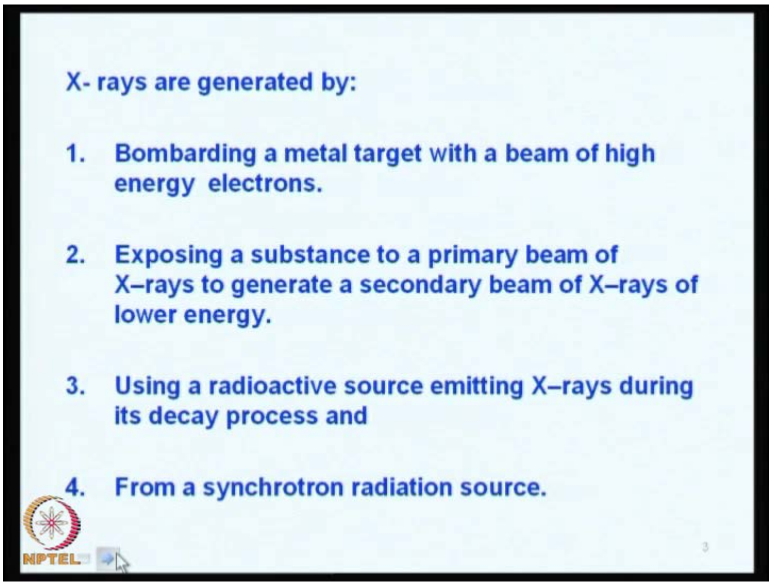
Modern Instrumental Methods of Analysis

Prof. J. R. Mudakavi
Department of Chemical Engineering
Indian Institute of Technology, Bangalore

Lecture No. # 15
X-Ray Analytical Techniques-1
Instrumentation

Welcome to the fifteenth lecture of our course. In the last class, we had discussed about X-rays fluorescence; just for continuity sake I will quickly go through about some properties of the X-rays what we had discussed earlier only. So, basically X-rays are short wave length electromagnetic radiations produced by the deceleration of high energy electrons or by it can also be produced by transition electronic transition of the electrons in the inner orbital's of the atoms. The X-rays have a wavelength range of 10 raise to minus 5 angstrom units to 100 angstrom. Conventional X-rays spectroscopy is largely confined to 0.1 angstrom to 25 angstrom units.

(Refer Slide Time: 01:16)



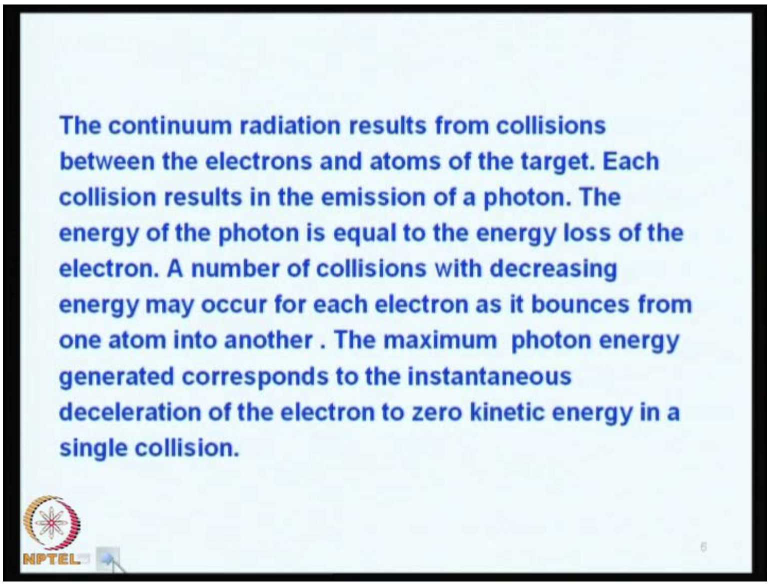
X- rays are generated by:

1. Bombarding a metal target with a beam of high energy electrons.
2. Exposing a substance to a primary beam of X–rays to generate a secondary beam of X–rays of lower energy.
3. Using a radioactive source emitting X–rays during its decay process and
4. From a synchrotron radiation source.

So, you can generate the X-rays by bombarding a metal target a beam of high energy electrons. You can also expose a substance to a primary beam of X-rays to generate secondary beam of X-rays of lower energy. You can use radioactive sources, some of the radioactive sources continuously emit X-rays like curium. By during it is and the adequate process and you can also generate X-rays from a synchrotron radiation source. So, the X-ray tube generates both continuum spectra as well as line spectra. Electrons are produced at a heated cathode and accelerated towards a metal anode with a potential difference of about 100 kilo volts.

And upon colliding with the anode part of the energy of the incident beam is converted into X-rays, and the continuum X-rays spectrum exhibits a well defined short wave length limit, which is characteristic of the applied voltage, but not of that of the chemical what you have element. So, you can see that if you use 50 kV, you will get 0.2; and 40 kV, we can get X-rays only starting from about 0.3 kV etcetera. These things we have seen in the last class with different applied potentials.

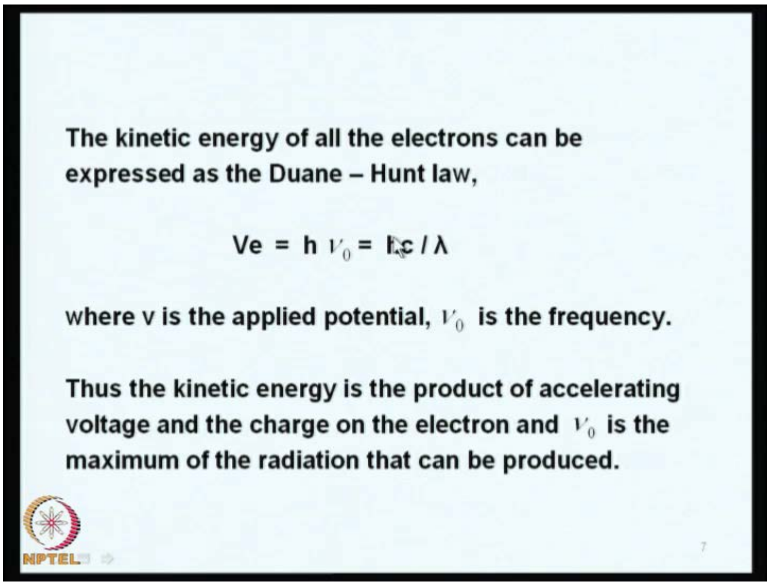
(Refer Slide Time: 02:50)



The continuum radiation results from collisions between the electrons and atoms of the target. Each collision results in the emission of a photon. The energy of the photon is equal to the energy loss of the electron. A number of collisions with decreasing energy may occur for each electron as it bounces from one atom into another . The maximum photon energy generated corresponds to the instantaneous deceleration of the electron to zero kinetic energy in a single collision.

So, the continuum radiation results basically from the collision between the electrons and the atoms of the target. Each collision results in the emission of a photon. The energy of the photon must equal to the loss of the energy when it collides with an electron. So, the number of collision with decreasing energy may occur for each electron as it bounces from one atom to another atom and this gives raise to continuum spectrum. So, the maximum photon energy generated corresponds to the instantaneous deceleration of the electron to zero kinetic energy - that is the basic difference. And the kinetic energy of all the electrons can be expressed as Duane hunt law - that is v e that is product of the applied potential multiplied by the electronic charge gives you radiation X radiation and the same h nu zero say notations.

(Refer Slide Time: 04:14)



The kinetic energy of all the electrons can be expressed as the Duane – Hunt law,

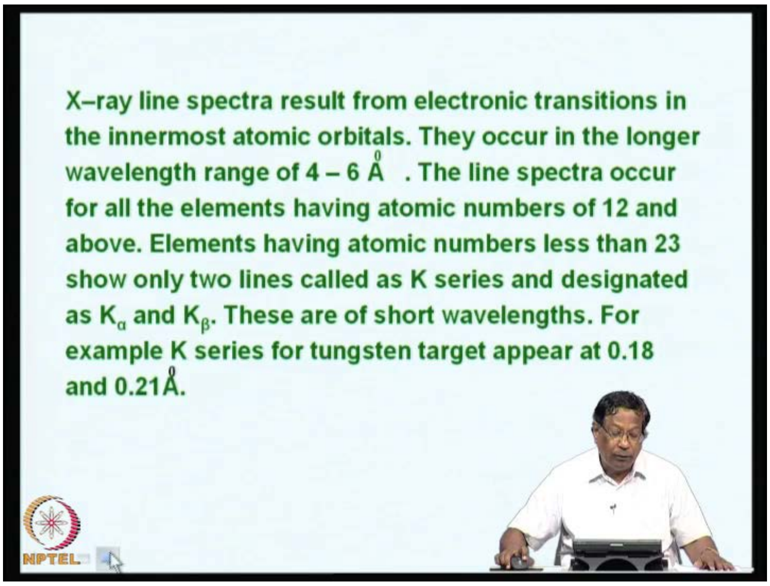
$$Ve = h\nu_0 = hc/\lambda$$

where v is the applied potential, ν_0 is the frequency.

Thus the kinetic energy is the product of accelerating voltage and the charge on the electron and ν_0 is the maximum of the radiation that can be produced.

You use to calculate the wavelength h nu 0 is nothing but h c by lambda; where h is planks constant and c is the velocity of light and a is the lambda is the wave length. So, the kinetic energy is basically the product…

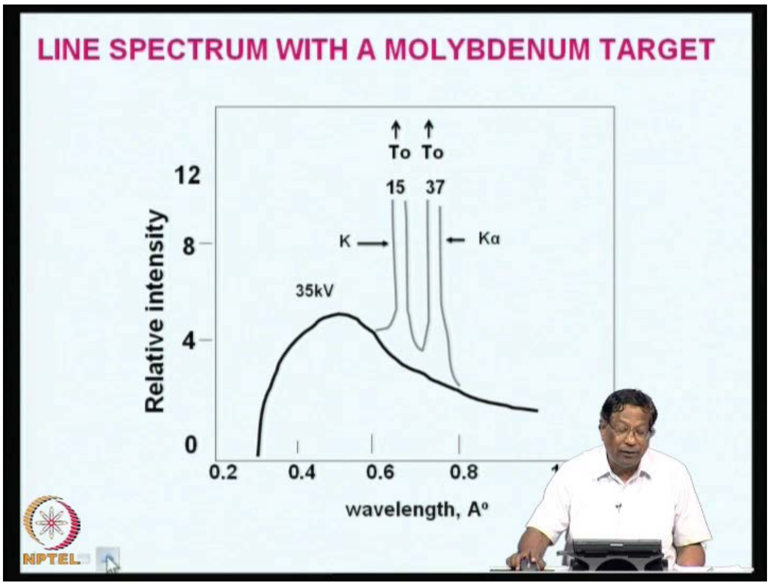
(Refer Slide Time: 04:30)



X–ray line spectra result from electronic transitions in the innermost atomic orbitals. They occur in the longer wavelength range of 4 – 6 Å . The line spectra occur for all the elements having atomic numbers of 12 and above. Elements having atomic numbers less than 23 show only two lines called as K series and designated as K_α and K_β. These are of short wavelengths. For example K series for tungsten target appear at 0.18 and 0.21Å.

Now, let us learn some more about the X-rays that is the X-rays lines spectra results from electronic transitions of the innermost atomic orbital’s, they occur in the longer wavelength range of 4 to 6 angstrom. The line spectra occur for all elements having atomic numbers of 12 and above below that you do not get line spectrum. So, usually atomic numbers having less than 23 show only two lines called as K series and designated as K alpha and K beta. These are of short wavelengths for continuum, for examples, K series for tungsten appears at 0.18 and 0.21 angstrom.

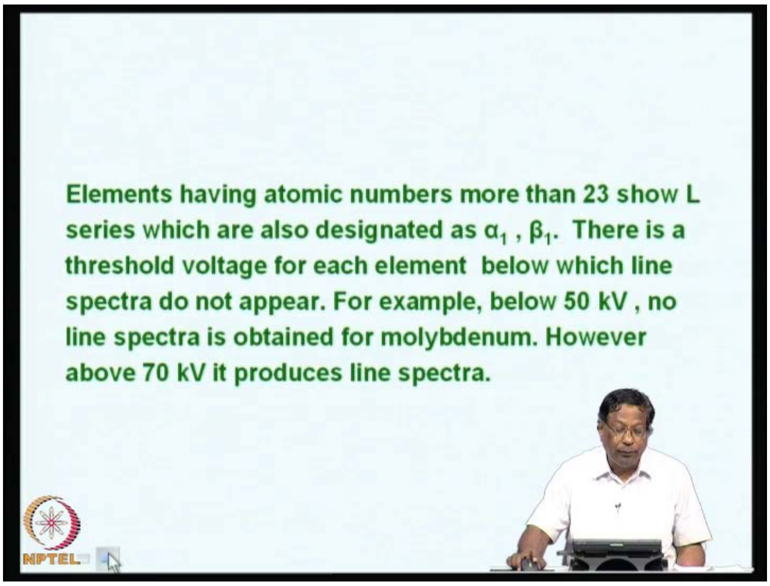
(Refer Slide Time: 05:14)



LINE SPECTRUM WITH A MOLYBDENUM TARGET

So, this is the figure we had shown you in the last class that there are two lines in this range, which are line spectra in super imposed on the continuum spectra like this.

