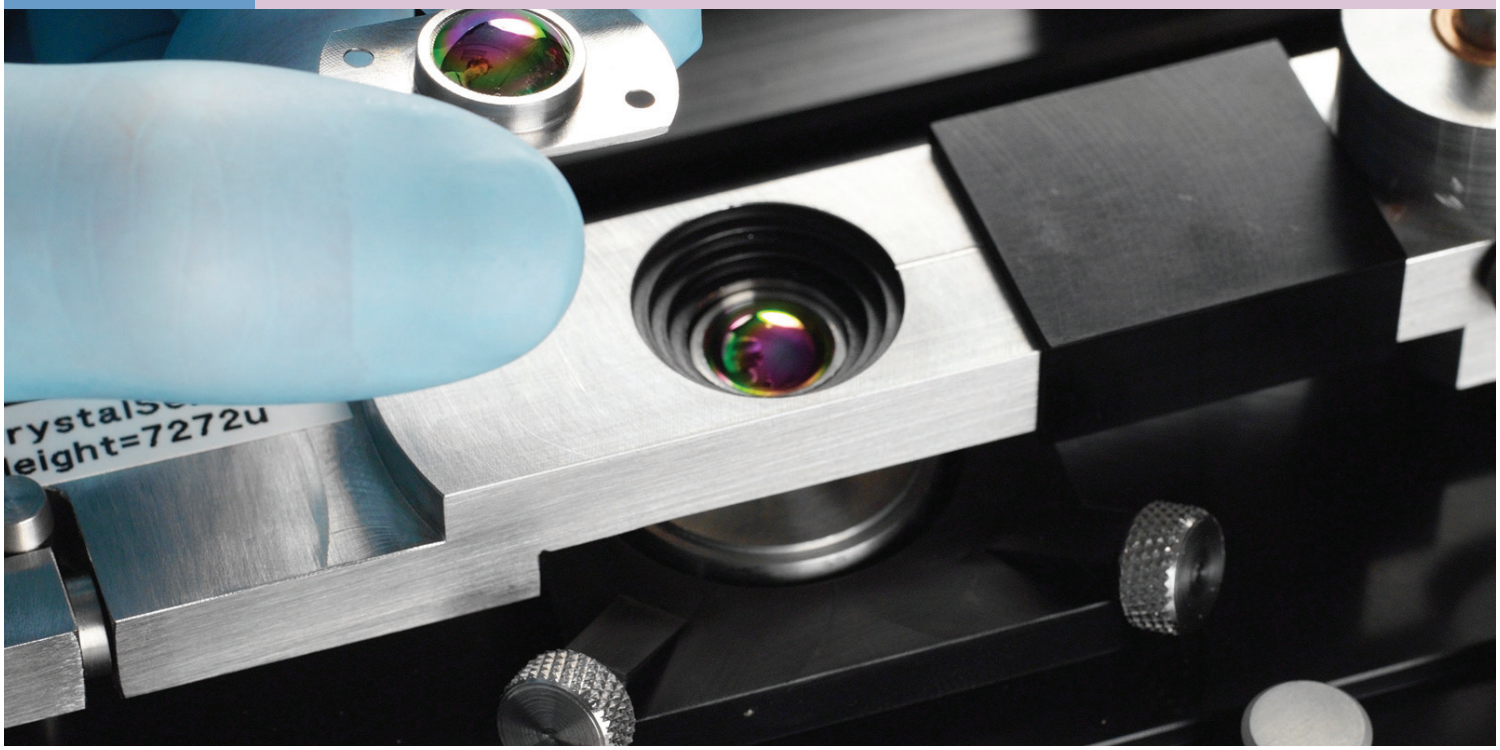
CASE STUDY

FT-IR Imaging



Reduced Sample Preparation and Increased Spatial Resolution with ATR FT-IR Imaging

Introduction

As a major producer of a wide range of consumer products, Unilever requires the ability to quickly test many different materials, including detergents, food, hair, packaging materials, and many others. The company has a long, successful history of using Fourier Transform Infrared (FT-IR) spectroscopy microscopy and imaging. Unfortunately, with FT-IR imaging, Unilever was only able to measure in transmission mode which severely limited the application range of this technology. Only recently, new instruments became available which could also measure in Attenuated Total Reflectance (ATR) mode. Unilever recently evaluated several suppliers offering high spatial resolution and reduced sample preparation ATR FT-IR imaging.

