Technical paper

Extraction and Preconcentration of Lead using Cloud Point Methodology: Application to its Determination in Real Samples by Flame Atomic Absorption Spectrometry

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Abstract

1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP) was used as a chelating agent in cloud point extraction (CPE) for the first time and applied for the preconcentration of trace levels of lead as a prior step to its determination by flame atomic absorption spectrometry using octylphenoxypolyethoxyethanol (Triton X-114) as a nonionic surfactant. The effect of the experimental conditions such as pH of the solution, concentration of the chelating agent and surfactant, equilibration temperature and incubation time on cloud point extraction, were evaluated and optimized. In the optimum conditions, an enhancement factor of 110 was obtained for only 10 mL of water sample in the presence of 0.05% (v/v) Triton X-114. The limit of detection (LOD) obtained in the optimal conditions was 1.49 μg L^{-1}. The calibration graph using the preconcentration system was linear at levels 5–200 μg L^{-1} with a correlation coefficient of 0.9995. The proposed method was applied to the trace determination of lead in biological and water samples.

Keywords: Lead; Cloud point extraction; FAAS; Triton X-114; PMBP

1. Introduction

Determination of trace metals in environmental samples is a subject of considerable interest, because trace metals play important roles in biological processes both as essential components and as toxins.[1] Among these, lead, even at very low concentrations, is a well-known element with toxic effects for animals and humans. It is confirmed that most of the lead contamination in humans is from foods and drinks consumed. A regular absorption of small quantities of lead may cause serious injuries to health such as encephalopathy, anemia, kidney damage, brain damage and damage to the body in several other ways. The threshold limit value in the environment is 4.83×10^{-7} mol L^{-1} and according to the US Center for Disease Control (CDC), the limit value of blood lead is 1.16×10^{-6} mol L^{-1}.[2] It is therefore important to monitor the levels of lead in environments.

Several sensitive methods such as ET-AAS,[3] ICP-AES,[4] ETV-ICP-MS,[5] ICP-OES,[6] anodic stripping voltammetry,[7] cathodic stripping adsorption voltammetry,[8] potentiometric stripping analysis,[9] stripping chronopotentiometry[10] and X-ray fluorescence spectrometry[11] have been developed for the determination of lead. However, direct determination of trace amounts of metals in natural water and biological materials is difficult. This is due to the low concentrations of the trace metals and the strong interferences from the sample matrix. Separation and preconcentration can solve these problems and lead to a higher confidence level and easy determination of the trace elements by less sensitive, but more accessible instrumentation such as flame atomic absorption spectrometry (FAAS). Many enrichment procedures such as liquid–liquid extraction,[12] coprecipitation,[13] ion exchange,[14] and also several systems of adsorption in sorbents such as polymeric resins,[15] activated carbon,[16] silica[17] and others, especially on-line solid phase extraction[18] have been reported in the literature.

The classical liquid–liquid extraction and separation methods are usually time consuming, labor extensive, and require relatively large volumes of high purity solvents. Of additional concern is disposal of the solvent used, which creates a severe environmental problem. In this sense, cloud point extraction (CPE) is an interesting and efficient alternative since it reduces the consumption of and exposure to solvents, the disposal costs and the extraction time. CPE is based on the fact that upon heating a non-ionic surfactant solution over a critical temperature

(cloud point), the solution easily separates into two distinct phases. The one contains a surfactant at a concentration below, or equal to, a critical micelle concentration (CMC). The other is a surfactant-rich phase. The mechanism by which this separation occurs is attributed to the rapid increase in the aggregation number of the surfactant's micelles, as a result of the increase of temperature or to critical phenomena. During the formation of two phases, the insoluble hydrophobic complex can be entrapped "in situ" in the surfactant-rich phase. The CPE in connection with FAAS can be a powerful analytical technique for metal preconcentration and trace analysis. The cloud point methodology has been used for the extraction and preconcentration of metal ions, after the formation of sparingly water-soluble complexes, as an initial step for their determination by FAAS.[19–23]

