Q. sample preparation for FTIR & How to sample introduce in the system?

FTIR SAMPLE PREPARATION

FTIR sample cell designed according to nature of a sample.

Sample may be liquid/solid/gaseous.

Sample preparation for Solid sample.

Sample is mixed with KBr powder, Blend is compressed under 10 ton pressure to a small tablet/disc (diameter=1 cm, thickness=1-3 mm). Disc is placed in a disc holder & measured. Best method for solid sample b’coz (over Nujol Mull process)…KBr is 100% transparent to IR radiation & shows no peak. So, peak will be obtained only because of sample. Method is used for qualitative analysis. It can’t be used for quantitative analysis, because solid dispersion are not 100% transparent.

Solution preparation for liquid analysis...

Sample is dissolved & diluted in a non-aqueous solvent to get a clear solution is placed in cell & measured

CCl₄ & CS₂ as solvent because not absorbing radiation range.

Nujol-Mull process

Sample is triturated with liquid paraffin to get paste, which is placed between kbr discs & measured process, (liquid paraffin(Mulling agent) which should be free from traces of H₂O). Bonds of liquid paraffin have their own absorption, by which more complex spectrum achieved.

For liquid Sample.....

Concentration should be in range mg/ml KBr cells.(gap thickness 0.01 to 1 mm)
Solution is prepared in non-aqueous solvent like CS₂ & CCl₄ etc...

Liquids are measured as such or after suitable dilution. But, solvent also shows absorbance peaks which is difficult to separate. Thus solvent should be so selected that it shows in overlapping spectrum for measurement of liquid, Sample cell made of NaCl should be used.
Gaseous Sample...
Measured directly after purification Gaseous Sample is made free from CO₂ & H₂O. That’s why, For CO₂--KOH is used & for H₂O---CaCl₂ used. Gaseous cell which pressured & certain volume (5-50 mm thickness)

FT-IR sample preparation

1. LIQUIDS:
Place a small drop of the compound on one of the KBr plates. Place the second plate on top and make a quarter turn to obtain a nice even film. Place the plates into the sample holder and run a spectrum. If the sample is too concentrated, separate the plates and wipe one side clean before putting them back together.

The KBr plates must be thoroughly cleaned after this procedure to prevent contamination of future samples. Wipe the windows with a tissue, then wash several times with methylene chloride (or another solvent that will take off you sample), then ethanol. Use the polishing kit in the lab to polish the window surface. Wear gloves to prevent fogging. The cleaned surface should be clear and free from scratches.

2. SOLIDS (in solution):
Prepare a concentrated solution of your compound in a suitable solvent (e.g. CH₂Cl₂).
Attention: Remember that all solvents containing water will either dissolve the KBr plates or make them fog up. The broad water band might also mask important bands of your compound.

There are several ways to do this depending how much material you have at hand: either you place a small amount (2-5 mg) of your compound directly on the plates and add one drop of solvent, or you dissolve it in a small test tube first and transfer this solution with a pipet onto the IR plates.

Reminder: Obtain a spectrum of solvent as well, or run the pure solvent as a baseline to automatically subtract it.

The KBr plates must be thoroughly cleaned after this procedure to prevent contamination of future samples. Wipe the windows with a tissue, then wash several times with your solvent, then ethanol. Use the polishing kit in the lab to polish the window surface. Wear gloves to prevent fogging. The cleaned surface should be clear and free from scratches.
3. SOLIDS (as Nujol mulls)

Alternative methods to obtain IR spectra of solids are Nujol (mineral oil) mulls between KBr plates.

Remember that Nujol by itself shows a characteristic spectrum!

Good results are obtained by this method only if the average particle size of the solid is somewhat less than the wavelength of light the particles are to transmit. Samples should therefore be ground in a mortar to reduce the average particle size to 1 to 2 microns. About 5 to 10 mg of finely ground sample are then placed onto the face of a KBr plate, a small drop of mineral oil is added and the second window is placed on top. With a gentle circular and back-and-forth rubbing motion of the two windows, evenly distribute the mixture between the plates. The mixture should appear slightly translucent, with no bubbles, when properly prepared.

Place the sandwiched plates in the spectrometer and obtain a spectrum. Ideally, the strongest band should have a transmission of 0 to 10% and should not be totally absorbing for more than 20 cm⁻¹.

Attention: If the bands are distorted (show fronting or tailing) the particle size is too great and some radiation incident on the mull has been scattered out of the sample beam (Christiansen scattering). If a better spectrum is required reduce the particle size further.

The KBr plates must be thoroughly cleaned after this procedure to prevent contamination of future samples. Wipe the windows with a tissue, then wash several times with methylene chloride, then ethanol. Use the polishing kit in the lab to polish the window surface. Wear gloves to prevent fogging. The cleaned surface should be clear and free from scratches.

