Trace and ultra trace analysis of metals Using atomic absorption spectrometry

Dr. J R Mudakavi
Department of Chemical Engineering
Indian Institute of Science, Bangalore

Lecture - 24
Interferences in AAS II

Zeeman splitting of common elements I am showing you now.

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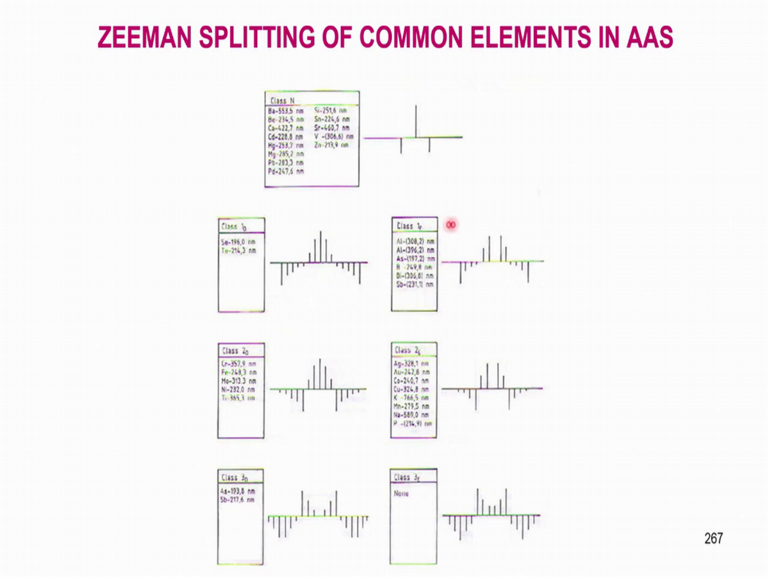

ZEEMAN SPLITTING OF COMMON ELEMENTS IN AAS

Class N
Ba-553,5 nm
Be-234,5 nm
Ca-422,7 nm
Cd-228,8 nm
Hg-253,7 nm
Mg-285,2 nm
Pb-283,3 nm
Pd-247,6 nm
Si-251,6 nm
Sn-224,6 nm
Sr-460,7 nm
V -(306,6) nm
Zn-213,9 nm

Class 1_0
Se-196,0 nm
Te-214,3 nm

Class 1_e
Al-(308,2) nm
Al-(396,2) nm
As-(197,2) nm
B -249,8 nm
Bi-(306,8) nm
Sb-(231,1) nm

Class 2_0
Cr-357,9 nm
Fe-248,3 nm
Mo-313,3 nm
Ni-232,0 nm
Ti-365,3 nm

Class 2_e
Ag-328,1 nm
Au-242,8 nm
Co-240,7 nm
Cu-324,8 nm
K -766,5 nm
Mn-279,5 nm
Na-589,0 nm
P -(214,9) nm

Class 3_0
As-193,8 nm
Sb-217,6 nm

Class 3_e
None

Because there are several classes of elements where the zeeman splitting is shown schematically. So, for example, on the top of this slide what you will be seeing class n that is very berrium, beryllium, calcium, etcetera, I have I written the wavelengths that is atomic absorption wavelengths for these elements here. And then here it contains silicon tin strontium vanadium etcetera, zeeman splitting of almost all elements Have been um have been studied since last more than hundred years.

So, you can also see we have here class, class 10, and then we have class, class 1 f here. And then 2 O 2 0 3 0 etcetera these are different classes. Typical notations for the zeeman splitting. For example, if you see here selenium and tellurium the zeeman splitting will be occurring like this. So, the upwards and downwards signals represent polarization. And here you can see for selenium and tellurium there are 1 2 3 4 5 pi components 5 sigma and 5 sigma plus and 5 sigma minus.

Similarly, for chromium iron molybdenum etcetera we have zeeman splitting occurring and their wavelengths are indicated here. You do not have to remember these numbers for examination or test because in general if you are remembering that some elements are having normal zeeman effect and some elements are having anomalous zeeman effect that should be good enough for your practice of atomic absorption.

Similarly, we have class 3 0 that is arsenic and antimony others are aluminum etcetera most of the other elements are defined here, the splitting is shown here.

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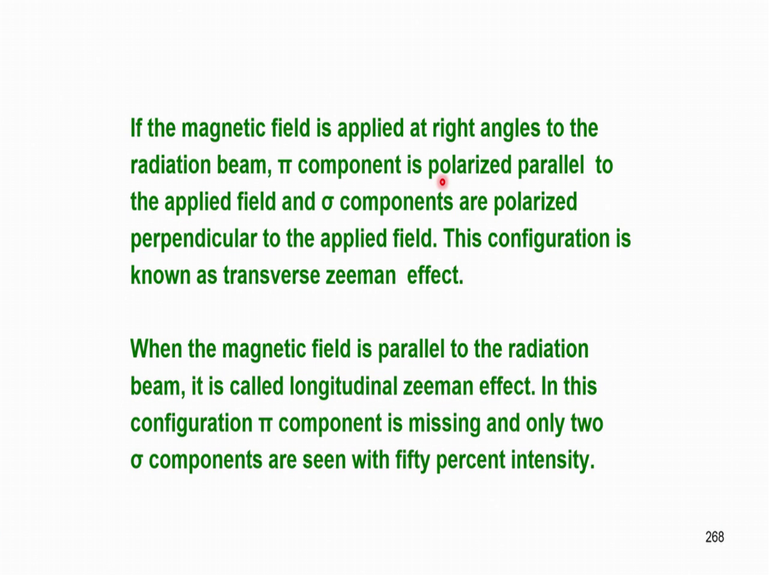

If the magnetic field is applied at right angles to the radiation beam, π component is polarized parallel to the applied field and σ components are polarized perpendicular to the applied field. This configuration is known as transverse zeeman effect.

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 two σ components are seen with fifty percent intensity.

So, if the magnetic field is applied at right angles to the radiation beam pi component is polarized parallel to the applied field, and sigma components are polarized perpendicular to the applied field. This is what I was telling you that, whenever there is a magnetic field around the flame the radiation from hollow cathode lamp split is into pi component and sigma component and I need a polarizer. Polarizer to separate the sigma and pi components otherwise we will not be able to see the effect of magnetic field ok.

So, this configuration is known as transverse zeeman effect; that means, put a magnetic field and put a polarizer, perpendicular to the applied field. So, this configuration is known as transverse zeeman field and if you put the polarizer and if the magnetic field is parallel to the radiation beam then it is called longitudinal zeeman effect; that means, if the flame is like this, you put the flame magnet around it and transverse is flame is like this you put the magnetic field up and below top and below, that is transverse zeeman effect and if you put along the flame horizontal then it is longitudinal zeeman effect.

In this component pi component is mixing because only 2 sigma components are seen with 50 percent intensity.

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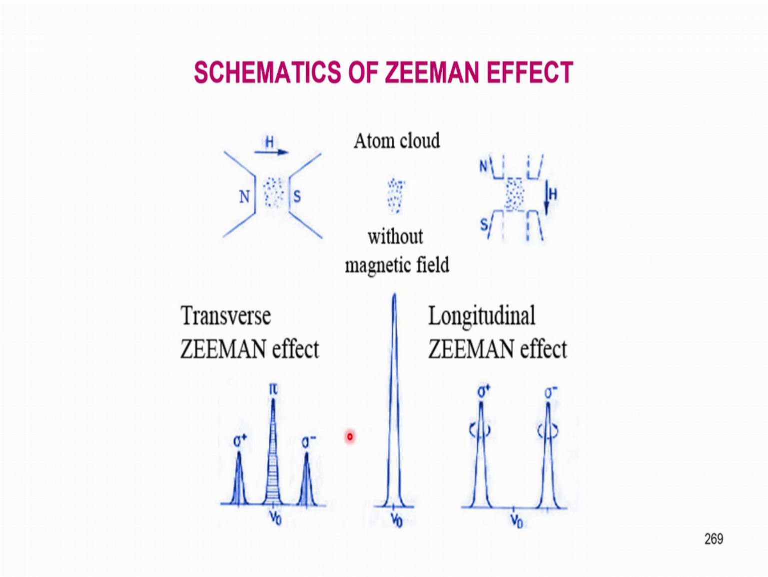

SCHEMATICS OF ZEEMAN EFFECT

Atom cloud

without magnetic field

Transverse ZEEMAN effect

Longitudinal ZEEMAN effect

So, this is the schematics of the zeeman effect, the I have to tell you at this stage that the zeeman effect background correction is one of the most important development in the atomic absorption spectrometry. And the signal measure is always less than the normal atomic absorption signal because the absorption line is split into 2 or 3 components. And we measure only one component that is pi component or sigma component, and the arrangement of atoms I am making it clear to you in this slide that is this is the atomic vapour or flame and the poles of the magnet are arranged perpendicular parallel to this.

This is without magnetic field and this is again with magnetic field, this is perpendicular, this is horizontally this is the sorry, this is horizontally this is perpendicular and this effect is known as transfer zeeman effect, here it is split into pi which is 50 percent stronger signal sigma plus and sigma minus are without the r on the left hand long shorter wavelength and longer wavelength ranges. And when the without the magnetic field my signal is double then this double than this and it is like this, and in the magnetically if I put a launch in the longitudinal effect, this pi component completely vanishes only the sigma plus and sigma minus are visible ok.

Now, is this clear to you. If it is not clear what I want you to do is imagine a flame and put 2 boxes around it and put 2 boxes on the top and bottom of the of the flame, and then you should imagine that this signal is split into 3 1 is pi when sigma plus and another is minus without the signal without the magnets only one signal is obtained and in longitudinal zeeman effect pi component is missing.