Several chelating agents such as O, O-diethyldithiophosphate (DDTP),[19, 24, 25] Ammonium pyrrolidineditiocarbamate(APDC),[26] Pyrogallol,[27] 1-(2-thiazolylazo)-2-naphthol (TAN),[28] and 2-(5-bromo-2-pyridylazo)-5-(diethylamino)-phenol (5-Br-PADAP),[29] have been used in CPE of lead. To the best of our knowledge, the use of 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP) as the chelating agent for metal ion extraction in cloud point preconcentration has not been reported. PMBP solution is very stable and forms strong complexes with various metal ions including lead[30]. Therefore, in the present work, we have developed and optimized a powerful CPE-FAAS combined methodology for lead determination, which shows excellent and rapid preconcentration. The stability of PMBP and its complex with Pb allow drying the surfactant-rich phase after CPE, which remove the remained water and leads to high enhancement factor. In the developed system, PMBP (Fig.1) was used as the chelating agent and Triton X-114 as the surfactant. The proposed method was applied to the determination of lead in biological (Urine, Hair and Liver) and water samples (Tap water, Rainwater and wastewater) with satisfactory results.

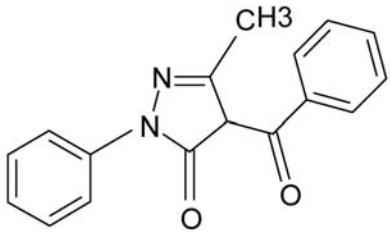

Figure 1. Structural formula of PMBP

2. Experimental

2. 1. Apparatus

A Shimadzu (Kyoto, Japan) Model AA-670G atomic absorption spectrometer with deuterium lamp background correction was used for the determination of lead in the surfactant-rich phase. A lead hollow cathode lamp (Hamamatsu photonics K.K., Japan) was used as the radiation source at the wavelength of 283.3 nm. The operating conditions were adjusted in order to obtain the maximum absorbance signal, while aspirating the analyte solution in methanol (Table 1). A thermostated bath (Tokyo Rikakikai Ltd., Japan) Model UA-1, maintained at the desired temperature, was used for cloud point preconcentration experiments and phase separation was assisted using a centrifuge (Hettich) in 15 mL calibrated centrifuge tubes (Superior, Germany). A Metrohm model 654 pH-meter was used for pH measurements. A balance (Libror, AEL-200, shimadzu) was used for weighting the solid materials.

2. 2. Reagents, Standard and Reference Material

The non-ionic surfactant Triton X-114 (Sigma, St. Louis, MO, USA) was used without further purification. Suprapur® HNO_3 (65%), $HClO_4$ (70%) and H_2O_2 (30%) (all from Merck, Darmstadt, Germany) were used for sample digestion. The chelating reagent PMBP was purchased from Fluka. A 100 mL of 1% m/v solution of PMBP was prepared daily by dissolving a 1g of the reagent in 2 mL of aqueous ammonia (25% Merck), diluting with water and adjusting the pH of the solution to 6.5–7.0 with dilute nitric acid. Thiourea and sodium fluoride (both from Merck) were used to remove the possible interference effects in the determination of Pb in real samples. Methanol (Merck) was used to decrease the viscosity of surfactant rich phase. All reagents were at least of analytical reagent grade and all solutions were prepared in deionized water.

A stock standard solution of lead at a concentration of 1000 mg L^{-1} was prepared from pure lead nitrate (Merck). Working standard solutions were obtained by stepwise diluting the stock standard solution.

A certified reference liver (TORT-1, National Research Council Canada) was analyzed in this study.

2. 3. Cloud Point Preconcentration Procedure

Aliquots of 10 mL of the standard or sample solution containing: Pb^{2+} (5–200 μg L^{-1}), acetate buffer solution (0.05 mol L^{-1}, pH = 5.5), PMBP (5.4×10^{-3} mol L^{-1}) and Triton X-114 (0.05% v/v) were subjected to CPE. In order to remove the possible interference effects in the determination of Pb in real samples, thiourea and sodium fluoride solutions (0.2 and 0.3% m/v, respectively) were added to solution. Fluoride as masking agent can form complexes with most of interferences, especially Ca^{2+}, Mg^{2+}, Fe^{3+}, Al^{3+} and Co^{2+}, and thiourea can mask Cu^{2+} which may present in biological or water samples. Then

Table 1: Flame atomic absorption spectrometer and cloud point extraction operating conditions

