

# Sensitive determination of Lead in Soil and Water samples by Cloud Point Extraction-Flame Atomic Absorption Spectrometry Method

Hossein Tavallali<sup>1\*</sup>, Elham Asrari, Abdol Mohammad Attaran<sup>2</sup>,  
Mahboobeh Tabandeh

<sup>1</sup>Department of Chemistry, Payame Noor University (PNU), Shiraz, 71365-944, Iran

<sup>2</sup>Department of Chemistry, Payame Noor University (PNU), Deligan, Iran

\*Corres. author: [tavallali@pnu.ac.ir](mailto:tavallali@pnu.ac.ir), [tavallali@yahoo.com](mailto:tavallali@yahoo.com),  
Phone: +989173153520, Fax: +98711622249

**Abstract :** Cloud point extraction has been used for sensitive pre-concentration of lead after complex with 1-(2-pyridylazo)-2-naphthol (PAN) followed determination of it's by flame atomic absorption spectrometry method. The analyte is quantitatively extracted to the phase rich in the nonionic Surfactant Triton X-114. The parameters which affecting the separation phase and detection process, were optimized under the optimum experimental conditions (pH=8,  $1 \times 10^{-1}$  mol l<sup>-1</sup> PAN, 0.5% w/v Triton X-114). Calibration graph showed linear trend in rang of 20-300  $\mu\text{g l}^{-1}$  with detection limit 8  $\mu\text{g l}^{-1}$  of lead (II). The enrichment, preconcentration factors achieved 50, 35 respectively. The proposed method was analyzed for soil and water samples which gave satisfactory results. Lead in soil and water samples, which gathered from petrochemical factory, has been measured approximately around 30  $\mu\text{g l}^{-1}$  and 1  $\mu\text{g l}^{-1}$  respectively. These amounts are more than limit threshold of lead. Regarding to achieved data, water and soil of case study is polluted.

**Key words:** lead concentration, Cloud point extraction, Flame atomic absorption spectrometry, PAN, soil and water samples.

## Introduction

Everyone is exposed to trace amounts of lead through air, soil, household dust, food, drinking water and various consumers. Inorganic lead arising from a number of industrial and mining sources occurs in water in the +2 oxidation state. Lead from leaded gasoline used to be a major source of atmospheric and terrestrial lead, much of which eventually entered natural water system. Lead in soil can come from the air or from erosion of lead-bearing rocks, and may be carried indoors as dust (1).

Lead may be absorbed into the body by ingestion, inhalation and through the skin. Absorption is governed by chemical structure. Short-term exposure to high levels of lead can cause vomiting, diarrhea,

convulsions, Coma or even death. However, ongoing exposure to even very small amounts of lead can be harmful, especially to infants and young children. Therefore it is very important to monitor the trace levels of it in environments (2).

In this aspect, reliable and sensitive analytical methods have an important role to evaluate the environmental impact of metal pollutants (3). Currently, the most common analytical methods for the lead trace determination are the flame atomic absorption spectrometry (FAAS) (4,5), the electrothermal atomic absorption spectrometry (ETAAS) (6-8) and the inductively coupled plasma emission spectrometry (ICP) (9). Flame atomic absorption spectrometry is by

far the most widely employed technique for analyte determination (10, 11) but is not sufficiently sensitive for the direct determination of lead and it needs previous separation and preconcentration.

Cloud point methodology has been used for the extraction and preconcentration of metal ions after the formation of sparingly water soluble complexes. Cloud point extraction and atomic spectrometry have been successfully employed for several elements in different matrices and it is an interesting alternative when a complex matrix has to be analyzed (12-14).

Several ligands such as 1-(2-pyridylazo)-2-naphthol (PAN), 2-(2-thiazolylazo)-4-methylphenol (TAC), 1-(2-thiazolylazo)-2-naphthol (TAN), dialkyldithiophosphates (DDTP), have been used in cloud point extraction of metal ions. (15)

Among various ligands used in separation procedures, including cloud point extraction, pyridyl azo reagent has been widely employed due several advantages obtained, such as, capacity to form complexes with each metal in suitable condition and low solubility in water. Some studies indicated that the hydrophobicity of ligands and complexes are the fundamental factors which regulate the extraction efficiency (16, 17). In this work, the complexation between lead and PAN has been extracted by CPE method and determined of it's by FAAS. The proposed method is also applied to determination of lead in soil and waste water samples. The samples have been gathered from polluted zone near petrochemical industry. It locked in Marvdasht city and near main city river, KOR. (The Kor River is the important river in Fars province). This river has been polluted by industrial and agriculture activities. One of the important industries in this area is petrochemical industry. Contaminates produced by petrochemical can be polluted this River. Then fast measuring of lead concentration in real samples has been played a major role to prevent of river pollution. Then this simple, rapid and new method can be used to determine of lead concentration in real samples to prevent polluted other resources.

