Determination of Trace Impurities in High-Purity Cadmium by High-Resolution Inductively Coupled Plasma Mass Spectrometry

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Trace impurities in high-purity cadmium were determined by high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS). To overcome some potentially problematic spectral interference, measurements were acquired in both medium and high-resolution modes. The matrix effects due to the presence of excess HCl and cadmium were evaluated. The optimum conditions for the determination were tested in this experiment and discussed. The detection limits ranged from 0.01 to 0.27 $\mu\text{g g}^{-1}$, depending on the elements. The results for the determination of 22 trace elements in high-purity cadmium are presented.

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The industrial and technical importance of high-purity cadmium has increased in recent years with the development of new techniques that require high-purity materials.¹ The determination of trace impurities in high purity cadmium is important because of their adverse effects on the quality of the final cadmium products. Thus, an analytical method is required, which achieves high accuracy, low detection limits and multi-element capability, even for the determination of trace impurities in the low ng g^{-1} range. Although there are some widely used methods for multi-elemental quantification that are based on inductively coupled plasma quadrupole mass spectrometry (ICP-QMS), or glow-discharge quadrupole mass spectrometry (GD-QMS),^{2,3} these often require considerable corrections for spectral interference in mass from other elements and poly-atomic molecules. High-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) provides several analytical advantages over ICP-QMS, which include: higher sensitivity resulting from higher transmission efficiency of ions passing through a mass spectrometer; reduced spectral interference problems owing to high resolution up to $m/\Delta m = 10000$. On the other hand, an analytical problem due to non-spectral interference, where analyte signals are suppressed or enhanced by matrix elements, remains unsolved, even in HR-ICP-MS.⁴

Since the matrix effects for ICP-MS were more serious than those for ICP-AES, many studies were reported in detail. Various mechanisms of matrix effects were proposed for ICP-QMS.^{5,6} However, only in a few HR-ICP-MS studies, were the matrix effects investigated.^{7,8} For high-purity cadmium, reports on the matrix effects for HR-ICP-MS were not found in the literature.

In the present work, using HR-ICP-MS, the matrix effects due to the HCl and Cd were examined. The trace elements (Be, Mg, Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Mo, Sn, Sb, Ba, Ce, Nd, Sm and Pb) in several high-purity cadmium samples were determined without matrix separation.

Experimental

Instrumentation

HR-ICP-MS of the Micromass Plasma Trace 2 (Micromass Ltd., Manchester, England) was used for the determination of trace elements. The instrument can be operated in a low-resolution mode (LRM, $m/\Delta m$ is about 600), a medium mode (MRM, $m/\Delta m$ is about 4000) and a high resolution mode (HRM, $m/\Delta m$ is about 9500). For a comparison of the analytical results, A HP4500 series300 ICP-MS (Hewlett Packard, USA) was used. Typical operating conditions for the HR-ICP-MS are listed in Table 1.

A 600 W microwave oven (Model MK-S, Xinke Institute of Applied Microwave Technology, Shanghai, China) was used for sample digestion.

Standards and reagents

All reagents used were prepared from analytical-grade/specpure chemicals (National Standards of China). Ultrapure water (specific resistance above 18.0 $\text{M}\Omega \text{ cm}^{-1}$) from a Milli-Q deionization unit (Millipore, Milli-Q SP) was used throughout

Table 1 Instrumental condition for the HR-ICP-MS

Operating condition	Parameter
Rf power	1350 W
Coolant gas flow	14.0 l min^{-1}
Auxiliary gas flow	0.6 – 0.8 l min^{-1}
Nebulizer gas flow	1.2 – 1.6 l min^{-1}
Sampling cone	Nickel
Skimmer cone	Nickel
Ion sampling depth	11 mm
Sample uptake rate	0.25 ml min^{-1}
Dwell time	20 ms
Accelerating voltage	6 kV
Resolution	400 – 10000
Scanning mode	Peak hopping transient
Ion lens setting	Maximum signal intensity

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Table 2 Isotopes of interest, mass resolution, some potential interferences and detection limits

