

Preconcentration system for cadmium and lead determination in environmental samples using polyurethane foam/Me-BTANC

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Abstract

In this work, polyurethane foam (PUF) loaded with 2-(6'-methyl-2'-benzothiazolylazo)chromotropic acid (Me-BTANC) was packed in a minicolumn and it was used in an on-line preconcentration system for cadmium and lead determination. Optimum hydrodynamic and chemical conditions for metal sorption were investigated. The effects of several foreign substances on the adsorption of cadmium and lead were also reported. The enrichment factor obtained was 37 (Cd and Pb) for 180 s preconcentration time. The proposed procedures allowed the determination of metals with detection limits (3σ) of 0.80 and 3.75 $\mu\text{g L}^{-1}$ (0.10 and 0.47 $\mu\text{g g}^{-1}$ of solid sample) for cadmium and lead, respectively. The precision of the procedures was also calculated: 3.1 (Cd 10 $\mu\text{g L}^{-1}$) and 4.4% (Pb 100 $\mu\text{g L}^{-1}$). The accuracy of the procedure was checked by analysis of the certified reference materials Spinach Leaves and Fish Tissue. Cadmium and lead contents in environmental samples (black tea, spinach leaves, natural and tap water) were determined by applying the proposed procedure.

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1. Introduction

Cadmium and lead, naturally occurring heavy metals, are two of the most hazardous elements to human health. Both metals causes adverse health effects in humans and their widespread presence in the human environment comes from anthropogenic activities. Cadmium is among the most dangerous of all the metal contaminants of food. Biological interest in lead has centred principally on its properties as a highly toxic cumulative poison in humans and animals. Contents of Cd and Pb in some matrices, such as foods, sediment or water can show pollution situation of an area [1].

In the determination of cadmium and lead in numerous real samples by atomic absorption spectrometry, there is a crucial need for a preconcentration step before their analysis due to their frequent low concentrations. Additionally, since high levels of concomitant components usually accompany analytes, a separation

step is often required [2]. Several enrichment procedures have been reported in the literature for cadmium and lead determination involving different analytical techniques, such as precipitation [3], liquid–liquid [4], cloud-point [5,6] or solid-phase extraction (SPE) [7,8]. Liquid–liquid extractions are generally time-consuming, labor-intensive and they require strict control of extraction conditions, such as temperature, pH and ionic strength. Solid-phase extraction is an attractive alternative in preconcentration procedures because it overcomes many drawbacks of liquid–liquid extraction. Other advantages in use of SPE are disposal costs, achievement of high recoveries, broader range of applications than liquid–liquid extraction due to the large choice of solid sorbents and easy recovery of the solid phase [9]. Among the sorbent materials most commonly employed for metal preconcentration are silica gel [10,11], polystyrene-divinylbenzene based sorbents [12,13], activated carbon [14], fullerene [15], naphthalene [16] and polyurethane foam [17,18].

Polyurethane foam is a interesting material for preconcentration and separation of a wide variety of inorganic and organic compounds in different media due to low cost, high available

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surface area and cellular structure and stability in acidic or basic media. Polyurethane foam has been used unloaded or associated to physically immobilised chelating reagents in preconcentration and sampling procedures [19,20].

Thiazolylazo and benzothiazolylazo reagents have been associated to solid supports employed in enrichment procedures due their capacity to form complexes with a large variety of metals [21–23]. Quantitative recovery of uranium from geological materials was achieved using TAR-XVI, a chelating resin containing TAR functional group [24]. 1-(2-Thiazolylazo)-2-naphthol (TAN) functionalized activated carbon was used to remove mercury(II) at trace and ultra trace levels from hazardous wastes [14]. Polyurethane foam (PUF) impregnated with the reagent 2-(2-thiazolylazo)-*p*-cresol (TAC) [20] has been used for lead determination in saline samples by ETAAS. TAC has been also used in an on-line preconcentration procedure based on the precipitation of cadmium(II) ions on a knotted reactor [25].

