Modern Instrumental Methods Of Analysis

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Lecture No 21

Atomic Absorption Spectrometry-5 Instrumentation

Will continue our discussions on the detection system in atomic absorption, I have shown you in the last slide that the detection system should include the detector associated power supplies and an amplifier

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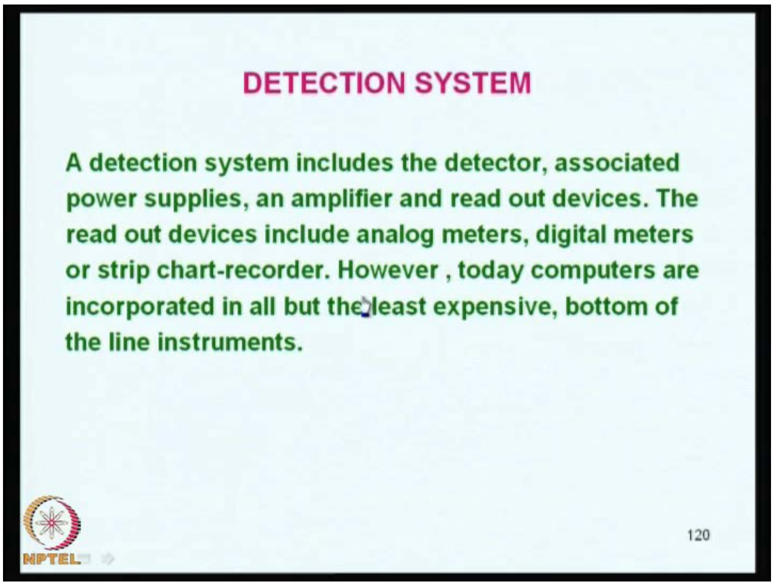

DETECTION SYSTEM

A detection system includes the detector, associated power supplies, an amplifier and read out devices. The read out devices include analog meters, digital meters or strip chart-recorder. However , today computers are incorporated in all but the least expensive, bottom of the line instruments.

and read out devices. The read out devices include analog meters digital meters or a strip chart recorder; however, today computers are incorporated in all, but the least expensive bottom of the line instruments the while continuing the our discussion on the detectors in the last class

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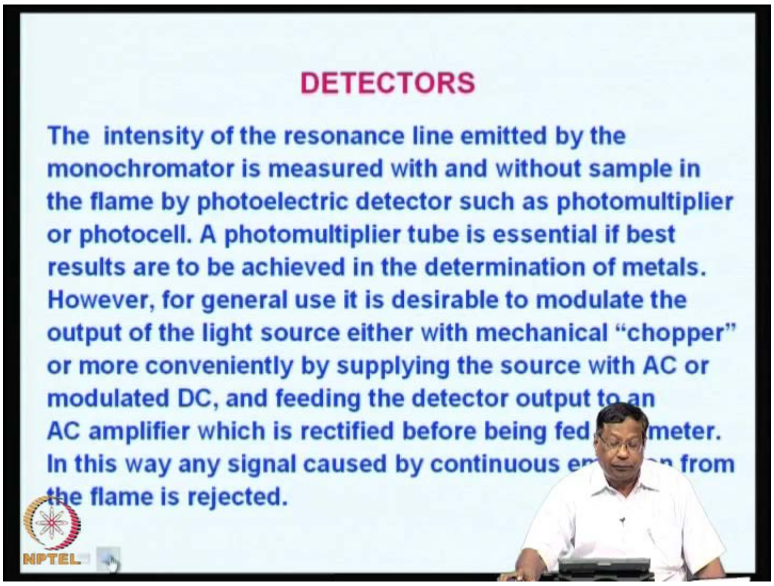

DETECTORS

The intensity of the resonance line emitted by the monochromator is measured with and without sample in the flame by photoelectric detector such as photomultiplier or photocell. A photomultiplier tube is essential if best results are to be achieved in the determination of metals. However, for general use it is desirable to modulate the output of the light source either with mechanical "chopper" or more conveniently by supplying the source with AC or modulated DC, and feeding the detector output to an AC amplifier which is rectified before being fed [illegible] meter. In this way any signal caused by continuous [illegible] from the flame is rejected.

I had explained that the intensity of the resonance line emitted by the monochromator is measured with and without the sample in the flame by the photoelectric detector. So, photomultiplier tube is essential if best results are to be achieved in the determination of metals. However, for general use it is desirable to modify modulate the output of the light source either with mechanical chopper or by supplying the source with AC and or modulated DC. Feeding the and feeding the detector output to an AC amplifier which is rectified before being fed to a meter. In this way any signal caused by the continuous emission gets attain a it or it gets rejected.

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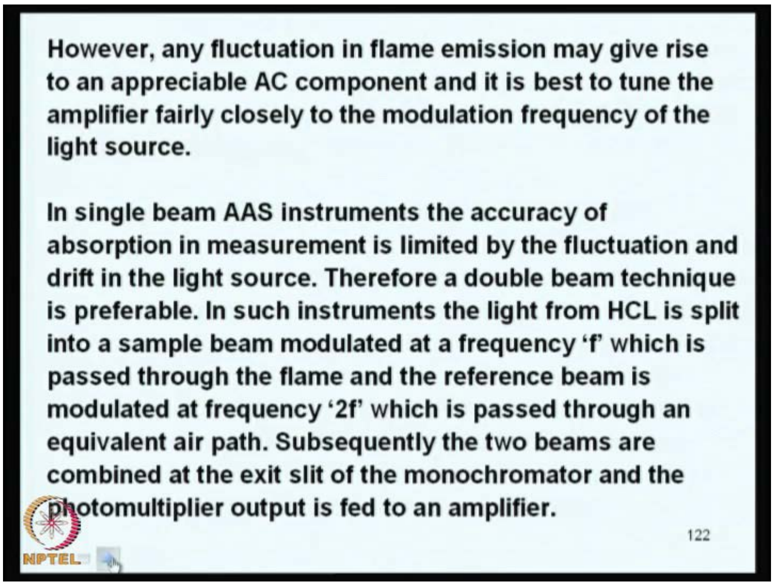

However, any fluctuation in flame emission may give rise to an appreciable AC component and it is best to tune the amplifier fairly closely to the modulation frequency of the light source.

In single beam AAS instruments the accuracy of absorption in measurement is limited by the fluctuation and drift in the light source. Therefore a double beam technique is preferable. In such instruments the light from HCL is split into a sample beam modulated at a frequency 'f' which is passed through the flame and the reference beam is modulated at frequency '2f' which is passed through an equivalent air path. Subsequently the two beams are combined at the exit slit of the monochromator and the photomultiplier output is fed to an amplifier.

However, any fluctuation in the flame emission may give raise to an appreciable a component and it is best to tune the amplifier frequency closely to that of the modulation frequency of the light source. In single beam instruments the accuracy of absorption is limited to the fluctuation and drift in the light source. Therefore, a double beam technique is preferable in such instruments the light from HCL that is hallow cathode lamp is split into a sample beam modulated way frequency f which is passed through the flame and another reference beam which is modulated at frequency 2f which is not pass through this we have discussed in the last class.

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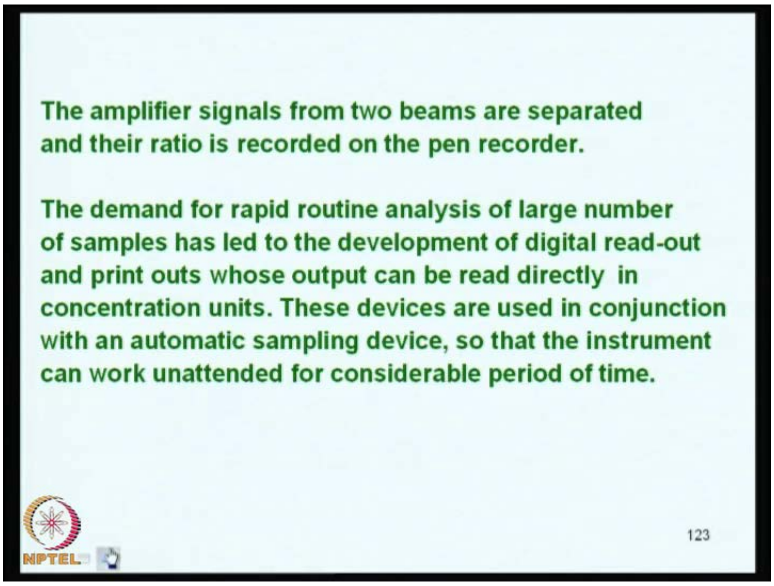

The amplifier signals from two beams are separated and their ratio is recorded on the pen recorder.

