Modern Instrumental Methods of Analysis
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Lecture No. # 22
Atomic Absorption Spectrometry-6 Signal handling

We were discussing about the oxide formation in flames, and we have discussed that spinal types of the type MeO metal oxide, Me 2 O 3 that is metal dioxide and of pervoskites MeOMeO 2 type; they form very stable lattices.

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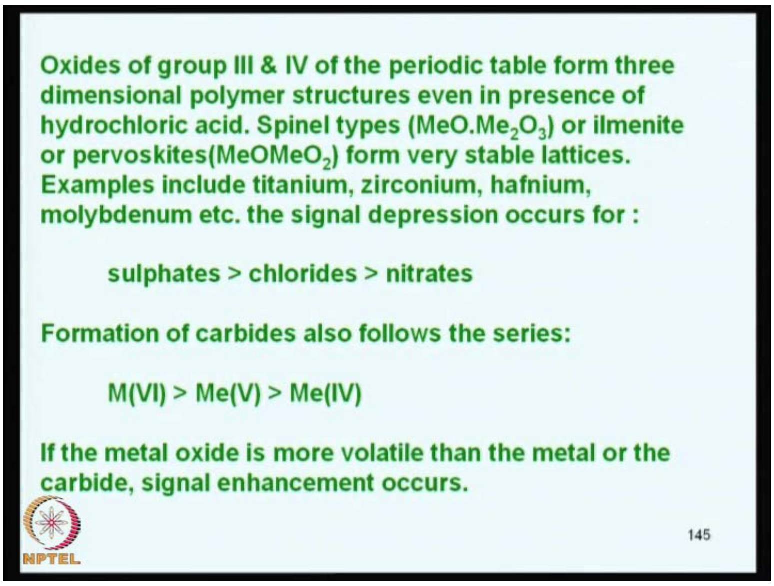

Oxides of group III & IV of the periodic table form three dimensional polymer structures even in presence of hydrochloric acid. Spinel types ($MeO.Me_2O_3$) or ilmenite or pervoskites($MeOMeO_2$) form very stable lattices. Examples include titanium, zirconium, hafnium, molybdenum etc. the signal depression occurs for :

sulphates > chlorides > nitrates

Formation of carbides also follows the series:

M(VI) > Me(V) > Me(IV)

If the metal oxide is more volatile than the metal or the carbide, signal enhancement occurs.

The examples include the metal such as titanium, zirconium, hafnium, molybdenum, etcetera and in all these cases the signal depression occurs if the salts are of the type of sulfides which gives maximum signal depression compared to chlorides, and that is much more than nitrates. So, the formation of carbides also follows a similar series that is 4th group elements are; they give you still smaller signal depression compared to the 6th group, 5th group and that is much more than 4th group; that is valancy four. If the metal oxide is more volatile than the metal or the carbide, usually signal enhancement occurs.

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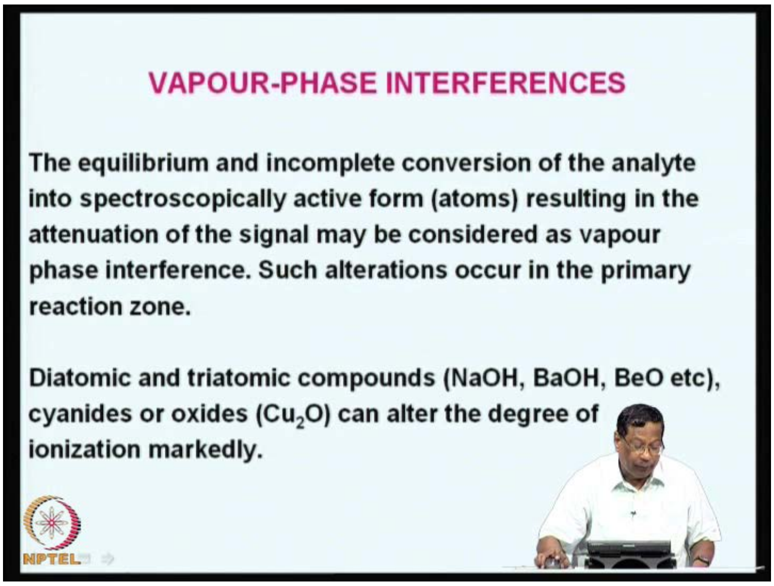

VAPOUR-PHASE INTERFERENCES

The equilibrium and incomplete conversion of the analyte into spectroscopically active form (atoms) resulting in the attenuation of the signal may be considered as vapour phase interference. Such alterations occur in the primary reaction zone.

Diatomic and triatomic compounds (NaOH, BaOH, BeO etc), cyanides or oxides (Cu_2O) can alter the degree of ionization markedly.

So, we will discuss now about vapor phase interferences; the equilibrium and incomplete conversion of the analyte into spectroscopically active form that is atoms resulting in the automation of the signal may be considered as vapor phase interference. First of all, we have to remember that the metal atoms formed they need to get into vapor phase system also. So, the equilibrium and incomplete conversion are the only factors that can change the concentration of the atoms in the vapor phase. So, such alterations usually occur in the primary reactions only.

So, diatomic and triatomic compounds such as sodium hydroxide, barium hydroxide, barium oxide, cyanides, oxides; they such compounds are readily formed in the flame and they can alter the degree of ionization markedly.

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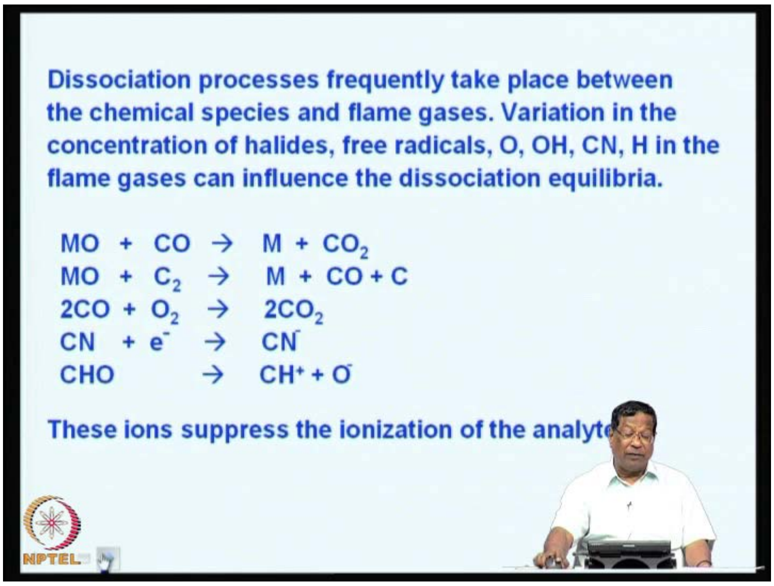

Dissociation processes frequently take place between the chemical species and flame gases. Variation in the concentration of halides, free radicals, O, OH, CN, H in the flame gases can influence the dissociation equilibria.

$MO + CO \rightarrow M + CO_2$

$MO + C_2 \rightarrow M + CO + C$

$2CO + O_2 \rightarrow 2CO_2$

$CN + e^- \rightarrow CN^-$

$CHO \rightarrow CH^+ + O^-$

These ions suppress the ionization of the analyt

So, this is another type of vapor phase interference. Usually, disassociation processes take place between the chemical species and the flame gases. Variation in the concentration of the halides, free air radicals, oxygen, and OH radicals, cyanogens radials, hydrogen it is all these gases are there present in the flame of the atomic absorption. So, there presence in the flame gases can influence the disassociation equilibria. Usually, we expect this kind of reactions; that is metal oxide reacting with carbon monoxide giving you metal plus CO 2; metal oxide reacting with carbon to give you metal and carbon monoxide plus carbon, and carbon monoxide can also react with oxygen to form CO 2. Cyanogens can pick up an electron from the flame to form cyanide ion; and CHO radical can change over to CH plus NO. These are ions if they form, they can readily suppress the ionization of the analyte.

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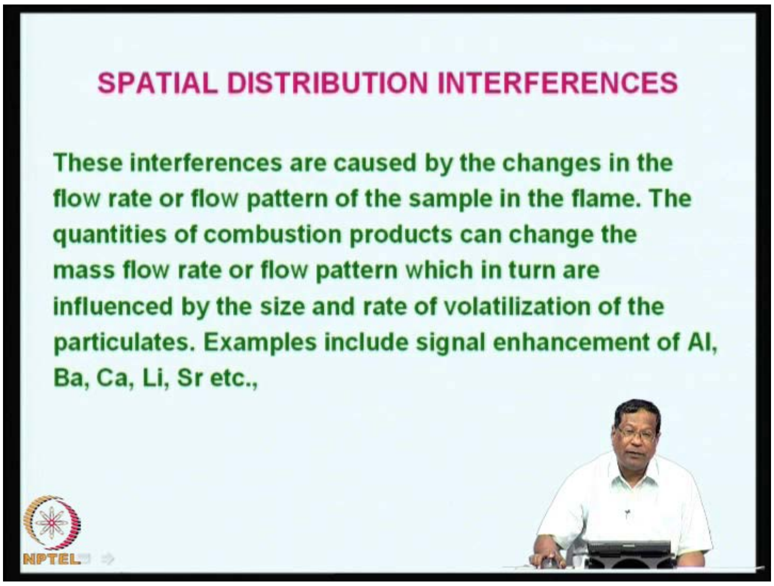

SPATIAL DISTRIBUTION INTERFERENCES

These interferences are caused by the changes in the flow rate or flow pattern of the sample in the flame. The quantities of combustion products can change the mass flow rate or flow pattern which in turn are influenced by the size and rate of volatilization of the particulates. Examples include signal enhancement of Al, Ba, Ca, Li, Sr etc.,

So that means, the signal will become smaller; that is it gets attenuated and then, we have other types of interferences that is special distribution of the interferences. These interferences are caused by the changes in the flow rate of or flow pattern of the sample in the flame. The quantities of combustion products can change the mass flow rate or flow pattern, which in turn are influence by the size and rate of volatilization of the particles. Examples of this type include signal enhancement of aluminum, barium, calcium, lithium, transom etcetera.

