Modern Instrumental Methods of Analysis

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Lecture No. # 31

Infrared Spectroscopy-1

Theoritical Aspects

Welcome to the thirty first lecture of this course. We are discussing about the infrared spectroscopy. In the last class, I was talking to you about the grating spectrophotometer ranges in infrared, and I had told you that the full range of grating spectrophotometer maybe 4000 to 600 centimeter inverse or better still would be 5000 to 200 centimeter inverse. Up to 200 centimeter inverse, you do get some useful i r peaks.

So, gratings are normally operated in the second and third order. Usually, spectrum is in the range of 4000 to 200 centimeter inverse range; 2000 inverse range is operated in the second order and 2000 to 400 centimeters range is obtain in the first order. A series of cut off and band pass filters are definitely therefore required and the detector must be synchronized to obtain the correct order of the grating. This is achieved by synchronizing the motor with the scanning of the grating. In more expensive instruments, we can use only first order gratings. For all the range, all over the range to provide optimum performance which is maximum over all the output range.

Now, what I want to convey at this stage is - a grating blazed at two angles performs as two gratings. So, you can manage with one grating blazed at two angles, that is, one, one higher and one smaller. The drive is reproducible in infrared spectrometry up by of the order of about 0.01 centimeters inverse; that means the increments what you use for infrared spectrum scanning should be of the order of about 0.01 centimeters inverse, but in can also be pre calibrated against a spectroscopic standard; that means the wavelength reproducibility should always be checked with a spectroscopic standard which will give you exact peak at a non wavelength, then you can synchronize the whole wavelength scan with respect to the standard compound and standard peak.

So, all other wavelength ranges are automatically pre calibrated. Modern monochromators are directly driven by spectrometer and stepper motor, and microprocessor controlled to provide high level of accuracy. This also provides a slit programming; that means you can increase or decrease the slit also depending upon the strength of the i r peak what you are getting. If the strength is weak, then you can allow more grating, more slit, and if the peak is very strong, you can go for a smaller slit and, the, such an arrangement provides you very high accuracy. This also provides a slit programming mechanism in modern instruments using the computer to give near constant energy.

So, single beam photometer posses the capacity for accurate measurement in quantitative analysis. That is important, because in i r as you will see later, the, the accuracy, quantitative accuracy is always slightly problematic, but they can be use for such systems in quantitative analysis single beam.

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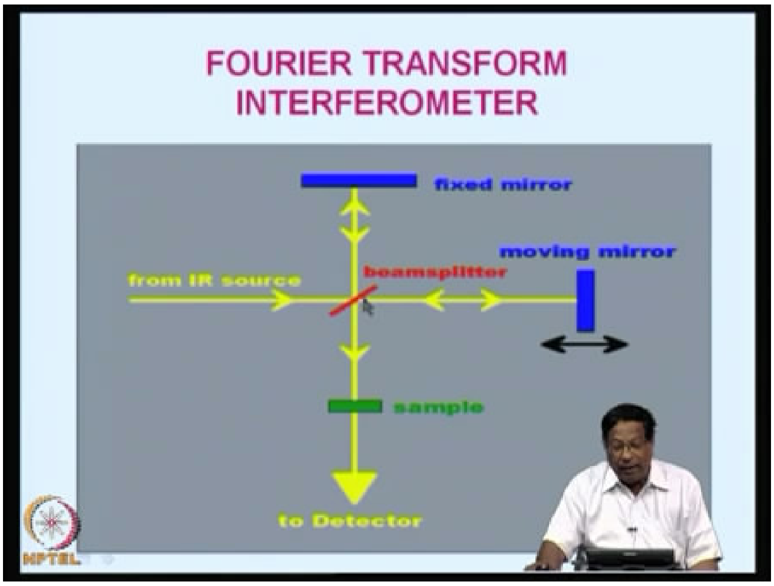

FOURIER TRANSFORM INTERFEROMETER

Now, let us discuss about the Fourier Transform spectroscopy. Now, here, the, I am showing you a figure of this Fourier Transform interferometer, and, the, you can see that from the i r source, there is a beam splitter here and part of the beam travels like this to a moving mirror where it gets reflected and comes back, and part of it goes to a fixed mirror on the top and then again it gets reflected. Both beams are combined here, and then, it passes through the sample to the detector. This is the general arrangement of a Fourier Transform f t i r.

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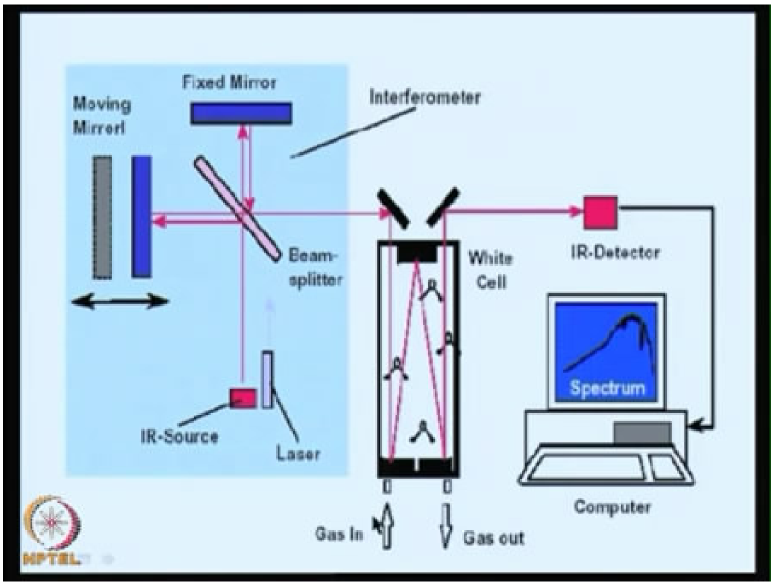

So, other arrangements are something like this where you can use a moving mirror on, the, this side, fixed mirror here and then beam splitter here and then i r source laser, etcetera. Here, the addition is a laser which is used to calibrate the wavelength, and then, all other things will remain the same, because this is for a gas sample to be taken for i r, and the gas comes here, gas goes out, but the beam splitter is always here and then it goes to i r detector which is totally controlled by the computer.

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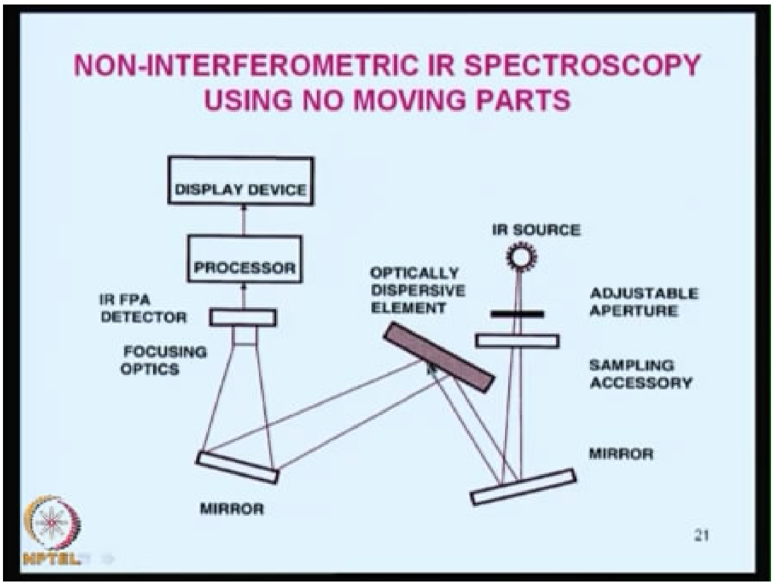
NON-INTERFEROMETRIC IR SPECTROSCOPY
USING NO MOVING PARTS

Now, this is a another arrangement where the i r source is passed through an adjustable aperture and sampling accessory mirror and then optical, other optical components like dispersive element, then mirror focusing processor, display device, etcetera. And non interferometric i r spectroscopy uses no moving parts. This a, that is the specialty of infrared spectrometer.

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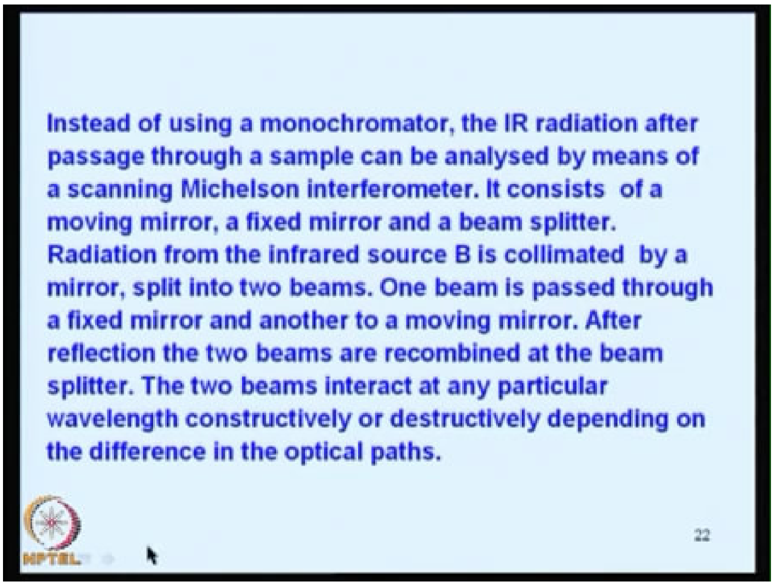

Instead of using a monochromator, the IR radiation after passage through a sample can be analysed by means of a scanning Michelson interferometer. It consists of a moving mirror, a fixed mirror and a beam splitter. Radiation from the infrared source B is collimated by a mirror, split into two beams. One beam is passed through a fixed mirror and another to a moving mirror. After reflection the two beams are recombined at the beam splitter. The two beams interact at any particular wavelength constructively or destructively depending on the difference in the optical paths.

