Modern Instrumental Methods of Analysis
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Module No 04
Lecture No 20
Atomic Absorption Spectrometry -4 Instrumentation

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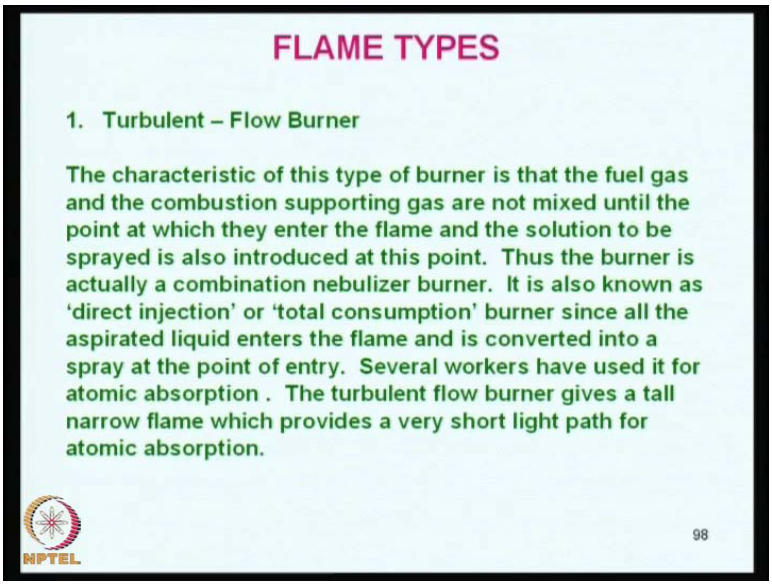

FLAME TYPES

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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We will continue our discussions on the flame types in atomic absorption spectrometry. We were discussing about the flow burners there are basically two types, one is a turbulent flow burner, another is pre mix burner. So, in the turbulent flow burner the characteristic of that type is that the fuel gas and the mixture combustion gas as well as, the sample are introduced only at the tip of the burner. That means, they come from different sources put into a uniform cone and then releasing simultaneously at the tip of the burner. So, the characteristic of this is a it is a combination of nebulizer as well as a burner. Because it has to break down the sample also into very small droplets for further reactions to occur as I have explained in the last class.

So, this burner is also known as, direct injection burner because we are introducing the sample also at the entrance of the flame. So, it is converted into a spray also at that point of entry. Several workers have used it for atomic absorption the turbulent flow burner usually gives a tall narrow flame, which provides a very short flight path for the atomic absorption. So, the idea is to introduce everything into the burner and let the burner take care of the atomization, because the sample is also sucked near the end point of the of the capillaritive and enters the flame along with the flame gas is also entering as well as the oxidizer.

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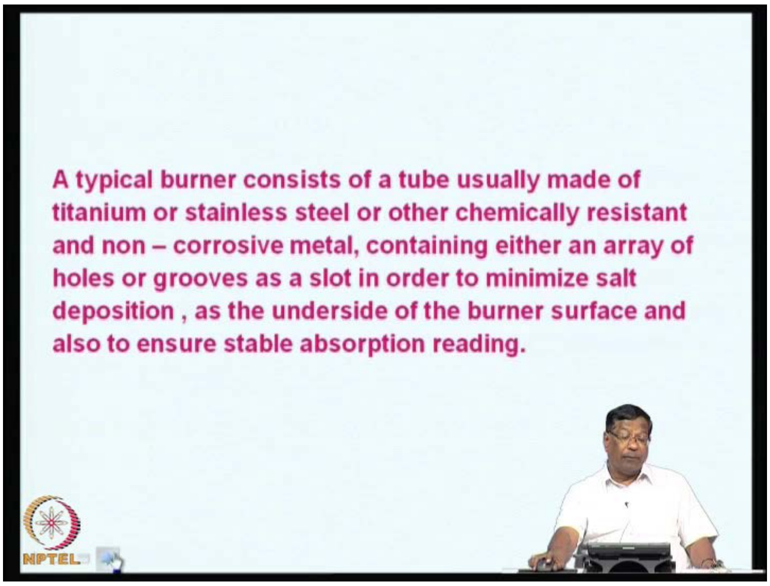

A typical burner consists of a tube usually made of titanium or stainless steel or other chemically resistant and non – corrosive metal, containing either an array of holes or grooves as a slot in order to minimize salt deposition , as the underside of the burner surface and also to ensure stable absorption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

So, a typical burner usually consists of a titanium base or a stainless steel base. So, other there are other chemically resistant and a non corrosive metals also have been used, but mostly titanium as well as, stainless steel burner seems to be of use. They contain either and array of holes or grooves as I slot in order to minimize salt deposition has the underside of the burner surface and also to ensure stable absorption.

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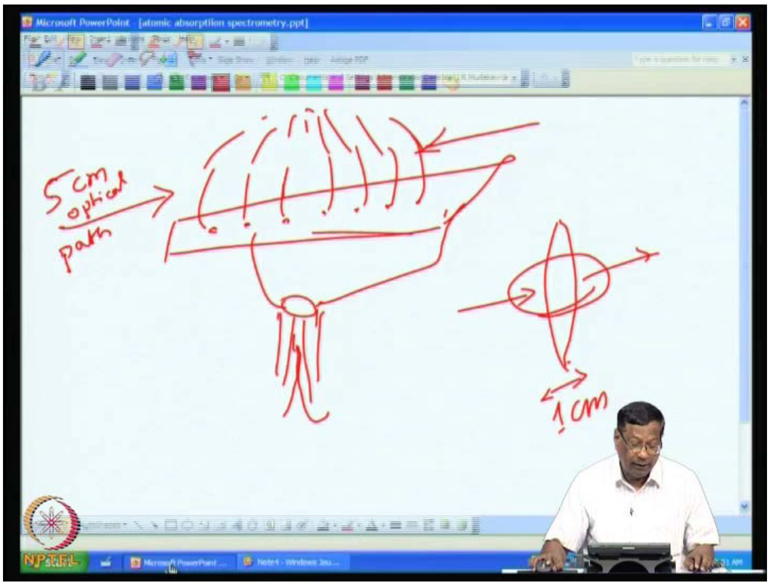

What we want to do? Is a take the burner introduce the gas, introduce the sample. So, here we are they are all burning and we draw a flame coming out through the flame into through a number of slots otherwise, what happens? You are having a flame like this and this provides a very small optical path only this much. The distance would be hardly one centimeter. So, this we do not want to happen, so, what you would like to do? Is take the burner and then, put it through titanium metal block in which, so many holes are made and then through the holes that will be flame coming out like this.

So, this will provide the optical path of the order of about five centimeter. If we do not do this, we have a burner going just like a candle burner the width of the burner would be hardly one centimeter. And compared to this the optical path would be less and sensitivity also would be five times less in the turbulent burner.

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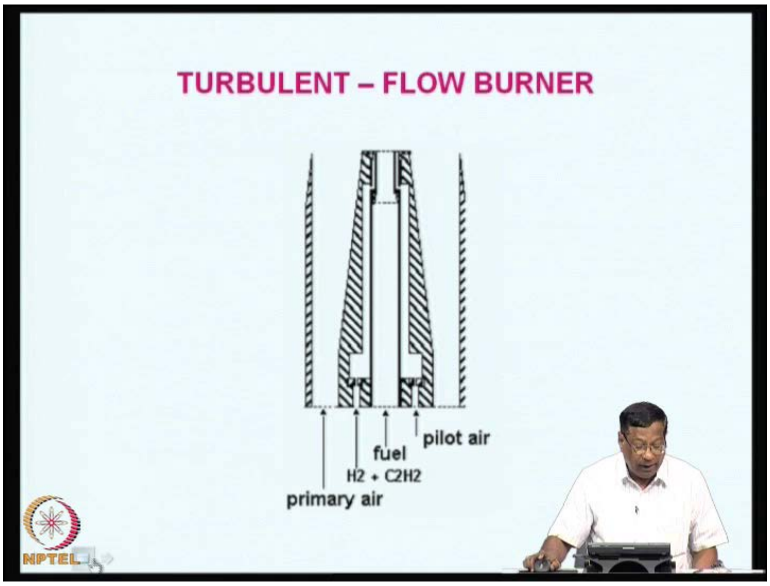

TURBULENT – FLOW BURNER

So, a typical burner we have to make it like this, and the actual design of the burner is like this, here we are introducing primary air and then there will be hydrogen possibility for introduction of hydrogen and acetylene and fuel also would enter like this. And pilot air, if we are using air as an oxidizer we are going to mix all of this is a material, which is at the edge is made of titanium here as well as outside.

