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Application of multivariate techniques in the optimization of a procedure for the determination of bioavailable concentrations of Se and As in estuarine sediments by ICP OES using a concomitant metals analyzer as a hydride generator

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ABSTRACT

A procedure has been developed for the determination of bioavailable concentrations of selenium and arsenic in estuarine sediments employing inductively coupled plasma optical emission spectrometry (ICP OES) using a concomitant metals analyzer device to perform hydride generation. The optimization of hydride generation was done in two steps: using a two-level factorial design for preliminary evaluation of studied factors and a Doehlert design to assess the optimal experimental conditions for analysis. Interferences of transition metallic ions (Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+} and Ni^{2+}) to selenium and arsenic signals were minimized by using higher hydrochloric acid concentrations. In this way, the procedure allowed the determination of selenium and arsenic in sediments with a detection limit of 25 and 30 $\mu g\,kg^{-1}$, respectively, assuming a 50-fold sample dilution (0.5 g sample extraction to 25 mL sample final volume). The precision, expressed as a relative standard deviation (% RSD, $n = 10$), was 0.2% for both selenium and arsenic in 200 $\mu g\,L^{-1}$ solutions, which corresponds to 10 $\mu g\,g^{-1}$ in sediment samples after acid extraction. Applying the proposed procedure, a linear range of 0.08–10 and 0.10–10 $\mu g\,g^{-1}$ was obtained for selenium and arsenic, respectively. The developed procedure was validated by the analysis of two certified reference materials: industrial sludge (NIST 2782) and river sediment (NIST 8704). The results were in agreement with the certified values. The developed procedure was applied to evaluate the bioavailability of both elements in four sediment certified reference materials, in which there are not certified values for bioavailable fractions, and also in estuarine sediment samples collected in several sites of Guanabara Bay, an impacted environment in Rio de Janeiro, Brazil.

1. Introduction

Determination of selenium and arsenic in sediments is of concern because it can reveal the degree of environmental contamination and its possible ecotoxicological effects. Selenium and arsenic are trace elements existing in multiple chemical forms in the environment, including different oxidation states and organic metalloid compounds that may be interconverted through chemical and biological activity [1].

Inorganic compounds are much more hazardous than organic compounds. Selenium is toxic at elevated concentrations [2,3]; however, when present in low concentrations, selenium is an essential element for living organisms. Arsenic contamination has a negative impact on the environment, as it can generate severe toxicological effects to both vegetation and animal organisms [4,5]. Discharge of arsenic compounds in the environment is associated with a variety of industrial processes: production of glasses, plastics, chemical and pharmaceutical products; semiconductor and electronic materials; mining; and the use of pesticides and herbicides based on arsenic compounds [6].

Sediments are normally considered a sink for trapping trace elements due to the presence of several geochemical phases (e.g., sulfides, oxides, and organic matter) that can bind to these species. In anoxic sediments, sulfides are perhaps the most important geochemical phases where selenium and arsenic can be found [7,8].

Selenium and arsenic are normally found in low concentrations in environmental samples. Thus, their direct determination by spectrometric techniques using pneumatic nebulization is not adequate because the limits of detection are relatively high for both elements. Sensitivity can be improved by one or two orders of magnitude by applying hydride generation (HG) sample introduction systems.

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This enhancement is due to the high efficiency of analyte transport under the form of gaseous hydride to the atomizer [9]. HG is usually coupled with detection techniques such as atomic absorption spectrometry [10–17], inductively coupled plasma mass spectrometry [18–21], atomic fluorescence spectrometry [22–25] and inductively coupled plasma optical emission spectrometry [26–28].

Hydride generation efficiency in a concomitant metals analyzer (CMA®) is dependent on a number of factors, including: flow rate and concentration of reagents (HCl and $NaBH_4$); pressure of nebulizer gas; and sampling flow rate. Moreover, the oxidation state of the element in solution, matrix constituents, and presence of interfering transition metals such as copper, nickel, cobalt, iron and cadmium can also influence the effectiveness of hydride generation. In order to obtain maximum efficiency using the hydride generation technique and guarantee the best figures of merit for the method, it is necessary to optimize all of these factors before determination of the elements of interest.

In the optimization of an analytical method, it is necessary to adjust several factors in order to establish optimal analysis conditions. This process can demand time, reagents and hard work if the univariate optimization method were to be utilized. Another drawback of the univariate optimization strategy is the neglect of interactions between the different factors that may affect the results [29]. In the past few decades, application of multivariate techniques for method optimization in analytical chemistry has increased substantially, owing to its economic and efficiency advantages. In addition, the method allows for simultaneous optimization of multiple factors [30–32].

This work describes the application of multivariate techniques (two-level factorial design and Doehlert matrix) in the optimization of a method for the determination of bioavailable concentrations of selenium and arsenic. A concomitant metals analyzer as a hydride generator and an ICP OES detector were applied for studying selenium and arsenic distribution in estuarine anoxic sediments.

