



Development of a sequential injection dispersive liquid–liquid microextraction system for electrothermal atomic absorption spectrometry by using a hydrophobic sorbent material: Determination of lead and cadmium in natural waters

Aristidis N. Anthemidis*, Kallirroy-Ioanna G. Ioannou

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

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ABSTRACT

A novel on-line sequential injection (SI) dispersive liquid–liquid microextraction (DLLME) system coupled to electrothermal atomic absorption spectrometry (ETAAS) was developed for metal preconcentration in micro-scale, eliminating the laborious and time consuming procedure of phase separation with centrifugation. The potentials of the system were demonstrated for trace lead and cadmium determination in water samples. An appropriate disperser solution which contains the extraction solvent (xylene) and the chelating agent (ammonium pyrrolidine dithiocarbamate) in methanol is mixed on-line with the sample solution (aqueous phase), resulting thus, a cloudy solution, which is consisted of fine droplets of xylene, dispersed throughout the aqueous phase. Three procedures are taking place simultaneously: cloudy solution creation, analyte complex formation and extraction from aqueous phase into the fine droplets of xylene. Subsequently the droplets were retained on the hydrophobic surface of PTFE-turnings into the column. A part of 30 μL of the eluent (methyl isobutyl ketone) was injected into furnace graphite for analyte atomization and quantification. The sampling frequency was 10 h^{-1} , and the obtained enrichment factor was 80 for lead and 34 for cadmium. The detection limit was 10 ng L^{-1} and 2 ng L^{-1} , while the precision expressed as relative standard deviation (RSD) was 3.8% (at $0.5 \mu\text{g L}^{-1}$) and 4.1% (at $0.03 \mu\text{g L}^{-1}$) for lead and cadmium respectively. The proposed method was evaluated by analyzing certified reference materials and was applied to the analysis of natural waters.

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1. Introduction

Modern trends in analytical chemistry are towards the simplification and miniaturization of sample preparation procedures as well as the minimization of solvent and reagent consumption [1,2]. Unconventional liquid–liquid extraction (LLE) methodologies have been arisen like: single drop microextraction (SDME) [3–5], wetting film extraction (WFE) [6], cloud point extraction (CPE) [7,8] and dispersive liquid–liquid microextraction (DLLME) [9–12].

DLLME is a miniaturized sample pretreatment technique based on a ternary component solvent system where the dispersion of the fine droplets of the extraction solvent is accomplished within the aqueous phase [13–15]. Consequently, vigorous shaking or mixing is not necessary. The principal advantage of DLLME is that the surface area between extraction solvent and aqueous sample initially is infinitely large, thus the equilibrium state is achieved quickly and the extraction time is very short. However, when

DLLME is performed in manual mode, is limited to a small number of extraction solvents (carbon tetrachloride, chlorobenzene and chloroform), since it is critical the extraction solvent to be heavier than water, in order to form stable cloudy solution capable of being separated by centrifuging [2]. In addition, the phase separation with centrifugation is a time consuming procedure including inherent problems of low precision. The principles and the applications of this new procedure have been reviewed recently by Bosch-Ojeda and Sanchez-Rojas [16] and Zang et al. [17].

The important role of flow injection (FI) and sequential injection (SI) techniques for automation, acceleration and miniaturization of solution handling in sample pretreatment has been well demonstrated [18].

Recently, an on-line sequential injection dispersive liquid–liquid microextraction (SI-DLLME) system for DLLME has been presented for metal preconcentration and determination using flame atomic absorption spectrometry (FAAS) [10] solving the above problems.

Electrothermal atomic absorption spectrometry (ETAAS) is an extremely sensitive technique capable for trace determination of many metals in various types of samples, however matrix

* Corresponding author. Tel.: +30 2310 997826; fax: +30 2310 997719.
E-mail address: anthemid@chem.auth.gr (A.N. Anthemidis).

Table 1
Graphite furnace temperature program for lead and cadmium determination in 30 μL of MIBK, without modifier.

Step	Temperature ($^{\circ}\text{C}$)		Ramp time (s)		Hold time (s)		Argon flow-rate (mL min^{-1})
	Pb	Cd	Pb	Cd	Pb	Cd	
Preheating	110	90	10	5	10	10	250
Drying	250	110	5	10	20	20	250
Pyrolysis	850	350	5	20	20	40	250
Atomization	1800	2200	0	0	5	5	0
Cleaning	2100	2400	1	1	3	2	250

interferences (e.g. from seawater) and/or very low analyte concentration usually cause difficulties in the direct sample analysis, requiring the use of matrix modifiers or various preconcentration techniques.

