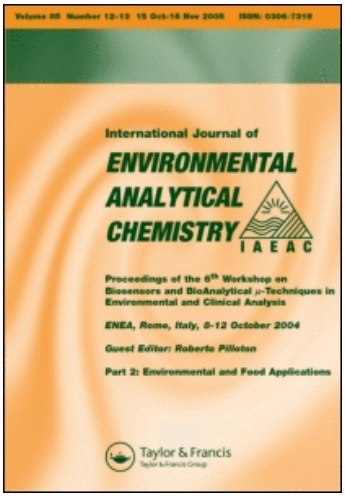

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Flotation separation and electrothermal atomic absorption spectrometric determination of lead in water samples

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A flotation method based on formation of an ion–associate complex between ferroin and Pb(II)–thiosulfate complex is proposed for the quantitative separation and preconcentration of Pb(II) content in water and some vegetable samples. The flotation process was carried out using a 250-mL aliquot of the aqueous solution at a buffering pH of 8.50. After separating the ion–associate complex, it was dissolved in 5 mL of heated 1 M HNO_3, and the Pb(II) content was determined by electrothermal atomic absorption spectrometry. The determination of Pb(II) was carried out in the range of 1.6×10^{-9} to 1.2×10^{-8} M. The limit of detection and relative standard deviation were obtained as 8.5×10^{-10} M and 1.73%, respectively. It was found that a large number of cations and anions, even at high much foreign ion/Pb(II) ratios, were not interfered. The validity of the method was confirmed by determining the Pb(II) contents in two Standard Reference Materials and a synthetic liquid extract of vegetable sample. It was then applied satisfactorily for determination of Pb(II) in several plant foodstuffs, drinking-water, and tap-water samples.

Keywords: Flotation; Preconcentration; Pb(II) determination; Ferroin; Thiosulfate; ETAAS

1. Introduction

The determination of heavy metals, especially some toxic metals which play important roles in biological mechanisms, has been receiving much attention. It has been found that even very low concentrations of these metal ions can cause serious biological disorders that can lead to serious diseases [1]. Usually, the direct determination of extremely trace level of these ions in such complex matrices containing high concentrations of salts is encountered with a ''classical'' difficulty due to their inherent low tolerance limit to the amount of total dissolved salts (TDS), which restricts application of instrumental sensitive techniques [2]. Lead is one of these toxic ions, which represents a potential problem because of its widespread distribution throughout the environment. Lead enters the organism primarily via the alimentary and/or

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respiratory tract. The main sources of this metal intake are air, drinking-water, and food [3]. The determination of extremely low levels of lead in complex matrices requires powerful techniques such as inductively coupled plasma atomic emission spectrometry (ICP-AES) [4–6], inductively coupled plasma mass spectrometry (ICP-MS) [7–9], and electrothermal atomic absorption spectrometry (ETAAS) [10–13]. Among these techniques, ETAAS is usually preferred because of the low sample volume requirements, low detection limit, relatively more simple treatment, and cheaper cost. The possibility of direct determination of lead by ETAAS has been investigated using various types of matrix modifier [14–16]. However, the appearance of errors in such determinations is inevitable due to the presence of several interference elements, especially with changing the sample matrices. For example, the presence of aluminium and iron give rise to severe interference so that the precise determination of extremely low concentrations of lead is impossible in such conditions [17]. Thus, a separation/preconcentration procedure is frequently used before the analytical measurement by ETAAS. Several methods including liquid–liquid extraction [18–21], ion exchange [22, 23], and functionalized chelating matrices [24–27] have been generally used for this purpose. Solvent extraction has several drawbacks like slow equilibrium attainment, mutual solubility of two phases, poor selectivity and emulsion formation. Indeed, several time multistage extractions are required for quantitative recovery. Ion exchangers and chelating resins also suffer respectively from insufficient selectivity and reproducibility.

Application of the flotation methods for separation/preconcentration of trace amounts has been developed in the last two decades [28, 29]. Among the various methods of the flotation techniques, the adsorptive droplet technique is one of the simplest to be developed as flotation spectrophotometry in treatment with ion–associate complexes [30–32]. The effective analytical characteristics of this technique are including no contamination of the organic phase, no requested to the carrier gas or surfactant, fast collection of the floated phase containing the analyte, simplicity, high enrichment factor, elimination of interfering component matrices, and good possibility to choice the solvent and the analytical measurement technique [33–40].

