Modern Instrumental Methods of Analysis

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Lecture No. # 19
Atomic Absorption Spectrometry 3 Instrumentation

We were discussing about the vapour discharge lamps as a source of radiation and atomic absorption spectrometry.

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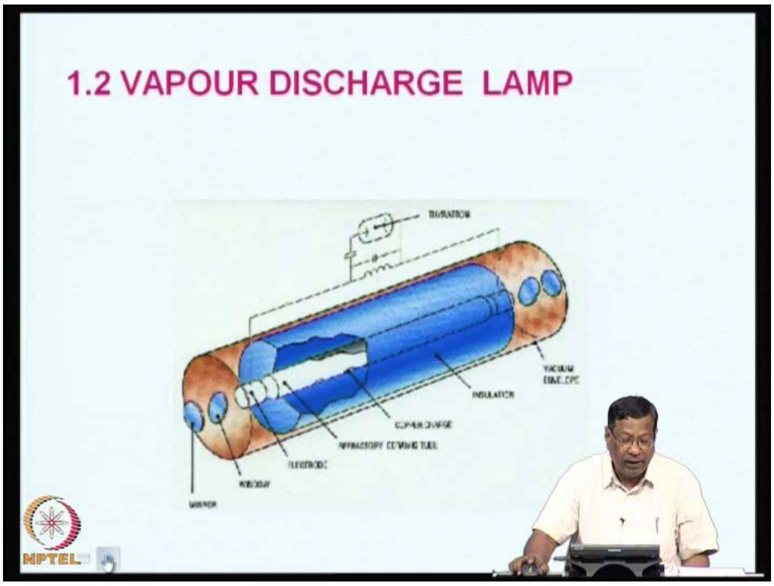

1.2 VAPOUR DISCHARGE LAMP

And I had shown you the slide in my last class, this is a very simple arrangement where the connectors are here in this range. Here we put some material and filled with argon, and then charge will be there, refractory material could be here. And with simple arrangement, we should be able to generate the, make the hollow cathode lamp, vapour discharge lamps.

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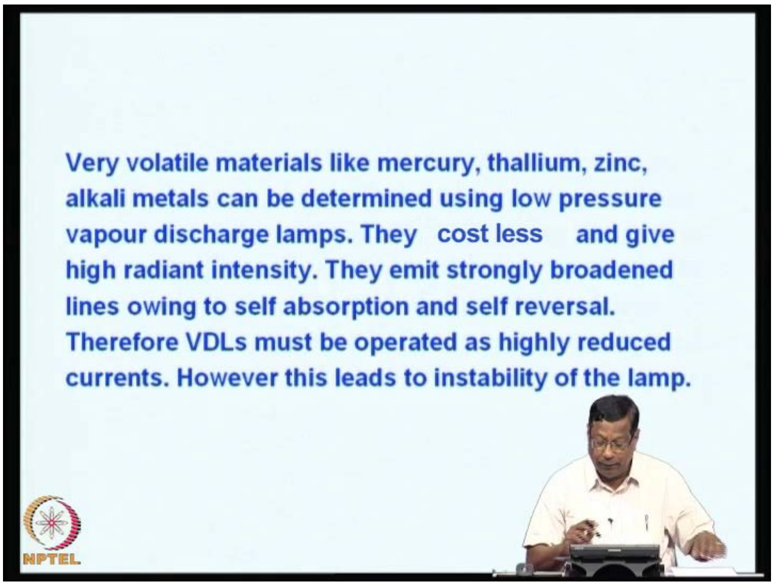

Very volatile materials like mercury, thallium, zinc, alkali metals can be determined using low pressure vapour discharge lamps. They cost less and give high radiant intensity. They emit strongly broadened lines owing to self absorption and self reversal. Therefore VDLs must be operated as highly reduced currents. However this leads to instability of the lamp.

So, very volatile materials like mercury, thallium, zinc, alkali metals, etcetera can be determined using low pressure vapour discharge lamps, they offer low cost and give high radiant intensity, they emit strongly broadened lines owing to self absorption and self reversal.

Therefore, vapour discharge lamps must be operated as at highly reduced currents, however this leads to instability of the lamp. So, it is important for us to operate them at high radiant intensity, at the same time the, another rider is the highly reduced currents if you operate, it leads to instability of the lamp.

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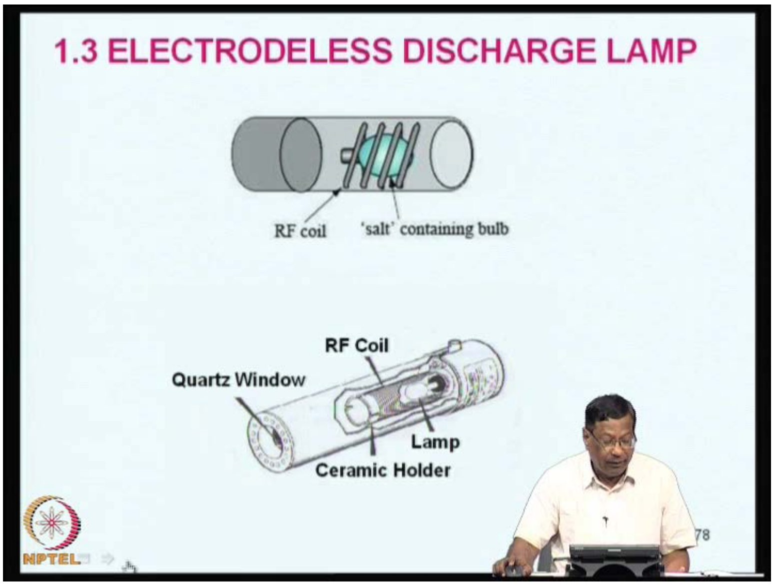

1.3 ELECTRODELESS DISCHARGE LAMP

So, now we will move on to electrode less discharge lamps another source, this is the picture of an electrode less lamp. So, what we have here in the slide is, we have a material which is put in this green region and then it is surrounded by RF coil. And then it contains the material, contained salt and it may be enclosed in a bulb and other other aspects remain the same, that is ceramic holder through which RF radiation is passed. And then we have the lamp, ceramic holder is required to give the structural stability, mechanical stability also and the, this part is glass and the window is quartz window, because most of the elements in the atomic absorption have resonance lines in the ultraviolet region.

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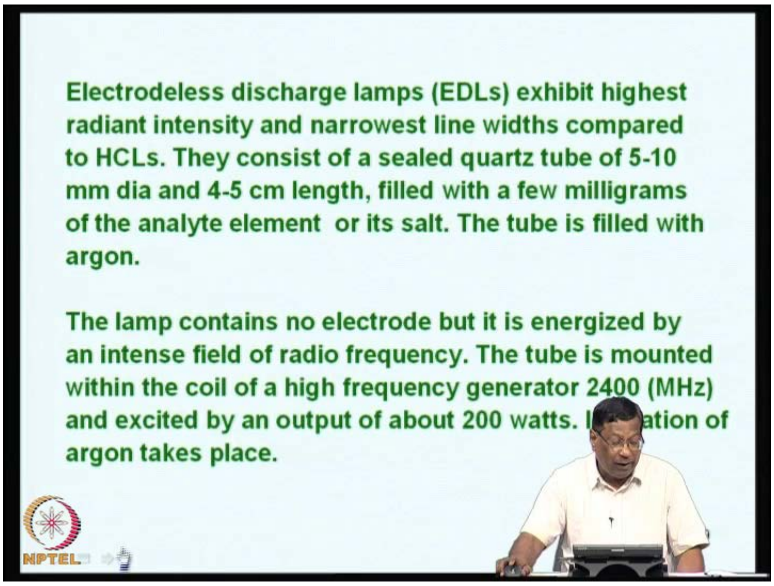

Electrodeless discharge lamps (EDLs) exhibit highest radiant intensity and narrowest line widths compared to HCLs. They consist of a sealed quartz tube of 5-10 mm dia and 4-5 cm length, filled with a few milligrams of the analyte element or its salt. The tube is filled with argon.

The lamp contains no electrode but it is energized by an intense field of radio frequency. The tube is mounted within the coil of a high frequency generator 2400 (MHz) and excited by an output of about 200 watts. I[illegible]ation of argon takes place.

