Neutron activation analysis

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Lecture-17, Module-1

Hello everyone. So today I discuss the sort of applications of nuclear chemistry in determination of analytes in different types of matrices using techniques called nuclear analytical techniques.



Nuclear analytical techniques

Analytical techniques based on nuclear phenomena

- 1. Neutron activation analysis
- 2. Ion beam analysis

Nuclear analytical techniques are those techniques which are based on a nuclear phenomenon, like for example nuclear reaction. So when we have a tool in the form of a neutron, you have a charged particle beam depending upon whether you have a neutron as a projectile and you want to do some analytical chemistry using neutrons, then we will call it neutron activation analysis. That means you activate a sample with neutrons and the radiations emitted by these activated products you are monitoring and that tells you about the concentration of the elements in the sample. So that technique is called neutron activation analysis.

And in today's lecture I will deal with neutron activation analysis. In the first part I will tell you about the principles, the fundamentals of this technique. And in the second part I will be talking about some of the applications of this technique just to bring home the point how important these techniques can be in solving many problems. And the second part I will take next time, that is the ion beam analysis where we use an accelerator providing the charged particle beams of protons, alpha particles or other ions, heavy ions.

And so these charged particle beams can induce reactions or they can be just simply scattered at a forward angle or backward angle. And based on these interactions again, we can characterize a sample for its constituent elements or you can even understand processes involving these techniques. So both these techniques are clubbed as nuclear analytical techniques. And in fact, you will see later on how kind of information that we obtain from these techniques, some of them are not possible by other techniques. So I will discuss both of them one by one.



Neutron Activation Analysis (NAA)

- 1. Simultaneous multielement determination in diverse matrices.
- 2. Highly sensitive → availability of high flux nuclear reactors and high efficiency HPGe detectors.
- 3. As many as 70% of the elements in periodic table are amenable to NAA, viz., Na, K, Mg, Ca, V, Al, Ti, Mn, Sc, Fe, Cr, Ni, Co, Zn, Ga, Se, As, I, Mo, Zr, Sn, In, Ta, W, Hf, Au, REEs (La-Lu).
- 4. Applications in many fields such as biology, geology, environment, forensic sciences, archaeology, medicine and nuclear technology.



George Hevesy (1936)



So the first technique as I was mentioning is the neutron activation analysis as the name itself implies that if you want to characterize a sample for its constituent elements, then we can activate the stable isotopes of the sample by neutrons. And as you know already that neutron is captured by the different isotopes and you can get radioactive isotopes. In some cases, even if you do not get radioactive isotopes, you can determine the prompt gamma ray to characterize the constituent elements. This technique was developed by George Hevesy, a scientist who in fact also gave the tracer concept which I discussed in the last lecture. George Hevesy along with Hilde Levy developed this technique in 1936.

And since then, it has become so popular among analytical chemists, not only analytical chemistry, but there are many, many fields in which this technique is being utilized. The best part of this technique is that of course, at the same time, you know, if you just irradiate one sample, you can determine simultaneously several elements in the sample. Whichever elements are amenable to neutron activation analysis, you bombard them and you get radioactive isotopes. Sometimes even if you can get prompt gamma rays, so then you can determine the concentration of these elements. And the diverse matrices can be studied by neutron activation analysis.

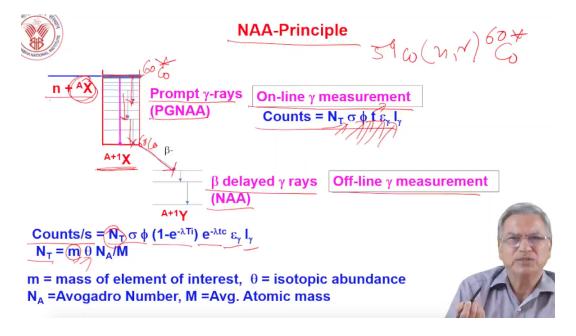
It is highly sensitive because the signal that we get in terms of the gamma rays, you will get high yield, particularly nowadays if you have availability of high flux nuclear reactors. So, the reactors these days give neutrons of the order of 10^{13} , 10^{14} neutrons per centimeter square per second. And because of that, you can assay even the nanogram, in some cases even picogram quantities of the isotopes. Secondly the availability of high flux nuclear reactors coupled with the high efficiency, high purity germanium detectors. So, they will require high efficiency.