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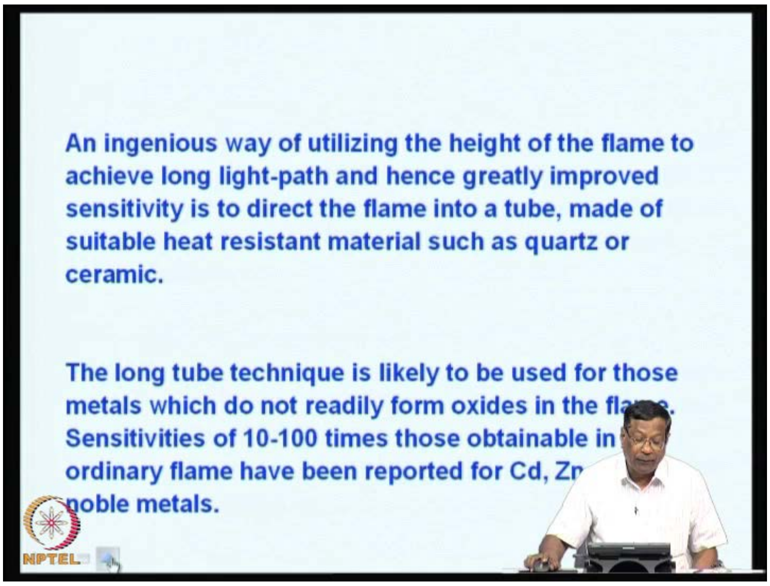

An ingenious way of utilizing the height of the flame to achieve long light-path and hence greatly improved sensitivity is to direct the flame into a tube, made of suitable heat resistant material such as quartz or ceramic.

The long tube technique is likely to be used for those metals which do not readily form oxides in the fla e. Sensitivities of 10-100 times those obtainable in ordinary flame have been reported for Cd, Zn noble metals.

So, this is a typical turbulent flow burner. So, how we increase this sensitivity is utilizing the height of the flame to achieve the long flight path. And hence greatly improved sensitivity is to direct the flame into a tube made of suitable heat resistant material. You can also use it as use quartz or ceramic they are also known to it is temp very high temperatures of the order of about 3000 degree centigrade. So, this long tube technique is likely to be used for those metals, which do not form oxidizes in the flame if they form oxidizes they will not higher nice.

So, that is very important in the analysis of oxidizes, oxide forming elements. If you have oxide forming elements and if you want to analyze them then you should use a smaller flame like here in this in what I have shown you here. So, we will get back to that the sensitivities of the order of about ten to hundred times are obtainable through an ordinary flame. These, sensitivities have been reported for cadmium, zinc and even some of the noble metals. So, it is very important for us to decide which type of burner we use.

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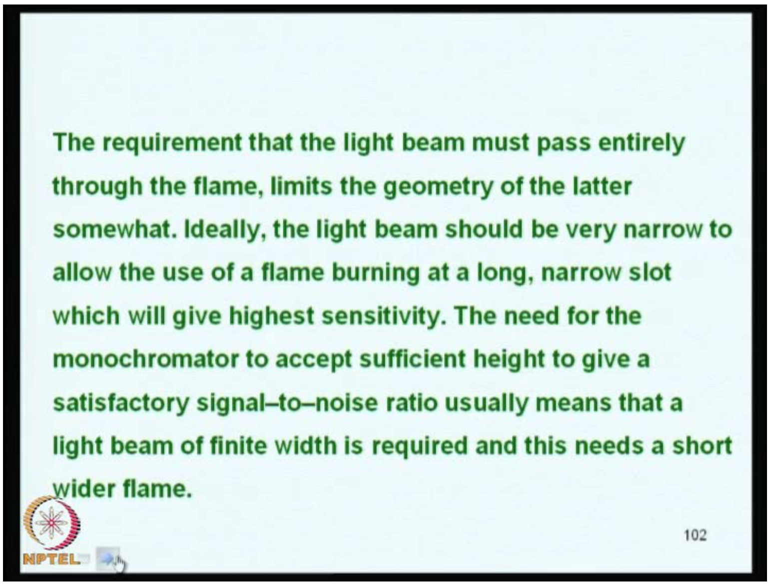

The requirement that the light beam must pass entirely through the flame, limits the geometry of the latter somewhat. Ideally, the light beam should be very narrow to allow the use of a flame burning at a long, narrow slot which will give highest sensitivity. The need for the monochromator to accept sufficient height to give a satisfactory signal–to–noise ratio usually means that a light beam of finite width is required and this needs a short wider flame.

So, the basic requirement is that the light beam must pass entirely through the flame. So, the light beam should be very narrow is another condition to allow the use of the flame burning at long narrow slot, which will give higher sensitivity. The need for the monochromator to except sufficient height of the flame to give a satisfactory signal to noise ratio usually means, that a light beam of finite width is required. So, to how do us increase the light beam of finite width is through take a titanium metal block with number of holes. So, that we have a flame, which is having an optical path of about 5 to 10 centimeter.

And then the turbulent flow burner it gives a flame which is a tall and narrow, while it is ideal for atomic absorption it provides a much shorter light path and hence exhibits poorer sensitivity compare to a laminar flow burner. The uptake of solution by the turbulent flow burner is also usually less than that of the laminar flow system and since all the aspirated solution is put it into enter the put into the flame or it enters the flame. It should be more efficient production producer of atoms then the laminar then the laminar flow systems.

But there is a small problem the problem is when you introduce the sample as a liquid more most probably ninety nine percent of the systems are introduced only as aqua solutions. So, the introduction of an aqua solution as a spray into a flame lowers the flame temperature, and this should not happen that is why turbulent flow burners have not. So, convenient and is a it is also not possible to make the turbulent flow burner into a laminar flow system unless you have one more attachment of the type what I had explained to you about titanium and steel burner stainless steel burner.

However, there is a evidence that is some of the aspirated liquid in the total consumption burner passes through the flame without being fully vaporized also. If the light path is very small very narrow; that means, much of the sample may pass through, because it is a very fast system burning system. So, the liquid without getting atomized it may go out of the systems also there by reducing the sensitivity. So, this some of the problems with turbulent flow burner, but otherwise premix flow burner is very ideal it is available as a routine component in almost all the atomic commercial, atomic absorption instruments.

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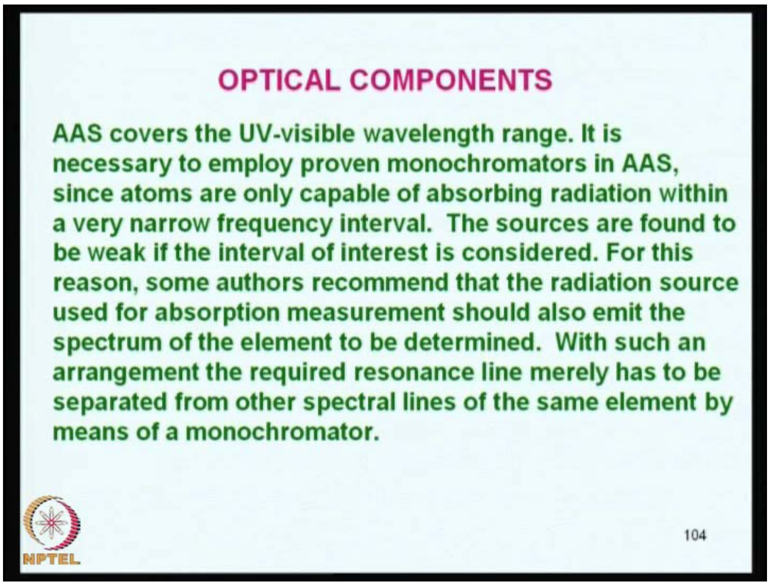

OPTICAL COMPONENTS

AAS covers the UV-visible wavelength range. It is necessary to employ proven monochromators in AAS, since atoms are only capable of absorbing radiation within a very narrow frequency interval. The sources are found to be weak if the interval of interest is considered. For this reason, some authors recommend that the radiation source used for absorption measurement should also emit the spectrum of the element to be determined. With such an arrangement the required resonance line merely has to be separated from other spectral lines of the same element by means of a monochromator.

