UNIVERSITY OF AGRICULTURE, ABEOKUTA
DEPARTMENT OF ENVIRONMENTAL MANAGEMENT & TOXICOLOGY

EMT 514: MISCELLANEOUS TECHNIQUES IN ENVIRONMENTAL ANALYSIS

COURSE OUTLINE
Neutron Activation Analysis
Radiochemical Methods
Enzymatic Methods

Recommended Textbooks for Further Reading

1. Principles of Instrumental Analysis by D. A. Skoog, F. J. Holler and T. A. Nieman. Brooks/Cole Thomson Learning, 5th Edition

2. Instrumental Analysis by H. H. Buaer, G. D. Christian and James E. O'Reilly

3. Instrumental Methods of Analysis by H. H. Willard, L. L. Merritt, Jr., J. A. Dean and F. A. Settle, Jr. Wadsworth Publishing Company.

4. Analytical Chemistry by F. W. Fifield and D. Kealey. Blackie.

5. Analytical Chemistry by Gary D. Christian. John Wiley & Sons.

6. Instrumental Analysis of Pollutants, edited by C. N. Hewitt. Elsevier Applied Science.

7. Quantitative Chemical Analysis by Daniel C. Harris. W. H. Freeman and Company. 5th Edition

8. Analytical Chemistry – An Introduction by D. A. Skoog, D. M. West, F. J. Holler and S. R. Crouch. Brooks/Cole Thomson Learning, 7th Edition

NUCLEAR STABILITY

Elements with atomic members greater than 83 (Bismuth) are radioactive and possess no known stable isotopes. On the other hand, all the lighter elements with the exception of Technetium (Tc) = 43 and Promethium (Pr) (Z = 61) have one or more stable non radioactive isotope. (I.e. lighter element is stable and non-radioactive). In addition, radioactive isotopes undergo nuclei transformation that leads ultimately to stable nuclei.

Sometimes, this is accomplished by a simple one-step process while in other cases a series of nuclear reactions occur before a stable isotope is reached. Since radioactivity is n nuclear phenomenon, it must be related to the number of neutrons or to the neutron/proton ratio (n/p concepts)

Indeed, if a n/p plot is made of stable nuclide the points tend to fall in a narrow band of stability which serves to demarcate the region of nuclei stability as shown in the diagram below.

For light nuclides, the n/p ratio is about unity (i.e. low atomic numbers, stable nuclei possess approximately equal numbers of protons and neutrons). Thus, the following isotopes are the most abundant for their respective elements, and those elements are: $^{12}_{6}C$ $^{16}_{8}O$ and $^{20}_{10}Ne$. Of course, there are other isotopes that deviate from this ratio e.g. ^{19}F. But they generally do so by having more neutrons than protons except in $^{1}_{1}H$ and $^{3}_{2}He$ which are special cases.

At about Z = 20, the number of neutrons always exceed the no of protons and the n/p ratio gradually increases to about 1.5 at the upper end of the band of stability. Apparently as the number of protons in the nucleus increases, there must be more and more neutrons to help overcome the strong repulsive forces between the protons. Nuclides that lie outside the band of stability are unstable and decay so as to bring n/p ratio back to within their range.

On this basis we can understand why certain nuclides undergo the type of radioactive decay that they do e.g. nucleus that has n/p ratio above the band of stability must either lose neutrons or

gain protons to achieve stability. Thus, we can understand why elements such as $^{14}_{6}C$ which lies above the band of stability must decay by β emission, because this process converts a neutron into a proton. This process is

$$^{1}_{0}n \longrightarrow \quad ^{1}_{1}P + ^{0}_{-1}\beta$$

e.g. $\quad ^{16}_{6}C \longrightarrow \quad ^{14}_{7}N + ^{0}_{-1}\beta$

Another way that an element located above the band can achieve a stable n/p ratio is by emitting a neutron although this particular mode of decay is rare e.g. decay of

$$^{137}_{53}I \longrightarrow \quad ^{136}_{53}I + ^{1}_{0}n$$
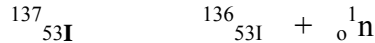
Therefore element located below the band of stability must increase their n/p ratio to achieve stability. This is accomplished generally in either of two ways.

1. This involves the emission of a positron, a particle having the same mass as the electron but with a unit positive charge. The ejection of a positron by an unstable nucleus converts a proton into a neutron.

$$^{1}_{1}P \longrightarrow \quad ^{1}_{0}n + ^{0}_{+1}\beta$$

$$^{11}_{6}C \longrightarrow \quad ^{11}_{5}B + ^{0}_{+1}\beta$$
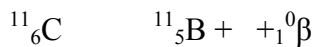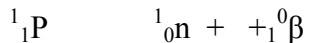
2. There is another mode of decay that results in an increase n/p ratio. It is called electron capture. In this case the unstable nucleus captures an electron usually from its own is orbit. The addition of this electron to the nucleus transforms proton to a neutron.

$$^{1}_{1}P + ^{0}_{-1}e \longrightarrow \quad ^{1}_{0}n$$
$$^{7}_{4}Be + ^{0}_{-1}e \longrightarrow \quad ^{7}_{3}Li$$
$$^{40}_{19}K + ^{0}_{-1}e \longrightarrow \quad ^{40}_{18}Ar.$$

where k is innermost shell.

