Effect of Sampling Depth on the Analyte Response in Laser Ablation Inductively Coupled Plasma Mass Spectrometry

Zhongke WANG*, Bodo Hattendorf and Detlef Günther

* *Laboratory for Inorganic Chemistry, Swiss Federal Institute of Technology (ETH Zürich), HCI, Hönggerberg, 8093 Zürich, Switzerland*
E-mail: z-wang@riken.jp

The dependence of analyte sensitivity and vaporization efficiency on the sampling depth of an inductively coupled plasma mass spectrometer (ICPMS) was investigated for a wide range of elements in aerosols, produced by laser ablation of silicate glass. The ion signals were recorded for two different laser ablation systems and carrier gases. Differences in atomization efficiency and analyte sensitivity are significant for the two gases and the particle size distribution of the aerosol. Vaporization of the aerosol is enhanced when helium is used, which is attributed to a better energy transfer from the plasma to the central channel of the ICP and a higher diffusion rate of the vaporized material. Stable signal is achieved at smaller particle size distribution in laser-generated aerosol. The sensitivity change with sampling depth variation is dependent on m/z of the analyte ion and the chemical properties of the element. Elements with high vaporization temperatures need longer residence time to be atomized and ionized in ICP plasma and reach a maximum at increasing sampling depth than easily vaporized elements, especially for bigger particle size distributions generated by 266 nm laser in Argon.

DOI: 10.2961/jlmn.2006.03.0003

Keywords: Laser ablation, inductively coupled plasma mass spectrometry, sampling depth, analyte response, signal sensitivity

1. Introduction

The quantification of solids using laser ablation inductively coupled plasma mass spectrometer (LA-ICP-MS) mainly depends on the acquired representative ion signal sensitivity. Therefore, any happened processes which affect the ion production and transmission in ICP can be expected to consequently influence the quantification accuracy. In recent studies, it has been shown that the ion formation in the ICP plasma significantly depends on the operating conditions of the ICP such as gas flow rates [1] and the particle size of the laser-generated aerosol [2]. When a large fraction of big particles is present in the laser generated aerosol, like for 266 nm ablation of transparent glass or silicate materials and ablation in Argon atmosphere, higher plasma temperatures and longer residence times are required to fully vaporize, atomize and ionize the aerosol [3]. The ICP plasma condition plays an important role to determine the aerosol vaporization, atomization and ionization. However, it is difficult to predict how a change in the individual ICP parameters will finally influence the sensitivity and mass response curves due to the complexity and interactions of the parameters. Nonetheless, the plasma temperature which every operating parameter of ICP can be expected to influence in some way is considered to be the dominant role influencing the analyte response. Very recently the influence of the ICP-operating parameters namely Rf-power, carrier gas flow rate and -composition on the sensitivity for different elements and the change in the mass-and element dependent response has been investigated when different particle size distributions are sampled into the ICP using Argon and Helium as carrier gases [4]. In all the ICP operating parameters, sampling depth is the distance between the edge of the load coil and the tip of the sampling cone. Therefore, it is expected to influence the ICP plasma size or confine the length of plasma, and accordingly influence the residence time of laser produced particles in ICP plasma. Thus, the vaporization efficiency of particles and accordingly ion signal sensitivity may change significantly with the various sampling depth.

The aim of this study is to investigate the influence of sampling depth on the analyte response: ion signal sensitivity, signal stability, polyatomic/oxide ion formation and vaporization, atomization and ionization efficiency of laser produced aerosols. A comparison was carried out between 193 nm and 266 nm ablation respectively in carrier gas Helium and Argon. Furthermore, the different behavior in ICP plasma between volatile elements (low temperature vaporization elements) and refractory elements (high temperature vaporization elements) is discussed at the various sampling depth.

