Atomic and Molecular Absorption Spectrometry for Pollution Monitoring

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Lecture – 14
UV-Visible spectrophotometry, instrumentation-II

We will discuss Slit Designs. The optimum slit to it is in any spectrophotometry you take there approximately between 0.2 to 0.7 millimeter.

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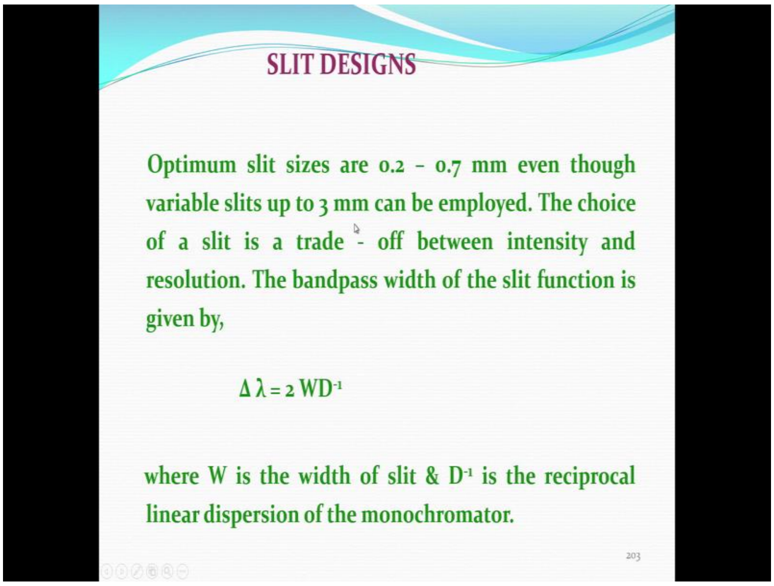

Basically what is a slit? A slit is a simple material a metal plate in which a hole is made that is a slit. I take a metal plate and make a small hole through which the radiation is coming. So, I put. So, I take the radiation source on the left side and then put a metal plate so that nothing comes out and all the radiation that is coming out will be only through the slit, and the slit designs are normally in the form of triangles.

So, optimum slit to its are 0.2 to 0.7 millimeters, even though variable slits are also employed, there what we do is we take two metal plates like this and then make them increase or decrease the width in between that is a variable slit width. So, the choice of a slit width, slit is a tradeoff between intensity and resolution. If I you choose a very small slit the intensity of the radiation coming out there will be much less, if I choose a bigger one then mono chromaticity will be lost. So, it is always a compromise. So, the band pa we define what is known as band pass width of a slit function as delta lambda, that is the each amount of radiation corresponding to different wavelengths is given by twice width twice this let width and reciprocal linear dispersion of the monochromator.

So, this is the very simple physical formula, physics formula and the effect of slit width what you can see is somewhere here.

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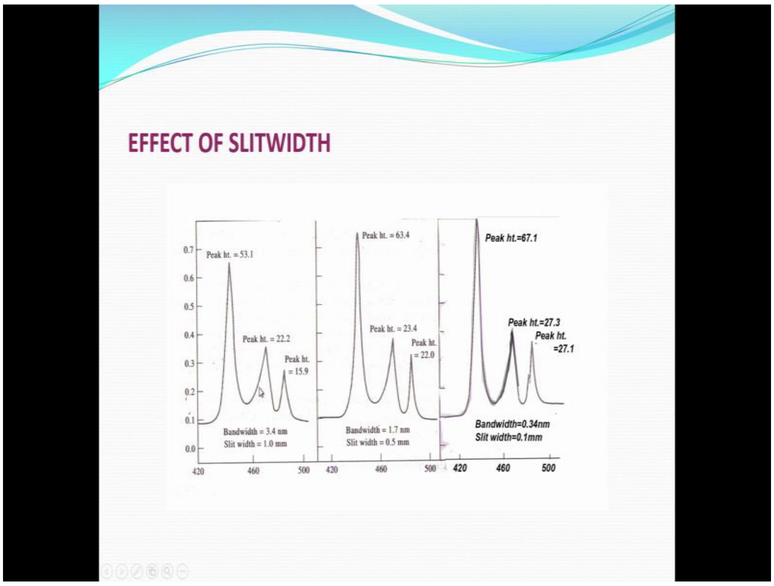

And here the peak things are normally you can see the sharpness of the peaks as the bandwidth varies from point 3.4 nanometer slit width is 1 nanometer this is 0.5, and this is 0.1 millimeter. So, here bandwidth is more 0.34 band width is well one plus I here it is 0.7 and it is 3.4 nanometers. So, you can see the peak heights entirely different for the same system.

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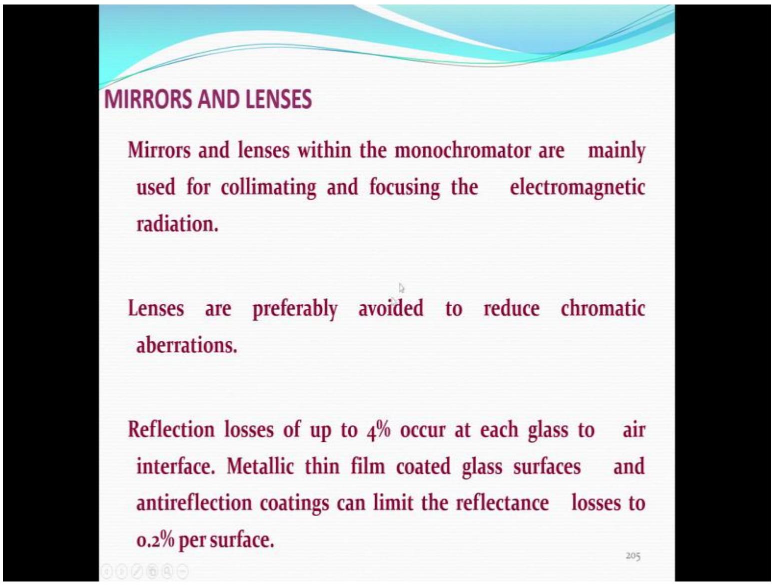

So, we also need mirrors and number of mirrors and the lenses in spectrophotometric optical arrangements, and they basically are used for collimating and focusing the electromagnetic radiation. Collimating means to get the wavelength set to get the radiation parallel and focusing means; we have to place that choose the place where the mirrors are kept so that the image of the radiation is sharp; and the lenses are pre preferably avoided because normally lenses as you we are our never knowledge of physics tells us that there will be normally chromatic aberrations associated with lenses.

