Simultaneous flow injection preconcentration of lead and cadmium using cloud point extraction and determination by atomic absorption spectrometry

Edson Luiz Silva*, Paulo dos Santos Roldan

Centro de Energia Nuclear na Agricultura, Universidade de São Paulo, Av. Centenário, 303, CP 96, 13416-000 Piracicaba, SP, Brazil

A B S T R A C T

A flow injection (FI) micelle-mediated separation/preconcentration procedure for the determination of lead and cadmium by flame atomic absorption spectrometry (FAAS) has been proposed. The analytes reacted with 1-(2-thiazolylazo)-2-naphthol (TAN) to form hydrophobic chelates, which were extracted into the micelles of 0.05% (w/v) Triton X-114 in a solution buffered at pH 8.4. In the preconcentration stage, the micellar solution was continuously injected into a flow system with four mini-columns packed with cotton, glass wool, or TNT compresses for phase separation. The analytes-containing micelles were eluted from the mini-columns by a stream of $3\,mol\,L^{-1}$ HCl solution and the analytes were determined by FAAS. Chemical and flow variables affecting the preconcentration of the analytes were studied. For 15 mL of preconcentrated solution, the enhancement factors varied between 15.1 and 20.3, the limits of detection were approximately 4.5 and $0.75\,\mu g\,L^{-1}$ for lead and cadmium, respectively. For a solution containing 100 and $10\,\mu g\,L^{-1}$ of lead and cadmium, respectively, the R.S.D. values varied from 1.6 to 3.2% ($n = 7$). The accuracy of the preconcentration system was evaluated by recovery measurements on spiked water samples. The method was susceptible to matrix effects, but these interferences were minimized by adding barium ions as masking agent in the sample solutions, and recoveries from spiked sample varied in the range of 95.1–107.3%.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Trace levels of heavy metals are widely distributed in the environment due to soil erosion and industrial and agricultural processes [1]. The contamination by heavy metals from various environmental sources including natural waters is a great concern nowadays [2]. Lead and cadmium are two of the most hazardous elements to human health, because both metals cause adverse effects on metabolic processes of human beings [3]. Lead is proved to be a carcinogenic agent and to cause disturbances to several organs. Cadmium is highly toxic even at low concentrations, causing damages to organs such as the kidneys, liver and lungs [4]. All theses facts cause alarming concern in public health, demanding accurate analytical procedures for the quantification of theses elements at trace levels [5].

Many methods for the determination of trace metals by atomic spectrometry techniques are still commonly carried out using a preconcentration step prior their detection [6]. Flame atomic absorption spectrometry (FAAS) has been a very attrac-

tive technique for routine metal determinations, owing to its ease of operation, its low acquisition and operating costs compared with inductively coupled plasma optical emission spectrometry (ICPOES) and graphite furnace atomic absorption spectrometry (GFAAS), and its high sample throughput [7]. However, there is a great necessity for the preconcentration of trace metals prior their determination, basically due to their low concentrations in aqueous sample [8]. For this reason, there is no decrease in the activity related to the development of new analytical methods for the preconcentration of metal ions [9,10].

Actually, separation/preconcentration procedures based on cloud point extraction (CPE) have attracted considerable attention mainly because it is in agreement with the principles of the "green chemistry". CPE is a green method for the following reasons: (i) it uses as an extractor media diluted solutions of the surfactants that are inexpensive, resulting in the economy of reagents and generations of few laboratory residues, and (ii) surfactants are not toxic, not volatile, and not easily flammable [11]. Micelle-mediated extraction procedures have found wide applications in different areas of analytical chemistry, and their advantages over the conventional liquid-liquid extraction technique have been well documented in the literature [12–14]. The formation of micelles consists on the aggregation of a certain num-

* Corresponding author.
E-mail address: edsonqmc@hotmail.com (E.L. Silva).

ber of surfactant monomers [15]. Aqueous solutions containing a non-ionic or zwitterionic surfactant above its critical micellar concentration (CMC) become turbid, because the surfactant molecules associate spontaneously, forming aggregates of colloidal dimensions [16]. Any species that originally present associates and binds to these micellar aggregates can be extracted from the initial solution and preconcentrated in a small volume of the surfactant-rich phase. The clouding phenomenon can be induced by changing the temperature, additive content, or pressure by which results the separation of a single isotropic micellar phase into two isotropic phases: (i) a surfactant-rich phase of small volume composed mainly of surfactant, and (ii) an aqueous phase containing surfactant with the concentration level near to CMC [14].

