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Final Research Report

Report Title: Application of Raman and Infrared Microscopy for the Forensic Examination of Automotive Clear Coats and Paint Smears

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Purpose of the Project

Modern automotive paints consist of a thin e-coat, primer, and color coat layer protected by a thicker clear coat layer. All too often, a clear coat is the only layer of automotive paint recovered at the crime scene of a "hit-and-run" where damage to a vehicle and/or injury or death to a pedestrian has occurred. However, clear coat formulations are too similar for commercial library search algorithms to generate accurate hit-lists of potential suspect vehicles by searching clear coat infrared (IR) spectra alone. The inability of Fourier transform infrared (FTIR) spectroscopy and the PDQ database to identify a vehicle from the clear coat layer alone using the text base searching system of PDQ or standard spectral search algorithms is a significant limitation in the use of FTIR spectroscopy and forensic automotive paint databases such as PDQ to obtain information about the model and the production year of the vehicle from an automotive paint sample. Recently published studies of pattern recognition methods applied to the IR spectra of clear coats [1-5] have shown that information about the line and model of the vehicle can be obtained from these spectra. To further enhance the general discrimination power of clear coats, Raman spectroscopy has been investigated as an alternative solution to the problem of extracting investigative lead information from automotive clear coats. The complementary nature of Raman and IR spectroscopy and the importance of IR spectroscopy in forensic automotive paint analysis

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suggest that Raman spectroscopy will also have the potential to extract investigative lead information from the clear coat layer of an automotive paint.

A second aim of this research project is the development of procedures to generate automotive paint smears (e.g., clear coat and color coat layers mixed together or clear coat, color coat, surfacer-primer, and e-coat layers mixed together). Realistic paint smears are difficult to create in the laboratory and have also proven challenging to analyze because of the mixing of the various automotive paint layers. To this end, an impactor has been designed and constructed for transferring a paint smear from an automotive sample to any surface of interest under conditions emulating a real car collision. The design involves the collision of two wedge-shaped steel blocks. An automotive paint sample containing all four layers is fixed on the lower wedge, while the paint-transfer substrate is fixed on the upper wedge. The impactor (because of its small foot print) can be operated in a laboratory as it is approximately 1 m in height with a metal base of 22 kg.

Product Design and Methods

Collection of Raman Spectra. Raman spectra of clear coats were obtained from metal or plastic substrates of General Motors (GM) vehicles manufactured at twenty-five assembly plants in North America (Arlington, Doraville, Fairfax, Moraine, Lansing, Ramos Arizpe, Ft. Wayne, Pontiac, Silao, Oshawa, Orion, Flint, Lordstown, Linden, Ingersoll, Oklahoma City, Janesville, St. Therese, Spring Hill, Baltimore, Fremont, Hamtramck, Lafayette, Shreveport, and Wilmington). The paint samples used in this study were provided by the RCMP and were either factory panels or street samples. Prior to sectioning each automotive paint sample, the outermost layer (i.e., the clear coat layer) was cleaned with methanol to remove dirt and oil. The clear coat layer was carefully scraped off the metal substrate using a blade under a stereo microscope. The sample was then transferred onto a glass microscope slide wrapped with aluminum foil.

Raman spectra of the clear coat layer were collected using a WITec alpha300 R confocal micro Raman spectrophotometer equipped with a 532nm ND: YAG laser and an 1800 lines/mm^{-1} grating. The ND: YAG laser, which was run at 10 or 40 mW, was focused on the paint sample using an objective lens of 20X. The integration time was 10s (for 40 mW laser power) or 30s (for 10 mW laser power), and the number of spectra accumulated was 20 (for 40 mW laser power) or 10 (for 10 mW laser power). For each paint sample, the laser was focused by moving the objective lens up and down until a clear image of the clear coat sample was observed on the screen of the computer used to collect the data. The spectra were collected at five different locations on the sample to obtain representative spectra. As Raman is sensitive to fluorescence, photo-bleaching was used to reduce the fluorescence background in samples that exhibited fluorescence due to the presence of a small amount of the color coat layer that was mixed with the peels of the clear coat layer. The fluorophore in the sample was saturated using a 40mW laser irradiation of the paint sample for five minutes to reduce the baseline followed by collection of Raman spectra at the same site. If peak shifting occurred in the Raman spectra, the sample was reanalyzed at a lower laser power, e.g., 10mW.