Now, let us move on to optical components and the AAS as, we see should also have some sort of optical components to direct the radiation from the source and to select the source radiation and then to pass through the radiation etcetera. Therefore, AAS covers UV visible wavelength range that is the range, which we need in atomic absorption spectrometers, because most of the atomic absorption lines resonance lines of most of the elements fall in the UV visible range. So, we need the visible range optics also, it is necessary to employ proven monochromators in atomic absorption. Since atoms are capable of absorbing radiation within a very narrow frequency interval. And these, intervals have frequency interval are of the order of 0.002 2.0 to a nanometers. And the source is found to be weak, if we considered the interval of the radiation frequency.

So, for this reason, it is not possible to use continues radiation sources. So, what do we do? I have explained to you this earlier some authors recommend that the radiation source use for the atomic absorption measurement should also emit the spectrum of the element to be determine. It will also have resonance line with such an arrangement the required only we need to separate the resonance lines and others from other spectral lines of the same element by means of a monochromator. So, what is the job of the monochromator it is to separate the resonance line that is all. So, you need not have a monochromator before the before the flame, because you are getting only one radiation from that is resonance radiation from the source. So, once we separate it other radiation coming from the flame or usually separated by the monochromator that is simple.

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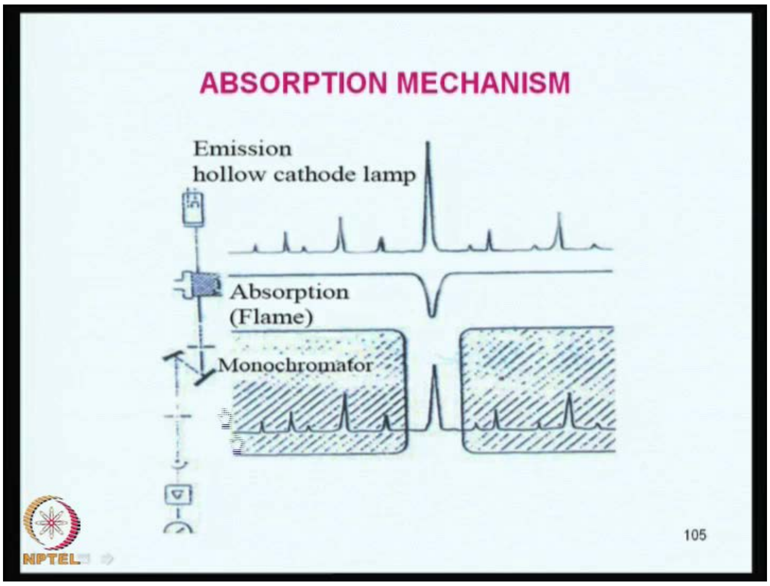

ABSORPTION MECHANISM

So, if you take a look at this figure, what we have here? We have source we have small filter and then optics and then it goes through a monochromator then absorption and this is the these, are the this is the hallow cathode lamp from the hallow cathode. Lamp we are getting number of lines spectrum lines like this, one two three four five this is the resonance line and these are nonresonance lines. Now, this is the first part what I am showing you here? Is the emission line and in the flame the atoms are produced and atomic absorption occurs since we are using only this radiation we do not need these radiations.

So, we need monochromator for blocking these radiations to enter and then we need a monochromator to block these also radiations also this we can stated through a monochromator. Now, what happens? Only this is the emission line and this is the absorption. So, the emission line gets attain attenuated by the amount of absorption that is taking place here in the flame. So, emission line intensity would be decreasing in this case that is atomic absorption.

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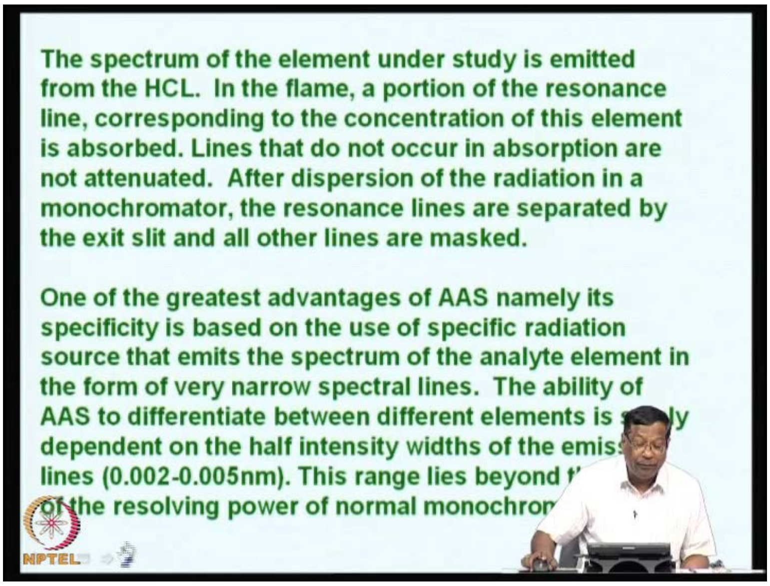

The spectrum of the element under study is emitted from the HCL. In the flame, a portion of the resonance line, corresponding to the concentration of this element is absorbed. Lines that do not occur in absorption are not attenuated. After dispersion of the radiation in a monochromator, the resonance lines are separated by the exit slit and all other lines are masked.

One of the greatest advantages of AAS namely its specificity is based on the use of specific radiation source that emits the spectrum of the analyte element in the form of very narrow spectral lines. The ability of AAS to differentiate between different elements is ly dependent on the half intensity widths of the emis lines (0.002-0.005nm). This range lies beyond t of the resolving power of normal monochrom

So, this is the mechanism the spectrum of the element under the study is emitted from the HCL. This we have already seen when we have been discussing about the hallow cathode lamps. So, in the flame a portion of the resonance line corresponding to the concentration of the element is absorb, lines that do not occur in the absorption are not attain attenuated what is mean by attention, is to reduce the intensity. So, lines after dispersion of the radiation in a monochromator there resonance lines are again separated by the exits slit we need a exit silt also. And all other lines do not pass through the exits silt, because we are allowing only the resonance line to pass through the flame.

One of the greatest advantages of atomic absorption spectrometry namely it is specificity; that means, one element, one technique and the response from other element for the same under the same conditions you almost zero that is what we call, specificity. That is the beauty as well as the attraction of atomic absorption. You want to determine any element you should simply choose atomic absorption, because any other element will not interfere in the process of the measurement. So, the specificity of atomic absorption is based on the use of specific radiations source that emits the spectrum of the element that is hallow cathode lamp.

And the ability of the AAS to differentiate between different elements is only again dependent upon the half intensity widths this we have discussed number of times. And of the emission line that is that gets half intensity widths we are getting due to du flora effect, isotropic effect, hyperfine effect and several other things. And that ranges from 0.0022 0.005 nanometer this range lies beyond the scope of the any known resolving power of a normal monochromator. We have seen when we have discussed in the spectra photometers also the best resolution you could get is of the order of about point two nanometer, but here what we need is 0.0022 0.005 nanometers.

So, the idea is hallow cathode lamp must be used as I source of radiation the monochromator as the most important task of separating the resonance line of the analyte element from other emission lines of the source. If silt widths are large in atomic absorption what happens, the sensitivity goes down. So, you will not be able to determine the element at lower levels that is what the atomic absorption are the quality of analysis is all about, what we want to say is you go down the concentration level. So, that you can determine parts per million, parts per billion, parts per trillion and femtogram levels, and etcetera.

And if we use the slit widths large silt widths than what happens, other radiations will be entry, they are all sort of spectral impurities. So, the sensitivity of the non resolvent multiples results in several resonance lines passing through the exit silt. So, the sensitivity goes down. So, it is absorb that for a number of elements a spectral bind pass width of point two nanometers is necessary to obtain good sensitivity. The requirement is of the order of point please go through the last slide what I showed you? Is the requirement is from 0.0022 0.005 nanometer requirement of this spectral separation.

