Volume 63B, No. 10, October 2008
ISSN 0584-8547

ELSEVIER

SPECTROCHIMICA
ACTA

PART B: ATOMIC SPECTROSCOPY
Including Spectrochimica Acta Reviews

SPECIAL ISSUE

A COLLECTION OF PAPERS PRESENTED AT THE

EURO MEDITERRANEAN SYMPOSIUM ON LASER INDUCED BREAKDOWN SPECTROSCOPY (EMSLIBS 2007)

Paris, France

11–13 September 2007

Guest Editors:
A. Semerok
P. Mauchien

Spectrochimica Acta Part B 63 (2008) 1145–1150

Contents lists available at ScienceDirect

Spectrochimica Acta Part B

journal homepage: www.elsevier.com/locate/sab

A comparison of laser ablation inductively coupled plasma mass spectrometry, micro X-ray fluorescence spectroscopy, and laser induced breakdown spectroscopy for the discrimination of automotive glass ☆

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ARTICLE INFO

Article history:
Received 22 December 2007
Accepted 30 July 2008
Available online 8 August 2008

Keywords:
LA-ICP-MS
LIBS
XRF
Glass
Forensic

ABSTRACT

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), micro X-ray fluorescence spectroscopy (μXRF), and laser induced breakdown spectroscopy (LIBS) are compared in terms of discrimination power for a glass sample set consisting of 41 fragments. Excellent discrimination results (>99% discrimination) were obtained for each of the methods. In addition, all three analytical methods produced very similar discrimination results in terms of the number of pairs found to be indistinguishable. The small number of indistinguishable pairs that were identified all originated from the same vehicle. The results also show a strong correlation between the data generated from the use of μXRF and LA-ICP-MS, when comparing μXRF strontium intensities to LA-ICP-MS strontium concentrations. A 266 nm laser was utilized for all LIBS analyses, which provided excellent precision (<10% RSD for all elements and <10% RSD for all ratios, $N=5$). The paper also presents a thorough data analysis review for forensic glass examinations by LIBS and suggests several element ratios that provide accurate discrimination results related to the LIBS system used for this study. Different combinations of 10 ratios were used for discrimination, all of which assisted with eliminating Type I errors (false exclusions) and reducing Type II errors (false inclusions). The results demonstrate that the LIBS experimental setup described, when combined with a comprehensive data analysis protocol, provides comparable discrimination when compared to LA-ICP-MS and μXRF for the application of forensic glass examinations. Given the many advantages that LIBS offers, most notably reduced complexity and reduced cost of the instrumentation, LIBS is a viable alternative to LA-ICP-MS and μXRF for use in the forensic laboratory.

1. Introduction

The evidential value of forensic glass analysis has increased over the past decade with the utilization of elemental analysis techniques, such as SEM-EDS, μXRF, ICP-MS, LA-ICP-MS, and more recently LIBS. The rise of elemental profiling for glass fragments collected at a crime scene is primarily due to the lack of discrimination power associated with refractive index measurements, which is the method typically employed by forensic laboratories for glass examinations [1]. Since glass manufacturers target a given refractive index to ensure optimum physical and optical properties, there exists only a very small degree of variation in glasses produced by the same manufacturer over time and glasses produced by different manufacturers, this is especially the case with float glass (i.e. automotive and architectural glass) [1]. Therefore, the forensic examiner must often utilize a complimentary technique in order to draw a valid association (or discrimination) between a glass fragment collected at a crime scene and its suspected source of origin. This paper compares two of the leading techniques in forensic trace elemental analysis, μXRF and LA-ICP-MS, to a less mature method, LIBS, for the analysis of automotive glass fragments collected from fourteen different vehicles in and around Miami, Florida, US. Each of these techniques requires little to no sample preparation and sample consumption is minimal; these attributes favor forensic analyses, where sample size is often an issue. The authors of this paper wish to primarily highlight the main advantages and disadvantages of the mentioned techniques in relation to forensic glass analysis, therefore bypassing the theory and background information behind such techniques. Nevertheless, an extensive review of the theory and application of these techniques as applied to the analysis of glass can be found in a paper by Almirall and Trejos [2].

Many laboratories employ μXRF for the analysis of different materials of forensic interest, including glass; this method offers lower detection capability versus some methods, such as SEM-EDS, which equates into

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☆ This paper was presented at the Euro Mediterranean Symposium on Laser Induced Breakdown Spectroscopy (EMSLIBS 2007) held in Paris (France), 11-13 September 2007, and is published in the Special Issue of Spectrochimica Acta Part B, dedicated to that conference.

