Trace and ultra trace analysis of metals Using atomic absorption spectrometry

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Lecture – 18

Instrumentation in AAS IV: Flame Processes

In the last class we were discussing about the flame that is the absorption cell it is called technically, but actually it is a space in where flame comes in the if optical path of the hollow cathode radiation.

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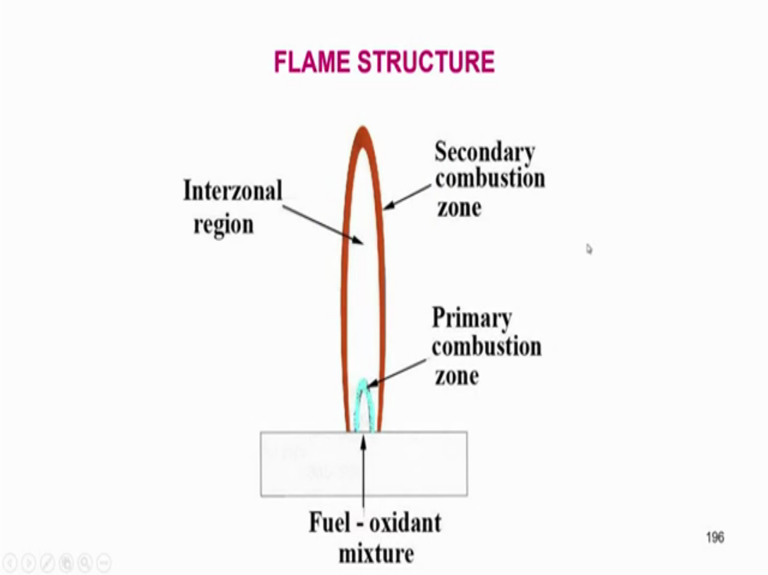

FLAME STRUCTURE

So, I had shown you this figure where I had shown you that there are primary combustion zone internal region secondary combustion zone etcetera these I had explained to you, and the temperature variations of this flame.

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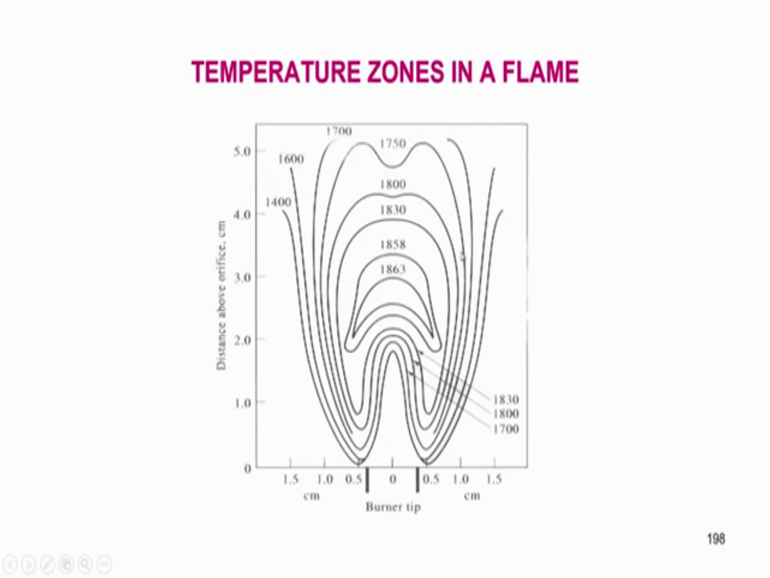

TEMPERATURE ZONES IN A FLAME

We have seen that the optimum temperature is somewhere around, around about 2 to 3 meters from height from the origin of the flame, and it extends the say 1860 range temperature extends from about 0.5 to 0.5 mm centimeter on the left and right of the flame.

