



Combination of dispersive liquid–liquid microextraction and multivariate optimization for separation–enrichment of traces lead by flame atomic absorption spectrometry



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ABSTRACT

This work presents a method for the preconcentration of lead using dispersive liquid–liquid microextraction. 2,2' Dithiobis (benzothiazole) was used as the chelating agent, and chloroform was selected as the extraction solvent. Parameters such as: pH, volume of ligand, volume of extraction solvent and dispersive solvent volume affecting on the extraction efficiency of method has been evaluated by Plackett–Burman design. The limit of detection and limit of quantification were $4.3 \mu\text{g L}^{-1}$ and $14.2 \mu\text{g L}^{-1}$, respectively. The accuracy of the method was evaluated by analyzing certified reference materials. Method was applied to the determination of lead in water samples.

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Introduction

Lead is one of the most ubiquitous elements in the environment and recognized as a major health risk to human metabolism [1–3]. Lead was classified as human carcinogen by the U.S. Environmental Protection Agency (EPA) [4]. Because of the health risk of the lead on human metabolism, the analysis of lead in water, food biological and environmental samples is an important part of public health studies [5–9]. Despite the increasing development of instrumental methods of analysis, direct determination of trace lead in complex matrices, is difficult due to the lack of sensitivity and selectivity. Hence the accurate and precise determination of lead concentration in real samples is one of the main parts of analytical chemistry [10–12]. A variety of techniques requiring expensive instrumentation have been applied for the determination of lead [13–16]. In contrast, flame atomic absorption spectrometry is distinguished by its low cost and the simplicity of its apparatus [17–22].

The recent trends of modern analytical chemistry following the requirements of green analytical chemistry (GAC) [23–25] have led to remarkable minimization of organic solvent, reagent and sample

consumption, cost and secondary waste. Microextraction techniques taking into account the advantages of green analytical chemistry (GAC) such as dispersive liquid–liquid microextraction (DLLME) [26,27], hollow-fiber liquid phase microextraction (HF-LPME) [28] and single-drop microextraction (SDME) [29] have been developed by scientists. Thus, since their introduction, liquid phase microextraction methods have been frequently used for the determination of organic and inorganic contaminants in liquid samples [26,30].

Several means of optimization can be used for the preconcentration techniques, but these methods are time-consuming, because they required the study of each variable separately. In contrast, procedures involving optimization by multivariate techniques have been increasingly used as they are effective, simple, faster and more economical and allow more than one variable to be optimized simultaneously [30]. Among the different groups of multivariate techniques, Plackett–Burman designs (PBDs), allow us to find the most significant variables for a certain system with only few experiments [30,31]. But the optimum value for each parameter cannot be found. Central composite design (CCD) is frequently used to optimize the significant factors for analytical procedure using k factor experiments [30,32].

According to our literature survey, the combination of DLLME, microsampling FAAS and multivariate optimization was used first time in the literature for the preconcentration–separation of

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lead(II) as 2,2' dithiobis (benzothiazole) chelates for the determination of traces lead in natural water samples from Turkey.

A new dispersive liquid liquid microextraction combined with microsampling flame atomic absorption spectrometry method (DLLME-FAAS) was developed for determination and extraction of lead in water samples.

Experimental

Apparatus

A Perkin Elmer 3110 flame atomic absorption spectrometer (Norwalk, CT, USA) equipped with lead hollow cathode lamp was used for absorbance measurements at wavelength of 283.3 nm according to the instrument instruction. The lead concentration in extraction phase extractant phase was measured by using the FAAS continuous aspiration mode. In this system, 100 μL of the extraction phase injected into the FAAS nebulizer by using a home-made microsample introduction system consist of Teflon funnel and Eppendorf pipette and the peak height was measured [33,34]. A centrifuge ALC PK 120 Model (Buckinghamshire, England) was used for centrifuging. All pH measurements were carried out using a Sartorius PT-10 digital pH meter (Germany) equipped with a combined glass-electrode.

Reagents and solutions

All used chemicals were of analytical-reagent grade and all solutions were prepared with ultra pure water (Millipore Milli-Q system 18 $\text{M}\Omega\text{ cm}^{-1}$ resistivity). Ethanol, methanol, dimethyl formamide, acetone, acetonitrile, chloroform, dichloromethane and carbon tetrachloride were obtained from Merck (Darmstadt, Germany). 2,2' Dithiobis(benzothiazole) solution (0.3%, m/v) was prepared weekly by dissolving 0.3 g in 100 mL dimethyl formamide and was stored in the dark.

