Automatic sequential injection liquid-liquid micro-extraction system for on-line flame atomic absorption spectrometric determination of trace metal in water samples

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ABSTRACT

An automatic sequential injection (SI) liquid–liquid micro-extraction system incorporating a dual-conical micro-gravitational phase separator is proposed as versatile approach for on-line metal preconcentration and/or separation. Coupled to flame atomic absorption spectrometry (FAAS) the potentials of this novel schema are demonstrated for lead determination in water samples at the $\mu g\,l^{-1}$ level. The non-charged lead complex with ammonium pyrrolidine dithiocarbamate (APDC) was extracted on-line into 300 μl isobutyl methyl ketone (IBMK) through the extraction coil. The organic phase containing the extracted metal complex is collected in the upper cavity of the phase separator and then forwarded to the nebulizer. All the critical parameters were optimized and offered good performance characteristics and high pre-concentration ratios. A sample consumption of 10.5 ml enabled the determination of Pb(II) in the range of 3.0–250.0 $\mu g\,l^{-1}$ with an enhancement factor of 120 and a sampling frequency of 25 h^{-1}. The detection limit and the precision were 1.4 $\mu g\,l^{-1}$ and 2.9% (at 50.0 $\mu g\,l^{-1}$ concentration level), respectively. The proposed method was evaluated by analyzing certified reference material and was applied successfully to the analysis of natural water samples.

1. Introduction

Despite its significant analytical chemical capacities for metal determination at low concentration levels, flame atomic absorption spectrometry (FAAS) often requires a suitable pretreatment step (preconcentration and/or separation) of the sample in order to facilitate the desired sensitivity and selectivity of measurement. Liquid–liquid extraction (LLE) is a widely applied and powerful pretreatment approach prior to analysis, which in batch mode procedures is labor intensive, time consuming, requires large reagent consumption, and suffers risks of sample contamination [1]. From this point of view, it is most beneficial to employ an automatic on-line procedure like flow injection (FI) or sequential injection (SI).

Since the introduction of flow injection liquid–liquid extraction (FI-LLE) as a mean for analyte preconcentration in FAAS by Nord and Karlberg [2], the applications of such systems for routine analysis are rather limited compared to other on-line preconcentration systems like solid phase extraction. This can be attributed to the complexity of the manifolds, which usually lack the ruggedness

and long-term stability [3]. In addition, there are significant difficulties in organic solvents transportation using conventional FI devices. Organic solvents like isobutyl methyl ketone (IBMK), which is the most widely used in FAAS cannot be reliably pumped even with solvent resistant pump tubes. In this case displacement bottles are required, which make the manifold more complicated, while technical skills are required for their manipulations [4]. In addition there are some limitations on the aqueous to organic phase ratios of segmented stream that on-line phase separators can handle successfully [5].

Most of FI procedures use continuous unidirectional pumping of sample and reagent streams, while SI is based on using programmable bidirectional discontinuous flow as precisely coordinated and controlled by a computer. SI systems have significant advantages over FI ones in the simplicity of manifold design, robustness and versatility [6,7]. The inert devices, glass syringe, PTFE tubing and PEEK multiposition valve make the SI systems feasible to manipulate all kinds of organic solvents in micro-scale. A significant advantage of the SI system is the ability for even small volumes (down to a few tenths of microliters) metering, thanks to the use of a syringe pump [8]. Moreover, SI is more economical regarding to the sample, reagents and hence the waste production, which is a significant parameter because it is getting almost more expensive to get rid of the wastes, than to buy the chemicals. Thus,

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SI technique is more suitable for on-line liquid–liquid extraction procedures.

The most critical component in on-line LLE systems is the phase separator of which various designs have been reported, such as: micro-porous membrane type [9–11] and gravitational ones [4,5,12–16]. The main drawbacks of the membrane type phase separators are: (i) insufficient separation of the phases when high segmented flow rates is required and (ii) limited lifetime of the membrane, resulting to the need of periodical change. On the other hand gravitational phase separators are more promising for large range of flow rate ratios of aqueous to organic phase and have previously been shown to be very efficient and easily operated [5,14].

