

Applications and Design of a Micro-ATR Objective

FT-IR Spectroscopy

Key Features

- No re-alignment required
- Spring-loaded crystal
- 100 μm contact area
- Applications
 - Thick samples
 - Non-reflecting samples
 - Contamination studies
- Depth profile studies
 - Contamination spots on paper
 - Paintings

Introduction

Attenuated total reflectance (ATR) techniques are well established in FT-IR spectroscopy for the direct measurement of solid and liquid samples without sample preparation. The technique requires good contact between the sample and a crystal made from a material which transmits IR radiation and has a high refractive index. When the IR beam enters the crystal at the critical angle, internal reflection occurs.

At each reflection, IR radiation continues beyond the crystal surface and enters the sample. The depth of penetration depends on the refractive indices of the crystal and the sample, the angle of incidence of the beam, and the wavelength of the IR radiation. For a germanium crystal, the penetration depth (for a sample of refractive index 1.4) between 3000 and 1000 cm^{-1} ranges between approximately 0.2 and 0.6 μm , allowing good spectra to be collected from optically thick, non-reflecting samples.

The multimode objective

For the analysis of microsamples using ATR, a small crystal allowing a single reflection is incorporated into the cassegrain objective of the PerkinElmer[®] microscopes. This forms the unique PerkinElmer multimode objective (Figures 1 and 2), in which the crystal has two on-axis positions, raised and lowered. When the crystal is raised, the sample can be viewed, brought into focus and centered in the field of view. The crystal is then simply lowered to contact the sample, and a spectrum can be collected. Importantly, when raised, the crystal does not obscure the optical path through the cassegrain. This allows the other modes of data collection, transmission and external reflectance, as well as viewing the sample, to be carried out without either removing the micro-ATR assembly or switching to another objective. Permanent alignment of all components in the multimode objective is therefore maintained ensuring reproducible and accurate measurements.

Germanium is usually the crystal of choice, as the short penetration depth provided by this material gives the widest range of possible applications, including carbon filled materials. Silicon is also available. The contact area of the crystal is a circular section with a diameter of 100 μm , although smaller samples can be measured using the apertures of the PerkinElmer microscopes.

Figure 1 shows that the crystal mount is spring-loaded. This ensures a high contact pressure at the sample, while at the same time, safeguarding against damage by ensuring that the crystal will automatically lift when excessive force is applied. Inconvenient contact alert or pressure sensing devices are not necessary for use with this design.

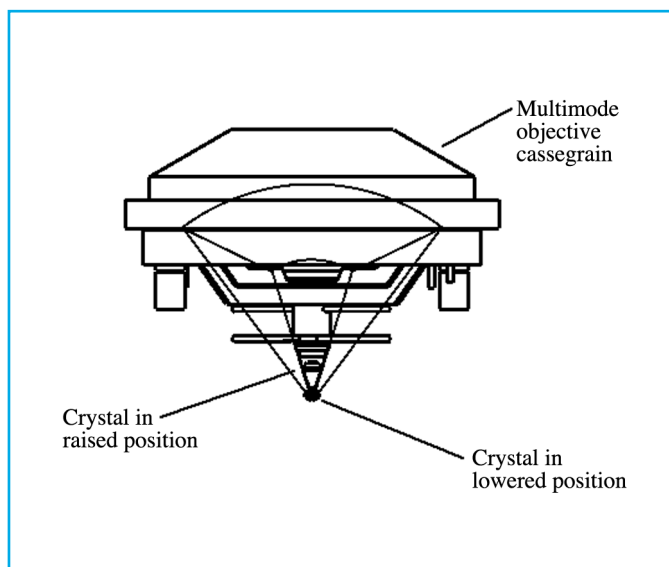


Figure 1: A schematic of the multimode objective

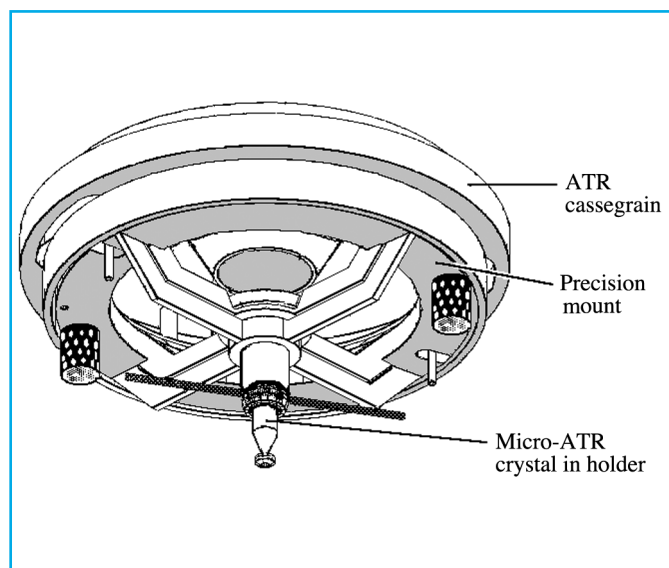


Figure 2: The multimode objective.

