**Trace and ultra trace analysis of metals Using atomic absorption spectrometry**

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**Lecture – 08**
**Interaction of EM radiation with matter III**

So, the quantum mechanical theory originally proposes for black body radiation was extended to the emission and absorption processes also. So, the essential postulates of quantum theory essentially include the interaction of the ions atoms molecules with respect to energy. So, what does it essentially say- that the energies of the atoms ions molecules electrons etcetera they are always in a fixed in a certain discrete energy levels.

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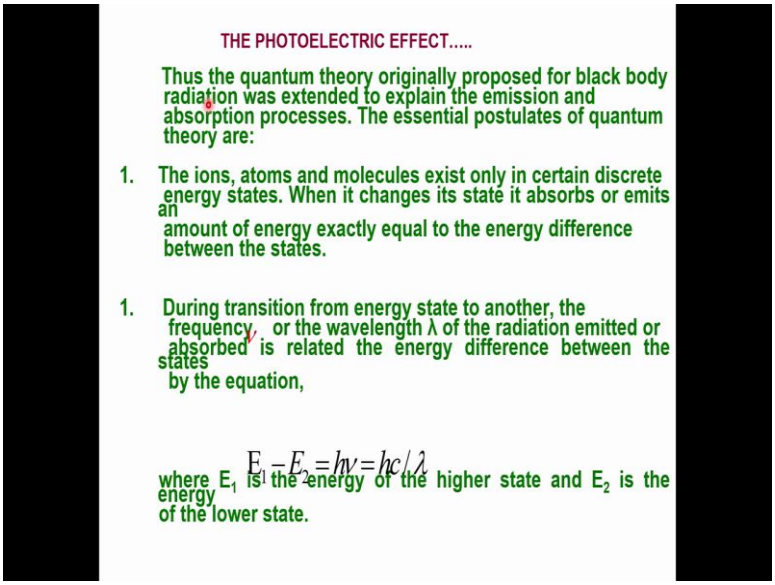


So, when it changes it state it absorbs or emits an amount of energy exactly equal to the energy difference between the two states. So, this is what we should be remembering.

So, during transition from the energy state to and from one energy state to another the frequency mu I have written here it as slightly come this side the frequency or the wavelength that is lambda denoted by lambda of the radiation a or absorbed radiation emitted or absorbed that is related to the energy difference between these states by the equation, E 1 minus E 2 is equal to mu that is equal to h c by lambda. Where E 1 is the energy of the higher state and E 2 is the energy of the lower state, this is essentially a statement of the quantum mechanical effect that is photo electric effect.

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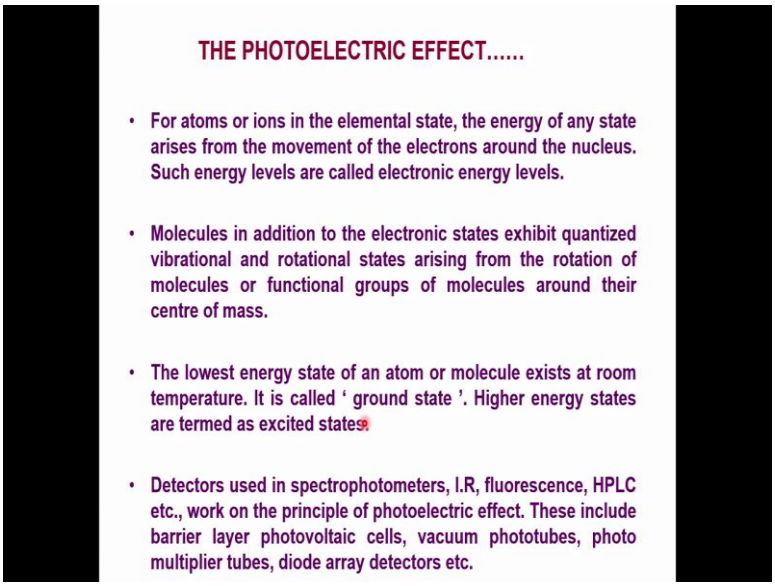


So, for atoms or ions in the elemental state, the energy of any state arises from the movement of the electrons around the nucleus, this we have already seen earlier in the on the discussion during the electronic structure.

