Modern Instrumental Methods of Analysis
J.R. Mudakavi
Department of Chemical Engineering
Indian Institute of Science, Bangalore

Lecture number # 27
Electrothermal Atomic Absorption Spectrometry-11 Practical Aspects

Welcome to the twenty-seventh lecture of the series on modern Instrumental methods of analysis; we were discussing about the electro-thermal atomic absorption.

In the last slide, I had explained to you that majority of the elements may be atomized around 2500 to 2800 Kelvin; both pretreatment and atomization curves must be optimized as a function of the absorbance signal. So, pretreatment temperature should be as high as possible without losing the atoms in the atomization stage. Similarly, atomization process should be the temperature of the atomization process, should be as low as possible, so that the life of the graphite tube will be extended.

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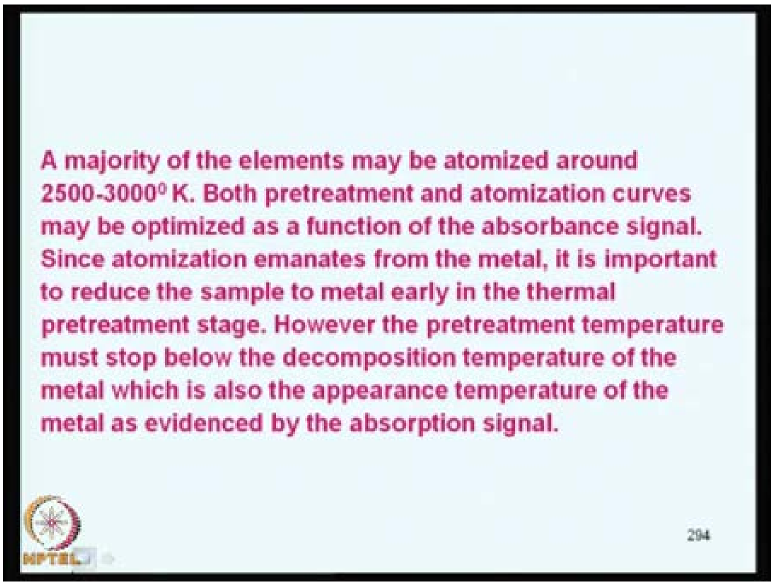

A majority of the elements may be atomized around 2500-3000^0 K. Both pretreatment and atomization curves may be optimized as a function of the absorbance signal. Since atomization emanates from the metal, it is important to reduce the sample to metal early in the thermal pretreatment stage. However 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.

Therefore, we would like to know the different conditions for each element, because for each element, pretreatment and atomization temperature would be different. So, what are the types of mechanisms that happen in graphite furnace technology?

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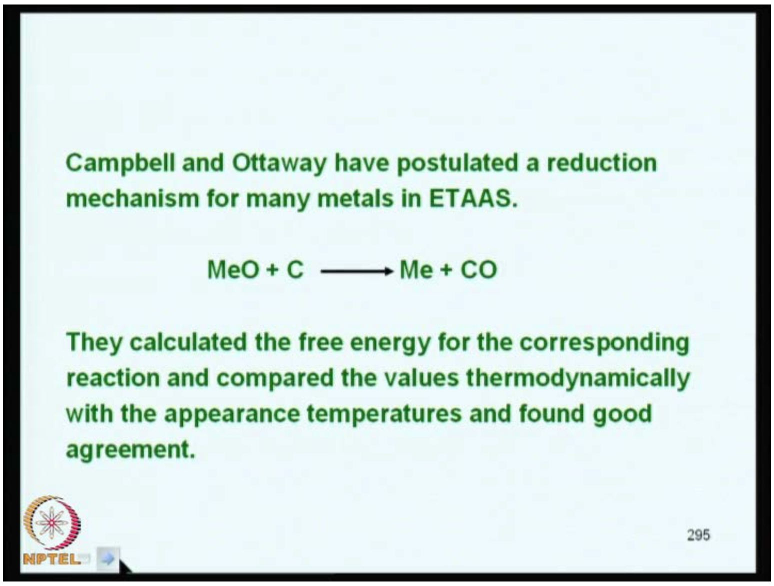

Campbell and Ottaway have postulated a reduction mechanism for many metals in ETAAS.

$$MeO + C \longrightarrow Me + CO$$

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

So, Campbell and Ottaway have postulated a reduction mechanism for many metals In the electrothermal atomic absorption; for example, if you are taking a small sample of a substance as a hydroxide or oxide, it would be reacting with the carbon of the graphite furnace to produce a metal. And then, the carbon would be converted into carbon monoxide or carbon dioxide, depending upon the free energy for the corresponding reaction. And they compare these values thermodynamically with the appearance temperatures of the metals and found good agreement; that means, the most of the reaction products are in would be metal and carbon monoxide in atomic absorption. So, how does this happen?

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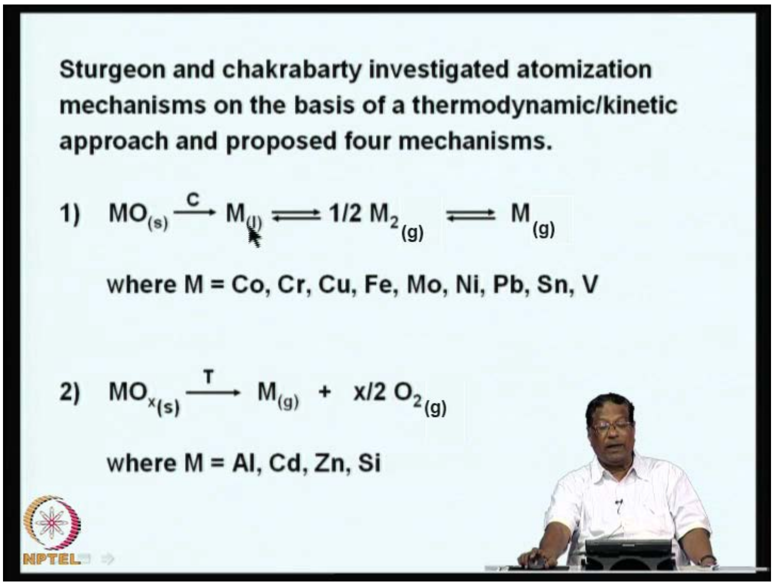

Sturgeon and chakrabarty investigated atomization mechanisms on the basis of a thermodynamic/kinetic approach and proposed four mechanisms.

1) $MO_{(s)} \xrightarrow{C} M_{(l)} \rightleftharpoons 1/2\ M_{2(g)} \rightleftharpoons M_{(g)}$

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

2) $MO_{x(s)} \xrightarrow{T} M_{(g)} + x/2\ O_{2(g)}$

   where M = Al, Cd, Zn, Si

Sturgeon and Chakrabarty have investigated the atomization mechanisms on the basis of a thermo dynamic and kinetic approach and they have proposed four mechanisms. And some of these mechanisms like what I had explained to you, this metal oxide reacting with carbon to produce metal, and then the metal would be in the initially in the liquid state and then it would be in the gaseous state, where m would be equivalent to, it could be cobalt, chromium, copper, Iron, molybdenum, nickel, lead, tin and vanadium.

So, for these elements, this mechanism is good, it holds good. suppose you have aluminum, cadmium, zinc and silicon; here, what you would be having as a sample would be a complex mixture of oxides. So, the composition is fairly not very specific. So, at high temperature, this would straight away decompose to metal and oxygen; this is another type of mechanism they had proposed.

Now, it is also possible, that metal oxide can get converted to metal oxide gas itself directly, and then the further reduction as usual, that is, metal in the metal atoms in the gaseous stage followed by little bit of oxygen, that is corresponding amount of oxygen that is present in the metal. So, this mechanism is prevalent, when metal atom is cadmium, magnesium, manganese and zinc.

Here you should imagine that the sample is not exactly in the form of a chloride or a nitrate, it could be in the form of oxide or a hydroxide; sometimes nitrate it can be, because some of the nitrates decompose to give you metal oxide, that is the starting equation for this third mechanism. Now, it is possible that salts like chlorides, etcetera, they react like this, m x two going to solid, going to liquid, that is melting stage followed by the gaseous formation, m x decomposition - partial decomposition - followed by metal and x 2. And if it is a chloride, you would have chlorine gas and bromide, etcetera, you would have bromine gas etcetera, so, where this mechanism holds good for most of the chlorides, especially cadmium, Iron and zinc.

So, mechanisms one and two what I had explained to you earlier, that is decomposition straight away into metal and of the oxides; decomposition of the oxides require intimate contact with the graphite surface for reduction to occur, but decomposition of oxides and halides can occur in the vapour stage itself, not necessarily in when it is in contact with the graphite material; therefore, these reactions are basically temperature independent temperature dependent reactions, because the decomposition of the halides at higher temperature, decomposition would be more. So, there is no Intimate contact with the graphite furnace necessary.

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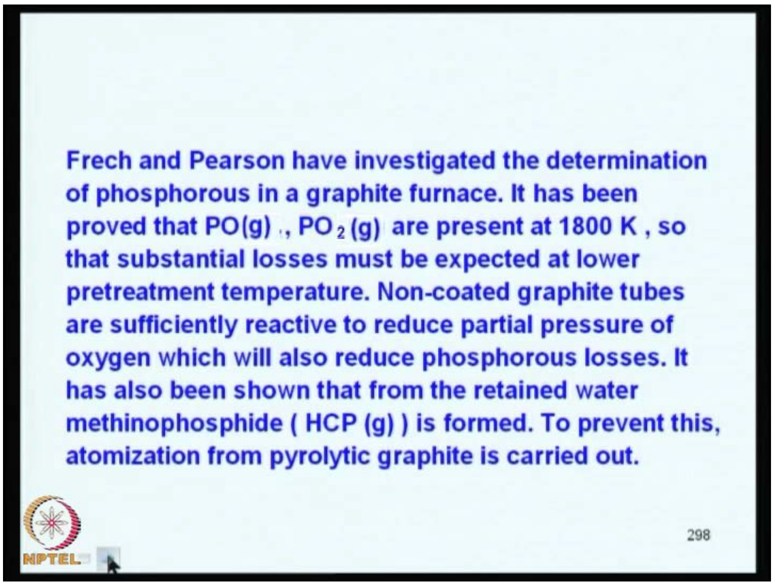

Frech and Pearson have investigated the determination of phosphorous in a graphite furnace. It has been proved that $PO(g)$, $PO_2(g)$ are present at 1800 K , so that substantial losses must be expected at lower pretreatment temperature. Non-coated graphite tubes are sufficiently reactive to reduce partial 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.

