Trace and ultra trace analysis of metals Using atomic absorption spectrometry

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Lecture - 33
Interference in ETAAS GF AAS: Individual elements

Greetings to you, we will we were discussing the volatilization interferences in graphite furnace. I think we had discussed the different kinds of interferences and the spectral interferences etcetera

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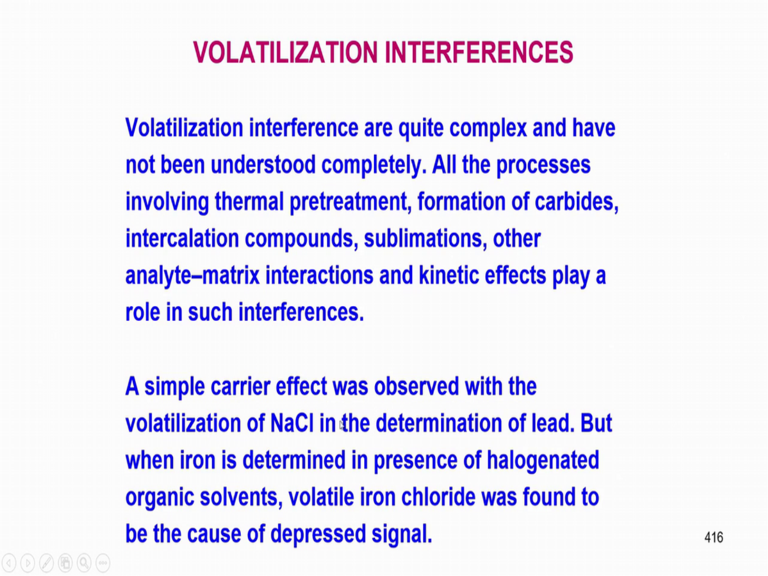

VOLATILIZATION INTERFERENCES

Volatilization interference are quite complex and have not been understood completely. All the processes involving thermal pretreatment, formation of carbides, intercalation compounds, sublimations, other analyte–matrix interactions and kinetic effects play a role in such interferences.

A simple carrier effect was observed with the volatilization of NaCl in the determination of lead. But when iron is determined in presence of halogenated organic solvents, volatile iron chloride was found to be the cause of depressed signal.

We had already discussed and I have told you that is as far as spectral interferences are concerned, they have the same effect as in flame. But in volatilization interferences they seem to be quite complex and they have not been understood completely. So, all the processes involving thermal pre treatment, formation of carbides, intercalation of compounds, sublimations and other analyte matrix interactions and kinetic effects, they all play role in such interferences.

So, a simple carrier effect was observed with the volatilization of sodium chloride in the determination of lead. We were doing the lead determination in sea water. So, lot of sodium chloride itself was getting volatilized. So, this kind of effect is always observed especially in electro thermal atomization, but when iron is determined in presence of halogenated organic solvents like methyl chloride, ethyl chloride, methyl chloride etcetera. Volatile iron chloride was found to be the cause of the depressed signal again we got very low value compared to normal iron and this we attributed to the presence of organic solvents containing chloride.

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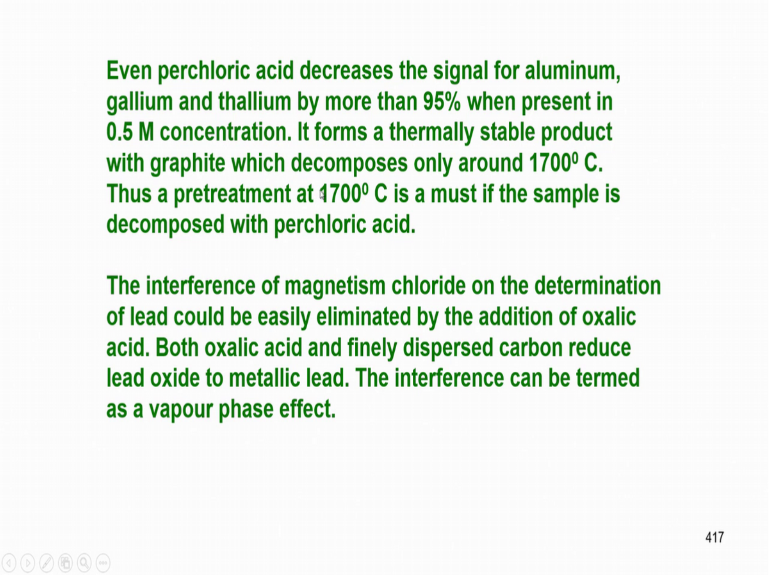