The demand for rapid routine analysis of large number of samples has led to the development of digital read-out and print outs whose output can be read directly in concentration units. These devices are used in conjunction with an automatic sampling device, so that the instrument can work unattended for considerable period of time.

So, the amplifier signals from the two beams are separated and the ratio is recorded on the pen recorder. The demand for rapid routine analysis of large number of instruments has lack to the requirement of digital read out and digital printouts whose output can be read directly in concentration units; because quite often people do not ah the operator of an atomic absorption spectrometry would be different from the actual scientist. So, the operator scientist who could can read any of the information from the from the data, but an operator can read more conveniently direct result that is concentration minutes. Such devices are used in conjunction with an automatic sampling device.

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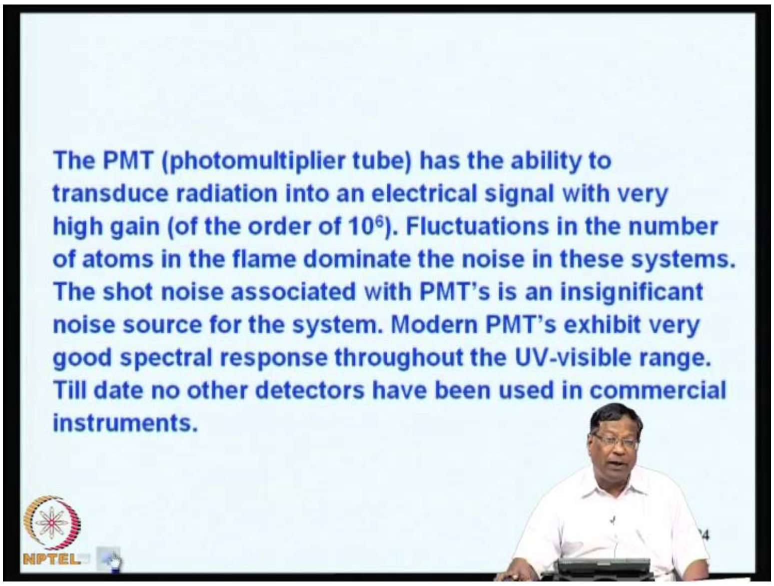

The PMT (photomultiplier tube) has the ability to transduce radiation into an electrical signal with very high gain (of the order of 10^6). Fluctuations in the number of atoms in the flame dominate the noise in these systems. The shot noise associated with PMT's is an insignificant noise source for the system. Modern PMT's exhibit very good spectral response throughout the UV-visible range. Till date no other detectors have been used in commercial instruments.

So, that instrument can work unattended for considerable period of time. The PMT has the ability to transducer radiation into an electrical signal these and all we have covered in the last class. What I wanted you to understand is the current slide what you are seeing as already I have already explained in the last class.

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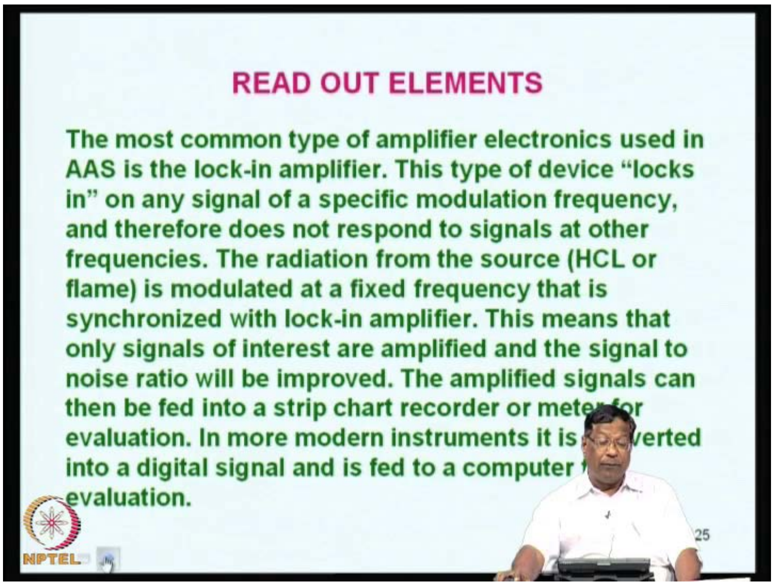

READ OUT ELEMENTS

The most common type of amplifier electronics used in AAS is the lock-in amplifier. This type of device "locks in" on any signal of a specific modulation frequency, and therefore does not respond to signals at other frequencies. The radiation from the source (HCL or flame) is modulated at a fixed frequency that is synchronized with lock-in amplifier. This means that only signals of interest are amplified and the signal to noise ratio will be improved. The amplified signals can then be fed into a strip chart recorder or mete for evaluation. In more modern instruments it is verted into a digital signal and is fed to a computer evaluation.

So, but just for the sake of brevity and putting most of the words into this slide to make it clear to you. So, the if you proceed to the read out elements again we have discussed that lock in amplifiers have got very important function to measure the response only at a particular frequency. And this frequency is locked; that means, the all other frequency would be rejected from the strip chart recorder.

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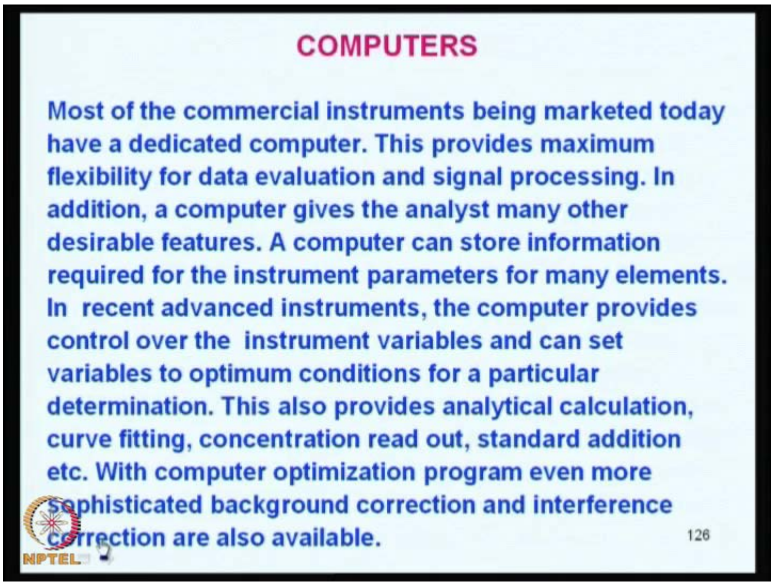

COMPUTERS

Most of the commercial instruments being marketed today have a dedicated computer. This provides maximum flexibility for data evaluation and signal processing. In addition, a computer gives the analyst many other desirable features. A computer can store information required for the instrument parameters for many elements. In recent advanced instruments, the computer provides control over the instrument variables and can set variables to optimum conditions for a particular determination. This also provides analytical calculation, curve fitting, concentration read out, standard addition etc. With computer optimization program even more sophisticated background correction and interference correction are also available.

So, the role of computers becomes very important especially when we look at the multiple types of functions and precautions and the requirement of data handling are taken into consideration. Therefore, most of the commercial instruments being marketed today have a dedicated computer. Which provides maximum flexibility for data evaluation and signal processing in addition computer gives the analyst many other desirable features such as storing of information, required for the instrument parameters for many elements. Suppose you want to determine copper, than you just press copper on the periodic table it will open a profile which will tell you what type of flame is to be used, and what is the wave length, what is the slide to it etcetera. What is the b r lamberts' law range, what is the linearity and what should be the flame temperature, what should be the gas flow rate like that several parameters required for the analysis can be ah exhibited just by choosing copper element on the periodic table.

Such information can be stored in the in the microprocessor and the computer also apart from giving this technical specifications it can also provide control over the instrument variables and it can set variable stop optimum conditions for example, if you want 324.7 nano meters you can just tell the enter the computer and go for slit go for wave length requirement simply type 324.4 it will start using stepper motor and move the wave length range to that value. So, such things are possible such process variables condition etcetera can be set by the computer. This also provides other types of analytical calculation curve fitting concentration read out standard addition etcetera.