Now, you can see from the previous figure that instead of using a monochromator, the i r radiation after passes through a sample can be analyze by means of a scanning michelson interferometer. It consist of a moving mirror as you have seen earlier, - fixed mirror and a beam splitter - you try to remember this figure.

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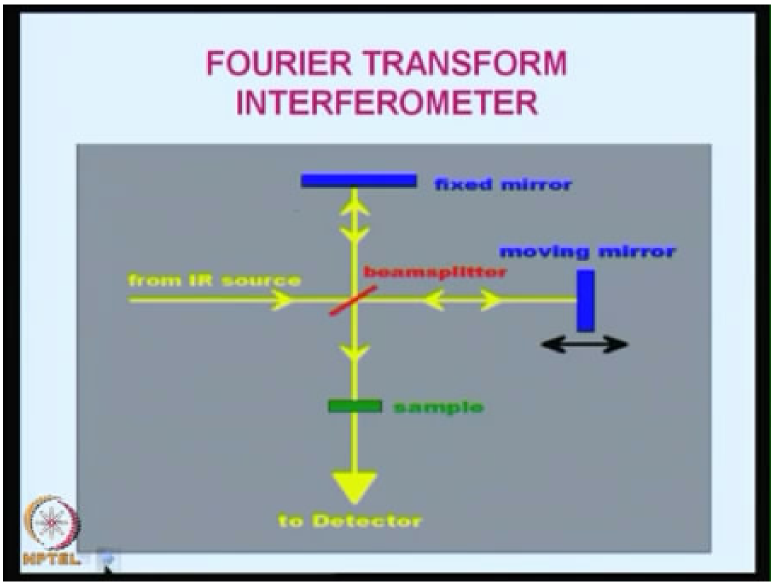

FOURIER TRANSFORM INTERFEROMETER

The figure what I am showing you in the slide, would you, you should try to remember this figure, where the moving mirror heats on continuing like this and then fixed mirror is like that, and then, we are discussing about this arrangement now.

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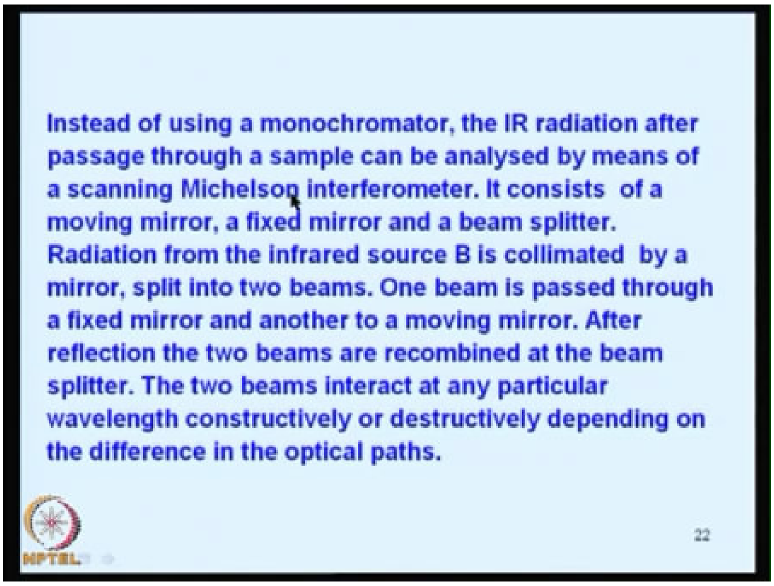

Instead of using a monochromator, the IR radiation after passage through a sample can be analysed by means of a scanning Michelson interferometer. It consists of a moving mirror, a fixed mirror and a beam splitter. Radiation from the infrared source B is collimated by a mirror, split into two beams. One beam is passed through a fixed mirror and another to a moving mirror. After reflection the two beams are recombined at the beam splitter. The two beams interact at any particular wavelength constructively or destructively depending on the difference in the optical paths.

So, here what is happening is moving mirror is there, a fixed mirror is there, a beam splitter is there, and radiation from the infrared source is collimated by a mirror, and then, it is split into two beams - one passes through a fixed mirror and another passes through a moving mirror, and after the reflection, the two beams are combined, recombined rather at the beam splitter. The two beams interact at any particular wavelength constructively or destructively depending upon the difference in the optical paths. So, the arrangement is always like, you know, it is a adjustment of the moving part against the internal standard.

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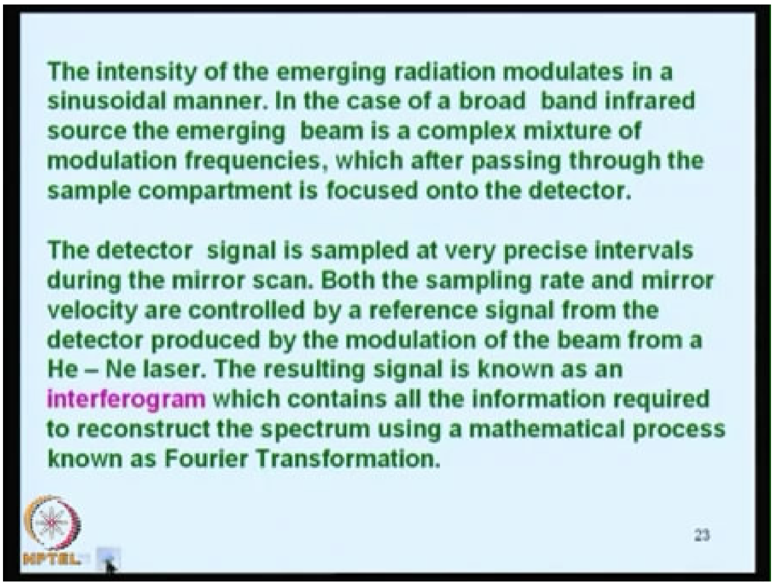

The intensity of the emerging radiation modulates in a sinusoidal manner. In the case of a broad band infrared source the emerging beam is a complex mixture of modulation frequencies, which after passing through the sample compartment is focused onto the detector.

The detector signal is sampled at very precise intervals during the mirror scan. Both the sampling rate and mirror velocity are controlled by a reference signal from the detector produced by the modulation of the beam from a He – Ne laser. The resulting signal is known as an interferogram which contains all the information required to reconstruct the spectrum using a mathematical process known as Fourier Transformation.

So, the intensity of the emerging beam radiation, I want to inform you that it is modulated in a sinusoidal sinusoidal manner, that is, in a, like a sign wave, the intensity of the beams that is coming out is modulated in the as a sign wave. In case of a broadband infrared source source, the emerging beam is a complex mixture of modulation frequencies, which after passing through the sample compartment is focused on to the detector; that means, all the information about the sample absorption of i r is contained in a single moving mirror operation, in which, all the beams are interacting constructively or destructively giving you peaks and no peaks.

So, the detector signal you will have to sample at precise intervals of the mirror scan. For each mirror scan, you have to scan the detector. The detector also should be able to should be synchronized. So, both the sampling rate and mirror velocity must be controlled by a reference signal from the detector using the modulation of the beam from a helium and neon laser, because lasers are known to posses very exact wavelengths and that is used for calibration. The resulting signal is known as an interferogram and which contains all the information require to reconstruct the spectrum using a mathematical process known as Fourier Transformation.

Now, it is not possible to go into tails of the mathematical operation of the mathematical principles of the Fourier transform operation, but it is a very well known operation in handling the mathematical expressions. You can look up any standard text books in mathematics like engineering mathematics. They will give you a detail description of what is a Fourier Transform. What are the, how the operation has to be conducted etcetera. We, I expect you to go through that and get a, in a, get a idea about what is Fourier transform infrared, Fourier Transform operation, and now, we have we are importing that idea from the Fourier Transform operation into infrared spectroscopy. So, basically it is mathematical operation conducted through a computer, but all the information is gathered through a simple arrangement like that Michelson Interferometer which I showed you like this.

So, what we are saying is - there are minimum moving parts and maximum information is opted; that means, the spectrum what you get in infrared is a pure spectrum and there are no distortions. There are other advantages of Fourier Transform infrared spectrometry.