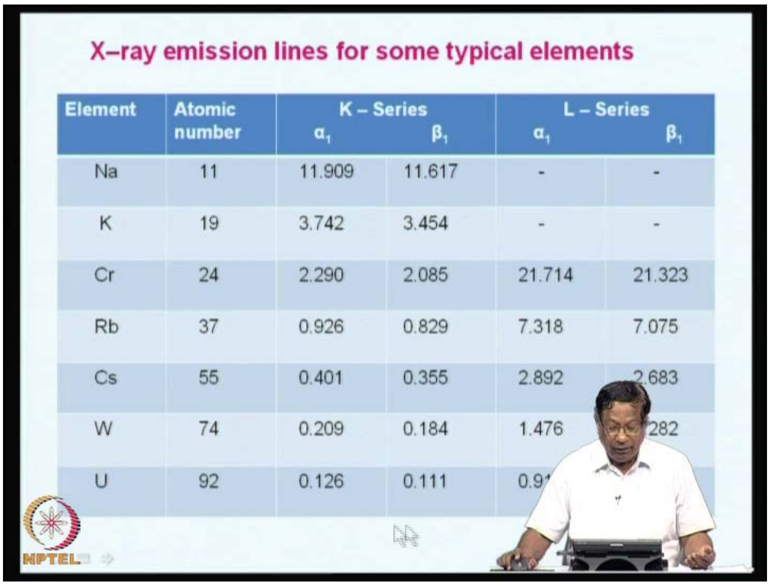
(Refer Slide Time: 05:30)



Elements having atomic numbers more than 23 show L series which are also designated as α_1 , β_1. There is a threshold voltage for each element below which line spectra do not appear. For example, below 50 kV , no line spectra is obtained for molybdenum. However above 70 kV it produces line spectra.

So, elements having atomic numbers more than 23 show L series which also designated as alpha 1 and beta 1. There is a threshold voltage for each element below which line spectra do not appear. For example, below 50 kV, no line spectra are obtained for the molybdenum; however, above 70 kV it produces line spectra.

(Refer Slide Time: 05:57)

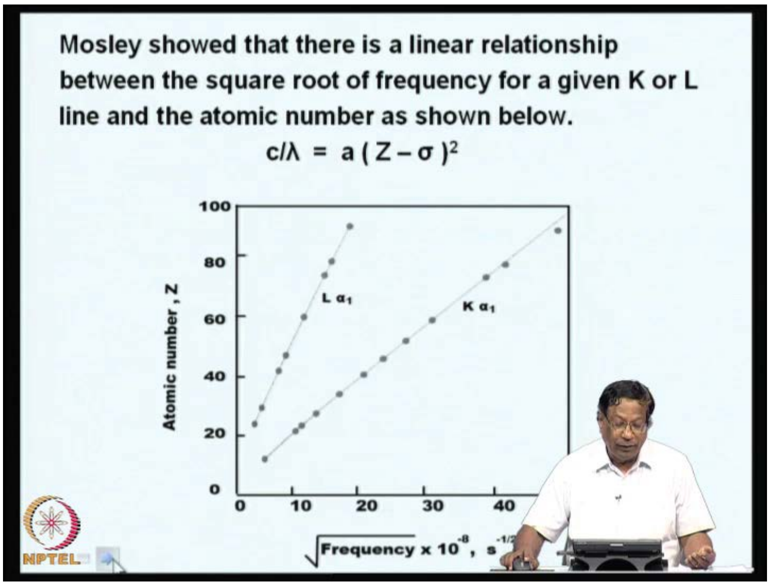


X–ray emission lines for some typical elements

Element	Atomic number	K – Series α_1	K – Series β_1	L – Series α_1	L – Series β_1
Na	11	11.909	11.617	-	-
K	19	3.742	3.454	-	-
Cr	24	2.290	2.085	21.714	21.323
Rb	37	0.926	0.829	7.318	7.075
Cs	55	0.401	0.355	2.892	2.683
W	74	0.209	0.184	1.476	282
U	92	0.126	0.111	0.91	[illegible]

Now, here are some elements and X-ray emission lines for some typical elements, for example, sodium - atomic number is 11; alpha 1 occur at 11.9 naught 9 and beta 1 occurs at 11.617. You will be surprised to see that we are able to calculate the wavelengths at such accuracy, only in the case of X-rays. Similarly, for potassium we have 3.74 to 3.454 etcetera. Above this level above atomic number 23 we have K alpha as well as L alpha L beta. So, we get four lines maximum, same with the case with rubidium, cesium, tungsten, uranium etcetera, where I have listed some of the X-ray lines obtained for these things.

(Refer Slide Time: 06:54)

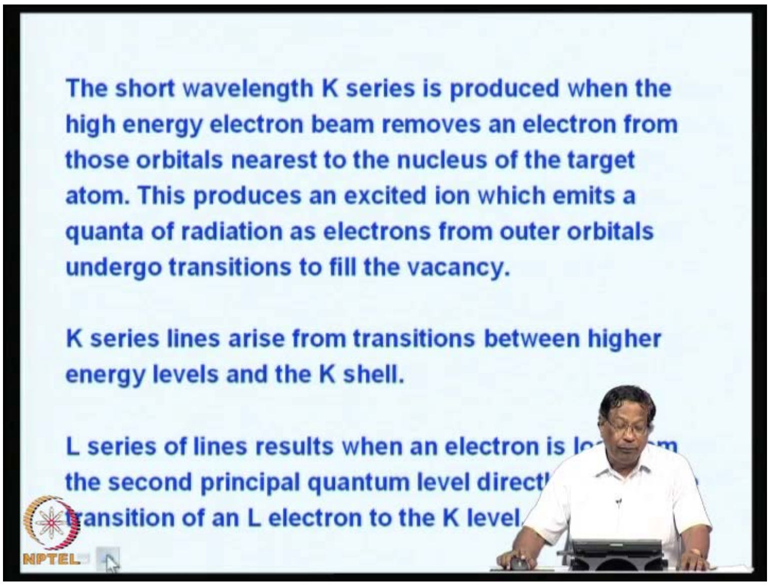


Mosley showed that there is a linear relationship between the square root of frequency for a given K or L line and the atomic number as shown below.

$$c/\Lambda = a(Z - \sigma)^2$$

Now, mostly has shown that there is a real linear relationship between the square root of the frequency for a given K or L line and the atomic number as shown below. For example, c by lambda is equal to a in to Z minus sigma whole square, where Z is the atomic weight. And you can see that the as the atomic number increases, there is a linear relationship in L alpha 1 as well as in the K alpha line frequency.

(Refer Slide Time: 07:39)



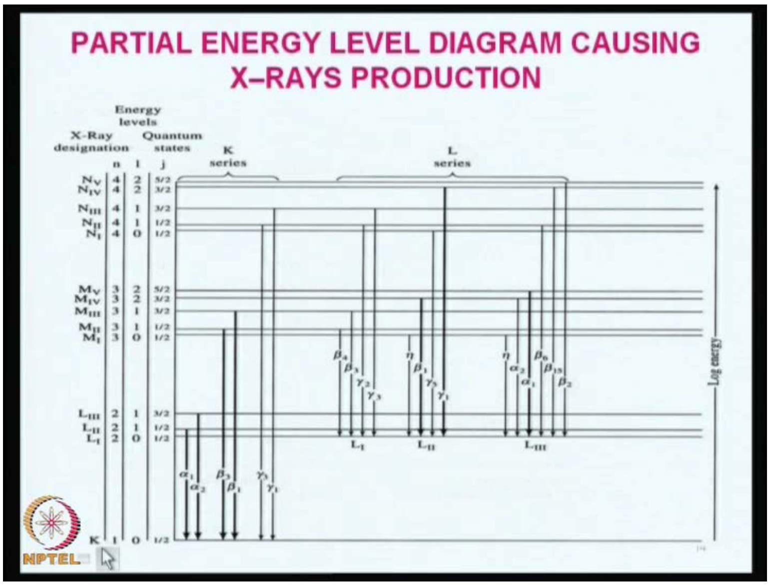
The short wavelength K series is produced when the high energy electron beam removes an electron from those orbitals nearest to the nucleus of the target atom. This produces an excited ion which emits a quanta of radiation as electrons from outer orbitals undergo transitions to fill the vacancy.

K series lines arise from transitions between higher energy levels and the K shell.

L series of lines results when an electron is lo m the second principal quantum level direct transition of an L electron to the K level

So, this is the very important property of all the X-rays and the short wavelength X-rays K series is produced when the high energy electron beam removes an electron the from the K orbit. This produces an exited ion which emits a quanta of the radiation as electrons from outer most orbital’s come back to the ground state. So, K series lines arise from transitions between the higher energy levels and the K shell. Similarly, L series of lines results when an electron is lost from the second principal quantum level directly or from the transition of element L electron from the K level.

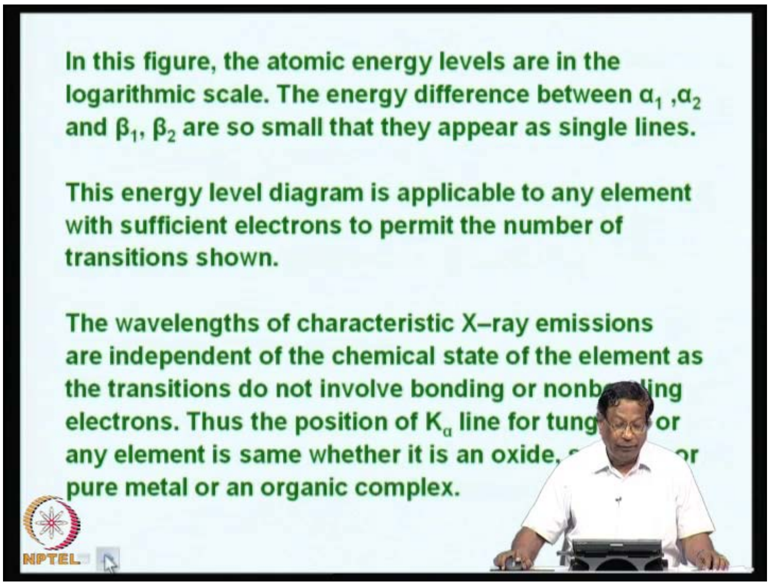
(Refer Slide Time: 08:24)



PARTIAL ENERGY LEVEL DIAGRAM CAUSING X–RAYS PRODUCTION

Now, this is the partial energy level diagram causing X-rays production, here I have shown you here alpha 1, alpha 2, beta 1, beta 2 etcetera. And these are all this series and the left part of this figure is K series, and the right part is the L series. They also contain some of the fluorescence lines.

(Refer Slide Time: 08:53)



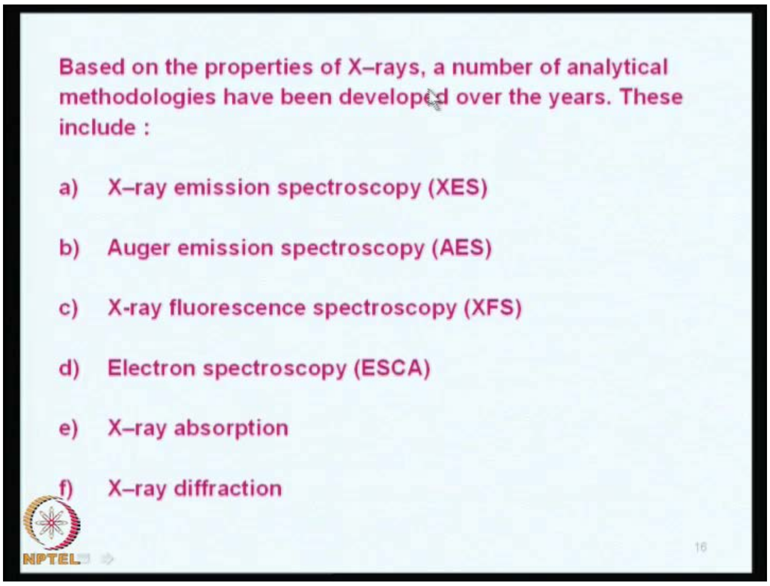
In this figure, the atomic energy levels are in the logarithmic scale. The energy difference between α_1 ,α_2 and β_1, β_2 are so small that they appear as single lines.

This energy level diagram is applicable to any element with sufficient electrons to permit the number of transitions shown.

The wavelengths of characteristic X–ray emissions are independent of the chemical state of the element as the transitions do not involve bonding or nonb ing electrons. Thus the position of K_α line for tung or any element is same whether it is an oxide, or pure metal or an organic complex.

