

Trace and ultra trace analysis of metals Using atomic absorption spectrometry

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Lecture – 32

GF AAS Interferences II

So, continuing our discussion on the temperature control. In electro thermal atomic absorption it is possible to heat that tube and hence the sample because, you put the sample inside the tube.

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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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So, we can heat it at a controlled rate in a series of stepwise increments. This is the beauty of electronics. This permit is the removal of unnecessary matrix components in the predetermined manner. So, it is possible suppose, you heat it to 100 degree centigrade nor 90 degree centigrade, within 1 second; that means, heating time is 1 second temperature is reached at 90 degree centigrade and then you can hold it up to for about 1 min, 1 second, 2 seconds, 3 seconds like that because you are handling microlitre quantities of the sample here ok.

So, I can heat it to 90 degrees within 1 second. And then raise it to 120 degrees at 2 degree centigrade per second; that means, from 90 to 120 degrees I can heat it at 15 seconds. So, within that time, I can I am the sample gets evaporated the all the moisture we will go. And I can hold it for 10 seconds to remove the remaining water. This is only

one example of how I can control the heating for different chemical removal, the one is water another is organic substances organic solvents etcetera. Similarly other temperature programs may be incorporated to remove organic matter, I can heat it to about 400 degree centigrade.

Suppose I am analyzing an organic compound like milk powder. So, milk powder mostly to will be organic material only lactose carbohydrates proteins etcetera. So, I can put that side dissolve it and put that sample in the graphite tube, heat it to 90 degrees and then all the water we will go. Whatever remains is organic matter around 120 degrees 92 and 20 degrees then I heat it to 400 degrees. Then what happens most of the carbon material protein and other tissue materials etcetera, they will burn off, they form vapor or burn off and then that will be swept away because I keep the organic argon flow constant; that means, a while heating I am keeping the argon flow. So, whatever comes out of the system inside the tube should be swept away.

So, I can heat it to 800 degrees, afterwards maybe 900 degrees. Then what happens? All other inorganic salts also like chlorides sulphates etcetera, they decompose and then chloride we will chlorine we will go away around 900, 800 degrees sodium chloride itself we will melt around one 800 degrees. So, any sample containing sodium and chloride we will go. So, if you want to analyze urine lot of sodium chloride we will be there right. One percent sodium chloride we will be there in almost every bodies urine, and then you can if I want to analyze some elements in seawater there 3.5 percent of chloride is there, sodium chloride is there.

So, I hold it to 800 degree centigrade, most of the sodium chloride we will go away. So, 1000 degrees most of the sulphate we will go away. So, the organic matter, inorganic matter and the salts and etcetera, and all other concomitants are removed by temperature programming. And only made suppose I heat it to around 1000 degrees, everything is gone, what remains? What remains is only metallic elements maybe there oxides. And the oxides get reduced to metal because of the carbon atmosphere. So, for the atomization a maximum heating rate we require, because after 1000 degrees nothing is left. Nothing organic is left. At that time I increase the heating rate to grow very fast to 3000 degree centigrade, 2000 degrees.

So, for the atomization, maximum heating rate is required; that means, ramping. So, within is here I had give mentioned that 2 degree heating rate per second. Here I heat from 1000 to 2500 in 1 second or 0 second; that means, maximum heating. So, then what happens? All the material that is present we will atomized. And the pretreatments such pretreatment procedures can be standardized for each and every matrix. For food, for blood, for metals, for environment samples, for all these things these pre treatment methods can be standardized, depending upon what they want to work with. And then in the preliminary experiments, before we can do the standardization before optimizing the temperature program.

So, what is a temperature program in graphite furnace is to a remove the concomitants. Concomitants means, other matrix elements that are present along with the sample without our intervention; that means, a plant extract we will have salt. So, organic substances etcetera all those things are called as concomitants.

