

Modern Instrumental Methods of Analysis

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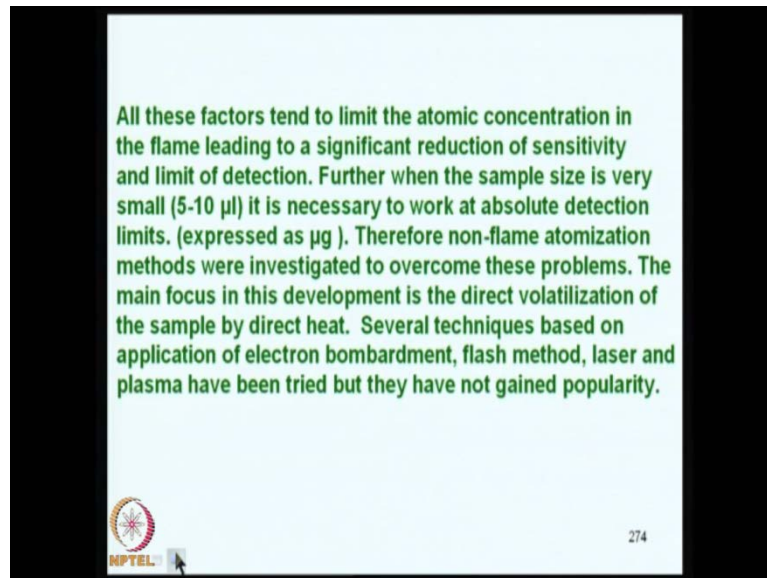
Lecture No. # 26

Electrothermal Atomic Absorption Spectrometry-10

Welcome to the next class. We in this class we will continue our discussion on the graphite furnace atomic absorption spectrometry or electro thermal atomic absorption spectrometry. As I was telling you in the last class, the atomic absorption analysis using flame atomization presupposes that the sample is in solution. For the analysis of solids in P P M level bringing the sample in solution itself involves a dilution. So that the concentration of the analytic will P P in P P M level will become a small fraction of the original content during dissolution itself. Plus you add the atomization efficiency that is only about 13 percent of the sample. So, part of it will go to again there is a loss in sensitivity plus you have you can assume that there are fair, there is a fair number of transitions of the metal atoms when they are produced into ions or molecules, refractory oxide.

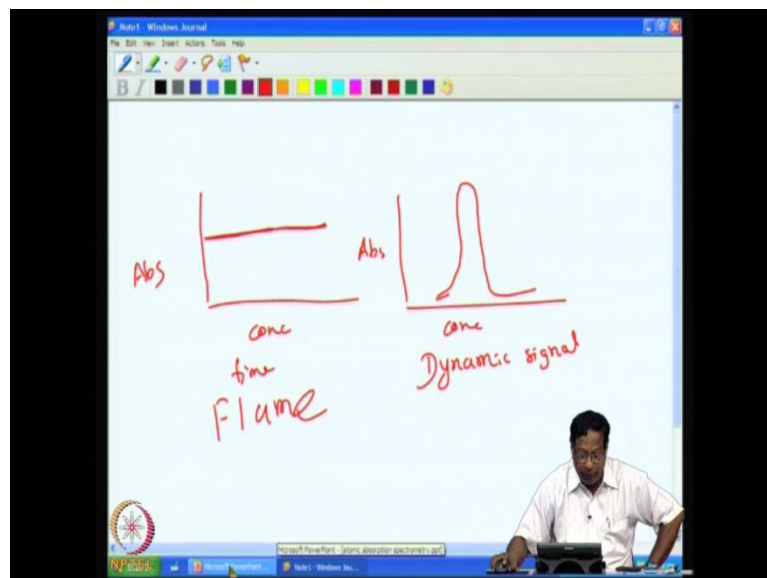
So, the atomic concentration keeps on coming down and the actual analysis of a sample in solid state will actually be a very very small fraction, when it comes to the final interpretation of the results in flame atomic absorption. So, the restriction of the burner design and other systems also causes a deterioration of the flame stability. So, all these factors tend to limit the atomic concentration in the flame, leading to a significant reduction of sensitivity and the limit of detection.

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Further when the sample is very small, let say about 5 to 10 micro liters it is necessary to work at absolute detection limits, express we can express that as the in the micro gram levels. Therefore, non flame atomization methods were investigated to overcome these problems. The main focus of this development is the direct volatilization of the sample by direct heating. So, in a atomic absorption, what do we have is a static signal. So, in the static signal means under equilibrium conditions we have a signal like this. (No audio from 03:21 to 03:29)

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So, in flame atomic absorption this is the absorbance signal and this is the concentration. So, under equilibrium conditions, what you see is the signal height as a constant value with respect to time also; that means, so long as you have the same sample being aspirated. You will have an equilibrium value and that equilibrium value of the [substance]- same solution is represented as a line of specific absorbance. But suppose you take a very small quantity of a sample and convert it into some sort of a total vapor. And introduce it into the optical path then what happens as the sample vaporizes the signal will increase and then it will reach a maximum and then come back to the ground (()). So, this is a dynamic signal, (No audio from 04:37 to 04:44) this happens in graphite furnace or electro thermal in the this is in the flame.

So, the possibility of absorbance value being much more nearer the realistic values is much more in electro thermal, you are not losing part of the sample during vaporization etcetera. The vaporization efficiency is always 100 percent if you take a small sample and vaporize it completely. So, this is what we are looking at. So, when we are working on non flame atomization methods. So, the main focus is always the direct volatilization of the sample. And several techniques have been tried for this depend[ing]- based on the application of electron bombardment, flash heating, you can use lasers, you can use plasma and many other techniques have been tried to convert a given small sample into a vapor, which can be introduced into the optical path of the spectrophotometer.

So, many of these techniques have not gained popularity, owing to several functional problems, but graphite furnace technology has gained wide popularity. So, among the graphite furnace technology, the pioneer is professor L'vov from Russia and he designed a graphite tube and which could be heated by a electrical resistance. And later Massmann designed an electrically heated graphite furnace based on the volatilization of the sample by direct heating of the graphite fluids. So, this with low voltage and high current and this he accomplished in argon medium. So that graphite substance when heated it should not form carbon dioxide and go away.

