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Article

Ligand-less Rapidly Synergistic Cloud Point Extraction as an Efficient Method for the Separation and Preconcentration of Trace Amounts of Lead from Food and Water Samples

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Um procedimento de extração no ponto nuvem de sinergia rápida foi desenvolvido para a separação e determinação de traços de chumbo em amostras de água e de alimentos antes da determinação por espectrometria de absorção atômica com chama (FAAS). A extração no ponto nuvem de sinergia rápida (RS-CPE) simplifica e acelera de forma eficiente o procedimento tradicional de extração no ponto nuvem (CPE). Este método é realizado em 1 minuto, a temperatura ambiente, na presença do surfactante não-iônico Triton X-114. Octanol atuou como reagente sinérgico para a extração no ponto nuvem, causando a diminuição na temperatura do Triton X-100, e contribuiu para o subsequente processo de extração. Alguns parâmetros que afetam a extração no ponto nuvem e a determinação do chumbo foram avaliados cuidadosamente, como o pH da amostra, a quantidade de octanol, a quantidade de Triton X-114, o tipo de solvente para a extração e a força iônica, bem como o efeito de interferentes. Nas condições otimizadas para a extração de chumbo (pH 8.5; octanol: 10 µL; Triton X-114: 0,04% w/v; e solvente de diluição: HNO_3 1 mol L^{-1} na presença de metanol) foi obtido um fator de enriquecimento igual a 40 e limite de detecção (LOD) de 1,6 µg L^{-1}. O desvio padrão para dez replicatas de uma solução contendo 100 µg L^{-1} de chumbo foi de 2,1%. O método proposto foi aplicado para a determinação de chumbo em amostras de água e de alimentos (espinafre, arroz e chá preto), com resultados satisfatórios.

A simple rapidly synergistic cloud point extraction procedure has been developed for the separation and preconcentration of trace amounts of lead from food and water samples by flame atomic absorption spectrometry (FAAS). Rapidly synergistic cloud point extraction (RS-CPE) greatly simplified and accelerated the procedure of traditional cloud point extraction (CPE). This method was accomplished in room temperature in 1 min. Non-ionic surfactant Triton X-114 was used as extractant. Octanol worked as cloud point revulsant and synergic reagent which lowered the cloud point temperature of Triton X-114 and assisted the subsequent extraction process. Some parameters that influenced cloud point extraction and subsequent determination were evaluated in detail, such as sample pH, amounts of octanol, amounts of Triton X-114, type of diluting solvent, extraction time and ionic strength, as well as interferences. Under optimized conditions (pH 8.5, octanol: 10 µL, Triton X-114: 0.04% w/v and diluting solvent: 1 mol L^{-1} HNO_3 in methanol), an enhancement factor of 40 could be obtained, and the detection limit (LOD) for lead was 1.6 µg L^{-1}. Relative standard deviation for ten replicate determinations of the standard solution containing 100 µg L^{-1} lead was 2.1%. The proposed method was applied for the determination of lead in food (spinach, rice and black tea bag) and water samples and satisfactory results were obtained.

Keywords: rapidly synergistic cloud point extraction, triton X-114, lead, food samples, water samples

Introduction

The environment and all the life on earth face a very serious threat due to heavy metal pollution resulting from rapid industrialization and increase in world population. It has been noted that some heavy metals (for instance lead, cadmium, and mercury) have an estrogenic activity; that is, they serve as an environmental endocrine disruptor.[1] Lead is one of the most abundant heavy metals in the environment and its toxic effects have been recognized since a long time.[2] Lead is released into the environment through several processes including waste and coal burning, industrial

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processes, volcanic emissions, metal mining, and smelting.[3,4] In 1991, the United States Environmental Protection Agency (USEPA) published a regulation to control lead in drinking water, which included an action level of 0.015 mg L^{-1}.[5] The World Health Organization (WHO) has released the guidelines for drinking water quality containing the guideline value 0.01 mg Pb L^{-1}.[6] Consequently, the accurate determination of lead at trace levels in environmental samples is a subject of great concern.

