

Determination of Pb^{2+} ion in water samples by CPE-FAAS using erythrosine as complexing agent

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Abstract: A cloud point extraction procedure was presented for the preconcentration of Pb^{2+} ion in various water samples. Pb^{2+} ion after complexation with Erythrosine, quantitatively extracted in Triton X-114. After centrifugation, the surfactant-rich phase was dissolved in acidified methanol prior to its analysis by flame atomic absorption spectrometry (FAAS). The influence of analytical parameters including ligand, Triton X-114, bath temperature, heating time, centrifuge rate and time were optimized. The effect of the matrix ion on the recovery of Pb^{2+} ion was investigated. The detection limit (3S.D.b/m, n=5) of $0.012 \mu\text{g mL}^{-1}$ along with preconcentration factor of 30 and enrichment factor of 15.07 with R.S.D. of 2.68% was achieved. The proposed procedure was applied to the analysis of various water samples.

1. Introduction

Water pollution by heavy metal ions is causing serious ecological issues in the globe, therefore, the determination of trace amount of toxic heavy metal ions such as lead, mercury, cadmium and etc. in the environmental samples is necessary, and requires analytical techniques exhibiting low detection limits¹. For centuries, lead toxicity has been one of the most significant preventable causes of neurologic morbidity from an environmental toxin. A heavy metal, lead is ubiquitous in our environment but has no physiologic role in biological systems. Its effects are pervasive yet often subtle; with consequences ranging from cognitive impairment in children to peripheral neuropathy in adults. Lead is one of the major heavy metals of the antiquity and has gained considerable importance as a potent environmental pollutant²⁻⁴.

Analytical methods such as graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma atomic emission or mass spectroscopy (ICP-AES, ICP-MS), and stripping voltammetry have been proposed for the determination of heavy metal ions at trace concentration level. But these methods need relatively high cost apparatus. Flame atomic absorption spectrometry (FAAS) is one of the most common analytical techniques for the determination of trace elements, but it often suffers from its low sensitivity. Because their amount is always lower than the detection limit of instruments and in addition, the problem of unsuitable matrix occurs. Therefore determination of this trace quantity of heavy metal ions which they are found at very low concentrations requires the use of preconcentration step prior to the determination step⁵⁻⁷.

Various separation and preconcentration methods have been used to achieve these goals. Among them are solid phase extraction^{8, 9}, liquid-liquid extraction¹⁰, cloud point extraction^{5, 11, 12}, ion exchange¹³ and coprecipitation¹⁴ techniques. The traditional liquid-liquid extraction and other conventional separation methods are time consuming and labor-intensive approaches, besides requiring relatively large amounts of high-purity and frequently toxic solvents, which have to be disposed of properly.

Cloud point extraction (CPE) is an attractive technique that reduces the consumption of and exposure to a solvent, disposal costs and extraction time. The CPE method has important practical application and used to separate and preconcentrate analyte compounds as a step prior to their determination after the formation of sparingly water-soluble complexes²⁻⁷. The non-ionic surfactant, Triton X-114, is the most frequently used surfactant to perform CPE experiments. A successful cloud point extraction should maximize the extraction efficiency by minimizing the phase volume ratio ($V_{\text{org}}/V_{\text{aqueous}}$), thus improving its concentration factor¹¹.

This paper reports the preconcentration of Pb^{2+} after the formation of a complex with Erythrosine as a proper complexing agent, and later analysis by flame atomic absorption spectrometry (FAAS), using TritonX-114 as surfactant. The proposed method was applied for the determination of pb^{2+} ion in several water samples successfully.

2. Experimental

2.1. Reagents and solutions

All chemicals were of analytical reagent grade and were used without previous purification. The laboratory glassware was kept overnight in a 1.4 M HNO_3 solution. Before the use, the glassware was washed with deionized water and dried. Stock standard solutions of Pb^{2+} at a concentration of $1000 \mu\text{g}\cdot\text{L}^{-1}$ were prepared by dissolving appropriate amounts of $\text{Pb}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$ in distilled water. A 1.0 % (w/v) Triton X-114 was prepared by dissolving 1.0 g of Triton X-114 in 100 mL volumetric flask. A solution of 0.001 mol L^{-1} of Erythrosine was prepared by dissolving appropriate amounts of this reagent in distilled water.

