# Characterization of Automotive Paint Clear Coats by Ultraviolet Absorption Microspectrophotometry with Subsequent Chemometric Analysis

Elisa A. Liszewski,[1] B.S., Simon W. Lewis,[2] Ph.D., Jay A. Siegel,[1] Ph.D.,

John V. Goodpaster,[1] Ph.D.*

[1] Department of Chemistry and Chemical Biology

Forensic and Investigative Sciences Program

Indiana University Purdue University Indianapolis (IUPUI)

Indianapolis, IN  46202

[2] Nanochemistry Research Institute, Department of Chemistry

Curtin University of Technology

GPO Box U1987

Perth, Western Australia 6845, Australia

1

**ABSTRACT**

Clear coats have been a staple in automobile paints for almost thirty years and are of forensic interest when comparing transferred and native paints. However, the UV absorbers in these paint layers are not typically characterized using UV microspectrophotometry, nor are the results studied using multivariate statistical methods. Measurements were carried out by UV microspectrophotometry on 71 samples from American and Australian automobiles, with subsequent chemometric analysis of the absorbance spectra. Sample preparation proved to be vital in obtaining accurate absorbance spectra and a method involving peeling the clear coat layer and not using a mounting medium was preferred. Agglomerative Hierarchical Clustering indicated three main groups of spectra, corresponding to spectra with one, two and three maxima. Principal Components Analysis confirmed this clustering and the factor loadings indicated that a substantial proportion of the variance in the data set originated from specific spectral regions (230 – 265 nm, 275 – 285 nm and 300 – 370 nm). The three classes were well differentiated using Discriminant Analysis, where the cross-validation accuracy was 91.6% and the external validation accuracy was 81.1%. However, results showed no correlation between the make, model, and year of the automobiles.

**INDEX HEADINGS:** forensic science, automotive paint clear coats, microspectrophotometry, agglomerative hierarchical clustering, principal components analysis, discriminant analysis

An original equipment manufacturer (OEM) automotive finish system is normally applied in several stages. The first stage applies the primer which is usually electrolyzed onto the body surface. Typically, above this are the finish layers, consisting of a color base coat followed by the clear coat. The clear coat is the top coat of paint that contains no pigmentation or color, provides the final appearance, and protects the base coat from degradation.[1] Clear coats were first developed in the late 1970s when the topcoat paint system was split into two parts, a pigmented base coat and a colorless clear coat. By the 1980s, the clear coat system became popular, and in the 1990s, new types of paint binders were introduced as well as paint that contained lower amounts of volatile organic compounds (VOCs) to meet new environmental standards.[2] Automotive clear coats currently used are applied either by a liquid application (i.e. acrylic melamine and acrylic carboxy epoxy) or a powder coating (i.e. acrylic carboxy epoxy and acrylic urethane).[3]

Almost all clear coats contain light stabilizers such as hindered amine light stabilizers (HALS). Clear coats also contain UV absorbers in order to protect the automobiles against UV light and weathering. UV absorbers must absorb light in the wavelength range of 290 to 350 nm because these photons can cause the photodegradation of polymers.[2] UV absorbers found in automotive clearcoats are often benzotriazoles and triazines, but benzophenones and oxalanilides can also be used.[2, 4] Clear coat binder chemistries are relatively simple, consisting of acrylics and polyurethanes, and are based on hydroxyl-functional polymers that react with cross linkers.[5] Both UV absorbers and UV absorptions of binder systems can contribute to the overall UV absorption of the clear coat layer.

Paint can be an important type of trace evidence in criminal investigations when it is found at the scenes of automobile crashes where one car hits another car, object, or pedestrian. In some cases, paint can be transferred between cars or from a car onto the

clothing or body of the person. In most situations, paint cannot be attributed back to a specific source. As a result, forensic testing focuses on generating as much physical and chemical data on the paint in question and comparing it to a known sample of paint from the automobile. Established procedures for analyzing paint evidence in normal casework follow guidelines originally developed by the Scientific Working Group on Materials Analysis (SWGMAT) as well as ASTM Standard E1610 (Standard Guide for Forensic Paint Analysis and Comparison).[6]

Mid-infrared spectroscopy and pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS) are two analytical tools that lie at the core of most paint examinations. Mid-infrared spectroscopy allows information to be obtained about the binders, pigments, and additives in coatings and it can provide structural information about organic and inorganic components.[7] Several authors[8-10] have presented results where mid-infrared spectroscopy of the clear coat was used to differentiate large collections of paint samples. Py-GC/MS is a valuable, albeit destructive, technique in the forensic examination of paint that has been frequently touted for its ability to differentiate and identify paint samples that were indistinguishable by IR.[11, 12] Burns[13] and Plage[14] demonstrated that this technique can also classify clear coats through visual inspection and/or library searching of the chromatograms and mass spectra.

