

# Analysis of automotive paint layers on plastic substrates using chemical imaging $\mu$ -FTIR and O-PTIR microspectroscopy

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## Abstract

Automobile paint chips are a crucial piece of trace evidence for forensic investigators. This is because automotive paints are composed of multiple layers, including the primer, basecoat, and clearcoat, each of which has its own chemical composition that can vary by vehicle make, model, year, and manufacturing plant. Thus, Fourier-transform infrared (FTIR) spectral databases for automobile paint systems have been established to aid law enforcement in, for example, narrowing search parameters for a suspect's vehicle. Recently, car manufacturers have implemented primers on plastic substrates that are much thinner ( $\sim 5\text{ }\mu\text{m}$ ) than those on metal substrates, making it more difficult to manually separate for analyses. Here, we evaluated FTIR microspectroscopy ( $\mu$ -FTIR) and optical photothermal infrared spectroscopy (O-PTIR) to chemically image cross sections of paint chips without manually separating the layers. For  $\mu$ -FTIR, transmission and transfection modes provided the highest quality spectra compared to reflection and  $\mu$ -ATR analyses. Point analysis was preferable to chemical imaging, as peaks were identified in the point (MCT) detector's lower spectral range that was below the imaging (FPA) detector's cutoff, such as those associated with titanium dioxide. Reduced spectral range can lead to a similar issue in O-PTIR analyses depending on instrument configuration. However, its complementary Raman spectra showed strong titanium dioxide peaks, providing an alternate means of identification. Both techniques are likely to become more relevant as they are non-destructive and avoid manual separation of the layers. O-PTIR is particularly well-suited for analysis of the thin primer layer due to its superior spatial resolution.

## KEY WORDS

automotive paint, chemical imaging, forensic analyses, FTIR microscopy, microspectroscopy, O-PTIR

## Highlights

- This is the first study evaluating O-PTIR for forensic car paint analysis.
- Of the  $\mu$ -FTIR modes, transmission yielded the best quality spectra but required more sample prep.
- $\mu$ -FTIR is suitable for the analysis of automobile paint layers, including primer layer  $>\sim 5\text{ }\mu\text{m}$ .
- O-PTIR offers high spatial resolution and simultaneous Raman data but a reduced IR spectral range.

## 1 | INTRODUCTION

When automobile paint is left at a collision scene or transferred onto other vehicles or objects, it can act as a crucial piece of evidence for law enforcement [1]. This is because automotive paints are made up of several layers, including the primer, basecoat, and clearcoat, each of which has its own chemical composition that can vary by vehicle make, model, year, and manufacturing plant (Figure 1) [2]. Thus, databases and Fourier transform infrared spectroscopy (FTIR) spectral libraries of the chemical composition of automobile paint systems have been established to identify the most likely source of an unknown paint system, which can narrow search parameters for a suspect's vehicle. Such databases include the Paint Data Query (PDQ) maintained by the Royal Canadian Mounted Police (RCMP), the National Automotive Paint File maintained by the Federal Bureau of Investigation (FBI), and the European Paint Group (EPG) maintained by the European Network of Forensic Science Institutes (ENFSI) for FTIR [3-5]. Though not maintained by a law enforcement agency, Microtrace LLC maintains a Raman library of automotive paints, and work has been undertaken to determine standardized parameters for use in creating a larger Raman database [6, 7]. These databases exist to assist law enforcement in linking automobile paint evidence to the types of vehicles that it may originate from. The PDQ, for example, is a text-based database that includes infrared spectra for layers of automobile paint systems together with vehicle source

information that is used by most North American countries [5]. Most of the samples in the PDQ are from metal substrates, where the paint layers are relatively thick and easy to separate for FTIR analysis. However, durable and light-weight plastic is increasingly being used in automobile exteriors to improve fuel efficiency, and vehicle collisions often leave plastic pieces behind [2]. Unfortunately, paint systems applied to plastics have recently begun using a very thin (~5 μm) and adhesive-like primer layer, which makes it difficult to physically separate and analyze [2]. Though the primer alone may not contain enough chemical information to identify a sample, especially in paint systems on plastic substrates, in combination with the clearcoat and basecoat, it can lead to specific vehicle parameters that are useful in database searching.

One way to avoid the difficulties associated with manually separating thin primers from adjoining paint layers is to analyze paint chips in cross section using FTIR microspectroscopy. This is a well-established technique that has been included in the standards for forensic paint analysis for many years as well as in published literature [4, 8-11]. While analysis in transmission mode is regarded as the gold standard for paint analysis, the use of attenuated total reflectance (ATR) mode is also common, with reflection mode being used less frequently [8]. However, the recent reduction in plastic substrate primer thickness has brought up a potential issue for the use of this technique. Car manufacturers are now utilizing primers on plastic substrates that are roughly 5 μm thick. As this is approximately equal to the limit of spatial resolution achievable for FTIR microscopes, there was a need to determine if it was still possible to collect good-quality spectra from the thin primer layers. Ultimately, the spatial resolution of a sample analyzed via μ-FTIR is based on the diffraction limit, which is itself a function of the IR light's wavelength [12]. If the ~5 μm spatial resolution limit means that it is not possible to resolve the primer layer from the adjoining layers using μ-FTIR, a new method will need to be investigated and validated for doing so.

