Document Title:	**Raman Spectroscopy of Automotive and Architectural Paints: In situ Pigment Identification and Evidentiary Significance**
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Raman spectroscopy of automotive and architectural paints: *in situ* pigment identification and evidentiary significance.

18 July 2013

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This report is respectfully dedicated to my colleague, uncle, and Godfather,

Mark Edward Palenik

who passed away early and unexpectedly.

I would not be where I am today without

his mentoring, knowledge, and integrity.

Our family and the staff at Microtrace will greatly miss

his scientific contributions, humor, and daily presence in our lives.

- Chris Palenik
  November 28th, 2012

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INTRODUCTION

Pigments are encountered in many kinds of trace evidence, including automotive and architectural paints, inks, fibers, and plastics. Traditionally, pigments have been studied by polarized light microscopy, microchemistry, infrared spectroscopy, py-GC/MS, SEM/EDS and X-ray diffraction. However, imitations inherent to each of these techniques have constrained the practical use of pigment identification in the analysis of trace evidence. Raman spectroscopy, which is becoming more widely available to forensic science laboratories, is the first analytical technique to provide the spatial resolution, sensitivity and specificity necessary to quickly and specifically identify a wide variety of pigments *in situ*.

The research presented here is a follow-up to internal research and a prior NIJ grant that resulted in a report entitled "Fundamentals of forensic pigment identification by Raman microspectroscopy" (Palenik et al., 2011). That initial research focused on developing the fundamental techniques that were required to identify pigments in microscopic specimens of forensic interest. This work involved extensive research into the following targeted areas:

- Validation and reproducibility studies to illustrate the reliability of pigment reference samples and Raman microspectroscopy as a pigment identification method.

- The development of a database of high quality Raman spectra, collected from verified reference samples, which represent approximately 300 commercial inorganic and organic pigments.

- The development of a systematic method for pigment identification from Raman spectra. This scheme was designed not only to identify pigments, but also to provide a way to determine the specificity of a pigment identification through a classification based on pigment chemistry and comparison to other pigments with similar chemistries.

- The production of a "Practical Manual of Pigment Identification" intended for use at the laboratory bench by trace evidence analysts. This manual provides the basic information needed to understand pigments, pigment nomenclature, pigment classification and best practices for reference pigment characterization.

This ultimate result of this research was the development of the largest and most complete, systematic, analytical organization of organic pigments ever directed specifically towards the forensic science community. It established the necessary background information required to solve practical questions regarding pigment identification involving actual forensic samples (a task that has been heretofore largely avoided or ignored because pigments are almost always encountered as near trace level components in mixtures encapsulated in a matrix).

The research that is the subject of this report, therefore, focuses on the identification of pigments as they occur in automotive and architectural paint samples and the development of practical forensic methods for pigment analysis and identification. This research focused primarily on automotive paints, since these are the most commonly encountered type of paint in criminal forensic cases; however, we have also studied various groups of architectural tinting pigments (which represent the colors added to white paint to make virtually every type of indoor and outdoor architectural paint produced in the United States) and a smaller set of architectural paints.

Several pigment analysis approaches were evaluated and these are presented here as practical methods that are ready for direct application to casework. These methods involve a) a fast screening method, which can be utilized at the beginning of an examination (prior to FTIR or SEM/EDS analysis) to conduct an analytical comparison on a sample, as received (no sample preparation required); b) a cross section preparation method, which has utility for routine identification of bulk pigments in a sample, and c) a thin section method utilizing two micrometer (2µm) sections and confocal Raman microspectroscopy for advanced characterization of individual pigment granules.

The data collected have been evaluated in terms of several possible applications and in light of other analytical methods (particularly FTIR) to see how they compare with traditional analytical methods for paint, if they are complementary to these traditional methods, and whether Raman spectroscopy ever provides discrimination beyond that provided by FTIR spectroscopy (which, as our examples prove, it does). The results presented here are not a final answer, but they do provide the first practical guidelines (supported by solid analytical data) for the application of these methods in a forensic laboratory, and establish applications where Raman spectroscopy could reasonably be expected to provide improved benefits in casework involving trace evidence containing pigments.

ANALYTICAL DETAILS

SAMPLE COLLECTION

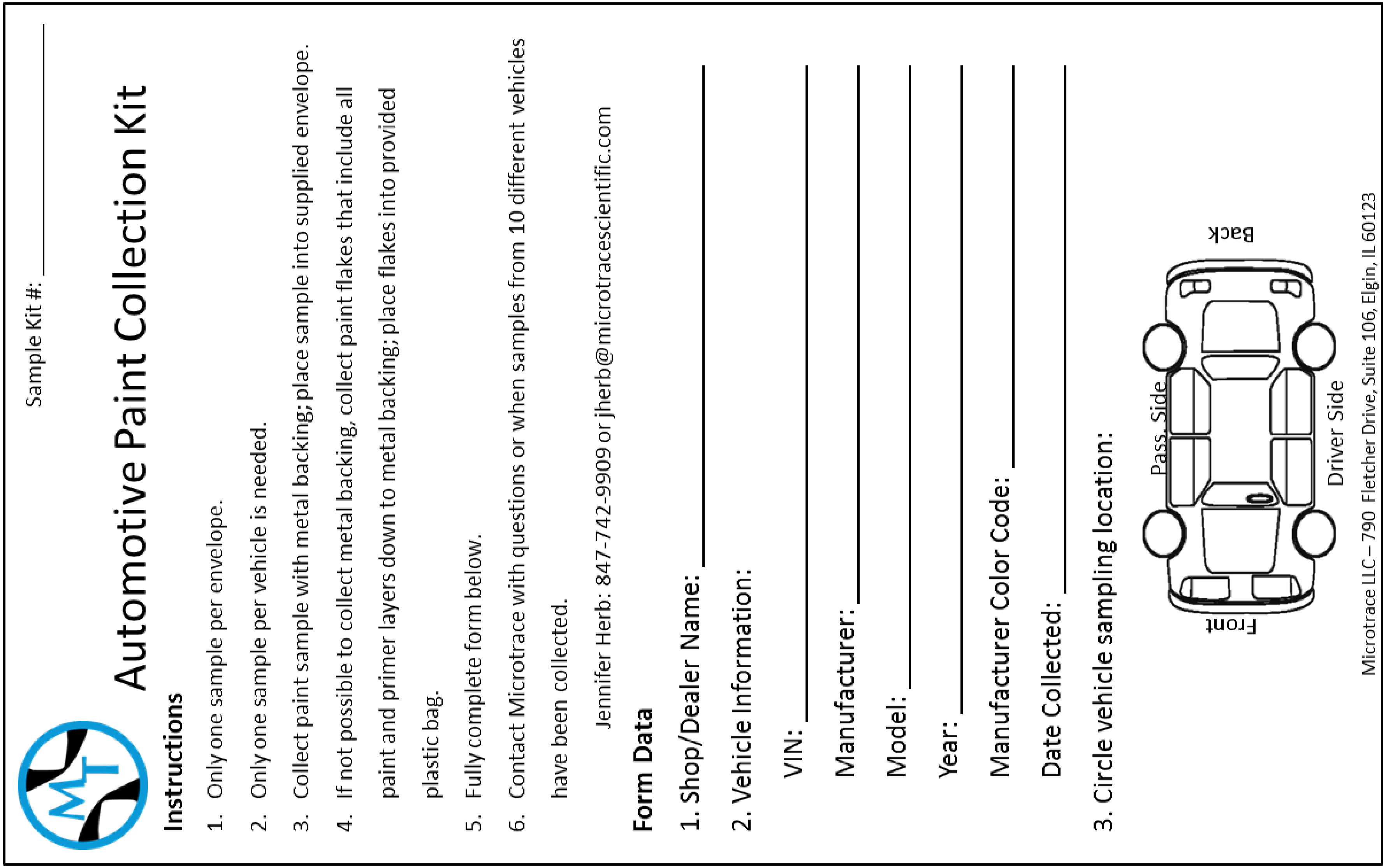
AUTOMOTIVE PAINT SAMPLES

The automotive paint samples utilized in this work are “street” samples collected by soliciting local body shops. These shops were asked to remove a small piece of paint, including the substrate (*i.e.*, plastic or metal backing) from vehicles requiring body repair. All samples were, therefore, collected from damaged areas of vehicles. In addition to the paint, shops were also asked to provide basic information about each vehicle. A total of 28 sources (*i.e.*, body shops, dealerships, junk yards, *etc.*) participated, resulting in the acquisition of 328 samples.

Sampling Kits

Each shop that agreed to participate was provided with a number of “Sample Kits” prepared by Microtrace. The sampling kit consisted of a 5” x 8” envelope with a label on the front. Inside of the envelope was a plastic bag to be used for smaller samples or samples that did not include the substrate (paint only). The front label provided space to fill in requested sample information (Figure 1):

- Body Shop/Dealer name (source of sample);
- Vehicle Identification Number (VIN)
- Year
- Make
- Model
- Manufacturer’s color code
- Date collected
- Area of vehicle sampled (circled on a graphic)



Sample Kit #: ____________

Automotive Paint Collection Kit

Instructions

1. Only one sample per envelope.
2. Only one sample per vehicle is needed.
3. Collect paint sample with metal backing; place sample into supplied envelope.
4. If not possible to collect metal backing, collect paint flakes that include all paint and primer layers down to metal backing; place flakes into provided plastic bag.
5. Fully complete form below.
6. Contact Microtrace with questions or when samples from 10 different vehicles have been collected.

Jennifer Herb: 847-742-9909 or jherb@microtracescientific.com

Form Data

1. Shop/Dealer Name: ____________

2. Vehicle Information:

VIN: ____________

Manufacturer: ____________

Model: ____________

Year: ____________

Manufacturer Color Code: ____________

Date Collected: ____________

3. Circle vehicle sampling location:

Microtrace LLC – 790 Fletcher Drive, Suite 106, Elgin, IL 60123

Figure 1. Automotive paint collection information page

Quality Index

The amount of information obtained with each sample varied greatly. In many instances, all of the requested information was provided; however, in some cases, only make and model were listed. As a result, a quality index rating was implemented to quickly assess the quality of samples. Samples received with all the requested information were given an index of "1"; samples with less information were labeled between 2 and 5. The matrix shown in Table 1 was created as a quick reference to indicate the quality index (Q.I.) rating per sample.

Table 1. Automotive paint sample quality index matrix; Y = Yes/Known, N = No/Unknown

Quality Index	Color Code	VIN	Year	Make	Model
1	Y	Y / N	Y	Y	Y
2	Y	N	N	N	N
3	N	Y	Y	Y	Y
3	N	Y	N	N	N
4	N	N	N	Y	Y
4	N	N	Y	Y	N
4	N	N	N	Y	N
4	N	N	Y	N	N
5	N	N	N	N	N

In the event sample information was not provided, an attempt was made to look-up missing information. If the sample was unique enough, the body shop/dealership was contacted and solicited for the additional information. Other samples required using a VIN decoding website to obtain a year, make or model (see Free VIN Decoder reference). Additional webpages were utilized to determine a likely color code based upon year, make and model information (AutomotiveTouchup.com and Expresspaint.com). Information that could not be solicited or found was ultimately left blank, resulting in a lower quality index rating. Information that was looked-up by Microtrace was noted as such in the database.

Color Codes

One obstacle encountered when researching color codes were the use of multiple alphanumeric codes for a single color. For example, a 2011 Chevrolet Impala, color name "Red Jewel Tintcoat Metallic," has four associated color codes: 301N; 80; GAQ; and WA301N. This is a common occurrence because many companies make more than one brand of car, and a single brand is produced in more than one factory. GM, for example, produces Buick, Cadillac, Chevrolet, GMC, Hummer, Pontiac, Saturn, *etc*. Chevrolet in return has factories in Michigan, Kentucky, and Canada, to name just a few. The various color codes were found to be synonymous within the same company or manufacturer but not necessarily across manufacturers (*i.e.*, WA301N by Chevrolet is equivalent to Pontiac's GAQ designation, but has no equivalent color code in a Chrysler model). All of this information was compiled in a database (described in a following section).

Sample Distributions

The collection of automotive paint samples from a variety of sources resulted in a broad distribution of collected samples. The three hundred paint samples used in this study span thirty-four manufacturers; the highest contributor being Toyota followed closely by Chevrolet (Figure 2). Figure 3 shows a comparison of paint samples by manufacturer compared to the distribution of automobiles sold in the US in 2011.

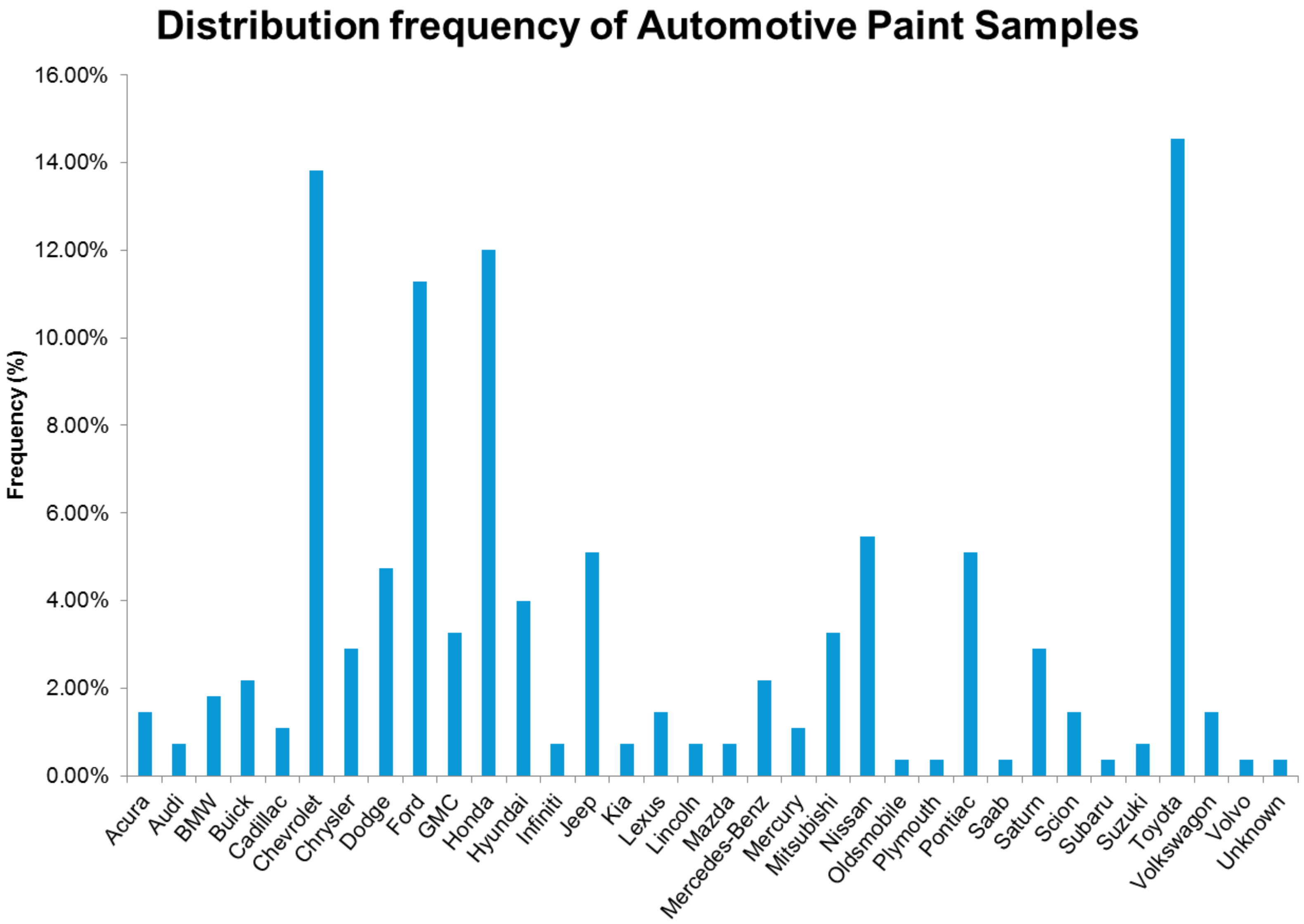


Figure 2. Histogram of Microtrace automotive paint sample population distribution by manufacturer.

2011 U.S. Top Selling Manufacturers

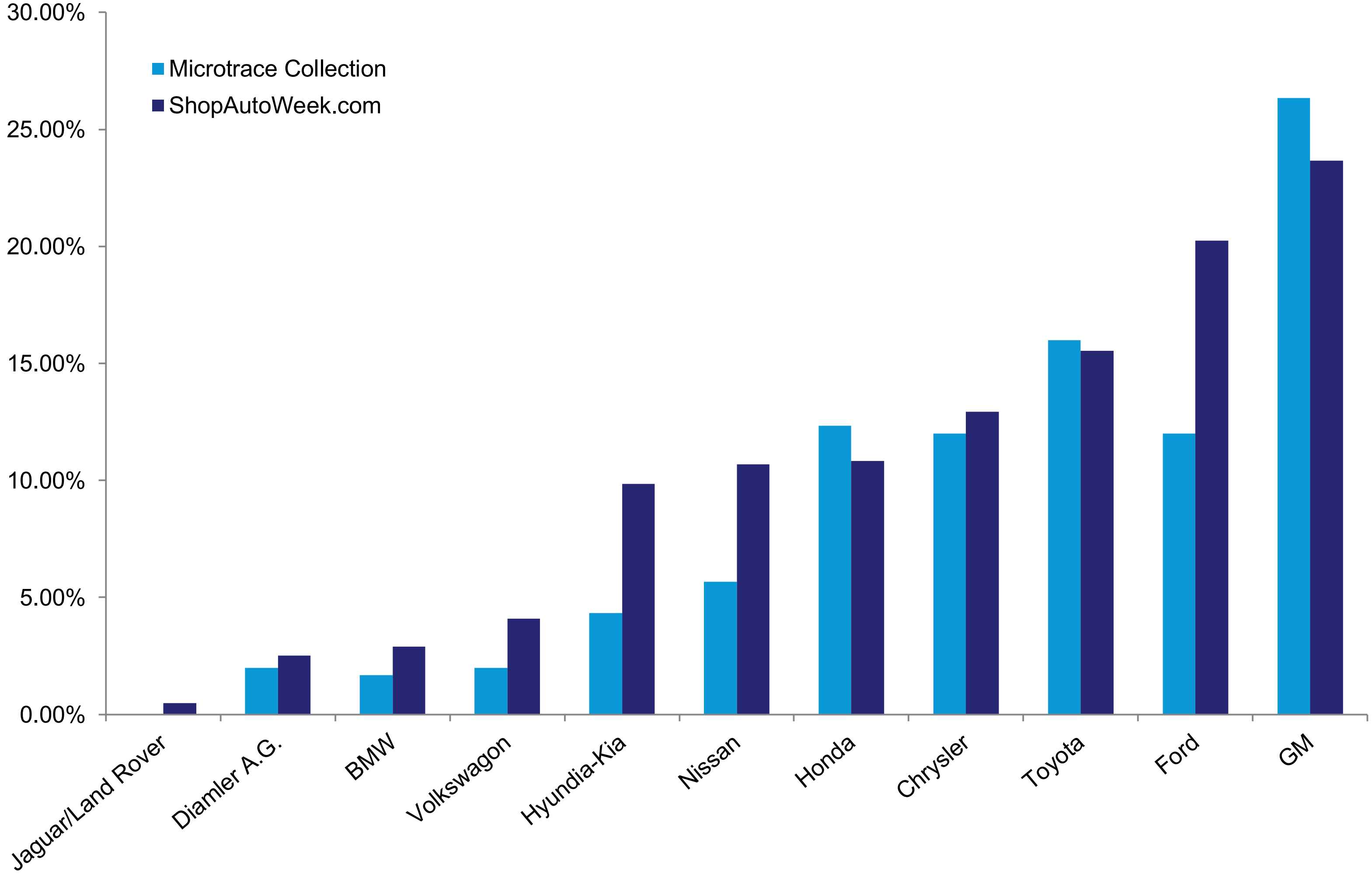


Figure 3. Comparison of 2011 distribution of US cars sold to the distribution of automotive paint samples collected here. Data are presented in percentage. The US car data is from shopautoweek.com (see references for link to data) and is based on a total of 12,048,673 cars sold (2011), and the auto paint samples data is based on a total of 300 samples collected by Microtrace LLC.

The distribution of nominal paint colors (as classified by Microtrace) is shown in comparison to the distribution of DuPont automotive paint sold in North America in 2011 (Figure 4.) In the samples collected here, a disproportionate number of silver colored automotive paints were returned, which may suggest a Midwestern color preference (samples were collected in the suburban Chicago area). Toward the end of our sampling period, we asked the sampling locations to limit or exclude white and black paint samples in order to bias the collection toward colors that we anticipated would contain a more diverse range of pigments. This ultimately increased the relative proportion of red samples. Yellow and orange paints were still more difficult to collect and are the least represented population of colors within this study.

Finally, the distribution of collected paint samples binned by year of production is shown in comparison to a histogram of car ages on U.S. roads (2011) (Figure 5). Since the number of data points being compared in this series of figures differs by several orders of magnitude, it is difficult to say that the samples collected truly represent current U.S. car demographics. We can state, however, that all major categories (as noted in each of these figures) are represented. Furthermore, the pigment data collected here is likely to be valid for some time into the future, considering that a significant percentage of cars on the road today are still older than 1999. Given these two factors, we believe that this is an adequate collection of paint samples for a study of this nature.

Once organized, the 328 samples collected were narrowed down to 300 samples, from 27 sources. Samples were removed from this study on the basis of a number of factors including the quality index number and the amount sample submitted. A summary of the paint samples studied is presented in Appendix A.

ARCHITECTURAL PAINT SAMPLES

Architectural paints were collected by Microtrace employees. In total 48 samples were collected, representing 10 different brands. Each sample was added to a database and assigned a colorant number to be used throughout this research. A quality index rating was assigned based on the information provided with the sample, which was then plotted on the matrix shown in Table 2.

Table 2. Architectural paint sample quality index matrix; Y = Yes/Known, N = No/Unknown

Quality Index	Tinting Pigments Known	Manufacturer	Manufacturer Color	Base Coat
1	Y	Y	Y	Y
2	N	Y	Y	Y
3	N	Y	N	Y
3	N	Y	Y	N
4	N	Y	N	N
5	N	N	N	N

The highest rating, "1", would include: tinting pigments (*e.g.*, C, KX, RU, T[1]), manufacturer (*i.e.*, Behr); manufacturer color (*i.e.*, Flaming Torch); and base coat (*i.e.*, Deep Base, Semi-gloss). As with the automotive paint samples architectural paints submitted for this project came with varying amounts of information. Architectural

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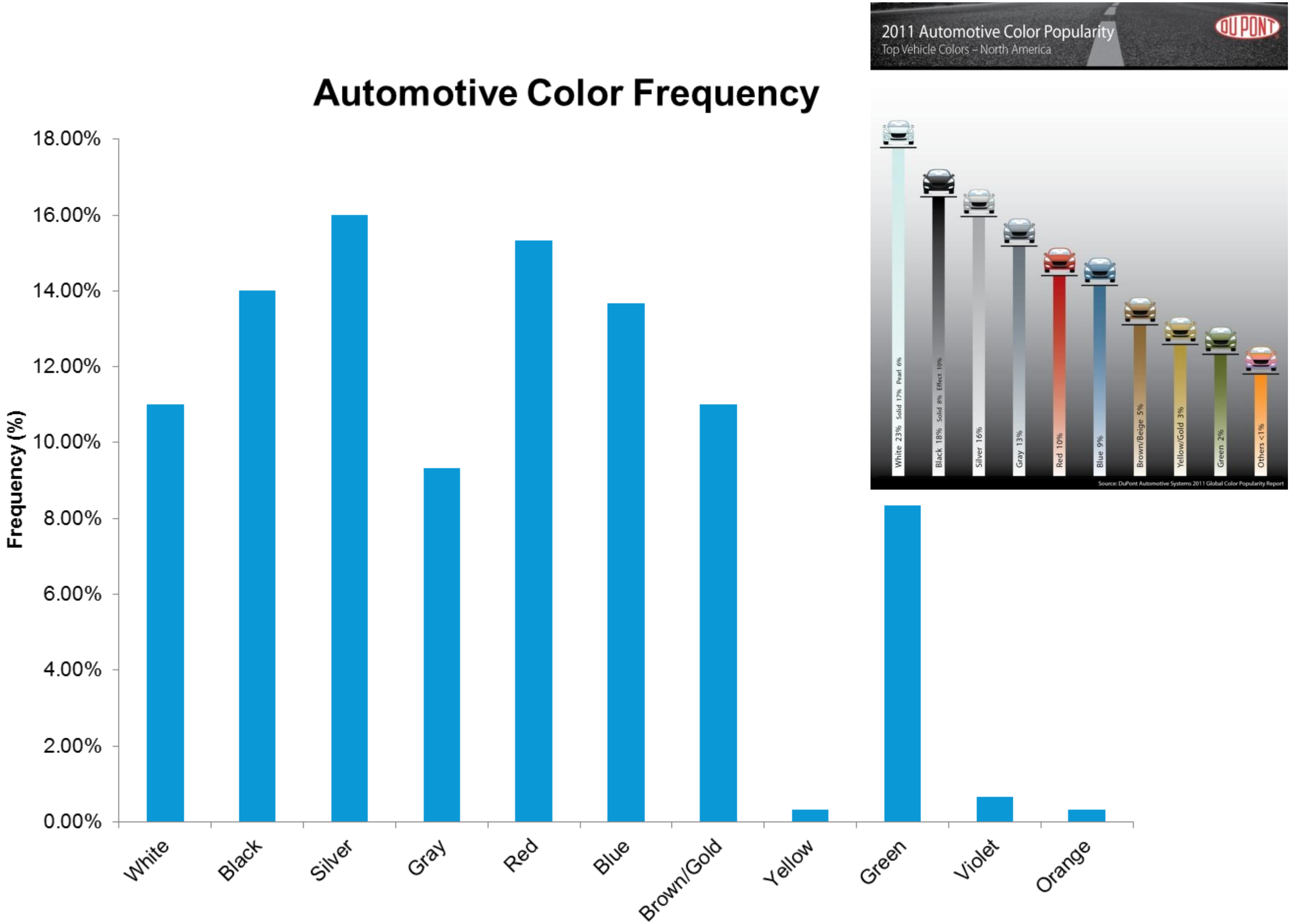
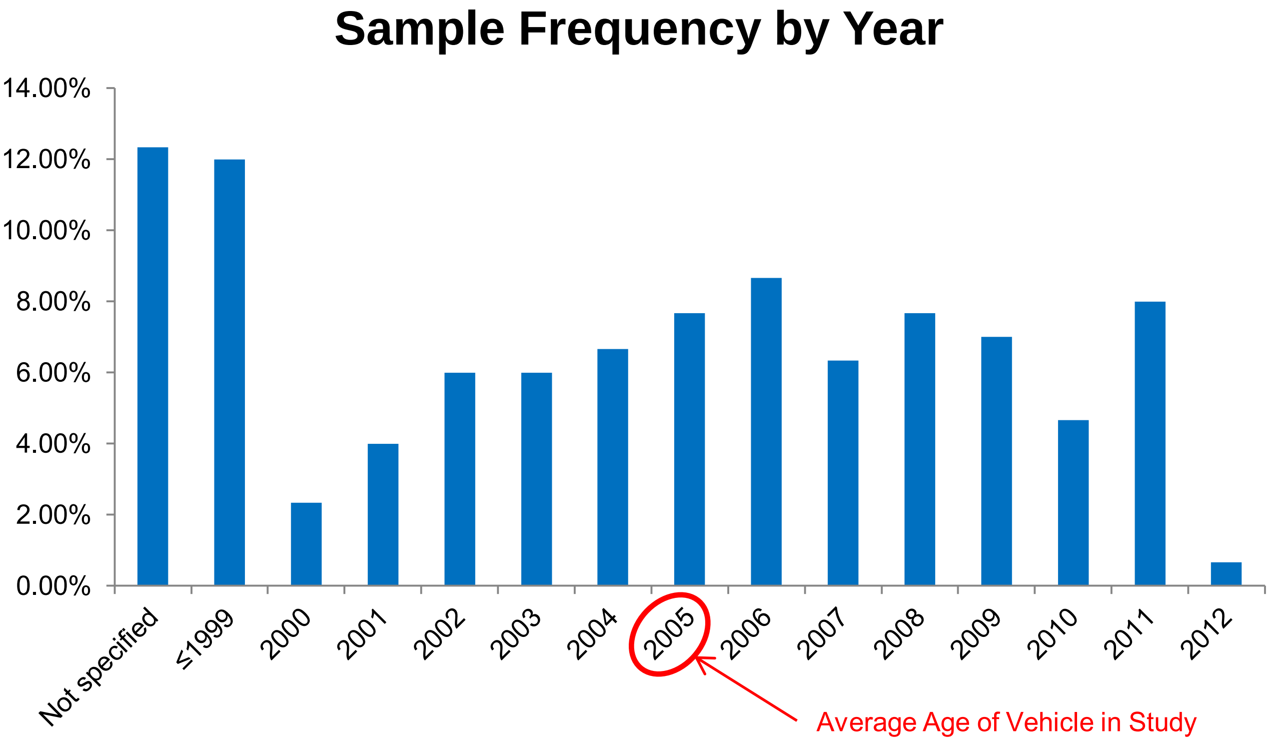
[1] These are examples of manufacturer tinting code designations of the type that would appear on custom architectural paint colors.



Source: DuPont Automotive Systems 2011 Global Color Popularity Report

Figure 4. Histogram of Microtrace automotive paint sample population distribution by color. Inset shows the DuPont automotive paint color production in North America in 2011.



Average Age of Vehicle in Study

Average Age of Passenger Cars and Light Trucks			
Year	Passenger Cars	Light Trucks	Total Light Vehicles
1995	8.4	8.3	8.4
1996	8.5	8.3	8.5
1997	8.7	8.5	8.6
1998	8.9	8.5	8.8
1999	9.1	8.5	8.8
2000	9.1	8.4	8.9
2001	9.3	8.4	8.9
2002	9.4	8.4	9.0
2003	9.6	8.5	9.1
2004	9.8	8.6	9.4
2005	10.1	8.7	9.5
2006	10.3	8.9	9.7
2007	10.4	9.0	9.8
2008	10.6	9.3	10.0
2009	10.8	9.8	10.3
2010	11.0	10.1	10.6
2011	11.1	10.4	10.8

Source: Polk
(note figures are from July 1 each year)

Figure 5. Histogram of Microtrace automotive paint sample population distribution by age. Inset is a table of the U.S. automobile age distribution as of 2011.

paints were selected for analysis on the basis of the quality index and color. Ultimately, 20 samples from 7 brands were studied (Figure 6). A summary of the paint samples studied is presented in Appendix A.

In addition to the field samples, a number of “tinting” pigments were also studied. Tinting pigments are valuable because they represent the actual colorants, which are added to a white base to produce custom interior and exterior paint colors. In this work, two sets of tinting pigments were analyzed. Thus the pigments identified in these two sets represent the majority of pigments that would be expected to be found in commercial and residential interior and exterior acrylic paints in the U.S. Figure 7 shows images of the various tinting pigments studied.

FIELD SAMPLE DATABASE

Microtrace developed and has maintained a colorant database for the past fifteen years, which has evolved into an increasingly complex relational database. This database consists of the following sub-databases:

- *Colorant Data*. Metadata concerning a specific colorant such as generic name, CI generic number, CI constitution number, chemical formula, structure, *etc*.

- *Colorant Reference Samples*. Data concerning individual reference samples including information such as manufacturer, quality index, source, trade name, manufacturer number, *etc*. This database consists of:

    - Pigment Reference Samples
    - Dye Reference Samples
    - Effect Pigment Samples

- *Field Sample Data*. This database concerning individual paint sample collected in the field is actually composed of two related databases, one that contains general sample information and cross section images, and the other that contains layer specific information permitting colorants and binders identified as well spectral data for individual layers. This permits extensive cross-referencing and summarization of data. Samples in this database include (but are not limited to):

    - Automotive Paint Samples
    - Architectural Paint Samples
    - Shade cards

For the samples collected for this project, each sample was assigned a unique identification number and all relevant data for each sample were added to our colorant database. The database provided a simple repository to organize and summarize all collected data. Through the relational nature of these databases, specific pigments can be associated with a specific sample layers, permitting samples and pigments to be cross referenced. For example, all automotive paint samples containing a specific pigment can be quickly tallied, or alternatively, information about all pigments in a given paint sample can be determined. This information was also grouped by layer, so that colorants within individual layers could be compared within a sample. As will be discussed later, paint specimens composed of multiple layers often contain layers with different pigment compositions.

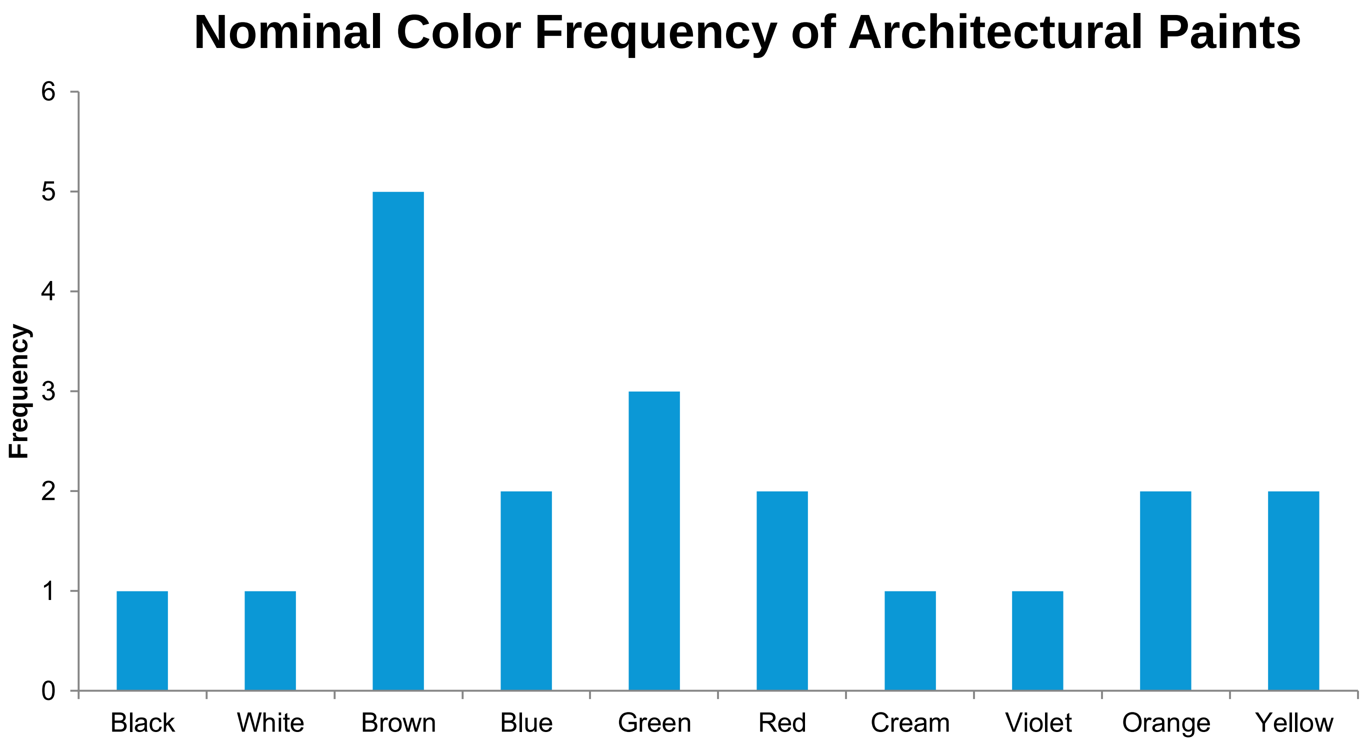


Figure 6. Nominal color distribution of 48 acquired architectural "field" samples.

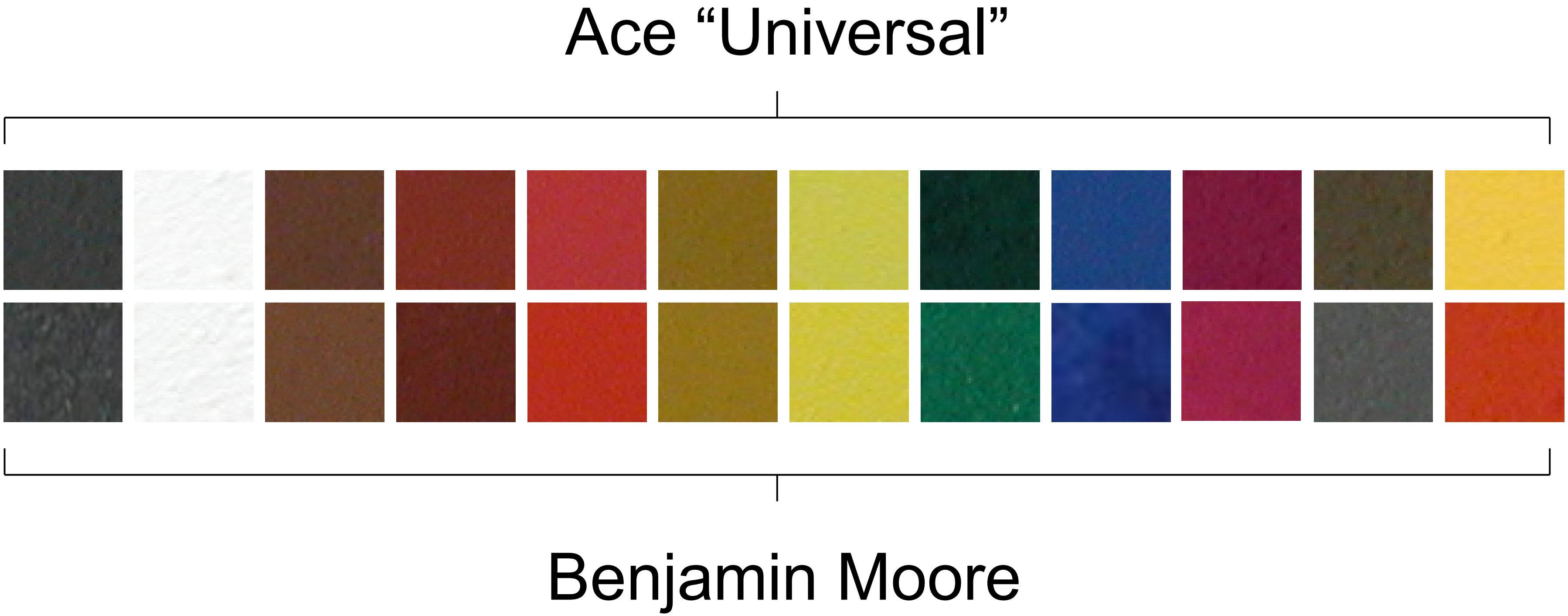


Figure 7. Tinting pigment colors analyzed.

SAMPLE PREPARATION

The methods described below were developed to allow automotive and architectural paint samples to be properly prepared for analysis by multiple analytical methods. As will be shown in later in this report, the level of information obtained from a sample is positively correlated with the amount of time spent on sample preparation. While a great deal of information can be obtained through the study of samples that have undergone no sample preparation, it is only with careful sample preparation that subtle differences can be exposed and relied upon for the highest levels of discrimination.

For example, a study of batch to batch differences in white and red automotive paints by Stocklein and Palenik (1998) showed that subtle but reproducible differences in both FTIR and MSP data could be used to consistently differentiate paints of the same color code, produced by the same manufacturer, at different times. Only through careful sample preparation, could these subtle differences be reliably interpreted and reproduced. This section discusses the approaches used in this study to prepare each sample for analysis by Raman and micro-FTIR spectroscopy.

SAMPLING PAINT FROM SUBSTRATE

Once each sample was given an ascension number, a subsample was removed for analysis. The paint systems sampled had been applied to either metal or polymer substrates. A different sampling approach was utilized to recover paint from each of the substrates.

To remove paint from a metallic substrate, the surface was scored with a cleaned razor blade, and the metal was bent back with a pair of pliers. In most cases, bending caused the paint to delaminate from the metal backing, releasing large flakes, which were isolated for later use. In cases where the paint could not be easily delaminated, a clean single edge razor was used to scrape paint from the substrate. Repaints were the most difficult to sample (especially if additional primer layers were present). It was our experience these paints tended to delaminate at the primer-paint interface (rather than the preferable paint-substrate interface). Once the sample was bent, a cleaned razor was scraped along the metal backing to isolate the paint from the substrate. Only chips with a complete layer structure were retained for analysis.

The removal of paint from a polymer backing was more straightforward. A cleaned razor blade was scraped along the sample so that it passed under the paint and along/through the polymer backing. It is important to pay special attention to ensure all layers of the paint are being removed. Repaint samples on a polymer surface were more easily sampled under a stereomicroscope, as it could be difficult to see that all layers had been sampled without additional magnification. Sampling from the edge of the paint flake was determined to be the best method for visualizing all layers being sampled. In one instance, a small square sample was removed from the larger piece with the use of heavy duty scissors. This paint sample had been repainted multiple times and trying to scrape all layers of the paint simultaneously caused a great deal of delamination. The polymer backing on the excised paint chip was removed with the use of a clean, single edge razor blade under a stereo microscope.

PREPARING EMBEDDING BLOCKS

Once the paint had been removed from its backing, a chip was placed on a glass surface and viewed under a stereomicroscope. A cleaned razor blade was used to cut a small rectangle from the larger chip. This rectangle was no more than a few millimeters wide and just slightly longer. The ultimate dimensions of the cut paint chip are limited by the size of the embedding mold being used. During sampling, the edges of the chip may not necessarily include all layers; for this reason, the embedded paint chip should be cut from an area where it is certain that all layers of paint are known to be present.

Multiple paint chips were embedded in a single mold utilizing a method developed by the paint examination section at the Bundeskriminalamt in Weisbaden (BKA), Germany. A small piece of double-sided tape is placed into the bottom of a silicone mold. The rectangular chips are placed into the mold on top of the piece of tape. Each paint chip is adjusted to sit vertically and be spaced evenly within the mold. When setting up the samples to be embedded, it is important to mount all the chips in the same direction. For these block preparations, the color face of each chip was always oriented so as to face the left. The block was then labeled using a small piece of paper with an identifier, which was then placed into the mold (Figure 8). The ascension number and location of each chip was recorded for future use.

The selection of an appropriate embedding medium is described in the following section of this report. The resin was slowly added from directly above the samples and allowed to flow into the mold without disturbing the chips. The mold can be placed in a bell jar under vacuum to force air bubbles out of the mold, if necessary. The resin was then cured according to the manufacturer's instructions. Excess resin was then trimmed from the preparation to present the smallest possible area to the microtome knife for sectioning.

EMBEDDING MEDIUM SELECTION

Sectioning paint has proven the best method for viewing complete layer structures and for generating reproducible analytical data. This reproducibility is of particular significance when attempting to make the most critical comparisons (such as the differentiation of two batches of the same paint applied at different times). While hand sectioning has been shown to be of utility in casework, generating thin, even sections of the highest level of reproducibility requires the use of a microtome and a sample mounted in an appropriate medium. Based on an informal study, it seems that every laboratory has its preferred embedding medium. Some are selected with good reasons and others for convenience. Regardless of the medium used, it is important to understand a) what the medium looks like by the instruments being utilized (*i.e.*, to ensure that the medium can be recognized by the analytical method being used) and b) whether traces of the resin can be detected in the sectioned samples (*i.e.*, whether the resin smears onto the sample). For the purposes of this, project several embedding media were evaluated and their various properties observed and evaluated to determine which medium would best suit the needs of this project. The following section describes the results of these tests.

Evaluated Resin Systems

Five different resin preparations were evaluated to determine which is best suited for the task of embedding multiple paint chips and cutting consistently reproducible good thin sections. Each resin was evaluated on the basis of clarity, hardness, curing speed and viscosity. Descriptions of each resin are listed in the table below.

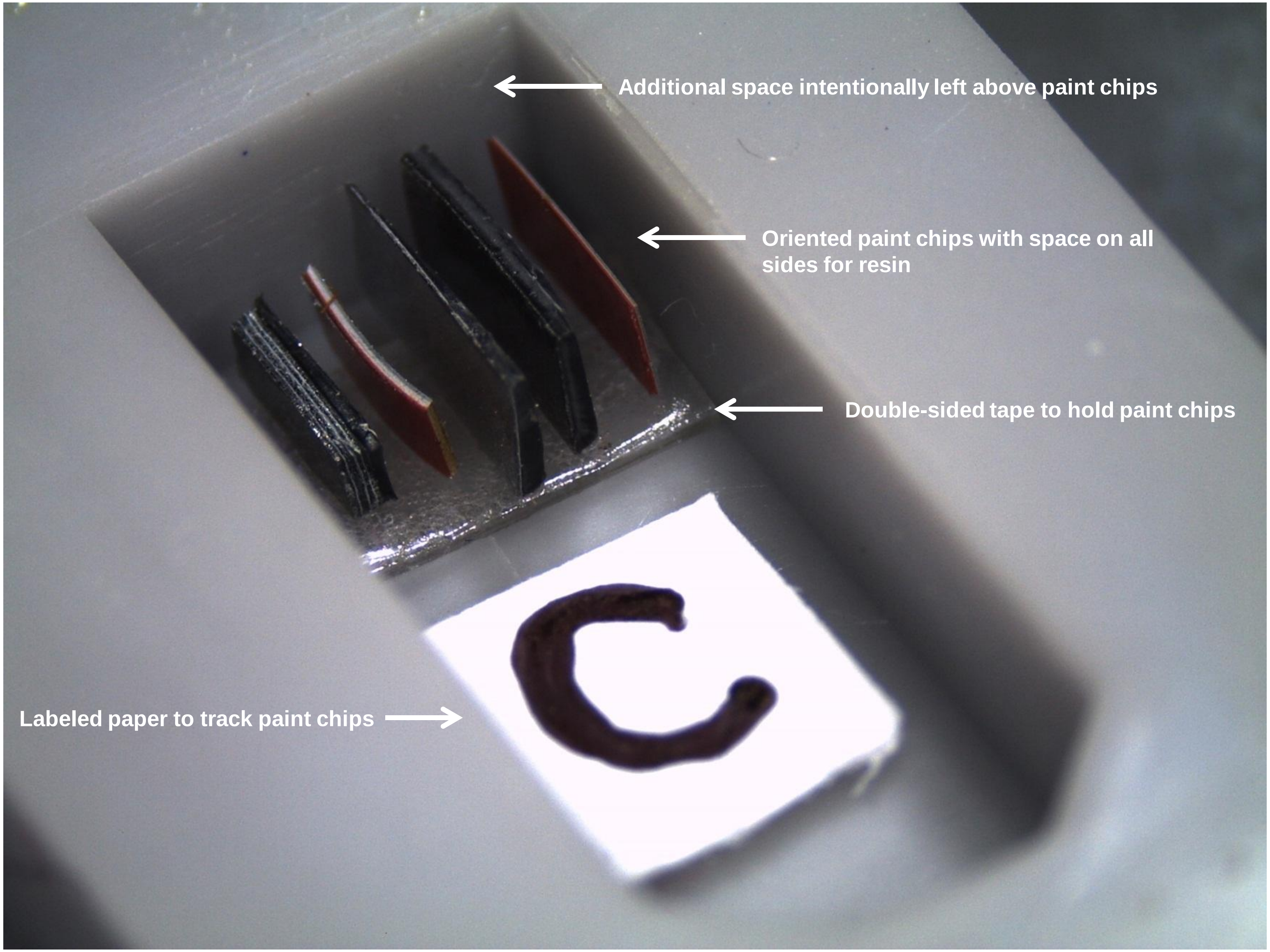


Figure 8. Silicone mold with paint chips mounted prior to the addition of embedding resin.

Table 3. Comparison of the properties of the five embedding resins evaluated.

Resin	Clarity	Color	Harness	Curing speed	Viscosity	Chemistry
Locktite® Heavy Duty	Cloudy	Yellow	Brittle	5 minutes	Medium	Epoxy
Tuffleye® Core	Clear	Colorless	Hard	$^{1}/_{3}$ minutes	Medium	Acrylic
Tuffleye® Finish	Clear	Colorless	Slightly Flexible	$^{1}/_{3}$ minutes	Medium	Acrylic
Double/Bubble® Extra Fast Setting	Cloudy	White	Hard	3-5 minutes	High	Epoxy
Double/Bubble® Dual Use – Adhesive & Coating	Clear	Colorless	Brittle	60 minutes	High	Epoxy

Air Bubbles

Upon preparation of samples using each resin, it was found that the Locktite® Heavy Duty and Double/Bubble® Extra Fast Setting epoxies each generated a large numbers of fine bubbles which disrupted the clarity of the preparations. While clarity is aesthetically displeasing, the bubbles create a more serious issue by preventing direct contact with the embedded chip. This lack of contact can lead to the chip being “plucked” from the mount during sectioning, which is a major issue, resulting in loss of time and potential sample loss or destruction.

Viscosity

The viscosity of the resin is important because the chips are placed into the silicone mold before the resin is introduced. If the viscosity is too high, it can displace the chips as is it flows into the mold, and/or trap air in the mold (at the bottom of the mold or in between the chips) resulting in incomplete bonding between the paint chips and resin.

Hardness

The Double/Bubble Dual Use and Locktite Heavy Duty epoxies both set as very hard and brittle solids. Extremely hard/brittle epoxies cause the microtome knife to chatter across, chip or splinter the blocks as it makes a pass. A complete thin and even section is difficult or impossible to cut when resins are overly hard. Over time, other resins can harden. The Tuffleye products which were selected for this study were sectioned over a 10 month period, which showed that even after aging for some time; good sections could still be cut.

Summary

On the basis of these criteria, the two Tuffleye products showed the best properties for our purposes. The Tuffleye resins are a blue-light curing acrylic, similar in composition to the acrylic bonding media used by dentists. Technovit®, a German company, also makes a blue light curing epoxy, LR White, which has been used for many years by the BKA paint section; however, it does not appear that this product is readily available in the U.S.

Ultimately, the Tuffleye Finish resin was found to be slightly more practical than the Tuffleye Core resin because the former has slightly fewer bubbles and is not as hard. The slight malleability of the Tuffleye Finish preparations seems to result in the best sections.

Spectral Evaluation

Once selected, the Tuffleye Finish resin was evaluated for its potential impact on analytical results. It is important that the medium holds the paint chip firmly, and does not smear or otherwise modify the sectioned paint sample. This is particularly important when attempting to compare minor spectral features, as any artifacts, particularly additions from the resin mount, could lead to confusion or errors. Since the Tuffleye is an acrylic resin, and paint systems are often based on an acrylic binders, the distinction between paint and resin becomes more difficult to detect, but is nonetheless of critical importance. To evaluate the potential for resin transfer, a series of embedded paint chips and polyolefin bumper fascia were sectioned and analyzed by the two vibrational spectroscopies utilized in this research. The results are detailed below.

Infrared Spectroscopy

The samples were prepared according to procedure outlined in the "FTIR Preparation Procedure" section of the report. A reference spectrum of the cured Tuffleye Finish resin was collected as a standard followed by all layers of the paint chip. The spectra were compared to see if the distinct peaks from the resin could be detected within any of the paint layers.

No definitive signs of the acrylic resin could be detected in any of the paint layers studied. Since the clear and color coats were composed of an acrylic polymer, complete distinction between the resin and paint was not possible; however, it is possible to say that no evidence of discrete absorption bands from the embedding resin could be seen in these spectra. The olefin bumper material could be evaluated more definitively. The major peaks present in the spectrum of the Tuffleye Finish were not observed in the polyolefin bumper spectrum (Figure 9). Also shown in this Figure is the spectrum of the polyolefin bumper material that was collected from a sample that had not been embedded (*i.e.*, the sample had been removed with a razor, flattened, and mounted directly on a salt plate). Taken together these experiments provide reasonable evidence that no detectable transfer of the Tuffleye Finish resin occurred during sectioning.

Raman Spectroscopy

Samples were prepared according to the procedure outlined in the "Raman Preparation Procedure" section of the report. Raman spectra of the tape adhesive and Tuffleye Finish resin were collected as background references. Raman spectra of all paint layers were then collected. The peaks present in the reference spectra were then compared to the peaks present in the sample spectra. Figures 10 and 11 show a comparison of typical spectra from the Tuffleye resin to those of strongly and weakly scattering paint layers. As can be seen in these spectra, the Tuffleye resin is a relatively weak Raman scatterer. Furthermore, there is no indication that the embedding resin was detected in the paint samples studied.