2. Experimental

2.1. Instrumental

The sequential inductively coupled plasma optical emission spectrometry instrument used in all experiments was a Jobin Yvon (Longjumeau, France) Ultima 2 equipped with radial viewing and automatic sampler AS 421. Analyst JY 5.2 software was employed for data acquisition.

A concomitant metals analyzer (CMA®), also furnished by Jobin Yvon, was used as a hydride generator. CMA is a modified cyclonic chamber developed by Jobin Yvon to measure both elements (forming and non-forming hydrides) simultaneously in a single run. For nebulized samples that do not go directly to the ICP torch (drops higher than 10 μm), a small cup located at the bottom of the cyclonic chamber allows for mixing of the sample with sodium borohydride and hydrochloric acid solutions before it is drained. Both solutions are delivered to the bottom of this small cup using a peristaltic pump and Teflon tubes (0.8 mm ID) in transmitting lines. A third line may be used for adding other solutions [33]; however, for this task (use of CMA only for hydride generator), the nebulization gas (argon) was used only as a carrier gas for hydride transport to the plasma. The inlet sample in the Meinhard nebulizer was closed off. The sample solution was inserted into the cyclonic chamber in the same way for both $NaBH_4$ and HCl solutions, using a Minipuls 3 multichannel peristaltic pump furnished by Gilson (Villiers le Bel, France).

Selenium and arsenic determinations were performed under the following conditions: power (1.2 kW), plasma gas flow (12.0 L min^{-1}), auxiliary gas flow (0 L min^{-1}), sheath gas flow (0.2 L min^{-1}), nebulizer gas pressure (245 kPa), integration time (4 s), stabilization time (10 s) and view height (15 mm). The analytical wavelengths (nm) used were: Se (196.026) and As (193.695).

A DGT-100 Plus (Provecto Analítica, Brazil) pressurized digestion system assisted by microwave radiation was used for sample treatment according to the US EPA 3051A method (0.5 g of sample extracted with 10 mL concentrated HNO_3) [34]. This digestion system was also used for the determination of the total concentration by employing the US EPA 3052 method (0.5 g of sample decomposed with 9 mL concentrated HNO_3, 3 mL concentrated HCl and 3 mL concentrated HF) [35].

2.2. Reagents

All reagents were prepared using ultra-pure water obtained from a purification system (Elix and Sinergy, Millipore, Bedford, MA, USA) and analytical quality chemicals. Nitric acid (Suprapur, Merck, Germany), hydrochloric and hydrofluoric acids (analytical grade, Merck, Brazil) were used as-is. Laboratory glassware was kept overnight in a 10% (v/v) nitric acid solution. Before use, the glassware was rinsed with ultra-pure water and dried in a dust free environment (laminar flow hood class 100).

Selenium and arsenic solutions were prepared by diluting 1 mg mL^{-1} standard solutions (SPEX, Metuchen, USA).

For the interference study, copper, cadmium, iron, nickel and cobalt solutions were prepared from 10 or 1 mg mL^{-1} stock standard solutions (SPEX, Metuchen, USA and Ultra Scientific, USA). The 2% (m/v) sodium tetrahydroborate solution (Vetec, Brazil) was prepared fresh every day by dissolving $NaBH_4$ in 0.5 mol L^{-1} NaOH (Merck, Germany) and then filtered before use.

2.3. Optimization

The optimization process was carried out using multivariate methodologies. A two-level full factorial design [36,37] was applied for preliminary evaluation of the significance of the factors involved in the analytical system. The Doehlert design [38] was performed in order to determine the optimum conditions to perform the analysis. $NaBH_4$, HCl and sample flow rates along with the nebulizer pressure were regarded as factors. The experimental data were processed using STATISTICA® software version 6.0 (StatSoft, Brazil). All experiments in this step were carried out in random order using 200 μg L^{-1} selenium and arsenic solutions.

In this work, selenium and arsenic responses are obtained as the corresponding net emission signal for each element. Both responses present a similar profile, which is an indication that there is the same tendency to a common optimal region. In order to obtain the conditions that simultaneously satisfy the hydride generation for both elements, the overall response equation was adopted (OR):

$$\mathrm{OR} = \frac{R(\mathrm{Se})}{\mathrm{HS(Se)}} + \frac{R(\mathrm{As})}{\mathrm{HS(As)}} \qquad (1)$$

where R (element) is the analytical signal for that element in a particular experiment and HS (element) is the higher signal in the set of experiments for that element.

2.3.1. Two-level full factorial design

This procedure was carried out using the experimental conditions described for each experiment (see matrix in Table 1). The maximum and minimum levels of each factor were established considering previous experiments. Replicates of all experimental points were performed to evaluate the pure error.

2.3.2. Doehlert design

The Doehlert design was used as the experimental matrix for the response surface methodology. The experimental conditions for $NaBH_4$ flow rate, HCl flow rate, sample flow rate, and nebulization

Table 1
Full two-level factorial design and responses (net emission intensity for duplicate analysis) for screening of principal factors that affect the determination of selenium and arsenic by HG ICP OES.

