

CHAPTER - 1

INTRODUCTION

CHAPTER - I

INTRODUCTION

Modern analytical chemistry can be called the 'Chemistry of traces' and a variety of analytical techniques are available for the determination of trace and ultratrace constituents. However, the choice of any particular technique is determined by its sensitivity, specificity, non-destructiveness, freedom from process blank, multielemental capability, precision and accuracy. Neutron activation analysis (NAA) technique fulfills most of the above mentioned conditions and is used for analysis of wide range of elements.

Activation analysis owes its origin in the paper of Hevesy and Levi¹ in 1936. They reported the determination of dysprosium in yttrium at the level of 0.1% using a portable radium-beryllium source. Later on Seaborg and Livingood² in 1938 showed the nondestructive aspect of activation analysis using charged particles. However, a first systematic presentation of activation analysis as a method was made by Clark and Overman³ in 1947 and Liddicotte and Reynolds⁴ have subsequently put the technique on routine use in 1952. The development of neutron activation analysis (NAA) into a powerful trace element analysis technique had to wait for nearly 20 years, until the high flux nuclear reactors were available for sample irradiation. With the growth of nuclear reactors and high resolution systems for radiation detection, now a days, the technique of activation analysis had gained wide popularity as a method for the determination of trace concentrations of wide range of elements.

1.1 THE PROCESS OF ACTIVATION :

In the process of activation, the analytes in the sample are converted into radioactive species, through bombardment with suitable particle. Radioactive nuclides, induced by nuclear reactions on the elements present, show different values of half-life, energy and kind of radiation, which enables one to identify the elements. The advances in the high resolution detector technology and the electronics for pulse height analysis have led to the use of γ -ray spectrometry as the principal mode for the quantitation of various elements in a sample, even though β -counting would be essential for certain nuclides, like ^{32}P which are pure β -emitters. The total activity produced for a specific nuclide for an irradiation time t in a particle flux ϕ is given by equation 1.1 which is directly related to the amount of target material.

$$A_t = \frac{W L r \phi \sigma (1 - e^{-\lambda t})}{100 M} \quad \dots\dots(1.1)$$

Where,

W = Weight of the target material, g.

ϕ = Particle flux, number of particles $\text{cm}^{-2} \text{s}^{-1}$.

σ = The capture cross section, cm^2 .

L = Avogadro's number (6.023×10^{23}).

r = Percentage abundance of the target.

λ = Decay constant of the radioactive product formed, time^{-1}

t = Time of irradiation, time.

M = Atomic weight of the target, g.

A_t = Activity of the nuclide at the end of irradiation, dps.

It should be noted that λ and t are expressed in the same units.

1.2 THE GENERAL TECHNIQUE OF ACTIVATION ANALYSIS :

The general technique of radioactivation analysis consists of a series of steps whose parameters are chosen to optimise the sensitivity and accuracy with minimum efforts and loss. These various steps are briefly discussed below :

1.2.1 The Choice of Optimum Nuclear Reaction :

Radioactivation analysis consists of three independent variables : the target nucleus, the irradiation particle and the product nucleus. In fact, these three variables are not absolutely independent. For elements having more than one major stable isotopes the target nucleus is still a variable, in such a case selection of a target nuclide depends upon its isotopic abundance and capture cross section. The type of activation reactions has to be selected from case to case. In general the following requirements are considered while selecting the activation reaction⁴ :

1. A suitable activation product has to be formed having sufficiently long half-life to allow for necessary treatments and/or transport of samples after the activation. However, half-life should not be too long which requires prolonged activation time.
2. The reaction has to exhibit an optimum sensitivity.

3. Interfering reactions forming or consuming the reaction products must not occur.
4. The treatment of the irradiated material must be as simple as possible. The chemical separation can often be avoided by a proper combination of individual factors.
5. The desired reaction should not involve other reactions producing competing radioactive isotopes of the same element as activation product.

1.2.2 Suitable Irradiation Facility :

The choice of a suitable irradiation facility depends on the type of irradiation particle required for the chosen nuclear reaction. The types of nuclear particles are classified as neutrons, charged particles, photons and electrons. The corresponding methods are then termed as neutron activation, charged particle activation, photon activation and electron activation analysis. After selecting a suitable projectile, other factors taken into consideration are energy characteristics of the irradiating particle. Irradiation geometry of the sample, specific regulations and encapsulation requirements, the location of the facility and the cost of irradiation also play an important role in the selection.

1.2.3 The Pre-irradiation Treatment :

Sample preparation consists of their weighing and packing. It is of vital importance to avoid any chemical treatment which could lead to a contamination with impurities from the reagents used. Only in the

case of solid samples the surface should be cleaned to remove surface impurities. Samples containing water (as e.g. biological materials) should be dried until a constant weight is achieved prior to the activation. Liquid samples can be activated either directly or after evaporation.