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doi:10.1016/j.sab.2008.07.005

Table 1
A comparison of various figures of merit for LA-ICP-MS, μXRF, and LIBS

Parameter	μXRF	LA-ICP-MS	LIBS
Operating principle	Highly energetic X-rays knock out an inner shell electron. Relaxation of an outer shell electron into the vacant position causes emission of characteristic X-rays	Laser photons remove material from sample. Submicron-sized particles are transported into the ICP which atomizes and ionizes the ablated material; ions are detected by MS	Laser photons induce matrix breakdown at sample surface. Characteristic emission lines are produced in the UV, VIS, and near IR range
Accuracy	Semi-quantitative	Quantitative	Semi-quantitative
Precision	Fair–good (5–10% RSD)	Excellent (<5% RSD)	Fair–good (5–20% RSD)
Sensitivity	100 ppm	<1 ppm	10–50 ppm
Discrimination	Very good–excellent	Excellent	Very good–excellent
Complexity	Easy to use	Difficult to use	Very easy to use
Sample consumption	Nondestructive	Almost nondestructive	Almost nondestructive
Throughput	~30 min/analysis	~3 min/analysis	~30 s/analysis
Cost	~$120,000	~$210,000	$50,000–$150,000

higher discrimination power. In addition, as mentioned previously μXRF is a non-destructive technique, which is an attractive feature for forensic analyses. Nevertheless, the technique has several drawbacks compared to the other competing techniques, such as increased sample analysis time (lower throughput), as well as sample orientation and size requirements. More specifically, the sample must contain a reasonably flat surface with a sampling area of at least 1 mm^2 and a thickness of at least 0.5 mm for optimal analysis; unfortunately, these requirements cannot always be met with glass evidence.

The figures of merit for LA-ICP-MS include excellent sensitivity, precision, and accuracy; in addition, the technique is almost non-destructive (μg of sample is removed), requires little if any sample preparation, and sample analysis is relatively fast. Due to its isotopic and multi-element capabilities, combined with the other figures of merit, LA-ICP-MS offers excellent discrimination power. Plus, given that matrix-matched standard reference materials are readily available (i.e. NIST 600 series glasses), quantitative analysis can be performed on respective unknown glass fragments, which is arguably the most advantageous factor LA-ICP-MS offers over the competing elemental techniques. The only disadvantages of this technique are instrumental cost and complexity of operation.

Laser induced breakdown spectroscopy (LIBS) is a relatively new application for the forensic analysis of glass. This technique offers a very sensitive and rapid approach to elemental analysis and, like LA-ICP-MS, small sample sizes can be analyzed with good precision. The main disadvantage of this technique is related to the “infancy” of the method, wherein the overall analytical approach (including data analysis and instrumental optimization) must be studied in order to achieve comparable discrimination power. Despite this drawback, the instrumentation is fairly inexpensive (compared to the more mature μXRF and LA-ICP-MS techniques), is less complex to operate, has the capability for portability, and can generate large quantities of data over a short period of time (high sample throughput). An overall comparison of these three techniques can be found in Table 1.

In recent publications by Bridge et al [3,4] the techniques of LA-ICP-MS and LIBS have been compared for the analysis of glass; however, the authors of this paper would like to point out several distinct differences in the approach reported by that group, as compared to the analytical approaches reported in this paper. With regard to the LIBS data, it was stated that the detector gate delay was varied depending on the sample matrix, between 2.0 μs to 6.5 μs [4]; this large variation in the delay ultimately affects the spectra generated such that different emission lines are present or absent (a dependence on plasma evolution characteristics). As a result, if samples are being compared for discrimination purposes, as they were in the referenced paper [4], it is absolutely necessary that all parameters remain constant in order to achieve the most accurate comparisons possible.

In relation to the LA-ICP-MS sections, the authors of this paper wish to reference several articles published by our group which depict a well established method for the analysis of glass, where excellent figures of merit were validated, such as accuracy, precision, and discrimination power [5–10]. With this in mind, the rastering technique (ablation mode/type) reported by Bridge et al has been proven by our group and others to provide less accuracy and precision for the analysis of glass when compared to single spot ablation [10,11]. Less accuracy and precision translates into an increased potential of committing Type I and II errors and hence incorrect discriminations or associations. More importantly, however, is that the LA-ICP-MS method developed and utilized by our group is based on quantitative analysis with use of an internal standard. Each sample is characterized based on the actual elemental composition and not intensities or ratios of intensities. The quantification approach with use of an internal standard has several advantages over using isotopic intensities. One advantage is that signal fluctuations are minimized and systematic errors are corrected for. In addition, there is less potential for inter-day and intra-day variation which translates into more accurate sample comparisons (discrimination). Additionally, a secondary source standard can be run daily to check instrumental and method performance. It is also important that one sample is selected and run twice to check the validity of the discrimination results; more specifically, the same sample (analyzed twice throughout a sequence) should be found indistinguishable from itself. These types of quality control measures are necessary, especially in the forensic community.

