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Amberlite XAD-2 functionalized with 2-aminothiophenol as a new sorbent for on-line preconcentration of cadmium and copper

Valfredo Azevedo Lemos*, Patrícia Xavier Baliza

Núcleo de Química Analítica da Bahia (NQA), Laboratório de Química Analítica (LQA), Universidade Estadual do Sudoeste da Bahia, Campus de Jequié, 45200-00 Jequié-BA, Brazil

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Abstract

A new functionalized resin has been applied in an on-line preconcentration system for copper and cadmium determination. Amberlite XAD-2 was functionalized by coupling it to 2-aminothiophenol (AT-XAD) by means of an −N=N− spacer. This resin was packed in a minicolumn and used as sorbent in the on-line system. Metal ions were sorbed in the minicolumn, from which it could be eluted directly to the nebulizer–burner system of the flame atomic absorption spectrometer (FAAS). Elution of Cd(II) and Cu(II) from minicolumn can be made with 0.50 mol l^{-1} HCl or HNO_3. The enrichment factors obtained were 28 (Cd) and 14 (Cu), for 60 s preconcentration time, and 74 (Cd) and 35 (Cu), if used 180 s preconcentration time. The proposed procedure allowed the determination of cadmium and copper with detection limits of 0.14 and 0.54 $\mu g\, l^{-1}$, respectively, when used preconcentration periods of 180 s. The effects of foreign ions on the adsorption of these metal ions are reported. The validation of the procedure was carried out by analysis of certified reference material. This procedure was applied to cadmium and copper determination in natural, drink and tap water samples.

Keywords: Preconcentration; Synthesis; Cadmium; Copper; Amberlite XAD-2; 2-Aminothiophenol

1. Introduction

Cadmium and copper determination in water and biological matrices is a good tool for environmental and toxicological monitoring. Generally, the determination of extremely low concentration of these elements is associated to separation and preconcentration steps due to insufficient sensitivity or matrix interference. The process based on solid phase extraction may be adopted as an alternative to solvent extraction due to a number of possible advantages including availability and easy recovery of the solid phase, attainability of large preconcentration factors and facility for separation and enrichment [1].

Development of chelating materials for solid-phase extraction has gained special attention due the advantages in the use of these substances in metal ion enrichment. These advantages include high degree of selectivity by controlling the pH, versatility, durability, good metal loading capacity and enhanced hydrophilicity [2]. Chelating ligands have been functionalized in several materials, such as silica-gel [3,4], polyurethane foam [5], cellulose [6,7] and styrene-divinylbenzene copolymer, commercially available as Amberlite XAD resin series. Amberlite XAD are resins widely used to develop several chelating materials for preconcentration procedures due to its good physical and chemical properties such as porosity, high surface area, durability and purity. Many ligands, such as chromotropic acid [8], α-nitroso-β-naphthol [9], salicylic acid [10], pyrocathecol [11], 1-(2-pyridilazo)-2-naphtol [12], *o*-aminobenzoic acid [13], 2-(methylthio)aniline [14] and 3,4-dihydroxybenzoic acid [15] were covalently coupled with a polymer backbone through an azo (–N=N–) [16,17], methylene ($-CH_2-$) [18] or other groups [19,20].

Preconcentration systems based on solid-phase extraction (SPE) have been used extensively for enhancing the selec-

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[*] Corresponding author. Tel.: +55 73 5256683; fax: +55 73 35256683.
E-mail address: vlemos@uesb.br (V.A. Lemos).