I will discuss the details, what are the factors that govern the sensitivity of this technique. In the periodic table, if you see as many as 70% of the elements in the periodic table are

amenable to neutron activation analysis, like for example sodium, potassium, magnesium, calcium, vanadium, aluminum and so on. So, there is an endless list, almost you know rare earths, many of the actinides, they are amenable to neutron activation analysis. You see, it is not necessary that every study has to be done using neutron activation analysis, but it has got an edge over other techniques in many cases. In those cases, you find this is very, very useful.

So, neutron activation, first of all it is not destructive because you can preserve the sample for subsequent analysis. That is why it is particularly useful, for like archaeological samples, geological samples, which you don't want to destroy, you don't want to dissolve and analyze. So, you want to preserve them for any sort of artifacts. So, such cases, neutron activation analysis finds a lot of applications. So, you can have biological samples, geological samples, environmental samples, forensic analysis samples, archaeology, even medicine, and of course, nuclear technology.

So, there are a lot of fields in which the determination of elements are required. It can be forensic application, it can be just chemical quality control of the materials, and even other areas like archaeology, geology. So, neutron activation analysis, if you see in analytical chemistry and other fields, you will find is very popular technique. Only thing is you require to have a source of neutrons.



So, let me just discuss what is the fundamental principle of neutron activation analysis. When an isotope captures a neutron, I have written it as mass number A, and X is the element. So, when it captures a neutron, the isotope of the same element is formed A+1X. And what I have shown is the sort of potential well of the compound nucleus that is formed. So, the reaction involves capture of neutron by AX to give you A+1X. And in this

capture reaction, energy equivalent to the binding energy of neutron in this nucleus is released.

Like when a neutron is captured by a nucleus ^{A}X , certain energy is released that Q value is positive for all neutron capture reactions. And so the energy that is released, the Q value is equivalent to the binding energy of neutron in that nucleus. So, this nucleus is excited. For example, you have a reaction $^{59}Co(n, \gamma)^{60}Co$. This cobalt-60 nucleus is excited; let us say ^{60}Co , excited state. And this is the ground state. So, this excited cobalt-60 nucleus having excitation energy of about 7 MeV, first will emit the gamma rays. So, these gamma rays that are shown here, they are called the prompt gamma rays. Because the excited state will de-excite its gamma ray within picoseconds. So, very quickly within picoseconds, either one or several gamma rays may be emitted.

These prompt gamma rays themselves can be counted online by a HPGe detector. So, you can determine the concentration of this isotope using the measurement of prompt gamma rays emitted by the sample. And this technique is called prompt gamma neutron activation analysis (PGNAA). Now, since these gamma rays are emitted instantaneously upon capture of a neutron, this is essentially an online measurement. Means while the neutrons are irradiating the sample in the reactor, you have to do the measurement.

So, how can you do that? So, for that neutron beams are taken out of the reactor and you have an arrangement where the neutrons are available to you outside the reactor hall and where you can put your sample and the detector system and then you can do the measurement of gamma rays. In such a situation, in PGNAA, so suppose you irradiate, your irradiation is going on, and you count the sample for, let us say, some time, say half an hour. So, the counts that you will get in that half an hour is $N_T \sigma \varphi \epsilon I \gamma Ti$, Where N_T is number of target atoms in the sample because all atoms are being exposed, σ is the cross-section for the neutron capture, φ is the flux of the neutrons in that position, T is the time of irradiation, ϵ is efficiency of detection of the gamma ray and $I\gamma$ the intensity of that gamma ray. So, you can see here, if you irradiate, if you do experiment for a certain time t and whatever counts you get, you can find out the number of atoms of the target element (N_T) and hence the concentration of element. The capture cross-section, which you know, you have to do some experiment, you need some monitors.

There are some flux monitors, some standard samples where concentration is known, you can find out the flux. Detection efficiency, you can determine using standards, you can find out and the intensity of the gamma ray per, say, how many times this gamma ray is emitted if that atom is formed. So, all these are nuclear data which are available in the literature. So, this is the prompt gamma neutron activation analysis. You need to do the experiment online, either in a reactor or if you have a neutron source like a Californium-252 neutron source or you can generate neutrons in an accelerator by spallation neutron sources. So, you can do it that way.

