Article

A New Chelating Resin Containing Indole-Methionine Composite: Synthesis, Characterization and Determination of Lead and Silver after Preconcentration in Biological and Environmental Samples

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O esqueleto indólico modificado com L-metionina foi imobilizado em uma matriz polimérica de poliestireno-divinilbenzeno e mostrou ser seletivo para a determinação dos íons Pb(II) em pH 8,0 e Ag(I) em pH 6,5. A capacidade máxima de adsorção da resina modificada é de 0,35 mmol g^{-1} para Pb(II) em pH 8,0 e de 1,5 mmol g^{-1} para Ag(I) em pH 6,5. A resina final e seus precursores foram caracterizados por diferentes técnicas instrumentais. O limite de detecção estabelecido (calculado como 3 vezes o desvio padrão do branco) foi de 30 ng mL^{-1} para o Pb(II) e de 38 ng mL^{-1} para Ag(I). Os percentuais de recuperação foram de 97,4 ± 2,6% para o Pb(II) ao nível da confiança de 98% e de 98,2 ± 3,4% para Ag(I) ao nível da confiança de 97%. O procedimento desenvolvido foi aplicado com sucesso para a preconcentração de Pb(II) e Ag(I) em diferentes amostras ambientais e biológicas. A quantificação de Pb(II) foi efetuada por espectrometria de absorção atômica com chama (FAAS) enquanto que para Ag(I) foi empregado um contador de cintilação no qual um cristal de iodeto de sódio dopado com tálio [NaI (Tl)] foi usado como detector.

Derivatized L-methionine having indole backbone has been anchored on polystyrene-divinylbenzene matrix and has been found to have selective binding ability for Pb(II) and Ag(I) ions at pH 8.0 and 6.5, respectively. Maximum capacity for Pb(II) at pH 8.0 is 0.35 mmol g^{-1} and for Ag(I) at pH 6.5 is 1.5 mmol g^{-1}. The final resin and its precursors are fully characterized by different instrumental techniques. Detection limits (3 × standard deviation of the blank signal) were 30 ng mL^{-1} for Pb(II) and 38 ng mL^{-1} for Ag(I). Recoveries were found to be 97.4 ± 2.6% for Pb(II) at 98% confidence level and 98.2 ± 3.4% for Ag(I) at 97% confidence level. The developed procedure has been successfully applied for preconcentration of Pb(II) and Ag(I) in different environmental and biological samples. The concentration of Pb(II) was determined by flame atomic absorption spectrometry (FAAS) and that of Ag(I) ion by using a scintillation counter equipped with a well type NaI (Tl) crystal detector.

Keywords: derivatized L-methionine, indole, chelating resin, polystyrene, lead, silver, FAAS, scintillation detector, application

Introduction

Heavy metal pollution of the environment, particularly by lead has received a considerable attention as it leads to many fatal diseases including dysfunction of renal blood and neurological systems.[1] Again, Pb(II) easily deposits in brain, kidney, reproductive and nervous systems. Acute lead poisoning can result severe anemia, colic shock and irreversible brain damage. Several works on the solid phase extraction of lead by incorporating different chelating groups on the polymer backbone has been reported. Among them, 2-aminothiophenyl-S-acetic acid,[2] dithiooxamide,[3] oxine,[4] resacetophenone,[5] o-aminophenol,[6] o-aminobenzoic acid,[7] zirconium phosphate,[8] pyrocatechol violet[9], quinalizarin[10] and imidazolylazo[11] anchored/supported polymers are noteworthy. Recovery of silver ion from photographic industrial wastes, selective removal of silver ion from medicinal samples and its ores have immense importance. Selective removal and preconcentration of silver from different samples were investigated by different workers.[12,13] Several analytical methods like

spectrophotometry, polarography, flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma optical emission spectrometry (ICP OES), inductively coupled plasma mass spectrometry (ICP-MS) are available for quantitative estimation of lead with different sensitivities. Different techniques used for the selective separation of lead include liquid-liquid extraction, solid-phase extraction, liquid membrane and cloud point extraction, etc.

