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Determination of Ag, Tl, and Pb in few milligrams of platinum nanoclusters by on-line isotope dilution in laser ablation inductively coupled plasma mass spectrometry

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Abstract

A new analysis procedure for determination of trace impurities in a few milligram noble metal nanoclusters, using on-line isotope dilution in laser ablation inductively coupled plasma mass spectrometry (LA–ICP–MS) was developed. During the laser ablation of investigated sample simultaneous the dry aerosol of nebulized enriched isotope spike solution was added and mixed in the laser ablation chamber. The capability of solution-based calibration by a modified isotope dilution analysis in LA–ICP–MS for the determination of selected elements was tested, using platinum reference material NIST SRM 681. A good agreement of measured with certified concentration for Ag and Pb was found. The detection limits for trace element determination of the developed analytical technique, using LA–ICP–MS with quadrupole analyzer varied between 6 ng g^{-1} for Ag and 90 ng g^{-1} for Pb. The analytical technique was applied for the determination of Ag, Tl, and Pb in a few milligram of platinum nanoclusters.

Keywords: Laser ablation inductively coupled plasma mass spectrometry; On-line isotope dilution technique; Platinum nanoclusters; Solution-based calibration; Trace analysis

1. Introduction

Biomolecular templating is a technique that allows fundamental aspects of biological self-assembly to be transferred to the emerging field of nanostructure formation and manipulation. It takes advantage of the well-defined chemical, physical, and structural properties of biomolecular templates used for a controlled deposition of inorganic material [1]. For example, the fabrication of regular arrays of metallic nanoparticles (Pt, Pd, or Ag) by biomolecular templating is of great interest in order to prepare nanometer structures for use in nanoelectronic devices (e.g., by deposition of nanoclusters on crystalline bacterial surface layers with well-defined cluster lattices or on stretched DNA to prepare nanostructures or highly conductive nanowires), optical devices and chemical devices (e.g., biosensors) [2,3]. As it is known, impurities due to contamination during device production can influenced the physical, electrical, and chemical properties of micro- and nano-electronic arrays (thin-layered systems or bulk) [4], therefore, powerful trace analytical techniques for the characterization of deposited noble metal layers in bioengineering are required. In order to avoid chemical digestion and contamination during sample preparation, direct solid-state

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analytical techniques, such as LA–ICP–MS (laser ablation inductively coupled plasma mass spectrometry) is gaining increasing importance. Trace impurities can be analyze in any solid samples by LA–ICP–MS rapidly with detection limits down to the sub ng g^{-1} range. LA–ICP–MS allows, in addition, a microlocal analysis and depth profiling with lateral resolution in the low μm range. One problem in trace analysis using LA–ICP–MS by analogy with the other solid mass-spectrometric techniques (glow discharge mass spectrometry (GDMS) or spark source mass spectrometry (SSMS)) — is the quantification of analytical results if no suitable certified reference material with a similar matrix composition is available [5]. In such a case, matrix-matched laboratory standards from high-purity compounds doped with the trace elements of interest [6] can be prepared. For example, an analytical procedure for the direct analysis of trace impurities, using such a platinum laboratory standard (high-purity Pt powder was doped with several elements) by GDMS was described by van Straaten et al. [7]. For the most important application field of LA–ICP–MS — geological research — the quantification is not so problematically because many different suitable geological and glass standard reference materials are available [7–9].

An alternative quantification procedure in LA–ICP–MS is possible, if the direct ablation of solid sample by a focused laser beam and the easy solution calibration in ICP–MS is combined, whereby an ideal matrix matching is achieved. The solution-based calibration uses standard solution with well-defined element concentrations nebulized by an ultrasonic nebulizer or microconcentric nebulizer with desolvator in order to produce a dried aerosol [10–12]. In comparison to the dual gas flow introduction in the inductively coupled plasma of ablated materials and nebulized standard solution via a Y-piece [10,11], we proposed a single gas flow introduction of a sample/standard mixture via an on-line coupling of the desolvating nebulizer together with the laser ablation chamber in order to yield an optimal mixing of aerosols nebulized from standard solutions and ablated material from solid sample in the laser ablation chamber [12–14]. An analogous experimental arrangement of solution-based calibration in ICP–MS was described by Bings [15] for determining of metals in lubricating oils. Three possible solution-based calibration procedures in LA–ICP–MS, namely, external calibration, analyte addition technique and isotope dilution are discussed in a recent review [4].