So, in this figure you can see that, the energy levels that is on the left axis versus or and the logarithmic scale. So, as the energy level increases the separation between the lines they also becomes less and they become crowded at higher energy levels at rather lower energy level, but between K shell L shell the energy levels are well separated. So, the wavelengths of characteristic X-ray emissions are also independent of the chemical element as the transitions do not involve bonding or non bonding electrons. For examples, the position K alpha line for tungsten or any element whether is exactly same whether it is an oxide, or whether it is sulphide or whether it is a pure metal or it could be an organic complex. So, whatever be the state chemical state of the atom the wavelength of characteristic X-ray spectrum, X-ray are always same; that means, irrespective of the state of the atom you should be able to determine the element by X-ray spectrum.

(Refer Slide Time: 10:39)



Based on the properties of X–rays, a number of analytical methodologies have been developed over the years. These include :

a) X–ray emission spectroscopy (XES)

b) Auger emission spectroscopy (AES)

c) X-ray fluorescence spectroscopy (XFS)

d) Electron spectroscopy (ESCA)

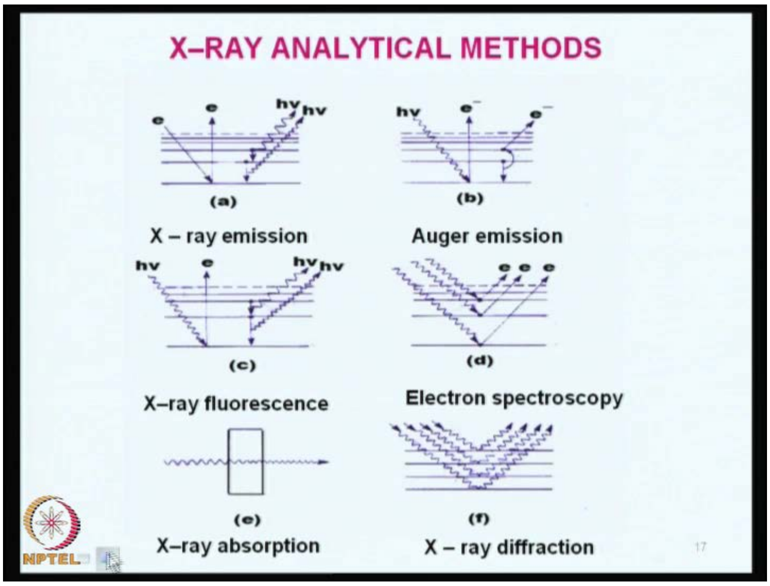
e) X–ray absorption

f) X–ray diffraction

Now, based on the properties of X-rays, a number of analytical methodologies have been developed and these are based on the atomic emission, for example, that is known as X-ray emission spectroscopy - XES, and then you can study the emission or surface emission that is known as auger emission spectroscopy. You can study the X-ray fluorescence spectroscopy, where the emitted X-rays have a wavelength longer than the excitation wavelength - that is X-ray fluorescence spectroscopy. Then you can have electron spectroscopy - that is ESCA. So, the here you are studying only the specific portion of the surface of the sample, what elements it contains etcetera using the X-ray line spectrum.

And you can also have X-ray absorption spectrometry - that is nothing but, you take a sample pass the X-rays whatever comes out the loss in energy of the X-rays can be determined as a function of a known element concentration. So, that is known as X-rays absorption. Another way of using another analytical technique very useful for X-rays is X-ray diffraction, that is you can study the crystal structure of the substance, where the elements, where the atoms are located. So, this you can do and we are not going into details of each of this technique, but we are going to concentrate only on the X-ray fluorescence technique, but this much of information is essential before you proceed into the analytical aspect. Now, here I am continuing where I left my last slide, that is I had described number of analytical technique that XES, AES, XFS, ESCA, X-rays absorption etcetera.

(Refer Slide Time: 13:06)



X–RAY ANALYTICAL METHODS

(a)
X – ray emission

(b)
Auger emission

(c)
X–ray fluorescence

(d)
Electron spectroscopy

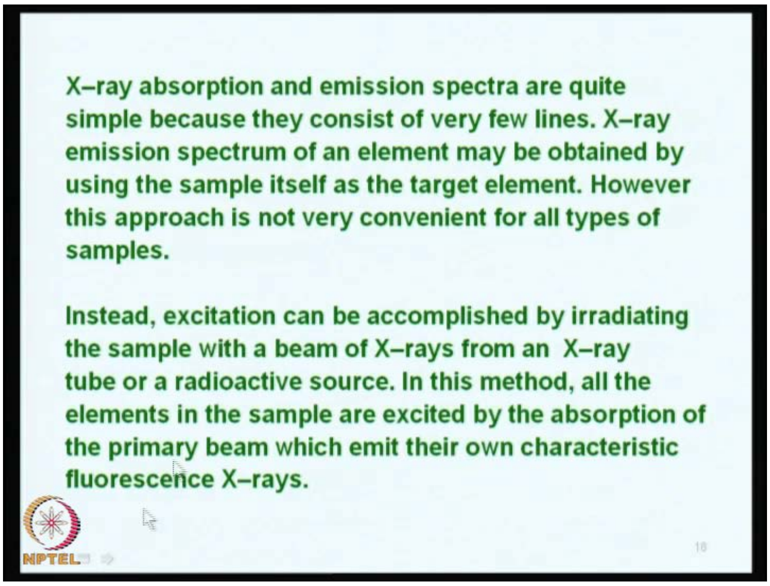
(e)
X–ray absorption

(f)
X – ray diffraction

The phenomenon that is occurring there, I am trying to show here. Here the X-ray is coming in the top figure – a, you can see that radiation is falling and then it gets excited and then it emits the radiation. And b is as hay the radiation is the falling on to the example, and again depending upon the X-ray properties you get as hay emission. And then X-ray fluorescence - the radiation X radiation falls on the sample, but the radiation emitted has a different wavelength.

Similarly, other electron spectroscopy: you take the electrons and then measure the wavelength of the different K lines L likes of the different elements that also you can take it to determine the concentration on the surface. Now, X-ray absorption like I was telling you to take the basic radiation, total energy of the bean passed through the sample loss of energy is determined just like molecular absorption. And electron spectra X-ray diffraction it gives you the atoms at different positions of the crystal and the crystal structure can be determined.

(Refer Slide Time: 14:34)



X–ray absorption and emission spectra are quite simple because they consist of very few lines. X–ray emission spectrum of an element may be obtained by using the sample itself as the target element. However this approach is not very convenient for all types of samples.

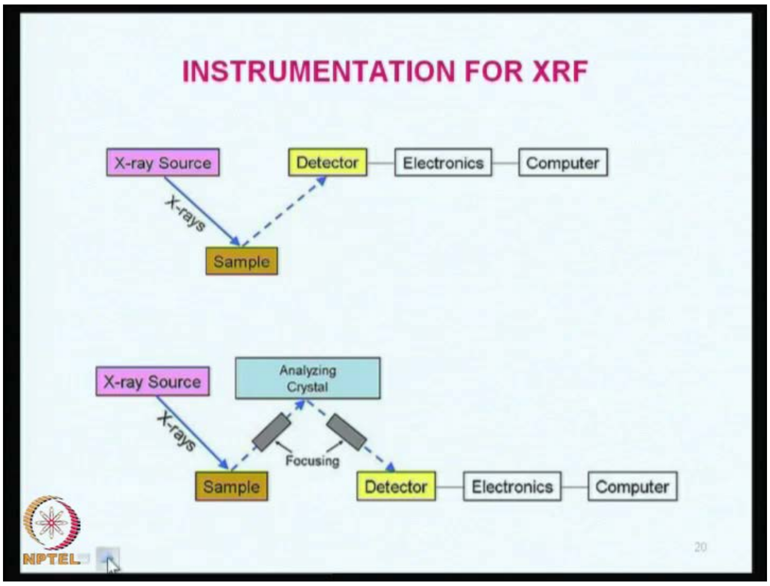
Instead, excitation can be accomplished by irradiating the sample with a beam of X–rays from an X–ray tube or a radioactive source. In this method, all the elements in the sample are excited by the absorption of the primary beam which emit their own characteristic fluorescence X–rays.

Now, the X-ray absorption and emission spectra are quite simple, but because they consists of very few lines, K alpha K beta L alpha and L beta. So, X-ray emission spectrum of an element may be obtained by using the sample itself as the target element. And this approach is not really convenient for all types of samples, because sometimes you may have a liquid sample, then it is not possible to fit it on to the position of the target directly. So, the sometimes you may have a powder that is also not easy that is unless you have a metal, which you can paste it and focus the incoming electronic beam on to the element.

Now, instead what we can do is? We can excite, you can achieve the same excitation by irradiating the sample with beam of X-rays from an X-ray tube or a radioactive source. And in this method all the elements in the sample are excited by the absorption of the primary beam which emit their own characteristic X-rays as usual fluorescence X-ray fluorescence. Now, therefore, the X-ray fluorescence is a powerful tool for the qualitative analysis that is pass fail test. Suppose, you are producing a metal in a foundry and then you would like to add some of the alloying elements and you would like to determine the concentration of the alloying element within a particular level.

All you have got to do is let the furnace run let the metal melt take a small amount of the melt and take it to a X-ray fluorescence just take the spectrum. If it shows you the X-ray fluorescence which is pre calibrated to the known concentration then you have a pass fail test ready, very quick method and very easy to control. So, most of the high Tec foundry have this kind of X-ray fluorescence lab attach to the foundry itself where they can control the composition of the metal. So, X-rays is also an non destructive technique, because the material does not get destroyed. So, unlike other element techniques where the, we have to either dissolve the sample or then extract the original nature of the sample is lost. So, there are two types of X-rays fluorescence spectrometers, one is you can monitor the wavelength of the dispersed red X-rays or you can monitor the energy of the X-rays.

(Refer Slide Time: 17:41)



INSTRUMENTATION FOR XRF

X-ray Source

X-rays

Sample

Detector

Electronics

Computer

X-ray Source

X-rays

Sample

Analyzing Crystal

Focusing

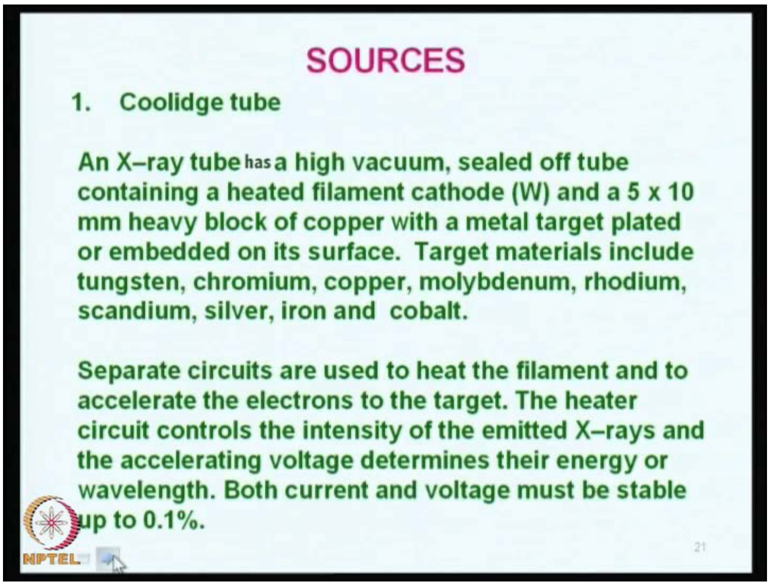
Detector

Electronics

Computer

So, important instrument components of a source X-ray XRF, I have shown here, here is an X-ray source that is X-rays will fall on the sample and then you have a detector followed by electronics and the computer. Then you can have another kind of arrangement, where X-ray source will fall on the sample and then you have a analyzing crystal through and the emitted X-rays are focused using metal thin metal films here. The one and two into and then on to the analyzing crystal from there again it is focused on to the detector followed by it is electronic and the computer to control the measurement.

(Refer Slide Time: 18:31)



SOURCES

1. **Coolidge tube**

An X–ray tube has a high vacuum, sealed off tube containing a heated filament cathode (W) and a 5 x 10 mm heavy block of copper with a metal target plated or embedded on its surface. Target materials include tungsten, chromium, copper, molybdenum, rhodium, scandium, silver, iron and cobalt.

