Trace and ultra trace analysis of metals Using atomic absorption spectrometry

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Lecture – 17
Instrumentation in AAS III: Burners

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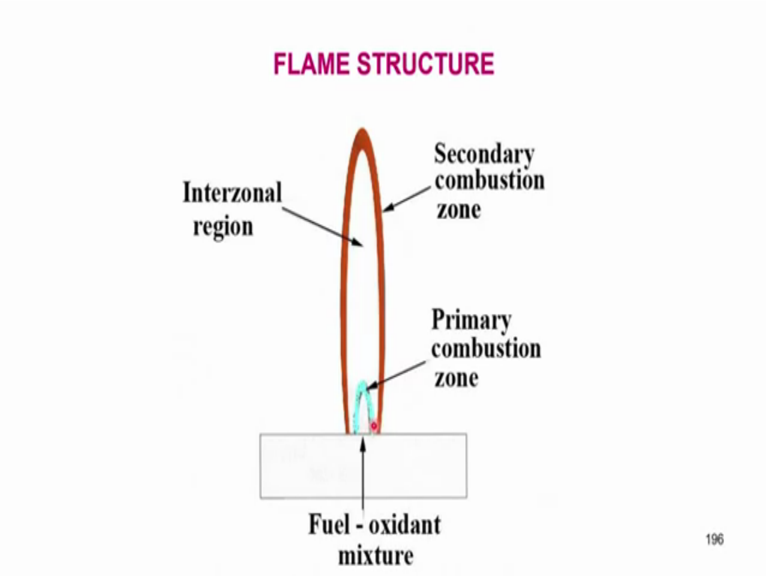

So, we were discussing about the fuel structure; flame structure. So, it contains the bottom blue portion and then a green portion and then there will be a red portion. One is primary combustion zone, another is green portion etcetera is secondary consumption combustion zone and the third is top portion; that is reddish flame and this is inter zonal region, so both of them will be there in this range.

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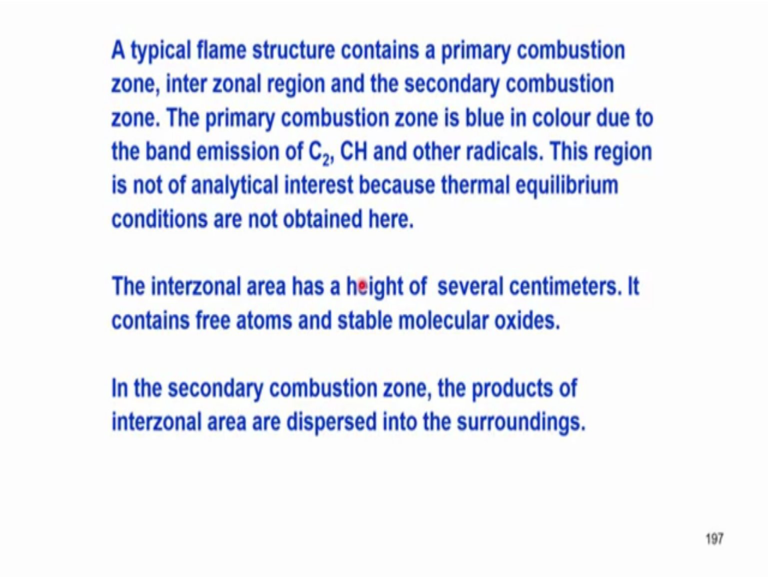

So, a typical flame structure contains a primary combustion zone and these two parts; the primary combustion zone is blue in color due to the band emission of C 2, CH and other radicals. Here there is not much oxygen available for the flame, for the acetylene gas to burn. So, whenever you use acetylene gas you will come across these radicals in the flame that is carbon CH and other radicals.

So, this region is not of analytical interest because thermal equilibrium conditions are not obtained here. What does it mean? Their flame is not steady; it does not have high temperature also in this blue region. So, the inter-zonal area has a height of several centimeter; it may be extend from 1 to 3 centimeters depending upon the flow of course, if the flow is very fast then the inter-zonal area will be extending several millimeters, several centimeters and if it is low, it can vary from 1 to 3 centimeters.

