

Laser induced breakdown spectroscopy as a tool for discrimination of glass for forensic applications

E. M. Rodriguez-Celis · I. B. Gornushkin ·
U. M. Heitmann · J. R. Almirall · B. W. Smith ·
J. D. Winefordner · N. Omenetto

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Abstract Materials analysis and characterization can provide important information as evidence in legal proceedings. The potential of laser induced breakdown spectroscopy (LIBS) for the discrimination of glass fragments for forensic applications is presented here. The proposed method is based on the fact that glass materials can be characterized by their unique spectral fingerprint. Taking advantage of the multielement detection capability and minimal to no sample preparation of LIBS, we compared glass spectra from car windows using linear and rank correlation methods. Linear correlation combined with the use of a spectral mask, which eliminates some high-intensity emission lines from the major elements present in glass, provides effective identification and discrimination at a 95% confidence level.

Keywords Glass · Forensic · Laser induced breakdown spectroscopy · Correlation analysis · Material identification

Introduction

Fragments of broken glass collected at crime scenes such as burglaries, car crashes, hit and runs, and vandalism constitute forensic evidence in criminal investigations [1]. These glass fragments can be compared with those found on the victim's body and/or the suspect's belongings. If they are found to come from the same source, they might associate a suspect with the perpetration of a particular crime. Hence, it is essential that the method chosen for the analysis is capable of handling small sample fragments to provide adequate confidence in the results.

A range of techniques are available for the forensic examination of glass. First, the possibility of a physical match between the fragments is explored. This requires the two broken edges to match perfectly, an outcome that is hard to find in real cases [2]. Next, physical properties such as color, thickness, refractive index (RI), and density are examined. Determination of the RI has been the technique of choice for many years. Nevertheless, technological improvements in the glass manufacturing process have led to less variability in physical and optical properties between manufacturers and different plants of the same manufacturer [3]. The reduction of the spread among RI values reduces the informing power of this technique and highlights the need for additional techniques to facilitate reliable identification.

Several elemental analysis techniques have been employed for the characterization and discrimination of glass fragments. These methods include flame atomic absorption spectroscopy, scanning electron microscopy combined with energy-dispersive spectrometry, X-ray fluorescence (XRF) spectrometry, neutron activation analysis, inductively coupled plasma (ICP) atomic emission spectroscopy, and ICP mass spectrometry (MS) [1, 4]. Each technique has its own advantages, but some of them are limited by sample size and shape,

E. M. Rodriguez-Celis · I. B. Gornushkin · B. W. Smith ·
J. D. Winefordner · N. Omenetto (✉)
Department of Chemistry, University of Florida,
P.O. Box 117200, Gainesville, FL 32611, USA
e-mail: omenetto@chem.ufl.edu

U. M. Heitmann
Department of Interface Spectroscopy,
ISAS–Institute for Analytical Sciences,
Albert-Einstein-Str. 9,
12489 Berlin, Germany
e-mail: uwe.heitmann@online.de

J. R. Almirall
Department of Chemistry and Biochemistry,
Florida International University, University Park,
Miami, FL 33199, USA

destruction of the sample, cost, and analysis time. The incorporation of laser ablation (LA) in ICP-MS has greatly simplified the analysis of glass samples. Advantages of this technique include minimal sample preparation, multielemental capability, greater sensitivity and better detection limits than conventional absorption and emission techniques, speed of analysis, and minimal sample destruction and contamination. However, in spite of its relatively high sensitivity, this technique is very expensive, which precludes its use in many forensic laboratories [2, 5–8]. In this study, laser induced breakdown spectroscopy (LIBS), an atomic emission technique, is proposed as a viable alternative for glass analysis. LIBS involves focusing a high-power, short-pulse laser (usually in the nanosecond range) on a sample surface. A very energetic plasma results which is rich in electrons, atoms, and ions. The plasma radiation, characteristic of the elements present in the sample, is observed and analyzed [9].

LIBS exhibits numerous appealing features that distinguish it from more conventional analytical spectrochemical techniques. For example, there is little to no sample preparation, which results in increased throughput and reduction of tedious and time-consuming sample digestion and preparation procedures. Virtually any kind of sample can be analyzed: solids, liquids, aerosols, or gases. In addition, it provides the possibility of simultaneous multielement analysis with low *absolute* detection limits. Through the use of conventional optics and fiber optics, LIBS can also be performed over a great distance, a technique referred to as remote sensing. Among a few disadvantages of LIBS are the poor precision (5–10%), poor *relative* detection limits (in the parts-per-million range), and matrix and spectral interferences [10, 11].

