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Lecture-17 Sample Handling in IR

Hello everyone, I think I will start a revision of yesterday's class and that we were discussing about the instrumentation in yesterday's class and I had told you that grating dispersive, filter dispersive, fourier transform IR in spectrometers are the currently have been evoked. And most of them contain the components one is optical source another is the optical system, one is optical system and other is the source sample compartment detector and electronics.

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INSTRU	MENTATION
	Modern commercial infrared instruments fall into three categories: Grating dispersive, filter dispersive and Fourier Transform (FT) infrared spectrometers.
	Essentially an infrared instrument consists of the following components:
	i) The main optical system
	ii) The source
	iii) Sample compartment
	iv) The detector and
	v) The electronics and data handling

These are common to all and then I had shown you this slide.

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Whatever the mode of operation, spectrometer or the spectrophotometer forms the heart of the instrument. It takes the broad band infrared radiation and splits it into ultimate discrete frequencies or wavelengths with a given spectral resolution. This may be performed directly with a monochromator in a dispersive instrument dr indirectly by a Fourier Transform instrument. In Fourier Transform, an interferometer assembly known as 'modulator' produces an output in the form of a modulated infrared beam which is decoded to produce the final infrared spectrum.

We had given you I had given you an introduction to fourier transform instrument and I had shown you couple of pictures about the fourier transform.

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And then prism grating, grating systems which are these are dispersive instruments. (Refer Slide Time: 01:22)

The full range of a grating spectrometer may be 4000 – 600 cm⁻¹ or 5000 – 200 cm⁻¹. Gratings are normally operated in second or third order. Usually spectrums in the 4000 – 2000 cm⁻¹ range is operated in second order and 2000 – 400 cm⁻¹ range is obtained in the first order. A series of cut off and bandpass filters are placed between the monochromator and the detector to ensure the correct order of the grating. This is achieved by synchronizing with the scanning of the grating. In more expensive instruments only first order grating is used for all the gratings to provide optimum performance which is maximum over all the output range.

And then had given I given you the range.

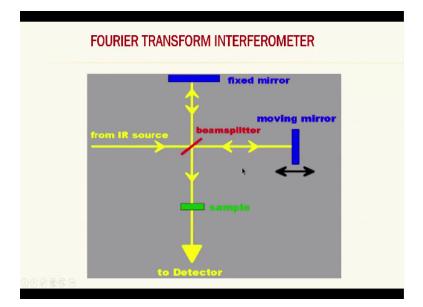
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A grating blazed at two angles performs as two gratings in one. The drive is reproducible by 0.01 cm⁻¹ but it can also be precalibrated against a spectroscopic standard. Modern monochromators are directly driven by a stepper motor and microprocessor controlled to provide high level of accuracy. This also provides a slit programming* mechanism to give near constant energy. Single beam photometers posses the capacity for accurate measurement in quantitative analysis.

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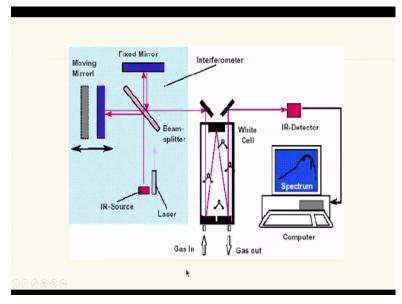
And then grating blazed blazing I had talked a little bit about it.

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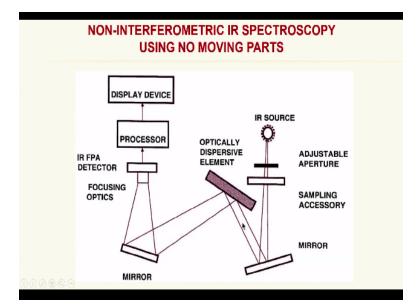
And then I have showed you this picture this is FT-IR instrument optics and contain the source and then beam splitter, moving mirror, and the fixed mirror and sample and detector as shown you this figure of the actual optical system existing in an instrument ok.

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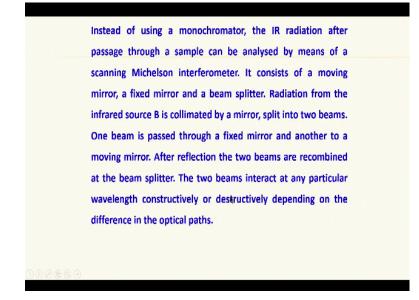
And then the non interferometry IR Spectroscopy.

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I had shown you this picture which contains grating as a dispersive element.

