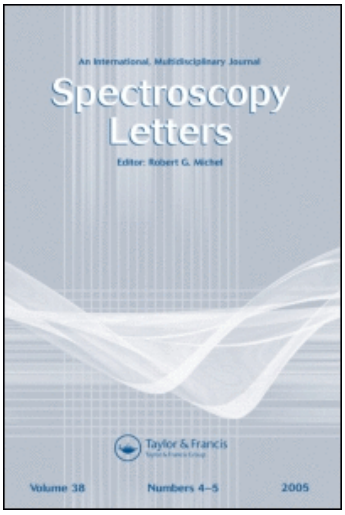

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Determination of Trace Elements in High-Purity Palladium by Inductively Coupled Plasma Mass Spectrometry Using an Internal Standard Method

Anding Zhang[a]; Xiangsheng Liu[b]
[a] Scientific Design Company, Little Ferry, New Jersey, USA [b] Beijing General Research Institute for Non-Ferrous Metals, Beijing, People's Republic of China

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Determination of Trace Elements in High-Purity Palladium by Inductively Coupled Plasma Mass Spectrometry Using an Internal Standard Method

Anding Zhang
Scientific Design Company, Little Ferry, New Jersey, USA

Xiangsheng Liu
Beijing General Research Institute for Non-Ferrous Metals, Beijing, People's Republic of China

Abstract: Method validation of inductively coupled plasma mass spectrometry analyses for trace impurities in high-purity materials is often limited not only by the lack of suitable reference materials with the same matrix composition but also by the lack of a significant number of certified trace element concentrations in the available reference materials. This paper demonstrates a new and simple method for the direct determination of 44 trace elements in high-purity palladium using inductively coupled plasma mass spectrometry and an internal standard method. Sc and In were employed as internal standards to effectively eliminate nonspectral interferences from the Pd matrix. The detection limits of the 44 trace impurities were from 0.00078 to 0.46 μg/mL and the relative standard deviations ($n = 6$) were below 3.5%. The method was further validated using a palladium standard material (Aldrich palladium standard material, CAS no. 7440053). The analytical results are in good agreement with the certified values.

Keywords: High-purity palladium, inductively coupled plasma mass spectrometry, internal standard method, trace impurities

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Address correspondence to Anding Zhang, Scientific Design Company, 49 Industrial Avenue, Little Ferry, NJ 07643, USA. E-mail: azhang@scidesign.com

INTRODUCTION

Palladium is an important noble metal and is widely used in the fields of catalysis, "green" energy (hydrogen separation and storage), electrical engineering, dentistry, and as an antitumor agent. Palladium of higher purity is demanded along with the expansion of its application. The presence of trace impurities in the high-purity palladium could significantly affect its physical and chemical proprieties. Thus, accurate determination of the impurities in a high-purity palladium sample is of great importance to major industrial sectors and the biomedical community.

Traditional techniques for the determination of trace impurities in metals are neutron activation analysis (NAA),[1] inductively coupled plasma optical emission spectrometry (ICP-OES),[2,3] glow discharge-mass spectrometry (GD-MS),[4] and so forth. However, among these techniques, NAA is very time-consuming and the limits of detection (LODs) of ICP-OES for certain rare earth and noble metal impurities are not low enough for ultratrace analysis. GD-MS is a well established technique for bulk solids analysis. Due to inherently short ablation time, the user is often limited in the number of elements that can be effectively monitored for a single run.

Inductively coupled plasma mass spectrometry (ICP-MS) has the advantages of high sensitivity, high speed, and low LODs. ICP-MS has already been used for determination of trace impurities in high-purity lead,[5] gold,[6] rhenium,[7] noble metals,[8] zinc,[9] cerium oxide,[10] and copper.[11] In this work, we have established a method of direct determination of 44 trace elements in high-purity palladium by ICP-MS using internal standard method.

