of the Rutherford type. These heavy primaries also allow the recoil angle to be larger than the critical angle for scattering of the primary particle. Using a gas detector, all elements could be resolved up to $Z = 15$.

The Bragg counter spectrometer (BCS) is a cylindrical gaseous ionization chamber with a Frisch grid (Fig. 3.10). The electric field is parallel to the axis. A thin aluminized mylar foil (1–2 μm) is provided for the entrance of particles to be detected. The foil also serves as grounded cathode. Uniform potential gradient is provided by the resistance chain and guard rings (closely spaced electrodes at different potential) between grid and the cathode. The electron collection is carried out along the direction of the incident particles. The ionization density distribution along the particle track follows the distribution of the energy loss. The Frisch grid screens the anode from charges and thus the charge collected at the anode generates a signal that is proportional only to the charge drifting between the Frisch grid and the anode. This means that the time dependent pulse height represents the ionization density as a function

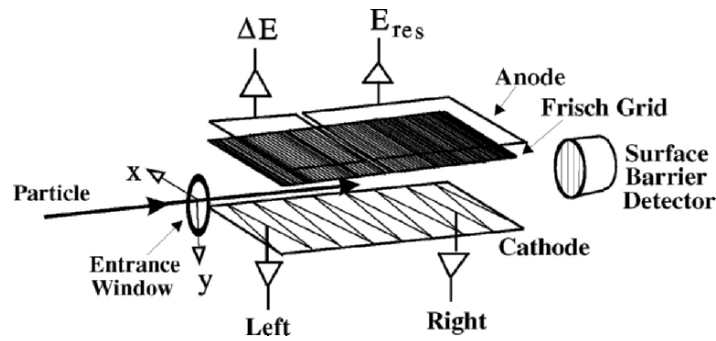


Fig. 3.10. Schematic view of Bragg counter spectrometer (BCS) with grided gaseous ionization chamber as ΔE detector with semiconductor detector as E -detector forming $\Delta E - E$ telescope

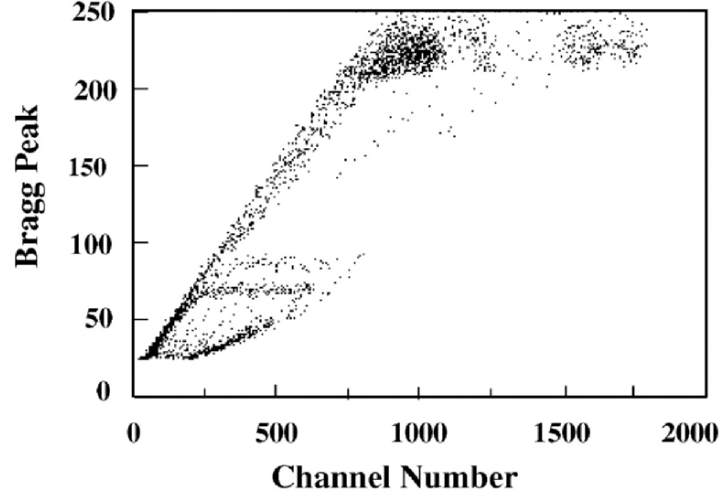


Fig. 3.11. Bragg peak (maximum value read out in the Flash ADC) vs. Energy (integrated area of the pulse) spectrum

of position, i.e., the Bragg curve. For particles stopped within the chamber this curve has a maximum near the end of the range, the so-called Bragg peak. Thus, if the signal is read out using a Flash ADC we get a complete information about the ionization density which lets us determine the energy, the Bragg peak, and the range of the particle. These quantities are then used to identify the particle. In Fig. 3.11, a typical Bragg peak vs. energy spectrum is shown. The Bragg Peak is the maximum value read out in the Flash ADC and the energy is the integrated area of the pulse.

In general, the measurement of a single energy loss signal, i.e., a subdivision of the anode into two electrodes (ΔE and residual energy E_{res}), is sufficient. However, for complex samples with a broad range of elements, two ERD measurements at different gas pressures are required for all elements to be resolved. An ERDA system using $\Delta E - E$ technique was assembled by Added et al. (2001) for stoichiometric and depth profile studies of materials formed by light elements. An ionization chamber with an SBD was used in this work. From the energy loss (ΔE) information obtained from the gas and the residual energy (E_{res}) obtained by the SBD, it was possible to identify atomic number of the arriving particles at the SBD. An incident beam of 58 MeV ^{35}Cl was used for the elastic scattering with the sample components. From the spectra obtained for carbon nitride thin films it was possible to clearly identify the elements carbon and nitrogen.

In the $\Delta E - E$ telescope, the dual ADC, that converts the signals of both detectors, is activated by the pulses from the stop detector. The most important reason for this choice is that the hydrogen recoils do not lose enough energy in the transmission detector to generate measurable pulses. It has also

an additional advantage that the numerous particles having an amount of energy too small to reach the stop detector do not contribute to the dead time of the ADC. These particles, however, do contribute to a background in the spectrum when they enter the telescope coincident with a particle that reaches the stop detector. This effect can be minimized by careful adjustment of the strobe pulse, which should be as short as possible, and by lowering the beam current.

The Bragg counter used by Siegle et al. (1994) consisted of a series of disks 75 mm in diameter and about 10 mm apart, each with a 38 mm hole in the center thus providing a homogenous field in which electrons produced by the detected particle are accelerated toward the anode. The detector with active area of 205 mm long, was filled with isobutene at a pressure of 120 torr. The cathode was biased to $-1,500$ V and had a 20 mm opening, which was covered with a fine grid. The entrance window was a $250 \mu\text{g cm}^{-2}$ mylar foil. A 12 mm gap between the window and the cathode resulted in an additional energy loss of the recoils.

With experimental geometry shown in Fig. 3.7, the target atoms recoil at an angle ' Φ ' with an energy $E_2 = KE_0$ with kinematic factor K_r as given by (3.3). According to (3.2), if $M_2 \ll M_1$, the recoils will have energies of ~ 3 MeV/u and ~ 1 MeV/u at a projectile energy of 1 MeV/u for $\phi = 30^\circ$ and 60° respectively. This approximation is correct for ^{28}Si recoils with ^{197}Au projectiles but does not hold good for recoils heavier than ^7Li with ^{59}Ni as projectile. With heavier projectiles, the maximum scattering angle for most elements gets so small that even at a 30° recoil geometry, the projectiles cannot be scattered into the detector (see (3.8) for maximum scattering angle). The detection sensitivity of the ERD is given by the solid angle of the detector and the scattering cross-section. In order to keep the data analysis simple, the cross-sections for the recoils of interest should still be Rutherford, which is always the case for heavy projectiles in the 1–2 MeV/u energy region. The sensitivity can be increased considerably by using heavier projectiles, since the cross-section (see (3.5)) increases not only with $(Z_1/E_0)^2$ but also with $(1 + (M_1/M_2))^2$.

To solve the problem of simultaneous detection of the full range of recoil atoms of all elements, from hydrogen to mass 100 ejected by heavy ion beams (since all low-mass surface recoils have almost identical velocity and also exhibit a wide spread of ranges in the detector since two or more gas pressures are often required to allow the detection of both low-mass and heavy recoil atoms), Siegle et al. (1996) have developed a simple $\Delta E - E_r$ detector. A combination of a gas detector (ΔE) and a solid state detector (E_r) leads to a very compact design. The capabilities of a compact ΔE (GIC) – E_{res} (solid state detector) telescope for simultaneous light and medium heavy element detection has been presented by Pantelica et al. (2006). An integrated preamplifier was mounted close to the ionization chamber by these authors to increase the resolution. The two outputs from the preamplifier have been fed into two main amplifiers, operated with high and low gain, respectively,

to achieve the simultaneous detection of very light elements (H and He) and of the heavier ones (C, O, Mg, Al etc.).

Since the detected particle is the recoil, it is possible to discriminate between different elements by their nuclear charge and mass. Different detection techniques such as ToF and gas detectors (Bragg detector or dE/dx detector) have been used to achieve the separation.

A large area two-dimensional position sensitive detector telescope described by Nageswara Rao et al. (2003) for performing ERDA-based material characterization experiments, consists of an anode, grid, Frisch grid, and a cathode. To obtain the ΔE energy signal, the anode is divided into two sections. The cathode signals from the backgammon-type structure, provide the position information. The position sensitive detector telescope has the advantage of detecting different recoil masses (with energies <1 MeV/u) with an energy resolution better than 1% and allows simultaneous depth profiling of several elements from mass 1 up to mass 150 or so. This gas ionization detector is working well with position resolution better than 2 mm and good z -separation in both high- and low-mass regions. Since large solid angle is a pre-requisite to minimize the possible unwanted radiation damage during the measurement, the consequent kinematic broadening has been corrected by recording the position information.

ERDA has been facilitated by the development of a large solid angle gas-ionization detectors with position sensitivity by Timmers et al. (2000). Their detector incorporates a segmented anode that consists of two ΔE electrodes and a residual energy (E_{res}) electrode as shown in Fig.3.12. Identification of both light and heavy ions within a single measurement has been achieved by subdividing the ΔE section of the anode. The lighter ions stop within the E_{res} section and the sum of ΔE_1 and ΔE_2 can be used

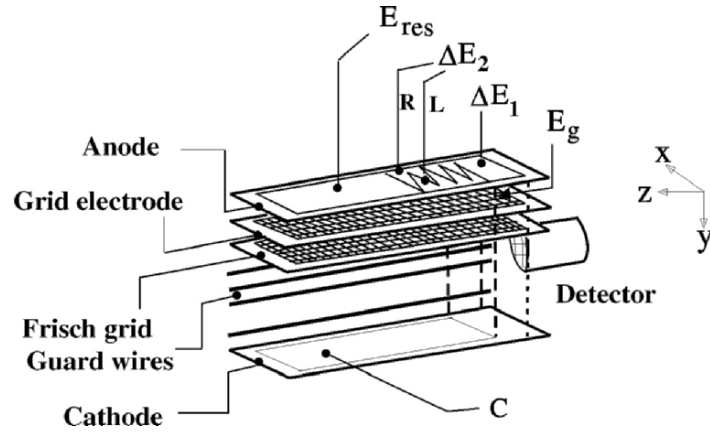


Fig. 3.12. Electrode structure of a gas ionization detector at Australian National University (Timmers et al. 2000; Elliman et al. 2004)

for Z separation. Heavier recoils stop within the ΔE_2 section and can be distinguished with regard to Z using the ΔE_1 signal. The ΔE_2 electrodes is further partitioned to provide position information in the scattering plane. This is used to correct the kinematic energy spread of ions entering the large solid angle detector. The total energy signal, which is the sum of all three anode signals, is provided as an independent total energy signal by a second grid electrode incorporated between the Frisch grid and the anode that measure the total ionization deposited by ions in the sensitive volume. The entrance aperture of the detector is 19 mm in diameter, providing an acceptance of ~ 4 msr for a distance of 280 mm between detector and sample.

The modified ERD parallel-plate gas ionization detector has been mounted on a movable arm inside a large scattering chamber (radius 1 m). The location of the detector can be varied between 10° and 170° relative to the beam direction. The sample can be rotated about an axis perpendicular to the detection plane. Ions recoiling from the sample enter the detector through a $0.5\text{ }\mu\text{m}$ thick mylar foil. Two tungsten collimators can be moved in front of the detector window: A central hole (diameter 2 mm) and a mask of nine rectilinearly positioned holes. Cathode has been divided into a left and right section using a sawtooth geometry. The total energy information (which can be obtained by adding the signals from the anode) is obtained directly from a grid electrode. The subdivision of the energy loss electrode, together with a carefully chosen position of the entrance window to maintain optimum resolution for two ΔE signals, enable light and heavy ions to be resolved at the same gas pressure. The placement of a saw tooth electrode within the anode gives position information, which is linear and independent of atomic number and ion energy.

Protons can be identified simultaneously with heavy ions by combining the information from the grid and residual energy signals, both amplified with high gain (Elliman et al. 2004). Two modes of operation are possible for hydrogen detection. A transmission mode in which the protons transit the active region of the detector and the energy is derived from an energy loss signal, and a stopped mode in which the protons are stopped in the sensitive gas volume of the detector and the energy is derived from the electrode signals in the usual way. The propane pressure in the detector was 70–100 mbar. For comparison with the heavy ion measurements, conventional ERD analysis was performed on the Al bilayer sample using 4.6 MeV He ions and an SBD located at a scattering angle of 30° . Scattering was symmetrical, with the incident and exit beams inclined at 15° to the sample surface. A $25\text{ }\mu\text{m}$ thick mylar stopping foil was used to exclude scattered primary ions. A symmetrical scattering geometry was employed in both cases with a scattering angle of 45° .

The relative signal heights of anode and grid electrode depend on the voltages applied. An optimum configuration was found by Timmers et al. (2000) with the grid electrode biased at 58% of the anode voltage (e.g., anode +450 V and grid +263 V). The pulse height of the signal from the grid electrode is about half of that obtained when all electrons are collected on the

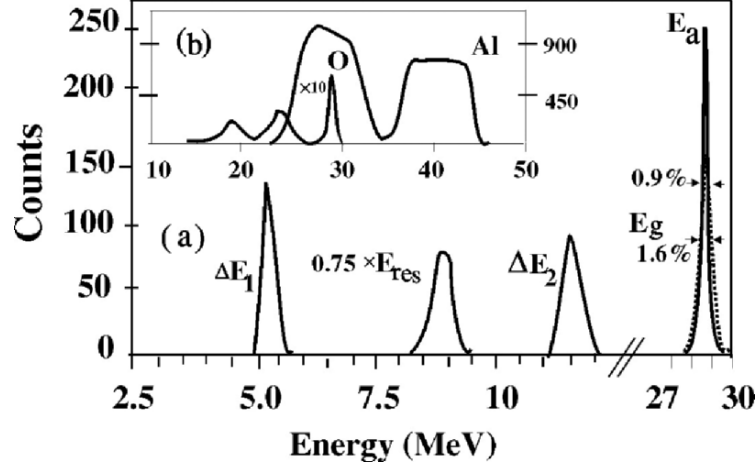


Fig. 3.13. (a) The anode signals ΔE_1 ; ΔE_2 ; E_{res} , their sum E_a (solid) and the signal from the grid electrode E_g (dotted). The resolution is indicated for E_a and E_g . (b) Kinematically corrected energy spectra for Al (dotted) and O (solid) recoil ions, which were obtained with the grid electrode for a double layer of Al separated by hydrogenated C using ^{197}Au at 216 MeV projectile beam was. The oxygen signal is due to surface oxidation of the Al layers and the Si substrate (Timmers et al. 2000)

grid (e.g., grid and anode both at +263 V). After passing the Frisch grid the drifting electrons induce a signal on the grid electrode. When the electrons have moved through the grid electrode, their drift toward the anode causes the immediate decrease of that signal. In contrast to the anode signals, the decay time of the signal from the grid electrode is therefore short and comparable to its rise-time. It can be amplified with a short integration time. Response of this modified detector for 28.6 MeV ^{16}O ions scattered from a thin Au target is shown in Fig. 3.13.

Time-of-Flight Spectrometry

With conventional ERD, all elements lighter than the incident ion are detected and all the other elements are blocked by the stripper foil. The use of a heavier mass incident ion beam, allows a multitude of other different elements to be recoiled forward and detected. In the conventional ERD, the different elemental spectra superimpose on each other and it becomes difficult to sort the separate masses so as to provide unambiguous data on the different elemental depth profiles.

In ERDA analysis, mass identification is done by means of the ToF method, i.e., the coincident measurement of energy and flight time for each recoil. Time-of-flight elastic recoil detection (ToF-ERD) is a powerful and complementary technique to Rutherford spectrometry for elemental analysis in surface

and thin films. Time-of-flight (ToF) spectrometers are based on the principle that the mass of the particle can be determined by the coincidence measurement of its velocity (flight time) and energy. There are a number of different measurement set-ups for ToF-ERDA. Since high-energy heavy ion beams are used for the ToF-ERD technique, there is always a maximum angle, depending on the target elements, at which the incident ion beam cannot be kinematically scattered past. The detector positioned at forward angles (say 45°), prevents the direct scattering of lighter elements, lighter than a particular Z -value, into the detector. Thus the stopper foil is not needed. The forward recoiled target atoms travel down the spectrometer tube and through two thin carbon foils, which are separated by about 50 cm. As the recoils pass through each of the carbon foils, a burst of secondary electrons is produced, which is then collected and amplified to produce ~ 1 ns wide fast timing signal. The time separation between these two timing signals is a measure of the atom's speed. The recoiled atoms then come to rest in a silicon detector, which measures their energy. From these two measured quantities i.e., speed and energy, the recoiled atom's mass is uniquely identified. From their energies and yield, elemental concentration and profile can be constructed for the sample.

A Time-of-Flight Energy Telescope

To increase the accessible depth of ERDA, a time-of-flight energy (ToF-E) telescope can be used at scattering angle of $\sim 45^\circ$. A thin carbon foil of $10 \mu\text{g cm}^{-2}$ near the target combined with microchannel plate (MCP) detector gives the start signal and an SSB detector after a flight path of about 100 cm provides both a time stop and energy signal of the detected particle. Two parameters are measurable with this telescope: The ToF of the particle, which is proportional to the mass number and the total energy of the particle.

As explained earlier, the amount of energy lost by the ions (dE) in a given thickness dx of stopping material is proportional to MZ^2 , on the basis of which the ions of different species are separated by using a transmission type thin ΔE detector and a thick E -detector. However, the isotopic separation above $Z = 5$ is not possible by $\Delta E - E$ telescope. Timing information from detectors is utilized to identify mass of the recoil ions. The ToF of different masses are measured for a given distance either by using two fast timing detectors or by using the pulsed beam and a fast timing detector (Fig. 3.14). In the second case, the recoil ions are all accelerated by a pulsed potential down an evacuated tube (drift region) and their time of arrival at detector D_1 is determined. This is a function of their M/Z values.

Ions of different masses have different flight times ($= d/v$) depending on the flight path d and velocity of the ion v or energy E given by $1.4(E/M)^{1/2}$. If the total energy E_t is known ($E_t = E + \Delta E$), the mass can be known from the energy by $M = 2Et^2/d^2$. Mass resolution is given by

$$\frac{\Delta M}{M} = \left[\left(\frac{\Delta E}{E} \right)^2 + \left(\frac{2\Delta t}{t} \right)^2 + \left(\frac{2\Delta d}{d} \right)^2 \right]^{1/2} \quad (3.14)$$

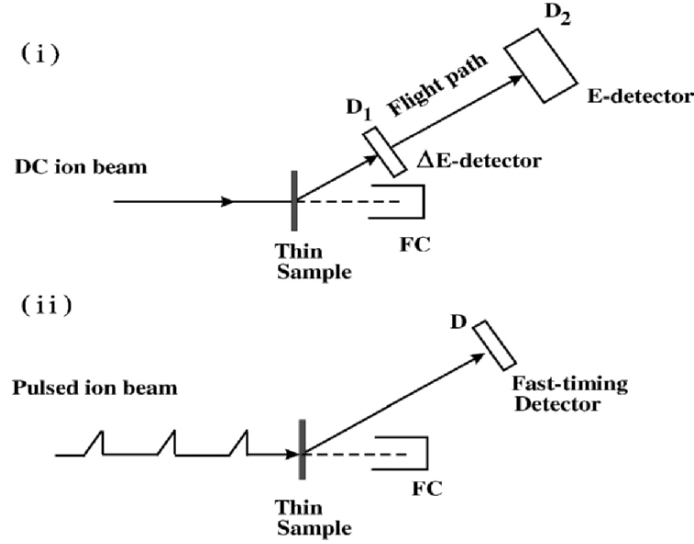


Fig. 3.14. Set-up for time-of-flight experiment

The uncertainty in distance measurement (Δd) is negligible as compared to energy and time uncertainty. It is either due to measurement error or due to different flight paths of ions between the timing detectors which further depends on detector solid angle and flight path. This is negligible only when the solid angle is small and flight path is large.

The energy spectra are generally deduced from ToF spectra because ToF detector has a linear calibration for all ions. The calibration is also independent of radiation damage contrary to the charged particle detectors. The energy resolution of the ToF detector for heavy ions is better and for light ions like C, N, and O of the same order than that of charged particle detector. A solitary high-energy resolution ToF-detector can also be used in forward or backscattering geometry (Bush et al. 1980). Owing to the specific energy loss of an element in the material, it is possible to know the depth dependent concentration distributions for all components of a sample to calculate from the measured energy spectra. The main advantage of ToF-ERDA lies in its capability of not only simultaneously depth profiling light elements ($3 < Z < 9$) but also with a superb depth resolution (a few nm). ToF telescopes have been successfully applied as tools for ion separation and depth profiling in ERDA at higher energies (Whitlow et al. 1987; Bohne et al. 1998). The two-dimensional plot showing time-versus energy of atoms from a $\text{SiN}_x\text{:H}$ layer on Si scattered to 60° relative to the direction of the irradiating beam of 230 MeV ^{129}Xe -ions, obtained by HMI Berlin group, has been shown in Fig. 3.15. However ToF-ERD is the only detection system that can be applied for light element detection in low energy (ion from accelerator with terminal

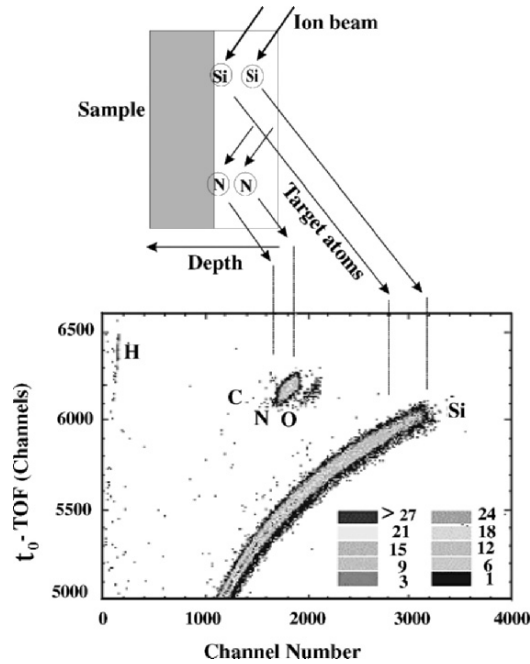


Fig. 3.15. Depth profiling through ToF-ERDA

voltages around 2 MV) regions although with lower detection efficiency and smaller accessible depths (Grigull et al. 1997).

The ToF can be determined by means of two identical timing gates (Whitlow et al. 1987; Arai et al. 1992) or an energy detector can be used to obtain timing signal (Groleau et al. 1983; Hong et al. 1997). Gujrathi et al. (1987) applied a carbon foil as the first time detector, measuring the secondary electron yield at the moment of transmission of a particle and an SSBD as a stop detector. One can also use two transmission time detectors and an SSBD stop detector (Whitlow et al. 1987). The time resolution of these ToF systems is in the range of 200–300 ps, and the flight time vary between 50 and 100 cm. In the analysis heavy ions are used (^{35}Cl , ^{79}Br). A mass resolution better than 1 amu for recoil masses smaller than about 30 has been demonstrated. Depth resolution and analyzable depth are improved, compared to the conventional set-up and the $\Delta E - E$ telescope, since the absorber foil or the transmission detector is omitted. Depth resolutions below 10 nm are reported by ToF technique. Using high-resolution ToF spectrometer, Zhang et al. (2002) have measured electronic stopping power of Be, C, Si, and Br in amorphous C over a continuous range of energies of swift heavy ions.

Elastic recoil detection analysis (ERDA) of a pyrex-glass sample has been carried out by Grigull et al. (1997) in the elemental range of $Z = 5 - 20$ using element dispersive ionization chambers and a time-of-flight (ToF-E) system,

respectively. It is shown that recoil identification with the gas detectors is limited to energies significantly higher than the values assigned to the maximum electronic stopping power of the different species in the detector gas. As a consequence, the in-target depth accessible for analysis decreases rapidly with increasing atomic number of the recoils in the case of the comparatively small projectile energies available from a 5 MV tandem accelerator. Mass discrimination using ToF spectrometry is effective down to significantly smaller energies, giving larger probing depths with unchanged beam and geometry parameters. This advantage over the gas detectors is most prominent with the heaviest recoils analyzed. Based on the multielement spectra obtained with 35 MeV ^{35}Cl and 210 MeV ^{127}I analyzing beams, respectively, an extrapolation onto a 2 MV tandem machine providing 12 MeV ^{35}Cl ions shows that element-discriminating analysis is possible also with small accelerators if ToF systems are employed for recoil detection.

The main problem with ToF detectors is the efficiency for detecting low- Z particles (Whitlow et al. 1989). It has been demonstrated that the detection efficiency for hydrogen can be as low as 30%. Further, it is difficult to apply a large acceptance angle in the detection since the distance of the stop detector from the sample surface is necessarily large. This increases the detection limit, as long as the quantity is determined by the stability of the sample under high-energy, heavy ion irradiation.

An ERDA detector telescope consisting of a ToF system combined with a GIC has been developed by Döbeli et al. (2005) and Kottler et al. (2006). This system is specialized for the identification of very low-energy ions. Equipped with a large area patterned silicon nitride entrance window of 130 nm thickness, the GIC allows heavy ion detection well below 1 MeV with sufficient resolution for particle identification. The ToF system has a start detector with a diamond-like carbon (DLC) foil of only $0.5 \mu\text{g cm}^{-2}$, which warrants excellent energy resolution for depth profiling. The system has been tested with ^{127}I , ^{197}Au , and ^{48}Ti projectiles of energies between 1.5 and 12 MeV. In the low-mass range (up to 30 amu) the mass resolution is better than 1 in 35 at a recoil energy of approximately 3 MeV. A depth resolution of 1.5 nm (FWHM) has been obtained at a TiO_2 surface using 1.5 MeV ^{127}I projectiles. The spectrometer is well suited for high resolution near-surface ERDA analysis even at accelerators with very low-beam energies.

A ToF spectrometer has been built for the ERD-ToF with a 1.7 MV tandem Van de Graaff accelerator by Kim et al. (1998a,b). The spectrometer consists of two time pick-off detectors and a silicon SBD with variable flight lengths. The time detector uses an electrode to accelerate and to focus the electrons from a thin carbon foil to an MCP. The advantage of this type of time detector is the good efficiency and no obstacles in the beam path at the cost of a small uncertainty in the flight length. The efficiency of the spectrometer measured for the ions lighter than Neon has been found to be better than 98% for the particles heavier than Boron. The intrinsic resolution of the time detector is about 220 ps. The time resolution of the spectrometer

was measured as a function of incident particle type and energy. The mass resolution is below 1 amu for the particles of interest.

Elemental characterization of electroluminescent SrS:Ce thin films using ERDA with an absorber and time-of-flight (ToF)-ERDA has been made by Li et al. (1998). The major impurities in the SrS bulk were found to be H, C, and O. The concentrations of these impurities in SrS:Ce films, the films prepared by the reactive evaporation, were found to be 0.6–1.8 at.% H, 0.2–0.7 at.% C and 0.5–1.8 at.% O.

ToF-ERD is a powerful technique for profiling multilayered, multielemental samples, and thin films as may be found in the microelectronic industry, to provide information about the film stoichiometry, homogeneity, surface, and interfacial properties, necessary to engineer the film to the desired functional properties.

ToF-Recoil Spectrometer

The fundamental task of ToF-E telescope is the measurement of a recoiled particle's flight time (t) over a flight length (d) and its energy (E). The particle's mass can be extracted from these quantities using the relation $M = 2E(t/d)^2$. Materials characterization using heavy ion elastic recoil ToF spectrometry has been described by Martin et al. (1994) at ANSTO who have used an electrostatic mirror, in which carbon foils act as a source of secondary electrons. When recoiled particles pass through it, these electrons are reflected into a set of MCPs. The anode signals are amplified by fast rise-time preamplifiers, and fed into fast constant fraction discriminators to produce a well-defined timing pulse, signifying the passage of a recoiled ion. Generally the time resolution Δt of a ToF detector (Kim et al. 1998a,b) is given by

$$\Delta t = (36.1 \times l \times \Delta E)^2 \cdot \left(\frac{M}{E^3} \right) + (\Delta t_i)^3 \quad (3.15)$$

where l denotes the flight length, M and E are the energies (MeV) of the projectile particle. Δt_i is the intrinsic time resolution (ns) of spectrometer. ΔE is the deviation of energy (MeV) of the projectile particle (contributed by incident beam energy spread, the geometrical contribution during a scattering reaction, the energy straggling in the carbon foil and surface contamination).

The ToF recoil spectrometer showing the two timing detectors separated by a flight tube is shown in Fig. 3.16. Recoiled target atoms enter the tube from the sample chamber, travel down the tube and finally into a silicon SBD (particle detector) at its end.

The detection efficiency of recoils with masses ranging from H up to Nb at energies from 0.05 to 1 MeV per nucleon has been investigated for ToF energy elastic recoil detection (ToF-E ERD) systems by Zhang et al. (1999). It is observed that the detection efficiency for the ToF-E detector telescope depends on the stopping power in the carbon foils, which in turn relies upon the recoil mass and energy. Furthermore, the limits of this behavior depend

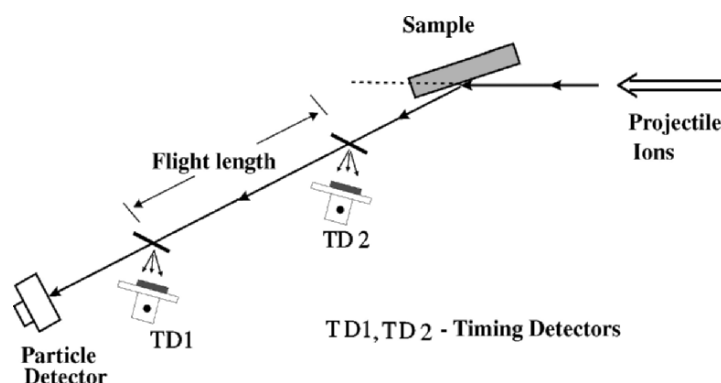


Fig. 3.16. Schematic diagram for time-of-flight recoil spectrometer

on the setting of the discriminator thresholds. The detection efficiency of a time detector could be fitted to a universal curve that can be described by a simple empirical formula as a function of recoil electronic stopping power in the carbon foil. This formula can be used to predict the detection efficiency by recoil energy for N, O, and other elements, for which it may not be easy to prepare suitable reference samples containing only that element.

Magnetic Spectrometry

In a magnetic field, the charged (in general) recoiled particles after emerging from the sample material, will follow a trajectory whose curvature depends on their mass and velocity, the magnetic field strength, and the charge state of the ion. Every trajectory is followed by all particles having the same momentum-to-charge ratio. The particles can be identified by the measurement of their energy by (say) SBD. A high resolution is achieved by determination of the position at which the relevant particles are projected in the detection plane by the magnetic field. A depth profile is then obtained by measuring the contribution of an element or isotope to the measured energy spectra in a position sensitive detector (Gossett 1986; Boerma et al. 1990; Dollinger et al. 1992) and/or as a function of a magnetic field settings depending on the depth range of interest.

Depth resolution of 8 nm for hydrogen and 2 nm for carbon on the surface of a sample have been demonstrated by Grossett (1986). Dollinger et al. (1992) have obtained better than 1 nm depth resolution for carbon at the surface of a carbon/boron multilayer sample applying magnetic spectrograph featuring a large acceptance angle and an overall energy resolution of 5×10^{-4} .

3.5 Heavy Ion ERDA

Heavy ion elastic recoil detection analysis (HI-ERDA) is a universal analytical probe capable of detecting virtually all elements simultaneously and with almost constant detection sensitivity. High energies of different ions are

preferred in HI-ERDA because of the greater analysis depths, better mass separation, and smaller multiple scattering effects. To reach the high energies, ions with high-charge states are required, and to obtain sufficient high-beam currents for the analysis, high-electron affinity elements are preferred. For example, the elements in the halogen group are especially suitable, because from them sufficiently high-negative ion currents can be produced by the ion source. Most of HI-ERDA in the literature has been done with Cl, Br, and I beams. Also Au has a high-electron affinity and is much used. Sajavaara et al. (2002) studied the suitability of different incident ions (43 MeV ^{35}Cl , 48 MeV ^{79}Br , 53 MeV ^{127}I , and 48 MeV ^{197}Au) in view of analysis and measurement fluency, accuracy, and ion-induced irradiation effects in ALD-grown Al_2O_3 , TiN, and TaN thin films. For Al_2O_3 films the atomic concentrations were obtained from the concentration distributions. All incident ions employed were found feasible in the analysis of these films, however a higher recoil energy leads to a better mass separation for light incident ions due to the scattering kinematics. For instance, the recoil energies for Al at the surface in a 40° scattering are 13.2 MeV and 24.8 MeV for 53 MeV ^{197}Au and 43 MeV ^{35}Cl ions, respectively. The low-beam currents obtained for $^{35}\text{Cl}^{8+}$ ions required longer measuring times while 43 MeV ^{35}Cl ions give more energy to light recoils and improve their mass separation as is illustrated for Al and Si signals in Fig. 3.17 where every detected recoil is visible in the histograms.

The stability of an implanted H distribution in diamond has been studied by Machi et al. (1997) by imaging with the micro-scanned Heavy-Ion Elastic

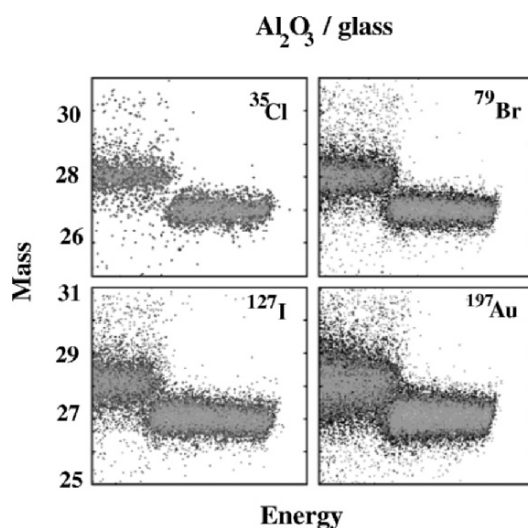


Fig. 3.17. ToF-ERDA energy vs. mass histograms showing Al and Si recoils from a 170 nm thick ALD-grown Al_2O_3 film on a soda lime glass substrate measured with 43 MeV ^{35}Cl , 48 MeV ^{79}Br , 53 MeV ^{127}I , and 48 MeV ^{197}Au ions

Recoil Detection Analysis (μ HI-ERDA) technique. A 25 MeV $^{35}\text{Cl}^{4+}$ beam was incident on the diamond sample at an angle of 70° (to the surface normal) and the ejected hydrogen ions were detected in a Si surface barrier detector at a recoil angle of 30° . A $10.5\text{ }\mu\text{m}$ aluminium foil was used in front of the detector to stop heavy recoils. Measurements on a Si standard sample implanted with a dose of $5 \times 10^{16}\text{ cm}^{-2}$ of 35 keV H^+ ions were used to convert the measured yields to concentrations. ERDA measurements were also performed on a $50\text{ }\mu\text{g cm}^{-2}$ carbon foil in order to estimate the detection limit for bulk hydrogen.

The use of very heavy ion beams such as ^{127}I or ^{197}Au with 1–2 MeV/u makes ERDA a quite universal technique for thin-film analysis capable of analyzing simultaneously light and heavy elements including H with almost constant sensitivity (Siegle et al. 1994; Assmann et al. 1996). Due to the strong increase of the recoil cross-section with the projectile atomic number typically less than 10^{12} ions are required to get sensitivities in the 100 ppm range. Detector systems with particle identification are advantageous for ERDA, which can be improved additionally regarding depth resolution and detection efficiency, if the kinematic energy spread is corrected.

ERDA with ^{209}Bi ion beams has evolved into a universal IBA technique for simultaneous analysis of almost all elements, with essentially constant detection sensitivity. With the large-solid-angle ($\sim 5\text{ msr}$) detectors, extremely small beam doses – typically less than 10^{11} ions per analysis, are required due to the strong Z_1 -dependence of ERDA cross sections. For this reason, the beam-induced damage effects are usually not serious. To confirm this, a series of HI-ERDA studies have recently been carried out by Davies et al. (1998) on various targets, using 1.1 MeV per amu beams of ^{79}Br , ^{127}I , ^{197}Au , and ^{209}Bi . Their comparative measurements show that the loss of volatile low- Z elements (H, N, O, etc.) is often smaller for 230 MeV ^{209}Bi than for 87 MeV ^{79}Br .

A spectrometer for low-energy HI-ERDA has been described by Kottler et al. (2006). This is an ERDA detector telescope consisting of a ToF system combined with a GIC which is specialized for the identification of very low-energy ions. Equipped with a large area patterned silicon nitride entrance window of 130 nm thickness, the GIC allows heavy ion detection well below 1 MeV with sufficient resolution for particle identification. The ToF system has a start detector with a DLC foil of only $0.5\text{ }\mu\text{g cm}^{-2}$, which warrants excellent energy resolution for depth profiling. The system has been tested with ^{127}I , ^{197}Au , and ^{48}Ti projectiles of energies between 1.5 and 12 MeV. In the low-mass range (up to 30 amu) the mass resolution is better than 1 in 35 at a recoil energy of approximately 3 MeV. A depth resolution of 1.5 nm (FWHM) has been obtained at a TiO_2 surface using 1.5 MeV ^{127}I projectiles. The spectrometer is well suited for high resolution near-surface ERDA analysis even at accelerators with very low-energy beams.

The applicability of HI-ERDA is evident from the measurements by many other workers. The analysis of silicon oxynitride ($\text{SiO}_x\text{N}_y\text{:H}$) films has been

made by Bohne et al. (2004) using 150 MeV ^{86}Kr ions. Since HI-ERDA provides absolute atomic concentrations of all film components including hydrogen with a sensitivity of at least 0.005 at.%, the data from this method were used as a quantitative reference to assess the applicability of RBS, EDX, and AES to the analysis of silicon oxynitrides. The analysis of a thin $\text{SiO}_2/\text{Si}_3\text{N}_4/\text{SiO}_2$ (in the range of 10 nm and less as this is important material in microelectronics) has been made by Brijs et al. (2006). Changes of elementary concentrations in dental enamel after a bleaching treatment with different products, have been measured by Added et al. (2006) with special focus on the oxygen contribution. Concentrations for Ca, P, O, and C and some other trace elements were obtained for enamel of bovine incisor teeth by HI-ERDA using a ^{35}Cl incident beam and an ionization chamber.

3.6 Data Analysis

For obtaining depth profiles, the basic idea in the most common methods, is the backward calculation of the recoiling depth. In the energy spectrum, a channel correspond to a certain depth slice. The depth is calculated using scattering kinematics and semiempirical stopping powers. The yield at different depths is then normalized using stopping powers and stopping cross-sections for a given incident ion and sample atoms. If all the sample elements can be analyzed, the final depth profiles can be normalized to unity and atomic ratios are obtained. A more sophisticated way to analyze ERDA spectra is to use simulation program which produces energy spectra and then compares the experimental and simulated spectra with each other. The final depth profiles of elements are obtained from the simulated depth distributions giving the best fit with the experimental ones. The advantage of this approach is to add the energy spreading factors like measurement geometry, beam divergence and energy deviation, detector resolution, and energy straggling to the program.

The analysis procedure (Machi et al. 1997) used to convert the measured yield to hydrogen concentration takes into account the energy loss of the incident projectile ion beam in the target, the scattering of hydrogen at a depth x by the projectile ion, and the energy loss of the ejected hydrogen in the foils in front of the detector.

If x is the depth from which the recoil atoms come out from the sample, the same can be determined from the incident energy E_0 , recoil energy E_2 , the stopping power of the recoils and the incident ions in the sample along the path $x/\sin\beta$ and $x/\sin\alpha$, respectively, and the kinematic factor K . The energy of recoils originating from a depth x and reaching the detector is given by

$$E_2(x) = K_r E_0'(x) - \Delta E_{A1} \quad (3.16)$$

where the kinematic factor K_r is given by (3.3). ΔE_{Al} is the energy loss of the recoils in the Al foil while $E_0'(x)$, is the energy of the projectiles at a depth x , which is given by

$$E_0'(x) = E_0 - \varepsilon_{in} (x / \cos \alpha) \quad (3.17)$$

where E_0 is the energy of the incident ion and ε_{in} their energy loss on the way in. The energy loss of the recoiling atoms on their way out of the surface is small compared to $E_r(x)$ and has been neglected.

The yield of the detected recoils $Y(x)$ in a detector solid angle $d\Omega$ (originating from depth x) during an irradiation of a sample of thickness Δx by N incident ions, is given by

$$Y(x) = N(x) \frac{d\sigma}{d\Omega} (E_0'(x)) n_i \Delta x d\Omega \quad (3.18)$$

where n_i is the number of incident ions, $d\Omega$ the detector solid angle, and $N(x)$ the H-concentration distribution in the sample, $d\sigma/d\Omega$ is the differential recoiling cross-section in $10^{-28} \text{ m}^2 \text{ sr}^{-1}$ (given by (3.5) and Δx is the ion path length in the sample (at. m^{-2}). Normally the measurements are made in a symmetrical geometry i.e., $\alpha = \beta$ (see Fig. 3.3). However, the depth resolution can be made better and scattering yields higher by tilting the sample (smaller α and larger β) without changing the total scattering angle θ .

In the analysis of the experimental yield for the ejected hydrogen energy, stopping power tables (estimated with TRIM by Ziegler 1998) can be used to calculate, for each energy bin, the ejected hydrogen energy just before the Al foil. Equation (3.18) is then used to calculate the energy of recoils emanating from a depth x . The energy of Cl projectiles at the interaction depth x is found by integrating the appropriate portion of the relevant stopping power table. The observed yield is converted into a quantity proportional to the areal concentration of hydrogen using (3.5) and (3.18).

Since the effects of straggling, stopping, multiple scattering, and roughness in the target and detectors contribute, the spectrum simulation is done taking all these factors into consideration. The ERD subroutine of GISA 3.95 (Saarrilahti and Rauhala 1992) calculates the recoil particle spectrum. The cross-sections are calculated using the general physical formula for Rutherford scattering of the recoiled particles or by using fitting functions.

Depth resolution better than 10 nm and sensitivity below $10^{14} \text{ at. cm}^{-2}$ have been achieved in ERDA of Al/Cu multilayers with 200 MeV Au ion beams by Assmann et al. (1994) using an ionization detector with 7.5 msr solid angle having particle as well as position resolution. In situ depth profile changes of Fe and O due to ion-induced oxygen absorption, have been measured by Avasthi et al. (1998) bombarding 243 MeV Au ions on a thin Fe film on Si and carrying out measurements with a large area position sensitive detector telescope.

3.7 Advantages and Limitations of ERDA

Using ERD one detects particles that are emitted from the sample surface. If the atomic identity of the particle is known, then the ERDA has the following *advantages* compared to RBS:

1. The depth dependent composition of the sample can be determined which is not possible with RBS technique.
2. The scattering probabilities are much larger with heavier projectiles.
3. Light elements become detectable because the scattering cross-section depends only very slightly on the atomic number of the target atom, whereas it depends quadratically on the atomic number in the case of RBS.

The *limitations of ERDA* are:

1. Recoiled particles usually have a smaller energy than backscattered particles from the surface. Since the recoil scattering cross-section is usually smaller than in the case of RBS cross-sections at forward angles ($<90^\circ$), the signal of the recoiled particles is covered by a huge background of backscattered particles in the energy spectrum recorded by a conventional ERD method. This is why one has to determine another particle parameter to determine the particle species.
2. Since the energy resolution of silicon surface barrier detectors is bad for heavier ions, more complicated methods such as time of flight measurements or magnetic spectrometers are required.

Mössbauer Spectroscopy (MS)

4.1 Introduction

Mössbauer spectroscopy is a versatile technique that is useful in many areas of science such as Physics, Chemistry, Biology, and Metallurgy. It yields very precise information about the chemical, structural, magnetic properties of a material. The basic feature of the technique is the discovery of recoilless γ -ray emission and absorption, now referred to as the “Mössbauer Effect,” after its discoverer Rudolph Mössbauer, who reported the effect in 1958 (Mössbauer 1958) and was awarded the Nobel Prize in 1961 for his pioneer work.

When a beam of electromagnetic radiation with a continuous frequency distribution is made to pass through a gaseous element or metallic vapor, certain frequencies will get absorbed. These frequencies correspond to the allowed excited states. Similarly the atomic nuclei will absorb the γ -rays as the atomic excited states fall in the γ -region. The important aspect of such absorption is that it is very sensitive to the γ -ray energy in the sense that if the γ -ray has frequency different from resonance by one part in 10^{12} , it will not be absorbed. Such sensitivity will not be realized unless the natural frequency spread (line width for atomic systems) of the γ -ray is small which will happen if the life time of the excited state emitting the γ -ray is long ($\geq 10^{-7}$ s).

When an isolated excited nucleus emits a γ -ray, it recoils in order to conserve the momentum. As a result of the motion, the energy of the emitted γ -ray is Doppler shifted to a somewhat lower value, which makes the absorption of that γ -ray impossible by some other nuclei of the same species. The recoil motion of the source can, however, be compensated by moving either the source or the absorber in a direction such that the total momentum of the nucleus plus γ -ray is zero.

Rudolf Mössbauer showed that if the excited nucleus is free, the recoil energy and momentum are taken by the nucleus itself. However, in a solid where the atoms are bound into a crystal lattice, momentum and energy go into lattice vibrations i.e., phonons. Since the entire lattice will absorb the

recoil momentum, therefore, the recoil energy is very small and the Doppler shift is likewise very small. The temperature dependence of the absorption cross-section of ^{191}Ir led Mössbauer to be the first to realize that a photon could be emitted with the entire solid recoiling as one rigid mass. In other words, a small fraction of nuclei held in a solid crystalline structure exhibit sharp-line absorption and emission spectra characteristic of no recoil. The spectral line widths have almost exactly the value predicted from the lifetimes of the states, rather than the much larger widths characteristic of when the nuclei can recoil individually. It is as if the entire massive solid structure of the crystal recoils, rather than an individual nucleus. The nuclei are strongly coupled to the crystal structure, rather than simply being locally constrained. In such situation, the energy lost to the recoil is negligible and the emitted photon may resonantly excite the absorber, i.e., the motion of the source or absorber would destroy the resonance condition; this motion could be used to “tune” the resonant frequency. That is, for no relative velocity between the source and the absorber, the counting rate of γ -rays transmitted through a moving absorber (or source) should be a minimum.

4.2 Concept and Theory

4.2.1 Nuclear Resonance Fluorescence

Mössbauer effect represents a phenomenon of recoil-free resonant interaction of γ -quanta with nuclei. It is impossible on free nuclei because during emission or absorption of a γ -ray, a free nucleus recoils due to conservation of momentum, just like a gun recoils when firing a bullet, with a recoil energy E_R . The emitted γ -ray has recoil energy E_R less energy than the nuclear transition but to be resonantly absorbed it must be E_R *greater* than the transition energy due to the recoil of the absorbing nucleus. These changes in the energy levels can provide information about the atom’s local environment within a system and ought to be observed using resonance-fluorescence.

Nuclear resonance absorption is expected to occur when γ -radiation emitted in a ground state transition is reabsorbed by another nucleus of the same kind. The two main obstacles in the path of achieving nuclear resonant emission and absorption are (i) the recoil energy shift (the recoil of the nucleus as the γ -ray is emitted or absorbed) and (ii) the nuclear thermal motion called Doppler broadening (the “hyperfine” interactions between the nucleus and its environment will change the energy of the nuclear transition) which destroy the delicate overlap of emission and absorption. To achieve resonance, the loss of recoil energy must overcome in some way. Consider a free atom with the mass M and impulse P emits γ -quantum with the energy E and momentum $\hbar k$ ($\hbar = \text{Planck constant } h/2\pi$). According to laws of conservation of momentum, the atom acquires the recoil impulse $p = \hbar k$. If E_e and E_g are the energies of the **excited** state and the **ground** state of the nucleus,

the nucleus remains in the excited state of energy $E_0 (= E_e - E_g)$ for the mean lifetime τ and then undergoes transition back to the ground state by isotropic γ -ray emission or a conversion electron due to internal conversion (energy transfer from the nucleus to the electron). When this excited nucleus decays to the ground state by emitting a γ -transition, the nucleus recoils with energy $E_R (= E_0^2/2Mc^2)$. The change in the energy E_γ of γ -quantum (defined by the change of nucleus kinetic energy under emission/absorption of γ -quantum) will thus be equal to $E_0 - E_R$ as shown in Fig. 4.1.

Mathematically, the γ -energy E_γ can be written as

$$E_\gamma = \left(\frac{(\vec{P} - \hbar \vec{k})^2}{2M} \right) - \frac{\vec{P}^2}{2M} = \frac{(\hbar k)^2}{2M} - \frac{\hbar(\vec{P} \cdot \vec{k})}{M} \quad (4.1)$$

The first term in Equality (4.1) describes the change of γ -quantum energy due to recoil. In a typical Mössbauer effect, the condition $\frac{(\hbar k)^2}{2M} \gg \Gamma$ (where Γ is the natural linewidth of nuclear level.) is usually implemented for the range of the energies of γ -quanta. Such a strong inequality makes great difficulty on observation of nuclear resonance fluorescence on free atoms.

The perfect resonance, which corresponds to total overlap of natural unperturbed emission and absorption lines at an energy E_0 is thus disturbed by the recoil caused by the emission line displaced from the resonance energy E_0 by an amount E_R . For a γ -ray with energy of 10 keV, E_R is in the millielec-

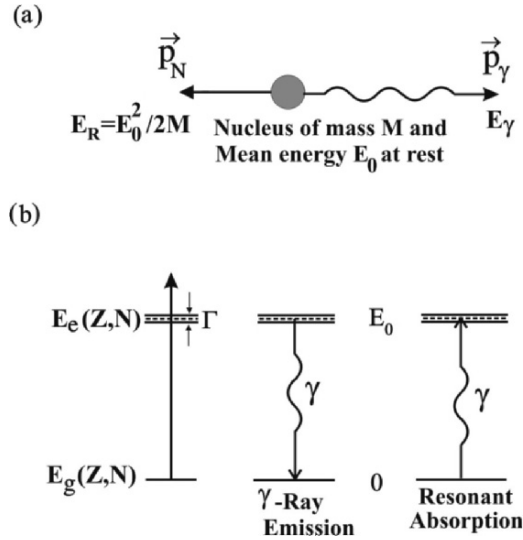


Fig. 4.1. (a) The effect of recoil of the nucleus on the energy of γ -rays and (b) schematic of the phenomenon of nuclear resonance fluorescence

tron volt (meV) range. Although the recoil energy is of the order of 10^{-3} to 10^{-2} eV yet it is sufficient to destroy the resonance in isolated atoms.

The second perturbation, namely the thermal motion of emitter nuclei, produce a Doppler-effect broadening of the emission line and causes it to extend in part beyond the energy E_0 even though centered at $E_\gamma (= E_0 - E_R)$. The γ -ray energy will be broadened into a distribution by the Doppler-effect energy, $E_D = MvV_x$, which is proportional to the initial velocity, V_x from the random thermal motion of the atom, and v from the recoil of the nucleus.

This can be expressed as $\overline{E}_D = E_\gamma \sqrt{2\overline{E}_k/Mc^2}$, where E_k is the mean kinetic energy per translational degree of freedom of a free atom. The Doppler shift due to thermal motion of atoms is described by the second term in (4.1).

For Maxwell distribution of the speeds of atoms, the emission and absorption lines also have a shape of Maxwell distribution with the Doppler width

$$E_D = 2\sqrt{E_R \left(\frac{3}{2} k_B T \right)} \quad (4.2)$$

where $E_R = \frac{1}{2} M v_R^2 \approx \frac{E_0^2}{2Mc^2}$, k_B is the Boltzman's constant and T is absolute temperature.

Since the γ -ray energy has a spread of values E_D caused by the Doppler effect, i.e., movement of the atoms due to random thermal motion, this produces a γ -ray energy profile for the emission as well as the absorption lines in free atoms as shown in Fig. 4.2. The area of overlap of the emission and absorption lines is extremely small but it is many orders of magnitude larger than the intrinsic energy width of the resonance $W = \hbar\Gamma$. To produce a resonant signal the two energies need to overlap. If the recoil energy is less than fairly large energy associated with lattice vibrations, no energy can be transferred either to or from the crystal lattice as a whole and consequently the

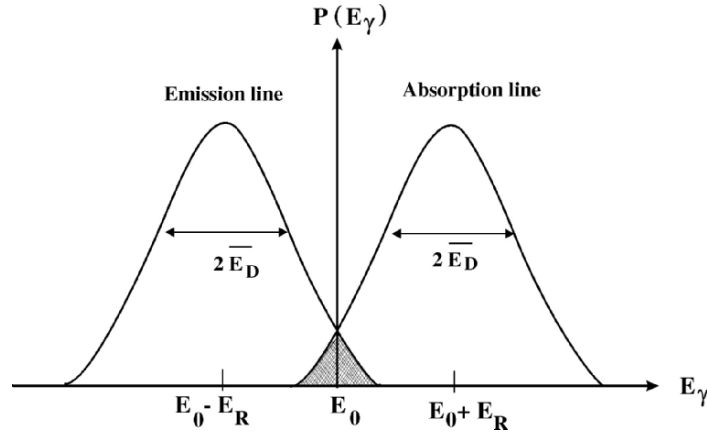


Fig. 4.2. γ -ray energy distribution for emission and absorption lines in free atoms. The emission and absorption lines are separated by $2E_R \approx 10^6 \gamma$ due to recoil effect. The overlap (extremely small) is not to scale

emission and absorption spectra display in common a recoilless component having the natural line width. Since the emitted photon can be absorbed by another nucleus of the same kind if the energy of the photon matches exactly the transition energy due to recoil of the nucleus with momentum $\vec{P} = \hbar\vec{k}$ and energy $E_\gamma = \vec{P}^2/2M = (E_e - E_g)^2/2Mc^2$, the photon has thus to be provided with this recoil energy in the absorption process.

If the γ -ray energy is small enough, the recoil of the nucleus is too low to be transmitted as a phonon (vibration in the crystal lattice) and so the whole system recoils, making the recoil energy practically zero: a recoil-free event. In this situation, i.e., if the emitting and absorbing nuclei are in a solid matrix, the emitted and absorbed γ -ray is of the same energy yielding resonance. The crystal takes up the recoil momentum as a whole, without the excitation of a phonon, in a certain fraction of emissions/absorptions, leaving the energy and width of the natural γ -line unperturbed. The recoiling mass is then so large that E_R is completely negligible compared with width $2E_D$. The overlap of broadened and displaced emission and absorption lines corresponds to resonance absorption as also illustrated in this figure. Doppler broadening can be appreciably reduced by cooling the source and absorber but cannot be fully eliminated.

When the atoms are within a solid matrix of crystal lattice, the effective mass of the nucleus is very much greater because the recoiling mass is now effectively the mass of the whole system, making E_R and E_D very small. In this case, an energy of crystal can acquire a set of discrete allowable levels according to quantum concept, and a minimal energy of excitation cannot be less than some magnitude ΔE_M . If $E_R \leq \Delta E_M$, then emission (absorption) process can occur without change of internal energy of the crystal. In such a case, a recoil impulse is delivered to the crystal as a whole. That is why we have to put $M = \infty$ in (4.1) and (4.2). One follows from there that $E_R = 0$, $E_D = 0$: emission (absorption) line is not shifted, and its width is near to natural. Probabilities of recoil-free processes of emission and absorption (f and f' correspondingly) are practically always less than unity. That is why an emission (absorption) spectrum represents a superposition of shifted line with Doppler width E_D (at $E_0 \pm E_R$, where E_0 is the energy of nuclear level) and nonshifted line with the width to be close to natural. From energy conservation, before and after emission of photon at the resonance energy E_0 ,

$$mc^2 + \frac{1}{2}mv^2 = \frac{1}{2}\left(m - \frac{E_\gamma}{c^2}\right)(v - v_R)^2 + E_0 + \left(m - \frac{E_\gamma}{c^2}\right)c^2 \quad (4.3)$$

we find that recoil-free emission occurs when $v \approx v_R/2$. Hence for resonance absorption, emitter and absorber must move towards one another with an overall relative velocity $u = 2v = v_R \approx E_0/mc$. The rotor-method of providing energy compensation, through a Doppler-shift, entails a peripheral velocity (u), which for a transition energy $E_0 = 0.412 \text{ MeV}$ in ^{198}Hg is

$$u \approx E_0/mc = 0.67 \times 10^5 \text{ cm s}^{-1} = 670 \text{ m s}^{-1}$$

which is in good accordance with observation of a resonance around 700 m s^{-1} .

After the recoil and Doppler broadening have been eliminated, the limiting resolution now is the natural linewidth of the excited nuclear state. This is related to the average lifetime of the excited state before it decays by emitting the γ -ray. A Lorentzian line is represented by the relation:

$$I(E) \approx \frac{\Gamma/2\pi}{(E - E_0)^2 + (\Gamma/2)^2} \quad (4.4)$$

where $\Gamma(=\Delta E)$ is the FWHM of the spectral line and is governed by the mean life time (τ) of the excited nuclear state by Weiskopf and Wigner relation $\Gamma\tau = \hbar$ (where $\hbar = h/2\pi$). Life times of excited nuclear states suitable for Mössbauer spectroscopy range from 10^{-6} to 10^{-11} s. Longer life-times produce too narrow transition lines, which no longer overlap sufficiently while life times shorter than 10^{-11} s give too broad transition lines; the resonance overlap between them would be too much smeared out and no longer distinguishable from the base line of the spectrum.

By achieving resonant emission and absorption for a particular γ -transition in a matrix, we can use it to probe the tiny hyperfine interactions between an atom's nucleus and its environment. In the case of the 14.4 keV transition of ^{57}Fe the resolution (line energy)/(line width) is so small (of the order of 10^{10} – a resolution only attainable by atomic beams, hydrogen masers, or trapped ions), this transition can therefore be used as an exceedingly sharp probe to investigate internal crystalline fields (hyperfine interactions, i.e., the small shifts or splitting of the nuclear levels caused by the interaction between the nucleus and the surrounding electrons) and magnetic dipole and electric quadrupole moments of nuclei as described in Sect. 4.2.3. The so-called isomer shift is due to the fact that the energy of a finite-size nucleus depends on the electron density at the nucleus. This shift will thus depend on the kind of material. Moreover, it will be different for the excited state and for the ground state. Consequently, the transition energies in emitter and absorber are generally different. Splitting arise through the electrostatic interaction between the quadrupole moment of the nucleus and the gradient of the electric field at the nucleus caused by the surrounding electrons (quadrupole interaction) or through the coupling between the nuclear magnetic moment and the magnetic field at the nucleus (magnetic hyperfine interaction).

4.2.2 Nuclear Physics of ^{57}Fe

As resonance only occurs when the transition energy of the emitting and absorbing nucleus matches exactly, the effect is isotope specific. The relative number of recoil-free events (and hence the strength of the signal) is strongly dependent upon the γ -ray energy and so the Mössbauer effect is only detected in isotopes with very low lying excited states. Similarly the resolution is dependent upon the lifetime of the excited state. These two factors limit the

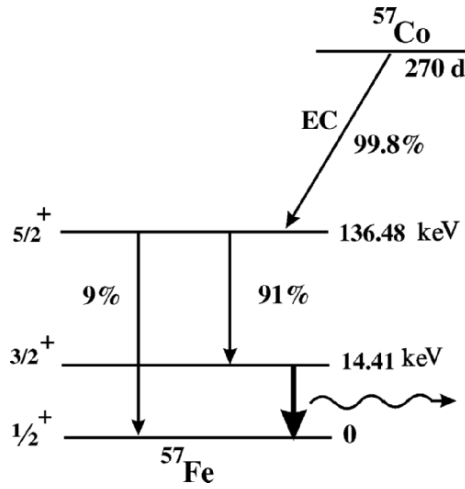


Fig. 4.3. Nuclear Decay of ^{57}Co to ^{57}Fe leading to 14.4 keV Mössbauer γ -ray

number of isotopes that can be used successfully for Mössbauer spectroscopy. The most used is ^{57}Fe , which has both a very low energy γ -ray and long-lived excited state, matching both requirements well. ^{57}Fe is the isotope with the highest recoilless resonant absorption. Since the vast majority of the work reported in the Mössbauer literature is for iron, the discussion here is restricted to this isotope. As shown in the level scheme of ^{57}Fe (Fig. 4.3), ^{57}Co isotope is a source of 14.4 keV γ -transition which is produced during the decay of 14.4 keV energy level of ^{57}Fe via γ -rays or conversion electrons and is used in Mössbauer spectroscopy of iron systems. The ^{57}Co source is generally produced from the nuclear reaction $^{56}\text{Fe}(\text{d}, \text{p})^{57}\text{Co}$ by electrodeposition of the carrier-free isotope on a metal or alloy, which acts as the matrix. Using the matrix like Pt or Pd, narrow emission lines are obtained, e.g., for a source in Pt, the measured line width is at most 10% broader than the natural line width. Of all the excited ^{57}Fe nuclei, about 10% will emit a 14.4 keV γ -ray via a magnetic dipole transition from the metastable $I = 3/2$ state to $I = 1/2$ ground state (I is the nuclear spin). The ratio of recoil-free 14.4 keV photons to all the 14.4 keV photons emitted is f , the recoil-free fraction of the source. The recoil free fraction varies with the properties of the solid and decreases monotonically with increasing temperature. In the case of ^{57}Fe in steel at room temperature, about 14% of the γ -rays are absorbed recoil free.

The line width of the emitted radiation is limited in theory by τ , the mean life of the $I = 3/2$ state. Since $\tau = 1.43 \times 10^{-7}$ s, the energy distribution is given by a Lorentzian with a fullwidth at half maximum of $\Gamma_{\text{nat}} (= \hbar/\tau) = 4.55 \times 10^{-9}$ eV.

To use the Mössbauer source as a spectroscopic tool we must be able to vary its energy over a significant range. This is accomplished by Doppler shifting the energy of the γ -beam. By moving the source, the energy of the

γ -rays is slightly changed. This movement adds or subtracts energy to the particles by way of the Doppler effect. Moving the source at a velocity of 1 mm s^{-1} toward the sample will increase the energy of the photons by $14.4 \text{ keV} \times (v/c) = 4.8 \times 10^{-8} \text{ eV}$ or ten natural linewidths. The “ mm s^{-1} ” is a convenient Mössbauer unit and is equal to $4.8 \times 10^{-8} \text{ eV}$ for ^{57}Fe . Mössbauer spectroscopy is thus useful due to its ability to measure the narrow line widths ($2\Gamma = 10^{-8} \text{ eV}$) of the γ -ray energy.

A ^{57}Fe source, which may be moved relative to the sample and a detector (to monitor the intensity of the beam after it has passed through the sample), will be an integral part of a Mössbauer spectrometer. We control the velocity of the source and thus know exactly the energy of the γ -rays as the energy of 14.4 keV γ -rays emitted by ^{57}Fe is distributed around the value of 14.4 keV with a small natural line width. These differences in the energy are so small that they are invisible in a γ -detector. Now the number of γ s which reach the detector are measured for each energy or each velocity. All the γ -rays with those different energies can be absorbed by another ^{57}Fe nucleus. If the γ s can be absorbed in the sample foil, the count rate in the detector goes down. The line width observed in the spectrum is not the natural line width but is due to the finite energy resolution of the detector used. The Mössbauer spectrum is thus a plot of the counting rate against the source velocity (v) i.e., the beam energy.

If the sample nuclear levels are not split and the $I = 3/2$ to $I = 1/2$ transition energy equals that of the source, then the effective cross-section for absorption is a function of gamma energy as given by

$$\sigma_{\text{eff}} = \frac{\lambda^2}{2\pi} \left(\frac{2I^* + 1}{2I + 1} \right) \left(\frac{f'}{2(1 + \alpha)} \right) \left[\frac{\Gamma_{\text{nat}}^2}{(E - E_\gamma)^2 + \Gamma_{\text{nat}}^2} \right] \quad (4.5)$$

where $I = 1/2$ and $I^* = 3/2$ are the ground and excited nuclear spins, $\alpha = 9.0$ is the internal conversion coefficient (ratio N_e/N_γ in the 14.4 keV decay), $\lambda = 8.61 \times 10^{-9} \text{ cm}$ is the wavelength of the radiation, $(E - E_\gamma)$ is the difference between mean incident and resonant gamma energy, Γ_{nat} is the energy width of the excited nucleus, and f' is the probability of recoilless absorption. The spectrum will be a single Lorentzian centered at $v = 0$ with a line width (FWHM) of $2\Gamma_{\text{nat}} = 0.19 \text{ mm s}^{-1}$. The line width is $2\Gamma_{\text{nat}}$ since the observed line arises from the convolution of the source energy distribution and absorber cross-section. As discussed below, the hyperfine interactions will split the nuclear levels of the sample and complicate the Mössbauer spectrum.