## Material and Method

### Reagents and solutions

All solutions were prepared with ultra pure water (obtained from HAMILTON, England) Laboratory glass was kept overnight in a 10% (V/V) HNO<sub>3</sub> solution and then rinsed with deionized water. All reagents were made from Merck.

The stock lead solution (1000 mg l<sup>-1</sup>) was prepared by dissolving 0.1598 gr of Lead nitrate with double distilled water in a 100 ml volumetric flask and then standardized solution immediately prior to analysis (18).

The nonionic surfactant Triton X-114, 0.5% (W/V) prepared by dissolving 0.50 gr surfactant Triton X-114

made up to 100 ml with distilled water. A solution of 1×10<sup>-1</sup> mol L<sup>-1</sup> PAN was prepared by dissolving 0.0249 gr of this reagent in 50 ml Ethanol. A buffer solution of pH 8 was prepared by using 0.07 mol l<sup>-1</sup> boric acid and sodium hydroxide adjusting to pH 8 by adding diluted HNO<sub>3</sub> 0.1 M solution.

### Apparatus

A SensAA GBC double beam atomic absorption spectrophotometer (AAS) with hollow cathode lamp operating at 5 mA was used for the determination of lead in the surfactant-rich phase, which was made at 217 nm. An adjustable-capillary nebulizer and supplies of acetylene and air were used for the generation of aerosols and atomization. Deuterium lamp background correction was employed to correct for the non-specific absorbance. Operation in a double beam-background correction mode was imperative due to the complexity of the aspirated sample, which apart from the target metal and excessive chelating agent, causing a suppression of the signal. Measurements were performed in the integration mode.

A centrifuge (Shimifan) was used to accelerate the phase separation process. A Jenway model 3510 pH-meter was used for pH measurements. An electronic analytical balance (220LA, ADAM) was used for weighting the solid materials. A thermostated water bath (Fater Ltd.) model W610B was employed to maintain the experimental temperature.

### Procedure

For the cloud point extraction, an aliquots of 10 ml of a solution containing lead, and 1 ml of buffer solution pH=8, 2 ml Triton X-114 0.5% (W/V), 0.5 ml of PAN 1×10<sup>-1</sup> mol l<sup>-1</sup> were placed in a centrifuge tube and heated in a thermostat water bath at 55°C for 15 min. After heated, the resultant solution was subjected to centrifugation at 4000 rpm for 10 min for phase separation, and then cooled in an ice-water for 10 min in order to increase the viscosity of the surfactant-rich phase. The supernatant aqueous phase was easily decanted by simply inverting the tube. To decrease the viscosity of the surfactant phase and rich facilitate sample handling, 1 ml of methanol was added. The resultant solution was introduced into the flame by conventional aspiration.

### Preparation of Real Samples

#### Soil samples

Accurately weighed 1.0 g of soil samples from near Shiraz petrochemical center, dried at 110 °C were poured into a 250-ml beaker and 10 ml concentrated nitric acid was added to it. The mixture was gently heated under a hood until drying. After complete drying and cooling to room temperature, a second 10-ml portion of concentrated nitric acid was added and

the procedure was repeated. Then 10 ml concentrated hydrochloric acid was added to the beaker and the mixture was gently heated until complete drying. After cooling, the residue was dissolved in 10 ml of 1 M HCl and the solution was then filtered into a 100-ml calibrated flask, using a syringe filter (0.45 mm pore sized). The sample was neutralized by proper amounts of a 1 M NaOH solution and finally prepared by purposed procedure.

#### Water samples

Water samples were collected from KOR River and Waste waters were collected from Shiraz petrochemical industry (These located in Marvdasht city and is the important river in Fars province). They were filtered through Watman No. 42 and stored in glass bottles at 4°C. Then the samples were ready for purposed procedure.