RADIOCHEMICAL METHOD
Radiochemical methods of analysis can be grouped according to whether one measures radioactivity present in sample or employ some means of introducing radioactivity into an otherwise non-radioactive samples in order to analyse for some components. An example of the first type is the determination of radioactive ^{40}K in rock samples. The second type is exemplified by using labeled $KI*O_3$ (I* denoting a radioisotope of iodine) to determine the concentration of SO_2 in air by the radio release method.

NEUTRON ACTIVATION ANALYSIS
A non-radioactive element sometimes becomes radioactive after bombardment with particles or γ radiation. This basis of activation analysis is the measurement of the radioactivity induced in a sample as a result of irradiation is particularly advantageous because the back of charge and the mass of neutron allows efficient penetration and energetic transfer to the target.

The analytical technique in which radioactive emissions are monitored from a sample that has been bombarded with neutron is called **NEUTRON ACTIVATION ANALYSIS**. The single most important advantage of activation method is high sensitivity which exceeds that of other methods for many elements by factor of 100 or more. Concentration determinations in the ppb range are common.

In neutron activation analysis, the standards and samples are simultaneously bombarded with neutron. Normally a single standard is used for quantitative analysis. The peak areas of the sample and the standard are used to calculate the number of nuclei of a particular type in the sample.

A direct proportion can be assumed between the peak area and the number of nuclei when equal irradiation times and neutron flexes are used; that is, when the samples and the standards are simultaneously bombarded.

CLASSIFICATION OF ACTIVATION METHODS.
Activation methods can be classified in several ways; one is based on the type of irradiation employed for excitation of samples. Slow neutrons, fast neutrons, γ-rays and various charged particles have been used. Most activation methods are based upon thermal neutrons, although - γ excitation appears to be a new method of growing interest.

A second variable which is used to characterize activation methods is the type of emission measured in the final step of the analysis. Here both β and γ -radiations have been monitored, the former is often more sensitive but, on the other hand frequently suffers from being less selective since the radiation is continuous rather than discrete.

Finally, activation method can be classified as being destructive or non- destructive of the sample. In destructive methods, the irradiated sample is dissolved and the element of interest is counted after it has been isolated by suitable chemical or physical means; possible interferences from other species made radioactive by the irradiation are thus eliminated. This method is called **RADIO CHEMICAL NEUTRON ACTIVATION ANALYSIS (RNAA).**

Prior to the development of high resolution Ge(Li) detectors the detector that were used for neutron activation analysis generally were incapable of resolving the peak in the γ -ray spectra obtained. Consequently it was necessary to use another method to distinguish between radio nuclide in the sample. Therefore, when this sample is chemically manipulated after bombardment but before counting the technique is called RNAA.

Any of several separatory methods has been used to remove potentially interfering radio nuclide prior to measuring the total particles or γ -ray emission. A typical procedure consist of
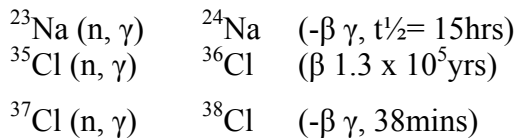
dissolving sufficient bombarded sample to contain about 5µg of the assayed element and adding a relatively large known amount (often 10 or 15mg) of a carrier. The carrier is a pure non-bombarded portion of the analyte. It is added to make the total concentration of the analyzed element in the sample solution sufficiently large to permit a simple separation.

After addition of the carrier, the analyte is separated from radionuclides that could interfere with the assay. The separation can be accomplished by performing a precipitation, a chromatographic separation or ion-exchange, an electro-chemical separation, an extraction or by using another procedure. After the separation is completed, the radio nuclide of interest is counted and the results are used to calculate the amount of the radio-nuclide in the original sample
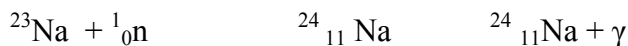
In the non-destructive procedure, the activated sample is counted without preparatory treatment. Hence the ability of γ -ray spectrometer to discriminate between radiations of different energies is called upon to provide the required selectivity. The non-destructive method is called INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS (INAA). It is a simple and direct method which offers the advantage of great speed (i.e. very fast). On the other hand, the resolution of a γ -ray spectrometer may sometimes be insufficient to eliminate all the interferences.

Potentially radiochemical methods enable us to detect exceedingly low conc. of material e.g. 10^{-12}g(pg). As stated earlier activation analysis involves creating radioactivity in the sample by irradiation (usually with neutrons) and comparing the level of induced activity with that of a standard. Thus e.g. to irradiate NaCl, the isotopes present are
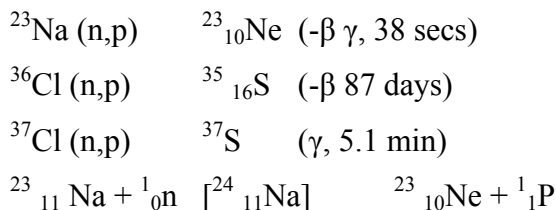
Irradiation of NaCl by neutrons (n, γ)

^{23}Na (n, γ)　　^{24}Na　(-β γ, t½= 15hrs)
^{35}Cl (n, γ)　　^{36}Cl　(β 1.3 x 10^5yrs)

^{37}Cl (n, γ)　　^{38}Cl　(-β γ, 38mins)

Equation of reaction

^{23}Na $+ {}^1_0$n　　　　$^{24}_{11}$ Na　　　$^{24}_{11}$Na $+ \gamma$
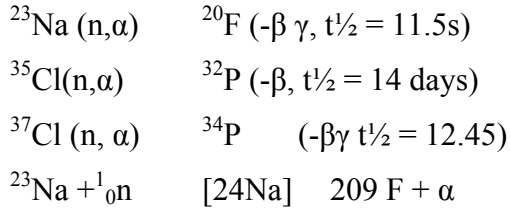
There is no simple way of ensuring the product except to control the experiment.

