ELSEVIER

On-line preconcentration using a resin functionalized with 3,4-dihydroxybenzoic acid for the determination of trace elements in biological samples by thermospray flame furnace atomic absorption spectrometry

Valfredo A. Lemos [a,*], Marcos A. Bezerra [a,b], Fábio A.C. Amorim [b,c]

[a] *Universidade Estadual do Sudoeste da Bahia, Laboratório de Química Analítica, Campus de Jequié,
45206-190 Jequié, Bahia, Brazil*
[b] *Universidade Federal da Bahia, Instituto de Química, Campus Universitário Ondina, 40170-290 Salvador, Bahia, Brazil*
[c] *Universidade Federal da Bahia, Instituto de Ciências Ambientais e Desenvolvimento Sustentável, Campus de Barreiras,
40805-100 Barreiras, Bahia, Brazil*

Abstract

In the present paper, an on-line preconcentration procedure for determination of cadmium, copper and zinc by thermospray flame furnace atomic absorption spectrometry (TS-FF-AAS) is proposed. Amberlite XAD-4 functionalized with 3,4-dihydroxybenzoic acid (XAD4-DHB) packed in a minicolumn was used as sorbent material. The metals were retained on the XAD-DHB resin, from which it could be eluted directly to the thermospray flame furnace system. The detection limits were 28 (Cd), 100 (Cu) and 77 ng L^{-1} (Zn) for 60 s preconcentration time, at a sample flow rate of 7.0 mL min^{-1}. Enrichment factors were 102, 91 and 62, for cadmium, copper and zinc, respectively. The procedure has been applied successfully to metal determination in biological standard reference materials.
© 2008 Elsevier B.V. All rights reserved.

Keywords: Cadmium; Copper; Zinc; Preconcentration; Solid-phase extraction

1. Introduction

Flame Atomic Absorption Spectrometry is a consolidated technique, but there is a great demand for improving its sensitivity [1,2]. A disadvantage of flame AAS is sometimes its relatively low power of detection for some elements. One of the main reasons for this is the low efficiency of the pneumatic nebulizer because only 5–10% of the primarily produced aerosol reaches the flame [3,4]. Another reason for the poor sensitivity is the short residence time of the atoms in the flame. Thus, thermospray flame furnace atomic absorption spectrometry (TS-FF-AAS) is a simple cost effective technique which improves the power of detection to more volatile elements because it allows the complete sample introduction and also

increases the residence time of the species in the light path [5].

Recently, preconcentration procedures have been coupled to the TS-FF-AAS technique to improve its sensitivity [6–9]. When TS-FF-AAS is coupled with a preconcentration procedure such as solid-phase extraction, it can reach a very low detection limit comparable to that obtained with Graphite Furnace Atomic Absorption Spectrometry (GF AAS) [10].

Solid-phase extraction has been performed by using several solid materials, such as multiwalled carbon nanotubes [11], microcrystalline naphthalene [12], polyurethane foam [13], silica-gel [14], styrene-divinylbenzene [15,16], chitosan [17] and other sorbents [18]. Styrene-divinylbenzene is commercially available as Amberlite XAD resin series. Many ligands were covalently coupled with a polymer backbone, such as 4,5-dihydroxy-1,3-benzenedisulfonic acid [19], 1-(2-pyridilazo)-2-naphtol (PAN) [20,21], 2-(2′-benzothiazolylazo)-*p*-cresol [22], 5-palmitoyl-8-hydroxyquinoline [23], pyrocatechol violet [24],

* Corresponding author. Tel.: +55 73 35289630; fax: +55 73 35256683.
E-mail address: vlemos@uesb.br (V.A. Lemos).

o-aminobenzoic acid [25], and 3,4-dihydroxybenzoic acid [26,27].

This paper proposes an on-line preconcentration system for determination of Cd, Cu and Zn in biological samples using thermospray flame furnace atomic absorption spectrometry (TS-FF-AAS). The procedure is based on the solid-phase extraction of these metals on a resin modified with 3,4-dihydroxybenzoic acid (XAD4-DHB). After on-line preconcentration, the elution of these ions using acid solution was performed, followed by detection using TS-FF-AAS.

2. Experimental

2.1. Instrumentation

A Varian Model SpectrAA 220 (Mulgrave, Victoria, Australia) flame atomic absorption spectrometer was used for the analysis. Hollow-cathode lamps were used as radiation source. Operational conditions of equipment were used according manufacturer recommendations (Table 1).

Two Alitea C-6 XV (Stockholm, Sweden) peristaltic pumps furnished with Tygon tubes were used to propel all solutions. A Rheodine 5041 (Cotati, California, USA) model four-way manual valve was used to select preconcentration/eluition 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.

