Trace and ultra trace analysis of metals Using atomic absorption spectrometry
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Lecture - 16
Instrumentation in AAS Radiation Sources: Sample introduction

So, we will continue our discussion on the nebulizer, but before I go on to this, I want you to take a look at the new slide which I am going to make for you.

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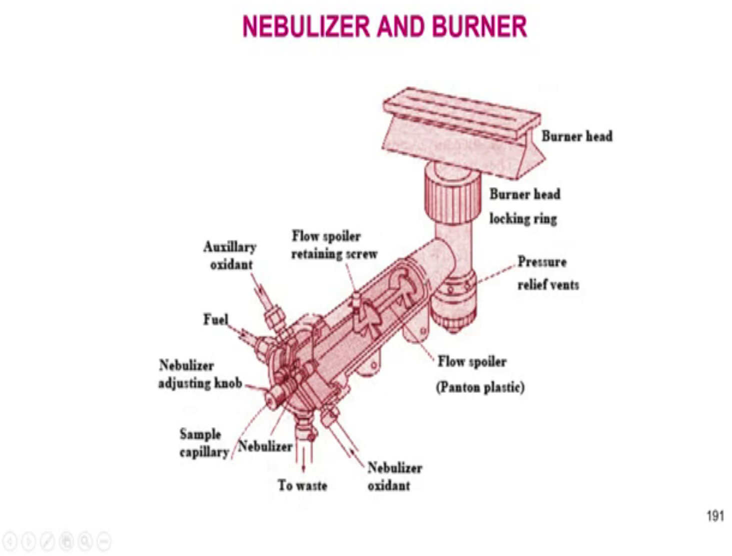

So, the actual layout of an atomic absorption for your convenience, I am going to write it here.

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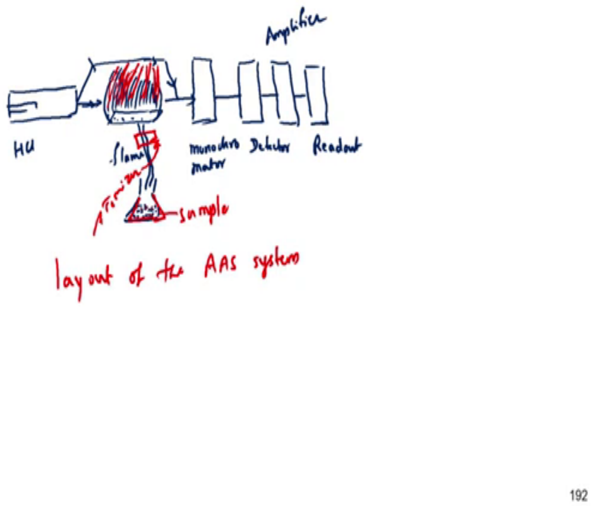

This is a hollow cathode lamp, and then this is the flame. So, the flame will be like this. This is the hollow cathode lamp and this will be the radiation passing through the flame. And this will be radiation going out of the flame. Here, I put a monochromator. This is flame, this is hollow cathode lamp or any other lamp for that matter. And then here I have the detector. And then one will pass through, one will put a mirror and then both here come back. This is double beam I am showing you detector and then a, what you call this would be amplifier, amplifier. And then we have a readout system readout. So, here I am going to put my sample, this is my flame. Here is my conical flask containing the sample. So, we are layout of the AAS system. So, what is what we are discussing is the layout of a AAS system, because you should not get confused what we are discussing about.

So, first we have we have discussed about the hollow cathode lamp we are go now going to discuss about the atomizer. This is the atomizer I should write it here. This is the atomizer. So, sample is taken through an atomizer into the flame. And then I have a monochromator I have a detector I have an amplifier and then I have a readout. So, we are going to discuss about the flame, and a atomizer now and then subsequently flame also. Afterwards we will discuss about monochromator detector amplifier and read out.

