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Use of the internal standardization for difficult sampling by graphite furnace atomic absorption spectrometry

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Abstract

This work shows the potentiality of As as internal standard to compensate errors from sampling of sparkling drinking water samples in the determination of selenium by graphite furnace atomic absorption spectrometry. The mixture $Pd(NO_3)_2/Mg(NO_3)_2$ was used as chemical modifier. All samples and reference solutions were automatically spiked with $500\,\mu g\,l^{-1}$ As and 0.2% (v/v) HNO_3 by the autosampler, eliminating the need for manual dilutions. For $10\,\mu l$ dispensed sample into the graphite tube, a good correlation ($r = 0.9996$) was obtained between the ratio of analyte absorbance by the internal standard absorbance and the analyte concentrations. The relative standard deviations (R.S.D.) of measurements varied from 0.05 to 2% and from 1.9 to 5% ($n = 12$) with and without internal standardization, respectively. The limit of detection (LD) based on integrated absorbance was $3.0\,\mu g\,l^{-1}$ Se. Recoveries in the 94–109% range for Se spiked samples were obtained. Internal standardization (IS) improved the repeatability of measurements and increased the lifetime of the graphite tube in ca. 15%.

Keywords: Internal standardization; Graphite furnace atomic absorption spectrometry; Complex matrices; Sparkling waters

1. Introduction

Flame (FAAS) and electrothermal (ETAAS) atomic absorption spectrometry are considered well-established analytical techniques and have been used in large-scale routine analysis [1,2]. Nevertheless, the quality of results can be usually impaired by random and systematic errors [3].

Internal standardization (IS) is an attractive, simple, and efficient strategy to compensate errors in atomic absorption spectrometry [4]. In a recent review [5], 11 articles were found on applications of IS in AAS for different matrices, including steel [6], zinc die cast [7], steel, steel alloys, and cement [8], steel, steel alloys, blood, and cement [9], natural waters [10], serum [11], blood [12], blood, urine, and placenta [13], wines [14]. From these, only three papers are related to GFAAS [9,10,14].

The fundamental principle of IS in chemical analysis is based on the addition of a known and fixed amount of one or more elements used as internal standards to all blanks, reference solutions, and samples. For elements similarly affected by changes in experimental conditions, use of the ratio of the analyte signal to the internal standard signal may compensate variations in the single signal of the analyte.

Aqueous, organic, emulsion or slurry samples presenting heterogeneous characteristics may change the amount of analyte inside the pipette of auto sampler of spectrometer. So, the mass of analyte dispensed into the atomizer will change accordingly to the portion of the sample volume. As a consequence, the repeatability and/or accuracy of measurements may depreciate. These drawbacks may be efficiently circumvented by adopting IS.

The benefits of internal standardization to compensate errors due to difficult sampling are illustrated here for samples containing high amount of gaseous bubbles. As example, arsenic was evaluated and used as internal standard for selenium determination in sparkling drinking water samples by graphite furnace atomic absorption spectrometry. The performance of the proposed method was checked after analyzing a sort of sparkling drinking water samples.

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2. Experimental

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, (Perkin-Elmer Part No. BO 504033) and an AS-72 autosampler were used. Electrodeless discharge lamps (EDL) were used for As (193.7 nm and slit 0.7 nm; Perkin-Elmer Part No. N 3050605) and Se (196.0 nm and slit 0.7 nm; Perkin Elmer Part No. N 305-0572), respectively, and they were operated according to the conditions recommended by the manufacturer. Atomic signals were measured in peak area mode. The EDL lamps were operated applying 380 and 290 mA for As and Se, respectively. High-purity argon (99.999%, White Martins, Brasil) was used as the purge gas. It should be pointed out that the experiments were carried out using the stabilized temperature platform furnace (STPF) conditions [2] including Zeeman-effect background correction.

2.2. Reagents, reference solutions, and samples

High-purity de-ionized water (resistivity 18.2 MΩ cm) obtained using a Milli-Q system (Millipore) was used throughout. All solutions were prepared with Suprapur® grade (Merck) nitric acid.

Reference solutions were daily prepared by dilution of the 1000 mg l^{-1} Se and As stock solutions (Normex®, Carlo Erba). All samples and reference solutions were automatically spiked with 10 μg l^{-1} As and 0.2% (v/v) HNO_3 by the autosampler, eliminating the need for manual dilutions.

The autosampler washing solution was composed by 0.1% (v/v) of Triton® X-100 in 0.2% (v/v) HNO_3. Chemical modifier solutions of 0.1% (m/v) Pd and 0.1% (m/v) $Mg(NO_3)_2$ were applied, both prepared from 1% (m/v) stock solutions (Perkin-Elmer Part No. BO 190635, Pd; Perkin-Elmer Part No. BO 190634, Mg).