Significant progress has been achieved in recent years regarding the application of LIBS to a number of analytical problems. This growing interest, together with the broad availability of less expensive and more robust lasers, higher-resolution spectrometers, and the ease of data collection and processing, will eventually convert LIBS into a routine analytical method in the laboratory and in the field. LIBS has also the potential to be an attractive technique that can be applied to forensic applications. A few forensic applications have been reported for the analysis of gun pulse residues [12], minerals in hair [13], and Rb traces in blood [14] and for detection of latent fingerprints [15].

Our group has evaluated the potential of LIBS for discrimination of glass samples of similar RI values by comparing the LIBS spectra over a short period of time (same day) [16]. Research by Bridge et al. [17] has recently focused on the characterization of automobile glass fragments by LIBS and LA-ICP-MS. For the LIBS analysis, 18 ionic and atomic emission lines, from the elements Al, Ba, Ca, Cr, Fe, Mg, Na, Sn, Si, and Ti, were evaluated and used to form ten different ratios of emission intensities. With use

of these ratios, 93 and 82% correct discrimination of 23 glass samples was achieved at confidence intervals of 90 and 99%, respectively. With the addition of RI data, the discrimination was improved to 100 and 99% for the confidence intervals of 90 and 99%. Later, this study was extended to the examination of four sets of glasses (automobile windows, headlamp, and side mirror, and drink container glasses). The use of LIBS in combination with RI determination provided 87% discrimination at a 95% confidence level [18].

Thus, good performance of LIBS is encouraging for its use in forensic laboratories. There have been previous studies of glass analysis by LIBS, although they did not focus on discrimination analysis for forensic purposes [19–28].

In this study, we examine the LIBS spectra of glass from a slightly different perspective. That is, we do not seek a detailed chemical composition or to calculate intensities or intensity ratios of some particular elements. Instead, we identify glass fragments from their unique LIBS spectral “fingerprints” by using statistical correlation methods.

The procedure used in this research is the following. First, an unknown glass fragment is identified by correlating its spectra against an available spectral database. Second, the spectra of the fragments are compared against each other to statistically determine if they originated from the same glass source. Third, the long-term reproducibility of the analysis is presented. Optimal sampling conditions for acquisition of accurate LIBS spectra are also reported. A summary of the results and their statistical significance is presented.

Experimental

Samples

A total of ten fragments from seven automobile glasses (side and rear windows) were used in this study. These ten fragments provide 45 possible pair comparisons. They were collected from automobiles at a local auto glass shop corresponding to 5 years of manufacturing and five vehicle manufacturers. Their height, length, and width were approximately 0.3, 1.0, and 0.9 cm, respectively. All of them were transparent and uncoated. A more detailed sample description is shown in Table 1.

All samples were mounted on a microscope glass slide using double-sided mounting tape and then placed on an XYZ translation stage that allows movement of the sample to a fresh spot. A laser positioning system consisting of a diode laser and a photodiode detector ensured a reproducible position of the sample.

Table 1 Information concerning the glass samples

Sample name	Vehicle information
A1	2007 Buick Lucerne, side window
A2	2002 Ford Focus, rear window
A3	2002 Ford Focus, rear window
A4	2003 Honda Accord, side window
A5	2003 Toyota Tundra rear window
A6	2003 Toyota Tundra rear window
A7	2002 Toyota Camry side window
A8	2004 Chevy Blazer side window
A9	2004 Chevy Blazer side window
A10	2003 Chevy Trailblazer side window

Instrumentation and data acquisition

The LIBS instrumentation used in this study consisted of an Ocean Optics (Dunedin, FL, USA) LIBS2000⁺ spectrometer coupled to a Big Sky (Bozeman, MT, USA) Ultra Q-switched Nd:YAG laser operating at 1,064 nm. This laser delivered a maximum of 50 mJ in 10 ns, providing an irradiance of approximately 5.2 GW/cm² on the sample surface. The laser beam was focused onto the glass surface using a 5-cm focal length lens. The radiation emitted by atoms ablated from the glass samples was collected by a quartz lens and guided into a seven-channel spectrometer. It is worth pointing out that the optical collection system used in this work was not achromatic: this may affect the line intensities obtained in widely different spectral regions and as a consequence also the discrimination power. Chromatic effects should then be taken into consideration when transferring different spectra from laboratory to laboratory. Each channel covered a spectral range of about 100 nm; the full range of the spectrometer was from 200 to 980 nm. The detector was a linear CCD with 2,048 pixels. The instrument spectral resolution (full width at half maximum) was 0.1 nm.