2. Experimental

Two different commercial laser ablation systems (LSX200, 266 nm Nd :YAG, Cetac, Omaha, NE, USA; GeoLasC, 193 nm ArF Excimer, MicroLas GmbH, Göttingen, Germany) were used for aerosol generation in this study. The laser crater on the sample surface was 50 μm for 266 nm ablation and 63 μm for 193 nm ablation, respectively. Both lasers were operated at a repetition rate of 10 Hz at a fluence 7 J/cm^2. Ablation was carried out in Argon and Helium atmosphere at carrier gas optimum flow rate 1.25 L/min for Argon only and 1.3 L/min when using He-

lium [4]. For Helium as carrier gas, a constant flow of 0.7 L/min Argon was added after the ablation cell to ensure stable plasma conditions.

The ICP-MS instrument used in this study was an Agilent 7500cs ICPMS (Agilent Technologies, Tokyo, Japan). The influence of sampling depth was studied at settings between 3 mm and 9 mm at a fixed Rf-power 1400 W. In the experiments presented here, the settings for ion optics were optimized to maximum signal intensity for entire mass range and used for all measurements.

Transient signals were acquired for 120 s, where 30 s background was measured before the laser signal for acquisition of the instrumental background (gas blank) and 30 s after the signal for monitoring aerosol washout. The laser signal intensity was generated over a period of 60 s as commonly used for analysis. Data reduction was carried out using the protocol as described elsewhere [5].

In total, 40 isotopes were measured and the operating conditions and the isotope selection are summarized in Table 1. Each data point represents the average of three replicates.

Table 1 Operating conditions used for laser ablation and ICP-MS lens settings

laser Ablation		
Type	ArF-Excimer	Nd:YAG
Wavelength	193 nm	266 nm
Pulse duration	13 ns	5 ns
Repetition rate	10 Hz	10 Hz
Energy density	7 J/cm^2	7 J/cm^2
Single spot ablation		
Background signal acquisition	30 sec.	30 sec.
Ablation signal acquisition	60 sec.	60 sec.
Sample used	NIST 610 SRM	
ICPMS Agilent 7500cs		
Typical ion optic settings		
Extraction lens 1	+ 4.2V	
Extraction lens 2	-103 V	
Omega Bias	-48V	
Omegas Lens	+ 8.2 V	
Cell Entrance	-34 V	
QP Focus	0 V	
Sampler	1 mm Pt	
Skimmer	0.4 mm Pt	
Isotopes measured		
m/z 5, ^{7}Li, ^{9}Be, ^{11}B, ^{23}Na, ^{25}Mg, ^{27}Al, ^{29}Si, ^{42}Ca, ^{43}Ca, ^{444}Ca, ^{55}Mn, ^{56}Fe, ^{57}Fe, ^{59}Co, ^{60}Ni, ^{65}Cu, ^{66}Zn, ^{85}Rb, ^{888}Sr, ^{89}Y, ^{93}Nb, ^{107}Ag, ^{133}Cs, ^{137}Ba, ^{139}La, ^{139}La, ^{159}Tb, ^{165}Ho, ^{175}Lu, ^{181}Ta, ^{197}Au, ^{205}Tl, ^{208}Pb, ^{209}Bi, m/z 220, ^{232}Th, ^{238}U, ^{248}ThO, ^{254}UO		

3. Results and discussion

3.1 Sensitivity

Figure 1 shows the typical profiles for background corrected signal intensity dependence on the sampling depth for volatile elements Li, Zn, Pb and refractory elements Be, Y, Ta. It has been shown that due to the stronger diffusion