Flow injection (FI) separation/preconcentration systems, which use a mini-column packed with a solid support loaded or functionalized with complexing reagents, has been much used to increase sensitivity and selectivity in the analytical determination of trace metals [17,18]. FI preconcentration procedures offer some very favorable features in relation to batch methods, because they comprise a cheap, versatile, and easy operation system that improves the analytical frequency and reproducibility. In addition, reagents and sample consumption and sample manipulation are reduced, minimizing the risks of contamination and analyte loss [19,20]. However, these advantages have been very little explored in CPE procedures, hence only a few published works with regard to micelle-mediated extraction procedures describe a FI preconcentration system for the determination of trace metals [21–25]. Therefore, the incorporation of CPE to a FI system is a very interesting alternative in the field of separation methods, joining the advantages offered for both methods.

The aim of this work was to develop a new FI separation/preconcentration procedure in combination with the CPE technique for lead and cadmium determination by FAAS. Phase separation was performed by using mini-columns packed with cotton, glass wool, or TNT compresses, which were tested as filtering material for effective retention of micellar aggregates. Operations generally employed in bath CPE such as the heating of micellar solutions in thermostatic bath, the use of a centrifuge and a ice bath, and the dilution of the surfactant-rich phase were not necessary, so the proposed procedure improved significantly the performance of bath CPE methods.

2. Experimental

2.1. Instrumentation

A model 3110 flame atomic absorption spectrometer (PerkinElmer – Norwalk, USA) operating with an air-acetylene flame, was used for lead and cadmium determination. Electrodeless discharge lamps (EDL) for lead and cadmium (PerkinElmer – Norwalk, USA) were operated at 10 and 4 mA, respectively, with a spectral bandwidth of 0.7 nm. The selected wavelengths were 283.3 and 228.8 nm for lead and cadmium, respectively. The acetylene flow rate, the burner height, and the aspiration rate of the spectrometer were adjusted in order to obtain the maximum absorbance signal. Signals were measured as peak height by using instrument software (WinLab^{TM}). All solutions were propelled by using an Ismatec-IPC peristaltic pump (Ismatec – Glattbrugg, Switzerland) with eight channels and provided with Viton® or Tygon® tubes. A homemade injector-commutator was used to select preconcentration/elution steps. A Model Tec-3MP pH-meter (Tecnal – Piracicaba, Brazil), equipped with a glass-combination electrode, was used to adjust the pH of solutions.

2.2. Reagents, solutions, and samples

High purity water (resistivity 18.2 MΩ cm) obtained by a Milli-Q® water purification system (Millipore, Bedford, MA, USA) was used throughout this work. All chemicals were of analytical-reagent grade and were used without previous purification. The laboratory glassware was kept overnight in a 1.4 mol L^{-1} HNO$_3$ solution. Before the use, the glassware was washed with deionized water and dried in a class 100 laminar flow hood.

Stock solution of lead and cadmium at a concentration of 1000 mg L^{-1} was prepared by dissolving appropriate amounts of Pb(NO$_3$)$_2$ and CdO, respectively (Johnson & Matthey, Royston, England). Working reference solutions were obtained daily by stepwise dilution from stock solution. A solution of 1.57 mmol L^{-1} TAN (Merck, Hohenbrunn, Germany) was prepared by dissolution of 100 mg of the chelating agent in 100 mL of ethanol, and the volume was completed to 250 mL with 2.5% (w/v) Triton X-114. A solution of 2.5% (w/v) Triton X-114 (Sigma, St Louis, USA) was used as surfactant agent. A buffer solution of 0.2 mol L^{-1} sodium acetate (Merck, Darmstadt, Germany) was used to adjust the sample pH at 5. The pH of this buffer was adjusted at 5 with concentrated acetic acid (Merck, Darmstadt, Germany). Sörensen buffer solution was used to adjust the pH between 6 and 8.5, and it was prepared by mixing 0.065 mol L^{-1} of Na$_2$HPO$_4$ and KH$_2$PO$_4$ (both from Merck, Darmstadt, Germany) in an adequate ratio. A solution of 0.1 mol L^{-1} tris(hydroxymethyl)aminomethane (Merck, Darmstadt, Germany) was used as buffer for the pH interval of 8.5–10. A 3 mol L^{-1} HCl solution used as eluent was prepared by direct dilution from the concentrated acid (Merck, Darmstadt, Germany) with deionized water.

River water and lake water samples were collected from the Piracicaba River and from a lake at ESALQ, respectively, from the city of Piracicaba, São Paulo state, Brazil. Mineral water samples were acquired from a local market and drinkable water samples were collected in our laboratory. The samples were filtered before analyses through a cellulose membrane (Millipore) of 0.45 μm pore size.

