# 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 – 21

## Instrumentation in ASS VII : Optics and Detectors

Greetings to you, is in my last class we had discussed about the atomic absorption spectrometry, instrumentation, automation and role of computer in the atomic absorption.

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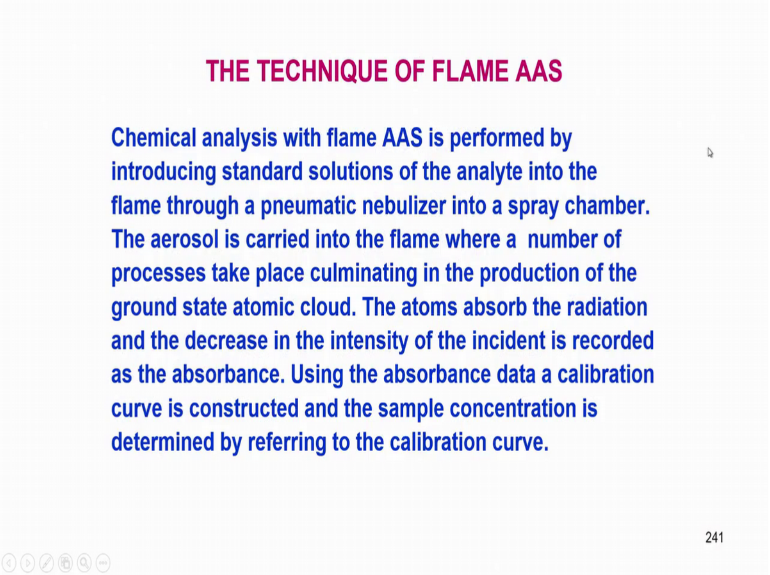

THE TECHNIQUE OF FLAME AAS

Chemical analysis with flame AAS is performed by introducing standard solutions of the analyte into the flame through a pneumatic nebulizer into a spray chamber. The aerosol is carried into the flame where a number of processes take place culminating in the production of the ground state atomic cloud. The atoms absorb the radiation and the decrease in the intensity of the incident is recorded as the absorbance. Using the absorbance data a calibration curve is constructed and the sample concentration is determined by referring to the calibration curve.

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Today, we will continue our discussion regarding the technique of flame ASS. If you remember, what I had told you earlier that there are about 4 systems of atomic absorption spectrometry, one is flame atomic another is graphite atomic absorption another is hydride generation, another is cold vapor mercury. So, now, we are going to discuss the technique of flame atomic absorption spectrometry.

So, just like any other spectrometric technique, what you should do is you have to switch on the instrument, and then prepare your standards. If you want to determine copper you have to prepare the copper standards of 1 to 5 ppm 1 ppm, 2 ppm, 3 ppm, 5 ppm etcetera. And then make they insert the sample into the flame record the absorbance. So, then you take it out put your second sample 2 ppm record the observed, 3 ppm record then you plot all the absorbances versus concentration, that is you are working curve. Then you put your unknown sample record the absorbance and refer it to the calibration curve that will tell you what is the concentration of the element. This is the general principle of all spectrometer photometric spectrometric techniques, where including spectrophotometry in infrared or atomic absorption flame emission, whatever it is we have to prepare the standards and refer the standard curve versus standard curve corresponding to the concentration versus response and to the to your sample.

So, chemical flame atomic absorption is no exception. So, chemical analysis with flame analysis, with flame atomic absorption is performed by introducing standard solutions of the analyte into the flame through then your nebulizer. Into the spray chamber the aerosol is carried into the flame, where a number of processes take place we already discuss, but we will discuss it once again. And culminating in the production of the ground state atomic cloud. And at these atoms absorb the radiation coming from the, hollow cathode lamp coming from the hollow cathode lamp, there therefore, the intensity of the hollow cathode lamp decreases whenever there is absorption.

So, the absorbance of the given sample corresponds to beer lamberts law, that also we have derived earlier and you have to plot the absorbance. So, the decreasing the absorbance is your concentration response. So, using the absorbance data, a calibration curve is constructed and the sample concentration is determined by referring to the calibration curve ok.