4.2.3 Lamb–Mössbauer Factor (Recoil-Free Fraction)

In Sect. 4.2.1, we have studied that nuclear resonance absorption of γ -rays does not occur between nuclei of isolated atoms or molecules (in gaseous or liquid state) because of the large energy loss of the transition energy E_0 due to recoil effects.

Because $E_R = E_0^2/2Mc^2 \approx 5.37 \times 10^{-4}(E_0^2/A)$ eV where $E_0 = > \text{keV}$, therefore for ^{57}Fe (14.4 keV), $E_R = 1.95 \times 10^{-3}$ eV (This is 10^6 times larger than width of spectral line as $\Gamma = 4.55 \times 10^{-9}$ eV).

If nucleus is moving at velocity v_N in the direction of γ -ray propagation, the γ -photon of energy E_γ receives a Doppler energy $E_D (= v_N \cdot E_\gamma/c)$. Therefore $E_\gamma = (E_0 - E_R) + E_D$ i.e., there will be Doppler broadening of the transition line

$$\begin{aligned} E_D &= 2\sqrt{E_K E_R}, \text{ where } E_K = 3k_B T/2 (\text{K.E. of nucleus}) \\ &\cong 10^{-2} \text{ eV for } 14.4 \text{ keV } \gamma \text{ in } ^{57}\text{Fe} \\ &\text{(a very low probability even in case of large recoil loss)} \end{aligned}$$

In solid state, Mössbauer atom is rightly bound to the lattice; therefore

$$E_R = E_{\text{tr}} + E_{\text{vib}}$$

where

E_{tr} = translational energy transferred through linear momentum to the crystallite as a whole and is very small; hence neglected
 E_{vib} = lattice vibrational energy

In case, E_R is smaller than the characteristic phonon energy ($\sim 10^{-2}$ eV for solids), E_{vib} causes a change in the vibrational energy of the oscillators by integral multiples of phonon energy i.e. $0, \pm 1 \hbar\omega_E, \pm 2 \hbar\omega_E$ etc. (where $\hbar = h/2\pi$ and ω_E is the Einstein frequency i.e. frequency with which each atom vibrates).

Probability f is an important characteristic of the Mössbauer effect. For a single atom crystal with cubic symmetry, the expression for f is $f = \exp\left(-\frac{4\pi^2}{\lambda^2} \langle x^2 \rangle\right)$ where $\langle x^2 \rangle$ is the average square displacement of atoms at the direction of emission of γ -quantum, and λ is the wavelength. Factor f under room temperature has a comparably high value only for restricted number of isotopes (^{57}Fe , ^{119}Sn , ^{181}Ta and some others) and depends on the temperature of crystal.

Maximum cross-section σ_0 of resonant absorption, usually some orders of magnitude, exceeds another cross-sections of interaction of γ -quanta with matter. That is why the Mössbauer effect is easily observable for ^{57}Fe and ^{119}Sn , despite their small content in natural isotope blend ($^{57}\text{Fe} \sim 2.2\%$, $^{119}\text{Sn} \sim 8.5\%$). Cross-section of resonant interaction reaches a maximum value for the energy $E = E_0$. Dependence of σ on E is given by the Wigner formula

$$\sigma(E) = \frac{\Gamma^2}{4} \frac{\sigma_0}{(E - E_0)^2 + (\Gamma^2/4)} \quad (4.6)$$

Here the width of nuclear level is related with its lifetime τ by Heisenberg's interval of uncertainty $\Gamma\tau \approx \hbar$.

Thus there is a certain probability that no lattice excitation (energy transfer of $0 \times \hbar\omega_E$, i.e., zero phonon process) takes place during γ -emission

or γ -absorption process. If f is the recoil-free fraction (a fraction of the γ -rays exempt from the effect of recoil energy and Doppler broadening)

$$E_R = (1 - f) \hbar\omega_E \quad \text{for} \quad E_R \ll \hbar\omega_E$$

$$\Rightarrow f = (1 - E_R) / \hbar\omega_E = 1 - k^2 \langle x^2 \rangle \approx \exp(-k^2 \langle x^2 \rangle) \quad (4.7)$$

Here x is the vibrational amplitude and $k(=2\pi/\lambda)$ is the propagation vector.

Debye model for solids leads to the following expression for Lamb–Mössbauer factor (called Debye–Waller factor f in Atomic Physics)

$$f = \exp \left[-\frac{E_R}{k_B \theta_D} \left(\frac{3}{2} + \frac{\pi^2 T^2}{\theta_D^2} \right) \right] \quad \text{for} \quad T \ll \theta_D$$

and

$$f = \exp \left[-\frac{6E_R T}{k_B \theta_D^2} \right] \quad \text{for} \quad T \gg \theta_D \quad (4.8)$$

Here the Debye temperature $\theta_D = \hbar\omega_E/k_B$ is the measure of the strength of the bonds between Mössbauer atoms of the lattice. The Debye–Waller factor f increases with (a) decreasing E_R , i.e., decreasing γ -photon energy E_γ , (b) decreasing temperature and (c) increasing Debye temperature.

$$f = 0.91 \text{ for } 14.4 \text{ keV } \gamma\text{-ray in } {}^{57}\text{Fe}$$

$$f = 0.06 \text{ for } 129 \text{ keV } \gamma\text{-ray in } {}^{191}\text{Ir}$$

4.2.4 Some Other Mössbauer Isotopes and their γ -Transitions

Apart from the 14.4 keV γ -transition of ${}^{57}\text{Fe}$, the following listed transitions from the radioisotopes ${}^{129}\text{I}$, ${}^{149}\text{Sm}$, ${}^{161}\text{Dy}$, ${}^{169}\text{Tm}$, and ${}^{181}\text{Ta}$ are also useful:

- (1) The 27.8 keV γ -transition of ${}^{129}\text{I}$ from the decay of ${}^{129}\text{Te}$ ($T_{1/2} = 69.6 \text{ m}$)
- (2) The 22.5 keV γ -transition of ${}^{149}\text{Sm}$ from the decay of ${}^{149}\text{Eu}$ ($T_{1/2} = 93.1 \text{ d}$)
- (3) The 74.6 keV γ -transition of ${}^{161}\text{Dy}$ from the decay of ${}^{161}\text{Tb}$ ($T_{1/2} = 6.9 \text{ d}$)
- (4) The 8.4 keV γ -transition of ${}^{169}\text{Tm}$ from the decay of ${}^{169}\text{Er}$ ($T_{1/2} = 9.4 \text{ d}$)
- (5) The 6.2 keV γ -transition of ${}^{181}\text{Ta}$ from the decay of ${}^{181}\text{W}$ ($T_{1/2} = 121.2 \text{ d}$)

For observing the Mössbauer effect, the reason for using a specified γ -transition is based on the following considerations:

- (1) The fraction (f) of recoilless transition should be adequately large (this corresponds to low transition energy E_0 and high Debye temperature θ_D) in order to attain low $E_R (= E_0^2/mc^2)$;
- (2) E_0 must be fairly large in order to furnish good precision (low Γ_0/E_0);
- (3) There must be few competing γ -transitions and small likelihood of internal conversion.

4.2.5 Characteristic Parameters Obtainable Through Mössbauer Spectroscopy

The nuclear energy levels are split by Hyperfine Interactions giving rise to quadrupole splitting, magnetic hyperfine interaction and combination of these. This resolution ($\Delta\gamma/\gamma$) of $\sim 10^{-12}$ in Mössbauer spectroscopy makes it possible to measure the various interactions of nuclear moments with extra nuclear electrons. Before going into the details of the characteristic parameters, let us try to understand an important term known as the electric field gradient (EFG). EFG is an important structural property of a crystalline solid, where it is defined at the location of a nucleus. The definition of the EFG is connected with the calculation of the electrostatic energy of a nucleus with the electrostatic potential in the fixed charge distribution of the electrons around that nucleus. The EFG is nonzero only if the charges surrounding the nucleus violate cubic symmetry and therefore generate an inhomogeneous electric field at the position of the nucleus. Mathematically, EFG is the Hessian matrix (the matrix of the second derivatives) of the electric potential V , i.e., $V_{ij} = \frac{\partial^2 V}{\partial x_i \partial x_j}$. If V_{ij} is EFG tensor at a nucleus, the components of the diagonalized EFG tensor fulfill the condition $V_{xx} + V_{yy} + V_{zz} = 0$ (s-electrons do not contribute to field gradient). They are by definition arranged so that $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$. Thus the asymmetry parameter (η) defined as $\eta = (V_{xx} - V_{yy})/V_{zz}$ we have $0 \leq \eta \leq 1$. EFG can be deduced from the symmetry properties of the crystal. If we choose the c-axis as the z-direction of the EFG tensor, i.e., $V_{xx} = V_{yy}$, then $\eta = 0$ (Axially symmetric field gradient).

The characteristic parameters, obtainable from the Mössbauer studies, are described in the following subsections:

Isomer Shift

The name isomer shift or isomeric shift is assigned due to the fact that this effect depends on the difference in the nuclear radii of the ground and isomeric excited states.

Isomer shift results from the electrostatic (electric monopole) interaction between the nuclear charge and electronic charges (those electrons which have a finite probability of being found at the region of the nucleus). The total electron density at the nucleus contributes to the isomer shift (Fig. 4.4). A change in s-electron density, which might arise from a change in valence electrons, will result in altered Coulomb interaction and manifests itself as a shift of nuclear levels (assuming nucleus to be spherical and charge density uniform).

The differences in isomer shift are observed between several oxidation states of iron differing only by the number of d-electrons, which do not themselves contribute to the electron density at the nucleus. For example the electronic configuration of the Fe-atom is $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^6, 4s^2$. Removal of sixth 3d electron in going from Fe^{2+} to Fe^{3+} increases the charge density at the nucleus and produces a sizeable negative isomer shift (-0.08 cm s^{-1}).

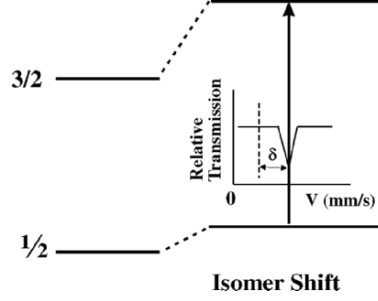


Fig. 4.4. Origin of Isomer Shift – electric monopole interaction between the nuclear charge and the electrons at the nucleus shifts nuclear energy levels without changing the degeneracy. Inset shows the schematic of the resultant Mössbauer spectrum

The isomer shift makes a change in the nuclear energy levels without changing the degeneracy and manifests itself as a shift from zero velocity of the centroid of the resonance spectrum.

Quadrupole Splitting

Non-spherical nuclei with a half-integer spin $>1/2$ possess a quadrupole moment Q , which interacts with the electric-field gradient (EFG) generated by their surroundings. The coupling of Q (a property of the nucleus) with an EFG (a property of a sample) is called the quadrupole interaction. The nuclear quadrupole coupling is expressed by the Hamiltonian

$$H = \frac{e^2 Q V_{ij}}{4I(2I-1)} \left[3I_z^2 - I(I+1) + \frac{1}{2}\eta(I_+^2 - I_-^2) \right] \quad (4.9)$$

where V_{ij} are the Cartesian components of $\mathbf{V}$, the EFG at the origin (a second-rank symmetrical tensor), η is the asymmetry parameter, and I_+ and I_- are the raising and lowering operators. For ^{57}Fe nucleus with spins $3/2$ and $1/2$, the solution of the equation gives

$$E_Q = \pm \frac{1}{4} e^2 Q V_{ij} \left(1 + \frac{1}{3} \eta^2 \right)^{1/2} \quad (4.10)$$

The nuclei whose spin is zero or $1/2$ are spherically symmetric and have $Q = 0$. The EFG is a 3×3 Tensor obtained by applying the gradient operator to the three components of the electric field. It is specified by V_{xx} , V_{yy} , V_{zz} , i.e.,

$$\frac{\partial^2 V}{\partial^2 x^2}, \frac{\partial^2 V}{\partial^2 y^2}, \frac{\partial^2 V}{\partial^2 z^2}$$

In case of ^{57}Fe , the levels of $I = 3/2$ and $I = 1/2$ are shifted by electric monopole interaction giving rise to the isomer shift. The quadrupole splitting

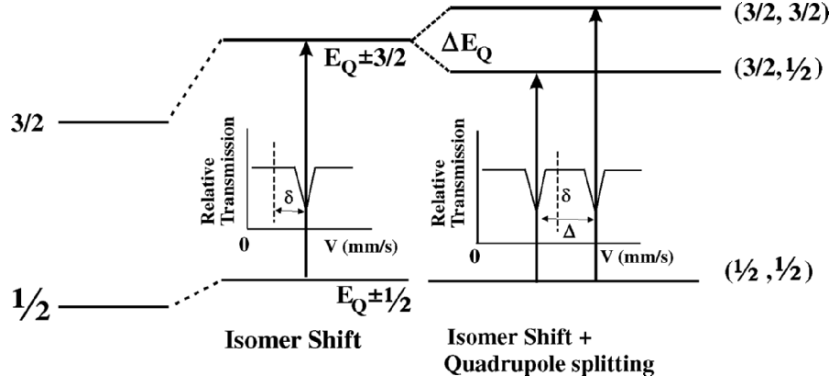


Fig. 4.5. Quadrupole Splitting in ^{57}Fe with $I = 3/2$ in the excited state and $I = 1/2$ in the ground state. The $I = 3/2$ level is split into two sub-levels by electric quadrupole interaction while the ground state with $I = 1/2$ does not split because there is no spectroscopic quadrupole moment in a nucleus with $I = 1/2$. The levels of $I = 3/2$ and $I = 1/2$ are shifted by electric monopole interaction (giving rise to isomer shift). Inset shows the schematic of resultant Mössbauer spectrum

with $I = 3/2$ in the excited state splits into two sub-levels while the $I = 1/2$ in the ground state does not split because there is no spectroscopic quadrupole moment in a nucleus with $I = 1/2$. The quadrupole splitting energy difference ΔE_Q between the two levels is given by relation

$$\Delta E_Q = E_Q(3/2, 3/2) - E_Q(3/2, 1/2) = (1/2)e^2q'Q(1 - \gamma_\infty) \quad (4.11)$$

The schematic diagram of quadrupole splitting in ^{57}Fe with $I = 3/2$ in the excited state and $I = 1/2$ in the ground state is as shown in Fig. 4.5.

Magnetic Hyperfine Structure

The splitting of spectral lines is caused by the interaction of nuclear magnetic dipole moment μ with the magnetic field H , due to the atom's own electrons-called "Zeeman splitting". The Zeeman splitting is always absent for those nuclear levels whose spin is zero, since their magnetic moment is identically zero. The Energy levels are given by

$$E_m = -\mu H m_I/I = -g \mu_N H m_I$$

where $m_I = I, (I-1), (I-2), \dots, (-I)$, and μ_N is the nuclear magneton.

Leaving aside external fields and bulk ferromagnetic fields, the various sources of magnetic interactions are:

- Direct coupling between the nucleus and the s-electrons called the Fermi contact interaction. This interaction gives the largest contribution to the internal field. It is a spin interaction between the nuclear and electron spin.

- Interaction between the nucleus and the orbital magnetic moment of the 3d electrons. For example, the magnetic hyperfine fields for ^{57}Fe in Fe-, Co- and Ni-host at 0 K is -342 , $+312$ and $+283$ kOe respectively, while it is 622 , 340 and 185 kOe in FeF_3 , FeF_2 and FeSO_4 host materials.
- Contribution from the dipole interaction with the moment of the electron spin.

The large negative part of this field is owing to core polarization. This results from the different exchange interactions of the 1s, 2s, and 3s electrons of parallel and antiparallel spin with the d-shell. The d-shell will effectively attract s-electrons having spins parallel to the d-shell spin. The paired s-orbitals of the two different “m” quantum numbers will then have different radial distributions resulting in a net unpaired spin density at the nucleus.

The term Internal field is used for the field resulting directly from the application of an external field H_0 , taking into account the Lorentz and demagnetizing fields, i.e., $H_i = H_0 + (4/3)\pi M - DM$. In case of ^{57}Fe , fields from 210 to 250 kOe per spin have been observed for various compounds of trivalent Fe. However, the fields are smaller for Fe-oxides and larger for Fe-fluorides. In divalent salts, the observations are as follows: Field of 220 kOe has been observed for Fe^{2+} in CoO, field of 330 kOe in FeF_2 and 485 kOe for Fe^{2+} in Fe_3O_4 .

Combined Magnetic and Electric Hyperfine Coupling

Suppose the hyperfine field is acting along the c-axis and one of the principal axes (say z-axis) of the EFG tensor (V_{zz}) is perpendicular to the mirror plane of the crystallographic iron site. This leads to $\theta = 90^\circ$ and $\phi = 0^\circ$ (for x//c) or $\theta = 90^\circ$ and $\phi = 90^\circ$ (for y//c) as shown in Fig. 4.6.

Here θ and ϕ are the polar co-ordinates of the hyperfine field direction in the principal axis system of the EFG tensor. In this case, therefore

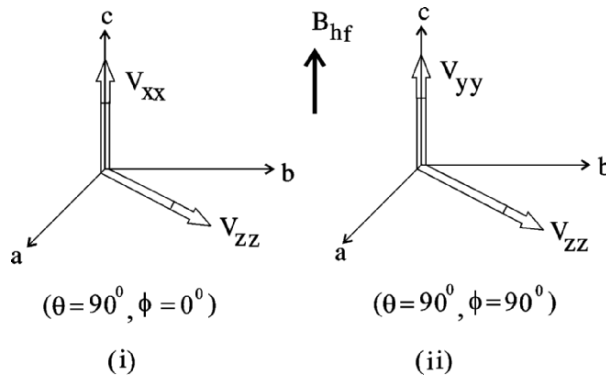


Fig. 4.6. Schematic diagram to show (i) the hyperfine magnetic field (B_{hf}) parallel to V_{xx} (ii) the hyperfine magnetic field (B_{hf}) parallel to V_{yy}

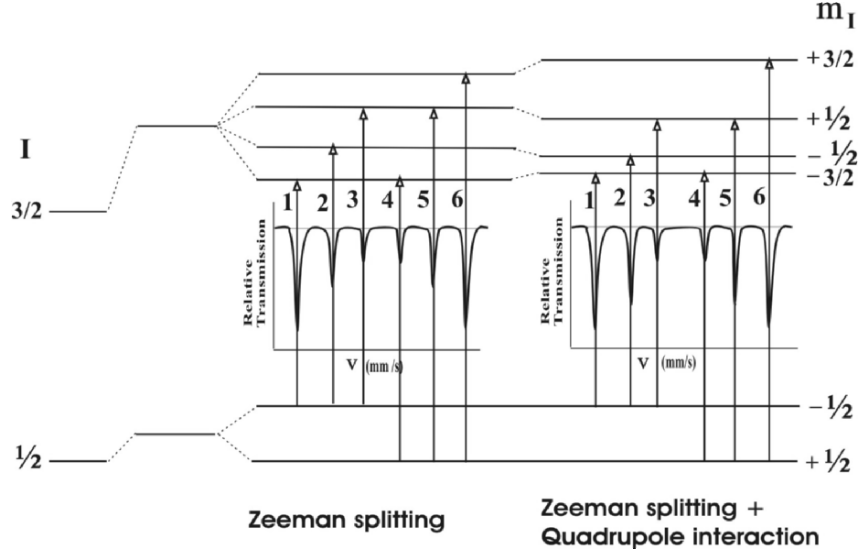


Fig. 4.7. Six allowed transitions in the Mössbauer spectrum of the 14.4 keV transition in ^{57}Fe . The internal/external magnetic field results in Zeeman splitting of the nuclear levels while an EFG interacts with the excited state level producing further shifts. The insets show the schematic of resultant spectra in both cases.

$$\Delta E_Q = \frac{eQV_{zz}}{2} (3 \cos^2 \theta - 1 + \eta \sin^2 \theta \cos 2\phi) \quad (4.12)$$

If B_{hf} and V_{zz} are parallel to c-axis, $\theta = 0^\circ$ and thus

$$\Delta E_Q = \frac{eQV_{zz}}{2} \quad (4.13)$$

All the four magnetic sub-levels of ^{57}Fe are displaced by the same amount by quadrupole interaction when the axially symmetric EFG tensor has its symmetry axis parallel to B_{hf} (Fig. 4.7).

A threefold axis (120° rotation) is also sufficient to ensure an axially symmetric field gradient

$$E_Q = \frac{eQV_{ij}}{4I(2I-1)} [3m_I^2 - I(I+1)] [1 + \eta^2/3]^{1/2} \quad (4.14)$$

where $m_I = I, (I-1), (I-2), \dots, (-I)$. The measurement of quadrupole coupling gives the product of nuclear moment and the field gradient at the nucleus.

In Fig. 4.7, the line positions are related to the splitting of the energy levels, but the line *intensities* are related to the angle between the Mössbauer γ -ray and the nuclear spin moment. The outer, middle and inner line intensities are related by $3 : (4 \sin^2 \theta)/(1 + \cos^2 \theta) : 1$ (where θ is the angle between

the magnetic field and the direction of propagation of the radiation) meaning that the outer and inner lines are always in the same proportion but the middle lines can vary in relative intensity between 0 and 4 depending upon the angle the nuclear spin moments make with the γ -ray. In polycrystalline samples with no applied field, this value averages to 2. In single crystals under applied fields, the relative line intensities can give information about moment orientation and magnetic ordering.

The hyperfine interactions, i.e., isomer shift, quadrupole splitting, and magnetic splitting, alone or in combination are the primary characteristics of many Mössbauer spectra. Some recorded spectra (shown in Sect. 4.3.1) illustrate how measuring these hyperfine interactions can provide valuable information about a material/system.

$$\begin{aligned}
 B_{\text{tot}} &= (V_6 - V_1) \text{ mm s}^{-1} \\
 B_{\text{hf}} &= (V_6 - V_1) \text{ mm s}^{-1} \times 3.097 \text{ (T)} \\
 B_g &= (1/2) [(V_5 - V_3) + (V_4 - V_2)] \text{ mm s}^{-1} \\
 B_{\text{hf}} &= B_g (\text{mm s}^{-1}) \times 8.430 \text{ (T)}
 \end{aligned} \tag{4.15}$$

The EFG due to partially filled nonspherical shells tends to be larger than that due to distant charges. This field gradient is also subject to shielding correction $V_{ij} = V'_{ij}(1 - \gamma_\infty)$ where V'_{ij} is the EFG due to distant charges and $(1 - \gamma_\infty)$ is the anti-shielding factor.

4.3 Experimental Set-Up

The energy changes caused by the hyperfine interactions are of the order of billionth of an electron volt. Such mini-scale variations of the original γ -ray are quite easy to achieve by the use of the Doppler effect, in the same way as the pitch of the siren of an ambulance gets raised when it is moving toward the listener and lowered when moving away from the listener. The hyperfine interactions are thus investigated in a Mössbauer spectroscopy experiment by varying the energy of source (called modulation) relative to the sample (absorber) and by counting of number of absorbed (scattered) photons according to the law of modulation. In order to modulate the energy of γ -radiation one usually uses the Doppler effect, i.e., the γ -ray source is moved toward and away from the sample called the absorber according to alternate/reciprocal law. This is achieved by oscillating a radioactive source with a velocity of a few mm s^{-1} due to extremely narrow width of resonant lines (10^{-8} – 10^{-7} eV). With an oscillating source we can modulate the energy of the γ -ray in very small increments. Where the modulated γ -ray energy matches precisely the energy of a nuclear transition in the absorber, the γ -rays are resonantly absorbed and we see the absorption peak. Fractions of mm s^{-1} compared to the speed

of light ($3 \times 10^{11} \text{ mm s}^{-1}$) gives the minute energy shifts necessary to observe the hyperfine interactions. The Mössbauer spectrum, which represents a dependence of number of registered γ -quanta on instant speed of source, is recorded in discrete velocity steps. The energy scale of a Mössbauer spectrum is thus quoted in terms of the source velocity (mm s^{-1}). Distribution of registered intensities is defined by a structure of Mössbauer lines. In general case Mössbauer spectrum contains several lines, since hyperfine interactions in crystal induce a shift and splitting of nuclear levels.

4.3.1 A Basic Mössbauer Spectrometer Set-Up

A basic Mössbauer spectrometer set-up (Fig. 4.8) consists of a ^{57}Co radioactive source mounted on a velocity transducer (drive unit), where it is repeatedly moved between zero and maximum velocity (typically a triangular wave of frequency 10–20 Hz), and a proportional counter, giving an absorption spectrum in the multichannel analyzer (MCA).

The Mössbauer effect is observed either in transmission or scattering geometry. In the first case, a part absorbed (by target) γ -quanta is measured while in the second case, a part of scattering γ -quanta is measured. In the transmission geometry, the γ -rays emitted from this source are passed through the sample, which contains the substance to be investigated, into a detector. The sample must be sufficiently thin to allow the γ -rays to pass through as the relatively low energy γ -rays are easily attenuated passing through the sample. The samples are studied from low temperatures going down to liquid nitrogen ($\sim 80 \text{ K}$) or still down to liquid helium (4.2 K) to high temperatures say $1,100 \text{ K}$ using a temperature controller. A new design for a Mössbauer in situ and versatile cell for the studies of catalysts and nanometer-sized particles has been described by Bødker and Mørup (1996) which can allow measurements

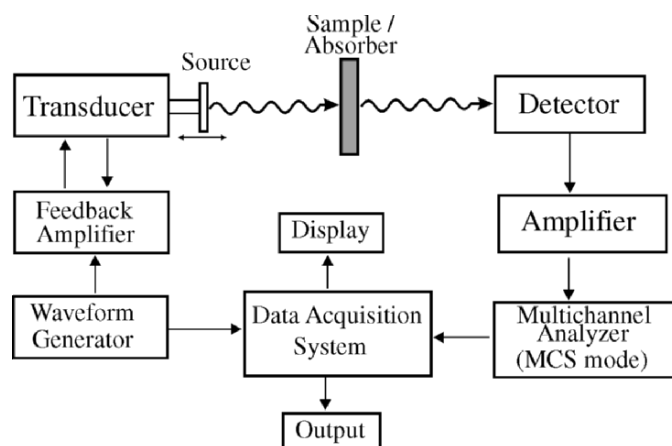


Fig. 4.8. Layout of Mössbauer spectrometer set-up

in the temperature range from below 5 K to about 800 K with the sample in vacuum or exposed to gases. The cell is designed to be used for Mössbauer studies in large applied magnetic fields.

The description of the components is presented in the following subsections:

Radioactive Source and Drive Unit

Mössbauer measurements are generally performed to analyze the samples containing iron. For this purpose, one uses a specially prepared “Mössbauer” source of 10–20 mCi (usually ^{57}Co diffused into Rhodium or Palladium foil) which emits the 14.4 keV photon by excited ^{57}Fe nuclei produced by the β -decay of ^{57}Co . Some of the 14.4 keV photons are emitted by nuclei that share the recoil momentum with macroscopic bits of the matter in which they are imbedded (“recoilless emission”) with the result that their fractional spread in energy, or line width $\Delta E/E$ is extraordinary narrow, of the order of 10^{-12} . A sample containing Fe-atoms in an environment that permits recoilless absorption of 14.4 keV photons, is placed between the source and the proportional counter. The sample of iron or compound of iron, which should be a thin foil (less than 20 μm), is placed at a distance of 5–10 cm from the Mössbauer source.

The source is mounted on the center rod of a piston that is connected to a velocity transducer/drive mechanism (a loudspeaker coil being forced to move with a triangular or sinusoidal velocity waveform due to the magnetic force produced by a drive current in the coil of the transducer). The piston thus moves back and forth with a velocity that is a periodic sawtooth function of time. The requirement of linear velocity scale means equal length of time spent in equal velocity increment, i.e., constant acceleration. Velocities in the mms^{-1} or cms^{-1} region are generally sufficient to cover the range of hyperfine interactions which can be achieved by moving the source toward the absorber with relative velocity v , causing the shift in energy equal to $dE = (E_e - E_g) \times (v/c)$. The resulting motion induces a current in a sense coil that is proportional to the velocity. This sense current is compared to a reference current ramp, and the difference (error) signal is fed back to the drive current amplifier in such a manner as to reduce the difference between the sense current and the reference current, keeping the velocity of the piston precisely proportional to the reference current. The reference current is a sawtooth function of time with a slow rise from $-I_0$ to $+I_0$ with a rapid flyback to $-I_0$. The corresponding velocity of the piston is therefore also a function of time with a slow linear rise from $-v_0$ to $+v_0$ and a rapid flyback. The drive circuitry starts the MCA sweep in the multiscaling mode and advances the channel number at fixed time intervals.

The motion of the Mössbauer source causes a corresponding sawtooth Doppler shift in the energies of the photons that traverse the sample. In effect, the narrow emission line is swept back and forth in energy over the recoilless

lines of the ^{57}Fe in the absorber. The analog signals of the detector channel are analyzed by discriminators for 14.4 keV and 6.4 keV peaks. Upper and lower threshold values of the discriminators are generated by digital to analog converters (DACs). These values can be changed automatically to follow the temperature drift of the amplifiers. Digital signals from the discriminators are sent to the velocity synchronized counters whenever a detected pulse is within the specified range. Counts are accumulated in a number of time bins (or channels), synchronized to the movement. A Mössbauer spectrum is a plot of the number of counts vs. the velocity between source and absorber. In transmission mode, the counts are due to γ -rays transmitted by the absorber and the recoilless absorption is observed as a dip in the spectrum. Mössbauer spectra for the two different energies of 6.4 keV and 14.41 keV are sampled separately. Since the experiment measures the width of the resonant absorption vs. the relative velocity curve for the 14.4 keV γ -rays from the first excited state of ^{57}Fe , it does not affect the result whether the source or the absorber is moved. It only depends on the availability of the equipment.

Detector and Electronics

The γ - and X-rays from the ^{57}Fe source, after passing through the absorber, are detected in a proportional counter, e.g., X-ray peak at 6.4 keV, given by the conversion of the Mössbauer transition and a 14.4 keV γ -peak, which is the Mössbauer transition. Normally, the 14.4 keV γ -ray from ^{57}Co decay can be detected with proportional counter, a small size ($1/2'' \times 1/2''$) NaI(Tl) scintillation detector or a Si(Li) detector. The proportional counter contains primarily Argon/Krypton with a small amount of methane gas at pressure of ≈ 800 Torr. The 14.4 keV photons enter the chamber through the mylar window and ionize some of the Krypton atoms. The creation of each ion/electron pair requires ≥ 30 eV. The positive ions drift to the outer wall while the electrons move to the central wire. In the vicinity of the wire, $E(\propto 1/r)$ is so high that electrons in one mean free path pick up enough energy to ionize more atoms, the effective gas gain being 1,000. The methane suppresses the sparking by absorbing the UV quanta generated in the process. The methane also suppresses the random motion of electrons, thus shortening the travel time to the center wire and the rise time of the signal pulse. The overall absorption efficiency at 14.4 keV is $\sim 30\%$. The 122 and 136 keV photons entering the counter Compton scatter and produce a broad background of lower energy signals. The SCA discriminates against most of these but about 20% of the pulses falling in the 14.4 keV window of the SCA are from this Compton background. The charge pulse from the counter is amplified and differentiated by the preamplifier, which is mounted as close to the counter as possible. The main amplifier, the output of which is applied to a single channel analyzer (SCA), provides further amplification. The SCA is set to discriminate against the non-14.4 keV signals. The signals accepted by the SCA are added to the current channel of the MCA.

An MCA records the detector pulses in a memory location that is synchronized with the velocity of the source. The photon pulses per velocity interval are summed up in the MCA connected to a PC over a USB bus, working in the multichannel scalar (MCS) mode. MCS is a device to store the instantaneous counting information in a large number of scalars. To count clock pulses in a scalar, the most significant bit of the channel address scalar of the MCS is used to trigger an independent ramp generator in the velocity circuit. The circuit is designed for a normal trigger rate of ~ 5 Hz. The counts of each count register are displayed on the computer monitor. In the absence of a Mössbauer absorption line, the average number of counts in the various velocity intervals will be equal within the Poisson statistics of counting. When a 14.4 keV photon, having traversed the absorber, triggers the proportional counter, the resulting pulse is counted in the memory channel of the MCS with the address given by the current number in the clock scalar. Thus after a given exposure, each channel of the MCS contains a number of photons that traversed the absorber within the narrow range of energies corresponding to the narrow range of velocities of the piston during which the clock scalar dwelled on the address of that channel. Due to the absorption line (at an energy equal to the Doppler-shifted energy at some particular velocity) the counting rate, during the time that pulses are addressed to that velocity channel, will be reduced and the accumulated deficiency of counts in that and neighboring channels will be seen as an “absorption line” on the screen of MCA as shown in Fig. 4.9.

User-friendly Mössbauer spectroscopy oriented analyzer card (MSPCA) with the standard software, the details of which can be found from the website: <http://alag3.mfa.kfki.hu/magnet/mossba/index.htm>, can be used to transform the personal computer into a full-featured Mössbauer spectroscopy analyzer. Any type of the Mössbauer function generators and driving units can be connectable to this analyzer card. The card is connectable to a Per-

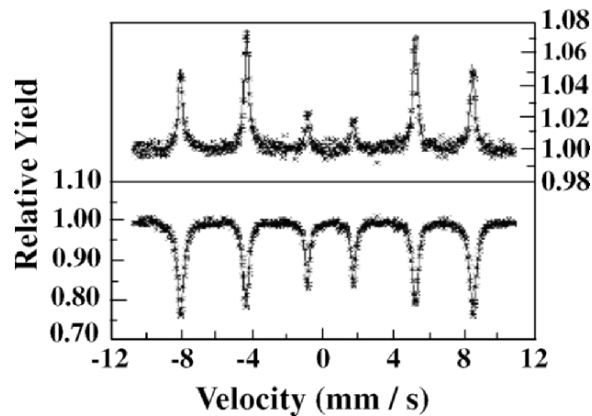


Fig. 4.9. Transmission spectrum (*top*) and absorption spectrum (*bottom*)

sonal computer (PC) ISA I/O slot and includes three important parts: a fast general purpose amplifier with computer controlled discrete gain values and SCA, a 4,096 channel Analog to Digital Converter (ADC) and two programmable logic arrays with memory to realize the PHA (Pulse Height Analysis) and MCS operation modes, and to build the interface between the card and PC. The minimum computer configuration required is 1 Mbyte memory, one floppy disk drive and any type of monitors but it is recommended to use a 486 main-board PC and color VGA monitor to exploit the software potentialities.

The Mössbauer spectrometer is calibrated against a metallic iron foil and zero velocity is taken as the centroid of its room temperature Mössbauer spectrum. In such calibration spectra, line widths of approximately 0.23 mm s^{-1} are observed. The master oscillator controls the source velocity as well as the address of the active channel of the MCA. This oscillator synchronizes the source acceleration and the sweep of the memory registers, causing the active channel address to be a linear function of the velocity. In other words, while the source is at a particular velocity, the pulses counted are always stored in a particular register. The master oscillator output is a rounded sawtooth or triangular wave and is applied to one of the driver inputs. The driver is essentially a difference amplifier with its output applied to the vibrator. A pick-up coil on the vibrator supplies a voltage proportional to the velocity of the source and is connected to the second input of the driver. The driver and vibrator form a tightly coupled, electro-mechanical, negative feedback loop, forcing the source velocity to be directly proportional to the master oscillator signal. The desired velocity range is selected by scaling the master oscillator signal before it is applied to the driver.

Converting Velocity into Channel Number by Multichannel Analyzer

First Procedure

The instantaneous velocity information is obtained from a (coil and magnet) velocity transducer; the resulting voltage is used to code the velocity information into the amplitude of the γ -ray counts, which are then stored by pulse height analyzer. The disadvantage of this method is that any nonlinearity in velocity appears as modulation of the no-absorption spectrum.

Second Procedure

The procedure is to use MCA as time analyzer, i.e., it is allowed to step at a clock-controlled rate through its channels. Synchronization between the mechanical motion and the analyzer is maintained by triggering the analyzer once per cycle or by using the analyzer as the waveform generator.

Typical Mössbauer Spectra of Some Iron-Compounds

The features of a Mössbauer spectrum depend essentially on the character of the magnetic state of the sample: paramagnetic, ferromagnetic or antiferromagnetic. This dependence is strictly connected with the electron spin lattice relaxation times of the material or the time between transitions from one orientation of the net electron spin S_L to another. Both the dipolar contribution H_D and the Fermi contact term depend on the orientation of the net electron spin S_L . The electron spin relaxation process can be thought of as flipping the direction and changing its magnitude of an effective magnetic field. If the frequency of the flip is comparable or smaller than the frequency of the nuclear spin, the spectrum will show a magnetic hyperfine interaction otherwise the hyperfine structure will be absent due to the zero mean value of the effective field seen by the nucleus.

To analyze the recorded spectra, the spectrometer needs to be calibrated. The three main calibration parameters are the velocity scale, the center point of the spectrum and the nonlinearity of the velocity/time profile of the oscillation compared to a standard reference. The calibration is performed using a spectrum recorded from an α -iron foil at room temperature using the well defined line positions of the sextet from α -iron, which occur at $\pm 5.312 \text{ mm s}^{-1}$, $\pm 3.076 \text{ mm s}^{-1}$, and $\pm 0.840 \text{ mm s}^{-1}$. The center of this α -iron spectrum at room temperature is taken as the reference point (0.0 mm s^{-1}) for isomer shift values of sample spectra. The typical Mössbauer spectrum of the 14.4 keV transition of ^{57}Fe in natural iron (Fig. 4.10) represents a simple example of pure nuclear Zeeman effect. Because of the cubic symmetry of the iron lattice, there is no quadrupole shift of the nuclear energy levels. The relative intensities of the six magnetic dipole transitions are

$$\begin{aligned} I_1 &= I_6 = 3(1 + \cos^2 \theta) \\ I_2 &= I_5 = 4 \sin^2 \theta, \text{ and} \\ I_3 &= I_4 = (1 + \cos^2 \theta) \end{aligned} \quad (4.16)$$

where θ is the angle between the magnetic field and the direction of propagation of the radiation. Lines 3 and 6 have right elliptical polarization with ellipticities equal to $\cos \theta$; lines 1 and 4 have left elliptical polarization with ellipticities equal to $\cos \theta$ while lines 2 and 5 are linearly polarized perpendicular to the direction of the field. If the magnetic and consequently, the internal fields are randomly oriented, the radiation is unpolarized and the intensities are 3:2:1:1:2:3 as follows from averaging (4.14) over a sphere. The internal field in metallic iron has been found to be $3.33 \times 10^5 \text{ kOe}$ at 300 K.

In the case of Fe_2O_3 (an antiferromagnet), which exists in two forms, i.e., $\alpha\text{-Fe}_2\text{O}_3$ (Fe^{3+} ions situated at a single type of lattice site) and ferromagnetic $\gamma\text{-Fe}_2\text{O}_3$ (Fe^{3+} ions situated in octahedral and tetrahedral lattice sites), the value of effective magnetic field is approximately the same in both types. The $\alpha\text{-Fe}_2\text{O}_3$ has a low symmetry structure; a mixed interaction of the magnetic dipole and electric quadrupole is expected. Since Fe^{3+} is in the $^6\text{S}_{5/2}$

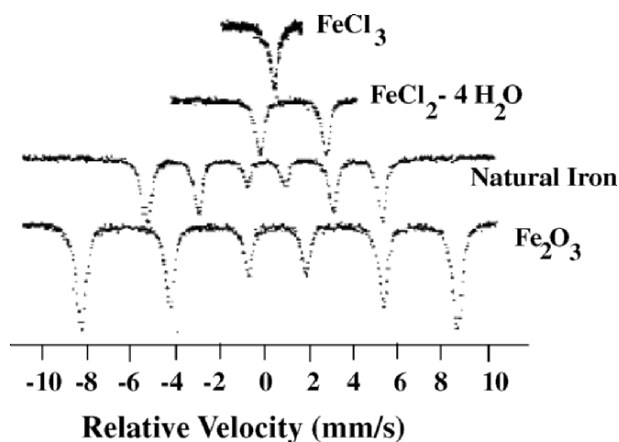


Fig. 4.10. The typical Mössbauer spectra of FeCl_3 , $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and Fe_2O_3 in comparison to natural-Fe

state, there is no contribution to the field gradient from the ion itself. The Mössbauer spectrum of Fe_2O_3 in comparison to natural-Fe as well as FeCl_3 and $\text{FeCl}_2 \cdot \text{H}_2\text{O}$ is also shown in Fig. 4.10. The Mössbauer spectrum for FeCl_3 (in which Fe^{3+} is in the ${}^6\text{S}_{5/2}$ state) clearly indicates that there is no contribution to the EFG from inner electron shells. There is also no quadrupole coupling due to octahedral symmetry of iron in this compound. On the other hand, there are two principal directions of the field gradient axis in a single unit cell of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ crystal which consists of Fe^{2+} ion surrounded by a distorted octahedral, constructed from two Cl^- ions and four water molecules.

4.3.2 Advances in Experimental Set-Up/Method of Analysis

In late 1970s, a few laboratories have replaced the conventional MCA system by a mini or microcomputer system (Window et al. 1974, Holbourn et al. 1979). Many isotopic sources like ${}^{119}\text{Sn}$ and ${}^{151}\text{Eu}$ have also been used for Mössbauer studies besides ${}^{57}\text{Fe}$. Not all isotopes exhibit resonant absorption at room temperature, so that studies at low temperature are carried out. The low and high temperature study is also carried out to investigate the internal magnetic field and the transition temperature. Even the external magnetic fields are used for obtaining additional information. In the nuclear solid state physics group of the Uppsala University, a state of the art data acquisition system, based on the general purpose low cost microcomputer was designed and constructed in 1982 by Sundqvist and Wäppling (1983) along with a simple multiscale interface for recording two Mössbauer spectra simultaneously (Linares and Sundqvist 1984) providing increased flexibility, improved capacity and ease of data handling. Mössbauer spectroscopy using 67.4 keV γ -radiation from ${}^{61}\text{Ni}$ source, produced using the reaction ${}^{64}\text{Ni}(p, \alpha){}^{61}\text{Co}$,

has been described by Häggstrom et al. (1984) in some Ni-compounds using NaI(Tl) and HpGe detectors. For ^{125}Te Mössbauer spectroscopy, the use of CdTe detector has been reported by Bargholtz et al. (2000). In their recent publication, Zhou et al. (2004) have described the remote data acquisition and control system for Mössbauer spectroscopy.

Conventional methods for $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio determination involve laborious wet chemical analysis or the recording of the full Mössbauer spectrum of ilmenite, which is an initial raw material in the synthesis of titanium white (TiO_2). The slowness (8–48 h are needed) of the conventional Mössbauer technique precludes its use as a control device in the manufacturing processes. A new algorithm for rapid determination of an $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio in ilmenite has been developed by Jancik et al. (2005) which is based on calculation of a ferrous to ferric ratio from the heights of spectral lines. The actual heights of spectral lines (heights with overlap correction) can be determined by using a constant velocity regime and measuring four points of the Mössbauer spectrum.

4.4 Evaluation of Mössbauer Spectra

The weighted mean square deviation χ^2 between the experimental data points N_i^{exp} and the corresponding theoretical values N_i^{theo} (as explained below) has to be minimized, i.e.,

$$\chi^2 = \sum_{i=1}^N \frac{1}{\sigma_i^2} (N_i^{\text{theo}} - N_i^{\text{exp}})^2 = \text{minimum} \quad (4.17)$$

Here $\sigma_i^2 = N_i^{\text{exp}}$ = square of the statistical variation of count rate in the i th channel, N_i^{theo} is the sum of K uncorrelated Lorentzian lines with different intensities and half widths

$$N_i^{\text{theo}} = N_{\text{base line}}^{\text{theo}} - \sum_{j=1}^k \frac{W_K}{\left(E_k - \frac{v_i}{c} \cdot E_0\right)^2 + (\tau_k/2)^2} \quad (4.18)$$

where $N_{\text{base line}}^{\text{theo}}$ is the count rate “off resonance.” The least square-fitting program for the evaluation of Mössbauer spectra needs the implementation of the Marquardt-Levenberg fitting procedure using Lorentzian or Voigt profile line shapes.

A versatile Mössbauer Data Analysis (MDA) user oriented computer simulation program was developed by Jernberg and Sundqvist (1983) in which the calculations consider a number of experimental situations and the comparisons is made by least squares sums or by plotting the simulated and the measured spectrum. The fitting routine minimizes the least square sums to find the parameters characterizing the measured spectrum.

4.5 Conversion Electron Mössbauer Spectroscopy

An additional technique, known as conversion electron Mössbauer Spectroscopy (CEMS), is applied to investigate the properties of physical surfaces (thin films) and the surface properties. To know about CEMS, we will have to understand what the conversion electron is?

We have seen in Fig. 1.1 of Chap. 1 that X-ray photons, Auger electrons, or both, can get emitted in the course of filling of the hole created after ejection of an electron from the inner-shell. The hole in an inner shell can also be created by a process called the internal conversion (a competing electromagnetic process to γ -ray emission) apart from X-ray/ γ -ray or charged particle bombardment. In this process of internal conversion, the excitation energy of the nucleus is transferred to one of the atomic electrons, causing it to be emitted from the atomic shells. The kinetic energy of the emitted electron (T_e) depends upon the electron binding energy, B_e and the transition energy ($E_i - E_f$) and is given by

$$T_e = (E_i - E_f) - B_e \quad (4.19)$$

Since there are several possible electron energies for a given transition, the electrons in a particular shell cannot be emitted if the transition energy in that shell is smaller than the electron binding energy. Conversion electrons are thus labeled by the atomic shell from which they originated. Conversion electrons from the L shell can be labeled L_I , L_{II} or L_{III} , if they originated from the $2s_{1/2}$, $2p_{1/2}$, or $2p_{3/2}$ atomic orbitals, respectively. The vacancy left in the atomic shell, by emission of a conversion electron, is filled by one from a higher shell and the difference in energy between the two shells appears in the form of an X-ray. Introduce the coefficient of internal conversion $\alpha (= \Gamma_e/\Gamma_\gamma)$, the total width of a nuclear level is $\Gamma = (1 + \alpha)\Gamma_\gamma$. The internal conversion coefficient depends on the energy of the transition (E_γ), the atomic number of the nucleus (Z) and principal atomic quantum number (n) in approximately as $\alpha \propto Z^3 / (n^3 E_\gamma^{2.5})$. Internal conversion coefficients are larger for magnetic transitions than for electric transitions, and increase with increasing multipolarity. For 14.4 keV level in ^{57}Fe , $\alpha = 9.0$.

Conversion Electron Mössbauer Spectroscopy (CEMS) is an alternative to normal Mössbauer spectroscopy. The γ -rays emitted by the source, enter the electron detector, through a thin Al window as shown in Fig. 4.11. The sample is mounted on the detector. Resonance absorption of γ -rays in the sample is followed by de-excitation of Mössbauer nuclei, as a result of which conversion and corresponding Auger electrons enter the detector volume, and trigger an electronic impulse. The recoilless absorption is observed as a peak in the spectrum.

The Conversion Electron Mössbauer Spectroscopy experiments are very useful, particularly in nondestructive testing and study of surfaces and thin layers because low-energy conversion electrons in matter have a limited range (typically 100 nm for the nucleus ^{57}Fe), the method is especially useful for the study of thin layers. Apart from the transmission spectroscopy, the

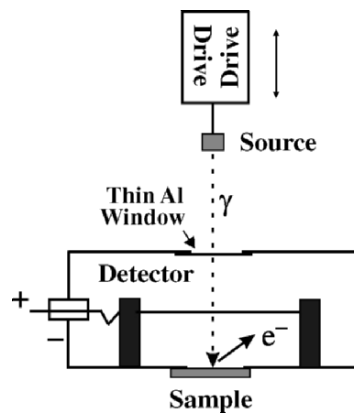


Fig. 4.11. Schematic diagram of a Conversion Electron Mössbauer Spectrometer

spectrometers have been used for scattering (CEMS) experiments between temperatures 4 K and 1,200 K. Systems use PC based data acquisition hardware and software and gas flow proportional counter. The high temperature data (300 K to 1,500 K) is recorded by using tube furnace.

Resonant electrons below 60 eV which are detected during CEMS provide surface-specific signals which decrease exponentially with application of metallic over layers up to 5.0 nm in thickness. Nonresonant electrons below 60 eV, arising from straggling and multiple-scattering events deep within the film, decrease only slightly in intensity with over layer thickness. Using this noted difference, two different empirical procedures have been developed/adapted to extract the CEMS spectrum of a 0.3 nm oxide surface layer from a bulk iron target by Zabinski and Tatarchuk (1990). Collection of low-energy electrons offers the advantages of short data acquisition times and increased surface sensitivity compared to established procedures relying on the collection of electrons near 7.3 keV. These techniques have proved to be useful for studies of surface reactivity, buried interfaces and surface magnetism.

Conversion Electron Mössbauer Spectroscopy of ^{197}Au and its application has been described by Sawicki (1994) who has used this technique for measuring Mössbauer spectra of the 77.35 keV γ -rays of ^{197}Au in very thin gold absorbers (in the conversion electron scattering mode) by detecting resonant re-emission of low-energy electrons at liquid helium temperature with a channel electron multiplier. The technique is best applicable to specimens of about $10\text{--}100\ \mu\text{g Au cm}^{-2}$, which is up to two orders of magnitude thinner than required for measurements in transmission mode. The sensitivity limits of the applicability of this technique have been examined. Using strong ^{197}Pt sources in a compact scattering geometry, they were able to obtain the spectra of gold absorbers even as thin as $5\ \mu\text{g cm}^{-2}$. Measurements of very thin films of pure gold and gold alloys, as well as the spectra of laser and ion beam-modified surfaces in a submicrometer range of depth have been presented as the examples.

The CEMS experiments are very useful, particularly in nondestructive testing and study of surfaces and thin layers because low-energy conversion electrons in matter have a limited range (typically 100 nm for the nucleus ^{57}Fe), the method is especially useful for the study of thin layers. Apart from the transmission spectroscopy, the spectrometers have been used for scattering (CEMS) experiments between temperatures 4 K and 1,200 K. Systems use PC based data acquisition hardware and software and gas flow proportional counter. The high temperature data (300–1,500 K) is recorded by using tube furnace.

It is possible to sample different depth regions with electrons by selecting the electrons emerging from the surface with particular energies. For the most promising isotopes, ^{57}Fe and ^{119}Sn , the main types of scattered photons or electrons, their intensities and their approximate ranges are given in Tables 4.1 and 4.2.

The fairly wide use of the ^{57}Fe , ^{119}Sn and ^{151}Eu source is due to the fact that these sources are long-lived and easily available. The spectra are normally recorded at room temperatures. If spectra have to be recorded at low temperatures (liquid Nitrogen 80 K or liquid helium 4.2 K) for the investigation of magnetic materials with low transition temperatures, it is common practice to keep the source at room temperatures and to cool the absorber only in a horizontal-beam transition cryostat.

Table 4.1. The photons/electrons emitted by resonant isotope ^{57}Fe (obtained from the decay of ^{57}Co), their intensities and their approximate ranges

Type of emitted radiation	E (keV)	Intensity	Range R in Fe-metal
γ -rays	14.4	0.10	$R \approx 20 \mu\text{m}$
K X-rays	6.4	0.28	$R \approx 20 \mu\text{m}$
K-shell conversion electrons	7.3	0.79	$100 \text{ \AA} \leq R \leq 4,000 \text{ \AA}$
L-shell conversion electrons	13.6	0.08	$200 \text{ \AA} \leq R \leq 1.3 \mu\text{m}$
M-shell conversion electrons	14.3	0.01	$200 \text{ \AA} \leq R \leq 1.5 \mu\text{m}$
K-LL Auger electrons	5.5	0.63	$70 \text{ \AA} \leq R \leq 2,000 \text{ \AA}$
L-MM Auger electrons	0.53	0.6	$10 \text{ \AA} \leq R \leq 20 \text{ \AA}$

Table 4.2. The photons/electrons emitted by resonant isotope ^{119}Sn , their intensities and their approximate ranges

Type of emitted radiation	E (keV)	Intensity	Range R in Sn metal
K X-rays	23.8	0.16	$R \approx 100 \mu\text{m}$
L X-rays	3.6	0.05	
L-shell conversion electrons	19.6	0.83	$300 \text{ \AA} \leq R \leq 5 \mu\text{m}$
M-shell conversion electrons	23.0	0.13	$300 \text{ \AA} \leq R \leq 7 \mu\text{m}$
L-MM Auger electrons	2.8	0.74	$50 \text{ \AA} \leq R \leq 500 \text{ \AA}$

Experimental techniques for the study of surfaces and thin films by the use of Mössbauer spectroscopy requires a detector that can isolate internal conversion electrons with energies of 7.3 keV or less. In addition, the changes occurring in a thin film, as the interface between the film and substrate is approached, can be observed if the detector is able to ‘energy-discriminate’ the electrons. This can be achieved by an electrostatic detector, employing parallel deflector plates and a channeltron electron multiplier which has the capability of detecting specific-energy electrons. This detector is capable of detecting the 7.3, 5.6, and 0.53 keV electrons emitted in the decay of Co^{57} . Isozumi et al. (1979) developed a proportional counter made of a Teflon frame for detecting backscattered electrons arising from the Mössbauer effect. This detector has been found to work well with a gas mixture of He + 10%CH₄ at 290°C.

A simple method of measuring the CEMS spectra at low temperatures down to 4.2 K has been presented by Sawicki et al. (1981). The method utilizes channel electron multipliers as high performance detectors of low-energy electrons at cryogenic conditions. The authors have described a versatile low-cost insert unit for Mössbauer effect measurements with the source, resonant scatterer and channel electron detector cooled down to liquid helium temperature.

Various authors (Bhandarkar et al. 1986, Vasconcellos et al. 1989, Marest et al. 1993, Inoue and Tanabe 1993, Terwagne and D’Haen 1997, Dobler and Reuther 1999) have applied the technique of CEMS for material science studies. Bhandarkar et al. (1986) have used CEMS for the study of thermal oxidation of $\text{Fe}_{67}\text{Co}_{18}\text{B}_{14}\text{Si}_1$ metallic glass while ^{57}Fe CEMS characterization of iron-aluminum thin-film alloys has been done by Vasconcellos et al. (1989). Nickel foils were implanted with $^{57}\text{Fe}^+$ in the range $0.1\text{--}2.5 \times 10^{17}$ ions cm^{-2} by Marest et al. (1993) and CEMS was used to identify various products of implantation. Inoue and Tanabe (1993) have measured microstructural variations with the annealing temperature in FeSiAl and FeSiAlN films using conversion electron Mössbauer spectroscopy. CEMS investigations of iron implanted with nitrogen have been done by Terwagne and D’Haen (1997) while the iron concentration profiles were studied by Dobler and Reuther (1999) after implanting doses of ^{57}Fe ions (from 2×10^{15} cm^{-2} to 2×10^{17} cm^{-2}) into n-type Si(111) at 350°C.

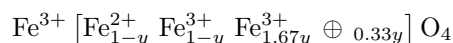
Nagy and Klencsár (2006) have developed a computer program, named BEATRICE (Backward Estimation of layer Thicknesses from transmission Integrals of Conversion Electrons) for the quantitative estimation of layer thicknesses of single- and multi-layers on the basis of their CEMS spectra. This software is able to estimate the individual layer thicknesses of multi-layers consisting of several homogeneous or mixed nanolayers. The program can also be applied for samples with composition varying continuously with depth, as well as for samples displaying columns of different layer structures.

4.6 Applications

Iron is the most common transition element on earth. Many minerals contain iron as a main or as a substitution ion. ^{57}Fe Mössbauer spectroscopy allows the identification of appropriate iron-bearing minerals, the determination of their oxidation states or nonequivalent positions of iron, and the investigation of their magnetic behavior. Mössbauer spectroscopy is used primarily to study the electron structure of materials. The extreme resolution (1 part in 10^{12}) allows the observation of hyperfine interactions between the nucleus and the surrounding electrons. Thus Mössbauer studies yield information about (a) structure, (b) quadrupole interaction, (c) magnetic ordering structure, (d) hyperfine field distribution, (e) temperature dependence of magnetic hyperfine field, (f) ordering temperature, (g) crystallization and crystalline phases. The link between the Mössbauer spectrum and the electron structure of the sample has been exploited in the study of many types of materials and thus the Mössbauer spectroscopy has been applied to the fields of solid-state physics, surface physics, metallurgy, chemistry, biochemistry, and geology.

4.6.1 Chemical Analysis

Mössbauer spectroscopy is being used to investigate the chemical state and local environment of Fe in a variety of synthesized and natural materials. The intensity of an absorption can be related exactly to the amount of the resonant isotope in the absorber. For example, Magnetite Fe_3O_4 , which is a member of the Spinel family of minerals can be represented by the formula



where $y=0$ represents pure **magnetite** and $y=1$ represents pure **maghemite**, and vacancies are represented by $\oplus$. Above 840 K, magnetite is paramagnetic with metallic-like conductivity. Between 120 and 840 K, the A sites are populated by Fe^{3+} ions and the B sites by Fe^{3+} and Fe^{2+} ions, with twice as many B sites populated as A sites. The Mössbauer spectrum displays two distinct components: one from the Fe^{3+} ions on the A sites and one from the $\text{Fe}^{2,3+}$ average on the B sites. Depending on the iron oxidation state, the values of the hyperfine parameters w.r.t iron metal are: For Fe^{2+} : Quadrupole Splitting (Δ) = 0.98, Isomer Shift (δ) = 1.26 mm s^{-1} while for Fe^{3+} , the isomer shift (δ) = 0.64 mm s^{-1} .

For $\text{FeTi}(\text{SO}_4)_3 \Rightarrow (\text{Fe}_{1-x}^{2+} \text{Fe}_x^{3+})(\text{Fe}_x^{3+}\text{Ti}_{1-x}^{4+})(\text{SO}_4^{2-})_3$, the studies on a number of naturally occurring silicate materials allow for a determination of the distribution of Fe environments in the material, including the relative proportions of different Fe oxidation states. The naturally occurring glassy silicate materials called tektites are characterized by very low concentrations of Fe^{3+} ions and very low water content. Mössbauer effect spectroscopy is a convenient way of observing the Fe states in tektites. Components of the

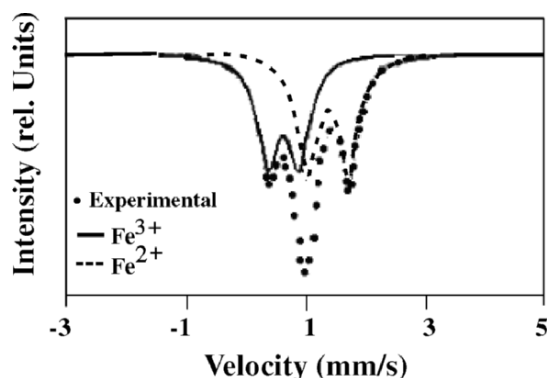


Fig. 4.12. The room temperature Mössbauer spectrum of ilmenite

spectrum due to Fe^{3+} ions and Fe^{2+} ions can be identified. The Fe^{2+} ions in tetrahedrally co-ordinated environments can also be distinguished from those in octahedrally co-ordinated environments.

Mössbauer spectroscopy in solid state chemistry under in situ conditions at high temperatures and at defined oxygen partial pressures have been made by Becker (2001) for order–disorder processes and their kinetics in nickel aluminate spinel and magnetite. The study has also been carried out for heterogeneous solid–solid and solid–gas reactions which relate to the formation of cobalt aluminate spinel and to redox processes in fayalite, Fe_2SiO_4 , respectively. The diffusion of the iron cations in Fe_2SiO_4 has also been observed by means of Mössbauer spectroscopy.

Through Mössbauer spectroscopy measurements on ancient Chinese glazes, Bin et al. (2004) detected that iron existed in the state of structural Fe^{2+} and Fe^{3+} ions. A relationship between λ_D of various colored glazes and the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio was established. The glaze color of Ru porcelain has been found to change gradually from pea green to sky green as the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio increased gradually.

The room temperature Mössbauer spectrum of ilmenite (Fig. 4.12), has been analyzed by Jancik et al. (2005) and found to consist of two partially overlapping doublets: an Fe^{2+} doublet with $\delta_{\text{Fe}} = 1.08 \text{ mm s}^{-1}$ and $\Delta = 0.66 \text{ mm s}^{-1}$ and an Fe^{3+} doublet with $\delta_{\text{Fe}} = 0.34 \text{ mm s}^{-1}$ and $\Delta = 0.53 \text{ mm s}^{-1}$.

4.6.2 Nondestructive Testing and Surface Studies

The Mössbauer (transmission and scattering) spectroscopy has been used for *in-situ* characterization of the micro structural properties of materials. For thick samples, the MS is done in reflection geometry. As shown in Table 4.1, the range with X-rays is $\approx 20 \mu\text{m}$, but with conversion electrons (CEMS)

it is $100 \text{ \AA} \leq R \leq 4,000 \text{ \AA}$. Most materials investigated have commercial or industrial applications with the research centering on the improvement in available materials or development of new materials. Several important aspects of research in material science, which are intimately concerned with the properties of surfaces, include such topics as corrosion, adsorption and catalysis at solid-liquid and solid-gas interfaces.

4.6.3 Investigation of New Materials for Industrial Applications

The Mössbauer spectroscopy helps to find new materials which have commercial or industrial applications with the research centering on the improvement of present or development of new materials. The characterization of new materials with commercially important properties is discussed in the following.

Hard Magnets

Rare earth-iron compounds are attractive for commercial applications as permanent magnet materials because of their low cost and high magnetization. Unfortunately these materials have two serious drawbacks: Planar (rather than uniaxial) anisotropy and low values of the Curie temperature. To understand the possibilities of overcoming these difficulties, $\text{Sm}_2\text{Fe}_{17}$ compounds with Ga substituted into the Fe show that uniaxial anisotropy is established in $\text{Sm}_2\text{Fe}_{17-x}\text{Ga}_x$ compounds for $x > 2$. The substitution of Ga is also seen to have the advantageous effect of substantially increasing the Curie temperature. The reasons for this behavior are related to the Fe neighbor environments. Mössbauer studies show that Ga substitutes preferentially for Fe in these sites and it is this behavior that is responsible for the changes in the magnetic properties of the Ga substituted compounds.

Mössbauer studies on a mosaic of single crystals of the layered compound $\text{TlFe}_{2-x}\text{Se}_2$ have been carried out by Häggström et al. (1986) at various temperatures between 100 and 460 K. A magnetic transition occurs at $\sim 450 \text{ K}$ and it has been found that the magnetic ordering within the Fe-Se layers is antiferromagnetic with the spins oriented along the tetragonal axis. The series of $\text{Nd}(\text{Co}_{1-x}\text{Fe}_x)_9\text{Si}_2$ compounds ($0 < x \leq 0.55$) have been characterized by Mössbauer (^{57}Fe) spectroscopy as studied by Berthier et al. (1988) under external magnetic fields. These authors have shown that the alloys are not suitable for permanent magnet applications because the Fe-moments are collinear with the bulk magnetization and that the Co-moments are canted.

Study of Conducting Solids

The application of Mössbauer spectroscopy to the characterization of new conducting solids has been illustrated by Berry (1993) in the investigation of three different types of materials. Firstly, the use of ^{125}Te Mössbauer spectroscopy

to examine the semiconducting compound Mo_6Te_8 and the newly synthesised related superconducting compounds of composition $\text{Mo}_{6-x}\text{Ru}_x\text{Te}_8$ is described. Secondly, the role of ^{151}Eu Mössbauer spectroscopy in the study of materials of composition $\text{La}_{2-x}\text{Eu}_x\text{CuO}_4$ which have structures related to those of the high temperature superconducting oxides is discussed. Finally, the important contribution which ^{119}Sn Mössbauer spectroscopy can make to the characterization of novel electrically conducting tin dioxide-pillared smectite clays, is described.

Study of Metallic Glasses

Metallic glasses (also known as amorphous metal) are the materials in which atoms are packed together in a somewhat random fashion, (unlike conventional metals, which have a crystalline structure) similar to that of a liquid. These materials have excellent mechanical properties, e.g., high tensile strength and large elastic strains, which arise in large part from their lack of grain boundaries. Unlike conventional metals, which are usually cooled slowly until they fully solidify, metallic glasses are to be cooled very rapidly and very uniformly to freeze their random atomic pattern in place before crystallization occurs due to the nucleation and growth of crystal grains. Metallic glasses are usually produced by splat cooling in which droplets of molten metal are quickly frozen on a cold surface. Continuous amorphous metal ribbons less than 0.1 mm thick can be formed at a cooling rate of one million $^\circ\text{C}$ per second. The ribbons are wear-resistant and possess interesting magnetic properties. Over the past decade, methods have been developed to produce metallic glasses in bulk based on mixes of zirconium, magnesium, aluminum, and iron.