FAAS parameters	
Wavelength (nm)	283.3
Lamp current (mA)	5
Spectral band pass (nm)	1
Flame	Air-acetylene
Acetylene flow (L min^{-1})	2.0
Air flow (L min^{-1})	8.0
Burner length (cm)	10
Burner height (mm)	6
Integrated time (s)	1
Aspiration rate (mL min^{-1})	8
CPE parameters	
Surfactant (%, v/v)	0.05
Chelating agent (mol L^{-1})	5.4×10^{-3}
Buffer solution concentration (mol L^{-1})	0.05 /0.05
Working pH	5.5
Ionic strength (mol L^{-1})	< 0.5
Equilibration temperature (°C)	40
Equilibration time (min)	15
Centrifugation time (min)	10
Cooling time (min)	10

the mixture (final volume = 10 mL) was heated for 15 min in a thermostated water bath at 40 °C. Separation of the two phases was accelerated by centrifugation for 10 min at 4000 rpm. The phases were cooled down in an ice-acetone mixture bath (10 min) in order to increase the viscosity of the surfactant rich phase. The bulk aqueous phase was easily decanted by simply inverting the tube. Any residue of water was removed from the surfactant rich phase by evaporation in water bath. To reduce the viscosity of the surfactant phase prior to FAAS analysis, 200 μL of methanol was added to the extract and the resultant solution was introduced into the flame by conventional aspiration. The optimized conditions are listed in Table 1.

2. 4. Preparation of Real Samples

2. 4. 1. Water Samples

Water samples were filtered using a 0.45μm pore size membrane filter to remove suspended particulate matter and stored in a refrigerator in the dark. Aliquots of 5 mL of water samples were subjected to the CPE methodology as described above.

2. 4. 2. Human Hair Samples

Hair samples were collected from the vertex of the scalp by cutting from the scalp region, and hair length varied between 3 and 5 cm. Prior to analysis, all hair samples were cut into 2 cm lengths with stainless steel scissors. The washing procedure carried out was that proposed by International Atomic Energy Agency (IAEA),[31] and thus, hair samples were first washed with deionized water, then washed three times with acetone and finally, they were again washed with deionized water (three times). The samples were then oven-dried at 100 °C.

Approximately 1 g of dried sample was placed in a 50 mL beaker and 12 mL concentrated HNO_3 (65%) and 2mL concentrated $HClO_4$ (70%) were added. The content of the beaker was heated on a hot plate (initially at 100 °C for 45 min and then at 150 °C for 45 min). After dissolution, the solution was cooled to 70°C and 5 mL of H_2O_2 (30%) was added. The mixture was heated to dryness at 200 °C to yield a whitish residue.[19] Approximately 5 mL of 0.1M HNO_3 was added to the resulting white residue and heated at 100 °C for 10 min. It was then dissolved in water and after the increasing of pH to about 4 with NaOH 2M, the volume made up to 25 mL in a volumetric flask. Aliquots of 5 mL of the resulting clear solution were analyzed according to the prescribed procedure.

2. 4. 3. Urine Samples

A 10 mL portion of a urine sample (or a spiked urine sample) was treated with 10 mL of concentrated HNO_3 (65%) and $HClO_4$ (70%) mixture of 2:1 in a 50 mL beaker covered with a watch glass. The content of the beaker was heated on a hot plate (100 °C 15 min, 150 °C 10 min). The watch glass was removed and the acid evaporated to dryness at 150 °C. $HClO_4$ (3 mL) was added to the resulting white residue and the mixture was heated at 160 °C to dryness. All heating steps were carried out under a hood with necessary precautions. Five milliliters of 0.1M HNO_3 was added, and the mixture was heated at 150 °C for 1 min and after the increasing of pH to about 4 with NaOH 2M, the volume was made up to the mark in a 25 mL volumetric flask. Aliquots of 5 mL of the resulting clear solution were analyzed according to the prescribed procedure.

2. 4. 4. Liver Samples

Exactly 100 mg of dried and powdered cow liver sample (or a certified reference liver) was treated with 10 mL of concentrated HNO_3 (65%) and an $HClO_4$ (70%) mixture of 2:1 in a 50 mL beaker covered with a watch glass. After 12 h, the resulting solution was digested according to above section.

