



Separation and solid phase extraction method for the determination of cadmium in environmental samples

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ABSTRACT

A solid phase extraction method was developed for the determination, preconcentration and separation of cadmium. The method is based on the adsorption of cadmium as 4-(2-pyridylazo) resorcinol (PAR) complex on Duolite XAD-761 resin. The extracted cadmium was determined by Flame Atomic Absorption Spectrometry (FAAS). The optimum experimental conditions for the cadmium assay were investigated. The optimum pH value for quantitative sorption of Cd-PAR was found between 3.5 and 5.5. Elution process was performed by using 5 mL of ethanol–2 mol L⁻¹ HNO₃ mixtures (1:3 v/v). The preconcentration factor was found as 160 for 800 mL aqueous solution containing 2.5 µg Cd. In optimized conditions, the detection limit for cadmium was found to be 0.38 µg L⁻¹. The method was applied to the determination of cadmium in different water samples.

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1. Introduction

Cadmium is an industrial waste or by-product, which has a great environmental concern. Cadmium is used in many industrial processes, such as a constituent of easily fusible alloys, soft solder, electroplating and deoxidizer in nickel plating, engraving processes, electrodes for vapor lamps, photoelectric cells, and nickel-cadmium storage batteries [1]. Although essential function of cadmium on human body is not clearly known, it may cause toxic effects even at very low doses. This toxicity could be due to a direct or an indirect interaction taking place between the metal and the biological system, as it could be the form of both extracellularly and intracellularly. Cadmium acts as inhibitor of sulphhydryl enzymes and has an affinity for other ligands in cells such as hydroxyl, carboxyl, phosphatyl, cysteinyl and histidyl side chains of proteins [2]. In cancer studies, it has been reported that this metal is a mutagen in mammalian [3,4] and at concentrations higher than the maximum permissible level, it may result in prostate, renal and lung cancers [5]. The FAO/WHO Joint Expert Committee on Food Additives recommended provisional maximum tolerable daily intake of Cd from all sources (food, air, and water) of 1.0–1.2 µg/kg mass of body [6]. Moreover, the national and international regulations on food quality are lowering the maximum permissible levels of toxic metals in human food; thus, the maximum

permissible level of Cd in drinking water is 3.0 µg L⁻¹ [7,8]. Therefore determination of trace amounts of cadmium in environmental samples has a great importance. The atomic absorption spectrometry is the most common technique used for the trace metals determination in different samples. There are some difficulties on determination trace quantities of some metals in environmental samples. Generally, the concentrations of some metal ions are lower than the detection limit of most instrumental techniques or metals usually exist in very complex matrix and matrixes generally have interferences on even the concentration of species under investigation is higher than the detection limit [9,10]. Because of these difficulties, a clean-up and preconcentration step is usually required to obtain more reliable data [11]. Thus, solid phase extraction (SPE) has become a preferred method for concentrating the analyte prior to its analysis by FAAS and other techniques. SPE has become to the forefront compared to other preconcentration and/or separation techniques, as it offers several advantages such as flexibility, higher enrichment factors, absence of emulsion, low cost, high speed and simplicity, safety with respect to hazardous samples and more importantly friendly to environment [12–14].

In the present study, a new method was developed for determination of trace amount of cadmium by using FAAS in water samples. Chelates of cadmium formed with 4-(2-pyridylazo) resorcinol (Cd-PAR) can be adsorbed on resin in column. The experimental parameters such as, pH of the solution, amounts of PAR and Duolite XAD-761, sample volume, elution process and the effect of diverse ions were investigated.

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2. Experimental

2.1. Apparatus

A Perkin Elmer (Shelton, CT, USA) Analyst model 700 Flame Atomic Absorption Spectrometer (FAAS) equipped with hollow cathode lamp and air-acetylene burner was used for the determination of Cd. The instrumental parameters were selected for given metal as follows: wavelength 228.8 nm, lamp current 7.5 mA, bandpass 0.5 nm. Schott Lab-Star pH meter was used to measure the pH of solutions.

