Trace and ultra trace analysis of metals Using atomic absorption spectrometry

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Lecture - 34
Individual Elements AAS

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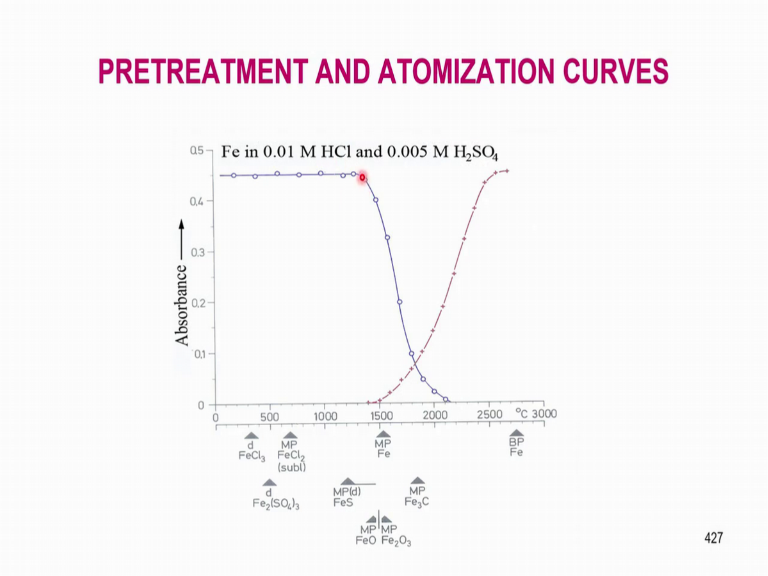
PRETREATMENT AND ATOMIZATION CURVES

So, for iron optimum temperature, pretreatment temperature is around 1500 and atomization temperature is around 2500. Similarly we are tried with antimony. Antimony again I have a slightly increased signal here, but for a known sample I can safely determine antimony up to pre do the pretreatment up to 1000 degree centigrade without losing any antimony, but if I preterit at a higher temperature it will reduce. And I will be losing most of the antimony by about 1500 or 1800 degree centigrade, most of the sample is lost and atomic absorption should not be carried out at all.

But the atomic absorption measurement I get optimum result somewhere around 2500 keeps on increasing but very slightly. If you look at the figure, let us say from about 2300 to 2500 it keeps on increasing because it forms a refractory oxide, so as you increase the temperature it increases. But you can see that the absorbance does not change very much from let us say 0.41 or 42 it increases between 2300 to 2700.

So, since this is not very significant what we can say is we can do the atomic; loose a little bit of sensitivity, but keep the graphite for a tube longer. So, do the atomization only around 2400 degree centigrade that should be ideal. So, this is how the pretreatment and atomization of different elements are carried out.

And that brings us to the end of our discussion about the electrothermal atomization of the sample. And what we want to say further is a very few small points.

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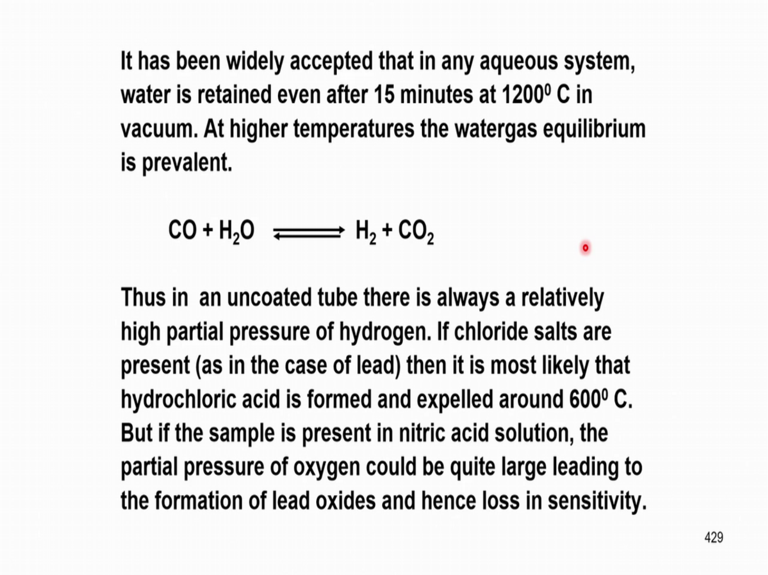

It has been widely accepted that in any aqueous system, water is retained even after 15 minutes at 1200^0 C in vacuum. At higher temperatures the watergas equilibrium is prevalent.

$$CO + H_2O \rightleftharpoons H_2 + CO_2$$

Thus in an uncoated tube there is always a relatively high partial pressure of hydrogen. If chloride salts are present (as in the case of lead) then it is most likely that hydrochloric acid is formed and expelled around 600^0 C. But if the sample is present in nitric acid solution, the partial pressure of oxygen could be quite large leading to the formation of lead oxides and hence loss in sensitivity.

