ORIGINAL ARTICLE

Applicability of cloud point extraction for the separation trace amount of lead ion in environmental and biological samples prior to determination by flame atomic absorption spectrometry

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Abstract A sensitive cloud point extraction procedure(CPE) for the preconcentration of trace lead prior to its determination by flame atomic absorption spectrometry (FAAS) has been developed. The CPE method is based on the complex of Pb(II) ion with 1-(2-pyridylazo)-2-naphthol (PAN), and then entrapped in the non-ionic surfactant Triton X-114. The main factors affecting CPE efficiency, such as pH of sample solution, concentration of PAN and Triton X-114, equilibration temperature and time, were investigated in detail. A preconcentration factor of 30 was obtained for the preconcentration of Pb(II) ion with 15.0 mL solution. Under the optimal conditions, the calibration curve was linear in the range of 7.5 ng mL^{-1}–3.5 µg mL^{-1} of lead with R^2 = 0.9998 (n = 10). Detection limit based on three times the standard deviation of the blank (3S$_b$) was 5.27 ng mL^{-1}. Eight replicate determinations of 1.0 µg mL^{-1} lead gave a mean absorbance of 0.275 with a relative standard deviation of 1.6%. The high efficiency of cloud point extraction to carry out the determination of analytes in complex matrices was demonstrated.

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The proposed method has been applied for determination of trace amounts of lead in biological and water samples with satisfactory results.

1. Introduction

The steady increase in pollution necessitates the analysis and monitoring of toxic species that could become a serious potential hazard if not controlled.

(Van Staden and Botha, 1999). Lead is one of the most toxic elements, has an accumulative effect and is an environmental priority pollutant (Chen et al., 2005). The harmful effects on human health, caused by lead contamination, are well-known and among them, the reduction of the enzymatic activity, the kidneys function and the neuromuscular difficulties have been reported (Comitre and Reis, 2005). The US Environmental Protection Agency (EPA) has classified lead as a group B2 (probable) human carcinogen (Naseri et al., 2008). Nowadays, there are legal restrictions concerning lead release to the environment. Nevertheless, it is used as a raw material in the manufacturing industry such as automotive batteries, ceramic and ink (Comitre and Reis, 2005). Furthermore, lead is a leftover of some industrial processes in the production of fertilizers and pesticides. In both cases, it could be either delivered to the environment by inadequate manufacturing processes or caused by accident (Naseri et al., 2008). The environmental and health problems arise fundamentally from the use of gasoline anti-knock products and paint pigments (Nezio et al., 2004). As a consequence, the world health organization (WHO) has established the maximum allowable limit of 10 ng mL^{-1} for lead in drinking water (WHO, 1996). It is, therefore, important to monitor the lead level in the environmental samples.

Many methods for the determination of trace metals by atomic spectrometry techniques are still commonly carried out using a preconcentration step prior to their detection (Tarley et al., 2004). FAAS has been a very attractive technique for routine metal determinations, owing to its ease of operation, its low acquisition and operating costs compared with inductively coupled plasma optical emission spectrometry (ICPOES) and graphite furnace atomic absorption spectrometry (GFAAS), and its high sample throughput (Tarley et al., 2006). However, there is a great necessity for the preconcentration of trace metals prior to their determination, basically due to their low concentrations in aqueous sample (Anthemidis and Ioannou, 2006). For this reason, there is no decrease in the activity related to the development of new analytical methods for the preconcentration of metal ions (Evans et al., 2004, 2005).

Cloud point extraction (CPE) has been used for the preconcentration of lead, after the formation of a complex with 2-(5-bromo-2-pyridylazo)-5-(diethylamino)-phenol, and later analysis by graphite furnace atomic absorption spectrometry using TritonX-114 as surfactant (Chen et al., 2005). Cadmium, copper, lead and zinc (Chen and Teo, 2001) were simultaneous preconcentrates after the formation of a complex with 1-(2-thiazolylazo)-2-naphthol, and later analysis by FAAS, using TritonX-114 as the surfactant. A CPE procedure has been developed for the determination of trace amounts of Cr(III), Pb(II), Cu(II), Ni(II), Bi(III), and Cd(II) ions by using FAAS without ligand using Tween 80 as the surfactant (Candir et al., 2008). A

CPE procedure has been developed for the determination of trace amounts of Pb(II) ions by using capillary zone electrophoresis without ligand using PONPE 7.5 as the surfactant (Luconi et al., 2006). A flow injection micelle-mediated separation/preconcentration procedure for the determination of lead and cadmium by FAAS has been proposed (Silva and Roldan, 2009). The analytes reacted with 1-(2-thiazolylazo)-2-naphthol to form hydrophobic chelates, which were extracted into the micelles of Triton X-114. Determination of Lead in Soil and Water samples by CPE-FAAS method was also reported (Tavallali et al., 2010).