2.2. Reagents and solutions

All reagents were of analytical grade and all solutions were prepared by using deionized water. Duolite XAD-761, an ester acrylic polymer, was used and purchased from Sigma-Aldrich. The PAR monosodium salt hydrate was purchased from Aldrich and standard PAR solution of 0.024% (w/v) was prepared by dissolving of 0.012 g PAR in 50 mL mixture of methanol and 0.2 mol L⁻¹ NaOH solution (55:45% v/v). Standard cadmium solutions were prepared in atomic absorption grade having the metal concentration of 1000 ± 2 mg L⁻¹ and other chemical reagents were purchased from Merck (Darmstadt, Germany).

Adsorption column were prepared according to literature [15]. The glass column was 12 cm in length and 1.0 cm in internal diameter. A small amount of glass wool was placed at the bottom of the column in order to held resin. 0.6 g of dried resin was placed and another small glass wool plug was inserted onto the tap of the resin. The bed height of the resin in the column was approximately 2.0 cm. It was washed successively with water, ethanol and 2 mol L⁻¹ HCl and HNO₃ solutions, respectively. After each use, the resin in the column was cleaned with 10 mL of ethanol, 10 mL of 2 mol L⁻¹ HNO₃ and deionized water and stored in water for the following experiment.

2.3. Preconcentration procedure

Standard test solutions were prepared as follows: 5 mL of 0.5 mg L⁻¹ of Cd (II) standard solution added to 1 mL of standard PAR solution and mixed with 2 mL buffer solutions in a volumetric flask. The pH of the solution was adjusted to optimum working pH. Afterwards, final volume was diluted to 50 mL with deionized water. This solution was permitted to flow through the column under gravity at flow rate of 3 mL min⁻¹. The adsorbed cadmium ions on the column were eluted with 5 mL of ethanol–2 mol L⁻¹ HNO₃ mixtures (1:3 v/v) at a flow rate of 4 mL min⁻¹. Cadmium was analyzed with direct calibration method. A blank solution was also run under the same conditions. In each experiment, reading was repeated three times by FAAS and mean of these reproducible measurements was used.

2.4. Analysis of water samples

A tap water sample was collected from Kirsehir, Turkey, a river water sample was collected from Kızılırmak River in Kirsehir, Turkey and geothermal water sample was collected from Terme, Kirsehir, Turkey. These water samples were filtered through Whatman No. 40 filter paper of 0.45 μm pore size to remove any particulate matter and 800 mL of water sample was transferred to a beaker. Then 1 mL of standard PAR solution and acetate buffer solutions were added. The pH of the solution was adjusted to 4.8 and passed through the Duolite XAD-761 column. After elution process, analyses of samples were performed according to recommended preconcentration procedure (Section 2.3).

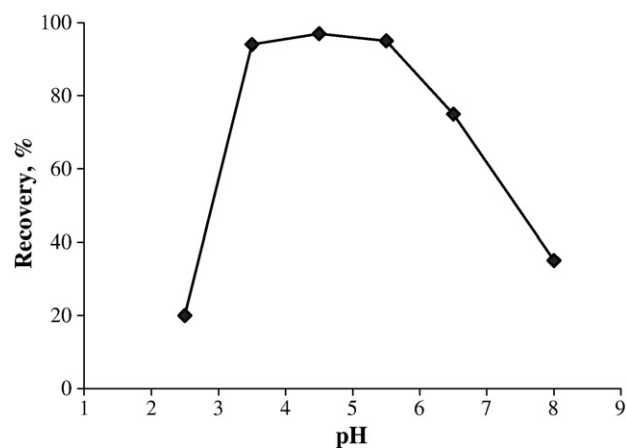


Fig. 1. The effect of pH on the recovery of cadmium (sample volume: 50 mL, amount of cadmium: 2.5 μg, eluent: 5 mL HNO₃-ethanol mixture, flow rate of sample: 3 mL min⁻¹, sorbent: 600 mg, N = 3).

3. Results and discussion

3.1. Effect of sample solution pH on recovery of Cd(II)

The adsorption of Cd-PAR chelates on Duolite XAD-761 resin at different pH ranges was investigated by using different buffers (citrate, acetate, phosphate and ammonia). The effects of pH on recovery values were summarized in Fig. 1. As shown in the Fig. 1, the optimum recoveries were found when the pH was adjusted between 3.5 and 5.5 and maximum recovery was established at the pH value of 4.8. Therefore, optimum pH value was chosen as 4.8 in sodium acetate-acetic acid buffer for preconcentration and determination of cadmium in further studies.