The TS-FF-AAS system consisted of a lab-made thermospray flame furnace unit, which included the ceramic capillary (0.5 mm i.d., 2.0 mm e.d. and 100 mm of length) and the Ni tube (10 cm) which is located on the burner by a lab-made stainless steel support fixed with four ceramic pins. The tube was laid on these pins and could be moved into and out of the flame. For increasing the temperature inside the tube, six holes of 2 mm diameter were drilled in the bottom part of the tube. Another orifice was drilled at $90°$ to the bottom holes for inserting the thermospray capillary. The capillary tip was about 1 mm inside the tube furnace. The manifold was assembled with 0.5 mm i.d. PTFE tubing.

A Digimed DM20 pH meter was also used. Digestion of certified reference materials was carried out in a Parr Instrument 4749 (Moline, IL, USA) Acid Digestion Bomb enclosing a chemically inert Teflon sample cup of 23 mL.

2.2. Reagents and solutions

All reagents were of analytical grade unless otherwise stated. Ultrapure water (resistance of 18.3 MΩ cm) was obtained from an EASYpure RF (Barnstedt, Dubuque, IA, USA) to prepare all solutions. Nitric acid was of Suprapur quality (Merck). Laboratory glassware was kept overnight in 10% nitric acid solution. Before use, the glassware was rinsed with deionised water and dried in a dust free environment.

Cadmium, copper and zinc working solutions were for the analysis were obtained from Merck. Acetate, phosphate and borate buffers were used to adjust the sample pH to the range 3.8–4.8, 6.5–7.0 and 8.0–9.0, respectively.

A laboratory-prepared XAD4-DHB resin was used as packing in a minicolumn. This material was synthesized as previously described in literature for similar resins [21,22,26]. The accuracy of the method was assessed by analysing the following certified reference material (CRM): NIST 1570a Spinach Leaves and NIST 1573a Tomato Leaves from the National Institute of Standards and Technology (Gaithersburg, MD, USA).

2.3. Column preparation

A cylindrical minicolumn with 3.50 cm length and internal diameter of 4.0 mm containing about 100 mg of XAD4-DHB was used in the on-line preconcentration procedure. A syringe was used to put the sorbent inside the minicolumn. Plastic foams were placed at the inlet and outlet of the minicolumn to avoid removal of the resin by carrier stream. Afterwards, the minicolumn was washed with ethanol 5% (v/v), nitric acid solution and deionizer water, respectively at 2.50 mL min^{-1} flow rate. The XAD4-DHB minicolumn was washed with nitric acid and ethanol to prevent any metal or organic contamination, respectively. All minicolumns prepared by this way shown good reproducibility.

2.4. On-line preconcentration system

A diagram of the on-line preconcentration system is shown in Fig. 1. The flow system was carried out using two peristaltic pumps fitted with Tygon tubes, a four-way valve and a minicolumn packed with XAD4-DHB resin, coupled to a thermospray flame furnace atomic absorption spectrometer (TS-FF-AAS). The flow system was operated in a time-based mode. A sample solution (S) containing the analytes was buffered at pH 7.0 with a phosphate buffer solution and pumped at 7.0 mL min^{-1}, percolating through a minicolumn that retains the Cd(II), Cu(II) and Zn(II) ions. The remaining solution was discharged (W). When the injection valve is switched, a stream of 1.0 mol L^{-1} nitric acid (E) flowing at 0.7 mL min^{-1} displaces the analytes. The eluate was taken directly into the thermospray flame furnace system. Signals were recorded as absorbance, using the instrument software. Achieved sampling rate was about 40 samples per hour for a preconcentration time of 60 s and an elution time of 30 s for each metal ion.
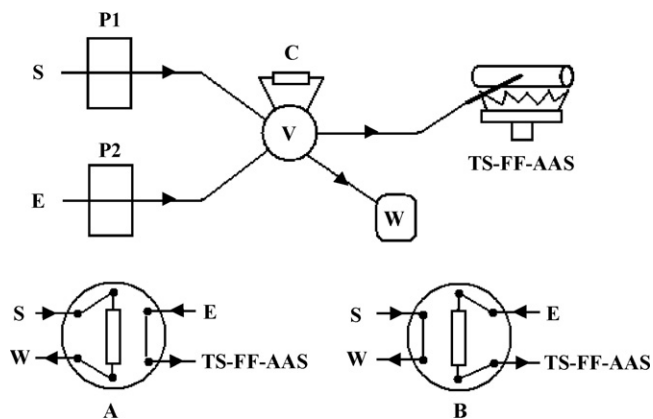
Table 1
Operating parameters of the flame atomic absorption spectrometer for cadmium, copper and zinc determination