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And then the IR radiation about passing through a Michelson interferometer, we have continued discussion.

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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.

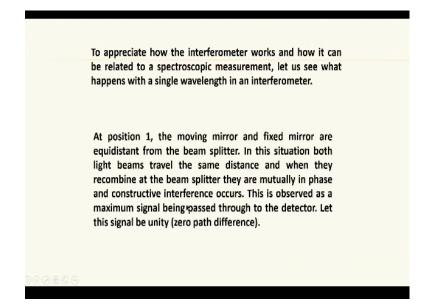
And then I had showed you the advantages of FT-IR.

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		ADVANTAGES OF FTIR
	I.	Only one moving part is involved which is mounted on a frictionless air bearing.
	Π.	Slits and filters are not needed which saves energy especially in the far IR region.
	Ш.	Near absolute frequency accuracy (better than 0.01cm^{-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 rationed against stored background in the memory which gives the double beam accuracy.
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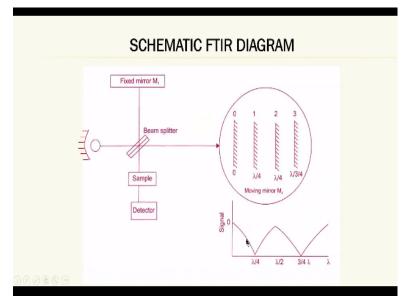
That is only one moving part is involved and things like that, one is near absolute frequency accuracy, this is one more advantage another is S/N signal to noise ratio that is held its advantage and then there are other advantages which I had listed here.

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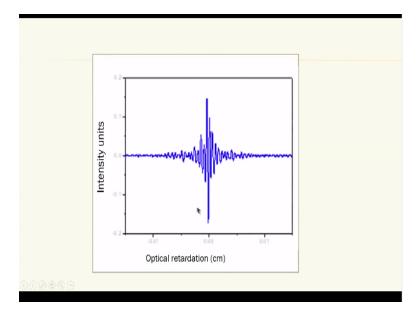
And then I had explained to you how the FT-IR functions the theoretical basis.

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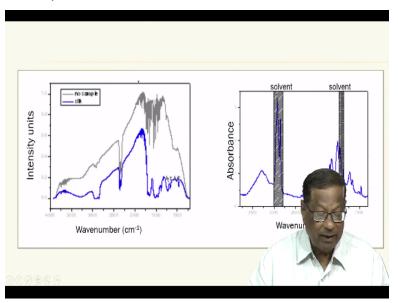
Now I then I had told you that moving mirror keeps on repeating at the moment only here which will represent a 1 degree lambda by 4 for each wavelength which will give you a cosin signal and when all the signals are sampled simultaneously.

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I get a figure like this, this is known as interferogram, this I had not shown you yesterday, so I had shown you this is the interferogram of the total IR radiation imposed on the sample simultaneously. So because all the frequencies are simultaneously measure the signal to noise ratio will be very like. So this interferogram when it is applied to the spectrum that is when we do this before year transformation what we get is something like this.



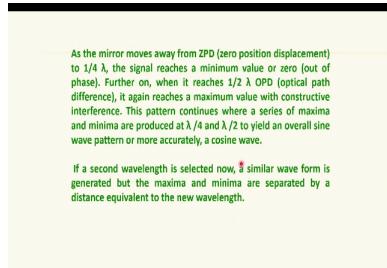


It is the intensity unit versus wavenumber, this is the simple sample reference beam that tis without the sample only the moving mirror etc. and this is with the sample. So when these 2 are ratioed what we get is the infrared absorption spectrometer. This is transmittance left side is

transmittance and right side is the absorption spectrometer, usually this absorption spectrometer also can be taken care of by the FT-IR.

So this is how the FT-IR spectrum looks like, this is wave number versus observance normally we put a plot transmittance versus absorbent because the amount quantity of absorbance will be very less. So 100% transmittance any aberration in the transmittance is normally recorded ok.

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So this picture slide also had shown you that is as the mirror moves away by 1/4 lambda 1/2 lambda etc.

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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 pe mathematically by a Fourier Transformation for fi analysis.

And cosine this thing as shown you.

