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## *FINAL TECHNICAL REPORT*

### **Application of Laser-Induced Breakdown Spectroscopy to Forensic Science: Analysis of Paint Samples**

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## **Abstract:**

A comparison has been made between laser induced breakdown spectroscopy (LIBS), X-ray fluorescence (XRF), scanning electron microscopy – energy dispersive X-ray spectroscopy (SEM/EDS) and laser ablation – inductively coupled plasma – mass spectrometry (LA-ICP-MS) for the discrimination of automotive paint samples. All discriminations were performed by hypothesis testing at the  $\alpha = 0.05$  significance level using both parametric and nonparametric statistical tests. Discrimination was tested across all paint samples, irrespective of paint color or other features, and in a more forensically relevant fashion, discrimination was determined for only those samples of the same color group, number of paint layers and the presence or absence of effect pigments in the paint. The paint samples came from automobiles manufactured in years 1985 – 2006, representing both original equipment manufacturers paint and repaint samples. The samples came from color groups that included black, blue, green, red, silver, tan and white. A total of 200 paint samples, comprising one group of 110 samples and one group of 90 samples were examined by the different analytical methods. Not all samples were analyzed by each method.

LIBS was determined to have a discrimination power of 90% (10% Type II errors) at a verified 5% Type I error rate. Discrimination was found to be slightly lower (86.6%) among the white color group. Variations in the LIBS signal over time led to same sample discriminations and an artificially high Type I error rate, which was overcome by attention to the sampling protocol and confining spectra collection on samples that were to be compared to a narrow time window. LA-ICP-MS was determined to give the best sample discrimination (100%), with XRF and SEM/EDS giving the lowest discriminations, 85% and 73% total discrimination respectively for each method. The results of this study suggest that LIBS may provide an important screening

tool in the analysis of automotive paint samples; however, careful attention to sampling protocols and statistical comparison of samples is recommended. In cases where two samples can not be discriminated, a more accurate comparison method or multiple comparison methods should be sought.

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## **Executive Summary:**

Laser induced breakdown spectroscopy (LIBS) can provide an inexpensive and rapid analytical method for the characterization of a sample's elemental composition. This research examines the application of LIBS for the analysis and pairwise comparison of automotive paint samples for the purpose of discriminating between two samples at a known level of statistical significance. In the absence of a uniquely identifying characteristic (i.e., matching fracture pattern, etc.), items of physical evidence are unlikely to found similar or different with a probability as high as that is enjoyed by biological evidence. This does not preclude the possibility of assessing the similarity of two items of physical evidence on a statistical basis. In order to achieve this goal, the analytical methodology used for the comparison must be characterized as to its ability to discriminate between different samples at a known level of statistical significance. The approach taken in this research was to utilize hypothesis testing to assess the ability of LIBS to distinguish between paint samples that came from different sources.

In the hypothesis testing approach, the null hypothesis ( $H_0$ ) is that a representative parameter measured for two samples (i.e.,  $\bar{X}_A$  and  $\bar{X}_B$ ) will be equal ( $H_0 : \bar{X}_A = \bar{X}_B$ ), and the alternate hypothesis ( $H_A$ ) is that they are not equal. When a Type II error (accepting  $H_0$  when it is false, or false inclusion) holds more serious consequences than a Type I error, as in the case of forensic science, it is common to hold  $\alpha = 0.05$ . Hypothesis testing is made in this research using parametric tests, which rely on an underlying normal distribution of the parameter of interest, and by a nonparametric permutation method that is free from any underlying assumptions of normality. Parametric tests used

for discrimination were the multivariate analysis of variance (MANOVA) as well as the t-test based on the hit quality index (HQI) and Fisher transformation of the Pearson product moment correlation ( $Z(r)$ ). The nonparametric method was a permutation test utilizing a test metric based on  $Z(r)$ .

As a measure of the forensic usefulness of LIBS, the discriminating power of LIBS was compared to that of X-ray fluorescence (XRF), scanning electron microscopy – energy dispersive X-ray spectroscopy (SEM/EDS) and laser ablation – inductively coupled plasma – mass spectrometry (LA-ICP-MS). Automotive paint sample were examined by each analytical method, making use of hypothesis testing at the  $\alpha = 0.05$  significance level, which sets the Type I error (same sample discrimination) at 5%. The power of each method is defined as the percent of different sample discrimination, at the defined significance level. The power of any test may be increased (higher different sample discrimination) at the expense of more Type I (false exclusion) errors. While neither one of these two errors is desired, it is important to know both error rates for a given analytical method. The typical approach is to hold the Type I error rate at a specified value while determining the Type II rate.

The discrimination power of each method was evaluated base on several methods of sample comparisons:

1. All pairwise comparisons of the analytical data from different samples (DS), irrespective of the color of the sample, the number of layers of paint or the presence/absence of effect pigments (metal flake, etc.).
2. Pairwise comparisons limited to samples from the same color group, e.g., black samples compared only to other black samples, etc.
3. The most forensically useful approach, where comparisons were limited to samples of the same color group that had the same number of layers of



paint. Samples with effect pigments were not compared to samples that did not contain effect pigments.

All samples came from different sources. Failure to discriminate different samples (DS) constituted a Type II error. The Type I error rate was nominally held at 5%; however, this assumption was tested in several cases by performing repeated analyses on the same sample and checking for statistical discrimination between the same sample (SS) comparisons. The paint samples examined in this research came from automobiles manufactured in years 1985 – 2006, representing both original equipment manufacturers paint and repaint samples. The samples came from color groups that included black, blue, green, red, silver, tan and white. A total of 200 paint samples, comprising one group of 110 samples and one group of 90 samples were examined by the different analytical methods. Not all samples were analyzed by each method. The following table summarized the analytical results.

**Summary of different sample (DS) and same sample (SS) discrimination by the analytical and data analysis methods utilized in this research.**

Analytical Method	Data Analysis Method	Number of Samples	Number of DS Comparisons	% Discrimination based on:			Number of SS Comparisons	Measured Type I Error Rate
				Total <sup>†</sup>	Color <sup>‡</sup>	Color + Layers + Effect Pigments		
XRF	MANOVA	102	5202	83.6	82.4	80.4	-	-
SEM/EDS	MANOVA	102	5202	73.3	71	70.3	-	-
SEM/EDS	HQI	101	5050	84.3	80.5	79.0	-	-
LA-ICP-MS	MANOVA	18	162	100	100	100	-	-
LIBS	MANOVA	20	780	87.3	78.9	84.4	20	5
LIBS	Z(r)	25	300	95.0	-	-	25	12 - 20
LIBS	Z(r)	93	4278	99.2	-	-	-	-
LIBS / log*	nonParametric	90	924	-	-	89.8	90	4.4

\* Log transformation of emission intensities used for sample comparisons  
<sup>†</sup> All pairwise comparisons irrespective of color, number of layers of paint or presence/absence of effect pigments  
<sup>‡</sup> Pairwise comparisons limited to samples of same color group, irrespective of number of paint layers and presence or absence of effect pigments

The results from these studies indicate that LA-ICP-MS analysis of automotive paint samples provides a very high discrimination. Although the total number of samples analyzed by LA-ICP-MS in this study was lower than by the other methods, the different sample discrimination was 100% of 162 different sample comparisons. The high discrimination by this technique is attributed to the reproducibility and accuracy of the method. Due to casework precedence and instrument repair issues, access to this technique was limited; however, the results reinforce the reports from other laboratories. The only issue of potential concern with this method is the untested level of Type I error. When the Type II error goes to 0%, as in this case, caution should be taken to insure that the Type I error is held at the nominal level (5% in our analyses). Although the MANOVA statistical method is considered to be highly robust, this is a potential topic to be considered in future research.

Comparison by MANOVA of the XRF spectra from 102 paint samples (5,202 unique different sample comparisons) resulted in an overall discrimination of 83.6% of the samples. Limiting the different sample comparisons to the more forensically realistic comparison of only samples of the same color, number of layers and presence or absence of effect pigments only lowered the discrimination to 80.4%. A discriminating power of 80% reflects a 20% chance of a committing a Type II error, and the associated social consequences.

SEM/EDS gave only a 73% overall different sample discrimination, based on 5,202 comparisons by hypothesis testing using the MANOVA approach. When the sample comparisons were limited to samples in the same color group, having the same number of layers of paint and the presence or absence of effect pigments, the

discrimination remained at 70%. The MANOVA discrimination was based on a series of elements in each of three paint layers, the clearcoat, color and primer. Again, the Type II error is higher than would be acceptable in most cases where the consequences of error can be high.

Analysis of paint samples by LIBS gave better discrimination than XRF, or SEM/EDS, but not as good as LA-ICP-MS; however, in this case the Type I error was verified. LIBS spectra of the paint samples were collected by a drill down technique, whereby spectra from successive laser ablations were collected from a single spot on the sample surface. When a series of 14 emission peaks were chosen from 20 LIBS spectra for the purpose of MANOVA discrimination between the paint samples, an overall discrimination of 87.3% was obtained for 780 different sample pairwise comparisons. Limiting the pairwise comparisons to the forensically more useful comparison to samples in the same color group and having the same number of layers and presence of absence of effect pigments lowered the discrimination slightly, to 84.4%. The Type I error rate was experimentally verified to be 5% based on the duplicate analyses and same sample comparison. Discrimination of paint samples by LIBS full spectral comparison using the HQI or  $Z(r)$  similarity metric gave very high different sample discrimination ( $> 95\%$ ) but also resulted in apparent Type I error rates as high as 20%. The apparent high Type I error rates were determined to be due to temporal variations or drift in the LIBS instrument. The problem of high apparent Type I error was corrected by limiting the sample analysis (with duplicate analysis) to a single group of samples, with each group comprised of samples having the same color, number of layers and presence/absence of effect pigments. With this modification in the spectral collection protocol, discrimination

of the log transformation of the emission intensities of 90 paint samples gave 89.8% discrimination of the 924 different sample comparisons for samples having the same color, number of layers and presence/absence of effect pigments. The Type I error rate was determined to be 4.4%, very close to the prescribed 5% level. The white paints were the least discriminated at 86.6% by the nonparametric permutation test. The Wald test achieved a power of 85.17% and an actual size of Type I error of 3.33%.

These results demonstrate that LIBS spectra obtained by drill down analyses can be used for the discrimination of automotive paint samples. The discriminating power is higher than that obtained by SEM/EDS or XRF; however, drift or temporal fluctuation in the LIBS instrument must be taken into account by a well planned sampling protocol. The results also demonstrate the importance of using hypothesis testing in sample discrimination as a method of controlling the Type I error rate. Likewise, it is important to experimentally know the Type II error rate given a prescribed significance level, e.g., at an  $\alpha$  of 0.05, LIBS discrimination of automotive paint samples can be expected to result in approximately 10% Type II errors by the statistical hypothesis testing methods used in this research. The level of Type II errors can be reduced at the expense of greater Type I errors.

While commercially available LIBS instruments are available at substantially lower costs than some other instruments that may be used for automotive paint analysis, these instruments should be carefully assessed for stability and protocols should be put in place to monitor the performance of the instruments over time. Automotive paint discrimination should be conducted with appropriate hypothesis testing and the level of

Type I error should be verified and the level of Type II error independently determined from a known sample set.

The results obtained in this research also point to one of the benefits of physical evidence questioned/known sample discrimination by hypothesis testing: the Type I error rate can be fixed and tested and the Type II rate can be independently determined. These methods should be extended to other physical evidence discriminations where they are applicable and the methodology verified through research and implementing proper laboratory protocols.

## **I. Introduction**

This section of the report gives a short background on forensic paint analysis, a brief introduction to LIBS, and a description of the data analysis methods used to determine the discriminating power of laser induced breakdown spectroscopy (LIBS), x-ray fluorescence (XRF), scanning electron microscopy-energy dispersive x-ray analysis (SEM-EDS), and laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) . The work reported here has resulted in one Forensic Science M.S. thesis by McIntee<sup>1</sup> and partial contribution to a Chemistry (Forensic Science emphasis) Ph.D. dissertation by Bridge.<sup>2</sup>

### **I.1 Statement of Problem**

Laser induced breakdown spectroscopy (LIBS) can provide an inexpensive and rapid analytical method for the characterization of a samples elemental composition. In order for LIBS to be useful in the forensic analysis of samples, e.g., for the comparison of questioned and known samples, it must possess the precision and reproducibility that permits the analyst to reach a match/no-match (sample discrimination) conclusion with

confidence. The sample discrimination question must be answered before any consideration of significance of association or probability of common source. The reproducibility of an analytical method can be taken into account when making a sample discrimination decision through the use of hypothesis testing statistical approaches.<sup>3</sup> In the hypothesis testing approach, the null hypothesis ( $H_0$ ) is that a representative parameter measured for two samples (i.e.,  $\bar{X}_A$  and  $\bar{X}_B$ ) will be equal ( $H_0 : \bar{X}_A = \bar{X}_B$ ), with the alternate hypothesis ( $H_A$ ) being that they are not equal. Statistical tests can not prove that two distributions or their representative parameters are equal, only that they differ, with a given probability of reaching an incorrect conclusion (see below). Hypothesis testing might become impossible when the sample quantity is so limited as to prohibit multiple analyses of each sample and therefore limit the ability to perform a hypothesis test; however, this is often not the case.

This research examines the use of LIBS spectra in hypothesis testing to make a match/no-match decision in the comparison of automotive paint samples. The performance of LIBS is compared with that of X-ray fluorescence (XRF), scanning electron microscopy – energy dispersive X-ray spectroscopy (SEM-EDS) and laser ablation – inductively coupled plasma – mass spectrometry (LA-ICP-MS) for the discrimination of automotive paint samples. Discrimination decisions are made at a 95% confidence level (significance level  $\alpha = 0.05$ ), e.g., such that in 5% of the cases  $H_0$  will be incorrectly deemed to be false (a Type I error). When a Type II error (accepting  $H_0$  when it is false, or false inclusion) holds more serious consequences than a Type I error (false exclusion), as in the case of forensic science, it is common to hold  $\alpha = 0.05$ . This is the practice taken in this research. Hypothesis testing is made in this research using

parametric tests, which rely on an underlying normal distribution of the parameter of interest, and by a nonparametric permutation method that is free from any underlying assumptions of normality. The probability of sameness is easier to establish than the probability of a common source in the case of mass produced items of physical evidence (i.e. fibers, glass, automobile paints, etc.). Statistical testing has been used to infer common sources in profiling illicit heroin and amphetamine samples.<sup>4,5</sup>

## **I.2 Literature Citations and Review:**

### ***I.2.1 Forensic Paint Analysis***

Automotive paint is comprised of three main components which are applied to the automotive substrate. The three components include the binder, pigment and solvent. The binder, which is responsible for ensuring that the paint remains attached to the substrate and keeping the pigment in the paint (adhesion and cohesion), is also known as the resin and contains the bulk of the solids in the paint. Binders are usually organic polymers, including epoxies, polyesters, alkyds (oil-included polyester), melamine and acrylics. The pigment primarily imparts color and opacity to the paint. The principle black and white pigments are inorganic, carbon black and titanium dioxide (TiO<sub>2</sub>) respectively, however, colored pigments are typically organic, which give truer, brighter colors. Effect pigments (EP) have become significant in the paint industry. Effect pigments giving special optical effects, referred to as a lightness or color “flop”, to the paint use a variety of substrates and coatings including coated mica platelets, silicate (SiO<sub>2</sub>) or alumina (Al<sub>2</sub>O<sub>3</sub>) flakes.<sup>6</sup>

Solvent is required as a vehicle for the application of the pigments and solid binder of all paints, with the exception of powder coatings. Heat may be applied to aid in the evaporation of the solvent, although heat is not required. Extenders are also included

in the paint to produce a less expensive product, and more recently their function has expanded to include affecting the drying, glossiness and interfacial and surface tension of the paint and retarding the growth of micro-organisms.<sup>7, 8</sup>

Paint chips from a vehicle coated with original equipment manufacturer's (OEM) paint will generally contain three or four layers, e.g.; a primer, surfacer, basecoat and clearcoat. The galvanized steel or plastic substrate is pretreated with a one micrometer thick phosphate conversion layer to help protect against corrosion and provide a layer for better adhesion of the paint layers.<sup>7,9,10,11</sup> An electrocoat primer layer is applied followed by an opaque surfacer to hide the substrate and primer. The pigment-containing basecoat is subsequently applied, and often effect pigments can be found in the colored basecoat. The clearcoat is applied last to complete the painting process. The clearcoat protects the underlying layers from mechanical damage while allowing the color from the pigments to be visible. The clearcoat also contains organic additives that absorb the sun's rays and protect pigments from UV degradation.

Car paint analysis has traditionally been carried out by polarized light microscopy or stereomicroscopy.<sup>12</sup> The number and thickness of the paint layers can be determined by examining a paint cross section under a stereomicroscope. A microspectrophotometer may be used to determine the color of the pigments found in each layer, although effect pigments can lead to significant light scattering. The resulting spectra, as well as Commission International de l'Éclairage (CIE) color coordinates from the microspectrophotometric analysis can be valuable in discriminating samples.