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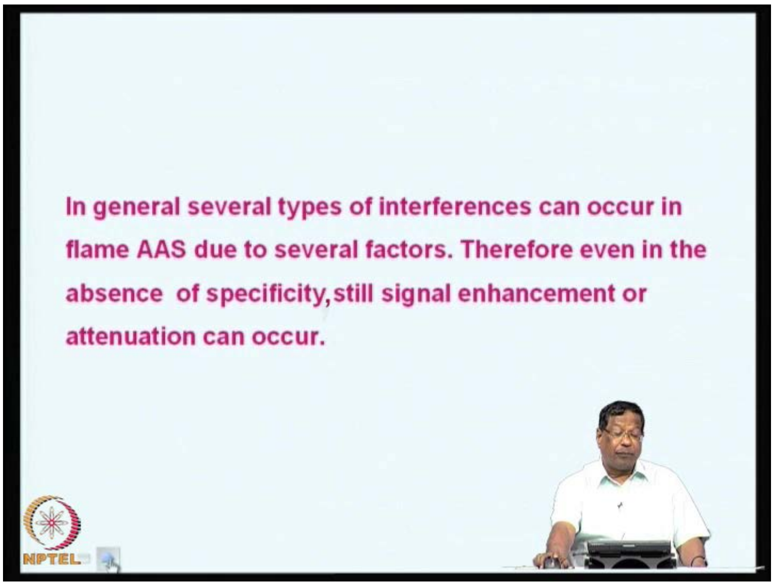

In general several types of interferences can occur in flame AAS due to several factors. Therefore even in the absence of specificity, still signal enhancement or attenuation can occur.

So, the… In general, several types of interferences can occur in flame AAS due to several factors. Therefore, even in the absence of specificity, still signal enhancement or attenuation can occur. This is what we want to understand in atomic absorption. That is even though it is an element specific technique, the signal at attenuation can occur due to various reasons that we had discussed so far. We will discuss again the actual chemical reactions that take place with specific metal ions in the later stages.

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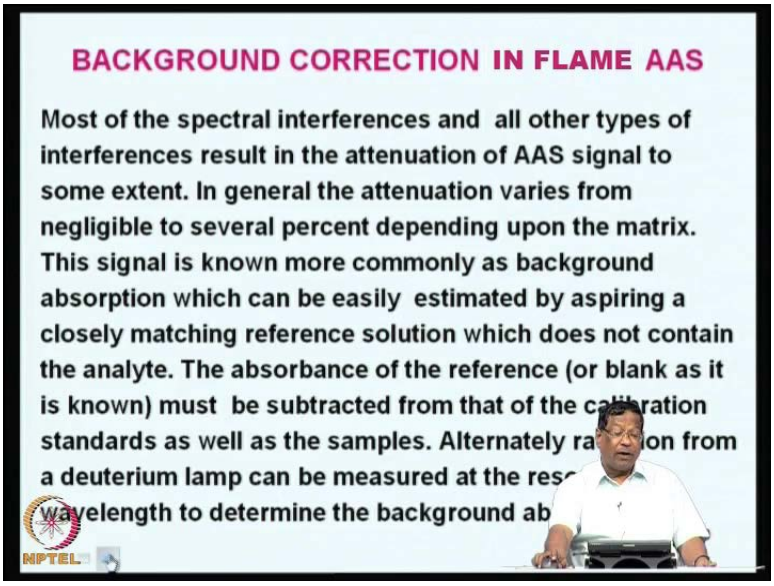

BACKGROUND CORRECTION IN FLAME AAS

Most of the spectral interferences and all other types of interferences result in the attenuation of AAS signal to some extent. In general the attenuation varies from negligible to several percent depending upon the matrix. This signal is known more commonly as background absorption which can be easily estimated by aspiring a closely matching reference solution which does not contain the analyte. The absorbance of the reference (or blank as it is known) must be subtracted from that of the calibration standards as well as the samples. Alternately ra ion from a deuterium lamp can be measured at the res wavelength to determine the background ab

Now, the back ground… Let us discuss about the back ground correction of flame AAS. So, the whenever there is signal attenuation the back ground correction also becomes very important because, will have to keep on adjusting the back ground depending upon the level of attenuation. Therefore, most of the spectral interference if they are there and all other types of interferences result in the attenuation on the AAS signal to some extent. In general, attenuation varies from negligible to several percent depending upon the matrix. So, if you are having very pure samples, standards etcetera where the matrix elements are much less; that is other types of elements which in which you are not interested as an analyte are much less then, the attenuation becomes much less. So, the signal is more commonly known as back ground absorption when there is no absorption no matrix element.

There is suppose, you use aqueous solutions only containing only one analyte or two analyte then, there is whatever signal you get without the sample is known as back ground absorption, which can be easily estimated by aspiring a closely matching reference solution or blank, we call it as blank. And, it becomes fairly important to run a blank in almost every determination. So, the absorbance of reference or the blank must be subtracted from that of the calibration curve as well as the samples. So, alternately what you can do, radiation from the deuterium lamp can be measured at the resonant wavelength only and to determine the back ground absorption because, the radiation from the continuum is almost represented by the deuterium lamp which is used for back ground this thing.

So, a schematic representation of a deuterium lamb back ground corrector can be measured at the reference wavelength to determine the back ground absorption. This is the figure of the back ground correction unit in atomic absorption.

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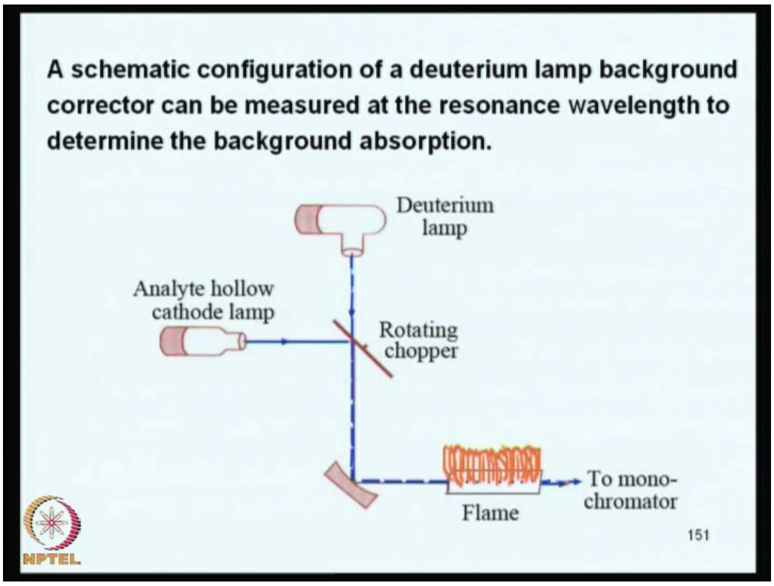

A schematic configuration of a deuterium lamp background corrector can be measured at the resonance wavelength to determine the background absorption.

So, I want you to see this figure. Here, what I have is an analyte hallow cathode lamb; that is the source and here, I have a deuterium lamb signals come from each site and then, there is a rotating chopper; both beams are combined and then passed through the flame and again they will be separated and then they lead to the monochromator. This is the schematic arrangement.

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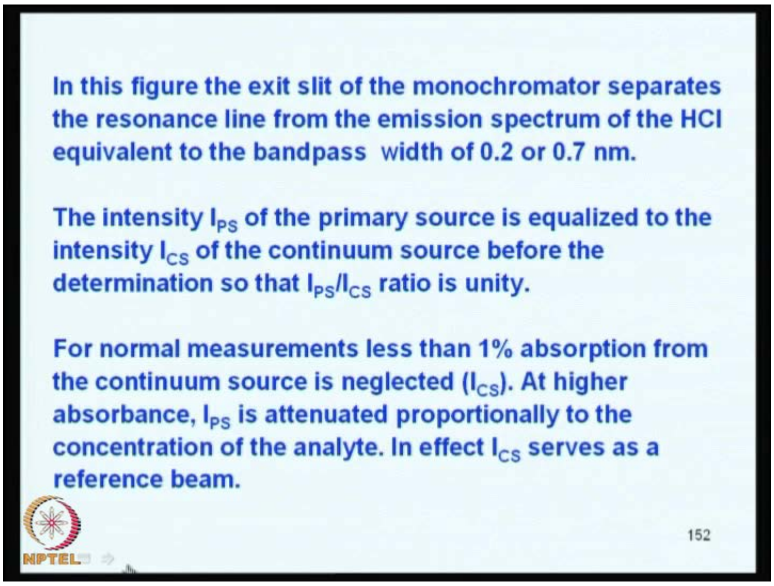

In this figure the exit slit of the monochromator separates the resonance line from the emission spectrum of the HCl equivalent to the bandpass width of 0.2 or 0.7 nm.

The intensity I_{PS} of the primary source is equalized to the intensity I_{CS} of the continuum source before the determination so that I_{PS}/I_{CS} ratio is unity.

For normal measurements less than 1% absorption from the continuum source is neglected (I_{CS}). At higher absorbance, I_{PS} is attenuated proportionally to the concentration of the analyte. In effect I_{CS} serves as a reference beam.

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And in this figure, the exit slit of the monochromator separates the resonance line from the emission spectrum of the hallow cathode lamp equivalent to band pass width of about 0.2 to 0.7 nano meter. This is this number 0.2 to 0.7 represents these actual slit width in the atomic absorption instruments which you can set manually or it you can change it automatically. The intensity I PS of the primary source is equalized to the intensity I CS; CS means continuum source. So, the primary source that is hallow cathode lamp intensity I PS is equalized to I CS before the determination so that I PS to I CS ratio is unity. This is very important for us to standardize the measurements. So, for normal measurements what we do is, we measure the usually less than 1 percent absorption if the back ground concentration back ground absorbent is less than 1 percent, we can neglect that. That is I CS that is continuum source. If the absorption of the reference relation is less than 1 percent you can neglect. At higher absorbance, the signal from the hollow cathode lamp is attenuated proportionally to the concentration of the analyte in this case. So, in effect I CS that is continuum source of the radiation serves as the reference beam.

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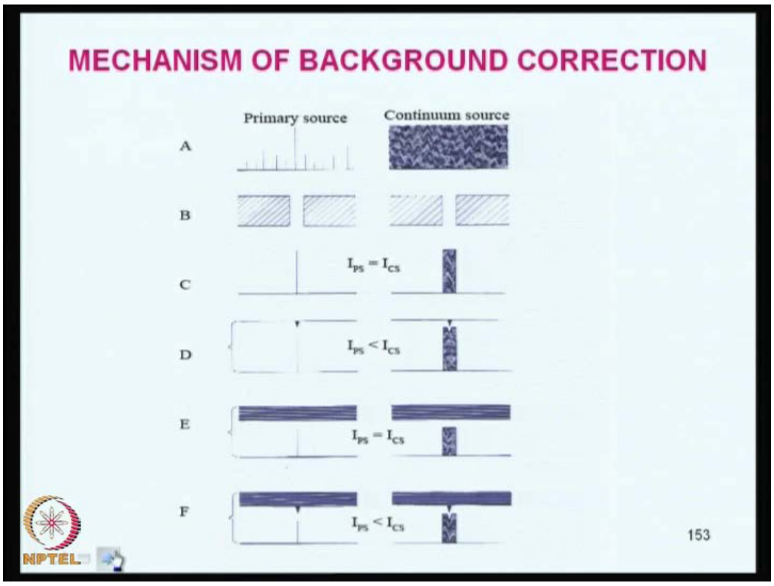

MECHANISM OF BACKGROUND CORRECTION

So, this is how the signal works; for example, here I have a primary source. This is a slit and then here, it is continuum source same slit and then I PS and I CS are equalized in height. And then, we have atomic absorption signal I PS is greater than I CS. So, the emission absorption occurs in this signal making a small gap here in the third figure. And then, the I PS and I CS are equalized again and then the atomic absorption occurs that is I PS is less than I CS. So, we have a atomic absorption signal; that is this is how the mechanism of back ground correction works.

