Modern Instruments Methods of Analysis

Prof. J R Madukavi

Department of Chemical Engineering

Indian Institute of Science, Bangalore

Lecture No. 23

Atomic Absorption Spectrometry-7 Interferences

We were discussing about the interferences and flame atomic absorption, and we are discussing about the elements like refectory oxides like this molybdenum, vanadium, titanium, etcetera and this slide I had shown you in the last class; that is a 1 number 184 slide.

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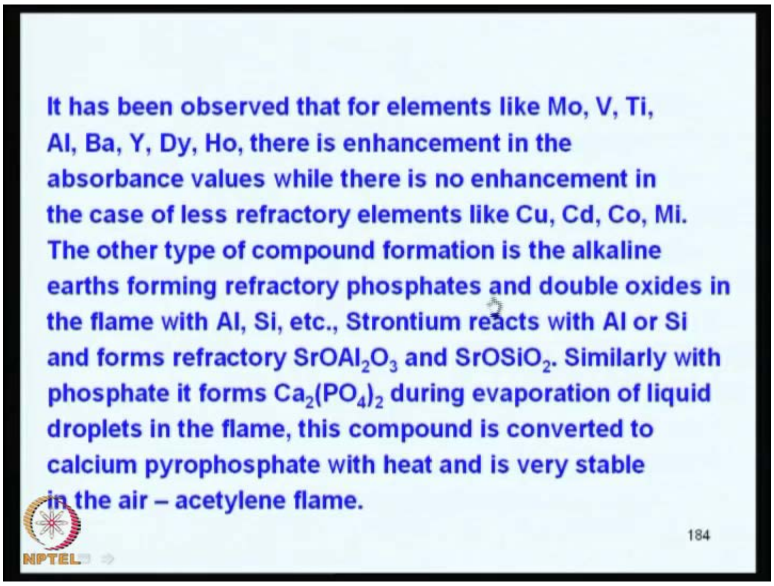

It has been observed that for elements like Mo, V, Ti, Al, Ba, Y, Dy, Ho, there is enhancement in the absorbance values while there is no enhancement in the case of less refractory elements like Cu, Cd, Co, Mi. The other type of compound formation is the alkaline earths forming refractory phosphates and double oxides in the flame with Al, Si, etc., Strontium reacts with Al or Si and forms refractory $SrOAl_2O_3$ and $SrOSiO_2$. Similarly with phosphate it forms $Ca_2(PO_4)_2$ during evaporation of liquid droplets in the flame, this compound is converted to calcium pyrophosphate with heat and is very stable in the air – acetylene flame.

184

This is we have maintain that little will been observed at for elements like molybdenum, vanadium, titanium, aluminum, barium, natrium, disposium, and holmium there is an enhancement in the absorbance values, while there is no enhancement in the case of less refractory elements like Cu, cadmium, cobalt, nickel, etcetera. The other type of compound formation is the alkaline earths forming refractory of phosphates and double oxides in the flame; for example, we have discussed that strontium reacts with aluminum or silicon to form refractory oxides of strontium aluminum that is SrOAl 2 O 3 and also it can form SrOSiO 2 these are double compounds. Similarly with phosphate, it forms calcium phosphate during evaporation of liquid droplets in the flame, and this compound is converted to calcium pyrophosphate in the flame with heat, and it is very stable in the air acetylene flame.

So, what we are essentially discussing is, if there is a possibility for the formation of the oxides refractory oxides, there is enhancement when do we increase the temperature and Co ratio, but in the case of elements like copper, cadmium, cobalt and nickel etcetera

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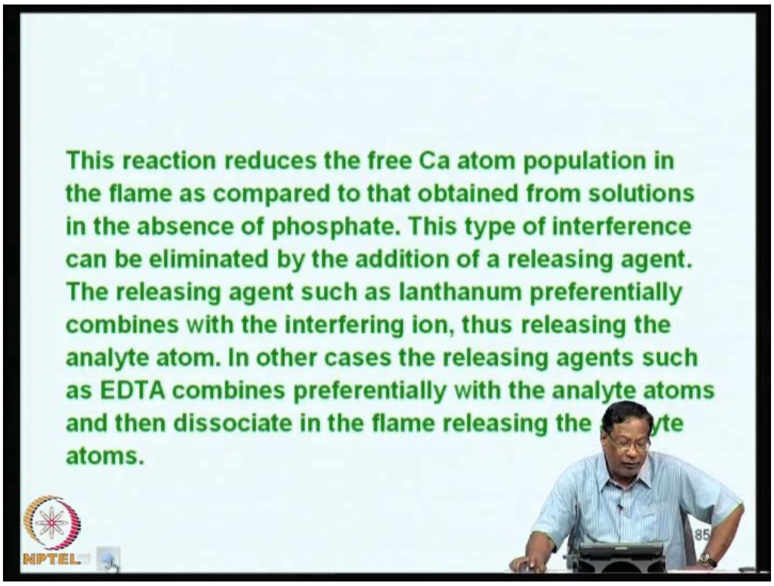

This reaction reduces the free Ca atom population in the flame as compared to that obtained from solutions in the absence of phosphate. This type of interference can be eliminated by the addition of a releasing agent. The releasing agent such as lanthanum preferentially combines with the interfering ion, thus releasing the analyte atom. In other cases the releasing agents such as EDTA combines preferentially with the analyte atoms and then dissociate in the flame releasing the yte atoms.

because, the elements do not form sufficient; do not form the refractory oxides. There is already enough carbon oxygen ratio to provide complete atomization of the sample. So, there is no further enhancement in the signal when we increase the flame temperature. How do we increase the flame temperature is by increasing the ratio of the ex or oxidant as well as fuel gas. So, when we are talking of calcium now, we have said that calcium phosphate forms during the evaporation and pyrophosphate during the when it is in the flame.

So, this reaction reduces the free calcium atom population also because, any compound formation reduces the atomic population, and this happens in the flame as compare to that of obtain from solutions in the absence of phosphate. So, if you want to analysis calcium in agricultural waters, you would normally have phosphates and this type of interference can be eliminated by the addition of a releasing agent. What do we mean by releasing agent is the we add another chemical which will preferentially form a complex with phosphate rather than with calcium.

So, when both calcium and releasing agent are added in a solution containing phosphate, it will react with phosphate releasing the calcium atoms for atomic absorption. So, this concept of releasing agent is a very important concept in atomizing atomic absorption spectrometry. So the releasing agent we usually use lanthanum and it preferentially combines with the interfering ion thus releasing the analyte atom. In other cases, what happens is the releasing agents we can add complexing agent like ADTA. So, ADTA will combine preferentially with several other elements to form compounds and then dissociate in the flame releasing the analyte element. So, this phenomenon of formation of a complex can also be used to release the atoms in the flame after complexization. So the addition of lanthanum releases the calcium atom you can… Are there any other elements any other salt which we can add as a releasing agent if the choice is there, you can add strontium also.

So, strontium also releases calcium ions form the calcium phosphate preferentially forming lanthanum or strontium phosphate. The addition of ADTA preferentially forms calcium EDTA complex if this is more volatile and therefore, it can dissociate relatively easily done calcium phosphate. So now, we have two choices; one is you add a releasing agent like calcium and calcium, lithium and strontium or you add a complexing agent forming calcium EDTA complex and then calcium phosphate; phosphate will remain in the solution and EDTA complex reaches the flame and then atomizes more easily.

So, you can eliminate the interference of phosphate. So, we have published research paper on the determination of indium in a geological sample by adding a mixture of citrate. So, tripotassium citrate and ascorbic acid also we have added in presence of in the in place of lanthanum. So, this approach also works to, but this approach is more useful because, it the try tripotassium citrate forms more complexes with other elements also. So, the it we can eliminate the interferences from several other elements, and it is possible to determine indium in presence of calcium potassium citrate and ascorbic acid.

So, another way of a looking at the interference is, you can go by the method of standard addition. Now, standard addition technique is a very simple technique. It can be used in any analytical technique for that matter, not just atomic absorption, it can be use for spectrophotometry. It can be used in electro analytical methods and several other methods and what we generally do is, we had a non amount of this standard increase the absorbance to all the sample solutions also. So the multiplicative interference can be taken care of in the method of standard edition. So, I will be dealing with standard edition technique, when I want to I will be teaching you with paleography not now because, they even though the principle remain the same, will have other aspects, a theoretical aspects will be dealing with that I will be doing in the when I am teaching paleography, but it does not mean that standard edition technique cannot be used in other spectrophotometer technique also.

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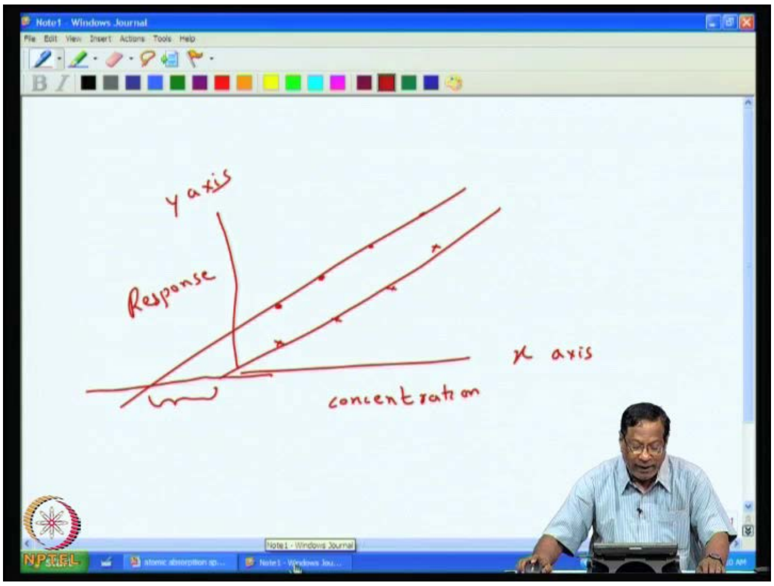

So, for the time being, I will only say that you prefer the standards; you first prepare a standard curve of response verses concentration and then, you will get some sort of a straight line and now what we do is, we had a known quantity of the standard solution to the samples also. So, we draw take the sample; add the same quantity of the known absorbance known standard then, you will get higher response somewhere like this and then, it may depending upon the matrix, you may get a response like this then, what you do is draw a standard curve like this, and the difference where it cuts the x axis; this is x axis and this is y axis. So, the difference is what it corresponds to the unknown.