So, such energy levels are called as electronic energy levels. Now molecules are aggregates of the atoms. So, molecules what they do is they in addition to the electronic states they exhibit quantized vibrational and rotational energy levels arising from the rotation of the molecules or functional groups of molecules around their center of mass. Here it needs a little bit of explanation. Normally what we expect is if it is only electron atom or an element, the electrons single element number of electrons are there, but electrons are located around the nucleus in a space and these electrons can go to next higher energy level or for fall down from the higher state to lower state by loosing or gaining the amount of energy that is equal to the quantum mechanical system that is whatever we depends upon the work function and things like that.

But the electrons by themselves of a an element do not in principle posses rotational and vibrational energy levels; that means, if you take pure atoms pure elements then you see the only energy levels 1 2 3 4 like that. Now if I take a group of molecules for example, nitride NO3 nitrogen is there oxygen is there they are combined into a mass, the total mass of nitrogen NO3 is 14 plus 48, 16 is the atomic weight three a oxygen, that is 48

plus 14 is nitrogen. So, 48 plus 14 is about 62. So, nitrogen NO3 the atomic mass is 62, it is a collection of 62 protons or a protons or neutrons together.

So, the electrons are not only affected by the nitrogen atoms or oxygen atoms, but all there are also affected by the NO3 molecule that is the bigger molecule. So, the electronic energy levels of each electron of nitrogen is the affected by oxygen atoms present in the at the center of the mass, and those a electrons of a oxygen are affected by the by the mass present with respect to nitrogen. So, they all energy levels of each electron is not only electronic, but there are sub divisions of electrons electronic energy level, where the electro can move with a little bit of freedom. This freedom in a levels of energy corresponding to different freedom are called as vibrational energy states and each vibrational energy state also is associated with a number of still smaller steps that is rotational energy levels.

So, the every electronic state is associated with number of vibrational energy states and each vibrational energy state is affected with the number of rotational energy levels. It is (Refer Time: 06:30) to imagining that you are standing on the first floor ground floor of a building, and you want to hit a food ball on the first floor. Now how do we reach the first floor there are number of steps right. So, when you kick a foot ball from the ground floor to the first floor it may not exactly land on the landing of the first floor, it may land two or three steps below or it may land two or three steps above. So, the possibility of the foot ball landing on the landing site of the first floor are more, but it will be very near that also need not be exactly on the first floor landing. So, that is vibrational. So, if each step is the again associated with number of smaller steps then the foot ball can land anywhere that is first floor that is it postal address and vibrational and rotational energy levels are like street address or house address.

So, basically what we have trying to say is an in electron associated with a molecule can exhibit number of electronic and vibrational and rotational energy levels. So, the lowest energy state of an atom or a molecule exists at room temperature. Again as I am explaining to you the element can be in it is natural state at room temperature; that means, at room temperature chlorine is a gas, oxygen is a gas, copper is a material like that the lowest energy is state of a molecule at room temperature is called it is ground state, whether it may be gas or it may be a soiled it may be a liquid also like mercury.

So, higher the energy state corresponding to the room temperature that is at higher temperatures, suppose from 25 to I heat a material to 35 degrees, they energy levels will definitely be disturbed. So, when these energy levels are disturbed the electrons will get excited to higher energy level, but it may not go to next electronic energy level it may just change it is position from one vibrational to another vibrational energy level. So, you supply enough energy for equivalent to the quantum mechanical difference between the two energy states, then it can move to higher energy level otherwise they will be moving in a small jumps from one vibrational to another and one rotational level to another (Refer Time: 09:41).

So, higher energy states are termed as exited states ground states. So, we have all the electrons located in the ground state when they are excited there at higher energy state they are excited states, and the detectors do the job of the electrons emitted from the photo electric materials like sodium, potassium, alkali metals etcetera they release the electrons and the released electrons get attracted towards the anode and generate the current, when it is maintained at slightly higher positive potential. So, they because they attract the electrons, so detectors used in spectrophotometers infrared spectrophotometers, visible spectrophotometers, florescence spectrometers, HPLC etcetera all work on the principle low photoelectric effect.

