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Development of a sequential injection dispersive liquid–liquid microextraction system for electrothermal atomic absorption spectrometry by using a hydrophobic sorbent material: Determination of lead and cadmium in natural waters

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ABSTRACT

A novel on-line sequential injection (SI) dispersive liquid-liquid microextraction (DLLME) system coupled to electrothermal atomic absorption spectrometry (ETAAS) was developed for metal preconcentration in micro-scale, eliminating the laborious and time consuming procedure of phase separation with centrifugation. The potentials of the system were demonstrated for trace lead and cadmium determination in water samples. An appropriate disperser solution which contains the extraction solvent (xylene) and the chelating agent (ammonium pyrrolidine dithiocarbamate) in methanol is mixed on-line with the sample solution (aqueous phase), resulting thus, a cloudy solution, which is consisted of fine droplets of xylene, dispersed throughout the aqueous phase. Three procedures are taking place simultaneously: cloudy solution creation, analyte complex formation and extraction from aqueous phase into the fine droplets of xylene. Subsequently the droplets were retained on the hydrophobic surface of PTFE-turnings into the column. A part of 30 µL of the eluent (methyl isobutyl ketone) was injected into furnace graphite for analyte atomization and quantification. The sampling frequency was 10 h⁻¹, and the obtained enrichment factor was 80 for lead and 34 for cadmium. The detection limit was 10 ng L^{-1} and 2 ng L^{-1} , while the precision expressed as relative standard deviation (RSD) was 3.8% (at $0.5 \ \mu g L^{-1}$) and 4.1% (at $0.03 \ \mu g L^{-1}$) for lead and cadmium respectively. The proposed method was evaluated by analyzing certified reference materials and was applied to the analysis of natural waters.

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1. Introduction

Modern trends in analytical chemistry are towards the simplification and miniaturization of sample preparation procedures as well as the minimization of solvent and reagent consumption [1,2]. Unconventional liquid–liquid extraction (LLE) methodologies have been arisen like: single drop microextraction (SDME) [3–5], wetting film extraction (WFE) [6], cloud point extraction (CPE) [7,8] and dispersive liquid–liquid microextraction (DLLME) [9–12].

DLLME is a miniaturized sample pretreatment technique based on a ternary component solvent system where the dispersion of the fine droplets of the extraction solvent is accomplished within the aqueous phase [13–15]. Consequently, vigorous shaking or mixing is not necessary. The principal advantage of DLLME is that the surface area between extraction solvent and aqueous sample initially is infinitely large, thus the equilibrium state is achieved quickly and the extraction time is very short. However, when DLLME is performed in manual mode, is limited to a small number of extraction solvents (carbon tetrachloride, chlorobenzene and chloroform), since it is critical the extraction solvent to be heavier than water, in order to form stable cloudy solution capable of being separated by centrifuging [2]. In addition, the phase separation with centrifugation is a time consuming procedure including inherent problems of low precision. The principles and the applications of this new procedure have been reviewed recently by Bosch-Ojeda and Sanchez-Rojas [16] and Zang et al. [17].

The important role of flow injection (FI) and sequential injection (SI) techniques for automation, acceleration and miniaturization of solution handling in sample pretreatment has been well demonstrated [18].

Recently, an on-line sequential injection dispersive liquid–liquid microextraction (SI-DLLME) system for DLLME has been presented for metal preconcentration and determination using flame atomic absorption spectrometry (FAAS) [10] solving the above problems.

Electrothermal atomic absorption spectrometry (ETAAS) is an extremely sensitive technique capable for trace determination of many metals in various types of samples, however matrix

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Table 1

Graphite furnace temperature program for lead and cadmium determination in 30 µL of MIBK, without modifier.

Step	Temperature (°C)		Ramp time (s)		Hold time (s)		Argon flow-rate (mL min ⁻¹)	
	Pb	Cd	Pb	Cd	Pb	Cd		
Preheating	110	90	10	5	10	10	250	
Drying	250	110	5	10	20	20	250	
Pyrolysis	850	350	5	20	20	40	250	
Atomization	1800	2200	0	0	5	5	0	
Cleaning	2100	2400	1	1	3	2	250	

interferences (e.g. from seawater) and/or very low analyte concentration usually cause difficulties in the direct sample analysis, requiring the use of matrix modifiers or various preconcentration techniques.