So, basically these EDLs as they are called, electrode less discharge lamps exhibit highest radiant intensity and narrowest line widths compared to hollow cathode lamps. They consist of a basically sealed quartz tube of 5 to 10 mm dia and 4 to 5 centimeter length. And they are filled with a few milligrams of the analyte element or its salt, the tube is filled with argon. The lamp contains no electrode basically, but it is energized by an intense field of radiofrequency. The tube is mounted within the coil of a high frequency generator of about 2400 megahertz and excited by an output of 200 watts. Ionization of argon takes place and sets up the radiation.

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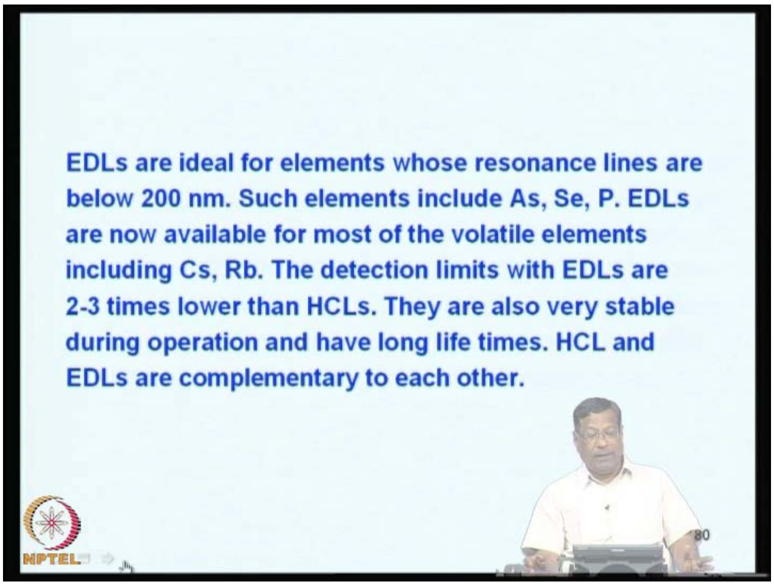

EDLs are ideal for elements whose resonance lines are below 200 nm. Such elements include As, Se, P. EDLs are now available for most of the volatile elements including Cs, Rb. The detection limits with EDLs are 2-3 times lower than HCLs. They are also very stable during operation and have long life times. HCL and EDLs are complementary to each other.

EDLs are ideal for elements whose resonance lines are below 200 nanometers. As I have explained earlier, below 200 lines, 200 nanometers we have the optical problems of selection of the wavelength. So, such elements usually include arsenic, selenium, phosphorus, and etcetera. And EDLs are now available for most of the volatile elements including caesium and rubidium, the detection limits what you obtain out of EDLs are about 2 to 3 times lower than hollow cathode lamps, to that extent they are superior to hollow cathode lamps.

But you cannot make EDLs for all kinds of elements, only some of the elements whose resonance lines are below 200 nanometer, 193.7, 197.5, like that. If the resonance lines are there, then we should go for EDLs the otherwise, suppose you use hollow cathode lamp for such elements, you will always end up with problems of the detection limits. So, the detection limit would be higher, spectral purity will not be there, etcetera, such problems such problems usually contribute to the general difficulties of the analysis.

They are the EDLs, are also very stable during the operation and they have long lifetimes, usually HCL hollow cathode lamps and EDLs, that is electrode less discharge lamps are complimentary to each other. That means, when you cannot use a hollow cathode lamp, look for EDLs or vapour discharge lamps. But the first choice is always hollow cathode lamps, followed by EDLs for specific elements. Now, we can take a look at other sources like continuum sources also, and we know that we have the continuum radiation from almost all elements including hydrogen, xenon and halogen lamps etcetera, they also offer good stability, they are cost effective and exhibit multi element capability.

However, there is again a rider owing to the low intensity of the chosen wavelength, high demands on the monochromator to produce wavelengths of 0.002 nanometer accuracy, so risk of spectral interferences are also there. So, in general continuum sources are not preferred, because when you select a wavelength band of about 0.002 2 nanometers, the intensity of the radiation is reduced to a large extent as compared to hollow cathode lamps.

Therefore, they have not become popular, but still they have been used for research purposes and several other things. But in general, most of the manufacturers do not give you continuum sources as a standard accessory, standard radiation source. They offer hollow cathode lamps and then EDLs, otherwise vapour discharge lamp, these three are safe enough for regular usage of atomic absorption spectrometer. So, now we move on to atomizers, that is second part of the instrumentation, atomizers usually the job is to transfer a liquid sample into atoms, that is why we call them atomizers, this is easily accomplished by spraying the analyte solution into the flame. So, you sprayed, the water will evaporate and then solvent will evaporate, salts will remain, the salts will decompose into ions which will pick up electrons from the flame and form the atoms.

So, other techniques of atomization include electro thermal evaporation and hydride technique also you can use, cold vapour technique you can use, these things we will be discussing later.

In general, the success or failure of atomic absorption determination of any element is virtually dependent upon the efficiency of atomization that is the total number of atoms that are formed in the flame environment; you can say that higher the atomization better is the sensitivity. That means, you can go down the lower order of determination that is most important in trace and ultra trace element analysis.

So, the, for this purpose we use nebulizers, pneumatic nebulizers and nebulizer is a very useful instrument to spray the sample into the flame in a continuous manner. So, we can maintain steady supply of the atoms, usually nebulizers are connected to the flame burner which can be considered as a single unit, that a nebulizer and the flame together constitute a single component of an instrument, even though both nebulizers can be nebulizer can be separated from the flame, flame attachment and the vice versa. So, you can take out the nebulizer, clean it and then refit it to the flame compartment and then you can use them.

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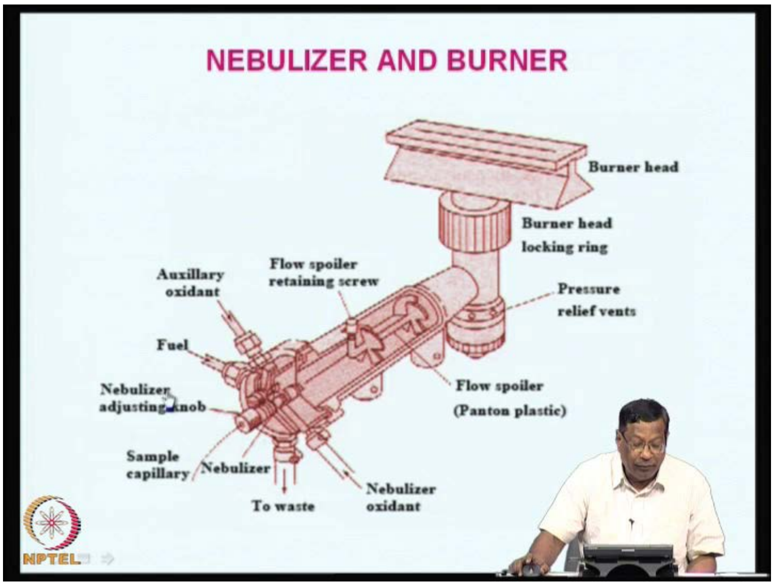

NEBULIZER AND BURNER

Typical design of a nebulizer is shown here, in this figure you can see the part on the left side is this part is nebulizer, here you can see lot of baffles, they are also called as flow spoilers.

So, the liquid will be sucked through a capillary, sample capillary and then released into this tube, which are fitted with flow spoilers or baffles. And then the required force to suck the liquid comes from the fuel and the auxillary oxidant and nebulizing, you can have a sort of a control to change the aspiration rate. So, what we have here is a nebulizer adjusting knob which connects the capillary and then some drops remain here, some drops will form really very small droplets and they are carried along with the auxiliary oxidant and fuel into the flame, into the burner.

And the force of the of the fuel and the oxidant is enough to suck the liquid into the nebulizer and usually the nebulizers have about 15 percent efficiency. And you can see that the, whatever is sucked along with the along with the gases is fed into this burner where it opens up in a flat steel plate or a titanium plate with a slotted burner, burner head. That means, there is a small opening of about 0.5 mm on the top of the burner which you can light it, just like you light it in your house any gas equipment. So, we have a burner head, locking ring, pressure relief vents and burner are the other components, burner head are the other components. In general, both these two units can be taken out, clean separately and used as such.