Time study of durability of blocks for sectioning

Over time, resins can harden (as they continue to cure) and become brittle. As discussed earlier, if a cured block is too brittle, it may not be possible to obtain good sections. A cured resin block that is too hard will chip or splinter as the knife of a microtome passes through it. Since Tuffleye Finish resin is a relatively untested product, blocks containing paint chips were sectioned periodically over the duration of this project to determine if useable sections could be produced months after the blocks were made. Since many of the preparations were made within a few days of each other, blocks were chosen at random for sectioning. At two months, the first few cuts from the exposed face showed a small amount of splintering. Once the exposed surface had been removed, however, excellent sections could still be cut from the block. At six months, the random block selected showed no signs of

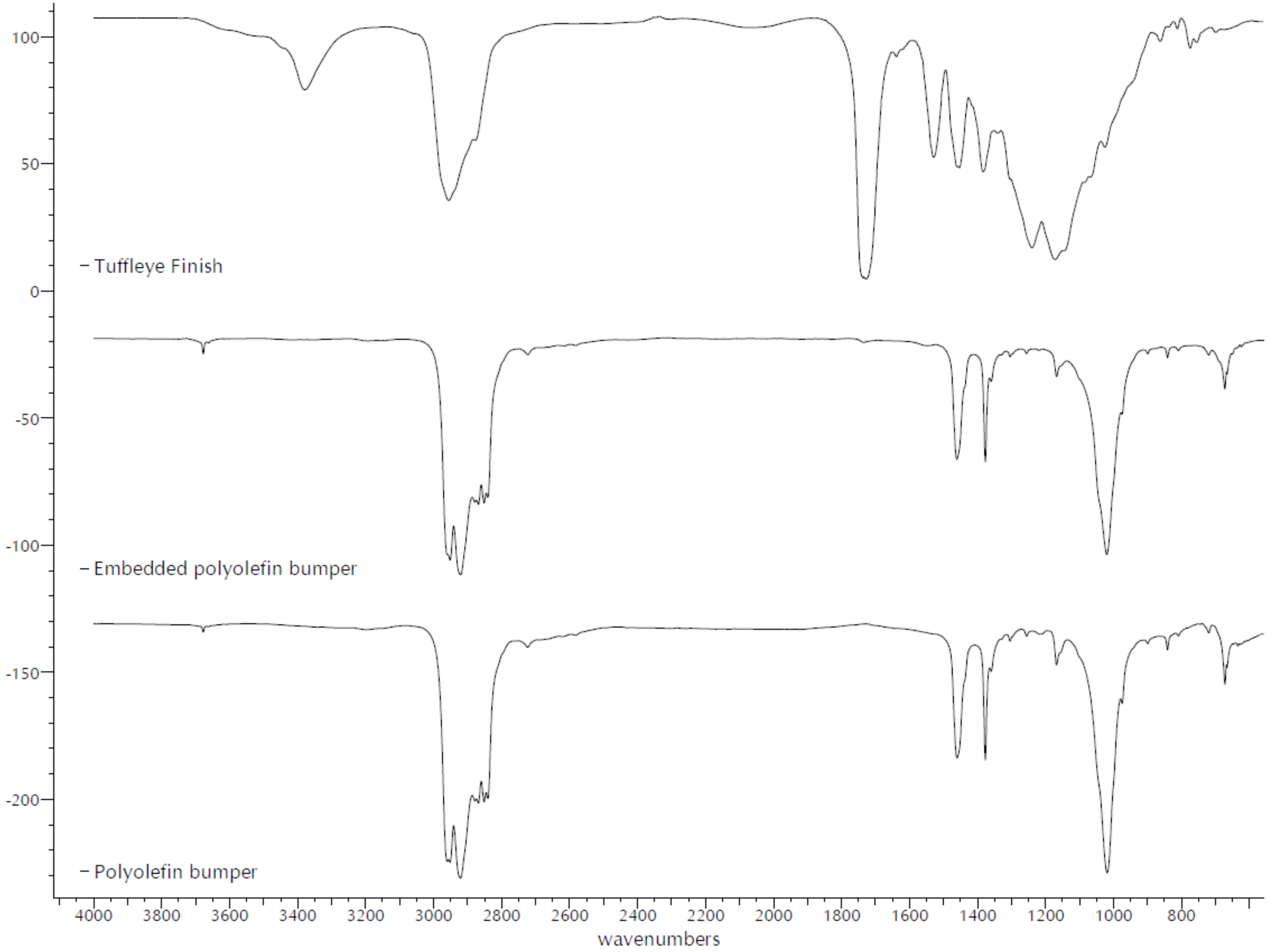


Figure 9. The infrared spectrum of Tuffleye Finish resin (upper) compared to a spectrum collected from a thin section of a polyolefin bumper embedded in Tuffleye resin (middle) and a spectrum of the polyolefin bumper.

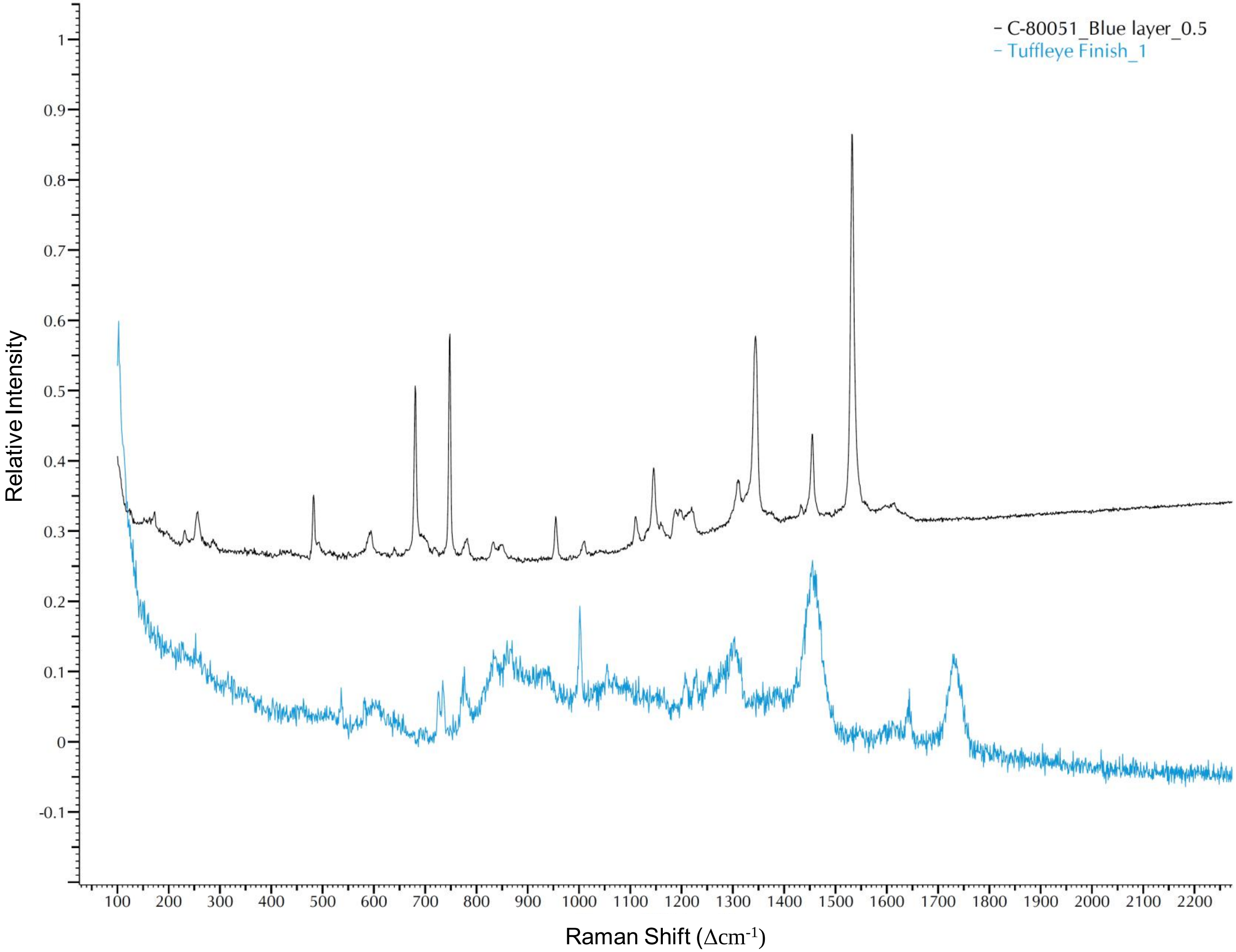


Figure 10. The Raman spectrum collected from a colored paint layer (upper, black) compared to a reference spectrum of Tuffleye Finish resin (lower, blue). Note that the scattering in the Tuffleye is extremely weak compared to that of the paint sample.

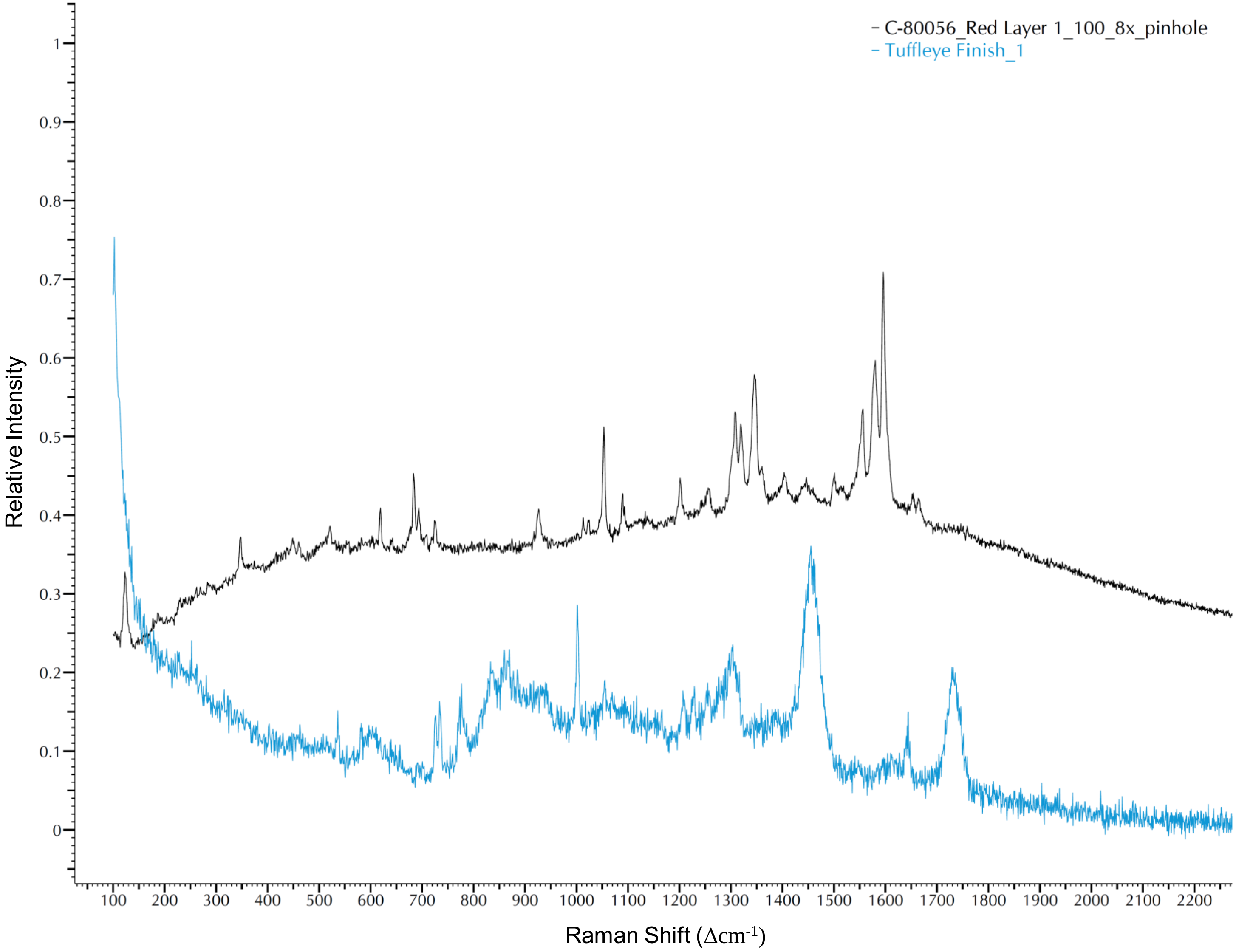


Figure 11. The Raman spectrum collected from a colored paint layer (upper, black) compared to a reference spectrum of Tuffleye Finish resin (lower, blue). In this case, a paint layer that exhibits relatively weak scattering is shown in comparison to the Tuffleye reference spectrum (785 nm laser).

splintering and thin, even sections were obtained. Even after nine months, useable sections could still be cut from the blocks. Therefore, it seems likely that paint chip mounts prepared using Tuffleye should last at least one year, if not longer. Nonetheless, since the shelf life of the resin mounts were not known at the early stages of this project, multiple thin sections were cut from each paint sample analyzed and archived for possible later use.

THIN SECTION PREPARATION

Currently, many forensic laboratories avoid thin section preparations when analyzing paint chips, as this method is more time consuming than producing thin peels using a scalpel and a stereo microscope. With layers approaching, or sometimes smaller than 10 µm in thickness, and with the presence of wet on wet applications, and tinted clear coats, layer recognition by stereomicroscopy alone is no longer adequate as a sole method for layer comparisons. While there are a variety of methods for exposing and preparing paint layers microscopical and instrumental analysis, preparation and evaluation of actual cross-sections by microtomy or hand sectioning has become more important in sample preparation. While sectioning can take more skill and/or more time than many of the cruder methods, mechanical sectioning provides several benefits, specifically: high quality results on even very small paint chips, recognition and access to the increasingly thin layers that are becoming more common in automotive paints, sections of uniform thickness necessary for photometric accuracy in microscopical and instrumental evaluation and analysis, and enhanced sample preservation (*i.e.,* minimal sample needed).

While there are several choices for exposing the layer structure of paint chips for analysis, two of the most commonly employed include the rotary microtome and hand sectioning. Hand sectioning is suitable for fast layer structure evaluation and IR sample preparation. For the most critical comparisons, such as those being conducted in batch-to-batch and research studies where minor differences must be evaluated for reproducibility, microtomed sections of samples cut from the same embedding block (and thus same section thickness) are optimal. Other methods such as cryo-, sledge-, and ultra-microtomy are all potentially useful; however, each carries additional time and materials requirements that make them inconvenient and outside the practical scope of the typical forensic science laboratory.

Equipment

Thin sections of the paint block preparations were cut using an American Optical Model 820 (rotary) Microtome with a steel knife. The micron selector offers 1 to 50µ sections in the following increments: 1-10 µm in 1µm increments, 10-20 µm in 2 µm increments, and 20-5 0 µm in 5 µm increments (GMI, Inc.).

The thickness of each section was selected based on the type of analyses to be performed. Nominal section thickness was set at 5 µm for Raman spectroscopy and EDS analysis; thinner sections (3 µm nominal selection) were cut for analysis by FTIR spectroscopy and PLM analysis. For confocal Raman microspectroscopy, the thinnest possible sections were cut to permit visualization of individual pigment clusters.

When a good section is cut, it can be picked up from the knife with a small piece of tape. The tape used to pick the sample should be touched to the portion of the section that consists of excess resin (as opposed to the area of the section containing the sample). The tape can then be attached to a glass slide for section storage and later retrieval. The process of sectioning and removal of good sections can be repeated so as to acquire multiple, serial sections. The slide is labeled and stored in a slide box to keep the sections free of dust and other contaminants. In this way, multiple sections were prepared from each sample and archived for future analysis.

Section Thickness Measurements

While knowledge of absolute thickness is not necessarily critical for comparative work, a dull blade can lead to substantially thicker sections than anticipated. Sections prepared using fresh and older areas of blade were turned on edge and placed on carbon tape for direct observation and measurement in the SEM.

SEM study of section thickness showed that sections prepared using a dull blade can be 3-5 times thicker than expected based on the nominal microtome setting (*i.e.*, the 3 µm sections were noted as large as 10-12 µm). Figure 12 shows an SEM image of one thin section cut at a nominal thickness of 2 µm, which is actually ranges from about 4-5 µm. Several factors are likely responsible for this difference, such as the knife sharpness, resin hardness, and microtome precision at thicknesses near the lower limits of its range. We found, not unexpectedly, that a fresh blade produced sections closer to the nominal microtome setting.

Based on this, the use of new sections of blade for final cuts is critical – particularly when preparing the thinnest sections. Metallic flake and other effect pigments caused a notable reduction in the number of quality cuts that could be obtained from a fresh area of blade. For this reason, fresh areas of the blade were always used for final cuts of each sample.

Ultimately, the absolute thickness of the prepared thin sections was less important than the production of consistent sections. The section thickness consistency was found to be adequate for spectroscopic reproducibility based on an empirical evaluation of multiple paint chips of the same sample cut from different sections.

POLARIZED LIGHT MICROSCOPY

Examination of Thin Sections by Light Microscopy

Each cross section was photo-documented using a polarized light microscope set up in Köhler illumination. Images were collected using a digital camera. Images were generally taken with transmitted light, oblique illumination, or a mixture of both to capture the paint color, reflection of metallic flake, or the color of individual pigments, as appropriate.

The length calibration of the ocular micrometer and camera images was established prior to analysis of samples. This calibration is checked on an annual basis. Post processing of the images, which consisted solely of a scalebar overlay, was completed using the Leica Application Suite (LAS).

Direct Examination of Pigments by Light Microscopy

Since many individual pigment particles are 1 µm or less in diameter, the direct visualization of pigmentation (see section "Identification of Minor Pigments") is at or below the resolving power of the light microscope. Nonetheless, pigments are generally not perfectly dispersed on the microscopic scale and these pigment agglomerates as well as larger pigments can be directly visualized by light microscopy. In such cases, the highest magnifications (100x objectives) and optical parameters (oil immersion) must be used to obtain the best possible images.

Under these conditions, as discussed in the section "Identification of Minor Pigments," a great deal of information that can be obtained by a direct examination of pigments (both visually and spectroscopically). While many

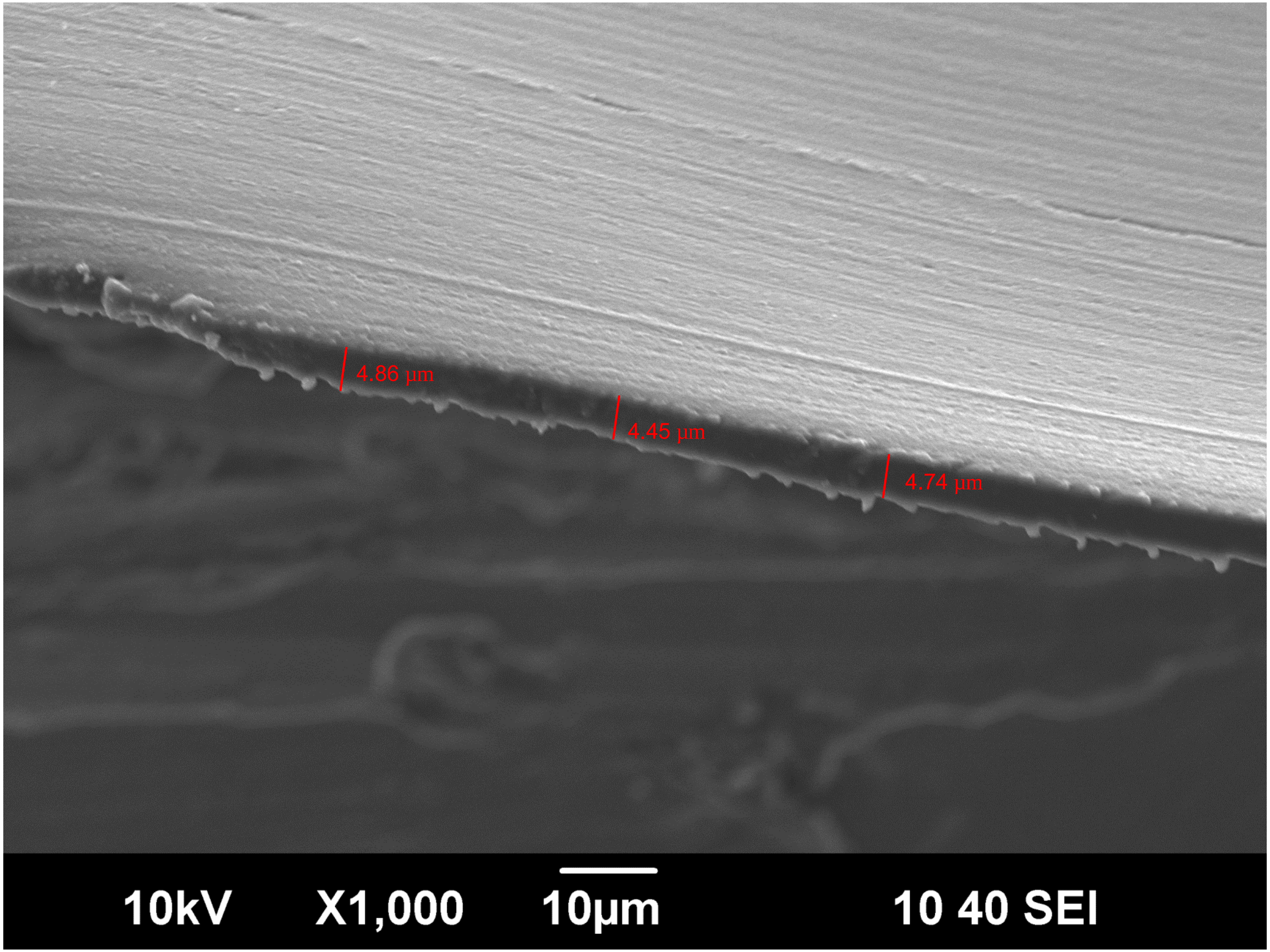


Figure 12. A section cut with a nominal microtome setting of 2 µm and a used section of blade (carbon coated).

laboratories have the capability to study samples by oil immersion microscopy, the technique is rarely utilized, due in part to a lack of education and in part to the additional steps necessary.

For oil immersion microscopy, it is advantageous to prepare such samples as permanent mounts, not for long term retention (as is the typical reason), but to eliminate coverslip (and particle) movement while moving a microscope slide that is oiled to the coverslip. The sections studied here were mounted permanently in Cargille Melt Mount 53 (n= 1.539), which is a thermoplastic resin. Once molten, a single drop is added to a coverslip and pressure is gently applied to it, permitting the medium to flow around the preparation (being cautious not to use too much pressure, as this can cause individual layers of the section to delaminate).

In some cases, where direct study of the pigment is the main focus, the colored layer of the paint can be separated mechanically and ground out in a permanent medium for direct examination. This is often the best way to observe and examine pigments microscopically, as it permits study of pigments in a monolayer, whereas even the thinnest rotary microtome sections results in layers of pigments instead of monolayers. If pigments are the only focus of an examination, a higher refractive index medium should be utilized (to correspond to the typically high refractive index of pigments).

Due the extremely small size of pigment crystals, it is necessary to optimize imaging conditions. At the highest magnifications, it can be difficult to collect enough light to obtain good resolving power. Oil immersion microscopy permits the highest resolutions to be obtained by exploiting the higher numerical aperture (and resulting increase in resolution) that can be obtained by optically coupling the slide and optics (condenser and objective) by a layer of oil (rather than air).

The paint samples and pigments where studied and photo-documented using oil immersion at a nominal magnification of 1,000x.

AUTOMOTIVE PAINT LAYER STRUCTURE

Layer Nomenclature

Each of the automotive paint samples studied in this project contains multiple layers. In many cases, a single paint sample contained multiple color layers.   As such, it was necessary to be able to reference and return to a specific layer in a given paint sample. To this end, various layer numbering schemes were considered. As we progressed through this research, it became clear that no layer number scheme is perfect.   Ultimately, we opted to partially adopt the PDQ layer numbering scheme, in large part due to the fact that it is the most widely recognized approach in use among forensic laboratories (RCMP, 2013).

The PDQ paint layer numbering system is based on a distinction between original undercoats, original topcoats and refinish topcoats. Since the purpose of this project was pigment identification (rather than paint system comparison), the greatest need was to assign a static layer numbering system immediately after cross section documentation and prior to spectroscopic analysis. As this point of an analysis, it is not always possible to discriminate between original and refinish coats, and as such, all layers were assigned as either an undercoat or topcoat (the refinish designation was not applied).

Even with this simplified layer numbering approach, it was necessary to distinguish between undercoats and topcoats. The continual development of layer system engineering and paint chemistry can result in the application of extremely thin layers (Figure 13), wet on wet applications where layer boundaries are unclear, tinted clear coats (Figure 14), and primerless systems (Figure 15). With these complications, layer designations were, at times, difficult to assign. A few notable examples are presented here.

With new ways to "hide" scratches, improve the covering power of more expensive top coat layers, or provide a "wetter" finish appearance, systems have been designed to utilize layer systems that contain coordinated primer layers and tinted clear coats (Figure 16). Many paint chips utilizing such systems were encountered in the course of this study. One flake, shown in Figure 17, combines a colored primer and tinted (by effect pigments) clear coat.

Layer Thickness Distribution

There are many design factors that impact layer thickness: paint technology, pigment covering power, location of the paint on the vehicle, and substrate (among others). For example, the use of plastic substrates on vehicles provides the benefit of easier adhesion compared to that of metal substrate counterparts, which, in turn, permits a thinner (or omitted) primer layer. The evolution of primer chemistry has resulted in better adhesion, allowed thinner layers to be consistently applied, and the use of "high-performance" pigments, which can result in better covering power further contributing to decreased layer thickness. Consumer preferences and environmental laws further drive these changes. Together, these factors along with more random variables such as OEM refinishes define the layer structure.

Based on photomicrographs of the cross-sections from each paint sample, the thickness of each layer (in all 300 samples) was measured. A great deal of information was obtained from these thickness measurements. The thickness of each layer is displayed in a histogram showing the frequency of different thicknesses for the three main layer categories (clear coats, top coats and primers) (Figure 18). Examination of the histogram shows that primer and colored layers are generally thinner than the clear coats. This is consistent with the requirement that clear coats provide a layer that is flat, absorbs sufficient UV light to protect the color layers and provides the desired "wet" look to a vehicle. It is also interesting to note that a significant percentage of layers (33%) fall in the category of less than 20 µm.

PREPARATION FOR ANALYSIS

Following layer characterization, samples were prepared for analysis by Raman and FTIR microspectroscopy.

Raman Preparation Procedure

A strip of double-sided tape (Scotch brand, cat. 665) was placed onto a polished aluminum slide. A section was then transferred from the glass slide (where it is stored after sectioning from the block) to the tape with a tungsten needle and lightly pressed onto the adhesive to ensure good adhesion contact and to generate a flat region to allow for easier analysis. A benefit of this preparation method is that it permits both Raman analysis and SEM/EDS analysis to be performed on the same specimen.

FTIR Preparation Procedure

As noted later, only select samples were prepared and examined by FTIR spectroscopy. While several valid and established sample preparation methods for infrared analysis of paint exist, all samples in this work were mounted

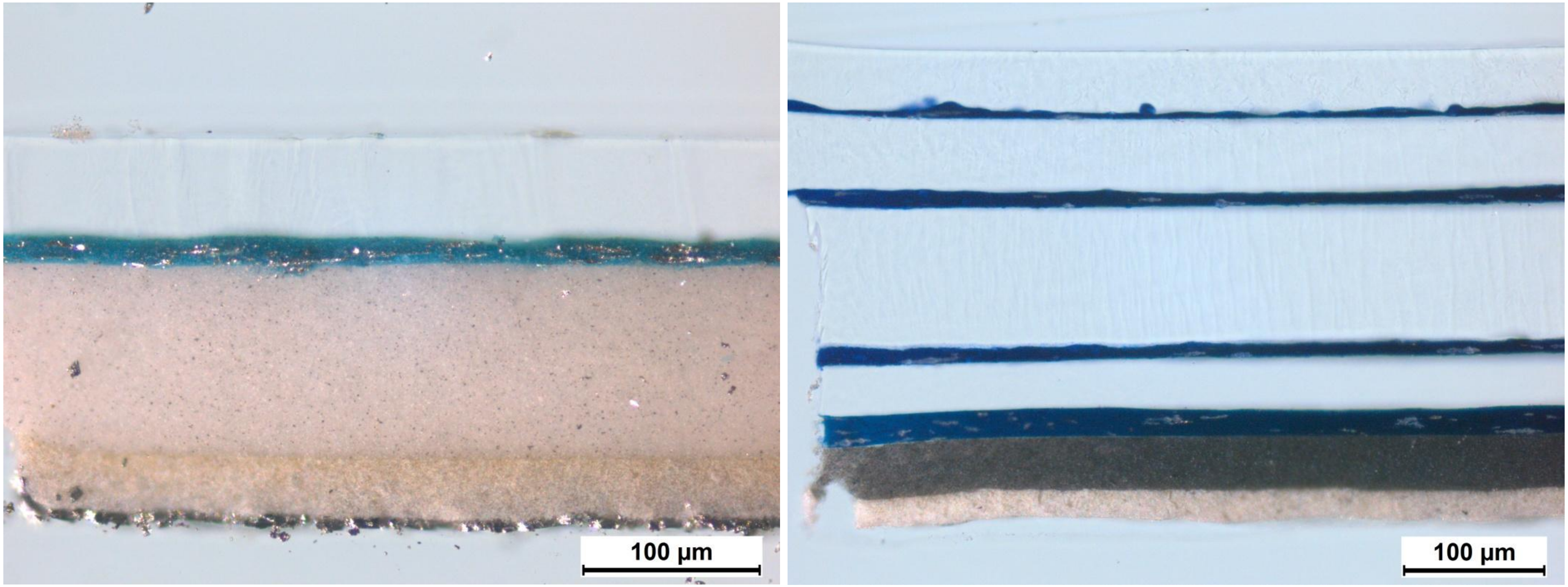


Figure 13. Examples of thin paint layers.

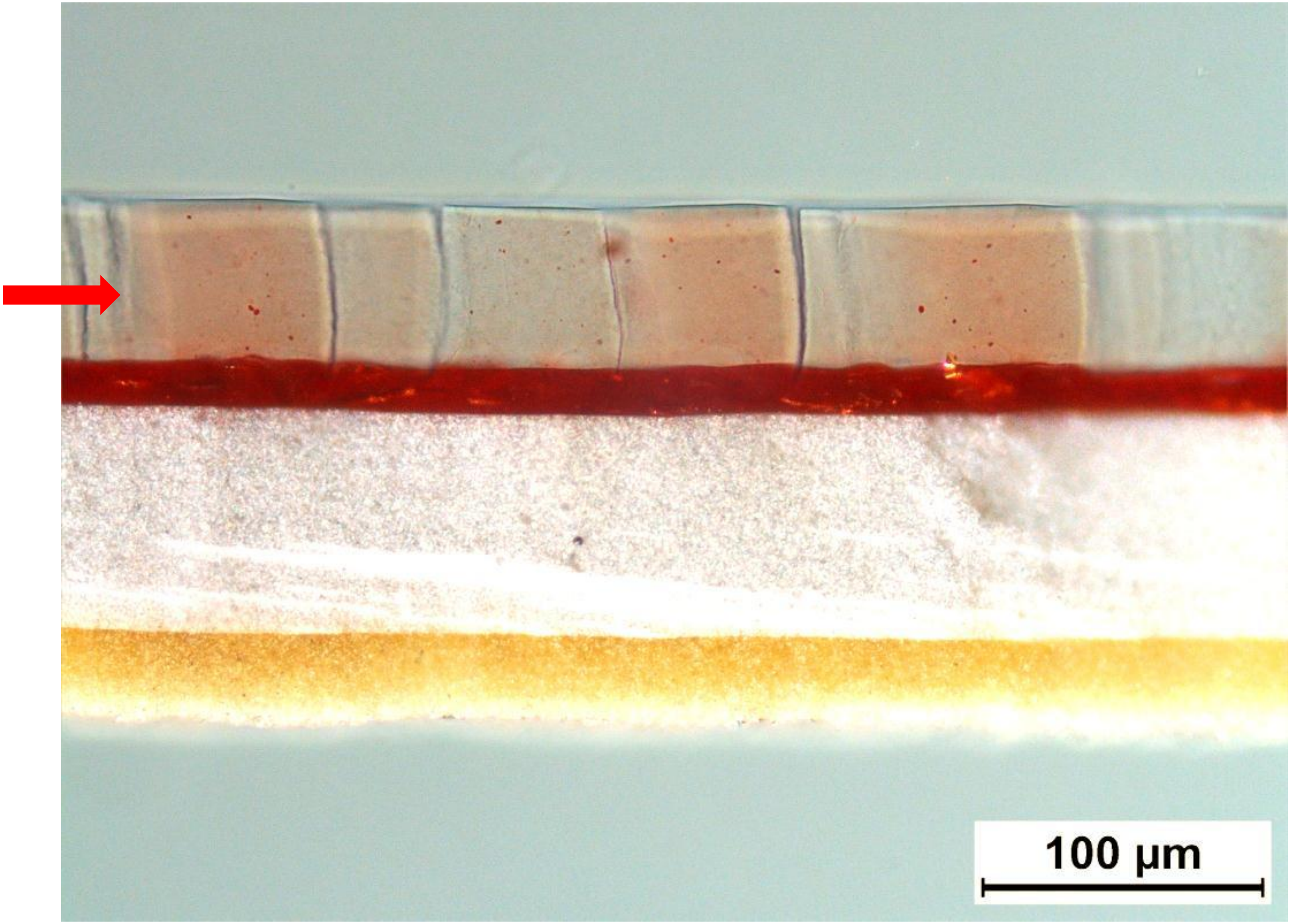


Figure 14. Example of paint showing a tinted clear coat (red arrow).

BLOCK BB – C-80484

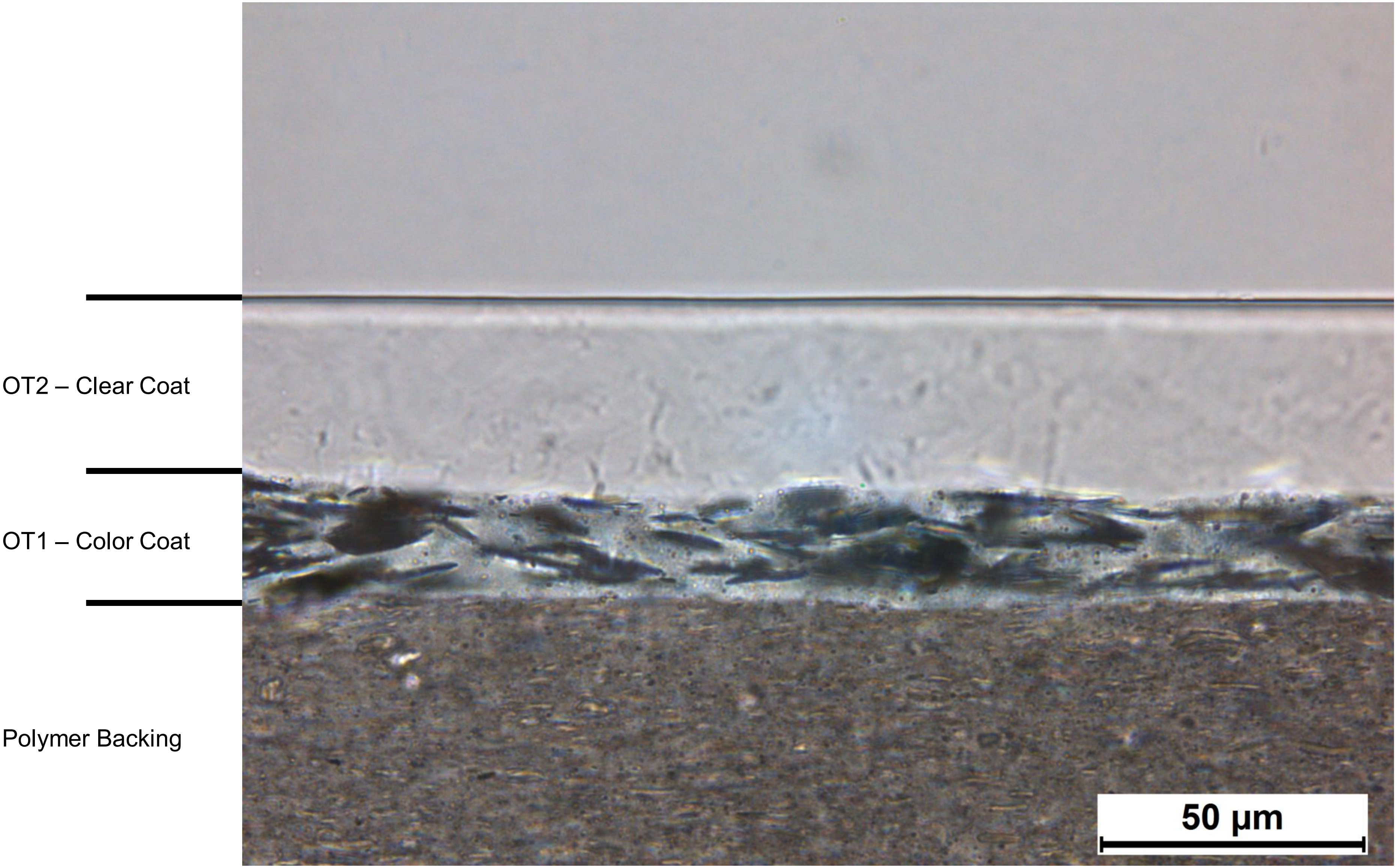


Figure 15. Example of paint samples showing no primer layer

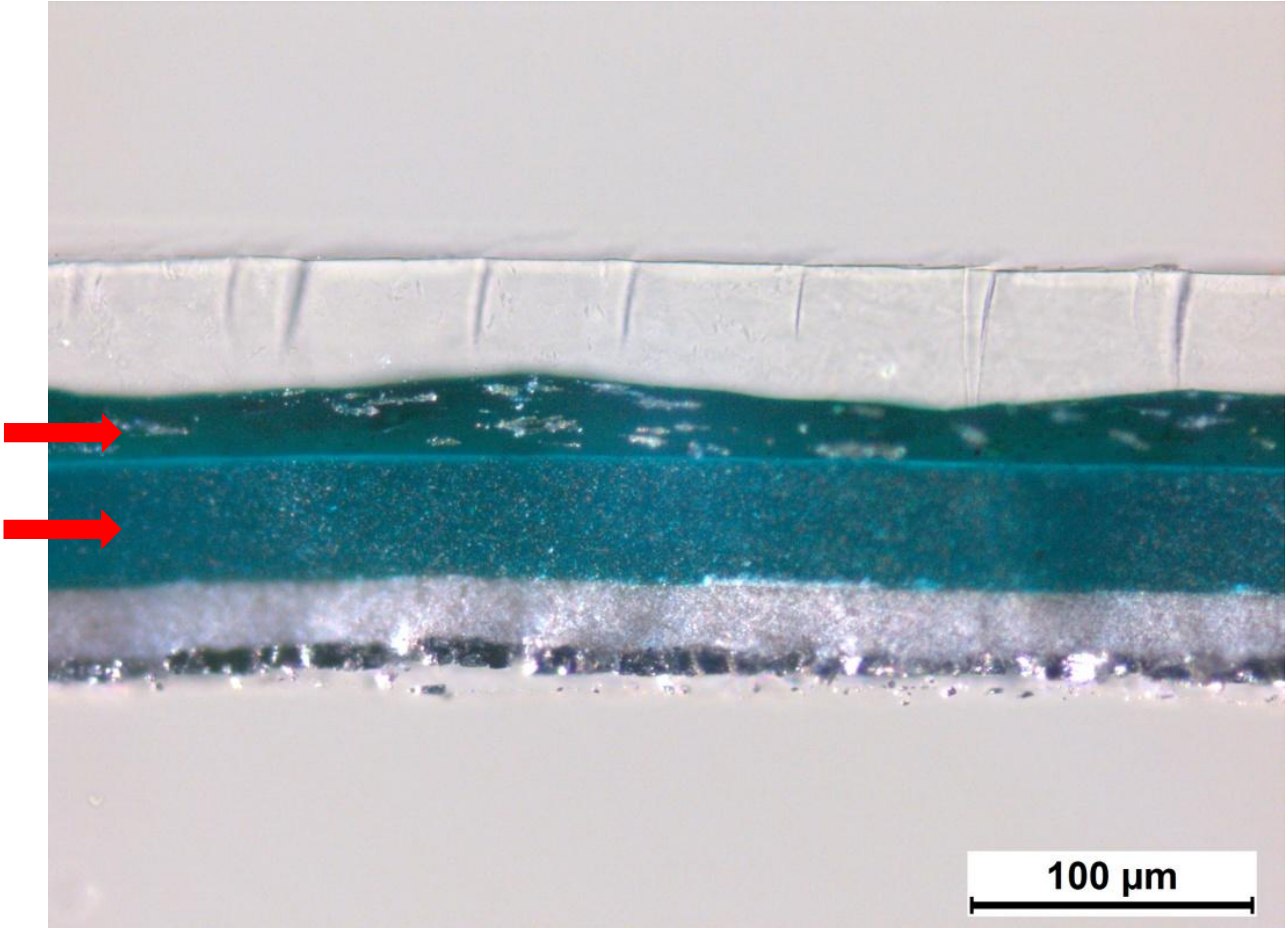
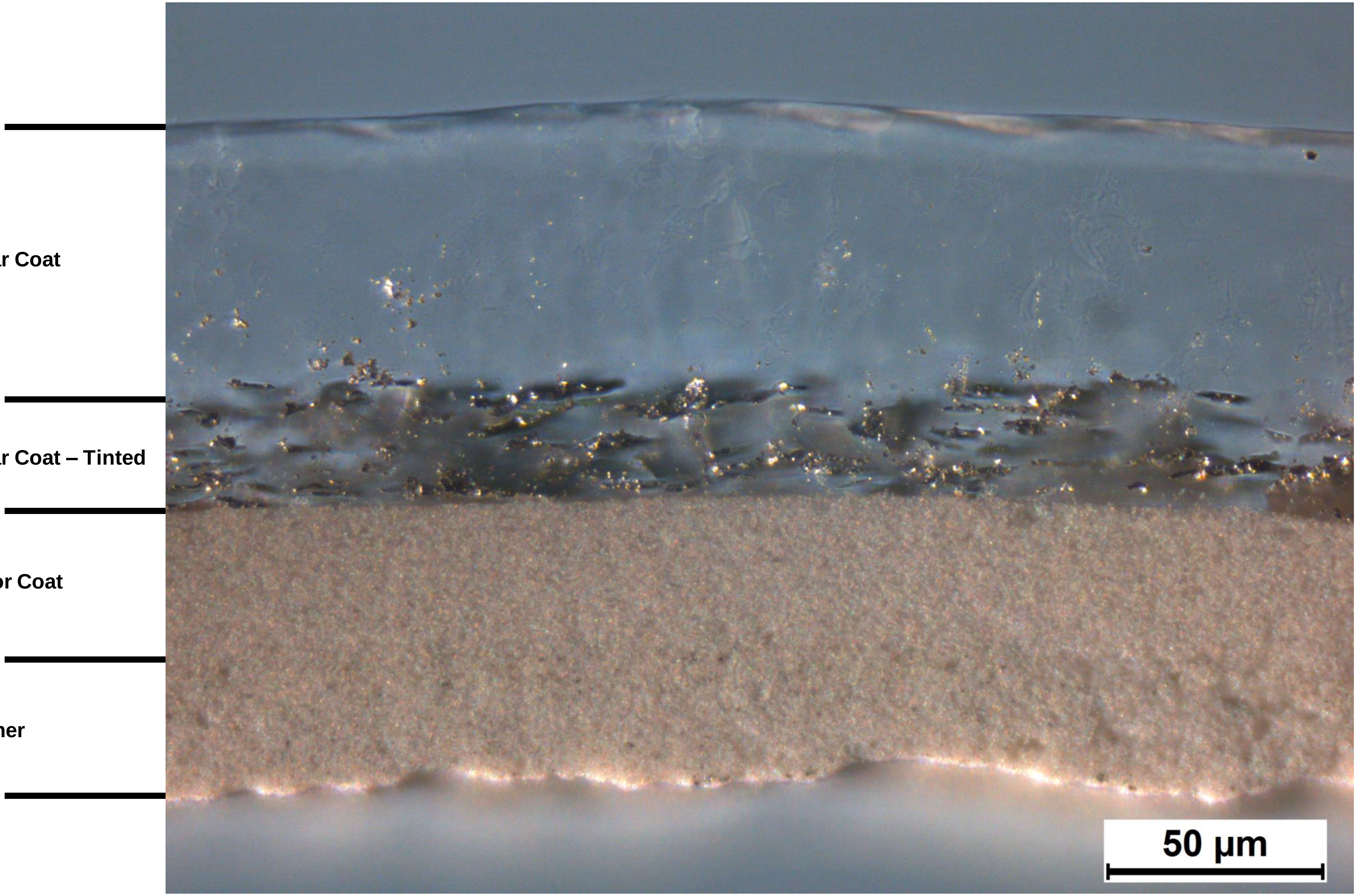


Figure 16. Example of paint showing a coordinated layer system (red arrows indicated coordinated layers).

BLOCK Q – C-80365



OT3 – Clear Coat

OT2 – Clear Coat – Tinted

OT1 – Color Coat

OU1 – Primer

Figure 17 Example of a clear coat paint layer containing metallic flake.

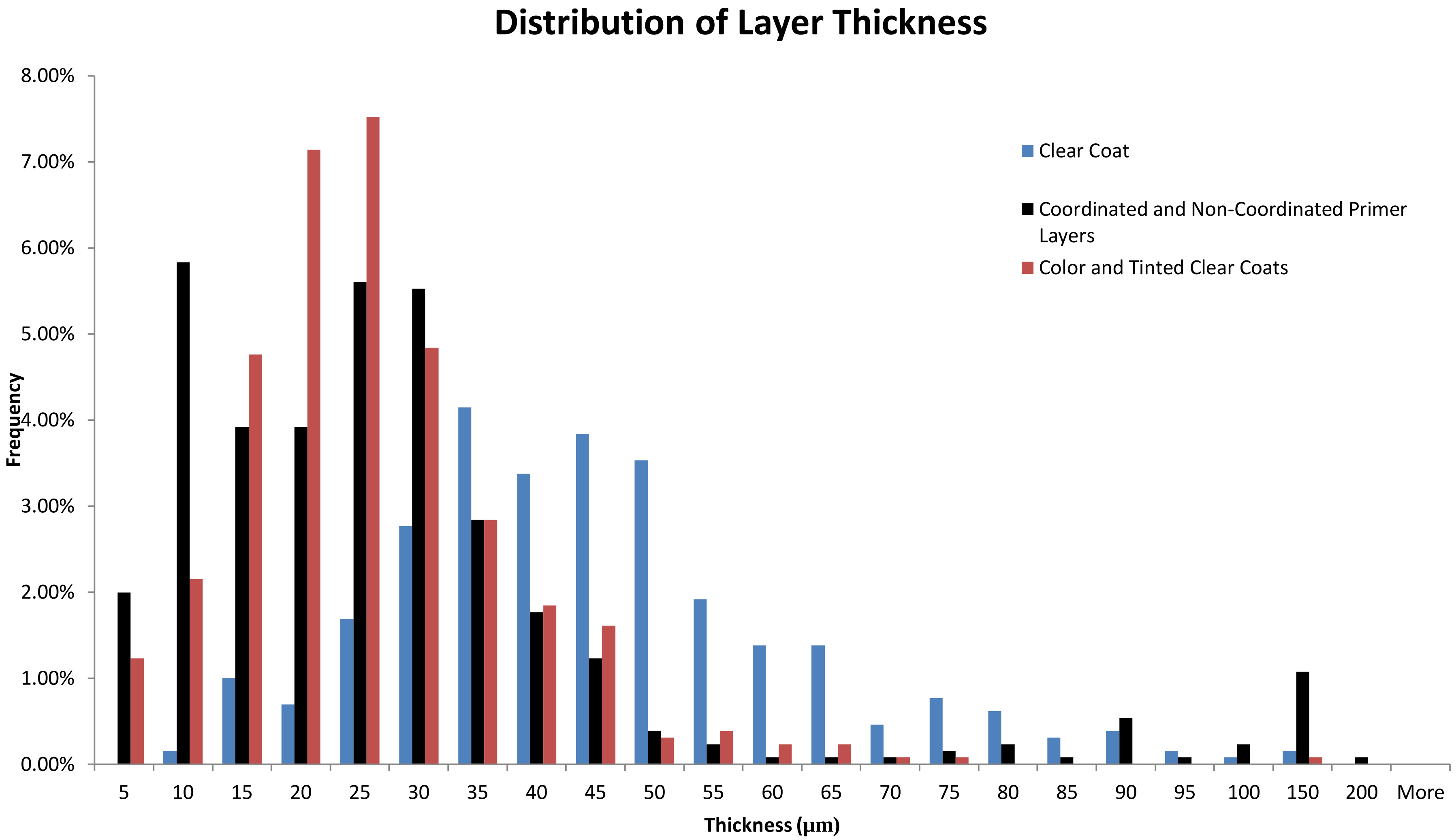


Figure 18. Histogram of automotive paint sample layer thickness distribution by layer type

on KBr salt plates and analyzed in transmission mode, which is generally agreed to give the best quality and most reproducible spectra. Prior to mounting the sample on the salt plate, the layer to be analyzed was physically isolated from the remainder of the paint system. Although this is not always necessary in casework, the approach was utilized here to ensure that adjacent paint layers did not contribute to the infrared spectrum. Preliminary experiments showed that this can occur for extremely narrow layers and when the analytical aperture is placed near a layer boundary.

Paint layers were isolated using a combination of forceps and tungsten needles. The sample is pressed down onto a cleaned microscope slide and viewed through a stereomicroscope. A clean razor blade is used to excise the color coat layer, paying careful attention to cut the layer within the boundaries of layer being sampled. The color layer is then lifted off the slide with a tungsten needle and placed onto a potassium bromide salt plate. A clean cover glass fragment is used to press the isolated layer directly onto the salt plate. Pressing the layer flat also increases its width, permitting a larger sampling aperture to be used, which results in a higher quality spectrum, which is especially beneficial with the thinnest layers.

Layers that were too thin to isolate by this method were not analyzed due to the uncertainty in knowing whether only layer of interest was being analyzed.

ANALYTICAL PARAMETERS

RAMAN SPECTROSCOPY

Instrument Specifications

The following instrument specifications were utilized for data collection in this research. The authors have utilized a wide variety of Raman instruments and have found that the specifications presented below represent a reasonable balance between performance and speed. Due to the fact that Raman spectroscopy is a relatively new application in forensic science, these specifications are presented as a starting point, rather than as a hard and fast rule. It is certain that other configurations could be utilized to produce similar results. Only with a community of scientists utilizing these methods on a regular basis will it be possible (or even necessary) to critically evaluate and specify optimal instrumental parameters more specifically. It is also likely that more detailed specification of instrumental parameters will become more sample (and pigment) specific as more experience in pigment identification is gained

- Instrument: Renishaw InVia Raman dispersive microspectrometer
- Lasers: 785 nm (diode)
- Gratings: 1200 lines/mm
- Laser power: 0.01 – 6 mW (at sample)
- Spot Size Diameter: ~1-2 µm (spot), 3 µm x 30 µm (line)
- Analytical Volume: ~3 µm^3 (confocal, @100x); ~360-450 µm^3 [rough approximation] (line, @50x)
- Spectral resolution: ~3 cm^{-1}
- Spectral range: 100 – 3500 Δcm^{-1} (used for pigment interpretation)

Stage and spectral mapping options continue to improve. While we have found little practical use for mapping results in paint analysis, there are some mapping applications that can effectively improve data collection times over traditional point analyses.

Instrument Validation

The following aspects of a Raman microspectrometer system should be established and verified on a regular basis. For the purposes of this work, the parameters were verified on the following basis:

- Wavelength Calibration: Verified on a daily basis
- Spectral resolution: Verified on a yearly basis
- Spot size location: Verified on a daily basis
- Spot size: Verified on a monthly basis
- Laser power (at sample): Verified on a yearly basis

The frequencies listed above were determined to be reasonable given the range of variations we have observed. In general, procedures for performing these verifications or instructions for adjusting alignments that optimize these parameters can be supplied by the instrument manufacturer. The laser power, at the sample, was verified prior to the start of this research using a handheld laser power meter.

Collection Methods

Given the heterogeneity of paint, we have found that not all samples can be analyzed under identical conditions. Each paint sample was, therefore, analyzed using optimized conditions (within the range of parameters presented in the “Instrument Specification” section). The optimal power was established as the highest laser power (modulated by a neutral density filter wheel) that does not saturate the detector or burn the sample. In some cases, multiple accumulations (on the same point) were used in lieu of higher laser powers. Some samples that showed strong fluorescence could be managed by “bleaching” the sample (*i.e.*, placing the beam on the sample prior to collection for a period of minutes for the purpose of reducing fluorescence).

For most paint layers, a confocal configuration was utilized due to the layer thinness. The confocal mode reduces the analytical sampling volume at the expense of signal strength. By using confocal mode, data is only acquired from the small sample volume (as small as 2-3 µm^3). In other cases, data was acquired using a “line” mode whereby the laser is projected as a line on the sample.

Spectral Acquisition

The microscope was first focused on the surface of a given paint layer. The spectral acquisition time was held fixed at 10 seconds; however, the laser power and number of accumulated spectra varied from sample to sample. The number of accumulations was increased in order to improve the signal-to-noise ratio. When multiple accumulations are collected, the system co-adds the intensity data within each pixel of the detector. Multiple accumulations improves the signal of a weak peak without saturating stronger peaks, whereas increasing the laser power or exposure time will generally serve to saturate the detector (for stronger peaks) or increase fluorescence.

Fluorescence occurs unpredictably in samples. The strength of fluorescence (and the strength of Raman scattering by the sample) will dictate whether all, some, or no peaks will be visible in the Raman spectrum. When fluorescence is strong, the detector will saturate and no peaks will be visible. Generally, a spectrum dominated by fluorescence will be shaped like a hill. Depending on the balance between the strength of sample scattering and strength of fluorescence, the Raman bands from the sample may or may not be visible. Generally, only the major peaks will be notable. In such cases, the background can be baseline corrected, which permits identification of at least some components in even a moderately fluorescing paint. Although fluorescence can be considered the "Achilles heel" of Raman spectroscopy, there are several approaches that can often be used to alleviate it:

- Reduction of laser power. Reducing the laser power can reduce the fluorescence.

- Sample bleaching (quenching). By exposing the analytical area to the laser for a period of time (minutes to an hour, typically), the fluorescence background will often be reduced, thereby improving the signal-to-noise ratio of the sample.

- Confocal mode (on a microscope) can reduce fluorescence by reducing the excitation volume.

- Excitation laser. Changing the excitation (laser) wavelength can help with fluorescence issues by collecting the Raman shift relative to a laser line in a portion of the spectrum that is removed from the location of the fluorescence. In general, excitation sources closer to the IR region are less susceptible to fluorescence than those approaching the UV.

In some cases, these approaches are not effective and no useful Raman data can be obtained from a sample.

Post Processing

All spectra collected are manually evaluated to determine what, if any, post processing is needed. A copy of all raw data is always saved; however, spectra are almost always baseline corrected. The most common exception to this occurs when the fluorescence of a spectrum is so strong that no Raman scattering is observed. In this case, the fluorescence spectrum is provided with no spectral processing.

Smoothing is the only other operation that is applied to spectra with extreme levels of noise or fluorescence. Smoothing improves the signal-to-noise ratio but degrades the spectral resolution. Smoothing should not be used as a substitute for obtaining a better measurement if that is possible.

Spectral Artifacts

A variety of spectral artifacts can be encountered during analysis (Palenik *et al*., 2011).

