Trace and ultra trace analysis of metals Using atomic absorption spectrometry

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Lecture – 19

Instrumentation in AAS V: Atomization Processes

So, having understood the mechanism of the production of atomic vapors for atomic absorption and subsequent measurement I want to tell you about the flame types. That is how do I inject the atomic sample in the flame.

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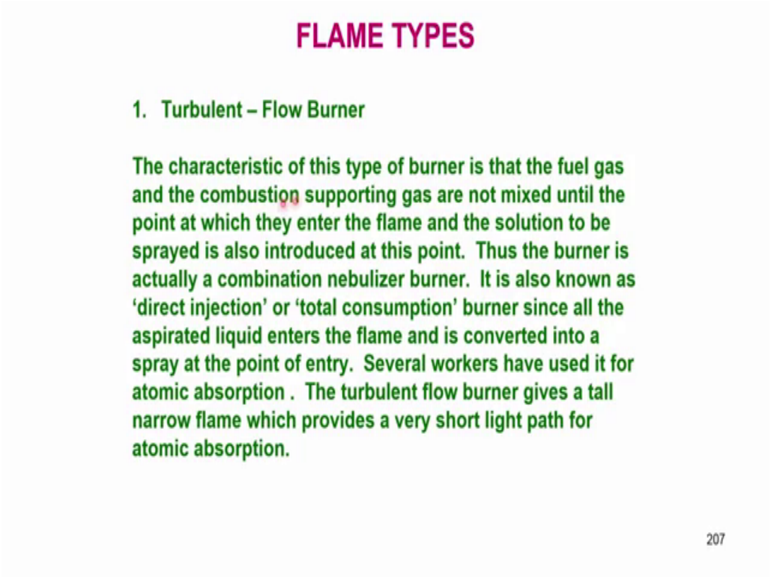

FLAME TYPES

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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So, the characteristic of this type: I have two types one is turbulent flow burner and another is premix that we have already discussed a little bit. And the characteristic of this turbulent flow burner is that fuel gas and combination gas 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, for burner is actually a combination of nebulizer cum burner- nebulizer burner. This is also known as direct injection or total consumption burner. Since all the aspirated liquid enters the flame and it is converted into a spray at the point of entry. The turbulent flow burner gives you a tall narrow flame which provides a very short light-path for atomic absorption.

I do not know whether I have this.

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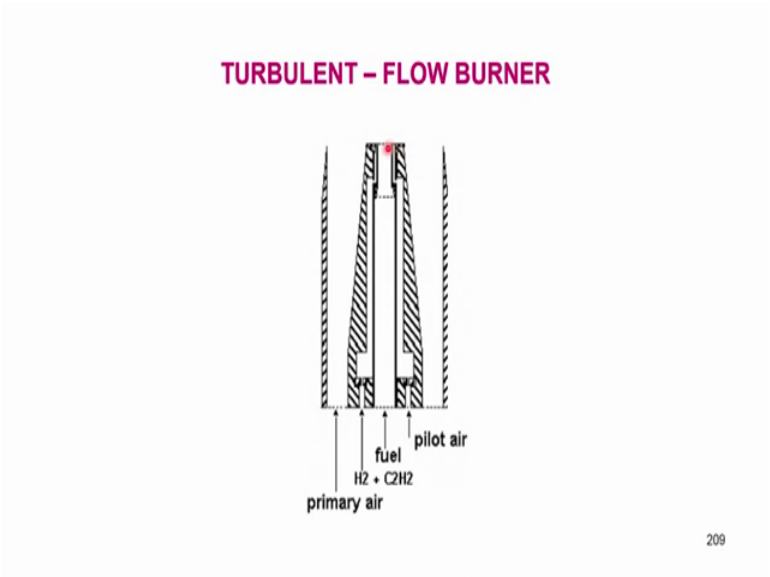
TURBULENT – FLOW BURNER

This is the turbulent flow burner. So, what I have here? I have a cylinder in which primary air is passing here it will come from the bottom from the compressor and it will reach here. And then I have the fuel coming insides in a separate channel from the cylinder both of them will mix here. I can have hydrogen coming up through this route and then entering here. Or I can have fuel acetylene gas coming through this or even they pilot the air through this. So, there are several combinations and designs of the turbulent burner.

The point to be noted here is that at the top of this there is an opening where all of them will mix together and the moment I light it, it will start burning; it is just like your Bunsen burner. So, in the Bunsen burner what is happening is the sample- I forgot to show you the sample; the sample also is go going to come through this one of these orifices and enters the burner somewhere here. That means, it will suck the sample through a small tube and then deliver the sample at the tip of the tube where burner is burning. So, this is known as direct injection or total consumption burner.

Since, all the aspirated liquid enters the flame and there are certain disadvantages.

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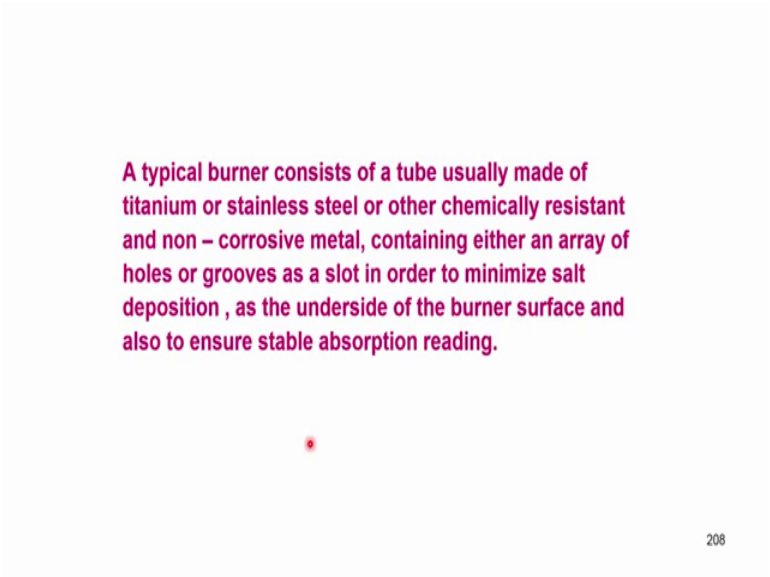

A typical burner consists of a tube usually made of titanium or stainless steel or other chemically resistant and non – corrosive metal, containing either an array of holes or grooves as a slot in order to minimize salt deposition , as the underside of the burner surface and also to ensure stable absorption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

So, a typical burner consists of a tube usually made of titanium or stainless steel or other chemically resistant and non-corrosive metallic can make it out of titanium also. Usually, titanium or stainless steel are the best. So, they contain either an array of holes or grooves as a slot in order to minimize salt deposition, because everything is coming into the burner. So, salt deposition also may take place. So, in order to minimize salt deposition what we do is; we on the top we make number of holes something like this through which the gas will enter.