And with computer optimization program even more sophisticated things like background correction this is very important. And interference corrections are also possible and therefore,

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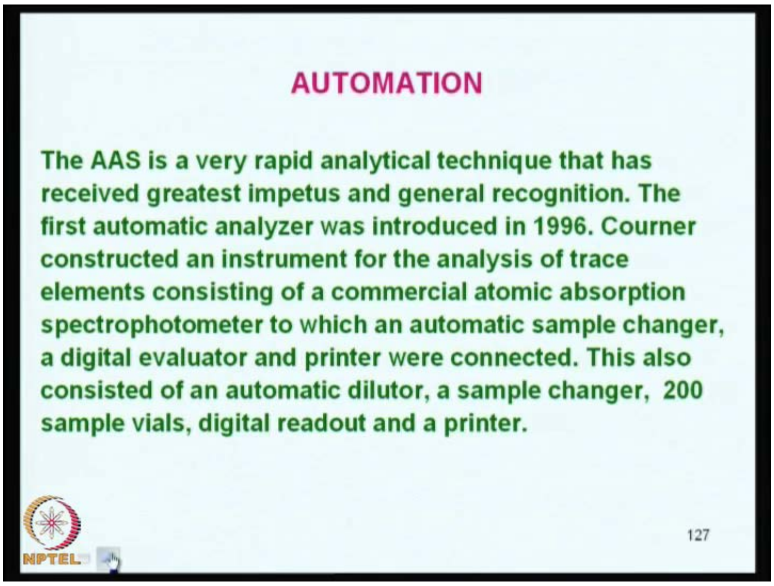

AUTOMATION

The AAS is a very rapid analytical technique that has received greatest impetus and general recognition. The first automatic analyzer was introduced in 1996. Courner constructed an instrument for the analysis of trace elements consisting of a commercial atomic absorption spectrophotometer to which an automatic sample changer, a digital evaluator and printer were connected. This also consisted of an automatic dilutor, a sample changer, 200 sample vials, digital readout and a printer.

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automation becomes very important and the requirement is in the field in the areas of agriculture, and then article chair, soil science, analytical laboratory, material science metallurgical laboratory like that, several thing are required where analysis of a large number of samples has to be done. So, a rapid analyzer with a computer for process automation also was introduced somewhere around 1996. The requirement added both an automatic sample changer a digital evaluator and printer.

So, this also consisted of an automatic dilutor, because sometimes you may when the signal is very high, you may not get the correct reading high absorbance then you will have to dilute. So, an automatic dilution facility was provided, and sample changer; that means, after one sample is done the sample rack should move or the sampler the nebulizer should move from the one sample to another sample that is known as sample changer, will take a look at it later attempt in a electro thermal atomic absorption option also. And then this instrument can take up to 200 sample vials and then view a digital read out and a print out also.

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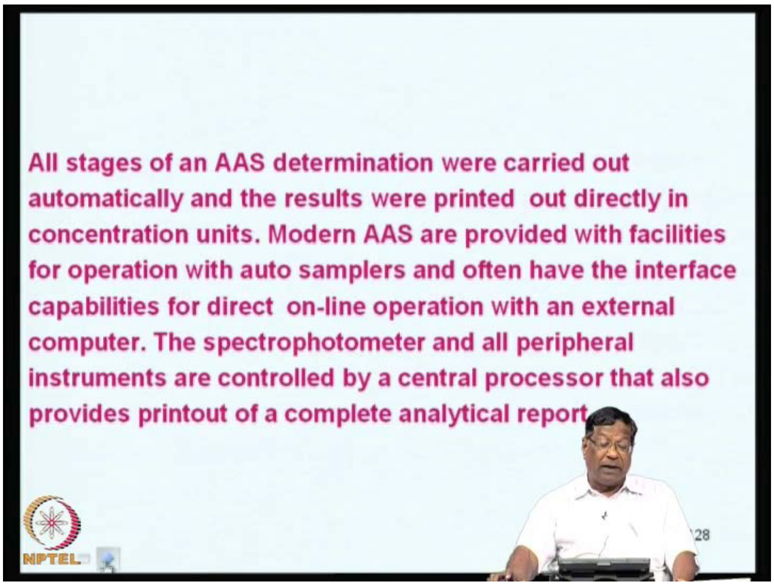

All stages of an AAS determination were carried out automatically and the results were printed out directly in concentration units. Modern AAS are provided with facilities for operation with auto samplers and often have the interface capabilities for direct on-line operation with an external computer. The spectrophotometer and all peripheral instruments are controlled by a central processor that also provides printout of a complete analytical report

So, such automation is system become available somewhere around 1996 and then all the stages of an atomic absorption where carried out automatically.

The results are printed out directly in concentration units. Modern atomic absorption spectrometers are provided with facilities like operation with auto samplers also. And you will have to program the auto sampler for your requirement; they have the interface capabilities for direct online operation with an external computer also. This spectrophotometer and all peripheral instruments are controlled by a central processor that also provides the printout of a complete analytical report.

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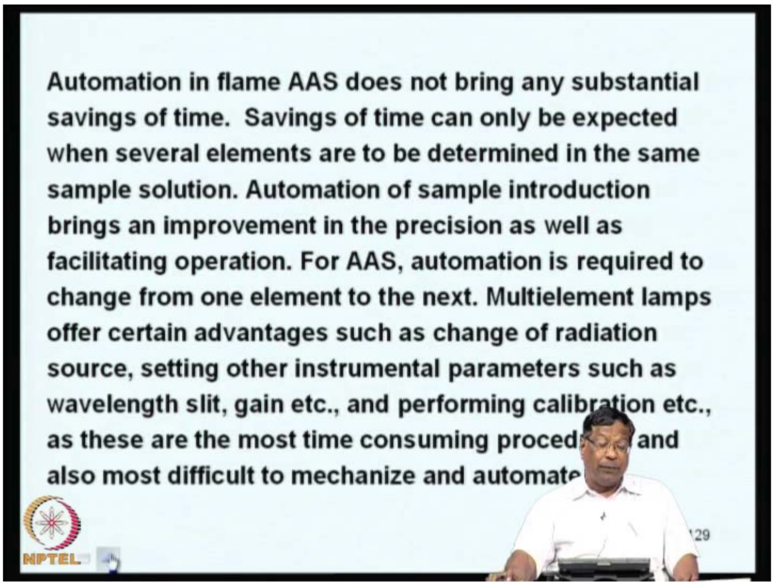

Automation in flame AAS does not bring any substantial savings of time. Savings of time can only be expected when several elements are to be determined in the same sample solution. Automation of sample introduction brings an improvement in the precision as well as facilitating operation. For AAS, automation is required to change from one element to the next. Multielement lamps offer certain advantages such as change of radiation source, setting other instrumental parameters such as wavelength slit, gain etc., and performing calibration etc., as these are the most time consuming proced and also most difficult to mechanize and automate

So, automation in flame basically does not bring any substantial saving of time. Savings of time can be only being expected when several elements are to be determined in the same sample solution. For example, the automation in a selection of the sample sucking and transporting the sample solution into the flame does not we say give you any savings, but you when there are several samples to be done then automaton helps. So, usually automation also brings in the precision as well as it facilitate the operation; that means, your results would be more reliable, if the machine takes over the process of sampling atomization putting it into the flame etcetera. So, that manual errors are minimized, for atomic absorption automation is require to change from one element to another for example, you may like to do copper for the first 20 elements, and then you may want to change the lamp to nickel for the same twenty samples. Than your sample you have to change the lamp, you have to change the lamp conditions current etcetera, and then you have to change the wave lengths slit etcetera, and then starts from the first sample to the same 20 sample.