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tivity and sensitivity of analytical methods. Automation of sorption separation procedures is very opportune for determinations of trace metals due to its flexibility, simplicity, high sampling rate and versatility which allow the method to be used in conjunction with different spectrometric detectors. The combination of on-line systems with flame atomic absorption spectrometry (FAAS) show good effects, such as strong tolerance to high concentrations of dissolved solids, use of organic solvents can enhance sensitivity and high selectivity of the detection technique. Generally, two simple steps, loading and elution, are used in most procedures. On-line column packings found on literature include chelating resins [21], silica [22,23],carbon [24], fullerene [25], activated alumina [26,27], ion-exchangers [28,29], polyurethane foam (PUF) [30–33] and polymeric resins [34,35]. This work aims to synthesize an 2-aminothiophenol functionalized Amberlite XAD-2 resin (AT-XAD) and to develop an on-line preconcentration method for cadmium and copper determination. The synthesis and characterization of the chelating resin was followed by the study of chemical and hydrodynamic parameters and application of the procedure in water and biological samples.

2. Experimental

2.1. Reagents

Deionized water from an water purification system was used to prepare all solutions. All reagents were of analytical reagent grade. Metal working solutions at $\mu g\,l^{-1}$ level were prepared daily by diluting a corresponding 1000 $\mu g\,ml^{-1}$ solution (Merck). Hydrochloric and nitric acid solutions used as eluents were prepared by direct dilution with deionized water from the concentrated solutions (Merck). The laboratory glassware was kept overnight in a 5% (v/v) nitric acid solution. Afterwards, it was rinsed thoroughly with deionized water and dried. Acetate, borate and ammoniacal buffers conveniently prepared [36] were used to adjust the sample pH in the range of 4.8–6.0, 7.0–8.0 and 9.0, respectively. Amberlite XAD-2 (Sigma, 20–60 mesh), 2-aminothiophenol (Sigma), nitric and sulphuric acids (Merck) and sodium nitrite (Reagen) were used for synthesis of the sorbent.

2.2. Instrumentation

A flame atomic absorption spectrometer of the Perkin-Elmer Instruments (Shelton, USA) model AAnalyst 200 equipped with air–acetylene flame was used for the analysis. Instrumental conditions used were those suggested by the manufacturer. Also the wavelengths had conventional values: Cd 228.8 nm and Cu 324.8 nm. Nebulizer flow rate was 5.0 ml min^{-1}. Infrared spectra were recorded in an ABB Bomen MB series model MB100 Fourier transform IR spectrometer. A Thermo Finnigan Flash elemental analyzer 1112 series was used for elemental analysis. A Digimed DM 20 (Santo Amaro, Brazil) pH meter was also used for pH measurements.

The manifold used for metal preconcentration was adapted to the nebulizer system of the flame atomic absorption spectrometer. Flow system was made up of a peristaltic pump (Millan, model 204, Colombo, Brazil) furnished with silicone tubes to delivery all solutions, two Rheodyne model 5041 six-port rotary valves (Cotati, USA) to select elution and preconcentration steps [37], and an AT-XAD packed minicolumn for the on-line preconcentration of the metals. The minicolumn has the following dimensions: 3.50 cm length and internal diameter of 4.0 mm. Mass of AT-XAD used was 100 mg. Plastic foams were placed at both sides of minicolumn to keep the packing material in the place. The minicolumn was firstly washed with ethanol, 5% (v/v) nitric acid solution and deionized water, respectively, at 2.50 ml min^{-1} flow rate. Washing with nitric acid and ethanol was necessary in order to prevent any metal or organic contamination, respectively. All columns prepared by this way shown good reproducibility. 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. To minimize dispersion, the length of the capillary PTFE tube between the end of minicolumn and the nebulizer was as short as possible (about 5 cm).

