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

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**Document No.:           237839**

**Date Received:           February 2012**

**Award Number:           2006-DN-BX-K251**

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## *FINAL TECHNICAL REPORT*

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

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Award number 2006-DN-BX-K251

Office of Justice Programs

National Institute of Justice

Department of Justice

Points of view in this document are those of the authors and do not necessarily represent the official position of the U.S. Department of Justice. The work was done at the national Center for Forensic Science.

## **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)***

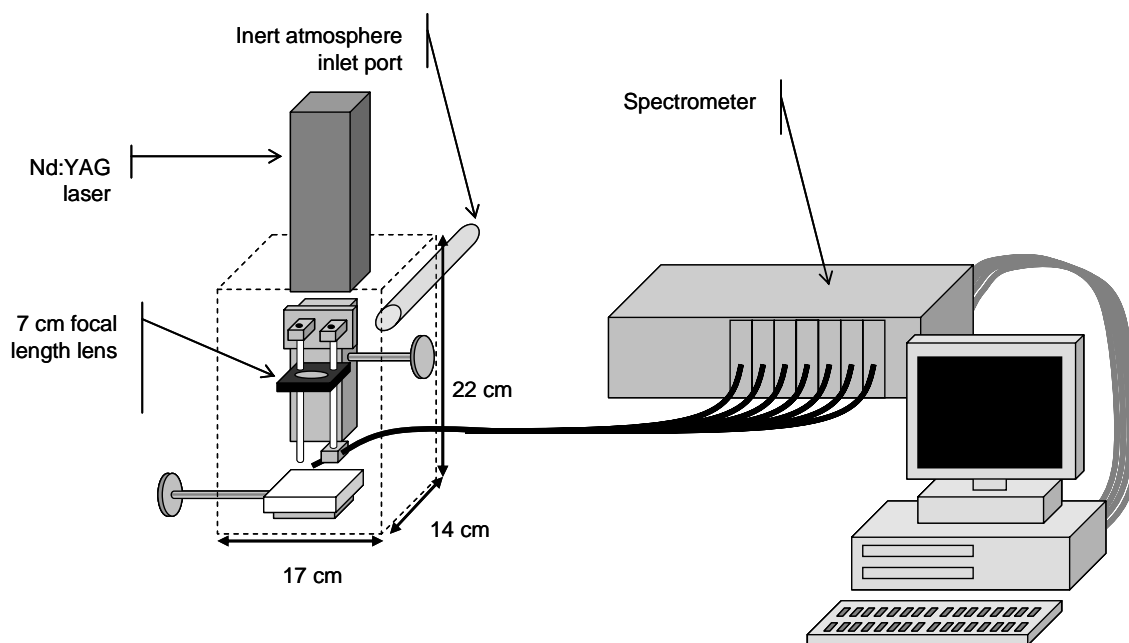
For this analytical technique, each layer of the cross section of each sample was analyzed. To obtain a viable cross-section, a thin layer of the cross section was removed with a scalpel, parallel to the direction of the layers. In the event that this method created curled, thin cross-sections, the ends 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



































































