A new benzothiazolylazo dye, [2'-(6-methyl-benzothiazolylazo)]-4-bromophenol (Me-BTAbR) was loaded on polyurethane foam as column packing in on-line preconcentration systems for zinc determination in natural waters [26]. The procedure presented in this work includes a description of an on-line preconcentration procedure using a minicolumn packed with a laboratory-made solid sorbent. The sorbent used was polyurethane foam loaded with 2-(6'-methyl-2'-benzothiazolylazo)chromotropic acid (Me-BTANC), a recently introduced reagent [27]. Optimum conditions, analytical features and selectivity were determined and the proposed procedure was applied to cadmium and lead determination in environmental samples.

2. Experimental

2.1. Reagents

Me-BTANC solution ($8.0 \times 10^{-4} \text{ mol L}^{-1}$) was prepared by dissolving 40 mg of 2-(6'-methyl-2'-benzothiazolylazo)chromotropic acid (laboratory-prepared, according to Section 2.3) in 100 ml of ethanol. Polyurethane foam, commercial open-cell polyether-type polyurethane foam (Atol, Simões Filho, Bahia, Brazil) was ground in a domestic blender with a large amount of deionized water, as previously described [26]. Afterwards, PUF was filtered off in a vacuum system and it was placed to dry in a stove at 80°C for 1 h. Acetate, borate and ammoniacal buffers [28] were used to adjust the sample pH in the range of 4.7–6.0, 7.0–8.0, and 9.0–10.0, respectively. Deionized water was used for all dilutions. Metal working solutions at microgram per liter level were prepared daily by diluting a corresponding $1000 \mu\text{g ml}^{-1}$ solution (Merck, Darmstadt, Germany). The laboratory glassware was kept overnight in a 5% (v/v) nitric acid solution. The following certified reference biological materials were analysed: NIST 1570a Spinach Leaves and MA-B-3/TM IAEA Fish Tissue purchased from the National Institute of Standards and Technology (Gaithersburg, MD, USA) and International Atomic Energy Agency (Monaco).

2.2. Apparatus

A Perkin-Elmer Instruments (Shelton, USA) model AAnalyst 200 flame atomic absorption spectrometer equipped with deuterium lamp background correction and an air-acetylene burner was used for absorbance measurements. Single-element hollow cathode lamps were used according the manufacturer's recommendations (Cd: 4.0 mA; Pb: 10.0 mA). Spectral bandwidth (0.5 nm), burner height (13.5 mm) and nebulizer flow rate (6.0 ml min^{-1}) had also conventional values. The flow system consisted of a four-channel peristaltic pump (Milan, model 204, Colombo, Brazil) furnished with silicone tubes to deliver the carrier, eluent and sample solutions, and two Rheodyne model 5041 six-port rotary valves (Cotati, USA) to select elution and preconcentration steps. A laboratory-prepared minicolumn packed with EPU/Me-BTANC (PVC, 3.50 cm length and 0.40 cm i.d.) and capillary tubes of PTFE were also used. All pH measurements were performed with a Digimed DM 20 model (Santo Amaro, Brazil) digital pH meter. The digestion of black tea, spinach leaves and certified materials was carried out in Parr Instrument 4749 (Moline, Illinois, USA) Acid Digestion Bombs enclosing a chemically inert Teflon sample cup of 23 ml.

The minicolumn packed with 100 mg of polyurethane foam has the following dimensions: 3.50 cm length and internal diameter of 4.0 mm. An $8.0 \times 10^{-4} \text{ mol L}^{-1}$ Me-BTANC solution was percolated through the minicolumn at a flow rate of 2.50 ml min^{-1} for 5 min. Afterwards, the column was washed with a 10% (w/v) sodium hydroxide solution until the black-purple effluent became colourless to remove the excess of Me-BTANC. A 5% (v/v) nitric acid solution and deionized water were used to wash the minicolumn before use. Reproducibility of the minicolumns prepared by this way was monitored by measuring analytical signals obtained for the same sample solution, using different minicolumns.

2.3. Synthesis of Me-BTANC

The synthesis of 2-(6'-methyl-2'-benzothiazolylazo)chromotropic acid involved diazotization with nitrous acid in acidic media at low temperature and coupling with chromotropic acid in basic media. Me-BTANC was synthesised and characterized according to a previously described procedure [27].