But if you measure the gamma rays that are emitted after beta minus decay, then these gamma rays are actually called offline gamma rays or beta delayed gamma rays. In that case, for example, Cobalt-60 having half-life of 5.27 years, you irradiate for some time, take the sample out of the reactor, take it to the laboratory and the half-life of Co-60 is 5.27 years. So, you can comfortably do the measurement in the laboratory. So, these are measurements of delayed gamma rays and this is the offline gamma ray measurement. The bulk of the neutron activation analysis is usually done using delayed gamma measurements. This is called NAA, neutron activation analysis. Now, you are actually measuring the concentration from a radioactive sample.

So, you are counting the radioactivity and what you get the counts per second. You take a gamma spectrum for a particular length of time and divide the peak area by the time you get counts per second. That count per second is a familiar equation

CPS =
$$N_T \sigma \phi (1-e^{-\lambda Ti}) e^{-\lambda t} \epsilon IV$$

 N_T σ ϕ is the rate of the reaction, neutron capture, (1-e^{- λ Ti}) the saturation time for particular irradiation time (Ti) , e^{- λ t} the decay after the end of irradiation, radioactive sample decaying with its own half-life, ϵ efficiency of detection and I γ the intensity of gamma ray. So, this you can get the number of target atoms (N_T) in the sample. So, how do you get the concentration? This is the mass of the element of interest.

$$N_T = m \theta N/A$$

m is mass of the target element of interest. Now, it can be a multi isotropic sample, like for example cobalt is monoisotopic. So, this is only one isotope, but you have tin, you have many isotopes, iron you have many isotopes. So, abundance of that particular isotope is theta, N_0 is Avogadro number and A is the atomic mass. So, if it is a multi-isotopic sample, then average atomic mass would be different from the mass number. And so, what you can determine is the concentration m, m is the parameter of interest to you.

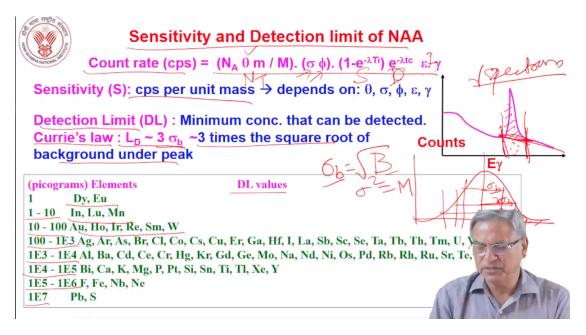
To start the start of the start	Nuclear data: NAA						
So di	Ιγ, %	Εγ (keV)	t _{1/2}	Activ. Prod.	σ (b)	θ %	Target Isot.
	100	1633.6	11.2s 🗸	20F	0.0096	100 /	¹⁹ F
	100	1368.5	15.03 h	²⁴ Na	0.513	100	²³ Na
Sensitivity depend	71.4	844	9.5 m	²⁷ Mg	0.0372	11.0	²⁶ Mg
upon θ, σ, lγ	100	1778.9	2.24m	²⁸ AI	0.23	100 🗸	²⁷ AI
, , , ,	94.1	3103.8	5.05 m	³⁶ S	0.16	0.02	³⁵ S
	32.5	1642.4	37.21m	38CI	0.423	24.23	³⁷ CI
	6.7	1524.7	12.40 h	⁴² K	1.45	6.73	41K
	56	142.5	18.7s	^{46m} Sc	9.8	100 🗸	⁴⁵ Sc
	92.1	3084.4	8.718 m	⁴⁹ Ca	1.12	0.19	⁴⁸ Ca
	93	320.1	5.76m	⁵¹ T i	0.17	5.4	⁵⁰ Ti
	100	1434.1	3.75m	⁵² V	4.92	99.75	⁵¹ V
	100	846.6	2.59 h	⁵⁶ Mn	13.3	100 🏑	⁵⁵ Mn
	7.4	1039.2	5.1 m	^{66m} Cu	2.48	30.83	⁶⁵ Cu
	39.9	834	14.10 h	⁷² Ga	4.61	39.9	⁷¹ Ga
	100 —	559.1	26.24 h	⁷⁶ As	3.86	100 🗸	⁷⁵ As
	52.4	162	17.4s	^{77m} Se	22	9.37	⁷⁶ Se