Even perchloric acid decreases the signal for aluminum, gallium and thallium by more than 95% when present in 0.5 M concentration. It forms a thermally stable product with graphite which decomposes only around 1700^0 C. Thus a pretreatment at 1700^0 C is a must if the sample is decomposed with perchloric acid.

The interference of magnetism chloride on the determination of lead could be easily eliminated by the addition of oxalic acid. Both oxalic acid and finely dispersed carbon reduce lead oxide to metallic lead. The interference can be termed as a vapour phase effect.

This I have we had completed earlier, and quite often we do come across situations where we have to dissolve the sample in perchloric acid.

So, if the sample is dissolved in perchloric acid, we again see a small amount of decrease in the signal for aluminum. So, same thing is true with gallium and thallium also; and but gallium and thallium the effect is much more significant where 95 percent of the signal goes away. So, but again it has to be correlated to the concentration here I had written that 0.5 molar concentration of per chloric acid can destroy the signal for gallium aluminum gallium and thallium etcetera; why means it forms a thermally stable product with graphite, which decomposes only around 1700 degree centigrade.

That means, once the thermal stable compound is obtained we have to the graphite itself will we have to raise it to such a high pretreatment temperature around 1700 degree centigrade that itself may not be very ideal for graphite furnace, graphite tubes rather the tubes will break very easily. So, it is no it is may not be ideal if we have the pretreatment with perchloric acid.

So, but still you want to determine 1700 degree centigrade is a must, if the sample is decompose the perchloric acid. Similarly, the interference of magnesium chloride on the determination of lead can be easily eliminated by the addition of oxalic acid. Both oxalic acid and finely dispersed carbon reduce the lead oxide to metallic lead itself. So, the interference can be termed as a vapour phase effect, because it is essentially a vapour phase reaction.

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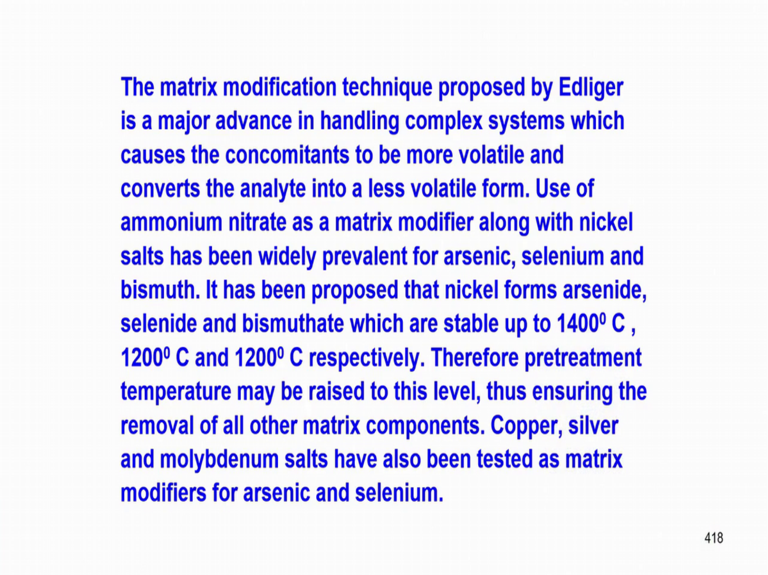

The matrix modification technique proposed by Edliger is a major advance in handling complex systems which causes the concomitants to be more volatile and converts the analyte into a less volatile form. Use of ammonium nitrate as a matrix modifier along with nickel salts has been widely prevalent for arsenic, selenium and bismuth. It has been proposed that nickel forms arsenide, selenide and bismuthate which are stable up to 1400^0 C , 1200^0 C and 1200^0 C respectively. Therefore pretreatment temperature may be raised to this level, thus ensuring the removal of all other matrix components. Copper, silver and molybdenum salts have also been tested as matrix modifiers for arsenic and selenium.

