



Development and optimization of analytical method for the determination of cadmium from mineral water samples by off-line solid phase extraction system using sisal fiber loaded TAR by FAAS

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ABSTRACT

In the present work, a minicolumn of sisal fiber loaded with tiazolyazo-Resorsinol (TAR) is proposed a preconcentration system for cadmium determination in drinking water samples by flame atomic absorption spectrometry. In the optimization was first of all a full factorial design of two levels (2^4) was used for preliminary evaluation of four factors, involving the variables: sampling flow rate, elution flow rate, buffer concentration and pH. This design has showed that, for the studied levels, buffer concentration and pH are significant factors. Using the established experimental conditions in the optimization step of: pH 7.0, buffer concentration of 0.009 mol L^{-1} for elution utilized HCl at 2.0 mol L^{-1} , this system allows the determination of cadmium with a detection limit (LD) ($3\sigma/S$) of $0.05 \mu\text{g L}^{-1}$ and a quantification limit (LQ) ($10\sigma/S$) of $0.17 \mu\text{g L}^{-1}$, precision expressed as a relative standard deviation (R.S.D.) of 2.9 and 3.4% for a cadmium concentration of 10.0 and $20.0 \mu\text{g L}^{-1}$, respectively, and a preconcentration factor of 30 for a sample volume of 50.0 mL. The accuracy was confirmed by cadmium with spike tests with recuperations varying from 92% to 103%, procedure was applied for cadmium determination in drinking water samples collected from Salvador City, Bahia, Brazil. From the five samples analyzed, the achieved concentrations varied from 0.10 to $0.54 \mu\text{g L}^{-1}$.

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1. Introduction

Toxic metals in the environment are generally a source of pollution because they present great risks to human health. Important anthropogenic sources of these elements are emissions from industrial plants [1,2].

The World Health Organization (WHO) has established 3 and $10 \mu\text{g L}^{-1}$ as the maximum permissible limits for cadmium and lead in drinking water. In uncontaminated soil, the concentration of lead is generally in the range of 20 to 50 mg kg^{-1} . However, these values can increase in soil exposed to atmospheric deposition of lead from emission of soot from the foundry industries or the addition of pesticides [3].

The direct determination of the micronutrients in waters by atomic absorption spectrometry (AAS) is very difficult due to the low levels of metal ions and also interfering because of influences of main components of the matrix. Despite the selectivity and sensitivity of analytical

techniques such as atomic absorption spectrometry, there is a crucial need for the preconcentration of trace elements before their analysis due to their low concentrations in numerous samples (especially water samples) [4–6]. In several instances, it has been necessary to use a preconcentration method prior to analysis. In this context, several methods have been proposed and used for preconcentration and separation of trace elements according to the nature of the samples, the concentrations of the analytes and the measurement techniques [7–9].

The application of solid-phase extraction technique for preconcentration of trace metals from different samples results in several advantages such as minimal waste generation, reduction of sample matrix effects as well as sorption of the target species on the solid surface in a more stable chemical form [10]. The normal and selective solid-phase extractors are those derived from the immobilization of the organic compounds on the surface of solid supports which are mainly polyurethane foams [11,12] and ion exchange resins [9]. Although most studies involving metal preconcentration have used commercially available sorbents; other materials known as “natural adsorbents” or “biosorbents” have recently been successfully employed in metal adsorption processes [13–20]. The biosorption process [21,22] involves

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a solid phase (sorbent or biosorbent; biological material) and a liquid phase (solvent, normally water) containing a dissolved species to be sorbed (sorbate, metal ions).

Algae, chitinous materials or cellulose containing biomass has been employed owing to the occurrence of one or more of the mentioned chemical groups in these materials [23]. Studies with lignocellulosic materials, a major component in the cell wall of plants, have determined the presence of carboxylic and hydroxylic functional groups.

Studies involving the use of sisal fiber for the treatment of water in terms of the removal of heavy metals have been published [24]. However, the use of this material in the pre-concentration of metals has reported rarely in the literature [25].

Multivariate techniques have been applied for the optimization of analytical methods [26,27]. Among these, the two-level full factorial design is one of the more used. It can be applied mainly for preliminary evaluation of the significance of experimental variables of the methods [18]. However, for determination of critical conditions, one of the options is the use of central composite, Box-Behnken, Doehlert matrix and the three-level full factorial design [28], which is a response surface methodology (RSM). However, among these RSMs, the three-level full factorial design has been used only infrequently, because it requires a relatively large number of experiments if the factor number is higher than 2 [28].