Instrumental parameters	Cd	Cu	Zn
Wavelength	228.8	324.8	213.9
Lamp current (mA)	4.0	4.0	5.0
Slit width (nm)	0.5	0.5	1.0
Burner height (mm)	10.0	10.0	10.0
Acetylene flow rate (mL min^{-1})	2.00	2.00	2.00
Air flow rate (mL min^{-1})	13.50	13.50	13.50

Fig. 1. Schematic diagram of the flow system used for the pre-concentration and determination of cadmium by TS-FF-AAS. S, sample, E, eluent (HNO$_3$ 1 mol L^{-1}), P1 (7.0 mL min^{-1}); P2 (2.0 mL min^{-1}); P, peristaltic pump; C, XAD4/DHB minicolumn; V, four-way valve; TS-FF-AAS, thermospray flame furnace atomic absorption spectrometer and W, waste. (A) Four way valve in the pre-concentration step and (B) four-way valve in the elution position.

2.5. Digestion of samples

For decomposition of CRMs, an amount of 0.1 g of the material was treated with 4.0 mL of 1:1 (v/v) nitric acid solution and kept overnight in Teflon vessel. Afterwards the Teflon vessel was closed and put into a pressurized digestion system. The thermal heating was carried out in a stove at 150 °C for 6 h. After cooling at room temperature these solutions were adjusted to pH with a 10% (w/v) sodium hydroxide. An appropriate buffer solution was added and the volume was diluted in a volumetric flask. At least one blank solution was run for each sample in order to evaluate metal contamination by the reagents used.

3. Results and discussion

In order to determine the best chemical and hydrodynamic conditions for cadmium, copper, and zinc preconcentration a 5.0 µg L^{-1} metal solution was employed.

The effect of pH on sorption of cadmium(II), copper(II) and zinc(II) ions onto resin inside minicolumn was studied within a pH range from 3.8 to 9.5 (Fig. 2). The pH control was kept
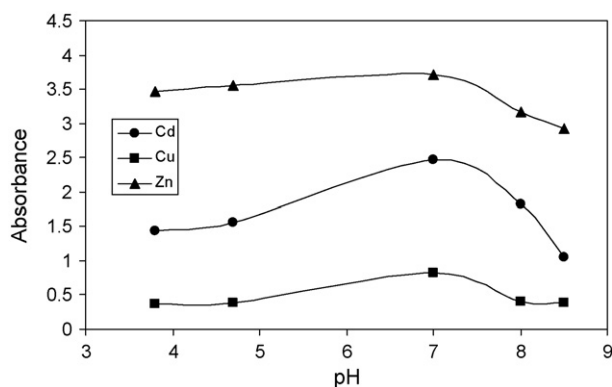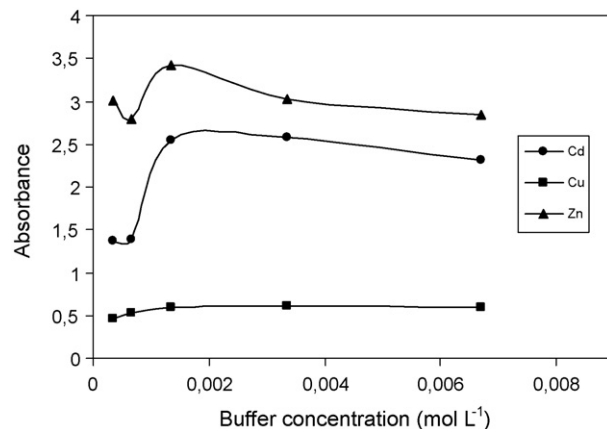

Fig. 3. Effect of buffer concentration on the retention of cadmium, copper and zinc in the minicolumn. Conditions: pH 7.0, sample flow rate 6.5 mL min^{-1}, eluent flow rate 2.0 mL min^{-1}, and HNO$_3$ concentration 1 mol L^{-1}.

by using pH 3.8 and 4.8 acetate buffer, pH 6.5 and 7.0 by using a phosphate buffer, pH 8.0 and 9.0 a borate buffer (all in the final concentration of 0.002 mol L^{-1}). The phosphate buffer pH 7.0 was suggested since this solution allows attain the higher analytical signal.

Final concentration of phosphate buffer (pH 7.0) in the sampled solutions was studied. An adequate buffer concentration is important to warrant the fast overhaul of column pH and allow the maximum efficiency in the extraction of metal ions. This study is shown in Fig. 3. As can be seen, from 0.002 mol L^{-1} buffer concentration the analytical signal attains its maximum values.