For example, you can see that here in the widely accepted that in any aqueous system water is retained even after 15 minutes at 1200 degree centigrade in vacuum. Some little tip bits I am giving you. So, do not be fooled that water can be removed completely in any given system easily.

So, at higher temperatures what happens is there is water gas equilibrium; carbon monoxide will react with water to give you hydrogen and carbon dioxide. So, in an uncoated tube there is always a relatively high partial pressure of hydrogen also, this can lead to explosion. So, one has to be careful, so you should use a pyrolytic coated graphite furnace. So, suppose there are chloride salts. For example, you want to determine lead in sea water, and then lead also chances are that lead will be present as lead chloride. Then it is most likely that HCL is formed, because whenever lead chloride decomposes into lead and chlorine gas releases, chlorine will react with hydrogen formed by this reaction inside the graphite tube and hydrochloric acid forms. Hydrochloric acid usually attacks the graphite tube. So, it cracks easily. But at lower temperature hydrochloric acid is expelled by about 600 degree centigrade.

So, the idea is you treat it to whenever you have chloride salts treat them around 600 degrees hold them for some time let is say 5 seconds or 10 seconds then go for atomization. So, if the sample is in nitric acid then what you would do, the partial pressure of oxygen could become important at that time. So, there that becomes quietly large, that leads to the formation of lead oxide because oxygen is there lead is there in the gaseous form both of them can react to form lead oxide.

So, again if lead oxide is formed the sensitivity decreases. So, we do not want that. That is why we need the oxygen are gone gas continuously passing through the system only until the atomization step. And during atomization make sure that it is 0; that is gas is not passing through, gas is stopped at that point.

So, if the formation of lead oxide takes place there will definitely be loss in the sensitivity.

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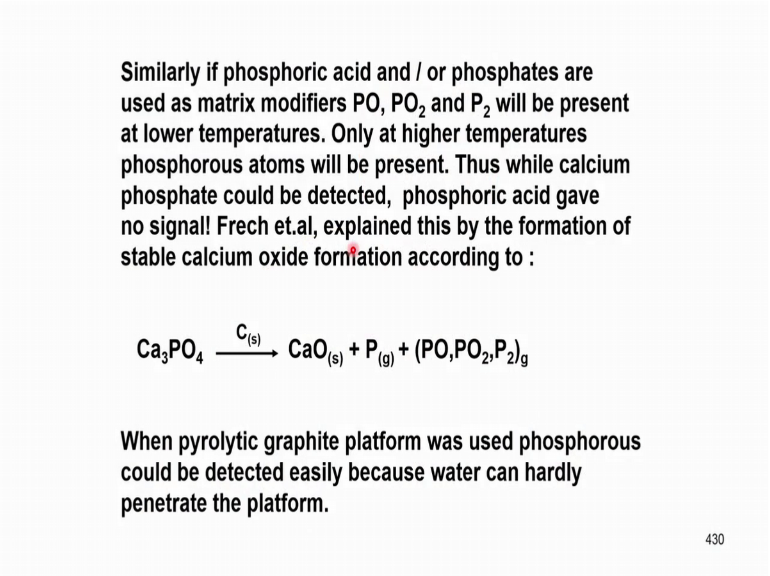

Similarly if phosphoric acid and / or phosphates are used as matrix modifiers PO, PO_2 and P_2 will be present at lower temperatures. Only at higher temperatures phosphorous atoms will be present. Thus while calcium phosphate could be detected, phosphoric acid gave no signal! Frech et.al, explained this by the formation of stable calcium oxide formation according to :

$$Ca_3PO_4 \xrightarrow{C_{(s)}} CaO_{(s)} + P_{(g)} + (PO,PO_2,P_2)_g$$

When pyrolytic graphite platform was used phosphorous could be detected easily because water can hardly penetrate the platform.

Now quite often we treat the samples with phosphoric acid. Or in that case phosphates are formed, no. So, phosphates are used as matrix modifiers quite often. So, phosphorous oxide PO 2 and P 2 will be present at lower temperatures, but only at higher temperature phosphorous atoms will be forming, because all these compounds will decompose. So, while calcium phosphate can be detected; calcium phosphate not phosphorous PO 2 or PO or something.