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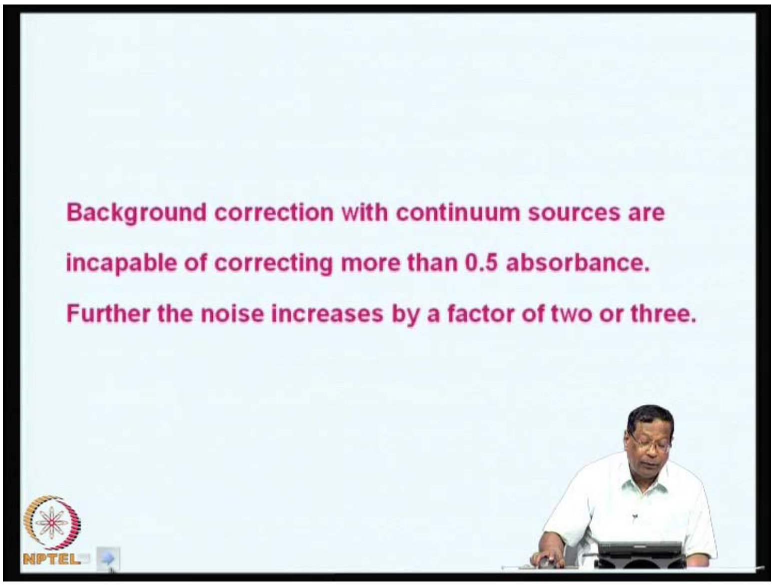

Background correction with continuum sources are incapable of correcting more than 0.5 absorbance. Further the noise increases by a factor of two or three.

So, back ground correction; it will work provided the continuum sources are less than 0.5 absorbance. If it is very high then, this technique will not work. Further suppose, it is very high then what happens; the noise also increases by a factor of two or three.

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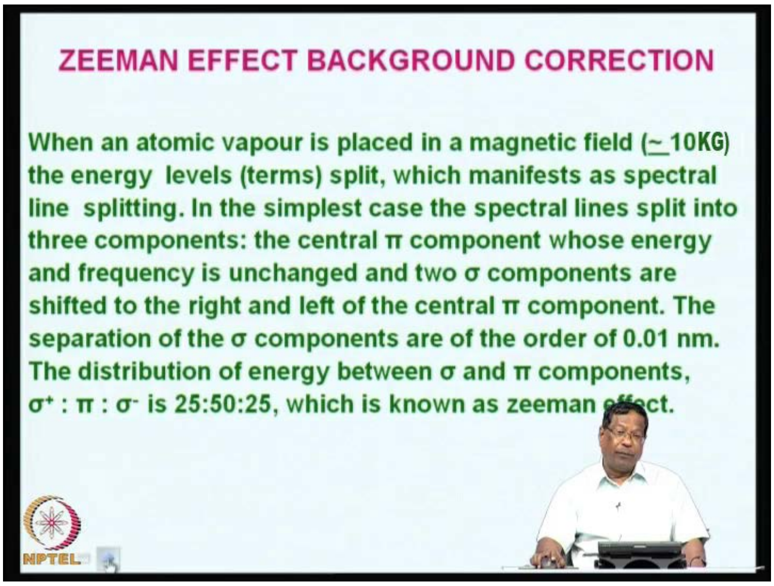

ZEEMAN EFFECT BACKGROUND CORRECTION

When an atomic vapour is placed in a magnetic field (≃10KG) the energy levels (terms) split, which manifests as spectral line splitting. In the simplest case the spectral lines split into three components: the central π component whose energy and frequency is unchanged and two σ components are shifted to the right and left of the central π component. The separation of the σ components are of the order of 0.01 nm. The distribution of energy between σ and π components, $\sigma^+ : \pi : \sigma^-$ is 25:50:25, which is known as zeeman effect.

So against this, we generally go for measurements with low back ground; that is the solutions should be as less as possible in terms of complexity; that means, it should not you should not determining the samples in very high salt water content such as body fluids or urine or sea water or several other alloys etcetera. So, another way of back ground correction is Zeeman effect back ground correction. So, let us discus a little more about the Zeeman Effect back ground correction. So, the basic theory is very simple. When an atomic vapor is placed in a magnetic field of the order of 10 kilo gauss, the energy levels split or terms split which manifest a spectral line splitting. In the simplest case, the spectral line split into three components. One is sigma component and other is pi component. So, pi component occurs at the exactly the same frequency as the original signal, and sigma components are separated slightly to the left and right of the pi component. The components are of the order of about the separation of the sigma components are of the order of about 0.01 nano meter.

So, if the energy level split, the energy also is split automatically and the ratio of sigma plus and sigma minus 2 pi corresponds to approximately 25 to 50 is to 25; that is pi component is maximum with 50 percent and the one which shifts to the left is a about 25 percent in intensity and which shifts to the right is also a approximately 25 percent intensity; that means, if the separation occurs only between sigma plus and sigma minus and pi component, you get three peaks in the presence of magnetic field and this is known as Zeeman effect.

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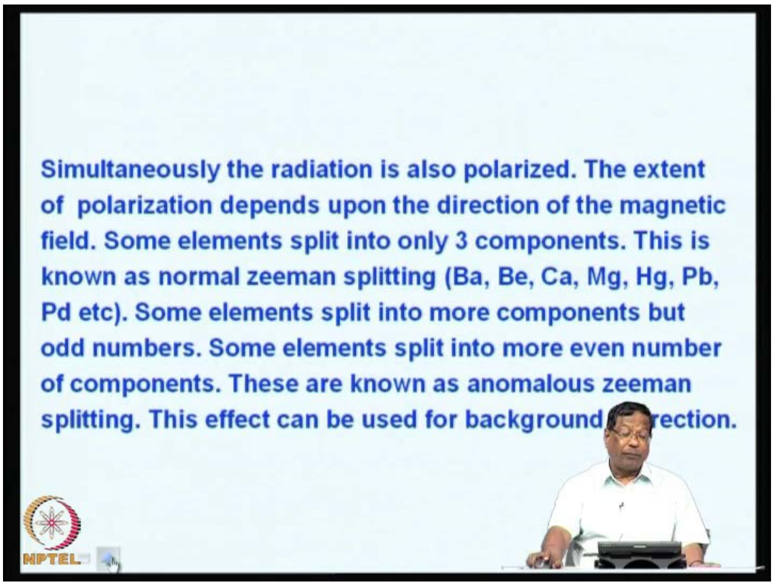

Simultaneously the radiation is also polarized. The extent of polarization depends upon the direction of the magnetic field. Some elements split into only 3 components. This is known as normal zeeman splitting (Ba, Be, Ca, Mg, Hg, Pb, Pd etc). Some elements split into more components but odd numbers. Some elements split into more even number of components. These are known as anomalous zeeman splitting. This effect can be used for background correction.

Now simultaneously, when you place a magnet in on the atomic cloud, the terms get split into three components. But simultaneously, the radiation also is polarized; that means, the direction changes of the direction of the radiation also changes. So, the extend of polarization direction change of direction depends upon the direction of the magnetic field. So, higher the magnetic field more is the rotation. Some elements split into only three components just like I was telling you and this is known as normal Zeeman splitting. Elements such as barium, calcium, beryllium, calcium, magnesium, mercury, lead, etcetera; they (( )) exhibit normal Zeeman effect splitting.

Some elements split into more components and but odd numbers. Some elements split into more even numbers of components. These are sort of enameling because the normal is only three components. So, when there are more components, the effect is known as anomalous Zeeman splitting. This kind of splitting can be used in atomic absorption measurement for back ground correction.

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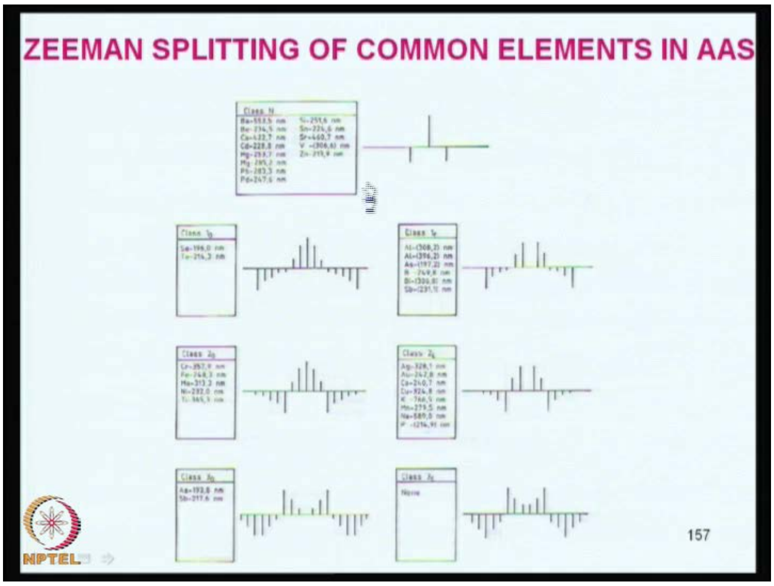
ZEEMAN SPLITTING OF COMMON ELEMENTS IN AAS



How? It is very simple. Here, I am showing you the normal splitting; that is the central component here is the pi component and here are two sigma components. One is sigma minus another is sigma plus. So, the elements corresponding to this are barium, beryllium, calcium, cadmium, mercury, etcetera, magnesium, etcetera; here are anomalous examples of anomalous Zeeman effect. Here, we can see that there are more number of pi components, more number of sigma components also.

Here, you can see again pi component is missing, but there are equal number of sigma components. The elements corresponding showing this type of pattern or splitting are aluminum, arsenic, beryllium and then bismuth, antimony etcetera and all in all most of the elements what I have listed here, there are about 35 elements which will show you different kinds of the splitting Zeeman splitting and this effect we can use it for back ground correction.

