

An on-line pre-concentration system for determination of cadmium in drinking water using FAAS

Walter N.L. dos Santos^{a,*}, Jorge L.O. Costa^a, Rennan G.O. Araujo^a,
Djane S. de Jesus^{a,b}, Antônio C.S. Costa^a

^a Universidade Federal da Bahia, Instituto de Química, Salvador, Bahia 40170-290, Brazil

^b Centro Federal de Educação Tecnológica da Bahia, Salvador, Bahia 40300-010, Brazil

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Abstract

In the present paper, a minicolumn of polyurethane foam loaded with 4-(2-pyridylazo)-resorcinol (PAR) is proposed as pre-concentration system for cadmium determination in drinking water samples by flame atomic absorption spectrometry.

The optimization step was performed using two-level full factorial design and Doehlert matrix, involving the variables: sampling flow rate, elution concentration, buffer concentration and pH.

Using the established experimental conditions in the optimization step of: pH 8.2, sampling flow rate 8.5 mL min^{-1} , buffer concentration 0.05 mol L^{-1} and elution concentration of 1.0 mol L^{-1} , this system allows the determination of cadmium with detection limit (LD) ($3\sigma/S$) of 20.0 ng L^{-1} and quantification limit (LQ) ($10\sigma/S$) of 64 ng L^{-1} , precision expressed as relative standard deviation (R.S.D.) of 5.0 and 4.7% for cadmium concentration of 5.0 and $40.0 \mu\text{g L}^{-1}$, respectively, and a pre-concentration factor of 158 for a sample volume of 20.0 mL. The accuracy was confirmed by cadmium determination in the standard reference material, NIST SRM 1643d trace elements in natural water.

This procedure was applied for cadmium determination in drinking water samples collected from Salvador City, Bahia, Brazil. For five samples analyzed, the achieved concentrations varied from 0.31 to $0.86 \mu\text{g L}^{-1}$.

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1. Introduction

Cadmium is one of the heavy metals more critical for the human health [1]. It enters the organism primarily via the alimentary and/or respiratory tract. It can be cause of diseases as: hypertension, arteriosclerosis, cancer, etc. [2]. Considering it, health organizations have established permissible limits for cadmium in food human, including drinking water [2,3]. The World Health Organization (WHO) established as $3 \mu\text{g L}^{-1}$ the maximum permissible for this element in drinking water [2]. The limit established by Environmental Protection Agency (EPA) is $5 \mu\text{g L}^{-1}$ [3]. In Brazil, the limit fixed by Health Organization Brazilian Govern is $5 \mu\text{g L}^{-1}$ [4].

Cadmium determination in drinking water samples could be carried out directly by electrothermal atomic absorption spectrometry (ETAAS) or by inductively coupled plasma mass spectrometry (ICP-MS), which have usually enough sensitivity. However, flame atomic absorption spectrometry (FAAS) and inductively coupled plasma optical emission spectrometry (ICP-OES), which are available techniques in most laboratories, require the use of a pre-concentration step in order to reach an appropriate level of sensitivity. Considering it, pre-concentration procedures for determination of cadmium traces by FAAS and ICP-OES are opportune and several pre-concentration procedures have been proposed for it [5–11].

Polyurethane foam has good properties as sorbent in solid phase extraction [12]. It was firstly used in on-line pre-concentration system in method for zinc determination using molecular absorption spectrophotometry [13]. However, in the last years this sorbent has been very used in on-line pre-

* Corresponding author. Tel.: +55 71 323 51 166; fax: +55 71 2355 166.
E-mail address: waltrs8@hotmail.com (W.N.L. dos Santos).

concentration system for metal determination using flame atomic absorption spectrometry [14,15].

Multivariate techniques have been very applied for optimization of analytical methods [16,17]. 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 [16,18]. However, for determination of critical conditions, one of the options is use of Doehlert designs [16,19], which is a response surface methodology (RSM) that have been very applied for optimization of analytical methods [20,21].