These include there are different types of photoelectric devices which can detect the radiation. So, we will study what are the different types of photoelectric materials, because they are the detectors used in spectrophotometry or in many other instruments. So, right now we have what is known as photovoltaic cells and then we have the vacuum phototubes, photomultiplier tube diodes array tubes and several other detectors perhaps you can look at this certain in table this slide in the last slide I have shown you that the different electron different detectors are barrier layers photovoltaic cells, vacuum phototubes, photo multiplier tubes diode array detectors etcetera.

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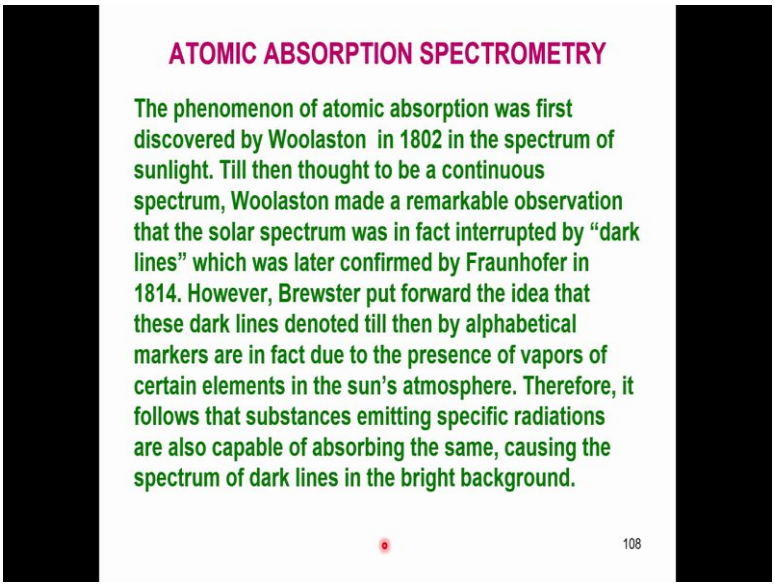


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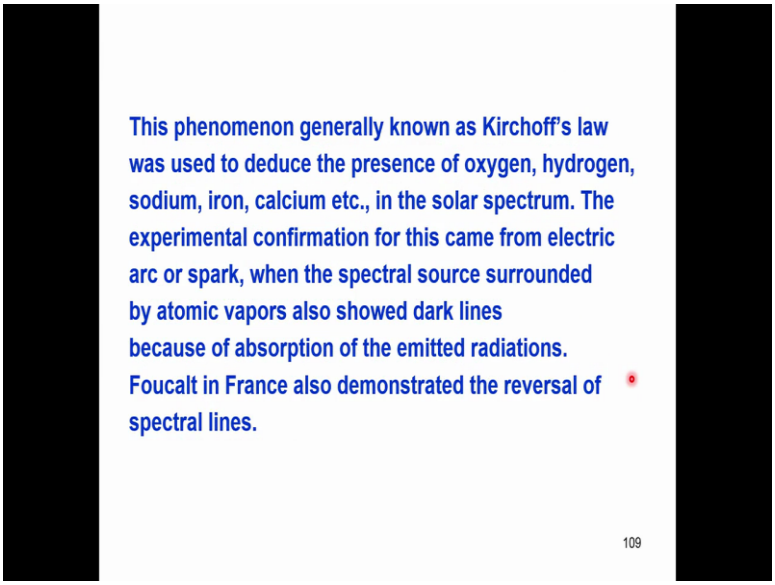


Now, we will study these will not be studying the barrier layer cells and other the cells expect the vacuum phototubes and photo multiplier tubes and diode array detectors in our next class to some extent. I will explain to you when we are discourse studying the instrumentation for a atomic absorption spectrometry. So, in a now we are entering the name topic of our discussion that is atomic absorption spectrometry.

So, far what we have studied are the atomic structure and the electromagnetic radiation, what are the effects of electromagnetic radiation upon the materials. So, that as given as

a little basis for describing the optical components of a spectrophotometer etcetera, that is important for as to understand the instrumentation of a instrument of a spectrophotometer or a automatic absorption. Now what we want to do you we want to concentrate on our main topic that is atomic absorption spectrometry for the determination of metal ions, and this one this is an important aspect as for as the elemental analysis is concerned.

I think all of you know that there are about 53 metals and the in the periodic table several of them are in the form of an ion also, I do not know how many of you are aware but copper ion hydrogen ion and metal cobalt like that you has to you would have studied in your text books, but you also are aware of a chromate ion that is anion is not it, chromate ion arsenate ion arsenate phosphate ion etcetera even such elements can be determined even if they are in the anionic form.