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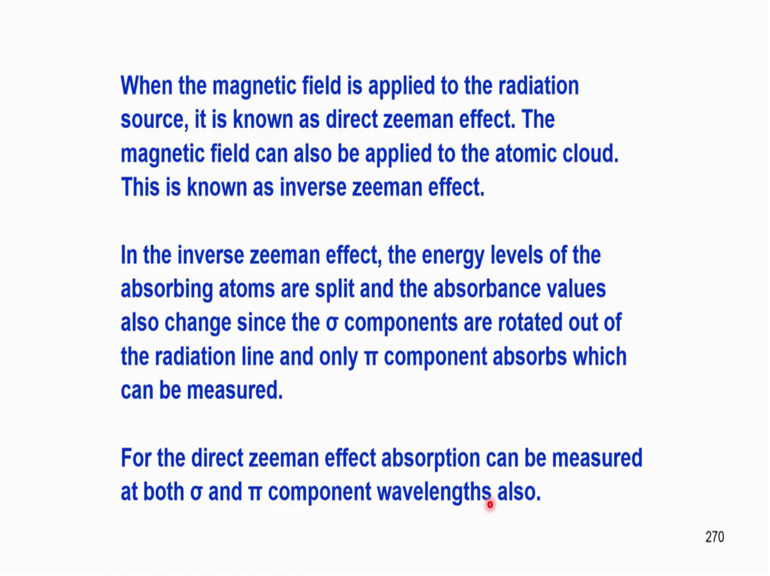

When the magnetic field is applied to the radiation source, it is known as direct zeeman effect. The magnetic field can also be applied to the atomic cloud. This is known as inverse zeeman effect.

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.

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So, you will see only 2 sigma components. And that is the central line is missing. So, when the magnetic field is applied to the radiation source, to the radiation source. Now we are talking about earlier I where talking about the applied application of magnetic field to the flame, where atomic vapor is disturbed whereas, now I am talking about magnetic field applied to the radiation source; that means, hollow cathode lamp itself. To the hollow cathode lamp if I apply a magnetic field then it is known as direct zeeman effect. The magnetic field can also be applied to the atomic cloud this I we have already seen, this is known as inverse zeeman effect. So, both these effects have been used in atomic absorption to a large extent and both are possible.

Nowadays the transverse zeeman effect is a more employed that is to the hollow cathode lamp itself. Or we can do it in the flame also and even in electrochemical electro thermal atomic absorption. I want you to remember that the zeeman effect is used very effectively for hollow for electro thermal atomic absorption. Because it extends the determination levels to parts per billion levels ppb.

So, in the universe zeeman effect the energy levels of the absorbing species as split absorbing atoms in the inverse zeeman effect that is atomic cloud. The at atoms and energy of the atoms are split and the absorbance values also change since the sigma components are rotated out of the radiation line by putting a polarizer. And only pi component absorbs which can be measured. Now for the direct zeeman effect absorption can be measured at both sigma and pi component wavelengths also; that means, in the direct one both are observe all the measurements are absorbed, all the wavelengths and in the universe zeeman effect only the pi component is absorbed is measured.

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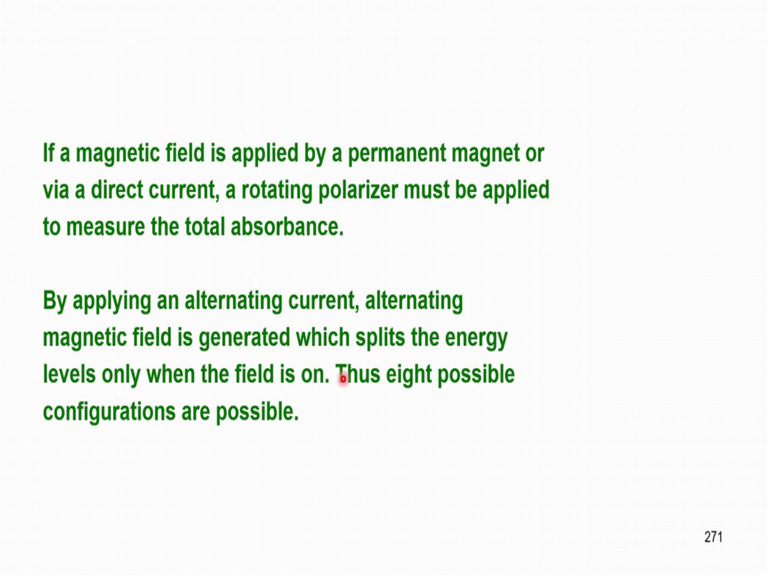

If a magnetic field is applied by a permanent magnet or via a direct current, a rotating polarizer must be applied to measure the total absorbance.

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, if a magnetic field is applied by a permanent magnet or via a direct current then a rotating polarizer must be applied to measure the total absorbance; that means, I apply a magnetic field permanent magnetic field or I can generate a temporary magnetic field by a passing current also, this effect is known it is a physical physics theory that you can generate magnets by passing electric current through a magnet. And a rotating polarizer I must apply then I can measure the total absorbance.

So, by applying alternating current, alternating magnetic field is generated which split is the energy levels only when the field is on; that means, AC current and the field is on, the it split is the energy when AC is not on, there is 0 current and the zeeman effect is not there; that means, you can measure the total background as well as the signal using these things. Thus 8 possible combinations are possible.

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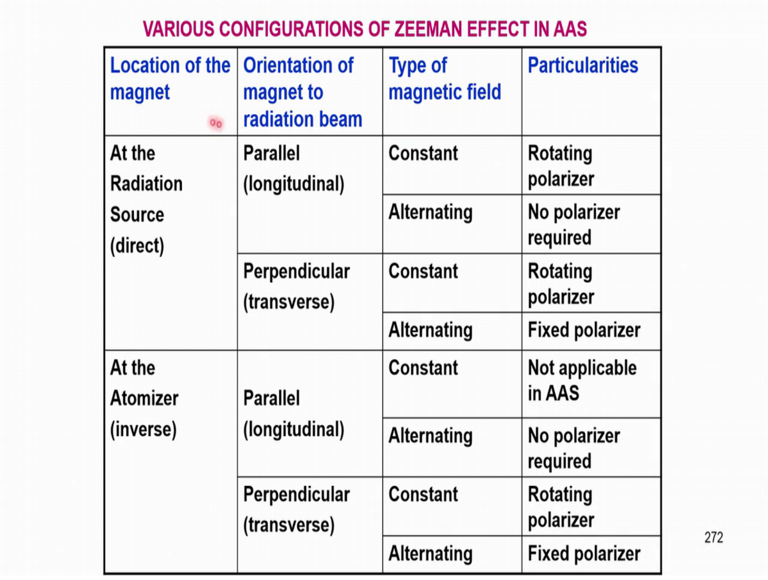

VARIOUS CONFIGURATIONS OF ZEEMAN EFFECT IN AAS

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 polarizer required
	Perpendicular (transverse)	Constant	Rotating polarizer
		Alternating	Fixed polarizer

What are those 8 combinations? One is I have made a small table here location of the magnet, orientation of the magnet, parallel or perpendicular type of the magnetic field and particularity.

So, at the radiation source if I apply a magnetic field, I can apply parallel or perpendicular to that, to their radiation source hollow cathode lamp. Then type of magnetic it can be constant alternating constant or alternating, that is with AC without AC direct. One is a constant means direct current another is with AC, then if it is constant I need a rotating polarizer. If I use alternating magnetic field using AC current I do not need a polarizer, this is a little tricky to understand, but I think most of you will appreciate if you look at this table a little critically.

So, suppose I go for perpendicular arrangement. Then also I can have a constant magnetic field or alternating magnetic field, in the case of constant magnetic field I need a rotating polarizer. And alternating field I need a fixed polarizer, because it is permanent. So, at the atomizers; that means, at least on the flame I can have similar combinations what I have here parallel the same as this and it is constant not applicable in atomic absorption inverse zeeman effect is not applicable in atomic absorption, but alternating current I can use to generate the parallel magnetic field that is longitudinal in that case I do not need a polarizer. Though I can have another combination that is perpendicular and here I have 2 possibilities one is rotating polarizer another is fixed polarizer. These particularities you need not remember, but these things can be determined easily ok.

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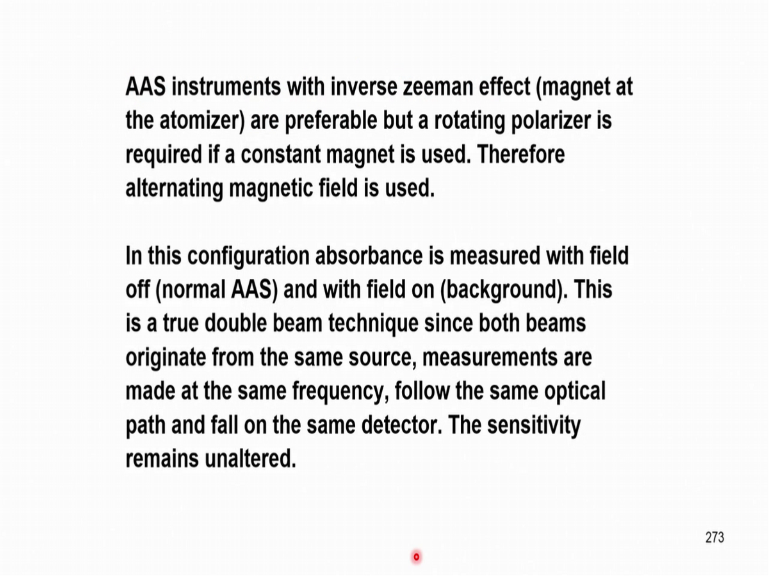

AAS instruments with inverse zeeman effect (magnet at the atomizer) are preferable but a rotating polarizer is required if a constant magnet is used. Therefore alternating magnetic field is used.

