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Final Summary Overview

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Purpose of the Project

Modern automotive paint systems consist of multiple layers of paint: a clear coat over a color coat, which in turn is over a surfacer-primer and e-coat layer. Since forensic laboratories analyze each layer of paint individually by FTIR, time must be spent to hand-section each layer and then present each separated layer to the spectrometer for analysis. Sampling too close to the boundary between adjacent layers can produce an IR spectrum that is a mixture of two layers. In the situation of searching an automotive paint data base, not having a “pure spectrum” of each layer prevents a forensic paint examiner from developing an accurate hit list of potential suspects. One way to minimize the time necessary for data collection is to collect IR data from all layers in a single analysis by scanning across the cross-sectioned layers of the paint sample using a FTIR microscope equipped with an imaging detector. Once the data has been collected, it can then undergo deconvolution using chemometrics to obtain a “pure” IR spectrum of each layer. This approach, not only eliminates the need to analyze each layer separately resulting in a considerable time savings, but can also ensure that the final spectrum of each layer is “pure” and not a mixture.

Project Design and Methods

Thirty-two automotive paint samples from six manufacturers (General Motors, Chrysler, Ford, Toyota, Nissan, and Honda) in a limited production year range (2000-2006) were obtained

from the RCMP. Each sample was removed from a metal substrate using a sharp knife, washed with methanol to remove dirt and particulate matter, and either embedded into a resin and sectioned by a microtome or sectioned without the use of embedding medium (Reichert-Jung 2050) to generate a thin cross-section which contained all four paint layers. Although several resins were investigated as embedding media in this project (including Tuffleye® Finish blue light – Wet A hook Technologies, Quick cure™ (Bob Smith Industries 5 min epoxy) and Embed-it™ Low viscosity epoxy kit (Polysciences®), Slow-cure™ (Bob Smith Industries) thirty minute epoxy was the resin selected for the embedding medium. The thirty minute epoxy resin and hardener mixture was poured into flat polyurethane embedding molds (BEEM®, Polysciences), and the paint sample was placed into the mold and oriented perpendicular to the bottom surface prior to polymerization of the epoxy. Paint samples in the thirty minute epoxy block were then placed in an oven at 60°C for ninety minutes to ensure total curing. After hardening, the epoxy block was removed from the mold and positioned in the microtome to ensure that a thin cross section (approximately 4 to 5 μm thick) cut by the microtome contained all four paint layers.

Each thin cross section was collected, placed on a barium fluoride disk, and examined for defects, which would appear as dirt or cracks and crevices in an otherwise smooth surface when examined under a Leica light microscope. For embedded paint samples, a portion of the barium fluoride disk covered with cured epoxy without sample was run for background at 4cm⁻¹ resolution before the image map of the embedded paint sample was obtained. Transmission IR image maps generated at 4cm⁻¹ resolution and attenuated total reflection image maps generated at 8cm⁻¹ resolution using an iN10 MX microscope (Thermo-Nicolet, Madison, WI) equipped with a liquid nitrogen cooled mercury cadmium telluride (MCT) single imaging detector were collected for each cross sectioned automotive paint sample. Both the aperture and step size of the single imaging

MCT detector (50 micron x 375 micron) have adjustable values. For the analysis of the automotive paint samples, a 20 micron aperture and 5 micron step size yielded the best results when the microscope was operated in transmission mode, whereas for ATR the best results were obtained using a 25 micron aperture and a 10 micron step size. For ATR imaging, it was necessary to locate the position of the paint sample using the linear array MCT detector prior to collecting the IR image of the automotive paint sample using the single imaging MCT detector.

For multivariate curve resolution (MCR), a line map was extracted from the IR image of each cross sectioned paint sample. To obtain a line map, a transit (line) was passed through an IR image map of each paint sample. All spectra in contact with the transit were extracted, and the resulting collection of spectra is referred to as a line map. The data for the line map was taken on an oblique transit in order to include all paint layers and as many spectra of each layer and of the mixed interfacial region between the layers. Because the spatial resolution of the imaging microscope in transmission mode (for example) is 25 microns, the likelihood of capturing spectra characteristic of the boundary between two layers using the set of criteria for defining the oblique transit is high as the thickness of the undercoat (e-coat and surfacer primer) layers are approximately 10 μm and 20 μm respectively and the clear coat layer is approximately 50 μm thick.