3.2. Influence of ligand amount

Different amounts of 4-(2-Pyridylazo) resorcinol were added to test solutions containing 2.5 μg of Cd (II) and then these test solutions passed through Duolite XAD761 column. The results were given in Fig. 2. Quantitative recovery was obtained for Cd (II) ions in the 0.1–0.50 mg range of PAR. At less amount of PAR than 0.1 mg and higher than 0.5 mg, the recovery was below 95%, due to competition on the

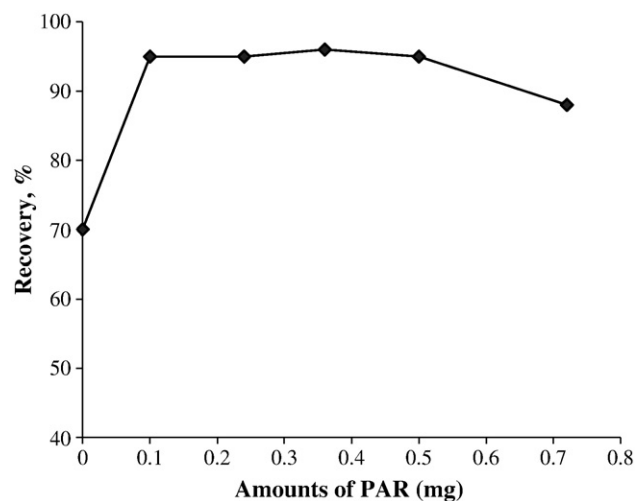


Fig. 2. The effect of PAR amounts on the recovery of cadmium (sample volume: 50 mL, amount of cadmium: 2.5 μg, eluent: 5 mL HNO₃-ethanol mixture, flow rate of sample: 3 mL min⁻¹, pH: 4.8, sorbent: 600 mg, N = 3).

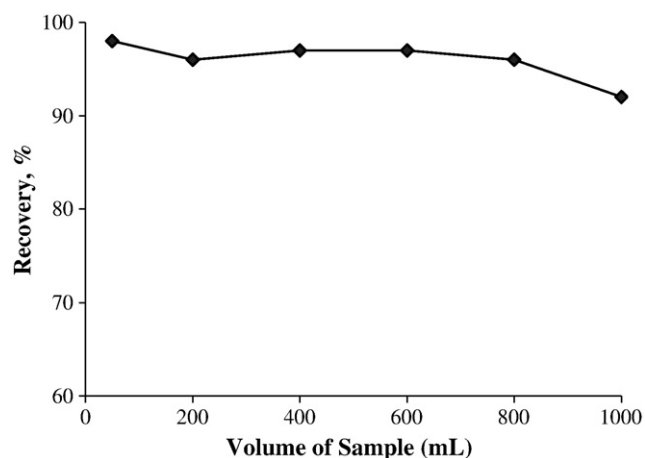


Fig. 3. The effect of sample volume on the recovery of cadmium (amount of cadmium: 2.5 μg , eluent: 5 mL HNO_3 -ethanol mixture, flow rate of sample: 3 mL min^{-1} , pH: 4.8, sorbent: 600 mg, $N=3$).

adsorption between PAR chelates and excess PAR in the solution. In further works, 0.24 mg of PAR was added to the solutions.

3.3. Influence of sample volume

To determine the influence of sample volume on recovery values were also determined. For this purpose, 50, 200, 400, 600, 800 and 1000 mL of the test solutions each contains 2.5 μg of cadmium passed through XAD-761 column at a 3.0 mL min^{-1} flow rate. The results were given in Fig. 3. Recovery of cadmium was found to be quantitative (>95%) when sample volume was chosen between the range of 50 mL–800 mL. By analyzing 5 mL of the final solution after the preconcentration of 800 mL of sample solution, an enrichment factor was found as 160.

3.4. Influence of flow rate

After optimization of the sample volume, the effects of flow rate on the adsorption of cadmium were also investigated. To obtain maximum recoveries for cadmium, different flow rates were used on the retention of the Cd-PAR chalets at optimum conditions. The cadmium was desorbed from the resin by using 5 mL HNO_3 -ethanol mixture. As shown in Fig. 4, optimum flow rate was found in the range between 1 and 3 mL min^{-1} . To decrease the time needed for analysis, flow rate was chosen as 3 mL min^{-1} .

