

COMBINATION OF FLAME ATOMIC ABSORPTION SPECTROMETRY WITH LIGANDLESS-DISPERSIVE LIQUID-LIQUID MICROEXTRACTION FOR PRECONCENTRATION AND DETERMINATION OF TRACE AMOUNT OF LEAD IN WATER SAMPLES

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ABSTRACT. A new ligandless-dispersive liquid-liquid microextraction method has been developed for the separation and flame atomic absorption spectrometry determination of trace amount of lead(II) ion. In the proposed approach 1,2-dichlorobenzene and ethanol were used as extraction and dispersive solvents. Factors influencing the extraction efficiency of lead, including the extraction and dispersive solvent type and volume, pH of sample solution, concentration of chloride and extraction time were studied. Under the optimal conditions, the calibration curve was linear in the range of 7.0-6000 ng mL⁻¹ of lead with R² = 0.9992 (n = 10) and detection limit based on three times the standard deviation of the blank (3S_b) was 0.5 ng mL⁻¹ in original solution. The relative standard deviation for eight replicate determinations of 1.0 µg mL⁻¹ lead was ±1.6%. The high efficiency of dispersive liquid-liquid microextraction to carry out the determination of trace amounts of lead in complex matrices was demonstrated. The proposed method has been applied for determination of trace amounts of lead in water samples and satisfactory results were obtained. The accuracy was checked by analyzing a certified reference material from the National Institute of Standard and Technology, Trace elements in water (NIST CRM 1643e).

KEY WORDS: Dispersive liquid-liquid microextraction, Lead determination, Preconcentration, Ligandless, Water analysis

INTRODUCTION

Lead mainly in inorganic form is used in a variety of products, but recently its impact as a major environmental pollutant was recognized. It virtually affects every system in the body. Blood lead levels as low as 100 µg L⁻¹ are associated with adverse health effects in children [1]. The World Health Organization (WHO) recommended a limit of 10 µg L⁻¹ of lead in drinking water [2], which requires a very sensitive measurement technique.

Currently, the most common analytical methods for lead trace determination are flame atomic absorption spectrometry (FAAS) [3, 4], electrothermal atomic absorption spectrometry (ET-AAS) [5], inductively coupled plasma atomic emission spectrometry (ICP-AES) [6] and inductively coupled plasma-mass spectrometry (ICP-MS) [7].

However, aforementioned methods except FAAS involve a greater cost and increased instrumentation complexity; consequently, their widespread application to routine analytical works was limited. FAAS is still being used because it combines a fast analysis time, a relative simplicity and a cheaper cost. Nevertheless, detection of metal trace elements in aqueous samples is difficult due to various factors, particularly their low concentration and the matrix effects [8]. Therefore, to determine trace amounts of Pb²⁺ ions in aquatic environments by FAAS, a preconcentration technique is usually required.

Recently, Anthemidis and Ioannou [9, 10] successfully applied an on-line sequential injection dispersive liquid-liquid microextraction (DLLME) system to preconcentration of lead. Also, Yousefi and Shemirani [11] developed an ionic liquid-based DLLME method for determination of Pb ion. Jia and coworkers combined a DLLME with flow injection ICP-MS for

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determination of Pb(II) ion [12]. Rivas and co-workers developed a DLLME combined with ET-AAS for determination of Pb(II) ion [13]. However, ICP-MS, ICP-OES and ET-AAS involve a greater cost and increased instrumentation complexity; consequently, their widespread application to routine analytical works was limited. Also, on-line sequential injection needs an intelligent interface that may not be available in all laboratories.

