Trace and ultra trace analysis of metals Using atomic absorption spectrometry
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Lecture - 30
Electrothermal AAS II

So, continuing our discussion on flame atomic emission, we will look at the history. A little bit flame emission spectrometry has been in used since 1900s, almost 100-115 years old technology.

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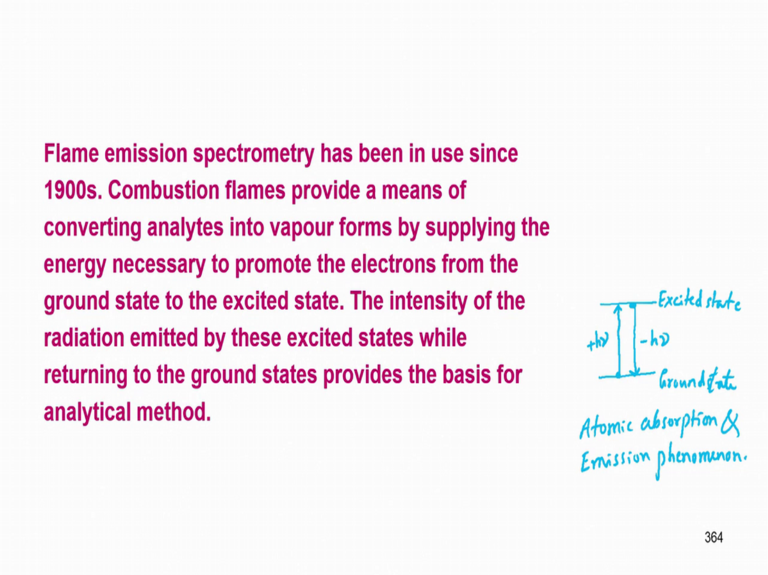

Flame emission spectrometry has been in use since 1900s. Combustion flames provide a means of converting analytes into vapour forms by supplying the energy necessary to promote the electrons from the ground state to the excited state. The intensity of the radiation emitted by these excited states while returning to the ground states provides the basis for analytical method.

364

So, combustion flames normally provide a means of converting analytes into vapour, 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 excited states while returning to ground state provides the basis for analytical methods. What we want to say essentially is, we have a ground state atom here and excited state is here and then, I have an electron here. This goes to next higher energy state if I put it in the flame. This is absorption.

So, the excited atom when it comes back to the ground state, this is ground state. This is excited state, this is the electron. We are talking about an electron is there and from here an electron can come back to the ground state. This is plus h mu and this is minus h mu. So, whenever there is absorption, it goes to the next higher energy state absorbing the energy. If it comes back, the energy is released. If the energy is released in the form of emission, in the form of radiation, then we have an atomic emission. So, this is atomic absorption and emission phenomena. So, this is the basis for atomic absorption and emission.

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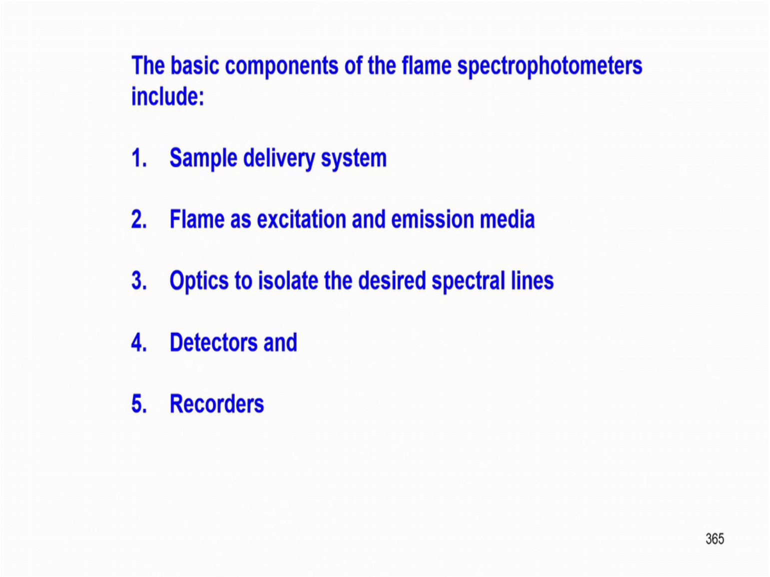

The basic components of the flame spectrophotometers include:

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, since we say that the technology is already there since 1900, but we want to tell you the basic components. We will define the basic components of the system and what will they contain. I need a sample delivery system and that means I have to provide means to convert the sample into small vapour droplets, small liquid droplets and deliver it into the flame. That is all that is required because flame itself can serve as an excitation source because we know that temperatures in gases can vary from 1000 to 1200-1500 etcetera. So, what we need is a sample delivery system which we have already described in atomic absorption, where we suck the sample and put it through a small nozzle as a spray. That is it basically and then, we need a flame as the excitation source and also the emission media because from the flame only radiation will be coming out in all directions. So, flame is not only an excitation source, but it is also the media for emission and then, what I need is the optics to isolate the desired spectral lines. I do not need a huge monochromator or grating or any of those things, but a simple filter because we know that sodium vapour lamp as you see on the straight, we using only yellow light. That means, all you need is a yellow filter.

Similarly, if it is potassium, it needs a violet filter. So, like that we need very simple optics to isolate only the desired spectral lines. Then, what we need once is the spectral line is separated from other electromagnetic radiation. We need to focus it on the detector and find out what the current is and then, what we need is a recorder if possible. Nowadays computers will do all that kind of job. So, basically sample delivery system to be introduced into the flame and from the flame, we need the optics, a filter, common filter to separate and then, that filter the radiation should fall on the detector. All other optics and electronics etcetera will remain the same.

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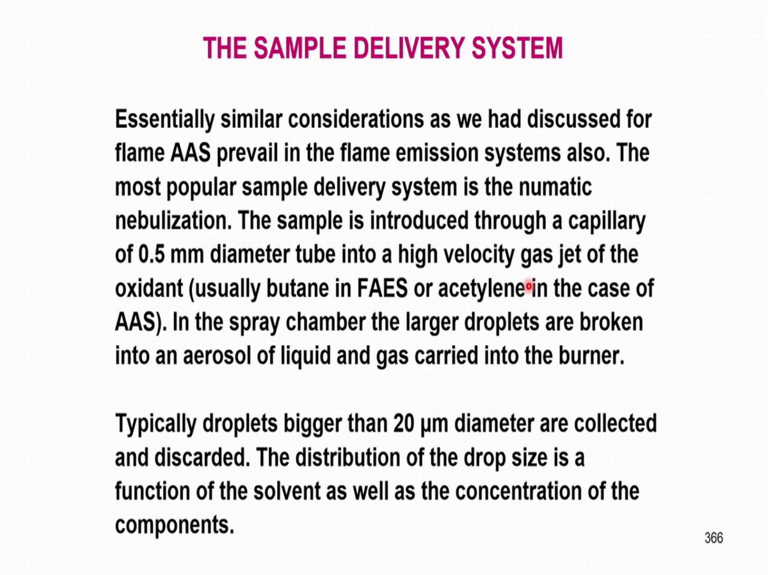

THE SAMPLE DELIVERY SYSTEM

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 diameter are collected and discarded. The distribution of the drop size is a function of the solvent as well as the concentration of the components.

