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Extraction Pb(II) by (Z)-Furan-2-carbaldehyde Thiosemicarbazone adsorbed on surfactant coated alumina before determination by FAAS

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ABSTRACT

A simple, highly sensitive, accurate and selective method for determination of trace amounts of Pb(II) in water samples is presented. The method is based on selective chelation of Pb(II) on surfactant coated alumina, modified with a Schiff's base (Z)-Furan-2-carbaldehyde Thiosemicarbazone (I). The retained ions were then eluted with 4 ml of 4 M nitric acid and determined by flame atomic absorption spectrometry(FAAS) at 283.3 for Pb. The influence of flow rates of sample and eluent solutions, pH, breakthrough volume, effect of foreign ions on chelation and recovery were investigated. 1.5 g of surfactant coated alumina adsorbs 40 mg of the Schiff's base which in turn can retain 15.0±0.9mg of each of the two ions. The limit of detection (3σ) for Pb(II) was found to be 5.57 ng l -1. The enrichment factor for both ions is 100. The mentioned method was successfully applied on determination of lead in different water samples. The ions were also speciated by means of three columns system.

Key words: Determination of lead, Pre-concentration, (Z)-Furan-2-carbaldehyde Thiosemicarbazone (I), FAAS.

INTRODUCTION

Trace amounts of metals are present in natural biosphere. Presence of some of these metals in very low concentrations and certain oxidation states are necessary. Higher concentrations and other oxidation states might be toxic and dangerous. Unfortunately the deference between these two levels are very small (Luoma, 1983; Forstner 1983). Lead occurs in nature mostly as PbS. It is used in batteries, tetraethyl lead, guns, solders and X-ray instruments (Kirk, Othmer, 1979). Copper on the other hand occurs as CuS, CuS2, CuFeS2, CuSO4. 5H2O and other forms. More than 75% of copper production is used in electrical industries. It is also used in pigments, metallic blends and household. Hence determination of lead and copper in industry and environment are both very important. A preconcentration step is advisable in trace analysis. Lead and copper have been so far determined by various methods such as spectrophotometry (Choi, Choi, 2003; Zaijan et al, 2003), liquid–liquid extraction (Kara, et al 2001; Sonawale 2001; Diniz 2004), cloud point extraction (Manzoori, 2002; Chen 2001), and electrochemical measurements (Yuan, 2004).

Some of these methods suffer from poor limit of detection and harmful solvents are being used in some others. On the other hand, effect of foreign ions on the analyte is not negligible in many instances. In such cases, preconcentration of the analyte makes the determination easier and the composition of the sample less complicated. In recent years, solid phase extraction (SPE) has offered attractive possibilities in trace analysis. It has reduced the solvent and time consumption drastically (Majors, 1989; Hagen, 1990). In order to increase the preconcentration or extraction power of SPE an organic or inorganic ligand is used in conjunction with the sorbont. Some of the ligands used for determination of lead

and copper are: Amberlit XAD-2 with 3,4-dihidroxybenzoic acid (Lemos, 2003), silicagel modified with 3-aminopropyl triethoxysilane (Tokman et al 2003), Levatit with di (2,4,4–trimethylpentyl) phosphinic acid (Castillo et al, 2001), silicagel functionalized with methyl thiosalicylate (Zougagh et al, 2004), silicagel modified with zirconium phosphate (Matoso et al, 2003) and C18 diskes modified with a sulfur containing Schiff's base (Hashemi et al, 2001; Groschner, 1994; Moghimi, 2006).

Comparing these examples with the presented method, they have either a lower enrichment factor or a higher limit of detection. On the other hand, the C18 disks can be used only a few times, while the proposed sorbent could be used more than 50 times without loss of efficiency. Surfactant coated alumina modified with chelating agents has been used for extraction and preconcentration of environmental matrixes and metals (Manzoori et al, 1998; Hiraide, 1999). Here, the surfactant molecules have been associated on the alumina surface forming an admicell or hemimicell. Organic molecules attach themselves on the hydrophobe part and low concentration of metallic elements also on the hydrophobe part, which includes the chelating agent (Hiraide, 1999). The Schiff's bases which are obtained from salisylaldelyde are known as multidentate ligands. These agents can form very stable complexes with transition metal ions (Calligaris, 1987; Alwood, 1997).

