Modern Instrumental Methods of Analysis

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Lecture No. # 25

Atomic Absorption Spectrometry-9

Cold Vapour Mercury AAS

Now, our discussion on the chemical interferences of the determination of mercury using cold vapour technique.

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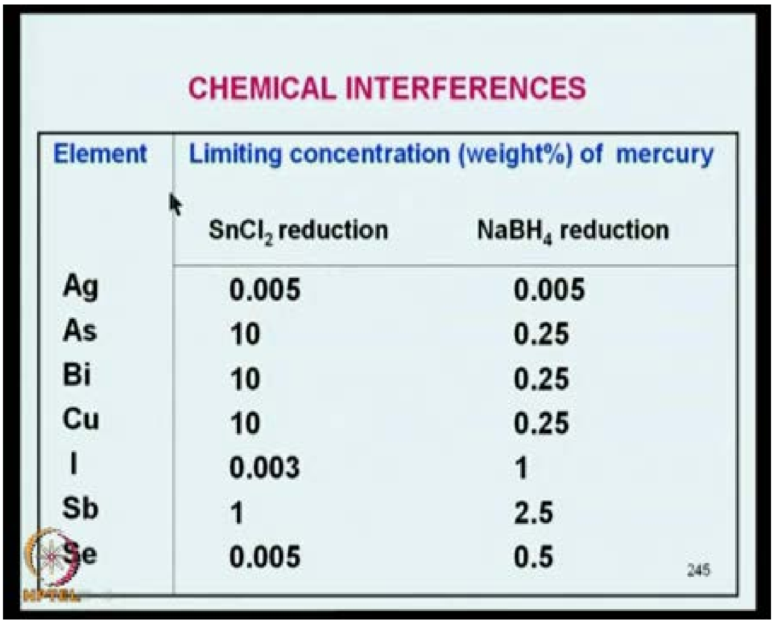

CHEMICAL INTERFERENCES

Element	Limiting concentration (weight%) of mercury	
	$SnCl_2$ reduction	$NaBH_4$ reduction
Ag	0.005	0.005
As	10	0.25
Bi	10	0.25
Cu	10	0.25
I	0.003	1
Sb	1	2.5
Se	0.005	0.5

I had shown you this slide about the chemical interferences in the last class; that is, silver, arsenic, bismuth, copper, iodide, antimony and selenium. If you use stannous chloride reduction and sodium borohydride reduction, the figures are fairly comparable, but you would see that the interference levels in sodium borohydride are much less here.

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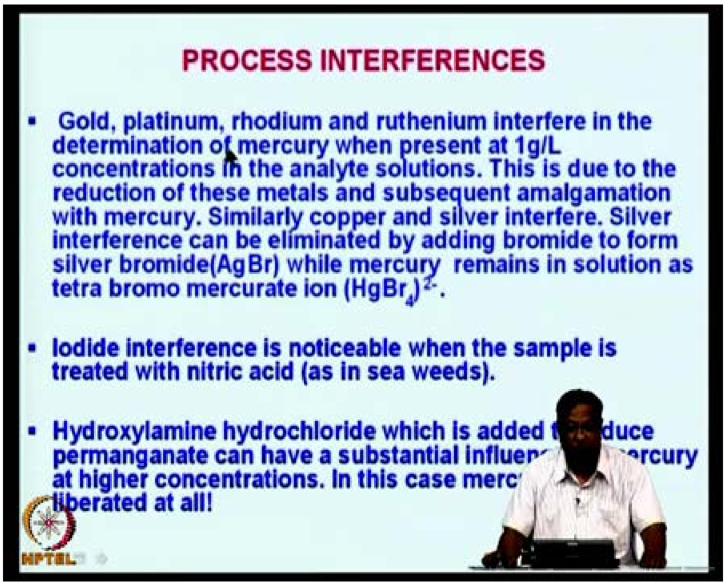

PROCESS INTERFERENCES

- Gold, platinum, rhodium and ruthenium interfere in the determination of mercury when present at 1g/L concentrations in the analyte solutions. This is due to the reduction of these metals and subsequent amalgamation with mercury. Similarly copper and silver interfere. Silver interference can be eliminated by adding bromide to form silver bromide(AgBr) while mercury remains in solution as tetra bromo mercurate ion $(HgBr_4)^{2-}$.
- Iodide interference is noticeable when the sample is treated with nitric acid (as in sea weeds).
- Hydroxylamine hydrochloride which is added t duce permanganate can have a substantial influen ercury at higher concentrations. In this case merc liberated at all!

And we had also discussed about the process interferences; that is, gold, platinum, rhodium, ruthenium, etcetera, they interfere in the determination of mercury, when present at 1g/l concentrations in the analyte solutions. This is due to the reduction of these metals and subsequent amalgamation with mercury; therefore, available mercury concentration decreases.

Similarly, copper and silver interfere. Silver interference can be eliminated by adding bromide to form insoluble silver bromide, while mercury remains in solution as tetra bromo mercurate ion. Ios Iodide interference is also noticeable, when the sample is treated with nitric acid, as if you this problem will be more noticeable, when you want to determine mercury in the sea weeds, because in sea weeds, iodide concentration is quite high.

So, hydroxylamine hydrochloride which is added to reduce permanganate can also have a some sort of a influence - substantial influence - on the mercury determination of mercury at higher concentrations. In this case, mercury is not detected at all.

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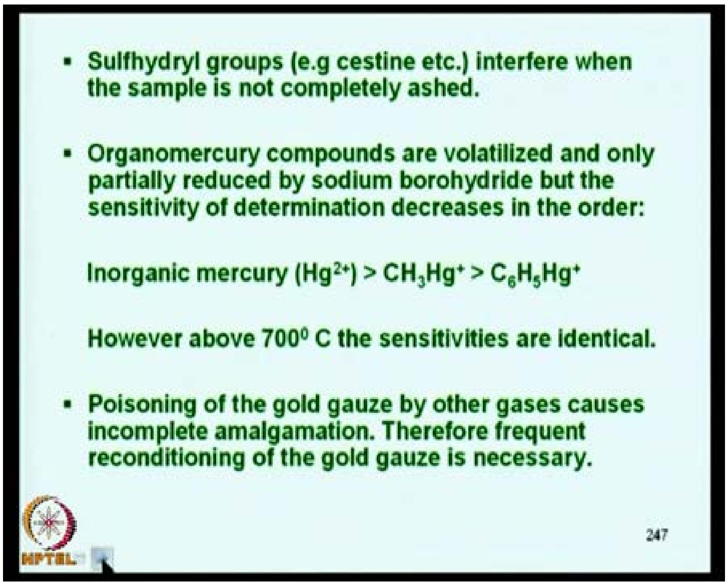

- **Sulfhydryl groups (e.g cestine etc.) interfere when the sample is not completely ashed.**
- **Organomercury compounds are volatilized and only partially reduced by sodium borohydride but the sensitivity of determination decreases in the order:**

  Inorganic mercury (Hg^{2+}) > CH_3Hg^+ > $C_6H_5Hg^+$

  However above 700^0 C the sensitivities are identical.
- **Poisoning of the gold gauze by other gases causes incomplete amalgamation. Therefore frequent reconditioning of the gold gauze is necessary.**

So, we will have to be careful regarding the chemicals present in the process matrix. Similarly, if you take a look at sulfhydryl groups present in the sample, they also interfere when the sample is not completely ashed.

Organomercury compounds are usually volatilized and only partially reduced by sodium borohydride, but the sensitivity of determination decreases in the order: inorganic mercury gives maximum sensitivity, and methyl mercury - that is mercurous ion - reduces is slightly much lower than that, and phenyl mercury is still less reacting; that means, it gives you a signal which is much less than inorganic mercury of the same concentration. However, above 700 degree centigrade, the sensitivities are identical, because in around 700 degree centigrade, both the all the organic components generally get converted into carbon dioxide and water, and only inorganic species would be present around this temperature.

So, the other problem associated with the cold vapour mercury are the poisoning of the gold gauze by other gases and that causes incomplete amalgamation; therefore, you will have to frequently recondition the gold gauze.

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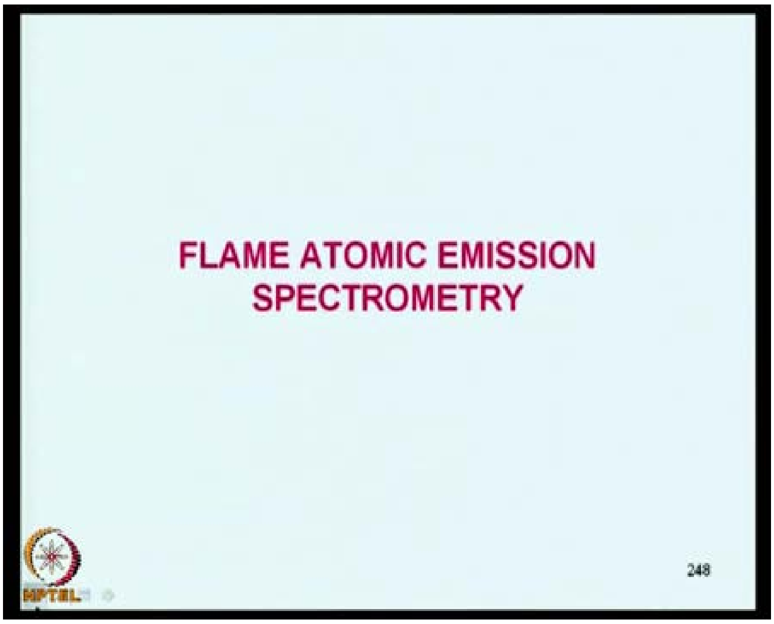

