6

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 looses 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 $\sim$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

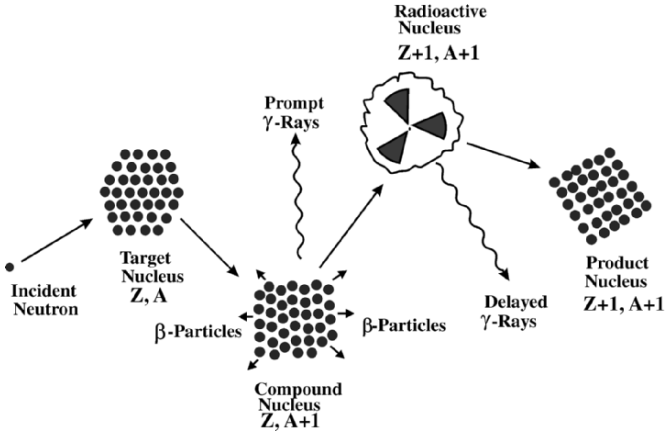


Fig. 6.1. Principle of neutron activation technique

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 l/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 $\sim 10^{13}\,\mathrm{n\,cm^{-2}\,s^{-1}}$ 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 Cockroft-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 PGNAA 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/D_2O 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 $\mathrm{N\,s^{-1}\,Ci^{-1}}$
^{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 Interacting With	Neutron Energy (MeV)	Yield ($\mathrm{n\,s^{-1}}$)
^{24}Na	15 h	2.75	Be	0.2	14
			D_2O	0.8	29
^{88}Y	108 d	0.9, 1.8, 2.8	Be	0.16	10
			D_2O	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 (^{3}H) target. The nuclear reaction carried out is $^3\mathrm{H(d,n)^4He}$. The energy of the produced monoenergetic neutrons is 14 MeV. The typical neutron yields of about 10^{11} neutrons $\mathrm{s^{-1}mA^{-1}}$ means a neutron flux of approximately 10^9 neutrons $\mathrm{cm^{-2}\,s^{-1}}$. 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, $^7\mathrm{Li(p,n)^7Be}$ 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 $^{28}\mathrm{Si(n,p)^{28}Al}$ and above the region where neutron capture reactions like $^{27}\mathrm{Al(n,\gamma)^{28}Al}$ 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 $\mathrm{N\,cm^{-2}\,s^{-1}}$	Moderator Material
$^{2}\mathrm{H(d,n)}^{3}\mathrm{He}$	3.25	$\sim 2.5 \times 10^{9}$	water or paraffin
$^{3}\mathrm{H(d,n)}^{4}\mathrm{He}$	17.6	–do–	–do–
$^{9}\mathrm{Be(d,n)}^{10}\mathrm{B}$	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}–$10^{15}\,\mathrm{n\,cm^{-2}\,s^{-1}}$. 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 $2{,}200\,\mathrm{m\,s^{-1}}$. 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 – $(\mathrm{n,p})$, $(\mathrm{n,n'})$, and $(\mathrm{n,2n})$ – 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 $1/E_{\mathrm{n}}^{1+\alpha}$ 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)	^{110m}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), $Be_4Ge_3O_{12}$ 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/cm^3. 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 $\sim$1 keV (at 122 keV) and $\sim$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 LN_2 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.

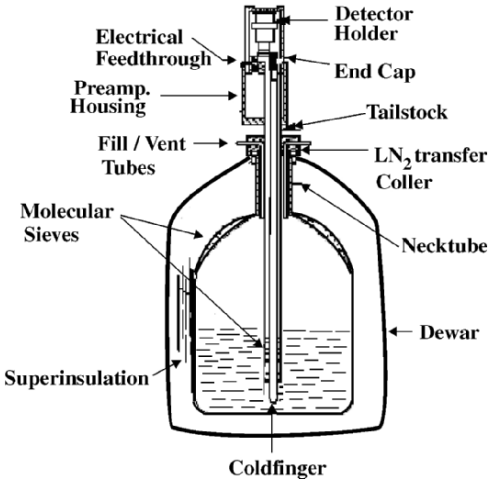


Fig. 6.2. Cross-sectional view of an HpGe/Ge(Li) semiconductors detector with a typical liquid nitrogen cryostat

In liquid nitrogen (LN_2) 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 LN_2 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 GΩ) 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. Ø × 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 ∼20% and the peak to Compton ratio ∼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. × 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.