Because, in our experiments only a few milligrams of platinum nanocluster are available a modified on-line isotope dilution analysis (IDA) in LA–ICP–MS will be applied. In IDA, which is a suitable quantification possibility in mass spectrometry for accurate trace element determination, a defined amount of an enriched isotope tracer of the element of interest was added to the ablated sample. The determination of trace element concentration is performed by measuring changed isotope ratios in the sample-spike mixture compared to those in the sample and highly enriched isotope tracer, using the equation of isotope dilution [16].

The aim of this work is to demonstrate the capability of on-line isotope dilution analysis in LA–ICP–MS for the determination of selected elements in a small amount of high-purity Pt nanoclusters or nanowires.

2. Experimental

2.1. Instrumental

In these experiments a commercial laser ablation (LA) system (CETAC LSX 200, Cetac Technologies, Omaha, NE, USA) is coupled to the inductively coupled plasma ion source of a quadrupole mass spectrometer (ICP–QMS, ELAN 6000, Perkin–Elmer, SCIEX Corp., Norwalk, CT, USA). The UV wavelength of a Nd-YAG laser (4th harmonic, 266 nm at pulse duration of 5 ns, repetition frequency of 20 Hz, energy per pulse of 4 mJ and laser power density of 1.1×10^9 W/cm^2) is used for laser ablation. For on-line isotope dilution analysis with LA–ICP–MS a microconcentric nebulizer with membrane desolvation (Aridus, Cetac) was directly coupled to the LA–ICP–QMS. The experimental arrangement is shown in Fig. 1.

The experimental parameters of the laser ablation system used and the mass spectrometric measurements are summarized in Table 1. The mass spectrometric measurements by LA–ICP–MS, using a quadrupole-based mass spectrometer were carried out at low mass resolution ($m/\Delta m \approx 300$). Laser ablation was performed in the single line scan modus at a scan speed of 10 μm s^{-1}.

2.2. Samples, standard reference material and highly enriched isotope tracers

Platinum nanoclusters were prepared by an electroless metallization procedure [2]. Small sample amounts of powdered platinum nanoclusters (only 1–5 mg were available) were placed on high pure carbon ribbon and analyzed directly by LA–ICP–MS without any additional sample preparation steps. In order to verify the accuracy of solution-based calibration in LA–ICP–MS, platinum standard reference material (SRM) NIST 681 was used with a certified concentration of Cu, Ag and Pb in the concentration range of 2.0 to 12 ng g^{-1}. Solutions of enriched isotopic tracer (^{65}Cu: 89.2%, ^{109}Ag: 95.6 %, ^{203}Tl: 97.8%, ^{204}Pb: 51.0%) in 2% nitric acid were prepared, using sub-boiled HNO_3 and deionized water. Final element concentrations in the isotope-enriched tracer solution range from 2 ng g^{-1} for Pb to 20 ng g^{-1} for Cu (tracer solution 1, used for trace element determination in NIST SRM 681) and from 0.002 ng g^{-1} for Tl to 0.12 ng g^{-1} for Pb (tracer solution 2, used for trace element determination in platinum nanocluster). Cu was used in this experiment as an internal standard element. The concentration of spike in solution was chosen so as to obtain an isotope ratio in the mixture of sample and isotope-enriched spike of about one. Abundances of enriched isotope spikes for isotope dilution

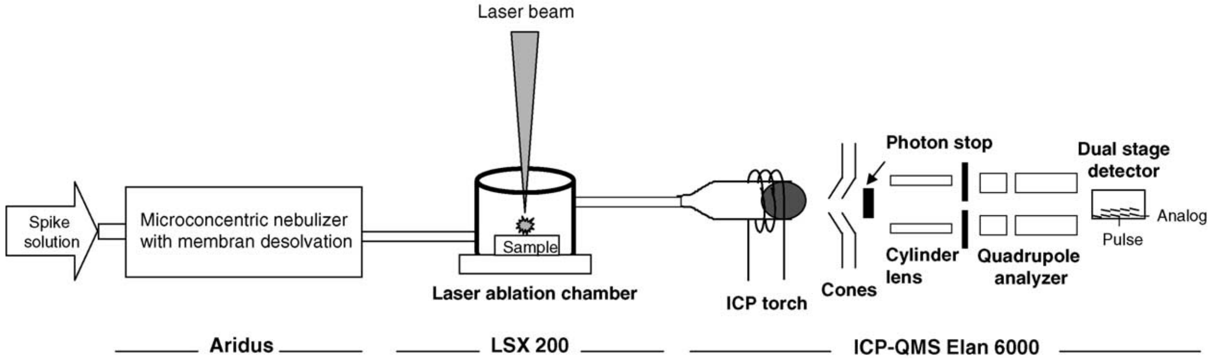

Fig. 1. Experimental arrangement for on-line isotope dilution analysis in LA–ICP–MS.