Supposing we irradiate with neutron and we get the proton i.e. an n/p reaction. (n, p)

^{23}Na (n,p)　　$^{23}_{10}$Ne (-β γ, 38 secs)

^{36}Cl (n,p)　　$^{35}_{16}$S　(-β 87 days)

^{37}Cl (n,p)　　^{37}S　　(γ, 5.1 min)

$^{23}_{11}$ Na $+ {}^1_0$n　$[^{24}_{11}$Na]　　$^{23}_{10}$Ne $+ {}^1_1$P

For irradiation with n to get α i.e. (n,α), we have

^{23}Na (n,α) ^{20}F (-β γ, t½ = 11.5s)

^{35}Cl(n,α) ^{32}P (-β, t½ = 14 days)

^{37}Cl (n, α) ^{34}P   (-βγ t½ = 12.45)

^{23}Na +$^{1}_{0}$n   [24Na]   209 F + α

(n, p) and (n, α) reactions can be suppressed by irradiation with thermal neutrons i.e. neutrons of low energy (0.01 eV). Cooling i.e. allowing to decay for 5 to 6 hours eliminates five nuclei by decay

RADIOACTIVITY SCHEME

In NAA the sample is normally bombarded with neutrons for a period that equals at least one and sometimes, several half lives of radionuclide. The bombarded samples are allowed to decay for a fixed period before measurement are made in order to allow emission from interference with short half – life's to decrease to a negligible value. Either β particle or γ -radiation is monitored. β particle emission is energetically continuous whereas γ -ray emission is discrete.

Consequently, γ –ray emissions are often preferentially measured. In most cases, relatively slow thermal neutrons are used for the bombardment. Thermal neutrons are those that have energies less than about 0.2eV. At room temperature thermal neutrons have energy of about 0.04eV. Neutrons that are emitted in reactors have energy in MeV region. They are slowed by collisions with a moderator to thermal velocities.

It is estimated that about twenty collisions are required to properly reduce the energy. The slowing process required less than a minute.
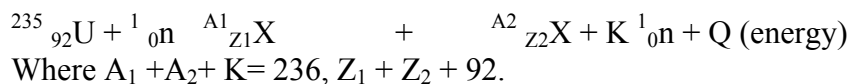
The most important type of reaction that occurs during neutron bombardment is capture reaction during which the neutron bombards and it is captured by the analyte nuclei The resulting excited radionuclide has a mass number that is one unit larger than that of the original nuclide. The energy impacted to the product nuclide by the neutron equals the sum of the kinetic energy of o the neutron and the binding energy of the neutron of the produced nucleus. The impacted energy excites the nucleus to a higher energetic level. Relaxation occurs by the emission of β particles α – particles, neutrons, protons or γ -radiation.

If sufficient energy is available, more than one emission can occur.

SOURCES OF NEUTRON
Three sources of neutron which are commonly used in NAA. Include
(1) Nuclear reactors: A nuclear reactor generated neutron by the process of fission. Although the actual working of nuclear reactors is quite complicated, the principles for the present purpose can be understood by considering a $^{235}_{92}$ U – fuelled nuclear reactor. Upon capturing a neutron, a $^{235}_{92}$U nucleus breaks up into several lighter nuclei and produces more neutrons

$$^{235}_{92}U + ^{1}_{0}n \quad ^{A1}_{Z1}X \quad\quad + \quad\quad ^{A2}_{Z2}X + K\,^{1}_{0}n + Q \text{ (energy)}$$
Where $A_1 + A_2 + K = 236$, $Z_1 + Z_2 + 92$.

The average value of K is 2.5. The fact that each nuclei of $^{235}_{92}U$ produces more neutrons than is required for fission is responsible for the copious production of neutrons by nuclear reactors.

The fission neutrons produced in nuclear reactors have a continuous kinetic energy spectrum, mostly in the range of 1 – 10 MeV. Since (n, γ) reactions have more wide spread analytical use, fission neutrons must be slowed to thermal energies by passing them thorough H_2O, D_2O, or graphite, which acts as moderator. Depending on the type of nuclear reactor and the irradiation position in the reactor, the neutron spectrum may vary widely.

2. **ISOTOPIC SOURCES OF NEUTRON:** Nuclear reactors are the only sources of copious quantity of neutrons. A typical research reactor might have a useful flux density of $10^{-11} – 10^{-13}$ n/ (cm^2-sec). However, moderate flux densities of neutrons can be obtained from isotopic sources of neutrons at relatively low cost and with minimal space and maintenance requirement.