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, atomic absorption spectrophotometers require inverse zeeman effect that is magnet at the hollow cathode lamp, magnet at the sorry, magnet at the atomizer are preferable, but for that we need a rotating polarizer, if constant magnet is used therefore, alternating magnet I can use comfortably. So, in this configuration absorbance is measured with field off; that means, no magnetic field total absorbance. And with field on the lines are split pi is missing. So, only the background correction background data is obtained. You understand? The logic field on pi is pi component is absorbance is measured and pi components are missing that is sigma components of pi is on sigma is off. And in field off the absorbance from the pi component is missing, because we will put a polarizer.

So, with field off and field on we measure the normal atomic absorption and field on we measure the background absorbent absorption. So, if you subtract normally as from the background if this is what you get the signal for the atomic absorption. This is a true double beam technique without using hydrogen lamp. Because there in the even in hydrogen lamp, what we normally measure is without this aspiration we are in deuterium lamp without aspiration, we measure the total absorbance with a hollow cathode lamp we measure the actual absorbance from the atom.

So, you have to subtract. Similarly with zeeman effect I do not need a hollow cathode lamp or sorry, I do not need a deuterium lamp. This is true double beam technique because both beams originate from the same source. So, any change in the signal is automatically attenuated, because with the field on, I measure the background with the field off I measure the background with a field on I measure only the background. Because the sigma are removed pi is rotated out. So, whatever is the remaining residual radiation I am measuring with field of I measure the normal layers.

So, it is just like deuterium lamp correction, but much better why we will see a bit later. So, the measurements are made at the same frequency, we follow the they follow the same optical path and fall on the same detector. So, the sensitivity remains unaltered. So, this aspect is to be very clear to you, because whenever you want to buy an atomic absorption spectrometer.

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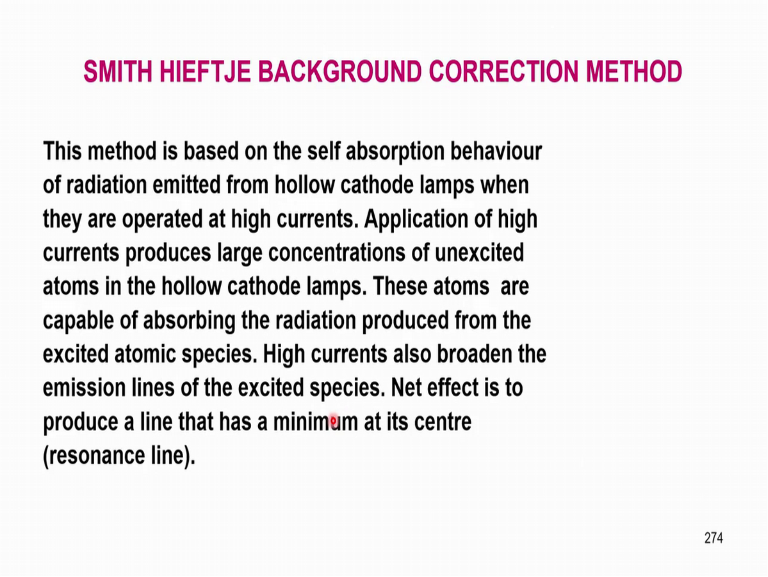

SMITH HIEFTJE BACKGROUND CORRECTION METHOD

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).

Whenever you want to buy an atomic absorption spectrometer the manufacturers will give you a choice of a background character, they will ask you sir do you need edit a deuterium lamp character or you need zeeman effect or you need some other effect that some other effect is know as smith hieftje background correction method. And depending upon the background character you choose the cost of atomic absorption also will vary.

So, it is important for you to understand the mechanism of background correction of deuterium lamp, mechanism of background correction of zeeman effect back zeeman effect, and the mechanism of background effect for the smith hieftje background correction method. Relatively smith hieftje background correction is somewhat of recent origin. And very few instruments are available nowadays quite a lot of instruments are available with smith hieftje correction also.

So, what is smith hieftje background correction method? This method is based on the self absorption behavior of radiation emitted from hollow cathode lamps when they are operated at high currents. I think you remember I had told you that whenever during the introduction of atomic absorption that whenever there is a change sodium lamp example I had given you there is change in the radiation, that is the lamp is coming on and off on and off it is due to the absorbance of the free atoms generated in the sodium vapour lamp.

So, sodium vapour lamp whenever you put it on the sodium will evaporate fill the lamp with lot of vapours from sodium atoms and they will there will be a light emission and after some time the absorb the generated atoms sodium atoms will absorb the same radiation lamp puts off. This you had seen your even see you can even see in the streetlights even now wherever sodium vapour lamps are on. As the temperature increases the absorbance increases this is known as self reversal.

So, application of. So, how do I increase the temperature in the hollow cathode lamp. What I do is at high temperature high current the hollow cathode lamps, whenever I operate with high current the self absorption behavior becomes more prominent because it gets heated more and the absorbance will be more. So, application of high current what does it do? It produces large concentrations of the unexcited atoms in the hollow cathode lamp.

So, these atoms unexcited atoms I think you should remember this. These atoms are capable of absorbing the radiation produced from the hollow cathode lamp. It is just like eating it is owner radiation. So, the these atoms are capable of absorbing the radiation produced from the excited atomic species. So, high currents also broaden the emission lines of the excited species this is another property. Whenever I apply high current they broaden the emission lines of the excited species. Net effect what is the net effect of both these thing s is to produce a line that has a minimum at it is center that is resonance line; that means, I take a hollow cathode lamp apply high current once and apply low current once.

So, whenever I have low current there is no self absorption. Whenever there is high current lot of free atoms are produced they absorb the radiation and then, they the signal from the hollow cathode lamp becomes less. It is just like putting off the lamp and whenever it reaches minimum that is the background absorbance. So, this is another way of making the background correction, net effect is to produce a line hollow cathode line that has minimum at it is center; that means, that is the background that is what is the center? That is the resonance line.

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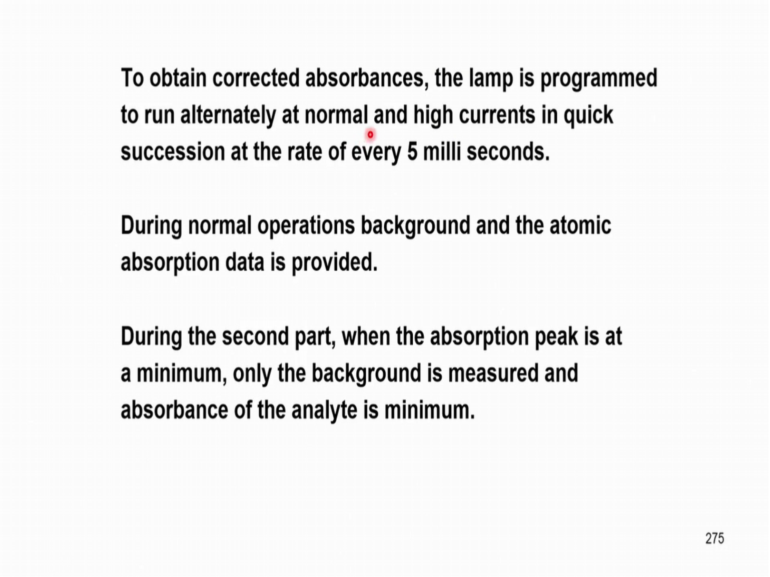

To obtain corrected absorbances, the lamp is programmed to run alternately at normal and high currents in quick succession at the rate of every 5 milli seconds.

During normal operations background and the atomic absorption data is provided.

During the second part, when the absorption peak is at a minimum, only the background is measured and absorbance of the analyte is minimum.

So, to obtain corrected absorbance the lamp is programmed to run alternately at normal and high currents, what we do? You take the hollow cathode lamp apply low current and high current, that is all we do. And measure the absorbance when it is high current and measure the absorbance when it is low current. When it is low current it is background plus sample when it is high current it is only the background. So, subtract the 2 you will get the atomic absorption signal. So, at what frequency we do this. We do this at the alternately at very high frequency for almost every 5 milliseconds I change the current high and low, high and low, high and low, every 5 milliseconds.

So, what happens you can extrapolate the difference of absorbance in the when you plot the absorbance curve. The total amount of absorbent because it is cut, cut. So, it will be like a square wave you can add up all that and draw a continuous curve that is some sort of theoretical extrapolation. And during normal operation background and atomic absorption data is provided. What do we do here? Normal operation no extra atom generation no self reversal.

So, the atomic absorption spectra absorption data of the whole species is obtained. Second part when the absorption peak is at a minimum only the background is measured. And the absorbance of the analyte is minimum. So, you subtract the 2 background is corrected that what we have been discussing. So, in the atomic absorption, why background? Because the background there is certain amount of absorbance at the resonance line from the flame, and from the other elements that may be present to some extent. That background correction must be subtracted from the sample atomic absorption and there are 3 mechanisms. One is deuterium lamp, another is zeeman effect and another is smith hieftje effect. Smith hieftje are the scientists who discovered this phenomenon and applied for the first time in atomic absorption measurements. And these were this type of correction has come only since last 20 years. Zeeman effect is there since last thirty years. Hydrogen deuterium lamp the background correction is there since almost 40, 45 years ok.

