CROATICA CHEMICA ACTA
CCACAA **80** (1) 17–23 (2007)

ISSN-0011-1643
CCA-3133
Original Scientific Paper

Determination of Lead and Cadmium in Different Samples by Flow Injection Atomic Absorption Spectrometry Incorporating a Microcolumn of Immobilized Ammonium Pyrrolidine Dithiocarbamate on Microcrystalline Naphthalene

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RECEIVED MARCH 4, 2005; REVISED MARCH 6, 2006; ACCEPTED SEPTEMBER 21, 2006

A new flow injection on-line preconcentration system adapted to flame atomic absorption spectrometry (FAAS) for lead and cadmium determination at the μg L^{-1} level was developed. Ammonium pyrrolidine dithiocarbamate was immobilized on microcrystalline naphthalene and was used as sorbent material in microcolumn preparation. Deposition of lead and cadmium was effected by processing a standard or solution of analytes at pH = 2–9 on the column. Injection of 500 μL of ethanolic solution of acetic acid (0.5 mol L^{-1}) and hydrochloric acid (0.25 mol L^{-1}) served to elute the retained species to atomic absorption spectrometry (AAS). A sample volume of 25 mL resulted in preconcentration factors of 65 and 53 for lead and cadmium, respectively, and precision at 60 μg L^{-1} was 2.7 % and 3.6 % (RSD) for lead and cadmium, respectively. The procedure was applied to tap water, river water, sea water, pine leaf and human blood samples. The accuracy was assessed through recovery experiments and independent analyses by furnace AAS.

Keywords
Pb and Cd determination
immobilized APDC
on-line preconcentration
flow injection
blood sample

INTRODUCTION

The role of trace and toxic levels of elements in human health has become an important area of scientific research. Lead and cadmium constitute the highest environmental hazard due to their extensive use, toxicity and widespread distribution. Heavy metals are non-degradable and so they accumulate in the environment.[1–2] The advent of atomic absorption techniques provided more accurate determination of low levels of metals in human body fluids and other complex matrices. Graphite furnace atomic absorption spectrometry seems to be the most suitable technique for trace determination of metal ions because of its excellent sensitivity, relatively simple operation, and low consumption of samples. However, it is an expensive analytical method and suffers from matrix interference. Flame atomic absorption spectrometry is often applied because of its speed and ease of operation, but it has the major drawback of low sensitivity for direct determination of low levels of heavy metals. Therefore, preconcentration and matrix elimination steps are required for ultra trace determination of elements.[3] Among different automated techniques for the determination of trace metals in a complex matrix, flow injection analysis (FIA)

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has attracted increasing attention because of its high precision, high sampling rate and the possibility of on-line sample pretreatment, including solvent extraction and sorbent preconcentration.[4–9] Among many sorbents reported in the literature for selective sorption of heavy metals,[10] only a limited number could be applied to FI on-line preconcentration. This is perhaps due to the requirement that in a FI on-line system sorption and desorption of analytes on the adsorbent must be fast. Hence, it is necessary to select and prepare sorbents suitable for on-line preconcentration. For determination of lead or cadmium utilizing flame atomic absorption spectrometry, different microcolumn enrichment systems have been developed, which include basic alumina powder,[11] CPG/quinolin-8-ol ion exchanger,[12] alumina fiber,[13] immobilized diethyldithiocarbamate[14,15] and dithizone[16] on C_{18} bonded to silica, adsorption of complexes of 1,10-phenanthroline on RP-C_{18}[17] and diethyldithiocarbamate on chromosorb 102,[18] polyurethane foam loaded with 2-(2-benzothiazolylazo)-2-*p*-cresol,[19] sorption of a complex of diethyldithiophosphates on C_{18} bonded to silica, activated carbon and polyurethane foam,[20] 8-hydroxi quinoline immobilized on vinyl co-polymer, Toyopearl gel,[21] natural sorbents such as vermicompost and humic acid.[22] In most of these methods cations form a complex with a chelating agent which was quantitatively sorbed by the column materials during a fixed sample loading period. The retained complexes are eluted by HNO_3, HCl,[11,13,19,21,22] MeOH, EtOH [14,17,18,20] or isobutyl methyl ketone.[15] Thus, the methods require considerable sample manipulation and contamination is possible. Enrichment factors in the above mentioned chemistry are typically 26–67 and 35–83 fold for lead and cadmium, respectively, while the detection limits for lead are between 0.7 and 10 μg L^{-1} and for cadmium between 0.8 and 3 μg L^{-1}.

