THE FOURIER-TRANSFORM INFRARED ANALYSIS OF COATINGS

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ABSTRACT

This paper is a descriptive statement of a talk presented to the Wood Artifacts Group at the American Institute for Conservation meeting in 1987. It describes how Fourier-Transform Infrared spectrometry (FTIR) operates, how FTIR differs from dispersive IR, and what the advantages and disadvantages of each type of analytical instrument are. Also included are some examples of how FTIR is used to identify various materials of interest to furniture conservators.

We begin by relating the infrared portion of the electromagnetic spectrum (EMS) to the rest of the types of radiation of which the EMS is I composed. The EMS is commonly presented as being divided into somewhat arbitrary regions of increasing radiation wavelength, a summary of which is given in Figure 1. Here it may be seen that radio and TV waves comprise the longest wavelength portion of the spectrum, while gamma radiation represents the shortest. Infrared waves, typically between 2 and 15 nanometers in length, represent that area of the EMS which falls between the microwave and visible light regions of the spectrum are usually described by the terms "wavelength" and "wavenumber". The wavelength is the actual length of one complete cycle in the sinusoidal path of transmitted energy. A radio wave with a 1 meter wavelength will complete one S-shaped wave as it travels along a path of 1 meter. The wavenumber is a frequency term in that it describes the number of waves that will be completed in a distance of 1 centimeter. For instance, an infrared beam with a wavelength of 0.01 cm (0.0001 m) will complete 100 waves in a distance of 1 cm, therefore it has a wavenumber of 100 cm⁻¹. In this paper, all infrared spectra will be described in terms of wavenumbers.

Microwaves provide energy to cause water molecules to spin (thus heating your food). Infrared radiation causes the bonds in molecules to vibrate. As shown in Figure 2, at room temperature different atoms in a molecule normally will move, stretching and twisting the bonds between them. For a specific pair of atoms bonded together (such as hydrogen-carbon pair shown in the figure), this movement is caused by a specific frequency of the EMS. The frequencies which cause these types of movements, or vibrations, fall within the infrared portion of the spectrum. By measuring the amount of infrared radiation absorbed by a sample at each frequency, we can infer the types of atoms which are bonded together and their arrangement with respect to other atoms in the molecules of the sample. That is easily said, but not as easily done.

A diagram of a conventional dispersive infrared spectrometer is shown in Figure 3. Here, infrared radiation is passed through the sample, then sent to the detector where it is compared to a reference beam which by-passed the sample. Differences between the two are due to absorption by the sample. The detector cannot differentiate between different wavelengths of infrared light, so a diffraction grating is used to disperse the light into its different wavelength components before the beam is sent to the sample and the detector. For each position of the grating, only a narrow band (usually 2, 5 or 10 cm⁻¹) is allowed through. As the gratings are moved, different, narrow portions of the EMS are sent to sample, with the detector measuring the amount of light passed at that band. This continues until all the bands in a certain range (such as 300 to 3000 cm⁻¹) have been collected. This is time consuming and wastes a majority of the signal, since all the light except the narrow band which passes through the grating is wasted.

On the other hand, FTIR's use the technology of the Michaelson Interferometer shown in Figure 4. A moving mirror causes the two halves of a split beam of infrared light to come back together slightly out of phase. Identical waves which meet when out of phase with each other will destructively interfere; that is, the intensity of the resultant joined beam will be less than the sums of the intensities of the two separate beams. For each frequency, there will be mirror positions that do not cause interference, so there will be a "bursts" at those frequency-mirror combinations. The detector records these signals as the mirror is moved repeatedly through its path.

A complete FTIR assembly is presented in Figure 5. There are two interesting differences to note between this type of IR spectrometer and a conventional one. The first difference is that the beam is modulated before being sent through the sample, so all the radiation which passes through the sample is seen by the detector. This is an obvious improvement over the wastefulness of the dispersive instrument. The other differences is that there is no reference beam. Since collection of a usable spectrum takes only a few minutes (as opposed to 20 minutes or an hour for conventional IR) the reference data may be collected immediately before or after the sample data without disturbances due to changing humidity, etc.

The output of an FTIR is an interferogram (Figure 6) and consists of a plot of detector signal versus the mirror displacement in the interferometer. The interferogram must be mathematically transform to a more conventional "% transmission versus wavelength" spectrum by means of Fourier-Transform methods. This is done in a computer which is also used to control the spectrometer.

