Trace and ultra trace analysis of metals Using atomic absorption spectrometry

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Lecture – 09
Interaction of EM radiation with matter IV

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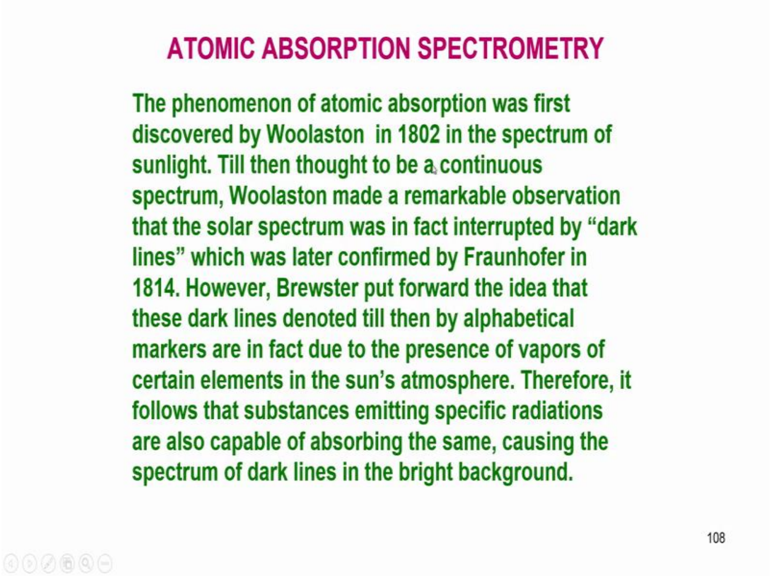

ATOMIC ABSORPTION SPECTROMETRY

The phenomenon of atomic absorption was first discovered by Woolaston in 1802 in the spectrum of sunlight. Till then thought to be a continuous spectrum, Woolaston made a remarkable observation that the solar spectrum was in fact interrupted by “dark lines” which was later confirmed by Fraunhofer in 1814. However, Brewster put forward the idea that these dark lines denoted till then by alphabetical markers are in fact due to the presence of vapors of certain elements in the sun’s atmosphere. Therefore, it follows that substances emitting specific radiations are also capable of absorbing the same, causing the spectrum of dark lines in the bright background.

So dear students, let us continue our discussion on Atomic Absorption. In the last class, I had told you about atomic absorption spectrometry, the phenomenon how it was discovered etcetera by Woolaston in 1802. Subsequently, Brewster put forward the idea that these dark spots, the lines denoted till then by alphabetical orders must be due to the presence of vapours of certain elements in the suns atmosphere.

So, the what it follows is the confirmation of quantum mechanical theory, that the atoms absorption and emission of the radiation is a quantamized system and the absorption of the vapours by the atoms causes the dark lines in the bright background of the suns this phenomenon was known as Kirchoff’s law.

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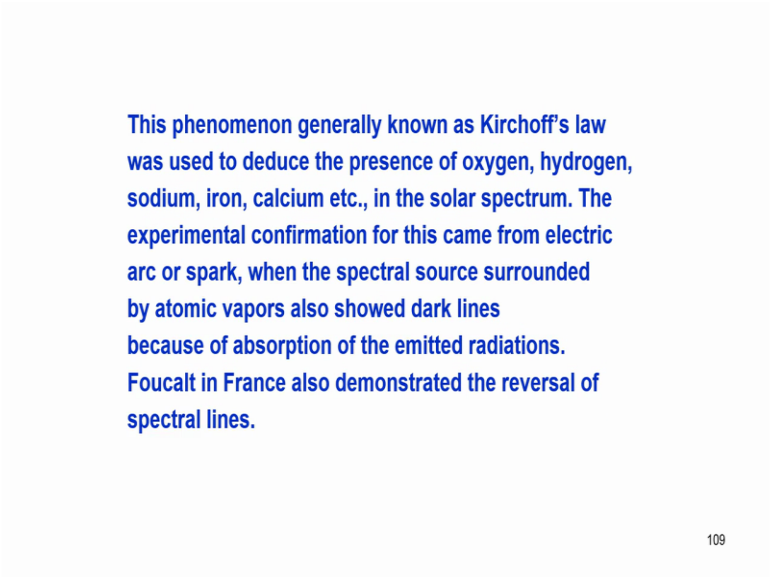

This phenomenon generally known as Kirchoff's law was used to deduce the presence of oxygen, hydrogen, sodium, iron, calcium etc., in the solar spectrum. The experimental confirmation for this came from electric arc or spark, when the spectral source surrounded by atomic vapors also showed dark lines because of absorption of the emitted radiations. Foucalt in France also demonstrated the reversal of spectral lines.

It was used to this deduce the presence of oxygen, hydrogen, sodium, iron, calcium etcetera in these solar spectrum. The experimental confirmation of this came from electric arc or spark, which was used to generate very high temperatures and when the vapours were introduced into the arc or spark, they also showed the spectrum showed dark lines similar to the radiations of observed in the sun's solar spectrum.