So, atomic absorption spectrometry is a tool for us to determine metal not only metallic elements directly, but non metallic elements also indirectly to some extent. So, regarding that chemical analysis technique which is fundamental to the chemical analysis of the environment and then materials and then water air etcetera with different applications automatic absorption spectrometry is essential. It is required for almost all chemical engineers, mechanical engineers, metallurgical engineers and then scientist and several other people's civil engineers also, everybody is concerned with the metal ions and their effect on pollution etcetera. So, we are going to study what is atomic absorption spectrometry it is instrumentation and how we go about understanding the phenomena in of the atomic absorption spectrometry.

Now, the phenomenon of atomic absorption was first discovered by Woolaston in 1802, what he did was in he found out that the solar spectrum is a all of you know what is solar system. Solar radiation also we have seen every day morning we get sunshine, and the sunshine what we get until 1802 was suppose to be a continuous uniform beam of radiation emanating from the sun, but in 1802 Woolaston has made an important discovery that he the solar spectrum was containing lot of darks lines which was later confirmed by Fraunhofer another scientist that was in 1814.

So, the discovery of atomic absorption was not known at that time so, but what was Tilden thought was a scientific thought was solar energy consist of a uniform bundle of

electromagnetic radiation, but then when he put it in a prism, put the solar radiation make it passed through a prism or something like that, he found out that apart from the different radiations there were also some darks lines in the solar spectrum, and that was in 1802 Woolaston and subsequently Fraunhofer took up the study of the solar radiation, and what he did was he confirmed that yes there are dark lines in the solar spectrum number of dark lines in fact. So, but again he did Fraunhofer did not give any explanation for the existence of such dark spots in the white back ground.

But down the line again after few more years Brewster put forward the idea that these dark lines are due to the presence of vapors of certain elements in the sunset atmosphere. So, till that time all the dark lines were studied extensively and people thought that we do not know what it is will call them a b c d etcetera and then. So, alphabetical mark are there they are all known as alphabetical markers, these alphabetical markers were suppose to be something which we do not know, but subsequently somebody emails may find out. So, the idea was what it could be due to? People did think I will quite a lot and, but only later it was found that the there may be certain elements substances emitting specific radiations of course, suns solar radiation is suppose to contain almost all the elements because it is a hot bed of very high temperature of several million degrees, and the even at the core outer core it is around 8000 Kelvin.

So, anything that is there in the solar system in the sun as a solar body, whatever is there on the earth must have been there because earth is born from the sun, but on the earth has cooled down and so many metals are formed. But there in the solar atmosphere solar disc the temperature of several million degrees exists. So, most of them would be either liquids or vapors.

So, the what the subsequent idea that the substance is emitting specific radiations they may be absorbing the same radiation, once the idea of quantum mechanics born was born and took shape and took firm roots, people thought that if an a substance is emitting certain amount of radiation at a higher energy, it can also absorb the same radiation why not if the it is comes across the amount of same amount of energy. So, if a substance is emitting certain amount of energy, but it re absorbs part of the energy then that portion of the spectrum looks darker. So, as plausible explanation was put forward what they said is substances emitting specific radiations are also capable of a observing the same radiation

causing the spectrum of dark lines in the bright back ground; this is the very important discovery as for as atomic absorption is concerned.

Now, we can see this phenomenon was generally known as Kirchoffs law. So, it is in Kirchoffs law was used to deduce the presence of oxygen using this law they said they what they did was they took oxygen, and then vaporized it passed to certain amount of radiation and without radiation oxygen intensity was high, when they passed certain radiation part of the radiation oxygen absorbed and they saw a dark line (Refer Time: 22:21) that is redaction in the intensity; similarly for hydrogen sodium iron calcium etcetera.

Now, the frequency what they obtained using synthetic materials on the earth, they were also the same frequency is used in the solar spectrum. What they observed they had observed I had explain to have those dark lines where called as a b c d etcetera, and those dark lines corresponded to the specific wavelength corresponding to oxygen, hydrogen, iron, sodium, calcium etcetera.