Now, coming back to this I want you to look at the design of the nebulizer and burner. As I told you it is the job of this nebulizer is to produce free atoms. So, from the conical flask you have a capillary, the sample capillary is shown here. This is the sample capillary and it is a plastic tube of about 1 mm may be less than 1 mm plastic tube which dips into the sample. So, from the sample it is sucked into this nebulizer. This nebulizer is a simple tube, but lot of engineering has gone into the design of the nebulizer and then the there is a nebulizer adjusting knob here. And then I have an air a fuel air fuel gas coming like this and then an oxidant auxiliary oxidant that is air or acetylene etcetera air or any other gas you want to introduce. So, both these gases are pro coming here and proceeding to the flame, follow my laser pointer both of them will come here auxiliary will come here they will mix and then proceed through this tube the gases will proceed through this tube into this burner and then the spray gas will be escaping which will be lie which will be lighted here on this course.

So, this is what I had shown you earlier how the flame will look like in the next slide it is there. So, what we have is a sample coming into this space. Here I put a small ball in this flow spoiler is there. So, I put a small ball. So, the liquid is coming, air is coming, gas is coming and the air and liquid and gas will mix together and the ball will be made to a rotate a little bit and then produce a fine stream of droplet us, which will be carried into this portion of the this is known as flow spoiler by putting a ball the this is a plastic ball.

Because there is no fire here and plastic ball is there and then this from the plastic ball a spray is carried into this cylindrical tube, and this is a pressure relief we went and this is a burner head this burner head connects to the a burner head that this is the locking ring; that means, you can change this burner to suit different kinds of burners. So, one may be 5 centimeter one may be 2 centimeters one may be 5 10 centimeter like that you can fit different burner heads to this; that means, the flame width will be 5 centimeter, if it is the 5 centimeter length. And the middle line what you see here in this block is a number of holes through which the gas is coming and the vapors are coming and the droplet us are also coming. So, once the gas is lighted you will be seeing a flame here.

So, this is the arrangement a, but I do no arrangement of the nebulizer, but all this will fit only somewhere here, before it enters the flame this is what we are discussing now. And the sample in the liquid form is taken in this conical flask.

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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 types: Pre-mix burner and total combustion burner.

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So, we need an air pressure nebulizer to take the sample into the flame. So, for this we need a fuel because just like your LPG at home we need a fuel that is it can be used LPG and here we use acetylene, air acetylene is the mixture fuel is the acetylene and oxidant is the air. So, we can change fuel and oxidant in different condition to suit different applications that we will see later also. So, both the fuel and oxidants are independently and accurately controlled. The flow rate flow rate will be about 6 liters per minute for air and 2 to 3 liters for acetylene that we will see later also. And the for the time being you consider that both the air flow and oxidant flow oxidant flow and fuel are independently and accurately controlled and combined in stoichiometric proportions.

We need a reproducible flame; the flame should be very steady that is why we need to control the fuel and oxidants. And they need to be combined in stoichiometric ray proportions. So, that the flame is continuous it does not put off by air, if the air is too much the fuel will put off if the oxidant is too much or if the fuel is too much air is less put off if air is more again put off and flame we want a continuous burning flame. So, the flow rates are usually controlled by double diaphragm pressure regulators, these are available in the market or they can be controlled by needle valves they are also available in the market, when you buy an atomic absorption you need a 2 cylinders. One is the acetylene cylinder or fuel cylinder; another is compressed air. So, the cylinders flow and the compressed air flow is connected to needle valves and needle valves are connected to rotameters, so that they can be adjusted to the desired volumes. So, the nebulizer and flame combination is of 2 types, one is pre mixed burner another is the total combustion burner.

Now you can imagine that before I proceed to the next slide I want you to understand that nebulizer is the heart of the atomic absorption spectrometer. You have to make a suction of the sample into the flame. Now the optimum nebulizers are of the order of about 20 percent of the liquid is a converted into a spray, normally.