Although microspectrophotometry (MSP) is a well established technique to distinguish dyes and pigments in paint,[15] it has not been fully exploited for analysis of UV-absorbing compounds in clear coats. Stoecklein and Fujiwara demonstrated that clear coats can be distinguished based on their UV absorption spectra.[2] While features in the UV spectra could arise from UV absorbers and/or binder systems, the authors largely attributed the spectral features of clear coats to the UV absorber itself. In this case, the UV absorbers were

found to contain one of three structural cores: hydroxyphenylbenzotriazole, benzophenone and oxanalide.

This study strives to assess the extent to which inherent diversity in a population of automotive clear coats can be reliably discerned by chemometric techniques. Prior studies of clear coats have used qualitative measures of discriminatory power by visually grouping samples[13, 14] or conducting pair-wise comparisons[9, 10]. In these approaches, there are no quantitative, objective measures of the underlying structure of a data set and they ultimately rely upon a human observer to decide if two samples are similar or dissimilar. In contrast, the application of chemometrics to samples of forensic interest is becoming widely accepted as means to improve the analysis of instrumental data.[16] Since MSP has already been shown to differentiate the UV absorbers in clear coats, it is the aim of this paper to demonstrate how chemometric techniques can provide a more quantitative way to distinguish samples by providing answers to the following questions:

1) How many groups of UV spectra can be reliably discerned in a population of automotive clear coats that have been analyzed by microspectrophotometry?

2) What general features of the spectra represent the groups so that an unknown spectrum could be tentatively classified?

3) What regions of the spectra are the most variable and therefore are the most reliable regions to inspect when comparing samples?

4) To what extent can additional samples be correctly and quantitatively assigned to a group?


**Materials and Methods**

*Instrumental Analysis*

Samples of paint were collected from automobiles from junkyards and automobile body shops. A scalpel was used to scrape the paint chips down to the underlying metal to guarantee that all paint layers were present in the sample. The make, model, and year of each vehicle were noted for each sample. Additional foreign exemplars collected from Australia were also included in this study. The foreign exemplars were collected by taking a disc of metal from discarded panels at an automotive repair shop or by taking samples from car roofs removed at a car sun roof fitting business.

The clear coat layer was shaved off with a sharp blade and analyzed directly. Using a coverslip was determined to be unnecessary so the shaved samples were placed directly on a quartz slide without a coverslip. It is important to note that this form of sample preparation is not typically used for comparison of a known (K) and questioned (Q) paint chip, where both would be simultaneously mounted and sectioned. This study is an attempt to use chemometrics to more quantitatively assess the diversity of clear coat samples, rather than conduct any so called "Q vs. K" comparisons.

A CRAIC QDI 2000 microspectrophotometer (CRAIC Technologies, San Dimas CA) was utilized with UV analysis being performed in transmitted light mode. Magnification was 35x. Prior to running samples, the microspectrophotometer was calibrated using NIST traceable standards. An autoset optimization, dark scan, and reference scan were run before each set of sample scans. Samples were taken as absorbance values, and five scans were taken at different locations for each paint sample.

*Data Analysis*

One feature of multivariate analysis is that relatively large sample populations are needed in order to confidently describe the organization of the data. In this paper, the sample collection consists of 355 spectra (71 total samples). The collection included a wide variety of cars; 18 different years are represented, 22 different makes, and 48 different models. Out

of these spectra, nine samples with five scans each (total of 45 spectra) were replicates of other samples, so this data was set aside to be used as supplemental data in an external validation study.  The entire dataset (wavelength range of 200 – 900nm) was first truncated to a range of 200 – 400nm (UV range), and this truncated data was baseline corrected. Following this, the data set was normalized by dividing it by the square root of the sum of the squares of all absorbance values.[17, 18]  This pre-treatment step eliminated variability in the data due to sample thickness.  Statistical evaluation of the data was performed using Microsoft Excel and an add-in, XLSTAT2008 (Addinsoft, Paris, France).  Agglomerative Hierarchical Clustering (AHC) and Principal Components Analysis (PCA) were used as unsupervised chemometric techniques, followed by Discriminant Analysis (DA) as a means to test the classification of samples.[17-19]  Averages of each group of five scans for each automotive clear coat sample were used when performing AHC.  For the purposes of PCA and DA, every scan was used rather than utilizing only the averages.