Recently we reported a new DLLME method for preconcentration of silver(I) and copper(II) without addition of chelating agent [14, 15]. In the first work, Ag⁺ ion was extracted at pH 5 and in the second work, Cu²⁺ ion was extracted at pH 10. According to obtained results, the presence of large amounts of copper had no significant effect on the LL-DLLME of lead (interference-to-analyte ratios = 1000). Although silver was also extracted by this method at pH 6, no interference in the determination of lead (interference-to-analyte ratios = 100) was noted. The aim of this work was to combine ligandless-dispersive liquid-liquid microextraction (LL-DLLME) with FAAS and developing a new method for determination of trace lead in environmental samples. All main factors were investigated and optimized. The LL-DLLME method was evaluated by analyzing two certified reference material.

EXPERIMENTAL

Instrumentation

A SensAA GBC (Dandenong, Australia) atomic absorption spectrometer equipped with deuterium background correction and lead hollow cathode lamp was used for absorbance measurements at wave length of 283.3 nm. The instrumental parameters were adjusted according to the manufacturer's recommendations. The acetylene flow rate and the burner height were adjusted in order to obtain the maximum absorbance signal, while aspirating the analyte solution. A Metrohm 692 pH meter (Herisau, Switzerland) was used for pH measurements.

Reagents and solutions

All reagents were of analytical grade and purchased from Merck (Darmstadt, Germany) unless otherwise specified. The laboratory glassware was kept overnight in a 1.4 M HNO₃ solution. Before using, the glassware was washed with deionized water and dried. The stock solution of lead at a concentration of 1000 µg mL⁻¹ was prepared by dissolving appropriate amounts of Pb(NO₃)₂, in 0.2 M of HNO₃. The working reference solutions were obtained daily by stepwise dilution from stock solution. A solution of 10% NaCl (Merck) was prepared by dissolution of 10 g of NaCl in 100 mL of deionised water. The solutions of alkali metal and various metal salts (0.1% w/v) were used to study the interference of anions and cations, respectively.

LL-DLLME procedure

All standards and samples were prepared for analysis according to the following procedure. Eight mL of each sample was placed in a screw cap glass test tube with a conic bottom. To each test tube, 1 mL of 0.2 M phosphate buffer (pH 6) and 1 mL of 10% (w/v) NaCl were added. Then, 2 mL of ethanol containing 15.0 µL of 1,2-dichlorobenzene (1,2-DCB) was rapidly injected into each solution. As a result, cloudy solution (water, ethanol, and 1,2-DCB) was formed in each test tube. In this step, lead reacted with chloride ion and was extracted into the fine droplets of 1,2-DCB. Then, the solution was centrifuged at 4000 rpm for 5 min, and the dispersed fine droplets of 1,2-DCB were deposited at the bottom of conical test tube. The sediment phase was removed by using a micro syringe and sediment phase dissolved in 0.5 mL of 0.5 M HNO₃ in ethanol. The final solution was aspirated directly into the flame of AAS.

Sample preparation

For evaluating the accuracy of the proposed method, one certified reference material furnished by the National Institute of Standards and Technology, Trace elements in water (NIST CRM 1643e) has been analyzed.

All water samples were collected in acid-leached polyethylene bottles. Kerman tap water and well water samples were collected from our University (Payame Noor University, Kerman, Iran). Mineral water samples were acquired from a local market. The only pretreatment was acidification to pH 2 with nitric acid, which was performed immediately after collection. The samples were filtered before analyses through a 0.45 μm pore size cellulose membrane (Millipore).

Extraction mechanism

At first, phosphate buffer and NaCl solution were added to lead solution. In this step, lead reacted with chloride ion to form PbCl_2 , then the aqueous, dispersive and extraction solvents were mixed and a cloudy solution was formed. After formation of cloudy solution, PbCl_2 diffuses into the extraction solvent quickly, because of the infinitely large surface area between extraction solvent and the aqueous phase. Then, the solution was centrifuged and the dispersed fine droplets of 1,2-DCB were deposited at the bottom of conical test tube. The sediment phase was removed and 0.5 mL of 0.5 M HNO_3 in ethanol was added to it. The final solution was aspirated directly into the flame of AAS. The extraction scheme of Pb(II) ion is shown in equation 1.

