

# Preconcentration and Determination of Lead for Trace Levels in Water and Wastewater Samples by Vortex-Assisted Microextraction Using TPAS as a New Synthetic Complexing Agent with Electrothermal Atomic Absorption Spectroscopy Detection

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**ABSTRACT:** A simple and rapid solidified vortex assisted 1-undecanol based liquid–liquid microextraction technique was proposed for preconcentration of trace levels of lead ions. The extraction solvent (1-undecanol) was dispersed into the aqueous samples by the assistance of vortex agitator. 100  $\mu\text{L}$  of 1-undecanol containing ethyl (2Z)-3-[(5-chloro-7-methyl[1,3]thiazolo[5,4-d]pyrimidin-2-yl)amino]-2-cyano-3-(methylsulfanyl)prop-2-enoate (TPAS) as a new chelating agent (0.1%w/v) was transferred to the water samples containing lead ions. The hydrophobic complex was extracted into 1-undecanol and the sample vial was cooled in an ice bath for 5 min. The solidified extract was transferred into a conical vial where it was melted immediately, and 20  $\mu\text{L}$  of this solution was injected and analyzed by Graphite Furnace Atomic Absorption Spectrometry (GFAAS). Several variables such as sample pH, concentration of TPAS, volume of 1-undecanol and extraction time were investigated in details and optimum conditions were obtained. Under the optimum conditions, the Limit Of Detection (LOD) was  $0.02 \mu\text{g L}^{-1}$  for lead and Relative Standard Deviation (RSD %) for five replicate determinations of  $1 \mu\text{g/L}$  of lead was 5.6%. The results for determination of lead in reference material, three samples of wastewater, well, tap, river and aqueduct water demonstrated the accuracy, recovery and applicability of the presented method.

**KEYWORDS:** Microextraction, water and wastewater analysis, Thiazolo[5,4-d] pyrimidine, Lead analysis, Graphite furnace absorption spectrometry.

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## INTRODUCTION

Lead is one of the most toxic elements and has accumulative effect. It is called environmental priority pollutants. Lead is a trace element of high interest, due to the toxicity of most of its compounds; lead poisoning adversely affects the central and peripheral nervous systems and the kidney[1], among others. Inorganic lead is distributed to soft tissue, bones and teeth. Organic forms of lead are fat soluble and therefore have a particular tendency to concentrate in brain. However, its unique properties make it to be used as an industrial material in a variety of fields, and hence it is released to the environment in considerable quantities [2]. Human activity increases the level of lead contamination in environmental water system, and this may greatly influence the quality of life, especially in developing countries. It is therefore important to monitor the levels of lead in environments[3].

In recent years there has been an increased concern over the content of lead in drinking and natural water. World Health Organization (WHO) recommended a limit of 10  $\mu\text{g/L}$  of lead in drinking water [4], which requires a very sensitive measurement technique. Thus, the determination of Pb in water has become increasingly important. Analytical methods for determination of trace levels of Pb have mainly used atomic absorption spectrometry,[5-7] inductively coupled plasma mass spectrometry [8] and spectrophotometry[9,10]. Graphite Furnace Atomic Absorption Spectrometry (GFAAS) is a sensitive technique for determination of trace of lead in several types of samples.

However, due the matrix effect, separation/pre-concentration steps are required before analytical measurements by GFAAS. Liquid phase extraction methods can effectively decrease the detection limit and eliminate matrix interferences, when coupled with the above-mentioned techniques, for the determination of lead ions in aqueous samples[11]. These methods include drop-in-drop system[12], Single-Drop MicroExtraction (SDME) [13,14], Homogenous Liquid-Liquid MicroExtraction (HLLME)[15,16], and Dispersive Liquid-Liquid MicroExtraction (DLLME)[17-20]. The main advantages of these techniques are: the negligible volume of solvents and their ability to detect analytes at very low concentrations. In recent years, *Khalili Zanjani* [21] reported a new liquid-liquid microextraction method

based on solidification of floating organic drop which was successfully used for the extraction and determination of Polycyclic Aromatic Hydrocarbons (PAHs). In this method, small volume of an organic solvent with a melting point near room temperature (in the range of 10–30  $^{\circ}\text{C}$ ) was floated on the surface of aqueous solution. The aqueous phase was stirred for a definite period of time, and then the sample was transferred into the ice bath. When the organic solvent was solidified (about 5 min), it was transferred into a small conical vial, and the melted organic solvent was used for determination.