ISOTOPIC NEUTRON SOURCES ARE OF TWO GENERAL TYPES
The first is man-made radio nuclide that undergoes spontaneous fission and produces neutrons. $^{252}_{98}Cf$ is a radio nuclide commonly used for this purpose; a 1mg $^{252}_{98}Cf$ source will produce 2.34×10^9n/sec. The neutron spectrum of this source is similar to that of reactor neutrons, and, therefore, for practical applications, the source is placed in a moderator or thermalizer. The useful thermal neutron flux density available in a typical facility is about 3×10^7n/ (cm^2-sec).

The second type of isotopic neutron source consists of a radionuclide emitting intense α or γ radiation, mixed with the element Be; one of the following reactions take place

$$^9_4Be + {^4_2He} \qquad {^{12}_6C} + {^1_0n}$$
$$^9_4Be + \gamma \qquad 2\,{^4_2He} + {^1_0n}$$
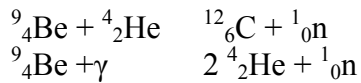
These neutrons also have a fast, continuous spectra distribution and are usually slowed (moderated) by placing the source in a hydrogen rich medium, such as water or paraffin.

3.   Accelerators; The accelerator most commonly used for the production of neutrons is the cock-croft-walton neutron generator. The Deuterium molecules are ionized in the ion source bottle of the generator, accelerated in an electrostatic field of $100 - 200kv$. and focused on a target containing tritium ^3_1H

The following nuclear reactions take place

$$^3_1H + {^2_1H} \qquad {^4_2He} + {^1_0n} + Q$$
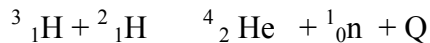
Where q is approximately 14 meV. The neutrons produced are nearly mono energetic at 14 meV. These neutrons are capable of inducing many thresh-hold reactions. Fore example, consider the reaction

$$^{16}_8O + {^1_0n} \qquad {^{16}_7N} + {^1_1H} + Q.$$
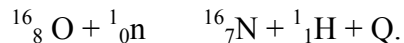
This method is widely used for the determination of oxygen, an element that is difficult to determine by other analytical techniques. Bench top sized sealed tube neutron generators are commonly employed.

LEVEL OF INDUCED ACTIVITY.

During bombardment with fast neutrons, the probability that a nuclear reaction will occur is nearly proportional to the cross sectional area of the target nucleus. Consequently, the reaction probability during nuclear bombardment can be expressed as a cross section (σ), which has area unit (generally cm^2). The cross section is associated with a single nucleus or atom. Even though the reaction probability is not directly proportional to the cross sectional area during bombardment with thermal neutrons or charged particles, the practice of expressing reaction probabilities as cross section persists.

A cross section that is $10^{-24}cm^2$ is considered large and consequently is termed a barn. The net rate (r) at which a target reacts to produce radio active atoms while being bombarded on all sides (e.g. in a reactor) with neutrons is given by

- $r = {}^{dN^*}/_{dt} \qquad = N\Phi\sigma - \lambda N^*$

- Where N is the no of nuclides in the sample; N* is the number of radionuclide formed by the reaction during time t, Φ is the neutron flux (particles per cm^2-sec); σ is the cross section (in cm^2); and λ is the nuclear decay constant (sec^{-1}).

The number of target nuclide can be calculated from the atomic wt of the target and the Avogadro's number. The first term on the far right of the equation (1) above $\Phi N\sigma$ is the rate at which the radionuclide are formed by the bombardment process, and the negative term is the rate ($-\lambda N$) at which the produced radionuclide decay.

Substitution of $Ne^{-\lambda t} = N^*$ in the above equation (1) followed by integration over the time interval from O – t during which the irradiation takes place result in $N^* = \Phi\sigma N(1-e^{-\lambda t})/\lambda$
Eq (2) can be used to calculate the no of radionuclide present at the end of the irradiation. Substitution of $0.693/t\frac{1}{2}$ for λ in equation (2) followed by the substitution of the resulting value of N* will yield an equation below;

$N^* = \Phi\sigma N (1-e^{-0.693t/t\frac{1}{2}})/\lambda$…………………………….(3)

Activity (A) $= \lambda N^* \ \Phi\sigma N (1-e^{-0.693t/t1/2})$……………(4)

The activity A in equation (4) is that of the radionuclide produced during the bombardment at the moment when the bombardment is stopped. Eq (4) assumes that the sample is sufficiently thin to allow attenuation of the neutron flux to be ignored. From eq (4) it is apparent that the activity increase as the bombardment time increases. Typical bombardment times range from 1 – 6 half-life's of the produced radionuclide. Bombardment times beyond 6 half-life do not significantly increase the activity because the relationship in equation (4) is exponential. Although neutron bombardment is most popular, bombardment with other particles, such as protons, also can be used.

QUANTITATIVE ANALYSIS.
In quantitative determination, the comparative method is used. Both samples and standards each sealed in polyethylene or quartz container are irradiated in the same physical location and therefore under the same flux condition. The relative activities are directly proportional to the respective concentration of parent nuclide.

