Multielement Analysis of Alkaline-Resistant Glass and Basalt Glass Fibers Using Laser Ablation ICP-MS: A Useful Tool in Technical Textile Quality Control

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ABSTRACT

A powerful multielement analytical technique using laser ablation inductively coupled plasma source mass spectrometry (LA-ICP-MS) for the sensitive determination of trace impurities in thin glass filaments, used as reinforcing material in the construction industry, was developed. The trace analysis was carried out directly on very thin solid strands (without any sample preparation steps) by LA-ICP-MS whereby a bundle of thin glass fibers (with a filament diameter of about 10 – 20 µm) was fixed on a thin, special tape of a target holder. The fibers were ablated in the ablation chamber with the aid of a commercial laser ablation system (using a Nd-YAG laser at a wavelength of 266 nm). In order to verify the trace analytical data, the ablated glass fibers were analyzed using a quadrupole (LA-ICP-QMS) and double-focusing sector field mass spectrometer (LA-ICP-SFMS). The detection limits of the trace elements in glass fibers using the LA-ICP-MS with a quadrupole analyzer were in the sub µg g^{-1} range, whereas using a sector field mass spectrometer (LA-ICP-SFMS) the detection limits could be improved by 3-4 orders of magnitude down to the low and sub ng g^{-1} range.

The multielement trace analytical method, developed for high-purity glass fibers, was applied to the determination of chemical composition on thin alkali-resistant glass and basalt fibers with finishing additives used in fine concrete for the building industry. The analytical results were quantified using standard reference materials (SRMs) of glass matrix, such as the NIST 612 glass SRM and the basalt geological reference glasses, KL-2G and ML3B-G, for the trace analysis of basalt glass fibers. The experimentally determined relative sensitivity coefficients (RSC) in LA-ICP-MS for both SRMs varied between 0.2 and 3 for most of the elements. An increase of the relative sensitivity coefficients was observed with increasing mass. The relative standard deviation (RSD) of most elements (N = 3) was between 2 and 10%. The results of the trace element concentrations by LA-ICP-MS using different instrumentation are in good agreement.

INTRODUCTION

Alkaline-resistant (AR) glass fibers are thin solid strands with a diameter of about 15 µm. The chemical composition of these fibers is of great interest (such as pure glass fibers with AR-increasing additives and basalt glass fibers), since they could have many future uses, such as reinforcing material in the construction industry. Such thin glass fibers (covered by a thin polymer film for better handling) should be alkali-resistant for application in reinforced concrete to ensure durability of the construction material.

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is a powerful and sensitive trace analytical technique which, within the last few years, has been gaining increasing importance for the sensitive trace analysis of solid non-conducting samples (1) in various fields of modern science and technology. The largest application field for LA-ICP-MS is geology and mineralogy (2-5). Jochum et al. (6) described the preparation and characterization of geological reference glasses (eight silicate glasses) for in situ microanalysis. In order to avoid inhomogeneous elemental distributions in geological samples, homogeneous geological glass targets were prepared by Jochum et al. (6) by direct fusion at 1400 – 1600°C using a special melting technique. The geological glass samples are well homogenized with respect to major and trace elements on the µm to mm scale. In general, the measurements by LA-ICP-MS yielded trace analysis results with good accuracy and precision on these geological glass samples in comparison to the recommended concentrations and the results of other bulk and microanalytical methods (XRF - X ray fluorescence analysis, SIMS - secondary ion mass spectrometry, SSMS – spark source mass spectrometry, LIMS – laser ionization mass spectrometry, NAA - neutron activation analysis, and others) used in this paper (6). The basalt glass fibers investigated in the present work are of similar matrix composition to that of the basalt glass targets studied in (6).

LA-ICP-MS can also be successfully used for characterizing the trace element composition of high-purity insulating materials without sample preparation (7,8). Due to its capability of complete ablation (evaporation) of any solid material (irrespective of its physical and chemical properties) by a focused laser beam and its sensitive detection of ions formed in the inductively coupled plasma, LA-ICP-MS is important for the direct multielement analysis of difficult-to-digest (chemically resistant) materials such as glasses, ceramics, or high-purity noble metals. Difficult and time-consuming sample preparation steps are not necessary and, therefore, possible contamination can be reduced to a minimum. Furthermore, LA-ICP-MS allows a rapid survey analysis of an unknown material with respect to its major, minor, and trace element composition (fingerprinting). Without any quantification procedure, the unknown sample can be characterized semi-quantitatively with respect to elemental concentration with an error factor of concentration of about 2 to 3 (9). The analytical results of LA-ICP-MS were mostly quantified by using suitable solid standard reference materials with similar matrix composition. The

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measured analytical results of LA-ICP-MS were corrected using experimentally determined relative sensitivity coefficients. With the application of a standard reference material (SRM), the RSC of a chemical element is defined as RSC = ratio of measured (experimental) to certified (true) element concentration in a given matrix (8). Fortunately for glass and basalt samples, standard reference materials are available which can be used for the purpose of quantifying analytical results.