At this point, the analysis may take two paths, one involving the analysis of the organic constituents and the second involving the analysis of inorganic components in the



paint. Fourier transform infrared spectroscopy (FTIR) may be used for the analysis of the clearcoat, the pigments and binders.<sup>13,14,15,16,17</sup> Infrared spectra may be collected in either transmission or reflectance mode.<sup>17</sup> The Paint Data Query (PDQ) Database, developed by the Royal Canadian Mounted Police (RCMP), can be search against FTIR spectra from an unknown to find the best possible match. Pyrolysis gas chromatography-mass spectrometry (GC-MS) has found limited use in automotive paint analysis.<sup>18</sup> Pyrolysis GC-MS has been reported to be slightly more successful than FTIR in discriminating between samples.<sup>19</sup> A modified pyrolysis method, laser micro-pyrolysis, requires a more time consuming sample preparation method, but provides an alternative to conventional pyrolysis methods.<sup>20</sup> Organic components in paint samples may also be identified by laser desorption time-of-flight mass spectrometry.<sup>21</sup>

Scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDS)<sup>22</sup> and laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS)<sup>23,24,25</sup> are commonly available analytical techniques that may be used for the analysis of the inorganic components of paint samples. Samples to be analyzed by SEM/EDS must be prepared for analysis by applying a sputter coating (typically carbon) to reduce or eliminate charging of the sample. The samples must be placed in the SEM and analyzed under vacuum. SEM/EDS has proven to be a useful technique for the analysis of paint.<sup>22</sup> Raman spectroscopy<sup>14</sup> has been applied to the analysis of extenders, inorganic pigments and effect pigments in automotive paints. X-ray diffraction (XRD)<sup>26,27</sup> and X-ray fluorescence (XRF)<sup>28</sup> are other commonly available techniques that have been utilized for the analysis of inorganic elements in paint samples. However, these techniques have limits of detection that are higher than SEM/EDS. Combining two

analytical methods, e.g.; FTIR with Raman or SEM/EDS, has been proposed as a method to identify both organic and inorganic components in a paint sample to give increased discrimination.<sup>29,30</sup>

This research focuses on the use of laser induced breakdown spectroscopy (LIBS), which is relatively inexpensive and commercially available, as an analytical method for the discrimination between paint samples. Discrimination by LIBS is compared with discrimination by SEM/EDS, XRF and LA-ICP-MS. A direct comparison of LA-ICP-MS and LIBS has previously been reported for the analysis of trace metals in a solid matrix of KBr and two oxides.<sup>31</sup> There have been previous reports of glass analysis by LIBS for non-forensic applications.<sup>32,33,34,35,36,37,38,39,40</sup>

### ***1.2.2 Laser-Induced Breakdown Spectroscopy (LIBS)***

Laser-induced breakdown spectroscopy (LIBS) is an analytical technique in which a high power laser pulse (e.g.; 1-10 MW/cm<sup>2</sup>) is focused onto a sample, resulting in dielectric breakdown and the formation of a plasma containing the atomized constituents of the sample, which emit light from various electronically excited states. Emissions may result from atomic, ionic, and molecular (typically only diatomic) species in the plasma, and appear at characteristic wavelengths in the 200 – 900 nm spectral region. The wavelength of the emission may be highly diagnostic for a specific element if the spectrometer resolution is sufficient high to determine the peak position. For emission classification or identification purposes (e.g.;  $\pm 0.02 \text{ cm}^{-1}$ ) it is recommended that the peak position be known with the following precision as a function of wavelength: 10,000 $\pm$ 0.02 Å, 6,000 $\pm$ 0.007 Å, 3,000 $\pm$ 0.002 Å and 2,000 $\pm$ 0.0008 Å.<sup>41</sup> The emission lines are spectrally resolved and recorded, typically about 1 – 5  $\mu\text{s}$  after the laser pulse. As an analytical

technique, LIBS is characterized by minimal sample preparation. Compact instruments have been demonstrated that allow for potential field portability. Reviews of developments in LIBS research address applications of the technique.<sup>42,43,44,45</sup> LIBS applications in forensic analysis have been reported for inks<sup>46</sup> and glass,<sup>47,48</sup> and in manufacturing applications for the analysis of paint<sup>49</sup> and pigments.<sup>50</sup> LIBS has also found use in environmental monitoring of soil<sup>51</sup> and water<sup>52</sup>, in the analysis and restoration of archaeological artifacts<sup>53</sup> and works of art<sup>54</sup>, and in the analysis of biological specimens.<sup>55</sup>

LIBS analyses can be hindered by high background continuum, line-broadening, and self-absorption in strong emission peaks, which manifests itself as a loss of intensity in the center of the peak and an apparent splitting of the emission peak. The precision of LIBS data can suffer as a result of shot-to-shot laser fluctuations (typically 1 – 5%) that can lead to experimental variations in atomic emission intensity that do not follow a normal Gaussian distribution.<sup>56,57</sup> Approaches that have been proposed to overcome these problems include “calibration free” LIBS,<sup>58</sup> semi-quantitative methods,<sup>59</sup> and correction for instrumental drift.<sup>60</sup> Multivariate data analysis approaches including principal components analysis (PCA) and partial least squares have been examined for the analysis of LIBS data;<sup>61, 62</sup> however, the accuracy of these analyses is dependent on either normally distributed data or a robust statistical method to overcome the lack of normality. Nonparametric statistical methods that do not rely on normal distribution of the data have also been examined for the analysis of LIBS results.<sup>57,63,64</sup> Both parametric and nonparametric statistical methods were employed to analyze the results in this research and both are addressed in section II.1 (Data analysis methods). The instrument used in

this work has previously been reported to give an average of  $6.5 \pm 1.4$  %RSD (relative standard deviation) for a set of 11 emission intensity ratios collected in a single day from averaged LIBS spectra from a NIST SR-610 glass sample.<sup>48</sup> The %RSD increased to  $24.5 \pm 29.2\%$  for spectra collected over a three day period, which favors limiting the use of this technique to comparisons of spectra collected on the same day and emphasizing the need for statistical testing for discrimination analysis. The precision of LIBS spectra is an important issue for forensic sample discrimination that was addressed in this research.

## **II Methods**

### **II.1 Data Analysis Methods**

Several data analysis methods have been utilized in the discrimination of paint samples based on the data collected in this research. Discrimination is accomplished by hypothesis testing at the 95% confidence level. The analyses can be split into two categories, those utilizing direct comparison of individual peak intensities or ratios of peak intensities and those that involve a comparison of the full spectrum obtained from the various analytical methods.

Discrimination based on a comparison of individual peak intensities or ratios of intensities was performed by multivariate analysis of variance (MANOVA) with either a Tukey honestly significant difference (HSD) post-hoc test or with the Bonferonni correction. Both approaches, Tukey HSD and Bonferonni, are designed to correct for inflated Type I error when discriminations are based on a comparison of multiple parameters, and will give highly similar results. Same-sample and different-sample spectral comparisons form the basis for pairwise discrimination between samples. Discrimination based on full spectral analysis is based on calculation of the Fisher

transformation of the Pearson product moment correlation between two spectra, calculation of a distance metric,  $D$ , and by a nonparametric permutation test. Each of these methods is described in this section of the report. Greater detail on each method can be obtained by accessing the referenced sources.

### ***II.1.1 Multivariate Analysis of Variance (MANOVA)***

Multivariate statistical methods allow for the comparison of samples based on multiple variables representing different criteria as a way of differentiating between samples. MANOVA is a technique that allows the determination of a statistically significant difference between samples when they are simultaneously compared across all variables.<sup>65</sup> The variables considered in this work are the intensities of peaks or peak intensity ratios, as described below. Discrimination between two samples from a set of samples using MANOVA involves three steps, the first of which is the MANOVA calculation. All MANOVA calculations were performed with the Statistical Analysis System or SAS software.

The null hypothesis for MANOVA states that all groups have the same mean ( $M_{ij}$ ), where the subscript  $i$  indicates the variable and the subscript  $j$  indicates the experiment group or sample.

$$\begin{pmatrix} M_{11} \\ M_{21} \\ M_{31} \end{pmatrix} = \begin{pmatrix} M_{12} \\ M_{22} \\ M_{32} \end{pmatrix} = \begin{pmatrix} M_{13} \\ M_{23} \\ M_{33} \end{pmatrix} \quad (1)$$

Wilks' lambda ( $W$ ) is calculated as the ratio of the determinants of the within-groups error SSP matrix ( $G$ ) to the total SSCP matrix ( $T$ ) as a measure of the level of association between the variables. SSCP is the sum of the squares and crossproducts.

$$W = \frac{|G|}{|T|} \quad (2)$$

An F statistic, calculated from the following equation, allows for evaluation of the significance of Wilks' lambda.

$$F = \frac{MS_{\text{between groups}}}{MS_{\text{within groups}}} \quad (3)$$

In equation 3,  $MS_{\text{between groups}}$  is the mean square that accounts for variability in error and variability due to differences in the means of the different groups, while  $MS_{\text{within groups}}$  accounts for only variability in error within each group.

A probability,  $p$ , of obtaining an F value greater than or equal to the calculated F value if the null were true is calculated. In order to reject the null hypothesis, if the calculated  $p$  value is lower than the established significance ( $\alpha$ ) value, the null hypothesis is rejected, i.e. all the groups do not have the same mean.

When the MANOVA null hypothesis is rejected, an ANOVA is performed for each variable (intensity at a given wavelength, ratio of intensities, etc.) The ANOVA proceeds by calculating an F statistic and probability,  $p$ , which can be used to reject or accept the null hypothesis ( $H_0 : M_{i,1} = M_{i,2} = M_{i,3}$ ), e.g.; that variable  $i$  is equivalent for each of the  $j=1,2,3\dots$  experimental groups. If the variable  $i$  is not equivalent across all experimental groups (samples), e.g.;  $H_0$  is not true, then variable  $i$  can be used to distinguish between samples. In this way, ANOVA is comparable to a t-test but it is able

to compare more than two samples at a time. Unlike MANOVA, ANOVA is used to indicate which variables can discriminate between samples.

If the ANOVA results are significant ( $H_0$  is false), Tukey's Honestly Significant Difference (HSD) test or the Bonferonni correction can be used to determine which samples are statistically different based on their means. Rejecting the null hypotheses of the MANOVA and ANOVA tests is required before performing the last step of the analysis.

### ***II.1.2 Full Spectral Comparisons***

While hypothesis testing based on individual peak analysis by MANOVA is a time tested statistical procedure, the method uses a limited portion of the dataset (only selected peaks or peak ratios), requires substantial data processing and requires well-behaved normally distributed data, although the method is known for being quite robust. Full spectral analysis methods can be straight forward and may require less data processing; however, these spectral comparison methods do not constitute a hypothesis test. In order to use these methods in a hypothesis testing scheme, the following approaches are taken.

#### ***II.1.2.1 Parametric Approaches***

A series of spectral measurements are made for each of two samples. The multiple measurements allow for an estimation of the precision of the measurement technique by making a set of same sample comparisons, e.g., calculating all unique pairwise same sample correlations, distance metric, etc. and denoted as  $D_{SS}$  and the associated standard deviation  $S_{SS}$ . The spectra from the two samples are then compared to generate a set of different sample comparisons, e.g., calculating the unique pairwise different sample correlations, distance metric, etc., denoted  $D_{DS}$  and the associated standard deviation  $S_{DS}$ .

Discrimination between samples is by a two-tailed t-test, a statistical method that can be used to compare two averages based on their standard deviations. The null hypothesis can be expressed as  $H_0: \bar{D}_{SS} = \bar{D}_{DS}$ , while the alternative hypothesis is  $H_A: \bar{D}_{SS} \neq \bar{D}_{DS}$ . If the samples are indistinguishable by the analytical method, the difference  $|\bar{D}_{DS} - \bar{D}_{SS}|$  will approach zero. The set of  $D_{SS}$  and  $D_{DS}$  comparisons are not strictly independent, as they are generated from comparisons of the same sets of spectra; however, the same sample and different sample comparisons do not share any common comparisons. An alternative approach, the Wald test, gives highly similar results. Discussion of the Wald test is given in section II.1.2.2.1 on nonparametric permutation test. One additional consideration is the normality of the distribution of  $D_{SS}$  and  $D_{DS}$ , a requirement for proper performance of the t-test. The distribution is discussed for each of the comparison method given below.

When  $i$  replicate spectra of sample A are compared with  $j$  replicate spectra of sample B, there will be  $n_{SS} = \frac{i(i-1) + j(j-1)}{2}$  values of  $D_{SS}$  and  $n_{DS} = i \cdot j$  values of  $D_{DS}$ , therefore the correct form for calculating t is the following.<sup>3</sup>

$$t_{calc} = \frac{|\bar{D}_{DS} - \bar{D}_{SS}|}{\sqrt{\frac{S_{DS}^2}{n_{DS}} + \frac{S_{SS}^2}{n_{SS}}}} \quad (4)$$

where  $\bar{D}_{DS}$  and  $\bar{D}_{SS}$  are the averages that are defined above,  $S_{DS}$  and  $S_{SS}$  are the associated standard deviations and  $n_{DS}$  and  $n_{SS}$  are the number of comparisons that were used to calculate the averages. This calculated value,  $t_{calc}$ , is then compared to a  $t_{table}$



value for a given significance level ( $\alpha = 0.05$ ) given the calculated pooled degrees of freedom ( $DF_{pooled}$ ).

$$DF_{pooled} = \frac{\left( \frac{S_{DS}^2}{n_{DS}} + \frac{S_{SS}^2}{n_{SS}} \right)^2}{\frac{\left( \frac{S_{DS}^2}{n_{DS}} \right)^2}{n_{DS} - 1} + \frac{\left( \frac{S_{SS}^2}{n_{SS}} \right)^2}{n_{SS} - 1}} \quad (5)$$

If  $t_{calc}$  is greater than  $t_{table}$ , the samples are statistically different,  $H_0$  is rejected.<sup>3</sup>

#### ***II.1.2.1.1 Pearson Correlation Spectral Comparison***

The Pearson product-moment correlation coefficient ( $r$ ) is calculated as a full spectrum comparison using equation 6.

$$r = \frac{\sum (a_i - \bar{a})(b_i - \bar{b})}{\sqrt{\sum (a_i - \bar{a})^2 \sum (b_i - \bar{b})^2}} \quad (6)$$

In equation 6,  $a_i$  is the  $i^{\text{th}}$  value in spectrum A and  $b_i$  is the  $i^{\text{th}}$  value in spectrum B while  $\bar{a}$  and  $\bar{b}$  are the intensities of each spectrum averaged over all wavelengths. As  $r$  approaches 1, the spectra are considered to be more similar and as  $r$  approaches 0, the spectra are highly dissimilar. Normalization of data does not affect the calculated correlation since the equation involves mean centering the data. It is assumed that the variables can assume a large number of values.

### ***II.1.2.1.2 Hit Quality Index (HQI)***

The Hit Quality Index (HQI), also known as the Euclidean Hit Quality Index, is a measure of distance between two spectra which is based on a dot product calculated between the spectra.<sup>56</sup> As the numerator in the HQI calculation approaches 0 (the angle between the vectors approaches 90°), the calculated value approaches  $\sqrt{2}$ .

$$HQI = \sqrt{2} \times \sqrt{1 - \frac{K \cdot Q}{\sqrt{K \cdot K} \sqrt{Q \cdot Q}}} \quad (7)$$

In the HQI calculation, K and Q represent the two spectra under comparison.

### ***II.1.2.1.3 Distribution issues:***

Parametric inferential statistic procedures for hypothesis testing rely on normally distributed data or nearly normal distribution of the data so that a robust test can perform correctly. Many parametric procedures that rely on normal distributions are addition-based procedures that facilitate easy calculation and allow the results to be stated in a concise manner.<sup>57</sup> If the data is not normally distributed, or very nearly normally distributed, the results can be misleading and ultimately inaccurate.

Most scientific data exhibits a log normal distribution, rather than a normal distribution.<sup>57</sup> In a log normal distribution, the values making up the distribution are positive and the mean is skewed from the mode. The log normal distribution represents a multiplicative version of the central theorem limit. The distribution can be converted into a normal distribution by taking the log of the values; however, the statistical calculations of the mean, standard deviation, etc. are somewhat different from the normal distribution

implied by the multiplicative term. Peak intensities in repeated LIBS spectra have been shown to exhibit distributions that are decidedly non-normal.<sup>57,66</sup> A few methods exist to address the problem non-normality regardless of the distribution, One approach is to convert the data using the Fisher's z transformation.

Fisher's transformation was developed for the purpose of dealing with a bivariate distribution. The transformation helps in converting a non-normal distribution to a more normal distribution, thereby facilitating the use of standard parametric statistical tests. The Fisher transformation is given by the following equation, where  $r$  is the value to be transformed and  $\ln$  is used to express the natural logarithm.<sup>65</sup>

$$Z = \frac{1}{2} \ln \left( \frac{1-r}{1+r} \right) \quad (8)$$

This transformation has classically been used with the Pearson correlation coefficient, which often exhibits a classic bivariate distribution. An alternative approach is to use a nonparametric statistical test that does not rely on a normal data distribution.

### ***II.1.2.2 Nonparametric Approaches:***

#### ***II.1.2.2.1 Nonparametric Permutation***

This analysis of full spectra is based on the same underlying principle as the parametric tests, namely that the similarity metric between spectra taken samples that have the same spectral profile, and presumably could come from the same source, will be larger than the similarity metric from samples with different spectral profiles and presumably from different sources. As in the parametric comparisons, a set of spectra are collected from each sample to be compared. Collecting multiple spectra from each sample allows for an

estimation of the variance in the spectra and therefore the variance in the similarity or distance metric used to compare the spectra. This knowledge is essential if we are to detect a statistical difference between spectra based on a given metric and hypothesis testing. The same sample comparisons, denoted  $D_{SS}$  above, specify the degree of similarity and variance in similarity between repeated spectra from each of the two samples. The different sample comparison, denoted as  $D_{DS}$  above, specify the degree of similarity and variance in similarity between the repeated spectra from one sample when compared only with spectra collected from the second sample. When the two samples have “identical” spectra,  $D_{SS}$  and  $D_{DS}$  will be indistinguishable at a given confidence level and  $H_0: D_{SS}=D_{DS}$  will be accepted. The same concepts apply here, but a different approach is taken to make the comparisons between the sets of spectra and a slightly different notation is used to explain the mathematical procedure.