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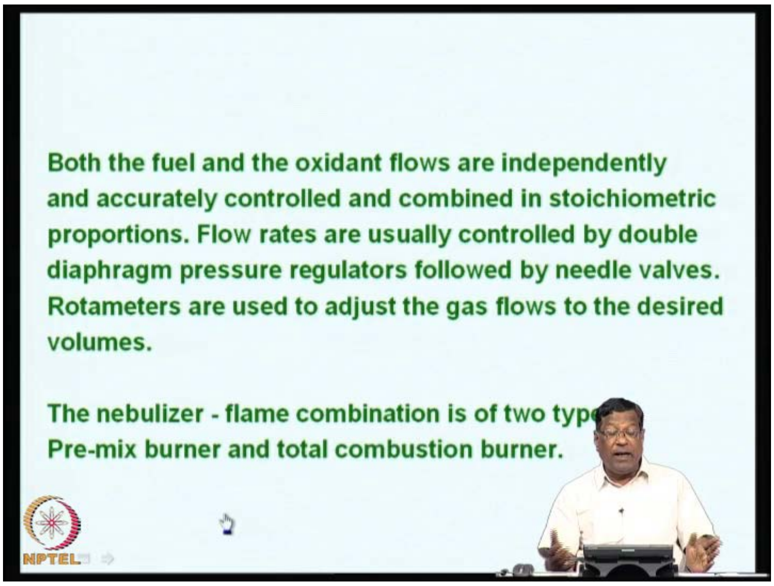

Both the fuel and the oxidant flows are independently and accurately controlled and combined in stoichiometric proportions. Flow rates are usually controlled by double diaphragm pressure regulators followed by needle valves. Rotameters are used to adjust the gas flows to the desired volumes.

The nebulizer - flame combination is of two typ
Pre-mix burner and total combustion burner.

So, both the fuel and oxidants are independently, accurately controlled, you have to control them very accurately, the flow rates. And you can combine them in stoichiometric proportions to light the fuel and when you light the fuel, you need oxygen. So, you call the other gas that is the auxillary gas as the oxidant, and the flow rates of both the oxidant gas, it can be air or it can be nitrous oxide or something like that.

And both these flow rates must be controlled very accurately and using double diaphragm pressure regulators followed by needle valves. So, it is an engineering component, well engineered component and to control the flow rates, you need rotameters, so to adjust the gas flows to the desired volumes. So, the nebulizer flame combination, there are two types; one is pre-mix burner, another is total combustion burner.

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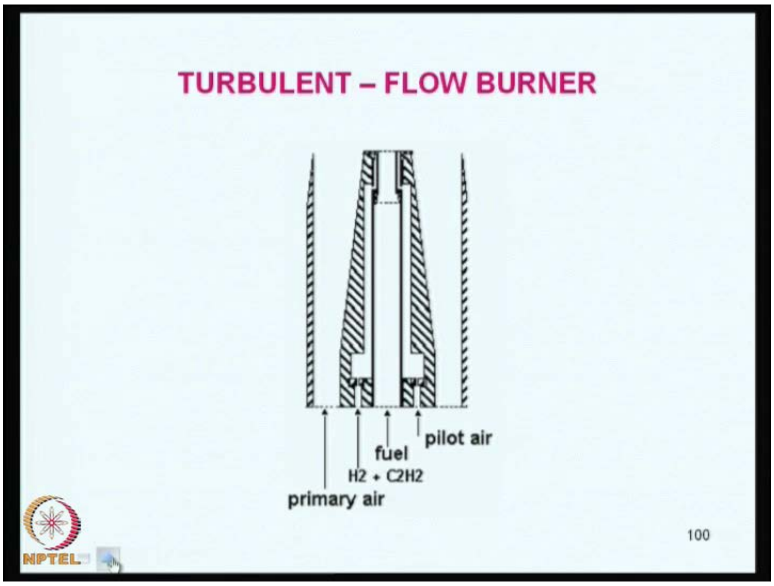

TURBULENT – FLOW BURNER

I will show you here in this figure, the oxidant and the fuel are premixed and then coming here together to burn at the slotted space, this is known as premix burner. And another way is to look a figure like this, you take the fuel hydrogen in one shot and pilot air in another slot, take the fuel that is a sickling gas and then you can also mix it to the air, here all of them are not being mixed initially.

So, all of them will come and join near the burner head, this is the slot and they will burn in a single as a single unit, but they will be mixing only at the time at the base of the burner. So, there are two types of burners, one is premixed another is total combustion burner and both have lot advantages as well as disadvantages.

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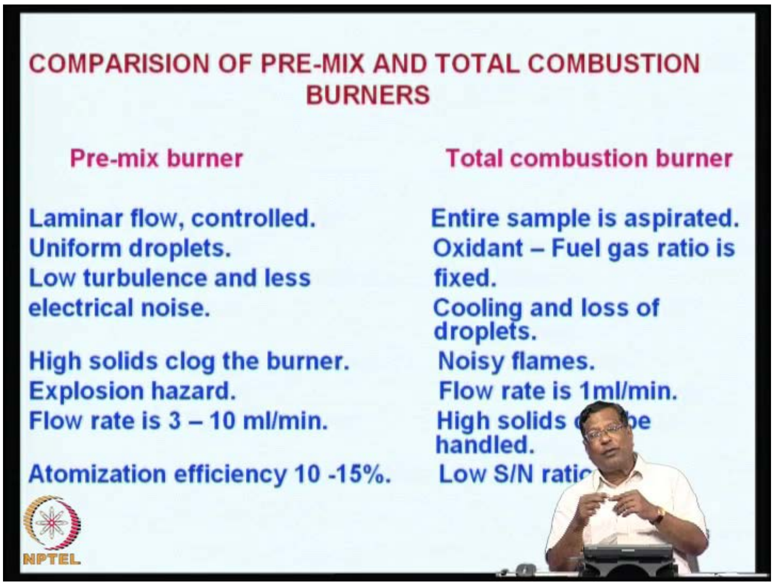

COMPARISION OF PRE-MIX AND TOTAL COMBUSTION BURNERS

Pre-mix burner	Total combustion burner
Laminar flow, controlled.	Entire sample is aspirated.
Uniform droplets.	Oxidant – Fuel gas ratio is fixed.
Low turbulence and less electrical noise.	Cooling and loss of droplets.
High solids clog the burner.	Noisy flames.
Explosion hazard.	Flow rate is 1ml/min.
Flow rate is 3 – 10 ml/min.	High solids [illegible] be handled.
Atomization efficiency 10 -15%.	Low S/N rati

So, a general comparison of the premix and total combustion burner, we can say that in the premix burner, we have laminar flow which is controlled and you get uniformed droplets and bigger droplets get collected contents and then they are removed as waste. So, low turbulence is another advantage and therefore, which leads to less electrical noise. So, suppose you have high solids, it clogs the burner, because when it comes near the edge of the burner, these high solids will stick to the burner slot and the gas will not be burning comfortably.

So, there will be gaps and then stop edges and then gas may extinguish or it may backfire due to pressure when the gas is not burning, but it is coming inside the burner. So, this is a slight disadvantage of the premix burner, now in the previous slide what we have seen is this may lead to explosion.

In general still it is preferred, because the burner heads are usually cleaned for almost every operation, if there is suspicion of clogging, this things happen only when you are analyzing high solids substances. That means, samples containing high solids such as sea water, urine, plasma, serum, etcetera, usually the flow rate in premix burner is of about 3 to 10 milliliter per minute. So, atomization efficiency is also of the order of about 10 to 15 percent only, remaining 85 percent goes waste, and this is one of the critical aspects of atomic absorption spectrometry. So, you should get very high efficiency, if you get very high efficiency if you get very high efficiency of atomization your deduction limit would be much better. That means, you can go down to very low levels of deduction of the order of 0.1 PPM, parts per million. So, in comparison, the total combustion burner its it has the sample also joins the burner head at the top along with the gases.

So, there is no question of wastage, but if the droplets become more, the temperature of the flame will get reduced. Because the (( )) parts etcetera, (( )) components, they need to be removed and evaporated by evaporation only. And the efficiency comes down, because the flame temperature comes down, even though we know the flame temperature does not have much influence on the production excited atoms, but still to some extent, this is always the problem in atomic absorption spectrometry.