The spectral discrimination problem posed in this study was intentionally challenging as the samples evaluated were all from the same manufacturer within a limited production year range (2000 – 2012). Using this set of clear coats helped to address many of the deficiencies of the experimental design used by previous workers [6] to assess the potential of Raman spectroscopy to extract investigative lead information from automotive clear coats. For example, many of the replicate spectra of the same clear coat were included in both the training and validation set and several automotive classes were represented by fewer than four clear coat samples. The large number of manufacturers (many of which were from different countries of origin), the automotive

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models surveyed and the small size of the data set used raised questions about the conclusions drawn by these authors.

Generation of Automotive Paint Smears. Automotive paint smear samples were generated by using a small footprint collider designed and constructed for transferring paint smears from an automotive paint sample to a steel substrate under conditions emulating an actual collision. The automotive paint sample was cleaned with methanol to remove any dirt or oil. The automotive paint sample was then mounted on the upper wedge i.e. a rounded stainless steel stage/base of which the sample is wrapped/covered by bending while the paint-transfer substrate is mounted on the lower wedge. The upper wedge was released from a set height and accelerated by gravity prior to collision with the lower wedge. It slides vertically on the guiding rods, but it transfers both vertical and horizontal momentum to the lower wedge upon collision, because the collision surfaces, or wedge surfaces are at 45$^\mathrm{o}$ to the horizontal/vertical. Upon collision, energy and momentum is transferred to the lower wedge, as it is allowed to translate vertically and horizontally on a rail guide. As a result, the lower wedge surface also slides against the upper wedge surface which creates friction. This frictional work is responsible for transfer of the paint, generating the paint smear.

Automotive paint smears generated were then analyzed with a Nicolet iN10-MX FTIR microscope equipped with an XYZ motorized sample stage and a Ge-tip ATR (tip diameter about 100 μm) as well as a mercury cadmium telluride (MCT) detector. The Ge-tip ATR and 150 x 150 micron aperture of the Nicolet iN10-MX microscope yielded an effective spatial resolution of 37.5 microns. The visual images were acquired using built-in camera of the Nicolet iN10-MX system. The target area was centered in the cross hairs and the aperture, and the Ge-tip ATR was inserted. A background spectrum of the clean ATR crystal (not in contact with the sample) was acquired

using the Thermo Scientific^{TM} OMNIC Picta^{TM} preview-mode spectroscopy software. Using the OMNIC Picta^{TM} preview mode, the microscope stage was slowly raised. The appearance of the spectrum and color change in the LED pressure indicator provided confirmation of the readiness for the data collection. The spectral acquisition was carried out using the Thermo Scientific ^{TM} OMNIC Picta^{TM} spectroscopy software. Each spectrum was the result of an average of 128 scans at 4 cm^{-1} resolution over a spectral range of 4000-675 cm^{-1}. The applied pressure was 15 psi.

Data Analysis

Analysis of Raman Spectra. OMNIC was used to transfer the raw data (txt files) into CSV files. Each CSV file was read into MATLAB and preprocessed for pattern recognition analysis using the PLS toolbox. The Whittaker filter was applied to each Raman spectrum for baseline correction, and smoothed using a Savitzky Golay filter followed by mean scatter correction to reduce noise. All Raman spectra were normalized to unit length and preprocessed using the discrete wavelet transform [7, 8] to enhance subtle but significant features in the Raman spectra. The Symlet mother wavelet (sixth smallest filter size, eighth level of decomposition) was chosen for preprocessing because the shape of its scaling function closely matched that of the shape of the band comprising the Raman spectra of the automotive paints. The wavelet transformed spectra were autoscaled to ensure that each coefficient has a mean of zero and a standard deviation of one throughout the entire set of transformed spectra. Autoscaling removed any inadvertent weighing of the data that otherwise would occur due to differences in magnitude among the wavelet coefficients comprising the spectral data. Applying a genetic algorithm for pattern recognition [9, 10], wavelet coefficients were identified that were characteristic of the assembly plant of the vehicle from which the clear coat layer originated. Enhancing the discrimination between spectra using wavelets for preprocessing and the pattern recognition GA to identify informative coefficients will permit more effective inter-comparisons of OEM clear coats.