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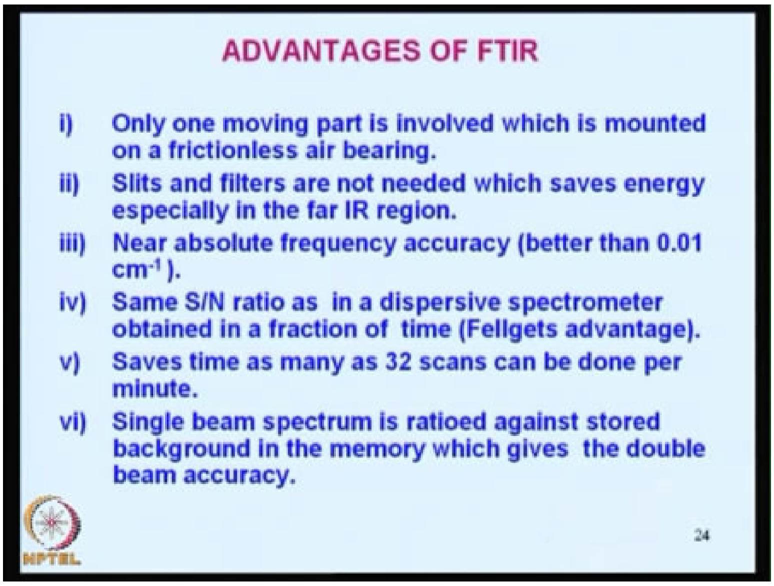

ADVANTAGES OF FTIR

i) Only one moving part is involved which is mounted on a frictionless air bearing.
ii) Slits and filters are not needed which saves energy especially in the far IR region.
iii) Near absolute frequency accuracy (better than 0.01 cm^{-1}).
iv) Same S/N ratio as in a dispersive spectrometer obtained in a fraction of time (Fellgets advantage).
v) Saves time as many as 32 scans can be done per minute.
vi) Single beam spectrum is ratioed against stored background in the memory which gives the double beam accuracy.

Now, you can see that there are there are only few moving parts, in the, in the, in using f t i r, there is actually one moving part in is involved, that is the moving mirror, which is mounted on a frictionless air barring; that means, the reproducibility is very high in that and then slits and filters are not needed; that is second advantage, which saves the energy especially in the far i r region, because the energy the energy of infrared and a far i r is much less than in the near i r or in the normal i r range. Then, the possibility is, advantage is near absolute frequency accuracy, that is, true spectrum, you will be getting and the error would be less than 0.01 centimeters inverse. That is third advantage. Fourth advantage is you will get the same signal to noise ratio as in a dispersive spectrometer using gratings and presumes, etcetera. You will get the same signal to noise ratio, but it is obtained in a within a fraction of a second.

So, this signal to noise ratio is quantitatively it is much less than a grating spectrometer, because to operate the, to complete the full range of grating, - grating infrared spectrum - you have to rotate the grating through the full range of i r starting from, let us say 4000 to 200 centimeter inverse, but here, what is happening is within a fraction of a second, whatever is the in signal to noise ratio is opted. So, it saves you the time. So, as many as thirty two scans can be done per minute.

So, this is known as Fellgett’s advantage, and then, single beam spectrum is ratioed against stored background. You can store the background and then use a single beam which gives you the double beam accuracy. This is another advantage. So, all in all, I have enumerated about six advantages of f t i r spectrum operations, and therefore, 90 percent of the commercial atomic commercial infrared spectrometer now a days are based on Fourier Transform infrared spectroscopy.

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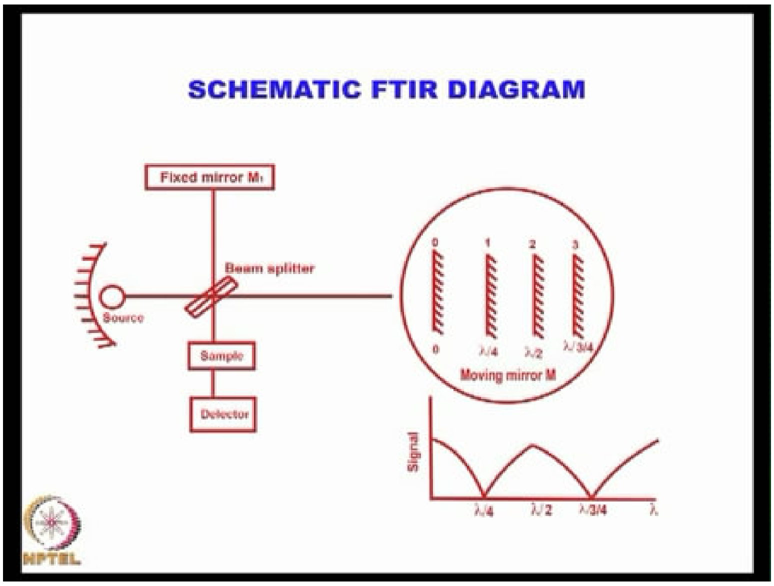

SCHEMATIC FTIR DIAGRAM

So, let us look at the how an interferometer works and how it can be related to spectroscopic measurement. Let us see what happens when a single beam wavelength is used in an interferometer, so, look at this slide, I am, I want you to, and I want to show you this slide, where I have schematized the whole process. Here is the i r source; here is beam splitter. What we had seen in the earlier figure? There is a fixed mirror m one here, and then, this is the moving mirror, I have put it in 0 1 2 3 operations, that is, positions, where it represents 0 lambda by 4 wavelength for a single one, single, and then lambda by 2 lambda by 4 and this is 3 lambda by 4, and then, the beam is reflected back and this beam is reflected back. It falls on the sample and then it falls on the detector. Now, you can see that lambda by 4 is here; lambda by 2 is here, and then, 3 by 4 lambda and then this is final position of the mirror, and then, again, from here, it moves back to 0 0 3 0 3 etcetera and continues like this.

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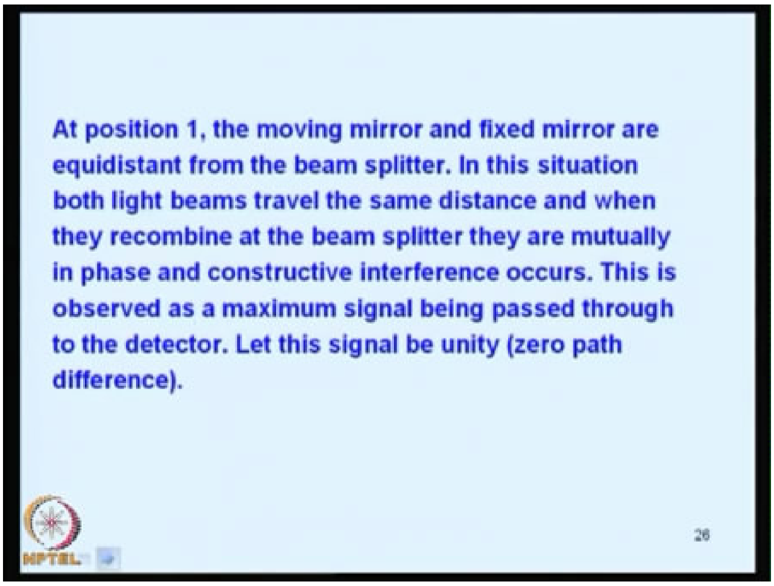

At position 1, the moving mirror and fixed mirror are equidistant from the beam splitter. In this situation both light beams travel the same distance and when they recombine at the beam splitter they are mutually in phase and constructive interference occurs. This is observed as a maximum signal being passed through to the detector. Let this signal be unity (zero path difference).

So, at position 1, the moving mirror and fixed mirror, that is, position one, they are at equidistant from each other. So, if there equidistant from the, from each other, then the signal in this situation, both lights, that is, coming from the fixed mirror and the moving mirror, they are they trouble the same distance, and when they recombined at the beam splitter, they are mutually in face and constructive interference occurs; that means, you will get a highest signal because everything is in face and everything is constructive. So, this would be there is no, destructive, destruction of the incoming radiation; that means you should get the highest signal when it falls on the detector. Now, this is observed as a maximum signal being pass through to the detector. So, let this signal be unity, that is, at zero path difference, the signal is unity. Now, look at this. As the mirror moves away from the, from zero position, that is, from zero position, it moves here.

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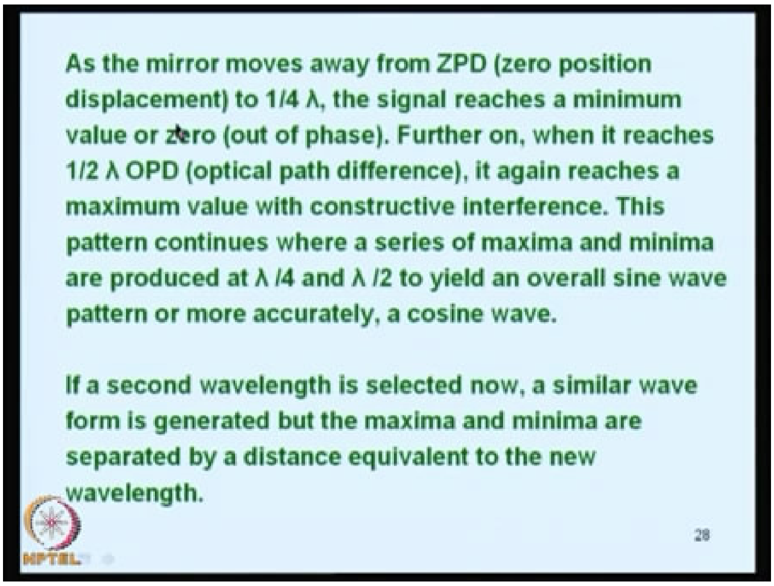

As the mirror moves away from ZPD (zero position displacement) to 1/4 λ, the signal reaches a minimum value or zero (out of phase). Further on, when it reaches 1/2 λ OPD (optical path difference), it again reaches a maximum value with constructive interference. This pattern continues where a series of maxima and minima are produced at λ /4 and λ /2 to yield an overall sine wave pattern or more accurately, a cosine wave.

If a second wavelength is selected now, a similar wave form is generated but the maxima and minima are separated by a distance equivalent to the new wavelength.

