International Journal of Mass Spectrometry 273 (2008) 151–155

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms

Short communication

Possibility of nano-local element analysis by near-field laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS): New experimental arrangement and first application

Myroslav V. Zoriy[a], Markus Kayser[b], J. Sabine Becker[a,*]

[a] Central Division of Analytical Chemistry, Research Centre Juelich, D-52425 Juelich, Germany
[b] Bruker Daltonik, D-28359 Bremen, Germany

ARTICLE INFO

Article history:
Received 14 February 2008
Received in revised form 13 March 2008
Accepted 14 March 2008
Available online 27 March 2008

Keywords:
Inductively coupled plasma mass spectrometry
Near-field laser ablation
Solid material
Thin Au layer

ABSTRACT

A near-field laser ablation inductively coupled plasma mass spectrometric (NF-LA-ICP-MS) procedure was created for element analysis in the nm resolution range. The method utilizes a well-known near-field effect in order to enhance the incident light energy on the thin tip of a Ag needle during the laser ablation process. A robust needle etching procedure was developed to produce the thin needles with a tip diameter in the range of hundreds of nm. An experimental arrangement was constructed to control the "sample-to-tip" distance via the measurements of tunnel current between the needle and sample surface. The NF-LA-ICP-MS technique thus developed was applied to analyze thin Au films deposited onto a Si substrate. The observed craters ranged from 500 nm to about 1 μm in diameter and were dependent on the needle used as well as on the "sample-to-tip" distance. These results were also confirmed by mass spectrometric measurements of the Au sample. Theoretical calculations performed showed that using the developed NF-LA-ICP-MS arrangement a detection efficiency of 2.7×10^{-5} cps per ablated Au atom can be achieved.

1. Introduction

Laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is becoming the method of choice for the trace, ultra-trace and isotope analysis of solid samples and is already the most important laser-induced technique in inorganic mass spectrometry due to the advantage of direct solid sampling by focused laser irradiation onto the sample surface and due to its ability to provide microscale information [1–5].

However, in spite of all the advantages of the LA-ICP-MS technique its application in some analytical tasks is limited by the restriction in focusing the laser beam due to the diffraction feature of the light, and therefore, a finite lateral resolution. The typical spatial resolution of LA-ICP-MS, achieved with most commercially available laser ablation systems, ranges from 5 to 300 μm [1,6–8], and in some cases this would be insufficient, for example, for the analysis of the fine structures of small regions of biological tissues and single cells [9–11] or in nanoelectronics [12]. The known near-field effect can be applied in order to improve the spatial resolution of the laser ablation, and this is being intensively investigated at present in several groups [13–17]. The idea of near-field laser ablation consisted in the formation of radiation intensity singularities by means of very small conductive objects (e.g., tip of a thin Ag needle) immersed in the radiation field. The resulting electric (linear or non-linear) polarization of such objects yields a considerable enhancement of the radiation intensity in the region comparable with the curvature radius of the object (near-field enhancement). Such an object can itself be treated as a very small but intense source of secondary evanescent near-field radiation, which can be considerably stronger than the field of the primary beam. If this source is brought so close to the target surface that this secondary radiation cannot diverge to any great degree during the transit between the two, it can cause a local laser-induced surface effect limited only by the object size rather than by diffraction effects [18,19]. Recently, the application of a near-field optical fiber probe coated with aluminum (SNOM tip had 170 nm diameter aperture) in the atmospheric pressure laser ablation of organic compounds combined with quadrupole-based mass spectrometry was proposed by Zenobi's group [16]. A heated stainless steel capillary was used as a nanosampling interface for the introduction of atmospheric laser-ablated organic material into the high vacuum of an electron impact ion source of the quadrupole mass spectrometer. On bis-(phenyl-*N*,*N*-diethyltriazene), the authors demonstrated three laser-ablated craters with a spatial resolution of about 200 nm and a depth of

* Corresponding author. Tel.: +49 2461 612698; fax: +49 2461 612560.
E-mail address: s.becker@fz-juelich.de (J.S. Becker).

1387-3806/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.ijms.2008.03.008

20 nm. However, this analytical technique was not able to give information on element concentration as well as was not possible to control "sample-to-tip" distance. In contrast to the application of aperture probes, Becker et al. [19] proposed using the near-field enhancement effect of the laser energy on the tip of a thin silver needle (apertureless probes) positioned on the surface of a biological sample to achieve material ablation. In this preliminary study, the near-field LA-ICP-MS (NF-LA-ICP-MS) technique was used for elemental and isotopic analysis at the nanometer scale on gels and biological samples [19,20].