MATERIALS AND METHODS

Instrument and Operating Parameters

A Perkin-Elmer Sciex Elan Model 5000 quadrupole ICP-MS (Perkin-Elmer, CT, USA) with a concentric nebulizer was used. Its operating parameters were optimized by univariate method (optimize one parameter while fixing all other parameters), and the optimal operating parameters are as follows. ICP source parameters: forward power is 1.0 kW; cooling gas flow is 12 L/min (15 L/min for torch ignition); auxiliary gas flow is 0.8 L/min; nebulizer gas flow is 0.96 L/min; sample uptake rate is 1.0 mL/min. Interface parameters: sampling position is 15 mm (from sampler cone orifice to coil); sampler cone (Ni) orifice diameter is 1.14 mm; skimmer cone (Ni) orifice diameter is 0.89 mm; dynamic pressure is about 140 Pa. Mass spectrometer parameters: dynamic pressure is 1×10^{-3} to 3×10^{-3} Pa; ETP potential is -2900 V; ion lens settings are B46, $E_1$17, P48, $S_2$47. Measurement parameters: resolution (10% peak height) is 0.8 ± 0.1 amu; scanning mode is element; measurement time is 0.3 s; measurements/peak is 3; repeat is 3.

Materials and Preparation of Standard Solutions

Standard solutions: Each individual element's primary stock solution is prepared at concentration of 1 mg/mL using its spectroscopy grade oxide. Then they were mixed and diluted so that each of the elements has a concentration of 100 μg/L as secondary stock solution, which was further diluted to make the final standard solution. Two milliliters of 49% HF solution was added in the secondary stock solution to ensure the stability of certain elements. Matrix solution: Pd solution (concentration of 2 mg/mL) was used as stock solution. Internal standard solutions: Internal standard stock solution was made so that each candidate internal standard element of Sc, In, Cs, Re, and Tl has a concentration of 100 μg/mL. All water used was HPLC grade. All reagents used were spectroscopy grade. All solutions have 2% HNO_3 (v/v).

Palladium Standard Material Sample Preparation

The palladium standard material used is the Aldrich palladium (product no. 203939, powder, 99.999%, MDL no. MFCD00011167, CAS no. 7440053). Six parallel digestions of the Pd powder were done. In each sample preparation, 10.00 mg of the Pd powder was weighed and put into a 25-mL beaker. Aqua regia, 2 mL, was added to the beaker to dissolve the sample at low temperature (the beaker was put into an ice bath). After dissolution, 2 drops of 49% HF solution was added to the sample solution. The completely transparent solution without residue ensures the completeness of the digestion. The fully dissolved solution was quantitatively transferred into a 10 mL volumetric tube and internal standard solution was also added, and finally the 10 mL volumetric tube was filled to the mark with water. The final sample solution has a palladium concentration of 1 mg/mL and each of internal standards has concentration of 50 μg/L.

RESULTS AND DISCUSSION

Isotope Selection and Spectral Interference

Spectral interferences always exist during ICP-MS analysis of high-purity materials. Spectral interferences could be summarized as follows: (1) isobaric interferences, which can be found in natural isotope fractional abundance table (e.g., Pd to ^{104}Ru and ^{110}Cd); (2) background atomic and molecular species (Ar^+, Ar_2^+) from the plasma gas; (3) air and impurities (O^+, O_2^+, CO_2^+, CO^+, N_2^+, N^+) in the carrier gas; (4) acids used for sample preparation, such as Cl^+, H_3O^+, NOH^+; (5) combinations of above, such as ArO^+, ArH^+, ArN^+, $ArOH^+$, $ArCl^+$, ClO^+; (6) combinations of sample matrix ion with above. The spectral interference of isotope of one element on isotope of

another element could be identified and calculated from natural isotope abundance table, and it is possible to eliminate most of those interferences by selecting appropriate isotopes for analysis. The selected analyte isotopes are listed as the first column of Table 1.

Table 1. A comparison of three different methods (μg/g)

Determined isotopes	Internal standard method	Matrix match method	Standard addition method
^{89}Y	5.5	5.3	5.1
^{139}La	4.5	5.1	4.9
^{140}Ce	5.0	5.3	5.6
^{141}Pr	4.7	4.9	5.7
^{146}Nd	4.4	5.4	5.6
^{147}Sm	4.9	5.1	5.6
^{153}Eu	4.3	5.4	5.2
^{157}Gd	4.8	5.4	5.8
^{159}Tb	4.8	5.5	5.4
^{163}Dy	4.8	5.9	5.0
^{165}Ho	4.9	5.7	5.2
^{166}Er	5.1	5.2	5.5
^{169}Tm	4.8	5.7	5.8
^{172}Yb	5.3	5.6	5.4
^{175}Lu	4.8	4.2	5.0
^{7}Li	5.0	5.6	5.2
^{9}Be	4.1	5.0	5.5
^{11}B	4.6	4.8	4.8
^{52}Cr	5.1	4.9	5.2
^{55}Mn	5.0	5.2	5.3
^{60}Ni	5.0	5.2	5.4
^{59}Co	5.2	5.6	5.6
^{63}Cu	5.8	4.4	5.6
^{72}Ge	5.4	5.0	5.1
^{88}Sr	5.1	4.9	5.1
^{111}Cd	4.5	5.5	6.1
^{118}Sn	4.5	4.9	5.6
^{121}Sb	4.5	5.3	5.2
^{137}Ba	4.4	4.8	5.7
^{208}Pb	5.0	5.2	4.9
^{209}Bi	4.7	4.8	4.8
^{47}Ti	5.8	5.8	5.0
^{90}Zr	5.2	5.2	5.4
^{93}Nb	4.9	4.2	5.2
^{95}Mo	4.6	5.4	5.1