So, Frech and Pearson have also investigated part of the mechanisms for other elements; for example, they have investigated the determination of phosphorous in a graphite furnace. it has been proved that, p o, p o 2 are present at 18 degree kelvin, so that substantial losses must be expected at lower pretreatment temperature; that means, whenever you have phosphorus in the form of an aqueous solution, the possibility is your pretreatment temperature should be much lower than the appearance temperature.

This they have calculated you only from the thermo dynamic principles. So, non-coated graphite tubes are sufficiently reactive, that is, we have been all the while telling, that we should use pyrolyticaly coated; but with respect to phosphorous, it is the non-coated graphite tubes are very reactive. So, to reduce the partial pressure of oxygen, which will also in turn reduce the phosphorous losses.

Suppose you use the pyrolytically coated graphite, you would have higher losses of phosphorous than the non-coated ones. So, it has also been shown that, from the retained water, methinophosphide gas is formed. To prevent this, atomization from pyrolytic graphite is carried out, but at a loss of sensitivity. So, it is a question of compromise between graphite furnace and non-coat pyrolytically coated graphite tube and non pyrolaytically graphite tube with respect to phosphorous.

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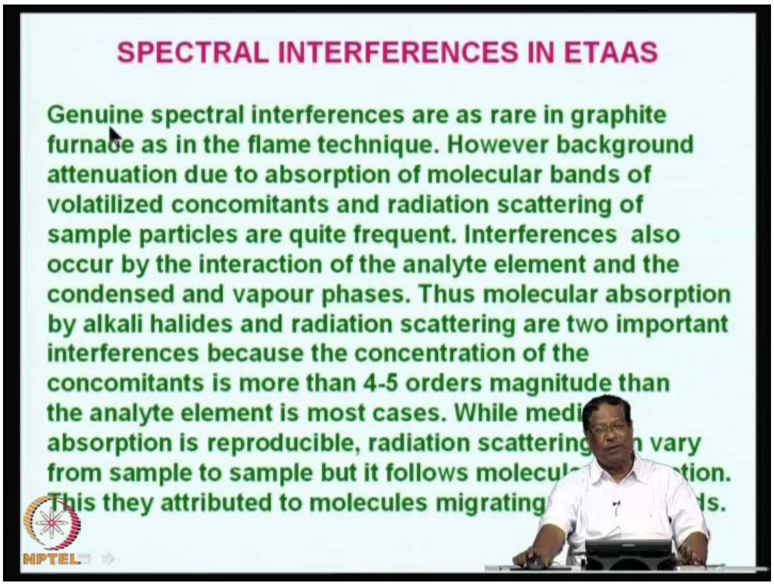

SPECTRAL INTERFERENCES IN ETAAS

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 is most cases. While medi absorption is reproducible, radiation scattering n vary from sample to sample but it follows molecul tion. This they attributed to molecules migrating ds.

So, if we take a look at the spectral interference, for example, we have already discussed the spectral interference in metal at a flame atomic absorption as well as in the hydride generation, and then cold vapour mercury, and also flame atomic emission.

Now, if we take a extend our discussion to spectral interferences in electro-thermal atomic absorption, you would not be surprised that, genuine spectral interferences are also as rare in graphite furnace as in the flame technique; that means, very few spectral interferences you should be expecting with respect to graphite furnace, because the hollow cathode lamp is same and then measurement wavelength is same. So, wherever there is a, wherever there is a overlapping of these spectral frequency, then only it will be spectrally interfering. So, whatever are the spectral interferences expected in flame atomic absorption, same thing you can expect in the graphite furnace also.

However, background attenuation due to absorption of molecular bands of the volatilized concomitants, that is, and radiation scattering of the sample particles are quite relevant and frequent in this case; what do we mean by that is, if the background attenuation due to molecular bands, for example, cyanogen is a big molecule with a broad lambda max, just like uv visible spectrometer. So, part of it would be measured at the spectral wavelength also. So, that increases the absorbance and that becomes significant especially in graphite furnace, because the residence time is longer in graphite furnace than in the flame atomic absorption. Same thing happens with respect to scattering of sample particles; if the sample particles are getting scattered, they would all be still in the optical path of the substance and scattering loses also are expected. So, interferences also occur by the interaction of the analyte element and the condensed vapour phase phases, and the sample also sample in the vapour phase and condense to vapour phases of the other concomitants.

For example, if you are you are dissolved the sample in hcl or in sulphuric acid, so part of it would be there in the graphite furnace as a cloud of hcl, before it decomposes. So, this kind of interaction is expected, that is molecular interference; therefore, molecular absorption by alkali halides and radiations scattering are two important interferences, because the concentration of the concomitants is usually more than four to five times the magnitude than the element in the most of the cases; whatever is the concentration of the element, the concomitants, acids, and then other dissolution aids what you have added, all the other things would be approximately four to five orders of magnitude, that is about ten thousand times higher than the metal element. So, obviously, the interference would be higher in this in such cases.

While medium absorption is reproducible; radiations scattering from vary from sample to sample; from one sample to another sample, they depending upon the concentration, radiation scattering also can change. So, there is some amount of non-linearity introduced, when you are doing graphite furnace, but it is a not very unusual, provided you correct the background absorbance due to scattering; it is possible.

So, you can correct it, only if there is it follows something like a molecular absorption; that means, a broad band peak, then it is possible to correct. So, this can be attributed to the molecules migrating to the cooler ends, you know, why it takes more time to remain in the graphite furnace, because the moment you are you are heating it, the vapour phase molecules will start migrating to cooler ends automatically. So, this is one of the important aspect; and the molecular spectra may be classified into dissociation continuum and broadband electronic spectra;

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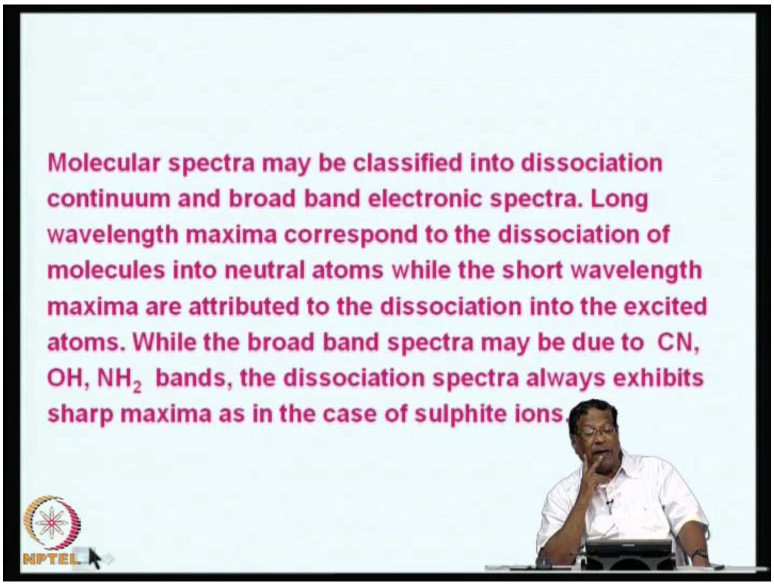

Molecular spectra may be classified into dissociation continuum and broad band electronic spectra. Long wavelength maxima correspond to the dissociation of molecules into neutral atoms while the short wavelength maxima are attributed to the dissociation into the excited atoms. While the broad band spectra may be due to CN, OH, NH_2 bands, the dissociation spectra always exhibits sharp maxima as in the case of sulphite ions.

For example, the broadband electronic spectra, it can be it is a structured material, it can be corrected straight away depending upon the, when the sample is not there, broadband electronic spectra will remain same, provided you make the sample matching; matrix also should be matching in your standards.

So, long wavelength maxima correspond to the dissociation of the molecules into neutral atoms, while the short wavelength maxima are attributed to dissociation into the excited atoms. Now, we are talking about the background absorption peaks. So, long wavelength maxima are they correspond to the dissociation of other concomitant molecules into neutral atoms.

Short wavelength maxima are attributed to the dissociation into the excited atoms. While the broadband spectra may be due to cyanogen, oh, nh 2 bands, the dissociation spectra always exhibits sharp maxima as in the case of sulphite ions, very sharp maxima.

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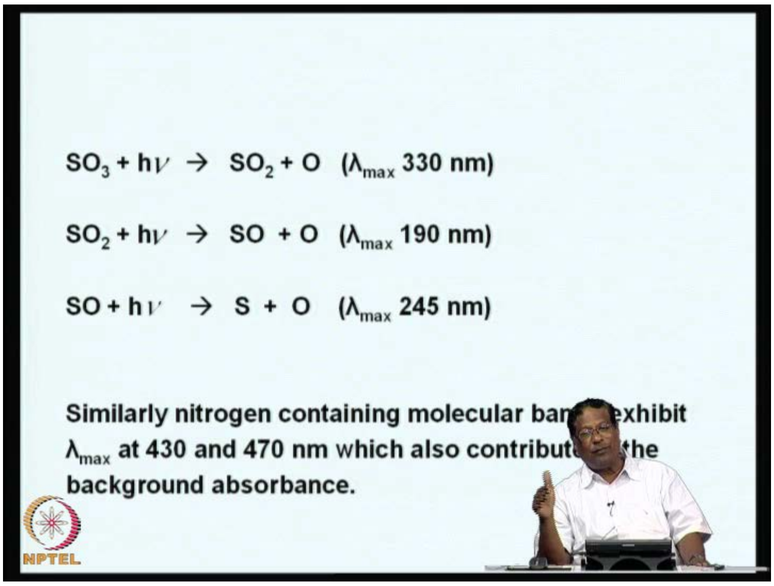

$SO_3 + h\nu \rightarrow SO_2 + O$ (λ_{max} 330 nm)

$SO_2 + h\nu \rightarrow SO + O$ (λ_{max} 190 nm)

$SO + h\nu \rightarrow S + O$ (λ_{max} 245 nm)

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

So, unless if you have a sulphite ion in the sample, it is it may not interfere because, it has got a very sharp maxima, unless it coincides with the measurement sig wavelength. So, here I have written the reaction of sulphite with electromagnetic radiation, the changes are expected are very simple; s o 3 will go to s o 2 and oxygen atom will be released, and s o 2 can further dissociate to give you s o, and s o can give you sulphur. And in gaseous state, such systems, such species can be stable, whereas in solution state, we do not expect such species s o 2, s o 3, s o and sulphur, but in gaseous state, such chemical species can and do remain in the gaseous state as a separate chemical entities itself.

