

On-line liquid–liquid extraction system using a new phase separator for flame atomic absorption spectrometric determination of ultra-trace cadmium in natural waters

Aristidis N. Anthemidis*, George A. Zachariadis,
Charalampos G. Farastelis, John A. Stratis

Laboratory of Analytical Chemistry, Department of Chemistry, Aristotle University, Thessaloniki 54124, Greece

Received 27 May 2003; received in revised form 10 July 2003; accepted 23 July 2003

Abstract

A robust flow injection (FI) on-line liquid–liquid extraction (LLE) preconcentration/separation system associated with a newly designed gravitational phase separator, coupled to flame atomic absorption spectrometry (FAAS) was developed. The performance of the system was illustrated for cadmium determination at the $\mu\text{g l}^{-1}$ level. The non-charged cadmium complex with ammonium pyrrolidine dithiocarbamate (APDC) was extracted on-line into isobutyl methyl ketone (IBMK). The organic phase was effectively separated from a large volume of aqueous phase and is led into a 100 μl loop of an injection valve before its introduction into the nebulizer. The system was optimized and offered good performance characteristics with unlimited life time of phase separator, greater flow rate ratios and improved flexibility, as compared with other solvent extraction preconcentration systems. With a sampling frequency of 33 h^{-1} , the enhancement factor was 155, the detection limit was $0.02 \mu\text{g l}^{-1}$, the relative standard deviation was 3.2% at $2.0 \mu\text{g l}^{-1}$ Cd concentration level and the calibration curve was linear over the concentration range $0.06\text{--}6.0 \mu\text{g l}^{-1}$. The accuracy of the proposed method was evaluated by analyzing a certified reference material of water and by recovery measurements on spiked samples. Finally, it was successfully applied to the analysis of tapwater, river and seawater samples.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Cadmium; Flow injection; Liquid–liquid extraction; Atomic absorption spectrometry; Phase separator

1. Introduction

Cadmium is a highly toxic and one of the most dangerous trace elements. Because of its extremely low concentration in environmental or biological samples with usually complicated matrices, preconcentration and separation techniques are often required.

Flame atomic absorption spectrometry (FAAS) is the most popular used technique for metals determination, but there are many limitations to determine traces of analyte in environmental samples due to insufficient sensitivity or, in some sample types, matrix interferences. Although the most extensively studied and widely applied preconcentration and/or matrix elimination technique is the liquid–liquid

extraction (LLE) [1], this procedure being operated in batch mode is time consuming, tedious, laborious and hence, potentially prone to sample contamination when ultra-trace determinations are required. The implementation of liquid–liquid extraction technique in continuous mode coupled to atomic spectrometry instruments eliminates many of these drawbacks and contributes advantages inherent in automatic methods of analysis [2].

Since the introduction of flow injection liquid–liquid extraction (FI-LLE) as a mean for analyte preconcentration in flame atomic absorption spectrometry (FAAS) by Nord and Karlberg [3,4], the number of contributions in this field was rather few compared to other on-line preconcentration systems [5]. This is due to the limited range of flow rate ratios of aqueous to organic phase of the segmented stream that on-line phase separators can handle and, in addition, the insufficient stability, versatility and robustness of them.

* Corresponding author. Tel.: +30-2310997707; fax: +30-2310997719.
E-mail address: anthemid@chem.auth.gr (A.N. Anthemidis).

Various types of phase separators have been reported, such as micro-porous polytetrafluoroethylene (PTFE) membrane types [6–8] and gravitational ones [9–13]. The main drawbacks of the membrane type phase separator is the short lifetime of the membrane and the permeation of small amount of aqueous phase especially, when high flow rate ratios of aqueous to organic phase and high segmented flow rate is required. Thus, it is difficult to maintain the hydrophobicity of membrane for long time and to prevent leakage of aqueous phase. On the other hand, gravitational phase separators are more promising for large range of flow rate ratios of aqueous to organic phase, but are difficult to be automated [5].

Among various dithiocarbamate agents, which have been widely used for on-line determination of various metals, ammonium pyrrolidine dithiocarbamate (APDC) is the most popular because its solutions are stable in acidic conditions, it operates in a broad pH range without any decomposition [14] and its complexation rate with various metals is very high.