You can see these are the monoisotopic elements where only one isotope is present in the sample. So, 100% abundance of arsenic-75, manganese-55, scandium-45, sodium-23 and the remaining ones you will find the even ones, even Z elements. So, they have more than one stable isotope, aluminum is monoisotopic. So, the abundance of the isotopes will vary. These are the cross sections for the particular isotope neutron capture reaction. And so, they are in barn and these are the products that are formed after neutron capture. They are formed, they are their half-lives, gamma ray and then the intensity of the gamma. So, you can see here, gamma ray intensity, some of them have 100%, means every decay will give you one gamma ray.

So, abundance is under gamma ray abundance or gamma ray intensity is 100%. So, you can see here, the sensitivity of the detection of the elements depends upon the isotopic abundance, the capture cross section and the intensity of gamma. So, essentially under the gamma ray peak, you get a peak area, the peak area will be more if the isotopic abundance is more, if the cross section for neutron capture is more and if the intensity of the gamma ray is more. Other parameter is flux, so that doesn't depend on nuclear data of the isotope. So, these parameters you need to maximize to get high sensitivity.

Even these are the other isotopes, so there are several isotopes as I mentioned are amenable to neutron activation analysis. You can see some of them, you see the monoisotopic ones, so they will have more sensitivity because there is only one stable isotope present in the element. So, let us discuss the sensitivity and detection limit of neutron activation analysis. As I mentioned, the count rate in the sample, when you irradiate a sample with neutrons, now we are discussing about now neutron activation analysis that means you do an irradiation, take the sample out of the reactor or neutron source and count the activity of the radioisotope in the laboratory.

That is the off-line measurement. So again, this is the same equation which I mentioned in the previous slide. This essentially gives you the number of target atoms. This is the cross section and the flux, saturation time, the cooling time, decay time, efficiency and abundance of the gamma ray, intensity of the gamma ray.



So, what is sensitivity? Suppose you irradiate one microgram of the sample, how many counts per second you get? That is called the sensitivity. So, counts per second per unit mass, let us say per microgram.

So, sensitivity can be written as cps per microgram or cps per milligram or cps per nanogram. If you have a sample containing one microgram or one nanogram or one milligram sample, what is the counts in your detectors? Suppose this is the gamma spectrum. So, this peak area, you can put the limits and so this is the peak area of the gamma ray peak and this is the background. Below this is the background. So, you have to subtract the background from the gross count.

So, when you put the two limits, area under this graph will be gross counts and then you do a linear subtraction of this background. So, this trapezium you subtract, you get the net peak area. So, this peak area will be high if flux is high, cross section is high, efficiency is high, gamma ray intensity is high, isotopic abundance is high. So, that determines the sensitivity of the technique.

Second quantity is the detection limit. How much is the minimum quantity that you can determine by this technique is called the detection limit. Now, how do you define the detection limit? So, normally now when there is no sample, you record the gamma spectrum, you will get a flat background count or there will be some bump here. So, that small bump, it may be confused as peak due to the sample, the gamma ray spectrum due

to the sample. So, we do not know how much of the amount that will give you a reasonable peak area. So, what is essentially done is, it's called the Currie's law.

That means if you take a background of a sample, suppose you have a blank, you don't have a sample, you just record the gamma ray spectrum. Then in the position of this gamma ray peak, you will get and you define these limits, upper limit and lower limit of the peak, you will get some background counts. And suppose you take multiple times the background, and then over, now next time you count the sample. So, suppose you get some higher counts, how do you make sure that there is a detectable amount of that particular element? So, the thumb rule for that is the level of detection is the three sigma background $(3\sigma_b)$. Now, three sigma, what is the significance of the background count? Standard deviation, σ_b means standard deviation of the background count.