Calcium phosphate can be detected; phosphoric acid cannot give any signal correct. So, this point has been explained by the formation of stable calcium oxide formation according to this reaction. So, Ca 3 PO 4 reacts with carbon to give a calcium oxide followed by phosphorous gas and then PO PO 2 P 2 all these are in the gaseous form. But so in normal graphite tube this reaction goes, but if you use pyrolytic graphite carbon phosphorus could be detected easily because water can hardly penetrate the top surface of the layer because it is very smooth.

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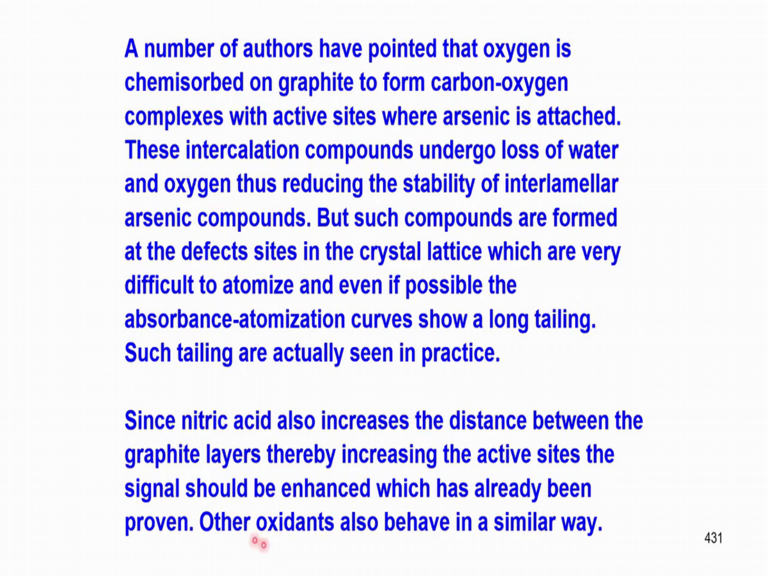

A number of authors have pointed that oxygen is chemisorbed on graphite to form carbon-oxygen complexes with active sites where arsenic is attached. These intercalation compounds undergo loss of water and oxygen thus reducing the stability of interlamellar arsenic compounds. But such compounds are formed at the defects sites in the crystal lattice which are very difficult to atomize and even if possible the absorbance-atomization curves show a long tailing. Such tailing are actually seen in practice.

Since nitric acid also increases the distance between the graphite layers thereby increasing the active sites the signal should be enhanced which has already been proven. Other oxidants also behave in a similar way.

So, these are some of the little tricks we understand, and number of authors also I have pointed out that oxygen is chemisorbed on graphite tube to form carbon oxygen complex with active sides where arsenic is attached. So, they do form some sort of intercalation compounds. They undergo loss of water and oxygen also, but reduce the stability of the interlamellar arsenic compounds.

So, such compounds are formed at the defect sides in the crystal lattice of the graphite’s which are very difficult to atomize they go inside the surface and do not get detected. Even if it is possible to determine the absorbance atomization curves show a long tailing. That means, a tailing curve cannot give you a deciding decision regarding the optimum temperature, because you do not know when to stop. So, such tailings are actually seen in practice for most of the elements such as arsenic.

Another point is, nitric acid also increase the distance between the graphite layers. Usually, if you understand the structure of graphite tube what happens is there is carbon plane in hexagonal shapes and the another carbon is attached to that like that carbon plane is there just like benzene ring, but put in a plane, and above that there is one more carbon plane like this. Now, if nitric acid is there it increases the distance between the two carbon planes it attacks the carbon basically, but the mode of attack is by increasing the carbon layer distance from each layer, from each other.

So, the nitric acid increases the distance between the graphite layers thereby increasing the active sides. So, signal should be enhanced. This is already proven. So, we do like nitric acid in graphite furnace, but again increased distance between the graphite planes leads to quicker destruction of the graphite tube, ok.