So, we will discuss a little bit about this sample delivery system. So, we have already discussed it. What we have already discussed earlier, similar concentrations in AAS prevail in the flame emission system also. That is why even in atomic absorption, we only have to change the switch. The most popular sample delivery system is then numatic nebulization, that is pass the air and then, allow the pressure to come out through a nozzle which will pick up and you would have seen such kinds of nebulization in your day to day life. Whenever you use a perfume spray, most of the perfume sprays what we normally use after bath etcetera, they all contain low boiling liquid. There are something like alcohol along with some perfume and with a small nozzle at the top, you just press it. The pressure, the liquid will be sucked and then, delivered through a small nozzle as a spray which we spray all around our body.

So, essentially that is what we are talking about. So, the sample introduced through the small capillary of about 0.5mm diameter tube. You would have seen this 0.5mm diameter tube in most of the perfumes sprays also. So, it is to be delivered into a high velocity gas jet of the oxidant that is in flame atomic absorption, we need the flame. So, in our body this thing just sprays into the atmosphere.

So, usually the gas what we need is butane in flame atomic emission FAES or acetylene as in the case of atomic absorption and then, you need some amount of air to make it burn. The dynamics of the flame we have already discussed earlier. So, in the spray system chamber, larger droplets are broken down into an aerosol and the gas is carried into the burner typically droplets bigger than 20 micrometer diameter are collected and discarded. So, the distribution of the drop size is a function of the solvent as well as the concentration of the component.

What you want to tell here is the drop size is a function of the solvent. If I use a very low boiling solvent with lot of vapour pressure, the drop size is smaller. If I use water drop size is bigger, if I use glycerol or something like that, drop size will be still bigger. So, it is better to use water or a mixture of water and alcohols which will give you smaller drop sizes. Smaller the drop size, less is the amount of heat required to convert it into vapour.

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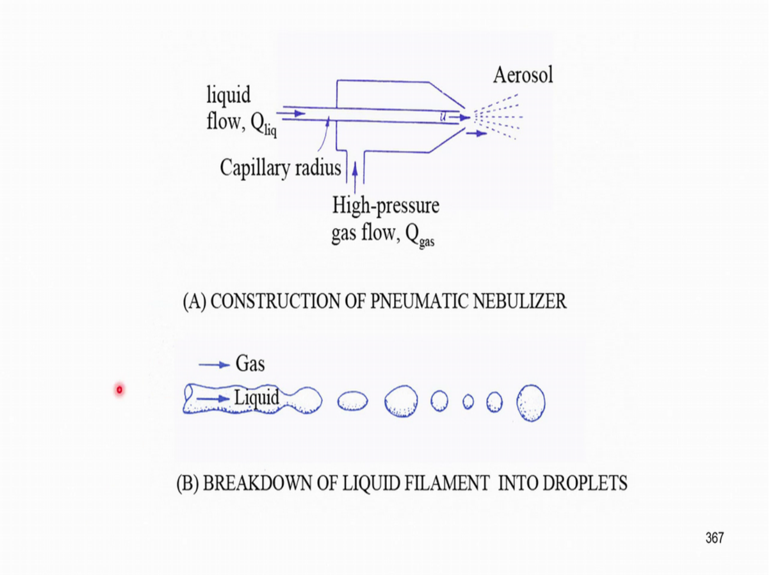

(A) CONSTRUCTION OF PNEUMATIC NEBULIZER

(B) BREAKDOWN OF LIQUID FILAMENT INTO DROPLETS

So, this is the typical break down of the construction of a pneumatic nebulizer. I have a liquid and then, coming through a small capillary and then, I put it an apparatus where high pressure gas flow is there. This gas flow is nothing, but butane and oxidant or acetylene and oxidant and all of them will be combining to form a small nozzle here and the nozzle aerosol is generated. It is a very simple arrangement and same thing is true once the gas aerosol comes out, what happens is initially it will be something like this.

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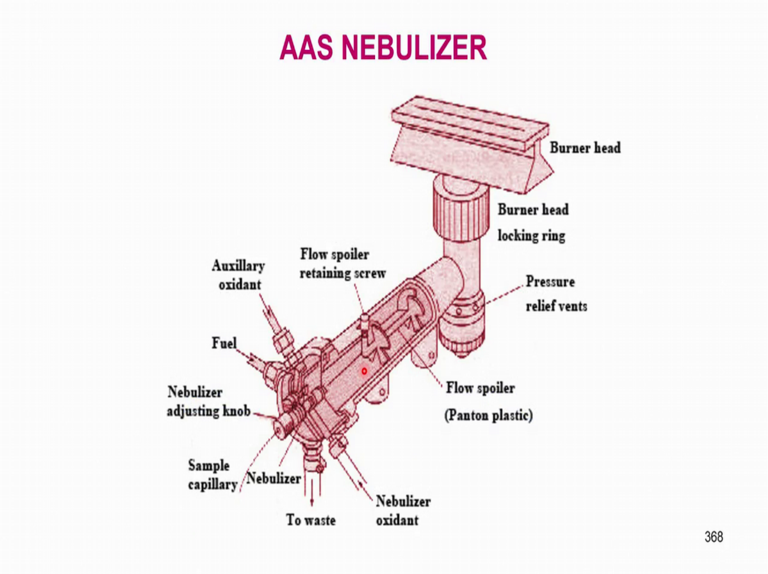

AAS NEBULIZER

Then, they breakdown into small droplets and their smaller droplets get carried into the flame and the bigger droplets are collected and discarded. So, the same thing modified form and more sophisticated. This we have already seen earlier. It is the nozzle sample comes, here ample air capillary, this one and then, there is fuel, there is oxidant, all of them are coming and mixing and then, there is a flow spoiler here and then, the bigger droplets are collected at the bottom of the cylinder and to waste remaining is carried into the burner head.