In the present work, a sequential injection on-line dispersive liquid–liquid microextraction system for electrothermal atomic absorption spectrometry (ETAAS) was developed. As far as we know, this work is the first description of combining sequential injection analysis (SIA), DLLME and ETAAS. For this purpose, an intelligent interface was developed using a column packed with PTFE-turnings for extraction solvent separation instead of the batch centrifuging. The effectiveness and efficiency of the proposed FI solvent extraction system were demonstrated for lead and cadmium determination in water samples, due to their high toxicity even in extremely low concentrations. The factors affecting the efficiency of microextraction were studied thoroughly. The developed method was successfully applied to environmental water samples and certified reference material.

2. Experimental

2.1. Instrumentation

A PerkinElmer, Norwalk, CT, USA (http://las.perkinelmer.com) model 5100 PC atomic absorption spectrometer with Zeemann effect background correction and a transversely heated graphite tube atomizer (THGA), equipped with AS-71 furnace auto-sampler and a circulating cooling unit, were employed throughout measurements. Pyrolytically coated THGA graphite tubes (PerkinElmer) with integrated L'vov platform were used. A cadmium and lead electrodeless discharge lamp (EDL) were used as light source operated at 10 W and 5 W respectively. The slit was set at 0.7 nm, while the wavelength was set at 283.3 nm and 228.8 nm resonance line for lead and cadmium respectively. The graphite furnace temperature program for Pb and Cd determination in the MIBK is summarized in Table 1. Two preheating/drying steps were necessary for gradual drying of the organic solvent. Argon 99.996% was used as purge and protective gas. Integrated absorbance (peak area) was used exclusively for signal evaluation.

A FIAlab[®]-3000 sequential injection system (Alitea FIAlab, USA) equipped with an internally incorporated six-port multiposition valve (MV) and a syringe pump (SP, Cavro, Sunnyvale, CA) with a capacity of 1000 μ L was adopted. The FIAlab[®]-3000 system was controlled by a personal computer and the FIAlab for windows v. 5.9.245 application software, written by FIAlab instruments (http://www.flowinjection.com). Two computers were used to communicate with the FIAlab[®]-3000 and the ETAAS 5100 PC, while the complete system was commanded by the computer that controlled the SIA system, as it has been reported elsewhere [19]. Thus, the computer that was operating the FIAlab[®]-3000 system.

The SI manifold and its operation for on-line sequential injection dispersive liquid–liquid microextraction (SI-DLLME) combined with ETAAS are presented schematically in Fig. 1.

The micro-column for retention of the extraction solvent, which includes the derivative chelate complex of metal with ammonium pyrrolidine dithiocarbamate (M–APDC), was fabricated by firmly packing 180 mg of PTFE-turnings in a piece of narrow PTFE tube (40 mm length, 2.1 mm i.d./3.2 mm o.d.). PTFE-turnings were mechanically produced in our laboratory by lathe as described elsewhere [20]. The performance of the column was stable during all experiments (over 1000 cycles).

A VICI AG (Valco International) three-section "Tee" type confluence connector (CC) made of PEEK, with 0.5 mm i.d. bore size was used for mixing of sample and disperser solution.

2.2. 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 was used throughout which was produced by a Milli-Q system (Millipore, Bedford, USA, http://www.millipore.com).

Stock standard solution (1000 mg L⁻¹ in 0.5 mol L⁻¹ HNO₃) of Cd(II) and Pb(II) were obtained from Merck Titrisol. Working standard solutions were prepared by appropriate stepwise dilution of the stock standard solution. Ammonium pyrrolidine dithiocarbamate (APDC) solution (0.2%, m/v) was prepared daily by dissolving an appropriate amount of APDC (Aldrich) in methanol. Methyl isobutyl ketone (MIBK) was previously saturated with ultra-pure water.

All glassware were rinsed with ultra-pure water, decontaminated for at least 24 h in 10% (v/v) nitric acid solution and rinsed again five times with ultra-pure water.

Natural water samples were filtered through 0.45 μ m membrane filters and acidified to ca. 0.01 mol L⁻¹ HNO₃ (pH ~ 2).

