

Factorial design in the optimization of preconcentration procedure for lead determination by FAAS

Mustafa Soylak^{a,*}, Ibrahim Narin^{a,1}, Marcos de Almeida Bezerra^{c,d},
Sérgio Luís Costa Ferreira^c

^a Department of Chemistry, Faculty of Art and Science, Erciyes University, Kayseri 38039, Turkey

^b Department of Chemistry, Faculty of Art and Science, Nigde University, Nigde 51100, Turkey

^c Grupo de Pesquisa em Química Analítica, Instituto de Química, Universidade Federal da Bahia, Campus Universitário de Ondina, 40170-290 Salvador, Bahia, Brazil

^d Departamento de Química e Exatas, Universidade Estadual do Sudoeste da Bahia, Campus de Jequié, 45200-000 Jequié, Bahia, Brazil

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Abstract

The present paper proposes a preconcentration procedure for lead determination using flame atomic absorption spectrometry (FAAS). It is based on lead(II) ions extraction as brilliant cresyl blue (BCB) complex and its sorption onto Diaion HP-2MG, a methacrylic ester copolymer. The optimization step was carried out using factorial design and the variables studied were pH, shaking time and reagent concentration. In the established experimental conditions, lead can be determinate with a limit of detection of $3.7 \mu\text{g L}^{-1}$ lead ($N = 20$) and a relative standard deviation of 7% for a lead concentration of $100 \mu\text{g L}^{-1}$. The accuracy was confirmed by analysis of a certified reference material, the stream sediment furnished by National Research Centre for Certified Reference Materials (NRCCRM), China (GBW 07310). Effect of other ions in the procedure proposed was also studied. The method was applied for lead determination in real samples of water, tea, soil and dust. Tests of addition/recovery in the experiments for lead determination in water samples revealed that the proposed procedure could be applied satisfactorily for analysis of these samples.

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1. Introduction

The principal sources of contamination into humans by lead are foods and drinks consumed. The presence of lead in aliments is due to environmental contamination associated with soil and also related to atmospheric precipitation, pesticides and materials used in its production. A regular absorption of small quantities of lead may cause serious injuries to health such as encephalopathy, kidney damage and several effects in the body [1,2]. This way, lead determination in al-

iments, drinks and its pollution sources like soil and dust are very important. However, lead is generally present in these samples as traces quantities, and the conventional techniques, such as flame absorption atomic spectrometry (FAAS) and inductively coupled plasma emission spectrometry (ICP-OES), have high detection limits for lead determination. Then, preconcentration procedures are opportune and several methods have been proposed with this objective [3–9].

Basic dyes, like brilliant cresyl blue, brilliant blue, methyl violet, etc., give ion-association complexes with a number of metal ions for their determination [10]. Various spectrophotometric studies have been performed for the determination of some metal ions by using brilliant cresyl blue [11–13].

Diaion HP-2MG is methacrylic ester copolymer, and has relatively hydrophilic nature. Its surface area, mesh size

* Corresponding author. Tel.: +90 3524374904; fax: +90 3524374933.

E-mail address: soylak@erciyes.edu.tr (M. Soylak).

¹ Present address: Faculty of Pharmacy, Erciyes University, 38039 Kayseri, Turkey.

and pore size is 500 g m^{-2} , 25–50 mesh and 170, respectively [14,15]. Diaion HP-2MG is relatively new resin for the solid-phase extraction of traces of heavy metal ions. Cysteamine-immobilized Diaion HP-2MG has been used for the preconcentration of Cd^{2+} and Pb^{2+} from aqueous solutions by Tanco et al. [16]. Kabay et al. [17] have used Diaion HP-2MG for the preconcentration of Cr (VI) from natural waters. Tuzen and Soylak [18] have proposed a preconcentration procedure from some metal ions on Diaion HP-2MG.

Chemometric techniques have been frequently used for optimization of analytical methods [19,20]. Among these, factorial design is used mainly for preliminary evaluation of the significance of the variables [21,22], but it can also be used for end optimization of analytical procedure [23].

The present paper proposes a procedure for lead determination in water, tea, soil and dust samples by flame absorption atomic spectrometry. It is based on sorption of lead(II) ions complexed with brilliant cresyl blue (BCB) onto a methacrylic ester copolymer (Diaion HP-2MG). The optimization step was carried out using factorial design.