Metallic glasses have been extensively investigated both from fundamental and technical points of view by Luborsky (1980). The amorphous metallic glasses $\text{Fe}_{75}\text{Al}_{15}\text{B}_{20}$ and $\text{Fe}_{75}\text{Al}_{10}\text{B}_{15}$ and the phases found after crystallization have been studied by Verma et al. (1985a) using Mössbauer spectroscopy between 80 and 1,025 K. The Mössbauer spectra were analyzed using six independent Gaussian distributions of Lorentzians to yield mean line positions and the FWHM. From the measurements, the Curie temperatures for these two glasses have been found to be 720 ± 5 and 685 ± 10 K respectively while the onset of crystallization has been found at 745 and 700 K respectively. In other studies relating to amorphous metallic glasses, Verma et al. (1985b, 1986) have reported the correlated hyperfine interactions in $\text{Fe}_{82}\text{P}_{11}\text{B}_7$ and the Mössbauer study of $\text{Fe}_{80}\text{Sb}_8\text{B}_{12}$ respectively.

Mechanical Alloying

Alloys are prepared by mechanical alloying by sealing powdered elemental components in a hardened steel or tungsten carbide vial with several hardened steel balls. The impact of the balls, when shaken by a high energy ball mill,

with the powder causes atomic diffusion between the powder grains and this results in the formation of an alloy. This method is suitable for producing several types of interesting structures including nanocrystalline materials, metastable alloy phases, and alloys with extended solubility limits. Mössbauer spectroscopic measurements are an important tool for understanding the alloying process, e.g., the systems Fe–Cu, Fe–Al, Fe–Si, and Fe–Sn systems.

4.6.4 Characterization of Nanostructured Materials

Understanding of nanostructured materials is often limited by experimental characterization methods that measure only bulk properties. For example, numerous studies have characterized nanostructured materials using X-ray diffraction for phases present, average grain size, internal strain, etc. Rawers et al. (1998) have used the Mössbauer analysis to characterize the local atomic site characterization, distribution, and concentrations of attrition milled nanostructure powder. Interatomic analysis has provided insight into the mechanical alloying process and the resulting nanostructure not reported previously. Iron powder, blends of iron with 2 wt% aluminum powder, and prealloyed iron–aluminum powder were processed with both argon and nitrogen gas as the processing environments. Mechanical processing resulted in micrometer-size particles with essentially defect-free nanograin interiors. Mechanical alloying iron powder with aluminum resulted in the aluminum being restricted to the grain boundary region. Mechanical processing of iron powder in a nitrogen gas environment resulted in nitrogen being either on the grain boundary or in the outer layer of the grain boundary distorting the local b.c.c.–Fe lattice into a b.c.t.–Fe lattice.

The magnetic properties of the nanocomposite $\text{Fe}_x(\text{SiO}_2)_{1-x}$ samples with different Fe contents have been studied by Xiong et al. (1999) using Mössbauer spectroscopy over a wide temperature range. These samples displayed the change of magnetic properties, which results from their unique nanostructure, the grain size effect, the strong interface interaction and the interface-osmosis effect at the Fe– SiO_2 boundaries.

4.6.5 Testing of Reactor Steel

The evaluation of the microstructure parameters of materials used in nuclear industry, has been made by Slugen et al. (2002) using Mössbauer spectroscopy. The usefulness of this method is documented on the evaluation of degradation processes going on in the nuclear power plant reactor pressure vessel (RPV) steels. Experimental MS results of different commercially used RPV-steels as well as results from the original irradiated Russian 15Kh2MFA RPV surveillance specimens have been used for inference. The systematic changes in the relative areas of Mössbauer spectra components due to irradiation with high energy neutrons ($E > 0.5 \text{ MeV}$) were observed mainly during the first period

(one-year stay in irradiation containers in operating conditions by a “speed factor” of about 10). It could be explained due to changes caused by precipitation of elements like Cu or Cr mainly in carbides to the surface. These results confirm that the close environment of Fe atoms, in bcc lattice of RPV-steels, remains almost stable after initial changes, which could perhaps be correlated with the ductile–brittle transition temperature curve in dependence to the increased neutron fluency.

4.6.6 In Mars Exploration

The Mössbauer Spectrometer was designed to determine the composition and abundance of iron-bearing minerals on Mars, with high accuracy, as many of these most important minerals that are difficult to detect, contain iron. The identification of iron-bearing minerals can yield information about early Martian environmental conditions. This Mössbauer Spectrometer is also capable of examining the magnetic properties of surface materials and identifying minerals formed in hot, watery environments that could preserve fossil evidence of Martian life.

Having already journeyed between fifty and hundred million miles from Earth, the twin Mars Exploration Rovers received their major instrument checkout. The Mössbauer spectrometer, on one spacecraft, called Spirit, returned test data that did not fit the pattern expected from normal operation. de Souza et al. (2003) have reported the surface analysis in archaeology using the miniaturized Mössbauer spectrometer MIMOS II while the investigation of the weathering of Fe-bearing minerals under Martian conditions has been reported by Schroder et al. (2004). Morris et al. (2004) have reported about the mineralogy at Gusev crater from the Mössbauer spectrometer on the Spirit rover.

4.6.7 Study of Actinides

Applications of Mössbauer spectroscopy to the study of electronic structure properties of nonconducting compounds of Neptunium have been reviewed by Kalvius (1986). A discussion of some recent results on neptunyl compounds along with some remarks concerning heptavalent Neptunium and the charge states of Neptunium incorporated in glasses are given. Some applications of Mössbauer spectroscopy to the study of insulating Neptunium compounds are reported by Jove et al. (1991) who have presented review of selected examples of recent studies regarding local order and isomer shift of Neptunium in crystallized or amorphous compounds for each charge state of Np(III–VII). They have correlated the electronic structure and bonding in insulating Neptunium compounds to isomer shift and EFG with calculations using the relativistic extended Hückel method.

4.6.8 Study of Biological Materials

The Mössbauer effect makes it possible to follow the biochemical transformation of some elements and to detect their inclusion in various cellular structures, since resonance absorption is a property of only certain definite isotopes (^{57}Fe , ^{119}Sn , ^{129}I , etc.). Because of the wide spread occurrence of iron compounds in biological materials, it can be used successfully in biology. The method of determination of the Mössbauer spectra of biological substances does not differ essentially from those used in studies of chemical compounds. However, difficulties are encountered due to relatively low iron content of biopolymers. Many of the large protein molecules which control biological functions utilize the oxidation–reduction properties of the transition metal atoms. One of the iron-containing proteins, without which the existence of living organism is not possible and is the constituent of red blood cells, is called hemoglobin, the iron content in which is only 0.34%. Therefore an important step in the investigation of biological materials is the establishment of conditions under which the iron atom can be exchanged by ^{57}Fe isotope without causing damage to the natural structure. In some cases, ^{57}Fe can be concentrated by cultivation of microorganisms in media which contain this isotope. The review presented by Oshtrakh (1999) relates to the study of the iron containing biological molecules and model compounds and considers the main results of biomedical applications of Mössbauer spectroscopy. The author has presented the various possibilities of this technique to study qualitative (structural) and quantitative changes of iron containing biomolecules during pathological processes or under effect of environmental factors.

The Mössbauer spectra of Fe^{3+} complexes with guanine, guanosine, and ribose have been investigated at 77 K. The study indicates the influence of the sugar on the shape of the spectra of the investigated complexes of iron. The Mössbauer spectra of complexes of Fe^{3+} with ribonucleic acid (RNA) and deoxyribonucleic acid (DNA) point to the difference in the electron donor properties of these biopolymers (caused by the structure of the sugar of the polymeric chain of nucleic acid).

The Mössbauer effect has also been useful in the study of the chemical states of iron in intact cells of nitrogen-fixing bacteria. Mössbauer spectroscopy has also been used to study iron uptake and translocation in rice plants by Kilcoyne et al. (2000) who have collected spectra from intact root and leaf tissue of rice plants grown in anaerobic $^{57}\text{Fe}(\text{II})$ -enriched nutrient solutions. The spectra obtained from root tissue of plants grown in nutrient solutions typical of paddy soils arise primarily from $\text{Fe}(\text{III})$ -oxide components precipitated on the root cell walls. In contrast, the spectra obtained from root tissue from plants exposed to lower, toxic, pH conditions show that, in addition to $\text{Fe}(\text{III})$, uncomplexed $\text{Fe}(\text{II})$ is taken up. No evidence of $\text{Fe}(\text{II})$ was seen in the leaf tissue of any of the plants, where the spectra are characteristic of $\text{Fe}(\text{III})$ in ferritin and other complex forms.

4.6.9 Investigation of Lattice Dynamics Using the Rayleigh Scattering of Mössbauer γ -rays

The 14.4 keV γ -ray has line width of $\sim 5 \times 10^{-9}$ eV. Since with neutron scattering experiments, the energy resolution is $\sim 10^{-6}$ eV, the energy resolution with Mössbauer spectroscopy is thus hundred times better. With this accuracy, one can distinguish between truly elastic and inelastic processes involving low energy phonons. Mössbauer scattering processes that change the nuclear spin orientation ($|i\rangle \neq |f\rangle$) have no electron counterparts since Rayleigh scattering leaves the nuclear spin unchanged.

The Mössbauer measurements makes it possible to study a variety of interesting effects that may be brought about by the introduction of impurity in the lattice as also the modifications brought about by imperfection in the crystal lattice, since the nuclei must be bound in a crystal for this study of resonant emission (or absorption) of γ -rays. Three dynamical quantities of interest, which are possible in the Mössbauer studies, are: (i) Zero-phonon absorption cross-section giving the Lamb-Mössbauer factor, (ii) One-phonon absorption cross section yielding the time information as well as the information of the localized modes and through this the information on the force constant between impurity and the host atom, (iii) the second order Doppler effect yielding information about the mean square velocity of the Mössbauer probe.

X-Ray Photoelectron Spectroscopy

5.1 Introduction

X-ray photoelectron spectroscopy (XPS) is an atomic spectroscopic technique, which is capable of providing atomic and molecular information regarding the surface of the material. Since the technique provides a *quantitative analysis of the surface composition*, it is also called electron spectroscopy for chemical analysis (ESCA). This technique was developed in mid-1960s by Prof. Kai Siegbahn at Uppsala University Sweden (Hagström et al. 1964, Siegbahn et al. 1970, 1972) who was later awarded the Nobel Prize for his pioneer work in 1981. In XPS, the sample surface is irradiated with X-rays and surface atoms emit electrons after direct energy transfer to the electrons. The electron energy is measured, and the emitting atom (except H and He) can be identified from the characteristic electron energy. Furthermore, the high energy resolution of the electron spectrometer makes it possible to obtain chemical information of the atomic bonds. Like XRF, XPS is based on the phenomenon of photoionization but the difference is that XPS makes use of soft X-rays in the range of 200–2,000 eV instead of relatively higher energy (in the range of keV) used in XRF analysis technique.

When the photon energy is smaller than the binding energies of the inner-shell electrons, the photon interacts with valence levels of the molecule or solid, leading to ionization by removal of one of these valence electrons. XPS is thus used to examine core-levels and subsequently to study the composition and electronic states of the surface region of a sample by energy-dispersive analysis of the emitted core photoelectrons. Since there is a characteristic binding energy associated with each core atomic orbital for every element, each element will, therefore, give rise to a characteristic set of peaks in the photoelectron spectrum at kinetic energies determined by the photon energy and the respective binding energies. The presence of peaks at particular energies therefore indicates the presence of a specific element in the sample under study – furthermore, the intensity of the peaks is related to the concentration of the element within the sampled region. It is

possible to identify the chemical state (e.g., valence) when the precision of the measurement is of the order of 0.1 eV. Small changes in binding energy (chemical shift) may be used to gain information regarding chemical environment of the element.

XPS is a surface-sensitive technique since the kinetic energy of the escaping electrons limits the depth from which it can emerge. It provides straightforward data interpretation and chemical bonding information. Although with the advent of synchrotron radiation (SR) sources, a much wider and more complete energy range of 5–5,000 eV of photons is possible yet it still remains a very small minority of all photoelectron studies due to the expense, complexity and limited availability of such sources.

5.2 Principle and Characteristics of XPS

The phenomenon of XPS is based on the photoelectric effect i.e., the ejection of electrons from a surface due to the impinging of photons as outlined by Einstein in 1905. The X-ray photons, whose absorption is very fast ($\sim 10^{-16}$ s), eject electrons from inner-shell orbitals of the atoms of the surface material and this technique is called electron spectroscopic technique. The kinetic energy, E_K , of these photoelectrons is determined by the energy of the X-ray, $h\nu$, and the electron binding energy, E_B (which represents strength of interaction between electron (n, l, m, s) and nuclear charge). The maximum kinetic energy (E_K) of the ejected electrons is given by:

$$E_K = h\nu - E_B \quad (5.1)$$

where h is the Planck constant (6.62×10^{-34} J s) and ' ν ' is the frequency (Hz) of the impinging radiation.

The binding energy (E_B) is dependent on the chemical environment of the atom making XPS useful to identify the oxidation state and ligands of an atom. Since the binding energies (E_B) of energy levels in solids are conventionally measured with respect to the Fermi-level of the solid, rather than the vacuum level, this involves a small correction to the equation given above in order to account for the *work function* (E_W) of the solid.

The experimentally measured energies of the photoelectrons are thus given by

$$E_K = h\nu - E_B - E_W \quad (5.2)$$

It is clear from the Fig. 5.1, that

- (a) No photoemission is possible for $h\nu < E_W$
- (b) In solids, no photoemission from levels with $E_B + E_W > h\nu$
- (c) The kinetic energy E_K of photoelectron increases as binding energy E_B of a solid decreases
- (d) A range of kinetic energies can be produced if valence band is broad

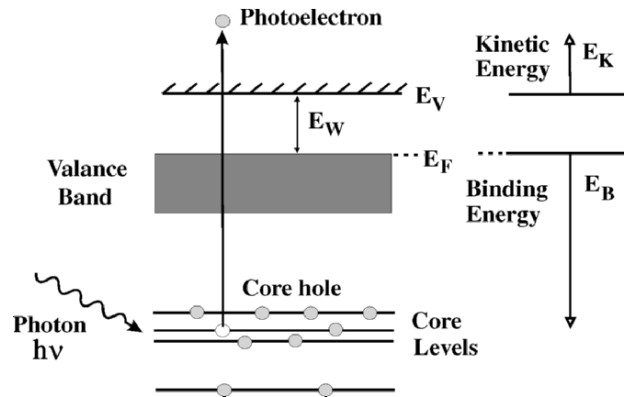


Fig. 5.1. Atomic energy levels and the ejection of electrons due to photon-impact

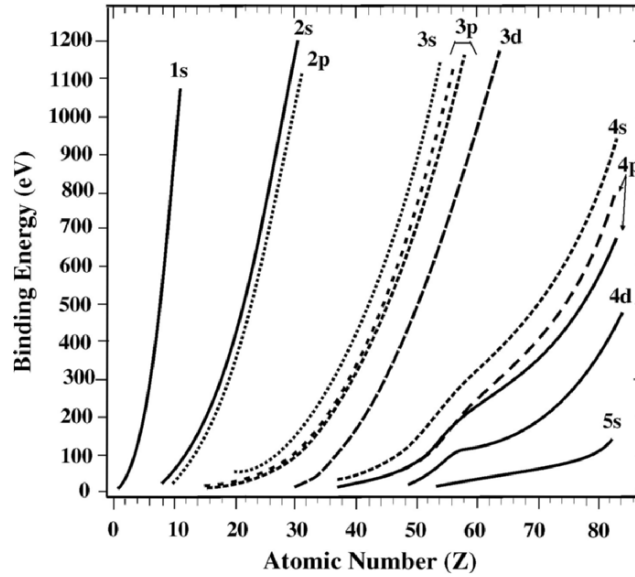


Fig. 5.2. Dependence of the binding energy (E_B) of different levels on the atomic number (Z) of elements

Since the binding energies of different levels (E_B) of an element depend on the energy level, it follows that (see Fig. 5.2):

- (a) For any particular element, $E_B(1s) > E_B(2s) > E_B(2p) > E_B(3s) \dots$
- (b) Binding energy of an orbital increases with atomic number (Z) of the element i.e.,

$$E_B(\text{Na } 1s) < E_B(\text{Mg } 1s) < E_B(\text{Al } 1s) \dots$$

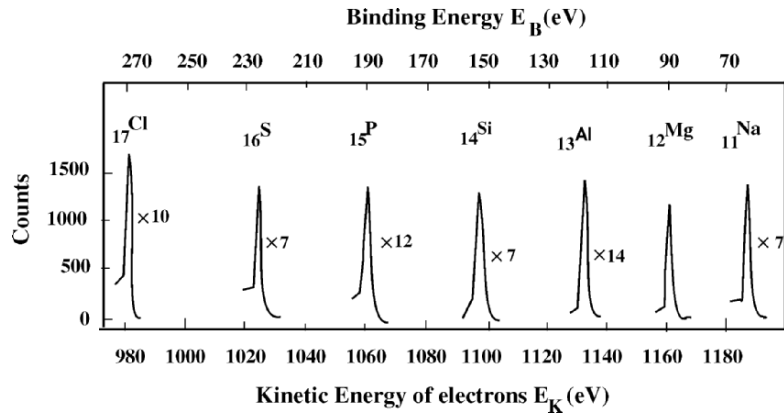


Fig. 5.3. Kinetic energies of emitted electrons (in eV) for a few elements excited by Mg K α (1253.6 eV) photons, and their corresponding 2s-binding energies (in eV)

- (c) Binding energy of an orbital is not affected by isotope effect. i.e., for all the isotopes of an element, the binding energy will be the same e.g.,

$$E_B (^7\text{Li } 1s) = E_B (^6\text{Li } 1s)$$

Figure 5.3 shows the photoelectron peaks of a few elements along with their kinetic energies (in eV) excited by Mg K α (1253.6 eV) photons, and the corresponding 2s-binding energies of these elements (in eV) according to (5.2). This figure clearly shows that as the binding energy values (depending on the atomic number of the elements) increase, for a fixed incident energy $h\nu$, the corresponding kinetic energy values of the photoelectrons decrease.

The XPS technique is highly surface specific due to the short range of the photoelectrons that are excited from the solid. For XPS, the Al K α (1486.6 eV), Mg K α (1253.6 eV) or Ti K α (2,040 eV) are often the photon energies of choice. The photoemission process is often envisaged as a three step-process:

- Absorption and ionization (initial state effects)
- Response of atom and creation of photoelectron (final state effects)
- Transport of electron to surface and escape (extrinsic losses)

All can contribute structure to XPS spectrum.

The energy values of the photoelectrons leaving the sample are determined using an electron detector (discussed in Sect. 5.3.2), which gives a spectrum with a series of photoelectron peaks. The binding energies of the peaks are characteristic of each element. Since the shape of each peak and the binding energy can get altered (slightly) by the chemical state of the emitting atom, hence the XPS technique provides information not only about the atoms on the surface but also about their chemical bonding. The peak areas can be used (with appropriate sensitivity factors) to determine the composition of

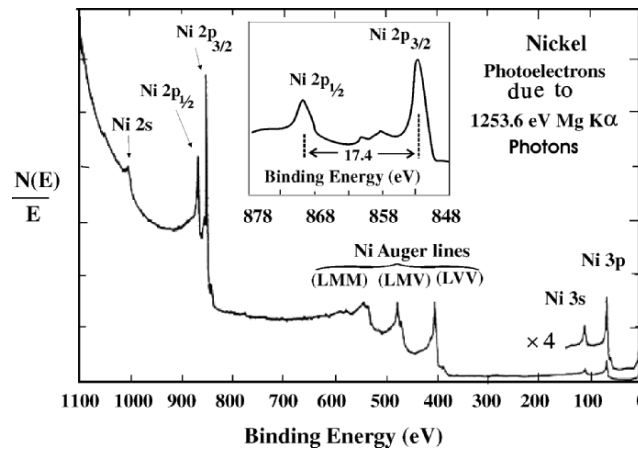


Fig. 5.4. Photoelectron spectrum of nickel ($Z = 28$) caused by 1,253 eV photon bombardment due to $\text{MgK}\alpha$ radiation

the surface of the material. XPS is not sensitive to hydrogen or helium, but can detect all other elements. However, XPS must be carried out in ultra high vacuum due to the low energy of the photoelectrons which easily get absorbed in air/poor vacuum.

As an example of the XPS spectrum, the photoelectron peaks of Nickel due to $\text{MgK}\alpha$ (1253.6 eV) photons are shown in Fig. 5.4. The spectrum indicates Ni 2s, $2p_{1/2}$, $2p_{3/2}$, 3s and 3p peaks. The Ni $2p_{1/2}$ and $2p_{3/2}$ are also shown in the inset of the figure for clarity. It is to be noted that Ni 1s peak is not present in the spectrum as the 1s electrons (having binding energy of 8332 eV) cannot be excited by 1253.6 eV photons.

Characteristic Features of XPS

- XPS is a surface-sensitive technique that provides spectral information. This information is collected from a depth of 2–20 atomic layers (less than 100 Å), depending on the material studied. The characteristic features of the technique include elemental surface analysis (except hydrogen), chemical bonding identification of surface species and compositional depth profiles.
- It is nondestructive technique in the sense that the material is not destroyed during the analysis.
- XPS provides information about the filled core states. Since each element has unique set of core levels (and hence the binding energy E_B), the kinetic energies (E_K) of photoelectrons can be used to fingerprint element (see (5.1) and (5.2)). The identification of the compound to which the element belongs, can be made from the fine shifts of E_B with chemical composition.

- (d) The XPS needs monochromatic (X-ray) incident beam. The intensity of photoelectrons depends on the intensity of photons. Atomic concentration can be deduced from the intensity of the photoelectron signal and empirically determined sensitivity factors.
- (e) The samples to be analyzed can be in the form of solids (metals, glasses, semiconductors, ceramics, polymers) or liquids (low vapor pressure oils) of small size.
- (f) Depth composition can be known from the analysis of photoelectron intensity vs. angle of observation.

There are three other broad electron peaks (in Fig. 5.4) between 400 and 600 eV, which have been marked as Ni-Auger lines. *Auger electron spectroscopy* (AES) is another form of electron spectroscopy which is based on the detection and measurement of the kinetic energies of the Auger electrons (instead of the inner-shell electrons). As usual, an inner-shell electron is ejected producing the photoelectron in the normal process of emission. To fill this hole in the core level (say K-shell), an electron drops from a higher level (say L_1 level) and the energy liberated in this process is simultaneously transferred to a second higher-shell electron (say L_{23}); a fraction of this energy is required to overcome the binding energy of this second electron, the remainder is retained as kinetic energy by this emitted second electron called the *Auger electron*. In the Auger process, the final state is a doubly-ionized atom with core holes in the L_1 and $L_{2,3}$ shells. As a rough estimate (since the KE of the Auger electron is independent of the mechanism of initial core hole formation), the KE of the Auger electron from the binding energies of the various levels involved will be $KE = (E_K - E_{L1}) - E_{L23}$. Auger transitions are given the notation ABC where A is the level initially ionized and B and C are, respectively, the level from which the electron falls to the inner hole and the level from which the Auger electron gets ejected. e.g., KLL, KL1V, KVV where V refers to the valence band in solids. Furthermore, the expected energy of Auger transitions ABC is given by

$$E_{ABC}(Z) = E_A(Z) - 0.5[E_B(Z) + E_B(Z + 1)] - 0.5[E_C(Z) + E_C(Z + 1)]$$

where Z is the atomic number of the atom emitting the Auger electron. $E_B(Z)$, $E_B(Z + 1)$, $E_C(Z)$ and $E_C(Z + 1)$ are the binding energies of B and C levels in atom of atomic numbers Z and $Z + 1$, respectively. Each element in a sample being studied by AES will thus give rise to a characteristic spectrum of peaks at various kinetic energies of the Auger electrons.

AES has the following features: 10–50 Å analysis depth, 100 Å spatial resolution, in-situ fracture analysis, large sample size, color maps and line scans. The AES provides depth profiling and formation about grain boundary particles. Like in XPS, there is a chemical shift, but the spectrum, in this case, is more complex because it involves three levels.

5.3 Instrumentation/Experimental

XPS apparatus consists of a source of fixed energy radiation (an X-ray source or synchrotron), an electron energy analyzer for the photoelectrons (which can disperse the emitted electrons according to their kinetic energy and thereby measure the flux of emitted electrons of a particular energy), a high vacuum environment (to enable the emitted photoelectrons to be analyzed without interference from gas phase collisions) and an electron detector. Since the photoelectron energy depends on X-ray energy, the excitation source must be monochromatic. The emitted photoelectrons will therefore have kinetic energies in the range of about 0–1,250 eV for $\text{MgK}\alpha$ photons or 0–1,480 eV for $\text{AlK}\alpha$ photons. Since such electrons have very short interaction range in solids, the technique is necessarily surface sensitive limiting to a few micrometers.

The schematic diagram showing the logical components of an XPS system is illustrated in Fig. 5.5. X-rays illuminate an area of a sample causing electrons to be ejected with a range of energies and directions. The electron optics, which may be a set of electrostatic and/or magnetic lens units, collect a proportion of these emitted electrons defined by those rays that can be transferred through the apertures and focused onto the analyzer entrance slit. Electrostatic fields within the concentric hemispherical analyzer (CHA) are established to allow electrons of only a given energy (the so called pass energy PE) to arrive at the detector slits and onto the detector.

Electrons of a specific initial kinetic energy are measured by setting voltages for the lens system (so as to focus the electrons of the required initial energy onto the entrance slit and to retard their velocity) so that the kinetic energy of these electrons, after passing through the transfer lenses, matches the pass energy of the hemispherical analyzer. To record a spectrum over a

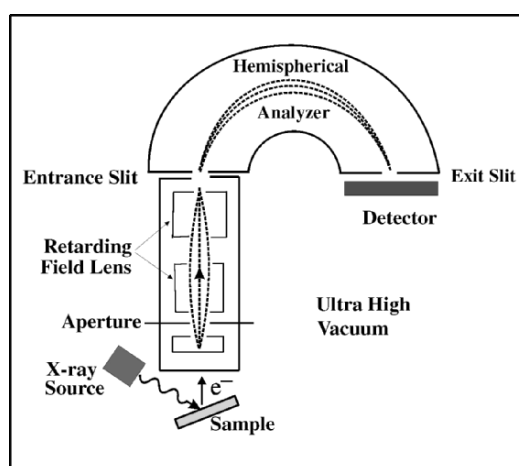


Fig. 5.5. Schematic diagram of X-ray photoelectron spectroscopic technique

range of initial excitation energies, it is necessary to scan the voltages applied to these transfer lenses and the prescription for these lens voltages is known as the set of lens functions. The efficiency with which electrons are sampled by a spectrometer is very dependent on these lens functions. The performance of the instrument can be severely impaired without properly tuned lens functions. It is necessary to characterize an instrument using a corresponding transmission function for each of the lens modes and energy resolutions since the collection efficiency varies across the many operating modes even with a well-tuned system.

An ESCA instrument with improved surface sensitivity, fast-imaging properties and excellent energy resolution (0.27 eV corresponding to the Fermi edge of silver and 0.44 eV corresponding to the Ag 3d_{5/2} line) has been described by Gelius et al. (1990) who have used a high-power monochromatic X-ray source and an electrostatic lens system permitting either large luminosity or high spatial resolution. The new geometry of their set-up allows excellent access to the sample area (30 $\mu\text{m} \times 30 \mu\text{m}$) and gives maximum surface sensitivity (spatial resolution of 23 μm) at glancing angles.

The working of each of the components of the X-ray photoelectron spectrometer is discussed in the following sections.

5.3.1 Commonly Used X-ray Sources for XPS Analysis

The commonly used X-ray sources are described as follows:

Radioactive Sources

The conventional XPS source makes use of Mg K α radiation: $h\nu = 1253.6 \text{ eV}$ and Al K α radiation: $h\nu = 1486.6 \text{ eV}$ which are produced by secondary fluorescence of Mg and Al targets placed before the ²⁴¹Am or ¹⁰⁹Cd or ⁵⁷Co radioactive source (for details, Chap. 1 be consulted). When using an Mg K α X-ray source, however, the XPS spectra of materials containing both magnesium and aluminum can exhibit a number of spectral artifacts. These artifacts described by Strohmeier (1994) are easily observed in XPS spectra of magnesium aluminate (MgAl₂O₄, also known as magnesium aluminum oxide). For example, the Al 2p peak is overlapped by the Mg K α X-ray satellites from the Mg 2s peak, and the Mg K α X-ray Mg KLL Auger peak. In addition, the Mg 2p peak can be overlapped by a C 1s X-ray ghost line caused by stray Al K α X-radiation when using a dual Mg/Al X-ray source. Because of these artifacts, the amounts of Mg and Al in such samples should be quantified (when using an Mg K α X-ray source) using the Mg 2s and Al 2s peaks, respectively, which are free of these artifacts.

For high-energy XPS studies, based on Cu K α_1 radiation ($h\nu = 8047.8 \text{ eV}$), an X-ray source has been constructed by Beamson et al. (2004). This source has been fitted to an ESCA electron spectrometer. The Fe 1s and Cr 1s core levels (at $\sim 7,112$ and $5,989 \text{ eV}$ binding energy, respectively) are readily observed at good resolution along with their KLL Auger series. It is concluded

that the new source shows much promise for investigation of the electronic structure of ferrous and other alloys of scientific and technological importance.

Dual Mg/Al Anode X-Ray Tube

The photon beam energy for XPS source is usually obtained from an X-ray tube with a hot filament at high voltage (10–15 kV) and current of 10–15 mA, which emits electrons. These electrons are accelerated to an anode at ground potential. The atoms of the anode may emit different X-rays from the excitation of different shells. Al and Mg give nearly mono-energetic (monochromatic) X-rays with $E_x = 1486.6$ eV and 1253.6 eV respectively. Since the use of two X-ray energies allow the elimination of ambiguities in the analysis, many XPS instruments have dual anodes (Al and Mg) that can be excited separately. The double anode X-ray source (shown in Fig. 5.6) is simple, gives high flux (10^{10} – 10^{12} photons s^{-1}) and is relatively inexpensive. It provides photon beam ~ 1 mm diameter size.

In dual Mg/Al X-ray tube, the anode is bombarded by electrons emitted from two independent filaments that are held at ground potential. The acceleration of electrons is caused by the positively biased anode at ~ 15 kV. The accelerated electrons hit only the nearest anode face. These electrons produce core holes in the anode target materials by electron impact ionization. The vacancies can relax by emission of characteristic X-rays that illuminate the sample. By switching the filament, one can get $MgK\alpha$ ($E_x = 1253.6$ eV) or $AlK\alpha$ ($E_x = 1486.6$ eV) lines with inherent resolution (ΔE_{FWHM}) of 0.7 eV

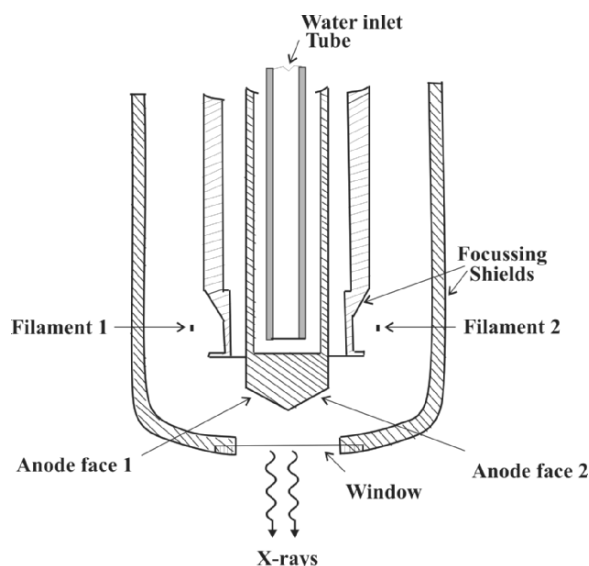


Fig. 5.6. Double anode X-ray source

and 0.85 eV respectively. For most line sources like the one shown in the figure, the emission of Bremsstrahlung together with the desired characteristic X-ray line cannot be avoided and produces a broad (but weak) background in the spectrum. A thin Al-window ($\sim 2\text{ }\mu\text{m}$) prevents secondary and backscattered electrons to reach the sample. Since considerable power is dissipated in the anode (100–1000 W), the heat generated is removed from the anode by internal water circulation. Body of the anode is made of copper having good thermal conductivity while the anode top is silver coated to prevent Cu X-rays ghost lines from complicating the spectra. The aluminum foil window at the exit aperture helps to reduce Bremsstrahlung radiation and to isolate the anode for differential pumping.

Hawn (1983) has described the performance of a dual-anode X-ray source for XPS using various un-collimated and collimated configurations to make it effective in increasing the signal-to-background ratio and reducing anode cross talk without substantial signal loss.

Monochromatic Source

An achromatic X-ray gun relies on narrow resonance peaks in the X-ray spectrum for the anode material and limits the energy resolution possible for a photoelectric line. Monochromatic X-ray sources eliminate satellites and provide improved energy resolution (although flux decreases by an order of magnitude) by filtering a narrower band of X-rays from the resonance peak. This is achieved by X-ray diffraction from a quartz crystal with $\langle 1010 \rangle$ lattice or from bent SiO_2 crystal (as shown in Fig. 5.7), which allows only certain wavelengths to be reinforced into a spot so that the monochromatic X-rays can be directed at the sample. The crystal spacing is such that X-ray wavelengths, that are multiples of the $\text{AlK}\alpha$ X-ray resonance, are reinforced by virtue of the Bragg relationship for X-ray diffraction. The fact that multiples

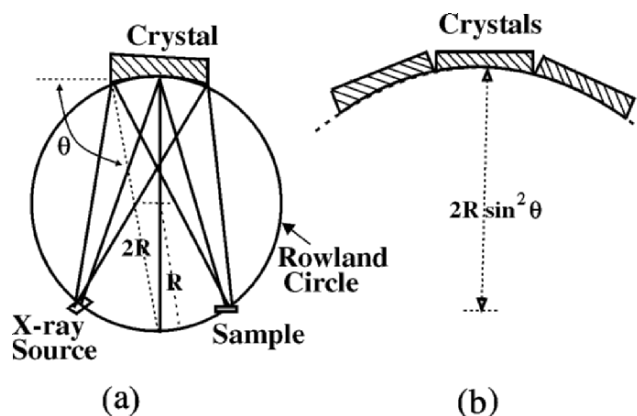


Fig. 5.7. X-ray monochromation (Johann focusing geometry)

of this wavelength are reinforced by the quartz crystal means that other anode materials, such as Ag and Cr, are possible sources for monochromatic X-rays. With commercially available X-ray monochromators, one has now the provision of using twice and four-times the energy of the Al K X-ray line (using Ag $L\alpha$ and Cr $K\beta$ characteristic X-rays respectively).

Synchrotron Radiation Source

When charged particles, particularly the electrons, are forced to move in a circular orbit, Bremsstrahlung (continuous) X-radiations of different energies are emitted. At relativistic velocities (when the particles are moving at close to the speed of light) these photons are emitted in a narrow cone in the forward direction, at a tangent to the orbit. In a high energy electron storage ring these photons are emitted with energies ranging from infra-red to energetic (short wavelength) X-rays. This radiation is called Synchrotron Radiation (SR). SR has a number of unique properties: (a) High brightness: SR is extremely intense (hundreds of thousands of times higher than conventional X-ray tubes) and highly collimated. (b) Wide energy spectrum: SR is emitted with a wide range of energies, allowing a beam of any energy to be produced. (c) SR is highly polarized. (d) It is emitted in very short pulses, typically less than a nanosecond (a billionth of a second).

Out of about 40 synchrotron light sources of the world, six are in USA, four in Germany and an equal number in Japan. Many of the European countries and big Asian countries including UK, France, Italy, Switzerland, Denmark, Sweden, Spain, India, China, Korea, and Thailand have their own synchrotron facilities, SR source is also available in Australia and Russia.

Kartio et al. (1994) and Laajalehto et al. (1997) have described the use of SR for exciting X-ray photoelectron spectra. The surface sensitivity of the measurement using SR is essentially better than the sensitivity obtained using Al $K\alpha$ or Mg $K\alpha$. However, the damage of the sample surface during the measurement may easily occur, probably, by sample heating when SR excitation is used.

To cite an example, to produce the soft X-rays for photoelectron experiments on surfaces, the light source at ELETTRA (Trieste, Italy) in Super-ESCA beam line is a 5.6 cm period undulator with 81 periods having minimum gap of 19.5 mm, gives a photon energy range of 120–2,100 eV at a ring energy of 2.4 GeV. The X-ray source covers an energy range of 200–1,400 eV using first, third, and fifth harmonic and is optimized for 400–700 eV. The peak brilliance is of the order of 10^{14} photons $s^{-1}/0.1\%bw/200$ mA with maximum power output of 1.9 kW. The monochromator with resolving power of the order of 10^4 at 400 eV, covers the whole photon energy range with a single plane grating.

5.3.2 Photoelectron Analyzers/Detectors

When an electron beam with a range of energies bombards a surface, it may escape or it may get absorbed after losing its energy. The distance that an electron can travel in solid depends on (a) material and (b) electron KE. The three loss processes (*inelastic scattering*) reduce the kinetic energy and can prevent escape from surface: (a) Phonon excitation – collective excitation of atoms in unit cell (0.01–10 eV). (b) Plasmon excitation – collective excitation of electrons (5–20 eV). (c) Interband transitions i.e., ionization. Many of these processes lead to the emission of electrons from the surface called secondary electrons. The large, broad peak at low energies is due to the secondary electrons, ejected in interactions with the primary beam. No electrons will be emitted when the primary energy is less than the work function. As the primary energy is increased, the number of secondary electrons increases. When the primary energy reaches into the 100 eV range, the number slowly decreases with increasing primary energy. The reason for the decrease is that the primary electrons penetrate deeper into the solid and the secondary electrons are less likely to escape. Figure 5.8 shows that the probability of escape from the sample without inelastic scattering is dependent on the energy of the electrons. For kinetic energy ~ 50 –100 eV (i.e., minimum λ of ~ 5 –10 Å) – the *surface sensitivity is maximum*.

The photoelectrons can be detected by a hemispherical analyzer or an electron multiplier tube or a multichannel detector such as a microchannel plate. The photoelectron detector usually has energy resolution of 0.3 – 0.4 eV, acceptance solid angle of 6% of solid angle 2π . The energy of the

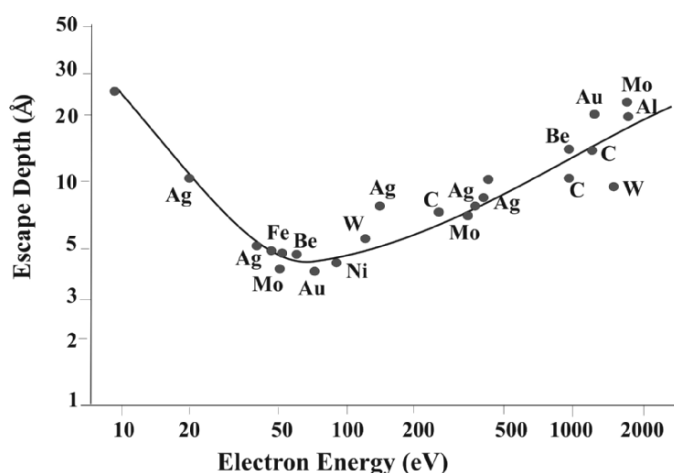


Fig. 5.8. “Universal curve” of electron escape depth (average distance between inelastic collisions (Å)) vs. kinetic energy (eV)

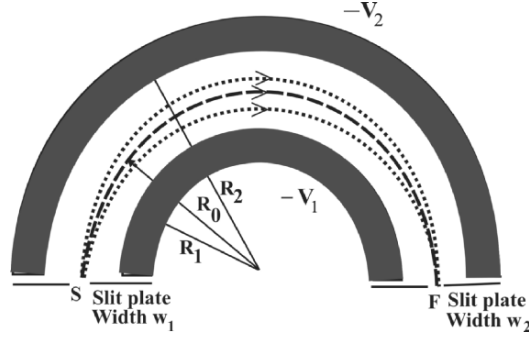


Fig. 5.9. Schematic representation of a concentric hemispherical analyzer

photoelectrons can be analyzed by hemispherical electrostatic analyzer or cylindrical mirror analyzer. In order to get good signal, Auger and photoelectron are differentiated from the core electrons due to their energy separation.

Concentric Hemispherical Analyzer

There are many different designs of electron energy analyzers but the preferred option for photoemission experiments is a Concentric Hemispherical Analyzer (CHA), which uses an electric field between two hemispherical surfaces to disperse the electrons according to their kinetic energy (Fig. 5.9).

Two hemispheres of radii R_1 (inner) and R_2 (outer) are positioned concentrically and potentials $-V_1$ and $-V_2$ are applied to these spheres, respectively, with $V_2 > V_1$. The potential of mean free path analyzer is

$$V_0 = \frac{V_1 R_1 + V_2 R_2}{2R_0} \quad (5.3)$$

An electron of kinetic energy $eV = V_0$ will travel a circular orbit through hemisphere at radius R_0 (radius of the medium equipotential surface). Since R_0, R_1 , and R_2 are fixed, changing V_1 and V_2 in principle, will allow scanning of electron kinetic energy following mean free path through hemispheres. The source S is located in the entrance slit of width W_1 and the focus F in the exit slit of width W_2 . The divergence of an electron entering the analyzer from the ideal tangential path is δx .

Total resolution of instrument is dependent on convolution of X-ray source width, natural linewidth of peak, analyzer resolution and is given by

$$(\text{FWHM})_{\text{total}} = \left[(\text{FWHM}_{\text{X-ray}})^2 + (\text{FWHM}_{\text{linewidth}})^2 + (\text{FWHM}_{\text{analyzer}})^2 \right]^{1/2} \quad (5.4)$$

We can only control the $(\text{FWHM})_{\text{analyzer}}$. The resolution of CHA (ability to separate closely spaced photoemission peaks) is given by $R = \Delta E/E$ where $\Delta E = \text{FWHM}$ (eV) and $E = \text{KE}$ of peak (eV). Since the resolution R is energy dependent (inversely proportional to energy E), it will not remain

uniform across the entire XPS spectrum. This can be achieved by retarding the electrons entering energy analyzer to fixed Kinetic Energy, called the *pass energy* E_0 , so that fixed resolution applies across entire spectrum $\Delta E/E_0 = s/2R_0$ where s = mean slit width. For this purpose either the pass energy can be decreased or R_0 can be increased. The increased resolution for an analyzer is typically $\sim 0.1\text{--}1.0\text{ eV}$.

The hemispherical analyzer and transfer lenses can be operated in two modes, namely, fixed analyzer transmission (FAT), also known as constant analyzer energy (CAE), or fix retard ratio (FRR) also known as constant retard ratio (CRR). In FAT mode, the pass energy of the analyzer is held at a constant value and it is entirely the job of the transfer lens system to retard the given kinetic energy channel to the range accepted by the analyzer. Most XPS spectra are acquired using FAT mode. The alternative mode, FRR, scans the lens system and adjusts the analyzer pass energy to maintain a constant value for the quantity “initial electron energy”/“analyzer PE”. This mode is typically used for Auger spectra since the energy interval accepted by the detection system (i.e., resolution) increases with kinetic energy and recovers weak peaks at high kinetic energies while restricting the intense low energy background that could do damage to the detection system.

The multielement electrostatic lens system (a) collects electrons of large angular distribution (larger flux) (b) focuses electrons at entrance slit (c) retards electrons to pass energy (d) can magnify image of sample for small spot XPS. Figure 5.10 shows the schematic diagram of a CHA with standard input lens system. The lens in this case is simply a transfer lens, which transfers an image of the analyzed area on the sample onto the entrance slit to the analyzer. Slight magnification is also performed.

To enable the study of gases, Gelius et al. (1984) have described the design and performance of high resolution multipurpose ESCA instrument with X-ray monochromator. Their instrument comprises of a high-power, fine-focusing electron gun, a high speed rotating anode, a double focusing multi-crystal X-ray monochromator, a monochromatic UV-source with a toroidal grating, a fine-focus variable energy electron-source, a four-element electrostatic electron-lens system, a large 36 cm hemispherical electrostatic analyzer, a 12 cm wide electron multidetector system and a dedicated computer system. The instrument is shown to reach an energy resolution of 0.23 eV with X-ray excitation at a sufficient intensity. For help in efficient designing and performance evaluation of an ideal ESCA-type hemispherical deflector analyzer (HDA) equipped with a zoom lens and a position sensitive detector placed at distance h from the exit focus plane of the HDA, Zouros et al. (2005) have optimized the base resolution.

Cylindrical Mirror Analyzer

The cylindrical mirror analyzer (shown schematically in Fig. 5.11) consists of a shield for electric field, two concentric cylinders, a pinhole with a diameter

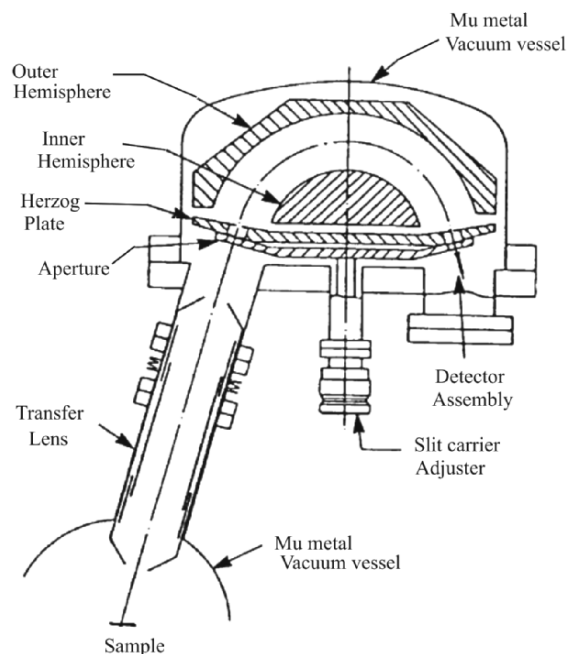


Fig. 5.10. Schematic diagram of a CHA with standard input lens system for XPS

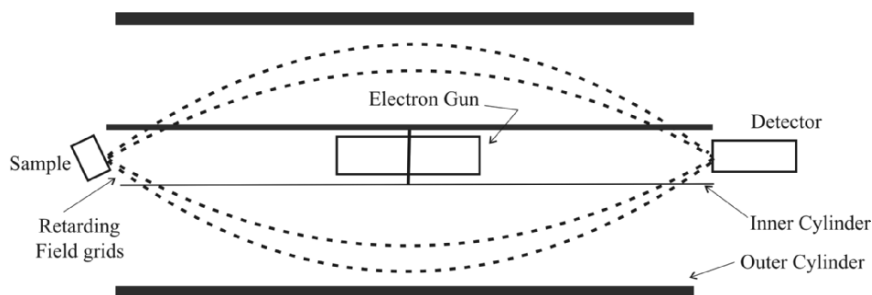


Fig. 5.11. Schematic diagram of a cylindrical mirror analyzer (CMA)

of ~ 2 mm and an electron multiplier. The inner cylinder is held at ground potential while the outer cylinder is at a certain negative potential. The electric field, between the cylinders, forces the electrons entering it to describe trajectories with a radius depending on their energy and the field in the analyzer. The ideal cylindrical mirror analyzer is simulated by allowing the electrons to pass through the charge sheet at the position of the inner cylinder. Only those electrons with a given energy, the so-called pass energy, are focussed onto the electron detector and are registered by the acquisition electronics.

The entrance aperture of the CMA is annular in shape. A second order focus is formed at the exit slit of each stage of the analyzer. In this case the pass energy is related to the potential at the outer cylinder and the radii of the cylinders. Since the solid angle of acceptance of a CMA is quite large ($\sim 0.5\pi$), the transmission of a CMA is relatively high and would optimally amount to $\sim 14\%$. This may constitute a major advantage over the CHA if sensitivity is a critical issue. Two drawbacks of the CMA needs to be mentioned: (i) Since the intensity and the energy calibration depend strongly on the sample analyzer distance, this not only necessitates a very careful adjustment of the sample but also poses significant geometrical limitations to an apparatus containing a CMA for energy selection, (ii) While a lens can be used to transfer the signal electrons to the spectrometer entrance in the case of a CHA (to make the distance between the analyzer and the sample $\sim$ a few tens of cm), this is strictly impossible in the case of the CMA. The typical energy resolution of CMA ($\Delta E/E$) is ~ 0.05 .

A double pass cylindrical mirror analyzer contains two identical segments in series through which photoelectrons are energy selected. Upon entering the first segment, photoelectrons are deflected by an energy resolving radial electric field between two coaxial cylinders and brought to a focus. The photoelectrons then enter the second segment, undergo the same deflection, are re-focused and then detected. This double focusing of electrons greatly improves the energy resolution obtained, as the second segment acts as an additional photoelectron filter. The enhanced resolution can be especially noticed when studying samples with rough surfaces and gas phase spectroscopy where the sample has a finite volume element. The high resolution, ease of construction and versatility make this double pass CMA an attractive device with many possible applications.

The energy analyzer consists of a cylindrical mirror analyzer and a multichannel detector. The multichannel detector provides enhanced sensitivity over a single channel cylindrical mirror analyzer by allowing the collection of several energy channels in parallel and has an overall gain of 10^6 – 10^7 .

Channel Electron Multiplier

Channel Electron Multiplier (CEM) or channeltron is an electron detector that is used to multiply each electron (up to 10^8 times) to provide a pulse output suitable for further amplification by conventional electronic circuits. This is a bent tube that is coated with a photoelectric material (of a specific work function) with a high secondary electron coefficient. The tube is kept at a potential of about 2.5 kV. When the electrons pass through the inlet aperture of the CEM and strike the surface of the CEM, a collision of sufficient energy between the ultraviolet radiation and the CEM wall will eject at least one electron. When an electron strikes the mouth of the tube, a number of secondaries is produced that is accelerated in the channeltron. A local electric field created by the bias voltage of the power source accelerates these

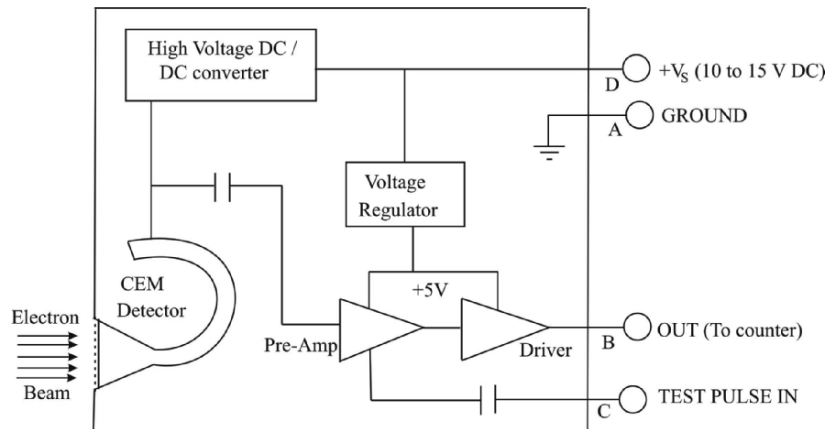


Fig. 5.12. Amptek electron detector using channeltron

electrons which gain enough energy to create secondary ejections from the wall of the CEM when they strike it again. These accelerated secondaries in turn produce further secondaries and so on. The energy required to produce these secondaries is supplied by the channeltron voltage supply. A single photon is capable of creating an output of 10 million electrons. In this way a pulse is produced that indicates the arrival of an electron in the detector. This process continues down the length of the CEM, creating more and more secondaries along the way. This amplified “cascade” passes through the preamplifier and is thus detected. This pulse is then shaped and ultimately registered by the acquisition electronics. In a similar way, pulses of electrons are produced in the microchannels of a microchannel plate (MCP). When this device is used in combination with a position sensitive anode, electrons can be detected with a lateral resolution of some tens of a micron.

The schematic diagram of an Amptek electron detector using CEM is shown in Fig. 5.12.

5.3.3 Experimental Workstation

The experimental workstation, a three level stainless steel ultra high vacuum (UHV) chamber whose pumping system permits to maintain a stable base pressure of $\sim 10^{-10}$ mbar, is equipped with hemispherical electron energy analyzer, variable entrance slit and a detector. The electrostatic lens transmits electrons to the spherical sector analyzer. The sample manipulator which could have either 3 degrees of freedom (x, y, z) or having 5 degree of freedom (x, y, z, θ, φ) and is either manual or computer controlled, allows the analysis in user-friendly way. A preparation chamber with less vacuum helps for precleaning of the sample before loading into the UHV chamber.

5.3.4 Data Acquisition and Analysis

To use the XPS technique, it is first required to make the data processing – analog and digital acquisition, background subtraction, measurement of peak area, X-ray satellite removal, curve-fitting, and deconvolution. The data processing leads to make (a) qualitative analysis – identification of elements, energy scale calibration, chemical shift, relaxation effects, Auger parameters, peak widths, and line shapes. (b) quantitative analysis – depth profiling, photoelectron cross-sections, asymmetry parameters, analyzer transmission, sensitivity factors, detection limits, and the effect of thin overlayers, (c) artifacts – X-ray satellites, ghost peaks, X-ray damage, and specimen charging and handling. The XPS has wide applications to solve surface-related problems such as determination of the atomic structure of surfaces and analysis of surface reactions by fast-XPS.

The various approaches employed for depth profiling through XPS are the angular studies, inelastic losses, and sputtering.

Quantification of XPS Data

The intensity of a given photoelectron line is proportional to the X-ray flux, cross-section for exciting the particular level, density of the particular atom in the lattice x , the escape depth for electrons of the resulting kinetic energy, asymmetry factor in the angular distribution of the photoionization event, transmission of the analyzer, which includes the acceptance angle and area, and the efficiency of the electron detector. In addition, there are several secondary factors, some of which depend on the matrix. The intensity of line is given by

$$I_a = \Phi_{X\text{-ray}}(x, y) \times C_a(x, y, d) \times \sigma_{ij}(h\nu) \times P_{\text{no-loss}}(\text{material}, d) \times A_{\text{analyzer}} \times T_{\text{analyzer}} \quad (5.5)$$

where $\Phi_{X\text{-ray}}$ is the X-ray flux, C_a the concentration of element a, $\sigma_{i,j}$ the subshell ionization cross-section, $P_{\text{no-loss}}$ the probability of no-loss escape, A_{analyzer} the angular acceptance of analyzer and T_{analyzer} is the transmission function of analyzer.

It is difficult to apply calculated $\sigma_{i,j}$ directly to XPS data. Other instrumental parameters need to be included about which enough information must be available to make an analysis from first principles.

Most analyses use empirical calibration constants, ASF (*called atomic sensitivity factors*) derived from standards

$$C_a(\bar{x}, \bar{y}, \bar{d}) = \frac{I_{\text{measured}}}{\text{ASF}} \quad (5.6)$$

The ASF for H, He is, however, very small (undetectable in conventional XPS). For applying ASF method, one should choose XPS peak with largest ASF to

maximize sensitivity. The accuracy is better than 15% with this method. Another method is to use standards to obtain sensitivity factors S_i for a particular line i , which are proportional to the intensity of line i for pure elements. As only ratios of factors are important, the proportionality factors as such are not needed and one can make them relative to the line of a particular element (say Si-2p). Dividing the intensity of the line i by the factor S_i one obtains R_i . Usefulness of XPS using standards, depends on sensitivity (minimum detectable concentration) as well as accuracy and precision. However, the accuracy of better than 5% can be achieved, if use of standards measured on same instrument is made.

For most elements, sensitivity factor S_i is $\sim 0.1 - 1\% \text{ ml}$ ($\equiv$ subnanomolar).

Depth Information From XPS Data

Let an X-ray photons be incident along AB at grazing angle δ (say with the sample surface of thickness d) as shown in Fig. 5.13, and the electron is emitted at an angle α with the sample surface. For off-normal *take-off angle* α , the probability (on average) that electrons can escape without losing energy is

$$P = \frac{I}{I_0} = \exp\left(\frac{1}{\lambda} \cdot \frac{-d}{\sin \alpha}\right)$$

or $d = -\ln(P) \cdot \lambda \cdot \sin \alpha = 3 \cdot \lambda \cdot \sin \alpha$

where d decreases by a factor of 4 on going from $\alpha = 90^\circ$ (normal) to 15° (grazing)

The effect of changing the grazing angle is evident from Fig. 5.14, which shows the effect of the variation of take-off angle on the Si 2p spectrum from silicon with a passive oxide layer. It is important to note the relative enhancement of the (surface) oxide signal at low angle (measured w.r.t the surface).

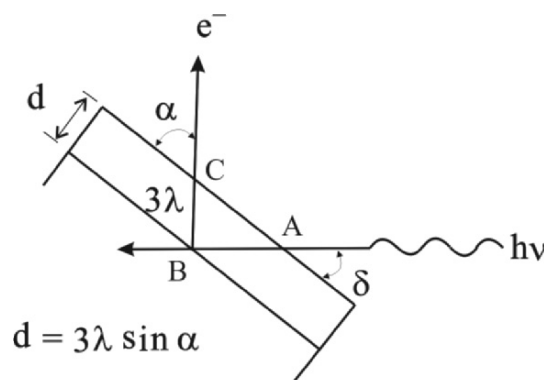


Fig. 5.13. Surface sensitivity enhancement by variation of the electron “take-off angle”

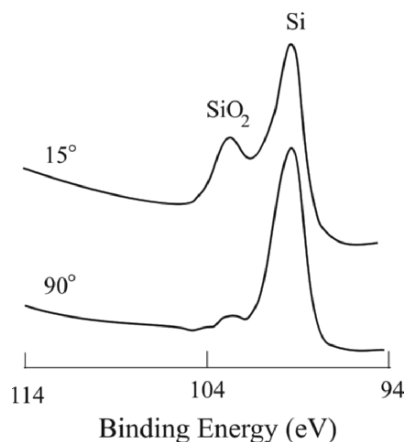


Fig. 5.14. Effect of the variation of take-off angle on the Si 2p spectrum from silicon with a passive oxide layer

5.4 Principle Photoelectron Lines for a Few Elements

The principle photoelectron lines for a few elements are presented in Table 5.1.

5.5 Salient Features of XPS and a Few Practical Examples

XPS, which is also known as ESCA, can be used to extract information of a chemical nature (such as atomic oxidation state) from the sample surface since the presence of chemical bonding (and hence the presence of neighboring atoms) will cause binding energy shifts. The binding energy is determined by the difference between the total energies of the initial-state atom and the final-state ion, which is roughly equal to the Hartree-Fock energy of the electron orbital. Hence the surface compositional analysis can be performed, by identifying the peaks with the specific atoms.

Measurement of the relative areas of the photoelectron peaks allows the composition of the sample to be determined. Because the photoelectrons are strongly attenuated by passage through the sample material itself, the information obtained comes from the sample surface, with a sampling depth of the order of 5 nm. Chemical bonding will clearly have an effect on both the initial state energy of the atom and the final state energy of the ion created by emission of the photoelectron. The changes brought about in the initial state energy by bond formation are well understood and can, in principle, be calculated by quantum chemical methods. They are basically due to the redistribution of electrons as the constituent atoms of a molecule or crystal come together in the solid state and will depend upon the *electronegativities* of the atoms involved.

Table 5.1. The principle photoelectron lines, with their energies, for a few elements

${}^4\text{Be}(1s) - 111.85 \text{ eV},$	${}^6\text{C}(1s) - 284.44 \text{ eV},$	
${}^{12}\text{Mg}(2p_{3/2}) - 49.79 \text{ eV},$	${}^{13}\text{Al}(2p_{3/2}) - 72.87 \text{ eV}$	
${}^{15}\text{P}(2p_{3/2}) - 130.01 \text{ eV},$	${}^{20}\text{Ca}(2p_{3/2}) - 346.61 \text{ eV}$	
${}^{21}\text{Sc}(2p_{3/2}) - 398.53 \text{ eV},$	${}^{22}\text{Ti}(2p_{3/2} \text{ and } 3p) - 453.98 \text{ and } 32, 47 \text{ eV}$	
${}^{23}\text{V}(2p_{3/2} \text{ and } 3p) 512.20 \text{ and } 37.17 \text{ eV}$		
${}^{24}\text{Cr}(2p_{3/2} \text{ and } 3p) 574.35 \text{ and } 42.27 \text{ eV}$		
${}^{25}\text{Mn}(2p_{3/2} \text{ and } 3p) 638.89 \text{ and } 471.17 \text{ eV}$		
${}^{26}\text{Fe}(2p_{3/2} \text{ and } 3p_{3/2}) 706.86 \text{ and } 52.48 \text{ eV}$		
${}^{27}\text{Co}(2p_{3/2} \text{ and } 3p_{3/2}) 778.35 \text{ and } 58.88 \text{ eV}$		
${}^{28}\text{Ni}(2p_{3/2} \text{ and } 3p_{3/2}) 852.73 \text{ and } 66.08 \text{ eV}$		
${}^{29}\text{Cu}(2p_{3/2} \text{ and } 3p_{3/2}) 932.67 \text{ and } 75.14 \text{ eV}$		
${}^{30}\text{Zn}(2p_{3/2}, 3p_{3/2} \text{ and } 3d) 1021.81, 88.63 \text{ and } 9.97 \text{ eV}$		
${}^{32}\text{Ge}(3d_{5/2}) 29.39 \text{ eV},$	${}^{33}\text{As}(3d_{5/2}) 41.65 \text{ eV},$	${}^{39}\text{Y}(3d_{5/2}) 155.90 \text{ eV}$
${}^{40}\text{Zr}(3d_{5/2} \text{ and } 4p_{3/2}) 178.78 \text{ and } 27.07 \text{ eV}$		
${}^{41}\text{Nb}(3d_{5/2} \text{ and } 4p_{3/2}) 202.34 \text{ and } 30.77 \text{ eV}$		
${}^{42}\text{Mo}(3d_{5/2} \text{ and } 4p_{3/2}) 227.95 \text{ and } 35.47 \text{ eV}$		
${}^{44}\text{Ru}(3d_{5/2} \text{ and } 4p_{3/2}) 280.08 \text{ and } 43.37 \text{ eV}$		
${}^{45}\text{Rh}(3d_{5/2} \text{ and } 4p_{3/2}) 280.08 \text{ and } 43.37 \text{ eV}$		
${}^{46}\text{Pd}(3d_{5/2}) 335.12 \text{ eV},$	${}^{47}\text{Ag}(3d_{5/2}) 368.27 \text{ eV}$	
${}^{48}\text{Cd}(3d_{5/2}) 405.12 \text{ eV},$	${}^{49}\text{In}(3d_{5/2}) 443.88 \text{ eV}$	
${}^{50}\text{Sn}(3d_{5/2} \text{ and } 4d_{5/2}) 484.98 \text{ and } 23.92 \text{ eV}$		
${}^{51}\text{Sb}(3d_{5/2} \text{ and } 4d_{5/2}) 528.25 \text{ and } 32.04 \text{ eV}$		
${}^{52}\text{Te}(3d_{5/2} \text{ and } 4d_{5/2}) 573.03 \text{ and } 40.41 \text{ eV}$		
${}^{59}\text{Pr}(3d_{5/2}) 931.89 \text{ eV},$	${}^{60}\text{Nd}(3d_{5/2}) 980.90 \text{ eV}$	
${}^{63}\text{Eu}(4d) 128.19 \text{ eV},$	${}^{64}\text{Gd}(4d) 140.37 \text{ eV}$	
${}^{65}\text{Tb}(4d) 146.01 \text{ eV},$	${}^{66}\text{Dy}(4d) 152.35 \text{ eV}$	
${}^{67}\text{Ho}(4d) 159.59 \text{ eV},$	${}^{68}\text{Er}(4d) 167.28 \text{ eV}$	
${}^{69}\text{Tm}(4d) 175.39 \text{ eV},$	${}^{70}\text{Yb}(4d) 182.40 \text{ eV}$	
${}^{71}\text{Lu}(4f_{7/2}) 7.19 \text{ eV},$	${}^{72}\text{Hf}(4d_{5/2} \text{ and } 4f_{7/2}) 211.50 \text{ and } 14.31 \text{ eV}$	
${}^{73}\text{Ta}(4d_{5/2} \text{ and } 4f_{7/2}) 226.40 \text{ and } 21.83 \text{ eV}$		
${}^{74}\text{W}(4d_{5/2} \text{ and } 4f_{7/2}) 243.50 \text{ and } 31.37 \text{ eV}$		
${}^{75}\text{Re}(4d_{5/2} \text{ and } 4f_{7/2}) 260.50 \text{ and } 40.34 \text{ eV}$		
${}^{76}\text{Os}(4d_{5/2} \text{ and } 4f_{7/2}) 278.51 \text{ and } 50.69 \text{ eV}$		
${}^{77}\text{Ir}(4d_{5/2} \text{ and } 4f_{7/2}) 296.31 \text{ and } 60.84 \text{ eV}$		
${}^{78}\text{Pt}(4d_{5/2} \text{ and } 4f_{7/2}) 314.61 \text{ and } 71.12 \text{ eV}$		
${}^{79}\text{Au}(4f_{7/2}) 84 \text{ eV},$	${}^{80}\text{Hg}(4d_{5/2} \text{ and } 4f_{7/2}) 359.32 \text{ and } 99.85 \text{ eV}$	
${}^{81}\text{Tl}(4d_{5/2} \text{ and } 4f_{7/2}) 385.02 \text{ and } 117.73 \text{ eV}$		
${}^{82}\text{Pb}(4d_{5/2} \text{ and } 4f_{7/2}) 412.03 \text{ and } 136.85 \text{ eV}$		
${}^{83}\text{Bi}(4d_{5/2} \text{ and } 4f_{7/2}) 440.13 \text{ and } 156.96 \text{ eV}$		

XPS is known for its weakly (usually non-) destructive nature and for its universal applicability to solid samples – be they metals, ceramics, or polymers. However, the samples must be solid and vacuum compatible. The most serious limitation is the ex-situ nature of the technique. The instrument is very costly and complex and the monochromatic X-ray sources have low flux.