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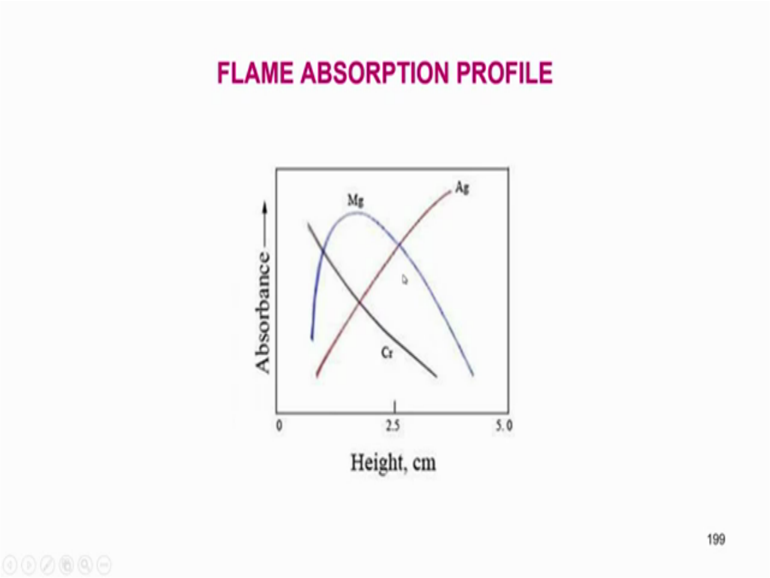

FLAME ABSORPTION PROFILE

So, we have also said that the optimum temperature for the production of vapor phase atoms are different. So, I had shown you this figure for example, chromium the optimum frame is optimum height is it should be as near the flame as possible, but for magnesium there is an optimum somewhere around 2 centimeters, and say for silver it is about two point may be about 3 to 3.5 centimeters. I had also explained to you that the height of the flame can be adjusted in almost all instruments to get the optimum response of the signal.

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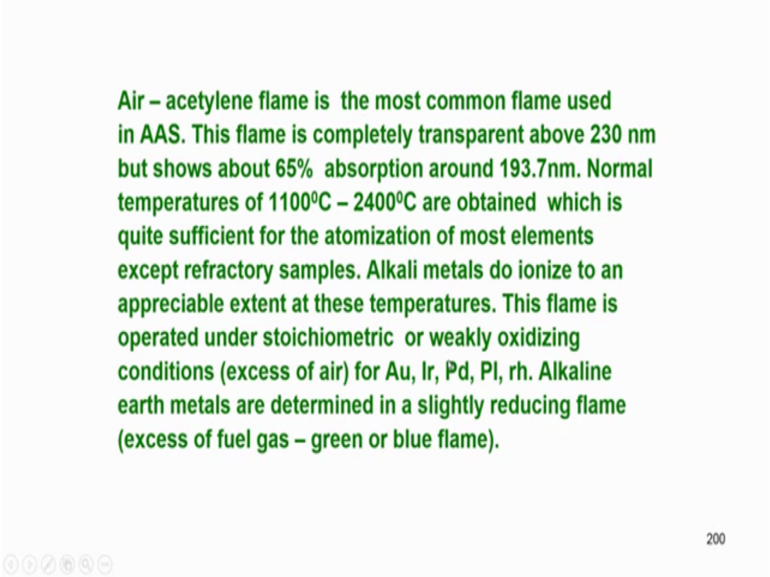

Air – acetylene flame is the most common flame used in AAS. This flame is completely transparent above 230 nm but shows about 65% absorption around 193.7nm. Normal temperatures of 1100^0C – 2400^0C are obtained which is quite sufficient for the atomization of most elements except refractory samples. 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, Pl, rh. Alkaline earth metals are determined in a slightly reducing flame (excess of fuel gas – green or blue flame).

Now, air acetylene we had discussed the flame air acetylene is the most common flame used in atomic absorption spectrometer, and this flame is completely transparent above 230 nanometers, but shows about 65 percent absorption around 193.7 nanometers. So, normal temperatures of about 2011 2400 degrees are obtained using air acetylene frame flame depending upon the flow rate of the gas and oxidizer. So, this is quite sufficient for the atomization of the most of elements except refractory elements. So, alkali metals sodium cesium potassium etcetera, they do ionize to an appreciable extent if I put it in the flame that is air acetylene flame.

If you have remember your high school chemistry or p u college chemistry, you will remember that is there is a test for the determination of sodium by putting it in the flame you will see yellow flame. Why does it happen? Because most of the atoms free atoms are produced they emit the radiation corresponding to different colours, and that is one of the qualitative method for the determination of sodium potassium etcetera that is also known as borax bead test also sometimes.