Multielement analysis on thin glass fiber samples by LA-ICP-MS without any sample preparation is unknown. The aim of the present work is to study the capability of LA-ICP-MS for the multielement determination of trace elements in glass and basalt fiber materials.

EXPERIMENTAL

Instrumental and Measuring Procedures

In these experiments, a commercial laser ablation (LA) system (Cetac LSX 200, Cetac Technologies, Omaha, NE, USA) is coupled to the inductively coupled plasma ion source of a quadrupole mass spectrometer (ICP-QMS, ELAN® 6000, PerkinElmer SCIEX, Concord, Ontario, Canada) and a double-focusing sector-field mass spectrometer (ICP-SFMS, ELEMENT, Finnigan MAT). The UV wavelength of a Nd-YAG laser (4^{th} harmonic, 266 nm) was used for laser ablation. The experimental parameters of the laser ablation system used and mass spectrometric measurements using two different ICP instruments are summarized in Table I. The mass spectrometric measurements of most elements were carried out at low mass resolution ($m/\Delta m \approx 300$). The rf power of ICP and the carrier gas flow rate are optimized using the NIST SRM glass 612 with respect to the maximum ion intensity of $^{88}Sr^{+}$. Three repetitions of LA-ICP-MS measurements at three different places on the glass and basalt fibers and the standard reference materials were performed.

TABLE I
Experimental Parameters

ICP-QMS (ELAN 6000, PerkinElmer SCIEX) ; ICP-SFMS (ELEMENT, Finnigan MAT)	
Rf power	1000 W
Coolant gas flow rate	14 L/min
Auxiliary gas flow rate	0.8 L/min
Carrier gas flow rate	0.6 L/min
Mass resolution $m/\Delta m$	ICP-QMS: 300 ICP-SFMS: 300 and 3000
Acquisition mode	Peak hopping
Detector mode	Dual
Points per peak	1
Dwell time	10 ms
No. of Sweeps	10
No. Readings	1
No. of Replicates	5
Sampling cone	Nickel with 1.1-mm orifice
Skimmer cone	Nickel with 0.9-mm orifice
Laser ablation	
Laser ablation system	CETAC LSX-200
Wavelength	266 nm (4^{th} harmonic of Nd:YAG laser)
Pulse duration	5 ns
Repition frequency	20 Hz
Pulse energy	5 mJ
Laser power density	$9*10^8$ W/cm^2
Spot diameter	340 µm
Pre-ablation time	10 s
Laser ablation mode	Single-line scan

Standard Reference Materials, Samples, and Sample Preparation

The standard reference material NIST SRM glass 612 and geological reference glasses [KL-2G and ML3B-G (6)] were used for the determination of relative sensitivity coefficients in LA-ICP-MS. Two glass fiber samples of different purity and two basalt fiber samples were investigated with respect to their trace element composition by LA-ICP-MS. The reference materials were also used for the determination of detection limits (3 σ criterion, the limit of detection is given by $m_b + 3\sigma_b$, where m_b is the mean value of the blank measurement and σ_b is the standard deviation of five independent measurements of this blank sample) of trace elements in different matrices. The fiber samples were fixed on the target holder by a special clean tape.

Silicon or lanthanum (if the concentration was known) were chosen as the internal standard elements for the determination of RSCs in both reference materials, the alkali-resistant glass, and basalt fibers.

