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Sampling strategies for the analysis of glass fragments by LA-ICP-MS Part I. Micro-homogeneity study of glass and its application to the interpretation of forensic evidence

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Abstract

The authors have previously reported the use of laser ablation ICP-MS as a powerful analytical tool for elemental analysis of glass. LA is a simpler, faster and less intrusive sample introduction method than the conventional solution ICP-MS. Due to the minute amount of material removed in LA (~300 ng, 50 μm crater size), the analyst should be aware of special sampling considerations such as characterization of the glass fragments originating from the "known" source, fragment size and selection of the area and surface of ablation.

The purpose of this work was to evaluate the micro-homogeneity of the elemental composition of glass samples commonly found in crime scenes like containers, architectural windows and windshields. The set of glasses under study was comprised of 56 fragments originated from glass containers, 28 fragments from automobile windshields and 20 fragments from architectural windowpanes. All fragments were selected with a size smaller than 2 mm^2 in order to simulate the typical glass fragments transferred from the crime scenarios. A Nd:YAG laser, 266 nm, flat top beam profile was used in single point mode sampling 50 μm spot size for 50 s at 10 Hz (500 shots). In this study, ^{29}Si was used as an internal standard and the standard reference material, SRM NIST 612, was used as a single point external calibrator. In addition, SRM 621 was used as another control standard for the containers set and SRM 1831 for the automobile and architectural window sets due to their very similar matrix with the samples of interest. For each set of glasses, the mean values and standard deviation of 10 replicates ($n = 10$) of a single fragment were compared with the values obtained from 10 ($n = 10$) different fragments of glass within the area of interest in order to evaluate whether or not the variation within a glass was bigger than the variation due to the method. In addition, a subset of tempered glasses was evaluated to perform an elemental composition profile within different depths of the fragments. Single shot (one laser pulse per analysis) was also evaluated and its limitations for the forensic analysis of glass are also presented. The results show that float glass is homogenous even at the micro-range level allowing LA-ICP-MS as an alternative technique to perform elemental analysis of glass. However, the variation of elemental composition of headlamps and containers is larger over the source than the instrumental variation due to inherent heterogeneity and therefore specific statistical methods are recommended to compare the glass samples.

Keywords: Glass; Laser ablation; ICP-MS; Elemental analysis; Trace evidence; Forensic science

1. Introduction

Glass as physical evidence could provide valuable information to assist criminal investigations. When a glass is broken during a car accident, a bombing, a robbery or a homicide, fragments are usually left at the crime scene. Those glass fragments can be compared with glass residues recovered from the body of the victim and/or suspect. If the fragments are considered to originate from the same source with a high degree of confidence, they can be used as strong scientific evidence to support the trial and to prove contact between the individuals [1]. In the same way, if the fragments are considered to originate from different sources, lack of guilty can also clarify a case.

In order for these scientific findings to have value at court the techniques used to perform the analysis should provide good discrimination and association power. Refractive index (RI) is a useful technique for the forensic examination of glass. Nevertheless, due to the narrow variation of the RI

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among glass samples, its discrimination power alone sometimes is not enough to generate a conclusive association [1–4]. As a consequence, it has become necessary to employ additional techniques such as elemental composition analysis to enhance the informing power of the comparison between fragments [5–17].

Elemental analysis by ICP-MS increases the value of the evidence because the method provides excellent accuracy and precision. In addition, it has been proved by analysis conducted by solution ICP-MS on glass that elemental composition of glass varies significantly between glasses that came from different sources, i.e. glass from automobiles with different manufacturing date, but does have a small variation within a single glass [5,7,18]. These characteristics make the analysis of glass by ICP-MS optimal for forensic analysis.

The typical digestion methods used for ICP-MS bulk analysis are time-consuming and involve complicated sample preparation steps to bring the sample into solution. Furthermore, the digestion step is destructive and ~6 mg of the sample is consumed during the analysis [3,17,19].