Factors	Low level (−1)	High level (+1)
(a) Studied factors and levels		
V1, sample flow rate (mL min^{-1})	1.0	1.5
V2, pressure of nebulizer (bar)	2.1	2.8
V3, $NaBH_4$ flow rate (mL min^{-1})	1.1	1.8
V4, HCl flow rate (mL min^{-1})	0.5	0.8

V1	V2	V3	V4	Net emission intensity (counting s^{-1})				Overall response	
				Se		As			
(b) 2^4 full factorial design									
−1	−1	−1	−1	135,158	116,648	97,876	81,218	0.92	0.77
+1	−1	−1	−1	270,073	269,807	155,671	156,092	1.62	1.62
−1	+1	−1	−1	223,703	176,307	96,742	88,704	1.16	0.98
+1	+1	−1	−1	260,899	242,926	116,271	115,499	1.37	1.32
−1	−1	+1	−1	111,755	124,589	110,479	111,523	0.92	0.96
+1	−1	+1	−1	151,455	153,207	139,787	126,044	1.20	1.12
−1	+1	+1	−1	143,147	145,905	64,502	63,718	0.76	0.76
+1	+1	+1	−1	131,733	138,989	126,088	112,306	1.07	1.01
−1	−1	−1	+1	213,908	184,420	116,494	114,254	1.24	1.15
+1	−1	−1	+1	357,875	327,175	157,578	149,181	1.87	1.74
−1	+1	−1	+1	143,309	172,275	70,690	70,228	0.79	0.87
+1	+1	−−1	+1	310,552	275,854	112,608	110,007	1.49	1.38
−1	−1	+1	+1	119,987	101,360	115,070	116,139	0.97	0.93
+1	−1	+1	+1	191,663	187,158	180,866	177,783	1.54	1.51
−1	+1	+1	+1	77,247	69,269	103,612	104,528	0.79	0.77
+1	+1	+1	+1	155,862	210,018	151,146	159,163	1.27	1.47

gas pressure were established considering the values required by the Doehlert matrix and are presented in Table 2a and b.

2.4. Extraction of bioavailable fractions of Se and As from sediments

To extract the bioavailable fractions of selenium and arsenic from sediment samples and certified reference materials, the US EPA 3051A method that employs concentrated nitric acid and microwave-assisted extraction was utilized [34]. The microwave-assisted acid extraction was performed at a temperature of 175 °C. Sediment samples (500 mg) to be evaluated were weighed in the perfluoralkoxy (PFA) vessels of the microwave oven. Concentrated HNO_3 (10 mL) was added to the samples as the extractor reagent. Six vessels were used simultaneously in each extraction cycle. Microwave digestion of the samples was carried out using a six-step program: 1 min at 100 W; 1 min at 200 W; 1 min at 300 W; 1 min at 400 W; 6 min at 500 W; and finally 30 min of ventilation. This heating program provided a temperature increase up to 175 °C in 4.5 min, and the temperature remained at 175 °C for 5.5 min in accord with the US EPA method 3051A [34].

A blank was carried out to evaluate the contamination possibilities for each analytical sample. After the vessels cooled down inside the microwave oven, the digested material was filtered (Macherey-

Table 2
Doehlert designs and responses for optimization of selenium and arsenic determination by HG ICP OES. Coded values are presented in parentheses.

Factors (mL min^{-1})		Net emission intensity (counting s^{-1})		Overall response
$NaBH_4$ flow rate	HCl flow rate	Se	As	
(a) Optimization of $NaBH_4$ and HCl flow rates				
1.7 (+1.0)	1.1 (0)	32,411.0	34,569.5	1.67
1.4 (+0.5)	0.5 (−0.866)	6,068.0	10,373.0	0.41
1.4 (+0.5)	1.7 (+0.866)	21,044.5	21,016.5	1.05
1.1 (0)	1.1 (0)	40,092.0	40,153.0	2.01
1.1 (0)	1.1 (0)	40,139.0	40,135.0	2.01
1.1 (0)	1.1 (0)	40,115.5	40,144.0	2.03
0.8 (−0.5)	0.5 (−0.866)	10,647.0	12,292.0	0.57
0.8 (−0.5)	1.7 (+0.866)	6,552.5	5,614.0	0.30
0.5 (−1.0)	1.1 (0)	9,451.0	9,131.5	0.46