Applications

Thick samples

In combinatorial chemistry, organic compounds are synthesized while bound to a base resin formed from polymer beads. Typically, beads have a diameter of 100 μm , which is too thick for meaningful transmission measurements, as many bands in the spectrum will totally absorb. However, using the micro-ATR objective, useful spectra can be obtained from a single bead. In the example shown in Figure 3, a compound containing an ether linkage and a carbonyl group was synthesized on a modified polystyrene resin. Spectra of the beads before and after the reaction are shown, along with a difference spectrum which shows a reduced contribution from the resin.

Non-reflecting samples

Carbon-filled rubbers and polymers present an additional problem if they are to be analyzed without any sample preparation. As well as being optically thick, they reflect little IR radiation which rules out direct external reflectance as a viable sampling method. However, with a germanium crystal, micro-ATR will quickly provide an excellent spectrum. Figure 4 shows the spectrum of a fragment of carbon-filled nylon.

Contamination studies

The micro-ATR objective is an essential tool for the analysis of contamination in final products and packaging materials, as no sample preparation is required. Contamination in paper presents a particular challenge as it can appear in many forms, including surface discoloration and embedded or surface particles. In many cases, it is impossible to cleanly remove the contamination from the paper without adhering fibers.

In Figure 5, spectra from a paper sample are shown. Small areas of the sample had a different surface texture, and had a very slight blue tint. Spectra from bulk and blue areas reveal that the blue area has a concentration of calcium carbonate filler on the surface.

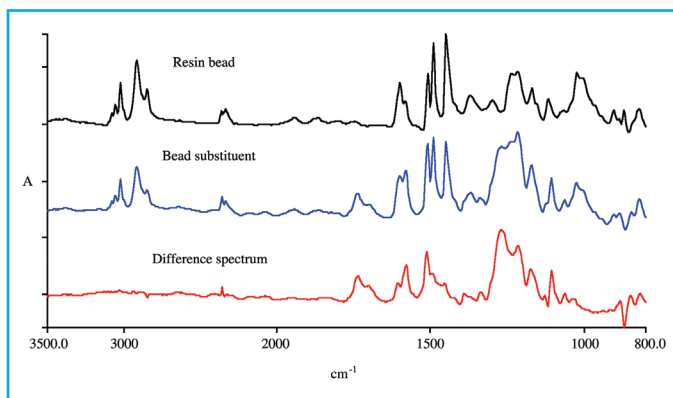


Figure 3: Micro-ATR spectra of organic substituents on resin beads. Collection time: 20 sec. Resolution: 8 cm^{-1} . Germanium crystal.

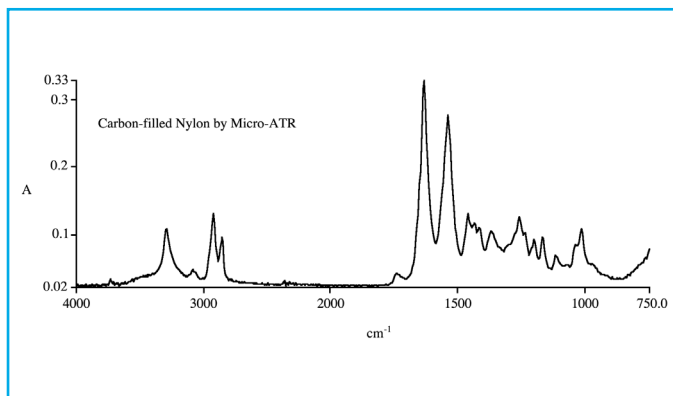


Figure 4: Micro-ATR spectrum of a fragment of carbon-filled nylon. Collection time: 15 sec. Resolution: 8 cm^{-1} .

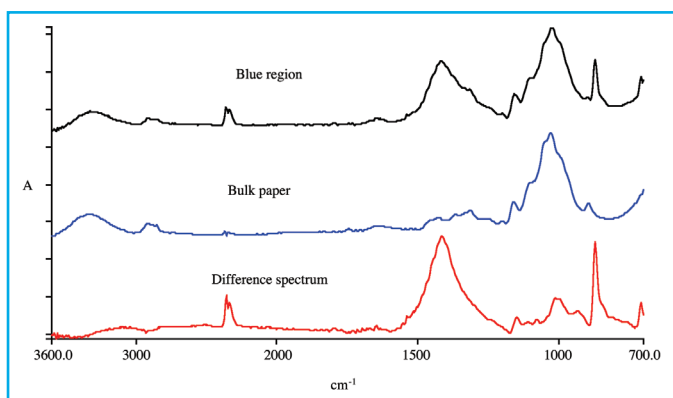


Figure 5: Micro-ATR spectrum of a paper surface. Collection time: 15 sec. Resolution: 8 cm^{-1} .

