

DISPLACEMENT-DISPERSIVE LIQUID-LIQUID MICROEXTRACTION BASED ON SOLIDIFICATION FLOATING ORGANIC DROP TRACE AMOUNTS OF LEAD IN WATER SAMPLE PRIOR TO FLAME ATOMIC ABSORPTION SPECTROMETRY DETERMINATION

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ABSTRACT

In this study, a novel method using displacement-dispersive liquid-liquid microextraction based on solidification of floating organic drop in complicated samples prior to flame atomic absorption spectrometry determination was developed. This method involves two consecutive dispersive liquid-liquid microextraction based on solidification. In step I, Zn(II) ions reacted with ammonium pyrrolidine dithiocarbamate (APDC) to form Zn-APDC complex and was extracted with the solidified floating organic drop microextraction procedure using 1-undecanol (extraction solvent) and ethanol (dispersive solvent). In step II, after centrifugation and solidification, the separated drop was dissolved in dimethylformamide (DMF) and then dispersed into the sample solution containing lead ion and another dispersive liquid-liquid microextraction based on solidification procedure was carried out. Due to the greater stability of Pb-APDC, Pb displaces Zn from the pre-extracted Zn-APDC and preconcentration of Pb was achieved. Under the optimized conditions, the calibration curve was linear in the range of 4-700 ng mL⁻¹ with detection limit of 0.7 ng mL⁻¹ (3σ_y). The relative standard deviation of ±1.6% was obtained (n=7) and the enrichment factor was found to be 35.0.

Keywords: Displacement extraction; Lead determination; Microextraction; Preconcentration

INTRODUCTION

Lead is known to be a toxic metal that accumulates in the human body. Its cumulative poisoning effects are serious hematological damage, brain damage, anemia, and kidney malfunctioning.¹ Allowed concentrations of lead in biological samples are as low as the levels of nanogram per kilogram or nanogram per milliliter. The World Health Organization (WHO) has established provisional tolerable weekly intakes of Pb of 0.025 mg kg⁻¹ body weight for all human groups.² In 1991, the United States Environmental Protection Agency (EPA) published a regulation to control lead in drinking water, which included an action level of 0.015 mg L⁻¹.³ WHO has released guidelines for drinking water quality containing the guideline value of 0.01 mg L⁻¹ for Pb.⁴ Due to the low concentration of lead and its matrix effects in environmental samples,⁵ separation and preconcentration steps are usually required for determination of trace amount of lead. Several procedures such as liquid liquid extraction (LLE),⁶⁻⁹ co-precipitation¹⁰ and solid-phase extraction¹¹⁻¹³ have been developed for the separation and preconcentration of lead from environmental matrices. Modern trends in analytical chemistry are towards the simplification and miniaturization of sample preparation, as well as the minimization of the organic solvent used. In this regard, several novel microextraction techniques have been developed for reducing the analysis step, increasing the sample throughput and improving the quality and the sensitivity of the analytical methods. Cloud point extraction (CPE),¹⁴⁻¹⁶ homogeneous liquid-liquid extraction (HLL),^{17, 18} liquid-phase microextraction (LPME),^{19, 20} and solid-phase microextraction (SPME)²¹ are some of the newer methods of sample preparation. Recently, Dadfarnia et al.²² developed a new liquid-liquid microextraction method based on solidification of floating organic drop, which was successfully used for the separation and preconcentration of lead. Solidified floating organic drop microextraction (SFODME) is a new microextraction technique in which a small volume of an organic solvent with melting point near room temperature (in the range of 10-30 °C) is floated on the surface of the aqueous solution. The aqueous phase is stirred for a prescribed period of time and then the sample is transferred into an ice bath. When the organic solvent is solidified, it is transferred into a small conical vial, and the melted organic solvent is used for analyte determination.²³ SFODME has the advantages of simplicity, low cost, short extraction time, minimum organic solvent consumption and high enrichment factor.²⁴ Dispersive liquid-liquid microextraction based on the solidification of floating organic drop (DLLME-SFO) is a combination of DLLME and SFODME in which the extraction solvent with properties similar to that of SFODME is dispersed into the aqueous sample.²⁵

