Trace and ultra trace analysis of metals Using atomic absorption spectrometry

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Lecture – 22

Interferences in AAS

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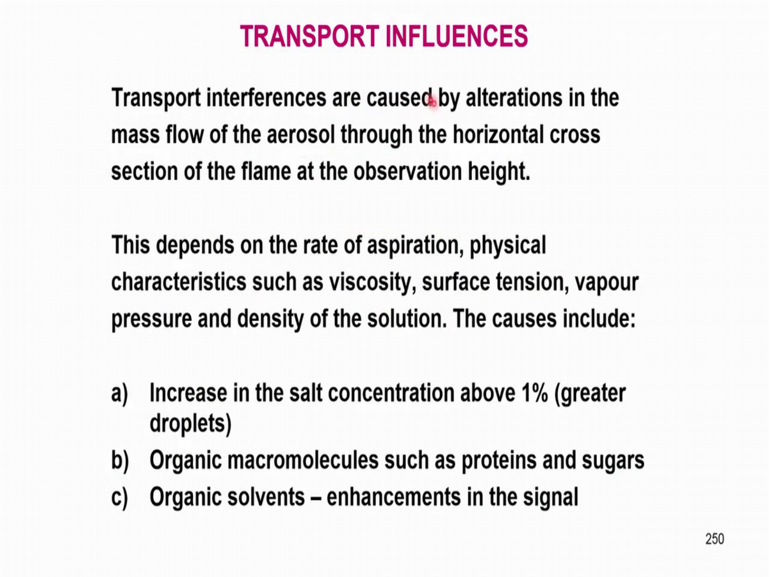

TRANSPORT INFLUENCES

Transport interferences are caused by alterations in the mass flow of the aerosol through the horizontal cross section of the flame at the observation height.

This depends on the rate of aspiration, physical characteristics such as viscosity, surface tension, vapour pressure and density of the solution. The causes include:

a) Increase in the salt concentration above 1% (greater droplets)
b) Organic macromolecules such as proteins and sugars
c) Organic solvents – enhancements in the signal

So, continuing our discussion on the other types of interferences. We will discuss about transport influences now. So, basically transport interferences are caused by alterations in the mass flow of the aerosol; that means, sample uptake of the sample uptake depending upon the flow rates of the auxiliary gas as well as fuel gas.

So, it has to happen through horizontal cross section of the flame also. Because once the elements once the metal atoms are there in the flame there is no reason that the flame atoms will pass through the flame vertically only. They can pass off horizontally also now, because flame is an open system in the atomic absorption. So, they may lose out the free atom concentration. So, the transport influences are basically dependent upon the rate of aspiration and physical characteristics. What are the physical characteristics? That is viscosity, surface tension, vapor pressure and density of the solution all these things. For example, if the sample is in glycerol, if the sample is resolved in grease glycerol the sample uptake in glycerol will be much lower compared to water. Because water is having a higher lower viscosity and then water is having say higher surface tension also.

So, if the sample is in methanol for example. Methanol is the density of methanol is very less compared to water so; the sample uptake will be more. So, less force is required to pull the sample. Similarly vapour pressure if the sample is have sample solvent is having a very low boiling point; that means, the aspiration and for other things will be affected, because increasing salt concentration. Density pressure all these things will increase. For example, I have written here increase in the salt concentration above one percent; that means, the droplet us will be bigger in size. This kind of situation occurs whenever we want to analyze seawater. And then human body solutions blood sugar blood sugar plasma and several other blood plasma serum all these biochemical samples will have more than one percent of the solids in their matrix, they in their composition.

So, in such cases transport influences are more; that means, interference will be absorbance will be lower than the expected. Similarly organic macromolecules proteins sugars and if such things are there they increase the viscosity. So, increasing viscosity; obviously, leads to lower absorbance and higher interference. Organic solvents normally 90 percent of organic solvents born with exothermic effect. So, organic solvents catch fire very easily that is our experience also. So, whenever there are organic solvents in our sample, for example, you may extract a sample in benzene toluene methyl isobutyl ketone or methanol isopropyl alcohol you could have dissolved, So many other organic solvents maybe there and whenever the samples containing organic solvents are introduced into the flame exothermic reaction takes place and production of with the production of carbon monoxide carbon dioxide.

