Ion beam analysis: Nuclear reaction analysis and Particle induced gamma emission

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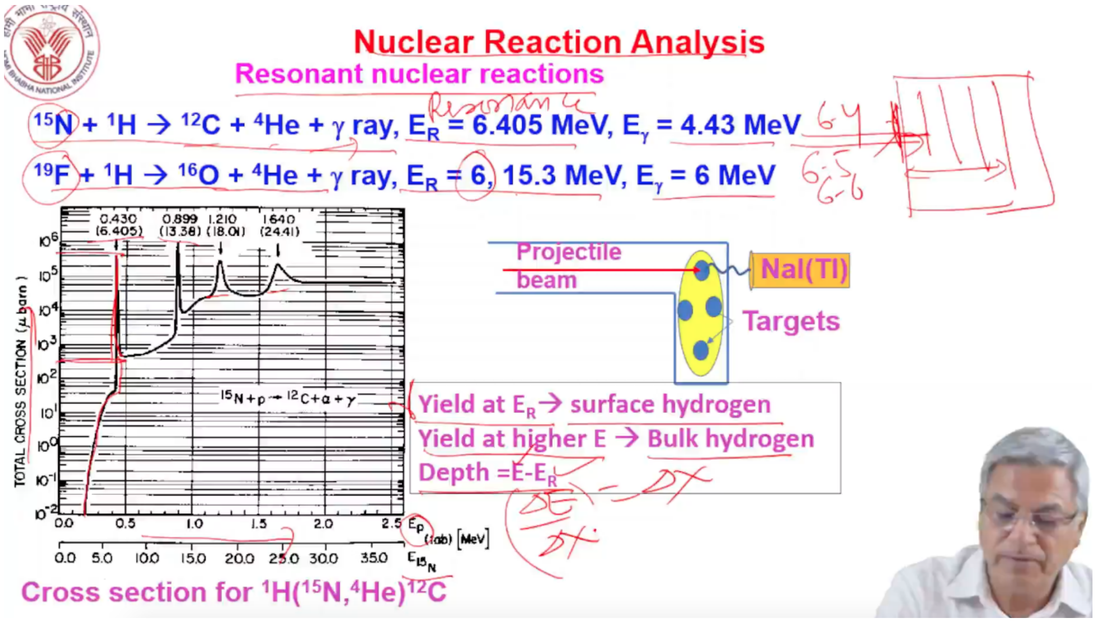
Lecture-18, Module-2

Hello everyone. In the previous lecture, I discussed about the two nuclear analytical techniques namely RBS and ERDA, which are based on a charged particle beam bombarding the target and we are measuring either the back scattered particle like in RBS or the forward emitted recoil in ERDA. Now I will discuss two techniques which are based on the measurement of the gamma rays that are emitted when the projectile reacts with the target. So they are called nuclear reaction analysis (NRA) and particle induced gamma emission (PIGE). In fact in particle induced gamma emission mostly we use proton as a projectile and so it can also be called as proton induced gamma emission but there are other PIGE reactions where the deuterium beam also can be used or even other beams can be used alpha can be used and so on.



Nuclear Reaction Analysis

Resonant nuclear reactions

$^{15}N + {}^{1}H \rightarrow {}^{12}C + {}^{4}He + \gamma$ ray, E_R = 6.405 MeV, E_γ = 4.43 MeV

$^{19}F + {}^{1}H \rightarrow {}^{16}O + {}^{4}He + \gamma$ ray, E_R = 6, 15.3 MeV, E_γ = 6 MeV

Yield at $E_R \rightarrow$ surface hydrogen

Yield at higher E → Bulk hydrogen

Depth = $E - E_R$

Cross section for $^{1}H(^{15}N,{}^{4}He)^{12}C$

Okay, so first let me discuss the NRA nuclear reaction. So there is a distinction between what NRA techniques I am discussing it basically they are based on the resonance in the nuclear reaction cross-section. Those techniques which are based on the resonances in the nuclear reaction cross-sections we will call NRA and other techniques so NRA and PIGE basically you have nuclear reactions involving emission of gamma ray but those techniques where there is an enhancement in the cross-section at particular energy of projectile that means there is a resonance we are clubbing as NRA as historically it has been called as NRA. So resonant nuclear reaction means at a particular energy of the projectile there is a significant enhancement in the cross-section of the reaction. The two most commonly used nuclear reactions are projectile is ^{15}N you take note of it, projectile is ^{19}F normally you know proton will be used as a projectile but here ^{15}N or ^{19}F is the projectile and we want to study hydrogen in the material so hydrogen is a target.

$^{15}N + {}^{1}H \rightarrow {}^{12}C + {}^{4}He + \gamma$ ray, $E_R = 6.405$ MeV, $E_\gamma = 4.43$ MeV

Now E_γ is 4.43 MeV and the E_R means the resonance energy. This is the resonance energy, the energy of ^{15}N at which resonance occurs. So I will elaborate this using this graph.