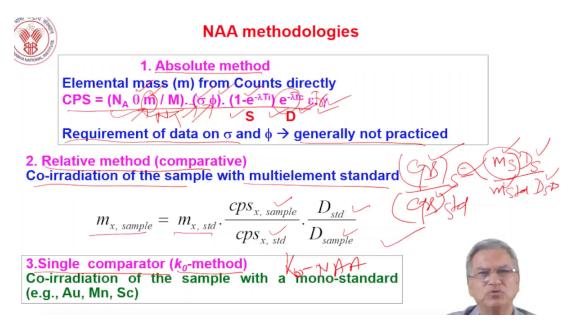
So, suppose you have b counts in the background, σ_b the square root of the counts is the standard deviation because variance is equal to mean when you are doing any counting, as they follow the Poisson's distribution. And so for Poisson's distribution, variance is equal to mean, that means $\sigma^2 = \text{mean}$. And so the standard deviation is equal to square root of the mean value. Now, how do you quantify that if it is this much times of standard deviation, we say there is a confidence limit, this much probability that the sample contains element of interest. So suppose you have a Gaussian distribution of the background counts. So, this is the mean background counts and this is the one sigma, σ_b , you have 2σ and you have 3σ . So, these are corresponding to different confidence levels. This is called the 68%, $\pm 1\sigma$, 95%, $\pm 2\sigma$ and 99%, $\pm 3\sigma$. So, 99% of the time, that means your sample contains that particular element. So, now, if the limit is three sigma means it has to be more than background $\pm 3\sigma$.

So, 3σ is essentially an indication of a confidence limit of 99%. You are 99% sure that your sample contains that element. That is the limit of detection. Three times the square root of the background counts under the peak. So, you can see here, the detection limits for different elements are given here in terms of picograms, elements, such as, dysprosium and europium have a detection limit of one picogram. That means if you have a picogram of these elements in a sample, by neutron activation you will get measurable counts. So, over the background, you will see a bump that you can quantify. So, this is called the detection limit, meaning you can detect that element.

There is something called limit of quantification that is more than 3σ and is actually six times the σ . Then you want to quantify concentration. Here you want to test if you can detect it. One to 10 picogram, indium, lutetium, manganese. So, this tells you about the favourable decay characteristics, the nuclear data, the cross section for neutron capture, the gamma ray intensity, isotopic abundance and so on. 10 to 100 gold, holmium, 100 to 1000, 1000 to 10,000, 10,000 to 1 lakh, 1 lakh to 1 million and 10 million. So, different elements have different sensitivity of detection in the neutron activation analysis.

So, you can choose. It is not necessary that we have to follow the neutron activation analysis technique to determine concentration. These days you will find there are very sensitive techniques like inductively coupled plasma mass spectrometry, Inductively coupled plasma atomic emission spectroscopy. You can have a source, you can excite, you can generate a plasma and the excited atoms decay and then you can measure the visible photons emitted by these atoms or you can generate plasma and then see emission lines of this one or you can do the mass spectrometry. So, depending upon what you measure, you can have ICP-AES or ICP-MS and this ICP-MS techniques can go up to picogram, picogram per gram, parts per billion. So, there are techniques now, but then what you need to do, you need to dissolve the sample and you need to do the analysis.

But in this particular case, you just take a solid sample, irradiate in the reactor and you can get the gamma rays. So, the sample is intact, you can repeat the experiment or you can preserve it for future analysis. That is the beauty of this neutron activation analysis. Let us discuss how do we determine the concentration.



So, there are mainly three methodologies I will be discussing. First is the absolute method of NAA, neutron activation analysis. Absolute method means you use this equation, counts per second.

$$CPS = (m \; \theta N/A) \; \sigma \; \phi \; (1 \text{-}e^{\text{-}\lambda T i}) \; e^{\text{-}\lambda t} \; \epsilon \; I \gamma$$

This is the amount of the isotope of element interest, isotopic abundance. So, this is the $N\sigma\phi$ saturation factor and the decay factor, efficiency and detection and the intensity of the gamma.

So, you want to determine m in the absolute method. So, you need to know the cross section, you anyway know in the reactor what is the flux at that position. This factor can be determined easily, detection efficiency, gamma ray intensity is known. These data are also known. So, we can find out m from this expression, provided you know σ and ϕ . So, sigma and phi sometimes you know you may not know exactly the flux.

The reactor is a big place where the flux in the particular position may not be accurately known because the flux is not constant all along the reactor. So, this absolute method requires that you should have the data on cross section and phi. So, generally you know this is not a preferred method, but sometimes you may not have any choice that you have to go for absolute method.