But even now these things are being produced and atomic absorption with all the 3, or any one of the 3 are usually marketed and you will have to choose and the proper background correction whenever you want to buy an atomic absorption system ok.

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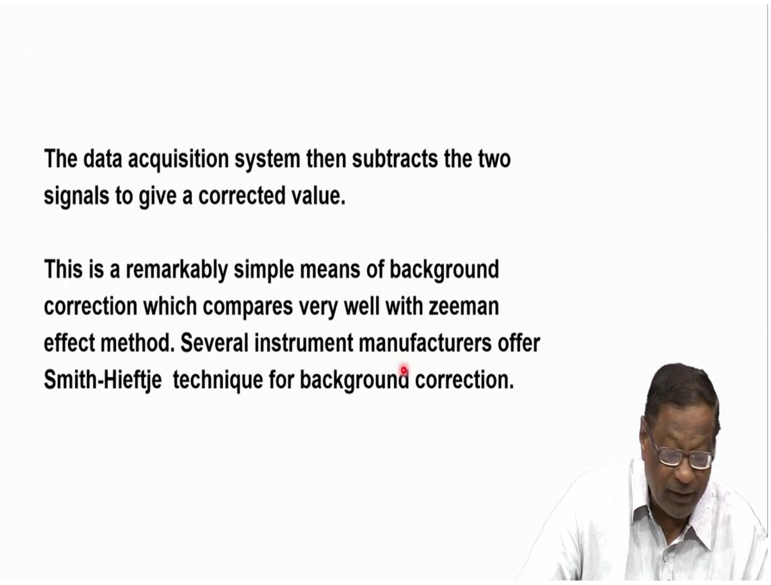

The data acquisition system then subtracts the two signals to give a corrected value.

This is a remarkably simple means of background correction which compares very well with zeeman effect method. Several instrument manufacturers offer Smith-Hieftje technique for background correction.

So, the data acquisition system in atomic absorption I have already told you that most of the time computers are being employed. And the plots and other things etcetera data everything is by computer nowadays. And the data acquisition system automatically subtracts the 2 signals in smith hieftje correction.

We have been discussing smith hieftje correction. So, normal observation background and atomic absorption and high current only background and we do a data acquisition system that subtracts the 2 signals to give the corrected value. So, this is a simple remarkable means of background correction which compares very well with zeeman effect method. Several instrument manufacturers offers smith hieftje technique for background correction. So, all these 3 are available.

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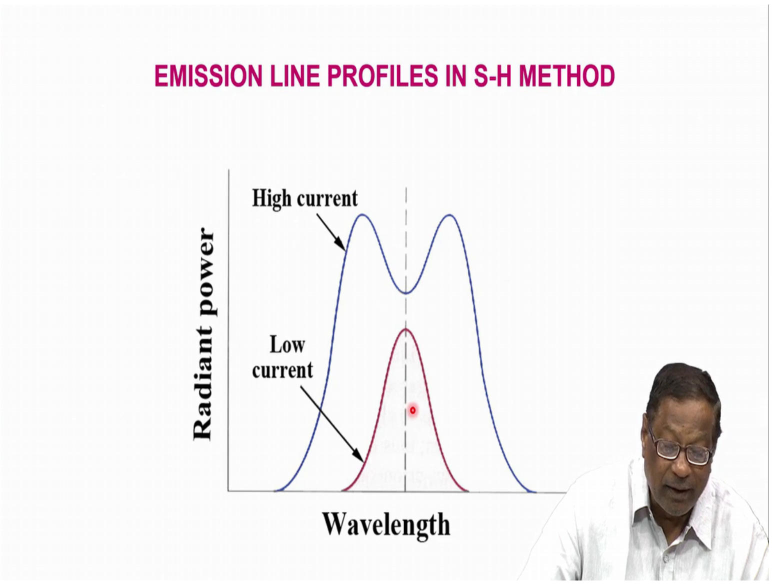

EMISSION LINE PROFILES IN S-H METHOD

So, this is what happens here, in the absorption at low current I have atomic absorption and in the high current level there is a reversal and then only the atomic absorption difference is measured in the smith hieftje correction ok.

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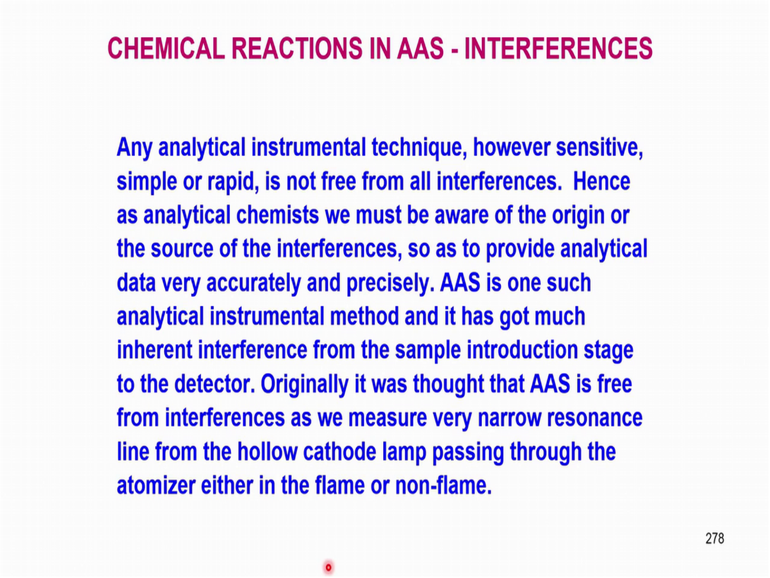

CHEMICAL REACTIONS IN AAS - INTERFERENCES

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 resonance line from the hollow cathode lamp passing through the atomizer either in the flame or non-flame.

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So, that is about atomic absorption in background correction. So, we will not discuss anything further than that, because there are other techniques that we need to discuss here and it is important for us to understand what are the chemical reactions taking place in atomic absorption interferences ok.

So, any analytical technique for that matter; however, sensitive any analytical technique it is simpler or rapid, whatever is their it is not free from all interferences definitely it would not be free from all interferences this we have been discussing since quite some time now. So, analytical chemist as analytical chemists or scientist we must be aware of the origin or the source of the interferences. Why? We have to provide an analytical data very accurately and precisely otherwise, kemeny chemical analysis will lose it is meaning.

So, atomic absorption spectrometry is one such analytical instrumental method and it has got much inherent interferences. From the sample introduction stage onwards to the detector level. Originally it was thought that a s is free from interferences and I have also told you a number of times that it is almost free from interference I never said it is totally free from interference if you remember my earlier sessions. But it is important that we measure very narrow resonance line from the hollow cathode lamp passing through the atomizer either in the flame or in the non flame that is a electro thermal atomic absorption.

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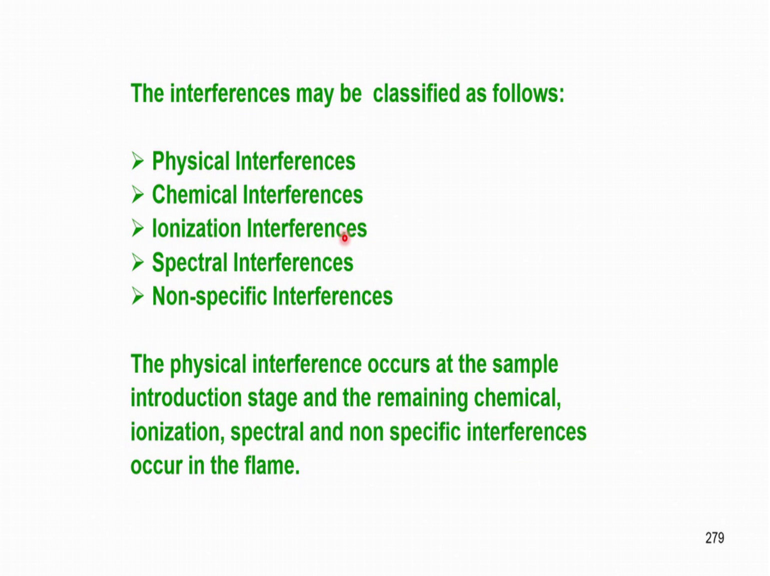

The interferences may be classified as follows:

- 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.

So, the interferences we have already seen this the chemical reactions and the interferences may be classified as follows physical chemical ionization spectral and nonspecific. The physical interference occurs at the simple introduction stage and the remaining chemical ionization spectral and nonspecific interferences occur in the flame ok.

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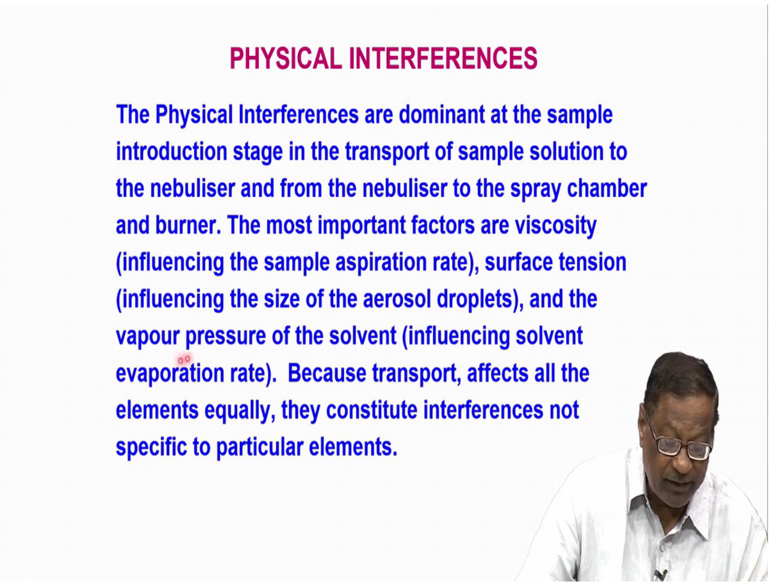

PHYSICAL INTERFERENCES

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, physical interferences are there in the sample introduction stage this we have already discussed a little bit earlier. And the it all depends upon viscosity, surface tension, vapor pressure etcetera, and because of the transport all the elements are effect it affects all the elements, but the signal becomes less.

