

Simultaneous pre-concentration procedure for the determination of cadmium and lead in drinking water employing sequential multi-element flame atomic absorption spectrometry

Lindomar A. Portugal^a, Hadla S. Ferreira^a, Walter N.L. dos Santos^b, Sergio L.C. Ferreira^{a,*}

^a Universidade Federal da Bahia, Instituto de Química, Campus Universitário de Ondina, Salvador-BA, 40170-290, Brazil

^b Universidade Do Estado da Bahia Rua Silveira Martins, 2555, Cabula. Salvador-Bahia CEP: 41.195.001, Brazil

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Abstract

In this paper is proposed a simultaneous pre-concentration procedure using cloud point extraction for the determination of cadmium and lead in drinking water employing sequential multi-element flame atomic absorption spectrometry. The ligand used is 2-(2-thiazolylazo)-*p*-cresol (TAC) and the micellar phase is obtained using non-ionic surfactant octylphenoxypolyethoxyethanol (Triton X-114) and centrifugation.

The optimization step was performed using two-level factorial design and Doehlert design. A multiple response function was established in order to get experimental conditions for simultaneous extraction of cadmium and lead.

The method allows the determination of cadmium and lead with detection limits of $0.077 \mu\text{g L}^{-1}$ and $1.05 \mu\text{g L}^{-1}$ respectively, precision expressed as relative standard deviation (RSD) of 1.5 and 3.3% ($n=10$) for cadmium concentrations of $30 \mu\text{g L}^{-1}$ and $50 \mu\text{g L}^{-1}$, respectively, and RSD of 1.8% and 2.7% for lead concentrations of $30 \mu\text{g L}^{-1}$ and $50 \mu\text{g L}^{-1}$, respectively. The accuracy was confirmed by analysis of a certified reference material of natural water.

This method was applied for the determination of cadmium and lead in drinking water samples collected in Jaguaquara City, Brazil. Tests of addition/recovery were also performed for some samples and results varied from 95 to 104% for cadmium and 96 to 107% for lead. The cadmium and lead concentrations found in these samples were always lower than the permissible maximum levels stipulated by Brazilian Health Organization.

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1. Introduction

The quantification of lead and cadmium in drinking water is very important considering the toxicity of these metals [1–3]. However, these determinations are generally difficult because the concentrations of these metals are low and the conventional analytical techniques do not present quantification limits necessary for these analysis. This way, several pre-concentration procedures have been performed in order to allow the determination of these elements in these matrices [4–6].

Cloud point extraction (CPE) is a separation technique that has been frequently applied in pre-concentration procedures for the determination of metal ions [7–12] and also other species

[13,14]. Advantages and limitations of this technique have been summarized in recent reviews [15,16].

The 2-(2-thiazolylazo)-*p*-cresol (TAC) is a ligand that has been used for the determination of metal ions using molecular absorption spectrophotometry [17] and also cathodic stripping voltammetry [18].

In the present paper, a simultaneous pre-concentration procedure using CPE is proposed for the determination of cadmium and lead in drinking water samples, employing the fast sequential flame atomic absorption spectrometry (FS-FAAS) as analytical technique [19,20]. The ligand is 2-(2-thiazolylazo)-*p*-cresol (TAC) and the micellar phase is obtained using the surfactant octylphenoxypolyethoxyethanol (Triton X-114). The optimization step was performed using factorial design and Doehlert matrix [21–23]. The method was applied for the determination of cadmium and lead in drinking water samples collected in Jaguaquara City, Brazil.

* Corresponding author. Fax: +55 71 32355166.

E-mail address: slcf@ufba.br (S.L.C. Ferreira).