**Table 1: Optimization of practical parameters**

CPE parameters	
Equilibration temperature	55 °C
Equilibration time (before and after centrifugation)	15 min
Centrifugation time	10 min
Centrifugation rate (rpm)	4000
Cooling time	10 min
Working pH	8.0
Non-ionic surfactant	0.5 % (w/v) TX-114

**Table 2. Properties of merit obtained by the proposed method**

Parameters	Pb
Linear Range ( $\mu\text{g L}^{-1}$ )	20-300
Correlation Coefficient	0.9998
Detection Limit ( $\mu\text{g L}^{-1}$ ) (n=5)	8
Enrichment factor <sup>a</sup>	50
Preconcentration factor <sup>b</sup>	35
RSD % (n=5)	2.7
Recovery %	97

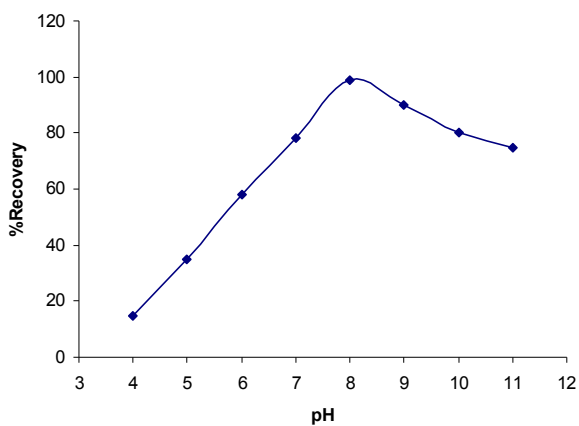
a) Enrichment factor as the ratio of the concentration of the analyte after preconcentration to that before preconcentration.

b) The preconcentration factors as the ratio of initial volume to final volume.

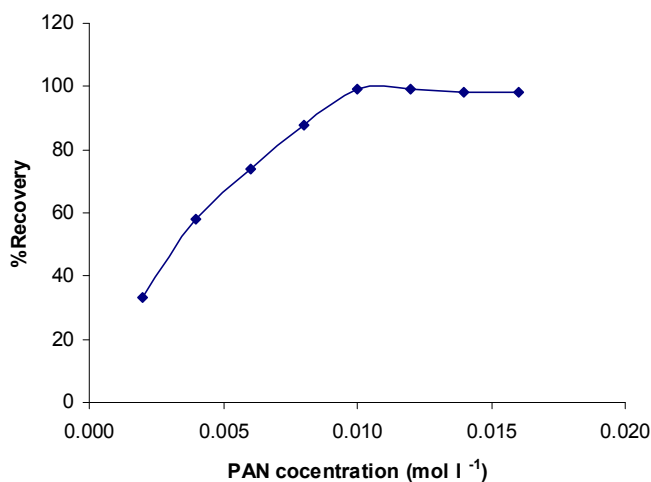
**Table 3. Determination of pb in soil and waste water samples**

Sample	Pb <sup>2+</sup> (µg L <sup>-1</sup> )		% Recovery
	Added	Found	
Waste water <sup>a</sup> 1	-	25.60±0.3	-
	20	47.32±0.3	108.6
	50	79.50±0.4	107.8
Waste water 2	-	ND <sup>d</sup>	-
	20	22.23±0.3	111.1
	50	54.51±0.4	109.0
Soil <sup>b</sup>	-	30.41± 0.4	-
	20	54.73±0.3	121.6
	50	86.24±0.4	111.6
Water <sup>c</sup>	-	ND	-
	20	19.00±0.5	95.0
	50	51.30±0.3	102.6

- a) From Shiraz petrochemical center
- b) From near Shiraz petrochemical center
- c) From Kor river water (local river)
- d) No detected



**Fig. 1 Effect of pH on the CPE-preconcentration performance**



**Fig.2 Effect of the PAN concentration on the recovery of Pb (II) ion.**

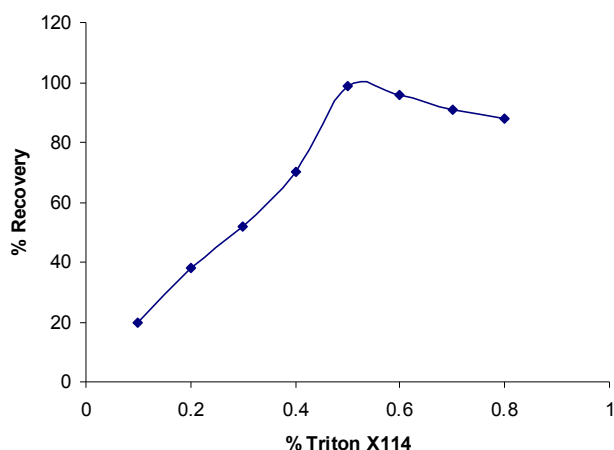


Fig.3 Effect of the Triton X–114 concentrations on the on the extraction recovery of lead.

## Results and Discussion

### Effect of pH

The pH plays a unique role on metal-chelate formation and subsequent extraction, and is proved to be a main parameter for CPE (19). The influences of pH of the aqueous solutions on the extraction yield of Pb (II) as PAN chelate was investigated in the pH range 4–11. For obtain better sensitivity pH values, several buffer agents such as phosphate, carbonate, boric acid / sodium hydroxide, and universal buffer were tested for pH adjustment, the best result was found for boric acid/ sodium hydroxide buffer solution. Fig. 1 shows that the best recovery is in pH 8 on extraction of lead complex. The maximum sensitivity can be achieved by using  $0.07 \text{ mol l}^{-1}$  boric acid/ sodium hydroxide buffer solution.