Ammonium pyrrolidine dithiocarbamate (APDC) is an efficient chelating agent. The standard method for determination of trace metals in an aqueous sample[23] recommends its use for complex formation, extraction of metal complex with MIBK and subsequent determination by FAAS. Complexes of metal-APDC have been also sorbed on a microcolumn of alumina coated with SDS,[24] PTFE [25,26] poly(octadecyl diitaconate) (PDI-18).[27] However, to the best of our knowledge, no study has been directed to immobilization of APDC and its use as a packing material for the microcolumn in a flow injection system. Thus, it was appropriate to investigate the possibility of preparing a microcolumn of immobilized APDC and assessing its capability of on-line trace enrichment of lead and cadmium. Studies confirmed the reliability of microcolumn enrichment/separation using APDC immobilized with microcrystalline naphthalene, and a rapid method for ultra-trace determination of lead and cadmium in different samples based on FI-FAAS has been developed.

EXPERIMENTAL

Apparatus

An instrumental laboratory AA spectrometer Buckscientific model 210 VGP, USA, furnished with a lead/cadmium hollow-cathode lamp and air-acetylene flame was used for all measurements. The operating currents and slit width were adjusted to the value recommended by the manufacturer. The wavelengths were set to 283.8 and 228.8 nm for Pb and Cd, respectively. The absorbance time responses were monitored on an x-t chart recorder (L-250) and quantitative analysis was based on measurement of the peak height of transient signals. A schematic diagram of the flow injection system used is presented elsewhere.[28,29] The manifold consists of a peristaltic pump (Ismatec, Ms-4 REG10/8-100, Switzerland), a rotary injection valve (Rheodyne, CA, USA) and a microcolumn of APDC immobilized on microcrystalline naphthalene (PTFE tube 3 cm, 2 mm id).

Reagents

All reagents used were of the highest purity available and at least of analytical reagent grade. High purity water was used throughout. Standard solutions were prepared daily by stepwise dilution of 1000 mg L^{-1} stock solutions (prepared from Titris concentrations, Merck). All solutions were stored in pre-cleaned polypropylene containers.

Microcolumn Preparation

A solution of naphthalene and APDC was prepared by dissolving 1 g of naphthalene and 0.5 g of APDC in 10 mL ethanol on a hot-plate stirrer at approximately 50 °C. The solution was then added dropwise into 40-mL of water at room temperature under continuous stirring. The mixture was stirred for 30 min and APDC was co-precipitated with naphthalene. The solution was filtered through a Millipore filter and air-dried prior to packing the column. The microcolumn was fabricated using PTFE (Teflon) tubing (3 cm in length, internal diameter 2 mm) and contained APDC immobilized with naphthalene (about 30 mg). The end of the tube was fitted with foam to retain the sorbent in the tube. The sorbent was stable for a few months.

Blood Preparation

4 mL of nitric acid was added to 5 mL of a blood sample and heated for ~15 min. Then, 2 mL of hydrogen peroxide was added and the mixture was heated for another 20 min. The digested sample was then diluted, the pH was adjusted to ~ 6, and the sample was quantitatively transported to a 25-mL flask and diluted to the mark with water. The sample was then treated according to the given procedure.

Pine Leaf Preparation

To 1 g of dried pine leaf, 4 mL of concentrated nitric acid was added and the sample was heated on a water bath for 15 min. Then, 2 mL of hydrogen peroxide was added and the mixture was heated for another 20 min. The sample was

then filtered through a Millipore filter, pH was adjusted to ~6, the sample was diluted to 200 mL and treated according to the given procedure.