What we have here is the cross-section versus the energy of the projectile, ^{15}N, and corresponding energy of proton is also shown. Suppose you want to detect ^{15}N using proton that also you can do but applications are more with regard to hydrogen determination using ^{15}N. So what I am showing here that the cross-section is going here and then there is a, see this is log scale. So here the cross-section is 100, 200 and here it is 2 lakh. So 200 to 2 lakh, 200,000.

So there is 3 orders of magnitude increase in the cross-section. 1000 times the cross-section is rising. So there is one more resonance at, so this is at 6.405 MeV of ^{15}N. This is at 13.38 MeV of ^{15}N and there are more resonances but we focus on the first resonance 6.405 MeV. So that means what? If you bombard a material containing hydrogen at the surface and at 6.405 MeV of ^{15}N you will get very high increase in the gamma ray yield. And so the moment the energy of nitrogen matches with the resonance energy then there will be 3-fold increase in the gamma ray yield, 3 orders of increase in the gamma ray.

Another reaction is

$^{19}F + {}^{1}H \rightarrow {}^{16}O + {}^{4}He + \gamma$ ray, $E_R = 6.153$ MeV, $E_\gamma = 6$ MeV

and the gamma ray of 6 MeV is emitted and this happens again at 2 energies, 6 and 15.3 MeV. Again we use the 6 MeV energy of the ^{19}F. So essentially you are using the resonance. So if the energy of the projectile is matching with the resonance energy there will be significant enhancement in the gamma ray yields.

So how do you get the information? Gamma ray yield at resonance energy gives you the concentration of the hydrogen. So when you are starting with the resonance energy 6.4 MeV for ^{15}N, resonance condition, this resonance condition is met at the surface. So you are probing the surface hydrogen. Then you increase the energy of ^{15}N in steps of 0.01 MeV or, 10 keV and so on. So you are gradually increasing the energy of the projectile, the resonance condition is met in the depth of the sample. So you understand this point if suppose this is the target and you start with the first 6.4 MeV you will see the hydrogen here. If you want to see the hydrogen here you have to have higher energy may be 6.5, 6.6 or so because the projectile will lose energy in this. So if you want to probe hydrogen at different depths you require to have higher energy. And you can calculate from the energy at which the resonance is achieved you can calculate what is the depth of that position. So that is the yield at higher energy gives you the bulk hydrogen. So that means at higher energy you are in the bulk, resonance condition is met in the bulk.

And what is the depth?

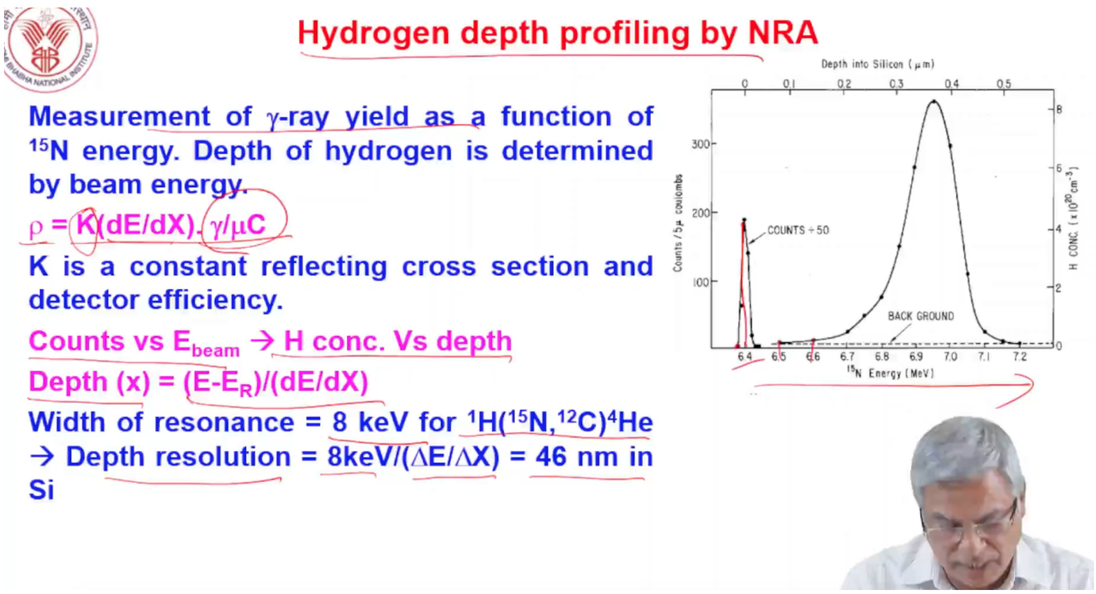
Depth (x) = $E-E_R/(dE/dX)$

So if you know the resonance energy, the energy of projectile at which the resonance occurs is divided by dE/dx is known. You can find out the depth at which the hydrogen was probed. So this is the principle of resonant nuclear reaction or NRA.