So, it is possible to record the absorbance maxima for s o 2, s o and sulphur also, if it is there in the vapour phase. So, that is why we have written that, s o 2 gives you lambda max of about 330 nanometers; for s o species, we have a lambda max of 190. So, if you are measuring absorbance at 190 for some element, then if there is s o 2, s o 3, there would be spectral interference almost.

So, we have to be very careful with such systems; that is why, in the dissolutions of samples, we do not prefer sulphur h 2 s o 4 as a solvent. Specially, if it is going to end up in the electrothermal atomic absorption for analysis, all these things are automatically expected. So, similarly, if you take a look at cyanogen bands, also molecular bands exhibit lambda max at 430and 470 nanometer; these things also contribute to the background absorption.

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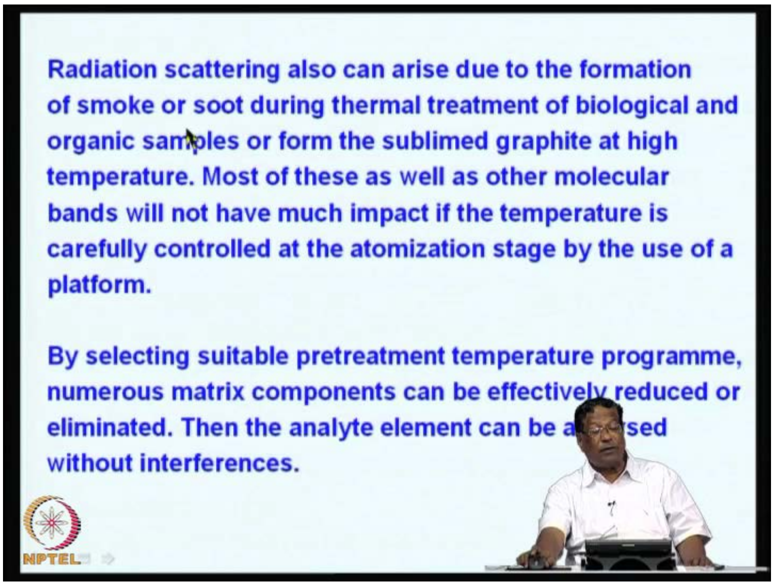

Radiation scattering also can arise due to the formation of smoke or soot during thermal treatment of biological and organic samples or form the sublimed graphite at high temperature. Most of these as well as other molecular bands will not have much impact if the temperature is carefully controlled at 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 a sed without interferences.

So, usually radiation scattering also can arise due to the formation of smoke or soot, these are also small small particles, they can also emit radiation or absorb radiation during the thermal treatment of the biological and organic samples; they may form sublimed graphite at high temperature, straight away from solid into the sublimed graphite. During that process, by the time they change over, there could be scattering.

And most of these as well as other molecular bands will not have much impact, if the temperature is carefully controlled at the atomization stage itself; that is why we prefer platform. So, there is no direct contact. So, the platform will be heated only by the radiation. So, that it will be sluggishly following the actual apply temperature; and if it is directly contact, then whatever is the temperature we give, it will follow fast, whereas, because it is radiation controlled, the platform temperature will slowly reach the applied temperature.

So, by selecting suitable pretreatment temperature programme, numerous matrix elements can be effectively reduced or eliminated. This is the greatest advantage of graphite furnace. So, the analyte element can be analyzed without the interference, because you would have eliminated most of the interferences before itself.

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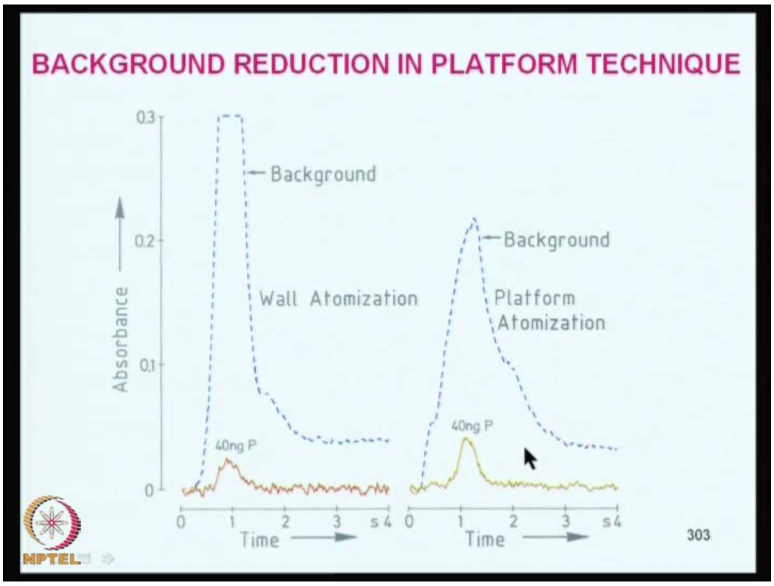

BACKGROUND REDUCTION IN PLATFORM TECHNIQUE

For example, take a look at the back ground reduction in the platform technique. See here, if it is directly 40 nanogram of phosphorous is, what you see at the bottom is the actual atomic absorption spectrum - AAS spectrum. So, people have done absorbance measurement with this curve and you can look at the background, background is 0.3 whereas, for 40 nanometer absorbance is only about 0.02 0r 0.03. So, you can correct background up to 0.3 also.

And then, suppose you use a platform, then what happens? Look at the figure here, to the right, the curve is much more symmetrical and much more smarter, and background has already gone; much of the background has already been sent out of the graphite furnace. So, this slide brings out the importance of pretreatment and different kinds of pretreatment procedures can be developed to handle specific concomitants.

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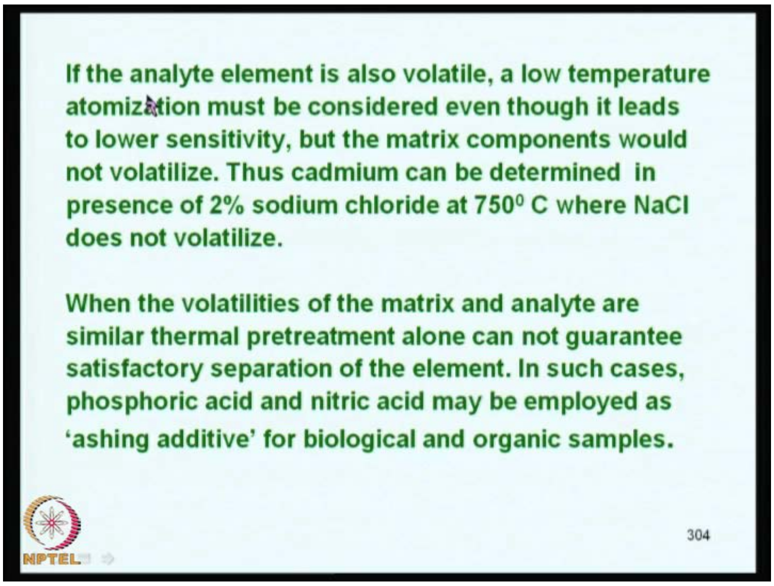

If the analyte element is also volatile, a low temperature atomization must be considered even though it leads to lower sensitivity, but the matrix components would not volatilize. Thus cadmium can be determined in presence of 2% sodium chloride at 750^0 C where NaCl does not volatilize.

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 suppose the analyte element is also a volatile, then low temperature atomization is a must, so that we do not lose the atoms in the pretreatment stage itself. So, even though, suppose you do the atomization at higher stage definitely, you will lose the sensitivity. So, we have to consider low temperature atomization, even though it leads to lower sensitivity, because part of it you would be losing anyway; for example, mercury, if it is there as a contaminant, you would start losing mercury right from 200 or room temperature itself. So, we will have to, still we will have to do the atomization at as low temperature as possible, that will not give you the freedom to pretreat at higher temperature. So, pretreatment temperature also comes down correspondingly.

So, the matrix component would not volatile should not volatilized; therefore, suppose you want to determine cadmium in sea water, so cadmium starts atomizing given around 900 degree kelvin. So, you should not, as you know most of the sodium sea water would be having between two to three percent or sometimes even 3.5 percent of sodium chloride. And the best way you can do is, pretreat at 750 degrees, you should not you should not be pretreating even for longer period, because you would be losing cadmium, if you hold the temperature of the pretreatment very high.

And what best we can do is, at 750 degree centigrade, we make sure that sodium chloride does not volatilize; you know do not aim for removing the sodium chloride from the matrix itself, atomize everything, pretreat around 600 degree or something, and let the sodium chloride will be, and then atomize along with that hope for better background corrections.

So, when the volatilities of the matrix and the analyte are similar, this tricks works. So, thermal treatment alone cannot guarantee satisfactory separation of the element. in such cases what we do? You can add a little bit of phosphoric acid or nitric acid to the sample in the graphite furnace, and they help in ashing easy; it is easier to ash in presence of phosphoric and nitric acids.

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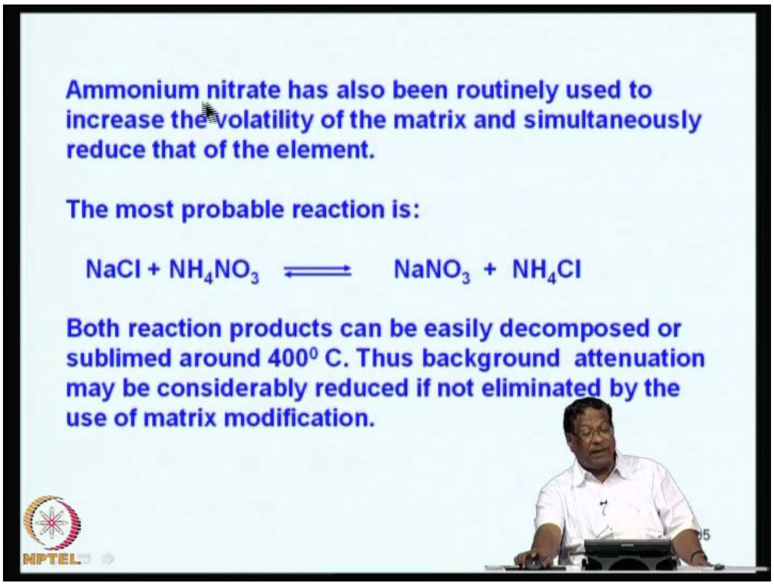

Ammonium nitrate has also been routinely used to increase the volatility of the matrix and simultaneously reduce that of the element.

