

## Evaluation of Arsenic and Selenium in Brazilian Soluble Coffee by Inductively Coupled Plasma Atomic Emission Spectrometry with Hydride Generation

Éder José dos Santos<sup>1\*</sup> and Elisabeth de Oliveira<sup>2</sup>

<sup>1</sup>Instituto de Tecnologia do Paraná (TECPAR), CP 357, CEP 81310-020, Curitiba, PR, Brazil; <sup>2</sup>Universidade de São Paulo (USP), Instituto de Química, CP 26077, CEP 05508-900, SP, Brazil

### ABSTRACT

*A method for the evaluation of arsenic and selenium in soluble coffee by inductively coupled plasma atomic emission spectrometry with continuous hydride generation to attend the Brazilian food legislation is described. Samples were digested with nitric acid and hydrogen peroxide in a focused microwave system. Slow heating eliminated nitric acid and selenium (VI) was reduced to selenium (IV) by addition of 6 mol/L hydrochloric acid and heating at 90°C under a reflux system. The influence of sample acidity on sensitivity was investigated. Hydrochloric acid 6 mol/L was the most suitable reaction medium. Practical detection limits of 2.0 mg/L for As and 1.0 mg/L for Se were achieved and attended the Brazilian food legislation. The results of recoveries on spiked samples demonstrate the reliability and accuracy of the procedure.*

**Key words:** ICP-AES, As, Se, soluble coffee

### INTRODUCTION

The production of Brazilian soluble coffee is almost entirely destined for exportation that was estimated to be 62 thousand tons in 1995 (Silva, 1996). The determination of macronutrients, micronutrients and toxic elements in soluble coffee is of great general interest, particularly because of the importance of coffee in nutrition to millions of people around the world (Krivan *et al.*, 1982). Previous work on the composition of coffee and its products is mainly concerned with the mineral contents and studies on toxic elements are scarcely reported (Clarke *et al.*, 1974; Gillies *et al.*, 1983; Horwitz *et al.*, 1974; Kuennen *et al.*, 1982; Kapur *et al.*, 1974; Koch *et al.*, 1989; Lara *et al.*, 1975/76). No information exists on the content of arsenic and selenium in this product although a

number of publications (Goulden *et al.*, 1981; Nakahara *et al.*, 1985; Nakahara, 1981; Nygaard *et al.*, 1982; Oliveira *et al.*, 1983; Pahlavanpour *et al.*, 1980; Ybanez *et al.*, 1992) demonstrated that hydride generation, followed by introduction of gaseous hydrides into an ICP was a suitable method for the determination of several trace elements, including arsenic and selenium, for which detection limits were inadequate for foods and related matrices when conventional pneumatic nebulization was used. The objective of this work was to develop a method for the evaluation of arsenic and selenium in soluble coffee by inductively coupled plasma atomic emission spectrometry with hydride generation in order to attend the Brazilian food legislation. The influence of sample acidity on sensitivity of the method was also studied.

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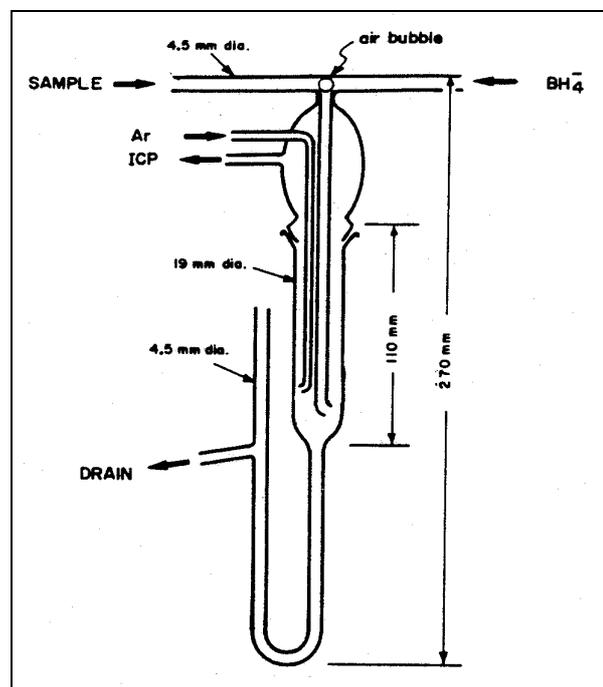
\* Author for correspondence