Cosmic Rays

Cosmic rays are random, high energy particle events originating from space. CCD detectors can be affected by these particles, which manifest themselves as sharp, random peaks in a spectrum. Most instruments have automated removal algorithms in their software that reject these rays (often through collection of multiple spectra). The fact that peaks due to cosmic rays are random means that they will almost certainly be absent from a second spectrum collected from the same specimen.

Monitor peaks. Many Raman systems are in enclosures designed to protect the user from stray laser radiation. An added benefit of an enclosure is the protection it provides the instrument optics from collecting stray light. The microscope objective has high collection efficiency and the CCD detector is extremely sensitive. As such, stray light (e.g., from the computer monitor) can result in unwanted spectral peaks. The peaks can vary from monitor to monitor, but are represented as sharp (often weak) peaks that are most notable when the spectral counts from the sample in the region of one of these peaks are otherwise low. Figure 19 shows the spectral contributions from two different monitors in use on our system. The easiest way to eliminate such peaks entirely is to turn off the monitor during data collection or purchase a privacy screen for the monitor.

Carbon Black

Carbon black has a recognizable spectrum that consists of two broad peaks (see the carbon tape spectrum in Figure 20). While these peaks can be quantitatively interpreted under proper conditions, the carbon black feature is qualitatively unmistakable when present. Analysis of various paint layers, including several white paints, showed a contribution due to carbon black in their Raman spectra. Carbon black, even at an extremely low (<< 1%) concentration, can cause a material to darken, and one would certainly not expect carbon black to be present in a white paint. Therefore, it appears that carbon black is sometimes present as a contaminant. The reason for such contamination is not clear; however, even a fresh white paint sample can show carbon black peaks. One possible explanation is that amorphous carbon is being deposited as a result of localized sample heating during analysis.

Polarization

Polarization is not an artifact, but can manifest itself as a notable effect in Raman spectra. While polarization is an optical property that forensic scientists most commonly associated with polarized light microscopy, the same principles apply to Raman spectroscopy (and other spectroscopies), where the laser light is inherently polarized. The effects of polarization in Raman spectroscopy manifest themselves most notably (as far as the forensic scientist is concerned) as changes in peak intensity or the complete disappearance of a peak. An example of this can be seen in the collection of a Raman spectrum from the mineral zircon, where the 1010 Δcm^{-1} peak intensity can range from 0 to 100% of the strongest peak in the spectrum based upon the orientation of the sample relative to the laser and system optics. While this can be used advantageously in certain academic/research studies, it is really more of an issue to be aware of when conducting phase identification. However, since it is unlikely that a single pigment particle is ever the sole object of an analysis, the random orientation of pigment particles in the sample usually results in an "average spectrum."

Stitching

In CCD based dispersive spectrometers, a Raman spectrum is collected by focusing the collected scattered photons onto a grating, which in turn, is projected onto a CCD chip. Only a portion of the entire spectrum is generally focused onto the CCD chip at any given time (based on the dispersion of the grating and the width of the CCD). As such, instrument designers have engineered various ways to scan a larger range of the spectrum than can be fit on the CCD at any one time. One of these methods involves collecting discrete images of adjacent regions of the spectrum, which are then stitched together based on a predefined overlap algorithm. Due to differences in the efficiency of the grating as a function of wavelength, stitching algorithms may not accurately capture data in the overlapping regions between two "frames." The principal author has used some spectrometers where peaks

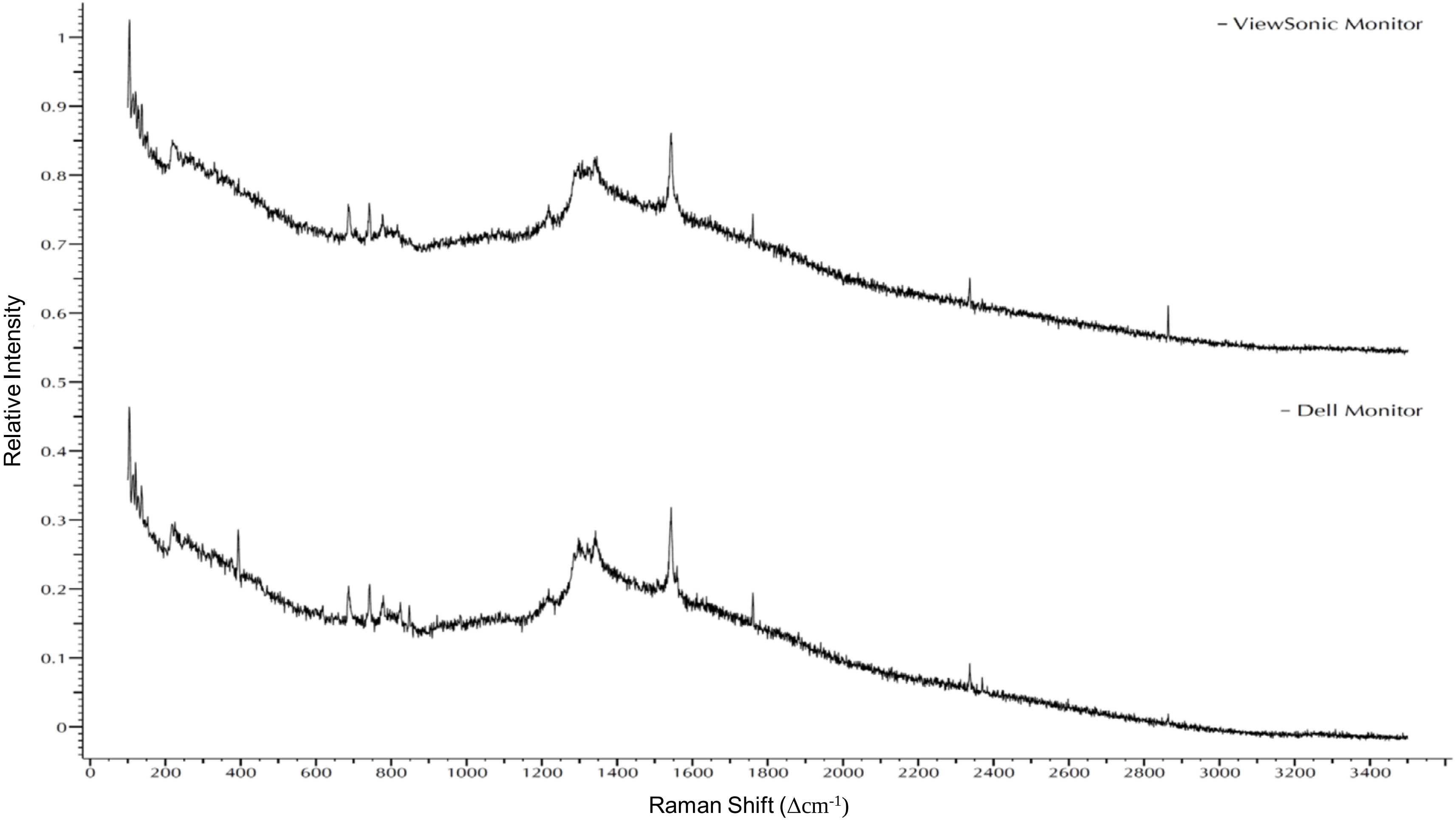


Figure 19. Raman spectra showing monitor peaks.

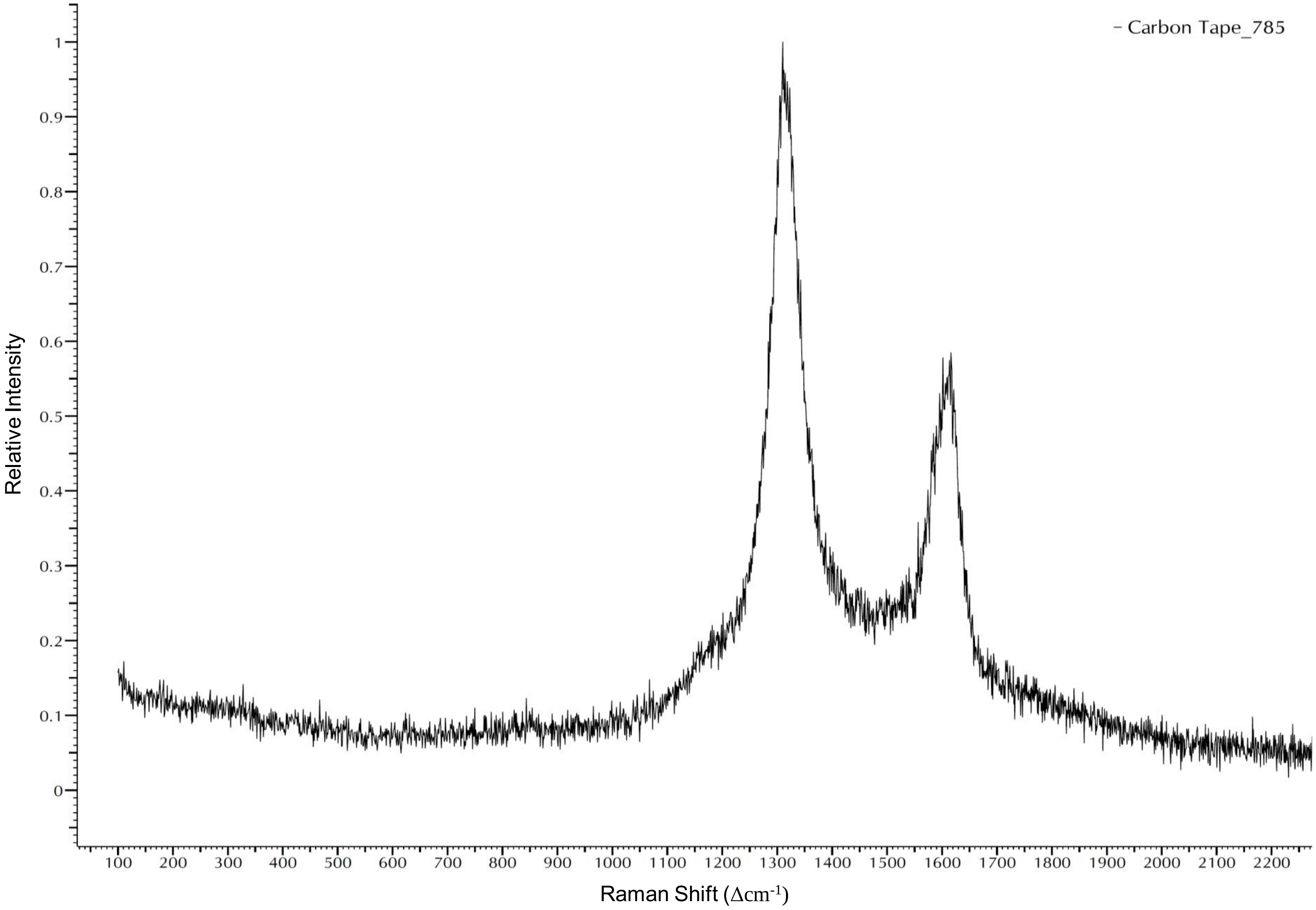


Figure 20. Raman spectrum of carbon tape, showing the two broad bands from amorphous carbon.

falling on these edges can change position or width. When attempting to collect data, it is generally a good idea to make sure that the final spectrum is collected in such a way that critical peaks do not fall on stitch boundaries.

FTIR SPECTROSCOPY

The analysis of paint by Fourier transform micro-infrared spectrophotometry (FTIR) is a well-established forensic approach to paint analysis based on polymer composition. (Ryland and Suzuki, 2012). In this project, FTIR spectroscopy was used to provide a detailed comparison between select paint layers with similar colors (as will be described in more detail later). Therefore, it is of foremost importance to ensure that no spectral interferences or contributions of adjacent paint layers are present in the area being analyzed. The preparation of each paint sample is described in the "FTIR Preparation Procedure" section of this report.

Instrument Specifications

The operating conditions of FTIR spectroscopy are very well established within the scientific community. Analyses of the paint sections were performed on a Perkin Elmer Spotlight 400 Fourier transform infrared microspectrophotometer with the following parameters:

Spectral range:	4000 to 550 cm^{-1}
Number of scans:	32
Spectral resolution:	4 cm^{-1}
Aperture:	Single, Rotatable, Variable in X and Y

Instrument Validation

The following aspects of an FTIR system must be established. For the purposes of this work, the following parameters were verified on a regular basis:

Wavelength Calibration:	Verified on a monthly basis
Spectral resolution:	Verified on a yearly basis
Aperture size location:	Verified on a daily basis
Aperture size and alignment:	Verified on a daily basis

The ranges listed above were determined in our laboratory as reasonable for the variations we have observed. In general, procedures for conducting these verifications or instructions for making alignments to optimize these parameters can be supplied by the instrument manufacturer.

Post Processing

Each spectrum collected is manually evaluated to determine what, if any, post processing is needed. A copy of all original raw data is always saved. Spectra are typically baseline corrected and smoothed when necessary, such as when large amounts of noise exist in a spectrum collected with a small aperture. The post processing of each spectrum was completed using PerkinElmer Spectrum software v6.2.0.

RESULTS AND DISCUSSION

The results presented here are discussed under two broad headings: automotive and architectural. Since automotive paints make up the great majority of paint casework in US forensic laboratories, this was the major area of focus for this grant. More specifically, this research focused on organic and inorganic pigments (this largely excludes pigments that would be considered effect pigments, which are less accessible by Raman spectroscopy alone).

The ultimate goal of the following analyses was determine where Raman spectroscopy might fit into a contemporary forensic laboratory, which already has an established core of preferred methods. This was accomplished by exploring various applications (ranging from fast screening through detailed analysis) and conducting an evaluation of the evidentiary potential for Raman spectroscopy compared to existing methods. It should be understood that this research (along with our proceeding publication) are the only ones of their kind as far we are aware. While the authors believe that they have provided a fair amount of insight into the forensic applications of Raman spectroscopy, there is still more work to be done in this area.

AUTOMOTIVE PAINT SAMPLES

The 300 automotive paint samples were analyzed by light microscopy, micro- FTIR, and Raman micro-spectroscopy, to identify components of the paint including, but not limited to: layer structure, binder chemistry and pigments. Results of these studies were interpreted to evaluate laboratory applications and evidentiary significance of data collected (with particular emphasis on pigment identification) by Raman micro-spectroscopy.

FORENSIC APPLICATIONS

Based upon our prior experience with Raman spectroscopy and forensic paint examination techniques in current use, we identified three areas where Raman could be of potential benefit in a forensic paint analysis scheme. The practical utility of these are: 1) Fast screening, 2) Routine discrimination based upon pigment identification, 3) High level discrimination and sourcing based on the identification of minor pigments. The pros and cons of each are discussed in more detail in the following sub-sections, but are summarized here in Table 4.

Table 4. Applications of Raman spectroscopy to paint characterization.

Method	Spatial Resolution	Laser Focus	Sample Preparation
Fast Screening	Low	Line	None
General Pigment Identification	Medium	Line	Cross Section
Trace Pigment Identification	High	Confocal Spot	Thin Section

Fast Screening

Forensic Benefit

The fast screening approach focused on whether it would be possible to identify pigments in a paint sample without sample preparation. This application would be intended for initial screening in the forensic laboratory, prior to any sample preparation for layer characterization, FTIR or SEM/EDS and would require collection of a Raman spectrum of the pigments through any existing clear coat. It is important to realize that such data would not necessarily originate from a single layer. However, the advantages of this method would be speed (<2 minutes per sample) and that the analysis could be conducted using any type of Raman spectrometer, including considerably less expensive macro Raman systems (if the chips were large enough).

Analytical Approach

To evaluate the potential of this method, a "directionality" study was conducted by analyzing a set of 30 multi-layered automotive paint samples. Each paint sample was studied in two orientations. The first orientation is how a paint chip would naturally rest on a horizontal surface and the laser beam was focused down through the clear coat into the interior color layers. The second orientation examined a single layer at a time from a cross section of the paint. At least two spectra from each sample were collected and compared. The results permitted the strengths and weaknesses of the fast screening method to be identified.

Results

Pigments could generally be identified in Raman spectra collected in both orientations. Figure 21 shows an example where the randomly positioned paint sample that underwent no preparation shows a spectrum that is extremely similar to the spectrum collected from the outermost color layer in a cross section preparation. Such examples, which constituted 19 of the 30 paint samples studied (63%), illustrate the potential benefit of a rapid analysis. Furthermore, each sample was studied in triplicate from each orientation (*i.e.*, a minimum of six analyses per sample). Comparison of the replicates from a given orientation of the same paint showed no qualitative differences in the pigments could be discerned, which suggests that the Raman sampling volume under the conditions used, effectively rendered the sample homogenous.

The disadvantages of this approach are the inability to determine which layer is being analyzed and the difficulty in seeing the color layer. Figure 22 shows examples of several paint samples viewed from the top down (through the clearcoat), by reflected light microscopy. These images reveal the lateral heterogeneity of the samples and the difficulty that can exist in trying to find the proper layer on which to focus. In summary, of the 30 paint chips analyzed, 19 showed no difference between the top down analysis and cross section analysis (though some of these showed only fluorescence). Of the remaining eleven samples, six showed that orientation led to major differences, while five showed minor differences in the spectra obtained. Some of these differences are highlighted by the following examples:

Example 1: Identification of pigments in multiple layers (C-80056). This red paint chip has a total of 7 layers (1 clear coat, 1 tinted-clear coat, 3 color layers, and 2 primers, in that order from top to bottom). The 3 color layers and the tinted clear coat are all adjacent to one another. Raman analysis thru the clear coat permits identification of the following components: PR170; PR254; polystyrene and/or polyethylene. Analysis of individual layers by cross section analysis identified the same two pigments; however, they were actually present in two separate layers. Pigment Red 170 was identified in OT1, while Pigment Red 254 was found in OT3 (Figure 23). Note that no colored pigments were identified in OT2.

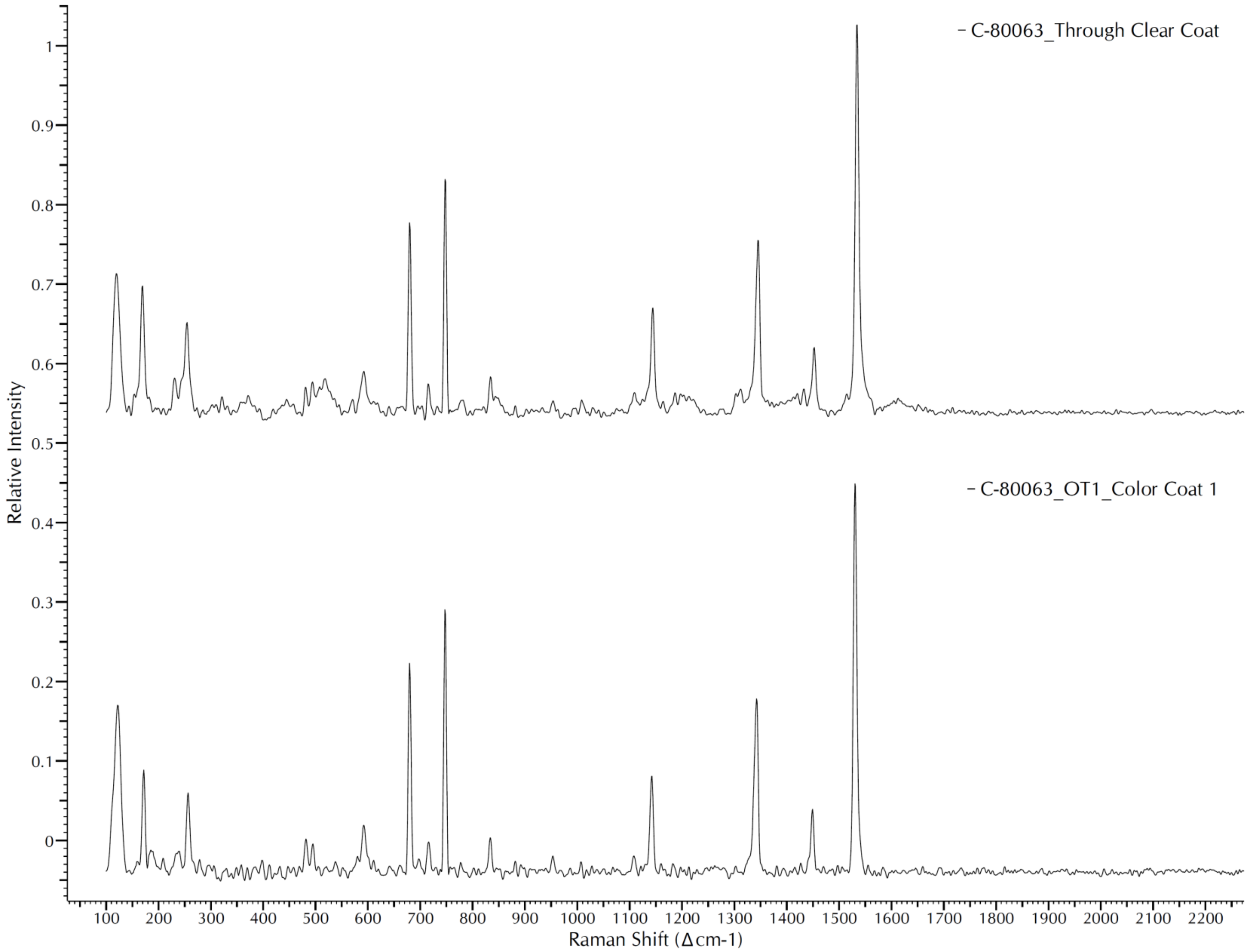


Figure 21. Two Raman spectra collected from the same paint sample as part of the directionality study. These two spectra show the case where the spectrum collected from a randomly positioned paint chip (that underwent no sample preparation) (top) is extremely similar to the spectrum collected from the outer color layer in a cross section preparation (bottom). Spectrum identified as Pigment Blue 15:6 (PB 15:6).

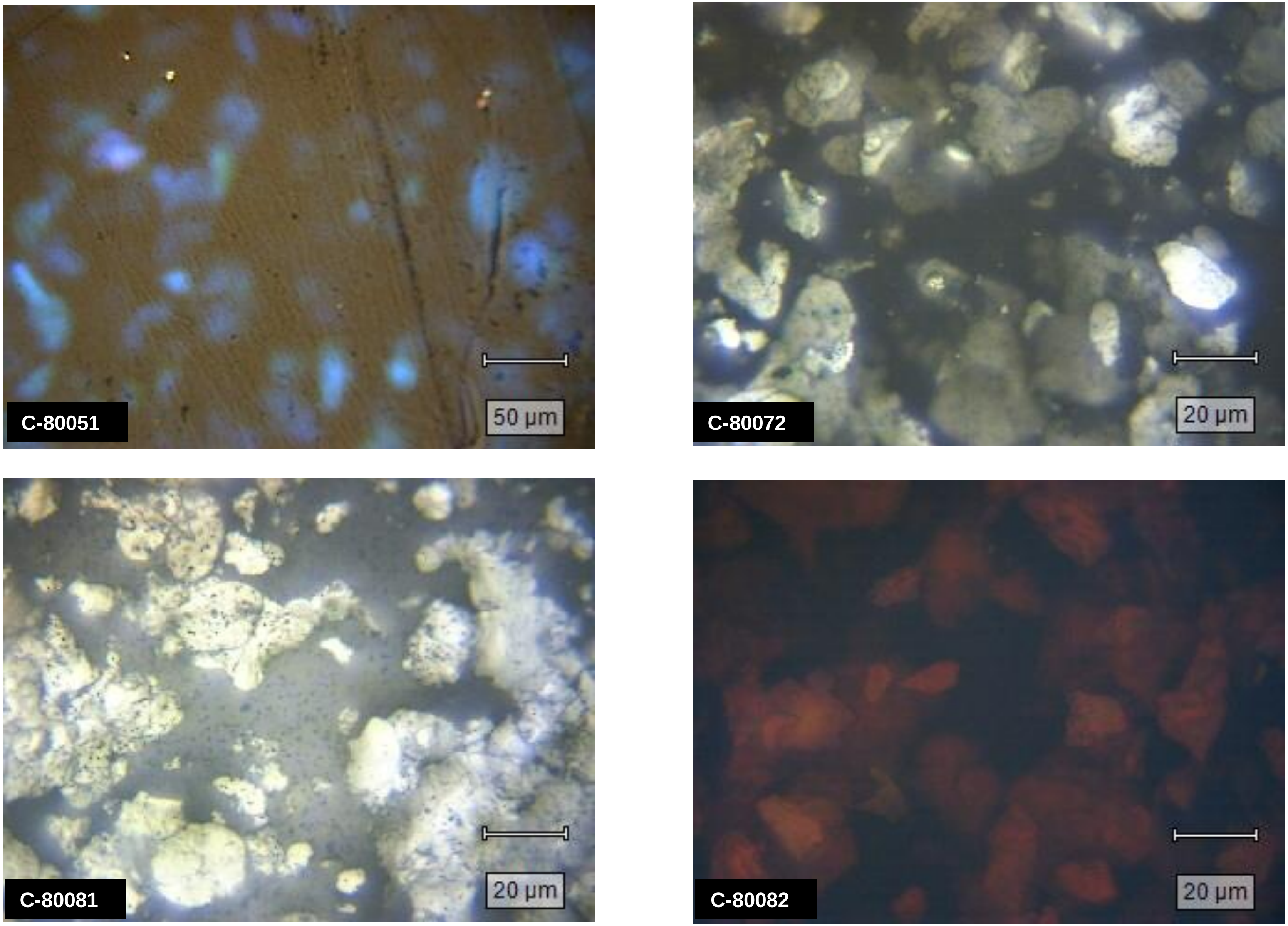


Figure 22. Reflected light Images taken through the Raman microscope through the clearcoat layer.

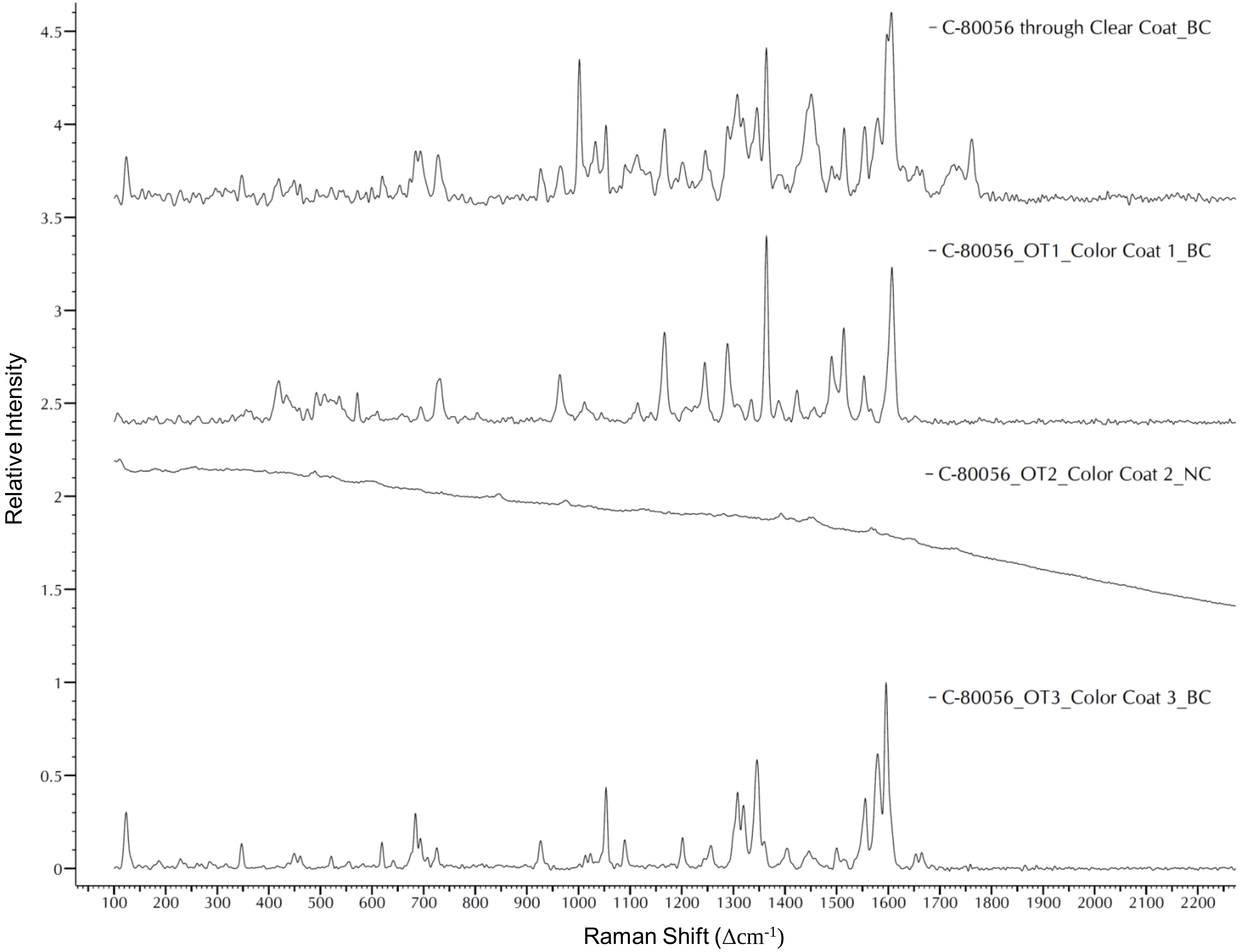


Figure 23. Comparison of spectra collected through the clearcoat (upper spectrum showing multiple components) and by cross section (showing the top three adjacent color layers (OT1, OT2, and OT3).

Example 2. Repaint Confusion (C-80066). This green paint sample shows three layers of repaint over the initial basecoat color layer, which resulted in 12 layers with 4 color layers (Figure 24). Each color layer is separated by a primer and clear coat. Based on analysis thru the clear coat, pigment PG7 (in layer OT10) was identified. Analysis of each colored layer in cross section showed that the uppermost green layer (OT10) contained PG7, the adjacent two green layers (OT7 and OT4) contained PG36, and the original green layer (OT1) contained a combination of PG36 and PG7 (Figure 25). PG7 and PG36 are both green pigments.

Summary

This sub-project showed that this quick screening process can provide spectral identification of pigments within a paint sample that has undergone no sample preparation. These results are not sufficient, in themselves, to determine the extent to which paints can be discriminated using this approach; however, they illustrate that the method should be considered as an early step in the comparison of paint samples of similar color– particularly, because of the fast nature of this analysis compared to other methods that require more extensive sample preparation. While this approach could likely be developed into a method to be used for eliminating samples from further consideration, it is not sufficient to confirm a comparison. For a more certain approach to paint comparisons, it is, we believe, necessary to conduct analysis on individual layers.

General Pigment Identification

Forensic Benefit

Given that the fast screening study shows the importance of performing analysis of individual layers, we formulated a plan to characterize the color layers in all 300 samples. The purposes of this exercise were to gain experience studying pigments in a variety of paint samples, be able to make some recommendations for best practices for such analyses, and obtain, for the first time, a sense of: 1) how often pigments could be identified in paint samples, and 2) how many different individual pigments could among a large set of paint samples. The goal was to develop a method that requires a level of effort on par with that used at present to conduct FTIR or SEM/EDS comparative analysis of paint in a forensic science laboratory.

Analytical Approach Development and Initial Results

Given that little experience existed in the *in situ* identification of pigments in automotive paints, we conducted an initial study of the color layers in 30 paint samples (10% of the total sample set) to refine our methods and obtain initial results. The initial 30 samples were selected from the 300 paint samples to represent the largest possible range of variation (color, make, model, age, *etc*.). Data for the first thirty paints underwent additional checks to ensure the heterogeneity of the results and overall consistency of data that was obtained.

A list of colors and layers represented by these 30 samples is presented in Table 5. Within the 30 samples, four had tinted clear coats, seven had multiple color layers, and two samples had been repainted showing multiple clear coats and primer layers.

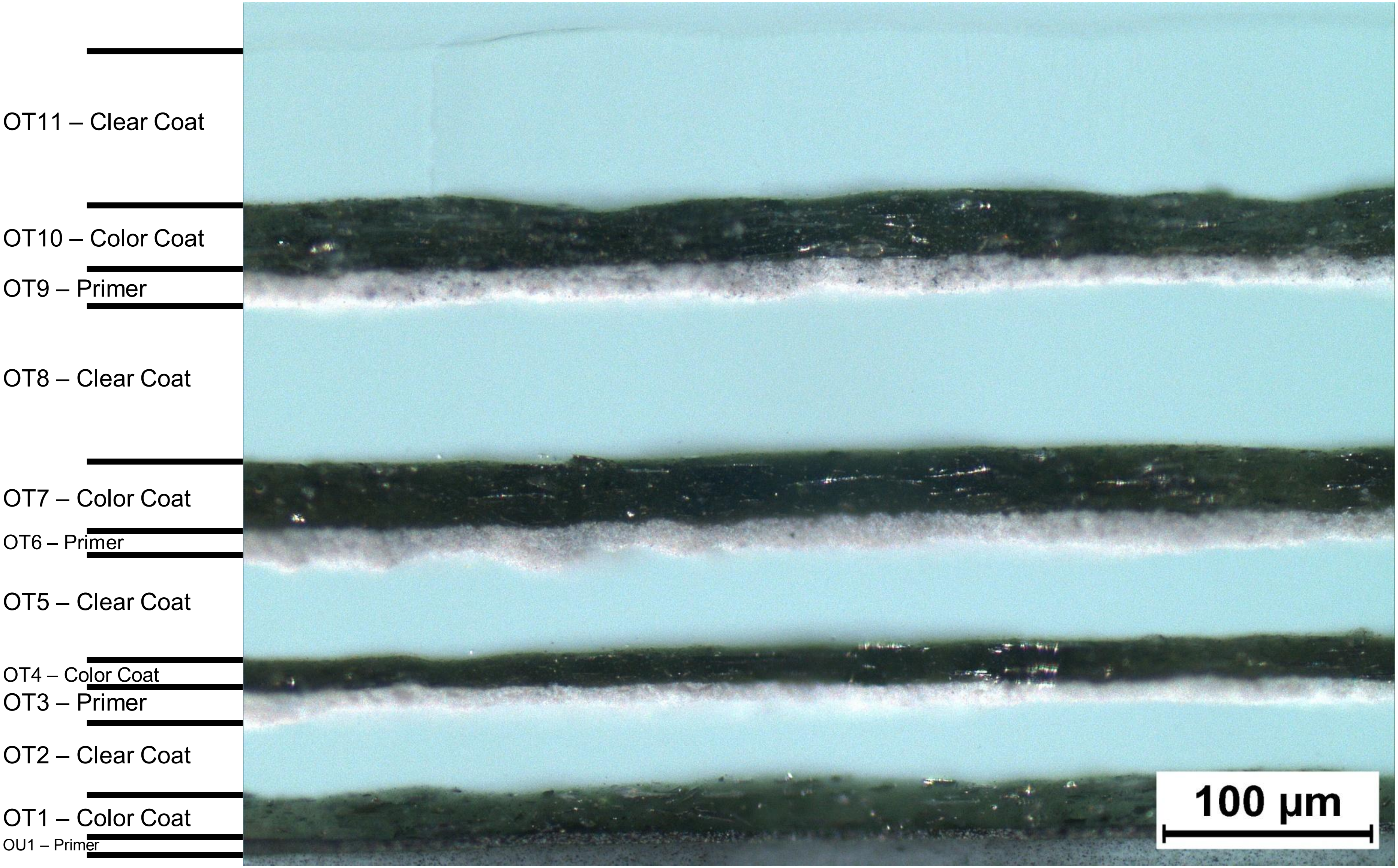


Figure 24. Photograph showing multiple layers within a single paint chip (*i.e.*, multiple primer and clear coats). BLOCK C – C-80066.

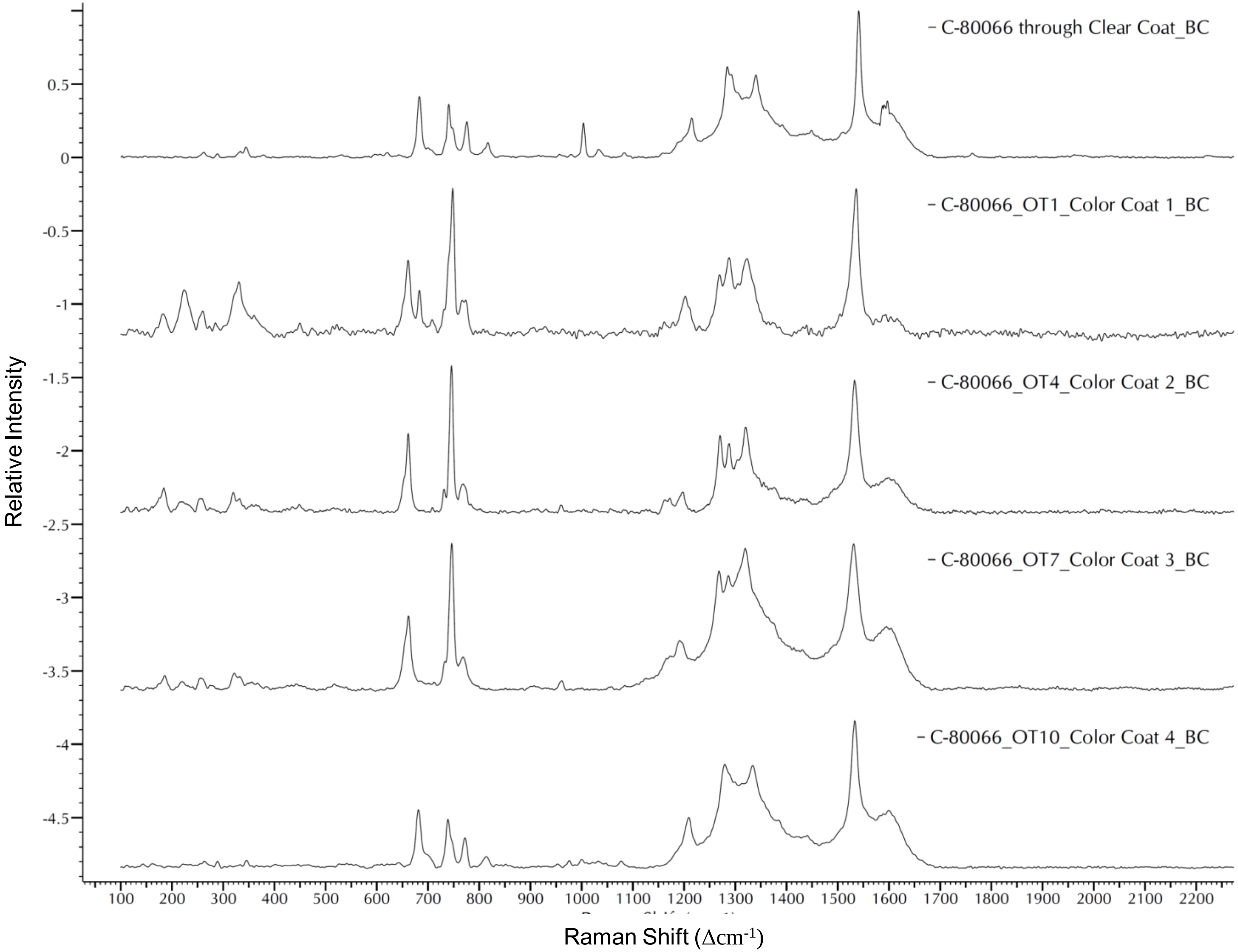


Figure 25. Raman spectra from colored layers in sample C-80066 showing that the outer layer contained Pigment Green 7 (PG7), while the inner color layers all contain Pigment Green 36 (PG36).

Table 5. Distribution of colors and layers within the 30 initial samples studied.

Distribution of colors	
Color	**Number of samples**
Blue	3
Red	10
Silver	5
Black	2
White	2
Green	4
Brown/Gold	4
Total	30

Distribution of Layer Types	
Layer designation	**Number of layers**
Clear Coat	34
Tinted Clear Coat	11
Color Coat	37
Primer Layers	50
Coordinated Primer Layers	0
Total	132

Paints were analyzed in cross section using a 785 nm laser focused to a line. Multiple analyses were performed on different areas in each layer, with a minimum of two replicates per layer. These results showed that in all cases, except one, the spectra collected from different areas of the same layer were qualitatively similar. That is, all pigments ultimately identified in a given layer could be identified in a spectrum collected from any location within that layer. This suggests that the use of a defocused laser (to a line) is generally sufficient in sampling volume to obtain a "bulk representative analysis" of a given layer.

In total, eleven unique pigments (or pigment groups) were identified within the 48 color layers that comprised the 30 samples. The identifications are based on the scheme devised in Palenik *et al*. (2011). The frequency of identification of those pigments is tabulated in the Table 6.

Table 6. Distribution of identified pigments in the 30 initial samples studied.

Pigment	Identification (Exact/Group)	Frequency
C.I. Pigment Black 7	Exact	12
C.I. Pigment Blue 15:3 (β)	Group	2
C.I. Pigment Blue 15:6 (ε)	Exact	1
C.I. Pigment Blue 60	Exact	6
C.I. Pigment Green 7	Exact	2
C.I. Pigment Green 36	Exact	3
C.I. Pigment Red 170	Exact	1
C.I. Pigment Red 224	Exact	2
C.I. Pigment Red 254 (α)	Exact	4
C.I. Pigment White 6 (Rutile)	Exact	9
C.I. Pigment White 26	Exact	1
No Colorant Identified	N/A	6
High Fluorescence	N/A	8

Identified Pigments

Following the analysis of the initial 30 samples and establishment of a firm approach, the color layers within the remaining 270 paint samples were analyzed. Within the three hundred automotive paint samples, a total of 498 colored layers were analyzed. A breakdown of these layers is presented in Table 7.

Table 7. Summary of layer statistics in the 300 studied paint samples.

Layer Type	Layers Analyzed
Tinted Clear Coats	82
Color Coats	405
Coordinated Primers	11
Total Colored Layers	**498**

Within these 498 layers, 496 pigment identifications were made. In addition to pigments, several other paint components were identified by Raman spectroscopy, which included some extenders, polymers, and modifiers. The 496 pigment identifications span eleven different chemical classes of pigments. These eleven classes of pigments can be sorted further into twenty-seven colorants. Twenty-one of the colorants have been identified to an exact pigment while six of the identifications can only be classified to a "chemical group" of pigments (as defined by Palenik *et al.* (2011)). "Chemical group" identifications are made when the Raman spectrum is not specific enough to differentiate between pigments with similar chemical structures or when the spectrum background is strong enough to limit the number of peaks that can be identified. A distribution of the colorants identified is presented as a histogram in Figure 26. In 13% of the 498 layers studied, no pigment could be identified. Such instances occur largely as a result of fluorescence; however, in some cases peaks existed that could not be attributed to a specific colorant or class of colorants and are likely related to the polymer composition of the sample.

In nearly seventy percent of the layers analyzed, only a single colorant was identified within a given paint layer. That number increases to just over ninety percent if carbon black is excluded as an additional colorant (see earlier Carbon Black section for discussion regarding potential contamination). The maximum number of colorants identified within a single paint layer was three, and several layers were identified that contained three colorants. Figure 27 shows a spectrum from a layer containing three pigments, while Figure 28 shows this same spectrum in comparison to reference spectra of the pigments it contains.

As one way to address the discriminating power of Raman spectroscopy for the analysis of automotive paints, the samples were grouped on the basis of colorants identified. This yielded forty-nine groups. When carbon black was excluded as a colorant (which is likely justified in some, but not all cases), this reduces that value to thirty-eight groups. Sixteen of those groups are composed of multiple pigments.

Pigment Specific Comments

Some details and additional observations concerning some of the more commonly identified pigments that arose out of our research are worth noting at this point:

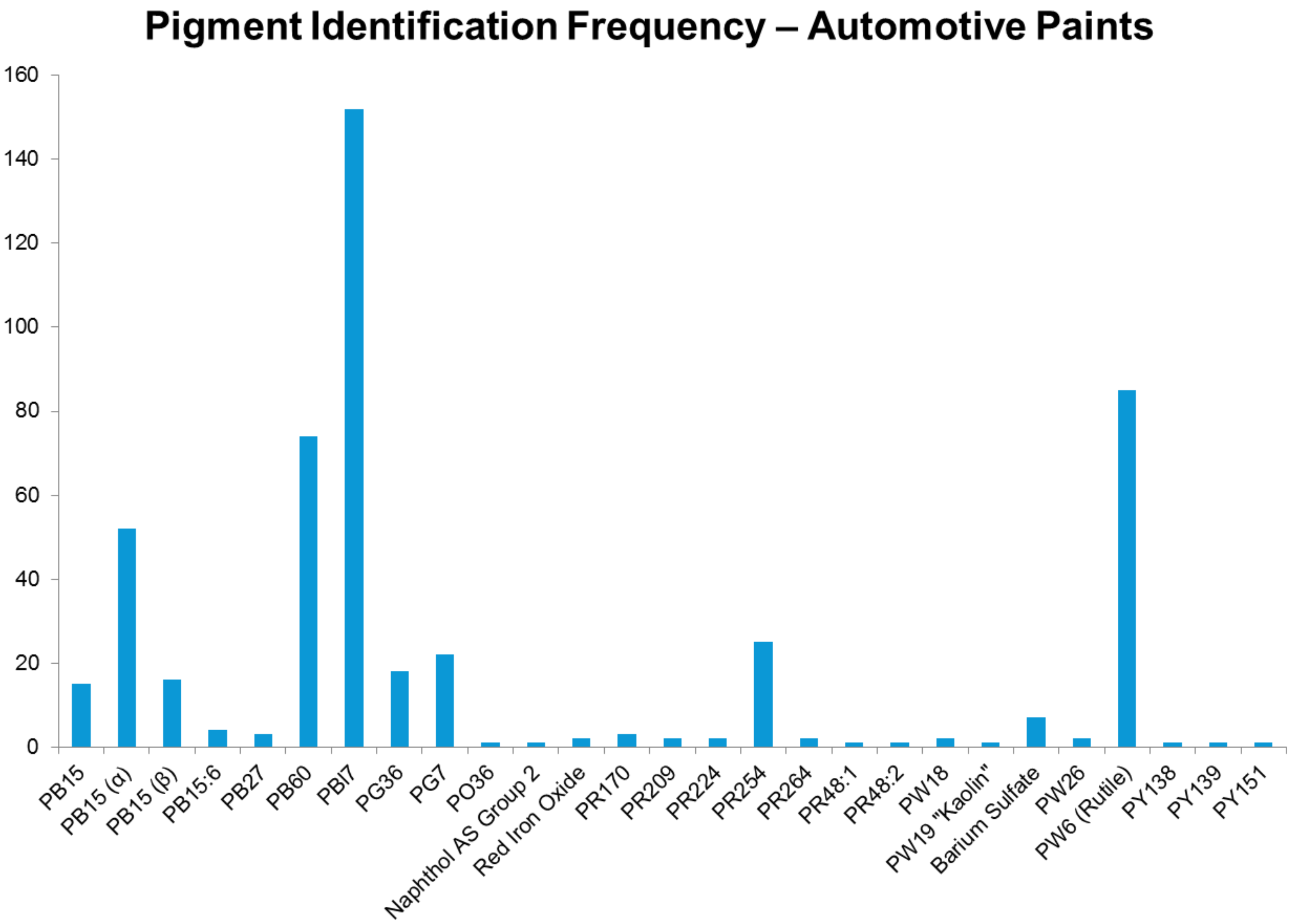


Figure 26a. Frequency distribution of pigments identified by Raman spectroscopy.

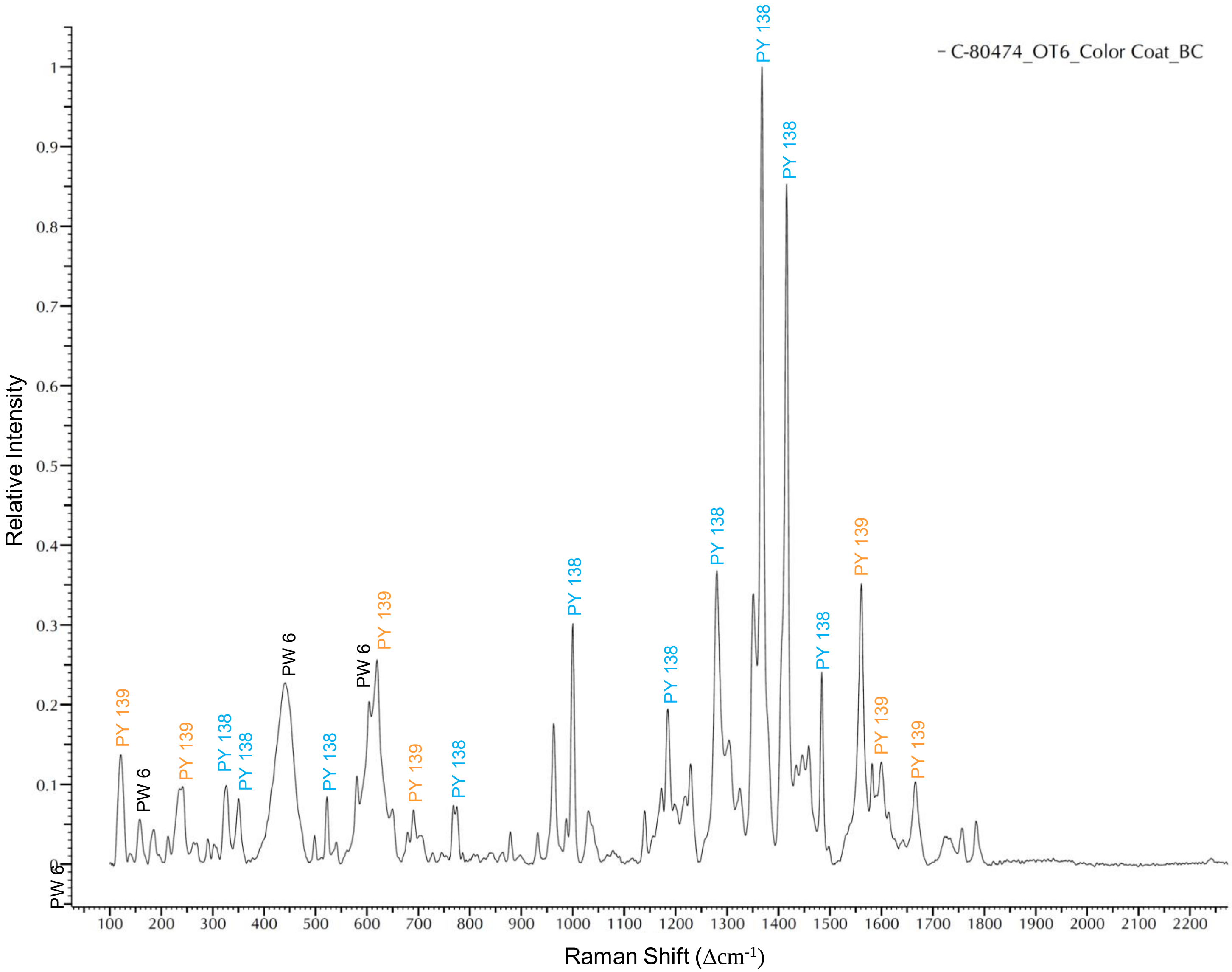


Figure 27. Raman spectrum of a color coat layer in which three pigments were identified. The peaks are labeled with the pigment to which they are assigned.

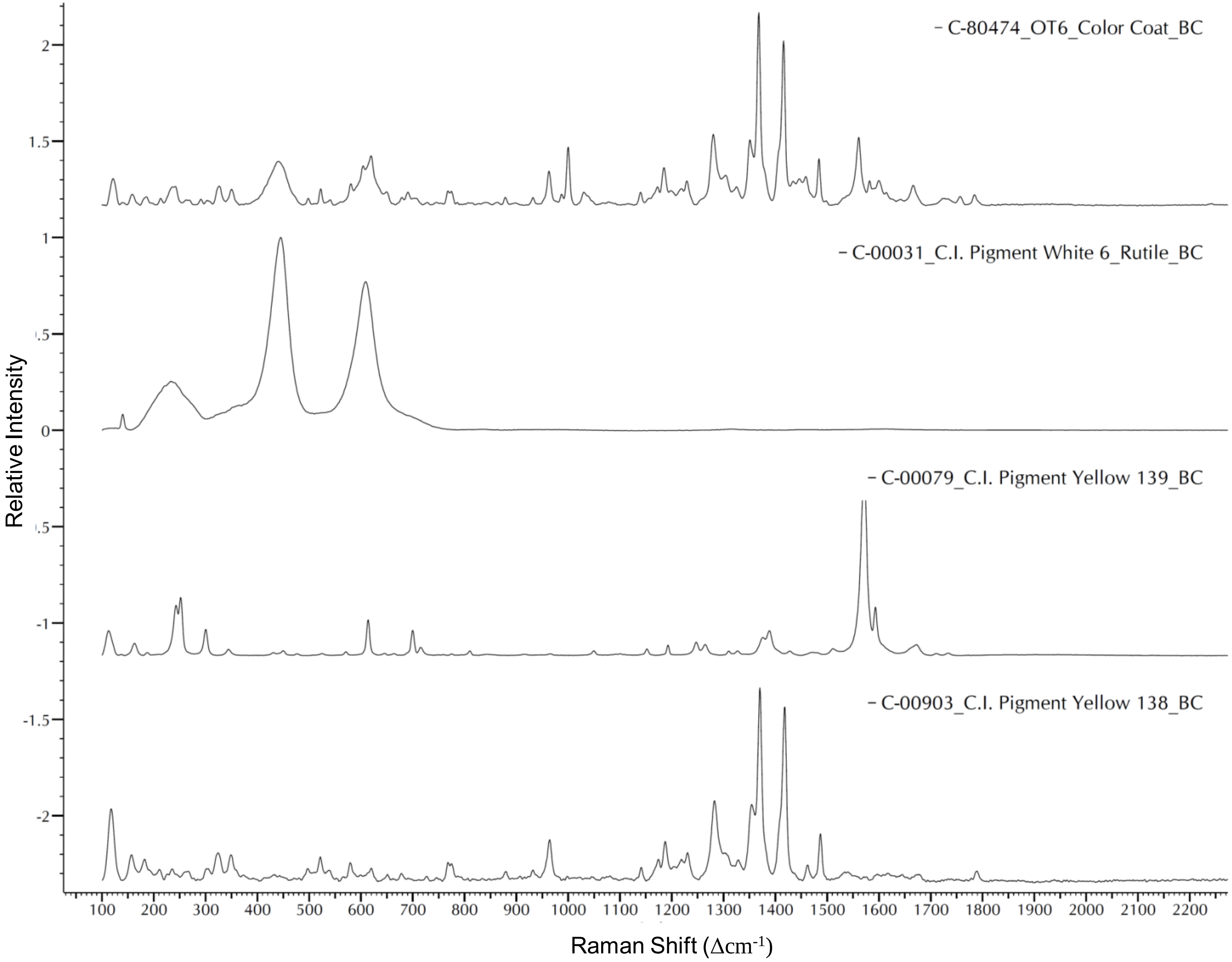


Figure 28. Raman spectrum of a color coat layer in which three pigments were identified. The spectrum is shown in comparison to reference spectra for the three identified pigments.