Our research goal is to synthesize different potential organic ligands which have specific metal ion binding affinity. The ligand then anchored to polymeric matrix to make a suitable platform through which the solution containing metal ions can pass through. Recently derivatized amino acids having a tripodal ligand motif have attracted immense interest as it is used in the development of chirality switch,[14-16] to modeling the structure and function of zinc enzymes like carboxypeptidase,[17] superoxide dismutase,[18] alkaline phosphatase,[19] L-fuculose-1-phosphate aldolase.[20] Because of its rich chemistry and the wide area that remains uncovered, we are presently working on the synthesis of different derivatized chiral amino acids, their structural characterization, metal ion uptake properties and applications of these new series of ligands.

Herein we report synthesis of indole containing derivatized L-methionine which has been incorporated to the polymeric framework to have an efficient trace level separation of lead and silver. It is found that incorporation of indole moiety into L-methionine part increases the absorption capacity of the soft metal ions like Pb(II) and Ag(I) over simply using L-methionine because indole contains a soft nitrogen donor site. Concentrations of lead and silver have been determined by FAAS and a scintillation counter equipped with a well type NaI (Tl) crystal detector, respectively. Because of high sensitivity, rapidity, operational simplicity, low operational cost of measurements over the other standard methods, estimation of silver was monitored radiometrically using [110mAg].

Experimental

Apparatus

A VARIAN (Spectra AA 55, Mulgrave, Australia) flame atomic absorption spectrometer was used. All measurements were performed using integrated absorbance (peak area). Hollow cathode lamp for Pb was operated at 10.0 mA and the wavelength 217 nm was selected using a spectral resolution of 1 nm. Air and acetylene gases have flow rates 3.5 and 1.5 L min^{-1}, respectively. The radioactivity was measured by a scintillation counter equipped with a well type NaI (Tl)

crystal detector (Nucleonix, India). IR spectra were recorded on a JASCO FTIR spectrophotometer (model FT-IR-H20, U.K.). Measurements of pH were performed with Systronics digital pHmeter (model 335, Systronics, India). UV-Vis spectra were obtained from a Shimadzu spectrophotometer (model UV2101PC, Japan). A Kratos MALDI-TOF 1 mass spectrometer using the matrix α-ACHC and an extraction voltage of 4 kV was used for mass spectrometry (Japan). ^{1}H NMR and ^{13}C NMR spectra were recorded on a 200 and 50 MHz Varian Gemini 200 and optical rotations were determined on a Perkin-Elmer model 341 polarimeter at 589 nm (U.S.A.). Thermogravimetric analysis was done on a Perkin Elmer TG/DTA Lab System l (Technology by SII). A domestic Samsung microwave oven (model CE2933) with a 2450 MHz frequency magnetron and 900 W maximum applied power and a polytetrafluoroethylene (PTFE) reactor (115 mL internal volume, 1 cm cell wall thickness and hermetic screw caps) were used for sample digestion.

Reagents and solutions

Stock solution of Pb(II) (1000 mg L^{-1} in 3% v/v HNO$_3$) was obtained from SOLUTIONS Plus Inc**.** (Missouri, USA) which was tested *versus* NIST SRM # 3108a (Gaithersburg, MD, USA). Then the solution was diluted 20 times for our practical work. All the working solutions were prepared by appropriate dilution with deionised water. ^{110m}Ag was supplied by Bhaba Atomic Research Centre, Trombay, and used as tracers. All other chemicals were reagent grade. Glass apparatus were soaked in 4.0 mol L^{-1} HNO$_3$ overnight and cleaned with double distilled water. Certified reference materials analyzed were: standard reference material (SRM) 1573 tomato leaves from National Bureau of Standards; pond sediment (NIES 2, Tsukuba-city, Japan); and igneous rock (JR-1) from National Institute for Environmental Studies. Different buffer solutions were used for adjusting the pH and prepared according to literature procedure, *i.e.* citrate buffer (pH 3.0-6.0), phosphate buffer (pH 7.0-8.0), boric acid-borax buffer (pH 9.0), glycine-NaOH buffer (pH 10.0) solutions.