In this paper is proposed an on-line pre-concentration system for cadmium determination in drinking water samples by flame atomic absorption spectrometry. In it, a minicolumn of polyurethane foam loaded with 4-(2-pyridylazo)-resorcinol (PAR) is used as solid phase. The optimization step was performed using factorial design and Doehlert matrix.

2. Experimental

2.1. Apparatus

A Varian (Mulgrave, Vic., Australia) Model SpectrAA 220 flame atomic absorption spectrometer was used for the analysis. The cadmium hollow cathode lamp was run under the conditions suggested by the manufacturer (current: 4.0 mA). Wavelength (228.8 nm), the bandwidth of the slit (0.5 nm) and burner height (13.5 mm) had suggested values. The flame composition was: acetylene (flow rate: 2.0 L min⁻¹) and air (flow rate: 13.5 L min⁻¹). Aspiration flow rate was 4.0 mL min⁻¹.

Two Alitea USA peristaltic pumps C-6 XV provided with Tygon tubes were used to propel all solutions and a Rheodyne 5041 model injection valve was used to switch the pre-concentration/elution steps. All connections were made using fittings, unions and tees made of plastic and PEEK materials. The manifold was built up with PTFE tube of 0.5 mm bore.

A 300 ANALYSER pH meter was used to adjust medium pH.

2.2. Reagents

Ultrapure water from a Milli-Q water purification system (Millipore) was used to prepare all solutions.

All reagents were of analytical grade. The laboratory glassware was kept overnight in a 5% (v/v) nitric acid solution. Afterwards it was rinsed thoroughly with ultrapure water and dried in a dust-free environment.

- *Cadmium(II) solution* (10.00 µg mL⁻¹) was prepared by diluting a 1000 µg mL⁻¹ cadmium solution with a 1% hydrochloric acid solution.
- *PAR solution* 0.01% (w/v) was prepared by dissolving 0.20 g PAR in 200 mL of ethanol.
- *Tris buffer solution* was prepared by dissolving 12.10 g of Tris-(hydroxymethyl)aminomethane (Merck) in 1000 mL of deionised water and pH was adjusted with hydrochloric acid.

- *Hydrochloric acid solution* (1 mol L⁻¹) was prepared by direct dilution with water from the concentrated suprapur solution.

2.3. Preparation of the minicolumn

PAR solution in a concentration of 0.01% (w/v) was percolated through the minicolumn containing about 0.1 g of polyurethane foam in a flow rate of 2.5 mL min⁻¹ for 5 min. After this system was washed with 1 mol L⁻¹ sodium hydroxide solution for elimination of the excess of PAR reagent and afterwards with 1 mol L⁻¹ nitric acid solution and water at the same flow rate in order to prevent any metal contamination [22].

2.4. Continuous flow system

The diagram of the flow system is shown in Fig. 1. The flow system was carried out using two peristaltic pumps fitted with Tygon tubes, one four-way valve and a minicolumn packed with polyurethane foam loaded with PAR, coupled to a flame atomic absorption spectrometer [14]. The flow system was operated in a volume-based mode, which a sample volume of 20.0 mL pumped at 8.5 mL min⁻¹ was percolated through a minicolumn. Then, cadmium(II) ions are retained in the minicolumn as cadmium(II)–PAR complex, and the remaining solution is discharged. By switching the valve a stream of 1.0 mol L⁻¹ hydrochloric acid (E) that flows at 5.5 mL min⁻¹ displaces the cadmium complexed. This eluate is taken direct to the nebulizer–burner system of a flame atomic absorption spectrometer. Signals were measured as peak area by using instrument software.

