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Determination of trace elements in high-purity platinum by laser ablation inductively coupled plasma mass spectrometry using solution calibration

J. Sabine Becker, Carola Pickhardt and Hans-Joachim Dietze

Central Department of Analytical Chemistry, Research Centre Juelich, D-52425 Juelich, Germany

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Multi-element trace analysis by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) of high-purity metals, semiconductors and insulators (*e.g.*, ceramics) is often limited by the lack of suitable standard reference materials (SRM) with the same matrix composition and also a lack of a significant number of certified trace element concentrations in the available SRMs. This paper describes a new and easy standard-free quantification strategy using solution-based calibration for the multi-element determination of trace impurities in high-purity platinum. For the mass spectrometric measurements, a quadrupole-based LA-ICP-MS instrument was coupled with an ultrasonic nebulizer (USN). Due to the lack of a high-purity blank platinum sample, quantification of the results of LA-ICP-MS measurements was carried out using the standard additions mode in solution-based calibration. In order to achieve matrix matching, the multi-element standard solutions (with different concentrations of analytes) were nebulized successively with a USN. Simultaneously the high-purity platinum target was ablated with a focused laser beam during solution calibration with the USN. The mass spectrometric method developed was validated using a platinum standard reference material (NIST SRM 681). The analytical results of the LA-ICP-MS of SRM 681 Platinum are in good agreement with the certified values. The relative standard deviation (RSD) of most elements ($n=3$) is between 2 and 10%. The proposed analysis method can be applied for other high-purity materials in a similar way, *e.g.*, for trace and ultratrace analysis of high-purity metals, semiconductors and insulators such as high-purity ceramics.

In the last 10 years—since the commercial introduction of laser ablation systems on the analytical market—laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has been gaining increasing importance. LA-ICP-MS is being developed for the sensitive trace analysis of solid samples in all fields of modern science and technology,[1,2] with most applications in geology and mineralogy[3–7] followed by environmental and biological research,[8,9] materials research for the characterization of high-purity materials,[10,11] glasses[12] and ceramics (including ceramic layers),[13,14] and for the determination of long-lived radio nuclides in non-conducting materials.[15,16]

In comparison to other powerful solid-state mass spectrometric techniques—such as spark source mass spectrometry (SSMS), laser ionization mass spectrometry (LIMS) and glow discharge mass spectrometry (GDMS)—for the determination of trace impurities in high-purity materials, LA-ICP-MS has the lowest detection limits in the ng g^{-1} and pg g^{-1} range.[1,15] As is well known, the lowest detection limits (down to pg L^{-1} concentration ranges and lower) were measured using ICP-MS on aqueous solutions. However, the detection limits in ICP-MS for high-purity solid samples are some orders of magnitude higher because of the dilution factor of the digested sample, the blank values of the chemicals used, and possible interferences by molecular ions.

Furthermore, a serious problem in LA-ICP-MS analysis of high-purity materials is the quantification of the analytical results, especially if no suitable standard reference material with the same or similar matrix composition and significant number of certified trace element concentrations is available. Without a suitable SRM, the semi-quantitative analysis by LA-ICP-MS of an unknown sample yields the major, minor and trace element composition very quickly with an error factor of an element concentration of 2 to 3 times. But such semi-quantitative results of LA-ICP-MS measurements are mostly not sufficient, because the users of high-purity materials (*e.g.*, the semiconductor industry) require accurate trace element concentrations. Therefore, for quantification of high-purity solid samples—if no standard reference material exists—we prepared matrix-matched synthetic laboratory standards from high-purity compounds doped with known concentrations of trace elements (*e.g.*, for GaAs[10] or for $La_{0.65}Sr_{0.3}MnO_3$ perovskites of solid oxide fuel cells[13,14]). For the analysis of solid high-purity platinum, a high-purity platinum powder (of 99.99% purity or better) should be available. Van Straaten *et al.*[17] described an analytical procedure for the direct analysis of platinum powder by GDMS where the relative sensitivity coefficients (RSC) of the elements of interest were determined on a platinum sample doped with impurities of several elements. The proposed preparation of synthetic laboratory standards and their characterization in connection with the quantification procedure is often the time-consuming step in solid-state mass spectrometry, and can lead to homogeneity problems.