The main goal of the present work is development of a fast, sensitive and efficient way for enrichment and extraction of trace amounts of Pb(II) from aqueous media by means of a surfactant coated alumina modified with ligand (Z)-Furan-2-carbaldehyde Thiosemicarbazone (I, shown in Fig. 1). Such a determination has not been reported in the literature. The structure of (Z)-Furan-2-carbaldehyde Thiosemicarbazone is shown in Fig.1.

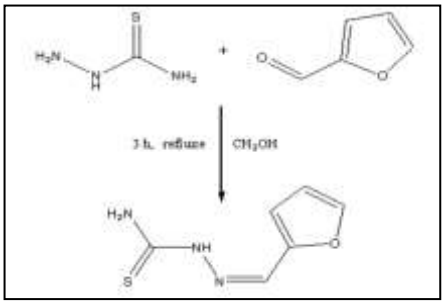

Fig.1. Synthetic and chemical structure of the compound (I)

The chelated ions were desorbed and determined by FAAS. The modified solid phase could be used at least 50 times with acceptable reproducibility without any change in the composition of the sorbent, ligand or SDS. On the other hand, in terms of economy it is much cheaper than those in the market, like C18 disks.

EXPERIMENTAL

REAGENTS AND APPARATUS

All solutions were prepared with doubly distilled deionized water. Alumina powder γ-type for chromatography with diameter of about 50 µm obtained from Katayama Chemicals. It was conditioned before use by suspending in 4 M nitric acid for 20 min, and then washed two times with water. Sodium dodecyl solfate (SDS) obtained from Merck and used without any further purification. Synthesis of sodium (Z)-Furan-2-carbaldehyde Thiosemicarbazone (Z)-Furan-2-carbaldehyde thiosemicarbazone (I) was prepared according to the modified procedure described in the literature (Dilovic et al, 2008). A solution of thiosemicarbazide (0.91 g, 10 mmol) in 40 mL of dry methanol was prepared with stirring and warming (about 40 oC) during 1 h. To the warm thiosemicarbazide solution, furan-2-carbaldehyde (0.96 g, 10 mmol) in 10 mL of dry methanol was added following by a 12 h reflux (Figure 1). The mixture was then slowly ooled own to room temperature until the yellowish needle crystals suitable for crystallography were obtained. Yield: 1.31 g (77%). Anal. Calcd for C6H7N3OS: C, 42.60; H, 4.16; N, 24.83; S, 18.94. Found: C, 42.41; H, 4.12; N, 24.76; S, 18.88 %. IR (KBr) (νmax/cm-1) :3135 (s), 2887 (m), 1620 (s), 1612 (s), 1575 (s), 774 (m). 1H NMR (δ, DMSO-d6, 25 oC, ppm): 11.40 (s, 1H, NHCS), 8.41 (s, 1H, H=N), 8.10 and 7.92 (2br s, 1H each, NH2), 6.11–7.54 (m, 3H, aromatic); 13C NMR (δ, DMSO-d6, 25 oC, ppm): 177.60 (C=S), 139.54 (CH=N), 148. 68, 142.8, 108.5, 109.01 (C-aromatic) as shown in Fig.1. Lead nitrate, copper sulfate pentahydrated, ammonium dihydrogen phosphate were of analytical reagent grade and RP-C18 silica (40-63 µm) obtained from Merck. The anion exchanger resin Dowex 1X-8 mesh 100-200 obtained from Fluka. The chelating resin, chelex-100, mesh 100-200 obtained from Bio Rad. Standard stock solution of 1000 µg ml -1of Pb(II) were prepared by dissolving appropriate quantity of their salts in water. A solution of 0.35 M of ammonium dihidrogen phosphate in water was prepared as the matrix modifier for determination of lead. A solution of SDS– I was prepared as follow: to a solution of 0.2 g of (Z)-Furan-2-carbaldehyde Thiosemicarbazone in 10 ml of ethanol, 5 drops of 1 M NaOH and 0.5 g of SDS were added, dissolved and its volume adjusted to 50 ml with water.