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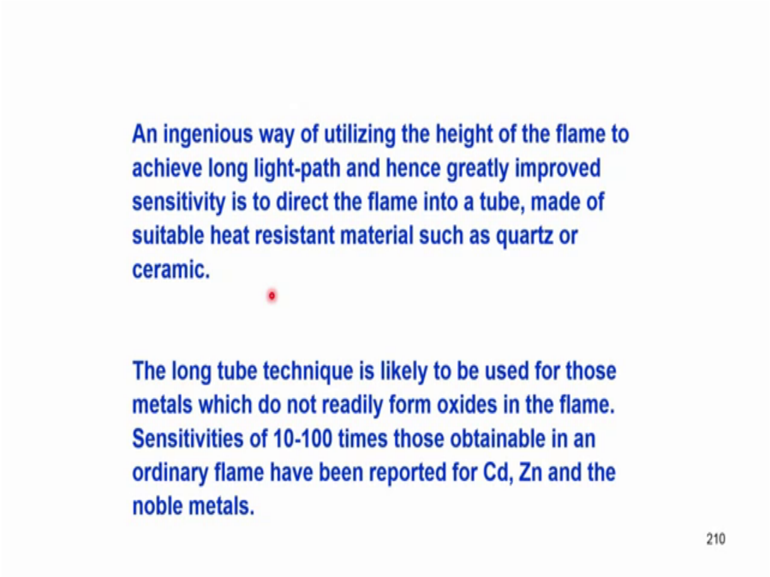

An ingenious way of utilizing the height of the flame to achieve long light-path and hence greatly improved sensitivity is to direct the flame into a tube, made of suitable heat resistant material such as quartz or ceramic.

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

So, it also leads to stable absorption reading, but all said and done the turbulent burner is not an ideal burner in most of the systems in atomic absorption. So, this is an engineer’s 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 then I can introduce make the optical path length longer. We will see how we can do that.

The long tube technique is likely to be used for those metals which do not form oxides in the flame. That means it cannot be used for refractory oxides that is chromium tungsten vanadium etcetera. But sensitivities of 10 to 100 times those obtainable in an ordinary flame have been reported. Why? See, I want you to understand when everything is burning the temperature is very high, I do not control; so whatever is the temperature the sample is burning. So obviously, the sensitivity would be very high because everything is getting converted into a vapor form.

So, approximately 10 to 100 times sensitivity is obtainable in ordinary flame, but for few elements like cadmium zinc and some noble metals. So, this is the important for us to understand; why we go for a total combustion burner.

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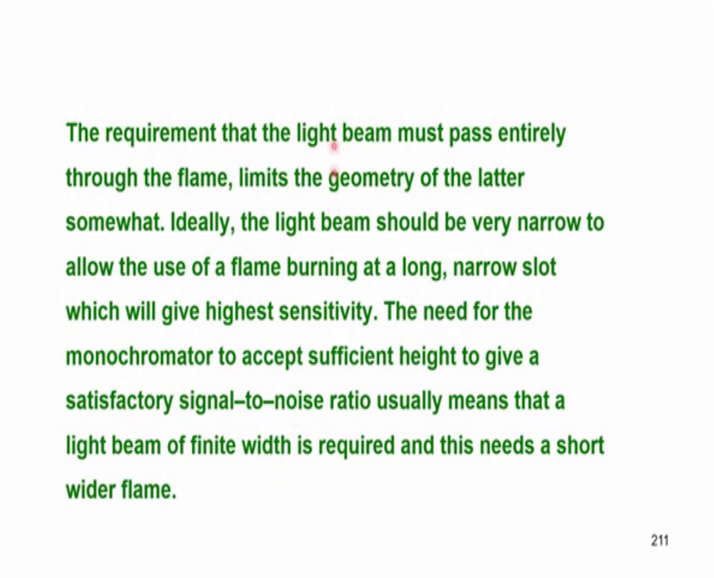

The requirement that the light beam must pass entirely through the flame, limits the geometry of the latter somewhat. Ideally, the light beam should be very narrow to allow the use of a flame burning at a long, narrow slot which will give highest sensitivity. The need for the monochromator to accept 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.

Now the requirement of the light beam must pass entirely through the flame, is it not? It is very important that the light beam, light from hollow cathode lamp should pass through the flame and then that limits the geometry of the total burner somewhat, because when the total burner is only just like a Bunsen burner light-path would be hardly about 1 centimeter. But if it is a 5 centimeter like what I had shown you in the premix burner it will be 5 centimeters or even 10 centimeters.

So, ideally the light beam should be very narrow light beam that is hollow cathode lamp come radiation coming from that it should be very narrow to allow the use of flame burning at a long narrow slot which will give the higher sensitivity. So, longer the path length higher is the sensitivity. So, the need for monochromator to accept sufficient height to give a satisfactory signal-to-noise ratio usually means that the light beam of finite width is required and this needs a short wider flame.

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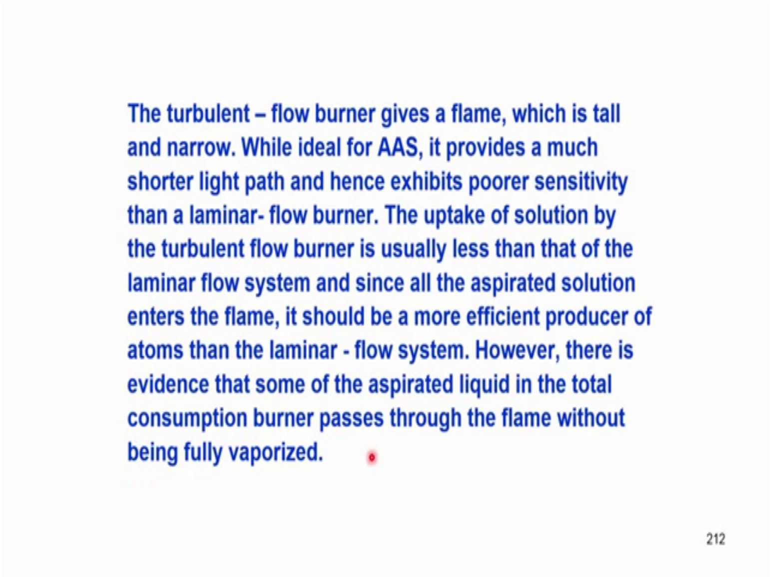

The turbulent – flow burner gives a flame, which is tall and narrow. While ideal for AAS, it provides a much shorter light path and hence exhibits poorer sensitivity than a laminar- flow burner. The uptake of solution by the turbulent flow burner is usually less than that of the laminar flow system and since all the aspirated solution enters the flame, it should be a more efficient producer of atoms than the laminar - flow system. However, there is evidence that some of the aspirated liquid in the total consumption burner passes through the flame without being fully vaporized.