In order to avoid the preparation of synthetic laboratory standards, different calibration techniques, using aqueous standard solutions, are the methods of choice.[18–20] Recently we proposed an easy solution-based calibration procedure, where the laser ablation chamber is directly coupled with an ultrasonic nebulizer (USN).[20] This procedure was applied for the trace analysis of geological samples fused with lithium borate. The solution calibration was performed by nebulization of the standard solutions with a USN. During solution calibration a lithium borate blank target is simultaneously ablated with a focused laser beam. The geological samples fused with lithium borate were measured under the same

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experimental conditions, where a 2% nitric acid solution is nebulized with the USN.[20]

Such a procedure could be applied for the determination of trace and ultratrace elements in high-purity materials if high-purity blank samples with the same matrix composition are available. If no high-purity blank material is available then the standard additions technique, which is well known in solution calibration, using a USN for the sensitive nebulization of aqueous standard solutions with different analyte concentrations could be applied. This technique would allow easy trace element analysis of difficult-to-dissolve high-purity noble metals.

The aim of this work is to apply LA-ICP-MS for the determination of trace elements in high-purity platinum using solution-based calibration with the standard additions technique.

Experimental

Instrumentation

In these experiments the laser ablation chamber is coupled to the inductively coupled plasma ion source mass spectrometer (ELAN 6000, Perkin-Elmer, SCIEX Corp., Norwalk, CT, USA). Fig. 1 shows the experimental arrangement for solution-based calibration in LA-ICP-MS using a commercial laser ablation system (CETAC LSX 200, Cetac Technologies, Omaha, NE, USA).[20] The UV wavelength of a Nd : YAG laser (4th harmonic, 266 nm) is used for laser ablation. The experimental parameters of laser ablation and mass spectrometric measurements are summarized in Table 1. Optimization of the rf power of the ICP, nebulizer gas flow rate for the USN, or carrier gas flow rate for laser ablation was carried out separately for both sample introduction systems (during optimization of the laser ablation parameters a platinum target was ablated and 2% nitric acid was nebulized simultaneously; when the experimental parameters for the ultrasonic nebulization were optimized a 1 µg L^{-1} standard solution was nebulized and the platinum target was ablated in order to perform matrix matching) and yielded the same values. The experimental parameters were optimized in order to achieve maximum ion intensity of ^{103}Rh$^+$ during laser ablation and ^{140}Ce$^+$ when using the USN. The mass spectrometric measurements were carried out at low mass resolution ($m/\Delta m \approx 300$).

No sample preparation is required before the trace analysis on compact high-purity platinum metals. Only the contamination on sample surfaces is removed by chemical etching.

Samples

A standard reference material of platinum metal (NIST SRM 681) was used to validate the accuracy of the developed solution-based calibration technique in the standard addition mode. Furthermore, the SRM 681 was used as a standard for a one-point calibration. Platinum (isotope ^{192}Pt was measured which led to 7×10^7 counts s^{-1} using the dual detector mode) was chosen as the internal standard element in order to correct for differences in the amount of ablated material.

Table 1 Experimental parameters of LA-ICP-QMS

Elan 6000 ICP-MS	
Rf power	1000 W
Coolant gas flow rate	14 L min^{-1}
Auxiliary gas flow rate	0.8 L min^{-1}
Carrier gas flow rate	0.78 L min^{-1}
Mass resolution $m/\Delta m$	300
Acquisition mode	Peak hopping
Detector mode	Dual
Auto lens	On
Points per peak	1
Dwell time	10 ms
No. of sweeps	5
No. of readings	1
No. of replicates	6
Sampling cone	Nickel with a 1.1 mm orifice
Skimmer cone	Nickel with a 0.9 mm orifice
Laser ablation	
Laser ablation system	CETAC LSX-200
Wavelength	266 nm (4th harmonic of Nd : YAG laser)
Pulse duration	5 ns
Repetition frequency	20 Hz
Pulse energy	5 mJ
Laser power density	1.4×10^9 W cm^{-2}
Spot diameter	300 µm
Pre-ablation time	40 s
Method	Single line scan
Ultrasonic nebulizer	
Sample uptake rate	2 mL min^{-1}
Heater temperature	140 °C
Cooler temperature	3 °C

Trace element concentrations determined using NIST SRM 681 can be used to validate results obtained by the LA-ICP-MS method with solution-based calibration.