So, alkali metals we know that they do ionize to an appreciable extent even around 2000 degree centigrade. So, if they ionize we have not much use of the metal because we want free atoms ions do not absorb radiation, but free atoms do absorb radiation so; that means, ions must pick up electrons to become atoms that is what happens in the flame because in the flame. There are lot of free electrons moving around and whenever I put an ion it must pick up the electron to form a metal atom that is in the ground state. So, this flame is alkali metals normally ionize quite a lot and therefore, alkali metals are not used for atomic absorption spectrometry, here using are not determined using atomic absorption spectrometry 99 percent of the time we have other techniques for that.

So, continuing this discussion we what we want to say is this flame air acetylene is operated under stoichiometric conditions or weekly oxidizing condition; that means, excess air for gold, iridium, palladium, platinum and rhodium. So, alkaline earth metals are determined in a slightly reducing flame, that is excess of fuel gas that is green or blue flame because these are the temperatures lower than the optimum temperature, but it is quite sufficient for alkali alkaline earth metals.

Now I had explained to you that there are air acetylene is one of the combinations, but I had also shown you that nitrogen oxide nitric nitrous oxide and acetylene are is another gas mixture which will give you temperature of about 3000 degree Kelvin centigrade. Now we make use of this system also in flame atomic absorption spectrometers; that means, the whenever you buy an atomic absorption people normally buy air acetylene, that is acetylene cylinders and also nitrous oxide cylinders. So, the advantage when I use nitrous oxide is it can give me temperatures of about 3000 degree Kelvin look at the next slide now.

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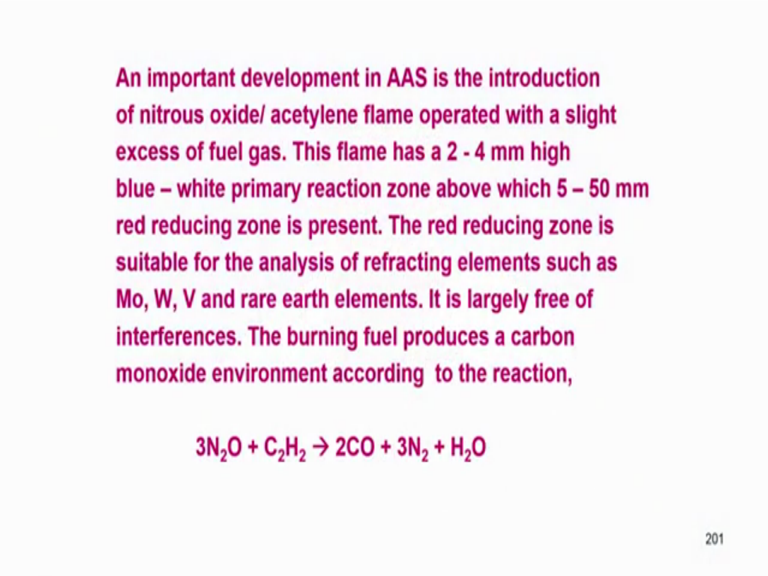

An important development in AAS is the introduction of nitrous oxide/ acetylene flame operated with a slight excess of fuel gas. This flame has a 2 - 4 mm high blue – white primary reaction zone above which 5 – 50 mm red reducing zone is present. The red reducing zone is suitable for the analysis of 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, an important development in atomic absorption spectrometry is the introduction of nitrous oxide and acetylene combination. This flame is operated with a slight excess of fuel gas; that means, the flame would be red colour. So, you have to adjust it in such a adjust the flow rate of nitrous oxide and acetylene to get a reddish flame and this flame has a 2 to 4 millimeter high blue zone blue white primary zone, above which 5 to 50 millimeter; that means, almost 5 centimeter red reducing zone is present. So, the red flame is the reducing flame.

So, if you use this most of the oxides can be reduced to metals, but these oxides belong to refractory elements. So, the red reducing zone is suitable for the analysis of refractive elements such as molybdenum, tungsten, vanadium chromium and several rare earth elements and this is largely free from interferences that is the beauty of this nitrous oxide acetylene flame. So, the burning fuel produces carbon monoxide environment according to this reaction that is nitrous oxide will react with acetylene to produce carbon monoxide which is a reducing agent and then the other products are nitrogen and water. So, all these things will be in the gaseous state whenever you are operating a nitrous oxide acetylene flame.