**RESULTS AND DISCUSSION**

In this study, combination of LL-DLLME with FAAS was developed for determination of trace amounts of lead. It is based on microextraction of lead chloride with ethanol as dispersive solvent and 1,2-DCB as extraction solvent. In order to reach optimum experimental conditions for quantitative extraction of Pb(II) ions via LL-DLLME, the influence of different parameters such as the extraction and dispersive solvent type and volume, pH of sample solution, concentration of chloride and extraction time was studied. The recovery percent was calculated through Eq. 2.

$$\text{Re } \% = \frac{C_0 V_0}{C_{\text{aq}} V_{\text{aq}}} \times 100 \quad (2)$$

where C_0 and C_{aq} ($\mu\text{g mL}^{-1}$) are concentrations of Pb ion in the organic and aqueous solutions, respectively, and V_0 and V_{aq} (mL) are volumes of organic and aqueous solution, respectively.

Type and volume of disperser solvent

For the DLLME method, the dispersive solvent should be miscible with both water and the extraction solvent. Therefore, acetone, methanol, ethanol and tetrahydrofuran were tested. The

effect of these solvents on the extraction efficiency of LL-DLLME of lead was investigated using 2.0 mL of each solvent containing 15.0 μL of 1,2-DCB as the extraction solvent. The extraction efficiency of LL-DLLME for lead in acetone, methanol, ethanol and tetrahydrofuran as disperser solvents were 78.1, 92.4, 98.7 and 88.9, respectively. Due to its lower toxicity as compared to methanol, ethanol was chosen as the disperser solvent for subsequent studies.

Also, the volume of the dispersive solvent is one of the important factors in DLLME. For investigating the effect of disperser solvent volume on extraction efficiency, various volumes of ethanol (0.5-3 mL) containing 15 μL 1,2-DCB were used. The results showed that the extraction efficiency increased with increasing volume of ethanol to 1.5 mL and remained constant to 2.5 mL. Reduction in the extraction efficiency was observed after the volume of ethanol exceeded 2.5 mL. At low volumes, ethanol could not disperse 1,2-DCB properly and cloudy solution was not formed completely. Reversely, at high volumes, the solubility of analyte in water increased. Therefore, 2 mL ethanol was chosen as the optimum volume.

Type and volume of extraction solvent

The selection of an appropriate extraction solvent was very critical for DLLME process. The most important point in the course of selecting extraction solvent for DLLME was that the extraction solvent must have higher density than water. Based on these facts, variety of water immiscible organic solvents, such as dichloromethane (CH_2Cl_2), chloroform (CHCl_3), carbon tetrachloride (CCl_4) and 1,2-dichlorobenzene (1,2-DCB) were investigated as the possible extraction solvents for LL-DLLME. The results showed that, after the addition of CH_2Cl_2 and CHCl_3 not only the cloudy state was formed but also no sedimentation phase on the bottom of the test tube noted after centrifugation. It was due to higher solubility of these solvents in water than the other tested solvents.

For this purpose, 1,2-dichlorobenzene (1,2-DCB) and carbon tetrachloride (CCl_4) were studied as extraction solvents. The effect of these solvents on the extraction efficiency of lead was investigated using 2.0 mL of ethanol containing 15 μL of each solvent. The extraction efficiencies of LL-DLLME for lead in 1,2-DCB and CCl_4 as extraction solvent were 98.7 and 88.9, respectively. Therefore, 1,2-DCB was selected as extraction solvent for subsequent experiments.

Also, in order to examine the effect of the extraction solvent volume, solutions containing different volumes of 1,2-DCB (15–100 μL) were subjected to the same LL-DLLME procedure. It was observed that the extraction efficiency was constant up to 30 μL and then, by increasing the volume of 1,2-DCB from 30 to 100 μL , the extraction efficiency decreased probably due to the decrease in the ratio between the dispersive solvent and the extraction solvent. By decreasing this ratio, the number of droplets available for extraction and the extraction efficiency decreased. Based on these observations, a volume of 15 μL was used for further experiments.