So, the cooling and loss of droplets, cooling of the flame and loss of droplets is always a problem in total combustion burners and another problem is it gives you a noisy flame, noisy means electrically noisy. It may burn silently, but the flame is not, does not have stability, sometimes it increases in length, sometimes it increases the, in different colours, oxidizing, reducing, and etcetera.

So, this flame character changes quite often in total combustion burner; that means, the temperature of the flame will not be very uniform. So, in general it leads to noisy flame and noisy flame means, electrical noise will be more and the deduction limits suffer.

So, the flow rate is also of the order of about 1 mL per minute, you have to be very careful to draw only 1 mL per minute of the sample so that you can atomize the sample. So, an advantage of this in comparison to premix burner is that, it can handle high solids, high percentage of solids and signal to noise ratio is always lower.

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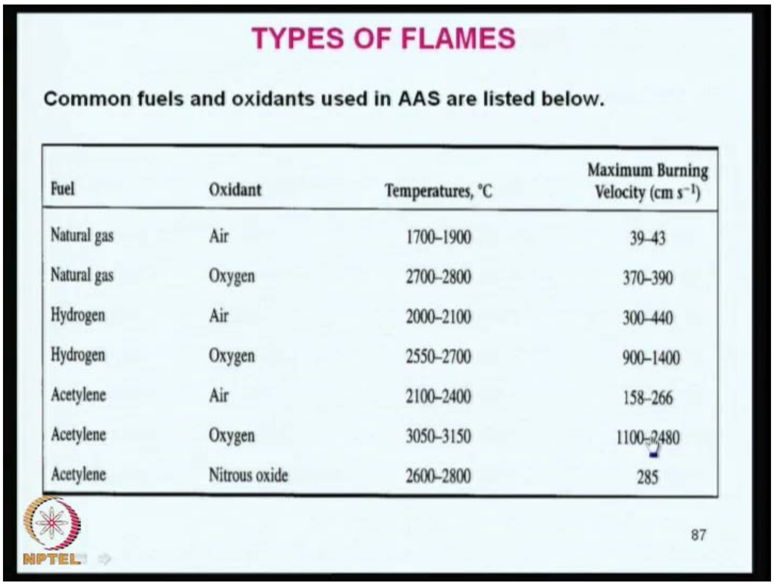

TYPES OF FLAMES

Common fuels and oxidants used in AAS are listed below.

Fuel	Oxidant	Temperatures, °C	Maximum Burning Velocity (cm s^{-1})
Natural gas	Air	1700–1900	39–43
Natural gas	Oxygen	2700–2800	370–390
Hydrogen	Air	2000–2100	300–440
Hydrogen	Oxygen	2550–2700	900–1400
Acetylene	Air	2100–2400	158–266
Acetylene	Oxygen	3050–3150	1100–2480
Acetylene	Nitrous oxide	2600–2800	285

So, you can choose different kinds of oxidant and fuels. In general natural gas can be used along with air and the temperature, what you are seeing here is of the order of about 1700 to 1900 degrees centigrade. So, the maximum burning velocity is also of the order of about 39 to 43 centimeters per second. Suppose, you replace air with oxygen, that means, you are giving more oxidizing capability, then the temperature of the flame increases to 2700 to 2800 and then burning velocity also you can see that, it increases almost 10 times from 39 to 370. Suppose, you use hydrogen and a hydrogen also burns in the burns giving water and air is the oxidizer, the normal flame temperature would be 2000 to 2100 and the burning velocity is about 300 to 440, you can replace again air by oxygen, then you get 2500 to 2700 degree centigrade in the flame.

But again, we look at this number that is burning velocity that is about 900 to 1400 centimeters per second. That means, we will be using an enormous amount of gas in the atomic absorption instrument.

So, for all these reasons, all the natural gas and hydrogen are not preferred even though studies have have been conducted, research has been conducted in using natural gas and hydrogen, air, oxygen mixtures. But if you use acetylene and air, you will almost end up with the same temperature like 2100 to 2400 and the burning velocity is also less of the order of about 115 158 to 266. That means, you will be consuming less acetylene and more more oxygen and your temperature also would be of the order of about 2400, that means, there is no loss of atomization efficiency.

You replace that with oxygen, you would have about 3050 to 3150 degree centigrade and again look at the burning velocity that is of the order of about 1100 to 2480 centimeters per second that is very high. You can choose acetylene nitrous oxide, nitrous oxide as the oxidant and you will see that the temperatures of the order of about 2600 to 2800 and the burning velocity is of the order of about 285 centimeters per second.

So, you have a choice of several gases as fuel as well as oxidizers, but regular in regular practice, acetylene and air is preferred for most of the elements and acetylene oxygen is not preferred. But it can be employed, all we have to do is have two cylinders, one made of acetylene, another made of oxygen or simply use a compressor to pass the air or you can use a cylinder, compressed cylinder with oxygen cylinder, with oxygen another possibility, another good choice is acetylene and nitrous oxide. So, standard gases for atomic absorption are these last three, that is, acetylene air and acetylene nitrous oxide and acetylene oxygen in that order.

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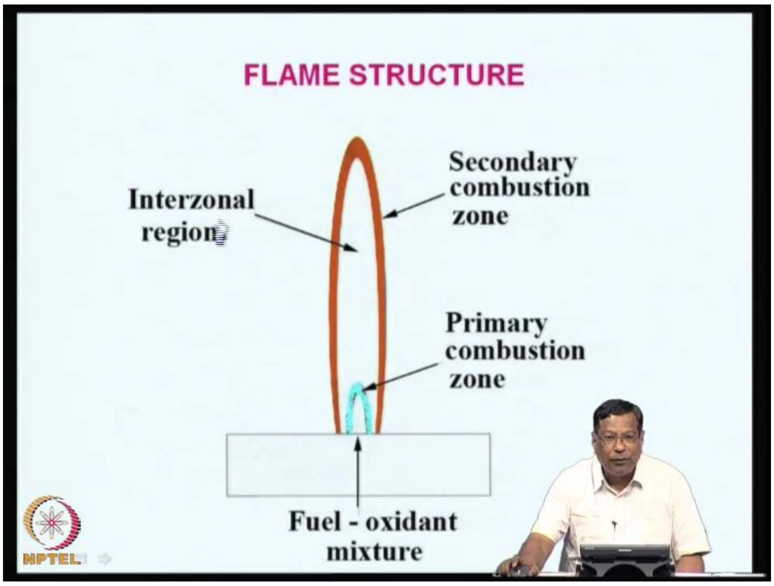

FLAME STRUCTURE

So, let us try to look at how a flame looks, this is a interesting aspect of the atomic absorption.

In general, if you try to remember how a flame looks in your gas in your gas at home, you would see that at the bottom of the burner, you would see a slightly greenish zone. It is burning with a green zone, and then there is another blue zone above that and then there is a red zone which is at the periphery of the flame (Refer Slide Time: 26:25).

So, this is now the green zone is known as primary combustion zone, this green one and this white one what I am showing is normally a blue flame, this is known as secondary combustion zone and at the edge you will see that the flame is burning with a reddish tinge, this is because it sucks oxygen from the air and the oxygen will combine to give you reddish flame (Refer Slide Time: 26:59). So, whenever you see any flame, you would be seeing all these three, if you have good observation power and provided the gas mixture is in proper proportion.

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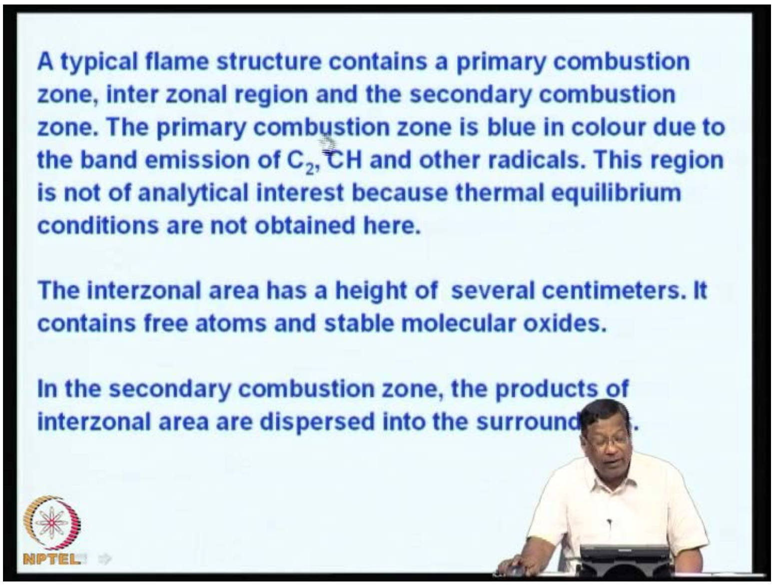

A typical flame structure contains a primary combustion zone, inter zonal region and the secondary combustion zone. The primary combustion zone is blue in colour due to the band emission of C_2, CH and other radicals. This region is not of analytical interest because thermal equilibrium conditions are not obtained here.