2. Experimental

2.1. Instrumentation

A Varian Model SpectrAA 220 (Mulgrave, Victoria, Australia) flame atomic absorption spectrometer with fast sequential module (FS-FAAS), equipped with a conventional system pneumatic nebulizer and nebulization chamber was used for the analysis. A multi-element silver, cadmium, lead and zinc hollow cathode lamp was run under the conditions suggested by the manufacturer applying a current of 10.0 mA. The most sensitive wavelengths for cadmium at 228.8 nm and lead at 217.0 nm were used with bandwidth of 0.5 nm and 1.0 nm for cadmium and lead, respectively. The flame composition was acetylene (flow rate 2.0 L min) and air (flow rate: 13.5 min⁻¹) and the burner height was 13.5 mm. The nebulizer flow rate aspiration was kept among 5.5 and 6.0 mL min⁻¹. A Fanem (São Paulo, Brazil) Thermostatic bath was used to reach the cloud point temperature. A Janetzki T 32 C (Berlin, German) centrifuge was used to accelerate phase separation.

2.2. Chemicals and reagents

Ultrapure water was used for the preparation of the standard solutions. Cadmium and lead solutions (10.0 g mL⁻¹) were prepared by diluting a 1000 g mL⁻¹ cadmium and lead solutions (Merck®) with 1% (v/v) nitric acid. A 0.025% 2-(2-thiazolylazo)-*p*-cresol (TAC) solution was prepared by dissolving 0.025 g of 2-(2-thiazolylazo)-*p*-cresol (TAC) in 3.2 g of Triton X-114 in 10 mL of ethanol and diluting to volume with ethanol in a 100 mL volumetric flask.

TRIS buffer solution (pH 10) was prepared by dissolving 24.2 g of Tris-(hydroxymethyl) aminomethane (Merck) in 200 mL of deionised water and pH was adjusted with hydrochloric acid.

2.3. General procedure

Into a centrifuge tube, transfer a sample volume of 50 mL, 1.0 mL of solution 2-(2-thiazolylazo)-*p*-cresol (TAC) in Triton X-114, 1.0 mL of buffer solution at pH 10.0 and dilute to the mark with demineralized water. This solution were kept maintained for 15 min in a thermostatically bath maintained at 40 °C. Separation of the two phases was achieved by centrifugation for 15 min at 2500 rpm. On cooling in an ice-bath for 15 min, the surfactant-rich phase became viscous. Then, the aqueous phase could be separated by inverting the tubes. In the later step, to reduce the viscosity and facilitate sample handling, 300 µL ethanol solution containing 1% HNO₃ was added. This final solution was introduced into the flame by conventional aspiration.

2.4. Sample preparation

The samples were filtered through 0.45 mm membrane immediately after sampling, and were acidified to pH 2.0 with nitric acid and stored at 6 °C. The bottles were previously washed with a 10% (v/v) nitric acid–water solution and afterward with ultrapure water.

3. Results and discussion

3.1. Optimization step for extraction of cadmium and lead

The optimization of the pre-concentration procedure was performed in two steps. Firstly, a two-level full factorial design [24–26] was carried out involving the followings factors: pH (in the range from 7.0 to 10.0); TAC reagent concentration (from 2.5 to 7.5 mg L⁻¹); sodium chloride concentration (from 0.04 to 0.10 g L⁻¹) and reaction time (from 30 to 90 min). The time and temperature of heating were fixed in 15 min at 40 °C as previous paper [27], which used also Triton X-114 as surfactant. A volume of 50 mL of a 30.0 µg L⁻¹ cadmium and lead solution was used in all experiments. The evaluation of this factorial design demonstrated that for these experimental conditions, only the factors pH and reagent concentration are significant for both metal ions and require a final optimization. Consequently, pH and reagent concentration were optimized using a Doehlert design [28,29]. The results obtained with this experimental design together with the coded and real values for the variables studied are shown in Table 1. The evaluation was done using a multiple response function (MR) in order to get a simultaneous condition for pre-concentration of lead (II) and cadmium (II) ions. MR was calculated by expression:

$$(MR) = \text{Abs Cd}/0.1176 + \text{Abs Pb}/0.0600,$$

where Abs is the analytical signal for each metal ion, 0.1176 and 0.0600 were the maximum values of absorbance obtained for cadmium and lead, respectively, during the experiment.

