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IR SAMPLE PREP: A PRACTICAL GUIDE

1 Plates and IR Optical Materials

Infrared spectroscopy is based on the same principles as ultraviolet-visible spectroscopy except instead of observing electronic absorptions, molecular vibrations are observed since they are of a lower energy. Likewise, different materials have different transparent regions based on their composition and the arrangement of the atoms that the materials are composed of. Most common materials used for infrared spectroscopy are binary salts. The absorption spectra of these materials are based on the reduced mass of the atoms in the salt as per Hooke's Law.

$$\bar{v} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}} \tag{1}$$

$$\mu = \frac{M_1 M_2}{(M_1 + M_2)(6.022 \times 10^{23})} \tag{2}$$

In this equation the frequency ($\bar{v}$ (cm^{-1})) of the oscillator is related to the square root of the force constant over the reduced mass (μ (amu)) of the molecular unit of the binary salt. A convenient rearrangement of Equation 1 gives 3.

$$\bar{v} = 4.12\sqrt{\frac{K}{\mu}} \tag{3}$$

Where μ has been redefined as Equation 4.

$$\mu = \frac{M_1 M_2}{M_1 + M_2} \tag{4}$$

The force constant depends on the bonding characteristics of the compound and is measured indirectly. For organic covalent compounds this value can be approximated as $n \times 5.0 \times 10^{-5} dyne/cm^{-1}$ where n is the number of bonds.

Table 1: Compounds for IR optics and their cutoffs

Material	Cutoff	Solubility	Notes
Sodium Chloride (NaCl)		H_2O	
Potassium Bromide (KBr)		H_2O, MeOH	
Cesium Iodide (CsI)		H_2O	Good for far-IR but may react with sample especially if a coordination complex.
Germanium (Ge)			
Silicon (Si)			
Diamond			

2 Preparation of Mulls

A common method of preparing solid samples for IR analysis is mulling. The principle here is by grinding the particles to below the wavelength of incident radiation that will be passing through there should be limited scattering. To suspend those tiny particles, an oil, often referred to as Nujol is used. IR-transparent salt plates are used to hold the sample in front of the beam in order to acquire data.

To prepare a sample for IR analysis using a salt plate, first decide what segment of the frequency band should be studied, for metal coordination complexes a far-IR transparent salt such as CsI works well, for organic compounds NaCl is sufficient.

Preparing the mull is performed by taking a small portion of sample and adding approximately 10% of the sample volume worth of the oil and grinding this in an agate mortar and pestle. The resulting mull should be transparent with no visible particles.

Another method involves dissolving the solid in a solvent and allowing it to dry in the agate pestle. If using this method ensure that all of the solvent has evaporated since the solvent bands will appear in the spectrum. Some gentle heating may assist this process. This method creates very fine particles that are of a relatively consistent size. After addition of the oil further mixing (or grinding) may be necessary.

Acquire the necessary plates. These plates should be stored in a desiccator to prevent erosion by atmospheric moisture and should appear roughly transparent. Some materials such as silicon will not, however. Gently wipe the plates with dry hexanes with a clean, lint-free paper cloth. In the United States a brand commonly used is Kimwipe from Kimberley-Clark.

This step should follow the preparation of the mull in order to maintain the integrity of the salt plates. Of course, if the plate is not soluble in water then it is still a good idea just to prevent the threat of mechanical trauma.

Once the mull has been prepared, add a drop to one plate, place the second plate on top of the drop and give it a quarter turn in order to evenly coat the plate surface. Place it into the spectrometer and acquire the desired data.

It is important to note that spectra acquired by this method will have strong C-H absorption bands throughout several ranges XXXX and may obscure signal.

Cleaning the plate is performed as previously mentioned with hexanes and a clean lint-free paper cloth. Place the salt plates back into the desiccator as soon as reasonably possible to prevent damage.

3 Preparation of Pellets

Along the same lines of the nujol mull except instead of the suspending medium being mineral oil, the suspending medium is a salt. Preparation of a salt pellet follows along the same lines as the preparation of a mull. The solid is ground into a fine powder with an agate mortar and pestle with an amount of the

suspending salt. Preparing pellets with diamond for the suspending agent is somewhat illadvised considering the great hardness of the substance. Generally speaking, an amount of KBr or CsI is used for this method.

Two approaches can be used to prepare pellets, one is somewhat more expensive but both usually yield decent results.

The first method is the use of a hydraulic press. The salt is placed into a cylindrical holder and pressed together with a hydraulic ram. Afterwards, the pellet, in the holder, is placed into the instrument and spectra acquired.

PHOTO: Hydraulic press, if I can find one.

An alternate, and cheaper method requires the use of a long large hex nut with a 0.5 inch inner diameter, two bolts, and two wrenches. One of the bolts is screwed into the nut and the salt is added through the other end. The second bolt is tightened with a body weight and left to sit. Afterwards, the bolts are removed, and the sample placed into the instrument.

SCHEMATIC: Not sure what kind of graphics to use here for this, maybe some pictures.

4 Preparation of Thin-Film Cells

Thin-film cells are a handy way of acquiring infrared spectra of compounds in solution and is particularly handy for monitoring reactions.

A thin-film cell consists of two salt plates with a very thin space in between them. Two channels allow liquid to be injected and then subsequently removed. The windows on these cells can be made from a variety of IR optical materials. One particularly useful one for water-based solutions is CaF_2 as it is not soluble in water.

SCHEMATIC: This will probably do here, it's a simple enough concept really.

4.1 Deuterated Solvent Effects

A problem emerges when dealing with these cells in that much like a nujol mull the solvent expresses strong absorption bands. These bands can be dealt with somewhat by using deuterated solvents. The difference in the absorption wavelength between a C-H and a C-D bond can be enough to see the absorptions caused by the sample. Additionally, isotopically labeled sample can help designate vibrations.

SPECTRA: Something should go here. I unfortunately don't have any at my disposal, gonna have to look around.

Table 2: Common solvents and their characteristic labeled and unlabeled IR absorptions

Solvent	Normal Bands	Labeled Bands	Notes
DCM			
Chloroform			
H_2O			
Acetone			
Ethyl Ether			
THF			
DMF			
DMSO			
Benzene			

5 Troubleshooting

Water vapor in the sample chamber can introduce significant noise if the chamber is not purged with a dry gas.

SPECTRA: Pt(pz)4 spectra with jaggy bits.

Scratches on salt plates can lead to diffraction of the beam leading to weaker signal and unwanted noise.

Particles that exceed the wavelength of the beam.

SPECTRA: Need to collect something like CuCl2 with large particles and see what happens.

Improper grinding of samples for oil-suspension or pellets can cause artifacts in collected spectra.

Too much or too little suspending agent can cause weak, or overly strong signal.

NOTE: Other bits will go in here too.

6 References and Further Reading