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An automatic countercurrent liquid–liquid micro-extraction system coupled with atomic absorption spectrometry for metal determination

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ABSTRACT

A novel and versatile automatic sequential injection countercurrent liquid–liquid microextraction (SI-CC-LLME) system coupled with atomic absorption spectrometry (FAAS) is presented for metal determination. The extraction procedure was based on the countercurrent flow of aqueous and organic phases which takes place into a newly designed lab made microextraction chamber. A noteworthy feature of the extraction chamber is that it can be utilized for organic solvents heavier or lighter than water. The proposed method was successfully demonstrated for on-line lead determination and applied in environmental water samples using an amount of 120 μL of chloroform as extractant and ammonium diethyldithiophosphate as chelating reagent. The effect of the major experimental parameters including the volume of extractant, as well as the flow rate of aqueous and organic phases were studied and optimized. Under the optimum conditions for 6 mL sample consumption an enhancement factor of 130 was obtained. The detection limit was 1.5 μg L^{-1} and the precision of the method, expressed as relative standard deviation (RSD) was 2.7% at 40.0 μg L^{-1} Pb(II) concentration level. The proposed method was evaluated by analyzing certified reference materials and spiked environmental water samples.

1. Introduction

The recent trends of modern analytical chemistry following the requirements of Green Analytical Chemistry (GAC) [1] have led to remarkable minimization of organic solvent, reagent and sample consumption resulting in microextraction techniques such as single-drop microextraction (SDME) [2,3], hollow-fiber liquid phase microextraction (HF-LPME) [4] and dispersive liquid–liquid microextraction (DLLME) [5,6]. A challenging task in analytical procedures is the controlled and robust solution handling, which significantly affects the sample preparation prior the final determination [7]. The automated systems, especially in the frame of flow and sequential injection (FI/SI) have attracted the researchers' attention over the past few years due to the fact that all chemical and physical manipulations can be made automatically in an enclosed environment. In this manner, the risk of sample contamination is minimized while the safety of the operator is increased.

Countercurrent extraction (CCE) is a separation technique that involves two immiscible liquid phases flowing in opposite directions in a single or a multistage mode. One of the key advantages of liquid–liquid extraction processes is the possibility to operate in a countercurrent mode resulting in high separation factors. Craig and Post introduced an intelligent glass apparatus [8] which could perform countercurrent (CC) liquid extraction in continuous multistage mode for separation of substances with similar distribution ratios. This system constituted the beginning of Countercurrent Supported-free Liquid–Liquid Chromatography (CCC) which later evolved in High Performance Countercurrent Chromatography (HPCCC) [9]. It is noteworthy mentioning that HPCCC methods require bulky instrumentation and also high reagent consumption. As far as we are concerned, although countercurrent extraction has been used for organic substances, only few works have been presented in the literature for metal separation [10,11].

Recently, an interesting study of countercurrent microflow on a microchip platform has been presented for liquid–liquid extraction [12,13]. Kitamori et al. presented a laminar countercurrent microflow system with a low Re on a glass microchip, which was obtained by selectively modifying the lower half of a microchannel with a hydrophobic group, and which was applied to recover a cobalt complex [12].

The main objective of this work was to develop an automatic sequential injection liquid–liquid microextraction (LLME) system based on countercurrent (CC) flow coupled with flame atomic absorption spectrometry (FAAS) for metal determination. A novel flow through microextraction chamber (EC) was designed and optimized for the purposes of the countercurrent extraction of

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metals (analytes) from aqueous to organic phase. The proposed EC is suitable for organic solvents either heavier or lighter than water. The study was focused on lead determination, while the effects of all significant experimental parameters including the dimensions of the EC and the sample flow rate were investigated and optimized.

2. Experimental

2.1. Reagents

All reagents were of analytical grade quality provided by Merck (Darmstadt, Germany, http://www.merck.de). Working solutions were prepared with Milli-Q water (Millipore, Bedford, USA, http://www.millipore.com). All standard solutions were prepared immediately before use by appropriate stepwise dilution of a 1000 mg L^{-1} Pb(II) stock standard solution in 0.5 mol L^{-1} HNO_3 (Merck Titrisol) to the required sub μg L^{-1} levels with water. The aqueous solution of 0.5% m/v ammonium diethyldithiophosphate DDPA (Aldrich, www.sigmaaldrich.com/european-export.html) was freshly prepared by dissolving the appropriate amount of DDPA without any further purification. Organic solvents were of analytical grade and were previously saturated with ultra-pure water. Glassware and pipettes were kept in 10% (v/v) nitric acid for at least 24 h and subsequently rinsed five times with ultrapure water.