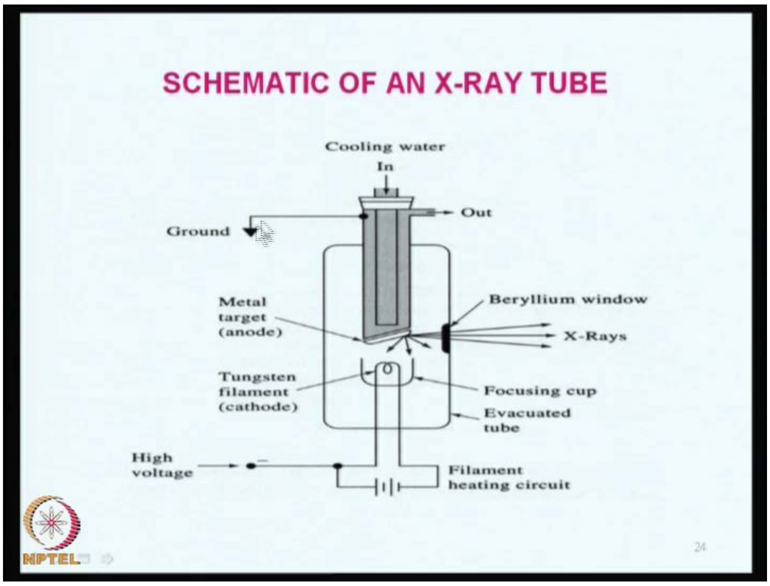
Separate circuits are used to heat the filament and to accelerate the electrons to the target. The heater circuit controls the intensity of the emitted X–rays and the accelerating voltage determines their energy or wavelength. Both current and voltage must be stable up to 0.1%.

So, what are the different types of sources for X-rays, how do you generate? The X-rays and other instrumental aspects are same whether it is auger, whether it is ESCA whether it is a X-ray absorption, emission etcetera. So, we are going to study the basic instrumentation for rays and then we will go on to the analysis of X-ray fluorescence technique other techniques. So, we are not studying right now. So, what does an X-ray tube has? Basically an X-ray tube is a high vacuum sealed off tube containing a the containing heated filament from, which we lead the electrons flow and these electrons need to be accelerated using hypo tension that is the requirement.

So, the filament cathode can be filaments which can simple generate the electrons when it is heated and the anode has to be a 5 by 10 mm heavy block of copper with a metal target plated or embedded on it is surface. And the target materials could be any element like tungsten chromium copper molybdenum rhodium scandium silver ion cobalt any element what you would like to study. So, you need two circuits one is for controlling the heating of the filament and another to accelerate the electrons and make them go and hit the cathode. So, the heat anode not the cathode, but it is the anode so, the heater circuit controls, the intensity of the emitted X-rays and the accelerating voltage determines the energy of the electrons or the wavelength.

So, both and current and the voltage must be stable up to point one percent accuracy that is very important otherwise, the energy of X-rays will not be constant and most of the measurements will go ovary. So, X-ray generation by this method is basically a inefficient process and much energy is wasted as heat so, cooling of the anodes is a must. So, the you will have to have a water cooling system to cool the anode and modern equipments what they do is they use highly sensitive transducers and hence they avoid cooling, cooling is not necessary. Some times in the such cases the X-ray beam generated in the source has to come out and fall on to the sample. So, we use a beryllium window or aluminum window or Parlodion films for this purpose, because you need to take out the X radiation from the source out of the source out of the tube and focus them on to the sample.

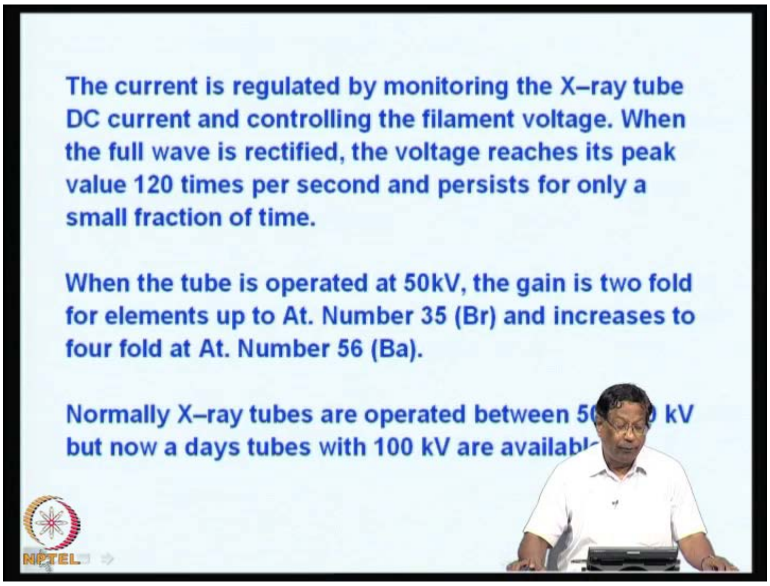
(Refer Slide Time: 22:14)



SCHEMATIC OF AN X-RAY TUBE

So, I am going to show you an X-ray tube here. The cooling water, there is cooling water in and cooling water out. So, the whole thing is cooled continuously during operation, and then we have a metal target anode here and this is the filament tungsten filament is we have used. And this is a focusing cup whatever are the electrons generated will be focused on to the target anode and then you have a circuit here, for accelerating the voltage, another for heating the element; this is for the heating, this is for the another circuit for the high voltage. And we have a beryllium window here through which X-rays are coming out you can have beryllium or any other element.

(Refer Slide Time: 23:17)



The current is regulated by monitoring the X–ray tube DC current and controlling the filament voltage. When the full wave is rectified, the voltage reaches its peak value 120 times per second and persists for only a small fraction of time.

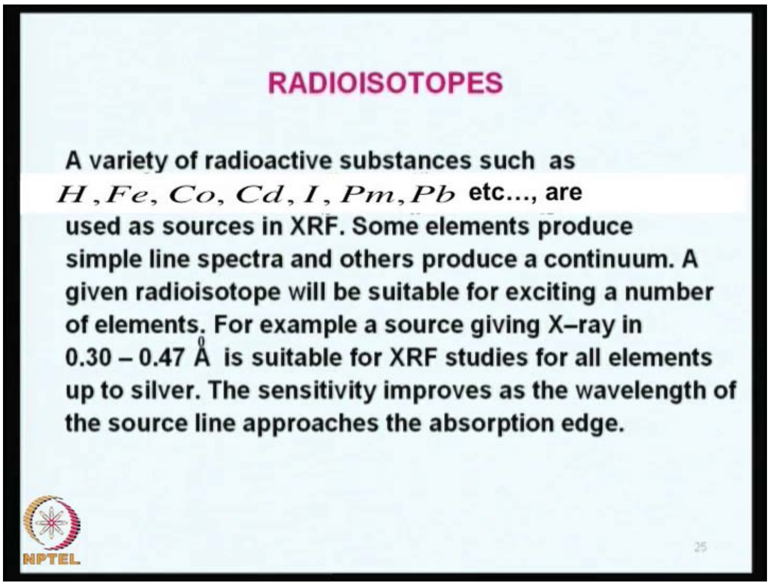
When the tube is operated at 50kV, the gain is two fold for elements up to At. Number 35 (Br) and increases to four fold at At. Number 56 (Ba).

Normally X–ray tubes are operated between 5 kV but now a days tubes with 100 kV are availabl

So, the current is basically regulated by monitoring the X-rays tube DC current and controlling the filament voltage. When the full wave is rectified? The voltage reaches it is speak value 120 times per second and persisted for a only a small fraction of the time; that means, 120 times per second you are going to get X-rays in per minute which is available to you. When the tube is operated at 50 kV the gain is approximately two fold for elements up to atomic number 25 and it increase to fourfold at beryllium. That is you keep on increasing the atomic number up to 25 increase, this to fold and then you take some other metal and reach up to other metals one by one.

And when you reach the atomic number 56 that is barium, the energy reaching the detector will be fourfold compare to bromine. So, normally X-ray tubes are operated between 50 to 60 kV source, power source, but nowadays you can operate tubes with 100 kV also for these are for high end elements. So, this is this I have shown you, another way of producing X-ray is to use radioactive substances such as hydrogen tritium and iron, cobalt, cadmium 1 naught 948, 1 naught 9 top numbers refer to top numbers refer to the atomic weight here I have written cadmium 1 naught 948.

(Refer Slide Time: 25:08)

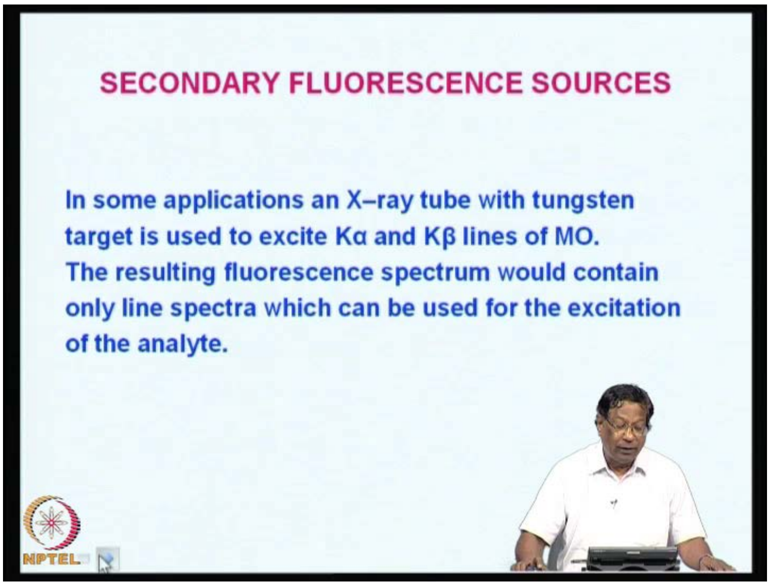


RADIOISOTOPES

A variety of radioactive substances such as H, Fe, Co, Cd, I, Pm, Pb etc…, are used as sources in XRF. Some elements produce simple line spectra and others produce a continuum. A given radioisotope will be suitable for exciting a number of elements. For example a source giving X–ray in 0.30 – 0.47 Å is suitable for XRF studies for all elements up to silver. The sensitivity improves as the wavelength of the source line approaches the absorption edge.

And then iodine is 125 53 like that there are number of elements which are radioactive, but they generate X-rays. So, some elements produce simple line spectra others produce a continuum a given isotope will be suitable for existing a number of limits for example, a source giving X-ray in 0.3 to 0.47 angstrom is suitable for a X-rays studies for all elements up to silver. The sensitivity improves as the wavelength of the source line approaches the absorption edge.

(Refer Slide Time: 25:56)



SECONDARY FLUORESCENCE SOURCES

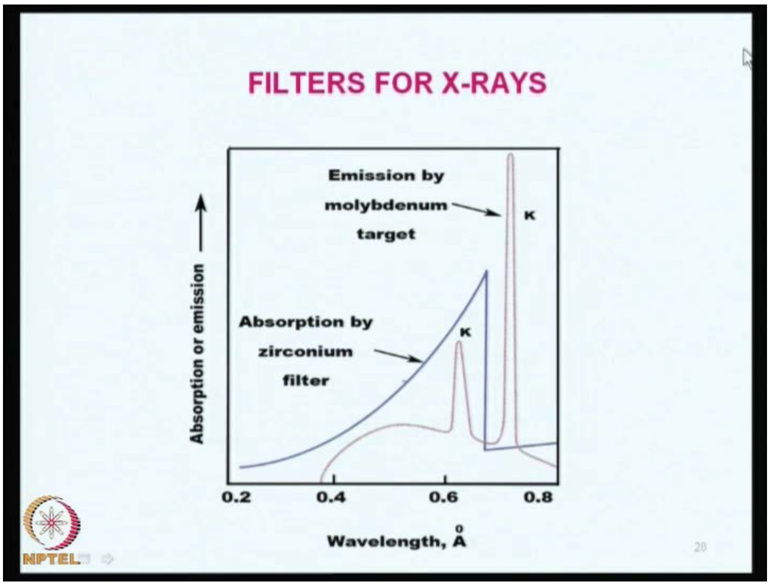
In some applications an X–ray tube with tungsten target is used to excite Kα and Kβ lines of MO. The resulting fluorescence spectrum would contain only line spectra which can be used for the excitation of the analyte.

Now, in some applications X-ray tubes with tungsten target is used to excite K alpha and

K beta lines of molybdenum. The resulting flow since spectrum would also contain only line spectrum which can be used for the excitation of the analyte. So, after you have X-rays generated from an X-ray tube or radioactive source and they come out you need to filter unwanted X-rays. So, just like in other electromagnetic radiation when you have you want to remove the unwanted the radiations here, also you need to use filters. So, the in some applications narrow ranges are required wavelength are required you do not need all the kinds of X-rays. So, you do not need continuum also so, both filters and monochromator are used for this purpose. So, zirconium filters are very ideal for these and they can be used in films for about 0.01 centimeter thickness to isolate K alpha line.

They not only eliminate the continuum, but they eliminate K alpha line also and you can see here in this figure that wave length is plotted again absorption of emission. So, here I have a filter in this range that is between 0.06 and 0.08 approximately around 0.07 there is continuum X-ray coming like this, and then there is K alpha line and then K beta line. And you need to use only K beta line, emitted by molybdenum target that is this line, but you do not need the other part. So, what I do is? I use a zirconium filter which will cut off all the radiation that is coming in this range including the K alpha line. So, this is what this is the job of the filter so, you what is available after using the filter is only the K line K beta line. So, several other filters are also available and basically thin strips of varies metal and you can choose their characteristics cut off wavelength is different for example, in this case.