So, it essentially a sequential operation. So, multi element lamp do offer certain advantages. Such as change of radiation source, setting of other important parameters, such as wave length, slide, gain etcetera. And it can also perform calibration and can do the statically fitting of the data, as these are the thing which takes most of most time desire. And they are time consuming process and they are most difficult to mechanize and automate also. So, with the computer all these things are become possible. Therefore, modern micro processor technology

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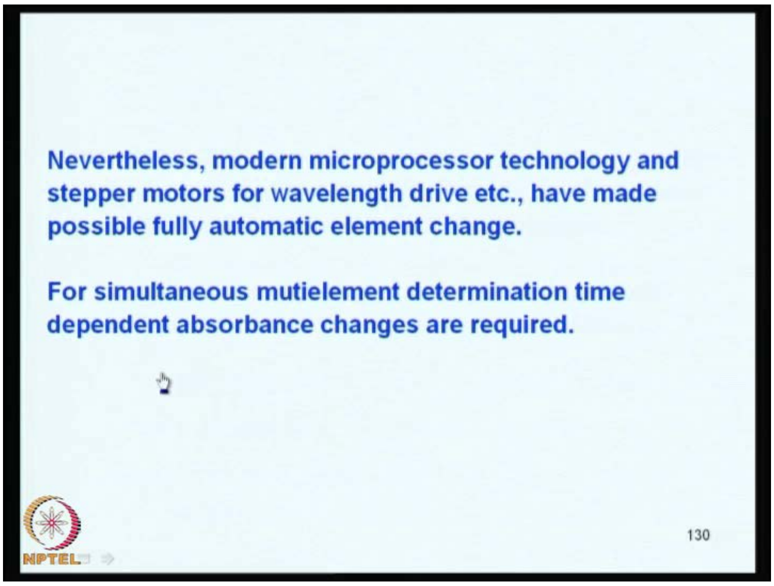

Nevertheless, modern microprocessor technology and stepper motors for wavelength drive etc., have made possible fully automatic element change.

For simultaneous mutielement determination time dependent absorbance changes are required.

and uses stepper motors for wave length and setting slide etcetera. They have they are now they are completely made automatic and for simultaneous multi element determination time dependent absorption changes are also required. For example, if you want to determine number of elements in the same sample, some it is possible to run through a sample number one to number 10.

And come back and change the lamp and again go with determine another element or in the same sample you determine all the elements simultaneously and then go to next sample like that. Several possibility exits when you have to do the number of analysis for different kinds of elements.

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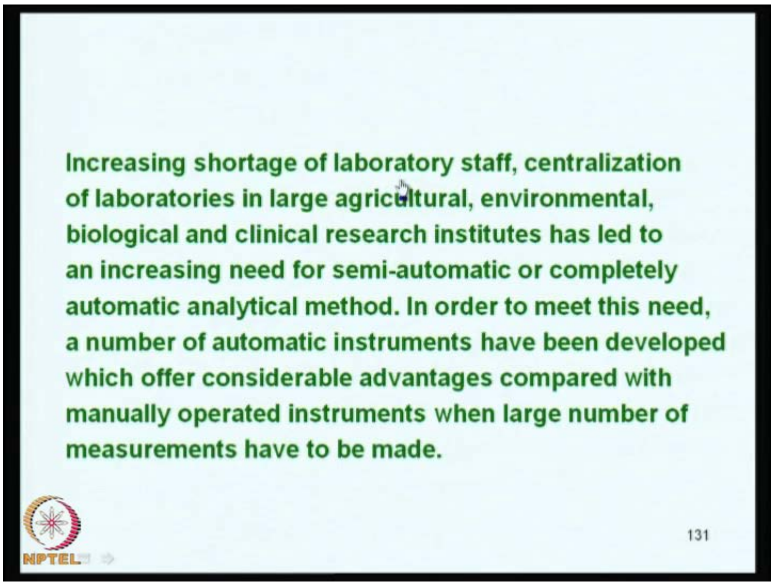

Increasing shortage of laboratory staff, centralization of laboratories in large agricultural, environmental, biological and clinical research institutes has led to an increasing need for semi-automatic or completely automatic analytical method. In order to meet this need, a number of automatic instruments have been developed which offer considerable advantages compared with manually operated instruments when large number of measurements have to be made.

Now, this increasing shortage of laboratory staff centralized of laboratories in large agriculture, environmental, biological, and clinical research institute has lead to an increasing need for semi automatic or completely automatic analytical method. This point I have been pressing again and again, because the amount of an effort that as gone into atomization automation is something phenomenal. Which as not being seen by any of the in any of the analytical technique. In fact, it was the atomic absorption spectrometer improvements in AAS that I like to automation in several other instruments such as spectrophotometer, ICP AAS etcetera. So, AAS is the leader where anything that required in terms of a process control or optimization data handling etcetera this as led the way. So, in order to meet this need a number of automatic instrument have been developed and that we have already discussed. Now what I want to discuss with you is the technique of flame AAS, because so for we have discussed the instrumentation in the atomic absorption. And now I would like to talk to you about the technique how to go about during atomic absorption analysis.

So, there are different components first of all you have to understand what is a actually happening in an atomic absorption. And how to measure the absorption, how to convert it into major able signal and concentration read out, but also you should understand the chemistry of atomic absorption. So, the chemical analysis with flame AAS is usually performed just like spectrophotometry you have to prepare standard solutions of the analyte; that means, you want to analyze copper, you will have to prepare standard copper solutions. There are a number of the instrument manufactures usually provide a cook book which tells you, what are the basic requirement for performing the chemical analysis. For example, if you want to determine copper it the cook book when you open the cook book the information there tells you.

What is the wave length required for copper. What is the gas combination air acetylene or acetylene nitro oxide like that, and then what is the slit, what are the what is the linearity range. And what are in what solution the samples have to be measured. Sometimes you may like to measure the sample in equest media, sometimes the standards lead to be made in acidic media like that, all the details are basically given and the cook book also tells you. What is the typical absorbance of a known concentration which has been done under laboratory guidance that is several laboratories combine together to produce the basic data for calibration? This cook book contains all such information the aerosol.

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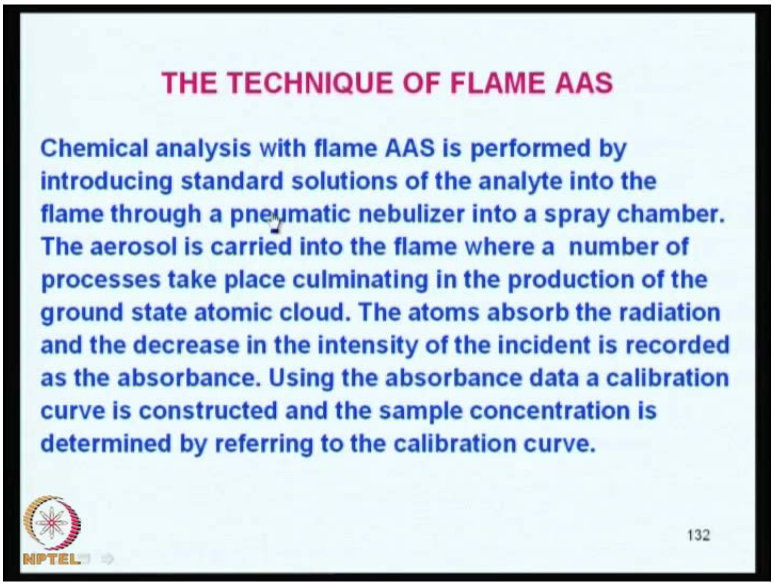

THE TECHNIQUE OF FLAME AAS

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.

So, first you have to prepare the standards and then you have to pass the samples through the pneumatic nebulizer into spray chamber. Then the aerosol is carried into the flame where a number of processes take place culminating in the production of ground state atomic cloud that is the essence of atomic absorption. The attempts absorb the radiation and the decrease in the intensity of the emitted radiation is recorded as the absorbance. So, using the absorbance data the calibration curve is to be prepared. And then you have to aspire the sample put it into the flame, and refer the absorbance data to calibration curve and find out what is concentration of the element corresponding to the absorbance what you have absorb it is just like spectrophotometer.

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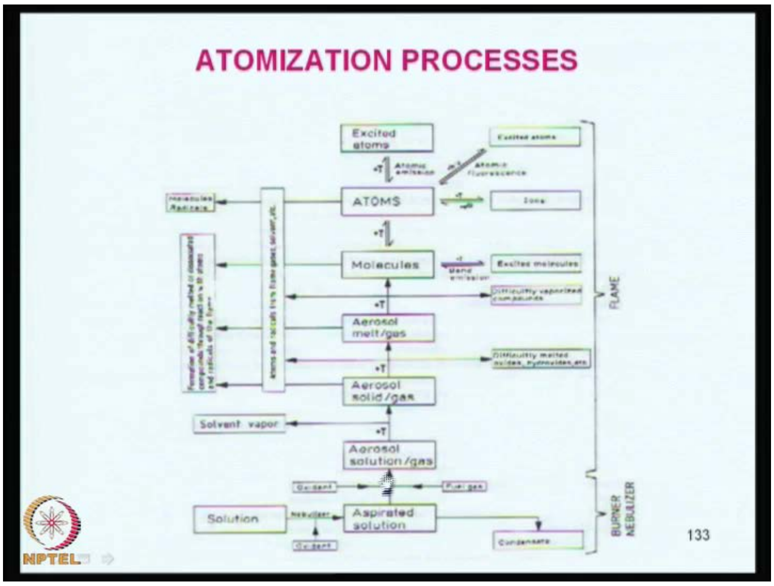

ATOMIZATION PROCESSES

Now, this is a presses I have prepared the difference stages of atomization and here we can see that here on this side I have put burner nebulizer and here I have put flame. The processes recorded on the left side of the burner in this area, corresponds to the nebulizer operations and in this area the processes are recorded with respect to flame when there sample enters the flame.

