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Flow injection on-line hydrophobic sorbent extraction for flame atomic absorption spectrometric determination of cadmium in water samples

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Abstract. A flow injection system was developed for on-line sorbent extraction preconcentration and flame atomic absorption spectrometric determination of cadmium in natural water samples. The non-charged cadmium complex with diethyl-dithiophosphate (DDPA) was formed on-line in $0.1\,mol\,L^{-1}$ HNO$_3$ and retained on the hydrophobic poly-chlorotrifluoroethylene (PCTFE) sorbent material. The adsorbed complex was eluted with isobutyl methyl ketone (IBMK) and injected directly into the nebulizer via a flow compensation unit. All major chemical and flow parameters affecting the complex formation adsorption and elution as well as interference were studied and optimized. By processing 2.4 mL of sample, the enhancement factor was 39 and the sampling frequency was $50\,h^{-1}$. For 30 s preconcentration time the detection limit was $0.3\,\mu g\,L^{-1}$ and the relative standard deviation at $5.0\,\mu g\,L^{-1}$ Cd concentration level was 2.9%. The calibration curve was linear in the range 0.8–$40.0\,\mu g\,L^{-1}$. The accuracy of the method was estimated by analyzing a certified reference material NIST-CRM 1643d (Trace elements in water). Good recoveries were obtained for spiked natural-water and waste-water samples.

Keywords: Cadmium; flow injection; solid phase extraction; atomic absorption spectrometry; poly-chlorotrifluoroethylene

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According to many regulations, the upper permissible level of cadmium in drinking water is $3.0\,\mu g\,L^{-1}$ [1]. Preconcentration and/or separation techniques are often required before metal determination, e.g. by flame atomic absorption spectrometry (FAAS). However, the determination of traces Cd in environmental samples is compromised by insufficient sensitivity or matrix interferences (in certain types of samples). Flow injection (FI) on-line sorption preconcentration and/or separation coupled with FAAS have shown to be very powerful for trace elements determination in a variety of matrices in terms of enhanced sensitivity and reproducibility, efficient matrix removal, diminished sample and reagent consumption, increased sampling frequency, reduced risk of contamination, and the feasibility for automation [2, 3].

On-line column preconcentration is based mainly on the implementation of mini-columns packed with various hydrophobic [4–7] or hydrophilic [3, 8–10] sorbent materials. The nature and the properties of the packing materials are of prime importance for effective fast and quantitative adsorption/elution of analyte, negligible swelling and shrinking, chemical resilience as well as regeneration ability and capacity [11].

Hydrophobic sorbents like octadecyl functional groups bonded on silica gel (C18) [7, 12], C60-Fulerene [6], Amberlite XAD-4 [13, 14], XAD-2 [15], Polyurethane Foam (PUF) [16, 17] and Poly(tetrafluoroethylene) (PTFE) as turnings [18], as beads [4] and as knotted reactor tubing [19, 20] have been

widely used for adsorption of non-charged chelating complexes. The applicability of poly-chlorotrifluoroethylene (PCTFE) beads as a packing material for FI on-line sorption preconcentration systems coupled with FAAS for trace metal (Cu, Pb and Cr) determination was successfully evaluated and demonstrated in previous works with various chelating reagents [21, 22]. The PCTFE packed column is easily reproducible in the laboratory due to the commercially availability of PCTFE in bead, while it offers high chemical resilience without the need of pre-conditioning or activation steps.

Among chelating reagents, dithiocarbamates like diethyldithiocarbate (DDC) or ammonium pyrrolidine dithiocarbamate (APDC), are the most widely used for on-line preconcentration. Alternatively ammonium diethyldithiophosphate (DDPA) has been used successfully, and compared with DDC proved to be more selective and stable for cadmium, copper and lead in very low pH values [12]. The main advantage of the DDPA is that form stable complexes with several metals even in strong acidic medium due to its resistance against hydrolysis, avoiding thus the addition of buffer solutions which are a significant source of contamination [13]. Another advantage of DDPA is that it does not react with alkali, alkaline earth metals and others such as Mn, V, Ti, Co, Cr, Zn allowing the separation of major components of the matrix after sorption of the analyte complexes on a column filled with a sorbent of low polarity [23].

