Talanta 84 (2011) 212–215

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Separation and preconcentration of Pb(II) using ionic liquid-modified silica and its determination by flame atomic absorption spectrometry

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ARTICLE INFO

Article history:
Received 2 September 2010
Received in revised form
31 December 2010
Accepted 7 January 2011
Available online 15 January 2011

Keywords:
Ionic liquid
Lead
Solid phase extraction
Silica
Flame AAS

ABSTRACT

A new method based on microcolumn packed with ionic liquid-modified silica combined with flame atomic absorption spectrometry has been developed for the determination of lead in environmental samples. Several factors influencing the preconcentration efficiency of lead and its subsequent determination, such as pH of the sample, flow rate, mass of ionic liquid, and interfering effect, have been investigated. Lead could be quantitatively retained by ionic liquid-modified silica in the pH range of 5–7, and then eluted completely with 3.0 mL 1.0 mol L^{-1} HCl. The detection limit of this method for lead was 0.7 μg L^{-1} with preconcentration factor of 185, and the relative standard deviation (RSD) was 4.2% at 0.1 μg mL^{-1} Pb(II). This method has been applied for the determination of trace amount of lead in NIST standard reference material 2709 (San Joaquin Soil) and river water samples with satisfactory results.

1. Introduction

Lead is a toxic metal, which accumulates in the vital organs of human and animals. Its cumulative poisoning effects are serious hematological damage, brain damage, anemia and kidney malfunctioning. In natural water its typical concentration lies between 2 and 10 ng mL^{-1}, whereas the upper limit recommended by World Health Organization is less than 10 ng mL^{-1} [1]. Thus, there is a great interest concerning the implementation of a reliable preconcentration system for lead(II) for analytical determinations.

Flame atomic absorption spectrometry (FAAS) has been widely used for the determination of trace quantities of Pb(II) because of the low costs, operational facility and high sample throughput. However, the direct determination of Pb(II) at trace level by FAAS is limited not only by insufficient sensitivity, but also by matrix interference. The most effective way to avoid these problems is to perform appropriate sample pretreatment, aimed at lowering the limit of detection, by both removal of interferences and increasing the concentration of the analyte. Various techniques for Pb(II) separation and preconcentration have been proposed, such as coprecipitation [2,3], liquid–liquid extraction [4,5], cloud point extraction [6–8], solid-phase extraction [9–13] and liquid phase microextraction [14,15]. Recently, solid phase extraction (SPE) have been extensively used for separation and determination of trace elements because this approach offers a number of important benefits, such as reducing of disposal costs, achievement of high recoveries and the sorbent easy to recover. SPE also offers broader range of applications than liquid–liquid extraction due to the large choice of sorbent.

Room temperature ionic liquid (IL) is a kind of burgeoning green solvent, and has aroused increasing interest for their promising role as alternative media in synthesis, separation, and electrochemistry applications as a result of its unique chemical and physical properties [16–18]. Its non-inflammability and non-volatility provided advantages for using it as a replacement to volatile organic compounds in solvent extraction processes [19,20]. On the analytical chemistry applications of supported ionic liquid phase, ionic liquid-modified silica particles were used as HPLC stationary phase to separate some familiar organic compounds [21] and as sorbent for solid phase extraction of organic compounds [22]. Ionic liquid impregnated resins were prepared for solid–liquid extraction of rare earth elements and noble metal ion [23]. However, there is no report for the application of supported ionic liquid phase for the preconcentration of trace metal ions.

In this work, ionic liquid-modified silica (IL-silica) was synthesized and characterized by FTIR. The potential of ionic liquid-modified silica for the preconcentration of trace Pb(II) was assessed using column method. The optimum conditions for sorption and enrichment of Pb(II) were studied. In addition, the possible

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0039-9140/$ – see front matter © 2011 Published by Elsevier B.V.
doi:10.1016/j.talanta.2011.01.006

use of the developed method for analyzing Pb(II) in synthetic and soil sample and water sample solutions were explored.

