X-Ray Crystallography
Prof. R. K. Ray
MN Dastur School of Materials Science and Engineering
Indian Institute of Engineering Science and Technology, Shibpur
Department of Metallurgical and Material Engineering
Indian Institute of Technology, Madras

Lecture - 24
Chemical Analysis by X-Ray Fluorescence

So far we have discussed different methods by which qualitative and quantitative phase analysis can be carried out by X-ray diffraction. Now I will tell you a method by which elemental chemical analysis can also be done using X-ray diffraction. The method is known as chemical analysis by X-ray fluorescence.

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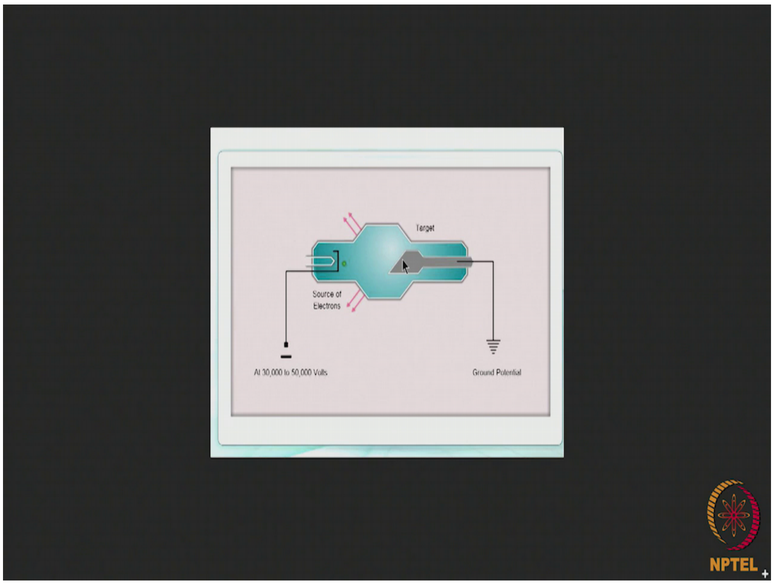

As we are all aware in an X-ray tube we have a target and we have a source of electrons. Now if a target is made up of a particular element then the striking electrons will produce in addition to the white radiation; characteristic radiations also depending on the excitation voltage.

Say if we have the element a that makes up the target then we will have the characteristic radiations of a notably k alpha and k beta radiations of a coming out of the X-ray machine. Now these characteristic radiations as a name implies are characteristic of the target material itself. That means, for a particular target made up of a particular element the characteristic radiations produced will have particular lambda values. Now this phenomena really tells us that we can use the X-ray machine itself for elemental chemical analysis.

Say for example, if we want to qualitatively identify an element a then we make a target made out of the element A and use it within an X-ray machine. So, when the excitation voltage is reached we will find k alpha and k beta radiations of a will come out. So, by analyzing these k alpha and k beta radiations we can easily say that- yes the material is made up of the element A. Again if there are more than one element say two elements: a and b which make up the target we will get the characteristic k alpha and k beta radiations, not only from element A but also from element B. Now analyzing the output from the target we can identify the wavelengths of those characteristic radiations and that will give us an idea about the identity of the elements present in the target material

It is not only a qualitative identification that you can do of a chemical species by making it the target in an X-ray machine, but by comparing the intensity of the k alpha or k beta radiations of a particular element in a mixture which makes up the target material. And if we compare it with the corresponding wavelength from a pure substance it is also possible to do some quantitative chemical analysis. But you see, if we want to make routine chemical analysis and if we want to use the elements to be made as target in an X-ray machine the process become very cumbersome.

Because every time we have to demount the target change into a new target etcetera, etcetera. So, that is the reason why chemical analysis you know by using this method cannot is not practiced nowadays. On the other hand what we do we use the element or a group of elements present in a substance as to be bombarded with X-ray from an X-ray machine and

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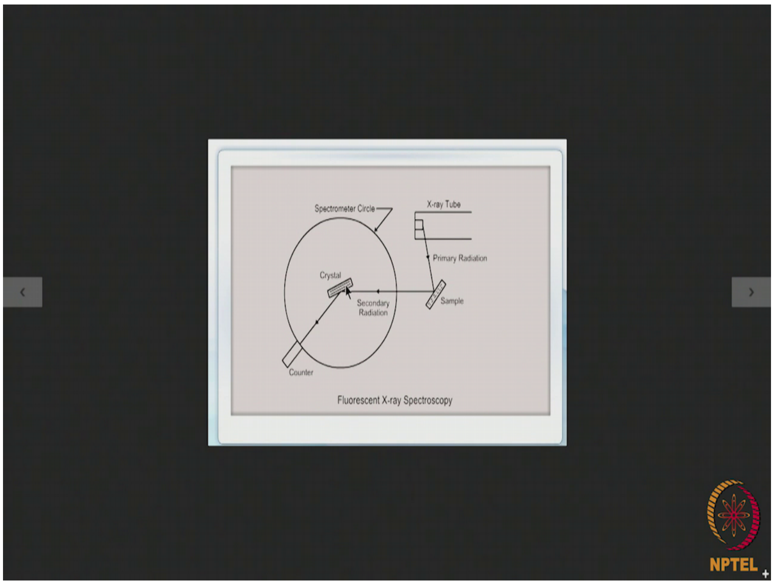

Fluorescent X-ray Spectroscopy

This bombardment of the sample by primary electron primary X radiation from the X-ray tube will produce the fluorescent radiation or secondary radiation.

