Talanta 97 (2012) 181–186

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Study of bond Elut® Plexa™ PCX cation exchange resin in flow injection column preconcentration system for metal determination by flame atomic absorption spectrometry

Aristidis N. Anthemidis*, Sofia Xidia, Georgia Giakisikli

Laboratory of Analytical Chemistry, Department of Chemistry, Faculty of Science, Aristotle University, Thessaloniki, Greece

ARTICLE INFO

Article history:
Received 17 January 2012
Received in revised form
28 March 2012
Accepted 4 April 2012
Available online 24 April 2012

Keywords:
Bond Elut® Plexa™ PCX
Flow injection
Column preconcentration
Metal determination
Atomic absorption spectrometry

ABSTRACT

A simple and sensitive on-line solid-phase extraction methodology for preconcentration and determination of trace amounts of Cd(II), Pd(II) and Cu(II) in natural water samples has been developed using the strong cation exchange capability of Bond Elut® Plexa™ PCX polymer resin. Plexa PCX is a mixed-mode sorbent, commercially available in a cartridge format and as far as we know, there is no application into the field of metal determination. The analytes were retained on the resin, eluted with 1 mol L^{-1} hydrochloric acid and subsequently directed to FAAS for quantification. The influence of chemical and flow variables which affect the performance of the system have been studied, providing the appropriate conditions for the analysis of real samples. For preconcentration time of 90 s, an enrichment factor of 90, 95 and 95 and a detection limit (3*s*) of 0.1, 1.8 and 0.5 μg L^{-1} for Cd(II), Pb(II) and Cu(II), respectively were obtained along with a sampling frequency of 30 h^{-1}. The accuracy of the proposed method was evaluated by analyzing certified reference materials. This procedure was successfully applied for metal determination in environmental and biological samples.

1. Introduction

Along with many other toxic compounds in the environment, a lot of heavy metals are present in our immediate environment. Human exposure to heavy metals has risen dramatically in the last 50 years, as they exist in virtually every area of modern consumerism from construction materials to cosmetics, medicines to processed foods, fuel sources to agents of destruction, appliances to personal care products. Metals like cadmium and lead are highly toxic and can cause damaging effects even at very low concentrations. On the other hand, copper is essential to life in tiny amounts, although in higher amounts it can be toxic as well. As levels rise in our air, water, and topsoil, they also rise within the human bodies via accumulation [1], affecting the central nervous system and contributing to serious chronic diseases, cancer, learning disorders, dementia, and premature aging.

Atomic spectrometry (AS) techniques such as flame absorption atomic spectrometry (FAAS), electrothermal atomic absorption spectrometry (ETAAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) and mass spectrometry (ICP-MS) are extensively employed for metal determination in various types of samples and matrices. The selection of an appropriate technique requires the consideration of a variety of important factors such as sensitivity, selectivity, ease-of-use, cost of analysis, availability and number of samples. FAAS is a relatively sensitive and available technique in many routine laboratories for metal determination. However, direct determination of trace elements in real samples is usually difficult due to the low analyte concentration and matrix interference. Therefore, a preconcentration and/or separation step prior to final measurement is usually required.

The combination of on-line preconcentration techniques with FAAS has proved to be of considerable interest, providing increased sensitivity and selectivity, higher recovery, speed low risk of sample contamination and reduced operational cost [2]. A common form of sample preconcentration and/or separation involves solid phase extraction (SPE), and particularly its on-line mode using a minicolumn packed with an appropriate sorbent material. On-line column preconcentration and FAAS determination of cadmium, lead and copper has been performed by using various sorbent materials such as ion exchangers [3], multi-walled carbon nanotubes (MWCNTs) [4–6], alumina coated [7], polyurethane foam (PUF) [8], polytetrafluoroethylene (PTFE) as turnings [9], polyetheretherketone (PEEK) [10], poly-chlorotrifluoroethylene (PCTFE) [11–13], ion-imprinted functionalized silica gel [14], modified silica gel [15], merrifield chloromethylated resin (MCR) [16], chloromethylated polystyrene [17,18], polystyrene divinylbenzene like Oasis HLB [19,20], XAD-2 [21] and XAD-4 [22]. For comparative purposes, the analytical

---

* Corresponding author.
E-mail address: anthemid@chem.auth.gr (A.N. Anthemidis).

0039-9140/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2012.04.014

Table 1
On-line sorbent extraction methods for cadmium, lead and copper determination with FAAS.