The interzonal area has a height of several centimeters. It contains free atoms and stable molecular oxides.

In the secondary combustion zone, the products of interzonal area are dispersed into the surround .

So, a typical flame structure is always like this, the primary combustion zone is blue in colour due to the band emission of C 2, C H and other radicals, the whenever gases burn, acetylene is basically C 2 H 2. And the carbon atoms burn and react with hydrogen coming from the coming from the acetylene only and they break into different small smaller smaller molecules like C 2 C H and other radicals.

And then these species, when they burn in the flame, they give rise to blue flame or green flame. This region is not of analytical interest, because the temperature is much lower at the base of the flame, slightly higher higher height of the flame, the temperature will be more. So, if you are looking to use this green flame, please do not, because thermal equilibrium conditions are never obtained at the base of the flame.

So, what you should look for is, the inter zonal area where you see blue flame which is steady and it has a height of a several centimeters. This contains free atoms coming from the sample as well as stable molecular oxides that is oxides C O, C O 2, etcetera and then metal oxides also could be there. And in the secondary combustion zone, where it mixes it air from the surroundings that is from the environment, the products of inter zonal area are dispersed outside to the environment.

So, all these gases will keep on coming out whenever you are aspirating a sample using acetylene as well as air or nitrous oxide. And these gases when they burn, they being lighter, they escape into the atmosphere, therefore above the instrument, above the flame you should have a suction so that all these species are sucked out and let out into the environment. So, a good suction unit is placed above the burner so that the flame can be maintained under controlled conditions.

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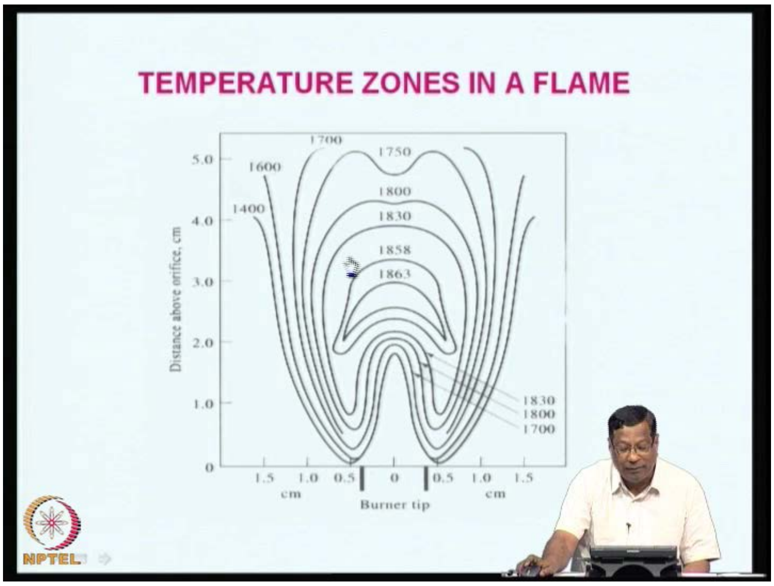

TEMPERATURE ZONES IN A FLAME

So, here I am going to show you the different temperature zones of the burner, here I am, here this is the burner tip and I have put here, the centimeter distance from the burner tip. This is 0.5, 1 and 1 .5, on the other side also you can we can have the same scale and on the (()) abscissa, I have put distance above the orifice where the flame is burning that is 1, 2, 3, 4, 5 centimeters.

Now, if you take the temporal spaces temporal space, you can see that temperature of about 1400 is obtained along these along the bottom line and then all over this you would, around this range you will get 1400 degree centigrade. Slightly inner, deeper if you go inside the flame, it increases to 1600 and then outs here it is 1700. So, it keeps on increasing and in the blue flame, somewhere around above 2 or 3 centimeters, you are you will end up with 1700 to 1800 degree centigrade.

So, this is the region of interest for us, where we need to pass the radiation from the hollow cathode lamp like this and then it must pass though the atom, atom population is mostly concentrated in this region (Refer Slide Time: 32:30).

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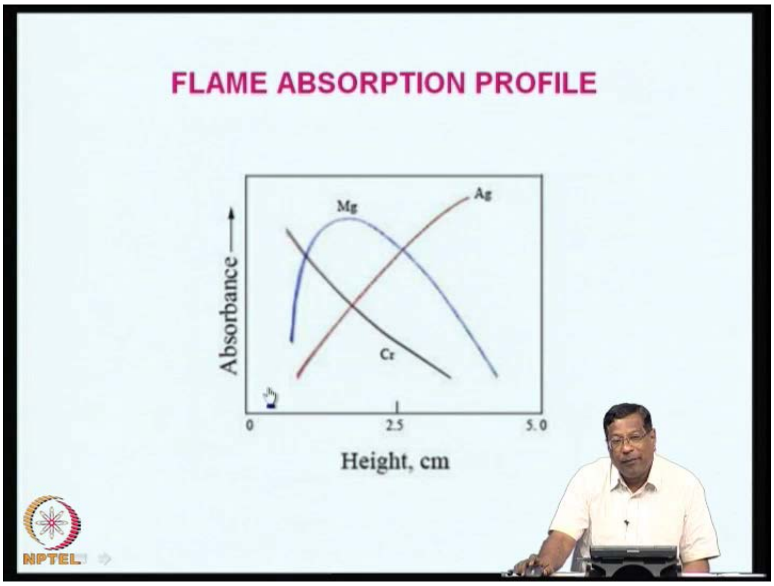

FLAME ABSORPTION PROFILE

So, sometimes it is important to decide the, at what height the radiation should pass through, like I was showing you that you can pass the radiation around 1 centimeter height, or 2 centimeter height, 3 centimeter height, 5 centimeter height, all you got to do is position your hollow cathode lamp at that height above the flame.

Now, if you do that, you can see that if the height is about 2.5, as you increase the height, for silver absorbance keeps on increasing, that means, it can the sensitivity increases. But for chromium, if you increase the height from 0 to about 3 centimeter, the sensitivity keeps on coming down, down and down. For magnesium it is the other way round, first it increases and up to after about 11.5 centimeter height, the signal keeps on coming down. Therefore, it is important for us to know at what height, the flame should be fixed through which the radiation is supposed to pass through. So, in general 5 centimeter about between 3 and 5 centimeters is the chosen height.

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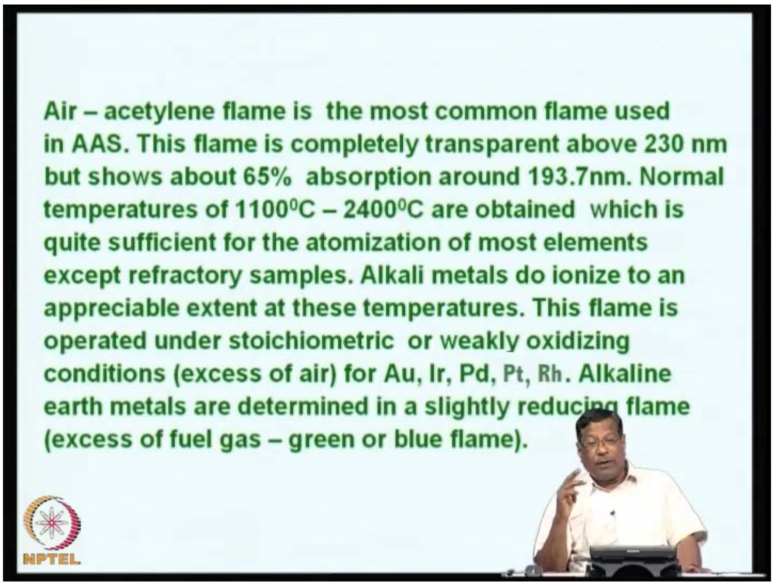

Air – acetylene flame is the most common flame used in AAS. This flame is completely transparent above 230 nm but shows about 65% absorption around 193.7nm. Normal temperatures of 1100^{0}C – 2400^{0}C are obtained which is quite sufficient for the atomization of most elements except refractory samples. Alkali metals do ionize to an appreciable extent at these temperatures. This flame is operated under stoichiometric or weakly oxidizing conditions (excess of air) for Au, Ir, Pd, Pt, Rh. Alkaline earth metals are determined in a slightly reducing flame (excess of fuel gas – green or blue flame).