The results outlined in this paper compare the discrimination results obtained utilizing μXRF, LA-ICP-MS, and LIBS, respectively, for

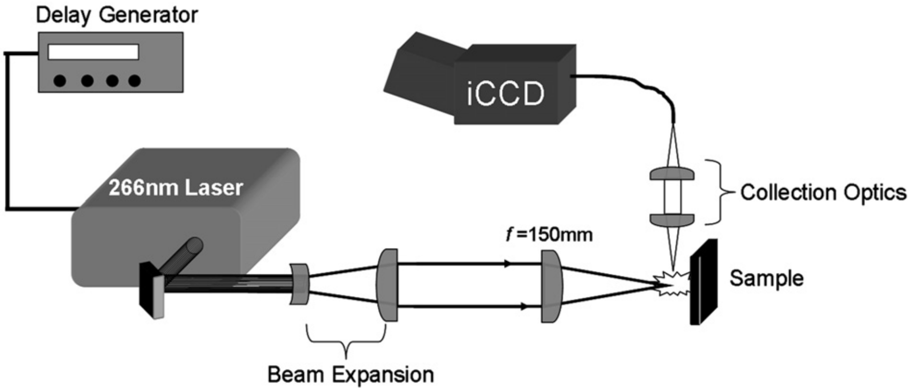

Fig. 1. Experimental setup for LIBS measurements. ICCD = intensified charge-coupled device; f = focal length.

Table 2
Description of the indistinguishable pairs found by μXRF, LA-ICP-MS, and LIBS

Pair #	Sample #	Vehicle make	Vehicle model	Year	Sample location
1[a, c]	6	Chevrolet	Cavalier	2004	Side window
	7	Chevrolet	Cavalier	2004	Rear window
2[a, b]	8	Chevrolet	Cavalier	2004	Outside winshield
	9	Chevrolet	Cavalier	2004	Inside winshield
3[a, b, c]	11	Oldsmobile	Intrigue	1998	Outside windshield
	12	Oldsmobile	Intrigue	1998	Inside windshield
4[a, b, c]	13	Dodge	Neon	2000	Outside windshield
	14	Dodge	Neon	2000	Inside windshield
5[a, b]	20	Chevrolet	Cavalier	2003	Outside windshield
	21	Chevrolet	Cavalier	2003	Inside windshield
6[a, b, c]	23	Dodge	Stratus	1998	Outside windshield
	24	Dodge	Stratus	1998	Inside windshield
7[a, c]	28	Ford	Expedition	2004	Inside windshield
	29	Ford	Expedition	2004	Outside windshield
8[a]	37	Jeep	Grand Cherokee	2001	Outside windshield
	38	Jeep	Grand Cherokee	2001	Inside windshield

[a] =indistinguishable pairs found by μXRF.
[b] =indistinguishable pairs by LA-ICP-MS.
[c] =indistinguishable pairs by LIBS.

an automotive glass sample set. The research presented in this paper is a collaborative effort between Florida International University (Miami, FL) and the Florida Department of Law Enforcement (Orlando, FL). All LA-ICP-MS and LIBS analyses were performed at Florida International University while the μXRF data was accumulated by the Florida Department of Law Enforcement. To the authors knowledge this is the first publication comparing these three techniques for the forensic analysis of glass.

2. Experimental

2.1. Sample and standard descriptions

The sample set of interest in this study is comprised of 41 different automotive glass fragments obtained from 14 different vehicles located in junkyards in and around Miami, FL. More specifically, the glass samples included 7 side window fragments, 6 rear window fragments, and 28 windshield fragments (14 inside windshield and 14 outside windshield samples) extracted from automotive vehicles spanning the years of 1995 to 2005. The non-float surfaces of the respective glass samples were examined via each of the three respective analytical techniques. Standard reference materials NIST 612 and NIST 1831 were utilized for optimization of each of the instrumental setups. In addition, NIST 612 was used as an external calibration source for quantification by LA-ICP-MS. NIST 1831 was used as a calibration verification sample (second source check standard) for LA-ICP-MS analyses to ensure accurate and precise results.