But exothermic reaction also means higher temperature of the flame. So, higher the temperature of the flame more would be the free atomic concentrate free atom concentration. So, this or if I use organic solvents I can use I can get higher sensitivity.

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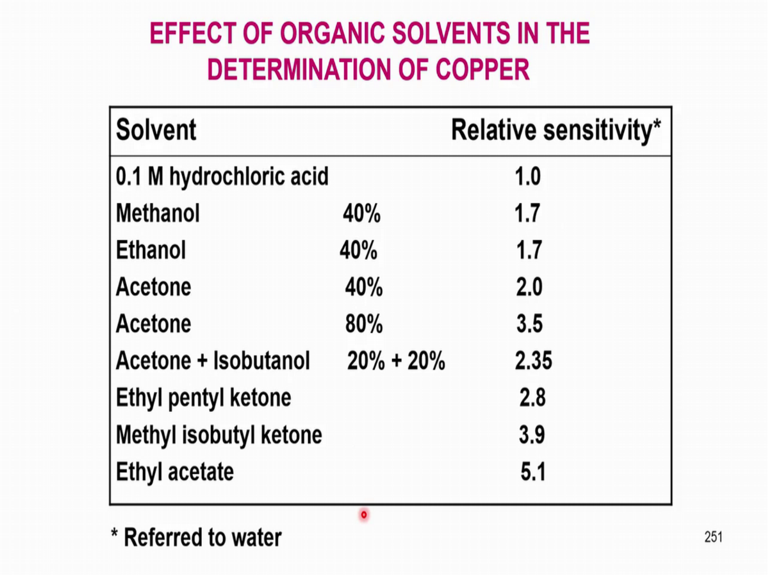

EFFECT OF ORGANIC SOLVENTS IN THE DETERMINATION OF COPPER

Solvent		Relative sensitivity*
0.1 M hydrochloric acid		1.0
Methanol	40%	1.7
Ethanol	40%	1.7
Acetone	40%	2.0
Acetone	80%	3.5
Acetone + Isobutanol	20% + 20%	2.35
Ethyl pentyl ketone		2.8
Methyl isobutyl ketone		3.9
Ethyl acetate		5.1

* Referred to water

So, it is important to remember such things and quite often the quite often we incorporate organic solvents in the standard method whenever we are trying to develop a new method we incorporate it, So that we can determine the sample at a still lower concentration that is higher sensitivity.

Now, I have I am giving you a list here the of solvent and relative sensitivity. Assume that I have dissolved a particular sample in hydrochloric acid 0.1 molar hydrochloric acid. And the relative sensitivity is 1. Then suppose I dissolve the same thing in 40 percent methanol; that means, I add hydrochloric acid 60 percent and methanol 40 percent. Then what happens the sensitivity that is absorbance will be 1.7 times more compared to hydrochloric acid.

Similarly, if I use ethanol it is almost same 1.7 percent because, it depends upon the density of ethanol. Suppose I use acetone is having a lower boiling still lower boiling point then ethanol methanol etcetera. So, the it is twice the sensitivity absorbance value will be twice same sample hydrochloric acid suppose it is 0.2 absorbance if I dissolve it in 40 percent acetone it will be 0.4 here, absorbance 0.2 to 0.4 double.

Suppose I increase the acetone to 80 percent, then what happens? I have the absorbance 3.5 times. So, you can feel the power of the organic solvents in the in atomic absorption; that means, 3.5 times lower concentrations can be determined in atomic absorption if I use acetone. Now sometimes it is possible to use acetone and isobutanol 20, 20 even then the value is almost double absorbance value would be double. And then ethyl pentyl ketone methyl isobutyl ketone ethyl acetate. So, use it I ethyl acetate you get 5 times sensitivity.

So, if it is for one ppm that can be determined minimum in a given sample. Then with if I use ethyl acetate I can determine 0.2 ppm, that is 200 ppb parts per billion. So, the determination interference, we can call it interference or increase in sensitivity whenever it is done deliberately we call it increase in sensitivity, but if we do not know that acetone is then I get a higher absorbance. So, I call it inference.

