

SHORT COMMUNICATION

Determination of lead in water resources by flame atomic absorption spectrometry after pre-concentration with ammonium pyrrolidinedithiocarbamate immobilized on surfactant-coated alumina

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Abstract: A rapid, simple, and sensitive procedure based on modified solid phase extraction was developed for the pre-concentration and determination of trace amount of lead in water resources. Lead was reacted with ammonium pyrrolidinedithiocarbamate (APDC) to make a complex. The complex was then collected in a column packed with surfactant-coated alumina. The parameters affecting the collection efficiency and desorption rate of the lead complexes from the column were investigated and optimized. The collection efficiency of the lead complex on the adsorbent was excellent under the optimized conditions. The results obtained from the recovery test showed the capability and reliability of the method for the analysis of trace amounts of lead. The proposed pre-concentration procedure made it possible to apply conventional flame atomic absorption spectrometry (FAAS) for the sensitive determination of trace amounts of lead in water resources.

Keywords: flame atomic absorption spectrometry, determination of trace lead, water pollution, pre-concentration of lead, solid phase extraction.

INTRODUCTION

Lead is a toxic heavy metal and can affect many organs in the human body. During the last decades, an extensive database has been published providing a direct link between exposure to low levels of lead and mental deficiency in children. Prolonged intake of even low concentrations of lead can cause serious problems for human health.¹

In recent years, concern has increased over the concentration of lead in drinking and natural waters. The international public health associations have reduced the permitted amount of lead in drinking water. For example, the European Community (EC) recommends a limit of 50 µg/L of lead in potable waters, which requires a method of lead determination with sensitivity much higher than that offered by con-

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ventional flame atomic absorption spectrometry. Although sensitive techniques for the determination of trace elements are available in the commercial market, these techniques require high primary investment, highly experienced technicians and are usually not available everywhere. Therefore, a preliminary pre-concentration of lead in environmental samples is necessary to improve the sensitivity of flame atomic absorption spectrometry for the determination of trace amounts of lead.²⁻⁴

The most frequently employed methods for pre-concentration are liquid-liquid extraction,⁵ sorption and chelating ion exchange,⁶ solid phase micro-extraction,⁷ *etc.* Among the different methods, much interest has recently been focussed on solid phase extraction, owing to its high enrichment factor, simplicity and possibility of automation.^{6,8} In any case, pre-concentration enhances the sensitivity of a determination method and enables the use of conventional flame atomic absorption spectrometry for the determination of trace amounts of lead in environmental samples.

In this work, the lead in an aqueous solution was reacted with ammonium pyrrolidinedithiocarbamate (APDC) and the formed lead complex was then pre-concentrated in a column packed with a surfactant immobilized on alumina. The method was applied for the determination of trace amounts of lead in natural waters.

EXPERIMENTAL

Reagents and chemicals

All chemicals were of analytical grade or better.

A commercial standard solution of 1000 $\mu\text{g mL}^{-1}$ of lead for atomic absorption spectrometry (BDH Ltd) was used as the stock standard solution. Working standard solutions were diluted from the stock standard solution with a 0.1 M nitric acid solution.

Sodium dodecyl sulfate (SDS) (Merck) was used without further purification. An APDC solution (0.1 % w/v) was prepared by dissolving the appropriate amount of APDC in distilled de-ionized water.

Gamma-alumina (10–50 μm) was used after washing with 5 ml of 3 M nitric acid and rinsing with distilled de-ionized water.

All glassware were cleaned before use by soaking overnight in 1.5 M nitric acid and triply rinsed with distilled de-ionized water and allowed to dry in a dust-free atmosphere.

Preparation of the surfactant-coated alumina column

2 g of alumina was suspended in 50 mL water and mixed with 100 mg SDS. The mixture was acidified to pH 2 with 3 M nitric acid. The mixture was then shaken for 15 min and the supernatant solution was then decanted and the surfactant-coated alumina was used for the preparation of the column.

Instrumentation

A Varian atomic absorption spectrometer, Model AA-220, equipped with a deuterium background correcting system was used for the determination of the lead concentration. A Varian standard premixed air-acetylene burner and a Varian hollow cathode lamp were used. The instrumental conditions for the determination of lead are given in Table I.