So, the matrix what we essentially conclude from this is of we add certain ashing agents; the ashing agents can to some extent overcome the deleterious effects of signal reduction in atomic absorption. So, what we do normally is along with the sample we add an another chemical that is known as matrix modifier. This matrix modifier essentially converts the substance into a more easily ashable oxide. Earlier we had discussed about lanthanum addition of lanthanum to the determination of copper and iron etcetera. Now we will discuss a little bit more about matrix modification.

So, this matrix modification technique was initially proposed by Edliger that is a major advance in handling complex systems that cause concomitance to be more volatile; that means, my other matrix elements will become more volatile compared to the metal ion which we which we are interested. We want to retain the metal ion, but interested in ashing the remaining things and remove them from the system. So, this matrix addition of a chemical is known as matrix modification.

This in matrix modification what we do is we add a substance something like magnesium nitrate to the sample itself that is in addition to the analyte. So, similarly we add it to the blank also. So, for all standard solutions we add the matrix modifier and then introduce the sample along with the matrix modifier into the graphite furnace and subject it to atomization treatment, that we will see how we plant the atomization in another slide ok.

So, the basic job of the matrix modifier is to convert it into a less volatile form that is oxide basically. So, uses of ammonium nitrate as a matrix modifier people have used it along with nickel salts. That means, whenever nickel slats need to be determined we had matrix modifier that is known that is ammonium nitrate. So, that has been it is widely prevalent for arsenic selenium and bismuth. So, what we do actually is whenever you want to determine arsenic, you add a little bit of ammonium nitrate and nickel chloride also some salt of nickel. So, both together will add as matrix modifier. So, you can see some of my publications on matrix modifier in which we have worked with palladium and magnesium salts as matrix modifiers.

But ammonium nitrate and nickel salts have been tried for arsenic selenium and bismuth. As you know most of the arsenic salts and selenium salts they are very volatile, so if you add the matrix modifier you can increase the pretreatment temperature so that we will come to that in a short while. So, it has been proposed that nickel when we add nickel to arsenic it forms nickel arsenide. In this nickel arsenide also sometimes it forms if you are determining selenium then it forms nickel selenide and nickel bismuthate are also known to form, but the beauty is these are stable up to 1400 degree centigrade, 1200 degree centigrade and bismuth is also stable up to 1200 degree centigrade respectively.

So, pretreatment temperature can be raised to this level without any loss of the metal up to 1200 degrees, you can pretreated in which case all other organic substances will evaporate. So, it ensures the removal of all other matrix components and this is one way, and the another way is we people have tried copper silver molybdenum salts along with ammonium nitrate. So, they have also been tested as matrix modifier for arsenic and selenium. It just not necessary that only arsenic and selenium bismuth etcetera are they need matrix modifier not necessarily we can try it for different elements also. So, several other matrix modifiers people have investigated.

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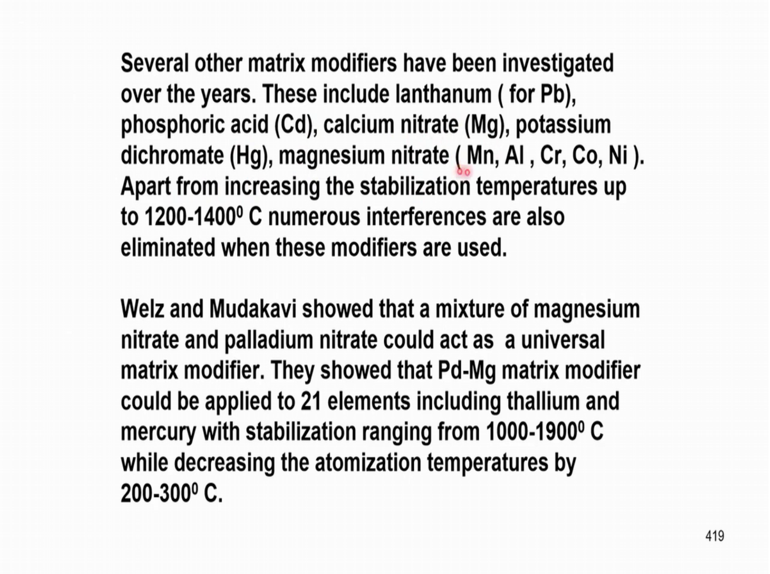