2.3. Procedure

The operation sequences of the on-line SI dispersive liquid–liquid microextraction method for lead and cadmium determination by ETAAS (SI-DLLME-ETAAS) are summarized in Table 2.

In steps 2 and 3 segments of air and disperser solution (methanol containing 2.0% (v/v) xylene and 0.2% (m/v) APDC) at volumes of $5 \,\mu$ L and $910 \,\mu$ L respectively were aspirated into the holding coil (HC). In step 4 (Fig. 1a), the multi-position valve (MV) was moved at port 4 and peristaltic pump (P) was activated for 90 s, transporting sample solution into the micro-column (C) through the confluence connector (CC). In the same time syringe pump (SP) was dispensing a part (900 μ L) of the disperser solution through the CC. By this procedure, the disperser solution was injecting into the moving sample solution, resulting thus a cloudy solution of fine droplets of extraction solvent (xylene). Under the above conditions the metal complexes were extracted continuously from aqueous phase to organic phase (xylene cloud). The extraction procedure performed for 90 s (extraction time). The xylene fine droplets (cloud) containing the metal complexes were retained on the PTFE-turnings into the micro-column (C).

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Fig. 1. Schematic manifold for SI-DLLME metal determination by ETAAS. (a) Step 4 extraction and (b) step 14, eluent into GF. For details see text and Table 2. S, sample; MeOH, solution containing 2.0% (v/v) xylene and 0.2% (m/v) APDC; W, waste; P, peristaltic pump; SP, syringe pump; MV, multi-position valve; IV, injection valve in "load: position; V, valve in "out" position; HC, holding coil; C, micro-column; CC, confluence connector; GF, graphite furnace of ETAAS.

As the injected volume of MIBK into the graphite furnace should be no more than 30 μ L, various sections of the eluent were tested. It has been revealed that the front portion (30 μ L) of the eluent contained the higher analyte concentration. Thus, the first 30 μ L section of the eluent was used for injection into the graphite tube of the ETAAS. In step 13 (elution), MV was moved at port 4 and 250 μ L was dispensed in order for the eluent (100 μ L MIBK) to get up to the end of the delivery tube (DT). In step 14, the DT was moved into the graphite tube of the ETAAS and the first part (30 μ L) of the MIBK was injected into graphite tube as it is shown in Fig. 1b. The atomization program was started and was running in parallel with the SIA program. Three replicate measurements were made in all instances.

2.4. Extraction and phase separation

In the proposed SI-DLLME method, a mixture of the disperser solvent which contains the complex reagent and the extraction solvent is mixed on-line with the aqueous sample solution. In that way a moving cloudy solution results from the formation of

 Table 2

 Operational sequence of the SI-DLLME-ETAAS method for lead and cadmium determination.

fine droplets of the extraction solvent, dispersed into the aqueous phase.

Some significant events are taking place simultaneously: formation of fine droplets of the extraction solvent, dispersion of the droplets into the sample solution (cloudy solution formation), analyte complex formation and extraction from aqueous phase into the extraction droplets. As the extraction procedure is very fast, extraction coil is not necessary. Thus, the tubing from the confluent connector (CC) up to micro-column (C) (Fig. 1), where the extraction procedure takes place must be short. In addition this connection tubing should be kept as short as possible due to the fact that an amount of extraction solvent could be retained on the inner surface of the tube resulting thus to inferior precision.

In conventional (batch) DLLME systems [9] the separation of the organic phase is accomplished by centrifuging, restricting by this way the number of the extraction solvents which could be used (they should have higher density than water). On the other hand, in the SI-DLLME system the extraction solvent is not necessary to have higher density than water, due to the fact that the extraction solvent (fine droplets) separation is accomplished by passing