Aunknown $=$ Nunknown
Astandard   Nstandard.
Consider the irradiation of the sample (containing nuclide x) and a standard (also containing x). If neutron flux and irradiation times are fixed for both of them, then the equation

D1 $=$ N1

D2   N2   is applied. That is

A sample   =   Mass of X in sample

A standard   mass of X in standard

The irradiation assembly must provide the same neutron flux for both sample and standard, or appropriate correction factor must be determined and used. The optimum irradiation time is a very important factor in activation analysis. The decision is based on the specific nature of the sample and the type of information desired. Generally, 2 factors are considered. First, longer irradiation times increase the activity produced. However as the equation (3) above shows that the factor $(1-e^{-\lambda t/t^{1/2}})$ approaches unity as the irradiation time becomes large with respective to the t1/2 of the product nuclide. Therefore irradiation times in excess of 3-5 half-life's of the product, results in little additional activity.

Secondly, the longer the irradiation time, the greater will be the induced activity due to the long lived radionuclide that may interfere with the specific determination.

Scheme for RNAA

The diagram above shows a complete NAA facility. As in any other analytical method, each step may introduce both random and determinate error, thereby affecting the overall precision and accuracy of the result. Problems associated with sampling are the same as in other method of analysis. Once the sample is obtained, it is packaged in appropriate container. An important point to keep in mind is that the sample and the standard should be as similar as possible in matrix composition e.g. when analyzing rocks, the sample is generally pulverized to a fine powder and the standard are also preferably made from finely powdered standard rocks. An alternate standard could be prepared by evaporating an aliquot of a standard solution of the element on a matrix of high purity prepared in a similar fashion as the sample. The size of the packaged samples should be as closed to that of the s standard as possible, so that self absorption of neutron flux does not introduce errors. When analyzing heterogeneous material complete mixing is very important. When irradiating organic materials decomposition of the sample may occur. This is essentially serious high fluxes of neutrons are employed since considerable heat may be generated inside the sample. Similar problem occurs with the irradiation of aqueous samples where the build up of pressure inside the container must be allowed for. In multi-element analysis of complex matrixes, detector resolution becomes critical and Ge(Li) detector must be used. NAAs have the important advantages of high sensitivity for many element and its

inherent freedom from problems of reagent and laboratory contamination; It is often the bench mark technique against which other trace element techniques are measured. The increasing availability of inexpensive, easily housed, isotopic neutron sources and sealed tube neutron generators can now put a reagent bottle of neutrons in even the most modest analytical laboratory.

CAPABILITIES & LIMITATIONS OF NAA

This technique is a method for determining the elemental content of the substances. Its fundamental limitation is its inability to distinguish among different chemical forms or oxidation states of an element. Like most analytical methods, this technique also suffers from possible interferences and matrix effects. Three types of interferences may occur

TYPE 1 INTERFERENCES

This arises from nuclear reaction in the other elements present in the sample that produce the same radionuclide as the one been measured. E.g., in determining Al in rock by reactor irradiation employing the reaction

$$^{27}_{13}Al(n, \gamma) \qquad ^{28}_{13}Al, \text{ a possible interference is } ^{28}_{14}Si (n, p)^{28}_{13}Al.$$
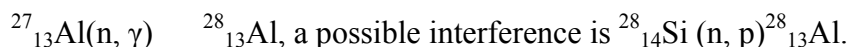
TYPE 2 INTERFERENCES

These are caused by the release of secondary nuclear particles from a primary reaction. For instance, when determining nitrogen in protein products with a neutron generator, the reaction employed may be $^{14}_{7}N (n,2n)^{13}_{7}N$. If the sample is package in polyethylene container, the incident neutrons may collide with hydrogen atoms present in the container material producing energetic protons which may in turn react with carbon in the sample according to the reaction $^{13}_{6}C(p,n)^{13}_{7}N$.

This type of interference is generally of limited significance because the flux density of protons is much less than that of the primary neutrons.

TYPE 3 INTERFERENCES

These are caused by the inability of some detectors to resolve closely similar γ ray energies e.g., when determing the Al content of a material by the reaction
$^{27}_{13}Al (n,p)^{27}_{12}Mg$, one employs the 0.842 MeV γ-ray emitted by $^{27}_{12}Mg$. Iron, if present in the sample, will undergo the reaction $^{56}_{26}Fe(n,p)^{56}_{25}Mn$ which emits 0.847 MeV gamma rays. If a NaI (T1) detector is used to detect the 0.842- MeV γ ray, the 2 γ-rays can not be resolved.

Sometimes, type 3 interference involves radionuclide with half life's different from those of the desired element and can be resolved by the decay curve method.

APPLICATION OF NAA
Some of the more interesting applications have been determining potentially toxic trace elements in natural waters and environmental samples, authenticating paintings and other objects of art, and studying impurities in semi conductor materials, trace element in plant and animal metabolism and trace element abundances in terrestrial rocks, meteorites and lunar samples. In the analysis of lunar samples more than twice as many trace element determinations have been reported by activation analysis than by any other techniques. In fact, the activation analysis determination on these rare samples probably exceeds those by all other techniques combined. Acceptance of evidence developed from activation analysis by court of law has led to its use in forensic chemistry.