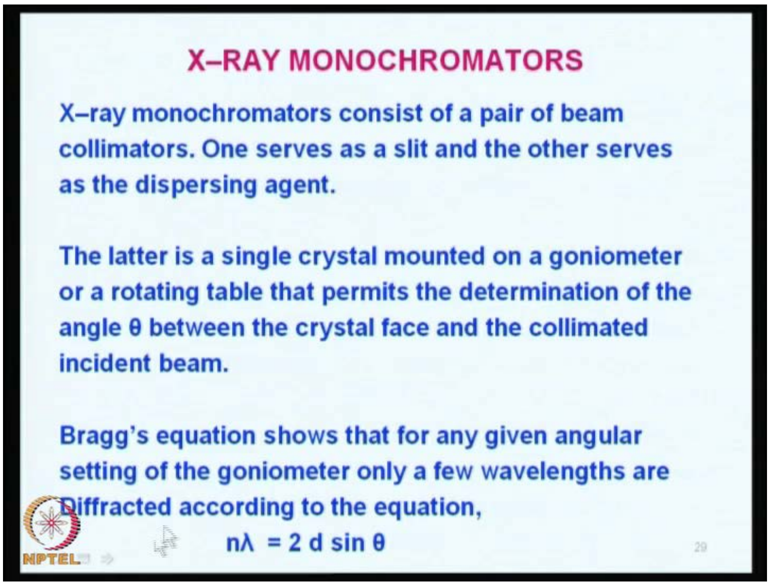
(Refer Slide Time: 27:29)



FILTERS FOR X-RAYS

It is around 0.65 or 0.7, but for some other elements it may be something else. So, depending up on your requirement you can choose the filter.

(Refer Slide Time: 28:59)



X–RAY MONOCHROMATORS

X–ray monochromators consist of a pair of beam collimators. One serves as a slit and the other serves as the dispersing agent.

The latter is a single crystal mounted on a goniometer or a rotating table that permits the determination of the angle θ between the crystal face and the collimated incident beam.

Bragg's equation shows that for any given angular setting of the goniometer only a few wavelengths are Diffracted according to the equation,

$$n\lambda = 2 d \sin \theta$$

Now, after choosing the filter you also need just like in you visible spectrophotometry monochromator systems. In X-rays monochromator, if you remember what I had thought you earlier? We had used the we had defined an X-ray monochromators system containing lens focusing lens a slate prism and the or a grating and then again refocusing slit etcetera, this is known as monochromator system. So, similarly, in X-rays also you need to have a monochromator system and this consists of a pair of beam of beam collimators that is to make the beam parallel. One serves usually you can use two filters one for as a slit one to serve as a slit and the other serves as the dispersing element.

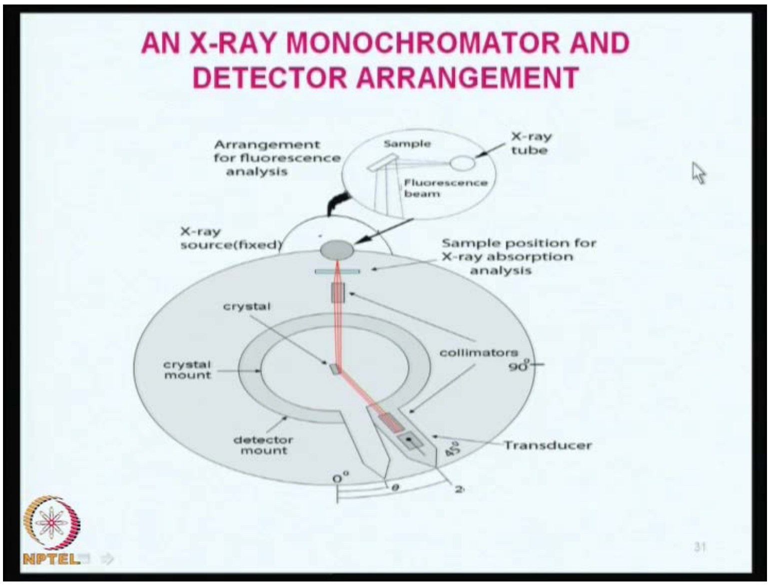
So, the dispersing element this is basically a single crystal mounted on a goniometer. What is a goniometer? A goniometer is a rotating table that permits the determination of the angle of theta that is the angle at which the radiation falls on the crystal and the then it gets reflected diffraction florist etcetera. And this angle you are you suppose your sample is on a rotating term stable the radiation will fall like this and then this angle can be varied from zero to ninety one eighty followed by three sixty. So, all the three sixty degrees you can vary the angle of incidence of X-rays.

So, the goniometer permits you disc arrangement it is nothing, but a circular arrangement on which the electrons are coming. And this angle of incidence from where the angle is from where the X-ray is coming is can be varied precisely for determining the X-ray and the detection and detector has to be located at twice the angle let us if I use Bragg's law L lambda is equal 2 d sine theta. Now, we have pour we have studied earlier, but it is also coming further; that means, for every angle of theta that the X radiation falls on the sample the detector has to be rotated to twice. Suppose, you are angle of incidence is 35 degrees the detector has to rotate at 70 degrees.

So, the both the turn table as well as the detector have to be rotated exactly one at half the speed one and another at twice the quantity of the theta, that is the between the crystal phase and the collimated incident beam. So, Bragg's equation shows, that for any given angular setting goniometer only a few lens are diffracted according to this equation, it is n lambda is equal to two d sine theta which I have explained just now. And to produce the spectrum again what you need? The exit beam also has to the collimated once again and the detector must be mounted on the another second table, that rotates at the twice the speed that I have told you.

And the modern X-ray monochromator systems have microprocessor controlled motors to drive the crystal to rotate the crystal and the detector independent of each other without gear based mechanism. What is the problem with gear based mechanism? If you use the gear based mechanism to rotate something gears can wear out. So, subsequently after you use it for sometime the gears can wear out and the precision of the angle would not be there at all. So, gear less mechanical systems is more comfortable in this kind of arrangements. So, they can scan rapidly if there are gearless we can scan the whole 360 degrees in a very short time because there are no gears involved. So, you can scan them at the rate of 240 degrees per minute, so these is the advantage of gearless this thing.

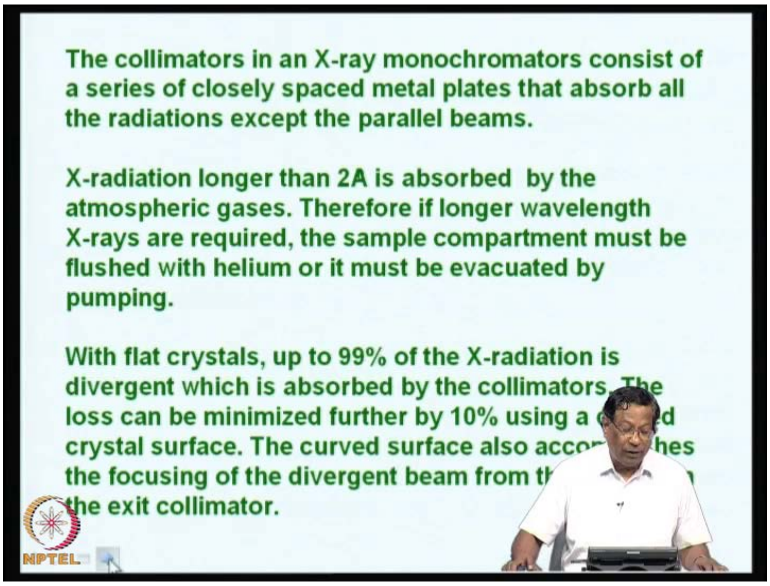
(Refer Slide Time: 34:31)



AN X-RAY MONOCHROMATOR AND DETECTOR ARRANGEMENT

Here I am showing you a monochromator system for X-ray - that is what we have here is an X-ray tube on this side, and the sample is here X-ray from the X-ray tube they fall on the fluorescence beam and then it the rotating table detector is located here. And then a sample position for X-ray absorption analysis etcetera are the X-ray sources there crystal is here and the transducer is here. So, the sample X-ray comes here falls on the there is collimators one for the incoming one for the outgoing and crystal is here and then detector amount are out here etcetera all around the turn table. And for this degree theta degree change in the X-ray angle the goniometer has to turn twice, this turn table has to turn twice the angle of incidence.

(Refer Slide Time: 35:46)



The collimators in an X-ray monochromators consist of a series of closely spaced metal plates that absorb all the radiations except the parallel beams.

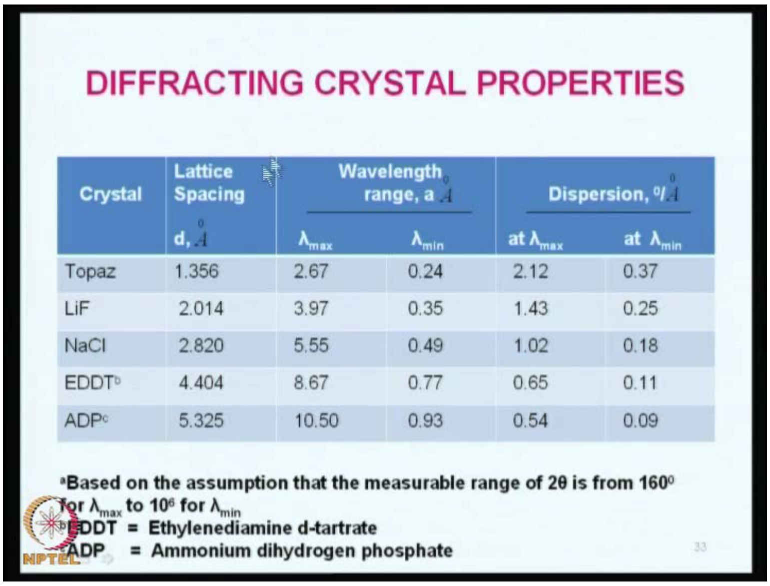
X-radiation longer than 2A is absorbed by the atmospheric gases. Therefore if longer wavelength X-rays are required, the sample compartment must be flushed with helium or it must be evacuated by pumping.

With flat crystals, up to 99% of the X-radiation is divergent which is absorbed by the collimators. The loss can be minimized further by 10% using a c d crystal surface. The curved surface also acco hes the focusing of the divergent beam from th the exit collimator.

So, this is what you have been talking about? The collimators basically consist of series of closely spaced metal plates that absorb all the radiations expect the parallel beams. Because the radiation scattered in other directions have no meaning for the chemical analysis what is coming out through a thin film of radiation, which is parallel that only use full. So, X radiation longer than two angstrom is absorbed the atmospheric gases this is another important concept you should understand. That means, longer than any X radiation longer than two angstroms should not be opened to atmospheric gases; that means, you need to have a vacuum system if longer wavelength are required.

So, the sample compartment must be fleshed with either helium or some other gas which does not absorb X-rays or it must be evacuated. So, with flat crystals, up to ninety nine percent of the X radiation is divergent which is absorbed by the collimators waste wastage twenty ninety nine percent. This loss can be minimized by about ten percent using a curved crystal surface suppose, your crystal is not exactly a ninety degree this thing we can machine it and shape it into a curved surface like this, then the loss can be minimized by about ten percent. So, and this divergent beam the curved surface also will help in accomplishing the divergent focusing further focusing it will any curved surface. If it X-ray falls on that it will act like a concave mirror or convex mirror, where it will try to focus the divergent beam from the source on to the exit collimators.