Preparation of the resin

Synthesis of N-(3-indolylmethyl) L-methionine (IM)

Method 1:[21] To a solution of 1.9 g of L-methionine (13.0 mmol) dissolved in 50 mL of 4.0 mol L^{-1} NaOH, 2.0 g of 3-indolecarboxyaldehyde (13.78 mmol, 1 equiv.) was added under stirring over a period of about 1 h. The stirring was continued for additional 2 h followed by addition of 0.5 g NaBH$_4$ in small portions. Stirring was continued till foaming ceases. Then the pH of the solution was adjusted to

3.0 with 6.0 mol L^{-1} HCl. Some suspended particulates were separated by filtration. The volume of the filtrate reduced to 20 mL by *vacuum* distillation and kept overnight. The orange crystalline product was isolated and dried. Yield was 55%; mp 112 °C.

Method 2:[22] To a 100 mL dichloromethane solution containing L-methionine methyl ester hydrochloride (1.0 g, 5.0 mmol), 1 equiv. of 3-indolecarboxyaldehyde (0.73 g, 5 mmol) was added. To this mixture, 20 mL triethylamine and 6.0 g anhydrous magnesium sulphate were added under stirring condition for 1 h at room temperature. Filtration, removal of solvent, water-ether partitioning and finally removal of ether yielded 70% of the Schiff base ester. A mass of 1.0 g of this ester was dissolved in THF and subjected to hydrolysis with 0.5 mol L^{-1} (20 mL) aqueous LiOH at room temperature for 4 h. The solvent was removed under reduced pressure and subjected to water-dichloromethane partitioning to remove any unreacted ester or other impurities. To the aqueous part, 0.4 g NaBH$_4$ in small portions was added under stirring condition till foaming ceases. The pH of the aqueous part was maintained at 7.0-7.5 with diluted HCl solution and extracted with ethyl acetate. Traces of water were removed by anhydrous Na$_2$CO$_3$. Solvent was removed under reduced pressure and the desired compound was crystallized from methanol. Yield was 65%; ^{1}H NMR (200 MHz, CDCl$_3$, peaks of the spectrum are relatively broad) δ 1.85 (2H, m, CH$_2$), 2.12 (3H, s, CH$_3$), 2.42 (2H, m, CH$_2$), 3.25 (1H, s, J 7 Hz, CH), 3.62 (2H, m, CH$_2$), 7.63 (1H, d), 7.15 (1H, t), 7.01 (1H, t), 7.35 (1H, d); ^{13}CNMR (50 MHz, CDCl$_3$) δ 15.95, 26.82, 34.05, 56.16, 64.18, 122.56, 130.15, 125.5, 132.3, 133; MS (*m/z*) 279.63 (M+H)$^+$. Calculated for C$_{14}$H$_{18}$N$_2$O$_2$S: C, 60.41; H, 6.52; N, 10.06. Found: C, 60.21; H, 6.62; N, 10.16%. FT-IR ν_{max}/ cm^{-1} 1622 (CO), 3393 (OH). UV-Vis λ_{max}/nm (acetonitrile) 392 (ϵ/dm^3 mol^{-1}cm^{-1} 87 × 10^3), 372 (ϵ/dm^3 mol^{-1}cm^{-1} 83 × 10^3); 354 (ϵ/dm^3 mol^{-1}cm^{-1} 78 × 10^3); 334 (ϵ/dm^3 mol^{-1}cm^{-1} 37 × 10^3); [α]^{25}$_D$ = +71°.

N-(3-Indolylmethyl) L-methionine (IM) 2.0 g is mixed with commercially available chloromethylated polystyrene-divinylbenzene (2%) (2 g) and NaHCO$_3$ (4 g) and refluxed for 8 h in dehydrated alcohol. The color of the insoluble desired resin becomes brown. The resin is filtered through sintered glass Gooch crucible (G 4), washed with double distilled water to free from alkali and dried under vacuum. The bead size of the resin is 120-140 mesh.

Stability of the resin

A mass of 250 mg of resin was shaken with 100 mL of acid and alkaline solutions (separately) of different concentrations for 7 days. Then filtered and washed with double distilled water to free from acid or alkali and dried under vacuum. The metal ion exchange capacity was measured. To study the effect of radiation on the resin matrix, the resin was exposed to γ-radiation for 48 h. As, measurement of water regain of the resin requires elevated temperature, so we have to be sure that resin remains unaltered at this elevated temperature (100 °C). The experiment was made thermogravimetrically (TGA / DTG).

Water regain

Air dried resin in basic form was stirred in double distilled water for 48 h, then filtered off by suction, weighed, dried at 100 °C for 48 h and reweighed.