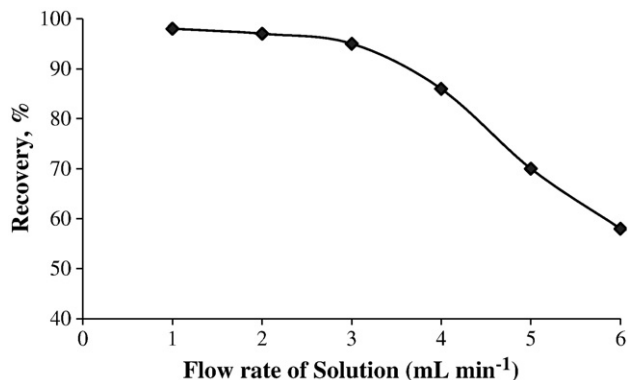


Fig. 4. The effect of solution flow rate on the recovery of cadmium (sample volume: 50 mL, amount of cadmium: 2.5 μg , eluent: 5 mL HNO_3 -ethanol mixture, pH: 4.8, sorbent: 600 mg, $N=3$).

Table 1

The effect of eluent types on the recovery of cadmium (sample volume: 50 mL, amount of cadmium: 2.5 μg , flow rate of sample: 3 mL min^{-1} , pH: 4.8, sorbent: 600 mg, $N=3$).

Eluent	Recovery (%)
2 mol L^{-1} HCl, 5 mL	60 \pm 1
2 mol L^{-1} HNO_3 , 5 mL	88 \pm 2
5 mL of ethanol-2 mol L^{-1} HNO_3 mixtures (1:3 v/v)	97 \pm 2
5 mL ethanol	32 \pm 1
5 mL acetonitrile	24 \pm 3

3.5. Choice of eluent agents

In order to obtain maximum quantitative recoveries of cadmium, various eluents and different volumes of reagents were studied. For this purpose ethanol, acetonitrile, HCl and HNO_3 solutions were tested. The results showed that the maximum recovery of cadmium was observed when 5 mL of ethanol-2 mol L^{-1} HNO_3 mixtures (1:3 v/v) was used. The effects of various eluent on recovery values are summarized in Table 1.

3.6. Influence of resin amount

The influence of XAD-761 resin amount on recoveries was studied. For this aim different amounts of sorbent was added in the range of 200 and 800 mg into the adsorption column. The test solution of 50 mL sample including 2.5 μg of cadmium was passed through the column at optimum conditions. The results showed that the amount of optimum sorbent was in the range of 500–800 mg of XAD-761 for maximum extraction of Cd (II) (Fig. 5). From these results, 600 mg of resin has been used in all further experiments as an optimum one.

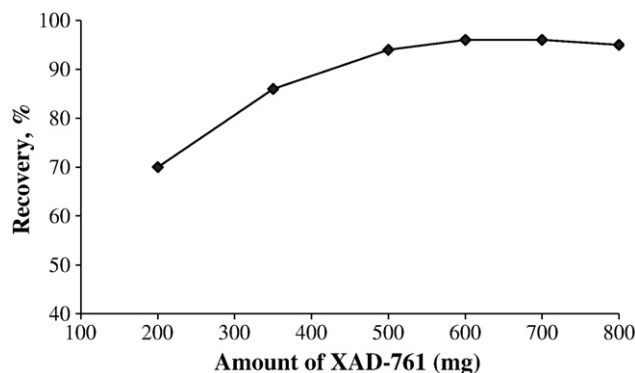


Fig. 5. The effect of XAD-761 amount on the recovery of cadmium (sample volume: 50 mL, amount of cadmium: 2.5 μg , eluent: 5 mL HNO_3 -ethanol mixture, flow rate of sample: 3 mL min^{-1} , pH: 4.8, $N=3$).

Table 2

The effect of some ions on the recovery of cadmium.