Step	V position	MV position	SP flow-rate $(\mu L s^{-1})$	SP operation	SP volume (µL)	P operation	Commentary
1	IN	2	50	Aspirate	80	OFF	Water into SP
2	OUT	2	3	Aspirate	5	OFF	Segment of air into HC
3	OUT	3	50	Aspirate	910	OFF	Disperser solvent into HC
4	OUT	4	10	Dispense	900	ON ^a	Cloudy solution formation/extraction
							(90 s)/retention on the column
5	OUT	1	20	Empty	95	OFF	Discard of air segment
6	OUT	2	50	Aspirate	500	OFF	Air into HC
7	OUT	4	20	Empty	500	OFF	Evacuate column by air
8	IN	4	50	Aspirate	280	OFF	Water into SP
9	OUT	2	3	Aspirate	5	OFF	Segment of air into HC
10	OUT	5	80	Aspirate	600	OFF	Methanol for cleaning
11	OUT	2	3	Aspirate	5	OFF	Segment of air into HC
12	OUT	6	20	Aspirate	100	OFF	MIBK into HC
13	OUT	4	20	Dispense	250	OFF	Elution—Eluent move up to the end of DT
-	-	-	-	-	-	-	Delivery tube movement into GF
14	OUT	4	10	Dispense	30	OFF	30 μL of eluent into GF
-	-	-	-	-	-	-	Delivery tube movement to waste
-	-	-	-	-	-	-	Starting of the atomization program/measurement
15	OUT	4	80	Empty	710	OFF	Cleaning of column

^a Sample propulsion with flow-rate, 5.4 mL min⁻¹ (90 µL s⁻¹); V, valve of syringe pump; MV, multi-position valve; SP, syringe pump; P, peristaltic pump; GF, graphite furnace of ETAAS.

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the cloudy mixture through a column packed with a hydrophobic sorbent material like PTFE-turnings.

After an adequate extraction time, the retained extraction solvent can be eluted with an suitable eluent such as MIBK.

3. Results and discussion

In order to obtain high enrichment factor for metal determination with the developed SI-DLLME method, the effect of different parameters influencing the complex formation and the extraction conditions, were optimized. These parameters were the type and concentration of extraction solvent, the flow-rate of the disperser solvent and sample, the nature and volume of the eluent as well as the sample acidity and ionic strength. Standard aqueous solutions $0.3 \,\mu g \, L^{-1}$ Pb(II) and of the $0.05 \,\mu g \, L^{-1}$ Cd(II) in 0.01 mol L^{-1} nitric acid were used throughout the optimization study. A solution 0.2% (m/v) APDC in disperser solvent (methanol) was adopted as optimum for all study, as it has been proved from preliminary experiments.

3.1. Effect of extraction solvent

For the selection of the extraction solvent some particular properties should be considered. It must have highly immiscibility with aqueous solution (aqueous phase), high extraction efficiency and hydrophobicity. Also it should be capable to form cloudy solution in a ternary system (water/methanol/extraction solvent). Various organic solvents like carbon tetrachloride, toluene, xylene and diisobutyl ketone (DIBK) have been examined in preliminary studies as extraction solvents and the results revealed that xylene offers the highest extraction efficiency. Thus, it was selected as extraction solvent in the present study. The concentration of the xylene in methanol (disperser solvent) is very important aspect because affects the volume of the dispersed droplets into the ternary system, as well as the preconcentration factor. The effect of the xylene concentration on the integrated absorbance was studied from 1.0% (v/v) to 4.0% (v/v). The maximum signal was obtained for xylene concentration 2.0% (v/v). Thus, xylene concentration 2.0% (v/v) in methanol was adopted for all experiments. In the absence of xylene the recorded absorbance was negligible indicating that the retention of the metal complex on the column was not achieved.

3.2. Effect of disperser flow-rate

The flow-rate of disperser solvent defines the volume of it in the ternary system for a fixed preconcentration time. It affects the volume and the formation of the extraction solvent droplets into the resulted cloudy solution and thus the extraction efficiency. In addition, it affects the linear velocity of the liquid mixture through the micro-column and thus the efficient retention of the xylene fine droplets on the sorbent material (PTFE-turnings). The effect of the flow-rate was examined in the range of $2-12 \,\mu L s^{-1}$. The recorded absorbance was greatest in the range of $6-10 \,\mu L s^{-1}$ as it is shown in Fig. 2. A flow-rate of $10 \,\mu L s^{-1}$ was selected as optimum for the rest of the study.