The Solidified Floating Organic Drop Microextraction (SFODME) is a modified solvent extraction method, and has the advantages of simplicity, short extraction time, low cost, minimum organic solvent consumption, and high enrichment factor. In this study the possibility of implementation of SFODME in combination with GFAAS in trace element analysis has been evaluated.

The applicability of the approach was demonstrated for the determination of lead in water and wastewater samples. Factors affecting the extraction efficiency, such as solution pH, concentration of organic ligand, extraction time, 1-undecanol volume, and ionic strength were optimized.

## EXPERIMENTAL SECTION

### Equipment

The experiments were performed using a Zeeman Varian atomic absorption spectrometer (Spectr AA 220 Z-type), equipped with a graphite furnace atomizer GTA-110. Zeeman background correction was employed to correct non-specific absorbances. All measurements were performed using the peak height method. A lead hollow cathode lamp (Photron Co. Ltd., L233-series) and a pyrolytic coated graphite tube (Shimadzu part No. 206-69984-02) were used. The sample injection volume was 20  $\mu\text{L}$  in all the experiments. The instrumental parameters and temperature program for the graphite atomizer are listed in Table 1. Argon gas with 99.999% purity was purchased from Sabalan Gas Co. (Tehran, Iran) and was used as protecting and purges gas.

The pH values were measured with a pH-meter (Metrohm 632, Switzerland) supplied with a glass-combined electrode. A vortex Gilson mixer (Villiers Le Bel, Germany) was used for thoroughly mixing of the solutions.

Phase separation was assisted using centurion scientific centrifuge (Model Andreas Hettich D72, Tuttlingen, Germany).

The electron impact mass spectra (MS) was obtained on a CH7A Varian Mat Bremem instrument at 70 eV, in m/z (rel %).

IR spectra were recorded on an Avatar 370 FT-IR Thermo Nicolet Infrared spectrophotometer.

The  $^1\text{H}$  NMR spectra was recorded on a Bruker AC 100 spectrometer in  $\text{CDCl}_3$  solution with TMS as an internal standard.

### Chemicals and Reagents

All reagents were of analytical reagent grade and deionized water was used throughout. A stock solution of 1000 mg/L lead (II) ion was prepared for  $\text{Pb}(\text{NO}_3)_2$  purchased from Merck. Working standard solutions were prepared freshly at various concentrations by diluting the stock standard solution with deionized water. Acetonitrile was prepared for Merck. The chelating agent, ethyl (2Z)-3-[(5-chloro-7-methyl [1,3] thiazolo [5,4-d] pyrimidin-2-yl)amino] -2-cyano-3- (methylsulfanyl)prop -2-enoate (TPAS) was synthesized as a new ligand in our department (Fig. 1).

TPAS solution (0.1% w/v) was prepared by dissolving proper amounts of TPAS in 1-undecanol. 1-Undecanol was purchased from Merck and was used as the extracting solvent. The pH adjustment was made with 0.1 mol/L of nitric acid (for acidic pH values) or 0.1 mol/L of sodium hydroxide solution (for basic pH values).

A solution of 500 mg/L ammonium dihydrogen phosphate ( $\text{NH}_4\text{H}_2\text{PO}_4$ ) (Merck, Darmstadt, Germany) was used as chemical modifier and injected into the graphite furnace for efficient thermal stabilization of lead.

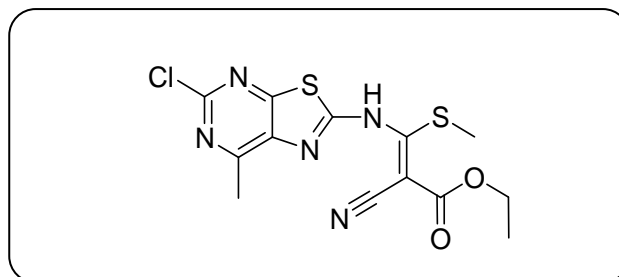
Sodium dodecyl sulfate (SDS, 0.4 % w/v, Merck), as antisticking agent, was prepared by dissolving 0.1 g of SDS in 25.0 mL ultra-pure water.