Now the turbulent flow burner gives a flame which is tall and narrow. While ideal for atomic absorption because everything gets evaporated it provides a much shorter light-path and hence exhibits poorer sensitivity, than a laminar flow burner. The uptake of solution also in the turbulent burner is usually less than that of the laminar flow system since all the aspirated solution a enters the flame, it should be a more efficient producer of atoms than the laminar flow system. However, there is evidence that some of the aspirated liquid in the total consumption burner passes through the flame without getting evaporated- vaporized.

Now you should imagine if I have a small flame burning like this and then all the sample is coming in part of it may not be vaporized at all, because there is a continuous supply of the liquid and the liquid droplets do not have sufficient time to vaporize and produce free atoms according to the mechanisms what we have already discussed.

So, there is evidence that some liquid does not get completely vaporized and some of it may fall down, it may reduce the temperature because it has not vaporized. So, if you throw water on a flame temperature gets reduced. Now that is the re reason. But not much especially whenever we are burning fuel gas along with air.

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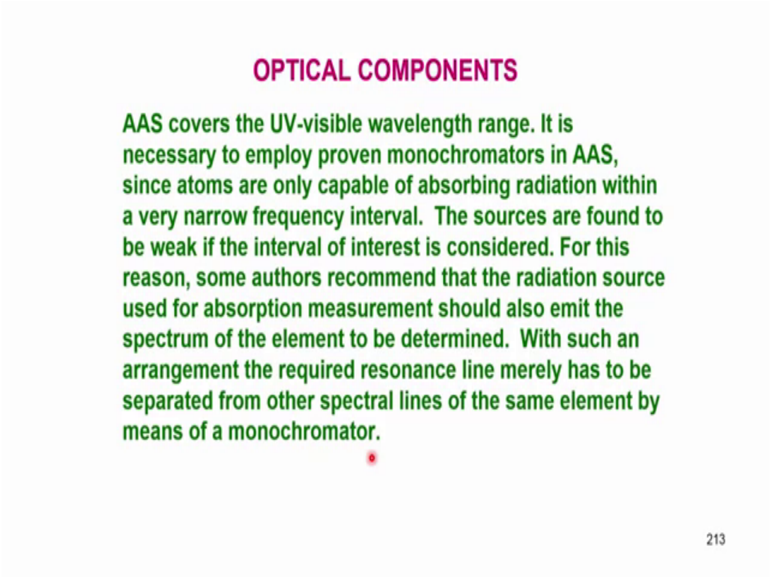

OPTICAL COMPONENTS

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, a premix burner I am not going to explain to you, because I had already explained to you about the premix burner when I was discussing about the nebulizer. If you remember that figure I will quickly go back and show you that.

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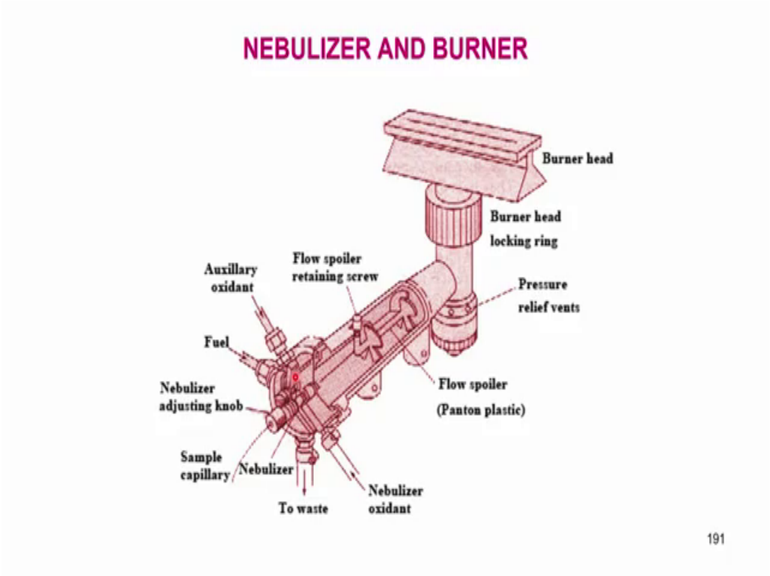

NEBULIZER AND BURNER

This is the nebulizer, this is the premix burner, long slot, number of holes and burning will be there, I had already explained to you. And we are not going to discuss this further.

Now, I want you to understand that the optical components are part and parcel of any spectrometer. Now, I had already explained to you that we are going to discuss different parts of components of the system: one component is hollow cathode lamp, second component is the nebulizer atomizer and fuel combination- that is second component, third component now we are going to discuss is the optical component of the spectrophotometer atomic absorption.

So, what you should remember now? You should remember that atomic absorption resonance lines occur in the UV and visible range. That means, I just need a radiation an optical component which can cover UV and visible range, I do not need to go to NMR higher wavelengths nor vacuum ultraviolet. So, it is necessary to employ proven monochromators in atomic absorption spectrometer.

So, atoms are only capable of absorbing radiation within a very narrow frequency range; that means, the sources are found to be weak if the interval of interest is concerned. So, for this reason some authors recommend that the radiation source use for atomic absorption should also emit the spectrum of the element to be determined. This we have already discussed number of times.

With such an arrangement the required resonance line merely has to be separated from all other radiations coming from the flame, because we have said radiation line is already coming from the hollow cathode lamp we need to separate only that line. That means, I just need a, but there are other radiations coming from the flame: blue radiation is coming, yellow radiation is coming, and red radiation is coming all these la radiations must be separated from the resonance line that is the requirement.

So, what we are looking at is a very simple monochromator.

