

Solid Phase Extraction and Determination of Traces Amounts of Lead(II) Using Octadecyl Membrane Disks Modified by a Novel Schiff's Base and Flame Atomic Absorption Spectrometry

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Dedicated to: Professor Kazem Kargosha

A highly selective, facile and reliable method for separation and preconcentration of the traces amounts of lead present in aqueous samples is introduced. By passing the solutions through an octadecyl silica membrane disk modified by a novel Schiff's base, Pb^{2+} ions are adsorbed quantitatively while almost all interfering ions pass through the disk. The retained lead(II) ions are then eluted from the disk surface by minimal amount of organic eluents. The influences of pH, sample flow-rates and interfering ions are also investigated. The proposed method permits an enrichment factor of about 500 or higher and a detection limit of $0.0065 \text{ ng.mL}^{-1}$.

INTRODUCTION

Lead chemistry is of prime interest because of its cumulative toxicity and harmful influences on animals and human health. Cumulative poisoning effect of lead causes hematological damage, anemia, kidney malfunctioning, brain damage, muscles sore, fatigue, irritation, and disturbance in central nervous system. ¹

Inorganic lead is attached with thiol group (-SH) in proteins or enzymes and hence considered as an inhibitor. This element disturbs calcium metabolism and deposits in the bone. Meanwhile, the organic derivatives of lead are highly toxic because the easiness of their absorption by the body through skin and mucus membranes. ² The typical level of Pb^{2+} in natural water lies between 2 and 10 ng.mL^{-1} , whereas, the upper limit recommended by world health organization (WHO) is less than 10 ng.mL^{-1} . The presence of lead in the industrial wastes is also undesirable. This is mainly because of the possibility of its passing onto foods or other products used or consumed by people. ³

The most common procedures and techniques for determination of lead involve spectrophotometry, ^{4,5} flame atomic absorption spectrometry, ^{6,7} electrothermal atomic absorption spectrometry (ETAAS), ^{8,9} inductively coupled plasma atomic emission spectrometry (ICP-AES), ¹⁰ inductively coupled plasma optical emission spectrometry (ICP-OES), ¹¹ inductively coupled plasma - mass spectrometry (ICP-MS), ¹² and non-dispersive atomic fluorescence spectrometry (ND-AFS). ¹³

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The major drawbacks of the mentioned methods are insufficient sensitivity and selectivity, inadequate concentration factor, unsatisfactory relative standard deviations and expensive instrumentation.

Regarding the lead presence in various environmental and biological samples at low levels, designing new approaches and development of the techniques concerning preconcentration, separation and determination of lead is necessary and has a vital and critical importance.

Solvent extraction methods of various metal ions have been widely utilized in literature.¹⁴

However, conventional classical methods are frequently time consuming, labor intensive, require too large volumes of ultrapure hazardous solvents, comprising elaborate experimental steps, encounter with emulsion formation, and suffer from elaborative automation, practically. An additional concern is the disposal cost of the solvents used which creates severe environmental problems. In order to reduce the risks of environmental pollution, exposure and consumption of poisonous organic solvents, disposal cost, extraction time and also improvement of the method efficiency, solid phase extraction (SPE) is considered as the best attractive alternative method.

In literature, there are numerous reports for efficient sorbents for SPE determination of the trace levels of lead in various samples. The most common employed adsorbents include co-crystallized naphthalene,¹¹ chelating resins (Amberlite XAD-2, Amberlite XAD-7, and Amberlite IRC-718),¹²⁻¹⁶ amino carboxylic acid-type cellulose known as Chelest fiber Iry,¹⁷ functionalized activated carbon,¹⁸ poly tetra fluoro ethylene (PTFE) turnings,¹⁹ immobilized C₁₈ on silica, activated carbon and polyurethane foam,²⁰ cellulose nitrate,²¹ rice bran,²² and silica gel chemically immobilized by 4-aminoantipyrine.²³