Procedure

100 mL of a standard solution of lead (30 ng/mL) or a water sample was transferred into a 250 mL beaker and the pH was adjusted to about 3 with nitric acid. 5 mL of APDC solution was added and the mixture was slowly shaken for 1 min. The solution was then passed through SDS-coated alumina packed column with the aid of a suction pump. The lead-APDC complex was absorbed in the

column. The column was then washed with 10 mL distilled de-ionized water. The lead complex was finally eluted from the column by washing with 4.5 mL of nitric acid (4M). The eluent was collected in a 5 mL volumetric flask and made to the volume with distilled de-ionized water.

TABLE I. Instrumental conditions for the determination of lead

Wavelength	217.0 nm
Slit	1.0 nm
Lamp current	5 mA
Flame type	Air-acetylene
Flame condition	Oxidizing
Background correction	On
Expansion factor	1

RESULTS AND DISCUSSION

Several parameters affect the pre-concentration efficiency of lead, including pH, flow rate of the analyte through the column, reaction time and the flow rate of the acid in the desorption stage. Therefore, the parameters had to be optimised in order to obtain an effective pre-concentration.

Effect of pH

100 mL of the standard solution of lead (30 ng/ml) was transferred into a 250 mL beaker and the pH adjusted to different values from 1 to 5. After adding 5 mL of APDC and shaking for 1 min, the solution was passed through the surfactant-coated alumina column to collect the lead complex. The column was then washed with nitric acid and the effluent analyzed for lead. The adsorption efficiency was then calculated. The effect of pH on the adsorption efficiency is shown in Fig. 1, which indicates that a high deposition efficiency was achieved at pH 3 and above.

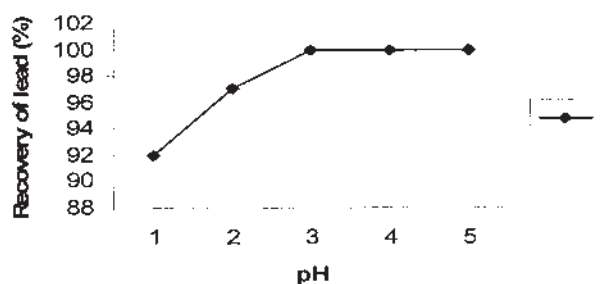


Fig. 1. Effect of pH on the pre-concentration efficiency.

Effect of the reaction time

The effect of the contact time between the reagent and sample before loading onto the column was studied and no considerable differences between the efficiencies obtained with different times of reaction in a range of 0.5 to 3 min were found.

Effect of the flow rate of the sample

The effect of the flow rate of the solution containing the lead complex through the column on the adsorption efficiency of the complex was investigated. As can be seen from Fig. 2, passing the analyte solution at higher flow rates through the column reduces the contact time between the lead complex and surfactant-coated alumina and reduces the recovery of the lead from the column.

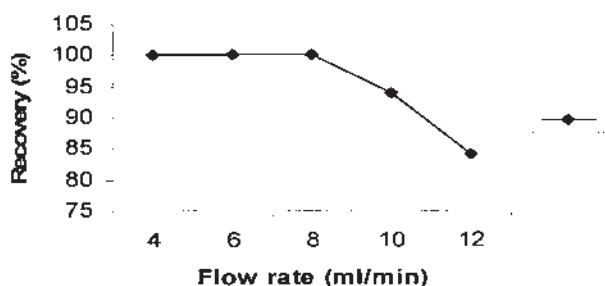


Fig. 2. Effect of the flow rate of the sample on the pre-concentration efficiency.

Effect of the flow rate of the acid solution

The effect of the flow rate of nitric acid used for the desorption of the lead complex from the column was investigated. The obtained results are shown in Fig. 3, from which it can be seen that at flow rates above 1.5 mL/min, the desorption of lead from the column was incomplete.

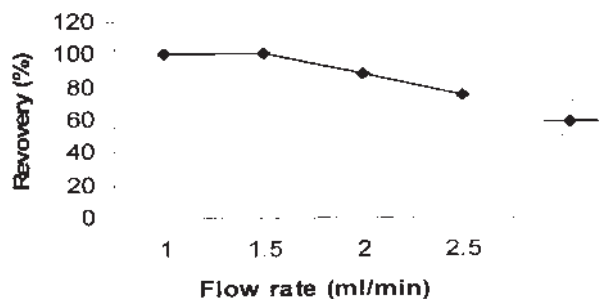


Fig. 3. Effect of flow rate of nitric acid on the desorption of lead.