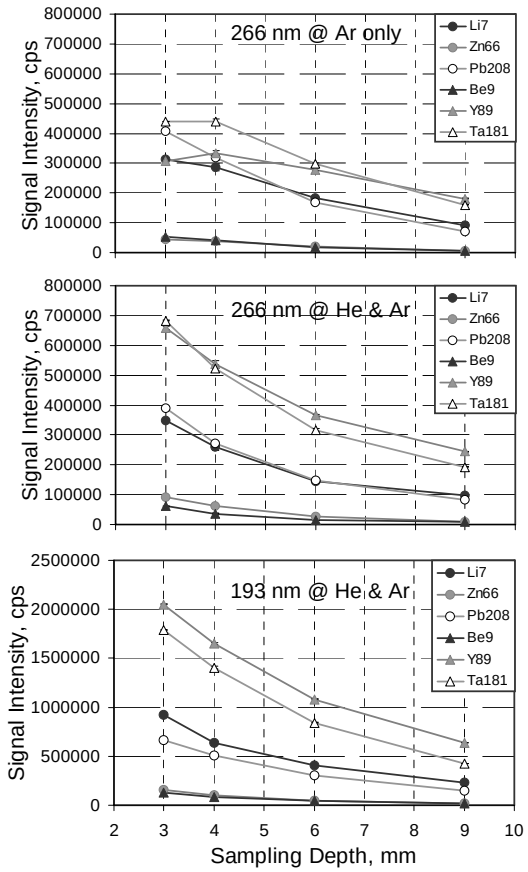

Fig. 1 Sensitivity in dependence on the sampling depth for the two lasers ablation in carrier gas Helium and /or Argon (Normalized to the identical crater size 50 μm).

of volatile elements, refractory elements like Y, Ta, etc. have the higher signal sensitivity compared with the volatile elements like Zn, Pb, etc. especially in carrier gas Helium. For example, sensitivity for Ta is by factor 1 to 2.3 times higher than Pb at the various sampling depth for 266 nm generated aerosols, by factor 2.5 to 3 for 193 nm generated aerosols. Furthermore, the high ionization energy (e.g. volatile element Zn, first ionization energy: 9.394 eV) further enhances the reduced sensitivity compared with the low ionization energy volatile elements like Pb (first ionization energy: 7.415 eV). The sensitivity difference between the two elements is by factor 8 to 12 higher for Pb than Zn at increasing sampling depth for 266 nm ablation in Argon, by factor 4 to 8 for 266 nm ablation in Helium, by factor 4 to 9 for 193 nm ablation in Helium, respectively. The low mass volatile elements Li has the relative high signal intensity compared to Zn, which is contributed to lower ionization energy (first ionization energy of Li: 5.392 eV). However, the high ionization energy of Be (first ionization energy of be: 9.323 eV) leads to by factor 80 to 90 % lower sensitivity compared to Li. These observations indicate that signal sensitivity is inherently related to the element volatility and the ionization energy if without considering the initial concentrations in the sample.

For the comparison between two lasers 193 nm and 266 nm, when Helium is used as the carrier gas, the sensitivity of all isotopes measured continuously decreases at increasing sampling depth (figure 1). So far it is quite clear that not all of the ions can be sampled into ion optics because ions

diffuse radially outward as they move in the plasma towards the sampling orifice and into skimmer cone [6], and the ion diffuses at a rate proportional to the inverse of the square root of the ion mass [7]. Due to the diffusion lose, ion signal is reduced with the sampling depth increasing. There are the similar various profiles for the two lasers. However, by factor 2 to 3 times higher signal intensity is obtained for 193 nm laser compared with 266 nm laser in carrier gas Helium. This is a result of the bigger fraction of smaller particles < 150 μm in aerosols generated from 193 nm laser ablation NIST 610 [8]. The different particle vaporization efficiency of the aerosol indicated by the U^+/Th^+ ratios (discussed later) is responsible for signal sensitivity difference between the two lasers. Smaller particles produced by 193 nm are more readily vaporized, atomized and ionized [2] and thus lead to a higher sensitivity. In contrast, for 266 nm laser ablation in carrier gas Argon, refractory elements like Y, Nb, La, Ta, etc. show a plateau or intermediate maximum intensity at increasing sampling depth. This indicates that refractory elements experience delayed vaporization compared with volatile elements, requiring longer residence times to be atomized and ionized, especially when the particle size distribution of the aerosol is bigger for 266 nm laser generated aerosols. At increasing sampling depth the enhanced vaporization and ionization efficiencies are achieved. When Helium is used as carrier gas and introduced to the central channel of the ICP after addition of 0.7 L/min of Argon for stable plasma operation, this leads to an increased transport efficiency of the aerosol from the ablation cell to the ICP and also reduces the energy and time required for efficient vaporization and atomization. The higher thermal conductivity of Helium may actually enhance notably the temperature in the central channel of the ICP [9]. Vaporization and atomization efficiency are improved due to the higher average temperature in the central channel and reduced temperature gradients compared to carrier gas Argon only. Thus enhanced sensitivity is obtained in laser ablation-ICPMS using Helium-Argon mixtures as aerosol carrier [10]. As shown in figure 1, the higher signal intensity is achieved for 266 nm ablating in Helium than in Argon, and the difference between two gases gets smaller with the sampling depth due to the accordingly efficient particle vaporization.