The aim of present work was to develop a novel robust with high reliability in wide range of phase ratios and long-term operational lifetime FI liquid–liquid extraction system for ultra-trace metals determination using flame atomic absorption spectrometry, as detection system. Thus, a new gravitational phase separator (PS) with dual PTFE conical cavity ends, was designed and elaborated in order to overcome all the above described limitations of other separators. The effectiveness and efficiency of the proposed FI-LLE system was investigated and demonstrated for cadmium determination, via its complexation with APDC and extraction of the on-line formed complex into isobutyl methyl ketone (IBMK). Being to the best of our knowledge this is the first time that an on-line liquid–liquid extraction system has been employed for cadmium determination with FAAS. The accuracy of the proposed method was tested by the analysis of certified reference materials and finally the method was successfully applied to the analysis of potable, river and seawater.

2. Experimental

2.1. Instrumentation

A Perkin-Elmer model 5100 PC flame atomic absorption spectrometer equipped with a deuterium arc background corrector was used as a detector. Cadmium electrodeless discharge lamp (EDL) was used as light source operated at 5 W. 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 IBMK, which serves as additional fuel. The air flow rate was set at 9.01 min^{-1} , acetylene flow rate at 0.91 min^{-1} and the resulting nebulizer's free uptake rate was 5.5 ml min^{-1} . A flow spoiler was employed in the

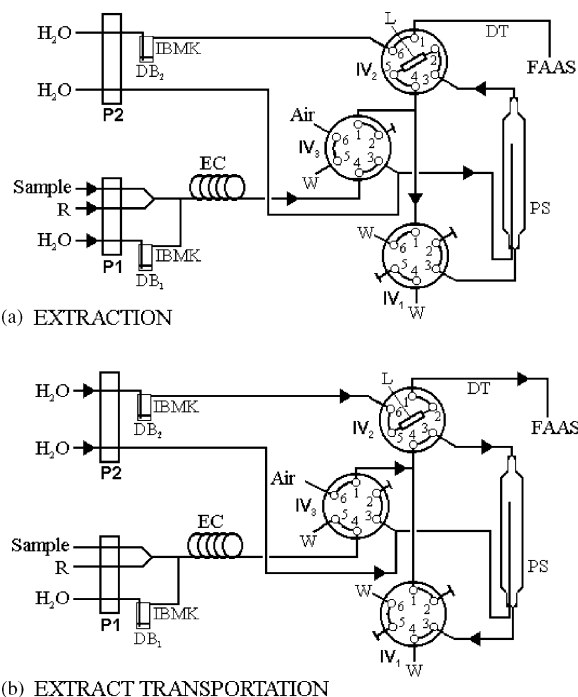


Fig. 1. FI manifold and operation of the liquid–liquid extraction system coupled to FAAS for cadmium determination. (a) Extraction; (b) extract transportation. For details see text. S, Sample; R, complexing agent, 0.5% mV^{-1} APDC solution; W, waste; P1, P2, peristaltic pumps; IV₁, IV₂, injection valves in (A) position and IV₃ injection valve in (B) position, as it is shown in (a); EC, extraction coil; L, extract loop; DB₁, DB₂, displacement bottles for IBMK propulsion; PS, phase separator; DT, delivery tube.

spray chamber for better nebulization conditions. An air compressor was used for PS evacuation with an air flow rate adjusted to 0.1 l min^{-1} .

The FI manifold and its operation for on-line liquid–liquid extraction and cadmium determination by FAAS is presented schematically in Fig. 1. It consists of two peristaltic pumps (Watson Marlow model 205U/BA and Gilson minpuls 3) and three six-port two-position injection valves (LabPro, Reodyne, USA). A $100 \mu\text{l}$ loop (L) of PTFE tubing was employed with the injection valve IV₂ in order to define the accurate volume of the collected extract for atomization.

The phase separator (PS) with the critical dimensions, which was designed and manufactured in our laboratory, is presented schematically in Fig. 2. The separating chamber was made of glass and the push-fit connections at upper and lower end was made of PTFE with internal conical cavities of ca. $30 \mu\text{l}$. The total volume capacity of the PS was 11.7 ml. The upper push-fit connection has a single outlet (0.3 mm i.d.) for the separated organic phase while the lower one has an inlet (1.0 mm i.d.) for the segmented flow and an outlet (1.0 mm i.d.) for the waste flow. During the collection time the low-density organic phase (i.e. IBMK) was directed to the upper region of the PS, while the aqueous phase to the lower one. In order to collect enough amount of organic phase to feed the nebulizer ($100 \mu\text{l}$) of the instrument the

