Modern Instrumental Method of Analysis

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Module No. 03
Lecture No. 16
X-Ray Analytical Techniques-2 Applications

We were talking about analytical methodology for X ray fluorescence, what I wanted to tell you is about the matrix effects. Usually absorption of X rays from the atoms occurs well below the surface. The extent of attenuation depends upon the mass absorption coefficient of the medium and its composition. Usually, signal decreases as the mass absorption component increases the signal decreases and sometimes enhancement of fluorescence may occur due to the secondary excitation of the analytical line signal. Suppose, the secondary excitation takes place then what happens there are more electrons, more photons which will hit the detector and these detectors will give you enhanced signal.

So, but they are not the real X ray fluorescence signals. So, you can minimize these effects by using closely matched standards, except the added element analyte. So, you can take a look at some of the composition of the standards and then use those standards except the enlighten element and then do the analysis using the standards. So, alternately you can use an internal standard that is introduced in all the standards and samples. So, one can also dilute the sample and standards that absorb X rays only weakly. Water organic solvents starch, lithium carbonate, alumina, boric acid, boride glass etcetera. The all such things can be analyzed very easily and here the matrix effect becomes essentially constant.

So, the applications of X ray fluorescence usually are occurring in different types of samples. When X ray absorption and enhancement effects are minimal XRF line intensity and element concentration curves are linear. So, to get such linearity N I s t standards provide such materials and in national institute of standards and testing. So, these standards are available you can buy them from the market, which will closely resemble your samples and they are all pre analyzed. So, that you can have about 95 percent confidence in their analysis results and when you get such analysis done then you can; if it matches your signal then you can go for the actual analysis.

So, such materials can be used to calibrate the instrument itself, alternately you can go for calibration as well as measurement. So, typical applications include the analysis of rock samples, there are about 22 elements that can be analyzed using XRF within a few minutes. And you can have alloy composition control during the manufacture, supposing you are manufacturing some alloys in a furnace then you have the raw material and then composition elements and then melt it. And then it will form a melt along with a slag floating on the top what you can do is take a small amount of the melt bring it to the laboratories by the time you bring it its already five cool it and then do the XRF analysis for composition of the alloys.

And if the alloys composition is matching, what you are planning what is your production line then you go ahead and take out the material and cast into different materials. Otherwise you if the analysis indicates that one or two elements are composing elements are in; are not in the expected concentration. You can add the alloying elements and then a rematch the standards and then cast it into different components, once the composition of the melt is akin to your samples. And then you can determine lead and bromine in aviation fields this is an application where the liquid samples are analyzed. So, you can use calcium, barium, zinc and lubricating oils.

We can determine and then pigments in paint samples also can be determined very easily. Another application is determination of chlorine, sulfides and sculpture dioxide using orthotolidine, silver nitrate and sodium hydroxide impregnated micro pour filter papers, what do we do? Actually is we take orthotolidine dip, it in micro pour filter papers and then expose it to the element. So, depending upon the amount of chlorine it will give you some colored complex. And that micro filter itself you can insert as a sample in XRF and determine the chlorine. Same thing is true of silver nitrate for sulphides; usually sulphides will react with silver nitrate to make them black producing silver sulphide.

And if you have the silver nitrate dipped micro pour filter you can expose it to the environment. If there is any hydrogen sulphide it will react producing a dark spot where the silver halide, silver sulphide would be held in the matrix and that sample can be straight away taken into the XRF. Then, sodium hydroxide works for sodium; sulphur dioxide. sulphur dioxide dissolves in sodium hydroxide and if you have a sodium hydroxide micro pour filter, again you can expose it to the sulphur dioxide concentration and determine. Similarly, you can determine the concentration of elements in food articles for example, iron, copper, zinc etcetera can be determined in rice samples.

So, such things are applications are also possible. So, the; in general, what I can tell you? Is that the applications of X rays are numerous and for the analysis is fast, you can complete the analysis within a few minutes. And then, they can determine number of elements either sequentially or in simultaneously. Sequential analysis is useful for single elements one after another you can go. And simultaneous and a X ray fluorescence analysis require different design and they are all almost; always dedicated instruments.

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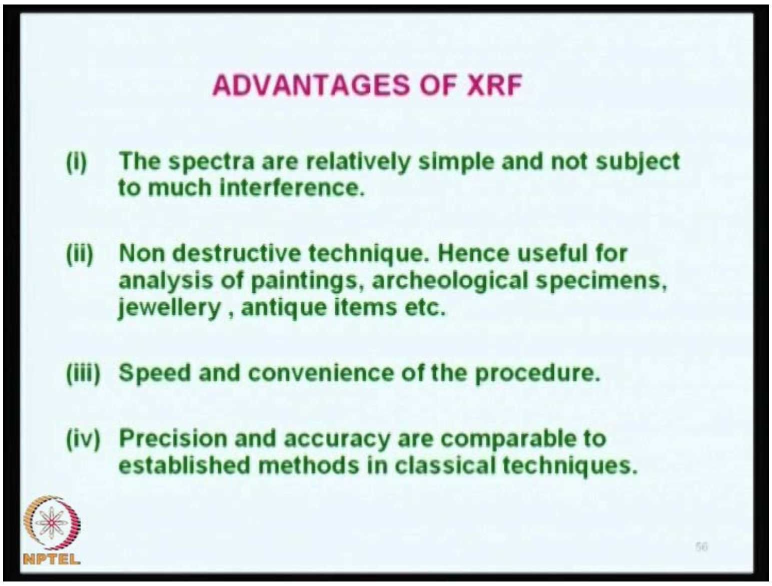

ADVANTAGES OF XRF

(i) The spectra are relatively simple and not subject to much interference.

(ii) Non destructive technique. Hence useful for analysis of paintings, archeological specimens, jewellery , antique items etc.

(iii) Speed and convenience of the procedure.

(iv) Precision and accuracy are comparable to established methods in classical techniques.

So, what are the advantages of XRF? Do you we can summarize it like this, the spectra are relatively simple and not subject to much interference. This is one of the important advantages, because there are not much complications and with a little training one can do the analysis. And then, basically it is a nondestructive technique so, you have not going to lose any sample. Therefore, they are useful for the analysis of paintings, paints in important paints. The paintings, we can analyze the paints and archeological specimens you can analyze, you can analyze jewelry, you can analyze antique items etcetera.

And then speed and convenience of the procedure is also one of the important advantages of XRF. And then precision and accuracy are comparable to established methods in classical techniques. This is very important because in classical techniques the chemical analysis might can match maximum PPM levels not lower than that. So, in general XRF can be used for the analysis of such substances in PPM levels. Now, they there are certain disadvantages also in XRF and these disadvantages I can only summarize like this, that the concentration range varies from 0.01 to 100 percent that is the analysis range, not lower than 0.01 percent.

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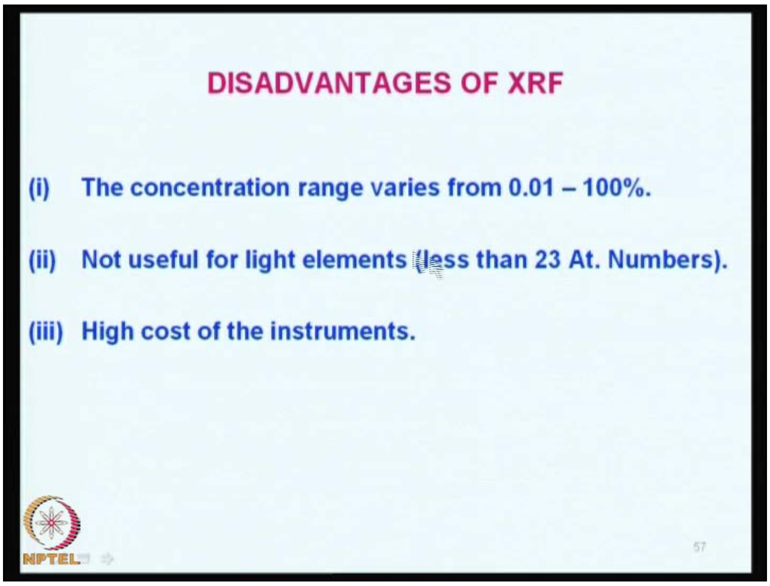

DISADVANTAGES OF XRF

(i) The concentration range varies from 0.01 – 100%.

