Available online at www.sciencedirect.com
SCIENCE DIRECT®
Talanta 67 (2005) 396–401
Talanta
www.elsevier.com/locate/talanta

Sampling strategies for the analysis of glass fragments by LA-ICP-MS Part II: Sample size and sample shape considerations

Tatiana Trejos, José R. Almirall *

International Forensic Research Institute and Department of Chemistry, Florida International University, University Park, Miami, FL 33199, USA

Received 1 September 2004; received in revised form 16 November 2004; accepted 17 November 2004
Available online 26 February 2005

Abstract

Glass fragments recovered from crime scenes are usually very small and therefore the amount of sample available to conduct forensic analyses is limited. Elemental analysis using conventional digestion methods consumes at least 2–3 mg of glass per replicate. LA-ICP-MS requires 10,000 times less glass consumption per analysis (~280 ng), and therefore the sample remains practically unaltered. Typically, the recovered fragments (unknowns) are 0.1–1 mm in length, while the "known" samples are usually larger, i.e. a broken fragment from a windshield (>3 mm). For bulk digestion analysis, the difference in fragment size does not present a problem for elemental comparisons – other than requiring at least 6 mg for triplicate analysis – because the sample is crushed and homogenized before weighing. Laser ablation sampling results in the creation of small craters (~50 μm diameter and 80 μm deep) drilled into the sample due to the interaction of the laser with the glass target. This study aims to evaluate whether the quantitative elemental analysis using the LA sampling method is affected by the size of the glass fragment due to differences in heat dissipation and surface–laser interaction. The analytical method employed for the analysis of glass by LA-ICP-MS had previously shown to possess the same or better performance than dissolution ICP-MS methods in terms of accuracy, precision, limits of detection and discrimination power. A 266 nm Nd:YAG laser with a flat top beam profile was used in single point mode sampling a 50 μm spot size for 50 s at 10 Hz. Standard glass reference materials SRM 612 and SRM 610 were selected to conduct this work in order to account for different concentration ranges and different opacities of the samples. The set under study was comprised of seven fragments originating from each standard at different sizes and shapes ranging from 6 to 0.2 mm length. Analysis of variance (ANOVA) followed by the Tukey's honestly significant different test (HSD) was used for data analysis. The results show that there is no significant difference in the elemental composition of different sized fragments. The conclusions, however, cannot be generalized for fragments measuring less than 0.2 mm × 0.1 mm.

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

1. Introduction

Forensics examiners usually combine the versatility of refractive index (RI) measurements with the discrimination power of elemental analysis in order to enhance the value of a comparison between glass fragments [1,2].

Elemental analysis of glass has been conducted by different techniques like atomic absorption [3,4], X-ray fluorescence [5,6], neutron activation [7,8], scanning electron microscopy [9], inductively coupled plasma atomic emission spectrometry (ICP-AES) [6] and ICP-MS [10–13]. Each technique has its own strengths and shortcomings [1,13], but ICP-MS has been shown to be the most effective analytical method for the comparison of trace elements in small glass fragments [14]. Some of the advantages of ICP-MS over the other analytical techniques include its multi-element capability, excellent sensitivity, high sample throughput and the capability to provide isotopic information.

Conventionally, the digestion methods used for ICP-MS bulk analysis are complex, costly and time consuming. Laser ablation is a sample introduction technique that overcomes

* Corresponding author.
E-mail address: almirall@fiu.edu (J.R. Almirall).

0039-9140/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2005.01.033

some of these disadvantages because the technique does not require sample dissolution. Furthermore, laser ablation eliminates the use of hazardous reagents such as hydrofluoric acid (HF) and significantly reduces the polyatomic interferences associated with solution analyses by ICP-MS [15–17].

Ablation can be defined as a progressive destruction of the surface of a material by different events such as fusion, melting, sublimation, erosion and explosion [17,18–20].

The use of LA has been applied to different matrices [15,21–32]. Glass analysis by LA-ICP-MS has been studied due to the current availability of matrix-matched certified standards like the SRM NIST series and the consistently high content of silica in the glass that make ^{29}Si a good choice for internal standardization. These features make glass a good model system to be explored for forensic applications of laser ablation. Nevertheless, the application of laser ablation for forensic analysis of glass cannot replace the accepted sample dissolution methods before it can be shown that it has the same or better analytical performance.

