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On-line isotope dilution in laser ablation inductively coupled plasma mass spectrometry using a microflow nebulizer inserted in the laser ablation chamber

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Abstract

Laser ablation ICP-MS (inductively coupled plasma mass spectrometry) is becoming one of the most important analytical techniques for fast determination of trace impurities in solid samples. Quantification of analytical results requires matrix-matched standards, which are in some cases (e.g., high-purity metals, proteins separated by 2D gel electrophoresis) difficult to obtain or prepare. In order to overcome the quantification problem a special arrangement for on-line solution-based calibration has been proposed in laser ablation ICP-MS by the insertion of a microflow nebulizer in the laser ablation chamber. This arrangement allows an easy, accurate and precise quantification by on-line isotope dilution using a defined standard solution with an isotope enriched tracer nebulized to the laser-ablated sample material. An ideal matrix matching in LA-ICP-MS is therefore obtained during the measurement. The figures of merit of this arrangement with a microflow nebulizer inserted in the laser ablation chamber and applications of on-line isotope dilution in LA-ICP-MS on two different types of sample material (NIST glass SRM 612 and NIST apple leaves SRM 1515) will be described.

Keywords: Microflow nebulizer; Laser ablation; ICP-MS; On-line isotope dilution analysis

1. Introduction

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has been established in analytical chemistry for sensitive and powerful multi-element analysis at the trace and ultratrace level [1,2] as well as for direct isotope ratio measurements on solid samples [3,4]. Fields of applications of LA-ICP-MS are geological research [5,6], materials research [7–9], environmental monitoring [10–14], characterization of radioactive waste [15,16] or biological research and life sciences [17–21]. Nowadays, LA-ICP-MS is attracting increased interest as a microlocal analytical technique for element determination (P, S and metals) in protein spots separated by 2D gel electrophoresis [22–25] and for imaging of elements, e.g., in thin sections of brain samples [26,27] where LA-ICP-MS is successfully employed.

A limitation in LA-ICP-MS analysis of solid samples is the quantification of analytical results, which is mainly due to a lack of suitable certified reference materials (CRM) with a matrix composition similar to that of the sample. Different quantification strategies have been investigated in order to solve this problem. Matrix matching as one way to overcome matrix effects was achieved, for example, by the preparation of homogeneous fused lithium borate targets of geological samples and geological reference materials. In this case, geological SRMs with a matrix composition different to those of the sample can be used for calibration [28,29]. Jochum et al. [30] prepared and characterized geological MPI-DING reference glasses for in situ microlocal-analysis [30,40]. It has been demonstrated for trace element determination in geological glasses that the use of a geological reference glass in comparison to NIST glass standard reference material (NIST SRM 612) for quantification of analytical results gives more accurate data due to a better agreement for the matrix composition of standard and sample [31]. Synthetic laboratory standards have also been prepared and successfully employed for quantitative analysis in the LA-ICP-MS of e.g., concrete matrix

