



Technical note

Detection efficiencies in nano- and femtosecond laser ablation inductively coupled plasma mass spectrometry

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ARTICLE INFO

Article history:

Received 12 March 2008

Accepted 4 October 2008

Available online 1 November 2008

Keywords:

Femtosecond laser ablation

Nanosecond

Inductively coupled plasma mass spectrometry

Detection efficiency

ABSTRACT

Detection efficiencies of laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), defined as the ratio of ions reaching the detector and atoms released by LA were measured. For this purpose, LA of silicate glasses, zircon, and pure silicon was performed using nanosecond (ns) as well as femtosecond (fs) LA. For instance, ns-LA of silicate glass using helium as in-cell carrier gas resulted in detection efficiencies between approximately $1\text{E-}7$ for low and $3\text{E-}5$ for high mass range elements which were, in addition, almost independent on the laser wavelength and pulse duration chosen. In contrast, the application of argon as carrier gas was found to suppress the detection efficiencies systematically by a factor of up to 5 mainly due to a less efficient aerosol-to-ion conversion and ion transmission inside the ICP-MS.

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1. Introduction

Only a few years after the invention of laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) in the late 1980s, several studies about the aerosol transport efficiency were launched [1–3]. In 1988, Arrowsmith et al. [1] and, in 1993, Huang et al. [2] reported on transport efficiencies of up to 60%. Based on theoretical considerations involving diffusion and gravitation effects the authors, in addition, calculated a transportable particle size range varying from $0.005\ \mu\text{m}$ to $2\ \mu\text{m}$ [1] which, ever since, has been confirmed in, for instance, Refs. [4–6]. Recently, Garcia et al. [7] found transport efficiencies of approximately 80% achieved by femtosecond (fs) LA of metal targets. However, data presented did not account for particle deposition on the sample surface, which was assumed to be negligible for LA using helium as carrier gas. Nonetheless, deposition can be quite severe, in particular, if LA is carried out in argon atmosphere. Therefore, additional efforts were made and revealed that roughly 30% of the ablated mass deposits on the sample surface under conditions typically applied for analysis [8].

Examining the different sources of material losses, eventually, aims to optimize the LA protocol or cell design and, thus, to enhance accuracy and sensitivity of ICP-MS analyses. However, as suggested in

[7] and [8], a significant increase of the transport efficiency cannot be expected, since values found for different cell designs, conventional ones as well as those assumed to be optimum, were almost equivalent at an already high level of 75%–95%. Consequently, the most promising strategies for increasing the sensitivity are, to shorten the wash-out time of the ablation cell and, thus, to increase the signal-to-noise-ratio [9] or to reduce ion losses inside the ICP-MS, i.e. improving the ion transmission. While the former approach can easily be accomplished using low-volume ablation cells as proposed in Refs. [1,7] or even in-torch LA, the latter one requires the utilization of sector field (SF) instruments, which are known to be the most sensitive instruments for MS-based analysis if operated in low resolution mode.¹

Alternatively, losses inside the ICP-MS interface and in front of the quadrupole filter must be minimized by increasing the over-all ion transmission which, however, would imply a redesign of currently available interfaces used in ICP-MS instruments. In order to assess the “hidden reserves” an improved ion throughput might offer, the detection efficiency (DE) defined as the ratio of ions reaching the detector and number of atoms released during LA needs to be known. According to the literature, there exist extensive data about DEs for solution nebulization (SN)-ICP-MS [10]. However, such values must not be understood as benchmark for LA as long as, e.g., aerosol losses

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¹ The ion transmission reported for SF-ICP-MS operated in low resolution mode is known to be roughly ten times higher than the one achieved by state-of-the-art Q-type instruments.

Table 1
LA settings, Q-ICP-MS conditions, and sample materials used throughout this study

	fs-LA	ns-LA
<i>LA protocol</i>		
Wavelength, pulse duration	795 nm, $\Delta t = 150$ fs	193 nm, $\Delta t = 15$ ns
Repetition rate	5 Hz	10 Hz
Spot size	20 μm –90 μm	127 μm
Fluence	1.9 J/cm ² –10.6 J/cm ²	4.7 J/cm ²
Beam profile	Gaussian	Flat-top
<i>ICP-MS settings</i>		
Rf power	1400 W	
Injection tube diameter	2.0 mm	
Nebulizer gas flow	0.5–1.0 L/min Ar	
Auxiliary gas flow	0.8 L/min	
Carrier gas supply	1.0 L/min He or 1.0 L/min Ar (LA)	
<i>Samples</i>		
Miscellaneous	Natural zircon, silicon wafer, object slide (silicate glass)*	
Silicate glass	SRM NIST610, 612, 614 [#]	