2. Experimental

2.1. Instruments

An Analyst 700 PerkinElmer flame atomic absorption spectrometer furnished with a lead hollow cathode lamp, operated with 10 mA, and with air–acetylene flame was used. The instrument was set at a wavelength of 217.0 nm and slit width of 0.7 nm. FTIR spectra of ionic liquid modified silica were recorded with a PerkinElmer Spectrum BX Fourier Transform IR spectrometer using KBr discs in the range of 4000–700 cm^{-1}. ^1H NMR spectra were measured on a Brunker 400 MHz spectrometer. The reported chemical shifts are against TMS. Microanalyses (C, H, and N) were carried out with CHNS-932 (LECO) elemental analyzer. pH measurements were made on a Lab WTW model digital pH-meter. A peristaltic pump was used in the separation and preconcentration process. For solid phase experiments a Varian cartridge (plastic container, 1.0 cm × 10.0 cm) equipped with 20 mm polypropylene frits was used. A PTFE tubing with i.d. of 0.5 mm was used for all connections.

2.2. Reagents and solutions

The stock metal ion solutions were prepared by dissolving analytical reagent grade metal nitrates, chlorides or sulfates in doubly deionized water. Stock standard solution (1000 $mg\,L^{-1}$) of Pb(II) was obtained from Certified Reference Material (Certificate #883-02) (Inorganic Ventures, USA). Working standard solutions were prepared by appropriate dilution of the stock standard solutions. Silica gel (Aldrich 70–270 mesh, 60 Å and surface area >500 m^2/g) was activated by treatment with HCl (5 $mol\,L^{-1}$) and dried in vacuum at 120 °C. Potassium bromide (Merck, for spectroscopy) was used for the preparation of pressed discs for the Fourier transform infrared (FTIR) spectrometer. 1-Methylimidazole and n-bromobutane were purchased from Aldrich. All other reagents and solvents used were of analytical reagent grade. The water used throughout the study has been deionized by means of a Millipore Milli-Q system. For pH adjustment, buffer solutions were used.

2.3. Synthesis of 1-methyl-3-butyl-imidazolium bromide

1-Methyl-3-butyl-imidazolium bromide was synthesized according to the literature [24], and its chemical structure was given in Fig. 1. A mixture of 21.48 mL (0.2 mol) of 1-bromobutane, 15.84 mL (0.2 mol) of 1-methylimidazole and 10 mL of toluene was refluxed for 12 h. After cooling to room temperature the yellow colored lower phase, which contains the product, was separated from the upper phase, and washed a few more time with 5 mL toluene. After the washing step the raw product was dissolved in CH_2Cl_2 and filtered. Following, the filtrate was evaporated to dryness in a rotary evaporator and a yellowish viscous liquid was obtained at a yield of 93% (40.7 g).

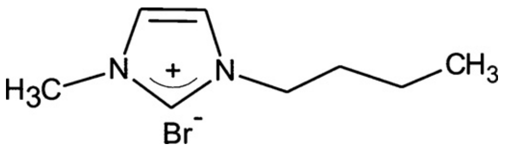

Fig. 1. The structure of 1-methyl-3-butyl-imidazolium bromide.

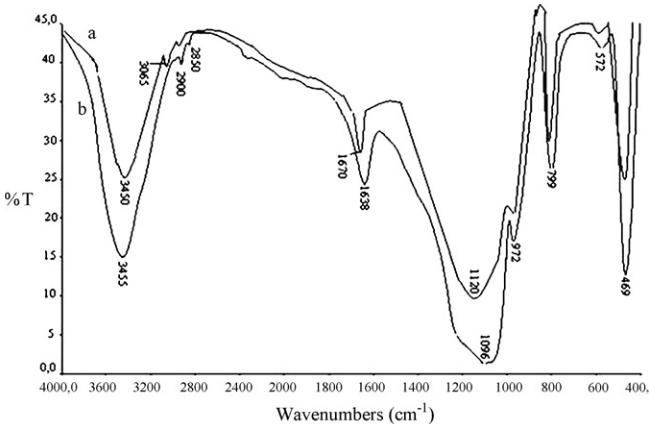

Fig. 2. FTIR spectra of ionic liquid-modified silica (a) and silica (b).