2.3. Synthesis of AT-XAD

For resin synthesis, a procedure for similar reagents [10,15] was performed. Concentrated nitric (10 ml) and sulphuric (25 ml) acids acid were added to Amberlite XAD-2 (5 g) and the mixture stirred at 60 °C for 1 h on an water bath. Thereafter, the reaction mixture was poured into an ice–water mixture. The nitrated resin was filtered, washed repeatedly with water until free from acid and added to a reducing mixture of 40 g of $SnCl_2$, 45 ml of concentrated HCl and 50 ml of ethanol. The system was refluxed for 12 h at 90 °C. The solid precipitate was filtered and washed with water and 2 mol l^{-1} NaOH. The amino resin was firstly washed with 2 mol l^{-1} HCl and finally with distilled water to remove the excess of HCl. For diazotization, the amino resin was suspended in 50 ml of a 6.0 mol l^{-1} hydrochloric acid solution at 0–5 °C. A solution of 2.1 g of sodium nitrite in 20 ml of water was added dropwise. The mixture was stirred and kept at 0–5 °C for 1 h. The diazotized resin was filtered off and washed with ice-cold water. For coupling, 3.0 g of 2-aminothiophenol was added to 20 ml of an 1.0 mol l^{-1} sodium hydroxide solution and the mixture was cooled to 0–5 °C. This solution was added dropwise to the above diazotized resin with vigorous stirring. The system was allowed stand overnight in refrigerator at 0–5 °C. The resulting dark-brown resin was filtered, washed with water and dried in air.

Infrared spectra of free Amberlite XAD-2 and AT-XAD resin were studied using the potassium bromide technique. Additional peaks in the IR spectrum of the AT-XAD resin that

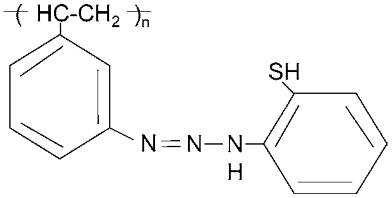

Fig. 1. Proposed structure for AT-XAD.

do not appear in the spectrum of the free Amberlite XAD-2 are at 2590, 1610 and 1525 cm^{-1} which appear to originate due to modification of resin by the ligand and are characteristic of –S–H, –N–H and –N=N– vibrations, respectively. Data obtained from CHN elemental analysis C 66.84%, H 6.37%, N 15.92% were comparable with the theoretically calculated values C 65.88%, H 5.10%, N 16.47%. The CHN analysis confirmed the presence of one 2-aminothiophenol molecule is present in the resin per repeat unit of the polymeric matrix. A structure according these data is shown in Fig. 1.

2.4. On-line system

The synthesized AT-XAD resin was packed in a minicolumn of the on-line preconcentration system. The manifold used is similar that described in a previous work for cobalt preconcentration [37]. An advantage of this system is the washing of the minicolumn with the carrier (water) before and after preconcentration, without damaging of the efficiency system. A sample solution containing metal ions was kept at convenient pH with a buffer solution and was percolated through the AT-XAD minicolumn that retained the cations. At this time, the remaining solution is discharged to waste. By sliding the two six-port valves simultaneously, a stream of water carries the acid eluent from the loop and column, displacing the ions. This eluate was taken direct to the nebulizer–burner system of the spectrometer. Signals were measured as peak height (or maximum absorbance). Peak height was used because it resulted in precision better than peak area.

2.5. Sample preparation

For accuracy studies, certified reference materials (CRMs) furnished by the National Institute for Environmental Studies (NIES), Japan, NIES 10b-Rice Flour unpolished, medium level of cadmium and the National Institute of Standards and Technology (Gaithersburg, MD, USA), NIST 1515 Apple Leaves were analyzed. For their decomposition [15], about 0.4 g of 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 12 h. After cooling at room temperature these solutions were adjusted to pH with a 10% (w/v) sodium hydroxide solution and appropriate buffer solution. The solution was made up to required volume with deionized water into a 100 ml volumetric flask.

Natural waters were sampled from river and well at Jequié city, Bahia state, Brazil. Mineral water sample was obtained in a supermarket at this city. For natural water samples, 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. Samples were filtered before analysis. A volume of 100 ml of the filtrate were taken and the pH was adjusted by addition of buffer solution. At least one blank solution was run for each sample in order to evaluate metal contamination by the reagents used.

