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Evaluation of internal standardization for the determination of semivolatile analytes in difficult matrices by simultaneous multielement atomic absorption spectrometry



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ABSTRACT

The aim of the present work is to investigate the use of the internal standardization technique combined with permanent chemical modification for the determination of two semivolatile analytes, such as As and Se, in difficult matrices by electrothermal atomic absorption spectrometry. Bismuth and tellurium have been evaluated as internal standards to minimize matrix effects on the direct determination of selenium and arsenic in sediments, by simultaneous electrothermal atomic absorption spectrometry using graphite tubes with integrated platform, pre-treated with different masses of Zr and Ir as permanent modifier. A Perkin-Elmer SIMAA 6000 simultaneous multielement spectrometer was used to study the correlation between two integrated absorbance signals. Matrix effects were evaluated by calculating the slope ratio between the analytical curve obtained from reference solutions prepared in 1.0% (v/v) HNO₃ and analytical curve obtained from IS additions in matrix solutions. The results showed that Te was the optimal internal standard and 200 μg Zr and 20 μg Ir was the optimal permanent chemical modifier for both analytes. The instrumental limits of detection for As and Se were 1.48 and 1.96 μg L⁻¹ without the use of an internal standard and 0.59 and 0.35 μg L⁻¹ when Te was used as an internal standard, respectively. Relative standard deviations for a sample with matrix effect containing 100 μg L⁻¹ As and 200 μg L⁻¹ Se were 1.3% and 2.3% (*n*=20) using 100 μg L⁻¹ Te, respectively, and for a standard solution sample containing 100 μg L⁻¹ As and 200 μg L⁻¹ Se were 3.0% and 1.2% (*n*=20) using 100 μg L⁻¹ Te, respectively. The accuracy of the proposed method was evaluated by an addition-recovery experiment and by the analysis of different certified reference materials. The recovered values were in the 95–100% range for both analytes.

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1. Introduction

Electrothermal atomic absorption spectrometry (ETAAS) has been widely used for the determination of trace levels of arsenic and selenium in a variety of matrices [1–4] because it offers excellent detection limits with minimum sample consumption, provides accurate measurement and is the most cost-effective among all the other modern techniques. However, this technique suffers from several drawbacks caused by high background levels, the interaction of arsenic and selenium with the heated carbon inside the atomizer and the volatilization losses of arsenic during the pyrolysis step. In order to overcome these difficulties several permanent or non-permanent chemical modifiers methods have

been proposed [2,5,6]. This study sought to propose alternative quantification techniques to solve these major problems in combination with permanent chemical modification. For this reason, the performance of internal standards for the determination of arsenic and selenium was tested by comparing parameters such as correlation coefficient, intercept and slope of matrix-matched standards calibration in order to investigate if the analytes and the chosen internal standard present comparable behavior.

Internal standardization (IS) is an attractive, simple and efficient method to compensate for random and systematic errors in atomic emission or absorption spectrometric analysis. The method is based on the addition of a constant amount of an element to all blanks, standard solutions and matrix samples in an analysis and when the analyte and the internal standard are similarly affected by the experimental and analytical procedure, the ratio of the analyte signal to the internal standard signal is then independent of the perturbation source.

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The main difficulty in applying IS to ETAAS was the unavailability of multi-channel instruments and the scarce knowledge on how to select internal standards properly. Internal standardization in atomic absorption spectrometry was introduced in 1965 by Massmann when he reported on the use of an internal standard to reduce the variability of sample introduction [7]. Since then, there is a lot of progress in the multi-element instrumentation making the internal quantification technique more useful [8,9]. Recently, the introduction of the simultaneous electrothermal atomic absorption spectrometry (SIMAAS) and high-resolution continuum source atomic absorption spectrometry (H-R CS AAS) systems [10–13], has increased the analytical potential of this quantification technique.

There are several articles concerning the application of an IS in SIMAAS for different matrices, including urine, blood, placenta [14], wine [15], whole blood [16], sparkling drinking water [17], nutritionally relevant foods [18], urine [19], milk [20], different reference solutions [21], and vinegar [22]. Among them there are 3 articles which are referred in the use of arsenic as internal standard for the determination of Se [17,18,20] and one which is referred in the use of Co as internal standard for the determination of As and Se [19]. In those researches the most important advantage of IS was the possibility to compensate for both random and systematic errors and to improve the precision and the accuracy in comparison to the method of addition. Internal standard also increases the lifetime of the graphite tube up to 40% and corrects the errors that cause the variations of the experimental conditions [17]. It should be emphasized that this is the first study concerning the use of Te and Bi as internal standards for the determination of As and Se by SIMAAS in heavy matrix samples, in the presence of Zr–Ir as permanent chemical modifier. Pd–Mg was also used as a chemical modifier for comparison reasons. The performance of the proposed method was checked by the analysis of different certified reference materials (CRM) and the analytical characteristics were compared with those obtained without IS.