Activation analysis is not without its own unique problem. However for the determination of elements at sub ppm level, it is certainly the technique against which other methods must be compared. Accuracy and precision of the order of a few percent are readily attainable at the monogram level for many elements. High sensitivity, multi element capability, and freedom from reagent and laboratory contamination problems are the major advantages offered. In addition, activation analysis is a very specific technique.

ACCURACY: The principal errors that arise in Activation analysis (AA) are due to shelf shielding, unequal neutron flux at sample and standard, counting uncertainties and errors in counting due to scattering, absorption, and differences in geometry between sample and standard. These errors can usually be reduced to less than 10% while uncertainties in the range of $1 - 3\%$ are frequently obtainable.

SENSITIVITY: The most important characteristic of NA method is its remarkable sensitivity for many elements e.g., as little as 10-5μg of several elements can be detected. Also about 50μg of Fe are required for detection in contrast to 10μg for europium; this shows a wide variation in sensitivity among the elements.

The sensitivity of the activation method for an element is a function of a number of variables. Some of these are associated with the properties of the particular nucleus. Others are related to the irradiation process; still, others have to do with the efficiency of the counting apparatus, e.g. in selecting the proper detector, the criteria used are detector efficiency and resolution. Where sensitivity is the overriding consideration, a Na I (Tl) detector is the detector of choice. If there are interferences RNAA must be employed to eliminate them. In multi element analysis of complex matrices detector resolution becomes critical and Ge(Li) detectors should be used

ADVANTAGES
One of the most important advantages of INAA over many other methods of analysis is that it is essentially non-destructive. Very often a complete analysis can be performed without appreciably altering the physical or chemical nature of the sample.

This is important for several reasons:
(1)   If may be imperative to preserve the sample, such as in forensic analysis where the sample is needed as evidence in the court room, or in the analysis of lunar samples or works of art

(2)   Non- destructive analysis involves minimum sample manipulation and therefore, a trace sample is not contaminated by regents and containers as in conventional destructive wet chemical techniques.

Other advantages include
1.   High sensitivity which exceed that of other methods for many elements by factor of 100 or more
2.   Conc. Determinations in the ppt ranges are common
3.   Accuracy and precision of the order of a few % are readily attainable at the ng level for many elements
4.   Very specific technique; nuclear properties such as β and δ energies as well as half-life's are all characteristic of particular element and may in fact, be used without resort to chemical separation.
5.   Speed: It is a very fast technique particularly where chemical separation is not necessary; the whole process may be carried out extremely rapidly

Limitations of NAA
1.   Requires the use of either the nuclear reactor or a machine produced neutrons. This is expensive to purchase and manage.
2.   Analysis gives only the total weight of an element irrespective of the state of combination (i.e.) inability to distinguish among diff chemical forms or oxidation states of an element)
3.   Spurious activities causing interference.
4.   Too many precautions are necessary to get good result.

Example 1:   Cal the activity for a 10mg sample of an aluminum alloy containing 0.041% manganese after a 0.5 hr irradiation in a flux of 5x 1013 neutron cm-2 sec-1. The t1/2 = 2.5 8 hr Neutron cross section = 13.3 barns

Example 2:   Using the data provided calculate the level of A induced in 1g sodium by an (n, γ) reaction.

Stable isotope = ^{23}Na, relative abundance = 100%
$t_{1/2}$ of product = 15.0hrs, n,γ (barn) = 0.534 barns
Irradiation time = 30hrs Neutron flux $\Phi = 10^{16}$nm^{-2}s^{-1}
1 barn = 10^{-28}m^2

METHODS INVOLVING ADDITION OF RADIONUCLIDES
The second general category of radio chemical analysis involves adding a radioactive substance to the sample, manipulating the sample by physical or chemical means, measuring the radioactivity and ultimately calculating the amount of the component of interest. This category includes. Direct and inverse isotope dilution analysis, radio chemical titration and radio release method of analysis

ISOTOPE DILUTION ANALYSIS (IDA).
IDA is a powerful method of determining small amount of material in a form where 100% separation and recovery of the material are difficult. In principle, a quantity of radioactive material of the same chemical form and of known specific activity is added to the unknown amount of inactive material.

Determination of the specific activity of the mixture then allows calculation of the quantity of inactive material present. The technique is based on the fact that the isotopic composition of an element remains constant throughout its series of chemical reaction. It is assumed that both the tracer (radioactive material) and the inactive isotope are in the same initial chemical state

THE THEORY OF IDA
Recall that in the method of activation analysis radioactivity is induced in the sample to be analysed. In the method of IDA, a radioactive form of the component of interest is added to the sample. The component is then exhaustively purified without regard to quantitative recovery and a fraction of the pure component is isolated.