(Refer Slide Time: 38:03)



DIFFRACTING CRYSTAL PROPERTIES

Crystal	Lattice Spacing d, Å	Wavelength range, a Å		Dispersion, °/Å	
		λ_{max}	λ_{min}	at λ_{max}	at λ_{min}
Topaz	1.356	2.67	0.24	2.12	0.37
LiF	2.014	3.97	0.35	1.43	0.25
NaCl	2.820	5.55	0.49	1.02	0.18
EDDT[b]	4.404	8.67	0.77	0.65	0.11
ADP[c]	5.325	10.50	0.93	0.54	0.09

[a] Based on the assumption that the measurable range of 2θ is from 160^0 for λ_{max} to 10^6 for λ_{min}

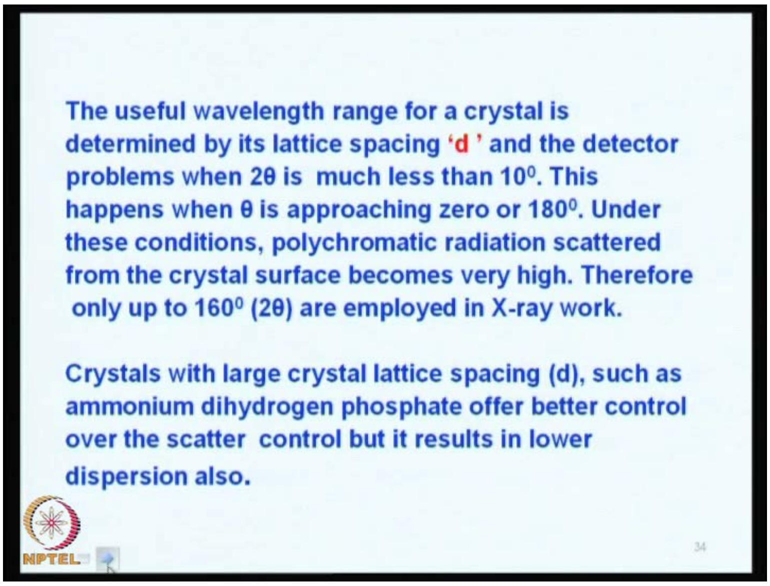
[b] EDDT = Ethylenediamine d-tartrate

[c] ADP = Ammonium dihydrogen phosphate

So, here there are some diffracting crystal properties like topaz, lithium fluoride, sodium chloride and then ethylene diamine tartrate ditartrate ammonium dyhydrogen phosphate etcetera, there lattice spacing’s are given here 1.356, 2.014 etcetera.

The wavelength ranges are given here, the dispersion is approximately in the third fourth column at lambda max and at lambda minimum. So, if you want to get X-rays of between two and between 2.67 angstroms and 0.24 you should go for topaz - this is how the table can be utilized. Suppose, you want 8.6 between 8 and 0.7 and 8 angstrom unit X-rays then you should go to this table, and look which of the material gives you the radiation corresponding to between 0.77 and 8.67 that corresponds to EDDT. So, depending upon the angle a wavelength, you should be able to choose the wavelength material crystal for X-ray collection.

(Refer Slide Time: 39:27)



The useful wavelength range for a crystal is determined by its lattice spacing ‘d ’ and the detector problems when 2θ is much less than 10^0. This happens when θ is approaching zero or 180^0. Under these conditions, polychromatic radiation scattered from the crystal surface becomes very high. Therefore only up to 160^0 (2θ) are employed in X-ray work.

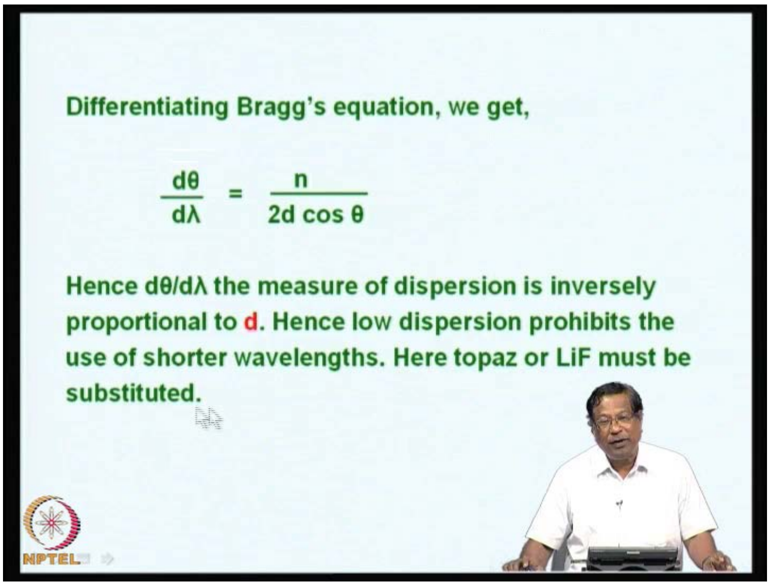
Crystals with large crystal lattice spacing (d), such as ammonium dihydrogen phosphate offer better control over the scatter control but it results in lower dispersion also.

So, the useful wavelength range for a crystal is determined by it is lattice spacing d - that is m lambda is equal to 2 d sine theta that what you mean by d; d corresponds to the lattice spacing in between the spacing in between the two element, two atoms rather. And this happens; the detector problems are more if the angle of incident is less than 10 degrees. So, if the angle of sometimes the angle may be 35 degrees, 90 degrees, 120 degrees like that below if it is almost parallel approximately 10 degree angle, the detector will have problems in collecting the collecting the X-ray emanating from the crystal, same thing happens when the detect angle approaches 180 degrees.

So, less between 170 and 180 detector will have problem in collecting the radiations quantitatively, between zero and ten as you have started from one end to the other end if this is zero and then slowly you will increase. First ten degrees there is a problem of collection, then it improves detection collection, it reaches 90 and then slowly when it comes to 170 degrees again it is almost parallel between 170 and 180 again the detection problem exists.

So, what we do is in between? We tried to work between only up to 160 degrees in an X-ray work. So, crystals with large spacing’s offer better kind of d spacing a lattice spacing offer better control over the scatter control, but it results in lower dispersion also, this is a consequence of the X-ray Bragg’s laws diffraction this thing.

(Refer Slide Time: 41:52)



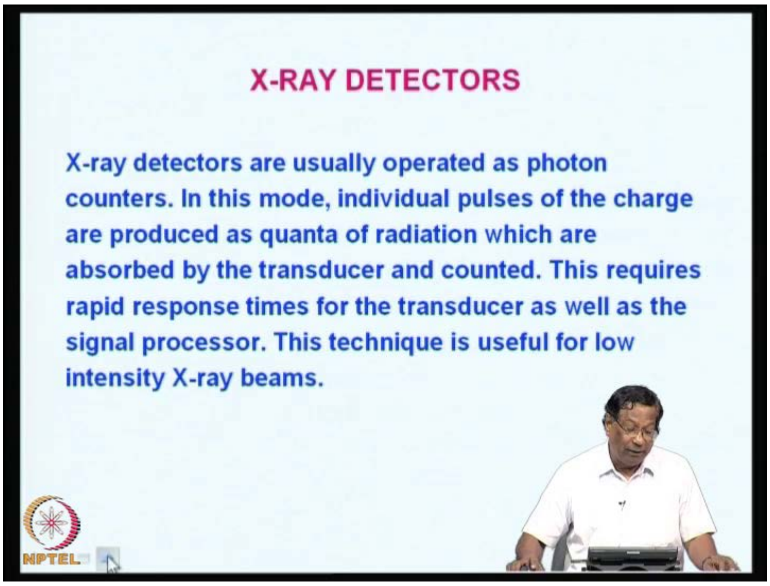
Differentiating Bragg's equation, we get,

$$\frac{d\theta}{d\lambda} = \frac{n}{2d\cos\theta}$$

Hence dθ/dλ the measure of dispersion is inversely proportional to d. Hence low dispersion prohibits the use of shorter wavelengths. Here topaz or LiF must be substituted.

If you differentiate Bragg's equation what do you get? Is d theta by lambda is equal to n over 2d sine theta and this 2d comes the denominator. Therefore, d theta by d lambda this dispersion is the measure of the dispersion that is inversely proportional to d, on the one hand when the d is large we get a better dispersion better collection. But because it is a measure of the dispersion which is inversely proportional you get other problems. So, low dispersion prohibits the use of shorter wavelength, hence topaz are lithium fluoride must be substituted in most of the X-ray fluorescence work.

(Refer Slide Time: 42:39)



X-RAY DETECTORS

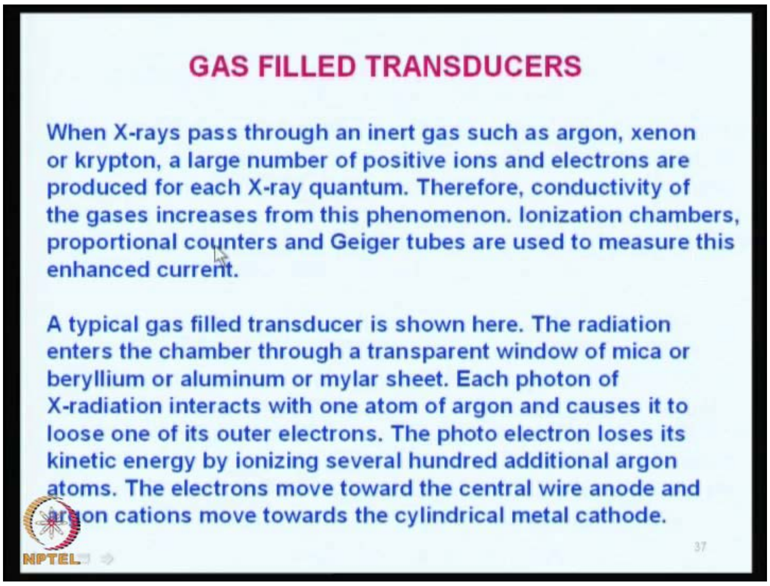
X-ray detectors are usually operated as photon counters. In this mode, individual pulses of the charge are produced as quanta of radiation which are absorbed by the transducer and counted. This requires rapid response times for the transducer as well as the signal processor. This technique is useful for low intensity X-ray beams.

So, X-ray, now we move on to we had discussed so far about X production of X-rays we had discussed so far about the use of filters. We had discussed about the monochromator system and how the sample has to be mounted, and how the angles and goniometer have to be arranged. Now, let us discuss about the detectors. In the X-ray detectors are usually operated as photon counter, in this mode individual pulses of the charges are produced as quanta of radiation, which are absorbed by the transducer. Basically, X-ray is nothing but the X-radiation has to come and hit a particular sensitive transducer and amount of energy has to be released quanta of energy that has to be counted.

So, this requires rapid response time because X-rays are very fast electrons are also very fast moving, X-rays also are very fast. And therefore, the transducers as well as a signal processor have to work in within micro seconds, the moment that hits within a few micro seconds the whole measurement and counting and all other related system must be completed before another photon comes and hits the detector. So, this technique is useful for low intensity X-ray beams, because in high intensity X-ray beams there is not much time for the each photon to be counted individually.

So, when X-rays pass through an inert gas such as argon and anon a or krypton a large number of positive ions are also generated electrons are there and then X-ray quantum is there. Therefore, the conductivity of the gases increases, because the positive ions and electrons have generated argon cation and electrons. So, electron is very light weight and argon cation is a higher rate samples.

(Refer Slide Time: 45:11)



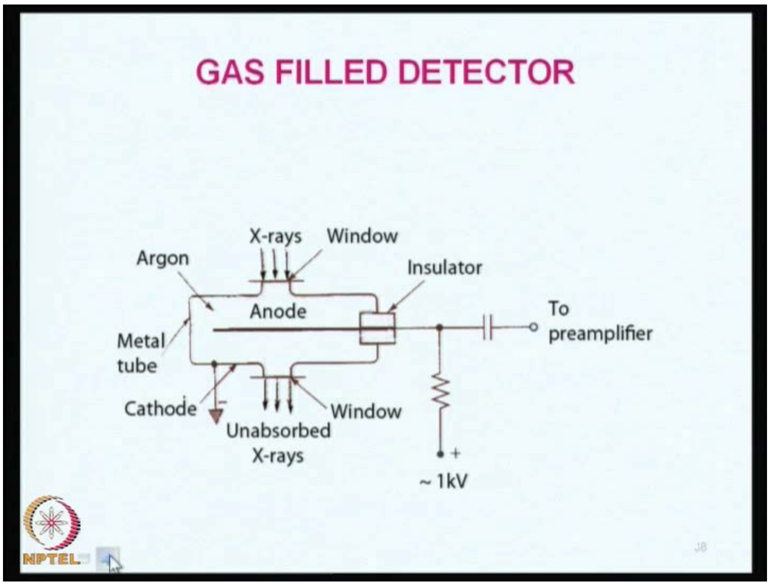
GAS FILLED TRANSDUCERS

When X-rays pass through an inert gas such as argon, xenon or krypton, a large number of positive ions and electrons are produced for each X-ray quantum. Therefore, conductivity of the gases increases from this phenomenon. Ionization chambers, proportional counters and Geiger tubes are used to measure this enhanced current.

A typical gas filled transducer is shown here. The radiation enters the chamber through a transparent window of mica or beryllium or aluminum or mylar sheet. Each photon of X-radiation interacts with one atom of argon and causes it to loose one of its outer electrons. The photo electron loses its kinetic energy by ionizing several hundred additional argon atoms. The electrons move toward the central wire anode and argon cations move towards the cylindrical metal cathode.

So, it moves slowly the electrons will move very fast. So, the conductivity of the gases increases from these phenomenon ionization chambers we use proportional counter we use and Geiger counters are used to measure this enhanced currents. So, basically X-ray measurement means we have to measure the current that is produced subsequently.