Otherwise, the tube deterioration is always a serious problem in graphite furnace. So, with this technique it is known as electro thermal atomic absorption spectrometry, he was able to obtain detection limits of about 10^{-12} to 10^{-14} grams per liter. That is less than parts per trillion. In the L'vov design graphite tube is mounted in a chamber filled with argon at reduced pressure. The sample is deposited in a

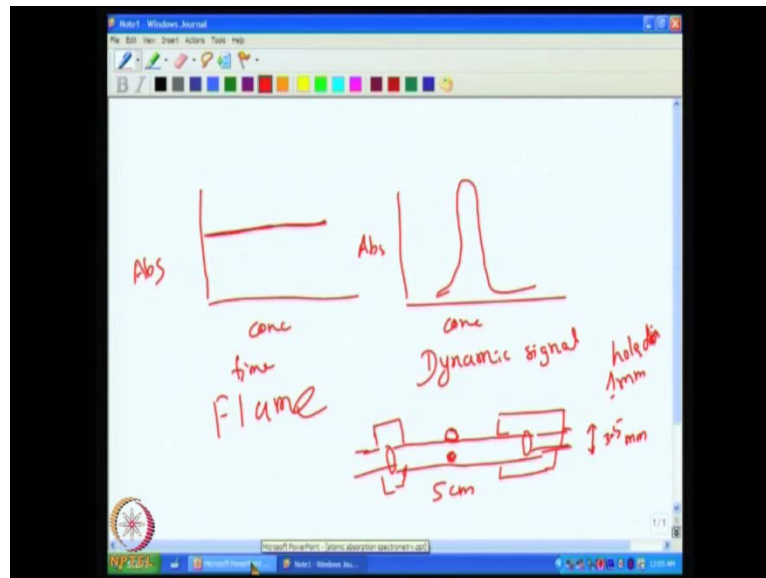
in the graphite volatilized and atomized by Joule heating that is Joule heating means resistance heating basically up to or around 3000 degree centigrade. L'vov obtained detection limits of about 10^{-12} to 10^{-14} with this design, but this apparatus is slightly complex not slightly, but actually more complex and slightly cumbersome in operation.

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Now, I will show you a Lvov's design. What he is what he has in this case here are where my arrow is pointing, you can see is graphite tube and this tube is in contact with two contactors. These two contactors are heated electrically, these round ones what you see here, they are in contact with the graphite tube and this he heated. And the whole system is the what you see on the top is a cover and that sits exactly on the circumference of this. And here there is no loss because most of the substa[nces]- most of the arrangement is air tight and he could evacuate it comfortably. and operate it under low pressure and give the heating also. So, with this design he was able to obtain 10^{-14} to 10^{-15} also in some cases.

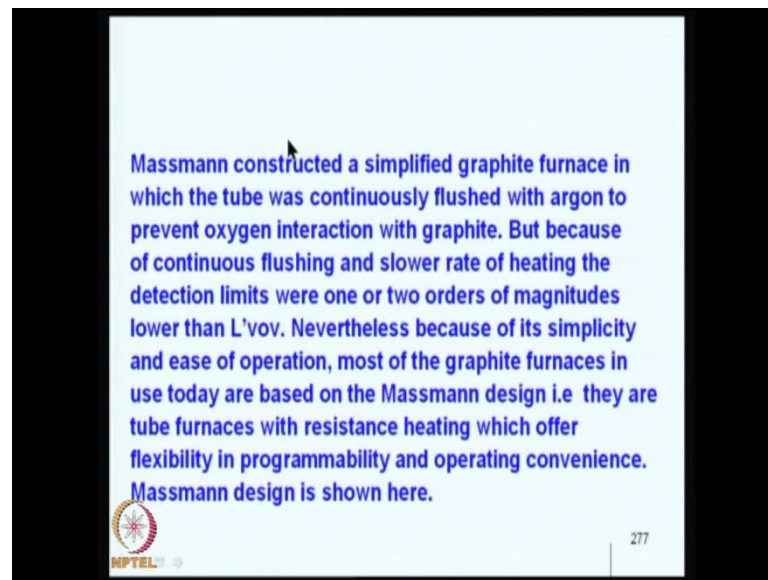
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Now, I want to show you actually, (No audio from 09:34 to 09:40) what is a graphite tube? Graphite tube is approximately about 5 centimeter length, it is a hollow cylinder, this is about 5 centimeter and there is a small hole at the top and the sample is deposited here. And when you heat this graphite tube with contacts like this, (No audio from 10:09 to 10:17) cylindrical contacts (No audio from 10:19 to 10:31) you will be able to this is 5 centimeter and the diameter of the tube is about 3 to 5 mm. So, he was able to introduce and then there is a small central hole here and this is of about [t]- the hole diameter is about 1 mm, (No audio from 11:58 to 11:11) the whole diameter is 1 mm.

So, let us get back to the graphite Lvov's graphite tube and this is the arrangement. But this design cannot be used for routine analysis, it was essentially a research instrument. But this; his experiments somewhere around 1965s spur the development of graphite furnace because it could extend the analysis to the range of parts per billion and parts per trillion straight away.

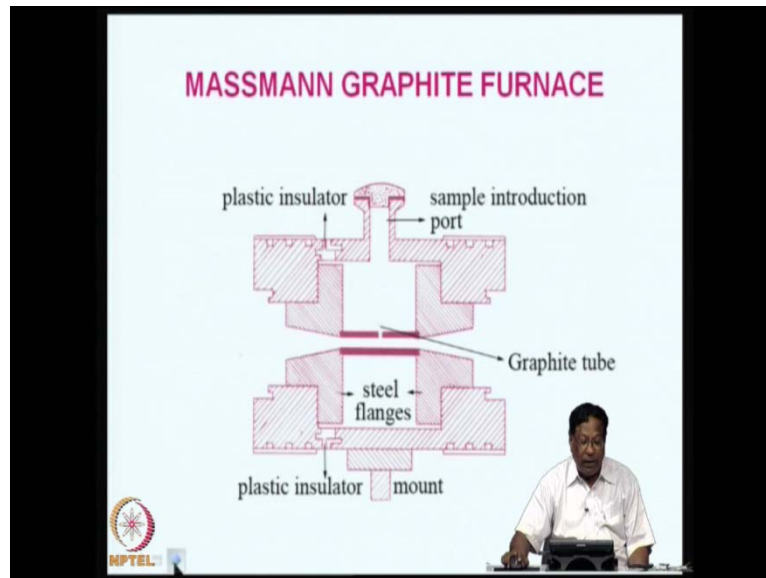
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So, Massmann improved on this design and he constructed a simplified graphite furnace in which the tube was continuously flushed with argon continuously. And to prevent oxygen ingestion into the carbon tube, thereby reducing the destruction of the graphite tube. But because of continuous flushing of argon and slower rate of heating, he obtained detection limits of the order of about 10^9 to 10^{10} that is 1 or 2 orders lower than professor L'vov's.

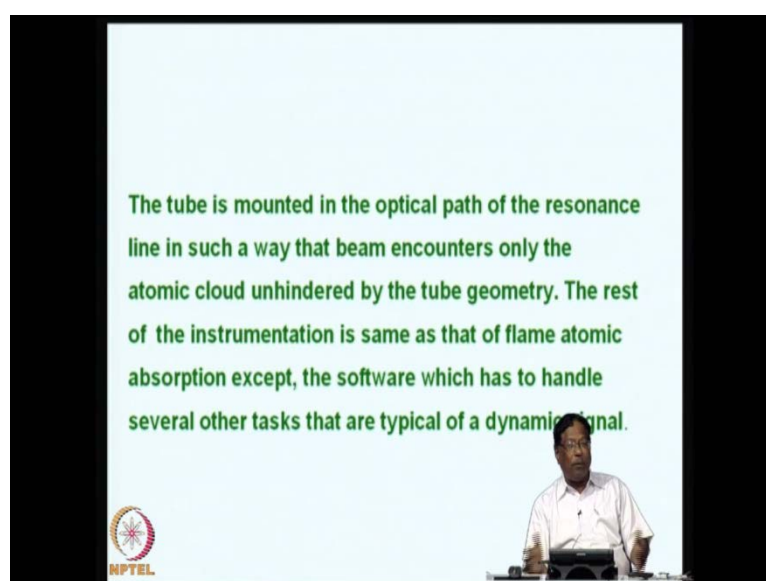
So, nevertheless because of its simplicity and ease of operation, most of the graphite furnaces in use today are based on the Massmann design. And that is there two furnaces with resistance heating which offer flexibility in heating rates also. So, because that is the populari[ty]- that is the reason for the popularity of Massmann design. And you can program the heating depending upon the amount of resistance, amount of voltage what you give and you can control the heating system also. So, it gives you an operating convenience also.