The XPS technique is not usually spatially sensitive, sampling depth varies with electron kinetic energy (and material) and the spectra is complicated by secondary features like X-ray satellites. The surface charging in insulators shifts binding energy scale. Hydrogen and helium can not be detected with good sensitivity.

Example 1. Study of the XPS spectrum of NaCl

Using the energies of core levels of various states (Fig. 5.15) and using energy of Mg $K\alpha$ radiation equal to 1253.6 eV, it is easy to find that the Na 1s, 2s and 2p photoelectron peaks resulting from photoionization of the 1s, 2s and 2p levels, respectively, level using (5.2).

Example 2. Study of the XPS spectrum of Pd metal

The XPS spectrum obtained from a Pd metal sample using Mg $K\alpha$ radiation is shown in Fig. 5.16.

From the spectrum given in Fig. 5.16, it is clear that the peaks occur at kinetic energies of about 330, 690, 720, 910, and 920 eV. These energies

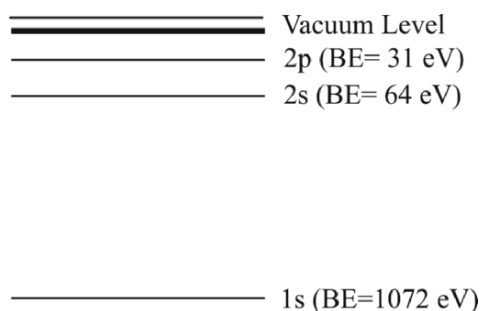


Fig. 5.15. Energy level diagram for sodium with approximate binding energies for the core levels

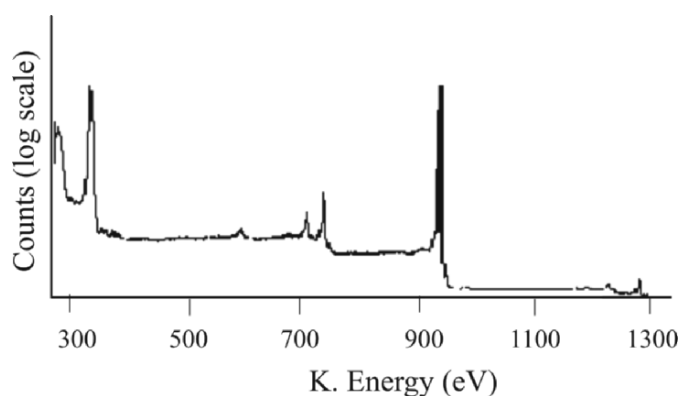


Fig. 5.16. XPS spectrum obtained from a Pd metal sample using Mg $K\alpha$ radiation

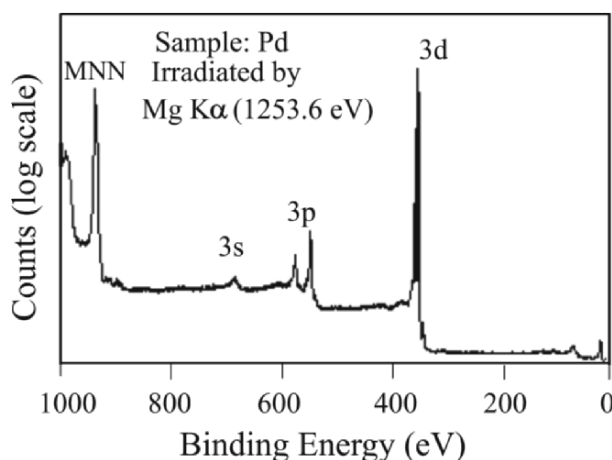


Fig. 5.17. Variation of photoelectron intensity vs. the binding energy in a XPS spectrum using sample of Pd and excitation by Mg K α X-ray of 1253.6 eV

can be transformed into the binding energy (BE) by taking into account the energy of Mg K α radiation which is 1253.6 eV. A plot of the intensity of the photoelectron vs. BE is shown in Fig. 5.17. Since the most intense peak is seen to occur at a binding energy of about 335 eV, it is easy to find that the valence band (4d, 5s) emission occurs at a binding energy of about 0–8 eV (measured with respect to the Fermi level, or alternatively at about 4–12 eV if measured with respect to the vacuum level) working downwards from the highest energy levels. The emission from the 4p and 4s levels gives rise to very weak peaks at 54 and 88 eV respectively. The most intense peak at about 335 eV is due to emission from the 3d levels of the Pd atoms, whilst the 3p and 3s levels give rise to the peaks at about 534/561 and 673 eV, respectively. The peak indicated as MNN is not an XPS peak. It is an Auger peak arising from X-ray induced Auger emission. It occurs at a kinetic energy of about 330 eV.

Example 3. Study of the hyperfine aspects in the XPS spectrum of Pd metal

The close examination of the 3d photoemission peak around 330 eV shows that it is a doublet with one peak at 334.9 eV BE and the other at 340.2 eV BE in the intensity ratio of 3:2 (Fig. 5.18). This arises from spin–orbit coupling effects in the final state. The inner core electronic configuration of the initial state of the Pd is:

$$(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^{10} \dots \text{ with all subshells completely full.}$$

The removal of an electron from the 3d subshell by photoionization leads to a $(3d)^9$ configuration for the final state – since the d-orbitals ($l = 2$) have nonzero orbital angular momentum, there will be coupling between the unpaired spin and orbital angular momentum values.

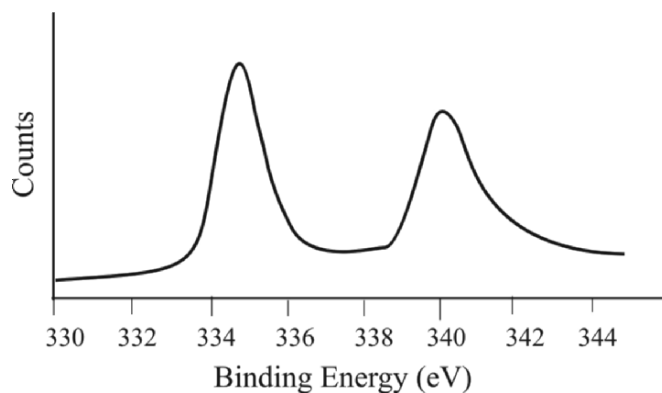


Fig. 5.18. Photoelectron spectrum of Pd restricted to energy range of 330 and 344 eV

We will now describe the following two parameters, which are important in the study of hyperfine structures:

Effect of Spin–Orbit Coupling

Spin–orbit coupling is generally treated using one of the two models, which correspond to the two limiting ways in which the coupling can occur. These are the LS (or Russell–Saunders) coupling approximation and the j – j coupling approximation.

If we consider the final ionized state of Pd within the Russell–Saunders coupling approximation, the $(3d)^9$ configuration gives rise to two states $^2D_{5/2}$ and $^2D_{3/2}$ with degeneracy values of 6 and 4 respectively, which differ slightly in energy. These two states arise from the coupling of the $L = 2$ and $S = 1/2$ vectors to give permitted J values of $3/2$ and $5/2$. Since the shell is more than half-full, the lowest energy final state is the one with maximum J -value i.e., $J = 5/2$. Hence this gives rise to the “lower binding energy” peak. The relative intensities of the two peaks reflect the degeneracies of the final states ($g_J = 2J + 1$), which in turn determines the probability of transition to such a state during photoionization.

The Russell–Saunders coupling approximation is best applied only to light atoms and this splitting can alternatively be described using individual electron l – s coupling. In this case the resultant angular momenta arise from the single hole in the d-shell; a d-shell electron (or hole) has $l = 2$ and $s = 1/2$, which again gives permitted j -values of $3/2$ and $5/2$ with the latter being lower in energy.

Effect of Chemical Shift

The exact binding energy of an electron depends not only upon the level from which photoemission is occurring, but also upon the formal oxidation state of

the atom and the local chemical and physical environment. Changes in either of these factors give rise to small shifts in the peak positions in the spectrum – called *chemical shifts*. Such shifts are readily observable and interpretable in XP spectra (unlike in Auger spectra) because the technique has high intrinsic resolution (as core levels are discrete and generally of a well-defined energy).

Atoms of a higher positive oxidation state exhibit a higher binding energy due to the extra Coulomb interaction between the photo-emitted electron and the ion core. This ability to discriminate between different oxidation states and chemical environments is one of the major strengths of the XPS technique.

In practice, the ability to resolve between atoms exhibiting slightly different chemical shifts is limited by the peak widths which are governed by a combination of factors; especially the intrinsic width of the initial level and the lifetime of the final state, the line-width of the incident radiation (which for traditional X-ray sources can only be improved by using X-ray monochromators) and the resolving power of the electron-energy analyzer. In most cases, the second factor is the major contributor to the overall line width.

5.6 Applications of XPS

The XPS is used for the determination of elements and their valence states in the surface of the material i.e., surface characterization to provide information about the chemical/oxidation states of various elements present in the surface (at depths $<1,000 \text{ \AA}$) of the material. This aspect is widely used in polymer chemistry, adhesive characterization, corrosion, and metallurgy.

5.6.1 Microanalysis of the Surfaces of Metals and Alloys

Effects of hydrogenation on the core and valence electronic structures of β (bcc)-stabilized Ti–V, Ti–Nb and Ti–Mo alloys have been studied with XPS technique by Tanaka and Aoki (1989) using monochromatic $\text{Al K}\alpha$ radiation. The oxide surfaces have been characterized by Bianchi et al. (1993) who have reported the results obtained by treating nickel and molybdenum oxides at a temperature of 523 K, at 10^{-4} Pa (in vacuum) and at 10^5 Pa (in hydrogen) to conclude that it is possible to completely reduce nickel oxide to metal by treating it in hydrogen and not in vacuum while on the other hand, for the two molybdenum oxides (MoO_3 and MoO_2) it is possible to notice the presence of a large amount of intermediate not reduced oxides, at 523 K, both in hydrogen and in vacuum. The surface analysis of black copper selective coating has been done by Richharia et al. (1991). Surface analysis of films formed on rolled and heat treated stainless steel 304 materials in air and in chloride solution was done by Phadnis et al. (2003) using XPS. XPS has also been used to analyze the oxidation state of palladium in dental alloys at the surface and at depths of 30–1,000 $\text{\AA}$ in order to understand the mechanism of oxide growth and development of new lower cost alloys.

From X-ray photoemission spectroscopy study, Biswas et al. (2003) found that the argon core levels exhibit a systematic shift in binding energy and change in the line shape as function of Ar-ion incidence energy on Al(111). This is related to the increase in size of the subsurface bubbles created by argon ion bombardment where the Ar atoms are trapped.

XPS was used by Huang et al. (2003) to analyze the chemical bonding states of C and Si in the 70% SiC–C films (deposited with radiofrequency magnetron sputtering on stainless steel substrates followed by ion beam mixing and then permeated by hydrogen gas under 3.23×10^7 Pa pressure for 3 h at 500 K) before and after hydrogen gas permeation. In addition to this, the chemical states of contaminated oxygen were also checked.

Trace element analysis of SiC-rich residue from the Murchison meteorite in presolar stardust grains was investigated by Bernhard et al. (2006) through XPS instrument. The micrometer-sized grains were deposited on a Si wafer from an aqueous suspension. Energy filtered ESCA images have been taken in the kinetic energy range from the threshold up to about 400 eV for various photon energies. A lateral resolution of the order of 120 nm along with a high energy resolution in the range of 100 meV provides the basis for chemical trace element analysis with maximum sensitivity. Apart from major (Si, C) and minor (N, Mg, Al, Fe) elements, the energy filtered images and local microspectra revealed the presence of a variety of heavy trace elements: Sr, Y, Zr, Nb, Mo, Ba and, interestingly the rare earth elements Dy, Er, and possibly Tm.

5.6.2 Study of Mineral Surfaces

Air oxidation of PbS and FeS₂ has been studied with SR source excitation (providing a continuous energy distribution over large energy region, instead of a fixed excitation energy source like Al K α or Mg K α radiation from sealed-off X-ray tube used in conventional XPS) with the purpose of increasing the surface sensitivity. In the case of identification of sulfur species, which often is the main task in surface analysis of sulfide surfaces, this leads to approximately an order of magnitude improvement in surface sensitivity and, hence, essentially better possibility to detect surface species of submonolayer coverage.

5.6.3 Study of Polymers

The XPS study of ion-beam irradiation effects in polyamide layers have been studied by Karpuzov et al. (1989). Thin polyamide films deposited on silicon or metal covered glass–ceramic substrates were exposed to ion bombardment at different fluences ranging from 1×10^{12} to 1.5×10^{16} cm^{−2}. The XPS technique was used to study the polymer stoichiometry of the near surface layers (~ 75 Å) before and after the bombardment. The results show that the stoichiometric ratio of O, N, and C-groups remains approximately constant with depth for unirradiated samples.

The work by Pireaux et al. (1995) on the so-called “reactive” (polytetrafluoroethylene) and even more “stable” (polypropylene and polyethylene) polymers based on the use of XPS *valence band* spectra, showed that irradiation can lead to superficial *structural* modification – lateral chain grafting, or cross-linking. This structural modification appears more pronounced for high fluence UV excimer laser irradiation in air, than for (more moderate) exposition to harder X-rays in vacuum.

XPS was used for determination of metal–polymer interaction and chemical state of atoms on metal–polymer interface after diffusion of Ag and Cu atoms in polyethyleneterephthalate (PET) and polyamide (PI) by Macková et al. (2005). XPS measurement gives an evidence of Ag clustering in Ag-PET samples prepared by cathode sputtering. In PI the Cu atoms exhibit higher diffusivity than Ag atoms due to their lower atomic radius.

Surface chemical structure of polycarbonate (PC) films after irradiation by $0.6 \text{ MeV u}^{-1} \text{ C}_n^+$ ($n = 1\text{--}5$) cluster ions of $5 \times 10^{12} \text{ ions cm}^{-2}$ was analyzed through XPS by Dai et al. (2006). The results show that the ratio of C 1s to O 1s (C/O) of PC surface irradiated by C cluster, with the same atomic energy and dose, gradually decreased with increasing of cluster size and then tended to a saturation. It indicates that the oxygen and carbon atoms contained in PC films were selectively sputtered by carbon cluster ions. As to the ratio of C/O of PC films irradiated by individual C decreased linearly with increasing of projectile energy. XPS results show that ion beams induce the change of chemical element ratio, restructure of near surface of PC and formation of new type of bond.

5.6.4 Study of Material Used for Medical Purpose

Corrosion characteristics of ferric and austenitic stainless steels have been studied by Endo et al. (2000) for dental magnetic attachment. The surface of the stainless steels was analyzed by XPS. The breakdown potential of ferric stainless steels increased and the total amount of released metal ions decreased linearly with increases in the sum of the Cr and Mo contents. The corrosion rate of the ferric stainless steels increased 2–6 times when they were galvanically coupled with noble metal alloys but decreased when coupled with commercially pure Ti. For austenitic stainless steels, the breakdown potential of high N-bearing stainless steel was approximately 500 mV higher than that of SUS316L, which is currently used as a component in dental magnetic attachments. The enriched nitrogen at the alloy/passive film interface may be effective in improving the localized corrosion resistance.

Iijima et al. (2001) has done the surface analysis of a commercial Ni–Ti alloy orthodontic wire and a polished plate, with the same composition, by XPS. The analysis demonstrated the presence of a thick oxide film mainly composed of TiO_2 with trace amounts of Ni hydroxide, which had formed on the wire surface during the heat treatment and subsequent pickling processes. This oxide layer contributed to the higher resistance of the as-received wire to

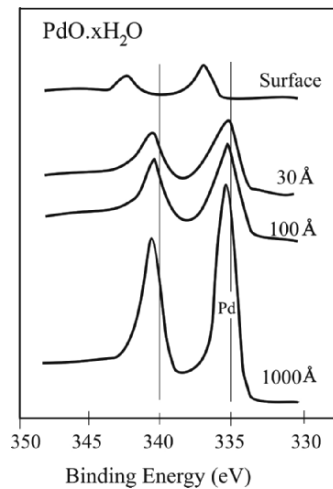


Fig. 5.19. Analysis of oxidation state of palladium alloy at the surface and at 30, 100, and 1,000 Å

both general and localized corrosion compared with that of the polished plate and the polished wire. The thick oxide layer, however, was not stable and did not protect the orthodontic wire from corrosion in 0.1% lactic acid solution.

In a pursuit to design new low cost alloys, XPS has been used to analyze the oxidation state of palladium in dental alloys at the surface and at depths of 30, 100, and 1,000 Å. The results are as shown in Fig. 5.19.

5.6.5 For Surface Characterization of Coal Ash

The surface chemical composition of brown coal ash particles formed during combustion has been determined by Ersez and Liesegang (1991) to detect any sputter-induced composition changes or to observe any difference between the surface and bulk compositions of the ash. They have observed that certain steels used for heat exchanger piping may well be predisposed to aluminosilicate fouling due to their intrinsic Al content.

5.6.6 Surface Study of Cements and Concretes

The study of the early hydration of Ca₃SiO₅ by XPS has been reported by Regourd et al. (1980) after detailed study of surface transformations of C₃S grains from very early ages of hydration.

5.6.7 Study of High Energy Resolution Soft X-rays Core Level Photoemission in the Study of Basic Atomic Physics

The use of XPS has been made to understand the mechanism of photoemission in finer details and the development of the basic atomic physics in order to

develop the technique itself and to make it applicable in different fields of study. The aim of this is also to optimize the analysis of surfaces with XPS in order to solve surface-related problems.

5.7 Advantages and Limitations of XPS

Since the strength of XPS is its ability to identify different chemical states, this ability is useful in a range of physical studies, for example, oxidation/corrosion products, adsorbed species, and thin-film growth processes. The advantages of the XPS technique, in general, are good surface sensitivity, rather straightforward elemental and chemical state analysis and reliable quantification of the data. The XPS technique is nondestructive and can be used for metal-, ceramics- or polymers-samples. However, the samples must be solid and vacuum compatible. XPS is a relatively straightforward quantitative method for elemental composition. Using ASF's, sensitivity $\sim 0.1\%$ ml., the chemical shifts give information about oxidation states and chemical environment. Sampling depth in XPS is typically $\sim 20\text{--}100\text{ \AA}$. There is extensive databases of chemical shift information. By changing take-off angle, one can have crude depth information.

The most serious limitation is the ex-situ nature of the technique. The instrument is very costly and complex and the monochromatic X-ray sources have low flux. The XPS technique is not usually spatially sensitive, sampling depth varies with electron kinetic energy (and material) and the spectra is complicated by secondary features like X-ray satellites. The surface charging in insulators shifts binding energy scale. It is not possible to detect hydrogen and helium using XPS.

Neutron Activation Analysis

6.1 Introduction

Neutron activation analysis (NAA) is a powerful technique to analyze the sample i.e., to identify the elements present in the sample both qualitatively and quantitatively. The technique is based on the principle of converting various elements of the sample to radioactive isotopes by irradiating the sample with neutrons in a nuclear reactor. During irradiation the naturally occurring stable isotopes of most elements that constitute the rock or mineral samples, biological materials, etc., are transformed into radioactive isotopes by neutron capture. The radioactive isotopes so formed decay according to their characteristic half-lives varying from seconds to years, emitting the γ -radiations with specific energies. For example, natural sodium ^{23}Na is converted to radioactive sodium ^{24}Na or natural aluminum ^{27}Al is converted to radioactive ^{28}Al or ^{63}Cu which is 69% of the natural copper gets converted to radioactive ^{64}Cu and so on, through the (n,γ) reaction. The characteristic γ -rays emitted by radioactive isotopes are subsequently measured with semi-conductor γ -ray spectrometers, to identify the source of these γ -radiations. Since each radionuclide emits γ -radiation of a specific wavelength(s) or energy(ies), the emitted γ -radiations are characteristic of the isotope formed and hence characteristic of the parent element. Furthermore, since the technique is primarily based on the measurement of prompt γ -radiations subsequent to neutron-induced nuclear reactions through radiative capture (for all elements and isotopes) or through fission (for actinides), this technique is also called neutron-induced prompt γ activation analysis (PGAA or PGNAA). NAA is a useful method for the simultaneous determination of about 25–30 major, minor, and trace elements present in geological, environmental, and biological samples in ppb–ppm range without or with chemical separation.

While studying the action of slow neutrons on rare earth elements, Hevesy and Levi (1936) found for the first time that the rare earth element Dy became highly radioactive after exposure to a source of neutrons - the principle on which the method of Neutron Activation Analysis is based.

These authors were able to detect Dy in Y matrix through this method. NAA is a very useful and sensitive technique for performing both qualitative and quantitative multielement analyses of major, minor, and trace elements in samples from various fields of scientific or technical interest. In comparison to well developed atomic analytical methods like PIXE and XRF, this nuclear analytical method, NAA, is still preserving its role as a ‘workhorse’ for the vast amount of analytical work because it is a nondestructive (sample loses almost all radioactivity after some time) and instantaneous (results appear promptly). Combined with computerized high-resolution γ -ray spectrometry, NAA offers multielement routine analysis needed in such areas as environmental monitoring, geochemistry, medicine, and technological processes. The favorable characteristics of NAA include the negligible matrix effects, excellent selectivity, and high sensitivity. For many elements and applications, NAA offers sensitivities that are superior to those attainable by other methods, of the order of parts per billion. Although the special capabilities of IBA methods like RBS, ERD, etc., give them the ability to provide information about surface composition and elemental distribution yet the NAA has been considered to be more mature and most widely applied nuclear technique for the analysis of samples (Watterson 1988). NAA is, however, a comparative technique. Standards are prepared from certified solutions of known concentration of the elements of interest. An extensive grouping of standard reference materials is incorporated into each analytical scheme. Orivini and Speziali (2001) have reviewed the applicability and limitation of instrumental NAA based on the data up to the year 2000.

6.2 Principle

The principle of NAA is the nuclear reaction, specifically the neutron capture and subsequent γ -emission through β -decay, called (n,γ) reaction. The radiative neutron capture has high probability for thermal (energy ~ 0.025 eV) neutrons due to very large cross-sections. When a neutron interacts with the target nucleus via a nonelastic collision, a compound nucleus (in an excited state) is formed. The excitation energy of the compound nucleus is due to the binding energy of the neutron with the nucleus. The compound nucleus will almost instantaneously de-excite into a more stable configuration through emission of one or more characteristic prompt γ -rays. In many cases, this new configuration yields a radioactive nucleus which also de-excites (or decays) by emission of one or more characteristic delayed γ -rays, but at a much slower rate according to the unique half-life of the radioactive nucleus. Depending upon the particular radioactive species, half-lives can range from fractions of a second to several years.

In principle, therefore, NAA falls into two categories with respect to the time of measurement: (1) PGNAA in which the measurements take place during irradiation and/or (2) DGNAA, where the measurements follow

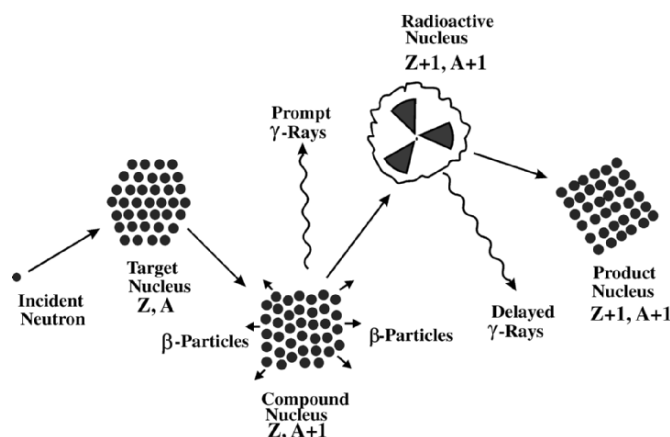


Fig. 6.1. Principle of neutron activation technique

radioactive decay (Fig. 6.1). The latter operational mode is more common. Thus, when one mentions NAA, it is generally assumed that one refers to measurement of the delayed γ -rays. About 70% of the elements have properties suitable for measurement by NAA.

The qualitative characteristics of NAA are the energies of the emitted γ -rays (E) and the half-life of the nuclide ($T_{1/2}$) while the quantitative characteristic is the intensity (I), which is the number of γ quanta of energy E measured per unit time.

To make NAA applicable for the determination of major and minor elements in any sample, data have been made available by various authors. Coming together with the data available in the literature, Ahmad (1983) reported the epithermal neutron activation data for ^{46}Sc , ^{51}Ti , ^{51}Cr , ^{52}V , ^{56}Mn , ^{59}Fe , ^{60}Co , ^{75}Se , ^{86}Rb , ^{95}Zr , ^{97}Zr , ^{124}Sb , ^{131}Ba , ^{134}Cs , ^{140}La , ^{141}Ce , ^{160}Tb , ^{181}Hf , ^{182}Ta , and ^{198}Au . The nuclear spectroscopy group of Prof. P.N.Trehan at Panjab University Chandigarh has made a significant contribution in this field of study by measuring energies and intensities of various γ -transitions emitted by different radionuclides (Kaur et al. 1980, Sharma et al. 1979, 1980, Sooch et al. 1980, Verma et al. 1978, 1979, 1980). Since the data about the decay schemes of various radioactive nuclei need addition and update from time to time, the same has been made available by hundreds of researchers working in the field of nuclear spectroscopy. The compilation of this data has been updated from time to time and the adopted data is available in the 2-volume set of the Table of Isotopes in the book form (Firestone and Shirley 1999) and also through Isotope Explorer (Chu et al. 1999a,b) or LBNL/LUND Table of Radioactive Isotopes (Firestone and Ekstrom 2004) or IAEA's NuDat (<http://ndsalpha.iaea.org>) on the Internet.

The evaluated database for prompt γ -rays from radiative capture of thermal neutrons, by elements from Hydrogen to Zinc, has been compiled by IAEA (Reddy and Frankle 2003). This database includes the energies of

the various emitted γ -lines, their relative intensities, partial cross sections and reaction identification for each γ -line along with the isotopic abundance, life-time of various energy levels, and total neutron radiative capture cross sections for various radioisotopes. The IAEA data base for PGAA (<http://www-nds.iaea.org/pgaa/databases.htm>) contains PGAA prompt γ data, PGAA decay γ data, most intense γ -rays, adopted prompt γ -ray cross-sections, and adopted decay γ -ray cross-sections in EXCEL Format Data Base files, PDF/PS Format Tables and Text-files.

6.2.1 Prompt vs. Delayed NAA

The NAA technique is categorized according to whether the γ -rays are measured during neutron irradiation (PGNAA) or at some time after the end of the irradiation (DGNAA). The PGNAA is performed by irradiating the sample using a beam of neutrons (from the reactor beam port) and simultaneous measurement of the characteristic γ -rays emitted by various short-lived radionuclides (so formed), to determine the concentrations of various elements in the sample. While DGNAA is more sensitive for the determination of most elements, it cannot be used for some elements which can be analyzed by PGNAA. The average kinetic energy (100 keV–10 MeV) of fast neutrons, produced in a nuclear reactor, can be lowered by passing the beam through a moderator. The collision of neutrons with atoms of the moderator material, changes these fast neutrons to epithermal ($E \sim 1$ keV) and thermal ($E \sim 0.025$ eV) neutrons. The average thermal neutron energy corresponds to velocity and wavelength values of 2200 m/s and 2 Å respectively. Since the application of NAA can be enhanced in some way by using sub-thermal i.e. “cold,” neutrons (with $E < 10$ meV), the same can be produced by using cryogenic moderators composed of solid or liquid CH_4 at temperatures ranging from 20 to 110 K.

Neutrons with sufficiently long wavelengths can be reflected from some surfaces in the same way as light can be reflected from the interface between two transparent media. Cold neutrons, then, can be guided down cylindrical wave guides without the normal $1/r^2$ attenuation and can be bent out of the line-of-sight paths followed by other radiation.

The usual neutron beams from a research reactor are contaminated by fast neutrons and γ -rays that originate in the core. Filters, collimators, and shielding can reduce these undesirable components to some extent. However, cold neutron beams have a much lower γ - and fast-neutron background. Thus, detectors for capture neutron and basic physics experiments can be placed closer to the sample, increasing sensitivity and making coincidence techniques feasible in many more situations.

Since guided cold neutron beams provide comparable neutron flux and lower background than thermal neutron beams, the detection limit of neutron absorption experiments, such as PGNAA, is decreased. This decrease in the

detection limit of absorption experiments is mainly due to the decrease in the γ -background.

Another major contribution of using cold neutrons is the ability to focus the neutrons to increase the flux on the sample. This will lead to a proportional increase in the reaction rate. Therefore, analytical techniques such as PGNAA which is exclusively dependent on the reaction rate and not on the direction of the incident beam will be enhanced considerably by neutron focusing.

Since the flux on samples irradiated by neutron beam is of the order of one million times lower than that on the samples inside a reactor, the detector can be placed very close to the sample compensating for much of the loss in sensitivity due to flux. The PGNAA technique is most applicable to elements with extremely high neutron capture cross-sections (B, Cd, Sm, and Gd); elements which decay too rapidly to be measured by DGNAA; elements that produce only stable isotopes; or elements with weak decay γ -ray intensities. DGNAA (sometimes called conventional NAA) is useful for the vast majority of elements that produce radioactive nuclides. The technique is flexible with respect to time such that the sensitivity for a long-lived radionuclide that suffers from interference by a shorter-lived radionuclide can be improved by waiting for the short-lived radionuclide to decay. This selectivity is a key advantage of DGNAA over other analytical methods.

6.2.2 Epithermal and Fast Neutron Activation Analysis

The NAA technique makes use of the slow neutrons. However, the epithermal and fast neutrons may also be used for the activation. An NAA technique that employs only epithermal neutrons to induce (n, γ) reactions by irradiating the samples being analyzed inside either cadmium or boron shields is called epithermal neutron activation analysis (ENAA). An NAA technique that employs nuclear reactions induced by fast neutrons is called fast neutron activation analysis (FNAA).

6.3 Experimental

The sample matrix plus standards for the elements of interest are irradiated for a select period of time in the neutron flux of a research reactor. After irradiation and appropriate radioactive decay, the γ energy spectrum is measured by counting the sample with a high resolution (to separate various γ -transitions of close-by energies) γ -detection system. The NAA technique provides highly resolved analysis of elemental composition by the identification of characteristic γ -ray energies associated with different isotopes. Quantitative analysis is provided by element-to-element comparison of the number of γ -rays emitted per unit time by the unknown sample to the number of γ -rays emitted per unit time by the calibration standards.

The technique of NAA can be applied to most sample matrices without any pre-treatment of the sample. This includes (a) solids such as coal,

metals, sediments, ores, tissues, bone, and synthetic fibers (b) liquids such as blood, water, manufacturing wastes, oil, gasoline (c) gases such as argon, chlorine, and fluorine, and (d) suspensions and slurries such as sewage sludge, river water, or foods.

Each sample and standard has its own characteristic γ -ray spectrum. The NAA technique provides highly resolved analysis of elemental composition by the identification of characteristic γ -ray energies associated with different isotopes. Quantitative analysis is provided by element-to-element comparison of the number of γ -rays emitted per unit time by the unknown sample to the number of γ -rays emitted per unit time by the calibration standards. The quantitative analysis is performed to give the elemental concentrations in nanograms, micrograms, or milligrams per gram or millilitre of unknown sample.

The procedure of NAA can be divided into three steps: preparing and irradiating the samples, performing Measurements and Interpreting the results.

Step 1. This involves pulverising, homogenising, mass determination, packing, and the preparation of the standards, if any. About 50–200 mg of the sample material (depending on the type of material), is packed in high purity polyethylene capsules. Because there is almost no sample preparation necessary, the chances of contamination are minimal. A maximum of 10–12 capsules filled with sample material, together with a capsule filled with a certified reference material and an empty capsule (the “blank”), are sealed together in polyethylene foil. Comparators are added in order to measure the neutron flux during irradiation. The whole package is packed in an irradiation container, and irradiated by shooting it to a position close to the reactor’s core by means of a pneumatic irradiation tube system. The transportation time to the irradiation sites and back is 10–15 s. Both unknown samples and standards of the elements of interest are irradiated from a few seconds to a few hours in the nuclear reactor to produce prompt γ -radiations characteristic of the parent isotope. The time of sample irradiation depends on the operation cycle duration of the reactor and is equal to 10–12 days. Neutron fluxes of $\sim 10^{13} \text{ n cm}^{-2} \text{ s}^{-1}$ exist in many irradiation facilities.

Step 2. After irradiation and appropriate radioactive decay of the sample and standards, these are measured on either a well-type or a coaxial large volume Ge(Li) γ -ray detector system coupled to a PC-based γ -spectroscopy system (explained in Sect. 6.3.4) to find out the energies of the γ -rays in the observed spectrum (and hence the corresponding isotopes of the elements present in the sample). The distance of the sample from the detector (and hence the solid angle) is adjusted depending on the count rate which should be about 100–500 counts per second.

For analysis by NAA, the information about the γ -radiations emitted by various radionuclides must be available at hand. This information in the form of compilation can be seen from the Table of Isotopes (Firestone

and Shirley 1999) or using chart of nuclides (Nuclear Data Section IAEA Vienna). Depending on the elements of interest, a waiting time is applied in order to let the nuclides with shorter half-life times decay, which gives a lower background and less interference. Samples are usually measured for 1 h, as goes for the reference material and the blank. The comparators are measured for 15 min.

Step 3. Using a computer software, the peaks are fitted, their peak areas (and hence the relative intensities of various γ -transitions) are determined to calculate the abundance of various elements present in the sample. The neutron flux is determined by analyzing the comparators. Finally all this information is converted into a list of elements and their concentrations.

In a full analysis i.e., the prompt as well as delayed γ -emission analysis, the short-lived nuclides are determined first. Actually the most intense γ -radiations are measured first and then observation about their decrease of intensity is made. (This will happen for γ -radiations of those isotopes which have short half-lives). Using a fast rabbit system, each sample is irradiated separately (but together with a comparator in order to calculate the neutron flux) for 5–30 s. Sample and comparator are measured separately after a waiting time from seconds (the element “selenium” has a nuclide with a half-life time of 17.5 s and thus needs to be measured as quickly after irradiation as possible) to as much as 20 min. After the analysis has been completed for all samples, a waiting time of 5–7 days is required before irradiating them again in order to determine the other elements with longer half-life times.

After this waiting period, the samples are packed together as described above, and irradiated for 1–4 h depending on the kind of material. To determine the elements with middle half-life nuclides, all samples are measured 3–5 days after irradiation. To determine the long half-life nuclides, the samples are measured again about 3 weeks after irradiation. After this third measurement, all three spectra of each sample are interpreted together.

The basic essentials required to carry out an analysis of samples by NAA are a source of neutrons, instrumentation suitable for detecting γ -rays, and a detailed knowledge of the reactions that occur when neutrons interact with target nuclei. Brief description of various neutron sources and γ -ray detection systems are given in the following subsections:

6.3.1 Neutron Sources

There are several types of neutron sources viz. radioisotopic neutron emitters like ^{239}Pu –Be, particle-accelerators (to produce high flux of neutrons through (p,n), (d,n), (α ,n) or other reactions) and nuclear reactors (which are sources of neutron due to fission reaction). Nuclear reactors with their high fluxes of neutrons from uranium fission offer the highest available sensitivities for most elements. Different types of reactors and different positions within a reactor can vary considerably with regard to their neutron energy distributions (thermal, epithermal, and fast) and fluxes due to the materials used to moderate the

primary fission neutrons. The neutron beam available at the nuclear reactor or accelerator site cannot be used in the field investigations. However, the fission neutron source like ^{252}Cf or the D–D/D–T fusion neutron sources or radioisotopic neutron sources like ^{239}Pu –Be can be used for field applications. Some of the neutron sources are described in the following sections.

Fission (^{252}Cf) Neutron Source

The spontaneous fission of some artificially produced transuranium isotopes can be applied as a small neutron source e.g., ^{252}Cf (half-life 2.6 y) undergoes fission, producing 3.76 neutrons of 1.5 MeV per event. ^{252}Cf (α -decay for $\sim 96\%$ and spontaneous fission $\sim 4\%$) is very strong neutron emitter (One mg of ^{252}Cf emits 2.28×10^9 neutrons per second). The major advantage of this neutron source is that it can be made portable and generate a stable neutron flux. But, as the neutron flux is rather low in comparison to a nuclear reactor, its use in NAA is limited to the determination of elements of high activation cross-section which are present in major concentrations. Pillay (2002) has used a 50 mg ^{252}Cf source, depleted about two orders of magnitude from its original neutron output to examine the sensitivity of NAA for selection of materials and compounds.

A comparison between ^{252}Cf and ^{238}Pu –Be for partial-body in vivo NAA (Morgan et al. 1981) shows that although the depth distributions of thermal neutron fluences in a water phantom are very similar for the two sources yet with respect to the fluence-to-dose ratio, the ^{252}Cf neutrons have an advantage of approximately 1.4 over the ^{238}Pu –Be source.

Fusion Type D–D/D–T Neutron Generators

These type of neutron generators are small accelerators which produce neutrons using the deuterium–tritium or deuterium–deuterium reactions. The neutron output from these generators may be pulsed or continuous. The small Van de Graaff or Cockcroft–Walton type accelerator of 400 kV (to produce deuteron beam) and a water cooled target of tritium to make fusion neutrons of 14 MeV. The yield of this source is between 1×10^{12} and 6×10^{12} neutrons per second. At the Japan Atomic Energy Research Institute, D–T neutron source has been employed to conduct benchmark experiment on silicon carbide (Maekawa et al. 2001). The experimental results on the use of compact high intensity D–D neutron generator in LBNL for PGNA and NAA techniques, have been reported by Reijonen et al. (2004).

Neutron Beam Using Radioisotopes Through (α, n) and (γ, n) Reactions

Neutron beam can be produced from (α, n) reaction using α -radioactive sources and Be-target or using photon-sources interacting on Be/D₂O targets are presented in Tables 6.1 and 6.2.

Table 6.1. Radioisotopic neutron sources

Name of α -source	Half-life	E_α (MeV)	Neutron Source	Neutron Flux $\text{N s}^{-1} \text{Ci}^{-1}$
^{210}Po	138 d	5.3	Po-Be	2.5×10^6
^{225}Ra	1,620 yr	4.5	Ra-Be	1.1×10^7
^{239}Pu	2.44×10^3 yr	5.1	Pu-Be	1.6×10^6
^{241}Am	433 yr	5.4	AmO ₂ -Be	2.2×10^6

Table 6.2. Photoneutron sources

γ -source	Half-life	Energy of γ -rays(E_γ) (MeV)	γ -rays Inter- acting With	Neutron Energy (MeV)	Yield (n s^{-1})
^{24}Na	15 h	2.75	Be	0.2	14
			D ₂ O	0.8	29
^{88}Y	108 d	0.9, 1.8, 2.8	Be	0.16	10
			D ₂ O	0.3	0.3
^{124}Sb	60.4 d	1.7	Be	0.02	19

Neutron Beam Using Protons, Deuterons or Other Charged Particles from Particle Accelerators

The particle accelerators are used to produce neutrons whereby a convenient target material is bombarded by accelerated charged particles and the neutrons are produced in a nuclear reaction. In the most frequently used and commercially available neutron generators, the accelerated deuterons are bombarded on the tritium (^3H) target. The nuclear reaction carried out is $^3\text{H}(\text{d}, \text{n})^4\text{He}$. The energy of the produced mono-energetic neutrons is 14 MeV. The typical neutron yields of about 10^{11} neutrons $\text{s}^{-1}\text{mA}^{-1}$ means a neutron flux of approximately 10^9 neutrons $\text{cm}^{-2}\text{s}^{-1}$. Due to the emitted fast neutrons, in NAA the neutron generators are used for the determination of elements of high cross-section in this energy region. The sources of neutrons using (d,n) reactions are presented in Table 6.3.

In an effort to produce neutrons for the selective excitation of nuclear isomeric states by inelastic scattering, $^7\text{Li}(\text{p}, \text{n})^7\text{Be}$ reaction has proved to be useful due to its relatively high yield and very narrow energy spread. To analyze silica and rocks for Si and Al concentrations, the neutron beam (below the energy region for the excitation of threshold reactions such as $^{28}\text{Si}(\text{n}, \text{p})^{28}\text{Al}$ and above the region where neutron capture reactions like $^{27}\text{Al}(\text{n}, \gamma)^{28}\text{Al}$ have large cross-sections) was produced by a suitable choice of proton energy and target thickness (Magagula and Watterson 1998).

Table 6.3. Neutron generation through (d,n)reaction

Reaction	Q-value (MeV)	Neutron Flux $\text{N cm}^{-2} \text{s}^{-1}$	Moderator Material
$^2\text{H(d, n)}^3\text{He}$	3.25	$\sim 2.5 \times 10^9$	water or paraffin
$^3\text{H(d, n)}^4\text{He}$	17.6	–do–	–do–
$^9\text{Be(d, n)}^{10}\text{B}$	3.79	–do–	–do–

Neutron Beam from Reactors

The neutron reactors produce neutrons due to the phenomenon of fission. The flux of neutrons produced by the reactors is of the order of 10^{12} – $10^{15} \text{ n cm}^{-2} \text{s}^{-1}$. Since the thermal neutrons are required for NAA due to their maximum absorption cross-sections, the neutron beam has to be thermalized as the neutron beam from the reactor consists of thermal, epithermal, and fast neutrons.

The thermal neutron component consists of low-energy neutrons with energies below 0.5 eV, which are in thermal equilibrium with atoms in the reactor's moderator. At room temperature, the energy spectrum of thermal neutrons is best described by a Maxwell–Boltzmann distribution with a mean energy of 0.025 eV and a most probable velocity of $2,200 \text{ m s}^{-1}$. In most reactor irradiation positions, 90–95% of the neutrons that bombard a sample are thermal neutrons. In general, a 1-MW reactor has a peak thermal neutron flux of approximately 10^{13} neutrons per square centimeter per second. The epithermal neutron component consists of neutrons with energies from 0.5 eV to about 0.5 MeV, which have been only partially moderated. A cadmium foil 1 mm thick absorbs all thermal neutrons but will allow epithermal and fast neutrons above 0.5 eV in energy to pass through. In a typical unshielded reactor irradiation position, the epithermal neutron flux represents about 2% the total neutron flux. Both thermal and epithermal neutrons induce (n, γ) reactions on target nuclei. The fast neutron component of the neutron spectrum (energies above 0.5 MeV) consists of the primary fission neutrons, which still have much of their original energy following fission. Fast neutrons contribute very little to the (n, γ) reaction, but instead induce nuclear reactions where the ejection of one or more nuclear particles – (n, p) , (n, n') , and $(\text{n}, 2\text{n})$ – are prevalent. In a typical reactor irradiation position, about 5% of the total flux consists of fast neutrons. Thermal and epithermal neutron fluxes are usually determined by $1/v$ – and resonance detectors (Fe, Al–Au, Al–Co, Nb, etc.) where the actual epithermal flux is approximated by the $1/E_{\text{n}}^{1+\alpha}$ function. Fast neutron fluxes are determined with a number of threshold reactions covering the 2–10 MeV energy range (Fe, Cu, Ti, Nb, Zr, etc.).

The samples for irradiation are normally put in glass, polythene, or aluminium containers. Comparison between these containers has been discussed by Sroor et al. (2000).

6.3.2 A Few Radioisotopes Formed Through (n, γ) Reaction (Used for Elemental Identification) and their Half-Lives

^{51}Cr (27.7 d)	^{76}As (26.3 h)	$^{110\text{m}}\text{Ag}$ (249.8 d)	^{177}Lu (6.7 d)
^{59}Fe (44.5 d)	^{82}Br (35.3 h)	^{113}Sn (115.1 d)	^{182}Ta (114.5 d)
^{60}Co (5.27 y)	^{86}Rb (18.6 d)	^{122}Sb (2.7 d)	^{198}Au (2.7 d)
^{65}Zn (243 d)	^{103}Ru (39.3 d)	^{131}Ba (11.8 d)	^{203}Hg (46.6 d)
^{65}Zn (243 d)	^{109}Cd (461.5 d)	^{134}Cs (2.06 y)	

6.3.3 Scintillation and Semiconductor γ -Ray Detectors

NaI(Tl) Scintillation Detector

NaI(Tl) scintillation detector consists of thallium (Tl) activated NaI crystal (having a small amount of impurity of Tl) which is optically coupled to a photomultiplier either directly or via a light guide. As the γ -rays interact with the scintillator material (through the process of photoelectric effect, Compton effect and pair production according to their energy range), the optical photons are produced due to fluorescence/phosphorescence. These light photons are then converted to an electrical pulse by the photomultiplier tube or a photo diode. The high atomic number of iodine in NaI gives good efficiency for γ -ray detection. The role of the impurity in inorganic scintillators is to produce luminescent centers energetically between the valence and conduction bands of the host crystal. The photomultiplier (PM) tube consists of a photocathode, a focusing electrode and 10 or more dynodes that multiply the number of electrons striking them several times each. The anode and dynodes are biased by a voltage divider circuit made through a chain of resistors, typically located in a plug-on tube base assembly. The commercially available NaI(Tl) detector includes a high resolution NaI(Tl) crystal, a photomultiplier tube, an internal magnetic/light shield and a chrome plated aluminum housing. The light shield around the photomultiplier is chrome plated (antimagnetic) mu metal. The tube base contains a high voltage divider network to supply all the necessary bias voltages for 10-stage PM tube and makes the integrally mounted assembly. A high voltage blocking capacitor is provided to couple the anode signal to a preamplifier. The best resolution achievable range from 7.5% to 8.5% for the 662 keV γ -ray from ^{137}Cs for 3 in. $\varnothing \times$ 3 in. long crystal, and is slightly worse for smaller and larger sizes. The bias supply needed for NaI(Tl) varies from 0 to $\pm 2,000$ V with current of 250 μA maximum.

The other inorganic crystals for γ -detection can be CsI(Tl), CsI(Na), LiI(Eu), $\text{Be}_4\text{Ge}_3\text{O}_{12}$ i.e., Bismuth Germanate (BGO), ZnS(Ag), and CdWO_4 . The energy conversion efficiency (or fraction of the γ -ray energy which appears as scintillation light) for NaI(Tl) is 12%, for CsI(Na) is 10%, and is 5% for CsI(Tl). Since the light output is low (about 200–300 eV is required for each optical photon), the energy resolution is also low. These detectors have

count rate capability up to 2×10^6 photons per second and for a scintillator thickness of more than 5 mm, the detection efficiency is essentially unity.

Ge(Li) and HpGe Semiconductor Detectors

Ge(Li) and hyper-pure Ge (HpGe) detectors are the semiconductor detectors. These are P–I–N diodes, in which the intrinsic (I) region is created by depletion of charge carriers when a reverse bias is applied across the diode. When a photon interacts in the intrinsic region, tracks of electron–hole pairs are produced (analogous to electron–positive ion pairs in a counting gas). In the presence of the electric field, these pairs separate and are swept rapidly to their respective collecting electrodes (detector contacts) by the electric field. The resultant charge is integrated by a charge sensitive preamplifier and converted to a voltage pulse with amplitude proportional to the original photon energy.

The average energy “ ϵ ” required to generate an electron-hole pair (2.95 eV for Ge) in a given semiconductor at a given temperature is independent of the type and the energy of the ionizing radiation. Since the forbidden band gap is 0.73 eV for Ge at 80 K, it is clear that not all the energy of the ionizing radiation is spent in breaking the covalent bonds. Some of it is ultimately released to the lattice in the form of phonons. To keep the leakage current low, the detector must have very few electrically active impurities. For example, Ge-detectors are made from zone-refined crystals that have fewer than 10^{10} electrically active impurities/cm³. They are usually cooled to reduce the thermal leakage current. Keeping the count rate limited to about 2×10^3 per second, the HpGe and Ge(Li) detectors have an energy resolution of ~ 1 keV (at 122 keV) and ~ 2 keV (at 1.332 MeV) respectively.

The attenuation of γ -rays in a material is caused by their interaction due to photoelectric, Compton and pair production effects and the total attenuation of the photon beam is given by $N = N_0 \exp(-\mu x)$. Since the depletion depth is inversely proportional to net electrical impurity concentration, and since counting efficiency is also dependent on the purity of the material, large volumes of very pure material are needed to ensure high counting efficiency for high energy photons. Prior to the mid-1970s the required purity levels of Ge could be achieved only by counter-doping P-type crystals with the N-type impurity, lithium, in a process known as lithium-ion drifting or lithium-drifting process for forming compensated material. This process is used in the production of Ge(Li) detectors but it is no longer required for HpGe detectors since sufficiently pure crystals have been available. Because of the greater sensitive region, the noise contribution from thermally generated electrons and holes is much reduced by cooling to liquid nitrogen temperatures. In intrinsic germanium detectors (called HPGe detectors) with impurity concentrations of less than 10^{10} atoms cm⁻³ have the advantage of not having to be kept at LN₂ temperature at all times. These are fabricated with n-type semiconductor rather than p-type required for the lithium drifting process. HPGe detector is used for low energy γ -ray detection.

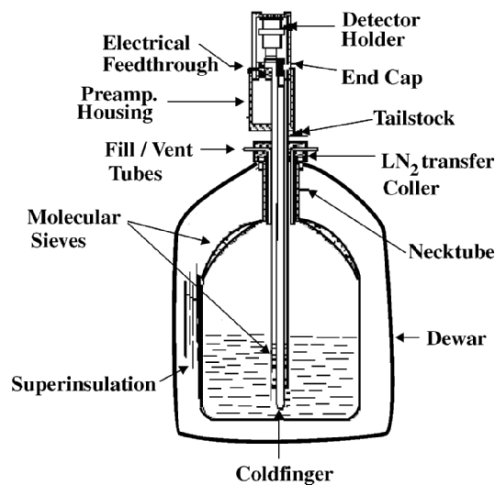


Fig. 6.2. Cross-sectional view of an HpGe/Ge(Li) semiconductors detector with a typical liquid nitrogen cryostat

In liquid nitrogen (LN₂) cooled detectors, the detector element (and in some cases preamplifier components), are housed in a clean vacuum chamber, which is attached to or inserted in a LN₂ Dewar. The detector is in thermal contact with the liquid nitrogen, which cools it to around 77°K or −200°C. At these temperatures, reverse leakage currents are in the range of 10^{-9} – 10^{-12} amperes. A cross-sectional view of a typical liquid nitrogen cryostat is shown in Fig. 6.2.

The first semiconductor photon detectors had a simple planar structure. The coaxial Ge(Li) detector was developed in order to increase overall detector volume, and thus detection efficiency, while keeping depletion (drift) depths reasonable and minimizing capacitance. The HpGe detector is made from germanium with impurity concentration in the range of 10^{10} atoms cc^{-1} which means that lithium drifting is not required to form sufficiently wide intrinsic or active region. The pure Ge-detectors can be warmed up or even stored at room temperatures. Semiconductor detectors provide greatly improved energy resolution over other types of radiation detectors for many reasons. Fundamentally, the resolution advantage can be attributed to the small amount of energy required to produce a charge carrier and the consequent large “output signal” relative to other detector types for the same incident photon energy. At 3 eV per e–h pair, the number of charge carriers produced in Ge is about one and two orders of magnitude higher than in gas and scintillation detectors, respectively. The charge multiplication that takes place in proportional counters and in the electron multipliers associated with scintillation detectors, resulting in large output signals, does nothing to improve the fundamental statistics of charge production. A Ge(Li) detector represents an extremely high source impedance ($\sim 10\text{ G}\Omega$) and appreciable capacitance (10–50 pF).

While Ge(Li) detectors are primarily used for γ -ray spectroscopy in the energy range of 50 keV to 10 MeV, the Planar pure Ge detectors have inherently good response down to very low energies (2–200 keV).

At low energies, detector efficiency is a function of cross-sectional area and window thickness while at high energies total active detector volume more or less determines counting efficiency. HpGe detectors, are usually equipped with a Be cryostat window to take full advantage of their intrinsic energy response. Coaxial Ge detectors are specified in terms of their relative full-energy peak efficiency compared to that of a 3 in. $\varnothing \times$ 3 in. thick NaI(Tl) scintillation detector at a detector to source distance of 25 cm. Because Ge has a lower Z than NaI, it will always have smaller interaction probability for photons and therefore smaller relative efficiency (the photoelectric absorption coefficient varies roughly as Z^5). While the resolution of a Ge(Li) detector at 1.332 MeV is ~ 2 keV, the efficiency of Ge(Li) detector is $\sim 20\%$ and the peak to Compton ratio $\sim 65:1$.

6.3.4 γ -Ray Spectrometer

The instrumentation used to measure γ -rays from radioactive samples consists of a semiconductor detector, associated electronics, and a computer-based multichannel analyzer as shown in Fig. 6.3.

Most of the NAA laboratories possess HpGe or Ge(Li) detectors which are used for the measurement of γ -rays with energies over the range from about 60 keV to 3.0 MeV. The two most important performance characteristics requiring consideration, when purchasing a detector, are its resolution and efficiency. Other characteristics to consider are peak shape, peak-to-Compton ratio, crystal dimensions or shape, and price. The detector's resolution is a measure of its ability to separate closely spaced peaks in a spectrum. In general, detector resolution is specified in terms of the full-width at half-maximum (FWHM) of the 122 keV photopeak of ^{57}Co , and the 1,332 keV photopeak of ^{60}Co . For most NAA applications, a detector with resolution of 1.0 keV or less at 122 keV and 2.0 keV or less at 1,332 keV is quite suitable. Detector efficiency depends on the energy of the measured radiation, the solid angle between sample and detector crystal, and the active volume of the crystal. A larger volume detector will have a higher efficiency. In general, detector efficiency is measured relative to a 3 in. $\times$ 3 in. NaI(Tl) detector using 1.332 MeV γ -ray from a ^{60}Co source placed at a distance of 25 cm from the crystal face.

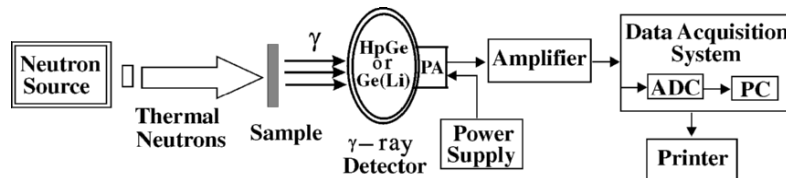


Fig. 6.3. γ -spectroscopy system used in neutron activation analysis

A general rule of thumb for germanium detectors is 1 percent efficiency per each 5 cc of active volume. As detector volume increases, the detector resolution gradually decreases. For most NAA applications, an HpGe detector of 15–30% efficiency is adequate. However, the Compton-suppression system comprising of the large area Ge(Li) detector surrounded by BGO/NaI(Tl) scintillation detectors is preferred to reduce the background and hence to improve signal-to-noise ratio. The comparative study for NaI, HpGe, and BGO carried out by Proctor et al. (1999) show that 5–10 times higher detection efficiency of a large size scintillation detector outweigh the resolution superiority of an HpGe detector for simple to medium complex bulk materials.

Since HpGe and Ge(Li) detectors require liquid nitrogen for cooling, these have the limitation to be used for field study. NaI(Tl) detectors do not require cooling but have the limitation of relatively poor resolution. For field applications e.g., the verification of nuclear material, the CdZnTe detectors have advantages of better resolution over NaI(Tl) detectors. However, since the CdZnTe detectors exhibit asymmetric peak shapes, particularly at high energies making automated peak fitting methods and sophisticated isotope identification programs difficult to use, Brutscher et al. (2001) have described the design and use of a semiautomated isotope identification program based on an interactive graphical method using CdZnTe detector.

For inter-comparison purposes of γ -ray spectra or for testing the computer software for γ -analysis, the IAEA has created a standard γ -spectrum using the progeny of ^{226}Ra i.e., decay chain products of ^{226}Ra including ^{222}Rn gas and other isotopes like ^{214}Pb , ^{214}Bi , ^{210}Pb , ^{210}Bi , etc. (Blaauw et al. 1997).

Typical γ -ray spectra from an irradiated pottery specimen are shown in Figs. 6.4–6.6 using two different irradiation and measurement procedures.

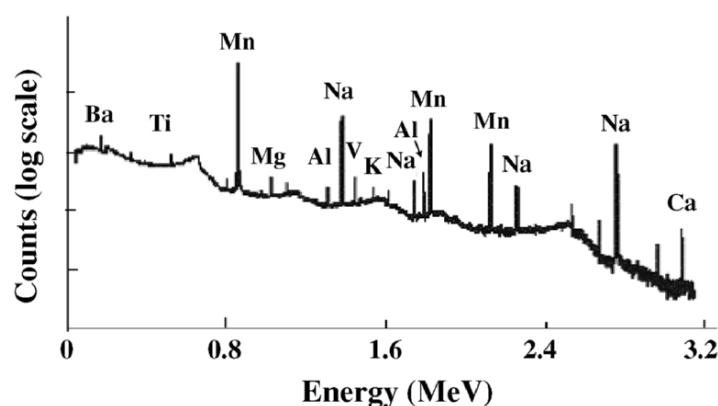


Fig. 6.4. γ -ray spectrum showing several short-lived elements measured in a sample of pottery irradiated for 5 s, decayed for 25 min, and counted for 12 min with an HpGe detector

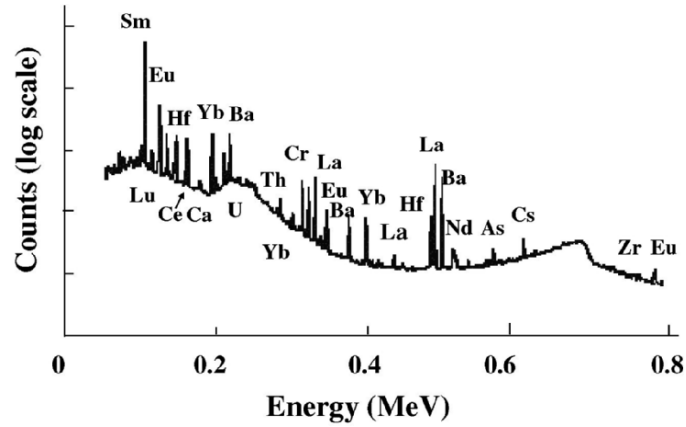


Fig. 6.5. γ -ray spectrum from 0 to 0.8 MeV showing medium- and long-lived elements measured in a sample of pottery irradiated for 24 h, decayed for 9 days, and counted for 30 min on an HpGe detector

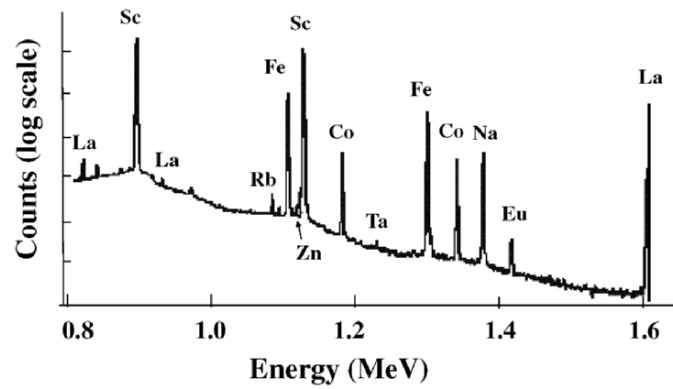


Fig. 6.6. γ -ray spectrum from 0.8 to 1.6 MeV showing medium- and long-lived elements measured in a sample of pottery irradiated for 24 h, decayed for 9 days, and counted for 30 min on an HpGe detector

6.4 Quantitative Analysis Using NAA

Assume that the sample has been activated and the measurements have to be done on this sample at $t = 0$. Since the induced activity is primarily the product of number of atoms ($\sim$ mass) of the element of interest, neutron capture cross-section and the neutron flux, this has to be corrected by multiplying with the fraction of the target isotope in the sample and saturation factor (determined by the half-life of the isotope formed and the time of irradiation). The induced activity of the sample will thus be given by

$$A_0 = \sigma \Phi \alpha S \left(\frac{m N_A}{M} \right) \quad (6.1)$$

where A_0 is the number of disintegrations per second of the element in the sample at $t = 0$ (when irradiation stops), σ is the neutron absorption cross-section in cm^2 ; $N (= mN_A/M)$ is the number of target elements (where m is the weight of the element in grams, N_A is the Avogadro number and M is the atomic weight of the element); Φ is the neutron flux in $\text{neutron cm}^{-2} \text{s}^{-1}$; α is the fraction of the target isotope in the sample (e.g. with an ordinary copper sample producing $^{63}\text{Cu}(n, \gamma)^{64}\text{Cu}$ reaction, $\alpha = 0.69$ since 69% of all natural copper is ^{63}Cu) and S is the saturation factor ($= 1 - e^{-\lambda t_i}$ where $\lambda = 0.693/T_{1/2}$, $T_{1/2}$ is the half-life for the reaction and t_i is the time of irradiation).

The activity of the sample after a cooling or delay period (t_d) from the end of the irradiation that lasted for time t_i is given by

$$A_{t_d} = \sigma \Phi \alpha S \left(\frac{mN_A}{M} \right) (e^{-\lambda t_d}) \quad (6.2)$$

Accounting for the number of radioactive nuclei that decay during counting interval t_c , the activity will be given as

$$A = \sigma \Phi \alpha S \left(\frac{mN_A}{M} \right) \cdot (e^{-\lambda t_d}) \cdot (1 - e^{-\lambda t_c}) \quad (6.3)$$

6.4.1 Absolute Method for a Single Element

If the irradiated sample is placed at distance 'r' from the detector of area D_A , the induced activity 'A' of the radioisotope formed in the sample, with N nuclei of a certain species as given by (6.3), can be measured through absolute method by measuring the area under the photopeak after subtracting the background i.e. ($\Sigma_p - \Sigma_b$) through the relation

$$(\Sigma_p - \Sigma_b) = \frac{A}{\lambda \cdot G \cdot \epsilon_p \cdot f} = \frac{\sigma \Phi \alpha S \left(\frac{mN_A}{M} \right) \cdot (e^{-\lambda t_d}) \cdot (1 - e^{-\lambda t_c})}{\lambda \cdot G \cdot \epsilon_p \cdot f} \quad (6.4)$$

where $G = D_A/2\pi r^2$; ϵ_p the intrinsic peak efficiency of the detector for the γ -ray energy; and f the decay fraction of the unknown activity. Since the nuclear decay processes occur at random and follow a Poisson distribution, the standard deviation (σ) equals to $(\Sigma_p - \Sigma_b)^{\frac{1}{2}}$. If μ is the mean of the distribution, the peak area, lying between $(\mu - \sigma)$ and $(\mu + \sigma)$, can be measured with 68% confidence. The confidence value becomes 95.5% for peak area lying between $(\mu - 2\sigma)$ and $(\mu + 2\sigma)$ and 99.7% for area lying between $(\mu - 3\sigma)$ and $(\mu + 3\sigma)$. The standard deviation is calculated by $\sigma = (\Sigma_p + \Sigma_b)^{\frac{1}{2}}$, where (Σ_b) is the background counts under the same number of channels for which the counts have been integrated to yield (Σ_p) .

The weight (m) of the unknown element in the sample can thus be calculated from (6.4). Apart from the counting statistics, the total error in NAA depends on a number of factors like sample preparation, weighing, and uncertainty in the basic parameters and amounts to $> 10\%$. This error can, however, be reduced by the comparison method described in Subsect. 6.4.2.

