Talanta 90 (2012) 57–62

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Determination of cadmium in food samples by ID-ICP-MS with solid phase extraction for eliminating spectral-interferences

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ARTICLE INFO

Article history:
Received 21 November 2011
Received in revised form
22 December 2011
Accepted 27 December 2011
Available online 2 January 2012

Keywords:
Cd
Spectral-interference
Solid phase extraction
ID-ICP-MS
Syringe driven chelating column
Certified reference material

ABSTRACT

A solid phase extraction (SPE) method using chelating resin was developed to separate Cd from spectral-interferences prior to the analysis of food samples by isotope-dilution inductively coupled plasma mass-spectrometry (ID-ICP-MS). Two syringe-driven chelating columns (SDCCs), Nobias Chelate PB-1M and InertSep ME-1, were investigated in the present experiment. The results of the pH dependence of Mo removal rates showed that separation of Cd and Mo could be obtained at pH conditions over 7. In addition, 0.6 mL of NH_4OH solution added into each 10 mL of digested sample solution (in 0.3 M HNO_3) followed by SPE was enough to remove the interfering elements, *i.e.* Mo, Zr, and Sn, in ID-ICP-MS analysis of Cd. Furthermore, it was found that InertSep ME-1 was more effective for separating Cd from the interfering elements, with removal rates approximately 100% for Mo, Zr, and Sn while the recovery of Cd was approximately 100%. The optimized SPE operations were as follows: 0.6 mL of NH_4OH was added into each 10 mL of digested sample solution; the sample solution was loaded into each pre-cleaned SDCCs at a flow rate of 5 mL min^{-1}; after 5 mL of ultrapure water was passed through the SDCC for washing, 2 mL of 0.3 M HNO_3 was passed through to elute Cd and the eluent was subjected to ICP-MS measurement. The present method was validated by analyzing five certified reference materials (CRMs) produced by the National Metrology Institute of Japan (NMIJ), and then was applied to a soybean powder sample.

1. Introduction

Cadmium is one of the hazardous heavy metals regulated by the World Health Organization (WHO) and the Food Agriculture Organization (FAO) [1]. Therefore, it is indispensable to inspect or monitor the concentration of Cd in various kinds of samples in relation to food and feed. Measurement of a certified reference material (CRM), with a similar composition to the sample, is one of the effective strategies for quality control in chemical analysis such as Cd measurement [2], since the reliability of measurement is one of the most important factors for the inspections related for food safety issues. In order to meet such a requirement, national (or regional) metrology institutes (NMIs) around the world have developed and/or are developing various kinds of CRMs for measurement of Cd and other trace elements.

Isotope-dilution (ID) is one of the well-established primary-methods in chemical analysis and is widely applied in development of CRMs for measurement of trace elements [3–10]. Particularly, ID with inductively coupled plasma mass-spectrometry (ICP-MS) as the detector, *i.e.* ID-ICP-MS, is widely used in the elemental analyses [3,5–10]. The application of ID-ICP-MS to an element requires that there are at least two stable isotopes being free from significant spectral-interferences. There are 8 stable isotopes of Cd, but each suffers from multiple spectral-interferences. The abundances and typical spectral-interferences (in the case of measurement by ICP-MS with argon gas plasma) of Cd isotopes are summarized in Table 1, where the information for isotopic compositions was based on the database provided by National Institute of Standards and Technology [11]. The spectral-interferences from Ge, Ga, Ru, Pd, Nb, Kr, and Th were not include in Table 1, taking into consideration the fact that the concentrations of these elements are extremely low in common food and feed samples. It can be seen from Table 1 that the Cd isotopes suffer spectral-interferences from Zn, Sr, Y, Zr, Mo, As, Se, and Sn when these elements appear at high concentration (similar to or higher than the concentration of Cd) in the sample. Moreover, all the Cd isotopes except for ^{106}Cd suffer spectral-interferences from Mo isotopes whose abundances are similar to those of Cd isotopes. Furthermore, a resolution of approximately 30 000–600 000 is required to separate the Cd isotopes from the Mo spectral-interferences, which cannot be accomplished with commercial ICP-MS. Considering the fact that there might be high concentrations of Mo in food samples such as cereal grains, potatoes, beans, nuts, seed, vegetables, and algae [12], development of separation techniques for Cd from Mo is required as a pretreatment of the sample prior to the measurement in ID-ICP-MS.