So, normally reflection losses of occur up to 4 percent at each glass to air interface. So, thin metallic films are coated on glass surfaces etcetera they can re limit the reflectance losses 2.2 percent. So, these are all technical details, but what is important is when you buy a spectrophotometer all these things you have to look into the technical specifications, so that get the optimum of be optimum instrumentation for the amount of money what you are spending to purchase a spectrophotometer.

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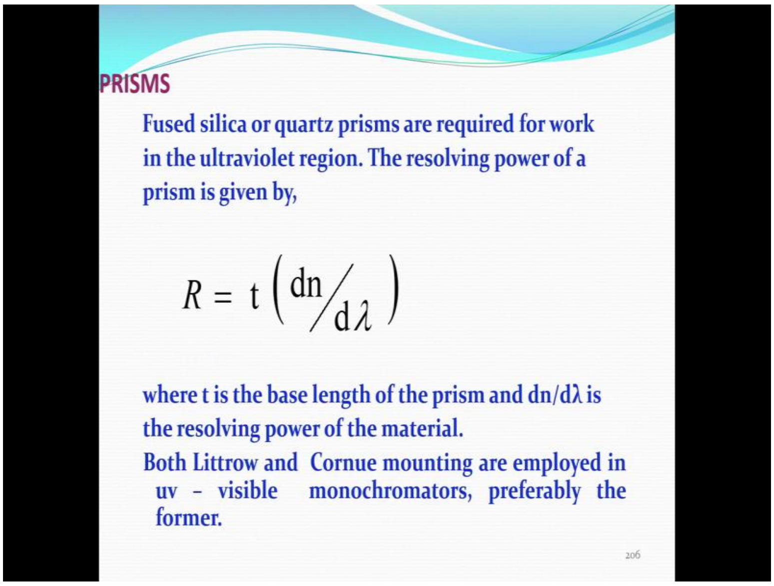

So, prisms apart from lenses and monochromators glass filters, we use prisms and prisms we have discussed earlier fused silica or quartz prisms are required, silica prisms are required for the visible range and quartz prisms are useful for the ultraviolet range.

The resolving power of a prism is given by this standard formula and both Littrow and Cornue mounting are employed in UV visible spectrophotometers preferably the former; that means, 32 half prisms are not preferred single half prism with a coated mirror surface on the back side.

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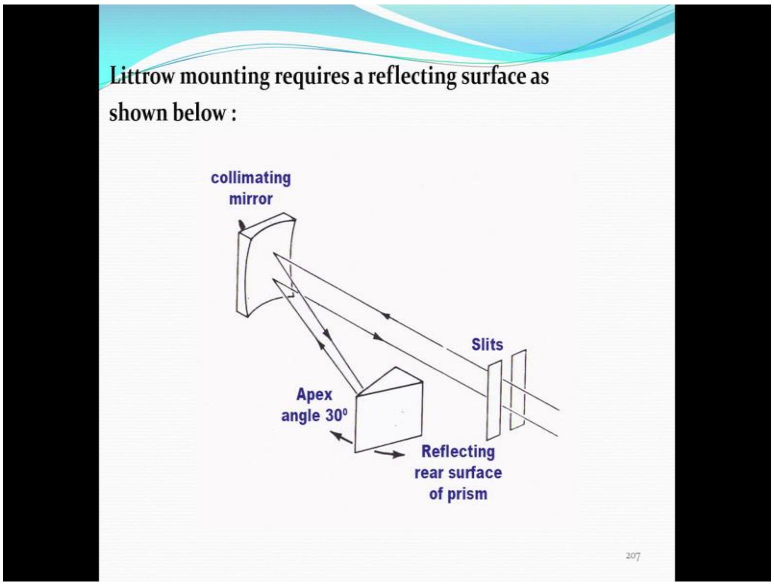

Now, the prisms there is an arrangement, typical arrangement I am showing you now here is the slit and from the slit I get a parallel radiation, here it is a collimating mirror and from the mirror the radiation is reflected back to a prism either it may be Littrow or Cornue mounting and the whatever radiation comes out should go should be a monochromatic radiation useful for measurement.

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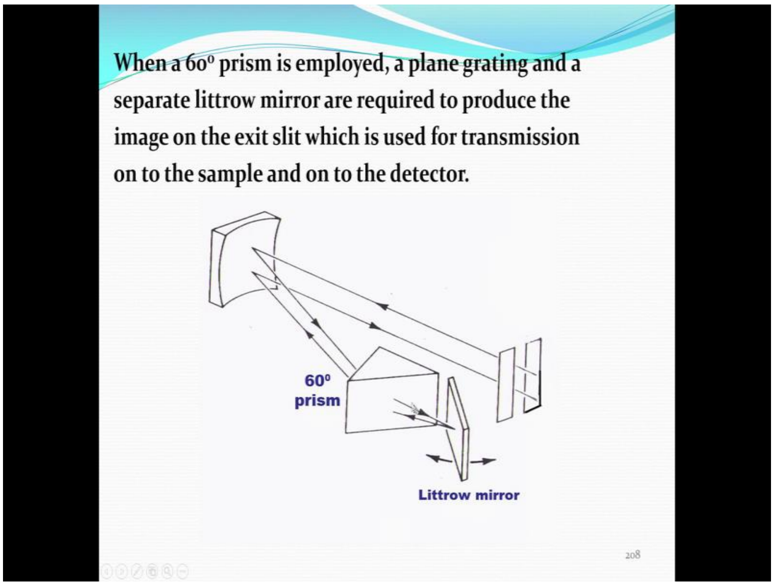

So, the 60 when a 60 degree prism is employed, I need a bigger space and then there is requirement of sharper dielectric constant material.