In conventional DLLME-SFO for preconcentration of metal ions, the first step is hydrophobic metal-chelate. Obviously, many ligands have little selectivity towards metal ions. In other words, competition for the complexing agent from

other co-existing transition metal ions with target analyte cannot be avoided and there may cause undesirable interferences. In fact, all metal-chelate based preconcentration systems have encountered this problem. Adding a masking agent or increasing the concentration of the complexing agent is a choice, but the effectiveness may be marginal and there is the risk of contamination. Recently, Yan et al. have successfully developed a displacement-sorption preconcentration protocol for highly selective quantification of metal ions in complicated matrices.²⁶ The principle of this technique is based on the stability difference of metal complexes. The target metal (M₁) with higher complex stability (M₁-L, L is the ligand) can replace another metal (M₂) with lower complex stability from its complex (M₂-L), whereas the reverse reaction cannot occur. Also, throughout the displacement reaction, interferences from the co-existing ions due to the competition for the ligand are largely eliminated. This displacement-sorption preconcentration method has been successfully applied for the determination of mercury in environmental and biological samples,^{27, 28} methyl mercury in fish samples,²⁹ palladium in road dusts³⁰ and silver in water samples.³¹ A displacement-cloud point extraction was also developed by employing the same principle and applied for the selective determination of silver.³² A displacement-dispersive liquid-liquid microextraction coupled with graphite furnace atomic absorption spectrometry has also been developed for the selective determination of silver.³³

In this work, the displacement reaction principle was employed in solidification of floating organic drop microextraction of metal ions, and displacement-dispersive liquid-liquid microextraction based on solidification of floating organic drop (D-DLLME-SFO) method was developed for the selective separation of lead. In this method, APDC was selected as the chelating agent and Zn(II) was employed as the pre-extraction metal ion for the best selectivity of displacement. The DLLME-SFO procedure was carried out twice during a single sample pretreatment process: firstly, Zn(II) was complexed with APDC and subjected to DLLME-SFO process. Then the solidified organic drop from the first DLLME-SFO was transferred into a small conical vial. After dissolving in DMF, it was dispersed into the sample solution containing lead ions and DLLME-SFO process was implemented for the second times. Because the stability of Pb-APDC is greater than that of Zn-APDC, Pb(II) replaces Zn(II) from the pre-extracted Zn-APDC complex and enters the extraction phase. Then the solidified solvent drop was transferred into a conical vial where it melts and was diluted with ethanol for FAAS determination.

EXPERIMENTAL

Apparatus

The lead measurements were performed with a Varian SpectrAA 220 flame atomic absorption spectrometer (Australia, <http://www.varianinc.com>)

equipped with a computer processor. A lead hollow cathode lamp, operated at 10 mA, was utilized as the radiation source. The analytical wavelength of 283.3 nm and a slit width 0.5 nm were used as recommended by manufacturers. A Metrohm 827 pH meter (model 827, Switzerland, www.metrohm.com) was used for pH measurements with a combined pH glass electrode calibrated against two standard buffer solutions at pH 4.0 and 7.0. An IEC-model HN-S centrifuge (New York, USA, <http://www.gsrtch.com/c/hns-ii.html>) was used to accelerate the phase separation.

Reagents and samples

The reagents used throughout this study were of the highest purity available and at least of analytical reagent grade. The standard stock solutions of lead ($100.0 \mu\text{g mL}^{-1}$) and zinc ($100.0 \mu\text{g mL}^{-1}$) were prepared using lead and zinc from Merck (Darmstadt, Germany). Standard solutions of lead and zinc were prepared daily by appropriate dilution of the stock solutions. 1-undecanol was obtained from Merck and used as extracting solvent. A solution of ammonium pyrrolidine dithio carbamate (APDC, 0.01% w/v) was prepared every day by dissolving an appropriate amount of APDC (99%, Merck) in double-distilled water. A solution of 10% (w/v) NaNO_3 was prepared by dissolving of 10.0 g of NaNO_3 (Merck) in 100.0 mL of double-distilled water. All vessels used for trace analysis were kept in a $1 \text{ mol L}^{-1} \text{HNO}_3$ solution for at least 24 h and washed twice with double-distilled water before they were used.