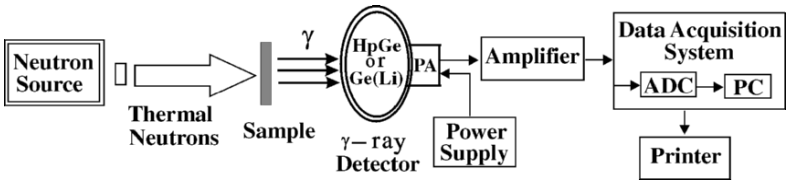


Fig. 6.3. γ-spectroscopy system used in neutron activation analysis

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.

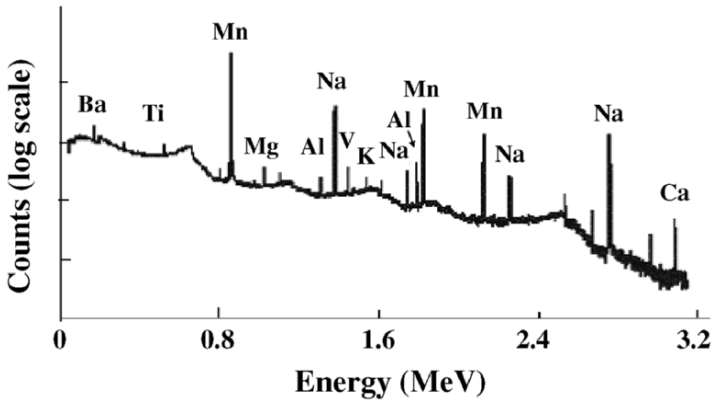


Fig. 6.4. γ-ray spectrum showing several short-lived elements measured in a sample of pottery irradiated for 5 s, decayed for 25 min, and counted for 12 min with an HpGe detector

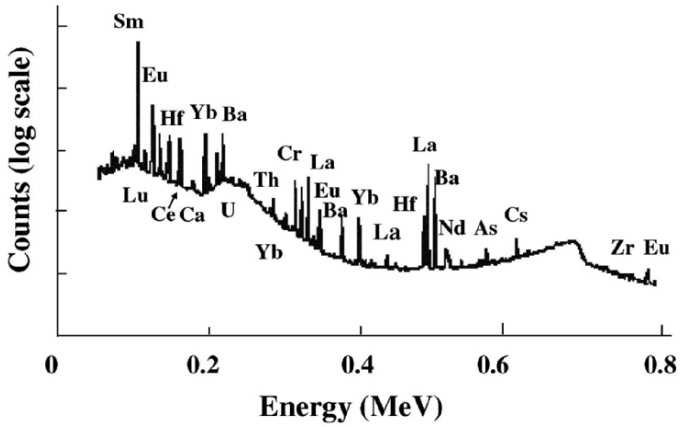


Fig. 6.5. γ-ray spectrum from 0 to 0.8 MeV showing medium- and long-lived elements measured in a sample of pottery irradiated for 24 h, decayed for 9 days, and counted for 30 min on an HpGe detector

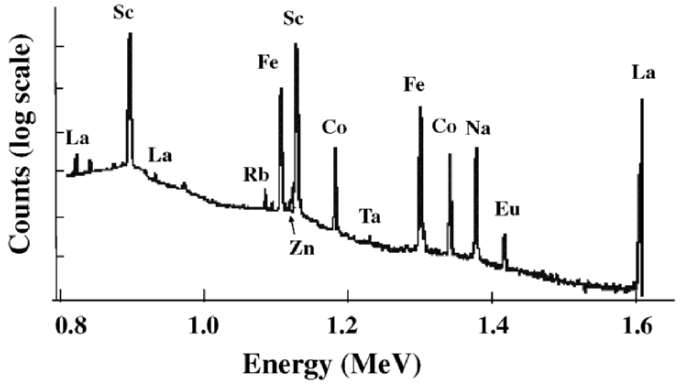


Fig. 6.6. γ-ray spectrum from 0.8 to 1.6 MeV showing medium- and long-lived elements measured in a sample of pottery irradiated for 24 h, decayed for 9 days, and counted for 30 min on an HpGe detector

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

$$A_0 = \sigma \Phi \alpha S \left(\frac{\mathrm{m\ N_A}}{\mathrm{M}} \right) \tag{6.1}$$