Effect of pH

The effect of pH of sample solution on the LL-DLLME of lead was studied in the range of 3 to 8.5, while keeping the other variable constant. The results are shown in Figure 1 and revealed that the recovery was nearly constant in the pH range of 5.7-6.5. Therefore, pH 6 was selected for further studies. In pHs lower than 5.7, PbCl_2 could not completely be formed and extracted into extraction solvent. In pHs higher than 6.5, $\text{Pb}(\text{OH})_2$ could compete with PbCl_2 , which might prevent complete transfer into extraction solvent.

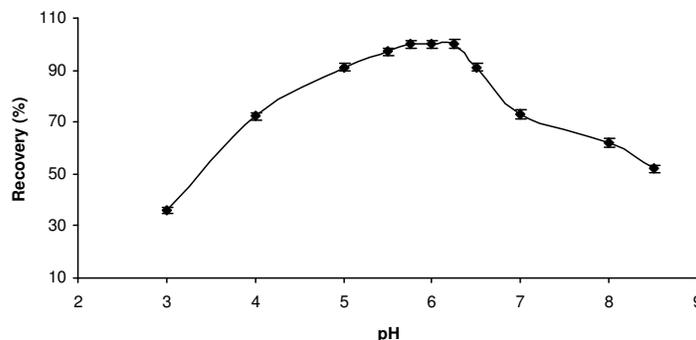


Figure 1. Effect of pH of the sample solution on the LL-DLLME extraction of lead. Conditions: Pb(II), 10.0 μg ; ethanol, 2 mL; NaCl 10%(w/v), 1 mL and 1,2-DCB, 15.0 μL .

Effect of chloride concentration

In the case of many microextraction procedures, Pb(II) ions should firstly form hydrophobic complex in the aqueous solution in order to be extracted into organic phase [14-15]. In this research, lead reacted with chloride ion for PbCl_2 formation, which then diffused into the extraction solvent quickly. Therefore, effect of chloride concentration on the LL-DLLME of lead should be studied. For this purpose, several experiments were performed by adding different amounts of NaCl ranging from 0.025 to 0.15 g, while keeping the other variable constant. The results showed that the extraction efficiency increased with increasing NaCl up to 0.1 g. Any amount in excess of 0.1 g NaCl showed no effect on the extraction efficiency. Therefore, 1 mL of 10% (w/v) NaCl was used in all further experiments.

Effect of extraction time

The extraction time was studied according to previous reports [14, 15]. The obtained results showed that the extraction time had no significant influence on the extraction. In this method, the most time-consuming step was the centrifuging of sample solution in the extraction procedure. The process took about 5 min.

Effect of foreign ions

To perform this study, diverse ions in different interference-to-analyte ratios were added to a solution containing 10.0 μg of Pb(II) and were subjected to the recommended procedure. Table 1 shows the tolerance limits of the interference ions (error $\pm 5\%$). The results demonstrate that the presence of large amounts of species commonly present in water samples have no significant effect on the LL-DLLME of lead.

Calibration, precision and detection limit

Repeatability, linearity, correlation coefficient and detection limit were investigated under the optimized experimental conditions. For a sample volume of 8.0 mL, the calibration curve exhibited linearity over the range of 7.0 ng mL^{-1} -6.0 $\mu\text{g mL}^{-1}$ with a correlation coefficient of 0.9995 ($A = 0.1646C + 0.0012$). Eight replicate determinations of 1.0 $\mu\text{g mL}^{-1}$ lead gave a mean absorbance of 0.165 with relative standard deviation of $\pm 1.6\%$. The detection limit was 0.5 ng

mL^{-1} . Enrichment factor was calculated as the ratio of the slope of calibration curve after and before microextraction step. The enrichment factor for lead was 15.5.

Table 1. Tolerance limit of foreign ions.