Hydrogen ion capacity

A mass of 0.5 g resin was first converted into its acidic form by treating with 6.0 mol L^{-1} HCl. The resin was first filtered off, washed with water and then dried at 100 °C for 6 h to remove any free HCl. The acidic hydrogen content of the resin was then determined by back titration with a standard alkali solution. The acidic form of the resin was equilibrated with 20 mL 0.1 mol L^{-1} NaOH solution for 6 h at room temperature under stirring condition. Then, the solution was filtered under suction, washed with deionised water and the excess alkali was titrated with 0.1 mol L^{-1} standard HCl solution.

Metal ion capacity as a function of pH

A batch technique was used by adding metal ion in excess to the resin. Capacities were determined in the pH range 3.0-10.0. To a glass stopper centrifuge tube (diameter 2.0 cm) containing 100 mg of the dry resin in basic form, 10 mL of the desired pH solution was added. After equilibration of this mixture, 1 mL of 0.2 mmol L^{-1} metal ion solution was added and the mixture was shaken for 24 h. The pH of the equilibrating solution was adjusted by appropriate buffer solution. After 24 h, the solutions were filtered under suction, washed with double distilled water and the amount of lead in the filtrate was determined by FAAS using air-acetylene flame whereas the amount of sorbed silver ion on the resin was determined by the measurement of the γ-activity of equal portions of the solutions, before and after the sorption.

Desorption of metal ions

Resin thus obtained after uptaking of Pb(II) and Ag(I) in the above mentioned batch technique was shaken with

30 mL of different eluents (0.01 to 2 mol L⁻¹ HNO₃ and also with 5% m/v thiourea in 0.1 mol L⁻¹ HNO₃) for 6 h and filtered. The concentration of the metal ion in the filtrate was determined.

Equilibration rates

Equilibration rates for Pb(II) and Ag(I) were studied at pH 8.0 and 6.5 respectively. The time required for 50% uptake of the metal ion was determined.

Kinetic studies

The concentrations of Pb(II) and Ag(I) absorbed/adsorbed by the resin at the pH where maximum sorption takes place were monitored at different time intervals. From those data, rate constants were determined for the sorptions of Pb(II) and Ag(I) on the resin using batch mode.

Column operations

Air dried resin (1 g) was immersed in double distilled water and allowed to swell for 24 h. A glass column (130 mm × 10 mm) was packed with swollen beads to a bed volume of 2 mL. Sorption and desorption characteristics for Pb(II) and Ag(I) in the column were studied at a flow rate of 0.5 mL min⁻¹. Lead(II) and silver(I) sorption capacity for the non-functionalized chloromethylated resin was measured at pH 8.0 and 6.5 to ascertain that it has no sorption for Pb(II) and Ag(I).

Analytical procedure

Portions (100-150 mg) of the certified reference materials were treated in a hermetically sealed PTFE (115 mL) reactor in sequence (450 W, 3.0 min each) with 2 mL of hydrofluoric acid (HF), 4 mL of aqua regia and 3 mL of H_2O_2. The digested sample was boiled with saturated boric acid (8 mL) for 12 min in a water bath to remove excess HF. Road dust samples from different places on G. T. Road, Burdwan (West Bengal, India) were also digested adopting the same procedure. Surely, safety aspects must be fully considered when working with a microwave oven not designed for laboratorial use and the use of a properly fabricated oven is strongly recommended. Two geological samples, obtained from Geological Survey of India, Kolkata, were also digested. Photographic washings from industrial exhaust and Silverex ointment containing silver were brought into solution by the usual method.[23]