Several other matrix modifiers have been investigated over the years. These include lanthanum (for Pb), phosphoric acid (Cd), calcium nitrate (Mg), potassium dichromate (Hg), magnesium nitrate (Mn, Al , Cr, Co, Ni). Apart from increasing the stabilization temperatures up to 1200-1400^0 C numerous interferences are also eliminated when these modifiers are used.

Welz and Mudakavi showed that a mixture of magnesium nitrate and palladium nitrate could act as a universal matrix modifier. They showed that Pd-Mg matrix modifier could be applied to 21 elements including thallium and mercury with stabilization ranging from 1000-1900^0 C while decreasing the atomization temperatures by 200-300^0 C.

Over the years that since 1980s and these include lanthanum as a matrix modifier for lead and phosphoric acid for cadmium, calcium nitrate for magnesium, potassium dichromate for mercury magnesium nitrate for several elements like manganese, aluminum, chromium, cobalt and nickel.

So, apart from increasing the stabilization temperatures up to 1200 to 1400 degree, numerous interferences are also eliminated when this matrix modifiers are used that is very very clear. So, we have worked I have worked with the doctor Welz and me Mudakavi we have showed that a mixture of magnesium nitrate and palladium nitrate they can act as a universal matrix modifier. So, why go for individual matrix modifier if we want to determine nickel bismuth you add nickel, if you want to determine lead add lanthanum, want to determine cadmium add phosphoric acid.

Like that there are several matrix modifiers available in the literature then what we thought is why not we develop a universal matrix modifier so that we do not have to go looking for a chemical every time we want to determine a particular element. So, what we tried a mixture of magnesium nitrate and palladium nitrate as matrix modifier. So, we have showed that palladium in carbon atmosphere both palladium and magnesium they nitrates get radius to palladium and magnesium alloy, and that modifier can be applied to 21 elements of the periodic table including thallium and mercury, with stabilization ranging from 1000 to 1900 degree centigrade. While decreasing the atomization temperature by about 200 to 300 degree centigrade this is also possible. Because any impurity in the formation of the alloy any impurity, it will reduce the melting point that is understood right.

So, matrix modifier essentially increases the step pretreatment temperature to remove most of the organic substances, but also it reduces the melting point so that atomization temperature decreases. So, that is the beauty of matrix modifier. With this information we want to know how it will help in the determination of metal elements, how do we do the temperature program. So, how do we do the (Refer Time: 13:26).

So, how do we do the temperature programming for electro thermal atomic absorption. So, what we do now is we make a temperature program.

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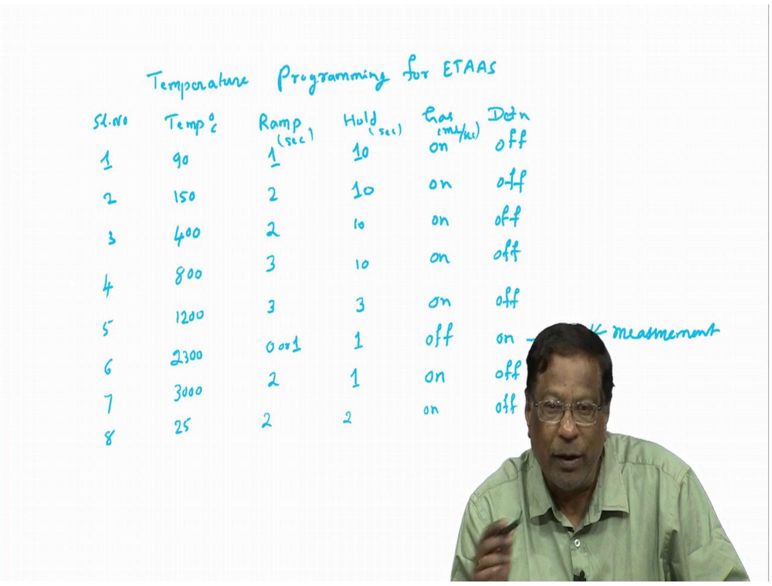

