



# Determination of cadmium, copper, mercury, lead and zinc mass fractions in marine sediment by isotope dilution inductively coupled plasma mass spectrometry applied as a reference method



Irena Wysocka<sup>a,b</sup>, Emilia Vassileva<sup>a,\*</sup>

<sup>a</sup> International Atomic Energy Agency, Environmental Laboratories, 4 Quai Antoine 1er, 98000, Monaco

<sup>b</sup> Polish Geological Institute-National Research Institute, Rakowiecka 4, 00-975 Warsaw, Poland

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## ABSTRACT

Isotope Dilution Inductively Coupled Plasma Mass Spectrometry (ID ICP-MS) has been applied for the determination of the total mass fractions of five trace elements (Cd, Cu, Hg, Pb and Zn) in marine sediment candidate reference material IAEA-458. Because of the rather complex matrix of the sample and the expected spectral interferences, special care was taken for the validation of the applied method, particularly for its measurement step. Reference isotopic measurements were carried out by quadrupole inductively coupled plasma mass spectrometer (ICP-QMS) or by sector field inductively coupled plasma mass spectrometer (ICP-SFMS). Comparative studies were performed with the aim to examine the degree of equivalence between employed techniques in terms of the high requirements for the quality of reference measurement data.

In order to reduce the number of analytical steps multiple spiking approach was applied. The measurements were performed after a microwave digestion of the blend samples assuring complete isotopic equilibration. Cd was determined after matrix separation by ICP-QMS or ICP-SFMS at low resolution mode. Additionally Cd isotopic ratios were measured by ICP-QMS operated in collision reaction mode, without separation of the matrix. ICP-SFMS at medium resolution and ICP-QMS methods were used for Zn and Cu determinations. Pb isotopic ratios were measured by ICP-QMS operated in standard mode. Because of the low Hg content in the sample Hg isotopic ratios measurements were carried out only by ICP-SFMS.

The entire ID ICP-MS measurement process was described by mathematical equations and the combined uncertainty was estimated. All factors influencing the final results and their uncertainties were systematically investigated. This included procedural blank, moisture content in the sediment material and parameters affecting the blend ratio measurements (instrumental background, spectral interferences, dead time and mass discrimination effects as well as the repeatability of measured isotopic ratios).

The excellent agreement between mass fraction values determined by different measurement techniques proved that all potential problems coming from the complex sediment matrix and the spectral interferences were solved. The consistency of the obtained results confirmed that ICP-QMS can be the method of choice even for the reference measurements, when the element content in a sample is sufficiently high and all steps in the analytical procedure are well described and understood.

The modeling of the analytical process resulted in adequate validation of measurement procedure, establishing traceability of the measurement results and estimating the realistic final expanded uncertainty. The combined uncertainties associated to the obtained mass fractions were considerably small (2% for Cd, Cu, Zn and Pb and to 4.9% in the case of Hg,  $k = 2$ ) and in line with the primary assumption to the reference measurements.

The developed procedure has been successfully applied for the characterisation of the IAEA-458 candidate reference material as well as used in the calculation of the assigned values in the frame of wide world IAEA-458 inter-laboratory comparisons study.

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## 1. Introduction

In the recent years, much attention has been paid to the chemical composition of the marine sediments in the coastal region due to the deterioration of oceanic ecosystems. The industrial and urban activities

\* Corresponding author.

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

have significantly contributed to the increase of element contamination (e.g. As, Cd, Cu, Cr, Hg, Mn, Ni, Pb, Sn, Zn) of marine environment and have directly influenced the coastal ecosystems. The major sources of pollution in the sea waters include municipal wastewater treatment and disposal, urban solid waste disposal, release of harmful concentration of nutrients, storage, transportation and disposal of hazardous waste and activities contributing to the destruction of the coastline and coastal habitats [1–9].

Marine sediments, especially estuarine and coastal, have been used to evaluate water quality because of a higher stability and lower variability of the sediment compared to the water column [5]. However, heavy metals are not fixed permanently in the sediment and the variation of the physico-chemical characteristics of the water column (pH, salinity, temperature, redox potential and the concentration of different organic ligands) can release part of the metal content trapped into the sediment to the water column making them available to living organisms [4,6]. Furthermore, the sediments integrate the concentration of pollutants throughout time and, therefore, this can be useful to study the historic evolution of contamination and to predict its future effects [10–12]. The vertical distribution of some trace elements in sediments can in fact be regarded as an historical record of environmental changes. Various studies have shown that trace element concentration profiles in sediments can be effectively used to assess paleo contamination events with the preindustrial concentration usually considered as the background [13]. Marine sediments are very important for any comprehensive marine monitoring program and the accurate determination of metal mass fractions in sediment cores is an issue of great environment significance. However, the determination of trace elements in marine sediment involves complex analytical methodology and still needs development of relevant analytical protocols. The application of appropriate sediment Certified Reference Materials (CRMs) or Reference Materials (RMs) can help to overcome some methodological problems in the procedures applied by the designated environmental monitoring laboratories [14,15].