As it moves away from this position, what happens? The, the zero position displacement to 1 4th lambda; the signal reaches a maximum minimum value of zero until it is totally out of face; that means, when it is totally out of face, no signal reaches the detector. This is further on when it reaches 1 by 2 - optical path difference - half of the moving mirror distance, that is 50 percent of the distance allocated for the moving mirror. Again, constructive interference occurs. This pattern continues until where a series of maxima and minima are produced at lambda by 4 lambda by 2 etcetera to yield an overall sign wave pattern or more accurately it is a cosine wave, because at 0, cosine 0 is 1.

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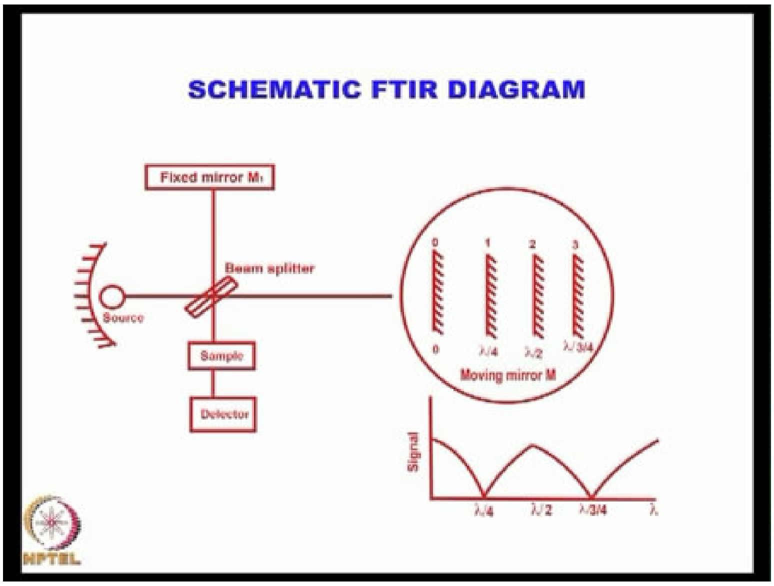
SCHEMATIC FTIR DIAGRAM

So, if you take a look at this, the signal is almost maximum here. So, we can call it 1 and from here lambda by 4, it comes to 0, and then, again lambda by 2, it reaches maximum; 3 by 4 lambda, it goes here and again it reaches like this.

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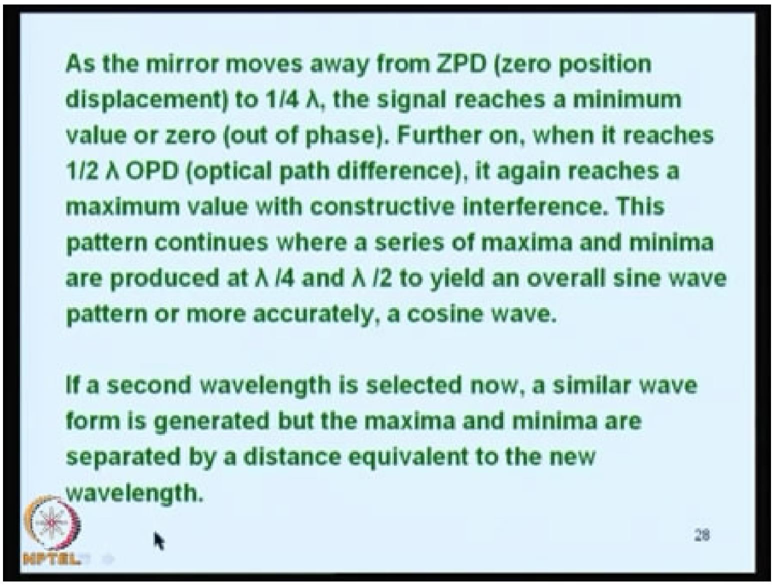
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If a second wavelength is selected now, a similar wave form is generated but the maxima and minima are separated by a distance equivalent to the new wavelength.

So, if a second wavelength is selected now, a similar wave pattern is generated and I want the maxima and minima to be separated by a distance equivalent to the new wavelength; that means for each wavelength, I am allowing it to pass through the beam splitter etcetera and then the sample. For each wavelength, I have now information totally collected as a single at single wavelength, and for each wavelength, I am measuring the total constructive and destructive interference. So, in this way, we are going to get a unique cosine design, cosine wave for each wavelength. The observed signal at the detector is thus therefore, for each wavelength is collected in the same detector. So, the observed signal at the detector is a summation of each of these cosine waves which gives a maximum at 0 position, and then, which rapidly decays into a complex overlapped signal which continues to decay with the increasing optical path difference.

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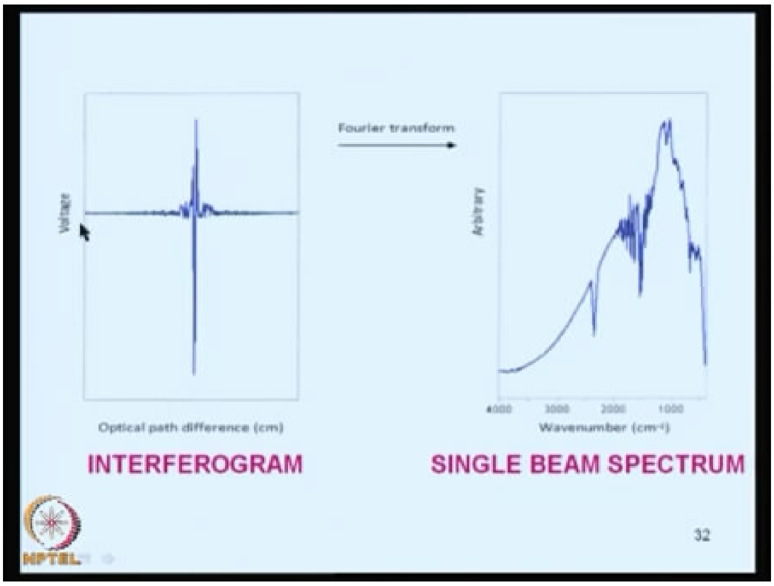

INTERFEROGRAM

SINGLE BEAM SPECTRUM

So, if the component cosine waves, I can now what I have is something like this. I am having a single way wave containing all the information plotted optical path difference here and vollume voltage is here, that is a detector voltage. You will see that a maximum signal is generated with the center and then slight variations on a either side of this. So, if you, this is the interferogram, if you transform this into single peaks into different wave numbers etcetera, you will you have to get the normal spectrum.

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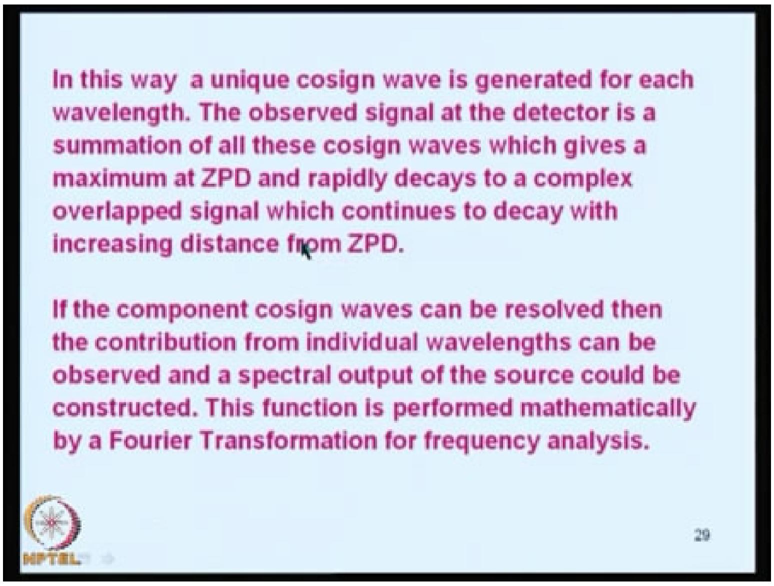

In this way a unique cosign wave is generated for each wavelength. The observed signal at the detector is a summation of all these cosign waves which gives a maximum at ZPD and rapidly decays to a complex overlapped signal which continues to decay with increasing distance from ZPD.

If the component cosign waves can be resolved then the contribution from individual wavelengths can be observed and a spectral output of the source could be constructed. This function is performed mathematically by a Fourier Transformation for frequency analysis.

So, again, going back to our discussion, we the observed signal at the detector is basically a summation of all these cosine waves which gives us a maximum at Zero Position Path Difference and rapidly decays into a complex overlapped signal which continues to decay with the increase in distance; that means one broad signal and then a simple noise like appearance, and then, if the component cosine waves, if we can separate them, resolve them from individual wavelengths, then we can put this spectral output of the source can be reconstructed. This function is performed mathematically by Fourier Transform transformation for frequency analysis; that means, first, what we are going to do is - put the sample and then pass the radiation, all infrared radiation from one source in one shot through the sample, and then, collect for each wavelength, total output as the mirror moves from 0 to lambda maximum position. Like that we are going to do number of operations to start starting from 4000 to 2000 centimeter inverse all that information is collected in one signal maxima.

And, so, to obtain that, you have to, first you have to you perform. Now, we have performed Fourier Transformation. Now, we have to defourier do defourier transformation Fouier detransformation to get back the original spectrum like what we are use to in normal spectrometry.