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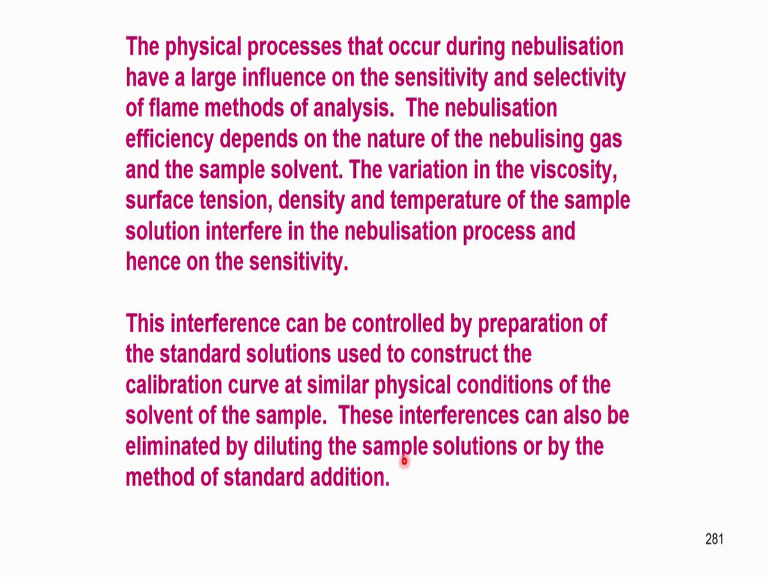

The physical processes that occur during nebulisation have a large influence on the sensitivity and selectivity of flame methods of analysis. The nebulisation efficiency depends on the nature of the nebulising gas and the sample solvent. The variation in the viscosity, surface tension, density and temperature 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 also be eliminated by diluting the sample solutions or by the method of standard addition.

So, physical processes occur during nebulisation. They have a large influence on the sensitivity. And selectivity nebulisation efficiency depends on the nature of nebulising gas and the sample solvent. So, the interference can be controlled by preparation of standard solutions and there by matching the solutions etcetera. And that is by standard deviation this we will discuss a little bit during the application of the atomic absorption.

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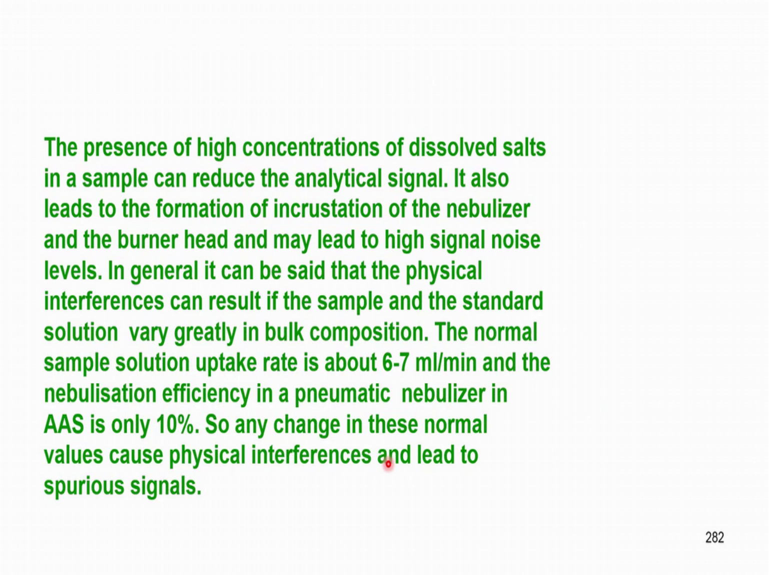

The presence of high concentrations of dissolved salts in a sample can reduce the analytical signal. It also leads to the formation of incrustation of the nebulizer and the burner head and may lead to high signal noise levels. In general it can be said that the physical interferences can result if the sample and the standard solution vary greatly in bulk composition. The normal sample solution uptake rate is about 6-7 ml/min and the nebulisation efficiency in a pneumatic nebulizer in AAS is only 10%. So any change in these normal values cause physical interferences and lead to spurious signals.

So, presence of high concentrations of dissolved salts etcetera, this we have already covered a little bit and So, I will not be covering much, but except to highlight the normal sample solution should be about 6 to 7 milliliters per minute. And nebulisation efficiency is about 10 percent. Nowadays, you get about 15 to 20 percent nebulisation efficiency is very well accepted.

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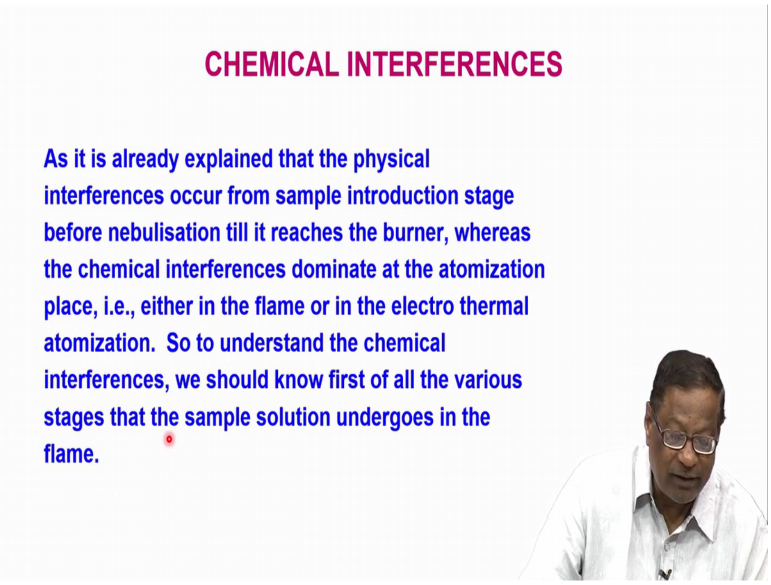

CHEMICAL INTERFERENCES

As it is already explained that the physical interferences occur from sample introduction stage before nebulisation till it reaches the burner, whereas the chemical interferences dominate at the atomization place, i.e., either in the flame or in the electro thermal atomization. So to understand the chemical interferences, we should know first of all the various stages that the sample solution undergoes in the flame.

So, as it is um it is physical interferences occurs from sample introduction stage before nebulisation. So, till it reaches the burners whereas, chemical interferences dominate in the atomization phase. That is in the flame or in the electro thermal atomization.

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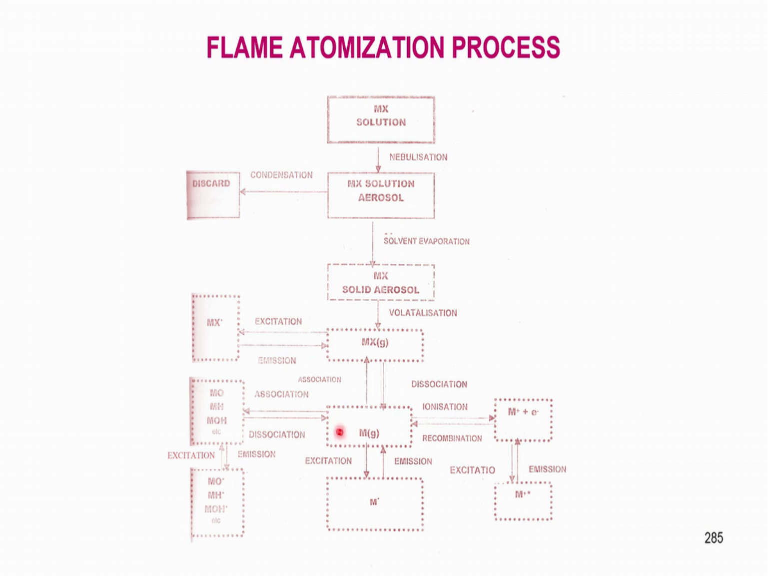
FLAME ATOMIZATION PROCESS



So, what happens is this? This I had shown you earlier, sample solution mx solution ionize solid aerosol solid from the solid aerosol gaseous formation from the gaseous. There is excitation, association, dissociation and ionization and recombination, but none of these things are suitable for atomic absorption. And these things are also not suitable for atomic absorption only the metal ions are suitable. Even if it forms a excited state and emission this is atomic absorption, but if the ions undergo excitation or emission this also does not lead to any atomic absorption.