FLAME ATOMIC EMISSION SPECTROMETRY

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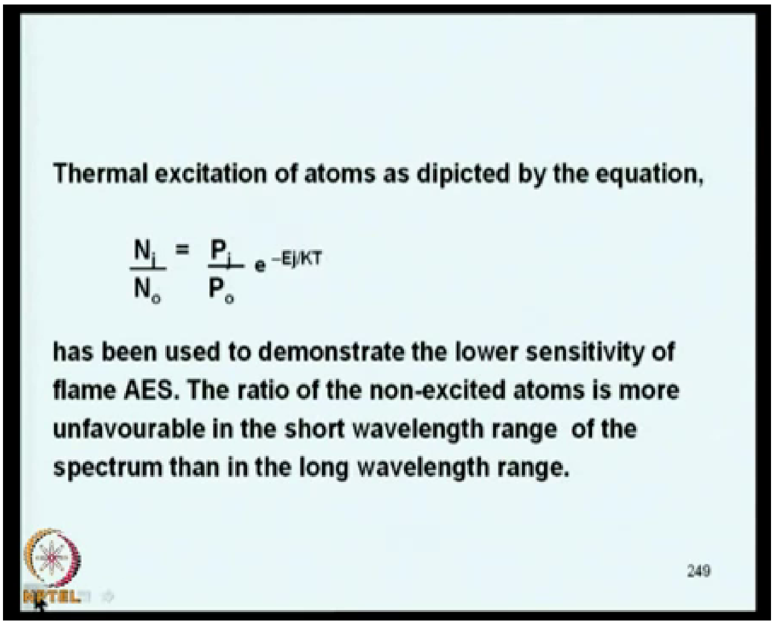

Thermal excitation of atoms as dipicted by the equation,

$$\frac{N_j}{N_o} = \frac{P_j}{P_o} e^{-Ej/KT}$$

has been used to demonstrate the lower sensitivity of flame AES. The ratio of the non-excited atoms is more unfavourable in the short wavelength range of the spectrum than in the long wavelength range.

That completes our discussion on the cold vapour mercury, which is essentially an accessory for atomic absorption spectrometry. Now, we will turn to another aspect of flame atomic emission spectrometry. Now, why I have included this topic at this stage is, earlier we had discussed about florescence and florescence analysis, and x-ray emission.

Now, I am introducing flame atomic emission spectrometry, which is almost similar to atomic absorption in terms of instrumentation, but you will have to remember that flame atomic absorption flame atomic emission spectrometry known was discovered and known since 1900. Since that time, flame atomic emission spectrometry has been used for the determination of alkali and alkaline earth metals like, sodium, potassium, lithium, strontium, etcetera.

Now, the reason to introduce flame atomic emission spectrometry at this stage along with atomic absorption is that, most of the atomic absorption instruments have a provision to perform flame at emission at the flick of a bottom. Even though flame atomic emission spectrometry can itself be is a separate technique, not necessarily connected with atomic absorption, but almost all commercial atomic absorption spectrometers available in the market today, give you an option to perform flame atomic emission.

Now, why is flame atomic emission is important? Because you will have to imagine several situations, where sodium determination is very very essential; it is required in the analysis of seawater, body fluids, soils, plants, and then in chemicals and several other samples, where the determination of sodium, potassium, lithium, etcetera become very important and routine. So, routinely in body fluids, sodium is determined and the other elements are also determined like potassium, etcetera. And I want to introduce this flame atomic emission to you at this stage, because we can combine flame atomic emission as well as atomic absorption into 1 unit; even though separate instruments for flame atomic emission are available, there not as costly as atomic absorption spectrometers, but it is the principles remains the same, except that, in flame in atomic absorption, the system is the principle is atomic absorption, but in flame emission, the system is emission phenomenon.

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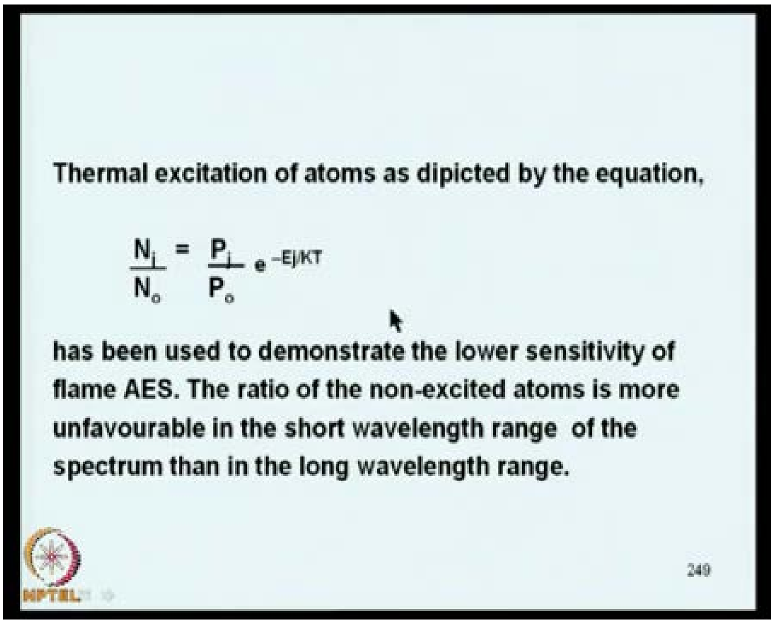

Thermal excitation of atoms as dipicted by the equation,

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has been used to demonstrate the lower sensitivity of flame AES. The ratio of the non-excited atoms is more unfavourable in the short wavelength range of the spectrum than in the long wavelength range.

So, I want to take you back to our discussion on the thermal excitation of the atoms, as depicted by the equation, when we are studying the atomic absorptions spectrometry. There we had described this equation, N j by N 0 should be equal to P j by P 0 into e to the power of minus E j by KT, where N j and N 0 are the number of atoms at the excited state and ground state, P j by P 0 is the probability statistical weights, and E j is the energy difference, and K is the boltzmann constant and T is the temperature.

This equation has been used to demonstrate the lower sensitivity of the flame AES. We had said that, the mini elements cannot be determined by atomic absorption because the by atomic emission, because the concentrations of the atoms at higher temperature - at this prevailing temperatures - are not enough to excite all the atoms and get significant atomic emission data. So, the ratio of the non excited atoms is more unfavorable in the short wavelength range of the spectrum than in the long wavelength range; this also we had discussed earlier.

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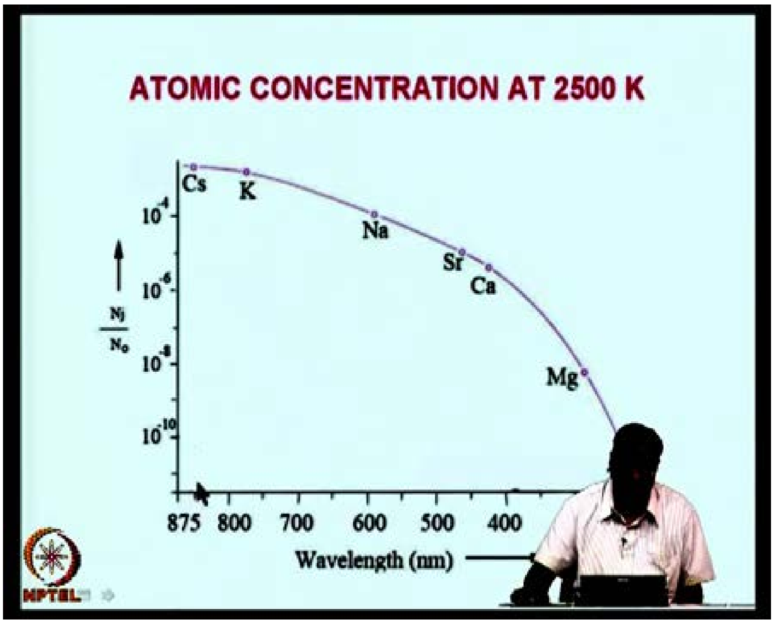

ATOMIC CONCENTRATION AT 2500 K

Now, if you take a look at this figure, you can see that, around I have plotted here, the wavelength 875, 800, 700, etcetera going up-to 200 nanometers, and N j by N 0, that is the ratio of the exited atoms to the ground state atoms. Now, you can see here that, Cesium alkaline alkali metal is having highest concentration at 875 nanometers; and then, concentration keeps on decreasing, and Na is somewhere around 10 raise to 3 or something, and then Sr are around 10 raise to minus 6; Ca would be around this much around 10 raise to minus 6; but if you come to Mg, that is, alkaline earth elements, these Sc, Ca, Mg, etcetera, the concentrations are of the order of about 10 raise to minus 8 for Hg. And Zn is almost of the order of about 10 raise to minus 15; that means, the 1 in 10 raise to 15 atoms would be in the ground state at this stage. So, the atomic emission is almost ruled out with respect to this equation using this equation.