Figure 2 shows the relative intensity changes with the sampling depth in the measured mass range. Signal sensitivity usually decreases at increasing sampling depth. The changed magnitude of the intensity at various sampling depth is significantly dependent on the m/z and elements. However, the sensitivities of measured isotopes are changing similarly at increasing sampling depth for 193 nm generated aerosols. In contrast, the intensity reaches a maximum at increasing sampling depth for refractory elements (e.g. Ca, Y, Nb, la, Ta) when using 266 nm ablation in carrier gas Argon. This indicates that refractory elements require longer residence times in the ICP especially when the particle size distribution of the aerosol is large at 266 nm laser ablation. As discussed before, this is a result of the different vaporization efficiency between refractory elements and volatile elements. Extending the sampling depth leads to a longer residence time, accordingly an improved ionization efficiency. Here the more interesting things,

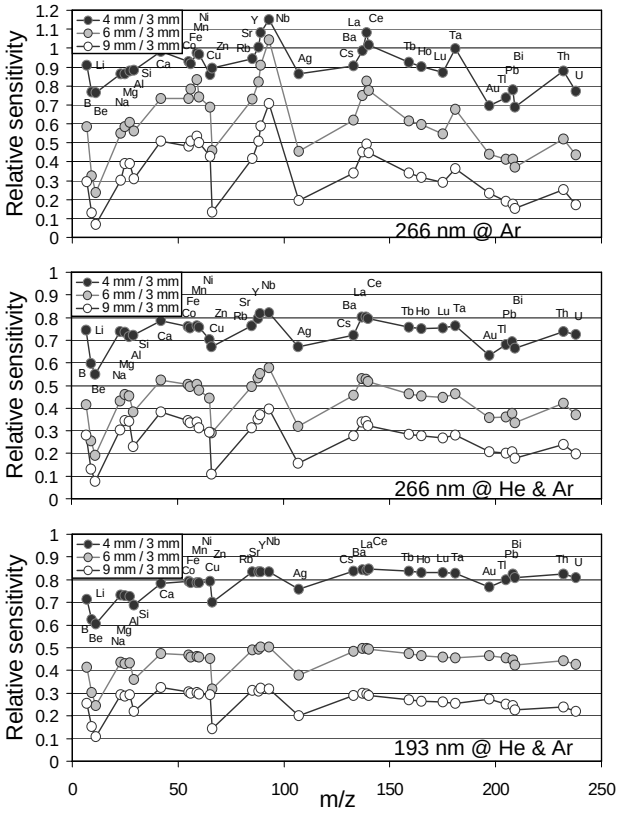

Fig. 2 Relative sensitivity at increasing sampling depth for the two lasers ablation in carrier gas Helium and/ or Argon.