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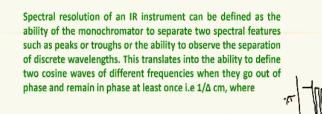
In mathematical terms, the Fourier relationship is defined as a pair of integrals.
$I(\delta) = \int_{-\infty}^{\infty} B(v) \cos 2\pi v \delta dv \text{and} \\ B(v) = \int_{-\infty}^{\infty} I(\delta) \cos 2\pi v \delta d\delta$
$B(v) = \int_{-\infty}^{\infty} I(\delta) \cos 2\pi v \delta d\delta$ where I(δ) is the intensity of the interferogram as a function
retardation and $B(v)$ is the source intensity as a function of the wave number.

And I had explain to you the how the fourier transform function and this is a interferogram which I did not draw it nicely in the yesterday's class, but anyway does not matter., I have shown your actual interferogram of a particular spectra a particular compound ok.

(Refer Slide Time: 05:35) An idealized interferrogram 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.

And then the ideal spectrograph interferogram has a unique centre burst which is corresponding to maximum intensity.

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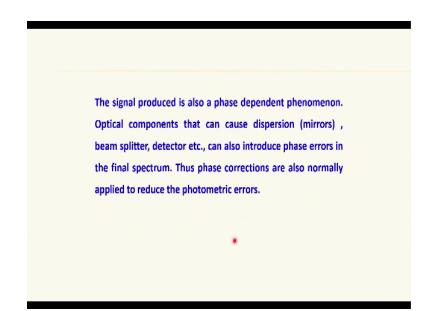
 $\Delta \nu = \nu_2 - \nu_1 (cm^{-1})$ Maximum resolution of a spectra is approximately defined as $1/\Delta_{max}$, where Δ_{max} is the distance of the moving mirror. Once data is obtained at a specific resolution, spectrum of lower resolutions can be artificially generated by using a subset of the data or by extrapolation.

Now I had explained to a little more about the frequency resolution and the purity of the spectrum ok. Now the I had also explain to you that FT fourier transform series is an infinite series. So we cannot apply directly to a system which is a finite system because in our interferogram we invite the mirror move only 1 cm or 2 cm. So it cannot be an infinite. Even though the steps can be infinite, steps of increase can be infinite.

But the IR spectrum we cannot sample infinite, otherwise the spectrum will never be completed. So we have to truncate the series to some extent this that I had shown you hear. This is known as apodization. This is also done mathematically with a computer program incorporated in the instrument itself microprocessor and 2 general apodizing functions are there that is it basically awaiting function or correction factor where to apply.

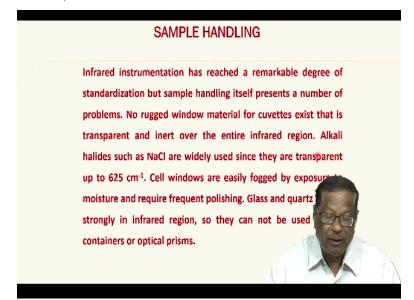
So hanging and Happ-Genzel are names these are the names of the apodizing functions based on the author of the algorithms and when you apply this the noise also reduces to a considerable extent.

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So the signal produced is also a phase dependent phenomena that is optical components of course still can cause a little bit of dispersion and beam splitter also can cause and then detector also can cause a little bit of this disruption etc. certain amount of optical aberration is always expected in all optical instruments ok. So you cannot have error free reflection refraction nothing like that.

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So the face corrections are normally applied to reduce the photometric errors basically I want to teach you about the sample handling the here that stop the yesterday and regarding the sample handling I have to tell you that infrared spectra instrumentation even though it has reached the remarkable degree of standardization. The sample handling itself presents a number of problems.

For example there is no regret window material for cuvettes just like in spectrophotometry we have quotes for ultraviolet and glass or polystyrene cells cuvettes for visible range.

Like that if I want to take an IR spectrum from 4000 to 200 or 10 cm inverse I do not have a single cuvette which can be transparent at all these wavelengths. So that itself is a big problem because depending upon the area where you want to region of infrared spectrum where you want to take the spectrum I have to choose the cell material ok. That is one problem and second problem is there is no universal cuvette.

So we have to choose cuvettes for different areas of infrared among these alkyl halides such a sodium chloride are widely used since they are transparent up to 625 cm inverse that means from 4000 to 625 cm inverse you can make a sample cuvette of sodium chloride. So sodium chloride will not absorb IR radiation and you will get the spectrum. But the problem is whenever you use sodium chloride you cannot have a moisture in the sample or the sample you cannot take the IR spectrum of water is it not.