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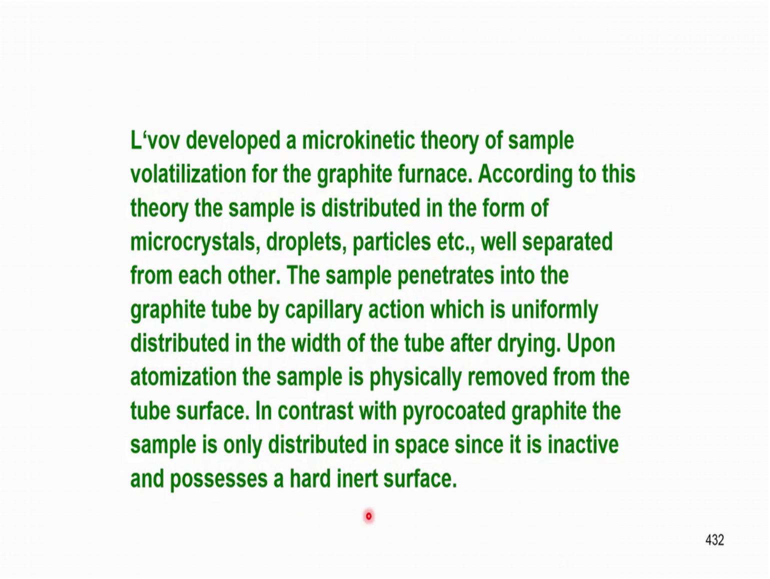

L'vov developed a microkinetic theory of sample volatilization for the graphite furnace. According to this theory the sample is distributed in the form of microcrystals, droplets, particles etc., well separated from each other. The sample penetrates into the graphite tube by capillary action which is uniformly distributed in the width of the tube after drying. Upon atomization the sample is physically removed from the tube surface. In contrast with pyrocoated graphite the sample is only distributed in space since it is inactive and possesses a hard inert surface.

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So, L'vov developed a microkinetic theory of the sample volatilization for graphite furnace. That is another contribution. According to this theory the sample is distributed in the form of microcrystals, droplets, and for particles etcetera. They are well separated from each other. So, the sample penetrates into the graphite tube by capillary action only. This is uniformly distributed in the width of the tube after drying. So, upon atomization the sample is physically removed from the tube surface. In contrast with pyrocoated graphite tube the sample is only distributed in space between the edges of the graphite tube and it is inactive and it possesses a hard inner surface, ok.

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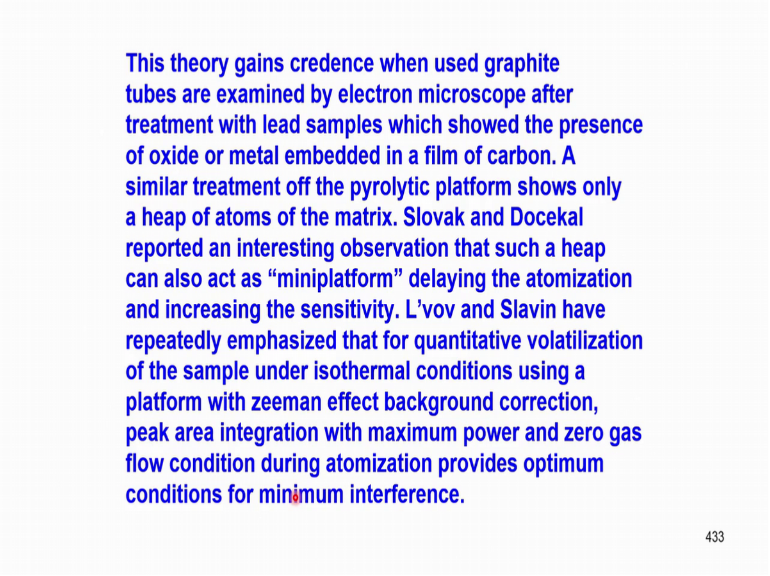

This theory gains credence when used graphite tubes are examined by electron microscope after treatment with lead samples which showed the presence of oxide or metal embedded in a film of carbon. A similar treatment off the pyrolytic platform shows only a heap of atoms of the matrix. Slovak and Docekal reported an interesting observation that such a heap can also act as “miniplatform” delaying the atomization and increasing the sensitivity. L’vov and Slavin have repeatedly emphasized that for quantitative volatilization of the sample under isothermal conditions using a platform with zeeman effect background correction, peak area integration with maximum power and zero gas flow condition during atomization provides optimum conditions for minimum interference.

So, this theory gains credence when used graphite furnaces: we have to examine them by electron microscope. After treatment with lead samples etcetera they show the presence of oxides or metal embedded in the carbon films. So, a similar treatment of the pyrolytic platform shows only a heap of atoms on the matrix.

So, after some time in general most of the graphite tubes become useless, so they become a consumable item in the atomic absorption. After some time they become useless, they will give you tailing they may not give you right signal etcetera, they may develop crack, they will give you enhanced signal because of the memory effect also because all of them they go sit on the surface of the graphite tube. Like that they act as a mini platform, because if I have carbon surface on that I put lot of metal atoms because of this graphite tube it cracks and metals go and sit inside the cracks active surfaces, since it acts as a mini platform for next sample.