In order to improve the ruggedness of FI-LLE system Tao and Fang [14] proposed the use of a gravitational phase separator with an internal conical cavity (ca. 45 μl), which is only effective for separation of low-density phase. Wang and Hansen proposed an alternative dual-conical gravitational phase separator, which facilitates the separation of both low- and high-density phase. The above phase separators have been tested coupled only with electrothermal atomic absorption spectrometry (ETAAS) for metals determination.

Hitherto, to the best of our knowledge, only one SI liquid–liquid extraction procedure with detection FAAS has been reported in the literature [17]. That procedure, instead of extraction coil and phase separator, uses a glass vial with porous ceramic plate inside, which allows solvents less dense than water to float above it.

In the present work, sequential injection is exploited for the first time as automatic and versatile approach for the implementation of liquid–liquid extraction in a simple low-cost manifold furnished with a dual-conical micro-gravitational phase separator (PS) for on-line metal flame atomic absorption spectrometric determination. In order to facilitate the on-line separation of micro-volume of a low-density organic solvent like IBMK, from a high flow rate segmented stream, a novel dual-conical micro-gravitational phase separator was designed and studied. The conical shape of the upper cavity combined with differences in density of the two phases and the hydrophobic nature of the cavity permits the continuous separation of the segmented phase.

The effectiveness and efficiency of the proposed SI-LLE system was investigated and demonstrated for lead determination, via its complexation with ammonium pyrrolidine dithiocarbamate (APDC) and extraction into isobutyl methyl ketone. The accuracy of the proposed method was tested by the analysis of certified reference material and the method was applied to the analysis of natural water samples.

2. Experimental

2.1. Apparatus

The SI manifold and its operation for on-line liquid–liquid extraction and lead determination by FAAS is depicted schematically in Fig. 1.

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 1.0 ml was used. The FIAlab®-3000 system was controlled by a personal computer and the FIAlab for windows v. 5.9.245 application program, written by FIAlab instruments (http://www.flowinjection.com).

A PerkinElmer, Norwalk, Connecticut, USA (http://las.perkinelmer.com) model 5100 PC flame atomic absorption spectrometer was exploited as detection system. Lead electrodeless discharge lamp (EDL) was used as light source operated at
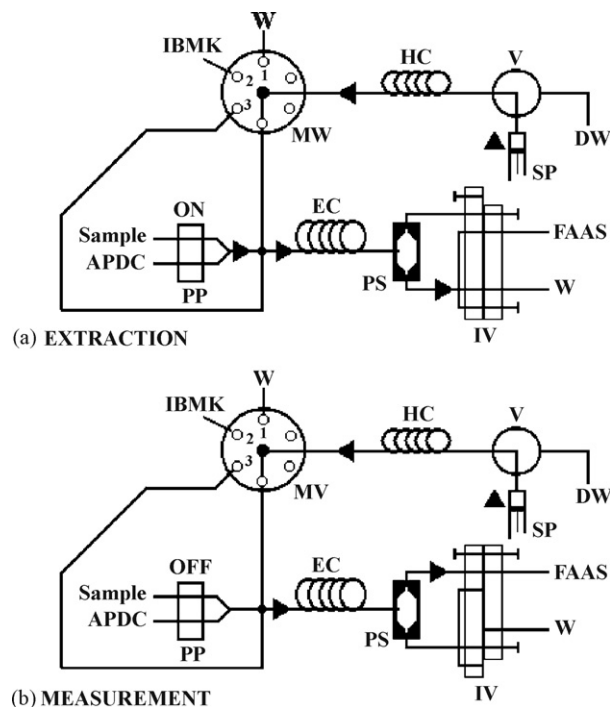
Fig. 1. SI-LLE system coupled to FAAS for lead determination. Two operation steps: (a) extraction (step 3) and (b) measurement (step 4). MV, multiposition valve; SP, syringe pump; V, syringe pump valve; PP, peristaltic pump; IV, injection valve; EC, extraction coil; HC, holding coil; PS; phase separator; DW, distilled water; W, waste.