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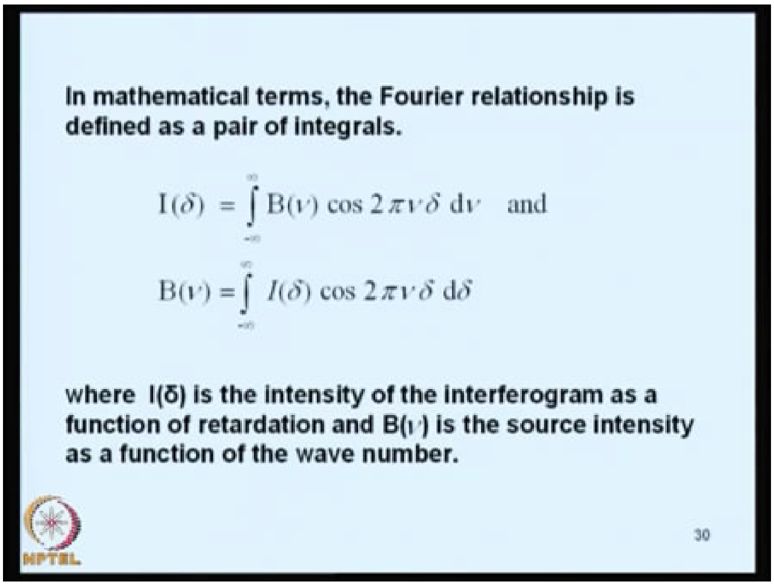

In mathematical terms, the Fourier relationship is defined as a pair of integrals.

$$I(\delta) = \int_{-\infty}^{\infty} B(\nu) \cos 2\pi\nu\delta \, d\nu \quad \text{and}$$

$$B(\nu) = \int_{-\infty}^{\infty} I(\delta) \cos 2\pi\nu\delta \, d\delta$$

where I(δ) is the intensity of the interferogram as a function of retardation and B(ν) is the source intensity as a function of the wave number.

So, in mathematical terms, the Fourier relationship is defined as a pair of integrals like this i delta is equal to, i delta is equal to minus lambda 2 in plus lambda; that means, we are assuming that the info the Fourier Transform series is an infinite series. That is given by b v b mew cosine 2 pie mew delta and d v and we define another term b mew is equal to again another Fourier Transformation from minus infinity to plus infinity i delta cosine two pie mew delta and d delta - where i delta, this one, is the intensity of the interferogram as a function of the retardation; retardation means, moving, moving mirror operations and b mew is the source intensity as a function of the wave number.

So, a Fourier Transform contains two in two parameters - one is the intensity of the interferogarm as a function of the moving mirror and another is the source intensity as a function of the wave number, because source intensity, the source gives you the total infrared spectrum containing all the wavelengths. That is why, the, the interferogram what we have seen earlier contains, two, two integrals - one is for i delta; another is for b v

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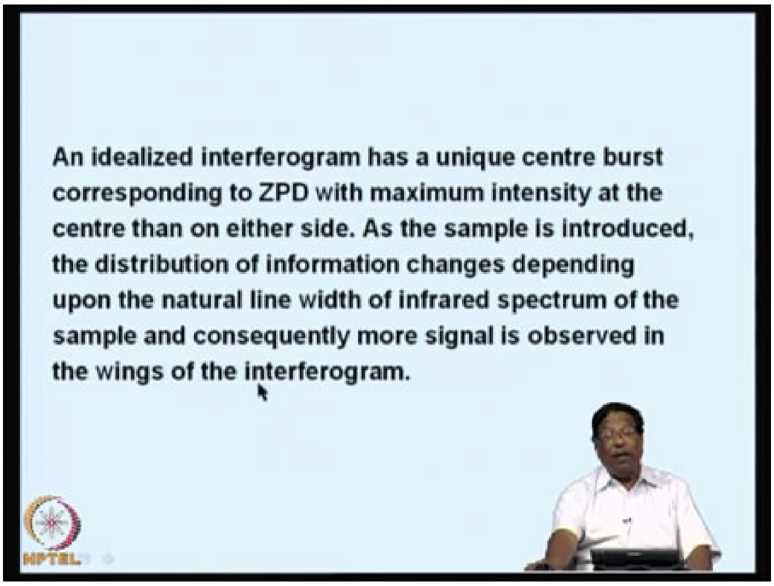

An idealized interferogram has a unique centre burst corresponding to ZPD with maximum intensity at the centre than on either side. As the sample is introduced, the distribution of information changes depending upon the natural line width of infrared spectrum of the sample and consequently more signal is observed in the wings of the interferogram.

Now, you can do this. Collect all the information and plot it. An idealized interferogram has a unique center burst, as I have already explained to you, corresponding to Zero Path difference with maximum intensity at the center than at the either side. As the sample is introduced, the distribution of information changes depending upon the natural line width of the infrared spectrum of the sample and consequently more signal is observed in the wings of the interferogram. The heart is always in the wings.

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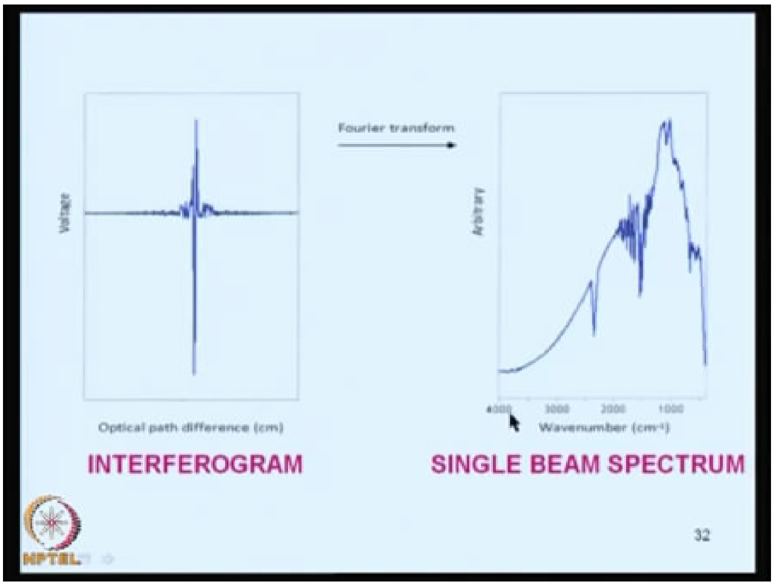

INTERFEROGRAM

SINGLE BEAM SPECTRUM

So, like this, you will see that information. This is the kind of information, where, if you look at it closely, you will see that it is not a straight line, but it is a noise like appearance with lambda, then coming out like this. So, if you do the Fourier transform, you will get the infrared radiation from 4000 to 15 100 or whatever is the range, you are operating into just like a single beam spectrum.

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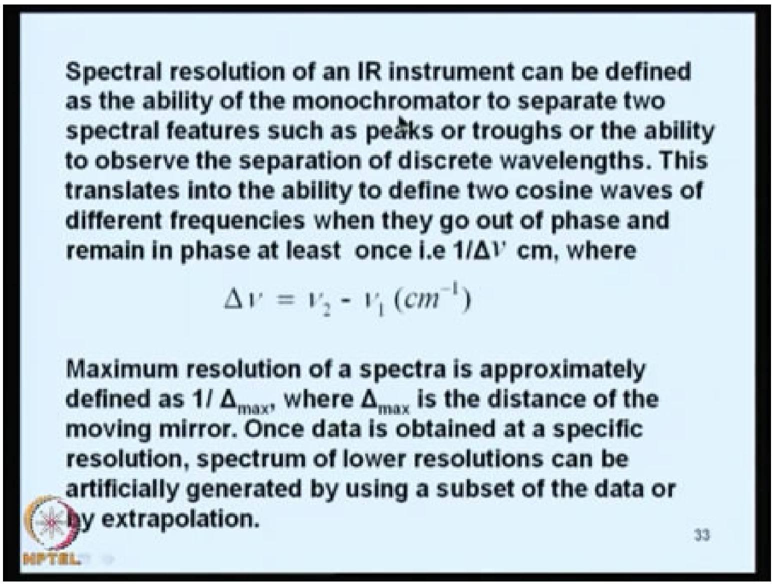

Spectral resolution of an IR instrument can be defined as the ability of the monochromator to separate two spectral features such as peaks or troughs or the ability to observe the separation of discrete wavelengths. This translates into the ability to define two cosine waves of different frequencies when they go out of phase and remain in phase at least once i.e $1/\Delta\nu$ cm, where

$$\Delta\nu = \nu_2 - \nu_1\ (cm^{-1})$$

Maximum resolution of a spectra is approximately defined as $1/\Delta_{max}$, where Δ_{max} is the distance of the moving mirror. Once data is obtained at a specific resolution, spectrum of lower resolutions can be artificially generated by using a subset of the data or by extrapolation.

So, spectral resolution of an i r instrument can be defined as the ability of the monochromator to separate two spectral features such as either a peak or a trough. That is the spectral resolution; we can define it as the ability to separate a peak or a trough, peak and a trough, peak and a trough like that, or the ability to observe the separation of discreet wavelengths. If we are able to operate the discreet wavelengths, that is fine, and then, this translates into the ability to define two cosine waves of different frequencies. When they go out of face and, they, when they remain in face, at least once, that is, 1 over delta mew centimeters inverse - where delta mew is defined as the second wavelength minus the first wavelength. That is the change, changing wavelength. So, the maximum resolution of a spectra is approximately defined as 1 delta lambda max. So, the wavelength difference one over divided by that wavelength difference which can be measure accurately - where delta max is the distance of the, moving is computed in terms of the distance of the moving mirror. Once the data is obtained at a specific resolution, spectrum of lower resolutions can be artificially generated using the Fourier Transform by using a subset of the data or by extrapolasion. These are all very simple systems and, the, theoretically the information should be collected at infinite retardation; that means, we should, I must take you back to this figure.

