

Forensic Discrimination of Automotive Paint Samples Using Pyrolysis-Gas Chromatography–Mass Spectrometry with Multivariate Statistics

Brian K. Kochanowski* and Stephen L. Morgan

Department of Chemistry & Biochemistry, The University of South Carolina, Columbia, SC 29208

Abstract

Analytical pyrolysis-gas chromatography (Py-GC) has been a standard method for the forensic analysis of automotive paint for a number of decades. Automotive paints are often identified by visual comparison of pyrograms for peak presence and intensities; however, such analyses can be subjective and time consuming. A preliminary investigation based on Py-GC–mass spectrometric analysis of 100 automobile paint samples of five different colors is presented. Designed experiments are employed to select pyrolysis conditions for adequate discrimination. Pattern recognition techniques including principal component analysis and canonical variates analysis are used to visualize clustering of pyrograms to validate comparisons between different automotive paint pyrograms. These methods have the potential to ease the interpretation task for data sets involving a large number of comparisons.

Introduction

Since its development, pyrolysis-gas chromatography (Py-GC) has been recognized as an informative technique for both the qualitative and quantitative analysis of polymers (1,2). Rapid heating decomposes a polymer into fragments characteristic of the original polymer structure. The reproducible nature of Py-GC allows for meaningful comparisons between different polymers based on differences in the chemical nature and varying amounts of their pyrolysis products. Automobile paint consists of several layers comprised of inorganic pigments contained in a polymer matrix. With minimal sample preparation, selected layers of a paint chip can be characterized, or all layers can be analyzed simultaneously by analytical pyrolysis.

Recognizable differences between automobile coatings are a result of variations in primers and topcoats. Some variations in paint formulation are due to requirements such as durability

and high quality physical appearance. Other considerations, such as lower cost, can lead one to change to a supplier whose formulation may differ from that of a previous supplier. Although care is taken to ensure that the paint does not vary between production sites, subtle differences can often be detected by chemical instrumentation.

Presently, automobile finishes can be classified into three major categories: acrylic lacquers, acrylic enamels, and alkyd enamels. For many years, automobiles from General Motors were coated with acrylic lacquers (3), but the current trend in automobile finishing involves the use of high-solid-content acrylic enamels with the clearcoat/basecoat system (4,5). Interests of a company usually influence changes in paint formulation, but other factors may also impact such decisions. Environmental concerns and regulations on solvent emissions from automobile plants has led to wider use of high-solids paint (6,7). The reduced solvent content precludes the use of paint containing the high-molecular-weight polymers typically found in the acrylic lacquers. High-solid-content automotive paint must be applied using relatively low-molecular-weight polymers and extensively crosslinked with compounds such as resins, urethanes, polyesters, and epoxies (8). Although the basic components are similar, differences exist in the paint formulations for different models of automobiles. Specific car models are produced at the same individual plant. Paint is usually purchased from the closest supplier, and the paint supplied to one plant may not be the same as a paint formulation supplied to another plant, even within the same model year. Different body styles often require a slightly different formulation (9). Sharp corners on the automobile frame require paint with high flexibility, and plastic parts require a special formulation. These factors combine to allow for discrimination and identification of an automobile's year and model.

Initial Py-GC analyses of paint used packed columns (10–16). Because of the limited resolution of packed columns, several columns of differing polarity were sometimes needed to completely differentiate between all paints of a given set. Analyses

* Current address: Solutia, Inc., 730 Worcester St., Springfield, MA 01151.

† Author to whom correspondence should be addressed: e-mail morgan@mail.chem.sc.edu.

typically involved visual comparisons of the presence or absence of prominent peaks. If necessary, relative intensities of certain peaks were also examined. Although not always able to completely differentiate automotive paint samples, these studies demonstrated the potential of using Py-GC for the forensic analysis of automobile paint chips.

The development of capillary columns renewed interest in the analysis of paints using Py-GC (17–18). The improved resolution of capillary columns provided pyrograms with more discriminating features, and multiple column analyses were no longer necessary to resolve the important components. However, as in previous work, the discrimination of paint samples was done by visual comparison. Even when performed by an experienced investigator, these comparisons are time consuming, and judging the degree of match between different samples is subjective.

The simplicity, ease of use, and lower cost of modern GC–mass spectrometry (GC–MS) instruments have led to an increase in the routine use of GC–MS for forensic analysis (19). Because of the complex nature of pyrograms, peaks with similar retention times might not represent the same pyrolysis product. Although a mass spectrum is often sufficient for tentative identification of a pyrolysis product, matching an unknown spectrum to that of a known standard can prove difficult, particularly for proprietary polymers for which standards are not available. Additionally, the ability to unambiguously interpret the mass spectrum of a pyrolysis product is not guaranteed. In these instances, the mass spectrum still provides a fragmentation pattern that characterizes the peak and allows the peak to be recognized in other chromatograms.

Because single GC–MS runs can generate megabytes of data, effective data handling methods are necessary. Principal component analysis (PCA) is widely employed for exploring relationships among samples by reducing the dimensionality of the data (20). PCA finds linear combinations of the original variables, known as principal components (PCs), that represent directions of maximum variability. If most of the variability is found to lie in the first two or three PCs, a projection of the data into this space may provide a useful graphic display of the relationship among samples. However, trends in the data that differentiate between different groups of samples may not coincide with the directions of maximum variability (21). For this reason, multiple discriminant analysis (also called canonical variates analysis or CVA) is also useful (22,23). Based on a prior knowledge of the identity of each sample in a training set, CVA constructs a new set of axes that best separates data into groups (in this case, different types of paint samples) by maximizing the ratio of the between-group to within-group variability. A projection of the data points in the space of the first several canonical variates can then be employed, which better displays the separation of group clusters. When the data set contains more variables (chromatographic peak areas) than samples, an orthogonal form of canonical variates is necessary (24).