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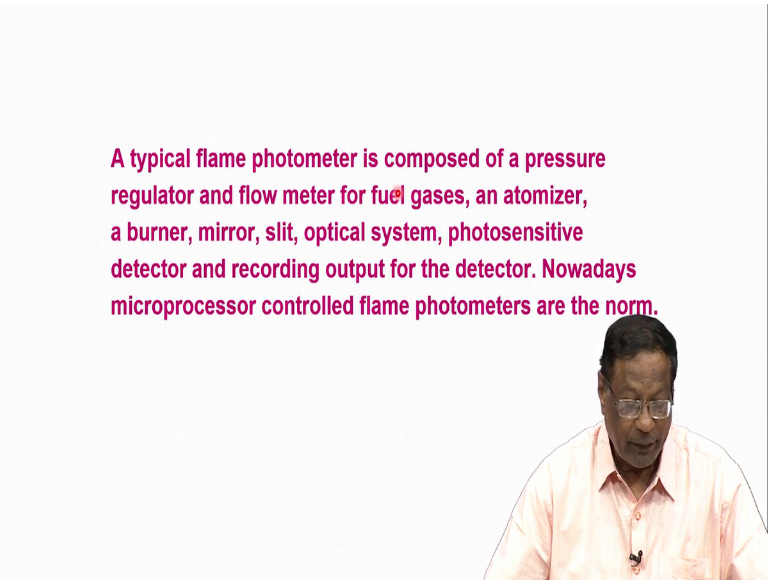

A typical flame photometer is composed of a pressure regulator and flow meter for fuel gases, an atomizer, a burner, mirror, slit, optical system, photosensitive detector and recording output for the detector. Nowadays microprocessor controlled flame photometers are the norm.

So, a typical flame photometer must normally therefore must be composed of a pressure regulator. We need flow meter for fuel gases, an atomizer, a burner, a mirror and slit optical that corresponds to slit optical system and the photosensitive detector and a recording output.

Nowadays microprocessor controlled instruments are available which we will do most of the jobs at the press of a button or turn of a screw.

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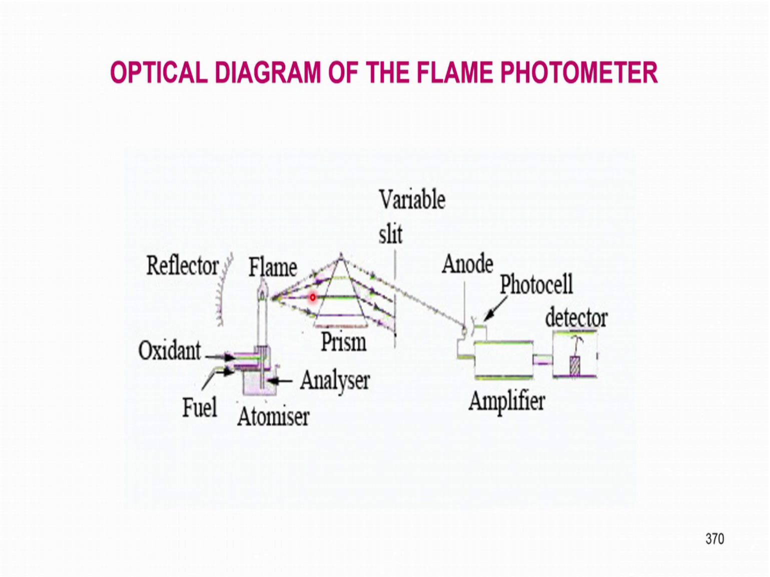

OPTICAL DIAGRAM OF THE FLAME PHOTOMETER

So, this is a typical arrangement of a flame photometer. As I told you may buy a flame photometer for about 5000 rupees with no source. You do not need hallow cathode lamp or electrode less discharge lamp or vapour lamp etcetera, but what is required available in the market is you need an atomizer basically and to be connected to a burner, this is the burner flame and then, this is just like a laboratory burner what you have in your laboratories and I put a flame mirror here, reflector and all the radiation coming backwards and other sides will be collected. This is fixed at the focal length of the mirror and then, all the radiation is pass through a prism. From the prism, the radiation will pass through a movable slit to collect different fractions of the electromagnetic radiation. If it is sodium, it is 589. If it is potassium, it is around 600 or something like that and for other elements, there will be other wavelengths.

Then, I need a photocell. It has got an anode and photocell etcetera. The electro radiations will generate photons. Photons will go down to the electrode of the photocell and current will be generated which will be amplified and detector will do the job of quantifying the current and converting it into concentration. So, this is the typical schematic diagram of flame photometer. So, there is nothing much to tell except that this is a very simple arrangement and most of the laboratories which are not sophisticated, especially soil laboratories, soil testing laboratories, water testing laboratories will be having a flame photometer in their laboratory.

So, it is a very common instrument, but if you have atomic absorption, you have this also. You do not need to buy separate lay of flame photometer, ok.

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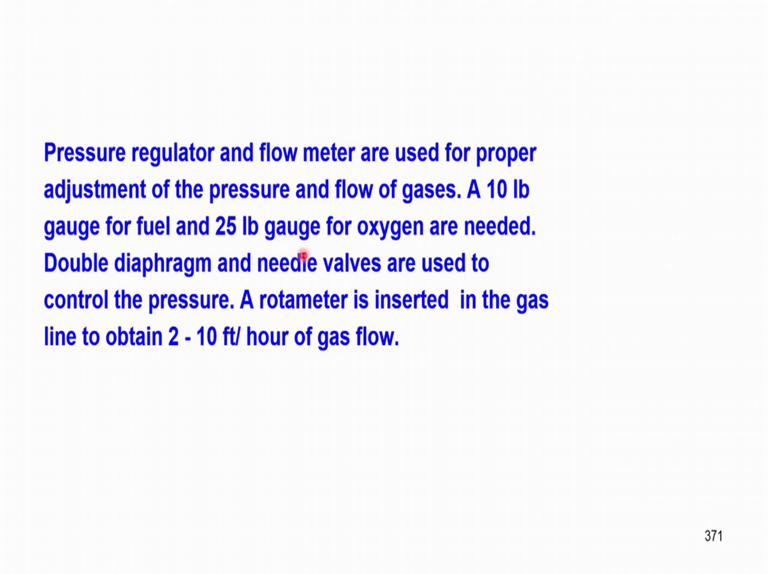

Pressure regulator and flow meter are used for proper adjustment of the pressure and flow of gases. A 10 lb gauge for fuel and 25 lb gauge for oxygen are needed. Double diaphragm and needle valves are used to control the pressure. A rotameter is inserted in the gas line to obtain 2 - 10 ft/ hour of gas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

So, pressure regulator and flow meter are used for proper adjustment of the pressure and flow of gasses. So, 10lb gauge for the fuel and 25lb gauge for the oxygen are required. You do not need oxygen. You can also use air and double diaphragm and needle valves are used to control the pressure.