2.2. Micro X-ray fluorescence (μXRF)

An EDAX Eagle Micro X-Ray Fluorescence Spectrometer (Mahwah, NJ) equipped with a rhodium X-ray tube was utilized for this part of the study. The instrument was operated with a 40 kV excitation potential, a 17 μs time constant, and 40–45% dead time. Other instrumental parameters included a 300 μm diameter focusing capillary and 1200 s of live count time; the chamber was operated under low vacuum conditions. Five replicate analyses were performed on each fragment with a sampling target area defined by the 300 μm diameter X-ray spot. The element menu consisted of six elements (K, Ca, Ti, Fe, Sr, and Zr), which were subdivided into six element ratios (Ca/Fe, Sr/Zr, Ca/K, Fe/Zr, Fe/Sr, and Fe/Ti) to be used for sample comparisons. The intensities of the K alpha peaks corresponding to each of the respective elements were determined following background subtraction utilizing peak deconvolution and generation software.

Table 3
Percent discrimination by element, LA-ICP-MS

Element	# Indistinguishable pairs	% Discrimination
Sr	76	90.7
Zr	127	85.5
Ti	142	82.7
Rb	176	78.5
Ba	191	76.7
All (5)	5	99.4

Table 4
Percent discrimination for the most discriminating ratios by LIBS

Sample #	Peak ratio	Description	# Indist. pairs	% Discrim.
1	394.4 nm/330.0 nm	Al/Na	70	91.5
2	766.5 nm/643.9 nm	K/Ca	84	89.8
3	394.4 nm/371.9 nm	Al/Fe	86	89.5
4	438.4 nm/766.5 nm	Fe/K	90	89.0
5	534.9 nm/766.5 nm	Ca/K	91	88.9
6	371.9 nm/396.2 nm	Fe/Al	91	88.9
7	766.5 nm/645.0 nm	K/Ca	93	88.7
8	394.4 nm/460.7 nm	Al/Sr	104	87.3
9	460.7 nm/766.5 nm	Sr/K	104	87.3
10	818.3 nm/766.5 nm	Na/K	141	82.8

2.3. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS)

A New Wave Research UP213 Laser Ablation system (Fremont, CA) coupled to a Perkin Elmer ELAN 6100 DRC II ICP-MS (Waltham, MA) was used for all LA-ICP-MS analyses. The laser is a Nd:YAG (4 ns) Q-switched laser operating at 213 nm and 100% energy (27.2 J/cm^2 fluence). The repetition rate utilized for this part of the study was 10 Hz and single spot ablation mode was used with a spot size of 55 μm. Helium with a flow rate of 0.9 L/min was the carrier gas into and from the ablation chamber, which then coupled to argon (1 L/min) prior to entering the ICP. The ICP-MS parameters included an RF power of 1500 W, a plasma gas (argon) flow rate of 16 L/min, an auxiliary (argon) flow rate of 1 L/min, and a dwell time of 8.3 ms. Three replicates (pertaining to different sampling spots) for each sample were analyzed. The element menu included five isotopes: ^{49}Ti, ^{85}Rb, ^{88}Sr, ^{90}Zr, and ^{137}Ba, with ^{29}Si used as the internal standard. The quantification of each elemental concentration was calculated using Glitter software (Macquarie Ltd, Australia), where a single point calibration source (NIST 612) and the internal standard (^{29}Si) were used to convert intensity (counts per second) via integration of time-resolved spectra into concentration (in ppm). The resulting elemental concentrations were then used to characterize the given samples and ultimately to associate and/or discriminate one fragment from another. This quantification approach has been described in more detail elsewhere [5–7].