So how do you get the depth profiling? As I already discussed you measure the gamma ray yield as a function of ^{15}N beam energy, I mean projectile beam energy. So you can see here that ^{15}N beam energy is increasing from 6.4 or you can go slightly low 6.3 or so, let's go 6.35. So you can see here each point, here the point will be 6.5, 6.6, so 100 keV. You can go even smaller steps. And so the experiment involves bombardment of the target.

In fact, I forgot to tell you about the experimental arrangement here that this projectile beam is passing in vacuum and you have the target on a rotating wheel, circular wheel and you have the targets at different positions, so we can have 4, 6 targets. At a time one of the target will come in the beam path and when you bombard, you will measure the gamma ray energy and intensity. Energy is known, and intensity with the NaI(Tl) detector. You don't need to have a HPGe detector because you are not interested in the energy measurement.

So you can have multiple targets and measure the gamma ray intensity using NaI(Tl). And so you can see this spectrum, this 6.4 MeV yield of hydrogen corresponds to surface because that is the resonance condition, initial beam energy. And as you increase the beam energy you are probing the bulk hydrogen. So this target actually they have implanted hydrogen in the sample at a particular energy and then you can probe it.



Hydrogen depth profiling by NRA

Measurement of γ-ray yield as a function of ^{15}N energy. Depth of hydrogen is determined by beam energy.

$\rho = K(dE/dX).\gamma/\mu C$

K is a constant reflecting cross section and detector efficiency.

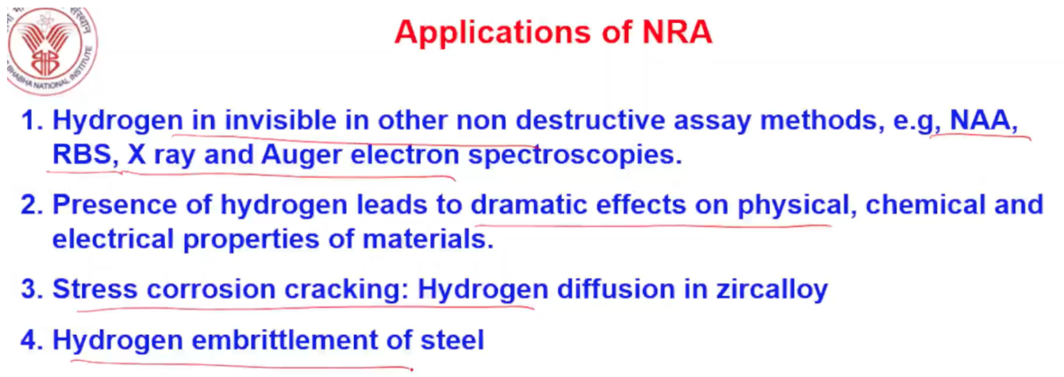
Counts vs E_{beam} → H conc. Vs depth

Depth (x) = $(E-E_R)/(dE/dX)$

Width of resonance = 8 keV for $^{1}H(^{15}N,^{12}C)^{4}He$ → Depth resolution = $8keV/(\Delta E/\Delta X)$ = 46 nm in Si

This is like a demonstration of the profiling of hydrogen in a machine. Okay, so the yield, the gamma ray yield depends upon some factor which is depends upon the cross section, detection efficiency, the stopping power and how many counts you get per micro Coulomb that gives you the hydrogen concentration. So counts versus energy gives you concentration versus depth as I mentioned just now and depth comes from the $E-E_R$ energy of incident energy minus resonance energy upon stopping power dE/dx. For this silicon carbon, this ^{15}N bombardment of hydrogen resonance, whatever resonance we saw in the previous slide, resonance width was only 8 keV and that width determines the depth resolution because that gamma ray yield if you vary by less than 8 keV it will not make a difference. So when you vary by 30 keV you will see the hydrogen at different depths.

So up to 10 keV you will see it is only same hydrogen you are probing by varying by 8 to 10 keV. So the steps of nitrogen beam energy will be 20 to 30 keV and so on. So this width of the resonance gives you the depth resolution 8 keV FWHM upon the stopping power of ^{15}N in that matrix and that happens to be 46 nanometers in silicon. So stopping power of ^{15}N in silicon is known and 8 upon that stopping power gives you depth resolution. So you can imagine at nanometer scale you can probe the hydrogen.