The incorporation of laser ablation greatly simplifies the analysis of glass samples. In LA-ICP-MS, a laser is used for the initial sample volatilization and direct introduction of solids into the plasma. A typical LA-ICP-MS setup consists of a laser, the ablation cell and the ICP-MS used as an ionization source and analyzer. The solid sample is placed inside the ablation cell and a laser beam is focused on the surface of the sample. The interaction of the laser with the sample produces a cloud of small particles that are transported to the ICP plasma by aims of a carrier gas, usually argon or helium [20–22].

Advantages of LA encompass minimum sample preparation, speed of analysis – up to eight times faster than conventional digestion methods, reduced consumption of sample and no need of using hazard materials such as hydrofluoric acid (HF) [23–26].

Recent comparisons between data generated using solution and laser ablation experiments were performed on 136 samples originated from different sources. The results have shown that LA-ICP-MS provides similar discrimination power and precision to the conventional digestion techniques for the analysis of glass [27].

As an extension of that study, the present work is focused now in the analysis of samples originated from the same source. Due to the minute amounts of material removed from glass during laser ablation where craters of only 50 μm are produced, it is necessary to extent the homogeneity studies into the micro-scale in order to demonstrate that this sampling is representative of the original piece of interest.

The homogeneity studies were conducted in glasses that usually are part of criminal investigations such as containers, architectural and automobile windows. Based on the variations due to sample heterogeneity and variations due to the method, matching criteria are proposed for the interpretation of glass comparisons by LA-ICP-MS.

Another glass of interest in forensic casework is the tempered glass. Tempered glass is ordinary glass that has followed a tempering process to provide additional strength and more safety breakage pattern and is widely employed in the manufacturing of automobile windows [28]. It has been found that the strengthening procedure conduct to differences in the refractive index of the surfaces and inner parts of the fragments generated from tempered glass. Consequently, studies of LA-ICP-MS within single fragments of tempered glass were perform to find if elemental composition suffers also from heterogeneity because of this process.

The aim of this work was to provide an overall study of the homogeneity of glass samples in order to propose sampling and statistical interpretation strategies for the forensic analysis of glass by LA-ICP-MS.

2. Experimental

2.1. Instrumentation

The ICP-MS used in this study was a Hewlett Packard, model HP-4500 Plus (Agilent Technologies, Palo Alto, CA, USA), with a quadrupole mass analyzer and equipped with an autosampler ASX-500 (CETAC, Omaha, NE, USA). Laser ablation analyses were performed with a CETAC (Omaha, NE, USA) laser ablation systems (model LSX-200 Plus) Q switched Nd:YAG, operating at 266 nm. The experimental parameters used for the analysis of the glass are summarized in Table 1. The elemental menu used for the quantification of the different glass sets is summarized in Table 2. For single shot studies, particle size measurements were done using a laser diffraction particle counter system (LASAIR 1001, Particle Measuring Systems, USA). The system analyzed and stored the data in eight size classes, from 0.1 to 2 μm, and produced real-time reports. The manufacturer calibrated the unit prior to its delivery to our laboratory. Performance checks were conducted daily and before each analysis; reference voltages were kept at 8.2 V and site elevation corrections

Table 1
Instrumental parameters used for elemental analysis by LA-ICP-MS

Parameter	Value
RF Power (W)	1302
RF matching (V)	1.95
Plasma gas ($l\,min^{-1}$)	16.0
Argon as carrier gas after cell ($l\,min^{-1}$)	0.95
Helium as carrier gas trough cell ($l\,min^{-1}$)	0.95
Ablation Cell volume (ml)	50.2
Ablation Mode	Single spot
Spot size (μm)	50
Dwell time (ms)	8.3
Energy output (%)	100
Frequency (Hz)	10
Ablation time (s)	50
Beam profile	Flat beam

Instrumental parameters used during the analysis by LA-ICP-MS.