2.2. Apparatus

An atomic absorption spectrometer (Perkin Elmer Co., USA) Model A analyst 800 with deuterium lamp background correction and lead hollow cathode lamps was used for absorbance measurements at wavelength of 217.0 nm according to instrument instruction. The acetylene flow rate and the burner height were adjusted in order to obtain the maximum absorbance signal, while aspirating the analyte solution in 1 mol L^{-1} HNO_3 in methanol. A Metrohm 827 pH meter furnished with a combined glass-saturated calomel electrode was used for pH measurements. A thermostatic bath (Peter Huber Co., Germany) maintained at desired temperature by circulating water was used for cloud point preconcentration experiments and phase separation was assisted using a centrifuge (Hettich) in 15 ml calibrated centrifuge tubes (Superior, Germany).

2.3. Cloud point extraction procedure

A typical cloud point experiment required the following steps: an aliquot of 15 mL of a solution containing $0.4 \mu\text{g mL}^{-1}$ of pb^{2+} ion, 0.067% (w/v) Triton X-114 and $5 \times 10^{-3} \text{ mmol L}^{-1}$ of Erythrosine was adjusted to pH 6.0 with the addition of NaOH. Then the centrifuge tubes containing the mixed solutions was shaken for 1 min and left to stand in a thermo-stated bath at 40°C for 5 min. Separation of aqueous and surfactant rich phases were accomplished by centrifuging at 3500 rpm for 5 min. On cooling in an ice bath (5 min), the surfactant-rich phase became viscous. Then, supernatant aqueous waste in the tubes was removed with a pipette pasture and 0.5 mL of 1.0 mol L^{-1} HNO_3 in methanol was added to it. The final solution was aspirated directly into the flame of FAAS.

3. Result and discussion

3.1. Effect of pH

The formation of metal–chelate and its chemical stability are the two important influence factors for CPE. The pH plays an unparalleled role on metal–chelate formation and subsequent extraction, and is proved to be a main parameter for CPE¹⁵. Extraction yield depends on the pH at which complex formation is carried out. In this view, a set of similar experiments in the pH range of 2–9 was conducted according to cloud point extraction method, and the obtained results are shown in Fig. 1. As the results showed the recovery of pb^{2+} are maximum when pH is 6.0. In more acidic solutions, deterioration of the signal occurs due to protonation of Erythrosine, while at $\text{pH} > 6$, the signal decreases and recovery is reduced due to precipitation of pb^{2+} ion in the

form of hydroxides or ternary complexes¹¹. Therefore, pH value of 6.0 seems to be optimum for the complete recovery of the analyte ions by the cloud point extraction method.

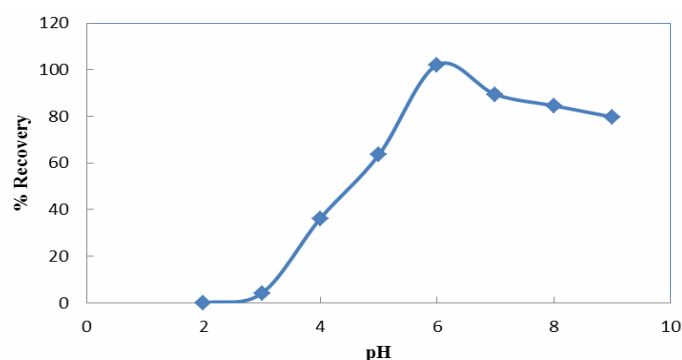


Fig. 1. Effect of pH on lead (II) ion recovery, Conditions: (15 mL $0.4 \mu\text{g mL}^{-1}$ Pb^{2+} ion, 0.067% (w/v) Triton X-114, and $5 \times 10^{-3} \text{ mmol L}^{-1}$ Erythrosine at various pH. Diluting solution: 1.0 mol L^{-1} HNO_3 in methanol.)

3.2 Effect of Erythrosine concentration

In order to study the influence of Erythrosine on the analytical response, different concentrations of the chelating reagent in the range of 2.5×10^{-3} to 0.1 mmol L^{-1} were used, and the general procedure was applied. The results (Fig 2.) showed that the signal is maximal when the concentration of Erythrosine is $5 \times 10^{-3} \text{ mmol L}^{-1}$. Therefore, a $5 \times 10^{-3} \text{ mmol L}^{-1}$ Erythrosine solution was selected as optimal. At lower than $5 \times 10^{-3} \text{ mmol L}^{-1}$ of Erythrosine, insufficient concentration leads to incomplete complexation. A possible explanation for the decrease in absorption with higher concentrations may be attributed to the formation of charged complexes with excess Erythrosine in the medium or with remaining excess Erythrosine in aqueous solution, competing with surfactant-rich phase for formation of complex with metal ion in aqueous phase¹¹.