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doi:10.1016/j.talanta.2011.12.071

Table 1
Abundance and typical spectral-interference of Cd isotopes.

Cd isotope	Mass [a]	Abundance[b] (%)	Spectral-interference [c]
^{106}Cd	105.9065	1.250	^{68}Zn^{38}Ar (6000), ^{66}Zn^{40}Ar (6000), ^{70}Zn^{36}Ar (8000), ^{90}Zr^{16}O (16,000), ^{88}Sr^{18}O (64,000), ^{89}Y^{17}O (73,000)
^{108}Cd	107.9042	0.89	^{68}Zn^{40}Ar (7000), ^{92}Zr^{16}O (26,000), **^{92}Mo^{16}O (44,000),** ^{90}Zr^{18}O (338,000)
^{110}Cd	109.9030	12.49	^{70}Zn^{40}Ar (8000), **^{94}Mo^{16}O (37,000),** ^{94}Zr^{16}O (62,000), ^{92}Zr^{18}O (93,000), **^{92}Mo^{18}O (38,000)**
^{111}Cd	110.9042	12.8	^{75}As^{36}Ar (8000), **^{95}Mo^{16}O (33,000)**
^{112}Cd	111.9028	24.13	^{76}Se^{36}Ar:7000, **^{96}Mo^{16}O (36,000),** ^{96}Zr^{16}O (267,000), **^{94}Mo^{18}O (76,000),** ^{112}Sn (55,000), ^{94}Zr^{18}O (42,000)
^{113}Cd	112.9044	12.22	^{75}As^{38}Ar (6000), ^{77}Se^{36}Ar (7000), **^{97}Mo^{16}O (33,000), ^{95}Mo^{18}O (189,000)**
^{114}Cd	113.9034	28.73	^{76}Se^{38}Ar (6000), ^{78}Se^{36}Ar (7000), ^{74}Se^{40}Ar (7000), **^{98}Mo^{16}O (38,000),** ^{114}Sn (197,000), **^{96}Mo^{18}O (238,000)**
^{116}Cd	115.9048	7.49	^{78}Se^{38}Ar (5000), ^{76}Se^{40}Ar (5000), ^{80}Se^{36}Ar (6000), ^{116}Sn (39,000), **^{100}Mo^{16}O (49,000), ^{98}Mo^{18}O (610,000)**

Bold font indicates spectral-interferences from Mo isotopes.

[a] Relative atomic mass cited from Ref. [11], the numbers are rounded-off to four decimal places.

[b] Cited from Ref. [11].

[c] The numbers in the brackets are the minimum resolution required to separate the Cd isotopes from the spectral-interferences, calculated based on the isotopic compositions in Ref. [11] and rounded-up the nearest 1000.

Mathematical correction and collision cell techniques could, to some extent, alleviate the spectral-interferences from measurements of Cd isotopes. However, these techniques might result in a relatively higher uncertainty of the results (either an additional factor is required to calculate the net signals of Cd isotopes or an additional gas was introduced into the mass analyzer to remove polyatomic ions), especially when the signal intensities of the spectral-interferences are significantly higher than those of the Cd isotopes. Coprecipitation with $Mg(OH)_2$ had been shown to be effective for separation of Cd from Mo [8]. However, relatively higher concentration of Mg appears in the analysis solution might affect the accuracy in ID-ICP-MS measurement [10] or result in cone-clogging and matrix sensitivity suppression [13].

Solid phase extraction techniques (SPEs) using chelating resins have been widely used in preconcentration and separation of trace elements, including Cd, from complicated matrices such as seawater [14–19]. Some studies showed that the optimum pH condition for adsorption of Cd and Mo differed from each other when a chelating resin with iminodiacetate functional-groups was applied as the solid phase [15,16]. These results indicate that SPE with a chelating resin could be used for separation of Cd from Mo. However, these researches were carried out to preconcentrate both Cd and Mo for their simultaneous analysis, which required a compromised condition (careful pH adjustment required) for a higher recovery of both of them. Besides, an SPE method using chelating resin (Chelex 100, 200–400 mesh) had been reported to be effective for separation of Cd from serum sample prior to the ID-ICP-MS analysis [20]. However, the operations were very complicated and time-consuming, which included loading the sample to the resin in 2 M NH_4COOCH_3, washing the resin with NH_4COOCH_3 and ultrapure water in sequence, eluting Cd with 2.5 M HNO_3, drying of the separated fraction and re-dissolving with 0.4 M HNO_3. A more effective and easy-operating pretreatment method is preferred for food and feed sample analysis.