These are all typical mechanical details which are fixed along the instrument and you do not have much to do with diaphragm and needle valves except just according to the specific instructions given along with the instrument, but what we need is a definitely a rotameter that is inserted in the gas line to obtain 2 to 10 feet per hour of the gas flow. The gas flow should be about 2 feet to 10 feet range. That means, it can be air recycling or it can be butane air also, ok.

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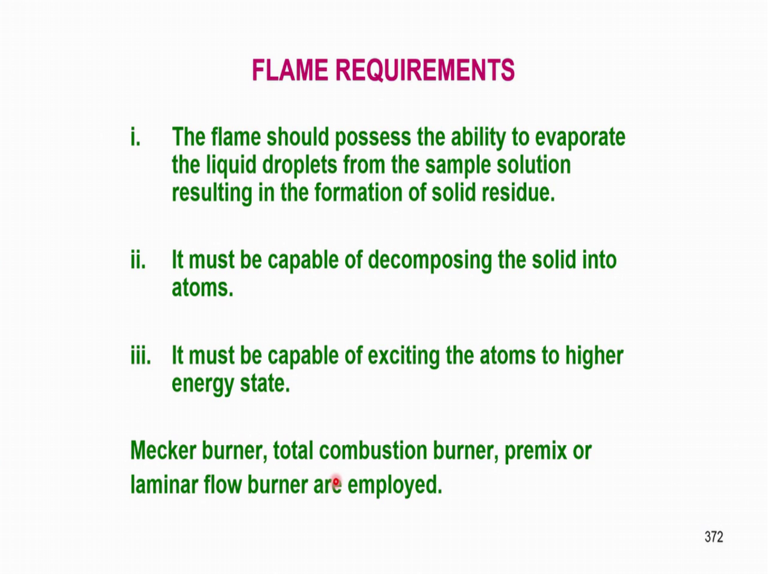

FLAME REQUIREMENTS

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.

So, what are the requirements of the flame, what kind of flame we do require in flame atomic emission spectrometry? First of all, the flame should posses the ability to evaporate the liquids droplets from the sample solution resulting in the formation of the solid residue. The mechanism of this I have already given earlier and it must be capable of decompose in the solid into the atoms and it must be capable of exciting the atoms to higher energy state.

So, a mecker burner which is quite common in laboratories or a total combustion burner or premix or laminar flow burner, this is in AAS. Mecker burner is a bigger version of your laboratory burner and total combustion burner is again the typical burner attached with a capillary at the nozzle.

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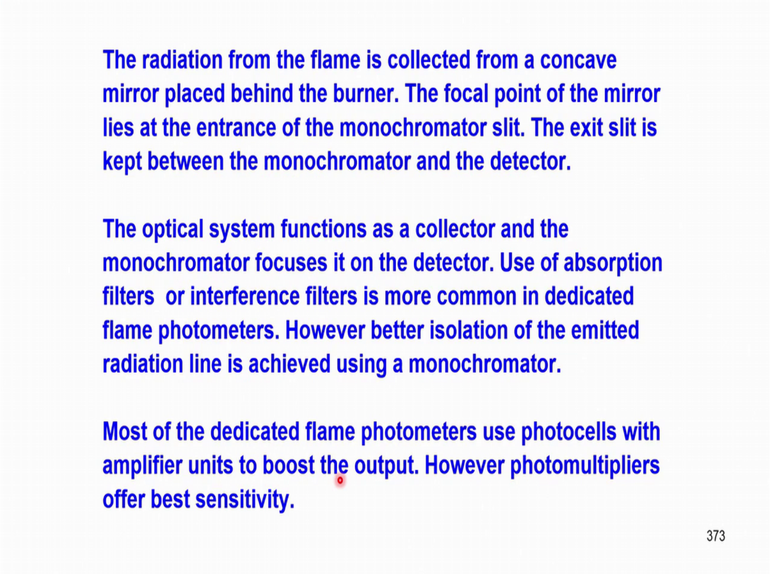

The radiation from the flame is collected from a concave mirror placed behind the burner. The focal point of the mirror lies at the entrance of the monochromator slit. The exit slit is kept between the monochromator and the detector.

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, these three kinds of burners are typically used in the flame atomic emission instruments. So, what we do is, we collect the radiation from the flame from a concave mirror placed behind the burner. The focal point is at the entrance of the monochromator slit exit. Slit is kept between the monochromator and you can refer the figure now and the optical system functions as the collector and a monochromator focuses on the detector use of absorption filters or interference filters is more common in dedicated flame of photometers. We had already discussed the different kinds of filters which are glass filters, colored glass filters or filter photometers, interference filters which have got a band pass width of about 15 nanometers, 5 to 10 nanometer band pass width. Interference filters are also quite common in flame photometer.

So, better isolation of the emitted radiation is the only m in the most of these flame photometers. So, that is achieved using a monochromator. You can use a prism and slit alignment or a grating or anything. You want quite common experience for physical physics experiment and the dedicated flame photometers, use photocells. That is enough. You do not need a photomultiplier tube also, but photocell does come, does have an amplifier units to boost the output, but now a days with atomic absorption instruments, photomultipliers are used. There is no need to use the photocells. Again a separately photomultiplier tube will do this job in atomic absorption instruments.

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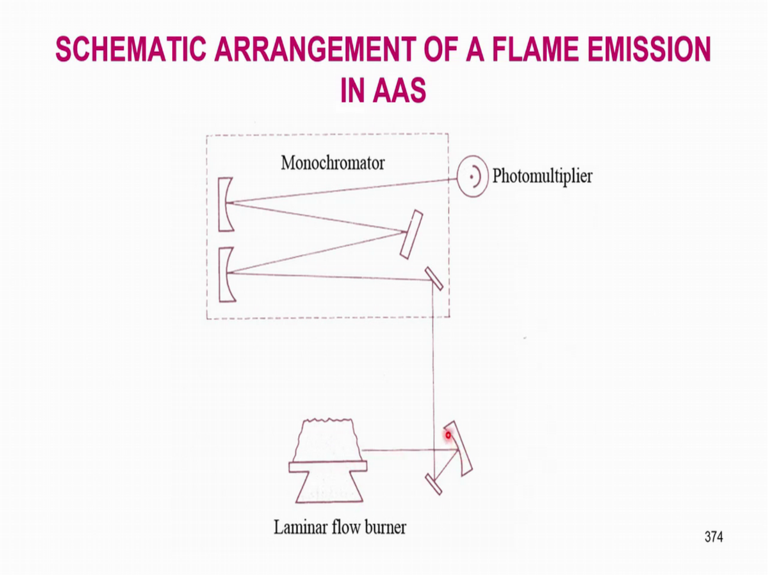

SCHEMATIC ARRANGEMENT OF A FLAME EMISSION IN AAS

So, this is the typical arrangement. Laminar flow burner, a concave grating and then, a line is chosen. It comes here and this is the monochromator arrangement. Then, it falls on the concave mirror collected here under mirror and then, again another mirror and it comes out onto the photomultiplier tube. This is schematic arrangement of flame emission. So, probably in the optics, there will be a small switch which will change the configuration in atomic absorption instrument, but otherwise this arrangement is suitable for flame photometer also.