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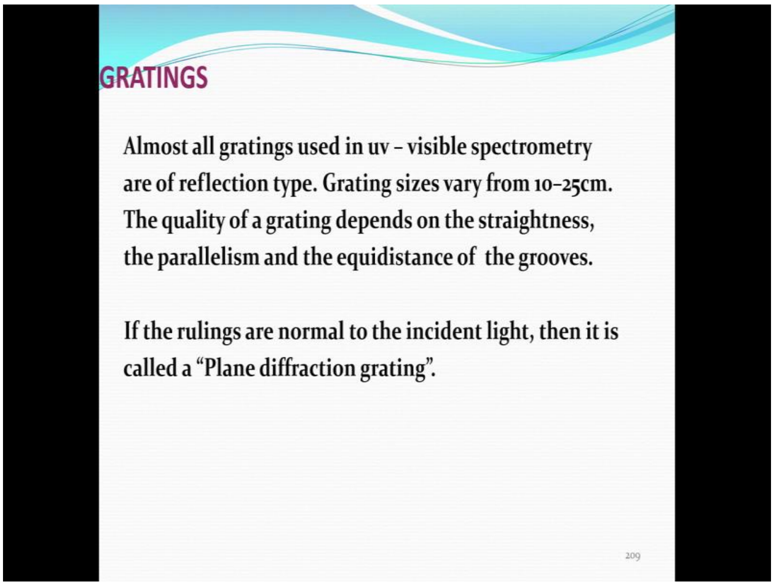

So, next thing is gratings; gratings are better than prisms to choose the correct wavelengths, almost all greetings are used in UV visible spectrophotometry are of reflection type; that means, the gratings are coated from the bottom so that the radiation that is falling simply gets reflected and grating size is varies from 10 to 25 centimeter the quality of a grating depends on the straightness parallelism and equidistance.

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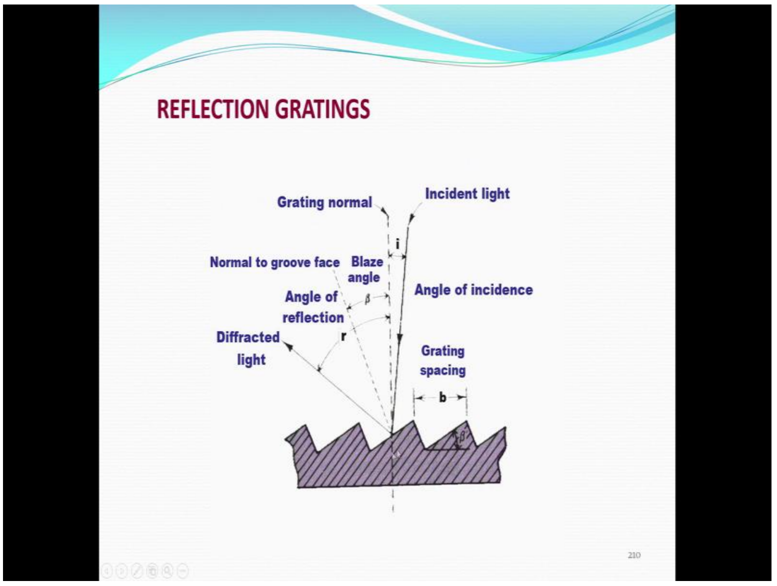

What is a grating a grating is a simple mirror glass as I am showing you in this figure with a number of grooves like this, and the number of grooves where is from 1200 to 30,000 groves.

So, basically whenever the radiation falls you see that number of it is as if a number of prisms are employed in choosing the wavelength. So, this is the if optics of the op grating and here there is a grating normal, and then the incident radiation is falling like this it gets it goes out like this and then it gets diffracted on the other side. So, this is the reflection this is diffraction. So, the distance between the gratings is known as grating spacing. So, angle of incidence need not be actually from the normal, but it can be true the different angle. So, what happens is as the gratings as the radiation falls on different rulings there is constructive and destructive interference and again we get a simple monochromatic radiation.

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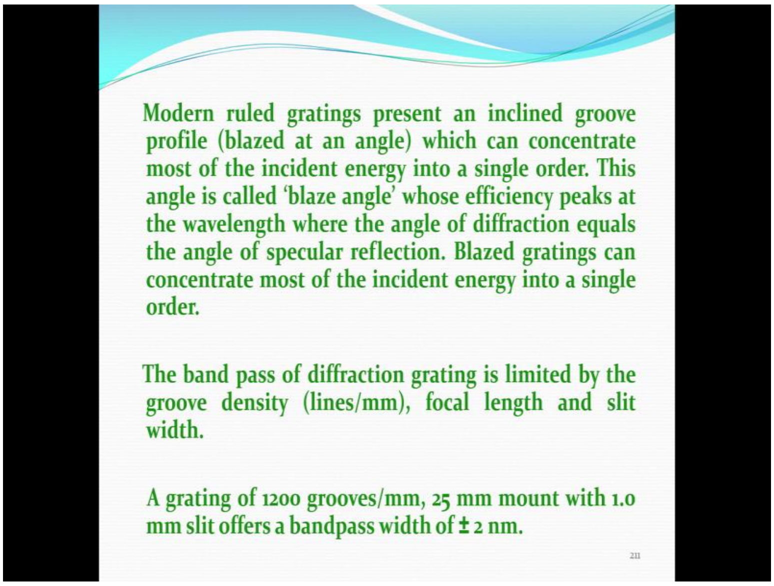

This is the optics of the grating. So, modern ruled gratings present an inclined group profile; that means, the gratings are not a perpendicularly drawn, but they are drawn at an angle. So, these can concentrate most of the energy into a single order, this angle is called as the blaze angle if it is drawn perpendicularly vertically then it is a normal grating, but if the if I hold the pen in a slanting position and draw a number of rulings then it is a blazed holographic grating; with their efficiency depends on the wavelength where the angle of diffraction equals the angle of specular reflection.

So, blazed gratings can concentrate most of the incident energy into a single order. The band pass width of a diffraction grating is limited by the groove density lines per mm as I had told you it is it varies between 1800 to 30,000 and then it also depends upon the fourth focal length and this lit width what you normally employ. So, a grating of over 1200 grooves per mm and 25 mm mount that is the size of the grating with 1 mm slit offers a band pass width of plus or minus 2 nanometers, that is excellent monochromaticity as far as spectrophotometry is concerned.