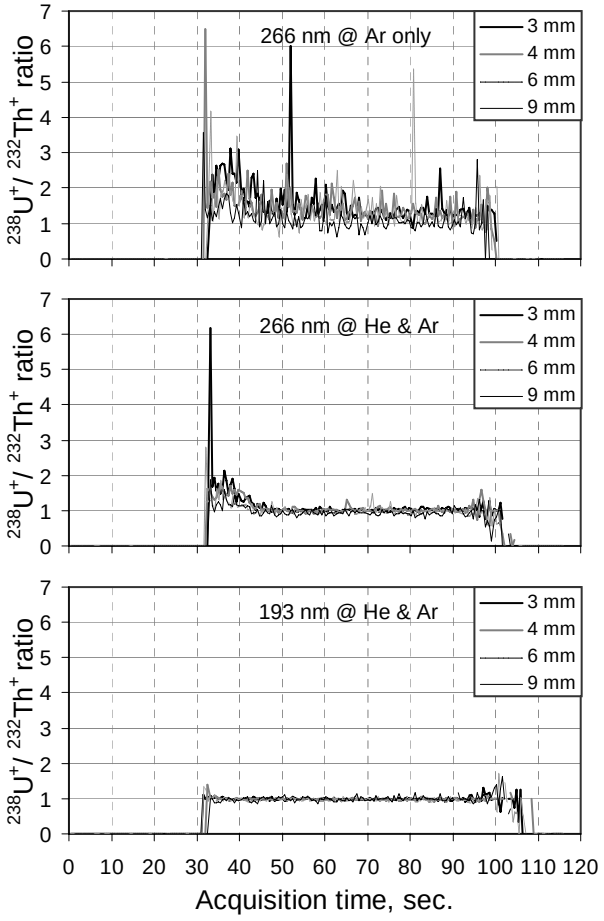

Fig. 3 Signal stability with the laser ablating for different sampling depth.

whether 266 nm or 193 nm ablation, carrier gas Argon or Helium, Be, B, Si, Zn and Ag typically show the negative relative signal in the measured entire isotopes, and this negative changing increases at increasing sampling depth (figure 2). We think this could be a result of convolution of the parameters: element volatility, ionization energy and diffusions occurred in the ICP. As the mass-dependent diffusion laws described by Dziewatkoski et al [7], light mass leads to a high radial diffusion, e.g. Li, Be, B. The high ionization energy reduces the ion production efficiency in the ICP compared to low ionization energy elements. High volatility leads to high vaporization efficiency but enhances diffusion as well. Refractory elements have the low vaporization efficiency but the low ion radial diffusion as well. However, at different conditions one of them could play a leading role to influence the signal behavior of element.

3.2 Signal stability and particle vaporization efficiency

The U^+/Th^+ ratio is a measure of the relative atomization efficiencies for laser-generated aerosols [11], and significately relies on the ICP operating conditions and the particle size distribution of the aerosol [4]. Figure 3 shows the variation of the ratio with the laser ablation time. The appeared irregular spikes in the plots clearly indicate the instibilities of ion signals with the acquisition time, which are attributed to the various atomizion efficiencies for different particle size generated by different laser wavelength. Especially when using 266 nm ablation in carrier gas Argon only, bigger particles significantly lead to the sharp spikes in the plots of signal to laser ablation time [12,13]. In contrast, the U^+/Th^+ ratio is much stable and typically closer to one with respect to changes of acquisition time and sampling depth when using 193 nm ablation. It indicates that 193 nm generated particles are vaporized efficiently and little variation of particle vaporization efficiency with the ablation time due to the smaller particle size.

Figure 4 shows the dependence of U^+/Th^+ ratio on the sampling depth and the signal sensitivities for U^+ and Th^+. The ratio exhibits significant positive deviations from the expected ratio of 1 at decreasing sampling depth, especially for 266nm laser ablation. Ablation in Argon produces a pronounced fraction of large particles and consequently the U^+/Th^+ ratio shows a pronounced deviation from the expected value. Bigger particle size leads to a delayed vaporization, the particle size-related vaporization was observed with sampling depth increasing. Using 266 nm laser ablation, an acceptable ratio is only obtained at significant expense of sensitivity. With the sampling depth increasing, the ratio decreases to get close to 1. This indicates that residence time significately influneces the particle atmoization in the ICP. In contrast, ablation using 193 nm in Helium typically yields a wider range of parameters where the ratio is close to 1. The expected U^+/Th^+ ratio is obtained for wide sampling distances. This shows that smaller particle size distribution of aerosols produced by 193 nm leads to a little variation of particle vaporization efficiency at various sampling depth.