We begin by denoting the sets of spectra from sample 1 and sample 2 as  $S_1 = \{1, 2, \dots, m\}$  and  $S_2 = \{m+1, m+2, \dots, m+n\}$ . The Fisher transformation  $z_{xy}$  of the Pearson correlation coefficient between two spectra,  $r_{xy}$ , will be used as the measure of similarity between the spectra and will take the mathematical form:

$$z_{xy} = 0.5 \ln[(1 + r_{xy}) / (1 - r_{xy})]. \quad (9)$$

A test statistic is constructed based on the difference between the average same sample and the average different sample, e.g.,  $\bar{z}_{SS} - \bar{z}_{DS}$ , as:

$$W_0 = \frac{\sum_{(i,j) \in S_1, i \neq j} z_{ij} + \sum_{(i,j) \in S_2, i \neq j} z_{ij}}{m(m-1) + n(n-1)} - \frac{\sum_{i \in S_1, j \in S_2} z_{ij}}{mn}, \quad (10)$$

Stated another way, the test statistic compares the average intra-sample similarity with the average inter-sample similarity. The null hypothesis, e.g.,  $H_0 : \bar{z}_{SS} = \bar{z}_{DS}$ , will be true when the two samples have the same profile and the intra-sample and inter-sample similarities behave the same leading to the expected value  $E(W_0) = 0$ . When the alternative, e.g.,  $H_0 : \bar{z}_{SS} \neq \bar{z}_{DS}$ , is true, the intra-sample similarities will be greater than their inter-sample counterparts and  $W_0$  will tend to be larger. It is important to assess the magnitude of  $W_0$  with respect to other groupings of the set of spectra collected from the two samples, therefore we reshuffle the spectra between two sets and recalculate the test statistic for each permutation of the spectra. A total of  $m+n$  spectra from the two samples will allow for  ${}_{m+n}C_m = (m+n)!/(m!n!)$  different unique permutations by selecting  $m$  out of  $m+n$  spectra. Since the test statistic is calculated for each permutation, this will result in  ${}_{m+n}C_m$  values of the test statistic. From the position of  $W_0$  in the ranked set of test statistic values it is possible to assign a p-value, without the need to make any assumptions concerning the normality of the distribution of  $W_0$ ,  $r_{ij}$ , or  $z_{ij}$ . The p-value for the test is defined as the fraction the  ${}_{m+n}C_m$  values that are no less than  $W_0$ , e.g., the percentage of the test statistic that are  $\geq W_0$  since  $W_0$  tends to larger values when the alternate hypothesis ( $H_a$ ) is true. If the p-value is less than the established  $\alpha$  value, traditionally set at 5%, the samples are discriminated. Given this definition of the p-value, it is obvious that the number of permutations will dictate the significance level at

which samples can be discriminated. In other words, when  $\alpha = 0.05$  a p-value smaller than  $\alpha$  would require greater than 20 test statistic values calculated from each of 20 unique permutations. In the samples compared by the nonparametric permutation method in this research, six LIBS spectra were measured for each sample giving  ${}_{12}C^6 = 924$  permutations (462 of which are unique), thereby allowing discrimination of the samples down to a significance level much lower than the traditional  $\alpha = 0.05$ .

It was important that the nonparametric permutation test performance be verified on a sample set that would be homogeneous with a high probability that the members of the data set from different sources would in fact be chemically different. To accommodate this requirement, the nonparametric permutation test was evaluated for the discrimination of a set of float glasses from different sources. The probability of two unrelated glass specimens having indistinguishable elemental compositions and refractive indices has been evaluated by several analytical techniques and calculated to lie between extremes of approximately  $10^{-5}$ – $10^{-13}$ .<sup>67,68,69</sup> Results from the glass study demonstrate the utility of the data analysis method.

As will be shown in the results section of this report, the nonparametric permutation test performs well in the discrimination of automotive paint and glass samples utilizing LIBS spectra, while holding the Type I error at the prescribed  $\alpha$  level. The parametric t-test described in section 3.2.1 does not perform well for the analysis utilizing LIBS spectra, in large part due to the deviation of the test statistic distribution from normality. As discussed above, the  $D_{SS}$  and  $D_{DS}$  comparisons are not strictly independent as required for the strictest application of the t-test. As an alternative to the t-test, a Wald test was performed on the LIBS data sets used to compare glass and

automotive paint samples. The results from the Wald test were nearly identical to the t-test results. A description of the Wald test is given in the following paragraph.

From the sample sizes used in this study, e.g.  $m=n=6$ , an estimate the variance of  $W_0$  can be calculated. We let  $E[z_{ij}] = \mu$ ,  $\text{var}(z_{ij}) = \sigma^2$ ,  $\text{cov}(z_{ij}, z_{kl}) = 0$ , and  $\text{cov}(z_{ij}, z_{jk}) = \delta^2$ , then the variance of  $W_0$  can be written as in equation 11.

$$\text{var}(W_0) = \left( \frac{2}{m(m-1) + n(n-1)} + \frac{1}{mn} \right) \sigma^2 + \left( \frac{-4mn(m+n-2)}{[m(m-1) + n(n-1)]^2} + \frac{m+n-2}{mn} \right) \delta^2 \quad (11)$$

The values  $\sigma^2$ ,  $\delta^2$ , and the  $\text{var}(W_0)$  are estimated from the sample spectra, and allows the Wald test to be performed with a test statistic  $x = W_0 / \text{sd}(W_0)$ , which is compared to a standard normal distribution. It is important to note that the Wald test statistic calculated from the comparisons of LIBS spectra does not exhibit a normal distribution. This result is discussed further in the results section of this report.

#### ***II.1.2.2.2 Alternative nonparametric approaches***

##### ***II.1.2.2.2.1 Spearman Rank Correlation:***

The Spearman rank correlation is a nonparametric measure of the correlation between two datasets. The method requires that the data from two spectral analyses be ranked and then the order of rankings for the two data sets is correlated. This method works best for datasets comprised of monotonic functions or smooth curves. Data sets comprised of a series of sharp peaks that are baseline resolved are less amenable to comparison by this technique because, although ranking of the peak intensities is straight forward, once the

noise level is reached, the rankings are meaningless. The alternatives are to either set an intensity or signal:noise ratio cutoff below which the spectral data is ignored or select those peaks that are to be correlated by some sort of masking method. Both of these approaches are less straight forward and more subjective than the full spectral perturbation method described in section 3.2.2.1. The Spearman rank correlation was not found to be useful in the comparison of LIBS spectra.

## **II.2 Experimental Approach**

### ***II.2.1 X-ray fluorescence XRF***

Access to the XRF used in this study was provided by the South Carolina Law Enforcement Department, Columbia, SC. The XRF system used in these analyses was an EDAX Eagle III microprobe with Vision 32 software. Samples were analyzed under low vacuum, which can enhance detection of aluminum, silicon and sulfur. Paint samples were analyzed with a 300  $\mu\text{m}$  spot size. A Rhodium (Rh) anode x-ray tube was operated at 40 kV and the current, in the  $\mu\text{A}$  range, was adjusted for each sample to maintain a dead time of less than 40%. The data collection rate was approximately 2000 counts per second.

Samples were prepared for XRF measurement by exposing the color, primer and base layers of each sample. The clearcoat layer was also analyzed. Analysis on the edge of a cross-cut sample was not possible since the beam spot size exceeded the individual layer thickness. Each layer of the sample was partially removed by scraping the layer away by hand using a diamond straight knife to expose the layers below. Removal of the layers was continued until the last layer was uncovered. In some cases, the primer layer was so brittle that it would break upon removal of the overlying layer. In these cases, the



bottom layer was accessed from the back of the paint chip. Each layer of every paint chip was analyzed in triplicate. In the case of repainted automobile samples, exposing each layer was problematic since the repainted layers were generally quite thin. In those cases, care was taken to ensure that only the original layers of paint were used for discrimination (e.g., those layers closest to the automobile substrate) even though every layer of the paint sample was exposed and analyzed. In some paint samples, more than one primer layer was present. In those cases, only the first primer layer (e.g., the primer layer closest to the automobile substrate) was used for sample discrimination.

### ***II.2.2 Laser ablation – Inductively coupled plasma – mass spectrometry (LA-ICP-MS)***

Access to the LA-ICP-MS used in this study was provided by the South Carolina Law Enforcement Department, Columbia, SC. The LA-ICP-MS system was equipped with a laser ablation unit (New Wave Research/Mechantek Fremont, CA, USA) model LUV 213 and an ICP-MS (Agilent Technologies, Palo Alto, CA, USA) model 7500s. The laser unit uses the 213-nm output of an Nd-YAG Q-switched laser (pulse width of 3-5 ns). The laser spot size is adjustable from 5  $\mu\text{m}^2$  to 400  $\mu\text{m}^2$ . Maximum laser energy output of 3 mJ/pulse was used for ablation.

The method used to sample the automobile paints is a drill down method, analyzing each sample at eight locations and incorporating all layers of the paint sample in each analysis. To prevent carryover of one sample analysis to the next, the data from the first position on each sample was discarded. The sampling at each position was comprised of seven acquisitions, in order to follow elemental trends through the sample. The method described above was developed from previous literature where LA-ICP-MS was used in a drill down method through the paint layers.<sup>23,25</sup> A time-resolved analytical method was

selected for this procedure to identify paint layers based on elemental trends through the sample. The time-resolved analytical method provides the instrumental responses to the elemental concentration in the sample without any further data processing. Therefore, the elemental responses can be followed in time and can identify “pockets” of excess elements through the analysis. The analysis time had to be adjusted for samples that were repainted, to account for the additional layers. The instrumental parameters for this analysis are present in Table 1.

**Table 1: Instrumental parameters for LA-ICP-MS drill-down method – automobile paint analysis**

Parameter	Value
Laser Output Energy	6 mJ/pulse
Laser Output Wavelength	213 nm
Sampling Energy	0.13 mJ (75%)
Raster Spacing	250 $\mu\text{m}$
Spot Size	50 $\mu\text{m}$
Ablation Depth	1 $\mu\text{m}$
Frequency	10 Hz
RF Power	1500 W
RF Matching	1.84 V
Carrier Gas	0.73 L/min
Ablation Cell Vol.	22 mL
Ablation Mode	Spot Drill Down
Sampling Time	10 minutes
Pre-ablation	No
Integration Time	0.1 sec/isotope
Dwell Time	61 sec

Three elements (Li, Y, and Tl) were used to check background counts of the instrument and to check the system parameters for maximum intensity. These elements were chosen to optimize the system for light, medium and heavy weighed samples. NIST standard SRM 612 was used to optimize the parameters of the system. Fifteen samples were analyzed by this method and all samples were analyzed in one day which reduces any

system drifts. Further analysis by this method was limited by instrument down time and precedence given to casework samples.

### ***II.2.3 Scanning electron microscopy – energy dispersive spectroscopy (SEM/EDS)***

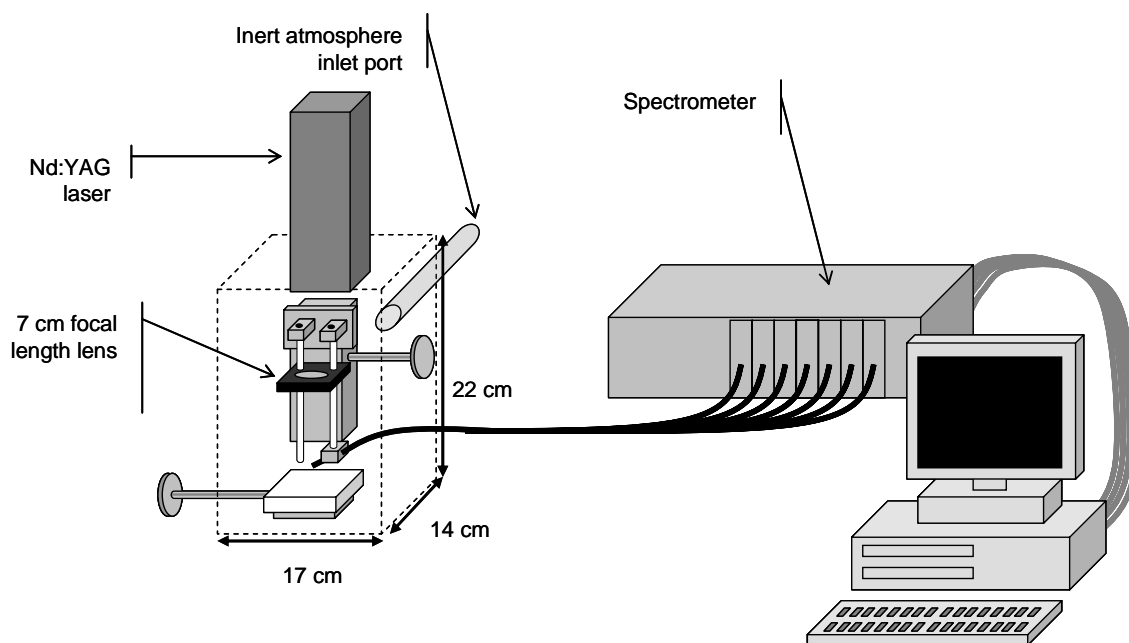
For this analytical technique, each layer of the cross section of each sample was analyzed. To obtain a viable cross-section, a thin layer of the cross section was removed with a scalpel, parallel to the direction of the layers. In the event that this method created curled, thin cross-sections, the ends were cut off to give flat cross section samples. Two to three cross-sections were cut per paint sample. Each thin layer of the cross section was placed on a carbon SEM dot for analysis. The samples were lightly coated in carbon to reduce electronic charging of the samples. For this reason, elements carbon and oxygen were removed from the analysis. Three measurements were collected per layer per sample.

### ***II.2.4 Laser induced breakdown spectroscopy (LIBS)***

The LIBS instrument used in this research was an Ocean Optics (Dunedin, FL, USA), model LIBS2000+, equipped with a Q-switched Nd-YAG pulsed laser (Big Sky Lasers, model CFR200, Bozeman, Montana, USA). The laser 1064 nm output pulse width was 9 ns. Spectra were collected at a laser output energies in the range of 20 - 98 mJ/pulse, and detector delay optimized to remove background continuum background while maintaining a strong signal. Detector delays were typically in the range of 1 - 15  $\mu$ s. The emission intensities in the 200 – 900 nm range were collected by a fiber optic bundle connected to seven linear CCD array spectrometers. The total spectral range was dispersed across 13,696 channels, giving a resolution of 0.05 nm/channel or 0.5  $\text{\AA}$ /channel. This resolution is insufficient for unambiguous identification of a given

elemental line, as described in section 2.2 based on recommendations from the “MIT Wavelength Tables”.<sup>41</sup> Since emission lines can not be unambiguously identified, full spectral comparison techniques which rely on comparison of a pattern of multiple peaks across the spectral range are deemed to provide more reliable discrimination. Analysis of LIBS spectra at higher resolution would obviate this problem.

The LIBS sample chamber consisted of a plastic box fitted with an x, y-adjustable sample stage, inert gas purge line and a safety interlock to prevent laser operation when the chamber door was open, see Figure 1. The laser pulse entered the chamber from the top and was focused on the sample by a 7 cm focal length lens, which was adjustable along the vertical axis to accommodate samples of variable thickness. The emission collection optic was optimized daily to give maximum signal intensity from a glass sample (microscope slide) and once fixed, the collection optic was held in position relative to the focusing lens and translated vertically with the lens. Data acquisition and some data analysis were performed using the Ocean Optics OOILIBS software.



**Figure 1. Diagram of the LIBS sample chamber, spectrometer and computer control.**

Two sample analysis methods were attempted. The first utilized an approach whereby a paint chip cross-section was analyzed by laser ablation of all layers in a single pulse by ablating perpendicular to the cross-section edge. This method of analysis was unsatisfactory due to reproducibility issues brought on by shot-to-shot variations which appeared to be due to difficulties reproducibly aligning the laser on center of the chip. The second sampling approach, which proved more useful, was to ablate the sample from perpendicular to the clearcoat surface of the sample, collecting repeated spectra in a drill-down procedure.

In the drill down procedure, samples were placed on a thin layer of poly isobutylene that had been softened at 200 °C and smoothed to allow for flat mounting of the paint chips. Poly isobutylene was chosen as a mounting medium because this elastomer does not produce a LIBS signal on the instrument used in these experiments when the elastomer is present in bulk or thick layers. This prevented the problem of contaminating the LIBS spectra from a paint chip when the drilldown experiment breached the bottom layer of the chip, exposing the underlying medium. The number of spectra averaged into each composite spectrum was varied in two ways for these analyses. In the first method, a single drilldown was performed to determine the number of laser pulsed required to breach the sample. Subsequent drilldown experiments on that sample were performed with the determined number of laser pulses and the spectra were averaged to give a composite spectrum of the sample. The 20 samples indicated in Table 2, Experiment 4, and the 93 samples indicated in Table 2, Experiment 5, were analyzed by this method. In the second data averaging method, each sample was interrogated with

five laser pulsed and the resulting spectra averaged to give a composite spectrum. The samples in Table 3 were analyzed by this method.

### II.3 Samples Analyzed

The following tables list the samples analyzed in this research. Table 2 lists a set of samples that were analyzed by several analytical methods: (1) XRF(MANOVA), (2) SEM/EDX(MANOVA), (3) LA-ICP-MS(MANOVA), (4) LIBS(MANOVA and t-test), 5 LIBS(t-test). Table 3 lists a second set of paint samples that were analyzed only by LIBS for data analysis by the nonparametric permutation method. The second set of LIBS samples were chosen to increase the number of samples in common paint groups having the same number of layers and to ensure that enough sample was available to allow repeat measurements to ensure that the Type I error rate was being held at the specified level.