2.4. Analysis of real samples

Accuracy of the procedure was evaluated by analysis of certified reference material. Real samples of black tea and spinach leaves were also analysed. These materials were digested using the following procedure: a portion of 0.2 g of dry sample was precisely weighted into a Teflon cup, 4.0 ml of 1:1 (v/v) nitric acid solution were added, and the acid digestion bomb was heated in a stove at 150°C for 5 h [29]. After cooling at room temperature the bomb was opened carefully in a fume cupboard. The pH of the final digests were adjusted by suitable addition of a 10% (w/v) sodium hydroxide solution and an appropriate buffer solution, and the mixture was finally diluted to 25 ml by double deionized water.

Tap and natural waters were sampled at Jequié city, Bahia state, Brazil. The only pre-treatment was acidification to pH 2.0 with nitric acid, which was performed immediately after collection, in order to prevent adsorption of the metal ions on the flask walls. Natural water samples were filtered before analysis. A volume of 100 ml of the filtrate was taken and the pH was adjusted by addition of buffer solution.

2.5. On-line preconcentration system

Preconcentration and determination of cadmium and lead were performed by using an on-line system previously described for lead analysis in natural waters [30]. The flow system was operated by a time-based mode. In the sorption step, the two six-port valves are in load position. The sample was pumped through the minicolumn, and metallic ions were retained by EPU/Me-BTANC. After 60 or 180 s, depending on the calibration mode, the valves were then switched to the elute position and a stream of water carried the acid eluent from the loop and column in order to release metal ions directly into the nebulizer of the spectrometer. The column was arranged in the manifold so that the eluent flowed through it, in reverse direction to that of the sample, minimizing thus the dispersion of the analyte. Total elution time is 15 s. Signals were measured as maximum absorbance.

3. Results and discussion

3.1. Elution

Dessorption of the metals was studied using solutions of eluents at several concentrations. Cadmium ($10 \mu\text{g L}^{-1}$) and lead ($100 \mu\text{g L}^{-1}$) solutions were used. Best results were obtained when used hydrochloric acid solutions at concentrations equal or higher than 1.0 mol L^{-1} , for both metals. These results are shown in Fig. 1. Similar results were found for nitric acid. Organic solvents, such as acetone or ethanol, were also tested as eluents, associated to acid solutions. However, the use of these solvents did not result in any significant increase in analytical signal. In posterior experiments, a 1.0 mol L^{-1} hydrochloric acid solution

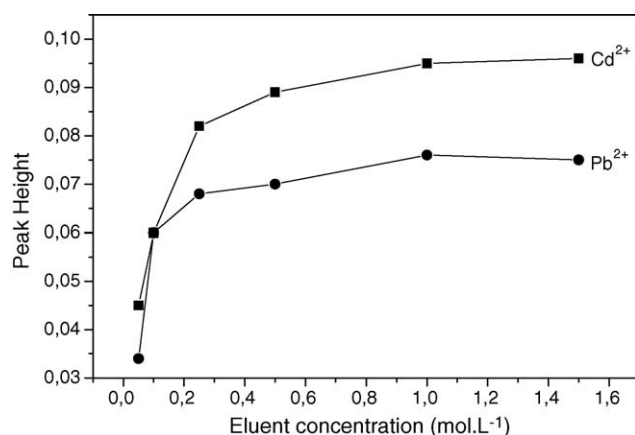


Fig. 1. Effect of eluent concentration on the preconcentration of Cd and Pb.

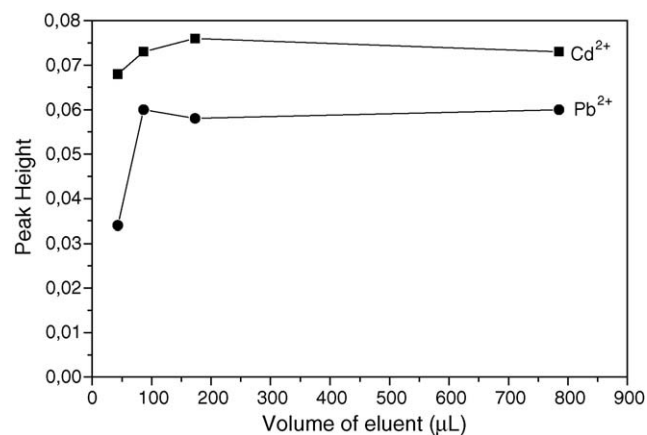


Fig. 2. Effect of eluent amount on the preconcentration of Cd and Pb.

was used in the elution of cadmium and lead from minicolumn. Amount of eluent necessary for a quantitative desorption of metals from minicolumn was studied, varying the eluent loop. According results shown in Fig. 2 elution is complete for eluent loops upper $80 \mu\text{L}$. It was used an eluent loop of $100 \mu\text{L}$ for cadmium and lead.

