

Cobalt as internal standard for arsenic and selenium determination in urine by simultaneous atomic absorption spectrometry

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Abstract

The effectiveness of internal standardization for simultaneous atomic absorption spectrometry (SIMAAS) was investigated for As and Se determination in urine. Co and Sn were selected as internal standard (IS) candidates based on the evaluation of some physico-chemical parameters related to the atomization. Correlation graphs, plotted from the normalized absorbance signals ($n = 20$) of internal standard (axis y) versus analyte (axis x), precision, and accuracy of the analytical results were the supportive parameters to choose Co as the most appropriate IS. The urine samples were diluted 1 + 2 to 1.0% (v/v) $\text{HNO}_3 + 80 \mu\text{g L}^{-1} \text{Co}^{2+}$. The mixture $20 \mu\text{g Pd} + 3 \mu\text{g Mg}$ was used as chemical modifier and the optimized temperatures for pyrolysis and atomization steps were 1400 and 2300 °C, respectively. The characteristic masses for As ($47 \pm 1 \text{ pg}$) and Se ($72 \pm 2 \text{ pg}$) were estimated from the analytical curves. The detection limits ($n = 20, 3\delta$) were 1.8 ± 0.1 and $2.6 \pm 0.1 \mu\text{g L}^{-1}$ for As and Se, respectively. The reliability of the entire procedure was checked with the analysis of certified reference material from Sero AS (Seronom™ Trace Elements in Urine). The obtained results showed the matrix interference disallowed the instrument calibration with aqueous standards. The best analytical condition was achieved when matrix-matched standards were used in combination with Co as IS, which improved the recoveries obtained for As. Under this experimental condition, eight urine samples were analysed and spiked with 10 and $25 \mu\text{g L}^{-1}$ As and Se. The mean recoveries were $96 \pm 6\%$ ($10 \mu\text{g L}^{-1}$ As), $95 \pm 6\%$ ($25 \mu\text{g L}^{-1}$ As), $101 \pm 7\%$ ($10 \mu\text{g L}^{-1}$ Se), and $97 \pm 4\%$ ($25 \mu\text{g L}^{-1}$ Se).

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1. Introduction

Despite its usual monoelement mode of operation, electrothermal atomic absorption spectrometry (ETAAS) is recognized as a robust technique for trace and ultra-trace element determinations [1]. The low detection limits, the high selectivity, and the possibility to carry out an in situ thermal sample pretreatment are important characteristics of ETAAS, which can be regarded as one of the most attested techniques for elemental determinations in a wide variety of samples [1,3], mainly for biological materials of clinical interest [2].

Simultaneous atomic absorption spectrometry (SIMAAS), commercially introduced during the last decade [4,5], adjoined the multielement capability to the ETAAS reducing analytical time and costs associated with the replacement of the graphite parts. Moreover, the multielement capability allows the use of internal standard (IS) in atomic absorption spectrometry, which can improve precision and accuracy in determinations by SIMAAS [6–9]. This strategy can also expand the graphite tube lifetime owing to the constant analyte/IS absorbance signal ratio [7,9]. There are two works dealing with the use of IS for the direct Pb determination in wine [7] and blood, placenta, and urine [6]. Significant improvements in precision were observed when Bi was adopted as IS, correcting the damaging effect caused by the high concomitant concentration still contained in the untreated sample solution introduced into the atomizer

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[6,7]. The Se determination in sparkling drinking water was carried out using As as IS, showing the benefits of internal standardization for correcting the sampling errors which may occur for heterogeneous samples [9].

In spite of the successful use of IS to improve Pb and Se determination in complex samples, the multielement capability of the instrument was not explored to determine more than one analyte. On the other hand, the internal standardization approach can be more useful when compromise conditions are really imperative, i.e. when two or more analytes are simultaneously determined in a complex untreated sample. In this context, Ag was proposed as IS for the simultaneous determination of Cd and Pb in whole blood samples. The accuracy of the analytical results was improved after the correction with IS, showing the possibility to minimize the interference effects caused by the concomitants [8]. Moreover, the development of a continuum-source spectrometer will enhance the multi-element capability of ETAAS in the near future, and the studies involving the use of IS can be useful in this context.