Temperature Programming for ETAAS

Sl.No	Temp °c	Ramp (sec)	Hold (sec)	Gas (ml/sec)	Detn
1	90	1	10	on	off
2	150	2	10	on	off
3	400	2	10	on	off
4	800	3	10	on	off
5	1200	3	3	on	off
6	2300	0 or 1	1	off	on ← measurement
7	3000	2	1	on	off
8	25	2	2	on	off

Temperature programming; this is this can be available on the computer itself, you have to go to that page and plan the temperature programming for each of these for each element. So, there will be number of steps. So, first step is you want to heat it to 90 degrees correct. So, temperature, this is a serial number I want heat it to let us say 90 degrees and then I want to heating time heating time is known as ramp.

So, I want to heat it in one second, now how long I want to hold it. That means, I want to heat it to 90 degrees in 1 second, but want to hold it for about 10 seconds. So, this is hold I let us say I want to hold it for 10 seconds. Now after holding it for 10 seconds during that time, do you want the gas on or off because every time a substance is the being heated you want the concomitance to go out of the tube. So, we have to put the gas on and that is argon gas.

So, gas we will say on and then you need a decision when to measure the atomic absorption right. So, then what we say is determination of we do not want. So, what is the next step the next step is serial number 2, we want to heat it to about 150 degree centigrade, and we want to heat it in 2 seconds hold it for about 10 seconds, gas should be on and determination should be off; that means we do not want to measure any signal during heating ok.

Now, third step I want to remove all the organic substances correct. So, organic substances if they are associated along with a sample, I may choose a temperature of about 300, 400, 500 600 also. So, let me choose a temperature of 400 degrees and I want to heat it within at a ferries steady rate. I do not want to heat it very fast nor do I want to heat it very slow, because if I give 2 degree centigrade per second it may take about 3 another 150 seconds, that is about 3 minutes we do not want that, but what I want to do is I want to heat it within 2 seconds and hold it for about 10 seconds; that means, after reaching 400 it will maintain the temperature of 400 degrees by that time all the almost all the organic compounds will go, and gas should be on and determination should be off, ok.

Now, the next step is I want to remove all the inorganic salts. So, I want to heat it to about 800 degree centigrade in about within about 3 seconds, this ramp time we can choose depending upon our requirement. And then I can hold it for about 10 seconds gas should be on and determination should be off we do not want that. So, last step last, but one step I want to remove whatever inorganic salts are there in the sample. So, I want to heat it to about 1200 degree centigrade and then ramp should be about 3 seconds, this is in seconds this is also in seconds, this is milliliter per second gas. So, in 3 seconds I am heating it and then taking it to holding it for about 3 seconds because most of the inorganics are remember we are adding only 10 micro liter of the sample. So, most of the inorganic salts would have gone by that time and gas should be on, and then determination also should be off.

Now, what remains is only the atomization step. So, in atomization step I want to heat it to very high degree say very high degrees; that means whatever is the sample remaining should go off the graphite tube correct. So, the metal should be atomized. So, I want to heat it very fast so that the sample is atomized. Now at the same time I want the metal vapour to remain in the optical path. So, I want to hold the metal vapour as long as possible inside the graphite tube so that atomization is always is held as long as possible. Now so the next step is I want to heat it to about 2300 degrees, but how slow or how fast I have to decide.

So, question of slowness does not arise I want to heat it as fast as possible. So, we will say maximum that is I give 0 or I can even say or 1 second, within 1 second let everything get evaporated. So, I can choose 0 or 1, and I want to integrate it integrate the signal for 1 second, 2 seconds, 3 seconds, 5 seconds etcetera. So, I have to hold it for about 1 second let us say that is a signal should be collected, and during that time I do not want the gas. So, gas should be off and what about determination? Determination should be on. So, this is the important step measurement.