So, first of all you start aspiring the solution here, and then there are the aspire solution go gives you a small droplets and bigger droplets, smaller droplets get carried into the nebulizer and then it proceeds to the it forms an aerosol in between the bigger drop condense and get out they are collected and thrown out and the nebulizer. So, a sample solution also can be taken up which forms the aerosol and solution aerosol of a solution and gas. So, the oxidant gas is coming here, that is air and then fuel gas comes here. So, all these three are mixed to form the aerosol solution gas, and a flame region it enter the flame region. And as the temperature increases the solvent vaporizes and everything becomes aerosol gas.

And this liquid droplet becomes a solid that is all the solvent gets evaporated. At this stage what happens is the real chemistry starts. Sometimes it form they formed oxides hydroxides etcetera, in the flame these are difficultly melted they have a high ob melting point basically. So, sometimes they formation of different substances also can take place and then aerosol they as the temperature increases, the solid sullied melt and aerosol melt gas is formed an aerosol of the melt and the gas. And again we have substances which form very difficultly decomposed vaporized, because oxides and other things do not vaporizes. So, easily and there could be some substances which are not. So, which are more easily converted into different kinds of molecules?

So, that is also not of much use. So, after these the substances will decompose and it forms the molecules. The molecules can get excited to higher energy straight that is of to forming excited molecules these are of no use for AAS atomic absorption and then there could be attempts the molecules will decomposed into attempts. And if the attempts pickup electrons then they form ions here, in this form in this way and then they can also form molecules radicals' etcetera in the flame. So, this process is also useless and the formation of ions is not ideal for our requirement.

So, only the atoms we are interested. So, these atoms whatever remain they get ex they form the excited atoms and then the excited atoms can absorb the radiation. And sometime there is florescence also and that is of no use again. So, the whole process of atomic absorbance involves the aspiring the solution to form a aspirated solution aerosol solution gas mixture, and then aerosol solid gas mixture, and aerosol of melt and melt and the gas, and then these should decomposed for molecules, and from the molecules atom percentage forms the atoms, and these atoms get excited and if they start florescence again it is of no use. So, this is basically the atomization process.

So, you would see that a very small portion of the sample what you are aspirating forms the atoms remaining all goes waste, because it there of no direct concerned to the atomic absorption process.

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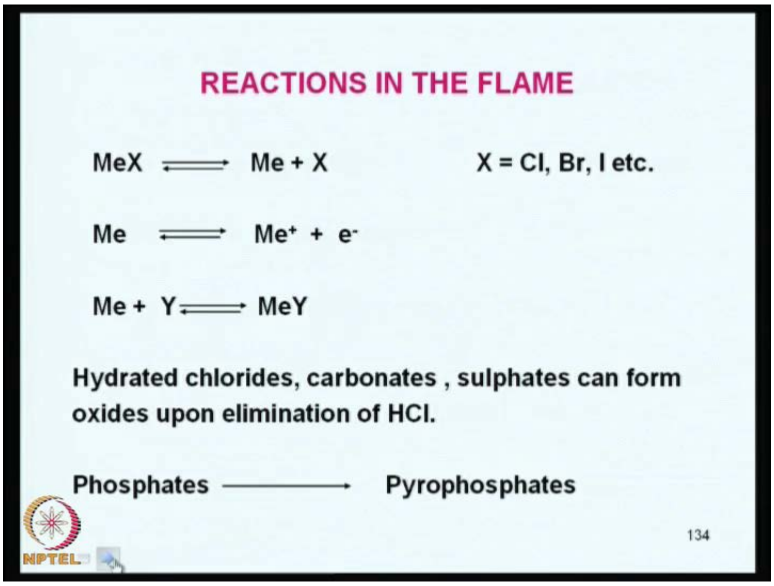

REACTIONS IN THE FLAME

$MeX \rightleftharpoons Me + X$ 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 ⟶ Pyrophosphates

So, you can see that number of reactions also can take place in the flame. For example, this slide I have written Me X that is metal halide and X is chloride, bromide, iodide some other salt. Basically that is what is dissolved in your sample solution; if you take a sample of copper dissolve in HCL it will form copper chloride. If you dissolve it in nitric acid it will form a metal nitric or if you do in the sulphuric acid it may form sulphides and the reaction in the flame is decomposition of the salts into metal and in salt. The metal gets excited to metal atoms ions. So, how does it happen? It happens by picking up by release in the electron this can this is known as ionization metal going to metal plaza positive charge releasing an electron or metal can also form another compound why react with another species to form metal m e y com type of salt this is of no use to us. So, hydrated chlorides, carbonates, sulphates etcetera they can form oxides also upon it is upon the elimination of HCL or sulphates carbonates when a high temperature. The solvent molecules and acid molecules when they go away what remains is only the metal salt it can decompose and react with oxygen and form carbonates oxides etcetera.

And phosphates can form pyrophosphates that are also another possibility. So, suppose you have basically phosphate salts they can form pyrophosphates. Now you would imagine that temperature of the flame would definitely have some important role in the volatilization of the salts, because as the temperature increases first metal salt has to decompose, and then for melt first it should melt then it should boil, and then it should decomposed and to constitute components after after wait thermal dissociation process of molecular molecules into atoms begins, before that it has to melt and then decompose then other process will start. This is a phase where non spectral interferences can occur, because the flame will have cyanogens CIH COO. So, many other radicals in the flame and variety of combustion products can also be present.

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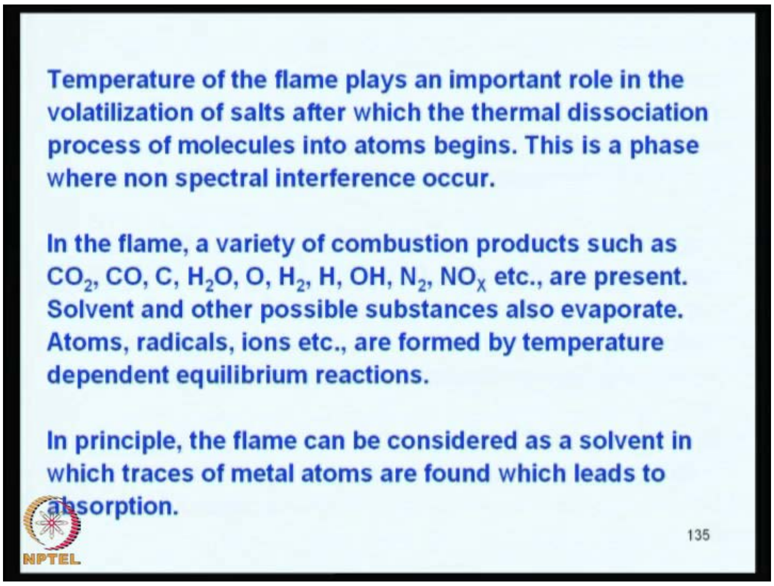

Temperature of the flame plays an important role in the volatilization of salts after which the thermal dissociation process of molecules into atoms begins. This is a phase where non spectral interference occur.

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.

For example, if you are passing acetylene and then air putting it into the flame variety of combination products such as carbon di oxide, carbon monoxide, simple carbon items, water vapor, oxygen, hydrogen, hydrogen ions atoms, OH radicals, OH atoms, nitrogen, NO nitric oxides, into 5 NO2, NO several types of nox compounds could be present. And then there will be solved also suppose you dissolve the sample in a in a solution and extracted into let us say methyl as. So, butyl ketone then the solvent also may will be there in your sample. So, the solvent and other possible substances also need to you operate and decompose forming atoms radicals' etcetera. They are formed by the temperature dependent equilibrium reaction; because most of the formations of such compounds are due to simple reactions, but their presence is govern presence.