In the present work, the authors describe a simplified SPE method, based on the characteristic behaviors of Cd and the interfering elements during the SPE operation using chelating resins, for removal of spectral-interferences on Cd in ID-ICP-MS analysis. The validation of the method was performed by analyzing NMIJ CRM samples. After that, Cd in a soybean powder sample was analyzed with the present method.

2. Experimental

2.1. Instrumentation

A double focusing single collector high-resolution (HR-) ICP-MS instrument of model Element 2 (Thermo Fisher Scientific, Germany) was used for the measurements of Cd isotopes and elements causing polyatomic interferences on Cd isotopes. The operating conditions of the ICP-MS instrument are summarized in Table 2. These operating conditions were chosen after the optimization of each instrumental parameter. An Ethos 1 Milestone (General K.K., Japan) microwave digestion instrument was used to digest the samples; the temperature was controlled by use of an ATC-400CE inner temperature sensor probe (General K.K.). An automatic-closed acid-reflux cleaning-system (TraceClean system, Milestone General K.K.) was used to clean digestion vessels.

2.2. Chemicals and materials

Single-element standards of Cd, Mo, and Zn (guaranteed by the Japan Calibration Service System, JCSS) were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). The following chemicals were also purchased from Kanto Chemical Co., Inc.: single-element standards of Sn and Zr (grade for atomic absorption spectrometry); Ultrapur® HNO_3, H_2O_2, and HF for digestion of the samples and for making solutions; Ultrapur® NH_4OH (approximately 28%) and acetic acid for pH adjustment of the sample solution prior to SPE. Enriched isotope ^{111}Cd (96.44%) was purchased from the Oak Ridge National Laboratory (ORNL, USA). The CRMs used in the present work were developed by NMIJ. Ultrapure water used throughout the present experiment was prepared by a Millipore purification system (Element, Nihon Millipore Kogyo, Japan).

Two kinds of syringe driven chelating columns (SDCCs) were tested in the present work. One is Nobias Chelate PB-1M (packed with 150 mg of chelating resins with ethylenediaminetriacetate (ED3A) and iminodiacetate (IDA) functional group) purchased from Hitachi High-Technologies Corp., Tokyo, Japan), and the other is InertSep ME-1 (packed with 280 mg of chelating resins with IDA functional group) purchased from GL Sciences Inc. (Tokyo, Japan).

Table 2
Typical operating conditions of HR-ICP-MS instrument.

Plasma conditions	
Incident power	1.35 kW
Coolant gas flow rate	Ar 16.0 L min^{-1}
Auxiliary gas flow rate	Ar 0.90 L min^{-1}
Sample gas flow rate	Ar 0.85 L min^{-1}
Additional 1 gas flow rate	Ar 0.28 L min^{-1}
Chamber	
Scott spray chamber (100 mL)	
Nebulizer	
MicroMist nebulizer	
Sample uptake rate	0.2 mL min^{-1}
Data acquisition (low resolution, $m/\Delta m = 300$)	
Mass window	10
Integration window	10
Samples per peak	100
Integration times (Runs × Passes)	10 × 600 times

2.3. Cleaning of sample bottles, pipette tips, and digestion vessels

Polypropylene sample bottles and single-use Eppendorf micropipette tips were used throughout the experiment. Prior to the experiment, all sample bottles and pipette tips were cleaned by soaking in a 3 M HNO_3 solution for one week, followed by rinsing 5 times with ultrapure water in a laboratory room. The PTFE digestion vessels used in microwave acid digestion were cleaned with the TraceClean system employing 50% aqua regia (450 °C, 3.5 h), followed by rinsing 5 times with ultrapure water.

2.4. Microwave acid digestion procedure

The samples were subjected to microwave acid digestion to obtain the sample solutions. The procedure for the microwave acid digestion was as follows. Approximately 0.3–0.5 g (depending on the sample) of the sample was precisely balanced and put into the digestion vessel, followed by immediate addition of the enriched isotope spike (^{111}Cd). After 6 mL of HNO_3 and 2 mL of H_2O_2 were added, the digestion vessel was sealed and left overnight. Then the sample was subjected to the first step of microwave irradiation (ramp: from room temperature to 150 °C for 30 min, hold for 5 min). After cooling down, 0.5 mL of HF, 1.5 mL of HNO_3 and 1.5 mL H_2O_2 were further added into the sample, which was then subjected to the second step of microwave irradiation (ramp: from room temperature to 220 °C for 25 min, hold for 20 min). After the second step of microwave irradiation, the acid solution in the digestion vessel was completely evaporated on a hot plate in a clean bench, and then 0.6 mL of HNO_3 and approximately 5 mL of ultrapure water were added into the digestion vessel to dissolve the digested sample. Finally, approximately 30 mL of the digested sample solution was obtained by adding ultrapure water.