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III THE STABILIZED TEMPERATURE PLATFORM CONCEPT

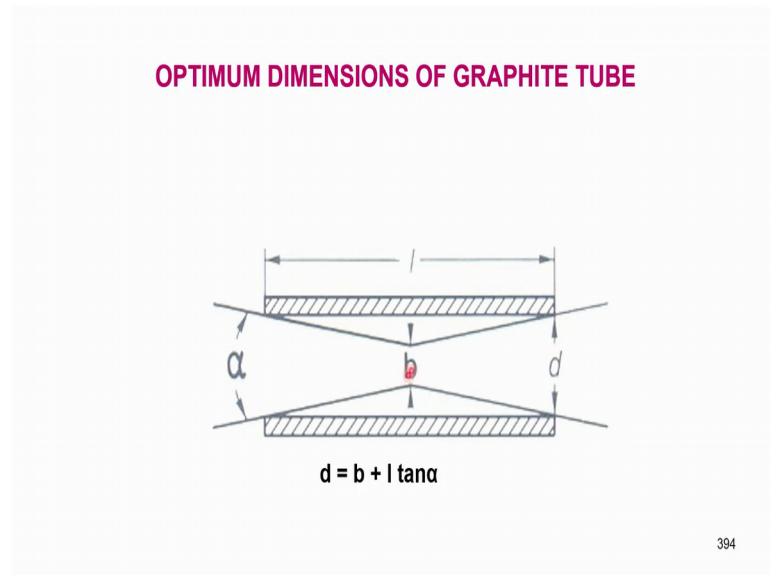
It has already been mentioned that the detection limits in L'vov furnace are 2-3 orders of magnitude higher than the Massmann design. This is because the sample after vaporization is not in equilibrium with volume or time and temperature. Sturgeon and Chakrabarty found that 60% of the atoms formed diffused 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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So, this already temperature programming has given rise to a sort of analytical concept, that is known as stabilized temperature platform concept. So, what you are doing is, because it has the detection limits of L'vov furnace are 2 to 3 orders of magnitude higher than the massmann design, because the sample after vaporization is not in equilibrium with the volume time of the volume or time or temperature.

So, the sturgeon and chakrabarty found that 60 percent of the atoms formed diffused to the cooler ends of the graphite tube, which was around 1500 degrees compared to the middle temperature of about 2000 degrees. If you go to massmann design you will see that the 2 ends of the yes.

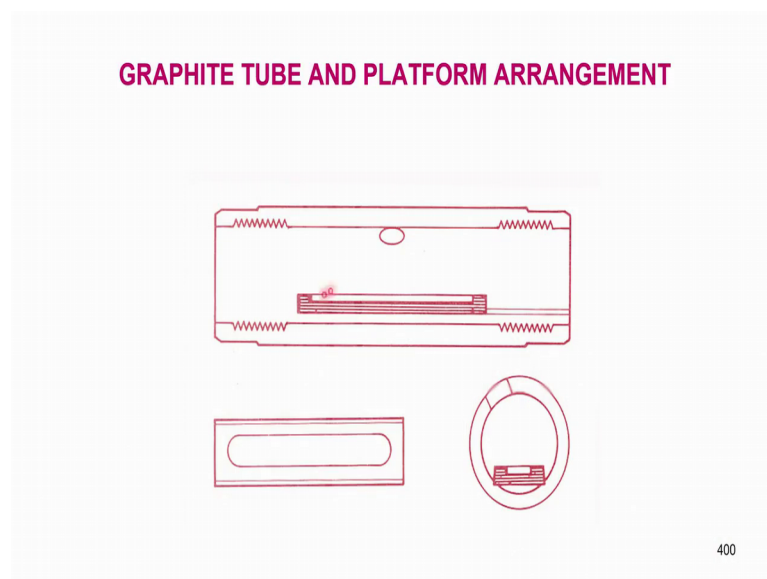
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This is the massmann design, if it is 2500 degrees in the range b here it will be 1500 near the edges. So, this is what chakrabarty found out, and this was not attainable because we want uniform temperature throughout the tube.

So, equilibrium which time is more difficult to achieve, but even then. So, this has given rise to the graphite tube and platform arrangement. What they did another improvement in the graphite furnace is they put a platform inside the tube. Around tube you put a insert a small graphite plate inside that make a groove and then inserted.

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So, that the plate is inserted it does not touch the bottom, it does not touch the sides it will take only the sides, but it can be it will be almost hanging in between; that means, I make a small groove here and then inserted this platform, and this is the whole through which the sample is put. So, I take a micropipette put the sample here on this platform instead of the graphite tube, if I do not put the graphite platform I will be putting it on the tube, and then the tube you will be heated more here and less here at the edges.

So, this problem is avoided because this platform is uniformly heated, because it is not in kids in contact only with the sides of the graphite tube. So, this is how it looks the inserted graphite tube. So, that the sample can be put here on this graphite tube, and this temperature is more uniform so it is called as stabilized temperature platform concept.

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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.

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STPF so, L'vov proposed that the sample must be dispensed on a loosely fitted pyrolytic graphite platform. They what is said is do not take the graphite tube which is pyrolytic, but make the pyrolytic platform also. The platform is a small 3 by 5 mm a graphite plate inserted into the tube ok.

So, he said even that platform you have to make it pyrolytic; that means, coat a carbon layer in permeable carbon later that is pyrolytic platform. What he said is coat that also with the carbon and that we will be heated only by the radiation and not by the direct contact. So, radiation heated material we will be heated uniformly instead of contact. So, such an arrangement does not permit heat conduction at right. Angles to the plane of graphitization. So, such an arrangement in temperature follows the tube temperature rather sluggishly, which permit is better equilibrium conditions because the tube gets heated fast, but platform gets heated slowly, so when the tube is at maximum this will slowly heat up to the temperature.