Sorbent	Ligand	Eluent	PT (s)	SC (mL)	c_L (μg L^{-1})	s_r (%)	EF	Ref.
Cadmium								
Alumina modified with SDS/1,10-phenanthroline	–	Ethanol	240	20.0	0.14	2.2	116	[7]
PCTFE	DDPA	MIBK	30	2.4	0.30	2.9	39	[12]
Hypersep SCX	–	2 mol L^{-1} HCl	150	15.0	0.14	2.8	92	[3]
Cd(II)-imprinted thiol-functionalized silica gel	–	0.5 mol L^{-1} HNO_3	45	6.6	0.07	0.9	56	[14]
Chloromethylated polystyrene functionalized with NAPdien	–	1 mol L^{-1} HNO_3	150	10.0	0.25	5.1	50	[17]
Oasis®–HLB	DDTP	Methanol	90	12.0	0.09	2.9	155	[20]
Bond Elut® Plexa™ PCX	–	1 mol L^{-1} HCl	90	18.0	0.10	2.9	90	**
Lead								
MWCNTs	–	2 mol L^{-1} HCl	90	1.5	1.0	4.6	15	[5]
MWCNTs	–	1 mol L^{-1} HNO_3	240	5.0	2.6	7.7	44	[6]
PEEK-turnings	DDTP	MIBK	120	11.0	0.32	2.2	110	[10]
PCTFE	APDC	MIBK	90	18.0	1.2	2.1	220	[11]
MCR-functionalized with DDTC	–	Methanol (acidified)	120	10.0	1.3	1.4	48	[16]
Hypersep SCX	–	2 mol L^{-1} HCl	150	15.0	2.1	3.1	97	[3]
Oasis®–HLB	DDPA	Methanol	90	12.0	0.92	2.6	180	[20]
Bond Elut® Plexa™ PCX	–	1 mol L^{-1} HCl	90	18.0	1.8	3.1	95	**
Copper								
MWCNTs	–	2 mol L^{-1} HCl	90	1.5	0.59	3.4	20	[5]
Alumina modified with SDS/1,10-phenanthroline	–	Ethanol	240	20.0	0.04	1.4	175	[7]
Polyurethane foam	APDC	MIBK	60	12.0	0.20	2.8	170	[8]
PTFE-turnings	APDC	MIBK	60	12.0	0.05	1.5	340	[9]
PCTFE	DDPA	MIBK	90	11.6	0.07	1.8	250	[13]
Hypersep SCX	–	2 mol L^{-1} HCl	150	15.0	0.47	2.5	93	[3]
Silica gel immobilized with dithizone	–	10% v/v HNO_3	50	5.4	0.20	1.7	43	[15]
Chloromethylated polystyrene modified with PPDOT	–	1 mol L^{-1} HNO_3	240	10.0	0.56	2.0	41	[18]
Oasis-HLB	DDTC	Methanol	90	10.0	0.10	2.9	195	[19]
XAD-4 functionalized with DHB	–	1 mol L^{-1} HNO_3	60	7.0	0.10	3.1	91	[22]
Bond Elut® Plexa™ PCX	–	1 mol L^{-1} HCl	90	18.0	0.50	2.7	95	**

SC: sample consumption, c_L: detection limit; s_r: relative standard deviation; EF: enhancement factor; NAPdien: N,N-bis(naphthylidenetriamine); SDS: sodium dodecyl sulfate; PPDOT: 1-phenyl-1,2-propanedione-2-oxime thiosemicarbazone; DDPA: diethyldithiophosphate ammonium; APDC: ammonium pyrrolidine dithiocarbamate; DDTC: diethyldithiocarbamate; MIBK: methyl isobutyl ketone.

** This work; PT: preconcentration (loading) time.

performance characteristics of some reported in the literature on-line SPE methods for FAAS determination of cadmium, lead and copper are given in Table 1.

Ion-exchange is an effective and easy to operate physicochemical process for uptake of trace metals from aquatic complex matrices. There are four main types of ion exchange resins differing in their functional groups: strongly acidic (typically, sulfonic acid groups, e.g. sodium polystyrene sulfonate or polyAMPS), strongly basic (quaternary amino groups, for example, trimethylammonium groups, e.g. polyAPTAC), weakly acidic (mostly, carboxylic acid groups) and weakly basic (primary, secondary, and/or ternary amino groups, e.g. polyethylene amine). Cationic exchange resins are polymers that are capable of exchanging positively charged ions with a solution passed through them. Some cation exchange resins dealing with their implementation for metal preconcentration are Hypersep SCX [3,23], Lewatit [24], Dowex 50 [25], Dowex 50WX4 [26,27], Dowex 50WX8-400 [28], Purolite C100 [29,30], D113 [31] and Amberlite IR 120 [32]. In addition, Chelex 100 (Bio-Rad Laboratories, Richmont, CA, USA) is a styrene divinylbenzene copolymer containing paired iminodiacetate ions which act as chelating groups in binding polyvalent metal ions. However, Chelex chelating resin is classed with the weakly acidic cation exchange resins by virtue of its carboxylic acid groups [33,34].