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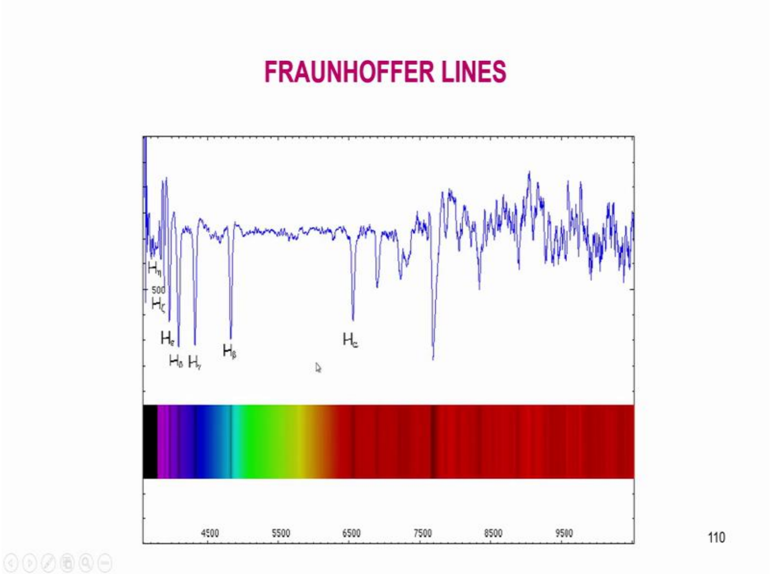

FRAUNHOFFER LINES

So, this is what I had shown you in the last class that the; so, how the solar has Fraunoffer lines are visible, you can see at the bottom that there are dark lines in the bright background.

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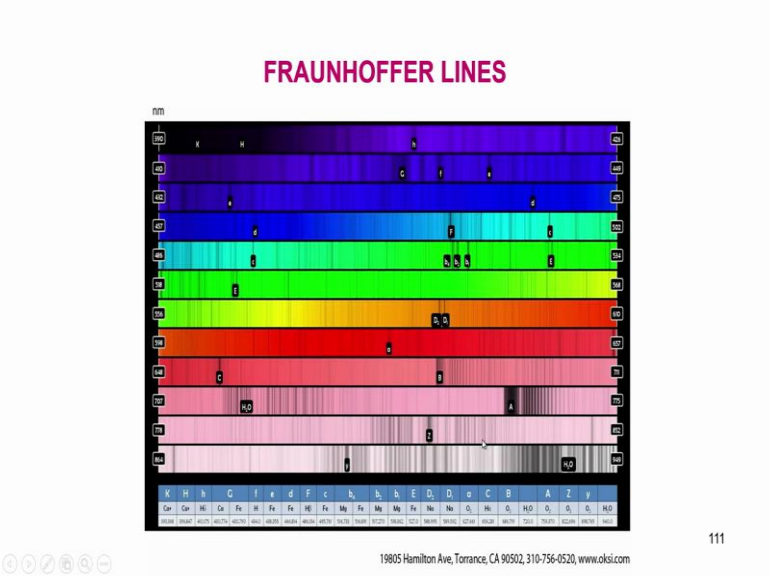

FRAUNHOFFER LINES

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And these are the different elements that have been detected calcium, holmium, calcium, iron and all these are these lines correspond to definite frequencies of the elements spectrum, which have been recorded elsewhere also. So, are the furs we assume that in the solar space atmosphere all these elements are present.

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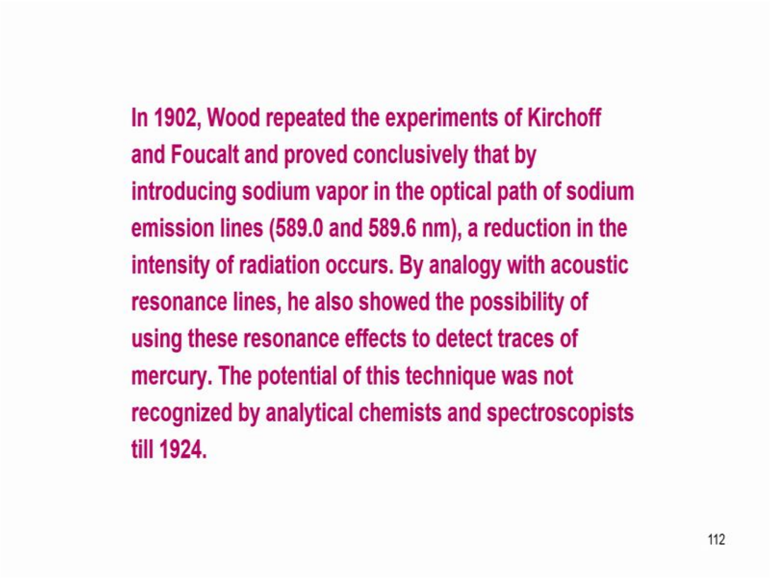

In 1902, Wood repeated the experiments of Kirchoff and Foucalt and proved conclusively that by introducing sodium vapor in the optical path of sodium emission lines (589.0 and 589.6 nm), a reduction in the intensity of radiation occurs. By analogy with acoustic resonance lines, he also showed the possibility 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.