Procedure

The FI manifold used was as described before.[28–29] The single line system was used to study the analytes breakthrough and to undertake initial method development studies. The two-line FI manifold was used to process real samples and to obtain performance data. The microcolumn was located in the sample loop of injection valves so that the sampling could be performed »off-line« and to prevent matrix constituents entering the AAS. At the end of sampling, the valve was switched »on-line« and the eluent was injected using a second valve to effect elution. The carrier and eluent solution were water and 500 μL of ethanolic solution of acetic acid (0.5 mol L^{-1}) and hydrochloric acid (0.25 mol L^{-1}), respectively. The solution pH was adjusted to ~3 by addition of nitric acid (0.1 mol L^{-1}). When using the FI manifold, standard solutions or samples (pH = 2–9) were passed through the APDC microcolumn (single line system, sample volume 500 μL, and double line system, time based sampling (*e.g.,* 90 at a flow rate of 3.5 mL min^{-1}) to effect analytes deposition. The adsorbed analytes were then eluted by injection of 500 μL of eluent solution and transported to the flame atomic absorption spectrometer for quantization. (For the FI double line system, the injection valve was switched to bring the microcolumn »on-line« prior to eluent injection). The transient signal was monitored for quantitative analysis.

RESULTS AND DISCUSSION

As already mentioned, APDC can form complexes with some metal ions, and it has mostly been used as a complexing agent in liquid-liquid extraction.[23] Its complexes with metal ions have also been retained on different bases in solid phase extraction[24–27] but, to the best of our knowledge, no attempt has been made to immobilize APDC. Therefore, the possibility of immobilizing APDC on a base and its suitability for on-line preconcentration of lead and cadmium in a FI-AAS was checked. It was found that APDC did not get immobilized on SDS coated alumina, but, when APDC was added to an alcoholic solution of naphthalene and diluted with water (according to the given procedure), it coprecipitated with naphthalene in a similar manner as already demonstrated for some other organic ligands.[30–31] The solid mass was then filtered, air dried and was used for microcolumn preparation.

In order to obtain a high capacity sorbent, different amounts of APDC were added to 1 g of naphthalene. It was found that the capacity of the sorbent reaches its maximum at the ligand to naphthalene mass ratio of 1:2. Furthermore, using the single-line FI system, it was confirmed, for a simple aqueous solution, that lead and cadmium underwent deposition/elution on a microcolumn of APDC immobilized with naphthalene. A typical absorbance time response for sequential injection of a standard solution (500 μL of 6 mg L^{-1} of Pb and 4 mg L^{-1} of Cd) and eluent (500 μL of ethanolic solution of acetic acid, 0.5 mol L^{-1}, and hydrochloric acid, 0.25 mol L^{-1}) is given in Figure 1 (A), and for comparison, equivalent transient signals for direct injection and pneumatic nebulization of samples (6 mg L^{-1} of lead and 4 mg L^{-1} of cadmium) are also included (Figure 1; B, C). The dispersion characteristics are significantly modified as a result of microcolumn deposition/elution, the elution peak being relatively sharp (*e.g.,* peak half-width of Pb signal, 6 s *versus* 9 s of direct injection) and intense (Figure 1, A), indicating the degree of preconcentration. Furthermore, the relatively sharp elution peak is an indication of fast exchange kinetics for the elution process. Based on the consideration of the peak height of conventional nebulization and the peak height of sequential injection with a microcolumn, dispersion coefficients (40/64 and 60/78) of 0.62 and 0.76 were calculated for lead and cadmium, respectively, even though the same volumes (500 μL) of solution (6 mg L^{-1} of lead and 4 mg L^{-1} of cadmium) were used in the deposition/elution step. Comparison of the area of signals of the microcolumn elution peak (Figure 1, A) and direct injection (Figure 1, B) indicates that a recovery of more than 97 % is obtained with a single injection of eluent.