## MATERIALS AND METHODS

**Reagents:** Distilled and deionized water (deionizing Permution); arsenic (V) and selenium (IV) stock standard solutions (1000 µg/mL) (Titrisol Merck); nitric acid, (Merck), 65%; hydrogen peroxide, (Merck), 30%; hydrochloric acid, (Merck), 37%, use of a 6 mol/L solution; Sodium borohydride, (Merck), 99.9%, use of a 1 % w/v solution in 0.1 mol/L NaOH.

**Apparatus :** Focused microwave system model 7400 Spex with 250 mL glass tubes; hydride generation was carried out in a continuous mode by using a two-channels peristaltic pump (Gilson Instrument Co., Minipuls) to introduce sample and borohydride reagent to a phase separator from Oliveira *et al.*, 1983 (Figure 1). The operating conditions for hydride generation system are summarized in Table 1. A Baird PSX sequential ICP spectrometer with a focal length Czerny-Turner monochromator, a holographic grating with a linear dispersion of 0.74 nm/mm (first order), a spectral resolution of 0.014 nm and a RF generator of 2.3

kW at 40.68 MHz were employed. The operating conditions are also summarized in Table 1.



**Figure 1** - Phase separator developed by Oliveira *et al.*, 1983.

**Table 1** - Standard operating conditions for the ICP and hydride-generation system.

PLASMA	
Plasma gas flow	8.5 L/min.
Auxiliary gas flow	1.2 L/min.
Observation height	12 mm above the load coil
Integration time	5 ds
Incident power	1.0 kW
Reflected power	< 5 W
Analytical lines	As -193.696 nm; Se - 196.026 nm
HYDRIDE-GENERATION APPARATUS	
Sample acidity	6 mol/L HCl
Sample flow	1.5 mL/min.
NaBH <sub>4</sub> flow	2.5 mL/min.
Carrier gas flow	0.6 L/min.

**Standard solutions preparation and calibration curves :** Calibration curves for the analytes arsenic (V) and selenium (IV) were made by using four different standard solutions: 0.0 µg/L, 5.0 µg/L, 10.0 µg/L and 20.0 µg/L in 6 mol/L HCl.

**Sample preparation:** Twenty-one samples of soluble coffee were collected from the Brazilian market and were used in the present work. Part one of sample preparation was developed in our laboratory (Santos *et al.*, 1997), and part two was adapted from Brimmer *et al.*, 1987.

Part one: Five gram of sample was introduced into a 250 mL glass tube (from the focused microwave

system model 7400 SPEX) and 30 mL of  $\text{HNO}_3$  was added. After 30 minutes of initial reaction at ambient temperature, the glass tube was placed on the focused microwave system, heated at 105 W power for 5 minutes, and allowed to cool for 5 minutes. This heating and cooling procedures were repeated. Then 2.5 mL of  $\text{H}_2\text{O}_2$  were added and the heating and cooling procedures were repeated once more.

Part two: The solution prepared above were transferred to a 100 mL boiling flask and evaporated at  $90 \pm 5$  °C to almost dryness. Twenty-five mL of 6 mol/L HCl were added to this and the solution was heated at  $90 \pm 5$  °C under reflux system for 30 minutes. Three replicate analyses were carried out.