You see if the excitation voltage you know if the primary X radiation has got wavelengths less than the k absorption edge wavelength of the elements in the sample then what will happen the k characteristic radiations of the elements in the sample they will be produced and those are known as the fluorescent X-rays. So, due to the impact of the primary X radiation on the sample made up of different elements the fluorescent characteristic radiations will be produced from those elements which is also known as the secondary radiation.

Now the group of characteristic radiations that are produced from the sample can be analyzed using a crystal in which a particular atomic plane is made parallel to the surface of the crystal and by rotation of the crystal or movement of the crystal around the central point it is possible to diffract the different wavelengths present in the fluorescent radiation at different points to be counted by the counter. So, in this way it is possible to obtain the intensities of the different characteristic radiations coming out from the sample by using this analyzing crystal and the counter.

Then it is a question of identifying know which elements produce that those kind of characteristic radiations. So, this is the basis of chemical analysis, by X-ray fluorescent method, we use such a setup for carrying out chemical analysis using an X-ray tube and also a diffractometer the arrangement is known as an X-ray spectroscopy.

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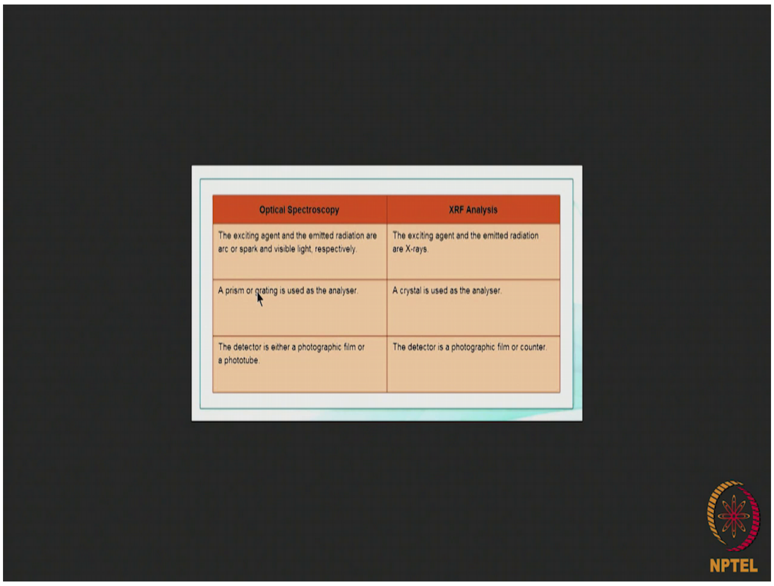

Optical Spectroscopy	XRF Analysis
The exciting agent and the emitted radiation are arc or spark and visible light, respectively.	The exciting agent and the emitted radiation are X-rays.
A prism or grating is used as the analyser.	A crystal is used as the analyser.
The detector is either a photographic film or a phototube.	The detector is a photographic film or counter.

So, in this case, it is fluorescent X-ray spectroscopy. Now optical spectroscopy has been known for a long time and routine chemical analysis used to be carried out by optical spectroscopy.

And even now it is being carried out in many plants and laboratories, but now gradually X-ray fluorescent analysis or X-ray spectroscopy is also come into existence and now it has established itself as a very important method of chemical analysis both qualitative and quantitative in different laboratories and industrial establishments. Now what is the basic difference between optical spectroscopy and X-ray fluorescence analysis or XRF analysis the excitation agent in case of an optical spectroscope are arc or spark and the emitted radiation is visible light on the other hand in case of the XRF analysis the exciting agent and the emitted radiation both are X-rays.

Now, in optical spectroscopy a prism or grating is used as the analyzer. On the other hand in XRF analysis a crystal is used as the analyzer. The detector is either a photographic film or a photo tube in case of optical spectroscopy and in case of XRF analysis the detector is a photographic film or a counter depending on the type of analyzing crystal used X-ray spectroscopy can be of 3 types namely.

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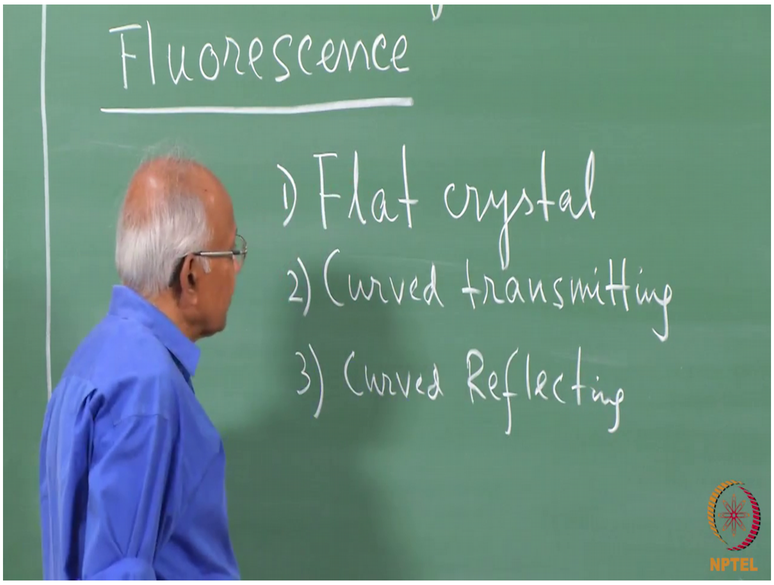