Remaining solution what happens it will remain as bigger droplet us and it will be it is a waste, because once I everything is introduced into the flame bigger droplet us will fall on their own or it may be collected in the nebulizer itself before it proceeds into the flame, a for this there is a waste a waste format in the nebulizer design itself, that I have not shown you, but I will show you now. See there is there is a waste here. So, whatever liquid is not converted into spray gets collected here and goes to waste. So, you need to keep a bottle to collect the waste and discard it during the time of at the time of analysis. So, the efficiency of the nebulization is again dependent upon the efficiency with which the ball disrupts the flow of liquid, from the conical flask. The efficiency of the flow of atomic absorption spectrometry or sensitivity depends upon the number of atoms that we produce, a best design. So, far is about 20 percent. Otherwise it is about 12 to 13 percent to efficiency is normally obtained over the year some improvements have been made, but now much.

It is not possible to convert a liquid into total a small volume of liquid into total spray. The liquid flow rate is also about 2 to 5 ml per minute that is quite large if you want to introduce it into a flame. Because water it a water itself may put off the flame. So, the waste is here and the waste liquid is collected and you need that and the efficiency, this is the matter of great research especially the efficient how to improve the efficiency of flame atomic absorption spectrometer we have talking about flame atomic absorption spectrometer how to convert maximum quantity of the sample into the vapor phase.

Now, we go back to this and the flow rates the nebulizer flame combination is of 2 types. One is premixed burner and another is combustion burner. If you remember this top portion, this is the burner in this burner there are 2 types one is premix and another is total combustion burner. So, what is a premix burner? A premix burner is one in which the fuel and the air are predetermined. The flow rates are predetermined that is a premix burner, and what is a total burner is the total burner is there is both of them are mixed at the point of burning burner. So, you can say that the one which I have described to you earlier, this one is a premix burner. Because both the gases are premixed and sent to the burner, but if I have 2, if I have 2 fuel and oxidizer coming together or I forget about this auxiliary oxidant I just take this fuel and put it into the flame, let the air in the available in the around the flame compartment.

All the air available just like in your LPG home what happens, we have a cylinder gas is coming inside in the at home, we have the gas cylinder when you light it the fuel comes, but air comes from different sides, from the side. So, it burns. So, that is a total combustion burner; that means, fuel is not regulated fuel quantity is fixed. And air available is approximately whatever is available at the room temperature and pressure. So, that is a total combustion burner I do not have any control over the flow of the fuel gas. So, these 2 types and here premixed burner the also there is there are several holes through which you can see the picture of the flame a; that means, it is a small length of burner, which will burn in at your home you see the circular burner is not it here. It is single line burner single all the air and fuel has to come only through this burner and burn. So, there are 2 types of burners one is premix another is total combustion burner.

Now, I want to give you a comparison of the premix and total burner, that is, in a premix burner because of this stoichiometry.

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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 can be handled.
Atomization efficiency 10 -15%.	Low S/N ratio.

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I have a laminar flow; that means, the flow is controlled; that means, I have a good control over the temperature of the flame and uniform droplet us are there because of the spoiler and other things. And low turbulence is there and less electrical noise. This is the property of the flame low turbulence and less electrical noise because smoothly both the gas and air are getting mixed. And then because of the small quantity of the small size of the holes, if I have a solution the particles when they are coming out of the burner they encounter a heated burner.

So, the liquid will evaporate solid will clog these small holes this you this you must have seen in the even in your houses, where LPG gases get clogged and you have to clean them mechanically. So, in premix burner you cannot use a very high solids content sample. It has to be very low, and then if it clogs the air will not escape the sample will not escape the pressure will be there fire will be there you know electrical fire etcetera. And then there may be an explosion hazard the whole thing may explode in a atomic absorption spectrometer if the burner is not maintained properly.