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So, in 1902 would repeated the experiments of Kirchoff and Foucalt and proved conclusively that by introducing the sodium vapour in the optical path of emission lines, a reduction in the intensity of radiation occurs. Now, you may be aware of this phenomenon in your day to day life also; for example, if you take a walk around your time; in the night whenever people use atomic; these street lamps, use sodium vapour lamps they are known as sodium vapour lamps.

The sodium vapour lamps sometimes you will observe that they are flickering, sometimes it gives bright light and then stops, it becomes dark and again it picks up; again it flicks picks up; this is due to the absorption of sodium vapour, usually what they what happens in sodium vapour lamp is there is a small amount of sodium kept in the street lamps and that when we heat it by electrical heating, it gives out emission. So, the emitted light is yellow light that you would see in all towns and wherever they use sodium vapour lamps.

Usually there are two types of lamps in the street; one is mercury vapour lamp which will give you very bright white light and the other is sodium vapour lamps. So, these sodium vapour lamps keep on occurring on and off; many people who do not know about it think that electric supply is erratic actually it is not so.

Quite often, the once the sodium kept in the street lamp evapourates; that vapour will absorb the; its own radiation and then the intensity of the light becomes less. So, this is the phenomenon which is we very commonly observed, but when we, during in Wood’s time that is in 1902; this phenomenon was observed, but by analogy with acoustic resonance lines; what he showed is the possibility that these resonance effects can be used to detect traces of mercury. The potential of this technique actually was not recognized by analytical scientist and spectroscopy also till 1924.

Later on the somewhere around 1913; somebody showed that mercury can be determined up to 10 raised to minus 13 grams in the environment using this technique, but as an analytical technique in the laboratory, it was not available for another 30-40 years.

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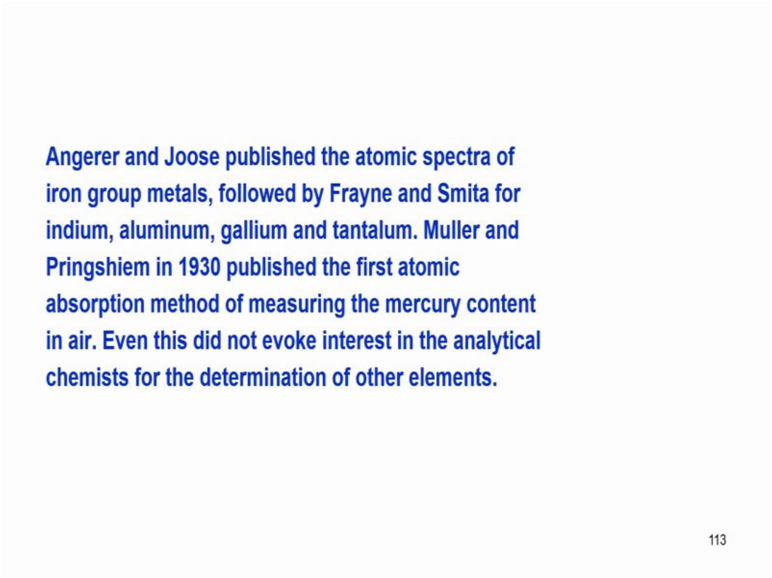

Angerer and Joose published the atomic spectra of iron group metals, followed by Frayne and Smita for indium, aluminum, gallium and tantalum. Muller and Pringshiem in 1930 published the first atomic absorption method of measuring the mercury content in air. Even this did not evoke interest in the analytical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

So, continuing our discussion Angerer and Joose published the atomic spectra of the iron grouped metals followed by Frayne and Smita for indium, aluminium, gallium and tantalum. Muller and Pringshiem in 1930 published the first atomic absorption method of measuring the mercury content in the air. Even this did not evoke interest in analytical chemist for the determination of other elements because the simple common laboratory instrument was not available for the determination of all metals; one auto metals in a research laboratory it is, but if the any analytical technique is not available in every laboratory that is not a universal technique.

So, until an instrument was developed to determine all these elements atomic absorption remained as a curiosity only; as far as the chemical analysis was concerned. So, Walsh was the person who discovered analytical potentials of atomic absorption and then he developed the first real application of atomic absorption to chemical analysis; that was in 1955. So, somewhere around in he is Walsh; he is an Australian scientist, we will find this information in several textbooks.