2.4. Preparation of ionic liquid-modified silica

IL-silica was prepared as described previously [25]. A typical example is as follows: to a stirred solution of 1-methyl-3-butyl-imidazolium bromide (0.25 g) in acetone, 1.0 g of silica powder was added. After stirring for 2.5 h, the volatile components of the mixture were evaporated by water bath. Then the resulting material was washed thoroughly with methylene chloride and distilled water, and dried under vacuum at 150 °C for 3 h, leading to a white powder. The total weight of the IL-silica is 1.18 g, so 0.18 g of ionic liquid was grafted on the surface of silica.

Fig. 2 shows the FTIR spectra of ionic liquid-modified silica (a) and silica gel before modification (b). It was seen that a new absorption peak at the position of about 1670 cm^{-1} appeared after silica gel being treated with IL-silica. This absorption peak could be attributed to the C–C vibration of imidazole ring. The peak at the position of 3065 cm^{-1} could be attributed to C–H vibration of aromatic cycle. These peaks indicated that ionic liquid has been grafted on the surface of silica.

2.5. General procedure

100 mg of IL-silica was introduced into a polyethylene column. Before use, 0.1 $mol\,L^{-1}$ HCl solution and methanol:water (10:90) and doubly distilled water were passed through the column to clean and condition it. Then, the column was conditioned to the desired pH by passing 10 mL of the corresponding buffer solution through the column. 100 mL of sample solution containing Pb(II) was taken and the pH adjusted to 6. It was then passed through the conditioned column at a flow rate of 1.5 $mL\,min^{-1}$ by means of a peristaltic pump. The metal ions were stripped from the column using 1 $mol\,L^{-1}$ HCl and determined by FAAS. A blank solution was also run under the same analytical conditions without adding any Pb(II).

2.6. Sample preparation

0.200 g of A NIST (National Institute of Standards and Technology) soil reference material (SRM 2709, San Joaquin Soil) was treated with 15 mL of 48% hydrofluoric acid in a PTFE beaker, and the mixture was allowed to rest for about 1 h at room temperature. After heating in a sand bath (150 °C) to dryness, an aliquot (15 mL) of the mixture containing concentrated nitric and perchloric acid at a ratio of 3:1 (v:v) was added and heated again to dryness. The residue was then treated with 2.5 mL of concentrated hydrochloric acid, water (2 mL) and four drops of 30% hydrogen peroxide under gentle warming to achieve complete solubility [26]. Then, the volume

Table 1
Eluent data (%) for Pb(II) sorbed on IL-silica.

Eluent	0.5 mol L^{-1}	1.0 mol L^{-1}	2.0 mol L^{-1}	3.0 mol L^{-1}	4.0 mol L^{-1}
HCl	75.0	96.2	96.0	96.5	96.2
HNO_3	16.5	25.0	32.6	45.6	50.1

Eluent volume: 3.0 mL.

was made up to 50 mL with distilled water, and this solution was used in the preconcentration step by applying the column concentration procedure given in Section 2. The analysis of SRM samples was repeated as triplicate. River water samples were taken from Meriç River, in Turkey, after allowing the water to flow for 5 min. All water samples were filtered through a 0.45 μm membrane filter and analyzed as soon as possible.

3. Results and discussion

3.1. Effect of pH

In order to evaluate the effect of pH on the preconcentration of Pb(II) on IL-silica, the pH values of sample solutions were adjusted to a range of 3–10. The results were shown in Fig. 3. The results obtained indicated that the ions could be retained quantitatively by silica modified ionic liquid at the pH range of 5–7. The decrease in signal at pH > 7 is probably due to the precipitation of ions as their related hydroxide and at pH < 7 may be due to competition of hydronium ion toward complexation with ionic liquid, which lead to the decrease in the recovery. To achieve high efficiency and good selectivity, a pH of 6 was selected for subsequent work.