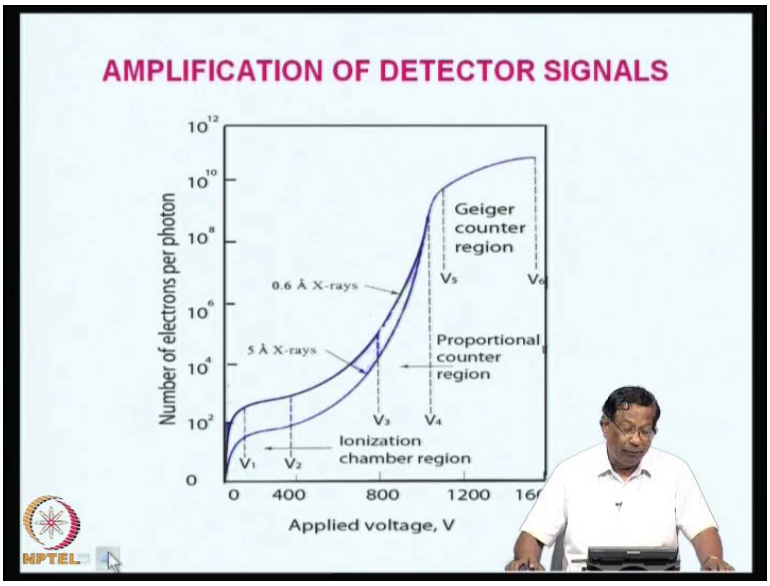
(Refer Slide Time: 45:36)



GAS FILLED DETECTOR

So, I typical gas filled transducer I am showing here, you can see here I have a gas filled material and anode is here X-rays are falling and this is a beryllium window parallel X-ray beam is falling here un absorbed X-rays are going out. And I need a metal tube here argon is filled and the window another window is here and the amount of radiation that is generated has two there is a cathode here there is a anode here. So, the electrons cations will move towards this side and electrons will move towards the cathode and the amount of current generated is to be amplified and used. So, this is how a gas filled detector works?

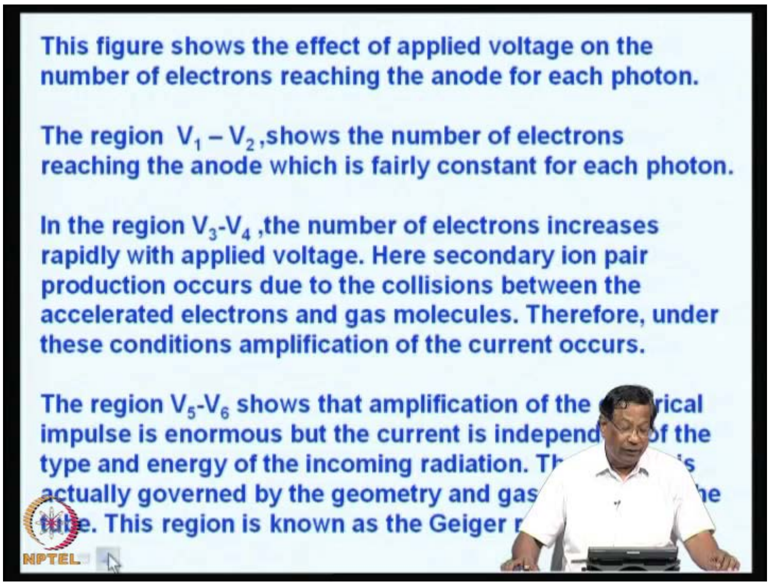
(Refer Slide Time: 46:31)



AMPLIFICATION OF DETECTOR SIGNALS

And if you look at the amplification of the detector signals, you will see three regions here in this figure, I am showing you one first bottom curve corresponds to 0.5 angstrom X-rays and the top curve this one corresponds to 0.6 angstrom X-rays. So, if you look at the applied voltage it varies from 0 to 1600 and number of electrons per photon has been plotted here. So, there are you can see that there are three regions - one is V 1 and V 2, and V 3 and V 4, another is V 5 and V 6. So, three regions different distinct regions can be identified in these systems.

(Refer Slide Time: 47:24)



This figure shows the effect of applied voltage on the number of electrons reaching the anode for each photon.

The region $V_1 - V_2$,shows the number of electrons reaching the anode which is fairly constant for each photon.

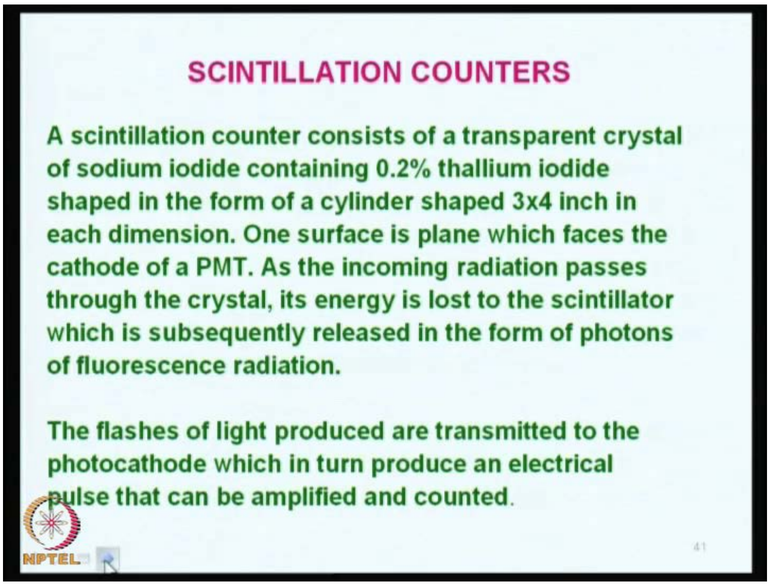
In the region V_3-V_4 ,the number of electrons increases rapidly with applied voltage. Here secondary ion pair production occurs due to the collisions between the accelerated electrons and gas molecules. Therefore, under these conditions amplification of the current occurs.

The region V_5-V_6 shows that amplification of the rical impulse is enormous but the current is independ of the type and energy of the incoming radiation. Th 's actually governed by the geometry and gas he tube. This region is known as the Geiger r

So, the first region shows the number of electrons reaching the anode which is fairly constant for each photon; that means the amount of energy is constant and it can be detected very easily. In the second region that is V 3-V 4 in this region. There is you can see that the slope has changed and it is it has increased enormously in this region range current. So, now this region number of electron release increase rapidly with applied voltage and here the secondary ion pair production occurs due to the collisions between the accelerated electrons and gas molecules.

Therefore, under these conditions amplification of the current occurs. So, the third region that is V 5-V 6 again here, there is a sort of saturation occurring and the amplification is enormous, but the current is independent of the type and energy of the incoming radiation. The current is actually governed by the geometry of then and gas pressure of the tube this region is known as Geiger region.

(Refer Slide Time: 48:53)



SCINTILLATION COUNTERS

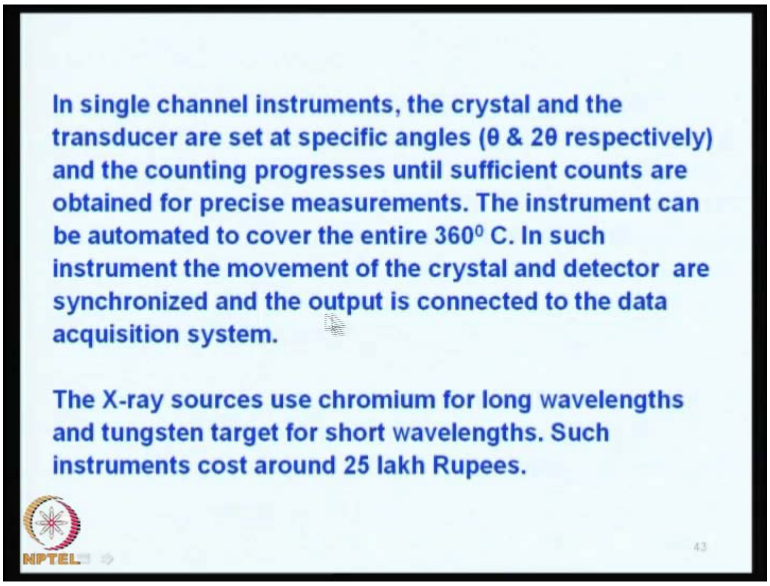
A scintillation counter consists of a transparent crystal of sodium iodide containing 0.2% thallium iodide shaped in the form of a cylinder shaped 3x4 inch in each dimension. One surface is plane which faces the cathode of a PMT. As the incoming radiation passes through the crystal, its energy is lost to the scintillator which is subsequently released in the form of photons of fluorescence radiation.

The flashes of light produced are transmitted to the photocathode which in turn produce an electrical pulse that can be amplified and counted.

So, scintillation counters are another type of electron of other types of detectors, where we use a sodium iodide crystal containing 0.2 percent thallium iodide shaped in the form of a cylinder and in about 3 to 4 inch in dimension. So, one surface is plane and the which phases is the cathode of a PMT as the incoming radiation passes through passes through the crystal its energy is lost to the scintillation, which is subsequently released in the form of photons of fluorescence radiation. So, the flashes of light produced are transmitted to the photo cathode which in turn produce an electrical pulse that can be amplified.

So, in X-ray now we come to these are the so far what I have covered is the basic instrumentation for X-ray fluorescence for all X-rays. Now, we come to X-ray fluorescence as I have explained to earlier, we have wavelength dispersive X-ray, WDXRF rays, energy dispersive. So, in both these systems radioactive sources are collimated and dispersed into its component wavelength both single channel and multichannel detection systems are possible. In what do we mean by single channel and double channel, multichannel and single channel elements you are going to determine only one element, and in multi channel elements you are going to determine number of elements simultaneously. So, the angles for each element have to be set specific for each element. So, the counting progresses until sufficient counts are obtained for précised measurements, the instruments can be automated to cover the entire three sixty range in such instruments.

(Refer Slide Time: 50:52)

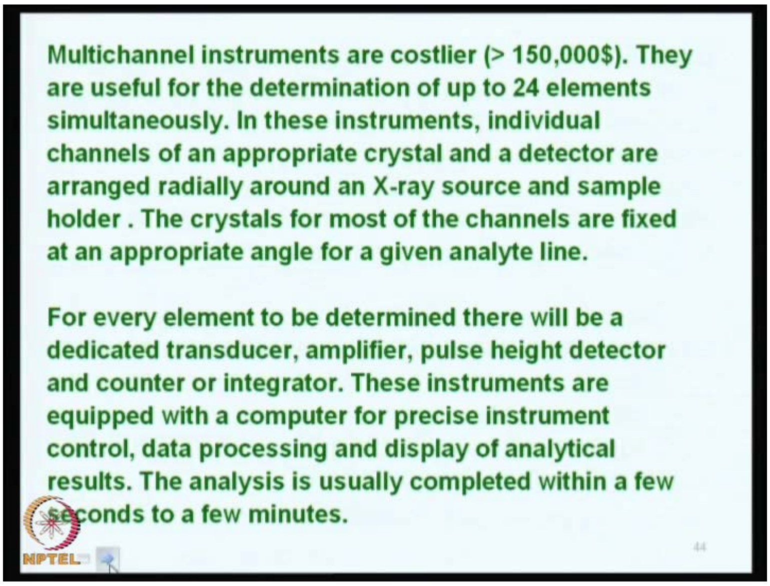


In single channel instruments, the crystal and the transducer are set at specific angles (θ & 2θ respectively) and the counting progresses until sufficient counts are obtained for precise measurements. The instrument can be automated to cover the entire 360^0 C. In such instrument the movement of the crystal and detector are synchronized and the output is connected to the data acquisition system.

The X-ray sources use chromium for long wavelengths and tungsten target for short wavelengths. Such instruments cost around 25 lakh Rupees.

The moment of the crystal and the detector and synchronized such instruments usually, cost around 25 lakhs of rupees and in multi channel instruments they are costlier the cost approximately 150,000 dollar's and there are useful for the determination of up to 24 elements simultaneously.

(Refer Slide Time: 51:05)

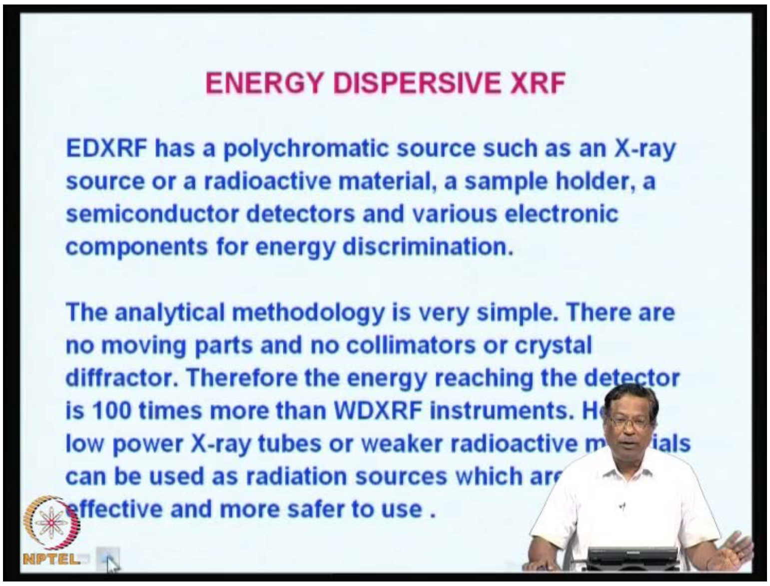


Multichannel instruments are costlier (> 150,000$). They are useful for the determination of up to 24 elements simultaneously. In these instruments, individual channels of an appropriate crystal and a detector are arranged radially around an X-ray source and sample holder . The crystals for most of the channels are fixed at an appropriate angle for a given analyte line.