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during transportation and incomplete evaporation of laser-produced particles inside the ICP cannot be excluded. In fact, data for LA-ICP-MS are limited because of the difficulties to determine the “true” material uptake with sufficient accuracy. To our knowledge, there have been only few attempts made yet to determine DEs for LA-ICP-MS. For instance, Boulyga et al. [11] found an ²³⁸U-specific value of 1.8E-3 using a 266 nm Nd:YAG ns laser source coupled to a first generation SF-ICP-MS instruments whereas Pisonero et al. [12] recently reported a ⁵³Cr-specific DE of 4.7E-5 on the basis of state-of-the-art UV-fs-LA-Q-ICP-MS. However, a systematic examination of the DEs achievable by LA-ICP-MS which covers a wider range of elements and materials has not been performed so far.

This study focuses on the determination of DEs applying ns- as well as fs-LA-ICP-MS. Values were measured for different materials and elemental masses ranging from 7 amu (⁷Li) up to 238 amu (²³⁸U).

2. Experimental

A chirped pulse amplification type (CPA), Ti-sapphire-based laser system (Legend, Coherent Inc., Santa Clara, CA, USA) operated at its fundamental ($\lambda = 795$ nm) was used for fs-LA. The pulse duration (150 fs) was calculated from the spectral broadening of the fundamental radiation assuming the temporal beam profile to be Fourier-

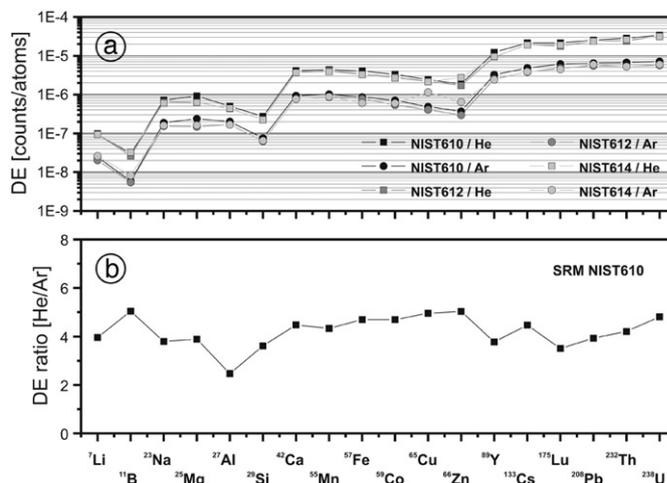


Fig. 2. Panel (a): DEs measured for ns-LA-Q-ICP-MS of silicate glass (SRM NIST610, 612, 614) using argon and helium as carrier gases. Panel (b): Ratio of DEs found for UV-ns-LA-Q-ICP-MS of SRM NIST610, as shown in panel (a).

limited. The radiation was delivered by dielectric mirrors and, subsequently, focused by a plano-convex UV-grade quartz lens ($f = 50$ mm) onto the sample surface. To avoid the formation of distorted crater shapes the beam focus was kept at or slightly below the sample surface. For ns-LA an ArF-excimer laser (GeoLas C, Microlas GmbH, Göttingen, Germany) emitting 15 ns long pulses at a wavelength of 193 nm was employed. In Table 1, a list of sample material, specifications and parameters used for LA are summarized. The composition of the object slide chosen for analysis was taken from the specification sheet provided by the manufacturer (e.g., Si content: 72.2%).

Samples to be ablated were positioned in a cylindrical ablation cell ($V = 40$ cm³) equipped with an inlet nozzle of 0.5 mm diameter. The cell was flushed with 1.0 L/min argon or helium. A list of all samples used to determine DEs is shown in the bottom part of Table 1. The count rate was determined by Q-ICP-MS (Elan DRC II, PerkinElmer SCIEX, Thornhill, Canada). Measurements of crater volumes were performed by a stylus profilometer (Dektak 8, Veeco Instruments Inc., Woodbury, NY, USA) or an atomic force microscope (AFM, Dimension 3000 M, Digital Instruments, Santa Barbara, CA, USA), depending on whether deep or shallow craters were formed. In order to keep the uncertainty of volume measurements to a minimum, the sample surfaces were thoroughly polished prior to LA, if necessary. Nevertheless, error bars of DEs calculated for both ns- as well as fs-LA were found to be in the range of 15% due to difficulties of measuring crater volumes with higher accuracy. In Fig. 1, examples of AFM and

