Preparation of a Modified Octadecyl Silica Membrane Disk for Solid Phase Extraction of Lead(II) Ions in Different Real Samples and their Determination with ICP-AES

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Abstract: A solid phase extraction and inductively coupled plasma atomic emission spectrometry (ICP-AES) for the determination of lead(II) ions with octadecyl-bonded silica membrane disks modified by 4-methyl-N-{2-(4-methylbenzothioyl)aminoethyl}benzenecarbothioamide (MMAB) was studied. Extraction efficiency, and the effects of parameters such as flow rate, pH, type and the least amount of acid for stripping of lead(II) from the modified disks and break through volume were examined. The maximum capacity of the membrane disks modified by 4.0 mg of MMAB used was found to be 527 ± 4 μg of lead(II) ions. The preconcentration factor is 440 (for 2200 mL water sample and flow rate of 12 mL min^{-1}) and detection limit of the proposed method is 85.4 ng mL^{-1}. The developed method was successfully applied to the determination of lead(II) ions in blood, spinach, bean, hair, milk, pepper and various water samples.

Keywords: Lead(II), Solid phase extraction, Benzenecarbothioamide, Preconcentration, ICP-AES.

1. INTRODUCTION

Lead is a neurotoxin and can enter the organism primairily *via* alimentary and/or the respiratory tract. It can be accumulated in skeleton and lead to behavioural abnormalities, retarding intelligence and mental development [1]. This element is listed by the Enviromental Protection Agency as one of 129 priority pollutants [2]. In trace level, it decreases enzymatic and chronic exposure to lead poisoning causes nephritis, scaring and the shrinking of kidney tissues, but it is an important constituent of some alloys too [3]. Thus, the determination of trace amounts of this element, is becoming increasingly important.

The most common methods for determination of lead(II) ions are including flame and graphite furnace atomic absorption spectrometry, spectrophotometry, constant current stripping analysis, differential pulse anoding stripping voltametry, inductively coupled plasma atomic emission spectrometry and potentiometry. The sensitivity of these methods is usually insufficient for very low level monitoring of lead(II) concentration in environmental samples. Consequently, a preconcentration and matrix elemination step is usually required. The most widely used techniques for the separation and preconcentration of trace amounts of this ion are liquid-liquid extraction (LLE), absorption on various adsorbents such as thiol cotton, silica gel, silanized glass beads and amberlite XAD-4. One of widely used and fast emerging preconcentrative separation techniques for this purpose is the solid phase extraction (SPE). It is an alternative technique due to the following advantages: higher enrichment factor, absence of emulsion, safety with respect to hazardous samples, minimal costs due to low consumption of reagents, flexibility and ease of automation [4, 5]. Hydrophobic SPE disks have been used extensively for the determination of organic environmental pollutents [6, 7]. These disks, made of 90% (w/w) octadecyl silane in an inert polytetrafluoroethylene (PTFE) matrix, have a typical diameter of 47 mm and a thickness of 0.5 mm. Typical capacity of a disk for well-retained compounds ranges from 10 to 20 mg. The proclaimed major advantages of the SPE disks include (1) shorter sample processing time due to the large cross-sectional area of the disk and decreased pressure drop, which allows the sample processing at higher flow rates, (2) decreased plugging by particles due to large cross-sectional area of the disk and (3) reduced channeling resulting from the use of smaller diameter sorbent and a greater mechanical stability of the sorbent bed [8].

We have modified the octadecyl silica membrane disks with some compounds for selective separation and preconcentration trace amounts of lead, copper

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and silver [9-12]. In the present paper, a simple SPE procedure has been developed using 4-methyl-N-{2-(4-methylbenzothioyl)aminoethyl}benzenecarbothioamide (MMAB) (Figure **1**) as modifier for lead(II) ions from aqueous solutions and real samples of blood, spinach, bean, hair, milk, pepper and various water samples. To the best of our knowledge, octadecyl silica membrane disks modified by MMAB have not been employed previously for selective separation and preconcentration of lead(II) ions from various samples. Presence of donor atoms (nitrogen and sulfur) in MMAB which form complexes with the lead(II) ions in solution, is the primary factor in extraction.

