Material analysis by infrared mapping: A case study using a multi-layer paint sample

Application Note

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Introduction

Agilent's 610 FTIR fourier transform infrared (FTIR) microscopes are routinely used for the analysis of heterogeneous materials. They provide an ability to characterize the spatial distribution of components as well as the ability to identify the specific chemical nature of a sample. Agilent's infrared microscopes can be used on both the microscopic and macroscopic scale using multiple measurement modes including:

- transmission
- reflection
- attenuated total reflectance (ATR)
- grazing angle reflection analysis
- 'large sample' mode using Agilent's large sampling side-port accessory

They are ideal for advanced materials characterization as they are simple to use, provide the best sensitivity and versatility, and can be customized to suit a desired area of analysis. By adding a motorized sample stage to an Agilent Cary 610 FTIR single-element detector microscope system, the capabilities can be extended to include automated infrared mapping analysis.

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Infrared mapping allows for multiple infrared spectra to be sequentially acquired from different spatially-resolved points on the same sample and provides both spectral and spatial information, thereby facilitating the study of within-sample chemical heterogeneity. Common infrared mapping applications in material sciences include simple material characterization, the analysis of the homogeneity of coating materials, the investigation of multi-layer sample interfaces such as polymer laminates and paint cross-sections, the automated screening of samples for defects or contamination, the characterization of the total reflectance of optical surfaces and other process control applications.

This paper highlights the simplicity and power of Agilent's Agilent Cary 610 infrared mapping microscope for the rapid and automated analysis of a multi-component paint sample.

Instrumentation

The infrared mapping experiment was conducted using a Cary 610 FTIR spectrometer, equipped with a 610 FTIR infrared microscope (containing a 250 micron single-element, narrow-band Mercury Cadmium Telluride detector and a motorized sample stage) operating under Resolutions Pro 5.0 software. A constant flow of dry air was used to purge the system, limiting the contributions from carbon dioxide and atmospheric water vapor.

The infrared map was collected in reflection-mode using a pre-loaded grid mapping template that was customized to collect a 19 × 19 grid (totaling 361 spectra) using a 20 µm step size from an area measuring 380 × 380 microns. The infrared spectra were sequentially recorded over the range of 4000–700 cm^{-1} at a spectral resolution of 8 cm^{-1} by co-adding 16 scans per point (~40 mins for the entire infrared map).

Sample preparation

The paint chip cross sections were prepared from vehicle paint fragments provided by a police forensic laboratory. Samples were mounted in a clear casting polyester resin, and then polished using a 12,000-mesh Micromesh polishing cloth. The embedded paint fragments were microtomed to a thickness of ~10 µm, and the samples transferred to a standard glass microscope slide that was covered with aluminum foil to allow for reflection/absorption analysis.

Results and discussion

Infrared mapping using Agilent's Cary 610 FTIR Microscope allows for the automated sequential acquisition of hundreds of high-quality infrared spectra from analytical samples. Using Resolutions Pro software, mapping experiments are extremely flexible. Users can either select individual spectral collection locations themselves or use one of several grid mapping templates that can be customized to a sample, saved and re-applied later. In this experiment, a paint fragment found at an automobile crime scene was embedded in a polymer resin, then microtomed to obtain an appropriate sample thickness. This sample was deposited onto the surface of a reflective infrared support slide which was then placed on the motorized stage of the microscope. A visual image of the paint sample was acquired, followed by the sequential collection of the 361 spectra (19 × 19 grid map; 380 × 380 µm area) using automated infrared mapping. The visual image of the sample and the spectral acquisition locations are shown in Figure 1. Each spectrum in the infrared map results from a spatial resolution of 20 µm.

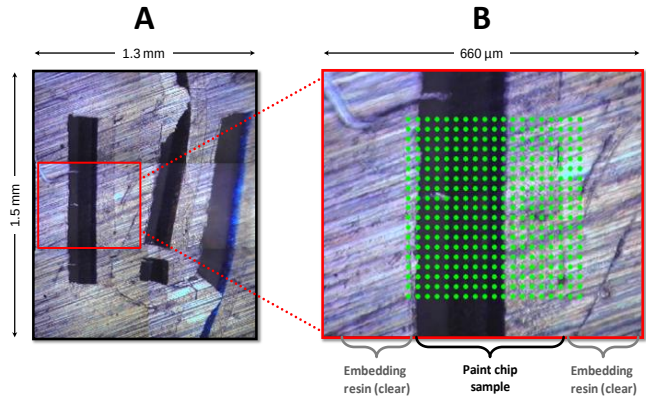


Figure 1. (A) Visual image of 3 sections of a paint chip sample (vertical bars), which were embedded into a polyester resin (clear). The reflective aluminum IR-slide upon which the samples are deposited can be seen through the resin. (B) Higher resolution view of a paint chip sample overlaid with the locations of spectral acquisition (represented by the grid of green circles). The overall area of analysis for the spectral map was 380 × 380 µm, yielding a total of 361 spectra.