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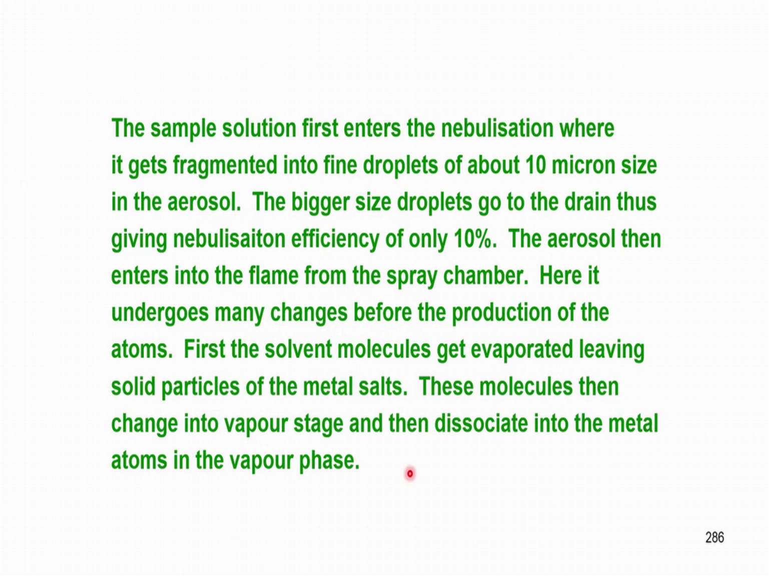

The sample solution first enters the nebulisation where it gets fragmented into fine droplets of about 10 micron size in the aerosol. The bigger size droplets go to the drain thus giving nebulisaiton efficiency of only 10%. The aerosol then enters into the flame from the spray chamber. Here it undergoes 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 enters the nebulisation where it gets fragmented into the fine droplets of about 10 micron size. The bigger sized droplets go waste and aerosol enters the flame and all the processes which I had discussed earlier occur.

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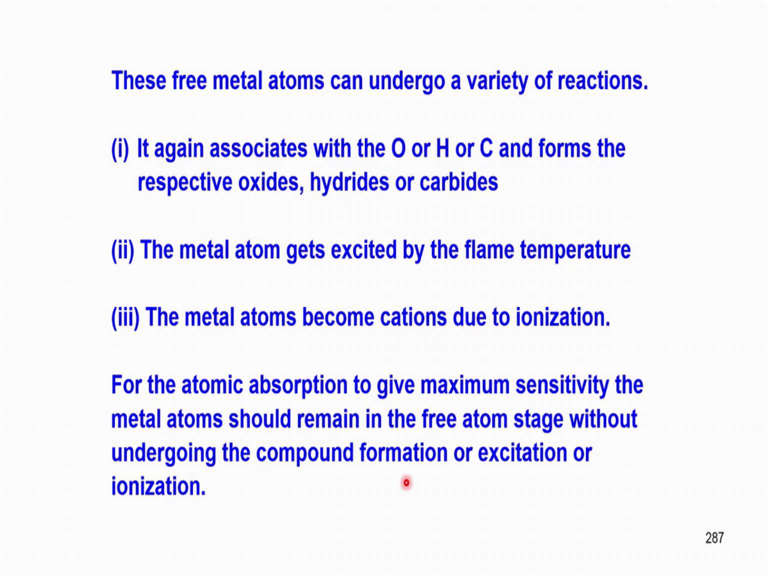

These free metal atoms can undergo a variety of reactions.

(i) It again associates with the O or H or C and forms the respective oxides, hydrides or carbides

(ii) The metal atom gets excited by the flame temperature

(iii) The metal atoms become cations due to ionization.

For the atomic absorption to give maximum sensitivity the metal atoms should remain in the free atom stage without undergoing the compound formation or excitation or ionization.

So, the free atoms undergo a variety of reactions all these things we already discussed there is not much to do discuss except that CH, NH, OH radicals are formed, and chemical interferences can occur And prevent enhance or suppress the formation of background interference.

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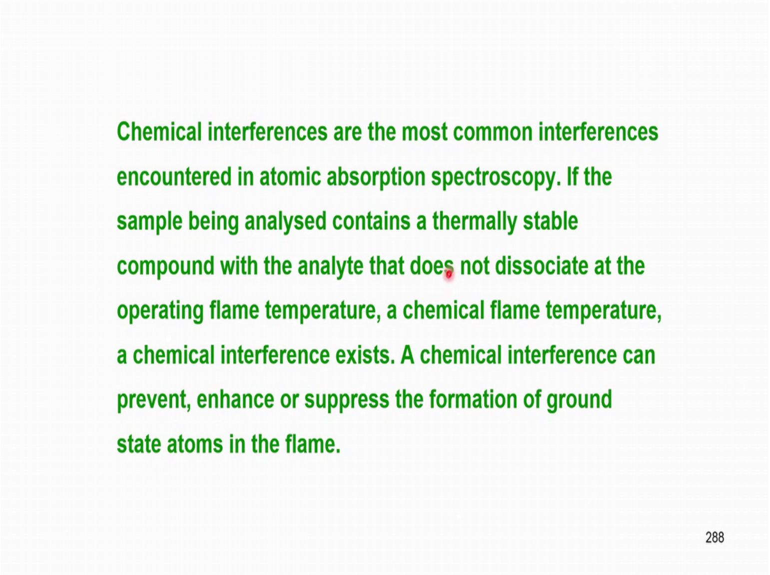

Chemical interferences are the most common interferences encountered in atomic absorption spectroscopy. If the sample being analysed contains a thermally stable compound with the analyte that does not dissociate at the operating flame temperature, a chemical flame temperature, a chemical interference exists. A chemical interference can prevent, enhance or suppress the formation of ground state atoms in the flame.

Background state atoms in the flame and we will consider this calcium atoms.

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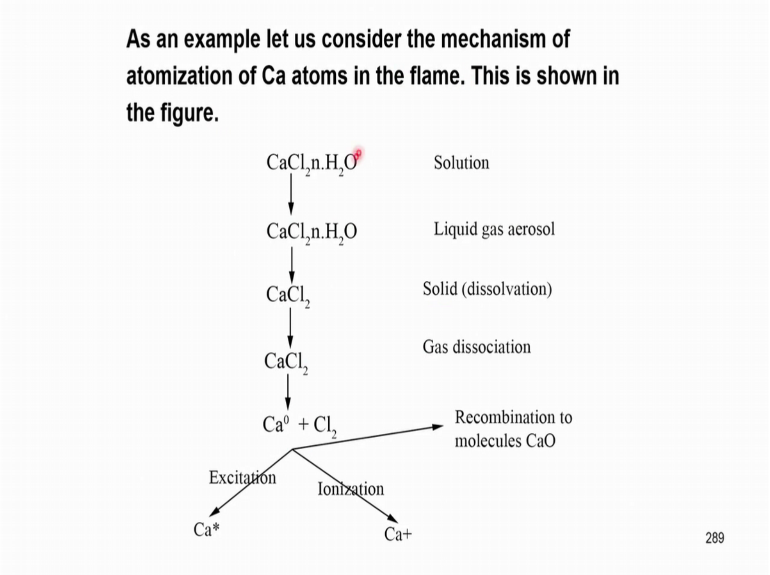

As an example let us consider the mechanism of atomization of Ca atoms in the flame. This is shown in the figure.

$CaCl_2 n.H_2O$ Solution

$CaCl_2 n.H_2O$ Liquid gas aerosol

$CaCl_2$ Solid (dissolvation)

$CaCl_2$ Gas dissociation

$Ca^0 + Cl_2$ Recombination to molecules CaO

Excitation Ca^*

Ionization Ca^+

And in calcium atoms I have this calcium chloride NH 2 a solution that n is not defined, because it is all solvated molecule.

So, in the solvated molecule from the solvated molecule in the sample, I produce a liquid gas aerosol and water will evaporate, I have a solid calcium chloride solution. From the solid I have a gaseous one from the gaseous this thing I have a concentration of calcium ions and chlorine gas and these 2 can combine, and from calcium I can get excited atoms here calcium and if it is the ionization it is waste recombination with oxygen coming from the flame or it from the air outside the flame, it leads to calcium oxide which is not good for atomic absorption.

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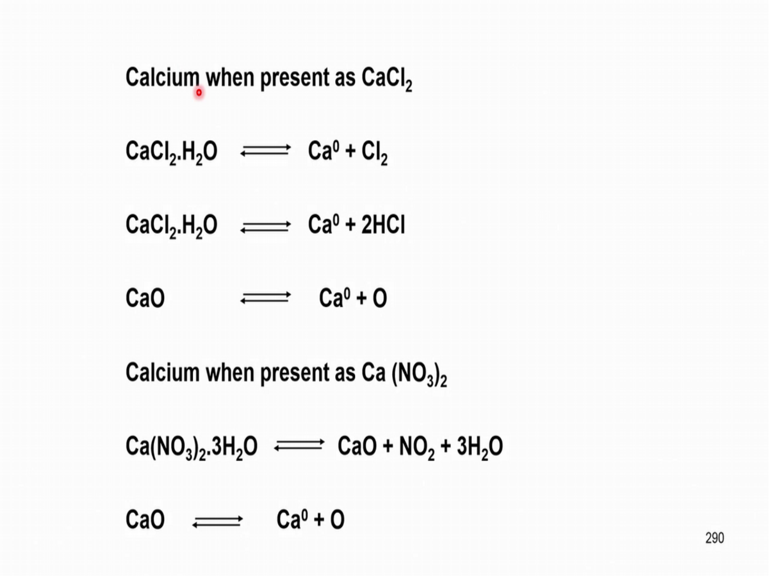

Calcium when present as $CaCl_2$

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

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

$CaO \rightleftharpoons Ca^0 + O$

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, this is a typical scheme. So, calcium when it is present as calcium chloride these are the reactions that take place. One is formation of calcium chloride waters and that is calcium atom and CaCl 2 h 2 O can also react to give you calcium and hydrochloric acid. See we can imagine that several types of reactions that do occur in the flame, and formation of hydrochloric acid is one of them. So, if you have a calcium nitrate solution then, nitric acid also may form in the flame.