One potential alternative option is optical photothermal infrared (O-PTIR) spectroscopy, a relatively new non-contact instrumental technique that can probe molecular vibrations at a submicron level, providing greater spatial resolution than traditional FTIR spectroscopy while also providing Raman spectra [13]. Raman spectroscopy is considered complementary to FTIR spectroscopy as some Raman peaks are not found in FTIR spectra and vice versa due to different selection and transition rules. This is particularly useful for paint analysis, as inorganic pigments such as  $TiO_2$  particles, which are commonly present in the car paint, strongly scatter light giving intense Raman peaks. O-PTIR works by using a combination of pulsing tunable IR lasers and a constant visible light (532 nm) probing laser. The pulsing IR laser shines on the sample at the same point as the visible probe laser; however, the visible light can be focused on a smaller spot (~0.5 μm) than the IR light (~5 μm) due to their different diffraction limits [14]. The interaction of the IR light with the sample results in thermal expansion of the sample when the IR laser is pulsed on and contraction when it is pulsed off. By measuring the difference in the visible probe signal when the IR laser is pulsed, an IR spectrum can be constructed [14]. While this is occurring, the

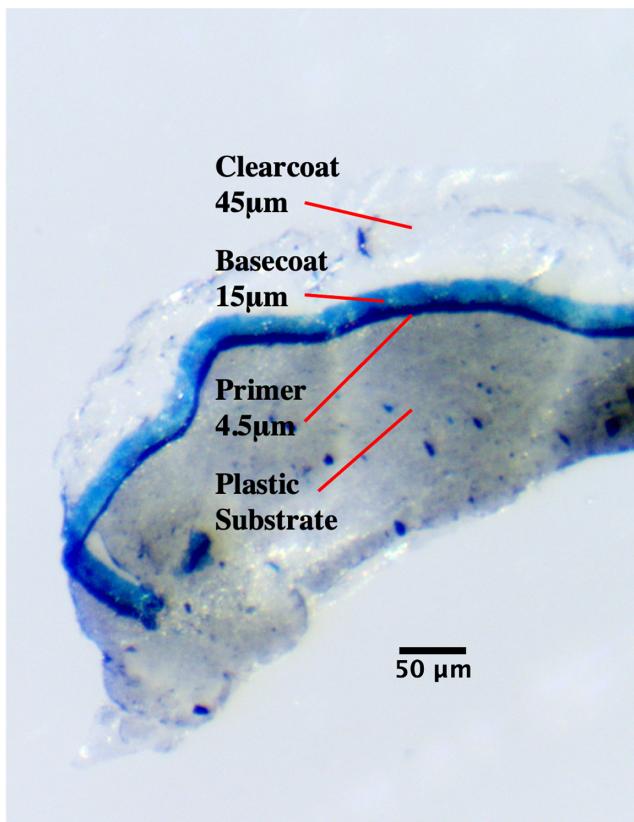


FIGURE 1 Stereomicroscope image of a cross section of an automobile paint chip showing typical layering including the plastic substrate and pigmented basecoat.

Raman-shifted scattered light from the visible probe is sent to a Raman spectrometer, which results in a Raman spectrum from the same area of the sample that the IR spectrum was collected. As of yet, the use of O-PTIR for paint analysis has focused on historical artwork with no papers published on O-PTIR analysis of automotive paint for forensic purposes [15, 16]. However, given that both FTIR and Raman microspectroscopy have previously been used to characterized car paint systems [17, 18] the technique shows great promise, especially for the characterization of thin primer layers.

The purpose of this project was to (1) explore the use of all three  $\mu$ -FTIR modes (reflection, transmission, and ATR) to chemically image and analyze automobile paint chip layers in cross section and (2) compare  $\mu$ -FTIR and O-PTIR for analyses of automobile paint chips on plastic substrates. To that end, we analyzed ten samples of automobile paint by  $\mu$ -FTIR and three of these by O-PTIR, with a special emphasis on characterizing the thinnest (primer) layer. Herein, we introduce and compare  $\mu$ -FTIR and O-PTIR for the chemical imaging and non-destructive forensic analyses of automobile paint chips. We also describe sample preparation and optimized analysis methods, compare reflection, transmission, and ATR modes of analyses in  $\mu$ -FTIR, highlight limitations of the methods, and suggest future work.

## 2 | MATERIALS AND METHODS

### 2.1 | Samples

Ten automotive paint chips were provided by a law enforcement agency that asked not to be identified. Each paint chip is from a different vehicle with varying thicknesses and components of their paint layers (Table 1). Each paint chip contained a full paint layer system (clearcoat, basecoat, and primer) on a plastic substrate. For samples that originated from the same manufacturer, samples were provided from different manufacturing plants.

Two different instruments were used to analyze the samples.  $\mu$ -FTIR analysis was conducted using the LUMOS II (Bruker Corp., Billerica, MA), while the mIRage (Photothermal Spectroscopy Corp.,

TABLE 1 Sample information for automobile paint chip samples analyzed in this study.

Vehicle ID	Manufacturer	Color	Finish
1	Honda	Blue	Metallic
2	Volkswagen	Red	Metallic
3	General Motors	Black	Metallic
4	Nissan	Black	Metallic
5	Ford	Black	Metallic
6	Honda	Silver	Metallic
7	Volvo	Silver	Metallic
8	Mercedes-Benz	White	Flat
9	Toyota	Blue	Metallic
10	Honda	Silver	Metallic

Santa Barbara, CA) was used for O-PTIR. As the LUMOS II was used in three different modes and the mIRage was used in reflection mode, the sample preparation required for these analysis modes differs and is discussed separately below. While all layers are important for vehicle identification, the sample preparation methods and analysis parameters reported here are focused on optimizing the primer layer spectra. For example, pressure was applied to samples in the diamond compression cell to achieve the optimal thickness of the primer, even if this meant that other layers remained too thick to yield optimal spectra. Similarly, O-PTIR Raman parameters were chosen to optimize the primer layer spectra, as other layers exhibited strong autofluorescence.

### 2.2 | Sample preparation

#### 2.2.1 | O-PTIR

Three paint chips (Vehicle ID 1, 2, and 3) were analyzed via O-PTIR. Since the O-PTIR technique involves reflection of both visible and IR light, the paint chips were superglued onto a magnetic sample holder and then sliced in cross section with a diamond-bladed microtome to create an extremely smooth surface. The sample holder was then placed on the sample stage for analysis.

#### 2.2.2 | $\mu$ -FTIR

Samples for analysis in reflection and  $\mu$ -ATR modes required little to no sample preparation. For  $\mu$ -ATR analysis, the bulk paint chips were placed in a microvise (PIKE Technologies, Madison, WI) with their cross section facing up. The microvise was then set directly in the LUMOS II sample stage holder for analysis. For the reflection samples, the bulk paint chips did not have a smooth enough surface to reflect the IR light properly. As such, the samples that were prepared for O-PTIR analysis by cross sectioning with a diamond edge microtome were used for this analysis mode. The thin-sliced cross-cut samples prepared for transmission mode were also analyzed via reflection mode. As the samples had a thickness of roughly 5  $\mu$ m, they were placed on MirrIR low E glass slides (Kevley Technologies, Chesterland, OH). This allowed the IR light to pass through the sample and reflect off the surface of the slide back through the sample. While these samples were still analyzed in reflection mode, this method is more commonly referred to as transfection.