So, they there is a certain amount of delay in which the platform gets heated, and the platform is under equilibrium condition. So, such a system has been proved that interferences are very low.

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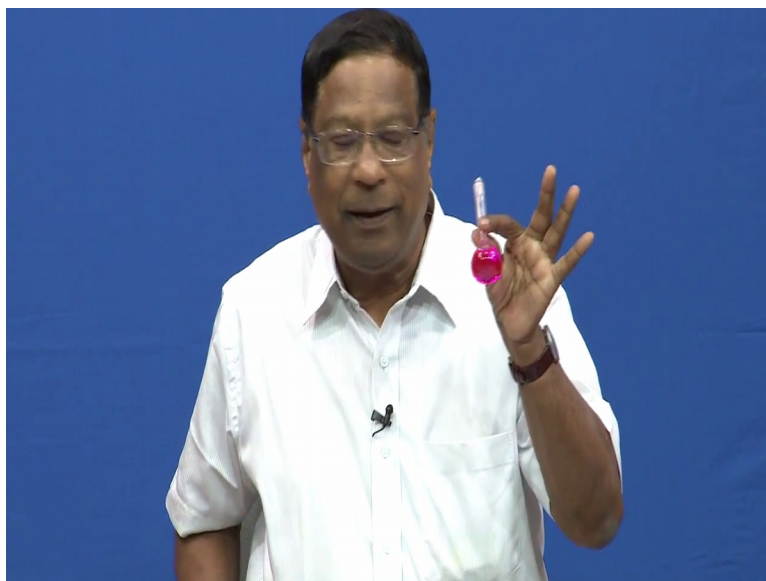
AUTOMATION

In graphite furnace the sample to be handled is rather small (5-100µl) 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%.

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So, this is the wonderful concept. And another concept, that is in graphite furnace technology is automation. So, what is required is the in graphite tube the sample must be invited through a micropipette every time we have to do analysis (Refer Time: 11:59) to your sample is in a bottle or like tube like this. Your time a sample is in a tube like this you have to open it put your micropipette suck the sample put it in the graphite tube.

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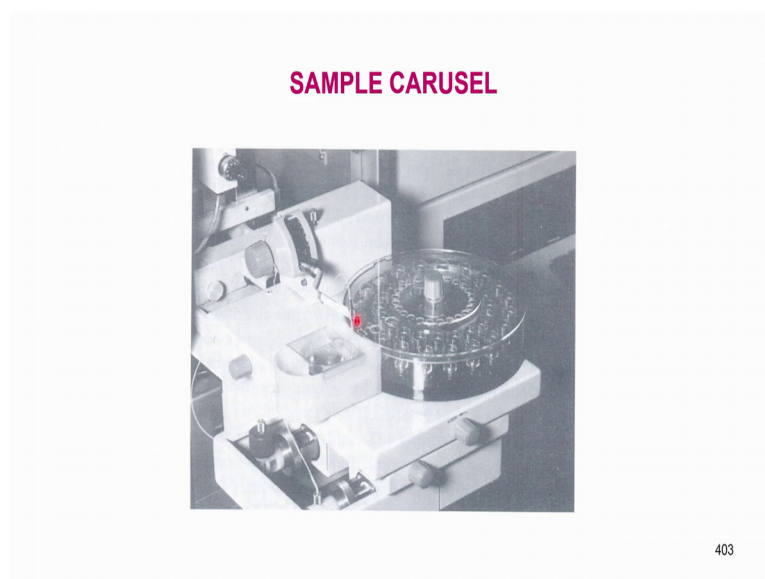
And the graphite tube then you close the massmann top cover and then do the heat temperature programming and heat it.

So, there is a certain amount of operator skill required because, the diameter of the tube in which the sample is put is about 1 mm. So, the micro tip should enter there so, to discharge the sample. So, what people did is they had a certain amount of difference in the sample delivery, even if it is of the order of 1 or 2 percent in the micropipettes. So, the sample to be handled is rather small 5 to 100 microlitre, but the sensitivity is rather high. The sample has to be introduced exactly in the same place that happened that is possible if you can put the sample on the platform. So, every time you are to insert it through the sample on to the graphite there is also the risk of sample contamination with the graphite hole edges. And pipette tips can get contaminated all these factors lead to poor precision with manual pipetting; that means, every time you do a manual this thing they are open to some sort of, some sort of interference or contamination.

So, moreover micropipette using taking sample putting it and then again analyzing doing this that etcetera it is cumbersome. So, what people thought is why not I design a carousel in which the sample is picked up and then a robotic arm can pick it up, take it there put it insert it into the graphite tube come back. And by the time it comes back at the carousel we will rotate another sample we will be ready for pickup. So, that kind of programming can be done that is known as automatic pipetting. So, this automatic pipetting concept is very new and now a days of course, it is being employed for all kinds of samples including spectrophotometry, gas chromatography, HPLC etcetera, but it all started with graphite furnace technology.