Depth profile studies

When working with soft materials, it is sometimes necessary to improve the contact between the sample and the crystal. This can be achieved by slightly raising the sample stage to increase the contact pressure. As previously discussed, there is no danger of either damaging the crystal or the cassegrain objective, as the crystal is spring-loaded. For many softer samples, once good contact has been made, it is possible to push the crystal further into the sample, and spectra may be obtained which contain information about sub-surface layers.

Contamination spots on paper

Spectra from a contamination spot on a paper sample are shown in Figure 6, along with a spectrum from the bulk paper. The contaminant has a carbonyl band at 1710 cm^{-1} which becomes relatively more intense than the band at 1650 cm^{-1} (from the bulk paper) as the sampling depth is increased. Similar changes are seen in the region $1300 - 1100\text{ cm}^{-1}$. The fact that the spectrum becomes less like the bulk spectrum indicates that the carbonyl containing contaminant is mainly embedded under the surface of the paper.

Paintings

A fragment from an ancient wall painting was analyzed in a similar way. Figure 7 shows five spectra from different depths, and a reference spectrum, also measured by micro-ATR, of a red ochre pigment used in the painting. The top four spectra show bands from the red ochre and a surface varnish. The intensity of the spectrum in the region $1050 - 1000\text{ cm}^{-1}$, where there are strong bands from the ochre, increases as the sampling depth increases. This is likely to be due to a greater contribution from the ochre deeper into the sample. In the fifth spectrum, an additional broad band is seen at ca. 1400 cm^{-1} , along with a much sharper band at ca. 870 cm^{-1} . These bands indicate that there is a lower layer of calcium carbonate onto which the pigment has been applied.

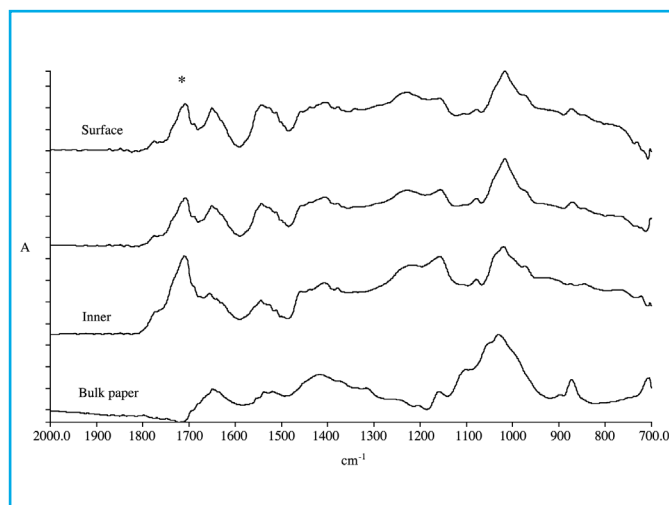


Figure 6: Micro-ATR depth profile spectra of a paper contaminant and bulk paper. Collection time: 20 sec each. Resolution: 8 cm^{-1} .

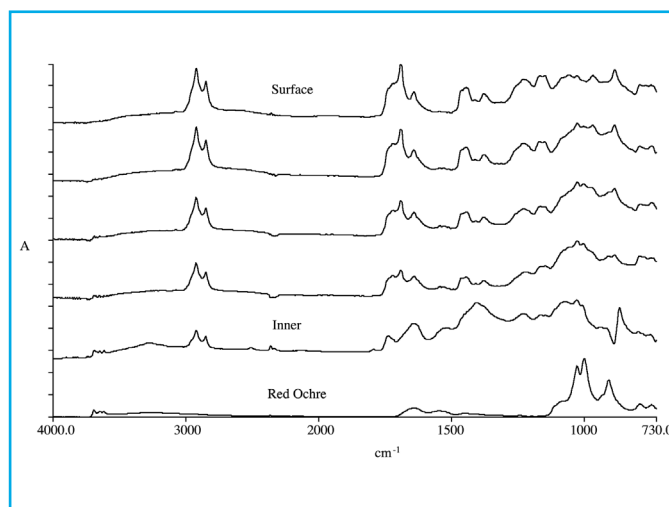


Figure 7: Micro-ATR depth profile spectra from a fragment of an ancient wall painting. Collection time: 15 sec each. Resolution: 8 cm^{-1} .

Conclusion

A multimode objective, which allows viewing and all IR modes of operation, has clear advantages over dedicated ATR objectives or clip-on devices. The spring-loaded micro-ATR crystal provides a simple measurement technique which does not risk damage to either the crystal or the cassegrain objective. The performance of the PerkinElmer microscopes permit the rapid collection of high quality micro-ATR spectra for a wide variety of samples, and measurements can be extended to include depth-profile studies.