So, air acetylene is the most common flame used, this is completely transparent above 230 nanometers. That means, you can see through the flame even though it is burning and but as you go down the wavelength, it shows about 65 percent absorption around 130 193.7 nanometer, this is the resonance line for arsenic.

So, you cannot use, you cannot determine arsenic using this radiation, air acetylene flame. So, normal temperatures of about 1100 to 2400 degree centigrade are obtained which is quite sufficient for the atomization, this point we have already covered, but this temperature you just, not good enough for refractory elements. So, refractory elements like vanadium, molybdenum, chromium, tungsten, etcetera, they form oxides. And oxides need higher temperature of the order of about 3000 degree centigrade to decompose and then produce atoms.

So, except alkali, except refractory metals, these these gases are fine, you can use them. Alkali metals present another kind of problem, because they ionize to an appreciable extent at these temperatures. We have seen in our previous discussion that at 2000 degrees, 3000 degrees, 4000 degree centigrade, the ionization increases much more for alkali metals and alkaline earth metals. So, that is also not very good, but we can sort out those problems provided we operate under stoichiometric conditions, this is very important for us.

So, we have to understand at what temperature, optimum burning takes place or we can go for weakly oxidizing conditions. That means, when you use gas you will get two types of fire, when you use oxidizing conditions more or reducing conditions more. So, when you get oxidizing conditions that you are using more air and less fuel.

So, the flame will be burning with a reddish reddish tinge and when you use excess fuel and less air, there is not enough oxidation. So, it is called a reducing flame and oxidizing conditions are good for gold, iridium, palladium, and then platinum, and rhodium, alkaline earth metals are determine usually in slightly reducing flame.

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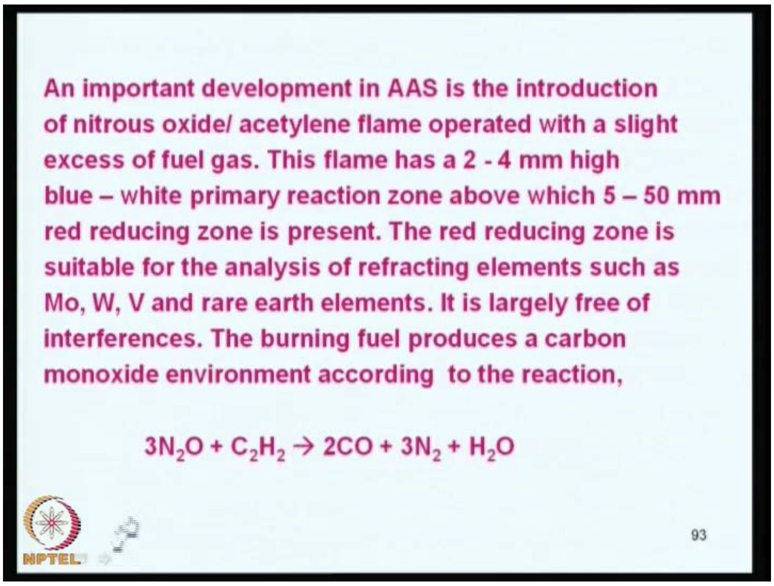

An important development in AAS is the introduction of nitrous oxide/ acetylene flame operated with a slight excess of fuel gas. This flame has a 2 - 4 mm high blue – white primary reaction zone above which 5 – 50 mm red reducing zone is present. The red reducing zone is suitable for the analysis of refracting elements such as Mo, W, V and rare earth elements. It is largely free of interferences. The burning fuel produces a carbon monoxide environment according to the reaction,

$$3N_2O + C_2H_2 \rightarrow 2CO + 3N_2 + H_2O$$

So, there is always a possibility for us to play around the composition of the gas sothat we can determine the element at its highest sensitivity. Now, another important development in atomic absorption occurred almost at the same time around 1960 s is that, the introduction of nitrous oxide and acetylene flame operated with a slight excess of fuel gas. This flame has a height of about 2 to 4 millimeter height, it shows high blue colour and white blue white primary reaction zone above which up to 5 centimeter, 5 to 50 centimeter it shows red reducing zone. And this temperature, the temperature here in this range between 5 and 50 millimeter is always very high.

So, the refractory elements also can be used and atomized at these temperatures, so molybdenum, tungsten, vanadium, many of the rare earth elements, they all form oxides when you burn them. And to analyze such elements, we need the nitrous oxide and acetylene flame; it is largely free of interferences also. And the burning fuel produces a carbon monoxide environment according to this reaction, that is, nitrous oxide and C 2 H 2, it produces carbon monoxide, nitrogen and water vapour. So, this is a very important development in the atomic absorption analysis.

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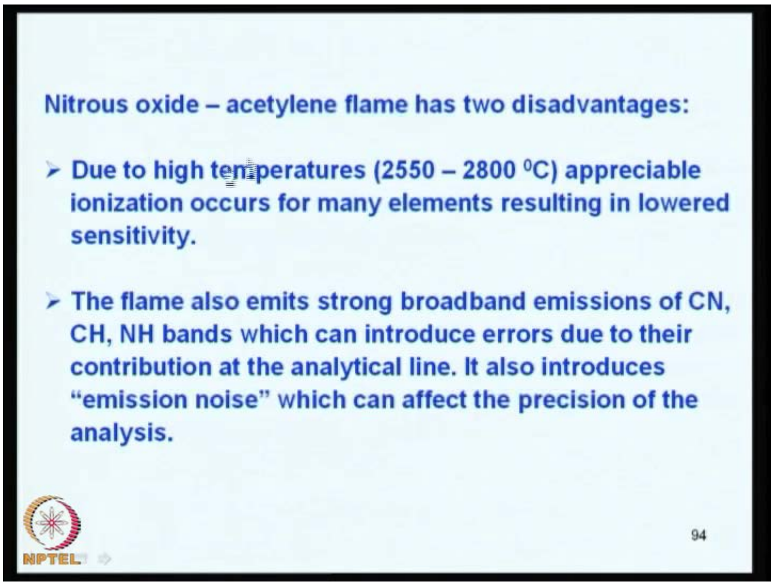

Nitrous oxide – acetylene flame has two disadvantages:

- **Due to high temperatures (2550 – 2800 ^{0}C) appreciable ionization occurs for many elements resulting in lowered sensitivity.**
- **The flame also emits strong broadband emissions of CN, CH, NH bands which can introduce errors due to their contribution at the analytical line. It also introduces "emission noise" which can affect the precision of the analysis.**

So, is it good? Yes basically it is good, but even nitrous oxide, acetylene flame has got two disadvantages, one is that due to high temperature employed that is of the order of about 2500 to 2800 degree centigrade, appreciable ionization occurs and to that extent, the production of the atoms decreases. So, your sensitivity decreases, because of the appreciably ionization.

So, another problem is the flame also emits strong broadband emissions, because you can see the red colour what you observed in nitrous oxide flame, also we will have some sort of absorption in the UV and visible range. So, these things produce cyanogen and then C H and N H bands which can introduce errors due to their contribution at the analyte line, it also introduces emission noise.