**Results and Discussion**

The AHC dendrogram for automotive clear coats is shown in Fig. 1.  AHC indicates that three distinct clusters are present based on the position of the truncation line, which was automatically determined by a histogram of node positions.  Bifurcations that occur to the right of the truncation line are more significant in determining the number of classes.  As shown in Fig. 2, the central objects of the AHC dendrogram (those samples that lie closest to the centroid of each class) differ in their relative absorptions at approximately 250 nm, 300 nm and 350 nm.

Following PCA, 78.68% of the total variance of the data set was captured in the first two principal components.  The factor loadings for these PCs can then be used to illustrate spectral regions that are most important in terms of explaining the variance in the data set.

The solid-lined bracketed areas in Fig. 2 indicate wavelengths that are positively or negatively correlated with PC1 (from 300 – 370nm and from 230 – 265nm, respectively). This could be due to the light absorbers found in clear coats, which typically absorb between 290 – 350nm.[2] An additional area of positive correlation for PC2 is highlighted on the central objects plot by a dotted box (from 275 – 285nm).

Discriminant analysis was then performed using the data from PCA. In this case, the first nine PCs were retained so that a set amount of cumulative variance was captured (95%). The results of DA using the first nine principal components are shown in Fig. 3, with 100% of the variance accounted for in two dimensions. Three distinct groups were used to be consistent with AHC. Overlap can be seen between the three groups, which affects the cross-validation results as seen in the confusion matrix results in Table I. Samples located along the diagonal represent those that were correctly classified, while samples in bold outside of this diagonal are incorrect classifications. Overall, 91.61% of the samples were correctly classified, which is considered to be an excellent result.

The additional replicates were used as a form of external validation and the results are shown in Table II. DA predicted which class the supplemental samples should be placed in and the correct placement was determined by where the original (non-replicate) sample was placed. The bolded diagonal numbers are samples that were placed correctly in the proper class. Other bolded numbers outside of the diagonal indicate samples that were incorrectly classified. Overall, the performance of the classification model was good, with 81.11% of samples correctly assigned. In this external validation, the samples that were misclassified had absorbance spectra that more similarly resembled the absorbance spectra of the central object of a different class.

Given that DA is a supervised technique, the number of classes and their composition can have a large effect on the results. Furthermore, the use of internal versus external

validation can also result in overly optimistic estimates of the accuracy of the DA model. Therefore, an additional study where the number of classes was varied demonstrated the validity of external samples. As is evident in Figure 4, the external validation had very high accuracy for three classes (81.11%), whereas the accuracy was significantly lower and never reached over 80% for all other number of classes. The estimation and cross-validation accuracy did not vary significantly when class number was changed and offered a clearly inflated view of the classification accuracy. Based upon external validation, three classes can be claimed to reasonably exist whereas larger number of classes have too low of an accuracy to say for certain that they exist.

Overall, chemometric analysis indicated three distinct groups that produced reliably discernible spectra. Using these results, the question of whether make, model, and year could be affecting the formation of these groups was addressed. However, cars of the same make and model but different year exhibited varying trends. For example, cars of the same make and model but different year had visually dissimilar spectra and were placed in different classes. In contrast, some cars of the same make and model but different year were placed in the same class. Overall, these results indicate that there is not a correlation between the make, model, and year of the automobiles.

It is important to note some limitations in this type of study. First, the initial conditions of the clear coats are unknown and environmental factors such as exposure to sunlight are likely to affect the clear coat. This could become relevant in cases where an unknown sample is collected from a crime scene, but a corresponding known sample is not collected immediately and undergoes significant photodegradation. There can also be differences in the finishes that are used on different parts of the automobile body, such as plastic and metal parts. Since a majority, if not all, of our samples were removed from the same part of a car, this limitation was avoided. Lastly, it is possible that more than one

manufacturer could supply the finish for a given vehicle.  Therefore, a given make, model, and year could easily have two or more types of finishes.  Overall, these limitations could explain why a correlation is not seen between year, make, or model in the collection of clear coats analyzed here.

