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Investigating automobile paint chip layers with FTIR and Raman microscopy

Introduction

Forensic labs are often asked to piece together evidence from hit and run incidents where one of the vehicles involved has fled the scene. Evidence left behind can include fragments of glass, pieces of the bumper, headlights, or tail lamps, as well as skid marks and paint residues. Collisions between a vehicle and an object or person can result in the transfer of paint, either as chips or smears.

Automobile paint is often a complex mixture of various components applied in multiple layers. While this complexity presents a challenge for analysis, it also provides a wealth of potential information for vehicle identification. Fourier transform infrared (FTIR) and Raman microscopy are some of the critical techniques used to address this challenge and provide non-destructive analysis of individual layers within the total paint structure.

Paint chip analysis begins with the collection of spectral data, which can be directly compared to a control sample or used in conjunction with a database to identify the make, model, and year of the vehicle. One such database is the Paint Data Query (PDQ) Database, which is maintained by the Royal Canadian Mounted Police (RCMP). Access is available to forensic laboratories who participate in the program to maintain and grow the database. This application note will focus on the first step in the analysis process; collection of spectral data from paint chips using FTIR and Raman microscopy.

Paint chip sample preparation

FTIR data was collected using a Thermo Scientific™ Nicolet™ RaptIR™ FTIR Microscope; Raman data was collected using a Thermo Scientific™ DXR3xi Raman Imaging Microscope. The paint chips were obtained from damaged sections of an automobile; one paint chip is from a door panel, and the other is from a bumper. Embedding samples in epoxy resin is a common way to mount them for cross-sectioning, but there is a risk that the resin penetrates the sample and complicates the analysis. To avoid this, the paint chips were sandwiched between two sheets of poly(tetrafluoroethylene) (PTFE) while being cross-sectioned.

The paint chip cross-sections were manually separated from the PTFE prior to analysis and pieces were placed on a barium fluoride (BaF_2) window. FTIR mapping was done in transmission mode using the optimized 15x objective and condenser, a 10 x 10 μm^2 aperture, and 5 μm steps. The same samples were used for Raman analysis for the sake of consistency, even though it was not necessary to have thin cross-sections on BaF_2 windows. It should be noted that BaF_2 has a Raman peak at 242 cm^{-1} that can be observed as a weak peak in some of the spectra. This signal should not be attributed to the paint chips. Raman images were collected using image pixel sizes of 2 μm and 3 μm. Spectra were analyzed for key component peaks and compared to commercially available libraries by employing techniques such as multi-component searching to help with identification.
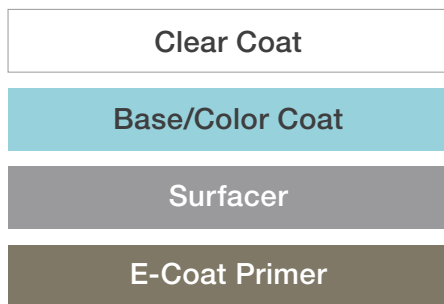
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Figure 1. Schematic of a typical four-layer automobile paint sample (left). Video mosaic image of a paint-chip cross-section taken from the door of an automobile (right).

Automobile paint composition

While the number of layers in a paint chip can vary, samples typically have about four layers (Figure 1). The layer applied directly to the metal is an electro-coat primer layer (approx. 17-25 µm thick), which is used to protect the metal from the environment and to provide a surface for the subsequent paint layers to adhere to. The next layer is the surfacer layer (approx. 30-35 µm thick) that acts as an additional primer and provides a smooth surface for the paint layers that follow. Next, there is a basecoat or color coat (approx. 10-20 µm thick), which contains the primary pigments of the paint. The final layer is a clear coat (approx. 30-50 µm thick), which protects the paint layers beneath it and provides a glossy finish. Part of the challenge of analyzing trace paint evidence is that paint chips and smears will not always contain all the layers present on the source vehicle. Additionally, samples from other areas might have different compositions. For instance, a paint chip from a bumper may contain bumper materials as well as the finish.

FTIR paint chip analysis – automobile door

A visible image of the paint-chip cross-section is shown in Figure 1. Four layers can be seen in the visual image, corresponding to the four layers identified by infrared analysis. The whole cross-section was mapped, and individual layers were defined using FTIR images of different peak areas.