In the present study, a new experimental arrangement for the application of the near-field effect in the LA-ICP-MS technique (using apertureless probes with the aid of a thin robust Ag needle) was created and successfully used in order to achieve a spatial resolution of the method in the hundreds of nm range. In the proposed arrangement, the superior probe handling (e.g., application of new low-volume ablation chamber; controlling of "sample-to-tip" distance, more stable arrangement to the disturbing entourage vibration, sample observation apparature, etc.) was established as well as improved method measurements conditions. The results of this study are presented as well as a detailed explanation of the NF-LA-ICP-MS experimental set-up.

2. Experimental

2.1. Set-up of NF-LA-ICP-MS method

The schematic arrangement of the established procedure is shown in Fig. 1. A Nd:YAG "Continuum Surelite™" (Santa Clara CA, USA) laser was used to produce a laser beam of 532 nm. No focusing lenses were applied at a laser energy of 5 mJ. The unfocused laser beam was enhanced onto the analyzed surface by means of a thin silver needle. To detect the quantity of material ablated during near-field laser ablation, a double-focusing sector field inductively coupled plasma mass spectrometer (ICP-SFMS) "Element, ThermoFisher™" (Bremen, Germany) was applied. The optimized experimental parameters are summarized in Table 1. The laser-ablated material (with and without near-field enhancement) was transported with argon to the inductively coupled plasma mass spectrometer and analyzed. A low-volume LA chamber embedded with a piezo manipulator (z-direction) was constructed. For better observation of the sample, the LA chamber was designed to be angular (internal volume of about 40 cm^3) and was made of a transparent quartz glass. To avoid leakage in the LA chamber the

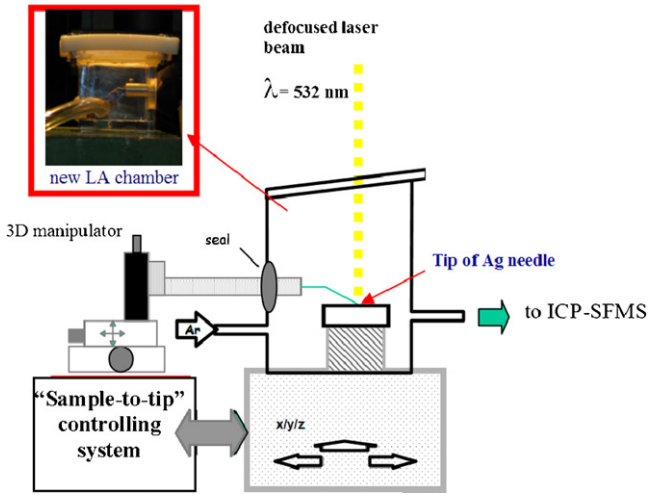

Fig. 1. Schematic arrangement of established NF-LA-ICP-MS procedure.

Table 1
Optimized operating conditions of the NF-LA-ICP-MS procedure for analysis of thin Au film deposited onto Si substrate

	LA-ICP-SFMS
Inductively coupled plasma mass spectrometer	Element (Finnigan)
RF power (W)	1200
Cooling gas flow rate (L min^{-1})	18
Auxiliary gas flow rate (L min^{-1})	0.65
Nebulizer gas flow rate (L min^{-1})	1.1
Extraction lens potential (V)	2000
Sampler cone	Nickel, 1.1 mm orifice diameter
Skimmer cone	Nickel, 0.9 mm orifice diameter
Mass resolution, $m/\Delta m$	300
Mass window (%)	10
Runs	1200–1400
Passes	1
Scanning mode	Peak hopping

hole through which the needle entered was gasketed with an elastic bellow. The needle was connected to an $x/y/z$ micromanipulator from "NewPort™" (Darmstadt, Germany) in order to roughly position it on the sample surface during experiments. In contrast to our previous work [19], a significant improvement was achieved in controlling the "sample-to-tip" distance (see Fig. 1). For this purpose, the scanning system for STM (Anfatec Instruments AG, Oelsnitz, Germany) was adapted and modified for the present experiments to adjust the piezo movement by measuring the tunnel current between the sample and the needle. All the movements were automated and controlled via computer software, so that it was possible to adjust and control the different "sample-to-tip" distances (1, 50, 100, 150 and 200 nm).