**Conclusions**

Based on the results discussed above, MSP is capable of analyzing automotive clear coats, but proper sample preparation has been shown to be vital in obtaining accurate spectral data.  The comparison of automotive clear coats using AHC, PCA, and DA resulted in several findings.  Three distinct groups formed within the collection of automotive clear coats.  The central objects of the AHC dendrogram (Fig.2) illustrate that the three classes differ in their relative absorptions at approximately 250 nm, 300 nm and 350 nm.  The spectral regions that correlated most strongly with PC1, and hence represent areas of high variability between samples, were 230 – 265 nm and 300 – 370 nm.  Overall, the three classes were differentiated with high accuracy using both cross-validation and external validation samples.  Clear coats also varied widely by model and year, but no clear relationships were seen between these qualitative variables and MSP data.

**References**

1.      J. Bentley, "Composition, Manufacture, and Use of Paint", in *Forensic Examination of Glass and Paint - Analysis and Interpretation*, B. Caddy, Ed. (Taylor & Francis, London, 2001).
2.      W. Stoecklein and H. Fujiwara, Science & Justice **39**, 3, 188 (1999).
3.      J. I. Thornton, "Forensic Paint Examination", in *Forensic Science Handbook*, R. Saferstein, Ed. (Prentice Hall, Upper Saddle River, New Jersey, 2002), p. 429.
4.      P. Oberg, Polymeric Materials Science and Engineering **83**, 129 (2000).
5.      J. Huybrechts, A. Vaes, K. Dusek, M. Duskova-Smrckova, and R. Barsotti, Surface Coatings International Part B: Coatings Transactions **89**, B4, 275 (2006).
6.      SWGMAT, "Forensic Paint Analysis and Comparison Guidelines", in *Forensic Science Communications* (*http://www.fbi.gov/hq/lab/fsc/backissu/april1999/index.htm*) (1999).
7.      A. Beveridge, T. Fung, and D. Macdougall, "Use of infrared spectroscopy for the characterisation of paint fragments", in *Forensic Examination of Glass and Paint*, B. Caddy, Ed. (Taylor & Francis, London, 2001), p. 183.
8.      S. Ryland, G. Bishea, L. Brun-Conti, M. Eyring, B. Flanagan, T. Jergovich, D. MacDougall, and E. Suzuki, Journal of Forensic Sciences **46**, 1, 31 (2001).
9.      G. Edmondstone, J. Hellman, K. Legate, G. L. Vardy, and E. Lindsay, Canadian Society of Forensic Science Journal **37**, 3, 147 (2004).
10.     M. Eyring, M. Lovelace, and D. Sy, "A Study of the Discrimination of Some Automotive Paint Films Having Identical Color Codes", in *NIJ Trace Evidence Symposium* (Clearwater Beach, FL, 2007).
11.     D. T. Burns and K. P. Doolan, Analytica Chimica Acta **539**, 1-2, 145 (2005).
12.     J. Zieba-Palus, G. Zadora, and J. M. Milczarek, Journal of Chromatography A **1179**, 47 (2008).
13.     D. T. Burns and K. P. Doolan, Analytica Chimica Acta **539**, 1-2, 157 (2005).
14.     B. Plage, A.-D. Berg, and S. Luhn, Forensic Science International **117**, 146 (2008).
15.     D. R. Cousins, C. R. Platoni, and L. W. Russell, Forensic Science International **24**, 3, 183 (1984).
16.     S. L. Morgan and E. G. Bartick, "Discrimination of Forensic Analytical Chemical Data Using Multivariate Statistics", in *Forensic Analysis of the Cutting Edge: New Methods for Trace Evidence Analysis*, R. D. Blackledge, Ed. (John Wiley & Sons, New York, 2007), p. 333.
17.     K. R. Beebe, R. J. Pell, and M. B. Seasholtz, *Chemometrics A Practical Guide* (John Wiley & Sons, Inc, New York, 1998).
18.     R. Kramer, *Chemometric Techniques for Quantitative Analysis* (Marcel Dekker, Inc, New York, 1998).
19.     J. Miller and J. Miller, *Statistics and Chemometrics for Analytical Chemistry* (Pearson Education Limited, England, 2005), Fifth ed.

