Trace and ultra trace analysis of metals Using atomic absorption spectrometry

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Lecture – 15
Instrumentation in AAS I (Contd) Radiation Sources

Greetings to you all, we are discussing about radiation sources for atomic absorption spectrometry.

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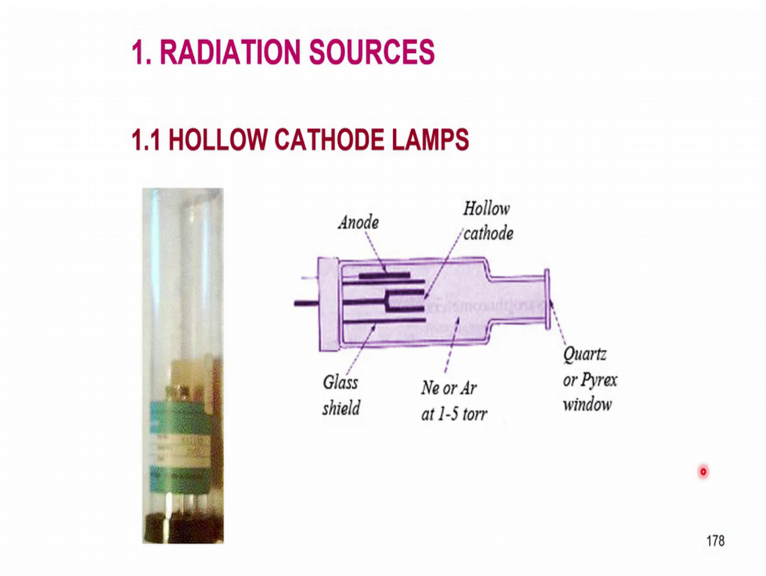

What we had discussed was about hollow cathode lamp as one of the sources of radiation which will give out the radiation of the same element which you want to determine and because the filament is made of the metal which you want to analyze the filament is in the form of a conical cylinder.

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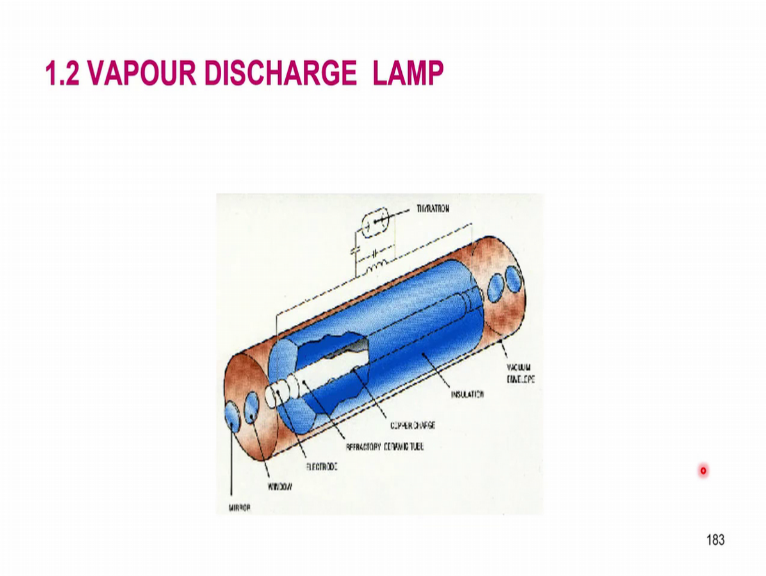

And we had discussed at length about these things I will do not want to repeat this, but we will move on to another source of the radiation that is known as vapor discharge lamp.

Here they you can see that the construction is almost similar in to the hollow cathode lamp it is a long tube and then made of Pyrex at the this end an or quartz window at this end. And then there is a vacuum inside and inside this hollow cathode tube we have the connectors here and then the sample is wound around this ceramic tube it is a refractory ceramic tube and if I want to make a copper estimation I wind a copper wire along this vapor discharge lamp. So, it is all insulated nicely and then we have; is lamp is ready for use.