Py-GC–MS and infrared reflectance spectroscopy followed by pattern recognition was previously applied to other forensic analytical chemical data (copy toners) (25,26). In the present article, we describe a preliminary investigation into the repro-

ducibility and discrimination ability of Py-GC–MS for the analysis of automobile paint. A major objective was to determine whether Py-GC–MS patterns are sufficiently reproducible yet different enough from one another to be relied upon for the identification of paints. A second objective was to evaluate the use of multivariate strategies for validating comparisons among different paints and objectively visualizing differences in their pyrograms.

Experimental

Paint samples were obtained from junkyard automobiles. A scraping to the metal body of the car ensured that all paint layers were sampled. A total of 100 samples of 5 different colors (20 each of white, red, black, blue, silver) were obtained. A smaller chip from the scraping, weighing less than 100 μg , was used for pyrolysis. Each sample was pyrolyzed in triplicate to give a data set of 300 pyrograms.

Analytical pyrolysis was performed using a CDS Analytical (Oxford, PA) model 2500 pyrolysis autosampler. Paint samples were loaded into quartz sampling tubes and placed sequentially in the autosampler tray. The pyrolysis chamber is arranged in a vertical configuration because the autosampler is a gravity fed device. Quartz rods measuring 19 mm were placed into the sampling tubes to secure the sample as the tube dropped into the pyrolysis chamber and ensure reproducible positioning of the samples in the center of the pyrolysis coil. Paint samples were pyrolyzed for 15 s at a final temperature setting of 650°C with the ramp rate set at 15°C/ms. The pyrolysis interface temperature was set at 250°C.

Capillary GC–MS was conducted using a Hewlett-Packard (Palo Alto, CA) series II GCD, which consists of a Hewlett-Packard series II GC and a quadrupole mass analyzer operating in electron impact mode (70 eV). A 5% phenyl–95% methyl polysiloxane-coated column (30 m \times 0.25-mm i.d., 0.25- μm film thickness, HP5-MS, Hewlett-Packard) was employed for all separations. The column oven program started at 50°C for 1 min and ramped at 10°C/min to a final temperature of 300°C for 10 min. The GC was operated in constant flow mode using helium at a flow rate of 1 mL/min. Injector and transfer line temperatures were set at 250°C and 280°C, respectively. Pyrolysates were transferred to the GC inlet using a 60:1 split ratio. The mass range was scanned from 45 to 450 amu under autotune conditions.

GC–MS data was translated from HP binary to ASCII text format by a program written in Visual C++ (Microsoft Corporation, Redmond, WA). The previously described GC–MS vector representation algorithm was employed to compile peaks from all 300 pyrograms into a standard vector containing all possible peaks and their associated mass spectra (27). A representation of each chromatographic pattern was then created by matching each individual GC–MS run to the standard vector. When the mass spectrum of a peak in a GC–MS pyrogram was found to match that of a peak in the standard vector (> 0.9 similarity), the integrated area of that peak was included in the final data matrix. If a peak was not present in a particular pyrogram, a

zero area was placed in the data matrix. The resulting data matrix consisted of 300 rows (100 samples \times 3 replicates) and a number of columns (peak areas) depending on the number of unique peaks found across the set of pyrograms.

Subsequent data analysis was performed using programs written in Matlab version 4.2c for Windows (The Mathworks, Cambridge, MA). The rows of the data matrix (representing

each pyrogram) were normalized to unit length to compensate for variations in sample size. The columns of the data matrix (each representing a different peak) were mean centered. The resulting normalized, mean centered data matrix was employed in all further analyses. Programs for PCA and orthogonal canonical variates analysis (OCVA) used singular value decomposition (28) for eigenanalysis and were validated by comparison with published literature results (20,23,24).

Table I. Factor Definitions, Coding Levels, and Design Points for $1/2 \times 2^5$ Fractional Factorial Design

Factor (original units)	Coded factor levels		
	(-)	(0)	(+)
Initial temperature ($^{\circ}\text{C}$)	100	125	150
Initial time (s)	0	7.5	15
Rate ($^{\circ}\text{C}/\text{ms}$)	0.9	7.95	15
Final pyrolysis temperature ($^{\circ}\text{C}$)	500	625	750
Final time (s)	5	12.5	20

Run	Coded factor levels				
	Initial temperature	Initial time	Rate	Final temperature	Final time
1	+	+	-	+	-
2	-	-	+	+	-
3	+	-	-	-	+
4	+	-	+	-	-
5	0	0	0	0	0
6	-	-	-	+	+
7	-	+	+	-	-
8	0	0	0	0	0
9	0	0	0	0	0
10	+	+	+	+	+
11	0	0	0	0	0
12	-	+	-	-	+

Results and Discussion

Selection of pyrolysis conditions for discrimination

Pyrolysis conditions should be selected to maximize the discrimination of samples. Although pyrograms are complex, some characteristic peaks should be readily apparent that are useful for characterizing samples into groups. In this work, designed experiments were conducted to find pyrolysis conditions that provided adequate discrimination among automobile paint samples. Two paints were arbitrarily selected for comparison: 1987 Buick Riviera and 1990 Geo Metro white paints. Five adjustable experimental factors (initial coil temperature, initial temperature hold time, temperature ramp rate, final coil temperature, and final temperature hold time) were varied in a $1/2 \times 2^5$ fractional factorial screening design (29). The eight design points were supplemented by four replicate experiments at the center of the design for a total of 12 experiments, carried out in a random order (Table I). At each set of conditions, the area difference between pyrograms of the two white paints was used to assess discrimination. Of the five factors, the final pyrolysis temperature and final hold time had the greatest absolute effects (Figure 1); the other three factors showed negligible effects and were held at constant levels in further experiments.

