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# On-line liquid phase micro-extraction based on drop-in-plug sequential injection lab-at-valve platform for metal determination☆

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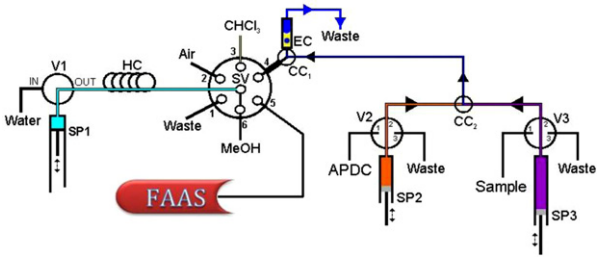
## HIGHLIGHTS

- Drop-in-plug micro-extraction based on SI-LAV platform for metal preconcentration.
- Automatic liquid phase micro-extraction coupled with FAAS.
- Organic solvents with density higher than water are used.
- Lead determination in environmental water and urine samples.

## GRAPHICAL ABSTRACT

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## ABSTRACT

A novel automatic on-line liquid phase micro-extraction method based on drop-in-plug sequential injection lab-at-valve (LAV) platform was proposed for metal preconcentration and determination. A flow-through micro-extraction chamber mounted at the selection valve was adopted without the need of sophisticated lab-on-valve components. Coupled to flame atomic absorption spectrometry (FAAS), the potential of this lab-at-valve scheme is demonstrated for trace lead determination in environmental and biological water samples. A hydrophobic complex of lead with ammonium pyrrolidine dithiocarbamate (APDC) was formed on-line and subsequently extracted into an 80 μL plug of chloroform. The extraction procedure was performed by forming micro-droplets of aqueous phase into the plug of the extractant. All critical parameters that affect the efficiency of the system were studied and optimized. The proposed method offered good performance characteristics and high preconcentration ratios. For 10 mL sample consumption an enhancement factor of 125 was obtained. The detection limit was 1.8 μg $L^{-1}$ and the precision expressed as relative standard deviation (RSD) at 50.0 μg $L^{-1}$ of lead was 2.9%. The proposed method was evaluated by analyzing certified reference materials and applied for lead determination in natural waters and urine samples.



## 1. Introduction

Complex matrices of the samples and the very low concentration of the analytes are still the main limitations for direct instrumental chemical analysis [1]. Liquid–liquid extraction (LLE) is a powerful and commonly used sample pretreatment technique for preconcentration and/or separation, which is included in many standard analytical methods especially for determination of metal and metalloids [2]. In batch operation, LLE is time consuming, tedious and laborious and has a number of severe restrictions, since it requires large amounts of toxic organic solvents, which are often dangerous and expensive.

Over the last few decades, there is an increasing necessity for the development of environmental friendly analytical methods. The aim of green analytical chemistry (GAC) is to reduce the amount of toxic solvents and reagents employed. Toward this direction, automatic and miniaturized analytical techniques

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have contributed significantly [3]. The progress toward greener extraction methods has led to remarkable reductions in the volume of organic solvents using various micro-extraction techniques based on solvent extraction as is presented in the literature [4,5]. Miniaturization of conventional LLE has led to some new liquid phase micro-extraction (LPME) methodologies such as single-drop microextraction (SDME) [6,7], hollow-fiber liquid phase micro-extraction (HF-LPME) [8], dispersive liquid–liquid micro-extraction (DLLME) [9,10] and solidified floating organic drop (SFO) [11] micro-extraction, which offer great reduction of organic solvents and increased sensitivity, due to the high ratio of donor to acceptor phase. The significance of these advantages is felt more in metal determination due to the increasingly enhanced demands for lower detection limits, and also due to the need for high sample throughput which is necessary in routine analysis.

In 1996, Liu and Dasgupta [12] presented the first on-line miniaturized solvent extraction system, the so-called "drop-in-drop", where a micro-drop of chloroform was immersed into a larger flowing aqueous drop to accomplish the extraction of ion-paired species. The evolution of this work was the single drop micro-extraction (SDME) technique where a droplet of an immiscible organic solvent was suspended at the tip of a syringe needle and immersed into the aqueous sample. The developments and advantages of this highly promising task, including applications and relative considerations, have been discussed in some comprehensive reviews [2,13].