In this work the performance of the PCTFE-beads packed column is studied by applying it in a FI-FAAS system for the determination of trace amount of cadmium in aqueous samples. All main analytical parameters such as sample acidity, ligand concentration, sample loading and elution flow rate and the preconcentration time were examined thoroughly. The effect of potential interferents occurring in environmental samples also studied. According to our knowledge, this combination of DDPA with PCTFE-beads was not proposed before for cadmium determination. The developed method was evaluated by analyzing certified reference material and environmental water samples.

Experimental

Instrumentation

A Perkin-Elmer, Norwalk, Connecticut, U.S.A. (http://las.perkinelmer.com) model 5100 PC flame atomic absorption spectrometer with deuterium lamp background corrector equipped with a

cadmium electrodeless discharge lamp (EDL) operated at 5 W was used as detection system. The wavelength was set at 228.8 nm resonance line and the slit at 0.7 nm. A time-constant of 0.2 s was used for peak height evaluation. The flame conditions were slightly leaner than those recommended by the manufacturer, in order to compensate the effect of organic solvent IBMK, which serves as additional fuel during elution step. The air and acetylene flow rate was set at 9.0 and 0.9 L min^{-1}, respectively. In that case the nebulizer's free uptake rate was 4.9 mL min^{-1}. A flow spoiler was employed in the spray chamber for better nebulization conditions. The spectrometer was set to work in the FI-FAAS mode.

A Perkin-Elmer Norwalk, Connecticut, U.S.A. model FIAS-400 flow injection analysis system was coupled to the flame atomic absorption spectrometer for automatic processing of the method and operated in preconcentration mode. The whole system was controlled by a personal computer and the AA Lab. Benchtop version 7.2 application program. The FIAS-400 system consisted of two peristaltic pumps P1, P2 and a 5-port 2-position injection valve and it was connected to the spectrometer's nebulizer using a short

a) **Preconcentration**

b) **Elution**
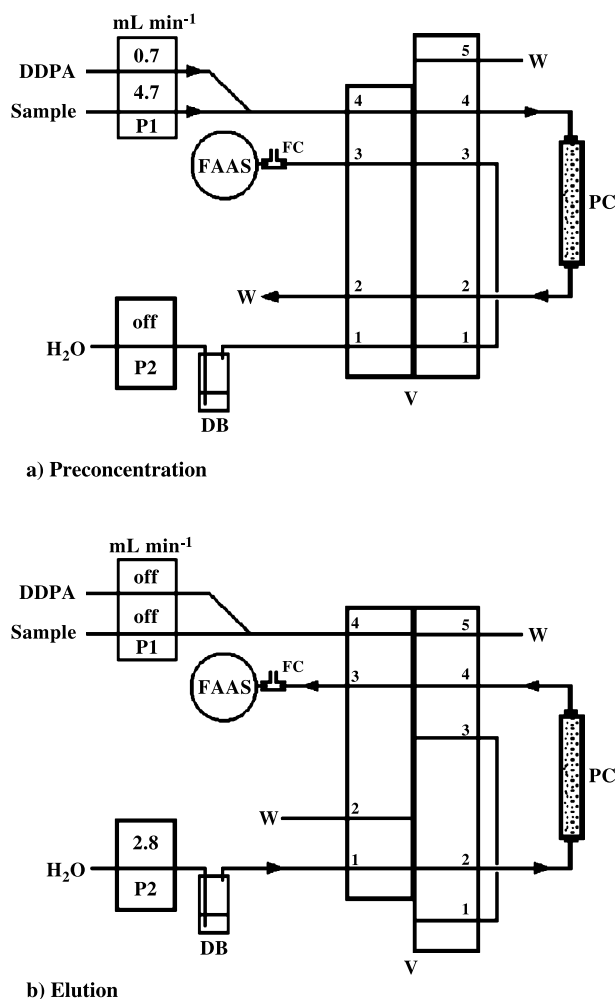
Fig. 1. Schematic diagram of the FI-manifold and the two operation sequences, for cadmium determination. *R* 0.6% m/v DDPA in 0.01 mol L^{-1} HNO$_3$; *P1*, *P2* peristaltic pumps; *V* injection valve; *DB* displacement bottle; *PC* packed column; *FC* flow compensation adapter; *W* waste

