Trace and ultra trace analysis of metals Using atomic absorption spectrometry

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Lecture - 31

GF AAS Interferences I

We are going to discuss electro thermal atomic absorption spectrometry today maybe for the next 2-3 classes also and what I want to tell you about this electro thermal atomic absorption spectrometry is, it started as a small modular attachment to the atomic absorption, flame atomic absorption, but now it has grown into a full fledge analytical technique itself by its own merit.

We have discussed hydride generation flame atomic absorption and cold flame atomic emission and cold vapor mercury has modular attachment for atomic absorption. Now, we are going to discuss electro thermal atomic absorption spectrometry, even though now it has become a full fledged analytical technique by itself for parts per billion and parts per trillion level detection of the metal ions.

The basic idea is only to ensure that maximize, maximum atomization takes place in the optical path of the atomic absorption spectrometer. That means, what we are going to do is, we are going to develop a small piece of equipment where we provide heat for sample vaporization instead of the flame. That means, if you remember the design of atomic absorption, schematic diagram in place of flame and nebulizer, we are going to put one heater. So, what difference it makes to the detection limit that is a very curious point.

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ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

Now, look at this slide.

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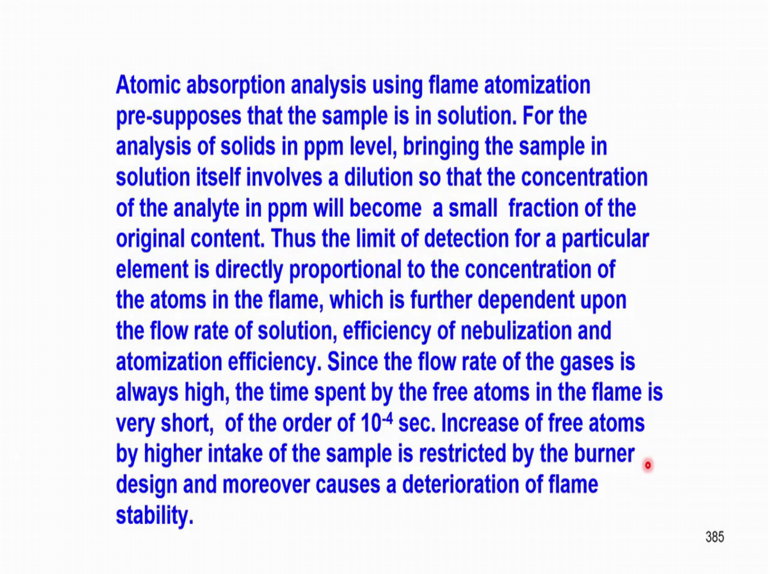

Atomic absorption analysis using flame atomization pre-supposes that the sample is in solution. For the analysis of solids in ppm level, bringing the sample in solution itself involves a dilution so that the concentration of the analyte in ppm will become a small fraction of the original content. Thus the limit of detection for a particular element is directly proportional to the concentration of the atoms in the flame, which is further dependent upon the flow rate of solution, efficiency of nebulization and atomization efficiency. Since the flow rate of the gases is always high, the time spent by the free atoms in the flame is very short, of the order of 10^{-4} sec. Increase of free atoms by higher intake of the sample is restricted by the burner design and moreover causes a deterioration of flame stability.

What do you want to say is using flame atomic absorption, we need to use nebulizer. If you remember our earlier discussion on nebulizers I told you that about 30 Y into 20 percent of atomic of the sample solution gets vaporized and forms an aerosol and then, the aerosol gets carried away with the oxidant gas and flame, oxidant gas and the acetylene gas, ok.

Now, it means that atomic absorption analysis using flame atomization, you are bound to use the sample as a solution because you had to form the aerosol. So, for the analysis of solids in parts per million level bringing the sample in solution itself involves a dilution, so that the concentration of the sample in ppm, we will go to parts per billion level. Suppose I get a small quantity of the sample let us say about 0.5 gram. You dissolve it in 100 ml 0.5. A solid sample is 0.5 and dilution is 100 ml. That means, the detection limits gets pushed. The analytical demand on the sample is more. You cannot dissolve 10 grams or 15 grams for chemical analysis. Many times you would not get that kind of samples. Suppose you want to do body analysis. How much blood you can take for analysis, a few milligram or few milliliters, right?

So, you cannot take 10 grams of blood sample and try to analyze the sample. It is not working. Same thing is true with respect to milk powder and food samples, tissue samples. You can get too much sample also from environment. You want to analyze the dust for 24hours. If you run the sample collection, you may end up with a few milligrams of the total dust and out of that you want to determine how much of nickel is there, how much of lead is there etcetera.

So, in the solid if you want to analyze solid samples dilution, it is a challenge because dilution pushes the analytical limits to parts per billion level. So, the limit of detection for particular element is directly proportional to the concentration of the atoms in the flame. This is understood because the limit of detection will always depend upon the concentration of the sample in the flame. The more sample I have in the flame, the more it will be detected.

So, that means it is further dependent upon the flow rate of the solution how fast or slow. We let the aerosol enter the solution. So, the flow rate of the both oxidant and acetylene gas are very high of the order of about 6 litres per minute and 3 to 4 litres per minute range. The time spent by the free atoms in the flame is very short. That time you can calculate and it comes to about 10 raise to minus 4 seconds. So, from the nebulizer into the flame and out of the flame, the total time spent by the aerosol particles is 10 raise to minus 4 seconds. Within that time all the reactions that I have described earlier must take place form ions. Ions have to react with electrons and then, if you should form atoms and those atom should get excited and reobserved and all that processes has to take place.