Fluorescence

1) Flat crystal
2) Curved transmitting
3) Curved Reflecting

Flat crystal type; the second one is curved transmitting type and the third one is the curved reflecting type. So, X-ray spectrometers can be of 3 types X-ray fluorescence spectrometers of our can be of 3 types the flat crystal type the curved transmitting type.

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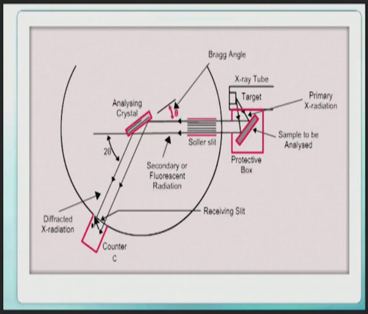

And the curved reflecting type. Now in the flat crystal type as you can see here from the X-ray tube X-rays are made to in the incident on the sample to be analyzed. So, these X-rays are what are known as the primary X-rays. Now these X-rays allow to pass through a solar slit in order to make the rays as parallel as possible these are allowed to fall on the analyzing crystal and depending on the angle at which these rays are incident these are diffracted into the counter. So, if there are several secondary X-rays or florescent X-ray wavelengths produced from this sample then one by one by changing the position of the analyzing crystal making different angles Bragg angles theta.

We can have the diffracted radiation intensity counted at different locations on the diffractometer circle by moving the counter. So, if the counter moves by an angle theta then if the analyzing crystal moves by an angle theta the counter moves by an angle 2 theta. So, whichever fluorescent or secondary X-ray wavelengths are able to diffract according to Bragg law. Those will be diffracted and those will be recorded in the counter normally sodium chloride or lithium fluoride crystals are used for analyzing purpose in the second type of X-ray fluorescence spectrometer known as the curved transmitting type this is the kind of arrangement we have.

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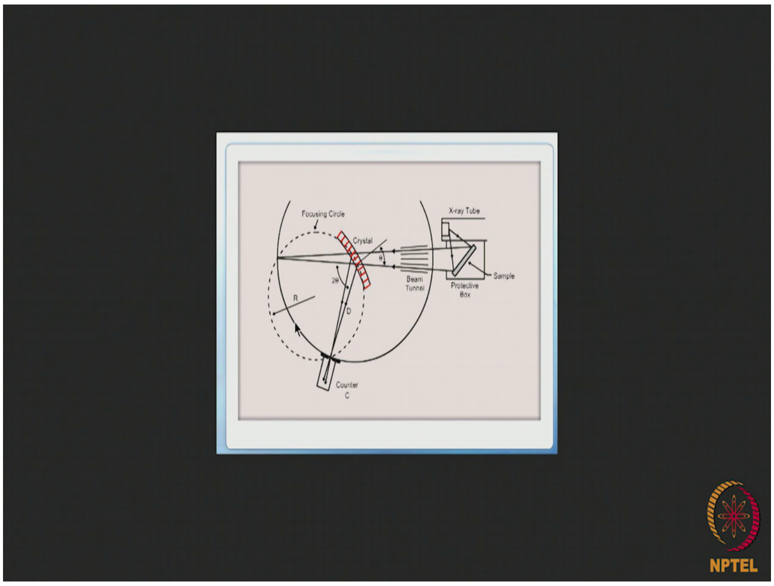

Here the fluorescent radiation or the secondary radiation produced from the sample, they are made to converge at a point on the focusing circle over here and the diffracted radiation from the transverse planes of the curved crystal are brought to a focus at the counter and the counter opening also lies on the focusing circle. So, the crystal or the curvature of the crystal can be changed and by doing that we can have different wavelengths of the fluorescent or secondary X radiation diffracted at different locations on the diffractometer circle to be measured by the counter.