The concentrations of Cd in the samples were obtained based on dry-mass. The dry-mass correction factor was acquired according to the certificate of each CRM.

2.5. Optimized procedure for SPE

Optimization of the procedure for SPE was carried out by testing the dependence of Cd recovery and Mo removal rate (or recovery) on the pH condition of the sample solution and on the amount of NH_4OH added into the sample solution. Eventually, the optimized SPE procedure was as follows. First, 0.6 mL of NH_4OH was added into each 10 mL of the sample solution, which was then passed through a SDCC at 5 mL min^{-1}. After 5 mL of ultrapure water was passed through the SDCC for washing, 2 mL of 0.3 M HNO_3 was passed through to elute Cd and then the eluent was subjected to ICP-MS measurement.

2.6. Calculation in ID-ICP-MS method

Calculation of analytical results was based on Eq. (1) following the instruction of EURACHEM/CITAC Guide CG 4 [21].

$$c_x = c_z \cdot r \cdot \frac{m_y}{wm_x} \cdot \frac{m_z}{m'_y} \cdot \frac{K_y \cdot R_y - K_b \cdot R_b}{K_b \cdot R_b - K_x \cdot R_x} \cdot \frac{K_{b'} \cdot R_{b'} - K_z \cdot R_z}{K_y \cdot R_y - K_{b'} \cdot R_{b'}} - c_{blk} \quad (1)$$

In Eq. (1), the subscripts x, y, z, b, and b' represent the sample, the isotope enriched spike, the standard, the mixed solution of x and y for ID, and the mixed solution of y and z for reverse ID, respectively. The meaning of other symbols are as follows: m_x and m_y, mass of x and y in mixed b [g]; m'_y and m_z, mass of y and z in mixed b' [g]; c_x, c_y, and c_z, concentration of Cd [ng g^{-1}] in x, y, and z, respectively; c_{blk}, observed procedure blank [ng g^{-1}]; R_x, R_y, R_z, R_b and R'_b, measured ratio of ^{110}Cd/^{111}Cd in x, y, z, b and b', respectively; K_x, K_y, K_z, K_b, and K'_b, mass discrimination correction factor of R_x, R_y, R_z, R_b, and R'_b, respectively. Because the isotopic ratio of natural Cd (R_x and R_z) was cited from International Union of Pure and Applied Chemistry (IUPAC), the values of K_x and K_z were equal to 1. The ratio of R_y was obtained from the certificate of enriched ^{111}Cd isotope, accordingly the value K_y equal to 1. The values of K_b and K'_b were obtained by dividing the theoretical Cd isotopic ratio (based on IUPAC data) to the observed Cd isotopic ratio of the standard solution. The w and r are wet factor (dry-mass correction factor) and repeatability factor, respectively.

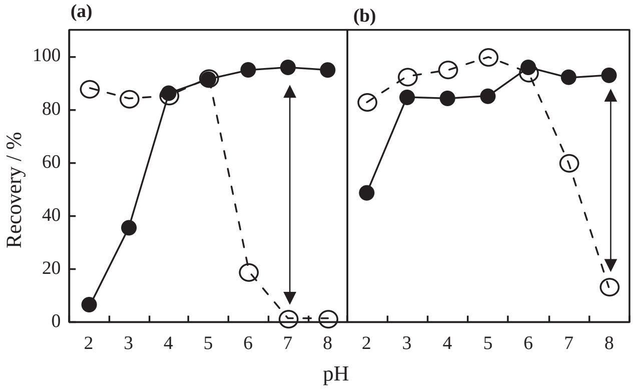

Fig. 1. Dependence of Cd and Mo recoveries on pH conditions of the sample. (●, Cd; ○, Mo. (a), InertSep ME-1; (b), Nobias Chelate PB-1M.)