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So, now I will show you Massmann's design here. The Massmann's design is essentially the graphite furnace is a tube what I had shown you here and there are contacts. This is the graphite tube, these two are the contacts and then here is a port and plastic insulator this side and sample introduction port and this is the mount. So, basically it is like two in the you have a box like this, in which you have a tube and over that sits another cover, which will totally seal off the graphite tube. From external, except that you will be able to send the argon gas through the hole here, continuously flush it. And you can introduce the sample only through the top that is sample introduction port.

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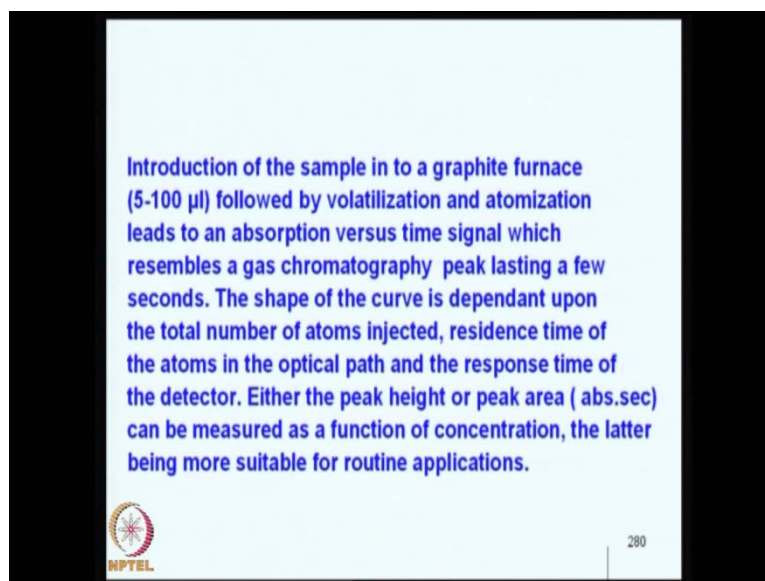


So, this is the design which is very popular and available in most of the graphite furnace atomic absorptions today. The tube is mounted in the optical path that is essential because in atomic absorption, we need to use the radiation coming from the hollow cathode lamp anyway. So, the optical path of the resonance line must be used in such a way that the beam encounters only the atomic cloud generated in the tube. It should be unhindered by the tube geometry. So, the hollow cathode radiation coming from the tube must not feel any obstruction except that of the vapour, vapour cloud not the graphite tubes.

So, the arrangement of the graphite tube becomes very important that is why we put a small piece of mirror, dentist mirror to see that the radiation is passing through. So, the rest of the instrumentation is same as that of flame atomic absorption except that there is a software which has to handle several other tasks that are typical of a dynamic signal. Because in flame atomic absorption, once everything is stabilized you just get a signal until the same signal until you change the sample. Where as in graphite furnace the once a sample is introduced vapour is there, vapour is measured and the signal dies down. So, again you have to introduce another sample if you want to have a repetitive analysis. This is the major difference between flame and non flame techniques

So, the again the introduction of the sample into a graphite furnace followed by volatilization and atomization leads to absorption versus time signal, which resembles a gas chromatographic peak just what you here.

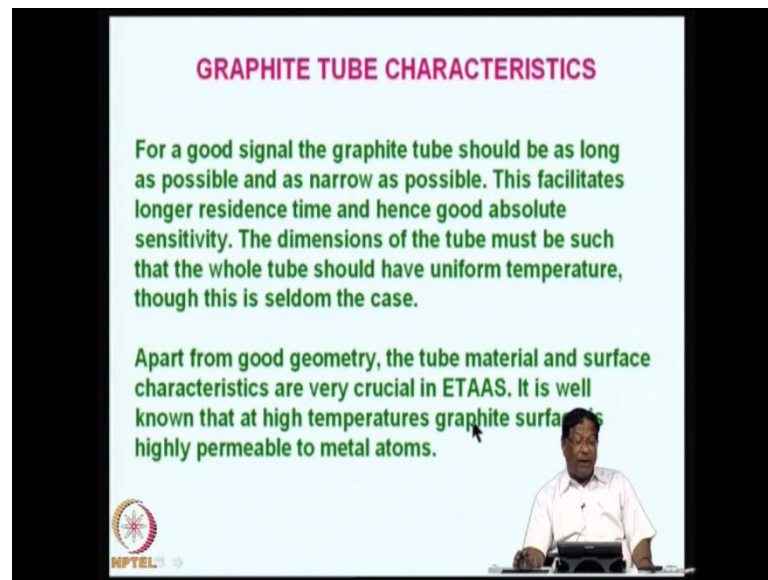
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The dynamic hear represents it just like any Gaussian curve it represents any gas chromatography it could be any figure. But it resembles approximately a signal that is rising from the blank value that is background, it reaches a maximum crescendo comes back to the base value. So, the shape of the curve is dependent upon the total number of atoms injected as well as the residence time of the atoms in the optical path. So, if you want to increase the absorbance, what you should do is you should the cloud the atomic cloud should be there for longer time before it dissipates away. That is why whenever we want to measure atomic absorption; we always want to stop the gas, argon gas. During heating, we do not want the carbon tube to get oxidize and decay. But during measurement, we do not want the gas because we want to retain the gas clouds as long as possible.

So, in graphite furnace, what we need is the height of the signal in flame photometry. Flame atomic absorption we measure the height of it because height or area does not matter in flame. Whereas, in graphite furnace depending upon the matrix part of it could be coming out early part of the analytic, may come out longer if it remains occluded in the given sample it may vaporize slowly. So, it is better to take the peak area as the basic measurement unit rather than peak height. So, the either the peak height also can be taken for atomic in graphite furnace, but peak area can be measured as a function of concentration. That is more suitable for routine applications because it takes care of the matrix variations. So, what are the characteristics of the graphite tubes?

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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 surfaces are highly permeable to metal atoms.