2.3. FI preconcentration system

The flow manifold is shown schematically in Fig. 1 and it was made up of a peristaltic pump, an injector-commutator, four mini-columns packed with filtering material, and polyethylene tubing with inner diameter of 8 mm. Tree filtering materials for mini-column packing were investigated: cotton (Apolo, Minas Gerais, Brazil – Lot: 031), glass wool (Technical and Applied Scientific Knowledge, Georgia, USA – Code: 3950), and TNT compresses (Bastos Viegas, São Paulo, Brazil – Code: 4391–503). The mini-columns made from PTFE tubes with 58 mm of length and inner diameter of 3 mm were sealed on both ends with glass wool. The performance of the mini-columns was stable during all experiments. The flow preconcentration system was operated in a time-based mode.

2.4. Procedure for lead and cadmium preconcentration

It was added to the analytical solution containing 0.2 mol L^{-1} NaCl and 3.25 mmol L^{-1} Sörensen buffer the complexing agent (3.92 μmol L^{-1} TAN) to react with the lead and cadmium ions. The pH of the reference and sample solutions was adjusted at 8.4 with a diluted nitric acid or sodium hydroxide solution. After 5 min, the surfactant agent was added to extract the metallic chelates into the micelles of 0.05% (w/v) Triton X-114, using an incubation time of 5 min. The cloud point phenomenon was obtained by NaCl already present in the micellar solution, which was then injected into the flow preconcentration system.
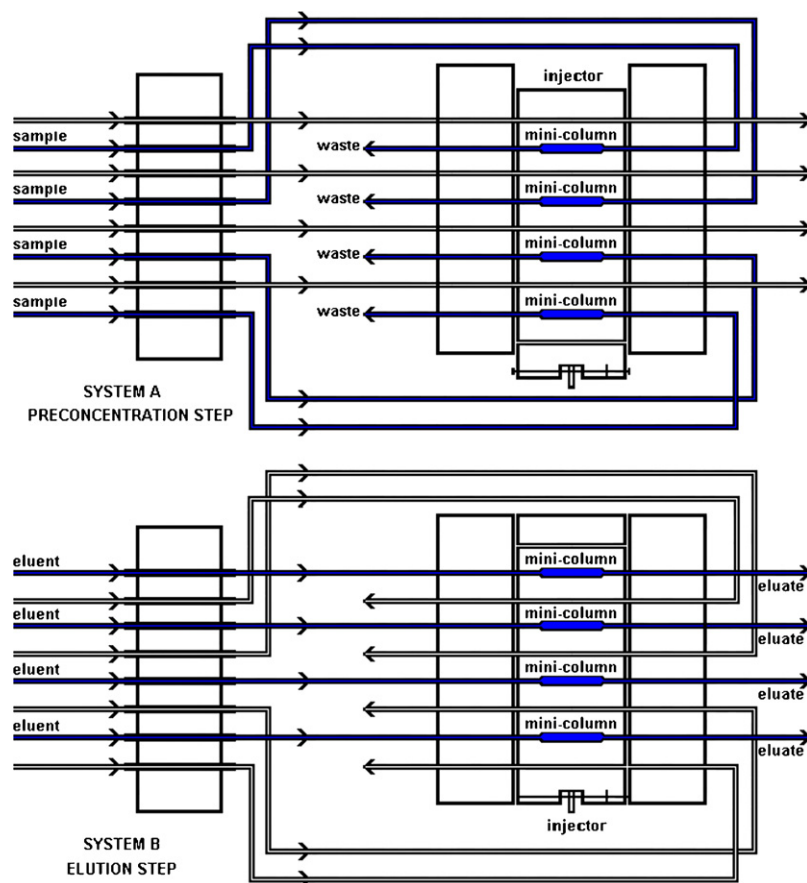
Fig. 1. FI preconcentration system. Two mini-columns packed with suitable filtering material were used for each analyte: cotton and TNT compresses for lead and TNT compresses and glass wool for cadmium.

In the preconcentration stage (Fig. 1, System A) with the injector-commutator in the loading position, a micellar solution was continuously pumped through the mini-columns at a flow rate of 3 mL min^{-1}, so that the analytes-containing micelles were collected inside the mini-columns, while the aqueous phase was sent to waste.

In the elution stage (Fig. 1, System B), the injector was then changed manually to its second position, and a 3 mol L^{-1} HCl solution was propelled through the mini-columns at a flow rate of 0.9 mL min^{-1}, eluting and carrying the micellar aggregates. During the elution step, the first 15 s had been discarded in order to eliminate larger part of dead volume from the mini-columns, following plus 40 s that was the enough time for quantitative recovery of the analytes. The elution was performed in opposite direction to sample loading in order to minimize the dispersion of the analytes through the eluent. The eluate was collected into 15 mL centrifuge tubes and later introduced into the nebulizer system of the spectrometer by direct aspiration. Finally, the filtering material was reconditioned by passing a 3 mol L^{-1} HCl solution through the mini-columns for 40 s at a flow rate of 3 mL min^{-1}.

