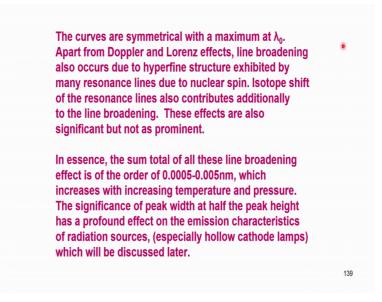
Trace and ultra trace analysis of metals Using atomic absorption spectrometry Dr. J R Mudakavi Department of Chemical Engineering Indian Institute of Science, Bangalore

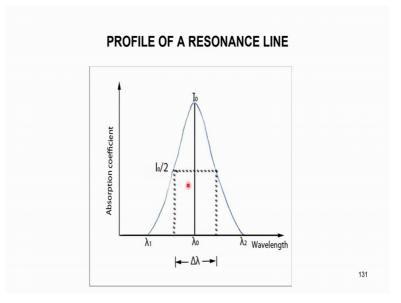
Lecture – 12 Theoretical basis of AAS III

So, a resonance line gets broadened by natural broadening, Doppler effects and Holtsmark effect, Lorenz effect and all of them put together means Voigt profile. In addition to these things, due to nuclear spin hyper splitting, again the spectral line purity gets affected that is nuclear spins and also isotopes. So, if you have the element, you want what you want to determine as number of isotopes then again they will or in the spectral line gets broadened.

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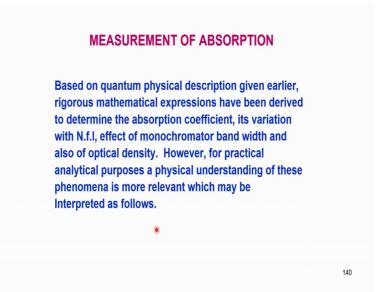
So, in essence putting together all these effects, what is the actual situation are in the field. So, we go back to this figure.



This figure, if you want to choose a spectral line from a given electromagnetic radiation, the half width due to all these pressure broadening, Lorenz pressure, Lorenz and Holtsmark and Voigt profile, nuclear spin and isotopes spin etcetera, this half width is of the order of 0.0005 to 0.005 nanometers that means, this increases with increasing temperature and pressure. The half width what you had shown in that figure if you want to choose 250 nanometers, you will be getting 250.005 nanometers plus or minus or 250.0005 nanometer; in this for all elements, the broadening is in this range apart from mechanical slits.

So, this increases with increasing temperature. Suppose, I increase the temperature from 500 to 1000 degrees of the vapour state then peak width also increases at half peak height it has a profound effect on the emission characteristics of radiation sources. So that means, the radiation coming from if any radiation is emitting a monochromatic radiation, and if the radiation source any light source for example, if it the temperature increases, it will have broader resonance line from the natural expected lines. So, this is what we have been discussing in the whole last class.

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And we will now move onto measurement of absorption. So, how do we measure the absorption of an atomic system so that is what this course is about? So, far we have been discussing only the electrical, only the electronic structure etcetera; and we would now move onto the quantization of the absorption. So, based on the quantum physical description given earlier so far what you had discussed rigorous mathematical expressions have been derived to determine the absorption coefficient that is Einstein absorption coefficient etcetera and its variation with number of atoms and then path length and then frequency etcetera. And effect of monochromator bandwidth and also of the optical density; and optical density is nothing but absorbance you should remember that.

However, for practical analytical purposes a physical understanding of all these phenomena is more relevant which may be interpreted as follows. So, so far all the theoretical discussions kept apart. What else we would like to know how to use this system for day-to-day analysis that is our main aim in the determination of metals and in trace and ultra trace quantities. So, mathematical expressions have been derived and we will be studying those mathematical expressions. (Refer Slide Time: 05:33)

A very narrow frequency interval is essential for the absorption of resonance radiation. However, it is impossible to isolate and obtain high intensity of illumination in the range of 0.0005 – 0.005 nm from continuum radiation sources. It would be too weak to be of any practical use. To overcome this difficulty, Walsh recommended that the radiation source should be made of the analyte element only. Therefore only the resonance line need to be separated from other spectral lines by a monochromator.