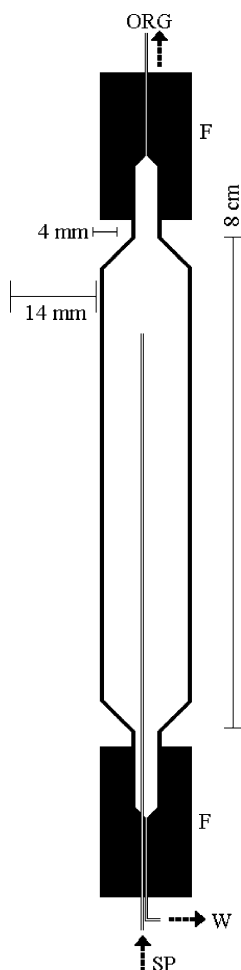


Fig. 2. Schematic diagram of the glass gravitational phase separator (PS). ORG, organic phase; SP, segmented phase; W, waste; F, PTFE push-fit connection with internal conical cavity.

aqueous phase flows to the waste through the lower outlet of the PS, by actuating the injection valve IV_1 for an appropriate time. The collected organic phase was completed free of aqueous phase and the aqueous one in the waste was also free of organic phase. The performance of the phase separator was stable during all experiments with unlimited lifetime.

A VICI AG (Valco International) trisection “Tee” type confluence connector with 0.50 mm i.d. bore size made of PEEK was employed for segmentation of aqueous and organic phase. The extraction coil (EC) was a PTFE tubing 300 cm length, 0.75 mm i.d., coiled at 2.5 cm i.d. The extract (concentrate) was transported to the nebulizer by a PTFE delivery tube (DT) 15 cm length, 0.3 mm i.d. in order to minimize the dispersion of the injected extract. Two displacement bottles (Tecator, Hoganas, Sweden) was used for propulsion of organic solvent streams (IBMK) due to its non-compatibility with Tygon peristaltic tubes. Loss or carryover of the analyte due to the complex retention on the walls of the PTFE before the segmentor and after the merging point of the sample with APDC was eliminated using as short as possible connection tube (5 cm length, 1.0 mm

i.d.). An Orion EA940 pH-meter was employed for the pH measurements being defined by NIST buffers.

2.2. Reagents

All chemicals were of analytical reagent grade and were provided by Merck (Darmstadt, Germany). Doubly de-ionized water was used throughout. Working standard solutions of cadmium were prepared by appropriate stepwise dilution of a 1000 mg l⁻¹ stock standard solution (in HNO₃ 0.5 mol l⁻¹) (Titrisol, Merck) to the required μg l⁻¹ levels just before use, and the pH of them was adjusted with dilute HNO₃. The chelating reagent, 0.5% mV⁻¹ APDC solution was prepared daily by dissolving the appropriate amount of APDC (Merck, pro analysi) in de-ionized water and was extracted with IBMK for further purification. Isobutyl methyl ketone (IBMK) was used without any other purification.

2.3. Procedure

The operation sequences for FI on-line LLE procedure preconcentration and determination of cadmium is summarized in Table 1 and runs through five steps.

In steps 1 and 2 (extraction, Fig. 1a), the sample stream was merged downstream with the complexing reagent (R) and the aqueous phase was segmented with the IBMK stream. The formed complex was extracted into the extraction coil for 60 s and during this period the extract (concentrate) was collected to the upper region of the PS. In step 3, the collected extract fills the loop (L) of the IV_2 by actuating pump P2. In step 4, a defined volume (100 μl) of the extract was transferred directly to the nebulizer of FAAS for measuring of the absorbance. Meanwhile the chamber of the PS was evacuated to the waste. In step 5, loop L of the injection valve IV_2 , which was already filled and washed by IBMK, was evacuated to the waste through the PS. During steps 4 (in case of a new sample) and 5 the segmented flow in the extraction coil was preconditioned before the next cycle. The peak height absorbance was proportional to cadmium concentration in the sample, and was used for all measurements. Five replicate measurements were made in all instances. The extraction was quantitative ($E > 99.0\%$) as was estimated by sequential extraction of aqueous cadmium standards.