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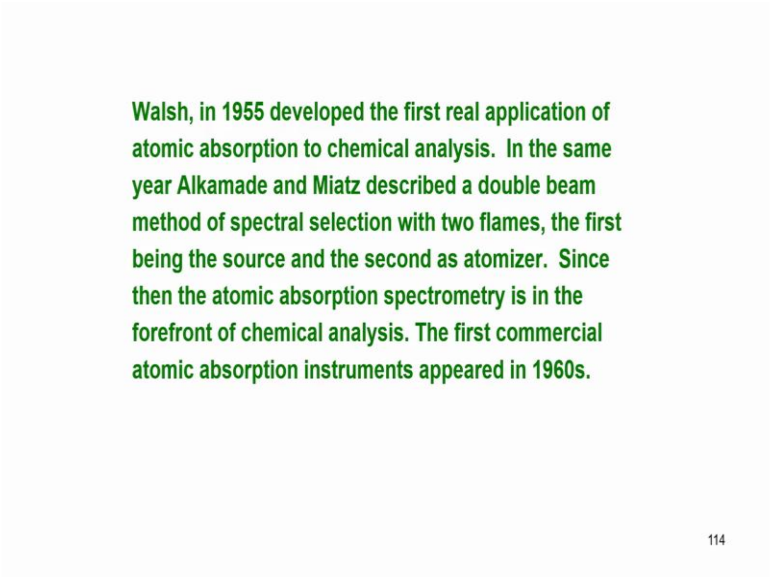

Walsh, in 1955 developed the first real application of atomic absorption to chemical analysis. In the same year Alkamade and Miatz described a double beam method of spectral selection with two flames, the first being the source and the second as atomizer. Since then the atomic absorption spectrometry is in the forefront of chemical analysis. The first commercial atomic absorption instruments appeared in 1960s.

But what is important is in the same year Alkamade and Miatz described a double beam method of spectral selection with two flames; the first being the source and the second is the atomizer.

So, we will see what is flayer source and atomizer and other aspects of atomic absorption and layers shortly, but ever since the Walsh developed this analytical technique, the atomic absorption spectrometry is in the forefront of chemical analysis. The first commercial atomic absorption instruments appeared in 1960’s; somewhere around 1970’s, they were there in several laboratories and by about 65 or so; instruments were available in India and right from 1970’s onwards; almost every University in India and elsewhere have got atomic absorption spectrometers in their laboratories, for their determination of metrics.

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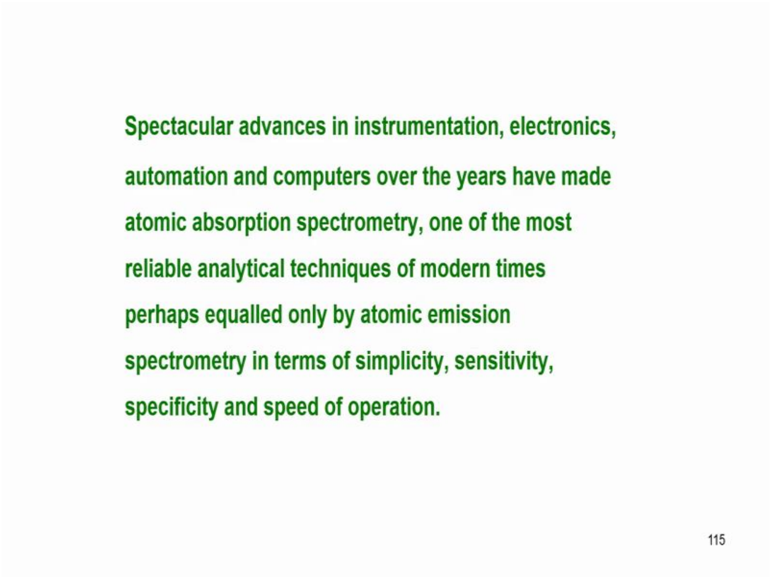

Spectacular advances in instrumentation, electronics, automation and computers over the years have made atomic absorption spectrometry, one of the most reliable analytical techniques of modern times perhaps equalled only by atomic emission spectrometry in terms of simplicity, sensitivity, specificity and speed of operation.

So, spectacular advances in instrumentation, electronics, automation and computers have taken over the complete overhauling of atomic absorption spectrometers and they have made atomic absorption spectrometry one of the most reliable techniques of modern times; perhaps equaled only by atomic emission spectrometry in terms of simplicity, sensitivity, specificity and speed of the operation. The most important aspect of atomic absorption spectrometry is its specificity; that means, if the element is there; it is detected, if it is not there; it is not detected. So, not only it is used for pass and fail tests, but also for the detection of metals and determination of course, is meant to be by quantization of the radiation.

So, the further development of atomic absorption was by Professor L’vovs and Massmann.

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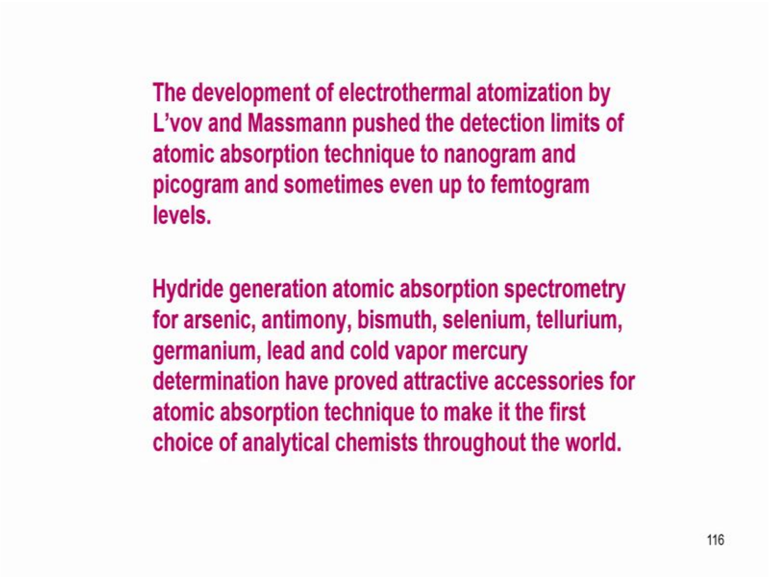

The development of electrothermal atomization by L’vov and Massmann pushed the detection limits of atomic absorption technique to nanogram and picogram and sometimes even up to femtogram levels.