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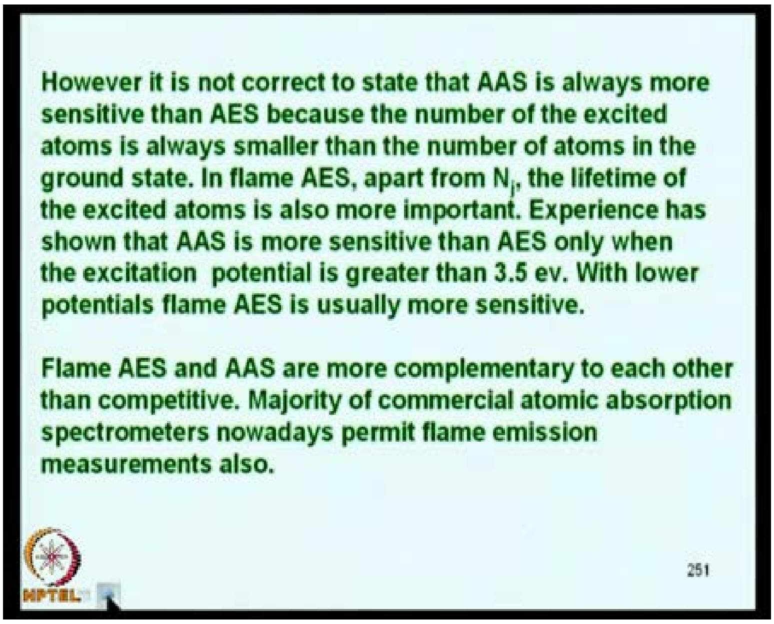

However it is not correct to state that AAS is always more sensitive than AES because the number of the excited atoms is always smaller than the number of atoms in the ground state. In flame AES, apart from N_j, the lifetime of the excited atoms is also more important. Experience has shown that AAS is more sensitive than AES only when the excitation potential is greater than 3.5 ev. With lower potentials flame AES is usually more sensitive.

Flame AES and AAS are more complementary to each other than competitive. Majority of commercial atomic absorption spectrometers nowadays permit flame emission measurements also.

However, it is not correct to state that, atomic absorption is always more sensitive than atomic emission spectrometry. AAS is always more sensitive than AES; this statement is made quite often; and that is not really correct, because the number of the excited atoms is always smaller than the number of atoms in the ground state. This is the basic premise that we work. But what happens is, in flame AES - atomic emissions spectrometry, apart from N j, that is exited atoms, the life time of the excited atoms is also more important; the atom should be in the excited state, but they also should be residing at the higher energy state for longer time. So, that aspect is not taken care of in the previous equation, that is, in this equation, the life time term does not appear.

So, apart from N j, the life time of the excited atoms is also more important. Experience has shown, that atomic absorption spectrometry is more sensitive than atomic emission, only when the excitation potential is greater than 3.5 electron volts. With lower electron potentials, electrode potentials flame atomic emission is usually more sensitive.

So, flame AES and atomic absorption are in a way complementary to each other than competitive. Majority of the commercial atomic absorption, as I have already told you a nowadays permit flame emission measurements also, because apart from the instrumentation, sources, nebulization and several other aspects of atomic absorption are common in atomic emission also.

So, flame emission spectrometry has been in use since 1900; this I have already told you. Combustion flames provide a means of converting the analytes into vapor forms, by supplying the energy necessary to promote the electrons from the ground state to the excited state. The intensity of the radiation emitted by these exited states while returning to the ground state, provides the basis of flame atomic emissions spectrometry. So, what are the basic components then and of the flames spectrophotometry?

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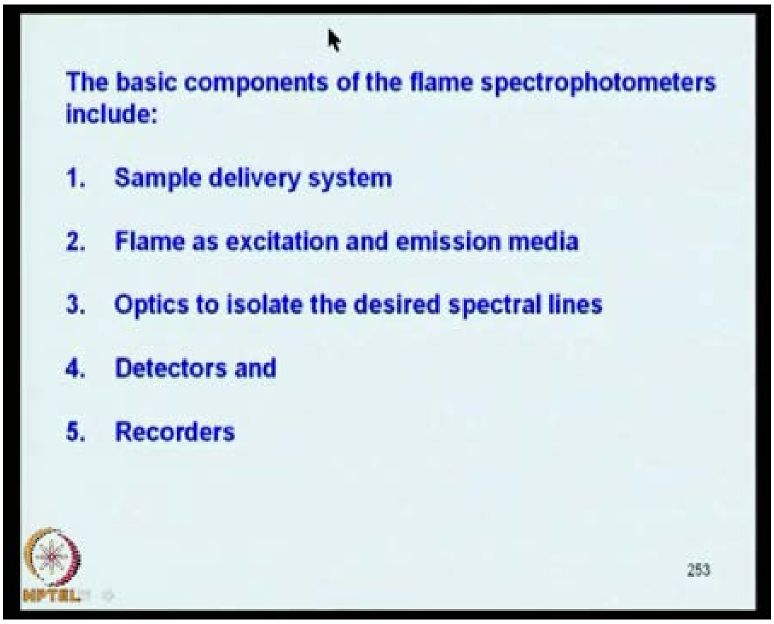

The basic components of the flame spectrophotometers include:

1. Sample delivery system
2. Flame as excitation and emission media
3. Optics to isolate the desired spectral lines
4. Detectors and
5. Recorders

Now, take a look at this slide that is in this slide. I would like you to compare the instrumentation common, for example, sample delivery system is almost similar in flame atomic emission as well as in atomic absorption. So, and flame also serve as excitation and emission medium. Optics, you need to isolate the desired spectral lines; these are also readily available in atomic absorption. And you need to use the detectors and recorders, etcetera, these are also quite common in flame atomic emission.

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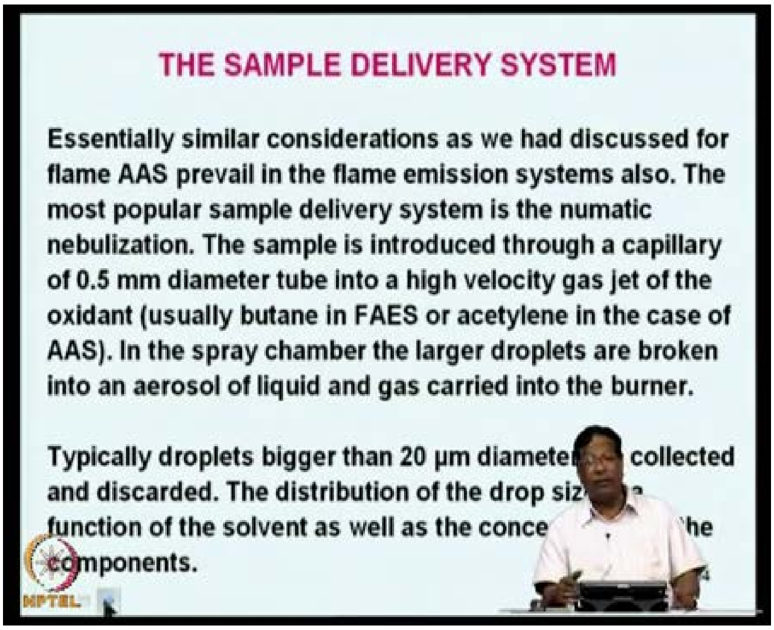

THE SAMPLE DELIVERY SYSTEM

Essentially similar considerations as we had discussed for flame AAS prevail in the flame emission systems also. The most popular sample delivery system is the numatic nebulization. The sample is introduced through a capillary of 0.5 mm diameter tube into a high velocity gas jet of the oxidant (usually butane in FAES or acetylene in the case of AAS). In the spray chamber the larger droplets are broken into an aerosol of liquid and gas carried into the burner.

Typically droplets bigger than 20 μm diamete collected and discarded. The distribution of the drop siz function of the solvent as well as the conce he components.

Now, let us take a look at the sample delivery system. Essentially similar considerations as we had discussed for the flame atomic absorption prevail in the flame emission system also. The most popular sample delivery system remains the numatic mode - numatic nebulization. And the sample is introduced as usual through a small capillary; take a beaker like this, take a beaker like this and introduce a small capillary, suck the sample into the nebulizer, where the liquid sample is broken down into smaller components and then it will be introduced into the flame.

So, the sample is introduced through a capillary tube of about 0.5 mm diameter, same as in atomic absorption. And the flame is produced by the use of air acetylene in the case of atomic absorption; but in flame, you can use ordinary butane glass, that is, what you use in the kitchens, the same gas can be used directly for flame atomic emission. In atomic absorption instruments, usually butane gas is not use, but in dedicated flame emission spectrometers, butane gas can be used very conveniently. There are certain differences in the design of the burners, when you use the butane, but otherwise, air acetylene is very fine with respect to atomic emission with of the alkali and alkaline earth metals.

So, in the spray chamber, the larger droplets are as usual broken down into very small droplets, and the gas in aerosol is formed and the gas is carried into the burner. Typically, droplets of 20 micro meters diameter are collected and discarded, that is wasted; you do not there not in introduced into the flame. And even if there introduced, they will cool down the flame temperature; so, that is not desirable also. So, we discard the droplets having more than 20 micro meters and the distribution of the drop size is basically a function of the solvent as well as the concentration of the components analyte.