For samples prepared for  $\mu$ -FTIR analysis in transmission mode, a scalpel was used to remove a portion of the plastic substrate, leaving the paint layers intact (Figure 1). This approach facilitated cross sectioning by making it easier to slice while also reducing the overall size of the cross section. Next, each paint chip was frozen at an angle in Tissue-Tek OCT (Sakura Finetek USA, Inc., Torrance, CA) and sliced to ~5  $\mu$ m in thickness with a cryostat. This approach was chosen to avoid the need to embed the samples in resin, which previous research has shown can affect the

paint layer's spectra [19]. A cryostat was used for sectioning due to its availability, but other studies have used an ultramicrotome to create thin cross sections [20]. Each cross section was placed in a plastic PetriSlide (MilliporeSigma, St. Louis, MO) using tweezers, washed with ultrapure water to remove the water-soluble Tissue-Tek OCT compound, and dried for 48 h in a vacuum oven at 40°C. Each paint chip cross-section was flattened in a Diamond EX'Press II 1.6 mm diamond compression cell (S.T. Japan-Europe GMBH, Köln, Germany), imaged with a SZMT2 stereomicroscope (AmScope, Irvine, CA), and analyzed with Bruker's LUMOS II FTIR Microscope.

## 2.3 | Sample analysis

### 2.3.1 | O-PTIR

Because both the IR and Raman spectra are collected at the same time using this technique, two sets of parameters were recorded for the samples analyzed with O-PTIR. The IR spectra were collected from 3000-2650  $\text{cm}^{-1}$  to 1800-950  $\text{cm}^{-1}$ . The gap from 1800 to 2650  $\text{cm}^{-1}$  is a consequence of using tunable lasers. At the time of measurement, there was not a tunable laser that covered the full mid-IR range, and there was a limited amount of physical space in the instrument for the tunable lasers. As a result, the specific instrument used for these samples sacrificed the triple bond region in order to include the fingerprint, single bond stretch, and the majority of the double bond regions. Recent improvements in laser technology allow for coverage of a much larger wavenumber range. Current options include a range of 3000-2700  $\text{cm}^{-1}$ , 2300-2000  $\text{cm}^{-1}$ , and 1800-950  $\text{cm}^{-1}$  or a range of 3600-2700  $\text{cm}^{-1}$ , 2300-2000  $\text{cm}^{-1}$ , and 1800-800  $\text{cm}^{-1}$ . Raman spectra were collected from 262.58 to 4082.58  $\text{cm}^{-1}$  with an excitation wavelength of 532.2 nm and a laser power of 0.49%. The spectral resolution for the instrument in both modes was 2  $\text{cm}^{-1}$ , while the spatial resolution was roughly 0.5  $\mu\text{m}$ . Both IR and Raman spectra were collected at the same time, with a speed of 25 s per measurement point. Similar to FTIR microscopy, both single-point and imaging modes are available for O-PTIR. The spectra shown herein were all extracted from hyperspectral images unless otherwise noted, which took roughly 15 min to acquire.

### 2.3.2 | $\mu$ -FTIR

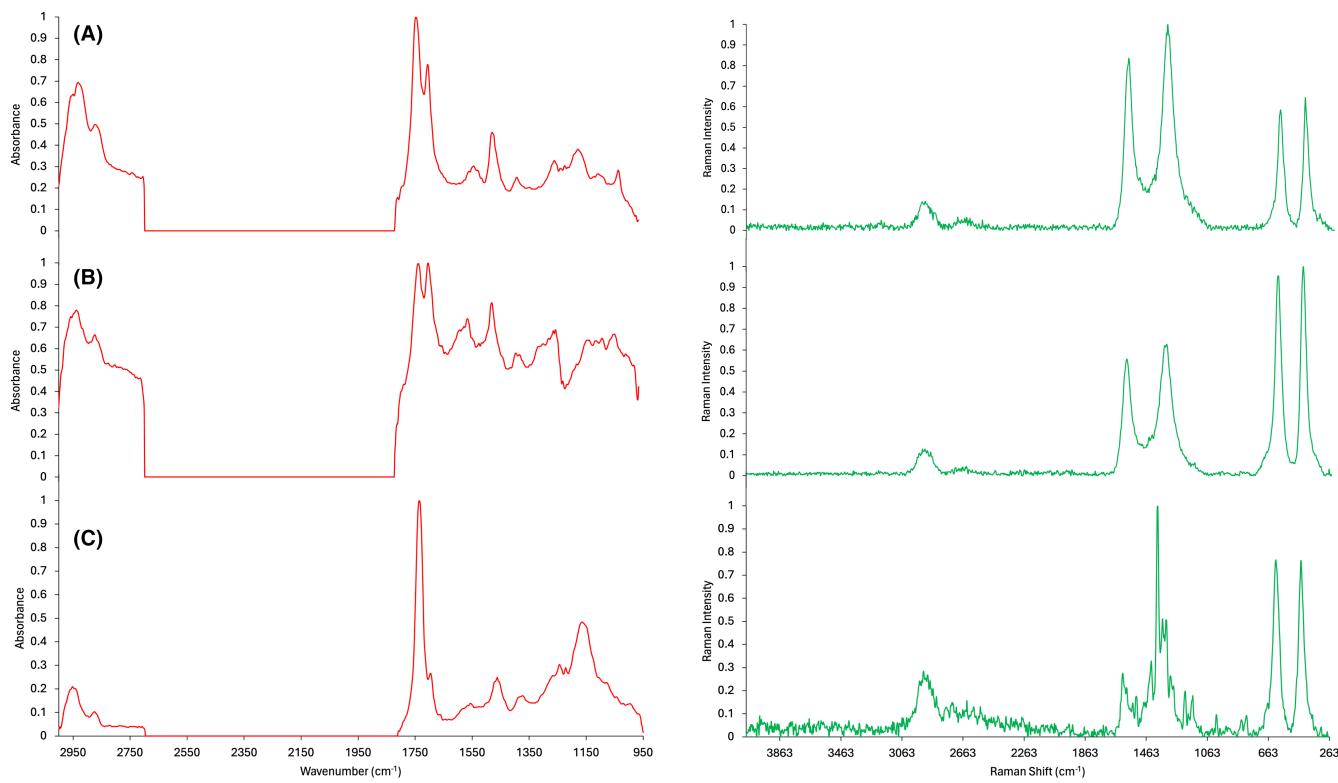
The LUMOS II is equipped with a focal plane array detector (FPA) for chemical imaging as well as a mercury cadmium telluride detector (MCT) for point analysis, both of which were used in this project. Spectra were collected and processed using the OPUS 8.7 software (Bruker Corp., Billerica, MA). All three modes of analysis (transmission, reflection, and ATR) were used to analyze the samples. All samples were run with 256 background scans, 100 sample scans, and a spectral resolution of 4  $\text{cm}^{-1}$ . The background scans were taken on