Table 1. Operation sequences of the FI-FAAS on-line sorbent extraction preconcentration system for cadmium determination

Step	Valve position	Pumps		Delivered medium	Flow rate (mL min^{-1})	Time (s)	Operation
		P1	P2				
1	load	ON	OFF	sample	4.8	25	preconcentration
				0.6% m/v DDPA	0.7		
2	load	ON	ON	sample	4.8	5	preconcentration
				0.6% m/v DDPA	0.7		
3	elute	OFF	ON	IBMK	2.8	10	elution/measurement
4	elute	OFF	ON	IBMK	2.8	30	washing

PTFE capillary 20 cm length, 0.35 mm i.d., to minimize the dispersion. A flow compensation (FC) unit was used just before nebulizer in order to compensate the lack of nebulizer free uptake flow rate as described elsewhere [22]. Peristaltic pump tubing of "Tygon" type was adopted to deliver the aqueous solutions and a displacement bottle (Tecator, Hoganas, Sweden http://www.foss.dk) was used to deliver the organic solvent isobutyl methyl ketone (IBMK). All other conduits used for various connections were of 0.5 mm i.d. PTFE tubing.

The packed column was made by a piece of polyethylene tube (60 mm length, 3.0 mm inner diameter) and filled with 600 mg of PCTFE-beads. The two ends of the column were blocked by glass wool. The performance of the column was stable at least for 500 preconcentration cycles.

Reagents and samples

All chemicals were of analytical reagent grade and were provided by Merck (Darmstadt, Germany, http://www.merck.de). Ultrapure quality water was used throughout which was produced by a Milli-Q system (Millipore, Bedford, U.S.A., http://www.millipore.com). Working standard solutions of cadmium were prepared by appropriate stepwise dilution of a 1000 mg L^{-1} stock standard solution (in HNO$_3$ 0.5 mol L^{-1}) (Titrisol, Merck) to the required µg L^{-1} levels just before use. The chelating reagent, 0.6% m/v DDPA was prepared fresh daily by dissolving the appropriate amount of ammonium diethyl-dithiophosphate (Aldrich) in 0.01 mol L^{-1} HNO$_3$. Isobutyl methyl ketone (IBMK) was used after saturation with water, without any other purification. Polychlorotrifluoroethylene (PCTFE) powder (Aldrich, Steinheim, Germany, http://www.sigmaaldrich.com) was sieved to obtain the PCTFE-beads fraction between 100 and 600 µm, and washed thoroughly by 2.0 mol L^{-1} HNO$_3$ followed by ethanol and finally with water.

Natural water samples (river, tap, and costal sea-water) were collected from Northern Greece as well as waste-water sample from an industrial area. All samples were filtered through 0.45 µm membrane filters, acidified to 0.1 mol L^{-1} HNO$_3$ and stored at 4 °C in acid-cleaned polyethylene bottles, in order to determine the "dissolved metal" fraction. The standard reference material NIST CRM 1643d (National Institute of Standard and Technology, Gaithersburg, MD, U.S.A., http://www.nist.gov/) containing trace elements in water was also analyzed.

Procedure

The on-line FI-manifold with the main operation parameters is presented in Fig. 1. The operation sequences and details of the FIAS-400 program are given in Table 1.