Following the screening design, a two-factor central com-

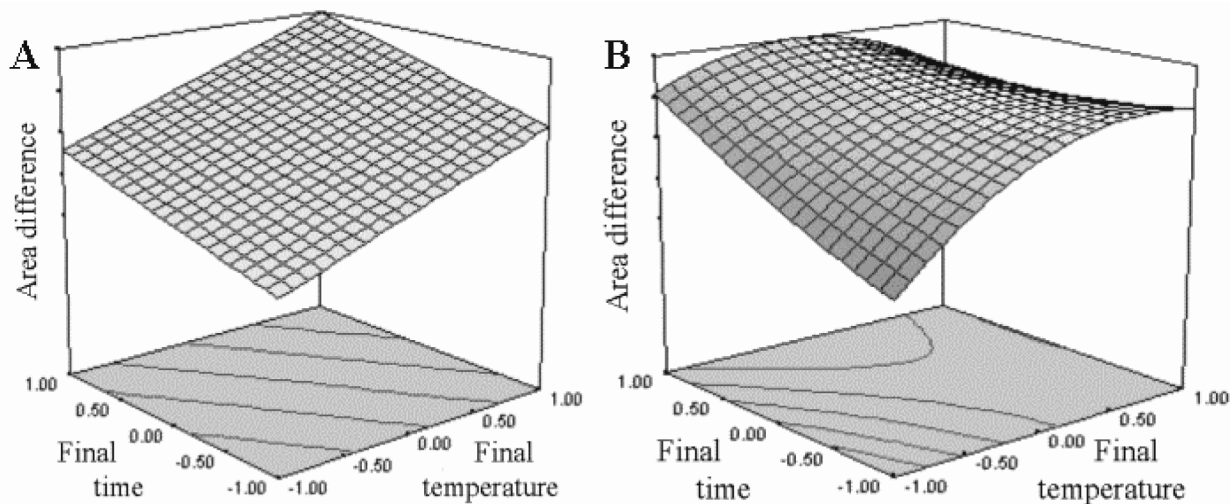


Figure 1. Fitted models for the difference in peak areas between pyrograms of 1987 Buick Riviera and 1990 Geo Metro white paints based on fractional factorial design (A) and central composite design (B). Effects are shown only for the final pyrolysis time and pyrolysis temperature; the remaining factors were held constant at their central values (Table I).

posite design was conducted to determine in greater detail the individual effects of final temperature and final hold time on discrimination between the two automobile paints. The design and coded factor levels for this 13-experiment response surface design (again carried out in a randomized time order) are summarized in Table II. Pyrograms of the two paints obtained at one of the experimental conditions from this design are shown in Figure 2. Pyrograms were divided into three areas:

Table II. Factor Definitions, Coding Levels, and Design Points for 2-factor Central Composite Design					
Factor (original units)	Coded factor levels				
	(-1.41)	(-1)	(0)	(+1)	(+1.41)
Final temperature (°C)	559	600	700	800	841
Final time (s)	12.36	14	18	22	23.64
Run	Final temperature (coded)		Final time (coded)		
1	0		0		
2	-1		+1		
3	0		-1.41		
4	+1		-1		
5	0		0		
6	0		+1.41		
7	0		0		
8	0		0		
9	+1.41		0		
10	-1.41		0		
11	+1		+1		
12	0		0		
13	-1		-1		

0–12.00 min, 12.01–24.00 min, and 24.01–36.00 min. With a nonpolar stationary phase, early portions of a pyrogram typically contain low-molecular-weight fragments that do not retain many features of the original polymer. Peaks appearing in the latter part of the pyrogram tend to be higher-molecular-weight fragments that are more indicative of the polymer structure. A full second-order model adequately described the difference in area response for the two paints in the last third of the pyrogram. A plot of the fitted response surface (Figure 1B) shows a local maximum with the greatest discrimination in the middle of the final pyrolysis temperature range studied. Discrimination increases only slightly with longer final pyrolysis times over the region studied. All further pyrolysis experiments were conducted using the following conditions: 250°C initial temperature, 15°C initial ramp rate, 650°C final temperature, and 15-s final time.

Reproducibility

Reproducibility has been of concern since the beginning of routine Py-GC analyses (1). Several studies have been conducted on the reproducibility of results using a standard sample (30–36). Coupe et al. (31) distributed the same sample to several analytical laboratories and compared both quantitative and qualitative results. Two stationary phases were recommended for the analysis, but the choice of pyrolysis and GC temperatures were left to the analysts' discretion. Variation of the results among the participating laboratories was quite high: the percent recovery of styrene monomer from polystyrene ranged from 26% to 102%. Subsequent studies specified pyrolysis and GC temperatures more stringently; although results improved, significant sources of variation originated from sample preparation and the pyrolysis instrument itself (33,36).