So, people deduced that the solar spectrum. So, solar matter suns sun must be having all these elements in the solar system. So, the experimental confirm you how do you conform it experimentally? See trying to do experiments in the on the earth is different, but to confirm we cannot really go and confirm physically, to the solar disc and try to conform. So, they experimental confirmation came only from electric arc or spark what they did is, they took two electric arcs and they bored them nearer produce very high temperatures and by applying electro high voltage. So, when the spectral source surrounded by vapors, so atomic vapors showed dark lines corresponding to different elements.

So, Foucault in France also demonstrated the reversal of spectral lines. So, what is reversal? What is being emitted is also being observed causing the radiation to look darker. So, the cycle law of observations started in 1802 was a completed with identification of different elements in the sunset atmosphere using Kirchoffs law and Fraunhofer lines etcetera.

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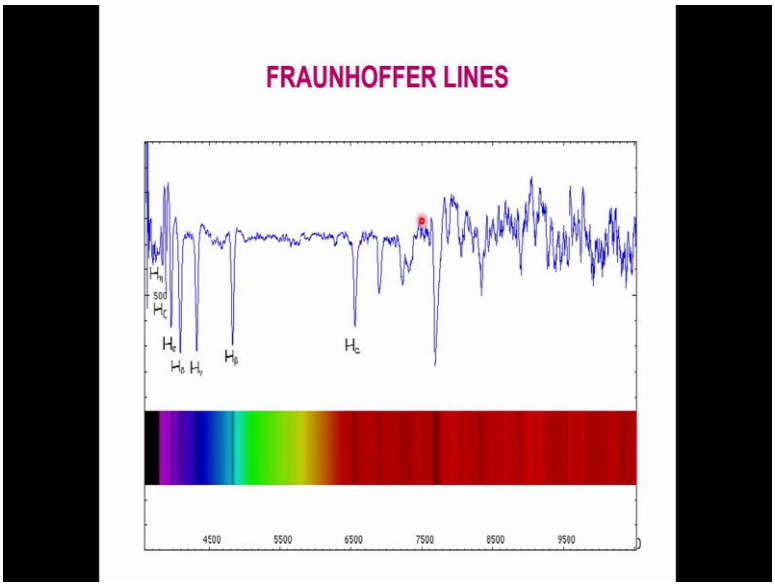


I will show you what is a Fraunhofer line, here you can you can see that solar spectrum contains dark lines like this is intend of the intensities. So, we initially intensity is very high suddenly there is a dip and then again a there is dip again it goes up again it goes in a steady, again it goes down like these we can see the whole solar spectrum. But if you take a photographic plate this is the energy figure drawn.

But if you take a photographic plate and then take the photograph of the solar radiation, he these are the dark lines what you would see corresponding to different wavelength. I have put the wavelengths here at 4500, 5500, 6500, 7000 etcetera and you can see that every line can be identified by a number of dark lines; that means, has there are has many elements as there are in the dark lines in the solar spectrum; that means, sun also contains the same elements from which earth is made of and from which we are also made of, that is what the Christian philosophy say earth to earth dust to dust.

So, we are all made of the same astronomic particles as earth and sun; that means, oxygen, hydrogen, nitrogen all of us we are all part of it we also have the same this thing.

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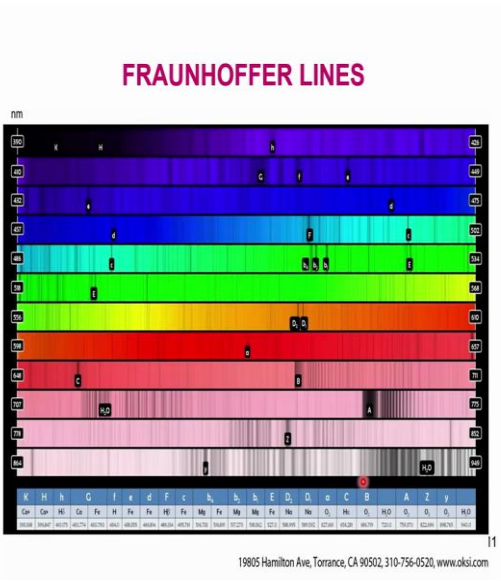


Now, this is a these are the Fraunhofer lines for different spectrum, again what are the elements identified are calcium, and then holmium, calcium, iron, hydrogen, iron these are all different irons lines frequencies, magnesium has been identified all the elements that we know of have been identified, apart from the molecules like oxygen O2 and water and H2O like this wherever when how whenever we study any astronomic body we look at this spectrum of these elements to find out whether such compounds are can exists on the Sun or Moon or Venus or Saturn or any other planet this is how it is being done.