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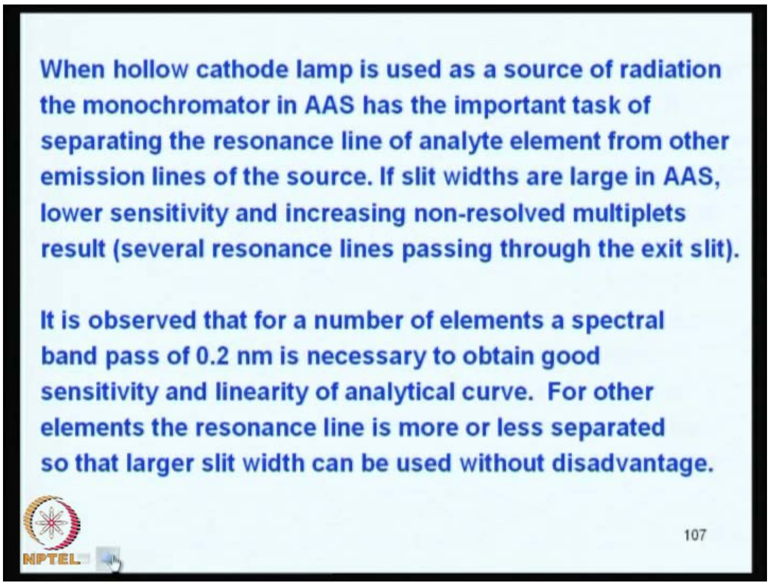

When hollow cathode lamp is used as a source of radiation the monochromator in AAS has the important task of separating the resonance line of analyte element from other emission lines of the source. If slit widths are large in AAS, lower sensitivity and increasing non-resolved multiplets result (several resonance lines passing through the exit slit).

It is observed that for a number of elements a spectral band pass of 0.2 nm is necessary to obtain good sensitivity and linearity of analytical curve. For other elements the resonance line is more or less separated so that larger slit width can be used without disadvantage.

And the instrumental requirement is about 0.2 nanometers it is necessary to obtain good sensitivity and linearity also of the analytical curve for other elements the resonance line is more or less separated. So, that larger silt width can be used without any disadvantage. So, you should not be worrying that, if are the requirement is only 0.002 to 0.005 nanometers, if I use 0.2 nanometers slit width. The other radiation lines may be coming in so, the sensitivity may go down, but this does not happen. Because the it is a other elements resonance lines are more or less well separated then 0.2 nanometers that is why there would not you will not be losing much of the sensitivity if you use 0.2 nanometers.

In some instruments you will see that there are people are using they give a choice to operate at 0.5 nanometers as well as 0.7 nanometers silt widths. So, that is also possible, but 0.2 nanometers is fairly sufficient to obtain fairly good analytical curves for other elements the resonance line is more or less well separated. So, that larger silt width also can be used without disadvantage this is the reason. Why they offer you 0.5 0.7 nanometer? Usually in most of the commercial instruments 0.2 and 0.7 are normally provided. And instruments now a days the modern instruments for a you a choice of slit widths in a continuous manner. You can use choose 0.2 0.8 0.5 0.4 0.7 like that the you can set the computer to that job.

So, the I want to show a figure subsequently shortly the influence of the spectral bind pass width on the sensitivity. And the signal to noise ratio also I want to show you as well as, the curvature of the analytical curve to prove that, if you use higher silt widths the sensitivity will not get affected in atomic absorption to a great extent. So, the for a I have chosen silica as the resonance as the element of a interest and silica as got spectral lines between 250 and 253 nanometers with such a small sufficiently small slit width. Every resonance line gives a linear analytical curve within the absorb range. Now, you can appreciate between 250 and 253 nanometers. There are several lines for silica for each of this silica, for each of this analytical line resonance line I what I do is? I had taken a small sample and using this wavelength I am going to determine the elements.

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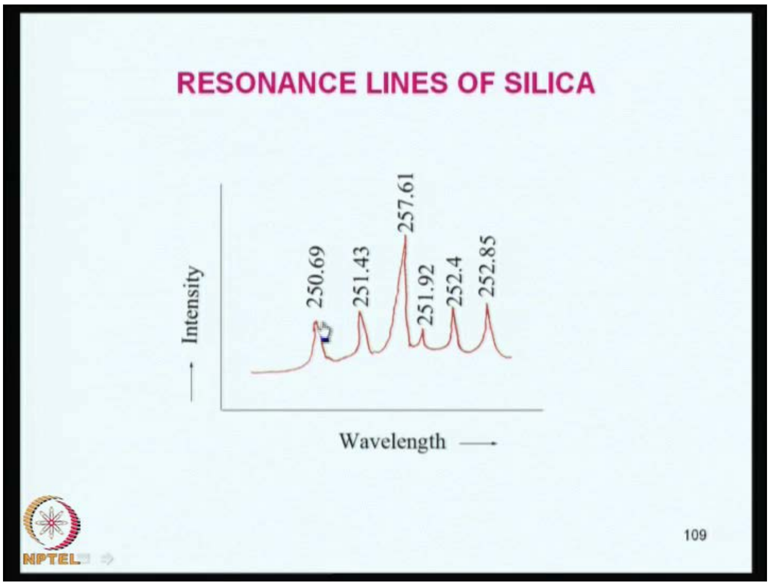

RESONANCE LINES OF SILICA

And draw calibration curve, when I do this calibration curve. You will see that there is not much difference for example, this silt will show you lines 250.69 and 251.43 is a another resonance line and 257.61 this is the resonance line of highest sensitivity you can see that the peak is very high here. And then there are other lines like 251.92 252.4 this one and the last 1 is 252.85. So, I have so, many resonance lines to prove the point that you can determine atomic absorption using all this resonance lines.

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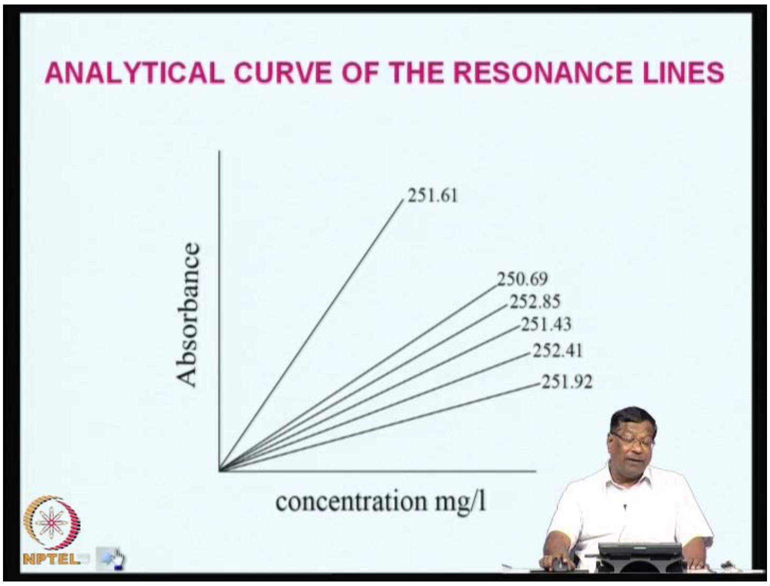

ANALYTICAL CURVE OF THE RESONANCE LINES

I draw a calibration curve, this is concentration in milligrams per liter and this is absorbance. So, you can see that if I use 251.61 that is corresponding to the highest sensitivity. This a resonance line if I draw a calibration curve you see that absorbance is a straight line corresponding to concentration in milligrams per liter. Similarly, at 250.69 this one and 252.85 is the next one like that, you will get slightly reduce absorbance, but the beauty is you can choose any of these wavelengths to determine the calibration curve. For example, the absorption in this case in 251.61 is about twice compare to absorption at 251.43 it is slightly more than 250.69 etcetera, but the point what I am trying to prove is you can choose any of these resonance lines.

And you can determine the concentration the calibration does not get affected, but the detection limits will definitely change, but not much also. Because the monochromator will allow all these radiations between 0.0022 0.005 or 0.2 nanometers you can see that all these are 0.6 0.69 0.85 0.43 0.41 and 0.92. So, if you choose 251.61 plus or minus 0.2 that is 0.43 as well as 0.85. All this lines will be permitted through the monochromator and you will get end up with an absorption curve somewhere in between these two in between this and this, because are many other resonance lines are also coming in this range.