The instrumental parameters used were as follows: laser power 50 mJ per pulse, detector delay time and gate width 1 μ s and 2 ms, respectively. For data acquisition, each sample was ablated at 15 positions; each position consisted of 130 ablation pulses at 1 Hz and the data were obtained at atmospheric pressure. The first 30 spectra were discarded and the next 100 were averaged, providing an individual spectrum per position on the sample. For the correlation analysis, 15 individual spectra per sample were averaged to create a sample library.

Software

A homemade program for correlation analysis written in Visual Basic 6.0 was used [29]. This program has already

been successfully applied to the identification of different classes of materials using their LIBS spectra [29–32]. The program allows creation of libraries by averaging individual spectra. Linear and rank correlation coefficients are calculated for each individual spectrum versus the library. Finally, a correlation plot is displayed, corresponding to the maximum correlation coefficient and the name of the sample associated with the highest correlation coefficient.

Results and discussion

Sampling considerations

Experimental conditions capable of providing high precision and repeatability between experiments are needed to obtain an accurate spectral fingerprint of each sample.

First, the effect of the laser power was studied. The Nd:YAG laser used has a specified maximum pulse energy of 50 mJ which can be changed in increments of 5 mJ. In our experiments, it was found that the highest laser power (50 mJ) resulted in better signal-to-noise ratios.

In LIBS, small unpredictable experimental fluctuations can cause a significant change in the appearance of the spectra. To check the stability of our measurement setup the following procedure is envisaged: the intensity of a Si atomic line at 288.16 nm is chosen and monitored at regular time intervals in a standard glass sample (NIST 612) used as a reference for the optimization of the experimental setup. The analysis is not continued and correlation is not performed if the difference in the intensities observed for this line exceeded the expected statistical variation of our method, $\sigma = \pm 15\%$. In this case, the entire experimental setup is inspected and optimized again until the results are satisfactory. In particular, three experimental parameters are checked, namely, the alignment of the collection optics with respect to the plasma volume observed, the focusing distance of the laser beam on the target, which affects the ablation efficiency, and the short-term pulse-to-pulse energy fluctuation of the laser.

A detector delay of 1 μ s and a fixed spectrometer integration time of 2.1 ms were used. These values resulted from an optimization study carried out for the detection of carbon in soils [33]. Although the choice seems to be arbitrary, in view of the different matrices examined, the optimization study was repeated with different samples such as glass and cast iron standards, confirming the choice of the values obtained previously. The repetition rate did not play a significant role during data acquisition and was set at 1 Hz.

No sample preparation is required for elemental analysis by LIBS. However, relatively low spectral intensities were recorded after the first laser pulse which slowly increased,

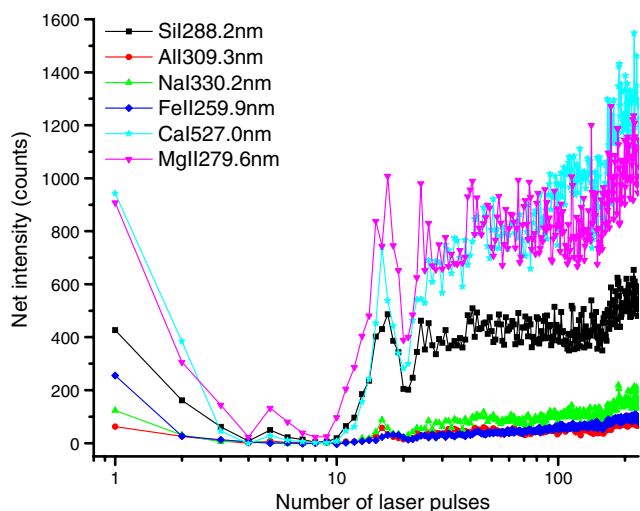


Fig. 1 Intensity dependence with the number of laser pulses

reaching a constant value after approximately 25 pulses on the same sample spot; this behavior is only observed when working with glass fragment samples. Figure 1 presents a typical plot of the variation of net intensities for the glass fragments (number of counts above the background level) for six emission lines versus the number of laser pulses (up to 250) at one spot on the sample. This behavior is caused by the laser–glass interaction [34, 35]. For the first few laser pulses, the samples were almost transparent and there was minimal ablation. However, as the glass interrogation progresses, defects in the glass are formed, making ablation stronger. Thus, about 25 preparation pulses were needed, in our case, to achieve reproducible ablation.