General procedure

1 mL of APDC solution and 0.6 mL of NaNO_3 (10 %) solution were added to 7.0 mL of $10.0 \mu\text{g mL}^{-1} \text{Zn(II)}$ solution. After pH adjustment at 5.0, the volume of the sample was raised to 10.0 mL in a 12 mL test tube. Then 0.5 mL of ethanol (dispersive solvent) containing 45.0 μL of 1-undecanol (extraction solvent) was rapidly injected into the sample solution using a 1.0 mL syringe. A cloudy solution was formed in the test tube and the complex of Zn(II) with APDC was extracted into fine droplets of 1-undecanol. This turbid solution was then centrifuged for 8 min at 2500 rpm leading to the aggregation of 1-undecanol as a floating drop on the surface of solution. The tube was now transferred to a beaker containing crushed ice and after 5 min; the solidified solvent drop was transferred to a conical vial where it immediately melted. The melted organic solvent was dissolved in 0.4 mL DMF and injected into the sample solution containing 0.24 mL of $10.0 \mu\text{g mL}^{-1} \text{Pb(II)}$ solution and 0.4 mL of NaNO_3 (10 %) solution. In this step, a cloudy solution was formed in which Pb replaced Zn from the pre-extracted Zn-APDC complex and entered into the extraction solvent phase. This turbid solution was also centrifuged for 8 min at 2500 rpm and then the tube was transferred to a beaker containing crushed ice. After 5 min, the solidified solvent drop was transferred into a conical vial where it melted and was diluted to 300 μL with DMF for FAAS determination.

Sample preparation

Preparation of water samples

Tap, rain and spring water samples from the Kerman and Sirjan were collected in acid leached polyethylene vials. Acidification to pH 1.0 with nitric acid was performed immediately after collection, in order to prevent adsorption of the metal ions on the vial walls. The samples were filtered before analyses through a cellulose membrane (Millipore) of 0.45 μm pore size.

Preparation of MA-1b standard samples

An accurately measured sample (500.0 mg) of gold ore sample (Canadian Certified Reference Material (MA-1b)) was dissolved completely by heating in a mixture of HNO_3 (~2 mL), HCl (~6 mL) and HF (~1 mL). To remove the excess HF the solution was evaporated to near dryness, then cooled, diluted and filtered. The volume of the filtrate was raised to 50.0 mL with distilled water in a calibrated flask.

RESULTS AND DISCUSSION

Effect of pH

The pH of pre-extraction solution (the acidity of Zn solution) influences the formation of the Zn-APDC complex, its pre-extraction and subsequent displacement extraction. So the effect of pH of Zn(II) solution on the D-DLLME-SFO of Pb was studied in pH range of 1.0 to 10.0. As can be seen in Fig. 1, the highest recovery of Pb extraction was obtained in pH range of 3.0 to 7.0. Therefore, pH of 5.0 was selected for further study. The pH of sample solution influences the stability of Pb-APDC complex and the displacement reaction. Again, the effect of the pH of sample solution on the extraction recovery of Pb was investigated in the pH range 1.5 to 9.5. The results (Fig. 1) show that the highest recovery was obtained in the pH range of 3.5 to 7.0.

Therefore, pH 5.5 was used for the sample solution in the second extraction process.