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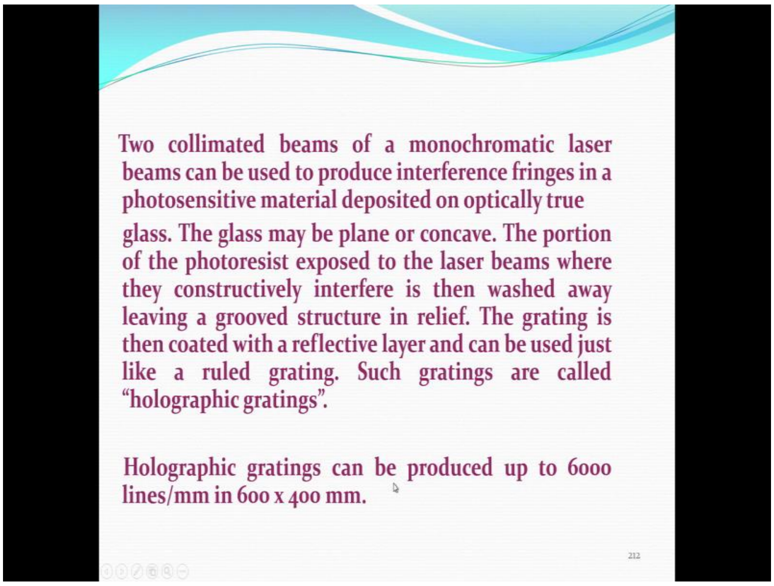

So, two collimated beams of a monochromatic laser beams can also be used to produce interference fringes on a photosensitive material, deposited on optically true glass.

This glass maybe plane or concave; the portion of the photo resist exposed to the laser beams where the constructively interfere is then washed away. I am what I am trying to do here is I am trying to teach you how to make a grating. So, what I want to do is I take a metal plate I like this and then draw the rollings with a diamond cutter or I or I take a glass plate draw a rolling with a diamond cutter which are parallel with a machine, and for your information I had to tell you that the first grating done in 1770 or something like that contain 30,000 gratings per centimeter; that means, 30,000 prisms where made on the grating at that time itself.

Nowadays, gratings are made by made in a factory where the ruling is automatic automated and then the greeting is coated for coated with in epoxy, and then done at a blazed angle etcetera. So, holographic gratings are also done on reflective layer, you might have seen stamps which will look different colour if you look at it different from different angles, that is a holographic grating; in your day today life holographic gratings are used on cars car light car headlights and car stamps 3-D designs, and all these things are use holographic gratings and they holographic gratings can be produced up to 6000 lines per mm and in sizes of 600 to 400 mm that is 60 to 40 centimeters.

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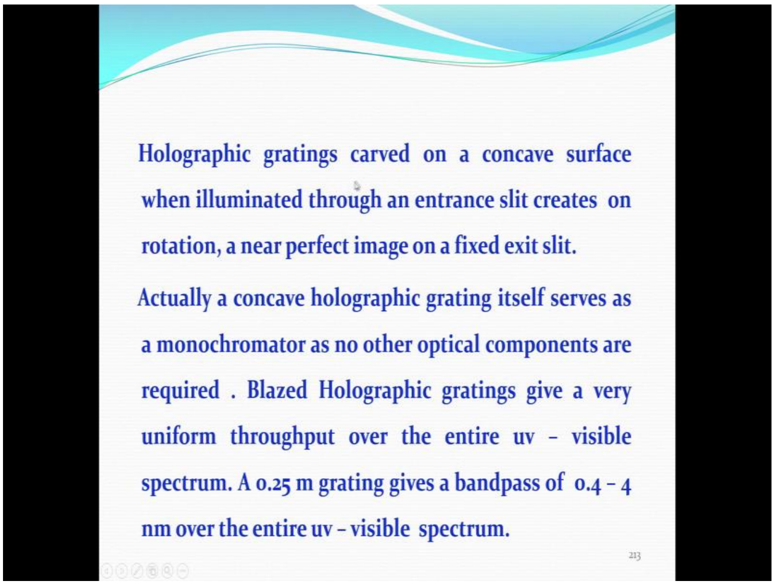

In a holographic grating carved on a concave surface when illuminated through an entrance slit, creates on rotation a near perfect image on a fixed exit slit. So, whenever you need a grating, you need an entrance slit as well as an exit slit. So, they blazed holographic gratings give a uniform throughput over the entire UV range that is the beauty of a holographic grating blazed holographic grating, they give you uniform output for the entire UV visible range. So, the band pass of 0.4 to 4 nanometers over the entire UV visible range is obtainable.

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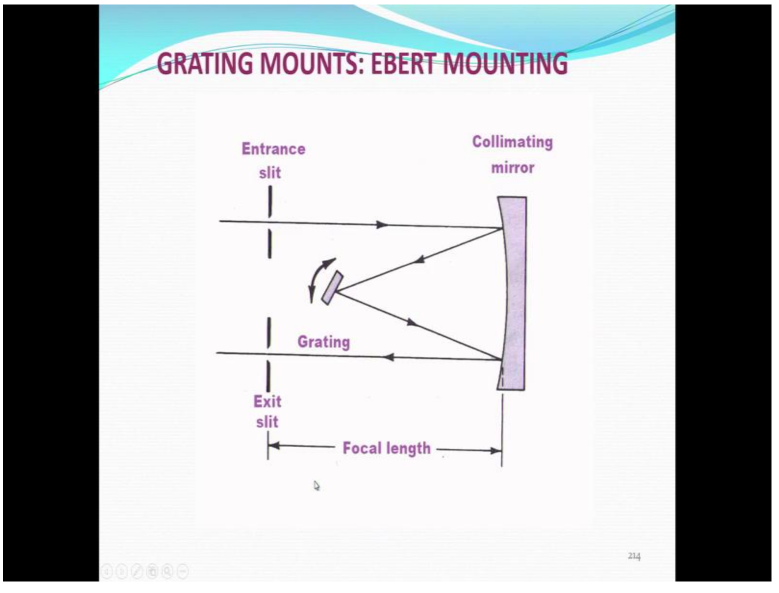

So, what I had told you so far is I want you to concentrate now the radiation that is normally I am coming from the radius from a spectro from a radiation source like tungsten lamp or something, that has to pass through a slit and then a monochromator a lengths or something to make the lines parallel.

They parallel lines are passed through the prisms or gratings to get desired wavelength and after the desired wavelength again we need a and exit slit, which is again triangular in nature and once that come through the exit slit what we get is the monochromatic radiation, that is the optics part of the spectrophotometer. Now in this optics part the arrangement of the exit slit and entrance slit is very important and that is known as mounting. So, the mount a mounting combination consists of an entrance slit a mirror and an exit re grating or a prism or something and then again transmitted light reflected light and that reflected light has to be collected back on the exit slit.

So, the combination of entrance exist slit and collimating mirror and the grating that is called as mounting. So, these are all things which are normally not disturbed by a spectrophotometer spectrophotometry user, it is all put it in a box and shield so that we do not disturb the thing; also there is certain amount of problem with dust and other things. So, the biggest enemies of spectrophotometric accuracy may accurate the measurements are the dust particles. So, the whole optics part must be housed in a box where there is no entrance of the dust, which is not always possible and quite often we have to open them and clean them etcetera that is a different science a service engineer will take care of that.