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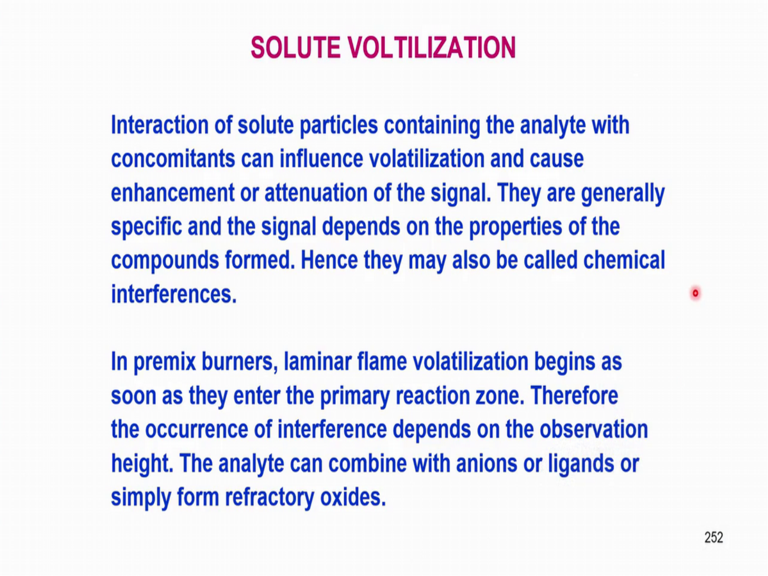

SOLUTE VOLTILIZATION

Interaction of solute particles containing the analyte with concomitants can influence volatilization and cause enhancement or attenuation of the signal. They are generally specific and the signal depends on the properties of the compounds formed. Hence they may also be called chemical interferences.

In premix burners, laminar flame volatilization begins as soon as they enter the primary reaction zone. Therefore the occurrence of interference depends on the observation height. The analyte can combine with anions or ligands or simply form refractory oxides.

252

So, is it can be interpreted either way. So, then we are discussing another point that is solute volatilization. So, in solute volatilization, what happens interaction of solute particles containing the analyte that is copper chloride cobalt chloride cobalt citrate or whatever it is we want to estimate. The with the other concomitant can influence volatilization. And cause enhancement or attenuation of the signal enhancement means increase in absorbance attenuation means decrease in the absorbance. They are generally specific to the matrix components; that means, the sample components will decide whether there is solute volatilization or not. And the signal depends upon the properties of the compounds that are formed. That is very simple instead of atoms if they if the free atoms combine to form another product, then the absorbance will definitely depend upon what type of compounds are formed exothermic, endothermic and then free atom concentration will be lowered, then also the absorbance will be more will be less.

So, they may also be called as chemical interference, because it is a basically formation of chemical compounds in the flame. So, in such things happen more in premix burners because in premix burner I do not have the control how much I am aspire rating the sample. All the sample is aspirated into the flame because it has got only one fuel box fuel cylinder and then sample also is introduced into the same cylinder through a capillary. So, everything will be burning at the top. So, in premix burner laminar flame volt realization begins as soon as they enter the primary reaction zone. In the primary at the blue flame range. So, the laminar flame volatilization begins as soon as they enter the blue flame range.

So, the occurrence of interference depends on the observation height the again we are coming back to this observation height which is very important. And the analyte can combine with the anions or ligands or simply from refractory oxides. So, the metal atom can combine with the anions chloride, bromide, sulfate, etcetera phosphate, carbonate, etcetera or ligands like EDTA NTA and other NH molecules etcetera, these are called as ligands or they may simply form refractory oxides platins. Vanadium of print oxide camille tungsten oxide chromium oxide like that they can form refractory oxides. If the refractory oxides are formed they do not dissociate. So, the absorbance will be absolutely nil or negligible.

So, we may not know, whenever we are determining an observer a substance containing aluminum or any other metal which are refractory chromium vanadium tungsten all these things. They may simply form the oxides and these oxides do not dissociate free atom concentration decreases absorbance decreases very simple.