Parameters of the proposed procedure were investigated by using the univariate method in order to determine appropriate chemical and flow conditions for analytes determination. A volume of 10 mL of work reference solution containing 500 μg L^{-1} of lead and 50 μg L^{-1} of cadmium was used for simultaneous preconcentration of the analytes. All assays were performed in triplicate and absorbance signals were measured as peak height.

3. Results and discussion

In this work, phase separation was performed by using mini-columns packed with a suitable filtering material. Three materials such as cotton, glass wool, and TNT compresses were studied in the flow system; hence the properties of a filtering material for effective retention of micellar aggregates are of prime importance. After performing some preliminary tests in the preconcentration system, two packing materials were selected for each analyte.

3.1. Effect of chemical and flow variables

The influence of chemical and flow variables on the simultaneous preconcentration of lead and cadmium was investigated. The pH was the first variable studied of the proposed procedure, since the extraction of metal ions by surfactant micelles generally occurs after the formation of a complex with enough hydrophobicity. According to the results shown in Fig. 2, the pH played an important role on extraction efficiency; since the maximum absorbance for lead and cadmium occurred at pH 8.4. It was found that the extraction efficiency was more favorable in slightly basic conditions, and a pH value of 8.4 was selected throughout, resulting in R.S.D. values ranging from 1.6 to 2.8%.

The clouding phenomenon is usually induced by an increase in temperature of the micellar solution; however, the addition of a salting-out agent has also proven to be an effective approach [25]. In this work, it was added a salting-out agent to the micellar solution in order to facilitate the phase-separation process. Fig. 3 shows the variation in absorbance as a function of NaCl concentration in
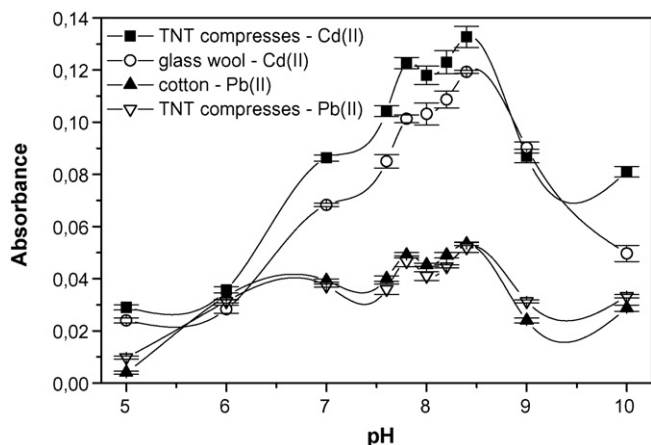
Fig. 2. Effect of pH on the preconcentration of 10 mL of a solution containing 500 µg L^{-1} Pb(II) and 50 µg L^{-1} Cd(II), 20 µmol L^{-1} TAN, 0.4 mol L^{-1} NaCl, and 0.15% (w/v) Triton X-114 at a flow rate of 3 mL min^{-1}. The micellar phase was eluted with 2 mol L^{-1} HCl at a flow rate of 0.9 mL min^{-1} for 40 s.

the range of 0.05–1 mol L^{-1}. The preconcentration of the analytes in the flow system occurred also in the absence of electrolyte; however, the analytical procedure was more efficient by using NaCl at concentrations of 0.1–0.3 mol L^{-1} for cadmium. Below or above this concentration range, it was observed a decrease on the absorbance for cadmium. As can be see in Fig. 3, the effect of NaCl concentration on the absorbance of lead was less pronounced. The maximum absorbance was obtained in the presence of NaCl at concentrations near to 0.2 mol L^{-1} for both the analytes, thus this concentration was selected for subsequent experiments, resulting R.S.D. values lesser than 3%.

The CPE efficiency depends of inherent interaction of analytes with micellar structures. The hydrophobic core in a micelle is the more employed binding site in CPE procedures for chelates extraction; however, the analytes were also extracted in the absence of chelating agent, probably due the existence of different solubilization sites in a micelle, such as on micelle surface, among the hydrophilic head groups, the space among the poly-oxy-ethylene groups, the interface between the head groups and the core, and hydrophobic core [9]. The method presented better sensitivity in the presence of TAN at concentrations near to 3.92 µmol L^{-1}. Above this concentration there was a decrease in the absorbance only for
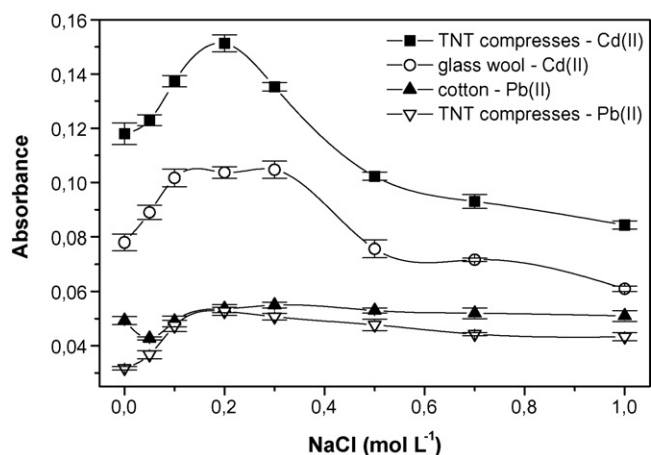
cadmium. A concentration of 3.92 µmol L^{-1} was selected in order to guarantee complete recovery of the analytes, and in this concentration the R.S.D. values varied from 1.4 to 3.3%.