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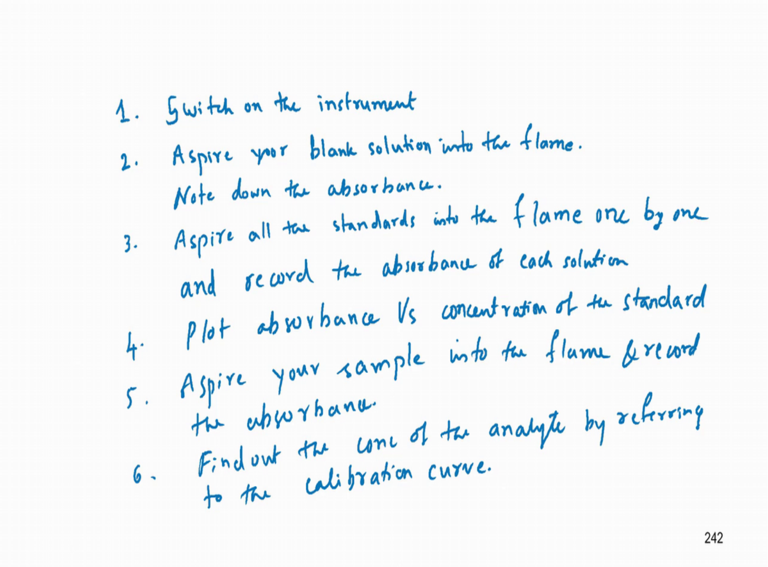

1. Switch on the instrument
2. Aspire your blank solution into the flame.
   Note down the absorbance.
3. Aspire all the standards into the flame one by one
   and record the absorbance of each solution
4. Plot absorbance Vs concentration of the standard
5. Aspire your sample into the flame & record
   the absorbance.
6. Find out the conc of the analyte by referring
   to the calibration curve.

So, the steps involved in atomic absorption are number one, switch on switch on the instrument. Number 2, aspire your blank solution into the flame, then note down the absorbance. This would be 100 percent transmittance; that means, no absorbance because there is no analyte element in your blank solution ok.

Once you do this aspire all the standards into the flame one by one and record the absorbances, absorbance of each solution. Afterwards plot absorbance versus concentration of the standard. This is the next step. Then what we will do we aspire your sample into the flame and record the absorbance. Last step would be I find out the concentration of the analyte by referring to the calibration curve.

So, this completes the analysis of atomic absorption analysis of a metal ion basically. So, first you switch on the instrument, aspire your blank solution into the flame note down the absorbance this is 100 percent or 0 concentration and then aspire all the standards and record the absorbance, and then followed by plot the absorbance versus concentration of the standard. Finally, we aspire your sample into the flame and record the absorbance, and from the absorbance you calculate the concentration by referring to the calibration curve.

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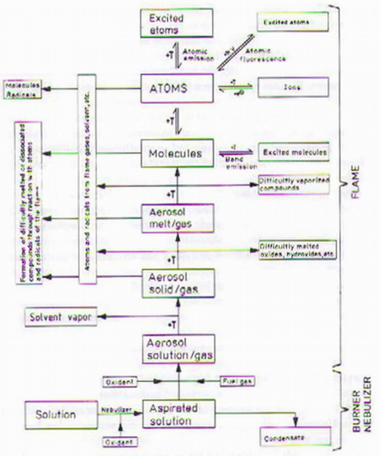
ATOMIZATION PROCESSES



So, again now we are going to discuss a little bit more in detail about the atomization process. So, atomization processes are excited atoms are the atoms are there, and then first we have the sample that you solution here, it is it comes in to the through the nebulizer and oxidizer is mixed aspirated solution, aerosol solution happens and then fuel gas and the oxidant gas are getting mixed. And then solid to vapour is formed aerosol or solid gas is formed, and these aerosols can undergo different kinds of chemical reactions which I have already discussed, the formation of difficulty melted oxides etcetera. Easily oxide So, all the oxides will form and then we have the aerosol melt gas molecules and from the molecules they pick up the electrons and these electrons, these electrons will react with the ions to form the molecules ok.