Ion	Concentration (mg L^{-1})	Recovery (%)	Ion	Concentration (mg L^{-1})	Recovery (%)
K^+	1000	97 \pm 1	Ni^{2+}	10	100 \pm 2
Na^+	1000	98 \pm 2	Zn^{2+}	10	96 \pm 2
Ca^{2+}	100	97 \pm 2	Mn^{2+}	10	98 \pm 3
Mg^{2+}	100	98 \pm 2	Pb^{2+}	10	96 \pm 2
Cl^-	100	97 \pm 2	Al^{3+}	10	98 \pm 2
Br^-	100	99 \pm 2	Fe^{3+}	10	96 \pm 3
SO_4^{2-}	100	101 \pm 2	Ag^+	10	97 \pm 2
Cu^{2+}	10	100 \pm 3			

Results are mean \pm standard deviation of three replicate analyses.

Table 3
Comparison of adsorption capacities and enrichment factors for cadmium.

Solid phase	Chelating agent	LOD ($\mu\text{g L}^{-1}$)	Adsorption capacity (mg g^{-1})	Enrichment factor	References
Polytetrafluoroethylene (knotted reactor)	Diethyldithiocarbamate	0.1	–	30	[17]
Mini-column packed with glass wool	1-(2-thiazolylazo)-2-naphthol (TAN)	0.76	–	20.3	[18]
Amberlite XAD-4	Ammonium pyrrolidine dithiocarbamate	0.1	9.47	180	[19]
Amberlite XAD-4	Piperidine dithiocarbamate	0.7	9.18	150	[20]
Amberlite XAD-7	Xylenol orange	9	1.6	200	[21]
Ambersorb 572	1-nitroso-2-naphthol-3,6-disulfonic acid	0.32	19.6	200	[22]
S. carlsbergensis immobilized on silica gel 60	–	1.66	–	50	[23]
Duolite XAD-761	PAR	0.38	12.4	200	Present work

3.7. Influence of interfering species

The interference studies were performed using various possible interfering ions on the retentions of the investigated analyte ions. For this purpose, influences of some cationic and anionic species were investigated. In these experiments, 50 mL of solutions containing 2.5 μg of cadmium and various amounts of interfering ions (in the form of their nitrate or chloride salts) were treated according to the preconcentration procedure. The results are given in Table 2.

3.8. Capacity of the resin

The adsorption capacity of the resin was calculated by the batch technique. For this process, 100 mg resin, 200 mg L^{-1} Cd ions and PAR solutions were stirred for 1 h with magnetic stirrer and filtered through a filter paper. Enriched cadmium ions onto polymer resin particles were stripped with 5 mL HNO_3 -ethanol mixture and were determined by FAAS [15,16]. As a result, capacity of the XAD-761 resin has been obtained as 12.4 mg g^{-1} . Different resins with their sorption capacities and enrichment factors were given in Table 3.

Table 4
Analytical performance and optimum conditions of the proposed method for determination of Cd.

pH (in sodium acetate-acetic acid buffers)	4.8
Amount of PAR 0.024% (w/v)(mL)	1
Amount of resin (mg)	600
Eluent volume (2 mol L^{-1} HNO_3 -ethanol mixtures 1:3 v/v) (mL)	5
Sample flow rate (mL min^{-1})	3
Maximum sample volume (mL)	800
Enrichment factor	160
Linear range ($\mu\text{g L}^{-1}$)	1.26–22
Regression equation ($\mu\text{g L}^{-1}$)	$A(10^{-3}) = 13.252C + 0.5635$
Correlation coefficient (R^2)	0.9973
Detection limit ($\mu\text{g L}^{-1}$)	0.38
Precision (R.S.D, N = 7) (%)	3.2

Table 5
The determination of cadmium in different water samples (initial volume for water samples: 800 mL).

Sample	Added	Found*	Recovery, %
Tap water	–	ND	–
	4.0 $\mu\text{g L}^{-1}$	4.2 \pm 0.3 $\mu\text{g L}^{-1}$	105
River	–	1.5 \pm 0.2 $\mu\text{g L}^{-1}$	–
	4.0 $\mu\text{g L}^{-1}$	5.4 \pm 0.4 $\mu\text{g L}^{-1}$	98.1
Geothermal water	–	2.1 \pm 0.3 $\mu\text{g L}^{-1}$	–
	4.0 $\mu\text{g L}^{-1}$	6.3 \pm 0.5 $\mu\text{g L}^{-1}$	103.2

ND: not detectable (below of LOD).