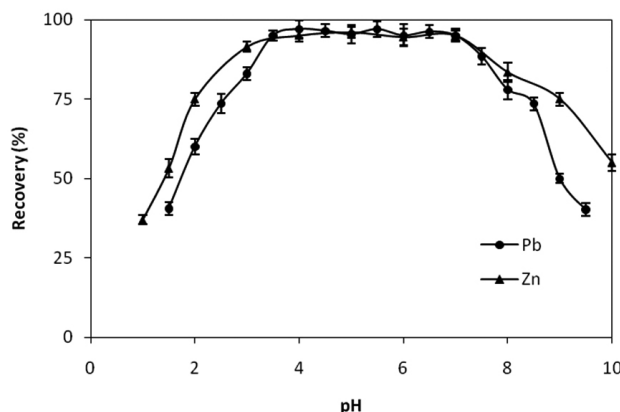


Fig. 1. Effect of pH on the extraction of $2.4 \mu\text{g}$ of Pb (II). Extraction conditions step 1: aqueous sample volume, 10 mL; APDC 0.01% (w/v), 1.0 mL; extracting solvent, 1-undecanol, 45 μL ; dispersive solvent, ethanol, 0.5 mL; amount of Zn, 7.0 mL; volume of NaNO_3 10% (w/v), 0.6 mL; centrifugation time, 8 min; Extraction conditions step 2, dispersive solvent, DMF, 0.4 mL; volume of NaNO_3 10% (w/v), 0.4 mL.

Effect of APDC amount

To examine the effect of ligand amount, different volumes of 0.01 % (w/v) APDC solution (0.4-1.3 mL) were investigated. Recovery of Pb increases with an increase in APDC volume up to 1.0 mL and then remains constant. Accordingly, 1.0 mL of 0.01 % (w/v) APDC solution was chosen as optimal volume for subsequent experiments.

Effect of Zn amount

Zn amount influences the amount of pre-extracted Zn-APDC and the subsequent displacement reaction. Different volumes of $10.0 \mu\text{g mL}^{-1}$ Zn solution were used in the first DLLME-SFO procedure and their effects on the extraction of Pb (the second DLLME-SFO procedure) were evaluated. Studies on the effect of Zn amount showed that the extraction recovery of Pb increased with the increase of Zn volume up to 7.0 mL and remained unchanged with further increase in Zn volume. For further experiments, a volume of 7.0 mL was used.

Selection of extracting solvent

The extracting solvent for DLLME-SFO should be able to form a cloudy solution in the aqueous phase. In addition, it must have a lower density than water, high extraction capability for the compounds of interest, low volatility, low water solubility and a melting point near room temperature.³⁴ Several extracting solvents, including 1-undecanol (mp 13–15 °C), 1-hexadecanethiol (mp 18–20 °C) and 2-undecanone (mp 11–13 °C) were investigated. 1-undecanol was selected because higher extraction efficiency, sensitivity, stability, lower price, low water solubility and low vapor pressure.

Effect of extraction solvent volume

In order to study the effect of the volume of the extraction solvent on the extraction efficiency, different volumes of 1-undecanol (20.0–60.0 μL) dissolved in a constant volume of dispersive solvent (ethanol, 0.5 mL) were tested. Extraction recovery increased with the increase of 1-undecanol volume up to 45 μL and then remained constant. Therefore, 45 μL of 1-undecanol was used as the extraction solvent in subsequent experiments.

Selection of disperser solvent

The miscibility of the disperser solvent in the organic phase (extracting solvent) and the aqueous phase (sample solution) is the main criterion for the selection of a disperser solvent. Several disperser solvents, including ethanol, acetonitrile, methanol and acetone were investigated for the first DLLME-SFO process. The effect of these dispersers on the extraction efficiency of D-DLLME-SFO of Pb was studied using 0.5 mL of each solvent containing 45.0 μL of 1-undecanol as the extraction solvent. The highest recoveries were obtained with ethanol; hence ethanol was selected as the optimal disperser

solvent in this process. For the second extraction process, ethanol, DMF, DMSO and acetone were used to dilute the separated drop from previous step and disperse it into Pb(II) solution. Since the highest recovery was obtained with DMF, it was selected as the optimal disperser solvent for further studies in second extraction process.

Effect of volume of the disperser solvent

After the selection of dispersive solvents for the first and second extraction processes, their volumes were also optimized. For this purpose, different volumes of ethanol in the range 0.2-0.9 mL containing 45.0 μL of 1-undecanol (as the extracting solvent) were used for the extraction of Pb ions using the D-DLLME-SFO procedure. The highest extraction recovery was obtained in the range of 0.4 to 0.6 mL. Therefore, 0.5 mL ethanol was selected for further study. In the second extraction process, the separated phase of the first extraction process was dispersed into the sample solution using DMF as the dispersive solvent. The effect of the volume of DMF on the recovery of Pb extraction was studied. The highest recovery was obtained in the range of 0.3 to 0.5 mL. Therefore, 0.4 mL DMF was selected.