Among the various SPE features, modified octadecyl silica membrane disks are known as excellent sorbents for trace amounts of metal ions and possess advantages as: shorter sample processing time and decreased plugging by suspended materials and matrix components due to the large cross-sectional area of the disk, more density; uniformity of packing; and decrease pressure drop which allows the sample processing at higher flow-rates; reduced channeling and favorable handling of small sample volumes resulting from facility of preparation of small diameter sorbent and a greater mechanical stability of the sorbent bed; selectively extraction and enrichment of the trace elements of interest thereby avoiding the presence of matrix ions; flexibility: supportable structure by using a porous glass or plastic supports; easiness of automation and possibility of on-line coupling to other analytical techniques; wide application domain including preconcentration of the trace metals and their organic compounds; determination of colloiddally associated polycyclic aromatic hydrocarbons (PAH); herbicides; drugs; natural and humic products; and higher preconcentration factor over similar adsorbents.^{1, 24-25}

We have recently modified and utilized C₁₈ disks for enrichment and monitoring traces of chromium²⁶⁻²⁷ and lead.²⁸

In recent years, different trapped Schiff's bases on octadecyl silica membrane disks have been successfully used for preconcentration, separation and determination of the trace amounts of lead,²⁹⁻³⁰ copper,³¹⁻³² and lead and copper, simultaneously.³³⁻³⁴

In Table 1, the typical structure and selectivity of the usual utilized Schiff's bases toward certain trace metal ions are compared. In the present report, we wish to describe an efficient, selective and concentrative method for assessment of trace levels of lead in different water samples. To the best of our knowledge, octadecyl silica membrane disks modified by the introduced symmetrical Schiff's base (NNDED) (Fig. 1) have not been used for isolation, preconcentration and monitoring of the lead traces, previously.

EXPERIMENTAL PROCEDURES

Reagents and materials

All chemicals were of analytical grade and used as received without any further purification. Ultra pure organic solvents and analytical grade nitrate salts of lithium, sodium, potassium, cesium, magnesium, calcium, strontium, barium, aluminum, mercury(I), mercury(II), thallium(I), thallium(III), tin(II), manganese(II), zinc, cadmium, lead, nickel, cobalt(II), copper(II), iron(II), iron(III), chromium(III) and potassium dichromate were of the highest purity and obtained from E. Merck, Darmstadt, Germany. Solid phase extractions were carried out by glassy membrane disks, ENVI-18DSK™ 47mm diameter × 0.6 mm thickness containing octadecyl silica bonded phase (irregular 30µm particles, 70 Å pore size) purchased from Supelco (Bellefonte, PA 16823). The typical composition of ENVI-18DSK™ membrane disks contain glass fiber embedded with surface modified silica having a disk void volume of 500 µL and a mean flow-through porosity of 5 µL. The typical capacity of an ENVI-18DSK™ for well retained species ranges from 10 to 20 mg. The employed disks are capable of separating bulky ion-pairs and neutral organic and organometallic molecules. The nylon filters (45 µm) used for filtration of water samples were obtained from S&S Company. Deionized water was prepared by passing of double distilled water through Nano-pure ultrapure water system from Barnstead Company (U.S.A) and was used throughout the experiments.

Apparatus

The NMR spectra were recorded on a Joel 90 MHz spectrometer, and TMS was used as internal reference. The FT-IR spectra were recorded on a Shimadzu 4300 instrument using KBr pellets. The MS spectra were recorded on a Shimadzu GC-14A gas chromatograph-mass spectrometer. Determination of chromium contents in working samples were carried out on a Varian spectra A.200 model atomic absorption spectrometer equipped with a high intensity hollow cathode lamp (HI-HCL) according to the recommendations of the manufacturers. These characteristics are tabulated in Table 2.

Solid phase extractions were conducted by the mentioned membrane disks, in conjunction with a standard Millipore 47mm filtration apparatus equipped with a desktop vacuum pump. The pH measurements were carried out by an ATC pH meter equipped with a combined glass calomel electrode (EDT instruments, GP 353).

NNDED: Synthesis and its spectral characteristics

The procedure for preparation of *N,N'*-disalicylideneethylenediamine (NNDED) is as follows: A mixture of 0.002 mol salicyl aldehyde and 0.001 mol of ethylene diamine in 10 to 15 mL of absolute methanol was refluxed in a round bottom flask for 1 h. The solvent was then evaporated and the residue was crystallized from 95% ethanol as a yellow

precipitate. The precipitate was thereafter recrystallized in absolute ethanol and finally dried in vacuum. The specifications of the yellow crystals obtained as product were: mp: 126-128 °C; IR (KBr) ($\nu_{\text{max}}/\text{cm}^{-1}$): 3050, 2932, 2901, 2870, 1636, 1497, 1283, 1149, 1042, 1021, 857, 749, 741; MS, m/z (%): 268 (M^+ , 23); Anal. Calcd for $C_{16}H_{16}N_2O_2$ (268.31): C, 71.62; H, 6.01; N, 10.44; O, 11.92. Found: C, 71.8; H, 6.05; N, 10.3; O, 11.8 %. ^1H NMR (250.1 MHz, DCCl_3): δ 3.9 (s, 4 H, CH_2), 6.8(m, 4 H), 7.3(m, 4 H), 8.3(s, 2 H), 13.2(brs, 2 H, Ar-OH)