Representative spectra from the four layers and corresponding FTIR images are shown in Figure 2. The first layer is consistent with an acrylic clear coat and includes polyurethane, melamine (peak at 815 cm^{-1}), and styrene. The second layer is the base (color) coat and is chemically similar to the clear coat. It also consists of acrylic along with melamine and styrene. While they are similar, and no specific pigment peaks were identified, there are still differences in the spectra, mainly in peak intensities. The spectrum from Layer 1 has more intense peaks at 1700 cm^{-1} (polyurethane), 1490 cm^{-1}, 1095 cm^{-1} (C-O) and 762 cm^{-1}. The spectrum from Layer 2 has more intense peaks at 2959 cm^{-1} (methyl), 1303 cm^{-1}, 1241 cm^{-1} (ester), 1077 cm^{-1} (ester) and 731 cm^{-1}.

Spectra from the surfacer layer matched with library spectra of an alkyd based on isophthalic acid. The final electro-coat primer layer consists of an epoxy and, potentially, polyurethane. Overall, results are consistent with what is typically found in automobile paints. The analysis of the different components in each layer was performed using commercial FTIR libraries rather than automobile-paint-specific databases, so while matches are representative, they may not necessarily be exact. Using databases specifically designed for this type of analysis would improve identification and could even be used to determine the make, model, and year of the automobile.
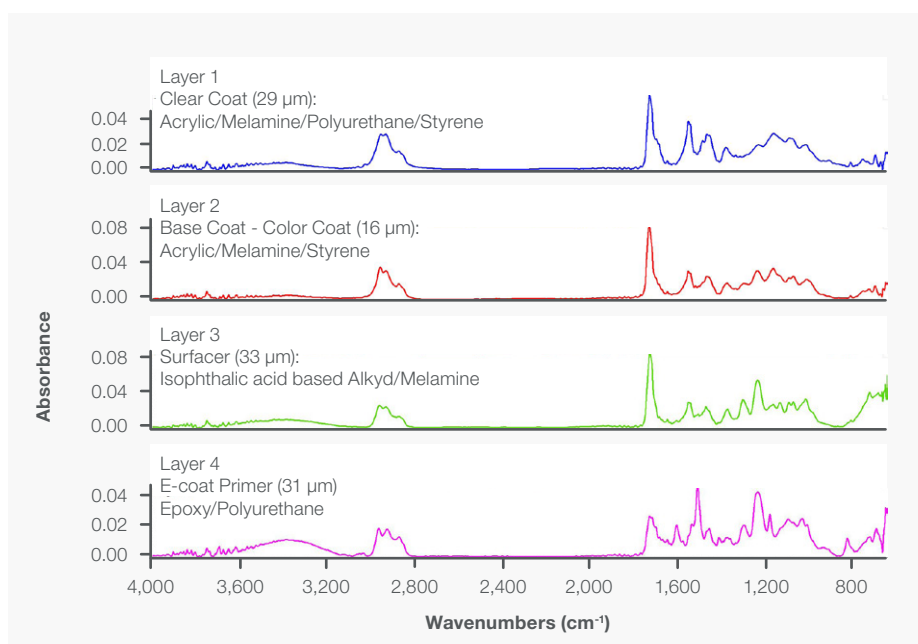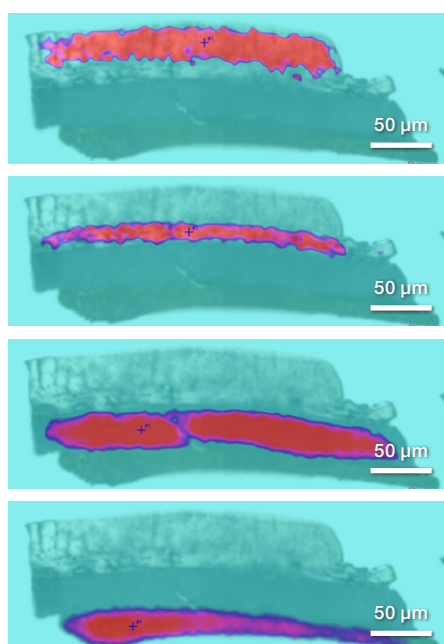