3.2. Sorption studies

Sorption in the minicolumn is based in the formation of chelates between Me-BTANC and cations. Therefore, The pH of the metal solution is an important parameter to study in this system because the formation of the complex species is strongly dependent of hydronium (or hydroxide) ions concentration in the media. The pH of cadmium ($10 \mu\text{g L}^{-1}$) and lead ($100 \mu\text{g L}^{-1}$) solutions was adjusted with acetate, borate and ammoniacal buffers. Analytical signals reached a maximum in pH value of 7.5 (Cd and Pb), according to the results shown in Fig. 3. These results are in good agreement with pH range favourable for Pb(II)/Me-BTANC complex [27]. Borate pH 7.5 was employed for pH adjusting of Cd and Pb solutions, in further experiments.

Studies about sorption capacity of EPU/Me-BTANC were performed by using 100 ml of Cd(II) 10 mg L^{-1} and Pb(II)

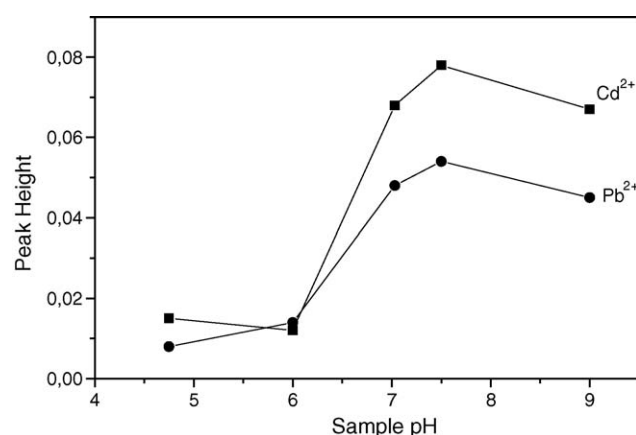


Fig. 3. Effect of pH on the preconcentration of Cd and Pb.

10 mg L⁻¹ solutions. The pH of these solutions was adjusted as in the anterior paragraph. Buffered metal solutions were added to plastic flasks containing 100 mg of the sorbent, and the systems were kept under agitation in a mechanical shaker for 4 h. Solid phase was separated by filtration and the metal contents in the liquids remaining were determined by FAAS. The sorption capacity calculated was 27.2 and 21.3 μmol g⁻¹ of EPU/Me-BTANC, for Cd(II) and Pb(II), respectively. The lifetime of the minicolumn was monitored by measuring the analytical signal of 10 μg L⁻¹ Cd(II) or 100 μg L⁻¹ Pb(II) at the end of each day of work and counting the number of preconcentration cycles. Minicolumn shown good reproducibility for about 500 cycles.

3.3. Hydrodynamic variables

The influence of the sample flow rate in the sorption of Cd and Pb ions on a PUF/Me-BTANC minicolumn was studied in the range of 1.5–15.0 ml min⁻¹. This study was made by pumping 5.0 ml of the solution containing Cd(II) and Pb into the system at various flow rates. The absorbance was linear up to 8.0 ml min⁻¹, implying that the complexation is complete and the contact time is sufficient. Above this value the analytical signal decreased because metal ions probably could not equilibrate properly with the resin due increasing in the velocity of the ions, that reduces the residence times. In posterior experiments, the flow rate was kept constant at 7.0 ml min⁻¹. In the on-line system, the carrier (water) flow rate controls the velocity of desorption. The effect of carrier flow rate was studied in the range of 2.0–7.0 ml min⁻¹. Best results were found within the range of 3.0–7.0 ml min⁻¹ for both metals. A flow rate of 5.0 ml min⁻¹ was selected in the subsequent studies, in order to match carrier and aspiration flow rates.