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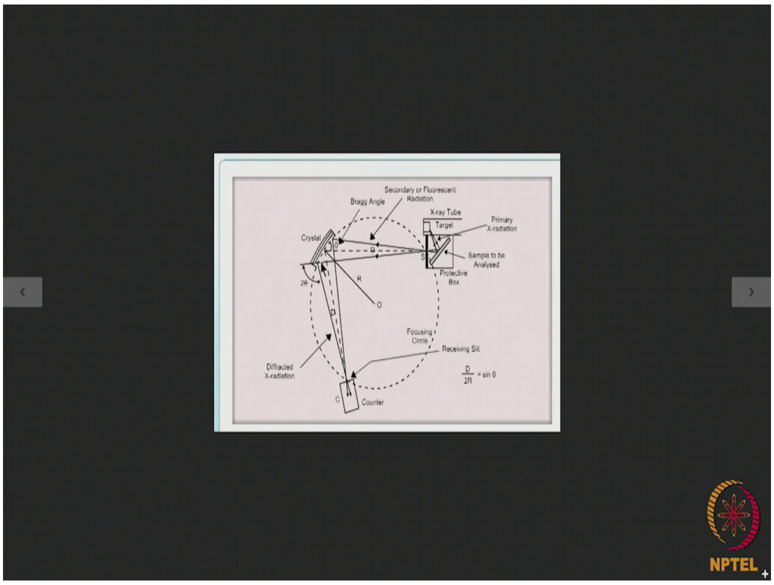

Now, in this method mica is a very general type of material which is used for analyzing purpose then comes the third type of X-ray fluorescent spectrometers this is the curved reflecting type as we can see here, here we use a slit to make the X radiation divergent, the fluorescent X radiation divergent and it falls on the crystal then it gets diffracted and the intensity of the diffracted radiation is measured by changing the curvature of the crystal. We can make different wavelengths of the fluorescent radiation to be diffracted at different locations on the diffractometer circle on the counter. Now in this case also we use sodium chloride or lithium fluoride crystal as the analyzer.

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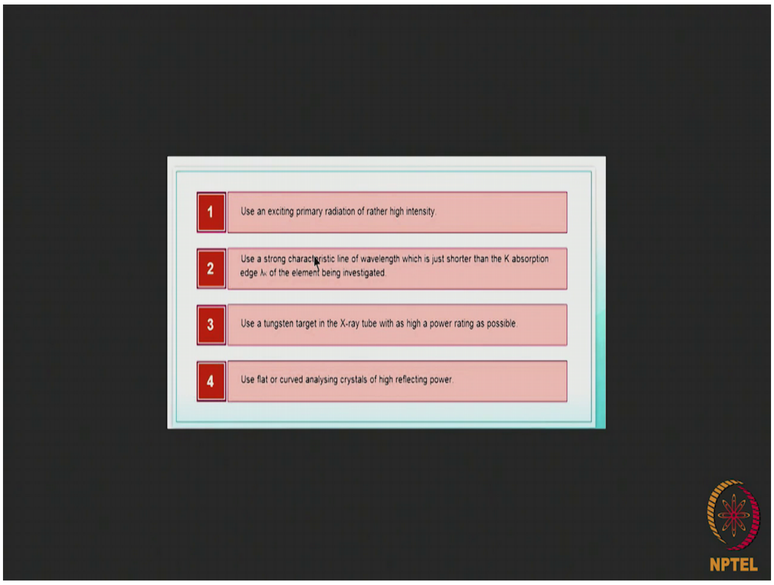

1 Use an exciting primary radiation of rather high intensity.

2 Use a strong characteristic line of wavelength which is just shorter than the K absorption edge λ_K of the element being investigated.

3 Use a tungsten target in the X-ray tube with as high a power rating as possible.

4 Use flat or curved analysing crystals of high reflecting power.

Now, while doing extra spectroscopy we must use an exciting primary radiation of rather high intensity why otherwise as you always know the diffracted intensity is very very low. So, if the primary radiation is of lower intensity the final diffracted intensity may be quite low and it may be difficult to detect the presence of some elements in the florescent radiation.

We should use strong characteristic line or wavelength which is just shorter than the k absorption edge of the element being investigated otherwise the florescent radiation will not be produced. We must use a tungsten target in the X-ray tube with as high power rating as possible. In fact, if tungsten is not available when molybdenum can be used and we must use flat or curved analyzing crystals of high reflecting power the most important.

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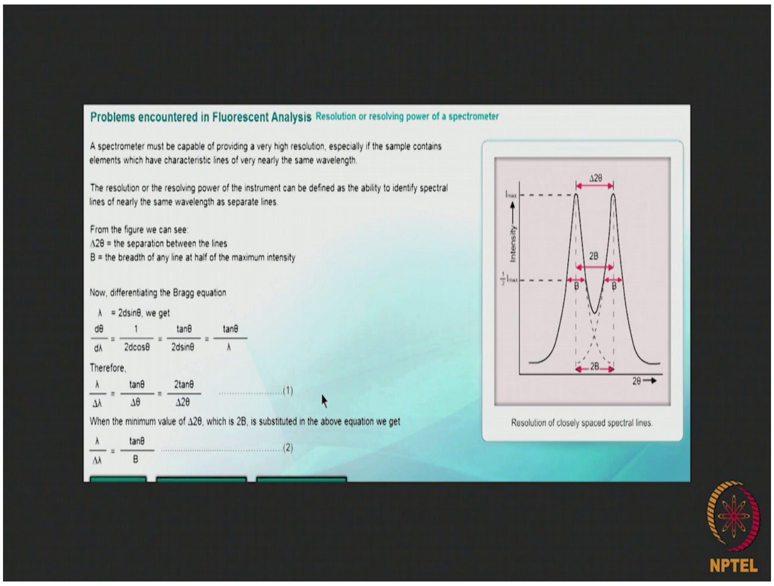

Problems encountered in Fluorescent Analysis Resolution or resolving power of a spectrometer

A spectrometer must be capable of providing a very high resolution, especially if the sample contains elements which have characteristic lines of very nearly the same wavelength.