**Table 2: Automotive paint set analyzed by (1) XRF, (2) SEM/EDX (3) LA-ICP-MS and (4 and 5) LIBS. Sample year of manufacture, make and model, generic color groups, the presence of effect pigments (EP) and the number of layers of paint are listed.**

No.	Year	Make	Model	Color Group	EP	Layers	1	2	3	4	5
1	2004	Chevrolet	Impala	white	no	2	x	x			
2	2003	Dodge	Neon	yellow	no	5	x	x	x		x
3	2001	Ford	F-series	white	no	3	x	x			
4	2002	Ford	Focus	tan	yes	2	x	x			
5	2002	Ford	Mustang	silver	yes	2	x	x			x
6	2003	Ford	Explorer	silver	yes	4	x	x			x
7	2003	Honda	CRV	white	no	4	x	x			
8	2004	Honda	Civic	red	no	2	x	x			x
9	2006	Kia	Sportage	silver	yes	3	x	x			
10	1998	Mazda	626	red	yes	3					x
11	2004	Nissan	Frontier	red	no	1	x	x			x
12	2004	Nissan	Infiniti G35	silver	yes	1	x	x			x
13	2004	Nissan	Pathfinder	silver	yes	6	x	x			x
14	2004	Nissan	Quest	blue	yes	2	x	x			x
15	2005	Nissan	Altima	black	yes	1	x	x			
16	1997	Oldsmobile	Regency	white	no	3					
17	2003	Pontiac	Grand Am	silver	yes	2	x	x			
18	2005	Pontiac	GTO	red	no	8	x	x			x
19	2003	Saturn	Ion	silver	yes	3	x	x			x
20	2005	Saturn	Ion	white	no	2	x	x			

21	2005	Subaru	Outback	black	yes	3	x	x			
22	1991	Toyota	MR2	silver	yes	2	x	x			
23	2003	Toyota	4Runner	silver	yes	4	x	x			x
24	2004	Toyota	Scion xB	silver	yes	2	x	x			x
25	2003	Volkswagon	Passat	silver	yes	3					x
26	2004	Dodge	Caravan	silver	yes	7	x	x	x	x	x
27	1995	Chevrolet	S-10	red	yes	3	x	x	x	x	x
28	1989	Chrysler	New Yorker	black	no	5	x	x		x	x
29	2004	Ford	Ranger Edge	blue	yes	4	x	x			x
30	1985	BMW	285i	black	yes	9					x
31	1987	Toyota	Std. 1/2 ton	white	no	9	x	x			x
32	1996	Ford	Explorer	red	yes	4	x	x			x
33	1987	Dodge	Ram	blue	yes	4	x	x		x	x
34	1999	Saab	9-3 S	green	yes	3	x	x			x
35	1988	BMW	325i	tan	yes	3	x	x	x	x	x
36	2001	Volkswagon	Golf	pink	no	2					x
37	2000	Toyota	Tacoma	white	no	3	x	x			x
38	1995	Honda	Civic	white	no	5	x	x			x
39	1999	Ford	Explorer	blue	no	4	x	x			x
40	1999	Dodge	Ram	black	no	3	x	x		x	x
41	1995	GMC	Jimmy	blue	yes	2					
42	1998	Dodge	Caravan	blue	yes	4	x	x	x		x
43	1999	Ford	Taurus	tan	yes	5	x	x	x	x	x
44	1995	Ford	Crown Victoria	white	no	3		x	x		x
45	1999	Hyundai	Sonata	black	no	1	x	x			x
46	2002	Kia	Rio	blue	yes	3	x	x	x	x	x
47	2000	Mazda	626	green	yes	4	x	x		x	x
48	1992	Toyota	Corolla	tan	yes	7	x	x			x
49	1997	Nissan	Sentra	red	yes	5	x	x			x
50	1993	Nissan	Maxima	red	yes	4	x	x	x		x
51	1998	Nissan	Altima	white	no	4	x	x			x
52	2001	Chrysler	PT Cruiser	silver	yes	4	x	x	x		x
53	2004	Chevrolet	Tahoe	green	yes	5	x	x		x	x
54	1996	Ford	Mustang	purple	yes	6	x	x			x
55	1994	Cadillac	Deville	green	yes	6	x	x	x		x
56	1997	Mercury	Grand Marquis	red	yes	3					
57	1994	Chevrolet	Camaro	blue	yes	4	x	x			x
58	1996	Ford	Mustang	purple	yes						
59	1994	Ford	Probe	blue	yes	2	x	x			x
60	1998	Ford	F150 Lariat	black	no	5	x	x			x
61	2003	Honda	Acura CL	silver	yes	4	x	x		x	x
62	2005	Chrysler	Pacifica	silver	yes	3	x	x		x	x
63	2006	Suzuki	Forenza	silver	yes	5	x	x			x
64	2000	Mazda	MPV	tan	yes	3	x	x			x
65	2006	Dodge	Ram	blue	yes	3	x	x			x
66	1998	Nissan	Infiniti I30	red	yes	5	x	x		x	x
67	2004	Mitsubishi	Lancer	black	no	4	x	x			x
68	2004	Kia	Spectra	tan	yes	5	x	x			x
69	2006	Nissan	Sentra	blue	yes	4	x	x			x
70	2005	Chevrolet	Tahoe	green	yes	4	x	x		x	x

71	1999	Subaru	Legacy	green	yes	3	x	x		x
72	2006	Toyota	Scion tC	silver	yes	4	x	x		x
73	2003	Mazda	Protégé	green	yes	4	x	x		x
74	2004	Chevrolet	Classic	white	no	3	x	x		x
75	2005	Toyota	Tacoma	red	no	4	x	x		x
76	2002	Kia	Optima	blue	yes	3	x	x		x
77	2004	Pontiac	Sunfire	black	yes	3	x	x		x
78	2001	GMC	Safari	tan	yes	4	x	x		x
79	2002	Buick	Century	tan	yes	3	x	x	x	x
80	2005	Ford	Excursion	white	no	3	x	x	x	x
81	2005	Nissan	Maxima	tan	yes	5	x	x		x
82	2004	Dodge	Grand Caravan	white	no	4		x	x	x
83	2005	Dodge	Stratus	blue	yes	5	x	x		x
84	1992	Mercedes	300E	silver	yes	3	x	x		x
85	2000	Nissan	Xterra	silver	yes	5	x	x		x
86	1998	Ford	F150 Lariat	red	yes	7	x	x		x
87	2005	Jeep	Liberty	red	no	5	x	x	x	x
88	2003	Mitsubishi	Galant	white	yes	3	x	x		x
89	2004	Chevrolet	Cavalier	silver	yes	3	x	x		x
90	2005	Mazda	Tribute	blue	yes	3	x	x	x	x
91	2002	Mazda	B3000	red	no	4	x	x		x
92	2002	Oldsmobile	Bravada	white	no	3	x	x		x
93	2004	Dodge	Dakota	silver	yes	4	x	x		x
94	2004	Toyota	Tundra	silver	yes	3	x	x		x
95	2002	Landrover	Discovery II	black	yes	2	x	x		x
96	2005	BMW	325i	black	no	3	x	x		x
97	2005	Lincoln	Navigator	white	no	3	x	x	x	x
98	2006	GMC	Canyon	black	yes	4	x	x		
99	2004	Ford	Ranger	white	no	3	x	x		x
100	2002	Chrysler	Voyager	red	no	4	x	x	x	x
101	2004	Chevrolet	Silverado	black	yes	3	x	x		x
102	2006	Honda	Pilot	red	yes	3	x	x	x	x
103	2004	GMC	Envoy	green	yes	3	x	x		x
104	2001	Dodge	Dakota	silver	yes	4	x	x	x	x
105	2002	Honda	Accord	blue	yes	3	x	x	x	x
106	2004	Chevrolet	Colorado	red	no	3	x	x	x	x
107	2006	Toyota	4Runner	silver	yes	4	x	x	x	
108	2004	Pontiac	Montana	tan	yes	5	x	x	x	x
109	2004	Chevrolet	Blazer	red	no	4	x	x	x	x
110	2002	Pontiac	Grand Am	red	no	4	x	x		x

**Table 3: Automotive paint set analyzed by LIBS for nonparametric permutation data analysis. Sample year of manufacture, make and model, generic color groups, the presence of effect pigments and the number of layers of paint are listed.**

No.	Year	Maker	Model	Color Group	Effect Pigment	Layers
1	2002	Kia	Rio	blue	yes	3
2	2006	Dodge	Ram	blue	yes	3
3	2002	Kia	Optima	blue	yes	3



4	2005	Mazda	Tribute	blue	yes	3
5	2002	Honda	Accord	blue	yes	3
6	1987	Dodge	Ram	blue	yes	4
7	1998	Dodge	Caravan	blue	yes	4
8	2006	Nissan	Sentra	blue	yes	4
9	2001	Chrysler	Concorde	tan	yes	3
10	2002	Chrysler	Sebring	tan	yes	3
11	2000	Saturn	SC2	tan	yes	3
12	1988	BMW	325i	tan	yes	3
13	1993	Toyota	Camry	tan	yes	4
14	2001	GMC	Safari	tan	yes	4
15	2004	Kia	Spectra	tan	yes	5
16	2005	Nissan	Maxima	tan	yes	5
17	1999	Ford	Taurus	tan	yes	5
18	2004	Pontiac	Montana	tan	yes	5
19	2002	Mazda	B3000	red	no	4
20	2002	Chrysler	Voyager	red	no	4
21	2004	Chevrolet	Blazer	red	no	4
22	2002	Pontiac	Grand Am	red	no	4
23	1995	Chevrolet	S-10	red	yes	3
24	2006	Honda	Pilot	red	yes	3
25	1998	Ford	F150	red	yes	3
26	1996	Ford	Explorer	red	yes	4
27	1993	Nissan	Maxima	red	yes	4
28	1997	Nissan	Sentra	red	yes	5
29	1998	Infiniti	I30	red	yes	5
30	2005	BMW	325i	black	no	3
31	1998	Nissan	Altima	black	no	3
32	2004	Mitsubishi	Lancer	black	no	4
33	2000	VW	Jetta	black	no	4
34	1997	VW	Jetta	black	no	4
35	2002	Nissan	Sentra	black	no	5
36	1997	Honda	Civic	black	no	5
37	2004	Pontiac	Sunfire	black	yes	3
38	1999	Honda	Accord	black	yes	3
39	2004	GMC	Envoy	green	yes	3
40	2001	Honda	Accord	green	yes	3
41	1996	Honda	Accord	green	yes	4
42	1993	Mitsubishi	3000GT	green	yes	4
43	2004	Chevrolet	Tahoe	green	yes	5
44	1995	Volvo	Wagon	green	yes	5
45	1999	VW	Passat	green	yes	5
46	2004	Chevrolet	Cavalier	silver	yes	3
47	2005	Chrysler	Pacifica	silver	yes	3
48	2001	Chrysler	PT Cruiser	silver	yes	4
49	2003	Acura	CL	silver	yes	4
50	2001	Dodge	Dakota	silver	yes	4
51	2003	Toyota	4Runner	grey	yes	4
52	2000	Nissan	Xterra	silver	yes	5
53	2006	Suzuki	Forenza	silver	yes	5
54	2003	Suzuki	Aerio	silver	yes	5
55	2000	Chrysler	Voyager	white	no	3

56	2002	Chrysler	Truck	white	no	3
57	1990	Dodge Ram	Van B250	white	no	3
58	1999	Chrysler	300M	white	no	3
59	1996	Dodge	Grand Caravan	white	no	3
60	1999	Ford	Expedition	white	no	3
61	1997	Ford	F150	white	no	3
62	1995	Ford	Crown Victoria	white	no	3
63	1995	Ford	Mustang	white	no	3
64	1998	Oldsmobile	Achieva	white	no	3
65	1998	Buick	Century	white	no	3
66	1997	Oldsmobile	88/LS	white	no	3
67	1997	Mercury	Grand Marquis	white	no	3
68	2000	Chevrolet	Camaro	white	no	3
69	2002	Pontiac	Grand Prix	white	no	3
70	2000	Ford	Focus	white	no	3
71	2001	Ford	Ranger	white	no	3
72	1998	Dodge	Ram 1500	white	no	4
73	1998	Ford	Expedition	white	no	4
74	1995	Chevrolet	Caprice	white	no	4
75	1998	Isuzu	Rodeo	white	no	4
76	2000	Kia	Sephia	white	no	4
77	2004	Dodge	Grand Caravan	white	no	4
78	1993	Ford	Mustang	white	no	5
79	2004	Ford	Econoline	white	no	5
80	1996	Ford	Mustang	white	no	5
81	1997	Buick	Lesabre	white	no	5
82	1995	Honda	Civic	white	no	5
83	1999	Honda	Civic	white	no	6
84	2002	Buick	Century	white	no	6
85	1997	Mercury	Cougar	white	no	6
86	1998	Chevrolet	Blazer	white	no	6
87	1995	Acura	Integra	white	no	7
88	2002	Dodge	Stratus	white	no	7
89	1999	Mitsubishi	Montero	white	no	7
90	1997	Ford	Explorer	white	no	7

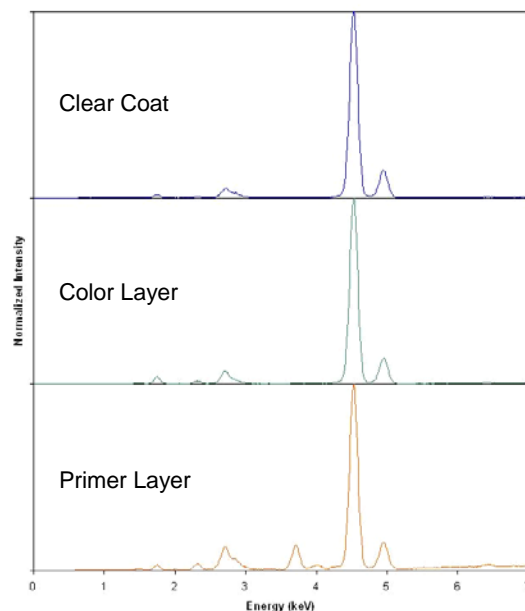
### III. Results:

#### III.1 XRF Discrimination:

##### III.1.1 ANOVA/Tukey HSD Data Analysis:

The automobile paint samples indicated under Experiment 1 in Table 2 were analyzed as described in section II.2.1. Only the clear, color and primer layers were use in the

discrimination. An example of XRF spectra from the clearcoat, color and primer layers of a single paint sample are shown in Figure 2.



**Figure 2: XRF spectra of the clear, color and primer layer of a paint sample.**

The most intense peak observed in each spectrum was titanium (Ti). The presence of metals in the clearcoat layer is attributed to environmental contamination that was not removed by surface cleaning and possible contamination from the underlying layers. Emission intensities from a series of elements were used to calculate discriminating ratios and the ratios were analyzed by ANOVA to determine an F value (ratio of between-group to within-group variance). Table 4 gives a list of the emission ratios used in the discrimination of each of the three layers examined, the associated F-statistic and the percent discrimination for each emission ratio within each of the three layers. The discrimination of the paint samples, given in Table 4, based on the clearcoat alone yielded 52.2% discrimination at a 95% confidence level. The samples were 42.9% discriminate based on the XRF of the color layer and 63.6% of the samples could be

discriminated by the first primer layer (also at the 95% confidence level). Overall, 83.4% of the samples were discriminated based on XRF elemental ratios. Since all of the comparisons were made between samples from different sources, each failure to discriminate represents a Type II error. The statistical test holds the Type I error at 5%.

**Table 4: XRF discriminating ratios for automobile paint samples at a 95% CL (only K lines included)**

Emission Ratios	Clear Layer		Color Layer		Primer Layer	
	F-Statistic	% Discrimination	F-Statistic	% Discrimination	F-Statistic	% Discrimination
Mg/Al	2.0	1.9	10.4	10.8		
Na/Mg					1.4	1.9
Si/Mo	4.0	5.1	2.7	3.7	3.0	2.6
S/P	10.8	9.5	2.2	1.7	3.8	5.6
Cl/K	6.2	6.2	2.6	6.2	2.2	1.3
Ti/Fe	11.6	11.7	19.7	31.7	16.12	28.0
Cr/Mn	8.4	5.7	44.4	10.6		
Ni/Co	3.4	3.5	2.4	5.4	3.0	3.6
Cu/Zn	2.1	3.3	10.3	6.9	62.1	9.3
Rb/Zn	6.4	9.8			8.1	8.7
Ti/Al	5.25	8.0	13.0	10.8	5.62	6.8
Ca/V			6.8	5.6		
Total Discrimination		52.8		42.9		63.6
Overall Discrimination				83.6		

The discrimination values given in Table 4 represent unique pairwise comparisons across all paint samples, irrespective of sample color, number of layers in the paint sample and the presence or absence of effect pigments. Ignoring these factors could give a discrimination level that exceed what would normally be expected in forensic practice, where two paints of different color, for example, would never be discriminated based on XRF. The factors of color, number of layers and presence of effect pigments are taken into account in Tables 5 – 12. For example, a paint with 3 layers and no effect pigments is indicated as 3n, 4 layers with effect pigment is 4y, etc.