6.4.2 Comparison Method

The method is based on the simultaneous irradiation of the sample with standards of known quantities of the elements in question in identical positions, followed by measuring the induced intensities of both the standard and the sample in a well-known geometrical position. A relative standardization can be performed by means of individual monoelement standards, or by using synthetic or natural multielement standards. In the comparison method, one needs to correct the difference in decay between the unknown sample and the comparator standard. One usually decay corrects the measured counts (or activity) for both samples back to the end of irradiation using the half-life of the measured isotope. The equation used to calculate the mass of an element in the unknown sample relative to the comparator standard is

$$\frac{A_{\text{sam}}}{A_{\text{std}}} = \frac{m_{\text{sam}} (e^{-\lambda T_d})_{\text{sam}}}{m_{\text{std}} (e^{-\lambda T_d})_{\text{std}}} \quad (6.5)$$

where A_{sam} is the activity of the sample and A_{std} the activity of the standard, m is mass of the element, λ the decay constant for the isotope and T_d is the decay time. When performing short irradiations, the irradiation, decay and counting times are normally fixed to be the same for all samples and standards such that the time dependent factors cancel. Thus (6.5) simplifies to

$$C_{\text{sam}} = C_{\text{std}} \frac{W_{\text{std}}}{W_{\text{sam}}} \cdot \frac{A_{\text{sam}}}{A_{\text{std}}} \quad (6.6)$$

where C is the concentration of the element and W the weight of the sample (sam) and standard (std).

The accuracy of the relative method depends on the standard preparation procedure (e.g., nonstoichiometry of the standard compound, dilution, and micropipetting uncertainties). The disadvantage of the classic relative method lies in the multielement application. The procedure of the standard preparation and counting is rather laborious, and this is coupled with the occasional loss of information if an unexpected element appears for which no standard has been irradiated.

There are commercial multielement Standards Reference Materials (SRM) available, however, the use of home-made multielement standards can be an answer to these problems.

6.4.3 Simulation: MCNP Code

In large samples, the γ -ray count rate of a PGNA system is a multivariable function of the elemental dry composition, density, water, contents, and thickness of the material. The experimental calibration curves require tremendous laboratory work using a large number of standards with well-known compositions. The Monte Carlo simulation code MCNP helps to reduce the experimental standards as described by Oliveira et al. (1997) in their attempt to optimize the PGNA instrument design for cement raw materials.

6.5 Sensitivities Available by NAA

The sensitivity of NAA for a particular element depends on the irradiation parameters (i.e., neutron flux, irradiation, and decay times), measurement conditions (i.e., measurement time, detector efficiency), nuclear parameters of the elements being measured (i.e., isotope abundance, neutron cross-section, half-life, and γ -ray abundance). The accuracy of an individual NAA determination usually ranges from 10^{-3} to 10^{-10} grams per gram of sample. Accuracy of a NAA determination is usually between 2% and 10% of the reported value, depending on the element analyzed and its concentration in the sample.

The lower limit of detection using NAA is given as (Kruger 1971)

$$C_{\min} = \frac{A_e A_m(t) e^{\lambda t_d}}{60 f N t \Phi \sigma (1 - e^{-\lambda t_i})} \cdot \frac{\text{UF}}{w_s} \quad (6.7)$$

where A_e is the atomic number of the element, $A_m(t)$ the minimum detectable counts, t_d the delay time between start of count and end of irradiation, f the isotope natural abundance, 60 the factor to change dPm to dPs, N the Avogadro's number Φ the neutron flux in $\text{n cm}^{-2} \text{s}^{-1}$, σ the cross-section for (n, γ) reaction, w_s the sample weight in gm and UF is the unit factor ($= 10^6$ if $C_{\min}$ is in ppm or mg L^{-1}) (10^2 if $C_{\min}$ is in percent).

Table 6.4 lists the approximate sensitivities for determination of elements assuming irradiation in a reactor neutron flux of $1 \times 10^{13} \text{ n cm}^{-2} \text{s}^{-1}$.

Choosing optimum irradiation, decay, and counting times can improve sensitivity for many of the above significantly. However, some of the elements namely B, Be, Bi, C, Li, N, Nb, Ne, O, P, Pb, S, Si, and Tl are not ordinarily detected by this method.

Table 6.4. Approximate sensitivities for determination of elements

Sensitivity (in μg)	Elements in Order of Increasing Atomic Number Z (in Each Row)
10^{-3}	^{23}V , ^{58}Ce , ^{62}Sm , ^{63}Eu , ^{66}Dy , ^{71}Lu , ^{75}Re , ^{77}Ir
10^{-3} – 10^{-2}	^{25}Mn , ^{49}In
10^{-2} – 10^{-1}	^{13}Al , ^{67}Ho , ^{74}W , ^{79}Au
10^{-1} –1	^{17}Cl , ^{18}Ar , ^{21}Sc , ^{23}V , ^{27}Co , ^{29}Cu , ^{33}As , ^{34}Se , ^{35}Br , ^{47}Ag , ^{51}Sb , ^{53}I , ^{55}Cs , ^{57}La , ^{65}Tb , ^{68}Er , ^{69}Tm , ^{70}Yb , ^{72}Hf , ^{73}Ta , ^{90}Th , ^{92}U
1–10	^9F , ^{11}Na , ^{24}Cr , ^{28}Ni , ^{30}Zn , ^{31}Ga , ^{32}Ge , ^{36}Kr , ^{37}Rb , ^{38}Sr , ^{40}Zr , ^{42}Mo , ^{44}Ru , ^{45}Rh , ^{46}Pd , ^{48}Cd , ^{52}Te , ^{56}Ba , ^{58}Ce , ^{60}Nd , ^{64}Gd , ^{76}Os , ^{80}Hg
10 – 10^2	^{12}Mg , ^{14}Si , ^{15}P , ^{19}K , ^{20}Ca , ^{22}Ti , ^{26}Fe , ^{39}Y , ^{40}Zr , ^{50}Sn , ^{54}Xe , ^{78}Pt , ^{81}Tl , ^{83}Bi
10^2 – 10^3	^{10}Ne , ^{16}S , ^{19}K , ^{41}Nb , ^{50}Sn , ^{82}Pb

6.6 Applications of NAA

NAA has been vastly used in many areas of fundamental and applied research as well as industrial applications. The theme work of NAA is trace element “fingerprinting.” The different areas in which NAA is applied are mentioned in the following sections.

6.6.1 In Archaeology

The use of NAA to characterize archaeological specimens like pottery and to relate the artifacts to source materials through their chemical signatures is a well-established application. For example, the “fingerprinting” of obsidian artifacts by NAA is a nearly 100% successful method for determining prehistoric trade routes since sources of obsidian are easily differentiated from one another through their chemical compositions. Over the past decade, large databases of chemical fingerprints for clays, obsidian, and basalt have been accumulated through analysis of approximately 30 elements in each of more than 42,000 specimens. Multielemental analysis of ancient Indian coins undertaken by Rajurkar et al. (1993) using NAA shows the presence of As, Au, Sn, Ag, and Sb apart from the major element copper.

6.6.2 In Biochemistry

High-specific activity radiotracers, produced by neutron activation, have been used with great success to study biochemical processes in the small animal model. For example, ^{75}Se , having a specific activity of $1,000 \text{ Ci g}^{-1}$ has been used to advance the discovery of dependent enzymes and other biologically important proteins. Trace-element and mineral nutrition are important aspects of human and animal health. NAA has been used to characterize a wide variety of samples for their elemental content. The basic nutritional requirement at the cellular level can be studied using NAA and radiotracer techniques. NAA is one of the important methods that has been used to study nutritional bio-availability and absorption of essential trace elements in the human using enriched stable isotopes.

The nutritional importance of trace elements has grown rapidly during the last years mainly because of a better understanding of their biological functions. For determination of low concentration levels of Se, NAA is very expedient a sensitive multielement technique which is valuable for both homogeneity testing and certification analyses due to its high precision and accuracy. NAA procedure using the ^{75}Se isotope is used to study the needs of the food samples and applied for the determination of selenium levels in basic food ingredients.

6.6.3 In Ecological Monitoring of Environment

NAA method has been applied to study the concentration distributions of typical toxic heavy metals in small amounts of industrial type air particulate fractions. Generally, toxic components are distributed in two forms in the particulates, e.g., in a matrix involved form and in a surface deposited form of which the latter one can be considerably enriched. Brune (1973) has listed various methods for the determination of interference-free trace elements in water, biological specimens, and food sources by means of NAA involving the use of a cold neutron irradiation procedure.

Johnston and Martin (1997) carried out ^{226}Ra analysis of uranium mine waters by measuring 186 keV γ -ray of ^{226}Ra or measurement of ingrowing ^{222}Rn progeny. NAA technique has been used by Shuvayeva et al. (1998) for atmospheric elemental composition, which varies between % and parts per trillion (ppt). Alemon et al. (2004) has found NAA to be particularly useful in the analysis of airborne suspended particles in a study undertaken to characterize the particulate material in the environmental samples of Mexico city's Metropolitan. To verify the sizes of particles collected and their elemental composition Coal-fly-ash particles collected on coated and uncoated impaction substrates in USA were analyzed by NAA to estimate the significance of bounce-off and re-entrainment on to back-up filters (Ondov et al. 1978). The results indicate the presence of 20–30% of the volatile species of Mo, As, Sb, and Se, and all of the refractory elements in the coal-fly-ash. Al-Jundi (2000) has reported the results of analysis of sediments from several sites of the Zarka river in Jordan. The author has attributed the presence of Zn, Cr, As, V, Co, and Zr from textile, paint, and tier plants into the river in addition to the wastage discharges and water treatment stations.

6.6.4 In Microanalysis of Biological Materials

Samples such as hair, nails, blood, urine, and various tissues are analyzed by NAA for both essential and toxic trace elements (Bhandari et al. 1987, Lal et al. 1987). The analysis can be related to determine their effect on disease outcomes. These authors have reported that the diet and environment contribute largely towards the trace elements in the human body. It has been demonstrated in other works that the selenium concentration in human nails is an accurate monitor of the dietary intake of selenium. As a consequence, the nail monitor has been extensively used to study the protective effect of dietary selenium against cancer and heart disease in numerous prospective case-control studies. In another study by Kanabrocki et al. (1979) on human thumbnails in USA, using thermal NAA technique, the average concentration of metals studied in clinically symptom-free adult female and male subjects were found to be zinc, 184 vs. 153 ppm; chromium, 6.8 vs. 4.2; selenium, 0.9 vs. 0.6; gold, 2.6 vs. 0.4; mercury, 1.9 vs. 0.4; silver 0.7 vs. 0.3; cobalt, 0.07 vs. 0.04. In another study, the fluorine concentration in bone biopsy samples was

measured by measuring F/Ca ratio after irradiating the samples in a reactor to induce the $^{19}\text{F}(n, \gamma)^{20}\text{F}$ and $^{48}\text{Ca}(n, \gamma)^{49}\text{Ca}$ reactions (Mernagh et al. 1977) with minimum detection limit of $50 \mu\text{g g}^{-1}$. To demonstrate the applicability of epithermal NAA method for biological samples, Chisela and Brätter (1986) have determined trace elements Br, Fe, Cs, Rb, Se, Zn, and Co in human erythrocytes, urine, and blood samples.

NAA has proven to be a most suitable method for the quantitative determination of a wide variety of trace ($0.01\text{--}100 \mu\text{g g}^{-1}$) and ultratrace ($< 0.01 \mu\text{g g}^{-1}$) elements in biological materials (Cornelis 1985). In his review article Cohn (1992) has illustrated the applications of this technique of NAA in nutritional research.

6.6.5 In Forensic Investigations

Forensic laboratories are often called upon to analyze evidence for the investigation and prosecution of criminal cases. The excellent sensitivity of detection available by NAA facilitates analysis of the extremely small evidence samples (e.g., gunshot residues, bullet lead, glass, paint, hair, etc.) typically found at crime scenes (Krishnan 1976, Guinn 1982). Elemental analysis of hair is an important screening test for determining specific nutrient minerals and trace elements, which a body may be lacking. It can also readily reveal what toxic element pollutants such as lead, cadmium, mercury, aluminum, or arsenic one may be exposed to unknowingly. Since mercury does not show up well in blood or urine samples, this is one reason why hair analysis is used in forensic medicine. Weider Ben and Fournier (1999) have revealed that activation analyses at the Harwell Nuclear Research Laboratory of the University of Glasgow in 1960 authenticated hairs of Napoleon Bonaparte, taken immediately after his death, confirmed Napoleon's chronic arsenic poisoning. The doctors drew the inference that since the arsenic was found to be present in the hair of Napoleon Bonaparte, it implies that it came from the blood and food ingested. Confirming to the high levels of arsenic in Napoleon's hair taken in 1805, 1814 and 1821, the report by *Science et Vie* magazine attributes the presence of arsenic to be from a hair ointment or gunpowder or wallpaper paste.

6.6.6 In Geological Science

Analysis of rock specimens by NAA is helpful to geochemists in research on the processes involved in the formation of different rocks through the analysis of the rare earth elements and other trace elements. For example, the discovery of anomalously high iridium concentrations in 65-million-year old limestone deposits from Italy and Denmark have been accomplished by NAA. The NAA findings support the theory that extinction of the dinosaurs occurred soon after the impact of a large meteorite with the earth. The study of low concentration of U in stony and meteorites and trace elements in Apollo-II lunar rocks (Ganapathy et al. 1970) have been undertaken through NAA. Detection

of As, Sb, W, and Mo in silicate rocks using epithermal neutron irradiation has been reported by Sims and Gladney (1991) with detection limits of 5 ng g^{-1} for As, 10 ng g^{-1} for Sb and W and 50 ng g^{-1} for Mo. The simultaneous analytical determination of the platinum-group elements Pd, Pt, Ir, Os, and Ru, as well as Au, Se, As, Re, and Sb, in common silicate rocks of Canada using NAA technique has been reported by Brüggmann et al. (1990) with detection limits of 0.004 ppb for Au, 0.03 ppb for Ir and Re, 0.05 ppb for Sb, 0.2 ppb for As, 3 ppb for Pd, 1 ppb for Os, 1.5 ppb for Pt, 2 ppb for Ru, and 5 ppb for Se.

The thermal neutron activation technique has been applied by Borsaru and Mathew (1980) to find the concentration of Al_2O_3 in coal measuring the 1.78 MeV γ -ray produced from the reaction $^{27}\text{Al}(\text{n}, \gamma)^{28}\text{Al}$. In another study, these authors (Borsaru and Mathew 1982) applied the thermal neutron activation technique to bulk samples ($\cong 11 \text{ kg}$) of Australian black coal for the determination of alumina, silica, and ash. The determination of alumina was based on the reaction $^{27}\text{Al}(\text{n}, \text{p})^{27}\text{Mg}$ and counted the 0.844 MeV peak ($t_{1/2} = 9.4 \text{ min}$). Silica was determined by means of the reaction $^{28}\text{Si}(\text{n}, \text{p})^{28}\text{Al}$ and counting the 1.78-MeV peak ($t_{1/2} = 2.3 \text{ min}$) applying correction for the interference from alumina.

Bauxite ores in Nigeria have been analyzed for investigation of Al using a 5 Ci Am-Be neutron thermalized source (Indris et al. 1998). Due to the very inhomogenous nature of Au occurring in heavy-mineral concentrates, it is imperative to analyze the whole concentrate. The only method which can provide a multielement analysis and still retain the sample intact is INAA. The quantitative detection of gold in two Egyptian ores has been carried out by El-Taher et al. (2003) apart from detecting 31 trace elements.

6.6.7 In Material Science (Detection of Components of Metals, Semiconductors, and Alloys)

The behavior of semiconductor devices is strongly influenced by the presence of impurity elements either added intentionally (doping with B, P, As, etc.) or contaminants remaining due to incomplete purification of the semiconductor material during device manufacture. Small quantities of impurities present at concentrations below 1 ppb can have a significant effect on the quality of semiconductor devices. The impurity levels of interest are such that the NAA technique is often the only method with adequate sensitivity for measuring the impurity concentrations. For example, NAA has been used to identify and eliminate the sources of contamination in semiconductor devices produced by several different companies. To investigate the effectiveness of purification, the impurity analysis in PbI_2 crystal semiconductor has been done using NAA technique (Hamada et al. 2003). Zn concentrations of $2\text{--}51 \text{ ng g}^{-1}$ has been determined in high purity GaAs with NAA by Köhler et al. (2000) with minimum detection limits of 0.018 ng g^{-1} .

Figueiredo et al. (2002) has reported the determination of lanthanides (La, Ce, Nd, Sm) and other elements in metallic gallium by NAA. Grossbeck et al.

(1998) has carried out analysis of V–Cr–Ti alloys in terms of activation of impurities while Nair et al. (2004) has used NAA technique to determine the composition of some alloys.

6.6.8 In Soil Science, Agriculture, and Building Materials

Many agricultural processes such as control of fertilizers and pesticides are influenced by surface and sub-surface movement, percolation and infiltration of water. Stable activateable tracers, such as bromide, analyzed by NAA, have allowed the soil scientist to quantify the distribution of agricultural chemicals under a wide variety of environmental and land use influences. In one of the study on phosphate fertilizers in Egypt using NAA, Abdel-Haleem et al. (2001) have reported the presence of heavy metals Fe, Zn, Co, Cr, and Sc as well as rare earth elements La, Ce, Hf, Eu, Yb and Sm in the samples containing the phosphate fertilizer components (e.g., rock phosphate, limestone, and sulfur) from which fertilizer is produced as final output product. The measurement of Ca/Si concentration ratio in the concrete samples has been carried out using NAA with 5 Ci Am–Be neutron source (Khelifi et al. 1999).

6.6.9 For Analysis of Food Items and Ayurvedic Medicinal Materials

The concentrations of Br, Ca, Cl, Co, Cu, K, Mg, Mn, Na, and V in cereals, oils, sweeteners, and vegetables sold in Canada were determined with absolute instrumental NAA. These items also indicated the presence of I, Rb, S, and Ti (Soliman and Zikovsky 1999).

Leafy samples often used as medicine in the Indian Ayurvedic system and vegetables were analyzed by Naidu et al. (1999) for 20 elements (As, Ba, Br, Ca, Ce, Cr, Cs, Co, Eu, Fe, K, La, Na, Rb, Sb, Sc, Sm, Sr, Th, Zn) using this technique. Multielement analysis using NAA on cereals and pulses have also been carried out by Balaji et al. (2000).

A study on spinach and cabbage by NAA method was found to be reliable as compared to atomic emission spectrometry for measurement of Ce, Co, Mn, Na, Rb, Th, and V (Andrasi et al. 1998).

In their attempt to find the difference between the essential elements of Indian and US brands of tea leaves, Kumar et al. (2005) have determined the relative concentration of Mn, Na, Cu, K, and Br.

Trace elements Co, Cr, Fe, Rb, Se, and Zn which are important for their nutritional and/or toxicological properties have been determined using NAA by Gambelli et al. (1999) in some Italian diary products in order to evaluate the contribution of this food group to the quality of the diet.

6.6.10 Detection of Explosives, Fissile Materials, and Drugs

Neutron activation is an important technique in the study of significant concentrations of actinide and rare earth elements in the nuclear weapon waste.

For example, epithermal NAA has been shown to be a powerful tool in the characterization of uranium over a wide range of concentrations (sub-ppm to several percent) in samples which may also have a rare earth content of 10 percent or greater. Neutron Activation analysis has been used for the detection of explosives, fissile materials, and drugs. The application of landmines detection with an isotopic source or pulsed generator has been discussed in detail by Hussein and Waller (2000) and Csikai et al. (2004).

6.7 Advantages and Limitations of NAA

6.7.1 Advantages of NAA

Activation analysis measures the total amount of an element in a material without regard to chemical or physical form and has the following advantages:

- (1) Samples for NAA can be liquids, solids, suspensions, slurries, or gases. Samples do not have to be put into solution or vaporized.
- (2) One of the most important advantage of NAA is that it is nearly free of any matrix interference effects because the atoms of matrix are composed of H, C, O, N, P, and Si that do not form any radioactive isotopes. This makes the method highly sensitive for measuring trace elements. Thus the vast majority of samples are completely transparent to both the probe (the neutron) and the analytical signal (the γ -ray).
- (3) NAA is nondestructive in that the integrity of the sample is not changed in any manner by pre-chemistry or the addition of any foreign materials before irradiation – thus the problem of reagent-introduced contaminants is completely avoided.
- (4) NAA requires only small amounts (100–200 mg) of sample material.
- (5) The analytical approach for NAA for most elements of interest is primarily an instrumental technique and does not require any post irradiation chemistry. The amount of technician contact time per sample analysis being low, makes NAA an efficient and low cost analytical approach.
- (6) NAA is a multielement analytical technique in that many elements can be analyzed simultaneously in a given sample γ -spectrum without changing or altering the apparatus as is necessary in atomic absorption.
- (7) NAA is fast in that many samples can be irradiated at a given time for many elements and counted later on a given decay schedule.
- (8) *Sensitivity to trace elements:* The sensitivity obtained by activation analysis is a function of the neutron cross-section of the element in question, available neutron flux, length of irradiation, resolution of the detector, matrix composition, and the “total” sample size. Hence, increasing neutron fluxes, increased irradiation times, and the major advances in nuclear detector technology in the areas of increased efficiency and resolution have pushed the detection limits of most elements of interest to the very low levels.

6.7.2 Limitations of NAA

- (1) Interferences can occur when different elements in the sample produce γ -rays of nearly the same energy. Usually this problem can be circumvented by choosing alternate γ -rays for these elements or by waiting for the shorter-lived nuclide to decay prior to counting. The limit of detection for a particular element will depend upon the measured count rate of the γ -ray being monitored and the background upon which that γ -ray peak sits. The measured count rate for a given isotope can be increased by (a) increasing the detector efficiency (moving the sample closer to the detector) (b) increasing the irradiation time and (c) decreasing the decay time. The sensitivity of the measurement can in many cases be improved by increasing the overall signal or total number of counts. This is accomplished by simply increasing the measurement time.
- (2) The limit of detection for an element can be lowered if we increase the ratio of the activity of the γ -ray of interest to the background through any combination of steps (a), (b) or (c) mentioned in (1). Conversely, changing the detector efficiency, irradiation time, or decay time to cause a lower peak-to-background ratio will worsen the detection limit. The change in peak-to-background ratio is primarily a function of the activity of other isotopes produced in the neutron irradiation of the sample.
- (3) The most important limitation is that it takes a lot of time to complete a full analysis. Because all radioactive isotopes have different half-life times, they can be divided into three categories: short-lived nuclides (half-life time from less than 1 s up to a few hours), middle-living nuclides (half-life time of a few hours up to several days), and long-living nuclides (half-life time of several days up to weeks, months or even years). When one wants to measure the elements which form long half life radionuclides, one has to wait for a few weeks in order that the nuclides with short- and middle half-life times can decay and should not cause any interference, and make the detection limits better.

A few elements like Pb, Cu, Al, P, S, etc. have small capture cross-sections and short radioactive half-lives and are thus difficult to detect. The XRF technique has an advantage over NAA technique due to these reasons.

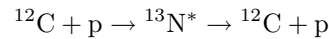
Nuclear Reaction Analysis and Particle-Induced Gamma-Ray Emission

7.1 Introduction

We have studied in Chap. 1 that the light elements, from hydrogen to fluorine, cannot be analyzed by PIXE and EDXRF techniques due to the limitation of detection by the Si(Li) X-ray detector. In Chap. 2, we have seen that the profiling of light elements in a heavy matrix by RBS method is limited since the RBS spectrum is dominated by the Z -dependence of the heavy element scattering cross sections. These low- Z elements can, however, be detected by carrying out nuclear reactions with accelerated particles, under resonance conditions, giving off secondary particles/ γ -rays. The nuclear reaction analysis (NRA) and particle-induced γ -ray emission (PIGE) are thus complementary to PIXE technique but unlike PIXE (which is based on X-ray emission i.e., atomic transitions), the NRA and PIGE are nuclear techniques as these are governed by the rules of nuclear reactions and kinematics. Contrary to PIXE and RBS where forces are electromagnetic and electrostatic, respectively, NRA and PIGE involve low-energy nuclear forces.

When the ion beam of energy more than the Coulomb barrier is made to impinge on the target, the energetic ions are able to perform nuclear reactions with target atoms, resulting in an excited nucleus. In NRA, the primary ion is absorbed by the analyte nucleus at some resonance energies and a different particle (usually a proton, neutron or α -particle) or γ -ray is promptly emitted. The recombination is monitored by means of the accompanying particle(s), which is then a measure for the amount of reaction partners in the sample. The energy of the reaction products is a function of the energy of the incoming ions. It is possible in this way to calculate the depth distribution of the atoms (that react with the incoming ions) from the energy distribution of the reaction products. The technique of NRA is also termed as nuclear resonance analysis if a nuclear reaction of the kind $^{12}\text{C}(\text{p}, \text{p})^{12}\text{C}$, which is carried out at the incident

protons of energy 1.7 MeV since in this case the elastic resonance occurs and scattered protons are emitted with the same energy but with much higher yield (as the cross-section is very high). The resonance is supposed to occur as follows:



The NRA technique is quite useful, though reactions are isotope specific and not broad based as in RBS. Most nuclear reactions have sharp resonance in the cross-section at certain energies. This fact is used to obtain a depth scale for the measured impurity concentration. Reactions with sufficiently large cross-sections exist for many elements. Among the light elements, there are several potentially useful reactions such as $^{19}\text{F}(\text{p}, \alpha)^{16}\text{O}$. In this case a ^{19}F nucleus absorbs a 1.25 MeV proton and promptly emits an 8.114 MeV α -particle. Measurement of the α energy thus indicates the depth from which it arose. Let us consider another example of the well-known resonance effect at 3.045 MeV for α -particles scattered from ^{16}O . The process is indistinguishable from elastic recoil except that the cross-section is many times greater. Although variable cross-sections resulting from higher beam energies complicate the analysis, the higher energies are useful in specific cases such as oxygen present as a single impurity in a thin layer.

The proton (particle)-induced γ -ray emission (PIGE) is restricted to the detection of γ -rays emitted in (p, γ) , $(\text{p}, \text{p}\gamma)$, and $(\text{p}, \alpha\gamma)$ reactions. The basic mechanism is the formation of a compound nucleus in a highly excited state that de-excites by the emission of gamma rays. Since all nuclear reaction processes do not result in the emission of γ -rays, the PIGE analytical technique can not be applied in every case. The limitation of this method is due to the fact that to have a nuclear reaction, the repulsive Coulomb barrier has to be surmounted. For light particles (proton, deuteron, He^3 , and He^4) of energy up to 3 MeV, the only accessible elements are the light elements with $Z < 15$. Indeed, the cross-sections become rapidly negligible for higher- Z elements. The similarity of NRA to PIGE lies in the fact that this technique is also restricted to the determination of light elements.

NRA is an excellent tool to study depth profiles of impurities in solids. It differs from charged particle activation analysis (CPAA) as the CPAA uses the accelerator to produce new radioactive nuclides, which are measured with the same instruments as used in the neutron activation analysis. This method is restricted to the determination of light elements. However, as the emitted charged particle reaction products have to exit from the material, the NRA method is more sensitive to the region near the surface. By measuring the energy spectrum of the emitted charged particles, a concentration vs. depth profile can be obtained for selected elements in the near surface region. The NRA technique has resolution of 50 Å, has sensitivity of 50 ppm (parts per million) and can detect up to 6 μm .

7.2 Principle of NRA

When the ion beam of energy more than the Coulomb barrier is made to impinge on the target, the energetic ions are able to perform nuclear reactions with target atoms, resulting in an excited nucleus. This is especially the case for light projectiles, impinging on light to medium heavy atoms, from accelerators used for material analysis in the energy range $\sim 1\text{--}5\text{ MeV u}^{-1}$. The yield of the prompt characteristic reaction products (γ , p, n, d, ^3He , ^4He , etc.) is proportional to the concentration of the specific elements in the sample. If γ -rays are among the reaction products the detection becomes extremely simple since a conventional detector (NaI(Tl), BGO, Ge(Li)) can be positioned outside the vacuum system. The products of the nuclear reaction or charged particles/ γ -rays, or both, are represented by an equation

$$a + X \rightarrow X^* \rightarrow Y + b + n\gamma \quad (7.1)$$

where “a” is the incident particle nucleus of mass M_1 impinging on the target nucleus “X” of mass M_2 . After the formation of compound nucleus X^* i.e., $(X + a)$, this transient nucleus dissociates to “Y”, the residual nucleus of mass M_3 called recoil nucleus and “b” is the emitted particle of mass M_4 along with “ $n\gamma$ ” cascade of n γ -rays emitted in the process due to the decay of excited compound nucleus. The principle of nuclear reaction analysis technique is shown in Fig. 7.1, where kinetic energy E_1 corresponds to impinging particle “a”, kinetic energy E_3 corresponds to scattered particle “b”, kinetic energy E_4 is carried by the recoil nucleus “Y”.

The excess kinetic energy of the final products or Q -value of the reaction corresponding to the excited state of the residual nucleus, is given by

$$Q = E_3 + E_4 + E_\gamma - E_1 \quad (7.2)$$

where E_1 and E_3 are the kinetic energies of the impinging and scattered particle, respectively, and E_4 is the kinetic energy of the recoil atom. E_γ is the energy of the emitted γ -ray. The nuclear reactions could be of endothermic ($Q < 0$) or exothermic ($Q > 0$) type. If $Q > 0$ then each E_1 generates

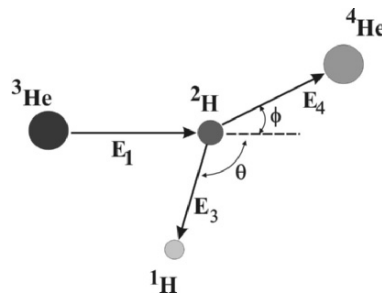
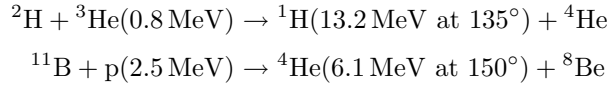
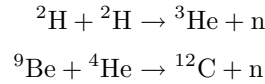


Fig. 7.1. Principle of nuclear reaction analysis technique

a reaction, but for low E_1 the cross-section is small. For $Q < 0$ there is a critical energy E_1 above which the reaction becomes possible. In the category of endothermic reactions, the important particle-particle reactions are $^2\text{H}(^3\text{He}, \text{p})^4\text{He}$, $^9\text{Be}(^3\text{He}, \text{p})^{11}\text{B}$, and $^{12}\text{C}(^3\text{He}, \text{p})^{14}\text{N}$ which take place at 800, 2,500 and 2,500 keV, respectively. Since the exothermic reactions result in high energetic reaction products, therefore for these types of reactions, the use of absorber foil in front of the detector and large area detectors (with large solid angles due to small reaction cross-sections) becomes necessary. A few examples of the particle-particle exothermic reactions are



The first reaction is used to measure concentration distributions of deuterium (^2H) beneath a surface by making the analysis through the $^2\text{H}(^3\text{He}, \text{H})^4\text{He}$ nuclear reaction. The problem with NRA is that it can result in high levels of radiations including the γ -radiations, neutron emission and the radiation caused by the activation of the sample. For example, the following unwanted reactions with deuterons and α -particles have high probability due to no energy threshold and high cross-sections above 2 MeV, respectively



NRA has the following characteristics:

Detectable Elements	H–Al
Standard conditions	~ 1 MeV proton beam (^{15}N , ^{19}F , etc. for H-detection) NaI-, Ge-detector ~ 15 min per measurement
Precision	composition: 5% relative
Sensitivity	ppm to % depending on element
Depth resolution	1–20 nm, probed depth $\sim \mu\text{m}$

7.2.1 Reaction Kinematics for NRA

If the total energy $E_{\text{T}} = E_1 + Q = E_3 + E_4$, it is simple to establish the following relations applying the laws of conservation of energy and momentum and using the reaction kinematics on the reactants and products (as shown in Fig. 7.1).

Ratio of the energy of light product w.r.t total kinetic energy

$$\frac{E_3}{E_{\text{T}}} = B \left[\cos \theta \pm \left(\frac{D}{B} - \sin^2 \theta \right)^{1/2} \right]^2$$

Ratio of the energy of heavy product w.r.t. total kinetic energy

$$\frac{E_4}{E_T} = A \left[\cos \phi \pm \left(\frac{C}{A} - \sin^2 \phi \right)^{1/2} \right]^2 \quad (7.3)$$

where

$$\begin{aligned} A &= \frac{M_1 M_4}{(M_1 + M_2)(M_3 + M_4)} \frac{E_1}{E_T} \\ B &= \frac{M_1 M_3}{(M_1 + M_2)(M_3 + M_4)} \frac{E_1}{E_T} \\ C &= \frac{M_2 M_3}{(M_1 + M_2)(M_3 + M_4)} \left(1 + \frac{M_1 Q}{M_2 E_T} \right) \\ D &= \frac{M_2 M_4}{(M_1 + M_2)(M_3 + M_4)} \left(1 + \frac{M_1 Q}{M_2 E_T} \right) \end{aligned} \quad (7.4)$$

It is to note that $A + B + C + D = 1$ and $AC = BD$. Most nuclear reactions, called resonant nuclear reactions, have sharp resonance in the cross-section at certain energies. The resonant cross-section width is of the order of several keV. This fact is used to obtain a depth scale for the measured impurity concentration and the technique is called *Resonant NRA*. Reactions with suitable cross-sections exist for many elements. The $^{15}\text{N}(^1\text{H}, \alpha\gamma)^{12}\text{C}$ nuclear reaction is widely used as a well established tool to measure hydrogen in all kinds of solids. On the other hand, in those cases where the nuclear reaction cross-sections vary slowly with energy, the technique employed is called *Non-Resonant NRA*. In such cases, taking NRA kinematics into account, the technique is identical to RBS.

For the nuclear reaction to take place, the kinetic energy E_1 of the charged particle must be sufficient to overcome the nuclear force, called the Coulomb barrier (B_C), given by

$$B_C = \frac{Z_1 Z_2}{\left(M_1^{1/3} + M_2^{1/3} \right)} \text{ MeV} \quad (7.5)$$

The Coulomb barrier is generally of the order of 1 MeV even in the case of interaction of singly charged particles with the lightest nuclei. Since the quantum mechanics provides with the finite probability for interaction, the under-barrier reactions (for impinging particles with energy below the potential barrier) are still possible. However, the penetrability of the Coulomb barrier increases very rapidly as E_1 approaches B_C .

The reaction (p, p'γ) can be a case of Coulomb excitation (inelastic Coulombs scattering) which occurs even if the energy of the projectile is below the Coulomb barrier. The projectile exchange energy with the target through the Coulomb interaction and the target is driven to excited state – therefore the de-excitation is through γ-emission. For nuclear reactions,

the impact parameter b [distance from the nucleus in the absence of the repulsive force which is further related to the distance of closest approach $d = Z_1 Z_2 e^2 / (8\pi\epsilon_0 \cdot E_1)$], should be less than the nuclear radius R and $E_1 > B_C$. Above the Coulomb barrier, the observed experimental spectra becomes more and more complicated due to overlapping energies of various reaction products (which are caused due to the opening up of more and more exit channels) because of large available excitation energy. As the emitted charged particle reaction products have to exit from the material, the NRA method is most sensitive to the region near the surface. By measuring the energy spectrum of the emitted charged particles, a concentration vs. depth profile can be obtained for selected elements in the near surface region.

The theoretical calculations for nuclear reaction probability can be made through optical model in which the target nucleus is represented by the complex potential comprising of the real and imaginary parts. The interaction of the projectile with the target nucleus is then reduced to de-Broglie's wave scattering (through real part of the complex potential) and absorption (through imaginary part of the complex potential) by the opaque sphere. The details of the optical model can be seen in the text book of nuclear physics. Calculations in the framework of the optical model are very sensitive to the parameters concluded as follows:

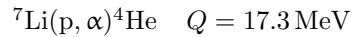
- (a) The strength parameter has strong energy dependence in the vicinity of the Coulomb barrier
- (b) The radial dependence of the real part of potential is more complicated than Saxon-Woods form
- (c) The imaginary part of the potential reveals nonsystematic dependence on nuclear mass number
- (d) Absorption is peaked at the nuclear surface

The reference input parameter library of optical model parameters for low energy proton scattering, required for calculation, is available with International Atomic Energy Agency (IAEA) Vienna Austria.

7.2.2 Examples of Some Important Reactions

Proton-Induced Reactions

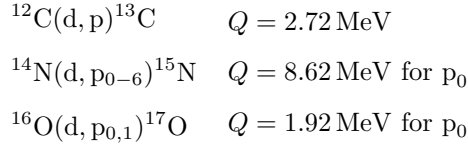
Proton-induced nuclear reactions, with positive Q -values, occur for almost all light elements. Some of these nuclear reactions are:



In some cases a number of reactions may be possible e.g., isotopic ratio of ${}^6\text{Li}$ and ${}^7\text{Li}$ has been determined by using the yield of ${}^6\text{Li}(\text{p}, {}^3\text{He})\alpha$, ${}^6\text{Li}(\text{p}, \alpha){}^3\text{He}$ and ${}^7\text{Li}(\text{p}, \alpha)\alpha$ reactions (Isobe et al. 2000).

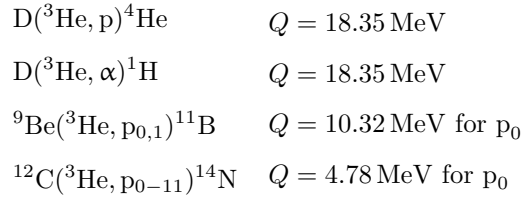
Deuteron-Induced Reactions

Deuteron-induced nuclear reactions, with positive Q -values, occur for almost all light elements. Although (d, p) , (d, α) and $(d, {}^3\text{He})$ reactions are possible but prominent among these are the (d, p) reactions. A few examples of the deuteron-induced reactions are



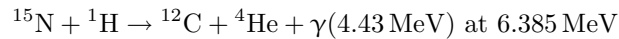
The (d, α) reactions are preferred over the (d, p) reactions because the later have low stopping power for incident deuterons and exit proton channels and are thus not suitable for depth profiling. Differential cross-sections for nuclear reactions ${}^{14}\text{N}(d, p_5){}^{15}\text{N}$, ${}^{14}\text{N}(d, p_0){}^{15}\text{N}$, ${}^{14}\text{N}(d, \alpha_0){}^{12}\text{C}$ and ${}^{14}\text{N}(d, \alpha_1){}^{12}\text{C}$ induced by deuterons from 0.5 to 2 MeV have been reported by Pellegrino et al. (2004).

${}^3\text{He}$ - and ${}^4\text{He}$ -Induced Nuclear Reactions



NRA for Analysis of Hydrogen

For hydrogen analysis, the NRA technique makes use of the following resonant reaction:



The beam energy is varied as in all resonance methods. The yield of γ -radiations becoming maximum at 6.385 MeV is indicative of the presence of hydrogen in the sample.

The ${}^1\text{H}({}^{15}\text{N}, \alpha\gamma){}^{12}\text{C}$ resonant nuclear reaction has been used by Fallavier et al. (1992) to measure the hydrogen coverage on the (110) and (111) faces of $\text{Pt}_{0.5}\text{Ni}_{0.5}$ single crystals. Similarly, the stoichiometry of the surface layer of Float glass (which is an important kind of commercial glass used in buildings and automobiles or other vehicles and is produced in the so-called float process, in which the glass melt floats on a bath of molten tin while cooling and solidifying) differs from that of the bulk and will sometimes change due to

subsequent high-temperature process steps and attack by water or humidity. Float glass samples which had undergone a defined hydration treatment were investigated by means of NRA (^{15}N technique) by Laube and Rauch (1995).

NRA for Analysis of Carbon

The reaction cross-section of the $^{12}\text{C}(\text{p}, \text{p})^{12}\text{C}$, $^{12}\text{C}(\text{d}, \text{p})^{13}\text{C}$ and $^{12}\text{C}(\alpha, \alpha)^{12}\text{C}$ at an angle of 150° have been measured by Jiang et al. (2004) over relevant energy regions using thin films of carbon ($5.8 \mu\text{g cm}^{-2}$) on silicate glass for NRA applications. A detailed study of the $^{\text{nat}}\text{C}(\text{d}, \text{d}_0)$ reaction has been presented by Kokkoris et al. (2006) for deuteron energy $E_{\text{d}} = 900\text{--}2,000 \text{ keV}$ and for detector angles between 145° and 170° . This reaction complements the implementation of the $^{12}\text{C}(\text{d}, \text{p}_0)^{13}\text{C}$, when NRA spectra are required for carbon profiling. Ion beam analysis of diamond-like carbon films have been done by Hirvonen et al. (1996) using a resonance of the nuclear reaction $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$.

NRA for Analysis of Nitrogen

The cross-section of the $^{14}\text{N}(\alpha, \text{p}_0)^{17}\text{O}$ reaction for NRA applications was measured by Giorginis et al. (1996) for α -particle energies between 4 and 5 MeV at laboratory scattering angle of 135° . The value of the resonance energy has been found to be $4,441 \pm 5 \text{ keV}$. The depth distribution of 30 keV implanted ^{15}N and ^{14}N were measured by using the resonance reaction $^{15}\text{N}(\text{p}, \alpha\gamma)^{12}\text{C}$ at resonance energy of 429 keV by Rose et al. (1993) while the depth profiling of implanted nitrogen isotopes, into Si/C and Zr/C bilayers, has been carried out by Miyagawa et al. (2000) using $^{15}\text{N}(\text{p}, \alpha\gamma)^{12}\text{C}$ and $^{14}\text{N}(^3\text{He}, \alpha)^{13}\text{N}$ nuclear reactions. To apply the data of nuclear reactions for NRA analysis, Pellegrino et al. (2004) have measured differential cross-sections for $^{14}\text{N}(\text{d}, \text{p}_5)^{15}\text{N}$, $^{14}\text{N}(\text{d}, \text{p}_0)^{15}\text{N}$, $^{14}\text{N}(\text{d}, \alpha_0)^{12}\text{C}$ and $^{14}\text{N}(\text{d}, \alpha_1)^{12}\text{C}$ using Si_3N_4 films (thickness 70 nm) induced by deuterons from 0.5 to 2 MeV.

NRA for Analysis of Oxygen

The reaction $^{16}\text{O}(\text{d}, \text{p}_1)^{17}\text{O}$ has been used by Wong et al. (1992) to measure the relative and absolute content of oxygen in thin films of superconductor YBaCuO grown on a substrate MgO, SrTiO_3 , etc. containing oxygen. The cross-sections for the analysis of oxygen using $^{16}\text{O}(\text{d}, \text{p}_1)^{17}\text{O}$, $^{16}\text{O}(\text{d}, \alpha)^{14}\text{N}$, $^{16}\text{O}(\alpha, \alpha)^{16}\text{O}$ over energies ranging from 0.701 to 1.057 MeV for d^+ ions and 2.949 to 3.049 MeV for H^+ ions have been reported by Jiang et al. (2003). The ^{18}O which has abundance of only about 0.2% of the natural oxygen, can be detected through the reaction $^{18}\text{O}(\text{p}, \alpha)^{15}\text{N}$, the resonance for which occurs at 629 keV.

7.3 Particle-Induced γ -Emission Analysis

In low energy encounters between ions and atoms, the Coulomb repulsion between the charged ion and the nucleus of the atom prevent any close interaction between the ion and the nucleus. However, MeV energy protons can penetrate the Coulomb barrier on light elements and induce various nuclear reactions. Thus the ions penetrate and excite the nuclei of specimen when irradiated with the ion beam. During the de-excitation process these excited nuclei emit γ -rays. The energies of these γ radiations are characteristic to the nuclei emitting them. The composition of the sample can thus be determined by measuring the yield of γ photons. The energy and intensity of the emitted γ photons is measured by Ge(Li) semiconductor detector which has energy resolution of about 2–3 keV at 1,173 keV of ^{60}Co photons. The best sensitivity can be reached for elements with atomic number in the range of $3 < Z < 20$. Since the heavier elements cannot be detected by PIGE, therefore the PIGE method is usually combined with the PIXE technique.

The PIGE technique is conveniently applied to the analysis of thick samples. The application of the PIGE technique to the multielement analysis of thin samples is most troublesome because of the strong energy dependence of prompt γ -reaction cross-section which makes it difficult to find an energy interval (as wide as the energy loss of protons in thin samples) where the cross-sections are high and constant enough. Compared to PIXE, the PIGE cross-sections are even some orders of magnitude lower and they drastically drop at increasing atomic number Z of the element due to increased Coulomb repulsion. Contrary to PIXE and RBS methods, PIGE does not show continuous sensitivity. Each element is a special case depending on the possibility or not of a reaction and furthermore on its cross-section which also depends on the energy of the impinging particle. The phenomenon of PIGE is shown in Fig. 7.2.

In the analysis of light elements by PIGE, the reactions by Coulomb excitation ($p, p'\gamma$) are common. The resonance nuclear reactions (p, γ), ($p, \alpha\gamma$) are used occasionally for the depth-profile.

Measurements of γ -ray emission induced by protons on fluorine and lithium have been carried out by Cacioli et al. (2006) who measured the γ -ray yields of the reactions $^{19}\text{F}(p, p'\gamma)^{19}\text{F}$ ($E_\gamma = 0.110, 0.197, 1.24, 1.35, 1.36$ MeV), $^{19}\text{F}(p, \alpha\gamma)^{16}\text{O}$ ($E_\gamma = 6.13, 6.92, 7.12$ MeV), $^7\text{Li}(p, n\gamma)^7\text{Be}$ ($E_\gamma = 429$ keV) and $^7\text{Li}(p, p'\gamma)^7\text{Li}$ ($E_\gamma = 478$ keV) for proton energies from 3.0 to 5.7 MeV using a $50 \mu\text{g cm}^{-2}$ LiF target evaporated on a self-supporting thin C-film. The γ -rays were detected by a 38% relative efficiency Ge detector placed at an angle of 135° with respect to the beam direction. Absolute γ -ray differential cross-sections were obtained for all the listed reactions with an overall uncertainty of $\pm 15\%$.

Table 7.1 lists some of the nuclear reactions which are commonly used in PIGE analysis.

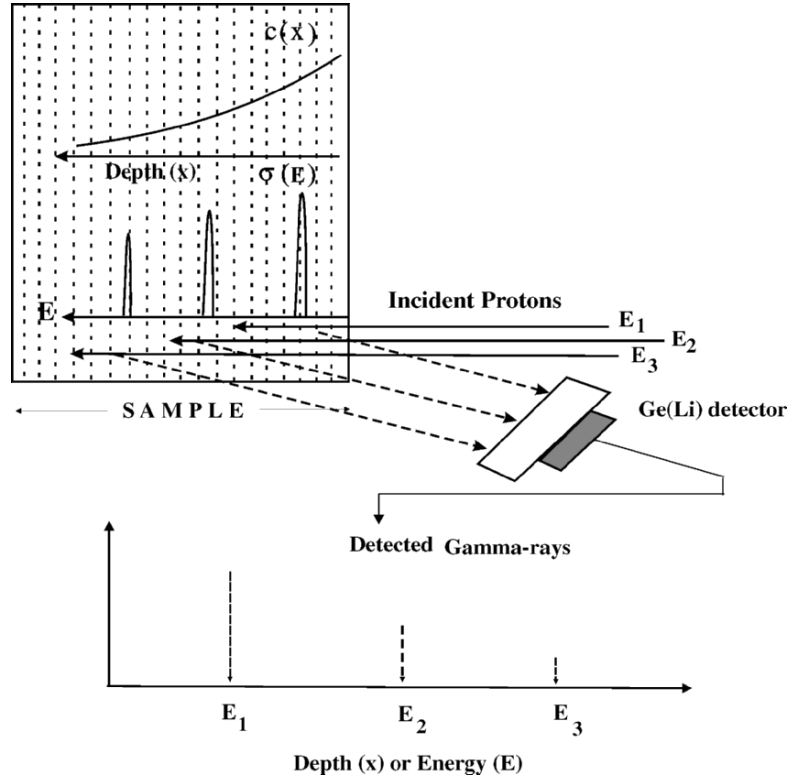


Fig. 7.2. Phenomenon of proton-induced γ -ray emission (PIGE)

7.4 Experimental Methods

Since the NRA and PIGE methods are based on the application of ion-beam for sample analysis, the basic experimental technique revolves around the use of accelerator, beam transport system, scattering chamber, detectors, and electronics circuitry. The experimental set-up has already been explained in Chaps. 1 and 2. For the detection of charged particles in NRA, one needs to employ the particle detection and energy measurement using solid-state surface barrier detector. In addition to this, one will need thicker detector or an absorber foil(s) in front of the detector. However this suffers from degraded depth resolution. More than one detector will be required due to the optimum reaction angle. Another method of particle detection can be by using magnetic or electrostatic analyzers. These type of spectrometers provide a very good resolution but suffer from their large and complicated set-up. Telescopes (combinations of two or more Si detectors) are also used to determine the charge (Z) and mass (A) of the particle by what is called the time-of-flight technique. This technique has excellent depth resolution but needs large particle flux due to small solid angle.

Table 7.1. Some of the commonly used nuclear reactions used in PIGE analysis

Reaction	E_γ (keV)	Reaction	E_γ (keV)
${}^7\text{Li}(\text{p}, \text{n}\gamma){}^7\text{Be}$	429	${}^{27}\text{Al}(\text{p}, \text{p}'\gamma)$	843, 1013
${}^7\text{Li}(\text{p}, \text{p}'\gamma)$	478	${}^{27}\text{Al}(\text{p}, \alpha\gamma){}^{24}\text{Mg}$	1368
${}^9\text{Be}(\text{p}, \gamma){}^{10}\text{B}$	3562	${}^{27}\text{Al}(\text{p}, \gamma){}^{28}\text{Si}$	1778
${}^{10}\text{B}(\text{p}, \alpha\gamma){}^7\text{Be}$	429	${}^{28}\text{Si}(\text{p}, \text{p}'\gamma)$	1779
${}^{10}\text{B}(\text{p}, \text{p}'\gamma)$	717	${}^{29}\text{Si}(\text{p}, \text{p}'\gamma)$	1273, 755
${}^{11}\text{B}(\text{p}, \text{p}'\gamma)$	2125	${}^{30}\text{Si}(\text{p}, \text{p}'\gamma)$	2234
${}^{15}\text{N}(\text{p}, \alpha\gamma){}^{12}\text{C}$	4439	${}^{31}\text{P}(\text{p}, \text{p}'\gamma)$	1266
${}^{18}\text{O}(\text{p}, \text{p}'\gamma)$	1982	${}^{31}\text{P}(\text{p}, \alpha\gamma){}^{28}\text{Si}$	1,778
${}^{19}\text{F}(\text{p}, \text{p}'\gamma)$	110, 197, 1236, 1349, 1357	${}^{31}\text{P}(\text{p}, \gamma){}^{32}\text{S}$	2,230
${}^{19}\text{F}(\text{p}, \alpha\gamma){}^{16}\text{O}$	6129	${}^{32}\text{S}(\text{p}, \text{p}'\gamma)$	2230
${}^{23}\text{Na}(\text{p}, \text{p}'\gamma)$	440	${}^{33}\text{S}(\text{p}, \text{p}'\gamma)$	841
${}^{23}\text{Na}(\text{p}, \gamma){}^{24}\text{Mg}$	1368	${}^{34}\text{S}(\text{p}, \gamma){}^{35}\text{Cl}$	1220
${}^{23}\text{Na}(\text{p}, \alpha\gamma){}^{20}\text{Ne}$	1635	${}^{35}\text{Cl}(\text{p}, \text{p}'\gamma)$	1220, 1763
${}^{24}\text{Mg}(\text{p}, \text{p}'\gamma)$	1368	${}^{37}\text{Cl}(\text{p}, \alpha\gamma){}^{34}\text{S}$	2127
${}^{25}\text{Mg}(\text{p}, \text{p}'\gamma)$	586	${}^{41}\text{K}(\text{p}, \alpha\gamma){}^{38}\text{Ar}$	2168

When neutrons are emitted as emergent particles, these are detected by nuclear interactions that produce secondary charged particles (e.g., BF_3 detector makes use of ${}^{10}\text{B}(\text{n}, \alpha){}^7\text{Li}$ reaction to detect neutrons). Liquid scintillators can measure both neutrons and γ -rays. However, by carefully measuring the shape of the electronic signal, it is possible to distinguish between these two types of particles.

Figure 7.3 shows the NRA spectrum using deuteron beam (E_d) of 650 keV. In this spectrum, since the peaks correspond to the line spectrum of ejected protons, the peak corresponding to ${}^{12}\text{C}(\text{d}, \text{p}){}^{13}\text{C}$, two peaks (p_0) and (p_1) corresponding to ${}^{16}\text{O}(\text{d}, \text{p}){}^{17}\text{O}$, and two peaks (p_{6-7}) and (p_8) corresponding to ${}^{28}\text{Si}(\text{d}, \text{p}){}^{29}\text{Si}$ have been observed. As shown in the level scheme of ${}^{17}\text{O}$ represented in Fig. 7.4, the two peaks (p_0) and (p_1) corresponding to ${}^{16}\text{O}(\text{d}, \text{p}){}^{17}\text{O}$ reaction, are the proton peaks corresponding to two proton groups: p_0 (ending in the ground state of ${}^{17}\text{O}$) and p_1 (ending in the 1st excited state of ${}^{17}\text{O}$, often denoted ${}^{17}\text{O}^*$). A γ -ray at 0.870 MeV is also observed when the ${}^{17}\text{O}$ decays to the ground state. In fact, at 150° and with deuteron beam energy (E_d) ~ 1 MeV, the intensity of p_1 is almost 10 times that of p_0 . Similarly, p_{6-7} and p_8 are the proton peaks in the reaction ${}^{28}\text{Si}(\text{d}, p_{6-7}){}^{29}\text{Si}$ and ${}^{28}\text{Si}(\text{d}, p_8){}^{29}\text{Si}$, respectively. From the observed spectrum, one can identify the presence of ${}^{12}\text{C}$, ${}^{16}\text{O}$, and ${}^{28}\text{Si}$ in the sample. The concentration of these elements, however, can be calculated using the data of reaction cross-section for each reaction.

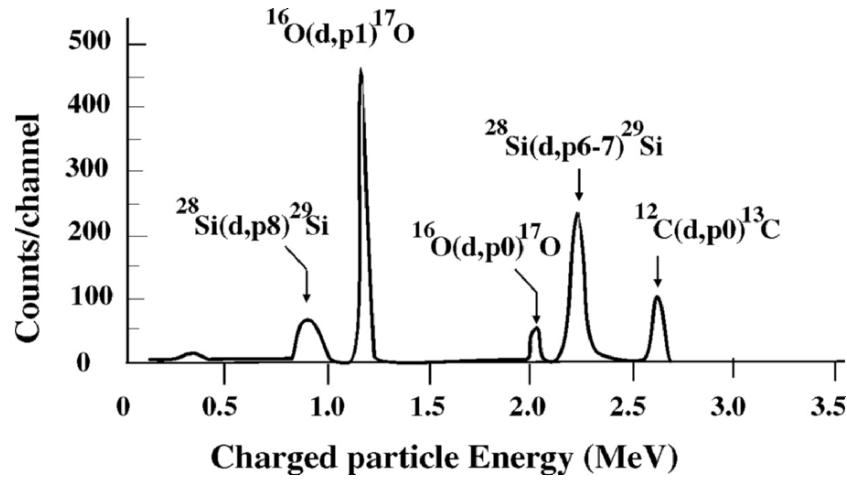


Fig. 7.3. Typical spectrum for a sample containing ^{12}C , ^{16}O and ^{28}Si using deuteron beam of 650 keV for nuclear reaction analysis

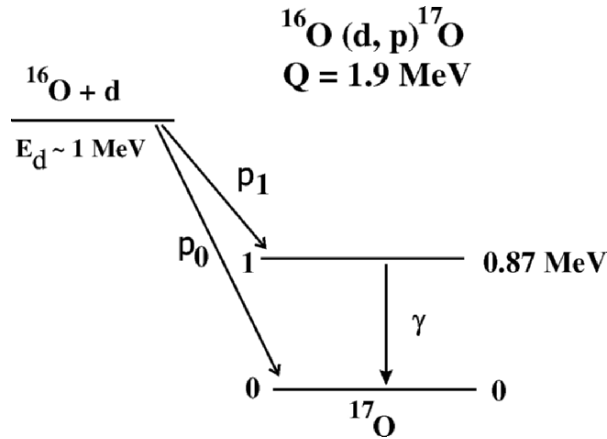


Fig. 7.4. Level scheme of ^{17}O to show two energies of protons emitted by $^{16}\text{O} + \text{d}$ in nuclear reaction $^{16}\text{O}(\text{d}, \text{p})^{17}\text{O}$

In the PIGE technique one needs to use the scintillation detector like NaI(Tl) or better resolution semiconductor detectors like HpGe or Ge(Li) for the detection of γ -rays. The detailed description of these detectors has been given in Sect. 6.3.3 of Chap. 6. The γ -rays are usually detected by Ge(Li) detector (FWHM ≈ 2 keV and 20% efficiency at 1.332 MeV). Although the NaI(Tl) detector has a better efficiency over Ge(Li) yet it is not preferred due to poor resolution. The energy and efficiency calibration of the γ -spectrometers can be done using the energy and intensity values of various transitions of the standard radioactive sources listed in the Appendix A.

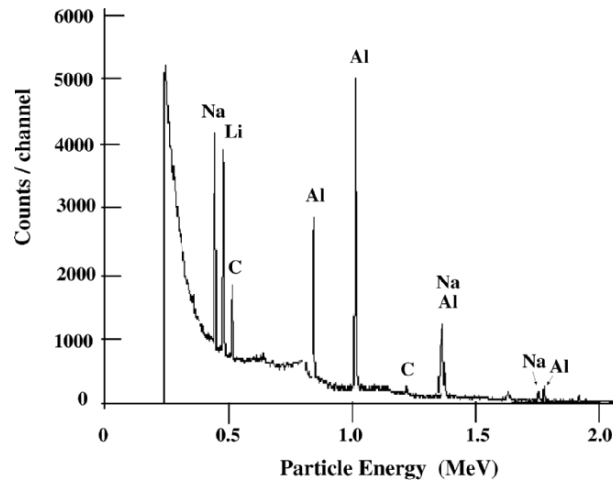


Fig. 7.5. Typical PIGE spectrum for a matrix composed of C, Na, Al, and Li using proton beam of 2.2 MeV

The PIGE method cannot determine profile concentration because the γ -ray beam is only attenuated in intensity and its energy is not diminished when it returns to the surface. Nonetheless, profile information can be obtained by using (p, γ) reactions with cross-sections that present a strong resonance. Since PIGE is also used to determine light element concentrations in surfaces, this makes it an ideal complementary technique to PIXE. A typical PIGE spectrum for a matrix composed of C, Na, Al and Li, is shown in Fig. 7.5. The peaks of 0.439 and 0.478 MeV used to determine Li and Na concentrations are well separated due to good resolution of the Ge(Li) detector.

In the case of overlap of γ -ray lines of different elements in a multielement sample, the elements are recognized from the nonoverlapping lines and the possibility of the existence of the corresponding line in the overlap. Bodart et al. (1977) have measured the intensity of the 439 keV γ -ray due to $(p, p'\gamma)$, 1368 keV γ -ray due to (p, γ) and 1634 keV γ -ray due to $(p, \alpha\gamma)$ reaction, caused by proton bombardment on the thick NaCl target, using a Ge(Li) detector placed at 90° . The 439 keV γ -ray is really characteristic of ^{23}Na and no interference is known for this γ -ray at proton energies lower than 3 MeV. Since the 1,368 keV γ -ray can also be produced by the bombardment of Al and Mg and the 1,634 keV γ -ray by the bombardment of F and Na, the 439 keV γ -ray can be used for trace analysis of Na, taking advantage of its high intensity.

Table 7.2 lists the prompt γ -reactions and the energies of the corresponding emitted γ -rays measured with the energy spread proton beam in the proton energy range 3.2–3.6 MeV with a 20 keV step for an irradiation of $60 \mu\text{C}$ proton.

Table 7.2. Prompt γ -reactions and the energies of the emitted γ -rays

Element to be detected	Nuclear Reaction	E_γ (keV)	Detection Limit ($\mu\text{g cm}^{-2}$)
Li	${}^7\text{Li}(\text{p}, \text{p}'\gamma){}^7\text{Li}$	478	0.001
B	${}^{10}\text{B}(\text{p}, \alpha\gamma){}^7\text{Be}$	429	0.3
B	${}^{11}\text{B}(\text{p}, \text{p}'\gamma){}^{11}\text{B}$	2125	0.6
F	${}^{19}\text{F}(\text{p}, \text{p}'\gamma){}^{19}\text{F}$	110	0.003
Na	${}^{23}\text{Na}(\text{p}, \text{p}'\gamma){}^{23}\text{Na}$	440	
Mg	${}^{25}\text{Mg}(\text{p}, \text{p}'\gamma){}^{25}\text{Mg}$	585	0.2
Mg	${}^{24}\text{Mg}(\text{p}, \text{p}'\gamma){}^{24}\text{Mg}$	1369	0.085
Al	${}^{27}\text{Al}(\text{p}, \text{p}'\gamma){}^{27}\text{Al}$	1014	0.09
Si	${}^{28}\text{Si}(\text{p}, \text{p}'\gamma){}^{28}\text{Si}$	1779	0.25
P	${}^{31}\text{P}(\text{p}, \text{p}'\gamma){}^{31}\text{P}$	1226	0.05

7.5 Detection Limit/Sensitivity

The sensitivity S is the yield measured as the ratio of the number of counts per unit charge to the element unit mass per unit sample area. The detection limits can be calculated as $3(N_b)^{1/2}/S$ where N_b is the number of counts in the background within an energy interval of FWHM both on left and right side around the γ -peak.

A special important advantage of the PIGE method is its ability to determine accurately at the same time C, N, and O, which are the major structural elements of biomedical and organic samples. However when analyzing such samples the use of an external beam is essential. The γ -ray spectrum analysis program such as SAMPO (Aarnio et al. 1984) can be used for photo-peak analysis of γ -ray spectra obtained with semiconductor detectors. This code includes subroutines for peak-search (which makes use of iterative least square fitting based on Marquardt algorithm), peak-fitting and peak intensity and energy determinations. It also makes complete statistical and calibration-error estimates. A linear or quadratic background function is used, while the peak shape is represented by an asymmetric Gaussian joined to an exponential right-hand tail and a double exponential left-hand tail. A subroutine of the program SAMPO-80 (developed at the Helsinki University of Technology, Finland) in Fortran IV carries out radioisotope identification and elemental mass determination after simple or cyclic thermal activation analysis.

Mateus et al. (2005) have recently developed a code for the quantitative analysis of light elements in thick samples by PIGE. The method avoids the use of standards in the analysis, using a formalism similar to the one used for PIXE analysis, where the excitation function of the nuclear reaction related to the γ -ray emission is integrated along the depth of the sample. To check the validity of the code, these authors have presented results for the analysis of lithium, boron, fluorine and sodium in thick samples. The experimental values of the excitation functions of the reactions ${}^7\text{Li}(\text{p}, \text{p}'\gamma){}^7\text{Li}$, ${}^{10}\text{B}(\text{p}, \alpha\gamma){}^7\text{Be}$,

$^{19}\text{F}(\text{p}, \text{p}'\gamma)^{19}\text{F}$ and $^{23}\text{Na}(\text{p}, \text{p}'\gamma)^{23}\text{Na}$ were used as input for this purpose. The agreement between the experimental and the calculated γ -ray yields have been found to be better than 7.5%.

The energies of the γ -rays and the detection limit obtainable from a typical thick biomedical sample are presented in Table 7.3.

