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 – 25

Interferencesin AAS III

We were discussing about the interferences in atomic absorption. Earlier I had told you that there are not many interferences to be expected in atomic absorption as for as analysis is concerned, but as far as signal is concerned there are different kinds of interferences which you have seen yesterday and there is some amount of certain amount of repetition earlier also I had shown you about the interferences and I was about to teach you about ionization interferences.

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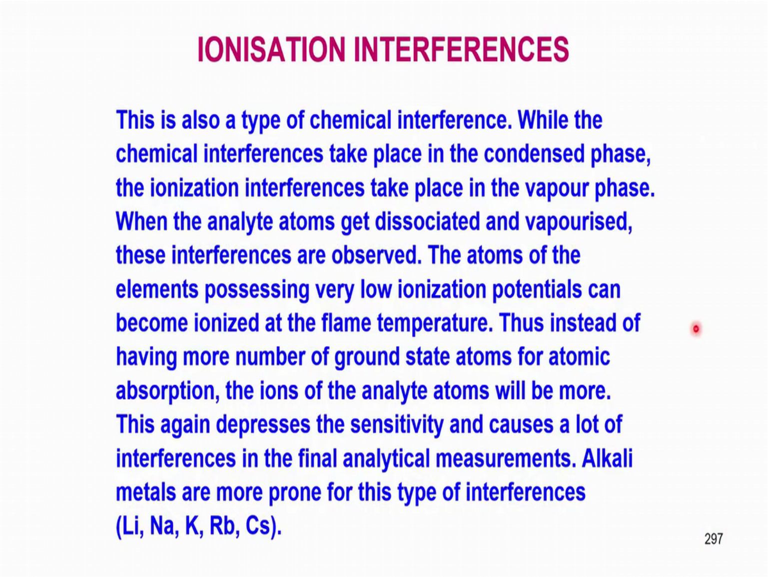

IONISATION INTERFERENCES

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, ionization interference is also a type of chemical interference while the chemical interferences take place in the condensed phase, but the ionization into interferences take place in the vapor phase. That means, during aspiration the chemical interferences can take place in the solution itself suppose you had certain reagents chemicals to dissolve a substance like sulfuric acid or a nitric acid. Sometimes we take the sample along with potassium carbonate sodium carbonate fusion reactions, sometimes we have perchloric acid all these additions of acids alkalis and then you know preservatives sometimes we take blood sample and then add tri tonics hundred that is a surfactant.

So, it keeps the blood in solution. So, the other chemicals the analyte as well as other chemicals can react in the solution itself for to form different types of compounds which will alter the number of free atoms in the vapor phase and that is the whole idea about atomic absorption. So, chemical interferences what we say is normally they all occur during in the solution phase itself and ionization interferences normally occur in the vapor phase, so why because only in the vapor phase inside the flame there is there are number of electrons available from the flame itself.

So, the combination, dissociation of electrons with the ions normally takes place in the vapor phase only. So, when the free analyte atoms what happens is when they sometimes they get dissociated and vaporized for example, in the case of sodium chloride. So, sodium chloride normally it gets dissociated in the vapor phase and then vaporized and then the interferences normally occur are observed only when there are, they are in the vapor phase.

So, the atoms of the elements possessing very low ionization potentials can become ionized at the flame temperature this sentence though it looks a little technical what it means is very simple, elements like sodium potassium cesium rubidium etcetera, they are all atoms of the elements possessing very low ionization potential. So, such elements can become ionized at the flame temperature that is around 1700 to 2300 degree centigrade lot of these sodium potassium calcium a calcium strontium and cesium etcetera they do get ionized and then instead of having more number of at ground state atoms there will be more number of ions in the vapor phase.

So obviously, the signal will drop. So, this depresses the sensitivity; that means, absorbance will become less and causes a lot of interferences in the final analytical measurements because normally what we do is whenever a sample is to be analyzed whenever a sample is to be analyzed the idea is we dissolve it take the sample dissolve it dilute it and then we take a small portion of the sample and then aspirate it. So, the actual analysis needs to a lot of multiplications etcetera to find out the actual concentration in the original sample.