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RESULTS AND DISCUSSION

The mean concentrations of major elements in AR glass and basalt fibers measured by LA-ICP-MS are summarized in Table II. It is possible to quantify the analytical results in LA-ICP-MS if a standard reference material with certified element concentrations and a similar matrix is available. Relative sensitivity coefficients (RSC = measured value / true value) in LA-ICP-MS, used as correction factors for the measured data, can therefore be determined (9). In Figure 1 the results of the determination of RSCs of 34 selected elements in NIST SRM glass 612 by LA-ICP-MS using two different mass spectrometers (LA-ICP-QMS and LA-ICP-SFMS) are compared. The measured RSCs varied between 0.4 and 2 for most elements in glass reference materials using LA-ICP-MS (except for Sn and Pb using LA-ICP-QMS). This means that a semiquantitative determination of trace elements without the use of SRM (glass matrix) is possible with an error factor in this range. In general, a similar dependence for RSCs on mass is found for different elements using both LA-ICP mass spectrometers in this work. Higher RSCs in LA-ICP-QMS in comparison to LA-ICP-SFMS are observed. Using the two different mass spectrometers, the RSCs of elements from Gd to Ta in NIST SRM glass 612 were determined by LA-ICP-MS to be approximately 1, which means no fractionation effects of these elements under optimized experimental conditions were observed in the glass matrix.

In comparison to NIST SRM glass 612, higher element sensitivity was measured on basaltic glass KL-2G in LA-ICP-SFMS (see Figure 2). This effect could be explained by the different matrix composition of these two reference materials and following differences in absorption and reflection of laser radiation.

TABLE II
Concentrations of Major Elements in AR Glass and Basalt Glass Fibers Measured by LA-ICP-SFMS

	Element concentration in %	
Metal oxide	AR glass fibers	Basalt glass fibers
SiO_2	50 - 62	26
ZrO_2	24 - 40	-
Na_2O	11 - 17	3
Al_2O_3	-	21
CaO	-	30
MgO	-	5
TiO_2	-	5
K_2O	-	5
FeO	-	3
MnO	-	2

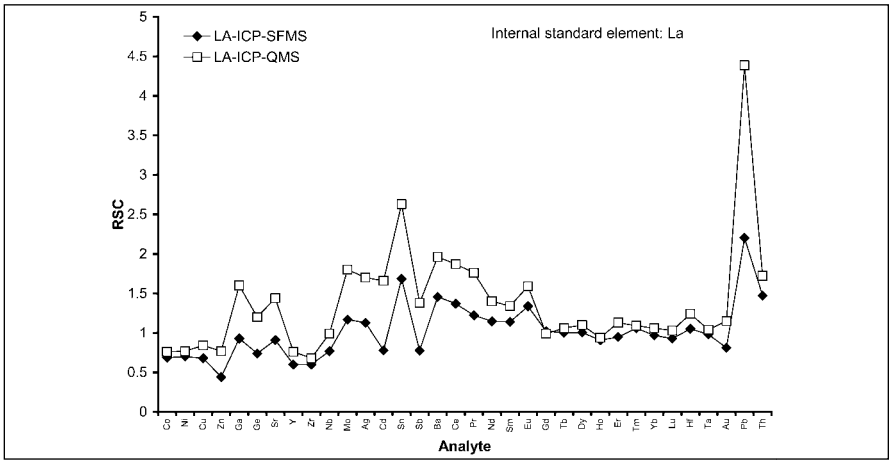

Fig. 1. Relative sensitivity coefficient (RSC) of elements in LA-ICP-QMS (ELAN 6000, PerkinElmer SCIEX) in comparison to LA-ICP-SFMS (Element, Finnigan MAT) for NIST SRM 612 glass matrix.

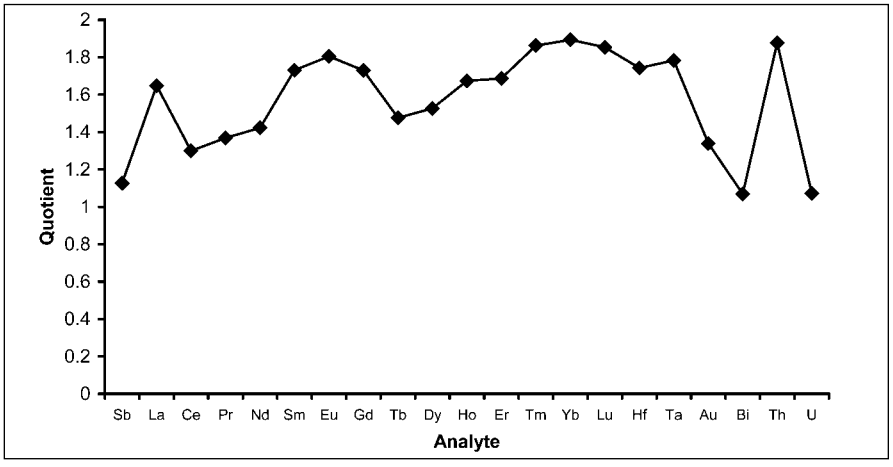

Fig. 2. Sensitivity measured on KL-2G (basaltic glass) divided by sensitivity measured on NIST SRM glass 612 using LA-ICP-SFMS.