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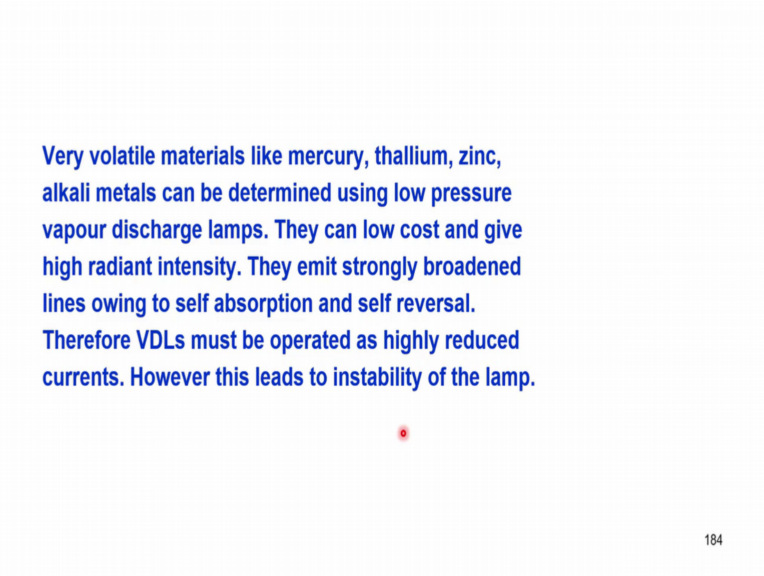

So, essentially the remaining part of the hollow cathode lamp remains the same and there is a glow discharge which from neon or argon which ever use whichever gas you use and later on them the initially glow discharge will start followed by the wire.

So, very volatile materials like mercury thallium zinc and alkali metals can be used can be determined using low pressure vapor discharge lamps why only these things because the we do not really create the discharge made by as like flame and we simply the use the materials as such they can they can be of low cost and give high radiant intensity because these elements are usually converted into vapor phase and they emit strongly broadened lines going to self absorption and self reversal because if the vapor concentration is more there will be lot of self absorption this we have already seen in the case of sodium lamps in our street light example. So, VDLs must be operated at highly reduced currents. So, the current requirement is very less, but if the current requirement is very less it leads to instability of the lamp poles.

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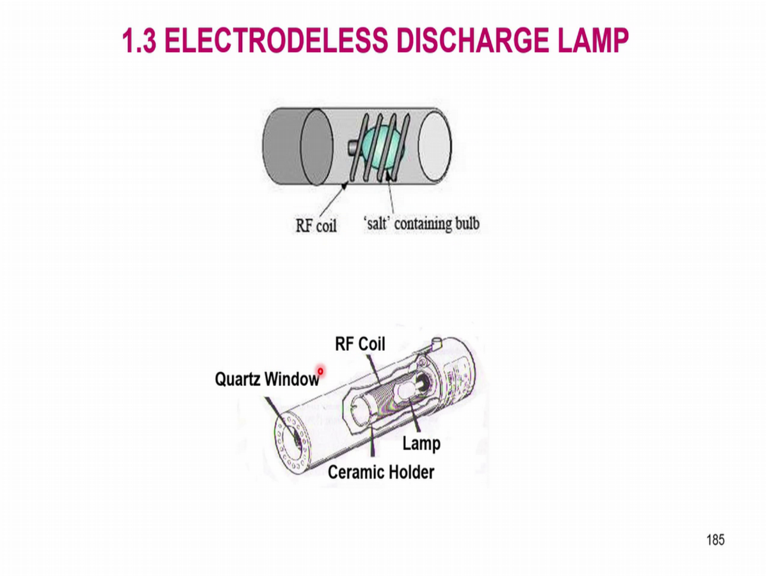

So, these are some of the problems with the material materials and they are not. So, common as a EDLs hollow cathode lamps because hollow cathode lamps are made of the same filament etcetera and they are made very easily and then it is difficult to make very few lamps are usually made of these are EDLs electrode less discharge lamps because only volatile materials need to be converted into vapor phase.

Now, the volatile materials means at very low temperature the material should be should vaporize that is the idea. So, we just go to the copper wire or some other wire with volatile materials like mercury this I already told you now this mercury thallium zinc and alkali metals etcetera and when we heat them; the discharge takes place. Now I am going to discuss another type of lamp that is known as electrode less discharge lamp. So, as the name suggests we have the there are no electrodes in this what we have we have a quartz window here in this side the you can see the plain portion of this region that is a quartz window and this is an RF coil radio frequency coil bound around a ceramic holder and then here you see there is a small cavity in this cavity we put our materials which we want to get discharge you can put any salt for example.