As shown in previous studies concerning microcolumn preconcentration,[28–29] the deposition/elution processes are influenced by FI parameters such as carrier stream flow rate, concentration of carrier stream/eluent, sample pH and composition, *etc*. Systematic studies aimed at optimizing the deposition/elution stages and identifying analytically

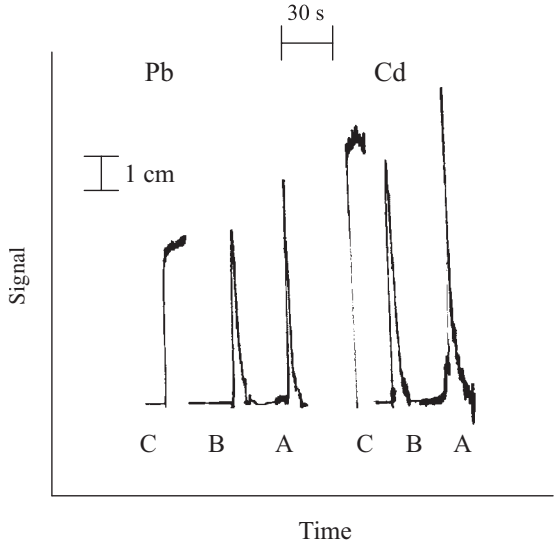

Figure 1. Absorbance-time response for: (A) sequential injection of Pb/Cd solution (500 μL of 6 mg L^{-1} of Pb and 4 mg L^{-1} Cd) and eluent (500 μL); (B) direct injection of Pb/Cd solution (500 μL of 6 mg L^{-1} of Pb and 4 mg L^{-1} Cd in eluent matrix); (C) Conventional nebulization of Pb/Cd solution (500 μL of 6 mg L^{-1} of Pb and 4 mg L^{-1} Cd in eluent matrix).

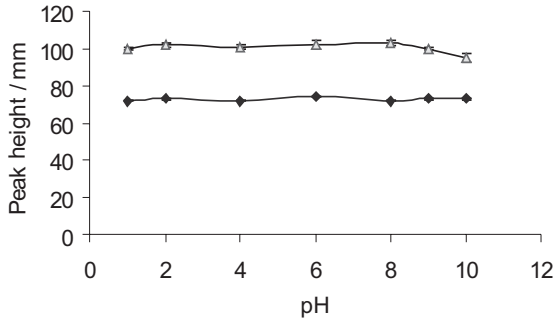

Figure 2. Effect of sample pH on analyte response; sample: 600 μg L^{-1} Pb, 400 μg L^{-1} Cd; sampling volume: 5 mL; eluent volume: 500 μl.

useful operating conditions were, therefore, performed. Analytes deposition was independent of sample pH in the range of 1–9, as shown in Figure 2; the small decrease in the cadmium signal at pH >9 is due to the precipitation of Cd as cadmium hydroxide. This result indicates the high affinity of microcolumn for lead and cadmium. The pH of ~6 was selected for subsequent work because it was more convenient.

The efficiency of analytes deposition was dependent on the carrier stream flow rate, as shown in Figure 3 for flow rates less than 4 mL min^{-1}; signal responses for cadmium and lead were independent of flow rate. Use of higher flow rates, however, resulted in a sharp decrease in signal, suggesting impaired deposition efficiency as a consequence of short contact time. Subsequent sample loading was performed at a flow rate of 3.5 mL min^{-1}.

Influence of the nature of eluent on deposition and measurement of analyte signals was considered. Different eluents such as acetic, nitric, perchloric and hydrochloric acids, EDTA, ethanol and acidified ethanol were examined. Signal enhancement for both analytes was observed with acidified ethanol. With ethanolic solution of acetic acid, complete recovery of lead but not of cadmium was possible, whereas with hydrochloric acid complete recovery of cadmium was possible. Further, the study confirmed that ethanolic solution of a mixture of acetic acid