Stock and standard solution preparation and regression equation

The stock solution of lead(II) was prepared by dissolving a proper amount of analytical grade lead(II) nitrate (159.8 mg) in 100 mL of deionized water. One mL of dilute nitric acid was added to this solution to prevent the hydrolysis of lead ions. The working solutions of lead were prepared by accurate stepwise dilution of the stock solution with double distilled deionized water. The linear regression equation of lead(II) standard solutions was as $A = 0.016C + 0.0032$ with a correlation coefficient of $r^2 = 0.9997$ using an external calibration curve. The linearity of the graph was in the range of $2.5\text{--}30\text{ }\mu\text{g}\cdot\text{mL}^{-1}$.

Sample extraction

The performance steps of the employed solid phase extraction - flame atomic absorption spectrometry (SPE-FAAS) technique were as follows:

1) *Sample treatment*: In order to eliminate small suspended materials, water samples were filtered through $45\text{ }\mu\text{m}$ nylon filters before extraction. Sampling vessels were polyethylene bottles soaked in $1\text{ mol}\cdot\text{L}^{-1}\text{ HNO}_3$ overnight, rinsed twice with deionized water, and dried in a dust-free environment.

2) *Disk cleaning and conditioning*: In order to remove potential interferences and to ensure optimal extraction of the analyte of interest, the disk cleaning and conditioning should be carried out before its use. Therefore, after placing the disk in the filtration apparatus, 10 mL of methanol was poured onto the disk and immediately drawn through the disk by applying a slight vacuum. When all the solvent passed through the disk, it was dried by passing air through it for a few minutes. The disk conditioning was done by introducing 10 mL of methanol onto the disk. Immediately a low vacuum was applied and the solvent was drawn through the disk until the solvent surface almost reaches the surface of the disk. The disk should not be allowed to soak without vacuum, and air contact with the surface of the disk should be avoided. This is to ensure complete wetting of the disk with the organic solvent. It is preferable to leave some extra methanol on top of the disk rather than allowing air contact. Immediately thereafter 20 mL of water was poured onto the disk and was drawn through it. The disk was then dried under the vacuum for 5 min or longer if necessary. This is especially important for the disks which are used for the first time.

3) *Disk modification*: This step could be performed by either of the following manners:

a) A solution of 4 mg of NNDED in 1 mL of CHCl_3 was introduced onto the disk and drawn slowly through it by applying a slight vacuum. The passed solution was collected in a test tube. Then, water was added drop-by-drop to the test tube until the formation of the suspension began and the subsequent solution becomes turbid. The resulting suspension was again introduced onto the disk and passed through the disk slowly. The

filtration and addition of water step was repeated until the passed solution becomes completely clear. The disk was then washed with 25 mL of water and dried by passing air through it.

b) A solution of 4 mg of NNDED in 1 mL of chloroform was added to the top reservoir of the apparatus and was drawn slowly through the disk by applying a slight vacuum until the ligand penetrates the membrane completely. The solvent was evaporated by a warm blower (at about 50 °C). The modified membrane disk is now ready for sample extraction. The activated and modified membrane disk is stable up to nearly two months and should be stored in a dry and dark place.

4) *Analyte elution*: The general procedure for the extraction of Pb^{2+} contents was as follows: after drying, the modified disk was washed with 25 mL of water to pre-wet the surface of the disk prior to the extraction. Then, 500 mL of the completely homogenized sample solution containing 10 µg of Pb^{2+} was passed through the membrane disk (flow-rate = 60 mL min⁻¹). After the extraction, the disk was dried completely by passing air through it and a 23 mm × 200 mm test tube was placed under the extraction funnel. The adsorbed lead was then stripped from the membrane disk using 5 mL of an appropriate organic solvent which is compatible with flame and does not change the signal to noise ratio, at a flow-rate of 5-15 mL min⁻¹. The lead content in the eluate was then determined by FAAS using an external calibration graph. To achieve higher selectivity and minimize the influence of the probable impurities present in acids used for pH adjustments, a blank determination was carried out.