Table 1
Optimized experimental parameters of LA–ICP–MS

ICP–QMS	(Elan 6000, PE Sciex)	Laser ablation (CETAC Technologies)	
Rf power	1150 W	Nd:YAG laser	
Coolant gas flow rate	14 L min^{-1}	Wavelength:	266 nm
Auxiliary gas flow rate	0.8 L min^{-1}	Pulse energy:	4 mJ
Dwell time	10 ms	Laser power density:	1.1×10^9 W cm^{-2}
		Repetition frequency:	20 Hz
		Spot diameter:	300 μm
Sweeps	15		
Replicates	100–200		
Microconcentric nebulizer Aridus with desolvator			
Nebulizer gas flow rate	1.2 L min^{-1}		
Sweep gas flow rate	7.0 L min^{-1}		
Solution uptake rate	90 μL min^{-1}		
Heater spray chamber	70 °C		
Heater desolvator	160 °C		

analysis in comparison to table values [17] and the concentrations of analytes in spike solutions are summarized in Table 2.

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

The new calibration strategy will be demonstrated for the determination of selected elements: Pb, Ag, and Tl in a small amount of platinum nanoclusters. In on-line isotope dilution analysis with LA–ICP–MS, an isotope-enriched tracer solution was nebulized by the microconcentric nebulizer Aridus with desolvator. After about 150 s laser ablation of the investigated platinum nanocluster sample was started and after an additional time of 150 s 2% nitric acid was nebulized instead of the tracer solution. The isotope ratios of lead (^{204}Pb/^{206}Pb), silver (^{107}Ag/^{109}Ag) and thallium (^{203}Tl/^{205}Tl), with ^{63}Cu/^{65}Cu for internal standardization, were monitored during the whole experiment. The measuring time for one experiment was no longer than 9 min.

The element concentration was determined via the formula for isotope dilution analysis (1):

$$Q_\mathrm{s} = Q_\mathrm{T}\frac{(T-X)}{(X-S)}\frac{m_\mathrm{s}}{m_\mathrm{T}} \qquad (1)$$

Table 2
Abundances of enriched isotope spikes for isotope dilution analysis in comparison to table values

Isotope	Spike		Concentration (spike in solution) ng g^{-1}		Sample[a]	
	Abundance (%)	Isotope ratio	Tracer solution 1	Tracer solution 2	Abundance (%)	Isotope ratio
^{65}Cu	89.2	8.3(^{65}Cu/^{63}Cu)	20.0	0.113	30.8	0.45(^{65}Cu/^{63}Cu)
^{109}Ag	95.6	21.7(^{109}Ag/^{107}Ag)	19.0	0.005	48.2	0.93(^{109}Ag/^{107}Ag)
^{203}Tl	97.8	45.1(^{203}Tl/^{205}Tl)	–	0.002	29.5	0.42(^{203}Tl/^{205}Tl)
^{204}Pb	51.0	2.4(^{204}Pb/^{206}Pb)	2.4	0.122	1.4	0.06(^{204}Pb/^{206}Pb)

[a] Table value (IUPAC) [18].

where Q_s is the element concentration in the sample; Q_T the element concentration in the highly enriched spike; X the isotopic ratio of the two selected isotopes in the mixture; T the isotopic ratio of the two selected isotopes in the spike; S the isotopic ratio of the two selected isotopes in the sample; m_s and m_T the atomic mass of the element in nature and of the isotopically enriched element, respectively.

Differences of sensitivity in LA–ICP–MS and ICP–MS were corrected with Cu as the internal standard element, whereby the correction factor is defined as the ratio of Cu concentration determined by solution-based LA–ID–ICP–MS to true Cu concentration in the sample. Cu is suitable as an internal standard element because its concentration in the sample has been determined by the use of platinum SRM NIST 681. If no trace element concentration is known in the sample a low abundant isotope of the matrix element Pt (e.g., ^{192}Pt) can be applied for internal standardization.