Suppose you want to take a analyze a plant material what do we do we take the plant material powder it and then right and then after drying the powder we take about point one gram or something like that or maybe 0.5 grams and then we dissolve it and then we analyze they after dissolving we dilute it to about 50 ml or 100 ml or what some standard volume and then that sample is atomized in the nebulizers.

So, the 100 ml of the sample corresponds actually to point one gram of the plant solid pearl material whatever you want it to analyze similarly for all chemical analysis we take a small sample of the of the actual analyte and then dilute it etcetera. So, there when we do the final analytically measurements we do not want the errors to be very high, but alkali metals are more prone to this type of interferences especially lithium, sodium, potassium, rubidium, cesium. So, it is better to avoid determination of these metals by atomic absorption atomic emission yes that will study a bit later.

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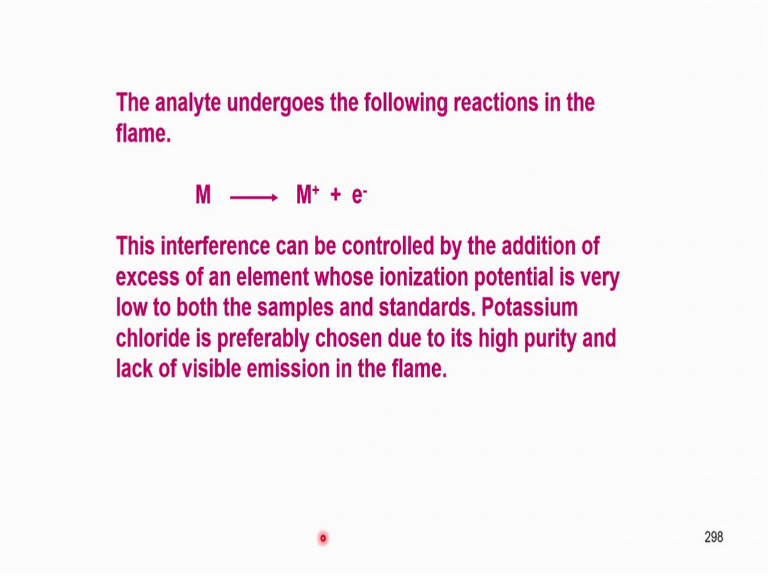

The analyte undergoes the following reactions in the flame.

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

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

So, the analyte undergoes this reaction that is material and goes to metal plus plus a minus and the ionization. So, this interferences I can easily control if they say absorbance signal is very low then what I can do is I can add an excess of an element whose ionization potential is very low to both samples and standards. So, what I do is if I want to analyze some other element sodium. For example, then I add potassium chloride because a potassium chloride will be more there is something like equilibrium and in the total equilibrium the concentration of sodium will be suppressed that is known as common ion effect.

So, if I take potassium potassium chloride when I want to analyze sodium chloride then potassium chloride is preferably chosen due to its high purity and lack of visible emission in the flame. So, this is one trick we normally employ in especially when we are determining the alkali metals.

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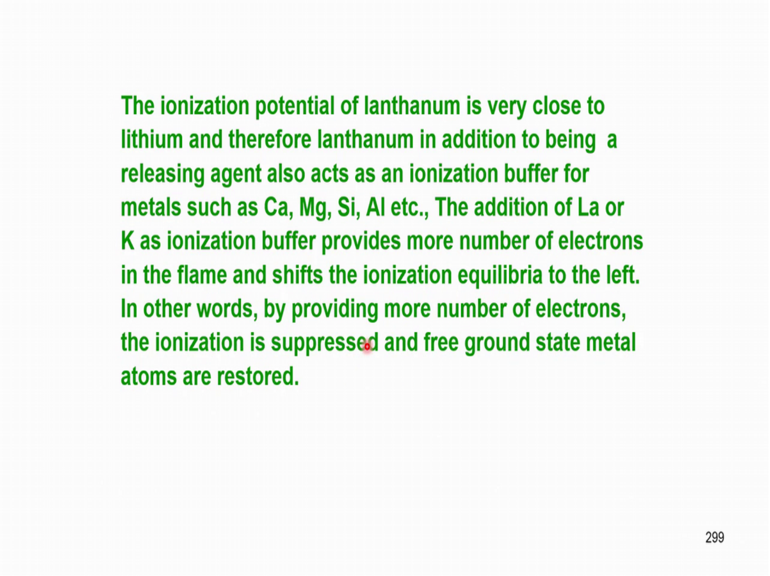