Applications of NRA

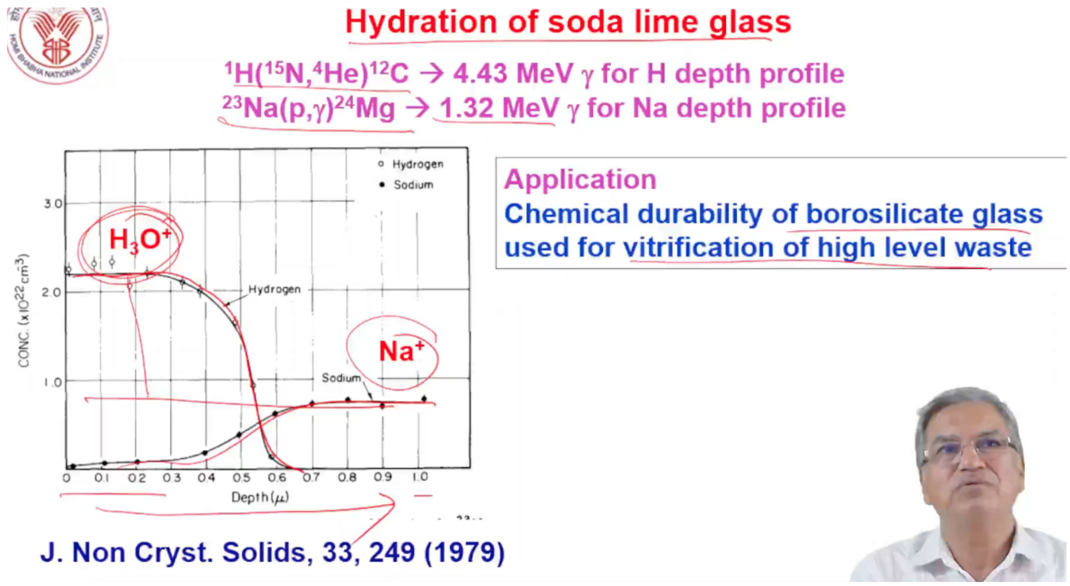
1. Hydrogen in invisible in other non destructive assay methods, e.g, NAA, RBS, X ray and Auger electron spectroscopies.
2. Presence of hydrogen leads to dramatic effects on physical, chemical and electrical properties of materials.
3. Stress corrosion cracking: Hydrogen diffusion in zircalloy
4. Hydrogen embrittlement of steel

So you will find there are not many techniques whereby you can probe hydrogen then normally you know you will see that you can like hot vacuum extraction and quadrupole mass spectrometry. For hydrogen isotopes you the hydrogen by heating it and then you evaluate them by mass spectrometry. But if you can do it non-destructively, nothing like that. So NRA is a unique technique to probe hydrogen because hydrogen is invisible in many other non-destructive techniques.

What are the other things? like neutron activation analysis. You cannot do NAA of hydrogen. By RBS, Rutherford back scaling spectrometry you cannot do because this is sensitive to heavier Z only. Then X-ray and Auger electron based X-ray fluorescence are. not suitable as hydrogen X-rays energies are very small you know. So most nuclear analytical techniques hydrogen is invisible and therefore NRA , in fact the growth of NRA technique was basically because of its potential to determine hydrogen in materials.

And also you will find technologically there are many materials which you know hydrogen may have dramatic effects on their physical, chemical, electrical properties and so it is important to know if there is a hydrogen impurity into this material. Particularly now in nuclear technology the hydrogen in Zr alloys. You are using water as a coolant. The hydrogen is generated it may diffuse into the zirconium and zirconium hydride will lead to stress corrosion cracking. Similarly, the steel is prone to embrittlement by hydrogen and so in many technologically important materials hydrogen induced embrittlement or corrosion is a big problem.

And so if you have a non-destructive technique this will be the best to determine hydrogen and its depth profiling in these materials. So mostly NRA is used for hydrogen profiling in technologically important materials.



Hydration of soda lime glass

$^{1}H(^{15}N,^{4}He)^{12}C \rightarrow$ 4.43 MeV γ for H depth profile

$^{23}Na(p,\gamma)^{24}Mg \rightarrow$ 1.32 MeV γ for Na depth profile

Application

Chemical durability of borosilicate glass used for vitrification of high level waste