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Analysis of Paint Smears. Paint smears containing one, two, three, or four distinct layers were identified when the transfer substrate was examined using an attenuated total reflection (ATR) infrared microscope. In many OEM paint samples, each layer was found in a separate region of the transfer substrate, which was visible using ATR infrared microscopy, but not with transmission infrared microscopy. For each sample, the IR spectra from the entire image generated using the ATR microscope was baseline corrected using MATLAB code developed in-house and smoothed u   sing OMNIC. The IR spectrum of each layer of the paint smear was then reconstructed using alternating least squares [11]. Our previous experience with ALS has shown that initial estimates of the concentration (score) or spectral (loading) matrices are crucial for rotating these two matrices towards a correct solution. For this reason, a varimax extended rotation that was used in previous studies [12, 13] to reconstruct transmission IR spectra obtained from line maps of IR spectral images of cross sectioned automotive paint samples was applied to spectra in the region of the transfer substrate that contained transferred paint. The spectral region used for decatenation was $4000cm^{-1}$ - $748cm^{-1}$. All library searches of the ALS reconstructed IR spectra against an in-house automotive paint infrared transmission spectral database was restricted to the region between 1641 and 860 cm^{-1} which has been shown to contain information about the manufacturer, line and model of the vehicle [4]. Outside of the fingerprint region, each IR spectrum contained only the carbonyl band and C-H stretching bands which are present in all IR spectra of OEM paint layers. For this study, it was necessary to convert the transmission spectra from the in-house spectral library to ATR spectra using an ATR spectral simulation algorithm developed in a previous study [14].

Project Findings

Raman Spectra of Clear Coats. 2216 Raman spectra of General Motors automotive paint clear coats were collected using a WITec alpha300 R confocal micro-Raman system. The Raman

spectra were analyzed in quintuplicates, quadruplicate or triplicates. The paint samples were from 23 assembly plants and spanned the production year range 2000-2012. There were a large number of lines and models represented in the data cohort. For pattern recognition analysis, our efforts were focused on the clear coats from Arlington, Doraville, Fairfax, Fort Wayne, Lansing, and Moraine assembly plants as our previous published studies had underscored the difficulty of this spectral discrimination problem. Binary classification studies were performed (e.g., one assembly plant versus the other five assembly plants) for each of the six assembly plants using the Raman spectra or the corresponding IR spectra of the clear coats. These binary classification studies demonstrated that all six assembly plants could be discriminated on the basis of their clear coat Raman spectra, whereas only clear coats from Moraine could be discriminated on the basis of their IR spectra. Given the challenging nature of this task, these results constitutes direct evidence of the potential advantages of Raman for forensic automotive paint analysis.

Paint Smears. Automotive paint smears consisting of the different paint layers were generated from OEM paint samples by the impactor at various levels of elastic force and damping. The collision parameters were controlled using replaceable springs at two different levels of stiffness and by changing the damping level (1 to 8) of the shock absorbers. The paint smears generated from the OEM paint sample onto the transfer substrate were analyzed with a Nicolet iN10-MX FTIR microscope equipped with an XYZ motorized sample stage, a Ge-tip ATR (tip diameter about 100 µm) and a mercury cadmium telluride (MCT) detector. Paint smears were generated from thirty General Motors automotive paint samples that represented a variety of paint chemistries. These samples were provided by the RCMP. For most of the automotive paint samples, only the clear coat layer was found in the paint smear when a soft spring was used to simulate the collision. When a hard spring was used and the damping factor was varied between 1

and 8, one could tune the number of paint layers discernable in the smear. The threshold value for the damping factor to produce specific paint layers was not fixed but appeared to be related to the specific automotive paint sample investigated and the corresponding chemistry of the manufacturer's paint system represented by this sample. The exception was UAZP00494 which produced a smear consisting of four distinct layers for both hard and soft spring configurations of the impactor. Evidently, this specific General Motors paint system does not adhere strongly to the surface of the automotive substrate. Paint smears containing one, two, three or four distinct layers could be identified using the infrared microscope and ALS. The IR spectrum of each layer generally compared well to corresponding spectrum of the same sample. For the topcoat layers, the matches against our in-house paint library for the clear coat was usually a first or second hits with the HQI value for a specific match often exceeding 97%. Performing a library search using our in-house General Motors paint library for the undercoat layers was more challenging as some matches were neither top five hit nor were their HQI values greater than 90%. This is due in all likelihood to the heat generated at transfer substrate and the resulting changes in the structure of the polymer comprising each of these layers.