So, increase of free atoms by higher intake of the sample is not possible. It is restricted for burner design and once you make a design, you are fixed for that flow rate. You cannot change the flow rate too much anyway. So, it causes a deterioration of flame stability. For example, instead of 3ml per minute if you increase these sample flow rate to 6ml, let us say double, then what happens is more aerosol, more liquid will move into the flame and flame may put off. You cannot increase it to 12 ml or something like that and the flame temperature will come down because you are interested in more liquid. Into that 99 percent of the time, the liquid is water or acid solution.

So, these water pre droplets reduce the flame temperature. So, the reduction of flame temperature causes a deterioration of flame stability. Also, flame my flicker, it may put off. Again you have to light it. Now, all those kinds of attendant problem will be there.

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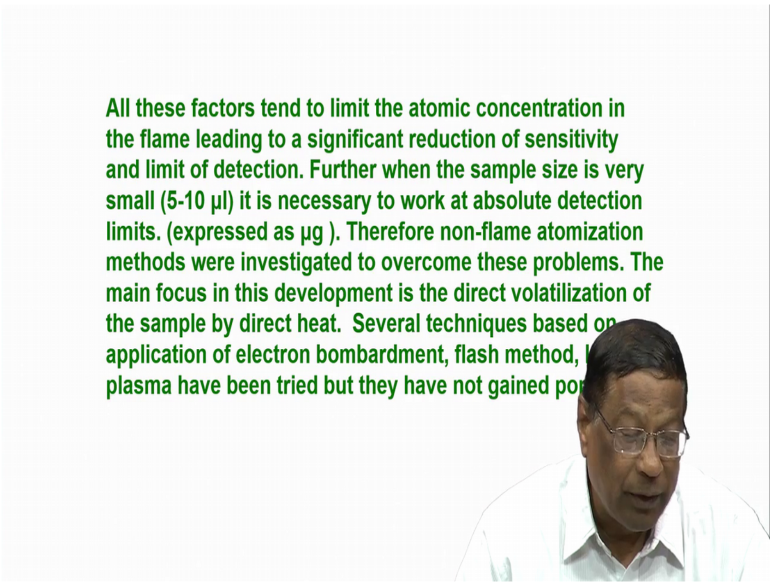

All these factors tend to limit the atomic concentration in the flame leading to a significant reduction of sensitivity and limit of detection. Further when the sample size is very small (5-10 μl) it is necessary to work at absolute detection limits. (expressed as μg). Therefore non-flame atomization methods were investigated to overcome these problems. The main focus in this development is the direct volatilization of the sample by direct heat. Several techniques based on application of electron bombardment, flash method, l plasma have been tried but they have not gained po

So, people thought all these factors tend to limit the atomic concentration in the flame atomic concentration. That means, detection limit also is rather limited. So, it lead to significant reduction of sensitivity also. Therefore, when the sample size is very small let say 5 to 10 microlitres, it is necessary to work at absolute detection limit. You have only 5 to 10 microlitres. 1000 microlitre is 1 ml, right. So, 5 to 10 microlitre sample like blood tissue, brain samples etcetera if you get, it is necessary to work at the absolute detection limit only that is expressed as micrograms absolute.

Therefore, non-flame atomization methods have been investigated to overcome these problems. So, why non-flame methods because if I heat a substance in an enclosure, convert it into vapor. 100 percent vaporization takes place instead of 20 percent of nebulization through that nebulizer and flame. So, people thought why not we introduce solid itself and then, into the flame and then, let us see how the detection limits are obtained. So, people made boats.

They took the sample in a small cup made of tantalum, introduce that cup into the flame by holding a tweezer or something, the fork. So, the solid sample itself gets vaporized. 100 percent not all the samples anyway, but atoms have been made. So, people made small cups of tantalum because tantalum is a material which can be obtained in a very pure form and then, it will not form reaction. It want form compounds with other metal ions.

So, tantalum is rather inert. People have tried platinum that is also an inert element, inert metal. So, if you take the sample in a platinum, small crucible of about 2 mm may be about 10 milliliter, 10 microlitre capacity, put the sample in that and then, you can evaporate it. So, several techniques based on the application of electron bombardment flash method, flash evaporation laser and plasma have been tried, but they are not gained popularity except the heating method electrochemical heating.

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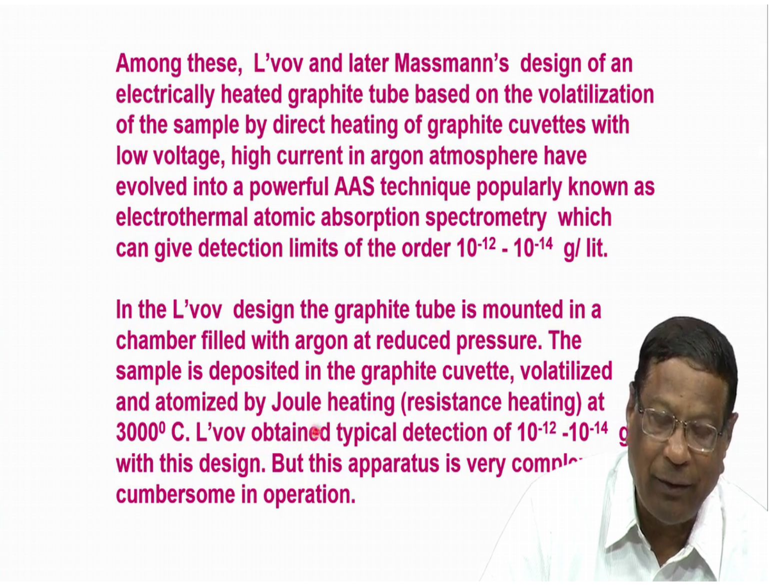