In a resistively heated filament pyrolyzer, solid samples are

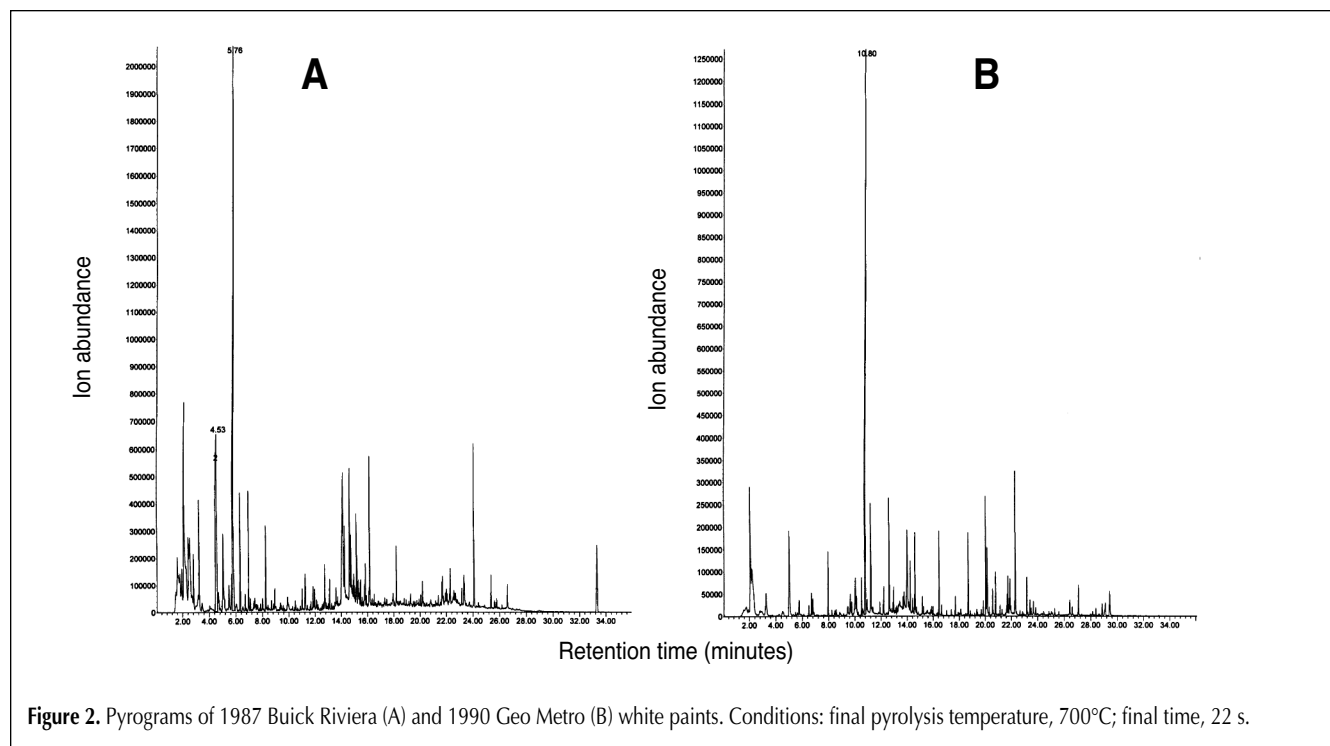


Figure 2. Pyrograms of 1987 Buick Riviera (A) and 1990 Geo Metro (B) white paints. Conditions: final pyrolysis temperature, 700°C; final time, 22 s.

typically placed in a quartz tube, which is then inserted into the coil of the pyrolysis filament. Samples must be placed reproducibly in the pyrolysis filament to avoid potential differences in temperature along the filament. The CDS 2500 pyrolysis autosampler positions the quartz tube in the same manner each time, thus exposing the paint sample to the same temperature. Placing a quartz rod inside the quartz tube also helps to position the sample reproducibly with respect to the heating coil. Care should also be taken that solid samples are of equivalent size, because this can also be a source of variation between pyrograms. Figure 3 displays three replicate pyrograms of white paint sampled from a 1989 Chevrolet Cavalier. Although some variations in peak intensity exist, excellent reproducibility is demonstrated. The similarity (or dissimilarity) of replicate pyrograms establishes the standard for judging the significance of observed differences between two or more Py-GC-MS patterns.

Comparison of pyrograms using multivariate statistics

Three stages of data analysis were conducted on the Py-GC-MS paint data set. The first stage involved the use of orthogonal canonical variates analysis (OCVA) on the entire data set to test the ability to separate pyrograms by paint color. A typical forensic paint analysis involves initial investigation by visual microscopy for the identification of such properties as color, texture, and layer structure. These initial visual inspections would typically be used to separate samples by color. Projections into the space of the first three canonical variates (plotted in Figure 4) reveal that all pyrograms of the same paint color cluster together and are almost completely separated from the other colors. The clusters of blue (C) and silver (E) paint pyrograms show some overlap.