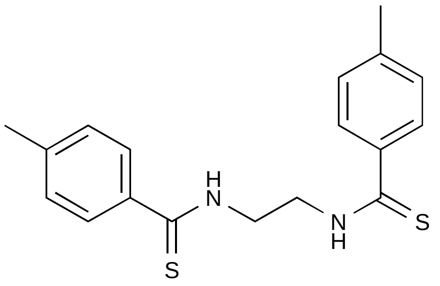

Figure 1: Structure of MMAB.

2. EXPERIMENTAL

2.1. Instruments

A Varian Liberty 150 AX Turbo ICP-AES was used for analysis. Determination of all other cations was performed under the recommended conditions for each metal. Extraction were performed with 47 × 0.5 mm (diameter × thickness) Empore membrane disks containing octadecyl-bonded silica (8-µm particles 60-Å pore size, 3M Co., Paul, MN). The disk was used in conjunction with standard Millipore 47-mm filtration apparatus. A Metrohm 691 pH/ion meter (Buchs, Switzerland) with a combined glass-calomel electrode was employed for measuring pH values of the test solutions.

2.2. Reagents and Materials

All solutions were prepared with deionized distilled water (Milli-Q Millipore 18.2 MΩ cm^{-1} conductivity). Otherwise stated, analytical grade acids, bases, nitrate salts of metals and other chemicals used in this study were obtained for Merck. All plastic and glassware were cleaned by soaking in dilute HNO_3 (1 + 9) and were rinsed with distilled water perior to use. MMAB was purchased from the Jaber Ibn Hayan research laboratories (Tehran, Iran).

2.3. Test Procedure for Solid Phase Extraction of Lead(II) Ions

After placing the membrane disk in the filtration apparatus, it was washed with 10 mL of methanol and methanol-ethanol (50-50 % V/V) to remove all contaminants arising from the manufacturing process and from the environment. After drying the disk by passing air through it for several minutes, a solution of 4.0 mg of MMAB dissolved in 4 mL of methanol was introduced onto the disk so that the solution was spread on the whole disk surface. The solution was allowed to penetrate inside the membrane completely without applying any vacuum. After about 1 min, the filtration funnel containing the modified disk was transferred into an oven and the solvent was completely evaporated at 60 ºC. Then the sample solution containing lead(II) ions with pH about 6.0 (that was chosen after investigation of pH effect) was passed through the membrane. After the extraction, the disk was stripped from the membrane disk using minimum 5 mL of a 2 mol L^{-1} nitric acid solution. The eluent was analyzed for determination of lead concentrations by inductively coupled plasma atomic emission spectrometry [11, 12].

2.4. Preconcentration Procedure

Standard test solution (containing 10 µg Pb^{2+}) was prepared and the pH was adjusted to optimum working pH. This solution was permitted to flow through the modified membrane disk at optimum flow rate. The adsorbed lead(II) ions on the membrane were eluted with 5 mL of 2.0 mol L^{-1} HNO_3 solution. Lead(II) ions were determined by ICP-AES. The preconcentration factor (PF) could be calculated from the ratio of initial volume of sample to the final volume after concentration.

2.5. Applications

3 mL of a freshly prepared mixture of concentrated HNO_3–H_2O_2 (2:1, v/v)was added to triplicate 0.2 mL of blood samples (were directly taken into PTFE flasks). The mixture kept for 15 min at room temperature and then heated following a 1-stage digestion programmed at 80% of total power (900 W), 1-2 min for blood samples. The resulting digested semidried mass was diluted up to 10 mL with 0.1 mol L^{-1} concentrated HNO_3. A blank extraction was carried out through the complete procedure. An aliquot of 100 mL total blood (previously homogenized) was diluted and lead(II) ions were determined by the general procedure.The

concentrations were obtained directly from calibration graphs after correction of the absorbance for the signal obtained from an appropriate reagent blank [13].

A 10 g of bean grain and 40 g leaves of spinach were heated in silica crucible for 3 h on a hot plate. The charred material was transferred to furnace and heating overnight at 650°C. The residue of bean grain was cooled, treated with 10 mL concentrated nitric acid and 3 mL of 30% H_2O_2, and again kept in furnace for 2 h. The residue of spinach leaves was cooled, gain kept in furnace for 2 h at the same temperature to decompose organic matter completely. The final residue was treated with 3 mL concentrated hydrochloric acid and 2-4 mL 70% perchloric acid and heated on hot plate to expel all acid fumes so that all the metals change to respective ions. The solid residue was dissolved in water, filtered and by adjusts pH at 6.0 by addition of KOH and phosphate buffer [14, 15].