Among these, L'vov and later Massmann's design of an electrically heated graphite tube based on the volatilization of the sample by direct heating of graphite cuvettes with low voltage, high current in argon atmosphere have evolved into a powerful AAS technique popularly known as electrothermal atomic absorption spectrometry which can give detection limits of the order 10^{-12} - 10^{-14} g/ lit.

In the L'vov design the graphite tube is mounted in a chamber filled with argon at reduced pressure. The sample is deposited in the graphite cuvette, volatilized and atomized by Joule heating (resistance heating) at 3000^0 C. L'vov obtained typical detection of 10^{-12} -10^{-14} g with this design. But this apparatus is very compl cumbersome in operation.

So, you can say that the idea was to put the sample whether it is liquid or solid in an atmosphere which can be heated electrical. There we put a small amount of this sample and when we heat it, all the sample gets evaporated and form the vapor cloud, ok.

So, there the atoms are also available and electrons are also available. So, as usual there will be formation of free atoms and atomic absorption can take place. So, among all these atoms L’vov and later Massmann, two scientists they designed and electrically heated graphite tube based on the volatilization of the sample by direct heating of the graphite cuvettes. You take a graphite cuvette, put it in the graphite cuvette and then, put it and introduce the cuvette into the flame. So, they found out that with low voltage and high current in argon atmosphere, they could get detection limits of 10 raise to minus 12 to 10 raise to minus 14 grams per litre. There is less than parts per trillion whereas, in flame it is parts per million.

So, the technique has evolved into a very powerful technique graphite furnace and this is known as electro thermal. At atomic absorption spectrometry, what they do is, they take a graphite tube, heat it electrically, insert it into the path of the flame. So, then you put the sample inside heated and then, converter make the atomic absorption measurement as usual. So, in the lab of design graphite tube is mounted in a chamber filled with argon at reduced temperature. The reduced pressure, the sample is deposited in the graphite cuvette.

As I told you volatilized and atomized by joule heating and that is resistance heating at 3000 degree centigrade. I can heat it to 2000, two and half thousand, 3000 anything because graphite can be heated to very high temperature without distraction because it is a conducting material. It does not burn when you pass electric current, but temperature can develop. So, L'vov obtained typical detection limit of 10 raise to minus 12 to 10 raise to minus 14 grams with this design.

L’vov is a Russian scientist and Massmann is an American scientist. I had opportunity to interact with both of them during the development of this graphite furnace and I had pleasure of working with them. Also, the graphite furnace developed by L’vov is slightly complex and cumbersome in operation actually. So, that is why that design was delta discarded by commercial manufacturers and then, was switched over to Massmann, but L’vov was the father of Electrochemi electro thermal atomic absorption spectrometry.

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L’VOV’S ARGON CHAMBER

So, this is the L’vov’s argon chamber. So, what happened here you see here two small electrodes and a small tube here. Look at the laser pointer. There are two electrodes and a small graphite tube here, where my laser is sitting laser point pointing and these are the guide pins and this is the base plate and then, this is the cover for this.

So, this cover moves and sits exactly in this, so that it does not disturb the touch. This graphite tube, it is just basically a small chamber or circular chamber which is air tight. So, this is the Massmann design and sorry, this is the L'vov’s design and because it has to every time, you have to open it and close it.

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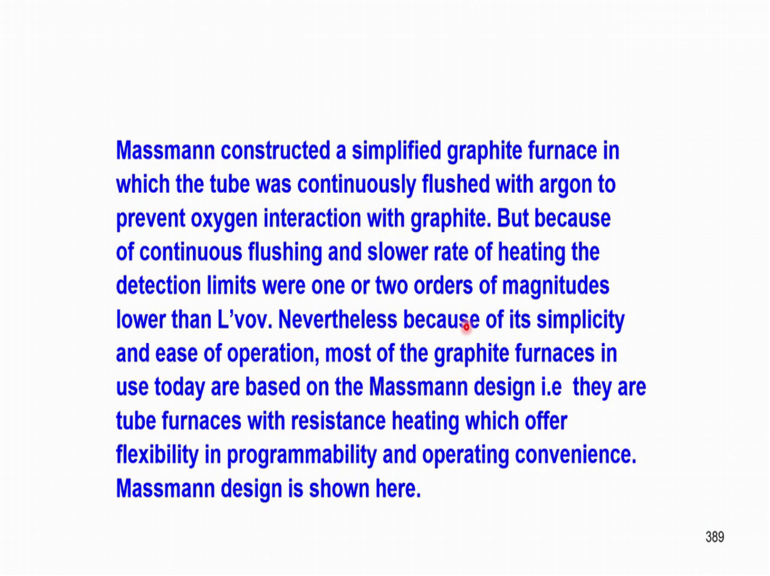

Massmann constructed a simplified graphite furnace in which the tube was continuously flushed with argon to prevent oxygen interaction with graphite. But because of continuous flushing and slower rate of heating the detection limits were one or two orders of magnitudes lower than L’vov. Nevertheless because of its simplicity and ease of operation, most of the graphite furnaces in use today are based on the Massmann design i.e they are tube furnaces with resistance heating which offer flexibility in programmability and operating convenience. Massmann design is shown here.