Previous research performed by our group has demonstrated that laser ablation provides similar accuracy, precision and discrimination power as the digestion methods. The study was performed for a set of over 130 glass fragments composed of a variety of containers, headlamps, windshields, side vehicle windows and architectural windows [30]. Fractionation has also presented an area of concern, and therefore a study indicating the non-effect of fractionation on the quantitative analysis of glass has also been reported [31].

Although these results are very encouraging, further studies regarding the particular interaction of the laser with the glass surface were also conducted to offer additional validation to the proposed method. These complementary investigations include a heterogeneity study of glass samples in the micro-scale range and the evaluation of the effect of fragment size on the quantitative analysis of glass for comparison purposes. The later is the aim of the present work.

Due to the differences in the samples submitted in casework involving broken glass, the sizes of fragments that arrive at the laboratory varies greatly. Samples recovered from a known source are frequently large (>3 mm) because they are sampled from the available original piece, i.e. fragments collected from the windowpane of a house in a breaking and entering case. On the other hand, the fragments collected from the suspect are usually recovered at the laboratory by shaking or brushing a garment over a sheet of paper and by using stereomicroscope to examine the debris. Typical sizes of these glass fragments are between 0.1 and 1 mm in length [33].

These differences in sample sizes does not make any effect in the comparison of fragments by the bulk digestion analysis other than the limitation of the amount of sample required for analysis, which should be at least 6 mg. However, for laser ablation, the amount removed is very small (∼280 ng) and the efficiency of the interaction of the beam with the surface depends on several factors.

The coupling of the laser energy to the surface of the material results in the formation of a micro-plasma during the ablation process, along with other mechanisms such as vaporization [18]. The thermo–optical properties of the sample are expected to influence these processes. The physical shape and size of the samples could eventually affect the dissipation of heat and cooling rates and the amount of material removed during the laser pulse.

In order to evaluate the impact of these concerns, the present work has evaluated the elemental composition of glass fragments between 6 and 0.1 mm in size to determine whether the ranges the size of the fragments affect the quantitative analysis of glass for forensic purposes.

2. Experimental

2.1. Instrumentation

A Leica microscope, model L2 was used to mount the glass fragments in labeled paper squares for LA analysis. 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 auto sampler ASX-500 (CETAC, Omaha, NE, USA). Laser ablation analyses were performed with a CETAC (Omaha, NE, USA) laser ablation system (model LSX-500) Q switched Nd:YAG, operating at 266 nm. Helium was used as carrier gas into the cell at 0.95 L min^{-1} and then mixed with make-up argon after the cell (0.95 L min^{-1}). Ablation was performed using single spot mode at 10 Hz for 50 s. The elemental menu used for the quantitative analysis of the glass standards is shown in Table 1. A scanning

Table 1
Elemental menu selected for LA data analysis of glass samples

Element	Isotope monitored
Li	^{7}Li
B	^{11}B
Mg	^{25}Mg
Al	^{27}Al
K	^{39}K
Si	^{29}Si
Ti	^{49}Ti
Mn	^{55}Mn
Fe	^{57}Fe
Co	^{59}Co
Rb	^{85}Rb
Sr	^{88}Sr
Zr	^{90}Zr
Sn	^{118}Sn
Ba	^{137}Ba
La	^{139}La
Ce	^{140}Ce
Hf	^{178}Hf
Pb	^{208}Pb
Th	^{232}Th
U	^{238}U

electron microscope (SEM/EDX) JSM-5900-LV (JEOL, Japan) from the FCAEM (Florida Center for Analytical Electron Microscopy at FIU) was used for the imaging of the craters on glass, operated at high vacuum and using secondary electron imaging at 20 kV and a spot size of 40 μm. The glass samples were coated with gold to prevent charging.