Factors		Net emission intensity (counting s^{-1})		Overall response
Sample flow rate (mL min^{-1})	Nebulization gas pressure (bar)	Se	As	
(b) Optimization of sample flow rate and nebulization gas pressure				
2.5 (+1.0)	2.45 (0)	89,238.0	94,041.0	2.00
2.0 (+0.5)	2.10 (−0.866)	81,695.0	80,725.0	1.77
2.0 (+0.5)	2.80 (+0.866)	69,086.5	78,180.5	1.61
1.5 (0.0)	2.45 (0)	80,221.0	82,103.4	1.77
1.5 (0.0)	2.45 (0)	80,004.0	82,305.3	1.78
1.5 (0.0)	2.45 (0)	80,112.5	82,000.5	1.75
1.0 (−0.5)	2.10 (−0.866)	37,221.0	42,383.0	0.87
1.0 (−0.5)	2.80 (+0.866)	27,456.5	34,797.0	0.68
0.5 (−1.0)	2.45 (0)	8,197.0	8,287.0	0.18

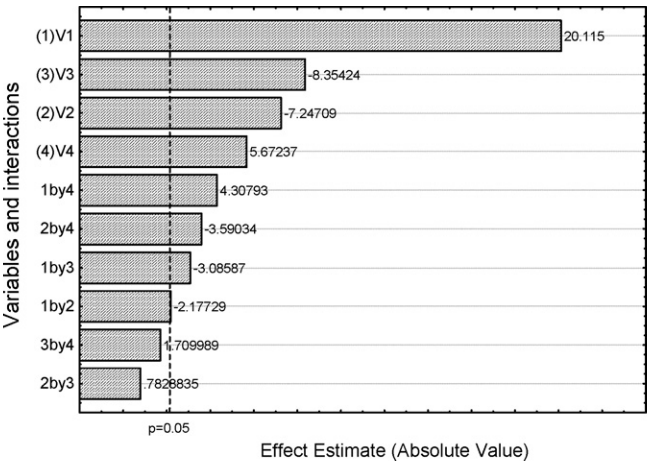

Fig. 1. Pareto chart of standardized effects for four variables studied. V1, sample flow rate ($mL\,min^{-1}$); V2, pressure of nebulizer (bar); V3, $NaBH_4$ flow rate ($mL\,min^{-1}$); V4, HCl flow rate ($mL\,min^{-1}$).

Nagel quantitative paper filters), transferred to 25 mL volumetric flasks, and filled to volume with ultra-pure water. The sample solutions were stored at 4 °C in polyethylene bottles until analysis.

2.5. Interference study

According to Pohl and Zyrnicki [39], transition metal ions cause serious interferences in hydride generation in the liquid phase. In this study, an evaluation of five such transition metal ions was performed. To each of the 200 $\mu g\,L^{-1}$ Se and As solutions, increasing amounts of interferent ions (Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+} and Ni^{2+}) were added in the following proportions: 1:10, 1:50, 1:100, 1:500 and 1:1000. These solutions were then analyzed using the optimized conditions.

Interference minimizations were tried with the obtained results by employing complexing agents such as thiourea, ortophenatroline, potassium iodide (0.1 $mol\,L^{-1}$) and HCl (3.0–6.0 $mol\,L^{-1}$).

3. Results and discussion

3.1. Factorial design

Table 2 shows the experimental design matrix, the results obtained from each duplicate run for selenium and arsenic determination, and the overall response which represents the sum of normalized signals for each element. Considering an analysis of variance (ANOVA), the results demonstrate that all four studied factors are statistically significant. As expected, the Pareto Chart (Fig. 1) clearly shows that sample flow rate provides the most significant effect on the response. The HCl flow rate has a less significant effect. As the four variables present significant effects, the Doehlert design for two factors was applied for the optimization of the following pairs: (1) $NaBH_4$ and HCl solution flow rates and (2) sample flow rate and nebulizer gas pressure.

3.2. Doehlert design 1: $NaBH_4$ and HCl solution flow rates

In this design, the optimized variables were $NaBH_4$ and HCl solution flow rates. The sample flow rate and nebulizer gas pressure were set at 1.5 $mL\,min^{-1}$ and 2.45 bar, respectively. The seven experiments required by the Doehlert design are presented in Table 2a. The $NaBH_4$ solution flow rate (f_{bor}) was studied over five levels from 0.5 to 1.7 $mL\,min^{-1}$. The HCl solution flow rate (f_{HCl}) was studied over three levels and varied from 0.5 to 1.7 $mL\,min^{-1}$. The HCl and $NaBH_4$ concentrations were fixed at 2.5 $mol\,L^{-1}$ and 2.0% (m/v), respectively. The sample flow rate and nebulizer gas pressure were fixed according to the procedure recommended by Tyler [40].