*Mean \pm ts/ \sqrt{N} with 95% confidence level.

3.9. Analytical performance

Optimized experimental parameters and analytical performance of methods were given in Table 4. Under these experimental conditions, analytical features of proposed method such as, linear range of calibration curve, limit of detection (LOD) and limit of quantification (LOQ) were also examined. LOD and LOQ for cadmium were obtained from calibration curve as 0.38 and 1.26 $\mu\text{g L}^{-1}$, respectively. Calculation of LOD and LOQ values were based on three and ten times the standard deviation of the blank signals, respectively (N=10). The response of analytical method used linearly changed with the concentration of cadmium in the range of 1.26 to 22 $\mu\text{g L}^{-1}$ with calibration equation given as: $A(10^{-3}) = 13.252C + 0.5635$, $R^2 = 0.9973$. In this equation $A(10^{-3})$ is absorbance corresponding to concentration $C(\mu\text{g L}^{-1})$ of Cd (II) after preconcentration process. The precision was tested from seven series of measurements of 100 mL of 5 $\mu\text{g L}^{-1}$ cadmium solutions. The precision of proposed method is obtained from relative standard deviation (RSD) values of 3.2%. These values show that, proposed method is suitable for determination of cadmium.

3.10. Determination of cadmium in real samples

Validity of proposed method was further proven by analyzing of spiked cadmium samples. For this aim, cadmium solutions having cadmium concentration 4.0 $\mu\text{g L}^{-1}$ was spiked into the mixture of 800 mL of water samples. Recovery of cadmium was determined by using proposed method. Experimental results corresponding to spiked cadmium in samples were given in Table 5. The levels of cadmium were found as 1.5 \pm 0.2 $\mu\text{g L}^{-1}$ and 2.1 \pm 0.3 $\mu\text{g L}^{-1}$ at 95% confidence level for river and geothermal water samples, respectively. Level of cadmium species in city line water could not be detected. Cadmium content of city line water is probably lower than the detection limit of proposed method.

Conclusions

A proposed procedure provides a simple, economical, rapid, and precise method for the preconcentration and determination of cadmium in water samples using 4-(2-pyridylazo) resorcinol as the chelating agent. The proposed solid phase extraction method due to advantages such as: high enrichment factor, high tolerance limit of interfering ions and low detection limit is a powerful tool for simple and sensitive determination of cadmium in water samples. This method could be combined with other methods of analysis, such as ET-AAS, ICP-OES, ICP-MS, and chromatographic methods, and used as an on-line preconcentration system.

References

- [1] S.N. Fatemi, S. Tubafard, S.J. Fatemi, B. Nadi, Evaluation of ATC as an orally administered drug in treatment of cadmium toxicity of rat organs, E-Journal Chem. 6 (2009) 504–510.