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So, what is required is a very narrow intense resonance line is required to make the atoms absorb the radiation. For atomic absorption, we need a source and then our sample and then a detector. So, the radiation source should emit a very narrow frequency interval essential for the absorption of radiation. It is not possible to get it from ordinary lamps like tungsten lamp or mercury lamp or even led's etcetera, because those things emit radiation of very broad frequency just like solar energy and you have seen how big is the Fraunhofer radiation. But what is required in atomic absorption is I want only one resonance line. I do not want any other radiation.

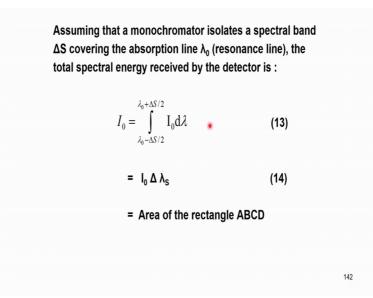
So, the accuracy what should be the accuracy, accuracy is determined by the resonance. Resonance line width half width that accuracy that is 250 plus or minus 0.005 nanometer that is what accuracy we need. To extract that kind of accuracy from to extract that kind of accuracy from a normal radiation source like tungsten lamp, mercury lamp etcetera are very difficult because the intensity of any frequency from those where lines would be very less, but we also need a very high intensity also. So, normal continuum radiation sources like tungsten lamp etcetera are too weak to be of practical use, this was the greatest difficulty in the development of atomic absorption spectrometer. Since the last say from 1920 to 1955 until Alan Walsh came up with a solution.

So, to overcome this difficulty what did Walsh recommend, he recommended that you need a radiation source of a particular frequency. We know that atoms emit radiation and

absorb radiation resonance frequency. So, why not make a lamp of the same element which you want to determine if you want to determine iron make an iron lamp you are all familiar with tungsten lamp. So, earlier people were using tungsten lamps to get radiation, mercury lamp you are all familiar like that if you want iron lamp, iron lamp. Iron lamp a filament having an iron as cathode will emit only those radiations corresponding to pure iron. Whereas, a tungsten lamp not we normally use in our day-today homes etcetera they emit radiation because of the blackbody radiation the tungsten wire gets heated in our normal circumstances and then it will emit radiation of all. What Alan Walsh said is you make sure that it is not the radiation that is heated filament, but you must generate excite the electrons to next higher energy state and let that come out from the lamp and that will be of single wavelength or it may contain only 3 or four resonance lines. So that was a revolutionary idea which made the atomic absorption a very versatile technique.

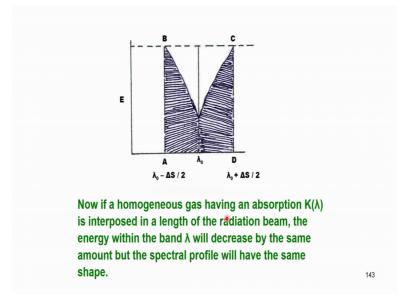
So, Alan Walsh said that you make we want a iron lamp make you want to determine iron, make an iron lamp; you want to determine cobalt, make a lamp made only of cobalt nothing else. So, the only job would be to separate the resonance line from other spectral lines by a monochromator, because that makes the job very simple, many lines do not are not emitted due to quantum mechanical problems, quantum probabilities and only resonance line will be coming from a lamp pure lamp. So, you get spectral lines, your job is only to separate the spectral lines of the resonance lines from the element.

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So, assuming such a monochromator, isolates a small spectral band delta S covering the absorption line lambda 0 that is the resonance line. So, what is the energy received by the detector. Now, you imagine I have a lamp some spaces there, I put a detector, and lamp made of this element. So, the total amount of energy the detector receives is nothing but the sum total of the all the wavelengths that is coming out from the system all resonance lines, so that is mathematically expressed as I 0 is equal to integral of lambda 0 plus or minus delta s by 2. And the total intensity I 0 and they multiplied by delta lambda that is the interval we choose. So, if you integrate this, what I get is I 0 is a constant, delta lambda s is the integral value; this is nothing but the area of the rectangle ABCD which I have shown in the next slide.