2.4. Laser induced breakdown spectroscopy (LIBS)

Experiments were conducted using a LIBS system constructed at FIU that was equipped with a New Wave Research Q-switched Nd:YAG Tempest laser (Fremont, CA) operating at 266 nm and a pulse width of 3–5 ns (full width half maximum). A 266 nm laser was chosen for this analysis due to an observed improved laser-to-sample coupling with glass (as compared to the more generally used 1064 nm irradiation for LIBS), which resulted in an increase in precision. A 3× beam expander was utilized to enlarge the beam diameter to approximately 11 mm; the laser beam was then focused perpendicularly to the sample using a plano-convex lens with a focal length (*f*) of 150 mm. An energy of 25 mJ per laser pulse and a spot size of approximately 190 μm remained constant throughout the analytical sequence and all LIBS analyses were conducted under atmospheric pressure in air. Light from the laser induced plasma

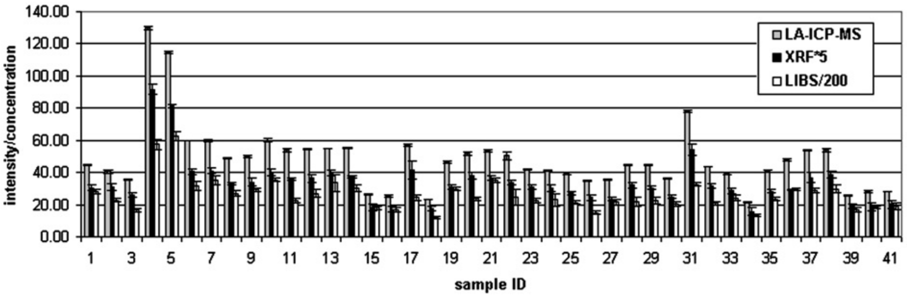

Fig. 2. Strontium distribution among the 41 glass set, a comparison of means for μXRF (signal intensity), LA-ICP-MS (concentration), and LIBS (signal intensity). Note that the μXRF intensities were multiplied by 5 and the LIBS peak areas were divided by 200.

was imaged from the side (90°) by a pair of plano-convex lenses (f=75 mm) into an optical fiber with a diameter of 50 μm. This fiber was coupled to the entrance slit of an Andor Mechelle 5000 spectrometer (South Windsor, CT) equipped with an Andor iStar intensified CCD, which converted the image into a spectrograph. The spectral range collected for each sample ranged from 200–950 nm with a resolution of ~5000. The repetition rate for the spectrometer was set at 0.67 Hz such that the spectrometer would capture a complete set of data for each laser shot. Both the laser flashlamp and the Q-switch were externally controlled using a Berkeley Nucleonics' Model 565 Delay Generator (San Rafael, CA). The emission lines were accumulated at a 1.2 μs delay upon plasma ignition, with an integration time of 3.5 μs. A schematic of the LIBS setup utilized for this part of the study can be found in Fig. 1.

Each sample replicate spectra was collected as a result of the accumulation of 50 laser shots. After each spectrum was acquired, the sample was rotated to a new spot for a total of 5 spots/replicate analyses per sample.

3. Results and discussion

3.1. Discrimination study

3.1.1. Micro X-ray fluorescence (μXRF)

The μXRF discrimination results found 14 indistinguishable pairs (98.3% discrimination) using a three-sigma criteria (three times the standard deviation), which is routinely used in casework by the