The resolution or the resolving power of the instrument can be defined as the ability to identify spectral lines of nearly the same wavelength as separate lines.

From the figure we can see:
$\Delta 2\theta$ = the separation between the lines
B = the breadth of any line at half of the maximum intensity

Now, differentiating the Bragg equation

$\lambda = 2d\sin\theta$, we get

$$\frac{d\theta}{d\lambda} = \frac{1}{2d\cos\theta} = \frac{\tan\theta}{2d\sin\theta} = \frac{\tan\theta}{\lambda}$$

Therefore,

$$\frac{\lambda}{\Delta\lambda} = \frac{\tan\theta}{\Delta\theta} = \frac{2\tan\theta}{\Delta 2\theta} \quad \text{..........(1)}$$

When the minimum value of $\Delta 2\theta$, which is 2B, is substituted in the above equation we get

$$\frac{\lambda}{\Delta\lambda} = \frac{\tan\theta}{B} \quad \text{..........(2)}$$

Resolution of closely spaced spectral lines.

Attribute of an X-ray spectrometer is the resolution or resolving power say for example, we have 2 elements a and b present in our sample if it. So, happens that the characteristic radiations produced from A and B are very very close together in norm in their wavelength unless the equipment has got the right kind of resolving power. Those 2 wavelengths may not be distinguished as 2 separate ones, but they merge into one.

So, resolution or resolving power must be high to resolve 2 closely spaced characteristic wavelengths as distinct wavelengths. Now in the figure suppose this is the profile of a characteristic wavelength; wave characteristic line. This is the profile of a nearby characteristic line suppose the half intensity breadth of both is equal to B. This axis is 2 theta. This is the intensity the angular separation between the 2 characteristic lines is say delta 2 theta and this distance can be taken as 2 B from you know similar triangle chronology. Now if we differentiate the Bragg equation lambda is equal to 2 d sin theta.

We can find out d theta by d lambda will be equal to one upon 2 d cosine theta equal to tan theta by 2 d sin theta which is equal to tan theta by lambda. So, we can write lambda by delta lambda is equal to tan theta by delta 2 theta when the minimum value of delta 2 theta which is 2 B is substituted in the above equation. We get lambda by delta lambda is equal to tan theta by B. Now lambda by delta lambda is what is known as the resolving power or resolution of the spectrometer here lambda is the average value of the 2 wavelengths of the 2 characteristic radiations and delta lambda is the difference in the wavelength of the 2 radiations which are close by.

So, we find that the resolution of an X-ray fluorescence spectrometer will become higher when theta becomes larger not only that this resolution resolving power will become higher when B decreases. So, if we use a crystal with smaller plane spacing or smaller d; smaller d means theta will be high. So, they will have a greater resolving power required to separate 2 spectral lines.

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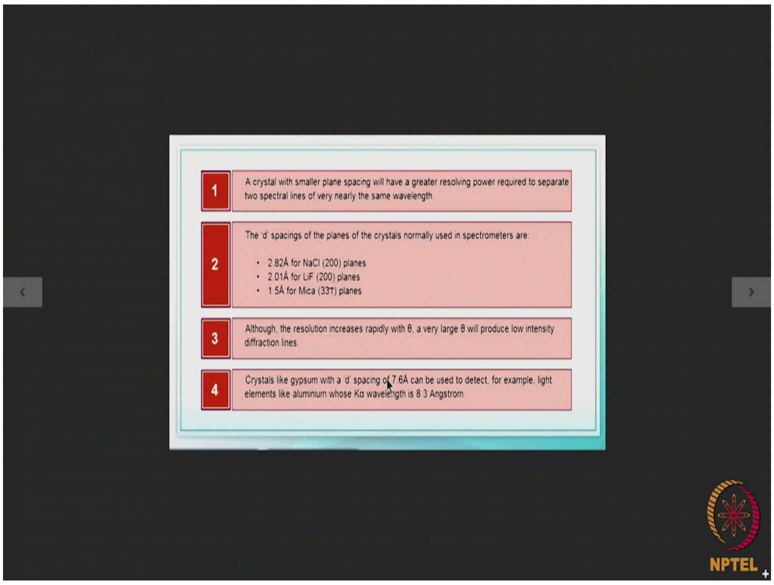

1 A crystal with smaller plane spacing will have a greater resolving power required to separate two spectral lines of very nearly the same wavelength.

2 The 'd' spacings of the planes of the crystals normally used in spectrometers are:

- 2.82Å for NaCl (200) planes
- 2.01Å for LiF (200) planes
- 1.5Å for Mica (33$\bar{1}$) planes

3 Although, the resolution increases rapidly with θ, a very large θ will produce low intensity diffraction lines.

4 Crystals like gypsum with a 'd' spacing of 7.6Å can be used to detect, for example, light elements like aluminium whose Kα wavelength is 8.3 Angstrom.

So, very nearly the same wavelength because smaller d means higher theta, so, we have seen that the resolution resolving power will increase as theta increases.