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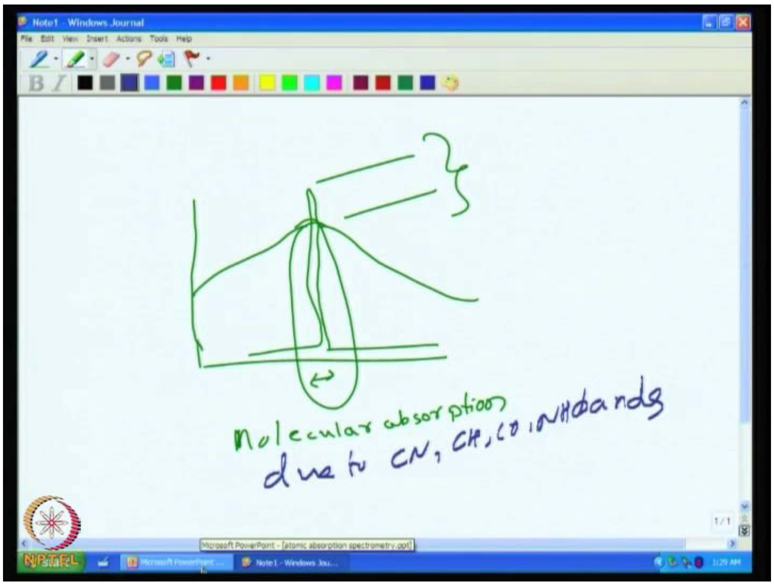

For example, if you have your emission line is like this, very small emission line and your molecular absorption due to cyanogens, etcetera, this is the absorbance (Refer Slide Time: 41:00). So, at this wavelength the signal will be attenuated to this level.

So, this can lead to reduction in sensitivity, because signal is already attenuated and what you will be measuring is only a small portion of the emission line, absorption line intensity. So, this should not happen especially, because of the molecular absorption (No audio from 49:54 to 42:05) due to (No audio from 42:07 to 42:17) C N, C H, C O, N H bands, this is a problem with with these nitrous oxide and acetylene flames. So, one has to use them very carefully, but the analytical sensitivity is always more whenever you are handling nitrous oxide and acetylene, for this reason it is a preferred combination.

In general, when you want to buy an atomic absorption spectrometer, you will have to decide which type of gas and oxidizer mixture you would like to be utilizing. So, for acetylene and air, premix burner is available and when you want to determine the refractory elements, you have to go for nitrous oxide and acetylene.

So, the burner design has to be changes, burner design changes in atomic absorption. So, when you want to buy an instrument, the manufacturer will ask what type of elements you want to analyze. If you want to analyze the non refractory elements, he will suggest, buy a premix burner and use it, it will be good enough, he will ask what what are the refractory oxides you would be analyzed, refractory metals. And if you are going to analyze molybdenum, molybdenum vanadium, tungsten, rare earth oxides, he would suggest nitrous oxide and acetylene and the you have to, the burner head also changes, burner design changes along with the nitrous oxide and acetylene. So, sometimes what people do is especially research organizations, they will they prefer to have both the sample, both the gases; in that case, you have to buy nitrous oxide acetylene burner head as an accessory. So, whenever you change over to from acetylene air to nitrous oxide and acetylene, you have to change the burner also, nebulizer also, that is why, nebulizer and burner are coming as a single unit, but they can be separated and cleaned that is an essential requirement of the burner.

So, this point if you remember, you would know which gases to buy and which burners heads you need to have. So, in addition to the composition of the gas mixture,. you will remember that I was talking about the burning velocities of the gases. If the gas flow rate does not exceed the burning velocity then what happens, the question is, will it burn or not? The flame, if the gas flame may extinguish if the gas flow rate is less; that means, the flow rate of acetylene, if it is less and if you are low only more air, the gas may not burn and the flame sometimes if it, the flame instead of extinguishing it propagates back into the nebulizer and into the cylinder and there are changes of explosion.

So, you must have good burning velocity recommended by the manufacturer to employ for the analysis. At high flow rates, suppose you use very high flow rates, then what happens, the flame will, flame height will increase and eventually it reaches a point where it blows off the burner. That means, it will be burning at very high, not very high at not at the slotted base, but it will burst out burning at a particular height, you will be able to see the flame only above 1 centimeter, 1.5 centimeter like that. And eventually if you still increase, you may not see the you may not see the flame at all. So, it blows off the burner, therefore it is very important to adjust the flow rate of the fuel oxidant mixture until it reaches a point just above the burner where flow velocity and burning velocity are equal.

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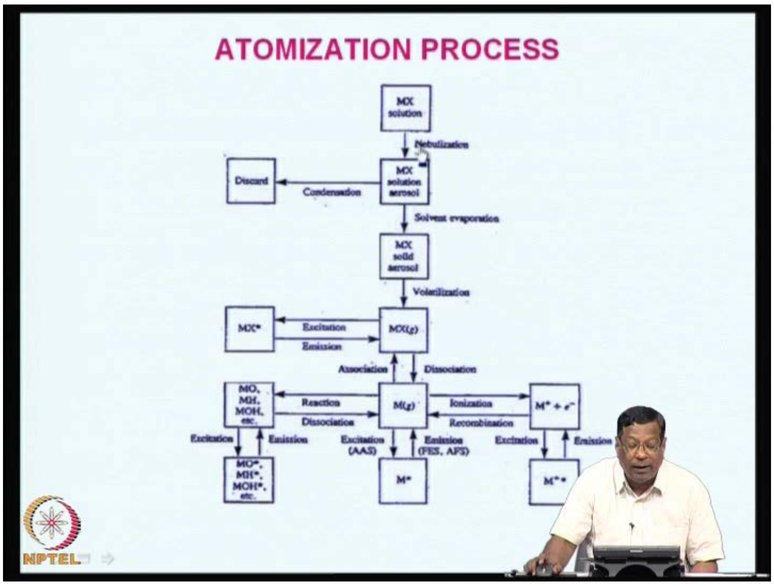

ATOMIZATION PROCESS

So, what happens in atomization process, very interesting situation here in the middle region, I have M X that is metal halide solution. So, you start from basically a solution which is to be analyzed that is at the top box; from the top box you are introducing through a capillary and nebulizer into the solution, into the nebulizer.

So, there you are having a composition of M X that is metal halide solution aerosol. So, the solution is converted into aerosol and during the conversion, there could be some losses, bigger droplets cannot cannot remain in the air. So, they they fall down due to gravity and that is to be taken for discarding, and the aerosol gets carried into the flame and the solvent evaporates, because of the high temperature prevailing in the flame. And when the solvent evaporates, you have an aerosol of metal halide solution, it can be metal carbonate also. I have taken as an example only the halide, but it can be any other salt also, it may be carbonate, it may be sulphate, if you have dissolve the sample in nitric acid it may be nitrite also. So, anyway it is the, after the solvent evaporates you have a solid salt and as an aerosol along with the burning mixture, now this volatilizes and you get the M X that is metal halide in the gaseous form. So, at this point it has to decompose and ions are produced.

So, these ions collect electrons from the flame and then they may get excited producing M X star, I have put it here as M X star and they can reemit the radiation. And so, there is a some sort of an equilibrium reaction between M X and M X star in this range.

Now, the this process is not good enough for our atomic absorption, it has to be, we need the atoms, not the salts. So, these atoms, these salts will decompose and the decomposition is again a an equilibrium process.

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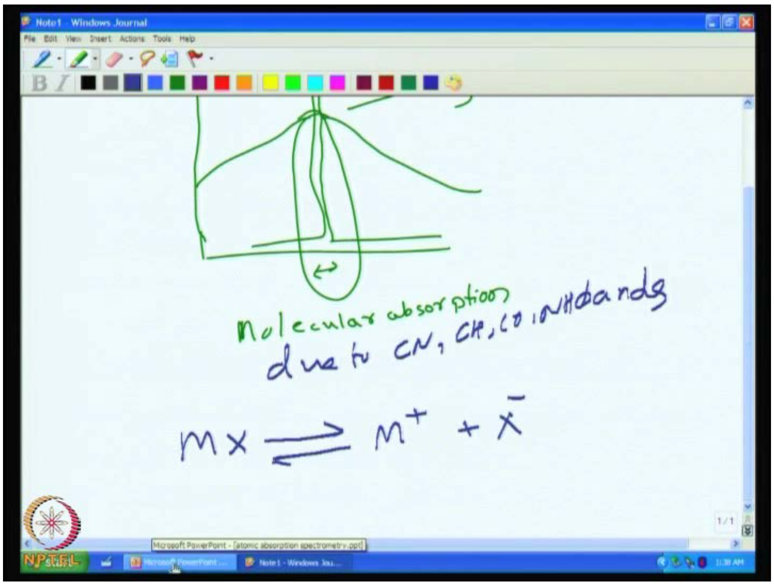

Molecular absorption due to CN, CH, CO, NH bands

$$MX \rightleftharpoons M^+ + X^-$$

One is it could be when the M x decomposes (No audio from 51:09 to 51:20), what we have (No audio from 51:22 to 51:29) M plus plus x minus. Now, these are the ions and these ions collect the electrons from the flame and we have in the gaseous form. So, in the (()) from the (()) ionization produces M plus e minus that I have put it on this slide (Refer Slide Time: 51:58). And then they can recombine also, another equilibrium reaction, not good for atomic absorption, this is a waste process again and this gaseous ions can also react with molecular species forming oxides, hydrides, M O H, metal hydroxides, etcetera and they may reduce, they may dissociate again to metal.