The equation below illustrates the relationship of the two variables pH and reagent concentration (RC) and the multiple response function (MR).

$$MR = -38.998 + 7.209(\text{pH}) + 1.898(\text{RC}) - 0.328(\text{pH})^2 - 0.119(\text{pH})(\text{RC}) - 0.074(\text{RC})^2$$

This equation shows a critical point in the surface response, which is a maximum for the pH of (10.14) and for the reagent concentration of (4.67 mg L⁻¹). These results (calculated using the multiple response function) agree with the results calculated for cadmium and lead separately, which were: pH 10.14 and RC: 4.84 mg L⁻¹ for lead, and pH 10.17 and RC: 4.55 mg L⁻¹

Table 1
Doehlert design for optimization of the extraction step

Experiment	pH	RC	Cd	Pb	MR
1	8.50	6.25	0.0692	0.0361	1.1902
2	9.50	7.50	0.0837	0.0505	1.5527
3	10.50	6.25	0.0903	0.0538	1.6643
4	8.50	3.75	0.0395	0.0357	0.9309
5	9.50	2.50	0.0654	0.0447	1.3019
6	10.50	3.75	0.1176	0.0600	1.9996
7 (C)	9.50	5.00	0.1128	0.0533	1.8477
8 (C)	9.50	5.00	0.1103	0.0571	1.8899
9 (C)	9.50	5.00	0.1077	0.0609	1.9313

RC: reagent concentration (mg L⁻¹).

MR: multiple response function for simultaneous extraction of cadmium and lead.

Table 2
Analytical characteristic of the method proposed

Parameters	Cadmium	Lead
Limit of detection	0.077 $\mu\text{g L}^{-1}$	1.05 $\mu\text{g L}^{-1}$
Limit of quantification	0.26 $\mu\text{g L}^{-1}$	3.5 $\mu\text{g L}^{-1}$
Precision as RSD	1.5 and 3.3% for concentrations of cadmium of 30 $\mu\text{g L}^{-1}$ and 50 $\mu\text{g L}^{-1}$.	1.8% and 2.72% for concentrations of lead of 30 $\mu\text{g L}^{-1}$ and 50 $\mu\text{g L}^{-1}$
Pre-concentration factor	22	56

for cadmium. The way of calculating these critical points has been published in previous papers [29,30]. All the experimental data were processed using a statistical program [31].

3.2. Validation studies

The limits of detection ($(3\sigma/S)$ and quantification ($(10\sigma/S)$, where (3σ) is standard deviation of the blank and (S) slope of analytical curve, were calculated as IUPAC recommendation [32]. The precision was also determined and expressed as relation standard deviation. All these parameters can be seen in Table 2.

The calibration equations obtained using the pre-concentration procedure were given as $\text{Abs}=0.0036 [\text{Cd}, \mu\text{g L}^{-1}]+0.0022$ to cadmium and $\text{Abs}=0.0017 [\text{Pb}, \mu\text{g L}^{-1}]-0.0004$ to lead with correlation coefficients (R) higher than 0.9993 for both metals. In order to determine the pre-concentration factor, analytical curves were prepared without the pre-concentration step. The calibration equations obtained were $\text{Abs}=1.1642 \cdot 10^{-4} [\text{Cd}, \mu\text{g L}^{-1}]+0.001$ and $\text{Abs}=3.06 \cdot 10^{-5} [\text{Pb}, \mu\text{g L}^{-1}]+0.0018$ to cadmium and lead respectively. The experimental enrichment factor calculated as the ratio of the slopes of the calibration graphs with and without pre-concentration were 22 and 56 obtained for cadmium and lead, respectively. The FS-FAAS system has a limitation. The burner position is fixed during the sequential determination. The adjustment is made by the element of smaller sensitivity and/or lower concentration in the samples. In this work, this optimization was made for the lead, because the sensitivity for this element is lower than the cadmium sensitivity. This explains because the pre-concentration for lead is higher than for cadmium.