3.2. Effect of flow rate

The dependence of metal ion sorption at various flow rates was studied at optimum pH. The sorption was highest and formed a plateau at the flow rates of 1.5; 1.0 and 0.5 mL min^{-1} for sorption ad stripping of Pb(II). A slight decrease at 2.0 mL min^{-1} and a gradual decrease in sorption above this flow rate were observed. The flow rate of 1.5 mL min^{-1} was preferred to subsequent work.

3.3. Effect of ionic liquid mass

Effect of the quantity of ionic liquid as chelating agent was also studied. In order to determine this, quantities of ionic liquid on the retention were examined from 0 to 300 mg. Without ionic liquid the preconcentration yields of Pb(II) ions were 15–20%. By the addition of ionic liquid up to 200 mg recovery of Pb(II) ions was quantitative and further addition has not significant change on recovery of ions. 250 mg of ionic liquid was recommended for subsequent works.

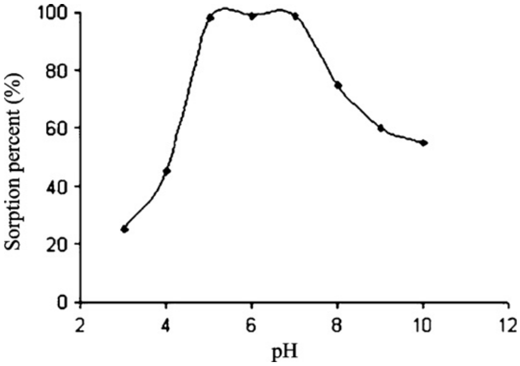

Fig. 3. Effect of pH on the sorption of Pb(II) on IL-silica. Pb(II): 100 mL, 1 μg mL^{-1}; flow rate: 1.5 mL min^{-1}.

3.4. Effect of eluent type and volume

As shown in Fig. 3, the sorption of Pb(II) is negligible at low pH. For this reason, various concentrations HCl and HNO_3 were studied for the elution of retained Pb(II) from the column at the flow rate of 1.5 mL min^{-1}. The results obtained were given in Table 1. As can be seen, quantitative recovery (>95%) could not be achieved when HNO_3 was used as eluent, 1.0 mol L^{-1} HCl was sufficient for complete elution of Pb(II).

The effect of eluent volume on the recovery of Pb(II) was also studied by keeping the HCl concentration of 1.0 mol L^{-1}. It was found that quantitative recovery (>95%) could be obtained with 3.0 mL 1.0 mol L^{-1} HCl. Therefore, 3.0 mL eluent was used in the following experiments.

3.5. Effect of sample volume

Due to the low concentrations of trace metals in real samples, by using samples with large volumes, the trace metals in these volumes should be taken into smaller volumes for high preconcentration factor. Hence, the maximum sample volume was optimized by the investigation of the recovery of Pb(II) ion in various synthetic sample volumes in the range of 250–2000 mL containing 0.5 μg of Pb. The recovery of Pb(II) ion from different volumes of aqueous solutions were shown in Fig. 4. The recovery was found to be stable until 1500 mL and was chosen as the largest sample volume to work. The preconcentration factor was found as 185 for Pb(II) ion.

3.6. Column reuse

The stability and potential regeneration of the column were investigated. The column can be reused after regenerated with 10 mL 2.0 mol L^{-1} and 20 mL double distilled water, respectively, and stable up to at least 10 sorption–elution cycles without significant decrease in the recovery of Pb(II).