This paper describes the selective separation/preconcentration of trace amounts of Pb(II) ions in some environmental samples by rapid flotation as an ion–associate complex using thiosulfate and ferroin agents before the determination by ETAAS. The analytical parameters relevant to the quantitative flotation of Pb(II) were investigated.

2. Experimental

2.1 *Instrumentation*

The measurements were carried out using a Shimadzu Model AA 6300 atomic absorption spectrometer with a deuterium background corrector and a Model GFA-EX7i graphite furnace with pyrolitic graphite tubes. The operating conditions of the spectrometer and the temperature programme used in the analysis were set as recommended by the company. A Corning model 130 pH-meter with a combined glass and calomel electrode was employed for measuring the pH values.

2.2 *Materials and solutions*

All chemicals were of analytical reagent grade (Merck, Darmstadt, Germany). Ultra-pure quality water was used throughout the experiments. Xylene (mixture of isomers) was dried prior to use by sodium twisted wire. Standard stocks solution of Pb (1000 mg/L) was prepared from Titrisol concentrate (Merck). The working solution of Pb(II) was obtained by diluting the stock solution with water. The thiosulfate solution (0.5 M) was made from sodium thiosulfate salt (pentahydrate). It was daily prepared and kept away from light. The ferroin solution (6.25×10^{-3} M) was prepared by stoichiometrically dissolving appropriate amounts of $FeSO_4$ and 1,10-phenanthroline (phen) in distilled water, addition of adequate volumes of the acetic/acetate solutions to adjust the pH of the solution to 5, and resting the solution for a few minutes. Solutions of 1 M acetic acid, sodium acetate, ammonium chloride, and ammonia were prepared separately for adjusting the pH of the experimental solutions. Solutions of 0.01 M and 1 M HNO_3 were prepared for dissolving the vegetable ash and the floated ion–associate complex, respectively. Solution of 0.001 M $Pd(NO_3)_2$ was used as the modifier for injection to the furnace. All the solutions were stored in stoppered flasks.

2.3 *Recommended procedure for the flotation process*

Six millilitres of thiosulfate solution was added to aliquot of solution (250 mL) containing up to 2.5 μg of Pb(II), and its pH was adjusted to 8.50 using the ammonium/ammonia solutions. The solution was then transferred to a separating funnel, and then 7.5 mL of ferroin and 20 mL of xylene were added to it, sequentially. The funnel was stoppered and shaken vigorously for 1 min, then left to rest for a few minutes. After the appearance of the floating ion–associate complex at the interface of the aqueous/organic phases, the stopcock of the funnel was slowly opened. The lower aqueous phase was discarded, and the upper organic phase was collected for drying and employing again. While draining off both the aqueous/organic phases, the floated layer containing the ion–associate complex completely remained in the funnel by adhering to its inner walls. It was first eluted with 5 mL of distilled water and then dissolved in 5 mL of 1 M HNO_3, which was warmed up to 80°C prior to use. By injecting 10 μL of this solution five times in conjunction with 5 μL of the Pd(II) solution into the prestandardized graphite furnace, the Pb(II) contents of the sample were measured at 283.3 nm against a reagent blank, which was prepared in the same manner.

2.4 *Sample collection and preparation*

To obtain the tap water samples, the tap was turned on and after running the water for 20 min, approximately 1000 mL of water was collected. The water samples were filtered through 0.45-mm-pore-size membrane filters immediately after sampling. All the glassware used was previously washed with a 10% (v/v) HNO_3 solution and then with ultra-pure water. The vegetable samples were obtained from a farmland around a parkway near to Brigand city. They were dried at 105°C, ground in agate, and homogenized. Samples (1 g) were weighed into a porcelain crucible and ashed at 500–550°C in a muffle furnace. The remaining ash was then dissolved with 100 mL of 0.01 M

HNO_3. To eliminate the interference of Hg(II), which could be present at trace levels in the real samples, the solution was passed through a fine sintered glass filter after adding thiosulfate and adjusting its pH. The recommended procedure was then followed on the filtrated solution for measuring the Pb(II) contents.