A mathematic correction method, where the samples were measured by ID-ICP-MS without separation by the present SPE, was also used for cross-checking of the significance of the present method. In the case of mathematic correction, the signal intensities of Cd isotopes were calculated with

$$S'_{\mathrm{Cd}} = S_{\mathrm{Cd}} - S_{\mathrm{Mo}} \times R^*_{\mathrm{Cd/Mo}}, \quad (2)$$

where S'_{Cd}, S_{Cd}, S_{Mo}, and $R^*_{\mathrm{Cd/Mo}}$ were respectively the net Cd isotope signal in the sample, the gross Cd isotope signal in the sample, the interfering Mo isotope signal in the sample, and the ratio of Cd isotope signal to the interfering Mo isotope signal in Mo standard solution.

All of the factors involved in calculating the concentration of Cd were considered to estimate the uncertainty of analysis in the following sections.

3. Results and discussion

3.1. Dependence of Mo and Cd recoveries on pH condition

All of the SDCCs in the present work were single-use and were preserved in ultrapure water. For the purpose of pre-cleaning, 5 mL of 0.3 M HNO_3 and ultrapure water were consecutively passed through each SDCC immediately prior to the experiment.

The solution of a tea-leaf sample after acid digestion was used as the test solution (1 ng mL^{-1} of Cd and 10 ng mL^{-1} of Mo spiked) to investigate the dependence of Cd and Mo recoveries on pH condition. The test solution was adjusted to pH 2.0–9.0 with an increment of pH 1.0 using acetic acid and NH_4OH solution. After that, 10 mL of each sample was respectively loaded to the SDCCs at a flow rate of 5 mL min^{-1}. After washing the SDCCs with 5 mL of ultrapure water, 2 mL of 2 M HNO_3 was passed through to recover the elements and the eluent was subjected to measurement by HR-ICP-MS.

The results obtained by InertSep ME-1 and Nobias Chelate PB1-M are respectively illustrated in Fig. 1(a) and (b). It can be seen from Fig. 1(a) that relatively higher recoveries of Cd were obtained when the sample pH was over 4. By contrast, the relatively higher recoveries of Mo were obtained when the pH of the sample were less than 5. When the pH of the sample was over 7, the recovery of

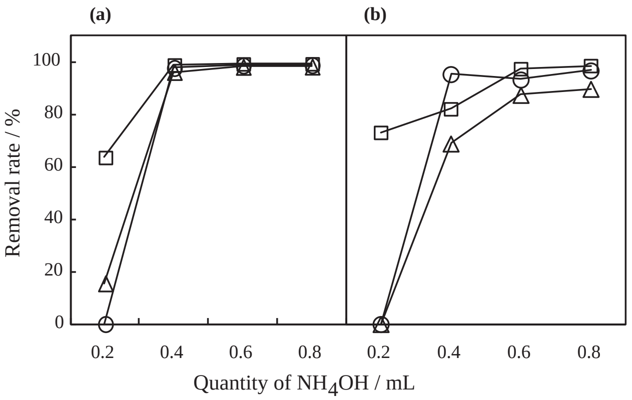

Fig. 2. The removal rates of interfering elements in relation to the quantity of NH_4OH added to the sample. (○, Mo; △, Zr; □, Sn. (a), InertSep ME-1; (b), Nobias Chelate PB-1M.)

Cd was close to 100% while that of Mo was close to 0%, which indicates that Cd and Mo could be completely separated. On the other hand, the plots in Fig. 1(b) showed that relatively higher recoveries of Cd and Mo could be obtained in a relatively wide pH range from 3 to 6. It is noted that the recoveries of Mo obtained at pH 8 was approximately 10%, which indicates that the separation of Cd from Mo was not as effective as that in Fig. 1(a).

It is noted that a relatively strong acid of 2 M HNO_3 was used to recover the elements in this test, since Mo could be adsorbed on the chelating resin at lower pH conditions. The results of a further preliminary test showed that 2 mL of 0.3 M HNO_3 was enough to elute Cd from the SDCCs. In the following experiment, 0.3 M HNO_3 was used to elute Cd from the SDCCs.

3.2. Dependence of removal rates of interfering elements on NH_4OH quantity

The results in Fig. 1 indicate that a better separation of Cd from Mo by InertSep ME-1 could be obtained in a relatively wide pH range over 7, which permitted the simplification of sample pH adjustment procedure. In the present work, optimization of NH_4OH quantity added to the sample was carried out by investigating the removal rates of interfering elements.