For atomic absorption spectrometry, we need to work; we need to get about 1 to 3 centimeters that is more than enough because only in that range, we need to pass the radiation; that means we have to adjust the height of the flame so that it passes through the radiation coming from the hollow cathode lamp. Refer to the structure schematic diagram I had shown you immediately after the nebulizer, so that height can be adjusted to get the optimum sensitivity. And this inter-zonal area has a height of several centimeters; it contains free atoms and stable molecular oxides this is what is of interest to us. We want free atoms in the flame and that happens in the inter-zonal area and molecular stable oxides are also there in this range.

For example, if you are using aluminum; it may form aluminum oxide goblets, so it is of no use. Mostly refractory elements are not useful because their temperature here is not good enough to vaporize them also. So, but molecular oxides apart from molecular oxides; any other element which does not form oxide should be present in the free atom, as a free atom in this range. So in the secondary combustion zone, the products of inter-zonal area are dispersed into the surroundings.

So, I want to show you go back here in this range; in this area all the products that are coming from this are dispersed into areas outside like this. So, that is of no use to us, so these are the three basic combustion zones and the inter-zonal area has height of this about these are 3 centimeter, secondary consumption zone is also good for us and if you look at the temperature of a flame coming from a burner, this is what happens.

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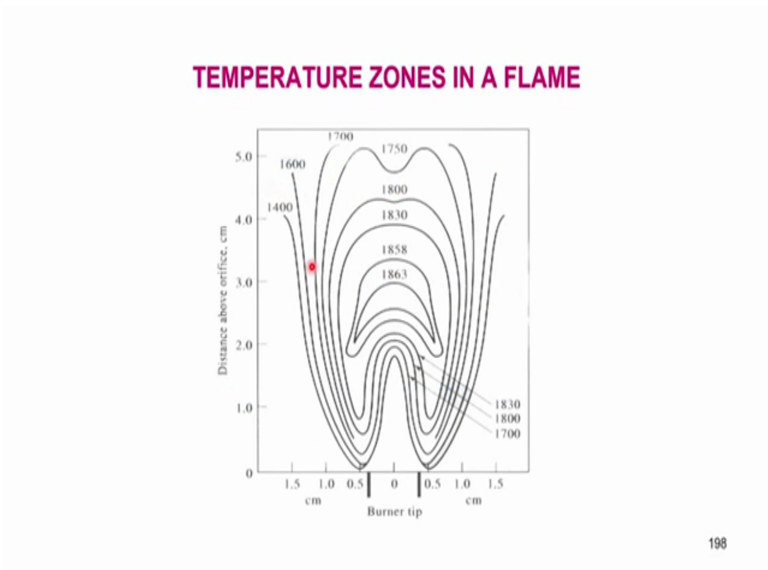

So, the internal combustion zone, if this is the burner tip, if you see here on the X axis 0 to 0.5 and these are in centimeters. This is the center of the flame; this line and 0.5 centimeter, what is the temperature, 1 centimeter, what is the temperature, along this line and 1.5 centimeter what are they temperatures, they have been plotted here. So, our interest is to know where we get maximum temperature so that we can make our hollow cathode lamp radiation pass through in that space. Now, this is the distance above the orifice; so, around 0.5 centimeter; width of the flame and distance about 1 centimeter above, what is the temperature here? We can see about, this is about 1800, so I am pointing it here and then corresponding to that is about 1800, 1830, 1700, around 0.5 centimeter away from the flame; flame orifice.

