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A rapid acid digestion method with ICP-MS detection for the determination of selenium in dry sediments

J. Pinho, J. Canário [*], R. Cesário, C. Vale

National Institute for Agronomy and Fisheries Research, IPIMAR, Av. Brasília, 1449-006 Lisbon, Portugal

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Abstract

Selenium (Se) is an essential element to organisms with the following peculiarity: at low concentrations anomalies are observed due to the specific biochemical changes, and at higher concentrations it becomes a toxic element. The interval of essential concentrations is in general very narrow. This dual Se behaviour has stimulated the development of numerous analytical methods for its determination in environmental and biological samples.

The baseline concentration of Se in sediments is low (0.05 $\mu g\,g^{-1}$), meaning that very sensitive analytical methods with low detection limits are required. We developed a simple and rapid method based on a pre-treatment/digestion of dry sediment samples with aqua-regia and HCl and quantification by ICP-MS using ^{82}Se. Obtained and certified Se concentrations for international certified reference materials MESS-1, MESS-2, BCSS-1 and 1646a, showed no statistically differences ($\alpha = 0.05$) between obtained and certified values. Low detection limits (approximately 0.03 $\mu g\,g^{-1}$), good repeatability (<1.5%) and recoveries (98–103%) made this method a useful tool for rapid selenium analyses in dry sediments. This method was applied to 50 surface sediments collected in the Tagus estuary giving a rapid image of the distribution of total selenium concentrations in the estuary.

Keywords: Selenium; Analytical method; Estuarine sediments; ICP-MS; Tagus estuary

1. Introduction

Selenium (Se) is an essential element to life [1–3], but at low concentrations it can cause anomalies in organisms and at high concentrations is toxic [4]. For each organism the interval for which Se is non-toxic is generally narrow [1–3]. Concentrations of Se in environmental compartments and biological samples should therefore, be determined with high degree of analytical confidence [5]. Selenium exists at low abundance in the earth's crust 0.05 $\mu g\,g^{-1}$ [6]. Contamination may result from mining, agricultural, petrochemical, and industrial manufacturing operations [7]. Sediments incorporate efficiently Se from anthropogenic sources and play an important role in the Se cycle [8–13].

Several methods have been used in the determination of Se concentrations, including gas chromatography [14], atomic [15] and molecular [16] fluorescence spectrometry, neutron activation analysis (NAA) [17,18], hydride generation (HG) [19,20] and graphite furnace (GF) [13] atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES) [21] and inductively coupled plasma mass spectrometry (ICP-MS) [22,23]. In general, sediment samples go through a pre-treatment procedure before Se quantification in order to solubilize it and to destroy organic matter due to its interaction with Se or chemical reagents used in the analytical procedure [24]. Organic matter is usually oxidised by hot nitric acid (HNO_3), hydrogen peroxide (H_2O_2) or aqua-regia ($3HCl{:}1HNO_3$) [25]. The analytical technique normally used in the determination of Se is the atomic absorption spectrometry (AAS), in particular hydride generation-AAS, although this technique may present kinetic, chemical or spectral interferences related

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[*] Corresponding author. Tel.: +351 213027191; fax: +351 213015948.
E-mail address: jcanario@ipimar.pt (J. Canário).

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with differences in the velocity of H_2Se formation, or the formation of a foam in the reaction vessel [26]. Inductively coupled plasma mass spectrometry (ICP-MS) has been used in the past years [27] with difficulties related to the large number of polyatomic ions interfering with Se isotopes [27,28]. Recent developments in ICP-MS technology like high resolution sector field ICP-MS and reaction/cell collision ICP-MS, improved significantly the selenium measurements capability [29–34]. In spite of the great analytical capability of the ICP-MS technique, this equipment are frequently coupled with different systems of sample introduction like electrothermal vaporization (ETV), liquid chromatography (LC), or hydride generation (HG) [35–37]. These systems are used to improve the efficiency of the sample introduction, better separation of Se from the matrix and to obtain lower detection limits [35].

In this work we propose a simple routine method for determination of selenium in dry sediments based on a digestion with aqua-regia and an HCl acid attack and on ICP-MS technique using the less abundant isotope ^{82}Se.