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See in this slide what I am showing you is this is the integration factor ABCD this is the half width figure which I have shown you, it is upside down now, because it is absorption; earlier it was emission. Now, this is the energy, this is wavelength. And if I isolate a particular line what I get is I choose a total intensity, this is the integral of the figure and part of it is absorbed by the radiation. So, the intensity becomes less corresponding to the amount of energy that is absorbed by the medium. So, if a homogeneous gas having an absorption K lambda is interposed in between in a length of the radiation beam, the energy within that band will decrease by the same amount of energy and similar shape. This is a bit difficult to understand, but if you imagine a rectangle and put that figure in this the amount of energy decrease is nothing but the

integral of this that you will understand very easily. So, instead of considering the radiation per unit volume, because if I had to quantify I may say per unit volume what is the amount of radiation decrease that is observed here is not it that is the idea of whole quantization analysis.

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Instead of considering the radiation per unit volume, if the total radiant flux (Φ) is considered, then it may be proved that the absorption factor and hence optical density is proportional to the concentration of the free atoms and to the path length in the absorbing medium provided that the concentration is low and the spectral bandwidth is narrow. This is nothing but Beer – Lambert's law which can be expressed as: $\Phi_{tr} = \Phi_0 e^{-x_r N T}$ (16)

Where Φ_0 and Φ_{tr} are the radiant fluxes before and after absorption in the path length I, x_v is the spectral absorption coefficient and N is the number of atoms. 144

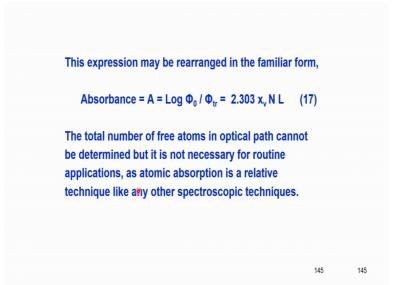
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So, I what I do is I consider the total radiant flux that is total ABCD, and find out how much is the reduction in the intensity, when I put my sample. So, if I put less sample, this BC the white portion in ABCD will become less and total integral will be more. If I put more sample, again it will decrease, and it will go like this. So, I consider the total radiant flux then I can prove that the absorption factor and which is nothing but optical density, absorption factor optical density are same. So, it is proportional to the concentration of the free atoms and to the path length in the absorbing medium. If I have longer path length, this dip will be bigger; if I have shorter path length dip will be smaller. If I have smaller concentration, dip will be smaller; if I have higher concentration, dip will be bigger that is what we are trying to quantify.

So, this is nothing but Beer-Lambert's law. So, Beer-Lambert's law should say that the decrease in the absorption of intensity should be proportional to the concentration of the absorbing species and the path length. Now, only difference is here we are considering total radiation flux that is transmitted light from the radiation source and this is the initial this thing the initial concern intensity that is proportional to the concentration of the

spectral absorption coefficient. And N is the number of atoms present in the ground state at that point and l is the path length. So, phi transmitted is equal to phi 0 into e to the power of minus chi v x v, and the total number of atoms multiplied by l.

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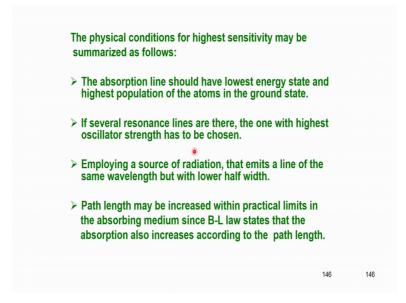
So, take logs now. And then if that comes to familiar term for us. Absorbance is nothing but denoted by A that is log of phi 0 divided by transfer phi transmittance total radiation intensity phi 0 divided by transmitted light total intensity of the radiation transmitted that is nothing but taking the logs e log e to the power of log e is 1. And then when we convert it into natural numbers, it is 2.303 chi v into N into L. So, where N is the total number of atoms and L is the path length