3.4. Selectivity

In order to investigate whether the described procedure suffers from interference, the effect of co-existing ions on the determination of 10 μg L⁻¹ cadmium and 100 μg L⁻¹ lead by the proposed method was studied. Any deviation >±5% from the absorbance value of cadmium or lead solution was taken as an interference. The results are given in Table 1. The interfer-

Table 1

Maximum tolerable quantities of foreign ions for the online system using polyurethane foam/Me-BTANC minicolumn for cadmium (10 μg L⁻¹) and lead (100 μg L⁻¹) determination

Substance	Maximum tolerable amount	
	Cadmium	Lead
Al ³⁺	1.0 g L ⁻¹	0.5 mg L ⁻¹
Br ⁻	0.1 g L ⁻¹	1.0 mg L ⁻¹
Cd ²⁺	–	0.5 mg L ⁻¹
Cl ⁻	0.1 g L ⁻¹	10.0 mg L ⁻¹
Co ²⁺	20.0 mg L ⁻¹	0.1 mg L ⁻¹
Cr ³⁺	20.0 mg L ⁻¹	0.5 mg L ⁻¹
Cu ²⁺	5.0 mg L ⁻¹	0.2 mg L ⁻¹
Fe ³⁺	1.0 mg L ⁻¹	1.0 mg L ⁻¹
K ⁺	0.2 g L ⁻¹	30.0 mg L ⁻¹
Mg ²⁺	0.1 g L ⁻¹	–
Na ⁺	0.1 g L ⁻¹	10.0 mg L ⁻¹
Ni ²⁺	20.0 mg L ⁻¹	0.1 mg L ⁻¹
NO ₃ ⁻	0.2 g L ⁻¹	30.0 mg L ⁻¹
Pb ²⁺	10.0 mg L ⁻¹	–
Zn ²⁺	20.0 mg L ⁻¹	1.0 mg L ⁻¹

ing substances examined were found not to impair the quality of the analytical signal when the chemical and hydrodynamic variables were maintained at the optimum levels.

3.5. Analytical features

Calibration graphs were run under the optimum conditions of the on-line preconcentration system for FAAS determination of cadmium and lead. Analytical characteristics of the procedure are given in Table 2. The data are shown for 60 and 180 s preconcentration time. Calibration graphs obtained for each metal by direct aspiration were $A = 4.40 \times 10^{-3} + 3.81 \times 10^{-4} C$ (Cd 10–1000 μg L⁻¹) and $A = 1.14 \times 10^{-3} + 4.08 \times 10^{-5} C$ (Pb 100–5000 μg L⁻¹) for cadmium and lead, respectively, where A is the absorbance and C is the metal concentration in solution.

The enrichment factors were calculated as the ratio of slopes of linear section of the calibration graphs before and after preconcentration [31] for 60 (Cd: 22, Pb: 20) and 180 s (Cd: 37 Pb: 37). In order to determinate the transfer phase factor, 25 ml of a 10 μg L⁻¹ cadmium or 100 μg L⁻¹ lead solution was percolated

Table 2

Analytical characteristics of the on-line cadmium and lead preconcentration system using polyurethane foam/Me-BTANC minicolumn (A: absorbance; C: metal concentration, μg L⁻¹)

Element	Cadmium		Lead	
Preconcentration time (s)	60	180	60	180
Enrichment factor	22	37	20	37
Concentration efficiency (min ⁻¹)	19	12	17	12
Transfer phase factor	0.93	–	0.95	–
Consumptive index (ml)	0.32	0.57	0.35	0.57
Sample frequency (h ⁻¹)	51	19	51	19
Eluent consumption (μl)	100	–	100	–
Limit of detection (μg L ⁻¹)	2.04	0.80	8.58	3.75
Precision (%)	2.0	3.1	2.9	4.4
Calibration function	$A = -8.51 \times 10^{-3} + 8.38 \times 10^{-3} C$	$A = 1.32 \times 10^{-2} + 1.41 \times 10^{-2} C$	$A = -2.15 \times 10^{-3} + 8.28 \times 10^{-4} C$	$A = 4.6 \times 10^{-3} + 1.51 \times 10^{-3} C$

Table 3
Metal determination in certified reference materials by proposed methodology* ($n=3$)

Sample	Cadmium amount ($\mu\text{g g}^{-1}$)		Lead amount ($\mu\text{g g}^{-1}$)	
	Found	Certified	Found	Certified
NIST 1570a Spinach Leaves	2.94 ± 0.15	2.89 ± 0.07	–	–
MA-B-3/TM IAEA Fish Tissue	–	–	4.49 ± 0.58	4.62

IAEA: International Atomic Energy Agency, Monaco; NIST: National Institute of Standards & Technology, USA.