Preparation of admicell column: to 40 ml of water containing 1.5 g of alumina, 10 ml of the above I solution was added. The pH of the suspension was adjusted to 2.0 by addition of 4 M HNO3 and stirred by mechanical stirrer for 20 min. Then the top liquid was decanted (and discarded) and the remained alumina was washed three times with water, then with 5 ml of 4 M HNO3and again three times with water. The prepared sorbent was transferred to a polypropylene tube (i.d 5 mm, length 10mm). Determination of Pb2+ contents in working samples were carried out by a Varian spectra A.200 model atomic absorption spectrometer equipped with a high intensity hallow cathode lamp (HI-HCl) according to the recommendations of the manufacturers. These characteristics are tabulated in (Table1).

Table.1.The operational conditions of flame for determination of lead

Slit width	0.7 nm
Operation current of HI-HCL	10 mA
Resonance fine	283.3
Type of background correction	Deuterium lamp
Type of flame	Air/acetylene
Air flow	7.0 mL.min-1
Acetylene flow	1.7 mL.min-1

A metrohm 691 pH meter equipped with a combined glass calomel electrode was used for pH measurements.

PROCEDURE

The pH of a solution containing 100 ng of each Pb(II) was adjusted to 2.0. This solution was passed through the admicell column with a flow rate of 5 ml min-1. The column was washed with 10 ml of water and the retained ions were desorbed with 1 ml of 4 M HNO3 with a flow rate of 2 ml min-1. The desorption procedure was repeated 3 more times. All the acid solutions (4 ml all together) were collected in a 10 ml volumetric flask and diluted to the mark with water. The concentrations of lead in the solution were determined by FAAS at 283.3.

DETERMINATION OF LEAD IN WATER SAMPLES

Polyethylene bottles, soaked in 1 M HNO3 overnight, and washed two times with water were used for sampling. The water sample was filtered through a 0.45 µm pores filter. The pH of a 1000 ml portion of each sample was adjusted to 2.0 (4 M HNO3) and passed through the column under a flow rate of 5 ml min-1. The column was washed with water and the ions were desorbed and determined as the above mentioned procedure.

SPECIATION OF LEAD IN WATER SAMPLES

This procedure is reported in several articles. The method has been evaluated and optimized for speciation and its application on complex mixtures (Abollino, 2000; Lewis, 1992). The chelating cation exchanger (Chelex-100) and anion exchanger, Dowex 1X-8 resins were washed with 1 M HCl, water, 1 M NaOH and water respectively. 1.2 g of each resin was transfered to separate polyethylene columns. Each column was washed with 10 ml of 2 M HNO3 and then 30 ml of water. The C18 bounded silica adsorber in a separate column was conditioned with 5 ml of methanol, then 5 ml of 2 M HNO3and at the end with 20 ml of water. 5 ml of methanol was added on top of the adsorber, and passed through it until the level of methanol reached just the surface of the adsorber. Then water was added on it and connected to the other two columns. A certain volume of water sample was filtered through a 0.45 µm filter and then passed through the three columns system, Dowex 1X-8, RP-C18 silica adsorber and Chelex-100 respectively. The columns were then separated. The anion and cation exchanger columns were washed with 10 ml of 2 M HNO3 and the C-18 column with 10 ml of 1 M HCl. The flow rate of eluents was 1 ml min-1. The lead content of each eluted solution were determined by FAAS.

RESULTS AND DISCUSSION

I is a Schiff's base. It is a four dentate ligand. It is insoluble in water, but soluble in slightly alkaline ethanol. Primary investigations revealed that surfactant coated alumina could not retain Pb(II) cations, but when modified with I, retains these cations selectively. It was then decided to investigate the capability of I as a ligand for simultaneous preconcentration and determination of lead on admicell. The alumina surface in acidic media (1<pH<6) attracts protons and becomes positively charged. The hydrophyl part of SDS(-SO3-), is attached strongly to these protons. On the other hand, the ligand molecules are attached to hydrophobe part of SDS and retain small quantities of metallic cations (Hiraide, 1999).