The molecules will revert to atoms and they from the atoms they can form ions or they can form molecules by combining again, and then there is also possibility that an excited atom is formed by absorbance of the radiation. So, the excited atoms can come back to the ground state by fluorescence or by atomic absorption. In the fluorescence what we have is another wavelength radiation is emitted is another wavelength, where as longer wavelength where as in the excited atoms there is no radiation coming out, but the intensity of the transmitted light reduces depending upon the concentration of the sample ok.

So, this is how the whole thing is organized, in this area there is burner nebulizer interaction and here the this area completely describes almost all the reactions that take place in the flame ok.

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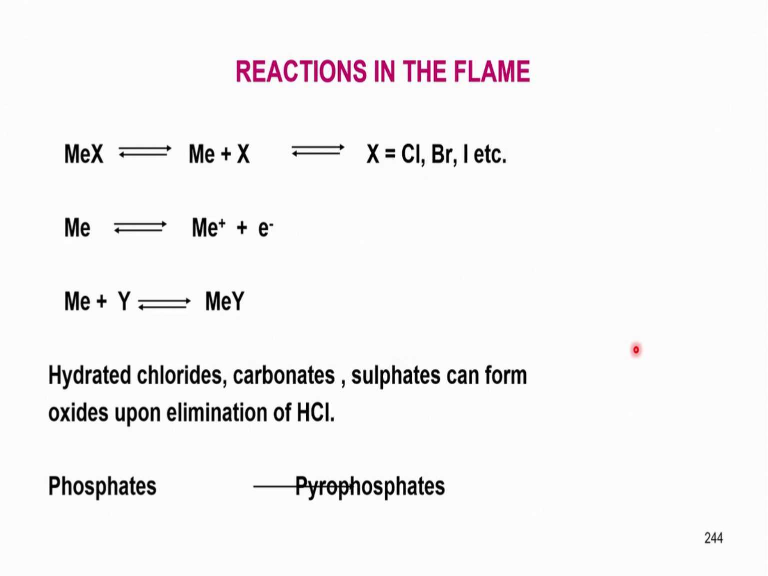

REACTIONS IN THE FLAME

$MeX \rightleftharpoons Me + X \quad \rightleftharpoons \quad X = Cl, Br, I$ etc.

$Me \rightleftharpoons Me^+ + e^-$

$Me + Y \rightleftharpoons MeY$

Hydrated chlorides, carbonates , sulphates can form oxides upon elimination of HCl.

Phosphates $\longrightarrow$ Pyrophosphates

So, what are the reactions in the flame we have assume we assuming that we have metal oxide metal hydro metal salt M e X, M e refers to metal, X refers to the salt for example, copper chloride, copper nitrate, or cobalt chloride, cobalt nitrate, cobalt bromide and it can be any salt ok.

So, in the flame the metal salt will ionize. That is in the solution itself the salt will ionize and same thing will be carried out into the flame. So, the metal ion will be there and metal atom and X that is halogen, where X can be chloride bromide etcetera. Now this metal will pick a can become an ion by losing and electron and this metal can combine with another halide ion producing M e Y another salt that is also possible. So, hydrated chlorides carbonates sulfates can form oxides this is the oxide M e Y upon elimination of HCL hydrochloric acid.