So, this is the salt containing bulb and this is the RF coil this is the front view. So, one side is by quartz window the other side is connected. So, essentially it is a very simple operation only thing is there are no electrodes here only the salt is deposited inside the cavity of the ceramic tube on which an RF coil is bound. So, how does it work?

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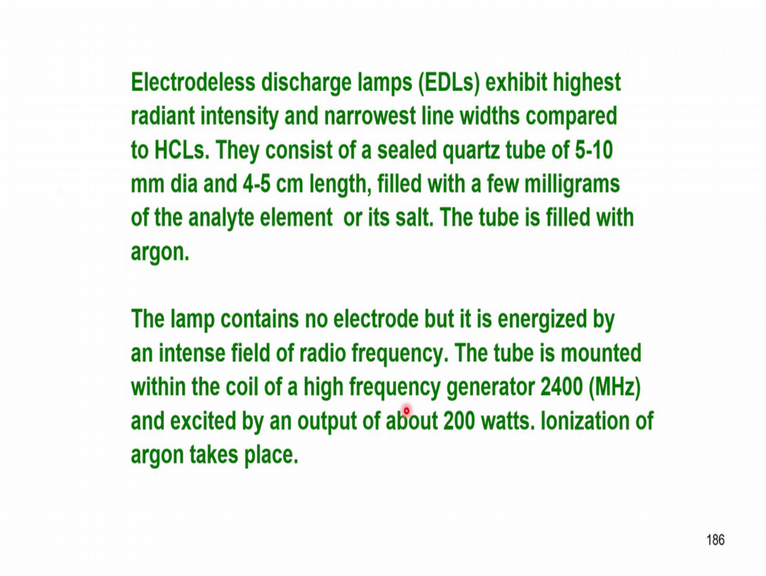

Yes electro this is known as electrode less discharge lamp because there are no electrodes and these things exhibit highest radiant intensity and narrowest line widths compared to hollow cathode lamps because basically the salts ionize and then they will pick up the electrons from the neon or argon glow discharges. So, it consists of a sealed quartz tube of about 5 to 10 mm dia 4 to 5 centimeter length and it is filled with a few milligrams of the analyte element this is a very important aspect of any analytic atomic absorption you need to have a salt of the and what you want to analyze you can put the element itself or its salt also this tube is filled with argon that is to set up the glow discharge.

So, the lamp contains no electrode, but it is energized by an intense field of radio frequency the tube is mounted within the coils of a high frequency generator their range is about 2400 megahertz and it is excited by an output of about 200 watts. So, these are the technical details of 2400 and 200 watts etcetera, they can vary for different elements this point you should remember and also you should remember that the design of this can vary from instrument to instrument. In fact, most of the instrument manufacturers change the design this length width and then the diameter and then connectors like that to suit their models. So, that they are also not applicable to other instruments. So, it is it becomes sort of intellectual property also the design.

So, we have this they may change this generator frequency they may change to a to from 200 to 150 watts or 250 watts. So, what happens is if the minimum if the if you want to fit the lamp of one instrument to another instrument for example, PerkinElmer to GBC or some other manufacturer they would set the limit at 2200 hertz then what happens if your instrument is not designed to take 2400; if it would not take 2400, but the EDL of another company another manufacturer would require 2400.

So, it would not work same thing is true with respect to weight edge also they will say we will set it up at 150 watts that they will not tell you in the technical literature it is only manufacturers data and they will say you buy our radial and then electrode less discharge lamp and use it and if you want to use somebody else's then it has to take 200 watts suppose the instrument itself is supplying only 150 watts definitely other EDL’s will not work plus there are other safeguards they normally employ such as position of the connector and other things.