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[15], ceramics [9], carbonates [11,14], tree rings [12], graphite [32], airborne particulate matter collected on PTFE-membrane filters [13] or thin sections of brain samples [26,27]. In the case of powdered samples, it is possible to apply the isotope dilution method by adding an isotope-enriched tracer solution to the sample powder followed by pressing targets [33,34]. However, preparation of synthetic laboratory standards or pressed sample targets is time consuming and not easy to perform for all kind of samples, e.g., high-purity metals, platinum nanoclusters or protein spots separated by 2D gel electrophoresis. An easy and rapid quantification procedure, especially if no suitable reference materials are available or preparation of synthetic laboratory standards is difficult or impossible, is solution-based calibration in LA-ICP-MS whereby a dual gas [35–37] and a mono gas sample introduction system [38,39] have been proposed. In the case of the mono gas sample introduction system, a nebulizer (e.g., ultrasonic [23,32,38,39], microconcentric [8], microflow [26] or Meinhard [41] nebulizer) is directly coupled to the laser ablation cell. By this means, the nebulizer gas flow coming from the nebulizer is used as the carrier gas flow for laser ablation. Using these arrangement measurements can be performed with optimized carrier and nebulizer gas flow rates [32]. However, during the measurement of the standard solutions matrix matching is necessary and can be performed by either laser ablation of a high-purity blank target [32,38] or by using the standard addition mode in solution-based calibration [26,39]. Neither method of matrix matching is applicable in the case of samples where no blank material exists or where the sample amount available (only a few mg) is not enough for the number of measurements required in the case of the standard addition mode. In order to overcome this problem a new strategy of solution-based calibration by performing on-line isotope dilution analysis (IDA) in LA-ICP-MS (on-line LA-ID-ICP-MS) combined with a microconcentric nebulizer was developed for the determination of Ag, Tl and Pb in a few milligrams of platinum nanoclusters [8]. Beside matrix effects also elemental fractionation has to be considered when performing solution-based calibration in LA-ICP-MS. The most important criterion in order to avoid fractionation effects in laser ablation ICP-MS is the laser power density, whereby elemental fractionation can be minimized at a laser power density of about 10^9 W cm^{-2} and higher [29,38,42,43]. Furthermore, different element sensitivities in ICP-MS and LA-ICP-MS have to be taken into consideration by applying a correction factor which is defined as the certified concentration of internal standard element divided by the measured concentration of internal standard element [32,38]. These differences in sensitivity depend on the nebulizer used for solution-based calibration in LA-ICP-MS and the sample to be analyzed (e.g., 15,000 for ultrasonic nebulizer, graphite samples [32]; 5000 for ultrasonic nebulizer, fused lithium borate targets [38]; 20,000 for ultrasonic nebulizer, high-purity platinum [32]). It would be advantageous to use a nebulizer with a low solution uptake rate in order to fit the nebulized solution to a small amount of ablated sample so that differences in element sensitivities in ICP-MS and LA-ICP-MS can be reduced. The microflow total consumption nebulizer DS-5 operates at solution uptake rates significantly below the 10 μl min^{-1} level and in combination with nano-volume flow injection in ICP-SFMS provides detection limits of 1.6 and 0.3 pg ml^{-1} in 54 nl sample volume for uranium and plutonium, respectively [44].

Applications of on-line isotope dilution in laser ablation ICP-MS using a special arrangement with microflow total consumption nebulizer DS-5 directly coupled to the laser ablation chamber (mono gas sample introduction) [45] will be presented in this work.

2. Experimental

2.1. Instrumentation

For on-line isotope dilution in laser ablation ICP-MS the microflow total consumption nebulizer DS-5 (CETAC Technologies, Omaha, NE, USA) was inserted in the laser ablation chamber as described elsewhere [26]. In brief, the microflow nebulizer was fitted into the laser ablation chamber on the opposite side of the outlet and transfer line to the ICP (see Fig. 1). A low and constant nebulizer solution uptake rate of 7 μl min^{-1} was provided by a high precision syringe pump (CMA-100, Carnegie Medicine, Solna, Sweden). In order to investigate this new arrangement for on-line isotope dilution two different combinations of laser ablation system and inductively coupled plasma mass spectrometer (ICP-MS) were employed. A photograph of the micronebulizer inserted in cooled laser ablation chamber is shown in Fig. 1. Determination of uranium in NIST glass standard reference material (SRM) 612 was performed using the laser ablation system Ablascope (Bioptic, Berlin, Germany) coupled to a double-focusing sector field ICP-MS (ICP-SFMS, ELEMENT 1, Thermo Electron Corp., Bremen, Germany) [20,22,26]. The ICP torch was shielded with a grounded platinum electrode (GuardElectrode, Thermo Electron Corp.). In order to determine the doped uranium concentration in NIST-SRM 1515 (apple leaves) the laser ablation system CETAC LSX 200 (CETAC, Technologies, Omaha, NE, USA) was combined with a quadrupole-based ICP-MS with collision cell (ICP-CC-MS, Platform, Micromass Ltd., Manchester, UK). Both laser ablation systems operate with a Nd:YAG laser, whereby in the case of the Ablascope a frequency quintupled laser wavelength of 213 nm is used (repetition frequency 20 Hz, spot diameter 50 μm, laser power density 3.5×10^9 W cm^{-2}) and the CETAC LSX 200 system is run with 266 nm (repetition frequency 20 Hz, spot diameter 300 μm, laser power density 1.1×10^9 W cm^{-2}). Ablation of sample material was performed by scanning the focused laser beam over the sample surface (single line scan modus). Experimental parameters of both laser ablation systems are summarized in Table 1. Experimental parameters in ICP-MS were optimized with respect to maximum ion intensity of $^{238}U^+$ using a 1 μg l^{-1} uranium solution nebulized with DS-5 directly coupled to the laser ablation chamber. This quick and easy way of optimizing ICP-MS parameters in LA-ICP-MS is possible using the mono gas sample introduction system because the optimized conditions (rf power, carrier or nebulizer gas flow rate) were found to be the same for nebulized solutions and ablated solid samples [32,38]. Furthermore, the mono gas sample introduction system offers optimum mixing of nebulized