10 W. The wavelength was set at 283.3 nm resonance line and the slit at 0.7 nm. A time-constant of 0.2 s was used for peak height evaluation. The air flow rate was set at $10.0 \, l \, min^{-1}$, acetylene flow rate at $0.9 \, l \, min^{-1}$ and the resulting nebulizer's free uptake rate was $92 \, \mu l \, s^{-1}$. The flame conditions were adjusted to be slightly leaner than those recommended by the manufacturer for aqueous samples, in order to compensate the effect of organic solvent isobutyl methyl ketone, which serves as an additional fuel. A flow spoiler was employed into the spray chamber for better nebulization conditions. A PerkinElmer Norwalk, Connecticut, USA model FIAS-400 flow injection analysis system was coupled to the SI system and to the FAAS for automatic processing of the whole procedure. The FIAS-400 system was controlled by a personal computer and the AA Lab. Benchtop version 7.2 software program. The FIAS-400 system consisted of two peristaltic pumps (only one, P is used for the proposed manifold) and a 5-port 2-position injection valve, IV. The connecting line between the IV and the FAAS nebulizer was a PTFE tube 20 cm long, 0.5 mm i.d.

A dual-conical micro-gravitational phase separator (Fig. 2) was incorporated within the SI system in order to accomplish the separation of organic or aqueous phases. The SP was fabricated from two "push-fit" conical (cavities of ca. 30 μl) shaped pieces of the hydrophobic material, polytetrafluoroethylene (PTFE) and one cylindrical shaped central union with perpendicular inlet bore size of 0.7 mm. The total inner volume of the PS was approximately 900 μl. The upper and lower pieces have an outlet bore size of 0.5 mm i.d. and 1.0 mm i.d., respectively. The extraction coil enters into the PS horizontally and that facilitates the fast separation and collection of organic phase free of aqueous phase in the upper conical cavity while the aqueous phase forwarded to the waste through the IV. The same PS can be used for organic solvents with either lower or higher density from water.

A VICI AG (Valco International) four-section "cross" type confluence connector made of PEEK, with 0.5 mm i.d. bore size was
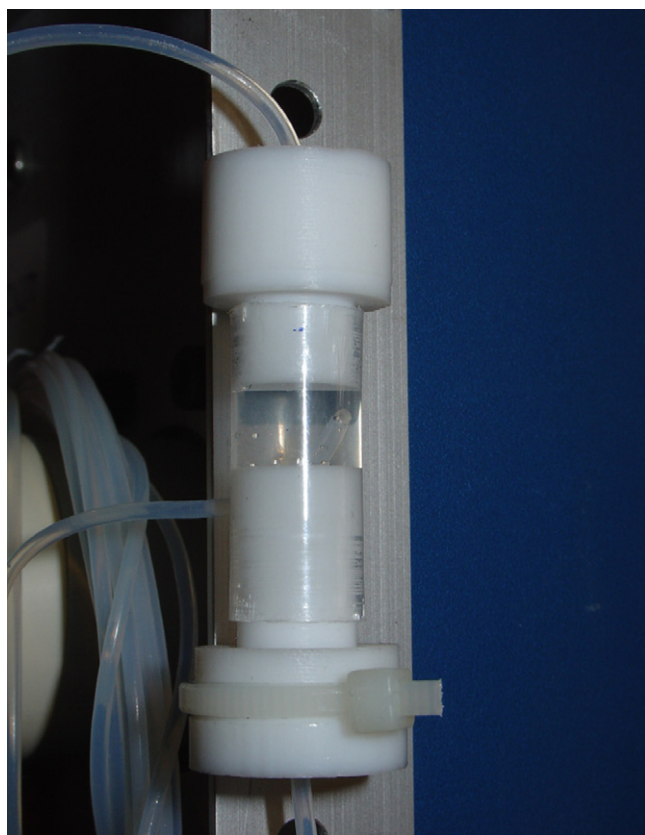
Fig. 2. Dual-conical micro-gravitational phase separator (PS).

exploited for segmentation of aqueous and organic phase. The extraction coil (EC) is advantageously made from PTFE tubing 300 cm length, 0.75 mm i.d. as a knotted reactor [15], which facilitates the dispersion of the two phases into each other so effectively that it is actually difficult to see them separately with the naked eye, that is, a very large area of interface between the two phases is generated, which in turn expedites the extraction.

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, 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). Working standard solutions of lead 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 pH of them

was adjusted with dilute HNO$_3$. The chelating reagent 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 was previously saturated with de-ionized water.

2.3. Procedure

The operation steps of the proposed SI-LLE procedure for lead determination are summarized in Table 1.