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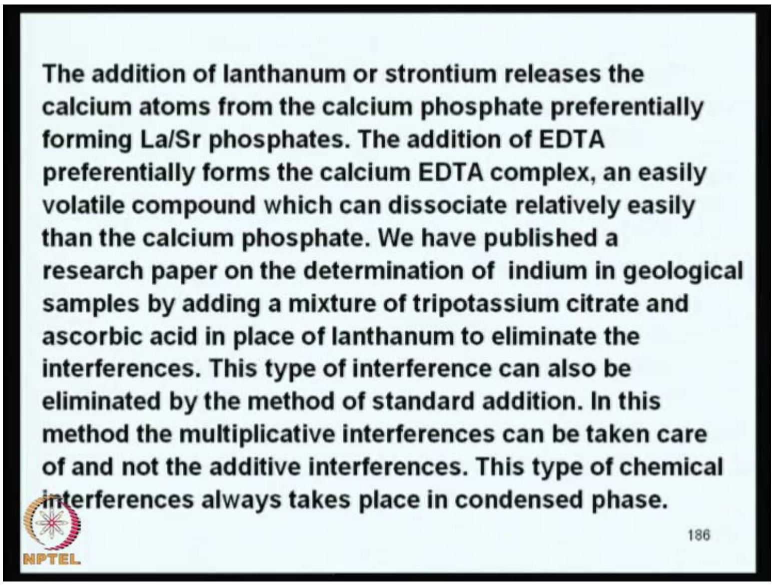

The addition of lanthanum or strontium releases the calcium atoms from the calcium phosphate preferentially forming La/Sr phosphates. The addition of EDTA preferentially forms the calcium EDTA complex, an easily volatile compound which can dissociate relatively easily than the calcium phosphate. We have published a research paper on the determination of indium in geological samples by adding a mixture of tripotassium citrate and ascorbic acid in place of lanthanum to eliminate the interferences. This type of interference can also be eliminated by the method of standard addition. In this method the multiplicative interferences can be taken care of and not the additive interferences. This type of chemical interferences always takes place in condensed phase.

So, this is in principle the standard method, standard edition techniques will study more about it later. Let us understand that this technique can be used to eliminate the interferences. But, to what we can eliminate is, we can eliminate the multiplicative inferences can be taken care of and not the additive interference. What we mean by this is, if this sample is more complicated in terms of presence of other concomitants then, we can take care of the interference by doing this standard edition technique and not the additive interference; additive interference means, you had the some reagent like releasing agent or complexing agent etcetera if that substance interference then, you cannot take care of that, but if the con sample itself is complicated like sea water, a plasma or urine or some other substance with high salt contained etcetera then, it is possible for us to determine the unknown using the standard edition technique.

So, this type of chemical interferences always takes place in the condensed phase that we should remember; that means, we do not have much choice over the interference control because of the complexity of the sample itself. Now, let us look at ionization interference.

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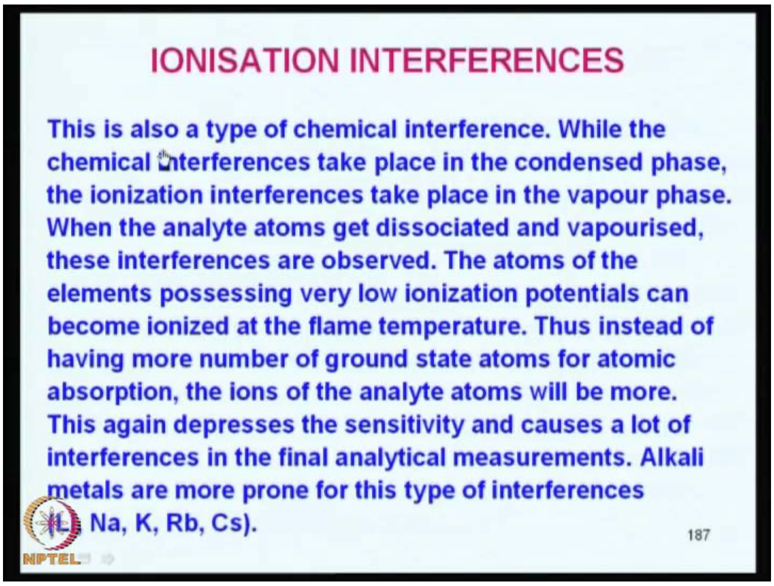

IONISATION INTERFERENCES

This is also a type of chemical interference. While the chemical interferences take place in the condensed phase, the ionization interferences take place in the vapour phase. When the analyte atoms get dissociated and vapourised, these interferences are observed. The atoms of the elements possessing very low ionization potentials can become ionized at the flame temperature. Thus instead of having more number of ground state atoms for atomic absorption, the ions of the analyte atoms will be more. This again depresses the sensitivity and causes a lot of interferences in the final analytical measurements. Alkali metals are more prone for this type of interferences Na, K, Rb, Cs).

So in this slide, I am giving small introduction in the slide; this is always also a type of chemical interference. Ionization interference is also a type of chemical interference, while the chemical interferences take place in the condensed phase. The ionization interferences take place in the vapor phase, this is the important difference. One is, its take place in the condensed phase whereas, ionization interference takes place in the vapor phase.

So, when the analyte atoms get dissociated and vaporized, these interferences are observed that is what it means in the interference in the vapour phases. The atoms of the elements possessing very low ionization potential like calcium, sodium, potassium, salts, etcetera they become ionized at the flame temperature itself. This we have flame temperature itself. This we have seen while we are discussing about the atomization of the alkali salts and alkaline earth salts and other salts. We have I had shown you a table where the sodium salts, concentration of sodium atoms become much more in the at the flame temperature itself.

So at the very like lithium chloride, lithium nitride, potassium chloride, potassium sulfide, potassium nitride many of these alkali salts have very low ionization potential. So, at the flame temperature itself, the concentration of the atoms goes up. So again, while read we will revert back to the slide. So what happens is, in this slide the I have shown you that a instead of having more number of ground state atoms for a atomic absorption, the ions of the analyte atoms will be more; that means, potassium, sodium etcetera atoms will be more. This again depresses the sensitivity because, it causes lot of interferences in the final analytical measurements. So alkali metals are more prone for this type of interferences like what I had told you like lithium, sodium, potassium, rhobidium, cesium, etcetera.

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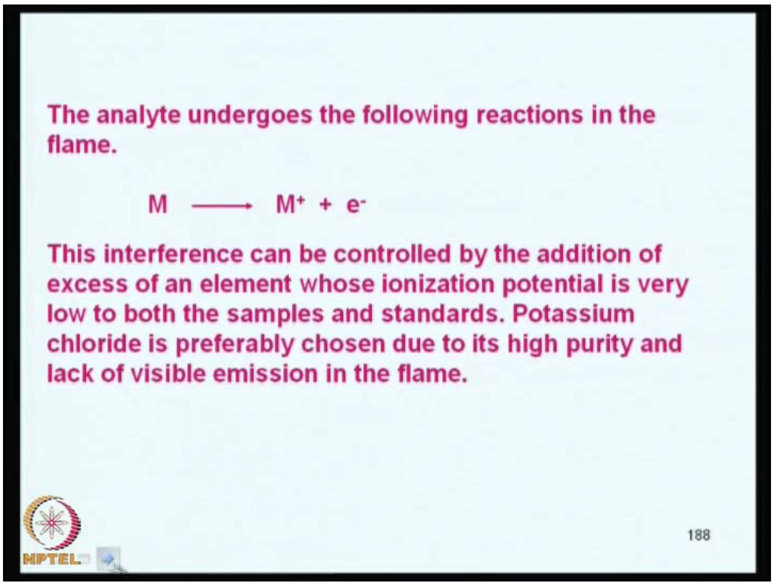

The analyte undergoes the following reactions in the flame.

$$M \longrightarrow M^{+} + e^{-}$$

This interference can be controlled by the addition of excess of an element whose ionization potential is very low to both the samples and standards. Potassium chloride is preferably chosen due to its high purity and lack of visible emission in the flame.

So, ionization interferences are cause by mostly by alkali and alkaline earth metal salts. You would know that many of the alkali and alkaline earth salts come from sea water and other sources. The analyte undergoes the following reaction that is M; M represents a metal ion; it goes to M plus and e minus metal ion plus electron. This interference can be controlled by the addition of excess of an element whose ionization potential is low to both samples and standards. This is a very important concept; that is you have to add the same interferent to the sample as well as standard. So what we do is, we take potassium chloride preferably due to its high purity which available in very purity, and lack of visible emission in the flame. This will reduce the band molecular band absorption.

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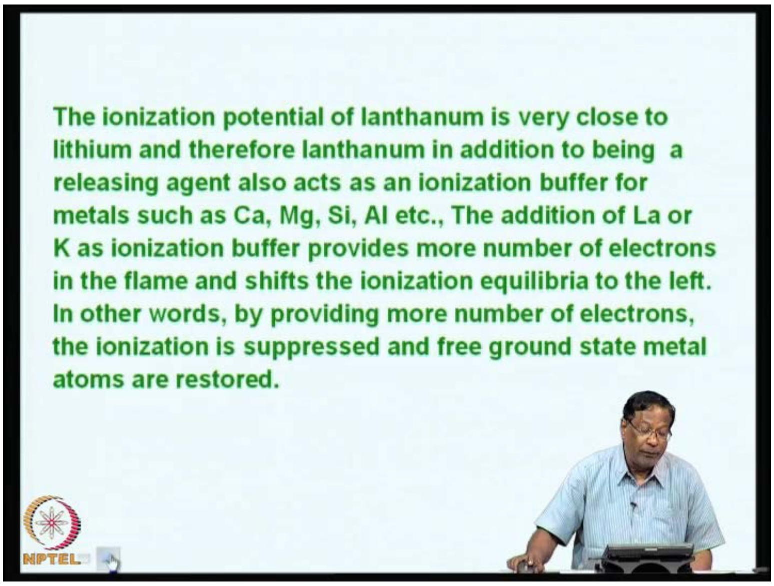

The ionization potential of lanthanum is very close to lithium and therefore lanthanum in addition to being a releasing agent also acts as an ionization buffer for metals such as Ca, Mg, Si, Al etc., The addition of La or K as ionization buffer provides more number of electrons in the flame and shifts the ionization equilibria to the left. In other words, by providing more number of electrons, the ionization is suppressed and free ground state metal atoms are restored.