Now, I want to tell you about sum of the mountings. So, as I told you mountings are they different arrangements and here I am showing you Ebert mounting, here what is happening and entrance radiations comes from the slit falls on a collimating mirror and collect the reflected light is collected a grating or a prism and then again it is collected on the same prism and once it comes out, the exit slit will be organized like this. So, this here the both entrance slit and exit slit are placed at the focal length of the collimating mirror.

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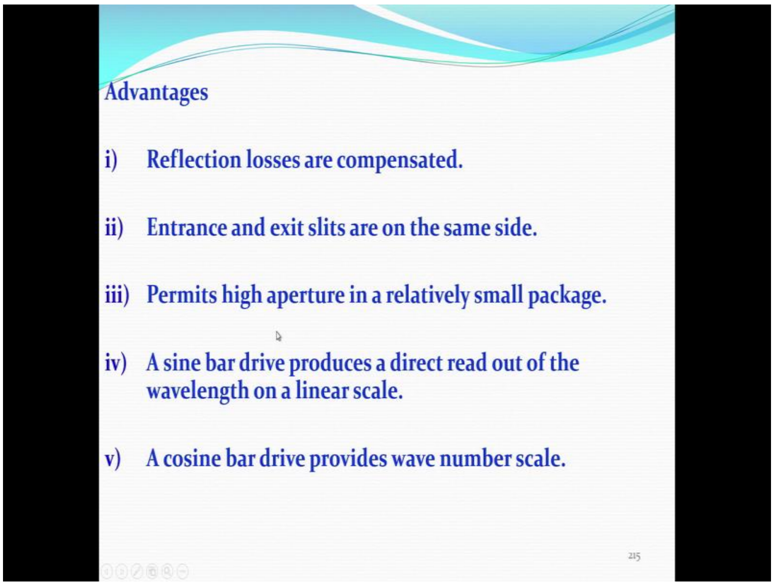

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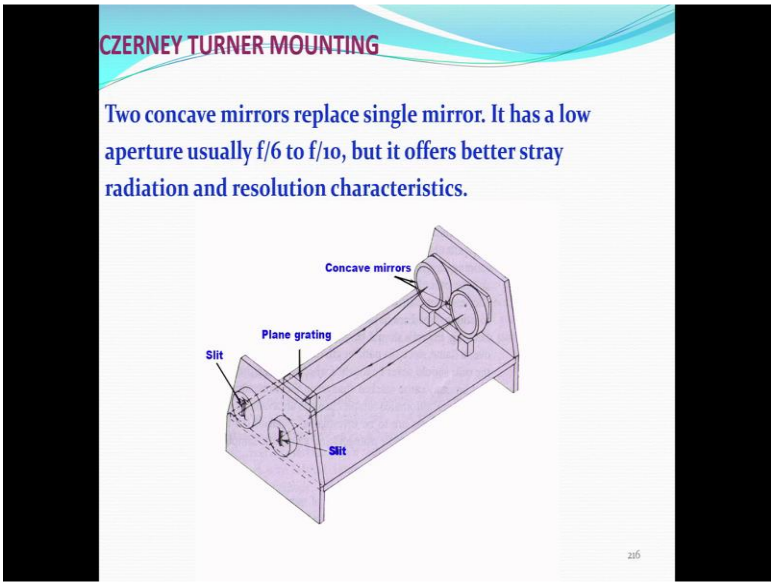

Now, I will show you another arrangement where the con mirrors there are two mirrors instead of one mirror.

Here you can see there are two mirrors. So, entrance slit is here it goes here collection the grating again goes to another mirror not on the same mirror like earlier, but comes out on the exit slip. So, going back to the Ebert mounting what we have here is, the using a single mirror and double mirror that is the difference between the two sets what I had shown you. The advantage of a single mirror is reflection losses are well compensated;

earlier I had told you that there will be about 4 percent error in the reflected losses and then entrance and exit slits are on the same side. That means, the instrument will become more compact and this permits high aperture in a relatively small package. That means, instrument become smarter and a sin bar drive produces a direct read out of the wavelength on a linear scale.

Suppose what is the wavelength coming out is depends upon how I rotate this grating; this grating is rotated the using a hand operation or automatic operation. So, the sine bar drive produces a direct read out of the wavelength. I can if I am rotating mechanically I can attach a wavelength scale as well, that is how the wavelength scale is made and it is a linear scale. So, cosine bar drive provides a wave number scale that is inverse of that. So, this is known as another arrangement known a Czerney turner mounting. Two concave mirrors are usually used here it has a low aperture f 6 to f 10, but it offers better stray radiation and resolution characteristics; stray radiation should be minimum and resolution should be optimum.

So, this is known as Czerney turner 99 percent of the spectrophotometer nowadays being produced in the market nowadays are based on Czerney turner mountings.

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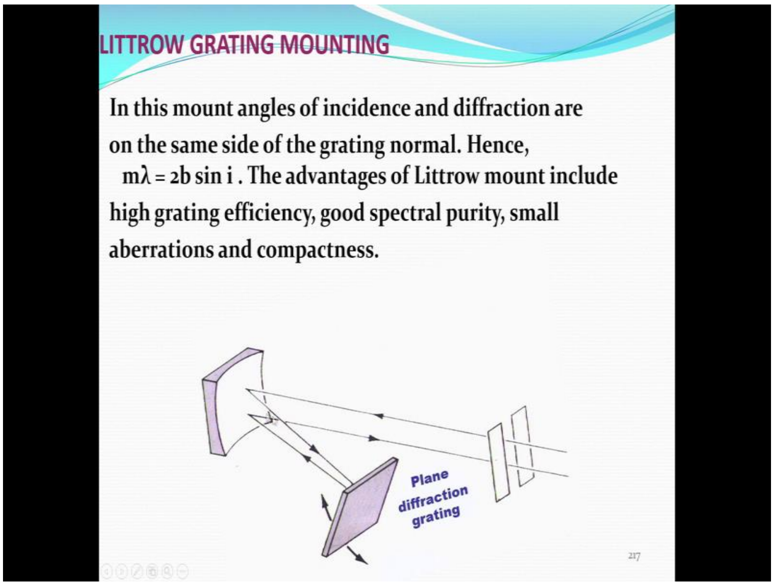

So, another arrangement is this is Littrow single entrance slit and exit slit, the difference is entrance slit is coming from the top and exit radiation is also is also coming through the same slit, but slightly at a lower level. So, this is known as Litrow grating mounting.