a clean portion of the compression cell that was close to the area of the paint chip that was being analyzed. Spectra collected with the FPA detector had a wavenumber range of 750-4000  $\text{cm}^{-1}$ , while those collected with the MCT had a range of 600-4000  $\text{cm}^{-1}$ . No binning was applied to the FPA data to maintain the maximum spatial resolution of 5  $\mu\text{m}$ . For samples analyzed with the MCT detector,  $\mu$ -ATR samples had a spatial resolution of ~40  $\mu\text{m}$  while the transmission samples had a spatial resolution based on their aperture window (<5  $\mu\text{m}$ ). There was a significant time difference for measurements taken with the two detectors. The FPA background (8.5 min) and sample (3.25 min/measurement position) scans took longer than the MCT background (1 min) and sample (45 s/measurement position) scans. Post analysis, spectra were subjected to both an atmospheric compensation and a rubberband baseline correction. Reflection spectra were also subjected to a Kramers-Kronig transformation. Spectra displayed in the figures below have also been smoothed using the Savitzky-Golay method.

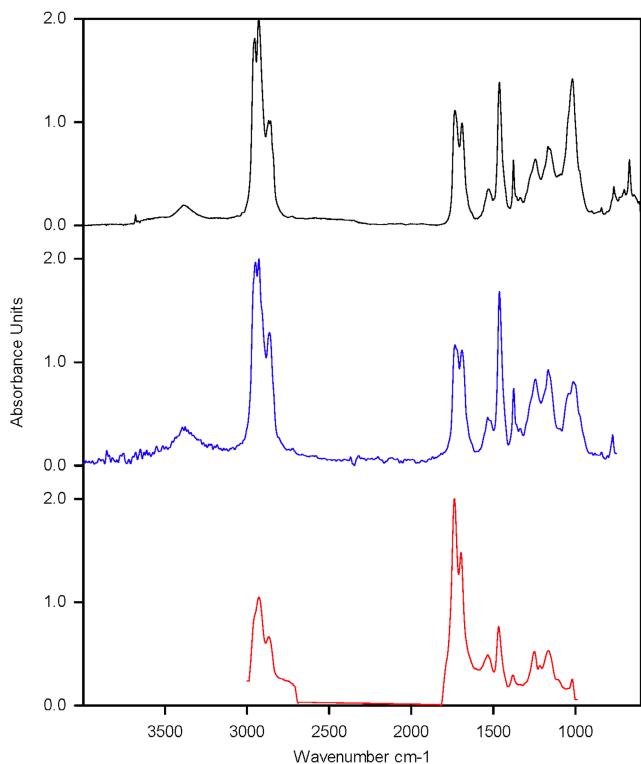
## 3 | RESULTS AND DISCUSSION

### 3.1 | O-PTIR

One major advantage of O-PTIR for forensic examiners is its ability to collect both infrared and Raman spectra from the same measurement point concurrently. [Figure 2](#) shows the simultaneously collected spectra from the primer layer for all three samples analyzed with this technique. Spectra from vehicle ID 1 and 2 were extracted from hyperspectral images, while spectra from vehicle ID 3 came from point measurements. The IR spectra clearly show a reduced spectral range for O-PTIR compared to the  $\mu$ -FTIR data which is further demonstrated in [Figure 3](#). As noted above, this is a result of using tunable lasers for the IR source. While technology has improved since these measurements were taken, at the time of writing, the latest models have a wavenumber range of 3600-800  $\text{cm}^{-1}$  but still have gaps from 2700-2300  $\text{cm}^{-1}$  to 2000-1800  $\text{cm}^{-1}$ . While the peaks present in the IR spectra may be used to identify major components, the reduced range makes it difficult to detect compounds with characteristic low wavenumber peaks, such as titanium dioxide. Here, the primer layers' Raman spectra provide complementary data to the IR spectra as they clearly show peaks associated with rutile, the most common form of titanium dioxide used in car paints, in all three samples. Furthermore, the chemical imaging results, when integrated for the 610  $\text{cm}^{-1}$  peak showed that titanium dioxide was localized only in the primer layer for Vehicle ID 1 ([Figure 4](#)). Given that the complementary nature of the IR and Raman spectra is a major advantage of the technique, it should be noted that the basecoat layer did exhibit autofluorescence in all three samples, though some peaks were still identifiable. There are two potential solutions to this issue. The first is that the hyperspectral image can be used to find a spot in the basecoat where the fluorescence is minimal. As depicted in [Figure 5](#), the autofluorescent peak at 2250  $\text{cm}^{-1}$  was integrated to create a chemical heatmap of the basecoat using its Raman data.