RESULTS AND DISCUSSION

Investigation of the ligand nature and role

The NNDED is a Schiff's base with 2N and 2S donating atoms and is slightly soluble in water at neutral pH. This reagent is quite stable in the pH range 3.0 to 8.0 and is washed out from the disk surface by the stripping solvents, sparingly. Our recent conductometric investigations in acetonitrile revealed that it can form a fairly stable and selective complex with Pb^{2+} ion.³⁵

Therefore, we decided to utilize of this reagent as a novel modifier for our studies. Additionally, some preliminary experiments were performed to evaluate the quantitative retention and subsequent clean-up and extraction of lead(II) traces in the absence and presence of NNDED by the octadecyl silica membrane disks. It was concluded that while the membrane disk does not show any tendency for the extraction of Pb^{2+} ions, the modified membrane disks are capable of quantitative extraction of the Pb^{2+} traces in sample solutions, satisfactorily. This is most probably due to the strong interaction between Pb^{2+} and the ligand. These observations are summarized in Table 3.

Elution of the retained Pb^{2+} ions

For selection of the proper stripping agent for desorption of the sorbed Pb^{2+} ions from the disk surface, after extraction of 10 µg of lead(II) content from a 500 mL water sample by one of the modified disks, desorption of Pb^{2+} ions was carried out by different volumes of several mineral and organic solvents. The results are tabulated in Table 4. As it is seen, among the 25 different stripping solutions used, the minimum volume required for quantitative desorption of Pb^{2+} ions is 5 mL of methanol, ethanol, 1-propanol, or 1-

butanol. It is noteworthy that methanol addition to each of the mineral eluting agents, leads to more efficient extractions. This is mainly because of the better contact of eluent with hydrophobic surface of the disk. To evaluate the percent extraction among the sequential volumes of appropriate and efficient eluting solutions, after the extraction of 10 µg of lead(II) from 500 mL of water sample (pH=4.0), the clean-up procedure was followed by five 1 ml portions of each. The related results are presented in Table 5.

Effect of pH on lead recovery

The pH influence on the recovery of 10µg of Pb^{2+} in 500 mL of water sample was investigated in the pH range of 1.0 to 8.0. The pH was adjusted by using 0.1M of either hydrochloric acid or sodium hydroxide solution. According to Fig. 2, the Pb^{2+} ions can be retained quantitatively by the modified membrane disk through the pH range 3.0 to 8.0. However, at lower pH (<3.0), nitrogen atoms of the NNDED could be protonated and the stability of complex is reduced. Meanwhile, the higher pH values (>8.0) were not tested because of the possibility of the hydrolysis of octadecyl silica bonded phase of the membrane disks.³⁶ To achieve higher selectivity and better results, it was decided to adjust the pH of the lead solution to 4.0 throughout the experiments.

Optimum amount of the modifier (NNDED)

In order to investigate the minimum amount of NNDED needed for quantitative extraction of 10 µg of Pb^{2+} from a 500 mL aqueous sample, the extraction was conducted by different amounts of the modifier from 0 to 10 mg (Table 6). As can be seen, the extraction of lead is satisfactory when 4 mg of NNDED is used. Hence, subsequent extraction experiments were performed with 4 mg of NNDED. It is also notable that as the amount of loaded ligand on the membrane disk increases, the required flow-rate of the solutions through the modified disk decreases.

The influence of the flow-rate

The effect of flow-rates of sample solutions on the retention and recovery of Pb^{2+} ions was examined. Under the optimum conditions, it was found out that in the range of 5-80 mL.min⁻¹, the retention of lead ions is hardly affected by the sample solution flow-rate (Fig. 3). The flow-rate was maintained at 60 mL.min⁻¹ throughout the experiments. In the other hand, quantitative stripping of Pb^{2+} ions from the modified membrane disks was obtained at a flow-rate ranging from 5-15 mL.min⁻¹ using 5 mL of each methanol or ethanol or their acidified solutions. A flow-rate of 10 mL.min⁻¹ was chosen for eluting solvents during desorption.