The ionization potential of lanthanum is very close to lithium and therefore lanthanum in addition to being a releasing agent also acts as an ionization buffer for metals such as Ca, Mg, Si, Al etc., The addition of La or K as ionization buffer provides more number of electrons in the flame and shifts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

So, look at this slide now the ionization potential of lanthanum is very close to lithium. So, what do we do if I want to add a determined lithium I add a lanthanum salt in addition to. So, which the lanthanum salt usually acts as a releasing agent for metals such as calcium magnesium etcetera it acts as an ionization buffer.

So, instead of really getting instead of ionizing the actual analyte this lanthanum oxide will ionize more. So, the supernal the ionization of calcium magnesium silicon etcetera all these things get suppressed; that means, there will be production of more atoms in the ground state. So, the addition of lanthanum or calcium also as ion this is called as ionization buffer. So, the ionization buffer provides more number of electrons in the flame, and shift the ionization equilibria to the left; that means, the analyte atoms do not ionize to the extent that they would analyze if I put lanthanum or calcium.

So, in other words by providing more number of electrons from some other source the ionization of the analyte element is suppressed and free ground state metal atoms are restored. So, this is one way of removing the interference from ionization potentials.

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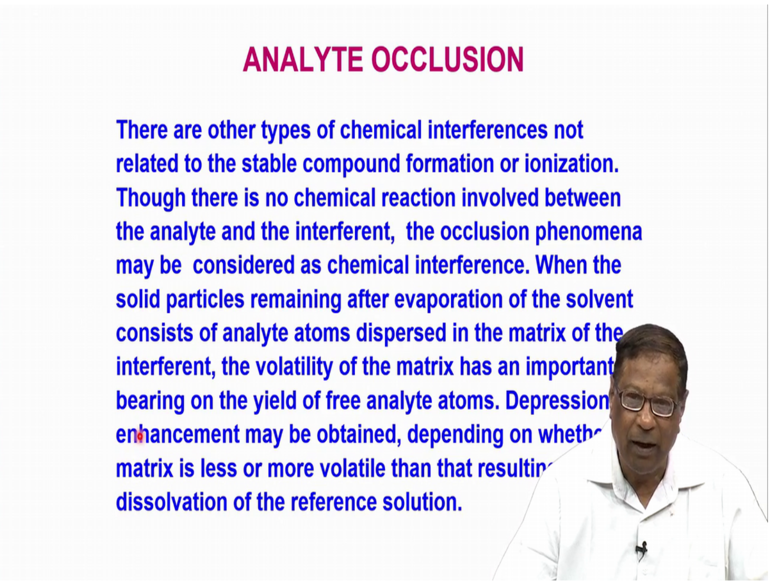

ANALYTE OCCLUSION

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

So, another way is analyte occlusion, sometimes there are other types of interval for chemical interferences not related to the stable compound formation or ionization also for that matter because there may not be any chemical reaction between the analyte and the interference, but the analyte may get uploaded get held up in a crystal cavity.

So, if it gets held up it does not get ionized nebulized at all. So, the when the solid particles containing a remaining after evaporation of the solvent if it contains analyte atoms dispersed will be matrix of the interference; obviously, the volatility of the matrix gets reduced. So, the volatility of the matrix has an important bearing on the yield of free analyte atoms; that means, suppose you want to analyze blood the volatility of the blood, blood is so thick that it is very difficult to atomized blood particles blood solutions.