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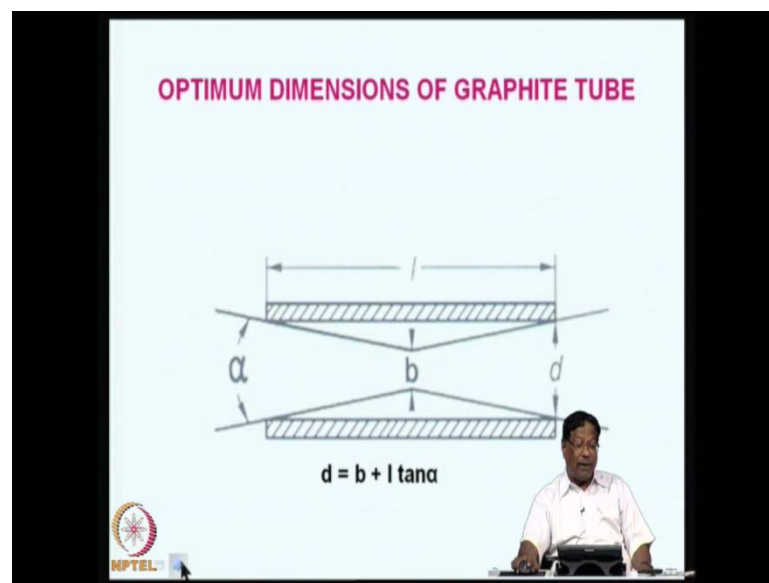
For a good signal, the graphite tube should be as long as possible. Because it can hold the vapour cloud in a longer path and optical path for measurement absorbance is a function of concentration wavelength as a less epsilon molecular extension co-efficient in this case, excitation co-efficient. So, and it should be as narrow as possible because then we can increase the absorption. And this facilitates longer residence time and therefore, good absolute sensitivity. We are talking about more absolute detection levels in graphite furnace compare to a relative concentration level in atomic absorption flame.

So, the dimension of (()) must be such that the whole tube should have uniform temperature that is one of the requirement, but the uniform temperature you will not get even if you heat it from both sides. So, there will always be some amount of variation near the end somewhere in the middle. So, the profile will always be changing if you plot temperature versus time current. So, somewhere in the middle it would be maximum near the end, it would be gases will be flowing so, it will be cooling down. So, there will always be a temperature profile which will limit the detection limits. Therefore, the dimensions of the tubes must such that it should not be too long and lead to positional errors with respect to temperature that is one thing. And that means, it should have uniform temperature though this is seldom the case.

Apart from good geometry, what else is important? The tube material and surface characteristics. So, the tube material you can use graphite furnace, you can use glassy

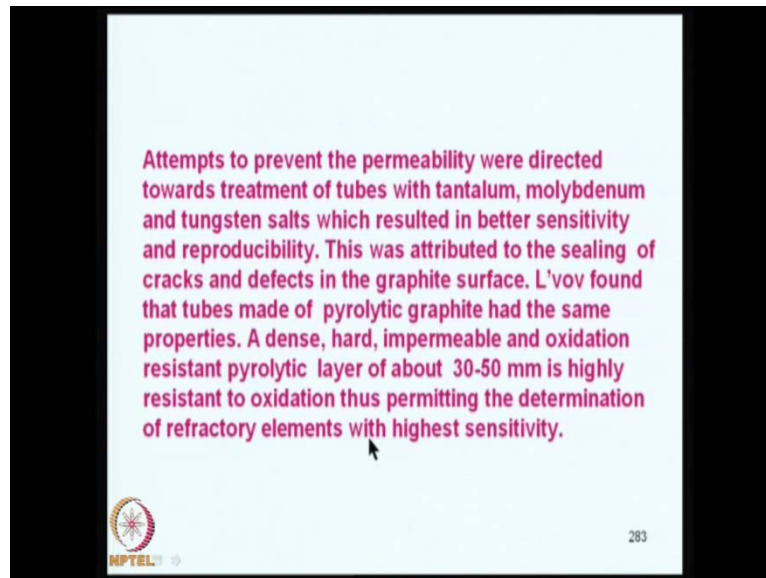
graphite, you can use any ordinary metal tube also. The earlier people had tried (C) niobium tubes of the same size, but subsequently graphite tubes have become more popular. But so, the tube material and surface characteristics are also very crucial in electro thermal atomic absorption spectrometry. It is well known that high at high temperatures graphite surface is highly permeable to metal atoms. Suppose, you put the sample and then you heat it metals will go into the graphite furnace, graphite surface rather than remain outside. So, it we need to have a surface where the metal atoms will not go into the matrix that is very important for us.

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So, what do we do for that is we might try to make graphite tube somewhere something like this in this range. Here, it is the central diameter, here it is the angle is alpha and here it is this thing so, d is b plus $l \tan \alpha$. These are the optimum dimensions to determine any metal for that matter.

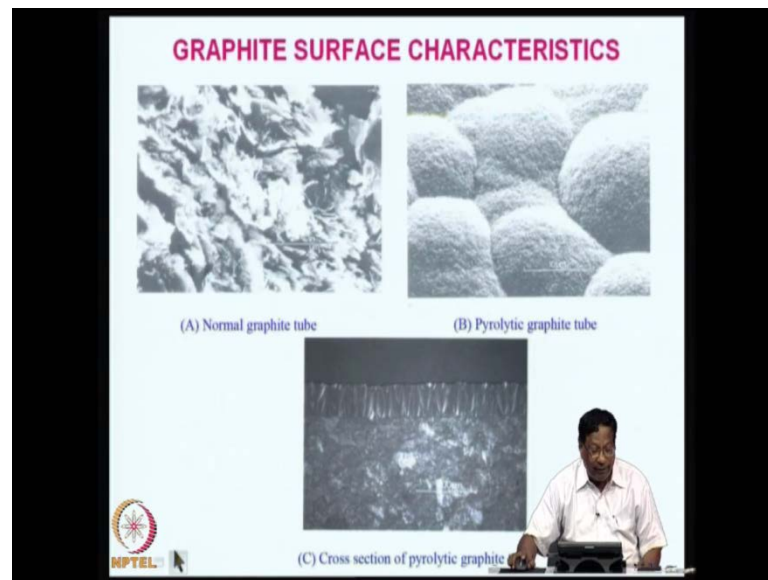
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And attempts to prevent the permeability, there were always problems initially especially from the first 10 to 15 years, the permeability was the biggest problem in graphite furnace. So, people have tried treatment of the tubes with tantalum, molybdenum and tungsten also, what you do is you take a graphite tube and dip it into tantalum salt. So that it gets a tan metallic finish. And people have tried tantalum, molybdenum and tungsten salts these things have resulted in better sensitivity and reproducibility also. This was actually attributed to the sealing of the cracks and defects in the graphite surface.

So, actually if you take a close look on the surface of the graphite tube, you would not see a very smooth this thing at a electron microscope level, you will see a lot of cracks and defects in the graphite furnace graphite surface. So, what transpires subsequently is L'vov found that the tubes made of pyrolytic graphite tube graphite had the same properties like; this tang tungsten and molybdenum coated salts. So, the paralytic graphite also prevented the permeation of the metals into the graphite surface matrix. So, a dense hard and impermeable oxidation resistant pyrolytic layer of about 30 to 50 nanometers is a highly resistant to oxidation. This permits the determination of refractory elements with highest sensitivity. So, this is what is being used now a days.

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So, the graphite surface characteristics are like this. Initially, if you take a normal graphite tube, you would always see that the whole surface is filled with cracks like this. If you take a pyrolytic graphite tube, you would see that the surface is very smooth and it is a there are not so many cracks and the defects are also very structural defects are also very minimum. So, if you take a look at a cross section of a graphite tube, here you would see that on the top in this range it is very smooth, this is the pyrolytic coating. And below that there is a inter facial layer and below that is the normal graphite.