In step 3 (Fig. 1 EXTRACTION), the sample containing the analyte is first mixed with 0.5% (m/v) APDC solution to form the metal complex and then intermixed with the extractant (300 μl IBMK) in the reaction coil (RC). Thereafter, the phases are separated in the micro-gravitational phase separator and the extractant collected in the upper cavity of the PS, while the aqueous phase was discarded to waste through the IV. In step 4 the collected IBMK is transported to the flame atomizer of FAAS detector with a flow rate of 92 μl s^{-1} for measuring the absorbance. In order to avoid a possible contamination between samples the extraction coil and the phase separator are washed during the last step. The peak height absorbance was proportional to lead 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 lead standards.

3. Results and discussion

3.1. Injection of the extractant into the atomizer

One of the major limitations of coupling continuous solvent extraction systems like FI and SI to FAAS, is the nonmatching of the uptake rate of the nebulizer, usually ranged between 66 and 133 μl s^{-1}, with the flow rate of the extractant, which is typically lower than 16 μl s^{-1}. In case the free uptake of the nebulizer exceeds that of the extractant flow, a random gaseous release of dissolved air during the delivery into the nebulizer could significantly deform the peak profile and degrade the readout precision [18]. Lower flow rate of organic solvent is necessary for higher flow rate ratios of aqueous to organic and thus higher preconcentration rates and sensitivity [5]. In this case it is more preferable to accumulate an appropriate amount of extractant in a holding coil and then to inject it into the nebulizer with a flow rate similar to the nebulizer's free uptake flow rate.

According to the proposed SI-LLE manifold, two points should be taken into account: (1) the lowest injected volume of extractant IBMK that is necessary to take the maximum absorbance, in order to reduce the reagents consumption and (2) the flow rate of the extractant that is needed for the nebulizer uptake flow rate compensation. The above considerations are achieved using the proposed dual-conical micro-gravitational phase separator.

The influence of the injected volume of the extractant into the nebulizer was examined in the range of 50–400 μl, with a fixed

Table 1
Operational sequence of the SI-LLE on-line preconcentration system for lead determination

Step	V	SP flow-rate (μl s^{-1})	MV	PP[a]	IV	SP action	Commentary
1	In	100	2	Off	Load	Aspirate 800 μl	Aspiration of water into SP
2	Out	50	2	Off	Load	Aspirate 300 μl	Aspiration of IBMK into HC
3	Out	3.0	3	On	Load	Dispense 300 μl	Extraction, collection of extract
4	Out	90	4	Off	Inject	Empty	Injection of IBMK extractant into nebulizer Absorption measurement
5	In	100	4	Off	Load	Fill	Repletion of SP with water
6	Out	100	4	Off	Load	Empty	Washing of extraction system

[a] Sample flow rate, 175 μl s^{-1}; [APDC] = 0.5% (m/v); APDC flow rate, 10 μl s^{-1}.
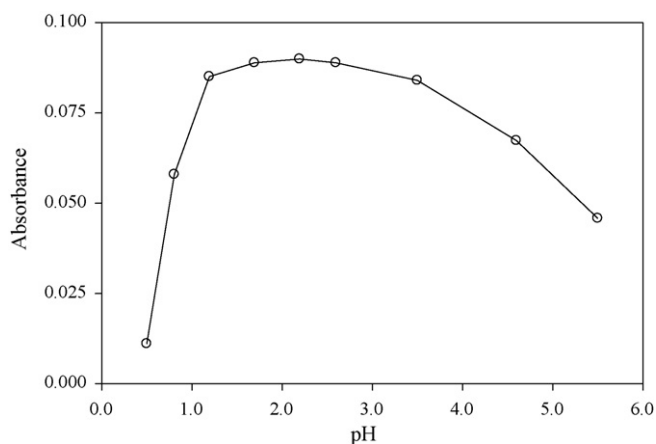
Fig. 3. Effect of sample pH on the absorbance of $90\,\mu g\,l^{-1}$ Pb(II). Sample flow rate = $137\,\mu l\,s^{-1}$. All other parameters as in Table 1.

Fig. 4. Effect of sample flow rate on the absorbance of $90.0\,\mu g\,l^{-1}$ Pb(II). IBMK flow rate = $3\,\mu l\,s^{-1}$; extraction coil: 300 cm length, 0.75 mm i.d. All other parameters as in Table 1.