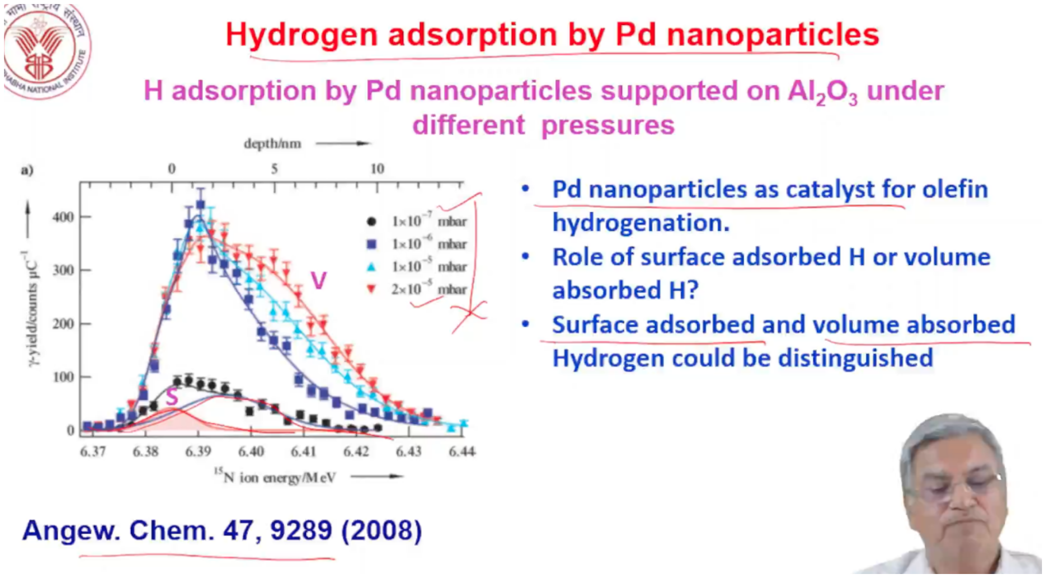
J. Non Cryst. Solids, 33, 249 (1979)

Okay so I will just give you a couple of examples of hydrogen determination in technologically important materials. One of the examples you know is the glass. The borosilicate glass is used for vitrification of high level waste. This high level waste is a waste material in nuclear technology. Now it is not called a waste because it contains lot of important isotopes which are useful. So when you irradiate uranium in the reactor to produce electricity and you get plutonium also and many fission products are produced. You want to recycle the uranium and plutonium in the subsequent reactors and therefore what you do is you separate uranium and plutonium from this spent nuclear fuel and then the raffinate of that repossessing can be evaporated to make what is called as the high level radioactive waste. This high level waste is a big problem but we know how to manage it.

So what they do they vitrify, immobilize in a glass matrix and the glass matrix should retain these radioactive isotopes for a time period of hundreds of thousands of years because it shouldn't come out. And therefore the chemical durability, the leach rate of the glass is determined as a function of radiation doses. People are studying radiation damage and even the glass can be attacked by water and therefore if you dip the glass in water then there could be leaching of sodium. Sodium from the glass goes to the water. So sodium is taken as a marker for leach rate determination.

When you put a glass in the water sodium will come out in the water and hydrogen will get into the glass. So that study was done. What is the mechanism of leaching of sodium from glass into the water? And you can see here depth profile by this reaction. So nitrogen-15 beam energy is increased. So they have directly put in terms of the depth in microns. So 0.1 to 1 micron thick, 1-micron thick glass sample and the depth profile of hydrogen is here and depth profile of sodium is here. So for sodium, ^{23}Na(p,γ)^{24}Mg, was used which is giving you 1.32 MeV gamma ray. So you can do sodium depth profile. It also has got resonance at particular energy of proton.

So what they see that from the bulk sodium is coming out into the water and hydrogen is getting into the bulk from the surface. So surface is in touch with the water, high hydrogen and gradually water is increasing into the glass, so you can find out the rate at which the exchange is taking place. And another important thing is that water, H^+ is coming as H_3O^+, From the ratio of the signal due to hydrogen and sodium in the NRA spectrum, you can find out what is the form in which hydrogen is getting into the glass. So this was a very important study way back in 1979 it was studied and it in fact led to the understanding the mechanism of inter-diffusion between the alkali metal in the glass and hydrogen in the water.



Hydrogen adsorption by Pd nanoparticles

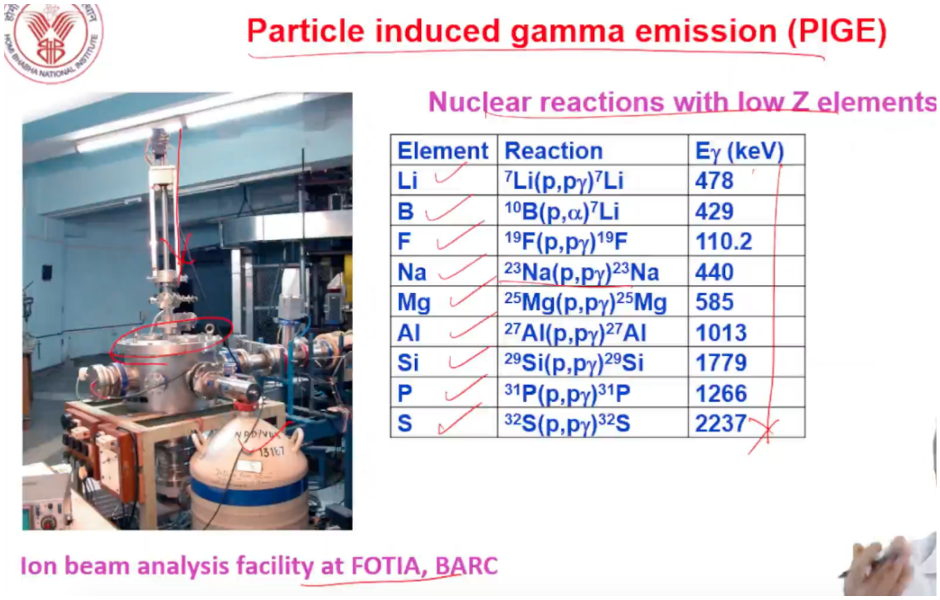
H adsorption by Pd nanoparticles supported on Al_2O_3 under different pressures