The second data analysis stage involved PCA performed separately on the Py-GC-MS data for each color group. The projections of the pyrograms for each type of paint (defined by the automobile model and year) for the five colors are shown in Figure 5. In each color subplot of Figure 5, the three replicate pyrograms for each paint sample are represented by the same alphabet letter. For the most part, each group of three replicate points cluster close together, with their variation indi-

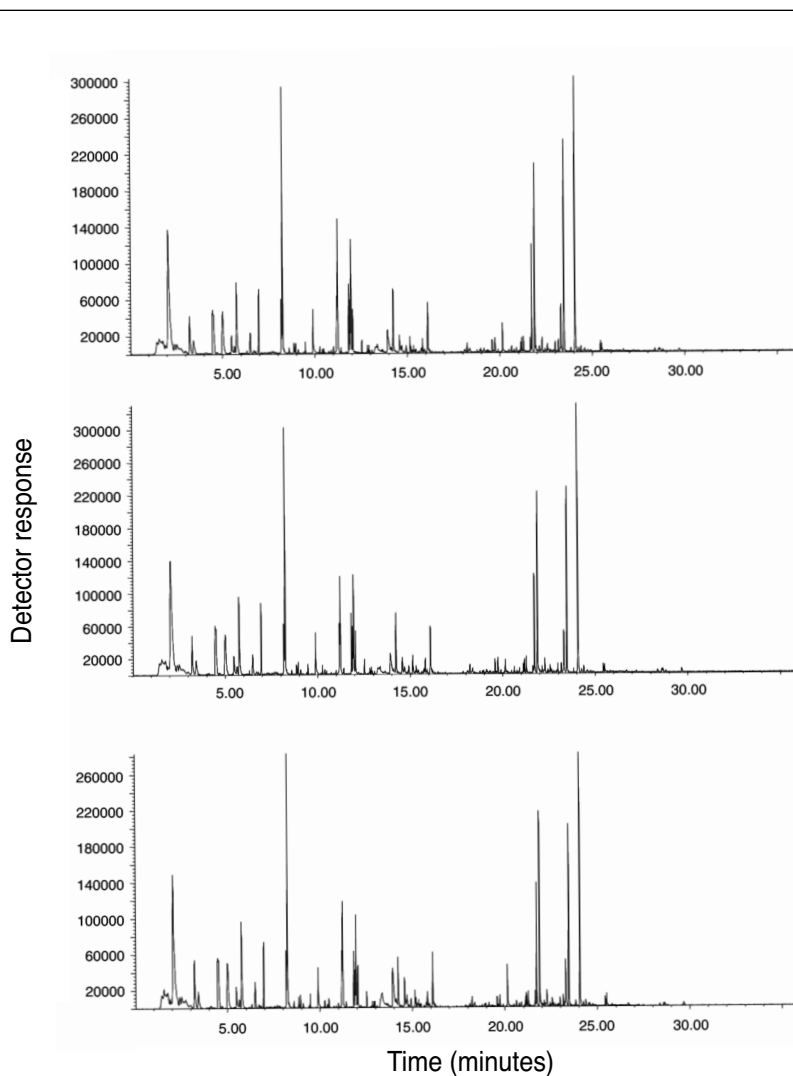


Figure 3. Replicate pyrograms for white paint sampled from a 1989 Chevrolet Cavalier automobile.

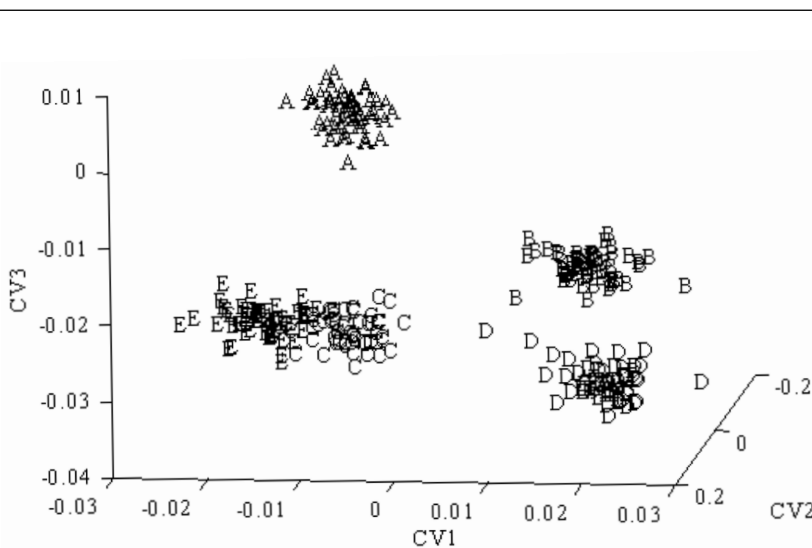


Figure 4. Projections of 300 automotive paint pyrograms into the space of the first three orthogonal canonical variates. Color identification: red (A), white (B), blue (C), black (D), silver (E).

cating the level of experimental variability.