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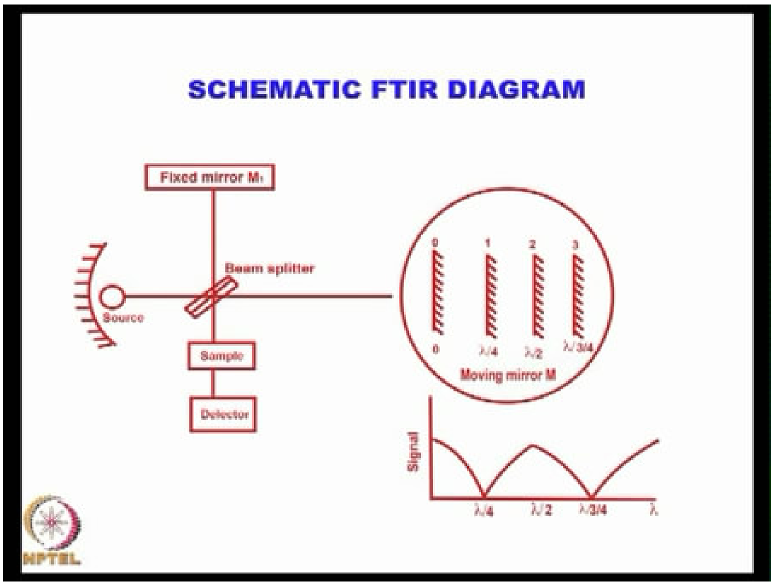

SCHEMATIC FTIR DIAGRAM

Here, the retardation should be infinite. It cannot be just fixed at a particular position and the increments also should be infinite. That is how we define the integrals from minus infinity to plus infinity and that is one requirement; that means, any Fourier Transform equation is always, is always defined for infinite never for particular movement, but that is not possible in infrared range.

So, in practice, the data is acquired at practical distances, as practical distances as possible which results in the truncation of the infinite series. At some stage, you should say stop this much of information for me and that is detected by one over data centimeters inverse. So, you say, this is minimum distance; I am going to major, and that the maximum distance of the moving mirror, I stop the interferogram and that is known as truncation; it does not continue up to infinity.

So, at some stage, and hence, the separation of the infrared, the quality of infrared spectrum would be always lower than the predicted value by to some extent. It is understandable, that is, if you do it infinite distance, you will get maximum signal. If you truncate it, you will get part of the signal is lost, and that part of the signal is lost, because we need to stop the interferogram at some stage. Otherwise, it would doing it infinitely; you will never get a spectrum.

So, we have to cut the wavelength Fourier Transform at some stage and this is known as apodization, where you decide to cut the integral to a particular value, and therefore, you have to do it again, do it mathematically and the apodizing function need to applied to reduce the effect of prematures truncation of the data; that means, part of the data you are losing if you are stopping the Fourier Transform. So, to correct what is lost and to get it back, we call it as the apodizing function; we apply small correction. So, if you cut a particular stage at the signal to so much like that, we can define an apodizing function, to, to get the true spectrum.

Now again, this apodizing function access a waiting function. If you cut it too short, then the correction required is more. If you cut the wavelength, cut the apordigation for long distances, more increments nearer the infinity area, then the apodizing function becomes smaller. So, the apodizing function, that is, the correction function to the infrared spectrum to be added to the i r spectrum is known as apodizing function. To apodizing, such, such apodizing function are very popular - one is known as hanning apodizing function; another is happ general apodizing function which are named after the in of after the inventers of these functions. They, they are basically mathematical functions corrections applied to it Fourier Transform. So, this also reduces; suppose, you applied these things without doing the actual movement where cutting the function.

Therefore, it reduces the noise. Since the noise is always uniformly distributed throughout the interferogram and you are cutting it at some stage. So, it reduces the noises to that extend, which you decide whether you use hanning function or happ general functions. So, it Is not the, it does not permit me to go more into details of this apodizing function also, but in general, I have explain to you the physical significance of these Fourier Transform and apodizing functions.

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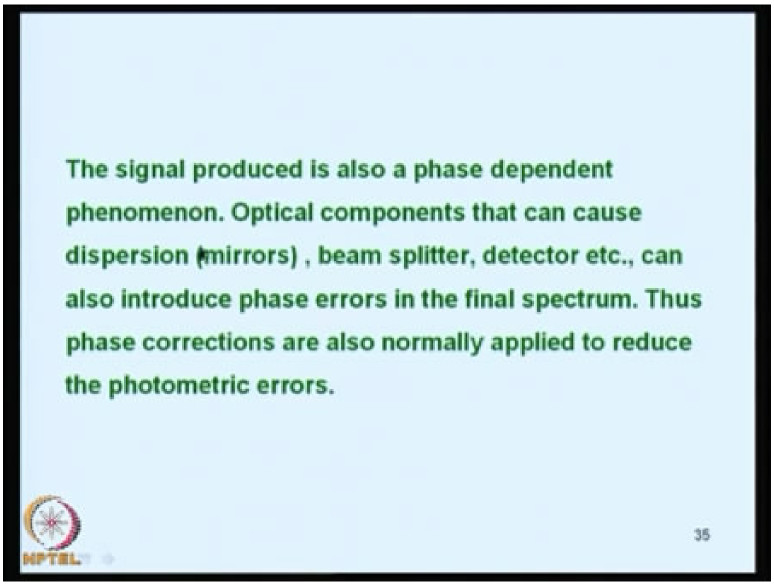

The signal produced is also a phase dependent phenomenon. Optical components that can cause dispersion (mirrors) , beam splitter, detector etc., can also introduce phase errors in the final spectrum. Thus phase corrections are also normally applied to reduce the photometric errors.

So, the signal produced in a f t i r transform is a phase dependent phenomenon. Optical components that can cause dispersion, beam splitter, detector, etcetera, they can also introduce phase errors in the final spectrum. Thus phase interferences are also normally applied phase corrections you have to apply to reduce the photometric errors to get a as true as possible i r.

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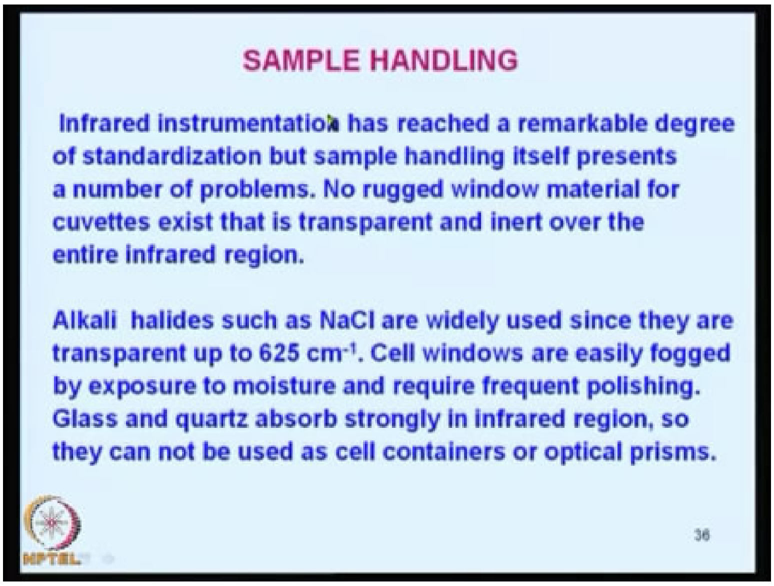

SAMPLE HANDLING

Infrared instrumentation has reached a remarkable degree of standardization but sample handling itself presents a number of problems. No rugged window material for cuvettes exist that is transparent and inert over the entire infrared region.

Alkali halides such as NaCl are widely used since they are transparent up to 625 cm^{-1}. Cell windows are easily fogged by exposure to moisture and require frequent polishing. Glass and quartz absorb strongly in infrared region, so they can not be used as cell containers or optical prisms.

Now, will stop discussion, on the, on the Fourier Transform. So far what we have discussed is the instrumentation of infrared - one is you can use either dispersive equipment monochromators using prism and then gratings, etcetera, that is one type of instrument; another type is Fourier Transform instrument, in which, beams splitter etcetera are there. There are no prisms, no gratings, etcetera in interferograms. So, but when you use prism etcetera, prism gratings etcetera, you will get a spectrum directly on the recorder, but when you use interferogram, you need a computer operation to convert the interferogram into spectral data, which can be done by the computer and the computer output will depend upon the type of function which you use to convert the interferogram data by using apodizing functions, which act as statistical widths. So, either way, whether you use grating spectrometer or an interferogram, you will get the same kind of information in infrared spectrometer. That is the gist of what we have discussed so far.

Now, I would like to move on to the aspect, another aspect of the infrared spectrometry, that is, sample handling. So, apart from regular precautions, what is required is - you need to develop instrumentations to handle the sample. How do you introduce the sample in an i r spectrometer? In generally, infrared instrumentation has reached such a remarkable degree of standardization, but sampling handle, sample handling itself presents problems a number of problems in fact, no raged. For example, no raged window material or quartz exist like in a spectrophotometer. You do not have a standard sample, in which, you can put a sample and take in infrared spectrum – no, that is not possible.