In the present work, CPE method has been used for the preconcentration of lead, after the formation of a complex with 1-(2-pyridylazo)-2-naphthol, prior to FAAS determination using TritonX-114 as the surfactant. The analytical conditions for the preconcentration of lead were investigated.

2. Experimental

2.1. Instrumentation

A Varian model SpectrAA 220 atomic absorption spectrometer equipped with deuterium background correction and lead hollow-cathode lamp was used for absorbance measurements at a wavelength of 283.3 nm according to instrument instruction. The instrumental parameters were adjusted according to the manufacturer's recommendations. A Metrohm 692 pH meter was used for pH measurements. A Centurion scientific centrifuge model 1020 D.E. (West Sussex, United Kingdom) was used to accelerate the phase separation.

2.2. 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 mol L^{-1} HNO$_3$ solution. Before the use, the glassware was washed with deionized water and dried. Stock solution of lead at a concentration of 1000.0 µg mL^{-1} was prepared by dissolving appropriate amounts of Pb(NO$_3$)$_2$ (Merck, Germany) in HNO$_3$ 0.2 mol L^{-1}. Working reference solutions were obtained daily by stepwise dilution from stock solution. A solution of 0.01 mol L^{-1} 1-(2-pyridylazo)-2-naphthol (PAN) (Merck, Germany) was prepared by the dissolution of 0.25 g of the chelating agent in 100 mL of ethanol. A solution of 0.3% (v/v) Triton X-114 (Sigma, St Louis, USA) in deionized water was used as the surfactant agent. Buffer solution was prepared from 0.2 mol L^{-1} acetic acid and 0.2 mol L^{-1} sodium acetate for pH 6. Solutions of alkali metal salts (1%) and various metal salts (0.1%) were used for studding the interference of anions and cations, respectively.

2.3. Procedure for cloud point extraction

An aliquot of water sample containing 10.0 µg of Pb(II) was pipetted to centrifuge tubes. Then, 1 mL of 0.2 mol L^{-1} acetate

buffer (pH 6.0), 1.0 mL of 0.3% Triton X-114, 0.1 mL of 0.01 mol L^{-1} PAN and 1 mL NaCl 3.5% (W/V) were sequentially added to it and the final volume was reached to 15 mL. The centrifuge tubes containing the mixed solutions were heated in a thermostatic water bath at 40 °C for 15 min. Separation of the aqueous and surfactant rich phases was accomplished by centrifuging at 3000 rpm for 5 min. After being cooled in an ice bath, the surfactant-rich phase became viscous, and the supernatant aqueous waste in the tubes was removed with a pipette. Then, to 0.50 mL of solution, 0.5 mol L^{-1} of HNO$_3$ in ethanol was added. The final solution was aspirated directly into the flame of AAS against the blank prepared in the same manner without the addition of metal ions.

2.4. Sample preparation

Tow certified reference material (CRMs) furnished by the National Institute for Environment Studies (NIES) No. 1 Pepperbush and NIES No. 7 Tea Leaves have been analyzed. Approximately 0.50 g of this material was weighed accurately into a Teflon cup and dissolved in concentrated nitric acid ($\sim$10 mL) with heating on a water bath. The solution was cooled, diluted and filtered. The filtrate was made up to 100.0 mL with deionized water in a calibrated flask. An aliquot of the sample solution was taken individually and lead ion was determined by the general procedure.

Tap water and well water samples were collected in acid-leached polyethylene bottles. Kerman tap water sample was collected from our Laboratory (Payame Noor University, Kerman, Iran). The well water sample was collected from Payame Noor University, Kerman, Iran. Mineral water samples were purchased from a local market. The only pretreatment was acidification to pH 2 with nitric acid, which was performed immediately after collection, in order to prevent adsorption of the metal ions on the flask walls. The samples were filtered before analyses through a cellulose membrane (Millipore) of 0.45 μm pore size.