See this one. Every time you put the same, you put the sample in this tube, you have to close it, open it, close it, open it. For after each measurement etcetera, there is some slight amount of combustion is involved. So, what happened was later Massmann constructed a simplified graphite furnace in which the tube was continuously flushed with argon to prevent oxygen interaction with graphite. When you do not pass the oxygen graphite, we will not burn fundamental truth, but because of continuous flushing and slower rate of heating, the detection limits were one or two orders of magnitude lower than L’vov.

So, here the point is in Massmann design. Argon is in Massmann design. Argon is continuously flushed through the tube, whereas in L'vov design it is just total argon atmosphere because argon is continuously flushed through the tube. The atomic vapor gets carried away out of the system just like in flame. In flame what happens is the particles themselves are moving. Aerosol particles, they move out of the flame and optical path here we are passing argon and pushing out the vapor. So, the detection limit in Massmann design are slightly lower than L’vov design.

Nevertheless because of its simplicity and ease of operation, most of the graphite furnace is in use today are based on Massmann design, that is they are tube furnaces with resistance heating which offer flexibility in the programmability and operating convenience.

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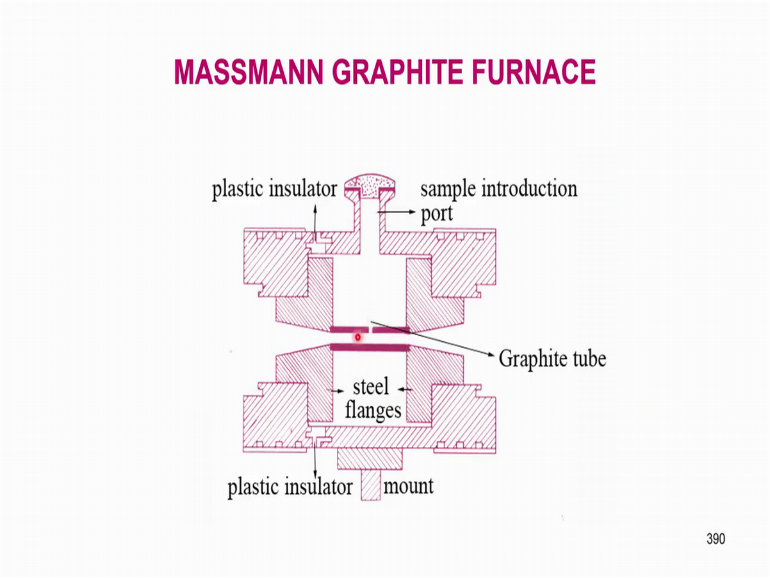

MASSMANN GRAPHITE FURNACE

I will show you the Massmann design here like this. Here the brown one, red, reddish brown area which I am pointing repre is the graphite tube. There is a small hole here and through this hole, we put the sample inside the tube where my laser is sitting now and this side the graphite tube is cylindrical and it is open at both ends, so that I can pass argon like through this hole and then, it comes out and goes out and the sample is either pushed through this way or it will go through, but this is closed.

So, the only way the sample part aerosols get out is through this. That means, there is a more possibility or spending more time inside the graphite tube and these 21234, the surroundings are steel flanges and these are the graphite tube, this is a plastic insulator and all that and these are heating plastic insulator here and these are the graphite connectors for electrical requirement.

So, what we have here is, I have a graphite tube which is fixed to the bottom of this part, bottom part and the top part you open and close the graphite tube. So, once I open this, put my sample and then, let over system run through and determine the atomic absorption reading as usual. So, this design 99 percent of the atomic absorption spectrometers are employing this design nowadays and it is good for routine analysis.

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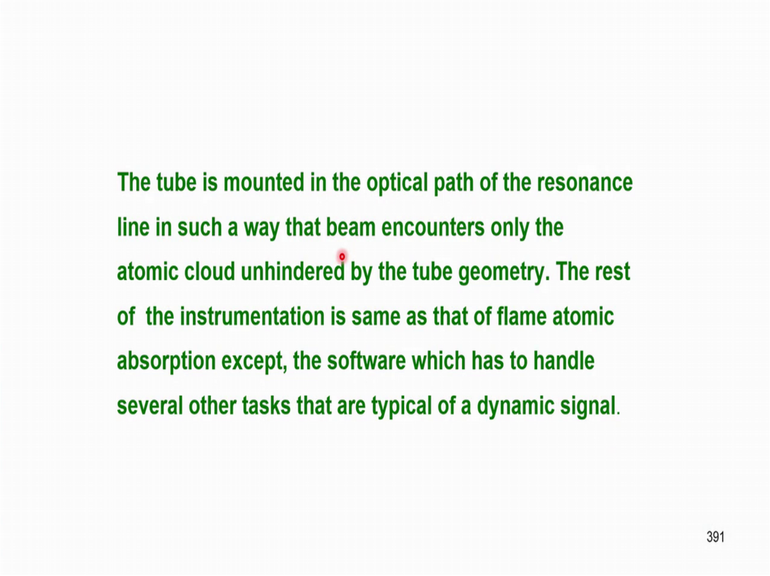

The tube is mounted in the optical path of the resonance line in such a way that beam encounters only the atomic cloud unhindered by the tube geometry. The rest of the instrumentation is same as that of flame atomic absorption except, the software which has to handle several other tasks that are typical of a dynamic signal.