2.2. Reagent, standards and sampling preparation

Standard reference materials SRM NIST 612 and SRM NIST 610 were crushed using a rubber-head hammer and disposable polypropylene weighing boats (Fisher, Pittsburg, PA, USA). The fragments were washed with 0.8 mol L^{-1} trace elemental grade nitric acid (Fisher, Pittsburgh, PA, USA) for 30 min followed by rinsing with deionized water and then let dry overnight. Seven fragments from different shapes and sizes (6–0.1 mm length) were selected from each standard. The fragments were mounted under a microscope into a small piece of "tacky blue" mounting medium (see Fig. 1). During LA-ICP-MS each fragment was analyzed in triplicate. The sequence of analysis was randomly selected and the order of analysis was fragment 3, 5, 2, 7, 4, 1 and 6 (fragment 7 was the smallest fragment). The calibrators SRM 612 or SRM 610 were analyzed at the beginning and at the end of the sequence in order to account for any drift and to correct the instrument for any drift.

2.3. Statistical analysis

Statistical analyses were carried out using analysis of variance (ANOVA) followed by the Tukey's honestly significant different test (HSD), using SYSTAT for windows 8.0 (SPSS Science, Chicago, IL). Data reduction of laser ablation data was performed using the GLITTER software (GEMOC, Macquarie University, Australia).

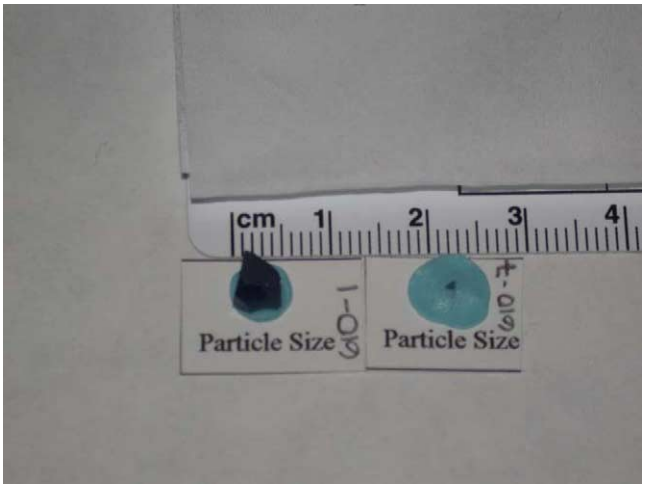

Fig. 1. Comparison of the fragment size 1 and fragment size 7 of SRM 610.

3. Results and discussion

The NIST standards SRM 612 and SRM 610 were used for this work in order to account for differences in the opacity of the sample as well as differences in concentration levels. The standard SRM 612 is more transparent than SRM 610 and depending of the laser used for the ablation could affect the efficiency of the coupling of the laser beam with the surface as well as loss of energy due to reflection. The sizes of the fragments were selected according to the typical sizes recovered from crime scenes. The smallest size of the fragments (#7) was limited by the minimum area that a glass fragment should have in order to perform the LA analysis of craters of 50 μm spot size in triplicate and leaving at least 50 μm of space between each ablation in order to avoid contamination due to depositions. Table 2 shows the size, mass and shape of the fragments used for the laser ablation analysis. The shape description is approximated because most of the fragments were amorphous. Fig. 1 shows the comparison of size between the largest and the smallest fragment sampled from SRM 610, in this example, fragment #7 had a length that is ∼25 times smaller than fragment #1. The SEM image on Fig. 2 shows the ablation of three craters on the fragment #6 of SRM 610, which is less than 1 mm in length. This fragment (#6) illustrates the clear advantages of LA over the digestion method because with the amount of material (∼1 mg) it would be impossible to run the digestion method that requires at least 6 mg to run the analysis in triplicate while laser ablation analysis was performed in triplicate and there is still enough glass left to conduct additional analysis, which may be critical for some forensic casework.

Analysis of variance (ANOVA) was conducted in order to determine if there was a significant difference in the elemental concentration of the fragments due to the size and shape of the glass piece. With a 99% confidence level ($p = 0.01$), there was no significant difference on the elemental concentration of any of the fragments originating from SRM 610 or SRM 612.