TABLE I – Confusion Matrix for the Cross-Validation Results from Discriminant Analysis (DA). The bolded diagonal numbers are samples that were placed correctly in the proper class. Other bolded numbers outside of the diagonal are where samples were incorrectly placed into classes. Overall, the percent correct classification was 91.61%.

| From/To | Class 1 | Class 2 | Class 3 | Total | % Correct |
|---|---|---|---|---|---|
| Class 1 | 72 | 6 | 2 | 80 | 90.00 |
| Class 2 | 15 | 145 | 0 | 160 | 90.63 |
| Class 3 | 3 | 0 | 67 | 70 | 95.71 |
| Total | 90 | 151 | 69 | 310 | 91.61 |

TABLE II – Confusion Matrix for the External Validation Results of the Supplemental Data from Discriminant Analysis (DA).  Replicate samples were removed and used for external validation.  DA predicted which class the supplemental samples should be placed in and the correct placement was determined by where the original (non-replicate) sample was placed. The bolded diagonal numbers are samples that were placed correctly in the proper class. Other bolded numbers outside of the diagonal are where samples were incorrectly placed into classes.  Overall, the percent correct classification was 81.11%.

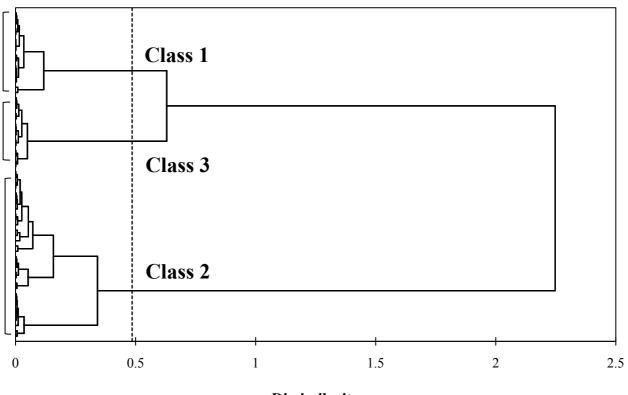| From/To | Class 1 | Class 2 | Class 3 | Total | % Correct |
|---------|---------|---------|---------|-------|-----------|
| Class 1 | 6 | 2 | 2 | 10 | 60.00 |
| Class 2 | 5 | 25 | 0 | 30 | 83.33 |
| Class 3 | 0 | 0 | 5 | 5 | 100.00 |
| Total | 11 | 27 | 7 | 45 | 81.11 |

**FIGURE CAPTIONS**


FIG. 1 – Dendrogram from Agglomerative Hierarchical Clustering of the averages of each clear coat sample. Three distinct classes are formed.
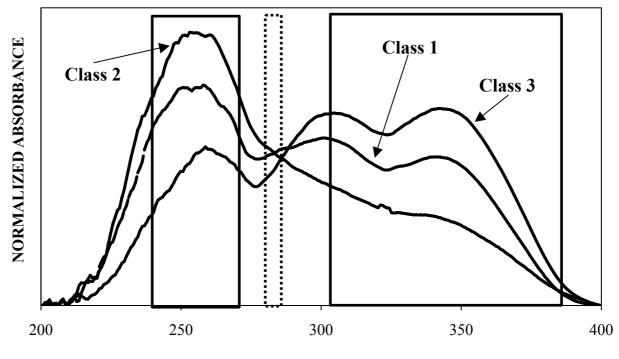

FIG. 2 – Three distinct spectra for the central objects of each of the three clusters that were defined in the dendrogram. The solid-lined boxed areas signify wavelengths whose factor loadings are highly correlated with PC1. The boxed area on the right contains wavelengths of positive correlation and the boxed area on the left contains wavelengths of negative correlation. The dotted-lined area signifies wavelengths that are highly correlated with PC2.


FIG. 3 – The observations plot from Discriminant Analysis (DA) illustrates the clustering of the three classes, similar to the AHC clustering. Using the first nine principal components, 100% of the variance is accounted for in two dimensions.


FIG. 4 – The percent accuracy for each DA testing technique is displayed for varying number of classes. Cross-validation and estimation techniques do not show significant changes when the number of classes is varied. However, the external validation only reaches above 80% accuracy when three classes are used (three classes results in 81.11% accuracy).

**Class 1**

**Class 3**

**Class 2**

Dissimilarity

0          0.5          1          1.5          2          2.5