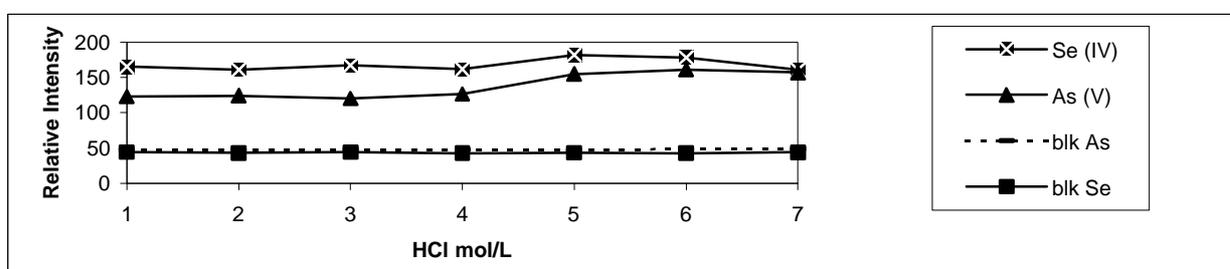
Spiked samples: Volumes of the standard solutions containing 0.25 µg of arsenic (V) and 0.25 µg of selenium (IV) were added to 1g of three samples (equivalent to 10.0 µg/L in the final solutions on which those analytes were determined). Two replicate analyses were carried out and these spiked samples were treated as described on sample preparation item (part one and two).

## RESULTS AND DISCUSSION

### Optimization of operating parameters

The phase separator constructed according to the specifications from Oliveira *et al.*, 1983, (Figure 1), was used with few problems in the operating conditions of the PSX-Baird spectrometer. Flow rates of 0.6 L/min., used at conventional solution nebulization by pneumatic nebulizer, were also suitable for determination of arsenic and selenium by hydride generation. At flow rates below 0.6 L/min., the formation of hydrogen bubbles was high, hindering the perfect operation of the drain. On the other hand, at flow rates higher than 0.6 L/min., the back pressure created tended to force all the waste liquid out of the U-tube in the phase separator and usually extinguished the plasma. A concentration of  $\text{NaBH}_4$  more than 1 % w/v also extinguished the plasma and at less than this value the signal was very poor (Oliveira *et al.*, 1983). The effect of the hydrochloric acid concentration on sensitivity was studied. The following solutions were prepared:

- 100 mL of 1 to 7 mol/L HCl (solutions of the blank);
- 100 mL of standard solutions of 50.0 µg/L of As (V) and Se (IV) in 1 to 7 mol/L HCl;
- 1 % w/v  $\text{NaBH}_4$  solution in 0.1 mol/L NaOH.



**Figure 2** - Effect of the acid concentration on sensitivity.

Figure 2 shows a plot of the different HCl concentrations versus the relative intensity of the analytes arsenic (V) and selenium (IV).

The base line represented by blank solutions (blk) showed invariable values at different concentrations of hydrochloric acid. The response had the best sensibility for selenium and arsenic with 5 and 6 mol/L HCl.

### Linearity, instrumental detection limits and practical detection limits

The parameters of analytical curve and detection limits were investigated under the conditions

detailed in Table 1 previously presented and are shown in Table 2. Typical calibrations were linear up to 20.0 µg/L. The instrumental detection limit is defined as the concentration that produces a net line intensity equivalent to three times the standard deviation of the blank or background signal (Oliveira *et al.*, 1983; Thompson, 1987). The blank was the ordinate intercept calculated from the linear regression analysis of the calibration data and showed in Table 2. However, under the conditions of this analysis, the background signal of the samples was different from that produced by the standard solutions and the blank, so the

practical detection limits used in this work were greater than instrumental detection limits by a factor of 2 since these results were better and a more realistic estimate for quantitative analysis.

#### Determination of arsenic and selenium

The results obtained for the arsenic and selenium in twenty-one samples of Brazilian soluble coffee are

presented in Table 3. The values were below the practical detection limits and were the following, in  $\mu\text{g/g}$  of soluble coffee: **As** not detectable up to  $0.010 \mu\text{g/g}$  and **Se** not detectable up to  $0.005 \mu\text{g/g}$ .