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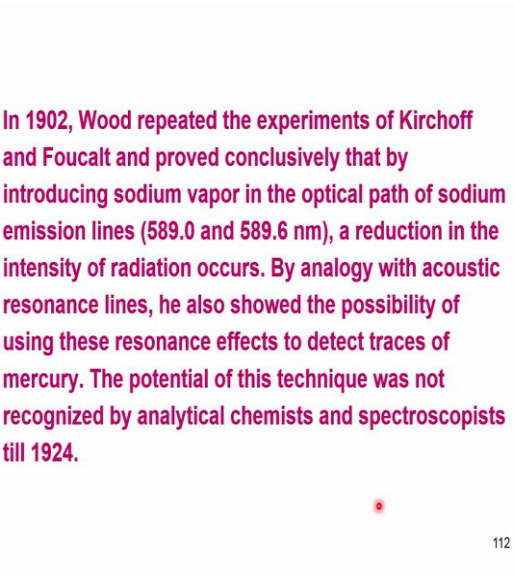

So, in 1902 wood repeated the experiments of co of Kirchhoff and Foucault and proved conclusively that by introducing sodium vapor in the optical path of sodium emission lines, what he did was he took certain amount of sodium burnt it, and then the it started burning emitting radiation then what he did was during in the path of a emission of the radiation he put sodium vapor. And this caused the sodium vapor absorbed that radiation and the intensity of the radiation coming out was much less. So, the idea of atomic atoms absorbing the same radiation that is emitted by the same element at higher temperature and absorbing the same at lower temperature proves the phenomenon of atomic absorption. So, the atomic absorption what is the end result? End result is a reduction in the intensity of the radiation that is important.

So, by analogy with acoustic resonance lines he also showed the possibility of using these resonance effects to detect traces of mercury that is in 1902 using the same similar principle he showed that traces of mercury could be detected in the environment. The Poto; however, potential of this technique was not recognized by analytical chemists and spectroscopists till 1924, but by about 1924 the idea of atomic absorption was fairly well known to the scientist, but still they did not know how it can be used it was till that time it remained a scientific curiosity rather than the atomic rather than a scientific fact.

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The facts that the atomic absorption phenomenon was known and the lines were available atomics lines were available and these were published subsequently by Angerer and Jose, and later by Frayne and Smita for indium aluminum etcetera.

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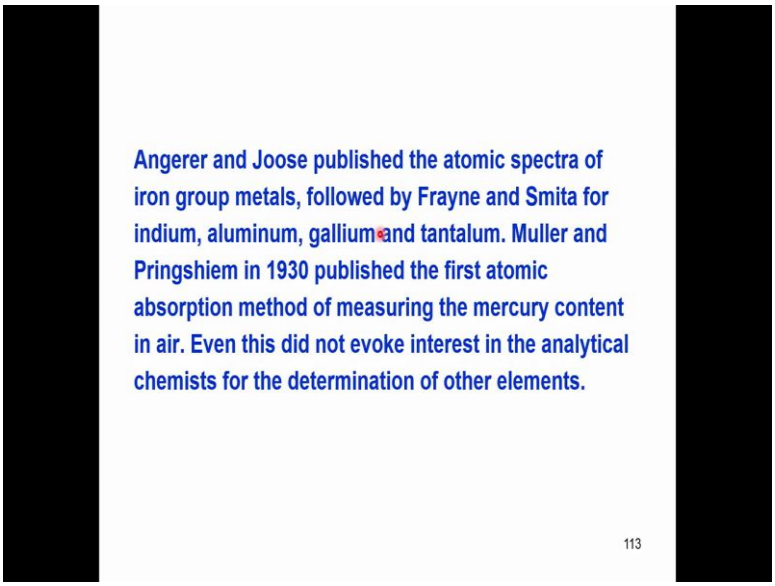


So, the idea of atomic absorption was fairly well established by about 1930. So, we will continue our discursion in the next class.

Thank you.