Results and Discussion

Synthesis and characterization of the resin

The resin was synthesized by coupling newly synthesized *N*-(3-indolyl) L-methionine (IM, II) with chloromethylated polystyrene-divinylbenzene (2%) as shown in Scheme 1. Elemental analysis, NMR, mass spectral data, FT-IR and UV-Vis spectra confirm the structure of *N*-(3-indolylmethyl) L-methionine (IM)
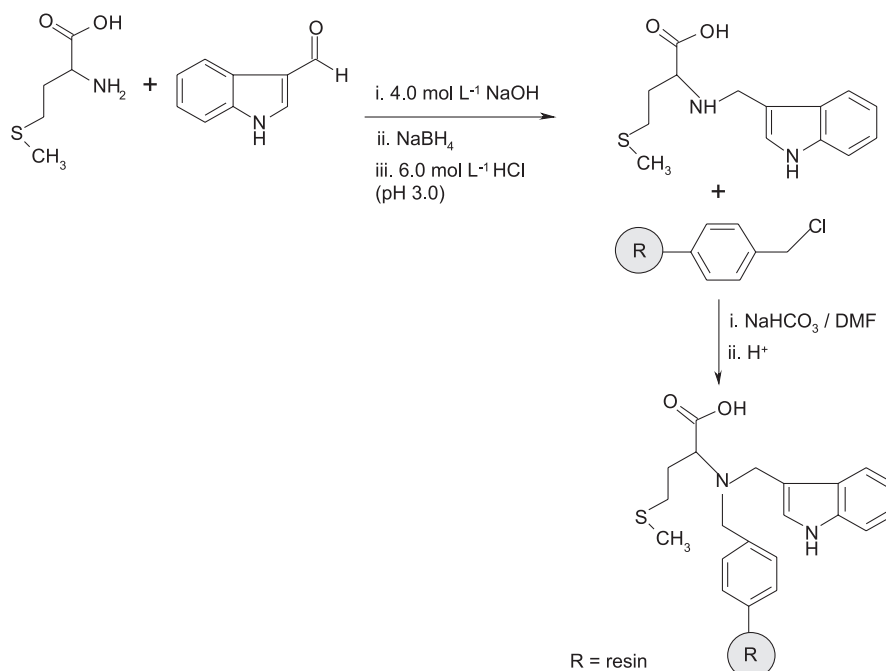
Scheme 1. Synthesis of the chelating resin containing *N*-methyl-3-indolyl L-methionine

whereas the FT-IR spectra of the final resin (S-1) shows all the characteristics stretching frequencies (v_{CO} 1602 cm^{-1}; v_{OH} 3426 cm^{-1} and fingerprint regions of methionine and indole *i.e.* 650-1200 cm^{-1}) present in compound (II), thereby indicating the incorporation of the IM moiety to the polymeric matrix.

The chemical stability of the resin in 0.01 to 6.0 mol L^{-1} HNO$_3$ and 0.1 to 6.0 mol L^{-1} NaOH was examined. No significant changes in the structure of the resin was observed as evident from comparison of FT-IR spectra as well as metal ion and hydrogen ion exchange capacities of the treated resin with the untreated one. Thus the resin is fairly stable in both acidic and alkaline conditions. Thermogravimetric analysis showed that the resin is fairly stable up to 130 °C (S-2). The time required for 50% uptake of the maximum capacity was found to be 28 and 32 min for Pb(II) and Ag(I) ions, respectively.

It is observed that the flow rate of the sample solution had an immense effect on the retention of metal ions on the resin. It was found that up to a flow rate of 5.0 mL min^{-1}, the sorption of Pb(II) is maximum, after that it decreases. The observed behavior for Ag(I) was similar. The water regain value for the resin is 12, which is satisfactory for column operation.

Sorption and desorption of metal ion

The hydrogen ion capacity of the resin was found to be 2.35 mmol g^{-1}. Maximum capacity for Pb(II) at pH 8.0 is 0.35 mmol g^{-1} and for Ag(I) at pH 6.5 is 1.5 mmol g^{-1}. The sorption capacity of the resin for Pb(II) and Ag(I) as a function of pH is shown in Figure 1. All the characteristics band of the IM resin undergo a red shift upon binding with Pb(II) and Ag(I) ions as evident from S-3 and S-4 respectively.
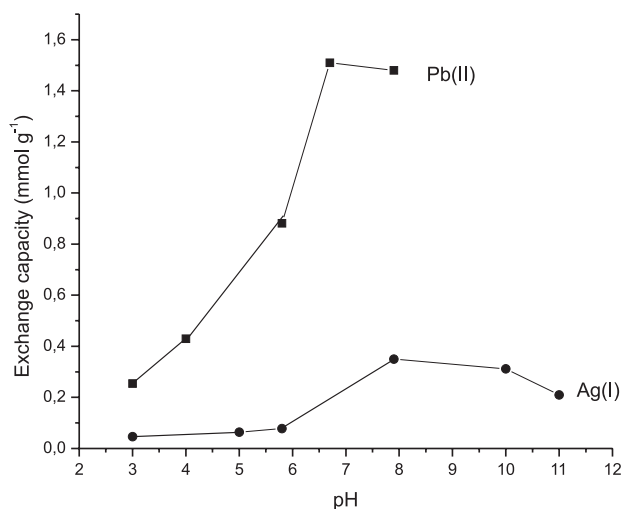

Figure 1. Sorption of Pb(II) and Ag(I) on the resin as a function of pH.