Furthermore, as shown in figure 4, the aerosol particles have the better vaporization efficiency in Helium, leading to reduced U^+/Th^+ ratios close to 1 compared to in Argon. Mostly due to the higher thermal conductivity of Helium

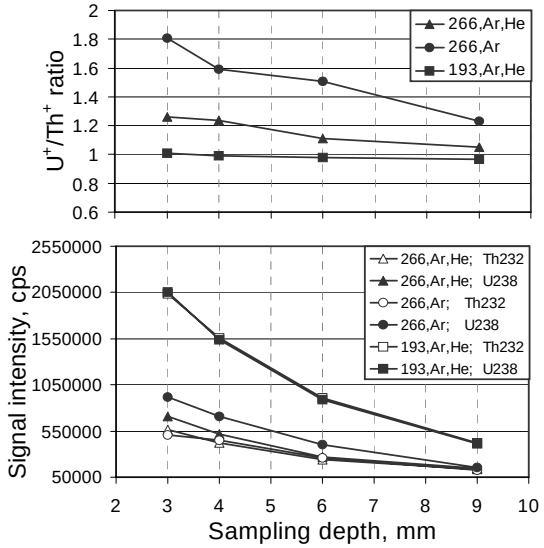

Fig. 4 U^+/Th^+ ratio in dependence on the various sampling depth.

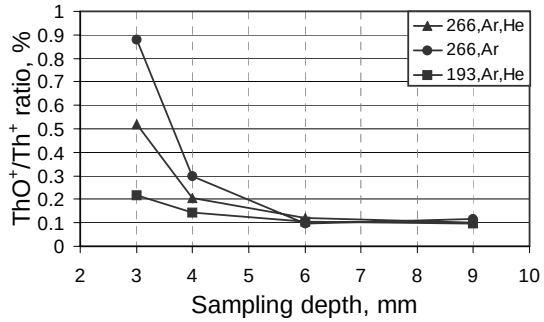

Fig. 5 ThO^+/Th^+ ratio in dependence on sampling depth.

compared to Argon, added Helium causes an increase in the gas-kinetic temperature [9, 14, 15], leading to higher average temperature in the central channel and reduced temperature gradients. Atomization of the particles can be accelerated by adding Helium to the plasma, which can assist evaporation by better energy transfer to the central channel of the ICP and also by faster transport of vapor away from the particle surface. Thus, better atomization efficiency and lower U^+/Th^+ ratios are observed for 266nm laser ablation in Helium than in Argon (Fig.4).

3.3 Oxide formation

Oxide formation is in a double-process in the ICP plasma. One side oxide is formed in the plasma, on the other side, oxide is dissociated in the plasma [14]. It mainly depends on the plasma temperature and also somehow on the residence time in the plasma. As indicated by the ThO^+/Th^+ ratios in figure 5, the higher ICP gas temperature and the reduced temperature gradients for carrier gas Helium significantly result in lower oxide formation or higher oxide dissociation and therefore the reduced ThO^+/Th^+ ratios. The ThO^+/Th^+ ratios decrease at increasing sampling depth, indicating that the formed oxide experiences a dissociation process and the dissociation is enhanced by extended residence time when using larger sampling depth.

This behavior is more pronouncedly at 266 mm ablation, which could be related to the particle size and vaporization efficiency, as indicated by the U^+/Th^+ ratio. For 193 nm laser ablation, the decrease in ThO^+/Th^+ ratios is unlike 266 nm laser ablation. Little variation of oxide abundance is found for 193 nm and with Helium as carrier gas. This would imply that the smaller particle size distribution in laser produced aerosols also could lead to a smaller oxide yield in the ICP. In the experimental conditions used it shows that the final yield for oxide ion formation is significantly influenced by sampling depth applied in the ICP.