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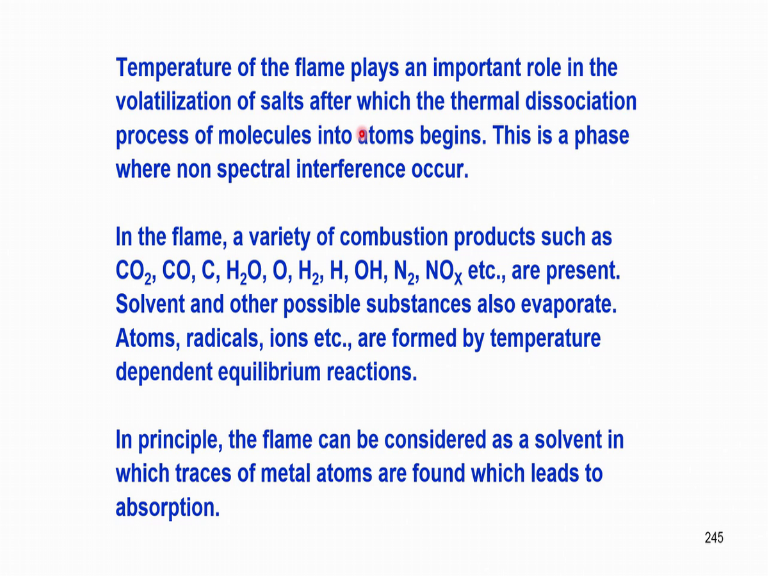

**Temperature of the flame plays an important role in the volatilization of salts after which the thermal dissociation process of molecules into atoms begins. This is a phase where non spectral interference occur.**

**In the flame, a variety of combustion products such as $CO_2$, CO, C, $H_2O$, O, $H_2$, H, OH, $N_2$, $NO_X$ etc., are present. Solvent and other possible substances also evaporate. Atoms, radicals, ions etc., are formed by temperature dependent equilibrium reactions.**

**In principle, the flame can be considered as a solvent in which traces of metal atoms are found which leads to absorption.**

So, what happens to phosphates? Phosphates will form pyrophosphates in the flame. So, temperature of the flame play plays an important role in the volatilization of salts after which the thermal dissociation processes of molecules into the atoms begins. Basically whenever we enter the sample, temperature will temperature of the flame will start all the reactions, but the all those reactions are So fast, that you may not be able to view them individually.

So, this is a phase where non spectral interferences occur. For example, I had already told you that in the flame there are cyanogens molecules and then CH molecules etcetera. Cyanogens CH, NH molecules all those things will be present and this is where molecular absorbance takes place. So, this can cause a little bit of interference as we have discussed earlier. Apart from that we have a variety of combustion products such as CO 2 carbon dioxide will form because the flame is open to atmosphere and acetylene is there. So, carbon will be there acetylene can burn into giving you carbon dioxide. It can also burn to give you carbon monoxide if the concentration of oxygen is less. And then it can get reduced to carbon, water molecules will be there oxygen molecules will be there, hydrogen and then hydrogen ions atoms OH molecules or OH radicals into NO x etcetera. Here you can see that the there are species like carbon, oxygen, H, OH etcetera. These are not stoichiometric combinations of the elements. So, they cannot be classified as compounds.

But in the gaseous state these species have been detected in the gaseous phase. So, as a even though there is lifetime could be short, you will see all kinds of spectral evidence in the flame that such compounds are formed being formed. They need not be stoichiometrically correct, but still they are present for very short time of course. So, solvent suppose you extract the sample in a solvent then solvent also will get into the flame and other possible substances present in the sample also will evaporate. For example, if you want to take a determine gold in silver or gold in seawater, then what happens? You want to determine gold, but along with the sample you will have So much of sodium chloride, magnesium chloride and several other elements in the seawater. So, all those things also will evaporate.

So, atoms radicals ions etcetera are all formed by a temperature dependent equilibrium reactions. So, in principle, the flame itself can be considered as a solvent. This is very interesting because flame on it is own does not give rise to any spectral features. So, it can be considered as a solvent. So, it is, but there are traces of metals could be there in the solvent also; that means, therefore, what we should do is if we are extracting the sample in a solvent we should aspire the solvent also to obtain the blank reading or reference reading ok.