(ii) Not useful for light elements (less than 23 At. Numbers).

(iii) High cost of the instruments.

Sometimes it is not useful for light elements having atomic number less than twenty three, this we have point we have discussed already. And third disadvantage is, it is the high cost of the instruments. Therefore, only when there are repetitive requirements and then multiple element analysis required, you should go for XRF that should be the natural choice and the concentration also should be very high. So, this completes our discussion on the X ray fluorescence. And now we will switch on to atomic absorption spectrometry. We will move on to another technique that is atomic absorption spectrometry, this is a very important technique for the analysis of number of elements.

And the phenomenon of atomic absorption was first discovered in as early as eighteen hundred and two. It was Wollaston who discovered the phenomenon of atomic absorption in the spectrum of sunlight, till then it was thought to be sort of a k sun solar spectrum was thought to be a sort of continuous spectrum, but Wollaston made a remarkable observation that the solar spectrum was in fact, interrupted by number of dark lines which was later confirmed by fraunhofer in eighteen hundred and fourteen.

So, fraunhofer reexamined this aspect and then he confirmed that the there were actually dark lines in the solar spectrum. However, the explanation for this, came forward by Doctor, Professor Brewster and who put forward the idea, that these dark lines in the solar spectrum denoted till then by usually alphabetical markers alpha, beta, A B C etcetera. They use to denote, but what he said; is that these dark lines in the solar spectrum are in fact, due to the presence of vapors of certain elements in the suns atmosphere. Very important observation, because it related to the absorption of solar radiation by these vapors therefore, it follows.

That the substance is emitting radiations, specific radiations are also capable of absorbing the same radiations causing the spectrum of dark lines in the bright background. If there was no absorption, the emission would be a very fine continuous spectrum and there should not be any dark lines at all. So, if there is there are certain elements in the sun, sun is core or atmosphere occurs on a somewhere. These elements are absorbing part of the radiations and then when they absorb the radiations the emitted intense; emission intensity becomes less. So, this is due to atomic absorption, because in the; at the temperatures prevailing in the sun is atmosphere there cannot be any molecules, but only the atoms.

So, this phenomenon is generally known as Kirchhoff’s law. It was used to deduce the presence of oxygen, hydrogen, sodium, iron, calcium etcetera. In the solar spectrum this is, how we came to know that oxygen, hydrogen, sodium, iron, calcium etcetera, are present in the solar atmosphere. The experimental confirmation for this came from the electric arc or spark, then these spectral source surrounded by atomic vapors also showed similar dark lines, because of the absorption of the emitted radiations. So, the same kind of temperatures prevailing in the solar atmosphere where generated by the arc or spark on the earth.

And when the generation of the spark was using the electrodes and if the electrodes contained particular elements, the same spectrum of the arc showed dark lines. Then, they thought yes; it must be due to the same element and if we can match the frequency of the elements absorption then we should be able to determine the elements even in the sun so, that was the thinking. So, because of the absorption of the emitted lines the vapors also showed dark lines in the arc or spark spectrum. So, this absorption leading to the decrease in the intensity of the emitted radiation was also demonstrated by Foucault in France, he showed the reversal of the spectral lines.

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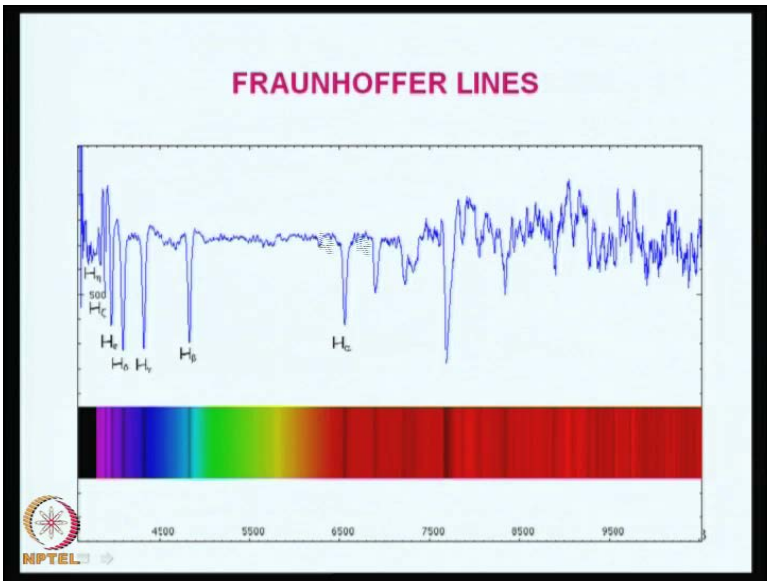

FRAUNHOFFER LINES

So, in essence what we are looking at is that the some of the elements in the sun are absorbing the same radiations that are present in the emission of the same elements. So, here you are; this is the; these are known as fraunhofer lines and here you can see the dark lines in the colored spectrum at the bottom. Here, I have put wave length this is 4500 5500 6500 like that up to 9500, here we have number of spectra and these spectra correspond to the dark lines, which are matched by the different kinds of elements. So, this is a very interesting observation, which co relates the atomic absorption to the elements present in the sun.

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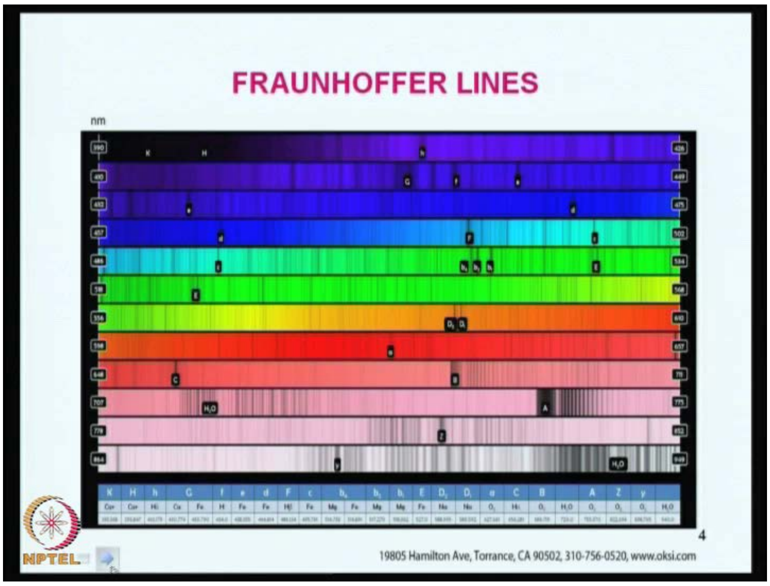

FRAUNHOFFER LINES

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This is actually a detailed diagram of the same, where we can see that the elements determined using these dark lines. You can dark lines all over this one is blue and then it is green and then it is orange red etcetera. And here you can that potassium, hydrogen and then calcium, cobalt, this is cobalt and then iron, iron lines are there hydrogen then magnesium then there is sodium and oxygen and water vapor all these elements are; all these molecules and elements are there in the solar spectrum..