Solution-based calibration procedure

In order to quantify analytical results of LA-ICP-MS, the standard additions mode is used. For the mass spectrometric measurements, a quadrupole-based LA-ICP-MS instrument is coupled with an ultrasonic nebulizer (U-6000AT, Cetac Technologies, Omaha, NE, USA). In order to arrange matrix matching, the multi-element standard solutions (with different concentrations from 0.01 to 3.5 µg L^{-1} of 50 analytes for each element in order to determine a suitable calibration range) are nebulized successively with a USN. Simultaneously the high-purity platinum target is ablated with a focused laser beam during solution calibration with the USN. The calibration curves for Ir and Pb in the platinum matrix are shown in Fig. 2. The correlation coefficient is better than 0.99 for all elements investigated. Differences of sensitivity in LA-ICP-MS and ICP-MS were corrected using Cu as the internal standard element, as described in detail elsewhere.[20] Calibration curves were also measured for the internal standard element Cu. In

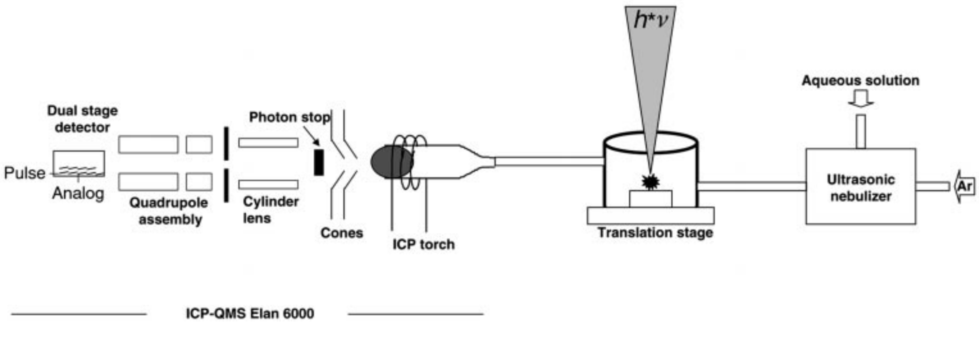

Fig. 1 Experimental arrangement of solution based calibration using a USN in LA-ICP-QMS.

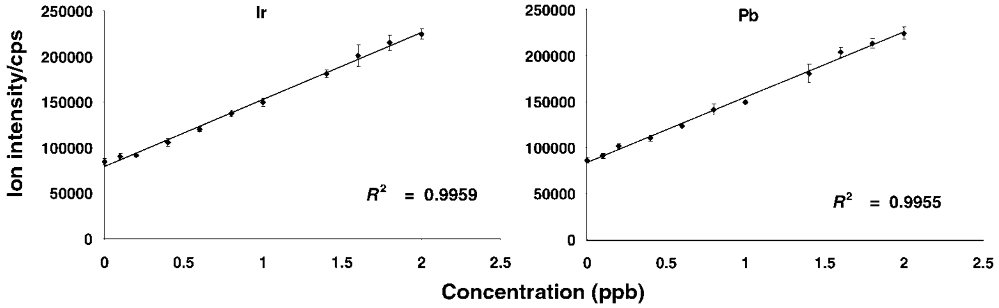

Fig. 2 Calibration curves for Ir and Pb in a platinum matrix (SRM 681) measured by LA-ICP-MS with solution-based calibration (standard additions mode).

Fig. 3 the calibration curve is given for Cu, obtained using the high purity platinum sample in the standard additions mode.