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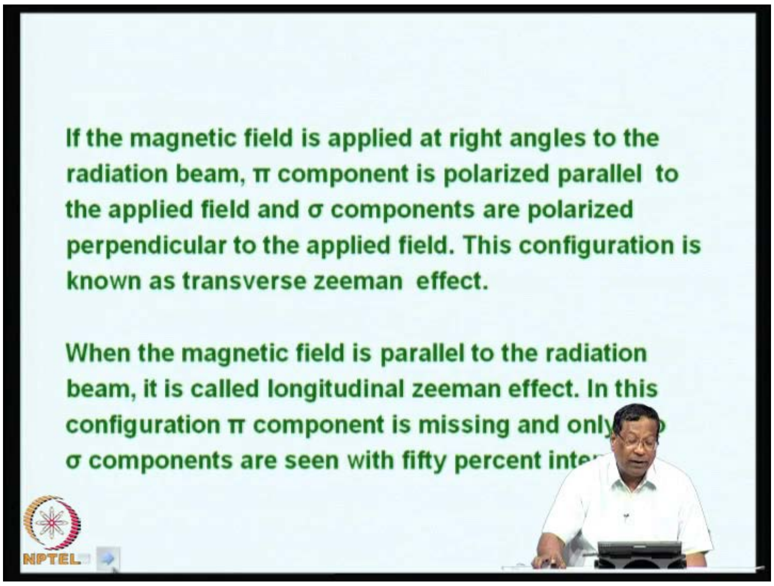

If the magnetic field is applied at right angles to the radiation beam, π component is polarized parallel to the applied field and σ components are polarized perpendicular to the applied field. This configuration is known as transverse zeeman effect.

When the magnetic field is parallel to the radiation beam, it is called longitudinal zeeman effect. In this configuration π component is missing and only σ components are seen with fifty percent inte

So, if the magnetic field is applied at right angles to the radiation beam; that is the radiation beam is going like this; I am going to put the magnetic field like this; one at the top; one at the bottom. So, the radiation is going in between these two magnetic fields.

So, that is a pi component is in such case; pi component is polarized perpendicular to the applied field; that means, it is rotated by 90 degrees. So this configuration is known as transverse Zeeman effect. So, when the magnetic field is parallel to the radiation beam then, it is called as longitudinal Zeeman effect. In this configuration, pi component is totally missing and only two sigma components you will be seeing. And, both of them would be having approximately 50 percent of the intensity because, the pi component is missing. So, the total of sigma plus and sigma minus would be 50 percent. Now, this is a schematic representation of the Zeeman effect.

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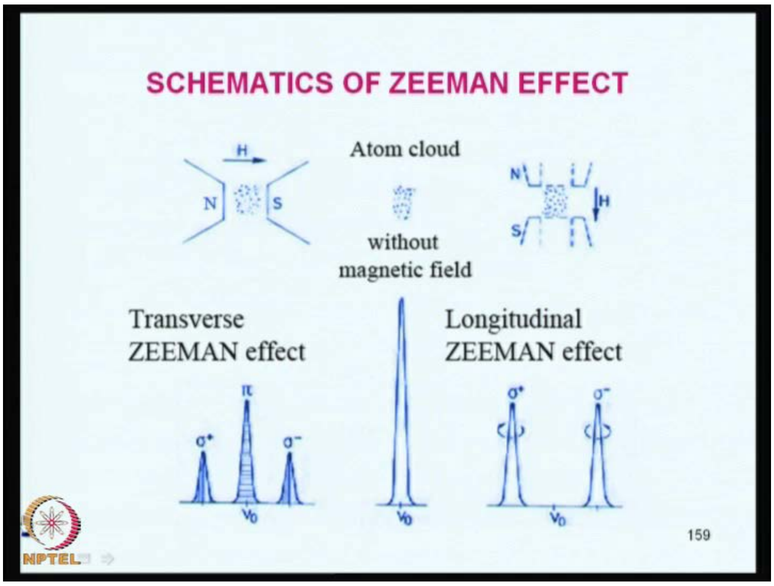

SCHEMATICS OF ZEEMAN EFFECT

Atom cloud

without magnetic field

Transverse ZEEMAN effect

Longitudinal ZEEMAN effect

This figure tells you that the atom cloud how it can affect the signal. Now, the in the center you will see there is an atom cloud here; there is no magnetic field. When there is no magnetic field, I get a signal at mu 0 which is approximately this side. Now, if I apply the field perpendicular to the direction of the beam; here is the direction of the beam and then what happens; I have a transverse Zeeman effect. The this is pi component; this is sigma minus; and this is sigma plus. So in longitudinal, how I am going to apply the field; put the magnet on the top and bottom and this is the magnetic field direction. So in this case, pi component is rotated out of the out of the beam and you will see only sigma plus and sigma minus peaks. So, this effect can be… Suppose, you put magnet like this and measure the absorbance; when the magnet is on, you will be measuring only the whatever signal you get will be the background because, the metal atoms signals sigma plus and sigma minus are already shifted away. So, what you see would be the pi component is missing because, it is already rotated ninety degrees. So, what you would be measuring is, whatever signal you get is only the sigma component.

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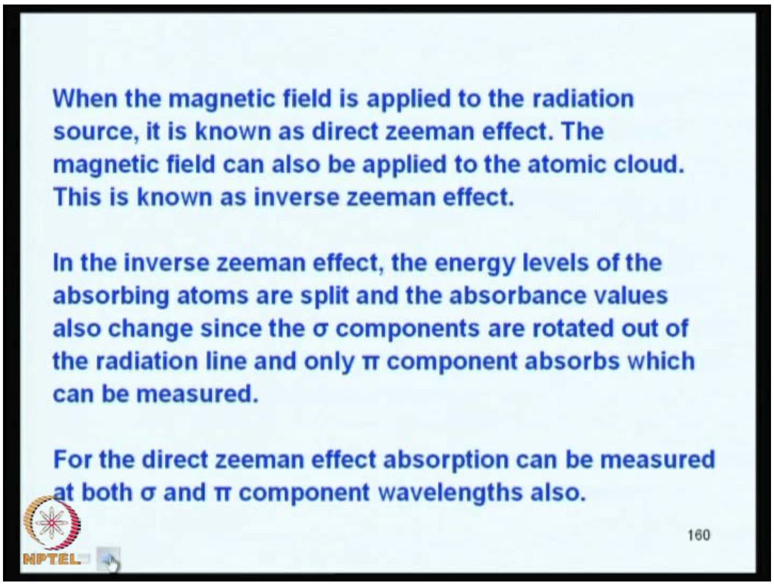

When the magnetic field is applied to the radiation source, it is known as direct zeeman effect. The magnetic field can also be applied to the atomic cloud. This is known as inverse zeeman effect.

In the inverse zeeman effect, the energy levels of the absorbing atoms are split and the absorbance values also change since the σ components are rotated out of the radiation line and only π component absorbs which can be measured.

For the direct zeeman effect absorption can be measured at both σ and π component wavelengths also.

So, when the magnetic field is applied to the radiation source. Now, in the previous figure I have shown you that this is the atom cloud on which the magnetic field has been applied. Now, what you want to do is suppose, we apply to the source that is hallow cathode lamp itself then, it is known as direct Zeeman effect. The magnetic field also can be applied to atomic could as we have seen earlier, this is known as inverse Zeeman effect.

So in the inverse Zeeman effect, the energy levels of the absorbing atoms are split and the absorbance values also change. Since sigma components are rotated out of the radiation line and only pi component absorbs which can be measured. For the direct Zeeman effect, absorption can be measured at both sigma and pi component wavelength also.

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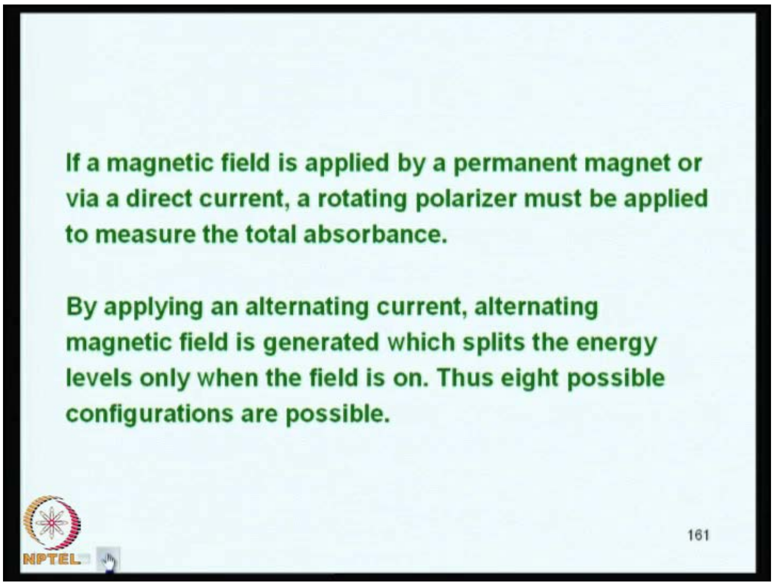

If a magnetic field is applied by a permanent magnet or via a direct current, a rotating polarizer must be applied to measure the total absorbance.

By applying an alternating current, alternating magnetic field is generated which splits the energy levels only when the field is on. Thus eight possible configurations are possible.

So, a number of possibilities exists in which we can organize the Zeeman effect application of the magnetic field to the either to the atomic could or to the source of radiation that is hallow cathode lamp. So, if a magnetic field is applied permanent magnet or by a direct current, rotating polarizer must be applied to measure the total absorbent because, when you apply a permanent magnetic field it is already rotated. So, you have to re-rotate it back to measure the absorbance. So, by apply… Suppose, you apply alternating current then, alternating magnetic field is generated which splits the energy levels only the field is on. So, you will have a continuous on off on off magnetic field.

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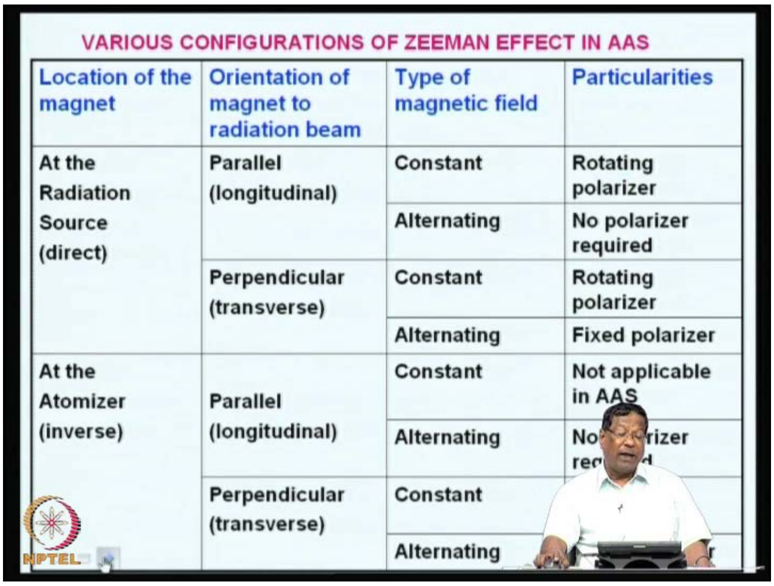

VARIOUS CONFIGURATIONS OF ZEEMAN EFFECT IN AAS

Location of the magnet	Orientation of magnet to radiation beam	Type of magnetic field	Particularities
At the Radiation Source (direct)	Parallel (longitudinal)	Constant	Rotating polarizer
		Alternating	No polarizer required
	Perpendicular (transverse)	Constant	Rotating polarizer
		Alternating	Fixed polarizer
At the Atomizer (inverse)	Parallel (longitudinal)	Constant	Not applicable in AAS
		Alternating	No [illegible]rizer req[illegible]d
	Perpendicular (transverse)	Constant	[illegible]
		Alternating	[illegible]r

So, if you look at all this possibilities, there are eight possible configuration of application of Zeeman effect back ground; for example, here you can see that the… We have at the… suppose, I apply to the radiation source that is on the hallow cathode lamp, I can orient the magnetic field parallel; that is longitudinal or perpendicular to the radiation source then, I can apply constant field or alternating field. So, rotating if I apply constant field, I need a rotating polarizer; if I apply a alternating field then, there is no polarizer required. Similarly, we have a… Suppose, I do with transverse magnetic field then again, I have a constant and alternating, but I need a rotating polarizer and fixed polarizer for the for measuring the signal.