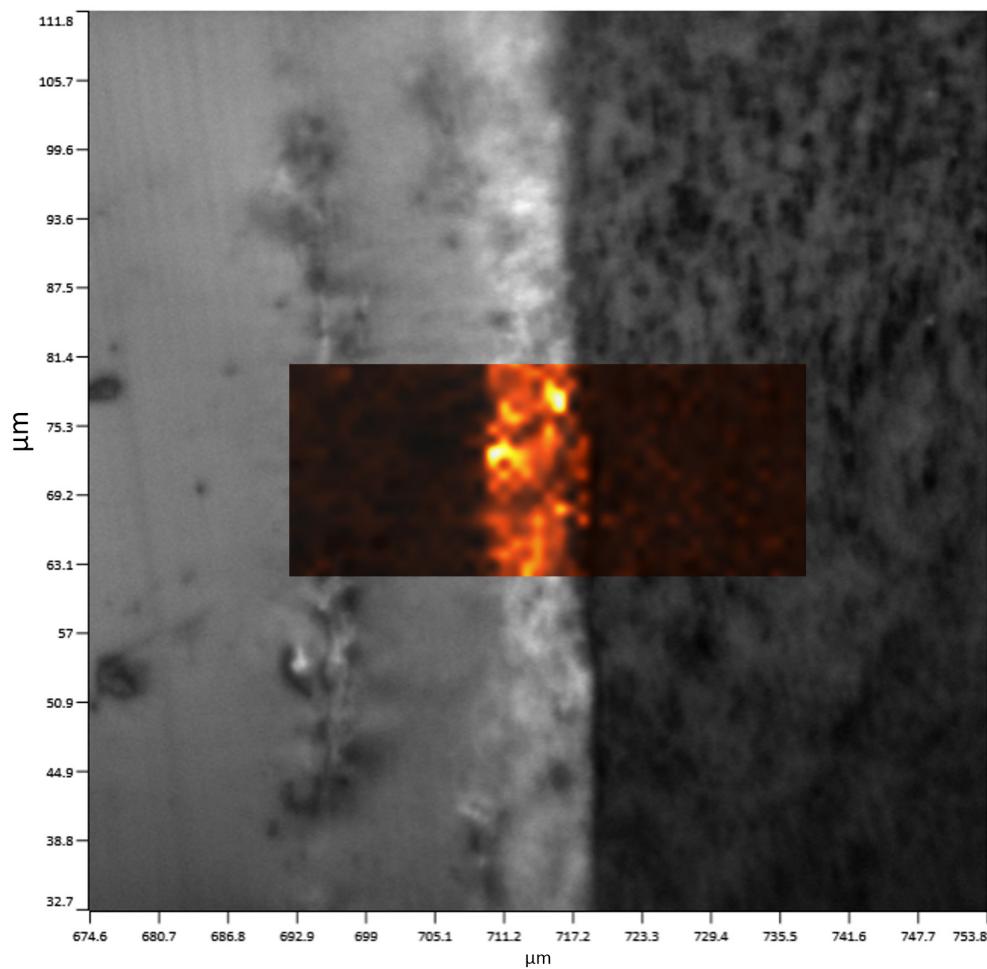
**FIGURE 2** IR (left) and Raman spectra (right) of primer layer from Vehicle ID 1 (A), Vehicle ID 2 (B), and Vehicle ID 3 (C). Titanium dioxide peaks are seen in the Raman spectra at roughly 610 and 450 cm<sup>-1</sup>.



**FIGURE 3** Comparison of normalized primer layer spectra of Vehicle ID 1 from  $\mu$ -FTIR point analysis (top, black),  $\mu$ -FTIR chemical imaging (middle, blue), and O-PTIR (bottom, red).

White and light yellow were used to depict areas where the auto-fluorescence was high, as seen in the Figure 5A spectrum. By contrast, the darkest areas of the chemical map had the lowest amount of autofluorescence, resulting in the significantly better-quality spectrum depicted in Figure 5B. An alternative method of dealing with this issue would be to use a different excitation source, such as a 785 nm laser, which may be able to reduce this fluorescence. Regardless of the method chosen, it is imperative to minimize the autofluorescence as failing to do so would force analysts to rely on the IR spectrum alone, with its reduced spectral range, for identifying components in the basecoat layer.

The other major advantage of O-PTIR over  $\mu$ -FTIR is its superior spatial resolution. Because its probe light is in the visible region, it has a much lower diffraction limit than IR light. This means that it is possible to collect spectra from areas that are only 0.5  $\mu$ m apart when using O-PTIR. As seen in the optical images shown in Figures 4 and 5, this makes it possible to chemically image samples while still resolving the primer layer. While the instrument used for  $\mu$ -FTIR could only collect a single spectrum across the primer layer, the instrument used for O-PTIR was able to collect seven spectra from the same area. By selecting spectra in the middle of the layer, it is possible to ensure that adjoining layers are not contributing to the primer layer's signal. This alone is likely not enough to justify the use of O-PTIR over  $\mu$ -FTIR for most samples given that it is not currently included in forensic standards, but the superior spatial resolution may become crucial as car manufacturers move towards thinner primer layers.