The most probable reaction is:

$$NaCl + NH_4NO_3 \rightleftharpoons NaNO_3 + NH_4Cl$$

Both reaction products can be easily decomposed or sublimed around 400^0 C. Thus background attenuation may be considerably reduced if not eliminated by the use of matrix modification.

So, most of the biological and organic samples are treated with nitric acid, because the aid in the ashing and most of the pretreatment components can be removed. Now, when we talk of ashing, it is also important for us to think about other substances, why nitric acid alone. Nitric acid is more corrosive, then people have tried ammonium nitrate routinely to increase the volatility of the matrix and simultaneously reduce that of the element.

So, the most notable probable reaction is this; the very simple reaction everybody knows this right from high school level, sodium chloride will react with ammonium nitrate exchanging the anions. So, we get sodium nitrate and ammonium chloride, ammonium chloride can be very easily separated from the matrix even at room temperature. So, the proposition of ammonium nitrate as an ashing aid has gained acceptance, since quite long time now.

So, both the reaction products can be easily decomposed, this n a n o 3 and ammonium chloride, and they can be or they can be sublimed around 400 degree centigrade; thus background attenuation may be considerably reduced, if not eliminated by the use of matrix modification. The addition of sodium, nitric acid, ammonium acetate and palladium nitrate, etcetera, these are all called ashing aids as well as matrix modifiers.

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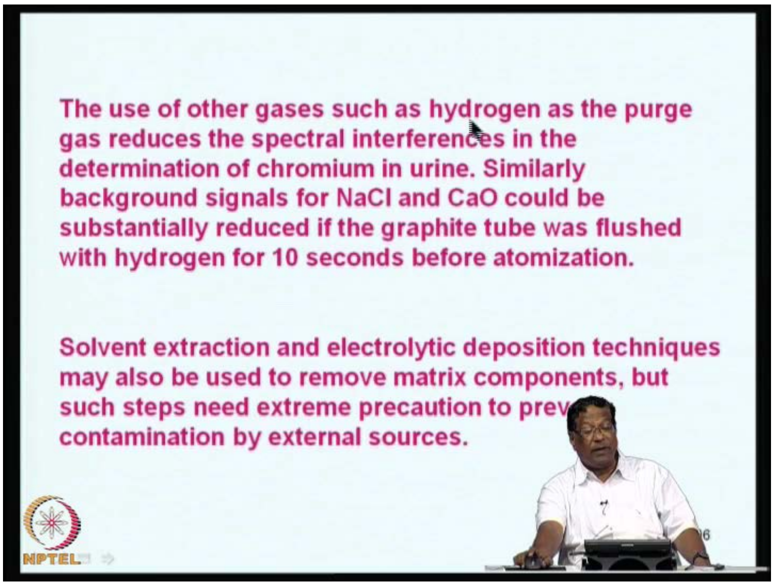

The use of other gases such as hydrogen as the purge gas reduces the spectral interferences in the determination of chromium in urine. Similarly background signals for NaCl and CaO could be substantially reduced if the graphite tube was flushed with hydrogen for 10 seconds before atomization.

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

So, the use of other gases, for example, such as hydrogen as the purge gas, that also reduces the spectral interference in the determination of chromium in urine; for example, urine is also supposed to be very high in sodium chloride contain, almost up to one percent and may be more. And similarly, background signals for sodium chloride and calcium oxide could be substantially reduced, if the graphite tube is flushed with hydrogen just for ten seconds before atomization.

So, how do you do that? That is during the optimization stage. So, you say a pass argon until 800 degree centigrade pretreatment, stop argon introduce hydrogen, it can be done with software and automatically it will pass hydrogen for ten seconds, then go for atomic absorptions with zero gas.

Sometimes it is useful to have solvent extraction and electrolytic decomposition techniques to remove the matrix components, but these are extreme steps. So, such steps need extreme precautions, because you are remember you are always working at nanogram levels. So, contamination is a distinct possibility, as well as loses of the analyte during experimentation is another reality. So, these things are one as to do with extreme precaution.

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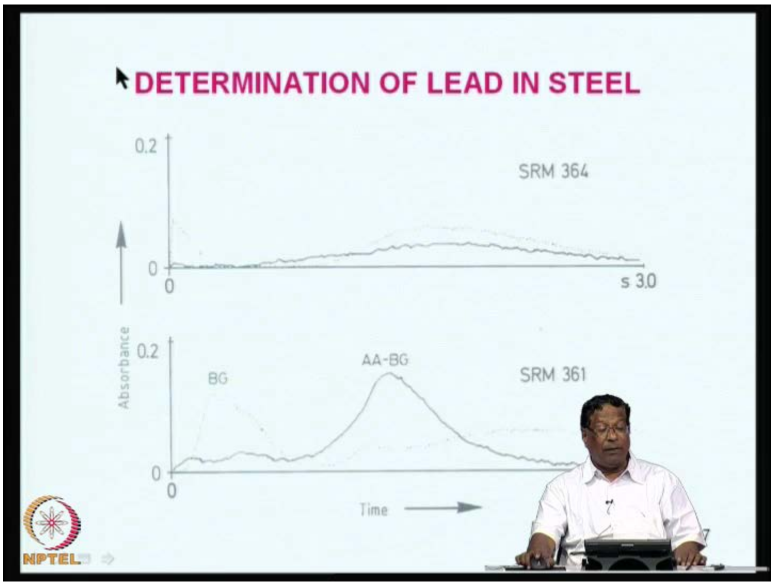

DETERMINATION OF LEAD IN STEEL

Now, I want to show you the determination of lead in steel; this I have tried in, when I was working on a graphite furnace and here you can see SRM 364 is the stainless steel - standard stainless steel - which has be analyzed by number of independent laboratories and each of these analysis are certified.

So, if you treat without background correction, then you have the signal like this and background is at the top; that means, background absorption is much more higher. So, after pretreatment, here what happens? Background is, I do the integration by adding the matrix modifier, I pushed the pretreatment to the right. So, background is already gone, most of the background concomitants, they are already gone by the time we do the integration by about, this is fully three seconds, this is one second.

So, I will say, start measurement after one second, then background is already gone, only the sample will be determined. So, you can see the sample signal which is enhanced. So, such tricks we do employ quite often.

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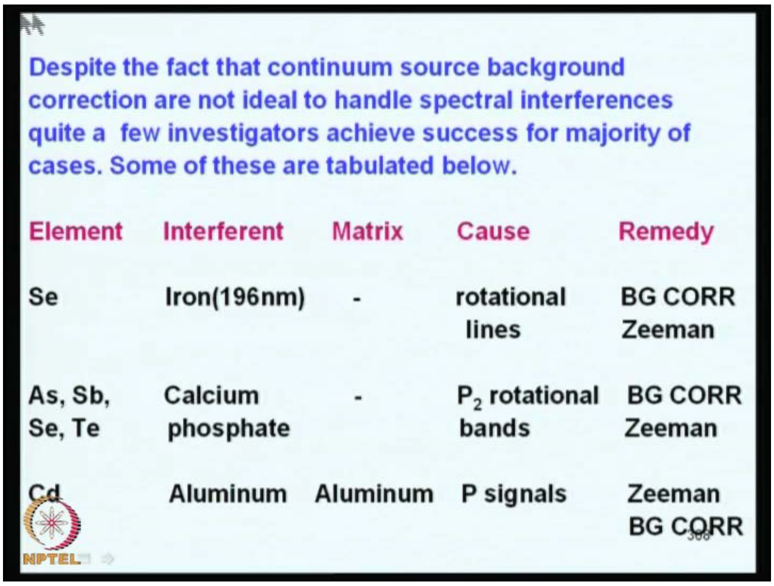

Despite the fact that continuum source background correction are not ideal to handle spectral interferences quite a few investigators achieve success for majority of cases. Some of these are tabulated below.

Element	Interferent	Matrix	Cause	Remedy
Se	Iron(196nm)	-	rotational lines	BG CORR Zeeman
As, Sb, Se, Te	Calcium phosphate	-	P_2 rotational bands	BG CORR Zeeman
Cd	Aluminum	Aluminum	P signals	Zeeman BG CORR

Now, I want to concentrate on the interference techniques how we can handle; for example, some of them I have listed here, this is selenium, interferent is iron; selenium is 196.7 and iron is 196. So, there will be interference and this interference is caused by rotational lines of the Iron, and then remedy, you just 196 and 196.7, it is quite large difference basically. So, spectrophotometer can monochromater can take care of this difference; so, simple background correction is more than enough or zeeman correction.

Now, arsenic antimony, they during their determination, calcium interferes due to the p 2 rotational bands, and then here also background correction and zeeman will take care. Similarly, selenium, tellurium, phosphate interferes zeeman correction; that means, we can conclude that it is something to do with the spectral interference. And the cadmium if you want to determine again aluminum and when the matrix itself is aluminum, you can see that, p signals are always cause the interference and zeeman is the more preferred one compared to normal background correction of deuterium.