2. Experimental

2.1. Instrumentation

A Perkin-Elmer Model 3110 atomic absorption spectrometer, equipped with a lead hollow cathode lamp operated at 7 mA, was used throughout this work. The wavelength and spectral band pass were set at 283.3 nm and 0.7 nm, respectively. The nebulizer uptake rate was adjusted to give the optimum response for conventional sample introduction, the resulting rate being 6.0 mL min^{-1} . An acetylene flow rate of 2.5 L min^{-1} was used with an air-flow rate of 8.0 L min^{-1} . A digital pH meter model Nel-900 was used for pH measurements. A Nuve ST 402 type shaker was used in all experiments.

2.2. Reagents and solutions

All chemicals used were of analytical reagent grade, unless stated otherwise, and aqueous reagents were prepared in double distilled deionized water. Laboratory glassware was kept overnight in 10% (v/v) nitric acid solution, rinsed with deionized water before use. Lead(II) standard solution was prepared from 1000 mg L^{-1} solution of lead(II) nitrate, and diluted as required with distilled water.

Diaion HP-2MG (25–50 mesh) was purchased from Supelco (no: 1-3601). In order to remove organic and inorganic contaminants, the resin was washed successively with methanol, distilled water, $1 \text{ mol L}^{-1} \text{ HNO}_3$ in acetone, distilled water, $1 \text{ mol L}^{-1} \text{ NaOH}$ and distilled water.

Brilliant cresyl blue solution (BCB) (Merck, Darmstadt) solution ($5 \times 10^{-3} \text{ mol L}^{-1}$) was prepared daily by dissolving in water. The stream sediment standard reference material

(GBW 07310) was obtained from National Research Centre for Certified Reference Materials (NRCCRM), China.

Ammonium acetate buffer (0.1 mol L^{-1}) was prepared by adding an appropriate amount of acetic acid to ammonium acetate solutions resulting in solutions of pH 6. For pH 7, a borate buffer was used. Ammonium chloride buffer solution was prepared by mixing appropriate amounts of 0.1 mol L^{-1} ammonia and 0.1 mol L^{-1} ammonium chloride solutions for pH 8.

2.3. General procedure

A sample volume of 100 mL or 250 mL, containing lead(II) ions, was transferred into a beaker; 10 mL of buffer solution and 1.0 mL of $5 \times 10^{-3} \text{ mol L}^{-1}$ brilliant cresyl blue (BCB) solution were added. After a fast shaking, 100 mg of Diaion HP-2MG was added and the mixture was shaken again for 30 min. The system was then filtered under vacuum through cellulose nitrate membrane (5 cm diameter). Then, the filter and constituents were washed with distilled water. In order to elute adsorbed lead on Diaion HP-2MG, 10 mL of $1 \text{ mol L}^{-1} \text{ HNO}_3$ in acetone was used. After elution, acetone content of the elution solution was evaporated near to dryness. The final volume was completed to 5.0 mL with $1 \text{ mol L}^{-1} \text{ HNO}_3$. Lead content of the final solution was determined by flame atomic absorption spectrometry. The same procedure was applied to the blank solution.

2.4. Optimization strategy

The optimization process was carried out using a two-level factorial design [24,25]. In this experimental design, the experiment number (N) is calculated by expression: $N = 2^k$, where k is the number of variables. The variables chosen were pH, reagent concentration (RC) and shaking time (ST). Maximum and minimum levels of each factor (Table 1) were established according to the data from previous experiments. Table 2 shows the experimental design matrix, using lead recovery (%) as analytical response. All the experiments were carried out in random order and in duplicates, using a solution volume of 250 mL containing $20.0 \mu\text{g}$ of lead.

2.5. Digestion procedure for the real samples

The stream sediment standard reference material, black tea, soil and dust samples were digested according to procedure given in literatures [26–28].

Table 1
Factors and levels used in the factorial design

Variable	Low (–)	High (+)
Reagent concentration (RC) (mol L^{-1})	5×10^{-6}	5×10^{-5}
pH	6.0	8.0
Shaking time (ST) (min)	10	30

Table 2
Design matrix and the results of the two-level factorial design

Experiment	RC	pH	ST	Recovery (%)	
				R1	R2
1	+	+	+	94.7	105.3
2	+	+	–	94.4	90.9
3	+	–	+	84.2	84.2
4	+	–	–	78.9	84.2
5	–	+	+	78.9	85.9
6	–	+	–	57.9	58.1
7	–	–	+	51.3	48.0
8	–	–	–	39.8	42.1

RC: reagent concentration; ST: shaking time.

