Reference measurements of cadmium and lead contents in candidates for new environmental certified materials by isotope dilution inductively coupled plasma mass spectrometry

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ABSTRACT

The analytical procedures for the reference measurements of cadmium and lead concentrations in four candidates for new environmental certified reference materials were developed. Cadmium and lead content was determined in bottom sediment (M-2 BotSed), Baltic herring tissue (M-3 HerTis), cormorant tissue (M-4 CormTis) and codfish tissue (M-5 CodTis). The measurements were carried out with the use of a direct isotope dilution inductively coupled plasma mass spectrometry (ID ICP-MS). The isotope dilution approach and the combined uncertainty of results are based on the mathematical equations as from definition of a primary method of measurement. All factors influencing the final results included: the procedural blank, the moisture content in the materials, the factors affecting the blend ratio measurements (instrumental background, spectral interferences, dead time, mass discrimination effects and the repeatability of measured isotopic ratios) as well as the isotopic equilibrium were systematically investigated and included in the uncertainty budget. The content of cadmium in candidates for new environmental reference materials, after correction for moisture contents, matrix separation on ion-exchange resin AG1-X8 of the blended samples and after using for the ICP-MS measurements ratio of pair of isotopes $n(^{110}Cd)/n(^{111}Cd)$ was found to be: $(2.18 \pm 0.06)\,\mu g\,g^{-1}$ in M-2 BotSed, $(337 \pm 2)\,ng\,g^{-1}$ in HerTis, $(16.4 \pm 0.6)\,ng\,g^{-1}$ in CormTis) and $(2.7 \pm 0.4)\,ng\,g^{-1}$ in CodTis, respectively. The content of lead in candidates for new environmental reference materials, after correction for moisture contents, matrix separation on ion-exchange resin AG1-X8 of the blended samples and after using for the ICP-MS measurements ratio of pair of isotopes $n(^{208}Pb)/n(^{207}Pb)$ was found to be: $(108 \pm 5)\,ng\,g^{-1}$ in M-3 HerTis, $(2.34 \pm 0.12)\,\mu g\,g^{-1}$ in M-4 CormTis and $(43 \pm 2)\,ng\,g^{-1}$ in M-5 CodTis, respectively. The Cd and Pb contents determined in this work were used as a contribution of the Faculty of Chemistry, Biological and Chemical Research Centre University of Warsaw in the characterisation of the abovementioned candidates for new certified reference materials in the frame of the Inter-Laboratory Comparison, organized by the Institute Nuclear Chemistry and Technology (Warsaw, Poland). The obtained excellent agreement within uncertainties with the reference values further validated the methods developed in this study.

1. Introduction

The accuracy and precision in the measurements of trace pollutants content in the environmental materials is crucial for the human health and from the environmental contamination control point of view. Both cadmium and lead have no known positive physiological functions and can become toxic at the higher concentrations [1]. The biota organisms (oysters, clams, mussels, *etc*.) and fishes with Cd and Pb accumulated in their tissues may act as dietary sources of those elements to human diet [2, 3]. Therefore, their content must be monitored in objects that can be a threat to the human health or can be dangerous from the ecological point of view.

The inductively coupled plasma mass spectrometry (ICP-MS) is often used for the determination of cadmium and lead concentration in various types of samples, *e.g.* fish tissue [1, 4–6], aquatic birds [7], various foodstuffs [8] and sediments [9, 10]. Despite its advantages, high sensitivity and precision, low detection limit (often in the ng L^{-1} range) and good precision of measurement ($< 1\%$ RSD), the ICP-MS has limitations such as the presence of interferences, especially in the case of cadmium determination. The possible sources of interferences include the formation of oxides and hydroxides of Mo and Zr as well as isobaric interferences from ^{112}Sn and ^{114}Sn. Although those

interferences can be eliminated by matrix separation with the use of ion exchangers [11, 12] however, to obtain true value using ICP-MS, 100% recovery of an element is required.

The isotope dilution mass spectrometry (IDMS) is regarded as a primary method of measurements. The main advantages of IDMS, in comparison with other calibration strategies, *e.g.* external calibration or standard additions, are: (i) once complete isotope equilibration between the sample and the spike has been achieved, there is no need to know the pre-concentration or dilution factor of the sample or to take into account any non-quantitative separation or evaporation process; (ii) any variation of the instrumental sensitivity such as signal drift has not influence on the final results; and (iii) the results are obtained with superior accuracy and precision, and with a small combined uncertainty [12, 13]. The use of IDMS enables the highest metrological quality of results [14] therefore, is often used for certified reference materials (CRMs) characterisation [11, 12, 15–17]. It should be noted that, as in the case for other calibration strategies, isotope dilution cannot compensate random contamination, which may occur during sample workup, thus a blank monitoring is necessary [18, 19].

The development and validation of ID ICP-MS reference measurement procedure for the quantification of Cd and Pb content in four candidates for new environmental reference materials with the objective of achieving an uncertainty target on final results of 1–5% ($k = 2$) and SI traceable values are described in this work. The systematic assessment of all factors influencing the measurement results as sample-spike isotopic equilibrium, factors affecting the blend ratio measurements, the efficiency of the sample digestion procedure, possible interferences, matrix effects, *etc.* was done through the present study. Modelling of the entire measurement procedures and the use of appropriate certified reference materials enable to assure the traceability of obtained values to the International System of Units (SI): the mole, the kilogram and the second [18, 20]. It should also be emphasised that reference materials are used for the method validation, calibration, estimation of measurement uncertainty and proficiency testing [21]. Therefore, different types of reference materials are required and there is still a need to introduce new CRMs to fulfill the demand of the environmentally oriented studies.