The percentage relative standard deviation (RSD) of the net intensity versus the number of laser pulses at one sample spot (in groups) is shown in Fig. 2. It is observed

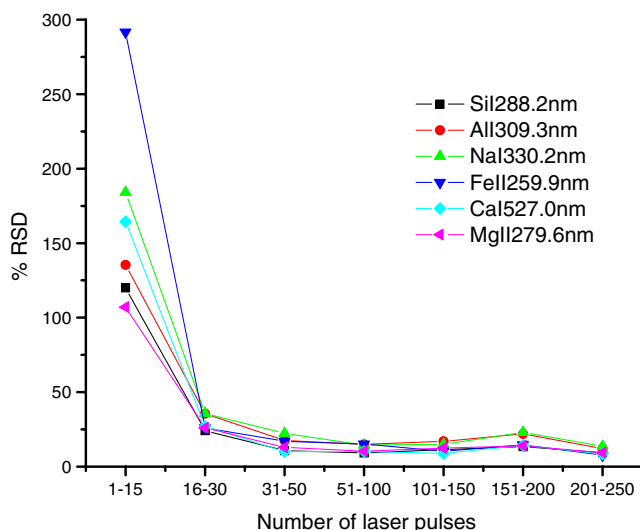


Fig. 2 Percentage relative standard deviation (% RSD) variability with the number of laser pulses on the same spot

that the RSD values decrease from 100 to 300% RSD for first 30 pulses to 15–20% RSD for the next 200 pulses. Consequently, the first 30 ablation pulses were discarded and considered as preparation pulses. The influence of the roughness of the glass surface was not examined but it has been reported not to cause significant changes in the emission spectra of glass [24, 36].

To determine the number of individual spectra to be averaged for the analysis, 180 pulse measurements were made at each position; ten positions per sample were examined. The first 30 spectra of each measurement were discarded and the remaining spectra were averaged in groups. The percentage RSD was calculated by using the averaged signals from each of ten sequential measurements. The plot of the percentage RSD against the number of averaged individual spectra is presented in Fig. 3 for some emission lines. It was found the percentage RSD reached a constant level of 10–20% after approximately 30 pulses; therefore, 100 individual spectra were averaged per position in our measurements.

Next, the effect of day-to-day changes in humidity, which might affect the laser air spark [37], was studied. The intensity of the hydrogen Balmer α emission line at 656.3 nm was monitored for this purpose since its variation is an indication of the changes in humidity of the ambient air. No significant changes in humidity were observed in 1-week period, and to simplify the sampling our experiments were performed in ambient air. In general, the overall reproducibility of the spectra taken on different days was within a variation of $\sigma = \pm 15\%$.

The effect of the offset distance or focal depth on pulse-to-pulse reproducibility was also considered. The offset distance is the difference between the lens-to-surface distance and the focal length of the lens [38]. It is an

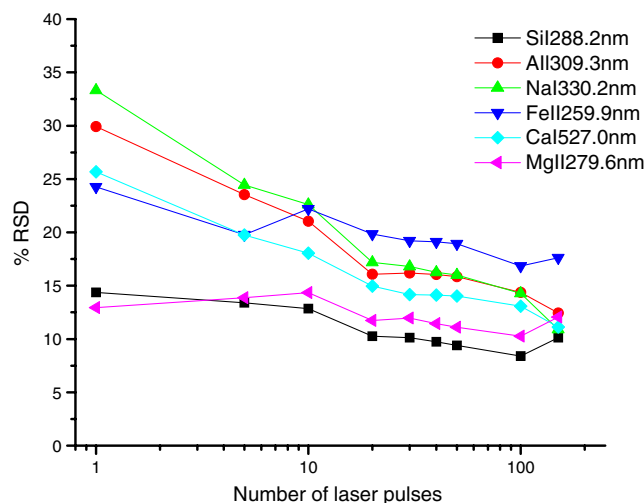


Fig. 3 % RSD variability with the number of laser pulses on separate spots

important parameter that must be held constant to obtain reproducible spectra [39]. No significant change in precision was found when moving the sample up or down 5mm relative to the focal point of the lens and we simply focused the laser on the sample's surface.

