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ATR Imaging Applied To the Analysis of Small Polymer Samples

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ATR imaging can improve spatial resolution in the infrared. Comparison of ATR imaging and transmission imaging illustrate this.

Infrared imaging using a focal plane array detector is now a mainstream spectroscopic technique. The method provides both spatial and spectral information. Traditionally, attenuated total reflectance (ATR) methods have extended the power of infrared spectroscopy to samples that are neither reflective nor thin enough to be examined in transmission.

ATR imaging (using an ATR crystal with a spectrochemical imaging system, US #6141100) is a relatively new technique that has the same ease of use and sampling capabilities as ATR does for single point analysis. In addition, ATR imaging provides increased spatial resolution. Coupled with a focal plane array detector, spectral and spatial information of a sample with domains on micron sizes can be obtained.

Experimental Conditions

Data was collected using a Stingray, spectrochemical imaging system from Digilab, LLC, Randolph, MA. The system consists of a rapid scan spectrometer (FTS-4000), a microscope (UMA 600) and a 32 x 32 Lancer™ mercury cadmium telluride (MCT) focal plane array detector. For the ATR measurements a germanium slide-on ATR was used with the UMA 600.

Spectra we acquired at 8 cm⁻¹ spectral resolution in a rapid scan mode and 32 scans were co-added for both transmission and ATR.

Results

In a single point analysis using an infrared microscope the aperture is closed down around the sample to isolate the area analyzed. The equation that governs the spatial resolution is:

$$R = 1.22 \lambda / 2 n \sin \theta$$

where λ = wavelength of light, n = refractive index of medium, and θ = half-cone angle of light captured by the objective. In transmission, at 1000 cm⁻¹, the calculated spatial resolution is 12 μm , the diffraction limit. In effect you will not get a good spectrum smaller than about this size. The ATR crystal, germanium, has a much higher refractive index (4) and the ATR technique

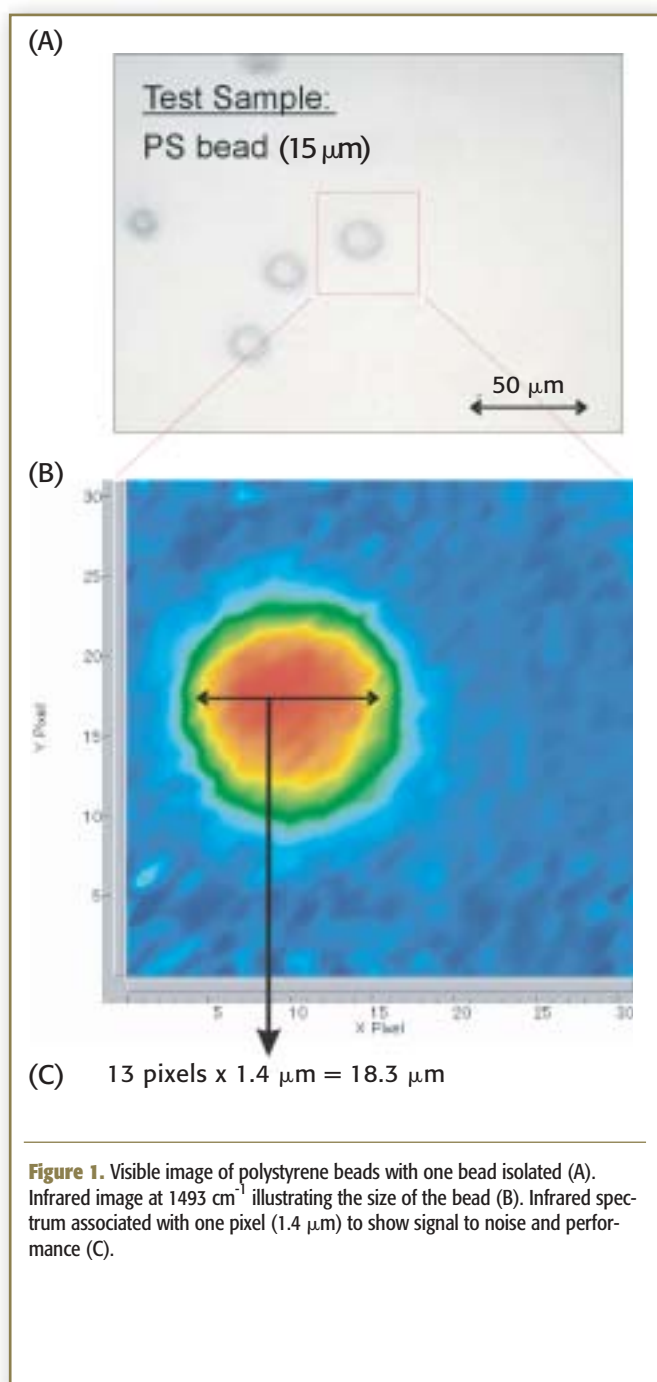


Figure 1. Visible image of polystyrene beads with one bead isolated (A). Infrared image at 1493 cm⁻¹ illustrating the size of the bead (B). Infrared spectrum associated with one pixel (1.4 μm) to show signal to noise and performance (C).