Table 2
Elemental ratios selected for LA data analysis of glass samples

Glass set			
Architectural	Windshield	Container	Tempered
Al/K	AL/K	Al/K	Al/K
Ba/La	Ba/La	Ba/La	Ba/La
Ce/La	Ce/La	Ce/La	Ce/La
Cs/Ba	Co/Sr	Fe/Mn	Co/Sr
Mg/Li	Mg/Al	Mg/Al	Mg/Al
Mn/Rb	Mn/Rb	Mn/Rb	Mn/Rb
Pb/Ce	Hf/Zr	Pb/Hf	Hf/Zr
Zr/Sn	Pb/Th	Rb/Sr	Pb/Hf
Sr/Zr	Rb/Sr	Sr/Zr	Rb/Sr
Ti/Mn	Sr/Zr	Ti/Mn	Sr/Zr
U/Th	Ti/Mn	U/Th	Ti/Mn
	U/Th	Zr/Sn	U/Th
		B/Li	

were performed to maintain the flow rate through the particle counter at 0.255 l min^{-1}. A T-connector was placed after the ablation chamber to split the flow of particles. Simultaneous measurements were then possible by the ICP-MS and in the particle measurement system. Blanks were run between each set of data to determine the background signal and samples were measured in five replicates.

2.2. Reagent, standards and sampling preparation

Standard reference materials SRM NIST 612, 621 and 1831 were used for this study. In order to improve focusing with the laser, the surface of the samples was slightly scratched with a sandpaper of 3600 mesh and then washed with methanol, followed by washing with 0.8 mol L^{-1} trace elemental grade nitric acid (Fisher, Pittsburg, PA, USA) for 30 min. The samples were rinsed with deionized water and then let dry overnight.

2.3. Glass sampling

A total of 104 fragments were used for the homogeneity evaluation, all of them were selected <2 mm^2 in size in order to be typical of those glass fragments transferred from the crime scenarios.

The homogeneity of the architectural windows subset was comprised of two sheet of glass, each one of 19 in. × 26 in. long. One of the sides of each sheet was covered with tape, enclosed in clean cardboard and broken with a hammer. Ten fragments from each sample were randomly selected for analysis. During LA-ICP-MS analysis, 10 measurements were performed on a single fragment in order to account for method variation. Ten different fragments were measured once by LA-ICP-MS in order to account for variations in the sheet of interest (see Fig. 1a). A total of 20 different fragments were used for this set.

The windshield set consisted of two windshields originated from different sources, one from a vehicle Chevy, year 1985 and the other from a vehicle Jeep Wrangler, year 1988. Each windshield consisted in a two window panels separated by a plastic film. One of the sides of each windshield was covered with tape, enclosed in clean cardboard and broken with a hammer. Seven fragments were randomly selected from each panel for a total of 14 fragments from each windshield. During LA-ICP-MS analysis, seven measurements were performed on a single fragment in order to account for method variation. Seven different fragments were measured once by LA-ICP-MS in order to account for variations in the panel of interest. The analysis was done independently for each panel of the windshields (inner and outer sides) (see Fig. 1b).

The container set was comprised of a four pack of green bottles, wine Bella Sera 2001, Merlot vinted and bottled in Italy (Villalta, Italy), and a six pack of brown bottles, beer Michelob 2003, brewed and bottled in USA (Anheuser-Bush, Inc., MO, USA). All bottles from the same pack contained the same bar code number. The homogeneity study of containers was divided into two subgroups: (a) homogeneity within a single bottle and (b) homogeneity between bottles from the same six (or four) pack. For the homogeneity within a single bottle 10 fragments were selected as shown in Fig. 1c. Each fragment was measured by triplicate. A total of 56 fragments were analyzed for this set. In addition, for the homogeneity between the bottles from the same pack three fragments from each bottle were measured by triplicate. A subset of 45 containers originated from the glass database at International Forensic Research Institute (IFRI) at Florida International University (FIU) was analyzed by triplicate in order to evaluate discrimination power for samples that came from different sources.

The tempered subset consisted of four window samples provided by the Center of Forensic Sciences (CFS), Toronto, Canada, from actual casework samples that were submitted to the laboratory. The elemental composition of the fragment was measured in the top surface by triplicate and compared with the side composition at different depths among the thickness of the fragment (see Fig. 1d).