- [2] S.S. Dara, Text book of environmental chemistry and its pollution control, second ed. S. Chand & Co. Ltd., New Delhi, 1997.
- [3] H. Ciftci, U. Bakal, The effect of lipoic acid on macro and trace metal levels in living tissues exposed to oxidative stress, *Anticancer Agents Med. Chem.* 9 (5) (2009) 560–569.
- [4] R.B. Hayes, The carcinogenicity of metals in humans, *Cancer Causes Control.* 8 (1997) 371–385.
- [5] G. Drasch, J. Schopfer, G.N. Schrauzer, Indicators for prostate cancer risk of smokers and non-smokers and relevance to the cancer protective effects of selenium, *Biol. Trace Elem. Res.* 103 (2005) 103–107.
- [6] FAO/WHO Joint Expert Committee on Food Additives, WHO Tech. Rep. Senal No. 505 (1972) 32.
- [7] WHO, Guidelines for drinking-water quality, second ed., Health criteria and other supporting information, vol. 2, Geneva, 1998, pp. 281–283.
- [8] S. Cerutti, M.F. Silva, J.A. Gasquez, R.A. Olsina, L.D. Martinez, On-line preconcentration/determination of cadmium in drinking water on activated carbon using 8-hydroxyquinoline in a flow injection system coupled to an inductively coupled plasma optical emission spectrometer, *Spectrochim. Acta B* 58 (2003) 43–50.
- [9] S.L.C. Ferreira, M.A. Bezerra, W.N.L. Dos Santos, B.B. Neto, Application of Doehlert designs for optimisation of an on-line preconcentration system for copper determination by flame atomic absorption spectrometry, *Talanta* 61 (2003) 295–303.
- [10] I. Narin, M. Soylak, Enrichment and determination of nickel(II), cadmium(II), copper(II), cobalt(II), and lead(II) ions in natural waters, table salts, tea and urine samples as pyrrolydine dithiocarbamate chelate by membrane filtration-flame atomic absorption spectrometry combination, *Anal. Chim. Acta* 493 (2003) 205–210.
- [11] H. Askun, B. Gulbakan, O. Celikbicak, C. Uzun, O. Guven, B. Salih, Preconcentration and Matrix Elimination for the Determination of Pb(II), Cd(II), Ni(II), and Co(II) by 8-Hydroxyquinoline Anchored Poly(styrene-divinylbenzene) Microbeads, *J. Appl. Polym. Sci. Symp.* 107 (2008) 2714–2722.
- [12] A.J. Bucheit, M. Witznbacher, Pesticide monitoring of drinking water with the help of solid-phase extraction and high-performance liquid chromatography, *J. Chromatogr. A* 737 (1996) 67–74.
- [13] H. Ciftci, Solid phase extraction method for the determination of cobalt in water samples on duolite XAD-761 resin using 4-(2-Pyridylazo) resorcinol by FAAS, *Curr. Anal. Chem.* 6 (2010) 154–160.
- [14] T. Prasada Rao, S. Daniel, J.M. Gladis, Tailored materials for preconcentration or separation of metals by ion-imprinted polymers for solid-phase extraction (IIP-SPE), *Trends Anal. Chem.* 23 (2004) 28–35.
- [15] E. Kenduzler, A.R. Turker, O. Yalcinkaya, Separation and preconcentration of trace manganese from various samples with Amberlyst 36 column and determination by flame atomic absorption spectrometry, *Talanta* 69 (2006) 835–840.
- [16] H. Ciftci, H. Yalcin, E. Eren, A. Olcucu, M. Sekerci, Enrichment and determination of Ni²⁺ ions in water samples with a Diamino-4-(4-nitro-phenylazo)-1H-pyrazole (PDANP) by using FAAS, *Desalination* 256 (1-3) (2010) 48–53.
- [17] Z. Fang, S. Xu, L. Dong, W. Li, Determination of cadmium in biological materials by flame atomic absorption spectrometry with flow-injection on-line sorption preconcentration, *Talanta* 41 (1994) 2165–2172.
- [18] E.L. Silva, P.S. Roldan, Simultaneous flow injection preconcentration of lead and cadmium using cloud point extraction and determination by atomic absorption spectrometry, *J. Hazard. Mater.* 161 (2009) 142–147.
- [19] A. Ramesh, K.R. Mohan, K. Seshiah, Preconcentration of trace metals on Amberlite XAD-4 resin coated with Dithiocarbamates and determination by inductively coupled plasma-atomic emission spectrometry in saline matrices, *Talanta* 57 (2002) 243–252.
- [20] P.K. Tewari, A.K. Singh, Amberlite XAD-7 impregnated with xylenol orange; a chelating collector for preconcentration of Cd(II), Co(II), Cu(II), Ni(II), Zn(II) and Fe(III) ions prior to their determination by flame AAS, *Fresenius J. Anal. Chem.* 367 (2000) 562–567.
- [21] E. Kenduzler, A.R. Turker, Determination of trace cadmium in waters by flame atomic absorption spectrophotometry after preconcentration with 1-Nitroso-2-naphthol-3, 6-disulfonic acid on Ambersorb 572, *Ann Chim-Rome.* 95 (2005) 77–85.
- [22] S. Baytak, E. Kenduzler, A.R. Turker, Separation/preconcentration of Zn(II), Cu(II), and Cd(II) by *Saccharomyces carlsbergensis* immobilized on silica gel 60 in various samples, *Sep. Sci. Technol.* 41 (2006) 3449–3465.