The amount and activity of the isolated component are measured and the quantity present in the original sample is calculated using that information. Consider a complex sample of Wgrams containing W_1grams of the component of interest. To this sample is added W_1*gm of a radioactive form of the component with a total activity of A_1. W_2 gram of the pure component is then isolated; it contains both the active and inactive forms and has an activity of A_2. The specific activity SA_1 of the radioactive ("spike") material before it is mixed with the sample is defined as:

$$SA_1 = \frac{A_1}{W_1*}$$

And SA_2, the specific activity of the recovered component, as $SA_2 = A_2/W_2$

SA_2 will remain constant regardless of how much of the pure component was isolated since it is activity per unit wt of recovered component. One can then write the following balance sheet:

	Weight of component	Specific Activity
Before mixing	W_1 (inactive form)	O
	W_1* (active mixture)	SA_1
After mixing but	$W_1 + W_1$* (mixture)	SA_2

Before purification

After purification $f(W_1 + W_1^*) = W_2$ SA_2
                        (Isolated component)

Note that f is the fraction of the component recovered and is unknown. Note also that the specific activity of the component of interest remains the same before and after purification.
It follows that $W_1^* \times SA_1, = (W_1^* + W_1) \times SA_2$ and solving this equation for W_1 we have,

$$W_1 = W_1^* \frac{(SA_1 - 1)}{SA_2}$$

The percentage of the component of interest in the original sample is then percentage unknown =
$$\frac{W_1^*}{W_1} \quad \frac{(SA_1 - 1)}{SA_2} \times 100$$
Since W_1, W_1^* and SA_1 are known and SA_2 can be determined experimentally, the amount of the component of interest in the original mixture can be easily calculated.

ADVANTAGES & LIMITATION OF IDA
In wet chemical analysis, exhaustive multi step purification procedures are often required to obtain the component in a highly pure form, and a quantitative yield is almost impossible to achieve. The main advantage of IDA is that no quantitative separation of the component of interest is necessary. The instrumentation required is usually quite simple, since measurement of gross activity with simple counting systems is sufficient.

Separated component must be in highly pure form; and once the pure component is obtained, its quantity must be accurately measured, or deduced from stoichiometry consideration.   The separated components must also have a high enough level of activity to minimize statistical counting error. (This is usually not a serious limitation; since the activity of the initial labeled compound can often be adjusted to compensate for a low efficiency in the purification step). The wt W_1^* should not be much larger than the W_1, and tracer solutions of high specific activity are ordinarily used.

A very important effect which could become either an advantage or a disadvantage is inherent in fundamental requirement of the method: Both the active and inactive forms behave identically in the subsequent purification step. This means either that the labeled component must be in the same chemical form as the inactive component, or that the mixture must be treated chemically to convert both forms into the same chemical compound. This situation can, of course, be of great advantage if one is trying to distinguish among different chemical forms of a given element. For instance, a solution containing both Cr^{3+} and $Cr_2O_7^{2-}$. Can be analysed for $Cr_2O_7^{2-}$ by adding $^{51}Cr_2O_7^{2-}$ tracer and excess NaOH, after which Ba^{2+} is added to precipitate $BaCrO_4$.

ADVANTAGES
1.   No quantitative separation of the component of interest is necessary
2.   Instrumentation required is usually quite simple since measurement of gross activity with simple counting systems is sufficient.
3.   The technique is highly specific for certain system.

LIMITATIONS
1.   Not very sensitive
2.   Labelled component must be in the same chemical form as the inactive component or that the mixture must be treated chemically to convert both forms into the same chemical compound.

INVERSE ISOTOPE DILUTION ANALYSIS. (IIDA)
In IDA, a radioactive form of the component of interest is added to the sample and the quantity of the inactive form initially present is determined. In some substances, one may wish to determine the amount of a radioactive substance in the sample. A method similar in principle to IDA can then be used wherein a quantity of an inactive form of the component of interest is added to the sample, the sample is purified without regard to quantitative recovery, and the amount of the recovered component and its activity are measured.

From this information, the quantity of the radioactive substance initially present in the sample is calculated. This method is referred to as: Inverse Isotope Dilution Analysis (IIDA)

THEORY OF IIDA.
Let W_1^* and SA_1 be the weight and specific activity, respectively, of the radioactive substance initially present in the sample. W_1 grams of an inactive form of the component is added, and some fraction of the pure component, having specific activity SA_2 is recovered. The balance sheet for this situation is as follows;

	Wt of component	Specific Activity
Before mixing	W_1^* (active form)	SA_1
	W_1 (inactive form)	O
After mixing but Before purification	W_1^* + W_1	SA_2
After purification	$f(W_1 + W_1^*) = W_2$ (isolated component)	SA_2

Note that f is less than unity and that SA_2 is the same before and after purification then,

$$SA_2 (W_1^* + W_1) = SA_1 (W_1^*)$$

Although, SA_1 is not known, the product $SA_1 (W_1^*)$ can be measured. This is the total activity of the component in the sample before any processing. Therefore, $SA_2 (W^*_1 + W_1) = A_1$ and $W^*_1 = (A_1/SA_2) - W_1$

Since $SA_2 = A_2/W_2$, where A_2 is the total activity of the recovered pure sample and W_2 is the wt of recovered sample: $W_1^* = (A_1/A_2) W_2 - W_1$

ADVANTAGES & LIMITATIONS OF IIDA

The main advantage of this method is that one can determine the quantity of the specific radioactive component of a sample without comparing it with a known radioactive standard. The method also avoids preparing standard with the same matrix as the sample in order to ensure equivalent counting efficiency. However, the method can not be applied if spectra interferences prevent the specific measurement of A_1.

Furthermore, the method is applicable only when W_1 does not differ greatly from W^*_1. In the case of trace analysis, the method offers the advantage of not requiring a quantitative separation of the component of interest.

