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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) HNO_3 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.

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 MΩ 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 μg L^{-1} As and Se plus 100 and 200 μg 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 μg Pd and 3 μg 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 ± 5 μg mL^{-1} $ZrOCl_2{\bullet}2H_2O$ in 0.5% HNO_3 (High Purity Standards, Charleston, SC), and 1000 μg 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 ± 0.010 mg As kg^{-1} and 6.70 ± 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 ± 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 μg Pd and 3 μg 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 ($n \sim 20$).

$$\text{Normalized signal} = PA_i/PA_{\text{mean}} \; (i=20)$$

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 appropriate element to be adopted as the IS. Correlation graphs were constructed by plotting the peak area (PA) or the response factor F (PA_{anal}/PA_{IS}) against the different concentrations of the analytes in matrix and standard solutions in order to compare the calculated recoveries with or without the use of an IS.

The developed method was validated. Quantification was performed with calibration curves constructed from integrated absorbance measurements and prepared by spiking 20 μL of different aqueous or matrix standard solutions of As or Se. The limits of detection (LODs) and quantification (LOQs) were calculated from the calibration curve. Precision and accuracy were also estimated from the matrix-matched calibration curves. Finally, the graphite coating stability was also examined for optimum mass combination of the permanent modifiers.

3. Results and discussion

3.1. Criteria for selection of IS

The major difficulty associated with the application of IS quantification technique in simultaneous atomic absorption spectrometry is the investigation for a suitable element to serve as internal standard. An internal standard (IS) should be chosen based on accepted IS selection criteria such as (a) the IS should not be present in the sample matrix and (b) the IS should have similar physico-chemical parameters to the analyte (Table 1). The most important of those parameters are (a) similar kinetic properties, (b) similar pyrolysis and atomization temperatures, (c) similar vaporization and dissociation heat for their oxides and chlorides, (d) similar activation energy for element atomization from respective oxides and (e) similar transient peak appearance. The appropriate concentrations of the internal standards were found as follows: the calibration curves of As, Se and the internal standards were constructed by at least 5 standard solutions in the linear range of all analytes and internal standards, and afterwards the correct concentration of the internal standard was the one that provided integrated absorbance of equal to the integrated absorbance of the analyte in the middle of the linear range of the analyte.

3.2. Modifier selection

There are many studies based on the permanent modifiers and varieties of element combinations have been tested [6,24,25]. The effect of various amounts of Zr and Ir ranging from 100 to 200 μg and 5 to 20 μg, respectively, was tested as permanent modifier and the results were compared to the Pd (5 μg)+Mg (3 μg) chemical modifier. The heating program for coating the integrated platform of a THGA with Zr followed by Ir was demonstrated by E.C. Lima et al. [6] and modified by Kalantzis et al. [26].

Pyrolysis and atomization curves were established to determine the optimum pyrolysis and atomization temperatures for each modifier. This study was carried out by pairs using As or Se in standard or matrix solutions containing 100 $\mu g\,L^{-1}$ and 200 $\mu g\,L^{-1}$, respectively spiked with 200 $\mu g\,L^{-1}$ Bi or 100 $\mu g\,L^{-1}$ Te. All results were based on peak area measurements. In the presence of the permanent Zr/Ir modifier, T_{pyr} for Se could be raised up to 1000 °C compared to the temperature achieved when Pd+Mg was used as chemical modifier (600 °C). These temperatures are within the optimum temperature range demonstrated by E.C. Lima et al. who used 250 μg W and 200 μg Rh for the determination of Se [6]. Similar T_{pyr} was also achieved for As (1100 °C) for all the different tested modifiers. The atomization temperatures (T_{at}) were 2200 °C for Se and 2000 °C for As. E.C. Lima et al. suggested that the optimum pyrolysis temperatures for the determination of As were 1100–1200 °C when used single noble metal permanent modifiers as well as mixed tungsten plus noble metals, whereas the achieved T_{atom} was 2300 °C [24]. By using 200 μg Zr together with 20 μg Ir as permanent modifier it was noticed that the atomic absorption (AA) profiles for all the elements were sharper and the background absorbance was decreased, significantly (Fig. 1). From the obtained results it seems that the optimum modifier mass for these determinations was the combination of 200 μg Zr and 20 μg Ir. This is also supported from the findings of Kalantzis et al. [26] who developed a method for the determination of As in leachate samples from sanitary landfills by ETAAS [26]. According to other works concerning the determination of As and Se using different permanent modifiers, there are many similarities between the achieved characteristic masses which are fluctuate around 40 pg for As and 50 pg for Se in standard solutions [6,24,26].