The aim of this work was to investigate the analytical performance and the potential applicability of Bond Elut Plexa PCX resin as sorbent for cadmium, lead and copper determination via an automatic flow injection (FI) on-line SPE–FAAS system. Although Plexa PCX has been employed for uptake of various organic compounds [35–37], this is the first reported application of the above resin in a micro-cartridge format for metal preconcentration. All major chemical and hydrodynamic factors affecting the analyte adsorption and elution were optimized, enhancing the effectiveness of the proposed method (FI–SPE–FAAS).

2. Experimental

2.1. Instrumentation

A Perkin-Elmer Model 5100 PC flame atomic absorption spectrometer (Perkin-Elmer, Norwalk, CT, USA, http://las.perkinelmer.com) was used as detection system. A Perkin Elmer Lumina™ single element hollow cathode lamp (HCL) for cadmium and lead operated at 4 and 10 mA respectively, and a Lumina™ multi element (Co–Cr–Cu–Fe–Mn–Ni) HCL at 30 mA for copper determination, were used as light sources. The wavelength/monochromator spectral bandpass (slit) was set at 228.8/0.7 nm, 283.3/0.7 nm and 324.8/0.7 nm for cadmium, lead and copper determination respectively. All spectrometric measurements were carried out using an air/acetylene flame at 10.0 and 1.0 mL min^{-1} flow rate respectively, according to the manufacturer recommendations. Under these conditions the nebulizer's free uptake rate was 5.5 mL min^{-1}. A flow spoiler inside the spray chamber resulted in better nebulization/atomization conditions. Peak height was used for signal evaluation throughout the study.

A Perkin Elmer FIAS-400 flow injection analysis system coupled to a 5100 PC was used for the automatic process of the proposed method. The FIAS-400 system comprised of a 5-port 2-position injection valve and two peristaltic pumps P1, P2 equipped with Tygon type peristaltic tubes for eluent and sample solution propulsion respectively. The FIAS-400 system was connected to the spectrometer's nebulizer via a short PTFE tube of

15 cm length and 0.35 mm i.d., for minimization of analyte dispersion into the eluent. A «T» type mixing device was utilized just ahead of the inlet of FAAS for flow compensation between elution flow rate and nebulizer aspiration as it has been reported elsewhere [11].

A micro-syringe pump (MicroCSP-3000, FIAlab Instruments, Bellevue, WA), equipped with a 2.5 mL glass syringe (TECAN) and a four-position Teflon/Kel-F valve at the top of it, was employed to deliver HCL solutions of concentrations higher than 2 mol L^{-1} due to the incompatibility of Tygon type tubes with high acidic solutions [38]. The micro-syringe pump was controlled by the FIAlab for windows v.5.9 application software coupled with the Perkin-Elmer AA Lab. Benchtop version 7.2, software. An Orion EA940 pH-meter was used for pH measurements.

2.2. On-line SPE cartridge

Bond Elut Plexa PCX is a mixed-mode solid phase extraction sorbent which contains a highly polar polymeric cation exchange resin that combines the outstanding properties of Bond Elut Plexa such as superior flow characteristics and improved analytical performance, with strong cation exchange functionalities. According to the manufacturer (Agilent Technologies, http://www.chem.agilent.com) Plexa PCX removes neutral and acidic interferences from the matrix, concentrates basic analytes and therefore improves sensitivity in the determination of basic compounds. The Plexa PCX particles are near mono-dispersed, resulting in much better homogenous packing efficiency. Reproducible results are the norm, with very good tube-to-tube and well-to-well performance. Ion suppression is reduced because the highly polar, hydroxylated polymer surface is entirely amide-free and does not provide binding sites for endogenous species such as proteins and lipids. The absence of particle fines dramatically reduces frit blockage and sample loss.

The Plexa PCX SPE cartridge (Bond Elut Plexa PCX, 30 mg/1 mL, Part Number: 12108301, Varian Inc.) was attached to the injection valve (IV) between ports 2 and 4 as presented in Fig. 1, in a readily exchangeable format presented elsewhere [20]. As it was shown from the experimental study, the performance of Plexa PCX microcolumn for on-line metal preconcentration remained constant for a number of preconcentration cycles higher than 600. This is an essentially important advantage for keeping the process cost down, in routine analysis.

2.3. Reagents and samples

All chemicals were of analytical reagent grade and were provided by Merck (Darmstadt, Germany, http://www.merck.de). Ultra-pure quality water, produced by a Milli-Q system (Millipore, Bedford. USA, http://www.millipore.com) was used throughout. All metal standard solutions were prepared by appropriate stepwise dilution of 1000 mg L^{-1} Cd(II), Pb(II) and Cu(II) stock standard solutions in 0.5 mol L^{-1} HNO_3 (Merck Titrisol) prior to use. The standard solutions and samples were acidified to 0.01 mol L^{-1} HNO_3 (pH ~ 2.0) by dilute HNO_3. Laboratory glassware were rinsed with ultra-pure water and decontaminated overnight in 10% (v/v) nitric acid solution.