The usual methods for the determination of lead in a solution involve spectrophotometric methods,[7] atomic absorption spectrometry,[8] inductively couple plasma-mass spectrometry[9,10] and electrothermal atomic absorption spectrometry.[11] However, due to the presence of lead in environmental samples at low levels, its separation from other elements present, and also the use of a preconcentration step prior to lead determination, can be necessary.

Various preconcentration techniques were used for the separation and preconcentration of trace amounts of lead such as liquid-liquid extraction,[12] dispersive liquid-liquid microextraction,[13,14] flotation,[15] coprecipitation,[16] solid phase extraction,[17,18] and cloud point extraction.[19,20]

Among the various kinds of preconcentration methods, cloud point extraction (CPE) has been well developed and applied in many fields of sample pretreatment and analysis in the recent decade[21] because it has several critical advantages such as low cost, safety, easier manipulation, no need for large amounts of organic solvents, less stringent requirements for separation, higher preconcentration factor, and easier attachment to analytical instruments such as graphite furnace and flame atomic absorption spectrometry.

Recently, rapidly synergistic cloud point extraction (RS-CPE) was introduced by Wen *et al.*[22,23] It is based on the use of a synergic reagent such as octanol[22,23] and 3,5-dichlorophenol,[24] for decreasing the cloud point temperature of surfactants in traditional CPE method. Triton X-114 was one of the most applied surfactants in CPE for its lower cloud point temperature (30 °C). In this method, octanol functioned as cloud point revulsant of Triton X-114 and synergic reagent for extraction. Rapid cloud point extraction was realized at room temperature (about 20 °C) without heating units or adding salts. Thus, traditional CPE pattern was considerably simplified and accelerated. Only 1 min was needed for the improved extraction compared with traditional CPE (about 40 min for heating, incubation and cooling). Compared to traditional CPE method, the proposed method is low time-and labor-consuming. There is no need to heat and/or cool solutions for separating phases which, as a result, avoids any possible losses due to volatilization and adds greater stability to phases once they have been separated.[22,23]

In this study, FAAS was investigated in order to be coupled with the proposed RS-CPE for the determination of lead. FAAS is used for determination because of its fast analysis time, relative simplicity, and lower cost. The proposed method was very simple and rapid. Various factors affecting extraction efficiency were evaluated and optimized. Under optimum conditions, the developed method was used for the preconcentration, separation, and determination of lead in food and water samples with satisfactory results.

Experimental

Reagents and solutions

All chemicals were of analytical reagent grade. Stock standard solution (1000 mg L^{-1} in 0.5 mol L^{-1} HNO_3) of lead was prepared using $Pb(NO_3)_2$ that was obtained from Merck (Darmstadt, Germany). The working standard solutions were prepared by appropriate stepwise dilution of the stock standard solution with deionized water.

Other reagents used namely nitric acid, perchloric acid, hydrochloric acid, hydrogen peroxide, sodium hydroxide, ethanol, methanol, acetone, tetrahydrofuran, and sodium nitrate were obtained from Merck (Darmstadt, Germany). Triton X-114 was obtained from Fluka Chemie AG, Buchs, Switzerland. All glassware was rinsed with deionized water, decontaminated for at least 24 h in 10 % (v/v) HNO_3 solution, and rinsed again five times with deionized water.

Instruments

A SensAA (GBC, Australia) atomic absorption spectrometer equipped with deuterium background correction and lead hollow cathode lamp was used for the determination of lead at a wavelength of 217.0 nm. The instrumental parameters were adjusted according to the manufacturer's recommendations (lamp current: 5 mA, band pass: 1 nm). Phase separation was assisted using a centrifuge (Hettich, EBA 20). The pH-meter model 827 from Metrohm (Herisau, Switzerland) with combined glass electrode was used for pH measurements.