So, in the slide what I am showing you number 6 step is the most important step, where the temperature reaches 2000 to 300 degree centigrade and ramp time is 0 or 1; that means, maximum amount of electricity is supplied to the graphite furnace. And then I am holding it for one second to get the signal and integrate it or make them a measurement peak height, then I can at that time the gas should be off because the atomic vapour should be in the graphite tube inside that 1 m for 3 by 5, 3 mm by 0.5 mm graphite tube, all the vapour should be inside that tube.

So, the at that time I want the hollow cathode lamp also to be on at I can plan it in such a way that only during step sects the lamp is on. So, that I do not have to waste the energy from the hollow cathode lamp that is a apart, but gas should be off that is most important determination should be on. Now after heating making the measurement the graphite tube is very hot, most of the metal vapour has gone out of the system and then I have to bring it down to room temperature so that I can put my next sample again. So, I need a cooling step.

Before that I want to heat it to a very high temperature still higher temperature to remove the remaining inorganic substances in the graphite tube. So, I will say that is known as firing step. Now my next step would be 3000 degree centigrade in about 2 seconds holding, our time also would be about one second, because I do not want any carbon to burn, but still I am heating it to 3000 degree centigrade. So, what is the best alternative for me? The best alternative for me is to heat it for very short time burn off everything put the gas on so that whatever comes out of the graphite tube also will be swept away out of the optical path of the system, at that time hollow cathode lamp can be off so gas also should be on. This gas will serve to remove the remaining inorganic substances out of the graphite tube and then determination we do not want any determination.

So, determination should be off. Now after heating it to 3000 degree centigrade what you would like to do? We would like to bring it back to room temperature. So, I need a cooling step and their power should be off. So, the if I specify the temperature let us say about 25 degree that is room temperature, I want it to cool very fast let us say about 2 seconds and then to help this I need the gas to be on hold down for about 2 seconds, I need the gas to be on determination to be off ok.

Now, at this stage the graphite tube is ready for the next sample now. So, now, what I want you to want you to understand is in a graphite tube atomic absorption spectrometer, you can plan all this temperatures depending upon your sample. For example, you may choose instead of 90 degrees you may chose 100 degrees for the first step, ramp you can choose 2 to 3 sometimes the sample spurts out, we do not want that it should be slowly heated and water vapour only should come out. So, you may ramp it for about 5 seconds, hold it for 5 seconds and then nest temperature if you do not have organic substances, then you can delete the second step simply go to 400 degree centigrade or 800 degrees and then do that ray process then finally, you go for removing the concomitance.

So, that can also be worked around 1000 degrees pretreatment, and after that you can go for atomic absorption sometimes you may do like to do it at 2300 degrees or 2500 degrees or may be 2000 degree itself. In 1200 degrees for example, if you want to determine mercury you may like to do for only 5 minute for 1200 degree, because mercury does not need even at room temperature you can determine now. So, mercury does not need very high temperature. So, you may like to do atomization itself at 1200 degree centigrade lead for example, similarly this lead also can be determined very easily because it is a very volatile element. Like that there are several volatile elements which will require still a rare temperatures. So, 2300 is not the all these temperatures in column 2 are adjustable according to your convenience ok.

And heating of up to 2500 or 2700 that is a mandatory, but again you may choose to if you heat it to 3000 degree centigrade and hold it for long time graphite tube may get destroyed faster. Normally a graphite tube in an electro thermal atomic emission atomic absorption spectrometer, last for about 300 determinations; so by that time graphite furnace graphite tube will destroy itself and breaks. So, if you want to prolong the life of the graphite tube you should not be heating it to 3000 degrees, but you may chose to heat it two if you heat it to 2500 or may be 2700, you may prolong the life of the graphite tube they are all very costly a typical graphite tube costs about 3000 to 4000 rupees with platform.