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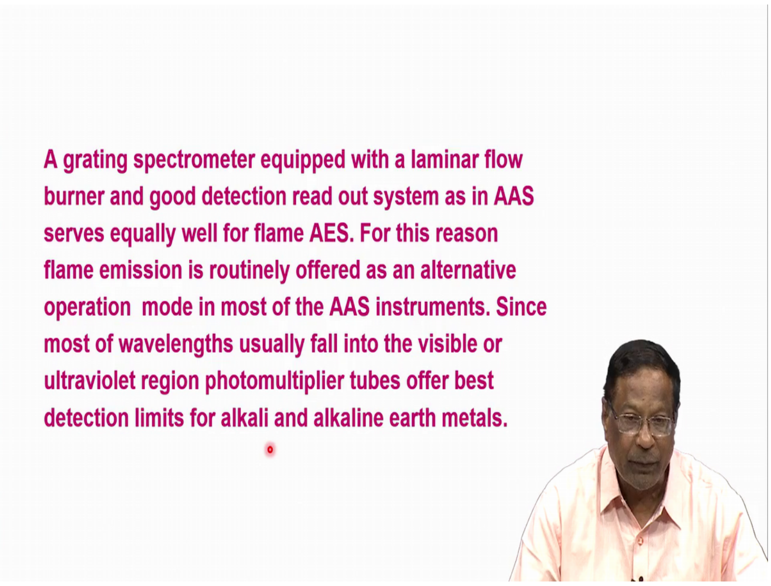

A grating spectrometer equipped with a laminar flow burner and good detection read out system as in AAS serves equally well for flame AES. For this reason flame emission is routinely offered as an alternative operation mode in most of the AAS instruments. Since most of wavelengths usually fall into the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

So, a grating spectrometer equipped with laminar flow burner and good detection read out system as in the atomic absorption serves very well for atomic emission also. For this reason, flame emission is routinely offered as an alternate technology in most of the atomic absorption. Even if you do not ask, the provision will be there. Whenever you buy an atomic absorption, since most of the wavelengths usually fall into the visible range above 500 nanometers, ultraviolet range is very less and photomultiplier tubes offer best detection limits for most of the alkali and alkaline earth metals.

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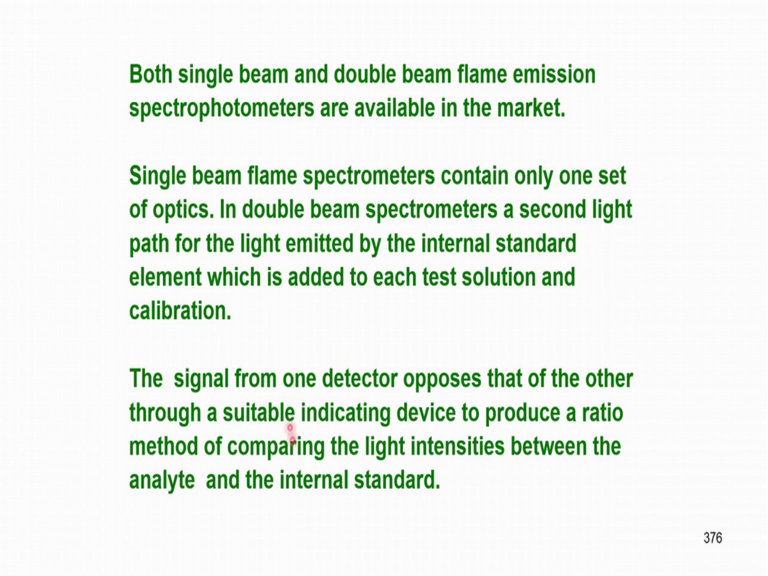

Both single beam and double beam flame emission spectrophotometers are available in the market.

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, both of you can use single beam and double beam flame emission. Spectrometers are available in the market. Of course, cost will vary depending upon what you are buying whether it is single beam or double beam. Single beam flame spectrometers contain only one set of optics. In double beam, a second path like path for light emitted by the internal standard element is added to each test solution and calibration. I think that is a little bit of more of analytic chemistry, that is if you add an internal standard, every time you do not have to worry about the instrument setting because with the inherent internal standard if you get the same absorbance reading, that means the machine is performing optimally.

So, signal from one detector opposes that of the other through a suitable indicating device to produce a ratio method. That is a very simple standard technique in almost all spectrophotometers including atomic emission, atomic absorption and spectrophotometry. So, that compares the light intensities between the analyte and the internal standard.

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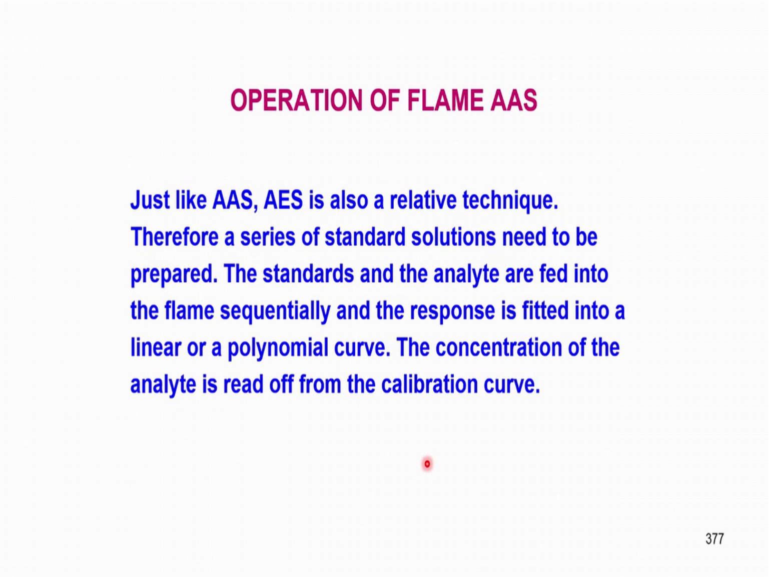

OPERATION OF FLAME AAS

Just like AAS, AES is also a relative technique. Therefore a series of standard solutions need to be prepared. The standards and the analyte are fed into the flame sequentially and the response is fitted into a linear or a polynomial curve. The concentration of the analyte is read off from the calibration curve.