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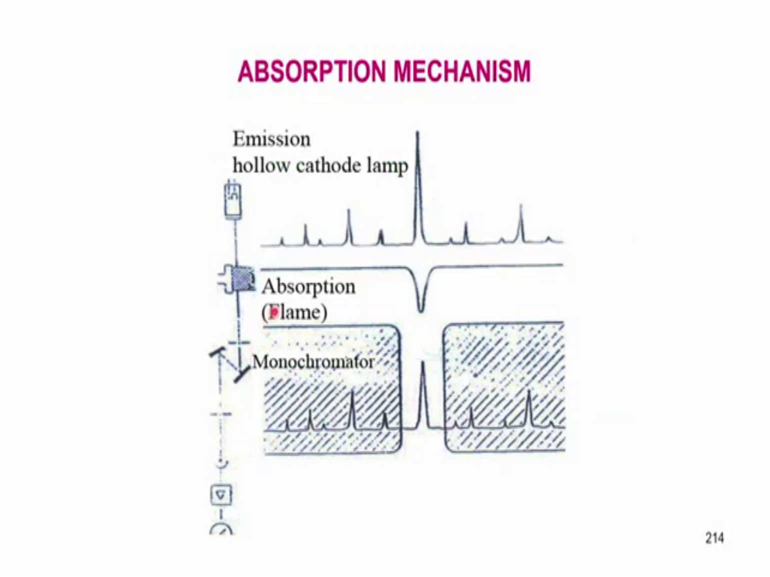
ABSORPTION MECHANISM

So, this is how the absorption mechanism occurs. Look I have drawn some the atomic absorption schematic diagram on the left side here and on the right side I am drawing several optical features. So, what I have on the left side here, look at the signal here I have a hollow cathode lamp, I have a flame; flame is burning this side I have shown it through a blue this thing. And through the flame the radiation is coming down. And this radiation apart from hollow cathode lamp also contains radiation from the flame of other elements. Maybe, from the flame molecular absorptions ch nh and c other cyanogen radicals etcetera all those radiations are coming.

Now I want to separate only this line coming from hollow cathode, I do not want others. So, what do I do? I just put a small slit here mechanical slit and then connect it to a diffraction unit or a prism and then that will give me exact wavelength. And then that we have already discussed the mechanism of optics in the earlier sections. And that radiation once it is separated this monochromator prism or a diffraction unit. Once it separates the line I do not have any other requirement of the optics. So, this line again I need to separate only collect only these radiations through a small slit connect it to a detector. Once I have the detector it is further signal is processed by amplification and the other things.

So, the left part is showing you the path of the radiation and the right path right side here on the top what I am showing you is the resonance lines from the element, from the hollow cathode lamp. There is one here, assuming that we are determining copper-copper has several resonance lines. One is here, one is here, one is here, one is here, one is here and another one is here, and there are several lines. These correspond to different wavelengths. Now among these which one you will choose for atomic absorption: obviously, this one, because it is the strongest absorption strongest line. Now when absorption occurs what happens, the intensity of this radiation becomes less. Is it not, so if the absorption is of this much then the intensity of this will be reduced by this much extent.

So, what I need is I need a monochromator which can separate this line, this line, this line, this line, this line on the left side. And on the right side I do not want this line, this line, this line, this line etcetera this part. So, the only thing I am interested is this line what is the difference in the absorption after the sample is put. If I do not put the sample I will get maximum intensity, the moment I put a sample some amount of absorption takes place and the intensity of this line resonance line decreases.

So, this is how if I put a monochromator these lines are separated. And on the right side this line these lines are also separated. So, this is the basic requirement of any atomic absorption measurement. So, you remove the all other resonance lines, remove on the left side that is on the shorter wavelength and on the longer wavelength and then collect the radiation only corresponding to the resonance line.

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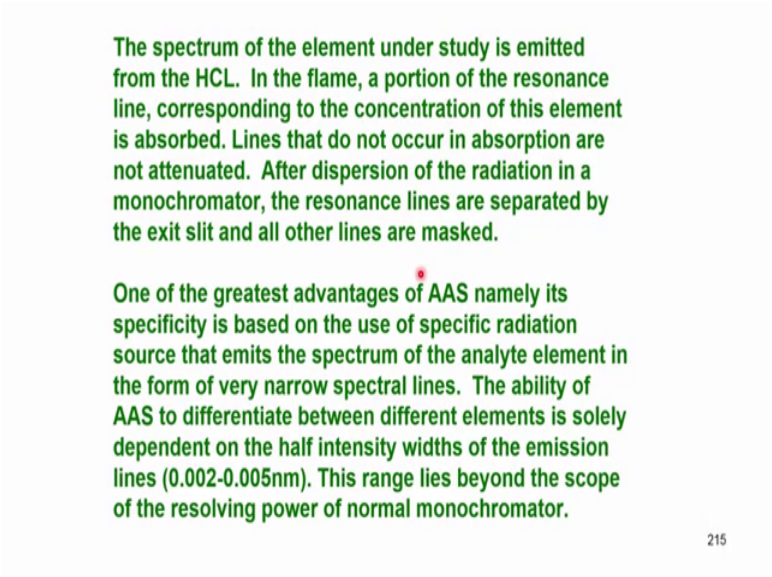

The spectrum of the element under study is emitted from the HCL. In the flame, a portion of the resonance line, corresponding to the concentration of this element is absorbed. Lines that do not occur in absorption are not attenuated. After dispersion of the radiation in a monochromator, the resonance 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 solely dependent on the half intensity widths of the emission lines (0.002-0.005nm). This range lies beyond the scope of the resolving power of normal monochromator.

So, the spectrum of the element under study is emitted from the hollow cathode lamp. So, in the flame a portion of the resonance line corresponding to the concentration of this element is absorbed- this I already told you. Lines that do not occur in absorption are not attenuated. So, what does it mean? So, these lines 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, is it not. We have already separated these lines and the radiation coming through this diffractometer lens, concave mirror and all the combinations will be there this only line will be measured.

So, one of the greatest advantages of atomic absorption spectrometer is its specificity based on the use of specific radiation source that emits the radiation of the spectrum of the analyte element in the form of very narrow spectral lines. So, the ability of atomic absorption to differentiate between different elements is solely dependent upon the half intensity widths of the emission lines. That means, if there are other elements in the sample all I need to know is whether other elements in the sample do they have a an absorption resonance line within to 002 to 005 nanometer. Because that we have already discussed what are the different Doppler Effect and all those things. And we have proved that the requirement is only 002 to 005.

Now in a given sample there may be several other elements also, and these things if they have got resonance line it within that 002; suppose I say 324.7 is the line for copper;

224.7. Now 224.7 plus or minus 0.005 nanometer is what I am going to choose from the spectrum. But all other elements if they do not have a resonance line they will not show absorbance, because there is no atomic absorption in that range. So, this range lies beyond this scope of the resolving power of the normal monochromator.