Those materials used for sample packing should not undergo activation and should show a remarkable resistance to heat and radiation. Silica ampoules and vials are most oftenly used. Polyethylene and aluminium have also found many applications as materials for packing samples and standards. In general preirradiation treatment should be always minimum, however, it is necessary if (a) sample is too bulky. (b) it is too inhomogeneous and (c) it is too radioactive after nuclear reaction.

1.2.4 Irradiation Time and Irradiation Conditions :

The irradiation time and flux of irradiating particle to be used for analysis are governed by the required sensitivity for the given experiment. In case of short lived activation products, the sensitivity is proportional to the intensity of the irradiation. For activation products with relatively longer half lives, the sensitivity depends on both the intensity and duration of irradiation. It is usually not desirable to irradiate to saturation activation in these cases. Therefore, a choice of irradiation condition is important, the choice being among several equivalent combinations of intensity and duration. The selection of the optimum irradiation conditions is usually based on the half lives of the major activation products in the sample. For

example, if these half-lives are relatively short with respect to those of the trace element activation products, it is advantageous to irradiate the sample for longer time at a lower flux to minimize the gross activation. For the opposite case, a shorter irradiation at higher fluxes may be preferable.

The sample must be prepared in a suitable form for irradiation and getting the sample container into and out of the irradiation facility must be smooth. If the flux is not uniform, the rotation of target assembly is necessary during the irradiation.

1.2.5 The Post Irradiation Assays :

After irradiation of the sample, selectivity in activation analysis is achieved by isolating the activity of the isotope of interest, from the activity of the rest of the nuclides in the sample. This can be done instrumentally by high resolution γ -ray spectrometry semiconductor detectors with time dependent measurements. The E_{γ} and $t_{1/2}$ aid in the selective estimation by this instrumental activation analysis approach. However, in cases of high matrix activity and short half-life of the analyte nuclides and in the cases of nuclides with overlapping gamma ray energies, chemical separations are must which further improves the selectivity and help to achieve improved practical detection limits compared to instrumental activation analysis (IAA). This approach is termed as the radiochemical activation analysis. Instrumental or radiochemical activation analysis are adopted depending upon the nuclear properties of the matrix, the analyte and the concomitant elements in the sample. IAA is perhaps the only approach

feasible in the cases of precious samples such as forensic exhibits, meteorites, archaeological specimens and ancient coins, which may require the preservation of the samples.

Another alternative for post-irradiation assay is absolute versus comparator method of analysis.

1.2.5.1 Absolute method :

The absolute activity formed in a sample from a given element is given by the equation :

$$A_t = \frac{W L r \phi \sigma (1 - e^{-\lambda t})}{M \times 100} \quad \dots\dots(1.1)$$

the meanings of different symbols being described earlier.

If all constants are known precisely, then by measuring the absolute activity, the amount of the element in the sample can be calculated by using above equation. This method of evaluation of an element has not been extensively used in practice.

This method has been developed mainly by the Girardi *et al.*⁵ They have determined 13 elements using a calibrated γ -spectrometer for the measurement of absolute activity. They reported that the random errors are not greater with this method than with activation analysis using standards; nevertheless, systematic errors may reach values upto 20%. These systematic errors are caused more by inaccuracy in the nuclear data determination, especially those of decay schemes and activation cross section values, than by inaccuracy in the neutron flux

or absolute activity determination.

1.2.5.2 Comparator method :

Comparator method of the activation analysis is essentially very simple, however, difficulties are encountered with respect to its reproducibility. The method is based on a comparison of the activity of the sample to be analyzed with the activity of a standard. The activation of both sample and standard have to be carried out under exactly identical conditions; their simultaneous activation represents the best approach. The standard should be situated as close as possible to the sample to eliminate the error that could arise due to any neutron flux inhomogeneity in the neutron source. Measurements must also be performed under identical geometrical conditions. Under such a situation, the several common parameters of the activation are equal, even if they are not sufficiently precise.

$$\frac{A_x}{A_s} = \frac{W_x \sigma_x \phi_x (1-e^{-\lambda t})}{W_s \sigma_s \phi_s (1-e^{\lambda t})} \dots\dots (1.2)$$

where, x and s stand for the unknown and known elements respectively. For equal irradiation times and irradiation flux conditions, other nuclear parameters being identical, one can calculate the amount of the element to be determined in the sample by :

$$W_x = W_s \frac{A_x}{A_s} \dots\dots (1.3)$$

Very often it is advisable to plot a calibration graph (activity against weight of target), particularly in the case of the quantitative analysis of samples showing different compositions.

The ease of the comparator method of activation analysis, which requires only relative measurements and eliminates the need for precise nuclear data, has resulted in its more widespread use compared with the absolute method. In this method, however, careful maintenance of equal conditions of sample and comparator is required.

1.2.6 The Measurement of Optimum Radiation :

Radiation measurement systems range from GM counters to high resolution gamma ray multichannel spectrometers. The optimum system will be that which measures radionuclides with maximum precision.