And concentration also is governed by the residence time in the flame. Therefore, they are formed the equilibrium constant and other chemical kinetics of the reactions. Usually are formed by the temperature depended equilibrium reactions. In principle the flame can be consider as a solvent, in which tresses of metal atoms are formed which relates to atomic absorption. This is the essences of atomic absorptions. The flame is a solvent not in the general sense of a solvent what we consider, but it is a medium in which tresses of metal atoms are found which relates of the radiation pass through them.

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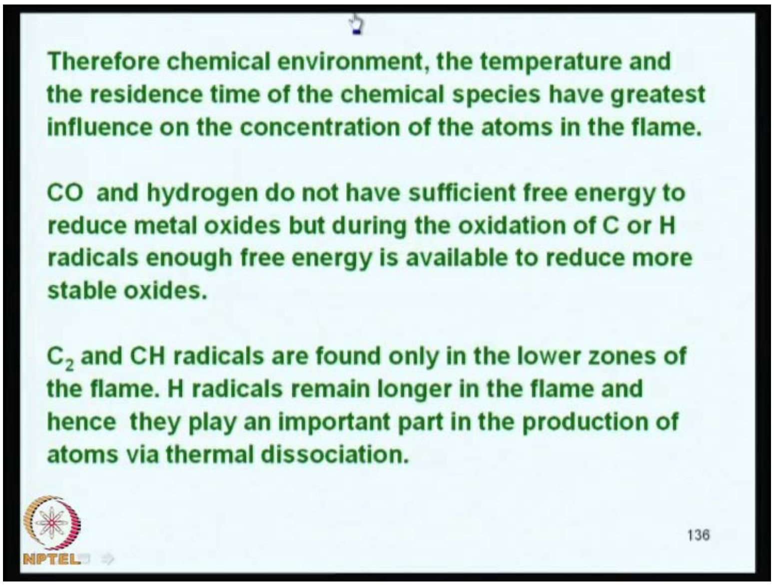

Therefore chemical environment, the temperature and the residence time of the chemical species have greatest influence on the concentration of the atoms in the flame.

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, the chemical environment of the temperature. The temperature and the residence time of the chemical species have greatest influence on the concentration of the atoms in the flame. This you have to understand, because all you are interested in atomic absorption is the concentration of atoms ground state atoms in the flame. So, the other components like this carbon monoxide and hydrogen, they do not have sufficient free energy to reduce metal oxides. You can look up the free energies of such species in a standard chemical tables in text books etcetera, and the amount of energy that is require to reduce metal oxides to metals is a very high and that much of energy is not supplied by the carbon monoxide and hydrogen etcetera. Therefore, a during the oxidation the res the energy released is only free energy is available to reduce more stable oxides.

So, the free energy released must be very high compared to the reduction energy compared to the energy require to reduce the stable oxides. So, c two and c h radicals are usually found in the lower zone of the flame. You remember that the flame as number of zones in which the lower zone which is not very high temperature medium zone and the diffusion zone etcetera who as discussed earlier. And I am referring to that figure than in the class about 3 or 4 classes before when we have discussed about these structure of the flame. And now I am referring to that figure if you remember that C 2 and CH radicals are found only in the lower zones of the flame, and hydrogen radical’s remains longer in the flame and therefore, they play an important part in the production of atoms, because one is through thermal dissociation and also hydrogen is a reducing agent.

So, most of the oxides that are formed they do get reduced to the metals where the presence of hydrogen atoms which have got a longer stain there is residence time of hydrogen in the flame is longer. Therefore, they are the active species which will decompose your metal oxides, because they reduce them.

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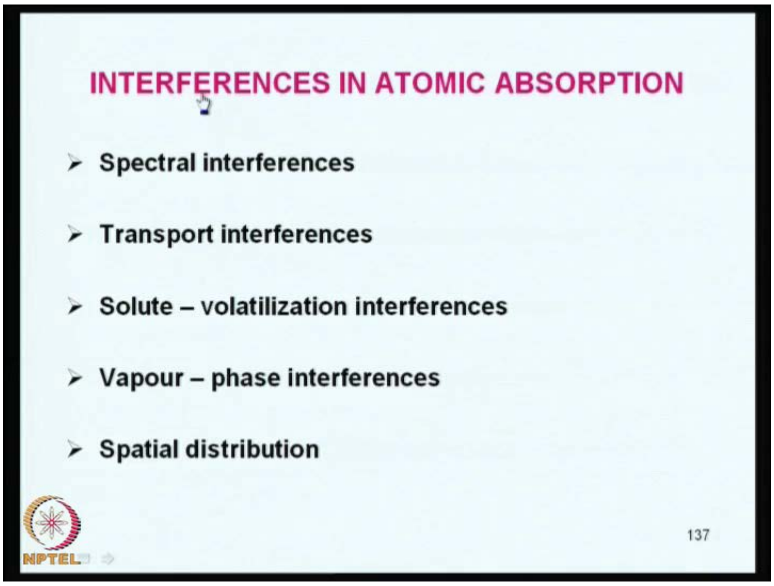

INTERFERENCES IN ATOMIC ABSORPTION

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

So, what are the types of interference? Now I am a now I am going to discuss with you the different types of interferences in atomic absorption, because all the while I have been saying that atomic absorption is the almost an ultimate technique, where the interferences is are minimal, and it is an element specific technique. The term element specific technique does not necessarily mean that there are no problems in the analysis there are. So, what are the types of inference? How does interference manifest in the determination of a metal. So, what I want trying to tell you is. So, long as you are measuring the absorbance of the sample using a standard and you get certain response reading 0.3 absorbance or 0.32 absorbance etcetera.

And you take your sample if they concentration is same as that of a standard it must show you the same absorbance like 0.3 or 0.32, but it does not and we call it interference of the method interference. So, the actual signal what you get is not exactly what is expected. Now what could be the reasons in spectrophotometry we have seen that interferences can occur due to formation of complexes.

And then association, dissociation, polymerization, PH effect, temperature effect, etcetera, but here in atomic absorption we have different kinds of inferences basically, because of the various processes that take place either during aspiration, during transport, during and during the residence, in the flame and also due to spectral aspects. So, we can consider the interferences in atomic absorption from their respective characteristics. For example, the first one I have put is spectral interference, and this could be due to your inability to separate this spectral line, if there are more than two substances which absorb at the same wave length there is nothing you can do about it, because you cannot change your renounce line, because it is the interning property of the element. And of course, you can always choose a second reference resonance line in atomic absorption, but the sensitivity goes down.

So, always you should choose the resonance line corresponding to the minimum energy. So, will discuss more about this shortly. So, there one part is spectral interference and another is transport interference, this is due to the transport of the sample and solvent etcetera. Then if you refer to the figure what I have shown you here, the solute and a other interferences formation of melts oxides etcetera. So, such interferences can also occur due to volatilization these are termed as volatilization interferences. Than you can have vapor phase interferences where the chemical species present in the flame, they can give you they can attend it the interferences and then spatial distribution.

That is height at which you absorb the signal that also can attend the signal to a considerable extended. So, will discuss these interferences slightly in more detail now, because these are all important one as to understand the basic the basic restriction that exit in the determination of the element.

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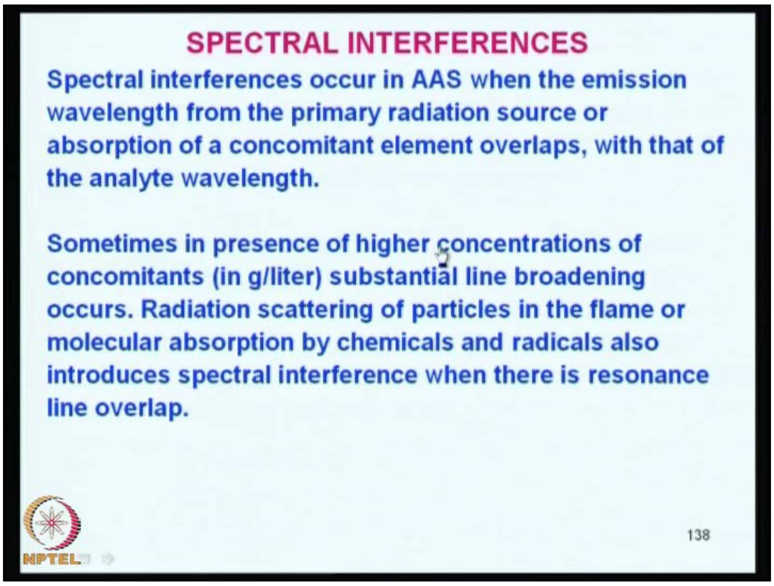

SPECTRAL INTERFERENCES

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.