Results and discussion

In Fig. 4, the different ion intensities for $^{85}Rb^+$, $^{88}Sr^+$ and $^{140}Ce^+$ in ICP-MS are demonstrated without and with the laser ablation of the platinum target. In this experiment a 1 μg L^{-1} standard solution was nebulized and, after 100 s, the laser ablation of a platinum target (Rb, Sr and Ce concentration in this platinum sample are not detectable with LA-ICP-MS, so changes in measured intensities are only caused by matrix effects) started. The intensities for all analyte ions decrease if the laser ablation of the high-purity platinum sample is started, *e.g.*, by a factor of 3.9 for Rb, 3.8 for Sr and 2.2 for Ce. The loss of sensitivity is different for each element and therefore no internal standard element can be used to correct for these matrix effects. Therefore, matrix matching must be performed during the measurement of the standard solutions.

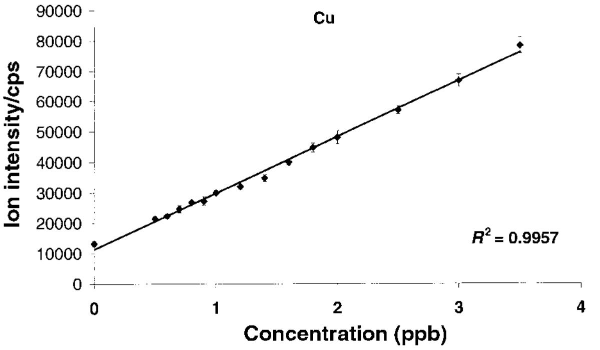

Fig. 3 Calibration curve for internal standard element Cu in a platinum matrix (high purity platinum sample) obtained by solution based calibration (standard additions mode) in LA-ICP-MS.

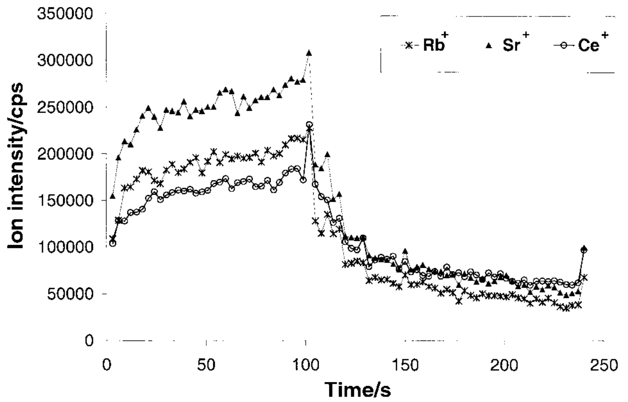

Fig. 4 Ion intensity for $^{85}Rb^+$, $^{88}Sr^+$ and $^{140}Ce^+$ in ICP-MS without and with the laser ablation of the platinum target (1 ng g^{-1} standard solution was nebulized using a USN, after 100 s the laser ablation of platinum started).

For the quantification of LA-ICP-MS results, with respect to the determination of trace elements in high-purity platinum metal, the quite different element sensitivities in LA-ICP-MS for platinum metal and the ICP-MS analysis of aqueous calibration solutions (using USN for solution introduction) listed in Table 2 must be considered using the standard addition mode. A further advantage of this proposed calibration is a nearly ideal mixing of ablated Pt material with the ultrasonic nebulized standard solution for calibration, which is transported by the argon nebulizer gas into the laser ablation chamber and is more completely compared to the mixing in a Y-piece.[19]

In Table 3 the results of the trace analysis of a platinum standard reference material (SRM 681) by LA-ICP-MS with solution-based calibration are compared with the certified concentrations. Only 12 elements in the medium and higher mass range are certified with concentration values from three noble metals (Rh, Pd and Ir). Cu is used as the internal standard element. The relative standard deviation of the measured element concentration in the low μg g^{-1} concentration range by solution-based calibration is about 5%. Considering the standard deviation of certified values (for the marked elements no standard deviation is given) and of measured concentrations the agreement of the data is good.

The experimentally determined detection limits (using the gas blank, due to the lack of a platinum blank target with higher purity compared to the sample) in LA-ICP-MS using an ELAN 6000 are summarized in Table 4. The detection limits using the 3σ criteria (the limit of detection is given by $m_b + 3\sigma_b$, where m_b is the mean value of the blank measurements and σ_b is the standard deviation of five independent measurements of the blank value) for the gas blank are in the ng g^{-1} range

Table 2 Sensitivity of selected elements (isotope corrected) in LA- ICP-MS and ICP-MS

	LA-ICP-MS of platinum SRM 681/kHz ppm^{-1}		ICP-MS^a/MHz ppm^{-1}
Element	With nebulization 2% nitric acid	Without nebulization	Nebulization of 1 μg L^{-1} standard solution
Cu	6	3.6	130
Zr	11	8.4	260
Rh	13	9.4	280
Ag	14	7.8	190
Pd	14	9.6	250
Ir	14	19	300
Pb	15	20	340

[a] Using USN for solution introduction.

