Cairo University

Journal of Advanced Research

ORIGINAL ARTICLE

Preconcentration of lead using solidification of floating organic drop and its determination by electrothermal atomic absorption spectrometry

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Abstract A simple microextraction method based on solidification of a floating organic drop (SFOD) was developed for preconcentration of lead prior to its determination by electrothermal atomic absorption spectrometry (ETAAS). Ammonium pyrolidinedithiocarbamate (APDC) was used as complexing agent, and the formed complex was extracted into a 20 μL of 1-undecanol. The extracted complex was diluted with ethanol and injected into a graphite furnace. An orthogonal array design (OAD) with OA_{16} (4^5) matrix was employed to study the effects of different parameters such as pH, APDC concentration, stirring rate, sample solution temperature and the exposure time on the extraction efficiency. Under the optimized experimental conditions the limit of detection (based on 3 s) and the enhancement factor were 0.058 μg L^{-1} and 113, respectively. The relative standard deviation (RSD) for 8 replicate determinations of 1 μg L^{-1} of Pb was 8.8%. The developed method was validated by the analysis of certified reference materials and was successfully applied to the determination of lead in water and infant formula base powder samples.

Introduction

Lead is one of the most common pollutants in the environment, toxic to the human beings and animals without any known physiological function, which accumulates in the organism [1]. At moderate levels of exposure, an important aspect of the toxic effects of lead is the reversibility of the induced biochemical and functional changes. Lead toxicity results in a wide range of biological effects in humans depending on its level and the exposure time. Lead in environment is a result of anthropogenic activities and when launched to the atmosphere, it does not undergo any degradation process, and remains available to human exposure [2–4]. Currently, the most common analytical methods for determination of lead at trace levels are flame atomic absorption spectrometry (FAAS) [5,6], electrothermal atomic absorption spectrometry (ET AAS) [7,8] and inductively coupled plasma emission spectrometry (ICP) [9]. ET AAS is the most sensitive technique with a detection limit in sub-picogram level for most

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Peer review under responsibility of Cairo University.

Production and hosting by Elsevier

metals. The inductively coupled plasma-mass spectrometry (ICP-MS) [10] has achieved a detection limit in the same range with ET AAS. However, the use of ICP-MS often involves a greater cost, higher sample volume and increased instrumentation complexity hence limiting its widespread application to routine analytical works. ET AAS is still being used because it combines a fast analysis time, a relative simplicity, a lower cost, low sample volume requirements and lower detection limits. All of these features have been responsible for its broad utilization in the determination of trace and ultra trace elements in different samples [11].

However, there are some disadvantages with ETAAS such as chemical interference due to sample matrix. The greatest challenge in the direct determination of trace levels by ETAAS is the low concentration of metal ions in samples. Additionally, a careful and time consuming cleanup stage is often required because real samples such as waste water, river water contain high levels of non-toxic compounds [12]. Avoiding chemical interference becomes a particularly difficult task in the analysis of complex matrices, such as wastewater, river water, food samples, and vegetables. Preconcentration and separation techniques, such as liquid–liquid extraction [13], ion exchange [14], co-precipitation [15] and solid phase extraction (SPE) [16,17], could solve these problems, leading to a higher confidence level and an easy determinations of the trace elements. Each technique has its advantages and disadvantages and should be chosen according to the analytical problem.

Several novel microextraction techniques are being developed in order to reduce the analysis steps, increase the sample throughput and to improve the sensitivity of the analytical methods. The cloud point extraction (CPE) [18], homogeneous liquid–liquid extraction (HLLE) [19,20], the liquid phase microextraction (LPME) [21,22], dispersive liquid liquid microextraction [23] and solid phase microextraction (SPME) [24–27] are fairly new methods of sample preparation, and are employed in separation and preconcentration of environmental contaminants. Nowadays, a new mode of liquid-phase microextraction (LPME) named solidification of floating drop microextraction (SFODME) has been proposed as a high-performing, powerful, rapid and inexpensive microextraction method [28,29]. In this technique, a few microliters of a suitable organic solvent (having a melting point near room temperature in the range of 10–30 °C) is delivered onto the surface of the solution containing analytes and the solution is stirred for a desired time. The sample vial is cooled by inserting into an ice bath for 5 min and the solidified organic solvent is transferred into a suitable vial where it is melted and then a fraction of it is injected into the graphite furnace.