In this paper, we proposed an off-line pre-concentration system cadmium (II) for determination in mineral drinking water samples by flame atomic absorption spectrometry. A minicolumn of sisal fiber loaded with tiazolylazo-Resorsinol (TAR) is used as a solid phase. The optimization step was performed using full factorial design.

2. Experimental

2.1. Instrumentation

A Varian Model SpectraAA 220 (Mulgrave, Victoria, Australia) flame atomic absorption spectrometer (FAAS), equipped with a conventional pneumatic nebulizer system and nebulization chamber was used for the analysis. The flame composition was air/acetylene (flow rate: 1.40 L min⁻¹). Aspiration flow rate was 5.0 mL in⁻¹. A cadmium hollow cathode lamp was run under the conditions suggested by the manufacturer applying a current of 10.0 mA. The most sensitive wavelength for cadmium is 228.8 nm; the suggested value for the bandwidth of the slit is 0.5 nm.

2.2. Reagents and solutions

All chemical reagents used in the experiment were of analytical grade. Ultra-pure water (18.2 MΩ cm) from a Milli-Q system (Millipore, MA, USA) was used to prepare all solutions. Glass apparatus used was maintained in nitric acid solution (10% vol/vol) for 12 h for decontamination prior to use.

Doubly deionized water was used throughout this work. Acetate (pH 4.7–6.0), borate (pH 7.0–8.5) and ammoniacal (pH 10.0) buffers were used to adjust the pH of the solutions, wherever suitable. Cadmium (II) standard solutions (1000 µg mL⁻¹) for the analysis were purchased from Merck. Working solutions were daily prepared by appropriate dilution. Hydrochloric and nitric acid solutions used as eluents were prepared by direct dilution from the concentrated solutions (Merck).

2.3. Preparation of the minicolumn

TAR solution in a concentration of 0.01% (wt/vol) was percolated through the minicolumn of dimensions: 5.0-cm length and an internal diameter of 4.0 mm, containing about 0.1 g of Sisal fiber in a flow rate of 2.5 mL min⁻¹ for 10 min. After this, the system was washed with 1 mol L⁻¹ of sodium hydroxide solution for elimination of the excess

Table 1
Factors and levels used in the factorial design.

Variables	Low (-)	Central point (0)	High (+)
Buffer concentration (mol L ⁻¹)	0.0080	0.0240	0.040
pH	3.0	6.0	9.0
Sample flow rate (mL min ⁻¹)	2.0	5.0	8.0
Elution flow rate (mL min ⁻¹)	2.0	5.0	8.0

of TAR reagent and afterward with 1 mol L⁻¹ nitric acid solution and water at the same flow rate in order to prevent any metal contamination.

The sisal fiber used as bioadsorbent in minicolumn was manufactured from the vascular tissue from the sisal plant and has diverse applications. Studies showed that the sisal fiber possesses carboxyl group (C=O), phenolic group (-OH), the C-H group [24].

The sisal fiber was prepared in the following ways: triturate in balls mill, wash with nitric acid solution (10% vol/vol) soon after washing with ultrapure water in successive times for total acid re-treat. After this, put the sisal fiber on the stove at 60 °C for 12 h.

2.4. The system off-line

The off-line system was carried out using one peristaltic pumps fitted with Tygon tubes and a minicolumn packed with sisal fiber loaded with TAR, the eluted was collected in vial and then analyzed in flame atomic spectrometry absorption. The flow system was operated in a volume-based mode, where a sample volume of 50.0 mL pumped at 6.0 mL min⁻¹ was percolated through a minicolumn.

2.5. Sample preparation

In the laboratory, prior to the pre-concentration procedure, all the water samples were filtered through a 0.45-µm pore size membrane filter to remove suspended particulate matter and were stored at 6 °C.