So, there are the if we advantage of this is high grating efficiency, good spectral purity, small aberrations and much more compact then double slits very simple arrangement.

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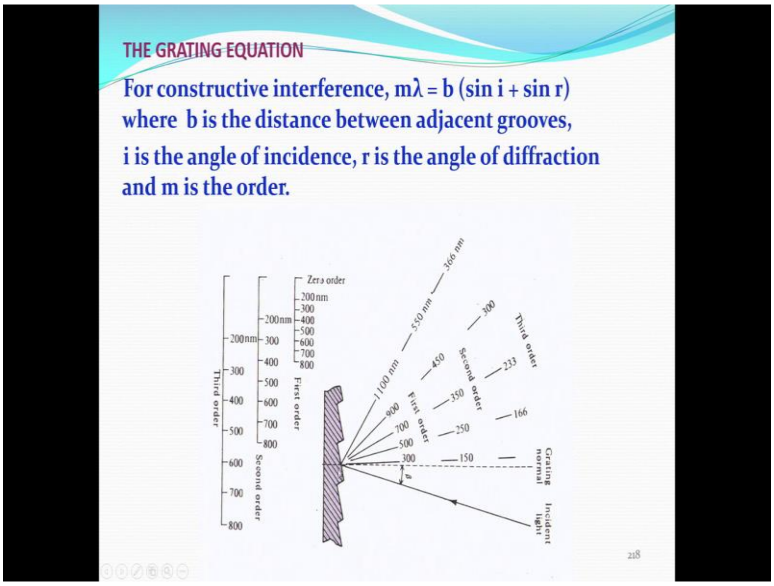

So, the grating equation basically is m lambda is equal to two d sin theta bar b into sin I plus sin r, where b is the distance between the adjacent grooves, and I is the angle this I have similar figure I have already shown you, but what is important in this case in this figure is here we will see the radiations wavelengths 300, 500, 700.

This is known as the first order wavelength any first order wavelength will also have half of that wavelength has second this is known as zero-order, this is a first order this is second order, third order like that. So, in any grating these are the basic problems with gratings, we have to minimize the second order and third order gratings because that is the wavelength that also comes out automatically along with any chosen wavelength. So, for example, if you choose 1100 it is always associated with 550 nanometer and half of that is again 366 nanometers and similarly 900 will be having 450 and 300 and it need not be in the same exactly half, but it will be a approximately.

So, this is the problem with gratings. So, there are lot of work has been done in reducing the higher order radiations coming from a grating, so that the wavelength accuracy is optimum; for actually if you are measuring around 1100 they will not be measuring 550 in general, but it will serve as a stray radiation which will help which will result in a slight aberration same as same thing is true with 360. Similarly if you go for 900 it is always associated with 450 and 300 nanometers, 700 with 350, and 233 like that.

It is a very simple calculation we can actually calculate the first order, second order, third order wavelengths using the simple formulas.

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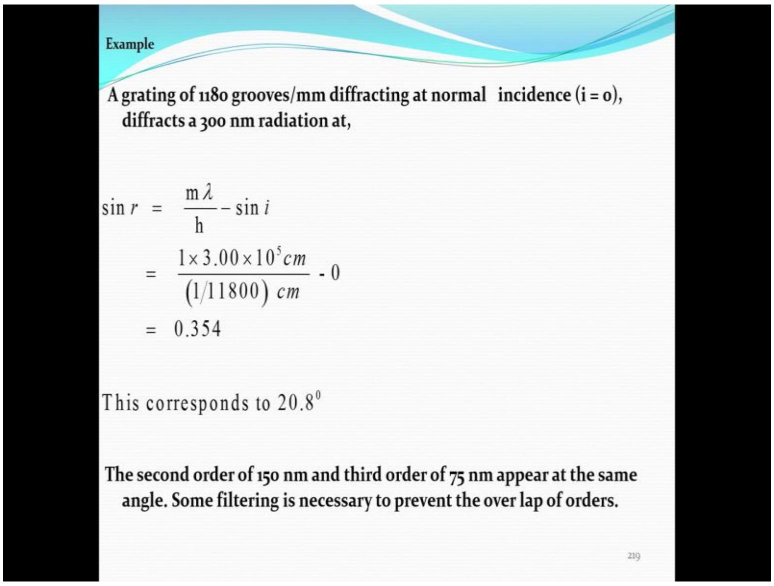

So, here is a small practical problem if I have a grating of 1180 grooves per millimeter diffracting at a normal incidence; that means, I is equal to angle of incidence is 0. So, it diffracts a 300 nanometer radiation I can simply calculate; what is the sin r, m lambda by h minus sin I, so this will be 0 sin angle of incidence is 0. So, sin I 0. So, m lambda by h is what I get here converting converted into centimeters, and then 1 into 3 into 10 raise to 5 divided by that is the centre convert everything into centimeter, what comes out is 0.354 and this corresponds to 20.8 degrees exit angle.

So, the second order of this would be 150 and third order would be 75 they appear at the same angle of 20.8 degrees. So, some amount of filtering is necessary if you want to prevent the overlap of the higher orders in a grating that is important.

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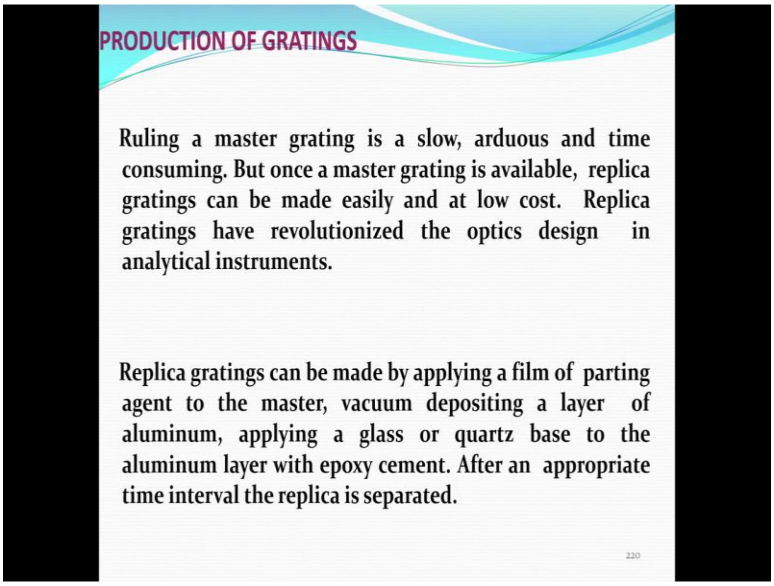

Now, how do I produce a grating? A grating is produced using a master grating once you know every time it is not possible to get the same quality of grating, by taking a machine and doing it. So, what we do normally is we take a master grating make a master grating and then produce there replicas. So, basically it is a slow arduous and time consuming, but once a master grating becomes available replica gratings can be made very easily and that to at low cost.