3. Results and Discussion

3. 1. Effect of pH on CPE

The formation of metal complexes and its chemical stability are the two important influence factors for the CPE, and the pH plays a unique role on metal chelate formation and subsequent extraction. The extraction depends on the pH at which complex formation occurs. The cloud point for

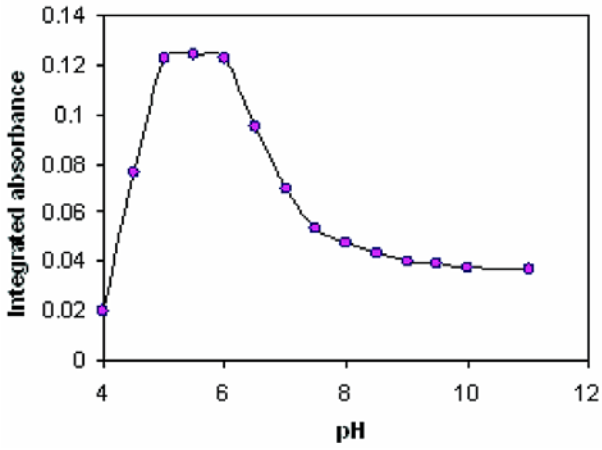

Figure 2. Effect of pH on the cloud point extraction of 100.0 μg L^{-1} Pb^{2+}. CPE conditions: PMBP (10^{-2} mol L^{-1}), Triton X-114 (0.05% v/v), equilibration temperature 50 °C and equilibration time 15 min. FAAS conditions as in Table 1.

lead preconcentration was performed at different pH values (4–11). Fig 2 shows the effect of pH on the integrated absorbance of the lead complex. It was found that the Pb-PMBP complex was quite stable in the range pH 5.0–6.0, and could be extracted completely in surfactant rich phase. As a result, pH 5.5 was chosen as the working pH.

3. 2. Effect of PMBP Concentration

The CPE efficiency depends on the hydrophobicity of the ligand and the complex formed, the apparent equilibrium constants in the micellar medium, the kinetics of the complex formation, and the transference between the phases.[32] In this work, PMBP was used as the chelating agent due to the highly hydrophobic nature of its metal complexes. Fig 3 shows the effect of PMBP concentration on the CPE of Pb^{2+}. The concentration of PMBP tested ranged from 0.02 to 0.22% (m/v). The integrated absorbance for Pb^{2+} increased as the concentration of PMBP increased from 0.02 to 0.12% (m/v), and then kept almost constant with further increase in the PMBP concentration up to 0.22% (m/v). Therefore, a PMBP concentration of 0.15% (m/v) was employed for further experiments.

3. 3. Effect of Triton X-114 Concentration

In CPE, since the temperature corresponding to cloud point is correlated with the hydrophilic property of surfactants, an appropriate surfactant is important. The surfactants, which have too high or too low cloud point, are not suitable for the CPE separation/preconcentration of trace elements. Triton X-114 was chosen for the formation of surfactant rich phase due to its recognized physicochemical characteristics: low cloud point temperature, high density of the surfactant rich phase; which facilitates phase separation by centrifugation, commercial availability, relatively low price and low toxicity. On the other hand, it is important to discuss the effect of surfactant concentration on CPE because a successful CPE would be that which maximizes the extraction efficiency through minimizing the phase volume ratio (ratio between the volume of the aqueous phase and the final volume of the surfactant rich phase), thus maximizing its concentrating ability. Hence, the variations in the integrated absorbance as a function of the concentration of Triton X-114 in the range of 0.005–0.3% (v/v) were investigated. As can be seen in Fig 4, Triton X-114 was found to effectively extract the Pb-PMBP complex from aqueous sample in the concentration range of 0.04–0.05%, using a single step extraction procedure. Above 0.05% surfactant, the analytical signal was deteriorate due to the increase in the final volume of the surfactant that was caused the preconcen-