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.

I had the opportunity to meet the Professor L’vovs and Massmann; sometime back in 80’s and these two gentlemen Professor L’vovs is from Russia and Professor Massmann is from Germany; both of them questioned the detection limits of atomic absorption to nanogram levels and picogram levels. Sometimes even up to femtogram level; that is I had already explained to you that it is up to 10 raised to minus 15 grams.

Then came another development that is hydride generation atomic absorption spectrometry, this technique could be used only for elements which produce hydrides metal hydrides these elements include arsenic, antimony, bismuth, selenium, tellurium, germanium, lead but it is a rarely used for lead nowadays, but for arsenic, antimony, bismuth, selenium, tellurium, and germanium in parts per billion level analysis; only hydride generation atomic absorption spectrometry is being used even now all over the world.

So, it is a very important development; we will be studying it in the course of this program and cold vapour mercury determination; that is another extension of the atomic absorption and that also has been nowadays pushed to the forefront of mercury determination up to 10 raise to minus 12 quantitatively; that means, 2 into 10 raised to minus 12; 5 into 10 raise to minus 12 grams of mercury can be determined; not detected, they can be determined quantitatively, we take accuracy and assurance and such advances have proved the attractiveness of the atomic absorption technique to make it the first choice of analytical scientists throughout the world.

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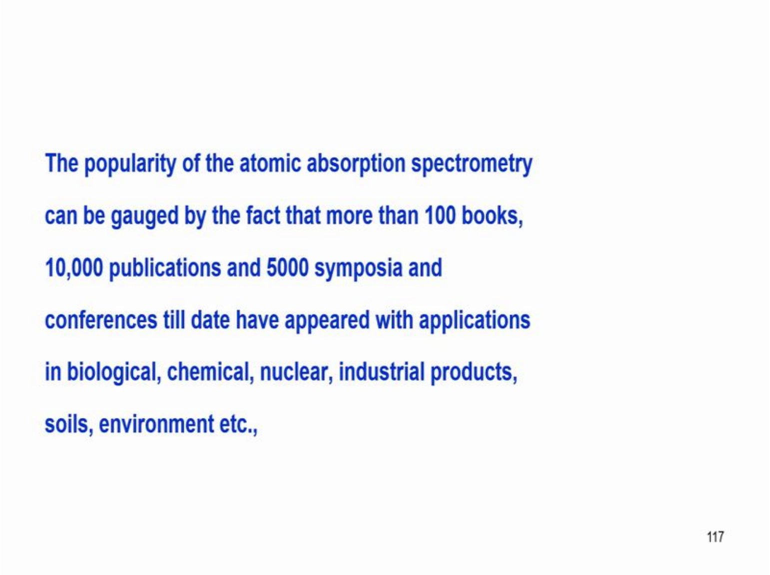

The popularity of the atomic absorption spectrometry can be gauged by the fact that more than 100 books, 10,000 publications and 5000 symposia and conferences till date have appeared with applications in biological, chemical, nuclear, industrial products, soils, environment etc.,

So, the popularity of atomic absorption spectrometry you can (Refer Time: 13:09) it by the fact that more than 100 books have been written on atomic absorption spectrometry so far; more than 100 and then more than 10000 publications have appeared in leading journals of analytical science and chemical analysis; reclaim chemical there are journals, scientific journals dedicated to atomic absorption also nowadays they are there and more than 5000 symposia, conferences and all the workshops have been conducted till date; they have appeared with applications in biological, chemical sciences, nuclear sciences, industrial products, soils and environment etcetera.

So, you should be feel happy that we are studying one of the most versatile techniques that will equip you for any job that you may undertake after your degree; if you are taking this course because I am going to make you an expert on atomic absorption spectrometry by the time; we are through with each other. So, please learn the subject very carefully and wish you all the best.

