



Reference measurements for cadmium, copper, mercury, lead, zinc and methyl mercury mass fractions in scallop sample by isotope dilution inductively coupled plasma mass spectrometry



Emilia Vassileva^{a,*}, Irena Wysocka^b, Maria Betti^c

^a International Atomic Energy Agency, Environmental Laboratories, 4 Quai Antoine 1er, 98000, Monaco

^b Polish Geological Institutes, Rakowiecka 4, 00-975 Warsaw, Poland

^c European Commission, Joint Research Center, Institute for Environment and Sustainability, Via E. Fermi 2749, 21027 Ispra (VA), Italy

ARTICLE INFO

Article history:

Received 26 February 2014

Received in revised form 12 May 2014

Accepted 12 May 2014

Available online 21 May 2014

Keywords:

Isotope dilution ICP-MS

Trace elements, biota sample

Certified reference material

Uncertainty, traceability, method validation

ABSTRACT

A marine certified reference material (CRM), IAEA 452, prepared with scallop (*Pecten maximus*) sample was recently produced by the Environmental Laboratories of the International Atomic Energy Agency (IAEA) and certified for trace elements and methyl mercury (MeHg) mass fractions.

The present work describes the certification of Cd, Cu Hg, Pb, Zn and MeHg in scallop (*P. maximus*) sample. The reference values for the Cd, Cu Hg, Pb, Zn and MeHg mass fractions were obtained with isotope dilution inductively coupled plasma-mass spectrometry (ID ICP-MS) applied as a primary method of measurement.

A procedure based on complete digestion of the samples and ID ICP-MS was developed with the objective of achieving expanded uncertainty of the final results of 1.5–4.56%. A systematic assessment of all factors influencing the measurement results as sample-spike isotopic equilibrium, homogeneity study, factors affecting blend ratio measurements, efficiency of the sample digestion procedure, possible interferences, matrix effects etc. was done throughout the present study. Modelling of the entire measurement process and the use of reference materials relates obtained values for Cd, Cu Hg, Pb, Zn and MeHg to SI units of the mole or the kilogram.

The agreement between obtained results and those derived from the worldwide Inter-laboratory Comparison between 146 laboratories, organised by IAEA on the same sample matrix (less than 1% difference), further validated the methods developed at Environment Laboratories of IAEA.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The continued release of metal contaminants into the marine environment from anthropogenic sources, including industrial process, waste streams and atmospheric emissions has led to an on-going requirement to develop analytical methodologies for their accurate determination in many sample types. Accurate determination of metal content in the reference marine species serves as an important step in pollution monitoring, food safety control and ecosystem conditions monitoring [1,2]. The low levels at which trace metals are present in marine environment and the thin line between acceptable and dangerous concentrations, mean that more accurate methods of analysis must be employed to control the content of metals in biota and particularly in seafood.

Important conclusions and decisions linked to the customer protection sphere derive from measurement results that have to be based on reliable data of adequate quality (traceable to SI and with sufficiently small uncertainty). Comparability of environmental results can only

be achieved when measurement results are traceable to a common system of reference; they are reported with combined uncertainty and produced with validated analytical methods [3].

The species selected was scallop (*Pecten maximus*), which is popular seafood in many countries in the world and is used to assess the potential transfer of toxic elements through the food chain. The scallop (*P. maximus*) is also used as bio-indicators for trace metal contamination in marine pollution studies. One of the outcomes from the Coordinated Research Project on seafood safety conducted by International Atomic Energy Agency (IAEA) was the identification of the need of seafood matrix CRM with elevated level of toxic elements.

The quality assurance of routine analytical measurements depends on traceability to the SI, which can be achieved by using certified reference materials (CRM's), comparing with primary methods, or the method itself having the potential to be a primary method. The Consultative Committee for Amount of Substance (CCQM) developed a definition for a primary method of measurement as a method having the highest metrological qualities, whose operation is completely described and understood, for which a complete uncertainty statement can be written down in terms of SI units [4,5]. The CCQM distinguishes within this definition the primary direct method, which measures the value of an unknown

* Corresponding author.

E-mail address: e.vassileva-veleva@iaea.org (E. Vassileva).

without reference to a standard of the same quantity, and the primary ratio method, which measures the value of a ratio of an unknown to a standard of the same quantity and whose operation must be completely described by a measurement equation [4,5]. Methods with empirical measurement equations, i.e. depending on calibration with one or more standards, are not primary methods because they do not meet the requirement of having full measurement equations in the sense of being fully described and understood in terms of SI units [13]. They can be called secondary methods, because they can only attain traceability to the SI when validated by a primary method of measurement or primary standard [13,14]. This classification of measurement methods is not intended to give a superior status to some methods or to devalue others that have demonstrated capability to produce high-quality data, but to provide a reference of a methods' ability to be traceably linked to the SI.

Isotope dilution inductively coupled plasma mass spectrometry (ID ICP-MS) is a powerful methodology based on the measurements of isotope amount ratios. The method is recognised as having the potential to be a primary method of measurement and is often used to produce reference values. If such a method is applied in a proper way the results are traceable to the International System of Units (SI). The characteristic of results that act as a reference is that they are reliable and have sufficiently small uncertainties. This is often advantageous for samples which induce strong matrix effects, such as some marine samples. Complete digestion of the sample following the spike addition ensures isotope equilibration and drastically reduces the matrix effects during the isotope ratio measurements. Measuring isotope amount ratios has the additional advantage of making the procedure independent from other possible sources of uncertainties, such as analyte loss occurring during the sample treatment [4,5].