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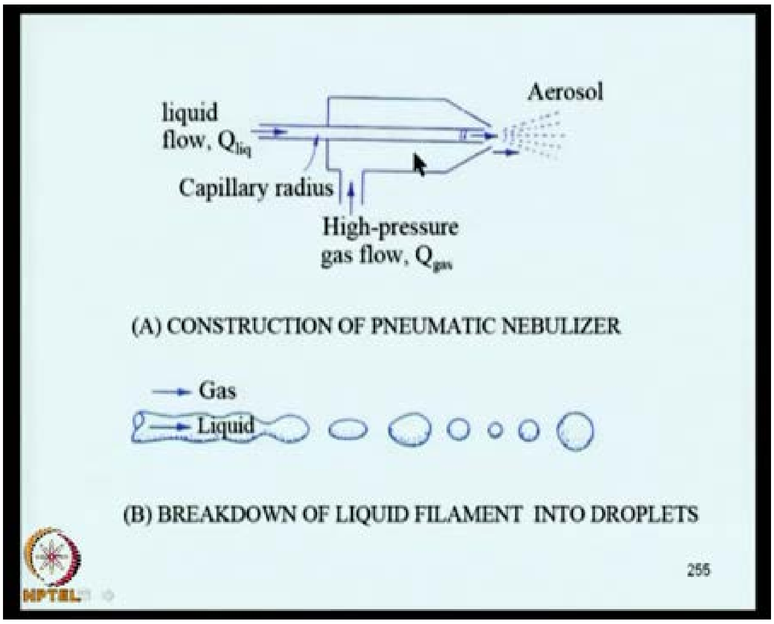

(A) CONSTRUCTION OF PNEUMATIC NEBULIZER

(B) BREAKDOWN OF LIQUID FILAMENT INTO DROPLETS

So, you can see here, I have drawn a simple burner construction of a pneumatic nebulizer I am showing here; the liquid is flowing through this and high pressure gas from a butane cylinder or something like that can be mixed; and both are allowed through an annular space, which immediately forms an aerosol. This is a very standard technique and very simple also; you do not have to do lot of engineering to arrange this type of sample delivery system. So, what happens is that, basically gas and liquids, liquid is flowing in a continuous system, and gas is coming out and it breaks down into smaller droplets, and liquid basically first it forms a liquid filament and then breaks into smaller droplets.

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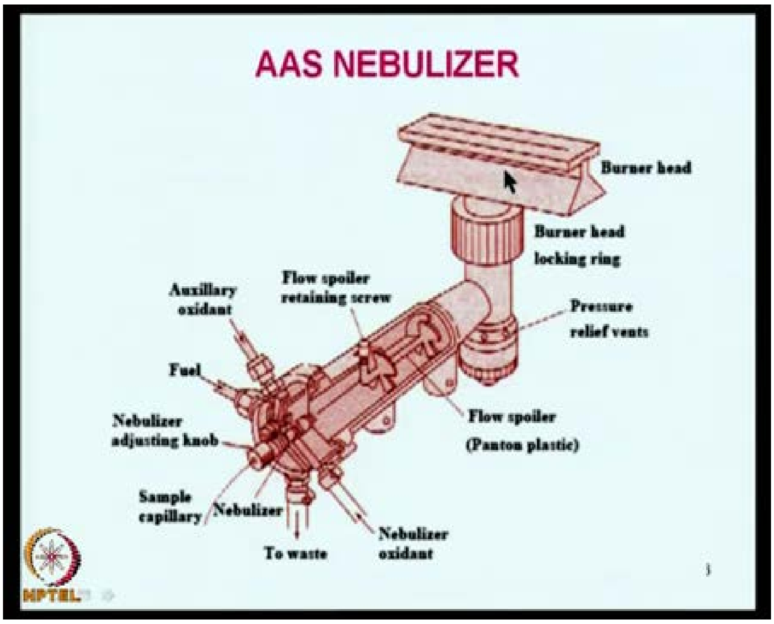

AAS NEBULIZER

Now, in atomic absorption nebulizer is slightly more complicated, but the principle remains the same; for example, this is for an atomic absorption nebulizer, here you have the capillary tube - this one sample capillary - and through a small teflon disc, the sample is introduced and let out into a chamber, where flow spoilers are there and fixed on a retaining screw. Fuel enters from here; auxiliary oxidant like air or nitrous oxide enters here, and then the bigger droplets fall down in this range, in this area. And here, you can adjust the screw to such an extent that, you get a satisfactory drop size, continuous aerosol of the specific quality. And then, you can introduce flow spoiler or even a small plastic bead, to reduce the flow and to reduce the particle size - aerosol size. And then, you can have pressure relief walls, and burner head and locking ring, which will open into the atomic absorption flame unit. This is slightly more complicated, but in dedicated instruments, you do not need so much of sophistication, because it is there in atomic absorption, we use that.

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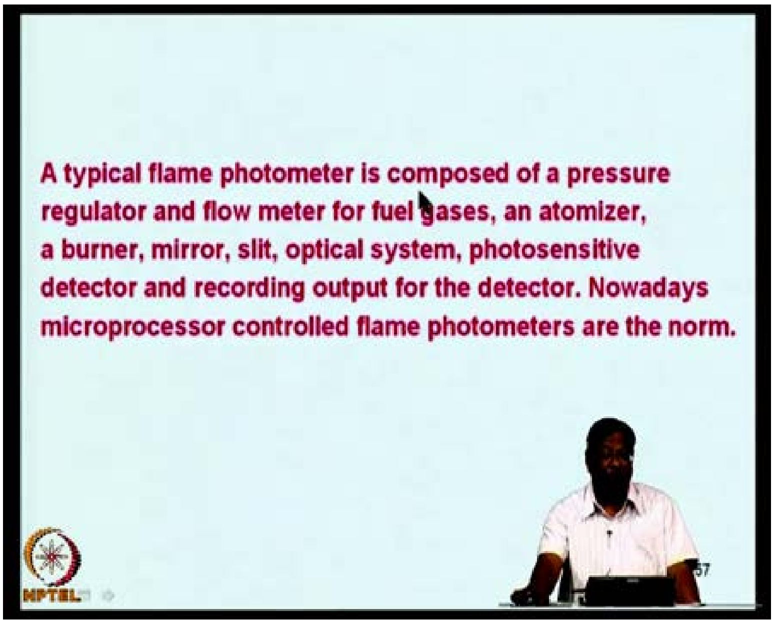

A typical flame photometer is composed of a pressure regulator and flow meter for fuel gases, an atomizer, a burner, mirror, slit, optical system, photosensitive detector and recording output for the detector. Nowadays microprocessor controlled flame photometers are the norm.

So, a typical flame photometer is composed of a pressure regulator, that is, I know I am talking about the dedicated flame photometers. So, it it has a pressure regulator, flow meter for the fuel gases, you need an atomizer, a burner, mirror and slits, optical systems to choose the wavelength of emission, and photosensitive detectors and recording output for the detector.

Nowadays, micro pressure control instruments are also available in the market and they are the norm. So, that will relieve you of the some of the routine statistical evaluation, that will take the averages and things like that.

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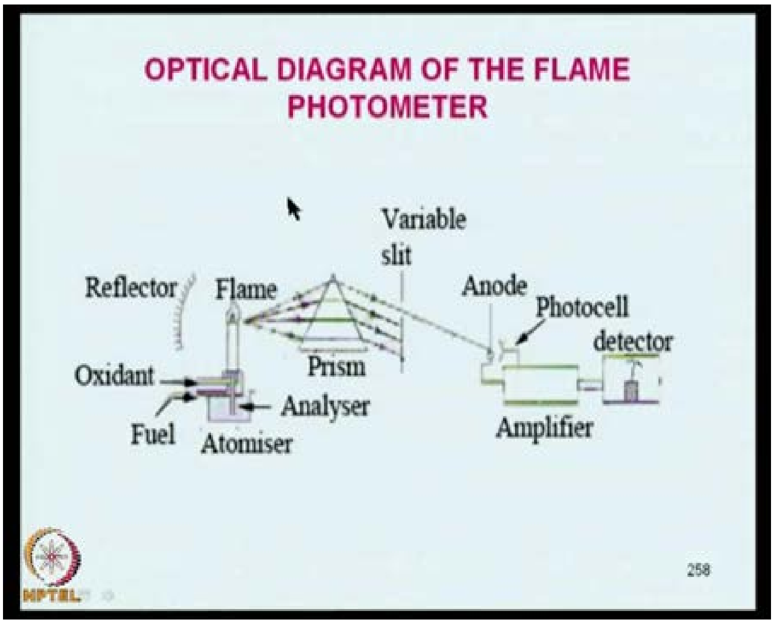

OPTICAL DIAGRAM OF THE FLAME PHOTOMETER

If you take look at the optical diagram of the flame, look here, I have put here the typical optical diagram and here is our nebulizer, fuel oxidant and analyzer, sample is taken up here and there is a flame here; into the flame, I am introducing the sample. So, I put a reflector here at the back and the reflector concentrates the radiations. And here, I have a prism and a variable slit, so that I can choose the wavelength what I need; it will be different for sodium, lithium, potassium, etcetera. And then, I have a photocell; the beam is made to fall on the photocell, where there is anode, photocell, detector, amplifier, etcetera; a very simple optical arrangement.