In this study SFODME was used for preconcentration of lead. The statistical optimization of the SFODME has been studied using Taguchi's experimental design, and from our best of knowledge, it has never been used to optimize the extraction of lead for infant formula samples.

The quantitative performance of the proposed SFODME, in terms of linearity, precision, and limit of detection (LOD), was validated under the optimal conditions. The capability of SFODME was also demonstrated by determining lead in a reference material (JR-1).

Experimental

Reagents and samples

A stock standard Pb (II) solution (1 mg mL^{-1}) was purchased from Merck (Darmstadt, Germany). Ammonium pyrrolidinedithiocarbamate (APDC) was obtained from Merck and its working solution (0.5%) was prepared by dissolving appropriate amounts of this reagent in ultrapure water daily. The organic extractant was 1-undecanol (Merck). Ultra-pure quality water was used throughout which was produced by a Milli-Q system (Millipore, Bedford, USA). The pH was adjusted with hydrochloric acid solution before use. The chemical modifier (5000 mg L^{-1}) for ETAAS was prepared by diluting Pd (NO$_3$)$_2$ stock solution (10.0 ± 0.2 gL^{-1}, Merck) with ultrapure water. Infant formula base powder samples were collected from local factory.

Instruments

A shimadzu AA-3600 atomic absorption spectrometer (Japan) equipped with a graphite furnace atomizer and an ACS-6100 auto-sampler was used. Deuterium background correction was employed to correct nonspecific absorbance. A Lead hollow cathode lamp (analytical wavelength 283.3 nm) from HAMAMATSU (Japan) was employed as the radiation source and operated at 10 mA with a spectral bandwidth of 0.7 nm. Pyrolitic graphite-coated tubes were used. The graphite furnace temperature program for determination of lead in 1-undecanol is summarized in Table 1. Two preheating/drying steps were necessary for gradual drying of the organic solvent. With regards to the boiling point of 1-undecanol (243 °C), it was proved that for evaporation of the solvent, an ashing temperature of 600 °C with a hold time of 10 s is necessary. Argon of 99.996% purity was used as purge and protective gas. Integrated absorbance (peak area) was used exclusively for signal evaluation. The use of a chemical modifier is required to allow lead determination in real samples as it increases the analyte thermal stability [30] and decreases the matrix effects and the background signal. Aliquots of 10 μL of Pd modifier and 10 μL of sample or standard solutions were directly injected into the graphite tube and operated at the temperature program, as shown in Table 1. A Wisestir, witeg (Germany) magnetic heater-stirrer using a 12 mm × 4 mm stirring bar was used for heating and stirring of the sample solution. Also a simple water bath was used for controlling the sample solution temperature. A Brand micro-sampler (Germany) was used for handling of APDC and 1-undecanol.

SFODME procedure for determination of lead

10 mL of the standard solution containing 1 μg L^{-1} of lead was transferred into a screw caped vial and its pH was adjusted to 3 with HCl. 50 μL of APDC solution (0.5% w/v) was added and the vial was kept in water bath at 55 °C for 10 min while stirring the solution. 20 μL of 1-undecanol was then placed on the surface of the sample solution and it was stirred for 30 min at 800 rpm. The test tube was transferred into a beaker containing ice and the organic solvent was solidified after 5 min. The solidified solvent was then transferred into a vial, where

Table 1 The graphite furnace temperature program for Pb determination.

Step	Temperature (°C)	Time (s)		Gas flow (L min⁻¹)
		Ramp	Hold	
Drying I	80	15	–	1
Drying II	150	30	–	1
Drying III	250	20	–	1
Pyrolysis	600	20	10	1
Gas stop step	600		3	0
Atomization	2000	–	2	0
Cleaning	2500	–	2	1

it melted immediately at room temperature. The extraction solvent was dissolved in 80 µL of ethanol to decrease its viscosity. 10 µL of diluted extractant and 10 µL of modifier was injected to furnace for subsequent analysis.