1.2.7 Precision and Accuracy :

The quality of determination of some specific elements or components is the function of the precision and accuracy obtained. The need for precision and accuracy may be divided into four categories.

1. Qualitative - Is element Z present in the sample?
2. Threshold - Is element Z present in amounts greater than some given amount?
3. Relative - Is element Z present in small or large amount?
4. Absolute - Exactly how much of the element Z is present in the sample?

Neutron activation analysis being based on nuclear reactions is not influenced by the chemical form in which the analyte is present and as such does not suffer from the common matrix effects. If measurements are made at levels sufficiently above the bare limits of detection, precision and absolute accuracies of about $\pm 2-3\%$ of the value are readily achieved and with a little extra care; these can be improved further even to $\pm 0.5-1\%$.

1.3 NEUTRON ACTIVATION ANALYSIS (NAA) :

The most extensively used form of activation analysis is due to the thermal neutrons. This is because of the following reasons.

1. The high neutron fluxes of the order of 10^{12} to 10^{14} n cm⁻²s⁻¹ are readily available.
2. Uniform neutron flux intensity.
3. The reduction of errors due to uncertainties of the energy spectrum.
4. Activation cross-sections are generally higher by a factor of thousand as compared to charged particles or gamma photons.
5. The elimination of many radionuclides produced through endoergic reactions.

Neutron activation analysis is not only capable of high sensitivity for large number of elements but also allows accurate determination as a non-destructive method of analysis. This was clearly demonstrated by several authors, among them were Leliaert *et al.*⁶⁻⁸ who determined vanadium and tungsten in high alloy steels using an internal

standard technique. The radioactive isotopes whose half-lives ranging between hours and years can be determined with precision of the order of 10^{-12} g, the technique is well suited and extremely efficient for a large number of elements.

1.4 NEUTRON SOURCES :

A wide range of devices are used to produce the neutrons needed for activation analysis. Some are sophisticated and extremely expensive while others are rather simple and modest. A variety of commonly used neutron sources are discussed briefly below.

1.4.1 Neutron Reactors :

A nuclear reactor produces neutrons as a by-product of uranium fission processes occurring within the reactor core. Nuclear reactors emit neutrons that have a wide range of energies. The fission process itself results in the emission of fast neutrons, moderation of these fast neutrons produces thermal, epithermal and resonance neutrons at the available NAA irradiation positions.

The largest research reactors can produce thermal neutron flux densities upto $\sim 10^{15}$ n cm⁻²s⁻¹ and are most often located at national laboratories. Smaller reactors produce useful flux densities at the order of 10^{11} to 10^{13} n cm⁻²s⁻¹ and are most often found in University and industrial research facilities.

Nuclear reactors are equipped with irradiation channels into which sample to be activated are inserted, possibly by means of a pneumatic transfer system. These channels can pass through reactor core, thermal

column (which contains prevalently thermal neutrons) or reflector. Channels can pass in either horizontal or vertical direction.

1.4.2 Isotopic Neutron Sources :

These are quite simple in design and operation compared to the other sources of neutrons. They rely on spontaneous nuclear processes for neutron production. The isotopic sources are classified as α -emitter, photon and spontaneous fission sources.

1.4.2.1 α -emitter sources :

These sources are the oldest isotopic neutron sources. As energetic α particles are available from the direct decay of a number of convenient radionuclides, it is possible to fabricate a small self-contained neutron source by mixing an α emitting isotope with a suitable target material. Several target materials can lead to (α, n) reactions, the maximum neutron yield being obtained with Be target. The α -emitter sources produce neutrons of varying energies and flux ranges from $10^5 - 10^7 \text{ n cm}^{-2} \text{ s}^{-1}$. These are simplest, least expensive and require relatively little shielding.

1.4.2.2 Photon sources :

Some γ -ray emitting radioisotopes can also be used to produce neutrons when combined with an appropriate target material. The resulting photoneutron sources are based on supplying sufficient excitation energy to a target nucleus by absorption of a γ -ray photon to allow the emission of a free neutron.

1.4.2.3 Spontaneous fission neutron sources :

Many of the transuranic heavy nuclides have an appreciable spontaneous fission decay probability. Several fast neutrons are promptly emitted in each fission event. Hence a sample of such a radionuclide can be a simple and convenient isotopic neutron source. Other products of the fission process are the heavy fission products, prompt γ -rays, β and γ activity of fission products accumulated within the sample when used as a neutron source, the isotope is generally encapsulated in a sufficiently thick container so that only the fast neutron and γ -ray emerge from the source. The most common spontaneous fission neutron source in use is Cf-252. Characteristics of some of the neutron sources classified under above heads are listed in Tables 1.1 - 1.3⁹.

