

Infrared Sample Preparation Techniques

Or, It's Not the Same Old Grind

I recently received a bundle in the mail from the editor of this fine journal that contained many comment cards from readers. I was quite pleased to discover that I seemed to have touched a positive nerve with my "primer" articles that have appeared during the past six months or so. My goal has always been to offset other journals' attitude that "if you have to ask how a technique works, you can't possibly understand it." I had grown tired of articles that assumed I knew all about a technique and all prior work done with it. Perhaps you, gentle readers, don't mind such statements as "Building on the work of Smith and Wesson (220-234), we proceeded to..." but I really don't have time to look up endless references while reading an article for general knowledge.

That brings us to the topic of this month's column. When I was teaching in college, I observed an organic chemistry teacher showing her students how to make a mull. She placed a few milligrams of material on a salt plate, covered it with a few drops of mineral oil, then placed a second plate on top. She proceeded to grind the two plates together. This, she claimed, was a proper mull. Fanning and smelling salts brought me around, but I promised that, someday, I would set this "difficulty" to rights.

I am lucky enough to have taken a Coblentz Society course in sample preparation at Pittcon in the early 1970s. I would like to share what I learned there and in the lab during the intervening 20 years.

IR SAMPLE PREPARATION

Infrared (IR) is the most versatile spectrometric method for structure elucidation — if used correctly. If we remember that the energies are low and the extinction coefficients relatively high, much of what I am discussing will make sense. The majority of sample preparation techniques in IR are designed to dilute the sample; for example, a mull, KBr pellet, thin film (plates or ATR), or a dilution in a liquid cell.

Thin films. The fastest sample preparation technique is simply to place a drop of liquid sample between two salt plates (KBr, AgCl, and so on) and squeeze gently. If this is done properly, the film has enough surface tension to hold the plates together. Various attachments from reputable companies (see annual product guides for examples) allow thin films to be introduced into the light beam.

Caution should be used to prevent air from getting back into the sample after it has been compressed. These bubbles cause edge effects and possible fringe effects along the baseline. Care should also be taken to avoid evaporation of volatile samples. The cooling effect of evaporation may cause condensation and create water peaks in the spectrum or cloud the salt plates. Evaporation could also cause a disproportionation of materials in a mixture by concentrating the less volatile ones.

Attenuated total reflectance (ATR). This is a simple and elegant method to create a short pathlength without destroying the sample. The cell usually consists of a trapezoidal prism of IR-transparent material. The sample (liquid or solid) is placed on one or both parallel faces.

The light beam is introduced so that it "grazes" the sample at a critical angle, creating a sawtooth pattern through the cell. The beam impinges on the sample once with a shorter cell or many times with a longer cell (a frustrated multiple internal reflection optical flat). Because the IR beam doesn't penetrate very deeply into the sample, dilutions are not needed.

One consequence of this is that the optical flat may be the side or bottom of a chemical reactor. This allows a reaction to be followed without withdrawing samples. Another use is to analyze coatings on paper, metal, or glass without the interfering spectrum of the matrix on which the sample is coated.

Some precautions are in order. First and foremost, the depth of penetration will vary with wavelength. This could cause problems if you are using a set of standards developed on pure samples through another technique. A computer search usually consists of peak intensity ratios. In ATR, the ratios differ from transmission spectra. This causes even worse problems in qualitative work (for which near-IR is the preferred mode of analysis), where ratios could be truly skewed if wavelengths used for quantification are relatively far apart in the spectrum. However, if precautions are taken, this is a great technique.

Mineral oil mulls. A relatively simple sampling method for softer organic samples is a mull. The proper approach is to use an agate mortar and pestle (small, of course). Place a few milligrams of the sample into the mortar and grind it until it looks like a thin film. At this point, add a drop of mineral oil and

continue to grind. The particle size must be reduced before the sample can be lubricated. It is nearly impossible to grind a sample while it is sliding all over the mortar.

When the paste is placed on the salt plates, use as little force or lateral motion as possible. Even in its finely ground state, the sample is merely a suspension of particles. This mix makes a fine abrasive. Unless you have an unlimited supply of salt plates (in which case, send me some, please), care must be taken at this step. Clearly, this technique causes less chance of evaporation of the solvent, but loss of film contact with both plates should be prevented as well. (Edge effects, and all that, you know.)

Of course, you might guess that the mineral oil has a considerable spectrum of its own, being a hydrocarbon of high molecular weight. The C-H peaks are off the chart. A second spectrum of the unknown must be taken using a solvent with no C-H peaks to speak of, such as CCl₄. The portions of the two spectra that are "solventless" are then combined. This little fact is sometimes lost in the heat of discovery.