Table 1
Physical and chemical parameters for the elements under study.

Parameter	*As*	*Se*	*Bi*	*Te*
Wavelength (nm)	193.7	196.0	223.1	214.3
Atomic number Z	33	34	83	52
Melting point (K)	814	217	271	452
Boiling point (K)	613	680	1420	1087
ΔH_{vap} ME (g)	72.3	54.3	49.5	47.0
$D^{o}_{298\,K}$ MO ($kJ\,mol^{-1}$)	481	464.8	337.1	376.1

3.3. Electrothermal behavior

Using the heating program shown in Table 2, the electrothermal behavior of As, Te, Bi and Se in different matrices was studied in a THGA tube containing an integrated platform pretreated with 200 μg Zr together with 20 μg Ir as permanent modifier. Pyrolysis curves were also constructed by plotting the ratio of analyte peak area to internal standard peak area as x values with the pyrolysis temperature as y values, for all tested pairs. The optimum pyrolysis temperature in standard solutions was 1200–1300 °C. However, when Bi was tested as a potential internal standard the optimum pyrolysis was 700 °C for both analytes. For higher temperatures, there is an abrupt drop in Bi absorbance. It seems that using Te as IS better thermal stability was achieved for both analytes in the temperature range 400–1200 °C, whereas thermal stability of Bi was adversely affected in the presence of matrix (Fig. 2). Better signal profiles and more repeatable measurements for As and Se in all matrices were obtained at the atomization temperatures of 2000 °C and 2200 °C, respectively.

3.4. Efficiency of tellurium and bismuth as IS for Se and As

The efficiency of tellurium and bismuth as ISs was examined using peak area (PA) and response factor (F) correlation graphs between matrix effect samples and standards to compare the variation of the calculated recoveries among the different quantification techniques.

Calibration curves for the different matrices were established using the ratio analyte absorbance to IS absorbance ($PA_{analyte}/PA_{IS}$) vs analyte concentration, and typical linear correlations of $r \geq 0.99$ were obtained. The recoveries were calculated from the analytical curves, plotting the analyte absorbance or factor F in standard solutions and the analyte absorbance or the factor F in matrix solutions (PA_{matrix} vs $PA_{standard}$ and F_{matrix} vs $F_{standard}$). The use of internal standard increased the recovery as it extracted from the increase of curve's slope. More precisely, Te contributed considerably to the improvement of the calculated recovery for both analytes and for both chemical modifiers, whereas Bi appeared