### Characteristic of TPAS

Compound 3 (TPAS) was synthesized from the reaction of 5-chloro-7-methyl[1,3]thiazolo[5,4-d]pyrimidin-2-amine (compound 1) and ethyl 2-cyano-3,3-bis(methylsulfanyl)prop-2-enoate (compound 2) in the presence of triethylamine (Scheme. 1). Starting materials 1 and 2 were prepared according to the previously reported methods[22,23].

**Table 1: Applied conditions for lead determination with GFA system.**

Optimum analytical conditions			
Lamp current		4mA	
Wavelength		283.3	
Spectral bandwidth		0.5 nm	
Signal processing		Peak height	
Purge gas		Ar	
Back ground correction		$\text{D}_2$	
Furnace program for GFAAS			
Steps	Temperature/c	Time/s	Argon flow rate,L/ min
1	85	5	3
2	95	40	3
3	120	10	3
4	600	20	3
5	2100	3	0
6	2100	2	3



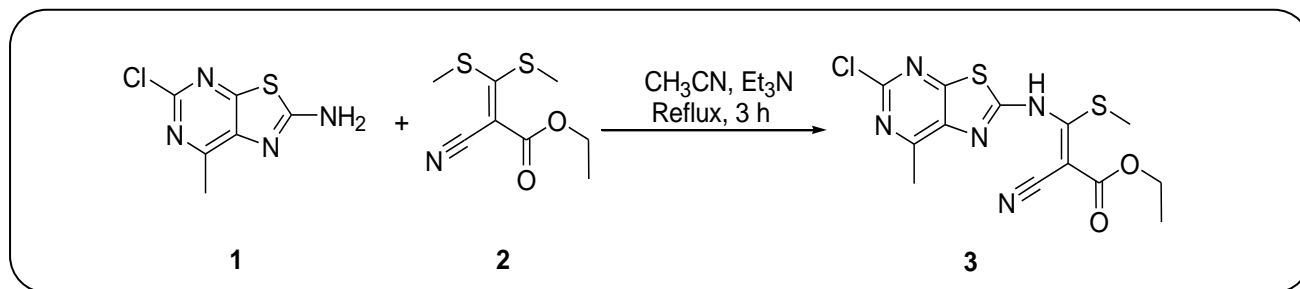
**Fig. 1: Structure of TPAS.**

A mixture of compounds I (1 mmol, 0.20 g), II (1 mmol, 0.217 g) and triethylamine (1.2 mmol, 0.16 mL) was refluxed in acetonitrile (10 mL) for 3 h. The reaction was monitored by thin layer chromatography using mixture of ethylacetate and n-hexane (1:8) as eluent. After the completion of the reaction, the mixture was cooled and the solvent was evaporated in vacuum. The residue was then washed with water and recrystallized from ethanol to afford compound III (0.31 g) as yellow solid in 84% yield.

Characterizations of TPAS are as follow:

1- Melting point 202-203 °C.

2- Mass spectrometer (MS) for  $\text{C}_{13}\text{H}_{12}\text{ClN}_5\text{O}_2\text{S}_2$ : m/z  $[\text{M} + 4]^+$ : 373,  $[\text{M} + 2]^+$ : 371,  $[\text{M} + 1]^+$ : 370,  $[\text{M}]^+$ : 369,  $[\text{M}-2]^+$ : 367. Mass spectrum was shown in Fig. 2.



Scheme 1: Synthesis of TPAS.

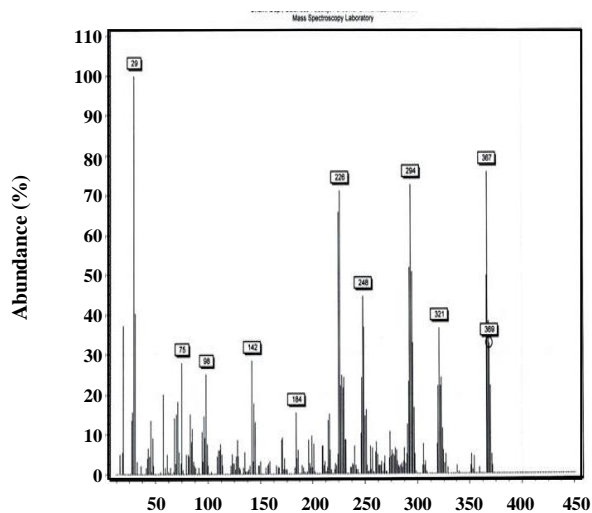


Fig. 2: Mass spectrum of TPAS.