2. Experimental

2.1. Chemicals and materials

Trace analysis grade reagents of 65% nitric acid (Suprapur, Merck, Germany), 35–38% hydrochloric acid (J.T.Baker, USA) and 49% hydrofluoric acid (Fluka, Germany) were used for digestion of the samples.

Four reference materials were used for the evaluation of digestion conditions assuring the quantitative recovery of cadmium and lead: (i) marine sediment IAEA-457 (International Atomic Energy Agency, Monaco) with the certified cadmium and lead content of $(1.09 \pm 0.08) \, \mu g \, g^{-1}$ and $(105 \pm 7) \, \mu g \, g^{-1}$, respectively; (ii) sediment HR-1 (National Water Research Institute, Canada) with the certified cadmium and lead content of $(3.88 \pm 1.24) \, \mu g \, g^{-1}$ and $(139 \pm 37) \, \mu g \, g^{-1}$, respectively; (iii) non defatted lobster hepatopancreas LUTS-1 (National Research Council, Canada) with the certified cadmium and lead content of $(2.12 \pm 0.15) \, \mu g \, g^{-1}$ and $(0.010 \pm 0.002) \, \mu g \, g^{-1}$, respectively; and (iv) bovine liver SRM-1577c (National Institute of Standards and Technology, USA) with the certified cadmium and lead content of $(0.097 \pm 0.0014) \, \mu g \, g^{-1}$ and $(0.0628 \pm 0.0010) \, \mu g \, g^{-1}$, respectively.

Isotopic standard IRMM-622 (Joint Research Centre Geel, Belgium) enriched in 95,7% of ^{111}Cd with cadmium concentration of $(1.1288 \pm 0.0020) \, \mu g \, g^{-1}$ was used for spiking the samples. Cadmium single component standard ICP (TraceCERT, Merck, Germany) with the concentration 1000 $mg \, L^{-1}$ was used for the correction of mass discrimination effects and for the calibration curve ICP-MS measurements.

The standard solution was appropriately diluted gravimetrically before use.

Isotopic standard IES-Pb207 (Innovative Solutions in Chemistry ISC-Science, Spain) enriched in 94,9% of ^{207}Pb and with concentration of $(100.02 \pm 2.65) \, \mu g \, g^{-1}$ was used for spiking the samples. Standard Reference Material SRM-981 (NIST, USA) – common lead isotopic standard certified for isotopic composition of lead was used for the correction of mass discrimination effects. Lead single component standard ICP (TraceCERT, Merck, Germany) with the concentration of 1000 $mg \, L^{-1}$ was used during the measurements by calibration curve ICP-MS. The standard solution was appropriately diluted gravimetrically before use.

Rhodium single component standard ICP (TraceCERT, Merck, Germany) with the concentration of 1000 $mg \, L^{-1}$ during the measurements by calibration curve ICP-MS was used.

ICP multi-element standard solutions (CertiPUR, Merck, Germany) for monitoring of sample matrix composition were used.

The working standard solutions and blend solutions were prepared gravimetrically using an analytical balance (Mettler Toledo, Switzerland).

The ion exchanger AG1 X-8 (Bio-Rad) was converted from chloride to nitrate form by shaking it with 2% nitric acid. The ion exchanger was allowed to deposit, and the acid was decanted off. This procedure was repeated several times. For the matrix separation procedure, diluted 65% nitric acid (Suprapur, Merck, Germany) and diluted 35–38% hydrochloric acid (J.T.Baker, USA) were used.

Four candidates for environmental reference materials with different matrix composition identified as: M-2 BotSed, M-3 HerTis, M-4 CormTis and M-5 CodTis (see Table 1) were examined for cadmium and lead concentration.

2.2. Instrumentation

Inductively coupled plasma mass spectrometer NexION 300D (Perkin Elmer, USA) was used for the ICP-MS measurements. The optimized working conditions used for cadmium and lead determination are listed in Table 2.

In case of IDMS approach, the signal intensities per replicate were corrected for dead time, and instrumental background before calculating an average isotopic ratio and its relative standard deviation. The dead time value and its associated standard uncertainty for every element were determined according to correction method described by Nelms et al. [22]. The ratios of $n(^{110}Cd)/n(^{111}Cd)$ and $n(^{113}Cd)/n(^{111}Cd)$ were selected for the cadmium concentrations determination (cross-validation purpose as all isotopes are affected by spectral interferences). In case of lead the ratios of $n(^{208}Pb)/n(^{207}Pb)$ and $n(^{206}Pb)/n(^{207}Pb)$ were chosen for the lead concentrations determination (cross-validation purpose, all isotopes are free from significant spectral interferences). The cross-validation is often use in IDMS measurements to validate results obtained from different pairs of isotopes and to eliminate random error. The mass discrimination effects during cadmium measurements were evaluated by measuring the ratio of $n(^{110}Cd)/n(^{111}Cd)$ and $n(^{113}Cd)/n(^{111}Cd)$ in the diluted cadmium single

Table 1
List of candidates for new environmental certified reference materials.

No	Code	Matrix
1	M-2 BotSed	Bottom sediment (from Vistula river near Włocławek city, Poland)
2	M-3 HerTis	Baltic herring tissue (*Clupea harengus*) (from the North Sea)
3	M-4 CormTis	Cormorant tissue (*Phalacrocorax carbo*) (from Czech Republic)
4	M-5 CodTis	Codfish tissue (*Gadus morhua*) (from Baltic Sea)