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For the Better

Research, development and problem solving

Developing new products and improving existing products generates great challenges. As new products structures and compositions are developed, it becomes critical to accurately characterize them to better understand their performance and to control the production to ensure quality products for customers. Sample preparation is often critical. Products can be fragile or heat/cold sensitive.

Unilever uses many different analytical methods to identify chemical structures and the distribution of chemical constituents. FT-IR spectroscopic imaging allows the visualization of the spatial distribution of chemical constituents within a sample. A further advantage of this technique is elucidation of product defects. In its current application, however, solid samples have to be embedded and thin slices have to be cut to prepare the sample for analysis. Obtaining evenly sliced layers is often very difficult.

Semi-liquid samples like spreads are usually squeezed between two IR transparent windows administering a certain amount of shear. One of the windows can be removed; however, this may influence the layer thickness of the spread. An option would be to measure with ATR-contact which is less labor intensive.

Transmission mode sampling vs. ATR for microanalysis

Traditional FT-IR spectrometers analyze solids, liquids and gases by transmitting the Infrared radiation directly through the sample. The thickness of the sample has a bearing on the intensity of the spectral features and therefore samples cannot usually be more than a few microns thick. This creates challenges in analyzing many materials whose properties might be altered when slicing them this thinly. Another limitation of standard sampling on all FT-IR microscopy or FT-IR imaging systems is that their spatial resolution is constrained by diffraction effects and has a lower limit of 8 or 9 microns. Spatial resolution is important because FT-IR can only reliably identify an object that is larger than the spatial resolution of the instrument. Consumer products manufacturers often desire to identify objects that are smaller than 10 microns, such as laminated samples with very thin layers.

ATR sampling has been used for many years in traditional FT-IR spectroscopy and FT-IR microscopy applications and operates by measuring the changes that occur in a totally internally reflected Infrared beam when a high refractive index crystal comes into contact with the sample. The Infrared beam is directed into an optically dense crystal with a high refractive index that is held in contact with the sample. This internal reflectance creates an evanescent wave that extends beyond the surface of the crystal into the sample. The evanescent wave extends only a few microns beyond the crystal surface and into the sample. In the regions of the Infrared spectrum where the sample absorbs energy, the evanescent wave is attenuated or altered. The attenuated energy from each evanescent wave is passed back to the IR beam, which then exits the crystal and is passed to the detector of the FT-IR imaging system. The system then generates an IR spectrum.

Testing the PerkinElmer Spotlight

Unilever tested several samples including detergents, spreads and a packaging foil in order to evaluate the ability of the PerkinElmer® Spotlight™ FT-IR Imaging System to handle the full range of Unilever's analyses tasks.

Transmission

A spread sample was squeezed between two BaF2 windows. A large area was analyzed in transmission mode as shown in Figure 1. The different fat and protein areas could be localized based on the wavenumber range between 1800-1710 cm^{-1} for fat and a single peak at 1652 cm^{-1} for protein. This sample was measured at room temperature but for future applications it would be preferable to use a temperature controlled stage where the sample can be measured at lower and higher temperatures.

Figure 1A

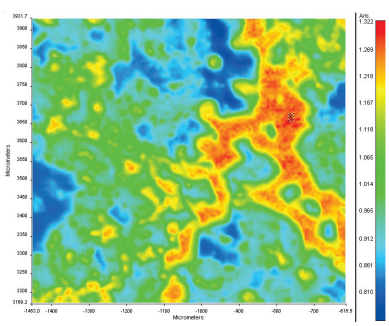

Figure 1B

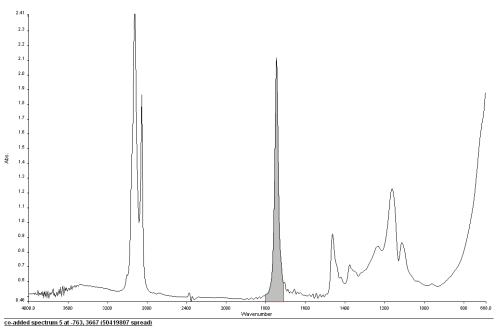

Figure 1C

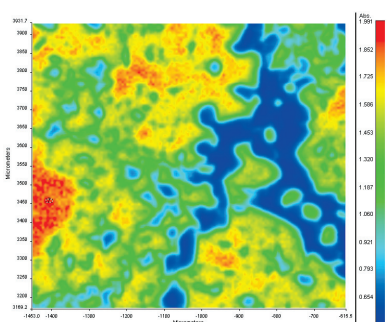

Figure 1: FT-IR transmission (A) image and (B) spectrum of a spread, based on fat, wavenumber range between 1800-1710 cm^{-1}, (C) image based on protein, for a single peak at 1652 cm^{-1}.