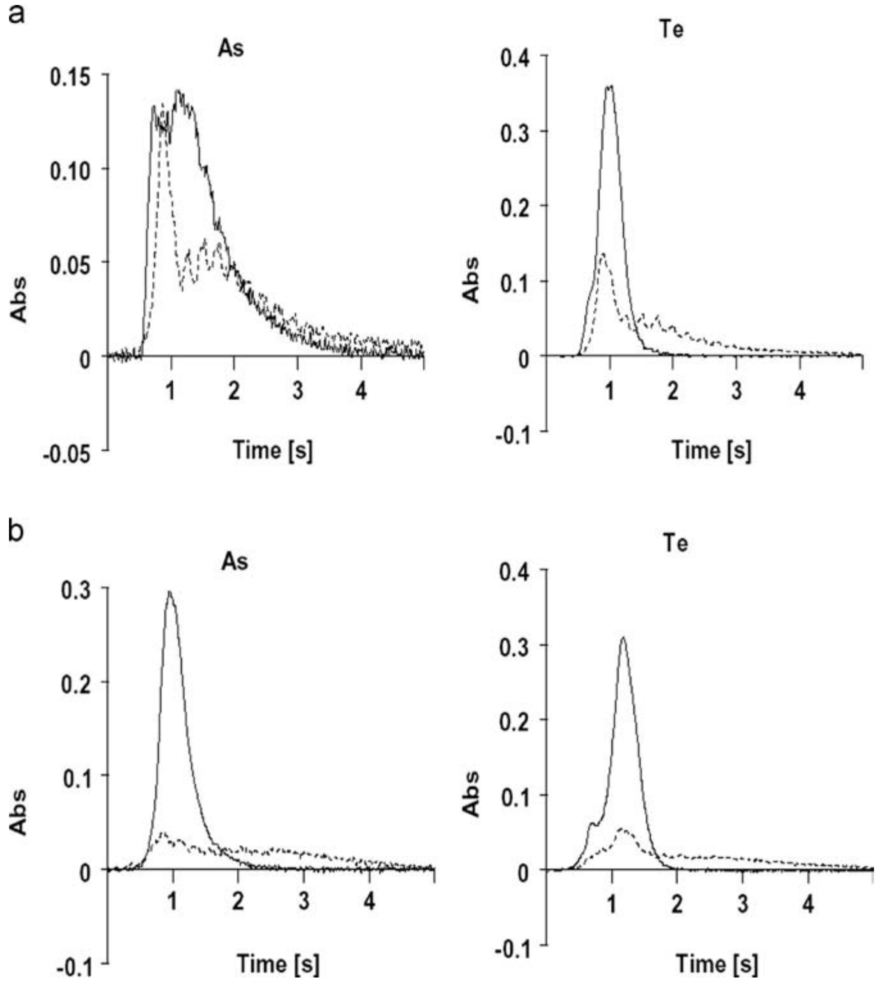

Fig. 1. Atomic absorption peak profiles (—) and background absorption (……) with different modifiers in matrix effect sample (a) Pd 5 µg+Mg 3 µg and (b) Zr 200 µg+Ir 20 µg.

Table 2
THGA heating program used for the SIMAA 6000 spectrometer.

Step	*As T* (°*C*)	*Se T* (°*C*)	*Ramp time* (*s*)	*Hold time* (*s*)
Dry	110	110	1	25
Dry	130	130	15	25
Pyrolysis	1100	1000	10	20
Atomization	2000	2200	0	5
Clean	2300	2300	1	3

to have a less repeatable attitude for the different modifiers and for both analytes (Table 3).

The efficiency of Bi and Te as internal standards for Se and As determination in different matrices was also evaluated by means of correlation graphs as suggested by Mermet and Ivaldi [23]. The correlation graph was plotted from the normalized absorbance signals (n=20) of internal standard (axis y) vs analyte (axis x). Twenty consecutive measurements of a matrix solution containing 200 µg L^{-1} Se or 100 µg L^{-1} As spiked with 100 µg L^{-1} Te or 100 µg L^{-1} Bi, in a new THGA tube containing an integrated platform pretreated with 200 µg Zr together with 20 µg Ir as permanent chemical modifier were performed. The absorbance values were normalized with respect to these consecutive measurements. Parameters such as correlation coefficient, intercept and slope were evaluated in order to verify the resemblance between simultaneous measurements obtained for the analyte and internal standard.

Plots of normalized absorbance of As and Se vs normalized absorbance of Te were constructed in order to obtain the correlation graphs in standard solutions as well as in solutions with matrix effect. The linear coefficient between normalized absorbance for As and Te were $PA_{As}=0.8439+0.1561PA_{Te}$, $r^2=0.0317$ for matrix effect and $PA_{As}=0.2805+1.2805PA_{Te}$, $r^2=0.3469$ for standard solutions, and for Se were $PA_{Se}=0.4977+0.5023PA_{Te}$, $r^2=0.5452$ and $PA_{Se}=0.6199+0.3801PA_{Te}$, $r^2=0.4157$. These results denoted that SIMAAS measurements do not show any drift.

3.5. *Method validation*

Calibration curves were constructed using Te as an IS for all the different matrices. Curves in the 10–50 µg L^{-1} As and 20–100 µg L^{-1} Se concentration range were established using the ratio analyte absorbance to IS absorbance vs analyte concentration, and typical linear correlations of $r \geq 0.99$ were obtained.