Hair samples (0.5 g) were cut into pieces no longer than 1 cm, thoroughly washed with a mixture of ethyl ether and acetone (3:1, v/v) under continuous stirring for 10 min, dried at 85°C for 1 h, and treated with a dilute (5%) aqueous solution of EDTA for 1 h. The pieces were repeatedly rinsed with distilled water, and finally dried at 85°C for 12 h in an oven to determine the dry weight of the sample just before the subsequent step. Hair digestion was based on irradiation with a microwave field at 2.45 GHz. The treatment steps have done as reported with HNO_3, H_2O_2 and HF [16].

1.5 mL of milk samples were transferred into previously decontaminated TFM vessels and digested by means of a Microwave oven. A number of five different portions of 1 mL, sampled from the same tube, were weighed in order to calculate the mean density of milk. The presence of fat in milk has required a strong digestion program with a reagents mixture of 5 mL of concentrated nitric acid 65% (v/v) and 1 mL of hydrogen peroxide 40% (v/v). After cooling, the digested solutions were quantitatively transferred in Falcon tubes of 50 mL by adding high purity deionized water up to a weight of 20 g [17].

A 100 mg pepper was taken in a beaker and dissolved in concentrated nitric acid (5 mL) with heating. The solution was cooled, neutralized with NaOH solution, diluted and filtered. The filtrate was made to 100 mL with water in a calibrated flask. An aliquot (10-20 mL) of the sample solution was taken and lead(II) ions were determined by the general procedure [12].

Tap, river and spring water samples used for development of the method were collected in PTFE containers. Before the analysis, the organic content of the water samples was oxidized in the presence of 1% H_2O_2 and then concentrated nitric acid was added. These water samples were then filtered using a 0.45 μm pore size membrane filter to remove suspended particulate matter and stored in a refrigerator in the dark before analysis [18].

3. RESULTS AND DISCUSSION

Normally, metal ions exist in hydrated form or as complexes associated with anions with little or no tendency of transformation to polymeric matrix. To convert the metal ion to an extractable species its charge must be neutralized and some or all water of hydration be replaced. Thus, the characteristics of metal ions and functional groups and/or donor atoms (such as O, N, P and S), which form complexes with the metal ions in solution, are the primary factors in extraction [19]. The selectivity of the surface with the immobilized functional groups towards metal ion(s) depends on factors like size of the modifier, activity of the loaded group and the characteristics of hard–soft acid–base [20, 21]. The insertion of suitable specific functional groups into the polymeric matrix makes them capable of reacting with metal species under certain favorable conditions to form metal complexes [19].

Despite great improvement in sensitivity and selectivity of modern instrumental techniques of analysis for the determination of trace metals in complex matrices, the crux is separation of analyte from the bulk matrix followed by concentration prior to instrumental detection. The use of C18 bonded silica phase, silica gel functionalized with silane reagents and/or organic chelating groups are in frontiers for the preconcentration. Development of silica supported molecular traps through covalent grafting of organic molecules on silica surface plays important role in elimination of toxic heavy elements from wastewater. Again there is a decrease in detection limit due to extraction of the analyte component from a relatively large volume of solution into the phase of the sorbent. Better selectivity results from the geometrical features of fixing chelating groups on silica surface and complex forming properties of the chelating group [19].

Some reaserches showed that, the schiff's base compounds can form a fairly stable and selective complex with transition and heavy metal ions [22, 23].

To the best of our knowledge, there is no report on the stability of MMAB complexes with metal ions. Thus, in preliminary experiments, the complexation of MMAB with a number of alkali, alkaline earth, transition and heavy metal ions was studied conductometrically in acetonitrile solution in order to obtain a clue to the stability and selectivity of the resulting complexes. In all measurements, the cell should be thermostated at the temperature of 25.0 ± 0.1 °C, using a Phywe immersion thermostat. Intypical experiments, 25 mL of an ion solution (1.0×10^{-4} M) is placed in a water-jacketed cell, equipped with a magnetic stirrer and connected to the thermostat, circulating water at the desired temperature. Then, a known amount of an MMAB (1.0×10^{-2} M) solution is added in a stepwise manner, using a calibrated micropipette. The conductance of the solution is measured after each addition. The MMAB addition is continued until the desired MMAB-to-ion mole ratio is achieved. The 1:1 binding of the different cations with MMAB can be expressed by the following equilibrium:

$$M^{n+} + MMAB \rightarrow M - MMAB^{n+} \tag{1}$$

$$K_f = \frac{[M - MMAB^{n+}]}{[M^{n+}][MMAB]} \times \frac{f_{(M-MMAB^{n+})}}{f_{(M^{n+})} f_{(MMAB)}} \tag{2}$$

The complex formation constancy in terms of the molar conductances, Λ, can be expressed as [24]:

$$K_f = \frac{[M - MMAB^{n+}]}{[M^{n+}][MMAB]} = \frac{(\Lambda_M - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_{M-MMAB^{n+}})[MMAB]} \tag{3}$$

$$[MMAB] = C_{MMAB} - \frac{C_M(\Lambda_M - \Lambda_{obs})}{(\Lambda_M - \Lambda_{M-MMAB^{n+}})} \tag{4}$$

Λ_M is the molar conductance of the metal ions before addition of MMAB, $\Lambda_{M\text{-}MMAB^{n+}}$ the molar conductance of complexed ions, Λ_{obs} the molar conductance of the solution during titration, C_{MMAB} the analytical concentration of MMAB added, and C_M the analytical concentration of the metal ions. The complex formation constants (K_f) were evaluated by computer fitting of equations (3) and (4) to the molar conductance-mole ratio data using a non-linear least–squares program KINFIT [25] and the results are summarized in Table **1**. This behaviour indicated that the MMAB complex was less mobile than the free solvated Pb^{2+} cation. As can be seen, the MMAB could act as a suitable complexing agent for preconcentration and separation of lead(II) ions *via* SPE, by using octadecyl bonded silica membrane disks.

Table 1: Formation Constants of Complexation of MMAB and Different Cations in Acetonitrile Solution

Cation	Log K_f	Cation	Log K_f
Na^+	2.11 ± 0.05	Zn^{2+}	2.83 ± 0.01
K^+	1.82 ± 0.06	Ni^{2+}	3.04 ± 0.05
Ca^{2+}	2.33 ± 0.03	Pb^{2+}	6.03 ± 0.02
Ba^{2+}	2.24 ± 0.07	Cd^{2+}	3.89 ± 0.03
Cu^{2+}	4.27 ± 0.06	Fe^{2+}	2.46 ± 0.02
Co^{2+}	3.41 ± 0.05	Mn^{2+}	2.92 ± 0.06

3.1. pH Studies on the Lead(II) Ions Removal

For solid phase extraction of the heavy metal ions based on chelating, the pH of the aqueous solution is one of the main factor quantitative recoveries of the analytes. Also, the formation of the metal ion complex and the maximum separation efficienncy can be achieved by optimization of pH. The influence of pH on the retention of lead(II) ions extraction was studied by applying the proposed procedure to 20 mL of sample solutions (1.0 µg L^{-1} Pb^{2+} ions). The pH of each solution was adjusted to values ranging from 2.0 to 8.0 with HNO_3 and KOH solutions. According to the results (Figure **2**), quantitative recovery values for the lead(II) ions were obtained through the pH range of 3.5-8.0. At lower pH (< 3.5), the nitrogen and/or sulfur atoms of the MMAB could be protonated and reduce the stability of complex formation between MMAB and lead(II) ions. The higher pH values (> 8.0) were not tested because of the possibility of the hydrolysis of octadecyl silica in the disks. Also, at pH values higher than 8.0, lead(II)