So, replica gratings can be made by applying a film of a parting agent; that means, I take a grating master grating, I take a master grating put a little bit of oil or butter or something you know which can be taken off, and then over that I put epoxy the epoxy will hard in, producing a replica of the grating on the epoxy on this epoxy is mounted on a aluminium plate. So, when you take it out I have the grating ready. So, that is the whole idea. So, glass or quartz base I can I need to take, and at the aluminum layer with epoxy cement after an appropriate time interval the replica can be separated. This is a very simple easy way of producing a grating which is a very high quality engineering material.

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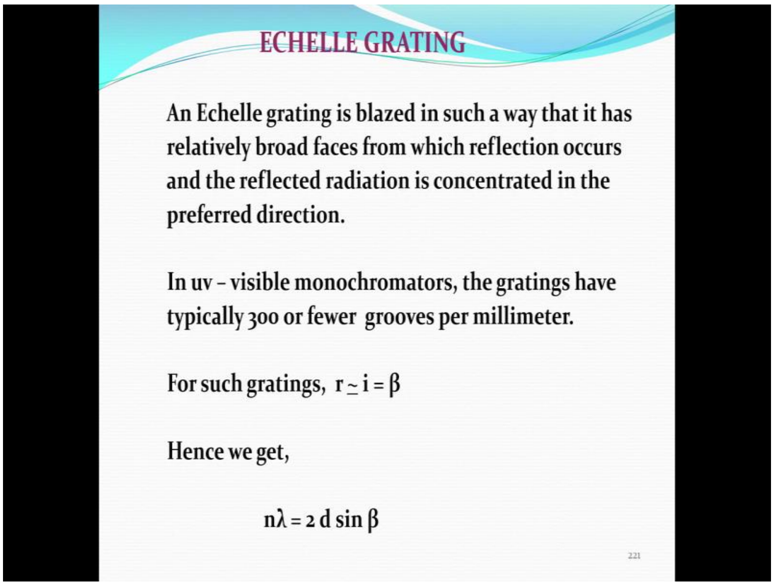

So, this grating coming back to the Echelle gratings, an Echelle grating you must know about it because lot of people were sales people etcetera when you bond a by an equipment they come and say sir ours is an Echelle grating, it is not blazed holographic grating or it is not a simple plain grating, but it is a Echelle grating. So, what is a Echelle greeting. So, an Echelle grating is blazed in such a way that it has relatively broader surfaces; that means, very few lines reflection lines. So, reflection occurs and the reflected radiation is concentrated in the preferred direction.

So, in UV- visible chromato monochromatars the grating usually you have bought 300 or fewer grooves maybe 75 grooves, 100 grooves like that instead of 1200, 1800 grooves in a normal blazed holographic gratings for spectrophotometer. So, for such gratings angle of reflection and angle of incidence are same fixed. So, you get m lambda is equal to 2-D sin beta that is whatever we are fixing the blazing angle.

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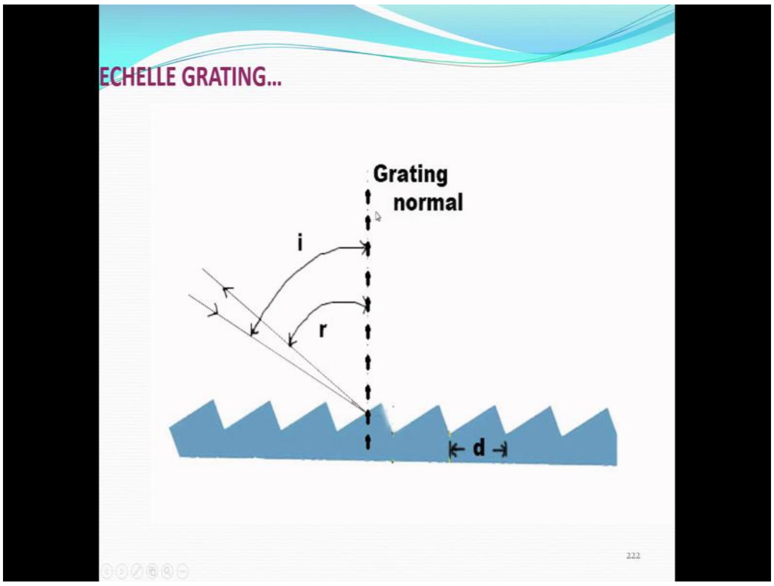

And then what happens is this the difference is like this this is normal grating normal, the angle of incidence is fixed and angle of this thing is reflection is also fixed like this this is the distance between their to.

So, the reflection losses in from this case are very less because it is not very near, instead of 1800 grooves like this like this we have only 75 or 80 grooves.

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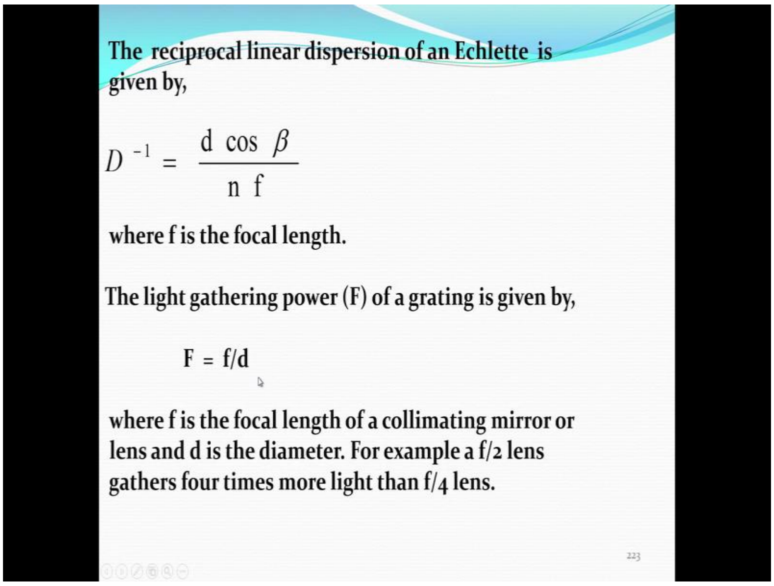

So, the reciprocal linear dispersion is given by this formula and light gathering power is better where f is the focal length.