$90\,\mu l\,s^{-1}$ flow rate using standard lead solution in IBMK without previous extraction procedure. By increasing the injected volume, the sensitivity was increased up to 100 μl and leveled off after this volume. Taking into account the extraction efficiency and in order to compensate the IBMK solubility in water, an IBMK volume of 300 μl was used for the subsequent studies.

The flow rate for transportation of the extractant (300 μl) to FAAS was studied in the range of 40–100 $\mu l\,s^{-1}$ using standard lead solution in IBMK without previous extraction. The absorbance initially increased with the increase of the flow rate and was leveled off at $80\,\mu l\,s^{-1}$. Finally, feed flow rate of $90\,\mu l\,s^{-1}$ which is similar with the free uptake flow rate ($92\,\mu l\,s^{-1}$) of the FAAS nebulizer was selected for all measurements.

3.2. Optimization of the extraction parameters

For the optimization of the different chemical and SI parameters which will be mentioned below, the univariant method was used, utilizing a standard aqueous solution of $90\,\mu g\,l^{-1}$ Pb(II).

The pH value of the sample solution effects significantly the Pb(II)–PDC complex formation, and also its extraction efficiency in the IBMK. Lead forms stable complexes with APDC over a wide pH range (0.1–6) [19] and can be readily extracted into IBMK. The pH of sample was studied in the range from 0.5 to 5.5 by adjusting it with dilute nitric acid or ammonia. The maximum signal was obtained within a pH range from 1.2 to 3.5 as it shown in Fig. 3. This fact shows that the method can be used directly in many aqueous samples after the common acid preservation, without any laborious precise pH adjustment. Thus, pH 2.0 was established for further study.

Ammonium pyrrolidine dithiocarbamate is the most popular dithiocarbamate agent due to the fact that its aqueous solutions are stable in acidic conditions, it operates in a broad pH range without any decomposition [20] and its complexation rate with various metals is very high. The effect of complexing reagent concentration was studied in the range of 0.1–1.0% (m/v). The absorbance was increasing for concentrations up to 0.3% (m/v) APDC, while for higher concentrations it remained constant. A concentration in excess of 0.5% (m/v) APDC was selected for subsequent studies due to the possible consumption caused by other extractable metals present in the sample.

In continuous liquid–liquid extraction systems the preconcentration factor is determined by the flow rate ratio of aqueous to organic phase, which is corresponding with the volume ratio of aqueous to organic phase in batch (off-line) extraction methods.
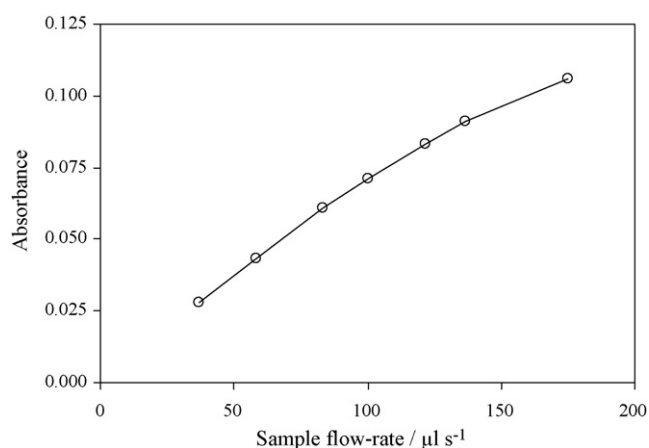
Generally, higher ratios give higher sensitivity. However, in flow systems there are practical limits to obtain very high flow rate ratios, due to the limited range of organic phase flow rate that peristaltic pumps can handle precisely and also due to the insufficient versatility and robustness of them at very low flow rates. The problem can be solved using stepper-motor driven syringe pumps and SI systems controlled by computer. On the other hand the aqueous phase (sample + complexing reagent) flow rate cannot be very high because in this case the resulted segmented (total) flow rate would be extremely high. Too high segmented flow rate causes significant disturbance 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 [5]. Moreover, the efficiency of the extraction procedure depends not only on the interface area but also on the time of contact.

According to the above considerations the effect of sample flow rate on the absorbance was studied in the range of 37–175 $\mu l\,s^{-1}$, while the APDC flow rate was fixed at $10\,\mu l\,s^{-1}$. The results are shown in Fig. 4. The absorbance increased with increasing the sample flow rate. Thus, a sample flow rate of $175\,\mu l\,s^{-1}$ was adopted in order to get higher sensitivity for the proposed method.