3. Result and discussion

3.1. Effect of PAN concentration on recoveries of the Pb(II) ion

In order to study the influence of PAN on the analytical response, different concentrations of the chelating reagent in the range of 2.5×10^{-3} to 4.0×10^{-2} mol L^{-1} were used, and the general procedure was applied. The results showed that the signal is maximal when the concentration of PAN is in the range of 7.5×10^{-3} to 1.5×10^{-2} mol L^{-1}. Therefore, a 1.0×10^{-2} mol L^{-1} PAN solution was selected as optimal.

3.2. Effect of pH

The formation of the metal–chelate and its chemical stability are the two important influence factors for CPE. The pH plays a unique role on metal–chelate formation and subsequent extraction, and is proved to be a main parameter for CPE (Shokrollahi et al., 2008). 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 3–9 was conducted according to the described procedure in Section 2.3. Diluted HNO$_3$ and NaOH solutions were used for pH adjustments. The results are shown in Fig. 1 and showed that,

pH value of 6 seems to be optimum for the complete removal of the Pb(II) ion concentration by CPE. The addition of 1–4 mL of acetic acid and sodium acetate buffer did not have any effect on the adsorption. Therefore, 1 mL of the buffer with pH $\sim$6.0 was used in all subsequent experiments.

3.3. 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 phases. It is reported that increasing the temperature or the equilibration time can decrease the amount of water in a surfactant-rich phase and hence the volume of that phase decreases. This is because dehydration between the hydrogen bonds occurs when increasing temperature (Jia et al., 2008). In an incubation time of 15 min, incubation temperature that varied between 20 and 60 °C was examined. The results showed that the optimum recoveries were obtained at 35–45 °C. So, an equilibration temperature of 40 °C was used.

3.4. 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 centrifugation (Tavallali et al., 2010). The effect of Triton X-114 concentration on the extraction efficiency was studied in the concentration range of 0.05–0.5% (v/v). The results showed that, highest Pb(II) ion recovery was obtained with 0.3% (v/v) Triton X-114. By decreasing the surfactant concentration to 0.05% (w/v) the recovery was reduced.

The Pb(II) ion recovery also decreased for a higher Triton X-114 concentration (0.3%, v/v). This result might be related to the presence of the high amount of surfactant, resulting in an increase in the volume of the surfactant-rich phase. In addition, the viscosity of the surfactant-rich phase increases, leading to poor sensitivity (Shokrollahi et al., 2008).

3.5. Effect of NaCl concentration

It has been reported that the presence of electrolytes decreases the cloud point temperature, resulting in more efficient
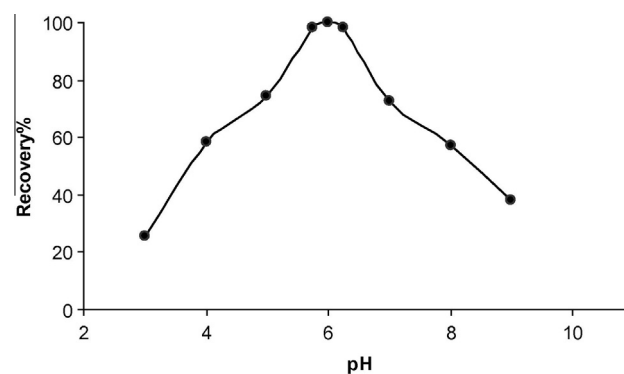
Figure 1 Effect of pH on recovery of Pb(II) ions. Conditions: 10.0 μg of Pb(II); buffer, 1 mL; PAN, 0.1 mL of 0.01 mol L^{-1} and 1 mL NaCl 3.5% (W/V).

extraction. The lower cloud point is attributed to electrolytes promoting dehydration of the poly(oxyethylene) chains. The salting-out phenomenon is directly related to desorption of ions from the hydrophilic parts of the micelles, increasing the inter-attraction between micelles and consequently leading to the precipitation of the surfactant molecules (Pourreza et al., 2008).

In order to study the effect of the addition of electrolyte on micellar solutions of Pb(II) ions, NaCl solution was investigated as electrolyte in the concentration range from 1% to 7% (w/v) and the highest sensitivity and Pb(II) ion recovery was obtained at 3.5% NaCl concentration. The signal decreased considerably for increasing NaCl concentrations (3.5–7%). This effect might be explained by the additional surface charge when the NaCl concentration is very high, thus changing the molecular architecture of the surfactant and consequently the micelle formation process. It is necessary to emphasize that different blank solutions were also evaluated and no significant signal was obtained. In this way, 3.5% NaCl concentrations were used in all further experiments.