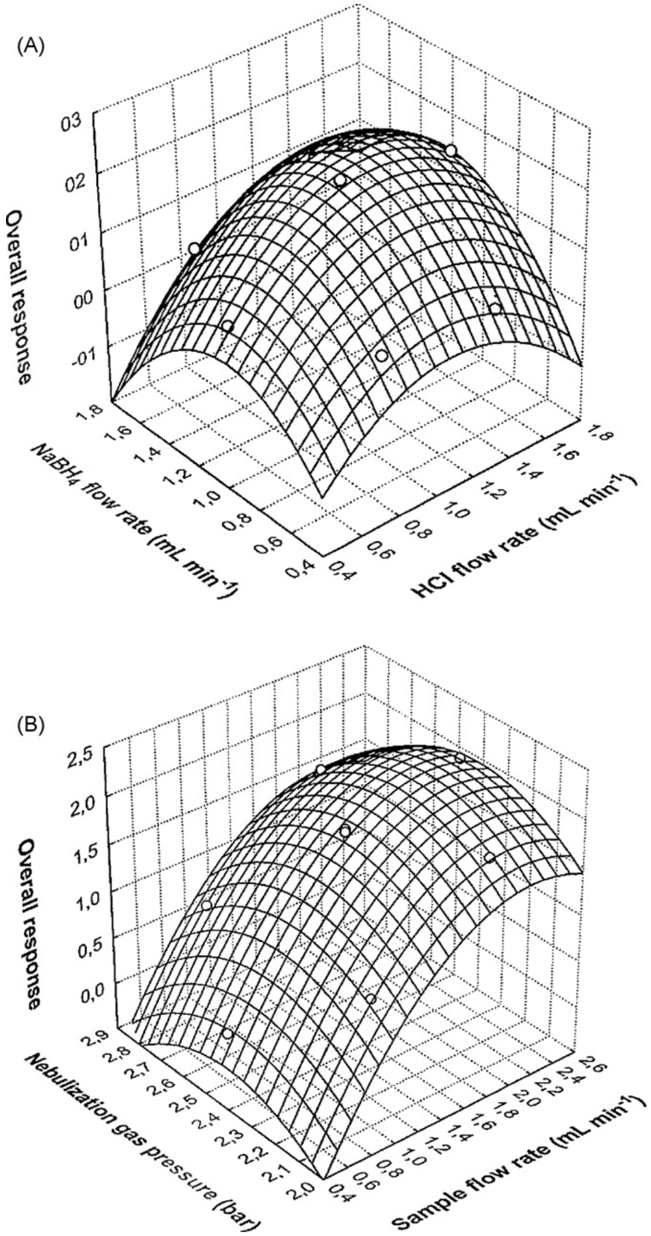

Fig. 2. Response surfaces (overall response) obtained for (a) HCl flow rate × $NaBH_4$ flow rate and (b) sampling flow rate × pressure of nebulizer.

The data obtained were used in the Doehlert matrix, and the following equation illustrates the relationship between f_{bor}, f_{HCl} and general response:

$$OR = -5.11(\pm 0.05) + 5.75(\pm 0.06) f_{bor} - 2.65\,(\pm 0.03) f_{bor}{}^2 + 6.15(\pm 0.05) f_{HCl} - 3.00(\pm 0.02) f_{HCl}{}^2 + 0.70(\pm 0.02) f_{bor} f_{HCl} \qquad (2)$$

The response surface described by this equation (Fig. 2a) shows a maximum point that was calculated using the following equations:

$$\frac{\partial f_{bor}}{\partial OR} = (5.75 - 5.30) f_{bor} + 0.70 f_{HCl} = 0 \qquad (3)$$

$$\frac{\partial f_{HCl}}{\partial OR} = (6.15 - 6.00) f_{HCl} + 0.70 f_{bor} = 0 \qquad (4)$$

Solving this system of equations, the optimum values were found to be $f_{\mathrm{bor}} = 1.3\,\mathrm{mL\,min^{-1}}$ and $f_{\mathrm{HCl}} = 1.2\,\mathrm{mL\,min^{-1}}$.

3.3. *Doehlert design 2: sample flow rate and nebulizer gas pressure*

In this design, the experimental conditions for f_{bor} and f_{HCl} were fixed in agreement with the optimal values found in Doehlert design 1 (1.3 and $1.2\,\mathrm{mL\,min^{-1}}$, respectively). The seven experiments required by this design are described in Table 2b. The sample flow rate (f_{sample}) was studied over five levels from 0.5 to $2.5\,\mathrm{mL\,min^{-1}}$. The nebulization gas pressure (p_{neb}) was studied over three levels and varied from 2.10 to 2.80 bar.

The data obtained were used in the Doehlert matrix, and the following equation illustrates the relationship between f_{sample}, p_{neb} and general response:

$$\begin{aligned}\mathrm{OR} = {} & -18.2(\pm 0.5) + 2.8(\pm 0.1) f_{\mathrm{sample}} - 0.68(\pm 0.01) f_{\mathrm{sample}}^{2} \\ & + 14.8(\pm 0.4) p_{\mathrm{neb}} - 2.98(\pm 0.09) p_{\mathrm{neb}}^{2} \\ & + 0.04(\pm 0.04) f_{\mathrm{sample}}\, p_{\mathrm{neb}} \end{aligned} \tag{5}$$

As can be seen by the standard error, the interaction term (f_{sample} p_{neb}) is not significant and can be excluded from the equation. These results indicated that there was a maximum surface response which can be calculated by the following system of equations:

$$\frac{\partial f_{\mathrm{sample}}}{\partial \mathrm{OR}} = (2.8 - 1.36) f_{\mathrm{sample}} = 0 \tag{6}$$

$$\frac{\partial p_{\mathrm{neb}}}{\partial \mathrm{OR}} = (14.3 - 5.96) p_{\mathrm{neb}} = 0 \tag{7}$$

Solving this system of equations, the optimum values were found to be $f_{\mathrm{sample}} = 2.2\,\mathrm{mL\,min^{-1}}$ and $p_{\mathrm{neb}} = 2.4$ bar.