Effect of salt addition

Depending on the nature of the target analytes, addition of salt to the sample solution can decrease their solubility and therefore enhance extraction efficiency due to the salting-out effect. Salting-out is a process of addition of electrolytes to an aqueous phase in order to increase the distribution ratio of a particular solute. The term also connotes reduction of mutual miscibility of two liquids by addition of electrolytes.³⁵ The effect of salt on extraction efficiency was studied by varying the volume of NaNO_3 solution (10%, w/v) in the range of 0.1–1.0 mL. The results show that the highest extraction recovery was obtained in the presence of 0.6 and 0.4 mL of NaNO_3 solution for the first and second extraction processes, respectively.

Effect of centrifugation time

Centrifugation was necessary to obtain two distinguishable phases in the extraction tubes. The effect of centrifugation time on the extraction efficiency was evaluated in the range of 4–14 min at 2500 rpm. The extraction performance reached its peak when the solution was centrifuged at 2500 rpm for 8 min. When the centrifugation time was longer than 8 min, the extraction recovery remained constant, so 8 min was chosen in the following study.

Effects of co-existing ions

In the conventional DLLME-SFO procedure,³⁶ most interference was the result of the competition of other heavy metal ions for the chelating agent and their subsequent co-extraction with the analyte. With the introduction of displacement reaction, the selectivity of displacement sorption preconcentration and displacement-cloud point extraction was largely improved. The same effect was also expected in D-DLLME-SFO method. The effects of several potentially interfering species were carefully studied. The corresponding results are compared in Table 1. Compared with the conventional DLLME-SFO method, the D-DLLME-SFO method shows an improvement in the tolerance limits of co-existing heavy metal ions. The high selectivity of the developed D-DLLME-SFO method for the determination of trace amounts Pb(II) is also clearly demonstrated.

Analytical figures of merit

The analytical figures of merit were evaluated for the determination of Pb(II) according to the recommended procedure under optimized conditions. Under optimal conditions, the calibration curve was linear from 4.0 to 700 ng mL^{-1} in the initial solution with a correlation coefficient of 0.9987 (R^2). The recommended procedure was repeated seven times for the determination of 240 ng mL^{-1} of Pb ion to obtain the relative standard deviation which was found to be $\pm 1.6\%$. The enrichment factor was 35.0 (enrichment factor (EF) = M_a/M_b , where M_a and M_b are respectively the slopes of the curves after and before preconcentration. The limit of detection, calculated as $3\sigma_b$ (σ_b is the standard deviation of the blank), was 0.7 ng mL^{-1} .

Application of the method

Application to real sample

To test the reliability of the recommended procedure, the method was applied to the determination of lead in tap, river, rain and spring water samples. For this purpose, a volume of 10.0 mL of each sample were preconcentrated with 45.0 μL of 1-undecanol according to the proposed method. The lead amounts in water samples are tabulated in Table 2.

Table 1. Tolerance limits of co-existing ion.

Ion	Tolerance limits ($\mu\text{g mL}^{-1}$)	
	Displacement D-DLLME-SFO ^a	Conventional DLLME-SFO ^b
Mn^{2+}	2000	500
Mg^{2+}	5000	4000
Co^{2+}	1000	-
Ca^{2+}	5500	4000
Al^{3+}	1000	500
Fe^{3+}	1500	500
Cr^{3+}	600	-
Bi^{3+}	1400	-
Ni^{2+}	800	-
Zn^{2+}	3000	2000
Cd^{2+}	3800	2000
Cu^{2+}	4000	2000
Br^-	1800	-
I^-	1700	-

^a APDC as complexing agent

^b 2-(5-bromo-2-pyridylazo)-5-(diethyl amino) phenol (5-Br PADAP) as complexing agent

Table 2. Determination of Pb (II) in water samples.