Important for trace analysis of glass fibers, especially of high-purity glass fibers used in information technology for transmitting information via light pulses, are the limits of detection (LODs) of the analytical techniques applied. In Figure 3 the limits of detection on high-purity glass fibers in LA-ICP-QMS are compared with those of LA-ICP-SFMS. Due to the higher element sensitivity and lower instrumental background of sector field ICP-MS, the limits of detection in LA-ICP-SFMS are 3 to 4 orders of magnitude lower than in LA-ICP-QMS. The lowest limits of detection were measured in high-purity glass fibers for Pr, U, La, and Th at about 20 – 40 ppt (pg g^{-1}). The detection limits of selected elements measured directly on basalt glass fibers by LA-ICP-SFMS are summarized in Table III. In contrast, the limits of detection in LA-ICP-QMS were determined to be in the sub µg g^{-1} range. These limits of detection are sufficient to measure trace element concentrations in basalt and AR glass fibers.

In principle, it is possible to determine ultratrace impurities in non-conducting materials in the low ppt range by LA-ICP-SFMS as demonstrated for the determination of certain long-lived radionuclides (e.g., LOD of ^{233}U as 1.3 pg g^{-1}) in a concrete matrix (7). Of special interest are the decreasing limits of detection due to increasing sensitivity using a shielded plasma torch in LA-ICP-SFMS. In Figure 4, the sensitivities measured in LA-ICP-SFMS are compared with and without a shielded torch (GE – guard electrode) on NIST glass SRM 612 at an rf-power of 1200 W and a carrier gas flow rate of 1.35 L min^{-1} (other experimental parameters are summarized in Table I). Using a plasma-shielded torch, an increase in sensitivity by a factor of 3 to 4 was observed for most of the analytes due to a reduction of secondary discharge and initial energy of ions in

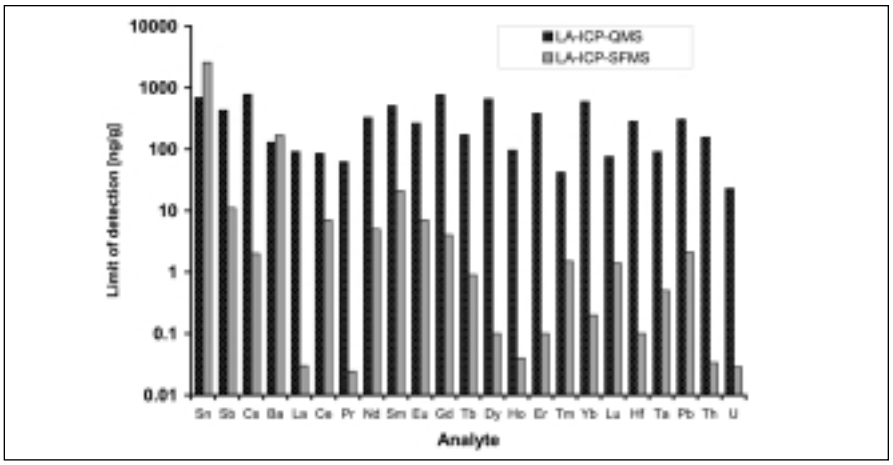

Fig. 3. Limits of detection on high-purity glass fibers in LA-ICP-QMS (ELAN 6000, PerkinElmer SCIEX) in comparison to LA-ICP-SFMS (Element, Finnigan MAT).