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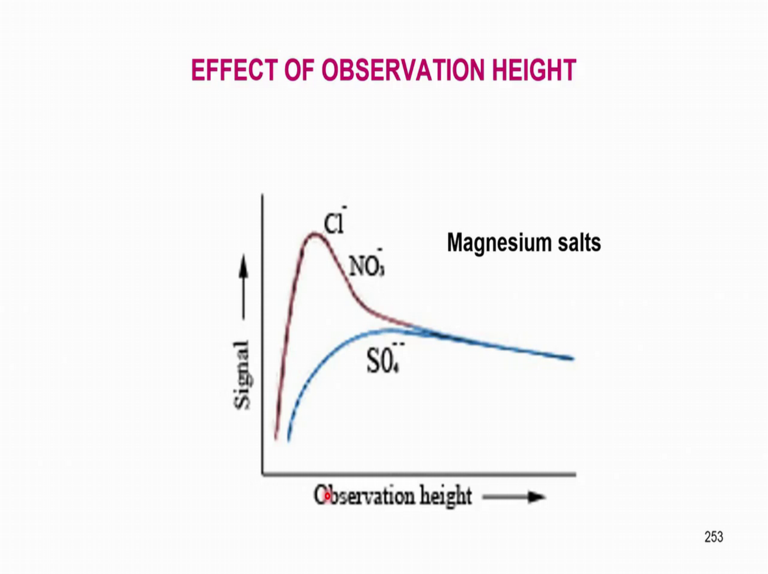

EFFECT OF OBSERVATION HEIGHT

So, this is the effect of absorber effect of observation height, now I have earlier I had given you for chromium magnesium and this chromium, magnesium and silver. Now I am giving you an observation height effect force chloride nitrate and sulfate. These are all magnesium salts. What we have done in this experiment is we are taken magnesium sulfate and magnesium nitrate and magnesium chloride, but we have increased the observation height whenever the solution contains sulphate. So, we take magnesium sulfate and aspire, I get a response figures like this whereas, if I take magnesium chloride or nitrate and the response is still higher, but the observation height is smaller. See observation height increases like this. So, here optimum reading is around this range, but for chloride it is almost the sensitivity is double, but the observation height is also is about half of the sulphate observation right about here.

Maximum chloride corresponds to half of observation height. So, if there is if you suspect there is sulfate in the sample, then what you should do observation height should be increased; that means, the flame should be raised further. So, if it contains chloride or nitrate the flame should be lowered. So, that the maximum sensitivity can be obtained or maximum absorbance can be obtained for lower concentration. So, this is the effect of observation height.

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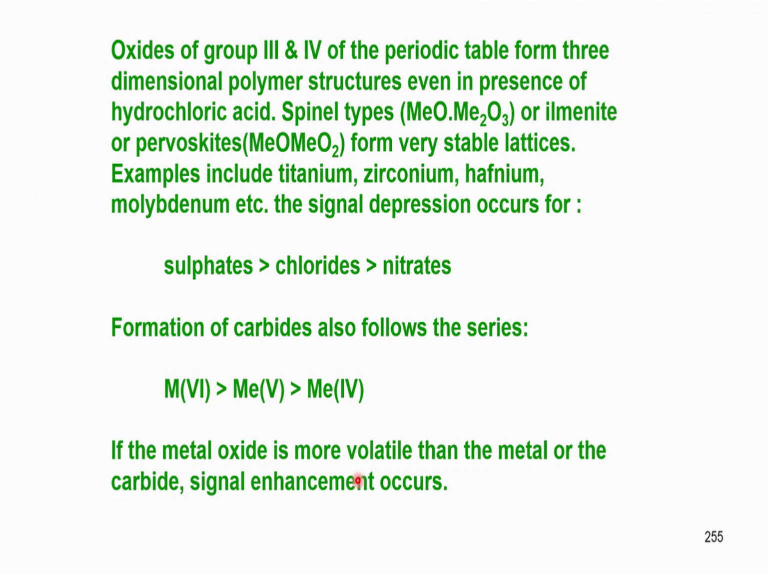

Oxides of group III & IV of the periodic table form three dimensional polymer structures even in presence of hydrochloric acid. Spinel types ($MeO.Me_2O_3$) or ilmenite or pervoskites($MeOMeO_2$) form very stable lattices. Examples include titanium, zirconium, hafnium, molybdenum etc. the signal depression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

Now, oxides of group 3 and 4 of the periodic table form 3 dimensional polymer structures. I think we all know about this, periodic table elements silicon it forms 3 dimensional polymer structures zeolites I think all of you must have heard of zeolites and such things structures persist even when we add hydrochloric acid to dissolve the sample.

So, spinal types are available like MeO.M e 2 O 3, these are the combined complexes metal oxide and metal oxide in 2 valency 3. Here metal oxide is 2, a metal valency is 2 oxygen is 2 here it is if So, it is both of them are combined. So, this metal and this metals could be different metals or they say they may be same metals. Like iron FeO Fe 2 O 3 or FeO and then al 2 O 3 something like this. These are called as spinal types. And there are other structures 3 dimensional polymer structures which are known as ilmenite pervoskites and several other structures. Mainly pervoskites are MeO MeO 2 type metal oxide metal dioxide. Here it is metal oxide metal ferric oxide something like this. They all these polymeric structures are known to occur and once they form it is very difficult to dislodge them from the structures.