Carbon Black (Pigment Black 7). Carbon black is used in virtually any application requiring true black (*e.g.*, tires, plastic products, inks and coatings). It is ideally pure elemental carbon and its elemental composition reflects this. Traces of sulfur, hydrogen, oxygen, and several inorganic elements can sometimes be detected in concentrated samples of carbon black. The trace element composition depends somewhat on the starting material, and there are six main types of carbon black produced worldwide: acetylene black; channel black; furnace black; gas black; lamp black; and thermal black. Differentiation of carbon black produced from different sources or as different grades (size range) made by a particular process requires analytical methods beyond the scope of this research and beyond the needs of a typical forensic examination (ASTM D1765).

Although detected in many samples, the presence of carbon black in a Raman spectrum appears to be of little evidentiary significance, since it shows up in colors that would not be expected to contain it (*e.g.* white paint layers). Thus, while it is necessary to note the presence of carbon black (so as to account for as many peaks as possible when interpreting a spectrum), the Raman identification alone does not appear to provide any value. However, if it is suspected from a spectrum that carbon black is present in a particular specimen, light microscopy (or x-ray diffraction if there is enough present) can be used to verify its presence. . Figure 29 shows an oil immersion images of carbon black particles in a gray architectural paint (Palenik and Bonta, 2008). The carbon black particles in the photomicrograph are actually clumps of still smaller particles. Transmission electron microscopy (TEM) is employed when it is necessary to confirm the identity of this pigment and compare it to a suspect source.

*Pigment White 6***.** Titanium dioxide occurs naturally in four polymorphs: anatase, brookite, rutile, and akaogiite. Anatase and rutile are industrially produced in large quantities, with the largest volume going into to paints and plastics. Both have a number of properties which are far superior to other white pigments, including: scattering power (which is directly related to hiding power); brightness; dispersibility; and weather resistance. Anatase and rutile have extremely high refractive indices of n = 2.55 and n = 2.80, which permit particles to be readily identified in a prepared specimen by polarized light microscopy. Rutile is more costly but has lower catalytic activity than anatase when used in polymers, which makes it a better choice and thus more common in automotive paints. In the modern automotive paints studied in this work, all of the titanium dioxide encountered was present as the rutile polymorph. No anatase was identified; however, analyses of paints from older vehicles have identified anatase. Today, it appears that anatase is more likely to be encountered in architectural and artist paints than in automotive ones.

*Pigment Blue 60***.** PB 60 is an organic pigment classified as indanthrone. It is primarily used in metallic automotive finished because it provides good transparency. It is often used today in place of PB 15 or the blend of PB 15 with PV 23, because of the weatherfastness[2] it provides.

Pigment Blue 15. These blue phthalocyanine pigments are widely utilized in blue paints with each crystal modification having its own application. The α (PB 15:1 and PB15:2) and β-modifications (PB 15:3 and PB 15:4), can be used to brighten white paints, including original automotive finishes and refinishes. The α-form provides a reddish shade of white, while the β is greenish white. Other applications include printing inks, spin dyeing of various fibers, and the coloring of plastics.

The ε-modification of this pigment, PB 15:6, has also been gaining interest in recent years. This copper based phthalocyanine pigment affords the reddest blue shade of this group. The ability to sufficiently heat stabilize this

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[2] Weatherfastness refers to the effects of irradiation and atmospheric impacts on a pigment vehicle system.

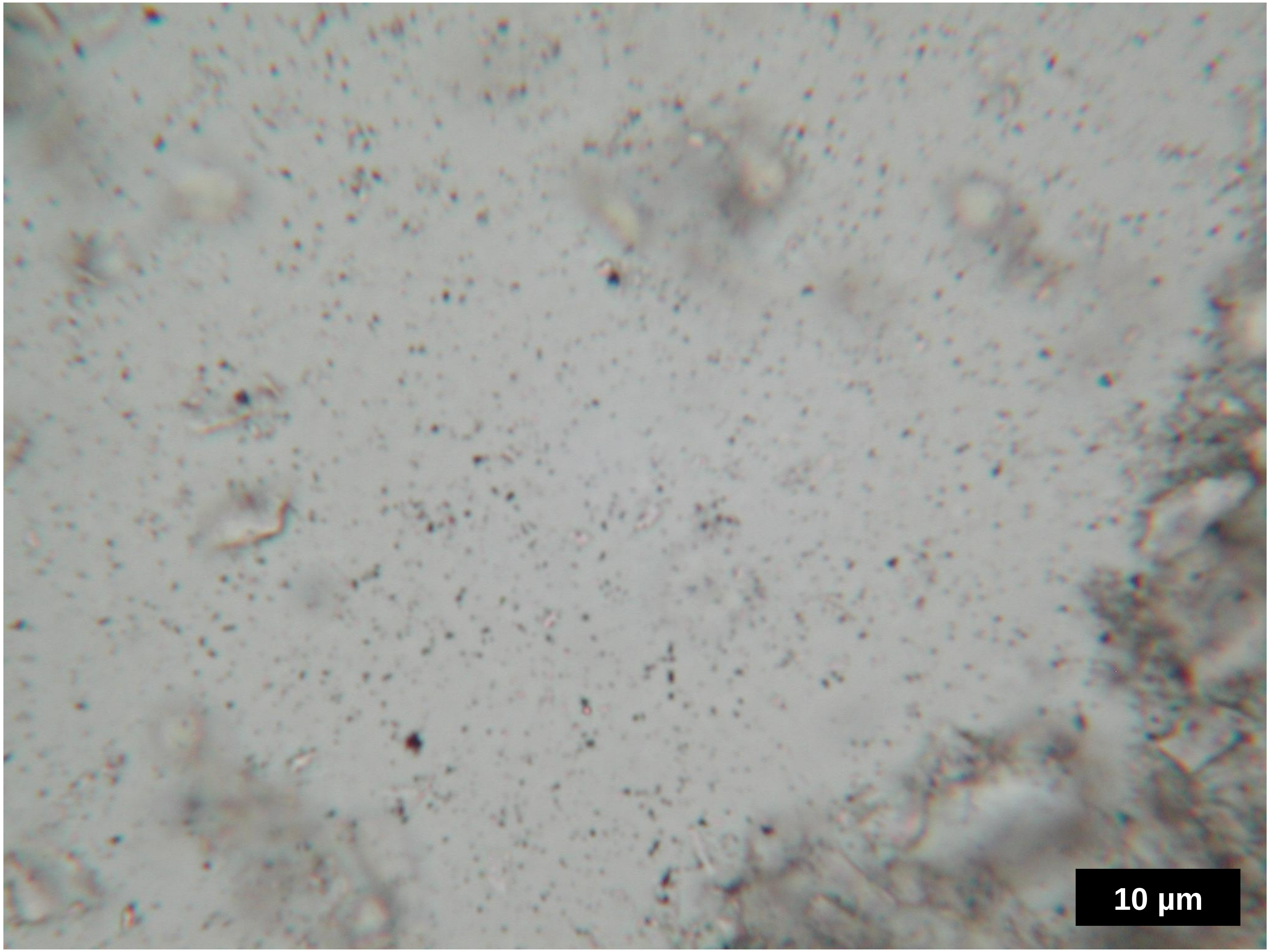

Figure 29. Smeared gray paint sample showing the presence of carbon black particles.

pigment has largely eliminated color unwanted effects during application. The most common use for PB 15:6 is in color filters for liquid crystal displays.
Halogenation of this pigment results in the production of various green pigments including PG 7 and PG 36.

Summary

This sub-section has shown that pigment identification in cross section is possible and at least one pigment can be identified in the majority of samples studied. The 27 identified pigments represent only a fraction of the pigments in production, nonetheless, this variety of pigments is a larger group than the total number of polymers and modifiers that are identified for differentiation by FTIR spectroscopy, which provides reason to believe that pigment identification can provide increased evidentiary significance for comparison and/or sourcing (as will be discussed later in the section on "Evidentiary Significance").

Thin section / Individual Pigment Identification

Forensic Benefit

Microscopical examination of paint thin sections performed prior to this research has shown us that pigments can be qualitatively recognized, grouped, and sometimes identified on the basis of color and other optical crystallographic properties. During these prior projects and internal research, we have recognized samples in which additional pigments are present at low concentrations (relative to any major pigments in the paint). In such cases, these pigments may not be detected by a "bulk" examination approach, such as that used in the "screening" section or in the "general pigment identification section." In cases where the most discerning and critical analysis is required, such as in a high level comparison or in an investigative examination in which one is attempting to establish the origin of manufacture of a product, a more detailed analysis can be performed that can, in many instances, result in the identification of such *trace* pigments.

Analytical Approach

The identification of trace and low minor pigments cannot be undertaken without first identifying candidate particles for analysis. . This can only be done by light microscopy using a very thin section (<2 µm) or a monolayer of paint prepared by smearing it as thin as possible. Examination of such smears or very thin sections at high magnifications in transmitted light permits the detection and recognition of particles with different colors, refractive indices, or birefringence than the principal pigments. Such particles can be optically compared in questioned and known samples, and when identification is required, confocal Raman spectroscopy provides the best chance of identifying them.

Results

Five examples that illustrate this very important technique are provided below. Using this method, confocal Raman spectroscopy was used to identify paint pigments that are present at extremely low levels compared to the primary pigments (the latter of which were identified with a defocused line analysis on a cross section).

Example 1. Analysis of Sample C-80400 using a defocused beam showed the presence of only one pigment (PB 15). Examination of a thin section revealed multiple colored pigments present in the colored layer. Blue, purple, black and red pigment can be observed in the thinnest section (Figure 30), whereas viewing the thicker section of that paint sample showed blue and some indications of a red secondary pigment (Figure 30 inset). With the beam of the laser focused onto one of the larger purple colored agglomerates, the purple could be identified as Pigment Violet 23 (β polymorph) (Figure 31). The spectrum obtained from the red pigment cluster is a mixture of signal

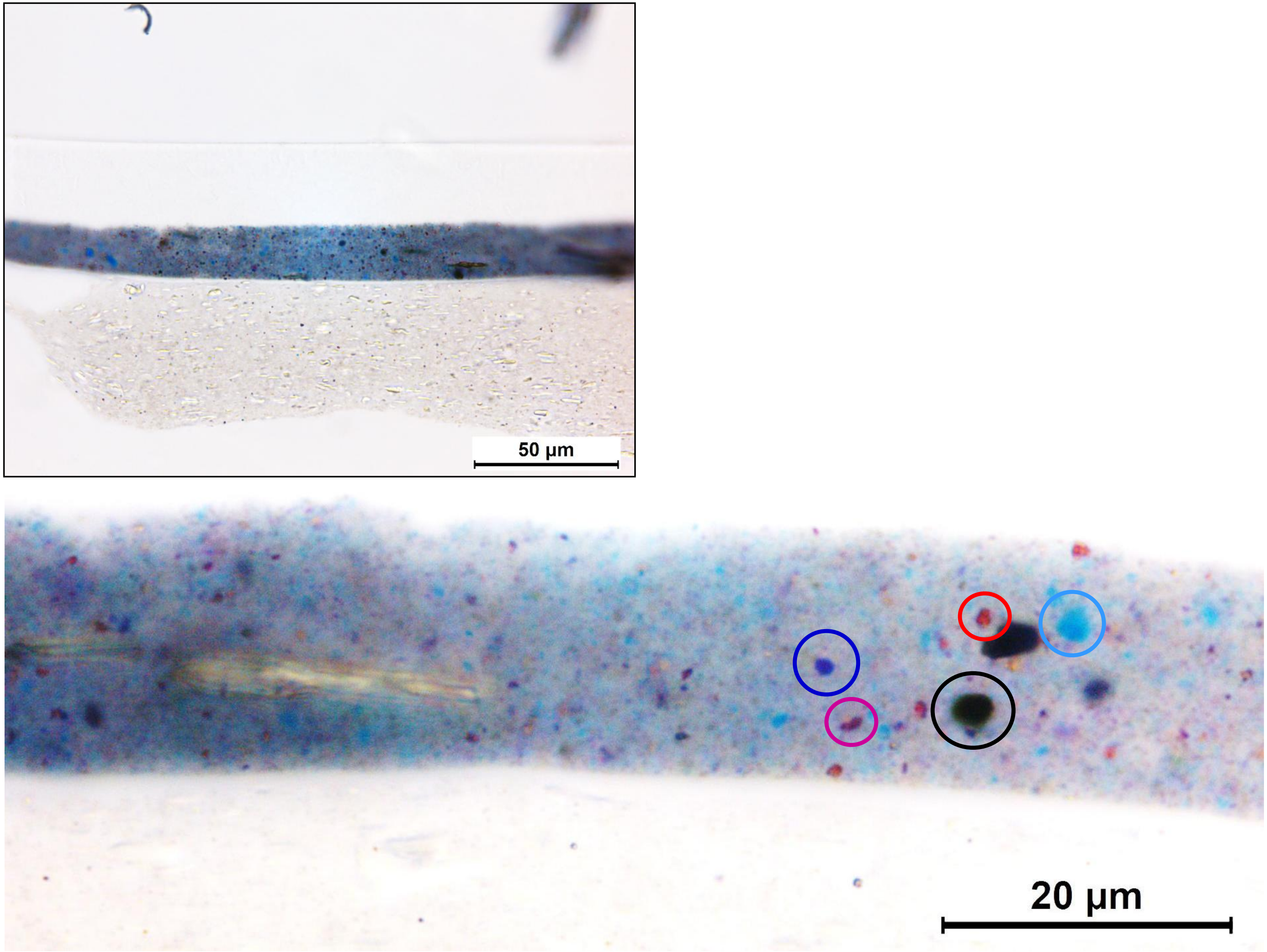

Figure 30. The inset (upper left) shows a typical thin section (~10 µm in thickness) from this sample. The larger image shows the same sample cut to a thickness of approximately 2 µm. Note that red, purple, blue, and black pigment particles can be visually observed in the section. The color of the outline indicates the color of the particle within the circle. (Sample C-80360).

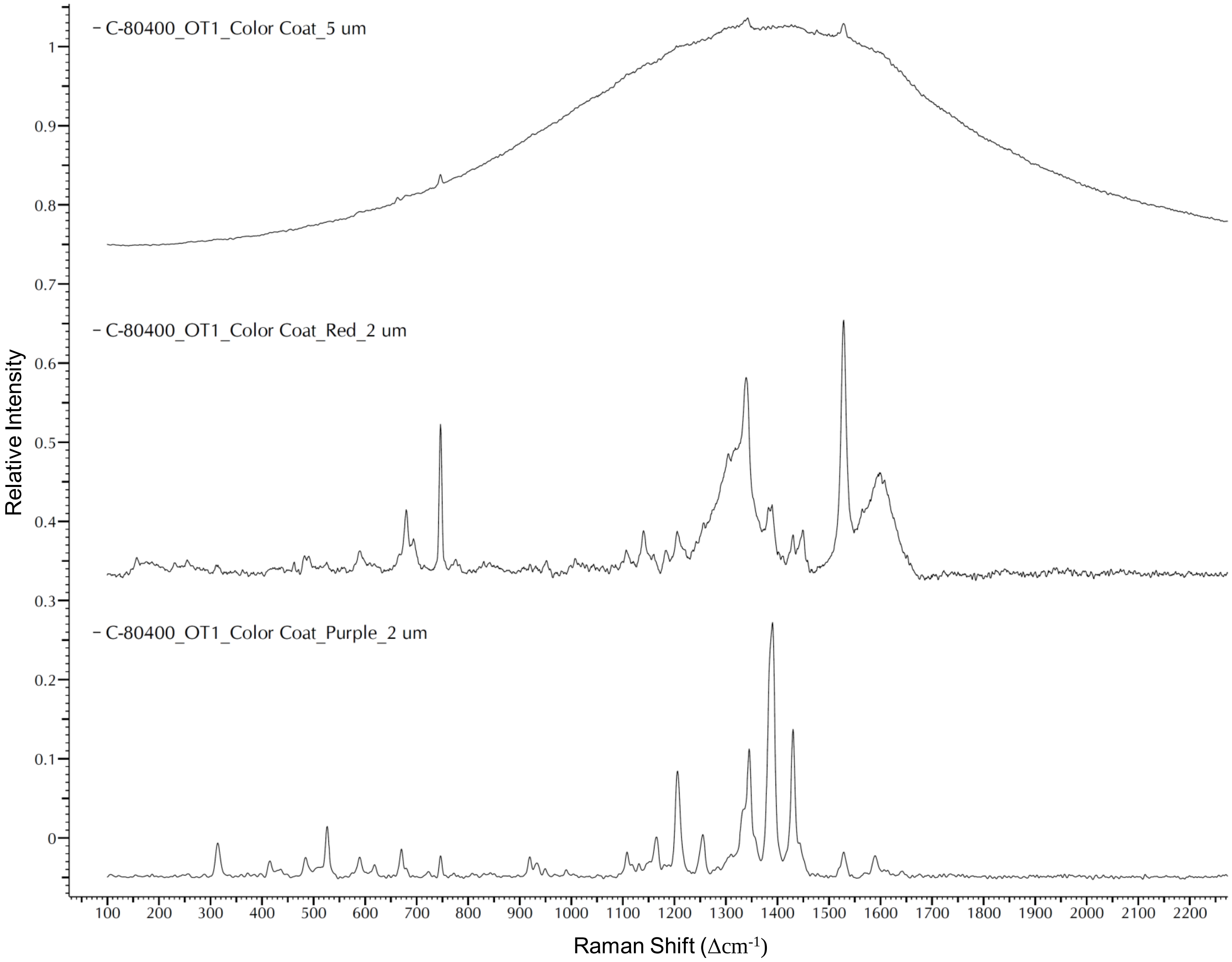

Figure 31. Comparison of Raman spectra collected from (top) a typical section, and the red and purple particles from the in the 2 µm section using confocal spectroscopy (C-80400).

from PV 23(β) and PB 15. There are small additional peaks present, but not enough information to conclusively identify the pigment; nonetheless, this could be used for comparison.

Example 2. A thin preparation of a paint layer revealed red pigmentation within sample C-80457 (Figure 32). Additionally black, blue and yellow pigments were seen in the colored layer of this thin section. Raman analysis of a larger undispersed cluster of the red pigment showed high fluorescence, which prevented its identification. The black pigment was identified as carbon black and the blue pigment as C.I. Pigment Blue 60, which is also present in a larger quantity. The blue pigment had already been identified by the defocused laser approach. Finally, no spectrum from the yellow pigment could be obtained, due at least in part to the fact that no larger clusters of this pigment were observed. This sample illustrates a case where Raman spectroscopy could not identify the trace pigments by name; however, light microscopy could be used to qualitatively illustrate their presence and permit comparison to be conducted.

Example 3. In the photomicrograph of the thin section of sample C-80366 (Figure 33), red, yellow, blue and black pigment clusters can be seen. Indications of the spectrum from the red pigment could be seen in the defocused laser spectrum (upper spectrum, Figure 34), however, it could not be identified definitively due to the strong carbon black (PBl7) and copper phthalocyanine (PB 15) signals. Analysis of individual particles by confocal spectroscopy permits identification of the red particles as Pigment Red 122 (lower spectrum, Figure 34). A spectrum could not be obtained from the yellow particles, possibly due to the fact that the individual particles were approaching the resolution limit of the light microscope.

Example 4. Microscopical examination of a black paint sample (Figure 35) showed that a fine green/blue pigment is dispersed throughout. Raman spectroscopy confirms that the pigment is Pigment Green 7 (a halogenated copper phthalocyanine).

*Example 5***.** In this example, we examined an unknown green smear. A portion of the smear was dispersed on a microscope slide. Microscopical examination showed the presence of green and yellow areas (Figure 36). No individual pigment particles were observed among the crystals of the calcite extender in the microscopical analysis. Thus it was not until examination by Raman spectroscopy that the presence of pigments, as opposed to a dye, was confirmed. Examination of the Raman spectrum of this pigment confirmed the presence of Pigment Green 7 and a diarylide yellow (a class of yellow pigments that is difficult to further sub-classify by Raman spectroscopy) (Figure 37).

In this example, the pigments were extremely well dispersed, making identification of a single pigment unfeasible; nonetheless, microscopy suggested that the Raman spectrum should contain two pigments. This orthogonal confirmation of identification by independent techniques is particularly helpful when conducting an investigative examination. The presence of high concentrations of other fillers (kaolin, talc and calcite) in the FTIR spectrum overwhelmed any polymer that was present. While pyrolysis GC-MS remains a viable option to compare polymers, Raman spectroscopy provided a fast and strong point of comparison along with additional investigative information in a short time.

Summary

The study of extremely thin sections and smears by confocal Raman spectroscopy offers what is arguably the highest level analysis in pigment identification[3], and as these examples show, the potential for identifying pigments

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[3] Since individual pigment particles are detected and identified.

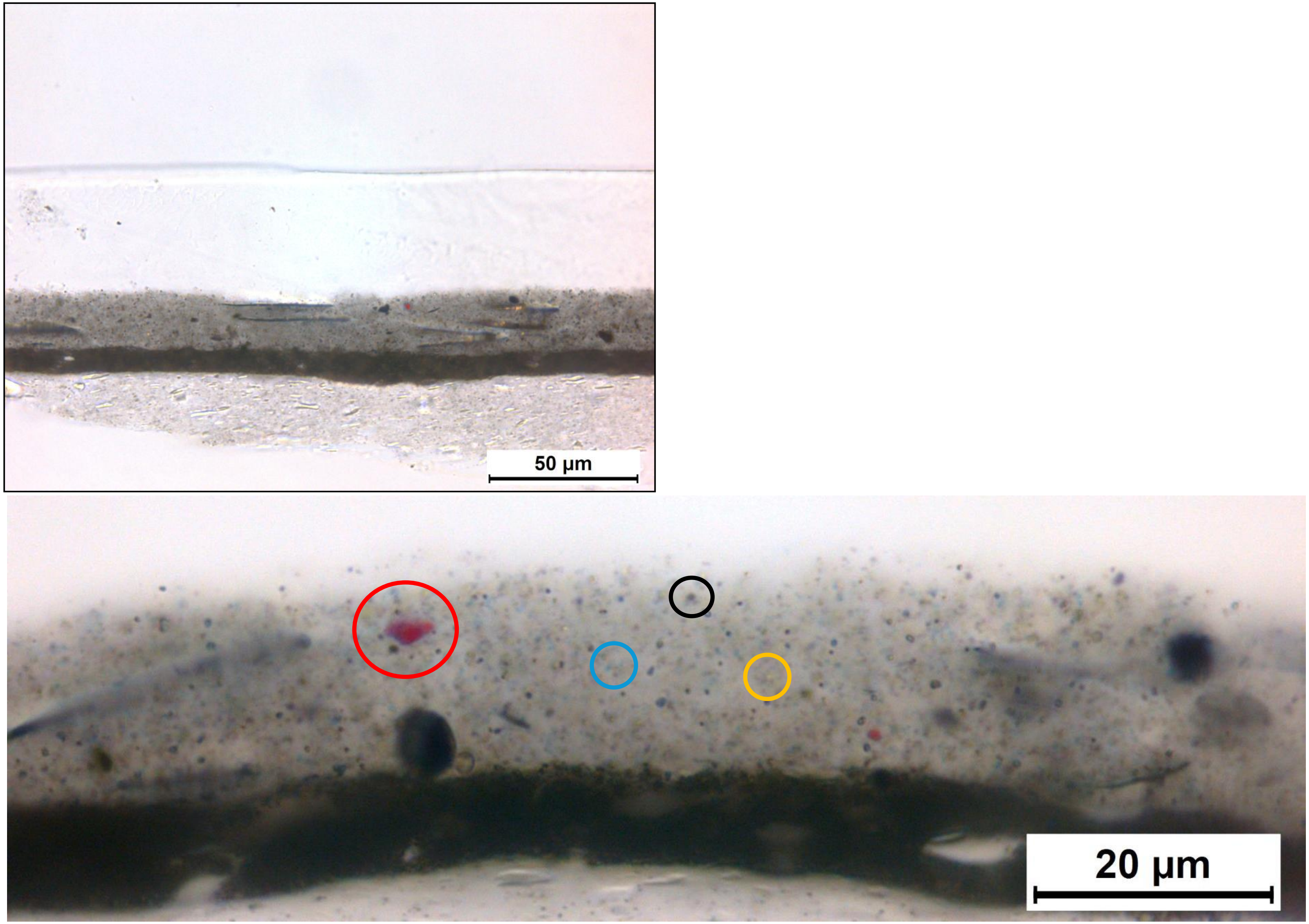

Figure 32. The inset (upper left) shows a typical thin section (~10 µm in thickness) from this sample. The larger image shows the same sample cut to a thickness of approximately 2 µm. Note that the red, yellow, blue and black particles can be visually observed in the section. The color of the outline indicates the color of the particle within the circle. (Sample C-80457).

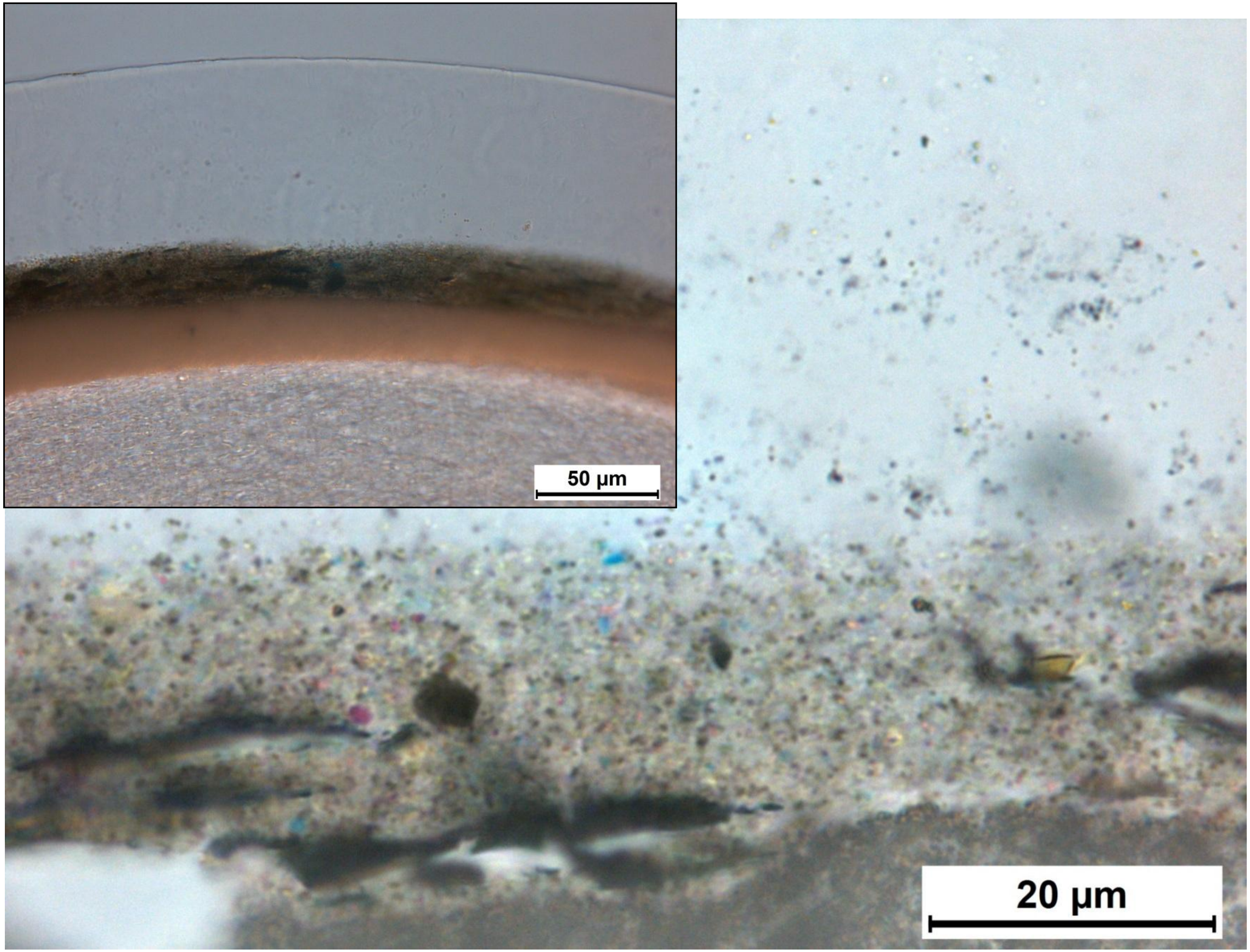

Figure 33. The inset (upper left) shows a typical thin section (~10 µm in thickness) from this sample. The larger image shows the same sample cut to a thickness of approximately 2 µm. Note that purple, blue, yellow, and black particles are visible in this section (C-80366).

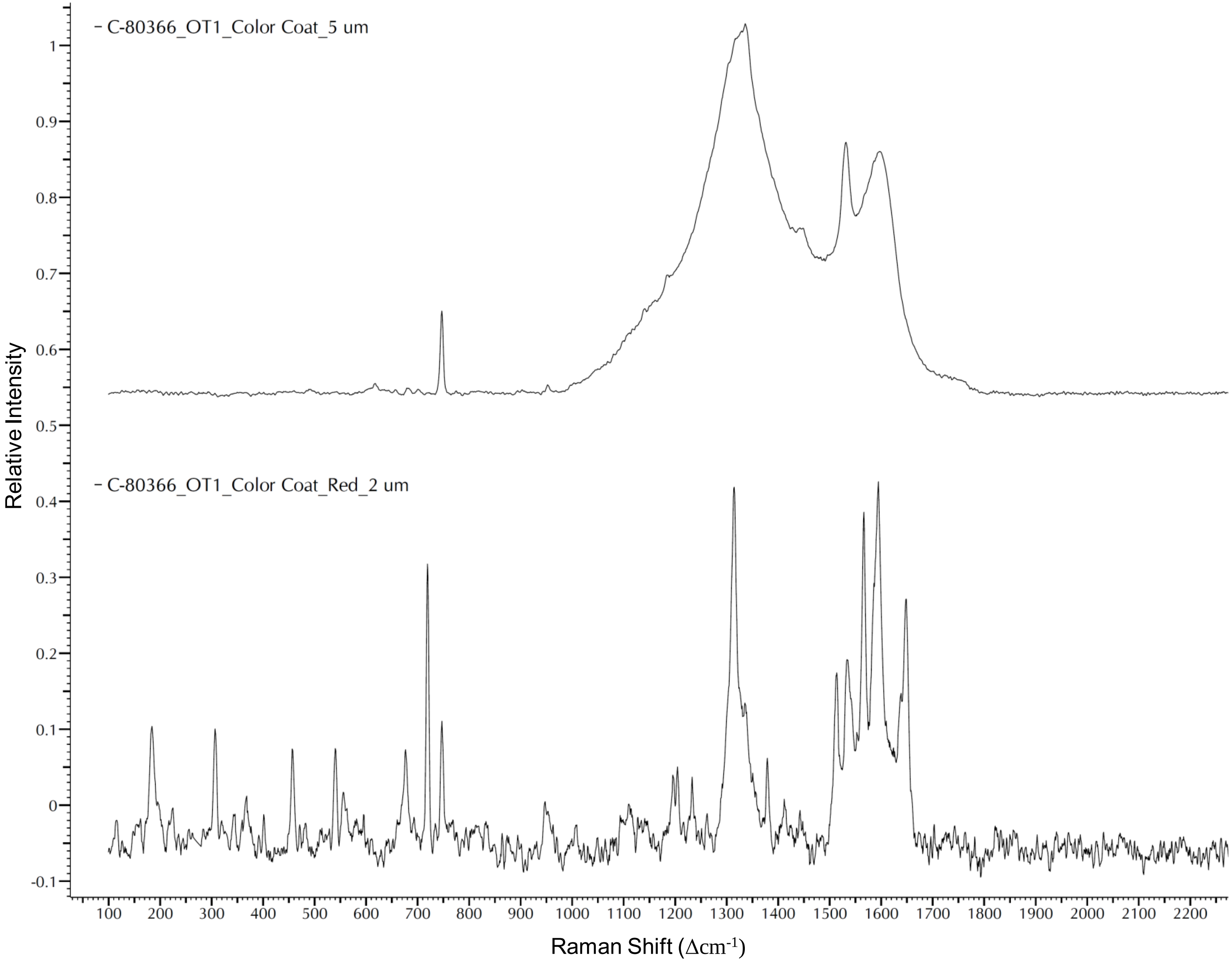

Figure 34. Comparison of Raman spectra collected from (top) a typical section, and one of a red particle observed in the thinner section.

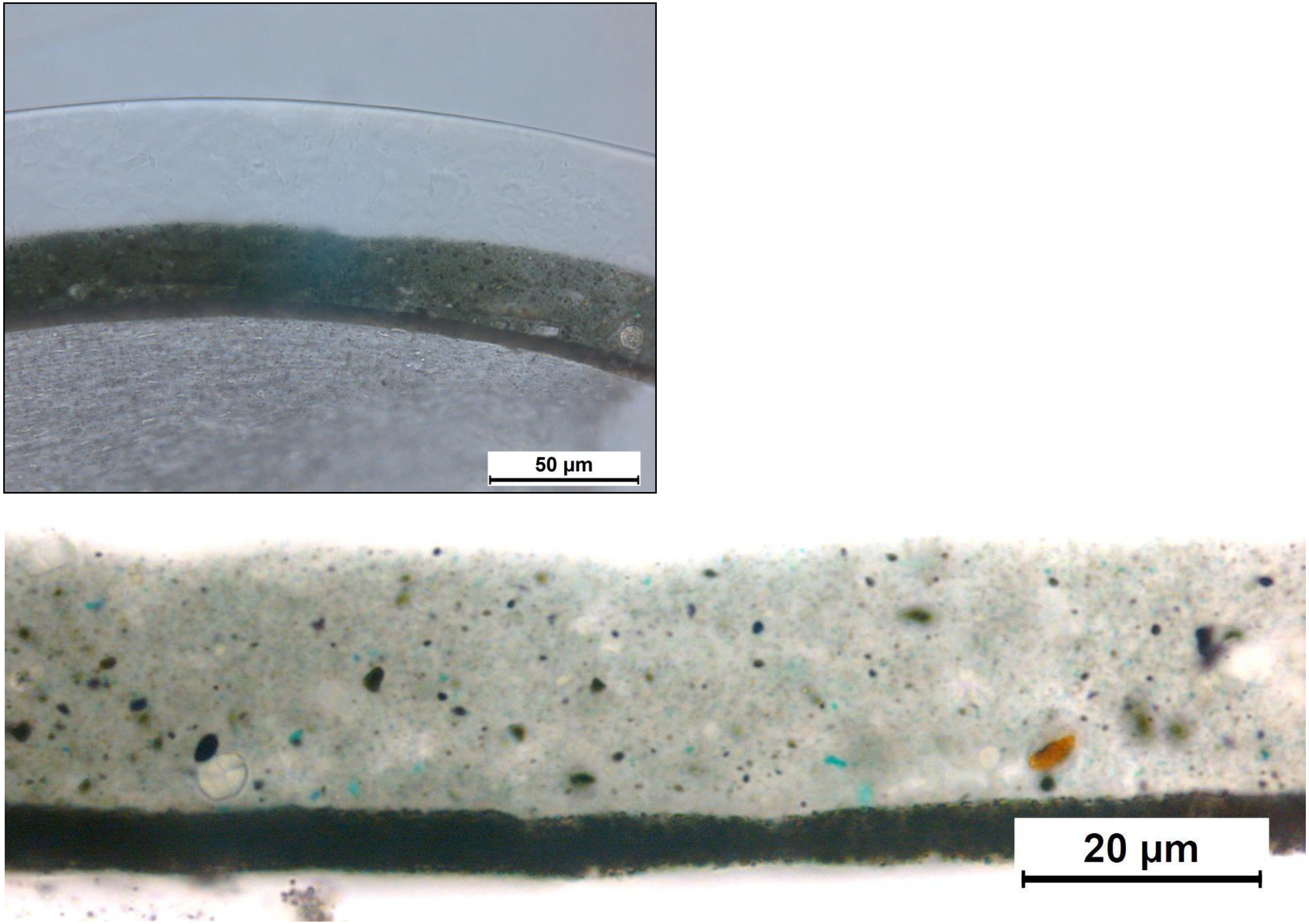

Figure 35. Black paint with green pigmentation (PG7) (C-80360).

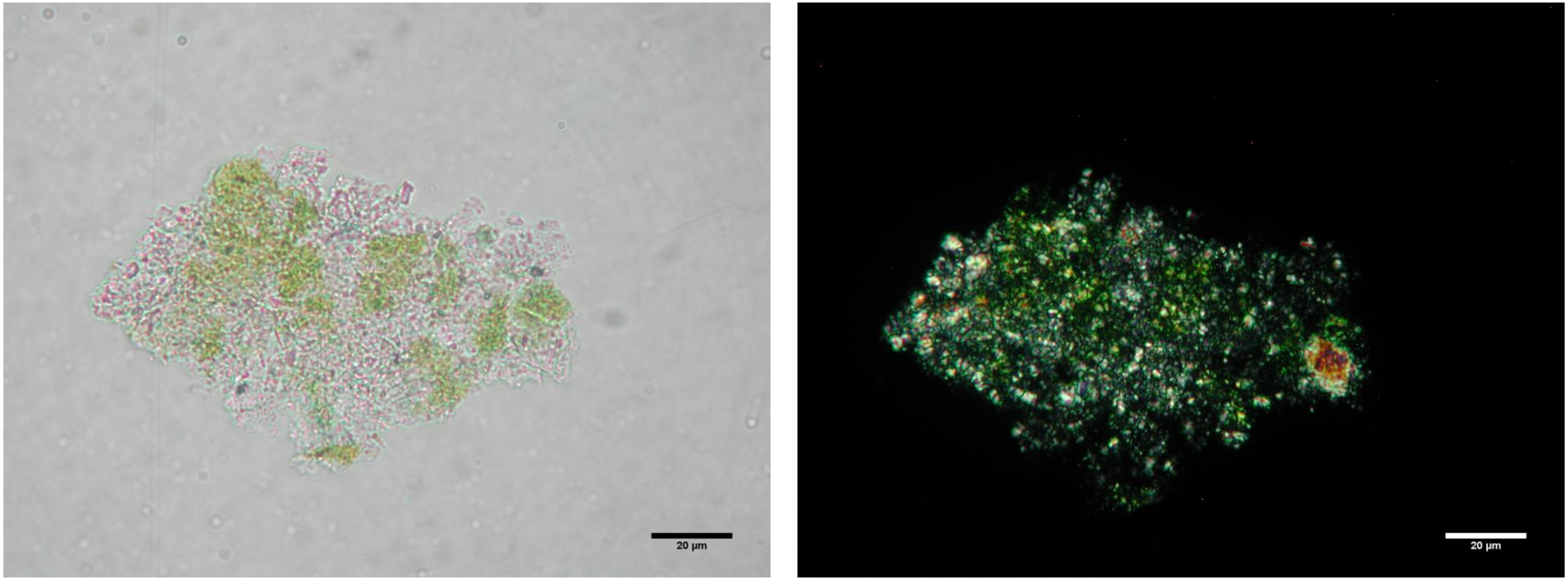

Figure 36. (Left) Plane and (Right) crossed polars images of a green residue as observed mounted in 1.660 refractive index liquid. The high birefringence of the particles is from a high concentration of calcite filler.

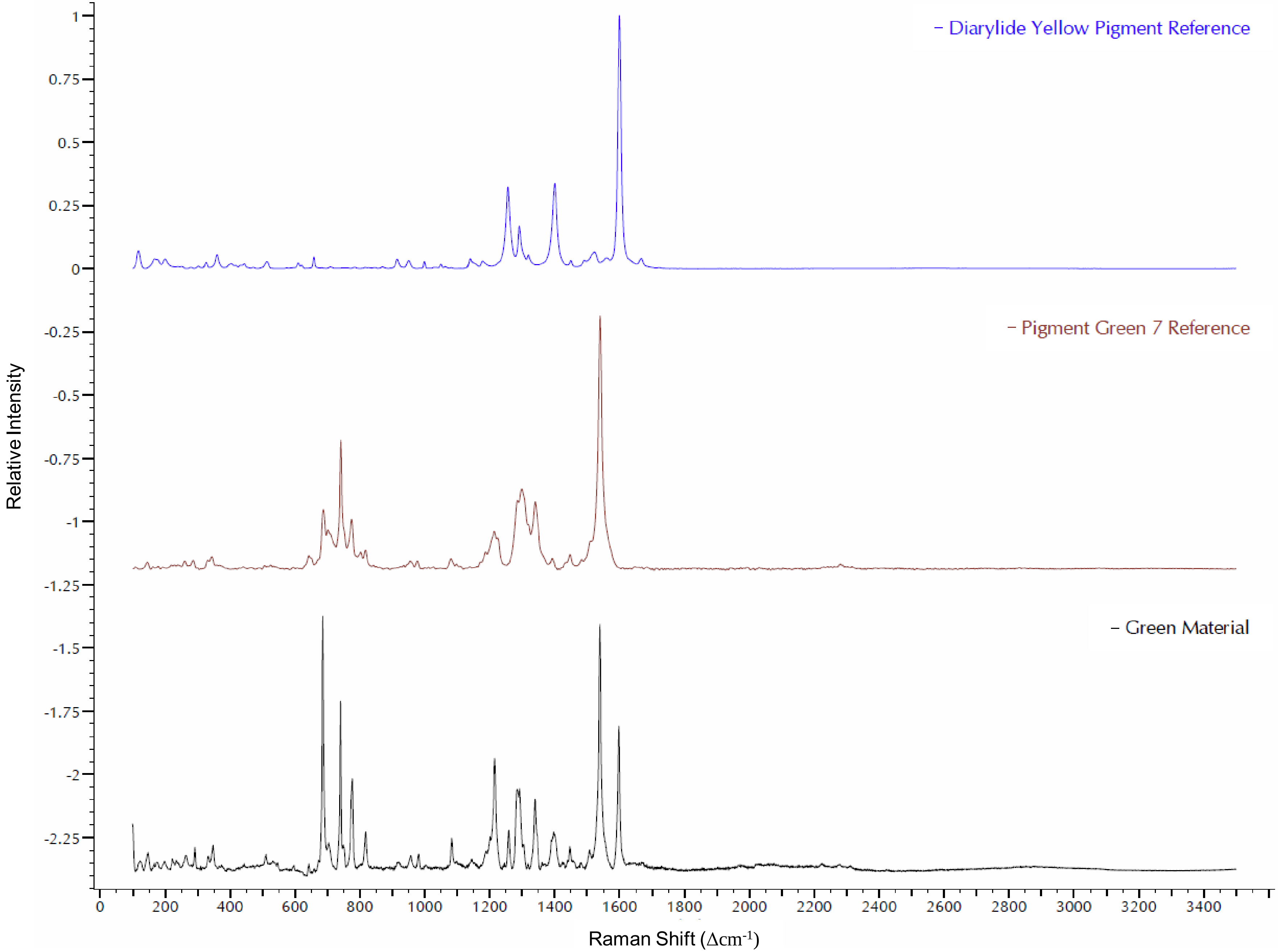

Figure 37. Confocal Raman spectrum of the green material compared to reference spectra of PG 7 and a typical diarylide pigment.

not even observed by less time consuming sample preparation methods. The use of microscopy in these cases is not difficult (as it does not require particularly advanced skill in microscopy) but the identification of trace-level pigments can provides a strong point of comparison that could not be made in any other way. This information is also known to be helpful in manufacturer sourcing activities.

Summary of Forensic Applications

Three approaches to sample preparation for Raman spectroscopy have been presented in this section. Each application has a potential application in the forensic paint analysis laboratory ranging from fast screening to high level analysis. Even the high level analysis just discussed requires little (if any) effort beyond that used to prepare samples for analysis by other methods currently in use in the forensic laboratory (*i.e.*, FTIR and SEM). The results provide additional points of comparison that can be used in addition to or in lieu of current methods for comparative analysis and paint sourcing.

EVIDENTIARY SIGNIFICANCE

Forensic Benefit

Given the nearly universal acceptance of FTIR spectroscopy and SEM/EDS as the principal analytical methods for paint comparison, many laboratories (ours included) have asked the question: “Does Raman microspectroscopy provide discrimination beyond that obtained FTIR spectroscopy alone?”

There are several direct and indirect responses to this question. The philosophical response is “Yes,” in theory, since pigments are commodities and as such, price and availability in addition to fashion and suitability may factor in to the decision to use a particular pigment (s) in a particular paint formulation. Even over relatively short periods of time, it doesn’t seems unlikely to expect that pigment compositions would be altered to adapt to changes in the supply stream (even in cases when the remainder of the binder chemistry remains constant). Of course, this might be expected to occur less for customized pigments with specifically tailored properties.

Secondly, while SEM/EDS may still provide elemental discrimination between two paints with similar or the same binders, elemental analysis cannot provide direct identification of a pigment or extender in any but the most exceptional cases. Elemental analysis cannot distinguish between rutile and anatase or PB15 α, β, and ε polymorphs. That is, Ti and O may suggest titanium dioxide but do not prove the presence of titanium dioxide let alone identify the polymorph in which it is present. Similarly copper, chlorine and bromine can be indicators of a halogenated phthalocyanine, but they can’t identify the specific pigment.

However, these responses still skirt the question of discriminating power. The work stemming from this grant, our prior grant (Palenik et al., 2011), and several years of internal research have been designed to build the framework necessary to finally address this question. While we don’t expect to answer it with finality, the approach presented below represents at least one way trying to do so. There are certainly other approaches, and hopefully this will encourage some of them to be explored in the future. The goal of this section is to specifically address the question as to whether instances can be identified where Raman spectroscopy provides discrimination beyond that provided by FTIR spectroscopy by means of specific examples.

Analytical Approach

Rather than conducting a comparison based on entire paint samples, we conducted a comparison between specific layers. The decision to use layers was made in an attempt to consider only the properties that are comparable by FTIR and Raman. Since these methods don't directly compare layer thickness or layer structure, those variables were eliminated.

A pairwise comparison of Raman and FTIR spectra originating from approximately 1000 layers was beyond the scope of this study and much of such data would, in any case, be irrelevant). As such, our approach was devised to identify and compare paint layers that were likely to share spectral similarities.

Automobiles sharing the same color code should give the greatest chance for finding samples that would be difficult to differentiate. Therefore, samples that shared a manufacturer color code were placed into groups. Within the total sample set of 300 paints there are 180 unique manufacturer color codes. Therefore, the samples could be divided into 181 groups (where 1 group contains samples that don't have a known color code). Within this set, 41 color code groups were found to contain multiple samples. Figure 38 provides a table of color code groups and the samples contained within each of them.

Each color code group contains between two and seven samples. Six of the forty-one unique groups contain samples that share "Year, Make, and Model" values. Nine of the forty-one groups contain samples that share only "Make and Model" information. Three of the forty-one groups contain samples that share only "Year and Make" information.

Each color layer within these samples had been previously examined by Raman microspectroscopy. Each color layer within these groups was then analyzed by FTIR spectroscopy as well. This resulted in a total of 173 colored layers in 120 individual paint samples that were analyzed and compared (resulting in 336 pairwise comparisons). It was necessary to analyze and compare all color layers because we had no way to know, *a priori*, which layer(s) corresponded to the color code of the paint sample (as some layers of paint were completely different colors from others in the same chip).

Results

Raman Spectroscopy

The Raman spectra from within each group were compared to each other. Comparisons were made on the basis of spectral overlay and pigments identified. No attempt to discriminate spectra on the basis of pigment quantities (*i.e.*, peak intensity) was made, as the groundwork for such a comparison has not been established. The results of the intra-comparison of spectra within each color code are presented in Figure 39. This table shows that 67% of comparisons could be discriminated by Raman spectroscopy (227/336). This comparison approach was biased toward false inclusions (*i.e.,* when a question arose, the pair was considered to be non-differentiated). For this initial study, we wanted to provide a conservative discrimination value (one that could be reasonably attained in a case working laboratory). It is likely that some of these spectra could be further discriminated using research-grade metrics, which is outside the practical scope of such an analysis.

FTIR Spectroscopy

Similarly, the FTIR spectra within each group were compared to each other. Comparisons were based on qualitative examinations of overlaid spectra and were performed by two experienced scientists working independently. Spectra that were difficult to distinguish were then examined by a third scientist to arrive at a

Manuf. Color	Nominal Color	Manufacturer	Model	Year	Ascension #
1E0	Silver	Scion	TC	2008	C-80343
		Toyota	Yaris	2010	C-80476
11	Brown	Chevrolet	Tahoe	2002	C-80268
		Chevrolet	Trailblazer	2003	C-80070
37	Blue	Buick	Lacrosse	2008	C-80516
		Chevrolet	Imapla lt	2008	C-80272
		Chevrolet	Cavalier	1996	C-80467
40	White	Pontiac	G6	2006	C-80388
		Toyota	Camry	2001	C-80224
		Mercedes	CLK 55 AMG	2001	C-80401
		Toyota	RAV4	2007	C-80050
		Toyota	Sienna		C-80414
41	Black	Chevrolet	Cavalier	1999	C-80468
		Chevrolet	Monte Carlo	2004	C-80430
		GMC	Sierra	2011	C-80392
		Pontiac	Grand Prix	2004	C-80475
		Pontiac	Grand Prix GTP	2001	C-80361
		Pontiac	Sunfire Coupe	2003	C-80061
		Saturn	Vue	2005	C-80514
46	Blue	Cadillac	CTS	2005	C-80357
		GMC	Sierra 1500	2009	C-80378
49	Red	Buick	Lucerne	2007	C-80390
		Chevrolet	Trail Blazer	2006	C-80417
50	White	Chevrolet	Impala	2006	C-80453
		Chevrolet	Silverado	2008	C-80374
		Chevrolet	Silverado	2008	C-80376
		Chevrolet	Silverado	2008	C-80377
		Chevrolet	Silverado	2009	C-80474
51	Gold	Chevrolet	Avalanche	2007	C-80363
		Chevrolet	HHR LT	2009	C-80274
		Saturn	L100	2002	C-80424
62	Silver	GMC	Envoy	2004	C-80426
		Saturn	LS1	2000	C-80387
63	Red	GMC	Yukon Denali	2004	C-80271
		Pontiac	Grand Prix	2004	C-80425
		Saturn	Ion	2005	C-80225
67	Silver	Buick	Lucerne	2006	C-80445
		Chevrolet	HHR	2007	C-80356
		Chevrolet	HHR LT	2006	C-80275
		Chevrolet	Impala	2006	C-80318
		Pontiac	Grand Prix	2007	C-80444
72	Red	GMC	Yukon	2002	C-80393
		Pontiac	Grand Prix	2000	C-80064
74	Red	Chevrolet	Cavalier	2004	C-80501
		Chevrolet	Cobalt	2010	C-80226

Figure 38. Table showing samples grouped by color code.

Manuf. Color	Nominal Color	Manufacturer	Model	Year	Ascension #
74	Red	Chevrolet	Cavalier	2004	C-80501
		Chevrolet	Cobalt	2010	C-80226
		Pontiac	Grand Prix GT	2003	C-80500
80	Red	Chevrolet	Impala	2011	C-80082
		Pontiac	Grand Prix	2008	C-80217
81	Red	Chevrolet	Camaro	1995	C-80482
		Chevrolet	Cavalier	2002	C-80442
		Oldsmobile	Alero	1999	C-80469
		Pontiac	Grand Prix	1997	C-80071
		Pontiac	Grand Prix GT	1997	C-80362
92	Green	Cadillac	CTS	2005	C-80066
		Chevrolet	Malibu	2004	C-80448
		Cadillac	Deville	1995	C-80418
98	White	Buick	Lacrosse	2011	C-80389
		Chevrolet	Traverse	2011	C-80519
202	Black	Toyota	Camry	2009	C-80053
		Toyota	Highlander	2006	C-80451
		Toyota	RAV4	2009	C-80403
1B2	Gold	Lexus	ES 300	1999	C-80380
		Lexus	ES 300	1999	C-80381
1F7	Silver	Toyota	RAV4	2007	C-80069
		Toyota	RAV4	2009	C-80369
3R3	Red	Toyota	Camry Hybrid	2007	C-80067
		Toyota	Camry Hybrid	2009	C-80055
		Toyota	Prius	2007	C-80398
B518P	Blue	Acura	MDX	2003	C-80280
		Honda	Odyessey	2003	C-80440
B537M	Blue	Honda	Civic	2010	C-80352
		Honda	Civic	2011	C-80408
B92P	Black	Honda	Accord	2007	C-80213
		Honda	Pilot	2004	C-80334
CX	Gray	Ford	Escape	2003	C-80333
		Ford	Focus	2006	C-80316
		Ford	Focus	2006	C-80439
G2	Red	Ford	Escape	2003	C-80431
		Volkswagon	New Beetle	2005	C-80276
JP	Silver	Ford	Expedition	2006	C-80432
		Ford	Explorer Sport Trac	2007	C-80525
K12	Silver	Nissan	Armada	2005	C-80279
		Nissan	Armada	2005	C-80353
KH3	Black	Nissan	Altima		C-80413
		Nissan	Sentra	2009	C-80351
		Nissan	Versa		C-80345
LD	Blue	Ford	Escape XLT	2001	C-80054
74	Red	Ford Chevrolet	F150 Cobalt	2004 2010	C-80273 C-80226

Figure 38 continued. Table showing samples grouped by color code.