So, there is no material which is transparent, over the, all over the infrared region and that is one of the problem, and then, the sample, the window material, the quart what you will call in spectrophotometry a similar equivalent of that where you insert put your sample, it must be inert over the entire infrared region; that means, it must not absorb any infrared radiation; that is another condition. So, usually, the, in spectrophotometry, we use glass cuvettes and then quartz cuvettes, plastic cuvettes, etcetera, but in infrared, such materials are not possible to use. Then what do you use as the sample container? The question is - is there any material which is transparent all over the infrared region where you want to take this spectrum? Unfortunately, the answer is no, and usually, we use alkyl halide such as sodium chloride, that is, common salt converted into cell which is widely used since they are transparent up to 625 centimeters inverse and you can see here.

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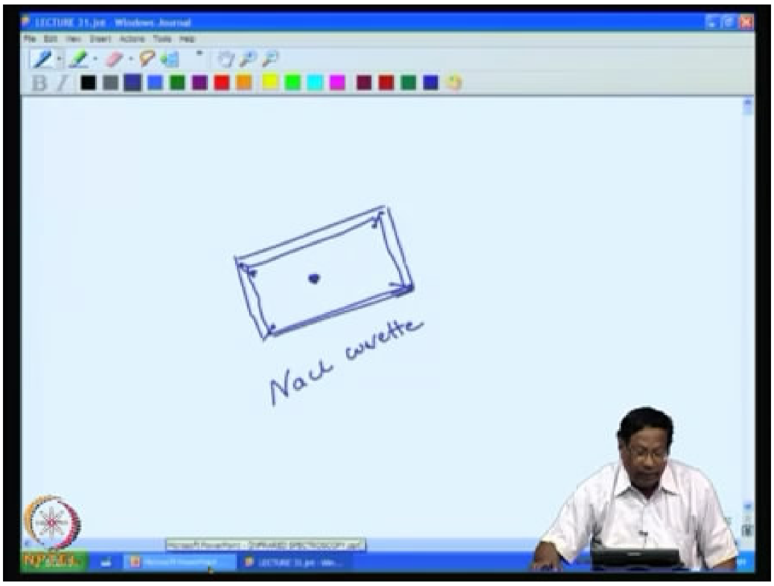

How do you make a transparent window of sodium chloride is - you make like this, a square box or rectangular box or a rectangular sheet you can make of sodium chloride, and then, on this, you put your sample here and, what you should, what you would like to do is over this, put another rectangular cell like this and then you have to fix this and this through a screw. This is a sodium chloride cuvette. So, you basically what you are going to do is take a sodium chloride sheet, put your sample on that, put another sheet over that and screw them at all the four corners. This is how after putting the sample, we are making the measurement. This is, this is sort of, sort of a sample holder as far as infrared is concerned.

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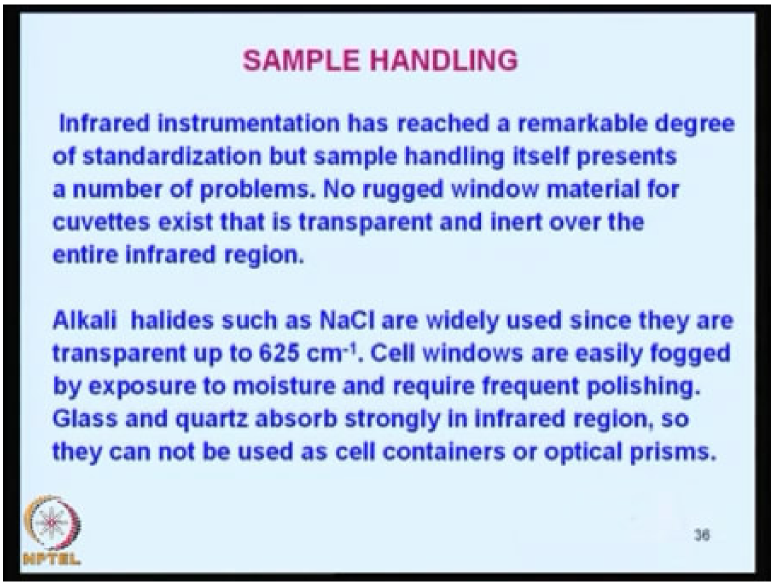

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So, such sample holders can be made of sodium chloride, that is, common salt which you have to dissolve and then make it into a solid. You operate the water and then make it into a cell, and these are widely used since they are transparent up to 625 centimeters inverse; that means, still you have another 4 to 400 centimeters inverse to go where sodium chloride is not useful for you, why? Because cell windows are easily fogged by exposure to moisture; sodium chloride dissolves in water.

So, what I would like to tell you is - if you keep on using sodium chloride, in, in the laboratory, due to moisture present in the laboratory, the sodium chloride window will no more be transparent but it will be pock mark with sodium chloride skills and then it will be no more be transparent. So, that is known as fogging. So, it want be transparent hundred percent transparent material and it requires frequent polishing; that means, you have to keep on wiping the fogged material to make keep it using.

And then, glass and the absorb unfortunately you cannot use in this infrared region, because the absorb strongly almost all the infrared radiation. So, they cannot be used as cell container or optical prisms also; that means, even quartz gratings, you cannot use in the infrared radiation, and almost invariably in all in dispersive instruments the sample compartment is positioned before the monochromator. In, if you recall our discussion on the arrangement of the source and then monochromoter, slit, and then sample and then detector, etcetera, in most of our discussion on the spectrophotometers, atomic absorption, etcetera, but in infrared, first comes the source and then immediately a slit followed by the sample container. You are not going to resolve individual i r wavelengths before; It will be, it it should better be done at the after the sample, after the radiation passes through the sample. That is because the i r energy itself is very weak so that you do not want to lose the intensity of infrared radiation before the sample. This is a major difference in the instrumentation of infrared spectrometers. So, the sample compartment is always position before the monochromator to conserve the weak infrared energy and reduce stray radiation. If you put the total, sample, radiation coming from infrared on to the sample, definitely stray radiation would also be reduced, because monochromator if it comes fast, you, you cannot avoid the stray radiation, and then, the optical libration also would be minimized if you use the source information, that is, source light containing all the wavelengths in the continuous operation, that is, without using any monochromator.

Then again, I take you back to the discussion what we are having regarding the sample cuvettes window materials. I discussed, told you that sodium chloride you cannot use, and because after 625 centimeter inverse, sodium chloride is going to absorb most of the radiation. So, you will not get any i r spectrum for any compound, but then, what are the other possibilities? You can use silver chloride.

Another promising material is silver chloride and this you can use it for moist samples, because even in infrared, when you want to take an infrared spectrum of a compound, the compound itself may contain some water, you know, we cannot always avoid it, because it could have been recrystalize from alcohol solution, and then, using water, etcetera, face separation, etcetera, and then, it can be silver chloride you can be use for moist sample, but it is not entirely satisfactory again either. It easily deforms; that means, when you tighten the screw the cell will became not flat but it will bend.

So, again, the, there is a problem; it is too soft, and another problem with silver chloride is that you keep it open into the air or light, it darkens because it is photo sensitive; on exposure to light, it becomes darker. So, again there will be loss of infrared radiation. So, for frequencies under 600 centimeters inverse, a polyethylene cell could be useful, and then, characteristic of other window material, there are several other window materials, I am showing in the next slide.

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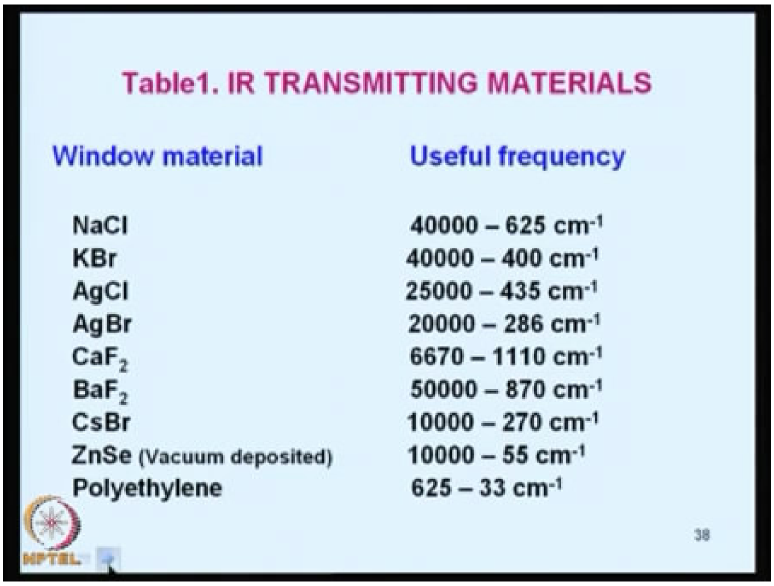

Table1. IR TRANSMITTING MATERIALS

Window material	Useful frequency
NaCl	40000 – 625 cm^{-1}
KBr	40000 – 400 cm^{-1}
AgCl	25000 – 435 cm^{-1}
AgBr	20000 – 286 cm^{-1}
CaF_2	6670 – 1110 cm^{-1}
BaF_2	50000 – 870 cm^{-1}
CsBr	10000 – 270 cm^{-1}
ZnSe (Vacuum deposited)	10000 – 55 cm^{-1}
Polyethylene	625 – 33 cm^{-1}

The, here I have made a small table of different window materials and their useful frequencies. Sodium chloride for example, is useful up to from 40,000 to 625 centimeter inverse; that means, it includes infrared, near infrared range also, and then, potassium bromide, up to 400, and then, silver chloride, up, it starts usefulness starts from 25,000, but ends around 435 centimeters inverse, and then, silver bromide, you can use it up to 286 centimeter inverse; calcium fluoride is useful up to 11 10; barium fluoride is up to 870 c c m bromide is good up to 270. Many times this is very nice to record spectrum up to 270 to 300 centimeters inverse, but vacuum deposited zinc sulfide the last but one. In this table is useful up to 55 centimeter inverse; this is fantastic. Another is polyethylene; it is useful from 625 to 33 centimeter inverse. So, such cells can be used for far i r also.