So, at that time the memory effects. Previous atoms coated in the previous determinations may also come out. So, that we call it as memory effect, so you may get enhanced signal also. So, this kind of enhance signal is actually wrong. So, your calibration may go haywire because you have to remember that you will be determining only the micro parts per trillion level; parts per million level ppb you will be determining. And parts per trillion will be the detection limit. So, ppt is the detection limit and ppb is the determination limit- 1000 times more.

So, all these things contribute the quantitative volatilization of the sample under isothermal conditions is the best way to handle such things. Because in general if we do this determination without the platform all these things what I have told you will happen. The metals go and sit in the carbon, on the carbon they defuse inside, etcetera. But if we use pyrolytic carbon that effect will be less, but if I use a platform I can simply remove the platform put one more platform. So, platform in a graphite tube always helps in the determination of substances without any contamination.

So, the zeeman effect background correction, peak area integration with maximum power, zero gas flow condition, and during the atomization, and the clean up step they provide the optimum conditions for minimum interference from other elements, ok.

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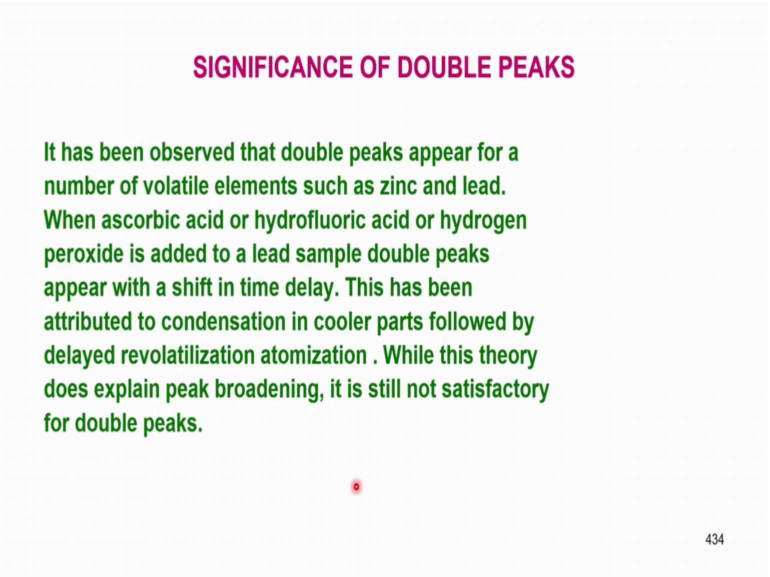

SIGNIFICANCE OF DOUBLE PEAKS

It has been observed that double peaks appear for a number of volatile elements such as zinc and lead. When ascorbic acid or hydrofluoric acid or hydrogen peroxide is added to a lead sample double peaks appear with a shift in time delay. This has been attributed to condensation in cooler parts followed by delayed revolatilization atomization . While this theory does explain peak broadening, it is still not satisfactory for double peaks.

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Now, sometimes we observe double peaks for a number of volatile elements, such as zinc and lead. That is again you do not know which peak to measure if there are two peaks. So, you cannot know which peak is being measured also. So, what we do is we when ascorbic acid or hydrofluoric acid or even hydrogen peroxide is assed top lead sample double peaks appear. You do not add ascorbic acid or HF directly, movingly, but sometimes if it is associated with a sample instead of seeing one peak you will see double peaks. So, what we do under such circumstances.

So, there will be two peaks, there will be a time delay. So, you have to integrate either both peaks or a take single peak. Single peak means again you need software to determine the peak area or peak height. So, this effect has been attributed to condensation in the cooler parts of the graphite tube. So, to avoid this go for STPF that is Stabilize Temperature Platform Concept.

So, while this theory does explain the peak broadening, quite often it leads to peak broadening sometimes elements with different valance state they also show different peaks. So, it is still not satisfactory explanation for the visibility of double peaks. It is a mystery, but lot of people have been working on that.