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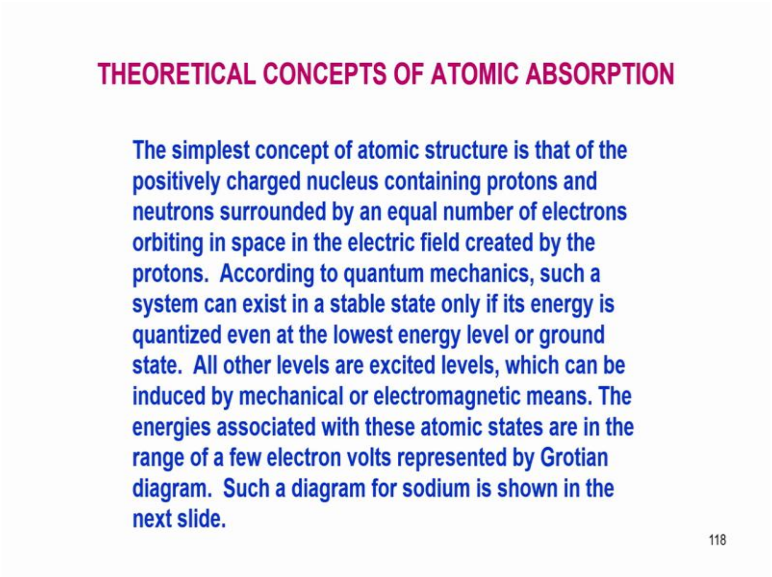

THEORETICAL CONCEPTS OF ATOMIC ABSORPTION

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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We continue our discussion on the theoretical concepts of atomic absorption now because so far I have given you only a small introduction of the atomic absorption spectrometry, now what is there; that is important in atomic absorption; what are the basic concepts we have to learn?

So, the simplest concept of atomic structure which we have already studied early is that, there is a positively charged nucleus containing protons and neutrons surrounded by an equal number of electrons; orbiting in space in the electric field generated by the protons; that means, in any atom atomic structure there is proton; proton is carrying large amount of electric weight and there is an positive electric field generated around the nucleus and this positive electric field is neutralized by an equal number of electrons. In terms of electrical charges, but weight of the electric electrons are they do not match with that of protons. So, the electrons are going round and round to balance the total electrical charge around an atom.

So, according to the quantum mechanics such a system can exist in stable state only if its energy is quantized. This we have already studied and even at the lowest energy level or ground state; that means, the atoms must be the quantized atomic energy is quantized at the lowest energy level or at the ground state or at room temperature. All other levels are excited levels, this means the electrons in the ground state of the atoms; this can be excited to higher energy level.

Because all other elements, all other electrons are at the ground state at room temperature in the in general system for example, in this room there is a would, there is metal and wherever there is metal; all the metal elements in this room or wherever you are sitting on the chair or you will clock or anything that contains the metal, all the atoms in that unit are at the ground state where there is no energy exchange.

But all the electrons are at the ground state; now if I supply certain amount of energy; that means, I can excite all the electrons to the next higher energy level; that is what it means. So, how do we do that? We can do it by inducing electrical energy or mechanical energy or I can simply heat it. So, the energy is associated with these systems are in the range of few electronic volts that is represented by a Grotian diagram, so what is a Grotian diagram? That I will show you in the next slide.

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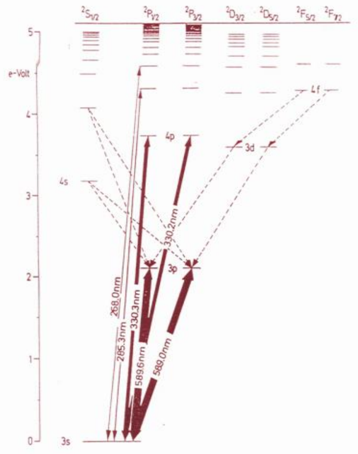
ENERGY LEVEL DIAGRAM FOR SODIUM



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This is the Grotian diagram energy level of sodium, you can see on the left side; I have plotted electron volts that is ground level is 0 and then 1, 2, 3, 4, 5 etcetera and these are the energy levels of the sodium atom. So, what are these energy levels that is 2 S by 2 S by 1 and half; 2 P 1 and half 2 P; 3 by 2 to the 3 by 2 to D S by 2 to F S by 2 to S 7 by 2 like that those are the energy levels; that means, there is one electron in the outermost orbital of the sodium atom you can look up the structure of sodium atom, it has 23 atomic absorption etcetera, it is in the outermost orbital; there is only one electron.

That one electron is having a spin of half; spin quantum number is half, but there are combined effects of the orbitals and those orbitals are designated as s n p orbital s p d f etcetera. This I have already explained to you in the earlier classes, so for sodium; it is 2 S half 2 P half; 2 3 2 P 3 by 2, 2 D 3 by 2; like that there will be different energy levels to which an electron can be excited; this is the ground state that is 3 S.

So, 3 S can be excited that is the ground state and when the electrons are excited it goes to 2 S by 2 etcetera; that is these S; in this S are different you should understand I have written here 3 S is a small letter here I written 2 S in the capital letter; that means, these energy levels are not the same. So, do not confuse that how it can happen from 3 S 2 S that is different entirely.

So, the current energy levels if the electron is to be excited it will go from 2 S half to 2 P 3 by 2; 2 P 1, 2 P by 2 and 2 P; 3 by 2; 2 D 3 by 2 etcetera. So, the energy levels if I take sodium atom and excite it, I will get frequency lines corresponding to this I have shown you different parallel lines here and 3 S is the ground state, from 3 S it goes up to 3 P here I am showing you it is 3 P and then there is 4 S is here and then 4 P is here 3 d and there are other 4 F etcetera other energy levels are shown all around here.