(*continued*)

Table 1. Continued

Determined isotopes	Internal standard method	Matrix match method	Standard addition method
^{178}Hf	5.0	5.1	5.1
^{181}Ta	5.1	4.9	5.0
^{182}W	4.9	5.1	5.1
^{101}Ru	5.7	5.6	5.4
^{103}Rh	4.4	4.2	5.4
^{189}Os	5.4	5.4	5.7
^{193}Ir	4.8	5.0	5.0
^{195}Pt	5.3	4.6	4.7
^{197}Au	5.0	4.9	5.9

All analytes have a concentration of 5.0 μg/g. Data are the average of three replicates. Uncertainties are all within ±3%.

Matrix Effect

The palladium matrix and the 20% aqua regia will suppress the signal of impurities and the higher the matrix concentration, the stronger suppression will be expected. When Pd matrix has a concentration of 1 mg/mL, the signal of impurities dropped to about 10% to 40%. Matrix separation is an effective way of eliminating matrix effect, but it is time-consuming and contamination-prone. Thus, a simple method for rapid direct determination is preferred. Internal standard method can effectively overcome matrix effect.[6] Our preliminary experiments have shown that all candidate internal standards (Sc, In, Cs, Re, and Tl) can reduce the Pd matrix effect to some extent, among them In gave the best recoveries for rare earth elements and Sc gave the best recoveries for all the other elements. Thus, in further experiments, In and Sc were used as internal standards for rare earth elements and the other elements, respectively. In matrix match method, all calibration samples were made so that they have the same matrix concentration as the analytes. In standard addition method, known amounts of standard were added in the analyte solutions to create a calibration and to calculate the analyte concentration by a simple linear least squares analysis. Table 1 is a comparison of several different methods for matrix effect correction. It may be seen from this table that internal standard method is an effective way to overcome matrix effect. In addition, matrix match method is often hard to apply for high-purity material analysis, because matrix matched material is not easily available. Also, standard addition method is very tedious if done by hand. From our study of internal standard concentration, the internal standard concentration between 30 to 500 μg/L can effectively compensate the matrix effect.

Internal standards of 50 μg/L were used in further study, because high concentration of internal standard could bring extra interference.

LOD, Precision, and Recovery

LOD is the minimum concentration of an analyte that an analytical process can reliably detect. Due to good stability of blank and calibration curve, reagent blank can be used as true blank to estimate the detection limits.[12] Recovery experiment was performed to validate the accuracy of the internal standard method. It was found that when Pd matrix concentration is 1 mg/mL, the recoveries are between 85% to 128% and the relative standard deviations (RSDs) are between 0.83% to 3.5% for all 44 impurities by using Sc and In as internal standards. LODs, RSDs, and recoveries of 44 impurity elements are listed in Table 2.

Table 2. LODs (3σ) of the impurity elements and RSDs (six replicates) and recoveries of standard addition method

Isotopes	LODs (μg/L)	Added (μg/L)	Detected (μg/L)	Recovery (%)	RSD (%)
^{89}Y	0.0045	5	4.66	93.2	0.85
^{139}La	0.0085	5	4.43	88.6	0.94
^{140}Ce	0.0020	5	5.14	102.8	0.83
^{141}Pr	0.0056	5	5.22	104.4	1.4
^{146}Nd	0.0016	5	5.32	106.4	0.97
^{147}Sm	0.0057	5	4.81	96.2	1.1
^{153}Eu	0.0091	5	4.50	90	0.96
^{157}Gd	0.0014	5	5.06	101.2	1.4
^{159}Tb	0.0066	5	5.35	107	1.1
^{163}Dy	0.0021	5	4.97	99.4	0.86
^{165}Ho	0.0035	5	5.41	108.2	1.3
^{166}Er	0.00078	5	5.68	113.6	1.6
^{169}Tm	0.0071	5	5.55	111	1.1
^{172}Yb	0.0073	5	5.53	110.6	1.2
^{175}Lu	0.0010	5	5.19	103.8	1.8
^{7}Li	0.048	5	4.95	99	1.6
^{9}Be	0.065	5	4.32	86.4	2.3
^{11}B	0.052	5	6.40	128	3.5
^{52}Cr	0.044	5	4.25	85	1.6
^{55}Mn	0.060	5	4.36	87.2	1.1
^{60}Ni	0.055	5	4.25	85	0.92