Kinetic parameters

The rate of exchange of metal ion by a chelating resin is controlled by a second order kinetic equation,[24] $\ln Z = 2kQ_0 (Q_0 - Q_\alpha)t / Q_\alpha$, where $Z = [Q_t (Q_0 - 2Q_\alpha) + Q_0 Q_\alpha] / Q_0 (Q_\alpha - Q_t)$ as developed by Turse and Rieman.[25] The rate constant k is calculated from the slope S of the equation: $S = 2kQ_0(Q_0 - Q_\alpha) / Q_\alpha$, where Q_t is the amount of metal ion (in mmol) exchanged at time t, Q_α is the maximum exchange capacity at equilibrium and Q_0 is the amount of chelating resin, in terms of milimoles of Na$^+$ exchanged after 24 h. Thus, a plot of ln Z *versus* t should be linear passing through zero for a second order exchange. We got the linear equations for Pb(II) as $\ln Z = 0.03607t + 0.364 \times 10^{-4}$ and for Ag(I) as $\ln Z = 0.03592t + 0.4704 \times 10^{-4}$ respectively. The values for rate constant (k) for the chelation of Pb(II) and Ag(I) by this new resin as obtained from the linearly fit second order plots are 1.134×10^{-3} and 1.31×10^{-2} respectively.

Effect of foreign ions

In column operation, the presence of macro amounts of diverse metal ions like alkaline and alkaline earth metal ions had no interferences. Amongst transition metal ions, Cu(II), Hg(II), and Cd(II) interfered, while others did not (Table 1).

Table 1. Tolerance limits of diverse ions

Diverse ions	Foreign ion to analyte ratio*	
	Pb(II)	Ag(I)
K$^+$, Na$^+$, Ca^{2+}, Mg^{2+}	5000	5000
Al^{3+}, Be^{2+}, Fe^{3+}, Cr^{3+}	1000	2000
Cu^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+}, Mn^{2+}	500	900
Hg^{2+}, Cd^{2+}	50	100
NO$_3^-$, SO$_4^{2-}$, Cl$^-$, Br$^-$, I$^-$,	5000	5000

* No interference observed.

Effect of eluent type and volume

In order to elute sorbed Pb(II) and Ag(I) from the resin, different eluting agents were tested as described in Table 2. It was observed that 5.0 mL of 5% m/v thiourea in 0.1 mol L^{-1} HNO$_3$ and 10.0 mL of 5% m/v thiourea in 0.1 mol L^{-1} HNO$_3$ can completely desorb Pb(II) and Ag(I) from the resin bed, respectively.

Effect of sample volume

In order to deal with real samples, the maximum applicable sample volume must be determined for the

Table 2. Percentual recoveries of Pb(II) and Ag(I) using different eluents (n = 4, mean ± standard deviation)

Eluent	Recovery % of Pb(II)	Recovery % of Ag(I)
0.01 mol L^{-1} HNO$_3$	60 ± 0.3	65 ± 0.5
0.1 mol L^{-1} HNO$_3$	68 ± 0.6	72 ± 0.8
1.0 mol L^{-1} HNO$_3$	72 ± 0.7	80 ± 0.9
2.0 mol L^{-1} HNO$_3$	82 ± 0.8	92 ± 0.8
0.1 mol L^{-1} HNO$_3$ + 5% m/v thiourea	99.2 ± 0.2	101 ± 0.5

solid phase extraction studies. A volume of 300 mL of stock solution (concentration 50 mg L^{-1}) of Pb(II) was passed through the column under the optimum condition of flow rate, *i.e.* 5 mL min^{-1}. The recovery of Pb(II) was quantitative (96%) up to 160.0 mL of sample volume for 1 g resin. Above 160.0 mL the recovery decreased quickly with increasing sample volume. Likewise 1000 mL stock solution (concentration 50 mg L^{-1}) of Ag(I) was passed through the column under the optimum condition of flow rate, again 5 mL min^{-1}. The recovery of Ag(I) was quantitative (97%) up to 435.0 mL of sample volume for 1 g resin.