So suppose, I apply the field magnetic field at the atomizer that is atomic could then again, I have parallel and perpendicular positions. I can use constant magnet or alternating magnetic field then off course, this is not applicable because to a flame you cannot apply constant magnetic field, but to the alternating field you can apply. So, no polarizer required. So, perpendicular transverse arrangement gives me a rotating polarizer and fixed polarizer.

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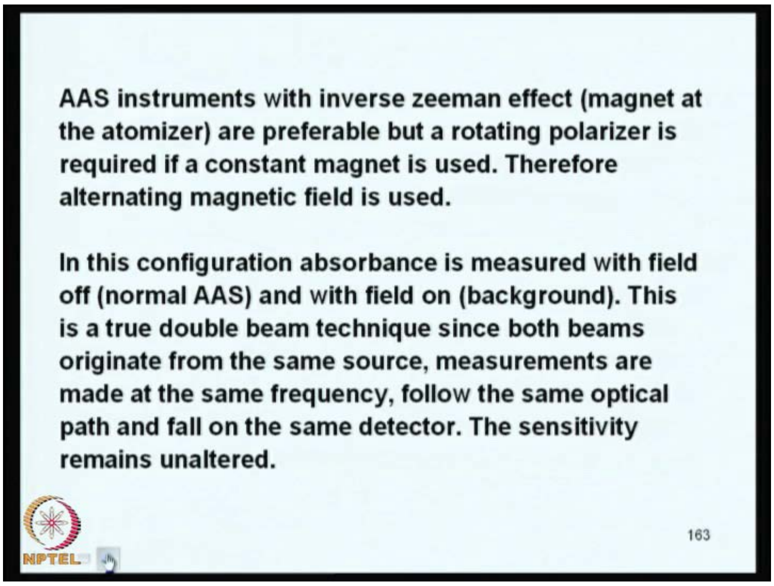

AAS instruments with inverse zeeman effect (magnet at the atomizer) are preferable but a rotating polarizer is required if a constant magnet is used. Therefore alternating magnetic field is used.

In this configuration absorbance is measured with field off (normal AAS) and with field on (background). This is a true double beam technique since both beams originate from the same source, measurements are made at the same frequency, follow the same optical path and fall on the same detector. The sensitivity remains unaltered.

So in all these cases, it is possible to measure. Now, in atomic absorption instruments inverse Zeeman effect; that is magnet at the atomizer are preferable compared to a source. So, what do to you would like to do is, around the flame we can put a magnet without touching the magnet, but keeping the field on at the same time. In that case, a rotating require is required if a constant magnet is used. Therefore, alternating magnetic field is used because, it does not require rotating polarizer also.

So, the addition of a rotating polarizer puts further restrictions of the servo mechanism to rotate the field, non rotate, d rotate the etcetera. In this case, configuration absorbance is measured with field off; that is when the field is off your measuring total absorbance that is normal AAS. And with field is on when the field is on, the sigma components are shifted, pi component is rotated. So, there is nothing at the at the measurement wavelength, and you will be measuring only the back ground. So, this is a true double beam technique since both beams originate from the same source. Usually, measurements are made at the same frequency therefore, they follow the same optical path, and they fall on the same detector. Only difference is, once we are measuring the total absorbance, once you are measuring the total back ground. So, the sensitivity remains unaltered and back ground gets corrected. This is the beauty of Zeeman atomic absorption and several commercial instruments are available with this type of arrangement.

And, another one is new way of measuring the absorbance; that is back ground correction is known as smith Hieftje back ground correction technique, and this method is based on the self absorption behavior of the radiation emitted by the hallow cathode lamps when there are operated at high currents. Now, I have referred to this self absorption earlier in my introductory remarks, and I have also mentioned that several of this street lights what you see sodium. In sodium, vapor lamps in the streets they switch on and off as if somebody is switching with a button you know on off. But actually, it is not so because, the at high currents the atomic could increases of atomic cloud of the sodium increases and it absorbs all the radiation emitted by the sodium vapor lamp. So, this principal is used in the back ground correction.

What happens; application of high current produces large concentration of the unexited atoms in the hallow cathode lamp itself. So, the these atoms are capable of absorbing the radiator; where ever you produce either in the flame or in the lamp if there are un exited atoms there would be absorbing the radiation. So suppose, you increase the concentration of the unexcited atoms in the hallow cathode lamp itself then, the hallow cathode lamp itself will absorb all the radiation and no radiation will pass through the optic flame and atomic could and reach the detector, this is the principal. Now what happens; these atoms are capable of absorbing radiation produced from the exited atomic spaces, and high currents also broaden the emission lines of the exited species; net effect is to produce a line that has a minimum at its center; that is the resonance line. So at the resonance line, when complete absorption takes place, there is no absorbance and only back ground gets measured.

So, what we had to do is to operate the hallow cathode lamp alternately with high current, low current, high current and low current like that. If you are able to do and measure then, the atomic absorption usually is can be measured with good back ground correction. This is known as smith Hieftje correction. I will show you a figure shortly corresponding to this. To obtain the correct absorbance, the lamp must be programmed to run alternately at normal current and high current in quick succession at the rate of every 5 milli seconds; 5 milli seconds you take one measurements and then apply high current no absorbance only back ground gets measured; again apply a low current. Like that, if you keep on doing every 5 milli seconds then, you can collect the all the back ground measurements for about 1 second or something like that add all of them then, add the signal without high current, that will give you back ground plus the atomic absorption signal. So, if you subtract the two what you will be getting is the normal atomic absorption signal which is corrected for the background, and during these first part back ground and atomic absorption is measured and during the second part only absorption peak use at the minimum and only the back ground is measured. So, the data acquisition system must be there to subtract the two signals to give a this thing.

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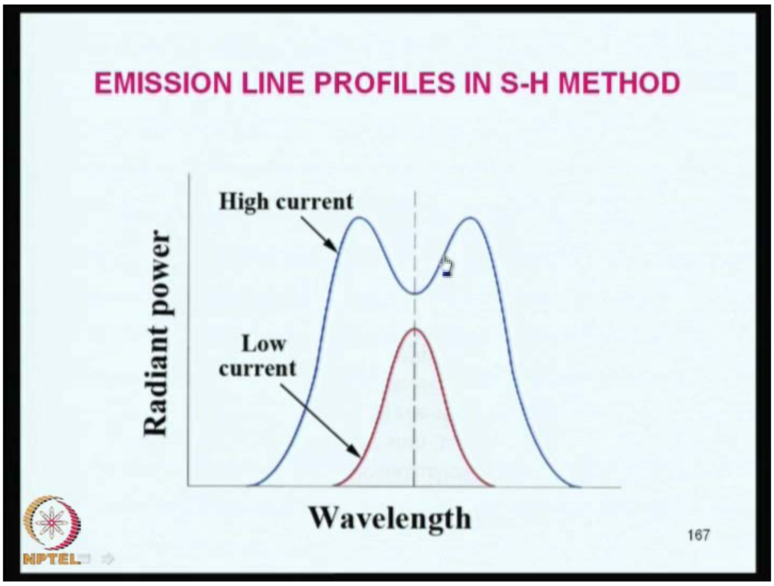

EMISSION LINE PROFILES IN S-H METHOD

So, if you take a look at this figure, this is a what I had discussed so far; it becomes fairly clear that is, when at low current, this is the atomic absorption signal. At high current, the signal gets submerged and only the what you will be measuring is only the difference that is there is no atomic absorption at all

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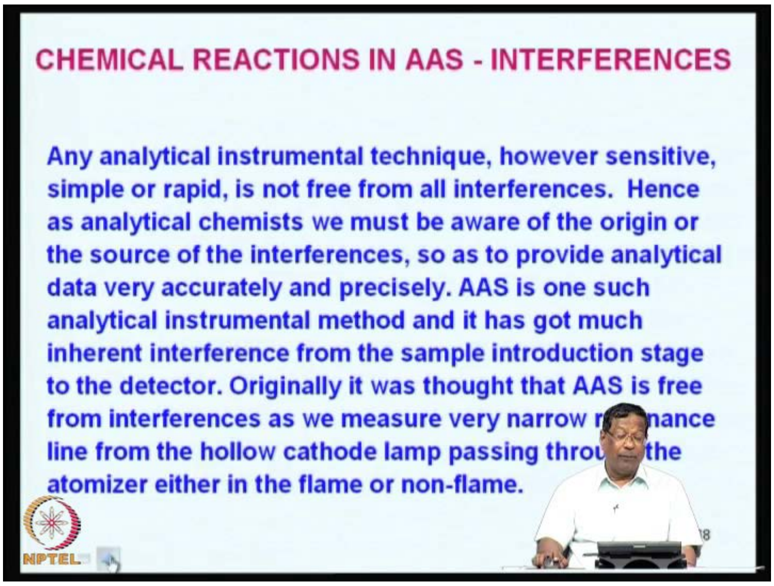

CHEMICAL REACTIONS IN AAS - INTERFERENCES

Any analytical instrumental technique, however sensitive, simple or rapid, is not free from all interferences. Hence as analytical chemists we must be aware of the origin or the source of the interferences, so as to provide analytical data very accurately and precisely. AAS is one such analytical instrumental method and it has got much inherent interference from the sample introduction stage to the detector. Originally it was thought that AAS is free from interferences as we measure very narrow r nance line from the hollow cathode lamp passing throu the atomizer either in the flame or non-flame.

and this is the mechanism of an atomic absorption. So, you can either use even the… Nowadays, instruments are available which will give you the an instrument which is automatically fitted with Smith Hieftje correction method; that is to supply electric current to the hallow cathode lamp alternately and such instruments are available in the market.