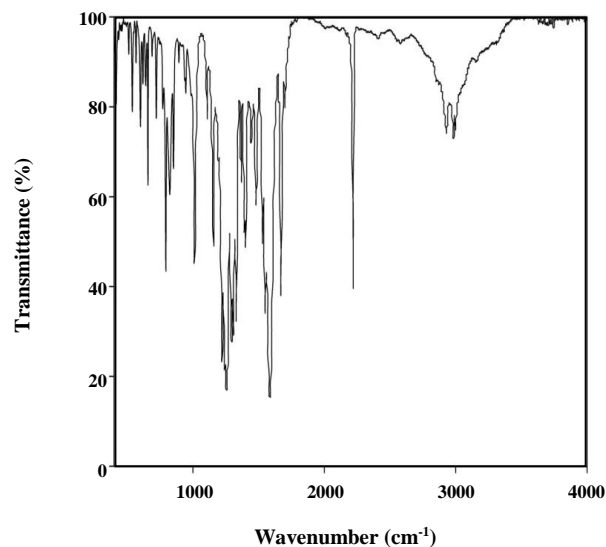


Fig. 3: The IR spectrum of TPAS.

3-  $^1\text{H}$  NMR (100MHz,  $\text{CDCl}_3$ )  $\delta$  1.38-1.42 (t, 3H,  $\text{CH}_3$ ), 2.69 (s, 3H,  $\text{CH}_3$ ), 2.78 (s, 3H,  $\text{SCH}_3$ ), 4.33-4.39 (q, 2H,  $\text{CH}_2$ ), 12.81 (brs, 1H, NH).

4- IR (KBr)  $\bar{\nu}$   $\text{cm}^{-1}$  3003, 2982, 2933, 2220, 1670, 1587, 1550, 1529, 1455, 1402, 1331, 1307, 1295, 1255, 1223, 1156, 1013, 809, 794, 723, 662, 604, 543.

The IR spectrum of TPAS was shown in Fig.3.

### Preparation of real samples

#### Water samples

Water samples including tap water, well water, aqueduct water and river water were collected from local sources. Seven milliliter of sample solution was used for the analysis after addition of TPAS and adjusting their pH to 6, with  $\text{HNO}_3$  solution.

#### Wastewater samples

Wastewater samples were collected from local

factories. Seven milliliter of waste sample was used for the analysis after addition of TPAS and adjusting their pH to 6, with  $\text{HNO}_3$  solution.

#### Reference material

In order to evaluate the accuracy of the proposed method, a standard rock reference material, JR-1, obtained from the geological survey of Japan was analyzed for lead content. The rock sample (0.5 g) was dissolved in 10 mL of a mixture of HF (12 M),  $\text{HNO}_3$  (14 M), and  $\text{H}_2\text{SO}_4$  (18 M) in a Teflon beaker, and heated until 2 mL of solution was remained. Concentrated  $\text{HNO}_3$  (8 mL) was added to this solution. After heating, it was treated with distilled water to give a clear solution and was finally made to 100 mL by further addition of distilled water. 10 mL of this solution was diluted to 100 mL and analyzed for lead content according to the proposed procedure.

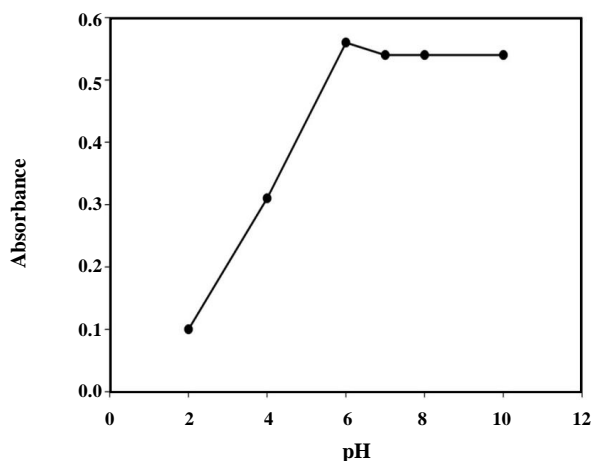


Fig. 4: Effect of pH on recovery of lead. Conditions: 4  $\mu\text{g/L}$   $\text{Pb}^{2+}$ , 0.1 % (w/v) of ligand, 100  $\mu\text{L}$  of undecanol, extraction time 1.5 min.