3.7. Effect of interferences

The effects of common coexisting ions on the sorption of Pb(II) on IL-silica were investigated. In these experiments, the solutions of 1 μg mL^{-1} Pb containing the interfering ions were treated according to the recommended procedure. The tolerance limits of the coexisting ions, defined as the largest amount making the recovery

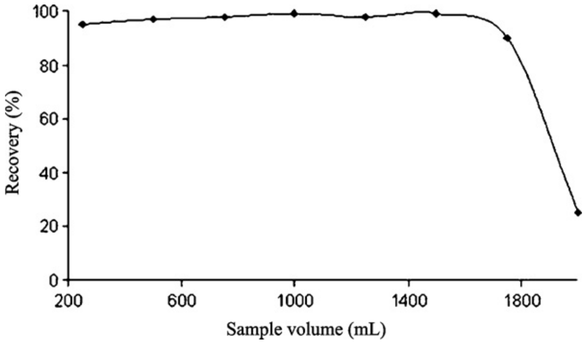

Fig. 4. Effect of sample volume on Pb(II) ion recovery.

Table 2
Tolerance limits for coexisting ions fort the sorption of Pb(II).

Coexisting	Tolerance limits of ions (μg mL^{-1})
Ca^{2+}, Mg^{2+}	2500
Zn^{2+}, Cd^{2+}, Ni^{2+}, Mn^{2+}, Cu^{2+}	400
Al^{3+}, Fe^{2+}	100
$SO_4{}^{2-}$, Cl^-, $NO_3{}^-$	2500
$PO_4{}^{3-}$	750

Table 3
Comparison of the published methods with the proposed method in this work.

Sorbent	Preconcentration factor	Detection limit (μg L^{-1})	Reference
IL-silica gel	185	0.7	This study
Thioureasulfonamide/ polymeric resin	60	0.15	[27]
Zr phosphate/silica gel	30	6.1	[28]
o-Dihydroxybenzene/ silica gel	250	4	[29]
Thioacetamide/silica gel	300		[30]
PAN/silica gel	100	0.13	[31]
Thiosalicylic acid/silica gel	150	3.7	[32]
Aspergillus niger/silica gel	50	5.2	[33]
5-Mercapto-1-methytetrazole/ silica gel	200	0.46	[34]

of Pb less than 95%, were given in Table 2. It can be seen that the presence of major cations and anions has no significant influence on the preconcentration of Pb(II) ion under the selected conditions.

3.8. Detection limits and precision

Under the optimum experimental conditions, the calibration curve for Pb was linear in the concentration range from 0.1 to 0.75 μg mL^{-1} with a correlation coefficient of 0.9965. The detection limit of this method, evaluated as the concentration corresponding to three times the standard deviation of ten replicate measurements of blank solution the precocentration method, was found to be 0.7 μg L^{-1} for Pb. The precision of this method (RSD), examined by ten replicate measurements of 0.1 μg mL^{-1} of Pb solution, was found to be 4.2%.

In Table 3, the characteristic data of the present method was compared with those reported in literatures. The preconcentration factor and the detection limit obtained by the proposed method are comparable to those reported methods.

Table 4
Determination of Pb(II) (μg mL^{-1}) in water samples.[a]

Sample	Added	Found[b]	Recovery (%)
River water	0	0.15 ± 0.12	–
	5	5.10 ± 0.17	99
	10	10.09 ± 0.22	98
	20	20.17 ± 0.25	100

[a] Sample volume, 100 mL.
[b] Mean ± SD, $n = 5$.

3.9. Analytical application

In order to establish the validity of the proposed procedure, the method has been applied to the determination of Pb in the sediment certified reference materials (SRM 2709, San Joaquin Soil). The analytical value (18.5 ± 0.2) is in good agreement with the certified value (18.9 ±0.5 μg g^{-1}).

The proposed method was applied to the determination of Pb in river water sample. In addition, the recovery experiments of different amounts of Pb were carried out; and the results were shown in Table 4. The results indicated that the recoveries were reasonable for trace analysis, in a range of 98–100%.

4. Conclusions

It can be concluded from the results that ionic liquid modified silica is an effective sorbent for Pb and can be used for its preconcentration from aqueous solutions. The proposed method based on preconcentration with IL-silica microcolumn and determinations in various samples. The precision and accuracy were satisfactory. The method can be applied to the separation, preconcentration, and determination of Pb in real samples.

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