Table 1.1 : Characteristic data of some (α, n) neutron sources

Radio-nuclide	Half-life/y	Target material	E_n/Mev	Neutron flux $/n \text{ s}^{-1} \text{ Ci}^{-1}$	Gamma dose rate/r h ⁻¹
²¹⁰ Po	0.38	Be	4.5	2.5×10^6	0.1
		B	2.5	5.0×10^5	--
		F	1.2	1.5×10^5	--
²²⁷ Ac	22	Be	--	1.5×10^7	80
²³⁸ Th	1.9	Be	--	2.0×10^7	300
²²⁶ Ra	1620	Be	4	1.3×10^7	600
²³⁹ Pu	24360	Be	4	1.6×10^6	10
²⁴¹ Am	458	Be	4.5	2.5×10^6	10
		B	--	5.0×10^5	
		F	--	1.5×10^5	

Table 1.2 : Characteristic data of some (γ, n) neutron sources.

Radio-nuclide	Half-life	E_{γ} /Mev	Target	E_n /Mev	Approximate yield/ $10^4 n s^{-1}$
^{24}Na	14.8 h	2.76	Be	0.83	13
			D_2O	0.22	27
^{72}Ga	14.1 h	1.87:2.21	Be	0.78	5
		2.51	D_2O	0.13	6
^{88}Y	108 d	1.84:0.90	Be	0.158	10
			D_2O	0.31	0.3
^{124}Sb	60 d	1.7	Be	0.024	19
^{140}La	40 h	2.5	Be	0.62	0.3
			D_2O	0.151	0.8
^{226}Ra	1620 y	2.42	D_2O	0.12	0.1

Table 1.3 : Spontaneous fission neutron sources

Nuclide	Alpha decay half-life/y	Fission half-life/y	Fission/ $10^6 \alpha$	Neutrons/ fission
^{238}U	4.5×10^9	6.5×10^{15}	5.6×10^{-1}	--
^{236}Pu	2.85	3.5×10^9	8.1×10^{-4}	1.89 ± 0.2
^{238}Pu	86.4	4.9×10^{10}	2.3×10^{-3}	2.04 ± 0.13
^{240}Pu	6580	1.3×10^{11}	5.4×10^{-2}	2.09 ± 0.11
^{242}Pu	3.8×10^5	7.1×10^{10}	5.3	2.32 ± 0.16
^{244}Pu	7.6×10^7	2.5×10^{10}	3.0×10^{-3}	--
^{242}Cm	0.45	7.2×10^6	6.2×10^{-2}	2.33 ± 0.11
^{244}Cm	17.6	1.3×10^7	1.3	2.61 ± 0.16
^{252}Cf	2.6	85	3.3×10^4	3.51 ± 0.16

1.4.3 Neutron Generators :

Neutron sources based on nuclear reactions facilitated with the aid of charged particle accelerators are termed neutron generators. These instruments produce neutrons by bombarding suitable targets with accelerated charged particles. Neutron yields obtained in neutron generators are proportional to the number of charged particles striking the target. The principle of the neutron generator operation may be described as follows.

An ion source generates charged particles which gain a velocity necessary in a focussing and accelerating unit and strike a suitable target. The high voltage necessary for accelerating the ions is most typically obtained on the basis of the van de Graaff accelerator or the other electrostatic accelerators.

The neutron generator produces fast neutrons whose energy is commonly of 14 MeV. By their slowing down to thermal velocities, the neutron flux is reduced by about two orders. Thus, it is more advantageous to exploit fast neutrons in the activation.

1.5 SPECIAL PRACTICES IN NAA :

Most activation analysis practices are based on radiochemical or gamma ray spectroscopy determinations of the radionuclides produced by thermal neutron irradiation. Many special practices are used to broaden the general scope of radioactivation analysis, some were developed to compensate for limitations inherent in routine neutron activation analysis. Others were developed as specific uses of activation

analysis, some of them are discussed briefly below.

1.5.1 Pulsed Neutron Activation Analysis :

The pulsing feature of some nuclear reactors has been used to increase sensitivity for activation analysis, especially for elements that produce short lived radionuclides. Such reactors have self regulating power operation. A reactor that operates at steady power of 250 kW with a total neutron flux of about $2.8 \times 10^{16} \text{ n cm}^{-2} \text{ s}^{-1}$, peak fluxes of $10^{17} \text{ n cm}^{-2} \text{ s}^{-1}$ can be obtained.

The advantage of using such high intensity neutron pulses for radioactivation analysis have been reported by Yule and Guinn¹⁰. It can be shown that the production of a radionuclide with a half life of one second in a single reactor pulse would be 54 times greater than the production from saturation irradiation at maximum steady operation power.

The system in which the irradiation sample can be transferred and counted readily, the method of pulsed neutron activation is obviously of benefit for those elements giving product nuclides with a half life smaller than about one minute.

1.5.2 Cyclic Neutron Activation Analysis :

Cyclic activation analysis is based on the concept of enhancing the sensitivity of the activation method for the determination of elements with short-lived indicator radionuclides by use of repetitive short irradiation and counting periods and summing of the γ -ray spectra obtained. This will result in an improved counting statistics for the

short lived species due to summing and thereby increase the effective signal-to-noise ratio in the determination of short half-life indicator radionuclides with respect to interfering longer lived radionuclides.