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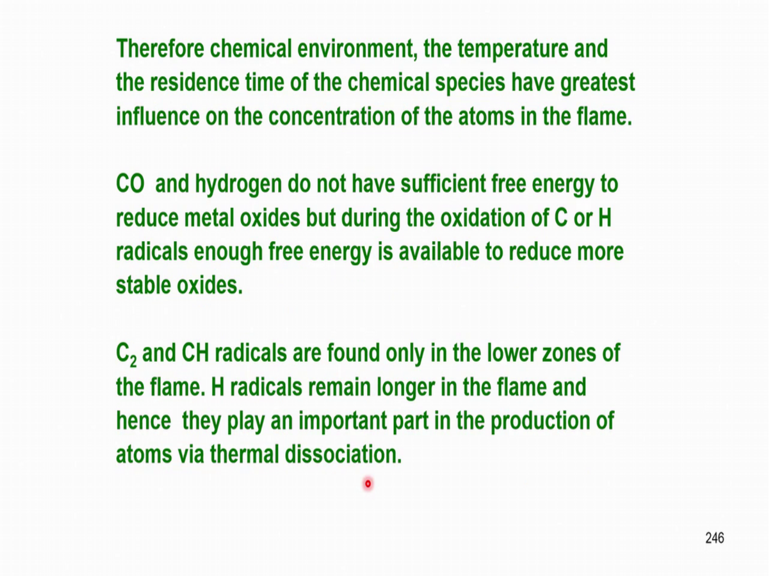

Therefore chemical environment, the temperature and the residence time of the chemical species have greatest influence on the concentration of the atoms in the flame.

CO and hydrogen do not have sufficient free energy to reduce metal oxides but during the oxidation of C or H radicals enough free energy is available to reduce more stable oxides.

$C_2$ and CH radicals are found only in the lower zones of the flame. H radicals remain longer in the flame and hence they play an important part in the production of atoms via thermal dissociation.

So, chemical environment the temperature and residence time of the chemical species have greatest influence on the concentration of the atoms in the flame. I want you to understand that in the flame the high temperature will be prevalent and then atoms will be there they are also coming and moving out of the flame, and then therefore, the residence time how long it remains within the 5 centimeter within the 5 centimeter flame, 5 centimeter length and 3 centimeter height of the flame, how long an atom can stay in the flame in the optical path?

So, that will be for a few microseconds maybe. So, all these parameters flame temperature, residence time and the chemical species whatever it forms. You know carbon monoxide, carbon dioxide elemental and all these things have greatest influence on the concentration of the atoms in the flame. So, what happens? Carbon monoxide and hydrogen they do not have sufficient free energy to reduce metal oxides on their own; that means, if you take a metal oxide if you take a metal oxide add a little bit of carbon monoxide expose it to carbon monoxide or hydrogen atmosphere, and then heat the mixture you may not get the metal oxide reduced to the metal. Because the free energy of these carbon or hydrogen radicals are not they do not have sufficient free energy. There should be for any chemical reaction free energy is involved.

So, if you read a little bit of thermodynamics, the free energy is the driving force for any chemical reaction. And free energy of the products minus free energy of the reactants gives is if it is known we can predict whether the reaction will proceed on the forward direction or on the backward direction, that is reduction or oxidation. So, that apart there is there are C 2 and CH radicals are found, only in the lower zones of this flame; that means, where there are blue flames. Hydrogen radicals remain longer in the flame and hence they play an important part in the production of atoms via thermal dissociation. So, thermal dissociation itself is a very important pathway for the production of atoms.

So, now what we are saying is, ever since I started this class I have maintained that atomic absorption is a specific phenomena and there is if the element is there you get a response if the element is not there you do not get a response; that means, the atomic absorption is essentially free from interferences. This statement is a little misleading, because while 99 percent of the atomic absorption measurements are interference free, but still we note quite often that there could be some sort of interferences, and in the determination. So, what we what do we mean by interference? What we mean is the absorbance of the sample is lower than what it is? What it should be? If it is lower than what it should be we call it interference.