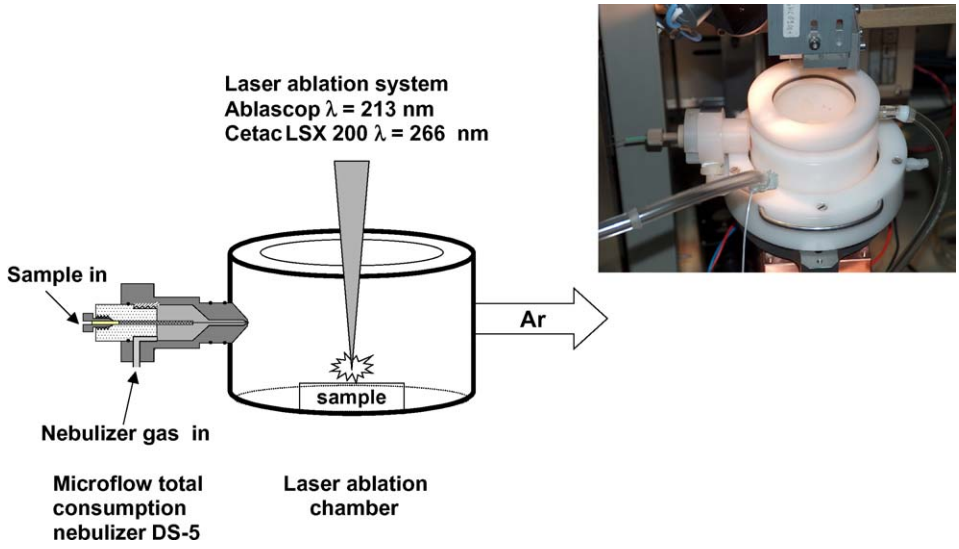

Fig. 1. Experimental set-up of laser ablation chamber with microflow total consumption nebulizer DS-5 for on-line isotope dilution analysis.

isotope-enriched tracer solution and laser-ablated solid sample directly in the ablation chamber, which is of importance in the case of isotope dilution analysis. Optimized ICP-MS parameters are given in Table 1. Replicates (given in Figs. 2 and 3 as measurements) in case of measurements using the ICP-QMS Elan 6000 and the ICP-SFMS Element 1, respectively, has been choosen according to the time needed for the measurement.

2.2. Samples, sample preparation and isotope-enriched tracer solution

Investigated samples were NIST glass standard reference materials (SRM) 612 (NIST, National Institute of Standards and Technology, Gaithersburg, MD, USA) and NIST apple leaves SRM 1515 with a certified uranium concentration of 37.4 and 0.006 $\mu g\,g^{-1}$, respectively. NIST glass SRM 612 was cleaned with 2% nitric acid and ethanol prior to measurements. In the case of apple leaves, uranium standard solution was added to the sample material in order to obtain a doped uranium concentration of 10 $\mu g\,g^{-1}$. The mixture was then homogenized, dried and placed on high-purity carbon ribbon for direct laser ablation measurements. A solution of isotope-enriched tracer ($^{235}U/^{238}U$: 0.5465) in 2% nitric acid was prepared from NIST U350 standard solution by diluting with high-purity deionized water (18 $M\Omega\,cm^{-1}$, Millipore Milli-Q-Plus water purifier, Millipore Bedford, MA, USA) and acidifying with sub-boiled nitric acid. Isotope-enriched tracer concentration in solution was chosen so as to obtain an isotope ratio in the mixture of sample and tracer solution as near as possible to one. For the investigation of NIST apple leaves SRM 1515 doped with uranium and NIST glass SRM 612, the U-concentration in the isotope-enriched tracer solution was 6 $mg\,l^{-1}$ and 1 $\mu g\,l^{-1}$, respectively.