For example, in the next slide I am going to show you that the spectral interferences in atomic absorption spectrometry occur. When the emission wave length from the primary radiation source or absorption from other element present in your sample the wave length of a measure maintain same, than there is spectral interference. So, some times in presence of higher concentrations for example, you want to determine gold in sea water. Gold in nano grams they all others salt are in grams per liter especially sodium chloride etcetera, and in urine small to thallium in urine you want to determine. Than the concentration of other salts are in grams per liter. Whereas, your analyte of interest is in nano grams or micro grams. So, substantial line broadening occurs. So, again the I have to remained you that line broadening means, the attenuation of the signal.

That means, you will get a lower absorbance value. So, sometimes radiation scattering of the practicals in the flame or molecular absorbance by chemicals and radicals also introduces spectral interference when there is resonance line over lap. For example, the resonance line very sharp, but the molecular bands are broad. So, part of the molecular absorbance usually gets measured along with the along with the spectral line. So, the such interference are also possible, because you cannot isolate only the spectral line from the analyte element from the other matrix elements that is not possible, because monochromator does not recognize an element, it just recognizes the wave length, if there is radiation in the wavelength, in the red there is radiation corresponding to the wave length. What you are measuring whatever is the source it will show you an enhancement if it is there if it is not there it will show you attenuation.

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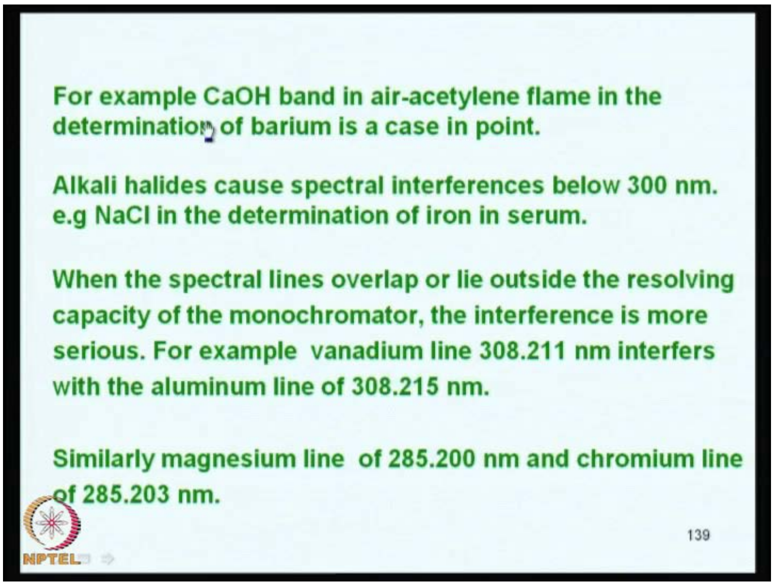

For example CaOH band in air-acetylene flame in the determination of barium is a case in point.

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.

For example, we can take a look at this calcium hydro oxide band in air acetylene flame indeed determination of barium there is calcium hydro oxides band CaOH and is broad and barium line atomic resonance line is very sharp, but there will be some amount of absorbance coming from calcium hydro oxide band when your measuring barium. So, the actual signal for barium increases, even though there is no barium so, but it does not happen all the time it happens only when there is calcium in the along with barium. And similarly, alkali halides causes spectral interference below 300 nano meter, in general this is a very general statement for example,

Sodium chloride if you want to determine iron sod iron in serum, sodium chloride is a constant spectral interferent. So, when the spectral line over lap or lie outside the resolving power of the monochromator. The interference more series, because it cannot differentiate and usually absorbance line, what we need the absorbance line plus or minus 0.005 nano meters. Now look at this example, of vanadium line this number is 308.211 for vanadium. And suppose you have aluminum in that aluminum along with vanadium and aluminum atoms also will absorb at 308.215 the difference between these two wave length is 0.004, but the your monochromator cannot differentiate between 0.30 8.211 or 308.215 till bunch all of them together and measure an absorbance. Similarly magnesium line and chromium line are having a difference of less than 0.005 nano meter see here 200 -203 which will give you these spectral interference,

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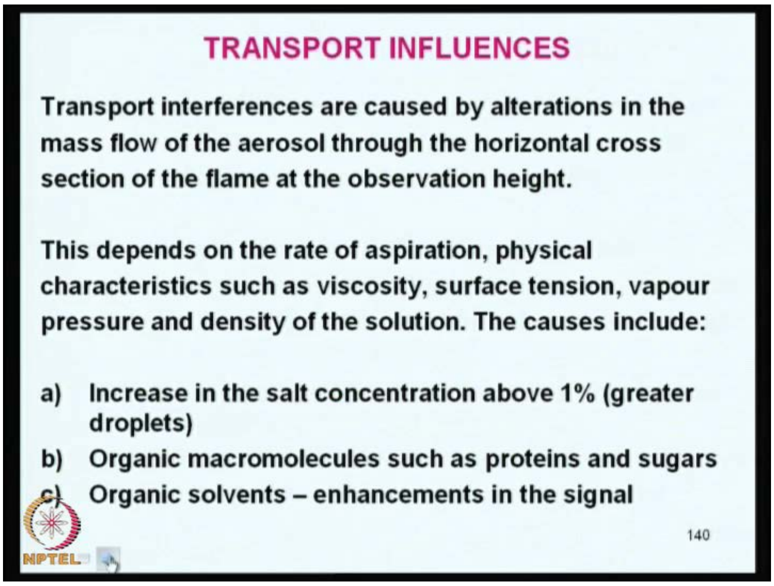

TRANSPORT INFLUENCES

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**

because the monochromator cannot handled this. Sometimes I have also told you that transporting infer influence. These transport interferences are caused by the alterations in the mass flow of the aerosol through the horizontal cross section of the flame, at the absorption height. This depends on the rate of aspiration physical characteristic such as viscosity, surface tension, vapor pressure, and density of the solution etcetera.

So, the causes usually include increase in the salt concentration above 1 percent and for example, if you the salt in sea water is 3.5 in urine it is about more than 1 percent, in plasma it is more than 1 percent. In several other element aligning metallurgical analysis the salt concentration could be much higher, and the result is they form greater drop droplets and reduce the number of atoms formed which is actually measure therefore, there will be attenuation of the signal; that means, we will get lower absorbance value sometimes you may have organic macromolecules such as protein and sugars. And these also will influence your these also will influence your absorbance.

So, organic solvents usually burn in the flame is not it organic solvents. When you are introducing along with equest they burn in the flame and most of the organic solvents burn with exothermic characteristic; that means, when they burn they give out more heat. So, the flame temperature itself will increase the number of atoms in the ground state we have seen in the introductory part of atomic absorption that as the temperature increases number of free items also increase. And this leads to an enhancement of the signal we can take it either as a positive or as a negative. Suppose you want to determine the element in a given matrix a solvent and you can an organic solvent present without without your knowledge can lead to enhance the signal that is higher absorbance.

Sometimes what you want to do is you want to increase the detection limits to still better values; that means, you want to work at very low concentration. Than you can even add additional additionally organic solvents to increase the flame temperature, and produce the atoms. So, the interference is either way it can be use for constructive as well as non constructive purposes. So, if the matrix is fixed then the interference is delete areas, if the matrix is not fixed you want to develop a method than you may like to deliberately add and give you get the higher absorbance for the same solution; that means, improve the sensitivity.