A 200 mg amount of a stream sediment standard reference material (GBW 07310) sample was decomposed with 15 mL of aqua regia and the solution was evaporated to dryness. This process was repeated twice. Ten milliliters of distilled water was added to the residue. The suspension was filtered through a blue band filter paper, and the insoluble part was washed with distilled water. Then the general procedure given above was applied to the final solutions. The same procedure was applied to the blank solution.

Two grams of black tea was digested in a quartz vessel with 10 mL of concentrated sulfuric acid and 40 mL of hydrogen peroxide 30% at 110 °C for 3 h. After digestion, the volume was made up to 50 mL with distilled water. Blanks were prepared in the same way as the sample, but omitting the sample.

A 1.0 g amount of soil or dust sample was decomposed with 15 mL of aqua regia and the solution was evaporated to dryness. This process was repeated twice. Ten milliliters of distilled water was added to the residue. The suspension was filtered through a blue band filter paper, and the insoluble part was washed with distilled water. Then, the preconcentration procedure was applied to the final solutions.

3. Results and discussion

3.1. Optimization of the experimental conditions using factorial design

Considering the preconcentration procedure proposed the variables chosen for optimization using factorial design were pH, reagent concentration and shaking time, using lead recovery (%) as analytical response. The data of this experiment were evaluated by analysis of variance (ANOVA). The Pareto chart (Fig. 1) shows these results. In this chart, it can also be seen that: (1) reagent concentration is the factor more significant for preconcentration procedure; (2) reagent concentration in the superior level is more convenient for this procedure; (3) the lead recovery increases with the increase of pH; and (4) the lead recovery increases with the increase of the shaking time. The interactions (ST) × (pH), (ST) × (RC) and (RC) × (pH) are significant. Considering this, the three studied variables have to be operated at their highest levels (+, +, +). The same conclusion can be showed geometrically by analysis of the graph present in Fig. 2. For three variables, corners of a cube can describe the eight experiments necessary to design application. The corner, which presents the recovery percent value of 101.38, is corresponding at levels combination (+, +, +) for all studied variables. In the opposite corner, the worst recovery can be found which possesses a value of 39.58%. This response corresponds at follow level combination (–, –, –). Thus, the two-level factorial design indicates that optimum values to develop solid-phase extraction procedure operation is $5 \times 10^{-5} \text{ mol L}^{-1}$ for reagent concentration, a buffer solution at pH 8.0 and a shaking time of 30 min for attain recoveries of 100%.

3.2. Matrix effects

The influences of some alkali, earth alkali and transition metals on the recoveries of lead ions on Diaion HP-2MG

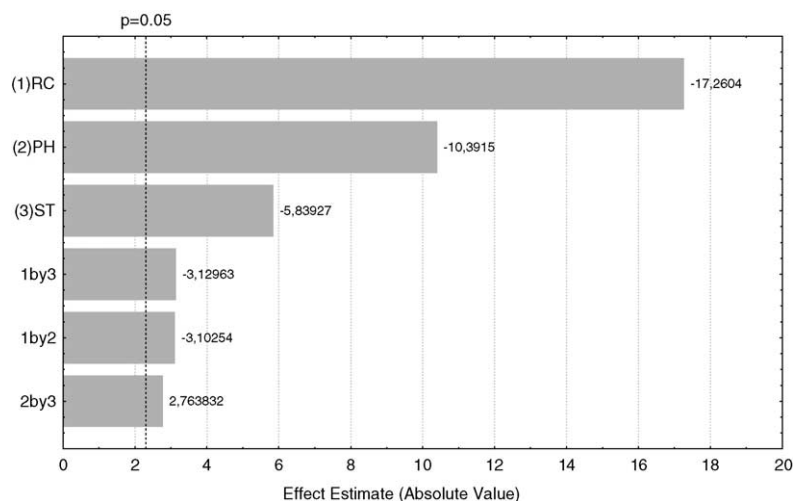


Fig. 1. Pareto chart of effects.