3. Results and discussion

3.1 *Optimization of conditions*

To obtain reliable results, 250-mL aliquots of the solutions containing 1×10^{-8} M of Pb(II) were prepared, and a series of effective parameters influencing the flotation process were investigated. The effect of pH on the flotation process was investigated within the pH range of 4.00–10.00. As shown in figure 1, the recoveries obtained exhibit a maximum value at the pH of 8.50, with respect to the other optimal conditions. Hence, further examinations were carried out at this pH value. The insufficient flotation efficiency at pHs below 8.50 is related to instability occurring for both ferroin and lead–thiosulfate complexes. On the other hand, the recovery decreasing at the pH values above 8.50 is due to the tendency of Pb(II) ions to precipitate as hydroxide or instability of thiosulfate agent.

The effect of thiosulfate agent was examined over the concentration range of 0.001–0.05 M in the solutions. Curve A, in figure 2, indicates that a maximum recovery occurs for the concentrations of 0.01 M of thiosulfate. The absorbance decreasing at the lower thiosulfate concentration is related to the lack of its adequate value to form the

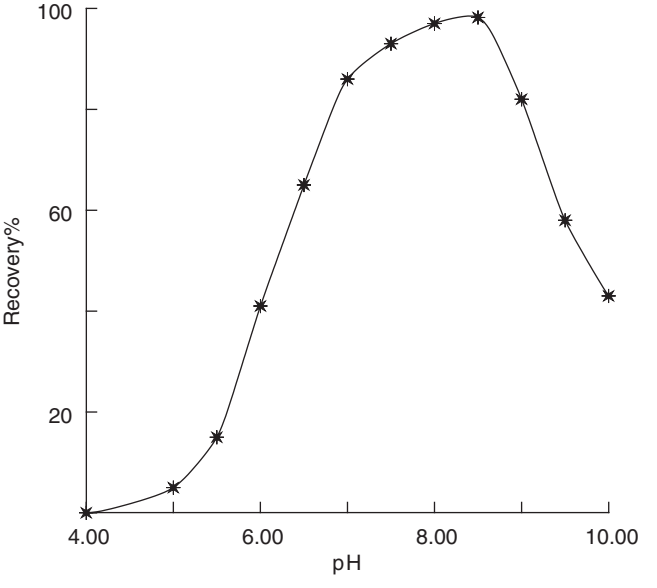

Figure 1. Effect of pH on the flotation process of Pb(II) for a fixed Pb(II) concentration of 1×10^{-8} M. The other conditions were according to the procedure.

lead–thiosulfate complex. On the other hand, the absorbance decreasing at higher concentrations is attributed to the formation of an alternate ion–associate between the excess amount of thiosulfate and ferroin, which prevents from associating the ferroin with the Pb-thiosulfate complex. Under such conditions, the ion–associate complex of interest can not be precisely formed.

The effect of ferroin content on the flotation process was also studied in the concentration range of 2.5×10^{-5} to 2.5×10^{-4} M. As shown in curve B, figure 2, a maximum absorbance was obtained at a concentration of 1.8×10^{-4} M, which was chosen for the future examinations. The absorbance decreasing in the presence of much excess amount of ferroin may be due to the tendency to form an alternate complex of Pb(II)–phen instead of Pb(II)–thiosulfate, which was not able to float at the interface of aqueous/organic phases.

The investigation to choose the favourable carrier to establish and collect the interested ion–associate complex was carried out using various agents including inert bubble gas (N_2), inert solid support (Amberlite XAD-4), polyurethane foam, cationic and neutral surfactants (*N*-cetyl-*N*,*N*,*N*-trimethylammonium bromide and Triton X-100), and various inert organic solvents. It was found that the appearance of ion–associate complex of interest is feasible mainly by employing dried aromatic solvents, such as benzene, toluene, or xylene as a floating layer. In so doing, xylene was chosen because of its lesser hazardous properties. Experiments showed that 20 mL is sufficient to obtain the maximum absorbance in treatment with 250-mL aliquots. It should be considered that the flotation efficiency is highly related to the degree of