So, how do we operate the atomic emission? In the atomic if you are using the atomic absorption, you just have to change the switch and start the operation just like AAS. AAS also is a relative technique. That means, the analysis is as good as your standards. If your standards are no good, your analysis is no good. So, depending upon what signal your standard gives is unknown. Signal is compared to that of the standard which is just like what you had discussed earlier. Prepare a calibration curve and then, put your unknown and measure the absorbance and then, relate it to concentration, but in atomic emission we do not measure the absorbance. We measure the transmittance.

Therefore, the standard solutions are there. They are fed into the flame sequentially and response is fitted to a linear or polynomial curve. It is not necessary that you should get only a linear curve. 99 percent of the time whenever you do atomic emission, you may end up with a polynomial curve, but one has to be a little careful especially when you are preparing a calibration curve, you should either refer to the text or standard text. And see what kind of response is expected for each element. So, the concentration of the element is rid of from the calibration curve. That is important. So, there are no interferences.

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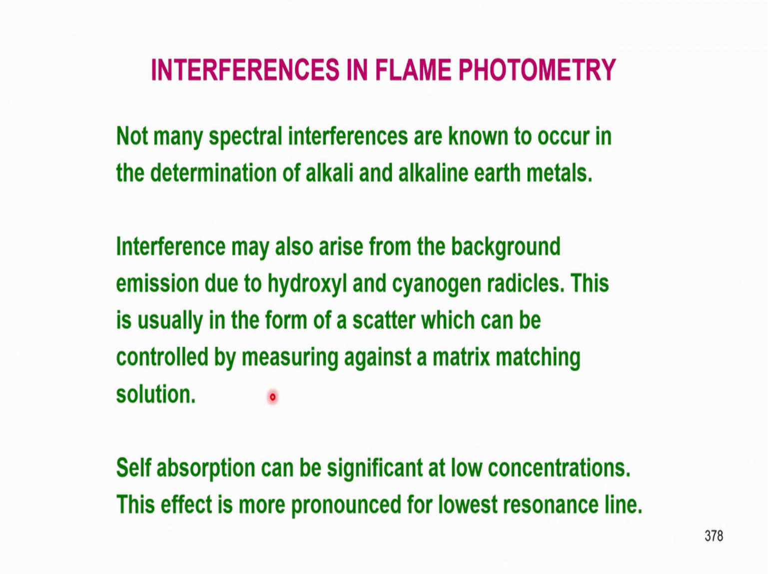

INTERFERENCES IN FLAME PHOTOMETRY

Not many spectral interferences are known to occur in the determination of alkali and alkaline earth metals.

Interference may also arise from the background emission due to hydroxyl and cyanogen radicles. This is usually in the form of a scatter which can be controlled by measuring against a matrix matching solution.

Self absorption can be significant at low concentrations. This effect is more pronounced for lowest resonance line.

We come to the other part. Obviously, that will be interferences, but not many interferences are known to occur in the determination of alkali and alkaline earth metals. So, it is almost a specific system. Interference may also arise from the background emission due to hydroxyl and cyanogen radicals. This we have seen earlier while we are discussing an absorption, atomic absorption.

This is usually in the form of a scatter which can be controlled by measuring against a matrix matching solution. So, suppose you want to determine sodium in the sea water or sodium in urine, you have to make the solution, standard solution also having almost the same ionic concentration except the analyte. So, if the sample solution is 1 percent salt solution, you have to prepare 1 percent salt solution of the standard also, but it should not contain the analyte.

So, basically it is to reduce the interference from other, all other unwanted components of the system. So, we measure basically analyte that is sodium potassium etcetera and match the salts with the similar concentrations. So, this is usually in the form of that we have seen self adsorption can be significant at low concentration self absorption. So, it can be significant at low concentrations.

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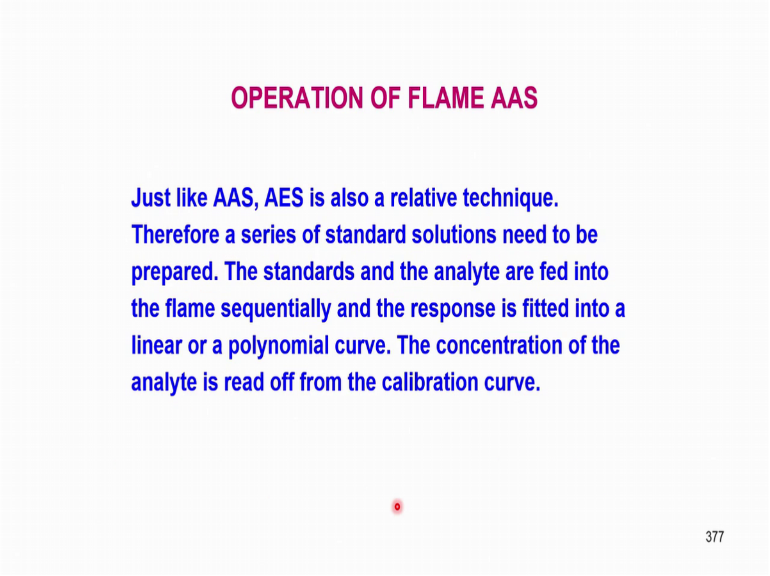

OPERATION OF FLAME AAS

Just like AAS, AES is also a relative technique. Therefore a series of standard solutions need to be prepared. The standards and the analyte are fed into the flame sequentially and the response is fitted into a linear or a polynomial curve. The concentration of the analyte is read off from the calibration curve.

So, this I have already explained to you with the example of sodium vapor lamp in the introduction of the atomic absorption. So, this effect is more pronounced for lowest resonance line.