So, it may be 5 percent it may be 10 percent or it there may not be any signal. So, all these things are possible, but rarely. Now rarely does not mean not there at all isn't it? Rarely means it will be there sometimes it will be significant, sometimes it will be most of the time majority of the time the interferences will not be there; that means, if the solutions are dilute and there are not many interfering species the absorbance will be as per your expectation. That we will discuss in the last part of this program what should what are a typical concentrations and typical observances.

Now, I want to spend some time on the interferences in atomic absorption.

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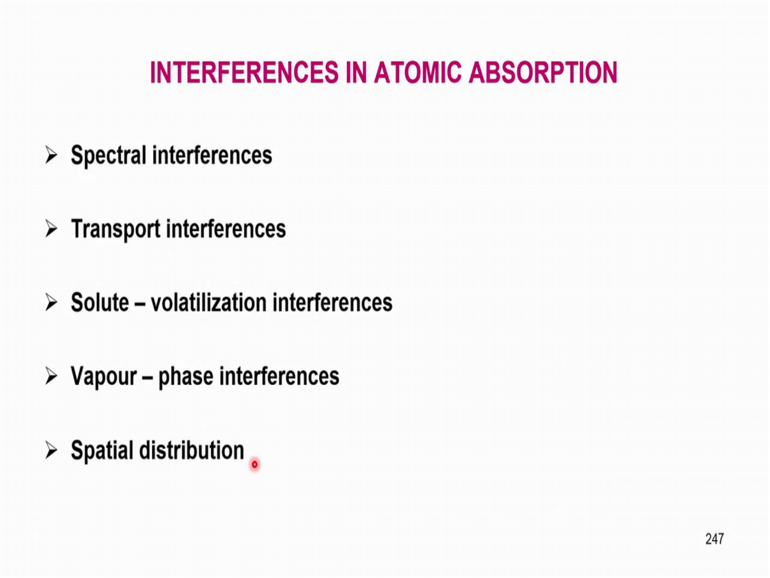

INTERFERENCES IN ATOMIC ABSORPTION

- Spectral interferences
- Transport interferences
- Solute – volatilization interferences
- Vapour – phase interferences
- Spatial distribution

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So, we can call, we can see here in this slide that there are different kinds of interferences. One is spectral interference and the second is transport interference. So, if the resonance lines of 2 elements are matching and we cannot separate them, then we call it spectral interference; that means, the reading may be higher and then transport intervals suppose the sample is not getting X getting introduced into the flame properly. So, these number of free atoms will reduce.

So, the absorbance will be reducing. Suppose there are more number more normal quantity of the sample is being aspirated, more free atoms, that also can give rise to higher absorbance. So, transport interference are also there and then solute volatilization interferences. Solute itself may volatilize and go off. So, that is the salt metal salt it may volatilize and go off. And then vapor phase interaction, when in the flame this is another type is vapor phase in the flame everything is in the vapor state. So, there could be interactions in the vapor phase there and the formation of CO, CO 2 CH no 2 NH 2 and all kinds of possible of vapor phase reactions are possible. And this may cause certain amount of error in the measurement and then finally, spatial distribution.

This is another aspect that is, we have a little discussed a little bit during a regarding the when we are discussing about the flame height. Typical flame height s for chromium silver and magnesium I had shown you. And depending upon the spatial distribution of the species the absorbance could be higher or lower. So, any change in the absorbance value from the expected is called interference. Sometimes interference may be significant sometimes it may not be.

So, what are these are the different kinds of interferences? A spectral transport solute volatilization vapor phase and spatial distribution, we should be aware as chemists and engineers. Otherwise we will be reporting wrong result. So, whenever we are talking about atomic absorption we talk of parts per million. And even if we go wrong in parts per million level, it can be cause significant changes it may have profound effects if we report wrong results also.