So, you go up still; what you get? Around 1863, still up 1858, 1830, 1800 and then 1750, so along this line maximum temperature is obtained and on the sides, you will get 1700, 1600, 1400. About 1.5 centimeter away from the tip, you are you are ending up about 4 centimeter height; you are ending up around 1400 degree centigrade. So, which is the most optimum area, through which the hollow cathode lamp should pass through, should it be 1700 or 1800, 1830, 1863, 1858. So, it is a very simple question it has to be maximum temperature, so the sample; the hollow cathode lamp radiation should come through and pass through this; around this range, about 3.5 centimeter from height above the flame and then it should pass through, pass out and in this there detect a monochromator and detector, so it will come something somewhere here and then detector etcetera.

But on the flame, the hollow cathode lamp should come somewhere here between 1858 and 1863. Now these figure, these numbers are not absolute numbers; for example, for a particular given condition, it is like this; where the authors have not specified what are the flow rates corresponding to this figure. So, but in general you can probably estimate the maximum temperature range according to this figure. So, it will be almost same for any other flow rates also, but numbers will differ, so this you should remember.

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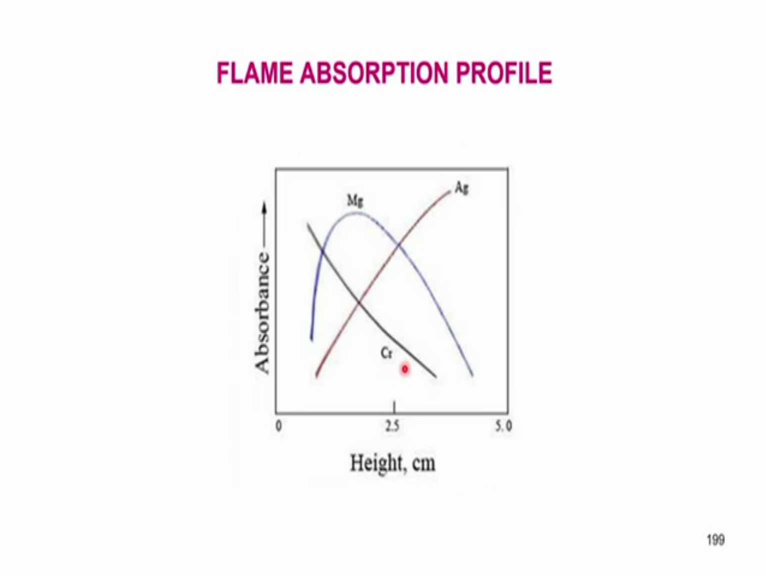

So, if you look at the flame absorption profile; what happens, suppose I want to determine this is the absorbance, this is the height; height from the burner. So, height from the burner here it is 0, here it is 2.5, here it is 5 centimeter above the burner and this is the absorbance recorded. Now, what you see from here is; if it is 2.5, this is about 1 centimeter; on the X axis. So, the absorbance increases as the height increases; if at 2.5, it is around this much and around 3 or 4 centimeter; this is the maximum absorbance.

Now, look at magnesium. Magnesium absorbance is starts from around 1 centimeter and then keeps on increasing, as I increase the height, it reaches a maximum around 2 centimeter and then if you increase the hollow cathode lamp radiation still higher; then the absorbance will be decreasing and it keeps on decreasing until you reach around 4, after that there want be any absorbance. So, you look at chromium; chromium maximum absorbance is obtained around 1 centimeter, this is where the maximum temperature is also there. But as the temperature decreases, chromium being a refractory element; it will the absorbance will keep on decreasing. So, until it reaches about 3 centimeter and if you increase the height of the hollow cathode lamp in the flame more than 3 centimeter, then you will not see any signal for chromium at all.

So, coming back to this figure now what do we understand; there is a certain range of height of the hollow cathode lamp that should pass through to get optimum absorbance. So, in atomic absorption they always give a small screw at the bottom of the nebulizer or the flame; burner so that you can increase the height of the burner to desired level, not much maybe 0.5 centimeter allowance up and down up and down. So, whenever you want to start a chemical analysis, what you should do is; your aim is for a standard, you should get maximum absorbance. So, the maximum absorbance you can adjust this is one of the parameters; another parameter is hollow cathode lamp, voltage, specifications etcetera. The second parameter is the nebulizer efficiency that you cannot do much because it is made by the factory.