Now, as I have already mentioned the materials which are used the crystals which are used in spectrometers are sodium chloride 2 0 0 planes of sodium chloride having a d spacing of 2.82 angstrom lithium fluoride the 2 0 0 planes of lithium fluoride having a d spacing of 2.01 angstrom and 3 3 bar 1 planes of mica having a d spacing of 1.5 angstrom we have to remember that although the resolution increases rapidly with theta a very large theta will produce low intensity diffraction lines and this is not good for chemical analysis.

Now, crystals like gypsum with a d spacing of seven point six angstrom can be used to detect for example, light elements like aluminum whose k alpha wavelength is 8.3 angstrom. Now when it comes to qualitative chemical analysis by X-ray spectroscopy the output from the counter is fed to a chart recorder and in the chart recorder.

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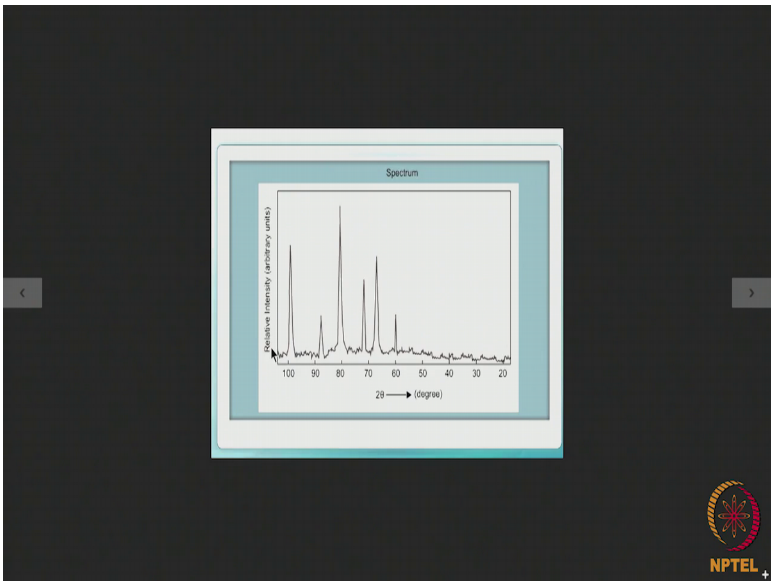

We record the relative intensity of the characteristic lines in the fluorescent radiation versus 2 theta. Now in order to do qualitative analysis; that means, identification of the elements we have to have 2 things with us one a table showing corresponding lambda and 2 theta values for the analyzing crystal once we have got that we can find out for every line here what is the lambda that the analyzing crystal has diffracted. So, all these lambdas will be known at the same time we must have a table of all the wavelengths of characteristic radiations.

Say k alpha and k beta radiations from different elements once we know that it becomes a simple comparison of the lambdas obtained in the spectrometer with the lambdas of the characteristic radiations of the different elements.

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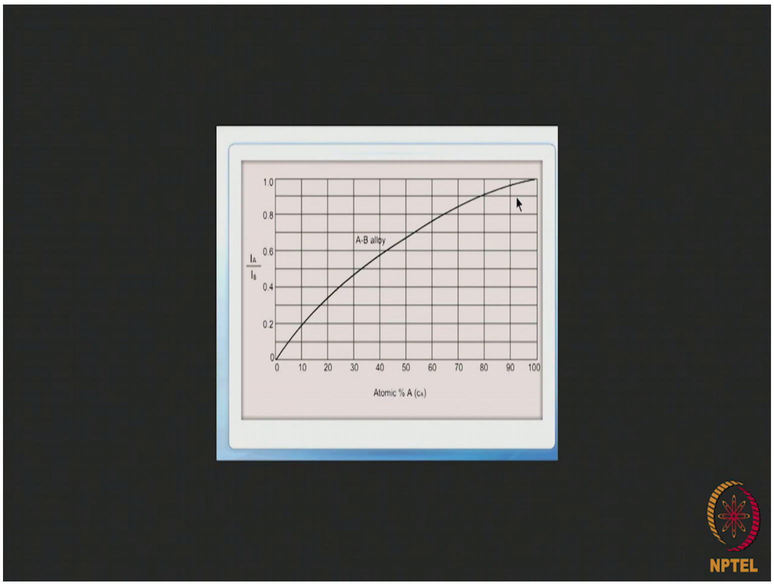

So, A 1 to 1 match will automatically give us an idea of which element is practically present in the sample. Now when it comes to quantitative chemical analysis by X-ray fluorescence say we have an alloy made up of 2 elements A and B; what we do? We make alloys of different compositions of A and B say for example, one with a ten atomic percent a twenty atomic percent a 30-40 etcetera, etcetera.

In each case we find out what is the intensity of a particular characteristic line coming out of a then compare it with the intensity of the characteristic line coming out from a pure sample of a then we can plot I A by I S. I A is intensity of the characteristic line from A and I S is intensity of the same characteristic line of pure A and if we plot it, we get a curve of this time. it is very difficult to predict the shape of the curve from theoretical consideration. In fact, that is the reason why you have to measure you have to take a number of alloys of A and B and construct this plot.