2.2. Certified reference materials and samples

The accuracy and precision of the proposed sequential injection countercurrent liquid–liquid microextraction (SI-CC-LLME) method were validated by analyzing two standard reference materials (CRMs): NIST CRM 1643e (National Institute of Standard and Technology, Gaithersburg, MD, USA) containing trace elements in water and BCR 278-R (Community Bureau of Reference Brussels, Belgium) containing trace elements in mussel tissue. An amount of ca. 0.4 g of mussel tissue was precisely weighed into sealed Teflon crucibles and wetted by a mixture of HNO_3–$HClO_4$–H_2O_2 in a volume ratio of 3:2:0.5. The digestion procedure was carried out in a stainless-steel pressurized bomb at 120 ± 5 °C for 2 h, according to the recommendations of the manufacture. After cooling the system, the digests were properly diluted in ultra-pure water and used for the total determination of lead.

The method was applied to the analysis of environmental water samples such as costal seawater and ditch water from the industrial area of Northern Greece region. The collected samples were acidified to 0.01 mol L^{-1} HNO_3 (ca. pH 2) with dilute HNO_3 and stored at 4 °C in acid-cleaned polyethylene bottles in order to be analyzed by the proposed method.

2.3. Instrumentation and software

The sequential injection countercurrent liquid–liquid microextraction (SI-CC-LLME) manifold used for lead determination is depicted in Fig. 1.

A Perkin-Elmer Model 5100 PC atomic absorption spectrometer (Perkin-Elmer, Norwalk, CT, USA, http://las.perkinelmer.com) was utilized as the detection system in flame mode. A Perkin Elmer Lumina™ lead electrodeless discharge lamp (EDL) operated at 10 mA was used as a light source. The monochromator spectral bandpass (slit) was set at 0.7 nm and the wavelength was set at 283.3 nm resonance line. A mixture of air and acetylene at flow rates of 10.0 L min^{-1} and 2.0 L min^{-1}, respectively, was used for atomization. In this case, the nebulizer's flow rate was 5.5 mL min^{-1}. The spray chamber of the burner was equipped

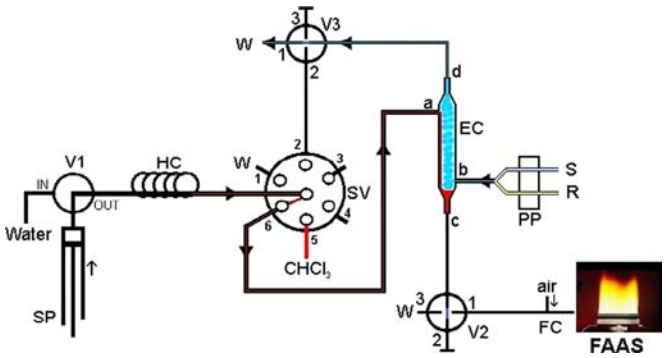

Fig. 1. Illustration of the SI-CC-LLME system coupled with FAAS for lead determination. SP, syringe pump; V1, 2-port valve; V2, V3, 3-port valves; HC, holding coil; SV, 6-port selection valve; EC, extraction chamber; FC, flow compensation unit; PP, peristaltic pump; a, b, c, d, inlet/outlet ports.

with a flow spoiler for better nebulization conditions. Integrated absorbance (peak area) was used for signal evaluation throughout the study. A confluence connector, acting as a flow compensation (FC) unit was adapted between the FAAS nebulizer and the on-line SI-CC-LLME system as it is shown in Fig. 1. It consisted of a VICI® (Valco Instruments Co. Inc. and VICI AG, http://www.vici.com/cfit/ctees.php) three-section "T" type (0.5 mm i.d.) connector made of polyether ether ketone (PEEK).

A FIAlab®-3000 (Alitea FIAlab, USA) sequential injection (SI) system comprising of a six-port multi-position selection valve, SV and a syringe pump, SP (Cavro, Sunnyvale, CA) with a capacity of 1000 μL was used for the automatic process of the proposed method. Two additional three-port Teflon/Kel-F selection valves, V2, V3 (MicroCSP-3000, FIAlab Instruments, Bellevue, WA) were employed. The FIAlab®-3000 SI system and the selection valves were controlled by a personal computer through the FIAlab application software for Windows v. 5.9.245 (http://www.flowinjection.com).