For MCR analysis, it is necessary for the data to have high signal to noise. For this reason, spectra were extracted from the line map and checked for artifacts that may have been a direct result of the extraction procedure used. Spectra with aberrant peak intensities were discarded and line maps comprised of spectra that exhibited signs of peak shifting were retaken. In addition, the region 700 cm^{-1} to 744 cm^{-1} was eliminated from spectra comprising the line map as data in this region was judged to be too noisy. The influence of CO_2 in the analysis was suppressed by directly

interpolating between 2280 and 2400 cm^{-1} . Automatic baseline correction was applied to all IR spectra in the line map prior to deconvolution by MCR.

Data Analysis

The IR spectrum of each layer of the automotive paint was reconstructed from the line map using the alternating least squares (ALS) algorithm [1] as the preprocessed raw spectra were either too noisy or were mixtures of the embedding material and the clear coat or e-coat layers or were mixtures of different paint layers. As each automotive paint sample is laminated, it is crucial to sample the layers in their actual order of presentation in the paint. For these reasons, ALS analysis was restricted to line maps.

Our previous experience with ALS has shown that initial estimates of the concentration (score) and spectral (loading) matrices are crucial for rotating these two matrices towards a correct solution. For this reason, a varimax extended rotation used in two previous studies [2, 3] to resolve severely overlapped liquid chromatographic peaks or deconvolute Raman images of oil in water emulsions was applied to the spectral line maps to compute the initial estimates of the concentration and spectral matrices for ALS. The spectral region for deconvolution of the IR spectra from each line map was 4000cm^{-1} - 748cm^{-1} . All library searches of IR spectra from the PDQ database performed in this study for the deconvoluted IR spectra were restricted to the spectral 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 the IR spectra of all paint layers.

Library searching of IR spectra from the PDQ database was performed using search prefilters (i.e., discriminants) to identify the vehicle manufacturer and assembly plant of the

vehicle from the reconstructed IR spectra of the clear coat, surfacer-primer and e-coat layers of the cross sectioned paint sample. To develop these search prefilters, the IR spectra were preprocessed using the discrete wavelet transform [5], which was applied to the fingerprint region of each layer to enhance subtle but significant features in the IR 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 bands comprising the IR spectra of the automotive paints. Three sets of wavelet coefficients, one for each layer, were concatenated (both approximation and detail coefficients) to form the sample pattern vectors used by the search prefilters. Wavelet coefficients characteristic of manufacturer or assembly plant were identified using a genetic algorithm for pattern recognition and feature selection [6]. 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. Search prefilters to identify automotive manufacturer [7] were developed using 1596 OEM paint systems from General Motors, Chrysler, Ford, Honda, Nissan, and Toyota within a limited production year range (2000-2006). Search prefilters for assembly plant [8-10] of a specific manufacturer were developed in a previously funded NIJ Project (2012-DN-BX-K059).

Project Findings

Initially, all cross sectioned paint samples were incorrectly classified by the library search prefilters for manufacturer and assembly plant when they were applied to the reconstructed IR spectra obtained from the transmission line maps. Almost all peaks in the reconstructed IR transmission spectra were shifted compared to the corresponding PDQ transmission spectra of the

same sample. The PDQ library consists of IR spectra collected by FTIR spectrometers, each equipped with a diamond cell. The diamond cell applies high pressure to the sample which causes shifts to occur in some IR bands due to a reduction in the free volume of the polymer [11]. For some peaks in the fingerprint region, these shifts are large ($\sim 3\text{cm}^{-1}$), whereas for others they are smaller ($\sim 0.3\text{cm}^{-1}$).

To solve this problem, IR transmission spectra from the PDQ library used to develop the search prefilters were converted into ATR spectra using an ATR simulation algorithm [12] developed in a previously funded NIJ research project (2012-DN-BX-K059). The ATR simulation algorithm, which was developed to convert transmission spectra from PDQ into ATR spectra, is able to compensate for most of these spectral shifts. The search prefilters were recomputed using the transformed IR spectral data, and the reconstructed IR spectra from the line maps were transformed to ATR spectra using the ATR simulation algorithm. The IR spectrum of each reconstructed paint layer was preprocessed in the same manner as the ATR spectra that comprised the training sets for the search prefilters. All thirty-two unembedded paint samples were then correctly classified as to the manufacturer, line, and model of the vehicle from which the paint sample originated.

This result is significant as there are clear advantages for cross sectioning paint samples without the use of embedding material in IR imaging. Sample preparation is faster and more straight-forward. Decatenation of the image data is also more straight-forward as spectral interference from the epoxy layer, which is a well-known problem among workers in IR and Raman microscopy, does not occur. Strict unimodality can be enforced in the mathematics of the decatenation process implemented in this study using ALS since there are no epoxy layers to model. (The epoxy is in contact with both the clear coat and e-coat layer as they are the outer- and

inner-most layers of the intact paint sample.) Third, library searches are also simplified as the number of components that need to be specified by the ALS algorithm are fewer and the accuracy of the reconstructed IR spectra for which the search is run is higher.