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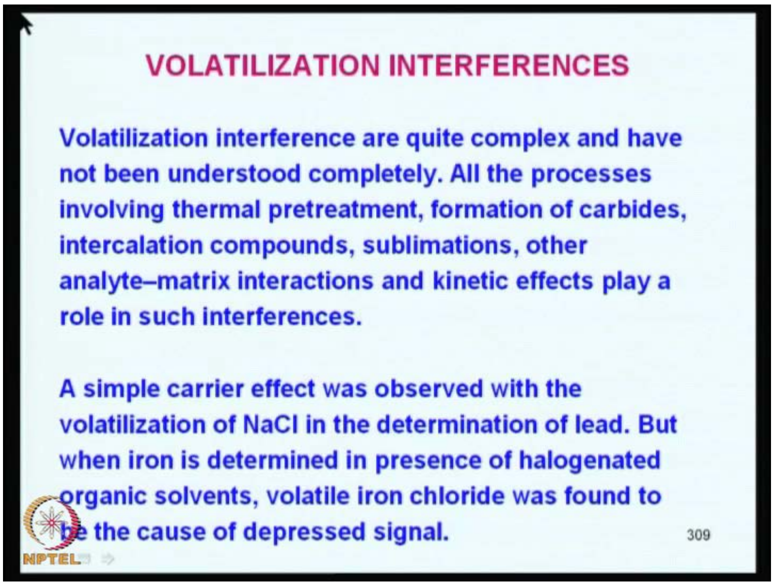

VOLATILIZATION INTERFERENCES

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.

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So, let us talk about volatilization interferences. I refer to this, when we were talking about sodium nitrate and ammonium chloride. And volatilization interferences are quite complex actually; they have not been understood completely. All the processes involving thermal pretreatment, formation of carbides, and then intercalation compounds, sublimations, and other analyte and matrix interactions, kinetic effects, they all play a significant role in such interferences, that is volatilization interferences.

A simple career effect was absorbed with the volatilization of sodium chloride in the determination of lead; just now I showed you that slide, this one lead. And when iron is determined in presence of halogenated organic solvents, volatile Iron chloride was found to be the cause; that means, if you cannot determine iron in presence of large quantities of chloride, because Iron chloride in the species as a species, it will not form iron atoms, it will form Iron chloride, that will give you absorbance. But because it is not atoms, it is not a signal. So, it causes lower signals; it gives you very low signal and depressed signal.

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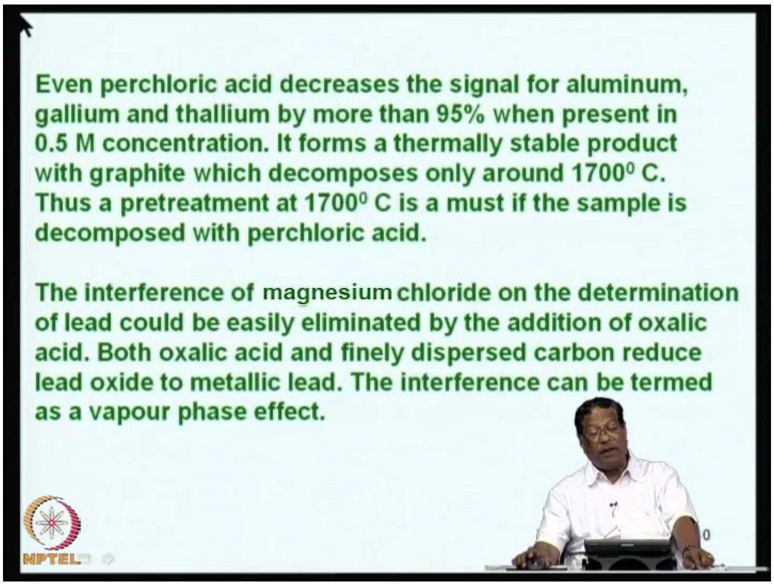

Even perchloric acid decreases the signal for aluminum, gallium and thallium by more than 95% when present in 0.5 M concentration. It forms a thermally stable product with graphite which decomposes only around 1700^0 C. Thus a pretreatment at 1700^0 C is a must if the sample is decomposed with perchloric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

The interference of magnesium 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.

So, even perchloric acid if you use the, it decreases the signal for gallium and thallium by more than 95 percent signal gone, when present in 0.5 molar concentrations; therefore, it forms a thermally stable product with graphite furnace, which decomposes only around 1700 degree centigrade.

Aluminum forms a thermally stable complex with graphite. So, a pretreatment temperature of 1700 degrees is a must, if you want to determine aluminum. And if the sample is decomposed with perchloric acid, aluminum chloride will be forming. So, the interference of magnesium chloride on the determination of lead can be easily eliminated, by the addition of oxalic acid.

These are all small little tricks; if you go through literature, you will know that, I am not getting a signal. So, the look up the literature, then they will say, yes, magnesium chloride can interfere in the determination of lead. So, what to do? So, oxalic acid they they have tried, and finally, dispersed carbon also reduces lead oxide to metallic lead. And once metallic lead is formed, there is no problem, the interference can be termed as a vapour phase interference.

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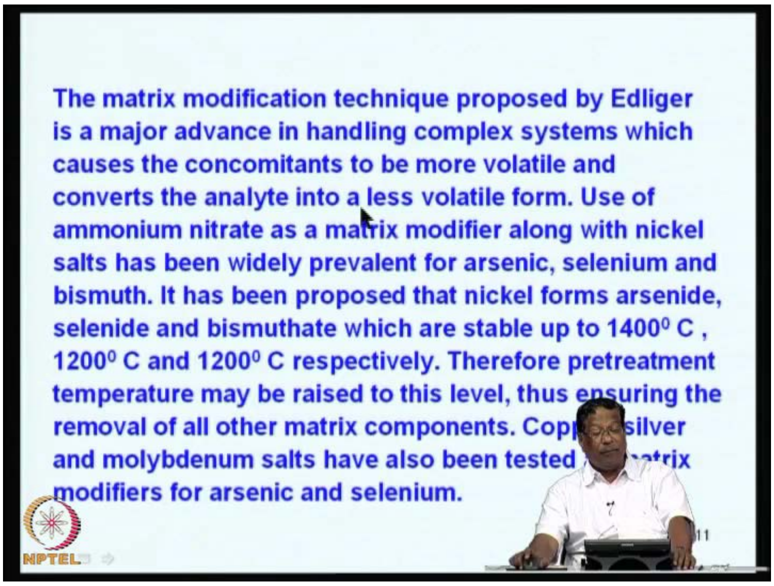

The matrix modification technique proposed by Edliger is a major advance in handling complex systems which causes the concomitants to be more volatile and converts the analyte into a less volatile form. Use of ammonium nitrate as a matrix modifier along with nickel salts has been widely prevalent for 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. Copp silver and molybdenum salts have also been tested atrix modifiers for arsenic and selenium.

So, the matrix modification technique what I was telling has been put on a very strong footing by Edliger. It is a major advance in handling complex systems, which causes the contaminants to be more volatile; and it converts the analyte into a less volatile form, that is a whole idea, you can form alloy. And when the alloy, whenever you form an alloy, alloy has to decompose and then form the metal and then form the metal atoms. So, if you are able to form a metal alloy, it is a good way of reducing the increasing the pretreatment temperature.

So, use of ammonium nitrate I have already explained to you; as a matrix modifier along with nickel, people have used along with nickel, because ammonium nitrite alone will not form a matrix with another metal element, you need another metal element. So, nickel has been tried by edliger.

So, what he did was, he tried nickel salts along with ammonium chloride. So, add 10 m - 10 microliter - of the nickel ammonium solution to your sample in the graphite tube and then start heating. So, as you heat, it will form the alloy. So, when other come alloy component, when other concomitants get out, this alloy composition will be strengthened, that is the logic.

So, it has been used as a matrix modifier with nickel and this he has used for arsenic, selenium and bismuth; it has been proposed that nickel forms nickel arsenide. If you want to determine arsenic, add nickel, nickel arsenide will form, and then nickel selenide will form and then bismuthate can form, which are stable up to 1400 degree centigrade; otherwise, by 900 degrees, you would be losing most of these metals. So, you add nickel salt along with ammonium nitrate, you can straight away increase the pretreatment temperature up to 1400 degree centigrade, without losing any arsenic; otherwise, arsenic is a very volatile element.

So, you would, it would not be easy to determine arsenic up to 1400 degrees, you cannot retain it; it would have gone by the time you reach, 600,700 itself. Similarly, with selenium, 1200 degrees; and bismuthate up to 1200 degrees, you can comfortably go.

Therefore, pretreatment temperature may be raised to this level; thus ensuring the removal of all other matrix element up to 1400, you can remove most of them anyway. So, copper, silver and molybdenum salts also, people have tried; you can use copper salt, you can use silver salt and you can use molybdenum salt along with ammonium nitrate; ammonium nitrate is, its function is basically as an ashing aid, nothing more than that and they have.

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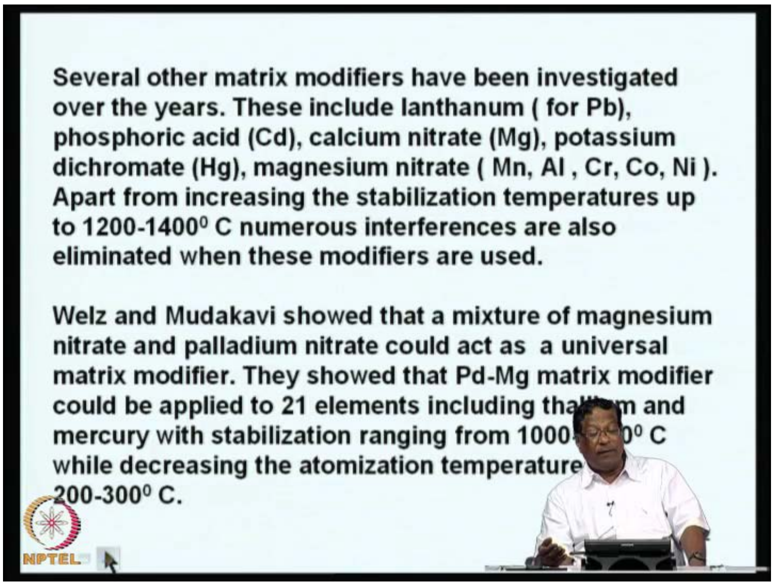

Several other matrix modifiers have been investigated over the years. These include lanthanum (for Pb), phosphoric acid (Cd), calcium nitrate (Mg), potassium dichromate (Hg), magnesium nitrate (Mn, Al , Cr, Co, Ni). Apart from increasing the stabilization temperatures up to 1200-1400^{0} C numerous interferences 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 tha[illegible]m and mercury with stabilization ranging from 1000-[illegible]0^{0} C while decreasing the atomization temperature [illegible] 200-300^{0} C.