PCA usually ranks principal components by the amount of variability accounted for by each PC. The first PC accounts for the greatest amount of explained variation, the second PC accounts for the second greatest amount of variation (in a direction orthogonal to the first PC), and so on as PCs are added in numerical order. Although variation in prominent

peaks that are present in every pyrogram may determine the first few PCs, peaks whose variation over the data set is numerically smaller may be important in distinguishing groups of samples. Within-group variability was calculated using the pooled variation of replicates. After PCA was performed separately on each color group, the PCs were ranked by the ratio of between-group to within-group variability for which each

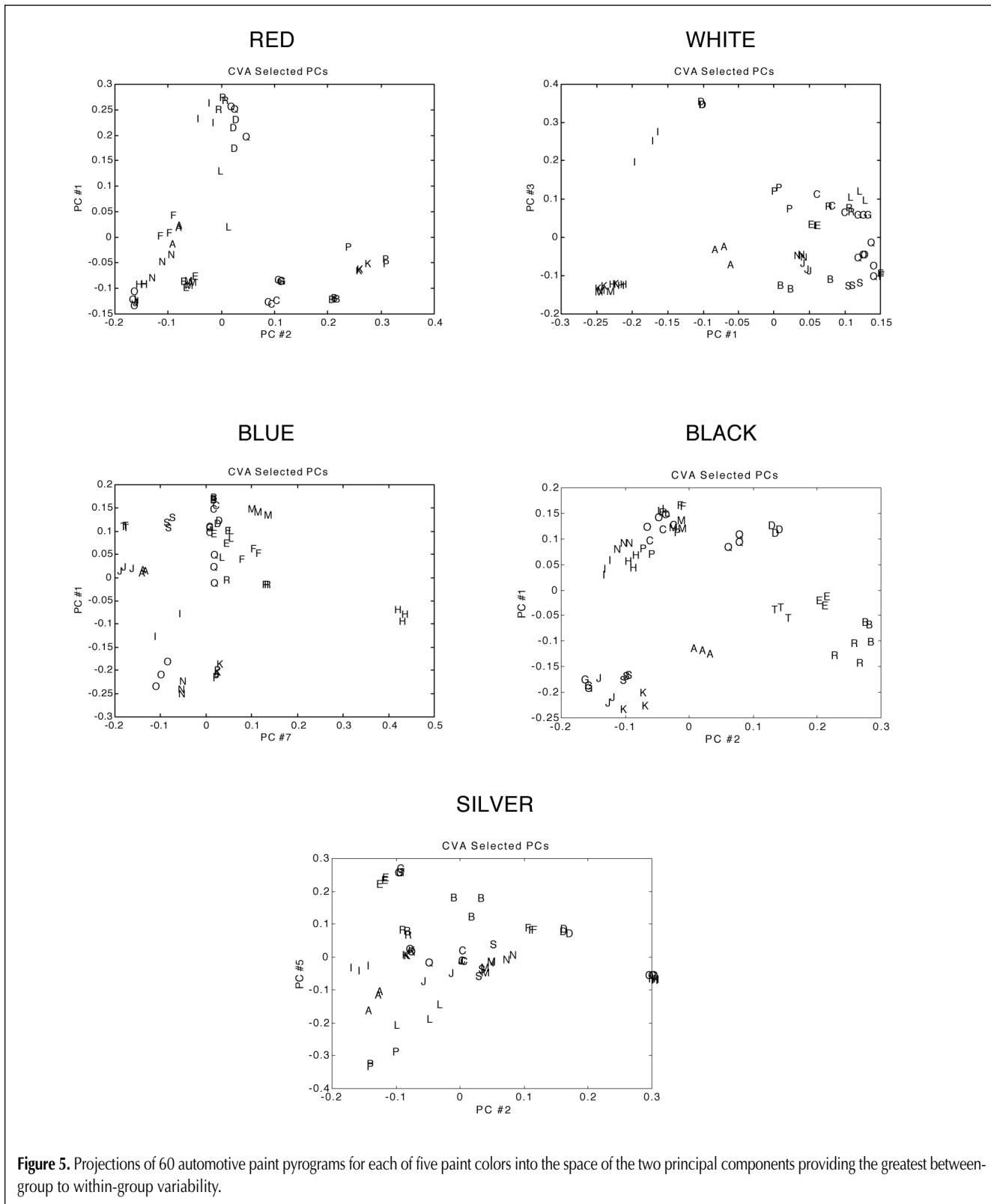


Figure 5. Projections of 60 automotive paint pyrogram for each of five paint colors into the space of the two principal components providing the greatest between-group to within-group variability.

was accounted (23). Thus, the two PCs used in the subplots of Figure 5 are not always PCs 1 and 2; instead the two PCs were chosen to best display the clustering of similar paint samples and the differences between different types of paints.

Pyrograms of five selected white paints are shown in Figure 6. Characteristic peaks that differentiate these samples can be visually identified. (Although beyond the scope of the present paper, mass spectra of these characteristic peaks may suggest underlying chemical differences in the different paints.) In the final data analysis stage, replicate samples were specified as groups for analysis by OCVA on each color separately. Results from OCVA of white automobile paints are shown in Figures 7 and 8. The labeled points correspond to the pyrograms shown in Figure 6. The axes used in these plots are based on an entirely different criterion than those of a PC space. The OCVA criterion produces uncorrelated axes that explicitly maximize separation between groups while minimizing differences within groups (in this case, with groups defined as replicate pyrograms of the same paint sample).

The two-dimensional plot (Figure 7) shows good separation of most of the groups. Note, for example, that the points representing the 1991 Oldsmobile Cutlass pyrograms are distinctly separated in the upper right corner of both plots. Almost every group of replicate paint pyrograms is distinctly separated from its neighbors, even more so than in the CVA-selected PC plots (Figure 5). In comparison to Figure 5, the within-group variability of each set of three replicates is smaller. Note that when the three replicates of a sample are not distinguishable in these plots (e.g., for sample K in Figures 7 or 8), it is because these three replicates agreed well enough with one another for the OCVA plot to superimpose the points. In Figure 6, the 1984 Volvo 245 (K) and 1981 Ford LTD (M) white paint pyrograms are substantially different by visual inspection. The separation between the points representing the pyrograms in Figures 7 and 8 (relative to the experimental variability of replicates) validates this discrimination.