The optimization of NH_4OH amount added to the digested sample solution was carried out with a test solution similar to that used for pH condition test. In addition to Cd and Mo, Zr and Sn (10 ng mL^{-1} each) were also added to the test solution. In the test, 0.2–0.8 mL of NH_4OH with an increment of 0.2 mL was respectively added into each 10 mL of test solution, which was then passed through the SDCCs at 5 mL min^{-1}. After washing the SDCCs with 5 mL of ultrapure water, 2 mL of 0.3 M HNO_3 was passed through to elute the elements and the eluent was subjected to measurement by HR-ICP-MS.

The removal rates of Zr, Mo, and Sn by InertSep ME-1 and those by Nobias Chelate PB1-M are respectively illustrated in Fig. 2 (a) and (b). As can be seen from Fig. 2, when the quantity of NH_4OH was less than 0.4 mL, the removal rates of Mo, Zr, and Sn were significantly worse than those obtained with 0.6 and 0.8 mL of NH_4OH, while the removal rates obtained with 0.6 and 0.8 mL of NH_4OH were equal. It is noted that when 0.6 mL of NH_4OH was used, removal rate of Mo, Zr, and Sn by InerSep ME-1 were extremely close to 100%, while the removal rates of Mo, Zr, and Sn by Nobias Chelate PB-1 was approximately 95, 90, and 97%, respectively. Therefore, InertSep ME-1 was used in the following experiment and 0.6 mL of NH_4OH was added into each 10 mL of the digested sample prior to loading to the SDCC. As addressed in Section 2.2, the InertSep ME-1 SDCCs have IDA as the functional chelating group while the Nobias Chelate PB-1 SDCCs have both IDA and ED3A as the functional chelating groups. Therefore, the above mentioned results might indicate that the ED3A functional groups in Nobias Chelate PB-1 contributed to the adsorption of Mo and affected the separation of Cd from Mo.

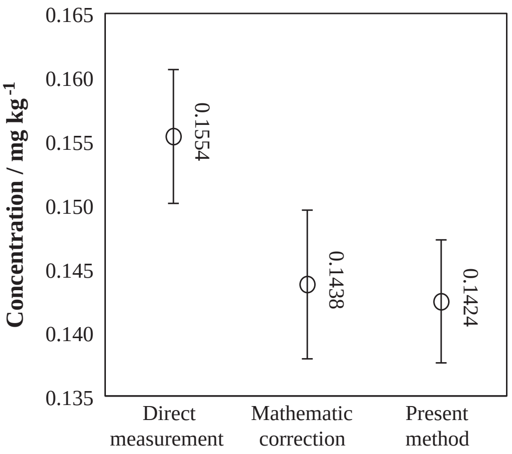

Fig. 3. A comparison of analytical results obtained by direct measurement, mathematic correction, and the present method. The error-bars are the expanded uncertainties with a coverage factor of $k = 2$.

3.3. Validation of the method

In order to validate the present method, determination of Cd in 5 food-relative CRM-samples from NMIJ was carried out. The observed values of Cd in these CRM-samples are summarized in Table 3 in comparison to the certified values. All of the values in Table 3 are shown as Mean ± *U*, $k = 2$, where *U* and *k* are the expanded uncertainty and the coverage factor which is corresponding to an estimated confidence interval of approximately 95%. The calculation of expanded uncertainty was carried out following the ISO GUM:2008 (Guide to the Expression of Uncertainty in Measurement) [22] considering all of the parameters in Eq. (1). It can be seen from Table 3 that the concentrations of Cd in these CRM samples covered a range from approximately 0.014 to 0.80 mg kg^{-1}. All of the observed values were in good agreement with the corresponding certified values taking into consideration the expanded uncertainties, where the expanded uncertainties of certified values covered the uncertainties of the homogeneity, the stability, and the methods for characterization.

It should be noted that the concentrations of Mo in white rice CRMs, NMIJ CRM 7501-a and 7502-a, were respectively 0.6 and 0.8 mg kg^{-1}. The concentrations of Zr and Mo in seaweed (Hijiki) CRM were approximately 3 and 1 mg kg^{-1}, respectively. By contrast, the concentrations of Zr and Mo were negligible in the tea-leaf CRM and the swordfish-tissue CRM. The concentration of Sn in all of the present CRM-samples was negligible. Nevertheless, the results in Table 3 showed that the results of Cd in white-rice CRMs and seaweed (Hijiki) CRM are reliable, without significant elevation of relative expanded uncertainties, as well as those in the tea-leaf CRM and the swordfish-tissue CRM. This fact indicates that the spectral-interferences were effectively removed in the present experiment and the present method is valid for determination of Cd in food and feed samples by ID-ICP-MS.