Evaluation of method performance

Calibration curve for quantitative analysis was linear up to 8 µg mL^{-1} with a regression coefficient $r^2 = 0.997$.

Detection limits (3σ of the blank signal) were 30 and 38 ng mL^{-1} for Pb(II) and Ag(I), respectively. Precision of the method was evaluated by successive retention and elution cycle with 0.1 g of the metal ions in 100 mL of solution. Recovery was 97.4 ± 2.6% for Pb(II) at 98% confidence level and 98.2 ± 3.4% for Ag(I) at 97% confidence level.

Real samples analysis

To establish the accuracy of the developed method, certified and real samples were digested using a microwave-assisted procedure and the separation of Pb(II) and Ag(I) were carried out using the newly synthesized resin, followed by its determination using FAAS and scintillation counter, respectively. Results are presented in Tables 3 and 4 and

Table 3. Analysis of certified reference materials and real samples for Pb(II) (µg g^{-1}, n = 4, mean ± standard deviation)

Sample	Certified or Reference Value	Determined Value	Error %
Tomato leaves	6.3 ± 0.3	6.5 ± 0.8	3.17
Pond sediment	105 ± 6	102 ± 2	2.65
Igneous rock	19.1 ± 0.3	20.0 ± 1.6	4.71
Road dust I	118 ± 6*	124 ± 0.9	5.08
Road dust II	59 ± 3*	62 ± 1.3	5.08

* Direct analysis.

Table 4. Determination of Ag(I) ion real samples (µg g^{-1}, n = 4, mean ± standard deviation)

Sample	Reference value	Determined value	% Error
Silverex	1.5[a] ± 0.3	1.6 ± 0.6	0.1
Photographic washings	59.31[a] ± 0.5	57.81 ± 0.8	1.5
Geological samples from G. S. I., Kolkata	600[a,b] ± 0.2	590 ± 0.8	10

[a] Gravimetry; [b] Recommended value from G. S. I., Kolkata

Table 5. Comparison of the developed procedure with some other proposed procedures

Resin	LOD for Pb(II) / Ag(I) (ng mL^{-1})	Sorption capacity (mmol g^{-1})	Samples
6-Mercaptopurine appended polystyrene-divinylbenzene through azo linker [ref. 26]	Ag(I): 29	Ag(I): 0.52	Geological, medicinal and environmental samples
Benzimidazolylazo appended polystyrene-divinylbenzene copolymer [ref. 13]	NA	Ag(I): 1.0	Rock samples, chawanprash (DABUR), sulfadiazine (Silverex), photographic washings
Imidazolylazo appended polystyrene-divinylbenzene copolymer [ref. 27]	NA	Ag(I): 1.49	Rock samples, chawanprash (DABUR), sulfadiazine (Silverex), photographic washings
2-Aminothiazole appended polystyrene-divinylbenzene through azo linker [ref. 28]	Pb(II): 25	Pb(II): 0.29	Tomato leaves, pond sediment, igneous rocks, road dust
2,6-Diacetylpyridine functionalized Amberlite XAD-4 [ref. 29]	Pb(II): 0.43	Pb(II): 238.1	Sea water, tap water
2-Aminothiophenyl S-acetic acid [ref. 2]	Pb(II): 40.6	Pb(II): 0.03	Road dust
This work	Pb(II): 30 Ag(I): 38	Pb(II): 0.35 Ag(I): 1.5	Tomato leaves, pond sediment, igneous rocks, road dust, geological sample, Silverex, photographic washings

NA = Not Available

they are in good agreement with with the certified and reference values; no significant differences have been observed at a 95% confidence level according to a t-test. Results for road dust samples are also included in Table 3.