Figure 2. Representative FTIR spectra from the four identified layers in the door paint-chip cross-section. Infrared images are generated from peak areas associated with the various layers, which are then superimposed on the video images. The red areas show the location of the various layers. The infrared image covers an area of 370 x 140 µm² using a 10 x 10 µm² aperture and 5 µm steps.
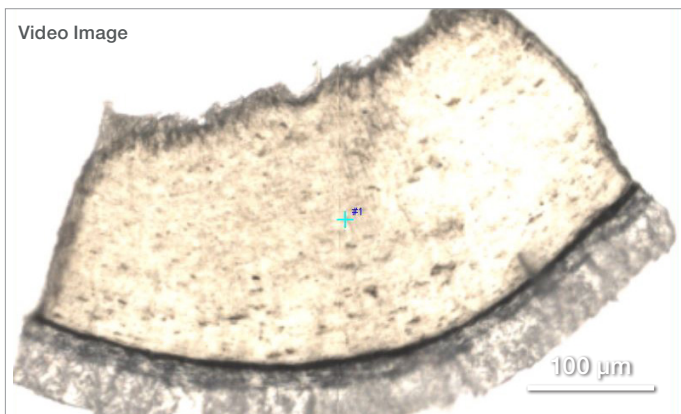
Figure 3. Video mosaic image of a paint-chip cross-section taken from the bumper of an automobile.
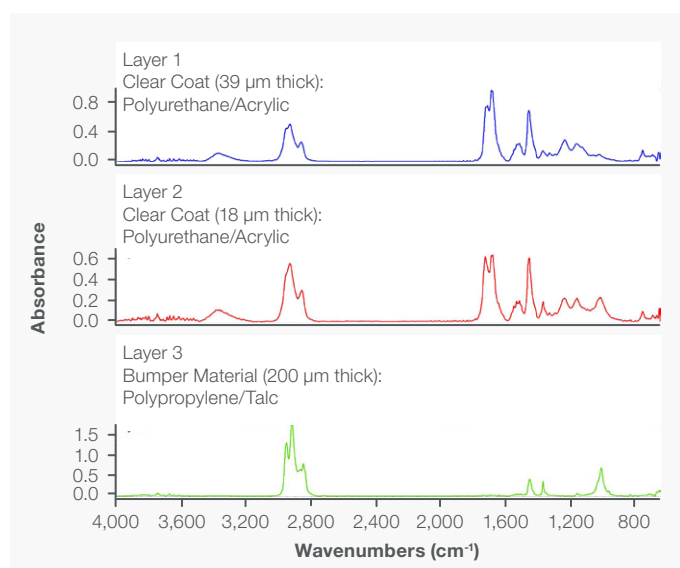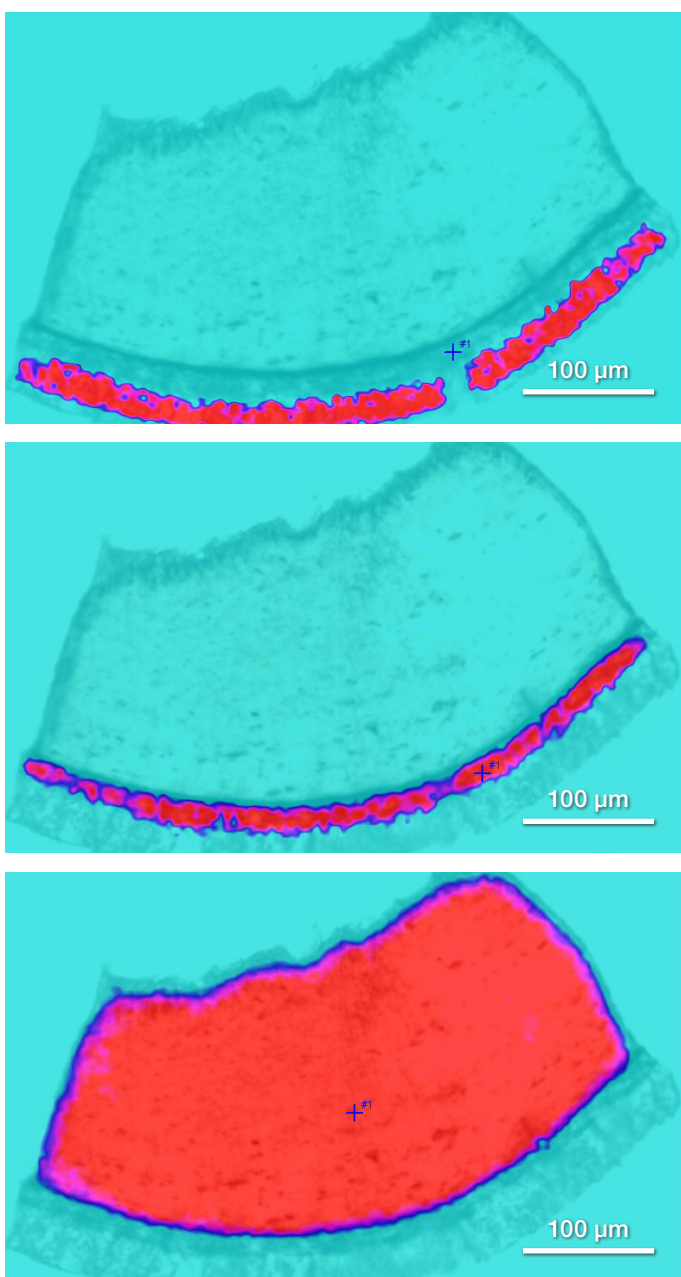