The Marine Environmental Studies Laboratory (MESL) of the International Atomic Energy Agency's Environment Laboratories (IAEA-EL) has the programmatic responsibility to provide assistance to Member State laboratories in maintaining and improving the reliability of analytical measurement results, both in trace elements and organic pollutants. This is accomplished throughout the production and provision of certified reference materials (CRMs) of marine origin, validated analytical procedures, training in the implementation of internal quality control, and through the evaluation of measurement performance by the organisation of worldwide and regional inter laboratory comparison exercises. IAEA's Analytical Quality Control Service (AQCS), now named Reference Products for Science and Trades, represents important bench mark in the upgrading the quality of laboratory performances and assessing the validity of the analytical methods used for marine monitoring studies in the Member States.

A procedure based on complete digestion of samples and isotope dilution-inductively coupled plasma mass spectrometry (ID ICP-MS), applied as a primary method of measurement, was developed with the objective of achieving an uncertainty target on final results of 1.5–3.5% ($k = 2$) and SI traceable values for the IAEA-452 CRM. Validation of the method developed was particularly emphasised. It included, apart from the comparison with results from worldwide inter-laboratory comparison, modelling of the entire measurement process allowing uncertainty estimations and systematic assessment of all factors influencing obtained measurement results.

The results obtained during this study contributed for the certification of trace elements mass fractions in the scallop (*P. maximus*) sample, which became IAEA-452 CRM.

2. Experimental

2.1. Chemicals and materials

High quality deionised water from Milli-Q system (Millipore, Bedford, MA, USA) was used throughout this work. Ultra-pure HNO₃ (Ultrex®, T. T. Baker, Phillipsburg, NJ, USA), hydrogen peroxide (p.a. from Merck)

and HF (p.a. from Merck, Darmstadt, Germany) were used for sample digestion. HCl (p.a. Merck, Darmstadt, Germany) was used for digestion of biota samples prior mercury determination.

Only new lab ware material (bottles, vessels, tips, syringes etc.) was employed and it was cleaned thoroughly following a procedure described elsewhere in detail [6]. In order to avoid risks of memory effects from previous experiments, digestion vessels were submitted to a supplementary hot cleaning procedure: first, addition of approximately 10 g concentrated HNO₃ to each vessel; second, microwave treatment at 350 W for 10 min; and third, the vessels were thoroughly rinsed with Milli-Q water.

All sample processing steps were performed in the Marine Environmental Studies Laboratory clean chemical laboratory (class <100 clean room) to reduce the risks of airborne contamination.

The following certified isotopically enriched materials were used to spike the samples: IRMM 622 (¹¹¹Cd), IRMM 632 (⁶⁵Cu), IRMM 6054 (⁶⁸Zn), ERM-AE 640 (²⁰²Hg) from the European Commission, Institute for Reference Materials and Measurements, Geel, Belgium (IRMM), NIST SRM-991 (²⁰⁶Pb) from National Institute for Standards and Technologies, USA and IES-MeHg (²⁰¹Hg enriched monomethylmercury standard) from Innovative Solutions in Chemistry, Oviedo, Spain. For the determination of mass discrimination effects during cadmium ICP-MS measurements, 5 ng g⁻¹ solution was prepared from single element commercial stock standard (Merck, Darmstadt, Germany). For lead, mercury and zinc certified reference materials NIST SRM 981, ERM-AE 639 and IRMM 3702 respectively were used for mass discrimination correction during ICP-MS measurements after appropriate dilution. Stock calibration standard of methylmercury chloride (CH₃HgCl, 1 mg L⁻¹ in 0.5% (w/w) acetic acid, 0.2% (w/w) hydrochloric acid) was obtained from Brooks Rand Laboratories, Seattle, USA. Working standard solutions were prepared gravimetrically weekly by diluting, in pre-cleaned Teflon vials, the stock calibration solution with a solution containing 0.5% (w/w) acetic acid, 0.2% (w/w) hydrochloric acid and Milli-Q water to a range of 5–10 µg/L, calculated as Hg. CH₃HgCl solutions were protected from light. The natural isotopic composition for Cd, Hg, Cu and Zn were taken from IUPAC tables [7].

The anion exchanger AG1X-8 (Bio-Rad, Hercules, USA) was used for matrix separation. AG 1X8 was converted from the chloride form to the nitrate form by shaking it with 2% nitric acid. The ion exchanger was left to settle and the acid was decanted off. This procedure was repeated six times to complete the conversion and to purify the ion-exchange resin.

2.2. Sample

A large quantity of scallop (*P. maximus*) was collected in December 2007 and January 2008 by scuba diving in the "Pertuis Breton," Western France. Organisms were immediately dissected. Soft tissue (adductor, muscle and gonads) were deep-frozen, freeze-dried, ground and sieved. The sieved material with a particle size of less than 40 µm was further homogenised. The homogeneity was performed by mixing the material in a stainless steel rotating mixer for 14 days in a clean atmosphere at a temperature of 20 ± 2 °C and relative humidity of 50%. After checking for the homogeneity of sample material, aliquots of about 8 g were packed into cleaned brown borosilicate glass bottles with polyethylene screw caps and then sealed in plastic bags. The sample material was labelled as IAEA 452 sample.

2.3. Homogeneity characterisation

The within bottle homogeneity was assessed by 15 replicate determinations of the content of investigated trace elements in one bottle. The final measurements were performed by direct solid sampling graphite furnace atomic absorption spectrometry (SS-GF-AAS) under repeatability conditions and in a randomised way in order to be able to separate a potential analytical drift from a trend in the filling sequence. The determination of mercury was done in solid subsamples

Download English Version:

<https://daneshyari.com/en/article/7643063>

Download Persian Version:

<https://daneshyari.com/article/7643063>

[Daneshyari.com](https://daneshyari.com)