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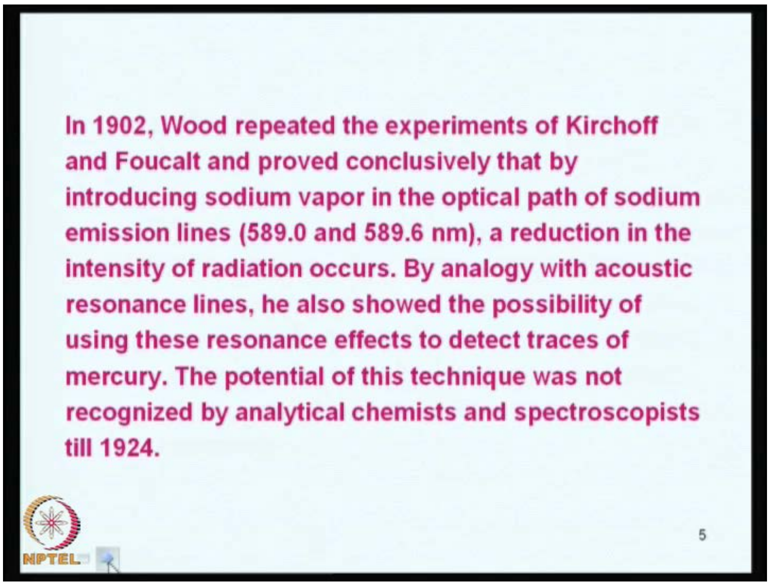

In 1902, Wood repeated the experiments of Kirchoff and Foucalt and proved conclusively that by introducing sodium vapor in the optical path of sodium emission lines (589.0 and 589.6 nm), a reduction in the intensity of radiation occurs. By analogy with acoustic resonance lines, he also showed the possibility of using these resonance effects to detect traces of mercury. The potential of this technique was not recognized by analytical chemists and spectroscopists till 1924.

So, it is a very interesting and confirming factor that the atomic absorption phenomenon. Even though known as early as eighteen hundreds is the known the scientist, but it was not repeated it was the significance of it was not known. So, in nineteen hundred and two would repeated the experiments of Kirchhoff and Foucault and he proved conclusively that, what he did? Is he introduced a sodium vapor in the optical path of sodium emission lines. And then what he noticed was a reduction in the intensity of the emitted radiation. Where you conclusive prove you take the sodium light, what you see in the street lights yellow bulbs which emanate radiation in yellow color they correspond to 589 and 589.6 nano meters.

It is a doublet two types of wavelengths are coming both of them are yellow light only. And in; if you take that radiation introduce sodium vapor in the optical path and measure the radiation intensity. We know how to make the measure the radiation intensity by photo multiplier tubes and other things. We have studied those things in our atomic absorption studies of molecular absorbance, photo aluminous sense etcetera. And if you do that, you will see a reduction in the intensity of the emitted radiation. That is before introduction of the sodium vapor you get certain intensity and you introduce the sodium vapor sodium vapor will absorb the part of the radiation.

And the out coming radiation will always be having lower intensity than the incident air radiation. So, by analogy with acoustic regiment is lines he also showed the possibility of using these regiments lines to detect traces of mercury, he extended the analogy to mercury suppose I have a mercury lamp then I introduce mercury vapor. Mercury vapor will generate mercury atoms and these mercury atoms will absorb part of the radiation. So, if you; if such a thing is actually happening, we should be able to determine mercury in different kinds of samples that was the logic.

So, he also showed the potential of this technique, but it was not realize; recognized by analytical scientist and spectroscope is till 1924 then only the thinking started yet yes we can use the; such a phenomenon for using these radiations atomic absorption phenomena to determine sodium, mercury, extra. Somewhere around that time around 1930, 25 and 30 Angarer and Joss published the atomic spectra of all iron group metals. So, now the; we know at what frequency iron atoms emit the radiations as well as absorb the radiations, it is like a dictionary so, data base. So, this was followed by he did for iron group metals and then Frayne and Smita published the similar data base spectrum for indium, aluminum, gallium and tantalum.

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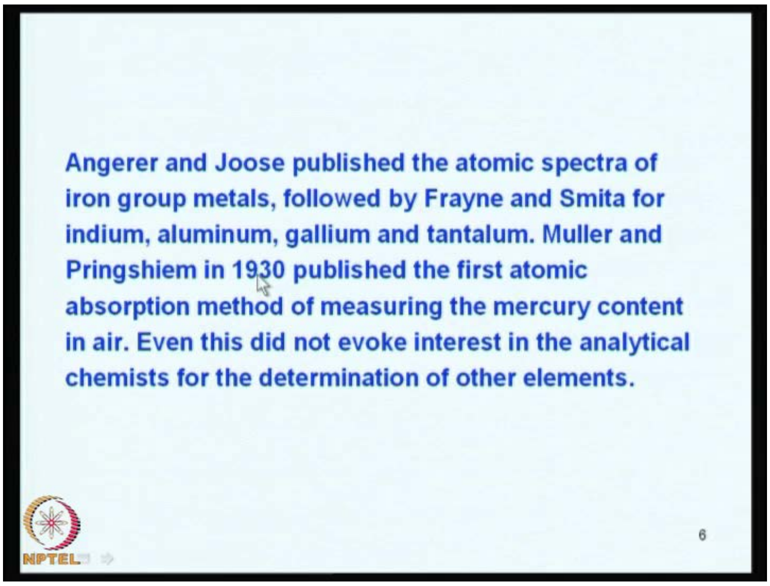

Angerer and Joose published the atomic spectra of iron group metals, followed by Frayne and Smita for indium, aluminum, gallium and tantalum. Muller and Pringshiem in 1930 published the first atomic absorption method of measuring the mercury content in air. Even this did not evoke interest in the analytical chemists for the determination of other elements.

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So, Muller and Pringshiem in nineteen thirty published the first atomic absorption method of majoring the mercury content in air. You will be surprised to know that the concentration of mercury determent in 1930 was of the order of phio PPB parts per billion, which you here doing now. But first time it was demonstrated that you could do PPM level analysis of mercury in air, in 1930. Even this did not evoke much interest in the analytical chemist for the determination of other elements. Because mercury we know that when it falls on the floor, the mercury vapor is automatically generated. So, if you just have a mercury source and a detector and put some mercury in the optical path it will always show some amount of absorption and that could be determined.

But for generating the atoms of other elements that was the big challenge and that is why atomic absorption did not take off as a real technique till late in 1955. In 1955 Walsh developed the first real application of atomic absorption to chemical analysis. In the same year Alcormade and Mitts described a double beam method of spectral selection with two flames, one for excitation another for absorption. The first being the source of atoms and the second as the atomizer, since then the atomic absorption spectrometry is in the forefront of chemical analysis.

The first commercial atomic absorption instruments appeared in the sixty is and due to the efforts of Alan Walsh in 1955 and subsequently commercial instruments appeared in the 1960. But then a revolution took place in the analytical front, spectacular advances in instrumentation electronics and then automation and computers. Over these all these years since last 5 decades, you have made atomic absorption spectrometry one of the most really reliable analytical techniques of modern times; it is perhaps equaled only by atomic emission spectrometry, which also has been developed only since last twenty years.

But atomic absorption and atomic emission both these techniques are; of recent origin atomic emission is slightly oh resent. But atomic absorption and atomic emission both of them hold the pride of place and first choice for the analysis of a number of elements, in terms sensitivity, simplicity, specificity and the speed of operation. Today the first choice of any analytical scientist, if you ask him to; the do a chemical analysis, first you will say yes sir I will do the atomic absorption method to determine the elements. So, it has come up to this state only because of the advances in instrumentation, electronics automation. And computers and the development of electro thermal atomization was the next big leap for the detection limits for increasing; decreasing detection limits of the order of few PPB parts per billion.

And sometimes even a pictograms, sometimes even femtograms that is ten raise to minus fifteen grams of the substance can be detected by; only by the development of a of an accessory known as electro thermal atomization. And this was prier headed by professor Labeouf of Russia.