So, it is a lot of safety regulations and precautions must be in place whenever you have an atomic absorption spectrometer in your laboratory or at your work place. And the flow rate for premix burner is also fixed 3 to 10 micro liters sorry 3 to 10 milliliters per minute. And the atomization efficiency as I have told you because of the spoiler it is 10 to 15 percent.

Now look at the slide that is I want to compare this with the total burner. In the laminar flow I have controlled flow, here entire sample is aspirated. Here flow rate is 3 to 10 here I have no control over how much I am aspirating. The how much sample I am putting into the flame that is one major difference. All they sample is aspirated here I can control it. And then there is uniform droplet us and cooling and loss of droplet us is more here in the total combustion burner. And then oxidant fuel gas ratio is fixed in the total burner because you do not have control over the oxidant nor in the fuel gas. So, everything as it comes out from the cylinder is burnt. Then because of this and because lot of sample comes into the flame the flame becomes noisy there noisy means, it is not sound based, but the quality of the flame sometimes it increases sometimes it decreases depending upon how much sample comes when the sample comes flame becomes cooler.

So, the flame becomes shaky and when the sample is less the flame becomes stronger like that the flame is called noisy, whenever there is a change in the structure of the flame in atomic absorption. And the flow rate flow rate is also fixed because we do not have a nebulizer. So, the flow rate is approximately set around 1 ml per minute, but because the burner is not of the laminar type there whole thing is burnt the clogging becomes very less. That is one advantage in total combustion burner and the point is in signal handling that is the radiation data collection transmitted light the signal to noise ratio becomes low, but what we want actually is the signal of the sample to electrical noise should be very less very high. So, this is one advantage where we can have signal to noise ratio is very low this is a basically a disadvantage only, but signal to noise ratio would be higher here in the premix burner. So, I wanted to explain to you about this low noise and high noise etcetera we will discuss it again further at the appropriate time.

So, there are 2 types of burners one thing common for both the burners is the use of a fuel and oxidant right. So, you need to have 2 one cylinder of the fuel and a compressor or an air cylinder nitro air cylinder also will do, but normally air is preferred because compressed air is very easy to produce. You just have to buy a compressor for about 2000 rupees or 3000 rupees collect it in a tank and from the tank you collect a needle valve and that is the end of the system. So, I have different I can choose different types of fuels and different types of oxidants. So, I have already told you air and oxygen and nitrous oxide are the oxidizers; that means, they provide support for the fuel to burn that is known as oxidant. And what is the fuel can also be a gas which burns. What are the fuels that burn one is natural gas, I can take a natural gas and make it burn. I can take hydrogen also burns high school chemistry.

And then I can have acetylene burns you must have seen the in your road sides lot of welding work etcetera they do it with acetylene. And then there are other gases which can be burnt. So, but among all these things natural gas hydrogen and acetylene these 3 are the most popular fuels now the point is I can have a combination of the fuels. These combinations of fuels normally give rise to various flame temperatures which are of use in the atomic absorptions spectrometry.

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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

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Look at the slide now, here I have made a list of natural gas and the oxidant if I use air I get a temperature of about 1700 to 1900 degree centigrade. For a good atomic absorption, we need around 2300 to 2500 or 3000 degree centigrade. And what I am getting here natural gas if I mix it with air, I get about 1700 to 1900 degree centigrade. And what is you burning velocity natural burning velocity in centimeters per second that is how it is expressed it is about 39 to 43 centimeters per second; that means, the flow of the combined air and natural gas should be 39 to 43. Below this it would not light higher than this there is wastage. So, another combination is natural gas and oxygen. What happens? 2700 to 2800 degree temperature centigrade I can achieve, if I use oxygen cylinder; that means, the auxiliary in the nebulizer should be connected to an oxygen cylinder fuels free is natural gas, but look at the burning velocity it is about 370 to 390 centimeters per second; that means, more fuel will be required here.