* Confidence interval 95%.

Table 4
Results obtained for determination of Cd and Pb in food samples ($n=4$)

Sample	Cadmium amount ($\mu\text{g g}^{-1}$)		Recovery (%)	Lead amount ($\mu\text{g g}^{-1}$)		Recovery (%)
	Added	Found*		Added	Found*	
Black tea	0.0	<LQ	–	0.0	2.38 ± 0.12	–
	2.0	2.04 ± 0.12	102	2.0	4.46 ± 0.09	104
	4.0	3.80 ± 0.09	95	4.0	6.42 ± 0.18	101
Spinach leaves	0.0	<LQ	–	0.0	<LQ	–
	2.0	1.96 ± 0.12	98	2.0	2.04 ± 0.15	102
	4.0	3.96 ± 0.10	99	4.0	4.28 ± 0.20	107

LQ: limit of quantification.

* Confidence interval 95%.

Table 5
Results obtained for determination of Cd and Pb in water samples ($n=4$)

Sample	Cadmium amount ($\mu\text{g L}^{-1}$)		Recovery (%)	Lead amount ($\mu\text{g L}^{-1}$)		Recovery (%)
	Added	Found*		Added	Found*	
River water	0.0	<LQ	–	0.0	11.31 ± 0.59	–
	2.5	2.65 ± 0.17	106	10.0	21.12 ± 0.15	98
	5.0	4.85 ± 0.19	97	20.0	30.51 ± 1.22	96
Tap water	0.0	<LQ	–	0.0	<LQ	–
	2.5	2.67 ± 0.06	107	10.0	10.47 ± 0.75	105
	5.0	5.21 ± 0.23	104	20.0	19.58 ± 1.11	98
Well water	0.0	<LQ	–	0.0	<LQ	–
	2.5	2.49 ± 0.21	100	10.0	9.86 ± 0.77	99
	5.0	5.25 ± 0.33	105	20.0	21.76 ± 2.02	109

LQ: limit of quantification.

* Confidence interval 95%.

by the column under optimum conditions. The desorption was carried out with 1.00 ml of 1.00 mol L⁻¹ hydrochloric acid solution and the metal was measured by FAAS. The transfer phase factor of the column is defined as the ratio between the analyte mass in original sample and that in the concentrate [32]. Other parameters used for evaluating preconcentration systems, such as concentration efficiency (CE) and consumptive index (CI) [32], were also determined. The detection limits were calculated as three times the standard deviation of the signals obtained from 15 sample blanks. The precision of the procedures were calculated as the relative standard deviation in 10 $\mu\text{g L}^{-1}$ cadmium or 100 $\mu\text{g L}^{-1}$ lead solutions ($n=7$).

To evaluate the accuracy of the present method, two certified reference materials were analyzed: NIST 1570a Spinach Leaves and MA-B-3/TM IAEA Fish Tissue. According to Table 3, the determined concentrations of cadmium and lead in these materials by developed procedure are in good agreement with the certified values. Confidence intervals are at 95% level. These

results indicate the applicability of the developed preconcentration system for interference-free determination of trace cadmium and lead in the biological samples analyzed.

3.6. Determination of cadmium and lead in real samples

The proposed analytical procedure was applied to the determination of Cd and Pb in black tea and spinach leaves. The results are described in Tables 4 and 5. Recoveries (R) of spike were quantitative. Results indicate that the proposed method can be reliably used for the determination of these metal ions in real matrices. Detection limits (3σ) expressed as microgram of metal per gram of solid samples in Table 4 were 0.10 and 0.47 $\mu\text{g g}^{-1}$, for cadmium and lead, respectively.