RADIOMETRIC TITRATIONS

In general, chemical methods of analysis for the natural radio elements are often replaced by measurement of intensity of radiation even when working with weighable quantity of the element in question. Radiometric analysis can also be used for the determination of a stable element if it can be combined with a radioisotope to give an insoluble compound e.g., determination of Ba^{2+} can be performed by adding excess SO_4^{2-} (labeled with ^{35}S) or chromate ion (labeled with ^{51}Cr) to precipitate the Barium. A comparison of the activity of the filtrate (containing excess anion) and initial specific activity will indicate the quantity of anion in the precipitate and hence, the quantity of Barium. This method has found many applications including the determination of Ba^{2+} (as it is discussed above), Mg^{2+} using $Na_2H^{32}PO_4$ and Ag+ using $Na^{131}I$ or $N^{125}I$.

The method is again applicable in case where total quantity involved is too small from normal measurement. All titrimetric methods of analysis require some means of detecting the equivalence point. This could be an abrupt change of colour (colorimetric titrations); a sudden change in the potential difference between 2 electrodes (potentiometric titrations), a change in current flow through 2 electrodes (amperometric titration) and so on. Similarly, the radioactivity of either the titrant or the substance titrated can be employed for detecting the equivalent point this type of analysis is called **RADIOMETRIC TITATION**

It should be noted that the sole purpose of the radioactivity is to signal the attainment of the equivalent point and that it takes no part in the titration. The technique can be applied in all cases of titration provided that a phase titration can be effected.

It is possible to carry out a titration using active solution or active titrant. If active titrant is used e.g Mg^{2+} by $Na_2H^{32}PO_4$, then curve A can be obtained.

That is, the count of he supernatant liquid remains equal to the background until excess ^{32}P is present, when count suddenly increases. If the magnesium salt is placed in the burette i.e. active solution in vessel, then curve. B is obtained.

Point P marks the end point of the titration. It is possible to use radioactive solution and titrant Curve C is obtained in this case

In all cases, it is not necessary to plot the whole curves but only to obtain 2 or 3 points on either side of the end point and extrapolate. Normally, if the whole curve is plotted, the end points are not as well defined as in the diagrams above.

The most straight forward application of radiometric titration is in precipitation titration, where phase separation occurs spontaneously. In order to understand the method, consider the titration of 50ml of a 0.001M Cl⁻ solution with a 0.001M solution of $^{110}_{47}Ag+$, with an activity of 1×10^9 dps/mol. The reaction is $Ag^+ + Cl^- = AgCl$ with ksp = 1.82×10^{-10}. The activity of the supernatant is monitored after equilibrium has been reached following each incremental volume of added titrant prior to the end point; the supernatant has very little activity because almost all of the radioactive Ag is present as precipitated AgCl.

A typical experimental arrangement for precipitation titration is shown in the figure below.

After each addition of titrant and attainment of equilibrium, an aliquot of the supernatant is drawn into the counting chamber and its activity measured. The solution is then ejected back into the titration vessel, and the next addition of titrant is made.

ADVANTAGES AND LIMITATION OF RADIOMETRIC TITRATION
Radiometric detection of the equivalence point is a general method that does not depend on the chemical reaction employed.

This contrast with other methods of detection, which depends on specific chemical or physical transition at the equivalence point. Amperometric titrations are applicable only to electrochemically active system; conductometric titration applies only to ionic solution and so on. In principle, any titration system in which a phase separation can be effected is amendable to radiometric defection provided there exist suitable radioactive labels. The major limitation of the method is the requirement for phase separation. In precipitation titration, the phase titration is automatic and the method is well suited to this class of titrations.

For other classes of titrations special phase separation methods such as solvent extraction need to be applied. At the present time, the method suffers from a lack of phase separation techniques suitable for continuous monitoring of the titration curves.

RADIO-RELEASE METHODS OF ANALYSIS

This method is based on the chemical reaction of the constituent of interest with a radio labeled reagent. The labeled component is then release either as a gas or in some readily extractable form. From a measurement of amount of radioactivity released and the stoichiometry of the reaction, the quantity of the constituent of interest is determined. Consider the determination of SO_2 in air by this method, If air is passed through a basic solution of $KI*O_3$, the following reaction takes place;

$$5SO_2 + 2KI*O_3 = 4H_2O \qquad K_2SO_4 = 4H_2SO_4 + I_2$$
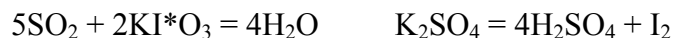
The solution is then acidified and the liberated I_2* is extracted into chloroform. The chloroform phase is separated and counted for its $I*_2$ content. From the stoichiometry of the reaction and quantity of liberated $I*_2$, the content of SO_2 in air can be determined.

The chief advantage of this method of analysis is its sensitivity, since highly active radio reagents are available. For instance, a micro mole of I_2 may easily have a 10^7 dpm activity. However, the method is chemical in nature and suffers from all limitations inherent in a particular chemical reaction involved. In the above example, any other substance that can reduce $KI*O_3$ to $I*_2$ will, of course, interfere with the determination (oxides of nitrogen are potential interferences). Furthermore, at trace levels, quantitative extraction of the released species becomes critical.