3. Results and discussion

3.1. Effect of pH on metal preconcentration

For this study, 10 ml of acetate, borate and ammoniacal buffers at different pH values were added to an 100 ml flask containing the metal and the volume was completed with deionized water. The effect of the sample pH on the copper response was investigated within the range of 4.7–9.2 using 10 $\mu g\,l^{-1}$ Cd(II) and 50 $\mu g\,l^{-1}$Cu(II). According these studies, the best intervals of pH for Cd(II) and Cu(II) preconcentration are 8.0–9.2 and 6.0–7.0, respectively, as shown in Fig. 2. In the posterior experiments, borate buffer pH 8.0 and acetate buffer pH 6.0 were used to adjust Cd(II) and Cu(II) solution pH, respectively.

3.2. Elution

Metal elution from the minicolumn was studied by using nitric and hydrochloric acid solutions, and it was not observed any significant difference between the results for the two acids. Hydrochloric acid solutions at different

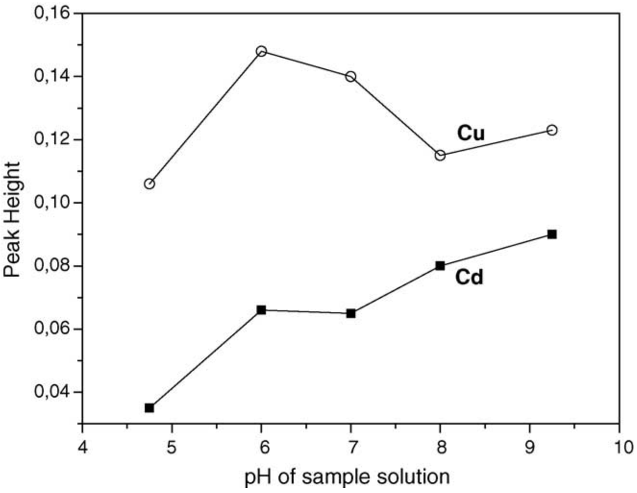

Fig. 2. Effect of pH on the preconcentration of Cd and Cu.

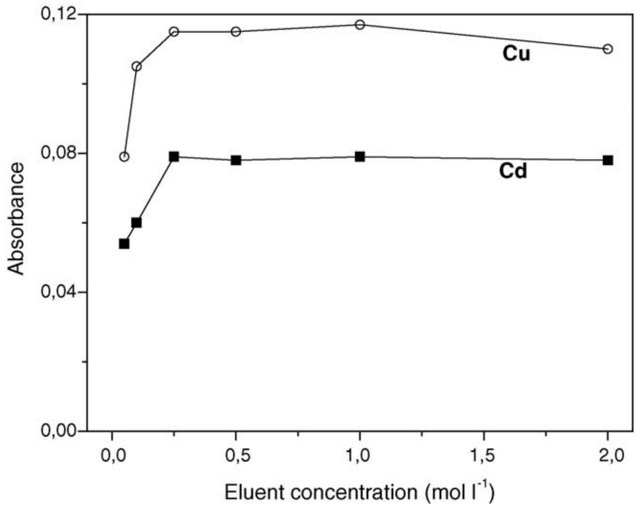

Fig. 3. Effect of eluent concentration on the preconcentration of Cd and Cu.

concentrations were used as stripping agent. Total elution was reached at concentrations over 0.25 mol l^{-1} for both metals, according Fig. 3. Addition of ethanol or acetone to acid solution have not resulted in any increasing of analytical signal. So, 0.50 mol l^{-1} hydrochloric acid was selected as eluent for further elution of Cd(II) and Cu(II).

The quantity of acid that passes by column is determined by volume of the eluent loop (L). Influence of this parameter in metal preconcentration is shown in Fig. 4. It was found maximum signal for eluent loop in the range of 80–1600 μl for Cd(II) and 40–350 μl for Cu(II). So, a volume of 80 μl of L was choosen for the two metals in posterior experiments in order to pass a minimum quantity of acid by the column.