So, this was around 1970s. And several programmable automatic dispensing unit is available now. And the tubes need to be made of teflon. And then they are available in the market and also they offer a standard accessory in graphite furnaces. So, the reproducibility with automatic dispenser is about one percent with an RSD of 0.4 percent compared with 5 percent is the reproducibility in manual pipetting; that means, 5 percent error is there for micropipette have which are handled by a person, but a RSD is about 3.2 percent. What is RSD? Relative standard deviation of the delivery of the sample ok.

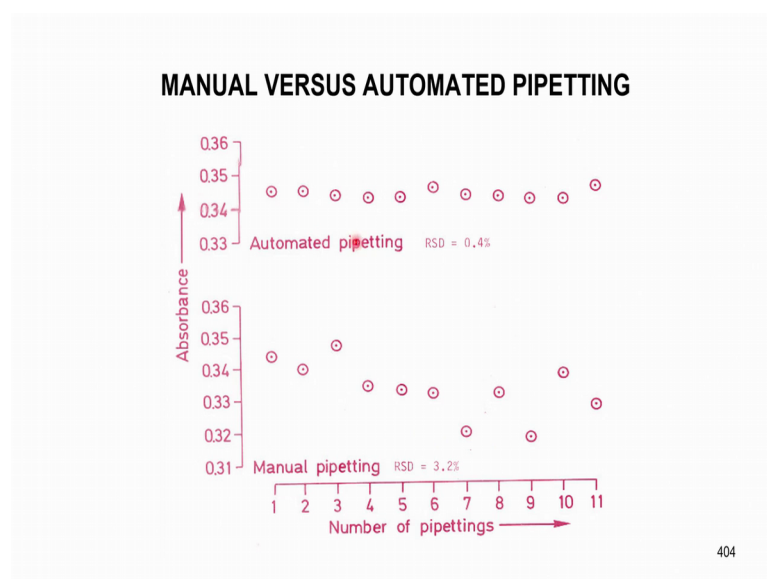
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For that is micro pipetting quantity. So, this is how the sample carousel looks, here you can see this is the robotic arm. Here you can see this is there is a teflon tube here and the robotic arm is here. Graphite tube we will be somewhere here inside on the optical path. So, this robotic arm we will come here, they come here pick up the sample rotate and deliver the sample there, comes back and here once it is in it is. So, (Refer time: 16:14) it a original place there will be water flushing. And this flashed water helps to clean up the tube. And then again when it is ready the robotic arm we lift and move into some other position and pick up the sample and read do the analysis; that means, hole auto operation of atomic absorption can be automated without any human interruption. The if I have prepare if all I have to is prepare all the samples to be put in these holes and then go for coffee or lunch or something and come back. By the time you come back when everything is automated or should be it would be ready for the interpretation.

So, the whole of atomic absorption process can be automated using this kind of samples.

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So, this is the difference between manual versus automated pipetting. So, you can see that I have plotted absorbance here and this is the I have taken. So, some sample and plotted the absorbance through the automatic pipetting that is through the carousel. And here I have done it manually. So, you can see that 99 percent of most of the time my reading CRR between 0.34 and 0.35. That is a absorbent seconds, but all of them are between 0.34 and 0.35, correct? So, but here if I do the same manual pipetting I have 0.34 3 4 here 3 4. And then some are here around 0.32.

Some of them are 0.35, and then some of them are somewhere here. But the spread is 0.318 or something like that they are also there. So, if I do ten determinations repeat samples of the same analysis, if I do it with automatic machine carousel. I always end up with between 0.34 and 0.35 whereas, with this I end up with 0.35 and 0.34 not only that, but I also get a reading of 0.32, 0.31, 0.33 you know. So, many differences, that is with a skilled person.

If a person is not skilled this can be even go up to 0.31 to 0.36, in that case you do not know where is the correct sample delivery. What is this thing?

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METHODOLOGY OF GRAPHITE FURNACE TECHNIQUE

The ETAAS permits the analysis of liquid and solid samples. A known volume or weighed quantity of the sample is deposited on to the platform or directly in the tube where it is subjected to a series of stepwise temperature programmes culminating in final rapid increase in temperature for atomization. Usually pretreatment steps are aimed at separating the concomitants or the matrix components as much as possible. The inert atmosphere enhances the reducing properties of carbon leading to better atomization.

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So, this brings us to the methodology of graphite furnace technique. So, how we go about doing the chemical analysis using graphite furnace atomic absorption. The electro thermal atomic absorption spectrometry permits the analysis of both liquid and solid samples. A known on volume of the weight quantity you have to take. The sample is dissolve it in a non volume and then deposit on to the platform or directly on to the tube both methods are available in the market, platform is better and if you do not have platform you can deposit on the a tube itself. And then it is subjected to a series of stepwise temperature programs; that means, heat it to 90 degrees remove water heat it to 120 degrees.