The influence of sample rate flow on the metal extraction was studied by varying the flow rate from 3.5 to 8.8 mL min^{-1}. Results presented in Fig. 4 demonstrated that the analytical signals were constant in the studied range for Cu and Zn. Absorbance of Cd is maximum at flow rates from 6.5 to 8.8 mL min^{-1}. High flow rates are limited by the back-pressure produced by the minicolumn. Otherwise, low flow rates decrease the sample throughput, resulting in long analysis periods. The flow rate of 7.0 mL min^{-1} was chosen for all metals in subsequent experiments as a compromise between efficiency and stability.

Fig. 2. Effect of pH on the retention of cadmium, copper and zinc in the column. Conditions: sample flow rate 6.0 mL min^{-1}, buffer concentration 0.004 mol L^{-1}, eluent flow rate 2.0 mL min^{-1}, and HNO$_3$ concentration 1.0 mol L^{-1}.
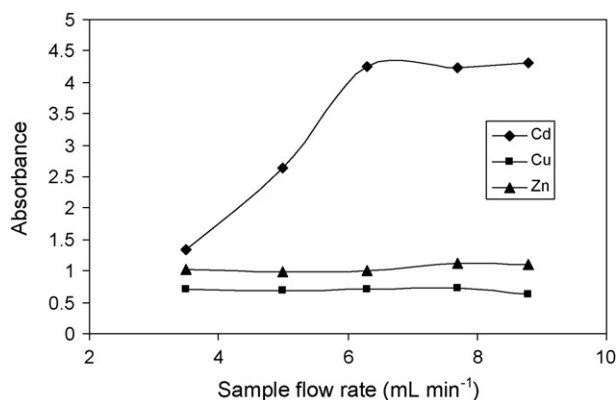

Fig. 4. Effect of sample flow rate on the retention of cadmium, copper and zinc in the column. Conditions: pH 7.0, buffer concentration 0.004 mol L^{-1}, eluent flow rate 2.0 mL min^{-1}, and HNO$_3$ concentration 1.0 mol L^{-1}.
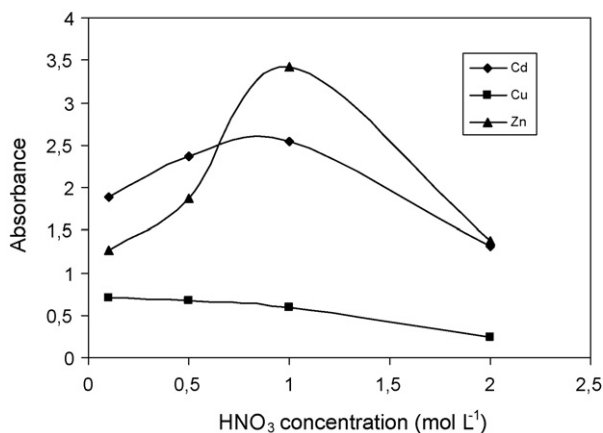
Fig. 5. Effect of eluent concentration on the retention of cadmium, copper and zinc in the column. Conditions: pH 7.0, sample flow rate 6.5 mL min^{-1}, eluent flow rate 2.0 mL min^{-1}, and buffer concentration 0.004 mol L^{-1}.

The effect of eluent concentration was considered. Nitric acid solutions at various concentrations (0.05–1.50 mol L^{-1}) were used as stripping agent for Cd, Cu and Zn. Results are shown in Fig. 5. It was found that with 1 mol L^{-1} nitric acid solution, the absorbance was maximum for Cd and Zn. For copper, maximum response occurred at concentration range of 0.05–1.00 mol L^{-1}. Therefore, for subsequent work, 1.00 mol L^{-1} nitric acid solution was employed as eluent.

3.1. Interference studies

The interference due to co-existing ions in the determination of 5.0 µg L^{-1} cadmium, copper or zinc was studied systematically using the on-line proposed procedure. A relative error of less than 5% was considered to be within the range of experimental error. The tolerance limits of several foreign substances in the preconcentration of each metal are given in Table 2. The effects of foreign ions at given concentrations are negligible. These concentrations are not the maximum allowed. Other amounts could be tested.