3.3. Lifetime and sorption capacity of AT-XAD

Lifetime of the minicolumn packed with AT-XAD used in the preconcentration system of Cd(II) and Cu(II) was monitored. It was made measuring the signal of 10 μg l^{-1} Cd(II) and 50 μg l^{-1} Cu(II) solutions at end of each day of work and counting the number of runs in that day. Results demonstrated that column shown good performance for at least 300 cycles. It indicates that material is very stable even under rough changes of pH and solvent conditions. The capacity of AT-XAD for both cations was determined by equilibrating 0.50 g of the resin with 100 ml of 5.0 mg l^{-1} Cd(II) at pH 8.0 or 5.0 mg l^{-1} Cu(II) at pH 6.0 for 4 h. Cadmium and copper were determined in each filtrate. The resin capacity was found to be 3.7 and 4.6 mmol g^{-1} for Cd(II) and Cu(II), respectively.

3.4. Flow rates

Sample flow rate is an important parameter in on-line systems because it determines the velocity of the cation on the minicolumn. In the proposed system, 5.00 ml of a solution containing 10 μg l^{-1} Cd(II) or 50 μg l^{-1} Cu(II) was pumped into the system at flow rates from 1.7 to 11.6 ml min^{-1}. Analytical signals decreased at 5.0 and 8.0 ml min^{-1} for Cd(II) and Cu(II), respectively. This study is shown in the Fig. 5. The difference in the optimum range for two metals is due the different kinetic properties. Metal sorption is minor at high flow rates due increasing in the velocity of the ions, that reduces the contact time between the phases, damaging the retention. High flow rates also increases back-pressure and this could cause leakage. Otherwise, low flow rates decreases sample frequencies, damaging system efficiency. Thus, flow rates of 5.0 and 8.0 ml min^{-1} were chosen for Cd(II) and Cu(II), respectively, in posterior experiments, as a compromise between efficiency and stability.

The effect of the eluent flow rate in the step of desorption of the metals from the minicolumn was also investigated. Experiments were carried out by pumping eluent in order to achieve an analytical signal as high as possible. Best results

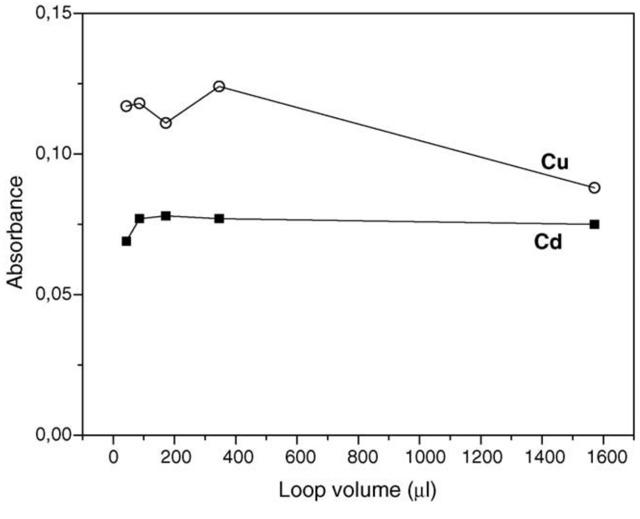

Fig. 4. Effect of eluent amount on the preconcentration of Cd and Cu.

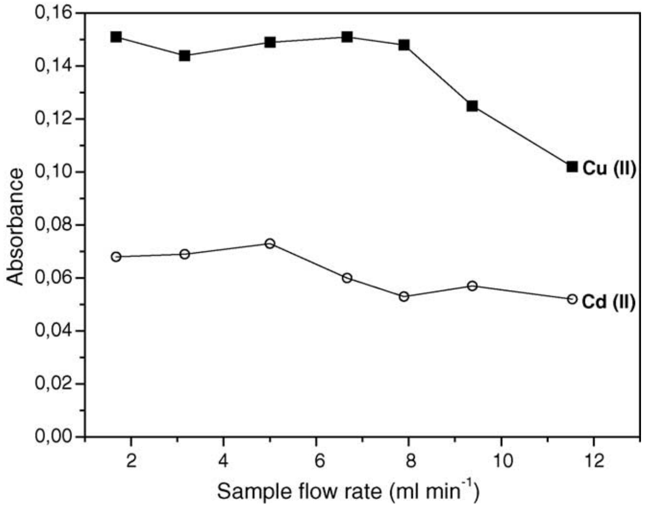

Fig. 5. Effect of sample flow rate on the preconcentration of Cd and Cu.