The accuracy of the developed method was estimated by analyzing the following standard reference materials (CRM): NIST CRM 1643e (National Institute of Standard and Technology, Gaithersburg, MD, USA) containing trace elements in water and BCR 278-R (Community Bureau of Reference Brussels, Belgium) trace elements in mussel tissue.

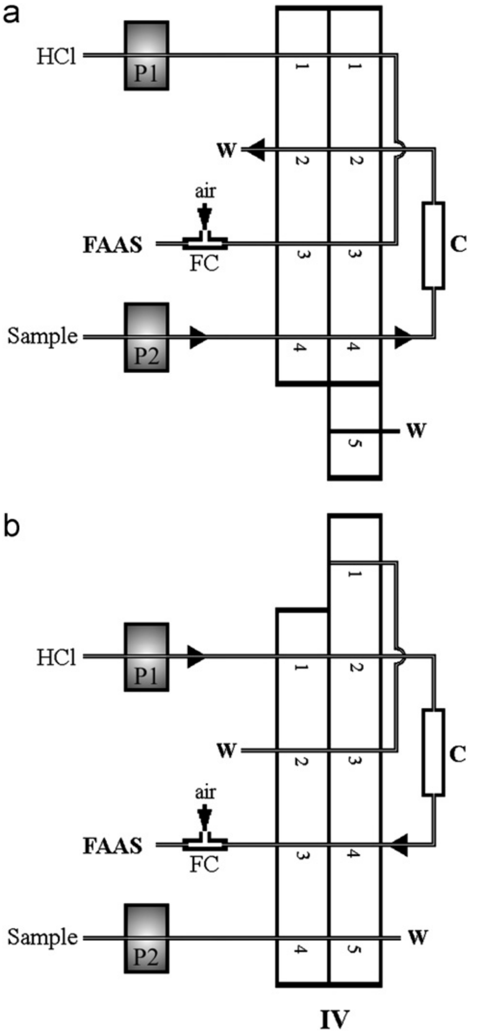

Fig. 1. Schematic diagram and the operation sequences of the FI–SPE–FAAS system for metal determination. IV, injection valve; P1, P2, peristaltic pumps; C, Bond Elut Plexa PCX microcolumn; FC, flow compensation device; w, waste. (a) Loading, (b) elution.

Water samples like river and lake water were collected from the area of Northern Greece. All samples were filtered through 0.45 μm membrane filters, acidified to ca. pH 2 with dilute HNO_3 and stored at 4 °C in acid-cleaned polyethylene bottles in order to determine the “dissolved metal” fraction with the proposed method. Urine sample (200 mL) was taken from a young healthy person. Mussel tissue and urine samples were digested using concentrated HNO_3. The digestion procedure was carried out at 130–140 °C in a stainless-steel pressurized bomb. The digestion parameters were selected according to the recommendations of the manufacture. After cooling the system, the digests were properly diluted in ultra-pure water and used for the analysis.

2.4. On-line preconcentration procedure

The manifold of the flow system is schematically presented in Fig. 1 and the operation sequences for the proposed method for metal determination are given in Table 2. Each analytical cycle consisted of two main steps: the preconcentration and the elution/measurement one. In the beginning (step 1), the injection valve (IV) was in “load” position and the sample solution was delivered through the microcolumn (C) by means of pump P2, for 90 s at a flow rate of 12 mL min^{-1}, for analyte preconcentration. Thereafter, the IV was switched to “elute” position (step 2) and pump P1 was activated to deliver the eluent (1.0 mol L^{-1} HCl) through the microcolumn towards the FAAS atomization system for measurement. The elution was performed in reverse direction

Table 2
Operational sequence of the FI–FAAS on-line microcolumn preconcentration system for metal determination.

Step	Function	Valve position	Pump operation		Delivered medium	Flow rate (mL min^{-1})	Time (s)
		IV	P1	P2			
	Pre-filling	Elute	OFF	ON	Sample or standard solution	12.0	10
1	Sample loading (preconcentration)	Load	OFF	ON	Sample or standard solution	12.0	90
2	Elution and measurement	Elute	ON	OFF	1.0 mol L^{-1} HCl	3.0	30

than that of loading to avoid analyte dispersion into the eluent. In case of a new sample or standard solution, an additional step named "pre-filling" was executed prior to the start of the analytical cycle in order to fill the tubing lines of the P2 peristaltic pump. The performance characteristics of the Bond Elut Plexa PCX microcolumn were consistent for at least 600 cycles.