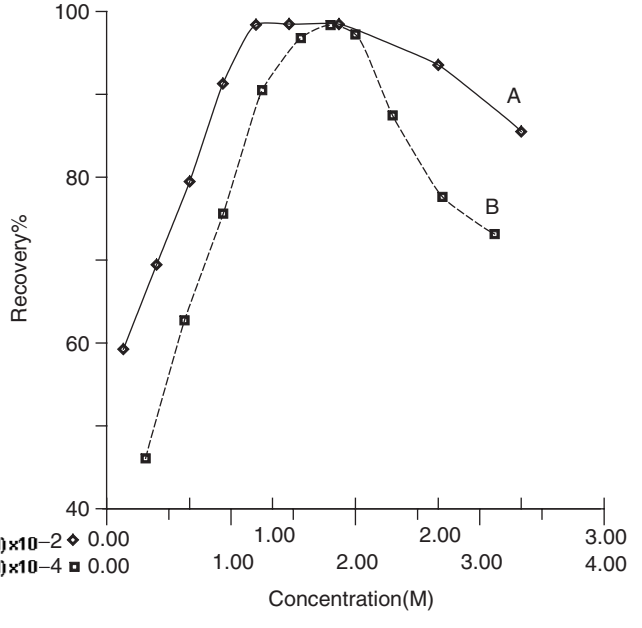

Figure 2. Effect of concentration of thiosulfate (A) and ferroin (B) on the flotation process of Pb(II) for a fixed Pb(II) concentration of 1×10^{-8} M. The other conditions were according to the procedure.

dryness of the xylene phase. Hence, it should be completely dried and kept away from air before use in the flotation process.

Initially, to dissolve the floating ion–associate complex, various experiments were carried out in which a series of organic solvents, such as methanol, ethanol, acetone, dimethylformamide, and dimethyl sulfoxide, were employed. It was observed that none of them were capable of dissolving the complex completely. Hence, the dissolution process was examined using oxidant agents including HNO_3, H_2O_2, and $KClO_3$ solutions, and it was found that a 5-mL aliquot of 1 M HNO_3 that was warmed up to 80°C is adequate for completely dissolving the complex. Aliquots of 10 μL of these solutions containing Pb(II) ions were injected into the furnace.

The breakthrough volume of sample solution was tested by performing the experiments under the optimum conditions in which the amount of Pb(II) ions was fixed (1.25×10^{-6} mmol), while the volume of the aqueous phase was varied over the range of 50–400 mL. It was found that the process could be carried out quantitatively up to volumes of 250 mL, and after that the reproducibility and recovery were put at risk. Hence, this volume was considered as the breakthrough volume for the process. In such a manner, by considering the breakthrough volume (250 mL) and the final dissolving volume (5 mL), a preconcentration factor of 50 was achieved.

3.2 *Analytical figures of merit*

Under the optimum conditions, a linear calibration curve was constructed using the equation $A = 4.20 \times 10^7 C_{Pb} + 0.067$ ($r^2 = 0.9989$), for the determination of Pb(II) by ETAAS at 283.3 nm over the range of 1.6×10^{-9} to 1.2×10^{-8} M (0.33–2.49 μg/L). The RSD obtained in the replicate treatments ($n = 7$) with 1×10^{-8} M Pb(II) was found to be 1.73%. In treatment with the blank solutions, the LOD was obtained as 8.5×10^{-10} M. The experiments also exhibit a linear calibration curve as: $A = 8.51 \times 10^5 C_{Pb} + 0.035$ over the range of 8.0×10^{-8} to 6.0×10^{-7} M with the correlation coefficient of 0.9991 for the direct determination of Pb(II) by the ETAAS technique. By considering that the experimental preconcentration factor is defined as the ratio of the slopes of the calibration graphs with and without preconcentration [41], the calculated ratio is 49.23, which is in agreement with the recovery obtained under optimal conditions.

3.3 *Effect of foreign ions*

The effects of several foreign ions were studied by introducing each one to 250-mL aliquots of the solutions containing Pb(II) with the concentration of 1.0×10^{-8} M. Each ion was considered as an interfering agent, when the absorbance value exhibited a deviation of more than ±5%. As shown in table 1, almost all of the cations and anions except Hg(II) did not interfere, even at considerably high foreign ion/Pb(II) ratios. The interference effect of Hg(II) is attributed to its oxidation which leads to a partial consumption of the thiosulfate content. In so doing, due to the presence of Cl^-, the produced Hg(I) ions precipitate as Hg_2Cl_2 in the medium, thus restricting

Table 1. Tolerance ratio of foreign ions in the determination of 5.0×10^{-9} M of Pb(II) in 250 mL of the aqueous phase.