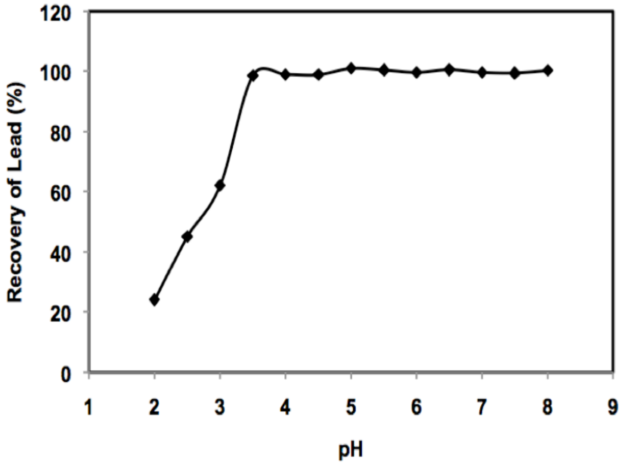

Figure 2: Effect of pH on recovery of the lead(II) ions (other conditions: 1.0 µg L^{-1} of Pb^{2+}; sample flow rate: 5 mL min^{-1}; eluent flow rate: 5 mL min^{-1}; sample volume: 20 mL; room temperature; n=3).

ions from complexes and precipitates with hydroxide ions and their retention is changed and the recovery of the method s decreased. So, all subsequent studies were carried out at pH 6.0.

3.2. Influence of Modifier Amount

The proposed method is based on sorption of lead(II) ions on modified membrane disk. In order to investigate the effects of the amount of modifier on the quantitative extraction of lead(II) ions by membrane disk, the extraction was conducted by varying the amounts of MMAB at 5.0 mL min^{-1} flow rates of sample and eluent solutions. Firstly, some works were carried out without ligand at pH 6.0. As seen in Figure **3**, the lead(II) ions were not quantitatively recovered (< 5%) without MMAB. The recovery values were found quantitative by using at least 4.0 mg of MMAB. With a lower amount, the recovery was decreased, because the extent of complexation and retention of lead(II) ions on the modified membrane is low. On this base, subsequent extraction experiments were carried out with 4.0 mg of MMAB.

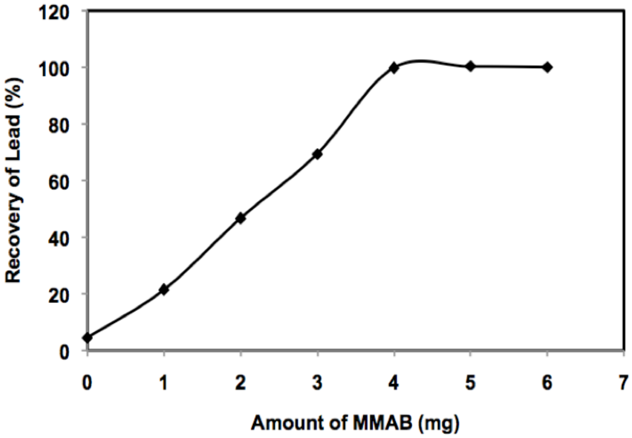

Figure 3: Influence of amount of MMAB on lead(II) ions recovery (other conditions: 1.0 µg L^{-1} of Pb^{2+}; sample flow rate: 5 mL min^{-1}; eluent flow rate: 5 mL min^{-1}; sample volume: 20 mL; pH = 6.0; room temperature; n=3).

3.3. Studies of Various Eluent Agents

The selection of suitable eluent was a difficult problem. The nature and concentration of eluting agents were found to have a significant effect on the desorption process of the adsorbed ions from the modified membrane. A satisfactory eluent should effectively elute the adsorbed analytes with small volume, which is needed for a high preconcentration factor, and should not affect the accurate determination of the analytes and destroy life time and reusability of SPE [26]. Because the adsorption of lead(II) ions is not acceptable at lower pH, various concentrations and various volumes of HCl, HNO_3 and CH_3COOH were tested for desorption of retained lead(II) from the modified membrane disk. As it is observed in Table **2**, HNO_3 showed the best quantitative elution effect in firs experiments and therefore it was selected as an eluent for further applications. After that, the experiments were carried out with acidic solutions at the concentration range of 1.0-3.0 mol L^{-1} and volume of 2-8 mL for selecting the best concentration and volume of HNO_3. The recovery values were increased with increasing of acid concentration and volume. As it is obvious that among three different acid solutions used, 5 mL of about 2.0 mol L^{-1} nitric acid can accomplish the quantitative elution of lead(II) from the membrane disk. The effect of HNO_3 as an eluent could be due to its ability to decompose the complex of lead(II)-MMAB and produce free lead(II) ions that can easily pass through the membrane.