So, how do we do this is you just take a graphite tube, put it in a furnace, pass methane gas. So, the methane gas will get reduced and then keep on depositing on to the graphite tube, normal graphite tube like this. And over a period of time you would get a surface like this. And if the surface is still smoother, then it is known as glassy carbon tube and glassy carbon tubes are not so preferable as pyrolytic graphite tube. Because this contains very small micron size less than micron size graphite atoms, graphite molecules carbon aggregates basically. And they are much more suitable because they are chemically reactive also to some extent. So, it is possible to absorb some of the acids and other things and release the metal atoms. So, these are very important characteristics of the graphite tubes.

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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 ingress 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.

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So, now let us move on to system considerations. What do we mean by system considerations? Basically, the introduction of graphite tube and heating etcetera it gives us lot of freedom when we want to operate the graphite furnace atomic absorption. So, the it is important to use argon in electro thermal atomic absorption. So, how do we use argon? We want argon when the sample is being heated, we do not want argon when the sample is being measured. So, you should have a control of argon flow and what are the advantages of argon? Being inert it prevents the ingress of atmospheric oxygen into the graphite furnace; this is the biggest problem basically, with respect to graphite furnace and it prolongs the life of the tube.

Usually, graphite tube cost about 3000 rupees in India. They are not being manufactured in India, we generally import them, but the graphite furnace you have to import even the contacts because contacts are have to be exactly matched with the graphite tubes. So, you import graphite tubes as well as graphite contacts. And it is very very important for us to use argon and thus prolong it prolongs the life of the tube. Usually, a carbon tube is good enough for about 300 firings because after heating to 300,000 centigrade to remove all the vapors, you again bring it back to room temperature to start the next analysis.

So, again heating cycle goes on. So, this constant heating and cooling heating and cooling, there has some deteriorating effect on the carbon. And after about 300 firings the carbon tubes deteriorates to such an extent. That it will be impossible to get the same

sensitivity at that time, it is time for changing the graphite tube. So, graphite also performs another important function. It prevents metal atoms also reacting with atmospheric oxygen to form refractory oxides. If you use argon there is no oxygen so, during evaporation or after during decomposition metals will not have a chance to react with the atmospheric oxygen and form the oxides. If they form the oxides the some of the elements like chromium, tungsten, niobium etcetera they all form refractory oxides. And even at 2500 degree centigrade they will not decompose, they need 3000 degree centigrade or more.

So, it is important for us to remove oxygen and this job argon does. It physically transports the matrix components out of the radiation beam, before atomization, thus eliminating much of the background radiation. This point I want to explain a little further because when you are introducing the sample in a graphite tube, you are introducing it as a liquid. And what we want to do now? We are passing the argon gas, we are heating the sample to get the atomic cloud. And this heating is important for us because we want to change the characteristics of the sample.

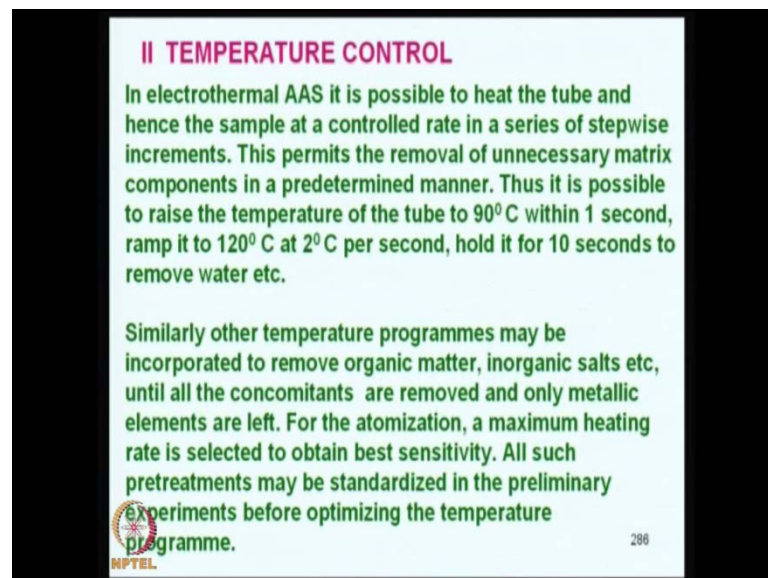
So, what we want to do basically is first remove the water that is this dissolution components. It will have acids, it will have metal salts, it will have water and all these things as a liquid sample we want to heat and remove the water as much as possible. And then water evaporates around 100 degree centigrade, but if it is held occluded etcetera etcetera, we heat the sample to 120 to 130 degrees to remove almost all the water, not exactly 100 degree centigrade. So, it is physically we are transporting the water from the matrix into the air removing.

Same thing happens with acids, you increase the temperature to around 200 300 degree centigrade, hydrochloric acid or Sulphuric acid or Perchloric acid, all these acids will evaporate. And because argon is flowing it helps to take out the acid vapors also out of the system. And then what happens? There will be salts like sodium salts suppose you want to determine gold in sea water. There is about 3.5 percent of salt, sodium chloride and suppose you we heat it to about 850 degree centigrade, salt will melt and boil and then it will evaporate. So, if around 1000 degree centigrade if I heat, there would not be any more sodium chloride, but gold will remain.

So, like that it is possible to remove most of the matrix components out of the radiation beam before atomization itself, this is part of the pretreatment program. So, thereby what we achieve is eliminating much of the background radiation due to all these effects. So, argon does another important function that is it is possible to precisely control the flow of the purged gas or argon or even reduce it to 0 during the measurement to obtain better sensitivity. During measurement we do not want argon so, if we stop the argon flow, no other gas also will enter because of the high temperature. And you would be having pure metallic cloud elemental cloud, during the measurement.

So, this brings us to another important aspect of electro thermal atomic absorption that is temperature control. So, in electro thermal atomic absorption, it is possible to heat the tube and hence the sample also at a controlled rate in a series of step wise increments. This permits the removal of unnecessary matrix components in a predetermined manner. Thus for example, just now I explained to you that it is possible to raise the temperature of the tube to 90 degrees within 1 second ramp it to 120 centigrade that means, I heat simply raise the temperature to 90 degrees.

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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°C within 1 second, ramp it to 120°C at 2°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.

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Afterwards I will say give a command heat the sample at rate of 1 degree per second. So, 20 seconds if I hold, the temperature will slowly raise in the graphite furnace up to 120 and then hold it for 7 10 seconds; that means, after reaching 120 I give an another computer command do not re increase the voltage. So, the temperature will be steady.

So, it will hold the same temperature for 10 seconds so, most of the water will be removed. So, like this temperature control becomes a very important aspect of graphite furnace.