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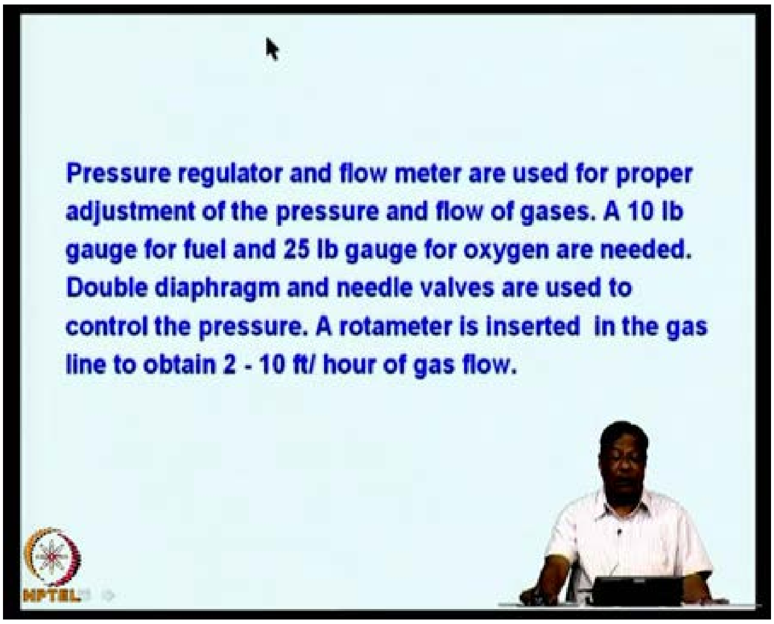

Pressure regulator and flow meter are used for proper adjustment of the pressure and flow of gases. A 10 lb gauge for fuel and 25 lb gauge for oxygen are needed. Double diaphragm and needle valves are used to control the pressure. A rotameter is inserted in the gas line to obtain 2 - 10 ft/ hour of gas flow.

And the only thing I would like to add now is that pressure regulator and the flow meter are used for proper adjustment of the pressure and flow of gases. A 10 lb gauge for fuel is required and 25 lb gauge for oxygen are needed. So, double diaphragm and needle valves are essential to control the pressure. A rotameter is also necessary to determine the flow rate of the gases. And the gas line should have the rotameter fixed on somewhere in between, through which the gas will be flowing at the rate of about 2 to 10 feet per hour. And if we have this kind of arrangement, then we can take a look at the flame requirements.

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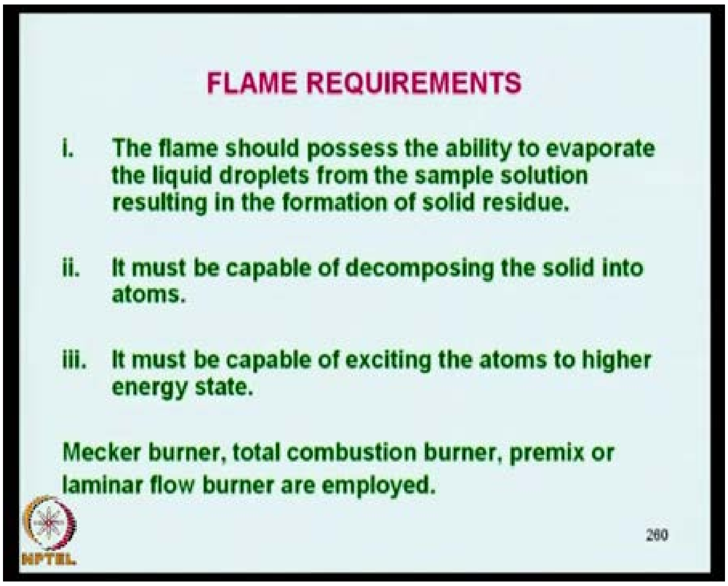

FLAME REQUIREMENTS

i. The flame should possess the ability to evaporate the liquid droplets from the sample solution resulting in the formation of solid residue.

ii. It must be capable of decomposing the solid into atoms.

iii. It must be capable of exciting the atoms to higher energy state.

Mecker burner, total combustion burner, premix or laminar flow burner are employed.

Now, what are the flame requirements? Very simple; the flame should possess the ability to evaporate the liquid droplets from the sample solution, resulting in the formation of the solid residue, because I would like to show that the basic job of the flame is to evaporate the sample. And the mechanisms we have seen earlier, that the liquid droplet should dry, it should loose the solvent, form a solid crystal, and then these crystals have to be melted, and then evaporated forming the atoms, ions, etcetera.

So, it must be capable of decomposing the solid into the atoms, that is another requirement; that means, the flame temperature should be high enough to decompose the solids; and for sodium potassium, sodium chloride, potassium chloride, they are all get decomposed very easily. And the flame should also be capable of exciting the atoms to higher energy state, that is very important, because we have seen that the samples must be only alkali and alkaline earth metals; this I have been stressing ever since the start of this lecture, because most of the flame photometers are use for the determination of metals in alkali and alkaline earth elements.

So, there are different kinds of burners, something known as maker burner, which you ordinarily see in your laboratory; and you can use a total combustion burner, that is another possibility. And if you have an atomic absorption instrument, a premics or laminar flow burners are usually employed. So, the radiation from the flame is collected from a concave mirror placed behind the burner as I told you, the focal point of the mirror lies at the entrance of the monochromator slit, that is the typical optical arrangement; and the exit slit is kept between the monochromater and the detector.

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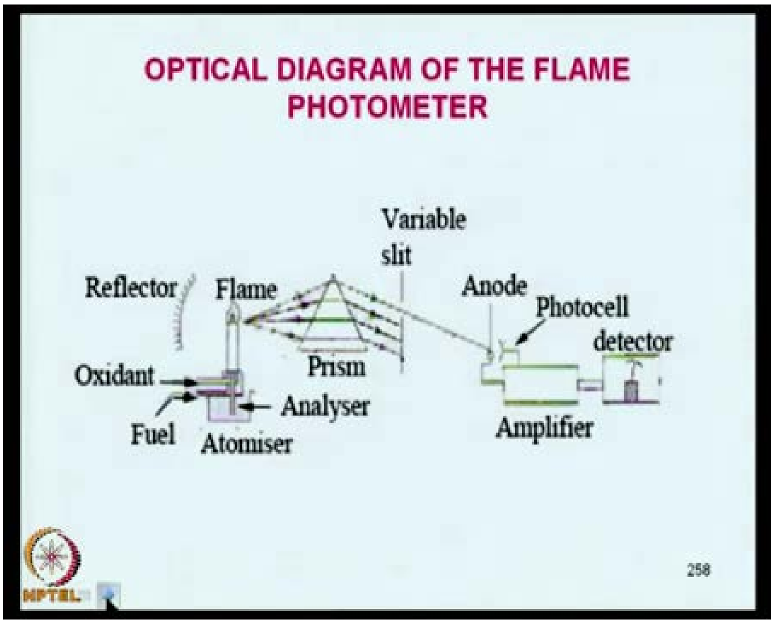

OPTICAL DIAGRAM OF THE FLAME PHOTOMETER

I hope you remember the figure, this is the exit slit, it has to between the monochromator and the detector.

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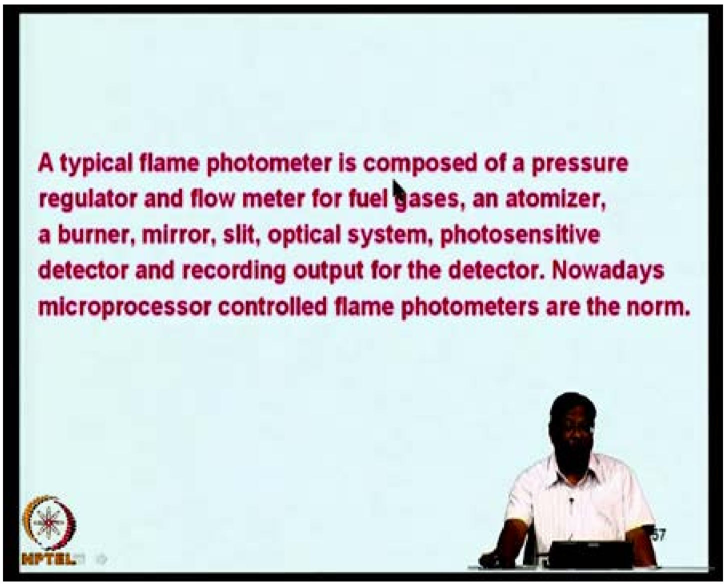

A typical flame photometer is composed of a pressure regulator and flow meter for fuel gases, an atomizer, a burner, mirror, slit, optical system, photosensitive detector and recording output for the detector. Nowadays microprocessor controlled flame photometers are the norm.

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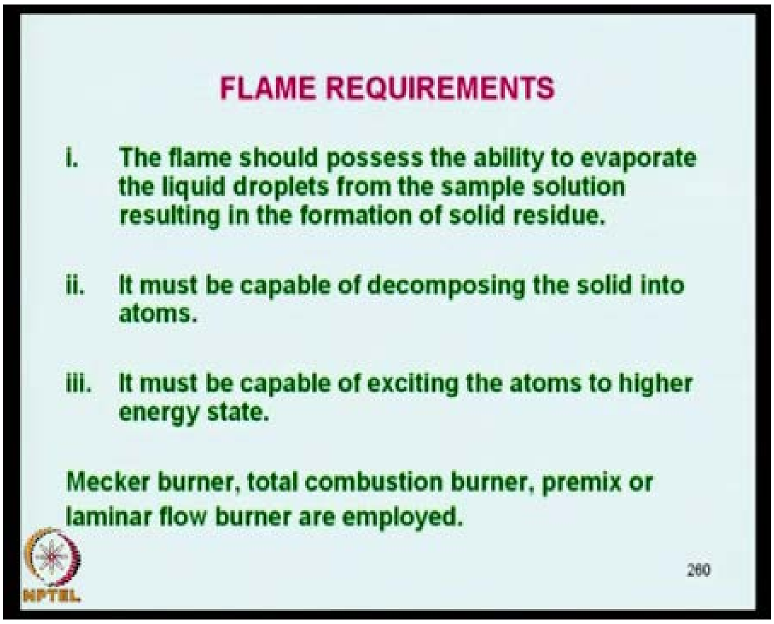