In order to raise the efficiency of the preconcentration system, the concentration of Triton X-114 was studied at concentrations of 0.025–0.5% (w/v). Maximum intensities of the analytical signals were attained at a concentration of 0.05% (w/v) Triton X-114. Above this concentration there was a decrease in the recovery of analytes, probably due to the competition for the filtering material between the analytes-containing micelles and the free micelles. Therefore, a concentration of 0.05% (w/v) Triton X-114 was chosen as appropriate.

The influence of sample loading flow rate on the preconcentration of lead and cadmium was studied. 10 mL of a micellar solution containing the analytes were injected into the flow system at flow rates of 1–6.5 mL min^{-1}. The absorbance signals decreased significantly only at flow rates higher than 3.5 mL min^{-1}. Therefore, a flow rate of 3 mL min^{-1} was found to be suitable for the proposed procedure.

In order to elute the analytes-containing micelles from the mini-columns, hydrochloric acid solutions at concentrations of 1–5 mol L^{-1} were tested as stripping agent. No expressive difference was observed on the analytical signals in the investigated concentration range. For concentrations below than 3 mol L^{-1} the cleanness of the mini-columns was slower, so a 3 mol L^{-1} HCl solution was selected for elution and cleanness of the mini-columns.

The incubation time of the micellar solution was investigated in order to employ a shortest incubation time. The absorbance of the analytes was practically constant in the range of 5–60 min, thus an incubation time of 5 min was considered appropriate for subsequent experiments.

Reaction kinetics was also studied in the proposed procedure, because complexes formation is the rate-determining step in several chelate extractions [14]. The kinetics of the complexation reaction between analytes and TAN has shown be fast, because it was not observed any pronounced effect on the absorbance of the analytes in the range of 5–60 min, so a time of 5 min was considered as appropriate for equilibration time.

3.2. Figures of merit of the FI preconcentration system

The analytical properties of merit were obtained by preconcentrating 15 mL of analytical solution under selected experimental conditions, using a preconcentration time of 5 min. All the statistical calculations were based on the average of triplicate measurements for each standard solution. The proposed analytical procedure provided linear calibration curves within the concentration range from 25 to 2000 µg L^{-1} for Pb^{2+} and from 2.5 to 500 µg L^{-1} for Cd^{2+}, according to the following equations:

$A = 0.00387 + 0.000145[Pb^{2+}, \mu g\,L^{-1}]$ with

$r = 0.99942$ (mini − column packed with cotton);

$A = -0.00118 + 0.000168[Pb^{2+}, \mu g\,L^{-1}]$ with

$r = 0.99918$ (mini − column packed with TNT compresses);

$A = 0.00082 + 0.0048[Cd^{2+}, \mu g\,L^{-1}]$ with

$r = 0.99937$ (mini − column packed with TNT compresses);

$A = -0.00858 + 0.00456[Cd^{2+}, \mu g\,L^{-1}]$ with

$r = 0.99802$ (mini − column packed with glass wool);

Fig. 3. Effect of NaCl concentration on the preconcentration of 10 mL of a solution (pH 8.4) containing 500 µg L^{-1} Pb(II) and 50 µg L^{-1} Cd(II), 20 µmol L^{-1} TAN, and 0.15% (w/v) Triton X-114 at a flow rate of 3 mL min^{-1}. The micellar phase was eluted with 2 mol L^{-1} HCl at a flow rate of 0.9 mL min^{-1} for 40 s.

Table 1
Properties of merit obtained by the proposed method

Ion	Range ($\mu g\,L^{-1}$)	Linearity[a] (r)	Slope (b)	LOD[b] ($\mu g\,L^{-1}$)	EF[c]	RF[d] (%)
Pb[e]	50–250	0.99993	0.000197	4.6	19.6	78.4
Pb[f]	50–250	0.99851	0.000204	4.4	20.3	81.2
Cd[g]	5–25	0.99942	0.00417	0.74	15.1	60.4
Cd[h]	5–25	0.99971	0.00448	0.76	16.2	64.8

[a] Linear correlation coefficient.
[b] Limit of detection.
[c] Enhancement factor.
[d] Recovery factor.
[e] Mini-column packed with cotton.
[f] Mini-column packed with TNT compresses.
[g] Mini-column packed with TNT compresses.
[h] Mini-column packed with glass wool.

where A is the absorbance signal and r is the linear correlation coefficient.