ATR accessories

A multi-layer packaging foil was used to test the ability of the ATR accessories. The layers consist of polyester with aluminium oxide ~12 µm, adhesive ~4 µm, oriented polyamide (OPA) ~15 µm, adhesive ~3 µm, and polypropylene (PP) ~70 µm.

The multi-layer packaging foil was tested in transmission as well as in ATR contact mode. Some of the results can be seen in the Figures 2 and 3. A part of the foil was embedded in a chemical compound (epoxyhars) and slices were obtained with a microtome. Of the remaining sample, a smooth surface was created which was used for the ATR imaging. Since the product composition was known, it was easy to determine where each layer would be found by using specific peaks. In the results, the use of a chemometric tool is shown, which can be used to identify different compounds within a sample. It was surprising that a clean Infrared spectrum could be obtained from every layer, even the two small adhesive layers by using this chemometric tool.

Advantages of ATR FT-IR imaging are that no thin sections are needed and images are obtained with a high spatial resolution.

In Figure 2A, the actual image obtained by the Spotlight is given, showing the dimensions of the image in micrometers.

In Figure 3, the first principal components of the image are given after some processing steps including 1st derivative, subtraction of average, CO_2 suppression and PCA with the given information that there are six principal components present.

The extracted spectra of the individual compounds are given in Figure 4 and can be matched with the library.

Additional tests were performed at a higher resolution giving more peaks details.

Conclusion

The Spotlight, in combination with the ATR accessory, provides a solution to a wide range of challenges. It enhances rapid understanding of product structures, which is a prerequisite for effective product development. Furthermore, it is a powerful tool in product manufacturing troubleshooting.

The substantially higher spatial resolution of the ATR accessory and its ability to scan a larger sample area is an advantage over conventional transmission measurements. The larger area offers a higher level of certainty that minor components as small as 5 to 10 micrometers are captured. On a 400 by 400 micron sample, one may see spots that would be missed on a 100 by 100 micron sample. The larger image area has proven very valuable in its ability to detect minor components that might not appear in a smaller sample. Analysis times increases proportionally; however, this is outweighed by the aforementioned advantages.

For further information regarding PerkinElmer's FT-IR ATR Image Accessory, please visit www.perkinelmer.com/atr

Figure 2A

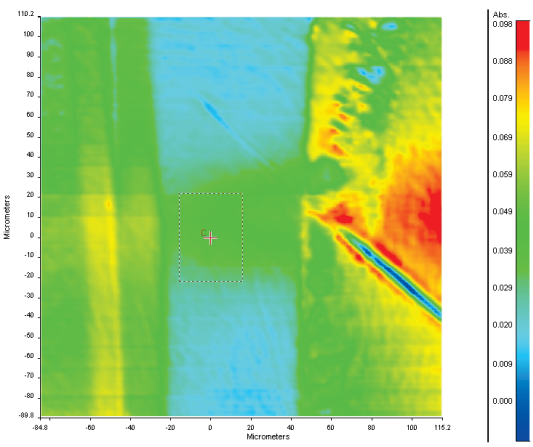

Figure 2B

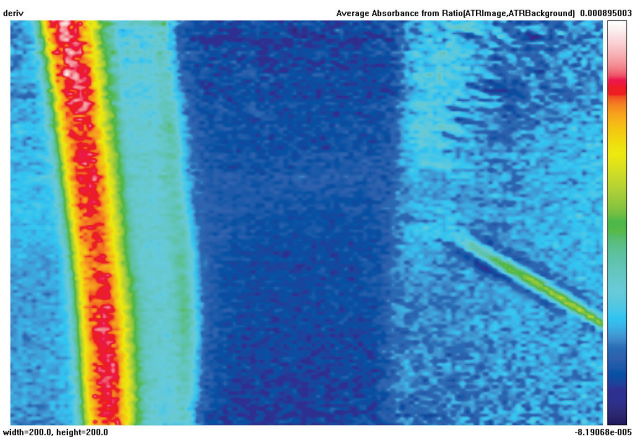

Figure 2: Summary FT-IR image of packaging material measured with prototype ATR equipment from PerkinElmer, image size (200 µm*200 µm, 128*128 pixels), overall image in Spotlight software (A). The standard deviation from the mean of baseline is subtracted from the spectra. The diagonal line is a scratch on the germanium crystal which generates mostly a sloping baseline which is not subtracted out here (B).