3.4. *Interference study*

It is essential that the developed method tolerates the presence of transition metal ions (normally interferents in the liquid phase) for the selenium and arsenic hydride generation, as the sediment samples chosen for analysis often have these elements in higher concentrations; this is especially true in environmental sites that are anthropogenically impacted. Thus, it is very important to evaluate the influence of potentially interfering ions such as cadmium, cobalt, copper, iron and nickel on the analytical signals of selenium and arsenic. Table 3 shows the results obtained when using a solution containing $10\,\mu\mathrm{g\,mL^{-1}}$ of each interfering ion (Cd, Co, Cu, Fe and Ni) in the presence of $200\,\mu\mathrm{g\,L^{-1}}$ of Se and As (50 times relationship interferent/analyte species), by using hydride generation and HCl concentrations of $2.5\,\mathrm{mol\,L^{-1}}$. As can be seen in the table, the interference is of concern for all ions except Co on Se and Cd on As. According to Pohl and Zyrnicki [39], the interfering ions react with the borohydride ions and precipitate in the form of metal-borohydride species. The precipitates then adsorb hydrides and cause their decomposition. Hence, the formation of volatile hydrogen selenate and arsine is suppressed, and a signal decrease is observed for both responses [41].

Table 3
Decreasing of analytical signal of selenium and arsenic ($200\,\mu\mathrm{g\,L^{-1}}$) in HG ICP OES caused by the presence of $10{,}000\,\mu\mathrm{g\,L^{-1}}$ interferent transition metal ion using $2.5\,\mathrm{mol\,L^{-1}}$ HCl.

Transition metallic ion	Decrease of analytical signal (%)	
	Se	As
Cd	45	5
Co	0	55
Cu	90	8
Fe	66	20
Ni	53	90

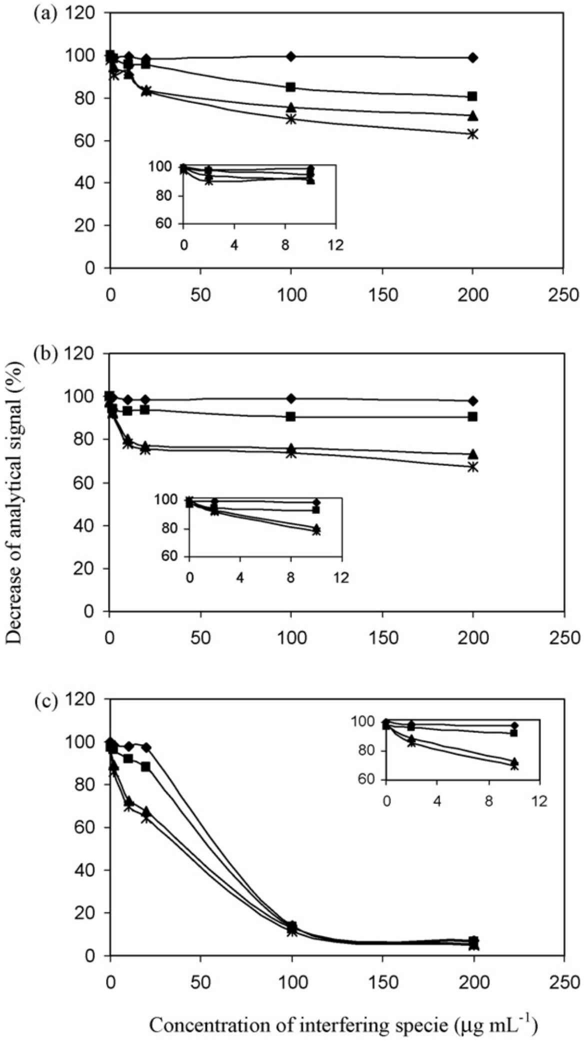

Fig. 3. Effect of several HCl concentrations on minimization of (a) copper, (b) iron and (c) nickel interferences on the analytical signal of arsenic by using HG ICP OES. Legend for HCl concentrations: ♦ $= 6\,\mathrm{mol\,L^{-1}}$; ■ $= 5\,\mathrm{mol\,L^{-1}}$; ▲ $= 4\,\mathrm{mol\,L^{-1}}$; and ✱ $= 3\,\mathrm{mol\,L^{-1}}$. Concentration of As: $200\,\mu\mathrm{g\,L^{-1}}$.