These things has been tested as matrix modifiers for arsenic and selenium. So, several other matrix modifiers have been investigated over the years. These include lanthanum salts for lead, phosphoric acid for cadmium; whenever you want to determine cadmium, simply add a little bit of phosphoric acid, so it forms cadmium phosphate and then you can increase the pretreatment temperature. Then, potassium, calcium nitrate has been tried potassium dichromate, that also is a very good one for mercury; magnesium nitrate has been tried for manganese, aluminum, chromium, cobalt, nickel; actually there is a vast literature available on the various types of matrix modifiers, which can be used to increase the pretreatment temperature up to 1200 to 1400 degrees for most of the elements now. So, numerous interferences are also eliminated, when these modifiers are used.

I have used Welz and Mudakavi, I have showed that, a mixture of magnesium nitrate and palladium nitrate can act as a universal matrix modifier. This was the theme on which I was working, so that we could use a single modifier instead of using one modifier for each element, why? We can as well use these two mixtures and then form matrix modifiers for many elements; we work down palladium magnesium matrix modifier on 21 elements, including thallium and mercury.

And with mercury, we could obtain stabilization ranging from thousand up to 1000 degrees and thallium up to 1200 degrees, but many of the other elements we were able to increase the pretreatment temperature to 1900 degree centigrade. While decreasing the atomization, because they are ashing aids, you can decrease also simultaneously atomization temperature. So, we were able to see the decreasing the atomization temperature by at least 200 to 300 hundred degrees, we could do the determination.

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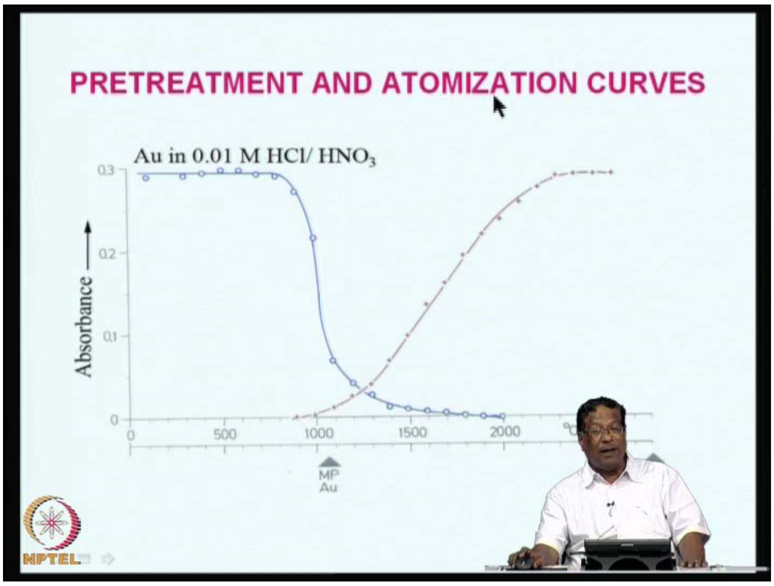

PRETREATMENT AND ATOMIZATION CURVES

So, this is one of the major advances, for example, here I am showing you a pretreatment and atomization curve for gold; in 0.01 h c l, h n o 3 and with matrix modifier, you can see that up to 1000 degrees, there is no loss, almost up to 900, without this. And then, atomization temperature you can see that, it starts from 900 itself; so, as it keeps on increasing, you should not be doing atomization at this stage somewhere around 1500 or 2000 also, because the atomization is not complete. So, it should be in the area of where the curve is becomes horizontal to the x axis.

So, somewhere around 2300, if you measure, you will get the proper absorbance; you can see that in the pretreatment that is in the blue color, the pretreatment atomization is kept maximum and then pretreatment is vary temperature. Here, pretreatment temperature is fixed and atomization temperature is varied. So, I can show you another one or two curves like this; for example, this is for Iron and then in 0.01 molar hcl and 0.005 molar h 2 s o 4 medium, you can see that atomization up to 1500 degrees, up to 1400, there is no loss of Ions, whereas atomization it starts only around 2500 degrees; till that time, we will not get a good signal.

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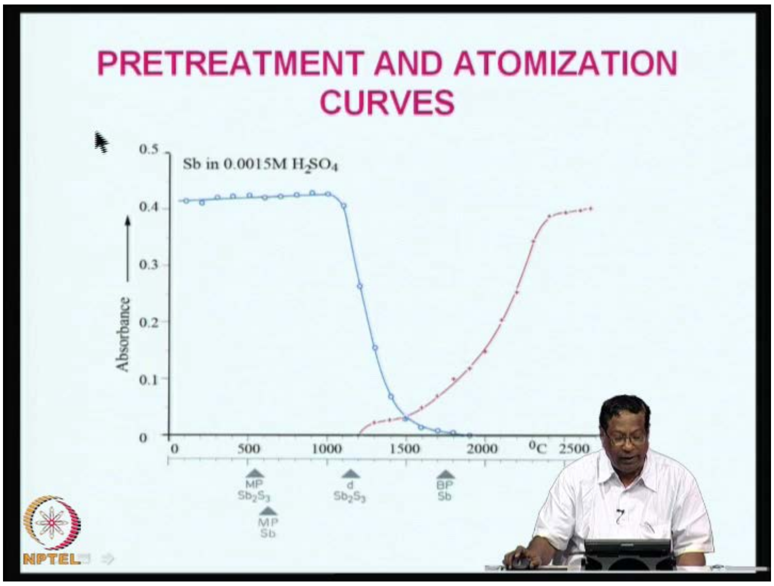

PRETREATMENT AND ATOMIZATION CURVES

So, we do have some more curve; this is for antimony. We can see that the different temperatures have been indicated for this thing; it is possible to determine the temperatures - specific temperature - for example, here I have written that the melting point this 500 centigrade matches with the melting point of antimony sulphide - s b 2 s 3.

We have checked that and then somewhere around 600, antimony melts; once it melts, the vapour pressure will start and you would be losing; but with matrix modifier, up to almost 1000 degree centigrade, antimony can be determined without much loses. So, this is the advantage of matrix modification.

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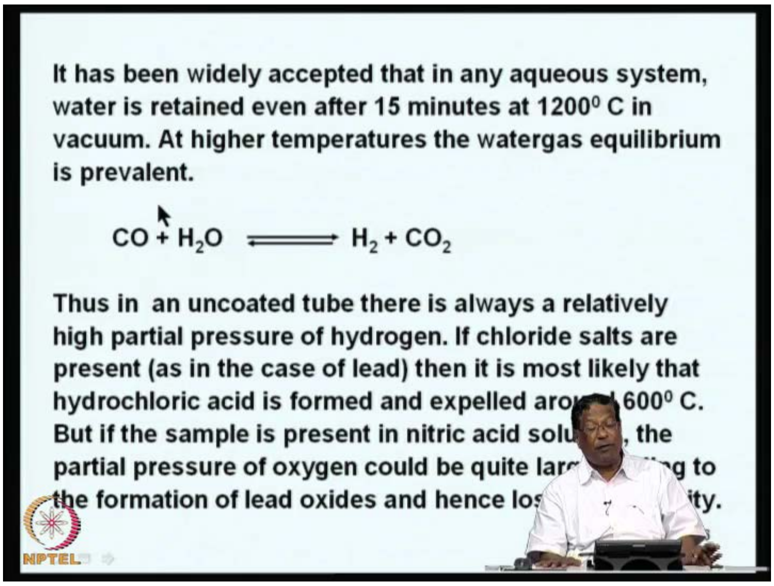

It has been widely accepted that in any aqueous system, water is retained even after 15 minutes at 1200^0 C in vacuum. At higher temperatures the watergas equilibrium is prevalent.

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

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 aro 600^0 C. But if the sample is present in nitric acid solu , the partial pressure of oxygen could be quite lar g to the formation of lead oxides and hence los ity.

So, in any aqueous medium system, water is retained even after 15 minutes at 1200 degrees centigrade. We have to understand that water does not go easily compared to our understanding of 120 degree centigrade, it does not go; still it will be retained in vacuum. At higher temperature, water gas reaction is always prevalent, that is, reaction of carbon monoxide with water to produce h 2 and c o 2.

Therefore, in uncoated tubes, there is always a relatively high partial pressure of hydrogen. So, if chloride salts are present, as in the case of lead we have seen, then it is most likely that hydrochloric acid forms in the graphite furnace coming from different sources, but in the vapour phase hydrochloric acid forms. So, if the sample is in the nitric acid, the partial pressure of the oxygen would be so large, that leading that leads to the formation of lead oxides, and therefore, loss in sensitivity.

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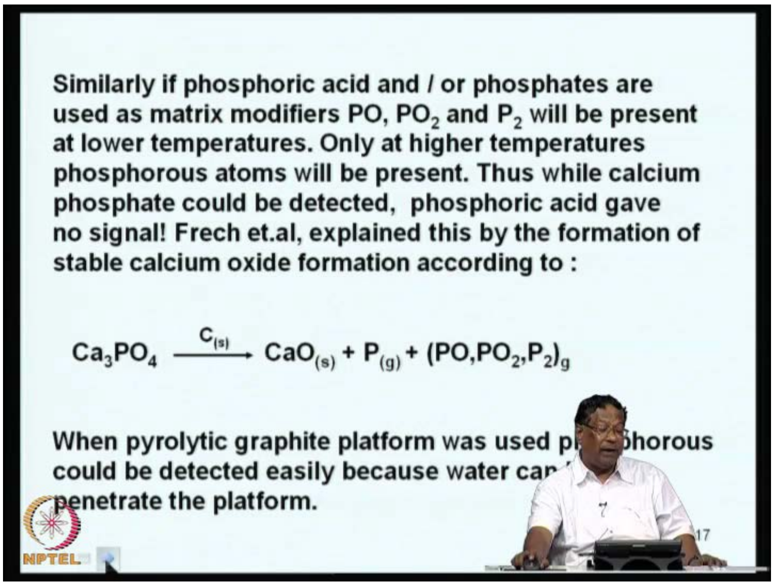

Similarly if phosphoric acid and / or phosphates are used as matrix modifiers PO, PO_2 and P_2 will be present at lower temperatures. Only at higher temperatures phosphorous atoms will be present. Thus while calcium phosphate could be detected, phosphoric acid gave no signal! Frech et.al, explained this 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 p horous could be detected easily because water can penetrate the platform.