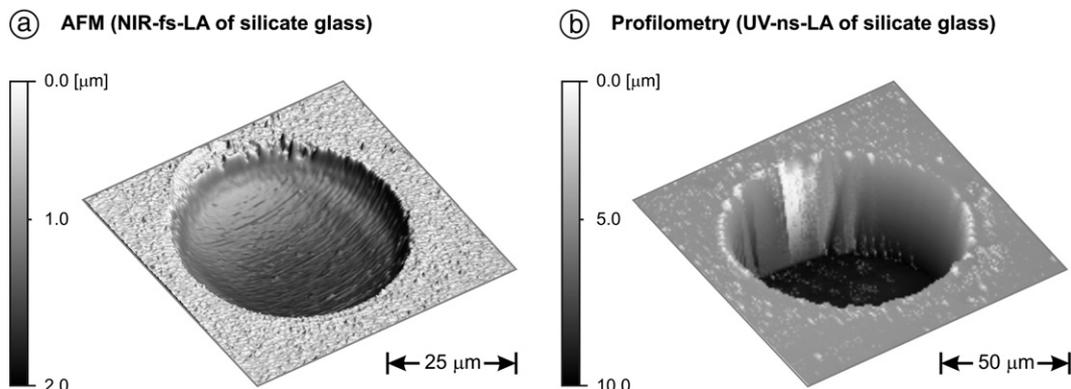


Fig. 1. (a) AFM micrograph of a crater produced by NIR-fs-LA of a polished object slide (carrier gas: helium, number of shots: 5) and (b) profilometry micrograph of a crater produced by UV-ns-LA of SRM NIST610 (carrier gas: helium, number of shots: 50). Note, that both lateral and depth scales of the craters shown are different.

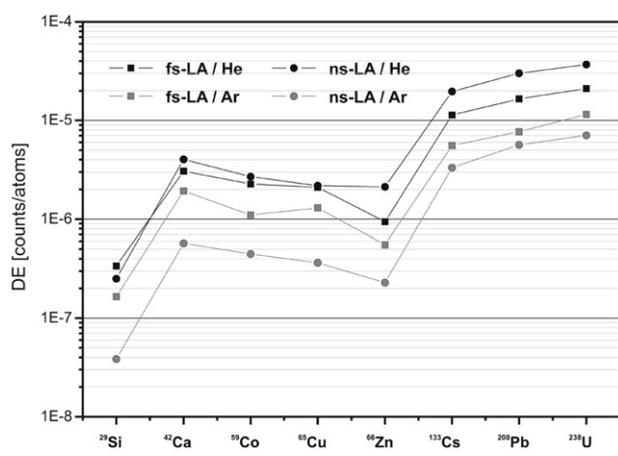


Fig. 3. Comparison of DEs measured for UV-ns- and NIR-fs-LA-Q-ICP-MS of SRM NIST610 of selected elements using argon and helium as aerosol carrier. The fluence was set to 4.7 J/cm² and 7.9 J/cm² for ns- and fs-LA, respectively.

profilometry micrographs of a craters produced by fs-LA and ns-LA of silicate glass are shown.

3. Results and discussion

3.1. Detection efficiencies of LA-ICP-MS

DEs were determined for UV-ns- and NIR-fs-LA of silicon, silicate glass, and natural zircon. Aerosols were analyzed by Q-ICP-MS and DEs, subsequently, calculated from crater volumes and the total number of ion counts detected. Prior to analysis, the ICP-MS instrument was tuned to maximum sensitivity within the intermediate mass range around 100 amu and minimum oxide formation (ThO/Th < 0.5%). In the upper panel of Fig. 2, DEs are plotted for ns-LA of silicate glass using argon and helium as carrier gas. As expected, values were highest for LA under helium atmosphere ranging from 9.8E-8 for ⁷Li up to 3.4E-5 for ²³⁸U. The application of argon as aerosol carrier made the DEs systematically decrease due to higher surface losses and, most probably, less efficient aerosol-to-ion conversion and extraction inside the ICP-MS. These findings are consistent with data reported by Eggins and co-workers [13]. The correlation of DEs in argon and helium, furthermore, indicates only minor compositional changes of aerosols generated by LA of silicate glasses entering the ICP. The trend shown in the upper panel of Fig. 2, thus, reflects the mass-dependent ion transmission curve of the Q-ICP-MS used for analysis.