To minimize the vibrations in the NF-LA-ICP-MS set-up, an Iso-Plate vibration damping system from "Thorlabs INC" (Newton, NJ USA) was applied. In addition, the LA chamber and the $x/y/z$-manipulator were installed onto two massive Pb bricks. The measurements were performed on the ground floor of the building in order to further suppress any possible vibrations of the apparatus.

2.2. Development of needle etching procedure

For the NF-LA-ICP-MS experiments, thin silver needles with a tip diameter in the range of hundreds of nm were electrolytically etched from silver wire (0.5 mm) in an electrochemical cell using a droplet of citric acid as the electrolyte. Under the applied DC voltage the needle was etched very slowly—the total time needed to produce one needle was about 50 min. At the end of the etching procedure, the prepared needle dropped into the vessel filled with water. This avoided any further damage to the needles. After preparation of the thin tip of the silver needle, the needle was further cleaned with pure MilliQ water (20 min, $T = 50\,^{\circ}C$).

2.3. Samples and measurement procedure

As analyzed samples, a 20 nm Au film deposited onto a Si substrate was used. A schematic representation of the sample is shown in Fig. 2a. In order to find the position of laser shooting during the measurements by scanning electron microscopy (SEM) on the analyzed sample a netting pattern was plotted (simply using an Edding marker) on the region of interest.

In general, three different experimental conditions were employed to study the figures of merit of the NF-LA-ICP-MS procedure. The basic principles are shown in Fig. 3a–c. Measurements were performed during "burst mode" (10 laser shots) of the unfocused laser when the needle was far away ($d > 10$ mm) – state 1 and at about 200 nm state 2 – from the sample surface (see

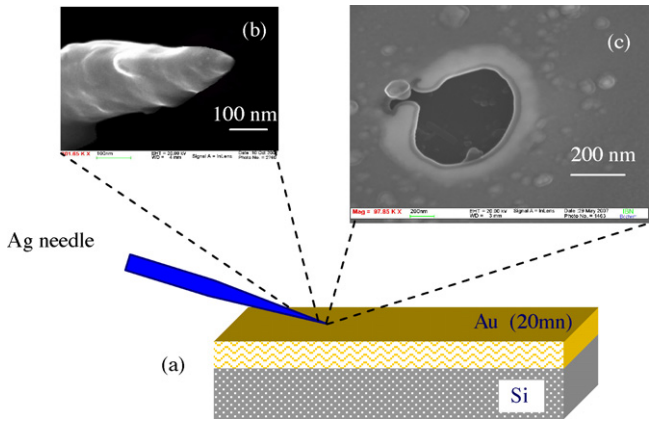

Fig. 2. (a) Schematics of analyzed sample (20 nm of Au deposited onto a Si substrate); (b) SEM image of thin silver needle typically obtained by etching using established needle etching procedure; (c) SEM image of observed crater produced by near-field laser ablation method developed here.

Fig. 3a and b, respectively). In addition, the experiments were performed with a continuously running laser at a repetition frequency of 10 Hz (state 3, Fig. 3). Under these experimental conditions, the needle approached the sample surface very slowly and the mass spectrometric signal was monitored with the running laser. Other details of the measurement procedure are summarized in Table 2.

3. Results and discussion

3.1. Near-field laser ablation and characterization of craters

The proposed new experimental arrangement of NF-LA-ICP-MS was employed to study a thin Au film (20 nm in a thickness) deposited onto a Si substrate. Thin Ag needles ($d \sim 180$–250 nm) for the current work were electrolytically etched in the electrochemical cell as described in the experimental section. A typical profile of the needles produced is shown in Fig. 2b. In all experiments, the distance between the needle and sample surface was controlled by measuring tunnel current. When the needle was at a defined distance from the sample surface (~200 nm) laser shots of defocused laser beam were performed, causing the a local enhancement of incident laser energy on the needle tip which was sufficient to ablate of the analyzed sample. Fig. 2c shows a typical form of ablated crater obtained under optimized experimental conditions and measured by scanning electron microscopy. As can be seen from the figure, all the analyzed Au (20 nm in depth) was ablated producing a crater of 500–600 nm in diameter. In addition, no scratching artifacts (lines and rows) were observed on the Si substrate nor in the vicinity of the ablated crater. This confirms the fact that during the experiments the needle was maintained at a distance from the surface and no contact with the surface occurred.