So, in general what we see across the market is most of the hollow cathode lamps or electrode less discharge lamps or vapor discharge lamps all these things normally are suitable for a particular model and for a particular company belonging to that company because models may change, but still the a material the electrical connectors and other things will remain the same. So, it becomes intellectual property. So, we will we are forced to buy EDL’s and the vapor discharge lamps from the same company if you are using a particular model. So, this point we should remember of course, there are nowadays there are interconnected which will help you to some extent, but not all the time.

So, these are the 3 main radiation sources for atomic absorption spectrometry there are others also for example, the a there where you can use a xenon lamp in a xenon lamp gives you very high intensity radiation at all wavelength frequencies right from UV to visible, but is a xenon lamp has short life etcetera there are other problems which have been solved to some extent in recent instruments, but before we go to that level.

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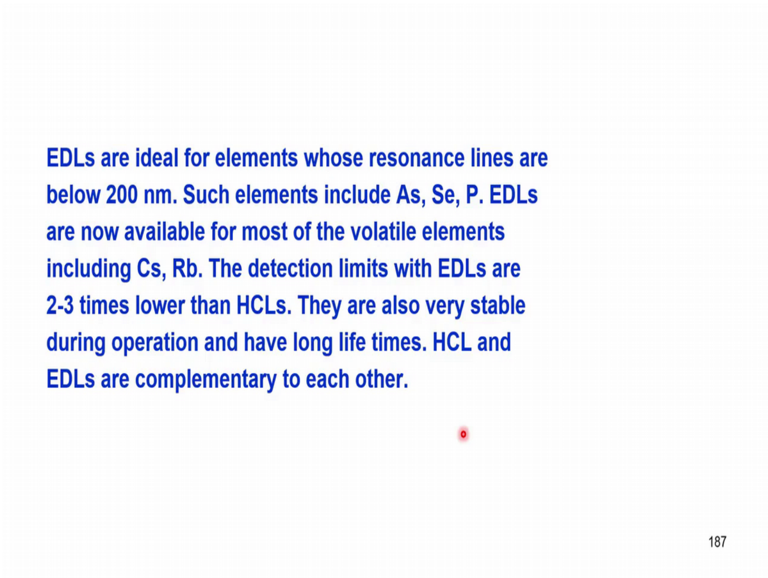

We will take a look at the chemical aspects of EDL. So, the EDLs for are ideal for elements whose resonance lines are below 200 nanometers this is an important aspect because earlier I had said that several elements like iodine arsenic etcetera they have resonance lines less than 200 nanometers.

Now, here we have if I use a vapor EDL electrode less discharge lamp I have a chance of using such a elements such EDLs light sources because EDLs give you very high intensity radiation and very narrow bandwidth. So, what are such elements these elements are arsenic selenium phosphorus iodine etcetera iodine is not there usually nobody determines iodine by atomic absorption, but EDLs are nowadays available for most of the volatile elements including c c m and rubidium actually the work function of c c m is very less, so it is used in detectors, but even for atomic absorption c c m and rubidium EDLs are available. So, if you use an EDL what are the detection limits? So, how do you compare the detection limit of EDL with anything else the only reason is to compare the sensitivity that is the lowest quantity of determination of the element with other radiation sources.

So, the what are the other radiation sources EDLs are not available for elements like arsenic etcetera the you have to compare only with hollow cathode lamps electro discharge lamps I have not available for all elements. So, we EDLs even though they are not so common for every element, but the detection limits what you are going to see are about 2 to 3 times lower then HCL for example, if with HCL we are able to determine about ten micrograms per liter or 10 PPB with EDL you can go to 3 micrograms per liter still lower quantities can be determined and we will discuss about the trace element theory of trace element determination at a later stage when we complete the atomic absorption studies and then after when we move towards applications.

So, they are also very stable EDLs are very stable and during operation and have long life times. So, HCL I had told you that they have a very short lifetime may be about 2 liter to 2 to 3 years, but EDLs have longer shelf life. So, what you what are the conclusions the conclusions are EDLs and HCL a hollow cathode lamp are complementary to each other what cannot be determined easily with hollow cathode lamp we should determine by electrode less discharge lamps or vapor discharge lamps also are possible.