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 neutron $cm^{-2}\,s^{-1}$; α is the fraction of the target isotope in the sample (e.g. with an ordinary copper sample producing $^{63}Cu(n,\gamma)^{64}Cu$ 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

$$A_{t_d} = \sigma\Phi\alpha S\left(\frac{mN_A}{M}\right)\left(e^{-\lambda t_d}\right) \tag{6.2}$$

Accounting for the number of radioactive nuclei that decay during counting interval t_c, the activity will be given as

$$A = \sigma\Phi\alpha S\left(\frac{mN_A}{M}\right).\left(e^{-\lambda t_d}\right)\cdot\left(1 - e^{-\lambda t_c}\right) \tag{6.3}$$

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

$$(\Sigma_p - \Sigma_b) = \frac{A}{\lambda\cdot G\cdot\epsilon_p\cdot f} = \frac{\sigma\Phi\alpha S\left(\frac{mN_A}{M}\right)\cdot\left(e^{-\lambda t_d}\right)\cdot\left(1 - e^{-\lambda t_c}\right)}{\lambda\cdot G\cdot\epsilon_p\cdot f} \tag{6.4}$$

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

$$\frac{A_{\mathrm{sam}}}{A_{\mathrm{std}}} = \frac{m_{\mathrm{sam}} \left(\mathrm{e}^{-\lambda T_{\mathrm{d}}}\right)_{\mathrm{sam}}}{m_{\mathrm{std}} \left(\mathrm{e}^{-\lambda T_{\mathrm{d}}}\right)_{\mathrm{std}}} \tag{6.5}$$

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

$$C_{\mathrm{sam}} = C_{\mathrm{std}} \frac{W_{\mathrm{std}}}{W_{\mathrm{sam}}} \cdot \frac{A_{\mathrm{sam}}}{A_{\mathrm{std}}} \tag{6.6}$$

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 PGNAA 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 PGNAA 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)

$$C_{\min} = \frac{A_{\mathrm{e}} A_{\mathrm{m}}(t) \mathrm{e}^{\lambda t_{\mathrm{d}}}}{60 f N t \Phi \sigma \left(1 - \mathrm{e}^{-\lambda t_i}\right)} \cdot \frac{\mathrm{UF}}{w_{\mathrm{s}}} \tag{6.7}$$

where A_{e} is the atomic number of the element, $A_{\mathrm{m}}(t)$ 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 $\mathrm{n\,cm^{-2}\,s^{-1}}$, 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 $\mathrm{mg\,L^{-1}}$) (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 1×10^{13} n $\mathrm{cm^{-2}\,s^{-1}}$.

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	$_{9}$F, $_{11}$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 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 is 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 $^{19}F(n,\gamma)^{20}F$ and $^{48}Ca(n,\gamma)^{49}Ca$ reactions (Mernagh et al. 1977) with minimum detection limit of $50\,\mu g\,g^{-1}$. 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 erthrocytes, urine, and blood samples.

NAA has proven to be a most suitable method for the quantitative determination of a wide variety of trace (0.01–100 μg g^{-1}) and ultratrace (< 0.01 μg 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 $5\,\mathrm{ng\,g^{-1}}$ for As, $10\,\mathrm{ng\,g^{-1}}$ for Sb and W and $50\,\mathrm{ng\,g^{-1}}$ 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 Brügmann 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 $^{27}\mathrm{Al(n,\gamma)}^{28}\mathrm{Al}$. In another study, these authors (Borsaru and Mathew 1982) applied the thermal neutron activation technique to bulk samples ($\cong$11 kg) of Australian black coal for the determination of alumina, silica, and ash. The determination of alumina was based on the reaction $^{27}\mathrm{Al(n,p)}^{27}\mathrm{Mg}$ and counted the 0.844 MeV peak ($t_{1/2} = 9.4$ min). Silica was determined by means of the reaction $^{28}\mathrm{Si(n,p)}^{28}\mathrm{Al}$ and counting the 1.78-MeV peak ($t_{1/2} = 2.3$ 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 2–51 $\mathrm{ng\,g^{-1}}$ has been determined in high purity GaAs with NAA by Köhler et al. (2000) with minimum detection limits of $0.018\,\mathrm{ng\,g^{-1}}$.

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.