2.4. Statistical analysis

All statistical analyses were performed by either the use of SYSTAT for windows 8.0 (SPSS Science, Chicago, IL) or Excel 2000 (Microsoft Corp., v9.0.2719). The statistical analysis was carried out using either analysis of variance (ANOVA) using the General Linear Model (GLM) tool from SYSTAT followed by the Tukey's honestly significant different test (HSD) or *t*-test. A thorough explanation of the statistical analysis of the comparison of glass analysis data can be found in previous reports [29,30]. Data reduction of laser ablation data was performed using the GLITTER software (GEMOC, Macquarie University, Australia). GLITTER was designed for data reduction of time-resolved signals obtained by LA-ICP-MS. The software provides real-time, on line data reduction based on the interactive selection of integration intervals from the time-resolved signal [31,32].

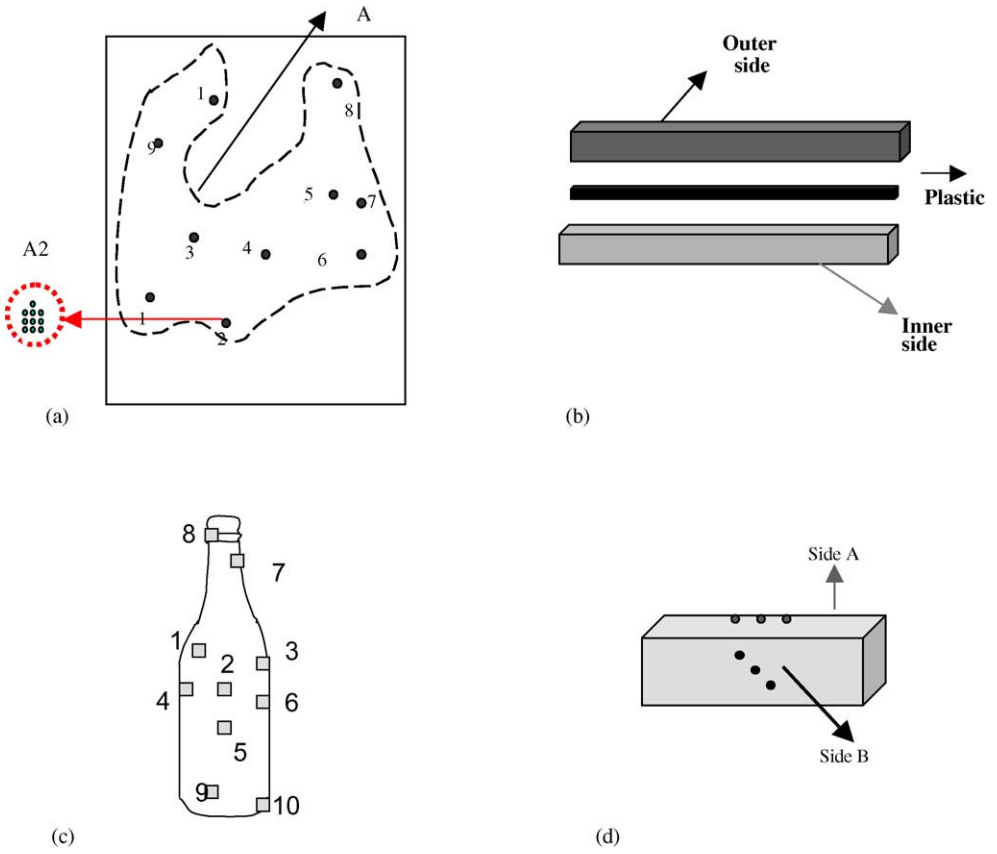

Fig. 1. Sampling diagram used for the homogeneity study of: (a) architectural glass, (b) windshields, (c) containers and (d) tempered glass.

3. Results and discussion

The homogeneity studies presented in this paper are intended to prove that even when very small amounts of sample are removed from a recovered fragment from a crime scene, the elemental composition could be representative of the original glass material, i.e. a whole window from a house, a windshield or side window from a vehicle or a container. Each of the distinct class of glasses has a different manufacturing process and therefore they have different opportunities to include contamination of trace elements into the final product.