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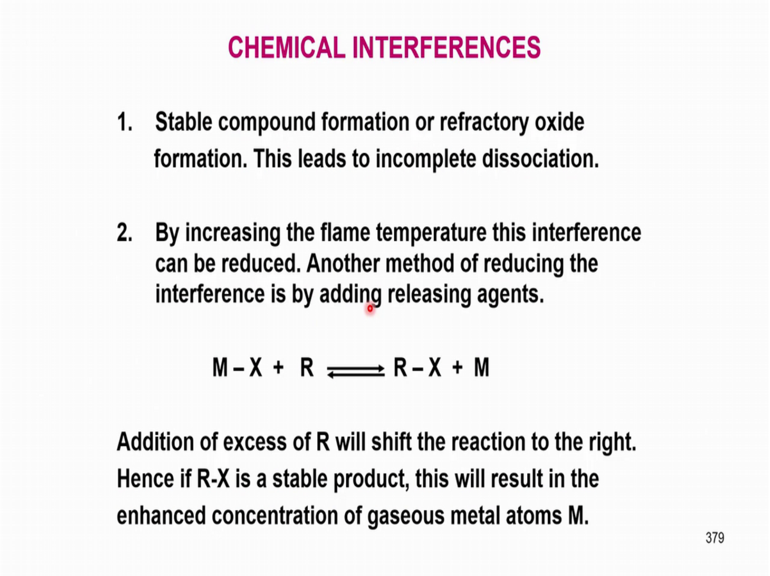

CHEMICAL INTERFERENCES

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, operation is a relative technique. Then, there could be some amount of chemical interference also. For example, some of the refractory oxide formation takes place that leads to incomplete dissociation does not melt refractory oxides, tungsten, chromium etcetera. We had discussed it earlier. So, if refractory oxide formation takes place like silicates etcetera; that leads to incomplete dissociation and lower absorbance reading, but we can increase the flame temperature by another small trick that is reducing by addition, reducing the interference by adding releasing agents.

Suppose releasing agents is R, suppose we want to analyze MX that is metal salt X is the anion part, M is the cation part. I add a releasing agent. So, what happens is, R will be replacing the X here. So, RX is formed and metal ion will be released and this addition of excess of R will shift to the reaction to the right because it is a chemical reaction controlled by equilibrium. So, if RX is a stable product, then metal will be more in the form of anion. So, it leads to enhanced concentration of the gaseous metal atoms in the flame also and that leads to enhanced transmittance reading.

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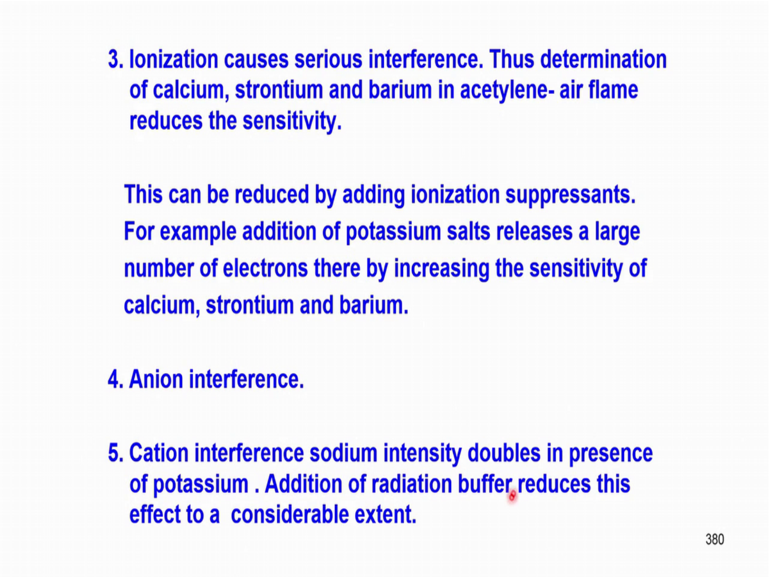

3. Ionization causes serious interference. Thus determination of calcium, strontium and barium in acetylene- air flame reduces the sensitivity.

   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.

So, ionization we do not want as usual. We do not want ionization because ionization cause a series. We want atoms and we do not want ions. That is the fundamental basis of all atomic absorption spectrometry because if ions are formed, it is useless as far as emission and absorption, we want atoms in the ground state. It should go to next higher energy state and the next higher energy state atoms have to come down to the ground state by lose of energy or through the emission in with model.

SSo, determination of calcium strontium and barium in acetylene and air flame reduces the sensitivity. Why because calcium strontium barium etcetera, they are all ions in summation. So, ionization causes serious interference. This can be reduced by ionizations suppressant also. All chemist have got small tricks up their sleeve especially with respect to interferences. For example, addition of potassium salts releases a large number of electrons which combine with the ions to form the metals.

So, if I add lithium salt, there will be lot of ions or potassium salts and these ions release number of electrons and the sensitivity of calcium, strontium and barium will increase. That means, if you want to analyze calcium strontium and barium, you add a little bit of potassium chloride or potassium nitrate. So, anion interference essentially acts the same way. We do not have the details here, but the additional details can be obtained by referring to AOSE literature, cation interference, sodium intensity doubles in front in presence of potassium.

So, you cannot determine sodium if there is potassium also. One has to be a little careful here. What you can do is, you can determine potassium first and subtract that quantity from sodium also. So, addition of radiation buffer is another trick that reduces the considerable emission from potassium.

So, some of these interferences are always you know it is a question of learning chemistry and applying the chemistry to the actual situations. Basically most of the interferences what I have already told that addition of potassium ionization suppressant, it all leads to chemistry only. So, if you know more chemistry, you will be more conversant with the use of the atomic absorption whenever there are problem cases. If there are no problem cases, instrument will do the job. So, interference due to other element lines, emission lines is quite possible

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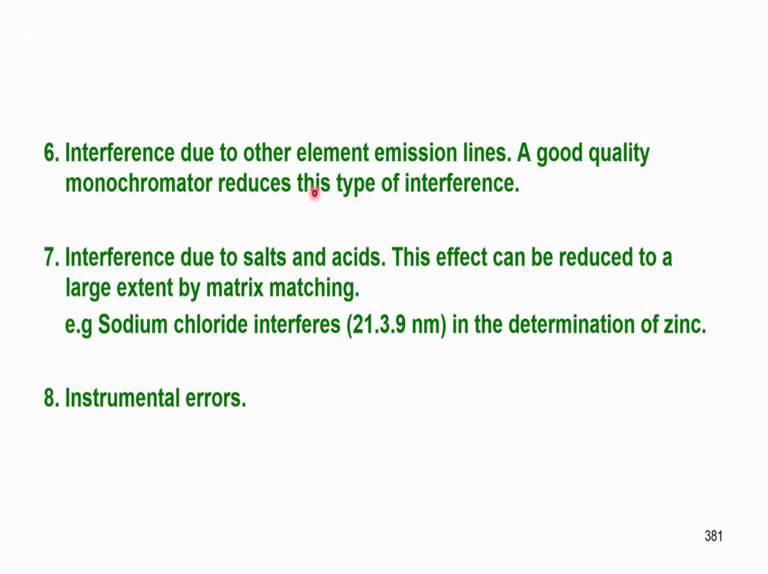

6. Interference due to other element emission lines. A good quality monochromator reduces this type of interference.

7. Interference due to salts and acids. This effect can be reduced to a large extent by matrix matching.
   e.g Sodium chloride interferes (21.3.9 nm) in the determination of zinc.

