LIBS-BASED APPROACHES FOR THE CLASSIFICATION OF GLASS MICROFRAGMENT SAMPLES

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1. INTRODUCTION

Glass is one of the most commonly used materials. Due to its various uses and numerous manufacturers, the elemental composition of glass objects varies at the level of main components and micro contaminations as well. Glass microfragments (<1 mm splinters) are generated in great number during a fracture, thus are commonly found on scenes of car accidents, burglaries, vandalism, assaults and many other, and therefore are often are the subject of forensic investigations. Glass fragments generated by breakage can be trapped by the cloth, shoes or even hair of people present at the crime scene, thus glass fragments frequently link people to each other or to locations [Caddy 2001]. Thus, the analysis of glass samples is important in forensic investigations.

Glass fragment analysis can be done in many ways. Non-destructive methods are preferred, such as refractive index (RI) measurement [Katz 2016], electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) [Ramos 2011], micro X-ray fluorescence spectroscopy (μ-XRF), but microprobe methods are utilized as well, such as laser-ablation inductively coupled atomic emission (LA-ICP-AES) or mass spectrometry (LA-ICP-MS) [Trejos 2013]. One promising microprobe method is laser induced breakdown spectroscopy (LIBS), which is a laser ablation based atomic emission spectroscopy technique with many practical features for the forensic analysis. It requires only simple sample preparation and the amount of the consumed sample is in the ng range only. It is sensitive for all elements, the typical detection limits are in the ppm range. LIBS spectra are very feature-rich which produces fingerprint-like spectra that are very characteristic for specific samples. Despite its advantageous properties, LIBS has only rarely been investigated as a possible instrument for forensic glass analysis (e.g. [Barnett 2008, El-Deftar 2014]).

In the current study, we set out to investigate the potential of LIBS for the qualitative discrimination of glass types, also including the investigation of their homogeneity and ablation properties.

2. EXPERIMENTAL

During this investigation, 131 glass samples, representing four major types, fused silica, borosilicate, soda-lime and flint glass (FS, BS, SL and FL), were analysed. Due to their widespread use our study focused mainly on soda-lime glasses, hence the majority, 96 of our glass fragment samples belonged to this type. Within the soda-lime type, float, container, patterned and security glass subtypes (SL/F, SL/C, SL/P, SL/S) were also sampled.

The surface contaminations of the fragments were removed by spectroscopy-grade acetone, followed by a wiping to dryness using Kimwipes tissues. The cleaned fragments were attached to plastic sample holder discs by a double-sided adhesive tape.

LIBS experiments were performed on a J-200 tandem LA/LIBS instrument (Applied Spectra, USA) equipped with a 266 nm, 6 ns Nd:Yag laser source and a six-channel CCD spectrometer with an average spectral resolution of 0.07 nm. LIBS spectra were recorded in the Axiom data acquisition software using 1 μs gate delay and 1 ms integration time, in the wavelength range of 190 to 1040 nm. The energy of laser pulses was 15 mJ (2% RSD), and the light was focused into a 40 μm wide focal point. The ablation chamber was rinsed by a 99.9995% purity argon gas (Messer Ltd., Hungary) flow at 0.5 L/min flowrate. 25 spectra of each samples were recorded (5 repetitions from 5 different locations).

Refractive index (RI) measurements were carried out on 589 nm by the oil immersion method, using a GRIM 3 system (Foster + Freeman, UK). The RI values were determined using temperature-matched calibration curve based on the measurement of 10 glass standards (Locke Scientific, UK). The laser ablation craters on the glass samples were investigated by using a Veeco Dektakt 8 contact profilometer (Vacuum Electronic Equipment Co., USA). The craters were fully mapped by 330 nm lateral and 400 nm vertical stepping resolution.

3. RESULTS AND DISCUSSION

Glass is produced by mixing and melting together the components, thus glass products are usually considered homogenous materials, and a shard may correctly represent the bulk. However, this property is crucial in glass microfragment analysis, thus we investigated the intra-fragment homogeneity of our samples by comparing the 5-5 LIBS spectra collected at different points of the sample. Linear correlation was used as a comparative function that produces a single numerical value (Pearson coefficient)

ranging from 1 to 0, representing full similarity and dissimilarity. Ray plots in **Figure 1.** show the observed intra-fragment spectral variation for some of selected samples. As expected, it was found that there is a reasonably good similarity between the spectra collected from different spots of the same sample (correlation coefficient was greater than 0.95), which indicates a generally good lateral homogeneity.

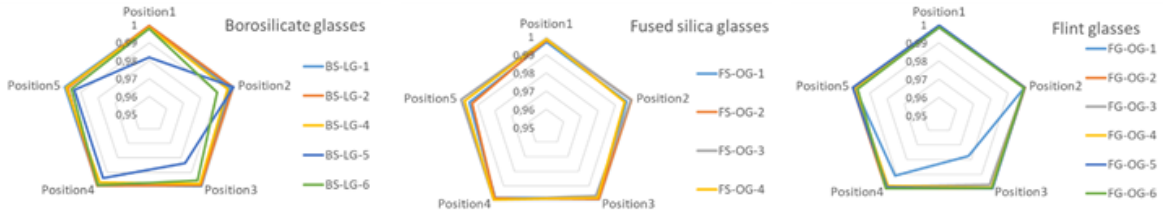

Figure 1. Intra–fragment compositional variations in different glass types.

We also studied the depth-resolved elemental distribution which revealed typically flat intensity profiles, expect for Sn. The concentration of this element gradually decreases with the depth in float glasses, which is an artifact caused by the production technology. Tin lines were therefore excluded from the spectra during our later investigations involving float glasses.