Sample preparation

Spinach, rice and black tea bag sample were purchased from the local supermarket at Sari in Iran. First, the spinach sample was cleaned with tap water and deionized water. Then, this sample was dried at 110 °C. The dried sample was ground to reduce particle size and then thoroughly mixed to ensure the homogeneity of the sample. A mass of

500.0 mg of spinach was transferred into a 250 mL beaker and 5 mL of 0.5 mol L^{-1} HNO_3 was added to moisten the sample thoroughly. This was followed by adding 10 mL of concentrated HNO_3 and heating it on a hot plate at 130 °C for 3 h. After cooling it to room temperature, 5 mL of concentrated perchloric acid was added to it drop wise. The mixture was heated gently until the completion of sample decomposition. In this step, a clear solution was obtained. This was left to cool down and then was transferred into a 100 mL volumetric flask by rinsing the interior of the beaker with small portions of 0.1 mol L^{-1} HNO_3 and the solution was filled to the mark with the same acid.[25]

The black tea bag sample was ground in a household grinder. 6.0 g of the sample was placed in a 100 mL beaker, and 10 mL of concentrated HNO_3 (65% w/w) was added to it. The mixture was evaporated to near dryness on a hot plate at about 130 ºC for 4 h. After cooling to room temperature, 3 mL of concentrated hydrogen peroxide (30%, w/w) was added. The mixture was again evaporated to near dryness. The resulting solution was diluted to 25 mL with distilled water. The result was filtered and diluted to 100 mL by double deionized water.[26]

5.0 grams of powdered rice sample was dissolved in 25 mL concentrated HNO_3 and heated on a hot plate at a low temperature. Then, 8.5 mL of concentrated HCl was added to the mixture and heated to near dryness. Under the heating conditions, 7.5 mL concentrated hydrogen peroxide was added and heated to complete the digestion. The solution was diluted to 100 mL with deionized water.[27]

Before doing the CPE procedure, the digested samples were neutralized with NaOH and then, the pH was reached to 8.5 by adding buffer.

Extraction procedure

For CPE preconcentration, 25 mL analytical solution containing lead ion, 0.04 mol L^{-1} phosphate buffer (pH = 8.5) and 0.04 % Triton X-114 was placed in a screw cap glass tube and 10 µL octanol was added. After shaking, the mixture solution became turbid because of the effect of octanol. The extraction was accomplished in 1 min under shaking. After centrifugation, the water phase was carefully removed with a syringe, and the surfactant-rich phase was diluted with 1.0 mL 1 mol L^{-1} HNO_3 in methanol. After that, the resultant sample was transported to FAAS for determination.

Results and Discussion

The extraction efficiency depends on some important experimental parameters. In order to obtain the maximal extraction efficiency, various parameters such as sample pH, amounts of octanol, amounts of Triton X-114, type of diluting solvent, extraction time, and ionic strength were investigated in detail. Triplicate extractions were performed for all experiments, and the average of these results was reported in figures or tables. Finally, these optimal conditions were applied to extract and detect lead in food and various water samples.

The effect of pH

The effect of pH on the cloud point extraction of 25 mL of lead standard solution (100 µg L^{-1}) was studied in the range of 4-11. Figure 1 shows the effect of pH on the extraction of lead. It can be seen that the recovery is nearly constant in the pH range of 8-10. At pH values below 8, however, the percent recovery is much lower. Triton X-114 forms a cationic complex with $[Pb(OH)]^+$ through their polyoxyethylene groups.[28,29] The lower extraction efficiency in acidic media may be due to the fact that H^+ ions can also bind to polyoxyethylene groups of surfactant, thereby hinders the complex formation of $[Pb(OH)]^+$ ions. The lower extraction efficiency in pH > 10 may be due to the formation of lead hydroxide. Therefore, pH 8.5 was chosen for further work. In further work, 0.04 mol L^{-1} of phosphate buffer (pH 8.5) was used for adjusting pH of the solution.

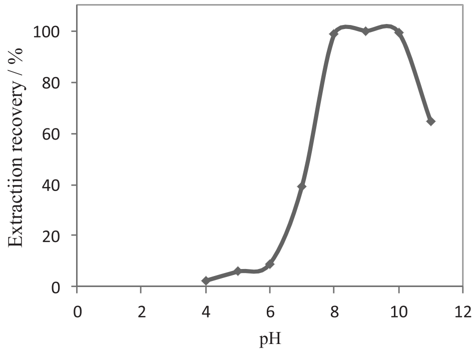

Figure 1. The effect of pH on extraction recovery of lead. (Sample volume: 25 mL; Triton X-114: 0.04 % (w/v); octanol: 10 µL; Pb: 100 µg L^{-1}).