Table 2: Effect of Type and Concentration of Eluting Agent on Recoveries of Lead(II) Ions[a]

Eluent	Volume (mL)	Recovery (%)[b]
HCl (1 mol L^{-1})	2	67.1 ± 0.7
HNO_3 (1 mol L^{-1})	2	74.3 ± 0.4
CH_3COOH (1 mol L^{-1})	2	61.6 ± 0.3
HNO_3 (1 mol L^{-1})	5	96.4 ± 0.1
HNO_3 (1 mol L^{-1})	8	99.5 ± 0.5
HNO_3 (2 mol L^{-1})	3	93.7 ± 0.5
HNO_3 (2.5 mol L^{-1})	3	98.3 ± 0.2
HNO_3 (3 mol L^{-1})	3	100.4 ± 0.6
HNO_3 (2.5 mol L^{-1})	4	99.5 ± 0.3
HNO_3 (2.0 mol L^{-1})	5	100.2 ± 0.4
HNO_3 (2.0 mol L^{-1})	6	98.8 ± 0.1

[a] Initial samples contained 1.0 µg L^{-1} Pb^{2+} ions (in 20 mL of solution).
[b] The values following "±" is the standard deviation (n = 3).

3.4. Influence of Flow Rate

After optimization of the eluent volume and concentration, the effect of flow rate on the adsorption of lead(II) ions was also investigated. It affects the retention of cations on the adsorbent and the duration of complete analysis. While the recovery increases with the decreasing flow rate, the preconcentration time increases. The influence of flow rates of the sample and eluent solutions from the modified membrane disk on the retention and recovery of lead(II) ions was investigated and the results (Figure **4**) showed that the retention of lead(II) ions is not affected by the sample solution flow rate in the range of 1-12 mL min^{-1}, by the membrane disk that modified with 4.0 mg of MMAB. At higher flow rate than 12 mL min^{-1} the extraction and stripping of lead(II) reduced considerably, because the sample solution passes through the membrane disk faster and there is not enough time for equilibration between the lead(II) ions and MMAB. Therefore, to increase the speed of operation, a sample flow rate of 12 mL min^{-1} was selected as the optimum value. The flow rate of eluent solution was examined in the range of 1-10 mL min^{-1}. After 8 mL min^{-1} of eluent solution, the recovery values were not quantitative. For the all experiments, 12 and 8 mL min^{-1} was selected as sample and eluent flow rate respectively.

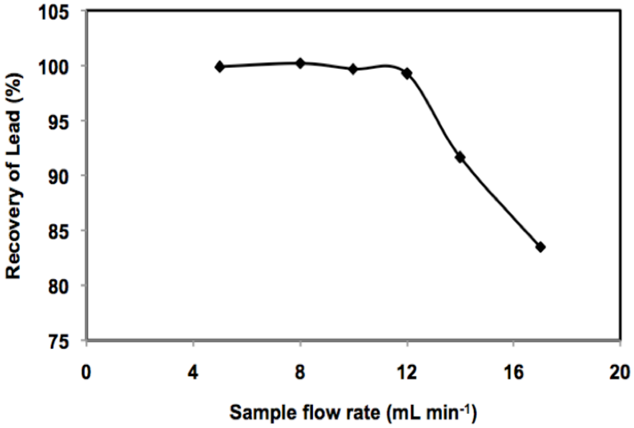

Figure 4: Effect of sample and eluent flow rate on adsorption of lead(II) ions (other conditions: 1.0 µg L^{-1} of Pb^{2+}; sample volume: 20 mL; pH = 6.0; room temperature; n=3).

3.5. Effect of the Volume of Sample Solutions

A higher preconcentration factor can be obtained by increasing the sample to eluent volume ratio by either decreasing the eluent volume and/or increasing the sample volume. Therefore, the effect of sample volume on the retention behavior of the lead(II) ions was investigated by passing 100-2800 mL of solutions. As shown in Figure **5**, the recovery was found to be stable until 2200 mL. Consequently, by considering the final elution volume of 5 mL and the sample solution volume of 2200 mL, an preconcentration factor 440 is obtained.