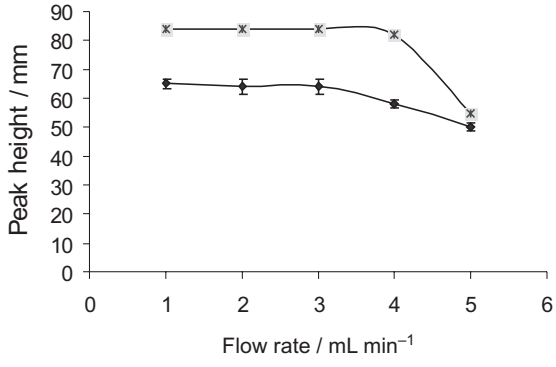

Figure 3. Analyte response to flow rate variation during deposition; sample: 600 μg L^{-1} Pb, 400 μg L^{-1} Cd; sampling volume: 5 mL; eluent: 500 μL.

(0.5 mol L^{-1}) and hydrochloric acid (0.25 mol L^{-1}) was the most suitable eluent for this propose, and was chosen for subsequent work. The aqueous chemistry of the processes is complex, and it is not possible to be precise about the mechanism of elution, but one possible explanation is that in acidified solution the hydrogen ion partially protonates APDC, whereas chloride and acetate ions form complexes with cadmium and lead, respectively; thus, the total effect is weakening the bond between the analytes and immobilized APDC, and thereby making quantitative elution of both analytes possible. When the flow rate during elution was varied, a virtually linear increase in the peak height response was observed that leveled off at a flow rate higher than the nebulizer uptake. This increase in peak height is due to starvation of the nebulizer at a low flow rate. The elution flow rate was chosen to match the recommended sample uptake of the atomic absorption spectrometer (4 mL min^{-1}). The effect of eluent volume on analytes elution was studied by varying the eluent volume between 250 and 1500 μL and the 500 μL eluent was found to be sufficient for quantitative recovery of analytes from the microcolumn.

The effect of column length on efficiency of analytes deposition and signal height was studied. When the length of the column was varied between 1 and 2 cm, the signal was constant but a further increase in column length caused a decrease in peak height (wider peak), so a 2-cm column (corresponding to a mass of ~30 mg) was chosen.

Analytical Features

The flow system showed good linearity for various sampling volumes (25 and 40 mL^{-1}) and typical results for the concentration range 10–400 μg L^{-1} of Pb and 10–200 μg L^{-1} of Cd are presented in Figure 4. Calibration slopes increased proportionally to increasing the concentrated volume, which indicates that the retention/elution efficiency of the process is constant (~100 %). The experimental preconcentration factor calculated as the ratio of the slopes of calibration graphs with and without preconcentration for a 25 ml preconcentration volume were 65 and 53 for lead and cadmium, respectively. The breakthrough capacity of the immobilized APDC microcolumn under the working conditions exceeded 2.5 mg of Pb^{II} and 1.0 mg of Cd^{II} per gram of packing material. This high value suggested high performance of the microcolumn even in the presence of competing ions.

The detection limit was evaluated as the concentration corresponding to a 3σ value of the blank signal and was found to be 4.6 μg L^{-1} for Pb^{II} and 3.2 μg L^{-1} for Cd^{II} for processing 25 mL of a synthetic sample solution blank. The precision of determination was measured by six successive retention and elution cycles of 25 and 40 mL of 60 μg L^{-1} of Pb^{II} and Cd^{II} and was found to be ±4.7 % and ±2.7 % for Pb^{II} and ±3.6 % and ±3.3 % for

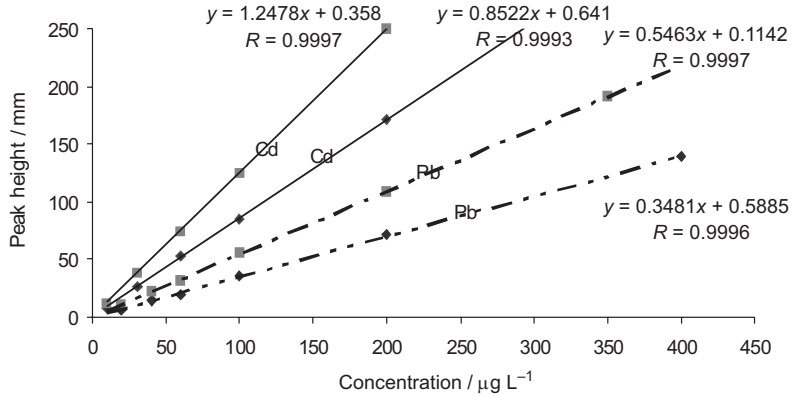

Figure 4. Lead and cadmium calibration curves; ◆ Sampling volume 25 mL; ■ Sampling volume 50 mL.