It is important to emphasize that although many articles have been devoted to the SDME system, only a few have dealt with the automation of SDME approach. In 2008, Pena *et al.* [14] combined the direct immersion-SDME technique with SIA for accurate and precise manipulation of sample and reagent, and ETAAS for chromium determination. A 3 μL micro-drop of toluene was suspended at the tip of a high-precision micro-syringe operated in manual mode. Recently, Anthemidis et al. [15] presented a completed automatic sequential injection single-drop micro-extraction (SI-SDME) system coupled with electrothermal atomic absorption spectrometry (ETAAS) for metal preconcentration/determination in water samples. A glass capillary tube with thick walls (0.15 mm i.d./4.5 mm o.d.), placed into a flow-through micro-extraction cell, proved to be the most appropriate means for organic solvent drop suspension due to the hydrophobic and hydrophilic nature of the solvent and glass respectively. It should be noted that, this system was convenient for organic solvents lighter than water. However, to the best of our knowledge, on-line SDME systems in automatic mode, adopting organic solvents heavier than water, have not been reported in the literature up to date.

Sequential injection analysis (SIA) has been evolved to miniaturization by Ruzicka who proposed the lab-on-valve (LOV) format in which an integrated micro-conduit is placed on the top of the selection valve of a SIA system to incorporate and handle all the necessary unit operations required for a given assay, which acts as a small laboratory, hence the name LOV [16]. Lab-at-valve (LAV) is another simple approach of SIA, firstly introduced by Grudpan's group [17,18], which becomes an alternative cost effective micro total analysis system. SIA-LAV uses a designed LAV component that can be constructed using an ordinary less precise machine tool, to have a suitable function for chemistry of interest and can be easily attached at a port of the multiposition selection valve in a usual way. This simpler approach was successfully demonstrated for online LLE based on flow reversal and the subsequent separation of the aqueous and organic phases in a conical separation chamber of the LAV unit attached to one port of the valve [18].

The aim of the present work was to develop a novel on-line LPME system, based on drop-in-plug micro-extraction, using a SI-LAV manifold for metal determination by flame atomic absorption spectrometry (FAAS). For this purpose, a newly designed flow-through micro-extraction chamber (EC), which was assembled at one port of the selection valve, was fabricated and optimized using only low cost commercially available components without any need for special LOV units. Another noteworthy feature of the proposed system is that water- immiscible organic solvents that are heavier than water are employed as extractants for the first time in such automatic micro-extraction systems. The effectiveness and efficiency of the developed system were demonstrated for lead determination using chloroform ($CHCl_3$) as extraction solvent.

## 2. Experimental

### 2.1. Reagents

All chemicals and solutions were prepared from analytical reagent grade and provided by Merck (Darmstadt, Germany, http://www.merck.de). Ultra-pure quality water throughout from a Milli-Q system (Millipore, Bedford, USA, http://www.millipore.com) was used throughout the work. All glassware were rinsed with distilled water, decontaminated for at least 24 h in 10% (v/v) nitric acid solution and rinsed again five times with ultra-pure water. The working standard solutions were prepared 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 acidity of the standard solutions and samples solutions was set by the addition of dilute $HNO_3$ of the appropriate concentration. The solution of the chelating agent, 0.4% m/v ammonium pyrrolidine dithiocarbamate (APDC), was prepared daily by dissolving the appropriate amount of APDC (Aldrich, www.sigmaaldrich.com/european-export.html) in ultra-pure water without any further purification. All organic solvents were previously saturated with ultra-pure water.

### 2.2. Certified reference materials and samples

The accuracy of the developed method was estimated by analyzing the following standard reference materials (CRM): 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. Natural water samples such as lake and costal seawater were collected from the Northern Greece region. They were filtered through 0.45 μm membrane filters, 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 determine the "dissolved metal" fraction with the proposed method. A urine sample (200 mL) was taken from a young healthy person. Mussel tissue and urine samples were digested using concentrated $HNO_3$. The digestion procedure was carried out at 130–140 °C in a stainless-steel pressurized bomb. The digestion parameters were selected according to the recommendations of the manufacturer. After cooling the system, the digests were properly diluted in ultra-pure water and used for the analysis.

### 2.3. Apparatus

A FIAlab®-3000 sequential injection (SI) system (Alitea FIAlab, USA) equipped with an internal incorporated six-port multiposition 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 microsyringe pumps (MicroCSP-3000, FIAlab Instruments, Bellevue, WA) SP2 and SP3, with a total capacity of 2.5 and 5.0 mL, equipped with a three-position Teflon/Kel-F valve each at the top of them, were employed to deliver the complexing reagent and sample solution respectively. The FIAlab®-3000 SI system and the