The effect of octanol amounts

In RS-CPE, octanol worked as cloud point revulsant and synergic reagent as mentioned before, which lowered the cloud point of the surfactant below room temperature and assisted the subsequent extraction process. Thus, this factor must be optimized. In this step, the volume of octanol was investigated from 10 to 500 µL. The lower volumes were not studied because at lower volumes cloudy solution is not formed completely. If no octanol was employed, the extraction could not be carried out. The results showed that, with the increase of octanol volume, the analytical signal decreased. It was found that 10 μL was the optimal condition, and excessive amounts of octanol led to remarkable decrease of signals. With larger amounts of octanol, the volume of organic phase increased. The larger volume of organic phase increased the viscosity of the resultant samples when diluted to 1.0 mL with 1 mol L^{-1} HNO_3 in methanol. The increased viscosity seriously decreased the sampling efficiency of pneumatic nebulization of FAAS.[22,23]

The effect of Triton X-114 amounts

The amount of surfactant used was a critical variable for the surfactant-rich phase volume and recovery obtained. Therefore, the effect of Triton X-114 concentration on the extraction recovery of lead was investigated between 0.002 and 0.06% (w/v). Figure 2 shows variation of the analytical signal of the analyte as a function of the surfactant concentration. As can be seen, the analytical signal increased as the concentration of Triton X-114 increased from 0.002 to 0.04% (w/v). However, further increase in the surfactant concentration resulted in a decrease in the analytical signal of lead, likely because the excessive surfactant could affect the room temperature RS-CPE efficiency.[22,23] So, a 0.04% (w/v) of Triton X-114 was used for further work.

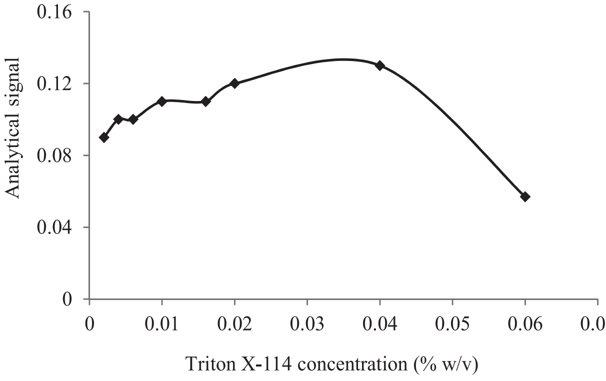

Figure 2. The effect of Triton X-114 concentration on analytical signal of lead. Sample volume: 25 mL; pH = 8.5; octanol: 10 μL; Pb: 100 μg L^{-1}.

The effect of the type of diluting solvent

Since the surfactant-rich phase obtained after cloud point extraction is very viscous and the demand of sampling volume for the conventional flame atomic absorption spectrometer is about 1.0 mL, it is necessary to dilute surfactant rich phase before detection. Hence, various diluting solvents were studied to achieve maximum analytical signal. The results are shown in Figure 3. It can be seen that maximum analytical signal was obtained by 1 mol L^{-1} HNO_3 in methanol. Thus, this solvent was selected for further experiments.

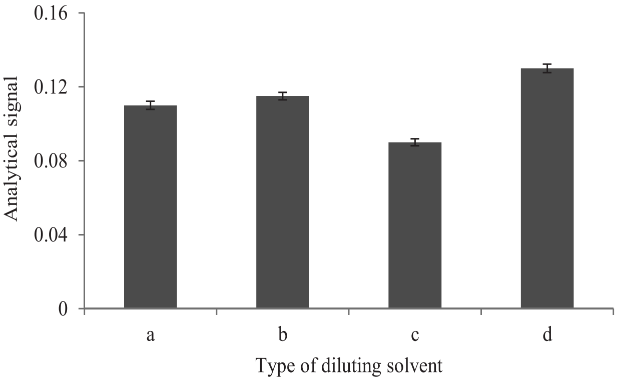

Figure 3. The effect of diluting solvent type on analytical signal of lead, (a) 1.0 mol L^{-1} HNO_3 in THF; (b) 1.0 mol L^{-1} HNO_3 in acetone; (c) 1.0 mol L^{-1} HNO_3 in ethanol; (d) 1.0 mol L^{-1} HNO_3 in methanol; sample volume: 25 mL; pH = 8.5; Triton X-114: 0.04% (w/v); octanol: 10 μL; Pb: 100 μg L^{-1}.