So, such a interaction reaction is always possible. And similarly, suppose we have phosphoric acid or phosphates, if you use them as matrix modifier p o, p o 2 and p 2 will be present at lower temperatures. And only at higher temperature, it forms calcium oxide, phosphorous and other gases. So, when pyrolytic graphite platform was used, phosphorous could be detected easily, because water can hardly penetrate the graphite furnace. So, with our matrix modifier, we have used graphite furnace for the determination of phosphorous.

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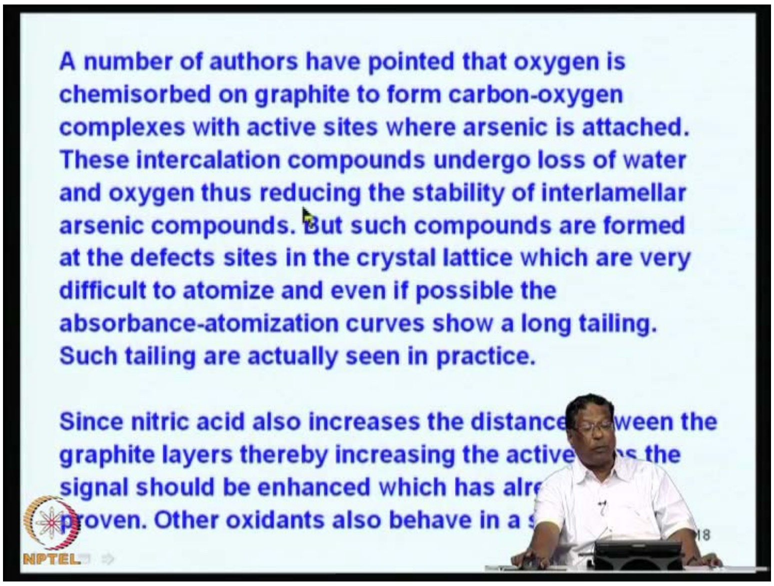

A number of authors have pointed that oxygen is chemisorbed on graphite to form carbon-oxygen complexes with active sites where arsenic is attached. These intercalation compounds undergo loss of water and oxygen thus reducing the stability of interlamellar arsenic compounds. But such compounds are formed 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 ween the graphite layers thereby increasing the active s the signal should be enhanced which has alr proven. Other oxidants also behave in a s

And number of other authors have pointed out that oxygen is chemisorbed on the graphite to form carbon-oxygen complexes; this is a very standard reaction. Whatever is the oxygen coming from the sample, it reacts immediately with the carbon surface to form carbon oxygen complexes, with the at the active sites. So, these intercalation compounds if arsenic you are determining, intercalation compounds also form; they undergo loss of water and oxygen, thus reducing the stability of interlamellar arsenic compounds formed on the surface of the pyrolytic graphite.

So, in the crystal lattice defects are the places, where such reactions can occur. So, it is possible, even if it is possible to determine the atomization absorption curves, they show a long tailing; this tailing we have observed especially in phosphorous this thing. You know, it does not, you do not get a sharp cut off, when you are doing the pretreatment with respect to such compounds. So, such tailings are actually seen in the practice.

Since nitric acid also increases the distance between the graphite layers you know nitric acid gets into the graphite layers and then there is swelling, and it increases the distance between different graphite layers; increasing in the active sides, the signal should be enhanced which has already been proven. So, other oxidants also behave in a similar way. Now, l'vov has developed a micro kinetic theory of sample volatilization for graphite furnace.

According to this theory, the sample is distributed in the form of small small micro crystals, and then small droplets, particles; they are all there well separated from each other, you know, it is not just a complex mixture of everything, but they are all well separated on the atomic scale. So, the sample penetrates into the graphite tube quite often by capillary action. So, the sample can be,if you have something like this, a small capillary will be there, the sample will start penetrating.

So, obviously, after sometime, you would see the graphite furnace in a different shape altogether. So, upon atomization, the sample is removed, but what goes inside the cracks, that cannot be removed, that will remain there. So, even though it may not interfere in the atomic absorption data, but it will deteriorate the quality of the graphite. We have seen even with a magnesium and palladium modifier, it still gets into this thing, we have broken them and looked at the structure in s c m; we still see part of that getting inside the cracks and other things.

So, it is always a compromise when you want to determine the sample in presence of matrix modifiers. This theory gains credence, when used graphite tubes are examined by electoral microscope. After treatment with lead samples which showed the presence of the oxide or metal embedded, this I already explained to you, but it happens with number of other elements also.

So, Slovak and Docekal, these are the two scientists who were working on a mini platform, and delaying the atomization and increasing the sensitivity.

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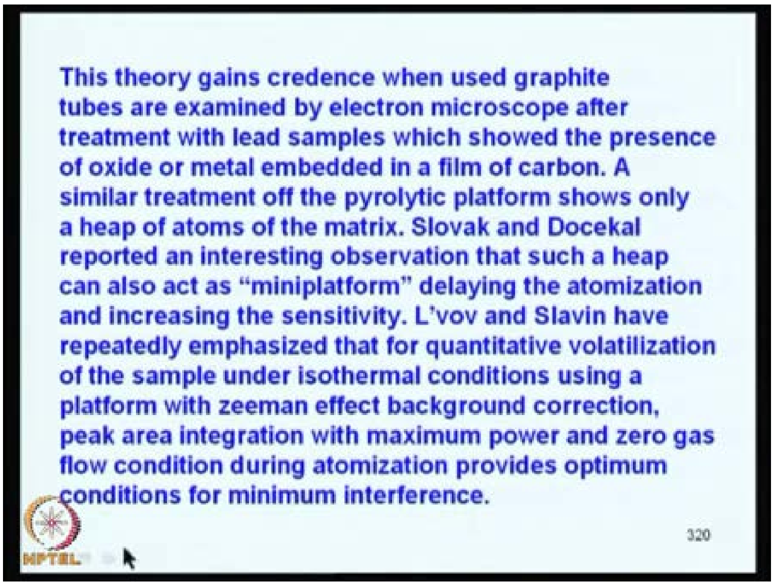

This theory gains credence when used graphite tubes are examined by electron microscope after treatment with lead samples which showed the presence of oxide or metal embedded in a film of carbon. A similar treatment off the pyrolytic platform shows only a heap of atoms of the matrix. Slovak and Docekal 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.

And all these people L'vov, Slavin and Chakrabarty, they have repeatedly emphasized that, 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 conditions during atomization it provides optimum conditions for with minimum interference.

So, what are we looking at now? A platform isothermal conditions, zeeman effect, background correction, peak area integration, zero gas at the time of measurement and interference optimum conditions with minimum interference, that is pretreatment optimization. So, you would see that, such a system would give you fairly good reproducible results. And it has been observed sometimes, that double peaks appear for number of volatile elements like zinc and lead; whenever you use antimony, you would see two peaks.

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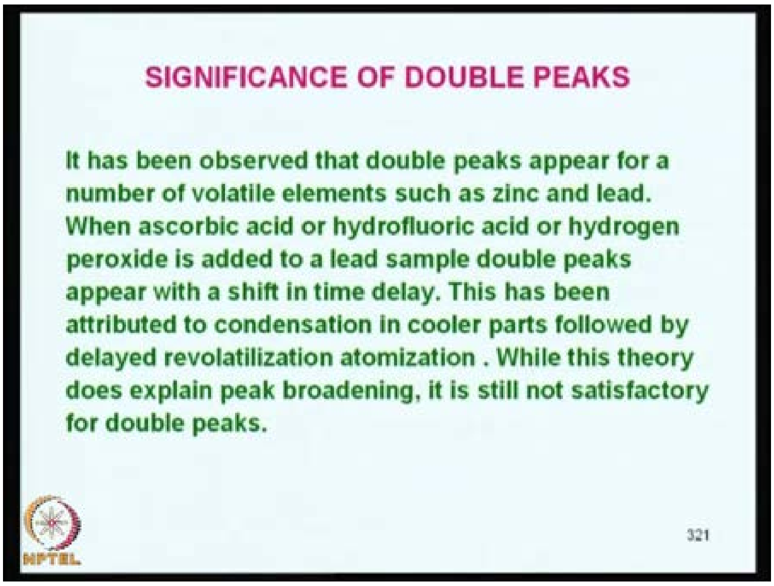

SIGNIFICANCE OF DOUBLE PEAKS

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.

For example, something like this, you would see a curve like this; this is for absorbance versus time signal; this is for antimony. Here, this one would be for antimony three and this one would be for antimony five. Even though it is a separate sig, these are combined still you can you will be able to see that, they form double peaks like this. And one should not confuse these things with a simple atomic absorption curve, so zinc lead etcetera

When ascorbic acid or something else is used to convert them into a single compound, inside the graphite furnace, you will see a single curve . So, the it, when it is added h f or hydrogen peroxide, you can add to a lead sample; the double peaks appear with a shift in the time delay. So, some amount of spaciation work can be done using graphite furnace; this is usually attributed to the condensation in cooler parts followed by delayed re-volatilization; while this theory does explain peak broadening, it is still not satisfactory for double peaks.

We are still very unclear why double peaks appear at all, because if you do the peak integration, you know with platform, people say that it migrates to the end of the tube end of the platform tube. But even when you do with platform, then you should be able to see the single peak, but it does not happen.

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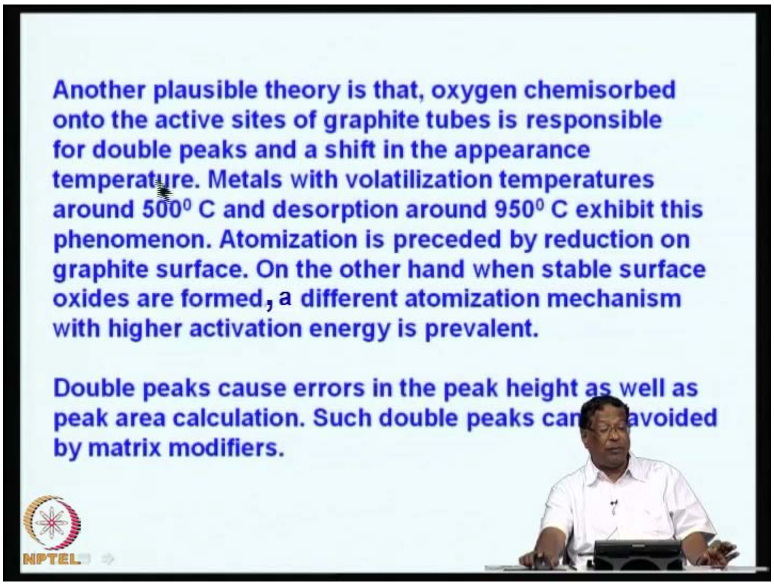

Another plausible theory is that, oxygen chemisorbed onto the active sites of graphite tubes is responsible for double peaks and a shift in the appearance temperature. Metals with volatilization temperatures around 500^0 C and desorption around 950^0 C exhibit this phenomenon. Atomization is preceded 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.