Table 2
Distribution of size and shape of the glass fragments selected for this study

Fragment	Surface size (mm)	Mass (mg)	Shape
SRM 612			
1	6.39 × 2.98	99.024	Triangular
2	2.25 × 3.14	35.080	Pentagonal
3	2.21 × 2.07	13.280	Irregular
4	2.02 × 1.64	11.834	Pentagonal
5	1.78 × 0.81	2.565	Rectangular
6	0.91 × 0.66	1.025	Rectangular
7	0.13 × 0.72	0.616	Rectangular
SRM 610			
1	3.6 × 3.5	45.020	Quasi-squared
2	3.8 × 1.97	33.841	Triangular
3	1.32, 1.44 × 2.2	15.284	Trapezoid
4	1.07 × 0.70	3.248	Pentagonal
5	1.31 × 0.6	2.280	Triangular
6	0.78 × 0.65	1.258	Irregular
7	0.11 × 0.20	0.907	Irregular

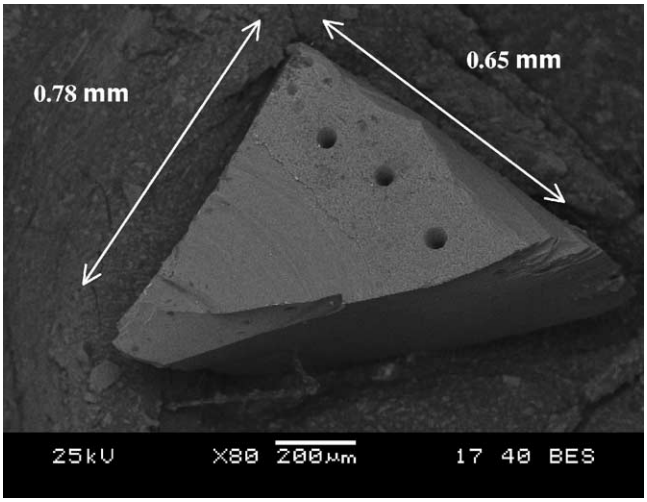

Fig. 2. SEM image of fragment SRM 610 # 6 after ablation.

Table 3 shows the elemental ratios for the different replicates in the fragments from both standards and a good correlation between fragments originating from the same standard can be observed. Fig. 3 illustrates an example of the comparison of mean values and precision of the elemental ratios between fragments originating from SRM 610. The RSD for the vast majority of elements was determined to be less than 6% when NIST SRM 612 (~40 $\mu g\,g^{-1}$) and SRM 610 (~500 $\mu g\,g^{-1}$) were measured.

In addition to the good association between fragments of different sizes, Fig. 4 illustrates the good accuracy of the elemental ratios for SRM 612 fragments compared to the reported values. Experiments conducted on the SRM 610 fragments have similar results.

The SEM images demonstrate that there was not a significant difference in the shape of the ablation craters and their immediate surrounding surface. Fig. 5 illustrates the comparison of crater images obtained for the biggest and the smallest fragments of SRM 612, where no differences in crater shape nor deposition of particles were observed.

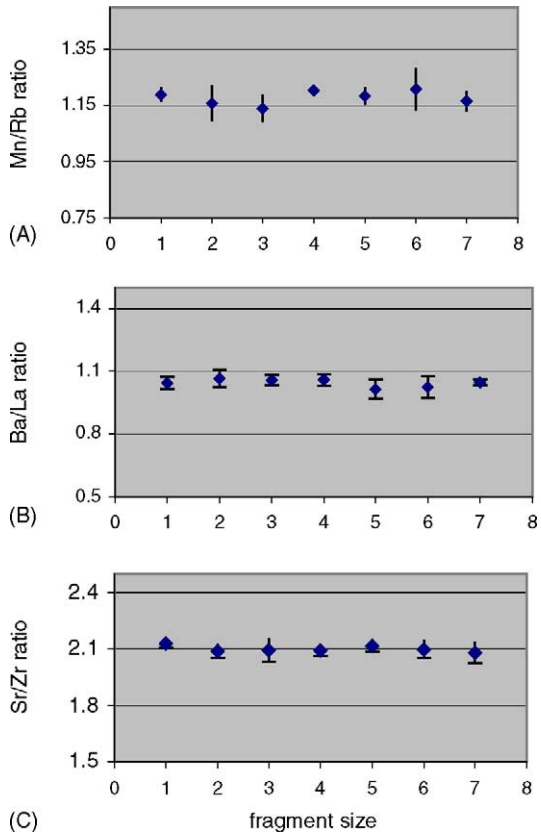

Fig. 3. Mean values and standard deviation ($n = 3$) of the elemental ratios of seven different glass fragments from SRM 612. (A): Mn/Rb, (B): Ba/La and (C): Sr/Zr.