So, the tube is mounted in the optical path of the resonance line in such a way that the beam encounters only the atomic cloud unhindered by the tube geometry because it is open at both ends. The rest of the instrumentation is same as that of flame atomic absorption except the software which has to handle several other tasks that are typical of a dynamic signal.

So, this we will explore now.

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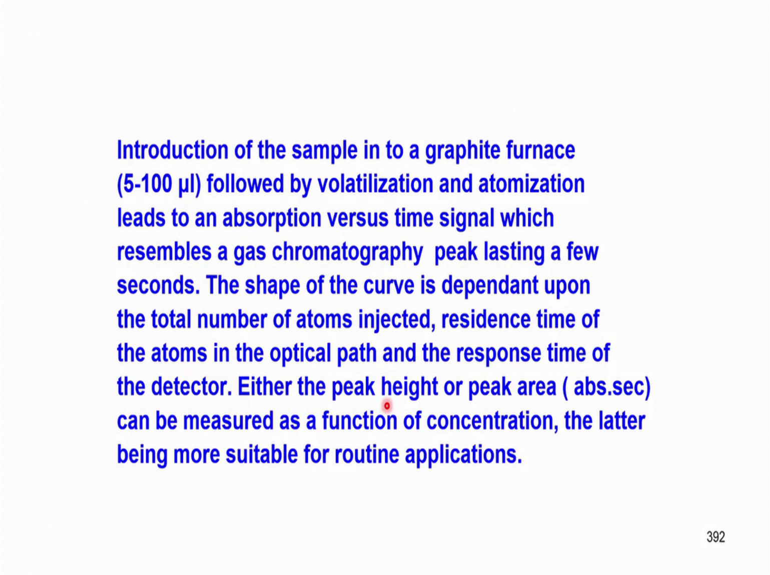

Introduction of the sample in to a graphite furnace (5-100 μl) followed by volatilization and atomization leads to an absorption versus time signal which resembles a gas chromatography peak lasting a few seconds. The shape of the curve is dependant upon the total number of atoms injected, residence time of the atoms in the optical path and the response time of the detector. Either the peak height or peak area (abs.sec) can be measured as a function of concentration, the latter being more suitable for routine applications.

So, what we mean is, we introduced the sample into a graphite furnace. The sample size can be 5 to 100 microlitres. That means, you have to use a micropipette here. You cannot use ordinary glass pipettes. So, it is volatilized and atomized and that leads to an absorption versus time signal which resembles a gas chromatography peak. It does not give you a line peak. Peak height is not very good. So, gas chromatography like peak lasting a few seconds and that means, the shape of the curve is dependent upon the total number of atoms injected residence time of the atoms in the optical path and response time of the detector, either the peak height, if the peak is very uniform and very sharp, we can use peak height or if it is not peak height, you can use peak area. The units of peak area are absorbent. That means, in the calibration curve, you plot absorbent seconds versus a concentration.

So, the peak area or peak height, we can measure as a function of concentration and latter being more suitable for routine and applications, why because peak area takes care of the dynamics of the situation. That means, the sample may volatized slowly. It may not volatilized slowly and the peak area may shift a little bit this side, that side depending upon our heating program. So, this we have seen in hydride generation. This I have shown you some of the peaks which are very sharp, some of the peaks which are not. So, sharp we have to use peak area and that is absorbance seconds as the measurement unit. So, 99 percent of the instruments, both peak area and peak height are measurable. You can choose either way depending upon the type of the signal.

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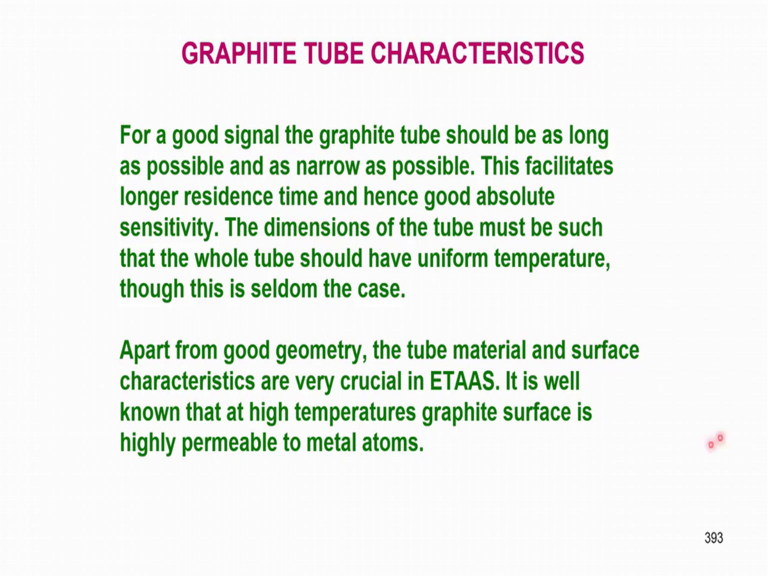

GRAPHITE TUBE CHARACTERISTICS

For a good signal the graphite tube should be as long as possible and as narrow as possible. This facilitates longer residence time and hence good absolute sensitivity. The dimensions of the tube must be such that the whole tube should have uniform temperature, though this is seldom the case.