#### Microextraction procedure

Twenty-five milliliter of aqueous sample solution containing 4  $\mu\text{g/L}$   $\text{Pb}^{2+}$  at pH 6 was prepared. 7 mL of this solution was transferred into a conical-bottom glass centrifuge tube and 100  $\mu\text{L}$  of TPAS solution in 1-undecanol (0.1%w/v) and 150  $\mu\text{L}$  SDS were added. The resulting solution was vigorously shaken with a vortex agitator for 1.5 min at 2500 rpm. Under the shaking, very fine droplets of 1-undecanol were formed through the solution and the lead-TPAS complex was extracted into the fine droplets of 1-undecanol at a relatively short time. In order to accelerate phase separation, the solution was centrifuged for 6 min at 4500 rpm and the 1-undecanol phase was floated on the surface of aqueous solution. After this process, the sample was transferred into an ice bath and the organic solvent was solidified after 5 min. The solidified solvent was then transferred into a conical vial where it melted immediately. 20  $\mu\text{L}$  of the extract and 10  $\mu\text{L}$  of 500 mg/L  $\text{NH}_4\text{H}_2\text{PO}_4$ , as chemical modifier, were subsequently injected into the graphite tube for determination of lead.

#### RESULTS AND DISCUSSION

There are different factors that affect the extraction process such as pH, concentration of chelating agent, amounts of 1-undecanol, extraction time and interfering ions. It is very important to optimize these parameters in order to obtain high recovery and enrichment factor.

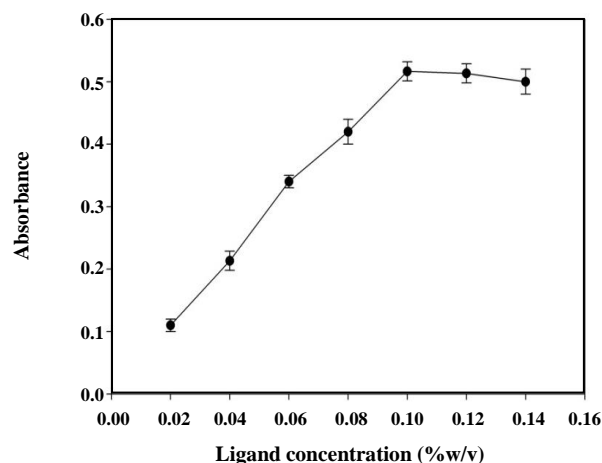


Fig. 5: Effect of ligand concentration on the recovery factor. Conditions: pH: 6, 4  $\mu\text{g/L}$   $\text{Pb}^{2+}$ , 100  $\mu\text{L}$  of undecanol, extraction time 1.5 min.

#### pH of solution

The pH plays a unique role on metal-chelate formation and subsequent extraction. The effect of pH on the solidified floating organic drop microextraction of lead was studied in the pH range of 2–10, using nitric acid or sodium hydroxide and keeping the other variables constant. The results demonstrated in Fig. 4 reveals that the absorbance of lead is maximum at the pH value of 6. So, pH 6 was chosen as the optimum value.

#### TPAS Concentration

The effect of concentration of TPAS was investigated in the range of 0.02% to 0.14% (w/v). The efficiency of lead extraction was dependent on TPAS concentration as shown in Fig. 5. The recovery was increased by increasing the TPAS concentration up to 0.1%w/v. Further excess of TPAS will cause a decrease in extraction probably due to the saturation of extracting solvent, which results in the introduction of TPAS into aqueous phase. Therefore a TPAS concentration of 0.1%w/v was chosen for further study.

#### Undecanol volume

The volume of 1-undecanol used in this procedure is a critical factor for obtaining high recovery of the analyte. The volume of 1-undecanol was studied in the range of 50–200  $\mu\text{L}$ . As can be seen in Fig. 6, by increasing the volume of 1-undecanol, the absorbance increased up to 100  $\mu\text{L}$  and then decreased by further increasing of the acceptor phase volume. Thus, 100  $\mu\text{L}$  of 1-undecanol was employed as the optimum value.