And final step is again it is at room temperature you may decide to do it around 20 degrees or so, but the whole graphite furnace should be in should be covered with a circulating water cooling water so that the can work faster. Heating at high temperature is no problem, but bringing it to room temperature fast it requires the help of a coolant. So, most of the electro thermal atomic absorption spectrometers are provided with coolers you know which ion which water of about 16 degree centigrade, circulates the graphite furnace all the time.

So, when you in the last step it gets activated and it cools faster and makes it ready for atomic absorption sample insertion once again. So, like this if you put first you should put blank, then you put the first sample standard second standard third standard etcetera make the absorption curve and then put your unknown sample make the determination. That is how most of the atomic absorption spectrometers will work and that is the whole system also that is how the atomic absorption is worked out.

Now, we will move on to the matrix modification, we have I had explained to you earlier that we have worked on my palladium and magnesium matrix modifier. So, what we want to do during matrix modification is we want to reduce the pretreat; increase the pretreatment temperature as much as possible, and reduce the atomic atomization temperature that is number 6 here in this slide, number 6 is a atomization and number 4 5, 3 4 5 are pretreatment temperatures.

So, whenever you want to work or develop any system for atomic absorption you have to optimize the pretreatment temperature and the atomization temperature. That is what we did for many elements using palladium nitrate and magnesium nitrate modifiers matrix modifiers.

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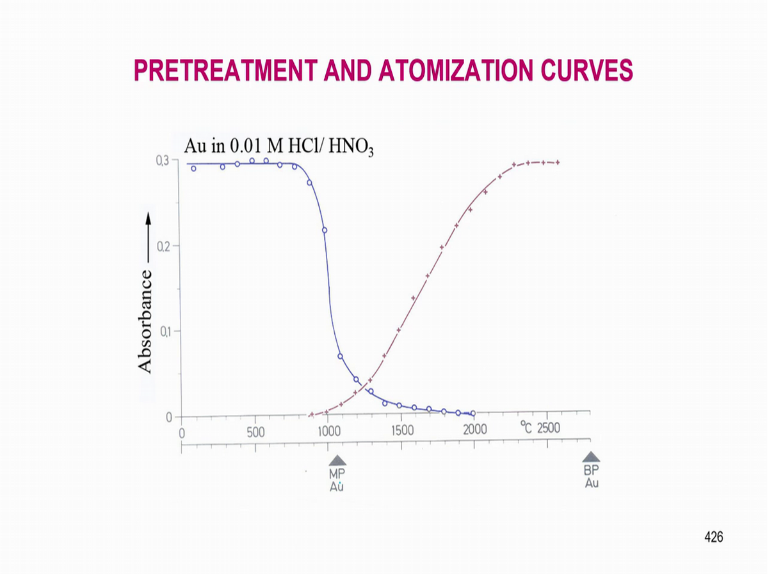

PRETREATMENT AND ATOMIZATION CURVES

So, this is the pretreatment and atomization curve for gold, I have written here gold and the melting point or of the gold is approximately around 1100 or something. This is the temperature. So, I have written here melting point of the gold around 1100 centigrade, what I have done is I have gone to gone through this procedure previous procedure, and kept the atomization temperature somewhere around 2200 or 2500. Now I increase the pretreatment temperature to about 5 200; 200, 300 500, 600, 800, 900 like that and my aim is to get maximum signal and maximum signal at higher temperature. So, what I did I do the increase the pretreatment temperature to around let us say 500 and then determine the signal.

So, what is the signal atomization signal? My atomization signal I chose a arbitrarily around 2000 year. So, I plot atomization signal. So, if it is 1000 degree, 500 degrees my atomization signal is maximum here. This is the atomization these are the this is the absorbance. So, the absorbance is maximum if I treat it to 500; that means, I am not losing any gold in during the determination suppose I do it up to 800, again the signal is almost 0.3 only. So, I am not losing, but the moment I come around 900 the signal dips here. So, I am it means that I am losing some of the gold here, similarly I can do this increase the temperature around 1000, I get very less reading and increase it to 1100 around the melting point I lose very fast signal becomes less than 0.1 compared to 0.3.