Pattern recognition was applied to the IR spectra of the smears that contained all four paint layers. A discriminant (search prefilter) to identify the automotive manufacturer was applied to the wavelet transformed reconstructed IR spectra of the recovered OT2, OU1, and OU2 paint layers. Of these seven paint smears, five were correctly identified by manufacturer. As for the other two paint smears, the HQI value of each of their undercoat layers was low (90% or less). Furthermore, visual examination of their ALS reconstructed spectra showed noise and absorption bands which were not present in the original intact paint samples. For one sample, there appears to be mixing of OT1 in the reconstructed OU1 spectrum. As for the other sample, the reconstructed OU2 layer

does not fully resemble the OU2 layer of the original sample suggesting that changes in this paint sample may have occurred because of heat generated during the collision as simulated by the impactor.

Potential Impact

The research project described in this final summary overview is directly targeted to the development of new approaches for the forensic examination of automotive clear coats and paint smears as well as aid in evidential significance assessment, both at the investigative lead stage and at the court room testimony stage. Direct impact on over 57 local, state, and federal forensic laboratories in the United States that are currently using the PDQ database is anticipated. There will also be impact on international forensic laboratories using the PDQ database including the Forensic Laboratory Services Division of the RCMP, the Centre of Forensic Science in Toronto, Canada, the ENFSI network of European forensic science institutes, the Australian Police Services, and the New Zealand Public Services. As of 2014, the Bundeskriminalamt (BKA) has started a European Automotive Paint Collection to analyze automotive clear coats by Raman spectroscopy. Currently, the BKA is in the process of collecting Raman spectra. The advantage of using Raman spectroscopy to analyze clear coats is expected to promote interest on the part of the BKA to analyze their spectral data once this work is published.

The research described in this overview is an international collaborative effort between the Lavine research group at Oklahoma State University (OSU) and Mark Sandercock and Kimberly Kenny of the Royal Canadian Mounted Police (RCMP). Pioneering studies performed by the Lavine research group at OSU and Mark Sandercock of the RCMP on Chrysler and General Motors clear coats in a very narrow production year range have demonstrated the advantages of using pattern recognition techniques to extract investigative lead information from IR spectra of clear coats, which all too often is the only layer of paint left at the crime scene. The methodology

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developed in this research project represents an improvement over the way clear coats and paint smears are currently handled by forensic paint examiners. This in turn will allow the forensic scientists to quantify further the general discrimination power of automotive paint comparisons of OEM paint samples encountered in actual casework and improve the forensic scientist's ability to succinctly communicate trace evidence to the courts.

Publications

1. K. S. Dahal, F. Kwofie, H. Zhong, K. Kalkan, and B. K. Lavine, "Application of Raman Spectroscopy to the Forensic Examination of Automotive Clear Coats," Talanta, in preparation.

2. G. Affadu-Danful, L. Zhang, K. S. Dahal, K. Kalkan, and B. K. Lavine, "Analysis of Automotive Paint Smears Using Attenuated Total Reflection Infrared Microscopy," Talanta, in preparation.

3. U. D. N. T. Perera, K. Kalkan, and B. K. Lavine, "Preparation of Automotive Paint Smears Using a Charpy Impact Tester," Forensic Chemistry, in preparation.

Dissemination Activities

1. B. K. Lavine, G. Affadu-Danful, H. Zhong, K. Kalkan, K. S. Dahal, and F. Kwofie, "Forensic Automotive Paint Analysis of Automotive Clear Coats and Paint Smears Using Infrared and Raman Spectroscopy," ACS National Meeting, San Diego, CA, March 20-24 2022, in preparation.