With the use of short irradiation times, saturation activity levels can be reached for the short lived species in each irradiation. In contrast, longer lived species activity levels increase only slowly with successive irradiations with the use of appropriate decay intervals between irradiations. The total detector response for a short lived indicator radionuclide determined by cyclic NAA will increase linearly with experimental time. Many short cycles are most desirable for discrimination from long lived interferences and optimum results may be obtained by setting the counting time equal to the time of irradiation in each cycle. Both reactor thermal neutrons and 14-MeV neutrons are used with cyclic NAA.

1.6 SENSITIVITY OF NEUTRON ACTIVATION ANALYSIS :

The smallest amount which can be determined by the activation analysis is limited by the minimum activity which can be determined with sufficient precision on the equipment used in measuring the radioactive radiation intensity. By inserting this minimum activity into activation equation (equation 1.1), one can calculate the limit of amount detectable under given conditions. From equation 1.1, one can see which quantities are governing the sensitivity of the method for individual elements. Elements with lower atomic weight and high relative isotopic abundance of the activated isotope will show a high sensitivity. Further the shorter the half life, the higher the

sensitivity.

The sensitivity is directly proportional to the flux of activating particles. Thus, analysts attempt to use as high fluxes as possible. Thus, the neutron activation analysis remarkably gained importance only after developing nuclear reactors yielding the highest neutron fluxes. The sensitivity is also directly proportional to the cross section of the activation reaction used. The sensitivity can be raised by prolonging the activation time to approach the saturation activity. However, this prolongation is of limited significance in many cases. In addition to the factors mentioned above, properties of the radiation emitted by the radionuclide formed and efficiency of the counting equipment used also affect the sensitivity.

1.6.1 LIMITS OF ESTIMATIONS WITH NAA :

With the neutron flux of 10^{12} n cm⁻²s⁻¹ sensitivities of elements are in the range of 10^{-5} to 10^{-12} g. Thus, activation analysis is used for the estimation of impurities present in parts per million, parts per billion or even as low as 10^{-12} g. The following Table (Table 1.4) gives the limits of detection for some of the elements¹¹.

Table 1.4 : Limits of detection for some elements by NAA at
neutron flux of 10^{12} n cm⁻²s⁻¹.

Elements	Limit of detection/g
Eu, Dy	10^{-12}
Mn, Pd, In, Sm, Ho, Re, Ir, Au	10^{-11}
Na, Sc, Cu, Ga, As, Br, Kr, Y, Sb, Pr Tb, La, W, Tu, Yb, Ta, Ta, Th, U	10^{-10}
P, Ar, K, Rb, Co, Ru, Cd, Cs, Ba, Ce, Gd, Hf, Pt, Hg	10^{-9}
Cl, Si, Ni, Zn, Ge, Se, Mo, Ag, Sn, Te, Xe	10^{-8}
Ca, Sr, Fe, Zr, Bi	10^{-7}
S, Pd	10^{-6}
Mg, Pb	10^{-5}

1.7 ADVANTAGES OF NAA :

1. The technique permits very high sensitivities for many elements in the periodic table. This is because there are many adjustable experimental parameters that can be exploited to achieve maximum sensitivity for the desired element.
2. As the quantification is mainly based on nuclear properties of the analyte the technique is highly specific, at the same time is capable of simultaneous multielement determination. Irradiation of a sample will induce activity in many elements. Use of multichannel analyzer to record all the γ -rays emitted by the sample permits the analyst to obtain information of many different elements.
3. The information obtained by nuclear analysis is generally independent of matrix or chemical form as the nuclear reactions are the basis of activation methods.
4. It is generally a non-destructive technique. The sample may not be visually or measurably chemically altered.
5. Many times capable of rapid analysis, particularly which based on use of short-lived indicator radionuclides.
6. A unique and basic advantage of NAA that has no parallel in the domain of analytical chemistry is its freedom from contamination. As the sample is generally not subjected to chemical treatment prior to irradiation, element contamination in post irradiation radiochemical treatment does not affect the property that is measured *viz.* induced radioactivity. The technique is also free from process blank.

1.8 LIMITATIONS OF NEUTRON ACTIVATION ANALYSIS :

As compared to several advantages, NAA has relatively few limitations. Some of the limitations are discussed below.

1.8.1 Elements for Which Neutron Activation is not Suitable :

Almost all elements become radioactive to some extent after irradiation, but some of the radionuclides formed are too short-lived to allow for removal of the sample from the irradiation facility followed by the necessary chemical separation and counting. For example, He, Li, B, O and Ne with half lives of seconds or less can not be analysed by normal activation technique.