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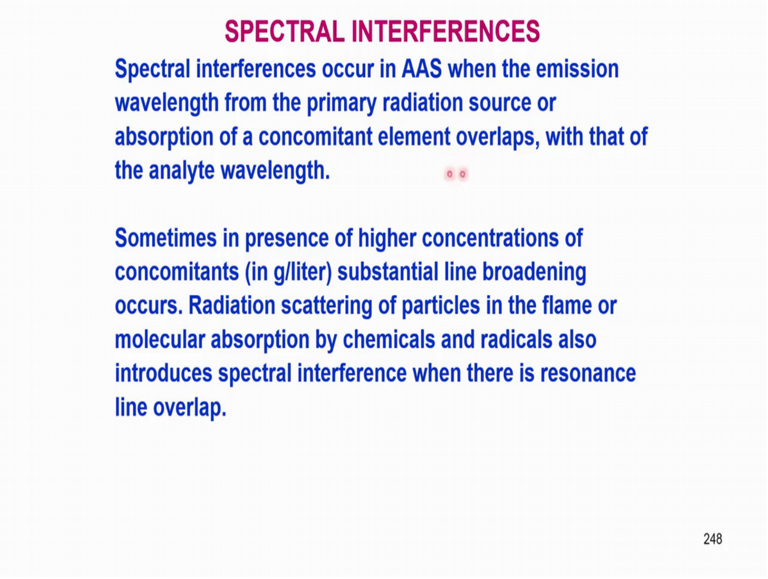

## SPECTRAL INTERFERENCES

Spectral interferences occur in AAS when the emission wavelength from the primary radiation source or absorption of a concomitant element overlaps, with that of the analyte wavelength.

Sometimes in presence of higher concentrations of concomitants (in g/liter) substantial line broadening occurs. Radiation scattering of particles in the flame or molecular absorption by chemicals and radicals also introduces spectral interference when there is resonance line overlap.

So, we will discuss these a little bit further now. So, what are spectral interferences? As I told you spectral interferences are when the emission wavelength from the primary radiation source or absorption of a concomitant element overlaps with that of the analyte wavelength; that means, 2 resin resonance lines 2 atom 2 elements will have same resonance line. So, the monochromator cannot do much it will measure the total absorbance. Sometimes in presence of higher concentrations of concomitant substantial, line broadening also happens.

So, whenever line broadening happens, what happens? An another resonance line of some other element may fall in the broadened resonance line. So, higher absorbance takes place. So, radiation scattering of particles here I have written the concomitant means other elements other compounds present in the sample, but if they are in grams per liter for example, like in sea water then, substantial line broadening happens and part of the measurement may fall into the resonance line where we are measuring the absorbance of a particular element.

So, radiation scattering of particles in the flame or molecular absorption by chemicals and radicals also introduces molecular interference whenever there is a resonance line overlap. This I had already explained to you once; that means, in the along with the spectral line there is a molecular absorbance line which encompasses totally the resonance lines resonance line is only about 0.002 plus or minus 0.005 nanometers accuracy.

But if there is a molecular absorbance which takes fully covers resonance line the absorbance at that wavelength adds to the actual interference actual measurement of the absorbance. So, you get a higher reading corresponding to the contribution of the molecular species at that wavelength, whatever is the concentration. Sometimes molecular absorption can be a source of error, but it can be taken care of. Now how we will see later. Whenever there is resonance line overlap we call it spectral interferences.

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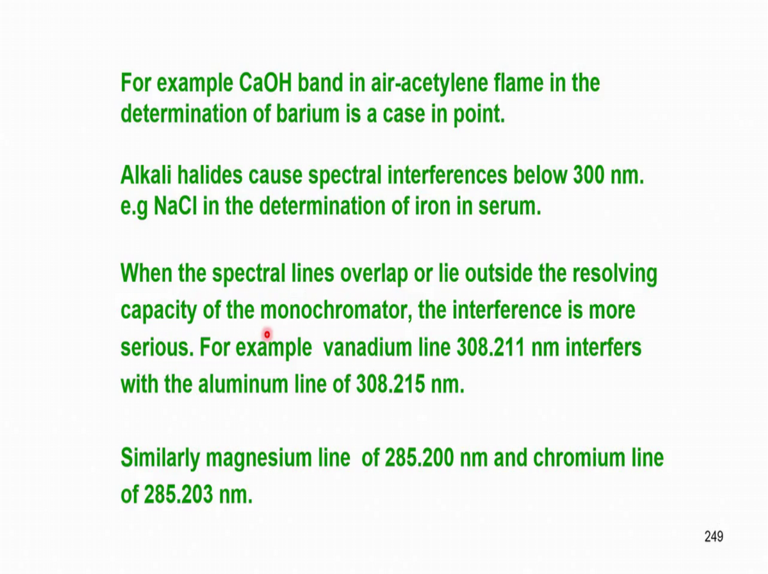

For example CaOH band in air-acetylene flame in the determination of barium is a case in point.