It is well documented that the use of thiourea [42], ortophenantroline [43] and potassium iodide [44] can solve these interferences; however, in the chemical conditions used in this work and employing these reagents, these interferences could not be suppressed successfully.

According to Welz and Schubert-Jacobs [45], an increase in the hydrochloric acid concentration improves the range of interference-free determination for both selenium and arsenic in the presence of transition metals. In this way, with the aim of verifying the range of the application of this methodology in contaminated anoxic sediments, the study of the effect of HCl concentrations on the minimization of the interferences caused by Co, Cu, Ni and Fe were assayed.

The effects of several HCl concentrations (3–$6\,\mathrm{mol\,L^{-1}}$) were studied for solutions containing between 2 and $200\,\mu\mathrm{g\,mL^{-1}}$ of each of four metallic species. These results can be seen in Figs. 3 and 4. Clearly, the best conditions for interference-free selenium and arsenic determination were obtained using a HCl concentration of $6\,\mathrm{mol\,L^{-1}}$.

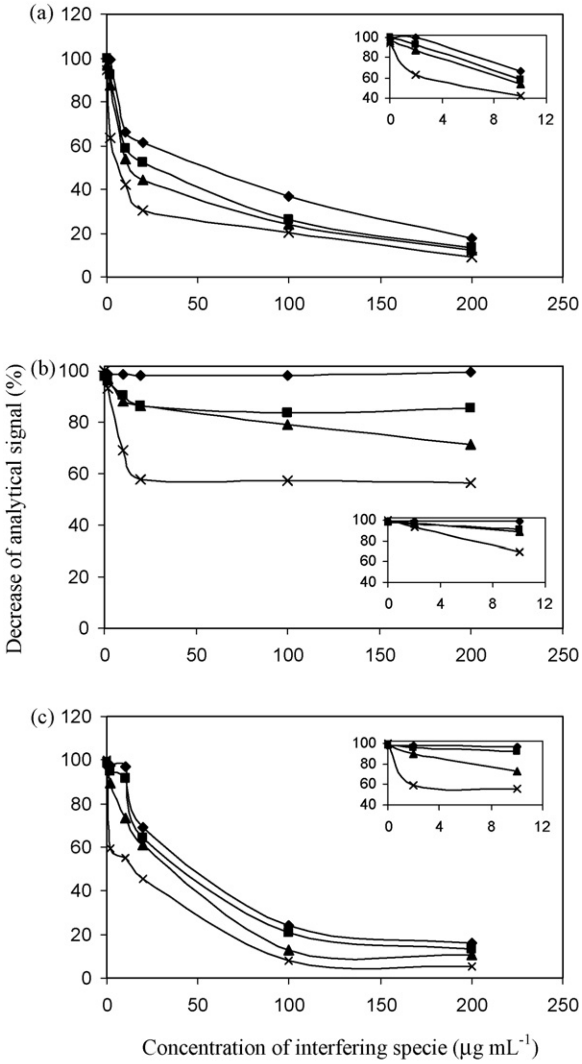

Fig. 4. Effect of several HCl concentrations on minimization of (a) copper, (b) iron and (c) nickel interferences on the analytical signal of selenium using HG ICP OES. Legend for HCl concentrations: ♦ = 6 mol L^{-}; ■ = 5 mol L^{-}; ▲ = 4 mol L^{-}; and × = 3 mol L^{-1}. Concentration of Se: 200 μg L^{-1}.

As can be seen in Figs. 3 and 4, an increase in concentration of these metallic species (copper, nickel, and iron) results in a decrease of the analytical signals between 0% and 90% for selenium and 5% and 90% for arsenic. It was observed that cobalt did not cause interference on selenium response and that nickel presented the more severe interference for both elements.

From the obtained results, it can be concluded that the use of hydrochloric acid in concentrations as high as 6 mol L^{-1} is more effective in the suppression of metallic ion interferences from iron, nickel and copper than the use of thiourea, ortophenantroline and potassium iodide.

The proposed methodology is able to provide accurate results when analysing anaerobic, impacted sediments containing as much as 1.5% Fe_2O_3, which is common in estuarine degraded environmental areas.

3.5. Analytical features

The proposed procedure using a concomitant metals analyzer (CMA®) as hydride generator and inductively coupled plasma optical emission spectrometry (ICP OES) showed linearity within the concentration range of 0.014–10 μg g^{-1} for selenium and 0.013–10 μg g^{-1} for arsenic, considering a sample dilution of 50 times. The precision expressed as relative standard deviation (RSD) was 0.2% for selenium and arsenic both at a concentration of 10 μg g^{-1}. The limits of detection (LD) and quantification (LQ) were determined following the IUPAC recommendation [46]. For selenium, the LD and LQ were 0.006 and 0.030 μg g^{-1}, and for arsenic the LD and LQ were 0.0055 and 0.025 μg g^{-1}.