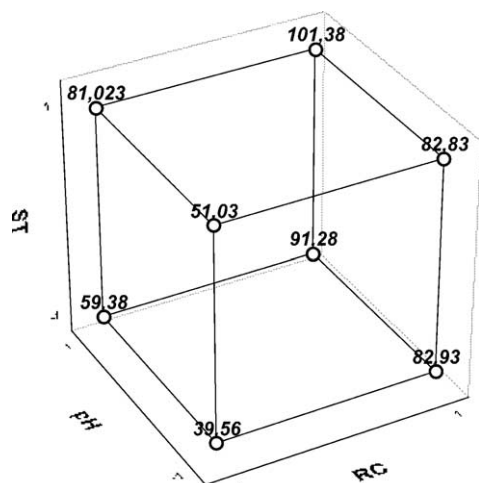


Fig. 2. Response cube graph of Table 2. The analyzed response was % lead recovery.

resin were investigated. The results are given in Table 3. The tolerance limit is defined as the ion concentration causing a relative error smaller than $\pm 5\%$ related to the preconcentration and determination of analytes. The tolerable levels of some heavy metal ions are suitable for the separation and preconcentration of the analyte ions in the real samples examined in the present study, because the levels of transition metals in these samples are lower than their interferic level.

3.3. Analytical performance

A relative standard deviation of 7% was obtained for a lead concentration of $100 \mu\text{g L}^{-1}$. The detection limit was determinate as IUPAC recommendation [29] for 100 mL of sample volume, based on three times the standard deviations of the blank. It was $3.7 \mu\text{g L}^{-1}$ ($N = 20$). The theoretical preconcentration factors found for this method were 20 or 50, considering sample volumes of 100 or 250 mL, respectively.

Tests of addition/recovery in the experiments for lead determination were performed in two water samples. The results are given in Table 4. Good agreements for lead ions were obtained between the added and measured analyte amounts.

Table 3
The influences of some ions on the solid-phase extraction of lead on Diaion HP-2MG ($N = 3$)

Foreign ion	Added as	Tolerable concentration (mg L^{-1})	Recovery (%)
Na^+	NaCl	10000	95
K^+	KCl	1000	100
Ca^{2+}	CaCl_2	1000	95
Mg^{2+}	MgCl_2	500	95
Co^{2+}	$\text{Co}(\text{NO}_3)_2$	50	95
Fe^{3+}	FeCl_3	10	100
Ni^{2+}	$\text{Ni}(\text{NO}_3)_2$	10	95
Cu^{2+}	CuSO_4	5	95
Mn^{2+}	MnSO_4	5	95
Cr^{3+}	$\text{Cr}(\text{NO}_3)_3$	1	95

Table 4

The results for tests of addition/recovery for lead determination in water samples (sample volume: 100 mL, final volume: 5 mL ($N = 3$))

Sample	Lead added (μg)	Lead found ^a (μg)	Recovery (%)
Anatolia bottled mineral water	0	—	—
	10	10.4 ± 0.1	104.0
	20	19.8 ± 0.8	99.0
	30	30 ± 2	98.7
A tap water	0	—	—
	10	9.9 ± 0.2	99.0
	20	19.7 ± 0.3	98.5
	30	29 ± 1	98.0

^a At 95% confidence limit.

The recovery values calculated for the added standards were always higher than 95%. In the light of these results, the proposed procedure could be applied satisfactorily for analysis of these samples.

3.4. Analysis of standard stream sediment reference material

The preconcentration procedure was applied for lead determination in a stream sediment standard reference material (GBW 07310). While the certified value was $27.0 \mu\text{g g}^{-1}$, the lead level found by proposed method was $27.2 \pm 2.4 \mu\text{g g}^{-1}$ at 95% confidence limit. The results are based on the average of five replicates, which show that the results are in good agreement with the certified values. If the concentration levels of the most common matrix constituents of the stream sediment reference sample and the accuracy of the presented method are considered together, it can be concluded that the proposed method is free from interferences of the various constituents.

3.5. Applications

The presented procedure was applied for lead determination in various samples including black tea, soil and house dusts. The results are given in Table 5. The results have been calculated by assuming 100% recovery of lead ions.

Table 5
The concentration of lead in the samples ($N = 5$)

Sample	Concentration achieved ^a ($\mu\text{g g}^{-1}$)
Black tea-1	3.3 ± 0.1
Black tea-2	3.7 ± 0.2
Soil sample from campus of Erciyes University	46 ± 4
Soil sample from Talas Road	42 ± 2
House dust-1	20 ± 1
House dust-2	24 ± 1

^a At 95% confidence limit.

4. Conclusions

The application of a two-level factorial design made possible a fast and economical optimization of a separation and preconcentration system based on solid-phase extraction phenomenon. The lead complexation by brilliant cresyl blue (BCB) reagent and its sorption onto Diaion HP-2MG was efficient to separate and preconcentrate this metal from several sample matrixes like tea, soil and water.

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