So the ionization potential of lanthanum is also very close to lithium and therefore, lanthanum in addition to being a releasing agent also acts as ionization buffer for metals such as calcium, magnesium, silicon, aluminum, etcetera. So, there we can use lanthanum also alternatively because, it in addition to being a releasing agent, it also acts as ionizations buffer. So the addition of lanthanum or calcium all as ionization buffer potassium as ionization buffer also, it provides more electrons in the flame, and shift the ionization equilibria to the left.

I have shown you a figure like this. If this reaction is for some other metal I had potassium, you can put a figure, you can put the reaction. Equilibrium can be shifted to the metal atoms to the left this side. So, this is the use of addition of lanthanum as well as potassium etcetera because, they act as ionization buffer. So in other words, by providing more number of electrons, the ionization is suppressed and free ground state metal atoms are restored.

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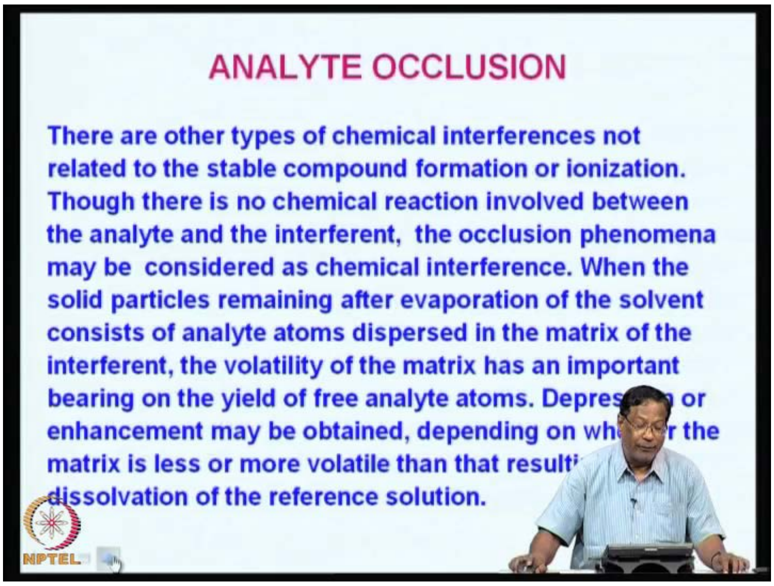

ANALYTE OCCLUSION

There are other types of chemical interferences not related to the stable compound formation or ionization. Though there is no chemical reaction involved between the analyte and the interferent, the occlusion phenomena may be considered as chemical interference. When the solid particles remaining after evaporation of the solvent consists of analyte atoms dispersed in the matrix of the interferent, the volatility of the matrix has an important bearing on the yield of free analyte atoms. Depres or enhancement may be obtained, depending on wh r the matrix is less or more volatile than that resulti dissolvation of the reference solution.

So, other ways of dealing with the interferences and atomic absorption are by analyte occlusion. That is sometimes, the analyte atom gets held up in the matrix and does not release in the flame. So, the… If it is not released in flame, you will definitely not get the atoms in the flame and subsequently, the signal will be lower than when the atom is not occluded. So, how does it happen? The it is not related to the stable compound formation or ionization, and there is no chemical reaction during occlusion between the analyte and the interferent; that means, the matrix. The occlusion phenomena may be considered as chemical interference, but it is not exactly chemical interference; it is actually physical interference. But, because of the nature of the complex sample what you are handling, it does not reach the flame and form the atoms.

So, when the solid particles remain in the flame after evaporation of the solvent, still it consist of the atoms analyte atoms dispersed in the matrix of the solid in the flame. So, the volatility of the matrix itself is a has an important bearing on the yield of free analyte atoms. So, depression or enhancement can happen depending upon whether the matrix is less volatile or more volatile, then that resulting from the dessolvation of the reference solution. It is a very simple concept that the sample if it gets held in the matrix, does not release than the occlusion interfere, we refer to a occlusion interference. It can be considered chemical interference because, the metal atoms do not form the do not form.

But, because of the presence of other elements the metal atoms can form if the occluded sample matrix if it blows up in the flame I may release the atoms also. So, it is a question of relative volatility. So, in this slide I have try put the my thoughts about the analyte occlusion and the depression or enhancement may be obtained depending upon whether the matrix is less volatile or more volatile, then that resulting from the dissolvation of the reference solution, dissolvation not dissolution an example.

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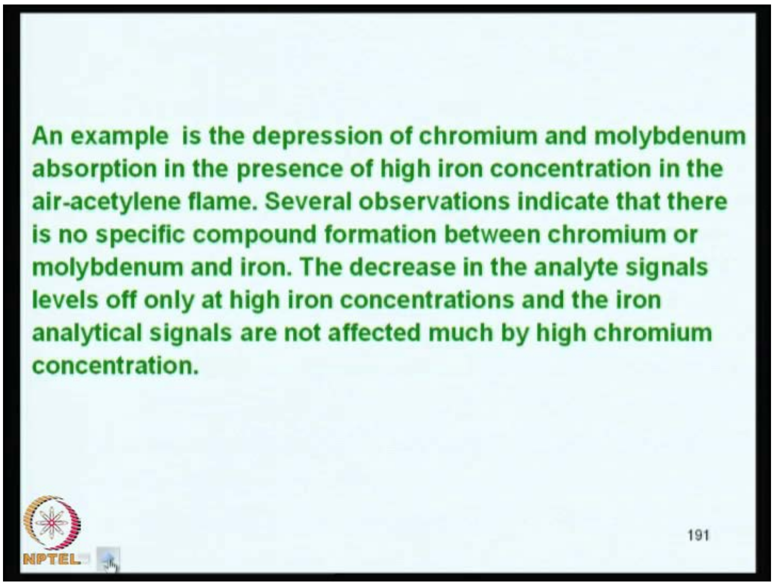

An example is the depression of chromium and molybdenum absorption in the presence of high iron concentration in the air-acetylene flame. Several observations indicate that there is no specific compound formation between chromium or molybdenum and iron. The decrease in the analyte signals levels off only at high iron concentrations and the iron analytical signals are not affected much by high chromium concentration.

Now, I want to give an example. It is the, when you are determining chromium and molybdenum absorption in presence of high iron concentration; that means, suppose, you are analyzing a stainless steel; they will contain chromium or molybdenum, but iron concentration would be very high. So, determination of chromium or molybdenum in presence of high iron concentration is the example. You generally, we do it by air acetylene flame. So several observation indicate that there is no specific compound formation between chromium and or molybdenum and iron; chromium and iron complex formation does not take place; molybdenum iron concentration does not takes place. But, you do get signal which is less than chromium for chromium.

So, they decrease in the analyte signals levels of only at high iron concentration. When the concentration of iron is more, they decrease; it gets you get lower signal and then, it slowly tappers of and the iron analytical signals are not affected because, if you want to determine iron in the same sample, they are not affected by high chromium. But, if you want determine chromium in the same sample, we have the problem of lower signal. So, this slides to give an example of this type of interference or chemical occlusion, chromium and molybdenum absorption in presence of high concentration.

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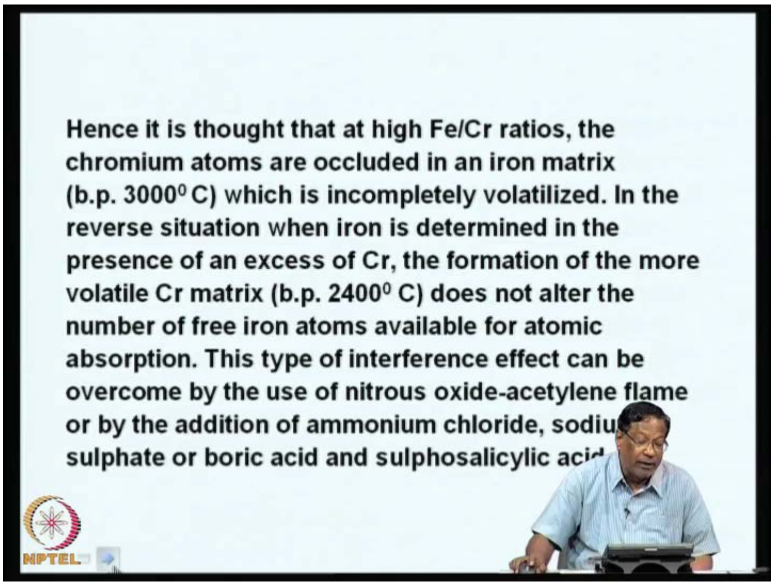

Hence it is thought that at high Fe/Cr ratios, the chromium atoms are occluded in an iron matrix (b.p. 3000^0 C) which is incompletely volatilized. In the reverse situation when iron is determined in the presence of an excess of Cr, the formation of the more volatile Cr matrix (b.p. 2400^0 C) does not alter the number of free iron atoms available for atomic absorption. This type of interference effect can be overcome by the use of nitrous oxide-acetylene flame or by the addition of ammonium chloride, sodiu sulphate or boric acid and sulphosalicylic aci

So this, it is thought that at high iron chromium ratios, the chromium atoms are occluded in the iron matrix. What is the boiling point of iron, is around 3000 degrees for this type of alloy which is incompletely volatilized because, the temperature of the flame is around 2400 to 2500 degrees. Definitely, if the boiling point is 3000 degree centigrade then, it will not be volatilized. In the reverse situation now, reverse situation means, when we want to determine iron, iron is determined in presence of excess of chromium that is when the chromium is there the formation of the more volatile chromium cum matrix does not alter the number of free iron atoms available for atomic absorption.

So, this type of interference can be overcome by using nitric oxide acetylene flame which will give you a very high temperature so that everything is volatilized. Alternately, you can add the addition of ammonia, ammonium chloride, sodium sulphate or boric acid or and sulphosalicylic acid to form the complexes. This way also you can handle this kind of interference.