Manuf. Color	Nominal Color	Manufacturer	Model	Year	Ascension #
LD	Blue	Ford	Escape XLT	2001	C-80054
		Ford	F150	2004	C-80273
NH578	White	Honda	Accord	2005	C-80211
		Honda	Civic	2010	C-80479
NH623M	Silver	Honda	Accord	2001	C-80311
		Honda	Odyssey	2002	C-80344
PB7	Blue	Jeep	Liberty	2002	C-80428
		Jeep	Liberty Limited	2005	C-80483
PB8	Blue	Chrysler	Pacifica	2006	C-80331
		Dodge	Grand Caravan	2004	C-80269
PDM	Gray	Dodge	Durango	2005	C-80502
		Jeep	Compass	2011	C-80074
PKJ	Gold	Dodge	Caravan	2002	C-80368
		Dodge	Caravan	2002	C-80410
PR4	Red	Jeep	Grand Cherokee	1997	C-80068
		Jeep	Liberty	2004	C-80076
PS2	Silver	Chrysler	300	2006	C-80341
		Chrysler	Sebring Sedan Ltd	2010	C-80485
		Jeep	Compass	2007	C-80526
PW1	White	Chrysler	Sebring	2002	C-80422
		Jeep	Grand Cherokee	2001	C-80375
		Jeep	Grand Cherokee	2004	C-80452
PX8	Black	Dodge	Dakota	1998	C-80075
		Dodge	Neon	2005	C-80384
PXR	Black	Chrysler	Sebring	2009	C-80509
		Chrysler	Town & Country	2006	C-80429
		Dodge	Caravan	2005	C-80421
		Jeep	Grand Cherokee	2011	C-80382
TS	Silver	Ford	Focus	2000	C-80210
		Ford	Focus	2007	C-80523
		Ford	Focus SE	2008	C-80419
		Mercury	Grand Marquis	1998	C-80506
UJ	Gray	Ford	Focus	2010	C-80326
		Lincoln	MKZ	2011	C-80435
63	Red	Pontiac	Grand Prix	2004	C-80425
67	Silver	Saturn	Ion	2005	C-80225
		Buick	Lucerne	2006	C-80445
		Chevrolet	HHR	2007	C-80356
		Chevrolet	HHR LT	2006	C-80275
		Chevrolet	Impala	2006	C-80318
		Pontiac	Grand Prix	2007	C-80444
72	Red	GMC	Yukon	2002	C-80393
		Pontiac	Grand Prix	2000	C-80064
74	Red	Chevrolet	Cavalier	2004	C-80501
		Chevrolet	Cobalt	2010	C-80226

Figure 38 continued. Table showing samples grouped by color code.

Manufacturer's Color Code	Samples in Group	Colored Layers in Group	Comparisons per Group	Number Differentiated (FTIR)	Number Differentiated (Raman)
1E0	2	2	1	1	1
11	2	2	1	1	1
37	3	4	6	5	3
40	5	10	45	45	40
41	7	8	28	27	12
46	2	2	1	1	1
49	2	2	1	1	1
50	5	7	21	20	4
51	3	3	3	3	2
62	2	4	6	5	4
63	3	4	6	6	3
67	5	5	10	10	10
72	2	3	3	2	0
74	3	6	15	14	0
80	2	4	6	6	0
81	5	8	28	27	21
92	3	6	15	13	11
98	2	4	6	6	5
202	3	4	6	6	3
1F7	2	3	3	3	3
3R3	3	5	10	10	8
AR	2	2	1	0	0
B518P	2	4	6	6	6
B537M	2	2	1	1	1
B92P	2	3	3	3	3
CX	3	4	6	6	3
G2	2	4	6	6	6
JP	2	3	3	3	3
K12	2	4	6	6	6
KH3	3	3	3	3	3
LD	2	3	3	2	0
NH578	2	4	6	6	6
NH623M	2	3	3	3	3
PB7	2	2	1	1	1
PB8	2	2	1	1	0
PDM	2	2	1	1	0
PKJ	2	3	3	2	2
PR4	2	2	1	1	1
PS2	3	6	15	15	15
PW1	3	5	10	10	7
PX8	2	2	1	1	1
PXR	4	4	6	5	1
TS	4	8	28	28	25
UJ	2	2	1	1	1
Total	**120**	**173**	**336**	**323**	**227**

Figure 39. Table showing discrimination among samples within a given group by FTIR spectroscopy and Raman spectroscopy.

consensus (*i.e.*, pair is discriminated or non-discriminated). Again, comparisons were biased toward false inclusions (*i.e.,* when a question arose, the pair would be considered non-differentiated). In total, 13 pairs of samples were identified that could either not be discriminated or had extremely similar FTIR spectra.[4] This works out to a discrimination value of 96% for the FTIR spectra alone.

Combined Data

Of these 13 layer pairs that shared similar FTIR spectra, five pairs could be discriminated by Raman spectroscopy. These five pairs originate from the vehicles listed in Table 8.

Table 8. Summary of vehicles/layers showing similar FTIR spectra.

Sample	Layer	Manufacturer	Model	Year	Pigments
C-80468	OT2	Chevrolet	Cavalier	1999	PBl7
C-80514	OT4	Saturn	View	2005	PBl7, PB15
C-80061	OT1	Pontiac	Sunfire	2003	PBl7
C-80514	OT4	Saturn	View	2005	PB15
C-80318	OT1	Chevrolet	Impala	2006	PBl7, PB15
C-80444	OT1	Pontiac	Grand Prix	2007	PBl7, PB15:1, UIP[1]
C-80666	OT1	Cadillac	CTS	2005	PBl7, PG36, PG7
C-80448	OT1	Chevrolet	Malibu	2004	PBl7, PG36
C-80448	OT1	Chevrolet	Malibu	2004	PBl7, PG36
C-80418	OT1	Chevrolet	Deville	1995	PG7

[1] UIP – Unidentified peak. Reproducible difference that could not be assigned to a specific component.

The data supporting each of these five comparisons is presented to show that the spectral similarities and differences are reproducible. The following data is provided for each comparison pair in Figures 40-44:

A) Cross section image showing the visual appearance of the layers being compared;

B) Comparison of Raman spectra of the two layers;

C) Three replicates of the Raman spectrum from layer 1,

D) Three replicates of the Raman spectrum from layer 2,

E) Comparison of the FTIR spectra of the two layers;

F) Three replicates of the FTIR spectrum from layer 1;

G) Three replicates of the FTIR spectrum from layer 2;

H) EDS spectrum from each of the layer 1;

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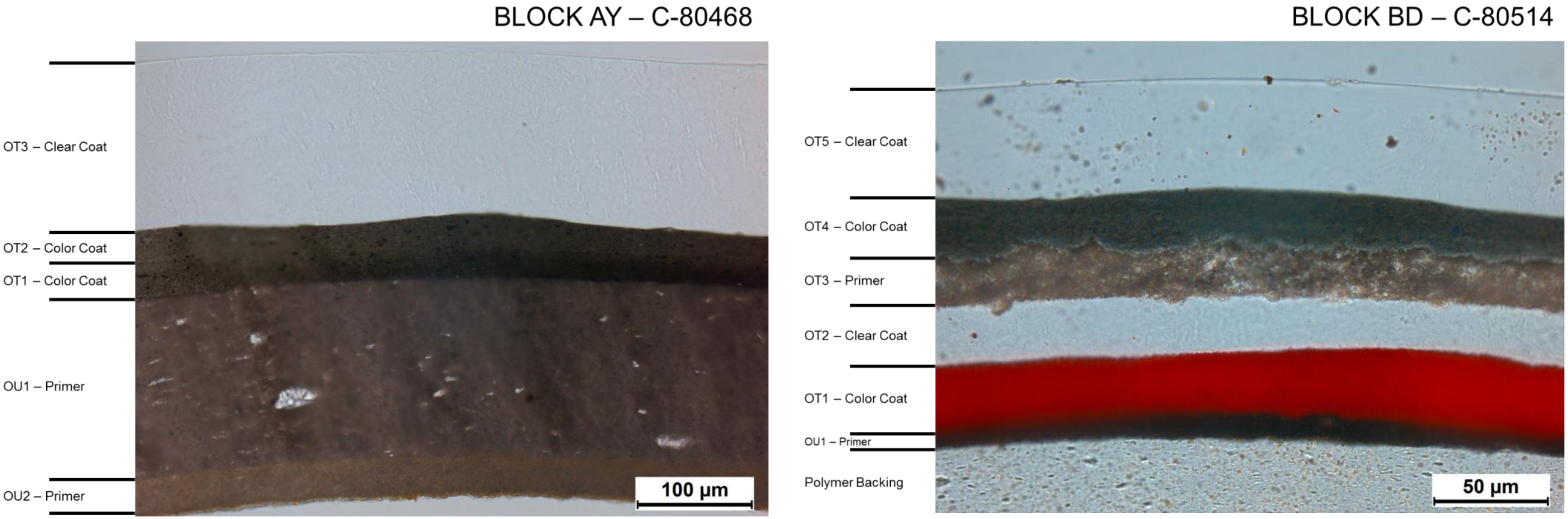
[4] The judgment of discriminated/non-discriminated by FTIR spectroscopy is qualitative and based upon the confidence of the examiner in the reproducibility of fine spectral features, some of which are likely not assignable to a known vibrational mode.



C-80468 – OT2 – Color Coat

1999 Chevrolet Cavalier

Color Code: 41

Sample Location: Rear Fender

Raman ID: PBI7

C-80514 – OT4 – Color Coat

2005 Saturn Vue

Color Code: 41

Sample Location: Front Bumper

Raman ID: PBI7, PB15

Figure 40A. Cross section images and meta-data for a comparison of the OT2 color layer of sample C-80468 and the OT4 color layer of sample C-80514.

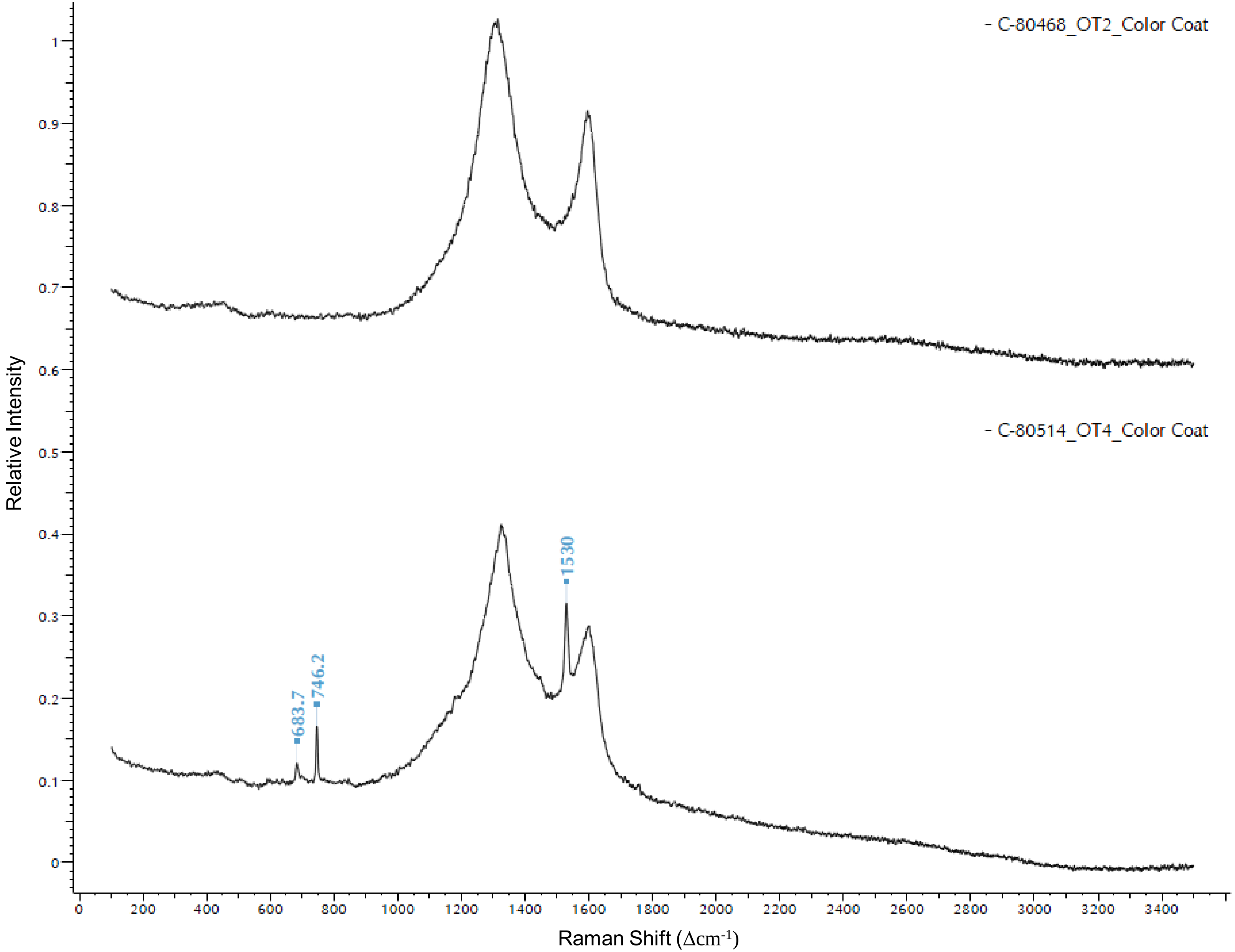


Figure 40B. Comparison of Raman spectra for the OT2 color layer of sample C-80468 and the OT4 color layer of sample C-80514.

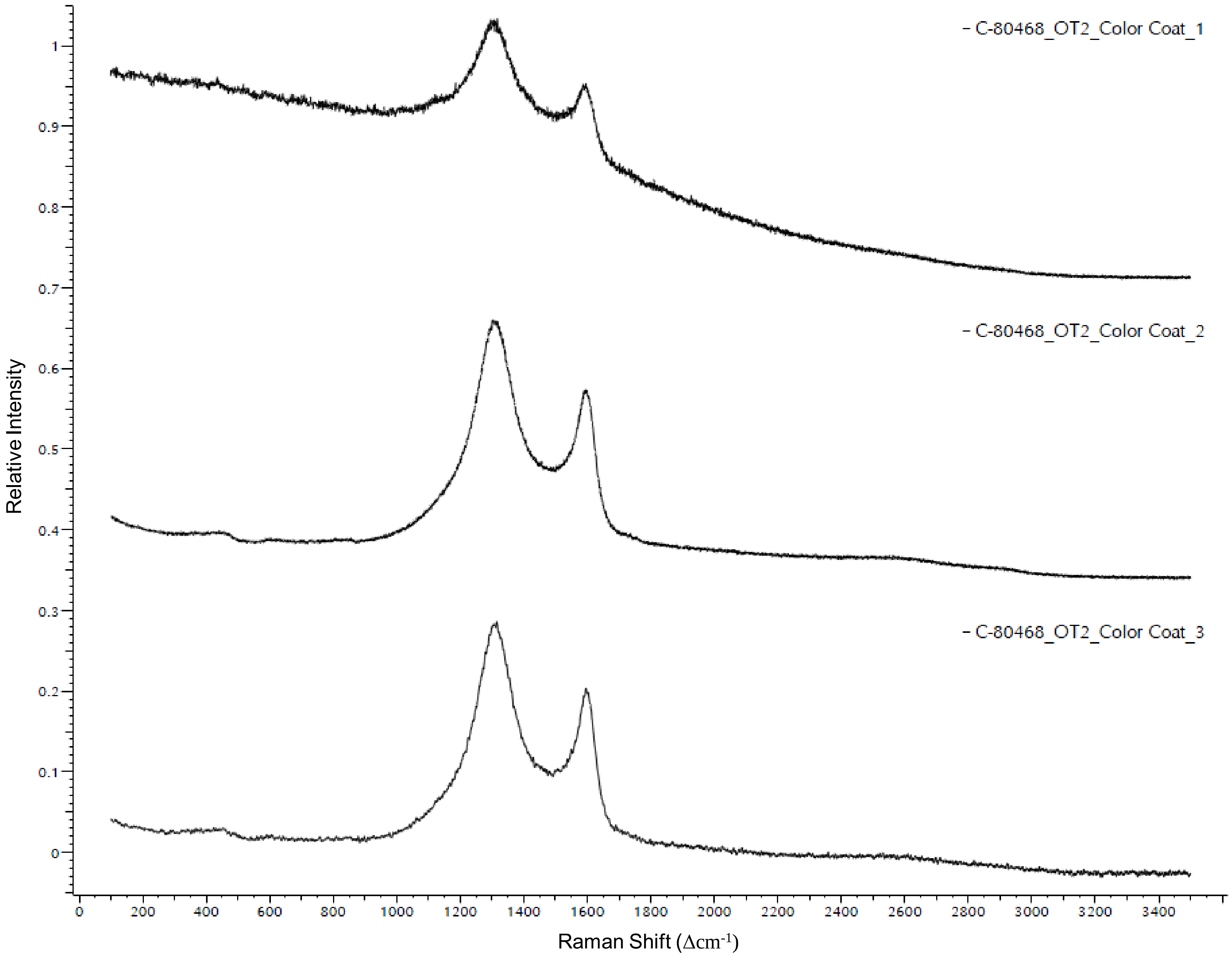


Figure 40C. Comparison of replicate Raman spectra for the OT2 color layer of sample C-80468.

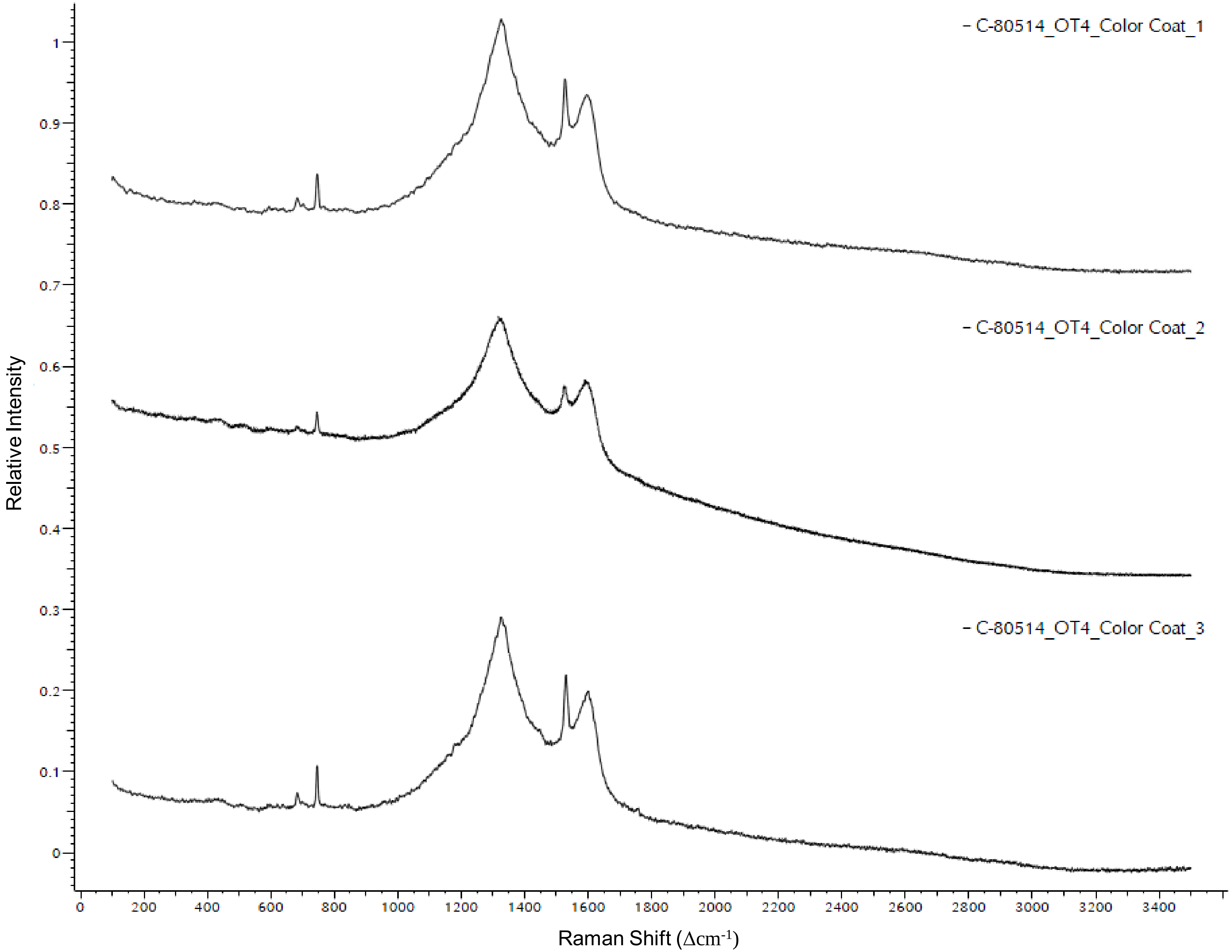


Figure 40D. Comparison of replicate Raman spectra for the OT4 color layer of sample C-80514.

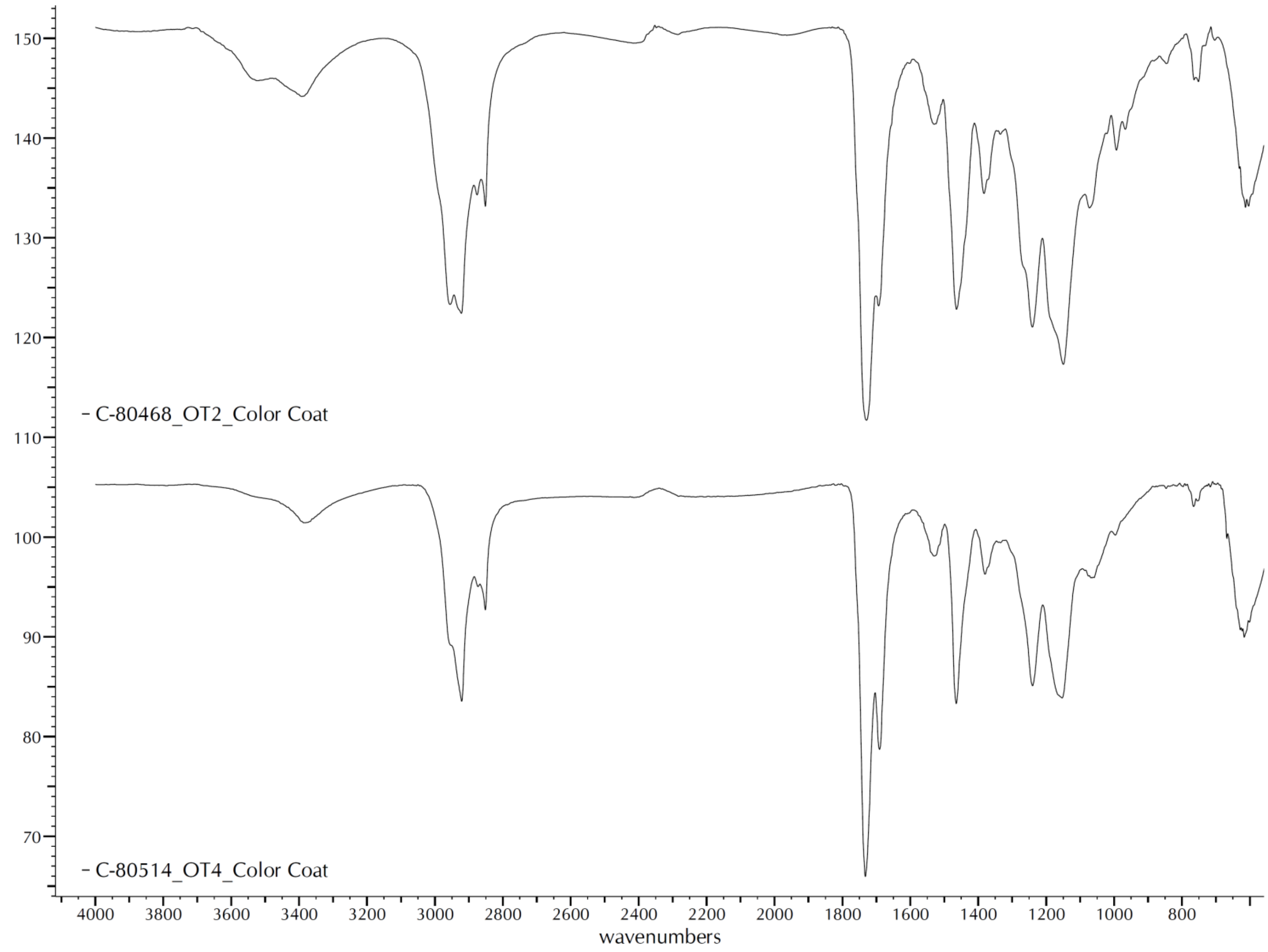


Figure 40E. Comparison of FTIR spectra for the OT2 color layer of sample C-80468 and the OT4 color layer of sample C-80514.

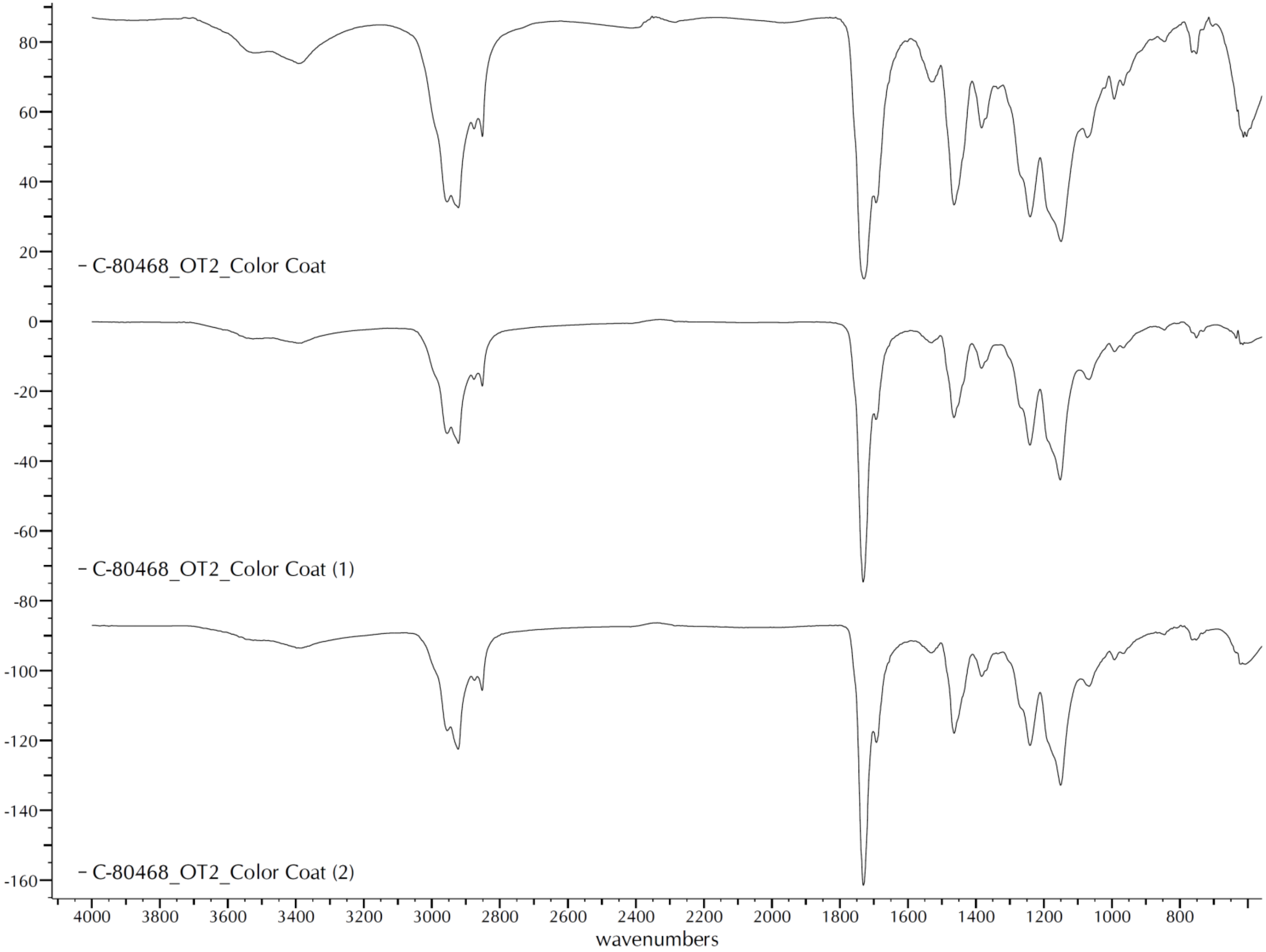


Figure 40F. Comparison of replicate FTIR spectra for the OT2 color layer of sample C-80468.

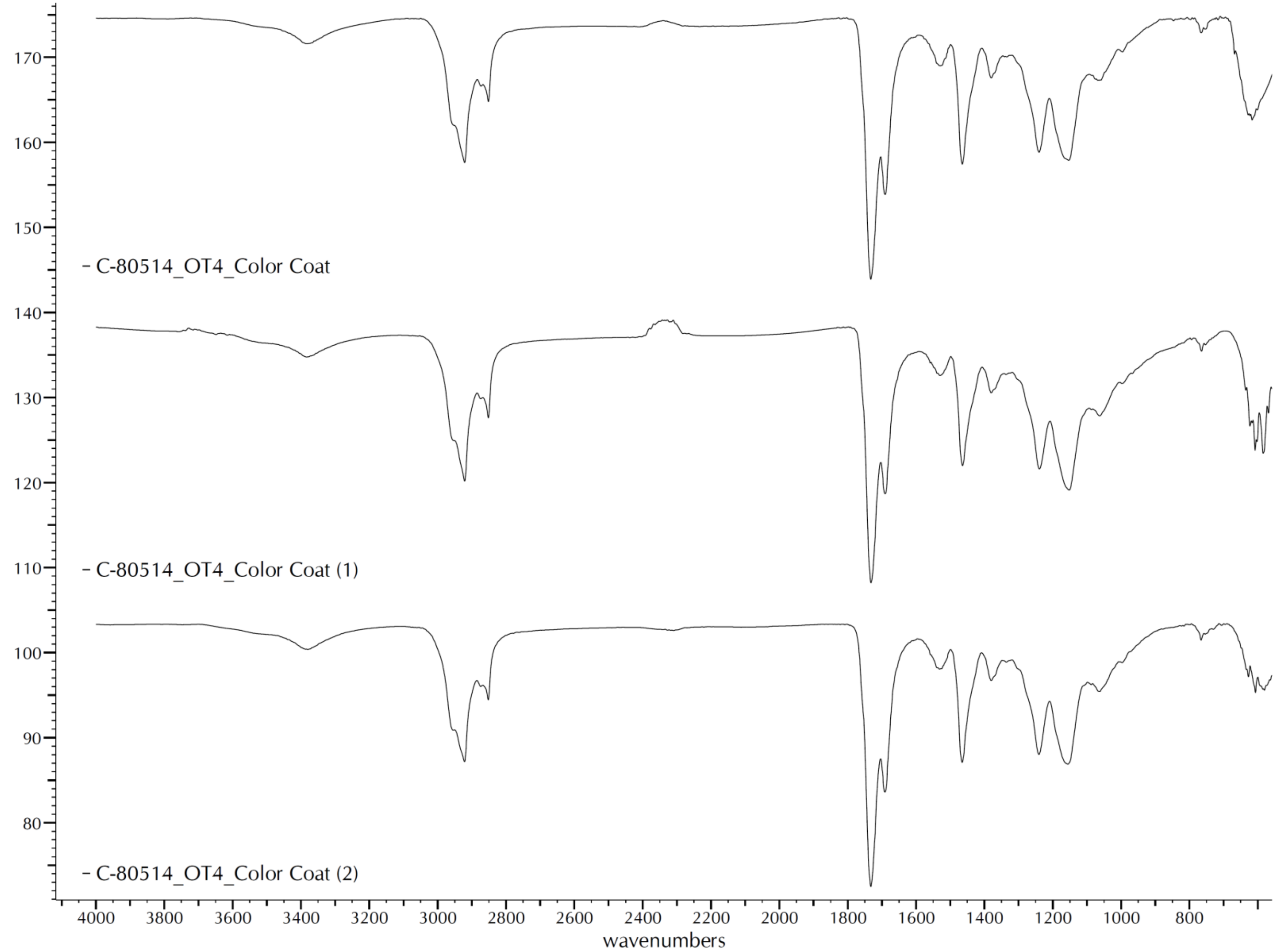


Figure 40G. Comparison of replicate FTIR spectra for the OT4 color layer of sample C-80514.

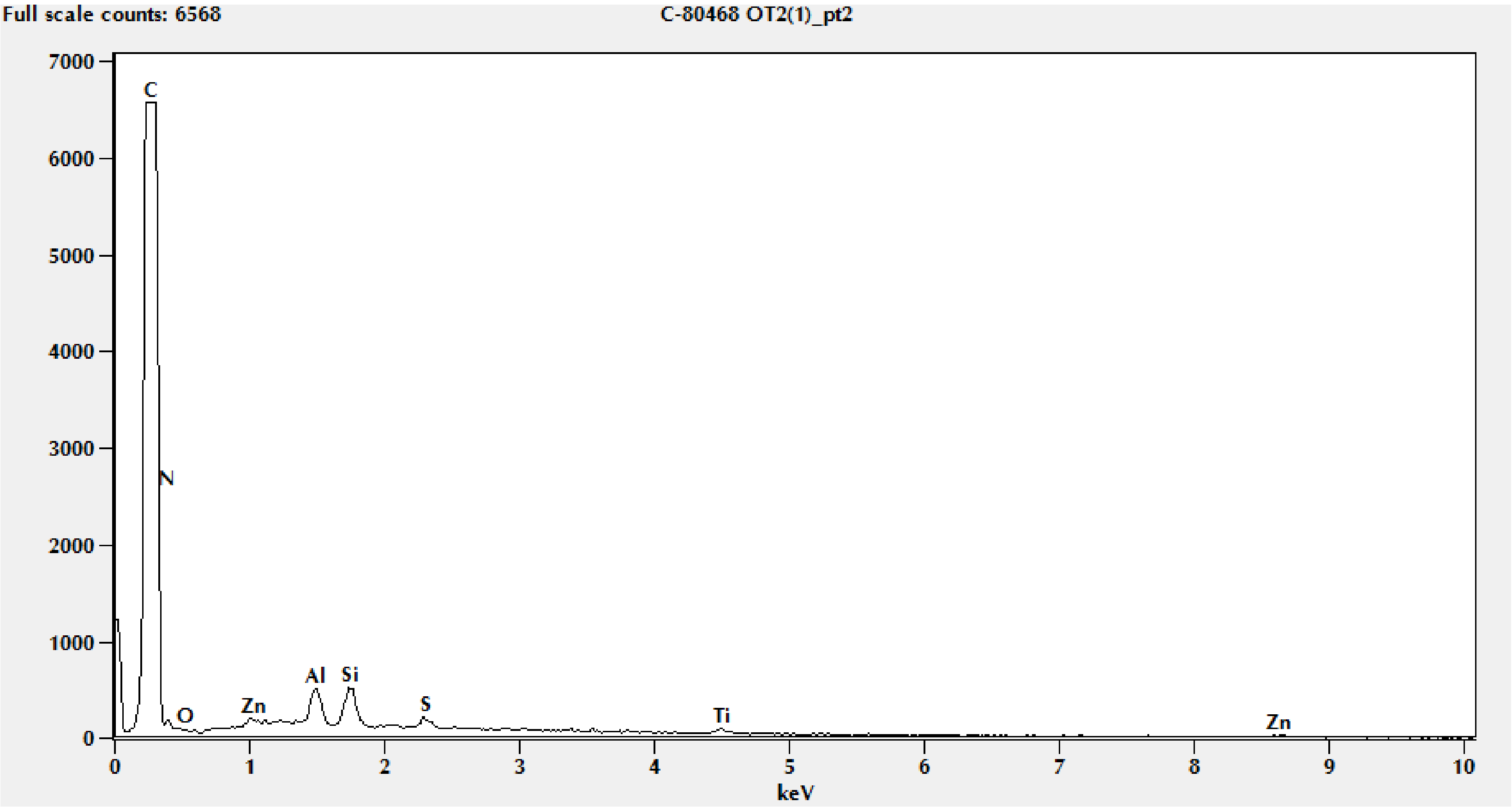


Figure 40H. Elemental analysis of the OT2 color layer of sample C-80468.

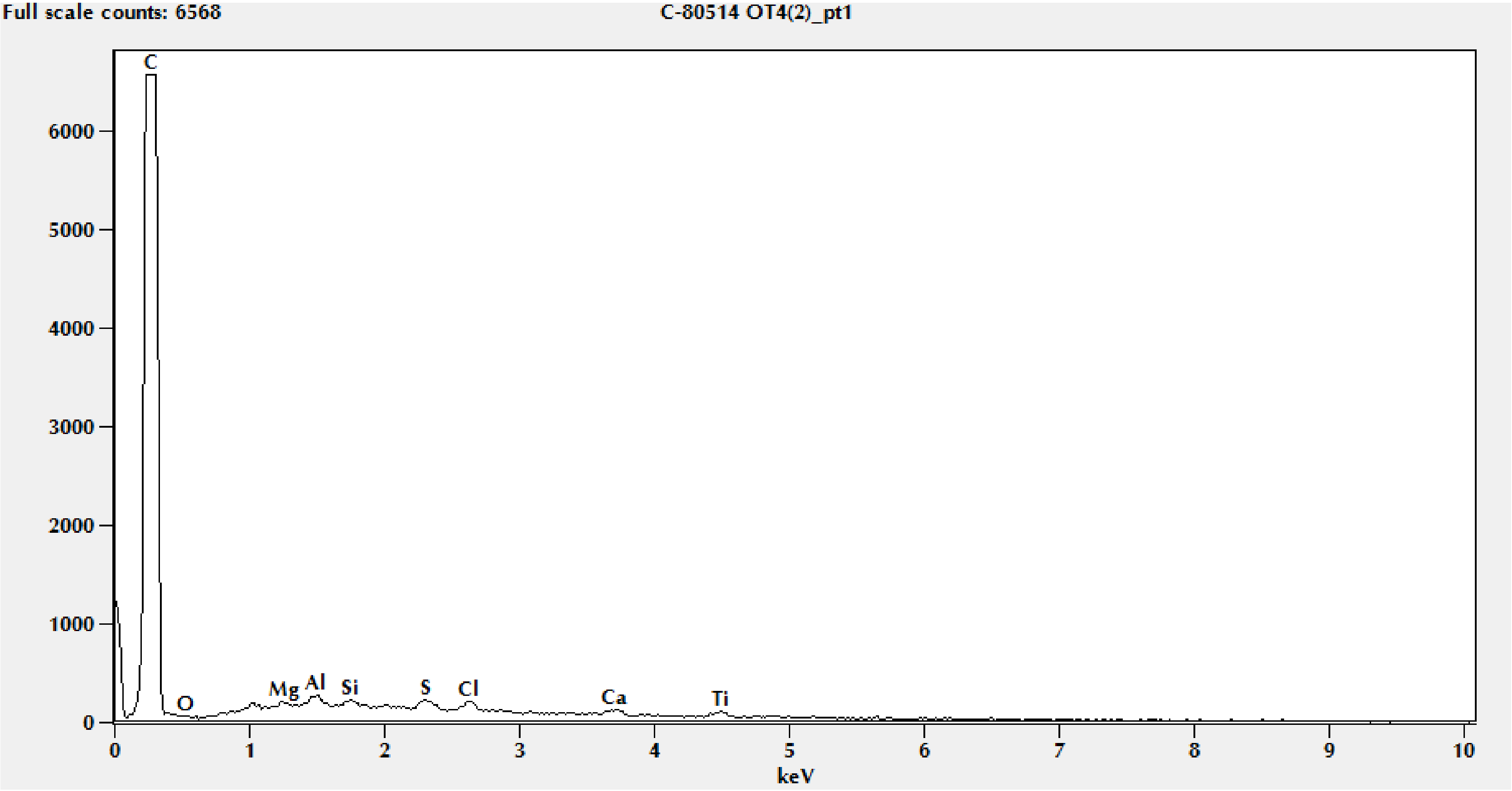
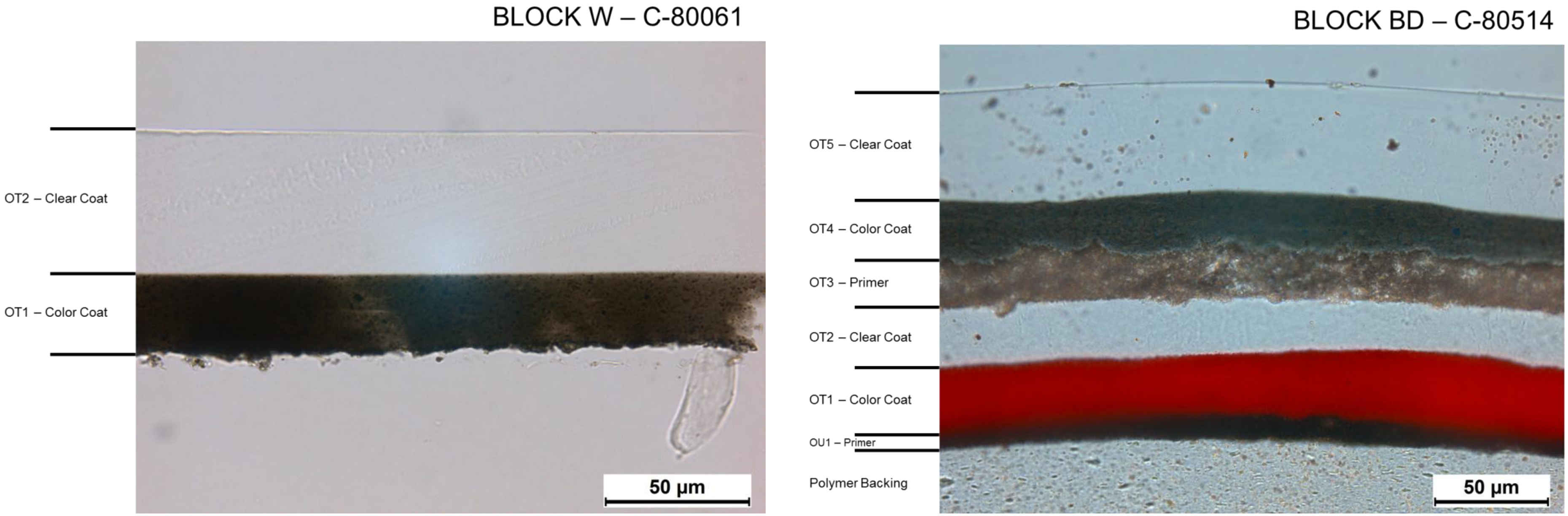


Figure 40I. Elemental analysis of the OT4 color layer of sample C-80514.



C-80061 – OT1 – Color Coat

2003 Pontiac Sunfire Coupe

Color Code: 41

Sample Location: Fuel Door

Raman ID: PBl7

C-80514 – OT4 – Color Coat

2005 Saturn Vue

Color Code: 41

Sample Location: Front Bumper

Raman ID: PBl7, PB15

Figure 41A. Cross section images and meta-data for a comparison of the OT1 color layer of sample C-80061 and the OT4 color layer of sample C-80514.

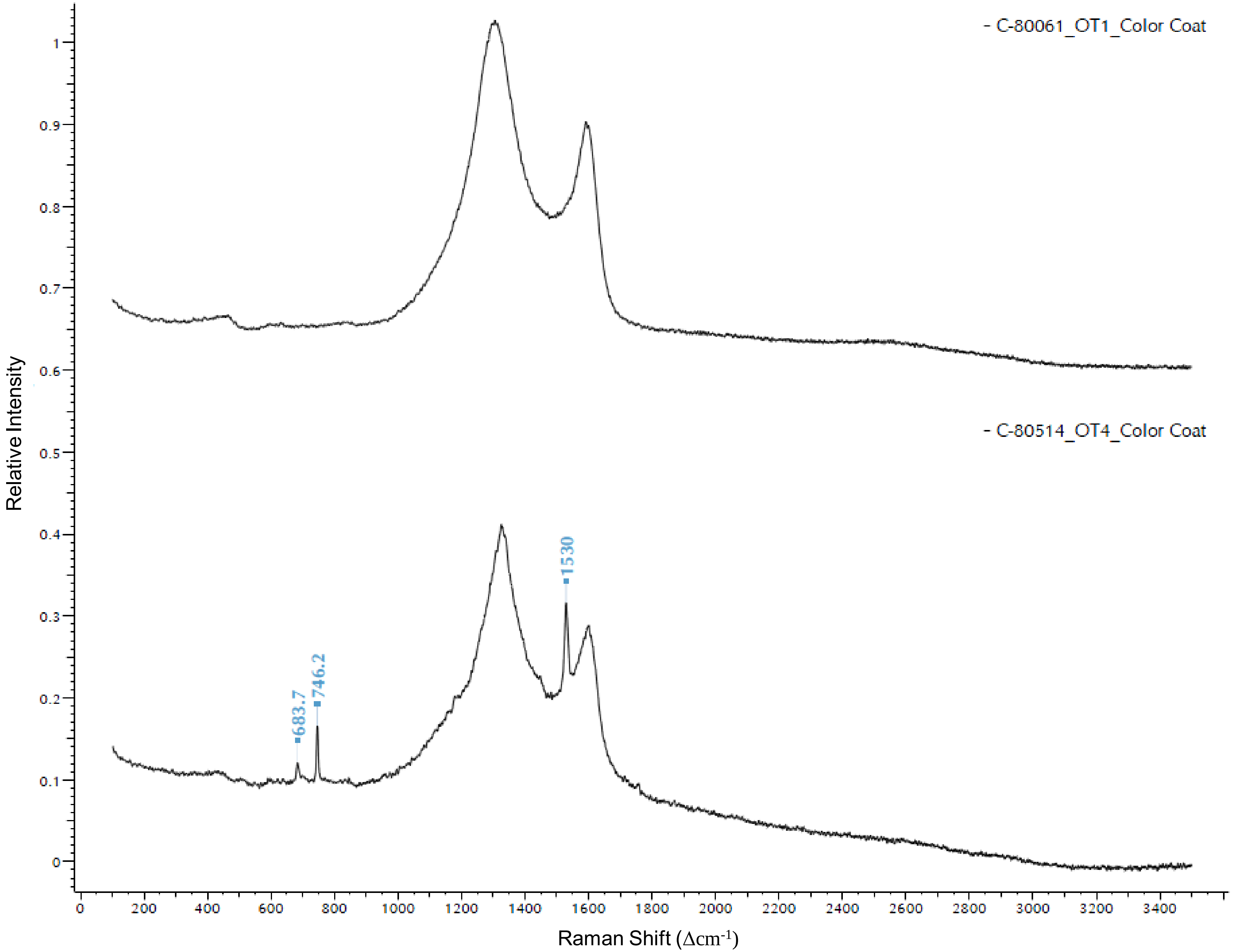


Figure 41B. Comparison of Raman spectra for the OT1 color layer of sample C-80061 and the OT4 color layer of sample C-80514.

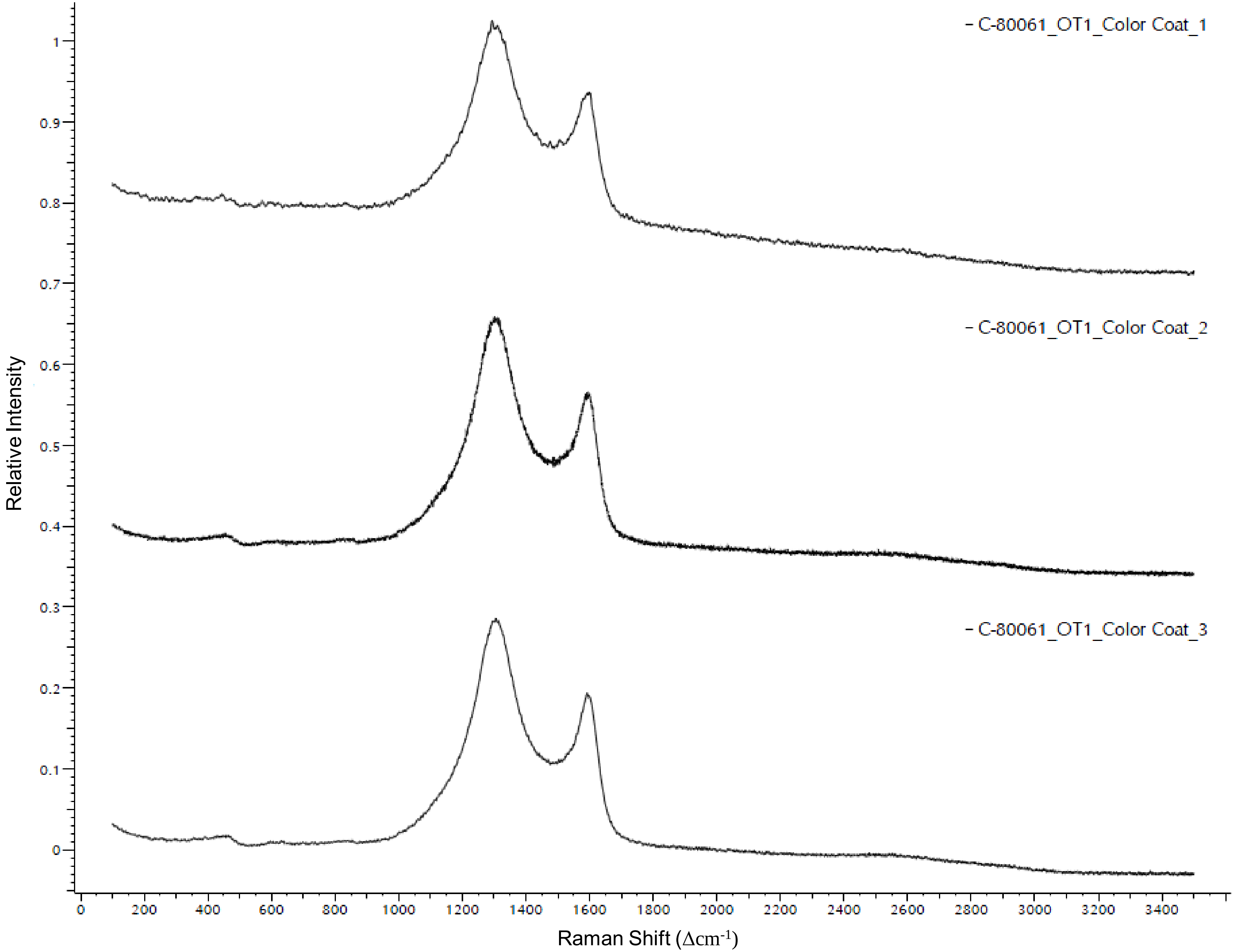


Figure 41C. Comparison of replicate Raman spectra for the OT1 color layer of sample C-80061.

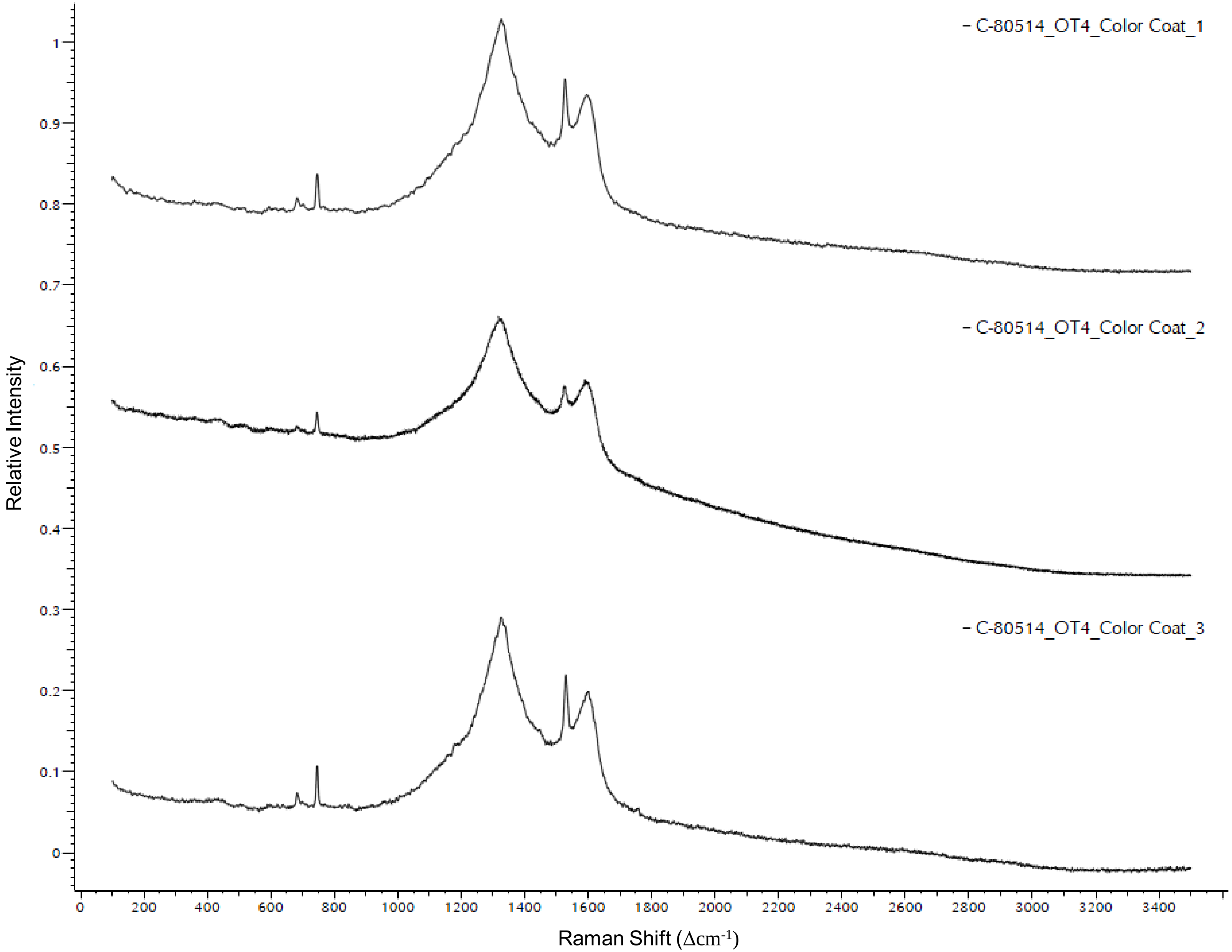


Figure 41D. Comparison of replicate Raman spectra for the OT4 color layer of sample C-80514.