Apart from good geometry, the tube material and surface characteristics are very crucial in ETAAS. It is well known that at high temperatures graphite surface is highly permeable to metal atoms.

So, what are the graphite tube characteristics, what kind of graphite tubes you should be using for a good signal? The graphite tube should be as long as possible because the longer the tube, more would be the vapor. It can hold as simple as that and it should be as narrow as possible. The whole should be as narrow normal dimensions of the tubes have should be such that the whole tube should have uniform temperature throughout its heating area, but though this is seldom the case.

Apart from good geometry, the tube material and surface characteristics are very crucial in electro thermal atomic absorption. It is well known that at high temperature graphite for surface is highly permeable to metal atoms. What does it mean? So, if I take the metal sample inside the graphite tube, if I take the metal inside the graphite tube, metal solution inside the graphite tube at high temperature, the metal may diffuse into the graphite material rather than form atoms and go out of the system. That is required in the atomic absorption whereas, at high temperature graphite surface itself can absorb the metals.

So, this is another problem, but it has been overcome using various techniques which will be discussing shortly and optimum dimensions of the tube.

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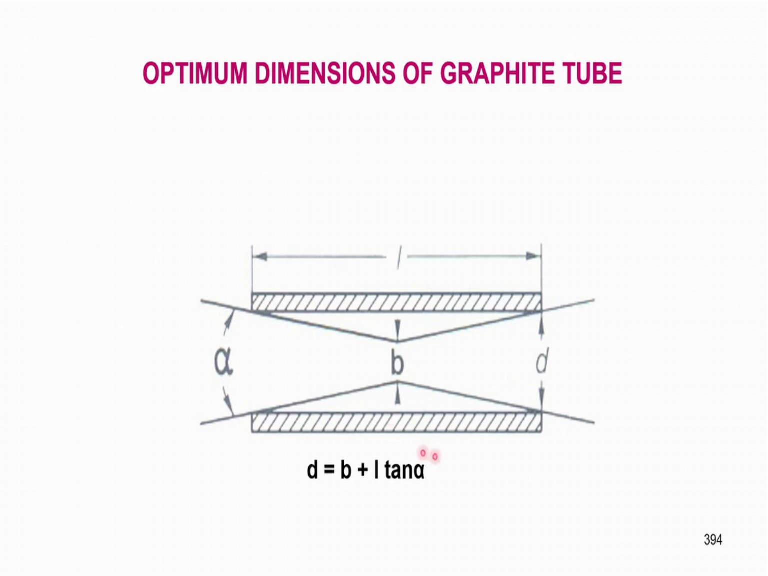

OPTIMUM DIMENSIONS OF GRAPHITE TUBE

$d = b + l \tan\alpha$

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This is the dimension of the tube, L is the length of the tube, this is the angle through which the sample is introduced somewhere here and this design is the graphite tube. It open at both ends, where I have written D and then, here also it is open at D and this is the sample, where it is put here below. There will be like a blob through a micropipette and the optical path radiation comes like this and then, goes out like this. This length is about 3 to 3.5 centimeter and this D, the distance is about 5ml, maximum 5 millimeters 0.5 centimeter.

So, it is 3.5 centimeter long and 0.5 mm diameter in the lab of design as well as in Massmann design, the sample is put here and electro thermist, ok.

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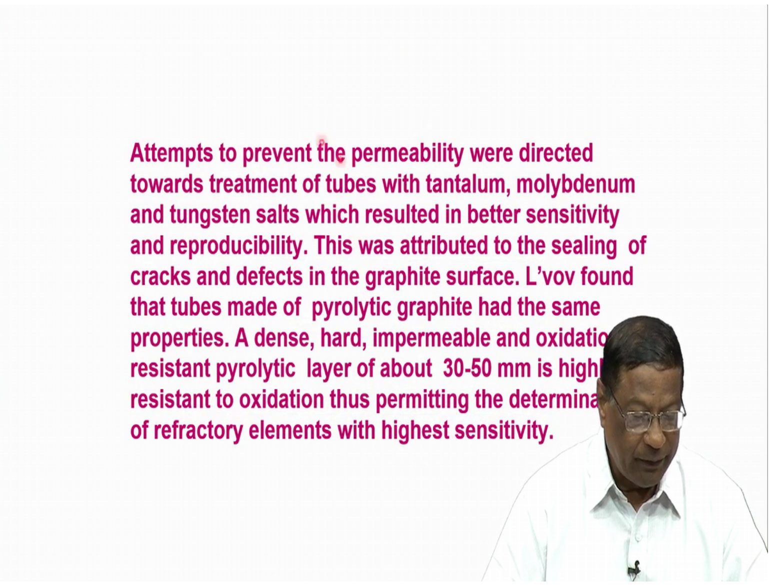

Attempts to prevent the permeability were directed towards treatment of tubes with tantalum, molybdenum and tungsten salts which resulted in better sensitivity and reproducibility. This was attributed to the sealing of cracks and defects in the graphite surface. L'vov found that tubes made of pyrolytic graphite had the same properties. A dense, hard, impermeable and oxidatio resistant pyrolytic layer of about 30-50 mm is high resistant to oxidation thus permitting the determina of refractory elements with highest sensitivity.