The investigation and interpretation of the infrared data was simplified by several intuitive software features. For example, the grid of green circles that is overlaid on the surface of the visual image of the sample can be used to extract spatially resolved data. Simply clicking on a desired sample location (or multiple locations) will fill in the green circle(s) and will display the corresponding IR spectra in the software's 'spectrum' display panel. Spectral peaks of interest can then be compared or used for quantitative analysis, and the selected spectra can be overlaid or stacked to facilitate visual interpretation. Upon cursory visual examination of the forensic evidence in Figure 1, the vertical black strip appeared to be uniform in composition with only minimal variations. However, infrared investigation revealed that the sample is heterogeneous and composed of multiple spatially-resolved vertical layers. Exploratory investigation of the spectra in the map revealed the presence of four chemically distinct layers. In addition, the high spatial resolution of the infrared map allowed for the identification of localized areas with different chemical compositions within the stratified layers. Figure 2 illustrates selected absorbance spectra from the paint chip sample.

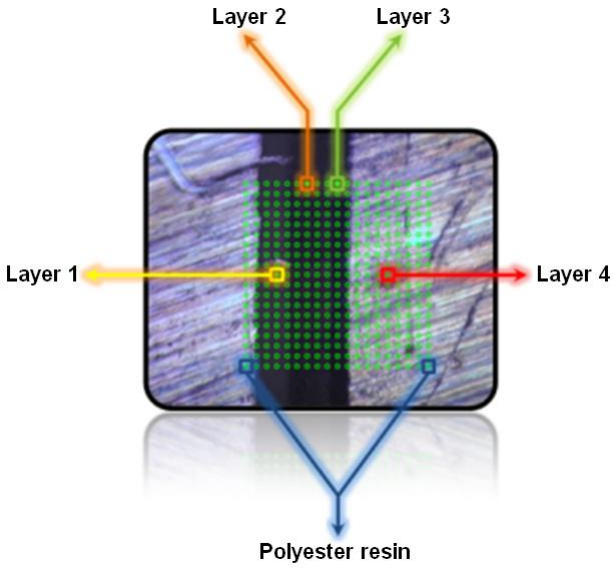
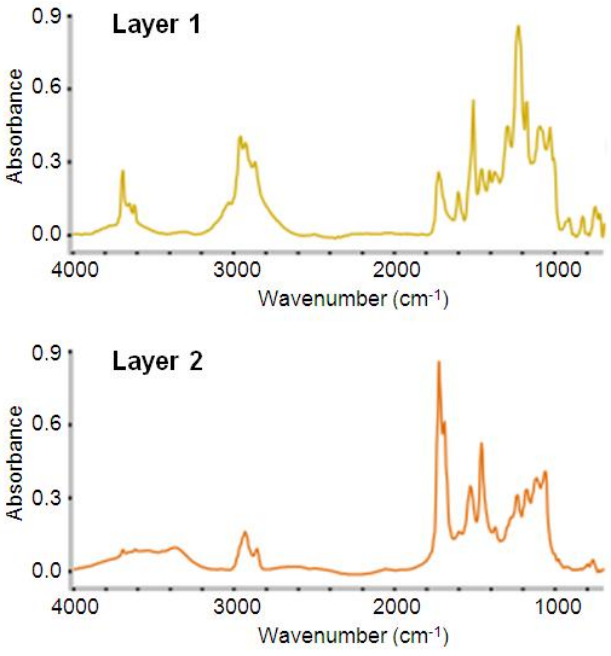
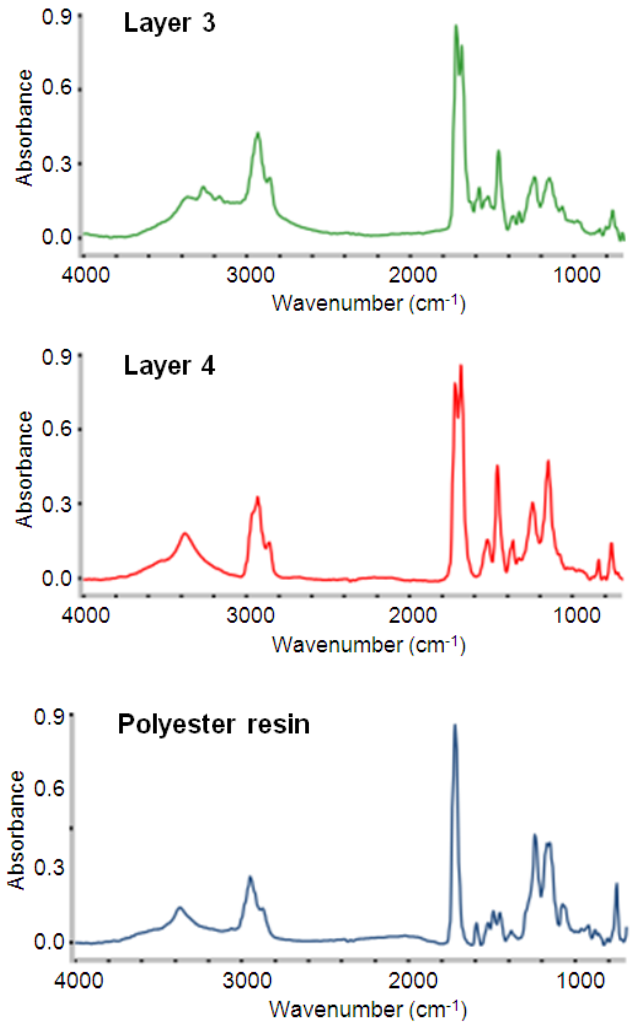