A PerkinElmer Norwalk, Connecticut, USA model FIAS-400 flow injection analysis system was coupled with the 5100 PC spectrometer and SI manifold for automatic processing of the whole procedure. The peristaltic pump PP of the above system was used for sample and reagent propulsion, throughout the experiments. The FIAS-400 system was controlled by a personal computer and the AA Lab. Benchtop version 7.2 software program.

2.4. The countercurrent extraction chamber

The extraction chamber, EC (Fig. 2), which was used for the operation of the countercurrent extraction, was designed and manufactured in the laboratory using a polyethylene tube (6.5 cm length/4.5 mm i.d.). Two pipette tips (1000 μL) were placed at both ends of the plastic tube in a push-fit manner. The EC involves four inlet/outlet ports (a, b, c, d) in a symmetrical arrangement design, as shown in Fig. 2, facilitating the CC extraction with organic solvent heavier or lighter than water.

Along the inner surface of the EC, there is an engraved channel, 6.2 cm length/1 mm width/0.5 mm depth, which is necessary to direct the organic phase downwards in a vertical flow as cataract. Thus, the stream of the organic phase is moving into the stream of the aqueous phase due to the gravity, as the organic solvent is heavier than water. The inlet port "a" constitutes the beginning of the above engraved channel and it is connected with the port 6 of the SV, as it is shown in Fig. 1. In case of an extractant lighter than water, the EC should be reversed from top to bottom, so that port "c" and "d" to be connected with V3 and V2 valve respectively. Thus, the organic solvent flows upwards and it is collected at the top of the EC.

The hydrophobicity or hydrophilicity of the EC material affects the form (width, thickness) of the generated cataract as well as its flow rate. Hydrophobic materials like polyethylene (PE) and polytetrafluoroethylene (PTFE) are the most suitable due to their high compatibility with the hydrophobic organic solvents like chloroform or methyl isobutyl ketone (MIBK), to produce a robust cataract flow. In case of a glass EC, several problems in maintaining the organic solvent flow rate either downwards or upwards were observed. Hence a polyethylene tube was adopted for the EC construction.

The effect of the EC inner diameter was examined for 5.5, 4.5 and 3.0 mm i.d. At small inner diameter (3.0 mm i.d.), the organic solvent collected, in the form of plug, at the inner space of the EC (port "a") preventing the formation of a vertical flow and consequently the CC extraction. For EC with 4.5 and 5.5 mm i.d., the obtained results were similar, although the linear velocity of the aqueous stream was increasing by reducing the internal diameter. In case of EC with a large internal diameter (5.5 mm i.d.), there was a high volume of aqueous phase which could not be in contact with the organic phase due to higher dead volume. Thus, an EC with internal diameter of 4.5 mm was adopted for the proposed method.

Fig. 2. Image of the countercurrent microextraction chamber.

2.5. Procedure

The SI-CC-LLME method is carried out through 13 operation sequences, which are summarized in Table 1 and presented in a video clip given as supplementary material.

Supplementary material related to this article can be found online at doi:10.1016/j.talanta.2014.04.091.

Initially, syringe pump (SP) was activated to aspirate consecutively 100 μL of water (step 1) and 120 μL of organic solvent into HC (step 2). Next, a small volume (10 μL) of organic solvent was dispensed to waste in order to fill the dead volume of the SV internal channel (step 3). In step 4, a volume of 120 μL of chloroform, at 1 μL s^{-1} feed flow rate was propelled into the EC through the inlet port "a". In the same time, the organic solvent is moving downwards along the engraved channel of the EC (from the port "a" to the bottom) thanks to the gravity. Meanwhile, the aqueous phase (sample + reagent) is flowing upwards, by means of the peristaltic pump, PP. During this step, on-line countercurrent extraction was taking place; the organic phase (120 μL) was collected at the bottom of the EC, while the aqueous phase was delivered to waste via V3 valve. Thereafter, the collected organic phase containing the extracted analytes was transported to FAAS for atomization and quantification by dispensing water through the EC by activating V2 and V3 (step 7). The following steps (step 8–13) were programmed for thorough cleaning of the EC and preparing it for the next analytical cycle.