The accuracy of the procedure was confirmed by determination of cadmium and lead in the certified reference material of natural water NIST SRM 1643d, supplied by National Institute of Standards and Technology. The results are shown in Table 3.

Table 3
Determination of cadmium and lead in certified reference material ($N=3$)

Sample	Cd ($\mu\text{g L}^{-1}$)		Pb ($\mu\text{g L}^{-1}$)	
	Certified	Found	Certified	Found
CRM 1643d	6.47 \pm 0.37	6.66 \pm 1.3	18.15 \pm 0.64	18.32 \pm 1.8

N Number of determinations.

Table 4
Determination of cadmium and lead in water samples ($n=3$)

Sample	Cd ($\mu\text{g L}^{-1}$)			Pb ($\mu\text{g L}^{-1}$)		
	Added	Found	Rec%	Added	Found	Rec%
1	0	<LQ	–	0	2.26 \pm 1.1	–
	1.0	1.04 \pm 0.07	104	2.0	4.40 \pm 1.0	107
2	0	<LQ	–	0	8.30 \pm 1.8	–
	1.0	1.0 \pm 0.10	100	8.0	16.10 \pm 1.3	98
3	0	2.72 \pm 1.0	–	0	6.58 \pm 1.7	–
	3.0	5.80 \pm 0.50	102	7.0	13.50 \pm 0.5	99
4	0	2.00 \pm 0.40	–	0	6.60 \pm 1.4	–
	2.0	3.90 \pm 0.90	95	7.0	13.70 \pm 0.9	101
5	0	0.80 \pm 0.19	–	0	4.61 \pm 1.5	–
	1.0	1.78 \pm 0.60	98	5.0	9.40 \pm 1.3	96
6	–	1.40 \pm 0.30	–	–	5.16 \pm 1.4	–
7	–	1.71 \pm 0.26	–	–	4.20 \pm 1.4	–
8	–	1.30 \pm 0.50	–	–	6.93 \pm 1.7	–
9	–	1.27 \pm 0.27	–	–	8.66 \pm 1.4	–
10	–	1.35 \pm 0.65	–	–	6.13 \pm 1.2	–

^aBelow limit of quantification, N number of determinations.

3.3. Effect of other ions

The effect of other metal ions was studied using 50 mL of a solution containing cadmium and lead (with concentration of 10 $\mu\text{g L}^{-1}$) and other metal ions, nickel, chromium cobalt, zinc, aluminum, iron, manganese, mercury, molybdenum, vanadium, (present in a concentration 100 $\mu\text{g L}^{-1}$). The results obtained showed that at these concentrations the other metal ions do not interfere in the procedure proposed.

3.4. Application

The proposed method was applied for the determination of cadmium and lead in drinking water samples collected in Jaguaquara City, Brazil. Ten samples were analyzed and the concentrations found for cadmium and lead varied from 0.08 to 2.72 $\mu\text{g L}^{-1}$ and 2.26 to 8.66 $\mu\text{g L}^{-1}$, respectively. Addition/recovery tests were performed for five samples and the recovery values achieved are in the range from 95 to 104% for cadmium and 96 to 107% for lead. These results are summarized in Table 4. These results demonstrate also that the content of lead and cadmium in these samples are lower than the permissible maximum levels by Health Organization of the Brazilian Govern, which are 5 and 10 $\mu\text{g L}^{-1}$ for cadmium and lead, respectively [33].

4. Conclusions

The fast sequential mode is a good alternative for multi-element determination using flame atomic absorption spectrometry. The limits of quantification obtained with this procedure allow the determination of cadmium and lead in drinking water samples considering the permissible maximum levels by Health Organization of the Brazilian Govern. The content of lead and cadmium in the drinking water samples collected in Jaguaquara City, Brazil were always lower than the permissible maximum levels stipulated by Brazilian Health Organization.

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