The three-dimensional plot in Figure 8 demonstrates the added discrimination ability provided by more dimensions. For example, in the two-dimensional OCVA plot (Figure 7), the pyrograms of the 1986 Chevrolet Celebrity (I) and 1987 Chevrolet Celebrity (J) were overlapped with one another; however, adding a third canonical variate (Figure 8) discriminates these two automobile paint sample pyrograms from one another.

Conclusion

Analytical pyrolysis followed by capillary GC and MS was employed to characterize different automotive paints of different colors and automobile types. In many instances, the chromatograms of pyrolysis products from paint chips are sufficiently reproducible to enable the user to make effective decisions concerning whether one pattern is distinguishable from another. The pyrolysis autosampler made possible the automated analytical Py-GC-MS on the large number of samples analyzed. Although not done here, interpretation of the mass spectra of characteristic peaks may also assist the forensic analyst in understanding the chemical differences that exist among different paints.

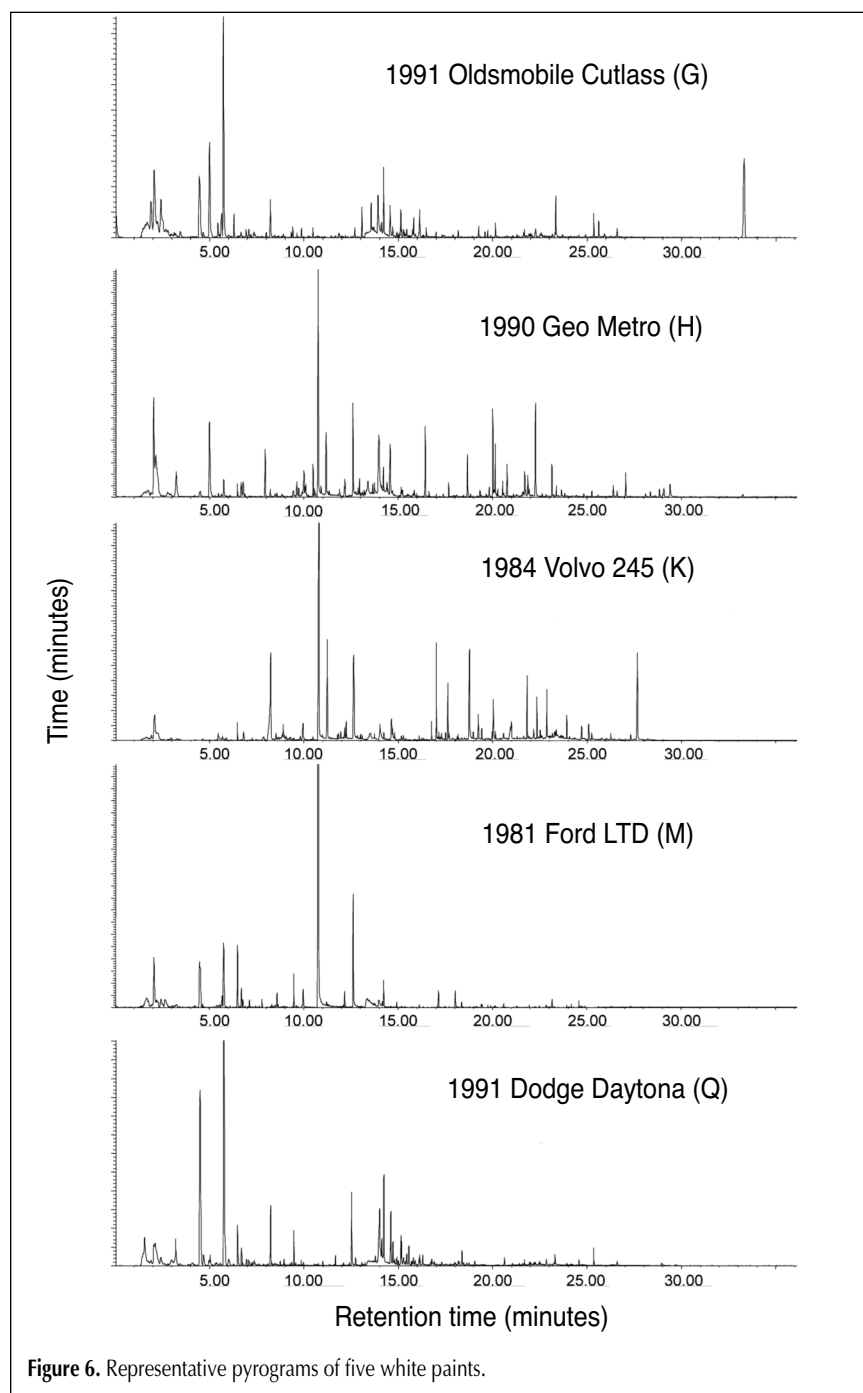
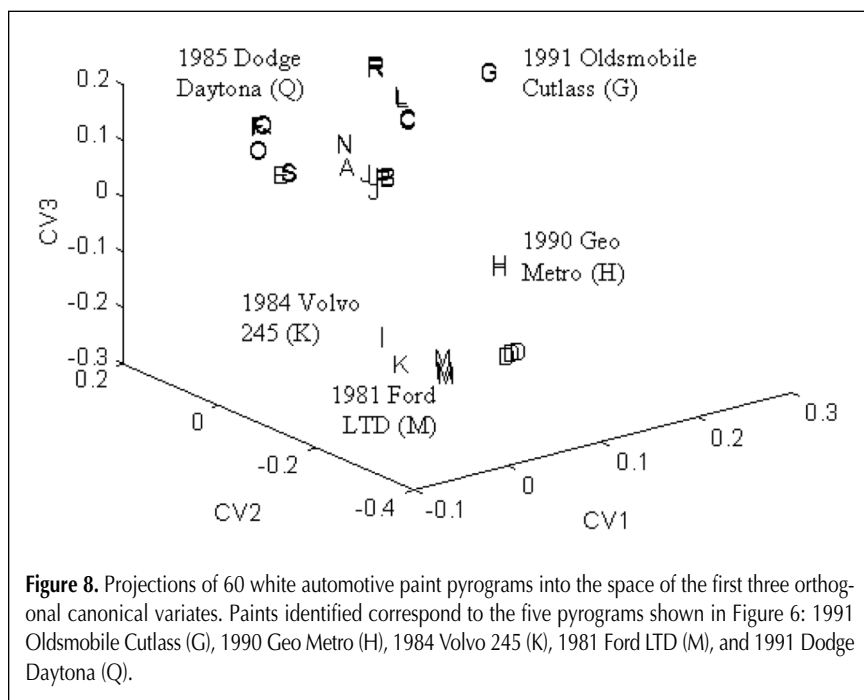
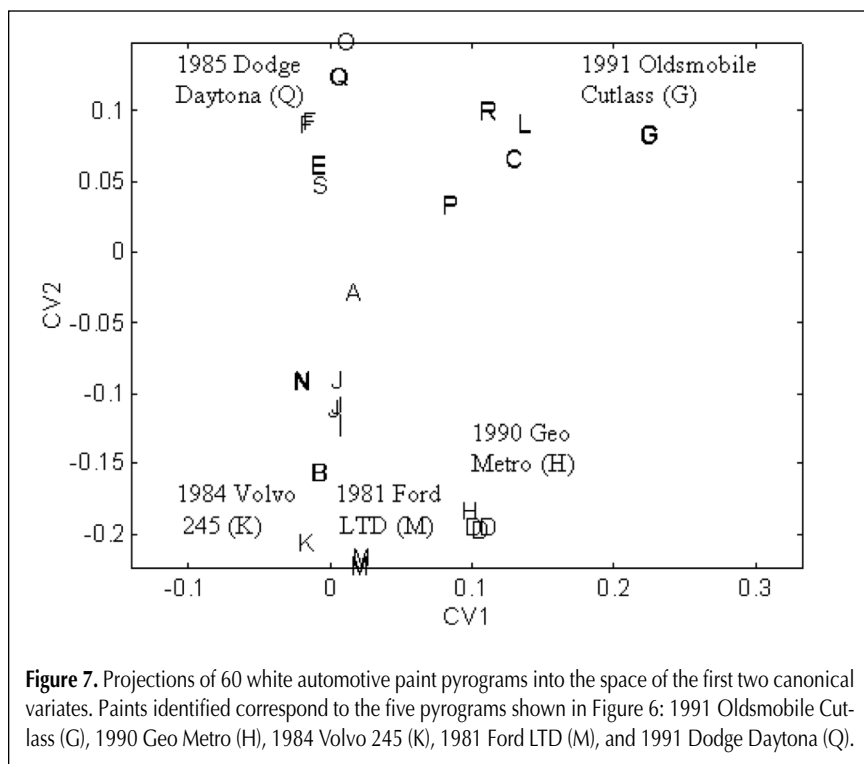