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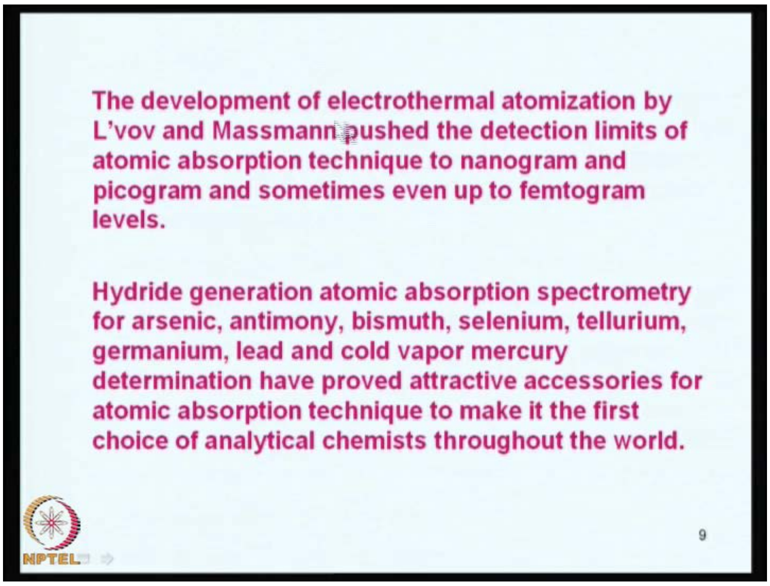

The development of electrothermal atomization by L'vov and Massmann pushed the detection limits of atomic absorption technique to nanogram and picogram and sometimes even up to femtogram levels.

Hydride generation atomic absorption spectrometry for arsenic, antimony, bismuth, selenium, tellurium, germanium, lead and cold vapor mercury determination have proved attractive accessories for atomic absorption technique to make it the first choice of analytical chemists throughout the world.

And a Professor Massmann developed the equipment to achieve electro thermal atomization. And he push the detection limits of atomic absorption technique to nano gram levels, picogram levels and femtograms levels. And other accessories for atomic absorption which have developed over the years include hydride generation. So, a hydride generation atomic absorption spectrometry is useful for the analysis of arsenic, antimony, bismuth, selenium, tellurium, germanium, lead etcetera, these are six or seven elements which form hydrides.

And this hydride generation atomic absorption spectrometry permits the determination of picogram levels of these elements arsenic, antimony, bismuth, selenium, tellurium, germanium, lead and mercury also to some extent. And you will appreciate that all these elements arsenic, antimony, bismuth, selenium, tellurium, germanium, lead, etcetera they are all environmentally very important elements. And we have strict standards for their presence in the environment and the standards refer to parts per billion level of existence in the air and water environment around us.

So, atomic absorption spectrophotometry using hydride generation atomic absorption works for these elements. And cold vapor, mercury vapor cold mercury what I what was described in 1920 that co; I had explained to you just now the cold mercury vapor determination. It is useful for picogram levels of, atomic of a determination of a mercury especially to make it the first choice of analytical chemist throughout the world..

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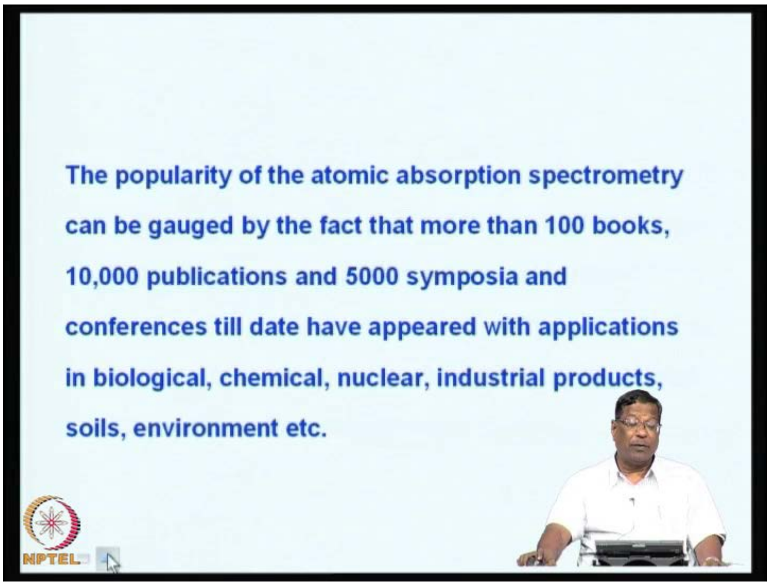

The popularity of the atomic absorption spectrometry can be gauged by the fact that more than 100 books, 10,000 publications and 5000 symposia and conferences till date have appeared with applications in biological, chemical, nuclear, industrial products, soils, environment etc.

So, these are the variants of atomic absorption and you can gauge the popularity of the atomic absorption spectrometry, by the fact that more than hundred books have been published only on atomic absorption spectrometry. And there are more than ten thousand research publications only in this area. And five thousand symposia in conferences including national, international conferences till date have happened. And these a symposia and conferences and publications most of them deal with atomic absorption analysis in a variety of methodizes.

Where biological, chemical, nuclear industry, industrial products, soil analysis, environmental analysis and several other applications where atomic absorption takes the leading roll in deciding which of the technique that can be utilized for the chemical analysis. So, now what we would like to do? Is I would like give you a some sort of a small introduction to the theoretical principles of atomic absorption. Sometimes a this may be slightly more involved and more mathematical, but really do not worry, because the all the theoretical considerations, what we are going to have discuss involve the applications of a subsequent development of the instrument and they are not really very rigorous in derivation.

But, to some extent they are because the atomic absorption spectrometry has been put on a very firm foundation since it is the preferred elemental technique and the; it may it may be slightly complicated. But I will try to make it as simple for you as possible and the basic ideas which have been developed using these theoretical aspects are put into operation it is an instrumental design and the chemical analysis etcetera. So, if you feel slightly overwhelmed by the derivation etcetera what I suggest is you take a look at it leisurely and them go through the; this lecture. And also you can go through other text books which will clarify your ideas, because in general at the first hearing you may feel slightly overwhelmed by the derivations. Especially the concepts and I will try to make it as simple as for you as possible.

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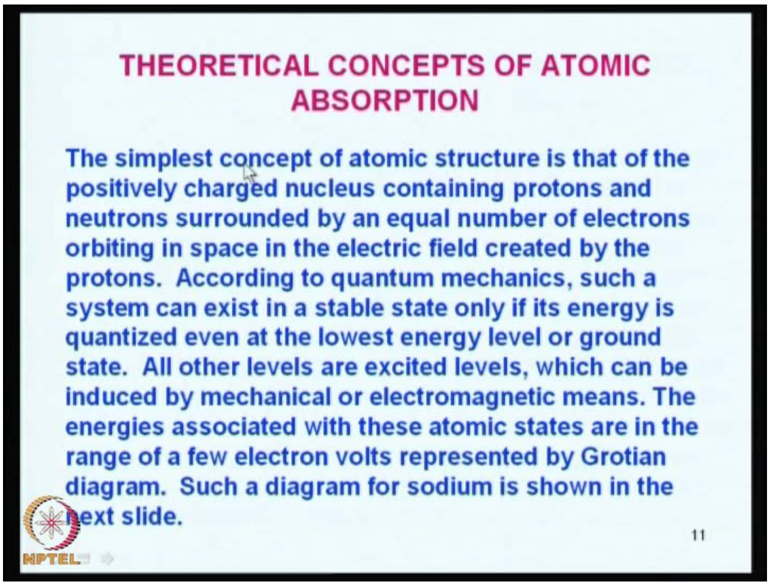

THEORETICAL CONCEPTS OF ATOMIC ABSORPTION

The simplest concept of atomic structure is that of the positively charged nucleus containing protons and neutrons surrounded by an equal number of electrons orbiting in space in the electric field created by the protons. According to quantum mechanics, such a system can exist in a stable state only if its energy is quantized even at the lowest energy level or ground state. All other levels are excited levels, which can be induced by mechanical or electromagnetic means. The energies associated with these atomic states are in the range of a few electron volts represented by Grotian diagram. Such a diagram for sodium is shown in the next slide.