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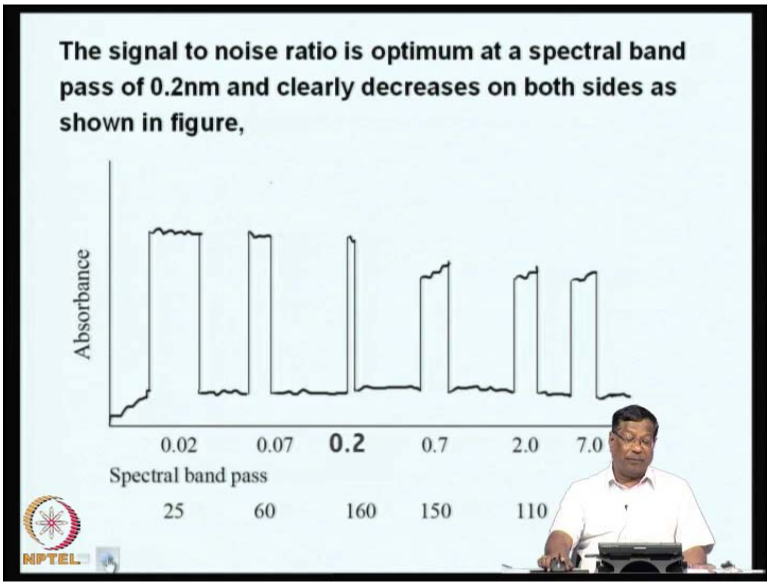

The signal to noise ratio is optimum at a spectral band pass of 0.2nm and clearly decreases on both sides as shown in figure,

Now, the signal to noise ratio is also optimum at a spectral bind pass of 0.2 nanometer this clearly decrease on both sides I shown in this figure you can see here. This signal 0.02 nanometer signals this things you are going to end up with very high signal and the 0.07 is a fairly broad. And signal to noise ratio is wear rate is to 25 that is lowest and if you keep on increasing you will end up with 61 61 51 10 like that difference signal to noise ratios.

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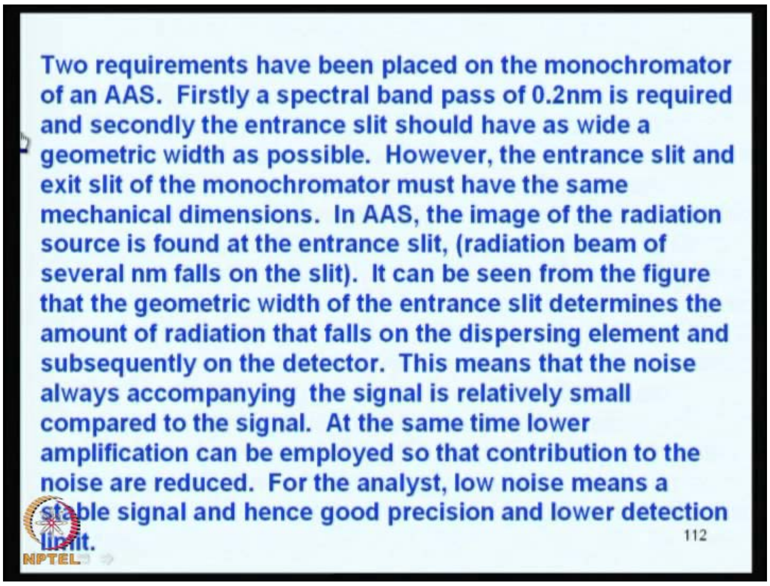

Two requirements have been placed on the monochromator of an AAS. Firstly a spectral band pass of 0.2nm is required and secondly the entrance slit should have as wide a geometric width as possible. However, the entrance slit and exit slit of the monochromator must have the same mechanical dimensions. In AAS, the image of the radiation source is found at the entrance slit, (radiation beam of several nm falls on the slit). It can be seen from the figure that the geometric width of the entrance slit determines the amount of radiation that falls on the dispersing element and subsequently on the detector. This means that the noise always accompanying the signal is relatively small compared to the signal. At the same time lower amplification can be employed so that contribution to the noise are reduced. For the analyst, low noise means a stable signal and hence good precision and lower detection limit.

So, the two requirements are placed on the monochromator of atomic absorptions. Firstly, a spectral line, spectral band pass width of point two nanometers is required. And secondly, the entrance slit should have as wide a geometric width as possible; that means, the mechanically it should allow as wide as possible radiation to pass through. However, the entrance silt and exit silt of the monochromator must have the same mechanical dimensions, that is entrance silt must form an image on the of the on the exit silt. So, if both of them entrance silt as well as the exit silt if they have the same dimensions that are the requirement in most of the atomic absorption spectrometers. So, in AAS the image of the radiation source must fall on the entrance silt, then only the image of the same thing will fall on the exit silt.

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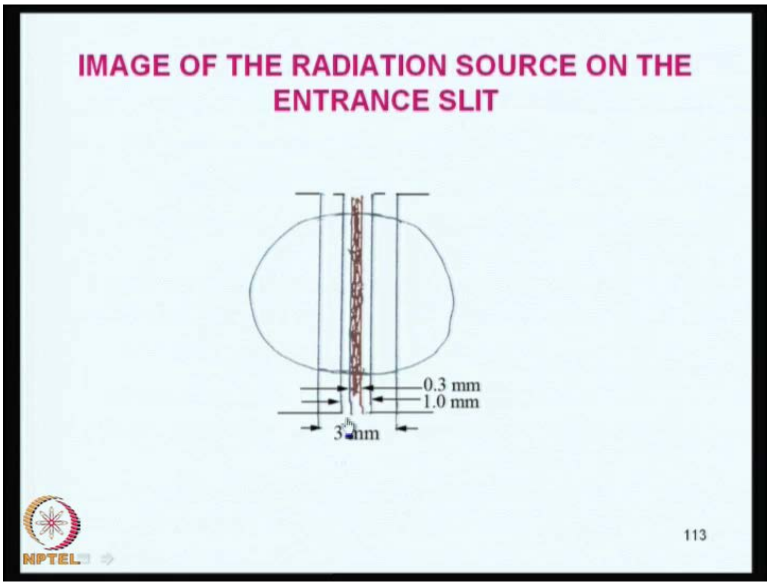

IMAGE OF THE RADIATION SOURCE ON THE ENTRANCE SLIT

So, we need to have slightly bigger entrance silt it can also been seen from the figure that the geometric width of the this is the entrance silt with 3 mm, 0.3 mm and 1 mm. So, I have take these are the images of the radiation source in the entrance silt this is what I am talking about right now. So, with 3 mm it is like this 0.3 mm, this is 0.3 middle one and outside one is 1 mm and the exterior most is 3 mm. So, the image of the entrance silt is also very important. So, I what I want to you convey to you at this stage is it can be seen from the figure the next figure, which I have already shown you that form the figure that geometric width of the entrance silt it determines the amount of radiation that falls on the exit silt.

And subsequently on the dispersing elements the aquariums and greetings etcetera and subsequently on to the detector also. So, this means that the noise always accompanying the signal is relatively small compare to the signal itself. The signal is large noise is always small and at the same time lower amplification can be employed. So, that the contribution to the noise are reduced that is the most important thing in atomic absorption we have to have a very high signal to noise ratio. So, the noise we need not amplify to the same extent as the signal.

So, long as we keep it below a particular level for the analyst, who does not understand much of electrical part? That is lock in amplification and things like that. Low noise means a stable signal that is what you should understand if it is a low noise signal; that means, it is a stable signal therefore, good precision is possible, because the signal will not very much. And if the noise is very low signal is low, very signal is very high that detection limit also would be still lower that is what we are looking for in most of the analytical techniques, what we have been using. So, this is the figure why which I had shown you, I hope it very fairly clear to you now.

That the entrance silt should be as small as possible, and exits silt should be same as entrance silt. So, if it is 0.3 you get a very sharp picture very high signal to noise ratio if it is one mm you will get a fairly bigger this entrance silt image and if it is 3 mm. You would get a still bigger this thing, but the signal to noise ratio also would be affected adversely. So, now, we move on to the presumes as well as, and gratings in the atomic absorption spectrometry. This are the job of the presumes and gratings is to disperse the radiation into individual wavelengths.

This we have seen right from our discussion from the optics of the spectrophotometers onwards in almost every instrument we have been discussing presumes and gratings. The repeated at your discussion only helps to clarify the points actually I am not introducing any special points here in the optics, because most of the optical components what we have discuss earlier there are coming in the in the current discussion. Therefore it is only sort of recapitulation of what you have already learned. So, this is not something new what I am teaching, but we have already discussed and we know about it just for the sake of ah completion of our discussion on the atomic absorption.