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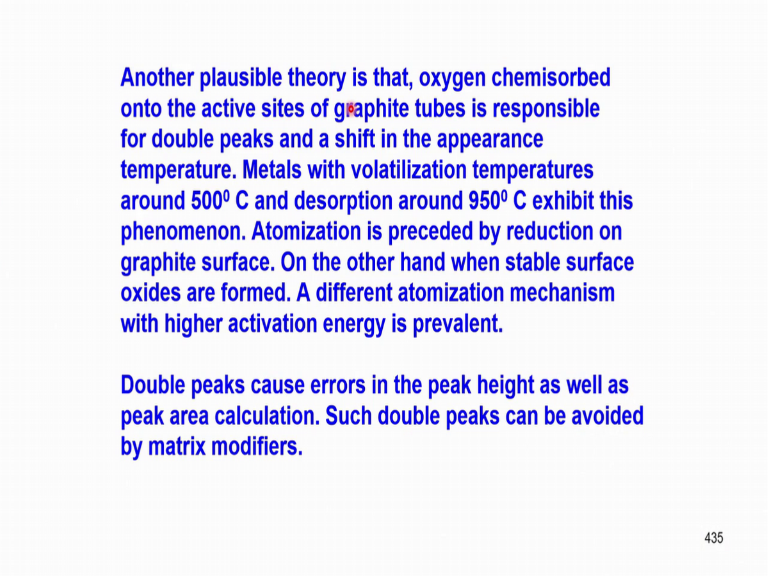

Another plausible theory is that, oxygen chemisorbed onto the active sites of graphite tubes is responsible for double peaks and a shift in the appearance temperature. Metals with volatilization temperatures around 500^0 C and desorption around 950^0 C exhibit this phenomenon. Atomization is preceded by reduction on graphite surface. On the other hand when stable surface oxides are formed. A different atomization mechanism with higher activation energy is prevalent.

Double peaks cause errors in the peak height as well as peak area calculation. Such double peaks can be avoided by matrix modifiers.

And, another theory has been proposed. That oxygen chemisorbed on to the active sides of graphite tubes could be responsible for double peaks. And there may be a shift in the temperature also. So, metals with volatilization temperatures around 500 degree centigrade and desorption around 950 degree centigrade exhibit this phenomenon. You have to remember this metals with volatilization temperature around 500. That means, mercury, antimony and all those things thallium, cadmium, some of the element. These are some of the elements they have volatilization temperature around 500 degrees including lead. And desorption can happen around 950 degree centigrade. So, such things show double peaks.

So, atomization is preceded by reduction on the graphite tube surface, on the other hand when stable surface oxides are also formed. In that case signal will become very weak. A different atomization mechanism with higher activation energy could be prevalent, it is not known exactly what are the real causes, but the fact remains that double peaks cause errors in the peak height as well as peak area calculation. The computer may do it correctly, but your calibration will go wrong.

So, such double peaks will we can avoid by matrix modifiers. That is one of the contributions from me towards the atomic absorption by electro thermal graphite technology.

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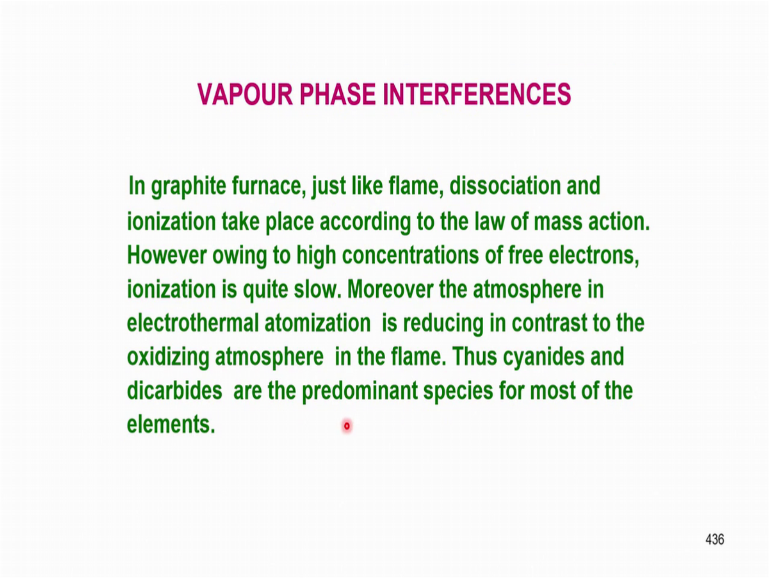

VAPOUR PHASE INTERFERENCES

In graphite furnace, just like flame, dissociation and ionization take place according to the law of mass action. However owing to high concentrations of free electrons, ionization is quite slow. Moreover the atmosphere in electrothermal atomization is reducing in contrast to the oxidizing atmosphere in the flame. Thus cyanides and dicarbides are the predominant species for most of the elements.

So, then there are vapour phase interferences. Just like in the flame dissociation ionization take place according to the law of mass action. However, owing to high concentration of free electrons ionization is quite slow. Moreover the atmosphere in electro thermal atomization is reducing in contrast to the oxidizing atmosphere in the flame. So, cyanides and di-carbides are the predominant species.