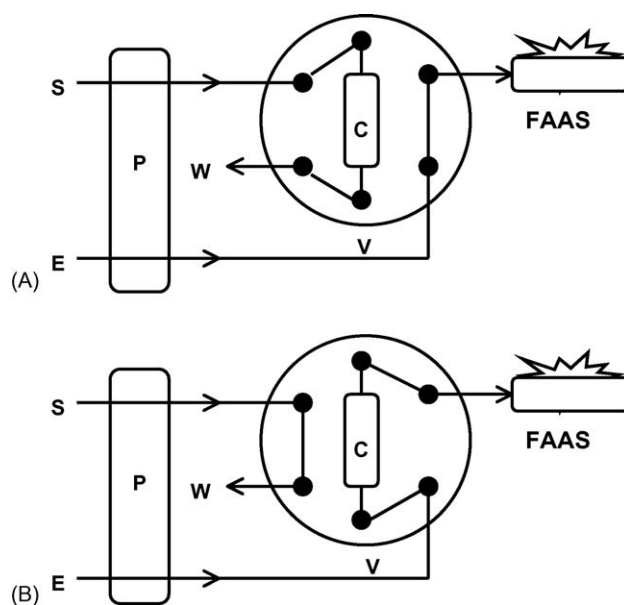


Fig. 1. System of on-line pre-concentration. Schematic diagram of the flow system used for pre-concentration and determination of cadmium by FAAS. P1 (8.5 mL min⁻¹); P2 (5.5 mL min⁻¹); P, peristaltic pump; C, polyurethane foam/PAR minicolumn; V, four-way valve; FAAS, flame atomic absorption spectrometer and W, waste. (A) Four-way valve in pre-concentration step and (B) four-way valve in the elution position.

The minicolumn was not reconditioned at the end of each cycle, since sample solution was buffered before pre-concentration. This strategy has been recommended [23] in order to simplify the on-line system (an additional line with buffer solution is avoided) and to increase the concentration efficiency (CE). This strategy caused a small loss of the analyte, but it did not deteriorate the pre-concentration system, since this loss might be always reproducible for both standards and samples.

2.5. Sample preparation

The samples were conditioned in PTFE bottles, according (USEPA) recommendations [24]. 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

The optimization step was performed using two-level full factorial design and Doehlert matrix. All the experiments were carried out in random order, using always 20.0 mL of 5.0 $\mu\text{g L}^{-1}$ cadmium solution. The variables regarded as factors in this step were: sampling flow rate, elution concentration, buffer concentration and pH. The elution flow rate was fixed at 5.5 mL min^{-1} because this is compatible with the aspiration flow of FAAS. The results of the factorial design and Doehlert matrix were evaluated using as response the analytical signal (absorbance).

3. Results and discussion

3.1. Two-level full factorial design

Considering the flow system, the variables chosen in the optimization step were: sampling flow rate (SFR), eluent concentration (EC), buffer concentration (BC) and pH. Firstly, a two level full factorial design was performed in order to determine the influence these factors on the on-line system. In Table 1 are the minimum and maximum levels of each factor, which were established according to data from previous experiments. Table 2 shows the experimental matrix and the results of this experiment. The evaluation considering the Pareto chart (Fig. 2) demonstrated that the interaction (pH \times buffer concentration) and the factors buffer concentration and pH are statistically significant. Sampling flow rate in the range from 7.0 to 10.0 mL min^{-1} and eluent concentration varied from 0.50 to 1.50 mol L^{-1} are not statistically significant.

Table 1
Factors and levels used in the factorial design

Variables	Low (–)	Central point	High (+)
Sampling flow rate (SFR), mL min^{-1}	7.0	8.5	10.0
Buffer concentration (BC), mol L^{-1}	0.010	0.055	0.100
Elution concentration (EC), mol L^{-1}	0.50	1.00	1.50
pH	7.0	8.5	10.0

Table 2
Two-level full factorial design

Experiment	SRF	BC	EC	pH	AS
1	+	+	+	+	0.1340
2	+	+	+	–	0.0546
3	+	+	–	+	0.1436
4	+	+	–	–	0.0812
5	+	–	+	+	0.1000
6	+	–	+	–	0.2482
7	+	–	–	+	0.1056
8	+	–	–	–	0.2510
9	–	+	+	+	0.0710
10	–	+	+	–	0.1367
11	–	+	–	+	0.1458
12	–	+	–	–	0.0785
13	–	–	+	+	0.1005
14	–	–	+	–	0.2570
15	–	–	–	+	0.1106
16	–	–	–	–	0.2482
Central point	0	0	0	0	0.2461
Central point	0	0	0	0	0.2570
Central point	0	0	0	0	0.2390

Solution volume: 20 mL; cadmium concentration: 5.0 $\mu\text{g L}^{-1}$; SRF: sampling flow rate; BC: buffer concentration; EC: elution concentration; AS: analytical signal (absorbance).