**Table 5: XRF Clear layer discrimination by color group, irrespective of the number of paint layers or the presence or absence of effect pigments.**

Total % Discrimination	0.528	Pairwise Comparisons (#PWC)						5202
Color	black	blue	green	red	silver	tan	white	Total
# PWC	66	91	28	136	253	45	120	739
% D	0.318	0.308	0.677	0.360	0.494	0.489	0.775	0.483

**Table 6: XRF Clear Layer discrimination by color group, number of paint layers or the presence or absence of effect pigments (designated y or n).**

Layers		black	blue	green	red	silver	tan	white	Total
2n	compared	0	0	0	0	0	0	1	1
	% Discriminated	0.000	0.000	0.000	0.000	0.000	0.000	1.000	1.000
2y	compared	0	1	0	0	6	0	0	7
	% Discriminated	0.000	1.000	0.000	0.000	0.833	0.000	0.000	0.857
3n	compared	1	0	0	0	0	0	28	29
	% Discriminated	1.000	0.000	0.000	0.000	0.000	0.000	0.786	0.793
3y	compared	3	10	3	1	15	3	0	35
	% Discriminated	0.333	0.200	1.000	1.000	0.333	0.000	0.000	0.343
4n	compared	0	0	0	10	0	0	3	13
	% Discriminated	0.000	0.000	0.000	0.200	0.000	0.000	0.000	0.154
4y	compared	0	10	3	1	28	0	0	42
	% Discriminated	0.000	0.400	0.333	1.000	0.286	0.000	0.000	0.333
5n	compared	1	0	0	0	0	0	0	1
	% Discriminated	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
5y	compared	0	0	0	3	1	6	0	10
	% Discriminated	0.000	0.000	0.000	0.000	1.000	1.000	0.000	0.700
Total	compared	5	21	6	15	50	9	32	138
	% Discriminated	0.400	0.333	0.667	0.267	0.380	0.667	0.719	0.471

**Table 7: XRF color layer discrimination by color group, irrespective of the number of paint layers or the presence or absence of effect pigments.**

Total % Discrimination	0.429	Pairwise Comparisons (#PWC)						5202
Color	black	blue	green	red	silver	tan	white	Total
# PWC	66	91	28	136	253	45	120	739
% D	0.439	0.275	0.464	0.426	0.368	0.200	0.683	0.418

**Table 8: XRF color layer discrimination by color group, number of paint layers or the presence or absence of effect pigments (designated y or n).**

Layers		black	blue	green	red	silver	tan	white	Total
2n	compared	0	0	0	0	0	0	1	1
	% Discriminated	0.000	0.000	0.000	0.000	0.000	0.000	1.000	1.000

2y	compared	0	1	0	0	6	0	0	7
	% Discriminated	0.000	1.000	0.000	0.000	0.667	0.000	0.000	0.714
3n	compared	1	0	0	0	0	0	28	29
	% Discriminated	1.000	0.000	0.000	0.000	0.000	0.000	0.786	0.793
3y	compared	3	10	3	1	15	3	0	35
	% Discriminated	0.000	0.000	0.667	0.000	0.000	0.000	0.000	0.057
4n	compared	0	0	0	10	0	0	3	13
	% Discriminated	0.000	0.000	0.000	0.300	0.000	0.000	0.000	0.231
4y	compared	0	10	3	1	28	0	0	42
	% Discriminated	0.000	0.400	0.000	0.000	0.214	0.000	0.000	0.238
5n	compared	1	0	0	0	0	0	0	1
	% Discriminated	1.000	0.000	0.000	0.000	0.000	0.000	0.000	1.000
5y	compared	0	0	0	3	1	6	0	10
	% Discriminated	0.000	0.000	0.000	0.000	1.000	0.000	0.000	0.100
Total	compared	5	21	6	15	50	9	32	138
	% Discriminated	0.400	0.238	0.333	0.200	0.220	0.000	0.719	0.333

**Table 9: XRF primer layer discrimination by color group, irrespective of the number of paint layers or the presence or absence of effect pigments.**

Total % Discrimination	0.6364	Pairwise Comparisons (#PWC)						5202
Color	black	blue	green	red	silver	tan	white	Total
# PWC	66	91	28	136	253	45	120	739
% D	0.7273	0.5604	0.7500	0.6471	0.5810	0.5556	0.7417	0.6346

**Table 10: XRF primer layer discrimination by color group, number of paint layers or the presence or absence of effect pigments (designated y or n).**

Layers		black	blue	green	red	silver	tan	white	Total
2n	compared	0	0	0	0	0	0	1	1
	% Discriminated	0.000	0.000	0.000	0.000	0.000	0.000	1.000	1.000
2y	compared	0	1	0	0	6	0	0	7
	% Discriminated	0.000	1.000	0.000	0.000	0.833	0.000	0.000	0.857
3n	compared	1	0	0	0	0	0	28	29
	% Discriminated	1.000	0.000	0.000	0.000	0.000	0.000	0.714	0.724
3y	compared	3	10	3	1	15	3	0	35
	% Discriminated	1.000	0.400	1.000	0.000	0.400	1.000	0.000	0.543
4n	compared	0	0	0	10	0	0	3	13
	% Discriminated	0.000	0.000	0.000	0.700	0.000	0.000	0.667	0.692
4y	compared	0	10	3	1	28	0	0	42
	% Discriminated	0.000	0.900	0.667	1.000	0.571	0.000	0.000	0.667
5n	compared	1	0	0	0	0	0	0	1
	% Discriminated	1.000	0.000	0.000	0.000	0.000	0.000	0.000	1.000
5y	compared	0	0	0	3	1	6	0	10
	% Discriminated	0.000	0.000	0.000	0.667	1.000	0.167	0.000	0.400
Total	compared	5	21	6	15	50	9	32	138
	% Discriminated	1.000	0.667	0.833	0.667	0.560	0.444	0.719	0.645

**Table 11: XRF total discrimination by color group, irrespective of the number of paint layers or the presence or absence of effect pigments.**

Total % Discrimination	0.836	Pairwise Comparisons (#PWC)	5202					
Color	black	blue	green	red	silver	tan	white	Total
# PWC	66	91	28	136	253	45	120	739
% D	0.818	0.703	0.857	0.897	0.771	0.756	0.967	0.824

**Table 12: XRF total discrimination by color group, number of paint layers or the presence or absence of effect pigments (designated y or n).**

Layers		black	blue	green	red	silver	tan	white	Total
2n	compared	0	0	0	0	0	0	1	1
	% Discriminated	0.000	0.000	0.000	0.000	0.000	0.000	1.000	1.000
2y	compared	0	1	0	0	6	0	0	7
	% Discriminated	0.000	1.000	0.000	0.000	0.833	0.000	0.000	0.857
3n	compared	1	0	0	0	0	0	28	29
	% Discriminated	1.000	0.000	0.000	0.000	0.000	0.000	1.000	1.000
3y	compared	3	10	3	1	15	3	0	35
	% Discriminated	1.000	0.600	1.000	1.000	0.600	1.000	0.000	0.714
4n	compared	0	0	0	10	0	0	3	13
	% Discriminated	0.000	0.000	0.000	0.900	0.000	0.000	0.667	0.846
4y	compared	0	10	3	1	28	0	0	42
	% Discriminated	0.000	0.900	0.667	1.000	0.607	0.000	0.000	0.690
5n	compared	1	0	0	0	0	0	0	1
	% Discriminated	1.000	0.000	0.000	0.000	0.000	0.000	0.000	1.000
5y	compared	0	0	0	3	1	6	0	10
	% Discriminated	0.000	0.000	0.000	0.667	1.000	1.000	0.000	0.900
Total	compared	5	21	6	15	50	9	32	138
	% Discriminated	1.000	0.762	0.833	0.867	0.640	1.000	0.969	0.804

Tables 5, 7, and 9 give the discrimination percentages and number of comparisons for each paint color group in the clear, color, primer and Table 11 breaks down the total discrimination across all layers based on the color groups. It is evident from these tables that while the total number of pairwise comparisons drops significantly, from 5202 to 739, the percent discrimination does not drop dramatically. The total discrimination drops from 83% to 82% (Table 11). Similar effects are seen for each of the individual layers,

with the largest decrease seen for the clear layer where the discrimination drops from 53% to 48%. Tables 6, 8, and 10 further breakdown the discrimination percentages for each paint color group in the clear, color, primer layers by limiting the comparisons to those samples with the same number of layers and the presence or absence of effect pigments. Table 11 breaks down the total discrimination across all layers based on the number of paint layers and the presence or absence of effect pigments. The total number of pairwise comparisons drops significantly, from 5202 to 138, yet the percent discrimination only drops from 83% to 80% (Table 12). Again, similar effects are seen for each of the individual layers; however, the largest decrease seen for the color layer where the discrimination drops from 43% to 33%.

These results show this analytical methods is giving an approximately 17% – 20% Type II error rate across all comparisons, despite limiting the comparisons to those samples with the same number of layers, the same generic color grouping and the presence or absence of effect pigments.

### **III.2 SEM/EDS Discrimination:**

The SEM image and EDS spectra of three layers from an automobile paint cross section are shown in Figure 3. The cross section shows three layers: a clearcoat, a color coat and the primer coat (from top to bottom). This image was obtained in the SEM with a backscatter detector. There is a significant difference between the spectra from each layer. The titanium peak at 4.5 keV present in the color and the primer layers but not in the clearcoat. There are a few peaks that differentiate the color and the primer, i.e. sulfur (2.4 keV) and tin (3.7 keV). The carbon and oxygen peaks are not used to discriminate



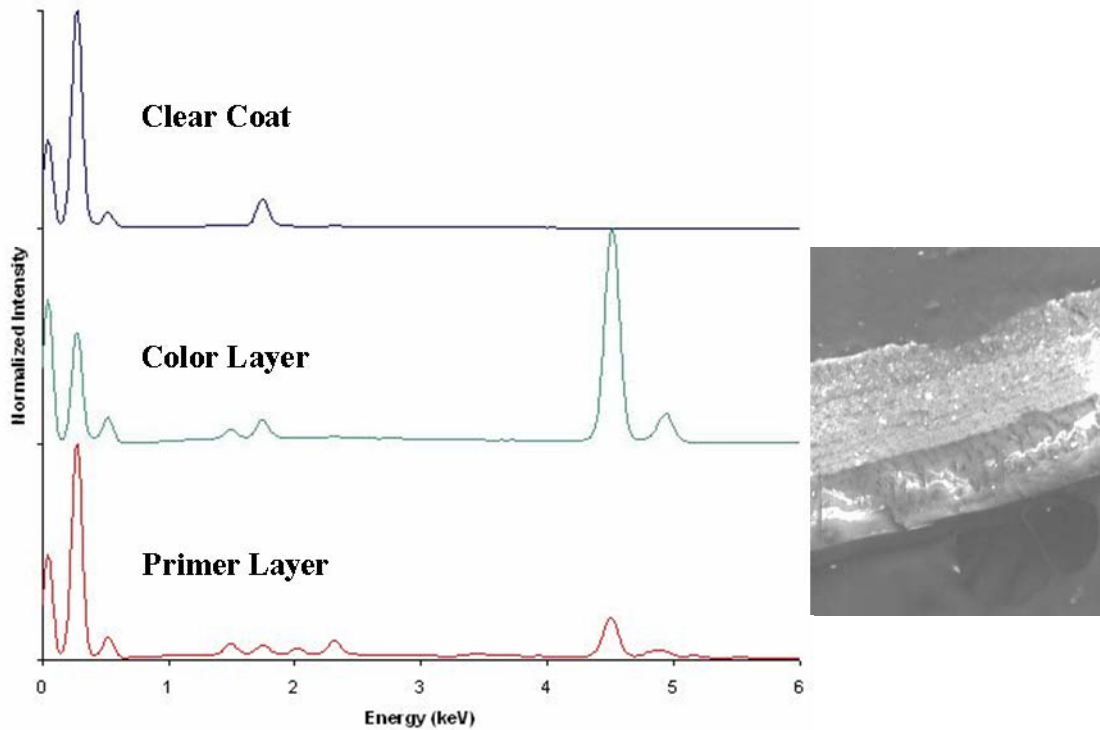


Figure 3. SEM image and EDX spectra of the cross-section of 2005 Ford Excursion (3 layers observed)

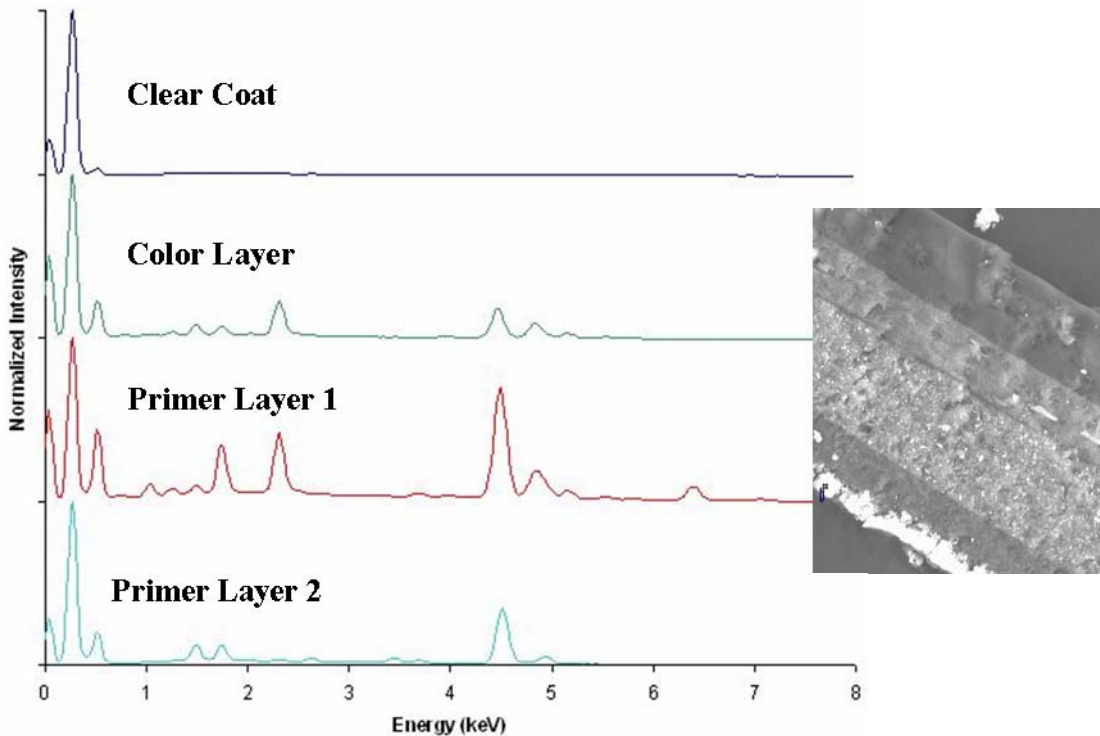


Figure 4. SEM image of cross-section and EDX spectra of 2005 Toyota Sienna five layer paint.

samples because each sample is coated lightly with carbon to prevent charging and oxygen is ubiquitous through the samples.

From the paint sample cross section imaged in Figure 4, five layers can be differentiated. The clearcoat is shown to be on the upper right, followed by the color layer, two primer layers and a metallic layer. The metallic layer is residual metal from the metallic substrate of the automobile. The clearcoat spectrum from the Sienna contains fewer peaks than the spectrum from the Ford Expedition clearcoat, which contains a silicon peak at 1.7 keV. The color and the first primer layer of the two samples are similar, with the exception of the iron peak (6.4 keV) present in Sienna's first primer layer. The first and second primer layers of the Sienna are differentiated by the sulfur peak (2.4 keV) and the barium (4.9 keV) both of which are located in the first primer layer. These two SEM images and the associated spectra show the potential for this method to differentiate automotive paint samples. Statistical discrimination of the samples listed as Experiment 2 in Table 2 by MANOVA of a set of element emission ratios and by a full spectral comparison method.

### ***III.2.1 ANOVA/Tukey HSD Data Analysis***

The set of 102 samples indicated under Experiment 2 in Table 2 were analyzed by SEM/EDX as described in section II.2.3. Only the clear, color and primer layers were used in the discrimination. Three measurements were obtained per layer per sample. A series of potential discrimination ratios were analyzed to determine those with the highest F-statistics and minimal linear correlation between the ratios to maximize the information content. The discrimination ratios used for the clear, color and primer layers are given in Table 13 along with the associated F-statistic. The discrimination ratios were analyzed by

the ANOVA/Tukey test at a 95% confidence level. Table 13 also lists the total discrimination for each layer. The highest discrimination was found in the color layer (43%) with the clear and primer layers providing 34% and 33% discrimination respectively. The overall discrimination was 73%. Since all of the comparisons were made between samples from different sources, each failure to discriminate represents a Type II error. The statistical test holds the Type I error at 5%.

The discrimination values given in Table 13 represent unique pairwise comparisons across all paint samples, irrespective of sample color, number of layers in the paint sample and the presence or absence of effect pigments. Ignoring these factors could give a discrimination level that exceed what would normally be expected in forensic practice, where two paints of different color, for example, would never be discriminated based on SEM/EDX. The factors of color, number of layers and presence of effect pigments are taken into account in Tables 14 – 21.