In summary, the basic advantages of an FTIR are that it is faster and more sensitive, so that smaller samples can be analyzed and a maximum signal can be collected in a minimum amount of time. The rest of this paper will deal with sample preparation and the spectra of typical samples analyzed at CAL; some of the reference spectra are from spectral libraries.

The most common sample preparation technique we use is to mix about 3 mg of the crushed sample with about 200 mg of potassium bromide (KBr). The mixture is pressed to form a clear pellet which is then put in the sample holder of the instrument. Clear films can also be put in the sample holder directly without any changes. Opaque films and surfaces can be put flat against a prism and the IR beam bounced along the interface between the two surfaces. The beam "catches" enough of the sample to obtain a spectrum. Finally, a very small sample can be compressed between the faces of two diamonds in a special cell and the IR beam passed through it. The diamond absorption frequencies do not interfere with the sample spectrum. This is especially useful for samples which are not brittle enough to grind well.

Figure 7 contains some examples of spectra with some interpretation of the peaks. While it is necessary to be able to assign the peaks in this manner, the final confirmation of an unknown structure is most effectively done by comparing the unknown spectrum to those of the likely knowns. An example of this is

illustrated in Figure 8. The spectra of the two waxes, beeswax and carnauba wax, are similar, except for the region between 1500

and 1650 cm⁻¹. The two peaks in that region which are present in carnauba wax but not beeswax might be due to olefinic C-C absorption or to an acid salt C-O. While both spectra are clearly those of waxes (a good clue is the double peak at 730 cm⁻¹), the identification as a specific wax is best left to matching spectra with those of known references. Additional data such as melting ranges may be needed.

Spectra of linseed oils are included in Figure 9 as a reference. Linseed oil spectra look very much like the spectra of other oils (tung, etc.) so that oils must be differentiated from each other by another method such as gas-liquid chromatography. However, the initial findings of an FTIR spectrum will indicate whether the sample is an oil or a wax, and therefore permit the researcher to decide which analytical method to use next.

Spectra taken in the laboratory from actual objects are not usually as neat and clean as those in Figures 8 and 9; consequently they are more difficult to interpret. The spectrum given in Figure 10 is that of a sample taken from the bottom of a Bugatti planter. It is a noisy spectrum, but the major peaks can be identified as shown in the Figure. The peaks seem to indicate the sample is a resin, and the spectrum indeed matches reasonably well with reference spectra of dammar. A spectrum of shellac is included in Figure 10 to show the slight differences which led us to chose dammar over shellac as the likely resin.

A waterproofing coating on the inside of a Southeast Asian pottery bowl also was analyzed. The resultant spectrum, presented in Figure 11, is similar to those of dammar, as well as having features which indicate that it might be rosin. At this point, the most straightforward way to get a definitive answer would be to obtain known samples of likely resins and take their spectra. This will allow for a closer match. If this fails or if the bowl coating seems to be a mixture of materials, an alternate technique such as GC/MS might be necessary.

As our last example, we present in Figure 12 the spectrum of an adhesive from a sickle found at the Middle-Eastern archeological site of Mahal Hemaz. The adhesive seems to be a protein glue; the spectrum compares best with that of bone glue, rather than those of gelatin or casein. Once again, matching spectra is best for a specific answer. In this case, further work with HPLC to identify the protein is a likely possibility.

We hope to continue collecting spectra and building a reference library of samples for the identification of samples from museum objects. The power, sensitivity and speed of the FTIR should prove to be an asset in the analysis of coatings and adhesives.



Figure 1. Electromagnetic spectrum.



Figure 2. Fundamental stretching and deformation vibrations for the methylene group.



Figure 3. Optical diagram for a double beam Infrared Spectrometer.



Figure 4. Diagram of a Michaelson interferometer.



Figure 5. Diagram of a typical Fourier Transform Infrared Spectrophotometer.



Fig. 1.13. Comparison of the interferograms of a broad-band initrated source: (a) with no sample in the beam, and (b) with a 0.05 mm sheet of polystyrene placed between the interferometer and the detector. (Small modulations just apparent in the wings of the upper signal are caused by a small amount of atmospheric water vapor in the beam.)

Figure 6. Interferograms of a) the background and b) a polystyrene film.



Figure 7. Interpretations of some example spectra.



Figure 8a. Carnauba wax.







Figure 9. Linseed oils.



Figure 10a. Unknown resin.



Figure 10b. Damars.



Figure l0c. Shellac.



Figure 11a. Coating from Southeast Asian bowl.

Figure 11b. Rosin.

Figure 12a. Adhesive from Mahal Hemaz sickle.

Figure 12b. Bone glue.