3.2. NF-LA-ICP-MS measurements of a thin Au film on silicon substrate

Fig. 4a presents a transient signal of $^{197}Au^+$ measured on thin Au film (20 nm) deposited onto Si substrate using the proposed NF-LA-ICP-MS procedure. All the observed transient signals of $^{197}Au^+$ correspond to the different places on the sample surface and the experiments were performed using different "states" (see Table 2). When in state 1 (see Fig. 3a; tip of the thin Ag needle is >10 mm above the sample surface), single laser shots were performed—only the background signals of about 500 cps were measured.

In state 2 (see Fig. 3b), the needle was positioned close ($d \sim 1$–200 nm, controlled via the tunnel current using the experimental arrangement presented) to the sample surface. In such a case with the single laser shots a strong increase of $^{197}Au^+$ ion intensity (up to 8000 cps) was observed (see Fig. 4a). This is the result of near-field laser ablation. In addition to the $^{197}Au^+$, $^{28}Si^+$ (from the substrate) was also monitored during all the measurements (see Fig. 4b). In contrast to state 1, in this experiment (state 2), the $^{28}Si^+$ signal was clearly detected during the laser shots (see Fig. 4b), which could be explained by the fact that the ablation crater produced was deeper than the thickness of the deposited Au film (>20 nm).

In state 3, the laser running mode was switched to the continuous mode ($f = 10$ Hz). ICP-MS measurements were started when the needle was far away from the sample ($d > 10$ mm). Then, under the running laser, the needle was slowly moved towards the sample surface. At the moment when the needle was in the vicinity to the sample surface (tunnel current was detected by the "sample-to-tip" distance controlling system) an increase of the signals was also found for both monitored $^{197}Au^+$ and $^{28}Si^+$ ion signals (see Fig. 4b). The measured intensity of $^{197}Au^+$ in this state 3 was similar to state 2, whereas the $^{28}Si^+$ signal was about 2.5 times higher.

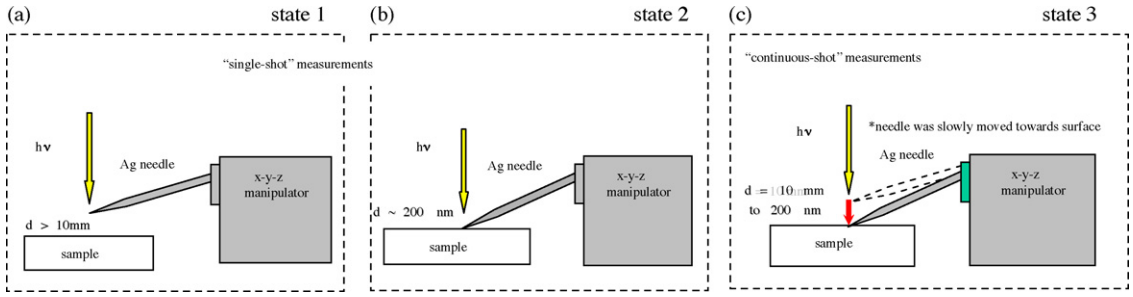

Fig. 3. (a) Needle is at a distance of about 10 mm from the sample; (b) needle is at a distance of about 200 nm from the sample; (c) needle is slowly approaching the sample (laser run in continuous mode, $f = 10$ Hz).

Table 2
Experimental parameters of measurement procedure applied in NF-LA-ICP-MS studies

	Laser running mode	Number of shots	Wavelength (nm)	Laser fluence (mJ cm^{-2})	Tip diameter (nm)
State 1	Burst	10 (1 Hz)	532	~5	~250
State 2	Burst	10 (1 Hz)			
State 3	Continuous	Continuous (10 Hz)		~6.4	