The effect of extracting solvent (300 μl IBMK) flow rate on the absorbance was studied in the range of 1–5 $\mu l\,s^{-1}$, while the sample flow rate was fixed at $175\,\mu l\,s^{-1}$. The absorbance decreased with increasing the IBMK flow rate, while a higher standard deviation was recorded at flow rate of $1\,\mu l\,s^{-1}$. An IBMK flow rate of $3\,\mu l\,s^{-1}$ was used as a compromise between the time consumption and the high sensitivity.

A selection of the appropriate extraction coil length at the used flow rates is important when maximum extraction efficiency is required. The dimensions (length and internal diameter) of the extraction coil define the time of contact (extraction time) and thus the extraction efficiency. In addition, the increase in coil length increases the extraction efficiency by providing larger contact area of the aqueous sample with a thin film of organic phase adsorbed on the inside wall of the coil, where partial transfer of analyte to the organic phase takes place [21]. The effect of the length of the extraction coil was studied in the range of 50–500 cm (0.75 mm i.d.). The absorbance was increased upon increasing coil length and reaches a maximum at length in excess of 300 cm. These results suggest that at shorter coils, the residence time of the analyte in the coil is short, resulting in incomplete extraction. A length of 300 cm was employed for the proposed method.

Table 2
Analytical characteristics of the SI-LLE on-line FAAS method for lead determination

Enhancement factor	120
Sample consumption (ml)	17.5
Sampling frequency (h^{-1})	25
Linear range ($\mu g\,l^{-1}$)	3.0–250.0
Regression equation ([Pb] in $\mu g\,l^{-1}$)	0.0012 [Pb] + 0.0021
Correlation coefficient	$r = 0.9995$
Detection limit ($3s$) ($\mu g\,l^{-1}$)	$c_L = 1.4$
Precision (RSD, $n = 11$; $50.0\,\mu g\,l^{-1}$) (%)	$s_r = 2.9$

Table 3
Analytical results of lead determination in natural waters by the proposed method

Sample	Added ($\mu g\,l^{-1}$)	Found[a] ($\mu g\,l^{-1}$)	Recovery (%)
Tap water	–	$<c_L$	–
	10.0	9.9 ± 0.6	99
River water	–	6.5 ± 0.5	–
	10.0	16.2 ± 0.9	97
Seawater	–	5.3 ± 0.5	–
	10.0	14.9 ± 1.2	96

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

3.3. Interference studies

The effect of potential interferents encountered in natural waters on the preconcentration and determination of lead were examined using the SI-LLE manifold shown in Fig. 1, under the optimum conditions described above for $50.0\,\mu g\,l^{-1}$ Pb(II). Taking as a criterion for an interference the deviation of the recovery more than $\pm 5\%$, Al(III) ($10\,mg\,l^{-1}$), Cd(II) ($0.5\,mg\,l^{-1}$), Co(II) ($1.0\,mg\,l^{-1}$), Cr(III) ($10.0\,mg\,l^{-1}$), Cr(VI) ($10.0\,mg\,l^{-1}$), Cu(II) ($1.0\,mg\,l^{-1}$), Fe(III) ($10.0\,mg\,l^{-1}$), Hg(II) ($0.5\,mg\,l^{-1}$), Mn(II) ($10.0\,mg\,l^{-1}$), Ni(II) ($1.0\,mg\,l^{-1}$), and Zn(II) ($2.0\,mg\,l^{-1}$) do not interfere. Although APDC does not form complexes with alkali and alkaline earth metals, high concentrations of them were tested because they are usually found in high concentrations in natural waters. Na^+ and K^+ up to $2000\,mg\,l^{-1}$ and Ca^{2+}, Mg^{2+}, Ba^{2+} up to $500\,mg\,l^{-1}$ and NaCl up to $30\,g\,l^{-1}$, did not caused any significant interference.