**Table 13. Element emission ratio F-statistic and percent discrimination of SEM/EDS spectra from the clear, color and primer layers of the paint samples indicated as Experiment 2 in Table 2.**

	Clear		Color		Primer	
	F-statistic	% Discrimination	F-statistic	% Discrimination	F-statistic	% Discrimination
Al/Ni	1.378	0.032				
Al/Si	2.133	0.043	5.733	0.019	2.210	0.019
Ba/Bi			1.551	0.018		
Ba/Ce	2.231	0.019	1.838	0.019		
Ba/Fe			18.078	0.104		
Bi/Mn			3.000	0.019		
Ca/Ti					5.530	0.038
Cl/Fe			1.713	0.019	3.518	0.034
Cl/K	1.611	0.019			2.434	0.019
Cr/Co	1.412	0.019				
Cr/Fe			2.704	0.054	2.542	0.019
Cu/Zn			3.902	0.019		
Fe/Cu	2.467	0.038	10.280	0.057	6.933	0.089
Mg/Na	1.913	0.019	1.367	0.019	3.134	0.038

Na/Al					1.420	0.019
Na/Si	6.030	0.093	7.382	0.111	5.065	0.038
Ni/Mo					1.464	0.037
P/Cl	1.402	0.038	2.300	0.029	7.346	0.019
Pb/Bi	1.325	0.019				
Pt/Fe			2.205	0.019	1.778	0.033
S/Cl			5.785	0.103	1.457	0.000
Si/Fe					1.862	0.019
Si/P			1.569	0.019		
Ti/Fe					2.330	0.030
Ti/V	1.717	0.036				
V/Cr	1.825	0.033				
Zn/Br			1.442	0.018		
Total Discrimination		0.345		0.439		0.337
Overall Discrimination				0.733		

**Table 14: SEM/EDX clearcoat discrimination by color group, irrespective of the number of paint layers or the presence or absence of effect pigments.**

Total % Discrimination	0.345	Number of Comparisons						5202
Color	black	blue	green	red	silver	tan	white	Total
# PWC	66	91	28	136	253	45	120	739
% D	0.485	0.495	0.250	0.419	0.146	0.578	0.242	0.315

**Table 15: SEM/EDS clearcoat discrimination by color group, number of paint layers or the presence or absence of effect pigments (designated y or n).**

Layers		black	blue	green	red	silver	tan	white	Total
2n	compared	0	0	0	0	0	0	1	1
	% Discriminated	-	-	-	-	-	-	0.000	0.000
2y	compared	0	1	0	0	6	0	0	7
	% Discriminated	-	1.000	-	-	0.000	-	-	0.143
3n	compared	1	0	0	0	0	0	28	29
	% Discriminated	0.000	-	-	-	-	-	0.464	0.448
3y	compared	3	10	3	1	15	3	0	35
	% Discriminated	0.667	0.000	0.000	1.000	0.267	0.667	-	0.257
4n	compared	0	0	0	10	0	0	3	13
	% Discriminated	-	-	-	0.400	-	-	0.000	0.308
4y	compared	0	10	3	1	28	0	0	42
	% Discriminated	-	0.900	0.667	0.000	0.000	-	-	0.262
5n	compared	1	0	0	0	0	0	0	1
	% Discriminated	0.000	-	-	-	-	-	-	0.000
5y	compared	0	0	0	3	1	6	0	10
	% Discriminated	-	-	-	0.333	0.000	0.500	-	0.400
Total	compared	5	21	6	15	50	9	32	138
	% Discriminated	0.400	0.476	0.333	0.400	0.080	0.556	0.406	0.304

**Table 16: SEM/EDX color coat discrimination by color group, irrespective of the number of paint layers or the presence or absence of effect pigments.**

Total % Discrimination	0.439	Pairwise Comparisons (#PWC)	5202					
Color	black	blue	green	red	silver	tan	white	Total
# PWC	66	91	28	136	253	45	120	739
% D	0.621	0.275	0.464	0.544	0.506	0.200	0.242	0.432

**Table 17: SEM/EDS color coat discrimination by color group, number of paint layers or the presence or absence of effect pigments (designated y or n).**

Layers		black	blue	green	red	silver	tan	white	Total
2n	compared	0	0	0	0	0	0	1	1
	% Discriminated	-	-	-	-	-	-	1.000	1.000
2y	compared	0	1	0	0	6	0	0	7
	% Discriminated	-	0.000	-	-	0.667	-	-	0.571
3n	compared	1	0	0	0	0	0	28	29
	% Discriminated	0.000	-	-	-	-	-	0.250	0.241
3y	compared	3	10	3	1	15	3	0	35
	% Discriminated	0.000	0.000	0.667	0.000	0.600	0.667	-	0.371
4n	compared	0	0	0	10	0	0	3	13
	% Discriminated	-	-	-	0.400	-	-	0.000	0.308
4y	compared	0	10	3	1	28	0	0	42
	% Discriminated	-	0.700	0.000	1.000	0.429	-	-	0.476
5n	compared	1	0	0	0	0	0	0	1
	% Discriminated	1.000	-	-	-	-	-	-	1.000
5y	compared	0	0	0	3	1	6	0	10
	% Discriminated	-	-	-	0.000	1.000	0.000	-	0.100
Total	compared	5	21	6	15	50	9	32	138
	% Discriminated	0.200	0.333	0.333	0.333	0.520	0.222	0.250	0.370

**Table 18: SEM/EDX primer coat discrimination by color group, irrespective of the number of paint layers or the presence or absence of effect pigments.**

Total % Discrimination	0.337	Pairwise Comparisons (#PWC)	5202					
Color	black	blue	green	red	silver	tan	white	Total
# PWC	66	91	28	136	253	45	120	739
% D	0.439	0.681	0.250	0.118	0.372	0.200	0.150	0.318

**Table 19: SEM/EDS primer coat discrimination by color group, number of paint layers or the presence or absence of effect pigments (designated y or n).**

Layers		black	blue	green	red	silver	tan	white	Total
2n	compared	0	0	0	0	0	0	1	1

2y	% Discriminated	-	-	-	-	-	-	0.000	0.000
	compared	0	1	0	0	6	0	0	7
3n	% Discriminated	-	1.000	-	-	0.500	-	-	0.571
	compared	1	0	0	0	0	0	28	29
3y	% Discriminated	0.000	-	-	-	-	-	0.250	0.241
	compared	3	10	3	1	15	3	0	35
4n	% Discriminated	0.667	0.700	0.000	0.000	0.533	0.667	-	0.543
	compared	0	0	0	10	0	0	3	13
4y	% Discriminated	-	-	-	0.000	-	-	0.000	0.000
	compared	0	10	3	1	28	0	0	42
5n	% Discriminated	-	0.400	0.000	0.000	0.357	-	-	0.333
	compared	1	0	0	0	0	0	0	1
5y	% Discriminated	0.000	-	-	-	-	-	-	0.000
	compared	0	0	0	3	1	6	0	10
Total	% Discriminated	-	-	-	0.000	0.000	0.000	-	0.000
	compared	5	21	6	15	50	9	32	138
	% Discriminated	0.400	0.571	0.000	0.000	0.420	0.222	0.219	0.319

**Table 20: SEM/EDX total discrimination by color group, irrespective of the number of paint layers or the presence or absence of effect pigments.**

Total % Discrimination 0.733 Pairwise Comparisons (#PWC) 5202

Color	black	blue	green	red	silver	tan	white	Total
# PWC	66	91	28	136	253	45	120	739
% D	0.848	0.890	0.643	0.750	0.743	0.578	0.450	0.710

**Table 21: SEM/EDS total discrimination by color group, number of paint layers or the presence or absence of effect pigments (designated y or n).**

Layers		black	blue	green	red	silver	tan	white	Total
2n	compared	0	0	0	0	0	0	1	1
	% Discriminated	-	-	-	-	-	-	1.000	1.000
2y	compared	0	1	0	0	6	0	0	7
	% Discriminated	-	1.000	-	-	1.000	-	-	1.000
3n	compared	1	0	0	0	0	0	28	29
	% Discriminated	0.000	-	-	-	-	-	0.643	0.621
3y	compared	3	10	3	1	15	3	0	35
	% Discriminated	1.000	0.700	0.667	1.000	0.867	0.667	-	0.800
4n	compared	0	0	0	10	0	0	3	13
	% Discriminated	-	-	-	0.700	-	-	0.000	0.538
4y	compared	0	10	3	1	28	0	0	42
	% Discriminated	-	1.000	0.667	1.000	0.607	-	-	0.714
5n	compared	1	0	0	0	0	0	0	1
	% Discriminated	1.000	-	-	-	-	-	-	1.000
5y	compared	0	0	0	3	1	6	0	10
	% Discriminated	-	-	-	0.333	1.000	0.500	-	0.500
Total	compared	5	21	6	15	50	9	32	138
	% Discriminated	0.800	0.857	0.667	0.667	0.740	0.556	0.594	0.703

Tables 14, 16, and 18 give the discrimination percentages and number of comparisons for each paint color group in the clear, color, primer and Table 20 breaks down the total discrimination across all layers based on the color groups. The total number of pairwise comparisons drops significantly, from 5202 to 739; however, the percent discrimination does not drop dramatically when taking into account the generic color group. The total discrimination drops from 73% to 71% (Table 20). Similar effects are seen for each of the individual layers, with the largest decrease seen for the primer layer where the discrimination drops from 34% to 32%. Tables 15, 17, and 19 further breakdown the discrimination percentages for each paint color group in the clear, color, primer layers by limiting the comparisons to those samples with the same number of layers and the presence or absence of effect pigments. Table 21 breaks down the total discrimination across all layers based on the number of paint layers and the presence or absence of effect pigments. The total number of pairwise comparisons drops significantly, from 5202 to 138, yet the total percent discrimination only drops from 73% to 70% (Table 21). Again, similar effects are seen for each of the individual layers; however, the largest decrease seen for the color layer where the discrimination drops from 44% to 37%.

These results show this analytical methods is giving an approximately 27% – 30% Type II error rate across all comparisons, despite limiting the comparisons to those samples with the same number of layers, the same generic color grouping and the presence of absence of effect pigments.

### III.2.2 SEM/EDS Full Spectra Discrimination by Student's t-test/HQI

The full spectra (0 to 10 keV) of each layer of the samples indicated as Experiment 2 in Table 2 were discriminated at a confidence level of 99% by the t-test using the HQI similarity metric. The Bonferonni correction was employed to combine the discrimination from each layer, giving a total discrimination at a confidence level of 97%. The overall discrimination of the paint samples, utilizing all three layers, was 84.3% ( $\alpha = 0.03$ ). This approach gives a higher discrimination than the MANOVA/Tukey HSD approach from section III.2.1. When the comparisons were limited to only those samples in the same color group, the percent discrimination dropped to 81%. When the comparisons were further limited to only those samples in the same color group that also had the same number of layers of paint and the presence/absence of effect pigments, the overall discrimination dropped to 79%, which still exceeds the discrimination by MANOVA/Tukey HSD. The increase in discrimination may be attributable to additional features in the spectral profile that are not taken into account in the MANOVA analysis, which only took into consideration the elemental ratios given in Table 13.

**Table 22: SEM/EDX (with HQI similarity metric) total discrimination by color group, irrespective of the number of paint layers or the presence or absence of effect pigments.**

Total % Discrimination	0.843	Pairwise Comparisons (#PWC)	5050					
Color	black	blue	green	red	silver	tan	white	Total
# PWC	66	91	28	136	253	36	120	730
% D	0.856	0.824	0.893	0.772	0.731	0.861	0.917	0.805

**Table 23: SEM/EDS (with HQI similarity metric) total discrimination by color group, number of paint layers or the presence or absence of effect pigments (designated y or n).**

Layers	black	blue	green	red	silver	tan	white	Total
2n compared	0	0	0	0	0	0	1	1



2y	% Discriminated	-	-	-	-	-	-	1.000	1.000
	compared	0	1	0	0	6	0	0	7
3n	% Discriminated	-	1.000	-	-	0.500	-	-	0.571
	compared	1	0	0	0	0	0	28	29
3y	% Discriminated	1.000	-	-	-	-	-	0.929	0.931
	compared	3	10	3	1	15	3	0	35
4n	% Discriminated	0.667	0.600	1.000	1.000	0.933	1.000	-	0.829
	compared	0	0	0	10	0	0	3	13
4y	% Discriminated	-	-	-	0.600	-	-	1.000	0.692
	compared	0	10	3	1	28	0	0	42
5n	% Discriminated	-	0.700	0.667	1.000	0.714	-	-	0.714
	compared	1	0	0	0	0	0	0	1
5y	% Discriminated	1.000	-	-	-	-	-	-	1.000
	compared	0	0	0	3	1	6	0	10
Total	% Discriminated	-	-	-	1.000	1.000	0.667	-	0.800
	compared	5	21	6	15	50	9	32	138
	% Discriminated	0.800	0.667	0.833	0.733	0.760	0.778	0.938	0.790

### III.3 Laser Ablation – Inductively Coupled Plasma – Mass Spectrometry (LA-ICP-MS)

The method of analysis chosen for this sample set was the ANOVA/Tukey HSD data analysis. Seven acquisitions were collected per position to collect isotopic intensities down through the sample. The first five acquisitions per position were used in the comparison of the paint samples. Paint layers could not be identified based on the repetitions alone. Hence, the intensities from each repetition were summed for each acquisition. The summed values were used to create discriminating ratios for each acquisition. Ratios were calculated between isotopes exhibiting a large response (> 100,000 counts) and between isotopes with a smaller response (< 100,000 counts). Isotopic abundance ratios were calculated for each of the five acquisitions and, in addition, the isotopic abundances were totaled through each of the five layers and the ratios calculated for the summed intensities. The summed intensities were calculated for LA-ICP-MS and not for XRF or EDS, because LA-ICP-MS data was collected as a drill down while the other data was collected on specific layers of the paint. The ratios used

for LA-ICP-MS analysis were chosen based on their F-statistic values and their Pearson correlation values such that redundant information from multiple ratios was reduced. The isotope ratios and associated F-statistic used for discrimination in each of the five acquisitions, and the summed intensities, are given in Table 24. Note that the F-statistic values listed in Table 24 are generally much larger than those listed in Table 4 (XRF data) and Table 14 (EDS data). Since the F-statistic is calculated as the ratio of the variance between groups (samples) to the ratio of variance within groups (samples), these values reflect a greater discriminating capability for LA-ICP-MS. Discrimination greater than 95% was achieved for each acquisition and overall from the summed isotopic intensity ratios at the 95% confidence level. This is due to the high precision of this instrument which yielded high F-statistic values for each discriminating ratio, Table 24.

**Table 24: LA-ICP-MS isotopic discrimination ratios and associated F-statistic for each successive acquisition (1-5) acquired during drill down analysis of automobile paints. The ratios were used to discriminate between paint samples by MANOVA/Tukey HSD data analysis at the 95% confidence level.**

Isotope Ratio	Acquisition 1		Acquisition 2		Acquisition 3	
	F-value	% Discrimination	F-value	% Discrimination	F-value	% Discrimination
Na/Mg	29.3	43.1	1.8	5.9	106.5	57.5
Al/Si	88.0	31.4	47.6	43.8	135.4	31.4
Pb/Ba	66.3	21.6	25.3	11.1		
Cs/Co			40.8	21.6	242.1	21.6
V/Cr	121.1	11.1				
Zr/Br	16.8	21.6	124.6	45.8	58.6	11.1
Zn/Cu						
S/Ni	22.4	11.1	6.3	11.1	13.4	35.9
Ca/Cl	13.1	32.0	17.2	38.6	180.4	73.2
Ti/Sn	35.7	55.6		0		
Fe/Mn	24.1	41.8	6.0	17.0	33.2	35.9
P/S	68.9	46.4	130.6	58.8	1547.8	36.6
Overall Discrimination		98.0		97.4		95.4

**Table 24 continued.**

Isotope Ratio	Acquisition 4		Acquisition 5		Summed Acquisitions	
	F-value	% Discrimination	F-value	% Discrimination	F-value	% Discrimination
Na/Mg	547.9	71.9	738.8	73.9	48.7	52.9

Al/Si	184.5	47.1	98.5	43.1	157.1	61.4
Pb/Ba			127.8	11.1		
Cs/Co	223.8	11.1			278.7	28.1
V/Cr	379.6	11.1				
Zr/Br	270.7	49.7	205.0	45.8	146.6	25.5
Zn/Cu					49.5	0.0
S/Ni	40.8	56.2	66.9	55.6	114.7	53.6
Ca/Cl	394.3	33.3	426.0	53.6	430.2	56.2
Ti/Sn					227.0	41.8
Fe/Mn	59.0	66.7	139.1	70.6		
P/S	223.9	29.4	172.9	43.1	367.3	49.0
Overall		100.0		100.0		100.0
Discrimination						

The discrimination percentages given in Table 24 are based on all sample pairwise comparisons and do not necessarily reflect the comparison percentages that might be expected in a forensic laboratory where comparisons would be limited to samples of the same general color group and probably samples with the same number of layers and the presence or absence of effect pigments. However, when the discrimination percentage is as high as shown in Table 24, it is probably unnecessary to further examine the discrimination as a function of color, number of layers and the presence of effect pigments. For the sake of completeness, analysis of the effects of color, number of layers and presence of effect pigments is shown in Tables 25 - 30 for acquisitions 1 – 3, which gave less than 100% discrimination.