The experimental results demonstrate that the proposed LA-ICP-MS method is not affected by the variability in fragment size of the samples and is reliable to perform routine forensic glass casework in these size ranges.

Table 3
Mean values ($n = 3$) of the elemental ratios of fragments of SRM 612 and SRM 610

Fragment #	B/Li	Mg/Al	Ti/Mn	Sr/Zr	Rb/Zr	Fe/Mn	Mn/Rb	Ba/La	Ce/La	Pb/Hf	U/Th	Zr/Sn	Al/K	Co/Sr
SRM 612														
1	0.824	0.007	1.211	2.129	0.413	1.691	1.189	1.044	1.082	1.134	1.078	0.907	168.2	0.472
2	0.834	0.007	1.203	2.090	0.415	1.498	1.158	1.065	1.050	1.121	1.071	0.979	162.9	0.467
3	0.877	0.007	1.534	2.092	0.416	1.529	1.140	1.057	1.073	1.085	1.026	0.970	157.3	0.478
4	0.884	0.007	1.209	2.093	0.415	1.495	1.204	1.059	1.067	1.079	1.043	0.931	178.9	0.460
5	0.837	0.007	1.318	2.117	0.418	1.696	1.184	1.014	1.042	1.144	1.096	0.907	168.1	0.451
6	0.828	0.007	1.315	2.097	0.418	1.696	1.207	1.024	1.027	1.095	1.025	0.933	177.1	0.466
7	0.819	0.007	1.282	2.081	0.422	1.721	1.165	1.047	1.055	1.098	1.040	0.951	180.7	0.461
SRM 610														
1	0.787	0.048	0.961	1.176	0.894	1.043	0.972	0.953	1.025	1.094	1.086	1.007	19.12	0.834
2	0.793	0.049	0.959	1.160	0.911	1.055	0.953	0.929	1.008	1.091	1.080	1.011	20.30	0.861
3	0.784	0.048	0.973	1.146	0.894	1.038	0.949	0.942	0.992	1.040	1.045	1.038	20.20	0.817
4	0.728	0.049	0.939	1.175	0.902	1.064	0.978	0.946	1.018	1.112	1.129	0.977	19.33	0.848
5	0.792	0.048	0.959	1.147	0.876	1.042	0.969	0.948	0.996	1.057	1.026	1.052	20.79	0.813
6	0.795	0.049	0.951	1.187	0.928	1.040	0.948	0.950	1.035	1.163	1.144	0.942	18.51	0.879
7	0.779	0.047	0.977	1.140	0.875	1.048	0.995	0.923	0.990	1.001	1.053	1.074	20.06	0.843