3. Results and discussion

3.1. Introduction of the extract into the atomizer

In the FI-LLE systems the flow rate of the organic extract is usually less than 1 ml min⁻¹ due to the high flow rate ratios of aqueous to organic phase required for higher sensitivity, and the limitation of the total flow rate. On the other hand, one of the main limitations on coupling FI-LLE systems to FAAS is the nonmatching of the free uptake rate

Table 1
Operating sequence of the FI-LLE on-line preconcentration system for FAAS cadmium determination

Step	Injection valves			Pumps		Delivered medium	Flow rate (ml min ⁻¹)	Time (s)	Function
	IV ₁	IV ₂	IV ₃	P1	P2				
1	A	A	B	ON	OFF	Sample APDC IBMK	17.0 1.0 0.45	38	Extraction/preconcentration Collection of extract
2	B	A	B	ON	OFF	Sample APDCI IBMK	17.0 1.0 0.45	22	Collection of extract
3	A	A	B	OFF	ON	H ₂ O IBMK	0.5 3.4	30	Loop filling of the IV ₂
4	B	B	A	ON	ON	Sample APDC IBMK H ₂ O IBMK	17.0 1.0 0.45 0.5 3.4	15	Transportation of the extract to FAAS Evacuation of the PS. Preconditioning of the segmented flow in the EC (for new sample)
5	B	A	A	ON	ON	Sample APDC IBMK H ₂ O IBMK	17.0 1.0 0.45 0.5 3.4	5	Evacuation of the L. Preconditioning of the segmented flow in the EC

A, B, position of injection valves as shown in Fig. 1(a).

of the nebulizer, which is usually ranged between 4 and 10 ml min⁻¹, with the flow rate of the organic extract. The introduction of a defined volume of extract into the atomizer of FAAS was achieved using a volume-based manifold employing an injection valve (IV₂) as it shown in Fig. 1, while an IBMK stream was used as carrier for the injected extract volume towards the nebulizer. The feed flow rate for transportation of the extract (300 µl) to FAAS was studied in the range of 1.2–5.8 ml min⁻¹. The absorbance was increased with the increase of the flow rate up to 3.4 ml min⁻¹ and was leveled off between 3.4 to 4.2 ml min⁻¹. Above this range, the absorbance was slightly decreased due to the higher dispersion at these feed flow rates. Finally, feed flow rate of 3.4 ml min⁻¹ was selected for all measurements for lower IBMK consumption.

The influence of the injected volume of the extract into the nebulizer was examined in the range of 35–500 µl, with a fixed 3.4 ml min⁻¹ carrier flow rate. By increasing the injected volume, the sensitivity was increased up to 100 µl and leveled off after this length, thus 100 µl was used throughout.

3.2. Optimization of the extraction parameters

Cadmium forms stable complexes with APDC over a wide pH range (1–6) [15] and can be readily extracted into IBMK which is the most popular organic solvent for FAAS. The pH value of the solution is one of the important parameters that have significant influence on the overall performance of the on-line liquid–liquid extraction affecting not only the

complex formation, but also the extraction efficiency in the IBMK. Therefore in this study the effect of the pH on the cadmium extraction was studied in the range from 0.0 to 8.1 by adjusting it with dilute nitric acid or ammonia. The maximum signal was obtained within a pH range from 0.4 to 3.4 as it shown in Fig. 3. This fact enables the use of the method directly in many aqueous samples after common acid preservation, without any laborious precise pH adjustment. Thus, the samples and standards were made up to pH = 2.0 for all measurements.

The effect of complexing reagent concentration was studied in the range of 0.05–1.0% mV⁻¹. The maximum signal was maintained over the APDC concentration range 0.3–1.0% mV⁻¹. Hence, aqueous solution of 0.5% mV⁻¹ APDC was chosen for subsequent studies.

In FI-LLE systems the degree of preconcentration is determined by the flow ratio of aqueous to organic phase and generally, higher ratios produce greater preconcentration factor. However, there are practical limits to this ratio, which are depended on the segmented (total) flow rate. Too high segmented flow rate causes significant derangement of the segmentation in the extraction coil leading to an inferior contact between the two phases and thus to a decrease of the extraction efficiency.

The effect of the segmented flow rate on the absorbance of cadmium was studied in the range 9.6–27.0 ml min⁻¹ while the flow ratio of aqueous to organic phase was kept constant at $Q_{aq}/Q_{org} = 30$. The results are shown in Fig. 4. The absorbance remains constant up to 18.4 ml min⁻¹ and above this value it starts to decrease.