So, typically we want to avoid as far as possible the formation of the acids in the sample. So, calcium oxide is dissociating to give you calcium and oxygen and when it is present as nitrate OH I already written here when it is nitrate it is calcium oxide nitrate and the water molecule. And calcium oxide also will go to calcium atoms and oxygen atoms ok.

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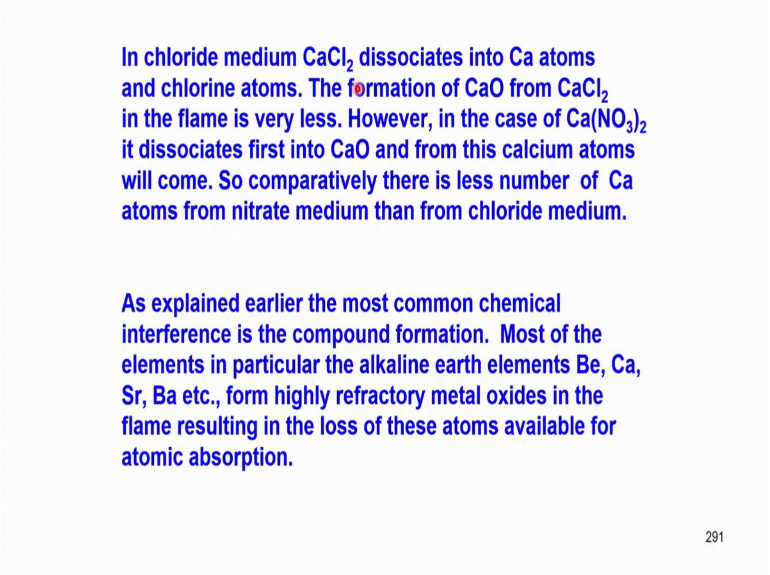

In chloride medium $CaCl_2$ dissociates into Ca atoms and chlorine atoms. The formation of CaO from $CaCl_2$ in the flame is very less. However, in the case of $Ca(NO_3)_2$ it dissociates first into CaO and from this calcium atoms will come. So comparatively there is less number of Ca atoms from nitrate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

So, in chloride medium calcium chloride dissociates to give you this, formation of calcium chloride in the flame is very less inside the flame; however, if you take calcium nitrate then the calcium atoms will come. This is the reason why we during in all atomic absorption spectrometers, what we do is we take the standard solution as nitrates instead of chlorides.

So, most of the nitrate salts are used as standard preparation solutions. So, if you want to prepare calcium go for calcium nitrate, want to prepare the coward determine copper prepare copper nitrate. Take analar grade copper nitrate solid dissolve it in water to give you one to 5 ppm or whatever is a beer law beers law range. So, the if you take sulphate there will be probability that these sulfates are not easily dissociated chloride if you take hydrochloric acid formation may take place etcetera. And then in the case of calcium nitrate it dissociates first into calcium oxide and from this calcium atom should come.

So, comparatively there is less number of calcium atoms, from the nitrate medium then from chloride medium. So, the most common chemical interferences is compound formation. So, most of the elements in particular, in particular alkaline earth elements, what are they? Beryllium, calcium, strontium, barium, etcetera. They form highly refractory metal oxides in the flame resulting in the loss of these atoms. If they form oxides there is loss of free atoms, that is understood ? Ok.

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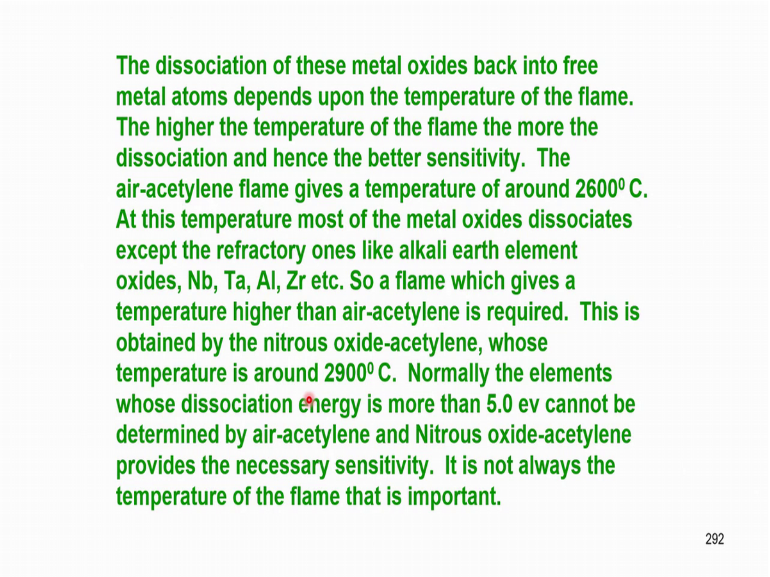

The dissociation of these metal oxides back into free metal atoms depends upon the temperature of the flame. The higher the temperature of the flame the more the dissociation and hence the better sensitivity. The air-acetylene flame gives a temperature of around 2600^0 C. At this temperature most of 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 ev 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 metal atoms depends on the temperature of the flame. If the flame temperature is high there is more absorb more dissociation more number of free atoms. The higher the temperature more is the dissociation and better sensitivity. Whenever we talk of atomic absorption what we talk is about the sensitivity. Especially interference means we are talking about the sensitivity; that means, absorbance should be as high as possible for a given sample.

So, the air acetylene gives a temperature of about 2600 degree centigrade. At this temperature most of the metal oxides dissociate except refractory in the metals like, niobium, tantalum, aluminum, zirconium etcetera, you know in we can include tungsten and all that. And alkali earth metal oxides also form some sort of a refractory compounds. So, a flame which gives a temperature higher than air acetylene is required. That is nitrous oxide, acetylene nitrous oxide is the one which gives you around 3000 degree centigrade whenever there is a possibility of the formation of oxides, you can study a little bit about the chemistry of these elements. And usually the atomic absorption whenever you buy in a atomic absorption they give you some sort of a cookbook which will recommend conditions for the determination of each element.

So, sometimes they are incorporated in the computer itself. So, the moment you select copper or calcium it will list all the things and precautions also. So, that comes on the computer screen, but let that apart the nitrous oxide acetylene flame either on 2900 degree centigrade which give it is a little better for us to understand, that the whenever there is possibility of oxide formation go for nitrous oxide acetylene flame. Normally the elements whose dissociation energy is more than 5 electron volts, they cannot be determined by a recipe. This is a general rule. Any element whose a dissociation energy is more than this we suggest go for nitrous oxide acetylene that provides the necessary sensitivity. It is not always the temperature of the flame that is important basically, what it means is quite often the ratio of carbon to oxygen in the flame determines the sensitivity.

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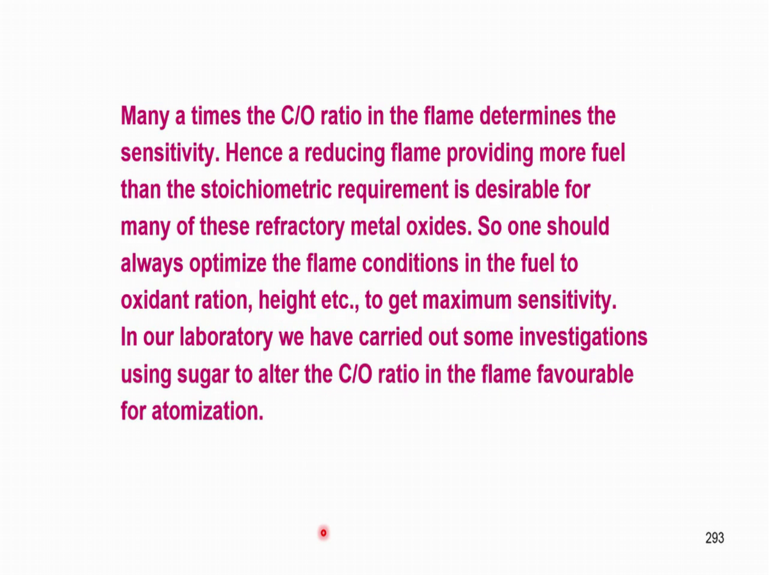

Many a times the C/O ratio in the flame determines the sensitivity. Hence a reducing flame providing more fuel than the stoichiometric requirement is desirable for many of these refractory metal oxides. So one should always optimize the flame conditions in the fuel to oxidant ration, height etc., to get maximum sensitivity. In our laboratory we have carried out some investigations using sugar to alter the C/O ratio in the flame favourable for atomization.

So, a reducing flame that provides more fuel then stoichiometric requirement is desirable; that means, for refractory metals what we need is a reducing flame, why? Because they are all oxides need to be reduced to the metals. So, a reducing flame that is a blue flame that is required in the case of refractory metal oxides. So, one should always optimize the flame conditions. In the fuel to fuel oxidant ratio and then you should also, optimize height because reducing flame any flame structure, we have seen earlier there is a reducing flame, then there is oxidizing flame, then there is secondary zone, where all other components from the air will come and mix and giving you a red flame. So, all these conditions need to be optimized in the case of every atomic absorption flame atomic absorption. That is where you should aspire rate, what is the height of the burner? To relate you to the hollow cathode lamp etcetera.