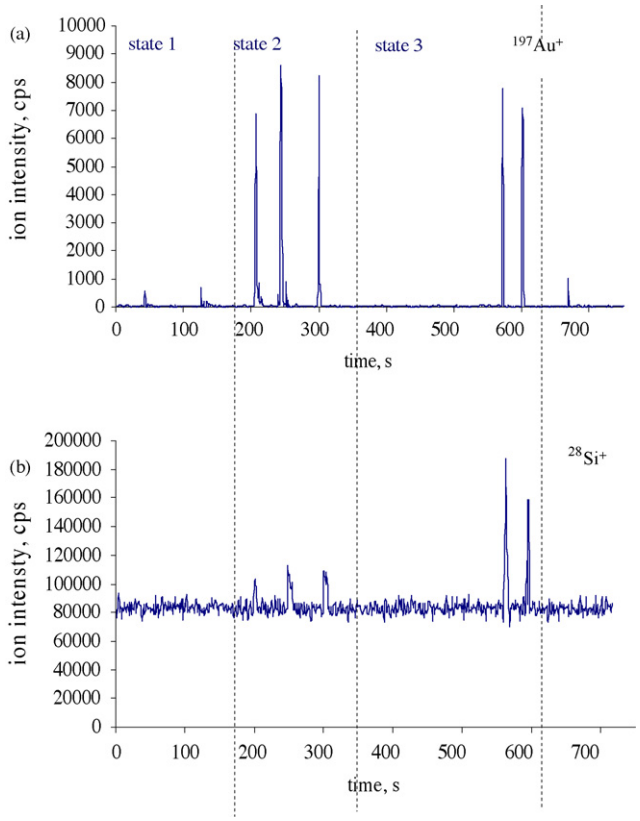

Fig. 4. Transient signals of $^{197}Au^+$ (a) and $^{28}Si^+$ (b) measured by proposed NF-LA-ICP-MS procedure. All observed peaks correspond to the different locations on the sample surface.

During different experiments laser craters in the sub-μm range (as a function of the tip diameter of the thin silver needle: from 200 nm to about 1 μm in diameter) were produced. These laser craters were observed by scanning electron microscopy. Additional experiments were performed to evaluate the capability of the NF-LA-ICP-MS procedure for isotope ratio measurements of copper as well for analysis of metals with relatively high melting points (e.g., W, Mo, etc.) [21]. The results of these studies will be presented in a forthcoming paper.

3.3. Theoretical calculation of ablated material and detection efficiency of the NF-LA-ICP-MS procedure

In addition to all the measurements, the theoretical calculation of quantity of ablated material as well as the current detection efficiency of the NF-LA-ICP-MS procedure was performed. The calculation algorithm was applied for both LA-ICP-MS as well as for the NF-LA-ICP-MS procedures used.

3.3.1. Calculation of detection efficiency for LA-ICP-MS

Using a small volume ablation chamber for LA-ICP-MS measurements of Au foil (laser crater diameter = 50 μm) an ion intensity of $^{197}Au^+$ of 1×10^{10} cps was observed.

- Ablated volume = $\pi r^2 \times L = 25^2 \times 3.14 \times 0.2 = 392\ (\mu m^3)$ (where L is crater depth).
- Density of Au foil = 19300 kg/m^3 = 19.3×10^{-12} (g/μm^3).
- Au concentration in Au foil = 1 g g^{-1} (100%).
- Detected signal = 1×10^{10} (cps/laser pulse).
- Ablated Au atoms per pulse = 19.3×10^{-12} [g/m^3] × 392 [μm^3] = 7.6×10^{-9} [g] Au = 7.6×10^{-9} [g] × 6×10^{23}/197 [g/mol] = 2.3×10^{13} [Au atoms].
- Detection efficiency = $1 \times 10^{10}/2.3 \times 10^{13} = 4.3 \times 10^{-4}$ [cps/ablated atom].

3.3.2. Calculation of detection efficiency for NF-LA-ICP-MS

The present calculation is performed from the NF-LA-ICP-MS measurements of thin Au film (20 nm) deposited onto a Si substrate. The laser crater diameter was determined to be 600 nm.

- Au density = 19300 [kg/m^3] = 1.93×10^{-20} [g/nm^3].
- Ablated volume = $3.14 \times 300^2 \times 20 = 5.7 \times 10^6$ [nm^3].
- Ablated Au atoms per pulse = 1.93×10^{-20} [g/nm^3] × 5.7×10^6 = 1.09×10^{-13} [g] Au = 1.09×10^{-13} [g] × 6×10^{23}/197 [g/mol] = 3.3×10^8 [Au atoms].
- Detection efficiency = 9000 [cps]/3.3×10^8 [atoms] = 2.7×10^{-5} [cps/ablated atom].