Potassium bromide pellets. My favorite sample preparation technique is the KBr pellet. In this method, a 0.3%–0.5% solid solution of the organic sample in dried potassium bromide is prepared. The two materials are ground to a fine powder either in a mortar and pestle (agate, again) or in a small stainless-steel or plastic container using hard balls of the same material and a reciprocal motion (a vibrating mixer seems to be the method of choice).

The mixture is then poured into a pellet press consisting of two "pis-

tons" in a smooth, cylindrical chamber. Pressure of up to 25,000 psi is then applied (under a vacuum, whenever possible, to remove solvents) for varying amounts of time. The pistons are removed and the pellet popped out and placed in a holder (some hand-tightened dies allow analysts to place the pellet in the sample beam while it is still in the holder). In most cases, a clear pellet is produced. However, several major faults may appear. I'll treat them by their appearance.

The first problem appears as a white, translucent pellet. You may have used too much sample. If the pellet is more than, say, 1-2 mm thick, you probably should regrind and remake it with less material. For "quick and dirty" scans, you could probably get away with the first pellet, but you may well lose fine details because of the lack of transmitted light.

The second problem I call the *half-moon*. The pellet displays a half-moon shape (or "Cheshire-cat" smile). This is simply due to the fact that you poured the powder down one side of the die. (You can assure yourself of this by measuring the thickness of both the clear and opaque sides.) Again, regrind and remake.

A third problem is the freckled look. Tiny but distinct spots are apparent throughout the pellet. This arises from insufficient grinding. The sample may be used, but a sloping baseline will be most obvious between 4000-3000 cm^{-1} . (This phenomenon also appears in mulls — a good diagnostic tool showing that more grinding is required.) Once more, regrind and remake.

Another common problem is one I call *chocolate chip cookies*. The spots in this case are larger than the previous case, more like chips in a cookie. They are caused by lack of or insufficient vacuum during pressing or poorly dried KBr; that is, the sample is wet. The extreme form of this is seen when a perfectly thin pellet comes out of the press cloudy. The water has been dispersed throughout the entire sample. You know the routine by now.

General caveats. Beware of cellulose peaks in an ATR of a polymer on paper. The light may penetrate just deep enough to "see" the matrix. Another common problem is cross-contamination from mortars. I didn't specify *agate* mortar and pestles because I own stock in them; I mentioned them because they aren't porous. Cheaper porcelain models can easily cross-contaminate your samples. They may be easier to use, but "cheap is cheap."

Another source of ghost peaks is the use of polypropylene balls and containers to grind the KBr and sample. These obviate the need to clean, but severely limit the grinding time to between "poorly ground" and "where the heck did these peaks come from?" (1). The stainless-steel containers and stainless-steel or agate balls should be used for sensitive work.

Sinusoidal waves may appear and coincide with the spectrum. These are most often caused by internal reflectance between two new or repolished parallel salt windows. I used to eliminate the waves by breathing on the windows to cause micropitting (garlic acts as a catalyst for this reaction, so don't perform this feat after shrimp scampi). These sine waves can even be used to measure the true distance between windows, but that should be covered in any good instrument text.

Basically, analysts must remember that the spectrum will only be as good as the effort put into the sample preparation. "No matter how hurried you are, you will always have time to do it right the second time" (2).

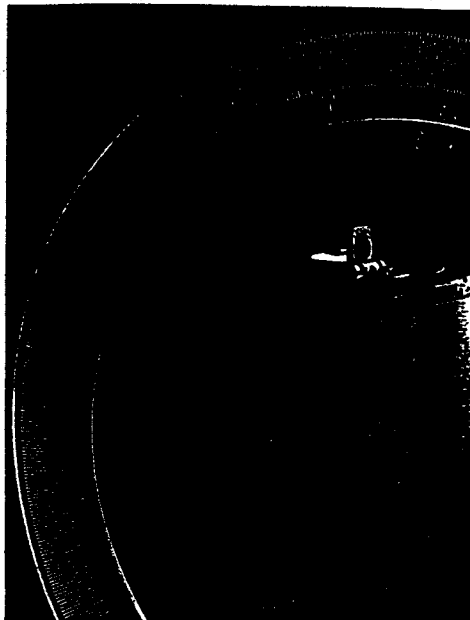
REFERENCES

- (1) Emil Ciurczak (the Elder) in a lecture to his stubborn son, Emil W. (the Lesser), Northern New Jersey, ca. 1961.
- (2) Emil Ciurczak (the Elder), later in the same lecture, regarding painting the house, if I recall correctly.

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