One can definitely go and choose between all the three all the that is deuterium back ground correction, Zeeman effect back ground correction or Smith Hieftje back ground correction all the systems are available, and one has to evaluate critically, what are the requirements of an analytical method and then go for the most suitable back ground correction system. I will be listing out the effects, the advantages and disadvantages of such back ground correction in the coming slides. So, what I want to do now is, I want to discuss with you the chemical reactions in atomic absorptions spectrometry. So, in the light of back ground correction how we can evaluate the chemical reactions and the types of interference also. Earlier, we had discussed solute vaporization etcetera and vapor phase and interference etcetera. But, in theory atomic absorptions spectrometry is an element specific technique; that means, there should not be any doubt regarding the presence of an element if you get an AAS signal. At the same time, it is element specific; that means, no other elements will interference.

Now, because of the chemical reactions in atomic absorptions flame, we will have interferences. So, any analytical instrumental technique; however, sensitive, simple and rapid it is not free from all interference. This point, I want to stress again and again that no instrumental technique is ever interference free. So as analytical scientist, we must be aware of the origin and source of such interferences to provide accurate analytical results and precise results also. So, atomic absorption spectrometer is one such analytical instrument and it has got inherent interferences from the sample introduction stages to the detector. Sometimes, even contamination during the preparation of the sample itself may occur and then originally, it was thought that AAS is basically free from all interferences as we measure only very narrow resonance lines from the hallow cathode lamp, but it is actually not so. So the interferences in chemical terms and physical terms,

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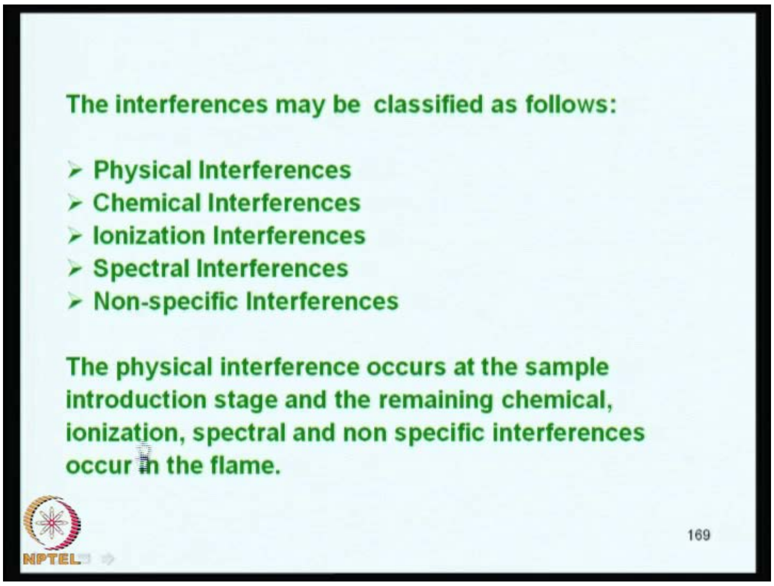

The interferences may be classified as follows:

- Physical Interferences
- Chemical Interferences
- Ionization Interferences
- Spectral Interferences
- Non-specific Interferences

The physical interference occurs at the sample introduction stage and the remaining chemical, ionization, spectral and non specific interferences occur in the flame.

we can classify like this; that is first is physical interferences, chemical interferences, ionization interference then, we have spectral interference we have discussed a little bit earlier and then non specific interference. So, the physical interference normally occurs at the sample introduction stage and the remaining chemical ionization etcetera, they the first one occurs at the sample introduction stage and all the other four occur during their stay in the flame.

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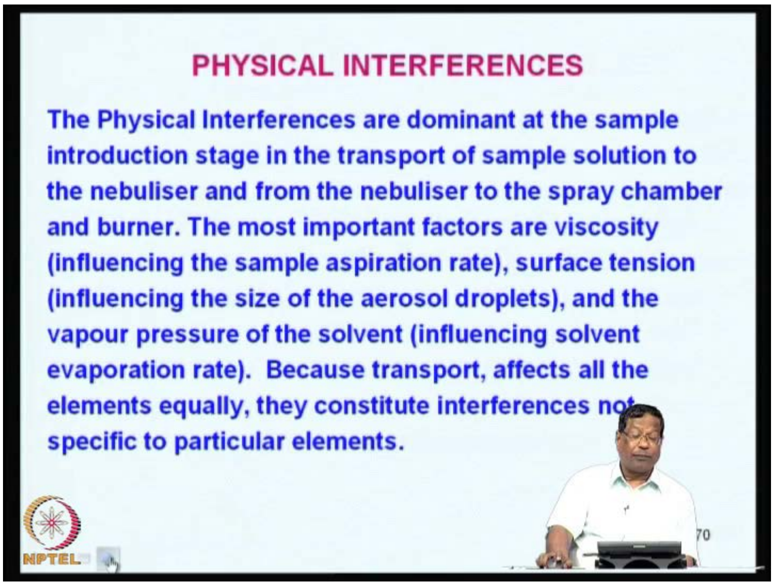

PHYSICAL INTERFERENCES

The Physical Interferences are dominant at the sample introduction stage in the transport of sample solution to the nebuliser and from the nebuliser to the spray chamber and burner. The most important factors are viscosity (influencing the sample aspiration rate), surface tension (influencing the size of the aerosol droplets), and the vapour pressure of the solvent (influencing solvent evaporation rate). Because transport, affects all the elements equally, they constitute interferences not specific to particular elements.

So, with this will not discuss physical interference because, we have already discussed the different types of interference that is due to viscosity and then transport and all these things. But, what I want to stress at this stage is that the transport and other aerosol effects etcetera, the all the effect all the instruments equally. So, the signal gets attenuated, but you cannot really call it an interference, but attenuation all the same. So, they constitute interference not specific to particular element this point will have to remember.

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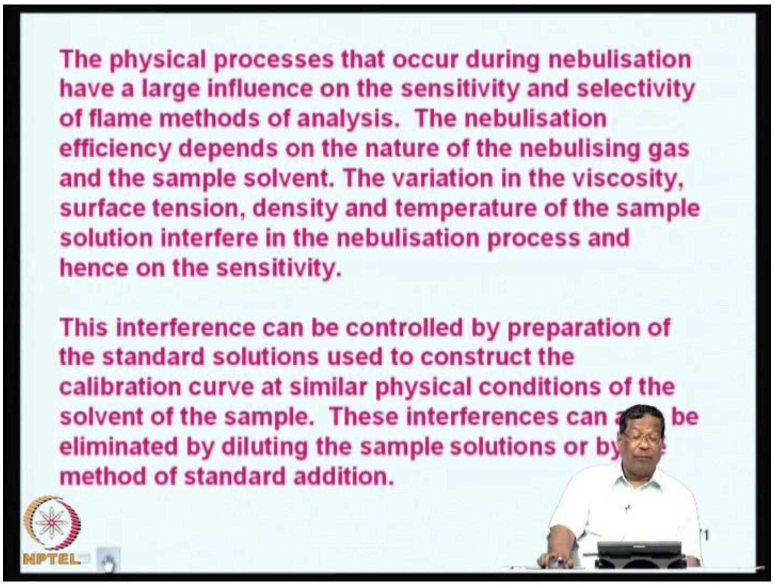

The physical processes that occur during nebulisation have a large influence on the sensitivity and selectivity of flame methods of analysis. The nebulisation efficiency depends on the nature of the nebulising gas and the sample solvent. The variation in the viscosity, surface tension, density and temperature of the sample solution interfere in the nebulisation process and hence on the sensitivity.

This interference can be controlled by preparation of the standard solutions used to construct the calibration curve at similar physical conditions of the solvent of the sample. These interferences can a be eliminated by diluting the sample solutions or by method of standard addition.

Now, the physical processes that occurred during nebulisation; they are large influence on the sensitivity and selectivity of the film methods. The nebulisation efficiency depends upon the nature of the nebulising gas and the samples solvent. The variation in the viscosity, surface tension, density and temperature of the sample all these things interference in the nebulisation process and therefore, they affect the sensitivity. This interference can be controlled to some extent by the preparation of standard solutions used to construct the calibration curve under similar physical conditions of the solvent of the sample. So, this interference can be eliminated by diluting the sample solutions also or by the method of standard addition. These things we will discuss later about the analytical techniques of analytical methodology how we go about doing this standard addition and other techniques.

Now, the presence of high concentration of dissolved salts; for examples, it can reduce an analytical signal. It also leads to formation and incrust station of the nebulizer and the burner head. You know burner head is a basically a small metallic piece with several salts and if the salts are there, they can block the gas passage. So, if it blocks the gas passage, you will not be getting the signal at all. So in general, it can be said that physical interferences can result if the sample and the standard solution vary in bulk composition. The normal sample solution up take in atomic absorption is about 6 to 7 milli liters per minute, and the nebulisation efficiency is of the order of about 10 percent maximum.

Nowadays, it is about 50 13 to 15 percent not more than; that means, only 15 percent of the 6 to 7 ml of the sample gets into the flame as aerosol. So, any change in these normal values causes physical interference and this can lead to spurious signals also. So, I do not want to say more about physical interference because, all these things are common to all elements. Therefore, good maintenance of atomic absorption should take care of such interference. Now, let us talk about chemical interference. We have already explained that the physical interference occur from sample introduction stage before nebulisation until it reaches the burner. Now, once the burner the sample reaches the burner then all types of chemical reactions can occurs. This we also we have discussed earlier with the flame component reactions. You remember, that I want to go back to the slide what I had shown you today only if you could look at this.

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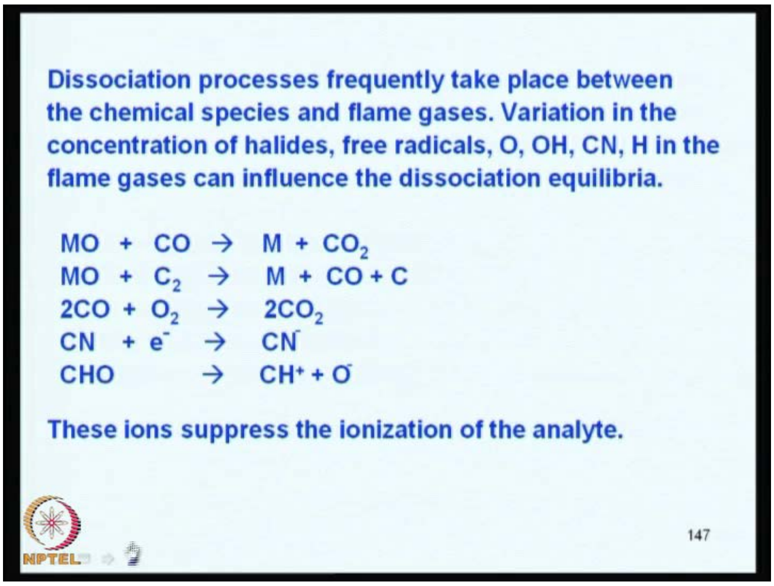

Dissociation processes frequently take place between the chemical species and flame gases. Variation in the concentration of halides, free radicals, O, OH, CN, H in the flame gases can influence the dissociation equilibria.