The minute amount of material removed per sample spot was approximately 3 μg . The mass ablated per spot was determined after examining the crater made with a calibrated optical microscope and using the known value of the density. The overall precision of these measurements was estimated to be approximately 10%. This mass of material has been proven to be representative of the whole piece of glass in studies using synchrotron micro XRF spectrometry [40] and LA-ICP-MS [7].

Sample identification by linear and rank correlation

Linear correlation measures the strength of the linear relation between two variables, in our case two glass LIBS spectra. The Pearson correlation coefficient, also known as linear correlation coefficient, is given by

$$r = \frac{\sum_i (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_i (x_i - \bar{x})^2} \sqrt{\sum_i (y_i - \bar{y})^2}}, \quad (1)$$

where \bar{x} represents the mean of the x values and \bar{y} is the mean of the y values from two data sets; x_i and y_i are intensities of the two spectra measured at the same pixel i .

We also used the rank (Spearman) correlation coefficient. The equation for rank correlation is similar to Eq. 1 but the values of the x and y distributions are replaced by their corresponding ranks R and S :

$$r = \frac{\sum_i (R_i - \bar{R})(S_i - \bar{S})}{\sqrt{\sum_i (R_i - \bar{R})^2} \sqrt{\sum_i (S_i - \bar{S})^2}}, \quad (2)$$

where the ranks have numbers 1, 2, 3, ..., N . The highest rank, N , is the total number of data points, or the highest pixel number. These ranks replace the true values of the x values and the y values in accordance with their magnitudes.

The value of r lies between -1 and +1. Values close to zero indicated uncorrelated data sets. The absolute value of r can be used as an indicator of the association between the data sets since the strongest correlation is represented by the absolute value of 1.

This study focused on the identification of ten glass fragments using linear and rank correlation coefficients. Fifteen individual spectra were collected from each sample. Each spectrum was the average of 100 ablation pulses. We refer to a library as the collection of averaged spectra; a

library was created containing ten averaged spectra (library 1). Each of the 150 individual spectra were correlated against the library spectra. The highest correlation coefficient indicated a similarity of a tested spectrum to one from the library. The difference between this and other correlation coefficients indicates spectral and, hence, compositional differences.

The results obtained on the “yes–no” basis for the identification of the 150 individual spectra (set 1) using correlation coefficients are presented in the top half of Table 2. These results include the name of the library the individual spectrum was “identified as” and the number of times (out of 15) correct identification was achieved. All the data points present in the spectra (13,701 pixels) were used for the correlation. From this table, linear correlation suggests that there is similarity between samples A2 and A3 and between samples A5 and A6, which is in fact correct since those glass fragments came from the same window. However, linear correlation did not identify similarities between samples A8 and A9, which also came from the same source. The rank correlation also indicates similarities for pairs A2 and A3 and A5 and A6, as does the linear correlation, but in addition suggests similarities for pair A1 and A9, which are not expected since these two samples came from different sources. Rank correlation also failed to identify similarities between samples A8 and A9. It is important to mention that all these ten samples have very similar LIBS spectra, and the correlation coefficients between these samples are all in the range of 0.9 or higher. This is understandable since all the samples have very similar elemental composition.

It is important that identification is reproducible within an arbitrary long time period, e.g., spectra from unknown samples taken on different days could be compared with the existing spectral library. For this purpose, a new experiment was performed in a period of 1 week. This time, however, only five individual spectra were collected from each sample, under the same experimental conditions reported earlier, and a new library was created containing ten averaged spectra (library 2). The identification of individual spectra for this second set of data compared with library 2 showed similar results to the results obtained previously and presented in the top part of Table 2. In addition, this set of individual spectra was correlated versus the library created the previous week (library 1). The bottom half of Table 2 shows that the correlation coefficients obtained by linear correlation indicate similarities for pairs A2 and A3, A5 and A6, and A8 and A9, which came from the same window; there were also no misidentifications. On the other hand, rank correlation also suggests similarities for the three previous pairs but in addition shows similarities for pairs A1 and A9 and A4 and A5, which are not expected since the samples were from different sources. So far, it is