Because water will dissolve the cuvette, so cuvettes will deformed and then there will be a lot of errors and spectrum will not be pure it out. So cell windows especially get fogged by exposure to moisture because they are all made of sodium chloride crystal. So fogging is a great problem. The most of the IR sample compartments contain chemicals which will absorb moisture normally use silicone or cobalt compounds for absorption of silicon.

Now water moisture, so the not only that when the cells do get fogged they need frequent polishing you have to remove that fogging by brushing abrasion and again after abrasion you need polishing to make the cuvette smooth. So glass and parts you cannot use in infrared because they absorb the IR radiation themselves. So they are not ideal for neither for prisms windows etc. glasses mirrors and you cannot use them nor you can use them as the cuvettes ok.

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Almost invariably in all dispersive instruments, the sample compartment is positioned before the monochromator to conserve weak IR energy and reduce stray radiation and optical aberrations.

AgCl is often used for moist samples but it is not entirely satisfactory. It easily deforms, is too soft and darkens on exposure to light. For frequencies under 600 cm⁻¹, a polyethylene cell is useful. Characteristics of other useful window materials are shown in the next table.

Now almost invariably in all dispersive instruments the sample compartment is positioned before the monochromator in spectrophotometer and other areas first we choose the wavelength and then put the sample compartment. So that the desired wavelength can be passed through the sample, but in infrared first I pass the IR radiation total through the infrared totally all the infrared radiation through the sample.

Then go for wavelength selection, this is a one major difference between IR instrumentation and spectrophotometry you can see. So the sample compartment is positioned before the monochromator to conserve the IR energy which is weak compared to UV and visible range. But also it will reduce these tray radiation and optical aberrations also become lesser because the radiation is falling on the infrared sample.

Quite often we do use silver chloride as a window material. I think you are all familiar with silver chloride because silver chloride is a precipitate generally obtained in the first group analysis of chemicals all college, schools and high school experiments involve the precipitation titration silver nitrate as a first group element using hydrochloric acid. So any sample you take dissolve it water.

And then add a little bit of sodium chloride you get precipitate it means invariably that the mail sample contain 3 silver or something like that. So silver chloride quite a few people are familiar

and silver chloride is often used for moist sample. But it is not entirely satisfactory other, quite often it is impossible to get a sample without moisture. So what to do, so sodium chloride cannot be used but silver chloride can be used to some extent.

But the problem is it easily deforms ok, so it is soo soft that it deforms and it is not nice, sometimes it is too soft silver chloride cells, cuvettes are not easy to handle because they are very soft, they may get pressed and then shape may change and quite often there are several things that can happen. So one has to be extra careful while putting the sample inside the silver chloride cells cuvettes.

And another problem with silver chloride is that it darkens on exposure to light, this is photosensitive I think most of your familiar with that because silver chloride is one of the chemical that is used in photography. So to get dark and white patches you will get you have to use silver chloride. So silver chloride it once it darkens you cannot make it white again. So unless you dissolve it and re-precipitate the things like that.

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			

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So for frequency is under 600 cm we can use those we cannot use both silver chloride and sodium chloride, but we can use a polyethylene cell that is useful. So characteristics of other useful window materials I am going to show you in the next slide that is so here I am plotting the

IR transmitting materials on the left side I have window material, on the right side I have the useful frequency in which range they are effective.

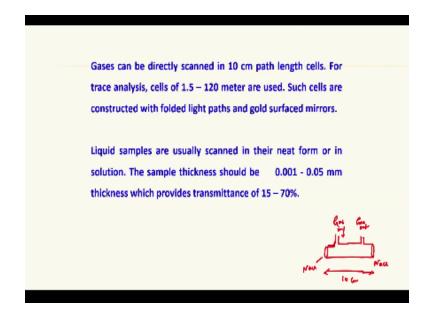
So here sodium chloride it starts from 40000 to 625 cm ok and then potassium Bromide is a good that is up to 400 cm inverse is better than type silver chloride. Silver chloride approximately same range but you cannot use it, it is not as versatile sodium chloride because its range is only 25000 to 435. Silver bromide essentially same thing but it expect the range of the lower range up to 286 cm inverse.

Below that they become not transmitter and they absorb the radiation, other material for calcium chloride at very good you have calcium fluoride works from 6000 to 1110 cm inverse, that means many bending vibrations if you want to see you cannot you is it not. So in bending vibrations 1110 is the last vibration that can be shown but many bending vibration do occur or less than around 800, 700 like that.