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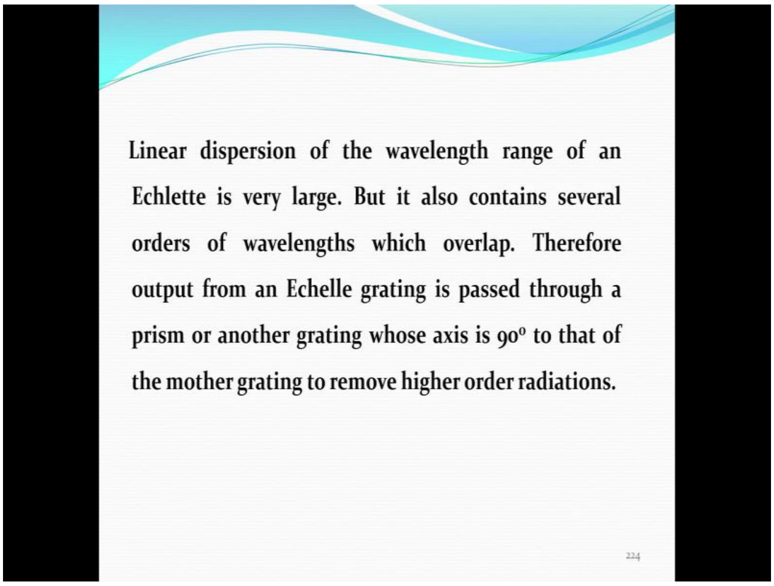

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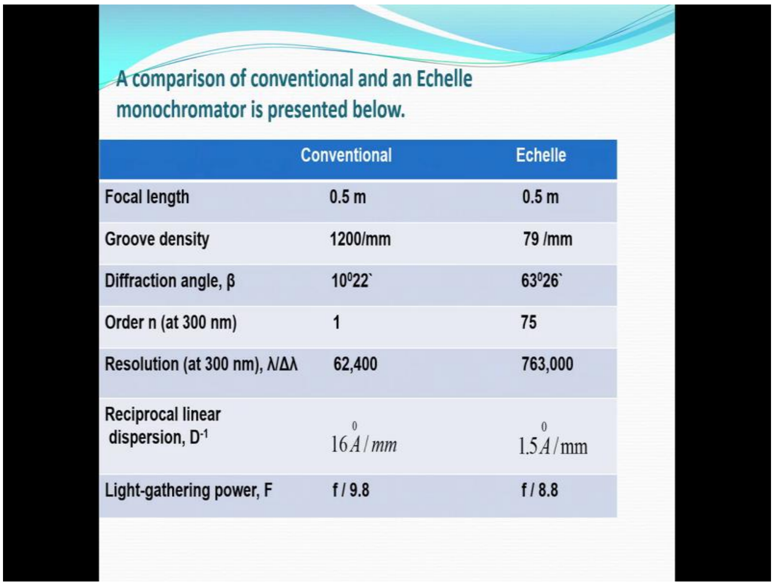

	Conventional	Echelle
Focal length	0.5 m	0.5 m
Groove density	1200/mm	79 /mm
Diffraction angle, β	10°22`	63°26`
Order n (at 300 nm)	1	75
Resolution (at 300 nm), λ/Δλ	62,400	763,000
Reciprocal linear dispersion, D^{-1}	$16 \overset{0}{A}/mm$	$1.5 \overset{0}{A}/mm$
Light-gathering power, F	f / 9.8	f / 8.8

And the linear dispersion is a of an Echelle is very large, it also contains several orders of wavelengths which overlap and the a comparison of the conventional and an Echelle monochromator is given here on conventional is 0.5 this is 0.5 1200 this become 1700 mm, this is 10 degrees, this is 63 degrees, that the diffraction angle order is one and here it is 75 resolution is 62,400.

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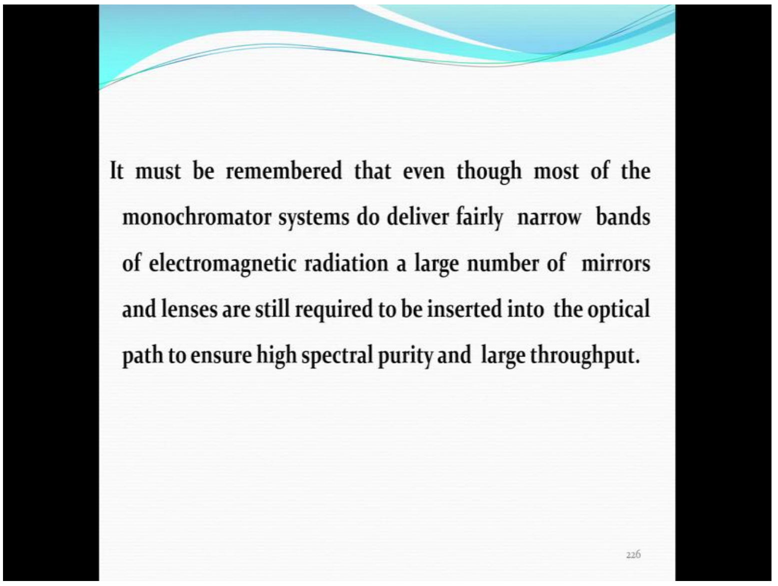

Whereas it is here in this case it is 763000. So, reciprocal in a accuracy what you can see here is the accuracy. So, it must be remember that even though most of the monochromator systems do deliver fairly narrow bands of electromagnetic radiation, large number of mirrors and lenses are still required in any spectrophotometer. So, if you happen to know by any chance open by any chance a spectrophotometer do not be bad feel if you see a number of small small mirrors and lenses.

So, that completes our discussion on the optics part, now we will concentrate on the absorption cells in the next class. Please remember that what we had discussed is the instrumentation of a spectrophotometer, we have discovered only half of it now will be discussing about the absorption cells as well as the detection and measurement of this spectrophotometry cells. And then we will discuss about the typical commercial instruments in the next class.