Tolerance foreign ion/Pb(II) ratio (mol/mol)	Ions
10 000	Cs^+, Li^+, K^+, Na^+, Cl^-, NO_3^-,
5000	Al^{3+}, As^{3+}, Cr^{3+}, Fe^{3+}, Ln^{3+}, Sb^{3+}, Ca^{2+}, Co^{2+}, Cu^{2+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, TiO^{2+}, Zn^{2+}, Rb^+, VO_2^+, $B4O_7^{2-}$, Br^-, I^-, MO_4^-, NO_2^-, OAC^-, SCN^-, CO_3^{2-}, SO_4^{2-}
1000	Hg^{2+}[a], Cd^{2+}
500	$C2O_4^{2-}$, PO_4^{3-}, VO_3^-, SeO_3^{2-}

[a]Tolerated in the presence of SCN^-.

Table 2. Determination and recovery study of Pb(II) content in SRM 1640, SRM 1643d, and a synthetic liquid extract of spinach sample in which the trace and minor elements concentrations were adjusted according to the literature [41, 42] (results are averaged over five replicate measurements, and standard deviations are indicated).

Sample	Certificated value (μg/L)	Found value (μg/L)
SRM 1640	27.89 ± 0.14[a]	28.91 ± 0.45
SRM 1643d	18.15 ± 0.64[a]	18.71 ± 0.32
Syn. Spinach	0.70 ± 0.01	0.73 ± 0.02
	1.40 ± 0.01	1.36 ± 0.02

[a]The treatment was carried out using aliquots of 20 mL of the stock solutions, which were diluted up to 250 mL.

flotation of the interested ion–associate complex. Fortunately, this interference can be easily eliminated via filtration of the solution before addition of phen and before performing the flotation process.

3.4 *Analysis of real samples*

In order to show the validity of the method, particularly in treatment with complicated matrices, the proposed method was carried out using two standard reference materials including SRM 1640 (Trace Elements in Natural Water), SRM 1643d (Trace Elements in River Water), and a synthetic liquid extract of plant foodstuff sample in which the trace and minor elements concentrations were adjusted according to the literature [42, 43]. The results of the determinations are summarized in table 2. As shown, irrespective of the complicated matrices, the recoveries obtained were quantitative in the range of 97.1–104.3%, thus confirming the validity of the method at 95% confidence limits. Subsequently, the proposed method was applied for the determination of lead in various samples including a commercial drinking-water, tap water (Birjand city), and three vegetable samples. The results are detailed in table 3. As it is shown, the recoveries for the spiked amounts of Pb(II) ions to the samples were more than 95%, which denote on satisfactorily application of the proposed method for such determinations.

Table 3. Determination and recovery study of Pb(II) in environmental samples with and without spiked lead contents (results are averaged over five replicate measurements and standard deviations are indicated).

Samples	Pb(II) spiked (μg/L)	Found (μg/L)
Drinking freshwater	1.0 ± 0.01	1.03 ± 0.02
	2.0 ± 0.01	2.08 ± 0.03
Tap water	–	2.18 ± 0.03
	2.0 ± 0.01[a]	4.27 ± 0.04
Cabbage leaves	–	1.87 ± 0.04
	2.0 ± 0.01[a]	3.91 ± 0.04
Lettuce leaves	–	2.36 ± 0.04
	2.0 ± 0.01[a]	4.28 ± 0.04
Spinach leaves	–	2.43 ± 0.05
	2.0 ± 0.01[a]	4.34 ± 0.04

[a]The spiking treatment was carried out using aliquots of 50-mL of the sample solutions, which were diluted up to 250 mL.

4. Conclusion

A simple, fast, highly sensitive and low cost flotation method is proposed for the determination of Pb(II) in various environmental systems including vegetable samples, sea and tap water samples. This method provides an appropriate selectivity for ultra trace determination of Pb(II) so that a number of metal ions and anions may be found in such complicated matrices are not interfering. For example, interference arising from the chlorinated compounds is one the main restriction in the determination of Pb(II) by ETAAS. In this method, the chlorinated compounds are totally removed from the media and no interference can be appeared by chlorine in the determination process. Unlike the solvent extraction determination methods of Pb(II) [44–46], which create a severe environmental problem due to the contaminated organic solvents; in this method, the organic solvent is mainly saturated with water and can be used repeatedly after a simple drying process. In comparison with the solid-phase extraction methods [47–50] in which the processes, such as sorption/desorption and regeneration are time-consuming, this method is more rapidly. The determination can be carried out with a good reproducibility and sample throughput. Finally, the moderately high preconcentration factor, recovery yield and the other figures of merit imply that the proposed method can be satisfactorily applied for the determination of extremely trace amount of Pb(II) in the natural environmental samples.

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