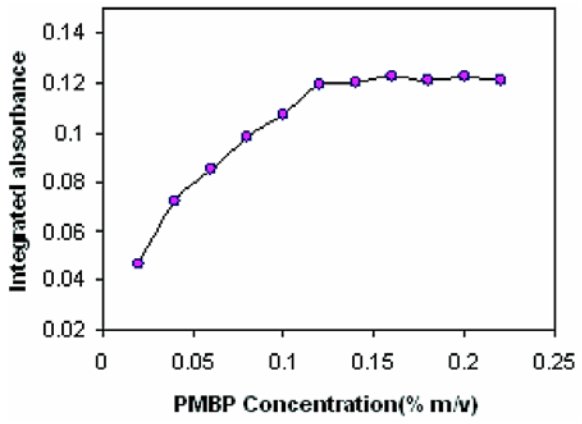

Figure 3. Effect of PMBP concentration on the cloud point extraction of 100.0 μg L^{-1} of Pb^{2+}. CPE conditions: Triton X-114 (0.05% v/v), pH 5.5, equilibration temperature 50 °C and equilibration time 15 min. FAAS conditions as in Table 1.

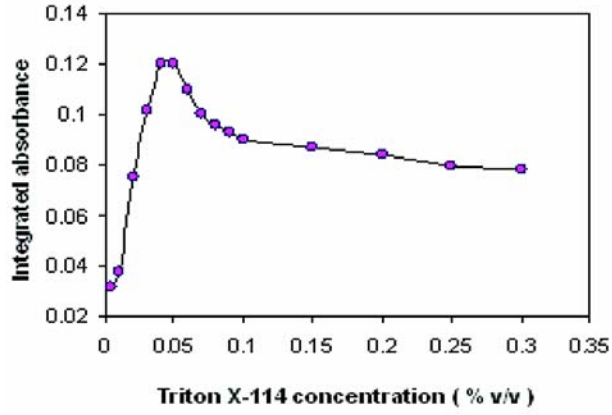

Figure 4. Effect of the concentration of Triton X-114 on the cloud point extraction of 100.0 μg L^{-1} of Pb^{2+}. CPE conditions: PMBP (5.4×10^{-3} mol L^{-1}), pH 5.5, equilibration temperature 50 °C and equilibration time 15 min. FAAS conditions as in Table 1.

tration factor(ratio between the analyte concentration in the surfactant rich phase after phase separation, and the analyte concentration in the initial solution before the preconcentration step) to decrease. Therefore, an amount of 0.05% Triton X-114 was chosen in order to achieve the greatest analytical signal and thereby the highest extraction efficiency.

3. 4. Effects of Equilibration Temperature and Time

Optimal equilibration temperature and incubation time are necessary to complete reactions, and to achieve easy phase separation and preconcentration as efficient as possible. The effect of the equilibration temperature was investigated from 20 to 80 °C. It was found that Pb extraction is significantly enhanced at temperatures above 35 °C. Keeping the temperature of 40 °C, the influence of incubation time on CPE was studied within a range of 2–30 min. An equilibration time of 15 min was chosen in order to achieve the highest extraction efficiency.

3. 5. Effect of Ionic Strength and Centrifugation time

The cloud point of micellar solutions can be controlled by addition of salts, alcohols, non-ionic surfactants and some organic compounds (salting-out effects). To date, most of the studies conducted have shown that ionic strength has no appreciable effect on the extraction efficiency. It was observed that the addition of NaF within the interval of 0.1–0.5 mol L^{-1} had no significant effect on the cloud point extraction efficiency.

In general, centrifugation time hardly ever affects micelle formation but accelerates phase separation in the same sense as in conventional separations of a precipitate from its original aqueous environment. The effect of centrifugation time upon analytical signal was studied for the range of 5–20 min. A centrifugation time of 10 min was selected for the entire procedure, since the analyte extraction during this time is almost quantitative.

3. 6. Effect of Viscosity on the Analytical Signal

Since the surfactant rich phase obtained after CPE is very viscous, methanol was added to the surfactant rich phase after the separation of phases in order to facilitate its introduction into the nebulizer of the spectrometer. The presence of methanol and surfactant in the aspirated sample solutions could change the physical properties of the liquid sample through altering the solution environment, and affect to some extent the resulting sensitivity. Methanol brings about some enhancement to the signal, which is more pronounced, when combined with the surfactant. Organic solvent in the flame increases atomization temperature; whilst both organic solvent and surfactant, as reported in the literature, can promote generation of small droplets during nebulization causing positive surface effects.[33] However, in this work enhancement factor is more than twice the phase volume ratio (Table 3). For added volumes of methanol of <200 μL, the signals are lower owing to the greater viscosity, which clearly predominates over the dilution, whereas for larger added volumes, the decrease in viscosity of the sample is less and it is essentially the effect of dilution that predominates. An optimal volume of 200 μL of methanol was added to surfactant rich phase. This added volume was chosen in order to ensure a sufficient volume of sample for direct aspiration.