3.2. Determination of the critical conditions using Doehlert matrix

Considering this result, a Doehlert design involving the factors buffer concentration (BC) and pH was carried out in order to determine the critical conditions of these variables for maximum signal of absorbance. In this design sampling flow rate and eluent concentration were fixed as 8.5 mL min^{-1} and 1.0 mol L^{-1} , respectively. Table 3 shows the matrix as coded and real values and the analytical signals (AS) obtained in the Doehlert design. These results are fitted as the following equation:

$$\text{AS} = -0.525 + 0.185\text{pH} + 1.018\text{BC} - 0.011(\text{pH})^2 + 0.068\text{pH BC} - 15.896(\text{BC})^2$$

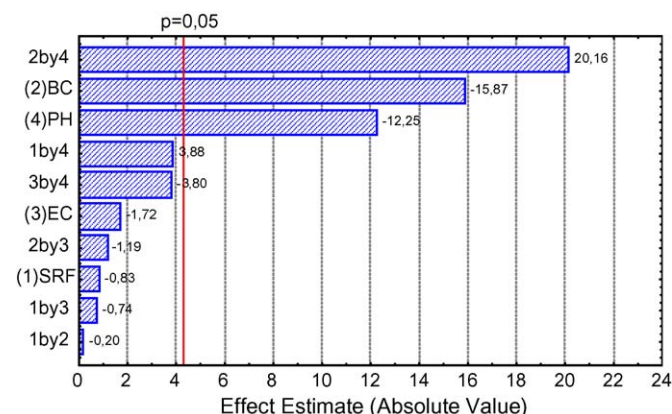


Fig. 2. Pareto chart of standardized effects. SRF: sampling flow rate; BC: buffer concentration; EC: elution concentration.

Table 3
Doehlert matrix for optimization of pH and buffer concentration

pH	BC (mol L ⁻¹)	Analytical signal (absorbance)
7.00 (-0.866)	0.070 (0.5)	0.2367
8.50 (0.000)	0.090 (1.0)	0.2358
10.00 (0.866)	0.070 (0.5)	0.2221
10.00 (0.866)	0.030 (-0.5)	0.2176
8.50 (0.000)	0.010 (-1.0)	0.2360
7.00 (-0.866)	0.030 (-0.5)	0.2403
8.50 (0.000)	0.050 (0.0)	0.2510
8.50 (0.000)	0.050 (0.0)	0.2651
8.50 (0.000)	0.050 (0.0)	0.2679

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

$$\frac{\delta AS}{\delta pH} = +0.185 - 0.022pH + 0.068BC;$$

$$\frac{\delta AS}{\delta BC} = +1.018 + 0.068pH - 31.792BC$$

The resolution of this equation system shows a maximum point for pH of 8.23 and buffer concentration of 0.049 mol L⁻¹. The corresponding surface response is shown in Fig. 3.

3.3. Final optimization

Considering the results obtained in the optimization step the conditions established in the procedure are: sampling flow rate of 8.5 mL min⁻¹, buffer concentration of 0.05 mol L⁻¹, pH 8.2, elution concentration of 1.00 mol L⁻¹ and elution flow rate of 5.5 mL min⁻¹. The volumes used for samples and standard solutions in the preparation of the analytical curves are 20 mL.

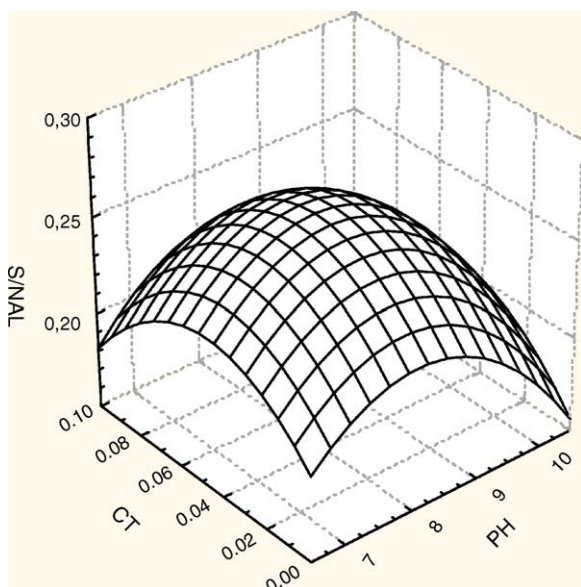


Fig. 3. Response surface for optimization of the variables pH and buffer concentration.