Foreign ions	Added as	Interference/Pb(II) ratio	Recovery (%)
PO_4^{3-}	$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	5000	96
H_2PO_4^-	$\text{K}_2\text{HPO}_4 \cdot 6\text{H}_2\text{O}$	5000	96
HPO_4^{2-}	$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$	5000	96
CH_3COO^-	CH_3COONa	1000	95
Na^+	NaCl	4000	104
K^+	KNO_3	4000	104
Ca^{2+}	CaCl_2	2000	105
Mg^{2+}	$\text{Mg}(\text{NO}_3)_2$	2000	105
Co^{2+}	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	1000	95
Cu^{2+}	$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	1000	95
Mn^{2+}	$\text{MnSO}_4 \cdot \text{H}_2\text{O}$	1000	95
Zn^{2+}	ZnCl_2	1000	95
Fe^{2+}	FeCl_2	200	95
Fe^{3+}	FeCl_3	200	95
Ni^{2+}	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	800	105
Al^{3+}	$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	50	96
Cr^{3+}	$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	600	95
Sn^{2+}	SnCl_2	700	105
Sb^{3+}	SbCl_3	500	96
Cd^{2+}	CdCl_2	500	96
Ag^+	AgNO_3	100	95

Conditions were the same as in Figure 1.

Accuracy of the method

For evaluating the accuracy of the proposed method, one certified reference material furnished by the National Institute of Standard and Technology, Trace elements in water (NIST CRM 1643e) has been analyzed. An aliquot of the certified reference material was taken and lead ion was determined by the LL-DLLME procedure. It was found that there is no significant difference at the 95% confidence level between results obtained by the LL-DLLME procedure ($19.81 \pm 0.8 \text{ ng mL}^{-1}$) and the certified value ($19.63 \pm 0.21 \text{ ng mL}^{-1}$).

Analysis of real samples

The proposed procedure has been applied to the determination of lead content in tap water, well water and two different mineral water samples. The results are given in Table 2. The recovery of lead from water samples spiked with Pb(II) samples was also studied. The results are given in Table 2. According to this Table, the added lead ion can be quantitatively recovered from the water samples by the proposed procedure. These results demonstrate the applicability of the procedure for lead determination in water samples. The recovery of lead added to the samples demonstrates the efficiency of the proposed method.

Comparison of LL-DLLME procedure with the other reported methods

A comparison of the current method with the other reported methods [16-19] is shown in Table 3. The results showed that, the enrichment factor and the detection limit obtained by the proposed method are comparable to methods reported in the literature.

Table 2. Determination of lead in water sample.

Sample	Lead amount (ng mL ⁻¹)		Recovery (%)
	Added	Found	
Tap water	0.0	7.8±0.3	----
	30.0	38.4±1.6	102
Well water	0.0	BLR [*]	----
	30.0	31.2±1.3	104
Mineral water 1	0.0	BLR [*]	----
	30.0	32.4±1.4	108
Mineral water 2	0.0	7.4±0.3	----
	30.0	37.2±1.7	99.3

^{*}Below linear range.

Table 3. Comparison of the reported methods with the proposed method.

Enrichment method	Detection method	Enrichment factor	Sample volume (mL)	Detection limit (ng mL ⁻¹)	Reference
CPE	FAAS	15.1	15	4.5	16
DLLME	FAAS	450	25	0.5	17
Coprecipitation	FAAS	125	50	16	18
LLE	FAAS	543	500	0.39	19
CPE	FAAS	50	10	8.0	20
LL-DLLME	FAAS	15.5	8	0.5	This work

CONCLUSIONS

It has been demonstrated that LL-DLLME combined with flame atomic absorption spectrometry provides a novel route for trace determination of lead in natural waters. The main benefits of the LL-DLLME methodology are minimum use of toxic organic solvents (15.0 µL of 1,2-dichlorobenzene), simplicity, low cost, enhancement of sensitivity, and rapid analysis time (maximum 10 min).

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