The improvement of the proposed methodology over the existing methods is the use of the ICP-MS without any introduction system, the minimization of some spectral interferences by a simple and adequate digestion procedure in order to remove the main interfering species, and can therefore, be easily used by a large number of environmental laboratories. This method was applied to 50 surface sediments collected in the Tagus estuary and provided a rapid image of the selenium distribution.

2. Experimental

2.1. Materials and decontamination

All the material used was decontaminated with the following procedure: 5 days soaking in HCl 20% (v/v) and another 5 days in HNO_3 20% (v/v), in closed recipients. Each soaking was followed by an intensive rising with ultra-pure water (Milli-Q). Finally, all material was dried in clean environment (Class 1000).

2.2. Reagents and standards

All samples, reference material and standards were pretreated with HCl 30% (Suprapur grade, Merck), HNO_3 65% (pro analyse and sub-distilled, Riedel de Haën) and ultrapure water Milli-Q. Elemental plasma standard solutions, Specpure®, of Ga, In, V, Cr, Co, Ni, Cu, As, Se, Mo, Ag, Cd and Pb with a concentration of 1000 mg L^{-1} (AlfaAesar) were used to prepare the internal standard (Ga/In solution) and the multi-elemental calibration solution with concentration of 1 mg L^{-1} with 2% (v/v) HNO_3. The internal standard solution was diluted to 100 μg L^{-1}. The calibration standards from multi-element stock solutions, with concentrations of 1, 10, 25, 50, 75 and 100 μg L^{-1}, were also prepared by diluting the multi-elemental calibration solution with 1 mg L^{-1} and adding the internal standard, with Ga/In in a final concentration of 2 μg L^{-1}. Finally a 10 mg L^{-1} AccuTrace™ reference standard quality control sample (QC-S), ICP Multi-element standard solution (AccuStandard Inc.), was diluted to 5 μg L^{-1} adding the internal standard, with Ga/In in a final concentration of 2 μg L^{-1}.

2.3. Samples pre-treatment

For the samples pre-treatment/digestion, approximately 1.5 g of a dry sediment sample was placed in 100 mL borosilicate glass tubes with 2 mL of water and 15 mL of aqua-regia. The moisture was refluxed (70 ± 1.5 °C) twice for 30 min in a heating block and 3 mL of water were added between the procedures. Then 2.5 mL of concentrated HCl was added and the solution heated for 2 h 30 min at 70 ± 1.5 °C. With this step all Se(VI) will be reduced to Se(IV) [18]. After cooling to room temperature the final volume was setup to 50.0 mL with Milli-Q water. Standard reference materials, marine and estuarine sediments MESS-1, MESS-2 and BCSS-1 from National Research Council of Canada and 1646a from U.S. Department of Commerce, National Institute of Standards and Technology, were also digested in order to ensure the accuracy of our procedure.

2.4. Instrumental

The results were obtained on a Thermal Elemental-X Series ICP-MS with a quadrupole reaction system, concentric nebulizer, impact pelletier nebulizer chamber and nickel cones. The operating parameters are shown in Table 1.

2.5. Sample preparation, measurement and calculations

The sample preparation for ICP-MS quantification was based on mass dilution. To approximately 1 mL of the digested sample was added 100 μL of the internal standard and 4 mL of Milli-Q water. In each of the mentioned additions the total weight was measured and the dilution factor was calculated. Two reagents blanks were prepared in the similar way for each 20 samples. For one batch (with ∼25 samples) analysis, two calibrations curves were obtained, one before the sample analysis and other in the end. No significant differences ($p < 0.01$) were found between calibration curve parameters. In every 10 samples a QC-S solution was measured in order to ensure the precision of the determinations (coefficient of variation less than 0.5%). All the solutions were analysed using the acquisition parameter outlined in Table 1. The raw data were exported to an Excel spreadsheet. All data were corrected for internal standard counts. We calculated the Se content in the sediment samples by using the average slope of each calibration curves and using the natural abundance of the ^{82}Se isotope, 8.73% (the Se isotope chosen for these determinations).