### Volume of surfactant (sodium dodecyl sulfate)

The influence of the Sodium Dodecyl Sulfate (SDS) volume was evaluated in the range of 0-200  $\mu\text{L}$  at constant experimental conditions. The results in Fig. 7 show that the absorbance has increased by increasing the surfactant volume up to 150  $\mu\text{L}$  and then remained constant up to 200  $\mu\text{L}$ . Therefore the surfactant volume of 150  $\mu\text{L}$  was chosen as the optimum value. 1-Undecanol is dispersed into aqueous solution with SDS. Therefore, the distribution of the analytes between organic solvent and aqueous phase is accomplished due to an additional interaction with the hydrocarbon chain of the surfactant.

### Extraction time

Optimum extraction time is the minimum time necessary to achieve equilibrium between the aqueous and the organic phase whereby the extraction of the analyte, the sensitivity, and the speed of extraction is maximized.

The influence of the extraction time was evaluated in the range of 1-2.5 min at constant experimental conditions. The results in Fig. 8 showed that the absorbance was increased by increasing the extraction time up to 1.5 min and then was remained constant up to 2.5 min. Therefore, in order to achieve a high enrichment factor, an extraction time of 1.5 min was chosen as the optimum value.

### Centrifuge time and speed

The effect of centrifugation rate on the absorbance was studied in the range of 1000–6000 rpm. It was found that over 4500 rpm, the organic phase was completely accumulated so that the rate of 4500 rpm was selected as the optimum point. At the optimum rate, the absorbance was studied as a function of centrifugation time. Six minutes was selected as the optimum centrifugation time, because complete separation occurred at this time.

### Ionic strength

The effect of salt on extraction was studied by varying the concentration of  $\text{KNO}_3$  within the range of 0-0.1 mol/L. The results showed that the addition of salt had no significant effect on the extraction efficiency.

### Coexisting ions

The coexisting ions commonly found in environmental samples were added individually to the

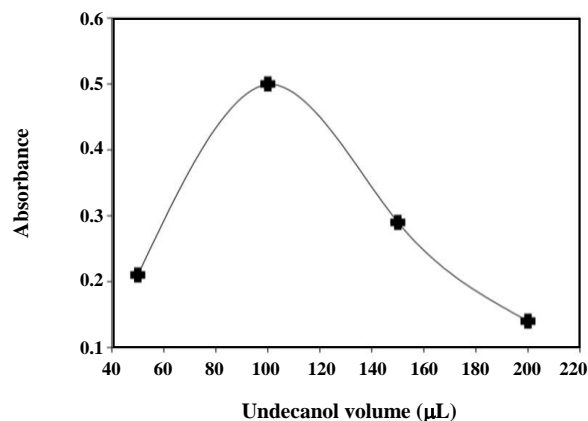


Fig. 6: Effect of amounts of undecanol on the recovery factor. Conditions: pH: 6, 4  $\mu\text{g/L}$   $\text{Pb}^{2+}$ , 0.1%(w/v) of ligand, extraction time 1.5 min.

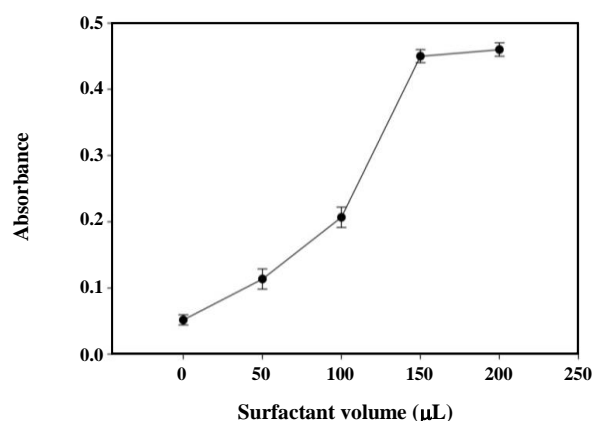


Fig. 7: Effect of volume of surfactant on the recovery factor. Conditions: pH: 6, 4  $\mu\text{g/L}$   $\text{Pb}^{2+}$ , 0.1%(w/v) of ligand, extraction time 1.5 min.