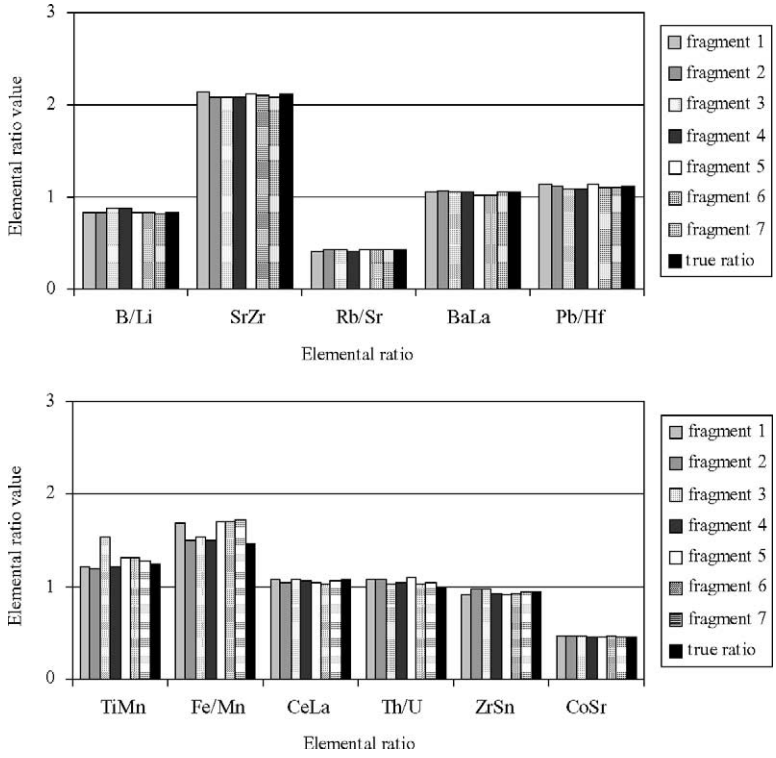

Fig. 4. Comparison of true values and experimental ratios in glass fragments of different sizes originated from SRM 612.

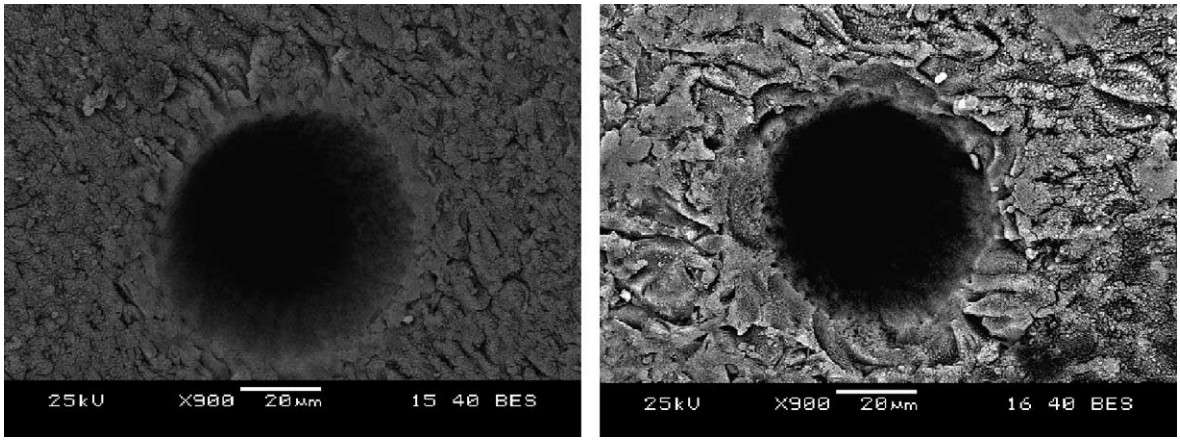

Fig. 5. Comparison of SEM image of the crater of fragment #1 (left) and #7 (right).

4. Conclusions

Laser ablation is the first choice as a sample preparation technique for elemental analysis of glass by ICP-MS because of the numerous advantages this technique has over the conventional dissolution methods.

The proposed method of LA-ICP-MS not only provides similar analytical performance to well-accepted digestion methods but also has been demonstrated to offer reliable comparisons of glass fragments that differ in size and shape.

One of the concerns of the application of laser ablation to forensic evidence is whether the surface interaction of the laser-target might be affected by the size and shape of the recovered material due to possible differences in heat dissipation. The results of this study indicate that the quantitative analysis of glass with internal standardization is possible for glass samples as small as 0.1 mm in length.

Acknowledgements

The authors would like to thank the Florida Center for Analytical Electron Microscopy (FCAEM at FIU) for using the SEM facilities and to Barbara Maloney and Thomas Beasley

for their technical support of the SEM imaging. CETAC, Inc. provided a partial instrument grant. The National Institute of Justice provided financial support of this work. The authors also want to acknowledge the efforts of the NITECRIME network and its members for the advancement of elemental analysis of glass fragments by LA-ICP-MS.