For the enforcement of regulations, and for studies at an international level, for example to assess the effects of pollutants on the environment, it is essential that measurements obtained in different laboratories on different occasions are comparable. Comparability can be achieved by making measurements traceable to a common system of a reference and providing measurement uncertainty statement to demonstrate the result's reliability [16–18]. The reliability and comparability of the analytical results, produced in this context are crucial points for management of the environment, taking decisions and meaningful actions in the remediation policy. The element determination in marine matrices typically relies on experimental processes using analytical instruments with a great level of complexity. Despite the improvements in methodologies and instrumentation, unanticipated problems with analysis of complex samples often become evident when the results are obtained by different analytical methods or different laboratories. The simplest way to verify the results for analytical laboratories is to use suitable standards, e.g. the reference materials for method validation, which already offer uncertainty and traceability of their stated quantities. By using reference materials for method validation, laboratories can demonstrate that their measurement results are traceable, or in other words that they are globally comparable [17,18,19].

The preparation of CRMs requires the application of the analytical reference procedures enabling to obtain low expanded uncertainty on the characterization component. The uncertainty budget of a CRM usually consists of three main components, which are contributions from the homogeneity, the stability and the characterization studies. This requires the application of analytical reference procedures enabling expanded uncertainties on the characterization component of the total uncertainty of 1–3% or preferably even below [20,21].

The calibration technique which is suited best for the quantification of trace element mass fractions is undoubtedly isotope dilution mass spectrometry (ID ICP-MS) [22,23].

The isotope dilution is based on a change of an element isotopic composition by adding an isotopic standard containing the same element, but with a distinct isotopic composition, and measuring the magnitude of the change induced. One of the significant advantages over other approaches, is that the analyte recovery does not have to be quantitative providing that isotopic equilibration has been achieved between all of the analyte and added spike material. Isotope dilution offers the possibility to determine major to trace element mass fractions of elements in any matrix, with superior accuracy and precision compared to the external calibration method and is often used for certified reference material characterization [22–26]. In this respect, a sector field mass spectrometer is preferable to quadrupole-based instruments because the resulting flat-topped peak shape obtained at low resolution mode enables a precise isotope intensity measurement to be achieved [26]. It should be noted that, as in the case for other calibration strategies, isotope dilution cannot compensate for random contamination which may occur during sample workup and an intensive blank monitoring is thus always necessary [27]. Moreover, problem of possible spectral interferences should be considered and the appropriate way of their correction has to be applied during ICP-MS measurements [24,25].

The development and validation of an ID ICP-MS based reference procedure for the quantification of Cd, Cu, Hg, Pb and Zn in marine sediment with the objective of achieving an uncertainty target on final results of 1.5–3.0% ( $k = 2$ ) and SI traceable values are described in this study. A systematic assessment of all factors influencing the measurement results as sample-spike isotopic equilibrium, homogeneity study, blend ratio measurements, efficiency of the sample digestion procedure, possible interferences, matrix effects etc. was done throughout the present study. Modeling of the entire measurement process and the use of reference materials, relates each of obtained results to SI units of the mole or the kilogram [19].

## 2. Experimental part

### 2.1. Chemicals and materials

High quality deionized water from Milli-Q system (Millipore, Bedford, MA, USA) was used throughout this work. Ultra-pure 70% HNO<sub>3</sub> (Ultrex®, T. T. Baker, Phillipsburg, NJ, USA), 30.5% H<sub>2</sub>O<sub>2</sub> (p.a. from Merck, Darmstadt, Germany), 40% HF (Suprapur®, Merck, Darmstadt, Germany) and 36% HCl (Ultrex®, T. T. Baker, Phillipsburg, NJ, USA) were used for sample digestion.

Only new lab ware material (bottles, vessels, tips, syringes etc.) was employed and it was pre-cleaned thoroughly following a procedure described elsewhere in detail [28]. In order to avoid risk of memory effects from previous experiments, digestion vessels were submitted to an appropriate cleaning procedure. To reduce the risks of airborne contamination all sample processing steps were performed in the clean chemical laboratory (class < 100).

The following isotopic reference materials were used to spike the samples: IRMM-622 (<sup>111</sup>Cd), IRMM-632 (<sup>65</sup>Cu), IRMM-654 (<sup>68</sup>Zn), ERM-AE640 (<sup>202</sup>Hg) from the European Commission, Institute for Reference Materials and Measurements, Geel, Belgium (IRMM) and NIST SRM-991 (<sup>206</sup>Pb) from the National Institute for Standards and Technologies, USA. For mass discrimination corrections during ICP-MS measurements single element standard solutions of cadmium and copper with natural isotopic composition (from Merck, Darmstadt, Germany) or certified isotopic reference materials (Hg from ERM-AE639, Pb from NIST SRM-981 and Zn from IRMM-3702) were applied.

Working standard solutions were prepared gravimetrically by appropriate dilution of stock standard solutions. The natural isotopic compositions for Cd, Hg, Cu and Zn were taken from IUPAC tables [29]. 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

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