We are going to say the following things that the presumes and gratings are to depressed the radiation into individual wavelengths. And presume based monochromators are basically wavelength dependent. They are wavelength dependent at a fixed geometrics silt width in gratings monochromators are dependent on the grating constants number of lines rolling grating angle, blazing angle and the holographic gratings etcetera. The quality of the gratings as well as, the quality of the selection of the wavelength improves as the number of lines passing through a grating increase this we have already discuss.

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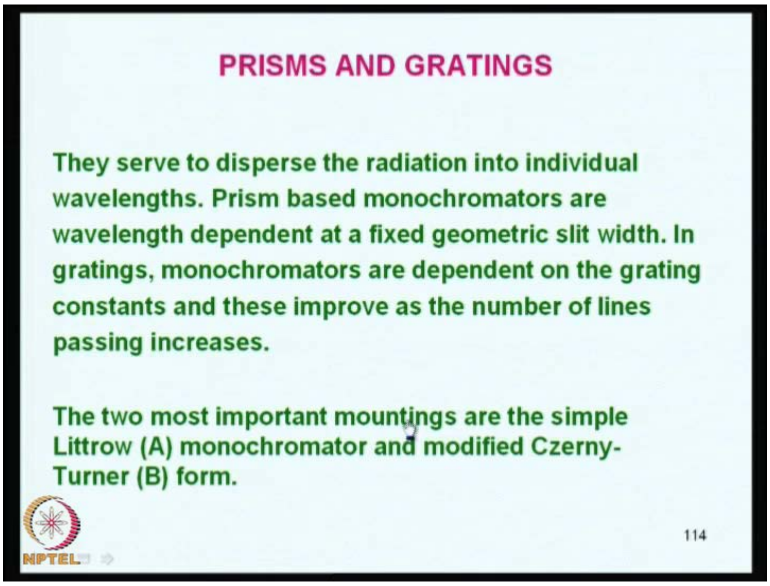

PRISMS AND GRATINGS

They serve to disperse the radiation into individual wavelengths. Prism based monochromators are wavelength dependent at a fixed geometric slit width. In gratings, monochromators are dependent on the grating constants and these improve as the number of lines passing increases.

The two most important mountings are the simple Littrow (A) monochromator and modified Czerny-Turner (B) form.

So, the two most important mountings this is also we had discussed are the simple Littrow monochromator as well as, a modified Czerny Turner system and two refresh your memory. I want to show you the next slide that is we have a plane diffraction rating.

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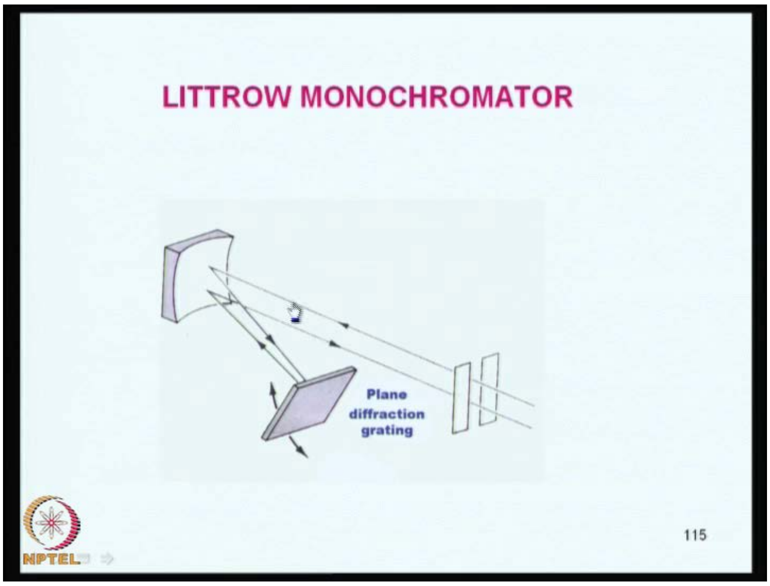

LITTROW MONOCHROMATOR

And this is mono Littrow monochromator we have an entrance exit silt here and this is Littrow mounting.

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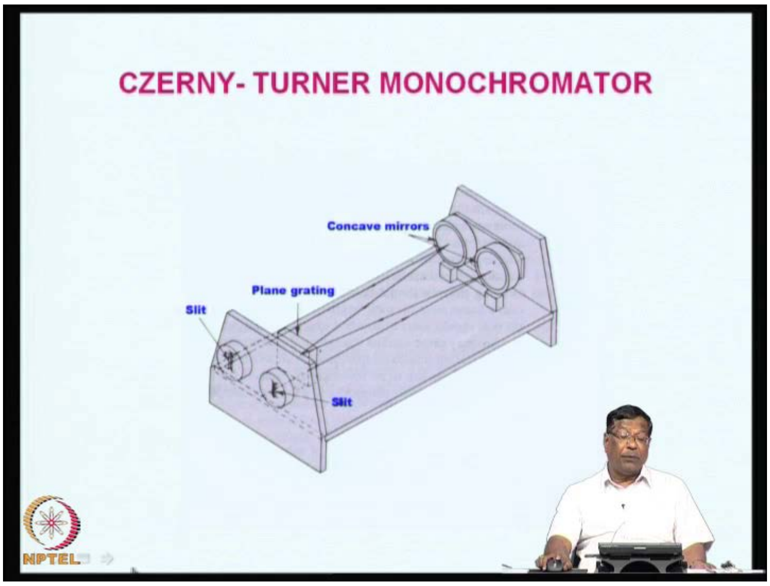

CZERNY- TURNER MONOCHROMATOR

And if we go to Czerny Turner mountain it is a again fairly simple arrangement. We have silts here one silt here, one silt here and a plane grating is placed in front of them and conquered mirrors are there. So, that radiation coming through this silt will go on to the conquer mirror reach the grating and then again go back to another mirror and it comes back through the exit silt. Very simple arrangement both these arrangements are useful for the atomic absorption spectrometer both of them are used dependants upon the model.

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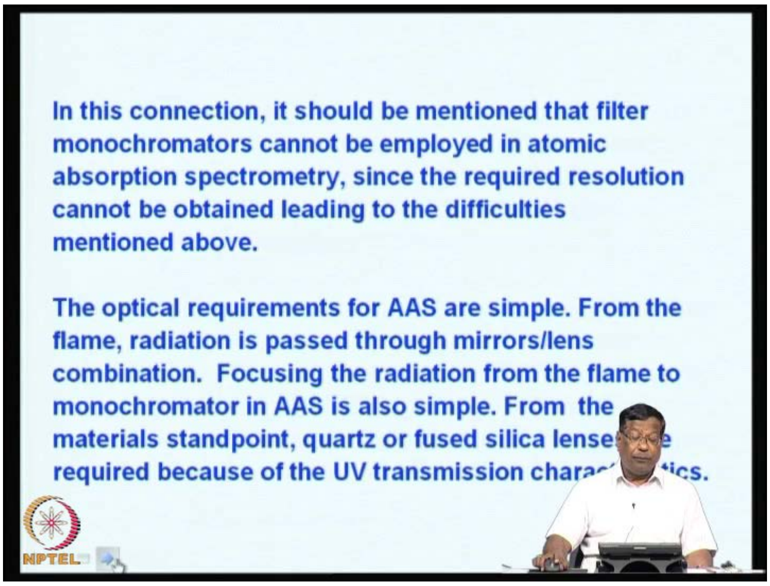

In this connection, it should be mentioned that filter monochromators cannot be employed in atomic absorption spectrometry, since the required resolution cannot be obtained leading to the difficulties mentioned above.

The optical requirements for AAS are simple. From the flame, radiation is passed through mirrors/lens combination. Focusing the radiation from the flame to monochromator in AAS is also simple. From the materials standpoint, quartz or fused silica lense e required because of the UV transmission chara tics.

So, when you are buying an instrument you should be aware of the Littrow mounting advantages as well as, Czerny Turner mounting advantages. So, you should look for what are the types of optics in a atomic absorption instrument, what you are buying, how many should get the technical specification and compare, what are the exit silts, what are the entrance silt, what are the optics, what are the whether it is presume based or either it is diffraction based and whether they are Littrow mounting as well as, whether it is a Czerny Turner mounting. So, in this connection I must mention to you here that filter photometers cannot be employed in atomic absorption spectrometry.