For the architectural set, a *t*-test for $n = 10$ was done to compare the mean value given by the instrument variation (10 replicates from a single fragment) and the mean value of the 10 fragments randomly selected from the sample, which represents the variation given by the natural heterogeneity within the whole piece of glass. The *t*-statistical analysis was performed for each of the 11 elemental ratios shown in Table 2 and in all cases they were not significantly different with a 99% of confidence ($p > 0.01$). Table 3 shows the elemental ratios obtained from the replicates of each architectural glass. The results show that the elemental composition within a single sheet of architectural window is homogeneous. Fig. 2 shows and example of the distribution of the values of Mn/Rb of 10 replicates from a single fragment versus 10 replicates made on different fragments among one of the architectural windowpanes.

The individual panels (outer and inner sides) for the two windshields were also evaluated for micro-homogeneity. Fig. 3 shows the elemental composition of fragments from the outside panel of the Chevy's windshield. According to the *t*-test performed the replicates from a single fragment were not significantly different from the replicates from different

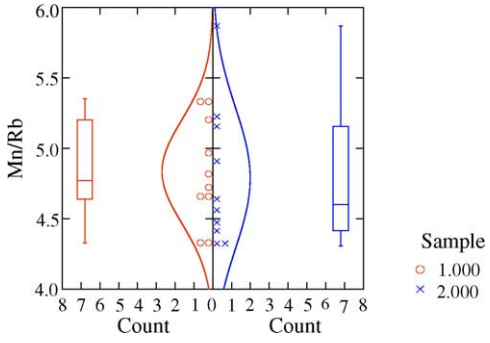

Fig. 2. Comparison of the distribution of values and standard deviations of the replicates within a single fragment and replicates within a whole architectural window. Sample 1 (circles) represent the values for 10 replicates of a single fragment and sample 2 (cross) represent the values for the measurements of 10 different fragments from the same glass source.

Table 3
Elemental ratios obtained for 10 replicates within a single fragment (samples 1) and 10 measurements among the architectural window pane number 1 (samples 2)

Fragment #	Th/U	Pb/Ce	AlK	AlCa	SrZr	ZrSn	Mg/Li	TiMn	MnRb	BaLa	CeLa	CsBa
1–1	1.629	1.348	1.258	0.041	2.014	4.032	5887	1.515	4.329	5.924	2.229	0.167
1–2	1.476	1.678	1.351	0.042	1.696	3.732	6110	1.000	5.203	8.505	2.602	0.125
1–3	1.750	2.212	1.304	0.041	1.851	3.511	5065	1.507	5.353	6.024	1.638	0.119
1–4	1.143	1.621	1.507	0.042	1.623	3.961	6303	1.272	4.662	18.736	2.019	0.040
1–5	1.548	1.398	1.379	0.043	1.700	3.373	5345	1.252	4.722	7.181	2.034	0.122
1–6	1.500	1.308	1.370	0.042	1.678	2.867	6754	1.350	4.967	5.295	1.837	0.120
1–7	1.031	1.315	1.408	0.043	1.559	3.844	6705	1.345	4.340	4.823	1.490	0.121
1–8	1.133	1.301	1.614	0.043	1.630	3.113	5802	1.568	5.314	5.864	2.000	0.145
1–9	1.286	1.537	1.599	0.042	1.700	3.120	6430	1.272	4.818	7.482	1.813	0.111
1–10	1.054	1.239	1.613	0.046	1.706	3.218	5204	1.346	4.640	6.398	1.737	0.101
Mean 1	1.355	1.496	1.440	0.043	1.716	3.477	5961	1.343	4.835	7.623	1.940	0.117
S.D. 1	0.258	0.292	0.133	0.002	0.129	0.402	608	0.164	0.370	4.052	0.317	0.033
2–1	1.294	1.301	1.522	0.043	1.812	3.704	6693	1.602	4.473	6.538	1.849	0.141
2–2	0.789	1.127	1.350	0.042	1.908	3.938	5945	1.362	4.909	5.482	1.789	0.150
2–3	1.353	1.460	1.265	0.041	1.773	3.232	5154	1.253	4.562	6.982	1.752	0.138
2–4	0.892	1.169	1.038	0.030	1.762	3.466	4218	1.681	4.306	6.524	1.905	0.123
2–5	1.237	1.316	1.265	0.041	1.845	3.337	5075	1.407	4.326	7.424	2.033	0.120
2–6	0.845	1.101	1.373	0.041	1.899	3.045	4415	1.321	4.415	7.118	2.039	0.125
2–7	1.123	1.231	1.217	0.040	1.868	3.189	6079	1.204	4.640	6.663	1.931	0.146
2–8	1.350	1.051	1.557	0.042	1.825	3.185	5452	1.464	5.870	7.788	2.438	0.127
2–9	1.409	1.178	1.554	0.046	1.621	4.096	5678	1.579	5.156	7.746	1.772	0.096
2–10	0.987	1.062	1.519	0.040	1.764	3.351	5206	1.331	5.226	4.747	1.500	0.142
Mean 2	1.128	1.200	1.366	0.041	1.808	3.454	5392	1.420	4.788	6.701	1.901	0.131
S.D. 2	0.233	0.129	0.173	0.004	0.084	0.348	751	0.158	0.502	0.967	0.245	0.016