$MO + CO \rightarrow M + CO_2$
$MO + C_2 \rightarrow M + CO + C$
$2CO + O_2 \rightarrow 2CO_2$
$CN + e^- \rightarrow CN^-$
$CHO \rightarrow CH^+ + O^-$

These ions suppress the ionization of the analyte.

These are some of the reactions we had discussed earlier metal oxide etcetera, but these are all general terms; that is M represents only a metal and CO, C 2, oxygen, electrons these are all these things represents the flame components.

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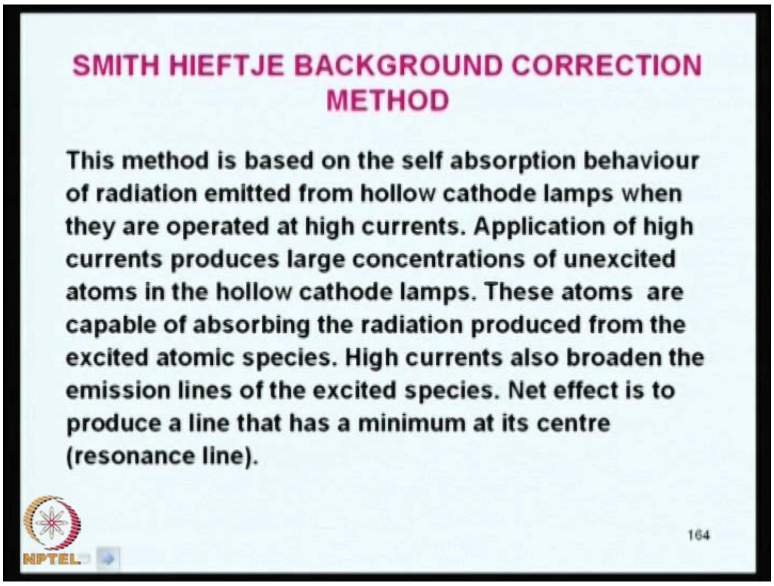

SMITH HIEFTJE BACKGROUND CORRECTION METHOD

This method is based on the self absorption behaviour of radiation emitted from hollow cathode lamps when they are operated at high currents. Application of high currents produces large concentrations of unexcited atoms in the hollow cathode lamps. These atoms are capable of absorbing the radiation produced from the excited atomic species. High currents also broaden the emission lines of the excited species. Net effect is to produce a line that has a minimum at its centre (resonance line).

So now, we will discuss a little more about the chemical interference in specific because, we feel that it is possible to know the reaction correction much more thoroughly if you understand the processes. So, the schematic diagram again I had shown you this figure earlier that, metal has to get evaporated; it must form a solution; and it must form an aerosol then, it forms a solid aerosol then, it comes to gaseous form and then, a metal atoms and then, metal atoms can form oxides and then, as they can get exited they can form react with carbide carbon to form carbides etcetera and are this reaction, this we have seen in earlier and discussed also.

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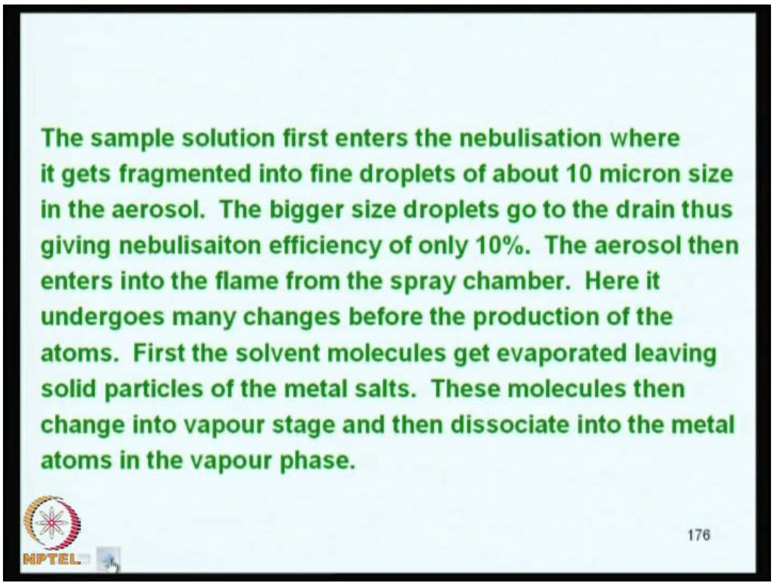

The sample solution first enters the nebulisation where it gets fragmented into fine droplets of about 10 micron size in the aerosol. The bigger size droplets go to the drain thus giving nebulisaiton efficiency of only 10%. The aerosol then enters into the flame from the spray chamber. Here it undergoes many changes before the production of the atoms. First the solvent molecules get evaporated leaving solid particles of the metal salts. These molecules then change into vapour stage and then dissociate into the metal atoms in the vapour phase.

So, the sample solution first enters the nebulisation where it gets fragmented etcetera. The bigger size droplets fall into the collection system and they get lose to drains and smaller 10 percent goes to the atmosphere goes into the spar chamber and then enters this thing enters the burner, and the… It is the free metals undergo a variety of reactions like oxygen, hydrogen, carbon, etcetera and the to get optimum sensitivity, we need the metal atom concentrations. So, chemical interferences are the most common interferences encountered in the atomic absorption spectroscopy. If the sample enters thermally forms a thermally stable compound then, the dissociation of the metal into atoms does not occur. This is a very simple very, straight forward interpretation of the interference in the atomic absorption.

So, if the signal gets attenuated, we have a chemical interference. So, chemical interference can either enhance a signal or attenuate the signal also. Now, let us take an example of calcium chloride. Now, the… In this exit slide,

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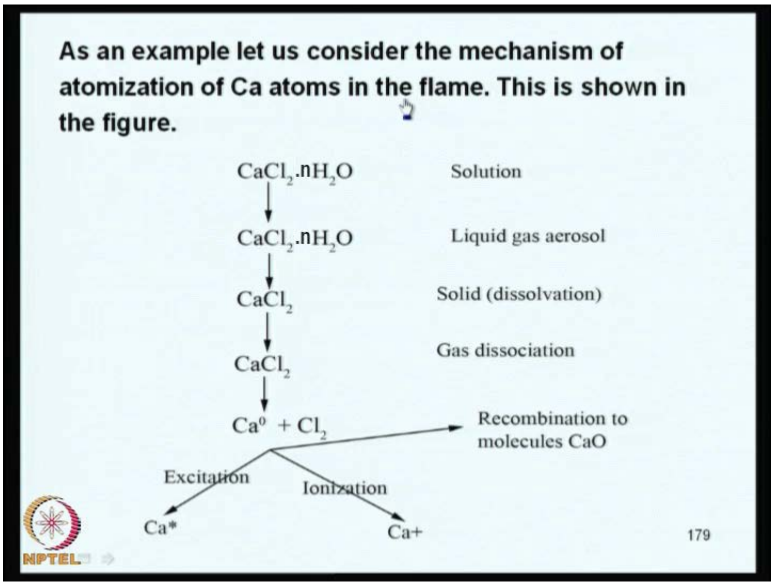

As an example let us consider the mechanism of atomization of Ca atoms in the flame. This is shown in the figure.

$CaCl_2.nH_2O$ Solution

$CaCl_2.nH_2O$ Liquid gas aerosol

$CaCl_2$ Solid (dissolvation)

$CaCl_2$ Gas dissociation

$Ca^0 + Cl_2$ → Recombination to molecules CaO

Excitation → Ca^*

Ionization → Ca^+

I am going to show you the calcium as an example what happens to the solution. Suppose, I start with calcium in solution, I can represent it as calcium chloride CaCl 2 nH 2 O and number of water molecules that is in solution. Now, it must form a liquid gas aerosol of calcium chloride nH 2 O and upon heating it must forms solid. So, the water molecules will evaporate and I have only calcium chloride here and then, the it must melt dissociate calcium chloride will form and calcium atoms will form and then chlorine atoms.

And, this calcium atom from can form exiting it can get excited and then ionized or recombined to form molecules. So, these are the waste techniques because, only the excitation is the one process where the atomic absorption can occur, but ionization and recombination are not concessive to good atomic absorption.

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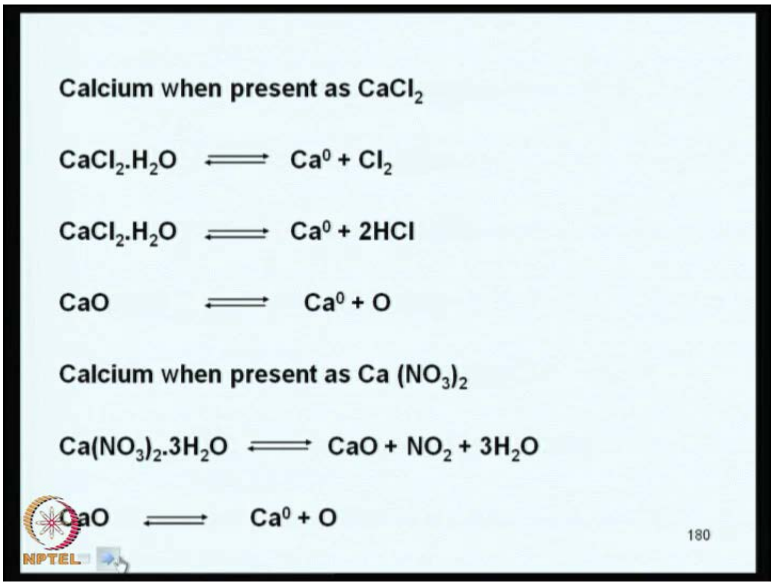

Calcium when present as $CaCl_2$

$CaCl_2.H_2O \rightleftharpoons Ca^0 + Cl_2$

$CaCl_2.H_2O \rightleftharpoons Ca^0 + 2HCl$

$CaO \rightleftharpoons Ca^0 + O$

Calcium when present as $Ca\ (NO_3)_2$

$Ca(NO_3)_2.3H_2O \rightleftharpoons CaO + NO_2 + 3H_2O$

$CaO \rightleftharpoons Ca^0 + O$

So, what are the types of the reactions? Here, it is CaO calcium atom and chlorine and it can also react with the acid present in the solution to form calcium atoms and 2HCl that is hydrochloric acid in the flame. All these reactions are occurring in the flame. So, you can see that calcium oxide suppose it forms because there is air in the flame also, and calcium oxide can get converted to calcium atom and oxygen atoms. So, when it is present as calcium nitrate then, we can expect nitrogenous gases; for example, I have written here that calcium nitrate CaNO 3 twice 3H 2 O gets dissociated into oxide calcium oxide plus NO 2 nitric oxide nitrogen dioxide plus three water molecules. So, if we do this calcium oxide can again decompose to calcium atoms and oxygen. So, I have shown you two types of reactions in which calcium chloride or calcium nitrate may be present as the analyte.