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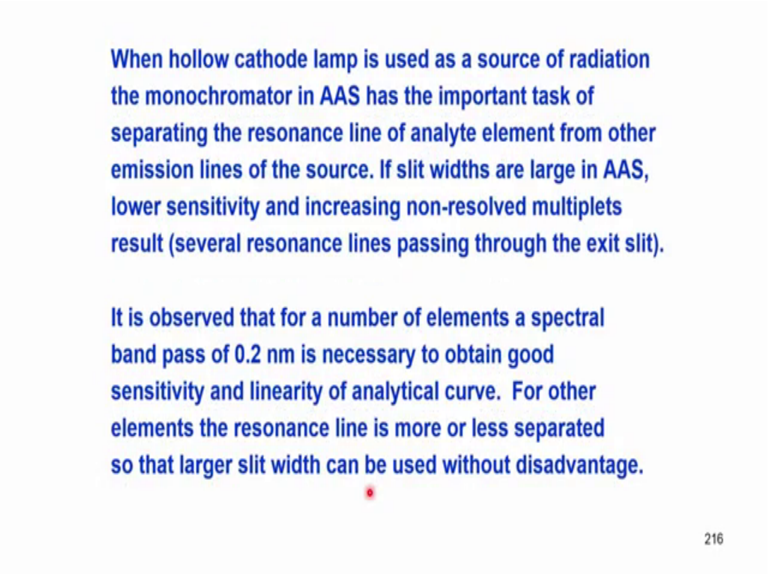

When hollow cathode lamp is used as a source of radiation the monochromator in AAS has the important task of separating the resonance line of analyte element from other emission lines of the source. If slit widths are large in AAS, lower sensitivity and increasing non-resolved multiplets result (several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

So, what essentially we are saying is- when hollow cathode lamp is used as a source of radiation the monochromator in atomic absorption has the job of separating only the resonance line of the analyte element from other emission lines of the source. That is there may be copper also will have several lines that we have already seen, flame will have several frequency that is wavelengths coming from the flame. So, if slit widths are large in atomic absorption; slit width mechanical slit width what I am talking about is this; this slit width. If this slit width is very large then other flame absorption may come in, but if this is narrow there will not be any other absorptions.

So, one of the greatest advantage of atomic absorption is its specificity based on the use of specific radiation source that emits the spectrum of the analyte element in the form of very narrow spectral lines. So, the ability of atomic absorption to differentiate between different elements is solely dependent upon the half intensity width of the emission lines. Ability of the atomic absorption, I am showing you here is to due to differentiate between different elements is dependent on the half intensity widths of other emission lines which are close to this range. So, this range lies beyond the scope of the resolving power of the normal monochromator. That means if the monochromator is not able to differentiate this range then it is not possible to determine atomic absorption.

So, the optics needs to be very accurate with respect to the choice of the wavelength within plus or minus 0.005 nanometers maximum. So, when hollow cathode lamp is used as a source of radiation the AAS atomic absorption it has the job of separating the resonance line only from other emission lines, if the slit widths are large lower sensitivity, if the slit widths are sharp then increased sensitivity.

It is observed that for a number of elements a band pass width of 0.2 nanometer is necessary to go obtain good sensitivity. Now I am talking of the mechanical slit whose hole size, the size of the hole should be 0.2 nanometer. Now I say copper should be three 224.7 plus or minus 0.005, but for that job is done by the lens or the concave mirror or a grating. But the mechanical slit through which the total amount of radiation is picked up is only approximately 0.2 nanometer that is more than enough to give obtain good sensitivity; hat means, in some instruments they will give you a choice of 0.2 nanometer or 0.7 nanometer; there will be a switch they we say choose 0.2 for good sensitivity.

Sometimes you can choose 0.7 also, but to obtain good sensitivity and linearity of the analytical curve what we need is the resonance lines are more or less separated so that larger slit width can be used without much disadvantage, but 0.2 is more than enough. It does not make much difference whether you use 0.2 or 0.7, but you will have a better feeling that if you use 0.7 but actually it does not increase in the sensitivity of the atomic absorption.

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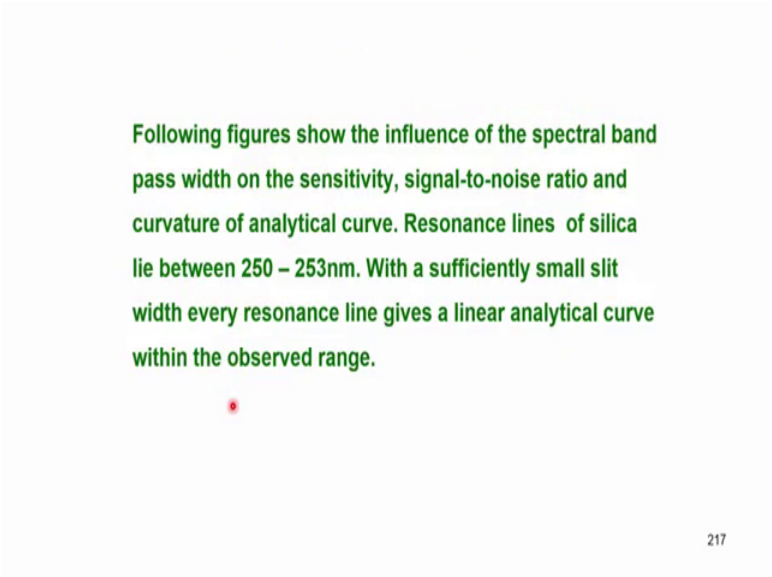

Following figures show the influence of the spectral band pass width on the sensitivity, signal-to-noise ratio and curvature of analytical curve. Resonance lines of silica lie between 250 – 253nm. With a sufficiently small slit width every resonance line gives a linear analytical curve within the observed range.

So, following figures will show you the influence of the spectral band pass width on sensitivity, signal-to-noise ratio, and curvature of the analytical line. This I am showing you especially for resonance lines of silica line between 250 and 253 nanometers. So, smaller slit, it gives a linear analytical curve within the observed range you should really concentrate on this these are the resonance lines of silica.