EFFECT OF PH

The effect of pH of the aqueous solution on the extraction of 100 ng of each of the cations Pb(II) was studied in the pH rang of 1-10. The pH of the solution was adjusted by means of either 0.01 M H NO3 or 0.01M NaOH. The results indicate that complete chelation and recovery of Pb(II) occurs in pH range of 2-4 and that of in 2-8 and are shown in Fig. 2.

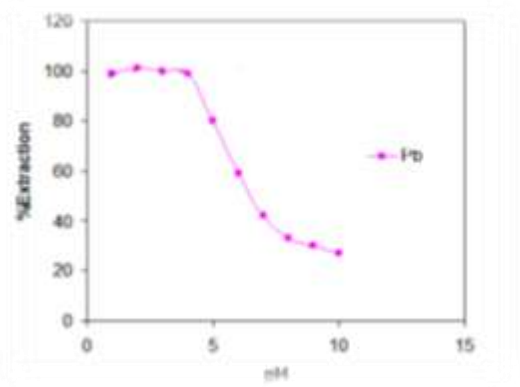

Fig. 2. Extraction percentage of Pb(II) against pH.

It is probable that at higher pH values, the cations might be hydrolysed and complete desorbeption does not occur. Hence, in order to prevent hydrolysis of the cations and also keeping SDS on the alumina, pH=2.0 was chosen for further studies.

EFFECT OF FLOW RATES OF SOLUTIONS

Effect of flow rate of the solutions of the cations on chelation of them on the substrate was also studied. It was indicated that flow rates of 1-5 ml min-1would not affect the retention efficiency of the substrate. Higher flow rates cause incomplete chelation of the cations on the sorbent. The similar range of flow rate for chelation of cations on modified alumina with SDS and a ligand has been reported in literature (Manzoori et al, 1998; Hiraide, 1999). Flow rate of 1-2 ml min-1for desorption of of the cations with 4 ml of 4 M H NO3has been found suitable. Higher flow rates need larger volume of acid. Hence, flow rates of 5 ml min-1and 2 ml min-1were used for sample solution and eluting solvent throughout respectively.

EFFECT OF I QUANTITY

To study optimum quantity of I on quantitative extraction of lead, 50 ml portions of solutions containing 100 ng of each cation were passed through different columns the sorbent of which were modified with various amounts, between 10-50 mg of the ligand. The best result was obtained on the sorbent that was modified with 40 mg of the ligand.

FIGURES OF MERIT

The breakthrough volume is of prime importance for solid phase extractions. Hence, the effect of sample volume on the recovery of the cations was studied. 100 ng of each cation was dissolved in 50, 100, 500 and 1000 ml of water. It was indicated that in all the cases, chelation and desorption of the

cations were quantitative. It was then concluded that the breakthrough volume could be even more than 1000 ml. Because the sample volume was 1000 ml and the cations were eluted into 10 ml solution, the enrichment factors for both cations are 100, which is easily achievable. The maximum capacity of 1.5 g of the substrate was determined as follow; 500 ml of a solution containing 50 mg of each cation was passed through the column. The chelated ions were eluted and determined by FAAS. The maximum capacity of the sorbent for three individual replecates was found to be 15.0±0.9 µg of each cation. The limit of detection (3σ) for the catoins (Skoog et al, 1998) found to be 5.57 ng l -1for lead ions. Reproducibility of the method for extraction and determination of 100 ng of each cation in a 50 ml solution was examined. As the results of seven individual replicate measurements indicated, they were 2.85% and 2.98% for Pb(II).

EFFECT OF FOREIGN IONS

Effects of foreign ions were also investigated on the measurements of lead. Here a certain amount of foreign ion was added to 50 ml of sample solution containing 100 ng of each Pb(II) with a pH of 2.5. The amounts of the foreign ions and the percentages of the recovery of lead are listed in Table 2. As it is seen, it is possible to determine lead without being affected by the mentioned ions.