2.3. On-line isotope dilution analysis in LA-ICP-MS

On-line isotope dilution in LA-ICP-MS as described in detail elsewhere [8] consists of three measurements one after the other:

1. Laser ablation of the sample and nebulization of 2% nitric acid in order to determine $^{235}U/^{238}U$ isotope ratio in the sample (S).

Table 1
Experimental parameters for on-line isotope dilution analysis in LA-ICP-SFMS and LA-ICP-CC-MS

ICP-SFMS "Element"		Laser ablation system "Ablascope"	
rf Power (W)	1200	Wavelength (nm)	213
Coolant gas flow rate ($l\,min^{-1}$)	18	Pulse energy (mJ)	6
Auxiliary gas flow rate ($l\,min^{-1}$)	1.25	Laser power density ($W\,cm^{-2}$)	3.5×10^9
Carrier gas flow rate ($l\,min^{-1}$)	1.20	Repetition frequency (Hz)	20
Dwell time (ms)	100	Spot diameter (μm)	50
ICP-CC-MS "Platform"		**Laser ablation system "LSX 200"**	
rf Power (W)	1200	Wavelength (nm)	266
Coolant gas flow rate ($l\,min^{-1}$)	13.55	Pulse energy (mJ)	4
Auxiliary gas flow rate ($l\,min^{-1}$)	1.09	Laser power density ($W\,cm^{-2}$)	1.1×10^9
Carrier gas flow rate ($l\,min^{-1}$)	0.85	Repetition frequency (Hz)	20
He gas flow rate ($ml\,min^{-1}$)	10	Spot diameter (μm)	300
Dwell time (ms)	200		

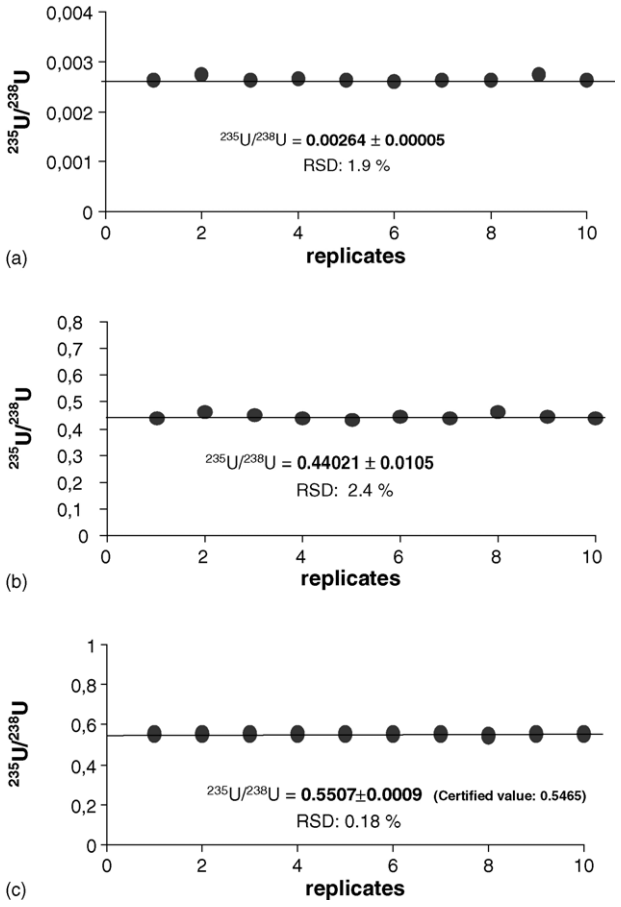

Fig. 2. Measurement of $^{235}U/^{238}U$ isotope ratios in (a) NIST glass SRM 612 (b) mixture of sample and isotope-enriched tracer solution and (c) isotope-enriched tracer solution by double-focusing sector field LA-ICP-SFMS (ELEMENT).

2. Nebulization of isotope-enriched tracer solution NIST U350 and simultaneous laser ablation of the sample for the determination of $^{235}U/^{238}U$ isotope ratio in the mixture (X).
3. Nebulization of isotope-enriched tracer solution NIST U350 while the laser is not operating thus allowing the measurement of $^{235}U/^{238}U$ isotope ratio in the isotope-enriched tracer solution (T).