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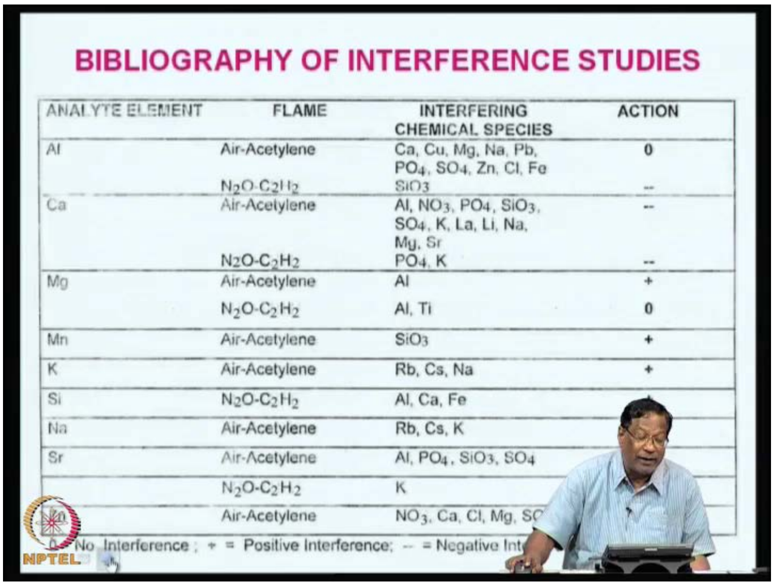

BIBLIOGRAPHY OF INTERFERENCE STUDIES

ANALYTE ELEMENT	FLAME	INTERFERING CHEMICAL SPECIES	ACTION
Al	Air-Acetylene	Ca, Cu, Mg, Na, Pb, PO_4, SO_4, Zn, Cl, Fe	0
	N_2O-C_2H_2	SiO_3	--
Ca	Air-Acetylene	Al, NO_3, PO_4, SiO_3, SO_4, K, La, Li, Na, Mg, Sr	--
	N_2O-C_2H_2	PO_4, K	--
Mg	Air-Acetylene	Al	+
	N_2O-C_2H_2	Al, Ti	0
Mn	Air-Acetylene	SiO_3	+
K	Air-Acetylene	Rb, Cs, Na	+
Si	N_2O-C_2H_2	Al, Ca, Fe	
Na	Air-Acetylene	Rb, Cs, K	
Sr	Air-Acetylene	Al, PO_4, SiO_3, SO_4	
	N_2O-C_2H_2	K	
	Air-Acetylene	NO_3, Ca, Cl, Mg, S	

0 = No Interference ; + = Positive Interference; -- = Negative Int

Now, I want to give you a bibliography of interference studies. In general, it is only a guideline that, if you want to determine aluminum, the typical flames are air acetylene, nitrous oxide, acetylene also can be used. The interfering chemical species I have listed out here calcium, copper, magnesium, sodium etcetera. And there is not much you can do the action and if I put 0; that means, if you see 0 in the action; that means, there is no interference; positive plus means positive, there is interference and negative means negative interference; positive interference means, there is enhancement of the signal and negative means, there is decrease in the signal. So, you can see that calcium, molly magnesium, manganese, excreta; so some of them are I have listed only for your guidance.

So, it is self exclamatory I do not have to say more regarding this because, the interference also depends upon the number of matrix size and then matrix type etcetera. This serve only as a general guideline; for example, your determining silicon with nitrous oxide air acetylene flame we can say, you can see some sort of enhancement of the signal due to aluminum, calcium and iron. So, if your determining silicon in air then obviously, there will be iron and aluminum in the samples, and you may get a signal like this. One has to slightly care full when you want to determine the elements, but more details can add from the regular text book regarding the interference.

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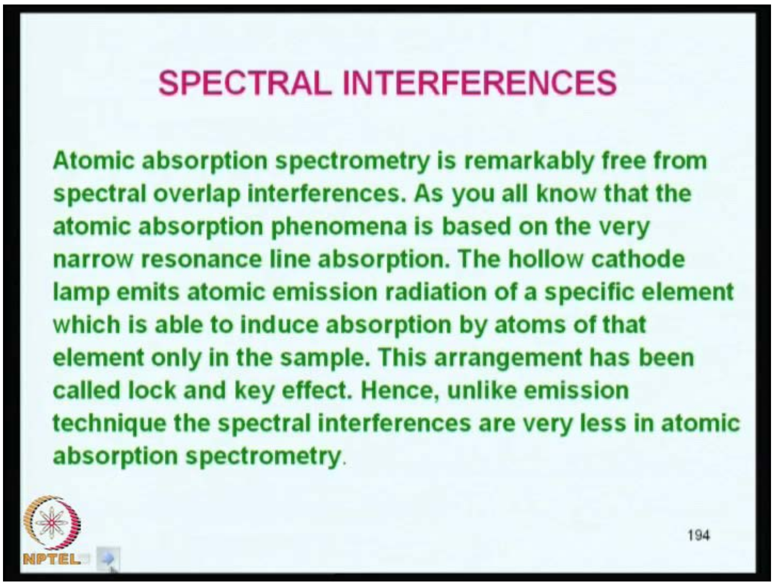

SPECTRAL INTERFERENCES

Atomic absorption spectrometry is remarkably free from spectral overlap interferences. As you all know that the atomic absorption phenomena is based on the very narrow resonance line absorption. The hollow cathode lamp emits atomic emission radiation of a specific element which is able to induce absorption by atoms of that element only in the sample. This arrangement has been called lock and key effect. Hence, unlike emission technique the spectral interferences are very less in atomic absorption spectrometry.

So, other way is another type of interference is spectral interference. This we have discussed earlier number of times; I will while discussing the interferences, I would like to include this spectral interferences. It is basically atomic absorption spectrometry is remarkably free from spectral overlaps. As you all know that the atomic absorption is based on the very narrow resonance line absorption. The hallow cathode lamp emits the emission radiation of a specific element. Therefore, it is supposed to be specific for the element and this arrangement where it absorbs the atoms of the same element, it is called lock and key effect. Hence, unlike emission technique, spectral interferences are very less in atomic absorptions spectrometry. I have given you earlier couple of examples also where spectral interferences do occur. So, when an absorbing element wavelength of an element is a in the present in the sample, but not being determine falls in the same bandwidth they have the spectra interference.

So, if there is spectral interference difference the absorbance value will be higher than the known standards. So, there is a whenever you want to determine any element using a atomic absorption, the manufactures will provide you a book which will give you a all the specific conditions for the analysis of a particular element; for example, if you want to determine copper, he will say copper you can determine if they information you will get is, what is the linearity range; what gas you should use; what should be the oxidant; what should be the reluctant; that is a oxidant and what should be the fuel. It could be either acetylene air or nitrous oxidize and acetylene like that and then, he will also tell you what is the medium of the medium in which the sample should be dissolved.

And, he will tell you that for a known concept typical concentration of let us say 5 PPM, they observe 1 PPM absorption should be about 0.3. Now suppose, you get higher absorbance 0.4 then, you known that there could be some spectral interference because, other than the spectral interference, the analysis will not be complete if you show higher absorbance; it means, either you have done a mistake while you preparing your standard solutions or there is sub element of uncertainty in your analysis, and the or there could be spectral interference. So, only three possibilities; one is element of uncertainty and you element of error or spectral interference.

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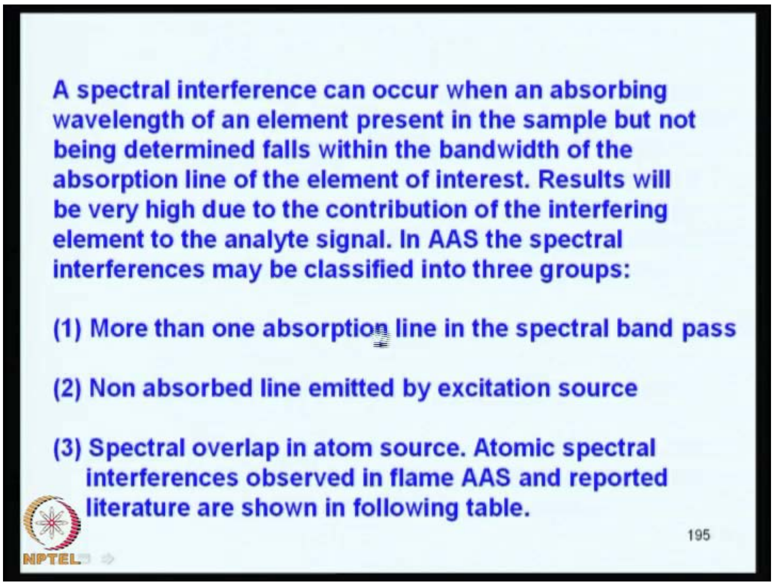

A spectral interference can occur when an absorbing wavelength of an element present in the sample but not being determined falls within the bandwidth of the absorption line of the element of interest. Results will be very high due to the contribution of the interfering element to the analyte signal. In AAS the spectral interferences may be classified into three groups:

(1) More than one absorption line in the spectral band pass

(2) Non absorbed line emitted by excitation source

(3) Spectral overlap in atom source. Atomic spectral interferences observed in flame AAS and reported literature are shown in following table.

So, because at the wavelength of measurement it is only the resonance line so, the… In AAS, spectral interference may be classified into three groups. More than one absorption line in this spectral band pass it can happen. Non absorbed line emitted by an excitation source; for example, flame this we have discussed earlier and spectral overlap in the atom source. So, atomic interference of absorbed in the flame AAS and reported in the literature. The non specific absorption, we have seen that scattering phenomena etcetera you can see in the slide also

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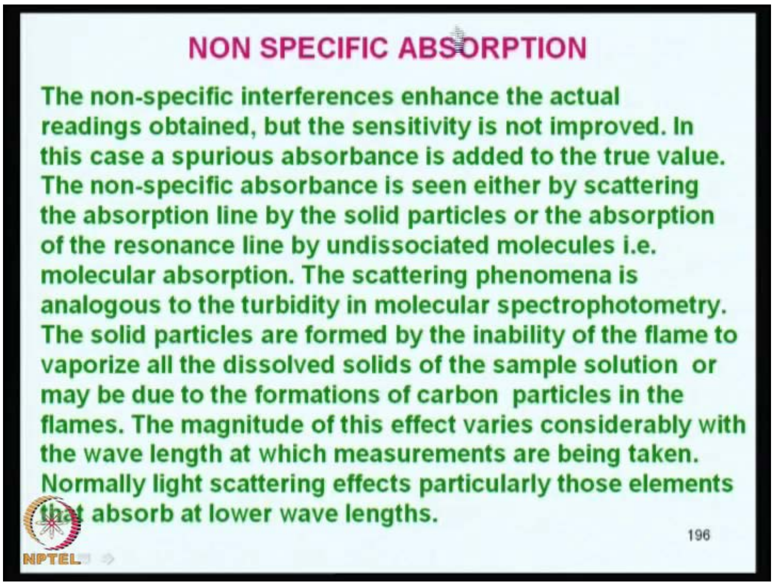

NON SPECIFIC ABSORPTION

The non-specific interferences enhance the actual readings obtained, but the sensitivity is not improved. In this case a spurious absorbance is added to the true value. The non-specific absorbance is seen either by scattering the absorption line by the solid particles or the absorption of the resonance line by undissociated molecules i.e. molecular absorption. The scattering phenomena is analogous to the turbidity in molecular spectrophotometry. The solid particles are formed by the inability of the flame to vaporize all the dissolved solids of the sample solution or may be due to the formations of carbon particles in the flames. The magnitude of this effect varies considerably with the wave length at which measurements are being taken. Normally light scattering effects particularly those elements that absorb at lower wave lengths.

this non specific interference enhance the actually readings obtain, but the sensitivity does not improve. In this case, a spurious absorbance is added to the true value.