The most common method is comparative method or relative method. That means if you have a sample where the concentration of that particular element is known that is called the standard. With respect to that you can determine the concentration in the sample of your interest. So, what you do in this you irradiate the sample and the standard together. So, the irradiation time is same. You are determining the gamma ray of the same isotope. The saturation factor is same. Detection efficiency, gamma ray intensity, cross section, flux all are same. What is different is the m. Now, this all will get cancelled what you have mx, sample equal to ratio of decay factor as you are counting at different times D(standard) upon D(sample) into mx, (standard).

$$m_{x, sample} = m_{x, std} \frac{CPS_{x, sample}}{CPS_{x, std}} \frac{D_{std}}{D_{sample}}$$

So, count rate of the sample, count rate of the standard, mass of the element in the sample, mass of element in standard, decay factor for the standard. So, what you get is the m this value, mass of the element in the sample, mass of element in standard which is known, count rate in the sample upon count rate in the standard, the decay factor. So, these are all very simple quantities. There are standard reference materials for which the concentrations are known. There have been inter laboratory comparison experiments done worldwide to establish the concentration of the analytes in standards and those standards can be now even purchased from the source.

Then there are certified reference materials and there are working standards. You can prepare a standard in your laboratory. Suppose you take a compound of known stoichiometry which is not hygroscopic, you can use that as standard for the particular element. Working standards, CRMs, certified reference material and standard reference materials, either of them we can use. So, this is the most commonly used method. But then there are situations where you do not know, suppose you have a new sample which you don't know what are the elements in that.

So, how can you have a reference for that? Unless you know the elements, you don't know how to chose the standard. So, for that this new development has taken place called single comparator K_0 neutron activation analysis. In the absolute method for every element you have to have a standard. You require concentration of the element to be known in the standards. So, suppose you have 10 elements, the standard should have all those 10 elements.

But if you have single comparator method, then you determine the concentration of all the elements with respect to the single comparator, like gold you can use as a single comparator or manganese or scandium. So, you irradiate a gold standard with the sample and you determine the gamma activity of gold and the sample. And there are now methodologies by which you can find out the concentration of the element with respect to gold. Gold amount is already known, so you can determine the concentration. So, the single comparator became very popular for unknown samples where you do not know what are the elements present in that particular sample.

I am not going to give details of this K_0NAA . This is a bit more elaborate methodology where you require to know the flux. In the reactor, you need to calibrate the reactor position for the flux, fast flux to thermal flux ratio. Because the cross-section follows 1/v-law, there are some resonances at higher energy. So, the flux as a function of energy of neutron, the cross-section of the the isotope as a function of neutron energy are required to be known. It is a little bit more elaborate.



Advantages of Neutron Activation Analysis

- 1. Simultaneous multi-elemental determination
- 2. Non-destructive
- 3. Negligible matrix effect
- 4. High selectivity
- 5. High sensitivity
- 6. High precision / accuracy
- 7. Considered as a Reference Technique

Lastly, what are the advantages of neutron activation analysis? One, it is the simultaneous multi-element determination. In the same time, if you irradiate a sample, whatever elements in that sample are amenable to NAA, it is determined by this technique.

It is generally non-destructive. There can be cases that you can introduce a lot of activity and you may not be able to handle it, but after some time, anyway, the activity will die down and so you can reuse the sample.

Matrix effects are largely negligible. Suppose this is like interference, there are very, very few isolated cases where the two elements will give the same gamma ray. Even if they give the same gamma ray, there may be different half-lives, so you can resolve them. That way, matrix effects are negligible. Unless you have an element which has got very high neutron absorption cross section, the flux may get reduced.

Highly selective because the radioisotopes that are formed, they have distinct gamma rays. Even if the gamma ray is same, you have different half-lives, hence highly selective,.

High sensitivity because of the high cross section, high flux, high detection efficiency, you have the high sensitivity. And so, high precision and accuracy, they are quite reproducible and the data can be obtained very accurately. So, because of these advantages, neutron activation analysis is called a reference technique.

That means for many, like, forensic applications or many applications, data provided by NAA are taken as reference data. Suppose you have forensic data in a court also, this data can be used, as an evidence. So, these are the advantages and NAA is well studied, very common technique, not only in the analytical chemistry, but many other areas which I will discuss in the next lecture. So, I will stop here. Thank you very much. Thank you.