4. Conclusion

The trends in optimization of sampling depth of the ICPMS show no significant differences when using 193 nm and 266 nm laser wavelengths respectively. The dependence of sensitivity and atomization efficiency on sampling depth leads to almost identical profiles. Major differences lie in the analyte sensitivities that are achieved and the vaporization and atomization efficiency of the laser generated aerosol. Higher sensitivities can be obtained when the aerosol contains mainly small particles which are atomized efficiently. Atomization can to some extent be enhanced by applying larger sampling depth, which is attributed to the longer residence time. The abundance of stable molecular ions, like ThO^+, increases remarkably at short sampling depth applied, is related to the residence time in the ICP but less dependent of the particle size distribution of the aerosol. Notable differences are found in the sampling depth profiles for elements with high and low vaporization efficiency respectively, high and low ionization energy respectively and for different particle size distributions. It is obvious that particle evaporation and atomization can be accelerated by adding helium to the plasma. This is most likely due to better energy transfer to the central channel of the ICP and faster transport of vapor away from the particle surface.

For ablation with 266 nm, the aerosol contains a significant fraction of bigger particles which need longer residence time in the ICP and high plasma temperature. The highest vaporization, atomization and ionization efficiency and analyte sensitivity for silicate samples is accordingly achieved using the 193 nm laser for ablation and helium as the carrier gas. This combination produces an aerosol which does not contain a significant fraction of bigger particles and the aerosol can be vaporized within a very narrow range of axial positions, minimizing analyte loss by the ions` radial spread within the ICP.

In general, when optimizing the ICPMS for operation with laser ablation sampling, the focus should be laid on reducing fractionation within the ion source by monitoring for example the U^+/Th^+ ratio than to focus solely on analyte sensitivity. Even with 266 nm laser ablation and argon as carrier gas, the difference in sensitivity will mostly be within a factor of 2 which in most cases has little impact on the limits of detection but certainly improves the reliability of the analytical data.

Acknowledgments

This work has been supported through funding by the World Laboratory Lausanne, the ETH Zürich and the Swiss National Science Foundation. Very valuable comments of the reviewers have helped to improve this manuscript and are highly appreciated.

References

[1] M. Rodushkin, D. Axelsson, D. Malinovsky and D. C. Baxter: J. Anal. At. Spectrom. **17,** (2002) 1223.
[2] H.R. Kuhn, M. Guillong and D. Günther: Anal. Bioanal. Chem. **378** (2004) 1069.
[3] M. Guillong, I. Horn, D. Günther: J. Anal. At. Spectrom., 18 (2003) 1224.
[4] Z. Wang, B. Hattendorf and D. Günther: J. Am. Soc. Mass Spectrom., **17** (2006) 641
[5] H. P. Longerich, S. E. Jackson and D. Günther: J. Anal. At. Spectrom., **11**, (1996) 899 .
[6] I. Stewart, C. E. Hensman and J. W. Olesik: Appl. Spectroscopy, **54** (2000) 164.
[7] M. P. Dziewatkoski, L. B. Daniels, and J. W. Olesik: Anal. Chem., **68** (1996) 1101.
[8] I. Horn, M. Guillong and D. Günther: Appl. Surf. Sci.; **182** (2001) 91.
[9] N.N. Sesi, A. Mackenzie, K.E. Shanks, P.Y. Yang, G.M. Hieftje: Spectrochim. Acta B; **49**, (1994) 1259.
[10] D. Günther and C. A. Heinrich: J. Anal. At. Spectrom., **14** (1999) 1363.
[11] Z. Wang, B. Hattendorf, M. Ramseier, M. Guillong and D. Günther: ICP-Inf. Newslett.; **30** (2005) 1042.
[12] M. Guillong, H.R. Kuhn and D. Günther: Spectrochim Acta B, **58** (2003) 211.
[13] M. Guillong and D. Günther: J. Anal. Atom. Spectrom., **17** (2002) 831.
[14] R. S. Houk and N. Praphairaksit: Spectrochim. Acta B; **56, (**2001) 1069.
[15] D.A. Wilson, G. H. Vickers and G. M. Hieftje: Appl. Spectrosc.; **41**, (1987) 875.

(Received: May 16, 2006, Accepted: September 26, 2006)