**Table 25: LA-ICP-MS acquisition 1 discrimination by color group, irrespective of the number of paint layers or the presence or absence of effect pigments.**

Total % Discrimination	0.980		Pairwise Comparisons (#PWC)					162
Color	black	blue	green	red	silver	tan	white	Total
# PWC	0	3	0	15	6	3	0	27
% D	0.000	1.000	0.000	0.933	1.000	1.000	0.000	0.963

**Table 26: LA-ICP-MS acquisition 1 discrimination by color group, number of paint layers or the presence or absence of effect pigments (designated y or n).**

Layers		black	blue	green	red	silver	tan	white	Total
3y	compared	0	1	0	1	0	0	0	2
	% Discriminated	-	1.000	-	1.000	-	-	-	1.000
4n	compared	0	0	0	1	0	0	0	1
	% Discriminated	-	-	-	1.000	-	-	-	1.000
4y	compared	0	0	0	0	3	0	0	3
	% Discriminated	-	-	-	-	1.000	-	-	1.000
5y	compared	0	0	0	0	0	1	0	1
	% Discriminated	-	-	-	-	-	1.000	-	1.000
Total	compared	0	1	0	2	3	1	0	7
	% Discriminated	-	1.000	-	1.000	1.000	1.000	-	1.000

**Table 27: LA-ICP-MS acquisition 2 discrimination by color group, irrespective of the number of paint layers or the presence or absence of effect pigments.**

Total % Discrimination 0.974 Pairwise Comparisons (#PWC) 162

Color	black	blue	green	red	silver	tan	white	Total
# PWC	0	3	0	15	6	3	0	27
% D	0.000	1.000	0.000	0.933	1.000	0.667	0.000	0.926

**Table 28: LA-ICP-MS acquisition 2 discrimination by color group, number of paint layers or the presence or absence of effect pigments (designated y or n).**

Layers		black	blue	green	red	silver	tan	white	Total
3y	compared	0	1	0	1	0	0	0	2
	% Discriminated	-	1.000	-	1.000	-	-	-	1.000
4n	compared	0	0	0	1	0	0	0	1
	% Discriminated	-	-	-	1.000	-	-	-	1.000
4y	compared	0	0	0	0	3	0	0	3
	% Discriminated	-	-	-	-	1.000	-	-	1.000
5y	compared	0	0	0	0	0	1	0	1
	% Discriminated	-	-	-	-	-	1.000	-	1.000
Total	compared	0	1	0	2	3	1	0	7
	% Discriminated	-	1.000	-	1.000	1.000	1.000	-	1.000

**Table 29: LA-ICP-MS acquisition 3 discrimination by color group, irrespective of the number of paint layers or the presence or absence of effect pigments.**

Total % Discrimination 0.954 Pairwise Comparisons (#PWC) 162

Color	black	blue	green	red	silver	tan	white	Total
# PWC	0	3	0	15	6	3	0	27
% D	0.000	1.000	0.000	1.000	1.000	0.333	0.000	0.926

**Table 30: LA-ICP-MS acquisition 3 discrimination by color group, number of paint layers or the presence or absence of effect pigments (designated y or n).**

Layers		black	blue	green	red	silver	tan	white	Total
3y	compared	0	1	0	1	0	0	0	2
	% Discriminated	-	1.000	-	1.000	-	-	-	1.000
4n	compared	0	0	0	1	0	0	0	1
	% Discriminated	-	-	-	1.000	-	-	-	1.000
4y	compared	0	0	0	0	3	0	0	3
	% Discriminated	-	-	-	-	1.000	-	-	1.000
5y	compared	0	0	0	0	0	1	0	1
	% Discriminated	-	-	-	-	-	0.000	-	0.000
Total	compared	0	1	0	2	3	1	0	7
	% Discriminated	-	1.000	-	1.000	1.000	0.000	-	0.857

The discrimination based on the data from acquisition 1 appears to decrease slightly from 98% to 97% when the comparisons are limited to the same color groups; however, the number of comparisons drops significantly from 162 to 27 and the difference in discrimination is due to 1 failed discrimination from 27 comparisons (3%). The failed discrimination is between two red paint samples that have different numbers of layers (samples 50 and 27). When the number of layers and presence or absence of effect pigments is included in the discrimination, the discrimination becomes 100%, Table 26, however, the total number of comparisons has dropped to seven. The discrimination based on the data from acquisition 2 follows the same behavior as the data from acquisition 1, with the same failed discrimination between two samples, 50 and 27. The discrimination based on data from acquisition 3 appears to decrease when the comparisons are limited to samples of the same color. In this case, the decrease results from the smaller number of comparisons and a single failure to discriminate between two tan paint samples that have different numbers of layers (samples 35 and 43). When the comparison is further limited to samples with different color, number of layers and presence or absence of effect pigments, the discrimination is 100%.

The time resolved analytical method was employed to allow identification of the layers of the paint sample by following the intensities of specified elements through the sample. This type of layer identification has previously reported with optimal results.<sup>23</sup> While this methodology worked for a few elements in a single paint sample, this method did not allow for layer identification. Nonetheless, the discrimination provided by LA-ICP-MS is quite high, in agreement with previous reports.<sup>23</sup>

### **III.4 LIBS Discrimination**

#### ***III.4.1 Laser Induced Breakdown Spectroscopy Discrimination (MANOVA)***

Twenty samples identified under Experiment 4 in Table 2 were analyzed by collecting triplicate drill down spectra per sample. The samples were then sampled a second time, in triplicate, so that the number of Type I errors could be rigorously determined.

It is important to note, as pointed out earlier in this report, the wavelength resolution of the LIBS spectrometer used for this research was insufficient to conclusively identify the origin of the emission. The spectra were baseline corrected to allow for peak intensities to be extracted without influence of the underlying continuum and 52 wavelengths were chosen for MANOVA analysis based on peaks that were common in five representative baseline corrected spectra. The intensities of these 52 wavelengths were analyzed by MANOVA to determine whether there was a significant difference between the intensities at different wavelengths and by a Tukey post hoc test to determine if there was sufficient difference between the samples. The Wilks' lambda value from the MANOVA was 0.00 while the p-value was  $<.001$ , indicating a difference between the emission intensities at a minimum of two wavelengths when compared simultaneously across all samples. The results warranted an ANOVA for each wavelength and it was found that each wavelength had a p-value of  $<.001$ , which

indicated that there was a significant difference between at least two of the samples. The F values obtained from each ANOVA indicated the relative strength of each wavelength's discrimination. The set of 52 wavelengths were reduced to 14 wavelengths that were able to discriminate the largest number of different sample comparisons while limiting the number of discriminated same sample comparisons to a minimum. Table 31 lists the 14 wavelengths that were used in the discrimination, along with the spectral assignment (where possible) and the respective F-statistic. Discrimination matrices were developed for each wavelength and combined to for each wavelength was combined with others by establishing that discrimination of one comparison by one wavelength meant that the samples were discriminated regardless of the result from other wavelengths.

**Table 31. Wavelengths used for MANOVA, their possible elemental identification and discrimination**

Wavelength (nm)	Emission Assignment <sup>41</sup>	F-Statistic	% Discrimination of Samples
394.43	Al	11.43	24.9
453.60	Ti	36.35	47.1
514.67	Co	50.08	55.1
517.31	Mg	67.61	61.4
519.23	NA	75.27	63.8
522.34	Ti	50.30	43.3
553.51	Ba	64.13	43.8
566.16	Ti	50.30	55.3
586.57	Ti	60.65	55.5
588.91	Na	9.80	19.7
599.67	Ni	39.36	53.1
614.09	Ba	23.61	38.3
626.04	Ti	40.09	47.2
670.70	Li	53.99	33.5

NA: Not assigned

A discrimination of 87.3% for different sample comparisons was found at the 95 % confidence while the same sample discrimination was limited to 1 in 20 (5%), the specified Type I error limit. The data is presented in Table 32 broken down by generic color group only. In limiting the comparisons within the same color group, the total

number of different sample (DS) comparisons was reduced to 76 and the percent discrimination remained high at 79%. The same sample (SS) discrimination did would not change, as the same sample comparisons do not change by limiting the comparisons to same color group. In this dataset, the different sample discrimination was lowest for the green paints (highest Type II error). The same sample discrimination was highest for the white paints (highest Type I error).

**Table 32: LIBS drill down total discrimination by color group, irrespective of the number of paint layers or the presence or absence of effect pigments.**

Total % Discrimination	0.873	Pairwise Comparisons (#PWC)	780					
Color	black	blue	green	red	silver	tan	white	Total
Different Sample								
# PWC	4	12	12	12	12	12	12	76
% D	1.000	0.833	0.417	1.000	0.750	0.750	0.917	0.789
Same Sample								
# PWC	2	3	3	3	3	3	3	20
% D	0.000	0.000	0.000	0.000	0.000	0.000	0.333	0.050

**Table 33: LIBS drill down total discrimination by color group, number of paint layers and presence or absence of effect pigments.**

Layers		black	blue	green	red	silver	tan	white	Total
3n	DS compared	4	0	0	0	0	0	12	16
	% DS Discriminated	1.000	-	-	-	-	-	0.917	0.938
	SS compared	2	0	0	0	0	0	3	5
	% SS Discriminated	0.000	-	-	-	-	-	0.333	0.200
3y	DS compared	0	4	0	0	0	4	0	8
	% DS Discriminated	-	0.500	-	-	-	1.000	-	0.750
	SS compared	0	2	0	1	1	2	0	6
	% SS Discriminated	-	0.000	-	0.000	0.000	0.000	-	0.000
4y	DS compared	0	0	4	0	0	0	0	4
	% DS Discriminated	-	-	0.500	-	-	-	-	0.500
	SS compared	0	1	2	0	1	0	0	4
	% SS Discriminated	-	0.000	0.000	-	0.000	-	-	0.000
5n	DS compared	0	0	0	4	0	0	0	4
	% DS Discriminated	-	-	-	1.000	-	-	-	1.000
	SS compared	0	0	0	2	0	0	0	2
	% SS Discriminated	-	-	-	0.000	-	-	-	0.000
5y	DS compared	0	0	0	0	0	0	0	0
	% DS Discriminated	-	-	-	-	-	-	-	-
	SS compared	0	0	1	0	0	1	0	2



7y	% SS Discriminated	-	-	0.000	-	-	0.000	-	0.000
	DS compared	0	0	0	0	0	0	0	0
	% DS Discriminated	-	-	-	-	-	-	-	-
	SS compared	0	0	0	0	1	0	0	1
	% SS Discriminated	-	-	-	-	0.000	-	-	0.000
Total	DS compared	4	4	4	4	0	4	12	32
	% DS Discriminated	1.000	0.500	0.500	1.000	-	1.000	0.917	0.844
	SS compared	2	3	3	3	3	3	3	20
	% SS Discriminated	0.000	0.000	0.000	0.000	0.000	0.000	0.333	0.050

When the pairwise comparisons are further limited to samples within the same color group that have the same number of layers and are similar in the presence of absence of effect pigments, the total number of different sample comparisons drops to 32. The percent discrimination increases slightly to 84% and the same sample discrimination stays at 5%, since limiting the comparison criteria does not change the number of same sample comparisons.

#### ***III.4.2 Laser Induced Breakdown Spectroscopy Discrimination (t-test)***

As pointed out in section III.4.1, the spectral resolution of the LIBS spectrometer used in this research does not meet the resolution recommended by Harris for the unambiguous identification of the emission.<sup>41</sup> In addition, the MANOVA/Tukey calculations can be involved, making an alternative discrimination method attractive. The method of linear correlation of two spectra is straight forward and well-known among forensic scientists; however, discrimination by hypothesis testing requires more than a single spectrum from each sample. In addition, it is known that correlations among repetitive data sets may not be normally distributed and may require transformation.<sup>70</sup> As an initial test of the discrimination power of Student t-test based methods, the samples corresponding to Experiment 4, Table 2, were analyzed by drilldown, three spectra per sample, and each sample was analyzed in duplicate to test for Type I errors. Similarly, the samples

designated as Experiment 5, were analyzed by drill down, three spectra per sample. The spectra from Experiment 5 were not repeated to test for Type I error. The spectra from both Experiments 4 and 5 were the basis for this analysis. Two different values based on the full spectrum comparison were calculated for subsequent t-tests: HQI and the Fisher transform of the Pearson correlation coefficient, Z(r). Both comparisons entailed using the full spectrum however the spectra were normalized prior to calculation of the HQI.

**Table 34. T-test results based on HQI values from drill down spectra**

Experiment	No. of samples	No. of spectra per file	HQI		Z(r)	
			Different Sample Discrimination (%)	Same Sample Discrimination (%)	Different Sample Discrimination (%)	Same Sample Discrimination (%)
4	25	3	95.0	16.0	95.5	20.0
4 (BC)	25	3	94.5	12.5	95.3	12.0
5	94	3	99.4		94.9	
5	94	5	99.2		99.6	
5 (BC)	94	5	99.3		99.7	

BC: Baseline corrected spectra

Results from the comparison across all samples, irrespective of color, number of paint layers, etc., are given in Table 34. The comparisons were performed at the 95% significance level and while the number of Type II errors are very low (e.g., >95% different sample discrimination), the Type I error (12 – 20%, Experiment 4) significantly exceeds the specified 5%, as shown for Experiment 4 results. This result is observed for both HQI and Z(r) similarity metrics. The Type II error remains low for Experiment 5 results, and while the Type I error was not specifically determined, it can be anticipated to be larger than the specified 5%. Baseline correcting (BC) the spectra did not appear to change the different sample discrimination, although the same sample discrimination decreased. Increasing the number of spectra per file decreased different sample discrimination only slightly (99.4 to 99.2). One possible explanation for the significantly

large Type I error is that the distribution of HQI is not normal and the statistical test is not robust enough to account for the lack of normality. The Fisher Z(r) transformation on the correlation coefficients is known to improve the normality of a distribution; however, the results in Table 32 do not indicate a significant decrease in the Type I error.

An alternative approach to the full spectral discrimination is to use a nonparametric analysis method that is not dependant on the assumption of normality in the distribution of the similarity metric. As a result of using the nonparametric method, you are guaranteed that the Type I error will not exceed the specified significance level. If the apparent Type I error is high, the repeat same sample analysis may be giving data that truly are different at the specified significance level. This was the case for the LIBS spectra used in the discrimination discussed in this section, which were taken in the following order. All samples were analyzed in triplicate and each sample was analyzed to comprise a set of analyses. In order to test the Type I error, the entire set of samples was analyzed a second time (each sample being analyzed in triplicate). By the time that the second set of measurements (the duplicate) was taken for each sample, instability in the LIBS instrument was giving spectra for the duplicate measurement that were statistically different from the original measurements. This effect became obvious through the use of the nonparametric data analysis method, as described below.

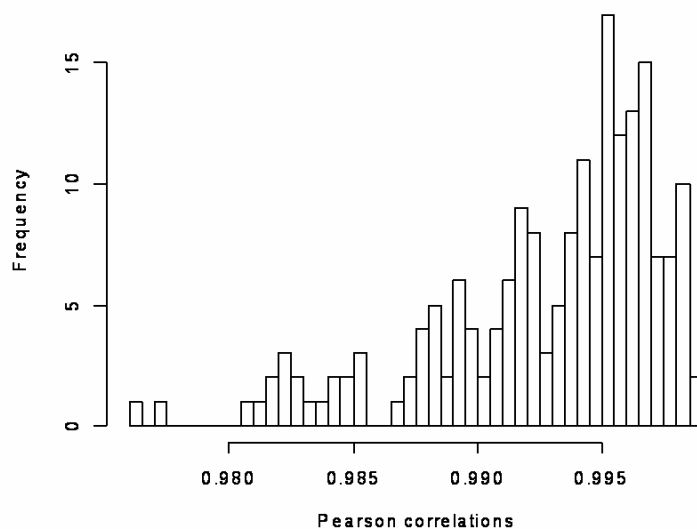
### ***III.4.3 Laser Induced Breakdown Spectroscopy Discrimination (nonparametric permutation test)***

#### ***III.4.3.1 Nonparametric permutation discrimination of glass samples***

In order to test the nonparametric permutation test, a set of LIBS spectra were collected from a set of float glass samples. Float glass samples were chosen because they are very homogeneous and are known to have a high probability of being chemically different

when they come from different sources. The composition of float glasses are known to be altered at their surface by corrosion,<sup>71,72</sup> but the probability of two unrelated float glass specimens having indistinguishable elemental compositions and refractive indices have been calculated to be less than  $10^{-5}$ .<sup>67</sup> Two experiments were conducted, the first to determine the distribution normality for the pairwise correlation of a set of LIBS spectra from a single source and the second to determine the discrimination capability of the nonparametric permutation test.

In the first test, a set of LIBS spectra were collected back-to-back from a single glass sample. A set of 20 averaged spectra, each the average of 10 single ablation spectra, was obtained from a 1990 Chevrolet Caprice glass sample. All of the unique pairwise Pearson correlations (190 comparisons in total) were calculated between the 20 average spectra. The Pearson correlations are evidently skewed as shown by the histogram in Figure 5, and remains skewed after the Fisher transformation, exhibiting a skewness of 0.11 and a kurtosis of -0.52.