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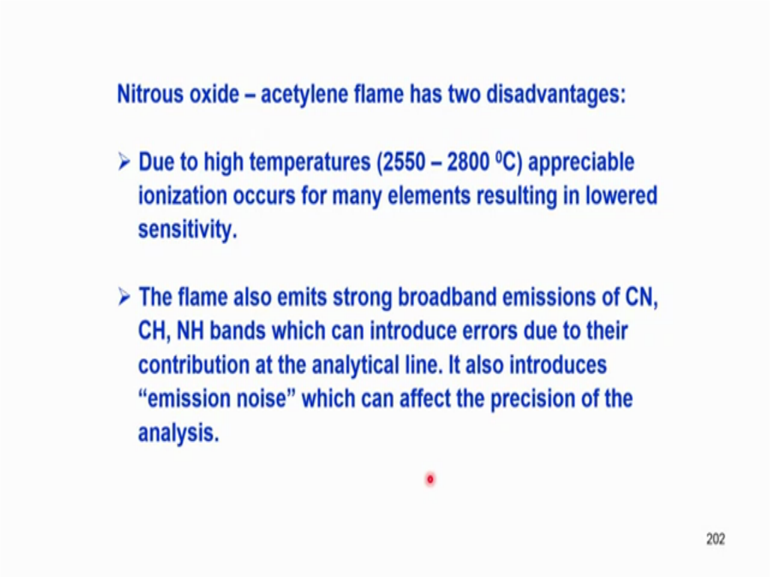

Nitrous oxide – acetylene flame has two disadvantages:

- 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, nitrous oxide acetylene flame has two disadvantages also, what are the disadvantages? Due to high temperatures that is almost 2500 to 2800, degrees appreciable ionization occurs for many other elements than your analyte. So, the resulting that results in reduced sensitivity; that means, the other elements do if you want to determine using nitrous oxide you want get the high sensitivity. Secondly, the flame also emits strong broadband emissions of cyanide CH and NH bands; that means, these are molecular absorption bands corresponding to carbon nitrogen combination in the air. So, it forms a cyanogen radical and then we also have carbon hydrogen combination CH and NH.

The all these bands have very short lifetime, but these bands do have a strong absorption band just like spectrophotometer it is a broad band it is not a very sharp band unlike atomic absorption what we are talking here because it is a resonance line and the requirement for atomic absorption is 0.002 nanometers, but if in the flame there is a broad band absorption. So, part of it will contribute to we will correspond to the atomic resonance line also. So, the, but it is not due to the element. So, this introduces a little bit of error due to their contribution to the analytical resonance line, that also introduces emission noise because noise is nothing, but additional signal that is picked up at the detector level.

So, this can affect the precision of the analysis because noise is not exactly same all the time. So, noise can vary. So, the signal also will vary. So, therefore, the emission noise is not desirable. So, I was telling you of that this broad band I want to make it a little more clearer by drawing this figure.

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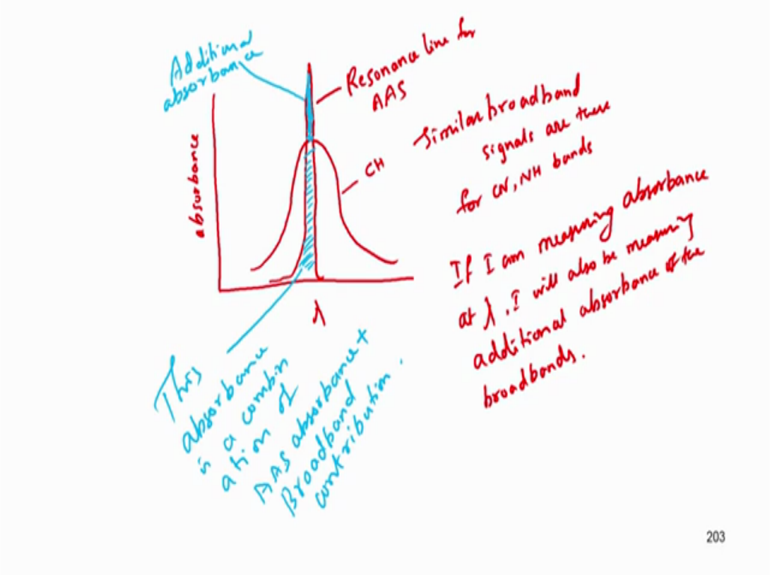

Similar broadband signals are there for CN, NH bands

If I am measuring absorbance at λ, I will also be measuring additional absorbance of the broadbands.

This absorbance is a combination of AAS absorbance + Broadband contribution.