3.2. Analytical performance

Analytical properties were obtained by submitting the calibration solutions of each metal (1.0–5.0 µg L^{-1}) to the preconcentration system under the variables of the procedure previously optimized. The calibration graphs under the optimum chemical and flow conditions with the manifold depicted in Fig. 1, were given as Abs = 0.5007 [Cd(II), µg L^{-1}] + 0.0284 ($R = 0.9995$); Abs = 0.0910 [Cu(II), µg L^{-1}] + 0.1368 ($R = 0.9983$) and Abs = 0.5957 [Zn(II), µg L^{-1}] + 0.3966 ($R = 0.9988$). By using of direct determination in TS-FF-AAS without preconcentration system, the linear range was between 20 and 100 µg L^{-1}. The calibration equations were Abs = 0.0049 [Cd(II), µg L^{-1}] − 0.0063 ($R = 0.9985$); Abs = 0.001 [Cu(II), µg L^{-1}] + 0.2109 ($R = 0.9993$) and Abs = 0.0096 [Zn(II), µg L^{-1}] + 0.2109 ($R = 0.9993$). The experimental preconcentration factor, calculated as the ratio of the slopes of the calibration graphs with and without

Table 2
Maximum tested quantities of other ions for the online system using XAD4-DHB minicolumn for cadmium (5 µg L^{-1}), copper (5 µg L^{-1}) and zinc (5 µg L^{-1}) determination

Substance	Maximum amount tested (mg L^{-1})		
	Cd	Cu	Zn
Al(III)	1.0	1.0	1.0
Ca(II)	25.0	5.0	1.0
Cd(II)	–	1.0	1.0
Co(II)	1.0	1.0	1.0
Cr(II)	1.0	1.0	1.0
Cu(II)	1.0	–	1.0
Fe(III)	1.0	1.0	1.0
Hg(II)	1.0	1.0	1.0
K(I)	50.0	10.0	20.0
Mg(II)	15.0	3.0	0.5
Mn(II)	1.0	1.0	1.0
Mo(VI)	1.0	1.0	1.0
Na(I)	30.0	7.0	1.0
Ni(II)	1.0	1.0	1.0
Pb(II)	1.0	1.0	1.0
Sb(IV)	1.0	1.0	1.0
V(V)	1.0	1.0	1.0
Zn(II)	1.0	1.0	–

preconcentration was 102, 91 and 62 for Cd(II), Cu(II) and Zn(II), respectively, for 60 s of preconcentration time. In these conditions, the phase transfer factor (defined as the ratio between the analyte mass in the original sample and that in the concentrate) was found to be 82, 100 and 68% for Cd, Cu and Zn, respectively. The concentration efficiency (defined as the product of the enrichment factor and the sampling frequency per number of samples analyzed per minute) was also calculated and was also found to be 53, 61 and 41 min^{-1} for Cd, Cu and Zn, respectively. The analytical frequency was 40 samples h^{-1}. The consumptive index is a parameter that informs which the amount of the sample volume is necessary to achieve a unit of enrichment factor. The consumptive index found for this preconcentration system was 0.081, 0.071 and 0.11 mL for Cd, Cu and Zn, respectively [28].

The limits of detection were calculated by the 3 s criterion as the concentration that gives a response equivalent to three times the standard deviation (S.D.) of the blank ($n = 12$). The limits of quantification were calculated as the concentration that gives a response equivalent to 10 times the S.D. of the blank ($n = 12$), and define the lower limit of the range. The limits of detection found were 28, 100 and 77 ng L^{-1}, for cadmium, copper and zinc, respectively. The limits of quantification were 93 (Cd), 330 (Cu) and 260 ng L^{-1} (Zn).

The precision of the procedure (defined as the relative standard deviation, $n = 10$) was also determined in sample solutions containing 1.0 (Cd: 4.8%, Cu: 3.1%, Zn: 6.7%) and 5.0 µg L^{-1} (Cd: 3.7%, Cu: 6.6%, Zn: 3.4%).

3.3. Analytical application

The proposed method has been applied to the determination of cadmium, copper and zinc in biological certified samples.

Table 3
Metal determination in certified reference materials using proposed methodology ($n = 3$, confidence interval 95%)

Sample	Cadmium amount ($\mu g\,g^{-1}$)		Error (%)	Copper amount ($\mu g\,g^{-1}$)		Error (%)	Zinc amount ($\mu g\,g^{-1}$)		Error (%)
	Found	Certified		Found	Certified		Found	Certified	
NIST 1570a Spinach Leaves	3.1 ± 0.3	2.89 ± 0.07	+7.3	12.9 ± 0.8	12.2 ± 0.6	+5.7	74.5 ± 9	82 ± 3	−9.1
NIST 1573a Tomato Leaves	1.4 ± 0.2	1.52 ± 0.04	−7.9	4.6 ± 0.5	4.70 ± 0.14	−2.1	32.0 ± 0.6	30.9 ± 0.7	+3.6

Table 4
Comparison of analytical characteristics of on-line preconcentration systems using chelating resins prepared with different ligands and supports