So; that means, I have lost about nearly 70 percent of the gold if I do the pretreatment up to 1100, similarly 1500 and all there is no signal at all. Now this curve tells me that the absorption is this sample can be pretreated without any loss of any signal up to 900 degree or 800 degrees. So, what I do is I fix the in all my future experiments, I fix 800 degrees as the pretreatment temperature; that means, say in the previous step here for gold I will say do not go to 1200 remove this keep only 800 for 3 minutes 3 seconds, and then go for atomization.

Now, what I do in all future experiments during for optimization, I keep 800 and start the atomization temperature. So, if I say atomize around 1000 degrees, around 900 degrees no signal thousand degrees no signal, almost 1500 degrees I get about 0.1 absorbance right. So, it that is not ideal. So, I increase it to 2000 what is the reading around 2000. 2000 is approximately 0.2 absorbance.

So, I increase it still further around 2005, 400 I get almost 0.3. So, 2 I increase it another 100, 2400 same reading, 2500 same reading. So, if I increase it higher I have to choose the life of the graphite tube whether is it worth it or not because signal is not increasing. So, my aim is to keep atomization as less as possible. So, I chose only around 2300 or 2400. So, this gives me this whole thing gives me a an idea of how a pretreatment and atomization can take place.

So, similarly we have to work for different elements in atomic absorption that especially graphite furnace.

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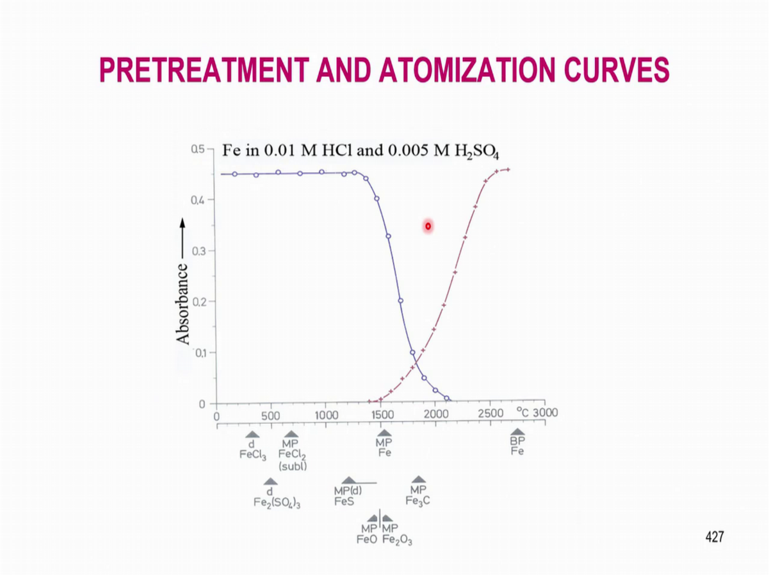
PRETREATMENT AND ATOMIZATION CURVES

Now I will show you one more slide like this is for iron. For iron we know that ferric chloride decomposes around 400 degree centigrade, around 300 melting point of ferric chloride is approximately here ferrous sulphate is here. So, most of the inorganic decomposition temperatures we have to avoid; that means, we have to make sure that the sample remains in the undecomposed state as far as possible right, but it can get reduced to the metal and remaining solution that is no problem.

So, what I did is I did again the same experiment increase the pretreatment temperature to 500, 1000, 1500, 100 and after 1500 I see that there is a dip in the absorbance signal. So, I can say with confidence that we can pretreat the sample without losing any iron up to 1400 degree centigrade. So, this that is the conclusion from this pretreatment curve and the atomization again I can start with around 21500 it is not signal is not good, 2000 signal is not good, but it reaches around 2600 or 2500 the it reaches maximum.

So, I fix the atomization temperature to about 2500, like this I can normally when you buy an instrument atomic absorption or with flame or without with graphite the cook book the manufacturer will give you a manual in which he will specify all these things. He will say atomization temperature for iron is approximately around 2500, and then it will help you in choosing the correct temperatures for atomization.