Remove some organic solvents, heat it to 400 or 500 degree centigrade to remove other organic compounds. And then finally heat it or around the 800 to 1000 degree centigrade to ah, convert all these chlorides and sulphates etcetera. To remove them from the sample matrix and in the finally, we make a rapid heating in temperature to 2500 degrees for atomization.

So, usually pretreatment steps are aimed at separating the concomitants or the matrix components as much as possible. So, the inert atmosphere enhances the reducing properties of carbon leading to better atomization ok.

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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.

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So, a majority of the elements of the periodic table may be atomized around 2500 to 3000 degree Kelvin. When you are talking about 2500 3 and 1000 degrees Kelvin or centigrade does not matter, but you can this is the normal practice whenever we talk of 2500 or higher range we talk of Kelvin. So, both pretreatment and atomization curves may be optimized as a function of the absorbance signal.

So, what we have been saying is, pretreatment, curve and atomization curve we can optimize to get the maximum signal. Since the atomization emanates from the metal there is no need to measure the absorbance during pretreatment. It is so it is important to reduce the sample to metal early in the thermal pretreatment stage. Before atomization get it reduced; however, the pretreatments temperature must follow it must be below the decomposition temperature of the metal; that means, it should not melt or something like that, which is also the appearance temperature of the metal as evidenced by the absorption signal. So, basically what we are trying to do is, we are converting the heating program into 2 parts. One is to remove the concomitances the other is to atomize. So, the appearance temperature of the metal should be should be optimum.

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Campbell and Ottaway have postulated a reduction mechanism for many metals in ETAAS.



They calculated the free energy for the corresponding reaction and compared the values thermodynamically with the appearance temperatures and found good agreement.

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That means pretreatment temperature should be very high, and appearance temperature should be very low.

So, Campbell and Ottaway have postulated a reduction mechanism for many metals in electro thermal atomic absorption. So, what we have here metal after all they concomitance are removed metal oxide for is there that we will react with the carbon to form the metal and giving you carbon monoxide. So, they calculator for this reaction they calculated the free energy for the corresponding this reaction and compared the values thermodynamically with the appearance temperatures and they found good agreement; that means, this reaction is one of the most important reaction in the third electro thermal atomization.

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Sturgeon and chakrabarty investigated atomization mechanisms on the basis of a thermodynamic/kinetic approach and proposed four mechanisms.

1) $\text{MO}_{(s)} \xrightarrow{\text{C}} \text{M}_{(l)} \rightleftharpoons 1/2 \text{M}_2(\text{g}) \rightleftharpoons \text{Mg}$

where M = Co, Cr, Cu, Fe, Mo, Ni, Pb, Sn, V

2) $\text{MO}_{x(s)} \xrightarrow{\text{T}} \text{M}_{(g)} + x/2 \text{O}_2(\text{g})$

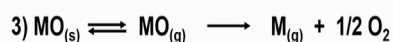
where M = Al, Cd, Zn, Si



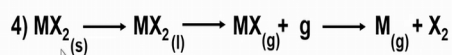
So, sturgeon and chakrabarty again the investigated atomization mechanism. How they get atomized on the basis of thermodynamic as well as kinetic approach. And they propose 4 mechanisms. What are the mechanisms? I have a metal oxide in the solid form and that reacts with the carbon to give material. And then the metal is converted into gaseous form and then it is metal in the gaseous form.

So, M can be cobalt, chromium, copper, iron, molybdenum, nickel and lead, tin and vanadium. Another mechanism what they said he suppose I have MO_x that is a variable form of oxides M_2O_3 or something like that. And then when I heat it the solid compound goes to material and releases oxygen, here there is no release of oxygen. But it forms carbon monoxide. Here it is releasing the oxygen. So, this kind of mechanism is prevalent for samples containing aluminium, cadmium, zinc, and silicon. So, different mechanisms they have studied and I think it is good for us to know what are the different kinds of ways in which metal is generated inside the graphite tube on the platform or on the graphite tube surface ok.

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where M = Cd, Mg, Mn, Zn



where M = Cd, Fe, Zn

Mechanisms 1 & 2 require intimate contact with graphite surface but decomposition of oxides and halides occur in the vapour stage and hence are largely temperature dependent.