Table 3 Results of trace analysis on a platinum standard reference material (NIST SRM 681) by LA-ICP-MS with solution-based calibration; Cu, internal standard element

	Concentration/μg g^{-1}	
Element	LA-ICP-MS	Certified value
Zr	9.7±0.5	11[a]
Rh	8.3±0.4	9[a]
Ag	1.93±0.10	2.0±0.5
Pd	5.7±0.3	6±1
Ir	11.1±0.6	11[a]
Pb	13±0.8	12±2

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

Table 4 Detection limit in platinum (μg g^{-1}), relative standard deviation (RSD, %) and accuracy of trace element determination in high-purity platinum and analysis time (h) for LA-ICP-MS and GDMS

Element	LA-ICP-MS	GDMS (ref. 17)
Co	0.05	nd
Ni	0.09	nd
Cu	0.04	0.009
Zr	0.01	nd
Ru	0.04	nd
Rh	0.003	0.006
Ag	0.002	0.01
Pd	0.003	0.005
In	0.03	nd
Sn	0.2	nd
Hf	0.006	nd
Ir	0.001	0.03
Pb	0.003	1
U	0.003	nd
RSD (%)	5	5–10
Accuracy (%)	<8[a]	<15
Analysis time/h	≈1	≈2

[a] For Zr<12%.

Table 5 Results of trace analysis on a high-purity platinum sample by LA-ICP-MS with solution-based calibration and one-point calibration using RSCs determined on NIST SRM 681

	Concentration/μg g^{-1}	
Element	Solution calibration	Calibration using SRM 681
Co	1.2±0.1	[a]
Ni	9.8±0.9	9.7±0.1
Cu	Internal standard element	17±0.5
Zr	1.8±0.2	1.4±0.2
Ru	3.2±0.3	[a]
Ag	10.0±1.0	9.7±0.7
In	2.5±0.2	[a]
Sn	3.1±0.3	[a]
Hf	0.51±0.05	[a]
Ir	13.6±1.2	18.3±0.8
U	0.23±0.02	[a]

[a] Non-certified in NIST SRM 681.

(varying from 1 ng g^{-1} for Ir to 200 ng g^{-1} for Sn). The detection limits and the accuracy of analytical results in LA-ICP-MS are mostly better than in GDMS[17] (except Cu). In general lower detection limits would be expected for the high-purity platinum by the application of the more sensitive LA-ICP-MS, using a double-focusing sector field instrument. The detection limits measured in this work by LA-ICP-MS using the ELAN 6000 are sufficient for the trace analysis of the investigated high-purity platinum samples (of 99.995% purity).

The results of trace element determination on a high-purity platinum sample using two different calibration procedures (by solution-based calibration with standard additions and by one-point calibration using SRM 681) are summarized in Table 5. Due to the limited number of elements for which the concentrations are certified in the platinum SRM 681, only a few elements can be determined. For these elements the results agree with those of solution calibration, except for Ir due to a possible inhomogeneous distribution of this noble element in platinum. The proposed technique which was developed for high-purity platinum allowed an easy trace analysis of difficult-to-dissolve high-purity metals.

Conclusions

Solution calibration in LA-ICP-MS is a possibility for a rapid and easy standard-free quantification strategy, especially if no suitable standard reference material with the same matrix composition exists or only certified reference materials with a lack of a significant number of certified trace element concentrations is available. Using a single gas flow (USN is directly coupled to the laser ablation cell), measurements can be carried out with optimised carrier and nebulizer gas flow rates. The accuracy of the analytical results using the standard additions mode in a solution-based calibration (due to lack of high-purity blank platinum sample) was improved by matrix matching. In future work this new strategy of solution calibration together with the isotope dilution technique will be applied.

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