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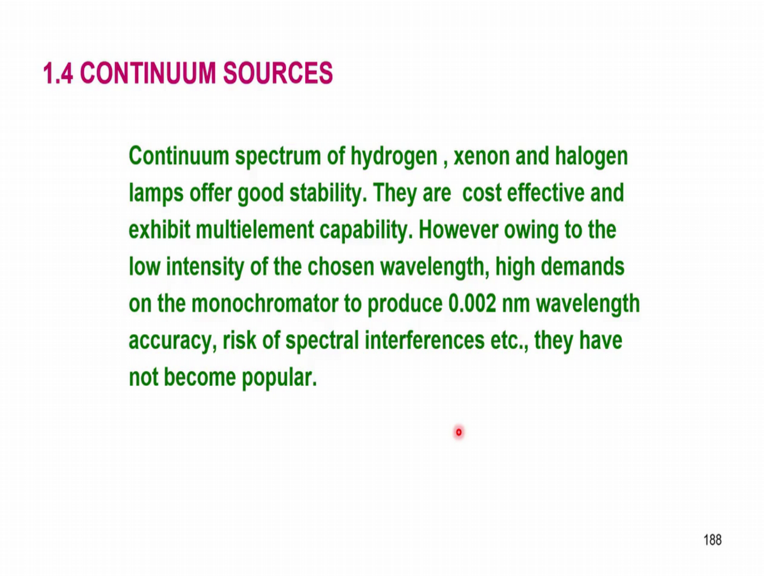

Now there are as I telling you we look at consist continuum sources. So, continuum spectrum of hydrogen xenon halogen lamps etcetera offer good stability they are cost effective and exhibit multi element capability they are; that means, you can because it is continuous several elements are detectable.

Because continuous spectrum means almost all lines are available in this spectrum. So, you can choose by putting a monochromator you can choose a any wavelength from the continuum corresponding to an element whose resonance line falls in that region. So, what we are saying is the whichever element gives you a continuum spectrum in the UV and visible range you should be able to determine theoretically atomic absorption and method you should be able to use atomic absorption for the determination of elements, but the only condition is the continuum portion of the spectrum must be also be very highly intense this does not happen.

For example even for hydrogen etcetera very few lines are really strong lines and; that means, they are when you collect on them photographic plate you should see a very dark line corresponding to that resonance line. So, the hydrogen xenon and halogen lamps normally offer good stability they give you continuum spectrum also, but among these only xenon lamp has picked up somewhat and now a days I am seeing in the market xenon lamps are being offered for atomic absorption spectrometry.

Now, what are the advantages of a xenon lamp one thing is it gives continuum. So, you can determine any element from UV if from the UV and visible rate range and one single source is enough that is xenon lamp correct. So, if I use a xenon lamp I do not need a hydro hollow cathode lamp I do not need electrode less discharge lamps I do not need vapor discharge lamps only one source will do. So, such instruments have become available since last 2-3 years only maybe earlier they were curiosities scientific curiosities, but nowadays commercial instruments have become available where you can use a xenon lamp which will obviate the necessity of purchasing a hollow cathode lamp for every element.

So, this is one advantage the other, but there are disadvantages with halogen lamps also what are they the lamp becomes very hot. So, you need to circulate cold water around the xenon lamp to keep the lamp in good working condition otherwise the lamp may be may not work for a long time. So, continuous cooling of these xenon lamps is necessary and also the optics will change because the same optics has to choose from a continuum spectrum particularly in hollow cathode lamp it is only one line 1 or 2 resonance lines maximum I can use. So, I can use a monochromator made of only glass filter or a simple quartz filter or a quartz prism I can use it, but from if you want to use a xenon lamp you need to have a proper monochromator which can give you very good accuracy of the wavelength what you want to choose.

So, these are the other things. So, if you take a look at this slide you will see that the low intensity of the chosen wavelength that is corresponding to hydrogen and halogen not xenon the intensity would be low. So, high demands on the monochromator; a monochromator performance should be extremely well. So, what it should produce it should produce an accuracy of 0.00 to nanometer wavelength and there will be risk of spectral interferences always and they had not become popular, but nowadays the technical problems of xenon lamps have been overcome and such instruments are available in the market.