fragments within the panel ($p > 0.01$), showing also good homogeneity within the sample. The same results were obtained for the other individual sheet of windshields analyzed. Nevertheless, when the elemental composition of the inside and the outside sheet of glass from the Chevy's windshield were compared versus each other, they were significantly different with a confidence level of 99% ($p > 0.01$). These results stress the importance of employing a good sampling strategy during collection of windshield fragments in a real casework. A good practice will be to collect, whenever possible, glass fragments from both sides of the windshield and identify them properly because the recovered fragment from victim(s) and suspect(s) could originate from a different side of the windshield or from a mixture of them. Therefore a proper identification of the "known" samples is definitive in providing a conclusion about the existence of a common origin between glass fragments.

Both set of containers (wine and beer bottles) shown a natural heterogeneity in the elemental composition within a single bottle that can be caused by the manufacturing process of the containers which involves the use of molding parts that allows more contamination of trace elements. Analysis of variance (ANOVA) was performed to the 10 fragments within the bottle, each one analyzed by triplicate. The varia-

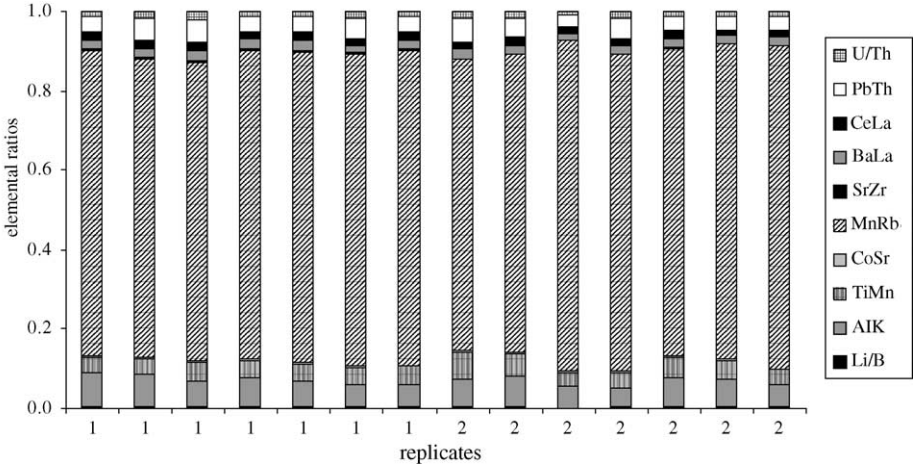

Fig. 3. Comparison of elemental ratios of seven replicates from a single fragment (sample 1) and seven measurements of different fragments within the outside pane of a Chevy's windshield.