What is important is I have an absorption signal this is absorbance this is my wavelength. An atomic absorption signal is a very sharp signal, now this is the broadband signal for CH it is also similar it may be somewhat similar for other NH ions similar broadband signals are there for cyanide NH bands. So, now, what I am saying there is a possibility of combine combining carbon atoms and hydrogen atoms to form a CH radical or it may be a CH molecule also, similarly CN is possible carbon nitrogen cyanogen it is called and then NH is called amine or something like that.

Now, consider my resonance line would be something like this, this is my resonance line for AAS for atomic absorption I have a resonance line. So, what happens if I am measuring absorbance at lambda, I will also be measuring additional absorbance of the broadbands.

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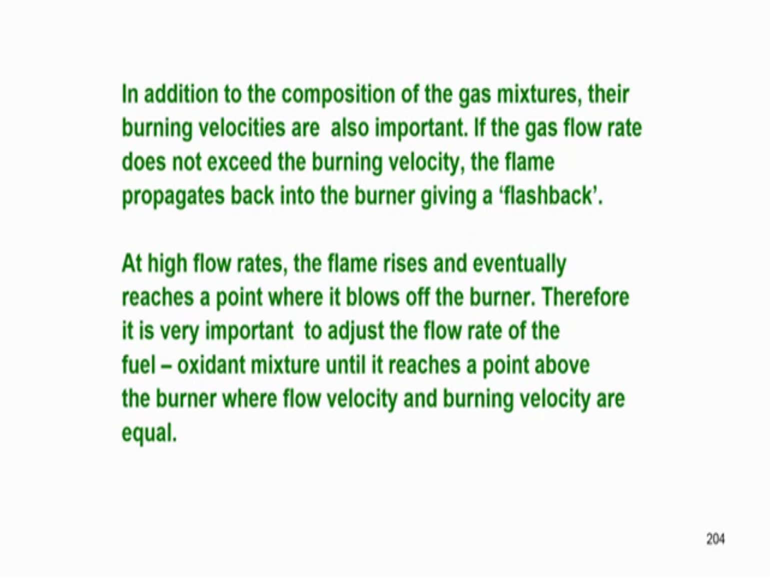

In addition to the composition of the gas mixtures, their burning velocities are also important. If the gas flow rate does not exceed the burning velocity, the flame propagates back into the burner giving a 'flashback'.

At high flow rates, the flame rises and eventually reaches a point where 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 above the burner where flow velocity and burning velocity are equal.

So, what is the additional absorbance I am going to measure? This is the additional absorbance this is the additional absorbance I am measuring at lambda, but it is not due to the element which I want to determine. So, this introduces a noise or an electrical noise which is not wanted therefore, what I have should be measuring I should be measuring an additional I want to measure only the resonance line, but this is the additional information that is that I am getting; because this portion also belongs to this absorbance is a combination of the AAS absorbance plus the broadband contribution. I think you are convinced of the problem here because all these broadbands have some amount of absorbance, the system cannot differentiate between the resonance line and the absorbance of the CH NH and the other bands at the resonance line.

So, the total absorbance would be the algebraic some of the signals at the resonance wavelength. So, they in addition to the composition of the gas mixtures their burning velocities are also important, if the gas flow and if the gas flow rate does not exceed the burning velocity the flame propagates back into the burner giving a flashback. So, what is a flashback? The flame will get sucked and then there will be an explosion. So, we should be very careful whenever we want to determine any element using atomic absorption because we do not want flashbacks and explosions occurring in the burner. So, at high flow rates what happens? If the high flow rates generally the absorbance that is the fuel gas is more. And eventually it reaches a point where it blows out of the burner blow it there are instances where the whole burner itself is blown off therefore, it is very important to adjust the flow rate of the fuel oxidant mixture, until it reaches a point above the burner where flow velocity and burning velocity are equal, both flow velocity and burning velocity should be equal.