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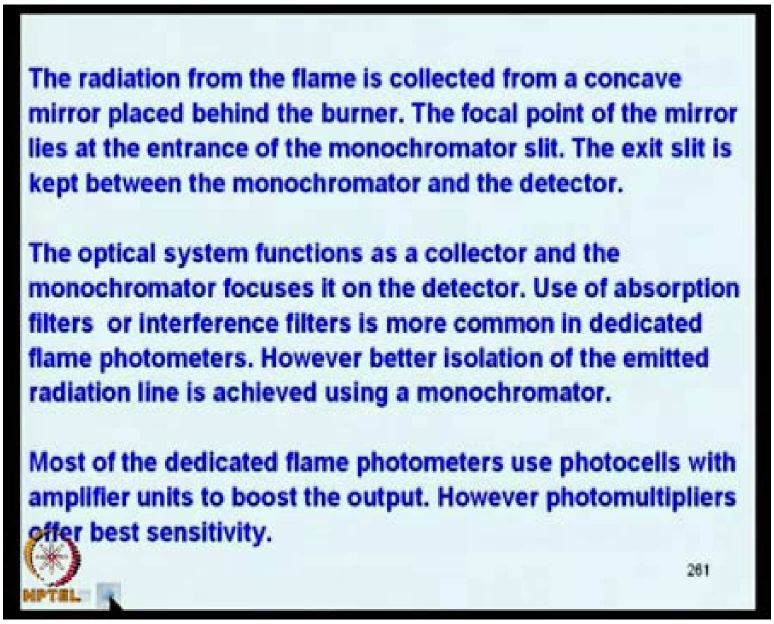

The radiation from the flame is collected from a concave mirror placed behind the burner. The focal point of the mirror lies at the entrance of the monochromator slit. The exit slit is kept between the monochromator and the detector.

The optical system functions as a collector and the monochromator focuses it on the detector. Use of absorption filters or interference filters is more common in dedicated flame photometers. However better isolation of the emitted radiation line is achieved using a monochromator.

Most of the dedicated flame photometers use photocells with amplifier units to boost the output. However photomultipliers offer best sensitivity.

So, the optical system itself functions as a collector of the radiation; and the monochromator, what is it do? It just focuses it on the detector. Use of absorption filters or interference filters is also more common in dedicated flame instruments, but not in atomic absorption, because most of the optics in atomic absorption is are optical components are mostly prisms and gratings, whereas interference filters are cheaper, they will give you similar capability, but you do not need prisms, etcetera, thereby you can reduce the cost of the dedicated flame flame atomic emissions spectrometer.

However, better isolation of the emitted radiation line is always achieved using a monochromator; its not the interference filters. Most of the dedicated flame photometers also use photocells with amplifier units to boost the output. For photo multiplier tubes, it offer better sensitivity, but if you use barrier layer cells, etcetera, there is no chance for amplification of the electrical signal. So, best thing is photo cells or photo multiplier cells.

Now, the schematic arrangement of a flame emission in atomic absorption, how does it look?

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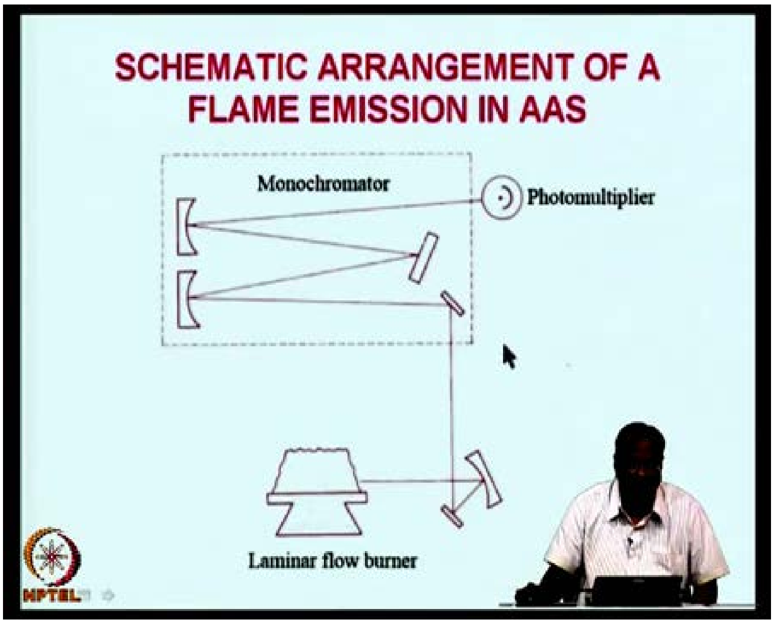

SCHEMATIC ARRANGEMENT OF A FLAME EMISSION IN AAS

Take a look at this figure. I have laminar flow burner, a beam splitter, and then I have a mirror, and then two concave mirrors and this is the grating, and it comes to the photomultiplier tube automatically. So, this is the typical arrangement of flame emission in AAS, except that, we’re not using a hollow cathode lamps source anywhere in the picture; that means, you do not have to light up the hollow cathode lamp, if you want to do sodium, lithium, potassium, cesium, etcetera.

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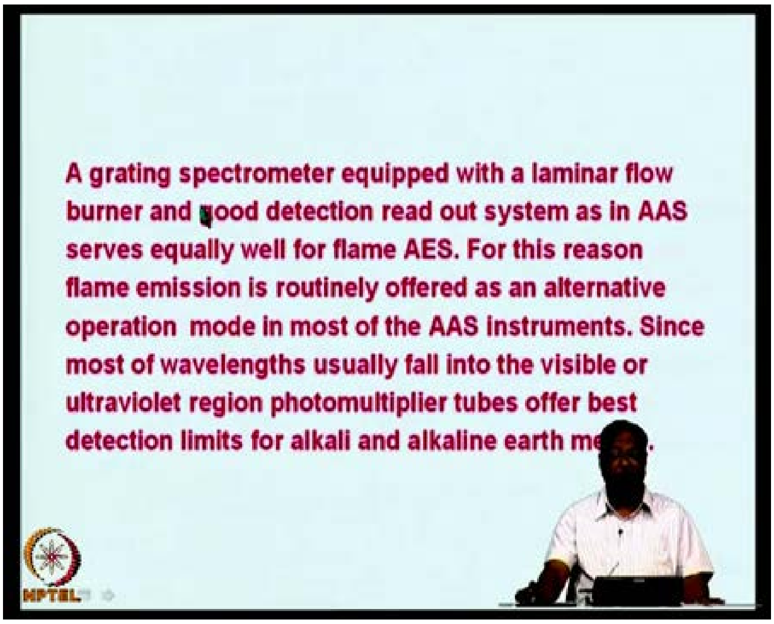

A grating spectrometer equipped with a laminar flow burner and good detection read out system as in AAS serves equally well for flame AES. For this reason flame emission is routinely offered as an alternative operation mode in most of the AAS instruments. Since most of wavelengths usually fall into the visible or ultraviolet region photomultiplier tubes offer best detection limits for alkali and alkaline earth me[illegible].

So, the existing optical system you can use it straight away. So, a grating spectrometer equipped with a laminar flow burner and good detection read out system, as in AAS serve equally well for flame AES - atomic emission spectrometer. For this reason, flame emission is routinely offered as an alternative operation in most of the atomic absorption instruments. Since most of the wavelengths usually fall into the visible region or ultraviolet region, I showed you a slide in the beginning of this lecture, when I was discussing about the ratio of the excited atoms to lower to the ground state atoms, where the wavelengths also I had indicated on the X axis; and usually photomultiplier tubes offer best detection limits for alkali and alkaline earth metals.

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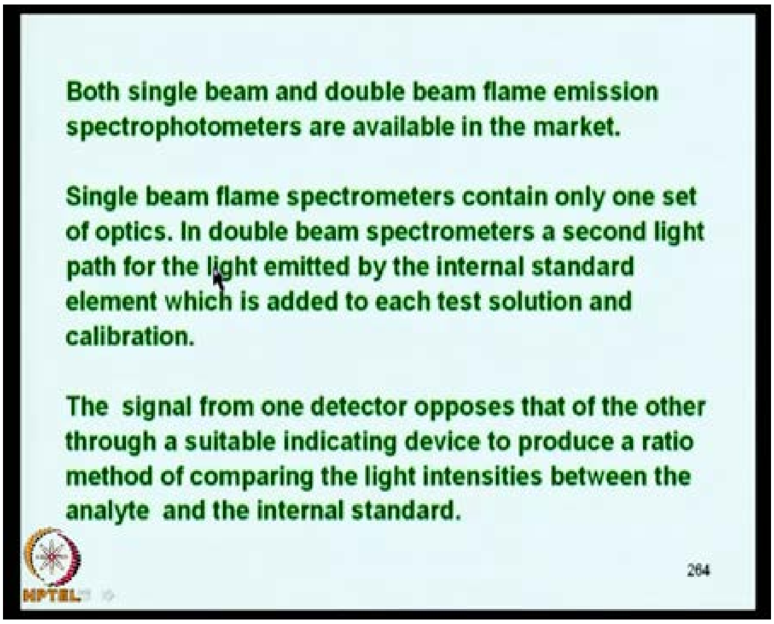

Both single beam and double beam flame emission spectrophotometers are available in the market.

Single beam flame spectrometers contain only one set of optics. In double beam spectrometers a second light path for the light emitted by the internal standard element which is added to each test solution and calibration.

The signal from one detector opposes that of the other through a suitable indicating device to produce a ratio method of comparing the light intensities between the analyte and the internal standard.