Solid matrix	Ligand	Metal	T (s)	EF	CE (min^{-1})	f (h^{-1})	LOD ($\mu g\,L^{-1}$)	Sample	Detection	Ref.
Styrene-divinylbenzene	AEE	Cu	120	21	8.7	25	1.1	Water	FAAS	[29]
			240	43	9.3	13	0.9			
		Zn	120	14	5.6	24	1.1	Water	FAAS	[30]
			240	26	5.6	13	0.98			
PTFE	Acrylic acid	Cu	45	43	–	55	0.20	Environmental and biological samples	FAAS	[31]
		Cd	45	73	67	55	0.10			[32]
Nb$_2$O$_5$-SiO$_2$	–	Cu	120	34	11	20	0.10	Water	FAAS	[33]
Chitosan biopolymer	HQ	Cd	90	24	10	26	0.10	Water	FAAS	[34]
		Cu	90	25	11	26	0.40			
	SAHQ	Cd	90	14	6	26	0.20	Water	FAAS	[35]
		Cu	90	19	8	26	0.30			
Amberlite XAD-2	DHB	Cu	120	33	14	28	0.27	Food	FAAS	[26]
	AT	Cd	60	28	24	51	0.89	Water	FAAS	[36]
			180	74	22	18	0.14			
		Cu	60	14	12	51	1.31			
			180	35	10	18	0.54			
	NN	Cu	60	29	24.6	51	1.1	Food	FAAS	[37]
			180	58	17.4	18	0.7			
	CA	Cd	60	21	18	51	0.40	Biological samples	FAAS	[38]
Amberlite XAD-4	DAP	Zn	30	–	–	–	0.20	Water	ICP-MS	[39]
	DHB	Cd	60	102	53	40	0.028	Biological samples	TS-FF-AAS	This work
		Cu	60	91	61	40	0.100			
		Zn	60	62	41	40	0.077			

EF: enrichment factor; CE: concentration efficiency; f: sampling frequency; LOD: limit of detection; T: time of analysis, considering elution and preconcentration; AEE: (S)-2-[hydroxy-bis-(4-vinyl-phenyl)-methyllpyrrolidine-1-carboxylic acid ethyl ester; DHB: 3,4-dihydroxybenzoic acid; NN: β-nitroso-α-naphthol; AT: 2-aminothiophenol; Nb$_2$O$_5$-SiO$_2$: silica gel-niobium(V) oxide; PTFE: polytetrafluoroethylene; CA: chromotropic acid; HQ: 8-hydroxyquinoline; SAHQ: 5-sulphonic acid 8-hydroxyquinoline; FAAS: Flame Atomic Absorption Spectrometry; ICP-MS: Inductively Coupled Plasma-Mass Spectrometry; TS-FF-AAS: Thermospray Flame Furnace-AAS; DAP: 2,6-diacetylpyridine.

The following certified reference materials were analyzed: NIST 1570a Spinach Leaves and NIST 1573a Tomato Leaves. Obtained analytical results are in good agreement with certified values, according results presented in Table 3. Results indicate the applicability of the developed procedure in cadmium, copper and zinc determination free of interference.

4. Conclusion

The developed procedure allowed a highly sensitive and simple approach for the determination of cadmium, copper and zinc determination at trace levels in biological matrices. Thus when on-line preconcentration using solid phase extraction of metals ions onto a modified resin (XAD4-DHB) is coupled

with thermospray flame furnace atomic absorption spectrometry technique it is possible to attain limits of detection more low then that obtained to GF AAS.

The developed procedure is very simple, sensitive, low-cost and the procedure show high tolerance to interference ions. Due to good analytical characteristics such as detection limit, enrichment factor and precision the method has been demonstrated to be promising for trace element analysis.

A comparison of the proposed procedure with other on-line systems for determination of cadmum, copper and zinc using chemically modified sorbents can be seen in Table 4. Analytical features, such as enrichment factor, detection limits or concentration efficiency are comparable to those presented by methods described in the literature.

Acknowledgements

References

[1] H. Matusiewicz, Atom trapping and in situ preconcentration techniques for flame atomic absorption spectrometry, Spectrochim. Acta B 52 (1997) 1711–1736.

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

[3] B. Welz, M. Sperling, Atomic Absorption Spectrometry, third ed., Wiley-VCH, Weinheim, 1999.

[4] S. Cerutti, L.D. Martinez, R.G. Wuilloud, Knotted reactors and their role in flow-injection on-line preconcentration systems coupled to atomic spectrometry-based detectors, Appl. Spectrosc. Rev. 40 (2005) 71–101.