Figure 2. Representative FTIR spectra from the four layers of the paint chip sample as well as a spectrum of the embedding resin. Three of the spatially-resolved layers are in the black vertical bar, while one layer is transparent, as is the polyester resin. See layer spectra in the five images below.





The spectra in Figure 2 are visually distinct and contain sufficient information to allow for the characterization of each individual layer. Based on these spectra, forensic scientists are able to search spectral databases of paint and coating samples to identify the vehicle's make, model, year, and color. In this instance, the ability to detect trace materials in the evidence proved to be very useful in extending the knowledge of the sample's composition far beyond that which could have been obtained by in-bench FTIR experiments or by other analytical techniques.

Without a clear delineation of the layers, it is difficult to study the variations in sample chemistry across the infrared map by using the spectrum display alone. Resolutions Pro software makes it easy to view chemical differences across an entire infrared map of a sample. One means of probing a sample is to generate a feature image based on one or multiple spectral peaks (one or multiple functional groups of interest). A feature image assigns a color to the absorbance value of a selected peak (or spectral region) and plots the intensity across the infrared map to easily view spatially-resolved chemical differences on the visual image of a sample. The color red indicates a high absorbance value, while the color blue indicates a lower absorbance value. Figure 3 shows a feature image generated from a spectral peak that is unique to one layer of the paint chip. It is equally possible to view the feature image without displaying the locations of spectra acquisition, or to view it as a '3D' chemical image as shown in Figure 3.

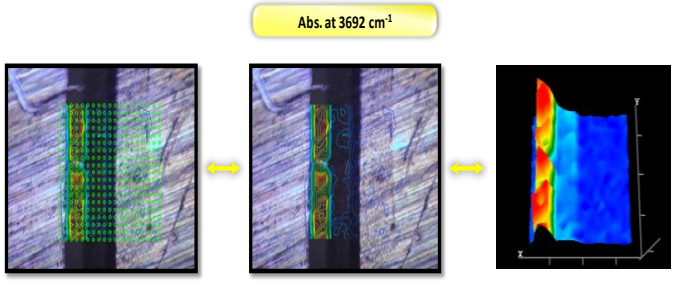


Figure 3. A feature image generated from a spectral peak that is unique to one layer of the paint chip (left), the same feature image shown without the spectral acquisition grid for clarity (center), and the 3-dimensional view of the feature image (right). These images were generated by plotting the intensity of the peak at 3692 cm^{-1} in the spectrum from each pixel across the entire infrared map.

Advantageously, feature images can be generated in real-time using any spectral range or absorbance peak to provide users with a better understanding of a sample's composition. Figure 4 illustrates the feature images generated from the four chemically distinct paint chip layers.