Table 7.3. Energies of the γ -rays and the detection limit obtained from a typical thick biomedical sample

Elements	Reaction	E_γ (MeV)	Detection Limit (ppm) By Weight)
C	$^{12}\text{C}(\text{p}, \text{p}'\gamma)$	4.439	100
N	$^{14}\text{N}(\text{p}, \text{p}'\gamma)$	2.313	100
O	$^{16}\text{O}(\text{p}, \text{p}'\gamma)$	6.130	300
Na	$^{23}\text{Na}(\text{p}, \text{p}'\gamma)$	0.440	300
Mg	$^{24}\text{Mg}(\text{p}, \text{p}'\gamma)$	1.369	200
P	$^{24}\text{Mg}(\text{p}, \text{p}'\gamma)$	1.266	500
Ca	$^{31}\text{P}(\text{p}, \text{p}'\gamma)$	3.736	5,000

Sulfur may be detected via the reaction $^{32}\text{S}(\text{p}, \text{p}'\gamma)$ ($E_\gamma = 2,230$ keV) at a level of 100 ppm from a thick organic sample. The optimum bombarding energy is about 4.9 MeV. However, care must be taken to compensate for the possible overlapping γ -ray peaks from the element of Phosphorous [$2,230$ keV $^{31}\text{P}(\text{p}, \gamma)^{32}\text{S}$ and $2,234$ keV $^{31}\text{P}(\text{p}, \text{p}'\gamma)^{31}\text{P}$], silicon [$2,233$ keV $^{30}\text{Si}(\text{p}, \gamma)^{32}\text{P}$ and $2,235$ keV $^{30}\text{Si}(\text{p}, \text{p}'\gamma)^{30}\text{Si}$], and chlorine [$2,230$ keV $^{35}\text{Cl}(\text{p}, \alpha\gamma)^{32}\text{S}$]. Since these elements have more dominating peaks at other energies which may be used for checking their presence in the samples. The strongest γ -ray peak for chlorine from the reaction $^{35}\text{Cl}(\text{p}, \text{p}'\gamma)^{35}\text{Cl}$ is at 1,219 keV but γ -rays of the same energy also originate from the reaction $^{34}\text{S}(\text{p}, \gamma)^{35}\text{Cl}$. A peak without overlapping may be observed at 1,763 keV due to the reaction $^{35}\text{Cl}(\text{p}, \text{p}'\gamma)^{35}\text{Cl}$. The intensity ratio of 16 has been measured for 1763 keV to 2230 keV chlorine-peaks at $E_p = 4.9$ MeV. In most cases the influence of overlapping peaks is not a problem, but should be taken into account.

A general problem in determining the absolute concentration of the major structural elements of biomedical and organic samples by PIGE work is the lack of suitable standard samples. For obtaining concentration value of C, N, and O in biomedical samples, one can develop a standard using glycine ($\text{C}_2\text{H}_5\text{NO}_2$) under the same experimental conditions as the actual samples. The known elemental composition of the compound can be used directly for the concentration calculation of the actual sample. The suitability of the method is based on the fact that there is an insignificant difference in the stopping power values of typical organic samples and the chemical compounds used along with the relative concentration of C, N, and O may differ significantly.

The γ -rays measured in $(p, x\gamma)$ reactions are used to show the absolute concentration of H on the surface. If the hydrogen is below the sample surface, then the impinging particle will not generate gamma rays unless the beam energy is increased to compensate for the slowing down of impinging particle by the sample. The depth of the hydrogen can therefore be determined by measuring the difference between the resonance energy and the beam energy (before it starts through the sample).

Based on the analysis made for thousands of thick obsidian and pottery samples analyzed over a 6-year period, the accuracy and precision of PIGE measurements have been found to be ranging from $\pm 5\%$ in thick samples to $\pm 15\%$ in thin samples or for low yield γ -ray production (Cohen et al. 2002).

7.6 Applications of NRA

7.6.1 For Material Analysis

Nuclear reaction analysis has mostly been applied to problems in material science, where the use of isotopically enriched compounds allows the profile of a specific element to be targeted by ion beam reactions with its isotopes. For example, in the thermal oxidation of silicon, the growth kinetics and diffusion of oxygen across the Si/SiO₂ interface region has been studied using sequential oxidations in natural and ¹⁸O enriched oxygen gas. The differentiation between possible pathways is due to the isotopic specificity of the NRA technique.

Stedile et al. (1992) have analyzed silicon nitride, aluminium nitride and iron nitride thin films grown by reactive sputtering on Si and polyimide substrates at various deposition conditions using ¹⁴N(p, γ)¹⁵O, ¹⁴N(d, p)¹⁵N, ¹⁴N(d, α)¹²C, ¹⁴N(α , α)¹⁴N, and ²⁷Al(p, γ)²⁸Si nuclear reactions while Bouchier and Bosseboeuf (1992) have used ¹⁴N(d, α)¹²C, ¹⁰B(d, α)⁸Be, ¹¹B(d, α)⁹Be, and H(¹⁵N, $\alpha\gamma$)¹²C nuclear reactions to measure the areal concentrations of nitrogen, boron, and hydrogen in films deposited on silicon to study the growth mechanism of boron nitride films. A technique allowing the simultaneous determination of the nitrogen and boron content of boron nitride thin films using (α , p) reactions on ¹⁴N, ¹⁰B, and ¹¹B has been developed by Giorginis et al. (1994). The cross-sections of the (α , p) reactions were measured by these authors in the energy range between 4.0 and 5.0 MeV in steps of 10–20 keV at the laboratory angle of 135° using thin polyimide, enriched boron-10 and natural boron targets. The uncertainty of the cross-sections determination is 7% for the ¹⁴N(α , p₀)¹⁷O, 5.5% for the ¹⁰B(α , p₀)¹³C and ¹¹B(α , p₀)¹⁴C and 6% for the ¹⁰B(α , p₁)¹³C reaction leading to an elemental composition determination precision of better than 10%.

Walker et al. (2000) used (d, p) and (d, α) nuclear reactions for quantitative analysis of silicon oxynitride films on silicon. They found that under optimum

analysis conditions (850 keV deuterons and 150° detector angle), the Si background level sets a lower detection limit of $\sim 1 \times 10^{16}$ nitrogen atoms cm^{-2} and $\sim 3 \times 10^{15}$ oxygen atoms cm^{-2} . They concluded that a comparison with data in the recent *Handbook of Modern Ion Beam Materials Analysis* shows reasonable agreement (10–15%) for the (d, p) reactions on oxygen and carbon. However, in the case of nitrogen, the measured cross-section values are $\sim 70\%$ larger than the handbook data. The resulting O/N-ratios agree to within 10%.

Characterization of two thin-film battery materials using neutron reaction analysis technique has been done by Lamaze et al. (2003) who have employed nitrogen depth profiling to determine the distribution of lithium and nitrogen simultaneously in lithium phosphorous oxynitride (LiPON) deposited by ion beam assisted deposition. The depth profiles are based on the measurement of the energy of the charged particle products from the $^6\text{Li}(n, \alpha)^3\text{H}$ and $^{14}\text{N}(n, p)^{14}\text{C}$ reactions for lithium and nitrogen, respectively. Measurements were made by Kennedy et al. (2002) on sets of amorphous GaN films prepared on Si(100) with varied deposition conditions. A typical NRA spectrum is shown in Fig. 7.6. The nuclear reactions $^{16}\text{O}(d, p_1)^{17}\text{O}$ ($E_p = 1.39$ MeV, $d\sigma/d\Omega = 4.6$ mb sr^{-1}), $^{14}\text{N}(d, \alpha_1)^{12}\text{C}$ ($E_\alpha = 5.63$ MeV, $d\sigma/d\Omega = 0.9$ mb sr^{-1}) and $^{12}\text{C}(d, p_0)^{13}\text{C}$ ($E_p = 2.7$ MeV, $d\sigma/d\Omega = 55$ mb sr^{-1}) were used to determine the concentrations of C, N, and O in the a-GaN films. The energy values are calculated for the particles after they have passed the $10.6 \mu\text{m}$ Mylar foil.

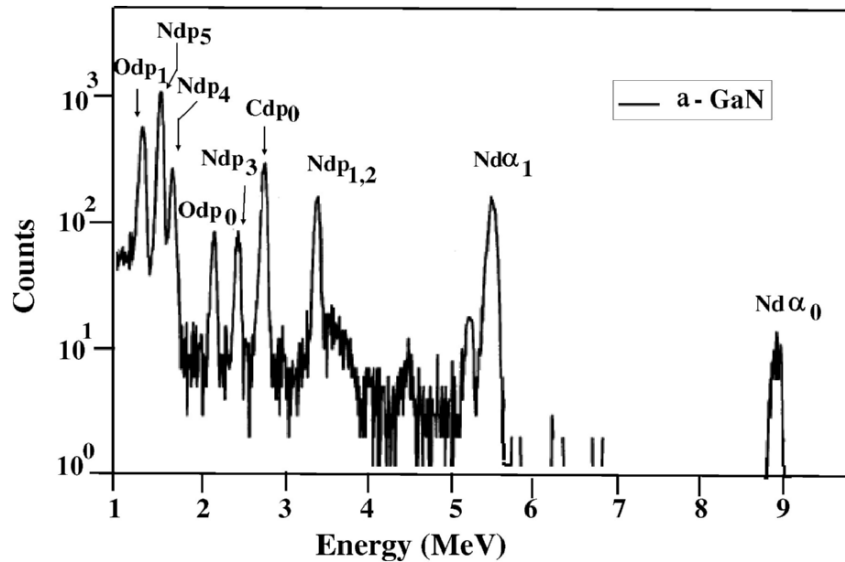


Fig. 7.6. Typical NRA spectrum of a-GaN by deuteron bombardment. The peak marked Odp_1 means that it is from nuclear reaction $\text{O}(d, p_1)$. Similarly, peak marked Ndp_5 means that it is from nuclear reaction $\text{N}(d, p_5)$ and so on

7.6.2 For Depth Profiling Studies

Another important application of the nuclear reaction analysis is depth profiling of polymer samples. In a certain depth of the polymer, the incoming ion beam particle can undergo a nuclear reaction with atoms of the film. The energy of the reaction products is a function of the energy of the incoming ions. It is thus possible to calculate from the energy distribution of the reaction products the depth distribution of the atoms that react with the incoming ions. Furthermore, as the nuclear reactions are isotope specific, one can use this analysis for binary blends of polymers, where one of the polymers is labeled with deuterium. The NRA gives us the depth distribution of the deuterium atoms and so of the labeled polymers.

The nuclear reaction analysis using ^{15}N ions provides depth resolution for the hydrogen distribution in a sample. Using deuterated polymers, concentration profiles and enrichment of components at buried interfaces can be detected for TiN thin layers on silicon as an illustrative example. Using nuclear backscattering with 2.7 MeV ^4He , the oxygen and nitrogen concentration standards have been precisely determined while 1.4 MeV deuterons have been found preferable as projectiles for simultaneous microanalysis of oxygen and nitrogen on silicon (Ivanov et al. 1994). Vickridge et al. (1995) have applied the nuclear reaction analysis with the $^{14}\text{N}(\text{d}, \alpha_1)$ reaction to the determination of ^{14}N depth profiles in the outer few micrometers of thermally nitrided titanium.

Depth profiling studies of ultra shallow implanted P using NRA has been made by Kobayashi and Gibson (1999) in the energy range of 5–80 keV using $^{31}\text{P}(\alpha, \text{p})^{34}\text{Si}$ reaction.

7.6.3 For Tracer Studies and for the Study of Medical Samples

Animals are dosed with small quantity of water enriched with the stable isotope ^{17}O and a blood sample is taken some hours later when isotopic equilibrium (^{16}O : ^{17}O : ^{18}O : 99.76%: 0.04%: 0.2%) is reached. The animals are then left to roam freely for a few days in their natural environment, before a second blood sample is taken. The ^{17}O content of the two blood samples is then measured. By measuring the loss of the stable isotopic tracer ^{17}O from the animal as a result of isotopic exchange with the environment, the rate of production of CO_2 can be estimated. This information leads to the metabolic rate of the free-ranging animal and hence the quantification of the animal's energetic requirements. Nondestructive determination of fluorine by nuclear reactions has made possible the study of the repeated application of fluoridated amalgams in cavities. Oxygen at trace level in calcium fluoride has been determined by instrumental deuteron activation analysis based on the $^{16}\text{O}(\text{d}, \text{n})^{17}\text{F}$ reaction by Sastri et al. (2000) using 2.5 MeV deuterons.

7.6.4 For the Study of Archaeological Samples

NRA technique has been used to characterize the obsidian samples from different mineral sites in Mexico by Murillo et al. (1998) who have determined the oxygen concentration by means of the $^{16}\text{O}(\text{d}, \text{p})^{17}\text{O}$ reaction. To determine the structure and composition of the patina through the depth profiles of the constituent elements like C, N, O, the (d, p) nuclear reactions have been employed using the external beam NRA measurements on copper alloys of archaeological significance with 3 MeV protons and 2 MeV deuterons by Ioannidou et al. (2000).

7.7 Applications of PIGE

7.7.1 For Material Analysis

Proton-induced γ -ray emission (PIGE) is especially useful for the analysis and the depth profiling of light elements like boron. One of the important applications of PIGE is the investigation of borosilicate samples that are used as insulator materials. The ZnO thin films, nominally undoped, or doped with Li, Al, Ga, and Sb and alloyed with Mg and Cd grown epitaxially on *c*-plane sapphire, were analyzed by PIGE using He^+ and H^+ ion beams by Spemann et al. (2004) in order to correlate the optical and electrical properties, e.g., the band gap energy and carrier concentration, to the elemental composition.

Chlorine in oil is very difficult to analyze by conventional methods. External beam PIXE-PIGE method is adequate for the fast simple analysis of a small amount of oil sample, especially for determining chlorine content. Choi et al. (1998) made analysis of chlorine in industrial oil samples by external beam PIXE and PIGE. It has been found that because of the presence of sulfur in most industrial oils, PIGE has usually better detection limit than PIXE.

7.7.2 For the Study of Medical Samples

Studying the biodistribution of boronated compounds for B neutron capture therapy (BNCT) requires the accurate detection of low levels of boron (^{10}B) in biological samples. PIGE analysis of ^{10}B provides viable for study of low-density lipoprotein (LDL), in tissue and blood samples. Analysis of ^{10}B by PIGE through γ -ray peak identification has been done by Savolainen et al. (1995). PIGE can be considered to be an appropriate reference method for boron analysis. In medical samples, protons and amino acids are determined by measuring the carbon/nitrogen ratio. Samples are often in liquid form but the ratio can be analyzed in either liquid or solid form. Solids are obtained by the lyophilisation of a sample prepared in such a way that it

contains only molecules with a molecular weight of more than 10,000 (centrifugation). The carbon and nitrogen contents are obtained by the $^{14}\text{N}(\text{d}, \text{p}\gamma)^{15}\text{N}$ and $^{12}\text{C}(\text{d}, \text{p}\gamma)^{13}\text{C}$ reactions; The γ -rays following these reactions are detected by the Ge(Li) detector and the ratio is directly obtained by comparison with a standard. Hall and Navon (1986) used a 4.1 MeV external proton beam to simultaneously induce X-ray emission (PIXE) and γ -ray emission (PIGE) in biological samples that included human colostrum, spermatozoa, teeth, tree-rings, and follicular fluids. The analytical method was developed to simultaneously determine the elements lithium ($Z = 3$) through uranium ($Z = 92$) in the samples.

Using 2.0–2.5 MeV proton beam, fluorine determination in human and animal bones collected from postmortem investigations was carried out by Sastri et al. (2001) based on the $^{19}\text{F}(\text{p}, \text{p}'\gamma)^{19}\text{F}$ reaction. Their results indicate that for 68% of the human samples the fluorine concentration is in the range $500\text{--}1,999\text{ }\mu\text{g g}^{-1}$. The variation of fluorine concentration among different types of teeth (canines and incisors, premolars, molars, etc.) and physical state (cariou and noncariou) have been examined by Carvalho et al. (2001). These authors have determined and compared the amount of fluorine in human healthy and cariou teeth using the PIGE technique using the nuclear reaction $^{19}\text{F}(\text{p}, \alpha\gamma)^{16}\text{O}$ from among the two groups of Portuguese people who are exposed to different levels of fluorine in drinking water.

7.7.3 For the Study of Archaeological Sample

A reliable knowledge of the composition of archaeological objects for major and trace elements is of primary interest for the archaeologists. The composition of the metal artifacts gives information on the ancient technological knowledge and helps to distinguish between various prehistoric cultural traditions. Analytical work on gold jewelery of archaeological interest has been performed by Demortier (1996) with an emphasis to solders on the artifacts and to gold plating or copper depletion gilding using PIGE along with other ion-beam analytical techniques like RBS, NRA, and PIXE. On the basis of elemental analysis, these authors have identified typical workmanship of ancient goldsmiths in various regions of the world: finely decorated Mesopotamian items, Hellenistic and Byzantine craftsmanship, cloisonne of the Merovingian period, depletion gilding on pre-Colombian tumbaga. Pieces of bronzes from two pre-Roman sites in Spain with different cultural traits have been analyzed by PIGE along with other ion beam analytical techniques (like PIXE and RBS) and Auger electron spectroscopy (AES) by Clement-Font et al. (1998) to extract complementary information on elemental composition and chemical state. The determination of the Na, Al, and Si content were carried out by PIGE analysis in the archaeological samples by Murillo et al. (1998) to characterize the obsidian samples from different mineral sites in México. PIGE technique has been extensively used for the investigation of several artifacts such as Roman

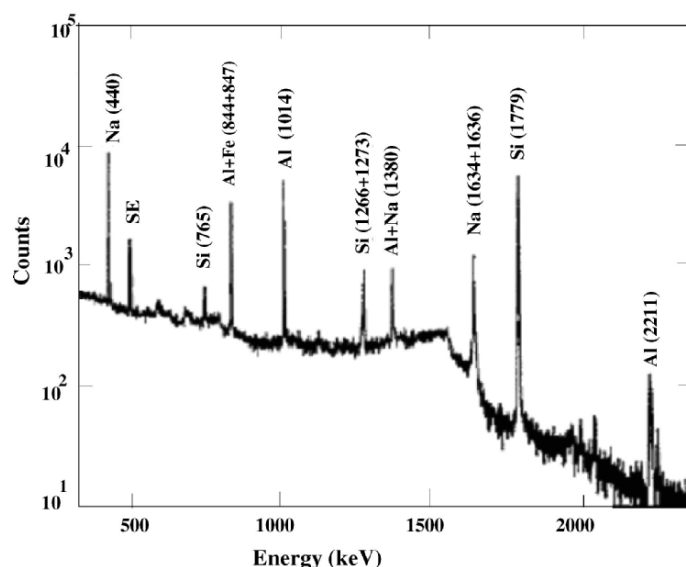


Fig. 7.7. PIGE spectrum of an archaeological sample (thick obsidian glass) induced by 4 MeV protons

glasses. A typical γ spectrum of an archaeological sample recorded by Murillo et al. (1998) is shown in Fig. 7.7. The important γ -peaks in the spectrum are due to $^{23}\text{Na}(p, p'\gamma)^{23}\text{Na}$, $E\gamma = 440$ keV, $^{27}\text{Al}(p, p'\gamma)^{27}\text{Al}$ ($E\gamma = 1,014$ keV), $^{28}\text{Si}(p, p'\gamma)^{28}\text{Si}$ ($E\gamma = 1,779$ keV). Because of the nondestructive character of PIGE-PIXE techniques which has been further strengthened by designing an external beam line permitting the in-air analysis of large or fragile works of art without sampling, the IBA facility has been operated in the Louvre (Paris) by Dran et al. (2004) for the study of works of art and archaeology for more than 14 years. This equipment has been chosen as the elemental maps can be drawn in PIGE mode by mechanically scanning the sample under the fixed beam within a lateral range much larger than conventional nuclear microprobes.

7.7.4 For the Study of Aerosol Samples

Atmospheric aerosols are small particulate matter with diameter of a few micrometer, which are caused by sandy dusts, smoke from factories, exhaust gas of cars and their deformed particles by photochemical reactions in the atmosphere. Elemental concentrations in atmospheric aerosol reflect air pollution and its generating process. The elements that may be found in dust samples range from hydrogen to uranium. However, the more common elements are H, C, N, O, F, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Co, Fe, Cu, Ni, Zn, Br, and Pb. While PIXE is generally used to determine concentrations of all elements with atomic number above Al ($Z = 13$), the

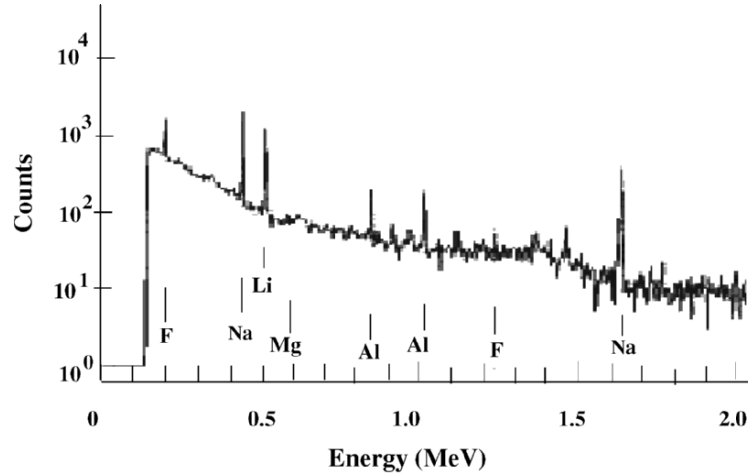


Fig. 7.8. PIGE spectrum of an aerosol sample. The elements corresponding to which the peaks appear, are shown below each peak

other IBA techniques are used to determine concentrations of light elements. The low- Z elements like boron and sodium, can be easily detected from the aerosol samples through $^{11}\text{B}(\text{p}, \gamma)^{12}\text{C}$ and $^{23}\text{Na}(\text{p}, \gamma)^{24}\text{Mg}$. The PIGE spectrum is shown in Fig. 7.8.

Air pollution measurements using external beam PIGE have been performed for fluorine determination in atmospheric aerosol by Calastrini et al. (1998) at Montelupo near Florence, characterized by the presence of a large number of ceramic and glass factories just inside the inhabited area. The minimum detection limit for the concentration of fluorine in air is of the order of 10 ng m^{-3} . The composition of particulate matter in the atmosphere of four major Italian towns (Florence, Genoa, Milan, and Naples) has been studied by Ariola et al. (2002) using the extensive applications of PIXE and PIGE techniques. Quantitative analysis of light elements in aerosol samples, collected on nuclepore polycarbonate filters, has been performed by Mateus et al. (2006) using PIGE technique but employing the method that avoids the use of comparative standards.

7.7.5 For the Study of Soil, Concrete, Rocks, and Geochemical Samples

Perdikakis et al. (2004) have used the PIGE technique to determine beryllium in light element matrices of soil and concrete samples (having complex matrix consisting of light elements in high concentrations), employing the deuteron beam at energies between 1.0 and 2.1 MeV, via the $^9\text{Be}(\text{d}, \text{n}\gamma)^{10}\text{B}$ reaction and subsequently detecting 718 keV γ -ray of ^{10}B using HpGe detector. PIGE

technique has been used by Pwa et al. (2002) in geochemical exploration for gold and base metal deposits.

There is a good correlation between the concentration of fluorine and that of phosphorus for igneous rocks, suggesting a control of apatite on the F content. In metamorphic rocks, amphibole and biotite besides apatite are the principal concentrators of fluorine indicating that fluorine in the system is controlled by granulite facies metamorphism conditions. Roelandts et al. (1986) analyzed more than 200 specimens from different occurrences of the Rogaland (Norway) igneous complex and surrounding granulite facies metamorphic rocks by PIGE technique and found that the fluorine contents vary from <25 to 3,500 ppm.

7.8 Common Particle–Particle Nuclear Reactions

7.8.1 Proton-Induced Reactions

Nuclear Reaction	Energy (MeV)	Reference
${}^4\text{Be}(p, p'){}^4\text{Be}$	2.3–2.7	Nucl. Instrum. Methods B29 (1988) 599
${}^7\text{Li}(p, p'){}^7\text{Li}$	0.45–2.9	Phys. Rev. 130 (1963) 2034
${}^6\text{Li}(p, {}^4\text{He}){}^3\text{He}$	0.100–1.0	Nucl. Phys. A326 (1979) 47
${}^7\text{Li}(p, {}^4\text{He}){}^4\text{He}$		Z. Phys. 327 (1987) 461
${}^{11}\text{B}(p, {}^4\text{He}){}^8\text{Be}$	0.163	Nucl. Phys. A233 (1974) 286
${}^{12}\text{C}(p, p'){}^{12}\text{C}$	0.7–2.5	Nucl. Instrum. Methods B12 (1985) 447
	2.7–3.1	Nucl. Instrum. Methods B61 (1991) 175
${}^{14}\text{N}(p, p'){}^{14}\text{N}$	0.7–2.5	Nucl. Instrum. Methods B12 (1985) 447
	2.7–3.1	Nucl. Instrum. Methods B61 (1991) 175
${}^{15}\text{N}(p, \alpha){}^{12}\text{C}$	0.9–1.3	Phys. Rev. 108 (1957) 1015
${}^{19}\text{F}(p, p'){}^{19}\text{F}$	1.00–1.875	Nucl. Instrum. Methods B44 (1989) 41;
${}^{19}\text{F}(p, \alpha){}^{16}\text{O}$	0.835–0.865	Lett. NuovoCim.11 (1974)33
${}^{23}\text{Na}(p, \alpha){}^{24}\text{Mg}$	0.3–1.75	Aust. J. Phys. 28 (1975) 369
${}^{16}\text{O}(p, p'){}^{16}\text{O}$	1.4–2.4	Czech. J. Phys. 41 (1991) 921
	2.7–3.1	Nucl. Instrum. Methods B61 (1991) 175
${}^{18}\text{O}(p, \alpha){}^{15}\text{N}$	0.620–0.900	Nucl. Instrum. Methods B51 (1990) 97
	1.730–1.760	
${}^{28}\text{Si}(p, p'){}^{28}\text{Si}$	4.8–7.0	Phys. Rev. 127 (1962) 947
	0.7–2.5	Nucl. Instrum. Methods B12 (1985) 447
${}^{35}\text{Cl}(p, p'){}^{35}\text{Cl}$	2.5–4.8	Nucl. Instrum. Methods B79 (1993) 524

7.8.2 Deuteron-Induced Reactions

Nuclear Reaction	Energy (MeV)	Reference
$^2\text{H}(\text{d}, \text{p})\text{T}$	0.025–0.080	Kasagi et al. (2000)
$^2\text{H}(\text{d}, \text{n})^3\text{He}$	0.052–0.692	Nucl. Phys. A245 (1975) 1
$^2\text{H}(\text{d}, \text{d})^2\text{H}$	0.08 to 0.36	Nucl. Phys. A255 (1975) L3
$^3\text{H}(\text{d}, \text{n})^4\text{He}$	0.2–1.0	Nucl. Phys. A244 (1975) 236
$^6\text{Li}(\text{d}, \text{n})^7\text{Be}$	0.5–3.8	Phys. Rev. C11 (1975) 370 Nucl. Phys. A289(1977)526
$^6\text{Li}(\text{d}, \text{p})^7\text{Li}$	0.5–3.8	Phys. Rev. C11 (1975) 370
$^6\text{Li}(\text{d}, \alpha)^4\text{He}$	0.5–3.8	Phys. Rev. C11 (1975) 370
$^7\text{Li}(\text{d}, \text{p})^8\text{Li}$	0.5–3.8	Phys. Rev. C11 (1975) 370
$^9\text{Be}(\text{d}, \text{p})^{10}\text{Be}$	0.9–3.1	Nucl. Phys. A250 (1975) 93
$^9\text{Be}(\text{d}, \text{n})^{10}\text{B}$		Nuclear Instrum. Methods A247 (1986) 359
$^{12}\text{C}(\text{d}, \text{p})^{13}\text{C}$	0.968	Nucl. Instrum. Methods B83 (1993) 47
$^{13}\text{C}(\text{d}, \text{p})^{14}\text{C}$	0.6–3.0	Phys. Rev. 103 (1956) 167
$^{12}\text{C}(\text{d}, \alpha)^{10}\text{Be}$		
$^{14}\text{N}(\text{d}, \text{p})^{15}\text{N}$	0.55–0.66	Nucl. Instrum. Methods 201 (1982) 476
	0.32–1.45	Nucl. Instrum. Methods 168 (1980) 107
$^{14}\text{N}(\text{d}, \alpha)^{12}\text{C}$	0.972, 1.200	Nucl. Instrum. Methods 218 (1983) 141
$^{15}\text{N}(\text{d}, \alpha_0)^{13}\text{C}$	0.972	Nucl. Instrum. Methods B15 (1986) 533
$^{16}\text{O}(\text{d}, \alpha)^{14}\text{N}$	0.84–1.03	Nucl. Instrum. Methods 149 (1978) 292
$^{16}\text{O}(\text{d}, \text{p})^{17}\text{O}$	0.55–0.66	Nucl. Instrum. Methods 201 (1982) 476
$^{16}\text{O}(\text{d}, \alpha)^{14}\text{N}$	0.8–2.0	Ann. Phys. 9 (1964) 297
$^{23}\text{Na}(\text{d}, \text{p})^{24}\text{Na}$	1.0–2.5	Nucl. Phys. 74 (1965) 225
$^{23}\text{Na}(\text{d}, \alpha)^{21}\text{Ne}$	1.0–2.5	Nuovo Cimento 38 (1965) 1082

7.8.3 ^3He -, ^4He -Induced Reactions

Nuclear Reaction	Energy (MeV)	Reference
$^1\text{H}(^3\text{He}, ^3\text{He})^1\text{H}$	3.5–5.0	Nucl. Instrum. Methods 218 (1983) 120
$^1\text{H}(^4\text{He}, ^4\text{He})^1\text{H}$		
$^2\text{H}(^3\text{He}, \text{p})^4\text{He}$	$0 < E < 2.5$	Nucl. Instrum. Methods 149 (1978) 61
$^2\text{H}(^4\text{He}, ^4\text{He})^2\text{H}$		Nucl. Instrum. Methods B6 (1985) 533
$^9\text{Be}(^3\text{He}, \text{p})^{11}\text{B}$	5.7–10.2	Proc. Phys. Soc. 75 (1960) 754
$^9\text{Be}(^3\text{He}, \text{d})^{10}\text{B}$	5.7–10.2	Proc. Phys. Soc. 75 (1960) 754
$^9\text{Be}(^4\text{He}, \text{d})^{11}\text{B}$	27	Nucl. Phys. A237 (1975) 1
$^{12}\text{C}(^3\text{He}, \text{p})^{14}\text{N}$	2.39	Nucl. Instrum. Methods B45 (1990) 91
$^{12}\text{C}(^4\text{He}, ^4\text{He})^{12}\text{C}$	5.50–5.80	Nucl. Instrum. Methods B85 (1994) 28
	7.35–7.65	
$^{13}\text{C}(^3\text{He}, \text{p})^{15}\text{N}$	1.0–3.0	Phys. Rev. 105 (1957) 961

$^{14}\text{N}(^4\text{He}, \text{p})^{17}\text{O}$	3.4–4.0	Nucl. Instrum. Methods B79 (1993) 498
$^{16}\text{O}(^4\text{He}, ^4\text{He})^{16}\text{O}$	3.045	Nucl. Instrum. Methods 83 (1993) 311
$^{14}\text{N}(\alpha, \text{p})^{17}\text{O}$	3.4–4.0	Nucl. Instrum. Methods B79 (1993) 498
$^{32}\text{S}(\alpha, \text{p})^{35}\text{Cl}$	6.0–12.0	Nucl. Instrum. Methods B113 (1996) 399

7.8.4 Some Important Reactions Used for NRA Analysis

Nucleus	Reaction	Incident Energy (MeV)	Emitted Energy (MeV)	Cross-section (Mb sr ⁻¹)
D	$^2\text{H}(\text{d}, \text{p})^3\text{H}$	1.0	2.3	5.2
D	$^2\text{H}(^3\text{He}, \text{p})^4\text{He}$	0.7	13.0	61
^6Li	$^6\text{Li}(\text{d}, \alpha)^4\text{He}$	0.7	9.7	35
^7Li	$^7\text{Li}(\text{p}, \alpha)^4\text{He}$	1.5	7.7	9
^{11}B	$^{11}\text{B}(\text{p}, \alpha)^8\text{Be}$	0.65	5.57 (α_0)	0.7
		0.65	3.70 (α_1)	550
^{12}C	$^{12}\text{C}(\text{d}, \text{p})^{13}\text{C}$	1.2	3.1	35
^{15}N	$^{15}\text{N}(\text{p}, \alpha)^{12}\text{C}$	0.8	3.9	15
^{18}O	$^{18}\text{O}(\text{p}, \alpha)^{15}\text{N}$	0.73	3.4	15
^{19}F	$^{19}\text{F}(\text{p}, \alpha)^{16}\text{O}$	1.25	6.9	0.5
^{23}Na	$^{23}\text{Na}(\text{p}, \alpha)^{20}\text{Ne}$	0.592	2.24	4
^{31}P	$^{31}\text{P}(\text{p}, \alpha)^{28}\text{Si}$	1.514	2.734	16

7.9 Some Important Reactions Used for PIGE Analysis

Some important reactions used for PIGE analysis, along with their excitation energy, reference cited in the journal and the concentration of particular isotope, are given in Appendix C.

The details about the reactions have been listed in the Nuclear Science References (NSR) file which is a bibliographic database covering low- and intermediate-energy nuclear physics. Currently it contains about 140,000 literature references. The NSR file originated during the mid-1960s at the Nuclear Data Project (NDP) at Oak Ridge National Laboratory as a part of a program of systematic evaluation of nuclear structure data. The NSR file contains references to published and unpublished work relevant to nuclear structure. At the same time the NDP created the Evaluated Nuclear Structure Data File (ENSDF) containing the physical data. Each reference in NSR has a unique identifier – the Key number. References since 1969 contain a Keyword Abstract and Keywords (which indicate the kinds of data contained in the article).

[<http://ie.lbl.gov:6023/welcome.htm>]

Accelerator Mass Spectrometry (AMS)

8.1 Introduction

Mass Spectrometry (MS) is the technique of separating and counting the constituent atoms of a sample according to their mass. Accelerator Mass Spectrometry (AMS) is a special tool for quantitative measurements of very long-lived radionuclides. This technique consists of counting the nuclides themselves instead of waiting for their decay. In AMS, a charged particle accelerator is added to the equipment conventionally used in mass spectrometry, increasing the sensitivity of the system (10^{-12} to 10^{-15}) for detecting very low concentrations (down to 10^3 – 10^5 atoms per sample) of a number of long-lived radioisotopes and stable isotopes.

One of the important applications of mass spectrometry is to determine the age of a material, which is known as radioactive dating. Many isotopes have been studied, probing a wide range of time scales. As an example of carbon dating, ^{14}C is made continuously in our upper atmosphere by $^{14}\text{N}(\text{n}, \text{p})^{14}\text{C}$ reaction. This isotope of ^{14}C is transported as $^{14}\text{CO}_2$, absorbed by plants, and eaten by animals. If we were to measure the ratio of ^{14}C to ^{12}C today, we would find a value of about one ^{14}C atom for each 10^{12} (one-trillion) atoms of ^{12}C . In matter undergoing active exchange of C with the environment, there is a steady state specific activity of about 7.15×10^6 decays per year per gram of carbon. This ratio is the same for all living things – the same for humans as for trees. Once living things die (consumption of food, which grew by C exchange with the environment, stops), they no longer can exchange carbon with the environment and the ^{14}C (which is radioactive, and beta-decays with a half-life of 5,730 years) will start decaying in the sample with its natural decay rate. This means that in 5,730 years, only half of the ^{14}C will remain, and after 11,460 years, only one quarter of the ^{14}C remains. Thus, the ratio of ^{14}C to that of ^{12}C will change from one in one-trillion at the time of death to one in two trillion 5,730 years later and one in four-trillion 11,460 years later. If we take one gram of carbon sample, it will contain 6×10^{10} atoms of ^{14}C , out of which only 14 decay per minute. Thus it will

need counting for about 48 h to achieve 0.5% statistical precision in this method of decay-counting. The decoupling of the “clocking function” from the “detection function”, and the resulting increase in sensitivity has allowed rapid dating of samples by mass spectrometry. However, in a conventional mass spectrometer, the ^{14}C ions are masked by relatively intense flux of the ^{14}N isobar by background from the stable isotopes ^{12}C and ^{13}C and also by molecular ions such as ^{13}CH and $^{12}\text{CH}_2$. In principle, it is possible to build a mass spectrometer which could resolve the interferences from the isobars and from molecular ions but the current of ^{12}C will be limited to 1 nA or less and thus the corresponding flux of ^{14}C would be less than one count per minute, making it a very time consuming method.

Accelerator Mass Spectrometry (AMS) was developed to overcome the fundamental limitations of both the decay-counting as well as conventional mass spectrometry. AMS method takes much less time, e.g., 10,000 atoms of ^{14}C can be counted in <30 s. Similarly, there are no molecular contaminants as ^{14}C is separated from ^{14}N as well as the molecular isobars $^{12}\text{CH}_2$ and ^{13}CH . AMS measurements have the advantage over the conventional method in that it enables samples a thousand times smaller (sample needed for dating <1 mg) to be dated. Very accurate measurements of the amount of ^{14}C by AMS allow one to date the death of the once-living things (the dating range back to >50,000 years). The ability to obtain a radiocarbon date using only a small quantity of material has made possible the direct dating of valuable art objects with the minimum of damage.

AMS is now a well-established highly sensitive method for counting atoms and it is used for detecting very low concentrations of mainly long-lived radionuclides (or stable isotopes) in small samples (Elmore and Phillips 1987). AMS makes use of the high-energy of a particle accelerator to produce positive ions of elements such as carbon, aluminum, calcium, chlorine, iodine, tritium, and plutonium. Carbon has two stable isotopes ^{12}C and ^{13}C having 98.89% and 1.11%. The $^{14}\text{C}/^{12}\text{C}$ ratio, which radiocarbon daters seek to measure accurately, is nearly double than that for $^{13}\text{C}/^{12}\text{C}$ ratio. Since AMS can separate the three isotopes of carbon, it is therefore an ultra-sensitive mass spectrometry method for determining radioactivity levels in samples. Using the AMS method, a much higher fraction of the ^{14}C can be achieved facilitating quick counting. The best estimate from AMS dating technique has been reported from the body of the “iceman” (the man lived between 3350 and 3300 BC in the Alps). The iceman died and was entombed in glacial ice until recently. When the ice moved and melted, iceman was recovered and pieces of tissue were studied for their ^{14}C content by AMS.

Through the AMS analysis technique, the isotopes typically measured include a handful of long-lived radioisotopes that are rare/scarcely due to their instability, yet difficult to measure by their infrequent decay. The negative ion source eliminates the interference of ^{14}N with ^{14}C . AMS has been successfully applied in the fields of archeology (Wendorf 1987, Zhou et al. 2000) and anthropology (Taylor 1987, Hofmeijer et al. 1987). The nondating

applications of AMS have also played a contributive role in many fields, such as nuclear physics, geology, and hydrology. Some new nondating applications in environmental science, material science, and biomedical sciences have got rapid developments in recent years. AMS has also been applied to stable-element analysis in electronic materials with detection limits of parts-per-trillion (system efficiencies similar to those of secondary ion mass spectrometry SIMS-typically 10^{-3} to 10^{-4}) and depth profiling capability (Anthony et al. 1987). The fact that AMS counts atoms rather than decays, results in great advantages compared to radiometrical techniques, such as highly reduced sample sizes and shortened measuring times. Since different cosmogenic radionuclides can be used for a wide variety of dating and tracing applications in the geological and planetary sciences, archeology, and biomedicine, the utility of AMS technique has been extended to include other isotopes like ^{10}Be , ^{26}Al , ^{32}Si , ^{36}Cl , ^{41}Ca , ^{44}Ti , and ^{129}I .

The applications of AMS in the major research areas are being undertaken in more than 50 research laboratories of the world. These works are published in all major international journals as well as presented in international conferences. The proceedings of the Ninth International Conference on AMS have been edited by Nakamura et al. (2004). The major areas of research, in which AMS has made significant impact, are described in Sect. 8.8.

8.2 Principle

As the name suggests, AMS is an extension of conventional MS by the inclusion of an accelerator, preferably an electrostatic tandem accelerator. In common with conventional MS, AMS is performed by converting the atoms in the sample into a beam of fast-moving ions (charged atoms) by placing the sample to be analyzed in an evacuated chamber, where it is bombarded with positive cesium ions Cs^+ in a cesium sputter source. Cesium lowers the work function of the material, allowing the release of negative ion beam of the sample material. These ions are then preaccelerated to energies in the keV range and a magnet is used for mass separation prior to particle detection. The mass of these ions is then measured by the application of magnetic and electric fields. The mass analyzed negative ions are accelerated to the positive high-voltage terminal (3–10 MeV) of the accelerator where they encounter either a thin carbon foil or low pressure gas. The stripper foil helps to convert negative atomic ions to multiply charged positive ions and also causing negative molecular ions to dissociate into their component atoms, which also emerge positively charged. The positive ions are now further accelerated back to ground potential in the second stage of the tandem accelerator. A magnetic field is used to analyze the ions of interest with a well-defined charge-state and energy and directs them to the ion detector which determines both Z and M of the individual ions. The rare isotope is thus identified and counted in a detector. Such identification is necessary because ions other than the

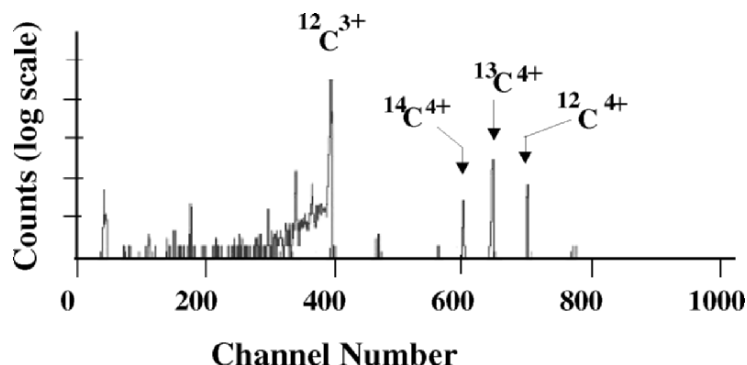


Fig. 8.1. Typical AMS energy spectrum of ^{14}C from sample and contaminants (from set-up)

AMS isotope may also reach the detector. The stable isotope is collected in a Faraday cup and its yield is determined from the accumulated charge.

Since the AMS generally determines the ratio of the rare isotope to the most abundant isotope of the same element (say $^{14}\text{C}/^{12}\text{C}$), this is accomplished by accelerating ions of the abundant isotope as well as the rare isotope. The rare isotope being examined is always measured as a ratio of a stable, more abundant (but not too abundant) isotope, e.g., ^{14}C as a ratio of ^{13}C , which acts as an internal standard and provides a clear signature to differentiate the rare isotope from the background. The ratio $^{14}\text{C}/^{13}\text{C}$ can be determined from the typical AMS spectrum shown in Fig. 8.1. In the high-energy mass spectrometer, the abundant isotope is removed from the ion beam and is measured as electric current in a Faraday cup being more intense (typically 10^{12}).

The isotopes in common AMS use are (see Table 8.1) ^{14}C (to date human relics), ^{59}Ni (to date meteorites), ^{14}C , ^{36}Cl , and ^{129}I (for tracing movements of ground water), ^{26}Al , ^{32}Si , ^{41}Ca , and ^{239}Pu (for human tracers and toxicity measurements), ^{10}Be , ^{26}Al , and ^{36}Cl (to date lava flow, land slides and erosion). The cosmogenic radionuclides, which are formed under influence of cosmic-rays, and occur in very small concentrations, can be used in a broad range of applications.

8.3 Experimental

A tandem accelerator based AMS system consists of the following components: (i) a Cesium sputter ion-source (SNICS) for producing negatively charged atomic or molecular ions. The typical beam currents are 1–20 pA, depending on the specific element to be measured and the composition of the target, (ii) an ion-injector consisting of a magnetic analyzer and sometimes a preacceleration system for negative ion beam, (iii) a Pelletron tandem accelerator including one section for negative ion acceleration and another section for

Table 8.1. Various radionuclides useful in the AMS studies

Radio-nuclide	Half-life (years)	Cosmogenic origin	Stable isotope	Extracted ion	Background	Overall efficiency
^{10}Be	1.6×10^6	N, O spallation	^9Be	BeO^-	$<10^{-14}$	10^{-5} to 10^{-2}
^{14}C	5,730	$^{14}\text{N}(\text{n}, \text{p})$ $^{16}\text{O}(\text{p}, 3\text{p})$	$^{12}\text{C}, ^{13}\text{C}$	C^-	$<10^{-15}$	0.5% to 5%
^{26}Al	7.2×10^5	^{40}Ar spallation	^{27}Al	Al^-	5×10^{-14}	10^{-4} to 10^{-1}
^{36}Cl	3.0×10^5	^{40}Ar spallation $^{35}\text{Cl}(\text{n}, \gamma)$ $^{36}\text{Ar}(\text{n}, \text{p})$	$^{35}\text{Cl}, ^{37}\text{Cl}$	Cl^-	$<10^{-15}$	10^{-3} to 2%
^{41}Ca	1.03×10^5		^{40}Ca	CaH_3^-	10^{-13}	
^{59}Ni	7.6×10^4	$^{58}\text{Ni}(\text{n}, \gamma)$	$^{58}\text{Ni}, ^{60}\text{Ni}$	Ni^-	$<10^{-9}$	
^{129}I	1.5×10^7	Xe-spallation U-fission	^{127}I	I^-	5×10^{-14}	10^{-3} to 10^{-2}

positive ion acceleration and an electron stripper in between, (iv) a positive ion analysis system for removing scattered particles, molecular fragments, and unwanted charge-states from the selected ion beam. A magnetic analyzer alone is not sufficient for that purpose and electrostatic analyzer or velocity selector is additionally used, and (v) an ionization detector for measuring the amounts of individual ions of different atomic number and mass. Sometimes a time-of-flight detector is also used. The schematic of AMS set-up is shown in Fig. 8.2.

The difference between the AMS and the other ion beam analysis methods (viz, PIXE, PIGE, RBS, ERD, etc.) is that in those Ion Beam Analysis techniques, the charged particles like protons, α -particles, Li^{n+} -, C^{n+} -, N^{n+} -, Ag^{n+} -ions, etc. are accelerated and bombarded on to the sample (to be analyzed) while in AMS, the beam of negative ions of the abundant and rare isotopes is generated from a small amount of the sample (to be analyzed) by the ion source, transmitted for acceleration and then analyzed. The functioning of the AMS technique thus mainly depends on the ion source to extract negative ions from the sample. The desirable criteria for the AMS accelerators are that transmission of ions through the accelerator should be high and reproducible, i.e., the transmission should be insensitive to small changes in the injection or accelerating parameters and that the terminal voltage should be very stable. The Pelletron accelerator (which normally has terminal voltage of 3–10 MV) is a two stage (tandem) electrostatic accelerator, in which the negative ions of the sample, produced in the ion source,

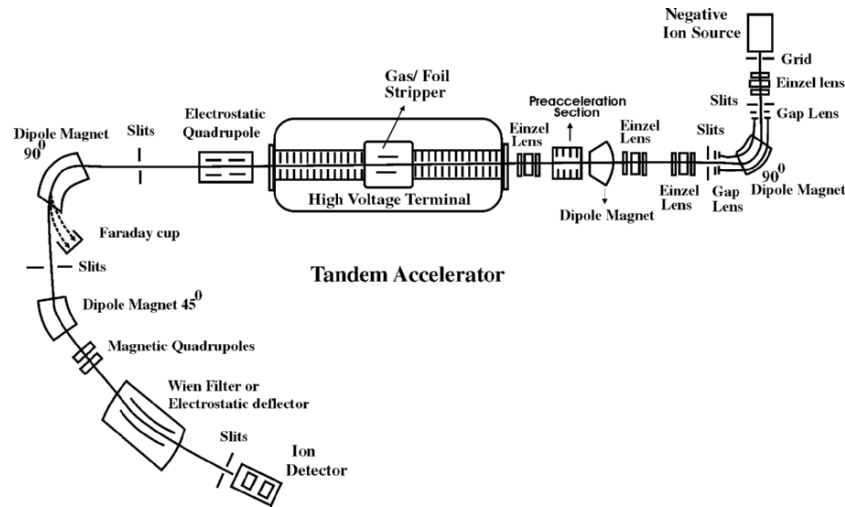


Fig. 8.2. Schematic of AMS set-up. Various parts like negative ion source, analyzing magnet, accelerating tube, carbon stripping foil, detector, and electrostatic analyzer are shown

are directed to the low-energy accelerator tube as explained in Sect. 1.4.3 of Chap. 1. The description of various parts of the tandem accelerator is being presented here with reference to the AMS technique.

The ion source produces a beam of ions from a few milligrams of solid material. The element is first chemically extracted from the sample (e.g., a rock, rain water, a meteorite) and then loaded into a sample holder and inserted into the ion source through a vacuum lock. Atoms are sputtered from the sample by cesium ions (using multicathode SNICS ion source), which are produced on a hot spherical ionizer and focused to a small spot on the sample. Negative ions produced on the surface of the sample are extracted from the ion source and sent down the evacuated beam-line toward the first magnet. At this point the beam current is about $10\ \mu\text{A}$ (mostly due to the stable isotopes), which corresponds to 10^{13} ions per second.

For carbon dating, the graphite or carbon dioxide sample is put into the ion source. A variety of organic materials, include bone, ivory, paper, silk, textile, wool, wood, etc. The amount of material required for AMS analysis depends on the composition. However, the approximate values for some common materials are: 20–50 mg for paper, textile, wool, wood, etc., and 200 mg to 2 g for bone, ivory, etc. Many other materials like food residues from ceramics can also be dated for which the quantity required depends on the carbon content. The sample is ionized by bombarding it with cesium ions and then focused into fast-moving beam of energy $\sim 25\ \text{keV}$. The ions produced are negative which prevents the confusion of ^{14}C with ^{14}N since nitrogen does not form a negative ion. The first magnet is used in the same way as the magnet in an ordinary

mass spectrometer to select ions of mass 14 (this will include large number of $^{12}\text{CH}_2^-$ and $^{13}\text{CH}^-$ ions and a very few $^{14}\text{C}^-$ ions).

The injector magnet bends the negative ion beam by 90° to select the mass of interest, a radioisotope of the element inserted in the sample holder, and reject the much-more-intense neighboring stable isotopes. A number of vacuum pumps are used to provide vacuum $\approx 10^{-6}$ Torr for the passage of ion beams. At this vacuum, there are still lots of molecules and isobars (isotopes of neighboring elements having the same mass) that must be removed by more magnets after the accelerator. In order to inject both the rare and the abundant isotopes into the accelerator, different approaches are adopted in the injection system. One approach is to inject the different isotopes sequentially, either by changing the energy of the ions prior to mass analysis, or by changing the field in the mass analyzing magnet. The former has the advantage of being fast and is normally used in dedicated AMS beam-lines while the later is slow and is employed where the beam-line of AMS experiments has to be shared with some other type of nuclear physics experiments.

The tandem accelerator consists of two accelerating gaps with a large terminal voltage (charged to high-voltage by two rotating chains) of the order of 3–10 MV in the middle is filled with CO_2 , SF_6 and N_2 insulating gases at a pressure of over 10 atm. The low voltage negative ions accelerated to a few KV travel down the beam tube and are attracted (and hence accelerated) toward the positive terminal. At the terminal they pass through an electron stripper, either a gas or a very thin carbon foil, and emerge as positive ions. These are repelled from the positive terminal, accelerating again to ground potential at the far end.

Since the beam currents of the stable isotopes can be as high as $100\text{ }\mu\text{A}$, therefore if injected for more than a few milliseconds, these cause the terminal voltage to drop because the charging system cannot adjust to the increased load (Suter et al. 1984, Hedges 1984). In the case of carbon dating, fast cycling sequences (like $20\text{ }\mu\text{s}$, $200\text{ }\mu\text{s}$, and 80 ms for ^{12}C , ^{13}C , and ^{14}C , respectively) are therefore chosen to ensure that the intense beam is in the accelerator for short enough time. Laboratories using slow cycling attenuate the prolific beam before injection into the accelerator with either a beam chopper (Fiefield et al. 1987) or “pepper-pot” attenuator (Kubik et al. 1987). Alternatively, the abundant and rare isotopes may be injected simultaneously. In such systems a sequence of dipole magnets and lenses are employed. These allow the different isotopes to follow different trajectories after leaving the ion source before being recombined at the entrance to the accelerator (Southon et al. 1990).

The tandem accelerators employed in AMS may be classified into three categories: (1) Accelerators from National Electrostatic Corporation called tandetrans which operate at terminal voltage of $\sim 2.5\text{ MV}$. Such machines are charged by a radiofrequency voltage doubling power supply and are not only used for high precision ^{14}C measurements, but also for measurements with ^{10}Be , ^{26}Al , and ^{129}I ions. (2) Machines working at terminal voltage between

4.5 and 9 MV (manufactured by NEC as well as by High Voltage Engineering Corporation) are extensively used as the full range of isotopes can be covered by these types of accelerators. (3) Machines operating with terminal voltage more than 10 MV manufactured by NEC and HVEC have advantage for ^{36}Cl .

As the ions collide with the gas molecules in the central “stripper canal”, the molecular ions (such as $^{12}\text{CH}_2$ and ^{13}CH) are broken up. The carbon atoms are stripped of three or four electrons making them into C^{3+} or C^{4+} ions, while the C^- ions are stripped of four electrons making them into C^{3+} ions. These are then accelerated down the second half of the tandem accelerator reaching energies of about 8 MeV. The second magnet selects ions with the momentum expected of ^{14}C ions and a Wien filter checks that their velocity is also correct.

The analyzing and switching magnets select the mass of the radionuclide of interest, further reducing the intensity of neighboring stable isotopes. In addition, they eliminate molecules completely by selecting only the highly charged ions that are produced in the terminal stripper (highly charged molecules are unstable since they are missing the electrons that bind the atoms together). Isotope ratios are measured by alternately selecting the stable and radioisotopes with the injector and analyzing magnets.

In the postacceleration analysis, the charge-state and hence the energy of interest is selected by magnetic analysis. In those systems employing fast cycling or simultaneous injection, the stable isotopes are collected in off-axis Faraday cups after the magnet since the radii of curvature of the AMS isotopes are different. The interfering ions are thus removed by the magnetic filter before the remaining ions finally slow to a stop in the gas ionization detector. The charge of individual ions can be determined from how the ions slow down. For example, ^{14}C slows down more slowly than ^{14}N , so those ions of the same mass can be distinguished from one another. Once the charges are determined, the detector can tell to which element each ion belongs and counts the desired isotope as a ratio of more abundant isotope. For example, the ions of the various isotopes of carbons, i.e., $^{14}\text{C}^{n+}$, $^{13}\text{C}^{n+}$, $^{12}\text{C}^{n+}$ having different m/z values, are brought down to ground potential and sent through an electrostatic analyzer and a high-energy magnetic sector to send (finally) only ^{14}C into the detector.

The electrostatic analyzer is a pair of metal plates at high voltage that deflects the beam to the left by small angle. This selects particles based on their energy and thus removes the ions that happen to receive the wrong energy from the accelerator. The electrostatic analyzer is an additional analysis stage to remove that small fraction of molecular fragments which have acquired the correct energy to follow the same trajectory as the AMS isotope through the analysis magnet. Finally the filtered ^{14}C ions enter the detector where their velocity and energy are checked so that the number of ^{14}C ions in the sample can be counted. Not all of the radiocarbon atoms put into the ion source reach the detector and so the stable isotopes, ^{12}C and ^{13}C are measured as well in order to monitor the detection efficiency. For each sample a ratio

of $^{14}\text{C}/^{13}\text{C}$ is calculated and compared to measurements made on standards with known ratios.

To identify and count the number of ions as they come down the beam-line, one could use either a silicon detector (which measures only the energy of the ions) or the ionization chamber (which measure not only the energy of the ions but also their rate of energy-loss as the ions slow down in the detector gas). In the ionization chamber, the ions are slowed down and come to rest in propane or isobutene gas. The isobutene gas has the advantage of a higher stopping power but is comparatively expensive while the propane gas is cheap and readily available. The gas confining window is usually made of Mylar, typically $1.5\text{ }\mu\text{m}$ thick. As the ions stop in the gas, electrons are knocked off the gas atoms. These electrons are collected on metal plates as they drift toward the anode in the transverse electric field. The anode is subdivided into sections, each of which collects these electrons produced beneath it, thereby measuring the energy lost by the ion along that portion of the track. The anode signal is amplified, and read into the computer. For each atom, the computer determines the rate of energy-loss and from that one can deduce the nuclear charge i.e. atomic number of the element. This energy-loss information permits the separation of interfering isobars since ions of different z -values lose energy at different rates.

The properties listed below, combined with those of the electrostatic and magnetic spectrometers, are crucial for reducing isobars and to make it possible to measure isotopic ratios down to 10^{-15} in an AMS-system:

- (1) Interferences from isobars can be avoided in many cases by using a negative ion source. ^{14}C analysis is facilitated due to the fact that the atomic isobar ^{14}N is eliminated because of the instability of negative nitrogen ions, while negative carbon ions are easily produced.
- (2) The stripping process at the accelerator high voltage terminal is of great importance since it breaks up molecules through the removal of three or more electrons. By selecting a high charge-state with a high-energy analyzing magnet, molecular isobaric interferences, such as ^{13}CH and $^{13}\text{CH}_2$, are removed.
- (3) The high final energy of the ions, in the order of tens of MeV, provides such a good resolution in energy or energy-loss measurements, that every single ion can usually be identified both by atomic and mass numbers.

8.4 AMS Using Low-Energy Accelerators

About half of the existing AMS facilities in the world are based on 3-MV tandem accelerators. These “work horses” of AMS allow for routine measurements of ^{10}Be , ^{14}C , ^{26}Al , and ^{129}I , with a large number of successful applications. The 3-MV tandems have achieved sufficient isobar suppression of ^{10}B for the lightest long-lived ^{10}Be radionuclide. The stable isobar ^{41}K can

be suppressed by using $^{41}\text{CaH}_3^-$ or $^{41}\text{CaF}_3^-$ ions. Using the Vienna Environmental Research Accelerator (VERA, based on a 3-MV tandem accelerator) Steier et al. (2005) have systematically explored the opportunities and limitations due to terminal voltage, both by modeling and by experiments. They have observed that if no stable atomic isobars exist, e.g., for ^{236}U or ^{244}Pu , the same detection limits as with large machines could be achieved. In cases where isobar separation is required, the achievable energy is the limitation.

In order to study the feasibility of AMS with very small accelerators, Suter et al. (1997) have performed ^{14}C test measurements at low terminal voltages of 0.5 and 1 MV. These experiments have demonstrated that molecules of ^{13}CH and $^{12}\text{CH}_2$ in charge-states 1^+ and 2^+ can get destroyed in an Ar gas stripper reducing their intensities by at least ten orders of magnitude at a stripper thickness of about $1\text{ }\mu\text{g cm}^{-2}$. It could be shown that particle identification and separation of $^{12}\text{CH}_2$ and ^{14}N from ^{14}C is possible with a ΔE - E gas counter for an energy of 3 MeV (using charge-state 2^+ at 1 MV terminal voltage). A Si detector combined with a time-of-flight system was used for the experiments at 1 MeV. At both energies, background has been found at levels below 10^{-13} . This is certainly sufficient for biomedical applications. For ^{14}C dating, further background reduction is required.

The 600 kV AMS facility has been upgraded to a universal platform for AMS at low energies by Stocker et al. (2005) allowing to perform studies of ^{10}Be , ^{14}C , ^{26}Al , ^{41}Ca , ^{129}I , ^{236}U , and ^{239}Pu . The most significant improvement in performance is due to a new gas ionization chamber of much better energy resolution. Performance for ^{10}Be , ^{14}C , ^{26}Al , ^{129}I , and ^{239}Pu isotopes is now competitive with larger AMS facilities. The background in ^{41}Ca measurements is sufficiently low to measure samples for biomedical applications. In order to obtain the necessary sensitivity for ^{10}Be with a low-energy AMS system not only the molecular background but also the very high intensity of the nuclear isobar ^{10}B has to be suppressed. By using BeF_2 instead of BeO as sample material the ratio of boron to beryllium in the beam can be reduced by 4 to 5 orders of magnitude. Grajcar et al. (2005) have shown that it is possible to suppress the remaining ^{10}B background by another 5 orders of magnitude in a high resolution ΔE - E_r gas ionization chamber even at a final beam energy of only 0.8 MeV. The necessary resolution has been obtained by a special choice of the detector entrance window and the preamplifier design. This allows now to detect ^{10}Be down to a $^{10}\text{Be}/^9\text{Be}$ level of 10^{-14} with the 0.6 MV Tandem accelerator. A total transmission of 50% is obtained in charge-state 1^+ , which makes such a facility competitive with much larger systems. Boron suppression by a degrader foil has also been investigated at the same terminal voltage and charge-state. With an overall transmission of about 5%, a $^{10}\text{Be}/^9\text{Be}$ level of 10^{-12} was reached. For both techniques the limiting background is most probably caused by scattered ^9Be from molecular components in the injected beam. In proof of the successful development, the compact AMS system has been used to measure ^{10}Be rainwater samples in the form of BeF_2 . Comparison

of the results to those obtained by a large 6 MV facility definitely confirms the competitiveness of this type of small scale equipment, now also for ^{10}Be AMS.

High Voltage Engineering Corp. USA has built a compact 1 MV multi-element AMS system (Klein et al. 2006) which is primarily designed for the analysis of light elements like beryllium, carbon, and aluminium. This system also supports the measurement of heavy ions like iodine and plutonium. The analysis of ^{14}C is done using the charge-state 1^+ . For this, the accelerator terminal is designed for high stripper gas thickness to efficiently destroy the interfering molecules like ^{13}CH and $^{12}\text{CH}_2$. For the analysis of ^{10}Be , suppression of the isobaric ^{10}B is achieved using an absorber foil that can be inserted in front of the electrostatic analyzer. The analysis of ^{26}Al can be done using 1^+ or 3^+ charge state. The rare isotopes are identified in a dual-anode high-resolution detector and a two-dimensional data acquisition system.

8.5 Sample Preparation for AMS

A sample for AMS analysis should be in the solid form and must be thermally and electrically conductive. All samples are carefully prepared to avoid contamination. They are reduced to a homogeneous state from which the final sample material is prepared. Carbon samples, for instance, are reduced to graphite. Usually just a milligram of material is needed for analysis. If the sample is too small, bulking agents are carefully measured and added to the sample. Careful sampling and pretreatment are thus very important stages in the dating process, particularly for archeological samples where there is frequent contamination from the soil. Before sampling, the surface layers are usually removed because these are most susceptible to contamination. Since only a very small quantity of sample (0.2–2 mg) is required for the AMS measurements, the damage to the objects can be minimized. The chemical pretreatment of the sample depends on the type of sample. For example, the bones are treated as follows: bone powder is produced by drilling the sample, acid is used to demineralize the bone, alkali is used to remove humic acids from soil, etc., the extracted “collagen” is converted to gelatin by heating, the gelatin is put through an ion exchange column to remove impurities, the purified sample is freeze dried. Several of these procedures are done in an automated continuous flow system.

After chemical pretreatment, the samples are burnt to produce carbon dioxide and nitrogen. A small amount of this gas is bled into a mass spectrometer, where the stable isotope ratios of carbon and nitrogen are measured. These ratios provide useful information on the purity of the sample and clues about the diet and climatic conditions of the living organism. The carbon isotope ratio is also used to correct for isotopic fractionation in the radiocarbon measurement. The carbon dioxide is collected in a glass ampoule or converted to graphite for radiocarbon measurement on the AMS system.

The sample preparation technique used for carbon samples is based on the production of elemental carbon by the catalytic reduction of carbon dioxide, mixed with hydrogen gas, over an iron catalyst. Two slightly different systems are used, one for samples with ^{14}C -activities above the contemporary atmospheric level and the other for dating purposes with samples of low ^{14}C activity. The two apparatuses are located in separate laboratories to avoid contamination of the low-activity samples. Carbon dioxide is released from the carbonate samples by adding phosphoric acid and organic matter is combusted in the presence of CuO . Samples of high activity can be diluted with ^{14}C -free CO_2 before being reduced to solid carbon. The total reduction time for each sample containing about 5 mg of carbon is about 3–4 h. By using a number of reduction units, which can be separated from the rest of the sample preparation system, several samples can be processed concurrently.

Since the isobaric interference, ^{36}S , is a main problem in AMS measurement of ^{36}Cl , the improvement in the sample preparation method of ^{36}Cl in natural environment have been reported by Jiang et al. (2004). The SO_4^{2-} ion exists in the natural environment with an amount compared with the chlorine concentration. Traditionally, precipitation of BaSO_4 is used to separate sulfur from the sample material. The sulfur reduction process should be repeated more than two times for measurement of the sample with a $^{36}\text{Cl}/\text{Cl}$ ratio down to 10^{-13} . After removal of SO_4^{2-} the sample solution is passed through the H column to absorb metal ions and transfer Cl^- to HCl . Then the HCl solution is passed through the Na column to convert HCl to NaCl . Finally, excess AgNO_3 is added to the NaCl solution and AgCl is precipitated for AMS measurement. The chemical process only takes ~ 6 h, the time much shorter than the traditional method, and the chlorine recovery is higher than $\sim 90\%$. The rainwater, groundwater, and seawater samples are prepared with this method. The $^{36}\text{Cl}/\text{Cl}$ ratios in those samples has been measured in range of 10^{-13} – 10^{-14} . The method can also be used for soil, sediment, and rock samples after extraction of chlorine (^{36}Cl) from the sample materials. The ^{36}Cl could be easily measured from the sediment and rock samples by the above described procedure.