1.8.2 Physical Limitations:

There are certain physical limitations in activation analysis, heat is being produced during the bombardment in a nuclear reactor, therefore, the sample should be such that it can withstand the higher temperature to which it is exposed. Further the sample must be enclosed in such a manner that there is no danger of contaminating the reactor, liquid must be sealed in silica containers.

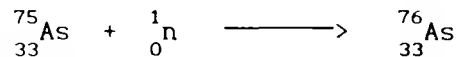
1.8.3 Chemical Limitations :

A sample put into a nuclear reactor will be bombarded both by gamma rays and neutrons. Structural damage and decomposition by these processes must be considered. Silica, for example, after a few hours of irradiation becomes almost black, so that one must take into account

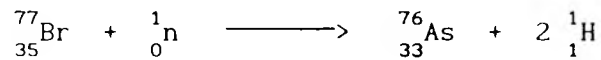
this effect while performing the activation analysis.

1.8.4 Nuclear Limitations :

One of the major nuclear limitations is that the radioactive nuclide which is being used as a measure of the mass of a given element in the activation analysis may be formed from different elements present in the sample to be estimated. For example, the determination of arsenic by reactor irradiation depends upon the formation of ^{76}As from the monoisotopic ^{75}As by the nuclear reaction :



However, ^{76}As can be formed by several other reactions starting with elements present in the sample to be analysed other than arsenic as :



1.9 RADIATION DETECTORS :

Radioactive nuclides are determined qualitatively and quantitatively by the interactions of their emitted radiations with materials used as radiation detectors. A radioactivity measurement system generally consists of two parts; the detector in which the radiations interact and the associated measuring device that gives the information from the detector in a suitable form.

These radiation detectors are classified as gas filled detectors, scintillation detectors and semiconductor detectors.

1.9.1 Gas Filled Detectors :

These are the old type of radiation detectors and are still widely used. All gas filled detectors consist of a volume of gas surrounded by a housing that may either be sealed or designed to permit a continuous flow of the counting gas. A voltage is applied across electrodes within the gas volume, creating an electric field. As radiation passes through the gas filled chamber, it ionizes the gas to form ion pairs consisting of an electron and positive ion. These are then attracted to the respective electrodes and this generates the electrical signal that indicates the passage of radiation. The electric signal that is measured may either be a current or voltage pulse or the total accumulated charge. The choice will depend on the way the instrument is configured. There are three types of gas filled detectors : ionization chamber, proportional counter and Geiger Muller counter. These differ primarily in the strength of electric field applied across the electrodes and hence lead to differences in the ionization processes taking place in the chamber.

1.9.2 Scintillation Detectors :

These detectors also have a long history in the study of radioactivity. The basis for scintillation detector is radiation-induced emission of light by the detecting material.

There are several substances, certain organic and inorganic materials, which emit light flashes or scintillations when charged particles, X-rays or gamma rays pass through them. These substances are called scintillators.

In a scintillation detector light flashes due to the interaction of radiation, are allowed to fall on the photocathode of a photomultiplier and a pulse is extracted out to signal the passage of nuclear radiation. The height of the output pulse is directly proportional to the energy dissipated by the ionizing radiation in the scintillator. Thus, a scintillation detector can be used not only for counting but for energy analysis also. Because of its versatility, there has been considerable development of scintillation detectors. The properties of some commonly used scintillators are given in Table 1.5.

Table 1.5 : Properties of some scintillators

Material	Density/ g cm ⁻³	Wavelength of maximum emission/Å	Relative beta rays pulse height	Decay time/s
Anthracene	1.25	4400	100	2.7×10 ⁻⁸
Trans-stibene crystal	1.15	4100	060	3-7×10 ⁻⁹
NaI (Tl)	3.67	4100	210	2.5×10 ⁻⁷
Plastics :				
(a) NE 102	1.03	4250	065	2.2×10 ⁻⁹
(b) NE 111	1.03	3700	055	1.7×10 ⁻⁹

1.9.3 Solid State Semiconductor Detectors :

Gamma ray spectrometry was advanced greatly by the development of solid-state semiconductor detectors in the 1960s and 1970s. These detectors offer a combination of good efficiency and high resolution for γ -rays that is not matched by the gas filled or scintillation detector.

A band structure exists in the semiconductor crystal similar to solid scintillator. However, the band gap is much smaller for semiconductors than NaI(Tl) detector. The passage of radiation injects enough energy into the system to raise an electron from the valence band to the conduction band, thus creating an electron-hole pair. The hole and the electron both migrate through the crystal in response to an electric field, and produce an electrical signal. The crystal used must have certain desirable properties :

1. The average energy required to produce a hole-electron pair should be as small as possible. This consideration would favour materials with small energy gaps but the choice is not so simple.
2. The crystal material should not contain large number of free carriers at room temperature.
3. The material should have a high atomic number so that it can stop nuclear radiation more efficiently.
4. The material should not contain many trapping centers because the holes and electrons should be free to move all the way to the collecting electrodes. The distance covered by the carrier is determined by its mobility life time product. The important desirable property of the material is that it should have a good

mobility life time product for the holes as well as for electrons so that they can be efficiently collected by the electrodes.