Counter ion influence on Pb^{2+} recovery

The interferences caused by different counter anions were examined under the optimal experimental conditions and the subsequent results are summarized in Table 7. According to these results, in presence of some counter ions such as nitrate, nitrite, salicylate, oxalate, vanadate, formate, acetate, perchlorate, dihydrogen phosphate and iodate, the extraction is complete and the subsequent recovery is quantitative. Most probably it indicates a strong interaction between Pb^{2+} ions and the employed NNDED. It should be noted that in some cases, the anion increases the efficiency of the modified disk.³⁷

Discussion on membrane efficiency

One of the main points that should be investigated for SPE determinations is the efficiency of the employed disks. Under optimized conditions, it was found out that each ENVI-18DSK™ disk could afford at least 22 replicate analyses when organic eluents are utilized, while acidic eluents practically lower the number of times of the quantitative extractions to a maximum of 16 replicates. The influence of the eluent type on percent recovery has been compared and demonstrated in Fig. 4.

Analytical performance

The maximum capacity of the modified membrane disk loaded with 4 mg of the NNDED, was determined by passing 500 mL portions of an aqueous solution containing 400 µg of lead at pH 4.0 followed by the determination of the stripped Pb^{2+} contents using FAAS by means of an external calibration graph. The maximal capacity of the used membrane disk was found to be 278 ± 1.9 µg of Pb^{2+} ion on the disk.

By passing different volumes of aqueous solutions, each of them containing 10 µg of Pb^{2+} ion in 50, 100, 500, 1000, 2000 and 2500 mL solutions under optimal experimental conditions, the Pb^{2+} ions were quantitatively retained in all cases. Hence, the breakthrough volume of the described method should be greater than 2500 mL. Therefore, by considering the final elution volume of the proper stripping agent (5 mL), an enrichment factor of about 500 is easily achievable.

The limit of detection (LOD) of the proposed procedure was estimated under the optimal experimental conditions. The LOD obtained from $C_{LOD} = K_b S_b \cdot m^{-1}$ ^{38,39} for a numerical factor of K_b and a concentration factor of about 500 is 0.0065 ng.mL⁻¹.

Separation and determination of lead in presence of interfering ions, synthetic and real samples

In order to discuss on the selective separation and monitoring of lead traces in the solutions containing different cations, an aliquot of aqueous solution (500 mL) containing 10 µg of Pb^{2+} and microgram amounts of other cations were chosen and the recommended procedure was followed. The results which are shown in Table 8 reveal that the lead ions in presence of foreign ions are retained completely under the experimental conditions by the modified membrane disk, while, the retention of the other cations are simultaneously negligible. Consequently, their interferences are omitted. Meanwhile, to assess the applicability of the proposed method to various matrices involving different amounts of interfering ions; it was applied for separation and extraction of Pb^{2+} ions from five synthetic samples (Table 9). Obviously, the results of five individual replicate analyses of each sample indicated that, in all cases, the lead recoveries are drastically quantitative. Meanwhile, to examine the applicability of the described method, it was employed for selective extraction and determination of lead in different water samples (Table 10) including tap waters (taken immediately and after 5 min operation of the tap), well water (Tehran, 10 February 2004), rain water (Tehran, 10 June 2004), snow water (Tehran, 20 November 2004), spring water (Oshan&Fasham, 16 December 2004), river water (Jajrood, 22 December, 2004) and two waste water samples (Tehranpars, 12 April 2004). As it is seen, the recovered lead ion reveals that the results are quite reliable.

CONCLUSION

The proposed method is facile, inexpensive, reproducible, highly selective, relatively fast in comparison with similar reports, and its reproducibility is at the most 2 %. The maximum time taken for the isolation, enrichment and analysis of 10 µg of lead in a 500 mL water sample is at the most 12 min. Table I clearly indicates the comparability or even superiority of the used NNDED as an excellent modifier for octadecyl silica bonded phase sorbents, favorable LOD and significant preconcentration factor which improves the LOD of the method by a factor of about 500. The suggested procedure is also free from interferences associated with lead in various samples and is capable for monitoring trace and ultra trace levels (sub-ppb) of inorganic lead, efficiently.

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Keywords: Lead(II), Schiff's base, Solid phase extraction, Flame atomic absorption spectrometry

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Table I. The effect of the different Schiff's base molecular structures on their selectivity toward different metal traces by using C_{18} octadecyl silica bonded phase sorbent.