For dating with bone samples, one is required to carry out chemical pretreatment of bone, removal of preservatives and contaminants from objects, radiocarbon calibration, stable isotope analysis, and interpretation of contaminants.

8.6 Time-of-Flight Mass Spectrometry (TOF-MS)

The time-of-flight spectrometry for ERD analysis has been discussed under Sect. 3.4.2 of Chap. 3. The TOF-MS system is employed in AMS, because of the reason that the energy resolution of a silicon detector or an ionization chamber is often insufficient to resolve neighbouring masses of heavier ions. Better separation is possible by combining the energy measurement with a

determination of the ions velocity via a time-of-flight measurement. The time of flight of the particle is proportional to the mass number and the total energy of the particle. A time-of-flight mass spectrometer uses the differences in transit time through a drift region to separate ions of different masses. The times of flight of different masses are measured for a given distance either by using two fast timing detectors or by using the pulsed beam and a fast timing detector. If operated in a pulsed mode, the ions must be produced or extracted in pulses. An electric field accelerates all ions into a field-free drift region with a kinetic energy of qV , where q is the ion charge and V is the applied voltage. Since the ion kinetic energy is 0.5 mv^2 , lighter ions have a higher velocity than heavier ions and reach the detector at the end of the drift region sooner. In the case of buckyball ^{60}C (fullerene) for example, whose mass is 720 amu, the transit time (t) through the drift tube of length L can be calculated using the relation, $t = L/v = L/[2V/(m/q)]^{1/2}$ (since $\text{K.E.} = qV = 1/2\text{ mv}^2$).

A time-of flight (TOF) system, using two fast timing detectors, consists of “start” and “stop” detectors separated typically by 2 m. Start detector consists of a thin carbon foil and a microchannel plate, which multiply the electrons liberated from the foil by passage of the ion. The electron collection is made isochronous with electrostatic mirrors, deflectors, or uniform magnetic fields employed to direct the electrons to the microchannel plate. The stop detector may be similar to the start detector, in which case it is backed by a silicon detector or an ionization chamber for energy measurements. Alternatively, a silicon detector is often used to provide both energy and timing signals. Typical time resolutions achieved with such devices are 300–500 ps, which is more than adequate to separate ^{129}I from ^{128}Tc and ^{127}I . The output of an ion detector is displayed on an oscilloscope as a function of time to produce the mass spectrum.

The TOF is a method for isobar separation at energies below 1 MeV amu^{-1} (Vockenhuber et al. 2005). The residual energy of initially mono-energetic ions is measured precisely with a time-of-flight detector. Differences in the specific energy-loss lead to a clear separation even at low energies. In this respect, TOF is superior to other methods, since angular straggling and charge-state fluctuations do not reduce the measurement precision. Additionally, the energy resolution can be made arbitrarily high by increasing the flight path. This allows studying the physical limitations due to energy straggling independently from detector properties, but reduces the efficiency. Silicon nitride foils (Doebeli et al. 2004) used both in the start timing detector and as degraders have proven to be extremely homogenous, and the peaks in the residual energy spectra are almost free of tails. Systematic studies have led to an optimized TOF set-up, which achieves a detector efficiency of $\sim 8\%$ for $^{41}\text{Ca}^{4+}$ (14.6 MeV) while suppressing $^{41}\text{K}^{4+}$ by a factor of $\sim 10^3$ (CaF_3^- is used for injection). For ^{36}Cl , where no suppression of the isobar ^{36}S is possible in the ion source, a similar suppression of ^{36}S of 10^3 was achieved, but will require improved chemical sulfur suppression before competitive measurements are possible.

8.7 Detection Limits of Particles Analyzed by AMS

The particles analyzed by AMS can be divided into three categories: (i) stable isotopes (elements), (ii) radioisotopes, and (iii) exotic particles. The detection limits of the three categories vary greatly depending on the corresponding level of background. The detection limits of stable isotopes can hardly be lower than the 10^{-12} (ppt) level due to the difficulties of establishing an ultraclean condition in an accelerator environment. For radioisotopes the sensitivities expressed as the concentration ratios of radioisotopes to their stable isotopes are in the range of 10^{-14} – 10^{-15} . The lowest detection limits can be reached for exotic particles, since the parameter of mass and charge (e.g., fractionally charged particles), where no known species exist, is scanned.

Long-lived radioisotope analysis is based on the measurement of a very small isotopic ratio. Usually, small amounts of chemically prepared “pure” samples (in the form of elements or compounds) rather than the original samples are used in the ion source. The element-preconcentration is performed during the preparation of the AMS sample. Since the natural abundances of long-lived radioisotopes are usually very low in terrestrial materials, the contamination by the radioisotope itself from the environment is not a severe problem. The background may come from interferences of atomic and molecular species, stable isobars and isotopes, which can be discriminated effectively by AMS. Consequently, high sensitivities can be achieved in the AMS measurements of the radioisotopes (^{10}Be , ^{14}C , ^{26}Al , ^{32}Si , ^{36}Cl , ^{41}Ca , ^{129}I , etc.) for tracer studies. The equivalent detection limits for these elements are generally a few orders of magnitude lower than those obtained in other analytical techniques. In the ^{10}Be measurement, as a prominent case, the element beryllium (composed of 100% stable isotope ^9Be) has a low concentration in nature, and hence an extremely high equivalent sensitivity *can* be obtained. Kusakabe et al. (1982) have detected 1% concentrations in seawater as low as ~ 500 atoms g^{-1} , which is equivalent to a sensitivity of about 10^{-20} g g^{-1} . Also, an estimated detection limit for ^{26}Al of 10^{-18} g (6×10^4 atoms) was gained when Barker et al. (1997) used ^{26}Al in medical tracer studies.

Accelerator Mass Spectrometry measurements of trace elements are concentrated on the studies of precious metals in minerals and impurities in semiconductors. Since the AMS measurement is based on single atom counting, it has much higher sensitivity than both conventional MS and low level β -counting of long-lived radioisotopes. A very small isotopic abundance of a long-lived radioisotope can be measured with high discrimination of the accelerator system against interferences from other species, such as molecules, isotopes, and isobars. The sensitivity limit reaches 10^{-15} for $^{14}\text{C}/^{12}\text{C}$, $^{10}\text{Be}/^9\text{Be}$, $^{26}\text{Al}/^{27}\text{Al}$, and $^{36}\text{Cl}/\text{Cl}_{\text{tot}}$.

8.8 Applications of AMS

Accelerator Mass Spectrometry is a special tool for quantitative measurements of very long-lived radionuclides. This technique consists of counting the nuclides themselves instead of waiting for their decay. As far as the tandem accelerator is concerned, no molecular background exists because of the stripping process. Any isobaric background is also drastically suppressed due to the nuclear techniques involved in the measurements. There occurs an extremely wide area of applications in different fields because of the capability of the AMS technique to determine the radioisotopes at the faintest level (the isotopic concentrations down to the range of 10^{-16} in some cases).

The AMS method has been applied in different areas of Science such as archeology, earth science, pollution, biomedicine, hydrology, material science, and geological science. More than one isotope may be used within a given area. Some of the areas of research in which AMS is presently having an impact, are explained in Sects. 8.8.1–8.8.10.

8.8.1 In the Field of Archeology

Before the birth of AMS technique, the radiocarbon dating has been widely used in the field of Archaeology. AMS has been regarded better than the conventional decay counting method since it has superior efficiency and is the most sensitive method for determining radioactivity levels in small samples. An archeologist is generally interested in the age of the sample in calendar years whereas from radiocarbon dating (decay-counting or AMS) one gets the $^{14}\text{C}/^{12}\text{C}$ ratio in the sample. The calibration of the time scale in terms of the calendar years can be achieved from tree rings or coral records. The exposure-age dating is facilitated as many radionuclides such as ^{10}Be , ^{26}Al , ^{32}Si , ^{36}Cl , ^{39}Ar , and ^{81}Kr , are produced in the terrestrial atmosphere as a result of nuclear reactions involving cosmic-rays (fast neutrons and muons) and suitable target nuclei on the surface of the rocks. For surface exposure-age dating (Dorn and Phillips 1991, Cerling and Craig 1994), the knowledge of production cross-sections of these radioactive isotopes due to reactions of cosmic-rays with the elements present in the rocks (such as silicon, oxygen, calcium, potassium, chlorine, etc.) as well as in the atmosphere (carbon, oxygen, hydrogen, nitrogen, Ar) must be accurately known.

8.8.2 In the Field of Earth Science

Concentration of in situ produced isotopes in rock surfaces are not only influenced by the exposure-age of the surface as illustrated earlier but also by the rate at which it is being eroded. The aspect of erosion which plays very important role in earth science, the same can be measured by the geomorphologist through cosmogenic-isotope method over a time scale determined by the characteristic time $1/(\lambda + \epsilon\rho/\mu)$ where ϵ is the erosion rate, ρ is the density of the

rock, λ is the decay constant of the isotope and μ is the attenuation length of the cosmic-ray in the rock (Lal 1991). Stone et al. (1994) and Bierman and Turner (1995) have measured erosion rates of lime stone features across a wide range of climatic regions using surface concentrations of ^{36}Cl and ^{10}Be , and ^{26}Al respectively.

Since many landscape surfaces are not bare rocks but have soils developed on them, soil loss is in the form of erosion. Soil is continuously created by weathering of the underlying bedrock and may accumulate due to transport by water or wind from elsewhere. Knowledge of the rates of bedrock-to-soil conversion and of soil losses due to anthropogenic influences is of vital importance in context of pastoral activity as well as agriculture in hilly areas. The rates of these processes of soil erosion can be measured by using either in situ produced ^{10}Be and ^{26}Al or “garden variety” ^{10}Be . The garden variety ^{10}Be is produced in the atmosphere by cosmic-ray spallation of nitrogen and oxygen nuclei which further get attached to aerosols and fall out in rainfall. The fall out rate appears to be correlated with precipitation and is about $1.5 \times 10^4 \text{ atoms cm}^{-3}$. After fall out, it attaches to soil particles and follows their subsequent history provided that the characteristic time for loss of ^{10}Be in solution is long compared to the soil residence time (Monaghan et al. 1983, 1986).

8.8.3 For Study of Pollution

Air Pollution

In urban areas, the air pollution is caused mainly because of the industrial and vehicle exhausts as well as the organic / inorganic molecules while in the rural areas it is due to the burning of biomass and fossil fuel. The remedial measures of air pollution in different urban areas requires knowledge of the contributions from different sources in those areas. Currie et al. (1994, 1997) have used the ^{14}C content of CO , aerosols and polycyclic aromatic hydrocarbons for the study of air pollution in various US cities.

Discharge from Nuclear Power Plants

The ^{14}C is one of the radionuclides produced by neutron-induced reactions in all types of nuclear reactors. In a nuclear power facility the production of ^{14}C can occur in the fuel, the moderator, the coolant, and the core construction materials mainly by the reactions $^{17}\text{O}(\text{n}, \alpha)^{14}\text{C}$, and $^{14}\text{N}(\text{n}, \text{p})^{14}\text{C}$. Part of the ^{14}C created in reactors is continuously released as air-borne effluents in various chemical forms (such as CO_2 , CO , and hydrocarbons) through the ventilation system of the power plant during normal reactor operation. Another part of the ^{14}C produced is released into the atmosphere from fuel reprocessing plants. The environmental release of this reactor-derived ^{14}C leads to an increase in atmospheric specific activity and hence, to an increased radiation dose

to man. Therefore, it is of interest to measure the ^{14}C releases, to study their pathways and to determine the chemical form of the effluents. Since ^{14}C is believed to produce one of the largest collective dose commitments as compared to all other nuclides released in the nuclear power industry, an extensive investigation of the ^{14}C releases from some Swedish nuclear power plants has been performed at the Lund AMS facility. The ^{14}C content in the samples of air emitted from the stacks was measured using AMS. The chemical form of the effluents has also been studied and the ^{14}C concentration in vegetation in the vicinity of a power plant has been measured.

^{36}Cl is another isotope which has been found in ground water and streams on and near the fuel reprocessing facilities. It has been estimated that release of ^{36}Cl to the atmosphere is due to escape of gaseous chlorine compounds which are formed when the fuel elements are dissolved in hot nitric acid. Direct release to ground water may occur as a result of effluent leakage.

In nuclear waste management ^{59}Ni is a most important radioisotope as it is produced by neutron activation in the stainless steel shielding surrounding the fuel. The total activity concentration of ^{59}Ni , as well as of other radionuclides, has to be established in preparation for final disposal. Furthermore, if the ^{59}Ni content in the steel can be measured, the integrated neutron flux at different positions in the reactor can be calculated. Because ^{59}Ni decays only via electron capture and has a very long half-life (7.6×10^4 years) it is very difficult to measure its radiation emitted in the radioactive decay. The atom counting approach of AMS would in this case be advantageous. However, for small tandem accelerators, the common energy or energy-loss detection techniques are not able to distinguish atomic isobars for heavy elements such as Ni. A new detection technique, suitable for heavier nuclei, has been proposed a few years ago in which the different atomic isobars can be distinguished by studying their characteristic X-rays. By applying this detection technique to AMS measurements of ^{59}Ni , the interfering isobar, ^{59}Co , can be suppressed.

8.8.4 In the Field of Biomedicine

The radioisotope ^3H is the most frequently utilized isotope in biomedicine, and has numerous applications, e.g., determination of total body water, metabolism studies, dosimetry measurements, etc. The development of tritium AMS is expected to have a great impact in biomedical research because tritium is the most widely used radioisotope in biomedicine. ^{14}C is widely used as a radioactive tracer in biomedical research and in drug testing. In clinical medicine, organic compounds labeled with ^{14}C are used to demonstrate metabolic abnormalities. One way of carrying out these studies is to use *breath tests*. The ^{14}C -labeled compound is ingested and metabolized, resulting in the end-product carbon dioxide, which is exhaled and easily collected for measurement. The decay of the radionuclide is usually measured by gas flow counters or liquid scintillators and the activity of the sample reveals the degree of say for example, fat malabsorption. Clinically useful information is obtained from

samples taken a few hours after the administration of the test compound, even if the total turnover time is much longer. A complete biokinetic study, needed for such purposes as the calculation of the radiation dose, requires sampling for a much longer time, up to several months or even longer. AMS offers the major advantage of much smaller doses than are required in the traditional scintillation counting apart from reduction in expenses as well as reducing the problem of disposal. Standard measuring methods, used in medical applications, are only capable of detecting increased levels of ^{14}C in expired air for a few days after ingestion. AMS which is much more sensitive technique has been used to study the long-term retention of ^{14}C after a fat malabsorption test (using ^{14}C -labeled triolein) by analysis of expired air. Studies on the long-term retention of ^{14}C after a ^{14}C -urea test are of vital importance because it can demonstrate abnormal activity of gastrointestinal bacteria. The ligand binding studies can be carried out on humans/experimental animals using ^{14}C , ^3H , and ^{129}I and the high sensitivity permits binding to be measured in-vivo or in-vitro.

To study a new drug using AMS, scientists modify just a few molecules of the drug to include a detectable atom such as ^{14}C . The amount of radioactivity in the drug dose is less than a person absorbs during a day on Earth from natural sources of radiation such as cosmic-rays. Using a radioactive isotope such as ^{14}C as a “tracer” is not new. What is new is the high sensitivity of AMS, which allows the use of much smaller drug doses and consequently less ^{14}C – from a thousand to a million times less than is used in studies that do not use accelerator mass spectrometry. Using AMS to count ^{14}C nuclei, researchers can follow the movement of the ^{14}C -tagged drug through the body, identifying how long it remains there, how much and when it is excreted, how much is absorbed, and what organs it affects. How does this work? ^{14}C is a naturally occurring radioactive isotope that can easily be incorporated into a drug or nutrient before a human ingests it. Counting ^{14}C atoms in urine samples will tell researchers how much of the chemical was digested and how long the ^{14}C -tagged drug was in the body before being excreted. Similar studies may be done with samples of blood or saliva. Studies over time can determine drug absorption and excretion and what the drug’s effects are. The tiny drug dose in this kind of study contrasts with the large quantities typically given to laboratory animals to determine dose-response relationships. Data from tests of potential carcinogens, toxins, and other compounds can serve as the basis for potency calculations and risk assessments relevant to humans. More tests of drugs using human subjects and the tiny doses that AMS can measure will expand the base of information on metabolism, efficacy, and toxicity. The time period for testing drugs can be shorter, which will decrease the cost of bringing new drugs to market. Definitive human data can give users a larger margin of safety than they have today. As the database on human metabolism grows, scientists will come ever closer to being able to tailor and individualize therapeutic treatments.

The AMS studies using ^{26}Al tracer is important due to toxic nature of aluminium and its low concentration in biological systems (1 ppm in tissues and 1 ppb in blood) whereas it constitutes about 9% of the earth's crust. Aluminum has several isotopes with half-life <6 min, this is too short for traditional exposition measurements. ^{26}Al has a half-life of 720,000 years, which is too long for exposition measurements, but quite ideal for AMS studies. The natural isotope ratio is $^{26}\text{Al}/^{27}\text{Al} = 10^{-14}$. Because the specific activity is so low, it is possible to give very low levels of ^{26}Al doses of $\sim 10^{15}$ atoms (~ 50 ng) to humans without causing any significant radiation impact. AMS can easily detect 10^6 atoms which opens the way for long-term studies using urine or blood samples. AMS measurements have been done by Barker et al. (1997) to study uptake and distribution of ^{26}Al in mice and the role of the transferrin receptor in aluminium absorption mechanisms. The procedure for sample preparation and use of AMS methodology for biomedical samples is given by King et al. (1997).

Unlike aluminium, calcium has a number of stable isotopes plus a radioactive isotope with a half-life of about a year. The AMS studies using ^{41}Ca has potential in the study of bone loss. The human calcium metabolism including bone resorption with ^{41}Ca tracer has been measured by Freeman et al. (1997). The other longer-lived isotope is ^{59}Ni ($t_{1/2} = 1.1 \times 10^5$ years) which can be used as a tracer for bioscience applications. ^{63}Ni ($t_{1/2} = 100$ years) is produced in copper samples via the $^{63}\text{Cu}(n, p)^{63}\text{Ni}$ reaction.

8.8.5 In the Field of Hydrology

^{36}Cl is the principle AMS isotope used in hydrology as it has found application in determining the ages of groundwater, in measuring recharge rates, in studying past climates and in investigating the hydrology of nuclear waste analogs and potential waste-disposal sites. The use of ^{36}Cl for dating the groundwater has been exemplified from the following data: $^{36}\text{Cl}/\text{Cl}$ ratios vary from $\sim 10^{-13}$ near recharge to $\sim 10^{-14}$ at discharge. This gives good estimate of the basin time in agreement with the ones based on hydrological model considering the difference in the ratio due to the decay of ^{36}Cl .

Although ^{14}C and ^{129}I have also been employed but the use of all these isotopes is to be regarded as complements to the more conventional tools employed by hydrologists rather than being used in isolation. Recent review on this application has been reported by Fontes and Andrews (1994).

8.8.6 In Material Analysis

The ultrasensitivity of AMS is useful to measure not only the long-lived radioisotopes but also ultratrace-concentrations (down to sub-ppb levels) of stable isotopes in minerals and semiconductors (Rucklidge et al. 1990, Kilius et al. 1990, McDaniel 1995). Since semiconductor devices are playing an increasingly important role in various fields of modern life, the purity of semiconductor

materials plays important role as the size of semiconductors decreases. There is strong need for a quantitative assessment of the contents of the trace impurities and their effects on the electronic performance of the semiconductors. The detection of trace elements in semiconductors by AMS technique has been reported by Anthony et al. (1987, 1990) who measured several impurities like B, Be, Si, Nb, Sb and Te in Si and GaAs crystals. The background level for most of these impurities was also a trouble problem due to contamination in the ion source. The results showed that the background ranged from 0.5 ppb for B in Si and in GaAs, and 40 ppb for Cr in GaAs; the background for other impurities lay in the 1–10 ppb range. This experiment demonstrated that the major constraint on the sensitivity of the system was the ion source contamination.

8.8.7 In the Field of Food Chemistry

An important topic in food chemistry technology is the interaction between foods and packaging materials, which can be defined as chemical and/or physical reactions between food, its package, and the environment. In this way the composition, quality or physical properties of the food and/or package can be altered. Knowledge of these interactions is of importance for the development of new packaging systems.

Several methods, each one having advantages and disadvantages, have been and are being used in studies of interactions between foods and packaging materials. One effect of the interactions is the absorption of aromatic compounds into plastic packaging materials, which can damage the package and impair its protective properties. If key aromatic compounds are absorbed, this can lead to a loss of aromatic intensity of the food, a change in flavor and hence a deterioration in quality of the food. In Lund (Sweden), the AMS technique has been introduced into food chemistry with the aim of demonstrating that AMS can be a complementary and suitable tool for investigations of the absorption of flavors in plastic packaging materials.

8.8.8 For Study of Nutrients

AMS is affecting the study of the effects of vitamins and minerals in our daily diet. We know that they are needed for healthy living but their effects are virtually unknown. Since the illnesses may result due to their absence from our diet, AMS is finally allowing researchers to trace such nutrients in the human body. A study of the dietary nutrient calcium is, for example, important as it is a key nutrient for bone health. Although understanding calcium metabolism is critical yet measuring calcium kinetics in bone directly was difficult until the advent of accelerator mass spectrometry. With decay-counting methods, only the short-lived radioisotopes of calcium can be used to trace the movement of calcium through the body. Very large amounts of the tracer must be used because ingested and absorbed calcium is only slowly

resorbed by the skeleton. For any of the tracers to show up in urine, which is where calcium appears that has been lost from bone, the patient must ingest a dangerously high radiation dose. An alternative testing method is the use of stable isotopes as tracers, but they are extremely expensive. If calcium with a ^{41}Ca tracer is given to a patient, the skeleton will become “tagged” with ^{41}Ca . The ^{41}Ca in subsequent urine samples will indicate how much ^{41}Ca is being lost from the skeleton. ^{41}Ca is an effective tool in testing drugs that may prevent osteoporosis. Some drugs are designed to “seal” the bone to reduce calcium resorption. When treatment with such drugs begins, calcium loss will slow, and the amount of ^{41}Ca in urine samples will be reduced. Various therapeutic dosages and formulations can easily be studied and compared. With ^{41}Ca and AMS, the kinetics of calcium in the human skeleton can be studied directly, enabling studies of fundamental bone processes and providing indicators of an individual’s bone health.

Elemental trace nutrients also yield to the new developments in AMS. Among those under investigation at the center are nickel, selenium, and iodine. The very long-lived isotopes of these elements that are detected through AMS will eventually be traced in humans at levels that present no discernible chemical or radiological danger. Tritium and radiocarbon are obvious labels in organic nutrition. The only other bulk nutrient elements having long-lived isotopes are chlorine and calcium. While measurement of ^{36}Cl is routine in many AMS facilities, it is primarily used in earth sciences. However, with its 350,000 year half-life, it is ideally suited for application to chlorine studies in animals, humans, or plants. ^{41}Ca is one of the most exciting isotopes to be made available to the nutrition and health communities. Although ^{41}Ca ($t_{1/2} = 1.16 \times 10^5$ years) is commonly used, there are the short-lived isotopes of ^{45}Ca and ^{47}Ca with 165 and 4.5 d half-life. Even with these high specific radioactivities, these isotopes have long been used in metabolism research and clinical testing (Elmore 1990, Fink et al. 1990, Freeman et al. 1997).

Among the trace nutrients, nickel is the most developed, with relatively simple sample definition and preparation for ^{59}Ni . While AMS detection of ^{53}Mn and ^{60}Fe has been accomplished in meteoritic samples, ^{59}Ni is the one readily available isotope for nutritional and detailed biochemical studies. Selenium is another trace nutrient element because of its position as an extremely important trace nutrient that is toxic at levels not much higher than nutrient levels, and which is found in nearly toxic levels. The element has been studied using the short-lived isotope ^{75}Se , but human research would benefit from the use of ^{79}Se whose half-life has recently been determined to be 2×10^6 years. Unfortunately, the nuclear isobar ^{79}Br contaminates our general purpose ion source to a very high level due to measurements of ^{36}Cl .

8.8.9 In the Field of Geological Science

Over the last one-and-a-half decade, the cosmogenic radionuclides based exposure dating technique has made a significant impact in our understanding

of the finer differences in the rates at which various landforms like river valley profile, change (Sharma 1999). Systematic analysis for different isotopes like ^{10}Be , ^{26}Al , and ^{36}Cl of air-borne and surface precipitation samples, from various distances from coast line can help to study ground water circulation, recharge and dating related problems.

^{10}Be has been shown to be useful for soil studies as it has affinity for particulate such as silicates and it rapidly participates from the atmosphere attached to such particles. The cosmogenic radionuclides ^{10}Be , ^{26}Al , ^{36}Cl , ^{129}I are being used for the study of ocean sediments due to the accumulation over millions of years. In addition to exposure ages based erosion, uplift, incision rates and slip rate along active faults, there are many more applications of AMS in geosciences, such as (i) glacier chronologies in Himalayas, (ii) fluvial system studies in Ganga basin, (iii) soil and desert sand studies, (iv) coastal morphological and sea level change related studies along vast coast line, and (v) time and space related weathering and erosion patterns.

8.8.10 For Study of Ice-Cores

Polar ice preserves record of atmospherically produced ^{10}Be and ^{36}Cl . The ice cores can be dated by a number of techniques including the counting of annual layers, the production rate and climatic factors that control the deposition of these isotopes in snow can be studied. Production is controlled by primary cosmic-ray intensity, modulation of the cosmic-ray flux by changes in the solar magnetic field and geomagnetic modulation of the cosmic-ray flux. The ^{10}Be concentration in ice cores does reflect changes in production rates due to solar activity as well as geomagnetic field intensity modulation. ^{36}Cl fall out is an order of magnitude less than ^{10}Be and therefore measurements of ^{36}Cl are as extensive as those of ^{10}Be (Yiou et al. 1997, Beer et al. 1990).

8.9 Use of Various Isotopes for Important AMS Studies

8.9.1 Use of ^{10}Be

S. No.	Application	Field of study
1.	Study of Glacial mountains	Palcoclimates
2.	Lake level changes	Palcoclimates
3.	Antarctic mountain summits	Palcoclimates
4.	Ice cores	Geomagnetism
5.	Lunar rocks	Geomagnetism
6.	Soils	Erosion studies
7.	Water sheds	Erosion studies
8.	Trace element cycling	Ocean sciences
9.	Past ocean productivity	Ocean sciences
10.	Dating and verifying impact events in rocks	Extraterrestrial materials

8.9.2 Use of ^{14}C

S. No.	Application	Field of study
1.	Study of tree rings	Solar variability and Geomagnetism
2.	Methane sources	Erosion studies
3.	Circulation (^{14}C in CO_2)	Ocean sciences
4.	Global warming rates (^{14}C in foraminifera)	Ocean studies

8.9.3 Use of ^{26}Al

S. No.	Application	Field of study
1.	Study of Antarctic mountain summits	Solar variability and Geomagnetism
2.	Lunar rocks	Solar variability and Geomagnetism
3.	To measure the distribution and uptake mechanisms of ^{26}Al in vivo in mice	Biomedicine

8.9.4 Use of ^{36}Cl

S. No.	Application	Field of study
1.	Study of Glacial mountains	Paleoclimates
2.	Pluvial lake sediments	Paleoclimates
3.	Lake level changes	Paleoclimates
4.	Antarctic mountain summits	Paleoclimates
5.	Ice cores	Solar variability and Geomagnetism
6.	Lunar rocks	Solar variability and Geomagnetism
7.	Volcanic rock exposure to cosmic-rays	Erosion studies
8.	Chlorine chemistry – ozone hole	Erosion studies
9.	Dating old ground water	Hydrology
10.	Brines in terminal lakes	Hydrology
11.	Dynamics of Antarctic ice (^{36}Cl in meteorites)	Extraterrestrial materials

8.9.5 Use of ^{41}Ca

S. No.	Application	Field of study
1.	Human calcium metabolism including bone resorption measured with ^{41}Ca tracer	Biomedicine

8.9.6 Use of ^{59}Ni

S. No.	Application	Field of study
1.	In nuclear waste management in the nuclear industry	Pollution

8.10 AMS of Molecular Ions

The use of tandem accelerators for AMS allows to literally “analyze” molecules. When a molecular ion with mass M and charge Q is injected at the low-energy side of the accelerator, it is broken up into its atomic constituents during the stripping process in the terminal. At the high-energy side, the positively charged atomic ions are analyzed by their mass-to-charge ratio and by their energy in the detector (and eventually by their nuclear charge). Since free doubly-charged negative molecules are a challenge for both theory and experiment, their stability depends on a very delicate balance between interatomic structure, electronic interaction and Coulomb repulsion. Detecting di-anions of mass M with conventional mass spectrometry always bears the risk of erroneously measuring contributions from singly charged negative ions near mass $M/2$, or from molecular fragments with different energy. Another possible source of errors is mass ambiguity, e.g., $M[(\text{CH}_4)_2] \approx M(\text{O}_2)$. Golser et al. (2004) have shown how one can overcome the methodical limits of conventional mass spectrometry by using AMS techniques for the analysis of very rare doubly-charged negative molecules. As an example, a new class of di-anions $(\text{OC}_n)^{2-}$, $n \geq 5$ has been presented, which were discovered by secondary ion mass spectrometry, and were analyzed in detail by AMS. In another study, Golser et al. (2005) have identified the doubly-charged negative molecule $(^{43}\text{Ca}^{19}\text{F}_4)^{2-}$. It considerably eases the task that the total mass $M = 119$ is odd, so the di-anion is injected at the half-integer mass-to-charge ratio $M/Q = 59.5$, where no singly charged ions can interfere.

Experimental investigation of the destruction of 1 MeV $^{12}\text{CH}_2$ molecules in single and double stripping foils was carried by Hughey et al. (1997) who performed experiments examining the destruction of mass-14 molecules in the 2^+ charge-state after passing through both single and double carbon stripping foils at 1 MeV. A background level of less than 2% of contemporary ^{14}C was

observed for a single foil with thickness $4.4 \mu\text{g cm}^{-2}$. Significantly increased attenuation of 1 MeV molecular ions after passing through a pair of thin carbon stripping foils was demonstrated, as compared to a single carbon foil of comparable total thickness. The detected molecular counts after passing through a single $4.4 \mu\text{g cm}^{-2}$ foil correspond to a surviving fraction in the 2^+ charge-state of less than 6×10^{-10} . No statistically significant molecular survival was observed for pairs of stripping foils with a combined thickness of $4.0\text{--}4.6 \mu\text{g cm}^{-2}$, with an upper limit on surviving molecular fraction a factor of 15 lower than for the single foil. These results show that a low-energy AMS system, based on the detection of ^{14}C in the 2^+ charge-state after a foil stripper, will provide more than adequate discrimination for the analysis of biomedical samples labeled at or above contemporary ^{14}C .

8.11 Advantages and Limitations of AMS

One of the main advantages of AMS over the conventional β -counting method is the much greater sensitivity of the measurement. In AMS the radiocarbon atoms are directly detected instead of waiting for them to decay. Sample sizes are thus typically 10^3 times smaller allowing a much greater choice of samples and enabling very selective chemical pretreatment. The fact that AMS requires only milligram-range, or smaller samples, has opened new possibilities in fields such as radiocarbon dating and biomedicine. For instance, in archeology single grains of corn can be dated, while in-vivo measurements of ^{14}C -labeled tracers can be performed. The AMS method is also much more efficient than radiometrical techniques, since each sample usually takes less than an hour to analyze. The capacity is thus highly increased and this makes it possible to conduct very thorough investigations as a result of the larger number of samples that can be analyzed by AMS than by conventional techniques. Another advantage is that the sample preparation for ^{14}C analyses with AMS is fairly simple. For instance, other radionuclides present will not interfere with the AMS measurements, as is the case in radiometrical techniques. An AMS facility is, however, a very expensive and a quite complicated and sensitive tool.

The distinct advantages of AMS in comparison with conventional mass spectrometry are:

- (1) Ultra-Sensitivity: The AMS measurement is principally based on single atom counting, allowing detection of a very small isotope ratio of a long-lived nuclide or a very low concentration of a stable isotope. The very high sensitivity results from the high discriminatory power of the facility against the interferences of molecular species, scattering particles, isotopes and isobars, which makes the sensitivity of AMS several orders of magnitude higher than the conventional mass spectrometry. For most of cosmogenic radionuclides, especially when their half-life is

greater than 10^5 years, the sensitivity of AMS measurements is much higher than that of β -counting method. For example, the lowest ^{10}Be concentration in a sample measured by β -counting is above 10^9 atoms g^{-1} , but AMS improves the detection sensitivity to 10^3 atoms g^{-1} or even less. The sensitivity limit, for example, for detecting $^{14}\text{C}/^{12}\text{C}$ ratio is down to 1.7×10^{-15} , and of the order of 10^{-15} for $^{10}\text{Be}/^9\text{Be}$, $^{26}\text{Al}/^{27}\text{Al}$ and $^{36}\text{Cl}/\text{Cl}_{\text{tot}}$. This rapidly growing technique increases the sensitivity of mass spectrometry by at least a factor of a thousand, and thus is often termed “ultrasensitive mass spectrometry.”

- (2) Reduction of Sample Size and Counting Time: In conventional low-level β -counting, a large sample is required. For instance, for ^{14}C counting in dating or tracer studies, several grams of a carbon sample is usually taken. For the longer-lived isotopes, even kilograms of samples are needed. AMS can often reduce the size of samples to a few milligrams and even to as little as 100 μg . Also, AMS shortens the measurement time considerably. For example, measurement of 10 ppt (parts-per-trillion) content of ^{77}Ir in an untreated mineral sample by AMS only takes 10 min, whereas the time spent to gather such data for Ir by neutron activation analysis is of the order of a couple of days. In particular, when a series of tests are made, AMS gives shorter turnaround time in measurements.

The limitations of AMS measurements are:

- (1) The obvious difficulty is the small choice of the appropriate elements to be studied, since only ^{10}Be , ^{14}C , ^{26}Al , ^{36}Cl , and ^{129}I can be routinely, and the other radioisotopes including ^{32}Si , ^{41}Ca , ^{44}Ti , ^{53}Mn , ^{59}Ni , ^{60}Fe as well as some stable isotopes of Os, Pt, Ir, B, P, Sb, etc. are seldom used.
- (2) The overall efficiency of AMS is the ratio of the number of atoms detected to the number of the same kind of atoms in the sample. It depends on the fraction of sample used, the efficiency of producing negative ions, the stripping yield in the particular charge selected and the transmission efficiency through the accelerator. The overall efficiency of AMS is lower than that of low-energy MS. The maximum efficiency among the accelerators ranges from 1.5×10^{-2} for ^{14}C to $10^{-6} - 10^{-5}$ for ^{53}Mn . This variation reflects the different efficiency for forming negative ions in the cesium sputter ion source. The efficiency for forming a negative ion depends not only on the element, but also on the sample matrix.
- (3) Background in AMS may arise from contamination and interference species. The contamination gets introduced into the sample from either the environment or other residual samples in the ion source. The interferences consist of unresolved molecular fragments, isotopes and isobars. Cross-contamination of different targets varies between 10^{-5} and 10^{-3} , depending on the geometry of the ion source. Special attention should be paid to the contributions by isobaric interferences from ^{10}B to the background of ^{10}Be , and ^{32}S to the background of ^{32}Si .

- (4) Factors that affect precision are counting statistics, isotope fractionation effects, frequency of cycling, and the effectiveness of blank and standard correction. Generally, the precision attained in AMS is comparable to or even higher than that of radioactive counting of natural samples for the long-lived radionuclides when the counting time available is not long enough, but lower than that of conventional MS.
- (5) Small sample sizes (considered as one of the major advantage) have their disadvantages i.e. greater mobility within deposits and more difficulty in controlling contaminants. In that case, the best conventional counters can achieve higher precision and lower backgrounds than an AMS system. For this reason, the calibration curves for radiocarbon have usually been measured using counters.

A

Appendix

A.1 Some Useful Data Tables

Table A.1. Binding energies of different subshells of various elements (in keV)

Z, Element	$1S_{1/2}$ (K)	$2s_{1/2}$ (L _I)	$2p_{1/2}$ (L _{II})	$2p_{3/2}$ (L _{III})	$3s_{1/2}$ (M _I)	$3p_{1/2}$ (M _{II})	$3p_{3/2}$ (M _{III})	$3d_{3/2}$ (M _{IV})	$3d_{5/2}$ (M _V)
1 H	0.0136								
2 He	0.02459								
3 Li	0.05475								
4 Be	0.1120								
5 B	0.1880								
6 C	0.2841								
7 N	0.4005								
8 O	0.5320								
9 F	0.6854								
10 Ne	0.8701								
11 Na	1.0721								
12 Mg	1.3050								
13 Al	1.5596								
14 Si	1.8389								
15 P	2.1455								
16 S	2.4720								
17 Cl	2.8224								
18 Ar	3.2029	0.320	0.2473	0.2452					
19 K	3.6074	0.3771	0.2963	0.2936					
20 Ca	4.0381	0.4378	0.3500	0.3464					
21 Sc	4.4928	0.5004	0.4067	0.4022					
22 Ti	4.9664	0.5637	0.4615	0.4555					
23 V	5.4651	0.6282	0.5205	0.5129					
24 Cr	5.9892	0.6946	0.5837	0.5745					
25 Mn	6.5390	0.7690	0.6514	0.6403					

Table A.1. *Continued*

<i>Z</i> , Element	$1S_{1/2}$ (K)	$2s_{1/2}$ (L _I)	$2p_{1/2}$ (L _{II})	$2p_{3/2}$ (L _{III})	$3s_{1/2}$ (M _I)	$3p_{1/2}$ (M _{II})	$3p_{3/2}$ (M _{III})	$3d_{3/2}$ (M _{IV})	$3d_{5/2}$ (M _V)
26 Fe	7.1130	0.8461	0.7211	0.7081					
27 Co	7.7089	0.9256	0.7936	0.7786					
28 Ni	8.3328	1.0081	0.8719	0.8547					
29 Cu	8.9789	1.0961	0.9510	0.9311					
30 Zn	9.6586	1.1936	1.0428	1.0197	0.1359	0.0866	0.0866	0.0810	0.0810
31 Ga	10.3671	1.2977	1.1423	1.1154	0.1581	0.1068	0.1029	0.0174	0.0174
32 Ge	11.1031	1.4143	1.2478	1.2167	0.180	0.1279	0.1208	0.0287	0.0287
33 As	11.8667	1.5265	1.3586	1.3231	0.2035	0.1464	0.1405	0.0412	0.0412
34 Se	12.6578	1.6539	1.4762	1.4352	0.2315	0.1682	0.1619	0.0567	0.0567
35 Br	13.4737	1.7820	1.5966	1.5499	0.2565	0.1893	0.1815	0.0701	0.0690
36 Kr	14.3256	1.9210	1.7272	1.6749	0.2227	0.2138	0.0889	0.0889	0.0240
37 Rb	15.1997	2.0651	1.8639	1.8044	0.3221	0.2474	0.2385	0.1118	0.1103
38 Sr	16.1046	2.2163	2.0068	1.9396	0.3575	0.2798	0.2691	0.1350	0.1331
39 Y	17.0384	2.3725	2.1555	2.0800	0.3936	0.3124	0.3003	0.1596	0.1574
40 Zr	17.9976	2.5316	2.3067	2.2223	0.4303	0.3442	0.3305	0.1824	0.1800
41 Nb	18.9856	2.6977	2.4647	2.3705	0.4684	0.3784	0.3630	0.2074	0.2046
42 Mo	19.9995	2.8655	2.6251	2.5202	0.5046	0.4097	0.3923	0.2303	0.2270
43 Tc	21.0440	3.0425	2.7932	2.6769	0.5449	0.4250	0.4064	0.2529	0.2500
44 Ru	22.1172	3.2240	2.9669	2.8379	0.5850	0.4828	0.4606	0.2836	0.2794
45 Rh	23.2199	3.4119	3.1461	3.0038	0.6271	0.5210	0.4962	0.3117	0.3070
46 Pd	24.3503	3.6043	3.3303	3.1733	0.6699	0.5591	0.5315	0.3400	0.3347
47 Ag	25.5140	3.8058	3.5237	3.3511	0.7175	0.6024	0.5735	0.3740	0.3680
48 Cd	26.7112	4.0180	3.7270	3.5375	0.7702	0.6507	0.6165	0.4105	0.4037
49 In	27.9399	4.2375	3.9380	3.7301	0.8262	0.7023	0.6640	0.4511	0.4440
50 Sn	29.2001	4.4647	4.1561	3.9288	0.8838	0.7564	0.7144	0.4933	0.4848
51 Sb	30.4912	4.6983	4.3804	4.1322	0.9437	0.8119	0.7656	0.5369	0.5275
52 Te	31.8138	4.9392	4.6120	4.3414	1.0060	0.8697	0.8190	0.5825	0.5721
53 I	33.1694	5.1881	4.8521	4.5571	1.0720	0.9305	0.8746	0.6313	0.6194
54 Xe	34.5614	5.4528	5.1037	4.7822	1.1490	1.0020	0.9410	0.6890	0.6773
55 Cs	35.9846	5.7143	5.3594	5.0119	1.2171	1.0650	0.9976	0.7395	0.7255
56 Ba	37.4406	5.9888	5.6236	5.2470	1.2928	1.1367	1.0622	0.7961	0.7807
57 La	38.9246	6.2663	5.8906	5.4827	1.3614	1.2044	1.1234	0.8485	0.8317
58 Ce	40.4430	6.5488	6.1642	5.7234	1.4346	1.2728	1.1854	0.9013	0.8853
59 Pr	41.9900	6.8348	6.4404	5.9643	1.5110	1.3374	1.2422	0.9511	0.9310
60 Nd	43.5689	7.1260	6.7215	6.2079	1.5760	1.4028	1.2974	0.9999	0.9777
61 Pm	45.1840	7.4279	7.0128	6.4593	1.6560	1.4774	1.3639	1.0605	1.0340
62 Sm	46.8342	7.7368	7.3118	6.7162	1.7278	1.5457	1.4248	1.1110	1.0852
63 Eu	48.5190	8.0520	7.6171	6.9769	1.8050	1.6189	1.4856	1.1656	1.1359
64 Gd	50.2391	8.3756	7.9303	7.2428	1.8878	1.6953	1.5510	1.2242	1.1922
65 Tb	51.9957	8.7080	8.2516	7.5140	1.9675	1.7677	1.6113	1.2750	1.2412
66 Dy	53.7885	9.0458	8.5806	7.7901	2.0468	1.8418	1.6756	1.3325	1.2949
67 Ho	55.6486	9.3901	8.9259	8.0868	2.1301	1.9271	1.7629	1.4000	1.3674
68 Er	57.5796	9.7424	9.2782	8.3919	2.2184	2.0144	1.8500	1.4700	1.4374
69 Tm	59.5791	10.1027	9.6335	8.7067	2.3117	2.1067	1.9429	1.5425	1.5099
70 Yb	61.6448	10.4720	10.0000	9.0217	2.4100	2.2040	2.0400	1.6175	1.5825
71 Lu	63.7741	10.8503	10.3750	9.3469	2.5133	2.3063	2.1425	1.6950	1.6599
72 Hf	65.9653	11.2386	10.7500	9.6217	2.6217	2.4137	2.2400	1.7775	1.7399
73 Ta	68.2271	11.6369	11.1250	9.9000	2.7350	2.5270	2.3825	1.8650	1.8250
74 W	70.5614	12.0452	11.5333	10.1833	2.8533	2.6453	2.5000	1.9575	1.9125
75 Re	72.9691	12.4645	11.9500	10.4717	2.9767	2.7687	2.6175	2.0550	2.0099
76 Os	75.4514	12.8948	12.3750	10.7650	3.1050	2.8970	2.7400	2.1575	2.1125
77 Ir	77.9991	13.3361	12.8083	11.0633	3.2383	3.0303	2.8675	2.2650	2.2200
78 Pt	80.6134	13.7884	13.2500	11.3667	3.3767	3.1687	2.9950	2.3775	2.3325
79 Au	83.2951	14.2517	13.7000	11.6750	3.5200	3.3120	3.1375	2.4950	2.4500
80 Hg	86.0464	14.7260	14.1583	11.9883	3.6683	3.4603	3.2850	2.6175	2.5725
81 Tl	88.8681	15.2113	14.6250	12.3067	3.8217	3.6137	3.4375	2.7450	2.7000
82 Pb	91.7614	15.7086	15.1000	12.6300	3.9800	3.7720	3.6000	2.8775	2.8325
83 Bi	94.7271	16.2179	15.5833	12.9583	4.1433	3.9353	3.7675	3.0150	2.9700
84 Po	97.7654	16.7392	16.0750	13.2917	4.3117	4.1037	3.9350	3.1575	3.1125
85 At	100.8771	17.2725	16.5750	13.6300	4.4850	4.2770	4.1175	3.3050	3.2600
86 Rn	104.0614	17.8178	17.0833	13.9733	4.6633	4.4553	4.3000	3.4575	3.4125
87 Fr	107.3181	18.3751	17.5917	14.3217	4.8467	4.6387	4.4825	3.6150	3.5699
88 Ra	110.6464	18.9444	18.1000	14.6750	5.0350	4.8270	4.6700	3.7775	3.7325
89 Ac	114.0471	19.5257	18.6167	15.0333	5.2283	5.0203	4.8625	3.9450	3.8999
90 Th	117.5214	20.1190	19.1417	15.3967	5.4267	5.2187	5.0600	4.1175	4.0725
91 Pa	121.0701	20.7243	19.6750	15.7650	5.6300	5.4220	5.2625	4.2950	4.2500
92 U	124.7844	21.3416	20.2167	16.1383	5.8383	5.6353	5.4750	4.4775	4.4325
93 Np	128.5641	21.9709	20.7700	16.5167	6.0517	5.8537	5.6925	4.6650	4.6200
94 Pu	132.4094	22.6132	21.3250	16.8983	6.2700	6.0770	5.9150	4.8575	4.8125
95 Am	136.3211	23.2695	21.8917	17.2833	6.4933	6.3063	6.1425	5.0550	5.0100
96 Cm	140.2994	23.9408	22.4600	17.6717	6.7217	6.5407	6.3850	5.2575	5.2125
97 Bk	144.4441	24.6271	23.0417	18.0633	6.9550	6.7800	6.6325	5.4650	5.4200
98 Cf	148.7554	25.3284	23.6350	18.4583	7.1933	7.0243	6.8850	5.6775	5.6325
99 Es	153.2331	26.0447	24.2417	18.8567	7.4367	7.2707	7.1425	5.8950	5.8500
100 Fm	157.8784	26.7760	24.8500	19.2583	7.6850	7.5200	7.3975	6.1175	6.0725
101 Md	162.6911	27.5223	25.4617	19.6633	7.9383	7.7733	7.6550	6.3450	6.3000
102 No	167.6724	28.2846	26.0750	20.0717	8.1967	8.0267	7.9125	6.5775	6.5325
103 Lr	172.8231	29.0629	26.6917	20.4833	8.4600	8.2700	8.1575	6.8150	6.7700
104 Rf	178.1434	29.8572	27.3100	20.8983	8.7283	8.5383	8.4300	7.0575	7.0125
105 Db	183.6341	30.6685	27.9317	21.3167	9.0017	8.8117	8.7025	7.3050	7.2600
106 Sg	189.2954	31.4968	28.5567	21.7383	9.2800	9.0900	8.9800	7.5575	7.5125
107 Bh	195.1281	32.3421	29.1850	22.1633	9.5633	9.3833	9.2725	7.8150	7.7700
108 Hs	201.1324	33.2044	29.8167	22.5917	9.8517	9.6817	9.5700	8.0775	8.0325
109 Mt	207.3091	34.0847	30.4517	23.0233	10.1450	9.9750	9.8625	8.3450	8.3000
110 Ds	213.6594	34.9830	31.0900	23.4583	10.4433	10.2733	10.1600	8.6175	8.5725
111 Rg	220.1841	35.8993	31.7417	23.8967	10.7467	10.5867	10.4725	8.8950	8.8500
112 Uub	226.8844	36.8336	32.3967	24.3383	11.0550	10.9000	10.7850	9.1775	9.1325
113 Uut	233.7601	37.7859	33.0550	24.7833	11.3683	11.2183	11.1025	9.4650	9.4200
114 Uuq	240.8124	38.7572	33.7167	25.2317	11.6867	11.5467	11.4300	9.7575	9.7125
115 Uup	248.0411	39.7485	34.3817	25.6833	12.0100	11.8800	11.7625	10.0550	10.0100
116 Uuh	255.4464	40.7598	35.0500	26.1383	12.3383	12.2183	12.0950	10.3575	10.3125
117 Uus	263.0291	41.7911	35.7217	26.5967	12.6717	12.5717	12.4475	10.6650	10.6200
118 Uuo	270.7894	42.8424	36.3967	27.0583	13.0100	12.9300	12.8050	10.9775	10.9325
119 Uuq	278.7271	43.9137	37.0750	27.5233	13.3533	13.2933	13.1675	11.2950	11.2500
120 Uub	286.8424	45.0050	37.7567	27.9917	13.7017	13.6617	13.5350	11.6175	11.5725
121 Uut	295.1351	46.1173	38.4417	28.4633	14.0550	14.0267	13.8975	11.9450	11.9000
122 Uuq	303.6064	47.2506	39.1300	28.9383	14.4133	14.3917	14.2725	12.2775	12.2325
123 Uup	312.2551	48.4049	39.8217	29.4167	14.7767	14.7700	14.6525	12.6150	12.5700
124 Uuh	321.0824	49.5802	40.5167	29.8983	15.1450	15.1533	15.0325	12.9575	12.9125
125 Uus	330.0881	50.7765	41.2150	30.3833	15.5183	15.5667	15.4450	13.3050	13.2600
126 Uuo	339.2724	51.9938	41.9167	30.8717	15.8967	15.9550	15.8225	13.6575	13.6125
127 Uus	348.6351	53.2331	42.6217	31.3633	16.2800	16.3233	16.2000	14.0150	13.9700
128 Uuo	358.1764	54.4944	43.3300	31.8583	16.6683	16.7117	16.5875	14.3775	14.3325
129 Uus	367.8961	55.7777	44.0417	32.3567	17.0617	17.1050	16.9800	14.7450	14.7000
130 Uuo	377.7944	5							

66 Dy	53.7885	9.0458	8.5806	7.7901	2.0468	1.8418	1.6756	1.3325	1.2949
67 Ho	55.6177	9.3942	8.9178	8.0711	2.1283	1.9228	1.7412	1.3915	1.3514
68 Er	57.4855	9.7513	9.2643	8.3579	2.2065	2.0058	1.8118	1.4533	1.4093
69 Tm	59.3896	10.1157	9.6169	8.6480	2.3068	2.0898	1.8845	1.5146	1.4677
70 Yb	61.3323	10.4864	9.9782	8.9436	2.3981	2.1730	1.9498	1.5763	1.5278
71 Lu	63.3138	10.8704	10.3486	9.2441	2.4912	2.2635	2.0236	1.6394	1.5885
72 Hf	65.3508	11.2707	10.7394	9.5607	2.6009	2.3654	2.1076	1.7164	1.6617
73 Ta	67.4164	11.6815	11.1361	9.8811	2.7080	2.4687	2.1940	1.7932	1.7351
74 W	69.5250	12.0998	11.5440	10.2068	2.8196	2.5749	2.2810	1.8716	1.8092
75 Re	71.6764	12.5267	11.9587	10.5353	2.9317	2.6816	2.3673	1.9489	1.8829
76 Os	73.8708	12.9680	12.3850	10.8709	3.0485	2.7922	2.4572	2.0308	1.9601
77 Ir	76.1110	13.4185	12.8241	11.2152	3.1737	2.9087	2.5507	2.1161	2.0404
78 Pt	78.3948	13.8799	13.2726	11.5637	3.2960	3.0265	2.6454	2.2019	2.1216
79 Au	80.7249	14.3528	13.7336	11.9187	3.4249	3.1478	2.7430	2.2911	2.2057
80 Hg	83.1023	14.8393	14.2087	12.2839	3.5616	3.2785	2.8471	2.3849	2.2949
81 Tl	85.5304	15.3467	14.6979	12.6575	3.7041	3.4157	2.9566	2.4851	2.3893
82 Pb	88.0045	15.8608	15.2000	13.0352	3.8507	3.5542	3.0664	2.5856	2.4840
83 Bi	90.5259	16.3875	15.7111	13.4186	3.9991	3.6963	3.1769	2.6876	2.5796
84 Po	93.0999	16.9393	16.2443	13.8138	4.1494	3.8541	3.3019	2.7980	2.6830
85 At	95.7240	17.4930	16.7847	14.2135	4.317	4.008	3.426	2.9087	2.7867
86 Rn	98.3972	18.0490	17.3371	14.6194	4.482	4.159	3.538	3.0215	2.8924
87 Fr	101.1299	18.6390	17.9065	15.0312	4.652	4.327	3.663	3.1362	2.9999
88 Ra	103.9162	19.2367	18.4843	15.4444	4.822	4.4895	3.7918	3.2484	3.1049
89 Ac	106.7563	19.8400	19.0832	15.8710	5.002	4.656	3.909	3.3702	3.2190
90 Th	109.6491	20.4721	19.6932	16.3003	5.1823	4.8304	4.0461	3.4908	3.332
91 Pa	112.5961	21.1046	20.3137	16.7331	5.3669	5.0027	4.1738	3.6064	3.4394
92 U	115.6006	21.7574	20.9476	17.1663	5.4480	5.1822	4.3034	3.7276	3.5517

Table A.2. K-Absorption edge and characteristic K X-ray emission energies (in keV)

Z, Element	K _{abs}	K α_2 (K-L _{II})	K α_1 (K-L _{III})	K β_1 (K-M _{III})	K β_2 (K-N _{I,III})
1 H	0.0136				
2 He	0.0246				
3 Li	0.055		0.052		
4 Be	0.116		0.110		
5 B	0.192		0.185		
6 C	0.283		0.282		
7 N	0.399		0.392		
8 O	0.531		0.523		
9 F	0.687		0.677		
10 Ne	0.874		0.851		
11 Na	1.08		1.041	1.067	
12 Mg	1.303		1.254	1.297	
13 Al	1.559	1.486	1.487	1.553	
14 Si	1.838	1.739	1.740	1.832	
15 P	2.142	2.014	2.015	2.136	

Table A.2. *Continued*

Z , Element	K_{abs}	$K\alpha_2$ (K-L _{II})	$K\alpha_1$ (K-L _{III})	$K\beta_1$ (K-M _{III})	$K\beta_2$ (K-N _{II,III})
16 S	2.470	2.306	2.308	2.464	
17 Cl	2.819	2.621	2.622	2.815	
18 Ar	3.203	2.955	2.957	3.192	
19 K	3.607	3.310	3.313	3.589	
20 Ca	4.038	3.688	3.691	4.012	
21 Sc	4.496	4.085	4.090	4.460	
22 Ti	4.964	4.504	4.510	4.931	
23 V	5.463	4.944	4.952	5.427	
24 Cr	5.988	5.405	5.414	5.946	
25 Mn	6.537	5.887	5.898	6.490	
26 Fe	7.111	6.390	6.403	7.057	
27 Co	7.709	6.915	6.930	7.649	
28 Ni	8.331	7.460	7.477	8.264	8.328
29 Cu	8.980	8.027	8.047	8.904	8.976
30 Zn	9.660	8.615	8.638	9.571	9.657
31 Ga	10.368	9.234	9.251	10.263	10.365
32 Ge	11.103	9.854	9.885	10.981	11.100
33 As	11.863	10.507	10.543	11.725	11.863
34 Se	12.652	11.181	11.221	12.495	12.651
35 Br	13.475	11.877	11.923	13.290	13.465
36 Kr	14.323	12.597	12.648	14.112	14.313
37 Rb	15.201	13.335	13.394	14.960	15.184
38 Sr	16.106	14.097	14.164	15.834	16.083
39 Y	17.037	14.882	14.957	16.736	17.011
40 Zr	17.998	15.690	15.774	17.666	17.969
41 Nb	18.987	16.520	16.614	18.621	18.951
42 Mo	20.002	17.373	17.478	19.607	19.964
43 Tc	21.054	18.328	18.410	20.585	21.012
44 Ru	22.118	19.149	19.278	21.655	22.072
45 Rh	23.224	20.072	20.214	22.721	23.169
46 Pd	24.347	21.018	21.175	23.816	24.297
47 Ag	25.517	21.988	22.162	24.942	25.454
48 Cd	26.712	22.982	23.172	26.093	26.641
49 In	27.928	24.000	24.207	27.274	27.859
50 Sn	29.190	25.042	25.270	28.483	29.106
51 Sb	30.486	26.109	26.357	29.723	30.387
52 Te	31.809	27.200	27.471	30.993	31.698
53 I	33.164	28.315	28.610	32.292	33.016
54 Xe	34.446	29.485	29.802	33.644	34.446
55 Cs	35.959	30.623	30.970	34.984	35.819
56 Ba	37.410	31.815	32.191	36.376	37.255
57 La	38.931	33.033	33.440	37.799	38.728
58 Ce	40.449	34.276	34.717	39.255	40.231
59 Pr	41.998	35.548	36.023	40.746	41.772
60 Nd	43.571	36.845	37.359	42.269	43.928

61 Pm	45.207	38.160	38.649	43.945	44.955
62 Sm	46.846	39.523	40.124	45.400	46.553
63 Eu	48.515	40.877	41.529	47.027	48.241
64 Gd	50.229	42.280	42.983	48.718	49.961
65 Tb	51.998	43.737	44.470	50.391	51.737
66 Dy	53.789	45.193	45.985	52.178	53.491
67 Ho	55.615	46.686	47.528	53.934	55.292
68 Er	57.483	48.205	49.099	55.690	57.088
69 Tm	59.335	49.762	50.730	57.576	58.969
70 Yb	61.303	51.326	52.360	59.352	60.959
71 Lu	63.304	52.959	54.063	61.282	62.946
72 Hf	65.313	54.579	55.757	63.209	64.936
73 Ta	67.400	56.270	57.524	65.210	66.999
74 W	69.508	57.973	59.310	67.233	69.090
75 Re	71.662	59.707	61.131	69.298	71.220
76 Os	73.860	61.477	62.991	71.404	73.393
77 Ir	76.097	63.278	64.886	73.549	75.605
78 Pt	78.379	65.111	66.820	75.736	77.866
79 Au	80.713	66.980	68.794	77.968	80.165
80 Hg	83.106	68.894	70.821	80.258	82.526
81 Tl	85.517	70.820	72.860	82.558	84.904
82 Pb	88.001	72.794	74.957	84.922	87.343
83 Bi	90.521	74.805	77.097	87.335	89.833
84 Po	93.112	76.868	79.296	89.809	92.386
85 At	95.740	78.956	81.525	92.319	94.976
86 Rn	98.418	81.080	83.800	94.877	97.616
87 Fr	101.147	83.243	86.119	97.483	100.305
88 Ra	103.927	85.446	88.485	100.136	103.048
89 Ac	106.759	87.681	90.894	102.846	105.838
90 Th	109.630	89.942	93.334	105.592	108.671
91 Pa	112.581	92.271	95.851	108.408	111.575
92 U	115.591	94.648	98.428	111.289	114.549

Table A.3. L-Absorption edges and characteristic L X-ray emission energies (in keV)

Z, Element	L _I abs	L _{II} abs	L _{III} abs	L α ₂ (L _{III} -M _{IV})	L α ₁ (L _{III} -M _V)	L β ₁ (L _{II} -M _{IV})	L β ₂ (L _{III} -N _V)	L γ ₁ (L _{II} -N _{IV})
11 Na	0.055	0.034	0.034					
12 Mg	0.063	0.050	0.049					
13 Al	0.087	0.073	0.072					
14 Si	0.118	0.099	0.098					
15 P	0.153	0.129	0.128					
16 S	0.193	0.164	0.163					
17 Cl	0.238	0.203	0.202					
18 Ar	0.287	0.247	0.245					
19 K	0.341	0.297	0.294					
20 Ca	0.399	0.352	0.349	0.341		0.344		

Table A.3. *Continued*

Z , Element	$L_{\text{I abs}}$	$L_{\text{II abs}}$	$L_{\text{III abs}}$	$L\alpha_2$ ($L_{\text{III-MIV}}$)	$L\alpha_1$ ($L_{\text{III-MV}}$)	$L\beta_1$ ($L_{\text{II-MIV}}$)	$L\beta_2$ ($L_{\text{III-NV}}$)	$L\gamma_1$ ($L_{\text{II-NIV}}$)
21 Sc	0.462	0.411	0.406	0.395		0.399		
22 Ti	0.530	0.460	0.454	0.452		0.458		
23 V	0.604	0.519	0.512	0.510		0.519		
24 Cr	0.679	0.583	0.574	0.571		0.581		
25 Mn	0.762	0.650	0.639	0.636		0.647		
26 Fe	0.849	0.721	0.708	0.704		0.717		
27 Co	0.929	0.794	0.779	0.775		0.790		
28 Ni	1.015	0.871	0.853	0.849		0.866		
29 Cu	1.100	0.953	0.933	0.928		0.948		
30 Zn	1.200	1.045	1.022	1.009		1.032		
31 Ga	1.30	1.134	1.117	1.096		1.122		
32 Ge	1.42	1.248	1.217	1.186		1.216		
33 As	1.529	1.359	1.323	1.282		1.317		
34 Se	1.652	1.473	1.434	1.379		1.419		
35 Br	1.794	1.599	1.552	1.480		1.526		
36 Kr	1.931	1.727	1.675	1.587		1.638		
37 Rb	2.067	1.866	1.806	1.692	1.694	1.752		
38 Sr	2.221	2.008	1.941	1.805	1.806	1.872		
39 Y	2.369	2.154	2.079	1.920	1.922	1.996		
40 Zr	2.547	2.305	2.220	2.040	2.042	2.124	2.219	2.302
41 Nb	2.706	2.467	2.374	2.163	2.166	2.257	2.367	2.462
42 Mo	2.884	2.627	2.523	2.290	2.293	2.395	2.518	2.623
43 Tc	3.054	2.795	2.677	2.420	2.424	2.538	2.674	2.792
44 Ru	3.236	2.966	2.837	2.554	2.558	2.683	2.836	2.964
45 Rh	3.419	3.145	3.002	2.692	2.696	2.834	3.001	3.144
46 Pd	3.617	3.329	3.172	2.833	2.838	2.990	3.172	3.328
47 Ag	3.810	3.528	3.352	2.978	2.984	3.151	3.348	3.519
48 Cd	4.019	3.727	3.538	3.127	3.133	3.316	3.528	3.716
49 In	4.237	3.939	3.729	3.279	3.287	3.487	3.713	3.920
50 Sn	4.464	4.157	3.928	3.435	3.444	3.662	3.904	4.131
51 Sb	4.697	4.381	4.132	3.595	3.605	3.843	4.100	4.347
52 Te	4.938	4.613	4.341	3.758	3.769	4.029	4.301	4.570
53 I	5.190	4.856	4.559	3.926	3.937	4.220	4.507	4.800
54 Xe	5.452	5.104	4.782	4.098	4.111	4.422	4.720	5.036
55 Cs	5.720	5.358	5.011	4.272	4.286	4.620	4.936	5.280
56 Ba	5.995	5.623	5.247	4.451	4.467	4.828	5.156	5.531
57 La	6.283	5.894	5.489	4.635	4.651	5.043	5.384	5.789

58 Ce	6.561	6.165	5.729	4.823	4.840	5.262	5.613	6.052
59 Pr	6.846	6.443	5.968	5.014	5.034	5.489	5.850	6.322
60 Nd	7.144	6.727	6.215	5.208	5.230	5.722	6.090	6.602
61 Pm	7.448	7.018	6.466	5.408	5.431	5.956	6.336	6.891
62 Sm	7.754	7.281	6.721	5.609	5.636	6.206	6.587	7.180
63 Eu	8.069	7.624	6.983	5.816	5.846	6.456	6.842	7.478
64 Gd	8.393	7.940	7.252	6.027	6.059	6.714	7.102	7.788
65 Tb	8.247	8.258	7.519	6.241	6.275	6.979	7.368	8.104
66 Dy	9.083	8.621	7.850	6.457	6.495	7.249	7.638	8.418
67 Ho	9.411	8.920	8.074	6.680	6.720	7.528	7.912	8.748
68 Er	9.776	9.263	8.364	6.904	6.948	7.810	8.188	9.089
69 Tm	10.144	9.628	8.652	7.135	7.181	8.103	8.472	9.424
70 Yb	10.486	9.977	8.943	7.367	7.414	8.401	8.758	9.779
71 Lu	10.867	10.345	9.241	7.604	7.654	8.708	9.048	10.142
72 Hf	11.264	10.734	9.556	7.843	7.898	9.021	9.346	10.514
73 Ta	11.676	11.130	9.876	8.087	8.145	9.341	9.649	10.892
74 W	12.090	11.535	10.198	8.333	8.396	9.670	9.959	11.283
75 Re	12.522	11.955	10.531	8.584	8.651	10.008	10.273	11.684
76 Os	12.965	12.383	10.869	8.840	8.910	10.354	10.596	12.094
77 Ir	13.143	12.819	11.211	9.098	9.173	10.706	10.918	12.509
78 Pt	13.873	13.268	11.599	9.360	9.441	11.069	11.249	12.939
79 Au	14.353	13.733	11.919	9.625	9.711	11.439	11.582	13.379
80 Hg	14.841	14.212	12.285	9.896	9.987	11.823	11.923	13.828
81 Tl	15.346	14.697	12.657	10.170	10.266	12.210	12.268	14.288
82 Pb	15.870	15.207	13.044	10.448	10.549	12.611	12.620	14.762
83 Bi	16.393	15.716	13.424	10.729	10.836	13.021	12.977	15.244
84 Po	16.935	16.244	13.817	11.014	11.128	13.441	13.338	15.740
85 At	17.490	16.784	14.215	11.304	11.424	13.873	13.705	16.248
86 Rn	18.058	17.337	14.618	11.597	11.724	14.316	14.077	16.768
87 Fr	18.638	17.904	15.028	11.894	12.029	14.770	14.459	17.301
88 Ra	19.233	18.481	15.442	12.194	12.338	15.233	14.839	17.845
89 Ac	19.842	19.078	15.865	12.499	12.650	15.712	15.227	18.405
90 Th	20.460	19.688	16.296	12.808	12.966	16.200	15.620	18.977
91 Pa	21.102	20.311	16.731	13.120	13.291	16.700	16.022	19.559
92 U	21.753	20.943	17.163	13.438	13.613	17.218	16.425	20.163

Table A.4. Energy and intensity values of various γ -transitions of a few standard radioactive sources for calibration of a γ -spectrometer

Parent isotope and daughter product	Half-life	Decay mode	γ - ray energies (in keV) and their uncertainties	γ - ray intensities with uncertainties (in the last digits)
$^{57}\text{Co} \rightarrow ^{57}\text{Fe}$	271.74 days	EC + β^+	14.4129(6) 122.06065(12) 136.47356(29)	9.16(15) 85.60(17) 10.68(8)
$^{75}\text{Se} \rightarrow ^{75}\text{As}$	119.79 days	EC + β^+	66.0518(8) 96.7340(9) 121.1155(11) 136.0001(6) 198.6060(12) 264.6576(9) 279.5422(10) 303.9236(10)	1.888(18) 5.807(33) 29.20(56) 98.9(11) 2.51(7) 100.0(3) 42.43(8) 2.235(8)
$^{133}\text{Ba} \rightarrow ^{133}\text{Cs}$	10.52 years	EC + β^+	400.6572(8) 53.1625(6) 79.6139(13) 80.9971(12) 276.3997(13) 302.8510(6) 356.0134(6) 383.8480(12)	19.47(11) 2.199(22) 2.62(6) 34.06(27) 7.164(22) 18.33(6) 62.05(19) 8.94(3)
$^{160}\text{Tb} \rightarrow ^{160}\text{Dy}$	72.3 days	β^-	298.5800(19) 309.561(15) 392.514(26) 765.28(4) 879.383(3) 962.317(4) 966.171(3) 1002.88(4) 1115.12(3) 1177.962(4) 1199.89(3)	86.8(6) 2.867(12) 4.44(3) 7.11(4) 100.0(2) 32.6(3) 83.4(4) 3.45(2) 5.20(5) 49.4(2) 7.92(4)
$^{60}\text{Co} \rightarrow ^{60}\text{Ni}$	1925.3 d	β^-	1173.228(3) 1332.49294	99.85(3) 99.9826(6)
$^{46}\text{Sc} \rightarrow ^{46}\text{Ti}$	83.8 d	β^-	889.287 1120.545	99.984 99.987
$^{59}\text{Fe} \rightarrow ^{59}\text{Co}$	44.495 d	β^-	142.65192) 192.343(5) 1291.590(6) 1481.7(2)	1.02(4) 3.08(10) 56.5(15) 43.2(11)
$^{88}\text{Y} \rightarrow ^{88}\text{Sr}$	106.65 d	EC + β^+	898.042(3) 1836.084(12)	94.4(3) 100.0(3)

$^{182}\text{Ta} \rightarrow ^{182}\text{W}$	114.43 days	β^-	65.7220(2)	8.38(13)
			67.7500(2)	118.1(18)
			84.6808(3)	7.58(14)
			100.1065(3)	40.4(3)
			113.6725(3)	5.40(5)
			116.4186(7)	1.234(14)
			152.4308(3)	19.85(13)
			156.3876(3)	7.57(5)
			179.3945(3)	8.83(6)
			198.3532(3)	4.13(4)
			222.3220(9)	21.45(13)
			229.3220(9)	10.40(6)
			264.0752(3)	10.33(2)
			1001.6950(19)	5.92(4)
			1121.3008(17)	100.0(3)
			1189.0503(17)	46.49(11)
			1221.4066(17)	77.3(3)
$^{94}\text{Nb} \rightarrow ^{94}\text{Mo}$	2.03×10^4 years	β^-	702.622(19)	98(2)
			871.091(18)	100

B

Appendix

B.1 Relation of Energies, Scattering Angles, and Rutherford Scattering Cross-Sections in the Center-of-Mass System and Laboratory System

Collisions can broadly be classified into two categories i.e., *elastic* and *inelastic*. In an elastic collision, total kinetic energy is conserved. When a light particle strikes a heavy particle, it is considered that the velocity of the light particle is only changed in direction, but not in magnitude, so its kinetic energy is conserved. In an inelastic collision, there is a decrease or increase in total kinetic energy that comes from the internal energy of the colliding partners. This may be rotation or vibration, or a change in structure, or even the disappearance of one particle.