2. Materials and methods

2.1. Instrumentation

A Perkin-Elmer SIMAA-6000 simultaneous multielement atomic absorption spectrometer with a longitudinal Zeeman-effect background correction system, equipped with a transversely-heated graphite atomizer, THGA, and an AS-72 autosampler were used. Electrodeless discharge lamps (EDL) were used for As (193.7 nm and slit 0.7 nm), Se (196.0 nm and slit 0.7 nm), and Te (214.3 nm and slit 0.7 nm) respectively, and a hollow cathode lamp was used for Bi (223.1 nm and slit 0.7 nm) and they were operated according to the conditions recommended by the manufacturer. Atomic signals were measured in peak area mode. It should be pointed out that the experiments were carried out using the stabilized temperature platform furnace (STPF) conditions and Zeeman-effect background correction. The digestions were performed on a microwave oven MARS X-Press (CEM Corporation).

2.2. Reagents, analytical solutions and samples

Ultrapure water (18.2 M Ω cm at 25 °C) from a Millipore Direct-Q-UV water purifier (Millipore) obtained using a Milli-Q system (Millipore). All solutions were prepared with Suprapur grade nitric acid (Merck, Darmstadt, Germany). Argon was of 99.999% purity.

The standard solutions containing 100 and 200 $\mu\text{g L}^{-1}$ As and Se plus 100 and 200 $\mu\text{g L}^{-1}$ Te and Bi, respectively, were daily prepared by appropriate dilution of 1000 mg L^{-1} As, Se, Te and

Bi stock standard solutions and acidified with nitric acid to 1% (v/v). The autosampler washing solution was de-ionized water acidified with 1% (v/v) HNO_3 .

The palladium/magnesium solution containing 5 $\mu\text{g Pd}$ and 3 $\mu\text{g Mg}$ was prepared by appropriate dilution of 10 g L^{-1} Pd (Merck) in HNO_3 and 1 g L^{-1} Mg in 1% (v/v) HNO_3 (High Purity Standards). The zirconium and iridium solutions were prepared by appropriate dilution of 1000 \pm 5 $\mu\text{g mL}^{-1}$ $\text{ZrOCl}_2 \cdot 2\text{H}_2\text{O}$ in 0.5% HNO_3 (High Purity Standards, Charleston, SC), and 1000 $\mu\text{g mL}^{-1}$ of Ir in 2% HCl (High-Purity Standards) with ultra-pure water. Likewise, HNO_3 65%, HCl 36% and HF 40% Suprapur[®] (Merck) were used for the digestion of the samples.

For quality assurance and accuracy estimation, the certified reference material BCR-402 (white clover with certified reference values of 0.093 \pm 0.010 mg As kg^{-1} and 6.70 \pm 0.25 mg Se kg^{-1}) was used. This material had been certified by Community Bureau of Reference and the certificate has been revised by the Institute for Reference Materials and Measurements. Furthermore, a river sediment test item used for an interlaboratory proficiency test organized by the project “Training courses on Analytical Quality Control and method validation in support to the Water Framework Directive (TAQC-WFD)” with assigned values for As equal to (24.1 \pm 2.9) mg kg^{-1} ($n=27$) was used as an in-house reference material.

2.3. Analytical procedure

All glassware and polypropylene bottles were cleaned with detergent solution, soaked in 10% (v/v) HNO_3 for 24 h, rinsed with Milli-Q water and stored into closed locker. 0.2000 g of the homogenized reference material BCR-402 was weighted into the Teflon vessels and 5 mL of 65% HNO_3 were added and the samples were left for 1 h at room temperature. Then the samples were digested using the MARS X-Press (CEM Corporation) microwave oven with a preselected program (first stage at 1600 W and 165 °C for 2 min; the second stage at 1600 W and 175 °C for 8 min) and then diluted to a final volume of 20 mL with ultrapure water. The river sediment sample was pre-treated following the same procedure as described above but 6 mL HF (40%) and 1 mL of a mixture of HNO_3 (65%):HCl (36%) 1:3 (v/v) were added.

The pyrolysis and atomization temperature curves were obtained by spiking 20 μL of a digested sample solution and 20 μL of each standard solution in order to investigate the electrothermal behavior of those elements. For this purpose, the elements were arranged in groups: (1) As (analyte), Bi (IS), (2) As (analyte), Te (IS), (3) Se (analyte), Bi (IS) and (4) Se (analyte), Te (IS). These curves were obtained in the presence of the selected chemical modifiers (5 $\mu\text{g Pd}$ and 3 $\mu\text{g Mg}$ or Zr and Ir as permanent modifiers in different mass combinations).

Repeatability experiments were carried out to verify the efficiency of the elements tested as IS using a diluted sample with the same spiked concentration. Twenty consecutive measurements of this solution in the presence of the optimum chemical modifier were simultaneously obtained for As, Se and one IS candidate. For all elements, the absorbance values were normalized with respect to the first result of the consecutive measurements ($n \sim 20$).

$$\text{Normalized signal} = \text{PA}_i / \text{PA}_{\text{mean}} \quad (i = 20)$$

Correlation graphs were obtained by plotting the normalized absorbance values of the IS (axis Y) vs the normalized absorbance values of the analyte (axis X) [23]. The comparison of the correlation graphs was done from the linear regression parameters (correlation coefficient, intercept and slope). In addition, the comparison of As and Se relative standard deviation (RSD) with and without IS correction was also used to choose the most

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