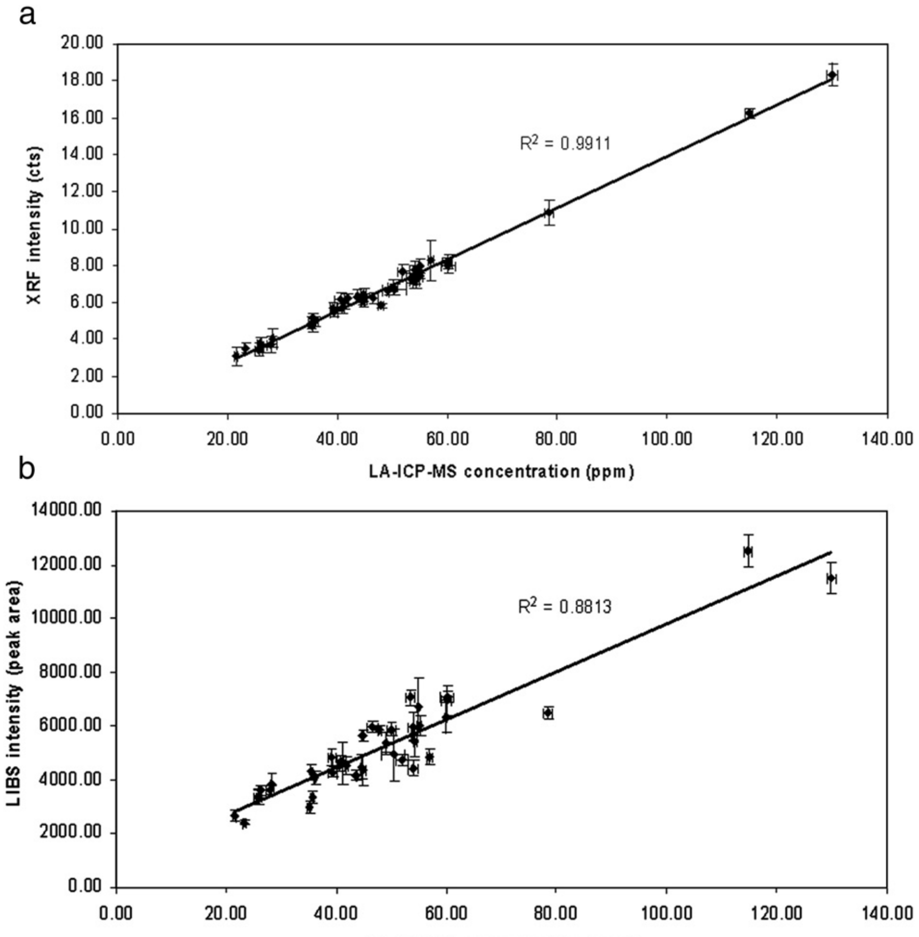

Fig. 3. (a) Correlation of LA-ICP-MS and μXRF strontium results, (b) Correlation of LA-ICP-MS and LIBS strontium results; concentration versus peak area.

Florida Department of Law Enforcement (FDLE). Of these pairs, only three originated from different vehicles. All of them were discriminated by application of the t-test at the 95% confidence interval. Application of the t-test at the 95% confidence interval to the remaining 11 pairs yielded 8 indistinguishable pairs out of a possible 820 comparisons (the number of possible pairs is equal to $N\ (N-1)/2$, where N is the number of samples). This combined approach demonstrated 99.0% discrimination for µXRF, which is excellent discrimination power. All of the indistinguishable pairs have explanation as to why they exhibit similar elemental profiles, namely that each indistinguishable pair originated from the same vehicle and were likely produced by the same manufacturing plant at approximately the same. Seven of the 8 pairs found indistinguishable were attributed to samples from the same laminated windshield (inside and outside fragments originating from the same windshield), while the eighth indistinguishable pair represents side and rear window fragments that also originated from the same vehicle. The pairs found indistinguishable by this method are listed and described in Table 2 with the indistinguishable pairs found by µXRF are labeled by the superscript “a”.

3.1.2. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS)

The data analysis utilized for the LA-ICP-MS results included a combination of pairwise comparison analysis using ANOVA and the General Linear Model (GLM) in Systat 11 (San Jose, CA) with Tukey's honestly significant different test (HSD). To the pairs found indistinguishable by pairwise comparison analysis a *t*-test at the 95% confidence interval was applied (via Microsoft Excel, Redmond, WA). A given pair found indistinguishable using the combination of the two data analysis strategies was ultimately determined indistinguishable, meaning the fragments have very similar elemental profiles. A more thorough review of this data analysis approach can be found elsewhere [5,7]. Pairwise comparison analysis alone yielded 11 indistinguishable pairs (98.7% discrimination); 6 of these pairs were discriminated by application of a t-test of which 3 pairs originated from different vehicles that were produced in different years. The other 3 pairs discriminated by *t*-test originated from the same vehicle. The reason why some glass fragments that originate from the same source can be discriminated is a result of sampling and/or precision across the entire pane of glass. If the precision of the measurement for a given fragment is smaller than the overall precision of the glass pane as a whole, it is possible that fragments obtained from the same source (i.e. inside and outside fragments from the same windshield) can be discriminated. Therefore, in forensic casework it is important that proper sampling techniques are followed to ensure that correct characterization of a glass source is achieved and that correct associations or discriminations are made. For LA-ICP-MS, combining pairwise comparison analysis and *t*-test, 5 indistinguishable pairs were found out of a possible 820 pairs (99.4% discrimination). Remarkably, these 5 pairs were identical to 5 (of the 8) pairs found indistinguishable by µXRF. Despite LA-ICP-MS showing slightly better discrimination power than µXRF (0.4% greater), the results are well correlated. The correlation between LA-ICP-MS and µXRF data for this sample set will be addressed later in this paper. The 5 indistinguishable pairs by LA-ICP-MS are summarized in Table 2 where the pairs marked with a superscript “b” represent the 5 indistinguishable pairs determined by LA-ICP-MS. The fact that both methods generated the same output, namely the same indistinguishable pairs, demonstrates the strength and validity of these two methods for forensic glass comparisons. Again, the indistinguishable pairs all had explanations as to why they exhibited very similar elemental profiles. The top discriminating elements by LA-ICP-MS and the associated results per element can be found in Table 3. Take note that the top discriminating element is strontium, which overall has been consistently a top discriminator for the trace elemental analysis of float glass. As a result, strontium was chosen for the correlation studies, comparing LA-ICP-MS concentrations to µXRF and LIBS signal intensities.