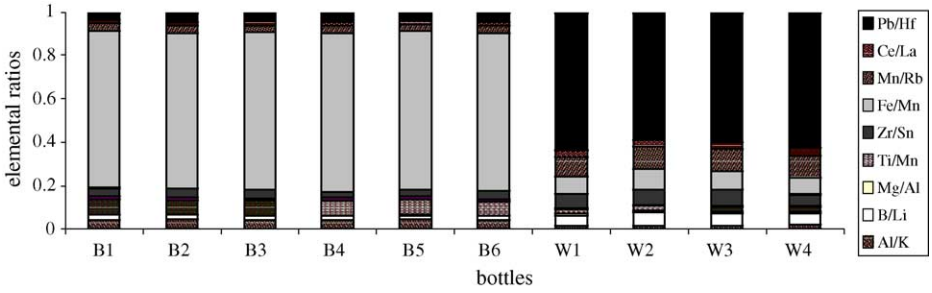

Fig. 4. Comparison of elemental composition of six beer bottles (B1–B6) and four wine bottles (W1–W4).

tion due to heterogeneity in the sample was bigger than the instrumental variation given by LA-ICP-MS and therefore different matching criterion was employed to process the data from containers. The mean squared error within the replicates from the fragments (MSEw) and the mean squared treatment between the fragments (MST) were provided by the output of the ANOVA. Each MST was used as a fixed mean squared error parameter in the general linear model (GLM) for further comparisons of containers samples.

Once this correction was done, three fragments from each of the beer bottles from the six-pack were analyzed by triplicate and ANOVA was performed. All six bottles were indistinguishable by elemental composition ($p > 0.01$). The same conclusion was obtained for the four wine bottles after the statistical analysis. Fig. 4 shows the mean values for the elemental composition of the bottles that comprises these sets. Furthermore, a pairwise comparison was run for the two set of bottles and also for a set of 45 containers originated from different sources, using the general linear model with the fixed MSE.

A comparison pair is a set of two samples that can be compared. To calculate the number of possible comparison pairs, the following formula is used: $n(n-1)/2$, where n is the number of samples. The six-pack can produce then a total of 15 pairs, the four pack set 6 pairs and the set of 45 containers can produce a total of 990 pairs. Table 4a and b shows that all of the possible 990 pairs originated from the 45-container set were distinguishable ($p > 0.01$) while the sets that came from the same source were indistinguishable by LA-ICP-MS, demonstrating that the MSE correction allows the association of samples known to come from a common source and the discrimination of samples that came from different sources without including any type II error.

Tempered glass is another class of glass that has a tremendous importance for forensic analysis and this study evaluated if there were differences in the elemental composition within the thickness of the fragment, especially in areas where different stages of tension were applied during the manufacturing. Four well-known and previously characterized samples were selected from the glass database at IFRI and the elemental concentration of the top surface of each sample was compared with the elemental composition among the thickness of the fragment using student t-statistic. Table 5 presents the summary of results for the t-test where p-values above 0.01 show no significant difference at 99% confidence level. No significant difference was found within the single fragments analyzed.

Special care should be taken when analyzing tin (Sn) in tempered glass and any other glass that has been manufac-

Table 4
(a) Relative discrimination capabilities of RI and LA-ICP-MS determined by pairwise comparisons of 45 container glasses originated from different sources (990 comparisons) using Tukey's test; (b) relative association capabilities of LA-ICP-MS determined by pairwise comparisons of fragments originated from 6 beer bottles from the same pack and 4 wine bottles from the same source

Number of Samples: 45, number of comparisons pairs: 990	No. of indistinguishable pairs ($p < 0.01$)
(a) Relative discrimination capabilities	
Ce/La	836
Fe/Mn	812
U/Th	515
Zr/Sn	471
Pb/Hf	443
Sr/Zr	392
B/Li	370
Rb/Sr	343
Mg/Al	225
Mn/Rb	191
Ti/Mn	96
All elements	4 (0.4%)
All elemental ratios + RI	0