3. Results and discussion

The analytical method developed was applied for the determination of selected elements in platinum standard reference material SRM NIST 681 and platinum nanoclusters. The application of on-line isotope dilution analysis for Pb determination by LA–ICP–MS in a platinum standard reference material was firstly demonstrated in [4]. Fig. 2 shows the isotope ratios measured during this procedure as demonstrated for ^{63}Cu/^{65}Cu starting with the analysis of the enriched isotope spike solution of Cu by ICP–MS, using the microconcentric nebulizer Aridus with membrane desolvator. During this experiment, enriched spike solution with trace element concentration in the sub ng ml^{-1} concentration range (Table 2) was nebulized, desolvated and the dry aerosol was transported with argon into the laser ablation chamber. After about 150 s the laser was switched on, the sample was ablated and mixed with the nebulized enriched spike solution in the gas phase. A change of ^{63}Cu/^{65}Cu isotope ratio from 0.12 to 1.59 was observed. 150 s later only 2% HNO_3 was nebulized and the sample ablation was continued. The isotope ratio for ^{63}Cu/^{65}Cu measured in the sample by LA–ICP–MS agrees well with the IUPAC table value of 2.24 [17]. The precision of the Cu isotope ratio measurements in the sample only by LA–ICP–MS was about 3.4% (relative standard deviation, R.S.D.). A relative worse precision of about 6.8% for determination of ^{63}Cu/^{65}Cu isotope ratio in the mixture of laser ablated sample and nebulized isotopic spike was observed because not real isotopic equilibrium in the laser ablation chamber was obtained. An quasi-equilibrium between isotopes of spike and sample could be achieved in the hot inductively coupled plasma. Also, in isotope dilution experiments, using capillary electrophoresis ICP–MS (CE–ICP–MS), described by Prange and co-workers [18] no isotopic equilibrium was achieved. In Table 3 the results of Pb and Ag concentration in platinum SRM NIST 681 obtained by modified on-line isotope dilution analysis with LA–ICP–MS were compared to those measured in a previous work by solution-based calibration in LA–ICP–MS, using standard addition mode [12]. The agreement of the analytical results, using the two different solution-based calibration techniques in LA–ICP–MS with certified values is good. The results of the quantitative determination of trace impurities in platinum nanoclusters, measured by LA–ICP–MS via the modified on-line isotope dilution analysis are compared with those obtained via external calibration, using SRM NIST 681 in Table 4. The detection limits for trace element determination in high-purity platinum measured by isotope dilution analysis, using a quadrupole-based LA–ICP–MS (see Table 4) are in the low ppb range. In comparison to GDMS (except Cu) in general, lower detection limits were observed. An improvement of detection limits in the sub ppb range was observed by

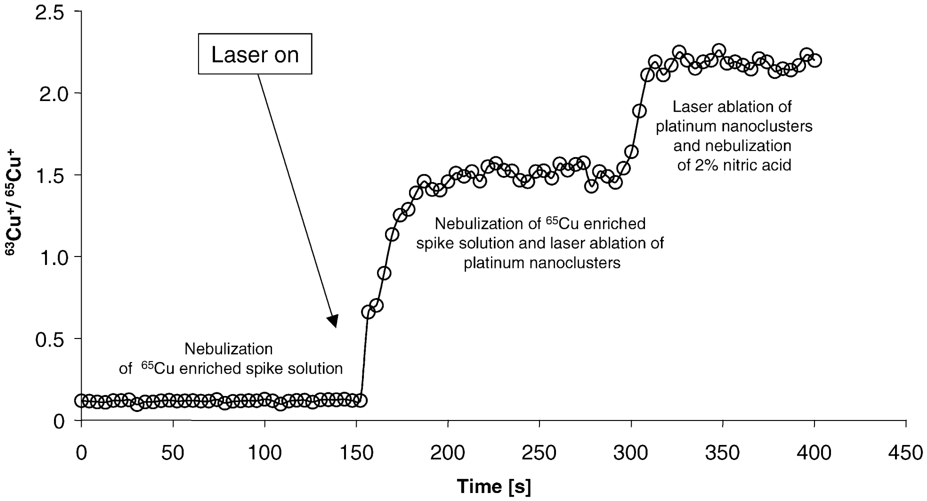

Fig. 2. ^{63}Cu/^{65}Cu Cu isotopic ratio for tracer solution, mixture and sample obtained by ratioing ion intensities of each measured replicate (before nebulization of spike solution 2% nitric acid was nebulized for 100 s in order to evaluate an average blank signal).