2. B. K. Lavine, G. Affadu-Danful, H. Zhong, K. Kalkan, and K. S. Dahal, "Raman Spectroscopy to Enhance Investigative Lead Information for Automotive Clearcoats," *2021 Online Forensic Symposium on Current Trends in Forensic Trace Analysis*," July 26-30, 2021.

3. B. K. Lavine, G. Affadu-Danful, H. Zhong, K. Kalkan, "Infrared Attenuated Total Reflection Microscopic Analysis of Simulated Automotive Paint Smears for Vehicle-Vehicle Hit-and-Run Collisions," *2021 Online Forensic Symposium on Current Trends in Forensic Trace Analysis*," July 26-30, 2021.

References

1. Barry K. Lavine, Nikhil Mirjankar, Scott Ryland, and Mark Sandercock, "Wavelets and Genetic Algorithms Applied to Search Prefilters for Spectral Library Matching in Forensics," Talanta**,** 2011, 87, 46-52.

2. B. K. Lavine, A. Fasasi, N. Mirjankar, and M. Sandercock, "Development of Search Prefilters for Infrared Library Searching of Clear Coat Paint Smears," Talanta, 2014, 119, 331–340.

3. B. K. Lavine, A. Fasasi, N. Mirjankar, and M. Sandercock, "Development of Search Prefilters for Infrared Library Searching of Clear Coat Paint Smears," Talanta, 2014, 119, 331–340.

4. B. K. Lavine, A. Fasasi, N. Mirjankar, and C. White, "Search Prefilters for Library Matching of Infrared Spectra in the PDQ Database using the Autocorrelation Transformation," Microchem. J**.**, 2014, 113, 30–35.

5. B. K. Lavine, A. Fasasi, N. Mirjankar, K. Nishikida, and J. Campbell, "Simulation of Attenuated Total Reflection Infrared Absorbance Spectra – Applications to Forensic Analysis of Automotive Clearcoats," Appl. Spectros**.**, 2014, 68(5), 608-615.

6. M. Maric, W. van Bronswijk, K. Pitts, and S. W. Lewis, "Characterization and Classification of Automotive Clear Coats for Forensic Purposes," J. Raman Spec., 47(8), 948-955.

7. J. S. Walker, Primer on Wavelets and Their Scientific Applications, Chapman & Hall/CRC Press, Boca Raton, FL 1999.

8. F. Chau, Y. Liang, J. Gao, and X. Shao, Chemometrics – From Basics to Wavelet Transform, John Wiley & Sons, NY 2004.

9. B. K. Lavine and C. E. Davidson, "Multivariate Approaches to Classification Using Genetic Algorithms," in: Brown S, Tauler R, Walczak R (eds.) Comprehensive Chemometrics, 2009, 3, pp. 619-646, Oxford-Elsevier.

10. B. K. Lavine, K. Nuguru, and N. Mirjankar, "One Stop Shopping - Feature Selection, Classification, and Prediction in a Single Step," J. Chemom., 2011, 25, 116-129

11. S. C. Rutan, A. de Juan, and R. Tauler, "Introduction to Multivariate Curve Resolution" in Comprehensive Chemometrics, Elsevier, Amsterdam, 2009, Vol. 2, pp. 249-260.

12. F. Kwofie, U. D. N. Perera, M. D. Allen, and B. K. Lavine, "Transmission Infrared Imaging Microscopy and Multivariate Curve Resolution Applied to the Forensic Examination of Automotive Paints," Talanta, 2018, 186, 662-669.

13. F. Kwofie, U. D. N. Perera, M. D. Allen, and B. K. Lavine, "Application of Infrared Microscopy and Alternating Least Squares to the Forensic Analysis of Automotive Paint Chips," J. Chemom., 2021, 35(1), e3277 (12 pages).

14. B. K. Lavine, A. Fasasi, N. Mirjankar, K. Nishikida, and Jay Campbell, ""Simulation of Attenuated Total Reflection Infrared Absorbance Spectra – Applications to Forensic Analysis of Automotive Clearcoats," Appl. Spect., 2014, 68(5), 608-615.