An analysis of the certified reference materials (industrial sludge, NIST 2782, and Buffalo River sediment, NIST 8704) demonstrates that the proposed procedure is accurate and that it can be used for selenium and arsenic determination in sediment samples. These certified reference materials were chosen because selenium and arsenic are certified for sample pretreatment using the US EPA 3051A method. The results obtained for the two certified reference materials are shown in Table 4.

3.6. Application

The proposed method was applied to the determination of bioavailable concentrations of selenium and arsenic in the certified reference materials and real sediment samples collected from several sites of Guanabara Bay, Rio de Janeiro, Brazil. Guanabara Bay is a eutrophic body of water that receives discharge from a drainage basin affected by over 7.8 million inhabitants, and evidence of trace metal contamination in anoxic sediments has been reported in the last decades [7,8,47].

The analysis results for four CRM sediments and for real sediment samples are shown in Table 5. According to the certified values, the total selenium content varies from 0.193 to 4.95 μg g^{-1}, and the total arsenic content varies from 6.23 to 45.3 μg g^{-1}. As can be seen, the bioavailable concentrations for these species represent a small percentage of the total mass in these samples. Bioavailable concentrations in the range of 0.11–1.2 and 2.8–22.2 μg g^{-1} were obtained for selenium and arsenic, respectively. The bioavailable percentage varied from 13% to 57% for selenium and 45% to 58% for arsenic. The analyte addition method was also applied to validate the developed method. The obtained results demonstrate that there are no significant differences between these two data sets, indicating that the proposed method could be satisfactorily used for the determination of bioavailable concentrations of selenium and arsenic in sediment samples. The developed procedure was applied to determine the bioavailable selenium and arsenic concentrations in five sediments samples collected from Guanabara Bay (Table 5). As can be seen, selenium presented bioavailability between 16% and 65% and arsenic presented bioavailability in the range of 31–41%.

Table 4
Results of analysis of two certified reference materials after samples digestion following US EPA 3051A method.

Certified reference material	Certified value (μg g^{-1})		Found value (μg g^{-1})	
	Se	As	Se	As
NIST 2782 (industrial sludge)	0.44 ± 0.11	166 ± 20	0.48 ± 0.05	167 ± 1
NIST 8704 (Buffalo River sediment)	–	17[a]	0.30 ± 0.04	17.2 ± 0.4

[a] Informed value.

Table 5
Evaluation of bioavaliable concentration and spiked tests of several sediments certified reference materials and real sediments samples collected in Guanabara Bay, Rio de Janeiro, Brazil.

Samples	Total concentration ($\mu g\, g^{-1}$)		Bioavailable concentration found by external calibration ($\mu g\, g^{-1}$)		Bioavailable concentration found by analyte addition method ($\mu g\, g^{-1}$)		Bioavailable fraction (%)	
	Se	As	Se	As	Se	As	Se	As
Certified reference materials								
NIST 1646a (estuarine sediment)	0.193 ± 0.028	6.23 ± 0.21	0.11 ± 0.01	2.8 ± 0.4	0.12 ± 0.02	2.9 ± 0.3	57	45
NIST 2702 (inorganic in marine sediments)	0.72 ± 0.05	21.2 ± 1.1	0.31 ± 0.02	12.3 ± 0.5	0.28 ± 0.03	12.7 ± 0.2	43	58
NRCC MESS-3 (marine sediments)	0.92 ± 0.22	26.2 ± 1.5	0.12 ± 0.03	11.8 ± 0.8	0.11 ± 0.01	12.2 ± 0.1	13	45
NRCC PACS-2 (harbour sediments)	4.95 ± 0.46[a]	45.3 ± 1.8	1.2 ± 0.3	22.2 ± 1.1	1.3 ± 0.1	22.6 ± 0.2	24	49
Guanabara Bay samples								
1	0.69 ± 0.05	8.2 ± 0.9	0.23 ± 0.02	3.0 ± 0.1	–	–	33	37
2	0.43 ± 0.02	6.0 ± 0.4	0.18 ± 0.06	2.4 ± 0.3	–	–	42	40
3	0.40 ± 0.03	8.7 ± 0.6	0.26 ± 0.02	2.7 ± 0.2	–	–	65	31
4	0.71 ± 0.04	7.5 ± 0.2	0.11 ± 0.06	2.90 ± 0.02	–	–	16	39
5	0.54 ± 0.05	13.1 ± 0.3	0.20 ± 0.03	5.3 ± 0.7	–	–	37	41

[a] Reference value.

4. Conclusions

An application of full factorial designs and Doehlert matrices allowed for the efficient optimization of a procedure for the determination of selenium and arsenic concentrations by ICP OES using a concomitant metals analyzer as hydride generator. Interference from transition metal ions such as cobalt, copper, iron and nickel can be avoided by using highly concentrated HCl solutions (6 mol L^{-1}). The proposed procedure was shown to be accurate, precise and have limits of detection and quantification adequate for the determination of bioavailable concentrations of selenium and arsenic in real sediment samples.

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