So, the ground state electrons are at 3 S, so if I start giving energy to this, I get different spectrum if the electron goes from 3 S to this line; somewhere around I supply 4.5 volts, the electron will jump to this higher energy this level from ground state and that corresponds to 268.0 nanometer energy. Similarly, if it goes here; it is 285.3 nanometers; next is 330.3 less energy I am supplying and then there is another one 330.2 and then 589.6; that is a around 2 electron volts and if it goes to 3 P; that is also approximately same that is 589.0; that means, the electrons in the electrons in atomic absorption spectrometry, whenever I am talking about the excitation of atoms; what I mean is this; that means, electrons will be excited to from 2 S to 3 S to 3 P; 3 D, 4 P etcetera.

But again, when I am supplying I have shown you in this figure; some of them are dark lines and some of them are thin lines. If you observe this figure carefully, you can see that some of them I have shown as dark lines and some of them are very thin lines. So, these dark lines are known as the resonance lines, so these resonance lines what do they represent is the energy can be excide the supplied from 3 S to 3 P and if I have an electron at 3 P level, it can absorb vapour and then it can lose its energy and come back to ground state; that means, absorption and energy will occur at the same wavelength; I have shown it by double lines, double arrows.

So, the lowest energy state is known as the resonance line; this resonance line is a basically it shows us that if I have a vapour, I supply energy the vapour can absorb that energy and come down to the ground state or if I have a ground state atom, I supply this much energy to excite the electron from this level to this level higher next resonance level. There are 1, 2, 3, 4 resonance lines in this spectrum of sodium, but you will see that in 3 P; there are two lines one is 589.6, another is 589.0; that means, both these lines are very very near each other; that means, quite often if I do not have a good spectrometer, it means that both lines will appear a single line.

But if I apply a magnetic field; I can separate them, so you will see two spectrums two peaks. So, this is the fundamental basis of all atomic absorption spectrometry; all other elements will show if you take the spectrum and plot electronic volts and energy levels like this; all of them will look approximately similar like this, but force the only differences is energy levels will be different for each element. So, that is how the Grotian diagram for any for a atomic absorption looks like.

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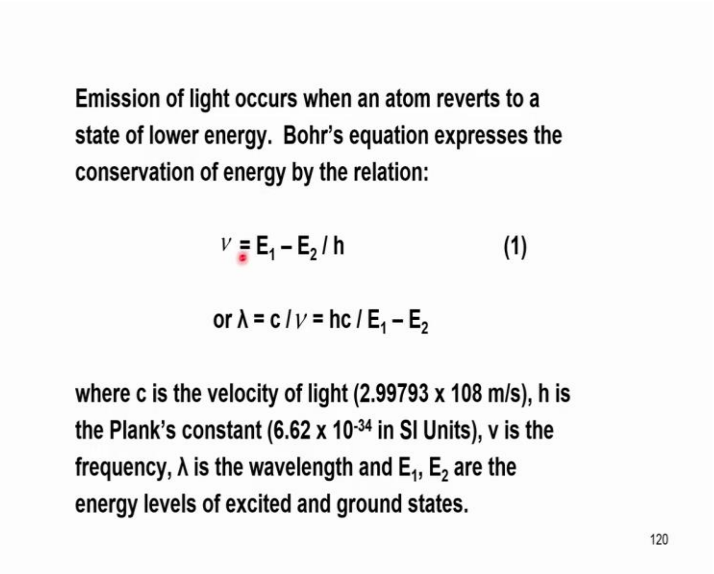

Emission of light occurs when an atom reverts to a state of lower energy. Bohr's equation expresses the conservation of energy by the relation:

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

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

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 is the frequency, λ is the wavelength and E_1, E_2 are the energy levels of excited and ground states.

So, what happens here emission of light occurs when an atom reverts to a state of lower energy; if an atom is at higher energy level, it falls down it has to emit to lose its energy sometimes it is emission. So, from the higher to lower energy there is emission lower energy to higher energy, it absorbs the radiation. So, Bohr's expression expresses the conservation of energy by a simple relation that is E 2 minus E 1 is equal to h nu.

So, you look at this figure I have written the same thing; the frequency that is wavelength is expressed by the energy difference between the two divided by Plank's constant or since frequency is limited to is a related to wavelength, which is a very measurable quantity simply for atomic absorption; lambda is nothing but velocity of light divided by frequency; that is the wavelength is given by h c divided by the energy difference that is E 1 minus E 2.

So, in this expression see the velocity of light this you know h is the Plank's constant it is a universal constant; that is 10; 6.62 into 10 raised to minus 4 unit 34 in the SI units; nu is the frequency, lambda is the wavelength and E 1 and E 2 are the energy levels of excited and ground states, I think you are all familiar and comfortable with so far.