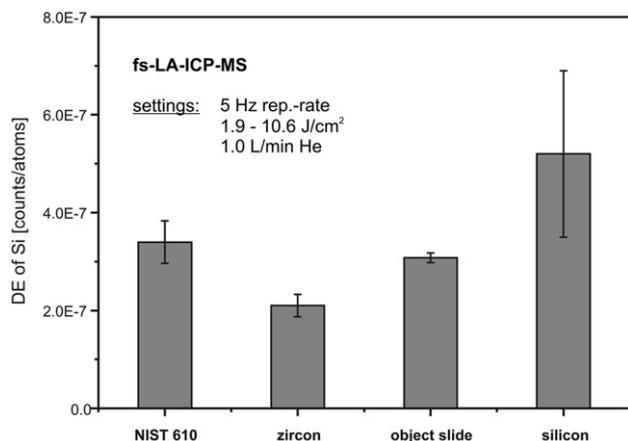


Fig. 4. Si-specific DEs calculated for NIR-fs-LA-Q-ICP-MS of silicate glass, silicon, and natural zircon. The large error specified for silicon mainly results from inaccuracies of the crater volume measurements carried out by AFM.

Table 2

Differences of the Si- and Zr-specific DEs and ablation rates achieved by NIR-fs-LA-ICP-MS of NIST SRM610 and natural zircon

Sample	Ablation rate [mg/shot]	DE _{Si}	DE _{Zr}
NIST610	1.9E-6 ± 1.5E-7	3.4E-7 ± 3.8E-8	6.7E-6 ± 6.4E-7
Zircon	4.3E-6 ± 3.3E-7	2.1E-7 ± 2.3E-8	3.4E-6 ± 2.9E-7

To better illustrate the correlation of DEs, in the lower panel of Fig. 2, the ratio of data points measured for UV-ns-LA of SRM NIST610 using argon and helium as carrier gases is shown as an example. Apparently, the DE for most of the elements decreased by approximately half an order of magnitude when performing LA in argon atmosphere, except for Al, whose sensitivity dropped by a factor of 2.5 only.

The utilization of fs-LA reduced the influence of the carrier gas on the DEs, although still present. Values varied from 3E-7 for ⁷Li up to 2E-5 for ²³⁸U which is in the same range found for ns-LA. A comparison of DEs measured for ns- and fs-LA of SRM NIST610 is shown in Fig. 3. Obviously, relative differences of the DEs measured by fs-LA-Q-ICP-MS decreased by about 50% suggesting the particle size distribution of aerosols produced by fs-LA to be less dependent on the carrier gas [5]. The slight shift of DEs for ns-LA using helium as aerosol carrier towards higher values indicate instrumental drifts, i.e. better system performance rather than substantial ion losses inside the ICP or varying transport efficiencies since the amount of debris formed can be disregarded. The error bars of data plotted in Figs. 2 and 3 were found to be less than 15%. Therefore, it can be concluded, that DEs are almost unaffected by laser wavelength and pulse duration chosen.

However, further Si-specific analyses of different materials, namely silicate glass, pure silicon, and natural zircon by fs-LA-Q-ICP-MS (carrier gas: helium) revealed pronounced variations of the respective DEs, as shown in Fig. 4. Although the value specified for pure silicon was subject to a comparatively large uncertainty these variations suggest DEs to be dependent on the aerosol composition and/or total mass supplied to the ICP since the material uptake of, e.g. zircon and silicate glass differed by a factor of 2.5. In Table 2 the differences of Si- and Zr-specific DEs and corresponding material uptakes are illustrated indicating that values found for silicate glass were about 40% higher. The origin of these discrepancies is still unknown but might be associated with the preferential release of Si due to phase changes of the original zircon matrix, namely ZrSiO₄ into ZrO₂, as demonstrated by Kosler et al. [14]. In addition, the particle size distributions shown