Table I. Effect of diverse cations and anions on the recovery of lead and cadmium

Ion	$\frac{c(M^{n+})}{c(Pb^{2+})}$	Pb recovery %	$\frac{c(M^{n+})}{c(Cd^{2+})}$	Cd recovery %
Na^+	1000	104	1000	105
K^+	1000	105	1000	102
Ag^+	250	95	100	95
Ca^{2+}	1000	100	1000	106
Mg^{2+}	1000	97	1000	104
Zn^{2+}	1000	96	1000	103
Ba^{2+}	1000	104	1000	98
Cu^{2+}	250	96	250	95
Mn^{2+}	1000	95	1000	104
Fe^{3+}	1000	102	1000	105
Al^{3+}	1000	95	50	95
Cr^{3+}	1000	96	1000	97
Ni^{2+}	500	98	500	95
Cl^-	1000	98	1000	103
Br^-	500	97	500	102
I^-	500	97	500	103
SO_4^{2-}	1000	96	500	102
$S_2O_3^{2-}$	1000	98	500	103
CO_3^{2-}	1000	105	1000	102
PO_4^{3-}	1000	104	1000	98
Tartarate	10000	104	10000	103
Citrate	10000	95	10000	92

[a] Lead concentration 100 μg L^{-1}, cadmium concentration 50 μg L^{-1}; concentrated volume 20 mL; pH ~6.5; flow rate 3.5 mL min^{-1}.

Cd^{II}, respectively. With a 10-mL sampling volume, up to 20 samples can be analyzed in one hour (analyzing each sample takes about 3 min).

Furthermore, deposition efficiency of the microcolumn in lead and cadmium preconcentration in the presence of various cations and anions was examined (Table I) and no significant interference was observed at the given level. These results indicate that high concentrations of matrix salts have a minimal effect on analytes species compared to matrix ions.

Real Sample Analysis

The FI-AAS procedure was applied to several categories of samples. Samples included tap water, river water (taken from the Karon river), sea water (taken from the Caspian Sea and Persian Gulf), and three human blood samples, with diverse matrix cation and anion concentrations. These results are given in Tables II and III. Reliability was checked either by spiking the sample or comparing the results with data obtained by the furnace atomic absorption analysis. As can be seen, the recovery of spiked samples is good. Also, there is satisfactory agreement between the results and data obtained by the furnace atomic absorption analysis, suggesting that the FI-AAS procedure is reliable for the sample type examined. The procedure was also applied to the determination of the content of lead pine in the leaf sample. The concentration of lead was found to be (26.1±0.7) mg kg^{-1}, which is in agreement with the results of independent analyses by furnace atomic absorption ((25.6±0.5) mg kg^{-1}).

Furthermore, the above procedure was applied to the determination of lead in a certified stainless steel sample (C_{12} E_{41}) (composition; C = 0.072, Si = 0021, S = 0.323, Mn =1.09, Ni = 0.01, Cr = 0.037, Cu = 0.006, Pb = 0.222). The concentration of lead in the sample was found to be 0.221±0.004, which is in good agreement with the accepted value (0.222 %; mass fraction, *w*). Thus, the procedure is reliable for analyses of a wide range of samples.