The laser ablation behaviour of glass fragments was found to be different from sample to sample. This is evidenced by the diagram in **Figure 2.** which indicates a great variety of crater volumes. In most cases, the crater volumes fall between $3 \cdot 10^5$ and $7 \cdot 10^5$ μm^3, but e.g. for container glasses it showed exceptionally high variation. It also has to be added that crater shapes show jagged edges, which is a clear sign of shock/stress-like fracture – as it is customary for glasses also in large pieces. This varying crater volume makes the accurate quantitative analysis and the qualitative discrimination based on concentration data difficult.

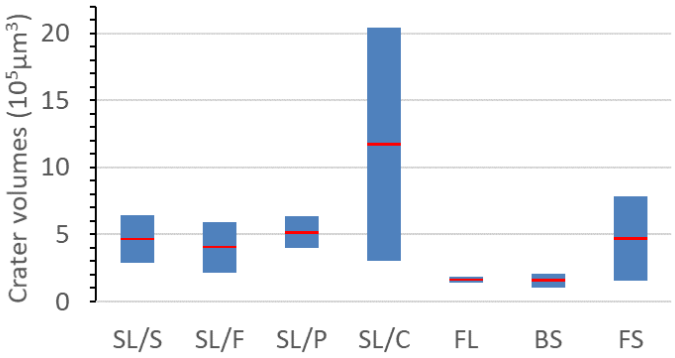

Figure 2. Mean and range values of laser ablation crater volumes for glass types.

The four investigated types of glass samples possess very different elemental composition. For example, fused silica glasses do not contain additives, soda lime glasses have a large Na, K and Ca content, borosilicate glasses contain considerable amount of boron and aluminium, while flint glasses are rich in Ba and Pb. Considering the large variation of compositions between the types, it seems as an easy task to differentiate

among the glass types using an element-sensitive analytical technique like LIBS. **Figure 3.** illustrates the potential of this approach for classification. In this graph, each glass sample is represented as dot placed in the space of their aggregated Ba+Pb, Ca+K and B+Al content. The sample points located close to each other usually belong to the same type group. As it can be noted, the automotive headlight shield glasses behave exceptionally. Although they were expected to be made of borosilicate glass (heat-resistant glass type), but some of them do not contain any boron or aluminium at all, whereas others contain significant amounts of barium and lead in addition to boron and aluminium. Overall, this group is widely scattered. This finding emphasizes that one must not base the discrimination on preconceptions about the composition of glass types.

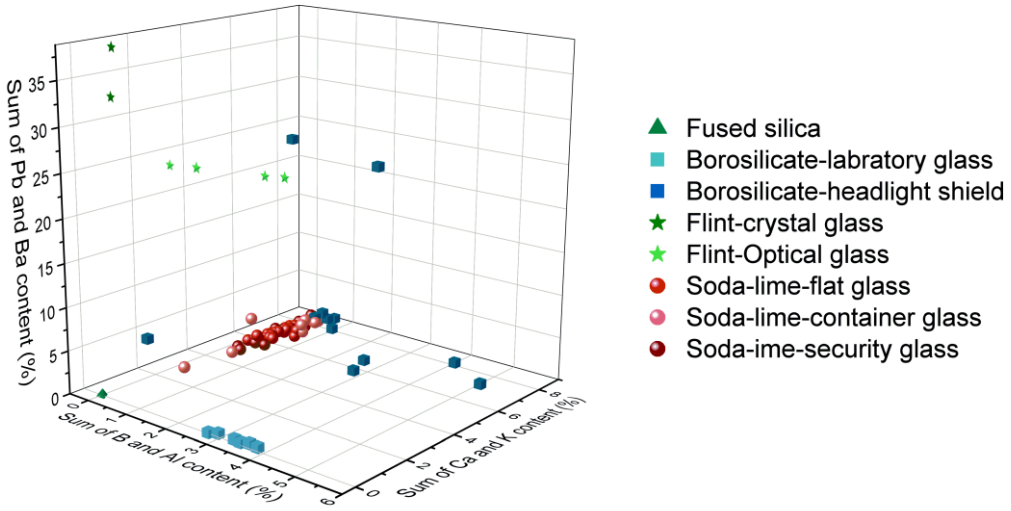

Figure 3. Classification of glass types based on their elemental composition.

Based on the above, we did not use any preliminary chemical information about the glasses during the qualitative discrimination attempts, during which we worked with four subtypes of the soda lime glasses only (SL/F, SL/C, SL/P, SL/S). We tested the accuracy of linear discriminant analysis (LDA), principal component analysis (PCA) and random forest (RF) methods on these data sets for the classification and managed to achieve around 90% of accuracy.

From a chemometric point of view, the identification of individual glass microfragment samples is a more challenging task. For this task, we had to implement a pre-sorting approach too, based on the refractive index in order to have enough "discriminative power" to tell apart individual glass samples. With this combined method, we achieved very satisfying results, which we will disseminate in our poster presentation.

4. CONCLUSIONS

LIBS spectra of numerous glass samples were recorded in this investigation, and a lateral and vertical homogeneity examination was carried out on them. It was found, as expected, that glass samples are generally quite homogenous, which allows the use of LIBS as a microsampling (microprobe) analytical method useful for the discrimination of small glass fragments. We also pointed out to some challenges that are faced when discrimination of glass samples based solely on the elemental concentration information is attempted. These challenges influence the performance of all widely used discrimination techniques, including LIBS. We found that discrimination accuracy is best if it is either based on direct (raw) LIBS spectra, or when LIBS data is combined with refractive index data, in which cases, better than 90% accuracy was achieved.

5. ACKNOWLEDGEMENTS

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