Isotope	Resolution mode	Example problematic interferences	Detection limit/ $\mu\text{g g}^{-1}$	Blank test/ $\mu\text{g g}^{-1}$
^9Be	LRM	O^{++}	0.04	< 0.04
^{24}Mg	LRM	Ca^{++} , BN	0.11	< 0.11
^{27}Al	MRM	CN, BO, Fe^{++} , CNH	0.15	< 0.15
^{51}V	MRM	CIO, CIN, SOH, ArNH, ArB	0.02	< 0.02
^{52}Cr	MRM	ArC, CIOH, ArO, ArN, ArNH	0.27	< 0.27
^{55}Mn	HRM	Cd^{++} , Sn^{++} , ArO, CaO, KO, ArN, ArNH, CIOH	0.06	< 0.06
^{56}Fe	HRM	Cd^{++} , ArO, CaO	0.14	< 0.14
^{59}Co	MRM	ArOH, CaOH, CaO, NaAr	0.02	< 0.02
^{60}Ni	MRM	CaO, NaCl	0.16	< 0.16
^{63}Cu	MRM	TiO, ArAl, TiOH, ScO, NaAr, PO_2	0.09	< 0.09
^{64}Zn	MRM	S_2 , ArMg, SO_2 , TiO, TiOH, Ba^{++} , VO, CrO	0.23	0.51
^{69}Ga	MRM	ClO_2 , Ba^{++} , Ce^{++}	0.01	< 0.01
^{74}Ge	MRM	ArS, Ar_2 , Cl_2 , KCl, FeO, CaO_2 , Sm^{++} , Nd^{++}	0.02	< 0.02
^{75}As	HRM	CoO, ArCl, ArK, NiO, CaO_2 , Sm^{++} , Nd^{++}	0.17	< 0.17
^{98}Mo	LRM	ArFe, ArNi, BrOH, BrO	0.04	< 0.04
^{120}Sn	LRM	CdN	0.23	0.35
^{121}Sb	LRM	ArBr, CdNH	0.09	< 0.09
^{138}Ba	MRM	CdO_2	0.01	< 0.01
^{140}Ce	MRM	CdO_2 , CdN	0.01	< 0.01
^{142}Nd	MRM	CdO_2 , CdAr	0.01	< 0.01
^{152}Sm	HRM	CdAr, CdCl	0.02	< 0.02
^{208}Pb	LRM	OsO	0.04	0.12

the experiment.

Single-element calibration solutions were prepared from 1000 $\mu\text{g ml}^{-1}$ stock solutions of Be, Mg, Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Mo, Sn, Sb, Ba, Ce, Nd, Sm and Pb in 10% HNO_3 by dilution with ultrapure water. The same procedure was followed to prepare a working solution to be used as the internal standard for mass spectrometric determinations. Multi-element standard solutions were prepared from single-element standard solutions. These solutions were freshly prepared.

Purifications of HNO_3 and HCl were carried out by the recycled sub-boiling distillation of analytical-grade acid three times. Glass containers were used throughout the work, and were cleaned by immersion in concentrated HNO_3 and concentrated HCl overnight, then successively steamed with HNO_3 and water vapor for 8 h.

Analytical procedures

Microwave digestion was used for sample preparation. Two kinds of high-purity cadmium samples were analyzed in this work. A 0.5-g sample of cadmium was transferred into a PTFE vessel. Then, 5 mL of HCl was added to the sample and, after 3 min of irradiation at 600 W, the reactor was cooled and 5 mL of HNO_3 was added while carrying out the second step of digestion for 2 min at a power of 450 W. Upon cooling at room temperature, the vessels were opened and the sample was diluted to 100 mL. The solution was further diluted 10 times with ultrapure water so that the concentration of cadmium was about 500 mg l^{-1} ; the solution was then led into the HR-ICP-MS. Corresponding blanks were also prepared in the same way without any sample material.

Results and Discussion

Selection of isotopes and resolution

One of the key features of ICP-MS is the ease with which a sample can be analyzed qualitatively. Especially, for HR-ICP-MS, it is easy to distinguish the peaks of analyte ions from those

of polyatomic ions. An increase of the mass resolution leads to a reduction in the number of transmitted ions so that, as a consequence, the sensitivity is reduced to a certain extent. Therefore, to measure the trace impurities, we must use sufficient resolving power to separate the analyte ion peaks from the interfering polyatomic ion peaks, but not more. HRM was used for ^{55}Mn , ^{56}Fe , ^{75}As and ^{152}Sm . MRM was used for ^{27}Al , ^{51}V , ^{52}Cr , ^{59}Co , ^{60}Ni , ^{63}Cu , ^{64}Zn , ^{69}Ga , ^{74}Ge , ^{138}Ba , ^{140}Ce and ^{142}Nd . LRM was used for other isotopes. The measured peaks used to determine the contents in the samples were isotopes whose abundances were maximum, or isotopes that were not overlapped by the polyatomic or doubly charged ion peaks of the matrix elements and Ar.⁴ The determined isotopes are given in Table 2, along with the resolution used and some of the potentially problematic interferences.