Sample	Found ($\mu\text{g L}^{-1}$) ^a
Rain water (Kerman)	4.68 \pm 0.08
Rain water (Sirjan)	B.L.R ^b
Tap water (Kerman)	5.20 \pm 0.07
Tap water (Sirjan)	5.83 \pm 0.09
Spring water (Sirjan)	4.10 \pm 0.06
Spring water (Kerman)	B.L.R
River water (Mahan, Kerman)	4.31 \pm 0.07
River water (Tangoyeh, Sirjan)	B.L.R

^a Mean \pm SD, n=3.

^b B.L.R: Below of linear range

Analysis of Pb in a MA-1b standard sample

The method was applied for the determination of Pb in Canadian Certified Reference Material (MA-1b) Project. An aliquot of this solution was taken and Pb was determined by the general procedure. Collective results, given in Table 3 indicate the applicability and accuracy of the D-DLLME-SFO method.

Table 3. Determination of lead ions in the Canadian Certified Reference Material.

Sample	Composition (% or $\mu\text{g g}^{-1}$)	Found ^a ($\mu\text{g g}^{-1}$)	Recovery (%)
MA-1b reference gold ore	Si; 24.5, Al; 6.11, Fe; 4.62, Ca; 4.60, K; 4.45, Mg; 2.56, C; 2.44, Na; 1.49, S; 1.17, Ti; 0.38, Ba; 0.18, P; 0.16, Mn; 0.09%, Cr; 200.0, Pb; 200.0 , Rb; 160.0, Zr; 140.0, Cu; 100.0, Zn; 100.0, Bi; 100.0, Ni; 90.0, Mo; 80.0, Te; 40.0, Co; 30.0, Y; 20.0, W; 15.0, Sc; 13.0, As; 8.0, Ag, 3.9, Sb; 3.0, Au; 17.0 $\mu\text{g g}^{-1}$	196.8 \pm 2.2	98.4

^a Mean \pm SD, n=3.

Comparison with other methods

Determination of lead in aqueous samples by the developed displacement-dispersive liquid-liquid microextraction based on solidification was compared with the other preconcentration methods used for determination of lead by flame atomic absorption spectrometry (FAAS). It is obvious from Table 4, the

limit of detection (LOD) and relative standard deviation (RSD) of D-DLLME-SFO is lower than co-precipitation-FAAS,¹⁰ off-line-SPE-FAAS,³⁷ on-line-SPE-FAAS,¹¹ CPE-FAAS,¹⁶ SPE-FAAS³⁸ and SPE-FAAS.³⁹ Moreover, this method has higher enrichment factor compared with off-line-SPE-FAAS,³⁷ SPE-FAAS¹¹ and CPE-FAAS.⁴⁰

Table 4. Comparison of the D-DLLME-SFO with other methods for preconcentration and determination of Pb.

Preconcentration/ determination method ^a	Enrichment factor	LOD (ng mL ⁻¹)	RSD (%)	Linear range (ng mL ⁻¹)	Ref.
Co-precipitation	125	16	3.0	-	[10]
On-line-SPE	330	0.8	2.6	1.6-100	[11]
CPE	50	1.1	3.51q	1.1-160	[16]
Off-line-SPE ^b	30	6.1	4.7	-	[37]
SPE	20	3.7	7	-	[38]
SPE	250	3.2	5.1	10.0-300	[39]
CPE	15.1	4.5	1.6	25.0-2000	[40]
D-DLLME-SFO	35.0	0.7	1.6	4.0-700	This work

^a Determination system: flame atomic absorption spectrometry

^b SPE: Solid phase extraction.

CONCLUSION

The proposed D-DLLME-SFO coupled with FAAS was successfully used for pre-concentration and determination of Pb(II) in complicated samples. The new method provides some operational advantages such as simplicity of experimental procedure, low cost, rejection of matrix constituent, enhancement of sensitivity and low organic solvent usage for routine trace Pb ion analysis. The interference from co-existing heavy metal ions is minimized effectively without the need of any masking reagents. The extraction solvent (1-undecanol) of this method has lower toxicity than DLLME, and thus this method is more environmental friendly.

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