2.6. Optimization strategy

In the optimization procedure, a full factorial design of two levels (2⁴) was used for preliminary evaluation of four factors, involving the following variables: sampling flow rate (SFR), elution flow rate (EFR), buffer concentration (BC) and pH, the data of this design are shown in Table 1. A full three-level factorial design was performed in order to determine the critical conditions of the method, which was carried

Table 2
The matrix of the 3² full factorial design.

pH	BC	SFR	EFR	Abs
3.0	0.008	2.0	2.0	0.0336
9.0	0.008	2.0	2.0	0.0256
3.0	0.040	2.0	2.0	0.0238
9.0	0.040	2.0	2.0	0.0140
3.0	0.008	8.0	2.0	0.0302
9.0	0.008	8.0	2.0	0.0348
3.0	0.040	8.0	2.0	0.0301
9.0	0.040	8.0	2.0	0.0158
3.0	0.008	2.0	8.0	0.0410
9.0	0.008	2.0	8.0	0.0228
3.0	0.040	2.0	8.0	0.0330
9.0	0.040	2.0	8.0	0.0180
3.0	0.008	8.0	8.0	0.0309
9.0	0.008	8.0	8.0	0.0310
3.0	0.040	8.0	8.0	0.0149
9.0	0.040	8.0	8.0	0.0251
6.0	0.024	5.0	5.0	0.0276
6.0	0.024	5.0	5.0	0.0313
6.0	0.024	5.0	5.0	0.0329

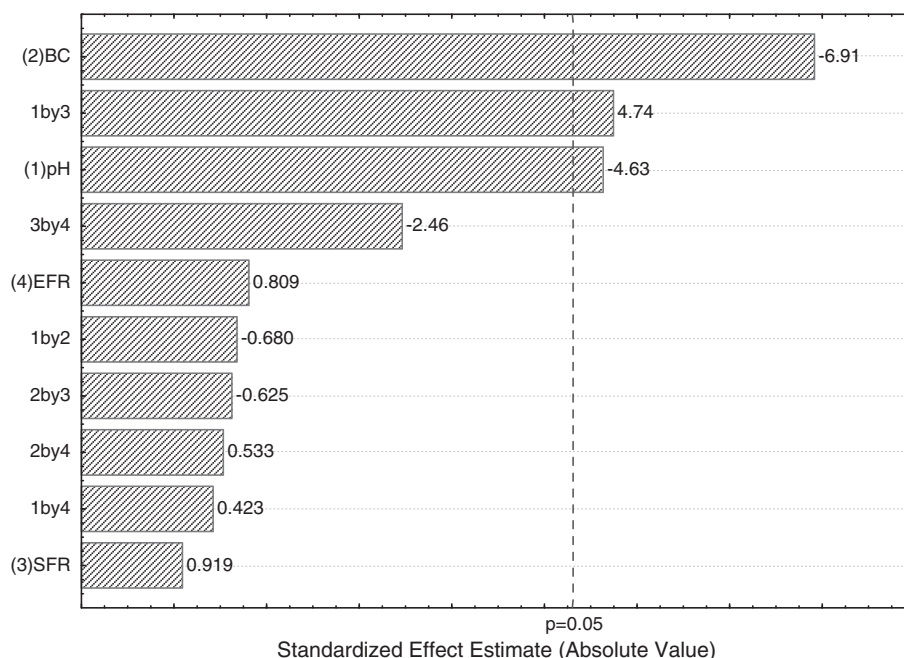


Fig. 1. Pareto chart of standardized effects. sampling flow rate (SFR), elution flow rate (EFE), buffer concentration (BC) and pH.

out in a random order. Triplicates of each point were performed to compute experimental variance. The analytical response was absorbance. The experimental data were processed using the STATISTICA computer program [29].

3. Results and discussion

3.1. Two-level full factorial design

The determination of the operational conditions sampling flow rate (SFR), elution flow rate (EFE), buffer concentration (BC) and pH was carried out in two steps. Firstly, a 2⁴ full factorial design was performed; the data of this design, with absorbance as response, are shown in Table 2. The evaluation of this experiment demonstrated that only the factors buffer concentration (BC) and pH are significant, as can be seen in the Pareto chart (Fig. 1) The negative values for the effects of buffer concentration (BC) and pH indicated that in the studied levels, the absorbance increased with the decreasing of BC and pH.

3.2. Determination of the critical conditions using 3² full factorial design

A 3² full factorial design was performed for the determination of the optimum conditions for the factors buffer concentration (BC) and pH, as described in Table 3, the factors and levels used in the factorial design.