So, the total number of free atoms in the optical path we cannot determine, there is a catch here we cannot determine the total number of free atoms. So, how do you quantify, but for a fortunately, it is not necessary for routine applications. You can imagine that routine applications, why do you want to know the total intensity, you will know only the difference correlated to concentration, this difference in intensity is related to so much of concentration. Therefore, that is eliminated as atomic absorption is a essentially a relative technique like any other spectroscopic technique. All spectroscopic techniques are relative techniques that means, if you take a known amount of sample take a spectrum the intensity of the peak is already a function of the total number of atoms, if you increase intensity will increase. So, the difference in increase can be calculated by how

much you have taken the sample that is a fundamental basis of all atomic absorption spectrometer.

So, the physical conditions of highest sensitivity may be summarized like this. What I do is I want to determine my element analyte element in parts per billion or parts per billion level that means, the sensitivity should be very high. So, only if the sensitivity is high, small change in the concentration can be determined at the end of the system.

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Now, for this the absorption line should have the lowest energy state maximum number of atoms should be in the lowest energy state that is first condition. And second condition is highest population of the atoms must be in the ground state. We do not want I want to make absorption measurement, if already the atoms are in the excited state, the concentration will not be it be sensitive. So, the first condition for all atomic absorption is that all the atoms must be in the vapour state and they should be in the ground state in the vapour state that is the first condition.

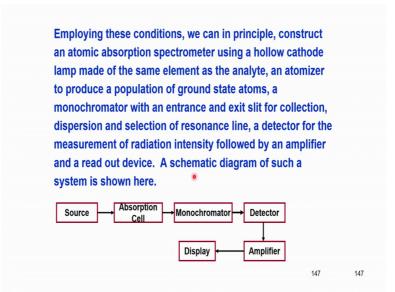
What is the second condition if there are 2 or 3 resonance lines, which one you will choose? The idea is the one with the lowest energy level, lowest energy of resonance line that should be chosen; only due to some reason if you cannot choose the lowest resonance line for some reason, then you go to the next higher resonance line. But because of the high energy requirement the sensitivity of the second resonance line will be lower than the smallest resonance line which we normally choose.

So, if several resonance lines are there this data is available in all data books, databases etcetera. If you take out to by any atomic absorption, the manufacturer will provide you the resonance lines of all the elements that you would like to determine. So, the resonance line with the highest oscillator strength should be chosen that means, the lowest frequency should be chosen between 200 and 600, 800 or whatever. It is suppose you choose a line which is below 200 then what happens you need to have a vacuum that is known as ultra vacuum ultraviolet range. Then it is a bit difficult to choose such lines because you need to have a vapour of the cloud you want to determine, but you also need a vacuum for the radiation. So, it is a little tricky, but in general choose a resonance line which corresponds to the lowest wavelength sure.

Then third point is employing a source of radiation that emits a line of the same wavelength, but with lower half width. You should choose a source of radiation that emits the same wavelength of determination, but with lower half width because smaller the half width better is the sensitivity. So, path length may be increased within the practical limits in the absorbing medium. Since, the Beer-Lambert law states that the absorption also increases according to the path length. Now, the idea is the there is a source of radiation in between I am sitting, I am the vapour state, this side there is a radiation.

Imagine my head as path length the radiation, this is my radiation, this is my detector, my head is this cell. So, the length path length is the space in between both my hands that in terms of centimetres, how far they are each other. So, this I can have 5 centimetres, 10 centimetres, 20 centimetres, 20 meters why not, but for all in all laboratories, you need a there is a certain amount of restriction. You cannot make a vapour cloud in a much larger than a particular limit. This limit is automatically set by the instrument's manufacturer, and the path length should be as long as possible as the instrument permits.