Figure 3A

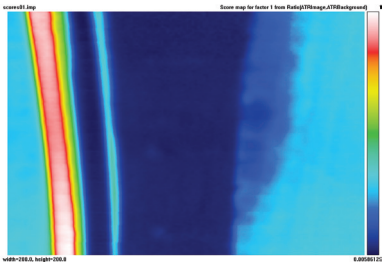

Figure 3B

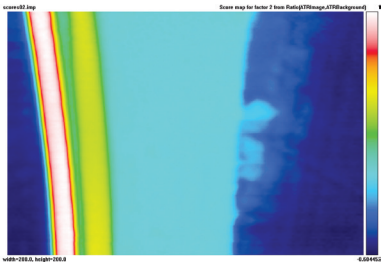

Figure 3C

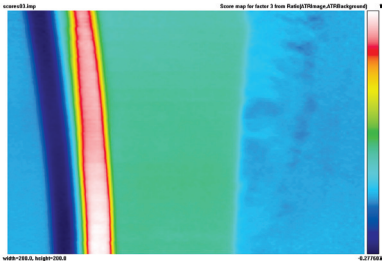

Figure 3D

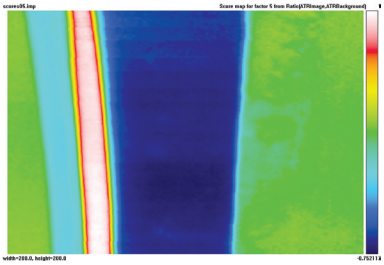

Figure 3E

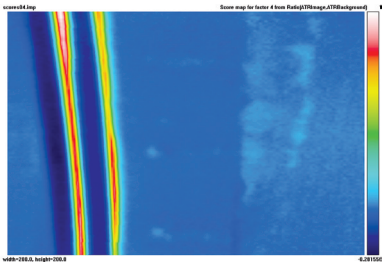

Figure 3F

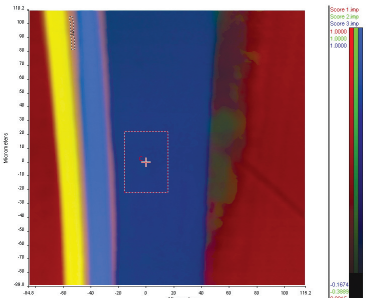

Figure 3: The first five principal component (factor images), showing clear evidence for all the layers resp. polyester with aluminium oxide ~12 µm (A), embedding material epoxy negatively correlated visualized by dark blue (B), oriented polyamide (OPA) ~15 µm (C), polypropylene (PP) ~70 µm negatively correlated visualized by dark blue (D), adhesive ~4 µm (E). An overlay spectrum of the five principal components is given in (F).

Figure 4A

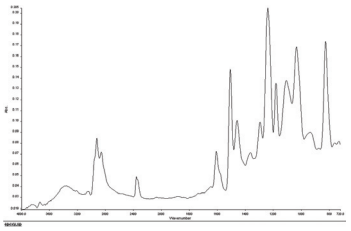

Figure 4B

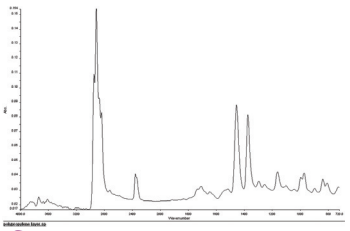

Figure 4C

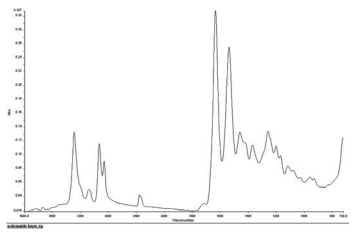

Figure 4D

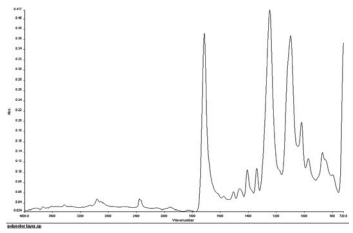

Figure 4E

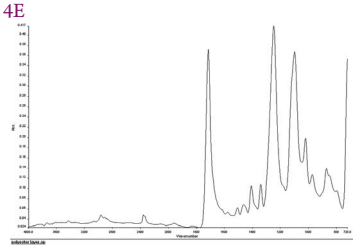

Figure 4: Library hits on the FT-IR spectra obtained from the different images, e.g.; epoxy (A), polypropylene (B), amide (C), ester (D) and adhesive (E).

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