Table 1
Analytical characteristics of the on-line cadmium and copper preconcentration system using AT-XAD minicolumn

Element	Cadmium		Copper	
Preconcentration time (s)	60	180	60	180
Enrichment factor	28	74	14	35
Concentration efficiency (min^{-1})	24	22	12	10
Transfer phase factor	0.98		0.92	
Consumptive index (ml)	0.21	0.24	0.43	0.51
Sample frequency (h^{-1})	51	18	51	18
Eluent consumption (μl)	150		150	
Limit of detection ($\mu g\, l^{-1}$)	0.89	0.14	1.31	0.54
Limit of quantification ($\mu g\, l^{-1}$)	2.96	0.38	4.38	1.81
Precision (%)	3.7	5.8	2.2	6.1
Calibration function	$A = 6.90 \times 10^{-3} + 8.90 \times 10^{-3} C$	$A = 3.10 \times 10^{-3} + 2.36 \times 10^{-2} C$	$A = 5.00 \times 10^{-3} + 2.40 \times 10^{-3} C$	$A = 1.67 \times 10^{-2} + 5.81 \times 10^{-3} C$

were found within the range of 3.5–6.0 $ml\, min^{-1}$ for both metals. At flow rates less than 3.5 $ml\, min^{-1}$ the analytical signal considerably decreased, resulting broader peaks. Probably, it is due to incompatibility between elution and nebulization flow rates, which cause significant dispersion when eluent flow rate is smaller than nebulizer flow rate. A flow rate of 5.0 $ml\, min^{-1}$ was selected in the subsequent studies, in order to match elution and aspiration flow rates.

3.5. *Analytical features*

Characteristic data under the optimum chemical and flow conditions of the manifold for cadmium and copper preconcentration were determined and are given in Table 1. The data are shown for 60 and 180 s preconcentration time, for both metal. Enrichment factors were calculated as the ratio of the slopes of the calibration graphs with preconcentration and direct aspiration, respectively [29,38,39]. By using direct aspiration in FAAS without the preconcentration system, the linear equation for cadmium determination was $A = 1.23 \times 10^{-2} + 3.17 \times 10^{-4} C$ and for copper determination was $A = 4.00 \times 10^{-4} + 1.68 \times 10^{-4} C$, where A is the absorbance and C is the metal concentration in solution ($\mu g\, l^{-1}$).

To determinate the retention efficiency of AT-XAD minicolumn, 25.0 ml of a 10.0 $\mu g\, l^{-1}$ cadmium or 50.0 $\mu g\, l^{-1}$ copper solution was percolated by the column under optimum conditions. The desorption was carried out with 1.00 ml of 0.50 $mol\, l^{-1}$ hydrochloric acid solution and the metals were measured by FAAS. In these conditions, the retention efficiency of the column, also known as transfer phase factor, defined as the ratio between the analyte mass in original sample and that in the concentrate [29], was 0.98 and 0.92 for Cd(II) and Cu(II), respectively. Other factors that characterize on-line preconcentation systems, such as concentration efficiency (CE) and consumptive index (CI) [29], were also determined.

The preconcentration time was also studied. The analytical signal increased proportionally with the preconcentration time up to 240 s for Cd 10 $\mu g\, l^{-1}$ and 180 s for Cu 50 $\mu g\, l^{-1}$. The retention efficiencies were constant within these time intervals. When used preconcentration times longer than these limits, signals decreased, probably, because occurs partial leaching of the ions from minicolumn. When more sensitive determinations were required, preconcentration time of 180 s was used. Using higher preconcentration time is not adequate in these systems because prejudices the efficiency, causing low sampling frequencies.