4. Conclusion

Using polyurethane foam loaded with Me-BTANC as solid sorbent, a new method for the determination of Cd and Pb was

successfully established. This is an alternative procedure for the preconcentration of cadmium and lead as a prior step to their determination by flame atomic absorption spectrometry. The determination involves a fast, easy and effective procedure for the preconcentration of the metals. The on-line preconcentration system is very economical, and simple in apparatus and manipulation. No severe sources of interference for the technique were observed from various tested substances. The high tolerance to interference, allied to presented advantages is very interesting for routine laboratories in trace element analysis.

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References

- [1] D.L. Tsalev, Z.K. Zaprianov, *Atomic Absorption Spectrometry in Occupational and Environmental Health Practice*, CRC Press, Boca Raton, USA, 1984.
- [2] B. Welz, M. Sperling, *Atomic Absorption Spectrometry*, Wiley-VCH, Weinheim, Germany, 1999.
- [3] S. Saracoglu, M. Soylak, L. Elçi, Separation/preconcentration of trace heavy metals in urine, sediment and dialysis concentrates by coprecipitation with samarium hydroxide for atomic absorption spectrometry, *Talanta* 59 (2003) 287–293.
- [4] M.C.T. Diniz, O.F. Filho, J.J.R. Rohwedder, An automated system for liquid–liquid extraction based on a new micro-batch extraction chamber with on-line detection: preconcentration and determination of copper(II), *Anal. Chim. Acta* 525 (2004) 281–287.
- [5] 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) 1–31.
- [6] V.A. Lemos, P.X. Baliza, J.S. Santos, Me-BTABr reagent in cloud point extraction for spectrometric determination of copper in water samples, *J. Braz. Chem. Soc.* 17 (2006) 30–35.
- [7] M. Tuzen, K. Parlar, M. Soylak, Enrichment/separation of cadmium(II) and lead(II) in environmental samples by solid phase extraction, *J. Hazard. Mater.* 121 (2005) 79–87.
- [8] Y. Liu, Y. Guo, X. Chang, S. Meng, D. Yang, B. Din, Column solid-phase extraction with 2-acetylmercaptophenyldiazoaminoozobenzene (ampdaa) impregnated amberlite xad-4 and determination of trace heavy metals in natural waters by flame atomic absorption spectrometry, *Microchim. Acta* 149 (2005) 95–101.
- [9] V. Camel, Solid phase extraction of trace elements, *Spectrochim. Acta Part B* 58 (2003) 1177–1233.
- [10] T. Madrakian, A. Afkhami, M.A. Zolfigol, M. Solgi, Separation, preconcentration and determination of silver ion from water samples using silica gel modified with 2,4,6-trimorpholino-1,3,5-triazin, *J. Hazard. Mater.* 128 (2006) 67–72.
- [11] G.G. Bortoleto, G.T. Macarovsky, S. Cadore, Determination of cadmium by flame-atomic absorption spectrometry after preconcentration on silica gel modified with cupferron, *J. Braz. Chem. Soc.* 15 (2004) 313–317.
- [12] S.L.C. Ferreira, V.A. Lemos, B.C. Moreira, A.C.S. Costa, R.E. Santelli, An on-line continuous flow system for copper enrichment and determination by flame atomic absorption spectroscopy, *Anal. Chim. Acta* 403 (2000) 259–264.
- [13] I. Narin, M. Tuzen, M. Soylak, Aluminium determination in environmental samples by graphite furnace atomic absorption spectrometry after solid phase extraction on amberlite XAD-1180/pyrocatechol violet chelating resin, *Talanta* 63 (2004) 411–418.
- [14] A.M. Starvin, T.P. Rao, Removal and recovery of mercury(II) from hazardous wastes using 1-(2-thiazolylazo)-2-naphthol functionalized activated carbon as solid phase extractant, *J. Hazard. Mater.* 113 (2004) 75–79.