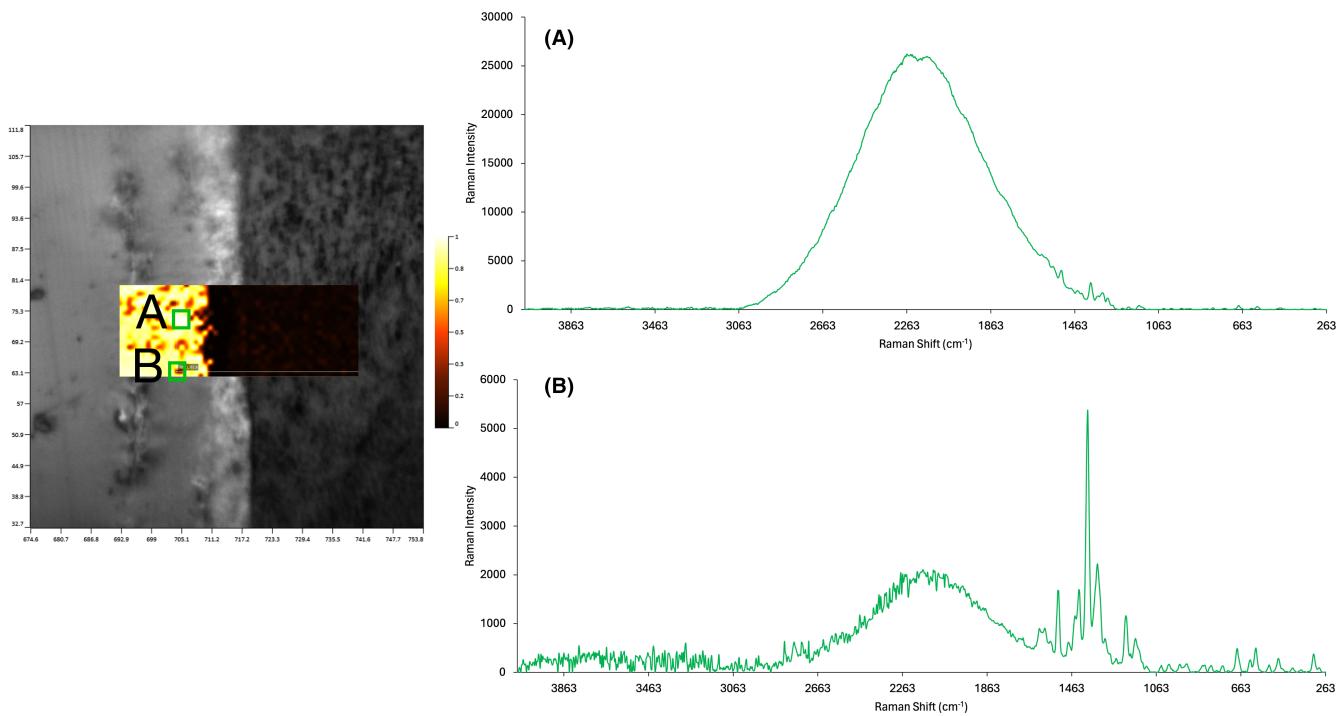


**FIGURE 4** Optical image of Vehicle ID 1 with overlaid Raman spectral data. The spectral heat map depicts the distribution of titanium dioxide within the primer layer and was created by integrating the peak at  $610\text{cm}^{-1}$ .

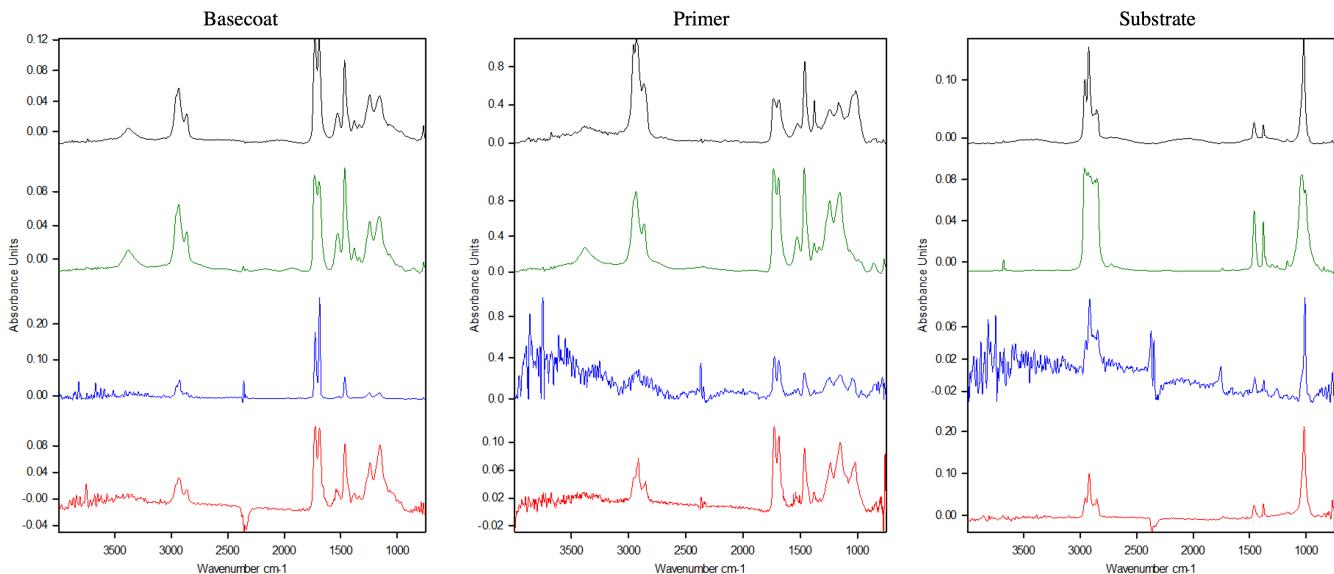
### 3.2 | Comparison of $\mu$ -FTIR modes of analysis

While FTIR microspectroscopy is a well-validated technique for the analysis of automobile paints, it was critical to determine if it still produced quality spectra for thin primer layers given that their size puts at the resolution limit of this technique. While the results of this analysis are not necessarily novel, they are presented here as confirmation that the norms associated with FTIR microscopy for automotive paint samples still hold true near the  $5\text{ }\mu\text{m}$  spatial resolution limit. To that end, Figure 6 shows a comparison of the spectra obtained from a single paint chip using all three techniques. As expected, the transmission and transflection modes produced better-quality spectra compared to the reflection and  $\mu$ -ATR modes. The peaks are sharp and well defined, and there is little to no atmospheric contamination. In all layers, the reflection and  $\mu$ -ATR modes show considerably more atmospheric peaks. This is problematic as the water peaks that appear from  $4000\text{-}3400\text{cm}^{-1}$  can hide the presence of peaks characteristic of paint components such as kaolin. Overall, the  $\mu$ -ATR spectra do show fewer and less intense atmospheric peaks than the reflection spectra. This makes  $\mu$ -ATR promising due to its lack of sample preparation. However, this is offset by

the fact that since the  $\mu$ -ATR crystal makes contact with the sample, it will result in an indentation on the sample's surface. While this may not be an issue for larger samples, it could make replicate analysis difficult to impossible for smaller paint chips. Additionally, the physical contact between the crystal and the sample carries the risk of contamination across multiple measurement points. As such, analysts choosing this method should clean the crystal thoroughly between measurements, especially when performing line scans. In contrast, the reflection mode required more corrections to obtain transmission-like spectra, resulted in very noisy spectra, and still showed atmospheric peaks after corrections were applied. These results demonstrate precisely why reflection is so rarely used in automotive paint analysis. In theory, transmission, transflection, and  $\mu$ -ATR modes all produce spectra that may be good enough to identify major components, but  $\mu$ -ATR mode may not allow all components to be identified due to atmospheric contamination and also carries the risk of physically contaminating the sample. Reflection mode did not produce good-quality spectra and should be avoided unless being used as transflection. Therefore, while transmission mode does require more sample preparation, the resulting spectral quality makes it the best choice for forensic analysts.