The instrumental LODs (µg L^{-1}) were calculated from the equation $\mathrm{LOD_{instr}}$ (µg L^{-1})=$3.3 \times S_{BL}/b$, where S_{BL} was the standard deviation of 10 blank determinations and the method LODs were calculated from the equation $\mathrm{LOD_{meth}}$ (ng g^{-1})=$\mathrm{LOD_{instr}}$ (ng mL^{-1})$\times$ $\mathrm{V_{dilution}}$ (mL)$\times$ m (g)$^{-1}$. For the As determination the LODs without and with the use of Te as internal standard were 1.48 µg L^{-1} or 148 ng g^{-1} and 0.59 µg L^{-1} or 59 ng g^{-1}, respectively. Finally, the LODs for the Se determination without and with the use of Te as internal standard were 1.96 µg L^{-1} or 196 ng g^{-1} and 0.35 µg L^{-1} or 35 ng g^{-1}, respectively. The results

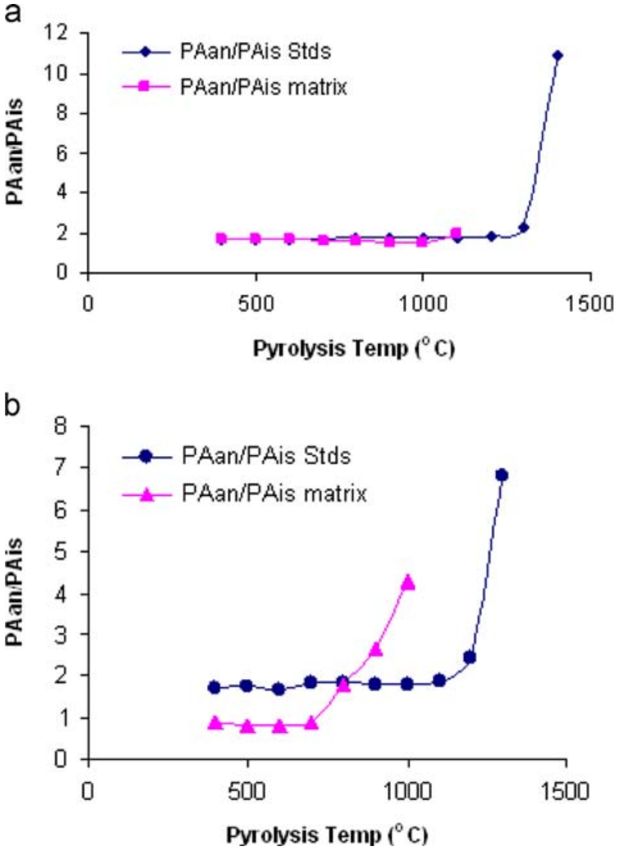

Fig. 2. Ratio of analyte area (PA_{an}) to internal standard area (PA_{is}) in correlation to pyrolysis temperature for (a) Se–Te and (b) Se–Bi. Using Te as IS better thermal stability was achieved for both analytes in the temperature range 400–1200 °C, whereas thermal stability of Bi was adversely affected in the presence of matrix.

Table 3
Slopes of the analytical curves ($n=5$), plotting the As and Se peak area measurements of different concentrations in aqua solutions as x values with the respective in matrix solutions as y values with and without the use of an internal standard in different modifiers.

Analyte-IS	*Chemical modifier*	*Slope based on PA measurements*	*Slope based on response factor F measurements*
As–Te	Pd+Mg	0.789 (±0.087)	0.861 (±0.085)
	Zr+Ir	0.723 (±0.052)	0.869 (±0.072)
As–Bi	Pd+Mg	0.684 (±0.051)	1.174 (±0.091)
	Zr+Ir	0.556 (±0.018)	0.370 (±0.013)
Se–Te	Pd+Mg	0.917 (±0.056)	0.949 (±0.034)
	Zr+Ir	0.470 (±0.016)	0.868 (±0.010)
Se–Bi	Pd+Mg	0.533 (±0.016)	0.763 (±0.023)
	Zr+Ir	0.714 (±0.041)	0.406 (±0.040)

show that the use of Te as internal standard improves significantly the calculated LODs and provide comparable values than other reported in the literature and concerning the determination of the same analytes by other techniques, such as hydride generation atomic fluorescence spectrometry (HG-AFS) [27], hydride generation inductively coupled plasma mass spectrometry (HG-ICP-MS) [28], inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) [29,30]. Moreover, in view of the content levels of As and Se in plant and sediment samples, it can be concluded that the limits of detection and quantification presented in this study are fit for their purpose.