So, the structures are stable very stable lattices. And the elements that combine to form spinals and ilmenite pervoskites are titanium zirconium hafnium molybdenum etcetera. Among these titanium and molybdenum are titanium zirconium oil these are all refractory elements only. So, the signal depression must occur whenever we have formation of spinals or ilmenite or pervoskites. So, when this happens whenever there is titanium and then zirconium, hafnium, molybdenum, aluminum etcetera silicon, yes I have not put all the elements here, but I may ask you questions in the examination.

So, sulfates the signal depression is maximum when sulphate is there. And then that is slightly more than chlorides and if it is nitrate the signal depression will not be So much. So, some types of elements form carbides for example, tungsten carbide very strong refractory element which is used in metal edges for metal cutting, tungsten carbide is quoted on even on our shaving blades. So, because it cuts very easily and it does not degrade very easily. So, the formation of carbide titanium carbide, molybdenum carbide, tungsten carbide. So, many elements form carbides and these carbides are also sort of refractory, boron nitride are also there and carbides nitrides etcetera. These decompose very less even at 3000 degree centigrade; that means, if we have such elements and you are doing it by flame you are bound to get lower absorbance.

So, the formation of carbides also follows this series that is, hexavalent is stronger then pentavalent then tetravalent metal ions. So, the absorbance decrease is maximum in hexavalent metal ions less is slightly less it is more than pentavalent which is more than tetravalent. So, if the metal oxide is more volatile, than the metal or the carbide then signal enhancement occur some elements form, if suppose there is a competition there is oxide there is also the carbon in the flame there is oxide oxygen there is carbon. So, if the metal oxide is more volatile the thermodynamically the formation of metal oxide will be favored because it requires less free energy. So, the signal enhancement occurs, but if it is a carbide decreasing the signal will occur.

So, such insights we can get depending upon the properties of the elements, but these elements are the concomitant elements, they could be there you along with the sample or they may be independently also. So, if you are determining titanium, zirconium, hafnium etcetera. We say a try do not try flame try some other method of analysis. Because the sensitivity is low interference is more.

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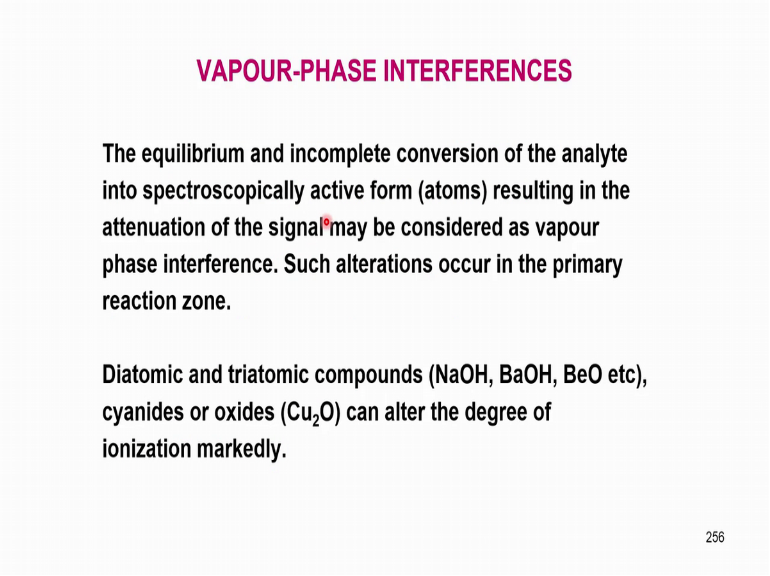

VAPOUR-PHASE INTERFERENCES

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, now we will talk a little bit about vapor phase interferences. The equilibrium and incomplete conversion of the analyte into spectroscopically active form that is atoms only resulting in the attenuation of the signal that is attenuation means decrease of the signal, may be considered as vapor phase interference; that means, what we are saying is the formation of the atoms and compounds. If the equilibrium is disturbed atom concentration will change and if the what is the spectroscopically activate term it means the atom formation. If the atom formation decreases absorbance decreases, if the atom formation increases absorbance increases.