3.4. Analytical characteristics

The on-line pre-concentration system proposed showed linearity within the concentration range from 64 ng L⁻¹ to 10.0 µg L⁻¹, with an analytical curve of $AS = 0.00122 + 0.0539 [Cd \mu g L^{-1}]$ ($R^2 = 0.9988$). The precision expressed as relative standard deviation (R.S.D.) was 5.0 and 4.7% for cadmium concentration of 5.0 and 40.0 µg L⁻¹, respectively. A limit of detection (LD) of 20 ng L⁻¹ and quantification (LQ) of 64 ng L⁻¹ were calculated as IUPAC recommendation [25] for sample solution of 20 mL. The experimental pre-concentration factor, calculated considering the ratio of the slopes of the analytical curves with and without pre-concentration was 158. The consumptive index [23] (defined as the sample volume, in millilitres consumed in order to achieve a unit of factor preconcentration) was also calculate and was 0.13 mL. The accuracy was confirmed by cadmium determination in the standard reference material, NIST SRM 1643d trace elements in natural water. Using the proposed method the cadmium concentration found in this SRM was $6.38 \pm 0.47 \mu g L^{-1}$ and the certified value of $6.47 \pm 0.37 \mu g L^{-1}$. The *t*-test demonstrated that there is no significant difference between these values.

3.5. 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 eighteen other metallic ions (each one at 10.00 µg L⁻¹) was prepared and cadmium was determined. The achieved results showed that in this concentration, the other metallic ions do not interfere in the cadmium determination. This experiment was carried out using a multielemental ICP-OES solution Quality Control Standards (QCS-19), which had arsenic, antimony, beryllium, cadmium, calcium, chromium, cobalt, copper, iron, molybdenum, nickel, thallium, titanium, zinc, lead, magnesium, manganese and selenium at the concentration of 100 µg L⁻¹ each one.

3.6. Cadmium determination in drinking water

The proposed method was applied for cadmium determination in drinking water samples collected in Salvador City, Brazil.

Table 4
Cadmium determination in drinking water samples

Sampling station	Cadmium content added (µg L ⁻¹)	Cadmium content achieved (µg L ⁻¹)	Recovery (%)
1	0.00	0.34 ± 0.03	–
	0.50	0.91 ± 0.01	114
2	0.00	0.51 ± 0.04	–
	0.50	1.04 ± 0.03	106
3	0.00	0.44 ± 0.03	–
	0.50	0.90 ± 0.05	92
4	0.00	0.86 ± 0.03	–
	0.50	0.31 ± 0.04	–

N, number of observations = 3.

The obtained results for analyse of five samples collected in several points of the city varied from 0.31 to 0.86 $\mu\text{g L}^{-1}$, as can be seen in Table 4. Recovery experiments were performed and the results varied from 92 to 114%. These results demonstrated that the cadmium concentration is lower than the maximum permissible level (5.0 $\mu\text{g L}^{-1}$) for drinking water considering the Health Organization of the Brazilian Govern [4].

4. Conclusion

The analytical features (precision, limit of detection and accuracy) achieved demonstrated the feasibility of the on-line system proposed for cadmium determination in drinking water samples using FAAS.

The Doehlert matrix allowed a fast and efficient optimization of the chemical and operational variables of the proposed procedure.

The cadmium content for the drinking water samples collected in Salvador City, Brazil were lower than the maximum permissible level (5.0 $\mu\text{g L}^{-1}$) for cadmium in drinking water as Health Organization of the Brazilian Government.

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