- [15] Y.P. de Peña, M. Gallego, M. Valcárcel, Fullerene: a sensitive and selective sorbent for the continuous preconcentration and atomic absorption determination of cadmium, *J. Anal. At. Spectrom.* 12 (1997) 453–457.
- [16] N. Pourreza, H.Z. Mousavi, Determination of cadmium by flame atomic absorption spectrometry after preconcentration on naphthalene-methyltriethylammonium chloride adsorbent as tetraiodocadmiate(II) ions, *Anal. Chim. Acta* 503 (2004) 279–282.
- [17] C.R.T. Tarley, W.N.L. dos Santos, C.M. Santos, M.A.Z. Arruda, S.L.C. Ferreira, Factorial design and doehlert matrix in optimization of flow system for preconcentration of copper on polyurethane foam loaded with 4-(2-pyridylazo)-resorcinol, *Anal. Lett.* 37 (2004) 1437–1455.
- [18] V.A. Lemos, S.L.C. Ferreira, On-line preconcentration system for lead determination in seafood samples by flame atomic absorption spectrometry using polyurethane foam loaded with 2-(2-benzothiazolylazo)-*p*-cresol, *Anal. Chim. Acta* 441 (2001) 281–289.
- [19] T. Braun, J.D. Navratil, A.B. Farag, *Polyurethane Foam Sorbents in Separation Science*, CRC Press, Boca Raton, 1985.
- [20] O.D. Sant'Ana, L.S. Jesuino, R.J. Cassella, M.S. Carvalho, R.E. Santelli, Determination of lead by electrothermal atomic absorption spectrometry employing a novel sampling strategy of polyurethane foam impregnated with thiazolylazo-*p*-cresol (TAC), *J. Braz. Chem. Soc.* 15 (2004) 96–102.
- [21] H. Onishi, *Photometric Determination of Traces of Metals, Part IIA*, Wiley, New York, US, 1986.
- [22] H. Onishi, *Photometric Determination of Traces of Metals, Part IIA*, Wiley, New York, US, 1989.
- [23] H.R. Hovind, Thiazolylazo dyes and their applications in analytical chemistry, *Analyst* 100 (1975) 769–796.
- [24] C.H. Lee, M.Y. Suh, J.S. Kim, D.Y. Kim, W.H. Kim, T.Y. Eom, Separation and preconcentration of uranium from geological materials with chelating resin containing 4-(2-thiazolylazo)resorcinol functional groups, *Anal. Chim. Acta* 382 (1999) 199–203.
- [25] S. Cerutti, S.L.C. Ferreira, J.A. Gásquez, R.A. Olsina, L.D. Martinez, Optimization of the preconcentration system of cadmium with 1-(2-thiazolylazo)-*p*-cresol using a knotted reactor and flame atomic absorption spectrometric detection, *J. Hazard. Mater.* 112 (2004) 279–283.
- [26] V.A. Lemos, W.N.L. Santos, J.S. Santos, M.B. Carvalho, On-line preconcentration system using a minicolumn of polyurethane foam loaded with Me-BTABr for zinc determination by flame atomic absorption spectrometry, *Anal. Chim. Acta* 481 (2003) 283–290.
- [27] V.A. Lemos, A.A. Jesus, E.M. Gama, G.T. David, R.T. Yamaki, On-line solid phase extraction and determination of copper in food samples using polyurethane foam loaded with Me-BTANC, *Anal. Lett.* 38 (2005) 679.
- [28] D.D. Perrin, B. Dempsey, *Buffers for pH and metal ion control*, Chapman and Hall, London, UK, 1974.
- [29] M.H.A. Melo, A.C.S. Costa, J.A. Nóbrega, S.L.C. Ferreira, The use of water soluble tertiary amine reagent for solubilization and metal determination in fish muscle tissue, *J. Braz. Chem. Soc.* 16 (2005) 69–73.
- [30] V.A. Lemos, J.S. Santos, L.S. Nunes, Synthesis and application of a new functionalized resin in on-line preconcentration of lead, *Sep. Sci. Technol.* 40 (2005) 1401–1414.
- [31] Z. Fang, L.P. Dong, S.K. Xu, Critical evaluation of the efficiency and synergistic effects of flow injection techniques for sensitivity enhancement in flame atomic absorption spectrometry, *J. Anal. At. Spectrom.* 7 (1992) 293–299.
- [32] Z. Fang, *Flow Injection Separation and Preconcentration*, Wiley, New York, USA, 1993.