The precision of the method was evaluated for a solution containing $100\,\mu g\,L^{-1}$ of lead and $10\,\mu g\,L^{-1}$ of cadmium, and their R.S.D. values varied from 1.6 to 3.2% ($n = 7$). Table 1 contains other figures of merit obtained by the FI preconcentration system shown in Fig. 1. The limit of detection (LOD) was defined as the analyte concentration, which resulted in a response equivalent to three times the standard deviation (S.D.) of the blank ($n = 11$) divided by the angular coefficient (b) of the calibration curve (LOD = 3 S.D./b). The enhancement factors (EF) were calculated as the ratio of the slopes of the calibration curves obtained with and without preconcentration. The recovery factors (RF) were obtained by the following equation: $EF = RF(V_S/V_E)$, where V_S is the volume of preconcentrated solution and V_E is the volume of eluate [19]. The overall time required for preconcentration of 15 mL of micellar solution for each mini-column of the proposed system was about 6.6 min; hence the system is composed of four mini-columns the sampling frequency was about 36.5 samples per hour.

The accuracy of the proposed procedure was investigated through the recovery test in water samples, adding known masses of analyte to the analyzed aqueous matrices. The analyses were
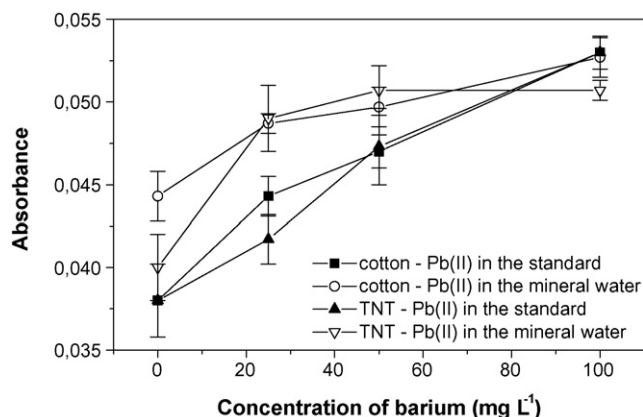

Fig. 4. Effect of barium ions on the recovery of lead in the reference solution and mineral water sample. The preconcentration was performed according to the optimized parameters.

performed in triplicate, using a preconcentration time of 5 min. Initially, the recovery of the analytes from spiked water samples by the preconcentration system was not appropriate due to matrix effects. In a previous work, we used barium ions as a masking agent to minimize matrix interferences on the preconcentration and determination of lead by FI-FAAS [26]. In order to obtain more accurate results, it was investigated the addition of barium chloride as a masking agent to the analyzed matrices. Analytical signals of both the reference and sample solutions were subtracted from their respective blanks. According to the results shown in Fig. 4, the addition of Ba(II) at concentration of $100\,mg\,L^{-1}$ increased the sensitivity and also improved the precision of the analytical measurements for lead, minimizing significantly matrix effects. Fig. 4 shows only the results for lead in the reference solution and in the mineral water sample. It was also necessary to add the barium ions in the samples of river water and lake water, except for supply water. A concentration of $100\,mg\,L^{-1}$ Ba(II) was selected for lead preconcentration.

Table 2
Recovery of lead and cadmium in water samples

Aqueous matrix	Pb^{2+} added ($\mu g\,L^{-1}$)	Pb^{2+} found ($\mu g\,L^{-1}$)	R (%)	Pb^{2+} found ($\mu g\,L^{-1}$)	R (%)
		Mini-column packed with cotton		Mini-column packed with TNT compresses	
Supply water	100.0	98.9 ± 7.7	98.9	97.9 ± 4.9	97.9
	200.0	208.9 ± 2.9	104.4	204.1 ± 2.8	102.1
Mineral water	100.0	103.9 ± 5.6	103.9	99.5 ± 2.8	99.5
	200.0	200.4 ± 7.7	100.2	212.3 ± 5.7	106.1
River water	100.0	97.2 ± 2.9	97.2	99.5 ± 7.5	99.5
	200.0	191.9 ± 5.1	96.0	192.7 ± 7.5	96.3
Lake water	100.0	98.9 ± 4.5	98.9	96.3 ± 2.8	96.3
	200.0	190.2 ± 7.7	95.1	191.0 ± 4.9	95.5