Table 3
Results of LA–ICP–MS, using solution-based calibration in LA–ICP–MS compared to certified values

	Concentration in platinum SRM NIST 681		
	Solution-based calibration in LA–ICP–MS		Certified value (μg g^{-1})
	By on-line isotope dilution (μg g^{-1})	By standard addition mode (μg g^{-1})	
Cu	Internal standard element		5.1 ± 0.5
Rh	–	8.3 ± 0.4	9[a]
Ag	1.91 ± 0.03	1.93 ± 0.10	2.0 ± 0.5
Pb	13.1 ± 1.1	13.0 ± 0.8	12 ± 2

[a] No estimate of accuracy is given in the NIST SRM 681 certificate.

Table 4
Results of quantitative trace analysis of platinum nanocluster by LA–ICP–MS

	Concentration (μg g^{-1})		Limits of detection (μg g^{-1})
	On-line LA–ID–ICP–MS	Calibration using SRM 681	
Cu	Internal standard	7.6 ± 0.5	0.009
Ag	0.050 ± 0.010	0.045 ± 0.003	0.006
Tl	0.102 ± 0.005	–	0.012
Pb	0.96 ± 0.03	1.03 ± 0.08	0.09

the application of double-focusing sector field LA–ICP–MS (e.g., Ir: 0.04 ng g^{-1} and Pb: 0.9 ng g^{-1}).

4. Conclusions

LA–ICP–MS, is a powerful tool for the determination of trace impurities in few milligram of noble metal nanoclusters. The quantification of analytical results for Ag, Tl, and Pb was performed with a modified on-line isotope dilution analysis in LA–ICP–MS which can be extended to other analytes of interest. In future work isotope dilution analysis with LA–ICP–MS will be used as microlocal analytical technique for multielement determination in thin layers or nanowires of high-purity platinum and palladium nanoclusters.

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References

[1] R. Wahl, M. Mertig, J. Raff, S. Selenska-Pobell, W. Pompe, Adv. Mater. 13 (2001) 736.
[2] M. Mertig, R. Kirsch, W. Pompe, H. Engelhardt, Eur. Phys. D 9 (1999) 45.
[3] J. Richter, Physica E 16 (2003) 157.
[4] J.S. Becker, Spectrochim. Acta 57 (2002) 1805.
[5] J.S. Becker, H.-J. Dietze, Int. J. Mass Spectrom. 197 (2000) 1.
[6] J.S. Becker, R.S. Soman, Th. Becker, V. Panday, H.-J. Dietze, J. Anal. At. Spectrom. 13 (1998) 983.
[7] M. Van Straaten, K. Swenters, R. Gijbels, J. Verlinden, E. Addriaenssens, J. Anal. At. Spectrom. 9 (1994) 1389.
[8] S.F. Durrant, J. Anal. At. Spectrom. 14 (1999) 1385.
[9] 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 (2000) 87.
[10] D. Günther, H. Cousin, B. Magyar, I. Leopold, J. Anal. At. Spectrom. 12 (1997) 165.
[11] J.J. Leach, L.A. Allen, D.B. Aeschliman, R.S. Houk, Anal. Chem. 71 (1999) 440.
[12] J.S. Becker, C. Pickhardt, H.-J. Dietze, J. Anal. At. Spectrom. 16 (2001) 603.
[13] C. Pickhardt, J.S. Becker, H.-J. Dietze, Fresenius J. Anal. Chem. 368 (2000) 173.
[14] S.F. Boulyga, C. Pickhardt, J.S. Becker, At. Spectrosc. 25 (2004) 53.
[15] N.H. Bings, J. Anal. At. Spectrom. 17 (2002) 759.
[16] K.G. Heumann, in: F. Adams, R. Gijbels, R. Van Griecken (Eds.), Inorganic Mass Spectrometry, Wiley, 1988, p. 301.
[17] IUPAC, J. Anal. At. Spectrom. 14 (1999) 5N.
[18] K. Polec-Pawlak, D. Schaumloeffel, J. Szpunar, A. Prange, R. Lobinski, J. Anal. At. Spectrom. 17 (2002) 908.