1000 mgL^{-1} Pb(II) of stock standard solution was prepared by dissolving nitrate salt of lead (E. Merck, Darmstadt, Germany). TMDA-64.2 Water, TMDA-53.3 (National Water Research Institute, Ontario, Canada) and SPS-WW2 Waste water (Spectrapure Standards AS, Oslo, Norway) certified reference materials were used.

DLLME procedure

10 mL of sample solution containing 50 μgL^{-1} of Pb(II), 2 mL of pH 7.0 phosphate buffer solution and 250 μL of 0.3% m/v of 2,2' dithiobis (benzothiazole) solution with adjusted pH 7.0 was placed in a 50 mL conical-bottom centrifuge tube. Then 0.5 mL of ethanol (dispersive solvent) containing 200 μL of chloroform (CHCl_3) (extraction solvent) was injected rapidly into the sample solution. A cloudy solution consists of water, chloroform and ethanol was formed in the test tube. In this step, lead ions complexed with 2,2' Dithiobis (benzothiazole) extract into the fine droplets of chloroform. The mixture was then centrifuged for 5 min at 4000 rpm. The volume of the sedimented extraction phase (chloroform) was determined using a micropipette. The sedimented phase was quantitatively transferred to another test tube and its volume completed to 300 μL with ethanol. For the measurement step, 100 μL of the extraction phase aspirated into the Flame AAS nebulizer by using a home-made microsampling introduction system explained Section 2.1 and the peak height was measured.

Procedure for lead determination in water samples

Samples of tap water, dam water and river water were collected from Kayseri, Turkey. Waste water samples were taken from

organized factory area in Kayseri, Turkey. Dem water sample was taken from Ankara, Turkey. Before use, each water samples were filtered through a cellulose membrane filter of 0.45 μm (Millipore) and subjected to the proposed method given in Section 2.3.

Results and discussion

There are several analytical factors such as the type and volume of extraction and dispersive solvents, pH of sample solution, the amount of ligand and sample volume that affect the extraction procedures. As an initial step, through the factorial design the suitable pair of extraction and dispersive solvents was selected out of several accessible solvents.

A Plackett–Burman design was applied to determine the main effects. Central composite design was used to optimize the preconcentration of Pb(II) by dispersive liquid–liquid microextraction. The factors studied were given Table 1 as low (–) and high (+) levels. For this purpose, A Minitab Version 5.1 (release 13 of MINITAB) computer programme at two levels with $2^4 = 16$ experiments for full factorial designs was carried out to eliminate the effects of extraneous or insignificant variables. The obtained recovery results were shown Table 2. Then, central 2^{3+} star, orthogonal composite design and Statistica computer program 2007 was applied for the development of interaction between factors and optimal conditions for the screening of three important factors, i.e., pH, chloroform volume, and ligand volume. The obtained results were given in Table 3.

Selection of extraction and dispersive solvents

Extraction solvent should have special properties such as low solubility in water, high efficiency in the extraction of the analyte and higher density rather than water [26]. Moreover, after centrifuge step, extraction solvent should produce settled phase in appropriate amounts. According to these criteria, CHCl_3 , CCl_4 and CH_2Cl_2 were tested as the extraction solvents. The recoveries obtained for CHCl_3 , CCl_4 and CH_2Cl_2 were 99%, 51% and 36%, respectively. Hence, CHCl_3 was selected as extraction solvent in subsequent experiment.

Dispersive solvent must be miscible in both aqueous and extractant phase and should have good dispersive ability [26]. Hence, Ethanol, methanol, dimethyl formamide, acetone, and acetonitrile were selected as dispersive solvents and the effect of these solvents on the recovery of lead was investigated. The results indicated that the maximum recovery was achieved by using ethanol as dispersive solvent (Fig. 1). Thus, CHCl_3 -ethanol as extraction-dispersive solvents pair was used for the further steps.

Optimization of parameters

In the suggested DLLME-FAAS method, four factors (pH (pH), volume of extraction solvent (EV), volume of dispersive solvent (DV) and volume of 0.3% m/v of ligand (LV)) were selected to optimize the % recovery of Pb(II) as analytical responses by Plackett–Burman design. The experiments were carried out with

Table 1
Experimental variable and levels used for the Plackett–Burman design in the factorial design for Pb(II).

Variables	Symbols	Low (–)	High (+)
pH	pH	3.0	7.0
Volume of extraction solvent, μL	EV	50	300
Volume of ligand, μL	LV	50	300
Volume of dispersive solvent, μL	DV	500	2000

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