So, attempt to prevent the permeability were talking about the permeability of the graphite surface at high temperature. So, people thought why not we use tubes made of tantalum or molybdenum or tungsten. So, they use, you quote them quote, the graphite tube with a tungsten salt, tantalum salt, molybdenum salts and the first to close the pores, then you put your sample. The sample we will not permeate. This is one way of doing it and this resulted in better sensitivity and reproducibility. See in graphite furnace whenever we are doing atomic absorption sensitivity and reproducibility is a very important factor. Every time you do the operation, you should get the same reading now and that is something to do with precision and accuracy, right.

So, recession should be good, accuracy also should be good. This problem was how we solve the problem of permeability. We attributed the sealing of the cracks and defects in the graphite furnace because graphite surface tube also is a surface basically and they thought that whatever is permeable material if I put some amount of tantalum salt, it will close these pores and then, they know more permeation is possible. So, L’vov found that tubes made of pyrolytic graphite had the same properties. This is L'vov contribution to the electro thermal atomic absorption and what he did was, he quoted the graphite tube with a dense hard impermeable oxidation resistant pyrolytic layer of carbon of about 30 to 50 mm.

He found out that such carbon tubes are highly resistant to oxidation and permit the determination of refractory elements also with high sensitivity because we know that refractory elements are not easy to determine in flame atomic absorption, but in graphite furnace if I use a pyrolytic graphite quoting, then I can get better detection limits.

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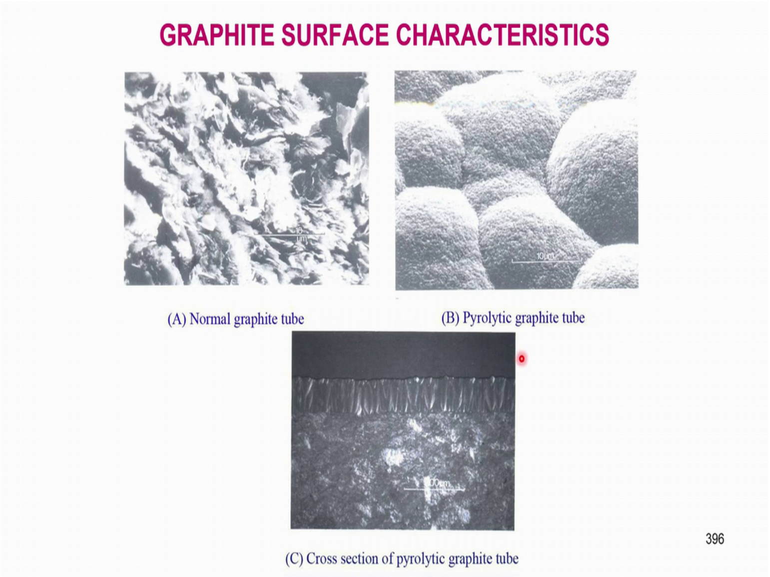

GRAPHITE SURFACE CHARACTERISTICS

(A) Normal graphite tube

(B) Pyrolytic graphite tube

(C) Cross section of pyrolytic graphite tube

So, this is the surface of graphite surface. Essentially it is a carbon surfac, this is the normal graphite tube. Now, this one is a pyrolytic graphite tube, the one on the right. So, you can see the surface of this tube is much more rougher than the pyrolytic graphite tube because it is very smooth compared to this. These are CM pictures, travelling microscope pictures of the order of about 10 micrometer. This is also 10 micrometer, this is also 10 micrometer area photographed through CM and you can see that this surface is much smoother than this surface.

That means, this has more crack sample can permit through the cracks here. It is not possible for the sample to permeate inside the surface and then, if I cut this pyrolytic graphite tube in what I have here is in the bottom portion of this tube. It is normal graphite tube like structure whereas, on the top it is very smooth carbon black area in the bottom. It is just like normal carbon and there is a permeation take quoting and then, above that impermeable quoting also of the same carbon atom. That means, the heating can be carried out much more easily, simpler with this type of a material.

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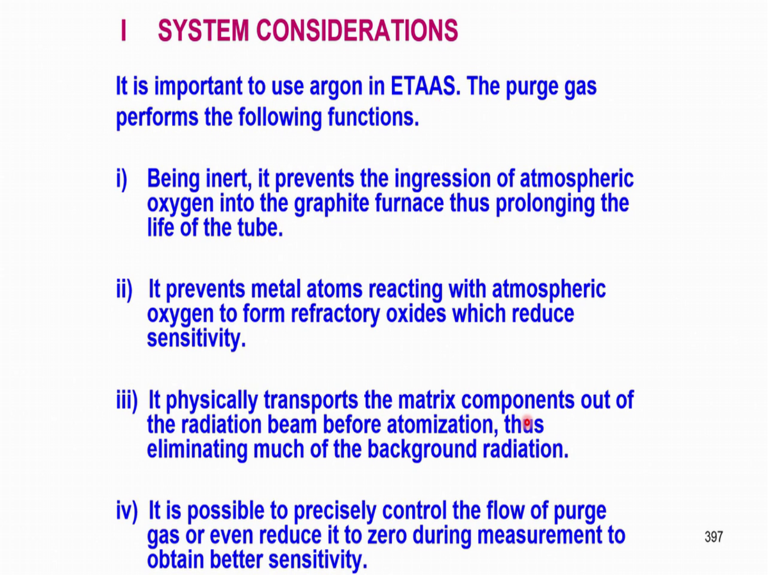

I SYSTEM CONSIDERATIONS

It is important to use argon in ETAAS. The purge gas performs the following functions.

i) Being inert, it prevents the ingression of atmospheric oxygen into the graphite furnace thus prolonging the life of the tube.

ii) It prevents metal atoms reacting with atmospheric oxygen to form refractory oxides which reduce sensitivity.

iii) It physically transports the matrix components out of the radiation beam before atomization, thus eliminating much of the background radiation.

iv) It is possible to precisely control the flow of purge gas or even reduce it to zero during measurement to obtain better sensitivity.