These theoretical results are in good agreement with our measured data (see Fig. 4a).

4. Conclusions

In this study, a new experimental arrangement of NF-LA-ICP-MS and an analytical procedure for the nanolocal analysis of solid samples were developed and successfully applied for measurements of thin Au film deposited onto a Si substrate. The observed ablation craters ranged from 500 nm to about 1 μm in diameter and were dependent on the needle used as well as on the "sample-to-tip" distance. The resulting mass spectrometric transient signals of $^{197}Au^+$ and $^{28}Si^+$ showed about a 100-fold increase of the ion intensity of the analytes when the needle was at a distance of about 200 nm from the surface in contrast to the case where it was far away from the sample. Based on these preliminary studies a further development and rigorous study of the proposed NF-LA-ICP-MS procedure will be of great importance in developing a quantitative nanoanalytical technique with multielement capability and the ability to measure isotope ratios.

Acknowledgment

The first author would like to acknowledge financial support for this research from the Deutsche Forschungsgemeinschaft (DFG, project: ZO256/1-1),

References

[1] J.S. Becker, Inorganic Mass Spectrometry: Principles and Application, John Wiley and Sons, Chichester, 2007.
[2] J. Pisonero, D. Fliegel, D. Guenther, J. Anal. Atom. Spectrom. 21 (2006) 922.
[3] M.V. Zoriy, J.S. Becker, Int. J. Mass Spectrom. 264 (2007) 175.
[4] B. Fernandez, F. Claverie, C. Pecheyran, O.F.X. Donard, TRAC 26 (2007) 951.
[5] X.Z. Pei, S.P. Ding, G.W. Zhang, H.B. Liu, Z.C. Li, G.Y. Li, Z.Q. Liu, Y. Meng, Sci. China Ser. D-Earth Sci. 50 (2007) 264.
[6] M.V. Zoriy, A. Matusch, T. Spruss, J.S. Becker, Int. J. Mass Spectrom. 260 (2007) 102.
[7] J. Koch, D. Guenther, Anal. Bioanal. Chem. 387 (2007) 149.
[8] M.V. Zoriy, M. Kayser, A.V. Izmer, C. Pickhardt, J.S. Becker, Int. J. Mass Spectrom. 242 (2005) 297.
[9] J.S. Becker, M.V. Zoriy, M. Dehnhardt, C. Pickhardt, K. Zilles, J. Anal. Atom. Spectrom. 20 (2005) 912.
[10] J.S. Becker, M. Zoriy, J. Dobrowolska, A. Matusch, J. Anal. Atom. Spectrom. 22 (2007) 736.
[11] M.V. Zoriy, M. Dehnhardt, G. Reifenberger, K. Zilles, J.S. Becker, Int. J. Mass Spectrom. 257 (2006) 27.

[12] B. Wolfrum, Y. Mourzina, D. Mayer, D. Schwaab, A. Offenhaeusser, Small 2 (2006) 1256.
[13] D.J. Hwang, C.P. Grigoropoulos, J. Yoo, R.E. Russo, Appl. Phys. Lett. 89(2006).
[14] D. Kossakovski, J.L. Beauchamp, Anal. Chem. 72 (2000) 4731.
[15] A. Rasmussen, V. Deckert, Anal. Bioanal. Chem. 381 (2005) 165.
[16] R. Stoeckle, P. Setz, V. Deckert, T. Lippert, A. Wokaun, R. Zenobi, Anal. Chem. 73 (2001) 1399.
[17] S.B. Wen, R. Greif, R.E. Russo, Appl. Phys. Lett. 91 (2007).
[18] M.A. Paesler, P.J. Moyer, Near-Field Optics. Theory, Instrumentation and Applications, John Wiley & Sons, Inc., New York, 1996.
[19] J.S. Becker, A. Gorbunoff, M.V. Zoriy, A.V. Izmer, M. Kayser, J. Anal. Atom. Spectrom. 21 (2006) 19.
[20] J.S. Becker, A. Gorbunoff, M. Zoriy, A. Izmer, M. Kayser, J. Anal. Atom. Spectrom. 22 (2007) 222.
[21] M. Zoriy, M. Kayser, J.S. Becker, Poster presented at 2008 Winter Conference on Plasma Spectrochemistry, Temecula, January 7th–12th, 2008.