3.4. Application of the method to a soybean powder sample

As an application of the present method, a soybean powder sample was digested and subjected to the analysis by direct measurement (without any correction and separation), mathematic correction method of spectral-interferences, and the present

Table 3
The observed values of Cd in CRMs in comparison to the certified values.

CRM code	Name	Cd mass fraction[a] (mg kg^{-1})		Mass fraction of interfering elements[b] (mg kg^{-1})		
		Observed value	Certified value	Mo	Zr	Sn
NMIJ CRM 7505-a	Tea leaf	0.0136 ± 0.0006	0.0139 ± 0.0012	ND	ND	ND
NMIJ CRM 7501-a	White rice	0.0511 ± 0.0010	0.0517 ± 0.0024	0.6	ND	ND
NMIJ CRM 7403-a	Swordfish tissue	0.159 ± 0.004	0.159 ± 0.006	ND	ND	ND
NMIJ CRM 7502-a	White rice	0.552 ± 0.008	0.548 ± 0.020	0.8	ND	ND
NMIJ CRM 7405-a	Seaweed (Hijiki)	0.800 ± 0.011	0.79 ± 0.02	1	3	ND

ND, not detected.
[a] Mean ± U, k = 2.
[b] The concentration in solid sample, not detected of each element after separation.

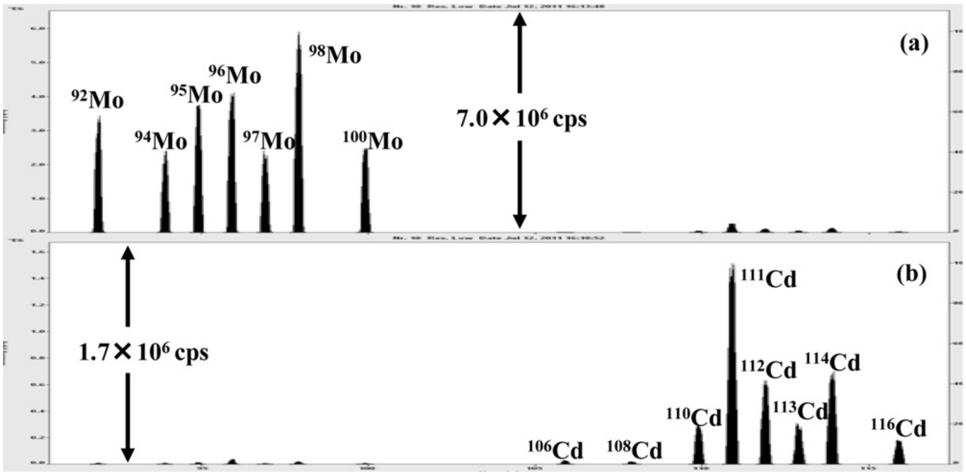

Fig. 4. Mass-spectra of Mo and Cd isotopes in a digested sample of the soybean powder sample. ((a) Before separation; (b) after the SPE separation.)

method. The results are illustrated in Fig. 3, where the error-bars are the expanded uncertainties with a coverage factor of k = 2. It can be seen from Fig. 3 that the result obtained by direct measurement was significantly higher (approximately 9%) than those obtained by the mathematic correction method and the present method, which indicates that the spectral-interferences with Cd isotopes were significant. The result obtained by mathematic correction method (0.1438 mg kg^{-1}) was in agreement with that obtained by the present method (0.1424 mg kg^{-1}) considering the expanded uncertainties of the values. However, the mean value and the expanded uncertainty obtained by mathematic correction method (0.0058 mg kg^{-1}) were slightly higher than those obtained by the present method (0.0048 mg kg^{-1}). The difference in the mean values could be attributed to the fact that the measurements in the present method were carried out at a spectral-interference-free condition, which could be confirmed by the comparison of mass-spectra of Mo and Cd isotopes in Fig. 4 (a) and (b) obtained by using a digested sample (^{111}Cd spiked) of the soybean powder sample. It can be seen from Fig. 4 that the spectra of Mo isotopes were effectively removed after the SPE separation so that clear spectra of Cd isotopes were obtained.