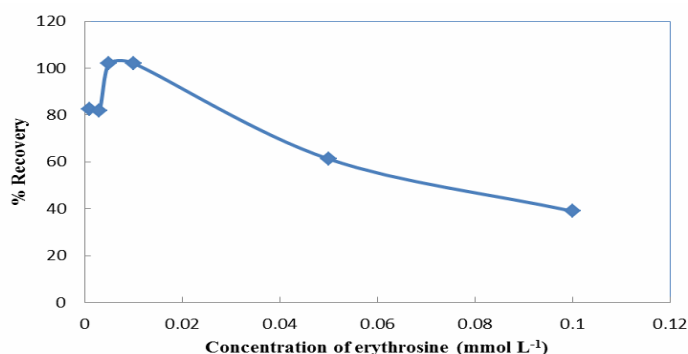


Fig. 2. Effect of Erythrosine concentration on lead (II) ion recovery, Condition: (15 mL $0.4 \mu\text{g mL}^{-1}$ Pb^{2+} ion, 0.067 (w/v) Triton X-114, at pH 6.0 and various concentrations of Erythrosine. Diluting solution: 1.0 mol L^{-1} HNO_3 in methanol.)

3.3. Effect of Triton X-114 concentration

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 centrifugation¹⁶. The effect of Triton X-114 concentration on the extraction efficiency was studied in the concentration range of 0.01– 0.24% (w/v). The results in Fig 3 showed that, highest Pb^{2+} ion recovery was obtained with 0.067 % (w/v) TritonX-114.

For concentrations lower than 0.067 % (w/v), the preconcentration efficiency of the formed complexes was very low, since the assemblies at low concentration were probably inadequate to preconcentrate trace amounts of Pb^{2+} ion. The decreasing of absorbance at a concentration higher than 0.067 % (w/v) is due to the

remaining of some part of Triton X-114 and Erythrosine in aqueous solution as this phase can compete with surfactant-rich phase to draw analyte ion. Therefore, in order to obtain optimum condition, a 0.067% (w/v) solution of Triton X-114 concentration was selected for further studies⁸.

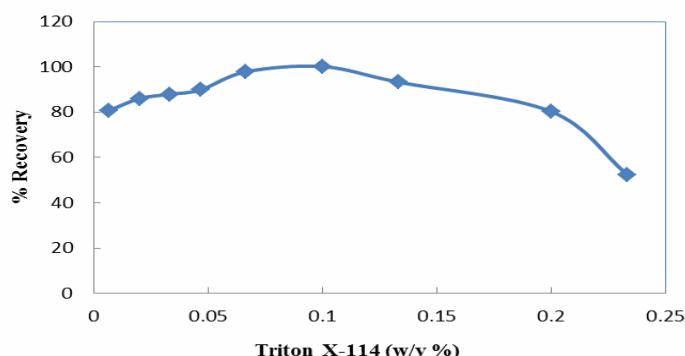


Fig. 3. Effect of amount of Triton X-114 on the recoveries of lead (II) ion, Condition: (15 mL $0.4 \mu\text{g mL}^{-1}$ Pb^{2+} ion, $5 \times 10^{-3} \text{ mmol L}^{-1}$ Erythrosine, at pH 6.0 and various concentrations of Triton X-114 Diluting solution: $1.0 \text{ mol L}^{-1} \text{ HNO}_3$ in methanol.)

3.4. Effect of incubation temperature and duration

It was desirable to employ the shortest equilibration time and the lowest possible equilibration temperature as a compromise between completion of extraction and efficient separation of phases¹⁷. The dependence of extraction efficiency upon equilibration temperature and time above the cloud point in the range of 30–50 °C and 5–20 min were thoroughly optimized, respectively. The results showed that an equilibration temperature of 40 °C was adequate to achieve quantitative extraction. Higher temperatures lead to the decomposition of Erythrosine– Pb^{2+} complexes and the reduction of analytical signal. At lower temperatures the separation of the two phases is not complete. The incubation time is kept at 5 min which is sufficient for the completion of the physicochemical processes.

