

FT-IR Spectroscopy

Author:

Ian Robertson

PerkinElmer, Inc.
Seer Green, UK

Attenuated Total Reflectance (ATR) Measurements into the Far-Infrared Spectral Region on a Multi-range FT-IR Spectrometer

Introduction

A typical FT-IR spectrometer will scan down to the long wavelength limit of approximately 400 cm^{-1} limited by the optical components such as the beamsplitter and detector which contain potassium

bromide (KBr). This optical range could be extended using caesium iodide optics that will extend the range down into the far-infrared region as far as about 220 cm^{-1} . However, there are a growing number of applications where the materials will exhibit spectral absorptions much further into the far-infrared region requiring instruments that can scan down below 100 cm^{-1} .

A multirange instrument, the PerkinElmer Spectrum 3™ (Figure 1), enables measurements to be performed from the near-infrared region all the way down to the far-infrared region using automatic switching of optical components to provide optimized performance for measurements in each spectral region.

The vast majority of FT-IR measurements on samples are now performed using Attenuated Total Reflectance (ATR) sampling accessories. However, the ATR accessories typically use optical components that have long wavelength cut-offs in the mid-IR spectral region. Advances in ATR sampling accessories have allowed for greatly improved spectral performance and made the far-infrared spectral measurements simpler compared to conventional far-infrared sampling techniques.

Far-Infrared Measurements on Spectrum 3

The Spectrum 3 tri-mode version allows for multiple optical components to be installed on a single instrument allowing for coverage of spectral range from 10,000 - 30 cm^{-1} . For the far-infrared region, an IR source, a multilayer FIR beamsplitter and FIR DTGS detector are utilised to provide a spectral range from 700 - 30 cm^{-1} . The interferometer area is sealed and desiccated to minimize spectral contributions from the strong atmospheric water vapor bands observed in the far-infrared spectral region. The sample compartment or sampling accessory can be purged if necessary, to further minimize these bands.

Sampling techniques for the far-infrared region of the spectrum have been somewhat limited and difficult in the past. For sampling of solids, the far-infrared equivalent of a mid-IR KBr disc is a disc made from fine powdered polyethylene. Polyethylene powder is a significantly greater challenge to grind than KBr and is extremely prone to electrical static problems. To achieve best homogeneity of these discs also requires heating the polyethylene/sample mixture to at least 150 $^{\circ}\text{C}$ during the pressing process. Recently, ATR sampling accessories have been improved to give extra spectral range into the far-infrared spectral region. The use of monolithic diamonds in ATR accessories has been a significant step forward. However, since these diamond ATR accessories are primarily used in the mid-IR spectral region, accessory manufacturers have tried to optimize the spectral throughput for this region using anti-reflectance coatings on the diamond at the expense of the far-infrared spectral throughput. Uncoated monolithic diamond top-plates are available on accessories giving improved spectral throughput in the far-infrared region as shown in Figure 2.

The pharmaceutical product sulfathiazole is often used as an example of a material with an interesting far-infrared spectrum, since it contains several spectral bands down into the far-infrared. Figure 3 shows the ATR spectra, after Advanced ATR correction, of sulfathiazole and sulfathiazole sodium salt demonstrating the differences within the spectra of these two very similar materials.

These ATR spectra were collected with no sample preparation and a measurement time of approximately one minute.

Far-infrared is particularly useful for studies of many inorganic materials, such as minerals used as pigments. Art conservationists and historians would like to discover the types of pigments used in art and manuscripts to determine the types of pigments used throughout history, and for authenticity testing. Mid-IR ATR measurements can be used for many pigment studies. However, there are a range of inorganic pigments that don't generate any mid-IR spectral bands. Figure 4 shows the mid-IR spectra of two such pigments.



Figure 1. The PerkinElmer Spectrum 3 FT-IR spectrometer.

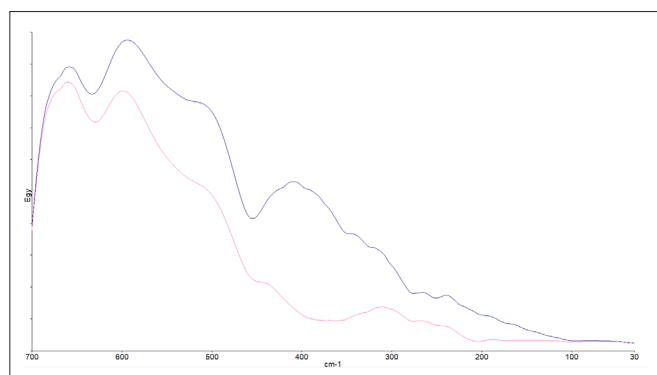


Figure 2. Single beam spectra of coated (red) and uncoated (blue) monolithic diamond ATR crystals.