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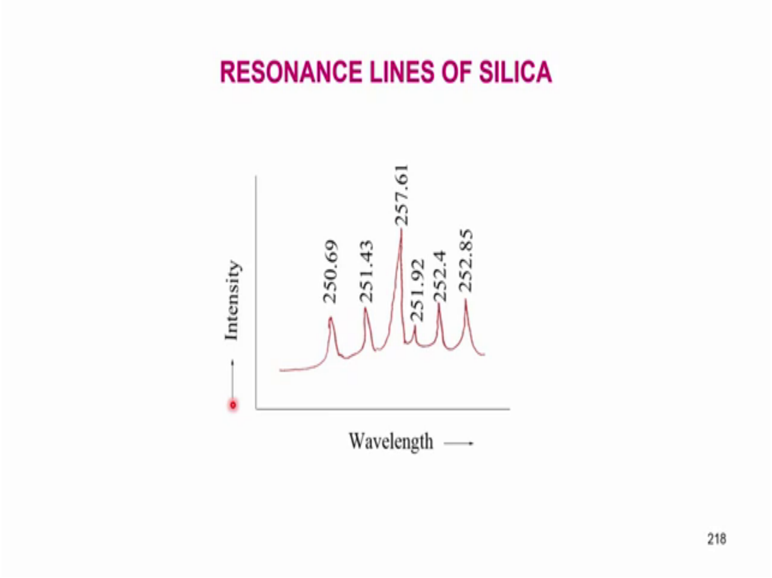

RESONANCE LINES OF SILICA

Now; that means atomic absorption analysis can be carried out using 250.69 nanometer, 251.4 I can choose any of these lines 251, 250, 257, 251, 252, and 252.85 all these are resonance lines, but you can imagine that they are all within 250 to 252 nanometers I can choose any line. These are the resonance lines.

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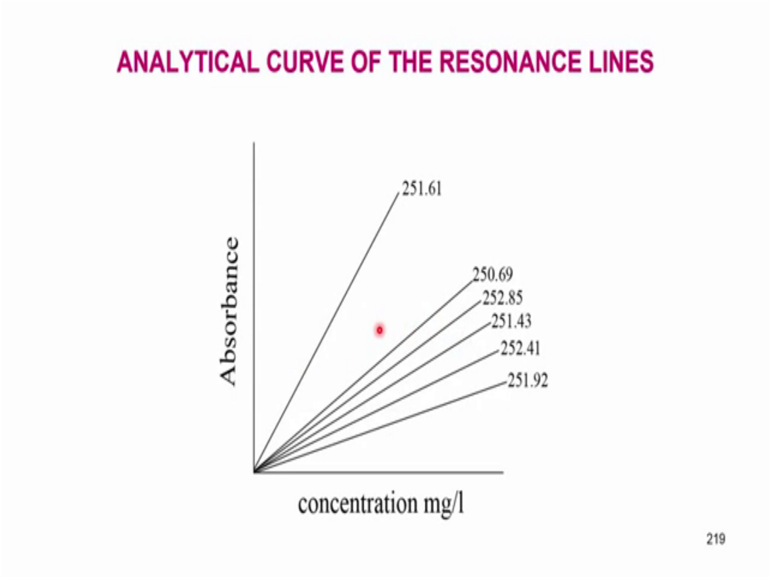

ANALYTICAL CURVE OF THE RESONANCE LINES

Assume I am choosing 251.61 nanometer for the determination, I draw a calibration curve of absorbance versus concentration. Because I have already told you that atomic absorption is a relative technique. Now you can see this line 251.61 is the sharpest, because the concentration range is over less than; let us say this is about 5 ppm, this will be up to 7, 8, 9, 10, 11 etcetera; that means linearity is observed in these things. But the most sensitive line what is the maximum absorbance you get in all these systems, if I in all these resonance lines corresponding to these wavelengths.

So, for 250.69 the absorbance is so high, and for 250.69 it is less and concentration is also more absorbance is less. So, you should normally for working in an atomic absorption system what you should choose is the one which gives you maximum absorption that line you should choose. So obviously, in this figure the optimum line should be 251.61 for working in the atomic absorption determination of silica. Of course, you can choose these things also but the sensitivity will be less, because at 251 the sensitivity would be double of what is at 250 or more than double of 252 and then somewhere here 251 and then 252 is here and then 251.9 to any other resonance line the absorption is less. So, you should choose an absorbance line which is higher; which gives you maximum absorbance on this scale y axis.

But if you look up the text books they will give you all these lines; it only means that several resonance lines are available if for some reason you are unable to obtain 251.61 we can choose other lines also for the emergency, but if you want very accurate results you should choose 251.61 according to this figure.

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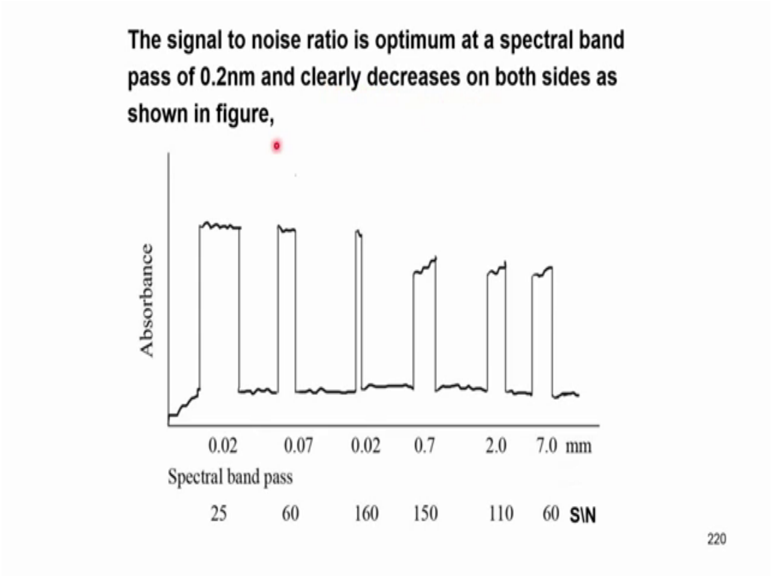

The signal to noise ratio is optimum at a spectral band pass of 0.2nm and clearly decreases on both sides as shown in figure,

Now, the signal-to-noise ratio is also optimum at a spectral band pass of 0.2 nanometer and clearly decreases on both sides. So, you can see the signal 0.02 band pass; that is this is the absorbance. If I use 0.7 0.02 this is the spectral band pass. For 0.07 it is this much. And 0.02 the signal is very sharp spectral band pass corresponding to these nanometers are 25 nanometers, 60 nanometers 160. Suppose you go to 0.7 then it is 150; 2 millimeter the now I am talking about the slit width for 2 it is about 110 and 7 it is about 60 sign that is the signal-to-noise ratio would be- which is best among these two the best is this 0.02.

But 0.02 to make a mechanical slit in using 0.02 mm is very difficult. So, what we normally settle is 0.2 and 0.7 these two are the most observed slit widths in atomic absorption spectrometry.