Figure 6. Representative pyrograms of five white paints.



The evaluation of automated, statistical-based strategies for data handling that offer improvements in method validation and ease of interpretation was a second focus of this work. Multivariate data analysis provides a much more efficient way to handle large amounts of data. In our work, 100 samples were analyzed in triplicate for a total of 300 pyrograms. Visual comparison and classification of this data would have been time consuming. Characteristic peaks would be hard to determine over this range of samples; judging whether one pyrogram is significantly different from another would be highly subjective.

Computer-assisted data interpretation of Py-GC-MS data clearly has the potential to facilitate identification of the questioned automobile paint chips. Principal component analysis and canonical variates analysis can be used to produce visually interpretable maps that display the quantitative similarity of pyrograms.

Further analysis of the present data is possible, and further studies are warranted. Unknown samples could be projected into these maps and classified by their proximity to known samples. For example, CVA axes that best discriminate between samples and directions between clusters of different samples are characterized by a linear combination of the original pyrolysis peaks. These "loadings" can be employed to identify which chromatographic peaks are useful for discriminating between groups. A larger library of paint pyrograms would make more reliable estimates of the accuracy of automotive paint classification possible. Unknown samples could be projected into these maps and classified by their proximity to known samples. Statistical measures of confidence in classification decisions could also be derived from more comprehensive data sets. Although not considered in this preliminary study, the influence of sampling variability and weathering on the ability of Py-GC-MS to identify paint chips is an additional consideration.

Acknowledgments

The Office of Justice Programs, National Institute of Justice, Department of Justice provided support for this work through award 97-LB-VX-0006. The points of view represented here are those of the authors and do not necessarily represent the official position of the U.S. Department of Justice. The authors thank Frederic Whitehurst and William J. Egan for their assistance.

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Manuscript accepted January 28, 2000.