Because of the requirement of 0.002 to 0.005 nanometer of the radiation to be separated filter photometers can never be able to do that job. Is it not? So, since the required resolution itself cannot be obtained leading to the difficulty therefore, filter photometers are out of question in atomic absorption. So, the optical requirements for atomic absorption are fairly simple from the flame the radiation is pass through mirrors and then lenses and it may be a combination of the two also mirrors or lenses and mirrors and lenses either way.

So, focusing the radiation from the flame to the monochromator in atomic absorption is also very simple. Because so long as you focus the radiation on to the entrance silt your job is done. So, focusing these also very simple, because all you got to do is position the hallow cathode lamp the filament will be there it take the radiation. And then put in entrance silt for the instrument, where the radiation from the hallow cathode lamp places outside on the other side of the entrance silt passes through the image. So, from the material stand point you can use quartz lenses or silica lenses both are required, because UV transmission characteristics or less there, for example, most of the lines what we have been discussing in atomic absorption.

They are all in the UV range expect alkali metals in the visible range. So, the optics if you use glass you are automatically going to cut off all the radiations coming from the hallow cathode lamp. If you use glass presumes they will all be cut off, because they where are not transferring, if you use quartz they are transparent to UV as well as, they are transparent to visible radiation.So, both quartz and pause this silica lenses are required, because of UV transmission characteristics. Now, spectral band selection so that again we are coming back to the same discussion.

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SPECTRAL BAND SELECTION

The term monochromator is in reality, a misnomer. Monochromatic radiation is the radiation with only one wavelength. All spectral band selection devices pass a band of wavelengths that may be larger or smaller according to the quality of the device.

The basic requirement for a wavelength selector is the ability to separate the desired resonance line from other lines emitted by the sharp-line source. If any background radiation is emitted by the source, a curved calibration graph will be obtained, but curvature can be minimized by using a narrow-pass monochromator to reduce the propagation of unabsorbed light.

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But what I want to tell now is the term monochromator is in reality a misnomer monochromatic radiation. Actually, it means the radiation with only one wavelength all spectral band selection devices pass a band of wavelengths that may be larger or smaller according to the quality of the device. That means, whatever, monochromator whatever, you use it will never give wavelength of single radiation. Because of the du flora effect, hyperfine effect, isotropy effect, white profile, orange profile and so many other profile you will never get a single wavelength radiation from any of the devices know to us so far.

So, the basic requirement of wavelength selector itself is defeated, because if you are looking for a single wavelength radiation of high intensity you will be disappointed. So, what is required is you take slightly increased band of radiation, and pass is through the optics to separate the desired resonance lines from other lines emitted by the sharp line source. That is happens, that happens because all hallow cathode lamps are made of the element, which we want to determine. So, there are well separated spectral lines if any background radiation is also emitted by the source. Then a cured calibration graph is required you will getting for example, in the previous slide what I had shown you?

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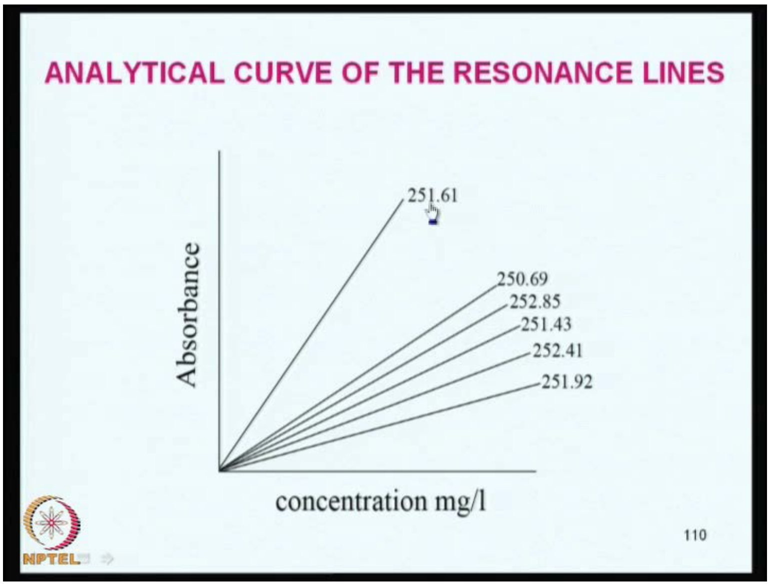
ANALYTICAL CURVE OF THE RESONANCE LINES

Here, these are all very straight line curves, but if you use a band of wavelengths you will get curved calibration curves. In this case, you are getting straight line, because all are resonance lines, but if you use a band of radiation with which are not we in which all the radiations are not resonance wavelength then you end up with a curved calibration curved, which is not linear. But you can minimize this curvature by using a narrow pass monochromator all the time you are going to get curved calibration curve, but you can minimize. It by passing through the narrow pass monochromator to reduce the propagation of the unabsorbed light that is, what I have put here? In this slide the last word is very important for us to understand a propagation of unabsorbed delight must be minimized.

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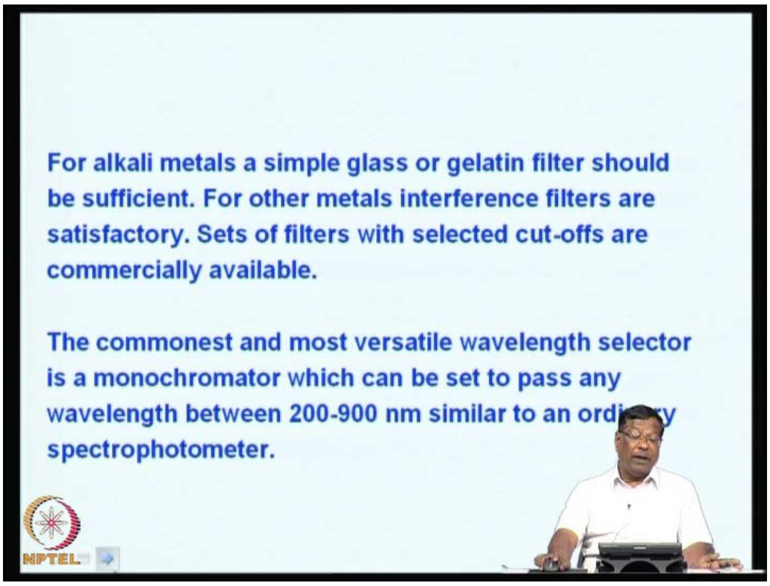

For alkali metals a simple glass or gelatin filter should be sufficient. For other metals interference filters are satisfactory. Sets of filters with selected cut-offs are commercially available.

The commonest and most versatile wavelength selector is a monochromator which can be set to pass any wavelength between 200-900 nm similar to an ordinary spectrophotometer.

Then the calibration curve would be linear what happens with alkali metals? A simple glass or gelatin filter itself is more than sufficient. Because most of the emission lines are in the visible range for other metals you can use interference filters fairly satisfactorily. But sets of filters with selected cut offs are commercially available you can use them as pre filters and then go on to presumes and gratings etcetera. So, the commonest and most versatile selector is again and again and again it is the monochromator, which can be set to pass any wavelength between two hundred to nine hundred nanometers similar, to an ordinary spectrophotometer.

So, the requirement is a pre filter and a monochromator and the job of the monochromator is to select only the radiation that is made of resonance line and you cannot use ordinary filters. But you are forced to use presumes and gratings and arrangement should be litho or Czerny Turner these two are the most simply as well as useful a components of all atomic absorption spectrometer. Now, let us talk about the detection system, a detection system usually includes the detector associated power supplies amplifier and read out the devices. So, what do we mean a detection system must be include a detector associated power supplies as well as, an amplifier and it must give a read out this all this put together is a detection system. But the detector is always a photomultiplier tube.

You usually, in almost all atomic absorption instruments photomultiplier tubes are used. And we have discussed about photomultiplier tubes earlier I suggest that you refresh yourself if you do not remember about the photomultiplier tubes. And I will not go into details, because of the requirement I would like to teach you much more the read out devices. Usually, include along with the photomultiplier tubes the analog meters, digital meters you can use or a simple strip chat required. As now a day’s most of this strip charge recorders are out of fashion. However, today computers have are incorporated in almost all atomic absorption instruments accept least expensive bottom of the line instruments.