Now similarly I can go for hydrogen and air mixture that gives me around 2000 to 2100 not so good, but it also gives you capability for 300 to 440 centimeters per second burning speed. I can go for hydrogen oxygen that gives me around 2700 900 to 1400 is the burning velocity quite high, and air acetylene is the combination which gives us 2100 to 2400 degree centigrade and the burning velocity is approximately 158 to 266 centimeters per second. I can have acetylene and oxygen that gives me almost 3000 degree centigrade and burning, but burning velocity should be much higher acetylene nitrous oxide is also gives us 2600 to 2800 degrees and it goes up to the burning velocity is 285.

So, among all these for natural for natural atomic absorption in your laboratory, which one you would choose the best choice is acetylene and air acetylene is quite economical reasonably available across all over the world and where even in small towns acetylene is a cylinders are available they can be used to connect. LPG gas may not be available in small towns. And LPG air if you remember the slide it gives you only 1700 to 1900 degree centigrade, but acetylene air will give you 2100 to 2400 degrees depending upon the burning velocity.

So, the most preferred fuel and oxidant in atomic absorption is air and acetylene. So, air and acetylene yes up to 2400 to 2500 good enough even though the free atom concentrations excited atoms are very less even at 2400 degree centigrade. You remember the example I had done in the last class about the typical concentrations of the different metal ions at higher temperature.

Now acetylene nitrous oxide is again a very good combination. You can look at the slide now the acetylene and nitrous oxide gives you 2600 to 2800 degree centigrade. And this is good enough for several refractory elements. I want you to remember that. So, in normal atomic absorption spectrometers what people do is for low temperature routine analysis they go for air acetylene combination, and for refractive elements like tungs10 chromium vanadium and many other elements refractor aluminum for example, that is also a refractory element and for such things, if you want to determine in parts per million level most of the flame atomic absorption is for ppm level parts per million that is my milligrams per liter or micrograms per milliliter. So, flame is operated using 2 combinations one is the natural gas sorry hydrogen acetylene and air another is acetylene and nitrous oxide, but if due to some reason nitrous oxide is not available, you can still I just for the time being and till you with natural gas until you get acetylene gas, but acetylene use of acetylene gas is very widely practiced.

So, how does a flame look like? You must have seen flame in your home try to remember any gas flame in your homes there is a small blue portion at the bottom, and then there is a green portion, and then there is a there is a red portion. On the top it will be red at the bottom there will be in the green, but at the start of the point it is mostly blue. If you remember this what I am going to show you we will exactly look the same there is no difference, but here.

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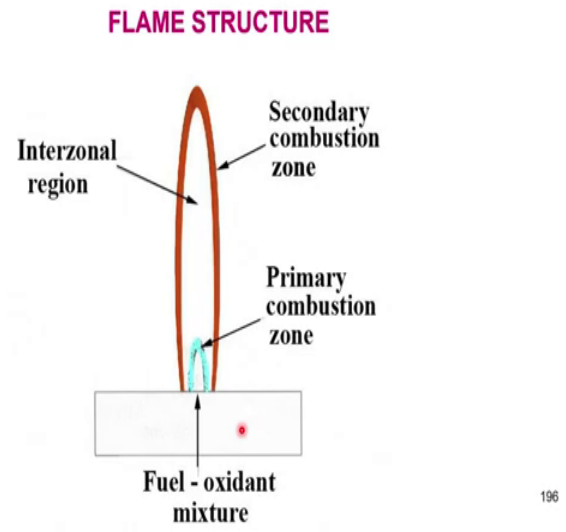

This is the flame burner in atomic absorption it is a rectangular block through which the flame is air a fuel and sample are is coming, and I am showing you a front view. So, the fuel oxidant mixture is coming from the bottom spreads through this and then it is horizontal and if you look at it there is a primary combustion zone, then there is an inter zonal section secondary consumption combustion zone and then there is inter zonal region. So, this is how a typical flame looks like now what is the importance of these flames. That we will see in the next class.