So, it is seen either by scattering absorbance line by the solid particles or absorption of resonance line by undissociated molecules that is molecular absorption. The scattering phenomenon is analogous to the turbidity in spectrophotometry. They are formed by the inability of the flame to decompose the dissolved solids, decomposed the solids or it may be due to the formation of carbon particles in the flame. So, the magnitude of this turbidity or solid particles scattering, where is considerably with the wavelength at which measurements are being made. So, scattering could be one of the important spectral interference. Normally, light scattering effects particularly those elements that absorbed at lower wavelengths.

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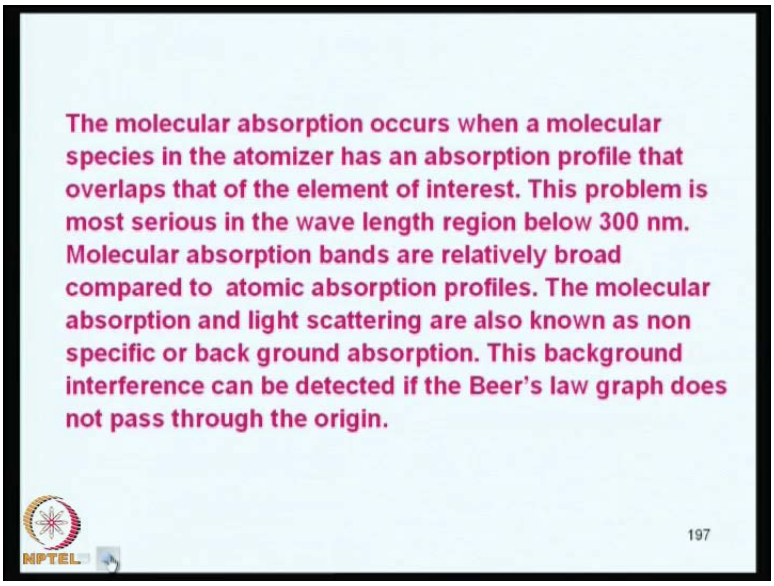

The molecular absorption occurs when a molecular species in the atomizer has an absorption profile that overlaps that of the element of interest. This problem is most serious in the wave length region below 300 nm. Molecular absorption bands are relatively broad compared to atomic absorption profiles. The molecular absorption and light scattering are also known as non specific or back ground absorption. This background interference can be detected if the Beer's law graph does not pass through the origin.

So, UV there could be lot of interference and molecular absorption occurs when the molecular species in the atomizer as an absorption profile that is measured at a they resonance wavelength. And this problem is more serious in the wavelength region below 300. That is why, we have a problem of analysis of elements like selenium and then arsenic, tellurium, etcetera because their absorb resonance lines are below 300 nanometers.

So, molecular absorption bands are relatively board compare to atomic absorption profiles. So, this you both these are known as non specific or background absorption. So it can be detected if the beer Lombard laws does not pass through the origin;

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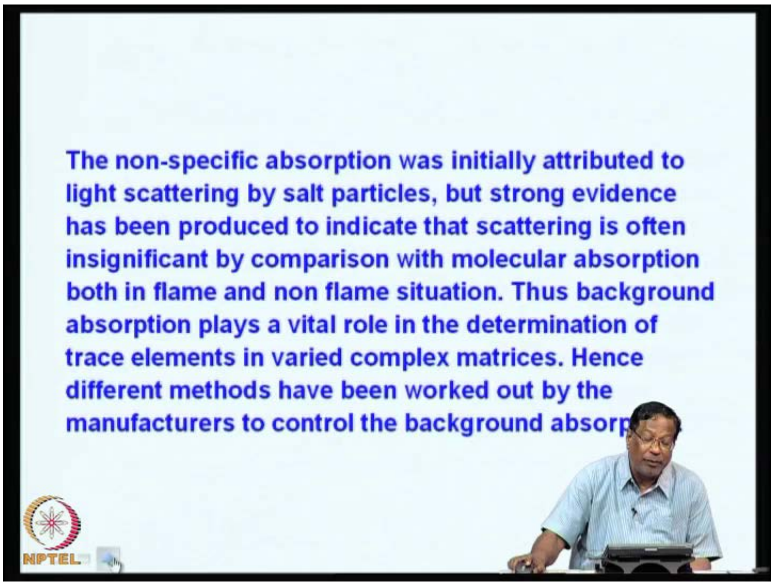

The non-specific absorption was initially attributed to light scattering by salt particles, but strong evidence has been produced to indicate that scattering is often insignificant by comparison with molecular absorption both in flame and non flame situation. Thus background absorption plays a vital role in the determination of trace elements in varied complex matrices. Hence different methods have been worked out by the manufacturers to control the background absorp

that means, there could be non-specific absorption and basically, it was attributed to light scattering by salt particles, but strong evidence has been produced to indicate that scattering is often in significant by compression with molecular absorption both in flame and non flame situation; that is electro thermal atomic absorption.

Thus background absorption plays a virtual role in the determination of trace elements in varied complex matrices. Therefore, different methods have been worked out by the manufacturer to control the background absorption because, spectral absorption nothing can be done,

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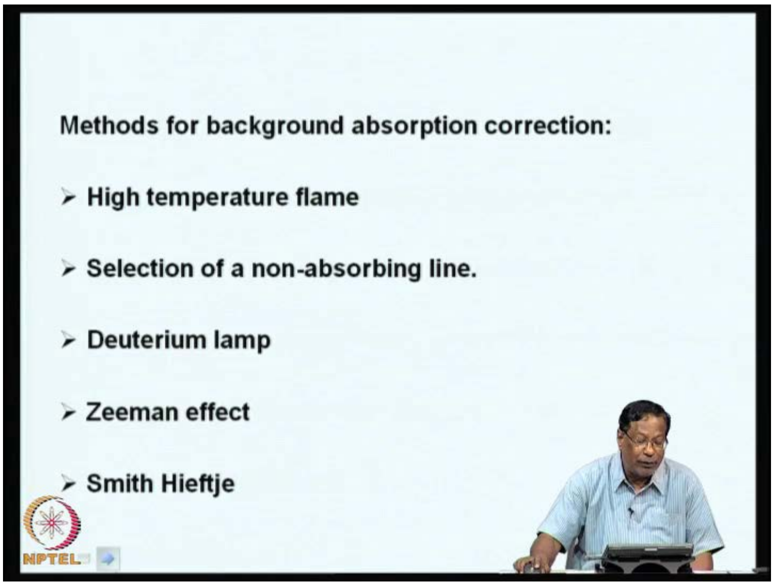

Methods for background absorption correction:

- **High temperature flame**
- **Selection of a non-absorbing line.**
- **Deuterium lamp**
- **Zeeman effect**
- **Smith Hieftje**

we are go for different types of Zeeman effect background correction etcetera. But, the important background corrections are high temperature flame, selection of a non-absorbing line you can go, deuterium lamp, Zeeman effect, Smith Hieftje the all things we have discussed earlier.

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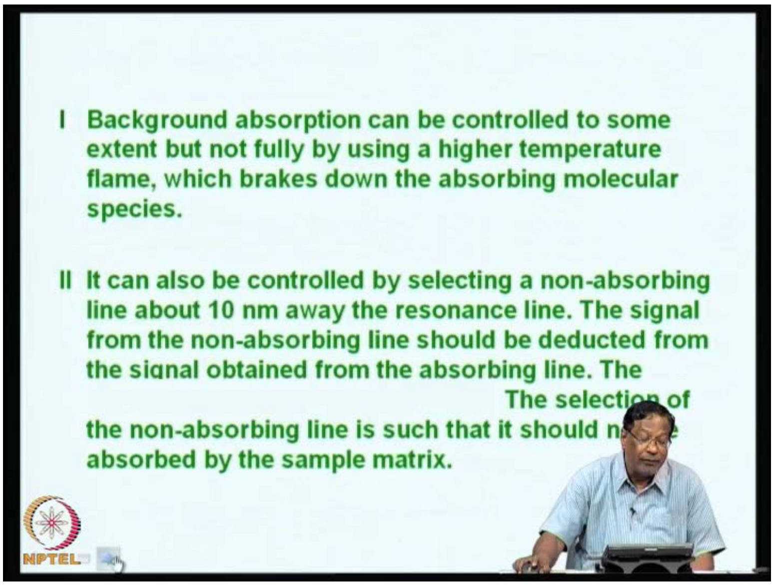

I Background absorption can be controlled to some extent but not fully by using a higher temperature flame, which brakes down the absorbing molecular species.

II It can also be controlled by selecting a non-absorbing line about 10 nm away the resonance line. The signal from the non-absorbing line should be deducted from the signal obtained from the absorbing line. The
The selection of
the non-absorbing line is such that it should n e absorbed by the sample matrix.

So, background absorption it can be controlled to some extent, but not fully by using high temperature flame, but which breaks down the molecular species itself can be destroyed. Then, molecular absorption does not take place. So, it can be controlled by selecting non absorbing line about 10 meter 10 nanometer away from the resonance line. So, they can measure the absorbance 10 nanometers away whatever is the absorbance subtracted from the known atomic absorption line at a resonance line because, it is fairly board; you will there will not be not much error in the background correction.

So, the signal from the non absorbing line should be deducted from the signal obtained from the absorbing line. This is a good way of treating the analysis data that is absorption of a background correction. So, the selection of the non absorbing line should be such that, it should not be absorb by the sample matrix that is only the criteria. That is very important in choosing this kind of background correction, but it is not very scientific. So, the most widely used system is deuterium lamp.