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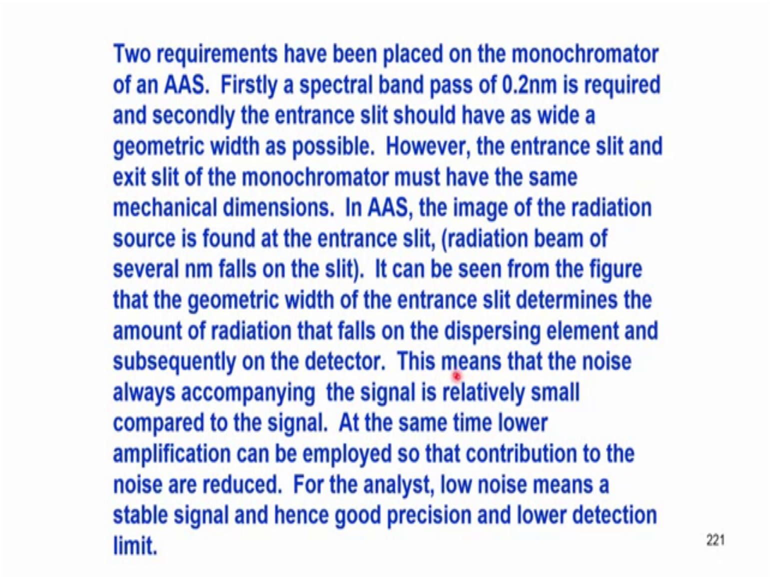

Two requirements have been placed on the monochromator of an AAS. Firstly a spectral band pass of 0.2nm is required and secondly the entrance slit should have as wide a geometric width as possible. However, the entrance slit and exit slit of the monochromator must have the same mechanical dimensions. 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, two requirements have been placed on the monochromator. Firstly, it is a spectral band pass of 0.2 nanometer is required, and secondly entrance slit should be as wide as possible. However, the entrance slit and exit slit of the monochromator must have the same mechanical dimensions. You see in whenever you want to determine radiation from this end to this end and flame is in between. The entrance slit, mechanical slit; that means, you take a metallic plate and make a hole that is the entrance slit radiation is at the back. So, you the all the radiation that is emitted comes through the mechanical slit metal plate with the hole. And the dimensions of this hole should be same as the collection after the flame; that is what we are talking about.

So, the exit slit of the monochromator must have the same mechanical dimensions. So, in atomic absorption image of the radiation source is found at the entrance slit. So, it can be seen from the figure I am going to show you a figure now that the geometric width of the entrance slit determines the amount of radiation that falls on the dispersing element; that is a grating and subsequently on to the detector. This means that the noise always accompanying the signal is relatively small compared to the signal, noise is very small actually.

At the same time lower amplification can be employed so that contribution to the noise are reduced. For the analyst if you are the chemist, you say I do not understand much of the what you are talking about. Low noise means a stable signal this is the bottom line actually it is a virtual bottom line also in this slide. So, low noise means stable signal, good precision and lower detection limit.

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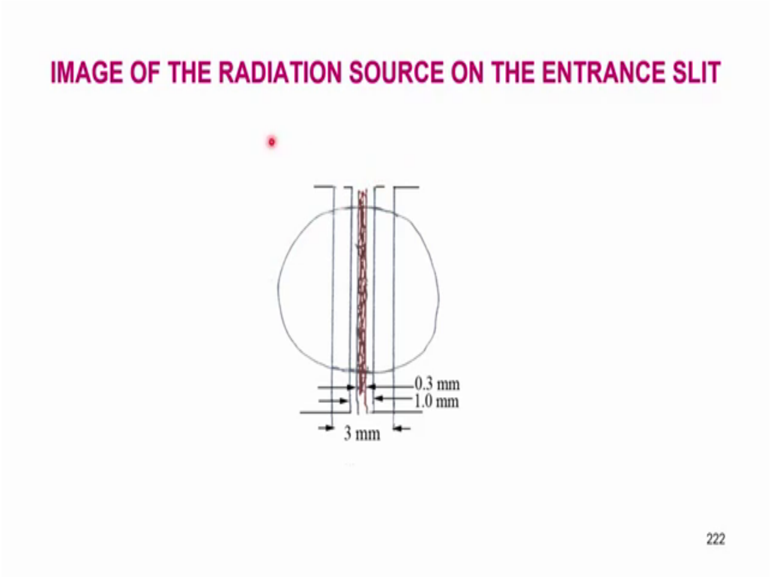

IMAGE OF THE RADIATION SOURCE ON THE ENTRANCE SLIT

So, this is what it means image of the entrance slit this is 0.3 mm, this is 1 mm, this is the entrance slit image and exit slit also should be same here.

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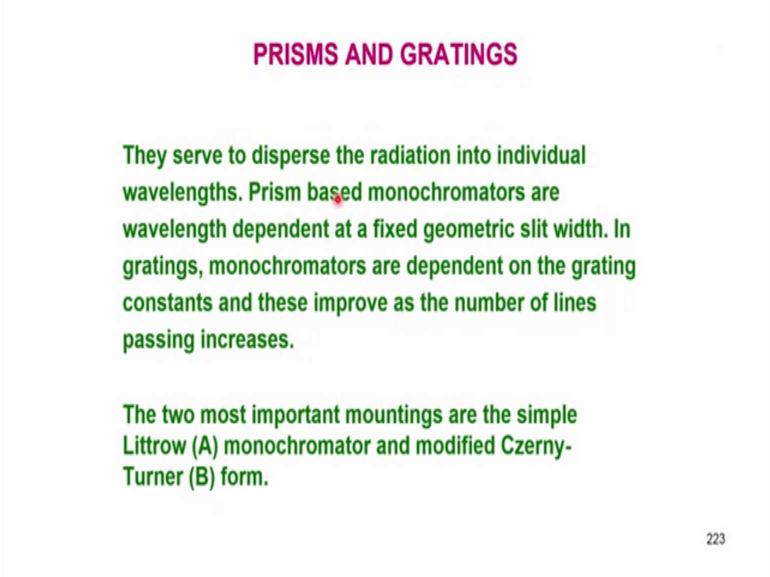

PRISMS AND GRATINGS

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, we are talking about prisms and gratings. Why? We need to separate the hollow cathode line for coming from the flame. And what is the hollow cathode line radiation source should be separated from? It is to be separated from emissions from the flame and emissions from other elements. And emissions from ch nh etcetera cyanogen broadband molecules.