So, same thing is true with sea seawater and say plasma human plasma bovine plasma and several other types of enema and other types of samples and then so if this happens if the analyte atom gets occluded or held up in the cavity crystal cavities of the molecular species then to that extent the production of vapours vaporized atoms becomes less. So, depression of or enhancement may be obtained when we get depression of the signal absorption signal if we get held up does not regret released into the flame or if it comes out suppose where you there is some additional element that is held in the matrix and when I aspire it that also comes out apart from this standard one then we get enhancement also.

So, the occlusion interference can work both ways it can be either increase or decrease ninety nine percent of the time it is decrease only. So, depending upon whether the matrix is less or more volatile, less volatile means more enhancement and more volatile more volatile means enhancement of the signals and less volatile means reduction of the signal. So, it all relates to the desolvation process of the reference solution in the flame after nebulisation.

So, this type of occlusion normally people come across especially when we want to do soil analysis blood analysis and things like that; that means, if the sample is very refractory in nature chances are many of the analyte elements are held in the held in the matrix of the silica matrix or alumina matrix and things like that.

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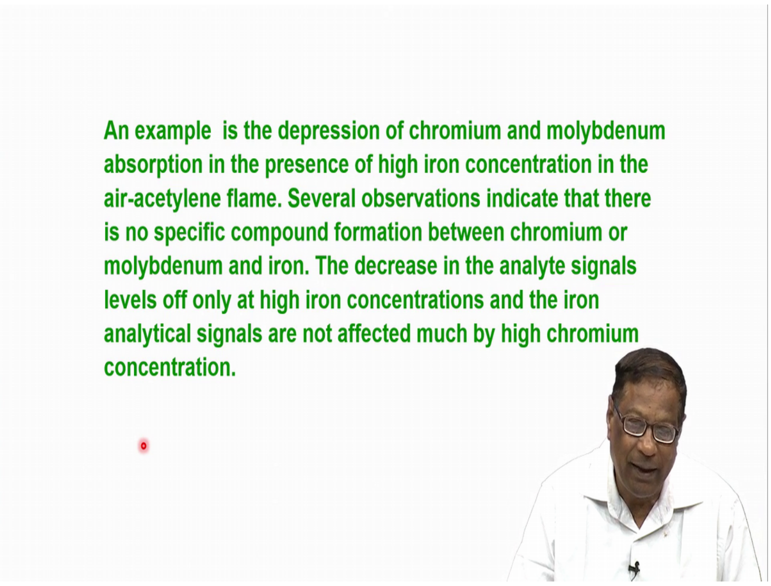

An example is the depression of chromium and molybdenum absorption in the presence of high iron concentration in the air-acetylene flame. Several observations indicate that there is no specific compound formation between chromium or molybdenum and iron. The decrease in the analyte signals levels off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

So, example is depression of chromium and molybdenum absorption in presence of high iron concentration in the air acetylene flame.

Now, we want to determine chromium and molybdenum in a given sample, but assume there is high iron concentration in the air acetylene flame when do you get such a situation the requirement is suppose you have an alloy and you want to estimate how much of chromium or molybdenum is there in the sample. So, the sample of make chromium and molybdenum may contain about one percent 5 percent 2 percent eighteen percent like that it may vary depending upon the alloy composition, but the remaining material is mostly iron. So, if it is an alloy of chromium molybdenum and iron; obviously, iron content will be more and the chromium and molybdenum will be less in concentration it depends upon the alloy composition whoever prepares the alloy will know how much they have put.

But in general stainless steel and several other kinds of steels contain chromium and molybdenum to the extent of maximum 20 percent more not more than that sometimes even one percent also will do. So, the analysis of chromium and molybdenum is done using air acetylene flame; that means, you take the alloy dissolve it in acid dilute it to a desired level aspirate it and then the aspirated solution will contain chromium molybdenum and then acids and then water and any other impurities that may be present in the alloy.