3. 7. Interferences

In view of the high selectivity provided by FAAS, the only interferences studied were those related to the preconcentration step, cations that may react with PMBP and anions that may react with lead and decrease the extraction efficiency. To perform this study, 10 mL of solution containing: 50 ng mL^{-1} Pb^{2+}, interferent ion in different interferent-to-analyte mass ratios in the absence and presence of masking agents, acetate buffer (0.05 mol L^{-1}, pH = 5.5), PMBP (5.4×10^{-3} mol L^{-1}) and Triton X-114 (0.05% v/v) were used for CPE. The results are given in Table 2. Column (A) and (B) are shown the interferent-to-analyte mass ratios in the absence and presence of thiourea 0.2% (m/v) and F^- 0.3% (m/v) as masking agents, respectively. Among the interfering ions tested; F^-, Cl^-, SO_4^{2-}, NO_3^-, CH_3COO^-, PO_4^{3-}, CrO_4^{2-}, tartarate, thiourea and ascorbic acid did not interfere at concentration 1000 times higher than the lead.

Table 2: Tolerance limits of foreign ions for the preconcentration and determination of 50 μg L^{-1} lead (results within 5% error).

Ions	Ion/Pb ratio (w/w)[a]	Ion/Pb ratio (w/w)[b]
K^+	> 1000	> 1000
Na^+	> 1000	> 1000
Mg^{2+}	200	1000
Ba^{2+}	200	1000
Mn^{2+}	150	1000
Al^{3+}	25	1000
Ca^{2+}	25	800
Cu^{2+}	25	800
Co^{2+}	10	500
Ni^{2+}	10	500
Cd^{2+}	10	500
Zn^{2+}	10	500
Cr^{3+}	10	500
Fe^{3+}	10	300

[a] Ion/Pb ratio in the absence of masking agents.
[b] Ion/Pb ratio in the presence of thiourea 0.2% (w/v) and F^- 0.3% (w/v) as masking agents.

3. 8. Figures of Merit of the Method

The limit of detection (LOD) of the proposed method for the determination of lead was studied in the optimal experimental conditions. The LOD was 1.49 μg L^{-1}, calculated considering three times the standard deviation of the background signal (3σ). Analytical characteristics of the method were summarized in Table 3.

Table 3: Analytical characteristics of the method.

Analytical parameters	Pb without preconcenteration	Pb with preconcenteration
Linear range (μg L^{-1})	1000–10000	5–200
Intercept	–0.0099	0.0107
Slope[a]	1×10^{-5}	1.1×10^{-3}
Number of points	10	12
Correlation coefficient	0.9984	0.9995
Detection limit[b] (μg L^{-1})	225.83	1.49
Quantification limit[c] (μg L^{-1})	752.77	4.98
Relative standard deviation[d] (RSD %) (n=/6)	2.11(5000 μg L^{-1})	2.43(10 μg L^{-1})
Phase volume ratio[e]	–	≈50
Enhancement factor[f]	–	110

[a] The slope of the calibration graph is the calibration sensitivity according to IUPAC definition.
[b] Detection limit calculated according to the IUPAC definition: 3 S_b/K, where K is the slope of the calibration graph.
[c] Quantification limit calculated according to the IUPAC definition: 10 S_b/K.
[d] Values in parentheses are the Pb concentration (μg L^{-1}) for which the R. S. D. was obtained.
[e] Ratio between the volume of the aqueous phase and the final volume of the surfactant rich phase.
[f] Ratio between the slope of the calibration graph for the CPE method and the calibration graph obtained without preconcentration.