Only twenty-eight of the thirty-two original paint samples were analyzed using epoxy resin because there was an insufficient amount of sample remaining after analysis in transmission and ATR modes with unembedded paint samples. Of the twenty-eight embedded paint samples, twenty-two were correctly identified as to manufacturer and assembly plant using the search prefilters. Although improvements in baseline correction and restricting the MCR analysis to the fingerprint region improved the decatenation of the spectral line maps for these six samples, the problems encountered with these samples - the mixing of IR spectra of the epoxy with the clear coat or e-coat layers or the mixing of IR spectra of adjacent paint layers - remained. These problems appear to be linked to the compression of the cross sectioned paint sample by the epoxy, which causes a decrease in the thickness of each layer of the automotive paint. For an OEM automotive paint system, embedding a paint sample in an epoxy may be problematic for some paint systems when one or more layers are too thin.

For the thirty-two unembedded automotive paint samples analyzed by ATR infrared imaging, twenty-one samples were correctly classified as to manufacturer and seventeen of the twenty-one were correctly classified as to assembly plant using the library search prefilters. The failure to correctly identify all paint samples using the search prefilters can be attributed to several problems. One problem is that the resolution of the ATR infrared spectrum of each paint layer reconstructed by MCR is 8cm^{-1} , whereas the resolution of the IR spectra comprising the search prefilters are 4cm^{-1} . If the resolution of the microscope was increased to 4cm^{-1} , the spectra would

be too noisy. Furthermore, using higher resolution in ATR would dramatically increase data collection times.

A second problem is that the reconstructed ATR spectra by MCR were often too noisy. The nature of the ATR measurement restricted the size of the sample interrogated by the IR beam. If the layer was too thin, the amount of polymer in the layer could have been insufficient to yield spectra with high signal to noise. Since a heat-map is used to identify the location of the sample, there was often ambiguity associated with the location of the sample in the ATR image, which further confounded the issue. However, decreasing the spectral interference from carbon dioxide and water vapor by covering the sample stage with plastic and waiting for approximately ten to fifteen minutes for the carbon dioxide and water vapor to diminish before collecting the data was beneficial for ameliorating some problems associated with signal to noise. Nevertheless, the net result was a degradation in both the quality of the IR spectra comprising the line maps and the performance of the MCR deconvolution algorithm including the signal to noise of the reconstructed IR spectra as compared to the corresponding IR transmission spectral line maps. The importance of signal to noise in spectral reconstruction by MCR is that search prefilters which utilize wavelet transformed IR spectra require unknown IR spectra to have very high signal to noise to ensure accurate predictions.

IR spectra obtained from the cross sectioned paint sample immobilized on the ATR crystal were also impacted by the position of the sample on the crystal. Changes in the absorbance values of the low wavenumber region were observed with spectra collected in the middle of the crystal versus spectra collected at the edge of the crystal. These changes vary as a function of the specific paint fragment employed, which can be attributed to differences in the contact angle between the crystal and the sample. This posed a problem when using the ATR simulation algorithm to

transform IR transmission spectra from the PDQ library into ATR spectra for the purpose of matching the ATR spectra obtained by the germanium hemispheres used for ATR imaging microscopy. This problem was partially ameliorated through improvements in the techniques used to cross section the paint sample and by placing the paint sample in the center of the germanium ATR crystal to improve the physical contact between the sample and the ATR crystal.

Implication for Criminal Justice Policy and Practice in the United States

The research project described in this final summary overview is directly targeted to enhance current approaches to forensic automotive paint analysis through decreased data collection times as compared to the current practices and to aid in evidential significance assessment, both at the investigative lead stage and at the courtroom testimony stage. Direct impact on over 75 local, state, and federal forensic laboratories that are currently using the PDQ database in the United States is anticipated. There will also be direct impact on international forensic laboratories using the database, including the Forensic Laboratory Services Division of the RCMP, the Centre of Forensic Sciences in Toronto, Canada, the ENFSI network of European forensic science institutes, the Australian Police Services, and the New Zealand Police Services. The research described in this report is an international collaborative effort between the Lavine research group at Oklahoma State University and Mark Sandercock of the RCMP. The use of the prototype pattern recognition assisted infrared library search system previously developed by Lavine and Sandercock in tandem with FTIR imaging will ensure that fewer hits are generated. This can translate into a significant time savings for the forensic scientist. Furthermore, information derived from the search prefilters for vehicle manufacturer can serve to quantify the general discrimination power of original automotive paint comparisons and further efforts to succinctly communicate the significance of the evidence.

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