8. Instrumental errors.

That is a good quality. Monochromator is required and other emission lines may be near by. So, if I use a filter emission will be more because there will be lot of more radiation falling on the detector. So, that is a type of interference only and then, there could be interference due to salts, acids etcetera. This effect can be reduce to a large extend by matrix matching.

So, for example, sodium chloride interferes in the determination of zinc. Instrumental errors can happen all the time and here there is a small error. The sodium chloride interferes in the determination of zinc. It is 213.9 nanometers and not 21.3.9 nanometer, but actually the wavelength range is 213.9 nanometer. Please excuse me for the error. If possible we will correct it, otherwise you can correct it in your notes.

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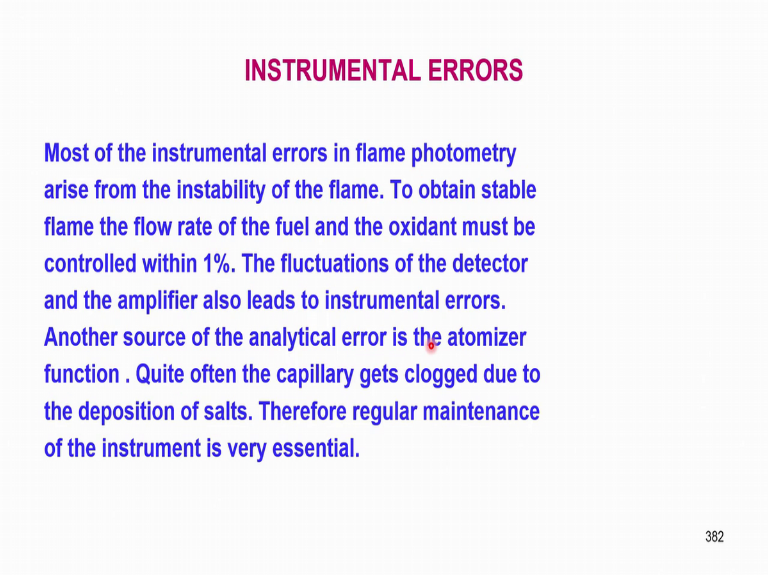

INSTRUMENTAL ERRORS

Most of the instrumental errors in flame photometry arise from the instability of the flame. To obtain stable flame the flow rate of the fuel and the oxidant must be controlled within 1%. The fluctuations of the detector and the amplifier also leads to instrumental errors. Another source of the analytical error is the atomizer function . Quite often the capillary gets clogged due to the deposition of salts. Therefore regular maintenance of the instrument is very essential.

So, instrumental errors arise from the instability of the flame because flame itself can vary like this and depending upon the gas film. So, oxidant flow and gas flow should be extremely steady during a flame atomic emission measurement. So, to obtain stable flame, what do we need is the flow rate of the fuel and oxidant must be accurately controlled within plus or minus 1 percent. If that is not the case, then there could be certain amount of variation in the flame stability.

So, the fluctuation of the detector and amplifier also leads to instrumental errors. So, we need a double beam instrument to take care of the detector and amplifier fluctuations from time to time. So, another source of analytical error that is the atomizer functions, if the nozzle gets blocked, obviously the atomic concentration in the flame will reduce the analyte. So, we have to clean the nozzle quite often and the capillary gets clogged due to the deposition of salts.

So, sometimes regular maintenance becomes very important because quite often you assume that everything is all right, but a small speck of dust or something like that if it gets into the capillary, nothing will be coming out or the sample errors all generation itself will be different.

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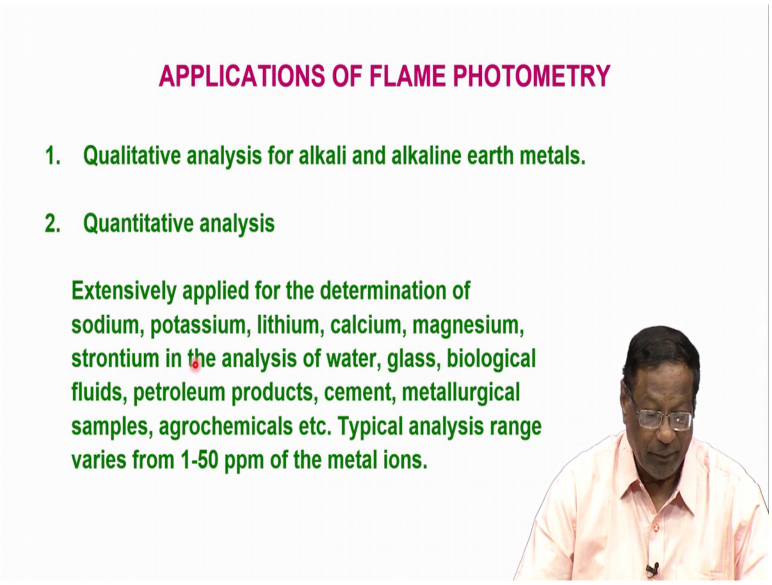

APPLICATIONS OF FLAME PHOTOMETRY

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.

So, in that case, the transmittance readings will be different. So, with this amount of knowledge we can look at the applications. One is qualitative analysis of alkali and alkaline earth metals and then, we can do the quantitative analysis, but flame atomic emission is extensively applied for the determination of only these elements sodium, potassium, lithium, calcium, magnesium, strontium, barium etcetera, but they are applied in the analysis of water glass biological fluids, petroleum products, cement, metallurgical samples, agro chemical.

The list is almost endless including even the pharmaceuticals people would like to determine the sodium and potassium concentrations. Typical analysis range varies from 1 to 50 ppm of the metal ions. Nowadays, there are instruments which will give you 1 to 5 ppm range very accurately.

So, whenever you want to buy the flame atomic absorption emission instrument independently of atomic absorption, you should check the specifications for the calibration range for all the elements that you are buying.

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ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

So, with this we will conclude our discussion on the atomic emission and then, from the next class for about 2 or 3 hours, we will discuss about electrothermal atomic absorption spectrometry which is a very good technique for the determination of elements by atomic emission, but without the flame we do it, do the vapour generation by heating. So, that is why it is known as electrothermal atomic absorption.

So, since last 30-35 years, may not be 35, but around 25 years, this technique, 30 years, this technique has gained wide popularity and commercial instruments are available that extends the determination to parts per billion level.

Thank you very much.