Only two materials silicon and germanium have these desired properties. They are semiconductors and are readily available in a state of high purity and crystalline perfection. Their properties are well known and their technology is well developed. Although silicon and germanium are not the most ideal materials, they have been used in the construction of semiconductor detectors by clearly doping them with proper type of impurity. Some commonly used semiconductor detectors are : silicon p-n junction, silicon surface barrier, high purity silicon, high purity germanium and lithium drifted germanium detectors.

Some characteristics of germanium semiconductor are given in Table 1.6

Table 1.6 : General properties of the germanium semiconductor

Property	Value
Atomic number	32
Atomic weight	72.59
Density/ g cm ⁻³	5.32
Dielectric constant	16.0
Energy gap at 300 K/eV	0.66
Energy required per (electron + hole) pair/eV	2.8
Electron drift mobility at 300 K/(cm ² V ⁻¹ sec ⁻¹)	3800
Electron drift mobility at 77 K/(cm ² V ⁻¹ sec ⁻¹)	36000
Hole drift mobility at 77 K/(cm ² V ⁻¹ sec ⁻¹)	42000
Intrinsic resistivity at 300 K/(Ohm-cm)	47
Intrinsic carrier concentration at 300 K/cm ³	2.35 x 10 ¹³

1.10 APPLICATIONS OF NEUTRON ACTIVATION ANALYSIS :

The application of the phenomenon of artificial radioactivity to analytical chemistry was first visualised and demonstrated by Hevesy and Levi¹ using neutrons. However, the first systematic presentation of this technique as a method was made by Clark and Overman³ in 1947. Over

the last five decades this technique has matured into an analytical competence providing not only rapid quantitative simultaneous multielement analysis down to ppb levels but also the crucial validation support to other techniques. The applications of NAA have been in chemical, biological, material, forensic, environmental and life sciences and in archaeology; to mention a few.

An optimum method for determination of rare earth elements is the neutron activation analysis¹². A precise instrumentation for NAA was developed for analysing Mn-Mg-Zn ferrites on a wide range, of macrocomponent concentrations¹³. Various elements in high purity aluminium by activation with a flux of $2 \times 10^{13} \text{ n cm}^{-2} \text{ s}^{-1}$, were detected by Azovsteva *et al.*¹⁴

Multielement analysis at trace levels on small amounts of samples has enabled the monitoring of pollutants in all spheres of the environment. The combination of multielement data and pattern recognition analysis have helped in establishing human head hair as an effective first level monitor^{15,16}, in a multilevel scheme of monitoring the exposure to inorganic pollutants and assessing the body burden.

Turel and coworkers¹⁷⁻¹⁹ had reported toxicity levels of several elements in aquatic environment of Bombay and in few other systems by substoichiometric NAA. Similarly Salagean *et al.*²⁰ reported 22 elements in geothermal water in Algeria, Nae²¹ reported 19 elements in water samples, dominant elements being Ca, Cl, Na, Mg and K.

The analysis of tissues and body fluids for specific elements and the monitoring of the intake of elements, for example through diet, are

examples of applications in in-vitro investigations that have helped to understand the role / effect of trace elements in human health. The more spectacular contribution of the activation analysis has been in in-vivo studies²² ranging from whole body measurements for elements like Ca, P, to specific measurements for elements like renal cadmium.

Concentrations of various elements viz. Na^{23,24}, Mg²⁵, Al²⁵⁻²⁷, K^{24,28}, Sc^{29,30}, Ni³¹, Cu³²⁻³⁷, Ga³⁸⁻⁴⁰, Rb⁴¹ and Zr⁴² in minerals, ores, rocks and sediments were determined by different workers using the method of NAA. The method also has been used for elemental analysis of agricultural soils for testing fertility of the soils by Benes *et al.*⁴³, Wang Yuqi,⁴⁴ Nilubol and Kaffkaffi⁴⁵ Diaz *et al.*⁴⁶, and Rajurkar *et al.*^{47,48}. Mineral nutrients of several food grains viz. wheat⁴⁹, rice⁵⁰⁻⁵², bengal gram⁴⁹ as well as that of oil seeds⁵³ also have been reported using this technique.

Many industries are making the use of activation analysis for quality control of finished products. Several elements viz. Mn, W, Mo, V, Cr, Ti etc. in steel samples⁵⁴⁻⁶⁵ of different series and in industrial alloys^{66,67} have been reported by different workers.

Non-destructive aspect of NAA has been used by several workers for the analysis of pottery⁶⁸, study of ancient ceramics⁶⁹, archaeological samples⁷⁰ and ancient coins.⁷¹

The method of NAA was applied for the determination of ultra trace amount of As in high purity trichloro silane medicinal samples.⁷² Similarly trace element impurities in aspirin tablets of Egyptian and American brands were reported by Iskander *et al.*⁷³ The method also has

been used for the analysis of several medicinal plants^{74,75} and herbal medicines⁷⁶.