CONCLUSIONS

Compared to the conventional liquid-liquid extraction with APDC, the proposed sorption method can be directly combined with atomic spectrometry, where the organic extracts can cause interference in the determination. Sorp-

Table II. Cadmium and lead determination in water samples[a]

Sample	Added		Found[b]		Recovery		GF-AAS[b]	
	Cd	Pb	Cd	Pb	Cd	Pb	Cd	Pb
	μg L^{-1}		μg L^{-1}		%		μg L^{-1}	
Tap water	–	–	>LOD	>LOD			0.49±0.03	3.70±0.10
	50	50	50.7±1.5	54.0±0.3	101.4	108		
Sea Water (Caspian)	–	–	>LOD	11.5±0.5			0.29±0.04	11.21±0.10
	50	50	50.3±1.5	61.7±0.2	100.6	100.4		
Sea Water (Persian Gulf)	–	–	>LOD	19.4±0.6			0.64±0.02	18.52±0.39
	50	50	50.6±1.8	68.3±0.2	101.2	97.8		
River Water (Karoon)	–	–	>LOD	6.0±0.4			0.46±0.06	5.24±0.01
	50	50	50.5±1.2	55.5±0.1	101	99		

[a] Concentrated volume 20 mL; pH ~6.5; flow rate 3.5 mL min^{-1}.
[b] Mean and standard deviation of three independent measurements.

Table III. Cadmium and lead determination in blood samples

Sample	Added		Found[b]		Recovery		GF-AAS[b]	
	Cd	Pb	Cd	Pb	Cd	Pb	Cd	Pb
	μg L^{-1}		μg L^{-1}		%		μg L^{-1}	
Sample 1	–	–	<LOD	15.97±0.4			2.65±0.25	18.06±0.34
	50	50	52.7±0.4	66.5±0.9	105.4	101.0		
Sample 2	–	–	<LOD	14. 9±0.5			3.80±0.10	14.85±0.09
	50	50	53.7±0.7	65.2±0. 8	107.4	100.6		
Sample 3	–	–	<LOD	23.9±0.9			4.12±0.01	25.92±0.39
	50	50	53.4±0.5	72.6±1.2	106.8	97.4		

[a] Concentrated volume 5 mL; pH ~6.5; flow rate 3.5 mL min^{-1}.
[b] Mean and standard deviation of three independent measurements.

tion and desorption and also preconcentration of analytes do not require any toxic organic solvents, which is an advantage from the viewpoint of solvent discharge into the environment. The proposed method proved to be simple, rapid, reliable and flexible for determination of lead and cadmium in a variety of samples, with limited interferences. Additional work will be directed to assessing the suitability of immobilized APDC microcolumn for field sampling of lead and cadmium.

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SAŽETAK

Određivanje olova i kadmija u različitim uzorcima atomskom apsorpcijskom spektrometrijom s protočnim injektiranjem i mikrokolonom od mikrokristaliničnog naftalena imobiliziranog amonijevim pirolidin ditiokarbamatom

Shayessteh Dadfarnia, Mostafa Talebi, Ali Mohammad Haji Shabani i ZahraAmani Beni

Razvijen je novi sustav ukoncentriravanja protočnim injektiranjem prilagođen metodi plamene atomske apsorpcijske spektrometrije za određivanje olova i kadmija na razini μg L^{-1}. Sorpcijska supstancija u mikrokoloni je amonijev pirolidin ditiokarbamat vezan na mikrokristaliničnom naftalenu. Izdvajanje olova i kadmija na koloni proučavano je u otopinama standarda i analita pri pH = 2–9. Eluacija sačuvane specije za atomsku apsorpcijsku spektrometriju postignuta je ucjepljivanjem 500 μL etanolske otopine octene kiseline (0,5 mol L^{-1}) i klorovodične kiseline (0,25 mol L^{-1}). Faktor ukoncentriravanja određen u 25 mL uzorku iznosio je 65 za olovo i 53 za kadmij, a preciznost određivanja (RSD) pri analizi 60 μg L^{-1} analita bila je 2,7 % za olovo i 3,6 % za kadmij. Postupak je primijenjen za analizu uzoraka vodovodne, riječne i morske vode, borovih iglica, i ljudske krvi. Točnost postupka provjerena je eksperimentima u kojima je određivana efikasnost izdvajanja te neovisnom analizom plamenom atomskom apsorpcijskom spektrometrijom.