[5] J. Davies, H. Berndt, Improvements in thermospray flame furnace atomic absorption spectrometry, Anal. Chim. Acta 479 (2003) 215–223.

[6] M.G. Pereira, E.R. Pereira, H. Berndt, M.A.Z. Arruda, Determination of cadmium and lead at low levels by using preconcentration at fullerene coupled to thermospray flame furnace atomic absorption spectrometry, Spectrochim. Acta B 59 (2004) 515–521.

[7] C.R.T. Tarley, M.A.Z. Arruda, A sensitive method for cadmium determination using an on-line polyurethane foam preconcentration system and thermospray flame furnace atomic absorption spectrometry, Anal. Sci. 20 (2004) 961–966.

[8] E. Ivanova, H. Berndt, E. Pulvermacher, Air driven on-line separation and preconcentration on a C18 column coupled with thermospray flame furnace AAS for the determination of cadmium and lead at $\mu g \, L^{-1}$ levels, J. Anal. Atom. Spectrom. 19 (2004) 1507–1509.

[9] L.M. Coelho, M.A.Z. Arruda, Preconcentration procedure using cloud point extraction in the presence of electrolyte for cadmium determination by flame atomic absorption spectrometry, Spectrochim. Acta B 60 (2005) 743–748.

[10] F.A.C. Amorim, M.A. Bezerra, Online preconcentration system for determining ultratrace amounts of Cd in vegetal samples using thermospray flame furnace atomic absorption spectrometry, Microchim. Acta 159 (2007) 183–189.

[11] M. Tuzen, M. Soylak, Multiwalled carbon nanotubes for speciation of chromium in environmental samples, J. Hazard. Mater. 147 (2007) 219–225.

[12] S. Dadfarnia, A.M.H. Shabani, Z. Dehghani, Immobilized stearic acid as a new sorbent for on-line preconcentration and determination of lead by flow injection flame atomic absorption spectrometry, J. Brazil Chem. Soc. 17 (2006) 548–554.

[13] W.N.L. dos Santos, C.M.C. Santos, S.L.C. Ferreira, Application of three-variables Doehlert matrix for optimisation of an on-line preconcentration system for zinc determination in natural water samples by flame atomic absorption spectrometry, Microchem. J. 75 (2003) 211–221.

[14] J. Fan, C. Wu, Y. Wei, C. Peng, P. Peng, Preparation of xylenol orange functionalized silica gel as a selective solid phase extractor and its application for preconcentration—separation of mercury from waters, J. Hazard. Mater. 145 (2007) 323–330.

[15] M. Dogru, R. Gul-Guven, S. Erdogan, The use of Bacillus subtilis immobilized on Amberlite XAD-4 as a new biosorbent in trace metal determination, J. Hazard. Mater. 149 (2007) 166–173.

[16] U. Divrikli, A. Akdogan, M. Soylak, L. Elci, Solid-phase extraction of Fe(III), Pb(II) and Cr(III) in environmental samples on amberlite XAD-7 and their determinations by flame atomic absorption spectrometry, J. Hazard. Mater. 149 (2007) 331–337.

[17] A. Sabarudin, O. Noguchi, M. Oshima, K. Higuchi, S. Motomizu, Application of chitosan functionalized with 3,4-dihydroxy benzoic acid moiety for on-line preconcentration and determination of trace elements in water samples, Microchim. Acta 159 (2007) 341–348.

[18] S. Cadore, R.D. Goi, N. Baccan, Flame atomic absorption determination of cobalt in water after extraction of its morpholinedithiocarbamate complex, J. Brazil Chem. Soc. 16 (2005) 957–962.

[19] V.A. Lemos, P.X. Baliza, J.S. Santos, L.S. Nunes, A.A. Jesus, M.E. Rocha, A new functionalized resin and its application in preconcentration system with multivariate optimization for nickel determination in food samples, Talanta 66 (2005) 174–180.

[20] M.A.H. Hafez, I.M.M. Kenawy, M.A. Akl, R.R. Lashein, Preconcentration and separation of total mercury in environmental samples using chemically modified chloromethylated polystyrene-PAN (ion-exchanger) and its determination by cold vapour atomic absorption spectrometry, Talanta 53 (2001) 749–760.

[21] S. Tokalioglu, H. Buyukbas, S. Kartal, Preconcentration of trace elements by using 1-(2-pyridylazo)-2-naphthol functionalized Amberlite XAD-1180 resin and their determination by FAAS, J. Brazil Chem. Soc. 17 (2006) 98–106.

[22] V.A. Lemos, J.S. Santos, L.S. Nunes, Synthesis and application of a new functionalized resin in on-line preconcentration of lead, Separ. Sci. Technol. 40 (2005) 1401–1414.