Table 3
The matrix of the 3² full factorial design.

pH	CT	Abs	Abs	Abs
3.0	0.008	0.0143	0.0132	0.0114
3.0	0.024	0.0038	0.0043	0.0045
3.0	0.040	0.0006	0.0016	0.0014
6.0	0.008	0.0453	0.0457	0.0450
6.0	0.024	0.0429	0.0434	0.0447
6.0	0.040	0.0311	0.0324	0.0322
9.0	0.008	0.0352	0.0357	0.0350
9.0	0.024	0.0337	0.0326	0.0339
9.0	0.040	0.0334	0.0336	0.0354
6.0	0.024	0.0489	0.0495	0.0495
6.0	0.024	0.0463	0.0460	0.0464
6.0	0.024	0.0415	0.0409	0.0425

The matrix of the design and the results are summarized in Table 3. The equation below illustrates the relation among buffer concentration (BC), pH and analytical signal (AS), considering the real values.

$$AS = 0.0602 + 0.0321pH - 0.0024pH^2 - 0.252BC - 8.94BC^2 + 0.0619pH \cdot BC$$

The derivation of this equation in terms of pH and also BC results in the following equation system:

$$\frac{\partial AS}{\partial pH} = 0.0321 - 0.0048pH + 0.0619BC$$

$$\frac{\partial AS}{\partial BC} = -0.252 - 17.88BC + 0.0619pH$$

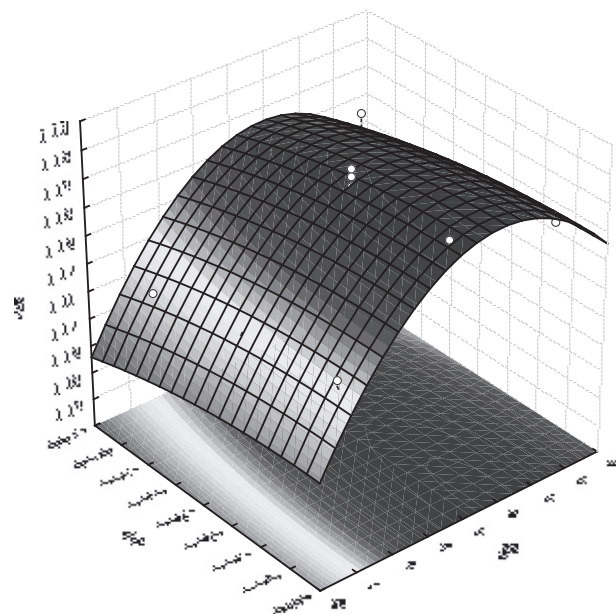


Fig. 2. Response surface for optimization of the variables pH and buffer concentration.

Table 4
Critical conditions.

Variables	Critical conditions
Buffer concentration (mol L ⁻¹)	0.0083
pH	7.0

This equation system shows a maximum point in the response surface (Fig. 2), therefore to determine the critical conditions, this equation was utilized. The method of calculating these optimal conditions has been published [30]. Considering the results obtained in the optimization step the conditions established in the procedure are as follows: sampling flow rate of 6.0 mL min⁻¹, buffer concentration of 0.009 mol L⁻¹, pH 7.0, elution concentration of 2.00 mol L⁻¹ and elution flow rate of 6.0 mL min⁻¹. The volumes used for samples and standard solutions in the preparation of the analytical curves were 50 mL.

3.3. Validation of the analytical methods

3.3.1. Analytical features

We used the established experimental conditions in the optimization step: pH 7.0 and buffer concentration of 0.009 mol L⁻¹; the cadmium was eluted with 1.0 mL of HCl (2.0 mol L⁻¹). This off-line preconcentration system allows the determination of cadmium with linear response from 0.1 to 800 µg L⁻¹, the analytical curve obtained was (Abs = 0.006 * Cd - 0.0016) with a correlation coefficient of 0.998.