3. Results and discussion

3.1. *Chemical and flow parameters optimization*

All chemical and flow parameters related to the loading and elution steps were thoroughly studied using the univariate methodology so that the optimum analytical conditions could be reached. Standard aqueous solutions of Cd(II), Pb(II) and Cu(II) at 10.0, 200.0 and 30.0 μg L^{-1} concentration level respectively were used for the optimization study.

3.1.1. *Effect of eluent type and concentration*

An ideal eluent for on-line SPE coupled to FAAS should offer fast and sufficiently strong elution ability. The recovery of the analytes from ion exchange sorbents depends on the eluting agent and its concentration. Preliminary experiments indicated that a volume of 1.0 mL of either hydrochloric or nitric acid at a concentration level of 2.0 mol L^{-1} could effectively elute the retained metals. Hydrochloric acid was adopted as eluent for subsequent experiments due to its less oxidation behavior. The effect of hydrochloric acid concentration on the recovery of the analytes was studied in the range 0.5–3.0 mol L^{-}. The results showed that complete elution was achieved for HCl concentrations higher than 1.0 mol L^{-}. Hence, 1.0 mol L^{-} HCl at a volume of 1.5 mL was chosen for total analytes desorption.

3.1.2. *Effect of sample acidity*

The acidity of sample solution is considered to be a significant variable controlling the sorption process. The effect of sample acidity on sorption behavior of Bond Elut Plexa PCX for all studied metals was examined in the range 1.0×10^{-4}–0.5 mol L^{-1} HNO_3 and the obtained results are illustrated in Fig. 2. Quantitative adsorption is accomplished in the range between 1.0×10^{-3} and 1.0×10^{-2} mol L^{-1} while at higher concentrations there is a clear decrease in the recovery of the analytes. The low sample acidity leaded to an inefficient adsorption of Cd(II), Pb(II) and Cu(II) due to their competition with the protons for the same binding sites on the surface of the cation resin. Taking into account the above results, sample and standard solutions were acidified with HNO_3 to the concentration of 0.01 mol L^{-1}. The above acidity is the most frequently recommended (APHA 1980, USEPA 1979) for the analysis of total and dissolved trace metal preservation. Therefore, in case of natural water samples analysis there is no need for additional precise pH adjustment.

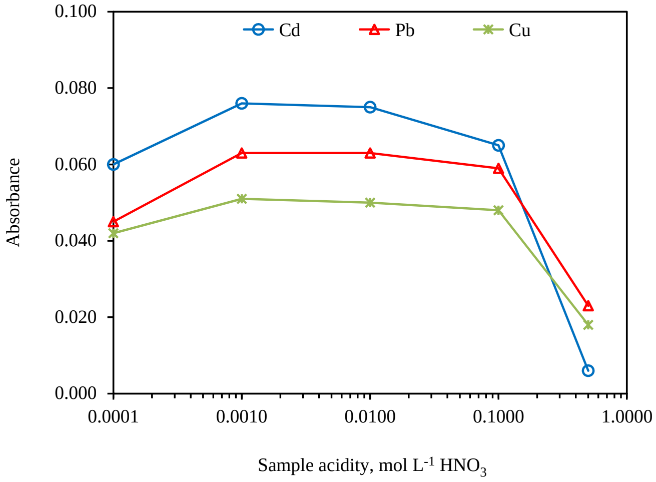

Fig. 2. Effect of sample acidity on the absorbance of Cd, Pb and Cu at 10, 200 and 30 μg L^{-1} concentration level. Experimental conditions: loading time, 60 s; loading flow rate, 8.8 mL min^{-1}; elution flow rate, 3.0 mL min^{-1}; eluent, 1.0 mol L^{-}.

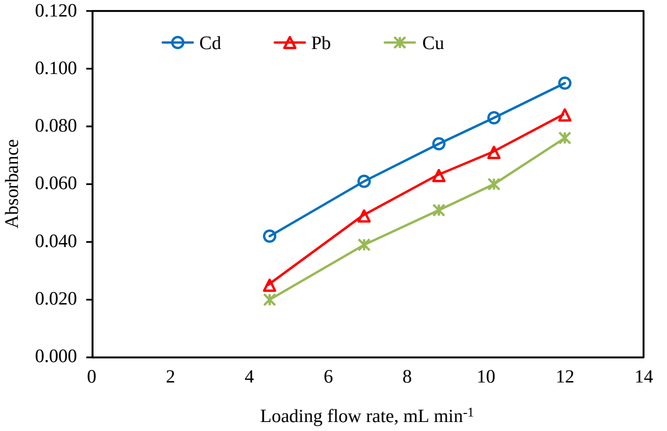

Fig. 3. Effect of sample loading flow rate on the absorbance of Cd, Pb and Cu. Experimental conditions as in Fig. 2.