4. KBr pellets/disks (for solid samples)

In order to prepare a KBr pellet, follow the procedure given below:

Sample/KBr ratio

The concentration of the sample in KBr should be in the range of 0.2% to 1%. The pellet is much thicker than a liquid film, hence a lower concentration in the sample is required (Beer's Law). Too high a concentration usually causes difficulties obtaining clear pellets.
The IR beam is absorbed completely, or scattered from the sample which results in very noisy spectra.

**Sample preparation**

Although a homogeneous mixture will give the best results, excessive grinding of the potassium bromide is not required. The finely powdered potassium bromide will absorb more humidity (it is hygroscopic) from the air and therefore lead to an increased background in certain ranges. Make sure to work fast. Transfer some KBr out of the oven (ATTENTION: the oven is at 100 °C - you can easily burn yourself!) into a mortar. Add about 1 to 2 % of your sample, mix and grind to a fine powder. For very hard samples, add the sample first, grind, add KBr and then grind again.

The sample must be very finely ground as in the Nujol mulling technique to reduce scattering losses and absorption band distortions.

Take two stainless steel disks out of the desiccator. Place a piece of the precut cardboard (in the tin can next to the oven) on top of one disk and fill the cutout hole with the finely ground mixture. Put the second stainless steel disk on top and transfer the sandwich onto the pistil in the hydraulic press. With a pumping movement, move the hydraulic pump handle downward. The pistil will start to move upward until it reaches the top of the pump chamber. Then, move the pump handle upwards and pump until the pressure reaches 20,000 prf. Leave for a few seconds and with the small lever on the left side, release the pressure (hold until the sample and pistil are all the way down). Remove the disks and pull apart. Remove the film, which should be homogenous and transparent in appearance. Insert into the IR sample holder and attach with scotch tape. Run the spectrum.

After use, the mortar and pistil should be cleaned with acetone and double distilled water, and be put back on top of the oven for drying.

**Reasons for Cloudy Disks**

1. KBr mixture not ground enough
2. Sample was not dry
3. Sample: KBr ratio high
4. Pellet too thick
5. Bolts not tightened sufficiently.
6. Sample has low m.p.
In order to obtain any meaningful information from your IR spectrum, you need to have a
decent spectrum with sharp peaks, i.e., with 'good' intensity and good resolution. Ideally,
the largest peak, which is caused by your compound, should have an intensity of 2-5%T.
Most detectors only respond linearly over a certain range (typically one magnitude). Keep
in mind that a transmission of 5% is equivalent to an absorption A=1.3, which is the upper
limit for most detectors. If you observe a higher intensity, all your impurities will seem to
be more significant than they really are. The peaks with the high intensity will be 'cut off'.
Therefore, it is very important to prepare the sample properly.

Q. KBr process

KBr Pellet procedure for solid samples

➢ Take about 1/8” of the solid sample on a microspatula and about 0.25-0.50
   teaspoons of KBr.

➢ Mix thoroughly in a mortar while grinding with the pestle. If the sample is in large
crystals, grind the Sample separately before adding KBr.

➢ Place just enough spl. to cover bottom in pellet die. Place in press and press at 5000-
10000 psi.

➢ Check pellet press brochure for details. Carefully remove the pressed sample from
die and place in the FTIR sample holder. The pressed disc should be nearly clear if
properly made. If it is translucent, Regrind and repress.

Q. Analysis of Rubber (FTIR Rubber)

Qualitative Analysis of Rubber (FTIR )

One method of qualifying rubber is measuring the attenuated total reflectance (ATR) using a fast and simple
infrared spectrophotometer (FTIR). Using the ATR method allows obtaining an infrared spectrum easily by
pressing the rubber tightly against a prism surface, which allows qualitative analysis of the rubber. In
addition, Energy Dispersive X-ray (EDX) fluorescence spectrometers can be used to easily, quickly, and non-
destructively analyze the constituent elements.

In this example, FTIR and EDX systems are used to qualify a rubber diaphragm sample.

Analysis Using the FTIR – ATR Method

The sample was measured using the Ge prism on the PIKE MIRacle single-reflection ATR accessory. Baseline
correction and a spectrum search were performed for the spectrum obtained from measurements. The
spectra below are for nitrile rubber containing PVC (polyvinyl chloride), where the lower spectrum is from measurement results and the upper spectrum is from the database search. (The presence of nitrile rubber can be confirmed from the peaks for the nitrile group near 2200 cm⁻¹ and the out-of-plane bending vibration from the =C-H bonds near 966 cm⁻¹, whereas PVC can be confirmed from the peak near 600 cm⁻¹, due to C-Cl stretching vibrations. However, since the spectrum from measurement results does not show measurements below 700 cm⁻¹, due to absorption by the Ge prism itself, it does not allow confirming the C-Cl peak.)