3. Results and discussion

3.1. Extractant volume

The extractant volume, which was collected at the bottom of the EC, depended on the time of extraction. It should be noted that the analyte concentration in the collected segment depends only

Table 1
Operation sequences of the SI-CC-LLME system for lead determination by FAAS.

Step	SV	V1	V2	V3	SP	PP	SP	SP	Description
	Position				Operation		Volume (μL)	Flow-rate (μL s^{-1})	
1	5	IN	2	1	Aspirate	OFF	100	50	Water into SP
2	5	OUT	2	1	Aspirate	OFF	140	50	Segment of organic solvent into HC
3	1	OUT	2	1	Dispense	OFF	10	5	Filling dead volume of SV valve with organic solvent
4	6	OUT	2	1	Dispense	ON[a]	120	1	On-line extraction / preconcentration
5	1	OUT	2	1	Dispense	OFF	110	50	Empty of SP to waste
6	1	IN	2	1	Aspirate	OFF	1000	80	Filling of Syringe pump with water
7	2	OUT	1	2	Dispense	OFF	1000	50	Transportation of extractant segment to FAAS / Measurement of absorbance
8	2	IN	3	2	Aspirate	OFF	100	50	
9	5	OUT	3	2	Aspirate	OFF	160	50	
10	6	OUT	3	2	Dispense	OFF	150	5	Purification of the extraction chamber and preparation for the next cycle
11	1	OUT	3	2	Dispense	OFF	110	50	
12	1	IN	3	2	Aspirate	OFF	1000	80	
13	2	OUT	3	2	Dispense	OFF	1000	60	

[a] Sample flow rate, 3.6 mL min^{-1}; DDPA flow rate, 0.4 mL min^{-1}.

on the volume ratio of aqueous to organic phase which takes place in the countercurrent extraction procedure.

On the other hand, in case of coupling such microextraction systems with FAAS, it should be taken into account the necessary injected volume into the burner/nebulization system for effective atomization and quantification [14]. The effect of the injected chloroform volume, on atomization and absorption, was examined in the range of 60–180 μL with a fixed flow rate (50 μL s^{-1}) and it was found that the absorbance (peak height) was increased for injected volumes up to 100 μL while for higher volumes it remained constant.

Due to the fact that in the present system the signal was evaluated by integrated absorbance (peak area), the effect of the injected chloroform volume on the sensitivity of the proposed method was examined in the range of 100–180 μL. The obtained results showed an increase of the sensitivity by increasing the injected volume as shown in Fig. 3. As a compromise between organic solvent and sample consumption, sampling frequency and sensitivity, a volume of 120 μL was adopted throughout the experiments.

3.2. Study of countercurrent flow rates

The flow rates of the aqueous and organic phases affect the preconcentration rate (expressed as the volume ratio of aqueous to organic phase) in dynamic on-line liquid–liquid extraction systems. Furthermore, in countercurrent extraction systems the flow rate affects either the relative linear velocity or the contact time between the two streams. By increasing the flow rate, the linear velocity was increased while the contact time was decreased. The influence of aqueous phase flow rate on the sensitivity was studied in the range of 2.0–5.0 mL min^{-1} keeping the organic phase feed flow rate constant at 1 μL s^{-1}. By increasing the aqueous phase flow rate up to 4.0 mL min^{-1}, the absorbance was increased with similar extraction efficiency, while for higher flow rates the extraction efficiency was decreased as shown in the diagram of Fig. 4. Taking into account the sample consumption and the sensitivity of the method, a flow rate of 4.0 mL min^{-1} was selected as optimum.

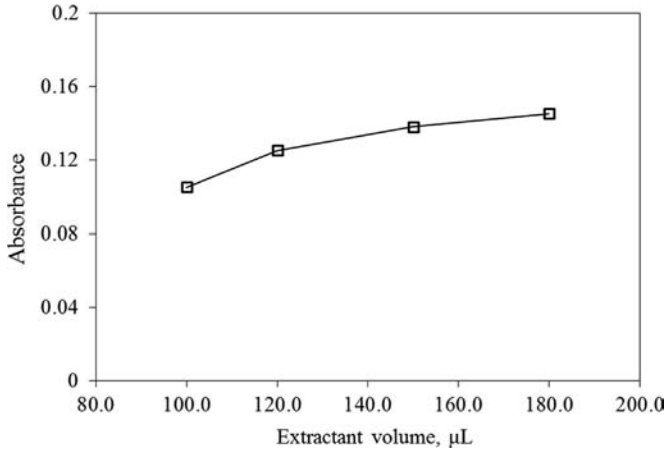

Fig. 3. Effect of extractant volume on the absorbance of 100 μg L^{-1} Pb(II). Other experimental parameters are presented in Table 1.