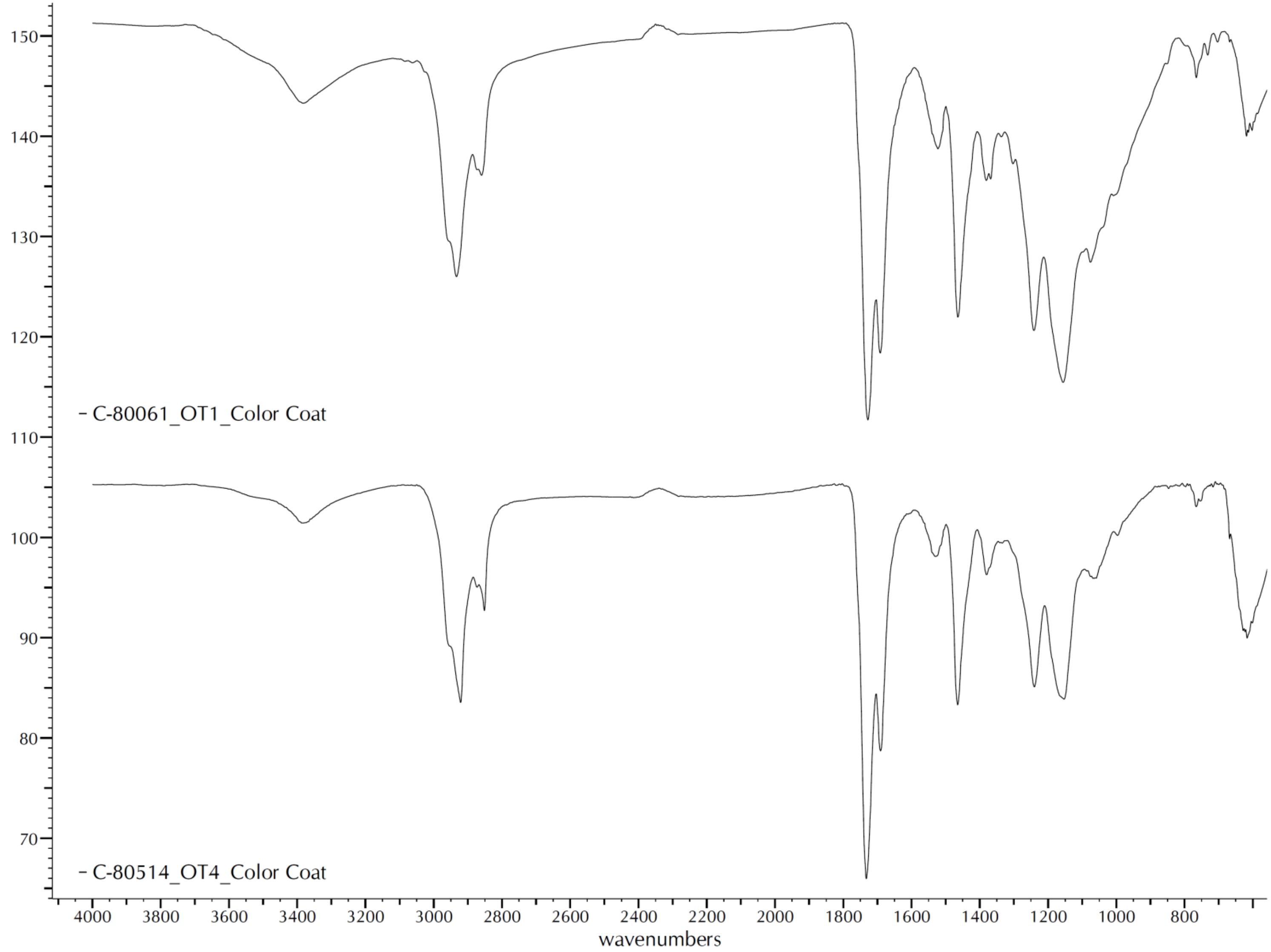


Figure 41E. Comparison of FTIR spectra for the OT1 color layer of sample C-80061 and the OT4 color layer of sample C-80514.

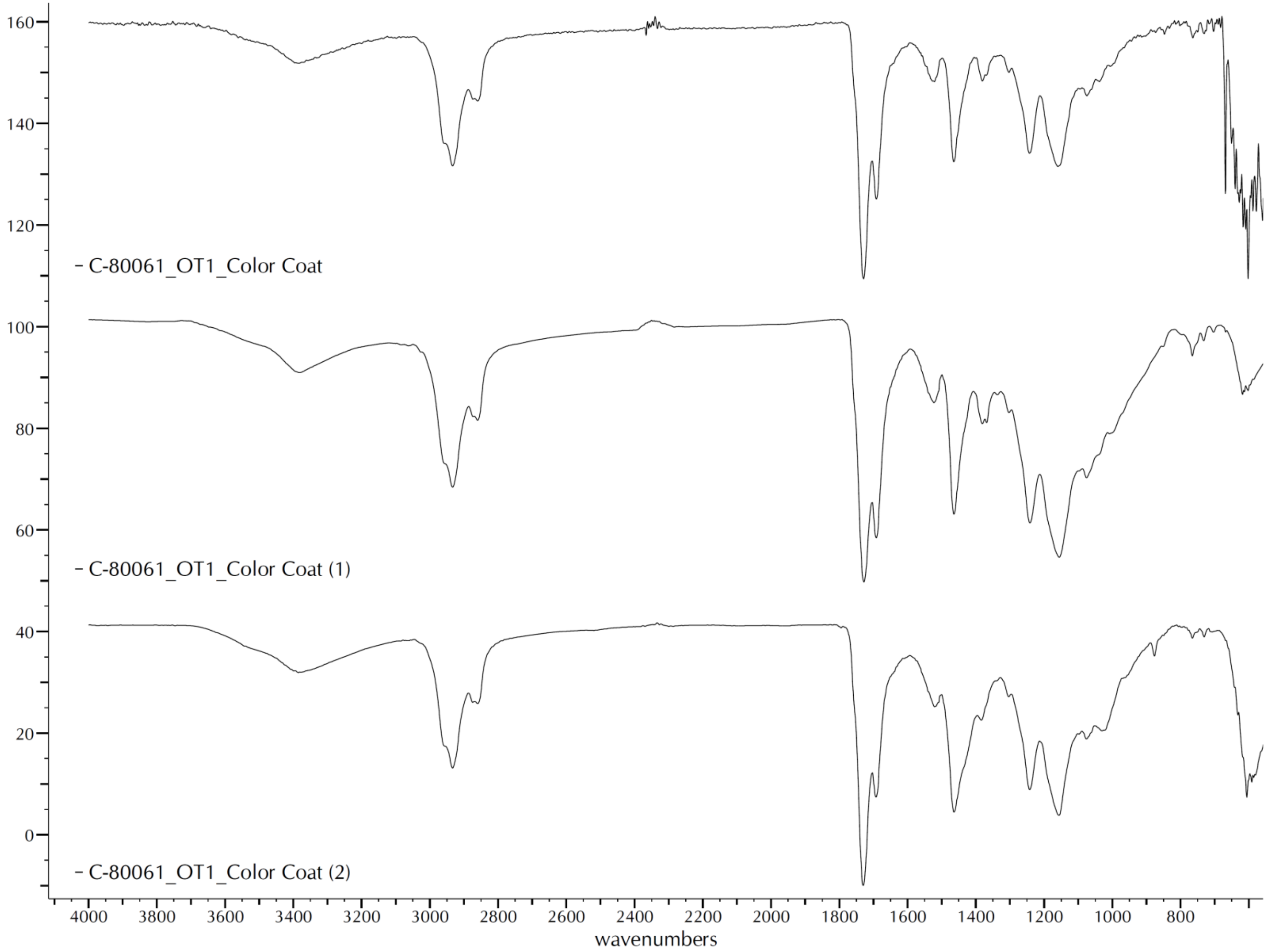


Figure 41F. Comparison of replicate FTIR spectra for the OT1 color layer of sample C-80061.

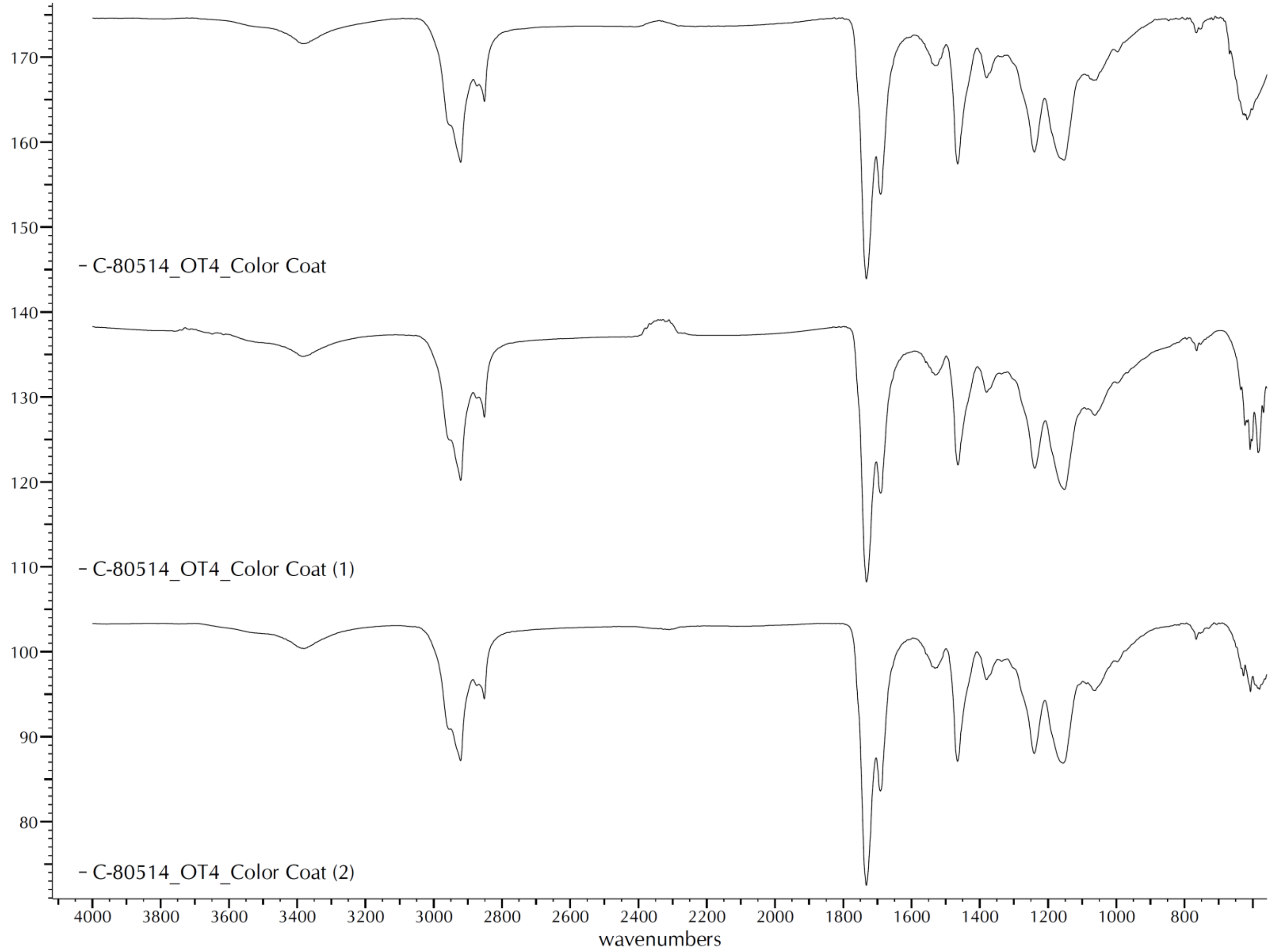


Figure 41G. Comparison of replicate FTIR spectra for the OT4 color layer of sample C-80514.

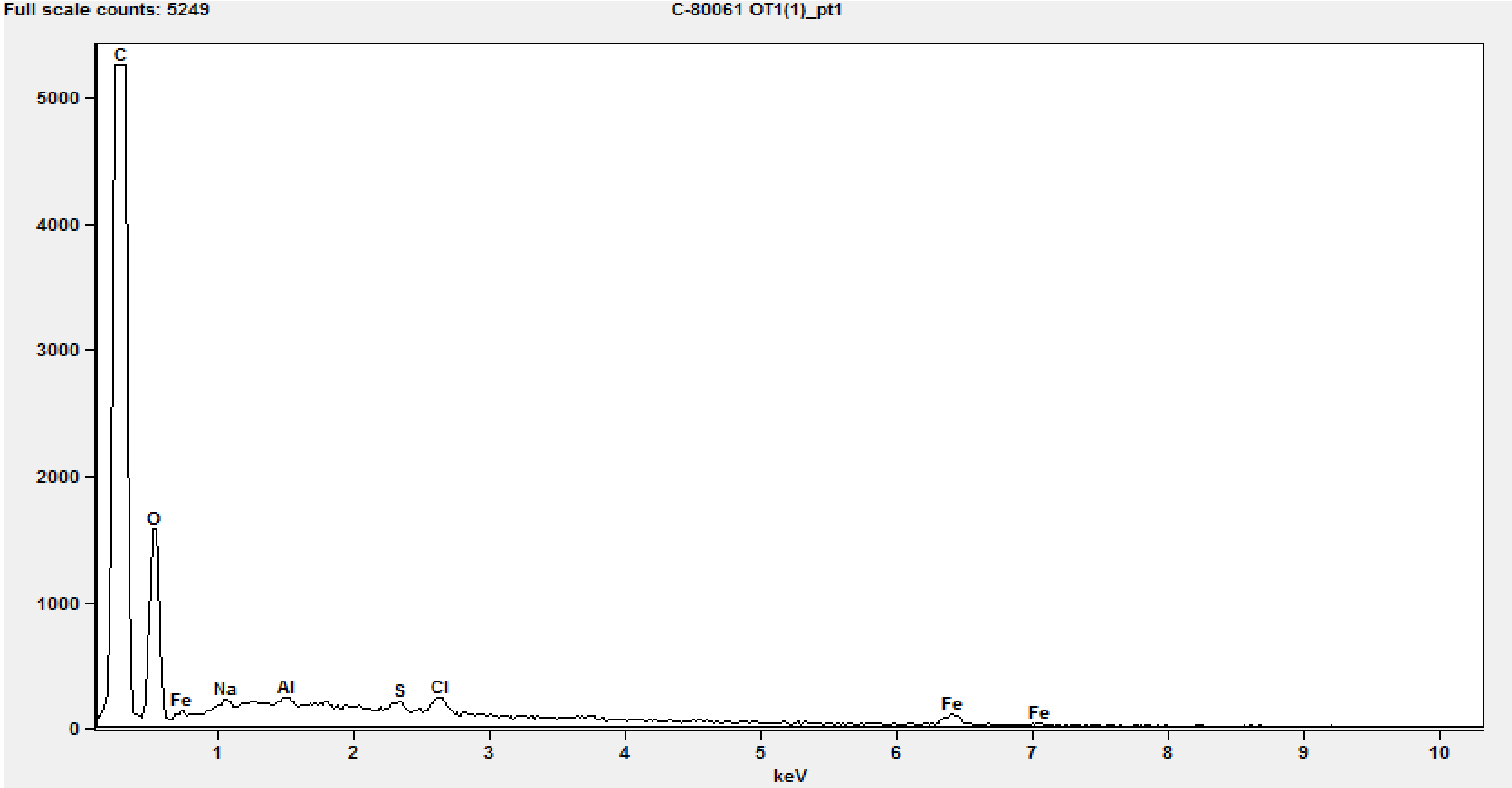


Figure 41H. Elemental analysis of the OT1 color layer of sample C-80061.

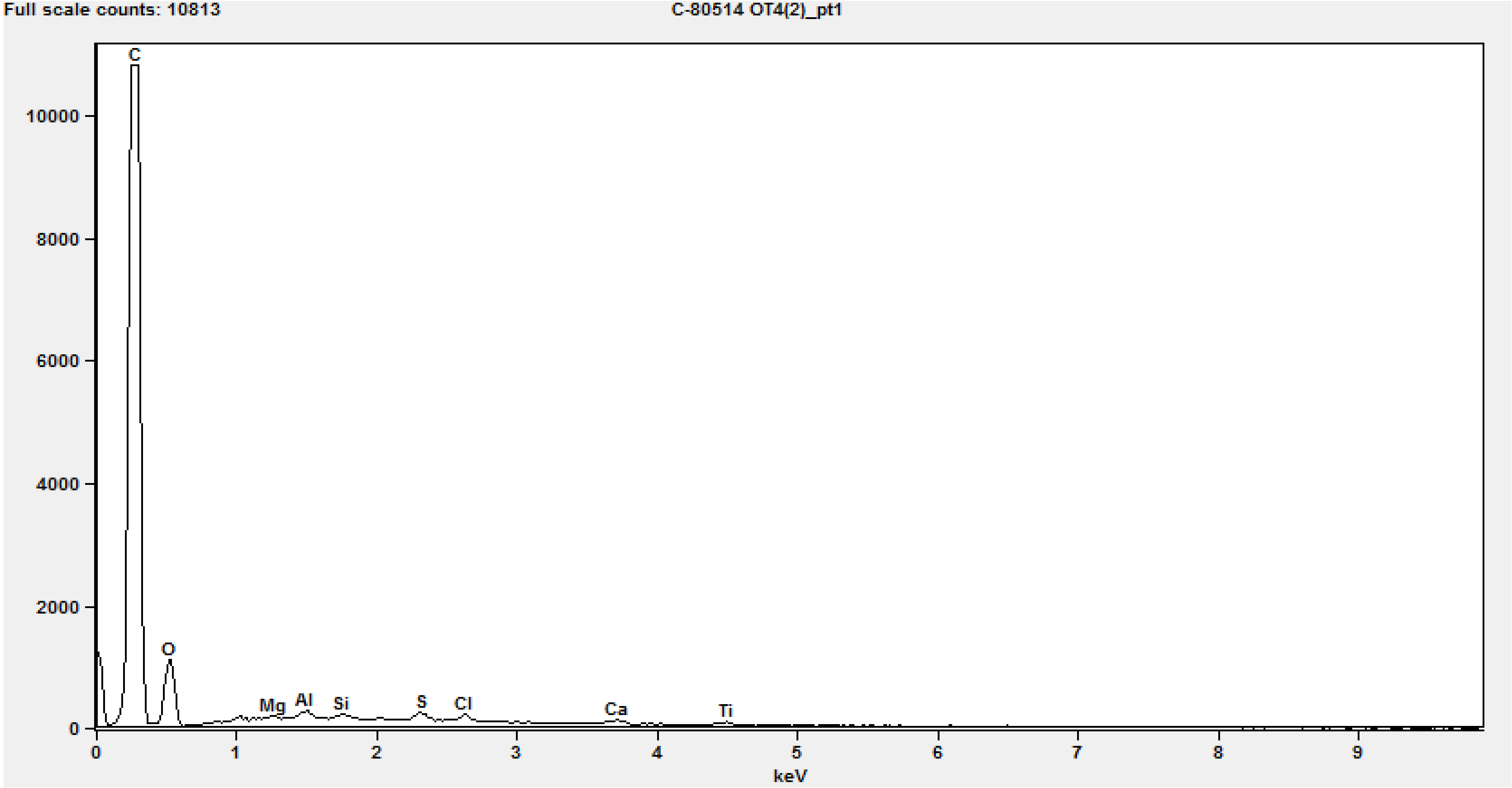
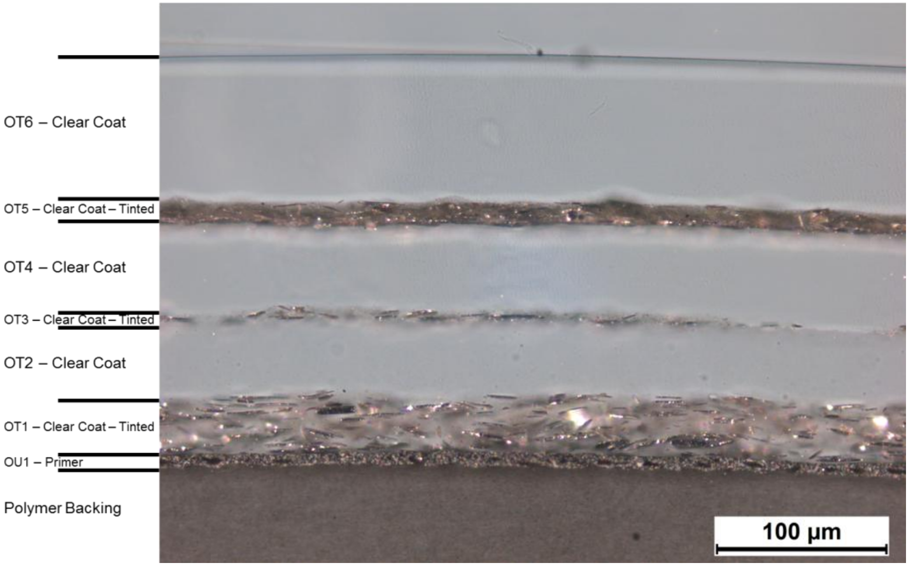
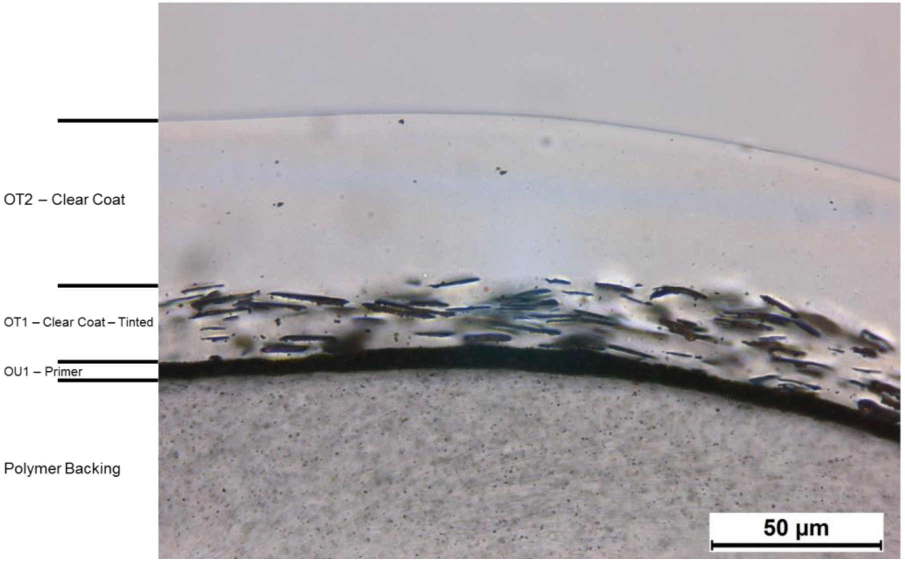


Figure 41I. Elemental analysis of the OT4 color layer of sample C-80514.

BLOCK K – C-80318



BLOCK AU – C-80444



C-80318 – OT1 – Tinted Clear Coat

2006 Chevrolet Impala

Color Code: 994L

Sample Location: -

Raman ID: PB15

C-80444 – OT1 – TInted Clear Coat

2007 Pontiac Grand Prix

Color Code: 994L

Sample Location: Bumper

Raman ID: PB15, PBI7

Figure 42A. Cross section images and meta-data for a comparison of the OT1 color layer of sample C-804318 and the OT1 color layer of sample C-80444.

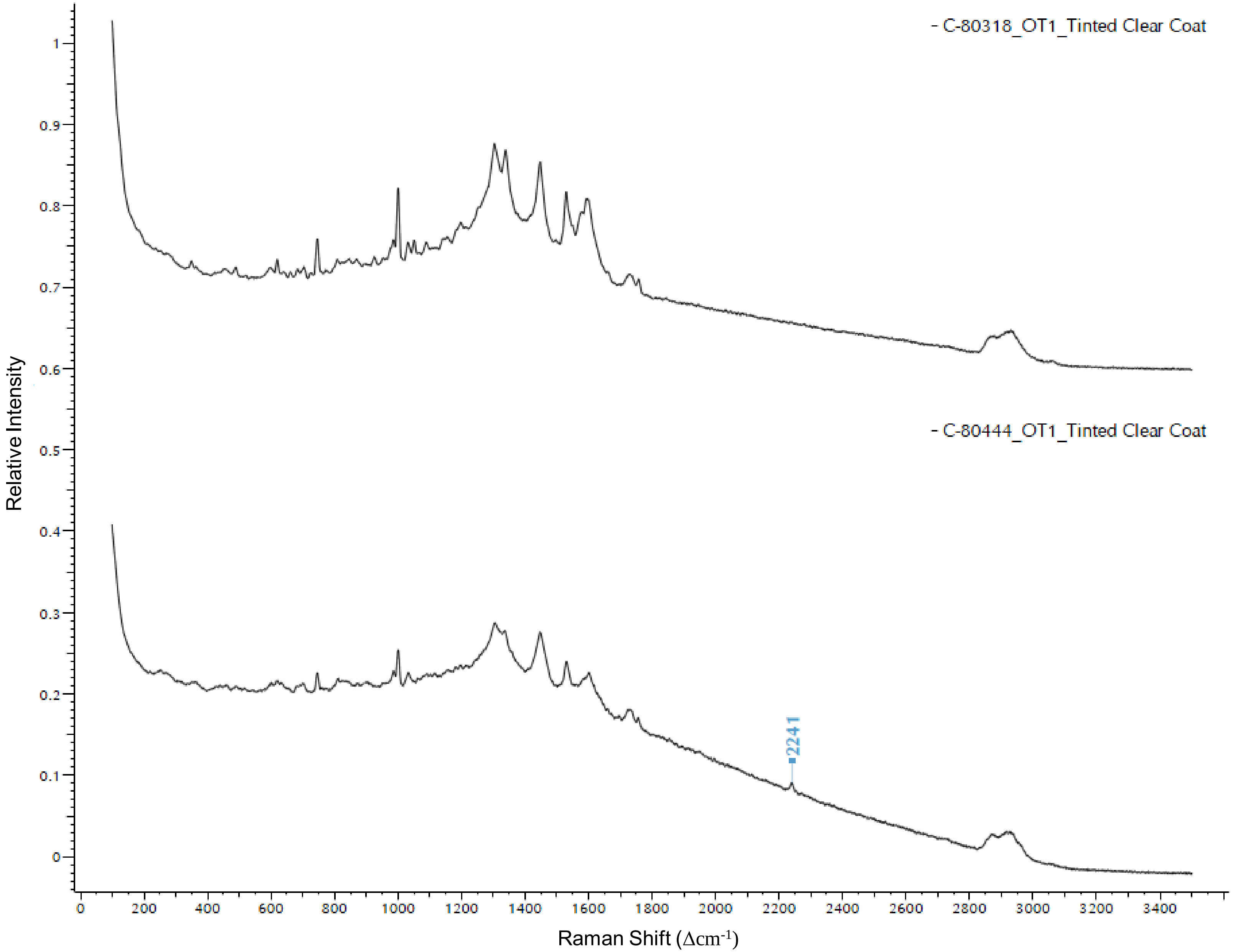


Figure 42B. Comparison of Raman spectra for the OT1 color layer of sample C-80318 and the OT1 color layer of sample C-80444.

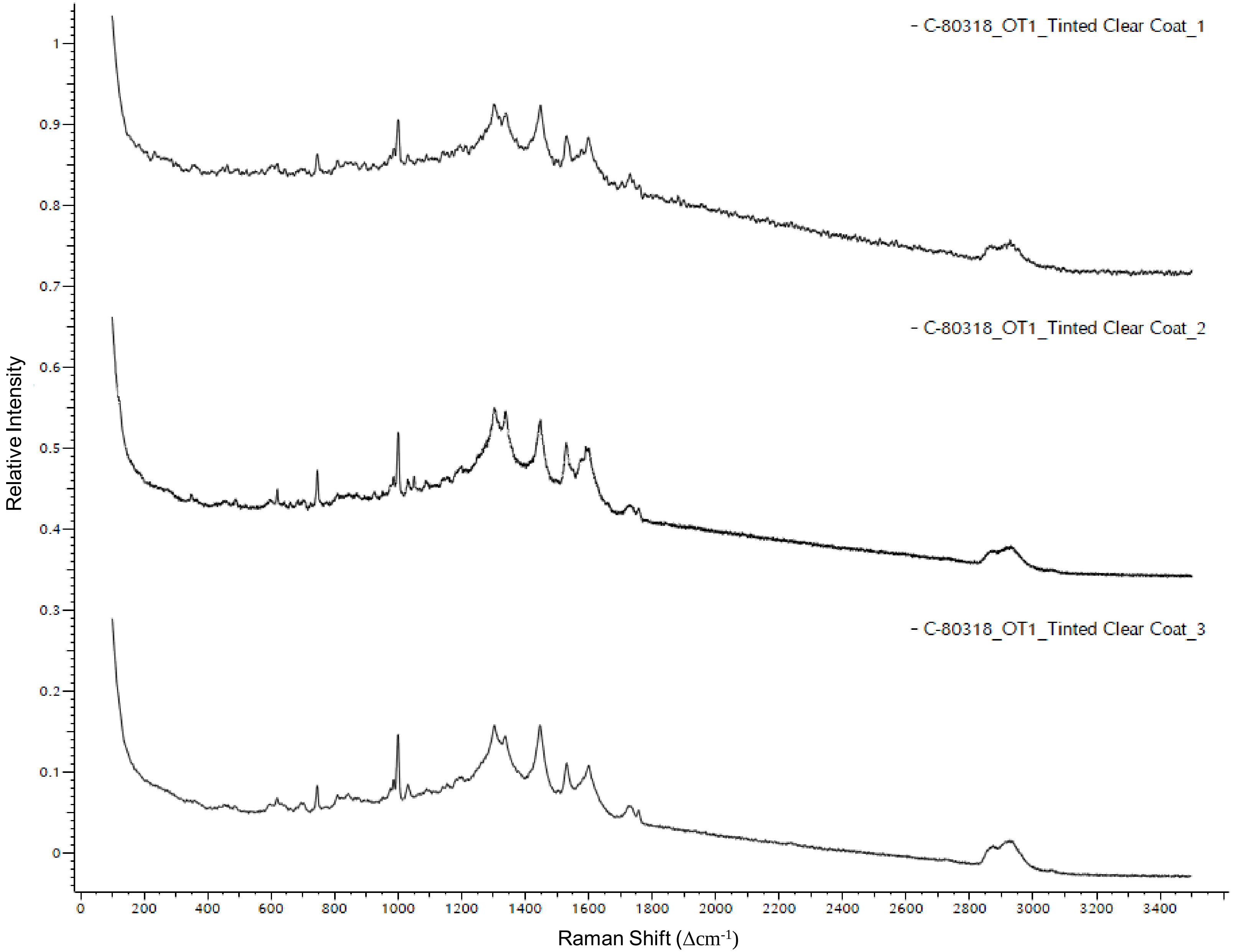


Figure 42C. Comparison of replicate Raman spectra for the OT1 color layer of sample C-80318.

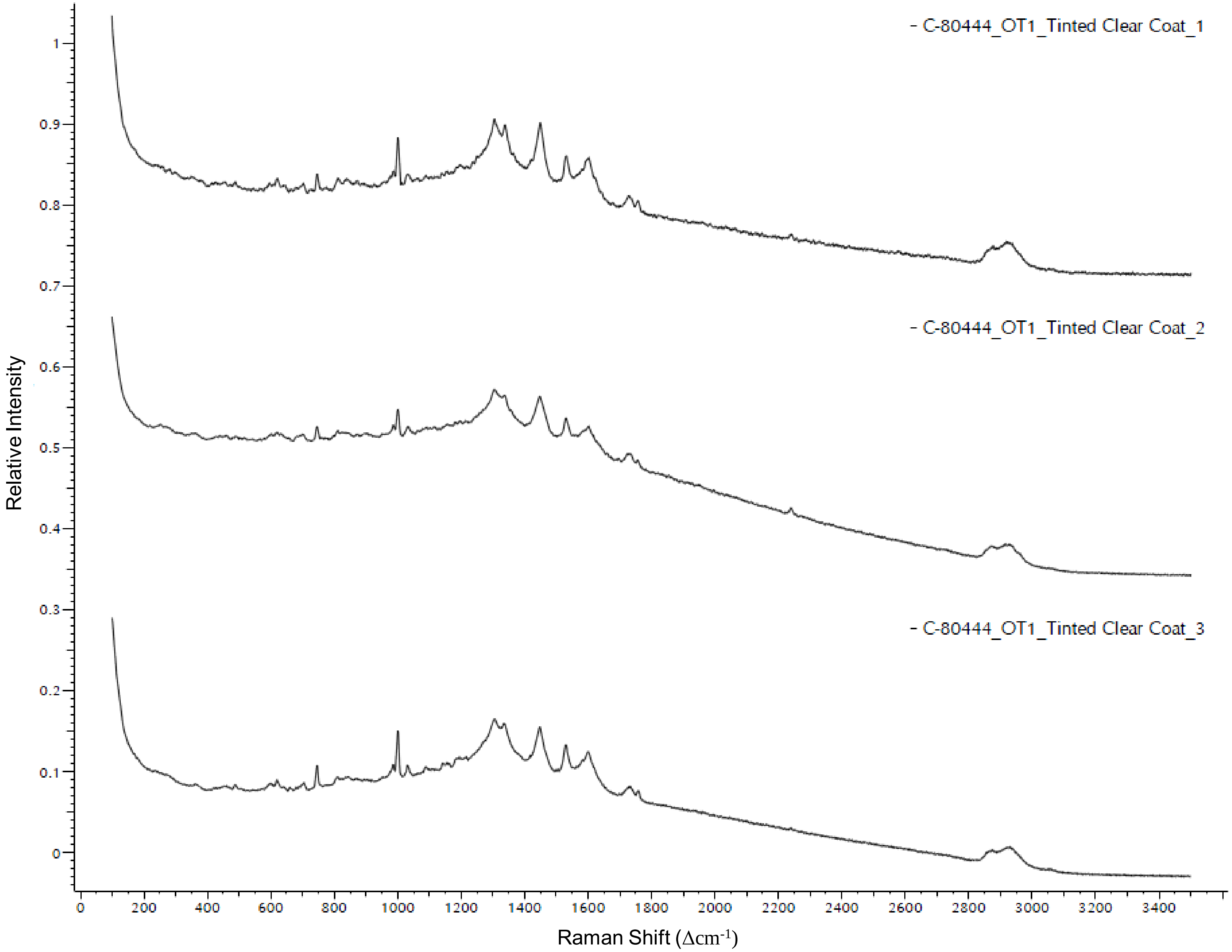


Figure 42D. Comparison of replicate Raman spectra for the OT1 color layer of sample C-80444.

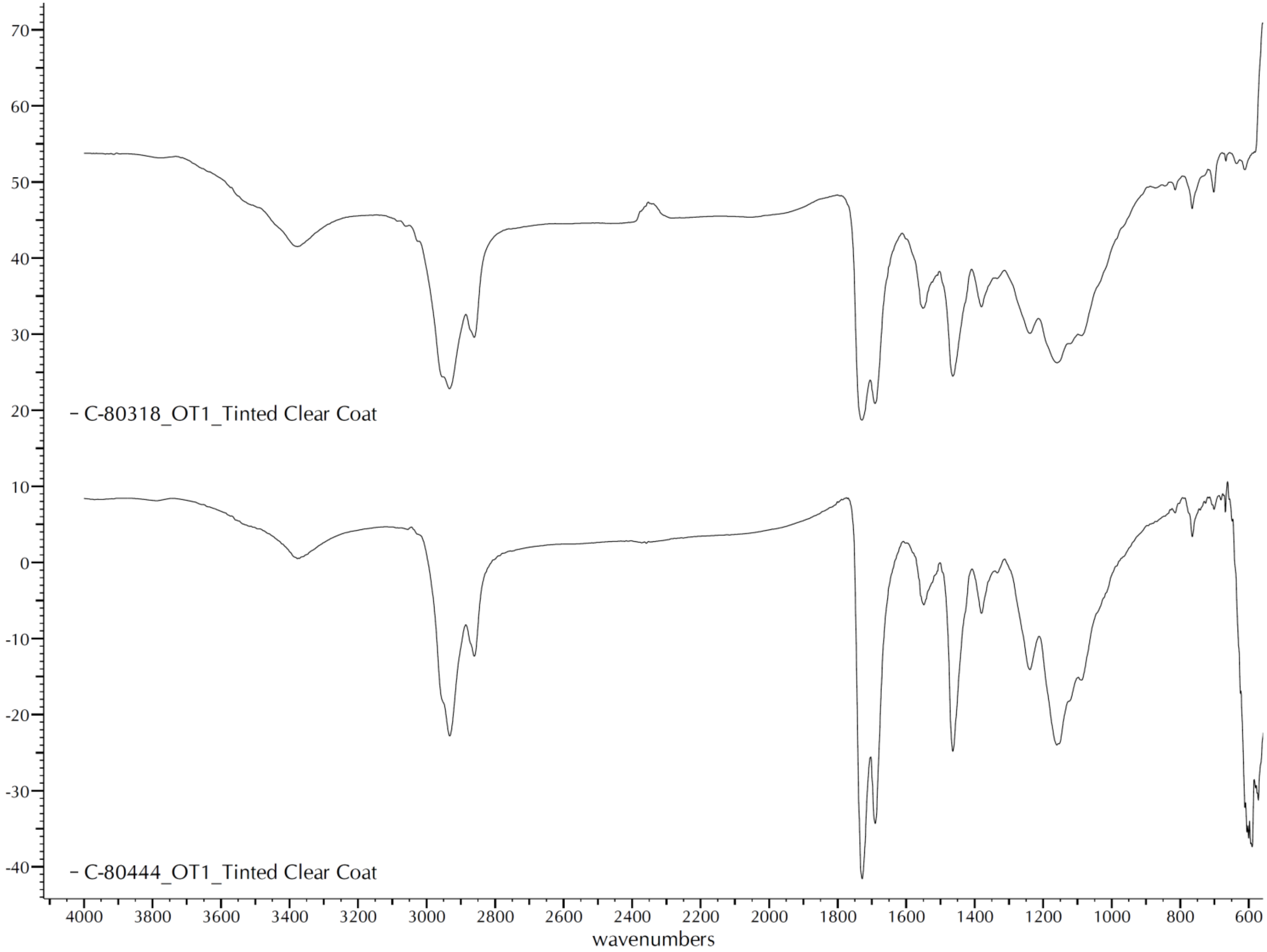


Figure 42E. Comparison of FTIR spectra for the OT1 color layer of sample C-80318 and the OT1 color layer of sample C-80444.

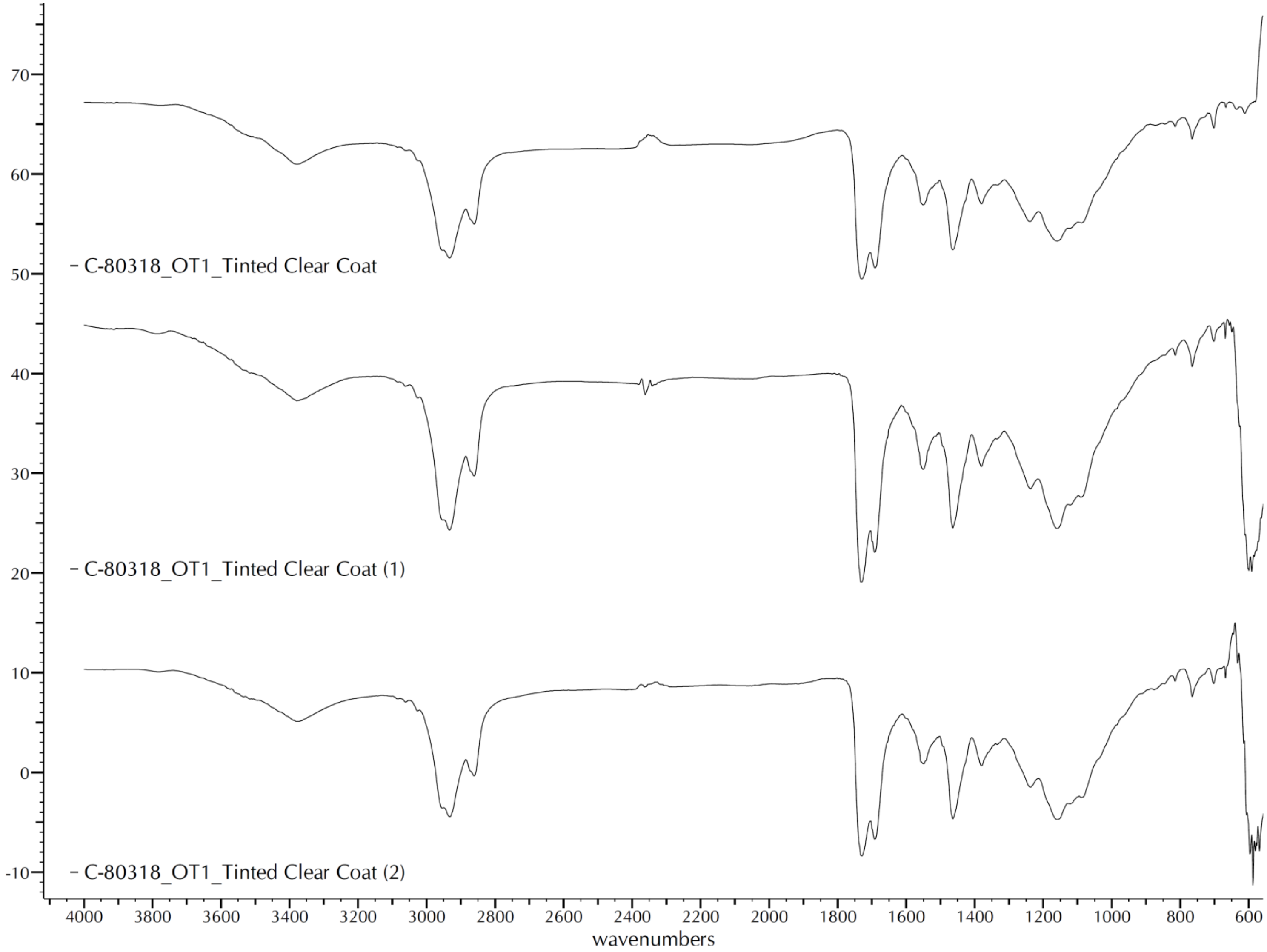


Figure 42F. Comparison of replicate FTIR spectra for the OT1 color layer of sample C-80318.

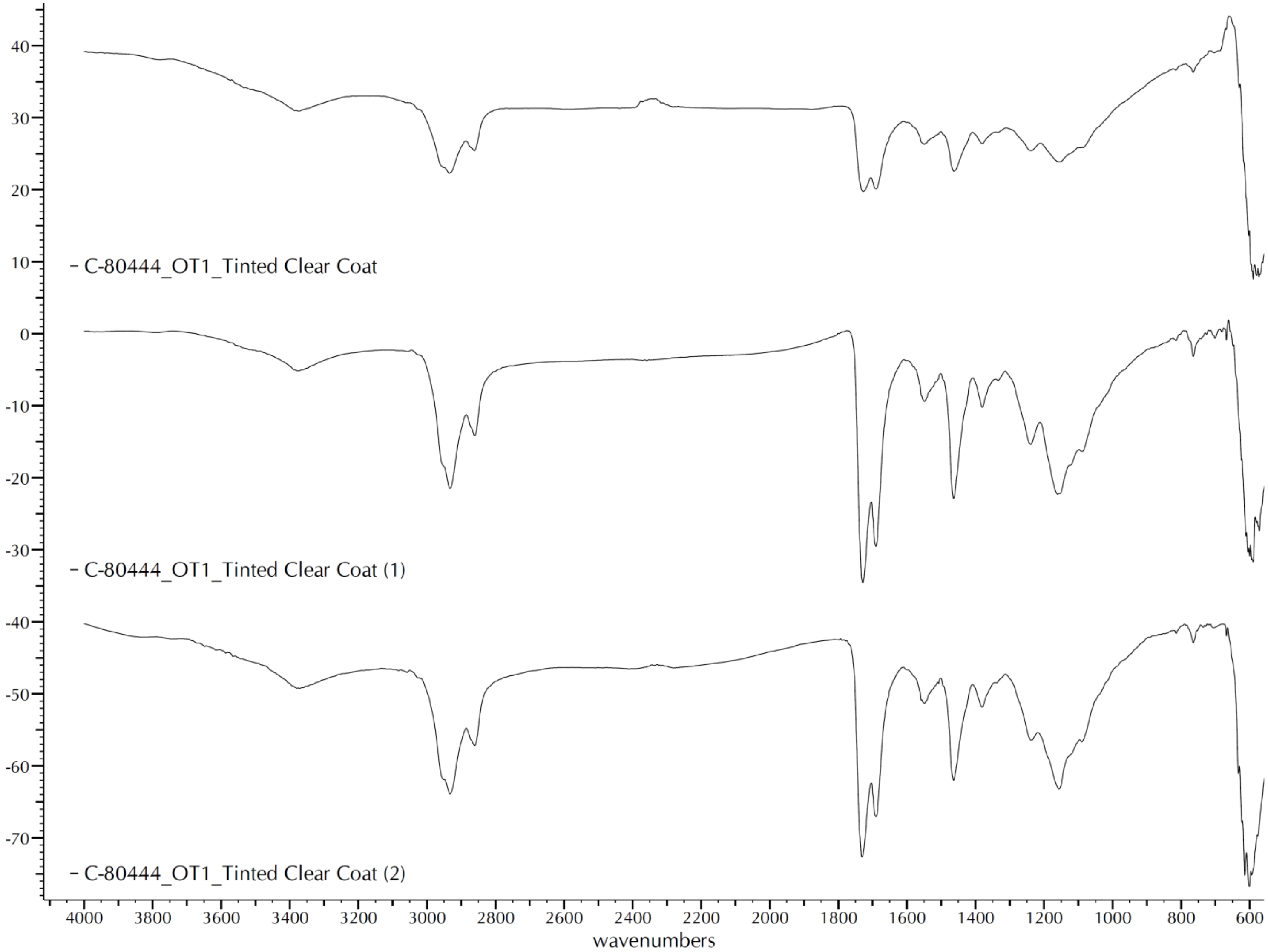


Figure 42G. Comparison of replicate FTIR spectra for the OT1 color layer of sample C-80444.

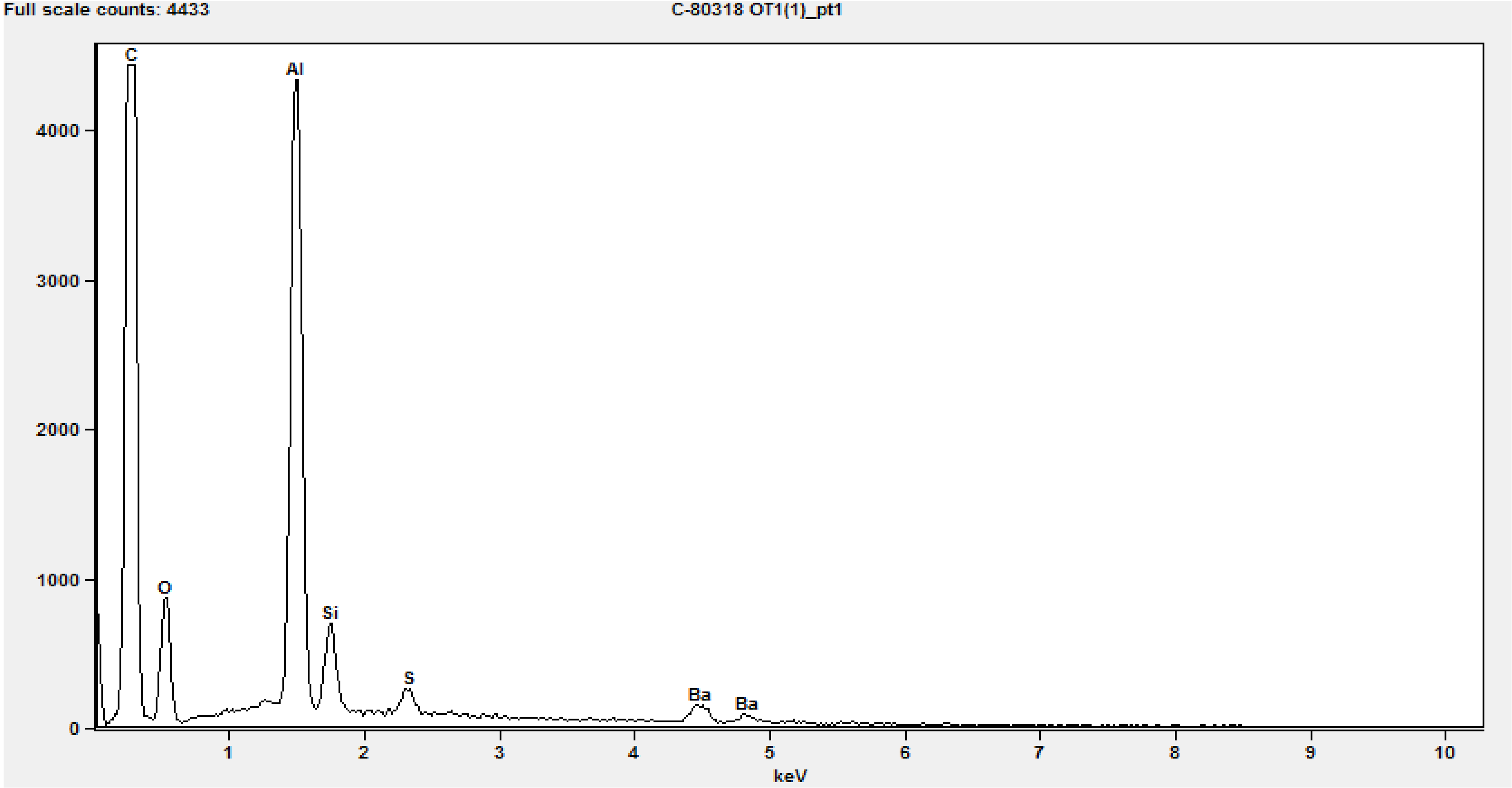


Figure 42H. Elemental analysis of the OT1 color layer of sample C-80318.

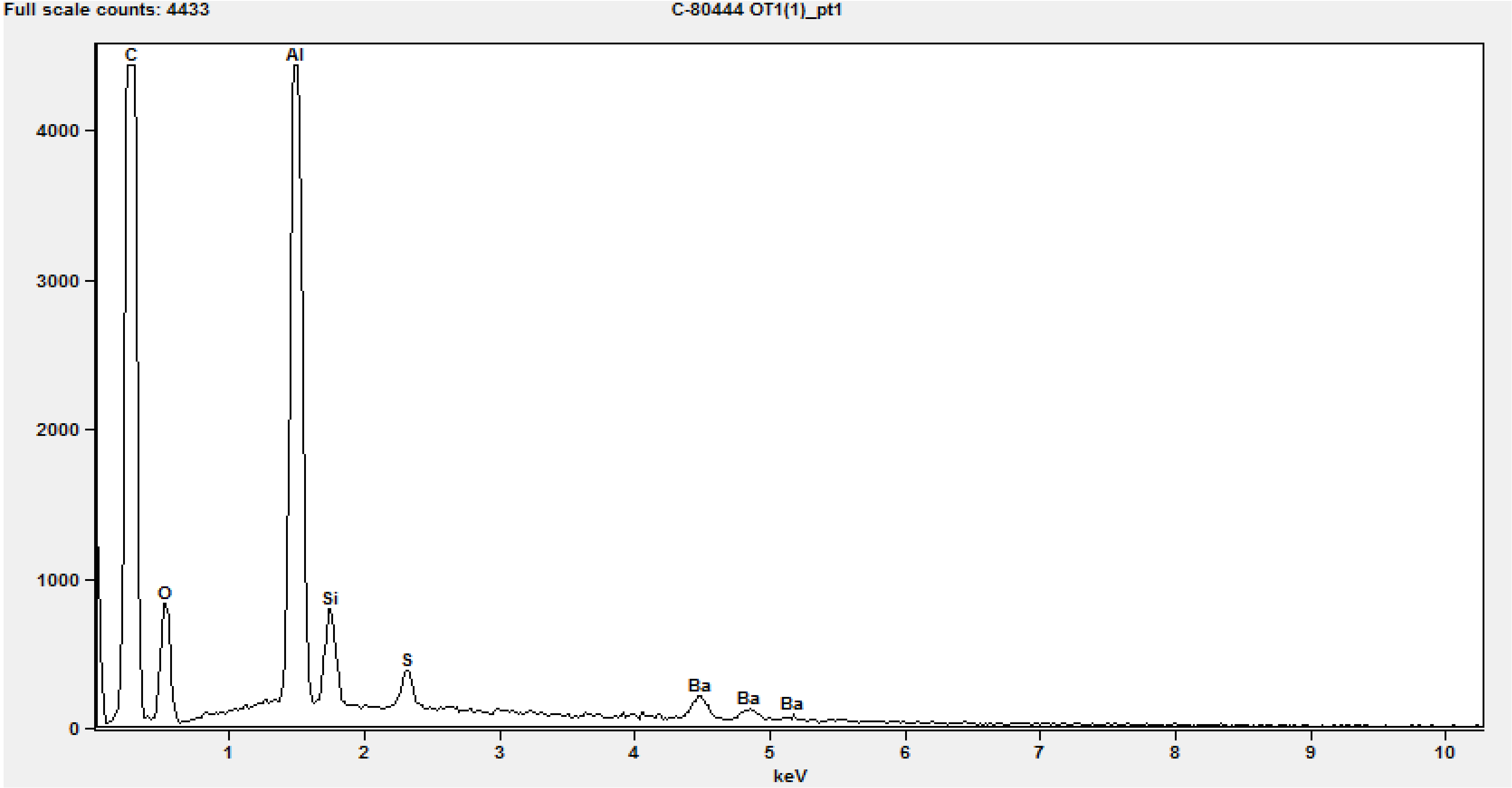
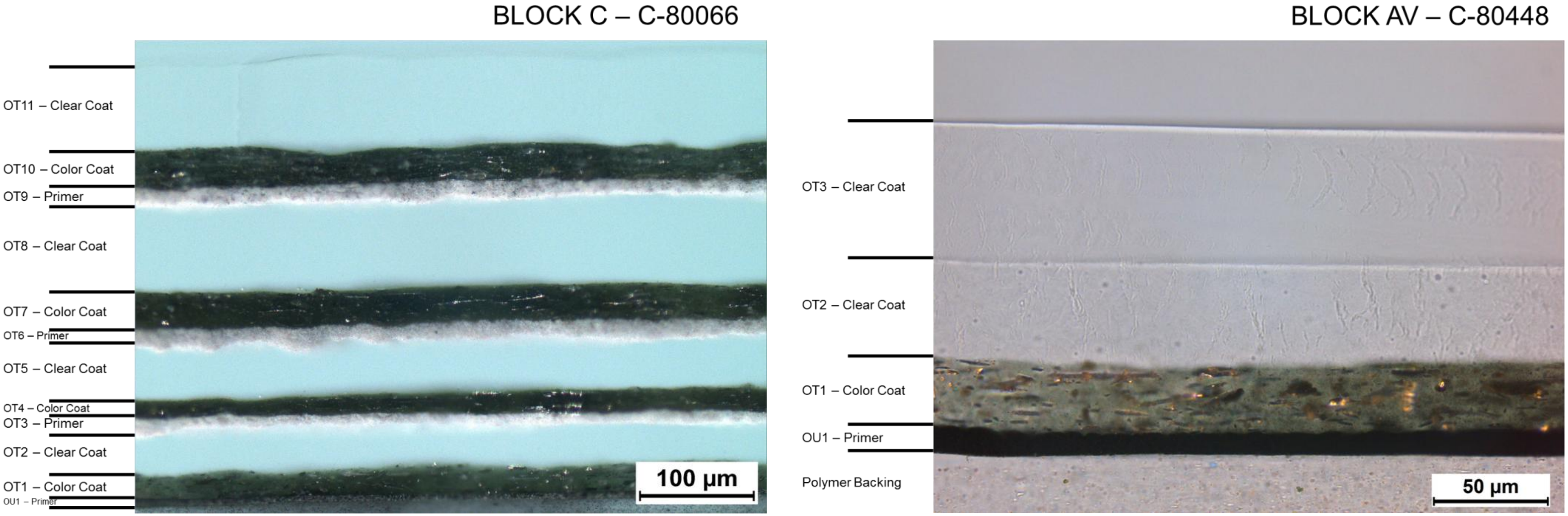


Figure 42I. Elemental analysis of the OT1 color layer of sample C-80444.