**FIGURE 5** Optical image of Vehicle ID 1 with overlayed with Raman spectral data. Integrating the peak at  $2250\text{ cm}^{-1}$  makes it possible to identify areas whose spectra display strong autofluorescence (A) as well as areas with better-quality spectra (B).

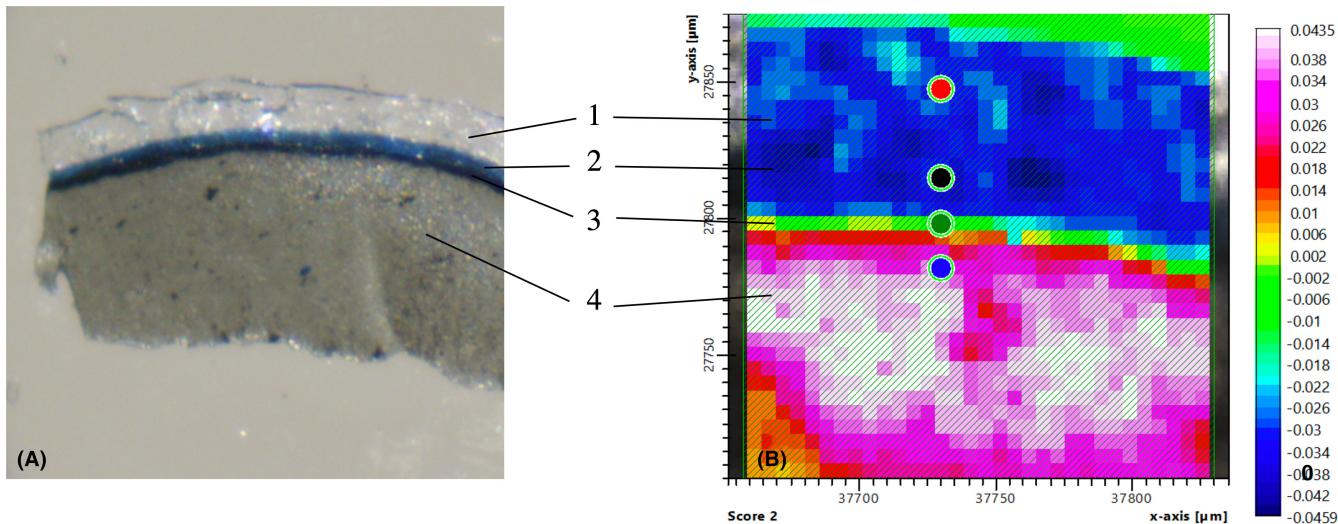


**FIGURE 6** Comparison of basecoat (left), primer (middle), and substrate (right) spectra using transmission (top, black), transfection (top middle, green), reflection (bottom middle, blue), and  $\mu$ -ATR (bottom, red) modes.

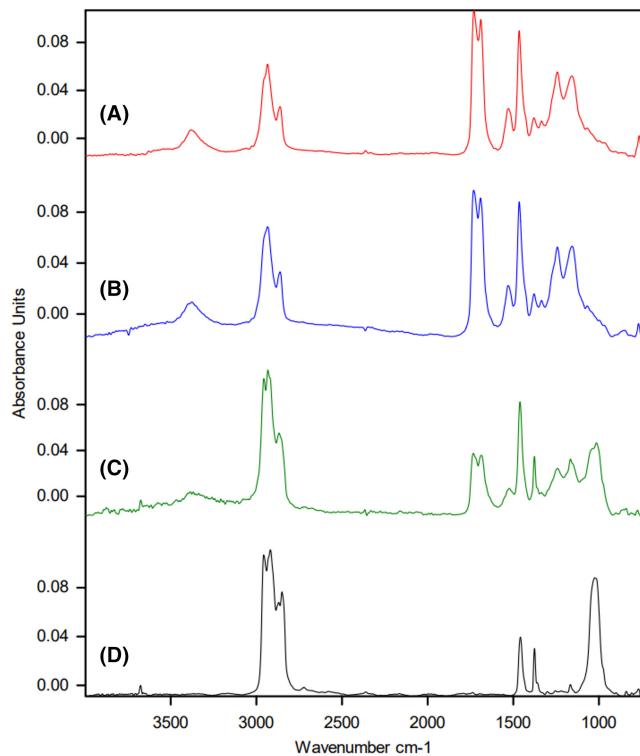
### 3.3 | Comparison of chemical imaging versus point analysis

Both optical and chemical images were taken of each sample with the LUMOS II and SZMT2 stereomicroscope in Figure 7. Figure 7A shows an optical image displaying the individual paint layers. Labeled as layer 3, the primer, which is the focus of this project, appears as the very thin,

barely visible black line between the blue-colored basecoat (Figure 7A, layer 2) and the plastic substrate (Figure 7A, layer 4). Figure 7B is created using the “Factorize 3D” macro in OPUS 8.7 to perform a factor analysis (FA) on the spectral data, which is similar to a principal component analysis (PCA). While both FA and PCA are useful for dimensionality reduction, FA is better suited for grouping samples that are highly correlated. By calculating a numeric factor loading for each



**FIGURE 7** (A) Stereomicroscope image of sliced paint chip for Vehicle ID 1. (B) Factorization plot of the spectral data overlaid on the physical image of the same paint chip, with colors indicating degrees of spectral differences. Individual layers can be seen by the following: (1) clearcoat (2) basecoat (3) primer (4) plastic substrate. Colored dots in 2B depict the location of the extracted spectra shown in [Figure 8](#).