So, we have already pointed out that, the atomic absorption lines are very narrow of the order of 10 to 50 nanometers. When an atomic line from hallow cathode line passes through an atom either, it will be absorb by the atoms. So by subtracting, you can pass through the radiation through the sample and once without the sample that is what deuterium lamp. So then, you can modulate it and it gives you a board spectrum deuterium lamp. So, you can correct the measure the absorbance at the deuterium using the deuterium lamp or a up to 300 nanometers without any problem; subtract that absorbance data from the atomic absorption signal.

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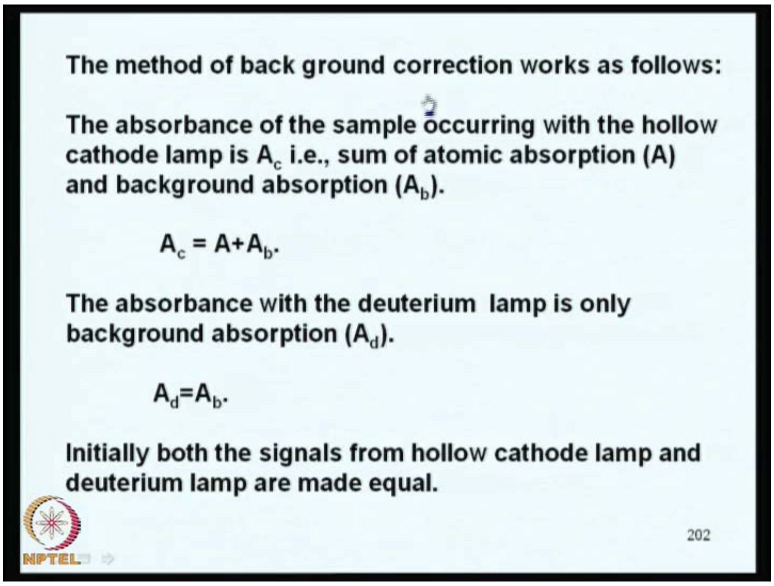

The method of back ground correction works as follows:

The absorbance of the sample occurring with the hollow cathode lamp is A_c i.e., sum of atomic absorption (A) and background absorption (A_b).

$$A_c = A + A_b.$$

The absorbance with the deuterium lamp is only background absorption (A_d).

$$A_d = A_b.$$

Initially both the signals from hollow cathode lamp and deuterium lamp are made equal.

So, the technique of a atomic absorption correction works like this. The absorbance of the sample occurring with the hallow cathode lamp is the sum of atomic absorption and background correction. This is very easy to understand for us. So, you can write A c is equal to A plus A b, where A is atomic absorption and A b is the background absorbance. So, absorbance of the deuterium lamp gives you only A d deuterium lamp, but that should be equivalent to A b. Initially, both the signals from the hallow cathode lamp and deuterium lamp are made equal. This also

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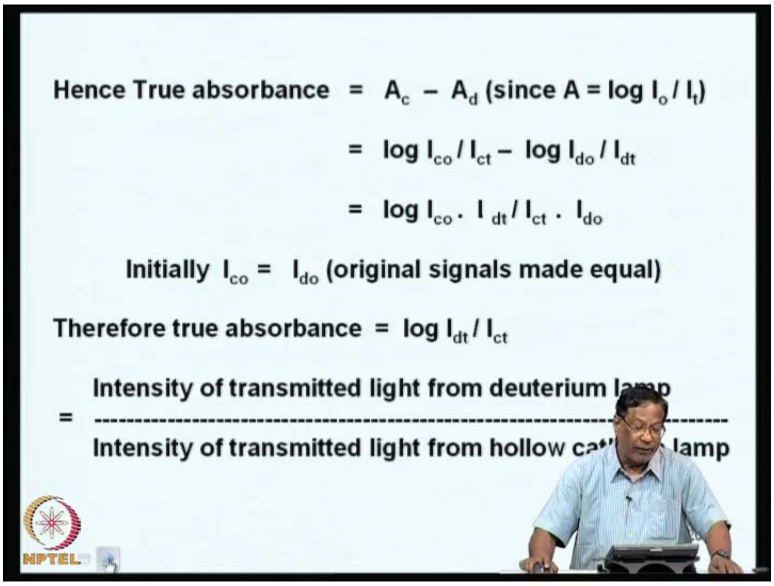

Hence True absorbance $= A_c - A_d$ **(since** $A = \log I_o / I_t$**)**

$= \log I_{co} / I_{ct} - \log I_{do} / I_{dt}$

$= \log I_{co} \cdot I_{dt} / I_{ct} \cdot I_{do}$

Initially $I_{co} = I_{do}$ **(original signals made equal)**

Therefore true absorbance $= \log I_{dt} / I_{ct}$

= Intensity of transmitted light from deuterium lamp / Intensity of transmitted light from hollow ca lamp

we have understood that the background correction should be first made equal when there is non-absorption.

So, the true absorbance would be basically absorbance minus that from the deuterium lamp. If you put it in terms of the ratio of absorbance's definitions, you will get log of I co divided by I ct minus log of I do by I dt. I am just expanding this terms A c as well as A d and this you can reorganized and which represents so, the log of I co I dt and then by I ct and I do. Initially, I co is equal to I do that is original signals must be made equal. Therefore, true absorbance would be nothing, but log of I dt by I ct; that means, intensity of the transmitted light from the deuterium lamp divided by the intensity of the transmitted light from the hallow cathode lamp; that is what we are aiming to measure.

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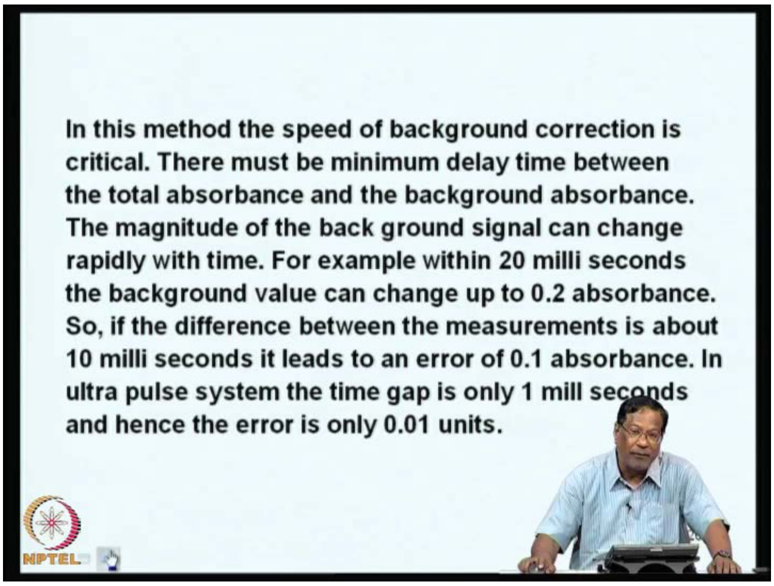

In this method the speed of background correction is critical. There must be minimum delay time between the total absorbance and the background absorbance. The magnitude of the back ground signal can change rapidly with time. For example within 20 milli seconds the background value can change up to 0.2 absorbance. So, if the difference between the measurements is about 10 milli seconds it leads to an error of 0.1 absorbance. In ultra pulse system the time gap is only 1 mill seconds and hence the error is only 0.01 units.

So in this method, the speed of background correction is very critical. There must be minimum delay between the total absorbance and the background correction. You understand this concept; the concept is the moment you make the measurement atomic absorption, it must be next second, next moment background should be measured. Again you can go for atomic absorption; again make the background correction after another time delay. So the time delay between the sample and the background is very important. So, it should be as small as possible to get as true a response as possible.

So, the magnitude of the background signal can change rapidly with time; for example, within 20 milli seconds, the background value can change up to 0.2 absorbance. This is very high because, in atomic absorption we are talking about only about 0.3, 0.4, 0.5 absorbance maximum. So, if the background itself can change within a few milli seconds by 0.2 absorbance the error could be quite large. So, if the difference between the measurements is about 10 milli seconds, it can lead to an error of about 0.1 absorbance. In ultra pulse system what happens is, the time gap is only 1 milli second and hence, the error is only 0.01 units. So, this is good because in 1 milli seconds if I keep on doing it, it would be nice.

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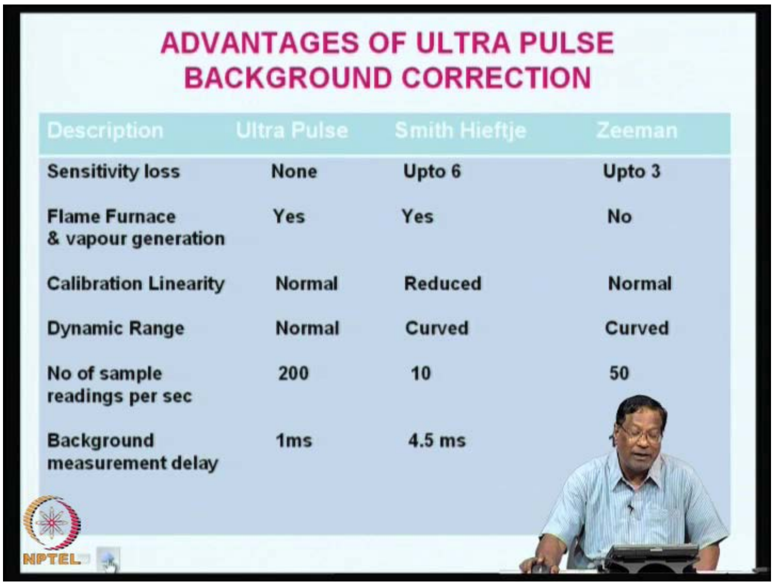

ADVANTAGES OF ULTRA PULSE BACKGROUND CORRECTION

Description	Ultra Pulse	Smith Hieftje	Zeeman
Sensitivity loss	None	Upto 6	Upto 3
Flame Furnace & vapour generation	Yes	Yes	No
Calibration Linearity	Normal	Reduced	Normal
Dynamic Range	Normal	Curved	Curved
No of sample readings per sec	200	10	50
Background measurement delay	1ms	4.5 ms	[illegible]

So, advantages of ultra pulse background correction I want to discuss with you. That is sensitivity loss, I have put 4 tables here. The top one is description and ultra pulse Smith Hieftje and Zeeman background correction. These three all these three we have discussed earlier and now I am trying to compare all that three. So sensitivity loss in ultra pulse background, there is a absolutely no sensitivity loss whereas, in Smith Hieftje correction up to 6 times the sensitivity loss can occur; that means, the detection limit can increase by about 6 times if you use Smith Hieftje, and if you do it with Zeeman up to 3 times the sensitivity loss can occur. So in flame and vapor generation, the if you use ultra pulse correction then, the there could be interference and then, there could be interference in Smith Hieftje, but in Zeeman it as no effect. So calibration linearity would be normal in ultra pulse slightly reduce in a Smith Hieftje, and normal in Zeeman Effect background correction. So the dynamic range is also very normal in this case, but in Smith Hieftje and Zeeman it is curved; that means, the linearity could get affected to some extent in both this systems.