Table 2. Effect of foreign ions on the recovery of 100 ng of Pb

Diverse ion	Amounts taken (mg) added to 50 mL	% Found	%Recovery of Pb2+ion
Na+	92.4	1.19(2.9)a	98.7(1.7)
K+	92.5	1.38(2.1)	98.9(2.2)
Mg2+	14.5	0.8(1.8)	98.7(1.7)
Ca2+	28.3	1.29(2.0)	99.0(1.8)
Sr2+	3.45	2.85(2.2)	98.2(2.0)
Ba2+	2.66	3.16(2.4)	98.3(2.0)
Mn2+	2.64	1.75(2.3)	98.5(1.8)
Co2+	2.17	1.4(2.3)	98.1(2.2)
Ni2+	2.65	2.0(2.14)	98.4(2.4)
Zn2+	2.74	1.97(2.1)	98.7(2.2)
Cd2+	2.53	1.9(2.0)	98.8(2.8)
Bi3+	2.55	2.7(1.4)	98.7(2.7)
Cu2+	2.46	2.81(2.3)	98.7(2.6)
Fe3+	2.60	3.45(2.4)	96.6(2.8)
Cr3+	1.70	2.92(2.2)	97.3(2.4)
UO2+	2.89	1.3(2.2)	98.3(2.2)
NO3-	5.8	2.3 (2.3)	98.3(2.6)
CH3COO-	5.0	2.2(2.6)	99.4(2.2)
SO42-	5.0	2.9(3.0)	98.7(2.1)
CO32-	5.6	1.8(2.5)	99.3(2.5)
PO43-	2.5	2.1(2.0)	98.9(2.0)

a:Values in parenthesis are CVs based on three individual replicate measurements.

ANALYSIS OF THE WATER SAMPLES

The prepared sorbent was used for analysis of real samples. To do this, the amounts of lead were determined in different water samples namely: distilled water, tap water of Tehran (Tehran, taken after 10 min operation of the tap), rain water (Tehran, 2۰ January, 2010), Snow water (Tehran, ۷ February, 2010), and two synthetic samples containing different cations. The results are tabulated in Table 3.

Table 3. Recovery of Pb contents of water samples

		Amount added(µg)	Found(µg)	%Recovery
Sample Distilled water (100mL)	Pb	-	-	-
		0.050	0.048(3.40)[a]	96
		0.100	0.097(2.90)	97
Tap water(100mL)	Pb	-	0.016(4.54)	-
		0.050	0.067(3.42)	96
Snow water(50mL)	Pb	-	0.048(3.25)	-
		0.100	0.151(2.65)	98.0
Rain water(100mL)	Pb	-	0.042(3.25)	-
		0.100	0.148(2.42)	98
Synthetic sample 1 Na^{+}, Ca^{2+}, Fe^{3+}, $Co^{2+}Cr^{3+}$, Hg^{2+}, 1 mg l^{-1}	Pb	-	-	-
		0.100	0.101(3.42)	98
Synthetic sample 2 K^{+}, Ba^{2+},Mn^{2+}, $Cd^{2+}Ni^{2+}$, Zn^{2+}, 1 mg l^{-1} of each cation	Pb	-	-	-
		0.100	0.101(2.73)	99

[a]: Values in parenthesis are CVs based on three individual replicate measurements.

As it is seen, the amounts of lead added to the water samples are extracted and determined quantitatively which indicates accuracy and precision of the present method. Separation and speciation of cations by three columns system It is possible to precon- centrate and at the same time separate the neutral metal complexes of organic ligands, anionic complexes and free ions from each other by this method (Liu, 1989). Water samples were passed through the three connected columns: anoin exchanger, C18-silica adsorber and chelating cation exchanger.

Each species of lead is retained in one of the columns; anionic complexes in the first column, neutral complexes of organic ligands in the second, and the free ions in the third. The results of passing certain volumes of different water samples through the columns are listed in Table 4.

Table 4. Results of speciation of Pb in different samples by three columns system

	Tap water (1000ml)	water sample (1000ml)a	River water (50ml)
Column	Pb(µg)	Pb(µg)	Pb(µg)
Dowex 1X8	-	-	-
Silica C-18	-	-	-
Chelex-100	0.012(4.5)b	0.105(3.0)	0.104(2.0)

According to the results, it is indicated that lead present only as cations. On the other hand the t-test comparing the obtained mean values of the present work with those published indicate no significant difference between them. We have proposed a method for determination and preconcentration of Pb in water samples using surfactant coated alumina impregnated with a Sciff's base. The proposed method offers simple, highly sensitive, accurate and selective method for determination of trace amounts of Pb(II) in water samples.

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