Figure 4. Representative FTIR spectra from the three identified layers in the bumper paint-chip cross-section. Infrared images are generated from peak areas associated with the various layers, which are then superimposed on the video images. The red areas show the location of the various layers. The infrared image covers an area of 535 x 360 µm² using a 10 x 10 µm² aperture and 5 µm steps.

FTIR paint chip analysis - bumper

A video image of a bumper paint-chip cross-section is shown in Figure 3; at least three layers are clearly visible. Infrared images of the cross-section confirmed three distinct layers (Figure 4). The outer layer is a clear coat that appears to be a polyurethane material with acrylic, which matched with clear coat spectra from a commercial forensic library. While the spectrum from the base (color) coat is very similar to the clear coat, it was still distinct enough to be differentiated from the outer layer. There are significant differences in relative peak intensities. The third layer is likely the bumper material itself and consists of polypropylene as well as what appears to be talc. Talc can be used as a reenforcing filler with polypropylene to improve a material's structural properties. The two outer layers are both consistent with paint layers found in automobile paint, but no specific pigment peaks were identified in the base coat layer.

Raman microscopy

To gather additional information on the samples, cross-sections were also analyzed using a Raman imaging microscope. The Raman analysis was complicated by fluorescence from the samples. Several different laser sources (455 nm, 532 nm, and 785 nm) were tested to evaluate the balance between fluorescence and Raman signal intensity. For the door paint chip, a 455 nm laser gave the best results; while there was still fluorescence present, it could be compensated for with a baseline correction. This approach, however, did not work with the epoxy layer because the fluorescence was too extreme, and the material was sensitive to laser damage. While some lasers worked better than others, none were a practical choice for analysis of the epoxy layer. A 532 nm laser was used for the Raman analysis of the bumper paint-chip cross-section. There were still fluorescence contributions, but these were addressed with a baseline correction.
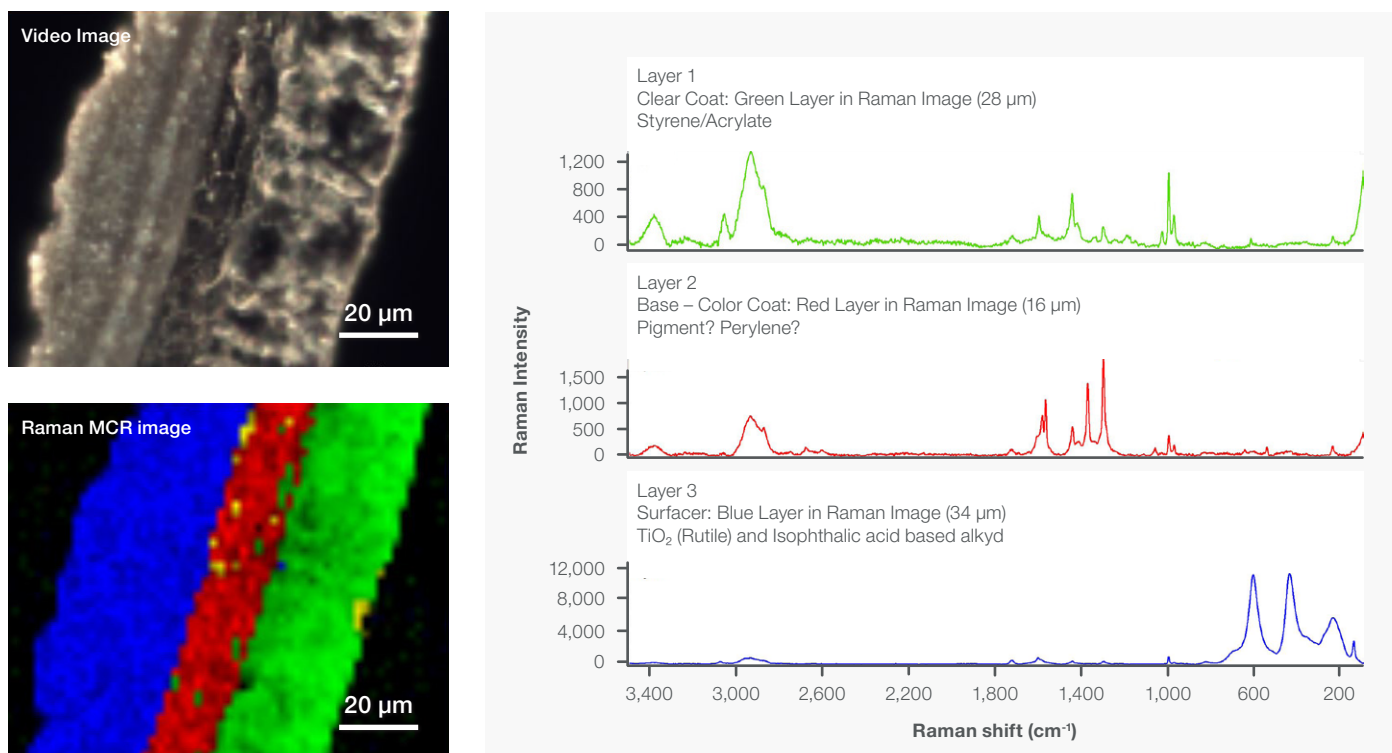
Figure 5. Representative Raman spectra from the first three layers of the door paint-chip sample (right). The fourth (epoxy) layer was lost during sample preparation. The spectra have been baseline corrected to remove fluorescence contributions and were collected using a 455 nm laser. An area 116 x 100 µm^2 was imaged using a pixel size of 2 µm. Video mosaic image of the cross-section (top left). Raman multivariate curve resolution (MCR) image of the cross-section (bottom left).