3.3. Effect of sample flow-rate

Generally, the ratio of aqueous to organic volume was increased by increasing the sample flow-rate, resulting to higher preconcentration factors. However, high flow-rate could lead to insufficient retention of the extraction droplets, resulting thus to lower enrichment factor. The effect of the sample flow-rate was studied in the range of 33–120 μ L s⁻¹. The integrated absorbance was increasing almost linearly up to 90 μ L s⁻¹ for both metals. For higher flowrate the absorbance was increasing with lower rate. A flow-rate



Fig. 2. Effect of the disperser flow-rate on the absorbance of $0.3 \ \mu g \ L^{-1}$ Pb(II) (- \bigcirc -) and $0.05 \ \mu g \ L^{-1}$ Cd(II) (- \square -). Extraction solvent: methanol containing 0.2% (m/v) APDC and 2.0% (v/v) xylene; 90 $\ \mu L \ s^{-1}$ sample flow-rate.

of 90 $\mu L \, s^{-1}$ was selected for high sensitivity and lower sample consumption.

3.4. Preconcentration time

In batch liquid–liquid extraction the extraction rate is reduced, as the system reaching to the chemical equilibrium. However, in the on-line systems, the equilibrium is not necessary, as long as the extraction conditions are extremely reproducible. Also the sorption procedure on the column, affected positively from the preconcentration time, because it defines the sample loading volume, which takes place in the extraction procedure. The effect of the preconcentration time (extraction time) on the absorbance was investigated in the range 30–90 s. The results proved, that the signal was increased almost proportional by increasing the extraction time. For higher sensitivity an extraction time of 90 s was adopted for the proposed method.

3.5. Sample acidity and ionic strength

The sample solution acidity is a key factor in the process of chelation of metal ions and in the consequent extraction procedure. Ammonium pyrrolidine dithiocarbamate (APDC) was selected as chelating agent due to its great ability to form stable complexes even in acidic medium with several metals [21]. The effect of the pH on the integrated absorbance was studied in the range from 0.2 to 4.0 by adjusting it (in metal solution) with dilute nitric acid. The obtained results have shown (Fig. 3) that, the absorbance was maximum and relatively constant in a wide pH range from 1.2 to 3.0 and gradually decreased at higher pH values. Therefore, a pH value of 2.0 ± 0.1 was selected for further studies.

To investigate the influence of ionic strength of the sample solution on the performance of on-line SI-DLLME, various experiments were performed by adding different amounts of NaCl from 0% (m/v) to 5.0% (m/v). The rest conditions experimental were kept constant. No significant impact on the enrichment factor was observed in the studied range enabling the possibility of utilizing the proposed method for saline samples.

3.6. Column elution

The effective elution of the column is a considerable task, because affects the final preconcentration degree. The eluent volume should be as small as possible and the elution as effective as possible. Methyl isobutyl ketone, methanol, ethanol and $3.0 \text{ mol } \text{L}^{-1}$

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Fig. 3. Effect of sample pH on the absorbance of $0.3 \,\mu g \, L^{-1}$ Pb(II) (- \bigcirc -) and $0.05 \,\mu g \, L^{-1}$ Cd(II) (- \Box -). Extraction solvent: methanol containing 0.2% (m/v) APDC and 2.0% (v/v) xylene. All other parameters as in Table 2.

nitric acid solution were studied as eluents. In all cases the flowrate and the volume of the eluent were fixed at $20 \,\mu\text{L}\,\text{s}^{-1}$ and $100 \,\mu\text{L}$ respectively. The results have shown that MIBK was the most effective eluent for the analyte complexes giving the higher absorbance. Besides, the effect of MIBK volume was examined in the range $100-300 \,\mu\text{L}$, taking into consideration the void volume of the column which is estimated at about $200 \,\mu\text{L}$. The integrated absorbance was slightly decreased by increasing the volume due to the higher dispersion of the analytes into the segment of MIBK. Thus, a segment of $100 \,\mu\text{L}$ MIBK was adopted as optimum.

3.7. Interference studies

The effect of potential interference encountered in natural waters samples on the recovery using the proposed SI-DLLME-ETAAS method were examined using $0.3 \,\mu g \, L^{-1}$ Pb(II) and $0.03 \,\mu g \, L^{-1}$ Cd(II) standard solution in the presence of various amounts of individual ions. A variation on the recovery higher than $\pm 5\%$ was considered as interference. The results have showed that, Al(III), Co(II), Cr(III), Cr(IV), Fe(III), Mn(II) and Zn(II) are tolerated up to $10 \, mg \, L^{-1}$ while Cu(II), Hg(II) are tolerated up to $1 \, mg \, L^{-1}$. Also the effect of common coexisting cations such as Ca(II), Mg(II), Ba(II), Na(I) and K(I) were also investigated in high concentration levels. No significant variation in the absorbance was observed at concentrations up to $1000 \, mg \, L^{-1}$ and NaCl up to $30 \, g \, L^{-1}$.