3.1.3. *Effect of sample loading flow rate*

Loading flow rate is one of the key factors in controlling the preconcentration efficiency and the time of analysis. The exchange kinetics and the overpressure of the column as well, depend on the speed and the sample volume that passes through the micro-column. Typically, in FI–SPE methods, larger sample volumes result in higher enhancement factors. The influence of loading flow rate on the retention efficiency of the studied metals was examined between 4.5 and 12.0 mL min^{-1}. As it is shown in Fig. 3, the analytical signals were increased almost proportionally with the increase of the flow rate for all analytes in the studied area indicating that the sorption was very fast even at relatively high loading flow rates through the resin beds. In order to achieve high enrichment factors a loading flow rate of 12 mL min^{-1} was selected for further experiments.

3.1.4. Effect of elution flow rate

The elution flow rate is an important parameter which seriously affects the efficient analyte desorption from the sorbent. On the other hand the elution flow rate should be combatable with the nebulizer uptake rate of the FAAS burner. The influence of HCl flow rate was tested within the range 1.8–4.5 mL min^{-1}. It was ascertained that quantitative recovery of all metals was achieved at a range of 2.4–3.6 mL min^{-1}. The decrease in the analytical signal at higher elution flow rates is probably due to slow elution kinetic and higher dispersion of analyte into the segment of eluent. Therefore, a flow rate of 3.0 mL^{-1} was used in further experiments.

3.1.5. Effect of preconcentration time

An efficient and sensitive on-line preconcentration system is largely depended on the sample loading time (defined as preconcentration time) which is directly related to the amount of analyte retained into the micro-column. The effect of loading time on metal sorption was studied at times ranging from 30 to 120 s using the optimized conditions. The experimental results showed a practical proportional increase in the analytical signal with the increase of the loading time. However, a long preconcentration time gives rise to a low sampling frequency. Therefore, considering the sample volume and time of analysis, a preconcentration time of 90 s was chosen as optimum.

3.2. Interferences

The interference of commonly encountered matrix components in natural water, i.e. alkali and alkaline earth elements, as well as some heavy metals, owing to their competition for the active sites on the sorbent, were examined for the determination of 5.0 μg L^{-1} Cd(II), 30.0 μg L^{-1} Pb(II) and 10.0 μg L^{-1} Cu(II) using the optimized method. A variation on the recovery greater than ±5% was considered as interference. Experimental results revealed that Al(III), Cr(III), Fe(III), Mn(II) and Zn(II) can be tolerated at least up to 5.0 mg L^{-1} for cadmium, lead and copper determination. Moreover, for each analyte the presence of the others can be tolerated up to 5.0 mg L^{-1}. The common matrix cations such as Na(I), K(I) Ca(II) and Mg(II) do not interfere up to a concentration level of 2000 mg L^{-1}.

3.3. Analytical features

The analytical performance characteristics of the developed FI–SPE–FAAS method for Cd(II), Pb(II) and Cu(II) determination under the optimal conditions are summarized in Table 3. The sampling frequency for the complete procedure and the enhancement factors (calculated by the ratio of the slopes of the calibration curves obtained with and without preconcentration using FAAS) achieved for each trace metal are also shown in Table 3. With a preconcentration time of 90 s, the detection limits (c_L) based on 3*s* criterion, were found to be 0.1, 2.2 and 0.5 for cadmium, lead and copper, respectively while the precision of the method, evaluated as relative standard deviation (RSD), was between 2.7 and 3.1%.

The retention efficiency of Bond Elute Plexa PCX microcolumn was estimated by the following procedure. 20.0 mL of 10.0 μg L^{-1} Cd(II) or 200.0 μg L^{-1} Pb(II) or 30.0 μg L^{-1} Cu(II) were percolated by the microcolumn under optimum conditions. The elution was carried out with 1.5 mL of 1.0 mol L^{-} HCl solution and the extracted analytes were measured by FAAS. The retention efficiency [21] is defined as the ratio between the analyte mass in the sample solution and the mass in the eluent and was calculated as 0.87, 0.92 and 0.94 for cadmium, lead and copper respectively.

In order to validate the accuracy of the proposed procedure, the FI–SPE–FAAS method was applied to the determination of cadmium, lead and copper in two standard reference materials, NIST CRM 1643e and BCR 278-R. Student *t*-test was employed to examine possible statistically significant differences between the recorded results and the certified values of the determined metals. The analytical values and $t_{\text{exp,}}$ values for Cd, Pb and Cu determination in the above CRMs are given in Table 4. Since all $t_{\text{exp,}}$ values are lower than the $t_{\text{crit, }95\%}=4.30$, no statistically significant differences were found at the 95% probability level, indicating the applicability of the developed method for metal determination in similar type of samples. The method was also applied to the analysis of river, lake water and urine samples. The results are presented in Table 5. The recoveries varied within the

Table 4
Analytical results of cadmium, lead and copper determination in CRMs using the proposed FI–SPE–FAAS method.