C-80066 – OT1 – Color Coat

2005 Cadillac CTS

Color Code: 92 (816K)

Sample Location: Bumper

Raman ID: PG7, PBl7

C-80448 – OT1 – Color Coat

2004 Chevrolet Malibu

Color Code: 92 (816K)

Sample Location: Bumper

Raman ID: PG36, PBl7

Figure 43A. Cross section images and meta-data for a comparison of the OT1 color layer of sample C-804066 and the OT1 color layer of sample C-80448.

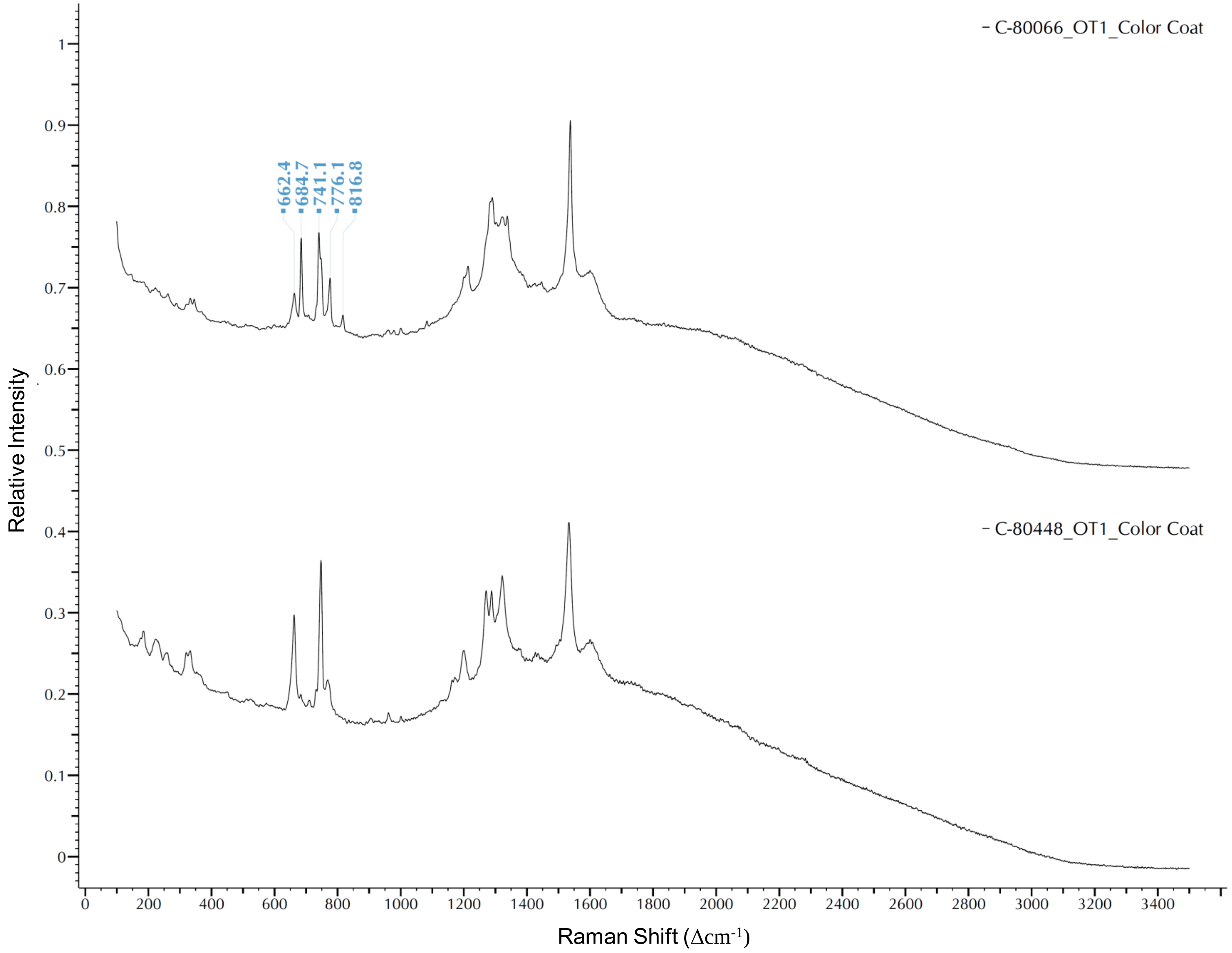


Figure 43B. Comparison of Raman spectra for the OT1 color layer of sample C-80066 and the OT1 color layer of sample C-80448.

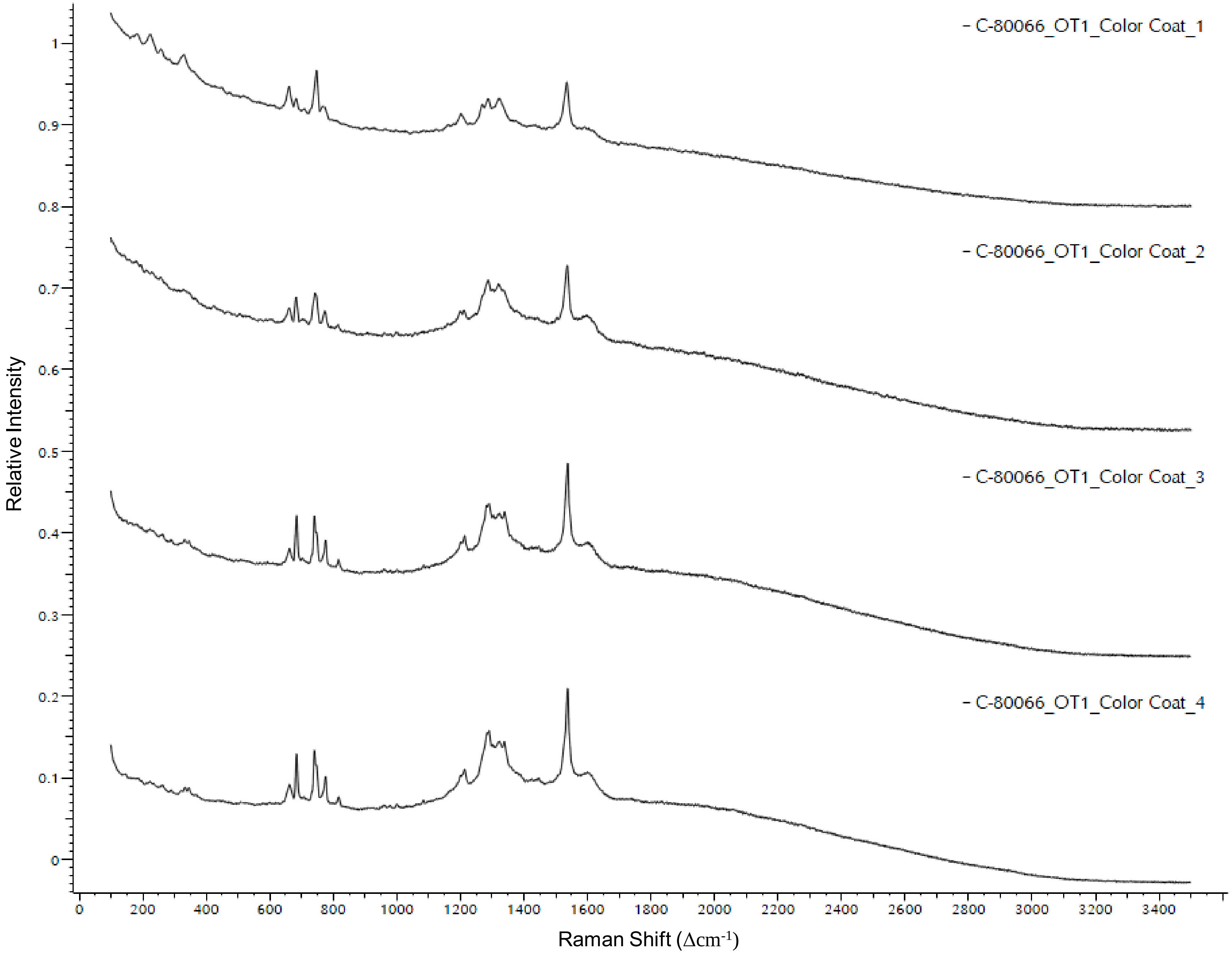


Figure 43C. Comparison of replicate Raman spectra for the OT1 color layer of sample C-80666.

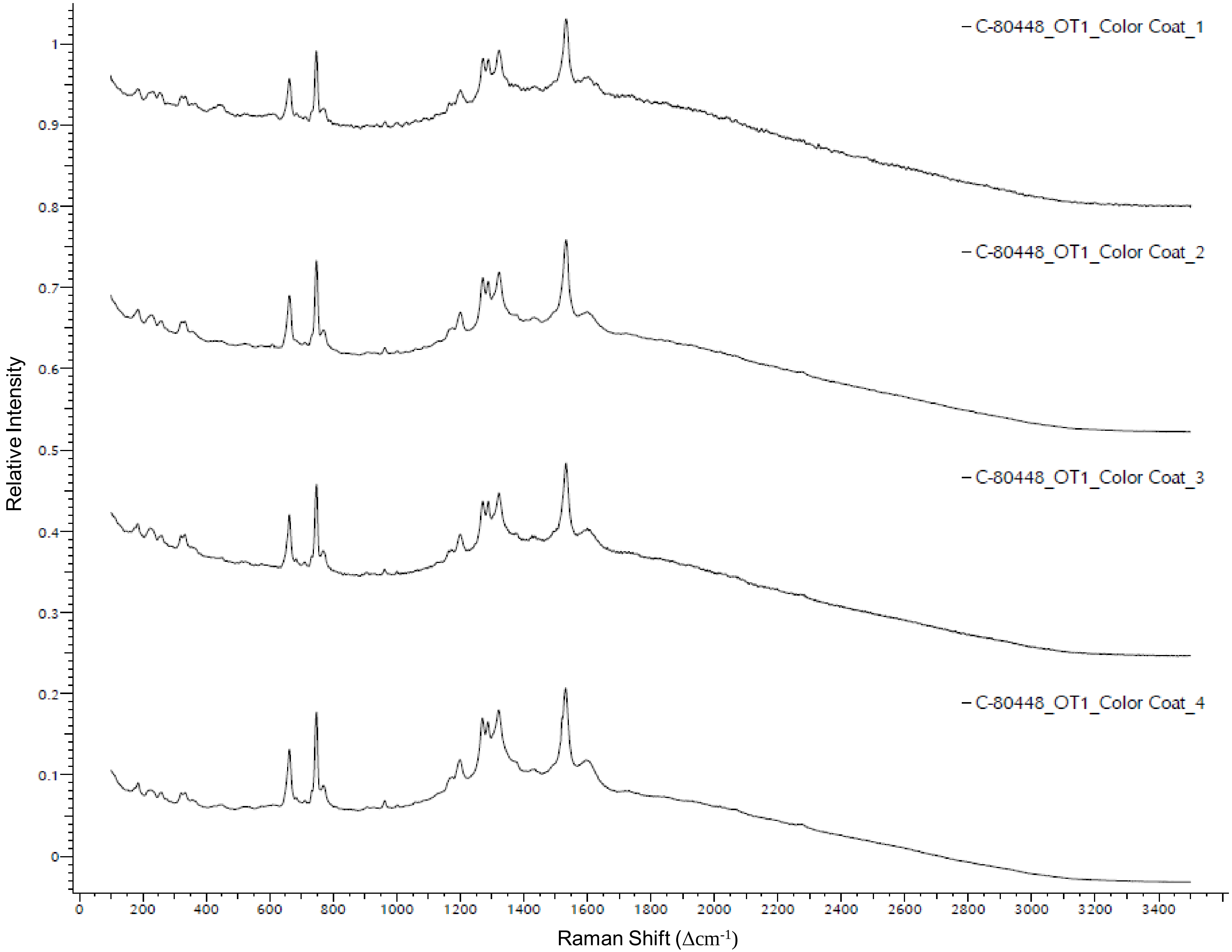


Figure 43D. Comparison of replicate Raman spectra for the OT1 color layer of sample C-80448.

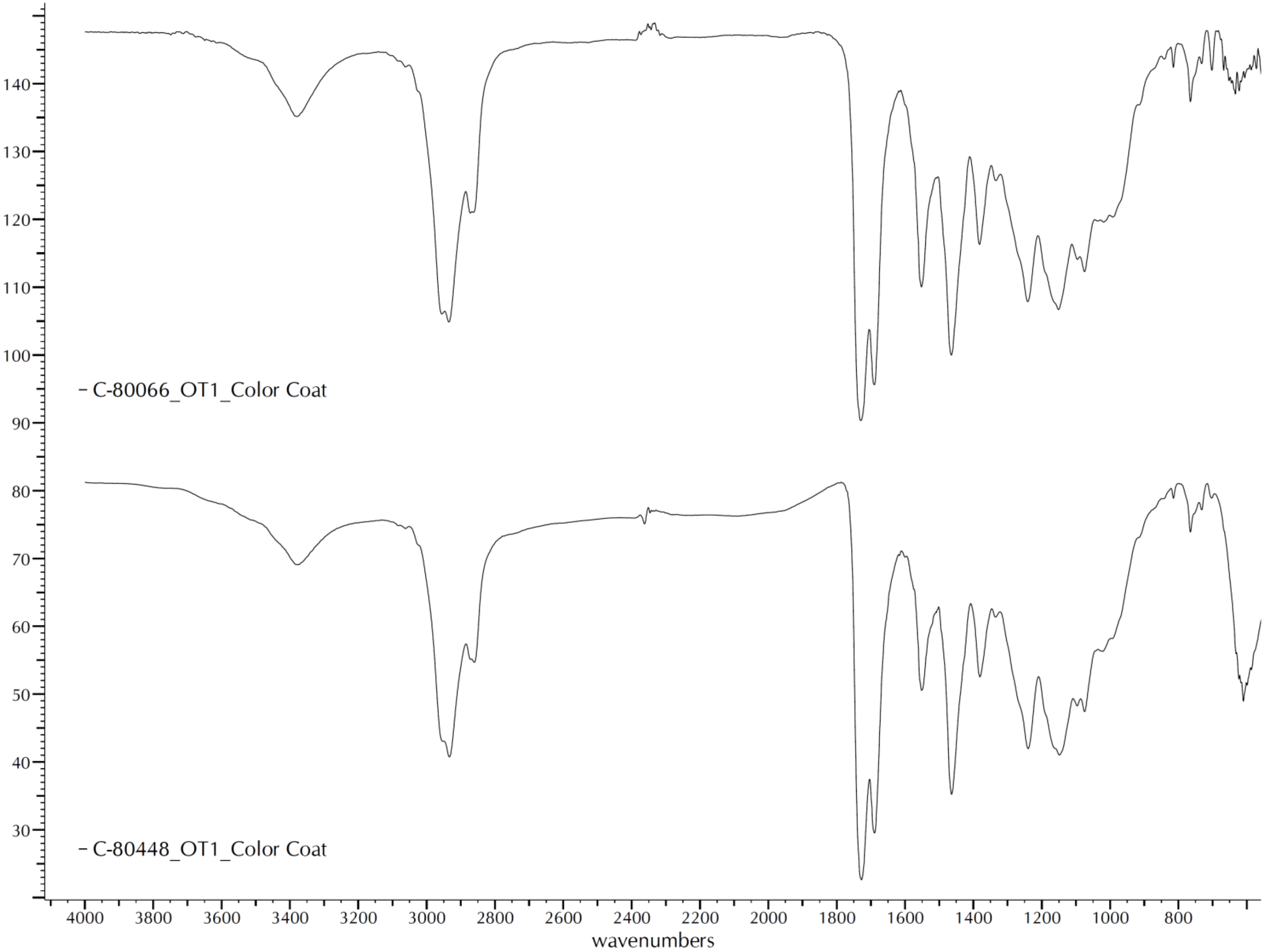


Figure 43E. Comparison of FTIR spectra for the OT1 color layer of sample C-80066 and the OT4 color layer of sample C-80448.

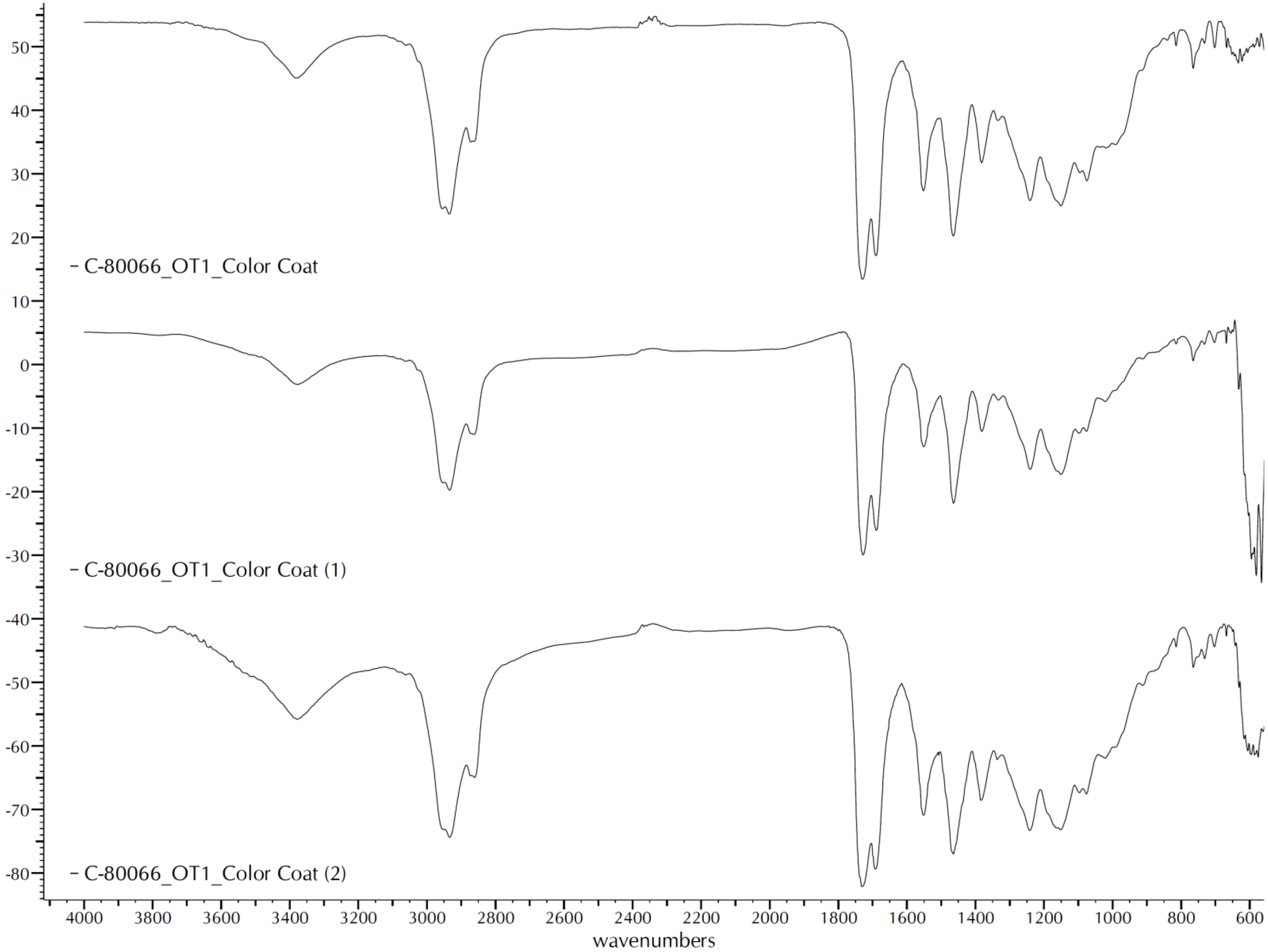


Figure 43F. Comparison of replicate FTIR spectra for the OT1 color layer of sample C-80066.

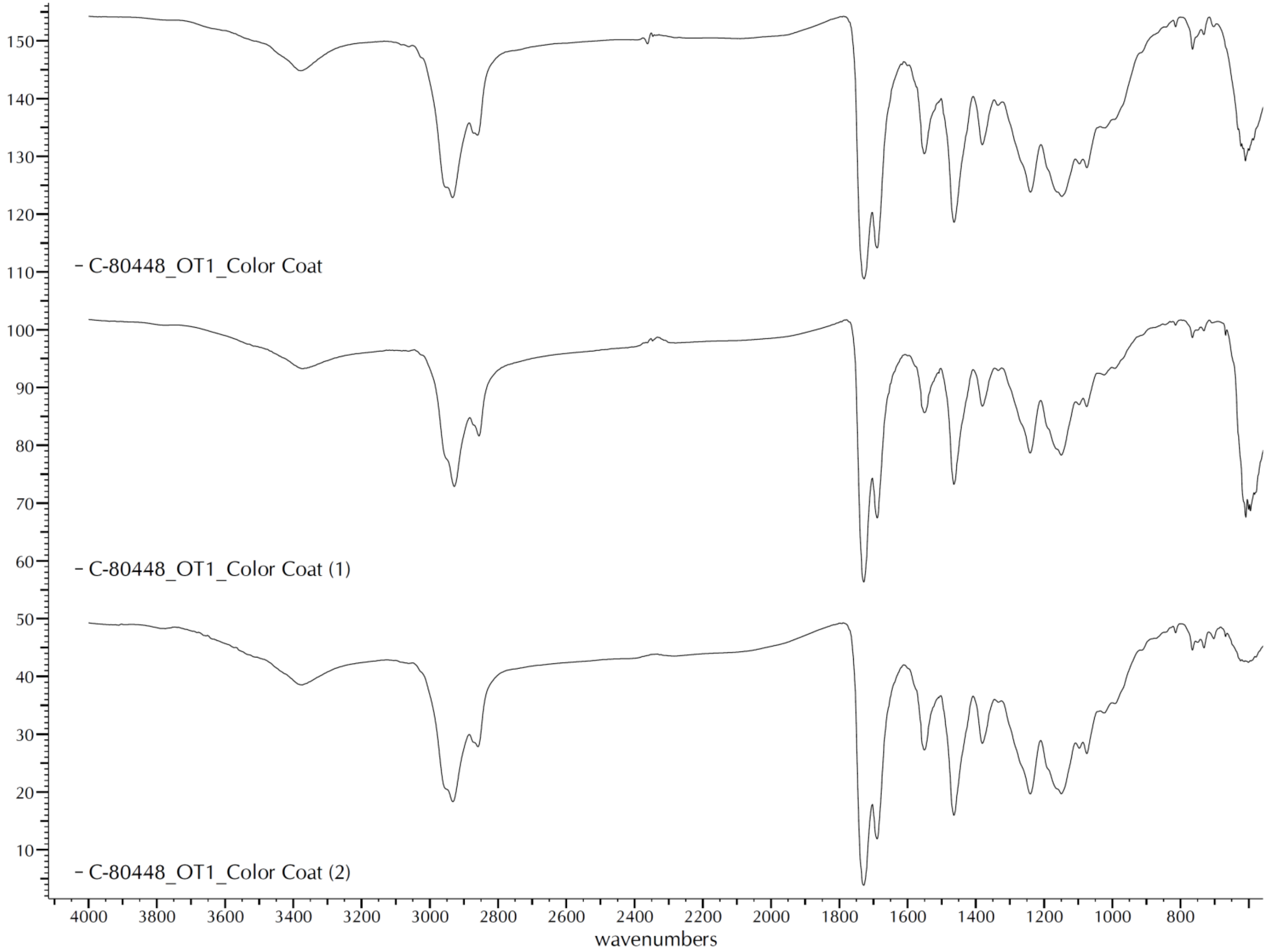


Figure 43G. Comparison of replicate FTIR spectra for the OT1 color layer of sample C-80448.

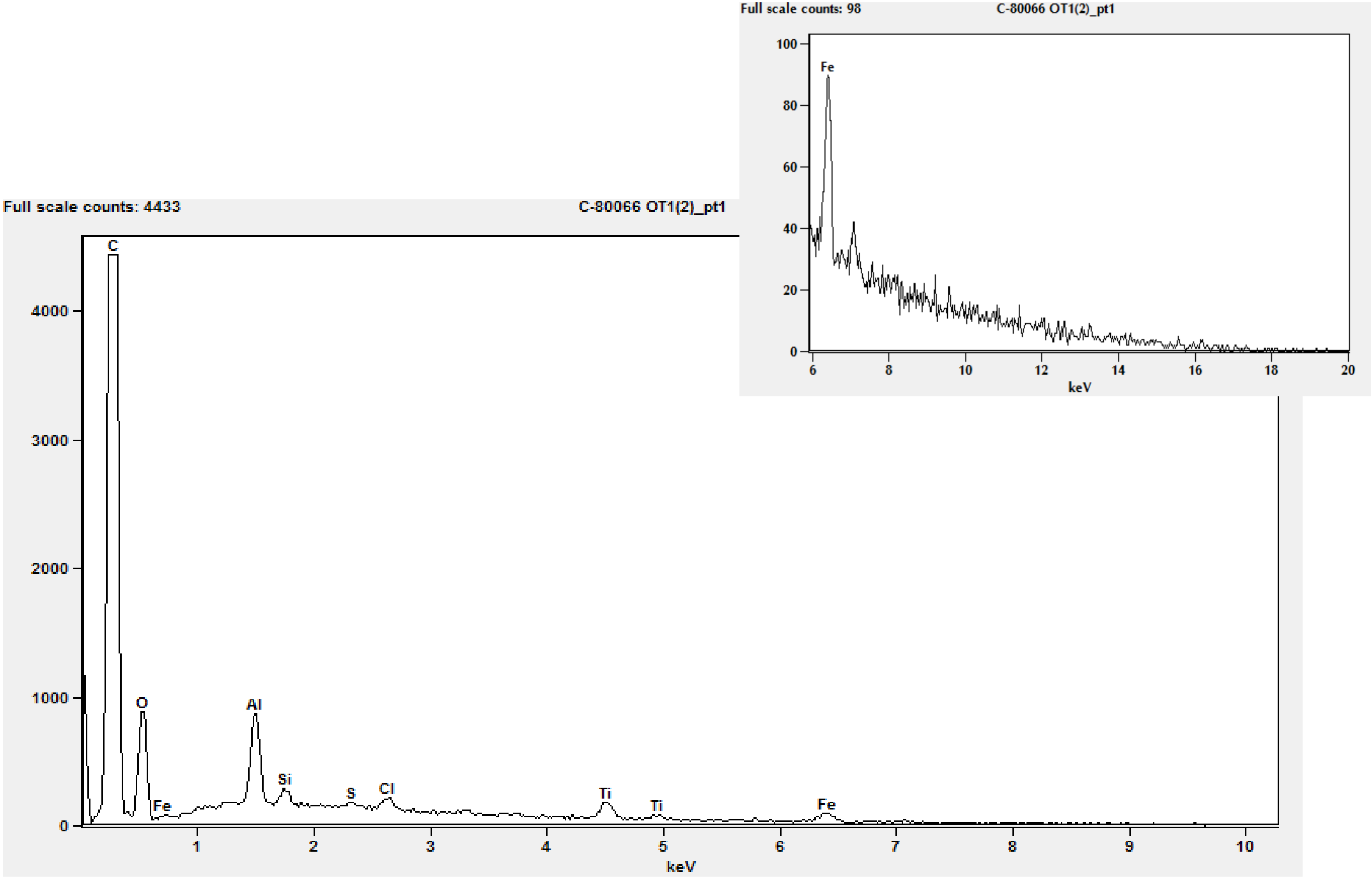


Figure 43H. Elemental analysis of the OT1 color layer of sample C-80066.

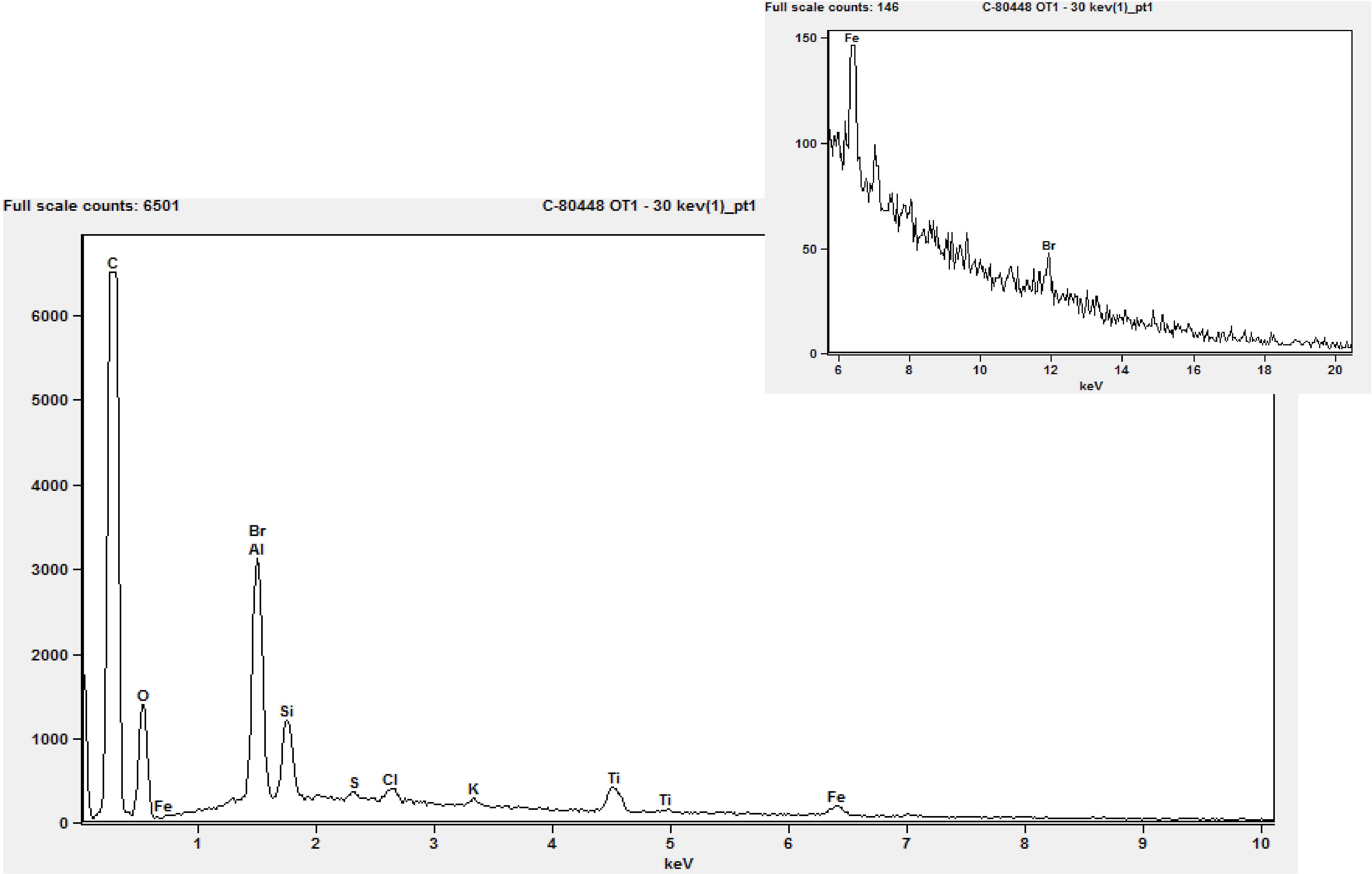
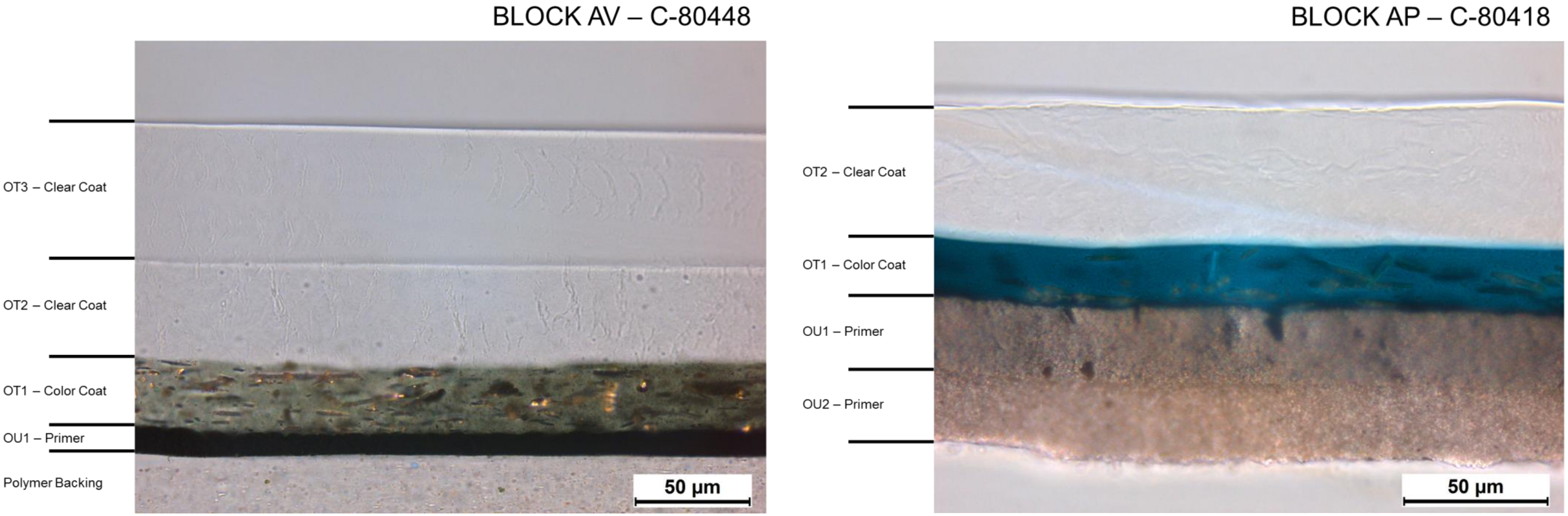


Figure 43I. Elemental analysis of the OT1 color layer of sample C-80448.



BLOCK AV – C-80448

BLOCK AP – C-80418

C-80448 – OT1 – Color Coat

2004 Chevrolet Malibu

Color Code: 92

Sample Location: Front Bumper

Raman ID: PG36, PBl7

C-80418 – OT1 – Color Coat

1995 Cadillac Deville

Color Code: 92 (115A)

Sample Location: Driver Side Door

Raman ID: PG7

Figure 44A. Cross section images and meta-data for a comparison of the OT1 color layer of sample C-80448 and the OT1 color layer of sample C-80418.

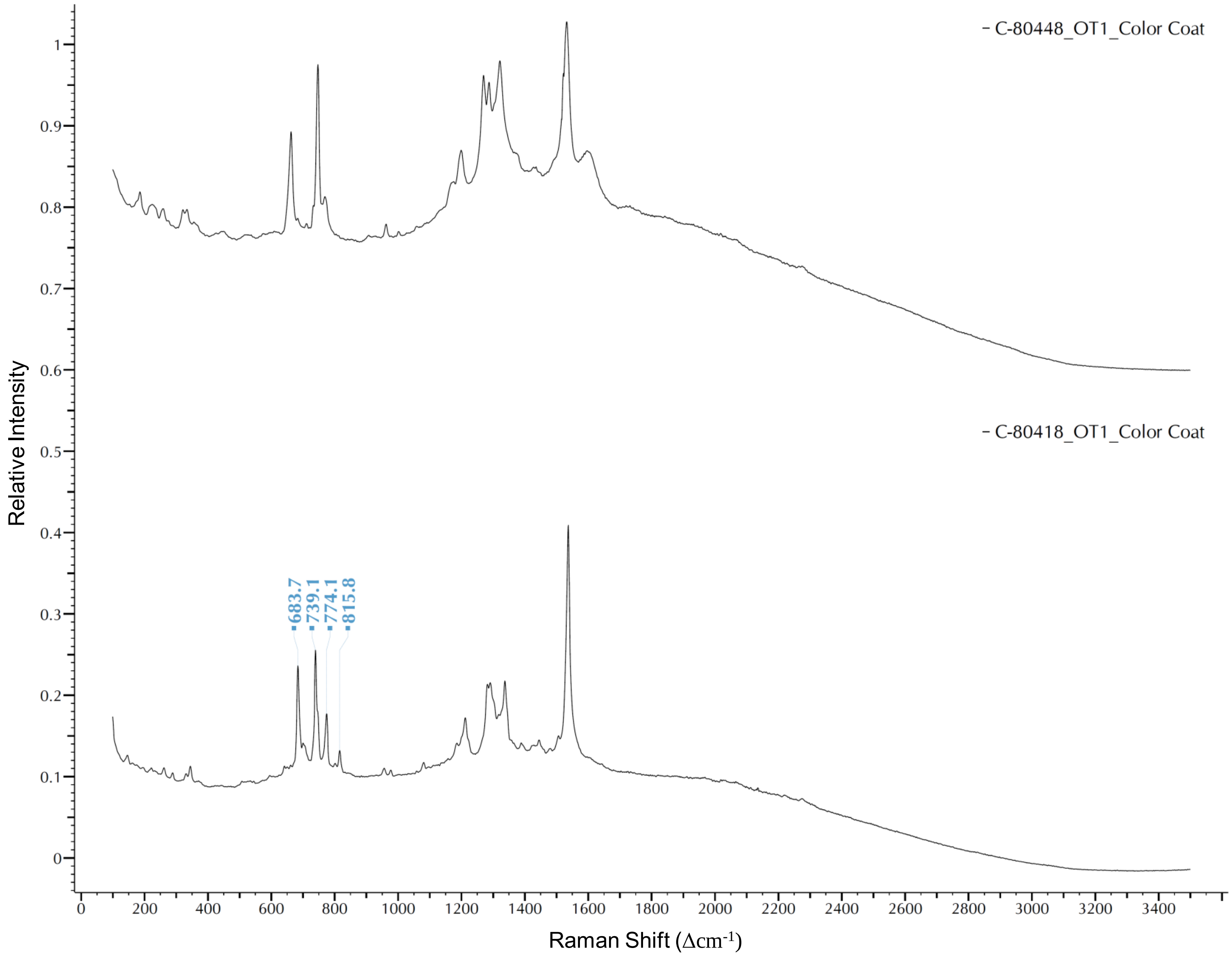


Figure 44B. Comparison of Raman spectra for the OT1 color layer of sample C-80448 and the OT1 color layer of sample C-80418.

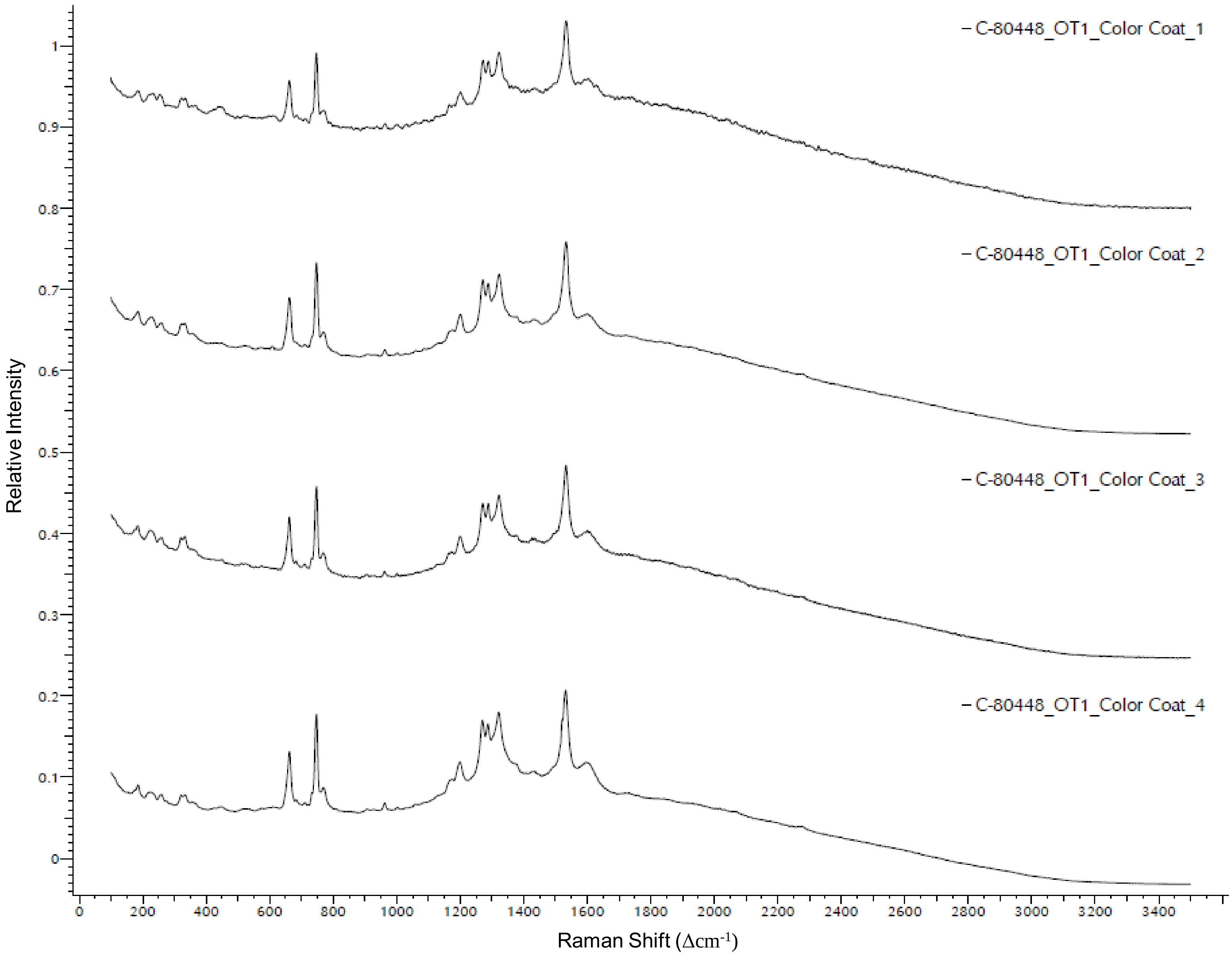


Figure 44C. Comparison of replicate Raman spectra for the OT1 color layer of sample C-80448.

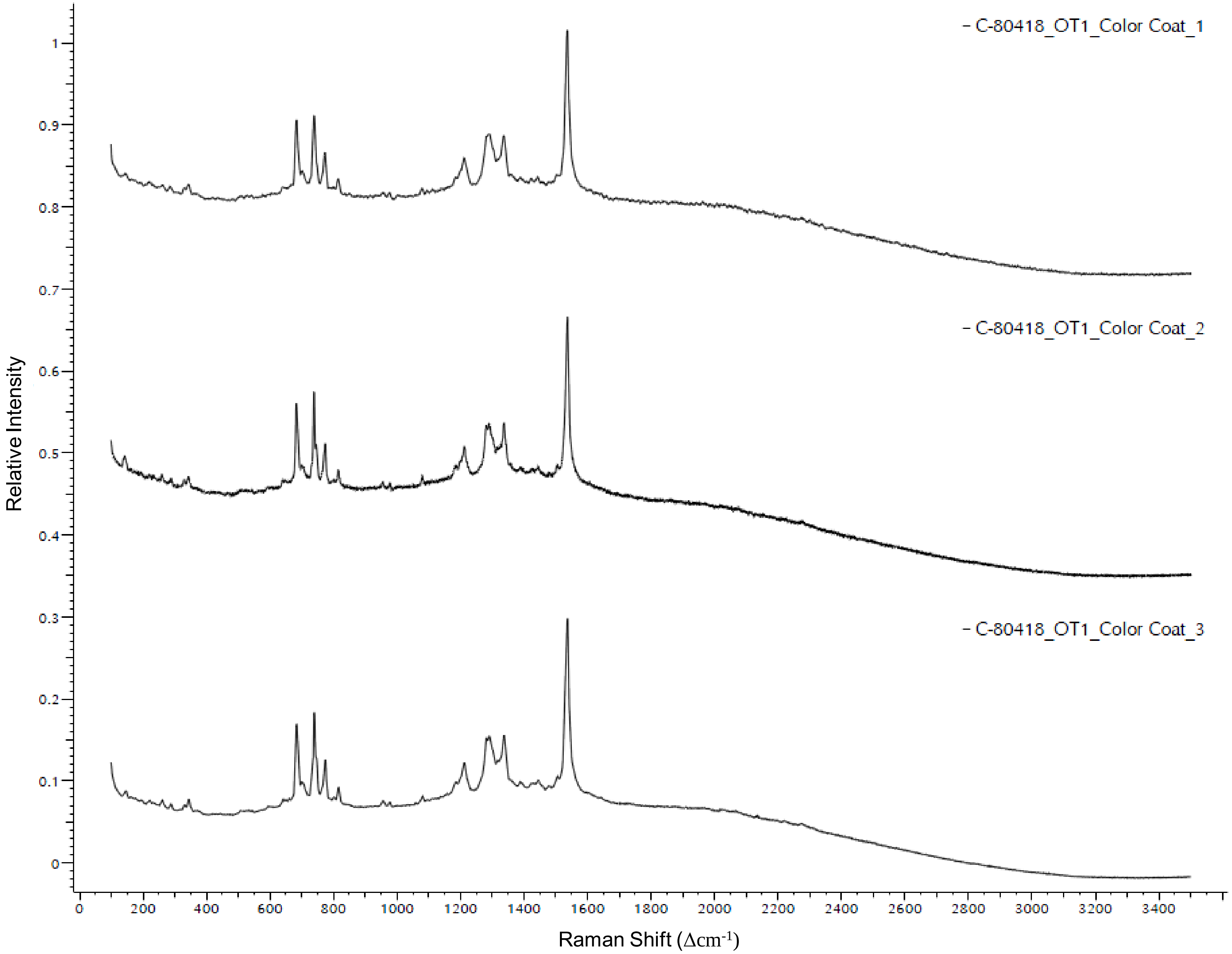


Figure 44D. Comparison of replicate Raman spectra for the OT1 color layer of sample C-80418.

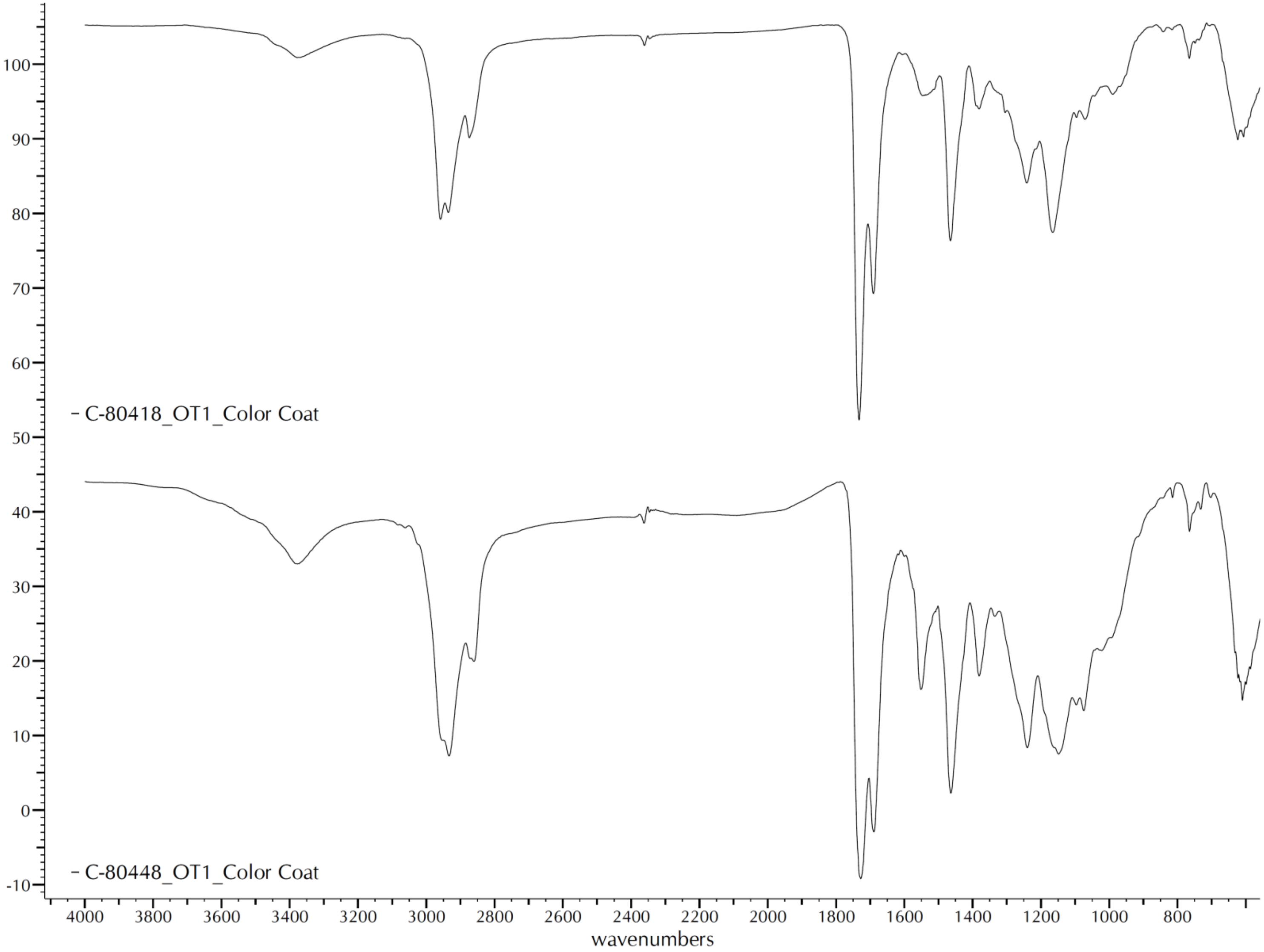


Figure 44E. Comparison of FTIR spectra for the OT1 color layer of sample C-80418 and the OT1 color layer of sample C-80448.