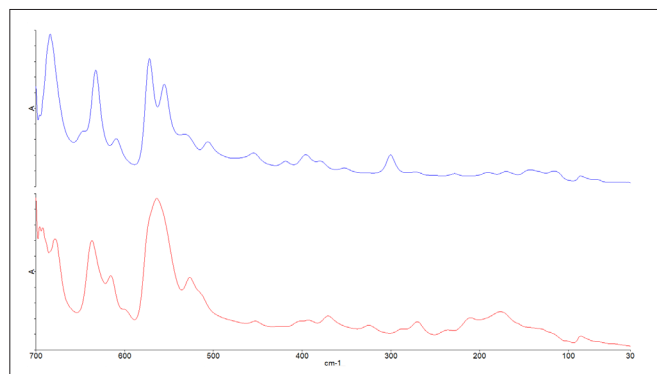


Figure 3. Far-infrared spectra of sulfathiazole (top) and sulfathiazole sodium salt (bottom).

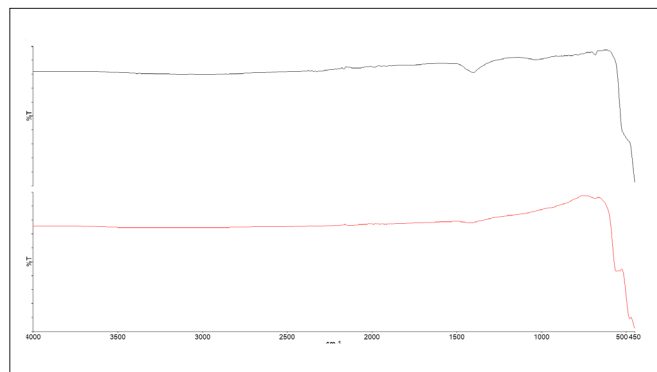


Figure 4. Mid-IR ATR spectra of 2 pigments.

There are potential spectral bands appearing in the region of 450 cm^{-1} , but these could also be spectral cut-offs as we would see in other inorganic materials such as KBr.

The same materials were measured, without removing the sample, in the far-infrared spectral region. The far-infrared spectra are shown in Figure 5.

The far-infrared spectra of the two materials exhibit significant differences below 450 cm^{-1} . The spectra from the different spectral regions can be combined using the Merge command in Spectrum 10 software to generate a single spectrum from $4000 - 30\text{ cm}^{-1}$ as shown in Figure 6.

By using the ATR for spectral measurements in both the mid- and far-infrared spectral regions, it is possible to make measurements for the complete spectral range without removing the sample. Near-infrared spectra could similarly be merged. However, the NIR sampling would have to be performed using a different sampling technique, not ATR.

Summary

High performance far-infrared measurements can be performed using optimized optical components on a multi-range Spectrum 3 FT-IR. Sampling by ATR offers a fast and easy method for measuring far-infrared spectra that has previously been unattainable, and expands upon the information obtained in the mid-IR region for the same sample.

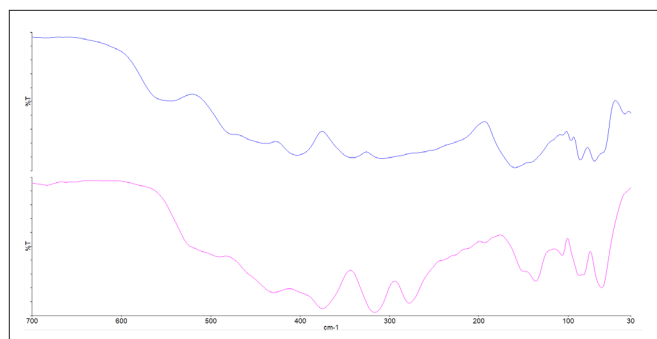


Figure 5. Far-Infrared ATR spectra of pigments.

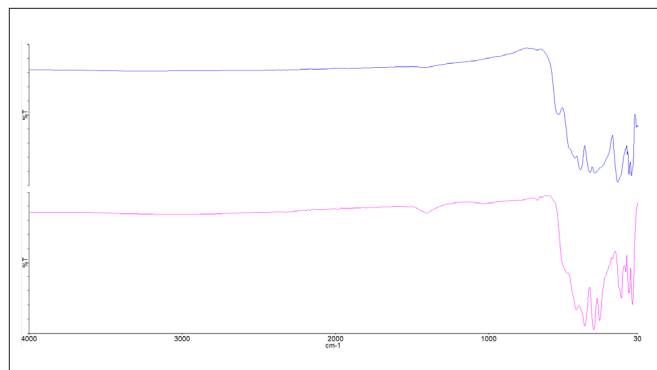


Figure 6. Merged spectra of pigments.