3.6. Effect of foreign ions

In view of the high selectivity provided by flame atomic absorption spectrometry, the only interference may be attributed to the preconcentration step, in which the cations may react with PAN which may lead to decrease in extraction efficiency. Interferences studied were those related to the preconcentration step, cations that may react with PAN or species that may react with analytes and decrease the extraction efficiency. To perform this study, interferents ion in different interferents-to-analyte ratios were added to a solution containing 10.0 μg of Pb(II) and were subjected to the complete procedure. Each experiment was repeated three times and averaged values are given as the results. Table 1 shows the tolerance limits of the interferents ions (error ± 5%). The results demonstrate that the presence of large amounts of species commonly present in water samples have no significant effect on the CPE of lead.

3.7. Calibration, precision and detection limits

Calibration curves were obtained by the preconcentration of 15.0 mL of a standard sample solution in the presence of 0.3% Triton X-114 at pH 6. The samples were introduced into the flame by conventional aspiration following the addition of 0.5 mL of 0.5 mol L^{-1} HNO_3 in ethanol. In this case, linear relationships between the absorbance measured and the concentration of metal placed in the solution were obtained. Linearity was maintained between 7.5 ng mL^{-1}–3.5 μg mL^{-1} with a correlation factor (r) of 0.9996 for the equation $A = 0.2781C$ ppm + 0.0013 where A = absorption and C = concentration. Eight replicate determinations of 1.0 μg mL^{-1} lead gave a mean absorbance of 0.275 with relative standard deviation of 1.6%. Preconcentration of 15.0 mL of sample in the presence of 0.3% Triton X-114 permitted the detection of 5.27 ng mL^{-1} for Pb(II) ion.

The preconcentration factors as the ratio of initial volume to final volume and enrichment factor as the ratio of the concentration of the analyte after preconcentration to that before preconcentration which give the same absorbance were 30 and 15.5 for Pb(II) ion, respectively. However, the higher preconcentration factors could be obtained by using larger sample volumes.

3.8. Accuracy of the method

The accuracy and applicability of the proposed method has been applied to the determination of Pb(II) ion in the National Institute for Environment Studies (NIES) No. 1 pepperbush and NIES No. 7 tea leaves. Results are given in Table 2. It was found that there is no significant difference at the 95% confidence level between results obtained by the proposed method and the certified results. These results indicate that the applicability of the developed procedure in lead determination is free of interference.

3.9. Analysis of real samples

The proposed procedure has been applied to the determination of lead content in tap water, well water and two different mineral water samples. Again, graphite furnace atomic absorption spectroscopy (GFAAS) was employed to check the accuracy. The t-test was applied to both sets of results and showed that there was no significant difference at the 95% confidence level. The results are given in Table 3.

The recovery of lead from water samples spiked with Pb(II) samples were also studied. The results tabulated 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.

3.10. Comparison of proposed method with the other sample reported methods

A comparison of the proposed CPE method with other reported CPE methods, for lead extraction from water samples, is given in Table 4 (Chen et al., 2005; Chen and Teo, 2001; Candir et al., 2008; Luconi et al., 2006; Silva and Roldan, 2009; Tavallali et al., 2010). The detection limits obtained, using the proposed CPE method, was better than some of the other reported CPE methods (Candir et al., 2008; Luconi et al., 2006; Tavallali et al., 2010). Based on the results

Table 1 Tolerance limit of foreign ions.

Foreign ions	Interferent/Pb(II) ratio[a]
PO_4^{3-}, $H_2PO_4^-$, $H_2PO_4^{2-}$	5000
NH_4^+	2000
CH_3COO^-	1000
Na^+, K^+	4000
Ca^{2+}, Mg^{2+}	2000
Co^{2+}, Cu^{2+}, Mn^{2+}, Zn^{2+}, Fe^{2+}, Fe^{3+}	1000
Ni^{2+}	800
Al^{3+}	100
Cr^{3+}	600
Sn^{2+}, As^{3+}	700
Sb^{3+}, Cd^{2+}	500

Conditions: 10.0 μg of Pb(II); buffer, 1 mL; PAN, 0.1 mL of 0.01 mol L^{-1} and 1 mL NaCl 3.5% (W/V).
[a] Average of three determinations ± standard deviation.

Table 2 Determination of Pb(II) ion in biological samples.