3.6. *Effect of foreign ions*

Solutions containing the metal (cadmium 10.0 $\mu g\, l^{-1}$ or copper 50.0 $\mu g\, l^{-1}$) and other ions in order to determine the selectivity of the analytical system were prepared and the developed procedure was applied. The effect of each species was considered interference when the signal in the presence of the species resulted in an absorbance deviation of more than ±5%. Results are shown in Table 2. The results indicates that various substances commonly present in biological or water samples do not interfere in the analysis of metals under the fixed conditions.

Table 2
Maximum tolerable quantities of other ions for the online system using AT-XAD minicolumn for cadmium (10 $\mu g\, l^{-1}$) and copper (50 $\mu g\, l^{-1}$) determination

Substance	Maximum tolerable ion amount	
	Cadmium	Copper
Na^{+} ($g\, l^{-1}$)	30	30
K^{+} ($g\, l^{-1}$)	12	12
Mg^{2+} ($g\, l^{-1}$)	2	4
Ca^{2+} ($g\, l^{-1}$)	2	4
Pb^{2+} ($mg\, l^{-1}$)	12	15
Al^{3+} ($mg\, l^{-1}$)	5	8
Co^{2+} ($mg\, l^{-1}$)	10	18
Ni^{2+} ($mg\, l^{-1}$)	10	20
Cd^{2+} ($mg\, l^{-1}$)	–	15
Cu^{2+} ($mg\, l^{-1}$)	5	–
Zn^{2+} ($mg\, l^{-1}$)	15	15
Fe^{3+} ($mg\, l^{-1}$)	10	2.5
Cr^{3+} ($mg\, l^{-1}$)	5	15
NO_3^{-} ($g\, l^{-1}$)	12	12
Cl^{-} ($g\, l^{-1}$)	30	30
SO_4^{2-} ($mg\, l^{-1}$)	50	100

Table 3
Metal determination in certified reference materials ($n = 4$)

Sample	Cadmium amount ($\mu g\,g^{-1}$)		Copper amount ($\mu g\,g^{-1}$)	
	Proposed methodology	Certified	Proposed methodology	Certified
NIES 10b-Rice Flour	0.34 ± 0.05	0.32 ± 0.02	3.6 ± 0.3	3.3 ± 0.2
NIST 1515-Apple Leaves	–	–	5.23 ± 0.45	5.64 ± 0.24

NIES: National Institute for Environmental Studies, Japan; NIST: National Institute of Standards & Technology, USA.

3.7. Accuracy of the method

The accuracy of developed procedure was evaluated by measuring the cadmium and copper amount in the following certified reference materials: NIES 10b-Rice Flour unpolished and NIST 1515-Apple Leaves. Confidence intervals are at 95% level. According Table 3, amounts of cadmium and copper determined in these materials are in good agreement with the certified values. Results indicate the applicability of the developed proce-

Table 4
Results obtained for metal determination in water samples ($n = 4$)

Sample	Cadmium amount ($\mu g\,l^{-1}$)		Recovery (%)	Copper amount ($\mu g\,l^{-1}$)		Recovery (%)
	Added	Found[a]		Added	Found[a]	
River water	0.0	1.09 ± 0.05	–	0.0	1.75 ± 0.09	–
	2.5	3.52 ± 0.19	97	5.0	6.70 ± 0.15	99
	5.0	6.39 ± 0.34	106	10.0	11.34 ± 0.22	96
Well water	0.0	<LOD	–	0.0	<LOD	–
	2.5	2.36 ± 0.09	94	5.0	5.26 ± 0.27	105
	5.0	5.23 ± 0.31	105	10.0	10.94 ± 0.22	109
Drink water	0.0	<LOD	–	0.0	<LOD	–
	2.5	2.45 ± 0.14	98	5.0	5.18 ± 0.20	104
	5.0	5.41 ± 0.11	108	10.0	9.28 ± 0.43	93
Tap water	0.0	<LOD	–	0.0	1.17 ± 0.07	–
	2.5	2.67 ± 0.23	107	5.0	6.04 ± 0.19	97
	5.0	5.27 ± 0.15	106	10.0	10.95 ± 0.31	98

LOD: limit of detection.