We need not worry too much about this. If we are concentrating on the atomization or only chemical analysis, but we should be aware of such interferences.

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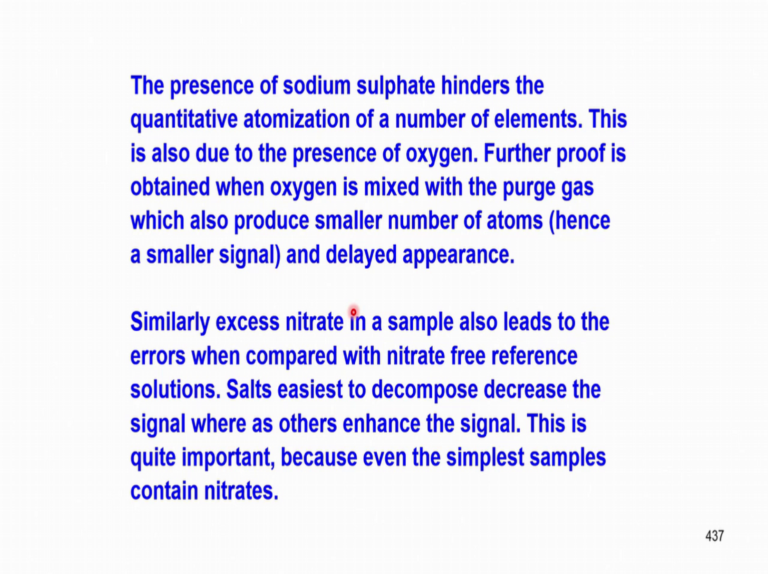

The presence of sodium sulphate hinders the quantitative atomization of a number of elements. This is also due to the presence of oxygen. Further proof is obtained when oxygen is mixed with the purge gas which also produce smaller number of atoms (hence a smaller signal) and delayed appearance.

Similarly excess nitrate in a sample also leads to the errors when compared with nitrate free reference solutions. Salts easiest to decompose decrease the signal where as others enhance the signal. This is quite important, because even the simplest samples contain nitrates.

So, presence of sodium sulphate normally; this is another aspect which I wanted to tell you. The presence of sulphuric acid or hydrochloric acid, perchloric acid, nitric acid, it is all very common in most of the atomic absorption sample handling. So, whenever we want to determine any element first here is to do is find out whether there is chloride or sulphate or nitrate in the sample, in the dissolved state.

And we have found out that presence of sodium sulphate hinders the quantitative determination itself for a number of elements. If there is high sulpahte, there is reduction in the signal. This is due to the presence of oxygen. Further proof is obtained by suppose I do the oxygen, I add the add oxygen along with the argon during the flow then what happens. I am mixing argon with the purge gas. That is argon, argon is known as purge gas. So, that also reduces the smaller they produce the smaller number of atoms, because they form oxides and they oxides will take longer time to decompose. So, the signal will appear at a longer distance or it may appear sluggish in that case peak area is the parameter which we chose to determine the elements.

That is absorbance seconds versus concentration. So, similarly if there is a lot of nitrate that also leads to errors when compared with nitrate free reference solutions. So, salts easiest to decompose decrease the signal. Whereas, others enhance the signal, this is quite important because even the simplest samples contain nitrates. Whatever is the sample you; whatever where the sampler you prepare they will either contain chlorides or sulphates or nitrates. Hydrofluoric acid and perchloric acid are a bit difficult. They may not be present in all the samples unless we deliberately add it. But, nitric acid hydrochloric acid they are all very common.

So, some other significant vapour phase interferences we have tabulated them here.

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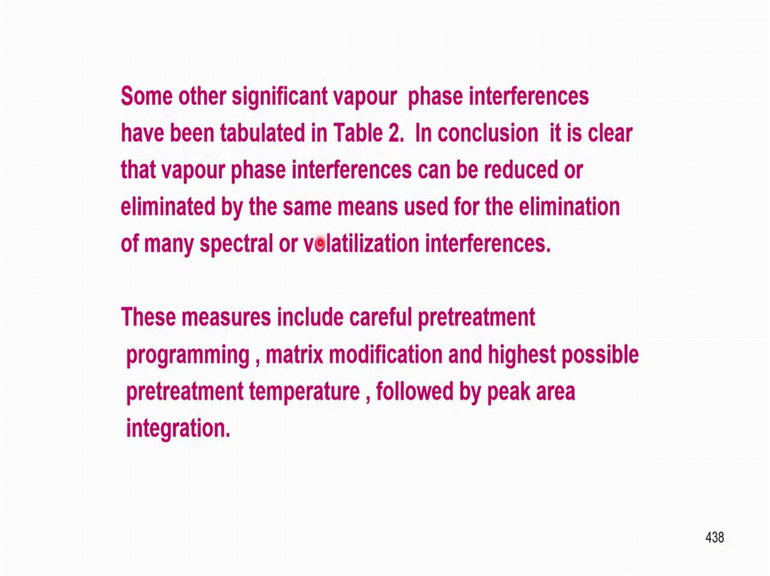

Some other significant vapour phase interferences have been tabulated in Table 2. In conclusion it is clear that vapour phase interferences can be reduced or eliminated by the same means used for the elimination of many spectral or volatilization interferences.