TABLE III
Detection Limits (in µg/g) for Trace Elements in Thin Basalt Fiber Samples Measured by LA-ICP-SFMS and LA-ICP-QMS

Element	LA-ICP-SFMS	LA-ICP-QMS	Element	LA-ICP-SFMS	LA-ICP-QMS
Sb	0.024	0.428	Dy	0.0002	0.654
Cs	0.0011	0.775	Ho	0.00004	0.096
La	0.00005	0.091	Er	0.0001	0.380
Ce	0.0062	0.085	Tm	0.0016	0.042
Pr	0.00005	0.062	Yb	0.0002	0.590
Nd	0.0073	0.326	Hf	0.0001	0.284
Sm	0.02	0.508	Ta	0.0006	0.090
Eu	0.0074	0.263	Pb	0.006	0.305
Gd	0.0047	0.762	Th	0.00003	0.156
Tb	0.0011	0.171	U	0.00003	0.023

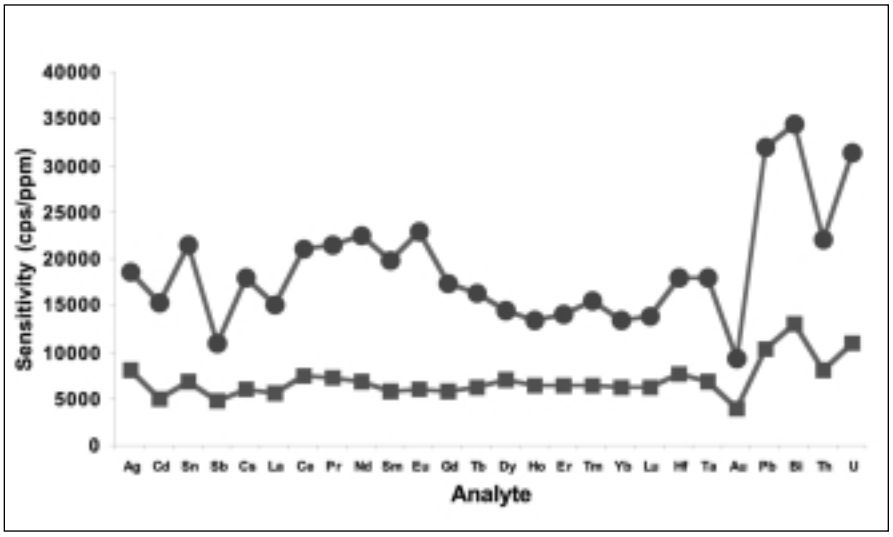

Fig. 4. Comparison of sensitivities measured in LA-ICP-SFMS with a plasma-shielded torch (●) and without a shielded torch (■) (GE –guard electrode) on NIST SRM glass 612 (rf-power: 1200 W; carrier gas flow rate: 1.35 L min^{-1}).

the plasma. The background intensities for measurements with and without plasma-shielded torch are in the same range (e.g., for $^{121}Sb^+$ - 700 cps, $^{141}Pr^+$ - 38 cps, $^{238}U^+$ - 2 cps with shielded torch vs. for $^{121}Sb^+$ - 680 cps, $^{141}Pr^+$ - 28 cps, $^{238}U^+$ - 1 cps without shielded torch). In order to verify the analytical data measured on glass fibers by LA-ICP-MS and to check the accuracy of the analytical results, the element concentrations in a glass fiber sample measured by LA-ICP-QMS (ELAN 6000, PerkinElmer SCIEX) are compared with those of LA-ICP-SFMS (Element, Finnigan MAT) in Figure 5. The results of the determination of trace element concentrations in this sample by LA-ICP-MS using different instrumentation are in good agreement.

The homogeneity of the investigated glass and basalt fiber materials is one of the most important features of the reference materials and was investigated by LA-ICP-MS measurements on different parts of samples. In general, the relative standard deviation of trace element determination is a measure of the inhomogeneities observed in the different glass fibers investigated.

Table IV summarizes the analytical results of element determination by LA-ICP-MS in two different AR glass fibers (doped with Na, Y, Zr, and Hf) measured by quadrupole LA-ICP-MS. The glass fiber sample 2, in comparison to sample 1, possesses a significantly higher Li and Ti concentration than non-alkaline-resistant glass fibers of about 4500 and 8260 µg g^{-1}. Titanium was added to the glass matrix in order to improve the alkaline resistance of the fibers. The relative standard deviation of the determination of the concentration in the investigated samples is mostly 2 to 10%. But the relatively high RSDs of the Zr, Hf, and Y concentrations determined demonstrate an inhomogeneous distribution of these