In the step (Fig. 1a, Preconcentration), the injection valve V is in the "LOAD" position. Pump P1 feeds sample solution mixed with complexing agent through the preconcentration column for 25 s. The on-line complexes formed are adsorbed on the surface of the PCTFE-beads of the packed column. Pump P2 is turned off to conserve organic solvent, while the nebulizer aspirates air through the flow compensation adapter (FC). For step 2, P1 functions as for step 1 and P2 is turned on to feed organic solvent to the nebulizer for 5 s to ensure that there the flame is stable before the preconcentration column is eluted. In step 3, the injection valve V is turned in the "ELUTE" position and pump P2 elutes the analyte complex out of the preconcentration column and delivers it to the nebulizer. The read cycle is started and measurement takes place. Pump P1 is turned off to conserve sample and complexing agent. For step 4, P1 and P2 function as for step 3 to wash the preconcentration column for 30 s. In order to keep the dispersion as low as possible IBMK flows through the column in reverse direction than that of the sample. The recorded transient signal of absorbance was sharp and the peak height was proportional to metal concentration. Five replicate measurements per sample were made in all instances.

Results and discussion

Optimization of chemical and FI parameters

It is well known that in acidic medium DDPA forms strong neutral complexes with Cd(II) that can be adsorbed onto C18 [12, 23], Amberlite XAD-4 [13], PTFE Algoflon® [4], PUF [16] and then eluted either with organic solvent (EtOH or MeOH) or with inorganic acids (HCl or HNO$_3$). In addition, it has been found that the sample acidity is not critical for the complexation of cadmium with DDPA and rigid control or buffer solution is not required [13]. Therefore, DDPA was chosen as complexing agent and IBMK as eluent in the present work.

The effect of nitric acid concentration on the absorbance was studied in the range 0.01–1.0 mol L^{-1} HNO$_3$. As it is shown in Fig. 2, no significant differences in the absorbance were recorded between 0.1–1.0 mol L^{-1} HNO$_3$. As a compromise a nitric acid concentration of 0.1 mol L^{-1} was used for further experiments.

In order to study the influence of the DDPA concentration on the absorbance it was varied from 0.05 to 1.0% m/v. The absorbance was increasing for con-
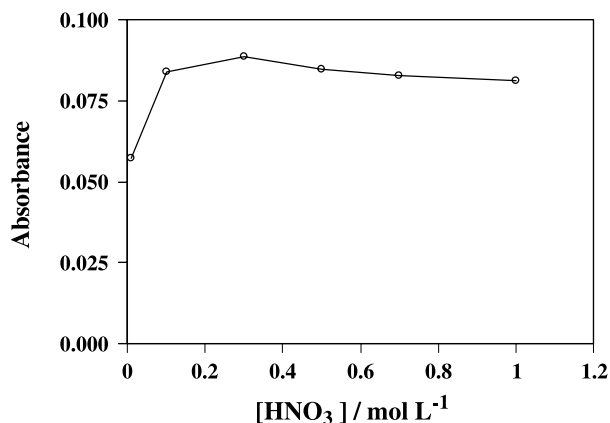
Fig. 2. Effect of nitric acid concentration on the absorbance of $10\,\mu g\,L^{-1}$ Cd(II). All other parameters as in Table 1
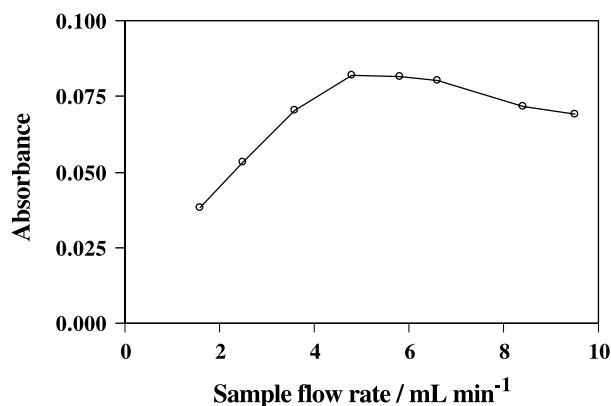