These measures include careful pretreatment programming , matrix modification and highest possible pretreatment temperature , followed by peak area integration.

In conclusion it is clear that vapour phase interferences can be reduced or eliminated by the same means used for the elimination of many spectral and volatilization interference. Do not worry about it, but if the signal gets reduced quite a lot then only you have to think about such things.

So, the best way to handle all these kinds of interferences is use zeeman effect background, and do a correct pretreatment programming, use matrix modification, highest possible pretreatment and lowest possible atomization, and do the peak area integration to take care of tailing, vapour phase interaction, decomposition and several other interferences which we have listed and talked about it.

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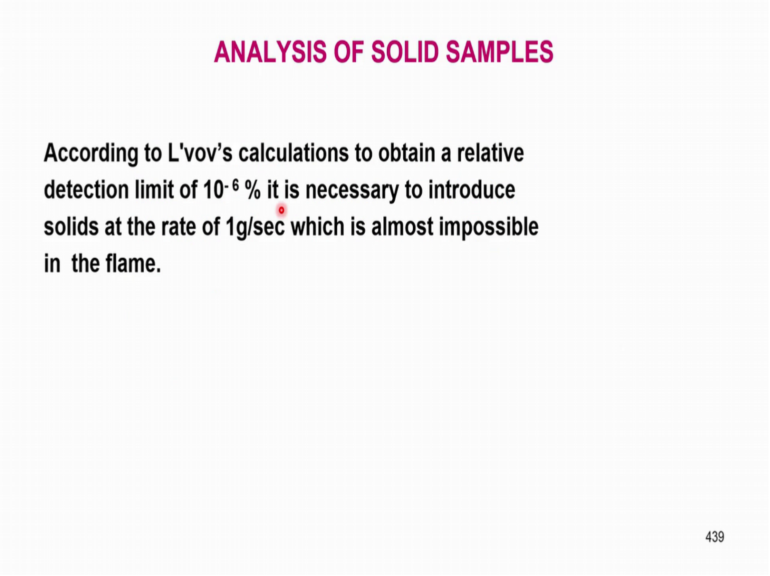

ANALYSIS OF SOLID SAMPLES

According to L'vov's calculations to obtain a relative detection limit of 10^{-6} % it is necessary to introduce solids at the rate of 1g/sec which is almost impossible in the flame.

So, the possibility of solid sample analysis is a very tempting thought, because if I can get a sample and directly put it in the analyzer; if it gives me this analysis nothing like that I do not have to do pretreatment, I do not have to dissolve it, I do not have to dilute it, I do not have to pipette it, and I do not have to worry about contamination. All these kinds of problems are avoided if you use solids as such. Sometimes it helps, but only problem is how do you introduce the solid sample in microgram quantities in a reproducible manner.

For example, it is very difficult to weigh so much and transfer exactly. Liquids are easy I can take 1 microliter also with correct accuracy and pipette it and depose it in the graphite furnace. But if it is a solid you have to weigh it and then transfer the whole weight without any loss after the weighing, back into the sample. That means you cannot have standard solutions, standard solids you cannot use.

So, solid solution analysis is a slightly tricky situation. So, according to L’vov’s trans calculation to obtain a detection limit of about 10 raise to minus 6 percent; that is almost 10 raise to minus 9 range. It is necessary to introduce solids at the rate of 1 gram per second, which is almost impossible in the flame. But same thing is true even with the graphite furnace, but people have done with: you take the sample in a capillary push it and then check the weight of the pipette itself after delivery. So, some amount of work has been done, but not very satisfactory maybe in the future time there will be method for the direct determination of solids using atomic absorption.

So, we will conclude our discussion about the sampling analysis about all flame and atomic absorption, flame cold vapour, mercury, and this hydride generation, and electro thermal, atomic absorption here. And in the next two lectures, we will talk about the potential of the method and how to go about doing the atomic absorption analysis in a systematic manner.