The effects of centrifuge conditions

Centrifugation was applied for separating Triton X-114 from the aqueous solution in the proposed method. In order to attain the best phase separation, the centrifugation rate and time was optimized. The results showed that 4000 rpm and 4 min were the optimum conditions.

The effect of ionic strength

The influence of ionic strength on the extraction efficiency of lead ions was examined by using aqueous solutions containing various concentrations of sodium nitrate (0.0-20.0%). The results showed that ionic strength had no significant effect upon extraction efficiency (at a 95% confidence level) and sensitivity up to 20.0%. This is in agreement with the results reported in the literature which demonstrate that increase in ionic strength in micelle mediated systems do not seriously alter the extraction efficiency of the analyte.[30,31]

Matrix effects

The effect of potential interference encountered in real samples on the recovery using the proposed method were examined using 100 μg L^{-1} lead standard solution in the presence of various amounts of individual ions. A variation on the recovery higher than ± 5% was considered as interference. The results (Table 1) indicate that lead recoveries are quantitative in the presence of interfering ions.

Table 1. Effect of interfering ions on the extraction of lead

Interfering ions	Ion/Pb(II) ratio / (w/w)	Recovery / %
K^+, Na^+, Li^+, Ca^{2+}, Mg^{2+}, Br^-, F^-, Cl^-, NO_3^-	1000	100.0
PO_4^{3-}, Ag^+, Cu^{2+}, Co^{2+}, Cr^{3+}, As^{3+}, Cr(VI)	100	99.7
I^-	80	99.3
Zn^{2+}	50	99.4
CO_3^{2-}, Hg^{2+}	30	100.0
Ba^{2+}, Cd^{2+}, Fe^{2+}	20	99.1
Ni^{2+}, Al^{3+a}, Fe^{3+b}	10	98.7
Mn^{2+}	5	98.4

[a] In the presence of 4.0×10^{-3} mol L^{-1} KSCN; [b] in the presence of 0.1 mol L^{-1} KF.

Figures of merit

The analytical performance of RS-CPE coupled with FAAS for the preconcentration and determination of lead was systematically investigated under optimized experimental conditions (Table 2). The results exhibited that there was an excellent linear correlation between the absorbance and the concentration of lead from 5 to 400 µg L^{-1} and a good correlation coefficient of 0.9988. The precision of this method was 2.1% (RSD, n = 10) at the spiked concentration of 100 µgL^{-1}. The detection limit (calculated as the concentration corresponding to three times the standard deviation of 10 runs of the blank samples) of the proposed method was 1.6 µg L^{-1}. The preconcentration factor (calculated as the ratio of the volumes of the solution before and after preconcentration) was 25 for 25 mL sample solution and the enhancement factor (calculated as the ratio of the slopes of the calibration curves with and without preconcentration) obtained was 40.

Table 2. Analytical characteristics of the method

Parameter	Analytical feature
Linear range / µg L^{-1}	5-400
Limit of detection / µg L^{-1} (n =10)	1.6
RSD[a] / %	2.1
Enhancement factor	40
Preconcentration factor	25

[a] Lead concentration was 100 µg L^{-1} for which RSD was obtained.

Comparison of the present method with other preconcentration methods

Comparative data from some recent papers on preconcentration of lead from various samples for the figure of the merits are summarized in Table 3. The proposed procedure shows better detection limit and precision compared to other preconcentration methods. A comparison of the enrichment factor of the proposed method with values reported from several other adsorbents is noteworthy. This methodology is a rapid, reproducible, simple, and low cost technique for the determination of lead in food and water samples.

Analysis of real samples

The method was applied for the determination of lead in food samples (spinach, rice, and black tea bag) as well as five kinds of water samples including tap, river, spring, mineral, and sea water, under the optimized experimental conditions. The results obtained for the samples are shown in Tables 4 and 5.