Elemental ratios	No. of indistinguishable pairs ($p < 0.01$) six pack of beer bottles $n = 6$, number of possible comparison pairs: 15	No. of indistinguishable pairs ($p < 0.01$) four pack of wine bottles $n = 4$, number of possible comparison pairs: 6
(b) Relative association capabilities		
Ce/La	15	6
Fe/Mn	15	6
U/Th	15	6
Zr/Sn	15	6
Pb/Hf	15	6
Sr/Zr	15	6
B/Li	15	6
Rb/Sr	15	6
Mg/Al	15	6
Mn/Rb	15	6
Ti/Mn	15	6
All elements	15 (100%)	6 (100%)

Table 5
Output from *t*-test analysis (*p*-values) for the comparison of elemental composition of different surface areas in the tempered glass samples CFS 143, CFS167, CFS 165 and CFS 594

Sample ratio	CFS 143	CFS 167	CFS165	CFS 594
Ti/Mn	0.210	0.391	0.116	0.991
Co/Sr	0.230	0.599	0.353	0.101
Rb/Sr	0.288	0.628	0.241	0.551
Sr/Zr	0.871	0.560	0.072	0.119
Ba/La	0.987	0.489	0.895	0.448
Ce/La	0.327	0.306	0.540	0.159
Pb/Hf	0.060	0.060	0.611	0.014
Mg/Al	0.152	0.191	0.377	0.232
Al/K	0.194	0.381	0.545	0.086
U/Th	0.292	0.327	0.757	0.946

tured using the "float" process because the side that is exposed directly to the tin pool could have 25–50 times more content of tin than the rest of the three faces of the fragment. For example, in the tempered glass sample CFS 143 the mean value of Sn in the "float" side was 1735 $\mu g\,mL^{-1}$ while the mean value for the other three sides was 36.90, 37.05 and 36.70 $\mu g\,mL^{-1}$, respectively. When the fragments recovered are big enough that they can be observed under a UV light, the non-fluorescent side should be used for analysis, if not the interpretation of tin content should be addressed carefully or not included at all.

4. Conclusions

Laser ablation is a sample introduction technique that has several advantages over the digestion-solution methods used for glass analysis. LA is faster, easier, less prone to contamination than solution ICP-MS. In addition, the laser removes minimum amounts of sample leaving the technique as almost non-destructive.

The amount of material removed from a glass sample fragment using laser ablation ICP-MS was proved to be representative from the whole piece of glass or known sample. Nevertheless, for forensic purposes is very important to provide a good sampling in order to arrive to accurate conclusions. It is recommended to sample the known material from different areas to account for natural heterogeneity within the glass piece (window, panel, container, etc.).

Architectural flat glass has shown to be homogeneous within a windowpane, therefore for comparison purposes it should be enough to sample five different glass fragments of the known source.

In the case of windshields there is a possibility of finding differences in the elemental composition of the two sides of glass separated by a plastic film and that should be taken into account also during the collection of evidence. It is recommended to sample at least five glass fragments from different areas of each of the known windshield panels.

When containers are involved in a crime is also necessary to address the natural micro-heterogeneity within a single bottle to the match criteria employed for comparisons. It is encouraged to take glass samples from the top, middle and bottom area of the known container. If the bottle or container is completely broken, the area of origin may be implied by the curvature and shape of the fragments. However, if that is not possible it is convenient to sample randomly at least five glass fragments from the known source.

The tempering process does not affect the elemental composition within glass fragments and therefore it is not a concern for forensic comparison of recovered fragments. Ablation of any of the surfaces of the glass must give the same elemental composition (except for the tin-side of float glass).

In general terms, an unknown glass fragment may be analyzed at least by triplicate in order to be able to apply statistical tools for comparisons with the known source. The natural elemental variation of the known source must be well characterized according to the recommendations given above.

It is convenient to avoid the tin-side of float glasses. When the fragments recovered are big enough that they can be observed under a UV light, the non-fluorescent side should be used for analysis, if not a high tin concentration during the ablation may indicate that the float side is being ablated, if that is the case, the side of the fragment must be flipped or the interpretation of tin content should be addressed carefully.

The limitations of size and shape of the glass fragments to conduct elemental analyses by LA-ICP-MS are presented in detail in the part II of this article.

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