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So, the third one is, metal oxide we have. It forms metal oxide gas straight away. And then that gets reduced to metal and then oxygen is released. This kind of mechanism is prevalent for cadmium, magnesium, manganese and zinc. Another one is suppose I take a chloride halogen salt, chloride bromides iodide etcetera, fluorides what I have is, MX₂ that is calcium chloride, magnesium chloride, copper chloride COCl₂ like that. And then that is a reminds a solid when I will finish when I am finished with a pretreatment temperature of about 800 degrees. And then that is all it we will melt forming MX₂ liquid and then it gets converted to MX gas. And then later on it will get reduced to metal, and then that is x₂. And then here M could metal could be cadmium, iron and zinc.

So, mechanisms 1 and 2 here, 1 and 2 are they require intimate contact with the graphite surface, but here it is only the conversion of solid into gas in third and fourth. So, the decomposition of oxides and halides occur in the vapour stage. It is not in the liquid stage and they may these mechanisms 3 and 4. So, they are these tempera these reactions which one the number 3 and number 4 above are largely temperature dependent because vaporized to decompose. It has nothing to do with the carbon contact with the graphite carbon of the graphite ok.

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Frech and Pearson have investigated the determination of phosphorous in a graphite furnace. It has been proved that PO (g) , $\text{PO}_2(\text{g})$ are present at 1800 K, so that substantial losses must be expected at lower pretreatment temperature. Non-coated graphite tubes are sufficiently reactive to reduce partial pressure of oxygen which will also reduce phosphorous losses. It has also been shown that from the retained water methinophosphide (HCP (g)) is formed. To prevent this, atomization from pyrolytic graphite is carried out.

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So, Frech and Pearson I have also investigated the determination of phosphorus in a graphite furnace. It has been proved that phosphorus oxide, phosphorus dioxide etcetera are present around 1800 degree Kelvin.

So, that substantial losses must be expected at lower pretreatment temperatures compare to metals. So, non coated graphite tubes are sufficiently reactive to reduce the partial pressure; that means, you need not go for pyrolytic carbon atom, pyrolytic carbon platform. You can it even with ordinary carbon tubes and that we will also reduce the phosphorus losses, because you can work at lower temperature. It has been shown that the from the retained water methinophosphides gasses formed to prevent these what we do is atomization from pyrolytic graphite is preferred and carried out.

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SPECTRAL INTERFERENCES IN ETAAS

Genuine spectral interferences are as rare in graphite furnace as in the flame technique. However background attenuation due to absorption of molecular bands of volatilized concomitants and radiation scattering of sample particles are quite frequent. Interferences also occur by the interaction of the analyte element and the condensed and vapour phases. Thus molecular absorption by alkali halides and radiation scattering are two important interferences because the concentration of the concomitants is more than 4-5 orders magnitude than the analyte element in most cases. While molecular absorption is reproducible, radiation scattering can vary from sample to sample but it follows molecular absorption. This is attributed to molecules migrating to cooler ends.

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So, now these are the discussions about atomic absorption using electro thermal heating. Now we will discuss a little about spectral interference in electro thermal atomic absorption. The point is genuine spectral interferences are as rare in graphite furnace as flame, because it has nothing to do with the sample right. Electro thermal spectral interference means the resonance line must match. It is it will match whether whatever is the form of vaporization or atomization new employee it has nothing to do. If the spectral interferences I have there for any element in flame the same spectral interference you will encounter in the graphite furnace also ok.

So, but the background attenuation to absorption of the molecular bands like nitrogen carbon CO and amino groups. So, those molecular bands are continuous in the flame during measurement, but here in electro thermal atomization, we treat them and remove them. So, the spectral interference from the molecular bands corresponding to resonance lines are reduced in graphite furnace. I think you should listen to this again and again. What I had told you and try to understand what I am planning to what I am meaning to say. So, spectral interferences from the molecular bands are minimum. So, interferences also occur, but by the interaction of the analyte element and condensed vapour phase ok.

So, molecular absorption by alkali halides and radiation scattering are 2 important interferences, because the concentration of the concomitant is more than 4 to 5 orders

of magnitude then the analyte element. In most cases you ponder over this sentence some more what we mean to say is, the scattering of radiation is more important and the background is higher. So, the background concentration or background M optical data is 4 to 5 orders of magnitude then the analyte element only in most cases. So, while medium absorption is reproducible, radiation scattering can be from can vary from sample to sample that is understood. But it follows molecular absorption, this what I have been trying to tell you throughout this slide presentation.

So, this the attributed to molecular molecules migrating to cooler ends. Only when they migrate to cooler ends they do not get removed so easily ok.

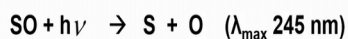
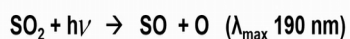
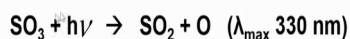
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Molecular spectra may be classified into dissociation continuum and broad band electronic spectra. Long wavelength maxima correspond to the dissociation of molecules into neutral atoms while the short wavelength maxima are attributed to the dissociation into the excited atoms. While the broad band spectra may be due to CN, OH, NH₂ bands, the dissociation spectra always exhibits sharp maxima as in the case of sulphite ions.