- Pd nanoparticles as catalyst for olefin hydrogenation.
- Role of surface adsorbed H or volume absorbed H?
- Surface adsorbed and volume absorbed Hydrogen could be distinguished

Angew. Chem. 47, 9289 (2008)

Another study was the hydrogen adsorption by palladium nanoparticles. This paper was published in Angew. Chem. You can imagine the kind of studies people are doing because the kind of information that you get from these techniques are unique. It is not a routine analysis but it is a very important technique, very, very useful information you get so let me try to explain this what is happening. These palladium nanoparticles are used as a catalyst for the hydrogenation of alkenes. So they wanted to study whether it is the hydrogen is getting adsorbed on the surface of nanoparticles or the bulk, there will be some hydrogen in the bulk of the nanoparticles. So what is the role of surface adsorbed hydrogen or and volume adsorbed hydrogen. So what they found that by this technique, NRA, one could distinguish between the surface adsorbed hydrogen and volume adsorbed hydrogen. You can see here the depth profile at a different function of the hydrogen pressure.

They studied 10^{-7} mbar to 10^{-2} mbar and the surface adsorbed hydrogen and the bulk hydrogen could be distinguished. You can deconvolute this depth profile of hydrogen and then as a function of the hydrogen pressure they found that the surface adsorbed hydrogen plays a role only at low pressure. High pressure, the bulk hydrogen also starts playing its role. So I will not go into the details. The point I wanted to emphasize was that you can study the role of surface and bulk hydrogen in understanding the particular chemical reactions that are taking place. This is the kind of study people are doing.



Particle induced gamma emission (PIGE)

Nuclear reactions with low Z elements

Element	Reaction	Eγ (keV)
Li ✓	$^{7}Li(p,p\gamma)^{7}Li$	478
B ✓	$^{10}B(p,\alpha)^{7}Li$	429
F ✓	$^{19}F(p,p\gamma)^{19}F$	110.2
Na ✓	$^{23}Na(p,p\gamma)^{23}Na$	440
Mg ✓	$^{25}Mg(p,p\gamma)^{25}Mg$	585
Al ✓	$^{27}Al(p,p\gamma)^{27}Al$	1013
Si ✓	$^{29}Si(p,p\gamma)^{29}Si$	1779
P ✓	$^{31}P(p,p\gamma)^{31}P$	1266
S ✓	$^{32}S(p,p\gamma)^{32}S$	2237

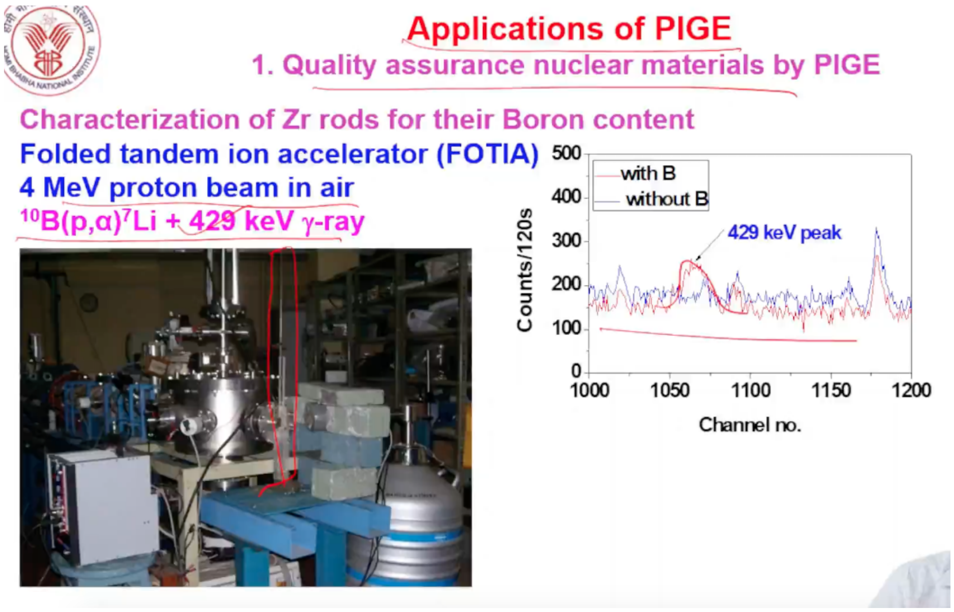
Ion beam analysis facility at FOTIA, BARC