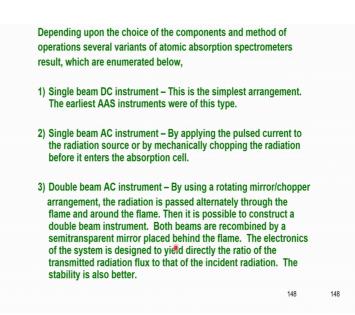
So, Beer-Lambert's law says if the path length is more sensitivity is more; if the path length is less sensitivity is less. So, the path length should be as long as possible; a resonance line should be as small as possible. And then several resonance lines are there we choose the smaller wavelength and we need an source of radiation that emits a line of the same wavelength that we want to determine that is also should be having lower half width.



So, under these conditions, we can in principle, construct an atomic absorption spectrometer using a hollow cathode lamp made of the same element of the analyte. I have been explaining to you that we need a lamp made of the same element, iron you want iron lamp we should have; tungsten you want tungsten lamp you should have; and then cobalt, cobalt lamp like that. You need a hollow cathode lamp made of the same element that is the radiation source and you need an atomizer to produce a population of ground state atoms in the vapour state vaporized form. And then you need a monochromator with an entrance slit and an exit slit for collection of the resonance line, and dispersion and selection of the resonance line is required. And then what you need is a detector now, and detector will detect the intensity of the radiation with the sample and without the sample. Without the sample is total amount transmitted; with the sample is some amount absorbed according to the figure what I had shown you that integral figure.

So, the essential components of a atomic absorption spectrometer would be source absorption cell and a monochromator and then the detector, and then detector can be connected to an amplifier they took a improve the electrical signal and then you need a display, this is how the source schematic diagram of an atomic absorption looks like. So, this absorption cell I have shown you is not an empty space, but it is a an instrument which generates the free atoms in the ground state as vapour that you should remember monochromator is nothing but a prism or a grating detector is some of the things which you have already discussed photomultiplier tubes etcetera. Amplifier and display are the electronic systems. And source is the lamp made of the same element, and we will be studying all these components in detail shortly.

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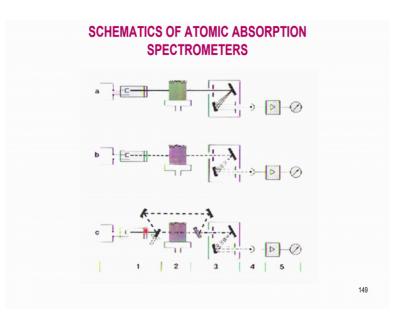
So, depending upon the choice of the components and method of operations, we can have different kinds of atomic absorption spectrometers these are enumerated below. What I can do is I can take a single source single line and then it make the measurement, but that means, I take a source collect determine the intensity without the sample and with the sample, but with the single wavelength. Now, what I can do is I can make a double beam instrument, this is known as sing single beam DC instrument this is what this is (Refer Time: 28:08) made this is the simplest arrangement earliest AAS instruments where of this type only; that means, one at a time. First you introduce water or something then you introduce your sample take the difference and make the calculation, because it is a relative technique. Assume that in water there is no element of your interest, which will should be 0.

Then I can have a single beam AC instrument - the alternating current. So, by applying the pulsed current, what happens to the radiation source or mechanically chopping their radiation before it enters the absorption cell? So, in the instrument you know AC, DC and all; in the AC what happens the current keeps on increasing reaching 0 increasing reaching 0 etcetera. When it reaches 0 there is no transmission, so that itself will serve as a blank. So, this is a single beam AC instrument.

Then I can have double beam AC instrument that is you split the radiation coming from the hollow cathode lamp in 2; one you make it pass through the sample, another simultaneously without the sample. So, what happens? Any change in the spectra hollow cathode lamp radiation will be simultaneously reflected during measurement that means, there would not be time lag or error between the stability of the instrument does not matter whenever a double beam instrument is used. Otherwise, whenever there is a high surge of the electric electricity electric current, the radiation source may in increase or decrease depending upon higher in 0, but in double beam instrument if I have the sample passing through and simultaneously another sample without another radiation passing without the sample it can be reflecting the changes in the hollow cathode lamp.