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So, molecular spectra may be classified into dissociation continuum and broadband electronic spectra. So, the long wavelength maxima correspond to the dissociation of molecules, into neutral atoms. While the short wavelength maxima are attributed to dissociation into the excited atoms. So, the broadband spectra may be due to cyanogen OH and NH₂ bands. The dissociation spectra always exhibit is a sharp maxima as in the case of sulphite ions, if it is sulphite ions you will see a sharp maxima.

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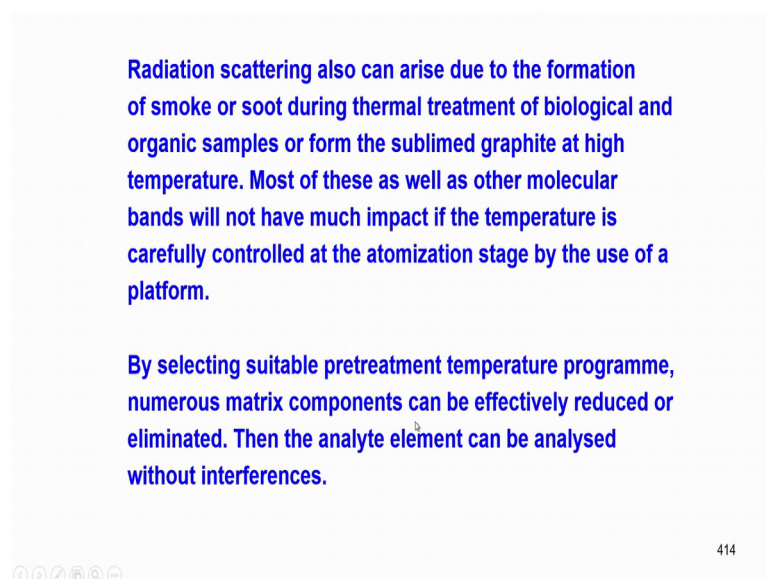
Similarly nitrogen containing molecular bands exhibit λ_{max} at 430 and 470 nm which also contribute to the background absorbance.

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So, these are the problems with sulphite, sulphite we will react with electromagnetic radiation. Whatever is the radiation coming from hollow cathode lamp and then they it reduces to sulphur dioxide and oxygen. And then sulf this can also form sulphur oxides or it can form sulfides, but the lambda max sharp peaks we will get 330, 190 to 45 etcetera.

Similarly, nitrogen containing molecular bands NH₂ groups, exhibit lambda max at 430 and 470 nanometer they also contribute to the background absorbance. You remember that in all atomic absorption backgrounds absorbance must be subtracted from the sample, to get the true analyses ok.

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Radiation scattering also can arise due to the formation of smoke or soot during thermal treatment of biological and organic samples or from the sublimed graphite at high temperature. Most of these as well as other molecular bands will not have much impact if the temperature is carefully controlled at the atomization stage by the use of a platform.

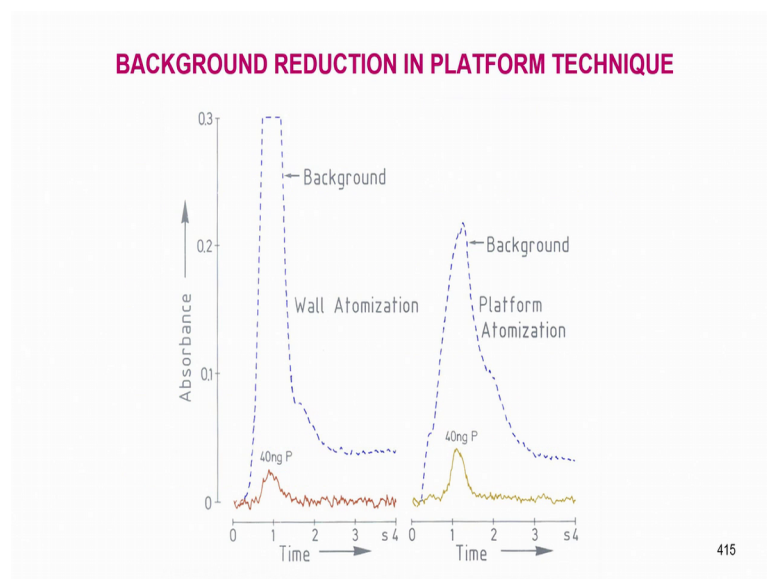
By selecting suitable pretreatment temperature programme, numerous matrix components can be effectively reduced or eliminated. Then the analyte element can be analysed without interferences.