So, what are the system considerations we require in electro thermal atomic absorption spectrometers? So, one thing is, it is important to use argon in electro thermal atomic absorption. This is known as purge gas. That means, you have to keep on using argon throughout the operation. Whenever you are measuring or performing atomic absorption, argon should be used because argon is an inert material. It will not allow the sample to oxidize that is number one, but it also several other functions. The first thing is being inert it prevents the ingression of atmospheric oxygen. Atmospheric oxygen does not enter the graphite tube. That means, oxygen is not available to burn the graphite say if oxygen comes burning taken take place on organized passing through, there is no oxygen available to the graphite tube.

So, it prolongs the life of the argon tube carbon, carbon tube. Secondly, it prevents metal atoms reacting with atmospheric oxygen to form refractory oxides because it is a carbon atmosphere, carbon surface. Atmospheric oxygen is not there. That means, refractory oxides cannot form. So, if the oxide refractory oxides form the radius, the sensitivity here, there is no chance for oxygen to enter. So, sensitivity remains high. Thirdly, it physically transports the matrix components out of the radiation beam before atomization, thus eliminating much of the background radiation. This point requires a little bit of explanation. What happens is if I can heat it before atomization to about 400 degree centigrade water, you operate organic substances and burn etcetera.

So, first if heat it to 400 degrees with argon passing whatever comes out of the system, acid vapors, this that and all those things will be swept away before measurement. That is one of the plus point of electro thermal atomic absorption and it is a merit, it is advantage. So, once most of these things are gone, what remains would be the metal, only the metal and not even metal oxides. Maybe metal chloride to some extent chloride sulphates etcetera, but in carbon atmosphere, the metal salts gets reduced to metals. Very simple fundamental truth if you want to break any metal, put a little bit of carbon into, any salt and then, heat it. Most of the jewelers do that. They take gold salt and things like that and then, add a little heat it in charcoal along with charcoal gets reduced to the metal.

So, it is a very well known metallurgical procedure also. So, it physically transports the matrix. Basically it physically transports the matrix component out of the graphite tube before atomization as long has organized flowing. So, it is also possible to precisely control the flow of organic gas or even reduce it to 0 during measurement to obtain better sensitivity. So, as long as I use organic argon, the materials whatever produced from our sample get swept away. Now, when I want to make a measurement, I can stop the argon flow and the atomic cloud that forms inside the tube. We will not move. That has to move only through diffusion because if I stop the argon flow atomic cloud, we will be held longer inside the tube. That means, I can make the measurement for longer time. So, this is one of the most important aspect of electro thermal atomic absorption.

So, system consideration is we need argon for preventing the injection of oxygen into the graphite furnace, prevent the oxidation, physically transport; the material out of the graphite tube. At the time of measurement, argon should not be there. Only the metal vapor should be there.

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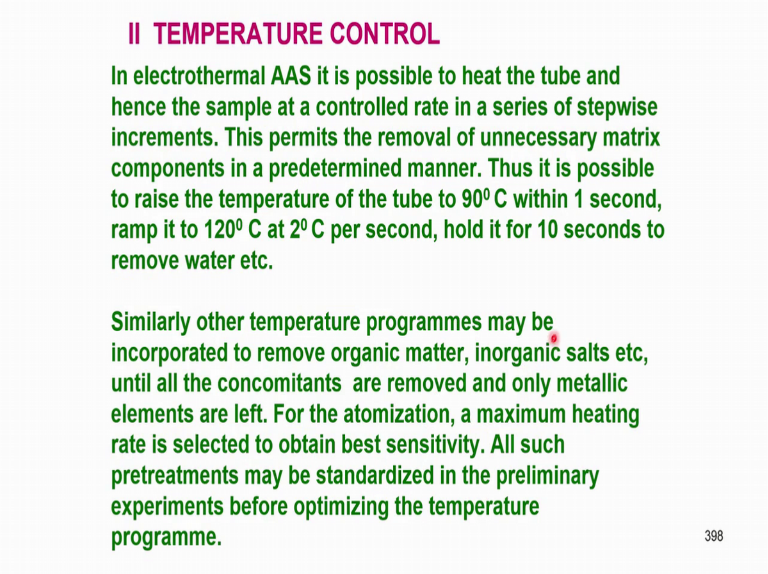

II TEMPERATURE CONTROL

In electrothermal AAS it is possible to heat the tube and hence the sample at a controlled rate in a series of stepwise increments. This permits the removal of unnecessary matrix components in a predetermined manner. Thus it is possible to raise the temperature of the tube to 90^0 C within 1 second, ramp it to 120^0 C at 2^0 C per second, hold it for 10 seconds to remove water etc.

Similarly other temperature programmes may be incorporated to remove organic matter, inorganic salts etc, until all the concomitants are removed and only metallic elements are left. For the atomization, a maximum heating rate is selected to obtain best sensitivity. All such pretreatments may be standardized in the preliminary experiments before optimizing the temperature programme.

We will discuss about the petro temperature control. We can do it you know in the next class.