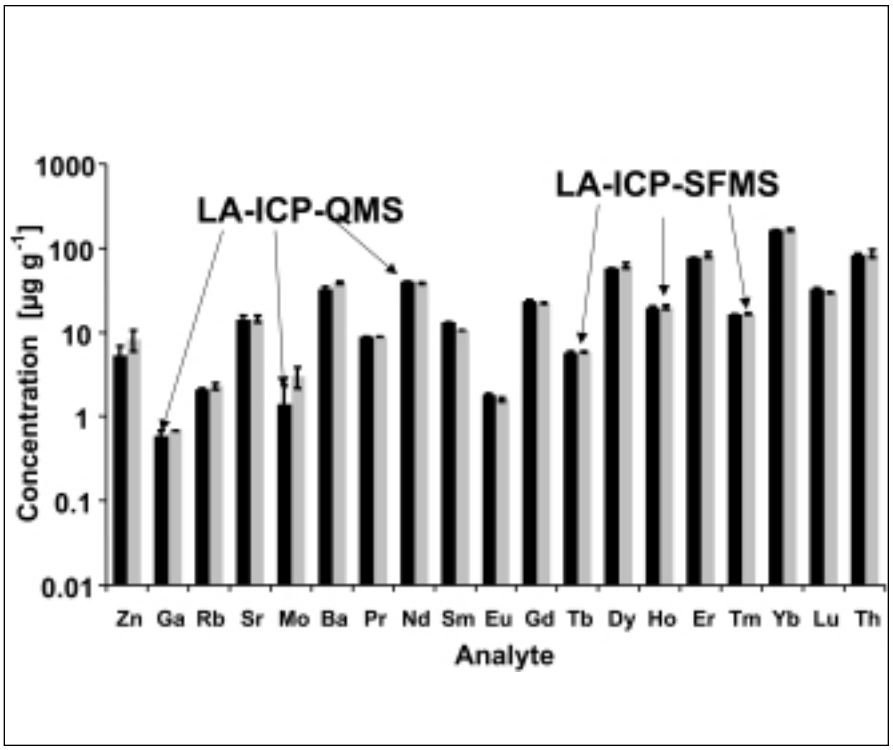

Fig. 5. Comparison of element concentrations in glass fibers measured by LA-ICP-QMS (left column: ELAN 6000, PerkinElmer SCIEX) in comparison to LA-ICP-SFMS (right column: Element, Finnigan MAT).

elements. The quantitative determination of problematic elements, which are disturbed by isobaric interferences with possible molecular ions (e.g., $^{56}Fe^+$ - $^{40}Ar^{16}O^+$; $^{52}Cr^+$ - $^{40}Ar^{12}C^+$, $^{64}Ni^+$ - $^{40}Ar^{24}Mg^+$ and $^{63}Cu^+$ - $^{23}Na^{40}Ar^+$ and others), is performed in LA-ICP-QMS after interference correction. Even an empirical correction of possible interferences, which is usually applied in quadrupole-based ICP-MS, is sometimes insufficient. An accurate determination of these elements can be performed by separating such interferences of molecular ions and atomic ions of analyte using a double-focusing sector-field mass spectrometer (LA-ICP-SFMS) at the required mass resolution.

The results of the trace analysis on one basalt glass fiber (with matrix element composition: Si > Ca > Al > Mg > Fe > Na > Ti > K) measured by LA-ICP-SFMS at low mass resolution are given in Table V. In this way, the concentrations of 18 selected trace elements were determined simultaneously whereas the content of rare earth elements (REEs) Cs, Hf, Pb, Th, and U in basalt glass fibers are in the low µg g^{-1} range. For the REEs, the typical concentration distribution in basalt was found with a lower concentration for elements with odd atomic numbers in comparison to the neighboring REEs and a decreasing concentration with increasing atomic number. Accuracy of the quantification method in LA-ICP-MS is better than 5% for most elements as demonstrated for several geological basaltic glasses in a previous work (10).

CONCLUSION

LA-ICP-MS is a very powerful multielement analytical technique for the simultaneous determination of major, minor, trace, and ultratrace elements in thin glass fibers used for communication technologies and glass and basalt glass fibers for future application in reinforced concrete in the construction industry. By optimizing the analytical techniques, detection limits in LA-ICP-MS in the sub ng g^{-1} range were observed. In comparison to more time-consuming measurements of trace impurities in glass fibers by LA-ICP-SFMS, especially if elements at higher mass resolution were determined, LA-ICP-MS using a quadrupole analyzer is very suitable for rapidly obtaining correct analytical data for trace element concentrations. The analytical method developed can be used for quality control of the glass fibers.