**Table 2** - Detection limits for the analytes and conditions of the analytical curve.

Analyte	Linear coefficient	Angular coefficient	Linear correlation ( r )	Instrumental detection limit	Practical detection limit
As	-24.1218	$5.744 \times 10^{-1}$	0.9982	1.0 $\mu\text{g/L}$	2.0 $\mu\text{g/L}$
Se	-13.8789	$3.625 \times 10^{-1}$	0.9976	0.5 $\mu\text{g/L}$	1.0 $\mu\text{g/L}$

**Table 3** - Results of determination of As and Se in samples of Brazilian soluble coffee ( $\mu\text{g/g}$ , n=3)

Sample	As ( $\mu\text{g/g}$ )	Se ( $\mu\text{g/g}$ )
1 (Iguaçu lot 04A/96)	<0.010	<0.005
2 (Iguaçu lot 04B/96)	<0.010	<0.005
3 (Iguaçu lot 09/96)	<0.010	<0.005
4 (Ariscafé lot 09/96)	<0.010	<0.005
5 (Ariscafé lot 08/96)	<0.010	<0.005
6 (Ariscafé lot 09/98)	<0.010	<0.005
7 (Ariscafé lot 04/96)	<0.010	<0.005
8 (Parmalat lot 08/96)	<0.010	<0.005
9 (Do Ponto liofilizado lot 06/96)	<0.010	<0.005
10 (Do Ponto descafeinado lot 08/96)	<0.010	<0.005
11 (Café Pelé lot 03A/96)	<0.010	<0.005
12 (Café Pelé lot 03B/96)	<0.010	<0.005
13 (Gran Classic lot 07/96)	<0.010	<0.005
14 (Nescafé tradição lot 06/96)	<0.010	<0.005
15 (Nescafé tradição lot 02/96)	<0.010	<0.005
16 (Nescafé tradição lot 12/96)	<0.010	<0.005
17 (Nescafé matinal lot 01/97)	<0.010	<0.005
18 (Nescafé matinal lot 06/96)	<0.010	<0.005
19 (Bassil coffee lot 09/95)	<0.010	<0.005
20 (Eldoro café lot 11/96)	<0.010	<0.005
21 (Café diana lot 01/96)	<0.010	<0.005

The results for three spiked samples treated as described on sample preparation are shown in the Table 4.

## CONCLUSIONS

The application of the hydride generation technique with inductively coupled plasma atomic emission showed to be suitable to determine arsenic and

selenium in soluble coffee with practical detection limits giving values below those specified in Brazilian food legislation (Compêndio da Legislação de Alimentos-Atos do Ministério da Saúde, 1988), that fixed the maximum arsenic content in  $1.0 \mu\text{g/g}$  and selenium in  $0.3 \mu\text{g/g}$ . The spiked samples treated as described on sample preparation showed acceptable results, indicating accuracy and precision of the present method of analysis.

**Table 4** - Results of the determination of As and Se in three spiked samples [0.25 µg/g of the As (V) and Se (IV) was added, n=2]:

Sample	As µg/g	Se µg/g
2 (Iguaçu lot 04B/96)	0.27 ± 0.02	0.25 ± 0.01
5 (Ariscafé lot 08/96)	0.23 ± 0.04	0.23 ± 0.02
17 (Bassil coffee lot 09/95)	0.26 ± 0.03	0.25 ± 0.02

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## RESUMO

O presente trabalho descreve um método para determinação de arsênio e selênio em café solúvel por espectrometria de emissão atômica com plasma acoplado a geração de hidretos, com o objetivo de atender aos limites estabelecidos pela legislação Brasileira de alimentos. Digestões das amostras foram realizadas com ácido nítrico e hidrogênio em sistema de microondas focalizadas. O excesso de ácido nítrico foi eliminado através de aquecimento lento e o selênio (VI) foi reduzido a selênio (IV) através de tratamento com ácido mol/L e aquecimento a 90 °C em sistema de refluxo. A influência da acidez na sensibilidade foi investigada, sendo o meio mais estável a concentração de ácido clorídrico de 6 mol/L. Os limites de determinação foram de 2.0 µg/L para o As e 1.0 µg/L para o Se. Os resultados das amostras enriquecidas demonstram a precisão e exatidão do método proposto.

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