Raman paint chip analysis – automobile door

Figure 5 shows the Raman imaging analysis of the door paint-chip cross-section; this sample did not have the epoxy layer attached, as it was lost during sample preparation. However, since the Raman analysis of the epoxy layer was already determined to be problematic, this was not considered to be an issue.

The presence of styrene was much more prevalent in the Raman spectra from Layer 1 while the carbonyl peaks were much less intense compared to the infrared spectra.

There was a much more dramatic difference in the spectra from the first and second layers in the Raman analysis compared to FTIR. The best Raman match to the base-color coat was perylene; while it not an exact match, derivatives of perylene are known to be used for pigments in automobile paint, so it could represent the pigment in the color layer. The spectra from the surfacer layer were consistent with an isophthalic acid base alkyd, but also showed the presence of titanium dioxide (TiO_2, rutile), which can be difficult to observe with FTIR, depending on the spectral cutoff.
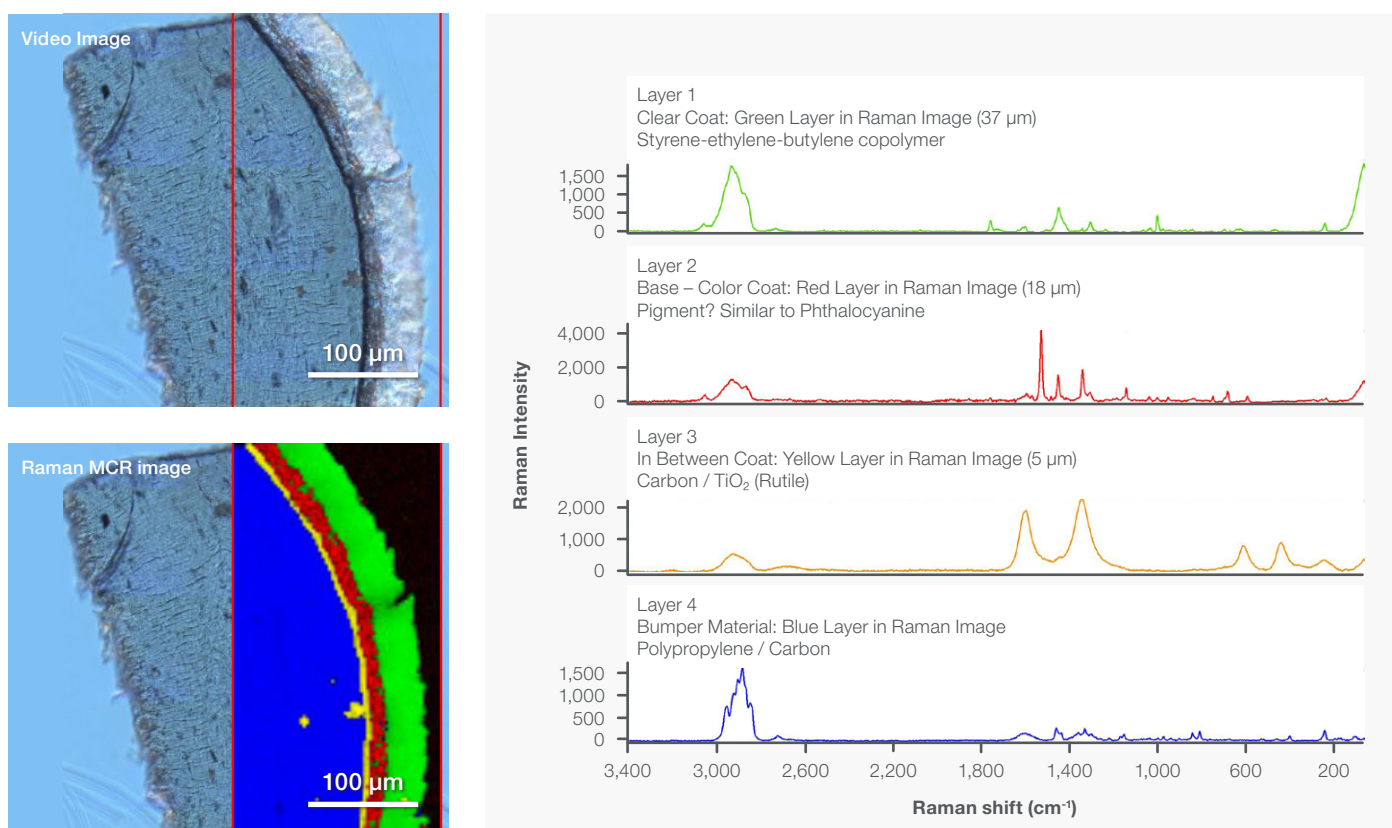
Figure 6. Representative Raman spectra from the bumper paint-chip sample (right). The spectra have been baseline corrected to remove fluorescence contributions and were collected using a 532 nm laser. An area 195 x 420 μm² was imaged using a pixel size of 3 μm. Video mosaic image of the cross-section (top left). Raman MCR image of a portion of the cross-section (bottom left).

Raman paint chip analysis - bumper

Figure 6 shows the Raman results for the bumper paint-chip cross-section. An additional layer (Layer 3) was observed, which was not detected with FTIR. The best match for the outer layer was a styrene-ethylene-butadiene copolymer, but there was also a small carbonyl peak that could not be accounted for, indicating an additional unidentified component. The spectrum from the base-color coat likely