Samples decomposition procedures

For infant formula base powder sample, 5 g of the sample was placed in a crucible and heated on an electric heater until smoking is ceased, then it was placed in a muffle furnace for 1 h in 550 °C and after cooling, the residue was dissolved in 5 mL HCl 6 M and 0.5 mL concentrated HNO_3 and diluted to mark in a 50 mL volumetric flask with pure water.

For validation purposes one standard reference material was studied; 0.5 g of JR-1 (Igneous rocks) was placed in a 100 mL Teflon beaker followed by addition of 7 mL of HF, 2.3 mL of H_2SO_4 and 0.6 mL of HNO_3. It was heated until small amounts of liquid remained and then cooled. 8 mL of HNO_3 was then added and diluted to 100 mL with pure water. Proper amounts of solid Potassium cyanide (KCN) were added to this solution before applying it to the microextraction procedure in order to mask the interfering ions. Because concentration of sample is not in the dynamic linear range of calibration curve, this sample was diluted 50-fold.

Result and discussions

In order to obtain high enrichment factor for lead determination with the developed SFODME method, the effect of different parameters influencing the complex formation and the extraction conditions, were optimized. These parameters include the pH of the sample solution, APDC's concentration, temperature of the sample solution, stirring rate and exposure time. 1 µg L⁻¹ lead standard solution was used throughout the optimization studies.

Experimental design and data analysis

Experimental design is an important tool for off-line and experimental quality control. The Taguchi orthogonal array design method is one of the efficient means for evaluation and improvement of the laboratory and continuous process efficiency [31].

In this study the effect of five important factors including the pH and the temperature of the sample solution, stirring rate, exposure time and APDC's concentration on the extraction of lead were studied using Taghuchi's method. A five-factor, four-level factorial design OA_{16} (4^5) was used to evaluate

the effects of these parameters. In order to estimate the best condition for extraction of lead, 16 experiments were performed. Each experiment was repeated twice and the factors and their respected levels are reported in Table 2. In this study, the focus was on the main effects of the five most important factors. The average responses for each factor at different levels were also calculated to probe the effect of each factor and to screen the optimum level.

The pH of the sample solution plays an important role on the metal-chelate formation and subsequent extraction. The extraction yield depends on the pH at which the complex formation occurs. In the present work, the effect of pH on the complex formation of target ion was studied within the pH range of 2.0–6.0, using either NaOH or HCl. Based on the ANOVA results, the effect of pH on the analytical signal of the metal ions was significant and at pH of 3, the highest signal was obtained. Hence, pH of 3 was chosen for subsequent extractions.

The effect of APDC concentration as complexing agent on the extraction efficiency of lead was investigated. The results indicated that the analytical signal was increased with increasing of APDC concentration from 0.01% to 0.5% as expected. It seems that the slight reduction of lead signal at higher

Table 2 The OA_{16} (4^5) matrix for optimization of SFODME of Pb.

Trial	A^a	B^b	C^c	D^d	E^e	Average signal
1	2	0.05	10	25	600	0.147
2	2	0.2	20	35	800	0.148
3	2	0.5	30	45	1000	0.360
4	2	1	40	55	1200	0.296
5	3	0.05	20	45	1200	0.250
6	3	0.2	10	55	1000	0.280
7	3	0.5	40	25	800	0.500
8	3	1	30	35	600	0.413
9	4	0.05	30	55	800	0.340
10	4	0.2	40	45	600	0.268
11	4	0.5	10	35	1200	0.168
12	4	1	20	25	1000	0.136
13	6	0.05	40	35	1000	0.118
14	6	0.2	30	25	1200	0.120
15	6	0.5	20	55	600	0.220
16	6	1	10	45	800	0.145

[a] pH.
[b] APDC concentration (W/V)%.
[c] Time.
[d] Temp.
[e] Stirring rate (rpm).

concentration of APDC is due to the extraction of APDC itself, which can easily saturate the small volume of the extracting solvent.

Generally, in most of the LPME experiments, higher enrichment factors can be achieved by increasing the sample solution temperature. Based on the extraction kinetics, higher temperatures would facilitate the diffusion and mass transfer of the analytes from sample solution into the organic solvent. According to the experimental results, the extraction efficiency increases by rising the sample solution temperature up to 55 °C. Thus by using a water bath, the temperature of the sample solution was adjusted to 55 °C for further studies.