Now, what about gases? So, I would like you to imagine that in a big industry, petrochemical industry for example, there will be different kinds of gases coming out and you would like to take this spectrum of the gas - production gas - infrared spectrum to find out what are the gases. So, there is a direct requirement for the analysis of gases. Sometimes people are constrained to major atmospheric gases. So, if the atmospheric gases are responsive to i r, several give you characteristic peaks, then they should be useful to be, it is, it would be useful to major gases directly.

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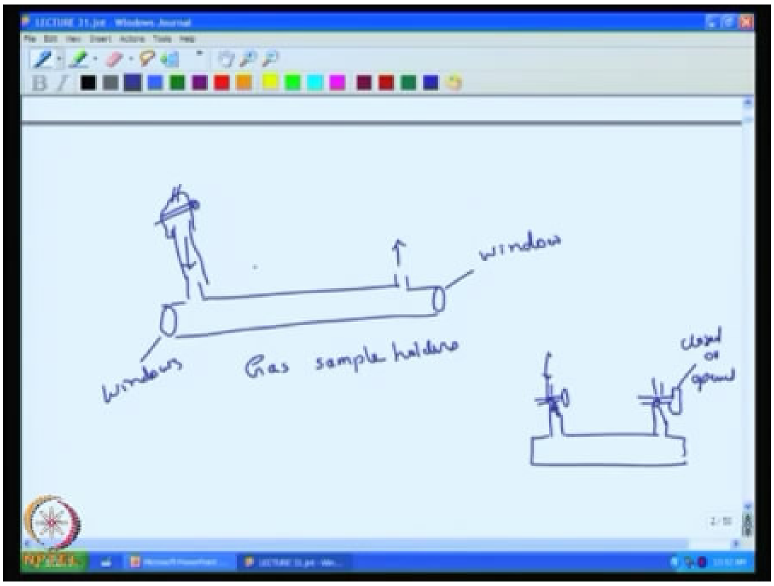

So, what we can do is take the gases in 10 centimeter path length cells, something like, you can design a cell like this. This is the gas. Coming in, this is the gas going out. If it is a continuous sample coming in air measuring i r, gas sample holders. These are known as, this is, these are the windows and this is another window. Now, you can seal this. If you want to do batch operation, what you should do is take this, then put a small rubber tube and then put a pinch cork or you can design a system like this, a three way cork, in which, you let the sample in and seal it off. Then, when you close this, this can be closed and opened; this can be closed or opened, or you can have a continuous system like this. In the typical the top figure, you can have a continuous system where it is connected to the process output.

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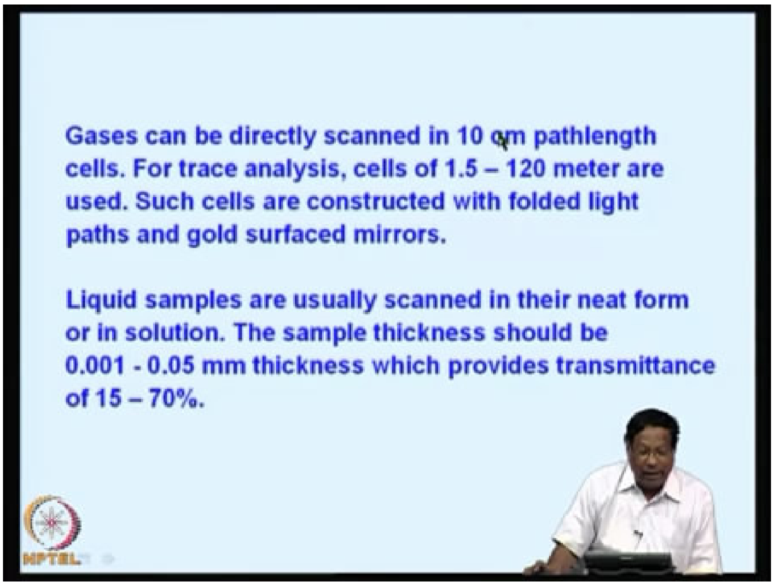

Gases can be directly scanned in 10 cm pathlength cells. For trace analysis, cells of 1.5 – 120 meter are used. Such cells are constructed with folded light paths and gold surfaced mirrors.

Liquid samples are usually scanned in their neat form or in solution. The sample thickness should be 0.001 - 0.05 mm thickness which provides transmittance of 15 – 70%.

So, like that, you can go for gas sample, gas analysis and samples such cells are constructed with folded like paths and gold surface mirrors. You can make it longer instead of 10 centimeter, you can go for 1.5 to 120 small cells with cells with very small diameter, diameter, but very long lengths; that means it can hold larger amount of the sample and infrared spectrum would be more responsive to the concentration, higher concentrations. So, such systems are also readily available for the process industries.

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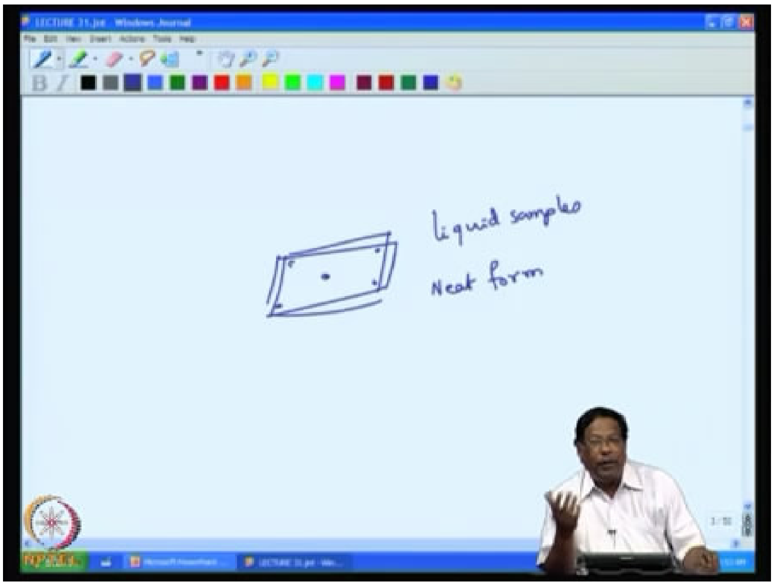

liquid samples

Neat form

Now, liquid samples are usually scanned in their need form; that means you can take the, take the liquid straight away. You can take the liquid on the window material and put it straight away and then fix it with another cell and then fixed them. This is known as neat form; that means, in the neat form, you do not do anything with the sample. You just take a drop and put it on the windows, just put another case and then seal it, and then, straight away insert it into the window, i r window. So, this is possible, and even for solids, you can go for dissolve, you can dissolve the sample and then put it for measurement as a solution, and sample thickness in the window should be of the order of 0.0012 to 0.005 millimeter thickness, which provides transmit of to about 15 to 70 percent range you can get form infrared if you use liquid directly, on to the window, on to the window material, but depending upon the thickness, the minimum can be 15 percent and maximum can be around 70 percent.

Now, what about the solutions? It solids a, you can make a solution in carbon tetra chloride. Carbon tetra chloride is c c l 4; it is an organic solvent; it is ideal for 4000 to 1333 centimeters inverse, because you can use alternately carbon disulfide also as a solvent; that means, if you have a solid powder, you can dissolve it in carbon disulfide, make a solution and put a drop on to the window material, and then, again put another one and seal the ends. So, you can use carbon tetrachloride 10 percent solution or carbon disulfide; you can use methylin chloride, acetonitrile and acetone, say any several useful solvents, but the only problem is you have to make sure that the samples which contain solvents, those solvent peaks, infrared solvent peaks should be discounted; that means subtracted from the solid sample to determined the spectrum of the solid samples; that means solvent should not be misinterpreted is as has part of the another component, because infrared cannot distinguish between the different spectrum interferences of mixers; it cannot be separated; it will, they will all give a peak.

So, you can take it for granted that carbon tetrachloride is always an interferent treated, but subtract the sample. Subtract the i r pick corresponding to these ranges. Now usually, i r cells are constructed with sealed windows which are separated by thin gaskets of copper i told you only two windows - one above the another screw it, but generally what we do is at the edge, we do use gaskets copper and led gaskets which are weighted with mercury; that means, the whole assembly is securely claimed in a stainless steel holder, and as the mercury penetrates, a gasket, penetrates a gasket, it expands and producing a tight, tight, seal; that means, atmospheric gases and other things should not be there. We will continue our discussions on the sampling and sampling of other substances in the next class.

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