**FIGURE 8** Spectral differences between paint layers. Spectra extracted from the correspondingly colored points in [Figure 7B](#) above. (A) Clear coat (B) Basecoat (C) Primer (D) Plastic Substrate.

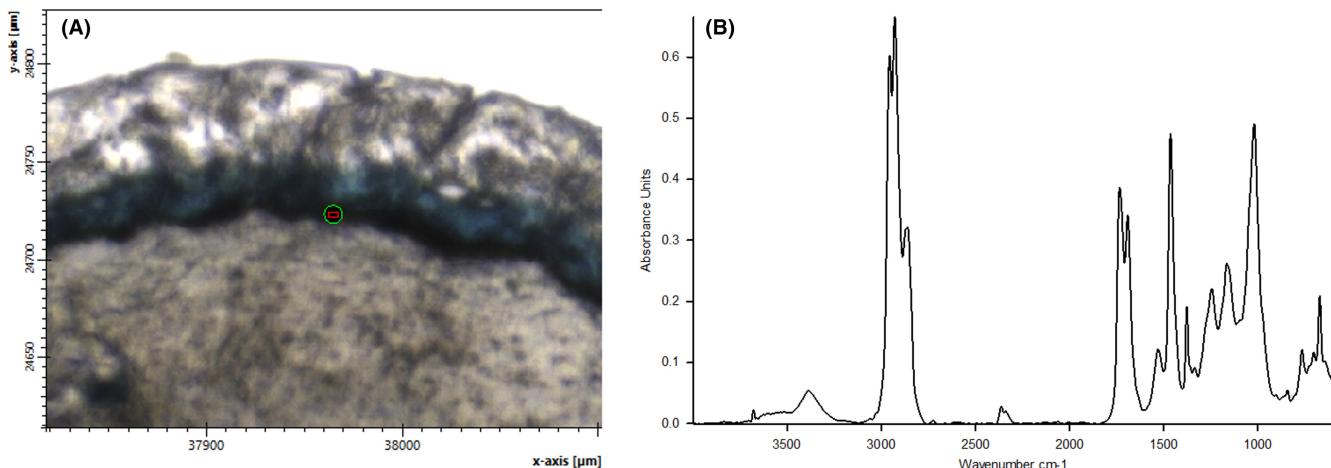
spectrum and then assigning a color to the loading values, a false color image can be created based on the spectral data and overlaid on the physical image of the sample. The use of these plots allows for a visual comparison of the chemical makeup of a sample. As seen in [Figure 7B](#), the chemical composition of the clearcoat and basecoat are extremely similar, while the composition of the substrate is markedly different.

Though the primer layer does not appear to group with either set of layers, spectra extracted from this area show only a mixture of peaks from the basecoat and substrate ([Figure 8](#)). While only a representative sample is shown below, all samples analyzed with the FPA detector showed similar non-unique primer spectra. This could either be because the primer composition is very similar to a mix of the substrate and basecoat or be due to the limited spatial resolution of the FPA detector. As seen in [Figure 7B](#), each single measurement point covers a  $5 \times 5 \mu\text{m}$  square. Given that most of the samples had primer layers that were approximately  $5 \mu\text{m}$  wide, it was difficult to tell if the adjoining layers had been entirely excluded using this method. Due to this, single-point measurements with the MCT detector were also collected.

While the FPA can collect many spectra very rapidly, the advantage of the MCT detector is that it can be used to analyze much smaller areas. While the spatial resolution of FTIR microscopy is limited to  $5 \mu\text{m}$  due to the IR light's diffraction limit, it is possible to analyze areas smaller than this by using a knife-edge aperture. As shown in [Figure 9](#), this feature along with using liquid nitrogen to cool the MCT detector, yielded good-quality spectra from the primer layer. Since the knife edge aperture was blocking the signal from the adjoining layers, it can clearly be seen that the similar peaks in the primer compared to the basecoat and substrate are likely due to similar chemical compositions. Additionally, the extended wavenumber range of the MCT showed peaks that were not seen in the FPA spectra. All ten samples displayed peaks below the  $750 \text{ cm}^{-1}$  cutoff of the FPA detector, which may provide crucial information on the inorganic components of the primer.

## 4 | CONCLUSIONS

We have investigated several promising new methods to collect FTIR spectra of the primer layer applied to plastic automotive bumpers via



**FIGURE 9** (A) Optical image of Vehicle ID 1 with the knife edge aperture shown in red and (B) its associated spectra collected using point analysis (MCT).

$\mu$ -FTIR and O-PTIR. Both techniques require very minimal sample preparation compared to conventional methods that require separating each paint layer manually. While these methods do require cutting the sample to expose a cross section, the analyses themselves are non-destructive, which allows the samples to be retained and reanalyzed as needed. In terms of characterizing all layers of the paint system, single-point analysis via transmission mode  $\mu$ -FTIR is still the best technique, with transfection and  $\mu$ -ATR also showing promise. However, O-PTIR may provide a suitable alternative method for primer layer characterization, especially for primers less than 5  $\mu$ m thick. Further work is needed to fully validate this new technique, but our results suggest that this technique shows enough promise to justify the time and resources involved in doing so. We think it is likely that the results of a full validation study would show that O-PTIR should be considered for inclusion in upcoming ANSI/ASB standards guidelines regarding the forensic analysis of automotive paint.

One limitation to this work is that as academic researchers, we did not have direct access to the car paint database systems maintained by law enforcement. This means that while we can make recommendations about the strengths and weaknesses of the methods based on their suitability for use with the current database systems, we cannot provide direct comparisons between the spectra collected in this study and the corresponding library spectra in these databases. This is less of a concern for FTIR microspectroscopy as it is already part of the published standards for forensic paint analysis. However, given the novelty of O-PTIR, future work should be undertaken to validate this technique for use with such databases before it is integrated into forensic workflows.

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#### CONFLICT OF INTEREST STATEMENT

The authors have no disclaimers or conflicts of interest to report for this work.

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