Aqueous matrix	Cd^{2+} added ($\mu g\,L^{-1}$)	Cd^{2+} found ($\mu g\,L^{-1}$)	R[a] (%)	Cd^{2+} found ($\mu g\,L^{-1}$)	R (%)
		Mini-column packed with TNT compresses		Mini-column packed with glass wool	
Supply water	10.00	13.15 ± 0.50	–	12.94 ± 0.22	–
	20.00	24.02 ± 0.28	103.8	24.62 ± 0.46	107.3
Mineral water	10.00	12.59 ± 0.63	–	12.41 ± 0.46	–
	20.00	23.22 ± 0.60	102.8	23.58 ± 0.34	105.2
River water	10.00	13.79 ± 0.24	–	13.53 ± 0.26	–
	20.00	25.30 ± 0.48	106.3	24.99 ± 0.59	106.2
Lake water	10.00	13.39 ± 0.55	–	13.53 ± 0.32	–
	20.00	24.74 ± 0.77	105.8	24.54 ± 0.59	104.3

[a] Recovery.

Cadmium was also susceptible to matrix effects, which were minimized with the addition of barium ions to the reference and sample solutions, except for supply water. A concentration of $100\,mg\,L^{-1}$ of barium was also selected for cadmium preconcentration, except for mineral water and river water, which presented better results at concentration of $60\,mg\,L^{-1}$ Ba(II).

According to the results contained in Table 2, the proposed procedure offered good accuracy for both analytes, presenting recoveries of 95.1–106.1% and 102.8–107.3% for lead and cadmium, respectively. The three materials employed to retain the micellar phase presented similar results as shown in Table 2, but cotton presented a more spoiled physical aspect at the end of this work. Although the cotton has been the most used material in FI-CPE procedures, TNT compresses have shown to be an excellent alternative as filtering material, since this synthetic material presented better physical conditions than cotton. Until recently, there were no reports in the literature concerning the use of TNT compresses as filtering materials for mini-column packing.

4. Conclusions

The separation and preconcentration of lead and cadmium in the proposed FI-CPE system, using mini-columns packed with cotton, glass wool, or TNT compresses, has shown to be an efficient, simple, and safe procedure for the determination of trace metals by FAAS. This procedure presented some very favorable features in relation to batch CPE methods by using collection mini-columns; hence some operations generally employed in bath CPE were not necessary for the proposed procedure, such as the heating of micellar solutions in thermostatic bath to induce phase separation, the use of a centrifuge to speed up the phase separation, an ice bath to facilitate the discarding of the aqueous phase, and the dilution of surfactant-rich phase to facilitate its introduction in spectrometric nebulizers, thus creasing the speed of analysis and decreasing the risks of contamination and analyte loss. The analytical procedure also presented low detection limits and good precision and accuracy.

Acknowledgements

References

[1] M. Tuzen, M. Soylak, K. Parlar, Cadmium and lead contamination in tap water samples from Tokat, Turkey, Bull. Environ. Contam. Toxicol. 75 (2005) 284–289.

[2] E. Melek, M. Tuzen, M. Soylak, Flame atomic absorption spectrometric determination of cadmium(II) and lead(II) after their solid phase extraction as dibenzyldithiocarbamate chelates on Dowex Optipore V-493, Anal. Chim. Acta 578 (2006) 213–219.

[3] E.M. Gama, A.S. Lima, V.A. Lemos, Preconcentration system for cadmium and lead determination in environmental samples using polyurethane foam/Me-BTANC, J. Hazard. Mater. 136 (2006) 757–762.

[4] T.A. Maranhão, D.L.G. Borges, M.A.M.S. da Veiga, A.J. Curtius, Cloud point extraction for the determination of cadmium and lead in biological samples by graphite furnace atomic absorption spectrometry, Spectrochim. Acta Part B 60 (2005) 667–672.

[5] E.L. da Silva, E.M. Ganzarolli, R.R.U. de Queiróz, Determination of aluminum traces in hemodialysis and tap water using standard method's procedure modified and flow injection ionic exchange preconcentration, Anal. Lett. 38 (2005) 2089–2101.

[6] C.R.T. Tarley, S.L.C. Ferreira, M.A.Z. Arruda, Use of modified rice husks as a natural solid adsorbent of trace metals: characterization and development of on-line preconcentration system for cadmium and lead determination by FAAS, Microchem. J. 77 (2004) 163–175.

[7] C.R.T. Tarley, A.F. Barbosa, M.G. Segatelli, E.C. Figueiredo, P.O. Lucas, Highly improved sensitivity of TS-FF-AAS for Cd(II) determination at ng L^{-1} levels using a simple flow injection minicolumn preconcentration system with multiwall carbon nanotubes, J. Anal. At. Spectrom. 21 (2006) 1305–1313.

[8] A.N. Anthemidis, K.-I.G. Ioannou, Evaluation of polychlorotrifluoroethylene as sorbent material for on-line solid phase extraction systems: determination of copper and lead by flame atomic absorption spectrometry in water samples, Anal. Chim. Acta 575 (2006) 126–132.