So, but to determine chromium and molybdenum what you need is a air acetylene flame this we know from the experience or from the cookbook when you want to analyze the instrument manufacturer will tell you when you want to analyze chromium you go for a air acetylene flamed that is simplest that is best. So, you normally end up doing chromium and molybdenum using air acetylene. Now several observations indicate that there are no specific compound formation between chromium molybdenum and iron in solution; that means, in solution chromium will not react with iron chromium will not react with molybdenum and chromium will no molybdenum will not react with chromium or iron all are independently existing in solution after the dissolution.

So, now what happens there is job is to aspirate it and determine chromium or molybdenum. So, the decrease in the analyte signal levels off only at high iron concentrations and the iron analytical signals are not affected much by high chromium concentration what does it mean this center last sentence in this slide says that there will be decrease in the analyte signal of chromium or molybdenum. And it increases only at high concentrations and the iron analytical signals are not affected, but chromium analytical signals are affected.

So, if you want to determine chromium and molybdenum you get a lower signal then actually what you should get; that means, lower concentrations, but iron if you want to analyse the remaining iron in the sample then there is not much effect on these sensitivity of the absorption line of iron.

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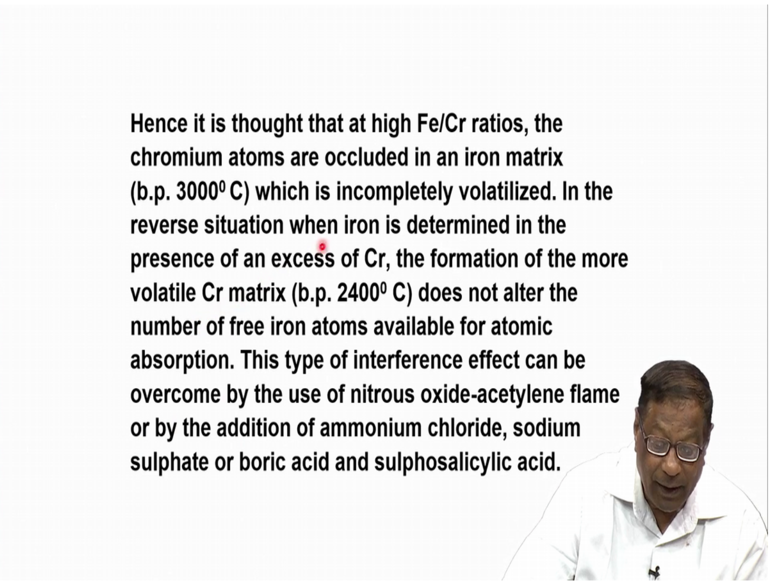

Hence it is thought that at high Fe/Cr ratios, the chromium atoms are occluded in an iron matrix (b.p. 3000^0 C) which is incompletely volatilized. In the reverse situation when iron is determined in the presence of an excess of Cr, the formation of the more volatile Cr matrix (b.p. 2400^0 C) does not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

So, it is thought that what people think or research points out is that it is at high iron chromium ratios suppose a chromium is also high and iron is also high chromium atoms are occluded in the iron matrix why because iron matrix will get destroyed only around 3000 degree centigrade it starts boiling.

So, which is income, so whatever is the temperature you use using air acetylene the; obviously, the iron chromium is in solution it is a metal melt of the iron chromium molybdenum (Refer Time: 18:30) alloy; that means, it is neither completely vaporized, but it is in the liquid state it is not boiling because it is boiling temperature is 3000 air acetylene is hardly around 2300 or 2500. So, what happens? The molybdenum chromium is held in the liquid state liquid form of the total alloy because all the alloy is not of is not vaporized; that means, it is occluded in the iron matrix that is what we say normally.

So, this is a; in the reverse situation suppose you want to a determine iron. So, an excess of chromium if it is there the formation of more volatile chromium matrix does not alter the number of three iron atoms available; that means, suppose you have an alloy where chromium is more iron is less than the you want to determine iron, iron does not it does not alter the number of free iron atoms, but if the ratio of iron to chromium is less; that means, if chromium is less then chromium a chances of 90 percent of the chances are chromium will be held in the melt of the alloy reverse situation you want to analyze iron in presence of high concentration of chromium it does not happen.