[23] H. Filik, Metal ion preconcentration with amberlite XAD-2 functionalized with 5-palmitoyl-8-hydroxyquinoline and its analytical applications, Anal. Lett. 35 (2002) 881–894.

[24] 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.

[25] S.D. Çekiç, H. Filik, R. Apak, Use of an o-aminobenzoic acid-functionalized XAD-4 copolymer resin for the separation and preconcentration of heavy metal(II) ions, Anal. Chim. Acta 505 (2004) 15–24.

[26] V.A. Lemos, P.X. Baliza, R.T. Yamaki, M.E. Rocha, A.P.O. Alves, Synthesis and application of a functionalized resin in on-line system for copper preconcentration and determination in foods by flame atomic absorption spectrometry, Talanta 61 (2003) 675–682.

[27] L.S.G. Teixeira, M.A. Bezerra, V.A. Lemos, H.C. dos Santos, D.S. de Jesus, A.C.S. Costa, Determination of copper, iron, nickel, and zinc in ethanol fuel by flame atomic absorption spectrometry using on-line preconcentration system, Separ. Sci. Technol. 40 (2005) 2555–2565.

[28] Z. Fang, Flow Injection Separation and Preconcentration, first edition, VCH Publishers, Weinheim, 1993.

[29] R.J. Cassella, O.I.B. Magalhães, M.T. Couto, E.L.S. Lima, M.A.F.S. Neves, F.M.B. Coutinho, Synthesis and application of a functionalized resin for flow injection/F AAS copper determination in waters, Talanta 67 (2005) 121–128.

[30] R.J. Cassella, O.I.B. Magalhães, M.T. Couto, E.L.S. Lima, M.A.F.S. Neves, F.M.B. Coutinho, On-line preconcentration and determination of Zn in natural water samples employing a styrene-divinylbenzene functionalized resin and flame atomic absorption spectrometry, Anal. Sci. 21 (2005) 939–944.

[31] Z.H. Whang, Z.P. Wang, Z.P. Zhang, L.W. Liu, X.P. Yan, Determination of trace copper and nickel in environmental and biological samples by flow injection on-line microcolumn preconcentration flame AAS using acrylic acid-grafted polytetrafluoroethylene fiber for column packing, Atom. Spectrosc. 26 (2005) 34–39.

[32] Z.H. Wang, Z.P. Zhang, Z.P. Wang, L.W. Liu, X.P. Yan, Acrylic acid grafted polytetrafluoroethylene fiber as new packing for flow injection on-line microcolumn preconcentration coupled with flame atomic absorption spectrometry for determination of lead and cadmium in environmental and biological samples, Anal. Chim. Acta 514 (2004) 151–157.

[33] E.L. Silva, E.M. Ganzarolli, E. Carasek, Use of Nb2O5-SiO2 in an automated on-line preconcentration system for determination of copper and cadmium by FAAS, Talanta 62 (2004) 727–733.

[34] A.O. Martins, E.L. Silva, E. Carasek, N.S. Gonçalves, M.C.M. Laranjeira, V.T. Favere, Chelating resin from functionalization of chitosan

with complexing agent 8-hydroxyquinoline: application for metal ions on line preconcentration system, Anal. Chim. Acta 521 (2004) 157–162.

[35] A.O. Martins, E.L. Silva, E. Carasek, M.C.M. Laranjeira, V.T. Favere, Sulphoxine immobilized onto chitosan microspheres by spray drying: application for metal ions preconcentration by flow injection analysis, Talanta 63 (2004) 397–403.

[36] V.A. Lemos, P.X. Baliza, Amberlite XAD-2 functionalized with 2-aminothiophenol as a new sorbent for on-line preconcentration of cadmium and copper, Talanta 67 (2005) 564–570.

[37] V.A. Lemos, E.S. Santos, E.M. Gama, A comparative study of two sorbents for copper in a flow injection preconcentration system, Sep. Pur. Techn. 56 (2007) 212–219.

[38] V.A. Lemos, L.S. Nunes, J.S. Santos, P.X. Baliza, R.T. Yamaki, A.A. Jesus, On-line solid phase extraction system for cadmium preconcentration and determination by flame atomic absorption spectroscopy, Can. J. Anal. Sci. Spect. 49 (2004) 24–30.

[39] D. Kara, A. Fischer, S.J. Hill, Preconcentration and determination of trace elements with 2,6-diacetylpyridine functionalized Amberlite XAD-4 by flow injection and atomic spectroscopy, Analyst 130 (2005) 1518–1523.