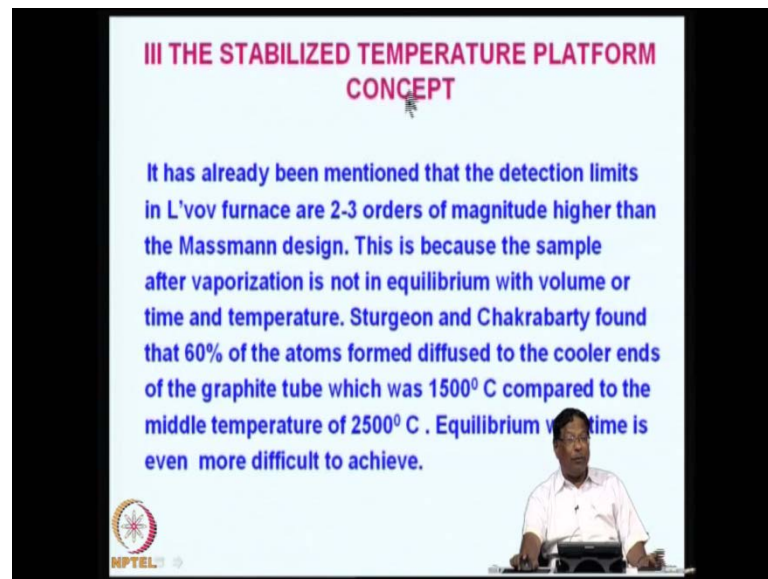
Similarly, other temperatures we can write, we can incorporate to remove the organic matter. We all know that, many of the organic substances present in a given sample will not survive more than 600 700 degree centigrade. So, if I heat the graphite tube containing the sample to 600 to 800 degree centigrade, then most of the organic substances complexes and other seaweeds, plants etcetera they will all get destroyed and they can be removed from the system. So, heating to higher temperatures about 400 to 600 degree centigrade makes lot of sense in electro thermal atomic absorption.

So, I can heat or plan in such a way that most of the organic matter also can be removed subsequently, inorganic matter like; Sodium Chloride, Potassium Chloride, Magnesium salts, Mercury if you are not analyzing, Mercury also can be removed by 200 230 degree centigrade, Thallium that also evaporates at very low temperature. So, all these concomitant elements can be removed by preprogramming. So, until at the end of it what remains is only the metallic element may be some of the nonvolatile other elements. And we know that atomic absorption is a technique where almost specific and other so long as there no spectral interferences, other metallic elements even if they remain at the atomization stage till they may not interfere. So, that is the idea.

So, for atomization a maximum heating rate is possible because we want the atom cloud to form suddenly, when we are atomizing. So, we give maximum heating power that is why I always wanted to use zero heating; that means, in PerkinElmer instrument if I say zero heating time ramping time; that means, it heats maximum, but in G V C atomic absorption graphite furnace we had to give minimum 1. So, in 1 second, you want to heat it to 2400 degree centigrade that is a major difference in G V C instruments as well as this PerkinElmer. Of course, there will sm[all]- slight differences in software, in most of the instruments. But what is important is at the time of atomization irrespective of the instrument you have to heat it at the maximum power. So that you form the atomic cloud for measurement and hold it for 1 second 2 second etcetera so that we can get a dynamic signal.

So, for the atomization maximum heating rate is selected to obtain best sensitivity. All such parameters may be standardized in the preliminary experiments you see, whenever you want to do a calibration, before that itself you standardized all these parameters. So that during the analysis the subject the sample also to the same pretreatments. So that there are not many differences between the operations the standards and calibrated standards and unknown standards undergo this difference. So, optimizing the temperature program is always a very important concept in atomic in graphite furnace.

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III THE STABILIZED TEMPERATURE PLATFORM CONCEPT

It has already been mentioned that the detection limits in L'vov furnace are 2-3 orders of magnitude higher than the Massmann design. This is because the sample after vaporization is not in equilibrium with volume or time and temperature. Sturgeon and Chakrabarty found that 60% of the atoms formed diffused to the cooler ends of the graphite tube which was 1500° C compared to the middle temperature of 2500° C . Equilibrium with time is even more difficult to achieve.

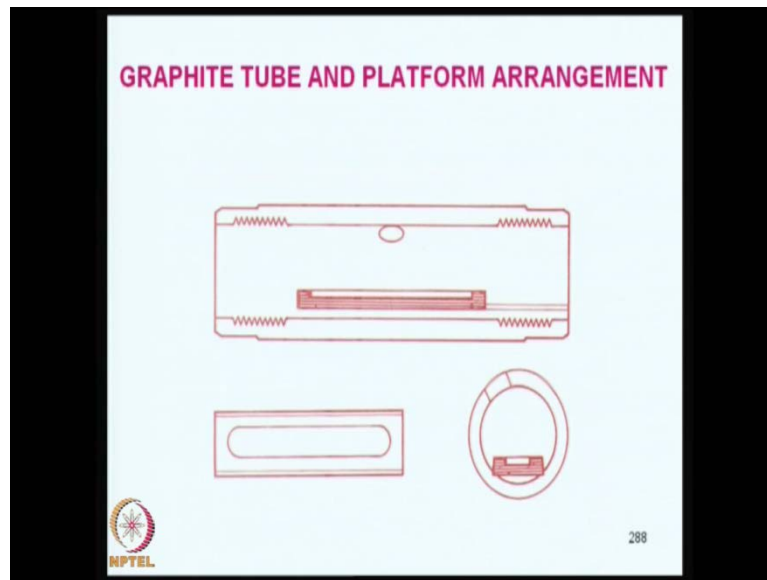
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Now, this brings us to an interesting concept that is known as stabilized temperature platform concept. In this case, the L'vov furnace it has already been mentioned that the detection limits in L'vov furnace are about 2 to 3 orders of magnitude higher than Massmann's design. Now, this is because of sample after vaporization is not in equilibrium with the volume or time or temperature. In L'vov furnace design also it is just heated and the he measures the peak height etcetera. And it is not a you know what you call 100 percent reproducible at that level 10 raise to minus 13 to minus 14.

But in Massmann's design, I have a lower order, but, there is better reproducibility. So, this is where Sturgeon and Chakrabarty, they did some research and found that 60 percent of the atoms formed defused to the cooler ends of the graphite furnace. So, the temperature of the graphite tube at the edges was 1500 when this temperature in the middle was around 2400 degree centigrade. Within that 3 centimeter there are so much

variation. So, obviously, this will lead to different configurations and then the vapour vaporization characteristics and then measurement characteristics etcetera. So, equilibrium with time is much more difficult to achieve we not we equilibrium with respect to temperature with time also.

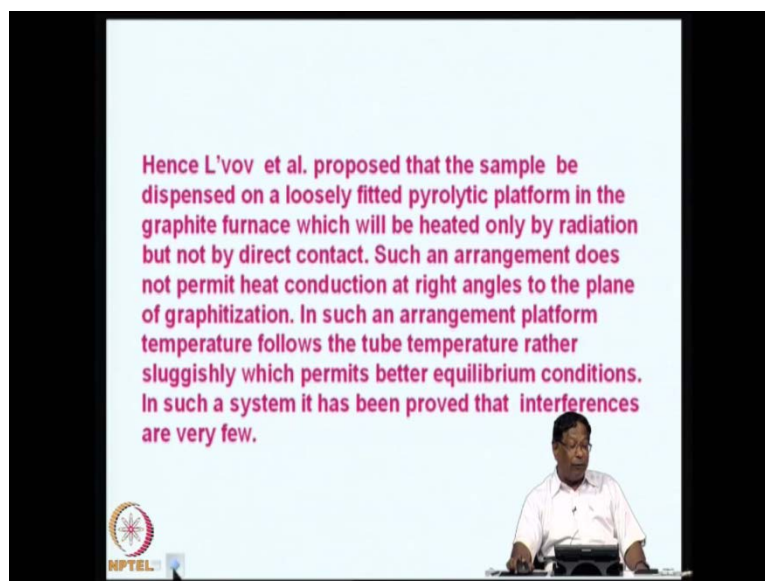
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So, all these considerations what we are going to do is avoid the variation in the temperature, variation in the time etcetera. And here a platform is introduced; that means, in the graphite tube I want to introduce a platform like this. So, this platform just slides into the graphite tube somewhere below the operator below the sample introduction point. So, when you have a platform, the platform is not heated directly by the electrical contact, but only by the radiations. Suppose, the whole tube is heated like this from the end, the platform is not heated so as the tube temperature increases platform gets heated so, it is heated by the radiation. Suppose, platform is heating around 300 the ends graphite tubes are heating around 300 degrees, platform would have been heated up to 250 because platform is not directly heated.