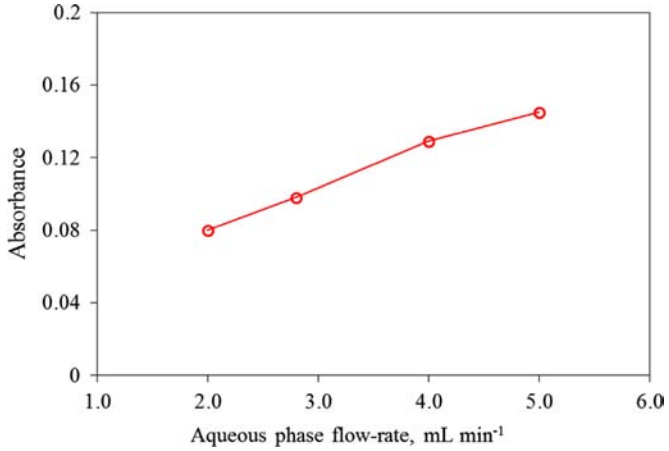

Fig. 4. Effect of aqueous phase flow rate on the absorbance of 100 μg L^{-1} Pb(II). Other experimental parameters are presented in Table 1.

In the proposed extraction chamber, the organic stream (cataract) was driven by the gravity and its flow rate depended mainly on the relative density of the organic solvent as well as on its chemical affinity with the material of the EC. On the other hand the organic solvent feed flow rate at port "a" of the EC defines the dimensions (width and thickness) of the countercurrent organic stream into the EC and thus the interfacial area between aqueous and organic phase. The influence of organic solvent feed flow rate on the sensitivity of the method was not significant for a fixed volume ratio of aqueous to organic phase as it was proved from preliminary experiments.

In order to get high preconcentration rate, the organic solvent feed flow rate in the countercurrent extraction should be kept as low as possible, for a fixed aqueous stream flow rate. Thus, for volume ratio of the two phases as high as possible the chloroform feed flow rate was fixed at 1.0 μL s^{-1} which was the lowest flow rate that could be used with the present configuration of the SI system. In case of a SI system with a syringe pump with smaller capacity, an even lower flow rate of the organic stream could be used in order to increase the sensitivity of the method.

3.3. Study of chemical parameters

Among various chelate agents such as dithiocarbamates and dithiophosphates, DDPA has been proved to be more selective and stable for toxic metals like cadmium, copper and lead under strong acidic conditions [15] due to its resistance against hydrolysis. This is a great advantage considering the fact that there is no need for pH adjustment by adding buffer solutions which are a significant source of contamination [16].

The effect of DDPA concentration was studied in the range of 0.1–1.0% m/v. The maximum absorbance was recorded over the range of 0.3–0.8% m/v. Taking into account the competitive complexation with other co-existing ions in the real samples, a concentration of 0.5% m/v DDPA was selected.

The effect of sample acidity on the sensitivity was studied over the range 0.5–1.0 × 10^{-4} mol L^{-1} HNO_3 preparing the standard solutions by adding proper amount of nitric acid. The obtained results showed that the absorbance was maximum and practically

Table 2
Analytical performance characteristics of the SI-CC-LLME method for lead determination.

Sample volume (mL)	6.0
Extractant volume (μL)	120
Sampling frequency (h^{-1})	13
Enhancement factor	130
Linear range (μg L^{-1})	5.0–280
Detection limit, c_L (μg L^{-1})	1.5
Precision, RSD, % (n=9)	2.7 (at 40.0 μg L^{-1})
Regression equation (10 standards; n=5; [Pb] in μg L^{-1})	A=(0.0013 ± 0.0001) [Pb(II)]+ (0.0020 ± 0.0080)
Correlation coefficient (r)	0.9987

Table 3
Analytical results for lead determination in CRMs using SI-CC-LLME method.