Alkali halides cause spectral interferences below 300 nm. e.g NaCl in the determination of iron in serum.

When the spectral lines overlap or lie outside the resolving capacity of the monochromator, the interference is more serious. For example vanadium line 308.211 nm interfers with the aluminum line of 308.215 nm.

Similarly magnesium line of 285.200 nm and chromium line of 285.203 nm.

So, for example, now I am going to give you an example here. Calcium hydroxide CaOH not OH twice, calcium hydroxide band in air acetylene flame in the determination of barium. I have a barium solution I want to determine barium, but suppose there is certain amount of calcium in the sample. So, I as a concomitant, because any sample nobody determines pure solutions you know 99 percent of the time nobody determines pure solutions. So, the aim of analysis itself is to determine a particular element in presence of other elements.

Now, I am giving you a situation, where barium is to be determined and calcium OH CaOH is band is there in the air acetylene flame. So, this causes spectral interference. Because the part of the band absorption spectrum of COOH and compasses the barium resonance line, it totally occupies. Similarly alkali halides cause spectral interferences below 300 nanometer whatever is the element you want to determine, if you if the resonance line is below 300 nanometers all alkali halides like sodium chloride, sodium bromide, potassium chloride, potassium bromide all kinds of things will form will cause error in the determination of iron, and yes this kind of interference is a especially noted in serum determinations ok.

So, people want to know how much of sodium is there in the case of blood pressure know. Somebody is having blood pressure they find out how much sodium is there in the serum. Let us see doctor will order so, but sometimes doctor will order determine iron hemoglobin what is the hemoglobin in the serum so, but serum itself will contain lot of sodium chloride. So, this kind of error happens here. So, when the spectral lines overlap or lie outside the resolving capacity of the monochromator the interference is more serious. Because monochromator can this can differentiate only plus or minus 0.2 nanometer, but even if you even if you use best monochromator like grating.

But if the monochromator is unable to differentiate between 2 lines then nothing can be done. There is spectral interference, both of them will add up. This example of vanadium for example, vanadium what is the spectral line resonance line I am showing here it is 308.211 nanometer, but what is aluminum is 308.215.

So, 0.005 both of them are if you choose point 308.211, 0.005 216 plus or minus 216 monochromator can differentiate, but this is less than 216. So, any determination of vanadium at 308.211 will cover the absorbance of the radiation line from 308.215 that belongs to aluminum.

So, the total absorbance of vanadium will be higher if there is aluminium. So, this is known as spectral interference; that means, whenever spectral interferences are there, what we should see is the a spectral line should not be more than should not be more than 0.005 nanometer from the resonance line of the 2 elements. So, if they are within 0.005 nanometers or something spectral interference will always be there. So, we have to be careful whenever you are I want I have to determine vanadium, first I check whether there is a aluminium is there or not. If aluminum is not that I do not have to worry, but if aluminum is there I will determine aluminum also and then subtract the absorbance from aluminum from the vanadium web service.

So, this is how we go about solving the interference problems. And similarly another example I am giving you is magnesium line of 285.200 nanometer and what is chromium? Chromium is 0.285, 0.203 the difference is 0.003 nanometer; that means, no amount of diffraction grating or monochromator can separate these 2 lines. So, there will be spectral interference of magnesium or chromium in presence of each other. If you want to determine magnesium chromium will interfere. If you want to determine chromium magnesium will interfere, if both of them they are there in the sample.