The budgets of combined uncertainties of the value obtained by the mathematic correction method and that obtained by the present method are summarized in Table 4, in which all of the parameters in Eq. (1) were considered. It can be seen from Table 4 that the present method significantly decreased the contribution of R_b, *i.e.* the measured ^{110}Cd/^{111}Cd ratio in the spiked sample, from 33.0% (in the case of mathematic correction) to 5.5%. It is noted that the major contribution to the combined uncertainty in the present method was the isotope composition of natural Cd isotope ratios (R_x and R_z), which was cited from the IUPAC. This contribution might be improved in the future with more precise techniques for measuring the natural Cd isotope ratios.

The procedure blank of Cd was 0.00046 mg kg^{-1} with a standard deviation of 0.00008 mg kg^{-1}, based on 5 individual blank tests (empty digestion vessel added with equivalent amounts of acid to the samples) to which the digestion and SPE operations were applied in the same manner to the samples. The detection

Table 4
A comparison of the budgets of combined uncertainty obtained by mathematic correction and the present method.

Factor	Contribution (%)	
	Mathematic correction	Present method
R_b	33.0	5.5
K_b	3.7	5.3
R'_b	3.2	4.5
K'_b	6.2	8.8
R_x	17.8	25.1
K_x	0.0	0.0
R_z	30.0	42.2
K_z	0.0	0.0
r	2.9	4.0
c_{blk}	0.0	0.0
c_z	3.0	4.3
R_y	0.0	0.0
K_y	0.0	0.0
m_x	0.1	0.2
m_y	0.0	0.1
m'_y	0.0	0.1
m_z	0.0	0.0
w	0.0	0.0
Combined uncertainty (%)	2.0	1.7

Table 5
Comparison of the operations in the present work with the reported methods.

	Present work	SPE-Chelex 100 [Ref. 20]	SPE-Anion Exchange [Ref. 20]
Starting solution	0.3 M HNO_3	2 M NH_4COOCH_3	HCl 1.5 M and HF 1 M
Pre-operation	Nothing	Nothing	Converting from the nitrate to the chloride form
Reagents used in the SPE procedure	28% NH_4OH Ultrapure water	2 M NH_4COOCH_3 Ultrapure water M HNO_3	HCl 1.5 M and HF 1 M HCl 1 M HNO_3 concentrated HNO_3
Post-operation	Nothing	Drying and re-dissolving	Drying and re-dissolving
Ending solution	0.3 M HNO_3 (*ca.* 0.15 M)	0.4 M HNO_3	0.4 M HNO_3

limit was 0.00023 mg kg^{-1}, corresponding to 3-fold of the standard deviation of procedure blank.

3.5. Comparison of the operations in the present method with reported methods

A comparison of the operations in the present method with reported methods are summarized in Table 5. It can be seen that the only required reagents in the present SPE operation are 28% NH_4OH and ultrapure water, in addition to 0.3 M HNO_3 (eluent). By contrast, relatively higher concentration of HNO_3 (2.5 M) was required in addition to NH_4COOCH_3 for the reported SPE-Chelex 100 method. Furthermore, SPE-Anion Exchange method required much more complicated reagents in the operations. Additional treatment was not required in the present method, while drying/re-dissolving were required in both reported methods and converting from the nitrate to the chloride form of the samples was required in the reported SPE-Anion Exchange method. Therefore, the operations of the present method are simpler and easier than the reported methods.

4. Conclusion

An SPE technique using SDCC was developed to separate Cd from spectral-interferences prior to the analysis of food samples by ID-ICP-MS. Complete separation of interfering elements (removal rates of Mo, Zr, and Sn close to 100%) from Cd could be achieved by simple operations. The suggested SPE operations could be easily performed by adding NH_4OH into the sample; loading the sample into the SDCCs; washing the SDCC with ultrapure water; passing 0.3 M HNO_3 through the SDCC to elute Cd. The present method was confirmed to be valid for highly precise and accurate analysis of Cd in food samples by ID-ICP-MS.

In the present method, both the starting sample solution and the ending sample solution in SPE separation were in 0.3 M HNO_3, which indicates that repetition of the SPE separation could be carried out easily on the ending sample to improve the separation effect when it is necessary.

It is noted that all of the present samples were in 0.3 M HNO_3, while the concentration of the NH_4OH were approximately 28%. Optimization of the NH_4OH quantity should be carried out when the present method is applied to a sample with a HNO_3 concentration higher than 0.3 M or when the concentration of NH_4OH is lower than 28%.

Acknowledgement

The authors express sincere gratitude to Mr. Alex Groombridge (The University of Sheffield) for preliminary grammatical check of the manuscript.

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