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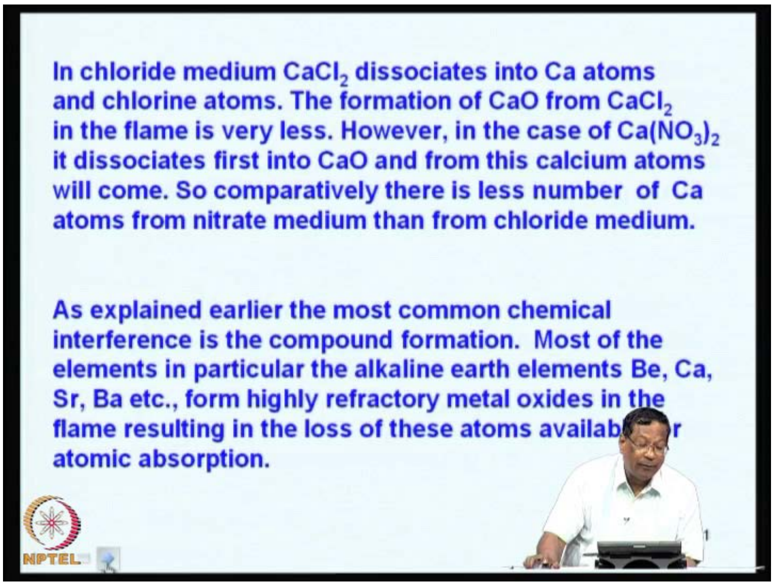

In chloride medium $CaCl_2$ dissociates into Ca atoms and chlorine atoms. The formation of CaO from $CaCl_2$ in the flame is very less. However, in the case of $Ca(NO_3)_2$ it dissociates first into CaO and from this calcium atoms will come. So comparatively there is less number of Ca atoms from nitrate medium than from chloride medium.

As explained earlier the most common chemical interference is the compound formation. Most of the elements in particular the alkaline earth elements Be, Ca, Sr, Ba etc., form highly refractory metal oxides in the flame resulting in the loss of these atoms availab r atomic absorption.

So in chloride medium, it forms calcium atoms and chlorine atoms and the in nitric acid medium, it forms calcium that is the mechanism. In chloride medium, it forms straight away disassociates into calcium atoms. In any acid nitric acid medium that is an oxidant, its gets converted to oxides and then it decompose. So, it is a two stage process. So as explained earlier, the most common chemical interference is the compound formation. So most of the elements in the alkaline earth elements such as beryllium, calcium, stroceium, barium etcetera; they form highly refractory metal oxides in the flame resulting in the loss of these metal atoms available for atomic absorption because, if they form the compounds, they are lost to the atomic absorption.

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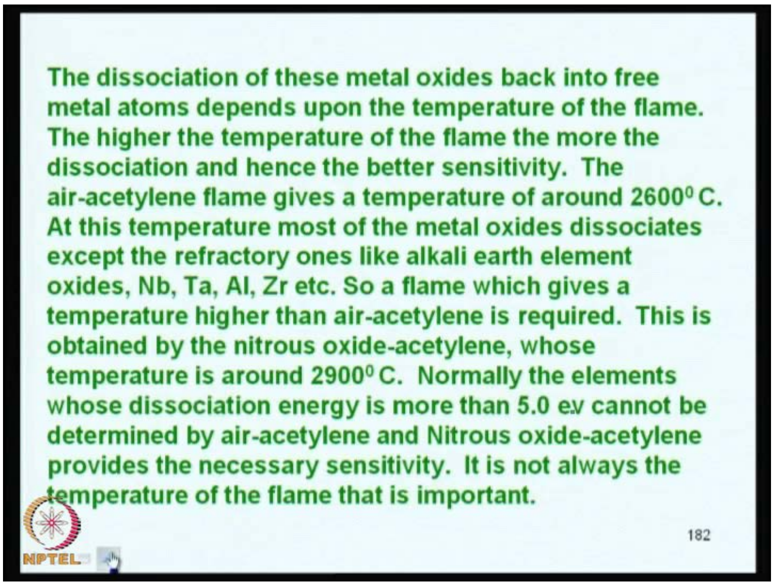

The dissociation of these metal oxides back into free metal atoms depends upon the temperature of the flame. The higher the temperature of the flame the more the dissociation and hence the better sensitivity. The air-acetylene flame gives a temperature of around 2600^0 C. At this temperature most of the metal oxides dissociates except the refractory ones like alkali earth element oxides, Nb, Ta, Al, Zr etc. So a flame which gives a temperature higher than air-acetylene is required. This is obtained by the nitrous oxide-acetylene, whose temperature is around 2900^0 C. Normally the elements whose dissociation energy is more than 5.0 e.v cannot be determined by air-acetylene and Nitrous oxide-acetylene provides the necessary sensitivity. It is not always the temperature of the flame that is important.

So the dissociation of the metal oxides back into free atoms depends upon the temperature of the flame. If the temperature of the flame is very high then, decomposition then always occur. The higher the temperature of the flame, the more is the dissociation and hence better sensitivity. So, it is a very simple logic that if a compound forms in the flame then, we have to raise the temperature of the flame to get the atoms back. So, the air acetylene gives a temperature of about 2300 to 2600 degree centigrade; that is depending upon the composition of the acetylene as well as air mixture. Now, at this temperature most of the metal oxides dissociate expect diffractions elements like alkali, alkaline earth elements also to some extent; niobium, tantalum, aluminum, zirconium, etcetera they form refractory oxides. So, a flame which gives a temperature higher than acetylene; that is 2600 degree is required if your sample contains any of the elements like niobium, tantalum, aluminum, zirconium, etcetera.

Now, this is… How do you get this higher temperature? Suppose, you want to analyze niobium only acetylene will not work, but it will give you very less sensitivity. So, change over to nitrous oxide gas. That we know that nitrous oxide gives you higher temperature up to 2900 centigrade. So, normally they are elements whose dissociation energy is more than 5.0 volts, they cannot be determined by acetylene. This is a very simple very simple logic and guideline for us. So, if the dissociation energy is more than 5 volts, you need air acetylene you do not air acetylene, but what you need is nitrous oxide acetylene gas. It is not always the temperature of the flame that is important, we have to understand this effect because, it is not always the temperature. Many times the carbon oxygen ratio in the flame also determines the sensitivity, not only the high temperature, but adjust the carbon oxygen.

So, if you have a reducing flame that is the reddish flame. Now, if you have a reddish flame that is oxidizing than you may get higher temperature even with the air acetylene also, but there are always limitations of up to maximum you could get is around 2600 degrees. But, higher than that, we have to go for no amount you have to go for nitrous oxides acetylene, but no amount of flow ratio of acetylene and nitrous oxides will change the temperature to the desired level. So, reducing flame providing more flue than the stoichiometric requirement is desirable for refractory metal oxides. So, one should only optimize the flame condition in the fuel to oxidant ratio, height etcetera to get maximum sensitivity. In our laboratory, we have tried some investigations using sugar to alter the carbon oxygen ratio in the flame in the flame for favorable for atomization because, it is very simple to use sugar along because, sugar dissolves in water or acids to large extend and when you introduced sugar in the flame; obviously, most of the sugar components will get decompose into carbon atoms. So, this is one way of adjusting the carbon component also in the flame by just by introducing the sugar.

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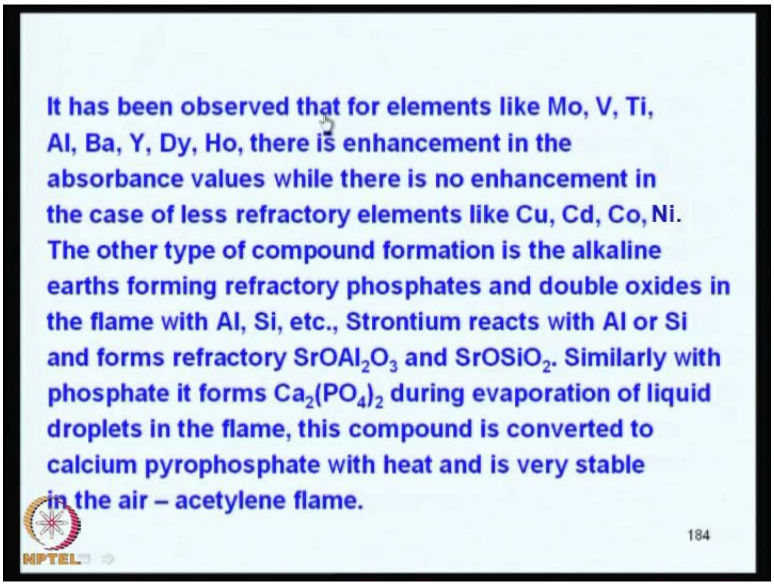

It has been observed that for elements like Mo, V, Ti, Al, Ba, Y, Dy, Ho, there is enhancement in the absorbance values while there is no enhancement in the case of less refractory elements like Cu, Cd, Co, Ni. The other type of compound formation is the alkaline earths forming refractory phosphates 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.

And, we have observed that for elements like molybdenum, titanium, menedium, aluminum, barium, atrium, dysprosium, aluminum, etcetera there is enhancement in the absorbance values, while there is no enhancement in the case of less refractory elements like copper, cadmium, cobalt, etcetera. A very this is a very interesting observation because, when we introduce sugar, the large amount of carbon atoms in the flame and they give a enhanced signal for refractory oxides; that is molybdenum, benydium, titanium, aluminum, all this form refractory oxides; the what do you mean by refractory oxides is very stable oxides which are having, which are stable up to 3000 degree centigrade etcetera.

Now, such elements give you higher signal when we put sugar, but when we do not put sugar, we have we have problems with ordinary elements like copper, cadmium, cobalt, nickel, etcetera. Now, it is very funny because, why there should not be a signal enhancement when we put sugar along with the solution. The answer is very simple. Then, with the even without sugar the dissociation of the salts is complete in the case of copper, cadmium, cobalt and nickel. So, any amount of addition of sugar is not going to increase the concentration because, the dissociation is complete. But, in the case of refractory oxides, we always get enhancement in the signal because, the refractory oxides start decomposing when we put sugar because of the reducing atmosphere. That is in addition to the gas and nitrous oxides flame.

So, the other type of compound formation is also possible where the elements can form refractory phosphates and double oxides in the flame; for example, aluminum, silicon, etcetera, strontium; they react with aluminum or silicon and forms refractory oxides such as SrOAl 2 O 3 strontium oxide aluminum oxide compound and then SrOSiO 2 strontium oxide silicon dioxide compounds. Similarly with phosphate, we have calcium phosphate during the evaporation of the liquid drop lets in the flame. This compound is converted into calcium pyrophosphate with heat and is very stable in the air acetylene flame. For the sake of privity, I want you to read the slide the to get the ideas clear because, in most of the systems, we do have a we do have a situation where refractory oxides give you higher signal when sucrose is the added, and normal elements do not give you sucrose higher significance, higher signal. So, we will continue our discussion in the next class.