Now I will come to another technique of nuclear reaction analysis called the particle induced gamma emission (PIGE) where some of our colleagues have done a lot of work in this area. So at the Bhabha Atomic Research Center we have an accelerator called FOTIA, folded tandem ion accelerator. It is a 6 million volt terminal, tandem accelerator. And so you can have (1+1)*6= 12 MeV proton beam. But normally you get 5 MeV proton beam and you can have heavier beams also, carbon, oxygen and so on.

So this is the photograph of the setup. We have a scattering chamber here, 50 centimeter diameter scattering chamber and for PIGE you have a HPGe detector at 90-degree and you have the target ladder. You can bring different targets in the position of the beam by raising and lowering this target holder. And the chamber is at vacuum because you may require to have, suppose you are doing RBS, you are determining the charged particles. So there are different nuclear reactions with low Z elements induced by mostly protons but there can be reactions induced by deuteron on sodium can be done. And so what is important is that you should have a suitable gamma ray in the range 100 to 1000 MeV or so.

So for low Z materials you will find lithium, boron, fluorine, sodium, magnesium, aluminum, silicon, phosphorus, sulfur. All of them have a suitable nuclear reaction with their isotopes and the gamma energy are also well resolved. So if you irradiate a sample with the proton beam of the order of 2 MeV and detect the gamma ray emitted by this reaction using a Germanium detector, you can do the determination of concentration of the elements present in a target material. So mostly these lighter elements, because once you go to higher target isotopes, let us say you want to do for iron, cobalt, nickel, so what happens? First of all, you have to cross the Coulomb barrier, you have to have higher energy. Once you have the high energy for proton beam, then the compound nucleus will be formed with higher excitation energy and so it will evaporate neutrons. So you will not have one reaction, you will have multiple reactions (p,n) (p,2n) (p,3n) and also you may have (p,p) (p,α) and so on with lighter ones. So for higher mass nuclei, the gamma spectra will be very complicated. Whereas for low mass nuclei, there are only simple, these are like inelastic scattering or low lying states are involved in the nuclear reaction. So gamma ray spectra are not very complex.

So PIGE is a very simple technique. You are not going for depth profiling because you are using protons. So the stopping power is not very high, you have a very low dE/dx, so resolution is not good. As I mentioned in the RBS also, that experiment for 4 MeV proton beam, that resolution was one micron. So normally you would look for a nanometer scale depth resolution to do depth profiling.



Applications of PIGE

1. Quality assurance nuclear materials by PIGE

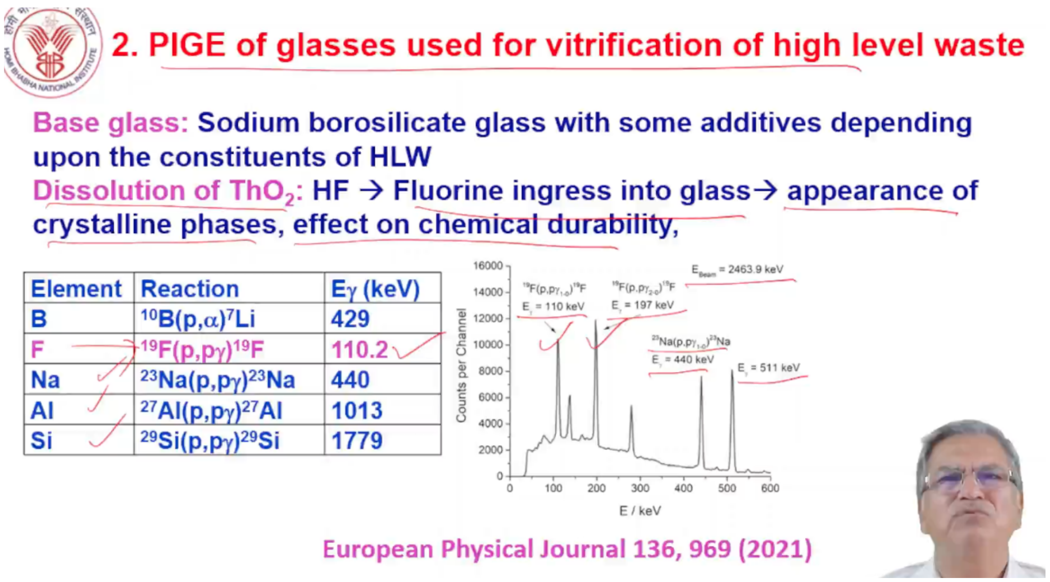
Characterization of Zr rods for their Boron content