For every element to be determined there will be a dedicated transducer, amplifier, pulse height detector and counter or integrator. These instruments are equipped with a computer for precise instrument control, data processing and display of analytical results. The analysis is usually completed within a few seconds to a few minutes.

In these instruments, individual channels for each crystal for each element are arranged radially around the X-ray tube and sample holder. The crystals for most of the channels are fixed at an appropriate angle for a given analytic. That means if you want to determine chromium you need one crystal and then one detector system one channel one amplifier 1 pulse side detector etcetera. And the similarly, every element to be determined there have to be so many different channels and they analysis the whole analysis would be completed within a few seconds or maximum a couple of minutes.

(Refer Slide Time: 52:03)



ENERGY DISPERSIVE XRF

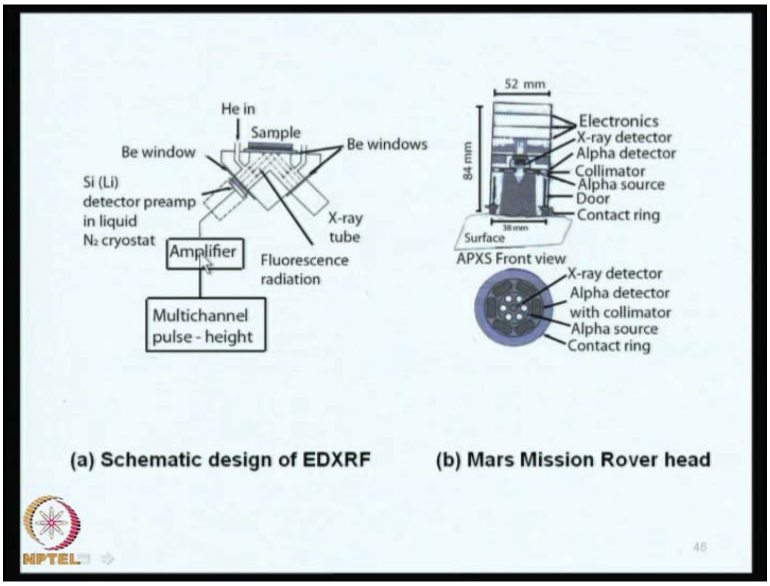
EDXRF has a polychromatic source such as an X-ray source or a radioactive material, a sample holder, a semiconductor detectors and various electronic components for energy discrimination.

The analytical methodology is very simple. There are no moving parts and no collimators or crystal diffractor. Therefore the energy reaching the detector is 100 times more than WDXRF instruments. H low power X-ray tubes or weaker radioactive m ials can be used as radiation sources which ar effective and more safer to use .

So, in energy dispersive X-ray fluorescence it has a poly chromatic source that is an X-ray source or a radioactive material a sample holder a semi conductor detector and various electronic components. So, the analytical methodology is also very simple here that is there are no moving parts - that is no collimators are crystal diffractions. Therefore, the entire energy reaching the detector is approximately 100 times more than wavelength dispersive hex rays instruments.

So, low power energy X-ray tubes or weaker radioactive materials can be used as radiation sources. Which are cost effective and safer to use why I am telling you all this is when you want to buy an instruments for your laboratory you should know what are the different sources? What are the detectors? What are their causes? What their collimators? What are their lines etcetera. So, this information would be very useful when you want to go for an instrument of this type.

(Refer Slide Time: 53:19)

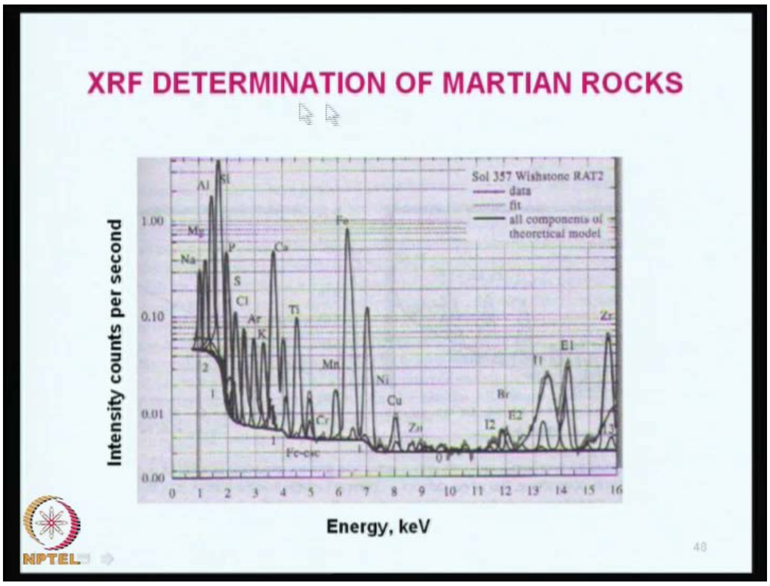


(a) Schematic design of EDXRF (b) Mars Mission Rover head

So, here you can see the amplifier is there, sample is here then helium cooling and then beryllium window is here, this is the beryllium window and then detector and then amplifier and multichannel pulse I am pulse height analyzer. So, fluorescence radiation keeps on coming like this; for each element you will have different kinds of the crystals and the detectors. So, this is the mars and rover detector mars machine rover detector, here we can see that X-ray detectors are all located around these six head APXS. This is a front view and alpha source is there, contact ring is there, and then door etcetera. Other things are all a set here this we had discussed in the first lecture also.

So, the sensor head the rower contains curium 244 sources that emits X-rays and five point eighty one m e v alpha particles. So, the multiple element determination can be obtained by particle induced X-ray emission method. So, the X-ray detector is a new room temperature type that exhibits very low noise the if the detector is at operating at very high temperature; that means, it is going for higher noise; that means, the detection limit will be lower.

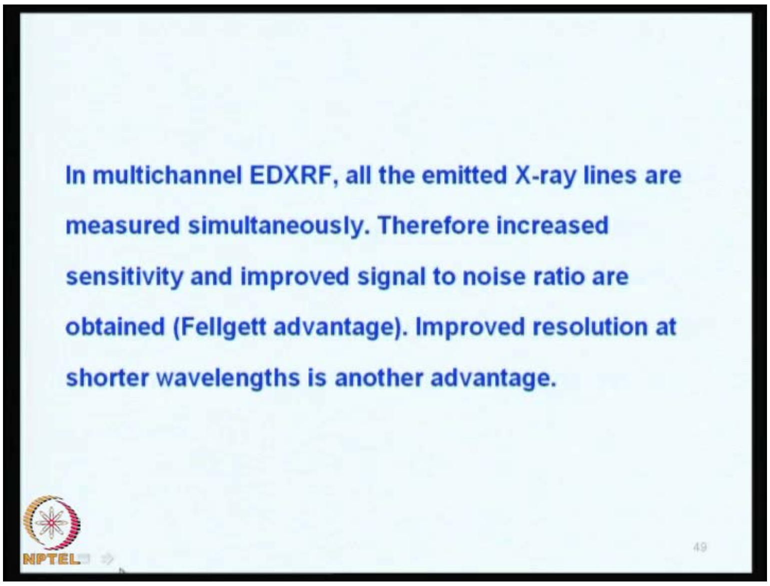
(Refer Slide Time: 55:01)



XRF DETERMINATION OF MARTIAN ROCKS

So, this is the XRF determination of the Martian rocks, we can see that in a single analysis sodium, magnesium, aluminum, silicon, phosphorus, sulphur, chlorine, argon potassium, titanium, calcium, manganese, iron, nickel, copper, zinc approximately about 24 elements have been determined in the martial rocks and they have been determined.

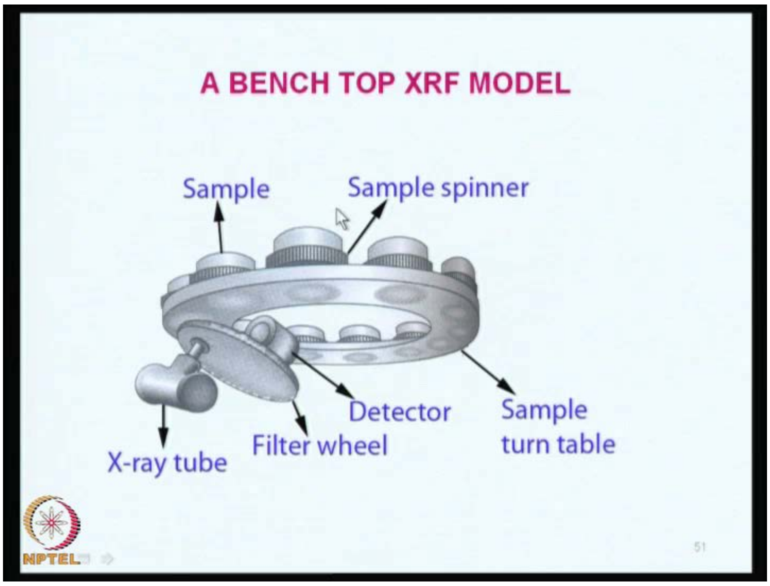
(Refer Slide Time: 55:26)



In multichannel EDXRF, all the emitted X-ray lines are measured simultaneously. Therefore increased sensitivity and improved signal to noise ratio are obtained (Fellgett advantage). Improved resolution at shorter wavelengths is another advantage.

In multi channel all emitted X-ray lines are measured simultaneously. So, improve the sensitivity is obtained and improved signal to noise ratio is obtained; this is known as Fellgett advantage. We will discuss about the Fellgett advantage in while you are talking about infrared radiation also. So, improved resolution a shorter wavelengths is possible nowadays, a bench top EDXRF is available for routine determination of up to twelve elements, ranging from sodium to uranium. The fluorescence signal is obtained by using appropriate filters and that strikes the bottom of the rotating table where the detectors is rotated located. And the rhodium X-ray tube five programmable filters helium per system is available twelve positive sample changer is there and a spinner to rotate.

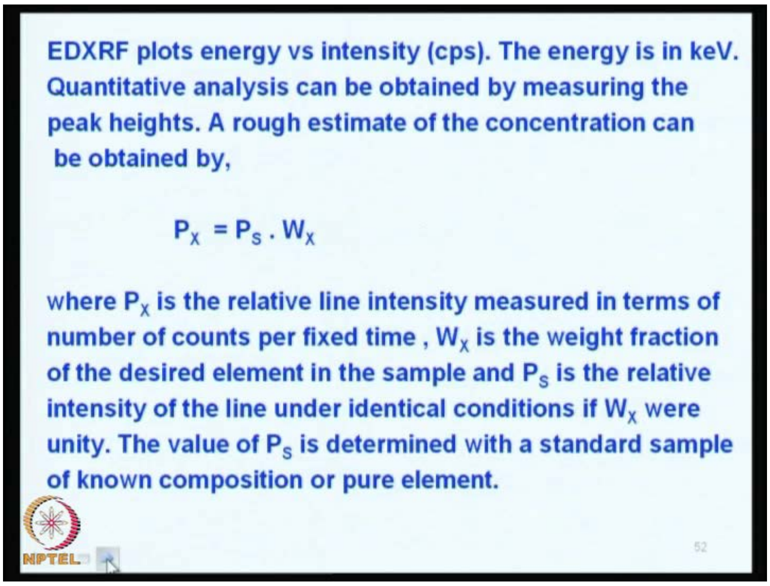
(Refer Slide Time: 56:33)



A BENCH TOP XRF MODEL

So, this is the picture of a bench top XRF model where you can see the different sample, samples spinner and then detector filter wheel ray tube and sample turn table.

(Refer Slide Time: 56:44)



EDXRF plots energy vs intensity (cps). The energy is in keV. Quantitative analysis can be obtained by measuring the peak heights. A rough estimate of the concentration can be obtained by,

$$P_X = P_S \cdot W_X$$

where P_X is the relative line intensity measured in terms of number of counts per fixed time , W_X is the weight fraction of the desired element in the sample and P_S is the relative intensity of the line under identical conditions if W_X were unity. The value of P_S is determined with a standard sample of known composition or pure element.

So, the EDXRF basically plots the intensity of the cps and with which can be quantified like this. The applications analytical methodology, we will continue in the next class. There is very little to be said about the analytical methodology and other systems analytical aspects that we will discuss in the next class and then continue on to atomic absorption spectrophotometric.