Sparkling drinking water samples were purchased at a local market in Araraquara city, São Paulo State, Brazil.

2.3. Selected parameters for evaluating internal standardization performance

As palladium nitrate plus magnesium nitrate is the combined modifier recommended for several analytes in different matrices [15], the electrothermal behavior of Se and As were investigated in 0.2% (v/v) HNO_3 with and without 5 μg Pd plus 3 μg Mg. For each measurement, 10 μl of the reference or sample solution, 5 μl Pd, and 3 μl Mg solutions were sequentially dispensed into the tube. Three replicates of each reference solution and sample were carried out. The optimized heating program used for simultaneous measurements is presented in Table 1. This program was used to study the electrothermal behavior of Se and As by means of pyrolysis and atomization temperature curves. This study employed the following solutions: aqueous solutions containing 25 μg l^{-1} Se plus 10 μg l^{-1} As in 0.2% (v/v) HNO_3, sparkling drinking water spiked with 25 μg l^{-1} Se plus 10 μg l^{-1} As in 0.2% (v/v).

Table 1
Heating program of the graphite tube atomizer

Step	Temperature (°C)	Time (s)		Ar flow (ml min^{-1})
		Ramp	Hold	
1	110	1	30	250
2	130	15	30	250
3	1200	10	20	250
4	2100	0	5	0 (read)
5	2550	1	3	250

The influence of variation of the injected sample volume on the absorbance signals of Se and As was investigated by dispensing 5, 10, 15, and 20 μl of sample (25 μg l^{-1} Se and 10 μg l^{-1} As) plus 8 μl of modifier into the atomizer.

The influence of the abrasion of the graphite tube platform on integrated absorbance of Se and As was studied by successive absorbance measurements of 25 μg l^{-1} Se and 10 μg l^{-1} As in sparkling drinking water in 0.2% (v/v) nitric acid until the rupture of the tube.

The influence of the sample matrix on Se and As absorbance signals was investigated by evaluating the accuracy and the precision of addition-recovery experiments and analysis of ten sparkling drinking water samples with and without IS. All samples were spiked with 25 μg l^{-1} Se and 500 μg l^{-1} As and three replicates were performed for each sample. The absorbance signal corresponding to each original sample was adopted as the blank. It should be mentioned that although Se concentration is usually lower than limit of detection for most samples, sparkling waters were only the type of samples selected to illustrate errors by sampling difficult samples by the auto sampler of the AA spectrometer.

3. Results and discussion

3.1. Electrothermal behaviors of selenium and arsenic

The electrothermal behavior of As and Se in diluted nitric acid (0.028 mol l^{-1}) and sparkling drinking water without modifier and in the presence of the mixture $Pd(NO_3)_2$ plus $Mg(NO_3)_2$ was evaluated. The amount of modifier (5 μg Pd plus 3 μg Mg) was added to a 10 μl sample volume. Pyrolysis and atomization curves were employed to determine the optimal pyrolysis and atomization temperatures with and without modifiers. For this study, 0.028 mol l^{-1} HNO_3 solution and sample were spiked with 25 μg l^{-1} Se and 25 μg l^{-1}

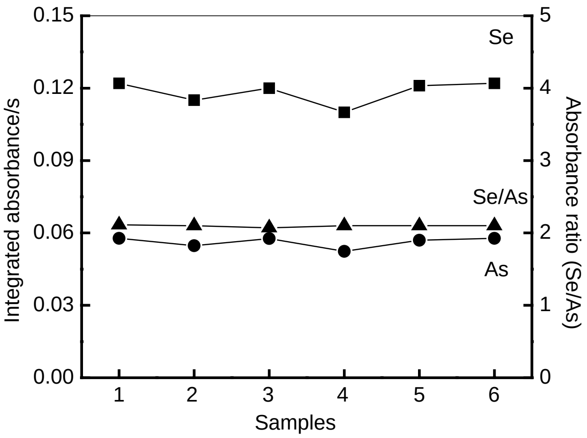

Fig. 1. Effect of the sample matrix on absorbance for Se and As, and corrected curve by internal standardization (Se/As). Spike signals in sparkling mineral water refer to 25 $\mu g\,l^{-1}$ Se and 10 $\mu g\,l^{-1}$ As.