So, it does not mean that in atomic absorption only linearity is required, but so long as we are able to give reproducible results, the curved range also can be used. So the number of readings when you take per second is about 200 in ultra pulse correct background correction. That is with the deuterium lamp every ultra 200 readings if you take per second, that is approximately about 3 readings per mile seconds and per second, and in Smith Hieftje, it is about 10 at 10 readings per second and in Zeeman, it is a approximately 50 times.

So the error would be much less in Zeeman than in Smith Hieftje as well as ultra pulse. So background measurement delay is 1 milli seconds here; here it is 4.5; here it is 10 milli seconds. So 90 percent of the atomic absorption instruments being sold today come with deuterium background correction. So, it is important for us to known what are the different types of, what are the advantages of deuterium background correction as well as disadvantages; advantages I had discuss with you earlier in the previous one; that is sensitivity losses nill then vapor generation, it is good and calibration is linear, normal

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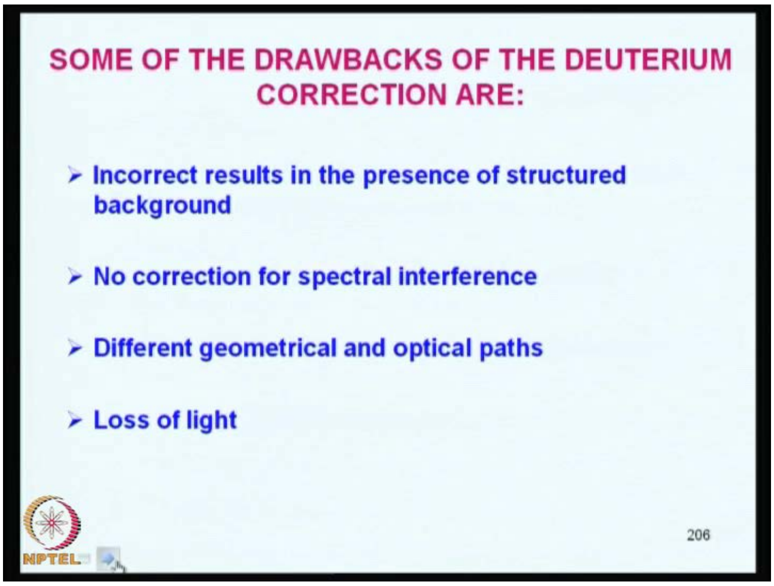

SOME OF THE DRAWBACKS OF THE DEUTERIUM CORRECTION ARE:

- Incorrect results in the presence of structured background
- No correction for spectral interference
- Different geometrical and optical paths
- Loss of light

and number of samples are 200; background measurement delay is only 1 milli second, but the associated advantages are incorrect results in presence of structured background; that means, if the molecular absorption as got a structure; that means, specific absorbance as specific wavelength then the background correction does not work So, spectral interference it is impossible to correct using deuterium lamp because, it is a board band absorption then, different geometrical and optical paths are required for a deuterium background. That is another at disadvantage; that means, it makes the optics more complicated then the Zeeman etcetera.

And then, there is sensitivity loss or intensity loss of the light; that is, it reflects on the calibration range. In spite of that, hydrogen deuterium background correction is most widely employed. Only since last 10 years, we have other types of atomic absorption background correction; that is Smith Heiftje as well as this Zeeman effect background correction. So, this Smith Hieftje we have discussed earlier; that is a brief pulse of a very high current is pass through those lamp causing self reversal, and we can subtract when self reversal occurs, there is only background correction and by subtracting one from the other, true absorbance is obtained. I would like to show

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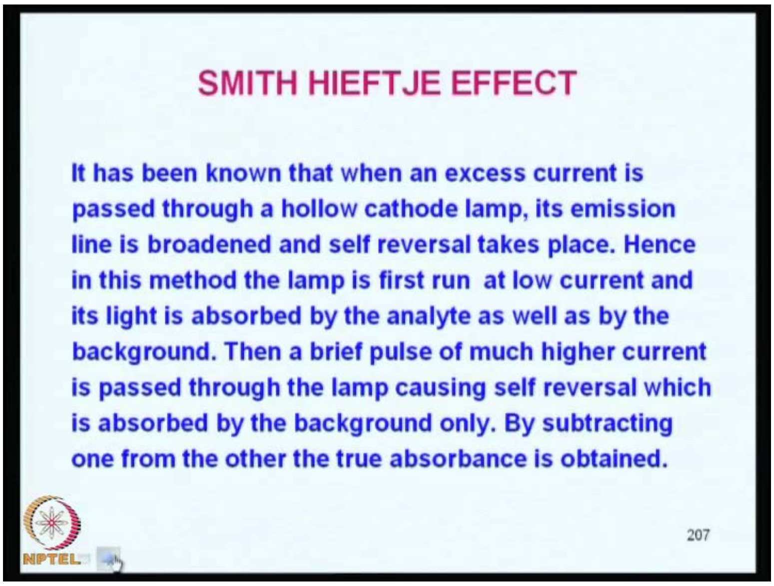

SMITH HIEFTJE EFFECT

It has been known that when an excess current is passed through a hollow cathode lamp, its emission line is broadened and self reversal takes place. Hence in this method the lamp is first run at low current and its light is absorbed by the analyte as well as by the background. Then a brief pulse of much higher current is passed through the lamp causing self reversal which is absorbed by the background only. By subtracting one from the other the true absorbance is obtained.

you the slide of what we have discussed for a brief this thing because, we have a discuss this already; I will not dwell more on this and then,

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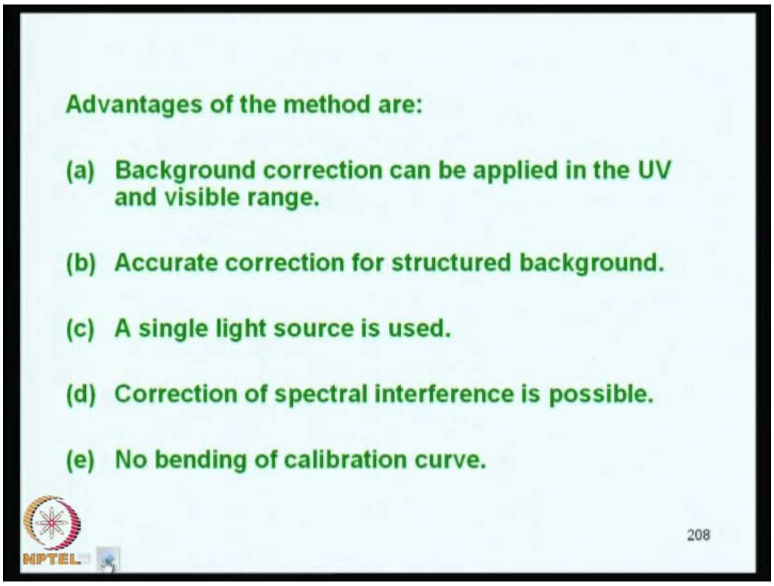

Advantages of the method are:

(a) Background correction can be applied in the UV and visible range.

(b) Accurate correction for structured background.

(c) A single light source is used.

(d) Correction of spectral interference is possible.

(e) No bending of calibration curve.

advantages of this methods are, it can be used in the UV visible range; accurate correction for structure background. This was not there in the deuterium background correction. So, a single light source is required; you do not need the deuterium lamp for this only the hallow cathode lamp. So, correction of spectral interference it is possible and calibration curved does not bend; that means, you will get a fairly linear calibration curve.

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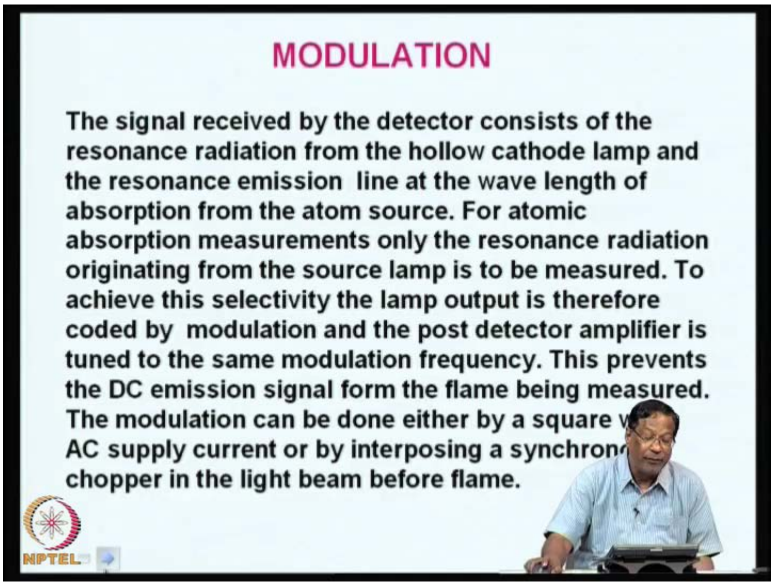

MODULATION

The signal received by the detector consists of the resonance radiation from the hollow cathode lamp and the resonance emission line at the wave length of absorption from the atom source. For atomic absorption measurements only the resonance radiation originating from the source lamp is to be measured. To achieve this selectivity the lamp output is therefore coded by modulation and the post detector amplifier is tuned to the same modulation frequency. This prevents the DC emission signal form the flame being measured. The modulation can be done either by a square
AC supply current or by interposing a synchron
chopper in the light beam before flame.