So, it is heated by radiation only. So, what happens at the platform? The temperature is much more steadier than at the ends. So, this concept of platforms stabilized temperature platform is a very important concept I have worked in this area.

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The image shows a video frame with a light blue background. On the left, there is a slide with red text. On the right, a man in a white shirt is seated at a desk, presenting. In the bottom left corner of the video frame, there is a logo for NPTEL (National Programme on Technology Enhanced Learning) featuring a stylized sun or star symbol.

Hence L'vov et al. proposed that the sample be dispensed on a loosely fitted pyrolytic platform in the graphite furnace which will be heated only by radiation but not by direct contact. Such an arrangement does not permit heat conduction at right angles to the plane of graphitization. In such an arrangement platform temperature follows the tube temperature rather sluggishly which permits better equilibrium conditions. In such a system it has been proved that interferences are very few.

And the other component of stabilized temperature system is that we introduce argon as flow gas. And then computer control the temperatures and then Zeeman effect background correction and followed by the area peak area integration. These are the four concepts of stabilized temperature platform system. And what L'vov's himself had proposed that the sample be dispensed on a loosely fitted pyrolytic tube platform, but he did not do much work. Because at the time there are somewhere in 19 platform sizes is also 2 mm by 3 mm that is all. It is a small platform which can be introduced into a slot inside the tube.

So, he is suggested that a loosely fitted pyrolytic platform in the graphite furnace, it should be heated only by radiation, but not by direct contact. Such an arrangement does not permit heat conduction at right angles to the plane of graphitization in such an arrangement. Platform temperature follows the tube temperature with a rather a little sluggishness, slowly it will try to come up to the tube temperature. So, this permits better equilibrium conditions. So that the vaporization, evaporation and all these things are slightly more under equilibrium conditions on the platform instead of it instead it was in the tube at the bottom. In such a system it has been proved that interferences are also very low in platform concept s 2 p f.

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AUTOMATION

In graphite furnace the sample to be handled is rather small (5- 10 μ l) but the sensitivity is rather high. The sample has to be introduced exactly in the same place every time through a small hole (about 1 mm dia) in to the graphite tube or on to the platform. There is also the risk of sample contamination with the graphite hole edges and pipette tips. All these factors lead to poor precision with manual pipetting. It is also cumbersome. Therefore automatic pipetting is preferred. Several programmable automatic dispensing units with teflon capillary are available in the market and also offered as a standard accessory with graphite furnaces. The reproducibility with automatic dispensers is about 1% with an RSD of 0.4% compared with 5% for manual pipetting with an RSD of 3.2%.

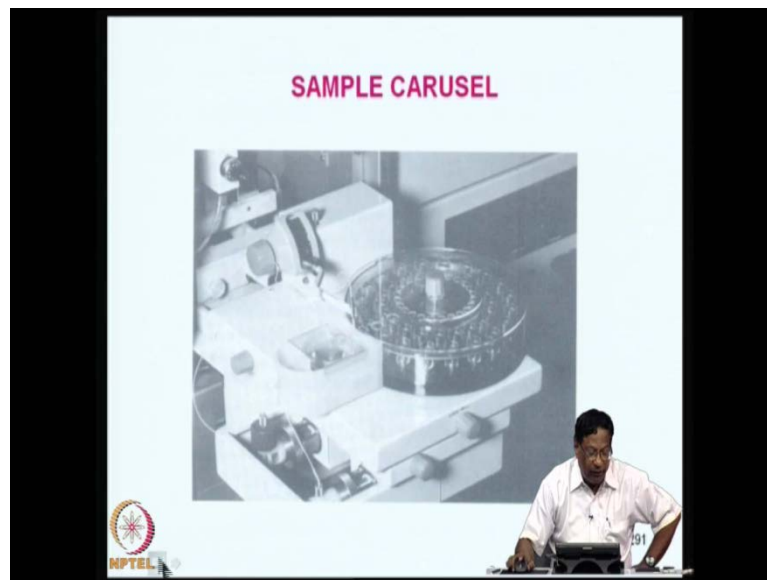
NPTEL 290

So, another concept is automation. So, in graphite furnace again the sample has to be handled is very small of the order of about 5 to 10 micro liters, but the sensitivity is very high. The sample has to be introduced exactly in the same spot through that through a small hole about 1 mm dia into the graphite tube or on to the platform, you can choose either way. But there is also the risk of sample contamination with the graphite hole edges if you take an ordinary micro pipette, you may touch the tube surface on the not inside, but the sample may be dispensed on the sides. And then there are other factors which will hand pipetting into the graphite tube is always a little problem. I will show you a slide shortly, what are the problems associated with hand pipetting inside the graphite tube.

But it is preferable to use an automatic pipettor into the graphite. So that will reduce the reproducibility irreproducibility problems. So, all the there is also the risk of sample contamination with the graphite tube, this time we introduced next time there could be contamination and again there will be a problem. So, these factors lead to poor precision with manual pipetting. So, as far as possible in graphite furnace we should avoid manual pipetting. It is also cumbersome actually to because first you have to if you want to make a calibration, first you introduce 10 micro liter, then you introduce 20 micro liter to make the calibration. And there could be errors manual errors or statistical errors in the incorporated in the pipette itself. Therefore, automatic pipetting is preferred.