For blank correction 2% nitric acid is nebulized and measured before and after this procedure.

Determination of element concentration is performed using the formula for isotope dilution analysis (1):

$$Q_S = \frac{Q_T(T - X)}{(X - S)m_S/m_T} \quad (1)$$

Q_S = element concentration in the sample; Q_T = element concentration in the highly enriched tracer; X = isotopic ratio of the two selected isotopes in the mixture; T = isotopic ratio of the two selected isotopes in the tracer; S = isotopic ratio of the two selected isotopes in the sample; m_S, m_T = atomic mass of the element in nature and of the isotopically enriched element, respectively.

In addition, the isotope ratio of two selected isotopes of an internal standard element is measured during this procedure and concentration of the internal standard element is calculated as described for the element of interest. Using the internal standard element differences of sensitivity in LA-ICP-MS and ICP-MS can be considered by employing a correction factor which is defined as the true concentration of internal standard element in the sample divided by the concentration determined via on-line isotope dilution in LA-ICP-MS. In order to demonstrate that different elements can be applied for this correction Ba (in the case of NIST apple leaves SRM 1515) and Th (in the case of NIST glass SRM 612) were used as internal standard elements. These elements concentrations are known in the samples investigated.

In case of employing this quantification procedure for element mapping the internal standard element has to be homogeneous distributed within the sample. Th and U were found to be homogeneous distributed in thin section of human brain samples and were therefore employed as internal standard element

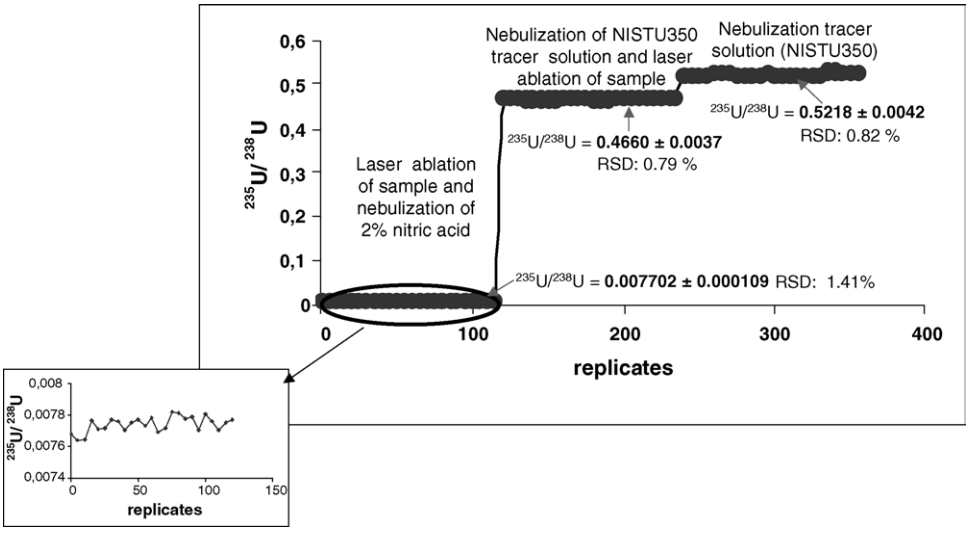

Fig. 3. Results of $^{235}U/^{238}U$ isotope ratio measurements for quantitative uranium analysis in NIST apple leaves SRM 1515 (doped U-concentration: 10 μg g^{-1}) via on-line isotope dilution technique in quadrupole-based LA-ICP-CC-MS (platform).

Table 2
Results of uranium determination in NIST glass SRM 612 and NIST apple leaves SRM 1515 doped with uranium by on-line LA-ID-ICP-MS

	Uranium concentration ($\mu g\,g^{-1}$)		
	Certified value	Doped U	On-line LA-ID-ICP-MS
NIST glass SRM 612	37.4 ± 0.1	–	36.2 ± 1.1[a]
NIST SRM 1515 apple leaves	(0.006)[b]	10 ± 0.5	11.19 ± 1.11[a]

[a] Mean ± 1 S.D. ($n = 3$).
[b] Information value.

for solution based calibration using standard addition mode [26]. Blank correction has been performed by subtraction of intensities determined for 2% nitric acid nebulized prior to and after measurement procedure shown in Figs. 2 and 3.