3.4. Analytical characteristics

The analytical characteristics of the proposed SI-LLE system for lead determination with FAAS are summarized in Table 2. For a 62 flow rate ratio of aqueous to organic phase, the sampling frequency was $25\,h^{-1}$. The enhancement factor, calculated from the ratio of the slope obtained with the proposed method to the slope without extraction (using aqueous standards solutions in batch mode), was 120. The linear calibration graph for lead determination was $3.0–250.0\,\mu g\,l^{-1}$. The limit of detection (c_L) defined by the $3s$ criterion and was found to be $c_L = 1.4\,\mu g\,l^{-1}$. The relative standard deviation (RSD) which define the precision was $s_r = 2.9\%$ at $50.0\,\mu g\,l^{-1}$ Pb(II) concentration level.

The accuracy of the proposed method was tested, by determining the lead concentration of a certified reference material NIST CRM 1643d (National Institute of Standard and Technology, Trace elements in water) with a certified content of lead, $18.15 \pm 0.64\,\mu g\,l^{-1}$ and the recovery obtained was 96% ($17.42 \pm 0.8\,\mu g\,l^{-1}$, $n = 3$). 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 tap water river water and coastal seawater samples collected from rivers and gulfs of Northern Greece. Natural water samples were filtered through $0.45\,\mu m$ membrane filters and acidified to $0.01\,mol\,l^{-1}$ HNO_3 (pH ≈ 2). The results are presented in Table 3. The obtained recovery varied from 96% to 99% showing that the performance of the method was very good in all types of natural waters.

4. Conclusions

The SI-LLE continuous extraction system with a dual-conical micro-gravitational phase separator has been evaluated and demonstrated to be promising for improving the sensitivity and selectivity of the FAAS method for routine determination of trace amounts of lead in water samples. A cost-effective simple fabricated micro-phase separator unit attached at the multiposition selection valve of the FIAlab®-3000 SI system offers an automatic on-line extraction in micro-scale by drastically reducing organic solvent volumes. The system versatility concerning the variation of the sample and organic extractant flow rate provides an expeditious way to control the sensitivity and high preconcentration factors.

It is further advantageous regarding the extraction with organic solvents denser than water like chloroform and feasibility of application to other metals determination with LLE and FAAS.

References

[1] Z. Fang, Flow Injection Atomic Absorption Spectrometry, John Wiley & Sons Ltd., West Sussex, England, 1995.
[2] L. Nord, B. Karlberg, Anal. Chim. Acta 125 (1981) 199.
[3] Z.-L. Fang, Anal. Chim. Acta 400 (1999) 233.
[4] J.-H. Wang, E.H. Hansen, Anal. Chim. Acta 456 (2002) 283.
[5] A.N. Anthemidis, G.A. Zachariadis, C.G. Farastelis, J.A. Stratis, Talanta 62 (2004) 437.
[6] J. Ruzicka, G.D. Marshall, Anal. Chim. Acta 237 (1990) 329.
[7] C.E. Lenehan, N.W. Barnett, S.W. Lewis, Analyst 127 (2002) 997.
[8] E.H. Hansen, J. Environ. Sci. Health 40 (2005) 1507.
[9] S. Motomizu, M. Oshima, Analyst 112 (1987) 295.
[10] K. Backstrom, L.-G. Danielsson, Anal. Chim. Acta 232 (1990) 301.
[11] T. Sakai, H. Harada, X. Liu, N. Ura, K. Takeyoshi, K. Sugimoto, Talanta 45 (1998) 543.
[12] S. Lin, H. Hwang, Talanta 40 (1993) 1077.
[13] S. Lin, Q. Shuai, H. Qiu, Z. Tang, Spectrochim. Acta Part B 51 (1996) 1769.
[14] G. Tao, Z. Fang, Spectrochim. Acta Part B 50 (1995) 1747.
[15] J.-H. Wang, E.H. Hansen, J. Anal. At. Spectrom. 17 (2002) 1284.
[16] A.N. Anthemidis, G.A. Zachariadis, J.A. Stratis, J. Anal. At. Spectrom. 18 (2003) 1400.
[17] R. Cerdeira de Campos Costa, A.N. Araujo, Anal. Chim. Acta 438 (2001) 227.
[18] G. Tao, Z. Fang, J. Baasner, B. Welz, Anal. Chim. Acta 481 (2003) 273.
[19] Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, Washington, 19th ed., 1995.
[20] Z.-S. Liu, S.-D. Huang, Anal. Chim. Acta 267 (1992) 31.
[21] R.H. Atallah, J. Ruzicka, G.D. Christian, Anal. Chem. 59 (1987) 2909.