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So, the simplest concept of atomic structure is that of the positively charged nucleus containing protons and neutrons, these are surrounded by an equal number of electrons orbiting in space, this we have discussed number of times how is in atomic atom is atomic structure is built. And according to quantum mechanics such a system can exist in a stable state only if it is energy is quantized. And at the lowest level as well as in the excited levels, the all other levels expect the ground state are referred as excited levels. Which can be induced to be occupied by the electrons to go to next higher energy level or excited levels by mechanical or electromagnetic means mechanically you can heat the substance.

And then produce the atoms which will get excited and go to the next higher energy level. Also we can use electromagnetic radiation make them fall on the atomic vapor and then excite the atoms. These are the things which we have discussed earlier with respective molecules in a spectrophotometry. But essentially the same discussion is taking place now, only thing is we are talking of the atoms now not the molecules. So, the energy is associated with these atomic states are in the range of few electron volts represented by grotrian diagram such a diagram for sodium I am showing in the next slide.

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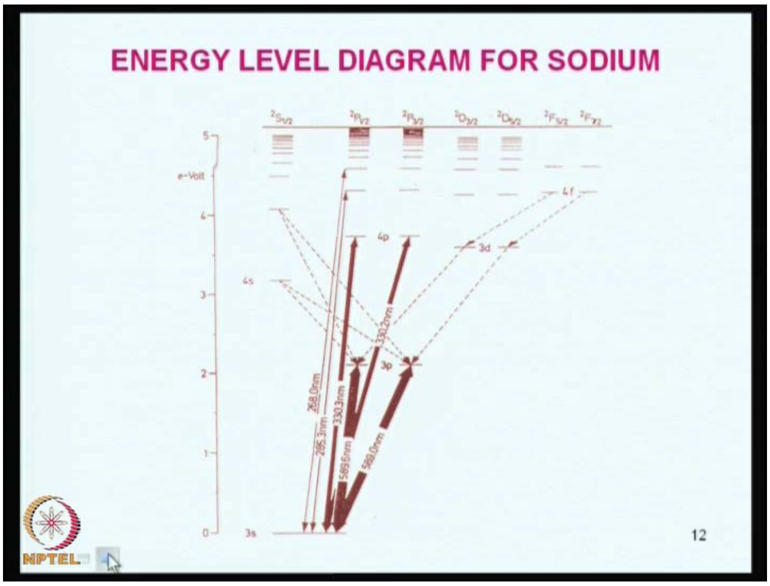

ENERGY LEVEL DIAGRAM FOR SODIUM

You can see here the energy level diagram for sodium. So, I have here the three s energy state and the bottom and then here it is 2 S 1 by 2 that is the excited state 2 p 1 by 2 2 p 3 by 2 2 D 3 E by 2 2 D 5 by 2 2 f 5 by 2 2 f 7 by 2. So, here are 3 S 4 S 5 S etcetera the energy excited energy are shown here by simple lines. And here you can see that the electrons the excited states are populated nearer and nearer in 2 p 1 by 2 and 2 p 3 by 2 etcetera. And the excess here is the ground state electronic levels and on the abscissa it is electronic volts. So, what is happening here is we are determining taking the sodium atom and determining, it is energy level.

For example, three s is occurring approximately at 0 electric volts 0 E volts. So, most of the electrons in the ground state are having energy of the ground state approximately 0 and then I have 1 2 3 4 5 electron volts; that means, I am exciting the atoms by applying one volt two volt three volts four electronic volts and 5 electronic volts and the electrons will be excited from here to the higher energy states described by 2 S by 2 2 p by 2 2 p 3 by 2 etcetera. So, the excitation can occur here like this from 3 S to 2 p 1 by 2. And this occurs around 200 and 60 80 nano meters next line is this line excitation and this occurs 285.3 E nano meters and 4 p levels occurs at 330.3 nano meters.

And then 330.2also there is 1 and 3 p 3 is 5 89 nano meters and another 3 p occurs at 330.3 nano meters. So, like that you can see that most of the excitations are starting from the ground state to higher energy states up to this and then here and then 4 p state 3 d state etcetera 4 f state also and all these transitions are coming back to 3 p and then falling back because they are I am showing all of them as the reversible reactions. That means an excited electron can also fall back to the ground state either it can fall back from the same level to which it is excited or it may be excited somewhere else some other line.

But it will fall back to 3 p and then from there it can fall down. So, I have shown here dark lines two dark lines at 3 p levels and two dark lines at 4 p levels. So, these dark lines represent what is known as resonance energy; that means, it is the lowest energy to which an electron can get excited up to this and then it can back to the ground state. So, the lowest is three p next lowest is 4 p. So, these are known as resonance lines. So, this is the energy level diagram of sodium this I have shown you even in when I was talking about atomic fluorescence similar diagram and I had made a statement that most of the elements the energy level diagrams are represented like this only and if you go back and check I had shown you.

The spectra for magnesium lithium cobalt etcetera. So, what we are looking at it is right now, our interest is in the dark lines that are taking representing the transition from the ground state to the next higher energy state that is 3 p and 4 p all others are non resonance lines; that means, the excitation and emission does not occur at the same wavelength and that is not the minimum.

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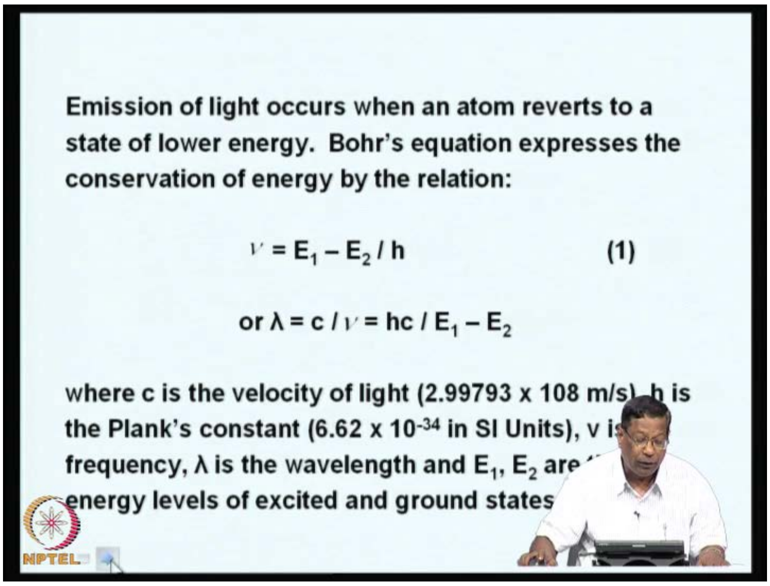

Emission of light occurs when an atom reverts to a state of lower energy. Bohr's equation expresses the conservation of energy by the relation:

$$\nu = E_1 - E_2 / h \qquad (1)$$

$$\text{or } \lambda = c / \nu = hc / E_1 - E_2$$

where c is the velocity of light (2.99793 x 108 m/s), h is the Plank's constant (6.62 x 10^{-34} in SI Units), v i frequency, λ is the wavelength and E_1, E_2 are energy levels of excited and ground states

So, if we use the minimum excitation then we should be able to determine what is the re what is the requirement of the electromagnetic radiation to excite an electron from the ground state to the next higher energy state. So, this can be calculated in terms electronic volts or in terms of radiation of particular wavelength. So, we are here it is very simple now to know that emission of light occurs when an atom reverts to a state of lower energy first the excite element has to excite go to next higher energy state and it has to return to the ground state and that time emission can occur this we know it as fluorescence or atomic emission. So, boar is equation expresses the conservation of energy by the relation E is equal to h mu.