How do you separate a radiation using an instrument? It is a basic physics of the system and any radiation can be separated using a prism into (Refer Time: 34:47) that we know. And for UV and other things we use concave length we have already discussed these points. So, I am only going to give you a glimpse of the prisms and gratings how they serve to disperse the radiation into individual wavelengths. So, prisms based on monochromators are wavelength dependent at a fixed geometric slit width. So, in gratings monochromators are dependent upon the grating constants and these improve as the number of lines passing increases.

So, the two most important mountings are the Littrow mounting monochromator and modified Czerny-Turner system. So, I have already explained to you what is litro and corneo mounting earlier when we were discussing the optics. And the idea is in atomic absorption Littrow mounting and modified czerny these two are these typical systems which will give you good separation.

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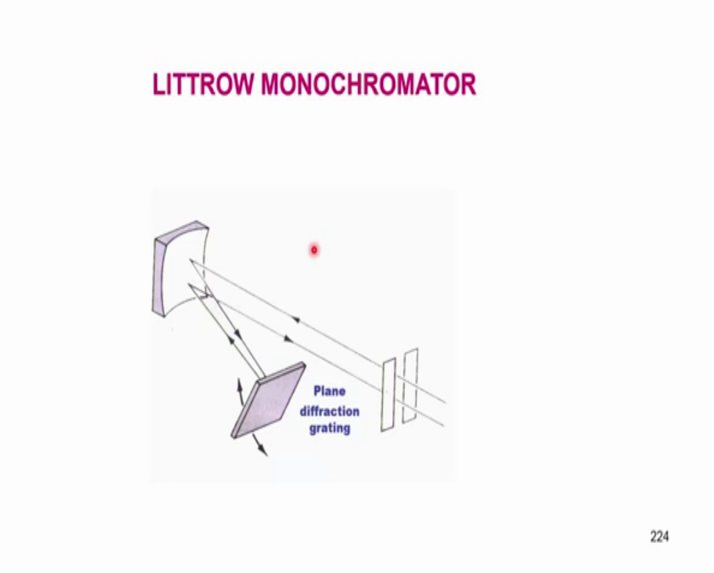

LITTROW MONOCHROMATOR

So, what is a Littrow monochromator? I just have a slit here, entrance slit radiation coming from the hollow cathode lamp moves like this and then hits a concave a mirror gets concentrated, all the concave mirrors have a property of concentrating the radiation at their wavelength. So, concentrated radiation falls on the plain diffraction grating. This is the diffraction grating which separates the wavelengths. So, this wavelength; this diffraction grating is fixed at the focal wavelength of the concave mirror here.

So, after separation all the radiation will again go back to the concave mirror and then it comes back through the same slit at a different angle of course, so that if I put a mechanical slit here I will be able to collect the radiation alone which is separated; what goes in is all the radiations, what comes out is only the resonance line radiation. So, this is the in Littrow monochromator system.

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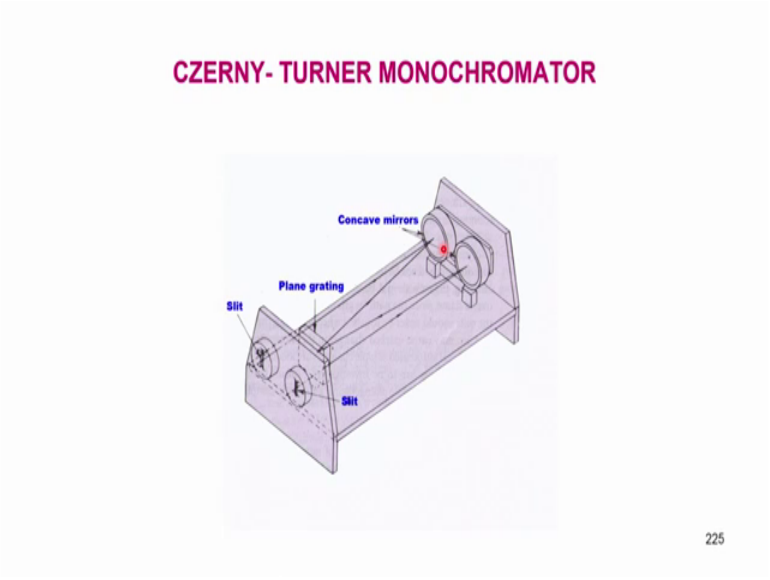

CZERNY- TURNER MONOCHROMATOR

And Czerny-Turner what I am doing is I am going to have a slit here, a plain grating is here, it goes to concave mirror, comes here to the plain grating. Again after their diffraction I have here and this is the exit slit. So, this is the entrance slit, this is the exit slit. So, plain grating is used and concave mirrors, two concave mirrors instead of only one here I has using only one that is Littrow and this is Czerny-Turner monochromator system.

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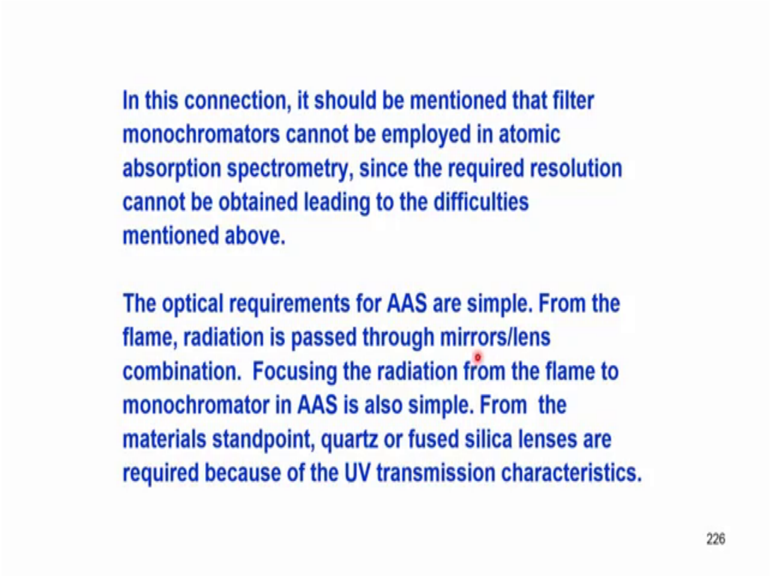

In this connection, it should be mentioned that filter monochromators cannot be employed in atomic absorption spectrometry, since the required resolution cannot be obtained leading to the difficulties mentioned above.

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 lenses are required because of the UV transmission characteristics.

So, we will continue our discussion on the monochromators in the next class.