Table 2 Identification using linear and rank correlation

	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10
First set of individual spectra correlated against spectral library 1										
Linear	A1 (15/15)	A2 (10/15)	A3 (13/15)	A4 (15/15)	A5 (8/15)	A6 (11/15)	A7 (15/15)	A8 (15/15)	A9 (15/15)	A10 (15/15)
Rank	A1 (12/15)	A2 (12/15)	A3 (14/15)	A4 (15/15)	A5 (11/15)	A6 (8/15)	A7 (15/15)	A8 (15/15)	A9 (13/15)	A10 (15/15)
	A9 (3/15)	A3 (3/15)	A2 (1/15)		A6 (4/15)	A5 (7/15)			A1 (2/15)	
Second set of individual spectra correlated against spectral library 1										
Linear	A1 (5/5)	A2 (5/5)	A3 (1/5)	A4 (5/5)	A5 (5/5)	A6 (1/5)	A7 (5/5)	A9 (5/5)	A9 (1/5)	A10 (5/5)
Rank	A9 (5/5)	A2 (5/5)	A2 (5/5)	A4 (5/5)	A5 (1/5)	A6 (3/5)	A7 (5/5)	A8 (5/5)	A9 (1/5)	A10 (5/5)
			A2 (4/5)		A4 (2/5)	A5 (2/5)			A8 (1/5)	
					A6 (2/5)	A5(2/5)			A1 (3/5)	

Az (x/y) means x out of y individual spectra are identified as sample z.

felt that linear correlation provides good identification for samples that are the same and distinction for the ones that are different even when the data are obtained on different days. Therefore, linear correlation is robust with respect to changes in spectral intensities on different days.

Besides the apparent differences and similarities between samples determined by the use of correlation coefficients, strict statistical criteria must be applied in order to quantify the level of significance. To do so, a simple analysis by Student's *t* test was applied. This hypothesis test determines whether two normally distributed populations are significantly different [41]. The normality of the distribution of the correlation coefficients was confirmed using normality plots (*Q-Q* plots). If the test's *p* value is less than the significance level chosen ($\alpha = 0.05$ to give a 95% confidence level) the null hypothesis is rejected and it is

concluded that the samples are different. Otherwise, the results suggest there is no significant difference between the two populations; in other words, there is no significant difference between the two samples.

Based on these *p* values, the top half of Table 3 presents the discrimination between glass fragments when the second set of individual spectra was correlated against the library created a week earlier (library 1). The *p* values for linear correlation coefficients indicate no significant difference for the means of pairs A2 and A3 and A5 and A6, which was expected. However, linear correlation also indicates that a significant difference exists between samples A8 and A9, which is not true. Therefore, linear correlation provides 98% correct identification at a 95% confidence level. On the other hand, the *p* values for rank correlation coefficients indicate no significant difference for

Table 3 Detected similarities between samples using *p* values obtained by Student's *t* test ($p > 0.05$)

	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10
All lines in the spectrum were used, no spectral mask										
Linear		A3	A2		A6	A5				
Rank	A8 A9 A10	A3	A2		A4 A6	A5		A9	A1 A8	
Selected lines in the spectrum were used, spectral mask is applied										
Linear		A3	A2		A6	A5		A9	A8	
Rank	A8 A9	A3	A2		A4 A6	A5		A9	A1 A8	

the means of pairs A2 and A3, A5 and A6, and A8 and A9, which is correct and expected. However, this analysis also indicates similarities for pairs A1 and A8, A1 and A9, A1 and A10, and A4 and A5, which is incorrect, providing an overall 91% correct identification at a 95% confidence level.

We conclude, therefore, that linear correlation provides better results than rank correlation but does not find similarities for samples A8 and A9. Rank correlation finds these pair to be similar but suggests that four other pairs are also similar.

To improve correlation analysis of spectra, “masking” the spectra prior to evaluation was chosen. Masking is a simple multiplicative process that retains only the selected peaks of the components to be analyzed, thus eliminating analytically useless parts of the spectra (e.g., peaks or bands from the matrix) [42, 43]. The criteria for choosing a valid mask is to strengthen spectral similarities between samples that are the same and improve differences for the ones that are different. One of the consequences of better quality control in the manufacture of glass is less variability between concentrations of major elements, e.g., Si, Mg, Na, Ca, Fe, and Al. As a result, analysis of trace element impurities within major materials emerges as a useful path for discrimination [44]. Some high-intensity lines from major elements present in glass are blocked since the concentrations of those elements are expected to be very similar among the glass fragments. By doing so, we focused our analysis on elements of lower concentration. Figure 4 shows the spectral lines that were masked for the analysis.