**Figure 5. Distribution histogram of the Pearson correlations from 190 pairwise comparisons of 20 LIBS spectra taken from a single glass sample.**

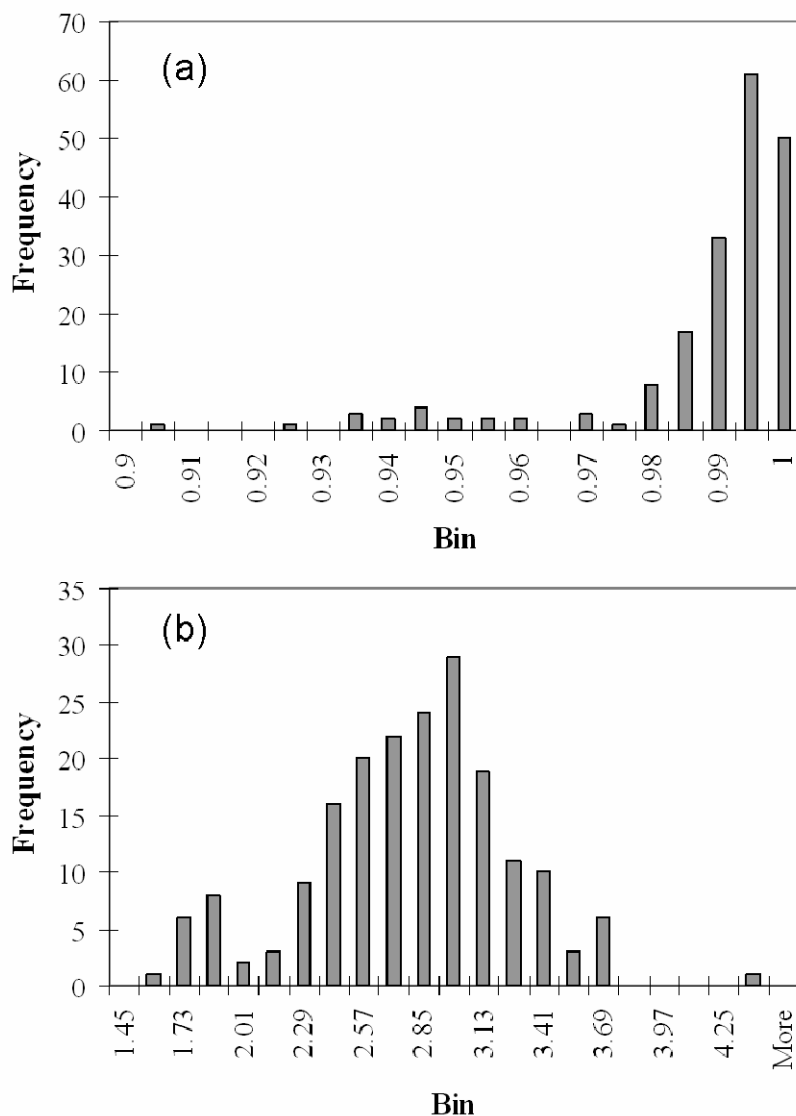
In the second test, LIBS spectra were collected over a period of several hours for a set of 20 automobile float glass samples. Six (6) average spectra were recorded for each glass sample, with each average spectrum comprised of 10 single laser shot spectra sequentially taken at different locations on the non-float side of the sample.<sup>73</sup> The power of differentiating samples from different profiles is 182/190 (96%) if the significance level is set at 0.05, and is 161/190 (85%) if the significance level is set at 0.01. A log transformation of the spectral intensity prior to the nonparametric permutation test resulted in an increase in the power of differentiating samples from different sources. The discriminating power increased to 189/190 (99%) at a significance level of 0.05 and 182/190 (96%) at a significance level of 0.01. The log transformation of the spectra has the effect of deemphasizing the most intense peaks and emphasizing the less intense peaks. These results provide significant evidence for the applicability of the nonparametric permutation test to the differentiation of samples analyzed by LIBS.

The spectra for each experiment (the first involving a single sample and the second involving 20 samples) were collected over a period of only a few hours. LIBS instrument drift was insufficient to lead to the discrimination of the same sample comparison of the first six and last six spectra collected from the 1990 Chevrolet Caprice glass sample.

#### ***III.4.3.2 Nonparametric permutation discrimination of paint samples***

Twenty drill down spectra, each an average of 5 single ablation spectra, were obtained from a 1999 Honda Civic white paint sample and the unique pairwise Pearson correlations (190 comparisons in total) were calculated. Figure 6a shows the

histogram of Pearson correlations between these 20 spectra. The Pearson correlations are not normally distributed (skewness of -2.59 and kurtosis of 6.81). Figure 6b shows the histogram for the Pearson correlation data following the Fisher transformation by equation 8. The transformation resulted in a distribution that is closer to normal (skewness -0.24 and kurtosis 0.60).



**Figure 6. Distribution of 190 unique pairwise comparisons of 20 sequentially collected drill down LIBS spectra from a white 1999 Honda Civic paint. The distributions are of (a) the Pearson correlation coefficients and (b) the Fisher transformation of the correlation coefficients, using equation 1 from the text.**

The sample set identified in Table 3 were analyzed by the drill down method described in section II.2.4, where each drill down spectrum was comprised of an average of five single laser ablation spectra repeated at the same location on the sample. The samples were grouped prior to analysis according to the color, the number of layers, and the presence of effect pigments.

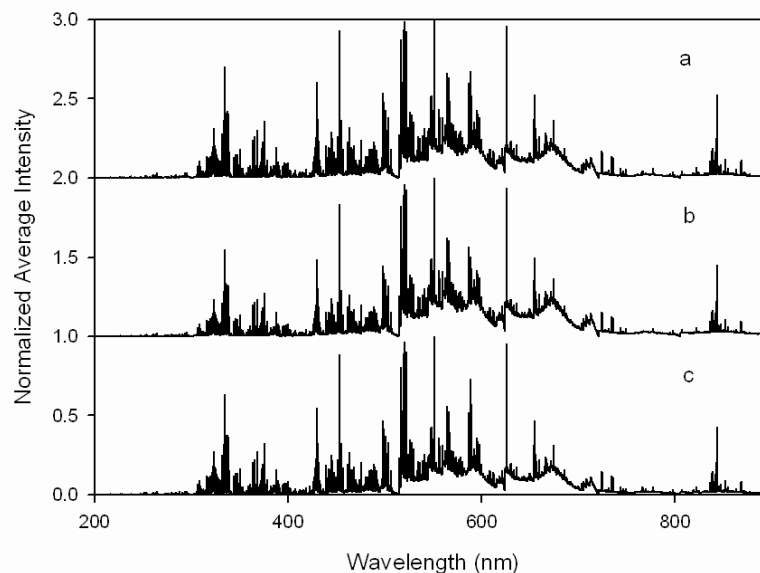
Initial attempts at discriminating the paint samples gave very high apparent Type I error rates at a significance level of 0.05. In those analyses, the samples were analyzed sequentially across all colors groups, number of layers and effect pigments (e.g. all samples were analyzed once before any duplicate analyses were made on any sample). Statistical analysis of the data continued to give very high different sample discrimination and an apparent Type I error near 20%. The order of sample analysis was modified as described below to give much better results.

In order to account for possible instrumental drift, paint samples were grouped by color, number of layers and presence or absence of effect pigments. The average spectra from each sample within the same “group” were obtained consecutively. This process was repeated until a total of 12 average drill-down spectra were collected from each of the samples within a group and then repeated for all groups of samples. Spectra from the complete set of all paints were collected over a period of four days; however, spectra from any single group of paint chips (those of the same color, number of layers, etc.) were collected over a period of only a few hours. The spectra collected from each sample were separated into two sets of six spectra to allow for an assessment of Type I errors. In order to take into account the possibility of instrumental drift; odd numbered spectra were

grouped together and even numbered spectra were grouped together. An alternative, and potentially preferable, method is to randomize the order of spectra collection from a set of samples.

A log conversion was applied to the spectral intensities from each sample and the samples were compared within groups according to their color, number of layers and the presence or absence of effect pigments. Table 33 displays the results from the permutation test. Overall the discrimination power was 830/924 (89.8%) at a significance level 5%. The Type I error was determined to be 4/90 (4.4%) which is very close to the nominal 5% level. Table 35 also shows the level of Type II and Type I error for color group, limiting comparison to samples with the same number of layers and those with and without effect pigments. The white paint chips exhibited the poorest different sample differentiation (87% overall), with the subgroup containing 5 layers having the lowest percent discrimination among samples from different sources at 70%, e.g., 30% Type II errors. The LIBS spectra for three white paint chips are shown in Figure 7. The Wald test or other parametric discrimination is not strictly valid because the distribution is not normal, nonetheless, the test can be performed on the data. The Wald test applied to the Fisher transformed data (distribution shown in Figure 6b) achieves a discrimination power of 85.2% (different sample discrimination) and Type I error of 3.33%.





**Figure 7: Libs spectra from three white paint chips taken from different automobiles.**

**Table 35: Discrimination of paint samples based on LIBS spectra and the nonparametric permutation hypothesis testing approach. Results show the percent discrimination broken down by the paint color, number of layers of paint and the presence or absence of effect pigments.**

Layers		black	blue	green	red	silver	tan	white	Total
3n	DS compared	4	0	0	0	0	0	544	548
	% DS Discriminated	1.000	-	-	-	-	-	0.875	0.876
	SS compared	2	0	0	0	0	0	17	19
	% SS Discriminated	0.000	-	-	-	-	-	0.000	0.000
3y	DS compared	4	40	4	12	4	24	0	88
	% DS Discriminated	1.000	1.000	1.000	1.000	1.000	1.000	-	1.000
	SS compared	2	5	2	3	2	4	0	18
	% SS Discriminated	0.000	0.000	0.000	0.000	0.000	0.000	-	0.000
4n	DS compared	12	0	0	24	0	0	60	96
	% DS Discriminated	0.917	-	-	1.000	-	-	0.833	0.885
	SS compared	3	0	0	4	0	0	6	13
	% SS Discriminated	0.000	-	-	0.000	-	-	0.000	0.000
4y	DS compared	0	12	4	4	24	4	0	48
	% DS Discriminated	-	1.000	1.000	1.000	1.000	1.000	-	1.000
	SS compared	0	3	2	2	4	2	0	13
	% SS Discriminated	-	0.000	0.000	0.500	0.000	0.000	-	0.077
5n	DS compared	4	0	0	0	0	0	40	44
	% DS Discriminated	1.000	-	-	-	-	-	0.700	0.727
	SS compared	2	0	0	0	0	0	5	7
	% SS Discriminated	0.500	-	-	-	-	-	0.000	0.143
5y	DS compared	0	0	12	4	12	24	0	52
	% DS Discriminated	-	-	1.000	1.000	1.000	1.000	-	1.000
	SS compared	0	0	3	2	3	4	0	12
	% SS Discriminated	-	-	0.333	0.000	0.000	0.250	-	0.167

6n	DS compared	0	0	0	0	0	0	24	24
	% DS Discriminated	-	-	-	-	-	-	0.917	0.917
	SS compared	0	0	0	0	0	0	4	4
	% SS Discriminated	-	-	-	-	-	-	0.000	0.000
7n	DS compared	0	0	0	0	0	0	24	24
	% DS Discriminated	-	-	-	-	-	-	0.958	0.958
	SS compared	0	0	0	0	0	0	4	4
	% SS Discriminated	-	-	-	-	-	-	0.000	0.000
Total	DS compared	24	52	20	44	40	52	692	924
	% DS Discriminated	0.958	1.000	1.000	1.000	1.000	1.000	0.866	0.898
	SS compared	9	8	7	11	9	10	36	90
	% SS Discriminated	0.111	0.000	0.143	0.091	0.000	0.100	0.000	0.044

## IV Conclusion:

### IV.1 Discussion of findings.

Automotive paint sample have been examined by XRF, SEM/EDS, LA-ICP-MS and LIBS with the use of hypothesis testing by several statistical methods to ascertain the sample discrimination capability. All hypothesis testing was done at the  $\alpha = 0.05$  significance level, which sets the Type I error (same sample discrimination) at 5%. The power of each method is the different sample discrimination, given the defined significance level. The power of a test may be increased (better different sample discrimination) at the expense of more Type I errors. We have chosen to compare the methods at a traditional significance level of  $\alpha = 0.05$ .

The emphasis of this work is on the comparison of LIBS to the other techniques across similar sample sets to allow for an evaluation of the utility of LIBS in forensic examination of automotive paint samples. The discrimination comparisons by LIBS are based on a comparison of spectra taken within a short period of time, as LIBS reproducibility over time remains an issue.<sup>48</sup>

The results from these studies indicate that LA-ICP-MS analysis of automotive paint samples provides a very high discrimination, as previously reported.<sup>23</sup> Although the total number of samples analyzed by LA-ICP-MS was lower than by the other methods, the different sample discrimination was 100% of 162 comparisons. The high discrimination by this technique is attributed to the reproducibility and accuracy of the method. Due to casework precedence and instrument repair issues, access to this technique was limited; however, the results reinforce the reports from other laboratories. The only issue of potential concern with this method is the potential level of Type I error. When the Type II error goes to 0%, as in this case, caution should be taken to insure that the Type I error is held at the nominal level (5% in our analyses). Although the MANOVA statistical method is considered to be highly robust, this is a potential topic to be considered in future research.

Comparison by MANOVA of the XRF spectra from 102 paint samples (5,202 unique different sample comparisons) resulted in an overall discrimination of 83.6% of the samples. Limiting the different sample comparisons to the more forensically realistic comparison of only samples of the same color, number of layers and presence or absence of effect pigments lowered the discrimination to 80.4%.

SEM/EDS gave only a 73% overall different sample discrimination, based on 5,202 comparisons, by hypothesis testing using the MANOVA approach. When the sample comparisons were limited to samples in the same color group, having the same number of layers of paint and the presence or absence of effect pigments, the discrimination remained at 70%. The MANOVA discrimination was based on a series of elements in each of three paint layers.

Analysis of paint samples by LIBS gave better discrimination than XRF, or SEM/EDS, but not as good as LA-ICP-MS. When a series of 14 emission peaks were chosen from 20 LIBS spectra for the purpose of MANOVA discrimination between the paint samples, an overall discrimination of 87.3% was obtained for 780 different sample pairwise comparisons from duplicate analyses. Limiting the pairwise comparisons to the forensically more useful comparison to samples in the same color group and having the same number of layers and presence or absence of effect pigments lowered to discrimination slightly, to 84.4%. The Type I error rate was experimentally verified to be 5% based on the duplicate analyses and same sample comparison. Discrimination of paint samples by full spectral comparison using the HQI or  $Z(r)$  similarity metric gave very high different sample discrimination ( $> 95\%$ ) but also resulted in apparent Type I error rates as high as 20%. The apparent high Type I error rates were determined to be due to temporal variations or drift in the LIBS instrument. This problem was corrected by limiting the sample analysis (with duplicate analysis) to a single group of samples, with each group comprised of samples having the same color, number of layers and presence/absence of effect pigments. With this modification in the spectral collection protocol, discrimination of the log transformation of the emission intensities of 90 paint samples gave 89.8% discrimination of the 924 different sample comparisons for samples having the same color, number of layers and presence/absence of effect pigments. The Type I error rate was 4.4%, very close to the prescribed 5% level. As a group, the white paints were the least discriminated at 86.6%. The Wald test achieved a power of 85.17% (compared with 89.8% by nonparametric permutation) and an actual size of Type I error of 3.33%.

These results demonstrate that LIBS spectra obtained by drill down analyses can be used for the discrimination of automotive paint samples, and therefore meet the goals of this study. The discrimination is better than by SEM/EDS or XRF; however, drift or temporal fluctuation in the LIBS instrument must be taken into account by a well planned sampling protocol. The results also demonstrate the importance of using hypothesis testing in the discrimination as a method of controlling the Type I error rate. Likewise, it is important to experimentally know the Type II error rate given a prescribed significance level, e.g., at an  $\alpha$  of 0.05, LIBS discrimination of automotive paint samples can be expected to result in approximately 10% Type II errors by the statistical hypothesis testing methods used in this research. The level of Type II errors can be reduced at the expense of greater Type I errors.

#### **IV.2 Implications for policy and practice.**

While commercially available LIBS instruments are available at substantially lower costs than some other instruments that may be used for automotive paint analysis, these instruments should be carefully assessed for stability and protocols should be put in place to monitor the performance of the instruments over time. Automotive paint discrimination should be conducted with appropriate hypothesis testing and the level of Type I error should be verified and the level of Type II error independently determined from a known sample set.

#### **IV.3 Implications for further research.**

The results obtained in this research point to one of the benefits of physical evidence questioned/known discrimination by hypothesis testing: the Type I error rate can be fixed and tested and the Type II rate can be independently determined. These methods should

be extended to other physical evidence discriminations where they are applicable and the methodology verified through research and implementing proper laboratory protocols.

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## VI Dissemination of Results

### Publications:

1. McIntee, EM “Forensic Analysis of Automobile Paints by Atomic and Molecular Spectroscopic Methods and Statistical Data Analyses,” University of Central Florida, 2008.
2. Bridge C “Discrimination of Forensic Trace Evidence using Laser Induced Breakdown Spectroscopy (LIBS),” University of Central Florida, 2007.
3. E. McIntee, E. Viglino, S. Kumor, L. Ni, M.E. Sigman, "Nonparametric Permutation Test for Discrimination of Float Glass Samples Based on LIBS Spectra" *Journal of Chemometrics* 2009, submitted.
4. E. McIntee, E. Viglino, C. Rinke, S. Kumor, L. Ni, M. E. Sigman\*, “Comparative Analysis of Automotive Paints by Laser Induced Breakdown Spectroscopy (LIBS) and Nonparametric Permutation Tests,” *Spectrochimica Acta, B*, 2009 submitted.

### Presentations:

1. Erin McIntee, Candice Bridge, Lt. Joseph Powell and Michael E. Sigman\* “Application of Laser-Induced Breakdown Spectroscopy to Forensic Science: Analysis of Paint Samples,” NIJ 2007 General Forensics R&D Grantees Meeting, San Antonio, TX, February 20, 2007.
2. E. McIntee, C. Bridge, M. E. Sigman “Application of Laser-Induced Breakdown Spectroscopy to Forensic Science: Analysis of Paint Samples,” Florida Annual Meeting and Exposition FAME 2007, American Chemical Society, Orlando, FL, May 10-12, 2007.
3. E. McIntee, C. Bridge and M. E. Sigman “Analysis of Automobile Paints by Laser-Induced Breakdown Spectroscopy (LIBS)” Trace Evidence Symposium, NIJ and FBI Laboratory Division, Clearwater Beach, Florida, August 13-16, 2007.
4. E. M. McIntee, C. Bridge, J. D. Powell, M. E. Sigman “ Evaluation of Laser-Induced Breakdown Spectroscopy as a Contributing Technique in the Analysis of Automobile Paint Samples,” American Academy of Forensic Sciences, Washington D.C., Feb. 18 – 23, 2008.