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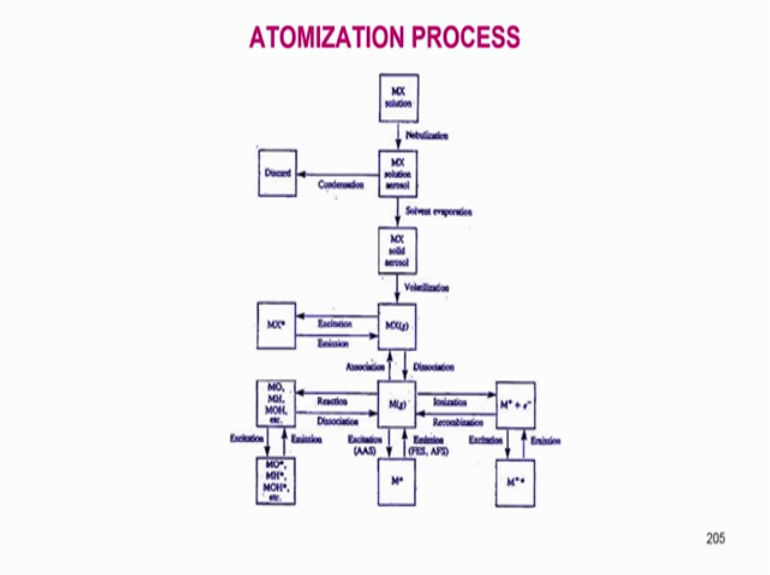

ATOMIZATION PROCESS

So, now we move on to another aspect of atomic absorption and that is to understand what exactly happens in an atomic absorption process that is we have already said negative we have already said.

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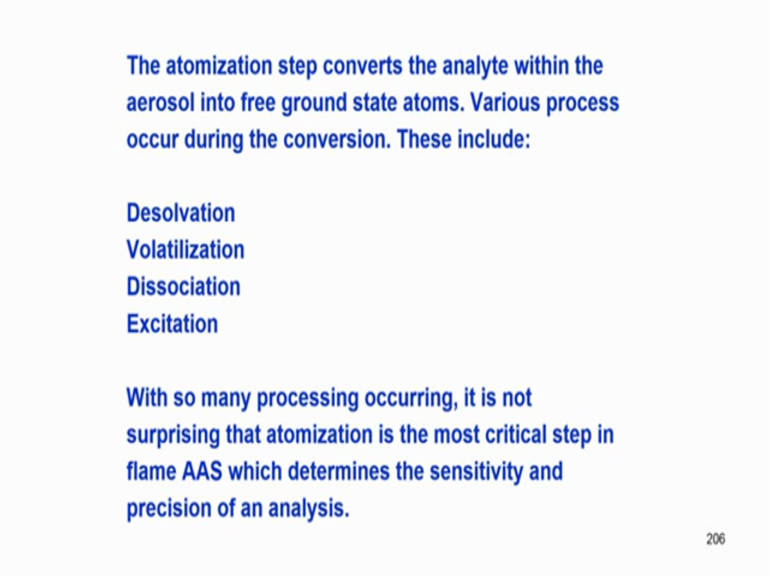

The atomization step converts the analyte within the aerosol into free ground state atoms. Various process occur during the conversion. These include:

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.

There is a need for nebulization and from the nebulization we want the free atoms in the space where flame is burning. So, we are introducing the sample in the form of vapor. So, what is the mechanism of atomic atomization? So, how does it happen? So, there are several theories and the most popular mechanism normally involves the desolvation that is there is a desolvation process, and volatilization process dissociation process, and excitation process. So, the whatever we are saying is whenever we introduce a vapor atomic solution into the atmosphere of the flame, the droplets what are that are being produced will normally have to undergo evaporation. So, the different steps are first it must be desolvated there is a almost every salt is having some amount of solvation water molecules around the ions. So, those water molecule should be removed that is desolvation, and then once the water molecules are gone then we want the atoms the water droplets to volatilize.

So, after it volatilizes all the liquid is removed what will remain the metal salt in the solid form. That solid form of the metal in the flame should be it goes it undergoes dissociation and once the dissociation is complete ions will be forming, and these ions will take up electrons and get excited to higher energy level etcetera etcetera free atoms etcetera and then we will have atomic absorption. So, with so many processes occurring it is not surprising that the atomization is the most critical step in the flame atomic absorption spectrometry which determines the sensitivity and precision of an analysis. So, this is the process here what I have is a solution of suppose I want to determine copper then I will have MX copper chloride. So, copper MX what we mean is it is a copper chloride solution. So, the moment I put it in nebulization whenever I have this MX solution, I put it through the nebulization and in the nebulization what is produced is aerosol. This aerosol is what is aerosol composition? It is the MX that is copper chloride in the I am only taking the example of copper chloride, but it can be any salt.