Effect of diverse ions

The effect of some ions which naturally exist in water resources on the sensitivity of determination of lead by the proposed method was also investigated.

TABLE II. Effects of different ions on the pre-concentration efficiency

Ion	Mole ratio	Recovery/%	Ion	Mole ratio	Recovery/%
Ca ⁺⁺	15	97.6	Cl ⁻	15	96.1
Mg ⁺⁺	15	98.2	NO ₃ ⁻	15	98.7
Fe ⁺⁺	15	97.5	SO ₄ ⁻	15	96.2
Ni ⁺⁺	10	96.7	HCO ₃ ⁻	15	97.8

TABLE II. Continued

Ion	Mole ratio	Recovery/%	Ion	Mole ratio	Recovery/%
Mn ⁺⁺	10	97.8	CO ₃ ⁻⁻	15	96.0
Cr ⁺⁺	10	96.8	F ⁻	10	96.3
Na ⁺	15	97.0	CrO ₄ ⁻⁻	10	95.9
Zn ⁺⁺	10	96.3	NO ₂ ⁻	10	97.2

100 mL of a synthetic water containing a lead concentration of 30 ng/mL at pH 3 in the presence of each diverse ion was pre-concentrated according to the proposed method under the optimized conditions. The recovery of lead was calculated for each solution. The results are summarized in Table II and no interference effect was observed with the different ions.

Analysis of real samples

The method was applied for the determination of lead in natural waters, including river water, tap water and ground water. The sensitivity of the method was evaluated by spiking lead into the sample. The results are shown in Table III. The recovery of spiked samples showed that the proposed method is sensitive and reliable for the determination of trace amounts of lead in water resources.

TABLE III. Determination of lead in natural waters

Sample	Added µg	Found µg	Recovery/%
River water	0	300	97.4
	200	487	
Tap water	0	3.6	96.5
	5	8.3	
Ground water	0	9.8	97.9
	10	19.4	

(Sample volume = 200 mL, pH 3, final volume 5 mL)

TABLE IV. Lead concentrations in Zayandeh-Rud and Bazoft Rivers, µg

Source	Site 1	Site 2	Site 3	Site 4
Zayandeh-Rud	320±3	438±5	590±5	694±6
Bazoft	74±3	102±5	83±3	98±3

The method was also applied for a comparison of the lead concentrations in two rivers: 1) Bazoft, and 2) Zayandeh-Rud. The river Zayandeh-Rud passes through highly industrialized and agricultural areas, while the river Bazoft flows through a non-industrialized area with no significant agricultural activities. The results of the analyses are shown in Table IV. It can be seen that the proposed procedure is a method which enables the sensitive determination of lead over a wide range. The results clearly show that industrial and agricultural wastes discharge a considerable amount of lead into the water resources.

ИЗВОД

ОДРЕЂИВАЊЕ ОЛОВА ИЗ ВОДЕ ИМОБИЛИСАНОГ НА
МОДИФИКОВАНОМ АЛУМИНИЈУМОКСИДУ ПОСЛЕ КОНЦЕНТРИСАЊА
СА АМОНИЈУМ-ПИРОЛИДИНДИТИОКАРБАМАТОМ МЕТОДОМ АТОМСКЕ
АПСОРПЦИОНЕ СПЕКТРОМЕТРИЈЕ

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Развијен је брз, једноставан и осетљив поступак за пре-концентрисање и одређивање олова у траговима у води, заснована на екстракцији модификованом чврстом фазом. Олово се преводи у комплекс у реакцији са амонијум-пиридиндитиокарбаматом (APDC) и комплекс хвата у колони са алуминијумоксидом прекривеним површински активном супстанцом. Испитивани су и оптимизовани параметри који утичу на колекциону ефикасност и брзину десорпције комплекса олова из колоне. На оптимизованим условима колекциона ефикасност за олово је била изванредна. Добијени резултати показали су могућности и поузданост методе за анализу олова у траговима. Предложени поступак пре-концентрисања омогућава примену конвенционалне пламене атомске апсорпционе спектрометрије (FAAS) за осетљиво одређивање трагова олова у води, односно различитим водним ресурсима.

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