Barium chloride is another one quite good but not very popular cesium bromide up to 270, zinc Selenium is good up to 55 cm inverse you that is almost into the for IR range. But the problem is it is a vacuum deposited cell. So in a vacuum deposited cells what happens is the deposit where is of after sometime, you know by handler frequent handling etc. the quality of the deposit goes down. So it is not very idle, but people do use them for a great work.

And polyethylene of course is quite good from 625 to 33 cm inverse. So with this information of what I have to tell you is silver sodium chloride is best and then we can go to polyethylene, you can use both sides, so you can use them in combination or alternately one can go for that others also are useful depending upon the particular area of research in which you may be interested area of IR for example frequencies ok.

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So how do I do the gas analysis in IR, initially I have told you in my first class on in this course that infrared analysis can be done on this glass, gases, solids and liquids. So gases how do we scan it is very simple, I have to just pass the gas in the sample compartment it fills the whole gas and the whole sample compartment is available for passing the IR radiation. So whatever is the part of it is observed and then it is simple or I can use a 10 cm cuvette a glass cell something like this.

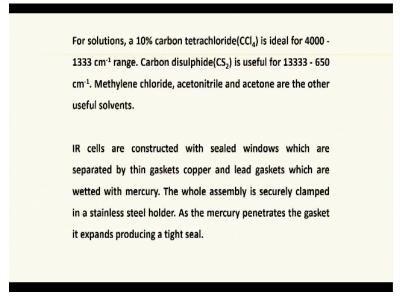
This is the gas in and this is the gas out, you can see them and then these are the windows sodium chloride windows or whatever real is 2 windows and then you can insert this into sample compartment. So gases can be used this can be 10 centimeter. So gases can be very easily measure, I can use even I can use a small capillary tube like this with about 1 mm dia you can use those small cylindrical things like what I should get my last slide.

But you can also use a simple tube at the end of the tubes you seal them with sodium chloride window and then the length of the tube you can even take make it in meter but roll them inside, so the infrared radiation will pass through 1.52 to 120 meters also. But diameter will be very small so the quantity of the gas held within the cell will be much less. So such cells are constructed with folded light parts also.

And gold surfaced mirrors they are all special equipment used in petrochemical industry online, so if it is normal laboratory gas analysis etc. you use a 10 cm cell like what I have shown you here in my previous slide ok. That is very simple ok. So this is a kind of gas vessel. So then how do you do liquid samples. Liquid samples are usually scanned in their need for orange solution. You can take the liquid directly in the sodium chloride cell.

Basically sodium chloride cell means it is a small plate of sodium chloride on which a drop of liquid is put and then I put one more sodium chloride plate and then seal it on both side on the four sides with screws. So that is the normal window cuvette ok. So I can use that kind of thing put a drop of a take one put a drop of the liquid put one more cell so the liquid will spread all over the cell. So that is also possible for that is known as neat form.

If it is any liquid we say take a neat infrared spectrum, that means it is directly as solution, sometimes if it is solid you can dissolve it in a liquid and take it in the neat form in a solvent. So in that case if it has IR spectrum here to subtracted from the actual IR spectrum because in IR spectrum cannot differentiate between the sample and solvent. So the sample thickness in between the 2 plates when I put it here with one drop the sample thickness becomes very small. **(Refer Slide Time: 24:17)**



So that could be from about 0.001 to 0.05 mm thickness but that provides you enough transmittance from about 15 to 78 cm inverse that is quite normal. So that much I wanted to tell

you about this thing. Now we will discuss about the solids. So what do you do with solids, one thing is we can discuss solids as a solution I can make a solution of 10% carbon tetrachloride.

Because this carbon tetrachloride is a symmetrical element, no dipole moment. So it becomes, it has no IR spectrum except 10% carbon tetrachloride if the sample is soluble you take it dissolve it in the liquid carbon tetrachloride and from 4000 to 1333 cm inverse range you can take the IR spectrum suppose you do not have carbon tetrachloride, then what do you do we can go for carbon disulphide that is also that also does not have dipole moment.

And it can be used in this range ok 13333 to 650 cm inverse we do not have any problem. Similarly I can go for methylene chloride is acetonitrile and acetone, these are all other useful solvent. So normally IR cells are constructed with sealed windows which I had already explain to you and we sealed windows like in sodium chloride windows their edges must also be sealed for that we need gaskets.

So the liquid does not out, so these gaskets are made of copper or even light small thin LED strips to be put in one glass of sodium chloride on that you put one more glass of sodium chloride and seal them with a little bit of pressure, you cannot use too much pressure because the sodium chloride cells may break. Once it breaks it is to be thrown out only they cannot be repaired.