Before the analysis of water samples, the collected water samples were filtered through a 0.45 µm Millipore

Table 3. Comparison of the presented method with other preconcentration methods for determination of lead

Method	LOD[a] / (µg L^{-1})	RSD[b] / %	LDR[c] / (µg L^{-1})	PF[d]	Sample volume / mL	Reference
SPE[e]-FAAS	16.7	–	–	120	1200	32
SPE-FAAS	5.5	–	–	200	2000	33
SPE-FAAS	6.1	4.7	–	30	300	34
Online-SPE-FAAS	1.8	3.4	3-250	131[g]	–	35
CPE-FAAS	5.27	1.6	7.5-3500	30	15	19
CPE- FAAS	3.42	4.8	500-10000	25	50	36
Coprecipitation-FAAS	2.0	2.45	2.5-200	400	1000	37
MF[f]-FAAS	31	–	–	150	300	38
RS-CPE-FAAS	4.3	4.9	up to 1200	39[g]	40	23
RS-CPE-FAAS	1.6	2.1	5-400	40[g]	25	This work

[a] Limit of detection; [b] relative standard deviation; [c] linear dynamic range; [d] preconcentration factor; [e] solid phase extraction; [f] membrane filtration; [g] enhancement factor (the ratio of slopes of the preconcentration and direct calibration equations).

Table 4. Determination of lead in water samples

Sample	Lead amount / (µg L^{-1})		Recovery / %
	Added	Found[a]	
Tap water (Drinking water system of Sari, Iran)	0.0 10.0 30.0	n.d.[b] 10.2 ± 0.2 29.6 ± 0.6	– 102.0 98.7
Mineral water (Damavand, mineral water, Iran)	0.0 10.0 30.0	n.d. 10.1 ± 0.2 29.6 ± 0.7	– 101.0 98.7
River water (Siahrood river, Larim, Iran)	0.0 10.0 30.0	n.d. 10.0 ± 0.3 29.8 ± 0.6	– 100.0 99.3
Sea water (Caspian sea water, Babolsar, Iran)	0.0 30.0 60.0	174.0 ± 3.5 206.3 ± 4.1 235.5 ± 4.9	– 107.7 102.5

[a]Mean of replicate experiments (n = 3) ± standard deviation; [b]not detected.

Table 5. Determination of lead in food sample

Sample	Lead amount / (µg g^{-1})		Recovery / %
	Added	Found[a]	
Spinach	0.00 4.00 8.00	3.90 ± 0.08 7.83 ± 0.18 11.84 ± 0.26	– 98.2 99.2
Rice	0.00 0.40 0.80	0.30 ± 0.01 0.71 ± 0.01 1.10 ± 0.02	– 102.5 100.0
Black tea bag	0.00 1.00 2.00	1.04 ± 0.02 2.10 ± 0.05 3.10 ± 0.08	– 106.0 103.0

[a]Mean of replicate experiments (n = 3) ± standard deviation.

membrane. The water samples were extracted using the proposed method and analyzed by FAAS. The results show that all water samples were free of lead contamination. The water samples were spiked at different concentration levels for evaluating the recovery. The recoveries for the spiked water samples were in the range of 98.7-107.7%. The RSDs were better than 2.7% for 3 replicate analyses. Also, in the analysis of food samples the relative recoveries at different spiking levels were obtained in the range of 98.2-106.0% and RSDs were better than 2.6%. Therefore, based on these analytical results, it was found that the preconcentration technique was suitable for the determination of ultra-traces of lead in food and water samples.

Conclusion

In the present work, the rapidly synergistic cloud point extraction (RS-CPE) method was successfully combined with FAAS for the determination of ultra-trace lead in food and water samples. The surfactant Triton X-114 was applied as the extractant and octanol worked as cloud point revulsant and synergic reagent for extraction, which lowered the cloud point temperature of Triton X-114 and assisted the subsequent extraction process. In this work, lead was extracted into micelle rich phase with octanol without adding any complexing agent. Besides displaying the advantages of traditional CPE, this method is fast, convenient, and low time-and labor-consuming. The proposed method displayed several good characteristics, such as fast extraction, low price, low LOD, and proper selectivity for lead determination by FAAS. The proposed method was used successfully for sensitive extraction and determination of lead ions from food and water samples.

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