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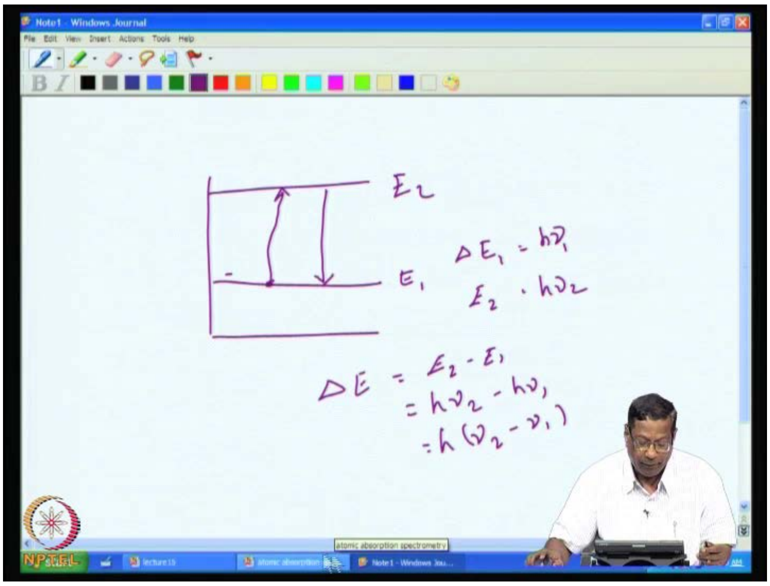

$\Delta E_1 = h\nu_1$

$E_2 \cdot h\nu_2$

$\Delta E = E_2 - E_1$

$= h\nu_2 - h\nu_1$

$= h(\nu_2 - \nu_1)$

So, suppose I have E 1 state another state is E 2 from E 1 and E 2 if the if there are 2 states one correspond to E 1 another corresponding to E 2 B I have an electron here. It can go like this and the excited electron can come back like this E 1 is equal to h mu or delta E can be h mu and E one is equal to h mu 1 and del E 2 is equal to h mu 2. So, the difference delta E is know is difference between E 2 minus E 1 and if you put h mu 2 minus h mu 1 they can derive that you can take out the difference h into mu 2 minus mu 1 and h you know that it is something to do with the energy.

And E 1 minus E 2 goes to mu and h. So, the wavelength can be simply calculated using this simple formula lambda is equal to c by v c by mu and which correspond to h c into E 1 minus E 2. So, where c is the velocity of the light h is the plank’s constant this all this we have discussed earlier and v is the if mu is the frequency lamed is the wavelength E 1 and E 2 are the energy levels of the excited and ground states.

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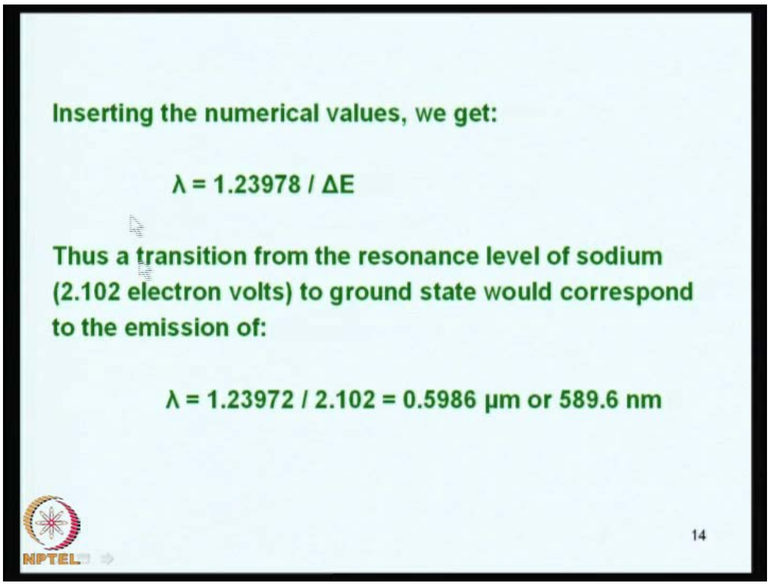

Inserting the numerical values, we get:

$$\lambda = 1.23978 / \Delta E$$

Thus a transition from the resonance level of sodium (2.102 electron volts) to ground state would correspond to the emission of:

$$\lambda = 1.23972 / 2.102 = 0.5986\ \mu m \text{ or } 589.6\ nm$$

Now, inserting the numerical values of h pi and other things etcetera we can calculate what is the wavelength of the emission that works out to some particular number 1.23978 divided by the energy difference between the ground and excited state that is E 1 and E 2. So, a transition from the resonance level of sodium to the ground state we can calculate we can go back to this figure from the ground state for sodium up to three p you can calculate. So, that where 3 5 use all these constants and it occurs at 2.10 electron volts and if insert those values I get 0.5986 micrometers or 589.6 nano meters. So, it is like this I can calculate the energy level or wavelength for each element any element I know if I know the difference between the two energy states..

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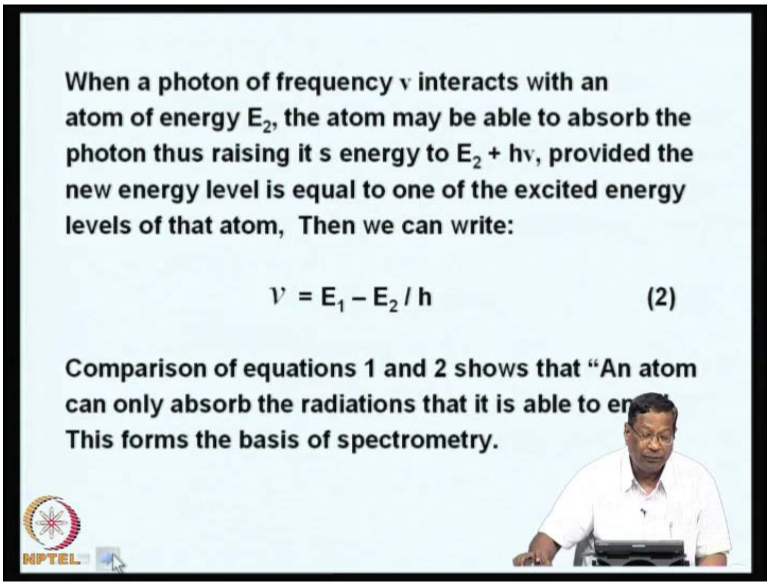

When a photon of frequency ν interacts with an atom of energy E_2, the atom may be able to absorb the photon thus raising it s energy to $E_2 + h\nu$, provided the new energy level is equal to one of the excited energy levels of that atom, Then we can write:

$$\nu = E_1 - E_2 / h \qquad (2)$$

Comparison of equations 1 and 2 shows that "An atom can only absorb the radiations that it is able to en

This forms the basis of spectrometry.

So, when an energy photon of energy frequency mu interacts with an atomic energy atom of energy E 2 the atom may be able to absorb the photon also thus raising its energy to E 2 plus h mu provided the energy level is equal to 1 of the excited energy level of that atom in the case of sodium. We know that, it is p an atoms p orbital. So, we can write E likes this very simple same thing what you have written earlier comparisons of equation one and two this is for absorption. Now, we are talking about absorption earlier equation one refers to emission.

So, it shows that an; a comparing these two expressions this one and the previous expression. This one expression, we know that the atom may be able to absorb the photon and an atom can only absorb the photons that it is able to emit, because the energy levels are fixed. So, it can either absorb if it the atom is in the ground state if the atom is in the excited state it can emit, but the radiation that it emits corresponds to the same energy level difference between the two this forms.