The (%) relative standard deviations (RSD) for a matrix solution containing 100 μg/L As and 200 μg/L 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 respective values when no internal was used were 4.1% and 4.2% ($n=20$) for a matrix solution containing 100 μg/L As and 200 μg/L Se, and 4.0% and 3.2% standard solution sample containing 100 μg L^{-1} As and 200 μg L^{-1} Se, respectively. These values are lower than the crucial values, as described by the Horwitz equation [31].

For quality assurance and accuracy estimation, different certified or in house reference materials were used. Using Te as the internal standard, the results of the analysis of the certified reference material BCR-402 for As (measured value 0.090 ± 0.014 mg As kg^{-1}, $n=6$; certified value 0.093 ± 0.010 mg As kg^{-1}, $n=15$) and Se (measured value 6.30 ± 0.45 mg Se kg^{-1}, $n=6$; certified value 6.70 ± 0.25 mg Se kg^{-1}, $n=15$) were in agreement with the certified values at a 95% confidence level. Moreover, the method was applied for the determination of As in a reference river sediment sample used for the proficiency test organized by "Training courses on Analytical Quality Control and method validation in support to the Water Framework Directive (TAQC-WFD)". The z-score value was 0.34, which is a highly acceptable value ($-2<z<2$). The (%) recoveries were also estimated by spiking different concentrations of the analyte and following the whole pre-treatment procedure. The (%) calculated recoveries were 95.8% for As and 99.9% for Se with satisfactory (%) RSD values.

3.6. *Coating stability experiment*

Coating stability experiment was carried out in order to investigate the Zr and Ir (200 μg and 20 μg) coating life time. 550 consecutive measurements of a matrix solution containing a known concentration of As and Te were performed. After these 550 firings, the THGA tube was destroyed. However, even at 530 firings, the absorbance for both elements was not decreased more than 10% of the initial absorbance value (Fig. 3). Afterwards, 20 μg

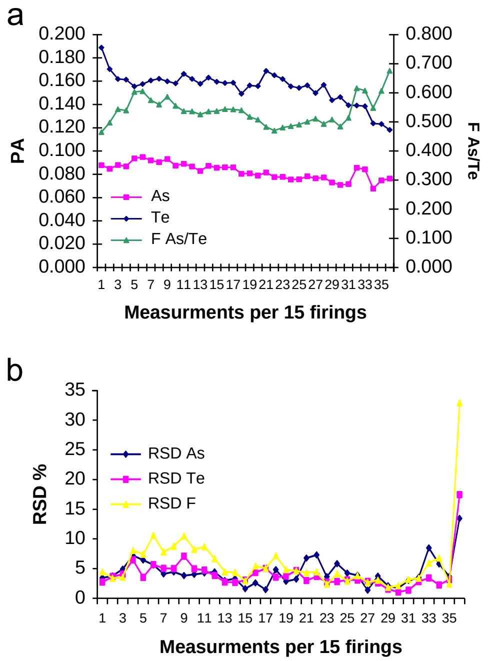

Fig. 3. Stability experiment for Zr+Ir coating: (a) Stability chart for peak area (PA) and response factor (F), (b) Stability chart for (%) RSD values.

of Ir were recoated in the THGA tube. In Meeravali et al. work [25], who used the same modifier and conditions, the coating lasted up to 500 firings, when they analyzed slurries samples, but it had to be recoated twice after 225 and 400 firings. The conclusion that was exported from this test was that the coating remained stable until the destruction of the graphite furnace.

4. Conclusions

Using Te as IS, satisfactory accuracy, repeatability and low LODs were achieved. More precisely, (%) recoveries had been significantly improved and they ranged from 95% to 105%. This means that Te can be used as a potential internal standard for the determination of As and Se by simultaneous electrothermal atomic absorption spectrometry in difficult matrices. Moreover, the Zr–Ir permanent modifier proved to be an appropriate modifier for the determination of As and Se, because it provided accurate and precise measurements, decreased the analysis time and cost, and increased the coating lifetime.

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