3. Results and discussion

On-line isotope dilution in LA-ICP-MS using this special arrangement with the microflow total consumption nebulizer DS-5 inserted in the laser ablation chamber (see Fig. 1) was applied for the determination of U concentration in NIST glass SRM 612 and NIST apple leaves SRM 1515 doped with uranium. The results of measured $^{235}U/^{238}U$ isotope ratios for the analysis of NIST glass SRM 612 are given in Fig. 2a (measured isotope ratio in the sample), Fig. 2b (measured isotope ratio of the mixture) and Fig. 2c (measured isotope ratio of the isotope-enriched tracer solution NIST U350). An interesting finding is that the U-isotope ratio was determined to be $^{235}U/^{238}U = 0.00264 \pm 0.00005$ in this sample versus the isotope ratio of 0.00725 in natural samples [46]. The $^{235}U/^{238}U$ isotope ratio obtained for the isotope standard reference material NIST U350 differs slightly from the certified value of 0.5465 because no correction for mass discrimination effects has been performed in the case of these measurements. This is not necessary due to the fact that the $^{235}U/^{238}U$ isotope ratio was measured for the sample (S), the mixture (X) and the tracer solution (T) and can therefore be applied uncorrected in the formula for isotope dilution analysis [see Eq. (1)]. Precision of measured isotope ratios was about 1.9% R.S.D. in the case of LA-ICP-MS of the glass sample and 0.18% R.S.D. for the nebulized tracer solution. A precision of 2.4% R.S.D. was observed for the determination of the $^{235}U/^{238}U$ isotope ratio in the mixture of laser-ablated sample and nebulized isotope-enriched tracer solution. This result indicates that the precision of the isotope ratio measurement in this case is mainly caused due to the laser ablation process and that an optimum mixture of ablated sample material and nebulized tracer solution in the laser ablation chamber is obtained. The application of on-line LA-ID-ICP-SFMS yielded a concentration of $36.2 \pm 1.1\,\mu g\,g^{-1}$ for uranium in NIST glass SRM 612, which agrees with the certified value (see Table 2).

In Fig. 3, the results of the measured $^{235}U/^{238}U$ isotope ratios obtained by quadrupole-based LA-ICP-CC-MS for the quantitative analysis of uranium via on-line isotope dilution in NIST apple leaves SRM 1515 (doped U-concentration: $10\,\mu g\,g^{-1}$) are summarized. In agreement with the measurements in LA-ICP-SFMS for NIST glass SRM 612, the precision for isotope ratio determination is better in ICP-CC-MS (0.82% R.S.D. for nebulization of isotope-enriched tracer solution) than in LA-ICP-CC-MS (1.41% R.S.D. for laser ablation of apple leaves). Furthermore, good precision for $^{235}U/^{238}U$ isotope ratio measurements performed during nebulization of NIST U350 tracer solution and laser ablation of NIST apple leaves SRM 1515 again indicates that solution and ablated sample are well mixed in the laser ablation chamber. Differences of uranium isotope ratios determined for laser-ablated sample from the isotope ratio in nature ($^{235}U/^{238}U = 0.00725$) and for the nebulized tracer solution from the certified isotope ratio in NIST U350 ($^{235}U/^{238}U = 0.5465$) are again due to the fact that no mass bias correction had to be performed for this kind of quantification procedure. As shown in Table 2, a concentration of $11.19 \pm 1.11\,\mu g\,g^{-1}$ was determined in the apple leaves sample investigated, which is in good agreement with the doped uranium concentration of $10\,\mu g\,g^{-1}$.

In future work, on-line LA-ID-ICP-MS will be applied for the quantitative element mapping of, for example, thin sections of brain samples.

4. Conclusions

The microflow total consumption nebulizer DS-5 inserted in the laser ablation chamber is a handy and low cost all-in-one arrangement for solution-based calibration in LA-ICP-MS. The low solution uptake rate of $7\,\mu l\,min^{-1}$ for DS-5 reduces the amount of isotope-enriched tracer solution needed for on-line isotope dilution in LA-ICP-MS. Furthermore, the low solution uptake rate allows a better fitting of small amounts of ablated material and nebulized solution. It was demonstrated that on-line isotope dilution analysis using this special arrangement allows quantitative uranium determination in different kind of samples with good accuracy.