Conclusions

Polymeric resin containing derivatized amino acid are scarce and it is found that the developed method, based on polymer anchored derivatized L-methionine can be used for selective separation of Pb(II) and Ag(I) from different environmental and biological samples. The functionalities present in the solid polymeric matrix contain thio-ether, tertiary nitrogen (from amino acid part) and soft nitrogen from indole moiety which probably are responsible for binding to Pb(II) ion as per HSAB principle *i.e.*, hard center always preferred to bind with hard center. Based on Table 5, it can be concluded that the present method is one of the most promising Pb(II) and Ag(I) SPE extraction methods found in the literature.[2,13,26-29]

Supplementary Information

Supplementary Information data are available free of charge at http://jbcs.sbq.org.br as pdf file.

References

1. Alegria, A.; Barbera, R.; Farre, R.; Lagarda, R.; Roig, M. J.; Romer, M. J.; *Int. J. Environ. Anal. Chem.* **1990**, *38*, 68.

2. Mondal, B. C.; Das, A. K.; *React. Funct. Polym.* **2002**, *53*, 45.

3. Dutta, S.; Das, A. K.*; J. Appl. Polym. Sci.* **2007**, *10*, 2281.

4. Gurnani, V.; Singh, A. K.; Venkataramani, B.; *Anal. Chim. Acta* **2003**, *485*, 221.

5. Goswami, A.; Singh, A. K.; *Anal. Chim. Acta* **2002**, *454*, 229.

6. Kumar, M.; Rathore, D. P. S.; Singh, A. K.; *Talanta* **2000**, *51*, 1187.

7. Cekic, S. D.; Filik, H.; Apak, R.; *Anal. Chim. Acta* **2004**, *505*, 15.

8. Matoso, E.; Kubota, L. T.; Cadore, S.; *Talanta* **2003**, *60*, 1105.

9. Saxena, R.; Singh, A. K.; *Anal. Chim. Acta* **1997**,*340*, 285.

10. Kumar, M.; Rathore, D. P. S.; Singh, A. K.; *J. Anal. Chem.* **2001**, *370*, 377.

11. Chattopadhyay, P; Sinha, C; Pal, D. K.; *Fresenius J. Anal. Chem.***1997**, *357*, 368.

12. Higuchi, H.; Matsufuji, T.; Oshima, T.; Ohto, K.; Inoue, K.; Tsend-Ayush, T.; Gloe, K.; *Chem. Lett.* **2005**, *34*, 80.

13. Das, D.; Das, A. K.; Sinha, C.; *Talanta* **1999**, *48*, 1013.

14. Das, D.; Dai, Z.; Holmes, A.; Canary, J. W.; *Chirality* **2008**, *20*, 585.

15. Holmes, A. E.; Das, D.; Canary, J. W.; *J. Am. Chem. Soc.* **2007**, *129*, 1506.

16. Zahn, S.; Das, D.; Canary, J. W.; *Inorg. Chem.* **2006**, *45*, 6056.

17. Rees, D. C.; Lewis, M.; Lipscomb, W. N.; *J. Mol. Biol.* **1983**, *168*, 367.

18. Borders, C. L.; Saunders, J. E.; Blech, D. M. Jr.; Fridovich, I.; *Biochem. J.* **1985**, *15*, 771.

19. Kim, E. E.; Wyckoff, H. W.; *J. Mol. Biol.* **1991**, *218*, 449.

20. Dreyer, M. K.; Schulz, G. E.; *J. Mol. Biol.* **1993**, *231*, 549.

21. Nakon, R.; Rechani, P. R.; Angelici, R. J.; *Inorg. Chem.* **1973**, *12*, 2431.

22. Stork, G.; Leong, A. Y. W.; Touzin, A. M.; *J. Org. Chem.* **1976**, *21*, 3491.

23. Vogel, A. I.; *A Textbook of Quantitative Inorganic Analysis*, 3rd ed., Longmans: London, 1961.

24. Frost A. A.; Pearson, R. G.; *Kinetics and Mechanism*, Wiley: New York, 1953.

25. Turse, R.; Rieman III, W. M.; *J. Phys. Chem.* **1961**, *65*, 1821.

26. Mondal, B. C.; Das, D.; Das, A. K.; *Anal. Chim. Acta* **2001**, *450*, 223.

27. Das, D.; Das, A. K.; Sinha, C.; *Anal. Lett.* **1999**, *32*, 567.

28. Dutta, S.; Das, A. K.; *J. Sci. Indian Res.* **2007**, *66*, 1025.

29. Kara, D.; Fisher, A.; Hill, S. J.; *Analyst* **2005**, *130*, 1518.