3.5. Effect of centrifuge time and rates

It is required to preconcentrate trace amount of pb^{2+} ion with high efficiency in short time. Therefore, CPE on a set of experiments of 15 mL sample at pH=6.0, $5 \times 10^{-3} \text{ mmol L}^{-1}$ of Erythrosine, $0.4 \mu\text{g mL}^{-1}$ of pb^{2+} ion and 0.067% Triton X-114 by heating at 40 °C and further centrifuging in various rates and times has been carried out. The results indicate the experiment in the optimized reagent concentration after heating for 5min at 40 °C and centrifuging by 5 min in 3500 rpm and cooling in 5 min.

3.6. Interferences

The effects of representative potential interfering species were tested. The tolerance limits of the coexisting ions, that defined as the largest amount making change the recovery of pb^{2+} ion less than 5%, are given in Table 1. They show that the recovery is quantitative and satisfactory in the presence of most foreign ions and the major ions in the water and real samples have no obvious influence on CPE of pb^{2+} ion under the selected conditions.

Table 1 Effects of the matrix ions on the recovery of the pb^{2+} ion

Foreign ion	Tolerance ratio
Na^+ , Ni^{2+} , Cu^{2+} , Mn^{2+} , CO_3^{2-} , PO_4^{3-} , NO_3^-	1000
Mg^{2+} , Zn^{2+} , Co^{2+} , Ca^{2+} , K^+ , SO_4^{2-} , CH_3COO^-	500
Cd^{2+}	250

3.7. Analytical performance

Calibration graph was obtained by preconcentration of 15 mL of several solutions under optimum conditions, containing various concentrations of analyte, with the process performed according to the general procedure section where the absorbance of the final solution was measured by FAAS. A linear relationship

between the measured absorbance and concentration of Pb^{2+} ion in the range 0.013-1.066 $\mu g mL^{-1}$ was obtained. Also, a calibration graph was obtained without preconcentration in order to calculate the enrichment factor. The equation of the regression line with and without the preconcentration was $Y = 0.1085 C + 0.0046$ and $Y = 0.0072 C + 0.0016$ (for R) respectively, where C is the concentration of Pb^{2+} in $mg L^{-1}$. The enrichment factor was calculated as the ratio of the slopes of the calibration curve with and without preconcentration, and factors obtained for Pb^{2+} ion was 15.07, respectively. Table 2 shows some of characteristics of proposed CPE method including the linear range, the relative standard deviation, the limit of detection and the preconcentration factor.

Table 2 Characteristics performance of the presented CPE method

Characteristic	Value
Linear range ($\mu g L^{-1}$)	0.013-1.066
Limit of detection ($\mu g L^{-1}$), (3S.D.b/m, n = 5)	0.012
Preconcentration factor	30
Enrichment factor	15.07
R.S.D. (%)	2.68

3.8. Analysis of real samples

The proposed procedure has been applied to the determination of lead content in city water, well water and spring water samples. The results are given in Table 3.

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.

Table 3 Recovery studies of lead in real samples

Sample	Added ($mg L^{-1}$)	Found ($mg L^{-1}$)	Recovery (%)
Tap Water (Firoozabad city)	0	Nd ^a	-
	0.267	0.271	101.49
	0.400	0.398	99.50
Wells water (University's wells)	0	Nd	-
	0.267	0.272	101.87
	0.400	0.400	100.00
Spring water (Atashkadeh spring)	0	Nd	-
	0.267	0.246	92.13
	0.400	0.380	95

a) Not detected

3.9. Conclusion

In this work, the use of micellar systems as a separation and preconcentration for Pb^{2+} ion offers several advantages including low cost, safety, preconcentrated Pb^{2+} ion with high recovery and very good extraction efficiency. We have proposed the use of cloud point extraction as an alternative method for the preconcentration of Pb^{2+} ion as a prior step for its determination by flame atomic absorption spectrometry. The proposed method can be applied to the determination of trace amount of Pb^{2+} ion in various water samples. The separation occurred efficiently, resulting in good enrichment factor and low LOD. In contrast to some other environmental pollution is limited to a small amount of surfactant. The methodology offers a simple, rapid, inexpensive and nonpolluting alternative to other preconcentration techniques¹⁸⁻²¹.

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