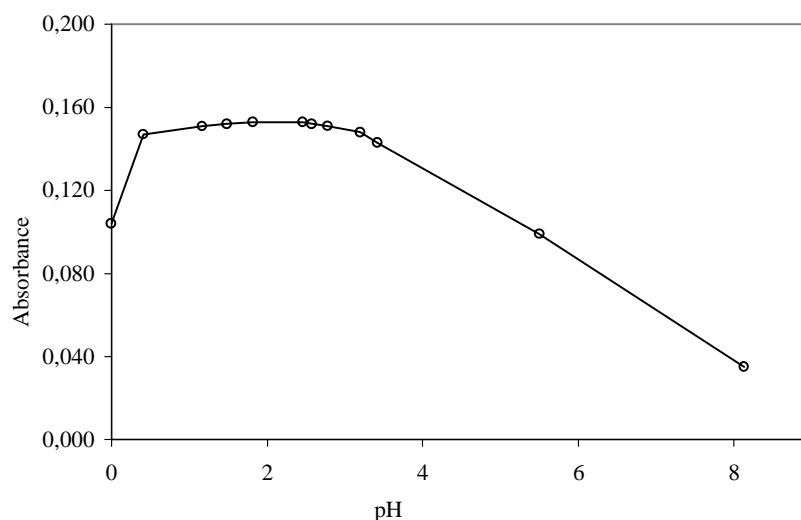


Fig. 3. Effect of sample pH on the absorbance of $4.0 \mu\text{g l}^{-1}$ Cd. All other parameters as in Table 1.

The effect of aqueous to organic phase flow rate ratio on the absorbance was investigated in the range 10–52, varying the aqueous flow rate while the organic one was kept constant. As it shown in Fig. 5, the absorbance increases by increasing the flow rate ratio up to value of 40, which corresponds to segmented flow rate of 18.5 ml min^{-1} but at higher flow rate ratios the sensitivity decreases because the disturbance effect of the high segmented flow rate compensates the gain from the preconcentration. In order to get the higher sensitivity a flow rate ratio of aqueous to organic phase of 40 was adopted for the proposed method.

In FI-LLE systems, both extraction coil dimensions and total (segmented) flow rate, define the extraction time, affecting the residence time and thus the extraction efficiency. The influence of the extraction time on the absorbance was studied by changing the length of the extraction coil in the

range 50–500 cm (0.75 mm i.d.), while the flow rate ratio of aqueous to organic phase was 40, for $4.0 \mu\text{g l}^{-1}$ cadmium determination. The absorbance was increased up to 300 cm, which corresponds to 4.3 s and remained almost constant over this value. Thus, a length of 300 cm, 0.75 mm i.d. was employed for this study.

3.3. Interference studies

The effect of potential interferences encountered in natural waters on the preconcentration and determination of cadmium were examined using the FI-LLE manifold shown in Fig. 1, under the optimum conditions for cadmium concentration of $2.0 \mu\text{g l}^{-1}$. The results are listed in Table 2 and indicate a relatively good tolerance to interference. Only Co(II), Cu(II), Hg(II) and Ni(II) were found to interfere at

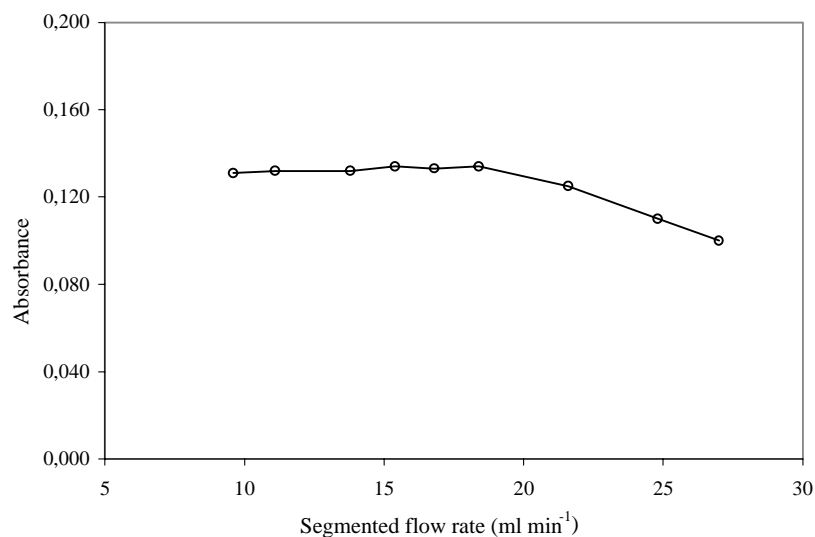


Fig. 4. Effect of the segmented flow rate on the absorbance of $4.0 \mu\text{g l}^{-1}$ Cd. $Q_{\text{aq}}/Q_{\text{org}} = 30$; extraction coil: 300 cm length, 0.75 mm i.d. All other parameters as in Table 1.