3.6. Linear Range and Detection Limit of the Proposed Method

By employing the optimum experimental conditions, the calibration graphs for lead(II) ions were obtained. The calibration graph exhibits linearity over the range of 0.1-250 µg L^{-1} with a correlation of 0.9997. The limit of detection (LOD) of the proposed method for the determination of lead(II) was studied. The LOD obtained from $C_{LOD} = K_b S_b m^{-1}$ for a numerical factor K_b = 3 and preconcentration factor of 440, is 85.4 ng L^{-1}. K_b is confidence factor (the factor K_b is most often chosen to be 2 or 3), S_b is the standard deviation of the blank measurement, and m is the slope of the calibration curve at particular concentration (n = 5).

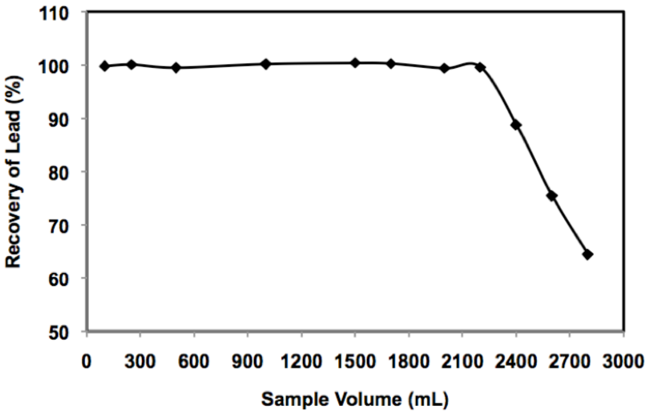

Figure 5: Effect of sample solution volume (other conditions: 10 µg of Pb^{2+}; sample flow rate: 12 mL min^{-1}; eluent flow rate: 8 mL min^{-1}; pH = 6.0; room temperature; n=3).

3.7. Retention Capaciy of Membrane

Retention capacity is an important parameter for the evaluation of adsorbent. It is the maximum metal ion quantity taken up by modified membrane disk. In order to study the maximum capacity of the membrane disk modified by 4.0 mg of MMAB, 50 mL portions of an aqueous solution containing 1500 µg lead(II) ions was passed through the disk, followed by determination of the retained lead(II) ions using ICP-AES. The maximum capacity was found to the 527 ± 4 µg of Pb^{2+} ions on the disk. This indicates that the membrane disk is capable of absorbing large amounts of lead(II) ions.

3.8. Effect of Interfering Ions

Because of the presence of other elements in real samples, the determination and preconcentration of lead(II) ions are difficult. Therefore, the effect of common coexisting cations (and anions) on the adsorption of lead(II) ions on the modified membrane disk were investigate. Metal cations were added individually to 50 mL sample solutions containing 1.0 µg L^{-1} Pb^{2+} ions. The tolerance limit was considered if it resulted in ± 3% variation in sorption efficiency of Pb^{2+}. It has been found (from Table **3**) that recovery of lead(II) was almost quantitative in presence of foreign ions and therefore useful for the analysis of this ions in real samples.

Table 3: Tolerance Limits for Coexisting Ions in Adsorption of Lead(II) Ions[a]

Foreign ion	Interferent / ion ratio (M^{n+}/Pb^{2+})	Recovery (%)[b]
Na^+	30000	100.2 ± 1.4
K^+	30000	100.0 ± 3.1
Ca^{2+}	30000	99.8 ± 2.2
Mg^{2+}	30000	99.8 ± 2.5
Sr^{2+}	30000	101.2 ± 1.3
Zn^{2+}	5000	99.9 ± 2.2
Ag^+	5000	99.7 ± 3.1
Fe^{2+}	5000	100.6 ± 1.8
Mn^{2+}	5000	100.4 ± 2.6
Co^{2+}	5000	99.5 ± 1.4
Ni^{2+}	5000	98.7 ± 1.6
Cd^{2+}	300	99.2 ± 1.5
Cu^{2+}	300	98.8 ± 1.0

[a] Initial samples contained 1.0 µg L^{-1} Pb^{2+} ions.
[b] The values following "±" is the standard deviation (n = 3).

3.9. Analysis of Real Samples

Various amounts of lead(II) ions were spiked to blood, spinach, bean, hair, milk, pepper and some water samples. Then the procedure presented was applied to the determination of lead(II) in these samples. The results are given in Table **4**. As can be seen, the results obtained by the proposed method and ICP-AES are in satisfactory agreement with the added lead(II) ions amounts. These results confirm the validity of the proposed method.