Sample	Composition	Found[a]
Pepperbush (NIES, 1)	K, 1.51 ± 0.06; Mn, 0.203 ± 0.17; Ca, 1.38 ± 0.07; Mg, 0.408 ± 0.020%; Cd, 6.7 ± 0.5; Ni, 8.7 ± 0.6; Cu, 12 ± 1; Cs, 1.2; Tl, 0.13; Fe, 205 ± 17; Co, 23.0 ± 3; Pb, 5.5 ± 0.8; P, 1100; Cr, 1.3; Zn, 340 ± 20; Ba, 165 ± 10; Sr, 36 ± 4; As, 2.3 ± 0.3; Rb, 75 ± 4; Na, 106 ± 13; Hg, 0.05 µg g-1	Pb: 5.6 ± 0.2 µg g^{-1}
Tea Leaves (NIES, 7)	Pb, 0.80; Cd, 0.030; Sb, 0.014; Zn, 33; Cr, 0.15; Al, 775; Mg, 1530; Ba, 5.7; K, 18600; Sc, 0.011; Na, 15.5; Sr, 3.7; Ca, 3200; Cs, 0.22 l; Co, 0.12; Mn, 7.00; Ni, 6.5 µg g^{-1}	Pb: 0.78 ± 0.04 µg g^{-1}

NIES: National Institute of Environmental Studies reference materials.
[a] Average of four determinations, ± standard deviation.

Table 3 Determination of lead in water sample.

Sample	Lead amount (ng mL^{-1})			Recovery%
	Added	Found by the proposed method[a]	Found by GFAAS[a]	
Tap water	0	8.6 ± 0.3	8.7 ± 0.5	–
	30	38.4 ± 1.6	39.1 ± 2.5	99.3
Well water	0	BLR[b]	4.3 ± 0.3	–
	30	30.9 ± 1.3	32.2 ± 1.9	103
Mineral water 1	0	BLR	3.7 ± 0.4	–
	30	31.8 ± 1.4	33.0 ± 2.7	106
Mineral water 2	0	9.1 ± 0.7	9.2 ± 0.8	–
	30	39.4 ± 1.7	38.7 ± 3.1	101

[a] Average of three determinations, ± standard deviation.
[b] Below of linear range.

Table 4 comparison of the reported methods with the proposed method.

Enrichment method	Detection method	Linear range (ng mL^{-1})	RSD%	Detection limit (ng mL^{-1})	Ref.
CPE	GFAAS	0.1–30	2.8	0.08	Chen et al. (2005)
CPE	FAAS	1.1–160	3.5	1.1	Chen and Teo (2001)
CPE	FAAS	2–12	⩽6	7.2	Candir et al. (2008)
CPE	Capillary zone electrophoresis	12–400	3.6	11.4	Luconi et al. (2006)
CPE	FI-FAAS	50–250	1.6–3.2	4.5	Silva and Roldan (2009)
CPE	FAAS	20–300	2.7	8.0	Tavallali et al. (2010)
CPE	FAAS	7.5–3500	1.6	5.27	This work

shown in Table 4, the linear range of the proposed CPE method was wider than all of the other reported CPE methods (Chen et al., 2005; Chen and Teo, 2001; Candir et al., 2008; Luconi et al., 2006; Silva and Roldan, 2009; Tavallali et al., 2010). The relative standard deviation of the proposed CPE method was lower than all of the other reported CPE methods (Chen et al., 2005; Chen and Teo, 2001; Candir et al., 2008; Luconi et al., 2006; Silva and Roldan, 2009; Tavallali et al., 2010).

4. Conclusions

Some advantages of CPE in comparison with similar extraction systems using organic solvents are: experimental convenience, low cost, easy and safe methodology for preconcentration and separation of trace elements in aqueous solutions. Triton X-114 was chosen for the CPE due to its excellent physicochemical characteristics; low cloud point temperature, high density of the surfactant-rich phase, which facilitates phase separation easily by centrifugation, commercial availability and relatively low price and toxicity. The obtained results showed that PAN is an efficient ligand for cloud point extraction of lead. The proposed CPE method is suitable for preconcentration of Pb(II) cations as a prior step to their determination by FAAS. Simple accessibility, formation of stable complexes, selectivity and enhanced analytical sensitively due to the fact that the complex can be easily extracted from the bulk aqueous solution into much smaller volumes of

the surfactant-rich phase are the major advantages of the CPE. In this method, a low limit of detection and good precisions (low RSD%) were obtained. The method was also verified with real samples and satisfactory results were obtained.

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