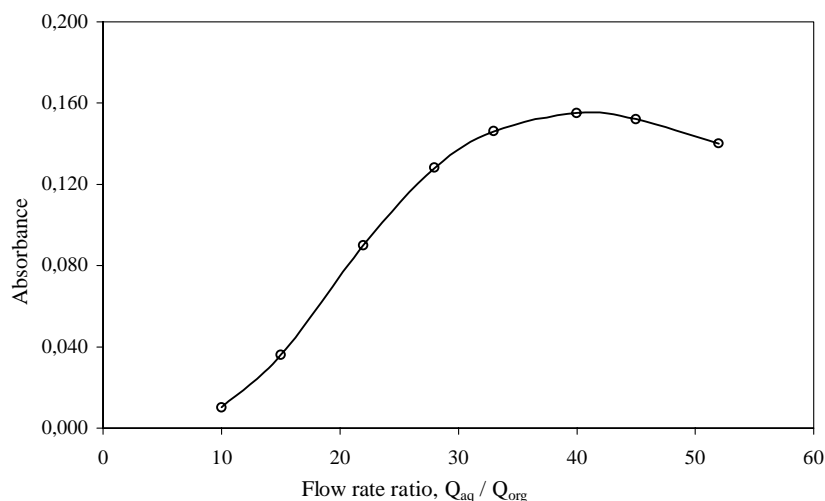


Fig. 5. Effect of the flow rate ratio on the absorbance of $4.0 \mu\text{g l}^{-1}$ Cd. $Q_{org} = 0.45 \text{ ml min}^{-1}$; extraction coil: 300 cm length, 0.75 mm i.d. All other parameters as in Table 1.

concentrations 1 mg l^{-1} , but such levels are not likely to be found in natural waters. It is well known that APDC does not form complexes with alkali and alkaline earth metals, which are usually found in high concentrations in natural waters. However, some common matrix cations such as K(I), Ca(II), Mg(II) and Ba(II) and same anions as Br^- , I^- , SO_4^{2-} , HCO_3^- , NO_3^- 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} .

3.4. Analytical performance

The analytical performance data of the FI-LLE preconcentration FAAS method for cadmium determination are

Table 2
Effect of interferences on the recovery of $2.0 \mu\text{g l}^{-1}$ Cd(II) by the proposed FI-LLE on-line preconcentration FAAS method

Interferent	Concentration (mg l^{-1})	Interferent/Cd(II) ratio	Recovery (%)
Al(III)	100	50000	101
Co(II)	1	500	78
	0.5	250	96
Cr(III)	1	500	99
Cr(VI)	1	500	96
Cu(II)	1	500	76
	0.5	250	95
Fe(III)	1	500	99
Hg(II)	1	500	82
	0.5	250	97
Mn(II)	1	500	98
Ni(II)	1	500	68
	0.5	250	94
Pb(II)	1	500	98
Zn(II)	1	500	96

summarized in Table 3. For a 40 flow rate ratio of aqueous to organic phase, the sampling frequency was 33 h^{-1} and the enhancement factor was 155. The detection limit was calculated by the $3s$ criterion and was found to be $c_L = 0.02 \mu\text{g l}^{-1}$ while the linear range of the method was $0.06\text{--}6.0 \mu\text{g l}^{-1}$. The precision at $2.0 \mu\text{g l}^{-1}$ cadmium concentration level was $s_r = 3.2\%$.

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, $6.47 \pm 0.37 \mu\text{g l}^{-1}$ and the recovery obtained was 97% ($6.27 \pm 0.30 \mu\text{g l}^{-1}$, $n = 5$). The result was in good agreement with the certified value and the calculated recovery was satisfactory.