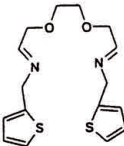
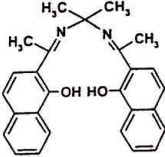
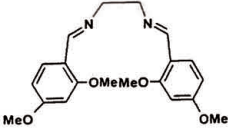
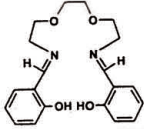
Schiff's base	Ion(s) of interest	Ref.
	Pb^{2-}	29
	Pb^{2-}	30
	Cu^{2-}	31
	Pb^{2-} & Cu^{2-}	33
	Pb^{2-} & Cu^{2-}	34

Table 2. The operational characteristics of flame.

Type of background correction	Deuterium lamp
Length of air -acetylene burner	13.0 mm
Operation current of HI-HCL	10.0 mA
Resonance line	217.0 nm
Slit width	1.0 nm
Type of flame	air/acetylene
Air flow	13.50 L.min ⁻¹
Acetylene flow	2.0 L.min ⁻¹

Table 3. The effect of NNDFD on extraction percent of lead(II) ^a

Ligand	pH range	Percentage recovery
Absence	1-8	0.00
Presence	1-8	35(2.1) ^b - 100(1.6)

^a Initial samples contained 10 µg of Pb²⁺ in a 500 mL of sample.

^b Values in parentheses are RSDs based on five individual replicate analyses.

Table 4. Percentage recovery of lead(II) through the modified disk using different eluting solutions^a

Removal solution	Recovery (%)		
	3 mL	5 mL	10 mL
CH ₃ OH	74.3(0.2) ^d	100.1(1.3)	99.9(2.2)
Acidified CH ₃ OH ^b	12.2(1.3)	34.5(2.6)	61.1(4.9)
Alkaline CH ₃ OH ^c	16.3(2.2)	75.3(5.5)	82.4(1.2)
C ₂ H ₅ OH	78.2(4.1)	99.8(0.6)	100.1(1.6)
Acidized C ₂ H ₅ OH	7.4(3.6)	48.2(1.7)	52.2(4.1)
Alkaline C ₂ H ₅ OH	17.6(2.4)	64.5(2.5)	71.5(3.1)
CH ₃ OHCH ₂ CH ₃	81.2(0.7)	100.2(2.0)	98.3(0.5)
HCOOH(1M)	10.3(0.3)	21.1(1.1)	27.4(1.9)
HCOOH(3M)	6.1(2.2)	14.9(0.7)	33.2(2.1)
CH ₃ OHCH ₂ CH ₂ CH ₃	66.9(1.4)	98.2(6.4)	96.9(0.7)
CH ₃ CHOHCH ₂ CH ₃	63.1(0.2)	80.1(1.1)	99.1(0.6)
HCl(1M)*	14.2(0.1)	54.1(0.7)	36.4(1.3)
HCl(3M)*	27.3(0.9)	9.5(4.2)	32.7(1.0)
HNO ₃ (0.5M)*	16.4(2.3)	26.3(4.1)	30.1(0.7)
HNO ₃ (1M)*	2.3(2.5)	7.0(2.0)	54.1(3.2)
HNO ₃ (3M)*	2.1(1.2)	4.1(2.8)	29.3(0.9)
CH ₃ COOH(1M)*	4.1(0.4)	6.2(3.6)	17.4(0.4)
CH ₃ COOH(3M)*	6.8(2.5)	8.5(0.3)	52.3(0.2)
H ₃ PO ₄ (1M)*	11.3(1.5)	34.8(0.1)	49.9(1.5)
H ₃ PO ₄ (3M)*	9.4(3.7)	43.8(0.7)	47.6(4.0)
HBr(1M)*	7.8(2.6)	7.2(1.6)	15.5(0.8)
HBr(3M)*	16.1(4.9)	14.7(0.3)	19.8(1.6)
Na ₂ S ₂ O ₃ (1M)	7.1(0.3)	10.1(0.4)	18.2(0.7)
NH ₄ SCN(1M)	2.1(1.4)	1.4(0.6)	6.8(3.3)
MIBK	32.4(8.7)	83.1(7.8)	71.7(5.6)

^a Initial samples contained 10 µg of Pb²⁺ in a 500 mL of sample.^b Acidified organic solutions with 0.1M HCl.^c Alkaline organic solutions obtained by using 0.1M NH₃.* Solutions containing methanol (5 % w.v⁻¹).^d Values in parentheses are RSDs based on five individual replicate analyses.