So, these reactions occur in the vapor phase; that means, in the flame where you have no control over the chemical reactions everything is thermodynamically dependent and upon the free energy changes. So, such alterations occur in primary reaction zone basically. So, the for example, diatomic and triatomic compounds like sodium hydroxide barium hydroxide beryllium oxide etcetera, cyanides oxides etcetera can alter the degree of ionization markedly.

Suppose you are taking copper it may form copper oxide or it may form copper chloride and the sample can give higher or lower reading depending upon the concentration of the free atoms. So, such elements like sodium such compounds like sodium hydroxide, barium hydroxide, the barium oxide, beryllium oxide, copper oxide cyanide etcetera can give rise to problems. So, whenever we want you to analyze samples, we simply we prefer to say you dissolve it in hydrochloric acid or nitric acid. Do not dissolve it in any other acids and make sure that the sample is in a reduction mode cyanides and other complexes are not there. So, that the absorbance can be maximum.

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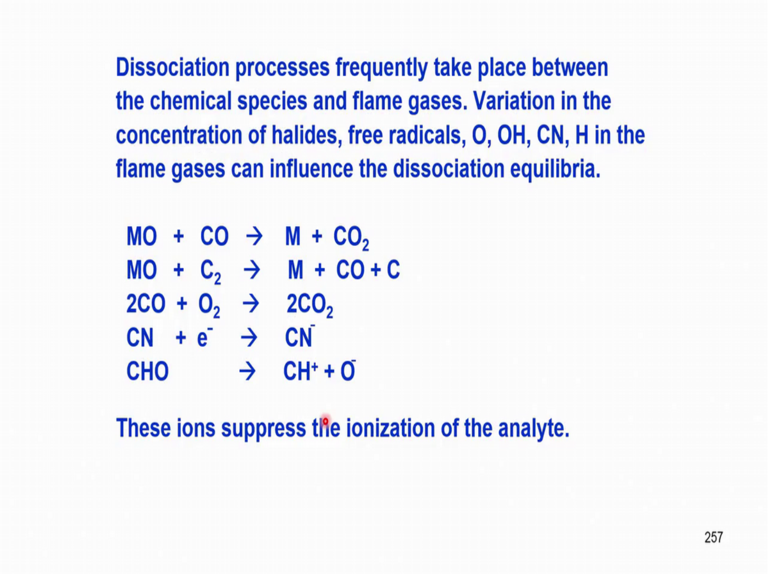

Dissociation processes frequently take place between the chemical species and flame gases. Variation in the concentration of halides, free radicals, O, OH, CN, H in the flame gases can influence the dissociation equilibria.

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

These ions suppress the ionization of the analyte.

So, what are the types of reactions that occur? Dissociation processes may take place frequently between the chemical species. For example, metal oxide plus CO goes to metal and CO 2 here production of metal atoms occurs, but this CO is there in the flame, metal oxide is there in the coming from the sample. So, even though it is metal chloride 90 percent of the time it is copper chloride, cobalt chloride, cobalt nitrate, etcetera the moment you introduce them into the flame metal oxide forms. So, the reaction of metal oxide with carbon monoxide gives you metal atom. This is a good reaction that is, beneficial for the production of atoms free atoms.

Similarly, metal oxide can react with C 2, carbon atoms and then producing metal plus carbon monoxide plus carbon dioxide. And then there are 2 CO, 2 CO molecules can give react with oxygen molecule to CO 2 this will have a broadband interference. Broadband means resonance line overlapping and there will be decrease in increase in the signal, but it is unnatural. Similarly cyanogens reacts with electron cyanide minus again this has got a broadband decrease in the absorbance CHO and dissociate to give you CH plus and O minus and this CH plus also reduces the signal; that means, most of the vapor phase interferences occur because of the presence of carbon monoxide, carbon atoms and oxygen etcetera. And they react with the metal oxides and sometimes there is increase in the concentration of the atoms for b due to the formation of metals, but if there is a formation of molecular species which have got broadband then there will be increase in the signal, but it is unnatural it is an interference.