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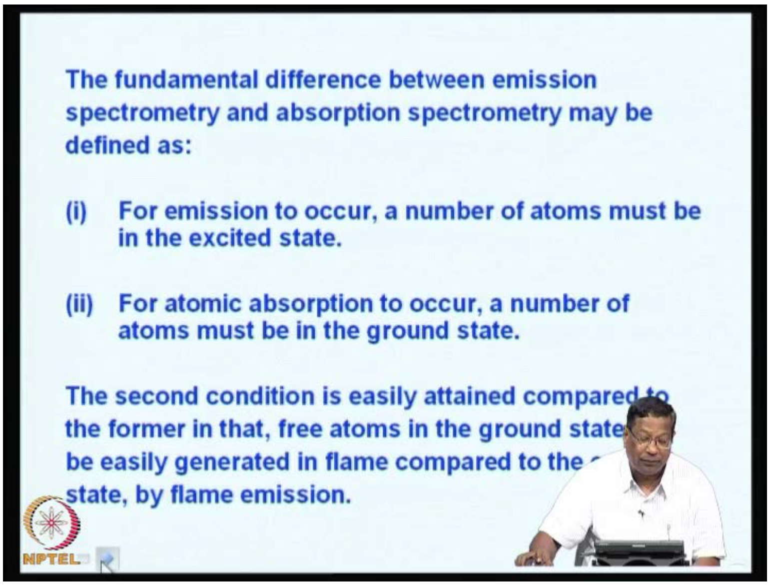

The fundamental difference between emission spectrometry and absorption spectrometry may be defined as:

(i) For emission to occur, a number of atoms must be in the excited state.

(ii) For atomic absorption to occur, a number of atoms must be in the ground state.

The second condition is easily attained compared to the former in that, free atoms in the ground state be easily generated in flame compared to the state, by flame emission.

The basis of atomic absorption spectrometry. So, the fundamental difference between an emission a spectrometry and absorption spectrometry we can define it like this for emission to occur number atoms must be in the excited state higher level. And then, only when the excited atoms come back to the ground state the energy will be released and it may in the form of emission. Now, for atomic absorption to occur where the number of atoms should be they should be in the ground state. So, that they can absorb the radiation and go to higher energy level. So, this second condition is easily attained compared to the former that is the; to have atoms in the ground state is simpler.

Then having atoms in the excited state it is very simple a logic basically, when you do not do anything almost of the atoms are in the ground state and to have more number of atoms in the excited state, you have to supply energy. So, without supplying the energy, it is possible to have the atoms in the maximum numbers of atoms in the ground state. So, this second condition is easily attained compared to the former in that free atoms in the ground state can be easily generated. We can generate the free atoms, how do you generate the free atoms in the ground state? We will see later, but if you are able to; if you have a choice between generating the atoms in the ground state or in the excited state the one which wins favor immediately is the ground state.

So, in the ground state, it is easier and we can produce atoms just by heating in a flame. So, compared to the excited state and that is what it means essentially. So, the characteristic absorption wavelength of an atom I have already demonstrated for sodium, that we can calculate the wavelengths and determine at what wavelength an element can absorb the radiation. So, the once we the energy levels are experimentally determine we can determine the wavelength of absorption also because the both of them mean the same, but several wavelengths are never observed even though you are able to calculate many of the wavelengths you do not see in the emission spectrum or in the absorption spectrum.

That is, because some sort of selection rules are there which will permit only certain transitions one the end those transitions are seen in the emission spectrum or in the absorption spectrum some of them are not permitted because they do not satisfy the quantum mechanical requirements the rules and these rules have were evolved empirically first and then subsequently confirmed by quantum mechanical calculations to the concept of transition probabilities. So, if the transition probably t if the quantum mechanical calculations permit a particular transition.

The probability is more, but if the quantum mechanical calculation does not permit the probability of a transition is always less that is how both of them are complementary to each other quantum mechanical calculations have to be supported by the probability and wise verse also. So, the probability of a spontaneous emission by transition between two energy levels E one and E two is how do you define it is defined as the fraction of number of atoms that drop to lower energy level per unit time off course you are if you are talking about the probability distribution rate etcetera we have no other recourse except to resort to equations and mathematical expressions.

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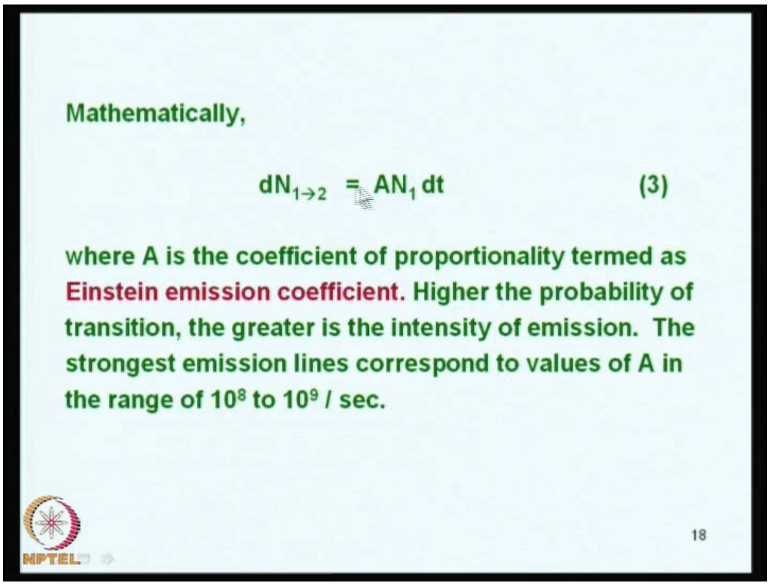

Mathematically,

$$dN_{1\to2} = AN_1\,dt \qquad (3)$$

where A is the coefficient of proportionality termed as **Einstein emission coefficient.** Higher the probability of transition, the greater is the intensity of emission. The strongest emission lines correspond to values of A in the range of 10^8 to 10^9 / sec.

So, the probability can be expressed as like this as an equation I have written here d N 1 these to two level one to level two the probably rate of pro transition is the denoted by a proportionality constant and number of atoms N 1 present at N 1. So, from N 1 they are going to N 2 and that is the transition when per unit time. So, as is the here in this equation three a is the coefficient of proportionality this is known as Einstein emission coefficient. So, higher the probability of transition the greater is the intensity of emission the strongest emission lines correspond to values of a in the range of about ten raise to eight to ten raise to nine per second.

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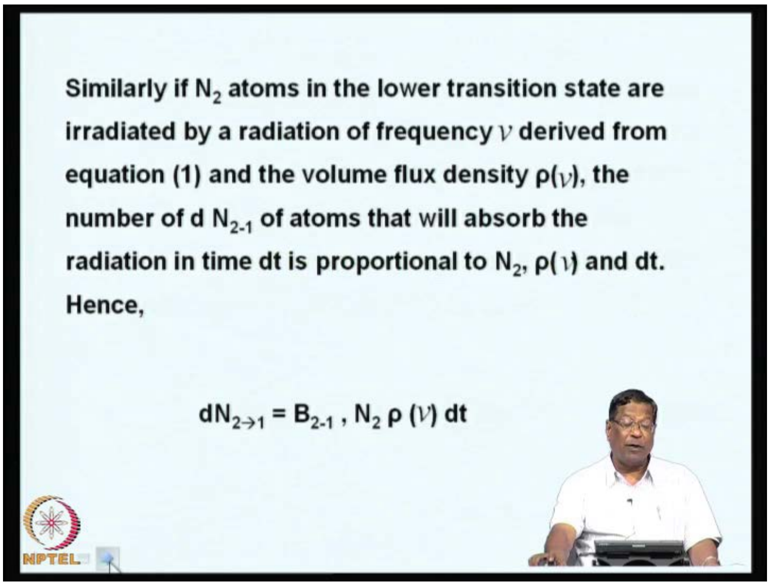

Similarly if N_2 atoms in the lower transition state are irradiated by a radiation of frequency ν derived from equation (1) and the volume flux density $\rho(\nu)$, the number of d N_{2-1} of atoms that will absorb the radiation in time dt is proportional to N_2, $\rho(\nu)$ and dt. Hence,

$$dN_{2\to1} = B_{2-1}\,,\, N_2\,\rho\,(\nu)\,dt$$

And the another aspect that is absorption similarly, if I have N 2 atoms in the ground in the lower transition state they are irradiated by radiation of frequency mu derived from equation one and if the volume flux density row v is the number of d N 2 to N 1 state that will absorb the radiation in the time fraction d t it should be proportional to the number of atoms in the high excited state N 2 o row v and d t. So, mathematically I can express this as d N 2 to 1 going to B 2 to 1 this is the proportionality constant N 2 and row v and d t that a row v represents the volume flux density of the transitions.