The limit of detection (LOD), defined as the cadmium concentration that gives a response equivalent to three times the standard deviation of the blank (n = 10), was found to be 0.08 µg L⁻¹ and quantification limit (LOQ) was 0.30 µg L⁻¹. Precision expressed as a relative standard deviation (R.S.D.) of 2.9 and 3.4% for cadmium concentration of 10.0 and 20.0 µg L⁻¹, respectively, were calculated as per IUPAC recommendation [31], and the pre-concentration factor for a sample volume of 50.0 mL was 30. The accuracy was evaluated using absolute recoveries comparing the concentrations found in five mineral water samples spiked with known amounts of standard of cadmium. The concentrations were obtained using the calibration curve, obtained values were about 92% to 103% of recuperation for cadmium (Table 4).

3.3.2. Tolerance of other metallic ions on the proposed procedure

In order to check the effect of other metallic ions on the method, a standard solution containing cadmium and other ions (F⁻, Cl⁻, CO₃²⁻, HCO⁻, Na⁺, SO₄²⁻, K⁺), each one at 24.0 mg L⁻¹, was prepared and cadmium was determined. The achieved results showed that in this concentration the other ions do not interfere in the cadmium determination.

3.3.3. Robustness test

The robustness [32] of the method (defined as the measure of its capacity to reproduce results when the procedure is performed under small changes in the nominal values established) was also evaluated. This test was carried out bearing in mind the following critical conditions: pH of 7.0 and buffer concentration of 0.009 mol L⁻¹

Table 5
Test spike and cadmium determination in mineral water samples.

Mineral water sample	Cadmium content added (µg L ⁻¹)	Cadmium content achieved (µg L ⁻¹)	Recovery (%)
1	0.0	0.47 ± 0.06	101.6
	10.0	10.63 ± 0.01	
2	0.0	<LQ	100
	10.0	10.02 ± 0.02	
3	0.0	0.52 ± 0.04	105
	10.0	11.02 ± 0.01	
4	0.0	0.64 ± 0.05	92.8
	10.0	9.92 ± 0.01	
5	0.0	2.02 ± 0.03	-

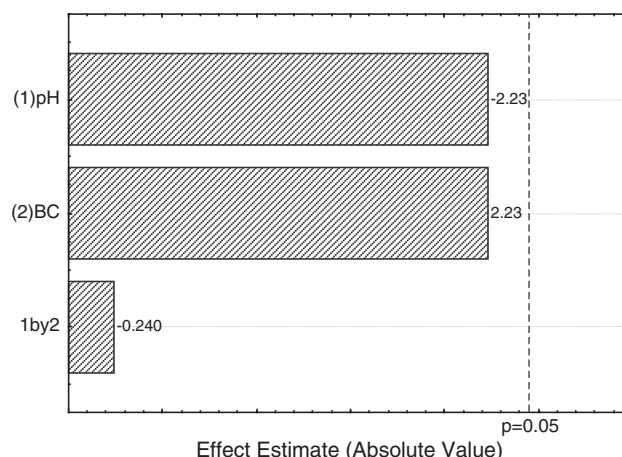


Fig. 3. Pareto chart for robustness test for a variation of 10% for the variables pH and buffer concentration.

(Table 6). For this test, we was used a two-level full factorial design involving these variables, centered on the experimental conditions described in Table 5. The analysis of variance (ANOVA) was used for interpretation of the data from this experiment, and the results demonstrate that this procedure is robust for a variation of 10% for the variables pH and buffer concentration (Fig. 3).

3.4. Cadmium determination in mineral water

The proposed method was applied for cadmium determination in mineral water samples collected in a supermarket in Salvador City, Brazil. The obtained results from the analysis of five samples collected in several supermarket of the city varied from 0.47 to 2.02 µg L⁻¹, as can be seen in Table 4. Recovery experiments were performed and the results varied from 92% to 103%. These results demonstrated that the cadmium concentration is very low.

4. Conclusion

Sisal fiber was successfully applied to the off-line preconcentration and determination of cadmium by FAAS in mineral water samples. The method is simple, inexpensive, precise and accurate. The cadmium content for the mineral water samples collected in Salvador City, Brazil was lower than the maximum permissible level (3.0 µg L⁻¹) for cadmium in mineral water as per Health Organization of the Brazilian Government (ANVISA).

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Table 6
Two-level full factorial design for robustness test.

pH	BC	Abs	Abs
-1.0	-1.0	0.1408	0.1289
1.0	-1.0	0.1287	0.1182
-1.0	1.0	0.1569	0.1411
1.0	1.0	0.1395	0.1302
0.0	0.0	0.1259	0.1389

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