In the present work, a sequential injection on-line dispersive liquid–liquid microextraction system for electrothermal atomic absorption spectrometry (ETAAS) was developed. As far as we know, this work is the first description of combining sequential injection analysis (SIA), DLLME and ETAAS. For this purpose, an intelligent interface was developed using a column packed with PTFE-turnings for extraction solvent separation instead of the batch centrifuging. The effectiveness and efficiency of the proposed FI solvent extraction system were demonstrated for lead and cadmium determination in water samples, due to their high toxicity even in extremely low concentrations. The factors affecting the efficiency of microextraction were studied thoroughly. The developed method was successfully applied to environmental water samples and certified reference material.

2. Experimental

2.1. Instrumentation

A PerkinElmer, Norwalk, CT, USA (<http://las.perkinelmer.com>) model 5100 PC atomic absorption spectrometer with Zeemann effect background correction and a transversely heated graphite tube atomizer (THGA), equipped with AS-71 furnace auto-sampler and a circulating cooling unit, were employed throughout measurements. Pyrolytically coated THGA graphite tubes (PerkinElmer) with integrated L'vov platform were used. A cadmium and lead electrodeless discharge lamp (EDL) were used as light source operated at 10 W and 5 W respectively. The slit was set at 0.7 nm, while the wavelength was set at 283.3 nm and 228.8 nm resonance line for lead and cadmium respectively. The graphite furnace temperature program for Pb and Cd determination in the MIBK is summarized in Table 1. Two preheating/drying steps were necessary for gradual drying of the organic solvent. Argon 99.996% was used as purge and protective gas. Integrated absorbance (peak area) was used exclusively for signal evaluation.

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 1000 μL was adopted. The FIALab[®]-3000 system was controlled by a personal computer and the FIALab for windows v. 5.9.245 application software, written by FIALab instruments (<http://www.flowinjection.com>). Two computers were used to communicate with the FIALab[®]-3000 and the ETAAS 5100 PC, while the complete system was commanded by the computer that controlled the SIA system, as it has been reported elsewhere [19]. Thus, the computer used to operate the 5100 PC was made a 'slave' of the computer that was operating the FIALab[®]-3000 system.

The SI manifold and its operation for on-line sequential injection dispersive liquid–liquid microextraction (SI-DLLME) combined with ETAAS are presented schematically in Fig. 1.

The micro-column for retention of the extraction solvent, which includes the derivative chelate complex of metal with ammonium pyrrolidine dithiocarbamate (M-APDC), was fabricated by firmly packing 180 mg of PTFE-turnings in a piece of narrow PTFE tube (40 mm length, 2.1 mm i.d./3.2 mm o.d.). PTFE-turnings were mechanically produced in our laboratory by lathe as described elsewhere [20]. The performance of the column was stable during all experiments (over 1000 cycles).

A VICI AG (Valco International) three-section "Tee" type confluence connector (CC) made of PEEK, with 0.5 mm i.d. bore size was used for mixing of sample and disperser solution.

2.2. Reagents and samples

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>).

Stock standard solution (1000 mg L^{-1} in 0.5 mol L^{-1} HNO_3) of Cd(II) and Pb(II) were obtained from Merck Titrisol. Working standard solutions were prepared by appropriate stepwise dilution of the stock standard solution. Ammonium pyrrolidine dithiocarbamate (APDC) solution (0.2%, m/v) was prepared daily by dissolving an appropriate amount of APDC (Aldrich) in methanol. Methyl isobutyl ketone (MIBK) was previously saturated with ultra-pure water.

All glassware were rinsed with ultra-pure water, decontaminated for at least 24 h in 10% (v/v) nitric acid solution and rinsed again five times with ultra-pure water.

Natural water samples were filtered through 0.45 μm membrane filters and acidified to ca. 0.01 mol L^{-1} HNO_3 (pH \sim 2).

2.3. Procedure

The operation sequences of the on-line SI dispersive liquid–liquid microextraction method for lead and cadmium determination by ETAAS (SI-DLLME-ETAAS) are summarized in Table 2.

In steps 2 and 3 segments of air and disperser solution (methanol containing 2.0% (v/v) xylene and 0.2% (m/v) APDC) at volumes of 5 μL and 910 μL respectively were aspirated into the holding coil (HC). In step 4 (Fig. 1a), the multi-position valve (MV) was moved at port 4 and peristaltic pump (P) was activated for 90 s, transporting sample solution into the micro-column (C) through the confluence connector (CC). In the same time syringe pump (SP) was dispensing a part (900 μL) of the disperser solution through the CC. By this procedure, the disperser solution was injecting into the moving sample solution, resulting thus a cloudy solution of fine droplets of extraction solvent (xylene). Under the above conditions the metal complexes were extracted continuously from aqueous phase to organic phase (xylene cloud). The extraction procedure performed for 90 s (extraction time). The xylene fine droplets (cloud) containing the metal complexes were retained on the PTFE-turnings into the micro-column (C).

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