The use of IS for analysing urine by SIMAAS was not investigated until now. In spite of being amenable to direct analysis, urine can cause intense matrix effects, damaging the accuracy and precision of the analytical results. For this reason, the objective of this work is evaluate the use of Co and Sn as IS for the simultaneous determination of As and Se in urine. They are important trace-elements and it is relevant to know their concentration in biological fluids accurately, to avoid misjudgement about the clinical diagnostics of deficiency or toxicity [10–13].

2. Experimental

2.1. Apparatus

All measurements were carried out by using a simultaneous line-source spectrometer (SIMAA-6000, Perkin-Elmer Life and Analytical Sciences, Shelton, CT, USA) equipped with a longitudinal Zeeman-effect background corrector, standard THGA tube with pyrolytically coated integrated platform, Echelle optical arrangement, and solid state detector. It was operated in four-element simultaneous mode using a hollow cathode lamp for Co ($\lambda = 242.5$ nm; $i = 25$ mA) and electrodeless discharge lamps for As ($\lambda = 193.7$ nm; $i = 380$ mA), Se ($\lambda = 196.0$ nm; $i = 290$ mA), and Sn ($\lambda = 286.3$ nm; $i = 325$ mA). The solutions were delivered into the graphite tube by means of a Perkin-Elmer AS-72 autosampler. Argon 99.996% (v/v) (Air Liquide Brasil S/A, São Paulo, Brazil) was used as protective and purge gas.

2.2. Reagents, solutions and samples

Only high-purity deionized water (18 M Ω cm) obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA) was used for preparing solutions and sam-

ples. Nitric acid (Synth, São Paulo, SP, Brazil) was purified by distillation in quartz sub-boiling stills (Marconi, Piracicaba, SP, Brazil). Analytical reference solutions were prepared by successive dilution of Titrisol stock solutions (Merck, Darmstadt, Germany) containing 1000 mg L⁻¹ of arsenic (As₂O₅), cobalt (CoCl₂), selenium (SeO₂) and tin (SnCl₄). The chemical modifier solution was prepared from high-purity Suprapur salts (Merck): Pd(NO₃)₂ and Mg(NO₃)₂. All solutions were stored in decontaminated polypropylene bottles (Nalge Company, Rochester, NY, USA).

Fresh urine samples were collected from laboratory personnel directly in disposable polypropylene containers (Sarstedt, Nümbrecht, Germany) and kept at 4 °C for until 48 h prior to the analysis. SeronormTM Trace Elements in Urine from Sero AS (Billingstad, Norway) was used to check the reliability of the entire proposed analytical method. SeronormTM Trace Elements in Urine Blank was used to prepare the matrix-matched standards for calibrating the spectrometer. Both SeronormTM urine materials were supplied in lyophilized form and reconstituted by dissolving the vial total content with high-purity de-ionized water.

2.3. Procedure

All glassware and polypropylene bottles were cleaned with detergent solution, soaked in 10% (v/v) HNO₃ for 24 h, rinsed with Milli-Q water, and stored into a closed polypropylene container. All solution and sample manipulations were conducted in a laminar flow bench (Veco, Campinas, SP, Brazil) to avoid the airborne contamination.

The instrumental conditions and the heating program for the graphite tube are showed in Table 1. The heating program optimization was carried out with a solution con-

Table 1
Spectrometer setup and atomizer heating program for the simultaneous determination of As and Se using internal standard

	Analytes		IS candidates	
	As	Se	Co	Sn
Spectrometer setup				
Wavelength (nm)	193.7	196.0	242.5	286.3
Bandpass (nm)	0.7	0.7	0.7	0.7
Lamp type ^a	EDL	EDL	HCL	EDL
Lamp current (mA)	380	290	25	325
Step	Temperature (°C)	Ramp (s)	Hold (s)	Argon flow rate (mL min ⁻¹)
Heating program for the atomizer				
Drying I	110	15	30	250
Drying II	130	10	10	250
Pyrolysis	1400 ^b	10	15	250
Atomization	2300 ^b	0	4	0
Cleaning	2450	1	4	250

Total program time: 99 s; sample volume: 10 μ L; chemical modifier volume (20 μ g Pd + 3 μ g Mg): 10 μ L; injection temperature: 20 °C.

^a EDL: electrodeless discharge lamp; HCL: hollow cathode lamp.

^b Parameters optimized after obtaining pyrolysis and atomization temperature curves.

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