It is advantageous to eliminate regions of the spectrum where no lines are present since the noise affects negatively the correlation coefficients. Another possibility of masking is to correlate lines from the trace elements present in the samples instead of just blocking the high-intensity lines; however, this might require a higher-resolution spectrometer capable of resolving and detecting K, Ti, Mn, Rb, Sr,

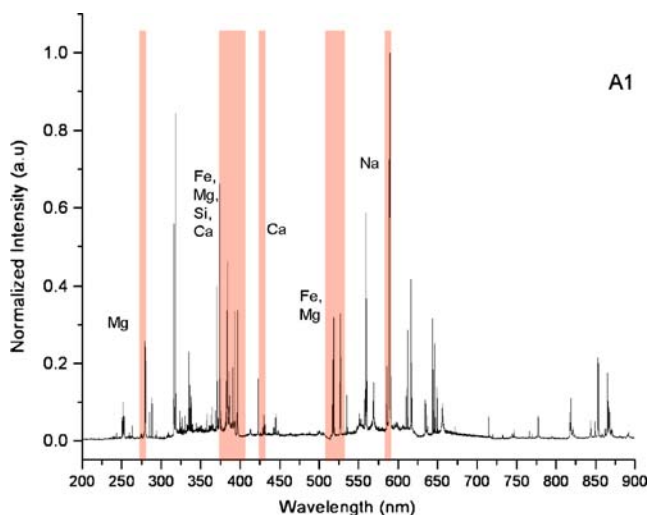


Fig. 4 Spectral lines that were masked for the analysis

Zr, Ba, La, Ce, and Pb, which have been proven to provide effective discrimination by LA-ICP-MS [6].

The results obtained when using the spectral mask are presented in the bottom half of Table 3. Linear correlation revealed that three pairs are indistinguishable (A2 and A3, A5 and A6, and A8 and A9); therefore, linear correlation together with masking provides 100% correct identification at the 95% significance level. By rank correlation, these pairs are also similar, but three pairs (A1 and A9, A1 and A8, and A4 and A5) out of 45 possible pair combinations are also judged to be similar, yielding 93% correct identification at a 95% significance level.

It is clear that masking improves the result by linear correlation. However, there is no significant improvement with rank correlation, probably owing to the nature of the mask itself, which only blocks high-intensity lines. Current research in our group suggests that rank correlation is very sensitive to noise and less sensitive to small systematic changes in line intensities [45]. Therefore, only linear correlation is the method of choice.

Conclusions

In this work, linear and rank correlation techniques were applied for discrimination of LIBS spectra from glass samples with similar chemical composition, some of them from the same source. The robustness of this technique was demonstrated by the 100% correct identification (95% confidence level for a type 1 error) obtained by linear correlation when used in combination with a spectral mask. The identification was reliable even when experiments were performed on different days when ambient conditions might be different and affect the line intensities in the LIBS spectra.

The rationale of using spectral masking is to eliminate regions of the spectra containing several intense lines common to all samples and to take advantage of the trace element impurities present in these glasses. We are aware of the fact that there are more sophisticated ways to generate a mask than the one used in this study. However, it was felt useful to focus at first on a simple masking procedure to see whether any further elaboration of this concept was worth pursuing. More refined procedures are planned for the future.

The main advantages of this LIBS method relative to other elemental analysis studies of glass for forensic applications are:

- Lack of sample preparation
- Short analysis time, since spectral acquisition and correlation analysis could be done in minutes
- No need for quantification or calculation of intensity ratios
- No need for supplemental measurements such as measuring RI values

The next steps in this study will involve the use of masks for spectral regions instead of lines, the use of background correction, and a study of different normalization procedures to assess the quantitative analytical performance of the technique.

In conclusion, elemental analysis of glass by LIBS has the potential of becoming a useful technique for the discrimination of forensic glasses. Its usefulness as an analytical method for legal purposes will be determined by its general acceptance in the relevant scientific community. Evidence of “general acceptance” normally includes known error rates and publication of the methods in peer-reviewed journals. These legal aspects and corresponding implications, which would require more in-depth statistical analysis, have not been considered in this work.

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