[9] E.H. Evans, J.A. Day, A. Fisher, W.J. Price, C.M.M. Smith, J.F. Tyson, Atomic spectrometry update. Advances in atomic emission, absorption and fluorescence spectrometry and related techniques, J. Anal. At. Spectrom. 19 (2004) 775–812.

[10] E.H. Evans, J.A. Day, C.D. Palmer, W.J. Price, C.M.M. Smith, J.F. Tyson, Atomic spectrometry update. Advances in atomic emission, absorption and fluorescence spectrometry, and related techniques, J. Anal. At. Spectrom. 20 (2005) 562–590.

[11] M.A. Bezerra, M.A.Z. Arruda, S.L.C. Ferreira, Cloud point extraction as a procedure of separation and pre-concentration for metal determination using spectroanalytical techniques: a review, Appl. Spectrosc. Rev. 40 (2005) 269–299.

[12] J.L. Manzoori, G. Karim-Nezhad, Development of a cloud point extraction and preconcentration method for Cd and Ni prior to flame atomic absorption spectrometric determination, Anal. Chim. Acta 521 (2004) 173–177.

[13] V.A. Lemos, J.S. Santos, P.X. Baliza, Me-BTABr reagent in cloud point extraction for spectrometric determination of copper in water samples, J. Braz. Chem. Soc. 17 (2006) 30–35.

[14] W.L. Hinze, E. Pramauro, A critical review of surfactant-mediated phase separations (cloud-point extractions): theory and applications, Crit. Rev. Anal. Chem. 24 (1993) 133–177.

[15] J.L. Burguera, M. Burguera, Analytical applications of organized assemblies for on-line spectrometric determinations: present and future, Talanta 64 (2004) 1099–1108.

[16] M.F. Silva, E.S. Cerutti, L.D. Martinez, Coupling cloud point extraction to instrumental detection systems for metal analysis, Microchim. Acta 155 (2006) 349–364.

[17] V.A. Lemos, E.M. Gama, A.S. Lima, On-Line preconcentration and determination of cadmium, cobalt and nickel in food samples by flame atomic absorption spectrometry using a new functionalized resin, Microchim. Acta 153 (2006) 179–186.

[18] V.A. Lemos, G.T. David, L.N. Santos, Synthesis and application of XAD-2/Me-BTAP resin for on-line solid phase extraction and determination of trace metals in biological samples by FAAS, J. Braz. Chem. Soc. 17 (2006) 697–704.

[19] E.L. da Silva, A.O. Martins, A. Valentini, V.T. Fávere, E. Carasek, Application of silica gel organofunctionalized with 3(1-imidazolyl)propyl in an on-line preconcentration system for the determination of copper by FAAS, Talanta 64 (2004) 181–189.

[20] T.D. Saint'Pierre, L. Tormen, V.L.A. Frescura, A.J. Curtius, The direct analysis of fuel ethanol by ICP-MS using a flow injection system coupled to an ultrasonic nebulizer for sample introduction, J. Anal. At. Spectrom. 21 (2006) 1340–1344.

[21] J. Nan, Y. Jiang, X.-P. Yan, A flow injection online micelle-mediated preconcentration and separation procedure without phase separation coupled with electrothermal atomic absorption spectrometry for determination of trace lead in biological samples, J. Anal. At. Spectrom. 18 (2003) 946–950.

[22] C. Ortega, M.R. Gomes, R.A. Olsina, M.F. Silva, L.D. Martinez, On-line cloud point preconcentration and determination of gadolinium in urine using flow injection inductively coupled plasma optical emission spectrometry, J. Anal. At. Spectrom. 17 (2002) 530–533.

[23] M. Garrido, M.S. Di Nezio, A.G. Lista, M. Palomeque, B.S.F. Band, Cloud-point extraction/preconcentration on-line flow injection method for mercury determination, Anal. Chim. Acta 502 (2004) 173–177.

[24] E.K. Paleologos, A.G. Vlessidis, M.I. Karayannis, N.P. Evmiridis, On-line sorption preconcentration of metals based on mixed micelle cloud point extraction prior to their determination with micellar chemiluminescence: application to the determination of chromium at ng L^{-1} levels, Anal. Chim. Acta 477 (2003) 223–231.

[25] Q. Fang, M. Du, C.W. Huie, On-line incorporation of cloud point extraction to flow injection analysis, Anal. Chem. 73 (2001) 3502–3505.

[26] A.O. Martins, E.L. da Silva, M.C.M. Laranjeira, V.T. de Fávere, Application of chitosan functionalized with 8-hydroxyquinoline: determination of lead by flow injection flame atomic absorption spectrometry, Microchim. Acta 150 (2005) 27–33.