So, another way of doing this is to do the modulation. The signal received by the detector consist of the resonance radiation from the hallow cathode lamp as well as the resonance emission line from the atomic source, and for atomic absorption measurements only resonance radiation originating from the source lamp is to be measured. To achieve this selectivity, the lamp output is therefore coded by modulation and the post detector amplifier is tuned to the same modulation frequency. This is called as lock in. This prevents the DC emission signal from the flame being measured.

From the flame we always get DC signal. So the modulation can be done only for the non continuous radiation. So, either by square wave technique AC supply current or by interposing, a synchronous chopper in the light beam. So, what I wanted to tell you regarding this modulation is that, whenever you are doing this atomic absorption by hydride generation sorry by deuterium background correction modulation is required whereas, for self reversal Smith Hieftje and Zeeman effect background correction modulation is not required.

So, the I have just try to put in exactly my thoughts about the about the background correction for your benefit so that, you should be aware of the different types of interferences that can occur which we have discussed so far. That we have discussed the instrumentation, we had discuss the mechanism, we had discuss the interference and we are fairly well aware that most of the atomic absorption systems can be used to analyze the elements in by using flame atomic absorption spectrometry. Now, this was flame atomic absorption spectrometry was the first AAS system that was commercialized since 1955, and the flame atomic absorption is not really useful for all the elements.

There are some elements which are not very ideal, which are not determined ideally by flame atomic absorption; for example, some of them could be non metals like carbon then, sulphur and the chloride, bromide, iodide, anions, phosphates these are not determined by atomic absorption only the metallic elements. Even among the metallic elements, the not all the metals can be determined by atomic absorption because, for sodium, potassium, etcetera they are all alcylane, alkaline metals. Fairly decent flame emission method itself can be used for PPM level of determination using atomic absorption flame atomic emission.

Now, below 300 nanometers there are certain elements which will provide which are not easily determined by atomic absorption whose resonance line less than 300 nanometers. Some of these include arsenic and selenium. How have we had I had mention to these things briefly in my earlier discussion today only, and some of these elements which are not conducive for atomic absorption by flame, they can be determined by slight modifications, and the elements who have got the capability to form hydrides are very easily determined by as an by using an accessory called as hydride generation accessory using flame atomic absorption spectrometry. So arsenic, selenium, titanium, germanium, antimony, lead etcetera they all form hydrides. So all these elements can be determined in parts per billion level using an accessory called as hydride generation accessory and normal flame atomic absorption.

So, we have three accessories like that; one is for the determination of hydride forming elements; another is cold vapor mercury determination; that is separate accessory available with atomic absorption spectrometers and in many of the atomic absorption spectrometers, you can have a just at the flick of a button, you can flip of a flick of a switch, you can measure the atomic absorption as well as atomic emission, you can choose what you want to measure. So, atomic emission you can do for sodium, potassium, lithium etcetera some of the alkali and alkaline earth metals. So, this also is available as an accessory or at the switch of a button. So, we will be discussing these hydride generation and cold vapor mercury and flame atomic emission in the next classes. Now, I want to continue give you a small introduction for the hydride generation AAS.

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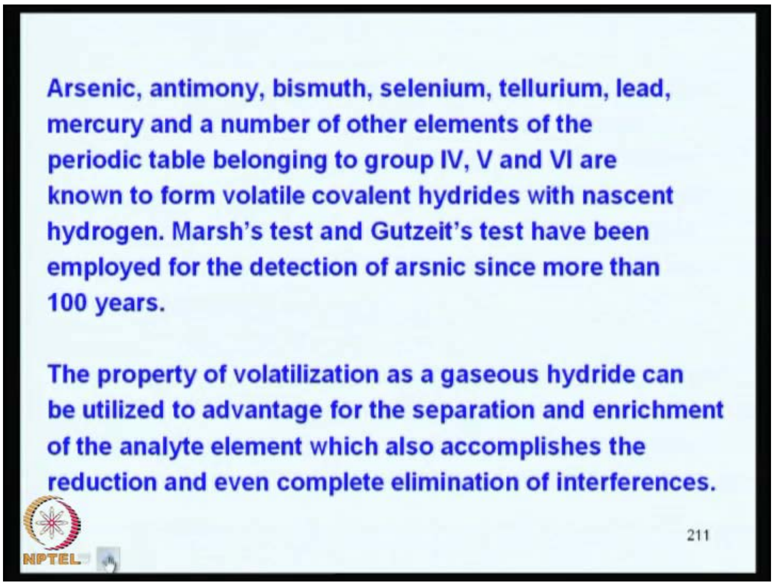

Arsenic, antimony, bismuth, selenium, tellurium, lead, mercury and a number of other elements of the periodic table belonging to group IV, V and VI are known to form volatile covalent hydrides with nascent hydrogen. Marsh's test and Gutzeit's test have been employed for the detection of arsnic since more than 100 years.

The property of volatilization as a gaseous hydride can be utilized to advantage for the separation and enrichment of the analyte element which also accomplishes the reduction and even complete elimination of interferences.

So in a hydride generation AAS atomic absorption technique, the elements what will be discussing are arsenic, antimony, bismuth, selenium, tellurium, lead, mercury and a number of other elements of the periodic table belonging to group 4, 5 and 6. These elements are known to form hydrides with they are known to react with hydrogen to form hydrides which are covalent compounds and they are volatile. If you take these metals solutions and bring them in intimate contact with nascent hydrogen, they form hydrides. There are some test known as Marsh's test and Gutzeit's test for the determination of hydride of a arsenic and they have been employed for the detection of arsenic since more than 100 years.

So, it is nothing new about it, but what is new is the utilization of the hydride generation property of the atomic absorption as an accessory to the flame AAS. The property of volatilization as a gaseous hydride can be utilized to advantage for the separation as well as enrichment of the analyte element corresponding to these elements arsenic, antimony, bismuth, selenium, tellurium, lead and mercury. They all it also accomplishes reduction and even complete elimination of interference can be obtained in using this accessory.

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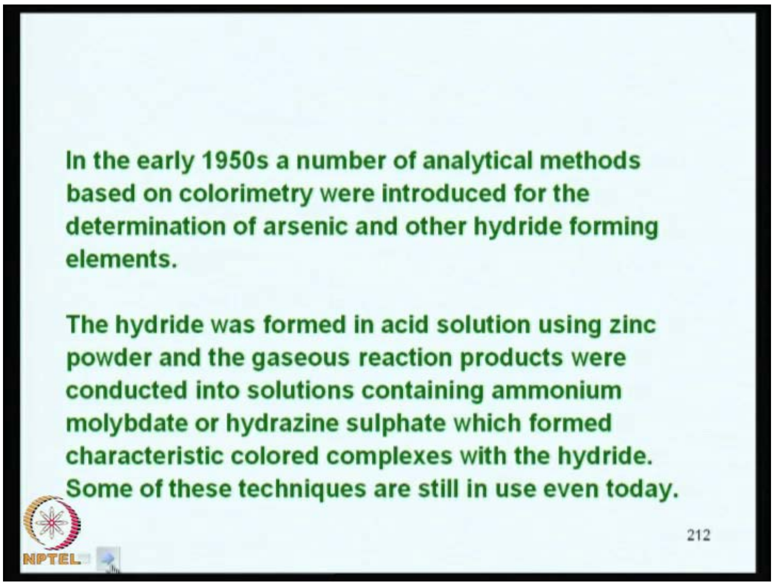

In the early 1950s a number of analytical methods based on colorimetry were introduced for the determination of arsenic and other hydride forming elements.

The hydride was formed in acid solution using zinc powder and the gaseous reaction products were conducted into solutions containing ammonium molybdate or hydrazine sulphate which formed characteristic colored complexes with the hydride. Some of these techniques are still in use even today.

So in early 1950s, a number of analytical methods based on the colorimetry were introduced for the determination of arsenic and other hydride. So the basic work was done much earlier for the determination of analyte elements. So the simplest way of forming hydride is to take an acid solution using zinc powder and the gaseous reduction reaction products are to be conducted into solutions containing ammonium, molybdate or hydrazine sulphate which formed characteristic colored complexes with the hydride. This was the spectrophotometric basis. Some of these techniques are still in use even today.

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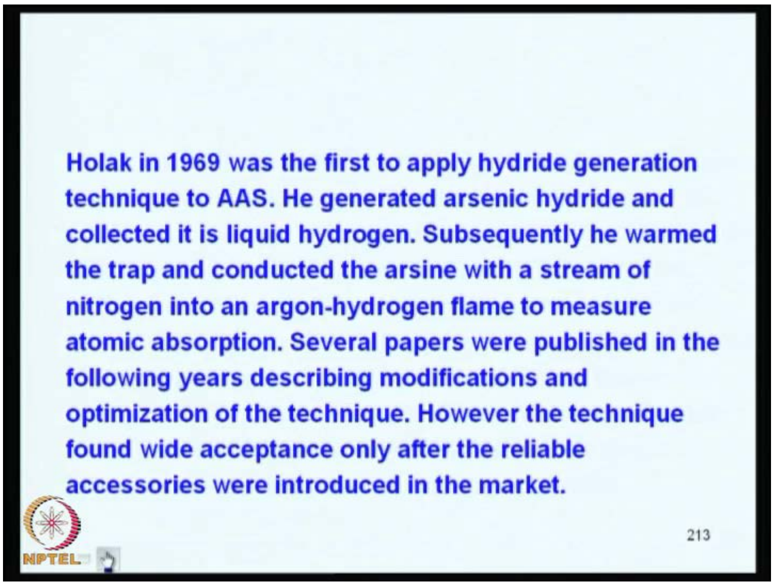

Holak in 1969 was the first to apply hydride generation technique to AAS. He generated arsenic hydride and collected it is liquid hydrogen. Subsequently he warmed the trap and conducted the arsine with a stream of nitrogen into an argon-hydrogen flame to measure atomic absorption. Several papers were published in the following years describing modifications and optimization of the technique. However the technique found wide acceptance only after the reliable accessories were introduced in the market.

But, in 1969 first attempt to apply hydride generation technique to AAS was used and he generated arsenic hydride and collected it in liquid hydrogen. Subsequently, he just warm the trap and conducted the arsine with a stream of nitrogen into an argon flame to measure atomic absorption. Subsequently, several papers were published in the following years describing modification and optimization. However, the technique has found wide acceptance only after the reliable accessories where introduced in to the market. Today, for the determination of arsenic, antimony, selenium, tellurium, bismuth, germanium and lead, hydride generation is the technique for the for parts per million or parts per billion level. We will continue our discussion in the next class.