For quantitative analysis it is necessary to allow a sufficient mass transfer into the drop in order to guarantee an efficient equilibrium between the aqueous and organic phases. The effect of the extraction time on the extraction efficiency was examined during 10–40 min period and it was observed that the analytical signal increased with increasing of the extraction time. In order to achieve a higher sample throughput, the extraction time of 30 min was selected for all subsequent works.

For SFOME, sample agitation is an important parameter that influences the extraction efficiency. Based on the film theory of convective-diffusive mass transfer for LPME system, high stirring speed could decrease the thickness of the diffusion film in the aqueous phase, so the aqueous phase mass-transfer coefficient will be increased with increasing of the stirring speed (rpm) and, also it depends on the size and shape of the stirring bar. The effect of stirring rate on the extraction efficiency of lead was investigated in the range of 600–1200 rpm. Despite the positive effect on the thickness of the diffusion film, stirring rates above 800 results in spattering of the microdrop where its collection becomes difficult.

The ANOVA results for the selected factor are shown in Table 3. 'It shows the percentage of contribution (P%) of each factor on the total variance and indicating the influence degree of each factor on the result. According to Table 3 the pH plays an important role in SFODME of lead from aqueous samples. The effect of other parameters was less significant. Further experiments were performed under the proposed conditions.

Optimization of ETAAS determination of lead

In order to decrease the possibility of chemical interference and reduce the magnitude of the background signal, the pyrolysis and atomization temperatures should be optimized. Here, these parameters were studied using 1 µg L^{-1} Pb solutions submitted to the SFODME procedure. It was found that at the pyrolysis temperature of 600 °C, the maximum absorbance

would be achieved. At lower pyrolysis temperatures, the background signal was too high, probably due to the vaporization of excess APDC and/or 1-undecanol itself at the atomization step. This causes a significant signal suppression, which resulted in low absorbance values for low pyrolysis temperatures. Increasing the pyrolysis temperature above 600 °C leads to the loss of analyte and hence decreases the analytical signal. Therefore, 600 °C was selected as the optimized pyrolysis temperature for determination of lead.

The effect of pyrolysis time on the absorbance of lead was also investigated. The results showed that the absorbance was increased with increasing pyrolysis time up to 30 s and no appreciable improvements were observed at longer times. As a result, a pyrolysis time of 30 s was chosen.

Also, the ramp temperature and the drying step time were optimized to reach a smooth and complete evaporation and removal of the liquid part of each sample without sputtering. The drying temperatures were set at 80, 150 and 250 with the ramp mode for 15, 30 and 20 s, respectively.

The atomization temperature was similarly optimized. According to the results, the signal was reached its maximum at about 2000 °C, and then decreased with further increasing of temperature, and hence the atomization temperature of 2000 °C was selected for further experiments. Since atomization time had little effect on the atomic signal, 2 s was selected for atomization of lead.

Study of interference effects

In order to demonstrate the selectivity of the developed microextraction method for determination of lead, the effect of some heavy metal concomitants with lead in environmental and food samples was investigated. The interferences may be due to the competition between lead and other metal ions for chelation with APDC and their subsequent coextraction with lead.

The effects of some potential interfering ions on the SFODME of Pb^{+2} (1 µg L^{-1}) were investigated. Results showed that Na^{+}, K^{+}, Mn^{2+}, Cl^{-}, SO$_4^{2-}$, PO$_4^{3-}$ up to 500 µg L^{-1}, Ca^{+2} up to 200 µg L^{-1} and Cd^{+2} and Cu^{+2} up to 100 µg L^{-1} cause no significant interference on the SFODME of Pb^{+2}. An ion was considered to interfere when its presence produced an error of more than 5%.

Analytical performance

The calibration curve was obtained by preconcentration of the standard solutions under the optimized preconcentration con-

Table 3 ANOVA results for experimental responses in the OA$_{16}$ (4^5) matrix.