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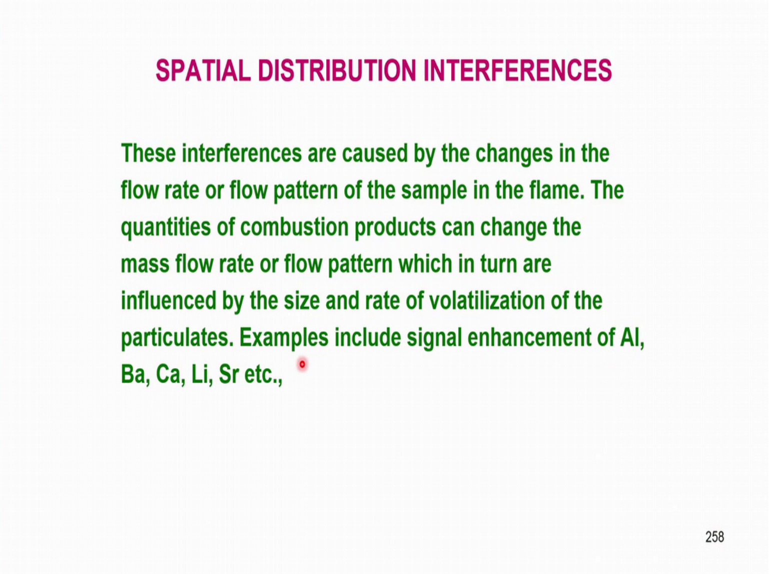

SPATIAL DISTRIBUTION INTERFERENCES

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, sometimes this distribution can take place, interference can take place in a special form. These interferences are caused by the changes in the flow rate or flow pattern of the sample in the flame. The quantities of kind of combustion products they can change the mass flow rate and flow pattern also, which in turn are influenced by the size and rate of volatilization of the particles, in particulate matter. So, examples include signal enhancement of aluminum, barium, calcium, lithium, strontium etcetera.

So, what we are saying is the formation of the combustion products into molecular species can change the absorbance. Examples include, either signal enhancement of aluminum and the other elements, but it can be it can lead to decrease also.

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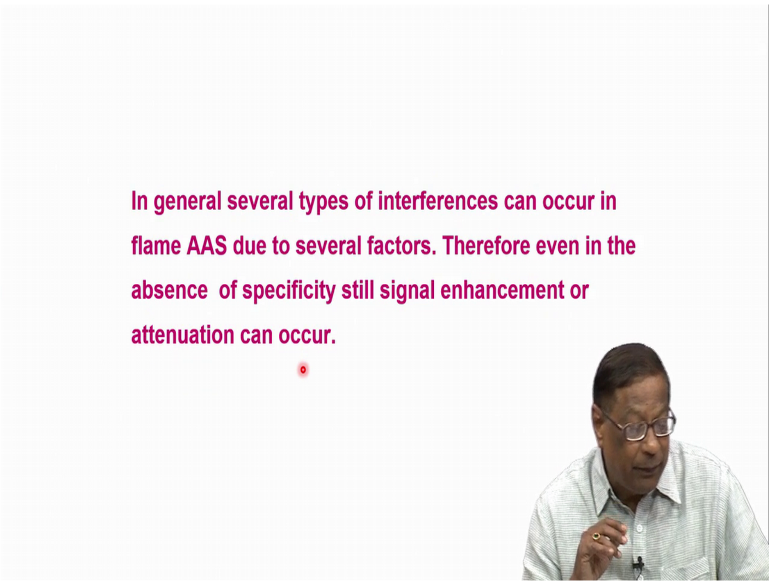

In general several types of interferences can occur in flame AAS due to several factors. Therefore even in the absence of specificity still signal enhancement or attenuation can occur.

So, in general what we want to say is, several types of interferences can occur and they do occur in flame atomic absorption due to several factors. Therefore, even in the absence of specificity still signal enhancement or attenuation can occur. This is the bottom line. We say like a panacea if you want to determine without knowing the chemistry of the substance go to atomic absorption. But knowledge of chemistry and the flame especially the flame chemistry, molecular species helps in proper handling of the signal; that means, you can expect interferences from spinal ilmenite and other structure gelolytype structures, vapor phase interferences could be there spectral interferences could be there.

So, just like a detective whenever a sample comes for analysis, what we want to know is what else it contains what are the possible other elements that are present in atomic absorption sample. A sample, that we asked sometimes if they do not know then we expect these interferences and try to make adjustments, how we make the adjustment? We will see later. So, we will discuss about the background correction of the flame AAS in the next class.

Thank you.