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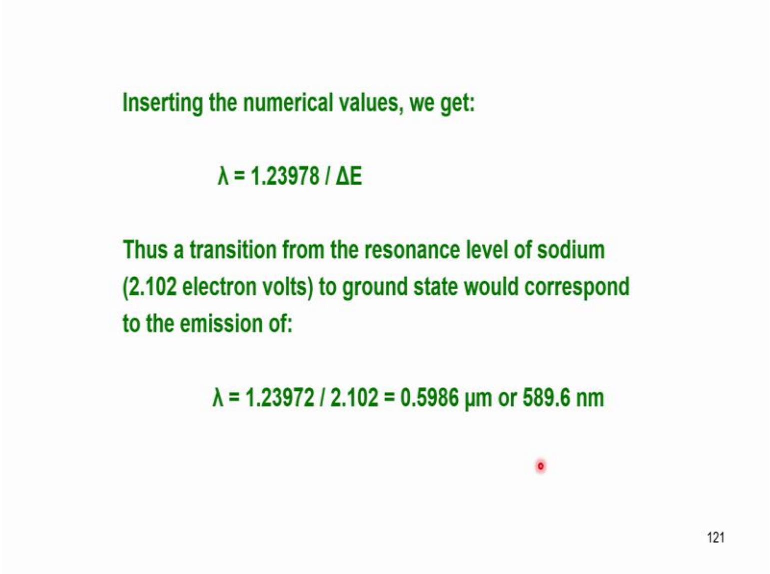

Inserting the numerical values, we get:

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

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

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

So, inserting the numerical values; what we get? You will put all those numbers and you get lambda is equal to 1.23978 and divided by delta E; delta E is nothing, but E 2 minus E 1, it is energy levels a difference of the energy levels. So, a transition from the resonance level of sodium that is occurs at 2.102 electron volts to the ground state that would correspond to the emission of 1.23972 divided by 2.102; that is the energy that corresponds to 0.5986 micrometer or 589.6 nanometers.

I have given you the conversion of micrometer, nanometer etcetera in the table; in the earlier version; earlier classes. So, there should not be any confusion with respect to this.

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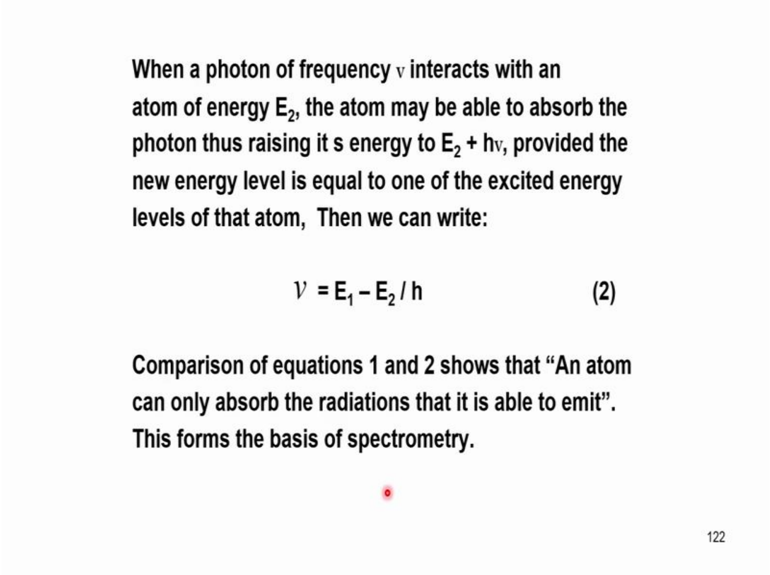

When a photon of frequency ν interacts with an atom of energy E_2, the atom may be able to absorb the photon thus raising it s energy to $E_2 + h\nu$, provided the new energy level is equal to one of the excited energy levels of that atom, Then we can write:

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

Comparison of equations 1 and 2 shows that “An atom can only absorb the radiations that it is able to emit”. This forms the basis of spectrometry.

So, when a photon of frequency nu interacts with an atom of energy E 2; the atom may be able to absorb the photon. So, it goes to E 2 plus h nu that is some amount of energy is absorbed and it goes to next time, the difference is h nu. So, provided the new energy level is equal to the one of the excited energy levels; in between energy if you supply nothing happens that is the beauty of quantum mechanics. So, we write this expression E 2; nu is equal to E 2; E 1 minus E 2 by h, so compare this equation with well first one; one here is same.

So, an atom can absorb; what it means? An absorption can also happen, an emission can also happen with the using the same amount of energy depending upon where the elect atom is there. So, if the atom is at higher state; it has only to absorb to come down to lower energy level and emit the radiation; that it has to emit to come down to lower energy level, if it is at lower energy level; it has to absorb to go to the next higher energy level and the both the energies are same for excitation and emission.

So, comparison of both equations shows that an atom can only absorb the radiation that it is able to emit; that means, if it is able to absorb; it can also emit, this is the beauty of Fraunhoffer lines because in the suns atmosphere; at around 2 million degrees Kelvin; everything is in vapour phase only, but they can absorb the radiation; other radiation corresponding to that their excitation energy levels and the concentration becomes less, so it appears as a dark line; so, this forms the basis of automatic absorption spectrometry also.