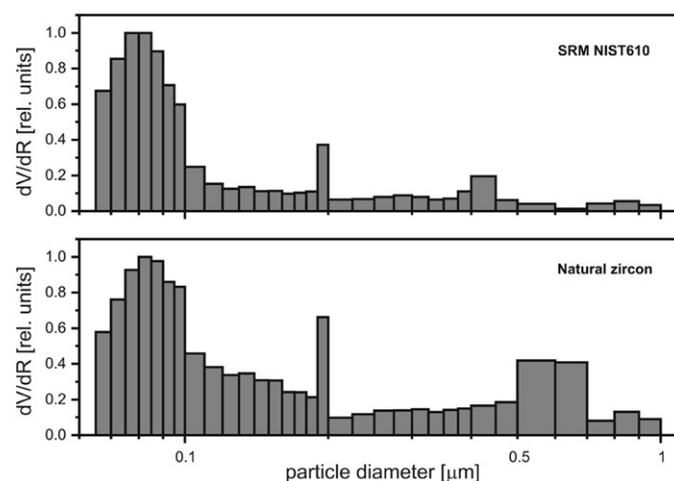


Fig. 5. Particle size distributions of aerosols formed by NIR-fs-LA of natural zircon and silicate glass SRM NIST610. Data were acquired using optical particle counting (OPC). For more details about the instrumentation used please refer to [15]. The peaks at 200 nm particle size originate from a significant change in channel width of the OPC device used and should, thus, be treated as artifacts.

in Fig. 5 suggest that a comparatively large number of particles larger than about 500 nm, i.e. well above the reported size limit for complete vaporization [16], are formed by NIR-fs-LA of zircon. An incomplete vaporization of such particles inside the ICP might, therefore, also contribute to the difference of the DEs observed, in particular, when assuming these particles to mainly consist of high melting point oxides. As demonstrated in [17] the utilization of UV-fs-LA reduces the formation of such particles and would have resulted in smaller discrepancies of the DEs shown in Table 2.

3.2. Analytical implications

Due to the difficulty of measuring the actual amount of debris formed during LA most of the data reported on the aerosol transport efficiencies only refer to the net mass uptake inside the ablation cell, i.e. without taking into account material losses arising from back-diffusion of particles towards the sample surface. According to the literature, such efficiencies vary from 60% up to 95% depending on the material, laser pulse duration and chosen carrier gas. In order to estimate the amount of debris occurring in argon atmosphere, recently Garcia et al. [8] performed LA of a thin Cr layer that allows the release of a well-defined aerosol mass and thus, the overall mass balance for material accumulating around the crater rim can be corrected. Based on the crater size and layer thickness, the relative amount of debris was found to exceed 30%, a value which should not be considered as a universally valid reference since the degree of material deposition is supposed to depend on the LA protocol including fluence, carrier gas etc. as well as geometrical issues such as layer thickness, crater depth and diameter. It is, however, obvious that even a “perfect” adaptation of the LA conditions using, e.g. helium as carrier gas, low fluence LA, low rep.-rate, etc., which hypothetically reduces the relative amount of debris to zero cannot substantially improve the amount of material reaching the ICP-MS and, thus, increase the DEs, as already stated above.²

4. Conclusion

The DEs for UV-ns- and NIR-fs-LA-Q-ICP-MS of silicate glass, zircon, and pure silicon were determined. It was shown that DEs of UV-ns- as well as NIR-fs-LA-Q-ICP-MS applying helium as carrier gas were similar and ranged from 1E-7 up to 3E-5. In contrast, the application of argon as carrier gas was found to suppress the DE by a factor of up to five.

These findings imply that, on the one hand, the utilization of argon generally results in higher surface losses and a less efficient aerosol-to-ion conversion inside the ICP-MS, especially when employing UV-ns-LA. On the other hand, the difference between DEs achieved by UV-ns- or NIR-fs-LA under argon and helium atmosphere is far lower than the “hidden reserve” an improved mass or ion throughput inside the ICP-MS would offer. However, DEs measured in this study differed by almost two orders of magnitude from those reported by Boulyga et al [11] who performed analyses by UV-ns-LA-SF-ICP-MS. Assuming SF-ICP-MS instruments to provide sensitivities approximately a factor of five up to ten higher than those achievable by quadrupole instrument,

the difference cannot totally be explained, in particular, since argon was used as aerosol carrier [11]. Nevertheless, for a DE of about 5E-5 which represents the largest value reported for Q-ICP-MS [12] and an instrumental sensitivity improvement by a factor of ten a “hidden reserve” of maximum four orders of magnitude can be assumed taking into account a theoretical limit of one.

Acknowledgements

Financial support by the Swiss Federal Science Foundation (SNF/project 200020 - 111825/1) is gratefully acknowledged.

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² A quantification of debris could have been accomplished by AFM or profilometry. However, the discrimination of deposited material turned out to be extremely demanding due to the limited AFM scanning range and a finite radius of curvature of the profilometry stylus used which did not allow for resolving morphology changes smaller than 1 – 5 µm.