So, now we move on to atomizers. So, what is an atomizer? The requirement of the production of free atoms in the optical path of the radiation coming from the hollow cathode lamp I need to put the mass of free atoms of the element which I want to analyze. So, the atomizer is a space in between the hollow cathode lamp and the monochromator and the detector on the other side and that atomizer should have a mechanism to produce free atoms from the sample which you want to analyze earlier I had told you that the most of the samples which we want to analyze in atomic absorption are in the aqueous state are in the liquid state most of the samples are dissolved in ethics and diluted to get solutions and this solution needs to be converted into fine vapor containing ions and those ions will pick up electrons from the flame and they have become atoms free atoms which is ready to absorb the radiation coming from hollow cathode lamp.

So, the job of the atomizer is to produce free atoms and the liquid must be converted into ions first vapor and then ions and then into atoms. So, this is easily accomplished by spraying the analyte you can look at this slide now.

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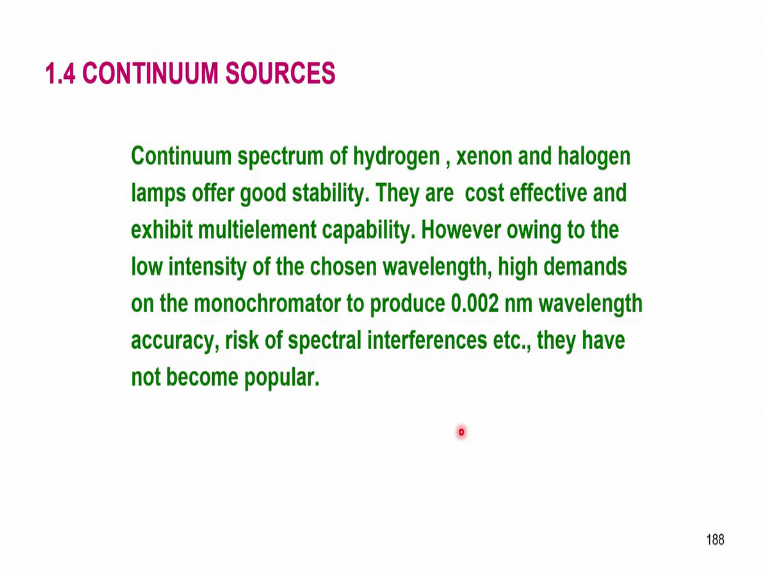

What I have written here the atomizer transformed a liquid sample into atoms this is easily accomplished by spraying the analyte solution into a flame where the ions or molecules are converted into atoms. So, is this the only mechanism that is available to convert a sample into a vapor; no, the answer is no there are other techniques of atomization that include I can heat it electro thermal evaporation I can produce a hydride generation which I had mentioned earlier a little bit a little bit earlier I had mentioned you and there is a cold vapor technique that is also we can we are going to discuss it later and the success or failure of atomic absorption determination is virtually dependent upon the efficiency of atomization. So, the total number of atoms that are formed determines the sensitivity.

Now we should imagine that there is a flame here space in which atoms are being produced here and then I have a small pipe from the bottom which will spray the liquid you would have seen number of sprayers gardens prayers this prayer and can sprayer a window cleaner most of them are sprayers. So, what I will do normally is I take a sprayer put the sample through the sprayer and press it. So, what happens a fine mist of the liquid will form and that liquid I am taking it into the flame space I will show you a diagram corresponding to that, but before that what you should realize is the since the job of the atomizer is to produce free atoms the more free atoms are produced more would be the absorbance more would be the number of atoms in the ground state which I we have already seen earlier that at any temperature the atoms in the ground state are at lower and ground state.

So, if my efficiency is more there are more atoms in the ground state. So, more atoms will absorb the radiation. So, if I am measuring the radiation if there are more atoms radiation coming out would be. So, much less if there are less atoms it a radiation will be more if there are more radiation; radiation coming out to will be less if there are no element if there are no free atoms then the radiation will remain unchanged that is 0 concentration at 0 concentration the radiation what we collect from the atomizer would not be affected because there are no free atoms suppose I may a I pass only water then what happens I want to determine copper there is no copper in water.