3.8. Analytical performance and analysis of natural waters

The analytical performance data of the proposed SI-DLLME-ETAAS method for lead and cadmium determination are listed in

Table 4

Analytical results of lead determination (dissolved fraction) in certified reference material and spiked natural waters samples with the SI-DLLME-ETAAS method ([Pb] in μ g L⁻¹).

Sample	Certified	Added	Found ^a	Recovery (%)
CRM 1643e Tap water	19.63 ± 0.21	- - 0.80	$\begin{array}{c} 19.22\pm1.6^{\rm b}\\ 0.65\pm0.04\\ 1.42\pm0.09\end{array}$	97.9 - 96.2
River water		- 0.80	3.40 ± 0.19 4.16 ± 0.26	- 95.0
Coastal seawat	er	- 0.80	$\begin{array}{c} 4.21 \pm 0.29 \\ 4.96 \pm 0.35 \end{array}$	- 93.7

^a Mean value \pm standard deviation based on three replicate measurements. ^b Not significantly different from the certified value, at the 95% level.

Table 5

Analytical results of cadmium determination (dissolved fraction) in certified reference material and spiked natural water samples with the SI-DLLME-ETAAS method ([Cd] in μ g L⁻¹).

Sample	Certified	Added	Found ^a	Recovery (%)
CRM 1643e	6.568 ± 0.073	-	6.305 ± 0.401^b	96.0
Tap water		-	0.032 ± 0.002	-
		0.050	0.081 ± 0.007	98.0
River water		-	0.160 ± 0.009	-
		0.050	0.208 ± 0.014	96.0
Coastal seawa	ter	-	0.190 ± 0.011	-
		0.050	0.237 ± 0.018	94.0

 $^{\rm a}\,$ Mean value $\pm\,$ standard deviation based on three replicate measurements.

^b Not significantly different from the certified value, at the 95% level.

Table 3. The enrichment factor (EF) was calculated by comparison of the slopes of the regression lines, which is obtained by the proposed method and the direct injection into graphite furnace of 30 μ L aqueous standard solution, correspondingly. The EFs were found to be 80 and 34 for lead and cadmium respectively. The differences between the EFs for the two analytes are due to the different metal-complex stabilities, the extraction rate and retention efficiency in the dynamic flow conditions. The precision was ascertained on the basis of 10 consecutive sample analyses.

The accuracy of the proposed method was tested by determining the trace level contents of Cd(II) and Pb(II) in a certified reference material, that is, NIST CRM 1643e (National Institute of Standard and Technology, trace elements in water). The proposed method was applied also to the analysis of tap water, river water and coastal seawater samples, which have been collected from Northern Greece. All the determinations were performed using aqueous standard solutions for calibration, without further matrix specific optimization for the samples. The experimental results are shown in Tables 4 and 5 for lead and cadmium respectively. Student's *t*-test was performed at 95% probability level, in order to test the significance of the differences between found and certified

Table 3

Analytical performance characteristics of the SI-DLLME-ETAAS method for lead and cadmium determination.

Parameter	Lead	Cadmium
Sample consumption (mL)	8.1	8.1
Extraction/preconcentration time (s)	90	90
Sampling frequency (h ⁻¹)	10	10
Enrichment factor ^a	80	34
Linear range (µg L ⁻¹)	0.04–1.50	0.006-0.150
Detection limit $(3 s, \mu g L^{-1})$	0.01	0.002
Precision (RSD, $n = 10$)	3.8% (0.5 μg L ⁻¹)	4.1% (0.03 μg L ⁻¹)
Regression equation ([M] in μ g L ⁻¹ , n=9)	$A = (0.2426 \pm 0.0119) [Pb(II)] + 0.0030 \pm 0.0085$	$A = (2.1836 \pm 0.1407) [Cd(II)] + 0.0021 \pm 0.0108$
Correlation coefficient (<i>r</i>)	0.9990	0.9989

^a Compared with the direct injection into graphite furnace 30 µL aqueous standard solution.