Table 4: Recovery Studies of Lead(II) Ions Determination in Real Samples[a]

Sample	Added value	Found value[b]	Recovery (%)
Blood	0.0	0.028 ± 0.007	-
	0.2	0.233 ± 0.010	102.5
Spinach	0.0	0.166 ± 0.008	-
	0.2	0.370 ± 0.034	102
Bean	0.0	0.083 ± 0.011	-
	0.3	0.395 ± 0.008	104
Hair	0.0	0.196 ± 0.021	-
	0.3	0.505 ± 0.085	103
Milk	0.0	0.061 ± 0.014	-
	0.3	0.375 ± 0.006	104.7
Hot pepper	0.0	1.250 ± 0.012	-
	0.5	1.769 ± 0.026	103.8
Tap water	0.0	0.024 ± 0.005	-
	0.5	0.519 ± 0.014	99
River water	0.0	0.043 ± 0.005	-
	0.5	0.545 ± 0.038	100.4
Spring water	0.0	0.034 ± 0.002	-
	0.5	0.542 ± 0.013	101.6

[a] The unit for solid samples is µg g^{-1} and for liquid samples is µg mL^{-1}.
[b] The values following "±" is the standard deviation (n = 3).

Table 5: Comparative Data from Published Methods on Solid Phase Extraction of Lead Ions

Adsorbent	pH	Eluent	Flow rate (mL min^{-1})	PF[a]	LOD[b] (μg mL^{-1})	Reference
Sodium dodecyl sulfate coated PVC	7	10 mL HNO$_3$ (3 mol L^{-1})	-	50	0.29	14
Graphene	6	2 mL HNO$_3$ (2 mol L^{-1})	2	125	0.61	18
Solid sulfur	8	2 mL HNO$_3$ (1 mol L^{-1})	1	250	3.2	27
Oxidized SWCNTs[c]	7-9	2 mL HNO$_3$ (0.5 mol L^{-1})	1.2	50	0.005	28
1-acylthiosemicarbazide modified activated carbon	3	3 mL CS(NH$_2$)$_2$ (2%) and HNO$_3$ (2 mol L^{-1})	1	100	0.45	29
2-aminoacetylthiophenol modified polyurethane foam	5	6 mL HNO$_3$ (1 mol L^{-1})	3	167	0.066	30
Modified nanometer alumina	7-8	2 mL HNO$_3$ (2 mol L^{-1})	3	250	0.17	31
MWCNTs[d]	9	5 mL HNO$_3$ (1 mol L^{-1})[e]	1	20	8.0	32
MnO$_2$ coated carbon nanotubes	6	1.5 mL HNO$_3$ (1.5 mol L^{-1})	2.5	100	4.4	33
2-(2,4-dichlorobenzylideneamino) banzenthiol modified Duolite XAD 761	7	10 mL HNO$_3$ (4 mol L^{-1})	2-3	150	2.9	34
Poly(2-amino thiophenol) modified MWCNTs	6	7.5 mL HNO$_3$ (10% (v/v))	0.5-2	280	1.0	35
Benzenecarbothioamide modified octadecyl silica membrane disk	3.5-8	5 mL HNO$_3$ (2 mol L^{-1})	12	440	0.085	Current work

[a] Preconcentration factor.
[b] Limit of detection.
[c] Single-walled carbon nanotubes.
[d] Multi-walled carbon nanotubes.
[e] in acetone.

4. CONCLUSION

A proposed procedure provides a simple, economical, rapid, and precise method for the preconcentration and determination of lead(II) ions using an SPE method with octadecyl-bonded silica membrane disks modified by 4-methyl-N-{2-(4-methylbenzothioyl) aminoethyl}benzenecarbothioamide. This technique was successfully applied for separation, determination and preconcentration of lead(II) ions in various samples, namely blood, spinach, bean, hair, milk, pepper and some water samples. A comparison of the pH, eluent flow rate, preconcentration factor and limit of detection of represented method with other SPE methods (with different adsorbent) reported in the literature [14, 18, 27-35] was given in Table **5**. Higher preconcentration factor, faster flow rate, wider pH range and comparable limit of detection are some of the advantaged of proposed method. In short, this method is suitable for preconcentration and separation of trace and ultra trace amounts of lead(II) ions in real samples.

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