If we have an unknown sample made up of A and B then again by measuring I A by I S for A, we can simply find out what should be the amount of A in that sample. So, this is how quantitative chemical analysis can be performed the shape of this curve will depend very much on the presence of other elements there are 2 different phenomena which influence the shape of this plot as we have shown here.

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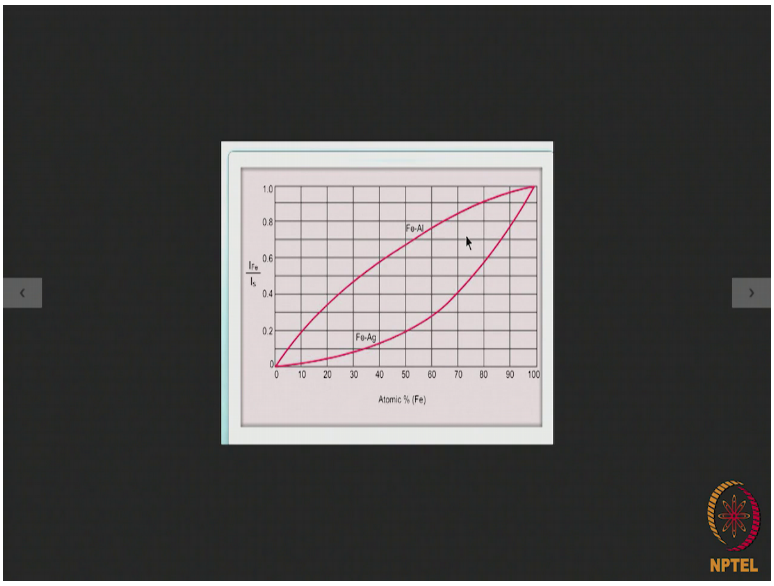

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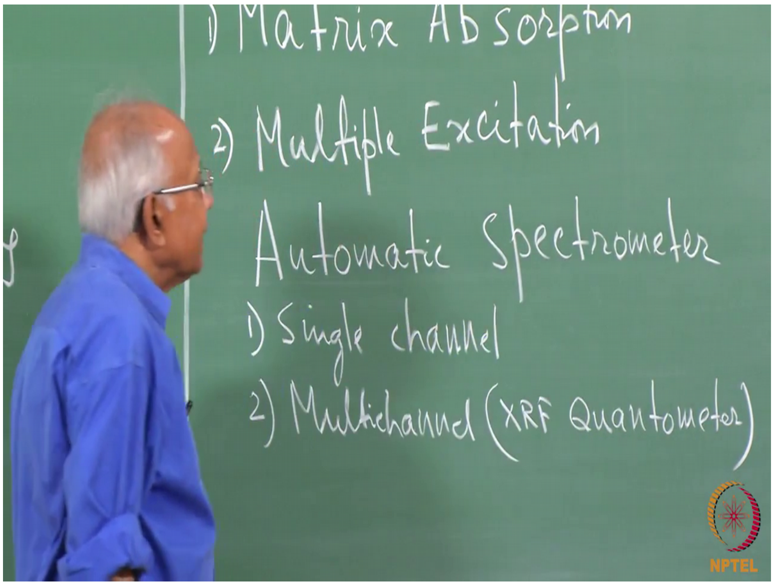

1) Matrix Absorption

2) Multiple Excitation

Automatic Spectrometer

1) Single channel

2) Multichannel (XRF Quantometer)

And those are known as matrix absorption and multiple excitation. Now in this figure we have plotted intensity of a characteristic line of iron divided by intensity of the same characteristic line of iron present in a standard sample this upper curve is for iron aluminum based alloys the lower curve is for iron silver based alloys.

Now, we see that for the same amount of iron in both iron silver and iron aluminum the IFE by I S value is much higher for FEAL than for FEAG why this is. So, the reason is simple iron silver has got a much higher coefficient of absorption than iron aluminum as a result the characteristic radiation of iron in iron aluminum alloys will show a much higher intensity than in an iron silver alloy of the same iron content. Now comes a second factor which is multiple excitation you see here we have plotted IFE by I S for iron nickel alloys of different compositions.

Now, if we look at this plot and when you go back to the previous one iron nickel the behavior the plot is very similar to f e l although coefficient of absorption wise iron.

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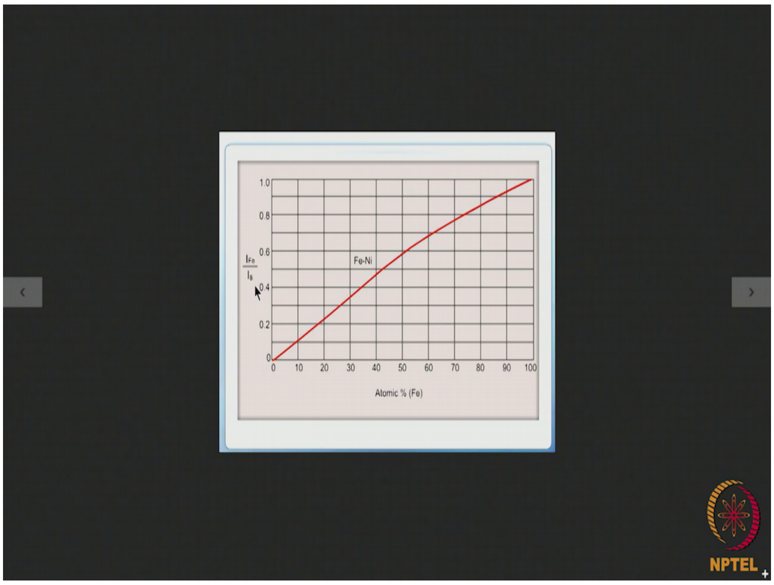