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6 Table 6

Comparison of analytical performance data of the proposed method with recently reported LLME-ETAAS methods for cadmium and lead determination.

Analyte	Preconcentration method	Chelating system	Sample volume (cm)	Linear range ($\mu g L^{-1}$)	$LOD(\mu gL^{-1})$	RSD (%)	EF	Ref.
Cd	Batch-DLLME	APDC	5.0	0.002-0.020	0.006	3.5	100	[11]
Cd	Batch-IL-USA-DLLME	DDTC	10.0	0.020-0.150	0.007	3.3	67	[12]
Cd	SI-SDME	DDPA	15.0	0.03-0.6	0.010	3.9	10	[3]
Cd	SI-SE/BE	APDC	13.0	0.05-0.8	0.0027	3.2	21.4	[22]
Cd	On-line LLE	DDPA	14.0	0.006-0.30	0.0028	3.2	24.6	[23]
Cd	SI-LOV	DDPA	1.25	0.05-1.00	0.005	4.3	17.2	[24]
Cd	SI-DLLME	APDC	8.1	0.006-0.150	0.002	4.1	34	a
Pb	Batch-SDME	DDTP	2.0	1.0-15.0	0.20	4.0	52	[4]
Pb	Batch-IL-SDME	$[C_4 MIM][PF_6]$	1.75	0.025-0.8	0.015	5.2	76	[5]
Pb	Batch-CPE	5-Br-PADAP	10.0	up to 30.0	0.08	2.8	50	[8]
Pb	Batch-DLLME	DDTP	5.0	0.05-1.0	0.02	2.5	150	[15]
Pb	On-line-SPE	PSTH-cpg	3.3	0.1-10.0	0.012	3.2	20.5	[25]
Pb	SI-LOV	Sepharose [™]	1.8	0.10-2.00	0.07	5.1	27	[26]
Pb	SI-DLLME	APDC	8.1	0.04-1.50	0.01	3.8	80	a

^a Present work—EF: enhancement factor; LOD: limit of detection; SI-SE/BE: SI on-line solvent extraction-back extraction; SFODME: solidified floating organic drop microextraction; [C₄MIM][PF₆]: 1-butyl-3-methylimidazolium hexafluorophosphate; DDTC: diethyldithicarbamate; DDPA or DDTP: ammonium diethyldithiophosphate; 5-Br-PADAP: 2-(5-bromo-2-pyridylazo)-5-(diethylamino)-phenol; Sepharose[™] Fast flow beads; PSTH-cpg: [1,5-bis(2-pyridyl)-3-sulphophenyl methylene] thiocarbonohydrazide on aminopropyl-controlled pore glass.

concentrations. Since both $t_{exp,Pb} = 0.44$ and $t_{exp,Cd} = 1.14$ are lower than the $t_{crit,95\%} = 4.30$, this reveals that the values obtained were in good agreement with the certified values. The recovery ranged between 94.0% and 98.0% showing the good performance of the method in all types of natural waters samples.

For comparative purposes, the performance characteristics of the proposed method and other selected liquid–liquid microextraction (LLME) preconcentration methods coupled with FAAS, reported in the literature are given briefly in Table 6. The proposed method shows good sensitivity and precision with reasonable preconcentration time, thus it is suitable for ultra trace analysis of cadmium and lead in the sample type examined.

4. Conclusions

A SI dispersive liquid-liquid microextraction system coupled with ETAAS for metal determination was developed for the first time. The proposed method was based on the metal extraction from aqueous phase into the fine droplets of extraction solvent (cloudy solution), which was formed on-line from a ternary component system (water-methanol-xylene). On-line preconcentration technique based on SI-DLLME offer great advantages, such as fully automated sample manipulation, relative short analysis time, low contamination, reduced sample/reagent consumption and waste production, thanks to the use of sequential injection manifold. In addition extraction coil and separation unit are not necessary. The proposed system seems to have easier linkage to atomic spectrometric detectors. The results have shown that SI-DLLME method is a precise, economic and reproducible way for trace cadmium and lead determination in natural environmental samples. The system could be readily applied to the determination of other metals using various ligands, extractable by other organic solvents.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.aca.2009.10.063.

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