3.5. Analysis of natural waters

The proposed method was applied to the analysis of coastal seawater, river water and tap water samples collected from rivers and gulfs of Northern Greece. Natural water samples were filtered through $0.45 \mu\text{m}$ membrane filters and acidified to 0.01 mol l^{-1} HNO_3 ($\text{pH} \approx 2$). The

Table 3
Analytical performance of the FI-LLE on-line preconcentration FAAS method for cadmium determination

Enhancement factor	155
Sample consumption (ml)	22
Sampling frequency (h^{-1})	33
Linear range ($\mu\text{g l}^{-1}$)	0.06–6.0
Regression equation ($[\text{Cd}] \mu\text{g l}^{-1}$)	$0.0372 [\text{Cd}] + 0.0027$
Correlation coefficient	$r = 0.9994$
Detection limit ($3s$) ($\mu\text{g l}^{-1}$)	$c_L = 0.02$
Precision (R.S.D., $n = 15$; $2.0 \mu\text{g l}^{-1}$) (%)	$s_r = 3.2$

Table 4
Analytical results of cadmium determination in natural waters by the proposed method ($\mu\text{g l}^{-1}$)

Sample	Added	Found ^a	Recovery (%)
Tap water	0	0.05 \pm 0.02	–
	0.50	0.53 \pm 0.04	96
	1.00	1.04 \pm 0.04	99
Seawater	0	0.07 \pm 0.02	–
	0.50	0.57 \pm 0.03	100
	1.00	1.09 \pm 0.06	102
River water	0	0.18 \pm 0.02	–
	0.50	0.67 \pm 0.03	98
	1.00	1.17 \pm 0.05	99

^a Mean value \pm standard deviation based on five replicate measurements.

results are presented in Table 4. The obtained recovery varied from 96 to 102% showing that the performance of the method was very good in all types of natural waters.

4. Conclusions

The FI-LLE preconcentration/separation system with a newly designed gravitational phase separator has been evaluated and demonstrated for cadmium determination to be an efficient and effective approach for improving the sensitivity and selectivity of the FAAS method. The main advantages of the proposed phase separator are: (i) the ability to be attained high preconcentration factors by directly adjusting the flow rates ratio of aqueous to organic phase, (ii) the ability to collect concentrate (organic) phase as much as required for accurate measuring, by controlling the collection time, (iii) The unlimited lifetime supplying 100% sep-

arated phases, compared to membrane phase separators and (iv) actually low cost manufacturing in the laboratory. The proposed method proved to be simple, sensitive and reliable for cadmium determination in natural water samples, with limited interferences. Although the obtained results in this work are related to cadmium, the system could be readily applied to the determination of other metals using APDC and IBMK. Additional work is in progress on testing the proposed phase separator and its performance employing various organic solvents with lower or higher density than water for on-line trace metals determination using either ETAAS or ICP-AES.

References

- [1] M.S. Cresser, Solvent Extraction in Flame Spectroscopic Analysis, Butterworths, London, 1978.
- [2] M. Valcarcel, M.D. Luque de Castro, Automatic Methods of Analysis, Elsevier, Amsterdam, 1989.
- [3] L. Nord, B. Karlberg Anal. Chim. Acta 125 (1981) 199.
- [4] L. Nord, B. Karlberg Anal. Chim. Acta 145 (1983) 151.
- [5] Z. Fang, Flow Injection Atomic Absorption Spectrometry, Wiley, West Sussex, UK, 1995.
- [6] S. Motomizu, M. Oshima, Analyst 112 (1987) 295.
- [7] K. Backstrom, L.-G. Danielsson, Anal. Chim. Acta 232 (1990) 301.
- [8] T. Sakai, H. Harada, X. Liu, N. Ura, K. Takeyoshi, K. Sugimoto, Talanta 45 (1998) 543.
- [9] S. Lin, H. Hwang, Talanta 40 (1993) 1077.
- [10] S. Lin, Q. Shuai, H. Qiu, Z. Tang, Spectrochim. Acta B 51 (1996) 1769.
- [11] G. Tao, Z. Fang, Spectrochim. Acta B 50 (1995) 1747.
- [12] J. Wang, E.H. Hansen, Anal. Chim. Acta 456 (2002) 283.
- [13] J. Wang, E.H. Hansen, J. Anal. At. Spectrom. 17 (2002) 1284.
- [14] Z.-S. Liu, S.-D. Huang, Anal. Chim. Acta 267 (1992) 31.
- [15] Standard Methods for the Examination of Water and Wastewater, 19th ed, APHA, AWWA, WEF, Washington, 1995.