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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 $1.5 \mu\text{g L}^{-1}$ and the precision of the method, expressed as relative standard deviation (RSD) was 2.7% at $40.0 \mu\text{g L}^{-1}$ Pb(II) concentration level. The proposed method was evaluated by analyzing certified reference materials and spiked environmental water samples.

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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 HNO₃ (Merck Titrisol) to the required sub µg L⁻¹ levels with water. The aqueous solution of 0.5% m/v ammonium diethyldithiophosphate DDDPA (Aldrich, www.sigmaaldrich.com/european-export.html) was freshly prepared by dissolving the appropriate amount of DDDPA 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 HNO₃–HClO₄–H₂O₂ 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 coastal seawater and ditch water from the industrial area of Northern Greece region. The collected samples were acidified to 0.01 mol L⁻¹ HNO₃ (ca. pH 2) with dilute HNO₃ 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

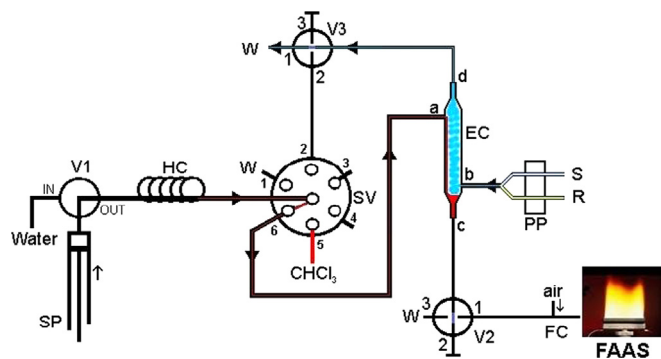


Fig. 1. Illustration of the SI-CC-LLME system coupled with FAAS for lead determination. SP, syringe pump; V1, 2-port valve; V2, V3, 3-port valves; HC, holding coil; SV, 6-port selection valve; EC, extraction chamber; FC, flow compensation unit; PP, peristaltic pump; a, b, c, d, inlet/outlet ports.

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/cft/tees.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.

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