CRM	Certified value (μg L^{-1})	Found*	Relative error (%)	t_{exp}
CRM 1643e				
Cd	6.568 ± 0.073	6.2 ± 0.3	5.3	2.01
Pb	19.63 ± 0.21	18.9 ± 0.6	3.7	2.11
Cu	22.76 ± 0.31	21.8 ± 0.7	4.2	2.38
BCR 278-R				
Cd	0.348 ± 0.007	0.34 ± 0.02	2.2	1.13
Pb	2.00 ± 0.04	1.9 ± 0.1	5.0	2.17
Cu	9.45 ± 0.13	9.1 ± 0.4	3.7	1.52

$t_{\text{crit.}}=4.30$ at 95% probability level.

* Mean value ± standard deviation based on three replicates.

Table 3
Analytical performance characteristics of the FI–SPE–FAAS method for cadmium, lead and copper determination.

Parameter	Cadmium	Lead	Copper
Preconcentration time, s	90	90	90
Sampling frequency (*f*), h^{-1}	30	30	30
Enhancement factor	90	95	95
Linear range ([M] in μg L^{-1})	0.4–20	7.5–450	1.8–100
Detection limit (c_L), μg L^{-1}	0.1	1.8	0.5
Precision (RSD, $n=10$) (%)	2.9% (at 2.0 μg L^{-1})	3.1% (at 30.0 μg L^{-1})	2.7% (at 10.0 μg L^{-1})
Regression equation ([M] in μg L^{-1}, $n=9$)	$A=(0.0170 \pm 8.3\times10^{-4})$ [Cd]$+(1.7\times10^{-3} \pm 5.6\times10^{-3})$	$A=(1.0\times10^{-3} \pm 4.6\times10^{-5})$ [Pb]$+(1.4\times10^{-3} \pm 8.9\times10^{-3})$	$A=(3.7\times10^{-3} \pm 1.6\times10^{-4})$ [Cu]$+(1.6\times10^{-3} \pm 7.6\times10^{-3})$
Correlation coefficient (*r*)	0.9991	0.9989	0.9991

Table 5
Analytical results of cadmium, lead and copper determination in lake, river and urine samples by the FI–SPE–FAAS method.

	Element	Added*	Found*	R (%)
River water	Cd	–	nd	–
		4.0	3.9 ± 0.1	97
	Pb	–	3.4 ± 0.2	–
		40	43 ± 2	99
	Cu	–	4.4 ± 0.2	–
		8.0	12.1 ± 0.4	96
Lake water	Cd	–	0.50 ± 0.02	–
		4.0	4.3 ± 0.2	95
	Pb	–	5.5 ± 0.2	–
		40	45 ± 2	99
	Cu	–	3.5 ± 0.2	–
		8.0	11.2 ± 0.4	96
Urine	Cd	–	nd	–
		4.0	3.8 ± 0.2	95
	Pb	–	nd	–
		40	39 ± 2	97
	Cu	–	nd	–
		8.0	7.6 ± 0.4	95

R, recovery; nd, not detected.

* Concentration in $\mu g\,L^{-1}$.

range 95%–98% showing the good performance of the proposed method.

4. Conclusions

The present work demonstrates for the first time the use of Bond Elut® Plexa™ PCX cation exchange resin in a microcolumn format for FI–SPE–FAAS metal determination. The proposed methodology was demonstrated for Cd(II), Pb(II) and Cu(II) determination in environmental and biological samples although it could be employed also for other metlas like Al(III), Cr(III), Fe(III), Mn(II) and Zn(II). The novel amide-free hydroxylated sorbent's surface in combination with a narrow particle size distribution minimize ion-suppression and ensure consistent flow rates, making Plexa PCX very attractive for on-line column preconcentration systems considering the availability in the market and the ease-of-use into the flow system. Multielement techniques like ICP-AES and ICP-MS could be used for simultaneous determination of various metals.