Table 5. Percent extraction of lead from modified C₁₈ membrane disk by using the sequential volumes of stripping solutions ^a

Eluent agent	Volume (mL)					Total
	First 1 mL	Second 1 mL	Third 1 mL	Forth 1 mL	Fifth 1 mL	
Methanol	33.2	21.1	16.8	19.4	9.6	100.1
Ethanol	29.8	13.6	18.4	23.3	14.7	99.8
1-Propanol	18.6	22.4	33.1	21.1	5.0	100.2
1-Butanol	14.1	20.2	26.7	18.3	18.9	98.2

^a Initial samples contained 10 µg of Pb²⁺ in a 500 mL of sample.

Table 6. The influence of NNDED amount on the recovery of Pb^{2+} ions using 5 mL of methanol as eluent ^a

Ligand amount (mg)	Recovery (%) of Pb^{2+}
0	0.00
1	58.7(1.1)
2	86.1(4.5) ^b
3	90.2(2.5)
4	99.9(1.6)
5	99.2(1.4)
7	98.7(3.1)
9	98.1(0.6)
10	99.3(2.2)

^a Initial samples contained 10 μg of Pb^{2+} in a 500 mL of sample.

^b Values in parentheses are RSDs based on five individual replicate analyses.

Table 7. Percentage recovery of lead in the presence of different counter anions ^a

Counter ion	Concentration (M)	Recovery (%) of Pb ²⁺
NO ₃ ⁻	0.01	99.2(0.6) ^b
NO ₂ ⁻	0.01	99.8(1.4)
C ₇ H ₅ O ₂ ⁻	0.01	98.6(2.1)
C ₂ O ₄ ²⁻	0.1	99.9(1.8)
VO ₃ ⁻	0.0001	100.1(0.7)
HCOO ⁻	0.01	99.8(0.5)
CH ₃ COO ⁻	0.1	98.4(1.6)
ClO ₄ ⁻	0.1	98.8(1.8)
H ₂ PO ₄ ⁻	0.01	100.0(2.3)
IO ₃ ⁻	0.1	99.9(1.2)

^a Initial samples contained 10 µg of Pb²⁺ in a 500 mL of sample.

^b Values in parentheses are RSDs based on five individual replicate analyses.

Table 8. The effect of interfering ions on recovery of Pb^{2+} ion ^a

Diverse ion	Amount taken (μg)	Found (%)	Recovery (%) of Pb^{2+}
Li^+	5000	NAOD ^a	100.1(0.3)
Na^+	5000	NAOD	100.2(0.7)
K^+	5000	NAOD	99.8(1.4)
Cs^+	5000	NAOD	98.4(2.8)
Mg^{2+}	2500	NAOD	99.2(0.9)
Ca^{2+}	2500	3.0(1.2)	99.2(1.1)
Sr^{2+}	2500	NAOD	97.4(1.8)
Ba^{2+}	2500	2.5(2.1)	100.1(0.2)
Al^{3+}	2500	8.0(1.9)	100.0(0.4)
Hg_2^{2+}	850	5.1(1.3)	100.0(2.1)
Hg^{2+}	2500	4.5(0.7)	98.6(2.5)
Tl^+	2500	NAOD	99.1(3.1)
Zn^{2+}	2500	NAOD	100.2(0.6)
Fe^{2+}	300	NAOD	97.4(0.7)
Fe^{3+}	100	NAOD	99.9(1.6)
Mn^{2+}	250	3.2(0.4)	98.2(3.3)
Sn^{2+}	800	NAOD	99.3(0.4)
Cr^{3+}	500	NAOD	98.5(0.9)
Cr^{6+}	500	NAOD	99.3(1.5)
Co^{2+}	200	NAOD	99.8(2.3)
Cd^{2+}	100	8.0(2.3)	100.3(1.1)

^a Initial samples contained 10 μg of Pb^{2+} in 500 mL of water.^b No adsorption occurred through the disk.^c Values in parentheses are RSDs based on five individual replicate analyses.