So, the both single beam and double beam flame emission spectrometers are available in the market. Single beams spectrometers contain only one set of optics, whereas in double beam spectrometers, a second light path a second light path for the light emitted by internal standard element, which is added to each test solution and calibration.

The signal from one detector opposes that of the other through a suitable indicating device, and it produces a ratio method of comparing the light intensities between the analyte and internal standard; this is a very standard technique, especially if you are doing high precision work. So, you can do either by calibration - simple calibration - or through a internal standard method; it may not be the same element, it can be any other element also. I will discuss this, when I am discussing at inductive couple plasma atomic emission.

So, operation of the flame AAS is very simple; flame AAS just like atomic absorption, atomic emission is also basically a relative technique; that means, you have to prepare the standards and the accuracy of your analysis depends upon the accuracy of the standards what you have prepared.

So, you should always use primary standards like sodium carbonate, etcetera, lithium carbonate, lithium chloride; lithium chloride is not a primary standard, but sodium carbonate is fine. Therefore, it can also be used for the as the internal standard for other elements. So, the standards and the analytes are as usual fed into the flame, that is, into the nebulizer sequentially and the response is fitted into a linear or polynomial curve.

The concentration of the analyte is read off from the calibration curve; this is a very standard technique. Now, you are all familiar with how to do a chemical analysis with known standards. Now, what about interferences? We have to discuss interferences, because flame emissions spectrometry is not without interferences, but not many spectral interferences are known to occur in the determination of alkali and alkaline earth metals. Therefore, for spectral interference to occur, the wavelength of the measurement should be same. So, if we are determining only 4 or 5 elements and their emission lines lie in this range, very few elements will have the same emission lines.

So, interference, but it may arise from the background emission due to hydroxyl and cyanogen radicals. Whenever you are taking burshane gas or butane gas, there will be always, nitrogen would be, when the gas is burning, nitrogen would be sucked from the surroundings. So, there is always an abundance of cyanogen and hydroxyl radicals; hydroxyl radicals come from the evaporation of water present in the sample, and cyanogens concentration comes from the suction of nitrogen air, basically during the flame process.

So, this is usually in the form of a scatter, which can be controlled by measuring against a matrix matching solution. So, if it is non-specific, so it can be controlled by making the standard also similar to the sample; for example, if you want to determine mercury in sea water, you your standard should also contain approximately 3.5 percent of sodium chloride. So, that is what we call standard matching.

So, you can also call it matrix matching. So, then what happens? Both the hydroxyl and cyanogen radical concentration would be approximately same in the sample. So, self absorption can be significant at very low concentration. This effect is more pronounced for the lowest resonance line; this is very easily understandable, because the lowest resonance line requires the least energy and flames do not produce very high energy also.

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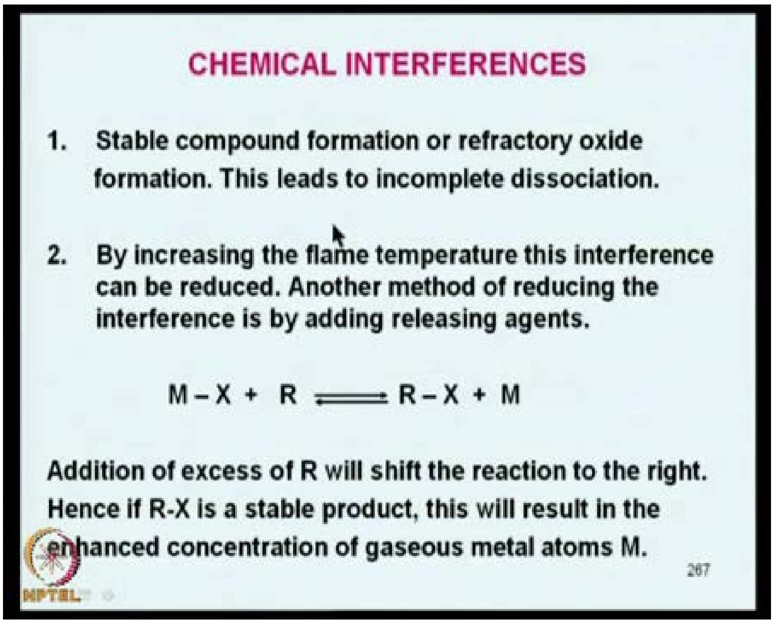

CHEMICAL INTERFERENCES

1. Stable compound formation or refractory oxide formation. This leads to incomplete dissociation.
2. By increasing the flame temperature this interference can be reduced. Another method of reducing the interference is by adding releasing agents.

$$M - X + R \rightleftharpoons R - X + M$$

Addition of excess of R will shift the reaction to the right. Hence if R-X is a stable product, this will result in the enhanced concentration of gaseous metal atoms M.

So, we can talk of chemical interferences. What are the typical types of chemical interferences, that we normally encounter in flame atomic emission. First thing is the compound formation. Whenever there is your sample, whenever there is air, whenever there is oxygen, and whenever there is flame, there is always a possibility that oxides are formed; we should never discount this possibility, when we are doing the chemical analysis with respect to flame flame atomic emission. So, stable compound formation or the formation of refractory oxides always leads to incomplete dissociation. Incomplete dissociation means less number of free atoms in the flame; that means, lower signal, simple.

So, the compound should not be forming an oxide; if it forms an oxide, then you have the problem. So, how do you do that? How do you control this kind of interference? We can do it by increasing the flame temperature; this, what happens? Most of the oxide again at higher temperature would decompose and atoms would be produced.

Another method of reducing the interference is by adding a releasing agents. I have put it as number 2 on in the slide. Now, the reaction you can see M X, that is, metal halite or any metal salt you can take, and I am adding a chemical known as R, it chemical represented by the symbol R. Now, there will be a chemical reaction in the solution itself. Now, what happens? The entity R will combine with X producing a sort of R X and metal ion would be released. So, the R is known as releasing agent. Now, if I add excess of R, the reaction equilibrium will be shifted to the right; that means, more metal ions will be there, then more R that is releasing agent.

So, if R X is a stable product, then this will result in the enhanced concentration of the gaseous metal atoms; very simple technique, very simple trick to make the analyte element by adding a reactive element known as releasing agent.

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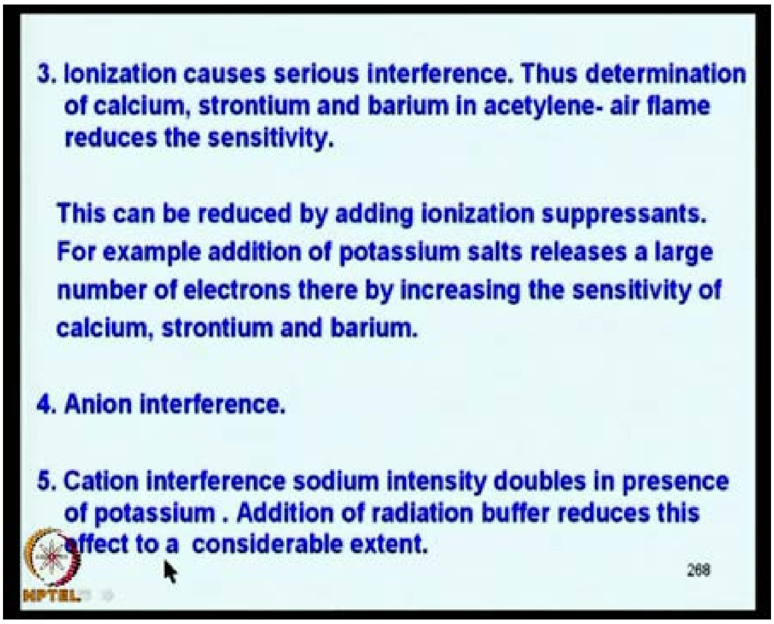

3. Ionization causes serious interference. Thus determination of calcium, strontium and barium in acetylene- air flame reduces the sensitivity.

This can be reduced by adding ionization suppressants. For example addition of potassium salts releases a large number of electrons there by increasing the sensitivity of calcium, strontium and barium.

4. Anion interference.

5. Cation interference sodium intensity doubles in presence of potassium . Addition of radiation buffer reduces this effect to a considerable extent.

Now, another possibility I must tell you is, that the ionization, because most of the atoms like lithium, sodium, potassium, etcetera, they ionize also in the flame. So, this ionization can cause serious interferences, because what we need are not the ions but the atoms. So, if the ions are formed using the electrons available in the flame, we are loosing a loosing the part of the signal corresponding to the formation of the ions.

Therefore, determination of calcium, strontium, and barium in acetylene and air flame reduces the sensitivity, because many of these atoms like calcium, strontium and barium, they form the ions; this can be reduced by adding ionization suppressant. I add a chemical which suppresses the ionization; for example, if you want to determine potassium, if you want to determine potassium, there is no problem, but if you want to determine calcium, strontium and barium, you add lot of potassium salt to the sample; then, what happens? The majority of the ionization process is consumed by potassium salts rather than calcium, barium and strontium. So, another small trick, that is, you add more easily ionizable salt to the sample as well as your standards; very simple trick.

Now, here, the it is there is no chemical reaction that you should remember.(No Audio: 41.35 to 41.43)

The addition of easily ionizable salt itself will do the job. Now, there could be some sort of anion interferences, and cation interference from sodium intensity doubles in presence of potassium. If you want to determine sodium, if there is potassium, there is intensity doubles; that means, you would be measuring higher signal than what it actually is.