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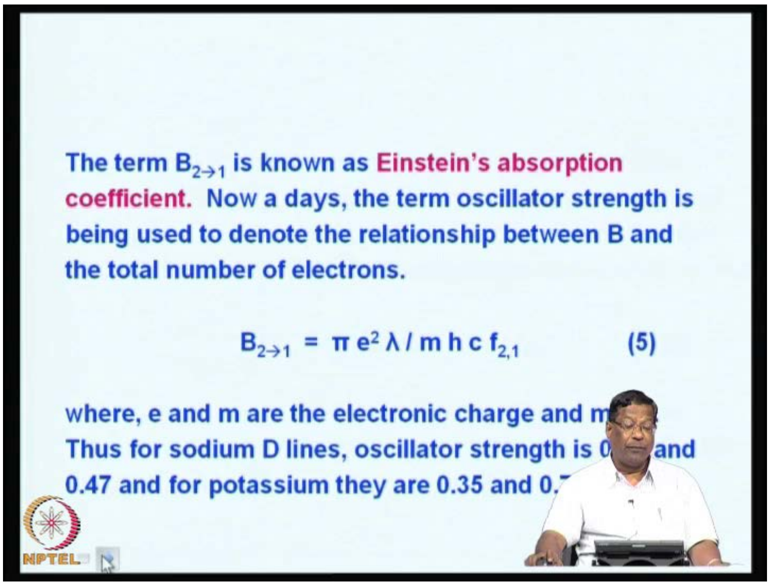

The term $B_{2\to1}$ is known as Einstein's absorption coefficient. Now a days, the term oscillator strength is being used to denote the relationship between B and the total number of electrons.

$$B_{2\to1} = \pi e^2 \lambda / m h c f_{2,1} \qquad (5)$$

where, e and m are the electronic charge and m
Thus for sodium D lines, oscillator strength is 0 and
0.47 and for potassium they are 0.35 and 0.

So, now we will have to define the B 2 to 1 this transition has to be different from Einstein emission coefficient. Because now, it the emission is not occurring, but absorption is occurring. So, we define this as Einstein absorption coefficient now days we do not use the Einstein absorption coefficient etcetera, but we simply term it as oscillator strength that is, it is being used to denote the relationship between the B and total number of electrons.

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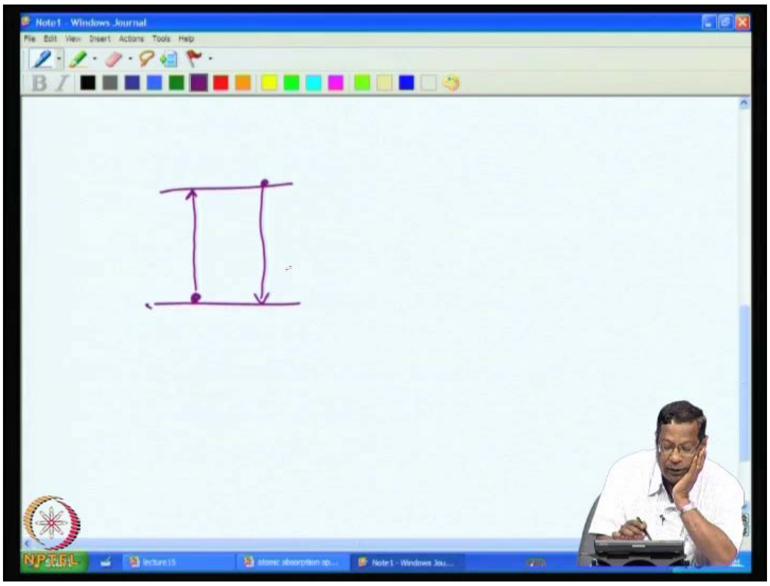

So, what we mean actually in this case is the is that, the electron is going from one state to another state I have two states this is an electron and it is going to the next end of the state it cannot remain there forever. So, it has to it from here it can come back to ground state. So, the electron is occurring is going from ground to excited, excited to ground state like this and then; that means, it is going according to a fixed plan like an oscillator it either goes from here from this point to the higher energy state and higher energy state to ground state and that one is known as oscillator; that means, it is oscillating only between the two possibilities now.

So, it is known as harmonic oscillator because it the oscillations are reproducible because the energy levels are fixed. So, the electron also has to go only between those two energy levels. So, in this equation we can say that the B 2 to 1 transition is nothing, but the Einstein absorption coefficient can be determined by pi E square lambda wavelength. And another is the mass other things are all known h c and f two to one is the probability therefore, for sodium d lines the oscillator strength is 0.23 and 0.47 to you remember there were two lines excitation lines of excitation from s to p. So, for potassium they are 0.35 and 0.7 similarly, for different elements their numbers will be different.

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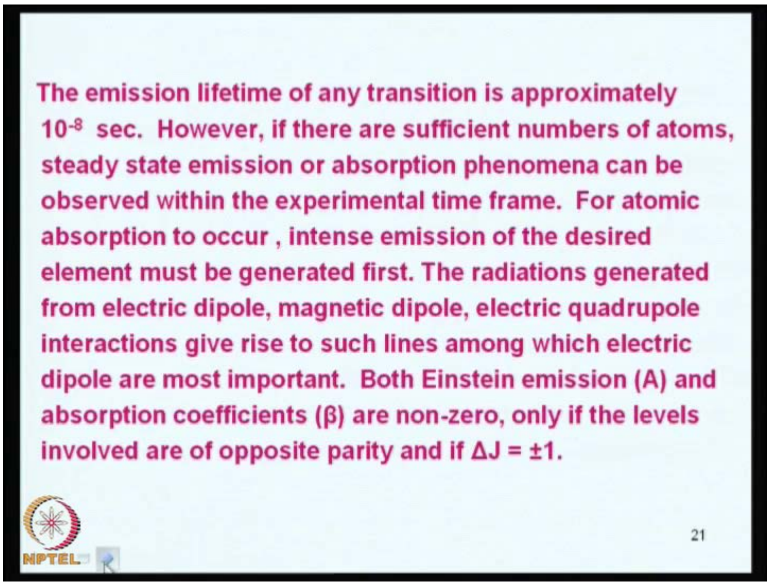

The emission lifetime of any transition is approximately 10^{-8} sec. However, if there are sufficient numbers of atoms, steady state emission or absorption phenomena can be observed within the experimental time frame. For atomic absorption to occur , intense emission of the desired element must be generated first. The radiations generated from electric dipole, magnetic dipole, electric quadrupole interactions give rise to such lines among which electric dipole are most important. Both Einstein emission (A) and absorption coefficients (β) are non-zero, only if the levels involved are of opposite parity and if $\Delta J = \pm 1$.

So, the emission life time of any transition is approximately ten raise to minus 8 seconds this we have seen in our discussion even in molecular spectrophotometry; however, if there are sufficient number of atoms are present steady state emission or absorption phenomena can be observed within the experimental time frame. So, what I want to tell you at this stage is the there are if there are sufficient numbers of atoms steady state absorption emission absorption emission absorption. So, the number of atoms that get excited to higher energy levels or equals the number of atoms getting de excited to lower energy level; that means, same number of atoms will be there in the excited and ground states.

So, for atomic absorption to occur what we need is intense emission of the desired elements must be generated first the radiations generated from the dipole magnetic dipole electrical dipole it is give raise to such lines which among which electric dipoles are most important. Both Einstein emission and absorption coefficients must be non 0 only if the levels involved are of opposite parity and if delta J is equal to plus or minus 1; that means, the selection rules should permit total quantization. Now, we will continue our discussion in the next class at this stage, we only have to understand that the number of elements must be more in the ground state?