Fig. 3. Effect of sample flow rate on the absorbance of $10\,\mu g\,L^{-1}$ Cd(II). All other parameters as in Table 1

centrations up to 0.5% m/v DDPA, while for higher concentrations it was almost stable. It was also found that the signals were higher when the DDPA solution was acidified. Thus a concentration of 0.6% m/v DDPA in $0.01\,mol\,L^{-1}$ HNO$_3$ was selected.

The effect of the sample flow rate during the preconcentration step was studied in the range 1.6–$9.5\,mL\,min^{-1}$ keeping chelating reagent flow rate constant at $0.7\,mL\,min^{-1}$. As it is shown in Fig. 3, the absorbance increased linearly with increase in the sample flow rate up to $4.8\,mL\,min^{-1}$, but for higher flow rates the absorbance decreases, probably due to insufficient contact time for achieving complete sorption or partial leaching of the complex [19]. A similar behavior was observed during the study of the preconcentration time in the range from 15 to 60 s. The absorbance increased up to 30 s and leveled off for further increase. Thus, sample flow rate of $4.8\,mL\,min^{-1}$ and preconcentration time of 30 s were

chosen as a compromise between sample consumption and high sensitivity.

Organic solvents like, ethanol, methanol and IBMK have been successfully employed as eluents to desorb metal-DDPA complexes from hydrophobic sorbent material [12, 16, 21]. The great advantage of IBMK is arising from its immiscibility with aqueous phase, its lower polarity, and its higher contribution to the flame atomization conditions. Thus, IBMK was adopted as eluent and the elution time was fixed at 10 s. The influence of the elution flow rate was studied within the range 1.5–$5.0\,mL\,min^{-1}$. The best analytical signals were achieved within the range 2.6–$2.9\,mL\,min^{-1}$. At low flow rates the signals decrease, probably due to significant dispersion produced from the high difference between elution flow rate and nebulizer free uptake. Above $2.9\,mL\,min^{-1}$ the absorbance decreases, mainly due to insufficient contact time. Thus, $2.8\,mL\,min^{-1}$ elution flow rate was employed throughout this work.

Interferences

It is well known that DDPA does not form complexes with alkali and alkaline earth metals, which are usually found in high concentrations in natural waters, or with other metals like: Al, Cr, Fe(II) [16]. However, some common matrix cations such as K(I), Ca(II), Mg(II) and Ba(II) at high concentrations were tested and found that they did not interfere at concentrations up to $1000\,mg\,L^{-1}$. Also NaCl did not interfere at concentrations up to $30\,g\,L^{-1}$.

The effect of potential interferents encountered in aqueous samples on the recovery of $5.0\,\mu g\,L^{-1}$ was

Table 2. Analytical results for the determination of cadmium in water samples (determination in "dissolved metal" fraction)

Sample	Added	Found[a]	Recovery (%)
River water	–	$<c_L$	
	5.0	4.8 ± 0.5	96
	10.0	10.3 ± 1.1	103
Tap water	–	$<c_L$	
	5.0	4.9 ± 0.4	98
	10.0	9.6 ± 0.5	96
Seawater	–	0.9 ± 0.2	
	5.0	5.6 ± 0.6	94
	10.0	10.6 ± 0.9	97
Waste water	–	3.4 ± 0.3	
	5.0	8.5 ± 0.7	102
	10.0	13.1 ± 1.4	97

[a] Mean value $\pm$ standard deviation based on three replicate determinations.