Optimized sample digestion conditions

In the present work, we selected HCl + HNO_3 (1:1, v/v) as a media for the digestion of Cd samples for elemental analysis. The experimental results show that the acid concentrations (HCl- HNO_3 , v/v) in the range of 3 – 15% did not affect the final determination result. In a following experiment, the total acid concentration was chosen as 10%.

Operational parameters

Before each measuring procedure, all of the operational parameters were optimized in order to give the maximum signal intensity for the analyte elements. The ion intensity, which is actually recorded by the detection system, depends on several operational parameters, of which the sampling distance, lens voltages, the forward power of the generator, sample uptake rates and aerosol carrier gas flow rates are the most important.⁹ The ion peak intensities of ^{24}Mg , ^{55}Mn , ^{75}As , ^{138}Ba and ^{152}Sm were measured with the variation of the Rf power ranging from 1000 to 1450 W. The ion peak intensities of the five elements were increased with increasing the Rf power. However, a few of the ion peak intensities were larger at 1400 W. Therefore, we used an Rf power of 1350 W. The ion peak intensities were

Fig. 1 Recoveries of a multi-element standard ($5 \mu\text{g l}^{-1}$) from 5% and 10% cadmium solutions.

measured with the variation of the auxiliary gas-flow rate ranging from 0.6 to 0.8 l min^{-1} , and the nebulizer gas flow rate ranging from 1.2 to 1.6 l min^{-1} . In the variation of the ion sampling depth ranging from 9 to 12 mm, the ion peak intensities of the five elements were maximized at 11 mm. Details of the operating conditions are summarized in Table 1.

Matrix effects

To access the effects of high cadmium concentrations on the determination of trace elements by ICP-MS, we measured the ion peak intensities of the analyte elements influenced by the cadmium matrix of several cadmium concentrations between 0 and 100 mg l^{-1} . HCl was used for samples decomposition. The matrix effect of Cl was negligibly small.¹⁰ For the elements studied, it was found that the relative intensities gradually decreased with increasing cadmium concentration for all elements. We tried to correct the matrix effects using ^{89}Y , ^{103}Rh and ^{115}In , respectively. These elements were frequently used as internal standards for drift corrections in mass spectrometric measurements.^{11–14} The relative intensities of five elements gradually decreased with increasing in the Cd concentration. The optimum internal standard elements could not be found. The standard addition method was used for each sample throughout this work.

The recoveries of different multi-element standards in 5% and 10% cadmium solutions were determined (Fig. 1). With the exception of Cr, all analytes exhibited excellent recoveries of $> 90\%$ from the sample matrix. The major error in Cr determination in particulate samples was Cr loss, incurred through volatilization during sample digestion.¹⁵

Detection limits and blanks

The detection limit was estimated as the analyte concentration corresponding to three-times the standard deviation (3σ) of the blank signals obtained in the replicate measurements ($n = 10$). The detection limits for analyte elements and blank tests are given in Table 2. The detection limits obtained by HR-ICP-MS were below $0.1 \mu\text{g g}^{-1}$ for most elements. The results of blank tests for all of the elements were below the detection limits, except for Zn, Sn and Pb. It was clearly shown that the samples were treated without any significant contamination.