CRM	Certified value	Units	Found*	Recovery (%)	t_{exp}
CRM 1643e (Trace element water)	19.63 ± 0.21	$\mu g\ L^{-1}$	18.8 ± 0.8	95.8	1.797
BCR 278-R (Mussel tissue)	2.00 ± 0.04	$mg\ kg^{-1}$	1.94 ± 0.15	97.0	0.693

* Mean value $\pm$ standard deviation based on three replicates; $t_{crit.}=4.30$ at 95% probability level.

stable in the range of $0.5–1.0 \times 10^{-2}$ mol L^{-1} HNO_3. Thus, the sample and standard solutions were fixed at 1.0×10^{-2} mol L^{-1} HNO_3 for further experiments. This is the recommended value of acidity for aqueous sample maintenance according to standard methods.

3.4. Interference studies

The interference from common potentially co-existing ions was examined under the optimum conditions using a 40.0 μg L^{-1} Pb(II) standard solution, in order to apply the proposed SI-CC-LLME method to environmental and biological samples. Variation of the recovery higher than $\pm 5\%$ was considered as interference. The experimental results revealed that Al(III), Cr(III), Cr(IV), Cu(II), Co(II), Fe(II), Fe(III), Mn(II), Ni(II) and Zn(II) could be tolerated at concentrations at least up to 2 mg L^{-1}, while Cd(II) and Hg(II) at concentrations up to 1.0 mg L^{-1}. Alkaline and alkaline-earth metals such as Ca(II), Mg(II), Ba(II), Na(I) and K(I) and some common anions like SO_4^{2-}, NO_3^- and HCO_3^- could be tolerated at concentrations up to 500 mg L^{-1}. In addition, NaCl did not cause any interference at concentrations up to 35 g L^{-1} which means that the method could be applied to the analysis of seawater samples.

3.5. Analytical performance and applications

The analytical figures of merit of SI-CC-LLME method for FAAS determination of lead under selected experimental conditions are presented in Table 2. The calibration graph was linear in the range of 5.0–280 μg L^{-1} with a good correlation coefficient (r) of 0.9987. The limit of detection (c_L), defined as 3s criterion (3 times the standard deviation of the blank solution measurements divided by the slope of the corresponding calibration curve), was 1.5 μg L^{-1}. The precision of the method, expressed as relative standard deviation (RSD), was 2.7% at 40.0 μg L^{-1} Pb(II) concentration level. For 6 mL sample consumption, the sampling frequency was 13 and the enhancement factor, defined as the ratio of the slopes of the calibration curves obtained with and without preconcentration (using aqueous standard solutions), was 130.

In order to estimate the accuracy of the SI-CC-LLME method for lead determination, two standard reference materials (NIST CRM 1643e and BCR 278-R) were analyzed. Student t-test was used to examine the statistically significant differences between the certified values and the obtained results. The measured concentrations and t_{exp}, values for lead determination are given in Table 3. Since all t_{exp}, values were lower than the $t_{crit,\ 95\%}=4.30$, no statistically significant differences were found at the 95% probability level. Due to the environmental significance of lead, representative samples of costal seawater and ditch water were analyzed to examine the applicability of the proposed SI-CC-LLME method in similar type of samples. The corresponding results are presented in Table 4. The recovery was investigated by spiking the samples with standard amount of lead before any pretreatment. The recoveries ranged between 95.0% and 102.4%, confirming the good performance of the method.

Table 4
Analytical results of lead determination in spiked environmental water samples by the SI-CC-LLME method.

Sample	Added*	Found*	R (%)
Ditch water	–	5.6 ± 0.4	–
	10.0	15.1 ± 0.9	95.0
	50.0	54.5 ± 2.8	97.8
Coastal seawater	–	$< c_L$	–
	10.0	9.6 ± 0.7	96.0
	50.0	51.2 ± 2.1	102.4

* Concentration in μg L^{-1}, mean value $\pm$ standard deviation ($n=5$); R, recovery.

4. Conclusions

In the present work, countercurrent extraction has been employed for the first time in an automatic on-line solvent extraction system. A novel flow through extraction chamber was designed and constructed for the countercurrent extraction facilitating the use of organic solvents heavier or lighter than water. A versatile SI-CC-LLME platform coupled with FAAS was developed and optimized for metal determination. The system requires very low volumes of organic solvent providing an environmentally friendly method, following the requirements of green analytical chemistry. The effectiveness and efficiency of the proposed SI-CC-LLME system was successfully demonstrated for lead determination and applied to environmental samples.

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