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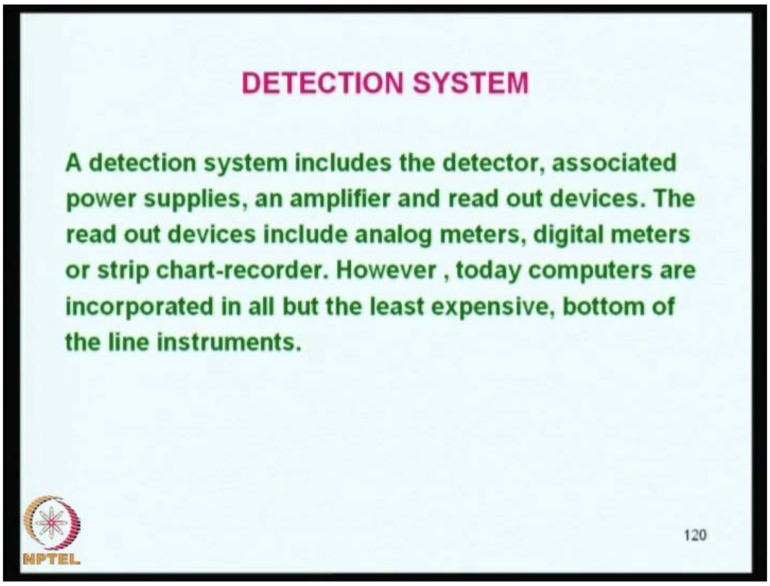

DETECTION SYSTEM

A detection system includes the detector, associated power supplies, an amplifier and read out devices. The read out devices include analog meters, digital meters or strip chart-recorder. However , today computers are incorporated in all but the least expensive, bottom of the line instruments.

So, what I would like to you to remember in this slide is to look through the requirements for the detection systems that most of the detection systems have got to do a set of electronics along with the photomultiplier tubes.

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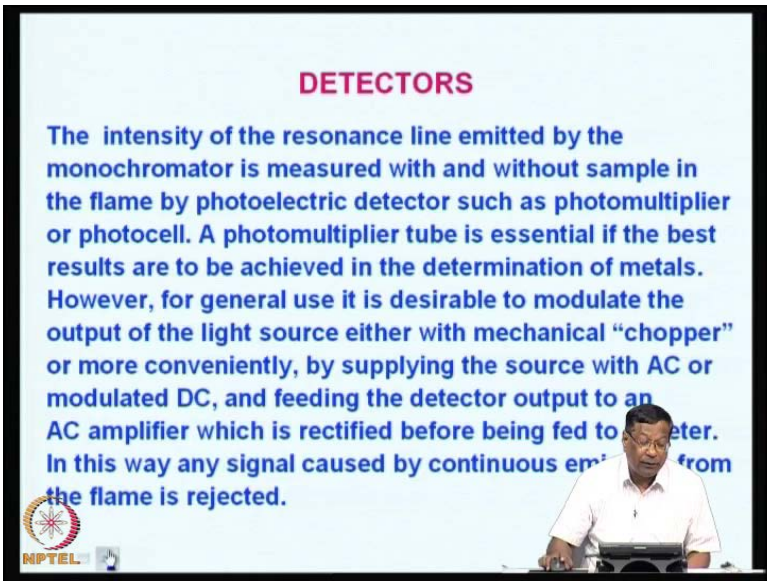

DETECTORS

The intensity of the resonance line emitted by the monochromator is measured with and without sample in the flame by photoelectric detector such as photomultiplier or photocell. A photomultiplier tube is essential if the best results are to be achieved in the determination of metals. However, for general use it is desirable to modulate the output of the light source either with mechanical "chopper" or more conveniently, by supplying the source with AC or modulated DC, and feeding the detector output to an AC amplifier which is rectified before being fed to [illegible]eter. In this way any signal caused by continuous em[illegible] from the flame is rejected.

So, the detectors intensity of the job of the detector that is PMT photomultiplier tube is to measure the intensity of the resonance line monochromator my resonance line emitted by the monochromator. And without the sample in the flame by the photoelectric detector once you have to measure without the sample, once you have to measure with the sample, when you measure without the sample you are getting a blank or reference reading. And if you are measuring with the sample then we are getting a sample reading. So, a photomultiplier tube is essentially, if the best results are to be achieve in the determination of metals. However, for general use it is desirable to modulate the output of the light source using either a chopper or supplying through AC or DC modulated electric supply.

And you have to feed the detector output to an AC amplifier, which is rectified before being fed into the meter. So, in this way any signal cause by the continues emission of the flame is rejected. Why? Because we are cutting the income radiation through a chopper a mechanical and what is continues is always not attenuated. So, it is rejected. So, this is the advantage of a chopper as well as a rectifier; however, any fluctuate on in the flame may give raise to appraisable AC component. And it is best to tune the amplifier fairly closely to the modulation frequency of the light source. What we mean is? The frequency the modulator should be locked to measure only one particular wavelength frequency.

So, that any fluctuation in the because flame also can be treated as a substance, which will give you radiations of many molecules like there is carbon, there is hydrogen, there is acetylene, there is water, there could be organic solvents and several other things. So, the since flame is also giving you radiations, it is better to block in the frequency of modulation to a particular value. So, that we measure only at the resonance wavelength. So, in single beam instruments the accuracy of absorption in the measurement is limited by fluctuation and also drifts in the light source. Therefore, a double beam technique is always preferable in atomic absorption spectrometer please; please, please, if you want to buy the good atomic absorption spectrophotometer look through the specifications.

And ask for a double beam instrument it is an always preferable always you will be comfortable in such instruments, what happens? The light from hallow cathode lamp is split into a sample beam modulated at a frequency let us say yes. Which is pass through the flame and the reference beam is modulated at a frequency of A 2 F. That is twice the frequency, which is pass through an equivalent of air path. Same radiation one is modulated a f another is modulated at F 2. And the when you are modulating the reference beam, it must be it must pass through an equivalent air path also; that means, without the flame. So, just behind the flame this arrangement is made.

So, the reference beam passes not through the flame does just back side of the flame. And which is pass through an equivalent air path that two beams are combined at the entrance silt of the monochromator again, and the photomultiplier output is spread into an amplifier that is a very simple system. At the amplifier signals from the two beams are separated and the ratio is recorded on the pen recorder or fed to the computer. The demand for routine analysis of large number of samples as relate to the development of digital read out and printouts, whose output can be read directly in concentration units not in absorption units.

Now, a day’s whenever I you want to buy an instrument you normal operation is you take the surface take your sample make a calibration curve. And then fire your sample take and then you want to measure the air you are measuring the absorbance let the computer do the concentration calculation also that is the advantage of computers. So, most of the instruments are geared to address this requirement and the output can be directly read in concentration units such units are available, when used in conjunction with automatic sampling device. So, that instrument can work an attendant for considerable period of time.

So, the photomultiplier tube as the ability to reduce the radiation into an electrical signal with very high gain of the order of about ten raise to six and then fluctuations in atoms cells dominate the noise in the systems. So, if the atom cells are more than the fluctuation will be more, if the production is not stable uniform etcetera. There will always be fluctuations the short noise associated with the PMT is basically not so significant. It is insignificant noise, but the spectral response for modern PMT exhibit very good sensitivity throughout, the wolf visible range.

So, till date no other detectors have been used in commercial instruments. So, the read out elements, if you have a computer the most common type of amplifier also can be computerized and the electronic used in the AAS should be is through a lock in amplifier. This device as I have explain to you already locks in at a particular modulation frequency. And therefore, it does not respond to signals from other frequency there by eliminating the noise from the flame. The radiation source is modulated and then that is synchronized with the lock in amplifier that is important.

And this means that only signals of interest are amplified and the signal to noise ratio will be improved the amplifier signals can then be fed into strip chat recorder or meter for evaluation. In more modern instrument, what we do is? It is we convert it into a digital signal. And feed it to a computer for evaluation will stop our discussion here and then we will discuss about the role of computers in the next class. And continue our discussion on atomic absorption because there is a there are lots of things to learn in this and will study about other aspects of atomic absorption techniques.