References

[1] J.R. Almirall, Elemental analysis of glass fragments, in: B. Caddy (Ed.), Forensic Examination of Glass and Paint, Taylor & Francis, London, 1999, pp. 65–80.
[2] J. Buscaglia, R. Koons, Forensic Sci. Commun. 1 (Jan 3) (2001).
[3] J.C. Hughes, T. Catterick, G. Southeard, J. Forensic Sci. 8 (1976) 217.
[4] T. Catterick, C.D. Wall, Talanta 25 (1978) 573.
[5] J. Buscaglia, Anal. Chim. Acta 288 (1994) 17.
[6] R. Koons, C.A. Peters, P.S. Rebbert, J. Anal. At. Spectrom. 6 (1991) 451.
[7] R.F. Coleman, G.C. Goode, J. Radianal. Chem. 15 (1973) 367.
[8] R.F. Coleman, N.T. Weston, J. Forensic Sci. Soc. 8 (1) (1968) 32.
[9] Kuisma-Kursula, Ray Spect. 29 (2002) 111.
[10] A. Zurhaar, L. Mullings, J. Anal. At. Spectrom. 5 (1990) 611.
[11] T. Parouchais, I.M. Warner, L.T. Palmer, H. Kobus, J. Forensic Sci. 41 (1996) 351.
[12] D.C. Duckworth, C.K. Bayne, S. Morton, J.R. Almirall, J. Anal. At. Spectrom. 15 (2000) 821.
[13] R. Koons, J. Buscaglia, M. Botrell, E. Miller, Forensic glass comparisons, in: R. Saferstein (Ed.), Forensic Science Handbook, Prentice Hall, New Jersey, 2002, pp. 180–211.
[14] D.C. Duckworth, S.J. Morton, K. Bayne, S. Montero, R. Koons, J.R. Almirall, J. Anal. At. Spectrom. 17 (2002) 662.
[15] S. Durrant, J. Anal. At. Spectrom. 14 (1999) 1385.
[16] R.E. Russo, X.L. Mao, H. Liu, J. Gonzalez, S. Mao, Talanta 57 (2002) 425.
[17] D. Günther, J.M. Mermet, Laser ablation for inductively coupled plasma-mass spectrometry, in: D. Barcelo (Ed.), Discrete Sample Introduction Techniques for Inductively Coupled Plasma Mass Spectrometry, Elsevier, London, 2002, pp. 445–501.
[18] R.E. Russo, Laser ablation, in: J. Holcome, G. Hiefte, V. Majidi (Eds.), Focus on Analytical Spectrometry: A Compendium of Applied Spectroscopy Focal Point Articles, Society for Applied Spectroscopy, MD, 1998, pp. 41–55.
[19] R.E. Russo, X.L. Mao, S.S. Mao, Anal. Chem. (1 Feb) (2002) 71A.
[20] R.E. Russo, X.L. Mao, H. Liu, O.V. Borisov, Trends Anal. Chem. 17 (8–9) (1998) 461.
[21] R.J. Wattling, B.F. Lynch, D. Herrring, J. Anal. At. Spectrom. 12 (1997) 195.
[22] R.J. Wattling, Spectroscopy 14 (6) (1999) 16.
[23] M. Guillong, D. Günther, Spectrochim. Acta 56 (2001) 1219.
[24] H. Scholze, E. Hoffmann, C. Luke, A. Platalla, Fresenius J. Anal. Chem. 355 (1996) 892.
[25] D. Devos, Ch. Moo, P. Lienemann, J. Anal. At. Spectrom. 14 (1999) 621.
[26] B. Flem, R. Larsen, J. Grimstved, J. Mansfeld, Geochem. Geol. 182 (2002) 237.
[27] E. Hoffmann, H. Stephanowitz, E. Ulrich, J. Skole, C. Ludke, B. Hoffmann, J. Anal. At. Spectrom. 15 (2000) 663.
[28] R. Jarowski, E. Hoffmann, H. Stephanowitz, Int. J. Mass Spectrom. 219 (2002) 373.
[29] P.M. Outridge, W. Doherty, D.C. Gregoire, J. Geochem. Expl. 60 (1998) 229.
[30] T. Trejos, S. Montero, J.R. Almirall, Anal. Bioanal. Chem. 376 (2003) 1255.
[31] T. Trejos, J.R. Almirall, Anal. Chem. 76 (5) (2004) 1236.
[32] A. Hobbs, J.R. Almirall, Anal. Bioanal. Chem. 376 (2003) 1265.
[33] P. Hamer, Microscopic techniques for glass examination, in: B. Caddy (Ed.), Forensic Examination of Glass and Paint, Taylor & Francis, London, 1999, pp. 48–50.