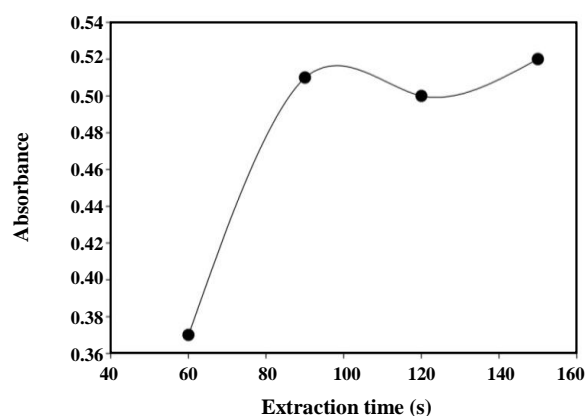


Fig. 8: Effect of extraction time on the recovery factor. Conditions: pH: 6, 4  $\mu\text{g/L}$   $\text{Pb}^{2+}$ , 0.1%(w/v) of ligand, 100  $\mu\text{L}$  of undecanol.

samples and their effects on the analytical signal intensity were investigated under the optimized conditions. The tolerance limit was set as the amount of ion required to cause an error of  $\pm 5\%$  in the determination of lead. The results of this investigation were summarized in Table 2, indicating that lead recoveries were almost quantitative in the presence of the excessive amounts of possible interfering cations and anions.

#### Analytical figures of merit

For a sample volume of 7 mL of lead, the calibration graph exhibited linearity over the range of 0.1- 4.5  $\mu\text{g/L}$  with a correlation coefficient of 0.9935.

The regression equation after the preconcentration procedure was  $A = 0.1449 C - 0.0089$ , where A is absorbance and C is lead concentration in  $\mu\text{g/L}$ . The equation of the calibration curve before the preconcentration procedure was  $A = 0.0049 C + 0.0019$  with a dynamic range from 3 to 100  $\mu\text{g L}^{-1}$ . The Limit Of Detection (LOD) and Limit Of Quantification (LOQ) based on  $3S_b/m$  and  $10 S_b/m$  ( $n = 8$ ) ( $S_b$  is the standard deviation of the blank and m is the slope of calibration curve after extraction), were 0.02 and 0.07  $\mu\text{g/L}$ , respectively.

The Relative Standard Deviation (RSD %) resulting from the analysis of five replicate solutions containing 1  $\mu\text{g/L}$   $\text{Pb}^{2+}$  was 5.6%. The enrichment factor, calculated as the ratio of the volume of the aqueous phase (7 mL) and the final volume of the organic phase (100  $\mu\text{L}$ ), was 70. The enhancement factor defined as the slope ratio of two calibration curves for  $\text{Pb}^{2+}$  with and without preconcentration step was 30.

#### Analysis of real samples

In order to evaluate the capability of the proposed method, the developed procedure was applied to determine lead in several samples including well water, tap water, aqueduct water, river water and three wastewater samples. In order to demonstrate the validity of this method, recovery experiments were also carried out by spiking the samples with different amounts of standard lead solution before any pretreatment. Table 3, shows the obtained results. The values of recoveries confirm the validity of the proposed method. Additionally, the accuracy of the proposed method was evaluated by analyzing a standard rock reference material JR-1,

**Table 2: Effect of diverse ions on the determination of 1  $\mu\text{g/L}$   $\text{Pb}^{2+}$ .**

Coexisting ions	Concentration ratio (ion/lead)	Recovery (%)
$\text{Ti}^+$	500	97.1
$\text{Sn}^{4+}$	500	98.9
$\text{Bi}^{3+}$	500	96.5
$\text{In}^{3+}$	500	97.2
$\text{Sb}^{3+}$	500	96.3
$\text{Cd}^{2+}$	500	98.1
$\text{Zn}^{2+}$	500	98.2
$\text{Cu}^{2+}$	500	97.8
$\text{Co}^{2+}$	500	99.1
$\text{Ni}^{2+}$	250	98.5
$\text{Fe}^{3+}$	250	98.1
$\text{Hg}^{2+}$	100	99.7
$\text{Ag}^+$	100	99.6
$\text{SO}_4^{2-}$	500	103.2
$\text{CO}_3^{2-}$	500	99.1
$\text{PO}_4^{3-}$	500	101.5
$\text{Cl}^-$	100	98.1

obtained from the geological survey of Japan. It was found that the analytical results were in good agreement with the certified values as shown in Table 4.