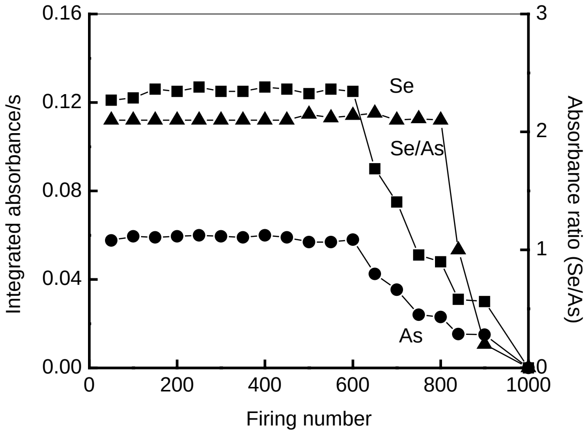

Fig. 2. Effect of the graphite tube abrasion on absorbance. Integrated absorbance refers to a reference solution containing 25 $\mu g\,l^{-1}$ Se and 10 $\mu g\,l^{-1}$ As in diluted gas water (1 + 1) in 0.2% (v/v) HNO_3.

As. The mixture Pd/Mg was a good modifier to thermal stabilization of As and Se up to 1600 and 1400 °C, respectively. It should be pointed out that absorbance for selenium abruptly drops for temperatures greater than 1400 °C. The selected pyrolysis temperature may be lower than 1400 °C in order to avoid Se losses when small variations in the pyrolysis temperature occur. Hence, 1200 °C was the pyrolysis temperature selected for further experiments. The atomization temperatures for As and Se in acidified water sample (0.028 $mol\,l^{-1}$ HNO_3) were within 2000–2200 °C. In this interval best signal profile and repeatability of measurements were obtained. So, the atomization temperature was fixed at 2100 °C.

3.2. *Effect of sample matrix on the absorbance signals of Se and As*

The correlation between Se and As absorbance associated to different sparkling drinking water samples is shown in Fig. 1. Signals correspond to the samples spiked with 25 and 10 $\mu g\,l^{-1}$ Se and As, respectively, and simultaneous detection of both elements. It was observed that the behavior of the absorbance for Se and As varied similarly for different samples. This suggests the feasibility of the use of arsenic as internal standard for Se (or vice-versa).

3.3. *Effect of variation of the injected sample volume*

Taking into account the influence of the variation of the injected sample volume on the repeatability of absorbance signals, measured absorbance of Se and As increased proportionally with injected sample volume (5–20 μl) of a reference solution containing 25 and 10 $\mu g\,l^{-1}$ Se and As, respectively. When internal standardization was applied, the ratio A^{Se}/A^{As} was independent of the injected volume. As a consequence, sampling of gaseous bubbles together with aqueous phase by the mechanical pipette of the auto sampler can be corrected by using internal standardization. Typical relative standard deviations (R.S.D.) of 20 successive measurements based on integrated absorbance observed for 25 and 10 $\mu g\,l^{-1}$ Se and As in drinking water with and without internal standardization varied up to 2 and ≤5%, respectively.

3.4. *Effect of the graphite tube abrasion on the absorbance signals*

Successive firings of the graphite tube cause abrasion of the surface. Among disadvantages of the tube deterioration are shorter lifetime, poor peak profile, and unsuitable sensitivity, accuracy, and precision. It is a good practice to replace the tube when either the integrated absorbance value falls ca. 20% below the original value or the relative standard deviation is higher than 10%. Successive simultaneous measurements of absorbance of Se and As could be done up to ca. 600 firings without adopting the internal standardization approach for corrections (Fig. 2). However, the lifetime of the tube was extended to 850 firings when the measurements were based on the ratio A^{Se}/A^{As}. This implies in a 40% increase of the tube lifetime.

3.5. *Figures of merit*

Accuracy and precision studies were carried out using addition-recovery tests for 10 sparkling drinking water samples. Selenium determinations in water samples carried out with and without internal standardization are shown in Table 2. Applying a paired *t*-test it was observed that all results are in agreement at a 95% confidence level. It is interesting to point out that relative standard deviations were 0.05 to 2.0% and 1.9 to 5.0% with and without internal standardization, respectively ($n = 12$, sample spiked with 25 $\mu g\,l^{-1}$ Se). Good recoveries (94–109%) for Se spikes were obtained.

Table 2
Comparative recovery results ($n = 3$) for sparkling water samples with and without IS

Sample	With IS		Without IS	
	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)
1	106	0.05	97	3.0
2	99	1.2	100	3.5
3	97	1.3	97	5.0
4	94	2.0	80	2.8
5	109	0.8	93	2.5
6	103	1.0	100	1.9

4. Conclusions

Internal standardization can be an alternative tool to solve, or circumvent to some extent, problems of sampling associated to heterogeneous solutions (in this case, solutions containing high concentrations of gases). In spite of the aspect that the selection of an internal standard is not trivial, the use of internal standardization to minimize random and systematic errors and improve the performance of simultaneous AAS techniques (SIMAAS) can be advantageous.

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