So, this is an equilibrium reaction, this is also not good for us and another possibility is these oxides, hydrides and hydroxides, they can get excited and emission, excitation and emission is possible in this process also. But what is of interest to us is this, M X should go to M plus and this M plus should form, pick up an electron and form metal atom (Refer Slide Time: 53:00).

The metal atoms are formed here and this is good for AAS, but if it emits the radiation, we go back to the same process. So, basically M X, M X solution aerosol, M X solid aerosol, M X gaseous and from the gaseous you can get excited, the molecular excitation which is not good for us, then it has to decompose, form metal in the gaseous form and then it can ionize which is not good for us, it can react not good for us, it can form excitation emission, not good for us. But only the metal atoms which pick up electrons, their concentration is important for our atomic absorption.

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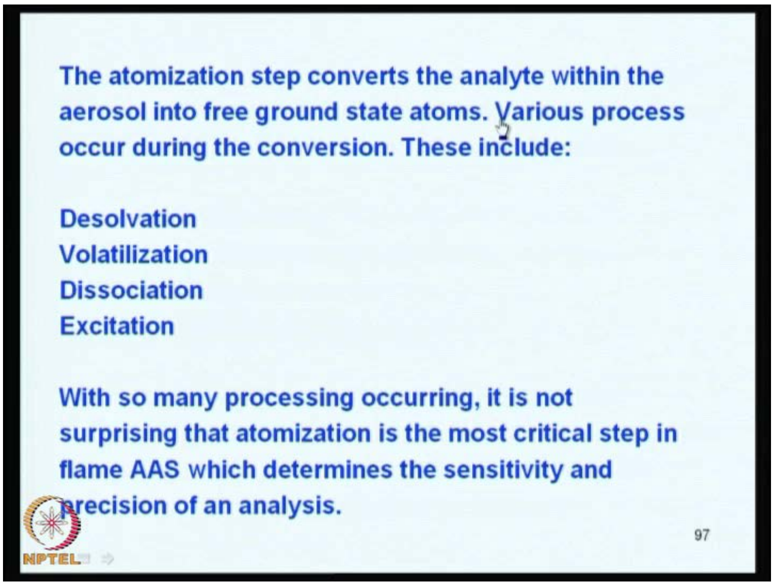

The atomization step converts the analyte within the aerosol into free ground state atoms. Various process occur during the conversion. These include:

Desolvation
Volatilization
Dissociation
Excitation

With so many processing occurring, it is not surprising that atomization is the most critical step in flame AAS which determines the sensitivity and precision of an analysis.

So, the atomization step basically converts the analyte into free ground state atoms, various processes occurs like what I have told you, these are processes are known as desolvation, volatilization and then we have dissociation and excitation. With so many processes occurring, it is not surprising that atomization is the most critical step in the flame atomization spectrometry, which determines the sensitivity and precision of analysis.

You have better atomization is using the good nebulizer and then good flow, good oxidant oxidant and gas combination, good flame, good height where the sample passes, the radiation passes through the sample, then only good atomic absorption analysis results can be obtained. So, these are the flame types, this we have already discussed the turbulent flow burner, it gives a tall narrow flame provided a very short light path for AAS.

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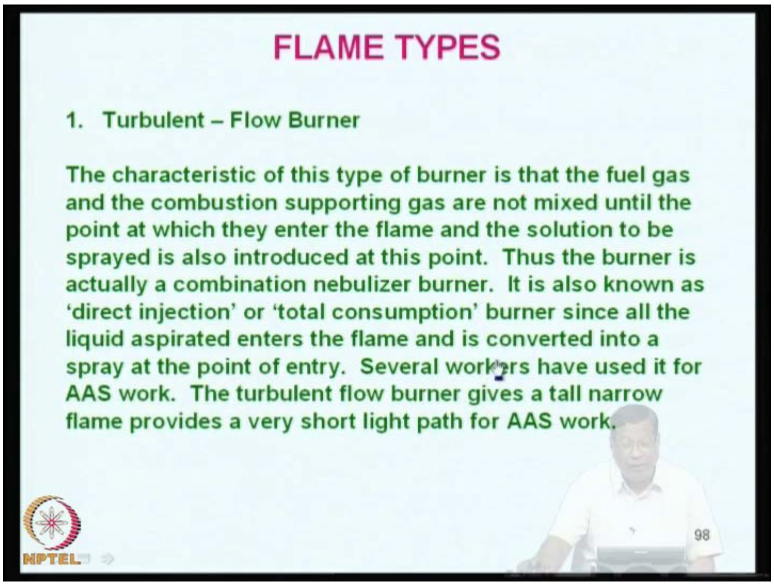

FLAME TYPES

1. Turbulent – Flow Burner

The characteristic of this type of burner is that the fuel gas and the combustion supporting gas are not mixed until the point at which they enter the flame and the solution to be sprayed is also introduced at this point. Thus the burner is actually a combination nebulizer burner. It is also known as ‘direct injection’ or ‘total consumption’ burner since all the liquid aspirated enters the flame and is converted into a spray at the point of entry. Several workers have used it for AAS work. The turbulent flow burner gives a tall narrow flame provides a very short light path for AAS work.

So, this is the reason why I have written here in this slide that the several workers have used it, even though they have used it for AAS work, the turbulent flow burner gives a tall narrow flame, but it provides a very short light path. Again this is a problem, because if the light path or absorption cell is more, then the absorption also can be higher.

So, turbulent flames, if they give you a sharp narrow flames like this, just like what you see in a candle, that is not good for analysis, it must burn with a long path and then in a single frame, a laminar jet is what we call it. In a laminar flow, the absorption can be of about 5 to 6 centimeters and then you get good atomic absorption data.

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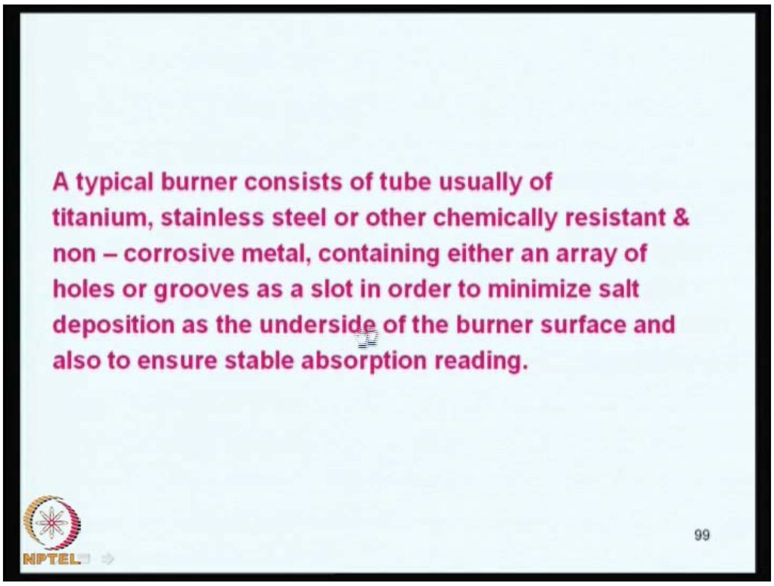

A typical burner consists of tube usually of titanium, stainless steel or other chemically resistant & non – corrosive metal, containing either an array of holes or grooves as a slot in order to minimize salt deposition as the underside of the burner surface and also to ensure stable absorption reading.

So, a typical burner consists of tube usually of made of titanium, stainless steel or other chemically resistant material. It should be non-corrosive, lot of requirements are there and this, we will discuss further about these flames a little more and then we will move on to other aspects of other aspects of atomic absorption measurement.