So, this type of interference can affect the interference effect can be overcome by the use of nitrous oxide acetylene flame simple whenever we have a situation like this we need a temperature of 3000, but at 2400 air acetylene does not work because the vaporization is not complete. So, how do we solve this problem you vaporize it you increase the higher temperature and then as usual ensures that all the will melt or alloy is vaporized using nitrous oxide acetylene flame this I have shown you earlier that nitrous oxide acetylene flame can give you up to 2800 to 2300 degree centigrade in the flame that is the temperature of the flame.

So, we can add this we can use determine chromium in presence of large quantities of iron using nitrous oxide acetylene even though the textbook says you use only the only air acetylene. Or I can do one more thing though what I do is by the addition of ammonium chloride sodium sulphate or boric acid and sulphosalicylic acid what I do is I convert the vapor into some sort of an organics of salt chromium or chromium chloride, chromel chloride sodium sulphate if I add chromium will react in the solution to form chromium sulphate or the chromium boric, chromium salicylate sulphosalicylate etcetera these organic and inorganic compounds ionize very easy, they do not need nitrous oxide acetylene flame.

So, these are all nuances of a atomic absorption especially you want to handle interferences there may be other methods of analysis, but atomic absorption is the ultimate in any chemical analysis and you can even say ICP also to some extent, but for the time being we are considering atomic absorption that ICP means inductive couples plasma atomic emission spectrometry that will may see later.

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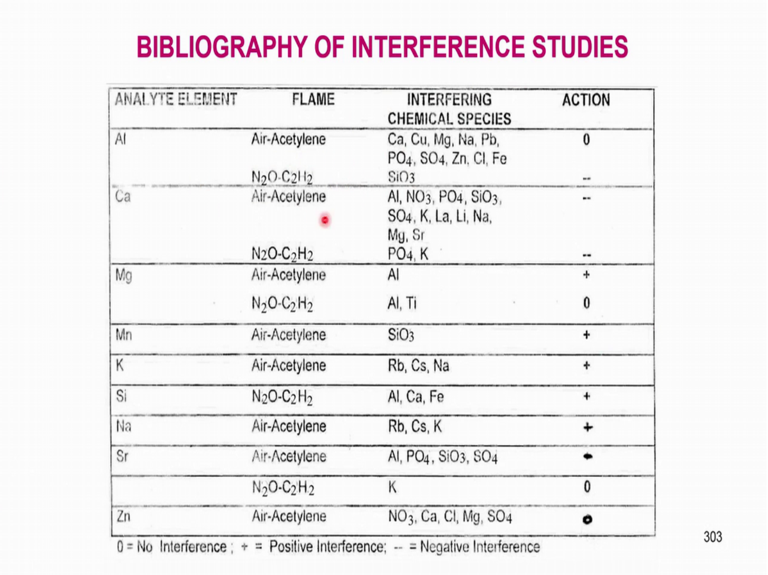

BIBLIOGRAPHY OF INTERFERENCE STUDIES

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

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

Now this the bibliography bibliography of interference studies what we have tried is we have I have I am trying to give you some sort of insight into different kinds of interferences that are normally expected. For example, take the first element aluminum normally it is determined by air acetylene chemical species all these things will interfere in the determination of such a element calcium copper magnesium sodium lead phosphate sulfate chloride zinc, SiO 3 etcetera.

So, the action if it is air acetylene we say do not bother, but if you use way a nitrous oxide and silicon all the interferences will you go away and only the SiO 3 could be of some interference, but if SiO 3 is there silicate in the sample then we say do not bother whatever is the reading you get you try to work it out. It may be small for small concentrations, but if it is not there we have to resort to some other kind of analysis rather than we rather than stick to atomic absorption obstinately that is not required there are there may be other simpler methods of analysis that we will have to look for as analytical scientists.