So the lead gaskets and copper gaskets are usually welted with Mercury so that it can expand and make a perfect seal between the 2 plates of sodium chloride. So the whole assembly is again security clamped in a stainless steel holder at the edge. So it is a very nice engineering arrangement you should go and see if you get an opportunity how the sample is handled in an IR instrument.

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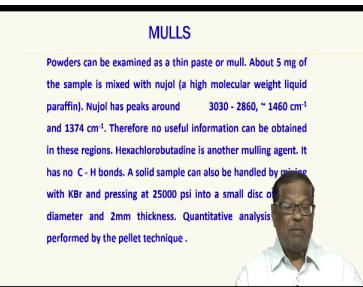


Then as the Mercury penetrates the gasket you know it expands, producing a very tight seal. So this is one way and films you can take the IR spectrum of the films also. Now a days you come across lot of films in your day to day life especially soaps and other things are all packed in thin films of plastics, milk comes in plastic packets and then your food when you order in a hotel it comes in cling film.

So it should be put that alright, so like that there are several kinds of films which we use in our day to day life, cellophane tape many of them are useful and the producers of those materials they do use IR for quality control. So for polymer, resin and amorphous solid, the sample is dissolved in a volatile solvent and you operate the solvent, you get a very thin film, very simple technique, simply dissolve it in solvent you operate, you get everything fill, that fill we can intercourse in between the 2 plates and take the IR spectrum as usual.

So you can even place the solution on the sodium chloride window and you can feel it that also will you operate slowly. So as the solvent operates I will get a very thin homogenous film that is deposited which can be scanned directly. So for liquids and polymers a drop of the solution may be placed and squeezed between the windows you can press them a little bit to get a thin film that is also possible.

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So mulls now I come to the solids, that is one way of taking IR spectrum is by taking these making a solution, but suppose you do not want to make a solution then how to take the IR spectrum, you can take the spectrum in a as a paste, how do you make a paste, you take a little bit of paraffin oil or even castor oil some paraffin oil just like castor oil. So you can take the sample in the bowl, put a drop of oil, put your solid and then make it a thin paste.

And take a scoop it a little bit with a metal spatula and smear it over the sodium chloride window smear it and then seal it as usual and take the spectrum ok. So the paraffin oil you can use or it is also known as nujol, so if you order nujol they would not ask you why you are doing nujol or what is nujol, they I almost everyone every chemical dealer knows nujol and what it is use for.

Nujol is a high molecular weight liquid paraffin that is used for exclusively for infrared Spectroscopy only. So nujol has it is not that it is fully transparent it has what specifically couple of weeks but for most of the part nujol does not have it is transparent it does not have absorption peaks higher. So but nujol has peaks around 3030 to 2860, there is one peak around 1460 cm inverse and 13 cm inverse.

There are 2 peaks, the 2 peaks are source near each other and it looks like a single peak single broad peak I will show you some of the IR peaks in using nujol. So actually no useful information can be obtained in these regions ok 3030 to 2816, 1460 1374 you will not get any

special information because nujol itself has got a peaks which is quite strong. So any IR peak that is available in that way gets mask it gets submerge with the nujol peaks.

So if you are interested in those regions better avoid nujol ok, so another then what else you can use you can use hexachlorobutadine that is another mulling agent and it is also a liquid at room temperature, it has no carbon hydrogen bonds hexachlorobutadine no hydrogen, carbon hydrogen. So you can see all the samples if it has got carbon nitrogen compounds, you can see all those peaks.

So a solid sample at another way of handling a solid sample is by mixing with potassium Bromide what we do if we take a bowl you know some marble bowl or something which is not reacting and I put a little bit of potassium chloride potassium Bromide and then put your solid sample also, mix them nicely as if they do it in Ayurvedic shop mixing and powdering. So when it becomes every thin nice uniform mixture all you got to do is put it in a small cavity press fit.

And then press it you will get a small 1 naya paisa size still smaller point 0.5 mm size disk containing potassium Bromide and your sample. So that you can use it directly into the IR sample compartment, holders are there which can hold them and such things are useful around 25000 PSI up to that is a pressure you have to apply make a small disc of 10 mm diameter that is 1 cm and you can make it up to 2 mm thickness also.

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So the IR radiation can pass through the disk and then quantitative analysis also we can do by the polytechnic ok. So I want to tell you so much about the infrared spectroscopy sample handling. Now I will continue in my next session regarding the radiation sources, so thank you very much.