Table 9. Percentage recovery from a synthetic sample containing 10 µg of lead (pH=4.0)

Synthetic sample	Ingredients	Recovery(%) of Pb
1	Al ³⁺ , Sr ²⁺ , Hg ²⁺ and Tl ¹⁺ (2.5mg) ^a	99.3(1.3) ^a
2	Ce ³⁺ , Ti(IV) and Zn ² (2.5mg)	100.1(1.2)
3	Fe ²⁺ , Fe ³⁺ and Mn ²⁺ (1mg)	99.8(2.4)
4	V ³⁺ , Tl ¹⁺ and Sn ²⁺ (1mg)	99.3(0.7)
5	Cr ³⁺ , Cr(VI) and Cd ²⁺ (5mg)	98.8(1.6)

^a Values in parentheses are mg amounts of each mentioned cation.^b Values in parentheses are RSDs based on five individual replicate analyses.

Table 10. Percent recovery of 10 µg of lead added to a 500 mL solution of real water samples

Sample	Pb content (µg)	Recovered amount (µg)
Tap water 1	BDL ^a	10.1(3.6) ^b
Tap water 2	BDL	10.0(2.7)
Well water	10	19.8(1.6)
Rain water	BDL	9.9(1.4)
Snow water	BDL	9.9(0.7)
Spring water	BDL	10.2(0.6)
River water	BDL	9.8(3.1)
Waste water 1	100	109.7(2.2)
Waste water 2	70	80.0(1.3)

^a Below detection limit^b Values in parentheses are RSDs based on five individual replicate analyses.

Table 11. Comparison of the efficiencies of the suggested method and published similar reports using octadecyl silica membrane disks

Ion(s) of interest	Enrichment factor			Sample flow-rate range (mL.min ⁻¹)	LOD (ng. mL ⁻¹)			Ref
	Pb ²⁺	Cu ²⁺	Ag ⁺		Pb ²⁺	Cu ²⁺	Ag ⁺	
Pb ²⁺	120	-	-	20	16.7	-	-	29
Pb ²⁺	100	-	-	1-30	0.075	-	-	30
Cu ²⁺	-	500	-	1-15	-	0.012	-	31
Pb ²⁺ , Cu ²⁺	200	200	-	1-20	0.9	0.2	-	34
Pb ²⁺	75	-	-	1-60	5	-	-	41
Ag ⁺	-	-	400	5-25	-	-	0.1	42
Ag ⁺	-	-	150	1-20	-	-	0.001	43
Pb ²⁺	>500	-	-	65	0.0065	-	-	proposed method

Fig. 1. The molecular structure of *N,N'*-disalicylideneethylenediamine(NNDED)

Fig. 2. Percent recovery of lead in the pH range 1.0 to 8.0.

Fig. 3. The influence of the sample flow-rates on percentage extraction

Fig. 4. The effect of number of extractions on disk efficiencies.

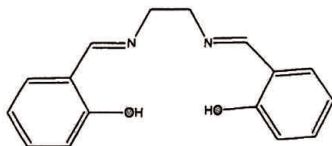


Fig. 1.

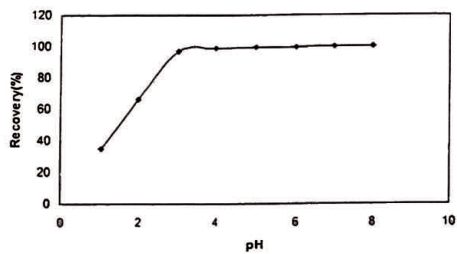


Fig. 2.

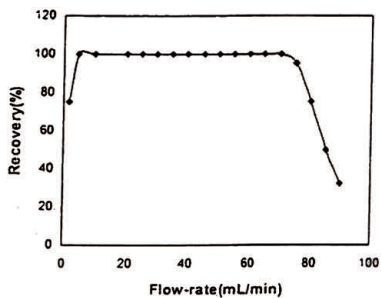


Fig. 3.

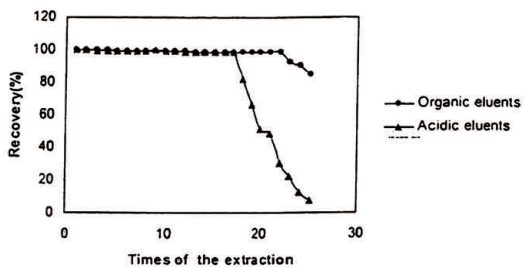


Fig. 4.