Similarly, calcium, calcium air acetylene is there and all these things aluminum nitrate phosphate silicate sulfate etcetera all these things will interfere. So, in general what we expect from atomic absorption analysis is that we very certain amount of concentrations of chloride, sulfate, nitrate, calcium, magnesium, sodium and phosphate to some extent iron is there most of the time there in the samples. So, in general we expect certain amount of interference from all these element only when you aspirate a standard solution containing only a living and then you get a higher one reading, but if you want to analyze all these things if analyze aluminium in several metals several samples containing chloride bromide sulfate etcetera because whenever you dissolve a given sample all these ions will be there all the time if you dissolve in alkali sodium put a calcium etcetera will be there sometimes people will treat these samples with lime etcetera in industries waste waters. So, calcium phosphate and other things will be there as impurities.

So, in general whenever the sample contains any of the interfering metals like any of the not only interfering any of the metals there will be certain depression in the analytical signal especially compared to a standard which does not have any of these impurities that is what it means. So, some amount of standardization is required in presence of all these interfering elements. So, now, we going we go back to this calcium determination what we want to tell you is aluminum nitrate phosphate silicate all these things will definitely give you a certain amount of attenuation of the signal, but if you want to avoid all that go for higher temperatures, but even there could be phosphate and potassium could be interfering species.

Similarly, for magnesium normally air acetylene aluminium will definitely interfere. So, this is the air acetylene we will take care of these things. So, aluminium is a positive interference; that means, the signal will be reduced if it is negative interference signal will be enhanced. So, nitrous oxide acetylene the signal will not be affected much in the case of magnesium. Similarly for air acetylene SiO 3 is the interference and it gives a positive interference. So, air acetylene potassium silicon sodium etcetera there is if I write zero there is no interference if I write positive, positive interference if I write negative it means negative interference.

So, positive interference means the interference signal will be less and negative interference will be the mean signal will be more. So, this is that is how we interpret the interference from chemical species, but what else what I want to tell you is people whenever they do any chemical analysis using atomic absorption large quantity of data is automatically generated. So, the table which I had shown you earlier does not represent the overall picture it varies from sample to sample and where it varies from operating condition to operating condition it varies from different composition of these standard and blank and reference etcetera.

So, it is best to match the standard also with the interfering species concentration; that means, you put the interfering species whatever you think it are possible in the standard also. So, the standard also absorbance from the standard also decreases and it can be analyzed to that extent the interference will be taken care of. So, that is what it means, but you have to remember that the interference list what I am giving you here is not at all exhaustive, but it is only an indicator. So, there are about 70 elements that can be determined by atomic absorption and the list is really exhaustive and if you want to know about every interference from chemical species etcetera you have to do some amount of certain amount of literature survey, but this is only an indicator of the things to come.

For example if you want to analyze particular element the cookbook will say these are the interferences expected. So, you study the cookbook choose the conditions make your standards then do the analysis that is the operating procedure. So, now, we will discuss about these spectral interferences and I have to tell you again that atomic absorption is remarkably free from spectral overlap interferences; that means, the resonance lines of each element is almost specific to the analyte atom you want to analyze almost specifically, but there can be some amount of exceptions.

So, we have been maintaining that resonance lines need to be chosen for atomic absorption measurements and spectral in; that means, or the resonance line what is the resonance line it is the lowest state of excitation where the excitation also can take place and absorption also takes place. So, from the free state atoms the electrons atoms go to higher excited state come back to the ground state and while coming back whatever is the amount of energy they absorb, but they come back and that much amount of energy is released their heat and that is a standard frequency at which the absorption and excitation takes place that is resonance line.

So, this kind of resonance line is different for every element and there may be 3 or 4 resonance lines of different sensitivity, the lowest resonance line will have highest sensitivity and higher the frequency the lower would be the sensitivity. Now what we want to tell is that the sometimes you come across situation where the monochromator with the resonance lines themselves can overlap for 2 or 3 elements sometimes it happens, exceptions do occur, spectral this is called as spectral interference we will the resonance line if it matches spectral interference; that means, we will be measuring the absorbance of the two elements if they are there of both the elements. So, this kind of interference will study in the next class.