Now, third is burner; the burner height can be adjusted to get maximum absorbance. So, that maximum absorbance you can see from this figure that it varies between 1 to 3 centimeters. So, the allowance given in most of the atomic absorption spectrometers; are of the order of about 1 to 3 centimeters. So, this is a good example of how flame absorption profiles can be made use of in the determination of metals, for using atomic absorption spectrometer. This kind of variation is not available in spectrophotometry; in which I have given a course earlier and you can take a look there or you can even see the; my NPTEL course on modern instrumental methods of analysis.

So, coming back to this; what we learn from this figure is, it is possible to adjust the flame height depending upon the where you get maximum absorbance.

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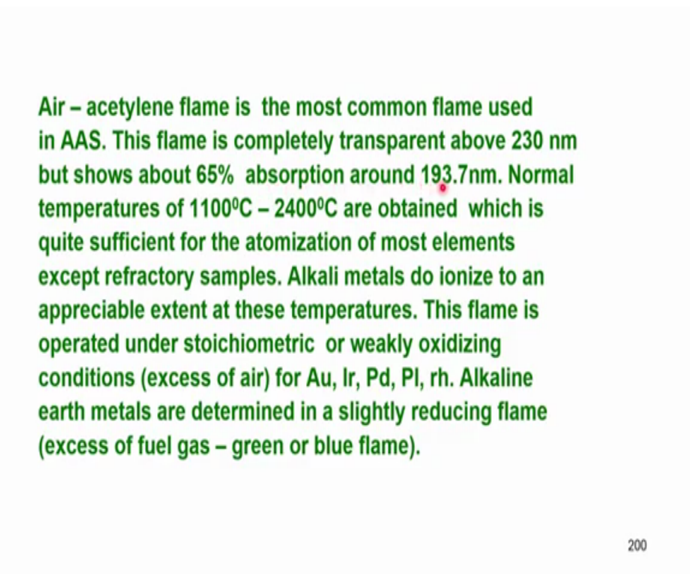

So, coming back to the gases air acetylene is the most common flame used in AAS. This flame is completely transparent above 230 nanometers; that means, it has no background;

the air acetylene does not show any absorbance of its own molecular species or the refractory oxides; air acetylene, so that is what it means. So, this flame is completely transparent above 230 nanometers; that means all the elements which have got resonance line above 230 nanometers, first resonance line above 230 nanometers can be used; can be determined using air acetylene mixture.

So, that is what the meaning of this flame is transparent above 230, some flame may be transparent above 300; that means, above 300, you can determine any resona element; if it has got a resonance line above 300. So, but air acetylene shows about 65 percent absorption around 193.7 nanometers. See, I have written here; it shows absorbance of about 65 percent around 193.7 nanometers. So, the temperatures obtained are around 1100 to 2400 degree centigrade, which is quite sufficient for the atomization of most elements, except refractory elements; that you cannot help it. So, it is the property of the refractory elements.

And alkali metals what happens? They not only form free atoms, but they also ionize to an appreciable extent at these temperatures. So, atomic absorption for alkali metals like sodium, potassium, lithium, cesium, rubidium etcetera is not easy using atomic absorption. Many people do not do the determination of these elements sodium, potassium, cesium, etcetera because of this reason; because they ionize and they absorption signal is smaller than emission signal. So, this flame is operated under stoichometric or weekly oxidizing condition that is at will slightly lower height and excess of air.

So, for gold, iridium, palladium, platinum, rhodium etcetera; this flame is fine and alkaline earth metals are determined in a slightly reducing flame. What are the alkaline earth elements; metals? Calcium, magnesium etcetera strontium all these thing barium; these are alkaline earth metals, they are determined in a slightly reducing flame. Reducing flame means somewhat bluish flame, not the reddish flame; so that means, excess of fuel gas that is either green color or blue flame is good for calcium, strontium, barium etcetera alkaline earth metals. We will stop here and continue our discussion in the next class.

Thank you very much.