On-line LA-ID-ICP-MS will be also applicable for single-shot analysis whereby isotope-enriched tracer solution is nebulized and the sample is ablated with a single laser shot. This procedure will allow quantitative analysis in the case of element mapping and imaging, e.g., in materials science or in biomedical applications. On-line LA-ID-ICP-MS is proposed to be the method of choice for quantitative element mapping and imaging even if reference materials are available. It is more convenient to use solution-based calibration because calibration can be performed easily, quickly and in any concentration range for almost all elements.

References

[1] J.S. Becker, H.-J. Dietze, Int. J. Mass Spectrom. 228 (2003) 127.
[2] S.F. Durrant, J. Anal. Atom. Spectrom. 20 (2005) 821.

[3] C. Pickhardt, H.-J. Dietze, J.S. Becker, Int. J. Mass Spectrom. 242 (2005) 273.
[4] J.S. Becker, J. Anal. Atom. Spectrom. 20 (2005) 1173.
[5] N.J. Pearson, O. Alard, W.L. Griffin, S.E. Jackson, S.Y. O'Reilly, Geochim. Cosmochim. Acta 66/6 (2002) 1037.
[6] P.J. Sylvester, M. Ghaderi, Chem. Geol. 141 (1997) 49.
[7] J.S. Becker, Spectrochim. Acta, Part B 57 (2002) 1805.
[8] J.S. Becker, C. Pickhardt, W. Pompe, Int. J. Mass Spectrom. 237 (2004) 13.
[9] J.Th. Westheide, J.S. Becker, R. Jäger, H.-J. Dietze, J. Anal. Atom. Spectrom. 11 (1996) 661.
[10] S.F. Boulyga, D. Desideri, M.A. Meli, C. Testa, J.S. Becker, Int. J. Mass Spectrom. 226 (2003) 329.
[11] W.T. Perkins, R. Fuge, N.J.G. Pearce, J. Anal. Atom. Spectrom. 6 (1991) 445.
[12] E. Hoffmann, C. Lüdke, H. Scholze, H. Stephanowitz, Fresenius J. Anal. Chem. 350 (1994) 253.
[13] C.-J. Chin, C.-F. Wang, S.-L. Jeng, J. Anal. Atom. Spectrom. 14 (1999) 663.
[14] V.R. Bellotto, N. Miekeley, Fresenius J. Anal. Chem. 367 (2000) 635.
[15] M. Gastel, J.S. Becker, G. Küppers, H.-J. Dietze, Spectrochim. Acta, Part B 52 (1997) 2051.
[16] J.S. Becker, C. Pickhardt, H.-J. Dietze, Int. J. Mass Spectrom. 203 (2000) 283.
[17] F. Lochner, J. Appleton, F. Keenan, M. Cooke, Anal. Chim. Acta 401 (1999) 229.
[18] T. Prohaska, C. Latkoczy, G. Schultheis, M. Teschler-Nicola, G. Stingeder, J. Anal. Atom. Spectrom. 17 (2002) 887.
[19] N.I. Ward, S.F. Durrant, A.L. Gray, J. Anal. Atom. Spectrom. 7 (1992) 1139.
[20] M.V. Zoriy, M. Kayser, A. Izmer, C. Pickhardt, J.S. Becker, Int. J. Mass Spectrom. 242 (2005) 297.
[21] J.S. Becker, M. Burow, M.V. Zoriy, C. Pickhardt, P. Ostapczuk, R. Hille, Atom. Spectrosc. 25/5 (2004) 197.
[22] J.Su. Becker, M. Zoriy, C. Pickhardt, M. Przybylski, J.Sa. Becker, Int. J. Mass Spectrom. 242 (2005) 135.
[23] J.S. Becker, S.F. Boulyga, J.S. Becker, C. Pickhardt, E. Damoc, M. Przybylski, Int. J. Mass Spectrom. 228 (2003) 985.