Another plausible theory is that, chemisorbed oxygen onto the active sides of the graphite tubes is responsible for double peaks and a shift in the appearance temperature also is possible. So, metals with volatilization temperatures around 500 degree centigrade and desorption around 950 degree centigrade exhibit this kind of phenomena; that is, antimony, arsenic and selenium sometimes. So, atomization is preceded by reduction on graphite furnace.

On the other hand, when stable surface oxides are formed, a different atomization mechanism itself is possible with higher activation energy. So, double peaks in general cause errors in the peak height, because you do not know how much, which peak to take, what should be the peak height, etcetera. But in peak area, the error can be minimized to certain extent, because when you are doing the atomic absorption in graphite tube, you cannot really control antimony three and antimony five formation; it is all in it all happens in such small interval of few seconds, that it is almost impossible. But these double peaks disappear with matrix modifiers, that is a very strange phenomenon.

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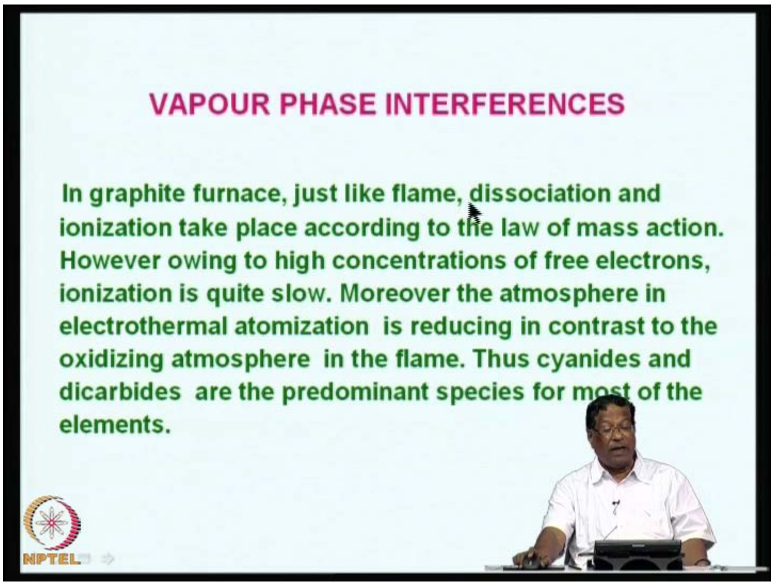

VAPOUR PHASE INTERFERENCES

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, we will also talk a little about a volatile phase interferences. So, just like flame, dissociation and Ionization take place in the graphite furnace, according to the law of mass action. However, owing to high concentration of free electrons, ionization is quite slow. Moreover, atmosphere in the electro-thermal atomization is basically reducing atmosphere in contrast to the oxidizing atmosphere in the flame; this is the difference. So, cyanides, dicarbides, etcetera are the predominant species for graphite furnace.

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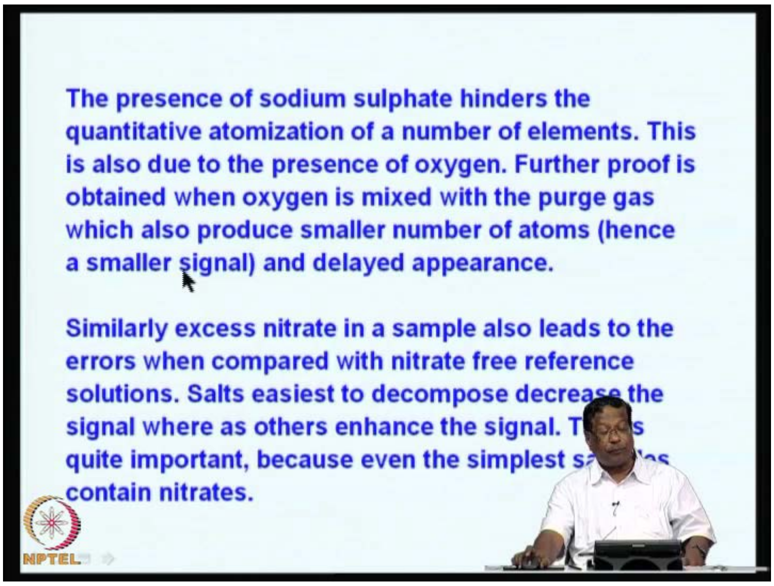

The presence of sodium sulphate hinders the quantitative atomization of a number of elements. This is also due to the presence of oxygen. Further proof is obtained when oxygen is mixed with the purge gas which also produce smaller number of atoms (hence a smaller signal) and delayed appearance.

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, the presence of sodium chloride hinders the quantitative atomization for number of elements; this is due to the presence of oxygen. Further proof is obtained, when suppose you mix oxygen with the gas, then what happens? You will see that the quantitative atomization is always affected in graphite furnace, with oxygen you should add. So, with the purge gas if you do that, it produces number of atoms and delayed appearance; it is a very common phenomena.

Similarly, excess nitrate in a sample leads to errors, when compared with nitrate free reference samples; that means, the absorbance will be different in nitrate samples and nitrate free samples. So, we have worked on the variation of sodium chloride itself, one percent, two percent, three percent, etcetera and we see large amount of volatilization signal attrition taking place and same thing happens with sulphate.

If you increase it up to one percent, above one percent signal gets absolutely dead. So, these things happen in most of the graphite furnaces and other significant vapour phase interference I have put it in table two.

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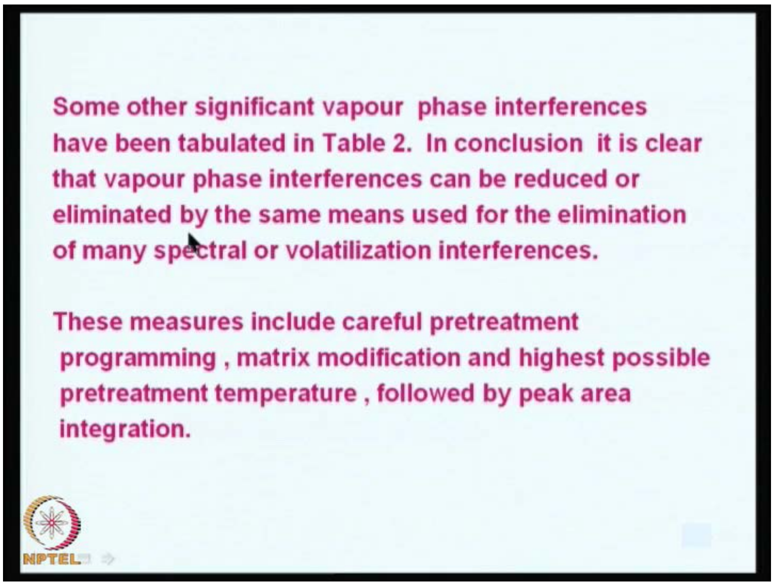

Some other significant vapour phase interferences have been tabulated in Table 2. In conclusion it is clear that vapour phase interferences can be reduced or eliminated by the same means used for the elimination of many spectral or volatilization interferences.

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

So, these systems always work whenever you operate with matrix modifiers. So, you can take care most of these things, and salts easiest to decompose the signal, they decrease the decompose decrease the signal.

So, you should always add salts which do not decompose easily, whereas others this is quite important, because even the simplest salt samples do contain nitrates. So, in conclusion, we can say that it is clear that vapour phase interferences can be reduced or eliminated by the same means, used for elimination of the many spectral and volatilization interferences.

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

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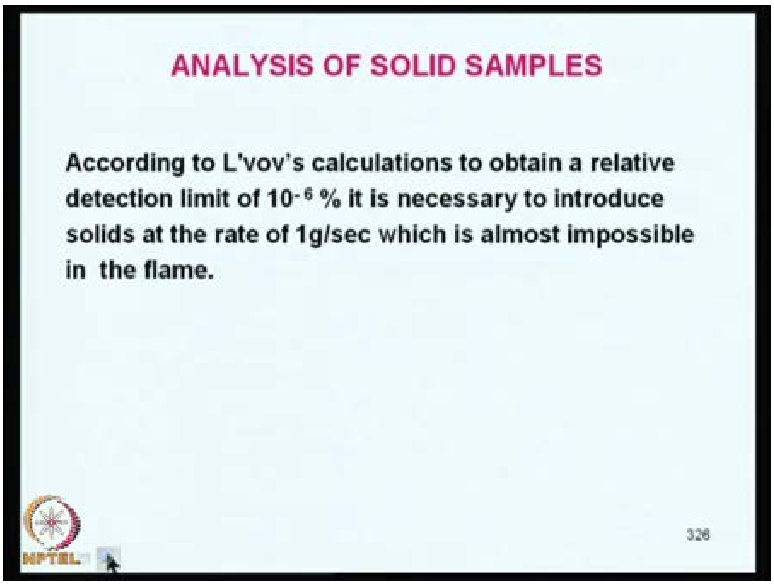

ANALYSIS OF SOLID SAMPLES

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.

At this stage, I just want to in in tell you, that analysis of solid samples can also be done directly in a graphite furnace; that is according to L'vov calculations, it is possible to obtain detection limits of about ten raise to minus six percent. And it is necessary to introduce solids at the rate of one gram per second, which is almost Impossible in the flame.

So, here, we will conclude our discussion on the graphite furnace, but we will refer to it back at the end of the next chapter, that is inductively couple plasma. What I would like to do at that stage is, compare the sensitivities of flame atomic absorption and I s graphite furnace and I c p, so that we can have a comprehensive view of which technique to choose, when we want to do the analysis at ppm ppb and ppt levels. So, we will continue our discussion in the next class.