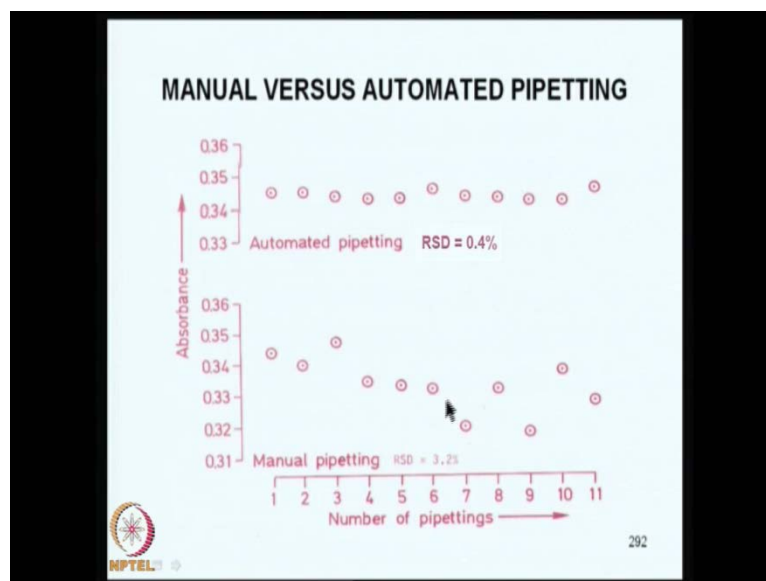
Several programmable automatic dispensable dispensing units with Teflon capillary are available now in the market, but just about 10 years before they were all curiosities. Even about 15 years before they were all curiosities people were still doing experiments. How to introduce the sample through a capillary whether to introduce through a metallic capillary or Teflon flexible Teflon tubing fitted to a metallic this thing, metallic support etcetera. So, the nowadays they have most of these problems have been solved and automatic pipetting is also part of the stabilized temperature concept. So, they are all available as standard accessory the reproducibility with automatic dispenser is about 1 percent with a relative standard deviation of 4 percent compared with 5 percent for manual pipetting and R S D approximately 3.2.

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For my next slide will show you this automatic system for sample introduction. This is a sample carousel and we have an arm with a tube here, the arm the sample carousel will rotate, the arm will come here take the sample. And then go up and introduce into the graphite furnace. So, this is a very standard configuration.

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But what I want to show you is the difference between manual pipetting and automatic pipetting. So, see look here in this figure I have drawn the determination of iron with manual pipetting. So, you can see that the absorbance is one is here 0.3345 another is 0.333 sometimes I have got 0.32, sometimes I have got less than 0.32 like that the variations are quite large. Remember we are talking about the third decimal second decimal and third decimal. Whereas, here the top one is the same sample when introduced using an automatic pipettor I have the fairly reproducible results. So, this is the advantage of automatic pipetting. So, because the capillary diameter is also very fixed and takes precisely it can be controlled using a stepper motor.

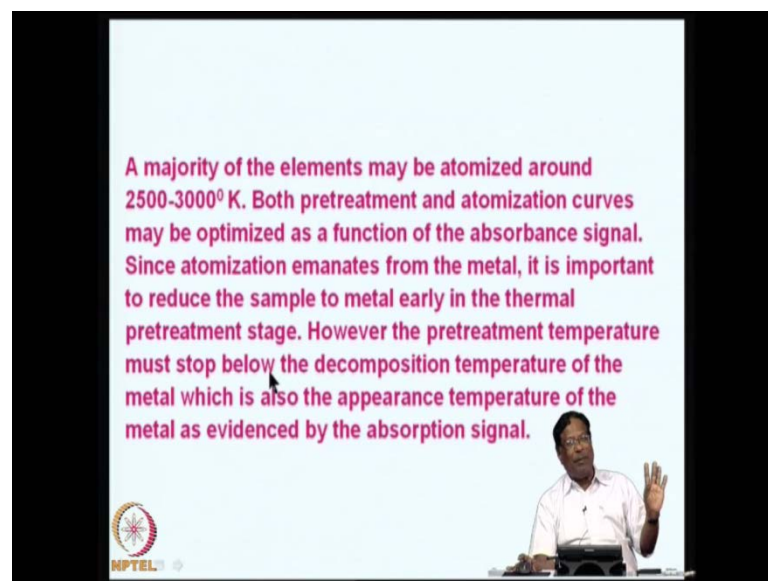
Nowadays, there are even machines available for dilution, automatic dilution. You take 10 micro liter and then dilute it to 1 ml that is 100 times dilution. Dilute it to 10 ml using the same capillary; that means, you will come to from 1000 P P M to 10 P P M straight away in one shot. And then you do repeat the operation with the same capillary again take 10 and then dilute to 100 1000 10 ml, again you will have you will straight away come to P P B level. So, that kind of machines are also been designed only after this automatic systems have been introduced. They are all available in the market where dilution can be very easily achieved with minimum errors.

So, how do we go about the graphite furnace technique, what is the methodology? The methodology is very simple, what we do is with the electro thermal atomic absorption;

we know it permits the analysis of liquids and solid samples. Solid samples also you can inject straight away into the graphite tube provided, you are able to introduce in a reproducible manner. For example, very fine solids like milk powder, you can straight away introduce using metal capillary piston syringes, such systems are available. You can introduce microgram of the sample itself. So, all you need is a microgram weighing balance. So, a known volume leaving that apart a known volume of or weight quantity of the sample is deposited on to the platform or directly into the tube where it is subjected to a series of step wise temperature programs culminating in the final rapid increase in temperature during atomization. That is the methodology.

So, usually pretreatment steps are aimed at separating the concomitants like; what I had explained to you about water, acids and other metallic salts, inorganic salts, organic salts like that. So, the inert atmosphere enhances the reducing properties of carbon leading to better atomization. So, a majority of the elements may be atomized around 2000 to 3000 degree centigrade including refractory elements maximum 3000. But if you operate it at 3000, there are more chances that graphite tube will deteriorate much faster within hundred firings the whole graphite tube will crack again there is a requirement for replacement. Both pretreatment and atomization curves should be optimized as a function of the absorbance signal.

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A majority of the elements may be atomized around 2500-3000° K. Both pretreatment and atomization curves may be optimized as a function of the absorbance signal. Since atomization emanates from the metal, it is important to reduce the sample to metal early in the thermal pretreatment stage. However the pretreatment temperature must stop below the decomposition temperature of the metal which is also the appearance temperature of the metal as evidenced by the absorption signal.

So, what I would like to impress upon you is that we have optimize for each type of sample, what should be the optimum drying, time drying temperature, pretreatment temperature, depending upon the matrix. So, there is always a certain amount of flexibility in incorporated during programming, in graphite furnace. In flame there is no flexibility, you just have to have the sample and fire it, there is no way to remove all these interferences. So, it is important to reduce the sample to metal early in the thermal pretreatment stage itself.

However, the pretreatment temperature must stop below the decomposition temperature of the metal. Pretreatment once the metal starts coming, you still cannot be doing pretreatment to remove concomitants. So, it must stop before you go for atomization. So, this is very important, this is where standardization with respect to every matrix is required. So, where is the drawing line, where do you draw a line? This is the end of pretreatment; this is the start of atomization. So, you should have two research programs; one for pretreatment, until you get you keep on increasing the temperature until you get the maximum signal and the moment the signal stops drying, drops slowly that is the your pretreatment limit.

Similarly, now that you have fixed the pretreatment until you get the maximum signal. Now, the same thing you can reproduce you can repeat by increasing the atomization temperature instead of 2100, you can try atomization at 2200. Suppose, you get the atomization at 2200 try it at 2300 at some stage it will start decreasing. But what is important is the requirement of heating temperature should be minimum during atomization. Not 2200 in if you have a choice of 2200 to 2400 you would rather fix the atomization temperature to 2200 to prolong the life of the this thing. So, pretreatment temperature should be highest, atomization temperature should be lowest. So, the pretreatment temperature should stop below the decomposition temperature of the metal which is also the appearance temperature of the metal as evidence by the absorption signal. So, we will continue our discussion in our next class.