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So, radiation scattering also can arise due to the formation of smoke or soot. During thermal pretreatment of the biological and organic samples or from the sublimed graphite at high temperature. Sometimes graphite also gets sublimed at high temperature. Most of these as well as other molecular bands will not have much impact if the temperature is carefully controlled by the STPF that is stabilized temperature platform concept and then it is carefully controlled at the atomization stage itself. Then there should not be any problem, but we should be aware of the interferences of this kind.

So, by selecting suitable pretreatment temperature programme numerous matrix components can be effectively reduced or eliminated. Then the analyte element can be analyzed without any interferences, analyte element can be analyzed without any interference, because we have removed most of the matrix components out of the system by pretreatment.

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Now this is how the background reduction in platform technique occurs. Look at this the I am trying to determine 40 nano grams of phosphorus. This is the signal peak 40 in this thing, but if I plot the background also you can see the background is So high it crosses c 1.3 absorbance whereas, the sample 40 nano grams of phosphorus is less than 0.01 absorbance here. For 0.01 absorbance a background is 0.3.

So, 0.3 minus the sample should be 0.3 plus 0.1, 0.31 out of 0.31 I am subtracting 0.3 background absorbance. So, this is occurs due to background and wall atomization. And if I do STPF my background is only about 0.25. Instead of 0.3, and signal is also for the same 40 is approximately about 0.04, 0.04 or 0.05 whereas, in this case it is just 0.01 or 0.02. So, this is how the platform stabilized platform concept helps. It removes the background too large extent as well as 40 nanogram sample is enhanced. So, you can imagine that the background is always he should higher than the sample signal, but it can be subtracted from the sample plus background.

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If the analyte element is also volatile, a low temperature atomization must be considered even though it leads to lower sensitivity, but the matrix components would not volatilize. Thus cadmium can be determined in presence of 2% sodium chloride at 750° C where NaCl does not volatilize.

When the volatilities of the matrix and analyte are similar thermal pretreatment alone can not guarantee satisfactory separation of the element. In such cases, phosphoric acid and nitric acid may be employed as 'ashing additive' for biological and organic samples.

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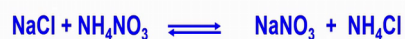
So, if the analyte element is also volatile, then what happens? A low temperature atomization must be considered because an element moves out of the system, because it is more volatile. So, we should ash it at lower temperature and then allow it to remain in the graphite tube for longer time. So, lower temperature is better, but the matrix components you will not be able to remove, because you are atomizing itself at lower temperature. So, the cadmium for example, it can be determined in presence of 2 percent sodium chloride at 750 degree centigrade whereas, sodium chloride does not volatilize. So, if you use some of the tricks that we employ depending upon the analysis and the sample matrix. So, when the volatilities of the matrix and analyte are similar thermal pretreatment alone cannot guarantee satisfactory separation. This is the very important point; that means, when the sample volatility of the analyte as well as matrix are similar. Then you have to do the typical normal background correction.

In such cases, what we can do is we can add a little bit of phosphoric acid and nitric acid to the sample that helps in ashing the biological and organic samples, to remove the volatility of the matrix by forming phosphates and nitrates. They are much more easily removed than the chlorides and sulphates. So, if there is a problem of equal volatility is there is a problem of equal volatility. Consider addition of phosphoric acid and nitric acid to remove the more volatile components than the analyte.

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Ammonium nitrate has also been routinely used to increase the volatility of the matrix and simultaneously reduce that of the element.

The most probable reaction is:



Both reaction products can be easily decomposed or sublimed around 400° C. Thus background attenuation may be considerably reduced if not eliminated by the use of matrix modification.

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So, ammonium nitrate people have tried, routinely to increase the volatility of the matrix and simultaneously reduce the element. So, what is the reaction in such cases. The reaction is sodium chloride we will react with ammonium nitrate simply it will form sodium nitrate, which is easily decomposing at around 400 degrees. It can be sublimed also it can be decomposed also. Sodium nitrite both these reactions both the reaction products are removed at 400 degrees instead of if you are taken sodium chloride alone, you would have needed 800 degrees. Whereas, if you just add a little bit of ammonium nitrate both these products can be removed at 400 degree only.

So, these are the typical chemical considerations that are required in atomic absorption measurement of typical elements. This is where the chemistry knowledge comes in useful than the instrument operation. So, at least the background can be considerably reduced, if not totally eliminated by the use of matrix modification. This is what we call matrix modification that is to the sample we are adding a modifier of the matrix is ammonium nitrate is a matrix modifier we call it matrix modifier.

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The use of other gases such as hydrogen as the purge gas reduces the spectral interferences in the determination of chromium in urine. Similarly background signals for NaCl and CaO could be substantially reduced if the graphite tube was flushed with hydrogen for 10 seconds before atomization.

Solvent extraction and electrolytic deposition techniques may also be used to remove matrix components, but such steps need extreme precaution to prevent contamination by external sources.

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And we will discuss little bit more about matrix modifier in our next class.