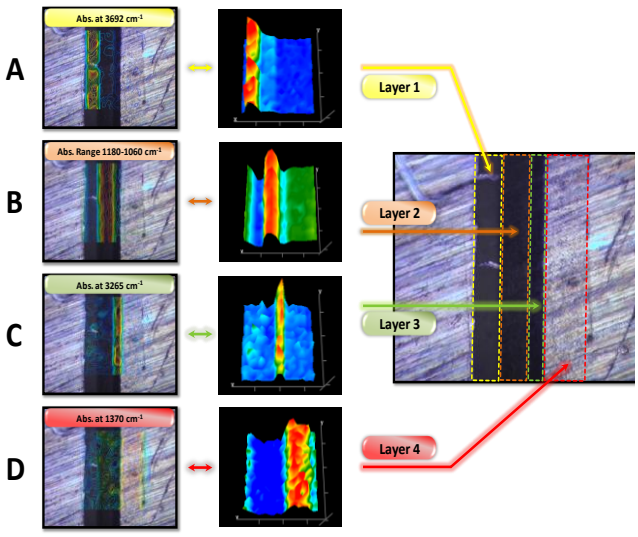


Figure 4. Feature images based on spectral peaks that are unique to each layer in the four-layer paint chip sample. The feature image in 'A' is based on the absorbance of the peak centered at 3692 cm^{-1}, which is primarily found in layer 1 of the paint chip; while the feature image in 'B' was generated from the absorbance peaks between 1180–1060 cm^{-1}, which are largely found in the second layer; 'C' shows the spatial distribution of the absorbance peak centered at 3265 cm^{-1}; while 'D' shows the feature image of the clear coating layer of the paint sample based on the absorbance at 1370 cm^{-1}. Legend for feature images: red = high intensity, green = medium intensity, blue = low intensity.

The chemical image display of the infrared mapping software was particularly useful to highlight the clear external coating of the paint sample, designated by layer 4 in Figure 4D. Depending on the visible contrast of a sample, it is occasionally easier to view the distribution of a selected spectral peak (or range) in different feature image views. From the feature images it is a simple task to estimate the approximate width of each stratified vertical layer; layer 1 is ~80 µm, layer 2 is ~80 µm, layer 3 is ~40 µm, while layer 4 is ~120 µm. It is equally possible to probe the heterogeneity within each layer for an improved characterization of the sample. For example, layer 1 in Figure 4A is not uniform in chemical composition and has a number of visible defects that can also be observed in the visible and feature images. With Resolutions Pro software, it is simple to investigate the chemical differences between adjacent spectra by displaying spectra simultaneously. However, for a more in-depth understanding of the samples' heterogeneity on the micro-scale, a higher spatial resolution infrared image would be required.

An alternate approach to acquiring IR spectra with a significantly higher spatial resolution involves the use of an infrared imaging system equipped with a focal plane array (FPA*) detector. An FPA-FTIR system would provide a superior means of investigating the subtle chemical differences found in each layer of the paint sample. Unlike infrared mapping using a single-element detector, an FPA* detector collects hundreds to thousands of spectra simultaneously within seconds, thereby providing dramatic savings in spectral acquisition time compared to infrared mapping techniques that perform sequential data collection. In practical terms, this infrared map required ~40 minutes acquisition time to collect 361 spectra for the area of 380 × 380 µm using a 20 µm spatial resolution; comparatively, Agilent's 128 × 128 FPA-FTIR system could acquire over 16,000 spectra with an identical signal-to-noise ratio from an area of 700 × 700 µm within a few seconds using an even higher spatial resolution of 5.5 µm per spectrum.

In addition, Agilent's FPA-FTIR imaging spectrometers have a number of easily user-changeable spatial resolution modes including: 1.1 µm (ATR Analysis), 5.5 µm, 11 µm, 22 µm and even larger sizes with pixel binning or macro imaging (for example, >40 µm). FPA-FTIR analysis would involve the same minimal sample preparation and could be used to reveal even the smallest features of the forensic evidence sample.

While this experiment focused on the characterization of a sample obtained from a crime scene, the application of FTIR microscopy and mapping in paint analysis extends far beyond forensic applications. They are commonly used for the characterization of historical art works, and for the development of conservation and preservation strategies for paintings and photographs. FTIR microscopy and mapping are equally important in the QC analysis of raw materials used in the manufacture of paints and inks, and are routinely applied to the analysis of resins, pigments, solvents and additives.

Conclusion

Agilent's Cary 610 FTIR Microscope provides the ability to collect high quality chemical information from multi-layer samples with a high spatial resolution. It provides an excellent means of probing a sample's chemistry as it can be used to visualize the relative distribution of specific components across a sample area of several centimeters. In this experiment, a 380 × 380 µm infrared map was automatically collected using a pre-defined acquisition grid to investigate the chemical heterogeneity of a paint chip sample. Four chemically distinct layers were resolved in the forensic evidence, including a miniscule layer measuring ~40 µm.

Feature images also were used to highlight each layer within the infrared map and to probe localized areas with varying chemical compositions within the stratified layers. The rapid nature and the simplicity of automated infrared mapping make it a key technique for the advanced characterization of material and polymer samples.

References

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