Folded tandem ion accelerator (FOTIA)

4 MeV proton beam in air

$^{10}B(p,\alpha)^{7}Li$ + 429 keV γ-ray

So this is one of the experiments we did at FOTIA, quality assurance of nuclear materials. As I mentioned, these are not meant for routine analysis, where we just want to determine concentrations. This is a specific application that certain rods, they contain boron and certain rods they do not contain. So you want to quantify them. You want to know that this rod contains boron or not. And so you use the nuclear reaction, $^{10}B(p, \alpha)^{7}Li$ and there is a 429 keV gamma ray is emitted and that is measured using this germanium detector. And the target, actually target is very long. So you cannot keep it inside the chamber because chamber height is only one or two feet. So what you do, you take out the proton beam in air by isolating the chamber with a tantalum foil and proton beam is not loosing much energy in air. So you can put this big sample at the surface and then determine the gamma ray that are emitted in the nuclear reaction. You can see here the 429 keV for the sample which contains boron and without boron you do not see a peak. So this is a kind of experiment where you do quality assurance experiments, means the manufacturer of the rods want to assure the user that this does not contain boron or this contains boron. So you have to provide a certificate of QA that this is meeting the requirement. So that is the kind of experiment people do using PIGE.



2. PIGE of glasses used for vitrification of high level waste

Base glass: Sodium borosilicate glass with some additives depending upon the constituents of HLW

Dissolution of ThO_2: HF → Fluorine ingress into glass → appearance of crystalline phases, effect on chemical durability,

Element	Reaction	Eγ (keV)
B	$^{10}B(p,\alpha)^{7}Li$	429
F	$^{19}F(p,p\gamma)^{19}F$	110.2
Na	$^{23}Na(p,p\gamma)^{23}Na$	440
Al	$^{27}Al(p,p\gamma)^{27}Al$	1013
Si	$^{29}Si(p,p\gamma)^{29}Si$	1779

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This is another important work for PIGE of glasses used for vitrification of high level waste. So again, let me try to give you some background to this study. As I was discussing in the previous one also that borosilicate glass is used to vitrify the high level waste. The high level waste is generated during the reprocessing of the spent nuclear fuel and there will be different types of fuels. And one of the fuels now for the future is thorium, thorium based fuels and that will contain ThO_2. Now when you dissolve thorium, particularly sintered thorium, very difficult to dissolve. And so to dissolve thorium there may be use of hydrofluoric acid, HF. HF is very reactive acid. And so when you do reprocessing, ultimately some fluorine may get into the glass matrix when you are immobilizing the HLW, you are supposed to remove fluorine, but suppose some fluorine is left, then this fluorine in the glass matrix may lead to appearance of the spline phases, calcium fluoride or others may precipitate out, like rare earth fluorides may precipitate out.

And so you want to know what is the tolerance of fluorine in your glass. Even the fluoride can affect the chemical durability of the glass because it may enhance the leachate. And so for the long term performance that this glass will retain the efficient products and actinides, it is important to again ensure that whatever content of fluorine is there in the glass, it is safe, it is within the tolerance. Though you can determine fluorine by ion selective electrodes, very simple, but then you have to dissolve the glass and do the study. So that is a very tedious and suppose you have multiple samples. Here is a very simple technique. You take the glass as it is, non-destructively just bombard with the proton beam for a few minutes, and the gamma spectrum tells you what is the fluorine content. So again, the same reactions I have shown for the constituents of the glass. You can have sodium borosilicate, it will have sodium, aluminum, silicon, moron, but there may be some extent of alumina also.

And if there is a fluorine, then you will get this 110 keV gamma. So in the one shot, all the constituents of the glass will give you the gamma spectrum. Again, there is one more reaction of fluorine with the proton, (p, p'γ). You have 197 keV, sodium 440 keV, there is 511keV gamma ray also. So by 2.4 MeV proton beam, you can determine the concentration of not only the constituent of the glass, like silicon, aluminum, sodium, boron, you can also determine the fluorine content and thereby quantify the fluorine content.

There is a threshold of 1%. You cannot have more than 1% of fluorine in the glass. You can quickly do the experiments and find out what the content of fluorine is. So I just gave you some of the examples of NRA and PIGE. Due to lack of time, I could not give more examples, but the point I wanted to emphasize was that these nuclear electrical techniques are not meant for routine analysis. They are meant for a very specific application in high technology areas. And it is not the only technique you will be using. There can be a combination of other techniques and to understand the process, to understand the mechanism also to qualify the high technology material.

So there are many other examples, but I do not have time to describe, but I hope that I am able to bring the point that ion beams, the low energy ion beams can be used in the analysis of materials which are being used in many, many applications. So that is all I have to say. Thank you very much.