Figure 2. Bright field image of the multi layer sample. Cross section of 4 layer laminate film Thickness: 3 μm (Picture taken with internal CCD of UMA600)

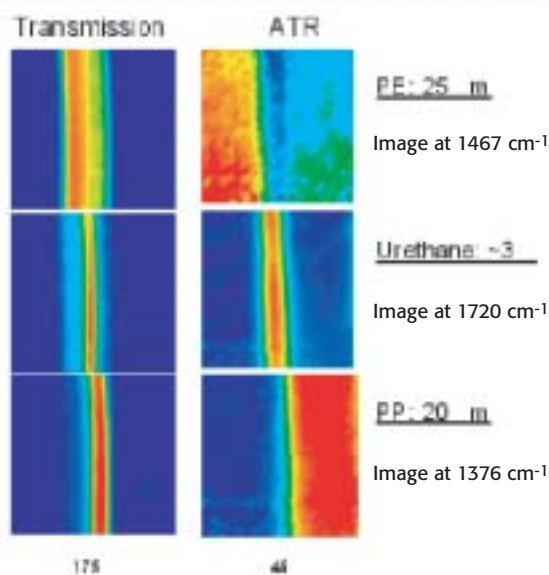


Figure 3. Comparison of images and field of view from the three layers of interest. In the image of the urethane layer, the transmission image is less than 2 pixels wide while the ATR image is 4 pixels wide. This gives both an improved spatial resolution as well as better images.

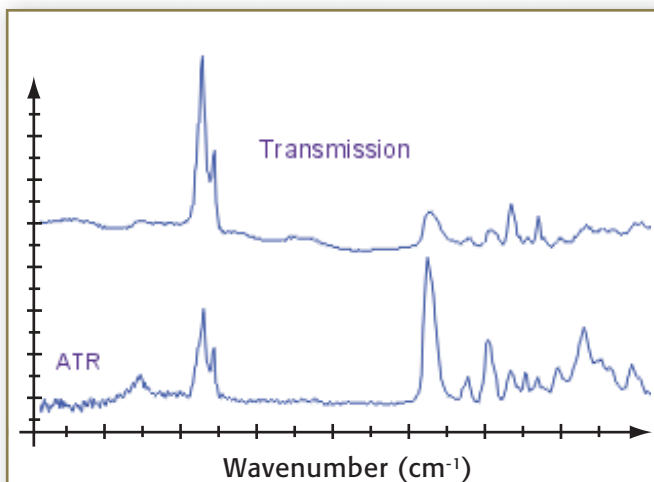


Figure 4. Showing a comparison of transmission and ATR imaging for the urethane layer (approximately 3 μm). Information from the neighboring polyethylene layer overlaps into the spectrum of the urethane layer in transmission imaging but not in ATR imaging.

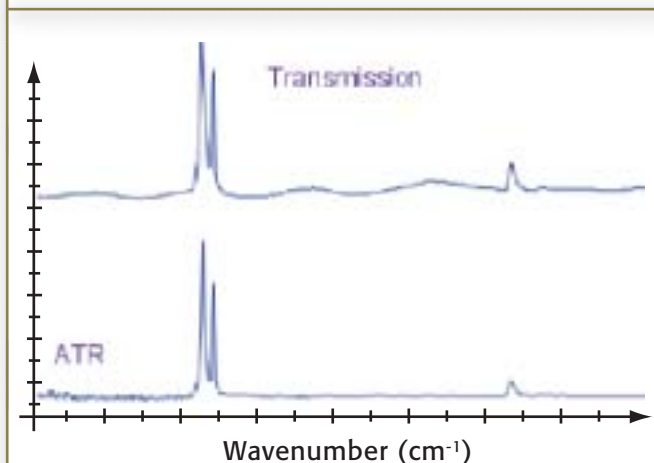


Figure 5. Comparison of baseline effects for transmission and STR imaging on the 25 μm layer of polyethylene.

provides a magnification effect and improved spatial resolution. Figure 1 illustrates this.

A multi layer laminate shows the practical applications by comparing the transmission and ATR analysis using a focal plane array, of a four component laminate. (Figure 2) The two polyolefin layers are large enough ($>15 \mu\text{m}$) that a pure spectrum of each layer can be obtained from a traditional ATR analysis. But the urethane layer is only 3 μm thick. ATR provides much higher spatial resolution. (Figure 3)

Finally there is an improvement in the actual spectra. Figure 4 shows a comparison of transmission imaging and ATR imaging on the urethane layer. Olefin is visible in the transmission spectrum but not in the ATR. Also, in the polyethylene layer, baseline effects such as fringes are eliminated. (Figure 5)

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