References

[1] S.B. Goldhaber, Regul. Toxicol. Pharm. 38 (2003) 232–242.
[2] K. Pyrzynska, K. Kilian, Water Res. 41 (2007) 2839–2851.
[3] A.N. Anthemidis, G. Giakisikli, C. Mitani, Intern. J. Environ. Anal. Chem. doi:10.1080/03067319.2011.603083.
[4] K. Pyrzynska, Trends Anal. Chem. 29 (2010) 718–727.
[5] X. Zhao, N. Song, Q. Jia, W. Zhou, Microchim. Acta 166 (2009) 329–335.
[6] A.F. Barbosa, M.G. Segatelli, A.C. Pereira, A.S. Santos, L.T. Kubota, P.O. Luccas, C.R.T. Tarley, Talanta 71 (1512–1519).
[7] A.M.H. Shabani, S. Dadfarnia, Z. Dehghani, Talanta 79 (2009) 1066–1070.
[8] A.N. Anthemidis, G.A. Zachariadis, J.A. Stratis, Talanta 58 (2002) 831–840.
[9] A.N. Anthemidis, G.A. Zachariadis, J.A. Stratis, Talanta 54 (2001) 935–942.
[10] A.N. Anthemidis, I.S.I. Adam, G.A. Zachariadis, Talanta 81 (2010) 996–1002.
[11] A.N. Anthemidis, S.-J.V. Koussoroplis, Talanta 71 (2007) 1728–1733.
[12] A.N. Anthemidis, C.-P.P. Karapatouchas, Microchim. Acta 160 (2008) 397–403.
[13] A.N. Anthemidis, K.-I.G. Ioannou, Anal. Chim. Acta 575 (2006) 126–132.
[14] G.-Z. Fang, J. Tan, X.-P. Yan, Anal. Chem. 77 (2005) 1734–1739.
[15] H.-M. Yu, H. Song, M.-L. Chen, Talanta 85 (2011) 625–630.
[16] R.S. Praveen, G.R.K. Naidu, T.P. Rao, Anal. Chim. Acta 600 (2007) 205–213.
[17] M.A. Chamjangali, S.T. Farooji, B. Bahramian, J. Hazard. Mater. 174 (2010) 843–850.
[18] M.A. Chamjangali, G. Bagherian, A. Mokhlesian, B. Bahramian, J. Hazard. Mater. 192 (2011) 1641–1649.
[19] A.N. Anthemidis, T. Maloumidou, Anal. Methods 3 (2011) 1392–1398.
[20] A.N. Anthemidis, G. Giakisikli, S. Xidia, M. Miro, Microchem. J. 98 (2011) 66–71.
[21] V.A. Lemos, P.X. Baliza, Talanta 67 (2005) 564–570.
[22] V.A. Lemos, M.A. Bezerra, F.A.C. Amorim, J. Hazard. Mater. 157 (2008) 613–619.
[23] A.N. Anthemidis, G. Giakisikli, G.A. Zachariadis, Anal. Methods 3 (2011) 2108–2114.
[24] N. Dizge, B. Keskinler, H. Barlas, J. Hazard. Mater. 167 (2009) 915–926.
[25] J.A. Perez-Serradilla, M.D. Luque de Castro, Anal. Bioanal. Chem. 389 (2007) 1541–1547.
[26] P. Pohl, Z. Bogdal, B. Prusisz, Microchim. Acta 150 (2005) 253–259.
[27] P. Pohl, B. Prusisz, Talanta 71 (2007) 411–418.
[28] P. Pohl, H. Stecka, P. Jamroz, Food Chemistry 130 (2012) 441–446.
[29] N.A. Badawy, A.A. El-Bayaa, A.Y. Abdel-Aal, S.E. Garamon, J. Hazard. Mater. 166 (2009) 1266–1271.
[30] S.A. Abo-Farha, A.Y. Abdel-Aal, I.A. Ashour, S.E. Garamon, J. Hazard. Mater. 169 (2009) 190–194.
[31] C. Xiong, Z. Zheng, J. Rare Earth 28 (2010) 862–867.
[32] S. Kocaoba, J. Hazard. Mater. 147 (2007) 488–496.
[33] A. Culetu, A.C. Ion, I. Ion, C. Luca, U.P.B. Sci. Bull., Series B 72 (2010) 139–146.
[34] Y. Song, Greg M. Swain, Anal. Chim. Acta 593 (2007) 7–12.
[35] C. Hubert, S. Houari, F. Lecomte, V. Houbart, C. De Bleye, M. Fillet, G. Piel, E. Rozet, Ph. Hubert, J. Chromatogr. A 1217 (2010) 3275–3281.
[36] H. Zheng, L.-G. Deng, X. Lu, S.-C. Zhao, C.-Y. Guo, J.-S. Mao, Y.-T. Wang, G.-S. Yang, H. Aboul-Enein, Chromatographia 72 (2010) 79–84.
[37] J. Zhang, J. Zhao, J. Zhou, X. Xue, Y. Li, L. Wu, F. Chen, Chin. J. Chem. 29 (2011) 1764–1768.
[38] B. Karlberg, G.E. Pacey, Flow Injection Analysis-A practical guide, Elsevier, 1989.