3.1.3. Laser induced breakdown spectroscopy (LIBS)

3.1.3.1. Data analysis approach. Twenty-two (22) peaks/emission lines were initially chosen for data analysis based on their presence across all 41 glass samples. The selected peaks represent 9 different elements; Al, Ca, Fe, K, Mg, Na, Si, Sr, and Ti. Both intensities by peak heights and peak areas (via integration) were evaluated statistically (between sample replicates) and it was observed that peak areas provided greater precision when compared to using peak heights or intensities. Since precision is one of the important factors in discriminating samples, peak areas were utilized for further data reduction purposes. From the 22 peak areas detailed above, every possible peak ratio (element/element) was evaluated to determine which ratio resulted in the best discrimination out of the 231 possible ratios [$N(N-1)/2$, where N is the number of peaks].

Discrimination for each individual ratio was conducted on the 41 different glass fragments, in the sample set, using a *t*-test at the 95% confidence interval to coincide with the 95% confidence interval utilized for both LA-ICP-MS and µXRF. In addition, a 42nd sample fragment was added as a quality control measure. This sample was the same sample analyzed twice during the analytical sequence, once towards the middle of the run and again at the end. Thus, the sample duplicate was treated as an unknown throughout the entire analytical scheme. The results related to this same sample analysis were then used to eliminate ratios that provided a false exclusion (or Type I error), meaning that the same sample was discriminated. A total number of 85 ratios produced no false exclusions following this format.

Of the 85 ratios, 10 were selected based on their respective degrees of discrimination for the glass sample set, with none of the ratios being repeated, such as 394.4 nm/460.7 nm (Al/Sr) and 460.7 nm/394.4 nm (Sr/Al). These 10 ratios and their individual discrimination results are reported in Table 4. The final step in this approach was to limit the number of ratios used in combination to only 6 ratios (of the 10), in order to remain consistent with the number of ratios used to discriminate the glass sample set by µXRF.

3.1.3.2. Discrimination results. All of the possible combinations of the 10 optimized ratios (using 6 different ratios in each combination) were assessed and further ranked in terms of discrimination power. In total, 210 different ratio combinations were evaluated [$n!/(n-m)!m!$ where n is the total number of ratios (10) and m is the number of ratios used per discrimination (6)], confirming that no Type I errors were detected.

Of the 210 combinations, 60 combinations provided one to six false inclusions (Type II errors), whereby these combinations resulted in the lack of discrimination of pairs originating from different vehicle makes/models manufactured in different years. In the worst case scenario, 9 indistinguishable pairs were found, 6 of which were false inclusions and 3 pairs with an explanation (same glass or same car origin). The authors wish to stress that this worst-case combination would not be used to discriminate glass samples and that none of the 60 combinations that produced false inclusions would be considered suitable for the discrimination of glass by LIBS.

It was determined that 150 combinations (of the possible 210) produced no Type I or Type II errors, with all associations resulting from plausible explanations (same glass or same car origin), which was the same result as with the µXRF and the LA-ICP-MS. Samples 6 and 7, which are fragments originating from the side and rear windows of a 2004 Chevrolet Cavalier, were indistinguishable by all 210 possible combinations with 36 combinations resulting with samples 6 and 7 as the only indistinguishable pair. In addition, this pair was also found to be indistinguishable by µXRF, as referenced in Table 2, which concludes that these two fragments share very similar elemental profiles. There were 4 other indistinguishable pairs that were found by several of the ratio combinations, which were also found indistinguishable by LA-ICP-MS and/or µXRF. These pairs and the associated frequency of occurrence (out of a possible 210 combinations) are: 11:12 (28 occurrences or 13.3%), 13:14 (7 occurrences or 3.3%), 23:24 (84 occurrences or 40.0%), and 28:29 (84 occurrences, or 40.0%). Actual sample descriptions for these pairs can be found in Table 2 with the pairs found indistinguishable by LIBS depicted by the superscript "c".