So, I have MX solution aerosol. So, part of bigger droplets condense and then get discarded here in this range. Now smaller droplets what happens they undergo solvent evaporation that is desolvation and then MX that is copper chloride solid aerosol will be there; that means, just like talcum powder in the air whenever you press it. So, the solid powders will be formed and this solid aerosol particles of copper chloride will continue to volatilize.

And MX gaseous next step is gaseous formation; gas a vapor formation of the copper chloride. So, I have written here MX g into bracket. So, this MX g gaseous form of the copper chloride can take up an electron go to next higher energy level, I denote this as MX star; that means, it has picked up an electron there and this excited electron can be lost by emission and again it forms the MX gaseous; that means, there is an equilibrium reaction between the MX g and MX star. That is one side reaction which is does not contribute to the atomic absorption. Now this MX g 2 aerosols of MX gaseous can combine to form association products and or it may undergo dissociation also because temperature is very high in the flame. So, this disassociation produces M g that is metal vapor in the gaseous form. In this form again it can pick up electrons or it can undergo chemical reaction with oxygen hydrogen etcetera in the flame.

So, if it undergoes chemical reactions with the flame elements I have MO metal oxide and metal hydrogen metal hydride MOH that is metal hydroxide etcetera and these things can also be dissociating to form Mg that is metal vapor; that means, this is another side reaction where there is loss of metal ions to some extent. And then another way of losing is they undergo ionization M plus e minus this is again an equilibrium reaction, and a they can combine M plus and e minus can combined to give you metal gases also gaseous if metal in the gaseous form.

Now this molecular orbitals molecular compounds excited molecular compound can get excited to higher energy level and emission. So, there is molecular ex excitation and emission process occurring in the flame for MO MOH, MH etcetera. So, this is again another equilibrium reaction which does not contribute to the atomic absorption measurement. Now similarly the metal ions if it undergoes excitation there is not much atomic absorption here. Now the other process is this metal gas metal in the gaseous form can undergo form atoms and this atom can get excited and it there will be an equilibrium between excited and non-excited metals, and it may lead to atomic absorption or it may lead to atomic emission depending upon on the temperature and property of the element.

So, among the emission is this fluorescence emission spectrometry and atomic fluorescence spectrometry both are possible and instruments are available to measure the atomic fluorescence and this flame emission, but right now we are talking about atomic absorption spectrometry that is we are interested only in this process. So, this is how the mechanism of atomic absorption takes place. So, this I have already explained to you that atomization step converts the analyte within the aerosol into the free ground state atoms several processes.

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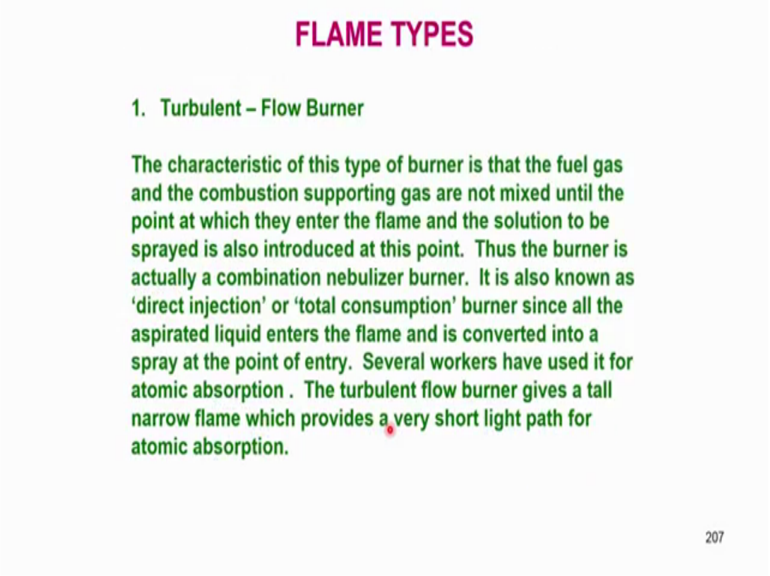

FLAME TYPES

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 aspirated liquid enters the flame and is converted into a spray at the point of entry. Several workers have used it for atomic absorption . The turbulent flow burner gives a tall narrow flame which provides a very short light path for atomic absorption.

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I have already described I think you are comfortable with the presentation.