[24] J.S. Becker, M. Zoriy, J.Su. Becker, C. Pickhardt, M. Przybylski, J. Anal. Atom. Spectrom. 19 (2004) 149.
[25] J.S. Becker, M. Zoriy, U. Krause-Buchholz, J.Su. Becker, C. Pickhardt, M. Przybylski, W. Pompe, G. Rödel, J. Anal. Atom. Spectrom. 19 (2004) 1236.
[26] J.S. Becker, M.V. Zoriy, C. Pickhardt, N. Palomero-Gallagher, K. Zilles, Anal. Chem. 77/10 (2005) 3208.
[27] J.S. Becker, M.V. Zoriy, M. Dehnhardt, C. Pickhardt, K. Zilles, J. Anal. Atom. Spectrom. 20 (2005) 912.
[28] M. Ødegård, S.H. Dundas, B. Flem, A. Grimstvedt, Fresenius J. Anal. Chem. 362 (1998) 477.
[29] C. Pickhardt, I.B. Brenner, J.S. Becker, H.-J. Dietze, Fresenius J. Anal. Chem. 368 (2000) 79.
[30] K.P. Jochum, D.B. Dingwell, A.W. Hofmann, B. Stoll, I. Raczek, A. Rocholl, J.S. Becker, A. Besmehn, D. Bessette, H.-J. Dietze, P. Dulski, J. Erzinger, E. Hellebrand, P. Hoppe, I. Horn, K. Janssens, G. Jenner, M. Klein, W.M. McDonough, M. Maetz, I.K. Nikogosian, C. Pickhardt, H.M. Seufert, S.G. Simakin, A.V. Sobolev, B. Spettel, S. Straub, L. Vincze, A. Wallianos, G. Weckwerth, D. Wolf, M. Zimmer, Geostand. Newslett. 24/1 (2000) 87.
[31] J.S. Becker, C. Pickhardt, H.-J. Dietze, Mikrochim. Acta (2000) 71.
[32] C. Pickhardt, J.S. Becker, Fresenius J. Anal. Chem. 370 (2001) 534.
[33] H. Scholze, E. Hoffmann, C. Lüdke, A. Platalla, Fresenius J. Anal. Chem. 355 (1996) 982.
[34] S.F. Boulyga, K.G. Heumann, J. Anal. Atom. Spectrom. 19 (2004) 1501.
[35] D. Günther, H. Cousin, B. Magyar, I. Leopold, J. Anal. Atom. Spectrom. 12 (1997) 165.
[36] S.A. Baker, M.J. Dellavecchia, B.W. Smith, J.D. Winefordner, Anal. Chim. Acta 355 (1997) 113.
[37] H.F. Falk, B. Hattendorf, K. Krengel-Rothensee, N. Wieberneit, S.L. Dannen, Fresenius J. Anal. Chem. 362 (1998) 468.
[38] C. Pickhardt, J.S. Becker, H.-J. Dietze, Fresenius J. Anal. Chem. 368 (2000) 173.
[39] J.S. Becker, C. Pickhardt, H.-J. Dietze, J. Anal. Atom. Spectrom. 16 (2001) 603.
[40] K.P. Jochum, B. Stoll, K. Herwig, M. Amini, W. Abouchami, A.W. Hofmann, Int. J. Mass Spectrom. 242 (2005) 281.
[41] N.H. Bings, J. Anal. Atom. Spectrom. 17 (2002) 759.
[42] E.F. Cromwell, P. Arrowsmith, Appl. Spectrosc. 49/11 (1995) 1652.
[43] D. Figg, J.B. Cross, C. Brink, Appl. Surf. Sci. 127–129 (1998) 287.
[44] D. Schaumlöffel, P. Giusti, M.V. Zoriy, C. Pickhardt, J. Szpunar, P. Łobiński, J.S. Becker, J. Anal. Atom. Spectrom. 20 (2005) 17.
[45] J.S. Becker, D. Schaumlöffel, C. Pickhardt, Verfahren und Vorrichtung zur quantitativen Elementanalyse in der Laserablations-ICP-MS mittels direkter on-line Lösungskalibration, Deutsche Patentanmeldung. 10 2004 048 380.9 vom 1.10.2004.
[46] International Union of Pure and Applied Chemistry, Isotopic composition of the elements, Pure Appl. Chem. 63 (1994) 991.