It should be noted that although the group at FIU (LA-ICP-MS and LIBS analyses) did know the origin of each fragment prior to instrumental analysis, the potential bias of comparison was avoided given that the data generation format (pairwise comparison analysis and/or t-test) treats each sample as if the identity is unknown and the user must decipher the results generated to determine which pairs are indistinguishable. Furthermore, with respect to the LIBS and LA-ICP-MS discrimination results, the analyst did not know which samples were associated (samples from the same vehicle) until after the discrimination results were generated. In the case of the µXRF analyses, the samples were analyzed as a blind study where the analyst did not know the origin of the samples until the final results were submitted. Overall, the discrimination results were well correlated, even though the methods for elemental analysis are different and each data analysis approach was performed by a different analyst.

3.2. Correlation study

The three analytical techniques are compared in terms of concentration (LA-ICP-MS) versus intensity (µXRF or LIBS), the results are summarized here. Fig. 2 shows the distribution of strontium (mean concentration or mean intensity), as determined by µXRF, LA-ICP-MS, and LIBS. The plot shows the variation (or in some cases the association) of strontium in the glass sample set analyzed for this study; also, it partially demonstrates the correlation of the strontium signal for the three methods. It can be observed in most cases that as a strontium concentration or intensity is increased for one method moving from one sample to the next, the strontium signal also increased in similar magnitude for the other methods. Nevertheless, a more descriptive (or visual) correlation of such results can be found in Fig. 3.

The correlation between LA-ICP-MS and µXRF data using strontium mean concentrations and intensities (with the associated error bars), respectively, for the 41 glass set was plotted and compared. As depicted in Fig. 3(a), a strong correlation between the two data sets is demonstrated, represented by a correlation coefficient of 0.9911. The excellent correlation between these two methods further establishes why similar discrimination results were obtained. A correlation between LA-ICP-MS and LIBS data was also plotted using LA-ICP-MS determined strontium concentrations versus LIBS intensities (mean values with respective standard deviations) for the 41 glass set. As observed in Fig. 3(b), the correlation for LIBS and LA-ICP-MS was determined to have a correlation coefficient of 0.8813. The correlation plot also illustrates the small degree of variation between sample replicates for LIBS using the setup described in this study.

4. Conclusions

Two of the leading techniques in elemental analysis, LA-ICP-MS and µXRF, were compared to the less mature technique, LIBS, in terms of discrimination power for a set of automotive glass samples. Significantly, all three analytical approaches yielded similar discrimination results with a percent discrimination of 99% or greater. The 5 indistinguishable pairs found by LA-ICP-MS were the same as 5 (of the 8) indistinguishable pairs determined by µXRF, and many of the ratio combinations used to discriminate the glass samples by LIBS resulted in the same pairs found to be indistinguishable by the other methods. In addition, the indistinguishable pairs obtained for LA-ICP-MS, µXRF, and LIBS had a good explanation as to why the elemental profiles were similar and thus could not be discriminated. These indistinguishable pairs originated from the same vehicle and thus were likely to have been manufactured in the same plant at approximately the same time. With respect to analyzing LIBS spectra and making sample comparisons, an extensive study was conducted comparing different data reduction procedures. The final approach resulted in good discrimination and was in agreement with the other elemental analysis methods. The probability of committing Type I or Type II errors is reduced and/or eliminated using the sample comparison approach for LIBS outlined in this paper. Avoiding such errors is a requirement for forensic casework. The best combination of ratios produced only 1 indistinguishable pair (out of the possible 820 pairs) and this pair was explainable. Based the data analysis study outlined, the authors suggest 10 ratios that are considered optimum for the analysis and discrimination of glass by LIBS. The proposed ratios include: 394.4 nm/330.0 nm (Al/Na), 766.5 nm/643.9 nm (K/Ca), 394.4 nm/371.9 nm (Al/Fe), 438.4 nm/766.5 nm (Fe/K), 534.9 nm/766.5 nm (Ca/K), 371.9 nm/396.2 nm (Fe/Al), 766.5 nm/645.0 nm (K/Ca), 394.4 nm/460.7 nm (Al/Sr), 460.7 nm/766.5 nm (Sr/K), and 818.3 nm/766.5 nm (Na/K). Given its low cost, high sample throughput, good sensitivity, and ease of use, the application of LIBS for forensic glass examinations has been shown to provide the same discrimination as other, more established methods and now presents a viable alternative to LA-ICP-MS and µXRF in the forensic laboratory.

Acknowledgment

The authors would like to gratefully acknowledge the financial support received through a grant awarded by the National Institute of Justice (NIJ), grant #2005-IJ-CX-K069. 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.

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