The description of the elastic collision is much simpler in the center-of-mass (CM) system, and the final velocities can be determined by the conservation of energy and momentum, and the scattering angle θ . Finally, the original velocity of the CM is added to all velocities to find the result of the collision in the laboratory system.

In the CM system, both the projectile (first particle) and the target atoms (second particle) are supposed to move in the opposite directions (as in the case of colliding beams) whereas in the laboratory frame, the target atoms are at rest. Referring to Fig. B.1, let v_1 and v_2 be the velocities of the projectile and target atoms in the opposite directions such that $E_1 = \frac{1}{2}m_1v_1^2$ and $E_2 = \frac{1}{2}m_2v_2^2$ be the kinetic energies of the first particle (projectile) and second particle (target atoms), respectively, before the collision. Likewise, let $E_1' = \frac{1}{2}m_1v_1'^2$ and $E_2' = \frac{1}{2}m_2v_2'^2$ be the kinetic energies of the projectile and target atoms, respectively, after the collision. If E is the total energy in the CM frame, the conservation of energies implies that

$$E = E_1 + E_2 = E_1' + E_2' \quad (\text{B.1})$$

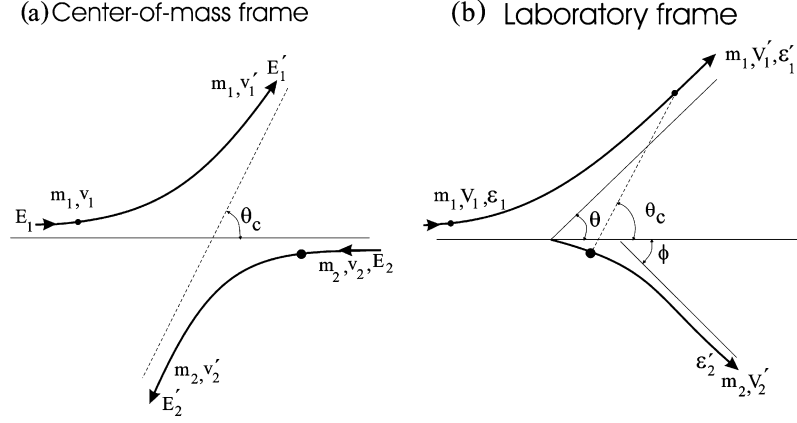


Fig. B.1. Relation of various parameters in CM system and laboratory system

Let ϵ be the total energy in the laboratory frame. This is, of course, equal to the kinetic energy of the projectile before the collision. Likewise, let $\epsilon'_1 = \frac{1}{2}m_1V_1'^2$ and $\epsilon'_2 = \frac{1}{2}m_2V_2'^2$ be the kinetic energies of the first and second particles, respectively, after the collision. Of course, $\epsilon = \epsilon'_1 + \epsilon'_2$.

The following results can be easily obtained:

$$\epsilon = \left(\frac{m_1 + m_2}{m_2} \right) E \quad (\text{B.2})$$

Hence, the total energy in the laboratory frame is always greater than that in the CM frame. Second,

$$\begin{aligned} E_1 &= E'_1 = \left(\frac{m_2}{m_1 + m_2} \right) E \\ E_2 &= E'_2 = \left(\frac{m_1}{m_1 + m_2} \right) E \end{aligned} \quad (\text{B.3})$$

These equations specify how the total energy in the center of mass frame is distributed between the two particles. Note that this distribution is unchanged by the collision. Finally,

$$\begin{aligned} \epsilon'_1 &= \left(\frac{m_1^2 + 2m_1m_2 \cos \theta_c + m_2^2}{(m_1 + m_2)^2} \right) \epsilon \\ \epsilon'_2 &= \left(\frac{2m_1m_2 \cos \theta_c + m_2^2}{(m_1 + m_2)^2} \right) \epsilon \end{aligned} \quad (\text{B.4})$$

Equation (B.4) specifies how the total energy in the laboratory frame is distributed between the two particles after the collision. Note that the energy distribution in the laboratory frame is *different* before and after the collision.

Some simple trigonometry and above equations, yield

$$\tan \theta = \frac{\sin \theta_c}{\cos \theta_c + (m_1/m_2)} \quad (\text{B.5})$$

and

$$\tan \phi = \frac{\sin \theta_c}{1 - \cos \theta_c} = \tan \left(\frac{\pi}{2} - \frac{\theta_c}{2} \right) \quad (\text{B.6})$$

which implies that

$$\phi = \left(\frac{\pi}{2} - \frac{\theta_c}{2} \right) \quad (\text{B.7})$$

Differentiating (B.5) with respect to θ_c , we obtain

$$\frac{d \tan \theta}{d \theta_c} = \frac{1 + (m_1/m_2) \cos \theta_c}{(\cos \theta_c + (m_1/m_2))^2} \quad (\text{B.8})$$

Thus, $\tan \theta$ attains an extreme value, which can be shown to correspond to a *maximum* possible value of θ , when the numerator of the above expression is zero i.e., when

$$\cos \theta_c = -\frac{m_2}{m_1}$$

Note that it is only possible to solve (B.8), when $m_1 > m_2$. If this is the case, then (B.5) yields

$$\tan \theta_{\max} = \frac{(m_2/m_1)}{\sqrt{1 - (m_2/m_1)^2}} \quad (\text{B.9})$$

which reduces to

$$\theta_{\max} = \sin^{-1} \left(\frac{m_2}{m_1} \right) \quad (\text{B.10})$$

Hence, we conclude that *when* $m_1 > m_2$ there is a *maximum* possible value of the scattering angle, θ in the laboratory frame. This maximum value is always less than $\pi/2$, which implies that there is *no backward scattering* (i.e., θ is always $< \pi/2$) when $m_1 > m_2$. For the special case when $m_1 = m_2$, the maximum scattering angle $\theta_{\max}$ is $\pi/2$. However, for $m_1 < m_2$ there is no maximum value, and the scattering angle in the laboratory frame can thus range all the way to π .

Equations (B.2)–(B.7) enable us to relate the particle energies and scattering angles in the laboratory frame to those in the center of mass frame. In general, this relationship is fairly complicated. However, there are *two special cases* in which the relationship becomes much simpler:

- (a) *When* $m_1 \ll m_2$. In this case, it is easily seen from (B.2) to (B.7) that the second mass is *stationary* both before and after the collision, and that the center of mass frame *coincides* with the laboratory frame (since the energies and scattering angles in the two frames are the same).
- (b) *When* $m_1 = m_2$. In this case, (B.5) yields

$$\tan \theta = \frac{\sin \theta_c}{\cos \theta_c + 1} = \tan(\theta_c/2) \quad (\text{B.11})$$

Hence,

$$\theta = \frac{\theta_c}{2} \quad (\text{B.12})$$

In other words, the scattering angle of the projectile in the laboratory frame is half of the scattering angle in the center of mass frame. The above equation can be combined with (B.7) to give

$$\theta + \phi = \pi/2 \quad (\text{B.13})$$

Thus, in the laboratory frame, the two particles move off at right-angle to one another after the collision.

$$\varepsilon = 2E \quad (\text{B.14})$$

In other words, the total energy in the laboratory frame is *twice* that in the center of mass frame. According to (B.3)

$$E_1 = E'_1 = E_2 = E'_2 = \frac{E}{2} \quad (\text{B.15})$$

Hence, the total energy in the center of mass frame is divided *equally* between the two particles. Finally, (B.4) gives

$$\begin{aligned} \varepsilon'_1 &= \varepsilon \left(\frac{1 + \cos \theta_c}{2} \right) = \varepsilon \cos^2(\theta_c/2) = \varepsilon \cos^2 \theta \\ \varepsilon'_2 &= \varepsilon \left(\frac{1 - \cos \theta_c}{2} \right) = \varepsilon \sin^2(\theta_c/2) = \varepsilon \sin^2 \theta \end{aligned} \quad (\text{B.16})$$

Thus, in the laboratory frame, the unequal energy distribution between the two particles after the collision is simply related to the scattering angle θ .

To find the angular distribution of scattered particles when a beam of particles of the first type scatter off stationary particles of the second type, we define a differential scattering cross-section, $d\sigma(\theta)/d\Omega$, in the laboratory frame, where $\Omega = 2\pi \sin \theta d\theta$ is an element of solid angle in this frame. Thus, $(d\sigma(\theta)/d\Omega) d\Omega$ is the effective cross-sectional area in the laboratory frame for scattering into the range of scattering angles θ to $\theta + d\theta$. Likewise, $(d\sigma(\theta_c)/d\Omega') d\Omega'$ is the effective cross-sectional area *in the CM frame* for scattering into the range of scattering angles θ_c to $\theta_c + d\theta_c$. Note that $d\sigma = 2\pi \sin \theta_c d\theta_c$. However, a cross-sectional area is not changed when we transform between different inertial frames. Hence, we can write

$$\frac{d\sigma(\theta)}{d\Omega} d\Omega = \frac{d\sigma(\theta_c)}{d\Omega'} d\Omega'$$

provided that θ and θ_c are related via equation i.e., $\theta = \theta_c/2$. This equation can be rearranged to give

$$\frac{d\sigma(\theta)}{d\Omega} = \frac{d\sigma(\theta_c)}{d\Omega'} \frac{d\Omega'}{d\Omega}$$

or

$$\frac{d\sigma(\theta)}{d\Omega} = \frac{\sin \theta_c}{\sin \theta} \frac{d\theta_c}{d\theta} \frac{d\sigma(\theta_c)}{d\Omega'} \quad (\text{B.17})$$

Equation (B.17) allows us to relate the differential scattering cross-section in the laboratory frame to that in the CM frame. In general, this relationship is extremely complicated. However, for the special case where the masses of the two types of particles are equal, we have seen that $\theta = \pi/2$, so that

$$\frac{d\sigma(\theta)}{d\Omega} = 4 \cos \theta \frac{d\sigma(\theta_c = 2\theta)}{d\Omega'} \quad (\text{B.18})$$

Let us now consider some specific examples. We saw earlier that, in the CM frame, the differential scattering cross-section for *impenetrable spheres* is

$$\frac{d\sigma(\theta_c)}{d\Omega'} = \frac{a^2}{4} \quad (\text{B.19})$$

where a is the sum of the radii. According to (B.18), the differential scattering cross-section (for equal mass spheres) in the laboratory frame is

$$\frac{d\sigma(\theta)}{d\Omega} = a^2 \cos \theta \quad (\text{B.20})$$

Note that this cross-section is *negative* for $\theta > \pi/2$. This just tells us that there is *no scattering* with scattering angles greater than $\pi/2$, (i.e., there is no backward scattering). Comparing (B.19) and (B.20), we can see that the scattering is *isotropic* in the CM frame, but appears concentrated in the forward direction in the laboratory frame.

We can integrate (B.20) over all solid angles to obtain the total scattering cross-section in the laboratory frame. Note that we only integrate over angular regions where the differential scattering cross-section is *positive*. Doing this, we get

$$\sigma = \pi a^2 \quad (\text{B.21})$$

which is the same as the total scattering cross-section in the CM frame. This is a general result. The total scattering cross-section is frame independent, since a cross-sectional area is not modified by switching between different frames of reference.

As we have seen, the Rutherford scattering cross-section takes the form

$$\frac{d\sigma}{d\Omega'} = \frac{1}{16} \left(\frac{Z_1 Z_2 e^2}{4\pi\epsilon_0 E} \right)^2 \frac{1}{\sin^4(\theta_c/2)} \quad (\text{B.22})$$

in the CM frame. It follows, from (B.18), that the Rutherford scattering cross-section (for equal mass particles) in the laboratory frame is written as

$$\frac{d\sigma}{d\Omega} = \left(\frac{Z_1 Z_2 e^2}{4\pi\epsilon_0 E} \right)^2 \frac{\cos \theta}{\sin^4 \theta} \quad (\text{B.23})$$

Here, we have made use of the fact that $\epsilon = 2E$ for equal mass particles [see (B.14)]. Note, again, that this cross-section is negative for $\theta > \pi/2$, indicating the absence of backward scattering.

If the masses m_1 and m_2 of the two particles are not equal, equation can be written as

$$\left(\frac{d\sigma}{d\Omega}\right) = \left(\frac{Z_1 Z_2 e^2}{8\pi\epsilon_0 E}\right)^2 \frac{1}{\sin^4 \theta} \cdot \frac{\left[\left\{1 - \left(\left(\frac{m_1}{m_2}\right) \sin \theta\right)^2\right\}^{\frac{1}{2}} + \cos \theta\right]^2}{\left\{1 - \left(\left(\frac{m_1}{m_2}\right) \sin \theta\right)^2\right\}^{\frac{1}{2}}} \quad (\text{B.24})$$

or

$$\frac{d\sigma}{d\Omega}(\theta) = \left(\frac{Z_1 Z_2 e^2}{8\pi\epsilon_0 E}\right)^2 \cdot \frac{1}{\sin^4 \theta} \cdot \frac{\left[m_2 \cos \theta + (m_2^2 - m_1^2 \sin^2 \theta)^{1/2}\right]^2}{m_2 \times (m_2^2 - m_1^2 \sin^2 \theta)^{1/2}} \quad (\text{B.25})$$

For heavy target nuclei i.e. $m_2 \gg m_1$, this reduces to the familiar Rutherford backscattering ($\theta > 90^\circ$) formula

$$\frac{d\sigma}{d\Omega}(\theta) \approx \left(\frac{Z_1 Z_2 e^2}{16\pi\epsilon_0 E}\right)^2 \frac{1}{\sin^4(\theta/2)} \quad (\text{B.26})$$

C

Appendix

Some important reactions used for PIGE analysis

Reaction	Energy/energy range (MeV)	Concentration	Reference
${}^6\text{Li}({}^4\text{He}, \gamma){}^{10}\text{B}$	3.75–5.2		Nucl. Phys. A242(1975)129
${}^9\text{Be}(\text{p}, \gamma){}^{10}\text{B}$	0.22–1.2		Nucl. Phys. A242(1975)129
${}^9\text{Be}(\text{d}, \gamma){}^{10}\text{B}$	0.56–3.56		Phys. Rev. C4(1971)1601
${}^{11}\text{B}(\text{p}, \gamma){}^{12}\text{C}$	0.163	${}^{11}\text{B} = 80\%$	Nucl. Phys. A233(1974)286
${}^{12}\text{C}(\text{p}, \gamma){}^{13}\text{N}$	0.48, 0.6, 1.75	${}^{12}\text{C} = 98.9\%$	Nucl. Instrum. Methods 113(1973)561
${}^{13}\text{C}(\text{p}, \gamma){}^{14}\text{N}$	0.48, 0.6, 1.75	${}^{13}\text{C} = 1.1\%$	Nucl. Instrum. Methods 113(1973)561
${}^{14}\text{C}(\text{p}, \gamma){}^{15}\text{N}$	0.25–0.67		Phys.Lett. 56B(1975)253
${}^{15}\text{N}(\text{p}, \gamma){}^{16}\text{O}$	0.15–2.5	${}^{15}\text{N} = 0.36\%$	Nucl. Phys. A235(1974)450
${}^{16}\text{O}(\text{p}, \gamma){}^{17}\text{F}$	0.83, 1.37, 1.96		Can. J. Phys. 53(1975)1672
${}^{20}\text{Ne}(\text{p}, \gamma){}^{21}\text{Na}$	0.37–2.1	${}^{20}\text{Ne} = 90.5\%$	Nucl. Phys. A241(1975)460
${}^{23}\text{Na}(\text{p}, \gamma){}^{24}\text{Mg}$	0.3–2.0		Nucl. Phys. A185 (1972)625
${}^{24}\text{Mg}(\text{p}, \gamma){}^{25}\text{Al}$	0.2–2.3	${}^{24}\text{Mg} = 79\%$	Nucl. Phys. A242(1975)519
${}^{25}\text{Mg}(\text{p}, \gamma){}^{26}\text{Al}$	0.3–1.72	${}^{25}\text{Mg} = 10\%$	Nucl. Phys. A230(1974)490
${}^{27}\text{Al}(\text{p}, \gamma){}^{28}\text{Si}$	0.5–2.5	${}^{27}\text{Al} = 100\%$	J. Radioanal. Chem. 12 (1972)189
${}^{27}\text{Al}(\text{p}, \text{p}'\gamma){}^{28}\text{Si}$			
${}^{27}\text{Al}(\text{p}, \alpha\gamma){}^{28}\text{Si}$			
${}^{28}\text{Si}(\text{p}, \gamma){}^{29}\text{P}$	0.724, 1.961	${}^{28}\text{Si} = 92.23\%$	J. Phys. 36(1975)913
${}^{29}\text{Si}(\text{p}, \gamma){}^{30}\text{P}$	0.4–3.6	${}^{29}\text{Si} = 4.67\%$	J. Phys. 36(1975)913
${}^{30}\text{Si}(\text{p}, \gamma){}^{31}\text{P}$	0.49–2.51	${}^{30}\text{Si} = 3.1\%$	J. Phys. 36(1975)913
${}^{31}\text{P}(\text{p}, \gamma){}^{32}\text{S}$	0.4–1.75		Aust. J. Phys. 28(1975)383
${}^{32}\text{S}(\text{p}, \gamma){}^{33}\text{Cl}$	0.588	${}^{32}\text{S} = 95\%$	Phys. Scripta 12(1975)280
${}^{34}\text{S}(\text{p}, \gamma){}^{35}\text{Cl}$	0.7–2.4	${}^{34}\text{S} = 4.2\%$	Sov. J. Nucl. Phys. 19(1974)603
${}^{35}\text{Cl}(\text{p}, \gamma){}^{36}\text{Ar}$	1.52–2.6		Nucl. Instrum. Methods 124 (1975)265
${}^{46}\text{Ti}(\text{p}, \gamma){}^{47}\text{V}$	0.7–3.7	${}^{46}\text{Ti} = 80\%$	Astrophys. J. 188(1974)601
${}^{47}\text{Ti}(\text{p}, \gamma){}^{48}\text{V}$	0.8–3.8	${}^{47}\text{Ti} = 7.5$	Astrophys. J. 188(1974)601

Some important reactions used for PIGE analysis

Reaction	Energy/energy range (MeV)	Concentration	Reference
$^{50}\text{Cr}(p, \gamma)^{51}\text{Mn}$	1.45–2.07	$^{50}\text{Cr} = 4.35\%$	Aust. J. Phys. 28(1975)263
$^{52}\text{Cr}(p, \gamma)^{53}\text{Mn}$	0.9–1.03	$^{52}\text{Cr} = 83.8\%$	Aust. J. Phys. 28(1975)263
$^{53}\text{Cr}(p, \gamma)^{54}\text{Mn}$	1.18–2.1	$^{53}\text{Cr} = 9.5\%$	Aust. J. Phys. 28(1975)263
$^{54}\text{Cr}(p, \gamma)^{55}\text{Mn}$	2.25	$^{54}\text{Cr} = 2.36\%$	Aust. J. Phys. 28(1975)263
$^{55}\text{Mn}(p, \gamma)^{56}\text{Fe}$	1.3–1.85	$^{55}\text{Mn} = 100\%$	Nucl. Phys. A235(1974)205
$^{54}\text{Fe}(p, \gamma)^{55}\text{Co}$	3.25–3.77	$^{54}\text{Fe} = 5.8\%$	Nucl. Phys. A249(1975)269
$^{56}\text{Fe}(p, \gamma)^{57}\text{Co}$	1.2–3.0	$^{56}\text{Fe} = 91.8\%$	Nucl. Phys. A240(1975)120
$^{57}\text{Fe}(p, \gamma)^{58}\text{Co}$	1.58–2.125	$^{57}\text{Fe} = 2.1\%$	Phys. Scripta 12(1975)95
$^{58}\text{Fe}(p, \gamma)^{59}\text{Co}$	2.20–2.25	$^{58}\text{Fe} = 0.3\%$	Z. Phys. A270(1974)129
$^{59}\text{Co}(p, \gamma)^{60}\text{Ni}$	1.365–2.15	$^{59}\text{Co} = 100\%$	Z. Phys. A272(1975)67
$^{58}\text{Ni}(p, \gamma)^{59}\text{Cu}$	1.376–2.275	$^{58}\text{Ni} = 68.27\%$	Nucl. Phys. A246(1975)457
$^{60}\text{Ni}(p, \gamma)^{61}\text{Cu}$	1.58–1.62	$^{60}\text{Ni} = 26.1\%$	Sov. J. Nucl. Phys. 20 (1975)567
$^{62}\text{Ni}(p, \gamma)^{63}\text{Cu}$	2.3–2.7	$^{62}\text{Ni} = 3.59\%$	Nucl. Phys. A233(1974)9
$^{64}\text{Ni}(p, \gamma)^{65}\text{Cu}$	1.1–3.7	$^{64}\text{Ni} = 0.91\%$	Phys. Lett. 58B(1975)420
$^{70}\text{Ge}(p, \gamma)^{71}\text{As}$	1.0–2.5		J. Phys. Soc. Jpn. 39(1975)1

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Chapter 1

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- RUNFIT: Schreiner WN and Jenkins R (1979) "A non-linear least squares fitting routine for optimizing empirical XRF matrix correction models" X-ray Spectrometry 8: 33
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- SIGMACALC: Gubrich AF (1996) “software for non-Rutherford elastic backscattering cross-sections” <http://www.ionbeamcentre.com/sigmacalc/>
- SIMNRA: Eckstein W and Mayer M (1999) Nucl. Instrum. and Methods in Physics Research B153: 337 (www.rzg.mpg.de/~mam)

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- MDEPTH: Szilágyi E, Pászti F and Amsel G (1995) “Theoretical approximations for depth resolution calculations in IBA methods” Nucl. Instrum. Methods in Phys. Res. B100: 103
- SIMNRA: Eckstein W and Mayer M (1999) Nucl. Instrum. and Methods in Physics Research B153: 337 (www.rzg.mpg.de/~mam)

Computer Codes Useful

In NRA Analysis

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Index

- Absolute method, 259
- Absorption Edges, 14, 15, 18, 59, 60, 88
- Accelerator, VII, VIII, 10, 11, 32–36, 71, 77, 89, 91, 113, 145, 150, 166, 168, 172, 249–251, 270, 271, 278, 295–304, 308, 309, 311, 312, 314, 315, 318, 320
 - Mass Spectrometry, VIII, 295–297, 299, 300, 306, 309, 312, 314, 315, 318, 319
 - Tube, 32–35, 300, 301
- Adiabaticity parameter, 75
- ADP, 21
- Advantages of
 - NAA, 267
 - thin foil technique, 52
 - using heavier ions, 129
- Aerosol samples, 80, 81, 289, 290
- AES, 83, 173, 218, 288
- ¹⁰⁹Ag, 12, 218
- Agriculture, 266, 310
- Air pollution, 289, 290, 310
- ²⁷Al, 64, 243, 251, 265, 279, 282, 284, 289, 299, 308, 313, 320
- ²⁸Al, 243, 251, 265
- Alloys, 44, 49, 51, 61, 79, 80, 202, 204, 207, 208, 221, 237, 239, 240, 265, 266, 287
- Alps, 296
- Aluminum, 13, 25, 34, 69, 77, 110, 116, 204, 208, 209, 220, 222, 243, 264, 296, 313
- ²⁴¹Am, 12–14, 27, 116, 220, 251
- AMS
 - of molecular ions, 318
 - using low energy accelerators, 303
- Analog to digital converter, 15, 37, 197
- Analysis, VII, 13, 48, 49, 70, 72, 136, 144, 213, 230, 244, 247, 248, 258, 282, 284, 290
 - Computer, 70
 - Qualitative, VII, 1, 13, 21, 48, 55, 89, 156, 211, 230, 243, 244
 - Quantitative, 13, 48, 49, 55, 65, 72, 80, 84, 89, 108, 136, 139, 143, 144, 150, 173, 204, 211, 213, 241, 243–245, 247, 248, 258, 264, 265, 282, 284, 290, 295, 309, 314
- Analyzing crystal, 20, 21
- Applications of, 76, 139, 237, 262, 284, 287
 - NAA, 262
 - NRA, 276, 284
 - PIGE, 287
 - RBS technique, 91, 139, 277
 - XPS, 237
 - XRF and PIXE, 76
- Archaeological samples, 37, 82, 83, 287, 288, 305
- Archaeology, 1, 76, 91, 210, 262, 289, 296, 309, 319
- Areal density, 56, 110, 126, 137–139, 141, 147, 154
- Argon, 83, 84, 195, 209, 238, 248
- Arsenic, 86, 264
- Artifacts, 82, 230, 262, 288

- Asymmetric system, 75
- Asymmetry parameter, 75, 187, 188, 230
- Attenuation coefficient, 14, 29, 51, 56, 60
- ^{198}Au , 245, 253
- Auger electron, 3, 5, 9, 54, 83, 201, 203, 218
- Avogadro Number, 59, 72, 95, 120, 259
- Ayurvedic medicinal materials, 266
- ^{131}Ba , 245, 253
- Background, 67
 - contribution of detection system, 67
 - contribution of scattering geometry, 67
 - due to insulating targets, 67
- Barkas correction, 95
- Battery material, 285
- Beam steerer, 35
- BGO detector, 257
- ^{210}Bi , 257
- Binary Encounter Approximation, 43, 73
- Binding Energy, 2, 3, 5, 9, 10, 43, 53, 73, 93, 104, 201, 213–218, 220, 232, 234–238, 241, 244
- Biochemistry, 205, 262
- Biological Sciences, 76
- Biomedicine, 31, 297, 309, 311, 317–319
- Bismuth Germanate, 253
- Bloch correction, 95
- Blood, 77, 211, 248, 264, 286, 287, 312, 313
- Born Approximation, 1
- Boron, 30, 170, 247, 282, 284, 287, 290, 304
- Bragg angle, 22
- Bragg equation, 19, 22
- Bragg Ionization Chamber, 156–158
- Bragg Peak, 158, 160
- Bremsstrahlung, 17, 19, 41, 43, 45, 46, 65–67, 90, 222, 223
 - Projectile, 65–67
 - Secondary Electron, 65–67
- Building materials, 266
- ^{14}C , 295
- Calcium, 286, 296, 309, 313–315, 318
- Capacitance, 255
- Carbon dating, 295, 300, 301
- ^{109}Cd , 220, 253
- CdZnTe detector, 257
- ^{141}Ce , 13
- ^{143}Ce , 13
- Cements and concretes, 240
- CEMS, 201–204, 206
- Centre-of-mass beam energy, 42
- Ceramics, 1, 79, 83, 139, 218, 233, 241, 300
- ^{252}Cf , 250
- Channeling, 119, 126, 134–136, 138
- Characteristics, 2, 18, 21, 32, 66, 89, 107, 108, 118, 149, 150, 192, 214, 239, 244, 245, 256, 272
- Charge State Effect, 2, 46
- Charged particles, VIII, 2, 3, 31, 32, 36, 39, 41, 44, 50, 51, 56, 59, 62, 66, 73, 91, 96, 114–117, 157, 201, 223, 251, 270, 271, 273, 274, 278, 279, 299, 308
- Chemical, 85
 - analysis, 85, 205, 213, 232
 - shift, 85, 214, 218, 230, 236, 237, 241
- Chlorine, 247, 248, 265, 283, 287, 296, 306, 309, 311, 315, 317
- ^{60}Co , 245, 253, 256, 277
- Coal, 240
- Collimator, 13, 21–23, 89, 163, 246
- Collision, 2, 5, 9, 10, 17, 32, 36, 43, 46, 47, 66, 74–76, 91–93, 95–97, 100, 104, 108, 109, 122, 129, 143–145, 147, 150, 154, 219, 224, 228, 244
 - elastic, 95
 - non-elastic, 95, 244
- Comparator, 248, 249, 260
- Comparison, 86
 - between EDXRF and WDXRF techniques, 86
 - of XRF and PIXE techniques, 87
- Comparison method, 260
- Compound nucleus, 244, 270, 271
- Compton Scattering, 14, 64, 65, 67, 68
- Computer codes, 38
- Computer simulation codes for RBS analysis, 362

- Computer software, 51
 - for PIXE spectrum analysis, 362
 - for XRF spectrum analysis, 361
- Concentric hemispherical analyzer, 219, 225
- Concept, 5, 10, 108, 145, 146, 150, 178
- Conclusion, 90
- Core states, 217
- Correction, 54
 - Barkas, 95
 - Bloch, 95
- Cosmic rays, 117, 298, 309, 312, 317
- Cosmogenic radionuclides, 297, 298, 315, 316, 319
- Coulomb, 25, 46, 73–75, 92, 100, 107, 110, 147, 269–271, 273, 274, 277
 - barrier, 11, 41, 42, 107, 110, 147, 269–271, 273, 274, 277
 - ionization, 46, 73
- ^{51}Cr , 245
- Criminology, 78
- Cross section, 11, 38, 39, 43, 51, 53, 58, 60, 64, 73, 87, 91, 99, 100, 102–104, 108–112, 120, 122, 125, 129, 137, 139, 141, 146, 147, 150, 161, 173, 175, 269
 - differential scattering, 91, 103, 109, 122, 129, 150
 - ionization, 11, 38, 43, 58, 64, 73, 87
 - non-Rutherford, 111, 112
 - photoabsorption, 53, 60
 - scattering, 51, 100, 102, 103, 107, 108, 111, 112, 120, 125, 137, 139, 141, 146, 147, 161, 175, 269
 - shielded Rutherford, 110, 112
 - stopping, 39, 99, 104, 108, 125, 149, 173
- Cryostat, 203, 255, 256
- Crystal spectrometer, 22, 23, 40, 85, 151
- Crystals, 20–22, 253
 - Analyzing, 21, 22
 - Diffraction, 20
 - Inorganic, 253
 - Organic, 300
- CsI(Na), 253
- CsI(Tl), 253
- ^{63}Cu , 243
- ^{64}Cu , 243
- Cylindrical Mirror Analyzer, 225–228
- Data Analysis, 161, 173, 200
- De-excitation, 3, 5, 22, 201, 273
- Dead layer, 25–27, 29, 115, 116
- Debye-Waller factor, 186
- Decay counting, 296, 309, 314
- Deconvolution, 72, 86, 230
- Delayed NAA, 246
- Depletion depth, 115, 116, 131, 254
- Depth, 71, 96, 108, 119, 122, 130, 133, 137, 138, 145, 147–150, 155, 158, 166, 168, 170, 172, 174, 218, 270, 273, 278, 286
 - Composition, 218
 - Profiling of Materials, 71
 - Resolution, 96, 108, 119, 130, 133, 137, 138, 145, 147–150, 155, 158, 166, 168, 170, 172, 174, 278, 286
 - Scale, 122, 270, 273
- Detection
 - Limit, 282
 - Range, 21
 - System, 37
- Detector
 - BGO, 271
 - Efficiency, 29
 - Gas, 159
 - Ge(Li), VII
 - Microchannel plate, 118
 - NaI(Tl), VII
 - Si(Li), VII
 - Surface-barrier, 114
- Deuteron, 10–12, 39, 42, 58, 91, 95, 97, 148, 250, 251, 272, 275, 276, 279, 280, 285–287, 290
- Dewar, 25, 255
- DGNAA, 244, 246, 247
- Diagram lines, 5, 22, 23, 41, 85
- Diffraction, 17, 19–21, 25, 67, 209, 222
- Dinosaurs, 264
- Dirac-Hartree-Slater, 38
- Disintegrations, 259
- Dispersing crystals, 21
- Distance of closest approach, 92, 105, 111, 140, 147, 274
- Doppler shift, 177, 178, 180, 181, 183, 194, 196

- Drive Unit, 193, 194
- Dual-anode tube, 18
- Duoplasmatron, 33, 34
- ^{159}Dy , 13
- Earth Science, 309, 315
- Ecological monitoring, 263
- ECPSSR theory, 41, 47, 58
- EDDT, 21
- Efficiency, 18, 21, 25–30, 44, 51, 52, 56, 59, 61, 72, 76, 79, 85, 87, 89, 118, 130, 167–170, 172, 195, 220, 230, 253–257, 259, 261, 267, 268, 277, 280, 299, 302, 307, 309, 320
- Einstein frequency, 185
- Elastic scattering, 91, 112, 133, 143, 144, 147, 149, 160
- Electric hyperfine coupling, 190
- Electron
 - capture, 74
 - cloud, 74
 - inner-shell, 2
 - promotion, 74
 - transfer, 2
- Electron-hole pair, 24, 29, 71, 254
- Elemental, 1, 29, 31, 40, 52, 55, 61, 64, 71, 76, 78, 80, 82, 83, 86, 87, 105, 127, 139, 143, 152, 164, 165, 167, 169, 208, 217, 241, 244, 247, 248, 253, 260, 262–264, 282–284, 287–289, 306, 315
- Elements, 44
 - High-Z, 44
 - Low-Z, 3, 21, 26, 172, 269, 290
- ENAA, 247
- Endothermic, 271
- Energy, 165
 - broadening, 123, 156
 - of backscattered particles, 140
 - Telescope, 165
 - transferred to electrons, 11
- Enhancement Effects, 43, 44
- Environment, 1, 89, 134, 178, 182, 194, 205, 209, 210, 214, 219, 237, 263, 286, 295, 306, 308, 314, 320
- ERDA
 - using E-detection, 151
 - using transmission telescope, 156
 - with particle identification and depth resolution, 155
 - with position sensitive detectors, 159
- Erosion, 79, 298, 309, 316, 317
- ESCA, 213, 220, 226, 232, 238
- ^{152}Eu , 13
- Excitation
 - characteristics, 2
 - functions, 282
 - Secondary, 13
- Excited state, 9, 12, 76, 97, 177, 178, 182, 187, 189, 195, 244, 270, 271, 273, 279
- Exciter, 13, 16, 18, 26, 31, 66, 69
 - Radioactive Source, 12
 - X-ray Tube, 12, 16, 69
- Exothermic, 271
- Experimental, 8, 9, 27, 41, 45, 47, 48, 50, 54, 97, 109–111, 113, 119, 126, 127, 130, 134, 137, 145, 150, 161, 173, 192, 199, 204, 209, 219, 229, 247, 259, 260, 278, 298, 318
- Explosives, 266
- Faraday cup, 34–36, 45, 298, 302
- Fast Neutron Activation Analysis, 247
- ^{57}Fe , 182–186, 188–191, 194, 195, 198, 199, 201, 203, 204, 207, 211
- ^{59}Fe , 40, 245, 253, 266
- Fissile materials, 266
- Fission Neutron Source, 250
- Flexibility, 16, 88, 199
- Float glass, 275
- Fluorescence Yield, 3, 8, 9, 13, 41, 53, 54, 56, 58, 76
- Fluorine, 73, 248, 269, 277, 282, 286, 288, 290, 291
- FNAA, 247
- Food chemistry, 314
- Food items, 266
- Forensic Investigations, 264
- Formalism, 52, 54, 56, 58
 - for thick-target PIXE, 58
 - for thick-target XRF, 54
 - for thin-target PIXE, 56
 - for thin-target XRF, 52
- Frisch Grid, 159, 162, 163
- Fundamentals, 107
 - of the RBS technique, 107

- Fusion type Neutron Generators, 250
- FWHM, 27, 29, 38, 48, 62, 71, 86, 109, 111, 168, 172, 182, 184, 208, 225, 256, 280
- Gamma-ray, 243, 253, 256
 - Detector, 253
 - Spectrometer, 243, 256
- Gasoline, 248
- Gaussian, 26, 29, 38, 49, 62, 70, 120, 208, 282
- Geo-chemical samples, 290
- Geological Science, 264, 309, 315
- Germanium, 29, 254, 255, 257
- Glasses, 83, 208, 210, 218
- Goniometer, 18, 21, 119, 134
- Ground water, 77, 298, 311, 316, 317
- Hair, 77, 264
- Half-lives, 243, 244, 249, 253
- Heavy Ion, 130, 131, 170, 172
 - ERDA, 131, 151, 170, 172
 - RBS, 130
- ^{181}Hf , 245
- HgI_2 crystal, 29
- HIBS, 129, 130
- High resolution, 85, 131, 167, 168, 170, 172, 226, 228, 244, 247, 253, 304, 305
- HpGe solid state detector, 29, 200
- Human, 77, 78, 80, 262, 264, 288, 295, 298, 312–315, 318
 - relics, 298
 - tracers, 298
- Hydrogen detection, 145, 150, 163
- Hydrology, 297, 309, 313, 317
- Hyperfine structure, 189, 198, 236
- Hyperpure Ge, 254
- Hypersatellite lines, 5, 22
- IAEA, 2, 28, 49, 245, 249, 257, 274
- IBA, VII, 113, 172, 244, 289, 290
- Ice man, 296
- Ice-cores, 316
- Imaging, 19, 30, 31, 72, 118
- Impact Parameter, 93, 100–102, 136, 140, 274
- Impurities, 25, 85, 92, 115
- In-vivo, 250, 312, 317, 319
- Induced Activity, 258
- Inorganic Crystals, 253
- Intensities, 8, 9, 13, 52, 55, 61, 63, 64, 66, 87, 149, 191, 198, 200, 203, 236, 245, 247, 260, 281, 304
 - relative, 8, 9, 13, 198, 236
- Intrinsic, 23–25, 27, 29, 32, 168, 169, 180, 237, 240, 254–256, 259
- Introduction, 1, 18, 29, 91, 143, 177, 213, 243, 269, 295
- Iodine, 253, 296, 305, 315
- Ion, 10, 11, 33, 34, 107, 124, 127, 134, 163
 - current, 10
 - Energy, 10, 107, 124, 127, 134, 163
 - velocity, 10, 11, 127
 - Sources, 33, 34
- Ionization, 119, 157–161, 167, 168, 172, 173, 303, 304, 306, 307
 - Chamber, 119, 149, 156–161, 167, 168, 172, 173, 303, 304, 306, 307
 - cross section, 58
- ^{191}Ir , 178, 186
- Irradiating, 243, 247–249
- Isomer-shift, 182, 187–189, 192, 198, 205, 210
- Isotope, 243, 247, 262, 286, 295–302, 305, 308, 313, 315, 319
 - abundant, 298, 299, 301, 302
 - rare, 297, 299, 301, 305
 - stable, 243, 247, 262, 286, 295, 296, 298, 300–302, 305, 308, 313, 315, 319
- Isotopic source, 199, 267
- Jewellery, 82, 288
- Jump ratio, 53
- $K\alpha$ photon, 2, 5
- K-shell, 2, 3, 5, 9, 11, 14, 28, 38, 42, 43, 53, 93, 203
- KAP, 21
- Kinematic factor, 93, 94, 105, 106, 108, 138, 140, 145–147, 150–152, 154, 161, 173
- ^{140}La , 245
- L-shell, 2, 14, 15, 22, 203
- Lamb-Mössbauer factor, 184, 186

- Lambert law, 14
- Land slide, 298
- Lattice dynamics, 212
- Lava flow, 298
- Leakage current, 116, 254, 255
- LiI(Eu), 253
- Limitations, 44, 140, 175, 241, 267, 268
 - of ERDA, 175
 - of heavy ions for PIXE, 44
 - of NAA, 267, 268
 - of RBS technique, 140, 241
 - of XPS, 241
- Line Intensities, 8
- Liquid Nitrogen, 15, 25, 29, 31, 193, 203, 254, 255, 257
- Liquids, 76, 77, 218, 248, 267
- Lithium, 25, 77, 130, 254, 255, 277, 282, 285, 288
- Magnet, 35, 113, 302, 303
 - Analyzing, 35, 113, 300, 302, 303
 - Switching, 35, 113, 302
- Magnetic, 114, 118, 119, 132, 145, 155, 303
 - Hyperfine Structure, 189
 - Spectrometer, 114, 118, 119, 132, 145, 155, 303
- Mars exploration, 210
- Mass spectrometry, VIII, 295–297, 299, 300, 306, 309, 312, 314, 315, 318, 319
- Material Science, 78, 204, 265, 284, 297, 309
- Matrices, 50, 52, 73, 77, 88, 247, 290
- Matrix elements, 30, 45, 61, 130
- MCNP-code, 260
- Medical purposes, 239
- MEIS, 133–135
- Mercury, 264
- Metals, 1, 13, 77, 79, 81, 86, 89, 139, 208, 218, 233, 237, 248, 263, 265, 266, 308
 - meteorites, 73, 264, 298, 317
- Mg/Al Anode X-ray Tube, 221
- Microanalysis, 30, 237, 286
- Microprobe, 32, 38, 72, 76, 289
- Mineral, 85, 238, 243, 320
 - samples, 85, 320
 - surfaces, 238
- ^{55}Mn , 12
- ^{56}Mn , 245
- Modulation, 192, 197, 316
- Molecular orbital, 5, 44, 74, 75
- Monochromatic, 12, 24, 55, 67–69, 218–223, 226, 233, 241
- Moseley Law, 7
- Mössbauer Spectrometer, 184, 193, 197, 202, 210
- Multichannel Analyzer, 15, 38, 126, 193, 194, 196, 197, 199
- Mylar foil, 153, 159, 161, 163, 285
- ^{23}Na , 64, 243, 279, 281–283, 289–293
- ^{24}Na , 243, 251, 292
- NAA, 243, 244, 246–251, 256–259, 261, 262, 264–268
- Nanostructured materials, 209
- Napoleon, 264
- Neutron, 246, 247, 249–252, 263, 265
 - Beam, 246, 250, 252
 - Cold, 246, 263
 - Epithermal, 245, 247, 249
 - Generators, 250, 251
 - Sources, 249, 250
 - Thermal, 265
- Neutron Activation Analysis, 243, 244, 246, 248, 250, 256, 261–264, 266, 267
- Neutron Sources, 250, 251
 - Radio-isotopic, 250, 251
- Non-characteristic, 5
- Non-destructive, 1, 84, 108, 133, 206, 241, 244, 286, 289
- Non-diagram lines, 2, 5, 22
- Notation, 4, 6, 7, 218
- ^{239}Np , 13
- NRA, 32, 51, 71, 82, 273
 - Non-resonant, 273
 - Resonant, 273, 275
- NRA for, 275, 276
 - Analysis of Carbon, 276
 - Analysis of Hydrogen, 275
 - Analysis of Nitrogen, 276
 - Analysis of Oxygen, 276
- Nuclear Reaction analysis, VIII, 32, 71, 269, 271, 280, 284, 286
- Nuclear Reactor, 243, 248–250, 310

- Nuclear resonance Fluorescence, 178, 179
- Nutrients, 314, 315
- Oils, 218, 266, 287
- Orbital electron velocities, 10, 11
- Ores, 85, 248, 265
- Parameters, 26, 38, 51, 55, 58, 61, 62, 70, 75, 97, 100, 101, 114, 125–127, 150, 158, 165, 168, 187, 198, 200, 205, 230, 236, 259, 261, 274, 299, 320
- Particle, VII, 2, 3, 31, 32, 36, 39, 41, 44, 50, 51, 56, 59, 62, 66, 73, 91, 96, 114–117, 119, 131, 133, 157, 166, 201, 223, 249, 251, 270, 271, 273, 274, 279, 295, 299, 308
- Accelerators, VII, 249, 251
- Charged, 2, 3, 31, 32, 36, 39, 41, 44, 50, 51, 56, 59, 62, 66, 73, 91, 96, 114–117, 133, 157, 166, 201, 223, 251, 270, 271, 273, 274, 278, 279, 295, 299, 308
- Detectors, 56, 114, 119, 131, 133, 166
- Elastic scattering, 91
- Particle-induced, 1, 85, 269
- Gamma ray emission, 269
- X-ray emission, 1, 85, 269
- Pauli's exclusion principle, 6
- ^{210}Pb , 257
- ^{214}Pb , 257
- Pd metal, 234, 235
- Peak, 70, 139, 216, 230, 237, 249, 259
- area, 71, 216, 230, 237, 249, 259
- centroid, 70
- width, 70, 139
- Pelletron, 31–33, 113, 298
- Penetration depth, 19, 87
- PET, 21, 239
- PGAA, 243, 246, 250
- PGNAA, 243, 244, 246, 247, 260
- Phonons, 177, 212, 254
- Photoelectric absorption, 14, 15, 53, 256
- Photoelectron Analyzer, 224
- Photomultiplier tube, 253
- Photoneutron Sources, 251
- Photons, 1–3, 5, 9, 13, 14, 17, 26, 30, 51, 53–55, 118, 183, 184, 192, 194–196, 201, 203, 214, 216, 218, 221, 223, 231, 253, 254, 256, 277
- photopeak, 29, 52, 55, 256, 259
- PIGE, VIII, 51, 77, 82, 269, 270, 277–283, 287–290, 293, 299
- PIXE, 39, 45, 89
- Applications, 89
 - Charging/Sparkling/Heating, 45
 - Some other Aspects, 39
 - Using Heavy Ion Beams, 39
- Plane-wave Born Approximation, 43, 74
- Planetary Science, 297
- Plutonium, 296, 305
- Pollution analysis, 80
- Polyethylene capsules, 248
- Polymers, 218, 233, 238, 286
- Position Sensitive Detector, 85, 116, 134, 135, 156, 158, 159, 162, 170, 174, 226
- Potential, 2, 10, 20, 25, 32, 35, 45–47, 69, 83, 89, 112, 113, 135, 136, 147, 156, 159, 165, 187, 221, 225, 227, 228, 239, 273, 274, 297, 301, 302, 312, 313
- Precision, 22, 45, 49, 64, 85, 108, 150, 186, 214, 231, 262, 272, 284, 296, 301, 307, 321
- Principle, 2, 104, 149, 214, 271
- and characteristic features of XPS, 214
 - and characteristics of ERDA, 149
 - and characteristics of NRA, 271, 272
 - of Rutherford Backscattering spectroscopy, 104
 - of XRF and PIXE techniques, 2
- Projectile Bremsstrahlung, 65, 66
- Prompt NAA, 246
- Proportional counter, 20, 22, 30, 85, 86, 193–196, 202–204, 255
- Proton, 10–12, 26, 31, 36, 39, 42–45, 47, 49, 56, 58, 60, 64–66, 72, 73, 77, 78, 85, 88–92, 95, 97, 111, 112, 115, 133, 148, 157, 163, 251, 269, 270, 272, 274, 275, 277–281, 287–289, 299
- Proton Gamma Activation Analysis, 243, 246
- Proton Microprobes, 72
- Protons, 1

- ^{238}Pu , 250
Pulsed Generator, 267
Pyrex glass, 167
- Quadrupole, 7, 35, 73, 182, 187–189, 191, 198
Coupling, 188, 191, 199
Lens, 35, 73
- Qualitative, VII, 1, 13, 21, 48, 55, 89, 156, 211, 230, 243–245
- Quantitative, 1, 13, 30, 48, 49, 55, 65, 72, 80, 84, 89, 108, 139, 143, 173, 204, 211, 213, 241, 243–245, 247, 248, 258, 264, 265, 282, 290, 295, 309, 314
- Quantum Mechanics, 2, 273
- Quantum Number, 5–7, 9, 11, 75, 190, 201
Azimuthal, 6
Magnetic, 6
Principle, 5
Spin, 6
- Quasi-molecular, 44, 74
- ^{226}Ra , 257
- Radiative, 3, 5, 9, 22, 54, 58, 76, 97, 243–246
Auger Emission, 235
decay, 97
- Radioactive isotope, 107, 243, 245, 267, 268, 309, 312, 313
- Radioactive Sources, VII, 12, 26–28, 220, 250, 280
as exciters, 12
- Range, 2, 8, 11, 12, 14, 16–21, 23, 27, 29–31, 36, 39, 43, 47, 50, 55, 56, 64, 65, 68–70, 72, 73, 76, 85, 87–91, 95, 96, 102, 108, 111, 115, 117–119, 124, 125, 127, 130, 132–135, 137, 144, 145, 147–152, 154, 156, 160, 161, 167, 168, 170, 172, 173, 179, 180, 182, 183, 194–197, 201–204, 206, 209, 213, 214, 216, 219, 220, 223, 224, 226, 236, 238, 241, 243, 244, 252, 253, 255, 256, 261, 267, 271, 273, 277, 281, 284, 286, 288, 289, 295–298, 302, 306, 308–310, 314, 319, 320
- Rayleigh scattering, 14, 212
- ^{86}Rb , 245, 253
- RBS spectrum, 119–124
from a thin layer, 119
from thick layers, 121
- Reaction Kinematics, 272
- Reactions, 274, 275, 291, 292
Deuteron-induced, 275, 292
 ^3He - and ^4He -induced, 275, 292
Proton-induced, 274, 291
- Reactor Steel, 209
- Recoil-free fraction, 183, 184, 186
- Recoil ions, 75, 145, 156, 158, 164, 165, 341
- Recoil particles, 146, 152, 155, 157
- Reference Books for further Reading, 359
- Reference Material, 244, 248, 249, 260
- References, 293
- Resolution, 15, 21–23, 26, 27, 29–31, 36, 38, 40, 48, 62, 66, 71, 85, 86, 88, 93, 96, 105, 106, 108, 113, 116, 118–120, 123, 129–133, 135, 137, 138, 143, 145, 147, 149, 150, 155, 156, 158, 159, 161–170, 172, 174, 182, 184, 187, 205, 212, 213, 218, 220, 222, 224–226, 228, 229, 237, 238, 240, 253–257, 267, 270, 272, 277, 278, 280, 281, 303, 304, 306, 307
- Resonance Fluorescence, 178, 179
- ^{222}Rn , 257
- Roman glass, 289
- Rutherford scattering, 56, 59, 91, 99–101, 103, 107, 108, 110, 137, 138, 141, 143, 147, 174
cross section, 99, 100, 107, 108, 110, 137, 141, 143
using forward angles, 137
- Rydberg constant, 8
- Sample Preparation, 89, 134, 248, 259, 305, 306, 313, 319
- Samples, 1, 2, 31, 32, 36, 37, 43, 45, 46, 49, 50, 52, 55, 58, 64, 73, 76–78, 80–85, 87, 89, 90, 124, 130, 134, 160, 169, 170, 192–194, 204, 209, 218, 233, 238, 239, 243, 248, 249, 256, 262, 266, 267, 276, 277, 282–284, 286, 288, 289

- Powdered, 84
- Thick, 49, 50, 52, 64, 87, 90, 206, 277, 282, 284
- Thin, 50, 52, 64, 89, 90, 277, 284
- Satellite lines, 5, 22, 40, 41
- Saturation factor, 258, 259
- Saxon-Woods, 274
- ^{124}Sb , 245, 251
- ^{46}Sc , 68, 245
- Scattering, 14, 36, 46, 67, 68, 91–94, 100–102, 105, 106, 109, 111–113, 133–135, 137–139, 143, 144, 147, 149, 150, 157, 158, 160, 161, 163, 165, 174, 193, 276, 278
- Angle, 91, 92, 94, 101, 102, 105, 106, 109, 111, 137–139, 147, 150, 157, 161, 163, 165, 174, 276
- Chamber, 14, 36, 113, 134, 150, 163, 278
- Elastic, 46, 91, 93, 112, 133, 143, 144, 147, 149, 160
- Fundamentals, 92
- Geometry, 67, 91, 100, 113, 135, 138, 144, 158, 193, 202
- Scintillation, 20, 22, 195, 253, 255–257, 280, 312
- Scofield, 38, 54
- ^{75}Se , 245, 262, 315
- Sediments, 248, 316, 317
- Semi-classical Approximation, 73, 217
- Semiconductor, 24, 29, 70, 79, 104, 114, 116, 139, 159, 218, 253–256, 265, 277, 280, 282, 308, 313
- Sensitive volume, 25, 26, 68, 114, 163
- Sensitivity, 1, 39, 64, 65, 69–71, 73, 88, 104, 108, 111, 129, 130, 135, 140, 151, 155, 158, 161, 162, 170, 172, 174, 218, 220, 224, 228, 231, 238, 247, 261, 265, 268, 295, 308, 313, 314, 319
- Shell, 2, 3, 5, 9, 11, 14, 15, 22, 28, 38, 40, 43, 53, 93, 201
- K, 2, 3, 5, 9, 11, 14, 28, 38, 40, 43, 53, 93, 203
- L, 2, 11, 14, 15, 22, 201, 203
- M, 3, 5, 9, 11, 14, 203
- Shielding, 112, 116, 192, 246, 311
- Si(Li) detector, 13, 15, 25–29, 36, 42, 44, 49, 56, 59, 61, 68, 70, 88, 195, 269
- Efficiency calibration, 26, 27, 280
- Siegbahn, 4, 213
- Signal background, 66, 67
- Signal-to-noise ratio, 257
- Silicate Rocks, 265
- Silicon, 24–26, 29, 49, 68, 71, 115–117, 119, 124, 126, 128, 130, 131, 144, 152, 153, 155, 165, 168–170, 232, 250, 283, 284, 286, 306, 307, 309
- Silicon drift detector, 31
- Simultaneity, 86
- Small size, 195, 218
- SNICS, 34, 298, 300
- Sodium, 13, 110, 234, 243, 282, 290
- Soil Science, 266
- Sollar slit, 21, 22
- Sources, 13, 14, 64, 65, 67, 220, 222, 233, 241
- Annular, 13, 116, 228
- Central, 13
- of background, 64, 65, 67
- X-ray, 14, 220, 222, 233, 237, 241
- Spallation, 1, 299
- Spectral, 7, 26, 30, 38, 45, 49, 86, 90, 154, 178, 182, 185, 200, 220
- overlap, 86
- series, 7
- Spectrometer
- Gamma-ray, 243
- Mössbauer, 193
- Spectrometry, 20, 21, 30
- Wavelength Dispersive, 20, 21, 30
- Spectrum Analysis, 38, 126, 282
- SRIM, 127
- SRM, 62, 260
- Standard deviation, 63, 120, 259
- Standardization, 259, 260
- Stopping, 42, 49, 50, 57, 59, 60, 95, 96, 114, 123, 126, 133, 144, 146, 148–150, 152, 154, 156, 167, 169, 170, 173, 174, 275, 283, 303
- cross section, 99
- power, 42, 49, 50, 57, 59, 60, 95–97, 114, 123, 126, 133, 144, 146, 148–150, 152, 154, 156, 167, 169, 170, 173, 174, 275, 283, 303

- Straggling, 95, 96, 108, 123, 126, 127, 143, 146, 149, 150, 169, 173, 174, 202, 307
- Stripper foil, 35, 47, 164, 297
- Study of
 - Actinides, 210
 - Biological materials, 211
- Sub-shell, 3, 5, 8, 14, 53, 54, 235
- Surface, 206, 214, 217, 219
 - sensitive, 214, 217, 219
 - studies, 206
- Surface Barrier Detector, 36, 106, 114–116, 130, 131, 144, 149, 151, 155, 159, 160, 163, 168–170, 278
- Synthetic fibers, 248
- ^{182}Ta , 245, 253
- TAP, 21
- Target, 16, 19, 36, 42, 54, 55, 66, 91, 95, 98, 99, 120, 122, 126, 149, 157, 251
 - holder, 36
 - material, 16, 19, 42, 54, 55, 66, 91, 95, 98, 99, 120, 122, 126, 149, 157, 251
- ^{160}Tb , 13, 245
- Technique, 1, 2, 9, 31, 32, 37, 46, 49, 52, 61, 71, 73, 76–80, 82, 83, 85–90, 140, 143–145, 147, 149, 151, 160, 162, 164, 165, 167, 169, 172, 175, 177, 200–202, 204, 211, 213, 214, 216, 217, 219, 230, 233, 234, 237, 238, 241, 243–248, 250, 262–271, 273, 275–278, 280, 281, 284, 285, 287–291, 295–297, 299, 300, 304, 306, 308, 309, 311, 312, 314–316, 318–320
- Telescope, 116–119, 144, 145, 148, 156, 159–161, 166, 168, 169, 172, 174, 278
- Theories of, 73
 - X-ray emission by charged particles, 73
- Thermal neutrons, 245, 246, 252
- Thick sample, 44, 49, 52, 58, 64, 87, 90, 206
- Thin sample, 52, 64, 89, 90, 277
- Time-of-flight, 107, 129, 130, 155, 156, 162, 164–168, 170, 172, 304, 306, 307
- Energy Telescope, 165
- Experiment, 166
- Mass Spectrometry, 306
- Spectrometry, 155, 164, 167, 168
- Timing Detector, 165, 166, 169, 307
- ToF-E detector, 155, 169
- Trace elements, 42, 43, 45, 49, 55, 69, 77, 81, 82, 84, 85, 105, 130, 173, 238, 243, 244, 262, 264, 267, 288, 308, 314
- Tracer studies, 286, 308, 320
- Transition probabilities, 9, 13, 58
- Transitions, 2, 4, 5, 7, 8, 22, 29, 41, 54, 64, 186, 191, 198, 201, 218, 224, 247, 269, 280
- Triaxial geometry, 18
- TRIM, 50, 59, 127
- Tritium, 148, 151, 250, 251, 296, 311, 315
- ^{237}U , 13
- Uranium, 47, 77, 249, 267, 288, 289
- Use of, 316–318
 - ^{26}Al , 317
 - ^{10}Be , 316
 - ^{14}C , 317
 - ^{41}Ca , 318
 - ^{36}Cl , 317
 - ^{59}Ni , 318
- Vacancy, 2, 3, 5, 10, 23, 41, 54, 56, 58, 75, 201
- Vacuum, 1, 16, 36, 61, 76, 81, 114, 255, 301
 - chamber, 1, 36, 61, 76, 114, 255
 - pump, 16, 36, 81, 114, 301
- Van de Graaff, 31, 32, 113, 168
- Wave-guide, 246
- WDXRF, 19, 20, 25, 80, 87, 88, 90
- Wet-ashing, 77
- X-Ray, VII, VIII, 1, 3, 5, 10, 12–19, 21–24, 26, 30–32, 36–41, 44, 45, 51, 54, 55, 58–62, 66, 68–70, 76, 79, 80, 82, 85, 87–89, 220–223, 233, 238, 311
 - Characteristic, 3, 5, 13, 15–19, 22, 30, 32, 36, 37, 44, 51, 55, 59, 87, 221, 222, 311

- Detection, 19, 31
- Fluorescence, VII, VIII, 1, 12, 18, 19, 23, 24, 30, 31, 38, 51, 60, 79, 80, 82, 85, 88, 89
- Production, 10, 18, 26, 31, 39–41, 44, 45, 54, 58, 59, 61, 62
- Sources, 14, 220, 222, 233, 237, 241
 - Spectra, 5, 23, 70, 85
 - Spectrometry, 19, 76
 - Tube, 12, 16–19, 21, 23, 24, 66, 68, 69, 89, 221, 223, 238
- XPS, 216, 217, 226, 230, 231, 234, 235
 - Applications of, 237
 - data, 230, 231
 - Features of, 217
 - spectrum, 216, 217, 226, 234, 235
- XRF, 12, 13, 19, 65, 66, 90, 213
 - Analysis, 12, 13, 19, 65, 66, 90, 213
 - Applications, 76
 - Modes of Excitation, 12
 - Principle, 2
- ^{169}Yb , 13
- Z-dependence, 269
- ^{95}Zr , 245
- ^{97}Zr , 245