### Effect of PAN Concentration

The amount of chelating agent is another important indicator as to whether the chelating action processed completely. The effect of PAN concentrations on the recovery were determined in the range of  $2 \times 10^{-3}$  to  $1.6 \times 10^{-2} \text{ mol l}^{-1}$ . As is shown in Fig. 2 on adding over  $1 \times 10^{-2} \text{ mol l}^{-1}$  PAN solution, the extraction efficiency was the most and close to 100%, hence,  $1 \times 10^{-2} \text{ mol l}^{-1}$  PAN solution in ethanol was chosen.

### Effect of Triton X-114 concentration

A successful cloud point extraction should maximize the extraction efficiency by minimizing the phase volume ratio (Vorg/Vaq), thus improving the concentration factor. Triton X-114 was chosen for the formation of the surfactant rich phase due to its low cloud point temperature and commercial availability in a high purified homogeneous form, low toxicological properties, cost and high density of the surfactant rich

phase, which facilitates phase separation by centrifugation.

Fig. 3 has shown the effect of TritonX-114 concentration on the CPE pre-concentration of lead. The signals of lead increased as the Triton X-114 concentration increased from 0.1- 0.5% (W/V) when, Triton X-114 concentration was increased larger than 0.5% (W/V), the signals was decreased. Hence a low concentration of Triton X-114, 0.5% (W/V), was employed for the rest of this work.

### Selection of the dilution agent for the surfactant – rich phase:

An organic solvent should have characteristics such as low viscosity, low surface tension and combustible for use in atomic absorption (20). Different solvents for the surfactant–rich phase were tested so as to select the one producing the optimal results regarding sensitivity. Acetone, methanol, ethanol and DMF were tested for this purpose. Methanol dissolved completely the surfactants which in its extracted complex of lead and PAN and the best recovery were obtained and an optimum volume is 1 ml.

### Practical parameter

The incubation time and equilibration temperature above the cloud point were thoroughly optimized. It is desirable to employ the shortest equilibration time and the lowest possible equilibration temperature, which compromise completion of the reaction and efficient separation of the phases. The dependence of extraction efficiency on equilibration temperature and time were studied within a range of 30 – 60 °C and 5–25 min, respectively. The results showed that an equilibration temperature of 55 °C and an equilibration time of 15 min are enough to get quantitative extraction of the ions. The effect of the centrifugation

time on the extraction efficiency was also studied within a range of 5–25 min. A centrifugation time of 10 min at 4000 rpm was selected for the entire procedure, since analyte extraction in this time is almost quantitative. The results were shown in Table 1.

#### Figures of merit

Calibration graph was obtained by pre-concentrating 10 ml of a sample containing known amounts of analysts in presence of 0.5% Triton X-114 in a medium buffered at pH 8. Final solution was introduced into flame atomic absorption spectrometry by conventional aspiration following the addition of 1 ml of methanol. Under the specified experimental conditions the calibration curve for pb was linear from 20 to 300  $\mu\text{g l}^{-1}$  with a correlation coefficient of 0.9998. The relative standard deviation (RSD,  $n=5$ ) for 50  $\mu\text{g l}^{-1}$  concentration of lead was 2.7% and the limit of detection (LOD) under the optimal condition was 8.0  $\mu\text{g l}^{-1}$ . The enhancement factor, calculated as the ratio of absorbance of preconcentration samples to that obtained without preconcentration, and the preconcentration factor is as ratio of initial volume to final volume, were 50 and 35, respectively (Table 2). Enhancement factor and the LOD have shown a good sensitivity of this method.

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#### Determination of lead in soil and waste water:

In order to test the reliability of the proposed methodology suitable for the assaying of lead in soil, waste water samples. For this purpose, 10ml of each of the samples were pre-concentrated with 0.5% (w/v) Triton X- 114 and a PAN concentration of 0.01 M, following the proposed procedure. The results are shown in Table 3.

#### Conclusion

Cloud point extraction using Triton X-114 shown to be an efficient, simple, easy, safe, rapid, inexpensive and versatile pre-concentration technique to determine pb by FAAS. In this method PAN is a reagent selectivity and sensitivity for determination of lead in soil, water samples. Phase separation can be achieved at relatively low temperatures and extraction efficiency is high, resulting in low detection limits and high enrichment factors and good R.S.D. The proposed method has promising application in environmental analysis for trace lead.

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