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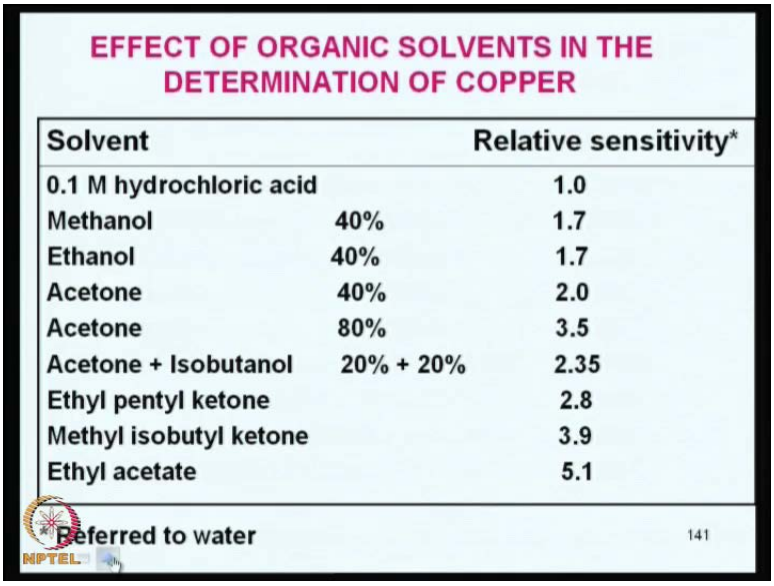

EFFECT OF ORGANIC SOLVENTS IN THE DETERMINATION OF COPPER

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, you can take a look in this table, which this is for the determination of copper. Suppose you determine in 0.1 molar hydrochloric acid assume that this is a relative sensitivity is one some value I call it relative sensitivity. Suppose you add 40 percent methanol to the same solution you will get 1.7 times higher absorbance than 0.1 molar hydrochloric acid. Suppose you take acetone 40 percent than you will get twice the signal is twice the absorbance value would be twice that. And suppose you do it increase the acetone concentration to 80 percent instead of 40 percent, than the signal get enhanced 3.5 times that is 350 times all, because the solve this solvents burn with exothermic energy increasing the temperature of the flame and subsequently increasing the atomic population which will result in an enhanced absorbance signal that is nice, because you can determine improve the sensitivity go to still aware concentration.

Suppose you take ethyl pentyl ketone than the signal enhancement around 2.8. Suppose you take methyl isobutyl ketone than the signal is 3.9, but look at the last figure ethyl acetate it is 5.1; that means, 5 times the signal you will get for the same element if you ads these organic solvents to the system you can do it by at the calibration stage itself or we can do it while preparing the solution.

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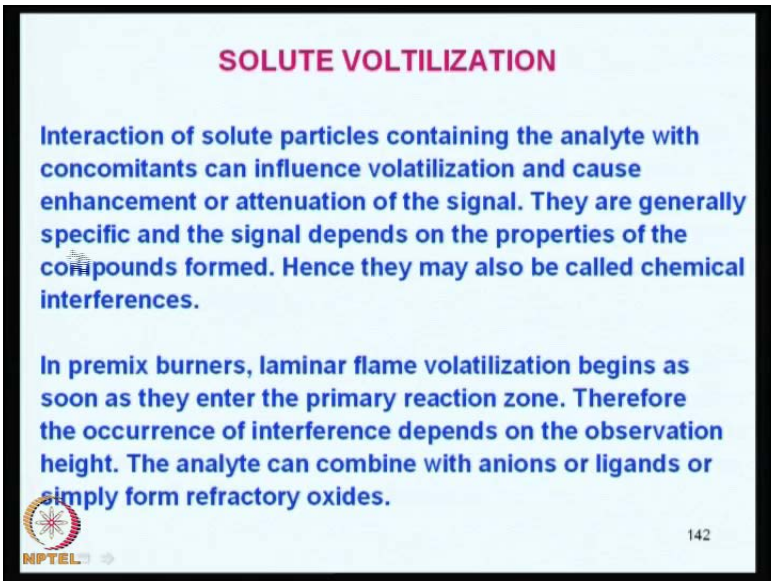

SOLUTE VOLTILIZATION

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.

So, now we look at another aspect of solute volatilization. You remember I talked about the formation of oxides the solute part of the sample that is used for aspiration it may form oxides instead of decomposing it into atoms, because air is generally for an oxidizer. So, there are several elements of the periodic table, which form referentially oxides and hydro oxides, when they are mixed with water and at high temperatures. So, the they are generally specific and the signal depends upon the properties of the compounds formed. Suppose your hydroxides melts at very high temperature or oxide melts at very temperature then the production of atoms would be affected adversely.

So, this type of interference can be called as chemical interference. In premix burners laminar flame volatilization laminar flame laminar flame volatilization begins as soon as they enter the primary reaction zone. Therefore, the occurrence of interference also depends on the observation height. So, wave the analyte can combine with anions or legends or simply form refractory oxides.

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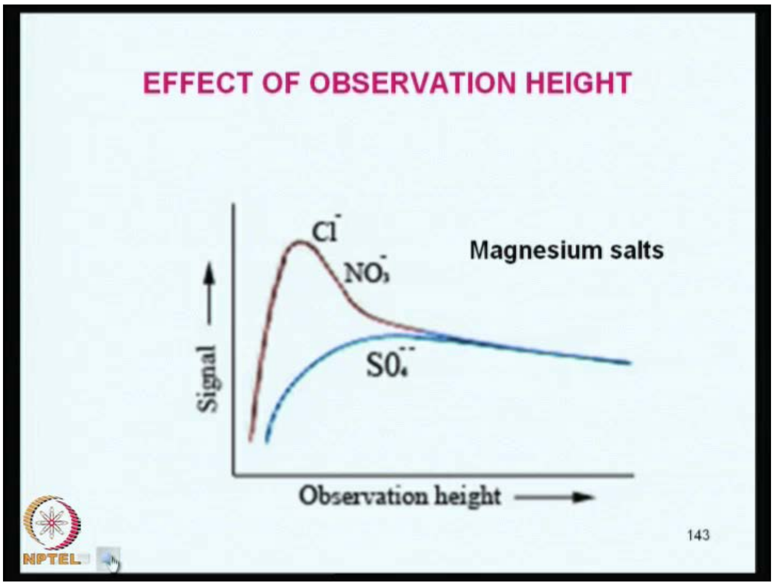

EFFECT OF OBSERVATION HEIGHT

Now, I have a slide for this which shows you the effect of observation of height on the determination of magnesium salts. Here we can see that this is the observation height and this is the signal. So, when the observation height is very small the signal is also a small; that means, if you allow the optical radiation to pass at this height then the signal is very small. If we increase the observation height let us say it 2 meter, 2 centimeter, 3 centimeter, 5 centimeter etcetera, then you will get maximum absorbance for sulphide somewhere around these region. Suppose you increase the height still further the atoms many other concomitant processes of the flame take place and the signal decreases, because it no longer the high temperature zone where the atom population is substantial.

Suppose you have chloride instead of sulphide than what happens look at this figure the observation height is a for optimum chloride signal is smaller than the observation height for nitrate as sulphide is not it. For sulphide optimum observation height is this much from here to here, were as pro chloride optimum height observation height is only one third of that this for magnesium salt actually, what I have done in this experiment is a taken sulphide and then you taken chlorides and nitrides and observe and measure the observance at let us say 1 centimeter, 2 centimeter, 3 centimeter, 5 centimeter height and recorded at the observance. So, the flame height where you make the observation depends upon the salts also.

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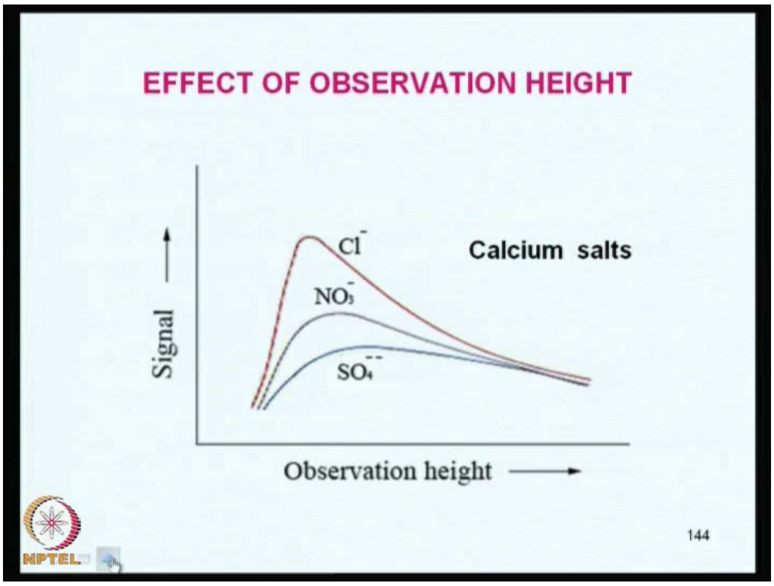

EFFECT OF OBSERVATION HEIGHT

And suppose you do the same thing with calcium salts again you have a similar, process taking place sulphide is lower it is optimum height is longer larger than that of nitrite and which is still smaller than the chloride. So, observation height is the one which determines the solute volatilization effects. So, the I am coming back to solute volatilization effect, I was giving you only an example of this. So, the oxides of group 3 and 4 of the periodic table they form polymers structures and they decompose more difficultly. So, we will discuss about these things in the next class an in more detail.