Factor	Dof [a]	Sum of Sqrs.	Variance	F ratio [b]	Pure sum of Sqrs.	Percent (%)
pH (A)	3	0.186	0.062	154.136	0.185	44.665
% APDC (B)	3	0.061	0.020	50.592	0.059	14.464
Time (C)	3	0.110	0.036	91.594	0.109	26.423
Temperature (D)	3	0.017	0.005	14.531	0.016	3.946
Stirring rate (E)	3	0.032	0.010	26.663	0.031	7.485
Error	16	0.006				
Total	31	0.414				

[a] Degree of freedom.
[b] F, critical value is 3.24 (p < 0.05).

Table 4 Comparison of the proposed method with other methods applied for extraction and determination of lead.

Method	LOD ($\mu g\ L^{-1}$)	Linear range ($\mu g\ L^{-1}$)	EF	Reference
SFOD	0.9 [a]	4–30 [a]		[28]
DLLME [b]	0.02	0.05–1	150	[32]
SDME [c]	0.2	1–15	52	[33]
CPE [d]	0.08	0.08–30	50	[34]
IL-SDME [e]	0.015	0.025–0.8	76	[35]
SPE [f]	0.007	–	21	[36]
SI-DLLME [g]	0.01	0.04–1.5	80	[37]
SFODME	0.058	0.2–10	113	This work

[a] $ng\ L^{-1}$.
[b] Dispersive liquid–liquid microextraction.
[c] Single drop microextraction.
[d] Cloud point extraction.
[e] Ionic liquid single drop microextraction.
[f] Solid phase extraction.
[g] Sequential injection (SI) dispersive liquid–liquid microextraction (DLLME).

Table 5 Analytical results for determination of lead in real samples.

Sample		Pb found	Pb Spiked [a]	Pb Found	Relative recovery (%)
Tap water [a]			–	2.63 ± 0.21	–
	–	–	5	7.24 ± 0.60	92
Infant formula base powder 1 [b]	–	3.10 ± 0.67			
	–		10	12.5 ± 0.9	94
Infant formula base powder 2 [b]	–	4.16 ± 0.38			
	–		5	8.90 ± 0.93	95

[a] $\mu g\ L^{-1}$.
[b] $\mu g\ kg^{-1}$.

ditions of the proposed method. The linear dynamic range (LDR) was between 0.2 and 10 $\mu g\ L^{-1}$ with a correlation coefficient of 0.997. The limit of the detection (LOD) (based on 3 s/m) was found to be 0.058 $\mu g\ L^{-1}$ and the limit of quantification (LOQ) (based on 10 s/m) was 0.2 $\mu g\ L^{-1}$. The relative standard deviation at 0.6 $\mu g\ L^{-1}$ of lead standard solution was calculated to be 8.8% ($n = 8$).

A comparison between the figures of merit for the proposed method and some of the published methods for extraction of lead are summarized in Table 4. The proposed method shows good sensitivity and precision with reasonable preconcentration factor, and makes it as a suitable method for ultra trace analysis of lead in the sample types examined.

Analysis of real samples

In order to verify the accuracy of the proposed method, it was applied to determine lead in one reference material, JR-1 Igneous rocks. The certified amount of lead in JR-1 is 19.3 ± 1.3 $\mu g\ g^{-1}$. The obtained values by using the proposed SFODME method was 17.62 ± 2.00 which is in good agreements with the certified value. The t-test was performed at 95% level and the results show that there is no significant difference between the two sets of results. (Experimental *t* value was 0.53 and critical *t* value for $p = 0.05$ was 2.78.)

The present method was also applied for determination of lead in tap water and infant formula base powder samples. The results and recoveries for the spiked samples are summa-

rized in Table 5. As seen, the proposed method is reliable for determination of lead in real samples.

Conclusion

This study shows application of Taguchi orthogonal array for screening the significant factors of SFODME for extraction and determination of lead in real samples. The effect of each factor was estimated using individual contributions as response functions. The results of ANOVA showed that pH has significant effect on this method. The results indicated that the Taguchi method is a suitable for optimization of SFODME for ions. This method is a modified liquid microextraction method and has advantages such as low organic solvent consumption, simplicity, low cost and relative high enrichment factor. This method allows determination of lead in different samples with good accuracy and reproducibility.

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