So, for this, what we do is, we add a radiation buffer, that is, we add a substance which gives you higher signal, but it does not go into your calculations; very simple technique. You can determine at higher concentration also, without adding the radiation buffer. Then, even though we say other element spectral interferences are not there, sometimes you do come across other element emission lines, so a good quality monochromator reduces this type of interference. That is why it is preferable to do the flame emission in atomic absorption, unless it is very high quality very low quality work required as in dedicated flame photometers.

So, interference can also come from salts and acids; this effect can be reduced to a large extent by matrix matching. Always remember that matrix matching is an accepted technique; you should always be doing it, whether it is something to do with specificity or not, to reduce the overall effect of the other concomitants present in the sample. So, for example, you can see here, sodium chloride at 213.9 nanometer interferes in the determination of zinc. So, best thing is to add sodium chloride and see how best you can determine zinc.

So, sometimes, apart from this chemical interferences, you can also come across instrumental errors. The instrumental errors are always drift and things like that, and nothing much can be said about it, because the instrumental errors arise from the instability of the flame; sometimes the more gas reaches, sometimes less gas reaches. If the flame is not laminar and very stable, then the the detector would receive a higher signal.

So, to obtain stable flame, the flow rate of the fuel and the oxidant must be controlled within 1 percent, then only you will get a very good signal; otherwise, more than one percent, the signal is not really very good. So, the fluctuations of the detector and the amplifier also leads to instrumental errors. Another source of analytical error is the atomizer function; we should never neglect that. Quite often the capillary gets cloaked; so, the capillary if it gets clogged, there is no way you can introduce the sample; obviously, you will end up with a very low signal, because the liquid is not passing through the capillary; therefore, regular maintenance of the instrument is very very essential. So, there is not much to explain more than this is not necessary, because as of now we are considering, the accessories available for atomic absorption.

So, we will straight away go into applications of flame photometry. Now, you can use this, see this slide.

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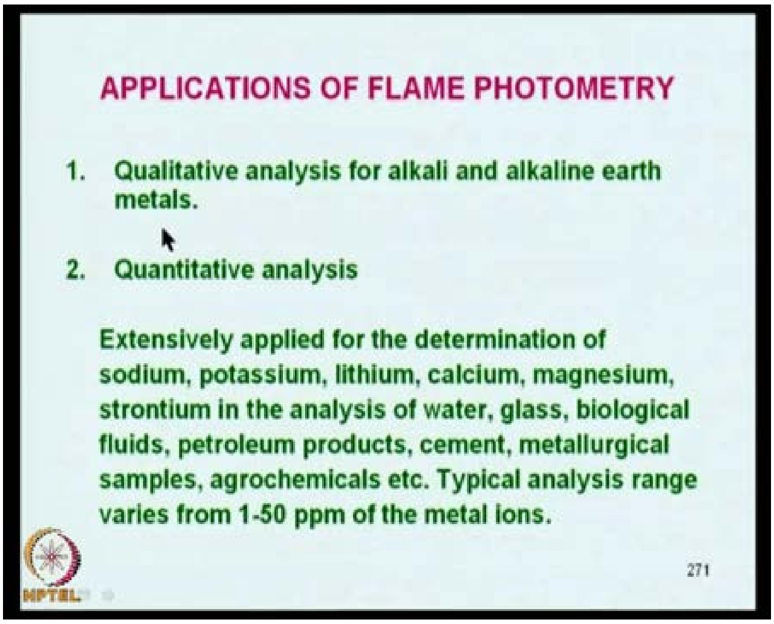

APPLICATIONS OF FLAME PHOTOMETRY

1. Qualitative analysis for alkali and alkaline earth metals.
2. Quantitative analysis

Extensively applied for the determination of sodium, potassium, lithium, calcium, magnesium, strontium in the analysis of water, glass, biological fluids, petroleum products, cement, metallurgical samples, agrochemicals etc. Typical analysis range varies from 1-50 ppm of the metal ions.

I have written here that qualitative analysis of alkali and alkaline earth metals is always possible; it is known even in qualitative analysis without flame photometry, that when sodium burns, it gives a yellow flame; and when there is potassium, it gives a reddish flame; and lithium will give you a violet flame. And these things are known, only thing is they have they are not used for the qualitative quantitative analysis, because for quantitative analysis, you will have to correlate the flame colour with the concentration, that does not happen.

But for qualitative analysis, you can always use a flame photometer, not the other way round. If there is a flame containing sodium, you cannot correlate it to concentration, but if in flame photometer, the concentration relations can be established. So, pass fail test, you can always do in flame photometry. So, for qualitative analysis, definitely alkali and alkaline earth metals, you can do the analysis to whether the sample contains sodium or not; if it gives yellow flame, yes, it contains; if it does not give yellow flame, you can say no, it does not contain sodium; this is pass fail test. Similarly, for potassium, a red flame, yes; non red flame, no; it is not possible.

Then, the other way is quantitative analysis; this we have been discussing, how to do using standard solutions. So, the quantitative analysis is extensively applied for the determination of sodium, potassium, lithium, calcium, magnesium and strontium; the analysis matrix can be water, you can analyze these elements in glass, and biological fluids like plasma, body fluids, urine, etcetera; petroleum products, it is always important to know the concentration of the elements; in cement, we do not want very high concentration of sodium, and metallurgical samples always contain sodium, potassium etcetera, calcium etcetera, and in agrochemicals, yes, many of the agrochemical contains sodium salts.

So, typical analysis range varies from 1 to 50 ppm of the metal ions. Now, you can always say that there is no fixed limit for the determination of these metals. You can make your calibration curve using 1 to 5 ppm of sodium also or you can make your calibration curve 1 to 50 ppm also, depending upon your system. So, in emission, there is nothing like fixed linear response system, but you can adjust the signal in such a way, that you can do the determination in the form of at very low concentrations as well as very high concentrations.

So, that completes our discussion on the flame photometry, because I do not want to convey to you more information, because it is basically it is a very simple system; anyone with a minimum educational qualifications who knows how to operate a flame photometer can keep on working, but to understand the complexities involved in the analysis of these things are more important, as a chemist for you as well as for others to interpret the results. See, basically, a chemical analysis is done not to know the concentrations, but also to adjust the concentrations in such a way that the functionality of the end material is always enhanced.

So, that is where the difference between an operator of an instrument and the chemist or the analytical scientist comes into play. An operator of the instrument simply will operate the instrument and give a result, whereas a scientist would like to know the type of the signal, the quality of the signal, the quality of the chemical analysis, and what to do with that information like that; there will always be decisions to be taken, whenever you are doing the analysis; analysis per say, just for it sake, nobody does, but whenever it is associated with a function - subsequent function - then the contribution from the analytical scientist become become significant.

So, now I will close our discussion on this atomic emission spectrometry, but I will come back to it again, whenever when I am concluding this chapter, that is, atomic absorption and inductive couple plasma, because there after this, I am going to talk to you one more technique about electro thermal atomic absorption spectrometry; that is known as ETAAS electro thermal atomic absorption spectrometry. And after that, we will be discussing about the inductively couple plasma AES - atomic emission spectrometry - ICPAES and atomic absorption spectrometry electro thermal. So, these two techniques will study; afterwards, again we will go ahead and compare the sensitivities of the determination of flame atomic absorption, and atomic absorption, atomic emission, electro thermal atomic absorption as well as the inductively couple plasma atomic emission spectrometry - that is ICPAES. So, please bare with me; when now I am going to talk to you about the electro thermal atomic absorption spectrometry.

So, what I would like to say to you at this stage is that, atomic absorption analysis using flame atomization presupposes that the sample is in solution, that is an easily understood; that means, before you attempt any chemical analysis using atomic absorption, you have to bring the sample into solution. For the analysis of solids at the ppm level, bringing the sample into solution involves a dilution; that means, the concentration of the analyte, whenever you dissolve, you are going to add liquids, acids, etcetera. So, the concentration comes down. So, that the concentration of the analyte if it is already in the ppm level, it becomes a small fraction of the original content, when you do the dilution; therefore, the limit of detection for a particular element is directly proportional to the concentrations of the atoms in the flame, which is again further dependent upon the flow rate of the solution, upon the atomization, efficiency of nebulization and atomization efficiency, flame temperature, and the instrumental errors, background corrections and all these things. So, there is always some loss of sensitivity, whenever you are doing a chemical analysis using the dilution technique.

Since the flow rate of the gases is always high, the time spent by the free atoms in the flame is very very short, that is of the order of about 10 raise to minus 4 seconds. Now, increase of free atoms by higher intake of the sample, you cannot keep on increasing; take more sample and introduce, so that we get a higher signal; that is not possible, because it is restricted by the burner design. If your burner contains only ten holes, the sample has to be introduced only through the ten holes in the sample in the flame. So, that you cannot increase indefinitely, and suppose you increase again, there it moreover causes a deterioration of the flame stability. Suppose you increase the increase the sample intake more, then the sample may cool may reduce the flame temperature and atomic concentration would again come down. So, what we want to do is, all these factors tend to limit the atomic absorption concentration in the flame, leading to a significant reduction of sensitivity and detection - limit of detection.

So, suppose the sample is very small, then what happens? Suppose it is only 5 to 10 microliters, suppose you want to analyze the brain - brain samples - liquid from the brain or from the human body, you would not be able to get too much of the sample, you may be always ending up with 5 to 10 microliters; therefore, it is necessary to work at absolute detection limits, that is, still lower levels, parts per billion, parts per trillion, etcetera. So, this atomic thermal atomic emission – ETAAS - is a step in that direction; we will continue our discussion on atomic absorption in the next class.