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REFERENCES

1. S.F. Durrant, J. Anal. At. Spectrom. 14, 1385 (1999).
2. D. Günther in Wilson and Wilson's Comprehensive Analytical Chemistry (D. Beauchemin et al. eds.), Vol. XXXIV, 445–501 (2000).
3. F.E. Lichte, Anal. Chem. 67, 2479 (1995).
4. C.-D. Garbe-Schönberg, C. Reimann, and V.A. Pavlov, Environ. Geol. 32, 9 (1997).
5. A.J. Campbell and M. Humayun, Anal. Chem. 71, 939 (1999).
6. K. Jochum et al., Geostandard Newsletter 24, 87 (2000).
7. J.S. Becker and D. Tenzler, Fresenius' J. Anal. Chem. 370, 637 (2001).
8. C. Pickhardt and J.S. Becker, Fresenius' J. Anal. Chem. 370, 534 (2001).
9. J.S. Becker and H.-J. Dietze, Int. J. Mass Spectrom. 197, 1 (2000).
10. J.S. Becker, C. Pickhardt and H.-J. Dietze, Mikrochim. Acta 135, 71 (2000).

TABLE IV
Results of Trace Analysis on AR Glass Fibers Measured by LA-ICP-QMS
(concentration in µg g^{-1})

Element	Sample 1	Sample 2
Li	9.4 ± 4.5	4515 ± 82
B	26.6 ± 6.0	20.4 ±3.5
Na	83970 ± 966	99100 ± 4840
Mg	215 ± 14	153 ± 3
Sc	55.9 ± 3.4	122 ± 10
Ti	138 ± 3	8260 ± 232
V	7.2 ± 0.3	63 ± 9
Mn	46.6 ± 1.0	73 ± 6
Fe	449 ± 150	556 ± 57
Co	1.4 ± 0.2	1.7 ± 0.5
Ni	22.3 ± 8.4	69 ± 32
Zn	4.3 ± 0.6	< 4
Ga	0.8 ± 0.07	1.7 ± 0.2
Rb	1.9 ± 0.1	4.0 ± 0.01
Sr	16.9 ± 1.2	4.0 ± 0.7
Y	12700 ± 1420	11640 ± 344
Zr	315080 ± 28490	293430 ± 40
Mo	1.5 ± 0.5	18.9 ± 0.4
Sn	6.3 ± 1.8	5.5 ± 0.1
Sb	3.7 ± 0.6	4.5 ± 2.2
Ba	34.8 ± 3.6	97 ± 14
La	45.2 ± 4.5	47.2 ± 5.1
Ce	57.7 ± 5.3	57.4 ± 5.1
Pr	9.6 ± 1.1	8.6 ± 0.3
Nd	48.4 ± 4.6	36.4 ± 3.3
Sm	14.6 ± 1.0	10.2 ± 0.9
Eu	2.0 ± 0.1	1.8 ± 0.2
Gd	26.7 ± 3.3	21.2 ± 2.7
Tb	7.1 ± 1.2	5.8 ± 0.5
Dy	68.4 ± 7	59.7 ± 6.9
Ho	25.1 ± 3.3	21.3 ± 0.8
Er	94 ± 15	76 ± 6
Tm	20.1 ± 2.2	18.0 ± 0.5
Yb	175 ± 22	173 ± 16
Lu	41.6 ± 6.1	33.7 ± 2.6
Hf	6180 ± 880	6553 ± 403
W	< 0.5	6.5 ± 1.2
Pb	3.3 ± 0.3	5.1 ± 1.4
Th	95 ± 9	122 ± 15
U	73 ± 5	75 ± 11

TABLE V
Results of Trace Analysis on Basalt Fibers Measured by LA-ICP-SFMS
(concentration in µg g^{-1})

Element	Basalt glass fiber
Cs	1.4 ± 0.2
La	9.8 ± 0.1
Pr	3.4 ± 0.8
Nd	14.4 ± 3.6
Sm	2.8 ± 0.4
Eu	0.81 ± 0.15
Gd	2.5 ± 0.4
Tb	0.5 ± 0.2
Dy	2.6 ± 0.3
Ho	0.48 ± 0.05
Er	1.5 ± 0.1
Tm	0.21 ± 0.03
Yb	1.5 ± 0.2
Lu	0.20 ± 0.03
Hf	2.9 ± 0.4
Pb	13.0 ± 1.7
Th	3.6 ± 0.04
U	1.0 ± 0.1