So, when there is no copper in water there are no free copper atoms. So, the radiation incoming and transmitted radiation will be same. So, if there are some about 100 atoms in the copper solution radiation will be. So, much less corresponding to 100 atoms if there are thousand copper atoms in the ground state I will have more absorbance and the radiate transmitted radiation will be. So, much less that is the logic of using an atomizer. So, you look at the slide now the success or failure of atomic absorption spectrometer is virtually dependent absolutely dependent upon the efficiency of atomization that is the total number of atoms that are formed.

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Numatic nebulizer is very useful to spray the sample into a flame in a continuous manner to maintain a steady supply of atoms. Usually nebulizers are connected to the flame burner which can be considered as a single unit even though, both parts are detachable and serviced independently and reconnected. Typical design of a Laminar flow burner is shown here.

Laminar flow burner uses a concentric tube nebulizer in which oxidizer and the fuel gas combine to produce an aerosol of the sample. The sample passes through a number of baffles and flow spoilers. Only the fine mist and mixture of gases are led into a slotted burner of 5 cm width. The flame height is approximately 5 – 10 cm.

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So, this point I hope I have driven well and the most easiest way of determining producing a free atom population in the optical path is a numatic nebulizer. So, what is a numatic nebulizers enable the nebulizer is one which converts a liquid into a spray a numatic nebulizer is it converts because of air pressure, because of the air pressure it will push out the liquid and produce a spray you can imagine any plastic simple plastic bottle in which liquid is put and you press it liquid will come out and if you put a at the exit point if you put number of holes small small holes vapor will come out into small jets and if the hole is small enough then it will produce small droplets in the space that is immediately outside.

So, that is a numatic nebulizer: numatic nebulizer is very useful to spray the sample into a flame in a continuous manner because we do not want to do it a manually every time we want to do it in a continuous manner. So, to maintain a steady state supply of atoms because in the flame if I if you remember a flame is a dynamic system flame is burning I want to introduce my sample. So, what happens to my sample my sample also keeps on flying out of the flame after some time may be a few microseconds it is there in residing in the flame and then it move a it will move out because more atoms are coming from the bottom. So, after some time what happens is the number of atoms coming into the flame and number of atoms going out of the flame will match.

If I have a steady supply of the liquid, so the because of the steady supply that is what we want the number of atoms entering the flame number of atoms leaving the flame are essentially same. So, this kind of steady state is required in atomic absorption spectrometry. Now, usually look at this slide now nebulizers what the job is to spray in a continuous manner look at the slide I want you to understand this continuous manner to maintain a steady supply of atoms is a must usually they are connected to the flame burner through a small capillary which can be considered as a single unit even though both parts are detachable and serviced independently and reconnected. So, typical design of a laminar flow burner is shown here.

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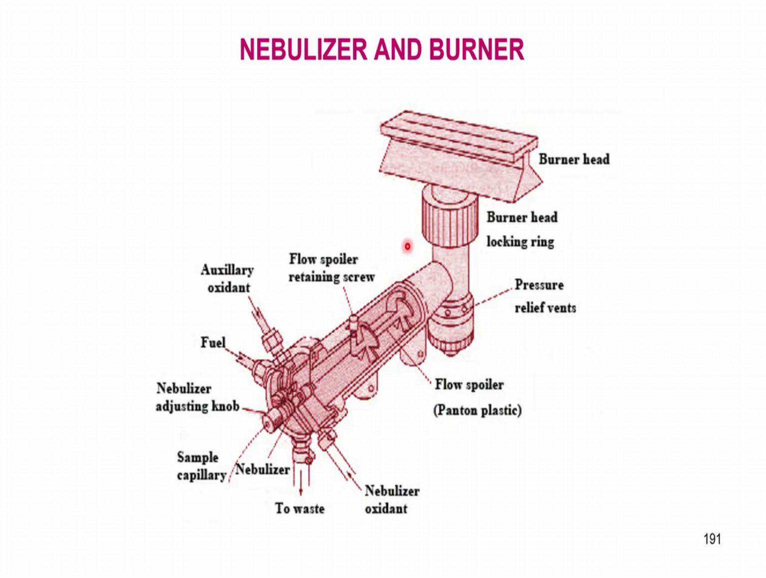

This is the atomizer or nebulizer and a burner assembly in atomic absorption spectrometer we will continue our discussion in the next class.