[a] Confidence interval 95%.

Table 5
Procedures for on-line preconcentration of cadmium and copper using chemically modified material and detection by FAAS

Sorbent	Analyte	EF	CE (min^{-1})	CI (ml)	f (h^{-1})	LOD ($\mu g\,l^{-1}$)	PT (s)	Reference
Silica gel/3(1-imidazolyl)propyl groups	Cu[a]	20–26	9–12	0.57–0.43	27	0.40	90	[40]
	Cu[b]	36–42	16–19	0.31–0.26	27	0.20	90	
Silica gel/niobium(V) oxide (Nb_2O_5–SiO_2)	Cd	33	11	0.44	20	0.10	120	[41]
	Cu	34	11	0.42	20	0.40	120	
Acrylic acid grafted PTFE fibers	Cd	73	67	0.10	55	0.10	45	[42]
Rice husks/NaOH	Cd	72	17	0.33	14	1.14	240	[43]
Chitosan biopolymer/8-hydroxyquinoline	Cd	24	10	0.42	26	0.10	90	[44]
	Cu	25	11	0.40	26	0.40	90	
Chitosan biopolymer/5-sulphonic acid 8-hydroxyquinoline	Cd	14	6	0.78	26	0.20	90	[45]
	Cu	19	8	0.56	26	0.30	90	
Amberlite XAD-2/3,4-dihydroxybenzoic acid	Cu	33	14	0.39	28	0.27	120	[15]
Amberlite XAD-2/chromotropic acid	Cd	21	18	0.33	51	0.40	60	[46]
Amberlite XAD-2/2-aminothiophenol	Cd	28	24	0.21	51	0.89	60	This work
		74	22	0.24	18	0.14	180	
	Cu	14	12	0.43	51	1.31	60	
		35	10	0.51	18	0.54	180	

EF: enrichment factor; CE: concentration efficiency; CI: consumptive index; f: sampling frequency; LOD: limit of detection; PT: preconcentration time.

[a] Response in peak area.

[b] Response in peak height.

dure in cadmium and copper determination free of interference.

3.8. Determination of cadmium and copper in water samples

The analytical system was used for cadmium and copper determination in water samples. The results are described in Table 4. Recoveries (R) of spike additions (2.5 or $5.0\,\mu g\,l^{-1}$ for Cd or 5.0 or $10.0\,\mu g\,l^{-1}$ for Cu) to water samples were quantitative. R was calculated as follows: $R\,(\%) = \{(C_m - C_o)/m\} \times 100$, where C_m is a value of metal in a spiked sample, C_o is a value of metal in a sample and m is the amount of metal spiked. These results demonstrate the applicability of the procedure for cadmium and copper determination in water samples.

4. Conclusion

AT-XAD was sucessfully applied to the on-line preconcentration and determination of cadmium and copper by FAAS. The system improved significantly the performance of the off-line FAAS method. A comparison of the proposed system with other on-line preconcentration procedures using several sorbents is given in Table 5. Enrichment factors (EF) obtained, especially for cadmium, was thus comparable to those presented by other methods described in the literature. Low detection limits and high tolerance to interferences from the matrix ions allows the application of the proposed procedure for cadmium and copper determination in a large range of samples. Lifetime of the AT-XAD column and simplicity of the manifold are also advantages of this procedure if compared to many methods existing to metal preconcentration. These characteristics are very interesting for routine laboratories in trace element analysis.

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