#### Comparison of the proposed procedure with other methods

A comparison of the represented method with the other reported preconcentration methods for lead extraction and determination from water samples is given in Table 5. Some of the preconcentration methods mentioned in this table are solidification of floating organic drop microextraction, [24] liquid-liquid extraction, [25] coprecipitation, [26] off-line-solid phase extraction, [27] on-line-solid phase extraction, [28] cloud point extraction, [29] dispersive liquid-liquid microextraction [30]. In this method, homogeneously solved 1-undecanol particles are accumulated on the top of the solution after centrifuging. Apparently, this work presented a high-enrichment factor (70), a short extraction time (7.5 min) and low sample consumption (7 mL).

**Table 3: Results (mean  $\pm$  standard deviation based on three replicate analysis) of determination of lead in real sample.**

Sample	Spiked( $\mu\text{g/L}$ )	Found( $\mu\text{g/L}$ )	Recovery (%)
Well Water <sup>a</sup>	0	0.15 $\pm$ 0.02	-
	0.20	0.33 $\pm$ 0.01	90
Tap Water <sup>b</sup>	0	ND	-
	0.20	0.22 $\pm$ 0.02	110
Aqueduct Water <sup>c</sup>	0	ND	-
	0.20	0.23 $\pm$ 0.03	115
River Water <sup>d</sup>	0	0.91 $\pm$ 0.02	-
	1	1.96 $\pm$ 0.02	105
Wastewater 1e	0	2.31 $\pm$ 0.1	-
	2.00	4.22 $\pm$ 0.1	95.5
Wastewater 2 <sup>f</sup>	0	1.52 $\pm$ 0.2	-
Wastewater 3 <sup>g</sup>	2.00	3.61 $\pm$ 0.1	104.5
	0	3.11 $\pm$ 0.1	-
	1	4.13 $\pm$ 0.2	102

a) Obtained from Khajeh Abasalt, Mashhad, Iran, b) Obtained from Mashhad, Iran

c) Obtained from Khashmar, Iran, d) Obtained from Khashaf Rood, Mashhad, Iran

e) Obtained from Toos Industrial Town, Mashhad, Iran, f) Obtained from Kalat Industrial Town, Mashhad, Iran

g) Obtained from Charm Shahr, Mashhad, Iran

**Table 4: Determination of lead in a certified reference material. Results (mean  $\pm$  standard deviation based on three replicate analyses).**

sample	Certificated( $\mu\text{g/g}$ )	Found( $\mu\text{g/g}$ )	Recovery (%)
JR-1	19.3 $\pm$ 1.3	20.7 $\pm$ 1.2	107.2

**Table 5: Comparison of SFODME with other methods for determination of lead.**

Method	LOD <sup>a</sup> ( $\mu\text{g/L}$ )	R.S.D. <sup>b</sup> (%)	Enrichment factor	Sample consumption(ml)	Time (min)	Calibration range ( $\mu\text{g/L}$ )	References
SFODME-GFAAS	0.001	5.4	500	10	5	0.004-0.03	24
Liquid-liquid extraction GF AAS	1	2.7	5	5.0	20	2-30	25
Co-precipitation-GF AAS	0.5	4.6	20	200.0	>20	-	26
Off-line-SPE-GF AAS	0.039	-	100	200.0	20	-	27
On-line-SPE-GF AAS	0.012	3.2	20.5	>3.3	2	0.1-10	28
CPE-GF AAS	0.08	2.8	50	10.0	30	1-30	29
DLLME-GF AAS	0.02	2.5	150	5.0	>3	0.05-1	30
SFODME -GF AAS	0.02	5.6	70	7.0	7.5	0.1-4.5	(Represented method)



These characteristics are of great interest for the routine laboratories in trace analysis of metal ions.

## CONCLUSIONS

It has been demonstrated that SFODME combined with graphite furnace atomic absorption spectrometry provide a novel route for trace determination of lead in several categories of wastewaters and natural waters. The main benefits of the SFODME methodology were: minimum use of toxic organic solvent, simplicity, low cost, rejection of matrix constituent, enhancement of sensitivity, and simple extraction procedure. The new ligand, TPAS, acts as a highly selective agent for  $Pb^{2+}$ .

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