So, to all these is to be done only because we need a higher sensitivity. So, in our laboratory we have carried out some investigations using sugar to alter the carbon oxygen ratio. So, why not we determine change in the carbon oxygen ratio? How best way is to introduce sugar along with the sample. Sugar resolves very easily in all water solutions acidic solutions etcetera. So, if you introduce sugar there will be lot of carbon atoms coming from the sample itself into the flame. So, the carbon oxygen ratio changes. So, this kind of experiments we have done in my laboratory. And we have seen some results that it has been observed that molybdenum, tungsten, titanium etcetera, for all these elements

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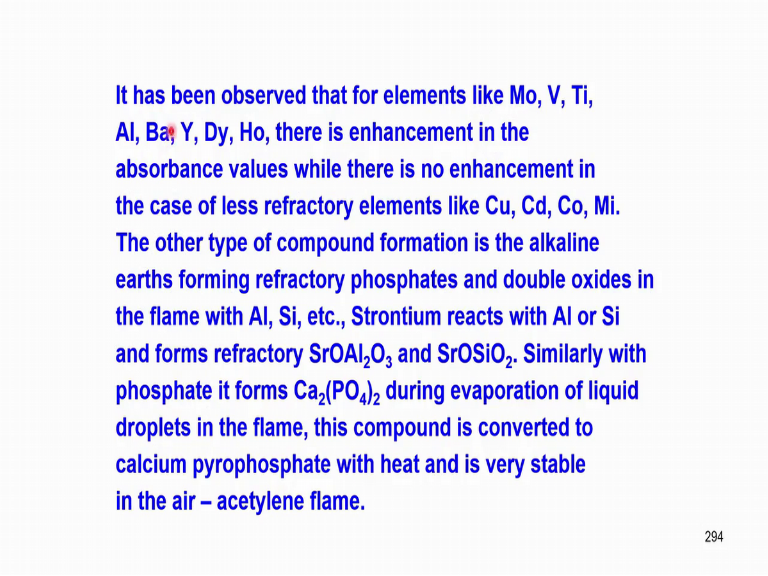

It has been observed that for elements like Mo, V, Ti, Al, Ba, Y, Dy, Ho, there is enhancement in the absorbance values while there is no enhancement in the case of less refractory elements like Cu, Cd, Co, Mi. The other type of compound formation is the alkaline earths forming refractory phosphates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

What you see in this slide molybdenum, aluminum, barium, atrium, dysprosium, holmium etcetera there is enhancement in the absorbance value whenever I put sugar.

But there is no enhancement in the refractory elements like copper, cadmium, cobalt and nickel. Other type of compounds formation is the alkaline earth forming refractory phosphates. For example, we can see that some elements form phosphate instead of oxide if you add a dissolve the sample in phosphoric acid. They form phosphates, quite often if you want to determine many elements in the soil calcium sodium etcetera, in the soil. Then soil also will have phosphate because, phosphorus phosphates are naturally fertilizers.

So, there is lot of fertilizer in the soil and whenever you aspire a dissolve the sample and aspire it they form phosphates also, sometimes they have form a double oxides that is with aluminum silicon etcetera, strontium reacts with aluminum or silicon to form metal occur mixed metal oxides that is SrO Al 2 O 3 SrO SiO 2 etcetera. Similarly with phosphate it forms calcium phosphate. So, during evaporation of liquid droplets in the flame, this compound is converted to calcium pyrophosphate instead of calcium atoms.

So, and, but it is very stable in the air acetylene flame. Therefore, you must be very carefully whenever you want to determine calcium etcetera, some elements which have got phosphate in the sample. Because the many of the elements form pyrophosphates which are very stable. So, this reaction. So, that is the formation of phosphates radius is the free atom population in the flame, compared to that obtained from solutions in the absence of the phosphate.

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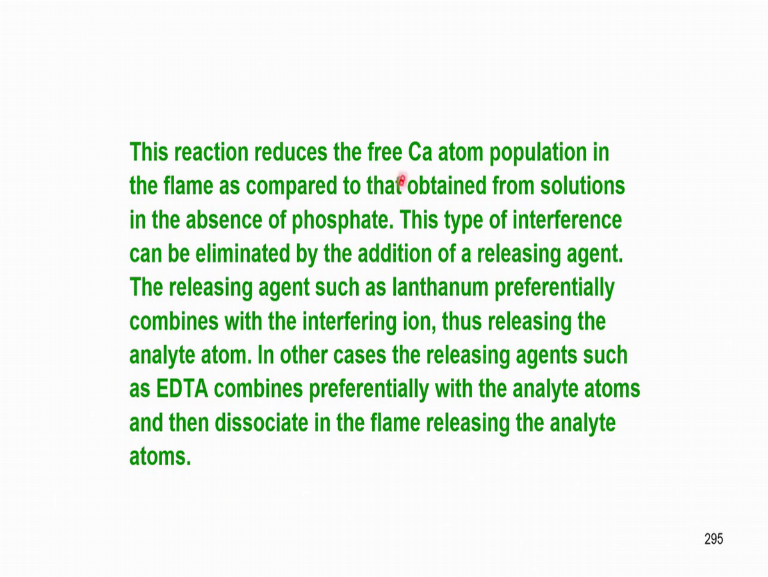

This reaction reduces the free Ca atom population in the flame as compared to that obtained from solutions in the absence of phosphate. This type of interference can be eliminated by the addition of a releasing agent. The releasing agent such as lanthanum preferentially combines with the interfering 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 analyte atoms.

So, this type of interference we can eliminate, why? Because phosphate radius the signal that is a bottom line. So, how do we take care of the phosphate interference and a releasing agent? So, what is the releasing agent? I just incorporate a little bit of lanthanum in this sample in this and in these standards, that combines with the interfering ion. So, it releases the analyte atom; that means, lanthanum pyrophosphate will form with releasing the calcium atoms. In other cases we can add EDTA that combines preferentially with elements and then that can dissociate in the flame that releases the analyte atoms.

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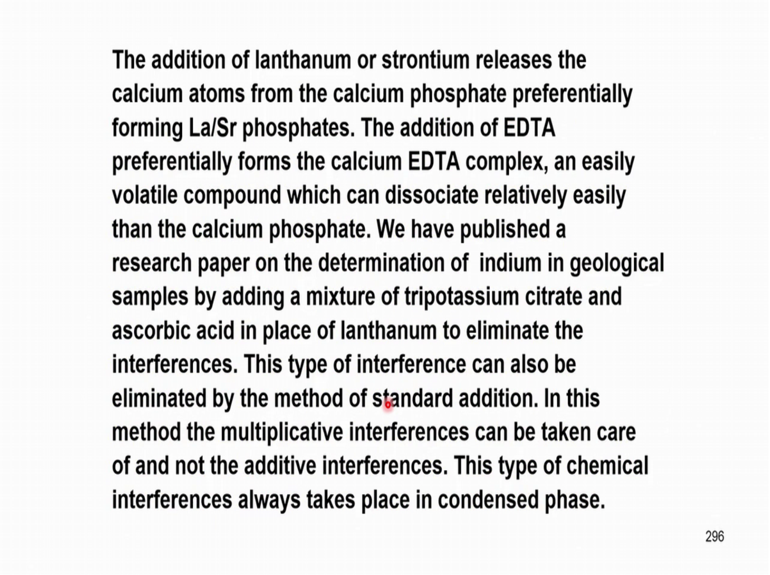

The addition of lanthanum or strontium releases the calcium atoms from the calcium phosphate preferentially forming La/Sr phosphates. The addition of EDTA preferentially forms the calcium EDTA complex, an easily volatile compound which can dissociate relatively easily than the calcium phosphate. We have 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, the addition of lanthanum or strontium that is also another releasing agent, that releases the calcium atoms from the calcium phosphate preferably forming lanthanum and strontium phosphates, addition of EDTA forms calcium EDTA complex and that is volatile we have published a research paper on the determination of indium in geological samples by adding a mixture of tri potassium citrate and ascorbic acid in place of lanthanum. Because lanthanum is very costly element.

So, this combination also we have tried. So, this type of interference can also be eliminated by the method of standard addition. This I will explain to you later when we discuss the atomic absorption spectrometer applications. So, in this method multiplicative interferences can also be taken care of and not the additive interferences.

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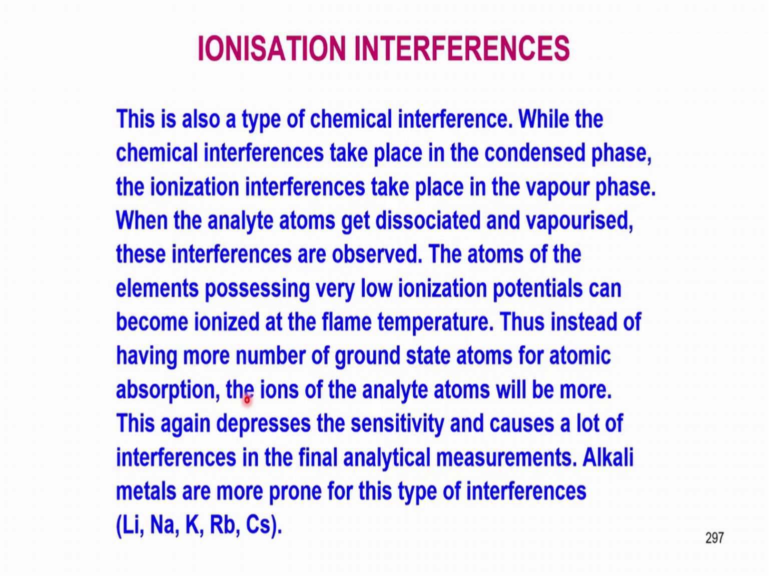

IONISATION INTERFERENCES

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 (Li, Na, K, Rb, Cs).

So, the additive interference always takes place in condensed phase, this you should remember. So, we will discuss the ionization interferences and other interferences in the next class.

Thank you very much.