Analysis of the reference materials

In order to validate the HR-ICP-MS method, two reference materials, namely WYG-02, were analyzed. The analytical results for the WYG-02 samples together with certified values

Table 3 Analytical results of the reference materials

Analyte	Observed value/ $\mu\text{g g}^{-1}$	Certified value/ $\mu\text{g g}^{-1}$	RSD, %
Be	0.13	— ^a	2.1
Mg	0.19	0.18	1.6
Al	0.43	0.41	2.3
V	0.25	— ^a	3.9
Cr	0.68	0.72	1.7
Mn	0.25	0.23	2.2
Fe	0.32	0.34	0.9
Co	0.25	0.27	2.6
Ni	< 0.16	0.15	—
Cu	< 0.09	0.036	—
Zn	0.81	0.79	3.2
Ga	0.33	— ^a	2.5
Ge	0.27	0.26	1.1
As	< 0.17	0.045	—
Mo	0.25	— ^a	3.5
Sn	< 0.23	0.13	—
Sb	0.25	0.24	3.4
Ba	1.39	1.42	2.8
Ce	0.17	— ^a	1.6
Nd	0.20	— ^a	4.0
Sm	0.15	— ^a	3.1
Pb	0.81	0.78	1.2

a. —, Denotes no certified value.

All the found values obtained were an average of 5 replicated measurements.

are presented in Table 3.

Table 3 shows that for analyte elements the measured concentrations are in good agreement with the certified values. The RSD of the observed values were within 5%. These results indicate that the present method was precise enough to apply to the multi-element analysis of the high-purity cadmium samples.

Analysis of high purity cadmium

The results concerning the determination of the 22 trace elements in two kinds of high-purity cadmium samples are given in Table 4. Each result is the average of five sample determinations. For those elements that can be determined by ICP-AES, the results are shown in parenthesis. There was a reasonable agreement between the results obtained by both methods.

Sample A contained comparatively high concentrations of

Table 4 Analytical results for high-purity cadmium samples (concentration $\mu\text{g g}^{-1}$)

Element	Sample A ^a	Sample B ^a	Element	Sample A ^a	Sample B ^a
Be	< 0.04 (< 1.1)	0.23 ± 0.05 (< 1.1)	Ga	0.71 ± 0.09 (< 6.4)	1.12 ± 0.24 (< 6.4)
Mg	3.67 ± 0.12 (3.9)	1.61 ± 0.28 (1.57)	Ge	0.26 ± 0.06 (< 8.3)	0.35 ± 0.10 (< 8.3)
Al	0.33 ± 0.08 (< 0.4)	0.75 ± 0.06 (< 0.4)	As	0.84 ± 0.15 (< 16.8)	1.36 ± 0.05 (< 16.8)
V	0.16 ± 0.03 (< 0.9)	< 0.02 (< 0.9)	Mo	< 0.04 (< 4.3)	0.09 ± 0.02 (< 4.3)
Cr	1.27 ± 0.05 (1.33)	0.69 ± 0.14 (< 0.8)	Sn	0.49 ± 0.06 (< 35.6)	0.76 ± 0.16 (< 35.6)
Mn	0.16 ± 0.02 (< 0.3)	0.22 ± 0.03 (< 0.3)	Sb	1.67 ± 0.19 (< 42.9)	0.85 ± 0.31 (< 42.9)
Fe	1.93 ± 0.22 (2.15)	0.57 ± 0.07 (< 1.1)	Ba	0.92 ± 0.21 (1.10)	0.74 ± 0.10 (0.68)
Co	0.04 ± 0.01 (< 0.4)	0.09 ± 0.02 (< 0.4)	Ce	1.33 ± 0.84 (< 4.5)	0.28 ± 0.04 (< 4.5)
Ni	0.42 ± 0.09 (< 1.8)	1.16 ± 0.25 (< 1.8)	Nd	0.26 ± 0.03 (< 7.7)	0.41 ± 0.03 (< 7.7)
Cu	1.26 ± 0.18 (1.72)	0.92 ± 0.13 (1.01)	Sm	0.19 ± 0.05 (< 12.6)	0.12 ± 0.02 (< 12.6)
Zn	0.85 ± 0.07 (< 1.5)	1.45 ± 0.01 (< 1.5)	Pb	0.77 ± 0.06 (< 31.2)	0.76 ± 0.19 (< 31.2)

a. Mean of 5 measurements standard deviation; values in parentheses were obtained by ICP-AES.

Mg, Cr, Fe, Cu, Sb and Ce. The total concentration of impurities in sample A reported by the producer was less than $50 \mu\text{g g}^{-1}$. Our analytical results were consistent with this value. For sample B, the purity reported by the producer was more than 99.999% (< $10 \mu\text{g g}^{-1}$). However, in our results, more than $20 \mu\text{g g}^{-1}$ impurities were recognized in sample B. The purity of cadmium samples A and B was determined to be 99.995% and 99.998%, respectively.

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