So, it is possible to construct a double beam instrument both beams are recombined by a semi transparent mirror placed behind the flame. And the electronics of the system is designed to yield directly the ratio of the transmitted radiation flux to that of the incident radiation the stability is also better in double beam instrument. So, how does it look like? Now, here absorption cell is nothing, but a flame. So, I need to have a flame just like in your house you have a Bunsen burner gas, I need a flame here to make the sample vaporize.

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So, these are the schematics of the absorption spectrometers. Here a, b, c; I have shown. And this part is the electronics part, and this is a hollow cathode lamp. Here you see the u type that is the hollow cathode lamp filament. This whole hollow lamp is vacuumized to the level of about 10 raise to minus 4 atmospheres. So, the radiation coming from this source is passed through a Bunsen burner or a burner which is having a flame like this. We will study more about the design of such instruments in due course. So, this is the design of the burner; from the burner, there is a flame burning continuously.

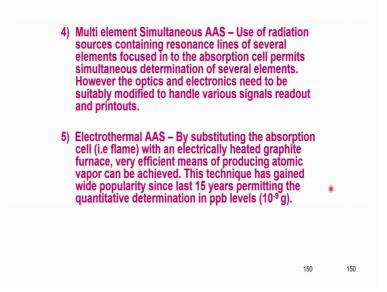
So, the radiation source passes through this burner and the sample is introduced from the bottom like this from a solution. And in the flame the sample, vaporizes. So, I have a vapour cloud in the flame of the atoms in the ground state. So, the radiation passes through the flame through the number of atoms and the path length is nothing but the width of the flame that is 1. And then I need a monochromator a wave layers split, a mechanical split and a grating and etcetera and then it is laid down to the detector, detector is here outside in this box. This is the optical box. And then there is the detector; from the detector, I have the amplification and other systems and readout systems.

So, the first part a is the monochromatic system; part b is a with c, I have shown this as a dotted line. So, in between the dashes, there is no current. So, the ones there is if I measure, when the beam is not when the current is not passing I have a 0 level reading that is a blank reading. And then when it is on, I have the sample reading. So, I get 2 types of readings at the difference I can determine here. But in the third system, where I divide the radiation by 2 beams this is double beam AC instrument I am using a rotating mirror or a chopper arrangement, the radiation is passed alternately. So, I have a hollow cathode lamp here, and then I have a beam here chopper. So, part of the chopper, there is a 50 percent goes through this, 50 percent goes through this, but it does not pass through the flame, but I combine this as well as this on this mirror. And then combine both calculate the take the ratio of the radiation, and then pass it onto the detector which will determine the current after using amplifier and readout technique.

So, using the radiation available for us from AC, non AC, the DC direct and AC with 2 double beam system. I can have different kinds of instruments which vary in complexity as well as in the accuracy of the level the quality of the instrument. I can have a single beam which is at the top a, I can have an AC single beam b, and I can have a double beam a c which is c. Now, lot of people come to you whenever they want to sell an atomic absorption spectrometer that saying that sir ours is AC single beam will do you do not need a double beam, never believe them. So, or whenever you want to buy an

instrument with a double beam what you should do is you want high accuracy go for double beam instrument, so that is an advice I want to give you whenever you want to buy an instrument. So, you know that there are single beam, double beam and single beam AC. So, always go for double beam AC, so that accuracy of the determination is more that means, reliability of your analytical value will be more.