Table 3. Procedures for on-line sorbent extraction preconcentration of cadmium and determination with FAAS

Ref.	Sorbent	Reagent	Eluent	PT (s)	SC (mL)	c_L ($\mu g\,L^{-1}$)	s_r (%)	EF
[3]	PAPhA	–	HCl	60	3.4	0.56	1.4	16
[6]	C_{60} fullerene	APDC	IBMK	120	6.0	0.3	1.9	110
[7]	C_{18}	DDC	EtOH	20	1.1	0.3	1.4	25
[12]	C_{18}	DDPA	MeOH	20	2.9	0.8	–	35
[13]	Amberlite XAD-4	DDPA	HCl	300	18	1.0	–	20
[9]	Nb_2O_5–SiO_2	–	HNO_3	120	14	0.1	1.6	33
[15]	AT-XAD-2	–	HNO_3	60	5.0	0.89	3.7	28
**	PCTFE-beads	DDPA	IBMK	30	2.4	0.3	2.9	39

** This work; *EF* enhancement factor; *PT* preconcentration time; c_L detection limit; s_r precision (relative standard deviation); *SC* sample consumption.

examined with individual interferents added. Taking as criterion for interference the deviation of the recovery more than ±5%, the obtained results showed that, Mn(II), Pb(II) and Zn(II) are tolerated up to $5\,mg\,L^{-1}$, Co(II), Hg(II) and Ni(II) are tolerated up to $2\,mg\,L^{-1}$, while Cu(II) is tolerated up to $0.5\,mg\,L^{-1}$.

Analytical features

The analytical performance of the developed method, under the optimized conditions, shows good linearity ($r = 0.9991$) within a linear range from 0.8–$40.0\,\mu g\,L^{-1}$, for 30 s preconcentration time. The regression equation of the calibration curve was calculated as $A = 0.00233 + 0.00835$ [Cd(II), $\mu g\,L^{-1}$, $n = 5$]. By using direct aspiration of aqueous standard solutions into FAAS without preconcentration the calibration curve was calculated as $A = 0.0018 + 0.000215$ [Cd(II), $\mu g\,L^{-1}$, $n = 5$] within a dynamic range from 0.015 to $1.2\,mg\,L^{-1}$. The enhancement factor, calculated as the ratio of the slopes of calibration curves with and without preconcentration, was 39 and the sampling frequency was $50\,h^{-1}$. The detection limit calculated by 3 s criterion was found to be $c_1 = 0.3\,\mu g\,L^{-1}$. The precision of the method evaluated as relative standard deviation (RSD), was $s_r = 2.9\%$, calculated from 10 replicate measurements at the $5.0\,\mu g\,L^{-1}$ concentration level of Cd(II).

The accuracy of the proposed method was tested, by determining the cadmium concentration of a certified reference material NIST CRM 1643d (National Institute of Standard and Technology, Trace elements in water) with a certified content of cadmium $6.47 \pm 0.37\,\mu g\,L^{-1}$ and the recovery obtained was 96% ($6.21 \pm 0.40\,\mu g\,L^{-1}$, $n = 5$). The result was in good agreement with the certified value and the calculated recovery was satisfactory.

The proposed method was applied also to the analysis of local natural water samples as well as waste-water and validated by spiking the examined samples with known amounts of Cd(II). The obtained results are presented in Table 2, and the recoveries were varied in the range 94–103%.

Conclusions

The results obtained in the present work, testify to the applicability of PCTFE packed column in FI on-line sorbent extraction preconcentration system coupled with FAAS for cadmium determination in aqueous samples. A comparison of the proposed system with other on-line sorbent extraction preconcentration FAAS methods using various packing materials is given in Table 3. The limit of detection (c_L) and precision (s_r) obtained, were thus comparable to those presented by other methods reported in the literature. The proposed method is simple and fast with reasonable sample throughput. The use of DDPA as chelating agent is advantageous since complex formation occurs at low pH values, not requiring buffer solution, and providing good selectivity to the method. The hydrophobic nature and excellent chemical inertness of the proposed sorbent material make it very attractive in on-line column preconcentration systems. It was also indicated that sample with difficult matrices like seawaters could be analyzed successfully by the proposed method.

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