3. 9. Determination of Lead in Biological and Water Samples

In order to test the reliability of the proposed methodology for the assaying of lead, it was applied to the determination of lead in biological (i.e., hair, urine and cow liver) and water samples (i.e., tap water, rainwater, and wastewater) and TORT–1 for verification of the proposed method and procedures. For this purpose, 5 mL of each of the digested biological samples and water samples were preconcentrated with acetate buffer (0.05 mol L^{-1}, pH = 5.5), PMBP (5.4×10^{-3} mol L^{-1}) and 0.05% (v/v) Triton X–114 in the presence of masking agents following the proposed method. The results were shown in Table 4. For calibration purpose, the working standard solutions were subjected to the same preconcentration procedure as applied to the analyte solutions. In addition, the recovery experiments of different amounts of Pb were carried out. The values of recoveries have confirmed the validity of the proposed method. It was noted that the assayed value of Pb of the TORT–1 are in close agreement with the certified value.

Table 4: Determination of lead in biological and water samples (results of recoveries of spiked samples)

Samples	Added	Found[a]	Recovery (%)
	Pb (μg L^{-1})		
Urine	0	15.85 ± 0.95	
	10	25.82 ± 0.09	99.9
	20	36.13 ± 0.21	100.8
Tap water[b]	0	ND[c]	
	10	10.13 ± 0.06	101.3
	20	19.8 ± 0.40	99.0
Rain water[d]	0	ND	
	10	9.86 ± 0.25	98.7
	20	19.83 ± 0.21	99.2
Waste water[e]	0	8.03 ± 0.15	
	10	17.6 ± 0.46	97.6
	20	27.9 ± 0.40	99.5
	Pb (μg g^{-1})		
Cow liver	0	ND	
	1	0.963 ± 0.030	96.3
	2	1.956 ± 0.023	97.8
Human hair[f]	0	0.131 ± 0.015	
	1	1.136 ± 0.015	100.4
	2	2.170 ± 0.026	101.8
	Certified values		Assayed values
TORT–1	10.4 ± 2.0		10.32 ± 0.23

[a] Mean of three experiments ± standard deviation.
[b] From drinking water system of Tabriz, Iran.
[c] Not detected.
[d] Collected at Tabriz city, Iran (3 May 2005).
[e] From waste water of local factory.
[f] Medium dark hair (man, 25 years old).

4. Conclusion

We have proposed the use of CPE as an alternative method for the preconcentration of Pb as a prior step to its determination by FAAS. The methodology offers a simple, rapid, sensitive, low cost, good extraction efficiency and lower toxicity than those using organic solvents. Environmental pollution is limited to a small amount of surfactant. This fact is particularly attractive, because the ''green chemistry'' concept can be employed here. From the results obtained, it can be considered that PMBP, which was used for the first time, is an efficient chelating agent for the CPE of lead with advantages such as; simple accessibility, the stable complex formation and consistency with the cloud point extraction method. The detection limit of the present CPE–FAAS method for the determination of lead was 1.49 μg L^{-1} with good R.S.D. The sensitivity of the method could be enhanced by using GF-AAS as the detection step. The proposed method can be applied for the determination of trace amounts of lead in various biological and water samples.

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Povzetek

Pri določevanju svinca z atomsko absorpcijsko spektrometrijo je bil, ob dodatku oktilfenoksietanola (Triton X-114) kot anionske površinsko aktivne snovi, prvič uporabljen 1-fenil-3-metil-4-benzoil-5-pirazolon (PMBP) kot ligand za ekstrakcijo in predkoncentracijo svinca v sledovih. Ovrednoteni in optimizirani so bili eksperimentalni parametri kot so pH raztopine, koncentracija liganda in surfaktanta, temperatura in čas inkubacije, ki vplivajo na ekstrakcijo. V optimalnih pogojih je bil za 10 mL vodni vzorec v prisotnosti 0,05 % (v/v) Tritona X-114 dosežen koncentracijski faktor 110 in spodnja meja detekcije 1,49 μg L^{-1}. Umeritvene premice so bile ob uporabi predkoncentracijskega postopka linearne v območju koncentracij 5–200 μg L^{-1} s korelacijskim koeficientom 0.9995. Opisana metoda je bila uporabljena za določevanje sledov svinca v vodah in bioloških vzorcih.