Nickel is close to iron silver, but how come the iron nickel plot becomes similar to iron aluminum here the reason is again simple when the primary X radiation falls on iron nickel, iron k radiation will be excited from iron and nickel k radiation will also be excited from nickel. Now the nickel k radiation that is excited that will be those radiations will again produce secondary or florescent radiation from iron. So, as a result the intensity or the characteristic line of iron will get enhanced as a result this plot instead of being coming over here it goes over there.

Because the intensity of the characteristic fluorescent radiation from iron gets enhanced due to the due to multiple excitation XRF method is used widely in industries. Nowadays the types of equipment that are used are known as automatic spectrometers there can be 2 variations of an automatic spectrometer the single channel type and multi channel type the second type is also known as X-ray fluorescence quantometers. So, X-ray fluorescence equipments are used widely as I said in industry for routine chemical analysis and for process control. Now in the single channel type machines the arrangement is shown here.

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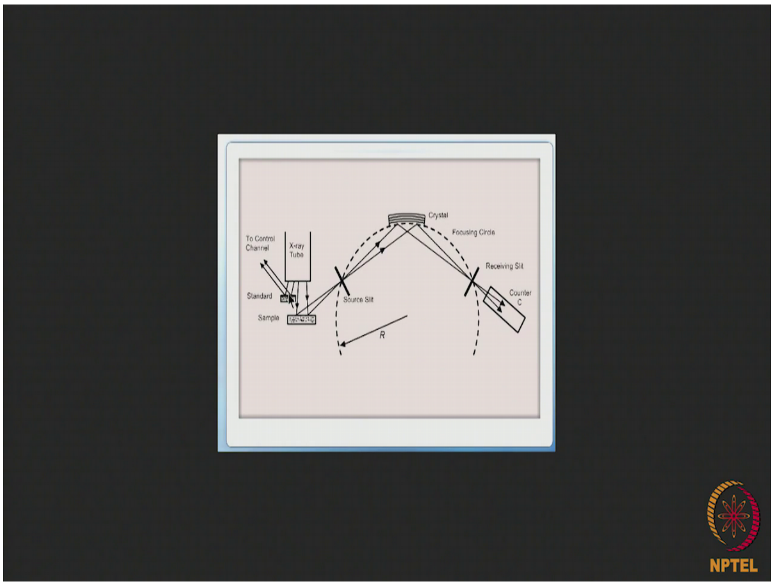

We have the X-ray tube primary X radiation is allowed to fall on the sample. So, the primary X radiation will produce the fluorescent or secondary X-rays from all the elements that are present in the sample and those will pass through the source slit and fall on the analyzing crystal as and when Bragg law is satisfied. You will get a diffracted beam and that particular wavelength will be diffracted. Now comparing that wavelength with the k characteristic radiations of different elements it is possible to figure out which element was that. Now in this equipment there is also a provision for the X-ray coming from the same X-ray tube to fall on a standard of the element concerned.

So, by comparing the intensity of the fluorescent radiation from the particular element with the fluorescent radiation coming from a standard of that element quantitatively it is possible to say how much of that particular element is present in this sample. Now for different elements different k characteristic radiations will be produced which can be brought to diffraction by different Bragg angles and as a result in this equipment it is possible to count a maximum of about 12 elements one after the other. So, for a particular element the counter is placed in the right position to count the diffracted radiation for a sufficient long time to give a good measure of the diffracted intensity.

Then it is moved along this circle to another position where the fluorescent radiation from a different element will get diffracted and again it will count the diffracted radiation over here in this way using the same equipment in a successive manner one after another we can count up to about 12 elements. Now this is called a single channel type X-ray spectrometer in a multi channel type machine what we have is a central X-ray generator there will be a central X-ray generator and this type of arrangement about eight such arrangements are positioned around the X-ray source.

So, there will be X-ray source of the central position and eight such arrangements of crystal and counter will be arranged around the central X-ray machine. So, about seven elements can be analyzed simultaneously by this process again the eight channel will be available for measuring the intensity of a characteristic line coming from the corresponding standards. So, XRF or X-ray fluorescence equipments are used or be used more and more to analyze different kinds of alloys say alloy steels or non ferrous alloys then oils then ores gasoline etc for liquid we you can produce you can have special holders made up of some other non absorbing material and used in the X-ray.

Now, X-ray fluorescence is used not only in industry it is used more and more in forensic sciences these days. So, it has got a wide application for both qualitative and quantitative determination of quantitative chemical analysis of materials.