(*continued*)

Table 2. Continued

Isotopes	LODs (μg/L)	Added (μg/L)	Detected (μg/L)	Recovery (%)	RSD (%)
^{59}Co	0.0092	5	4.83	96.6	1.4
^{63}Cu	0.033	5	4.86	97.2	1.1
^{72}Ge	0.039	5	5.73	114.6	1.2
^{88}Sr	0.0013	5	5.97	119.4	2.6
^{111}Cd	0.050	5	5.05	101	2.0
^{118}Sn	0.46	5	5.29	105.8	2.0
^{121}Sb	0.0083	5	4.69	93.8	1.8
^{137}Ba	0.0078	5	5.03	100.6	1.7
^{208}Pb	0.050	5	4.63	92.6	2.5
^{209}Bi	0.010	5	4.44	88.8	0.89
^{47}Ti	0.037	5	4.99	99.8	2.1
^{90}Zr	0.043	5	5.20	104	1.3
^{93}Nb	0.0026	5	5.84	116.8	2.8
^{95}Mo	0.042	5	4.31	86.2	1.3
^{178}Hf	0.0015	5	5.36	107.2	1.8
^{181}Ta	0.083	5	4.92	98.4	0.94
^{182}W	0.092	5	4.48	89.6	1.7
^{101}Ru	0.0027	5	4.56	91.2	1.5
^{103}Rh	0.0010	5	5.24	104.8	1.7
^{189}Os	0.064	5	4.66	93.2	0.85
^{193}Ir	0.0049	5	4.99	99.8	1.5
^{195}Pt	0.0050	5	5.67	113.4	1.6
^{197}Au	0.0070	5	4.97	99.4	1.0

LODs, limits of detection; RSD, relative standard deviation.

Palladium Standard Analysis

The availability of certified reference materials is of great value for laboratories engaged in analytical chemistry. For palladium analysis, there are only few international standard reference materials, which are directly traceable to a standard reference material of the U.S. National Institute of Standards and Technology. For example, single-element atomic absorption spectroscopy (AAS) standards are offered at 1 mg/mL by Aldrich or can be prepared according to APHA et al.[13] To our knowledge, interlaboratory comparison programs for the determination of environmental palladium are not yet available. Our ICP-MS results are in good agreement with the recommended values reported from Aldrich (see Table 3). Some impurities that do not have Aldrich values were determinated by ICP-MS as well. The analysis of the palladium standard further validates the accuracy and the detection power of ICP-MS coupled with the internal standard method.

Table 3. ICP-MS results (average of six independent sample preparations), standard deviation of the ICP-MS results, and the certified values of the Pd standard material from Aldrich (mg/kg, or ppm)

Element	ICP-MS	Standard deviation	Certified values (Aldrich)
Cu	0.4	± 0.01	N/A
Ge	0.19	± 0.01	N/A
Zr	0.2	± 0.02	N/A
Mn	0.7	± 0.03	0.3
Nb	0.04	± 0.002	N/A
Ta	0.06	± 0.002	N/A
W	0.1	± 0.01	N/A
Ru	2.3	± 0.07	N/A
Pt	3.8	± 0.1	4.1
Au	0.4	± 0.02	N/A

Results for all other impurity elements are lower than LOD of our inductively coupled plasma optical emission spectrometry (ICP-MS). It is also mentioned by Aldrich that this standard material has 20 ppm (maximum) total metallic impurities.

CONCLUSIONS

Direct determination of 44 trace impurities in high-purity palladium was achieved by ICP-MS using Sc and In as internal standard elements. LODs are $0.00078 \sim 0.46$ μg/L. Recoveries are $85 \sim 128\%$. Relative standard deviations are $0.83 \sim 3.5\%$. This method only requires 10 mg of sample, and the analysis time for each sample is about 3 minutes. The method was also validated using a palladium standard from Aldrich.

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