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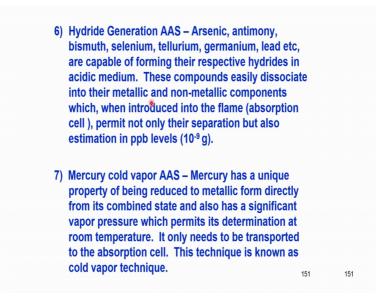
So, I can also have another system where the multi element I can choose. So, what I should I do is if this source is made of several elements. I had told you that if you want I have used only iron, but if you use an alloy of iron and manganese you can determine use the same lamp, but your job is only to separate the resonance lines of iron and manganese in this. So, if I use a hollow cathode lamp made of multi alloys, then I can determine both elements this is what I am talking about now. Multi element simultaneous AAS use of radiation sources containing resonance lines of several elements all of them pass through the absorption same absorption cell, but simultaneous determination of several elements can be done, this is a great advantage because otherwise it becomes a sequential technique one element at a time.

Now, you can use the same a hollow cathode radiation source that is known as hollow cathode lamp. However, the optics and electronics need to be suitably modified because you have to collect the radiation of 2 or 3 radiation lines resonance lines coming from the same source. So, one detector will determine one resonance line, another detector will be

dedicated to another resonance line, so that 2 elements can be determined like that I can go for 3, four, five depending upon our requirement. We will also study how all elements can be determined in one shot that we will study later.

Now, coming back to this, we study we can also have electro thermal atomic absorption spectrometry that is another variation what we do here is by substituting the absorption removing the flame, we want to heat a take an electrically heated graphite tube furnace. So, in that furnace, I heat the electric sample through electrical beams and a produce a vapour. See, you must have known several thing several systems in your home life also microwave and other things, where you can heat without the flame. So, essentially we are doing the same thing here I take a graphite tube pass current that raises temperature and the sample vaporizes. So, with an electrically heated graphite furnace very efficient means of producing atomic vapour can be achieved, this technique has gained wide popularity since last 15 years permitting the quantitative determination in parts per billion levels.

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Now, this is another variation of atomic absorption. Now, there is also another type that is known as hydride generation atomic absorption. What happens is you must remember that several elements for metallic hydrides, arsenic, antimony, bismuth, selenium, tellurium and germanium and led etcetera all these elements form a hydrate. So, the job is very simple. You take a sample, put a little bit of acid and then generate hydrogen. So, arsenic will form arsenic hydride, and antimony will form antimony hydrate, bismuth will form bismuth hydrates etcetera. You pass nitrogen through the sample, all these hydrates are vaporized and come out of the system as gas. And this gas is introduced into the graphite furnace or flame or whatever it is, and then the all other remaining substances which do not form hydrides except these 6, they will remain in the solution.

So, it is a very beautiful technique for the determination of arsenic etcetera. And these compounds when you heat them to around 1000 degrees, all the hydrates will decompose and to give the metallic elements in the ground state very important, do not forget the ground state. So, when introduced into the flame they permit not only their separation, but also estimation in parts per billion level.

So, the next technique we which is similar mercury; it has a unique property of being reduced to metallic form directly from its combined state and also has a vapour pressure; significant vapour pressure even at room temperature. So, you do not need a flame, you do not need higher electro thermal furnace also. So, it only needs to be transported into the absorption cell a space where mercury can be determined, this is known as cold vapour technique.

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Over the years atomic absorption spectrometry as an analytical technique has been accepted as a standard method of analysis all over the world. An enormous amount of literature on the instrumentation, radiation, sources, atomization techniques, optics, signal handling and data presentation has been developed. The advent of computers has made it possible for maximum use of automation, instrument control and statistical data evaluation. On an average, more than 500 research papers are being published on the application of AAS to various matrices every year. Now we shall discuss the detailed aspects of atomic absorption spectroscopy.

We will continue our discussion in the next class, but I want you to see this slide before I close that is over the years atomic absorption spectrometry using all these for a 6 techniques has been accepted as a standard method of analysis all over the world. And

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enormous amount of literature on instrumentation, radiation, sources, atomization techniques, optics, signal handling data presentation have been developed. So, the advent of computers has made it much more possible to make it for automation, and instrument control and statistical data evaluation are also possible. On an average, more than 500 research papers are being published on the application of AAS every year there are more than 500 applications. And now what we will do is from the next class onwards, we will discuss the detailed aspects of atomic absorption spectrometry.

Thank you very much.