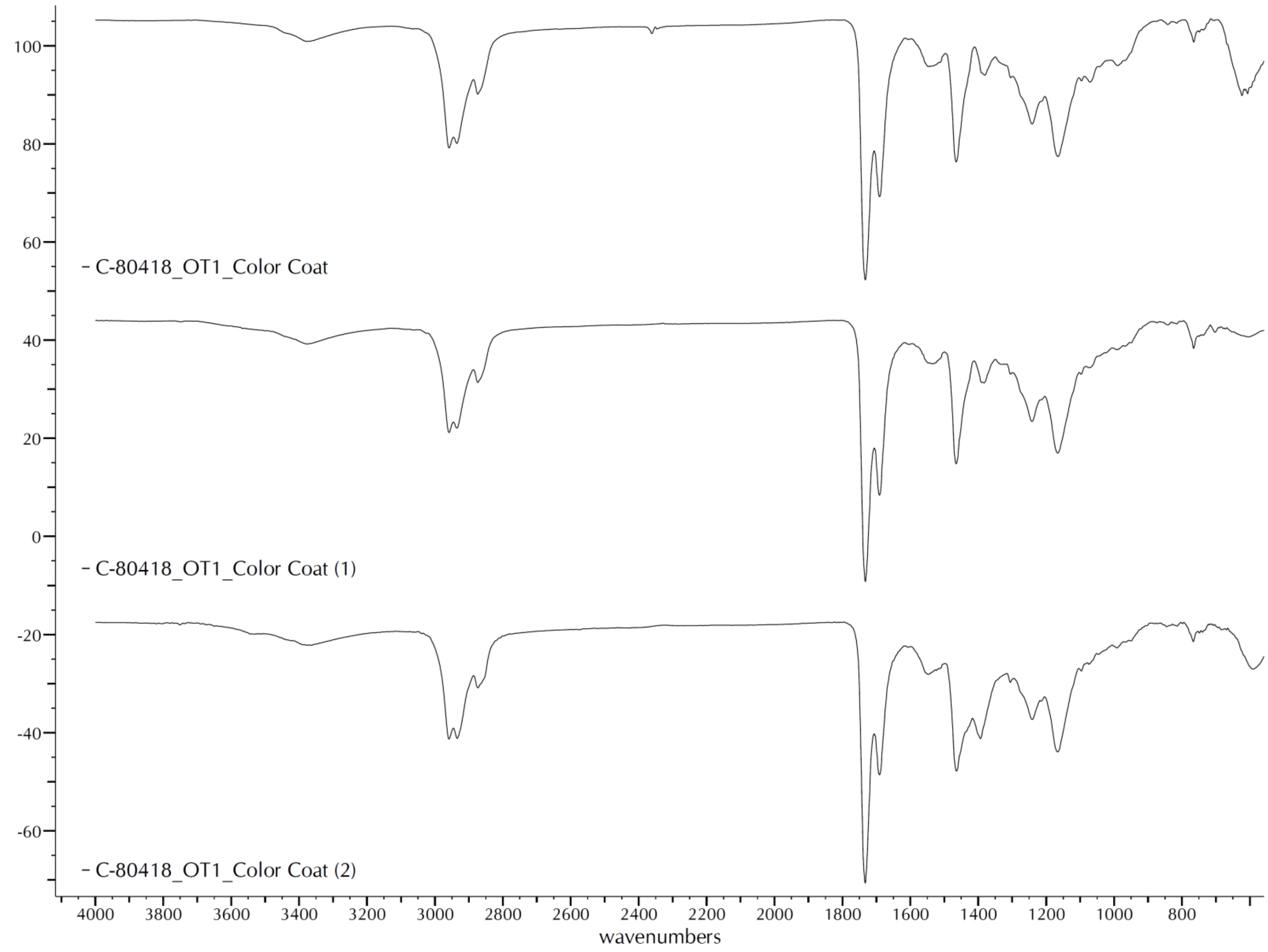


Figure 44F. Comparison of replicate FTIR spectra for the OT1 color layer of sample C-80418.

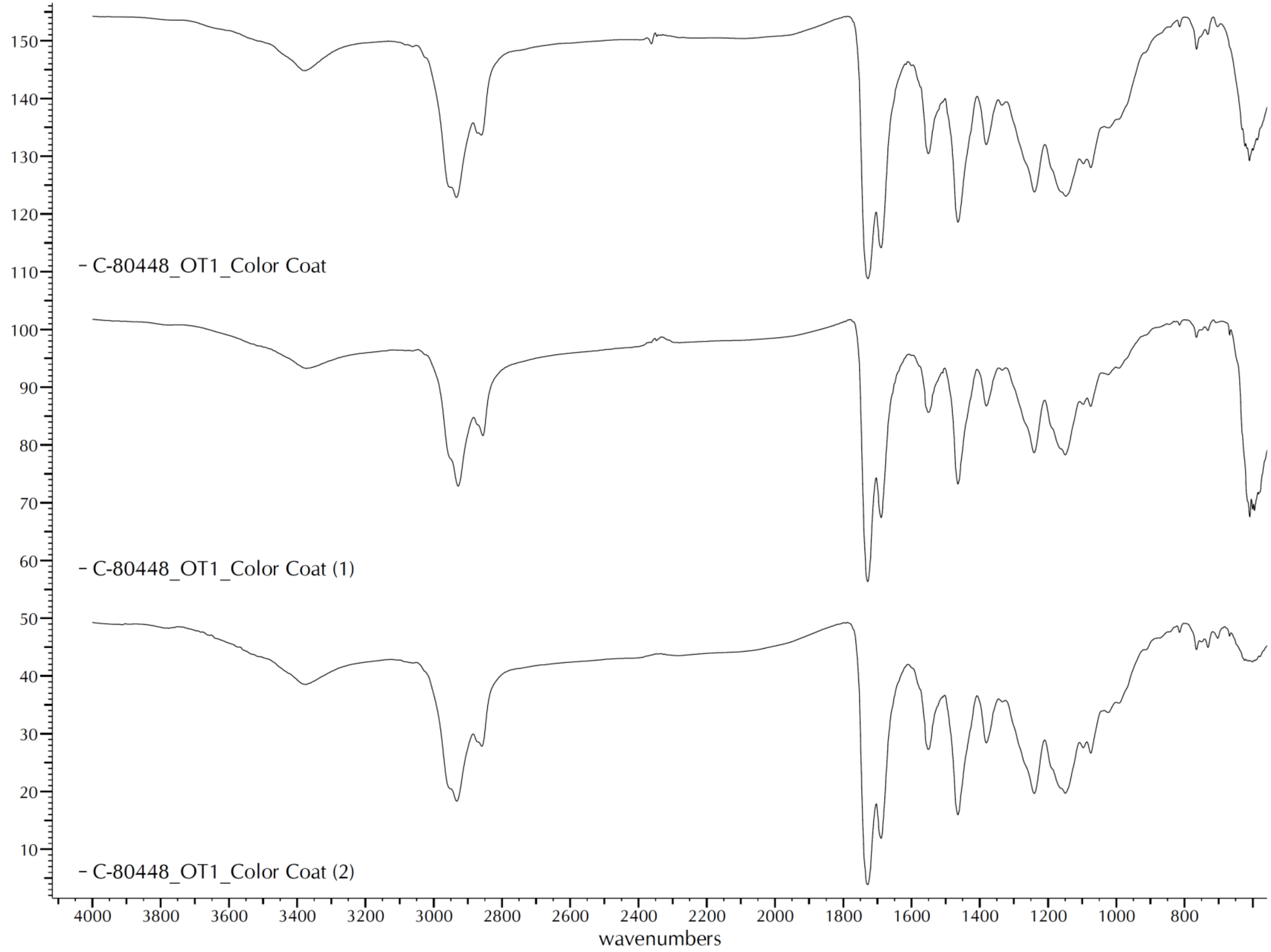


Figure 44G. Comparison of replicate FTIR spectra for the OT1 color layer of sample C-80448.

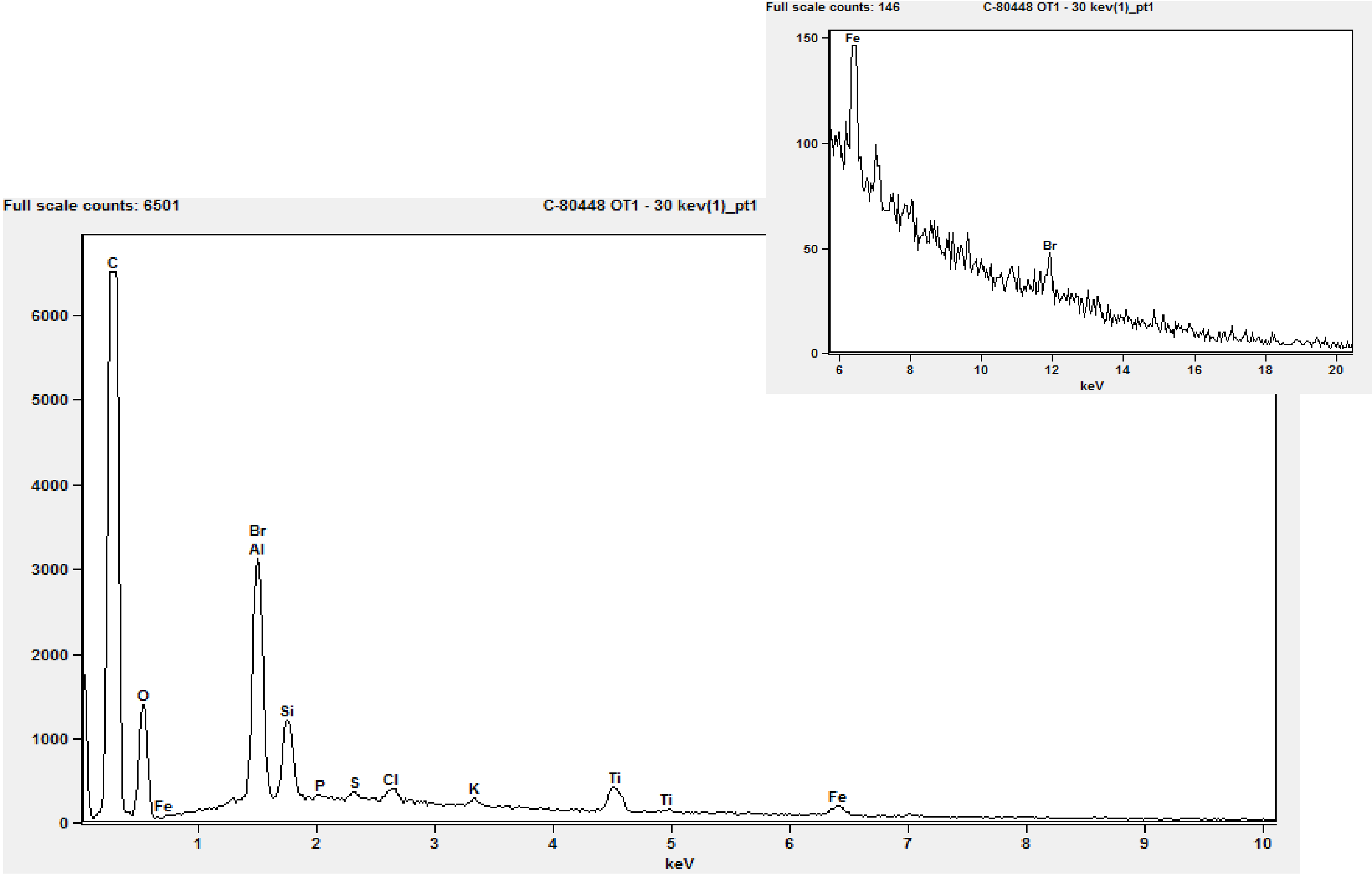


Figure 44H. Elemental analysis of the OT1 color layer of sample C-80448.

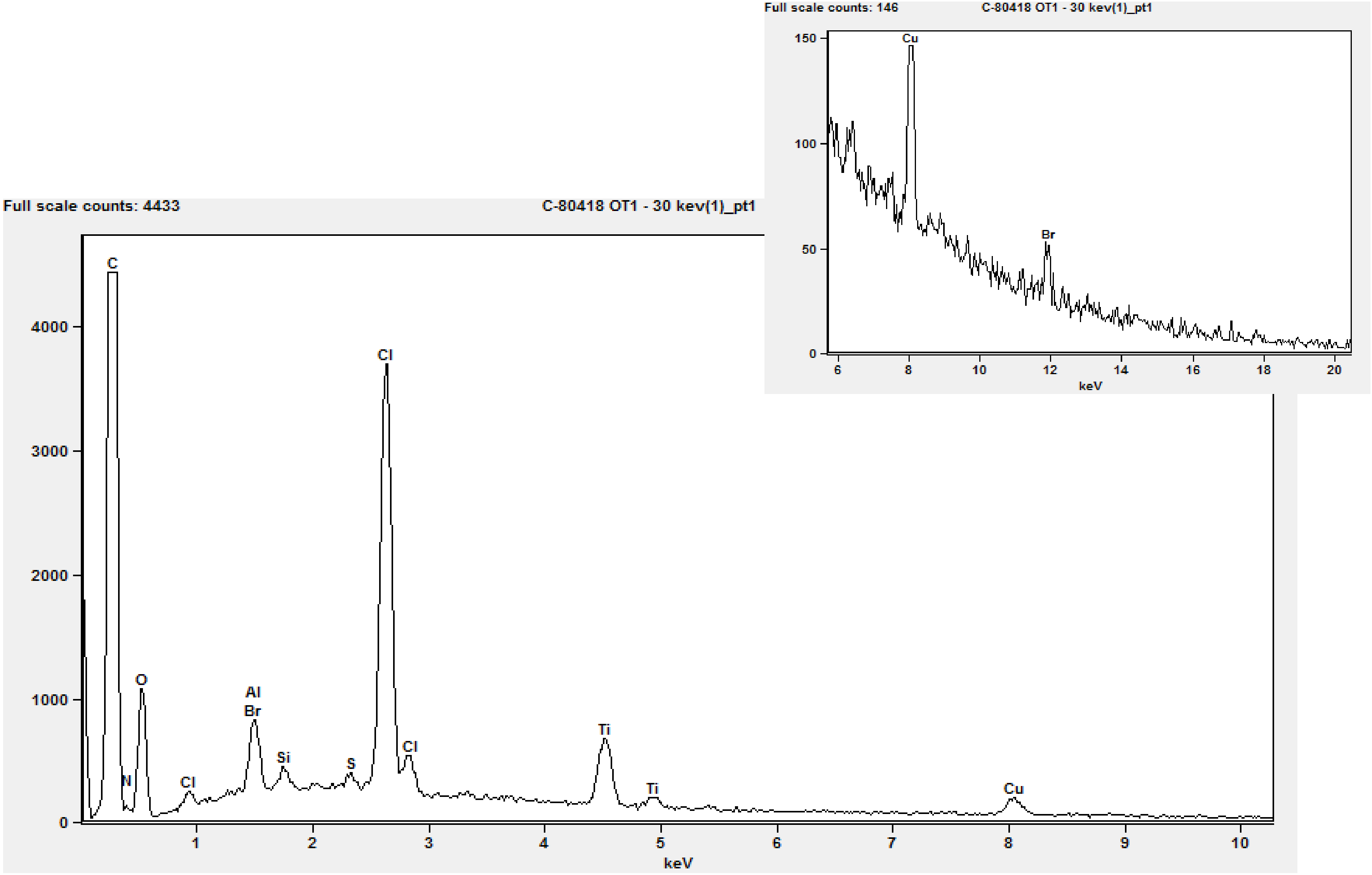


Figure 44I. Elemental analysis of the OT1 color layer of sample C-80418.

I) EDS spectrum from each of the layer 2;

Summary

Based the above data, the following statements can be made:

- Raman and FTIR spectra for each of the studied layers (even subtle spectral features) are reproducible.
- Some examiners may feel comfortable in distinguishing some of the pairs based on the FTIR spectra alone; however, we believe that it is fair to say that all of these layer pairs are extremely similar. The data are presented for the reader to make their own comparisons.
- The Raman data in five sample pairs that are difficult to distinguish by FTIR spectroscopy alone show that there are distinct differences in their pigment compositions.
- In four of the five samples, the discriminating Raman spectral feature(s) has been identified as an additional pigment. In the fifth sample, the difference is due to a reproducible, but unidentified peak.
- Elemental data (EDS spectra) collected for pairs that were similar by FTIR are an additional discriminating factor in four of the five samples.
- Raman Microspectroscopy can be especially helpful when attempting to determine if known and questioned paints, which appear to be the same based on their infrared spectra and elemental analyses, may still exhibit some difference based on a completely independent chemical property that is not easily observable using those two methods of analysis.

Since this study is the first of its kind, there are certainly other avenues that could be explored and different methods for quantifying discrimination. Regardless of other approaches, this study illustrates two main points. Raman spectroscopy does not appear to be as discriminating as FTIR spectroscopy; however, there are examples where Raman spectroscopy provides discrimination beyond the capabilities of FTIR. There is at least one example where the discrimination exceeds that of a combination of FTIR and EDS (C-80318 *vs*. C-80444).

OTHER LAYERS

In the course of this research, we explored the possibility of obtaining useful information from layers other than the main color coat. In this section we provide information resulting from these pilot studies to illustrate their potential for providing additional discrimination.

Tinted Clear Coat Study

Tinted clear coats are becoming more popular for vehicle paint systems. The Tri-Coat paint system uses a tinted clear coat to add depth to the color of the vehicle. The silver color of vehicles is achieved by silver colored effect pigment flake or aluminum flake embedded within a clear polymer. Within the three hundred paint samples studied eighty-nine, comprising nearly seven percent of all layers encountered, were found to have tinted clear coats.

Pigment concentration(s) within tinted clear coats is less than that of color coats. FTIR provides limited detection of pigments, especially when present at near trace concentrations within a polymer. Raman, on the other hand, has shown the capability of identifying pigment(s) within the polymers and in some instances, the polymer and/or modifiers to that polymer.

Within the population of tinted clear coats, identifiable pigments were detected forty-five times; the forty-five pigment identifications can be further broken down into twelve unique pigments or groups of pigments. Table 9 provides a list of the pigments we observed and identified in the tinted clear coat layers. There were many instances where the tinted clear coat showed a large amount of fluorescence and in all but a few of these cases, at least one pigment could be identified (despite the fluorescence).

Table 9. Summary colorants identified within tinted clear coats.

Colorant Identified	Exact/Group	Number of Identifications
C.I. Pigment Black 7	Exact	14
C.I. Pigment Blue 15	Group	4
C.I. Pigment Blue 15:1	Group	6
C.I. Pigment Blue 15:3	Group	4
C.I. Pigment Blue 60	Exact	4
C.I. Pigment Green 36	Exact	1
C.I. Pigment Green 7	Exact	1
C.I. Pigment Red 209	Exact	1
C.I. Pigment Red 254	Exact	1
C.I. Pigment White 19	Exact	1
C.I. Pigment White 21	Group	2
C.I. Pigment White 6 (Rutile)	Exact	6
No colorants identified	N/A	26
High fluorescence - no identifications	N/A	11

Coordinated Primer Study

Coordinated primer layers have been developed for a variety of reasons. It is our understanding that the two main reasons are 1) to reduce the thickness of the main color coat and 2) to reduce the impact of a scratch that penetrates the color layer.

Definitively identified coordinated primer layers were observed in twelve instances, which could be sub-divided further into five different pigments packages. This count does not include silver paints, which often consist of a clearcoat containing a metallic flake directly above a (typically) tan or gray layer. Inclusion of the silver paints would dramatically increase the number of coordinated primers encountered in this study.

Primer Layer Study

Primers were characterized by Raman spectroscopy as part of the initial study of thirty paint samples. Table 10 shows a summary of the pigments identified in these layers, which consisted exclusively of Pigment Black 7 (Carbon Black), Pigment White 6 (Titanium Dioxide), Pigment White 21/22 (Barium Sulfate), and Pigment White 26

(Talc). Various unidentified peaks were also observed; however, it does not appear that these are pigments but rather other components of the primer that are common to many of the samples studied. This group of fifty-one primer layers can be sorted into twelve groups with the potential of more categories as unidentified peaks are assigned.

Table 10. Survey of components identified in the primer layers of the first thirty paint samples by Raman spectroscopy. P = present. UI = unidentified peaks.

No.	Layer	Layer/Coat	Adjacent Layer	PBl 7	PW 6	PW 21/22	PW 26	UI
C-80050	OU1	Primer Layer 1	Bumper	P	P			P
C-80051	OU2	Primer Layer 2	Bumper	P	P			P
C-80052	OU1	Primer Layer 1	Paint	P				P
C-80055	OT3	Primer Layer 2	Paint		P	P	P	
C-80055	OT5	Primer Layer 3	Paint	P	P			
C-80055	OT6	Primer Layer 4	Paint	P	P		P	
C-80055	OU1	Primer Layer 1	Bumper	P	P	P		
C-80056	OU2	Primer Layer 2	Bumper	P	P			
C-80056	OU1	Primer Layer 1	Paint	P	P	P		
C-80057	OU2	Primer Layer 2	Bumper					P
C-80057	OU1	Primer Layer 1	Paint			P		P
C-80058	OU1	Primer Layer 1	Bumper	P				
C-80059	OU1	Primer Layer 1	Bumper	P				
C-80063	OU1	Primer Layer 1	Bumper	P	P			
C-80064	OU2	Primer Layer 2	Bumper	P	P			
C-80064	OU1	Primer Layer 1	Paint	P	P			
C-80065	OU2	Primer Layer 2	Bumper	P	P			P
C-80065	OU1	Primer Layer 1	Paint	P	P	P		
C-80066	OT3	Primer Layer 2	Paint	P	P			P
C-80066	OU1	Primer Layer 1	Bumper	P	P			
C-80066	OT6	Primer Layer 3	Paint	P	P			P
C-80066	OT9	Primer Layer 4	Paint	P	P			P
C-80068	OU1	Primer Layer 1	Paint	P	P			P
C-80068	OU2	Primer Layer 2	Bumper	P	P			P
C-80069	OU1	Primer Layer 1	Bumper	P	P	P		
C-80070	OU1	Primer Layer 1	Bumper	P		P		
C-80071	OU2	Primer Layer 2	Bumper					P
C-80071	OU1	Primer Layer 1	Paint	P	P	P		
C-80072	OU2	Primer Layer 2	Bumper					P
C-80072	OU1	Primer Layer 1	Paint	P				
C-80073	OU2	Primer Layer 1	Bumper					P

C-80073	OU1	Primer Layer 2	Paint					P
C-80074	OU2	Primer Layer 2	Bumper					P
C-80074	OU1	Primer Layer 1	Paint		P			P
C-80081	OU1	Primer Layer 1	Paint		P	P		
C-80081	OU2	Primer Layer 2	Bumper	P	P			P
C-80082	OU2	Primer Layer 2	Bumper					P
C-80082	OU1	Primer Layer 1	Paint		P			P
C-80211	OU1	Primer Layer 1	Bumper	P	P			
C-80212	OU1	Primer Layer 1	Bumper	P	P			
C-80213	OU2	Primer Layer 2	Bumper					P
C-80213	OU1	Primer Layer 1	Paint	P	P	P		
C-80214	OU2	Primer Layer 2	Bumper					P
C-80214	OU1	Primer Layer 1	Paint		P			P
C-80215	OU1	Primer Layer 1	Bumper	P	P			
C-80216	OU1	Primer Layer 1	Bumper	P	P			
C-80217	OU1	Primer Layer 1	Bumper	P				P
C-80218	OU1	Primer Layer 1	Bumper	P				P
C-80226	OU1	Primer Layer 1	Bumper	P	P			
C-80227	OU2	Primer Layer 2	Bumper					P
C-80227	OU1	Primer Layer 1	Paint	P	P			P

ARCHITECTURAL PAINT SAMPLES

TINTING PIGMENTS

Architectural (interior and exterior) paints are produced in a much wider range of colors than automotive paints. However, many architectural paints are produced from a white base to which measured quantities (volumes) of pre-dispersed pigments are added. As part of an internal research project several years ago, we visited several paint stores and with the assistance of management acquired aliquots of the “tinting” pigments used to produce the continuum of colors from which consumers and commercial painters can choose (Palenik and Bonta, 2008).

We found that these sets of tinting pigments are typically composed of around a dozen colors. Based on that research we learned there are at least four different sets of colorants used. At least two manufacturers produce a similar set of universal colors (used by most home improvement warehouses and several paint stores). Benjamin Moore® has at least two proprietary systems, one which is their traditional set of twelve colors and a newer fully aqueous collection. Due to differences between the systems, slightly different ranges of final colors can be produced.

By identifying the pigments used in the main “tinting” colors, one would, by definition, know which pigments are used in all colors produced from these pigments. Dry pigments were isolated from the store samples through a process of multiple extractions to remove solvents that had been added to ease mixing. Although these had been previously studied, they were re-analyzed to take advantage of the recent developments in classification of pigments by Raman spectroscopy (Palenik et al., 2011).

Table 11. Pigments identified in the two tinting systems studied here.

Pigments Identified within Ace Tinting System		
Universal Tinting System Color Code	**Nominal Color**	**Pigments Identified**
B	Black	PBk 7
E	Blue	PB 15(β)
L	Brown	PBr 6
D	Green	PG 7
F	Red	PR 101*
I	Red	PR 101, PBk 7
R	Red	U.I.
V	Violet	PR 122
KP	White	PW 6 (Rutile)
APP	Yellow	PY 74
C	Yellow	PY 42(α)
T	Yellow	PY 74, PY 65

Pigments Identified within B.M. Tinting System		
Benjamin Moore Tinting System Color Codes	**Nominal Color**	**Pigments Identified**
BK	Black	PBk 7
GY	Black	PBk 7, PW 26
BB	Blue	PB 15(α)
BR	Brown	PBr 43
TG	Green	PG 7, PG 36
MA	Magenta	PR 122
OG	Orange	PO 36**
RD	Red	
RP	Red	PR 101
WH	White	PW 6 (Rutile)
OY	Yellow	PY 42α
YW	Yellow	PY 74

*C.I. Pigment Red 101 has been identified to a group that includes PR101, PR101:1, PR102
**Additional peaks present that have not yet been identified, another pigment may be present

With an understanding of the pigments used in the different systems, this information can now be applied to architectural paint samples. See "Sample Collection – Architectural Paint Samples" for details on samples selected for analysis.

WALL SAMPLES

As discussed in the Sampling section, 48 architectural paint samples were studied by Raman spectroscopy for the purposes of pigment identification. Samples were studied with no sample preparation using a defocused laser. A summary of the pigments identified is presented in Figure 45. Note that the paints are dominated by whites (rutile – PW6, anatase – PW6, calcite – PW18, kaolin – PW19, and silica – PW27). The lack of variety in pigments suggests that it may be beneficial to use a smeared sample, critical microscopy, and a confocal laser to better classify pigments present at lower concentrations (such as the tinting pigments used to color the samples). Nonetheless, the variety of 14 pigments in 48 samples suggests there is a good deal of potential in studying architectural paint pigments by this approach.

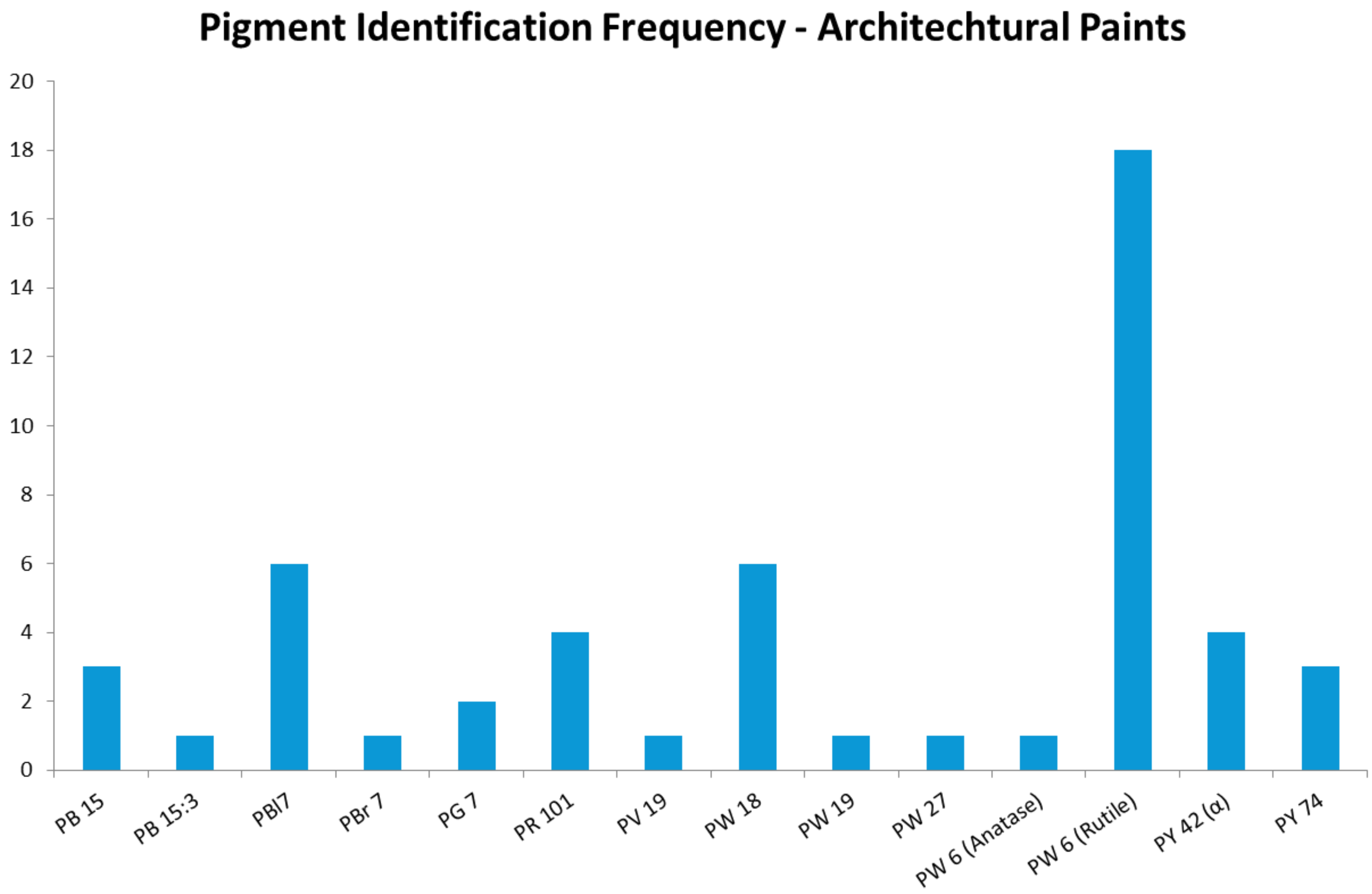


Figure 45. Summary of pigments identified in the 48 architectural paint samples studied.

CONCLUSION AND SUMMARY

This report is the culmination of approximately seven years of research into the characterization of pigments by Raman spectroscopy for forensic purposes. Part I of this research provided fundamental information regarding the chemical classification and identification of pigments, while Part II (this study) focused on the identification of pigments within paint samples and the evidentiary value of this information. Both parts of this research have attempted to be as pragmatic as possible, presenting results and information in a manner that would be obtainable and/or applicable in a forensic laboratory. Despite the length of both of these reports, they are organized in a manner such that a reader can reference only a portion of the work to obtain relevant information. Despite the amount of information, there is a great deal more to study and learn before this approach can be considered mature, in the way that this is currently understood for FTIR and EDS spectroscopies.

This report has attempted to remain unbiased toward the technique, presenting the data (both positive and negative) in a way which will allow the forensic community to determine its utility in practice. It is our belief that Raman spectroscopy has a place in all forensic laboratories – not exclusively for paint analysis, but for general classification purposes as it is fast and simple to use in comparison to other methods (including FTIR and EDS). For paint analysis, we have considered three levels at which it may see use – as a fast screening tool, as an intermediate characterization method, and as a high level characterization and identification method. There are potential applications for its use in all three areas, though the first and last seem to hold the most potential.

For some, the decision to employ Raman spectroscopy in casework will come down to the question of whether it will provide additional discrimination beyond currently used methods (namely FTIR and/or EDS). The answer to this question is 'yes,' however, this additional discrimination was observed so far in only a handful of samples. Regardless of the number, we believe this additional discrimination will be of special importance in certain instances. For example, in cases subjected to high scrutiny, in cases involving extremely small amounts of sample, in cases containing layers too thin to examine by FTIR spectroscopy (which will only become more common), and in cases where no comparison sample is available. Again, it is our belief that the use of pigment identification in conjunction with other analytical approaches can only improve the investigative information that can be obtained from a colored paint and polymer evidence.

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APPENDIX A – LIST OF AUTMOTIVE PAINT SAMPLES STUDIED

Year	Make	Model	Color Code	Nominal Color	Q.I.	MT Ascension Number
Field Sample						
	Paint					
		Architectural				
	Glidden	Interior/Exterior Gripper Grey Latex Primer & Sealer	GL3250	Black	1	C-80233
	Glidden	Eggshell Base 2	GL6012	White	1	C-80236
	Sherwin Williams	Latte	6108	Brown	1	C-80246
	Sherwin Williams	Blue Beyond	6961	Blue	1	C-80255
	Benjamin Moore	Saybrook Sage	HC-114	Green	1	C-80257
	Benjamin Moore	Candy Stripe	#2079-70	Red	1	C-80258
	Sherwin Williams	Promar 400 Interior Latex Eg-Shel	B20 W 4451	Brown	1	C-80299
	Benjamin Moore	Eggshell Aquavelvet Ultra Base	319 4B	Magenta	1	C-80300
	Benjamin Moore	SuperSpec Interior Latex Eggshell Finish	C274-1B Base Pastel	Blue	1	C-80301
	McCloskey	Suede Impressions Premium Acrylic Wall Finish	6400 Tinting Base	Brown	1	C-80302
	Benjamin Moore	Super Spec Premium Letex Interior Flat	pastel Base 275 1B	Cream	1	C-80303
	Benjamin Moore	Eggshell Aquavelvet Medium Base	319 2B	Brown	1	C-80306
	Lowes	Valspar Base 4 94101	1003-3A Purple	Violet	1	C-80464
	Lowes	Valspar Base 4 94101	6007-6A New	Yellow	1	C-80465
	Lowes	Valspar Base 4 94101	1008-9A Smoky	Brown	1	C-80466
	Valspar	Signature Series Brushed Suede Finish		Orange	2	C-80540
	Behr	Ultra Flat Sample		Yellow	2	C-80541
	Behr	Premium Plus Ultra Interior Semi-Gloss		Orange	2	C-80542
	Sherwin-Williams	Interior Latex Eggshell - Promar 200		Yellow	2	C-80543
	Behr	Self-Priming Interior Satin Enamel		Green	2	C-80544
		Automotive				
2006	Buick	Rendezevous		Brown	3	C-80048

Paint Sample Information

Field Sample - Paint - Automotive

Year	Make	Model	Color Code	Nominal Color	Q.I.	MT Ascension Number
2012	Hyundai	Elantra		Silver	3	C-80049
2007	Toyota	RAV4	040	White	2	C-80050
2005	Toyota	RAV4	8M6	Blue	2	C-80051
	GMC	Terrain		Red	4	C-80052
2009	Toyota	Camry	202	Black	2	C-80053
2001	Ford	Escape XLT	LD or M6763A	Grey	3	C-80054
2009	Toyota	Camry Hybrid	3R3	Red	2	C-80055
2001	Honda	CR-V Ex	R81	Red	2	C-80056
1999	Plymouth	Voyager	PG2	Brown	1	C-80057
1995	Mercury	Villager	DK	Silver	1	C-80058
2000	Ford	Focus SE	FL	Red	1	C-80059
2002	Buick	LeSabre Custom		Brown	3	C-80060
2003	Pontiac	Sunfire Coupe	WA8555/41	Black	2	C-80061
2000	Saturn	SL SL1	WA9554/75	Red	2	C-80062
2011	Subaru	Legacy 2.5i	E6F	Blue	1	C-80063
2000	Pontiac	Grand Prix	WA526F	Red	1	C-80064
1999	Infiniti	I30	CR0	Gold	1	C-80065
2005	Cadillac	CTS	816K	Green	1	C-80066
2007	Toyota	Camry Hybrid	3R3	Red	2	C-80067
1997	Jeep	Grand Cherokee	PR4	Red	1	C-80068
2007	Toyota	RAV4	1F7 - Silver	Silver	1	C-80069
2003	Chevrolet	Trailblazer	382E	Brown	1	C-80070
1997	Pontiac	Grand Prix	8774 - Red	Red	1	C-80071
2011	Toyota	Sienna	6T7 - Green	Green	1	C-80072
2006	Dodge	Caravan	PBE - Blue	Blue	1	C-80073

Paint Sample Information

Field Sample - Paint - Automotive

Year	Make	Model	Color Code	Nominal Color	Q.I.	MT Ascension Number
2011	Jeep	Compass	PDM - Green	Green	1	C-80074
1998	Dodge	Dakota	PX8	Black	2	C-80075
2004	Jeep	Liberty	PR4 / AY110PR4	Red	2	C-80076
2002	Hyundai	Elantra		Silver	3	C-80077
2007	Chevrolet	Traverse		Black	3	C-80078
2005	Pontiac			Black	4	C-80079
2011	Mazda			Blue	4	C-80080
2007	Toyota	Yaris	1E7	Silver	1	C-80081
2011	Chevrolet	Impala	301N	Red	1	C-80082
1989	Toyota	Camry		Blue	3	C-80083
1988	Honda	Accord		Red	3	C-80084
1987	Nissan			Red	4	C-80085
1993	Honda	Accord		Green	3	C-80086
1992	Nissan	Sentra	549	Black	2	C-80087
1992	Volkswagon			Green	4	C-80088
1985	Honda	Prelude	R51	Red	2	C-80089
2000	Ford	Focus	TS	Silver	2	C-80210
2005	Honda	Accord	NH578	White	1	C-80211
2008	BMW	328xi	475	Black	1	C-80212
2007	Honda	Accord	89ZPA	Black	1	C-80213
2008	Ford	Focus	2Y	Grey	1	C-80214
2006	Honda	Civic	NH700M	Silver	1	C-80215
2011	Audi	Q5	LX7W	Silver	1	C-80216
2008	Pontiac	Grand Prix	301N	Red	1	C-80217
2011	Nissan	Rogue	NAH	Red	1	C-80218

Paint Sample Information

Field Sample - Paint - Automotive

Year	Make	Model	Color Code	Nominal Color	Q.I.	MT Ascension Number
2006	Volkswagen	Jetta		Blue	3	C-80219
2002	Hyundai	Sonata	AR	Red	2	C-80220
2003	Saturn	L200	89/854J/WA854J	Blue	2	C-80221
1998	Jeep	Wrangler	PQ7/AY97TQ7	Blue	2	C-80222
2002	Mitsubishi	Eclipse	R70/AC11270	Red	2	C-80223
2001	Toyota	Camry	40/8554/WA8554	White	2	C-80224
2005	Saturn	Ion	63/817K/WA817K	Red	2	C-80225
2010	Chevrolet	Cobalt	WA9260	Red	1	C-80226
2010	Chevrolet	Colorado	WA726S	Brown	1	C-80227
1998	Saab	900 Talladega	8555/770/170B	Black	2	C-80228
	Toyota			Brown	4	C-80260
	Chevrolet	Cobalt		Silver	4	C-80261
	Honda	Civic		Blue	4	C-80262
	Mercedes			Red	4	C-80263
	Toyota	Camry		Grey	4	C-80264
	Toyota	Camry		Grey	4	C-80265
	Toyota			Brown	4	C-80266
	Mitsubishi	Eclipse		Black	4	C-80267
2002	Chevrolet	Tahoe	11	Brown	1	C-80268
2004	Dodge	Grand Caravan	PB8	Blue	1	C-80269
2008	Ford	Focus SE	ZY	Grey	1	C-80270
2004	GMC	Yukon Denali	63	Red	1	C-80271
2008	Chevrolet	Imapla lt	37	Blue	1	C-80272
2004	Ford	F150	LD	Blue	1	C-80273
2009	Chevrolet	HHR LT	51	Gold	1	C-80274

Paint Sample Information

Field Sample - Paint - Automotive

Year	Make	Model	Color Code	Nominal Color	Q.I.	MT Ascension Number
2006	Chevrolet	HHR LT	67	Silver	1	C-80275
2005	Volkswagon	New Beetle	L43D/G2	Red	1	C-80276
2005	Dodge	Stratus SXT	PRH	Red	1	C-80277
2000	Toyota	Sienna	6M3	Green	1	C-80278
2005	Nissan	Armada	K12	Silver	1	C-80279
2003	Acura	MDX	B518P	Blue	1	C-80280
	Toyota	Camry		Gold	4	C-80281
	Jeep	Cherokee		Gold	4	C-80282
	Mercedes	Benz		Black	4	C-80283
	GMC	Acadia		Grey	4	C-80284
	Toyota	Camry		Blue	4	C-80285
	Honda	Pilot		Blue	4	C-80286
	Mitsubishi	Eclipse		Silver	4	C-80287
	Chevrolet	Suburban		Green	4	C-80288
	Chevrolet	Suburban		Black	4	C-80289
	Toyota	Camry		White	4	C-80290
	BMW			Silver	4	C-80291
	Mercedes			Brown	4	C-80292
	Chevrolet			Black	4	C-80293
	Mercedes			Silver	4	C-80294
	Unknown			Red	5	C-80295
2007	Mitsubishi	Outlander	A39	Grey	1	C-80296
2004	Dodge	Stratus Sxt	PJR	Green	1	C-80297
2001	Honda	Accord	NH 623 M	Silver	1	C-80311
2003	Pontiac	Grand Prix	WA 519F	Silver	1	C-80312

Year	Make	Model	Color Code	Nominal Color	Q.I.	MT Ascension Number
1996	Mercury	Cougar	DZ	Cream	1	C-80313
2011	Nissan	Rogue	LAE	Violet	1	C-80314
2009	Chevrolet	HHR	636R	Silver	1	C-80315
2006	Ford	Focus	CX	Blue	1	C-80316
2001	Acura	MDX	YR530P-4	Black	1	C-80317
2006	Chevrolet	Impala	994L	Silver	1	C-80318
2008	Scion	TC	130	Grey	1	C-80319
2010	Chevrolet	Equinox	686H	White	1	C-80320
1997	BMW	318i	297	Blue	1	C-80321
2006	Nissan	Sentra	B14	Blue	1	C-80322
2006	Scion	XB	8P8	Blue	1	C-80323
2010	Mitsubishi	Galant	W55C	White	1	C-80324
1998	Dodge	Caravan	PPJ	Green	1	C-80325
2010	Ford	Focus	UJ	Grey	1	C-80326
2003	Toyota	RAV4	1D4	Silver	1	C-80327
2010	Hyundai	Elantra	NKA	Black	1	C-80328
2006	Lincoln	Zephyr	T7	Grey	1	C-80329
2001	Honda	Civic	G-95-P-4	Green	1	C-80330
2006	Chrysler	Pacifica	PB8	Blue	1	C-80331
2001	Toyota	Sienna	8L9	Blue	1	C-80332
2003	Ford	Escape	CX/M7039	Grey	2	C-80333
2004	Honda	Pilot	B92P	Black	2	C-80334
	GMC	G20		Red	4	C-80335
2003	Nissan	Frontier SE-V6		Blue	3	C-80336
	Ford	F250		White	4	C-80337

Paint Sample Information

Field Sample - Paint - Automotive

Year	Make	Model	Color Code	Nominal Color	Q.I.	MT Ascension Number
2004	Chevrolet	Avalanche	WA913L / 56	Orange	2	C-80338
1999	Honda	Civic	NH583M	Silver	1	C-80339
	Toyota	Camry		White	4	C-80340
2006	Chrysler	300	PS2	Silver	2	C-80341
2002	Ford	Focus	E4/M3470A	Red	2	C-80342
2008	Scion	TC	1E0, 001	Grey	2	C-80343
2002	Honda	Odyssey	NH623M	White	1	C-80344
	Nissan	Versa	KH3	Black	1	C-80345
2002	Toyota	Camry		Silver	3	C-80346
2004	Chrysler	Crossfire	960	White	2	C-80347
2009	Toyota	Sienna	070	White	2	C-80348
2007	Honda	Accord		Silver	3	C-80349
2008	Mercedes	Z350		Grey	3	C-80350
2009	Nissan	Sentra	KH3	Black	1	C-80351
2010	Honda	Civic	B537M	Blue	1	C-80352
2005	Nissan	Armada	K12	Silver	1	C-80353
2011	Hyundai	Sonata	WHC	White	1	C-80354
2009	Hyundai	Sonata	GP	Green	1	C-80355
2007	Chevrolet	HHR	994L	Silver	1	C-80356
2005	Cadillac	CTS	928L	Blue	1	C-80357
2009	Honda	Accord	NH731P	Black	1	C-80358
2003	Mitsubishi	Outlander	470	Grey	1	C-80359
2010	Ford	Fusion	UH	Black	1	C-80360
2001	Pontiac	Grand Prix GTP	41/WA8555	Black	1	C-80361
1997	Pontiac	Grand Prix GT	81/WA8774	Red	1	C-80362

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Year	Make	Model	Color Code	Nominal Color	Q.I.	MT Ascension Number
2007	Chevrolet	Avalanche	51/WA316N	Grey	1	C-80363
2009	Hyundai	Sonata	DS	Grey	1	C-80364
2000	Audi	A4	LY7W/5B	Silver	1	C-80365
2003	Nissan	Altima	KY2	Brown	1	C-80366
2011	Toyota	Sienna	1H1	Grey	1	C-80367
2002	Dodge	Caravan	PKJ	Gold	1	C-80368
2009	Toyota	RAV4	1F7	Silver	1	C-80369
2009	Nissan	Rogue	QX1	White	1	C-80370
2003	Jeep	Grand Cherokee	AY97XRV, PRV	Red	2	C-80371
1999	Ford	Windstar	FY	Green	2	C-80372
2009	Toyota	Camry	776	Green	2	C-80373
2008	Chevrolet	Silverado	8624	White	1	C-80374
2001	Jeep	Grand Cherokee	PW1	White	1	C-80375
2008	Chevrolet	Silverado	8624	White	1	C-80376
2008	Chevrolet	Silverado	8624	White	1	C-80377
2009	GMC	Sierra 1500	46/428L/928L/WA428	Blue	2	C-80378
2004	Pontiac	Grand Am	5322	Gold	1	C-80379
1999	Lexus	ES 300	1B2	Silver	2	C-80380
1999	Lexus	ES 300	1B2	Cream	1	C-80381
2011	Jeep	Grand Cherokee	PXR	Black	1	C-80382
2008	Jeep	Compass	PJC	Gold	1	C-80383
2005	Dodge	Neon	PX8	Black	1	C-80384
2007	Toyota	RAV4	8S6	Blue	1	C-80385
2011	Ford	Edge	L6	Blue	1	C-80386
2000	Saturn	LS1	110E	Violet	1	C-80387

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Year	Make	Model	Color Code	Nominal Color	Q.I.	MT Ascension Number
2006	Pontiac	G6	WA8554	White	1	C-80388
2011	Buick	Lacrosse	WA 800J	White	1	C-80389
2007	Buick	Lucerne	WA204M	Red	1	C-80390
2002	Acura	MDX	NH-638M-4	Silver	1	C-80391
2011	GMC	Sierra	WA8555	Black	1	C-80392
2002	GMC	Yukon	WA526F	Red	1	C-80393
2011	Ford	Fusion	WS	White	1	C-80394
2010	Dodge	Grand Caravan SXT	PRP	Red	2	C-80395
1997	GMC	Savana G3500	9225	White	2	C-80396
2005	Chrysler	Town & Country		Red	3	C-80397
2007	Toyota	Prius	3R3	Red	2	C-80398
2008	Hyundai	Azera	Y5	Silver	2	C-80399
2008	Honda	CRV	B536P	Blue	1	C-80400
2001	Mercedes	CLK 55 AMG	040	Black	1	C-80401
2005	Chevrolet	Silverado	9539	Green	1	C-80402
2009	Toyota	RAV4	202	Black	1	C-80403
2005	Mazda	3	29Y	Grey	1	C-80404
2002	Ford	Taurus	M6985	Brown	1	C-80405
2003	Ford	Windstar	WT	White	1	C-80406
2007	Toyota	Camry	1G3	Grey	1	C-80407
2011	Honda	Civic	B537M	Blue	1	C-80408
2009	Ford	Fusion	D2	Green	1	C-80409
2002	Dodge	Caravan	PKJ	Gold	1	C-80410
2006	Mitsubishi	Galant ES	A33	Silver	1	C-80411
1999	BMW	3 Series		Red	4	C-80412

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Year	Make	Model	Color Code	Nominal Color	Q.I.	MT Ascension Number
	Nissan	Altima	KH3	White	2	C-80413
	Toyota	Sienna	040	Black	2	C-80414
	Chevrolet	Trailblazer		Gold	4	C-80415
2008	Honda	Accord EX Sedan AT	R530P	Red	2	C-80416
2006	Chevrolet	Trail Blazer	WA204M	Red	1	C-80417
1995	Cadillac	Deville	115A	Green	1	C-80418
2008	Ford	Focus SE	TS	Silver	1	C-80419
2005	Nissan	Altima S	C12	Gold	1	C-80420
2005	Dodge	Caravan	PXR	Black	1	C-80421
2002	Chrysler	Sebring	PW1	White	1	C-80422
2005	Honda	Civic	YR528M4	Gold	1	C-80423
2002	Saturn	L100	WA257C	Red	1	C-80424
2004	Pontiac	Grand Prix	WA817K	Red	1	C-80425
2004	GMC	Envoy	WA805K	Grey	1	C-80426
2010	Mitsubishi	Lancer	A31	Silver	1	C-80427
2002	Jeep	Liberty	PB7	Blue	1	C-80428
2006	Chrysler	Town & Country	PXR	Black	1	C-80429
2004	Chevrolet	Monte Carlo Supercharged SS	WA8555	Black	1	C-80430
2003	Ford	Escape	G2	Red	1	C-80431
2006	Ford	Expedition	JP	Silver	1	C-80432
2008	Chevrolet	Equinox	23, 563Q, GBX,	Blue	1	C-80433
2011	Ford	Escape XLT	SZ	Blue	1	C-80434
2011	Lincoln	MKZ	UJ	Grey	1	C-80435
2011	Ford	Expedition	UG	White	1	C-80436
2004	Toyota	Seuoia	1D6	Silver	1	C-80437

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Year	Make	Model	Color Code	Nominal Color	Q.I.	MT Ascension Number
2001	Honda	Civic	YR525M	Gold	1	C-80438
2006	Ford	Focus	CX	Grey	1	C-80439
2003	Honda	Odyessey	B518P	Blue	1	C-80440
2008	Hyundai	Elantra	9F	Grey	1	C-80441
2002	Chevrolet	Cavalier	81, WA8774	Red	1	C-80442
2009	Toyota	Corola	4Q2	Gold	1	C-80443
2007	Pontiac	Grand Prix	994L	Silver	1	C-80444
2006	Buick	Lucerne	994L	Silver	1	C-80445
2009	Honda	Fit	B548P	Blue	1	C-80446
1998	BMW	528i	309	Silver	1	C-80447
2004	Chevrolet	Malibu	92, 816K, WA816K	Green	1	C-80448
2011	Acura	MDX	NH743M	Silver	1	C-80449
2011	Ford	Focus	JV	Red	1	C-80450
2006	Toyota	Highlander	202	Black	1	C-80451
2004	Jeep	Grand Cherokee	PW1	White	2	C-80452
2006	Chevrolet	Impala	50/8624/GAZ/WA8624	White	2	C-80453
2002	Toyota	Camry	6S7	Green	2	C-80454
2004	Toyota	Echo	068	White	2	C-80455
2009	Hyundai	Accent	3E	Blue	2	C-80456
2008	Kia	Sportage	9T	Grey	1	C-80457
2001	Mitsubishi	Eclipse		Black	3	C-80458
2008	Kia	Sportage	UD	White	1	C-80459
2005	Suzuki	XL7	ZA4	Gold	1	C-80460
2011	Honda	Pilot	B552P	Blue	2	C-80461
1996	Chevrolet	Cavalier		Green	3	C-80467

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Year	Make	Model	Color Code	Nominal Color	Q.I.	MT Ascension Number
1999	Chevrolet	Cavalier	41, 8555, WA8555	Black	2	C-80468
1999	Oldsmobile	Alero	81, 8774, WA8774	Red	2	C-80469
2009	Saturn	Vue	88, WA812K	Grey	1	C-80470
2003	Chevrolet	Corvette	21, 779J, WA779J	Blue	1	C-80471
2006	Honda	Odyssey	NH662P	Green	1	C-80472
2005	Suzuki	XL-7	Z2S	Silver	1	C-80473
2009	Chevrolet	Silverado	50/GAZ/8624/WA8624	Yellow	1	C-80474
2004	Pontiac	Grand Prix	41, WA8555	Black	1	C-80475
2010	Toyota	Yaris	1E0	Green	1	C-80476
2003	Honda	Pilot	YR542M4	Brown	1	C-80477
1996	Honda	Civic	G82P4	Green	1	C-80478
2010	Honda	Civic	NH578E	White	1	C-80479
2011	Honda	Odyssey	B564M	Blue	2	C-80480
2008	Saturn	Aura XE	58, 501Q, GAR,	Black	2	C-80481
1995	Chevrolet	Camaro	81, 8774, WA8774	Red	2	C-80482
2005	Jeep	Liberty Limited	PB7, AY112WB7	Blue	2	C-80483
	Volkswagen	Tiguan		Silver	4	C-80484
2010	Chrysler	Sebring Sedan Limited	PS2	Silver	2	C-80485
	Toyota	4-Runner		Grey	4	C-80486
	Jeep	Grand Cherokee		Brown	4	C-80487
	Toyota	Prius		Silver	4	C-80488
	Lexus	RX330		Silver	4	C-80489
	Chevrolet	Cruz		Blue	4	C-80490
2010	Honda	CRV	YR578M	Brown	2	C-80491
2003	Honda	Civic	B96P, DG758	Blue	2	C-80492

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Year	Make	Model	Color Code	Nominal Color	Q.I.	MT Ascension Number
1996	Volvo	850 GLT		Black	3	C-80493
2003	Pontiac	Grand Prix GT	9260	Red	1	C-80500
2004	Chevrolet	Cavalier	9260	Red	1	C-80501
2005	Dodge	Durango	PDM	Grey	1	C-80502
2004	Ford	Explorer Sportrac	P5	Green	1	C-80503
2005	Hyundai	XG350	AR	Cream	1	C-80504
2006	Nissan	Altima	KY1	Silver	1	C-80505
1998	Mercury	Grand Marquis	TS	Silver	1	C-80506
1997	Lexus	ES300	051	White	1	C-80507
2008	Honda	Accord	NH737MX	Grey	1	C-80508
2009	Chrysler	Sebring	PXR	Black	1	C-80509
2005	Saturn	Vue	74/GCN/WA9260/926	Black	1	C-80514
2006	Infiniti	QX56	G10	Black	1	C-80515
2008	Buick	Lacrosse	37	Blue	1	C-80516
2012	Ford	Fusion	HT	Brown	1	C-80517
2008	Scion	TC	209	Black	1	C-80518
2011	Chevrolet	Traverse	WA800J	White	1	C-80519
2007	Ford	Focus	TS	Black	1	C-80523
2006	Ford	Escape	DV	Green	1	C-80524
2007	Ford	Explorer Sport Trac	JP	Silver	1	C-80525
2007	Jeep	Compass	PS2	Silver	1	C-80526
2004	Toyota	Corolla	8P4	Blue	1	C-80527
2006	Dodge	Durango	PW7	White	1	C-80528
1999	Ford	Explorer	B2	Gold	1	C-80529