represents a pigment component because the spectrum matched, to some extent, phthalocyanine compounds that are used as pigments. The previously undetected layer is quite thin (5 μm) and contains carbon and rutile. Due to the thickness of the layer, and the fact that TiO_2 and carbon are more difficult to detect with FTIR, it is unsurprising that it was not captured by the infrared analysis. Consistent with the FTIR results, the fourth layer (bumper material) was identified as polypropylene, but Raman analysis also showed some carbon. While the presence of the talc seen with FITR cannot be ruled out, exact identification was not possible as the corresponding Raman peaks were too small.

Conclusions

Automobile paints are complex mixtures of components, and while this represents a wealth of identifying information, it also complicates their analysis. Paint chip evidence can be effectively probed using a Nicolet RaptIR FTIR Microscope. FTIR is a non-destructive analytical technique that delivers valuable information about the various layers and components in automobile paints. This application note focused on spectral analysis of paint chip layers, but further analysis of the results, either by direct comparison with a suspected automobile or dedicated spectral database, could provide additional information to match the evidence with its source.

Raman analysis with the DXR3xi Raman Imaging Microscope provided additional information on the paint chip samples. While FTIR and Raman are both vibrational spectroscopy techniques, this application note highlights how they can be used to identify different components of paints. Together, these techniques provide a more complete and complementary view of the samples. The extent of information that these techniques deliver from individual paint layers makes them valuable resources for the challenging task of forensic paint analysis.

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