1.11 A BRIEF REVIEW OF THE WORK DONE ON ANALYSIS OF ANCIENT COINS :

A survey of the literature reveals that a considerable amount of work has been done on Roman,⁷⁷⁻⁸⁰ Greek,⁸¹⁻⁸³ Korean^{83,84,85} and Chinese^{85,86} coins by using different destructive as well as non-destructive methods, Greek and Korean coins being analysed by chemical⁸² and polarographic analyses⁸⁴ and by non-destructive NAA^{83,85} and X-ray fluorescence techniques.⁸¹ Roman coins, on the other hand, have been analysed only by non-destructive techniques viz. XRF,⁷⁷ NAA⁷⁹ and laser microspectral analysis.⁷⁸

Studies on Roman coins⁸⁷ by different workers showed the presence of minor and trace elements such as gold, zinc, nickel, tin, bismuth and lead in the middle of 3rd century where as silver, gold, tin, antimony, cobalt, indium and copper were found to be present in the period of 250 A.D. to 500 A.D in these coins.⁷⁹ Bajnoczi and Major⁸⁸ studied the coins of lead-tin-copper and concluded that lead was in frequent inhomogeneity than tin. Further they observed that inhomogeneity was less in the side as compared to the face of the coins.

A detailed examination on bronze coins by Earle⁸⁹ showed that coins minted in the period 400 B.C. always contain high percentage of tin and low of lead while late coins have low tin (4 to 8%) and high lead (upto 32%). The high tin, low lead coins are known to be much more

resistant to corrosion. High percentage of lead coupled with moderate percentage of tin as well as presence of gold, silver and nickel is characteristic of antiquity especially of ancient Greek bronze coinage.⁹⁰ Ancient Greek silver coins⁸² were found to contain minor elements such as copper, gold, bismuth, lead and trace elements sodium, manganese, cobalt, nickel, arsenic, tin, antimony and iridium while trace elements were iron, cobalt, nickel, gold and silver in ancient Chinese coins⁹¹ which were containing copper, lead and tin in major proportions. A systematic study of ancient Korean coins by Chaul *et al.*⁸⁴ indicated that copper, lead and tin in earlier coins were present in approximate ratio 90 : 4 : 3 while those in later days it has been changed to 7 : 2 : 0. 17th century Korean brass coins were found to contain copper, zinc and lead as major constituents in approximate ratio of 7 : 1 : 1 while Japanese⁹² and Chinese⁹² coins showed the ratio of Cu : Zn as 7 : 2 and 1 : 1 respectively.

Though there are several reports on above mentioned coins only scanty reports are available for Italian⁹³, German⁹⁴, British⁹⁵, and Indian coins^{96,97}. Quantitative chemical analyses of some ancient Indian coins were carried out by Rao and Gayatri⁹⁷ using atomic absorption spectrometric method. They found that coins of Bahamani dynasty (1347 A.D. - 1526 A.D.) contain copper as a major component while addition of tin was found in the beginning of the dynasty and discontinued later, after 1435 A.D. concentration of other trace metals changes from year to year and have a large variation throughout the dynasty.

Analysis of some counterfeit coins from different countries also have been reported by some workers.^{94,95} Klockenkaemper *et al*⁹⁴ revealed that the chemical composition of the genuine gold coins is sufficiently uniform and the instrumental analysis sufficiently accurate to set up definite criteria for genuiness. A gold content of 90 % is a first criterion and a silver content of 0.4 % is further criterion. Counterfeits frequently show somewhat more gold and often less or more silver. Several counterfeits also have an additional gold enrichment at the surface.

In brief, overall review of coin analysis reveals that copper is the major component in all the ancient coins. Gold, tin, arsenic, antimony, nickel, manganese, lead and iron are present at tracer level while some exceptional elements like iridium, cobalt, calcium, Silicon, magnesium, ruthnium and iridium are found in some of the coins. Some of the ancient coins also contain silver as a major component along with the copper.

1.12 SCOPE OF THE PRESENT WORK:

Coins have been the principal source of our information about the various tribal and city republics and monarchical states that flourished in India during the pre-Christian centuries and after. In the history of Indian numismatics, study so far shows that coins are categorised mainly as copper, silver and gold alloys but detail metallurgical composition for most of the coins is not known. Hence it is thought of interest to study the elemental composition of ancient

Indian coins from different eras. As the conservation of ancient coins, which are of world wide interest, is important from numismatic point of view a non-destructive technique is demanded for such analysis. Instrumental neutron activation analysis provides a non-destructive, specific, multielemental and highly sensitive technique with good precision. The present work deals with the determination of elemental composition of ancient Indian coins from different eras by instrumental neutron activation analysis with respect to various parameters.