

ASSESSMENT OF THE TRACE LEVELS OF LEAD (II) USING SOLID PHASE EXTRACTION AND FLAME ATOMIC ABSORPTION SPECTROMETRY

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ABSTRACT

An efficient procedure for pre-concentration, separation and determination of the trace amounts of lead (II) ions in water samples has been established. The analyte is adsorbed on the surface of C₁₈ silica membrane disk modified with APDC, quantitatively, while other interfering ions pass through the disk to drain. The sorbed Pb²⁺ ions are then stripped by appropriate eluting agents followed by monitoring of the eluates by flame atomic absorption spectrometry (FAAS). The effects of sample pH, amount of the modifier, stripping agent types, sample flow-rates, and potential interfering ions were also investigated. The described method involves a pre-concentration factor of about 200. The detection limit of the procedure is 0.93 ng.mL⁻¹. The method was employed for isolation and determination of lead in different water samples.

Keywords: Lead, Flame Atomic Absorption Spectrometry & Solid Phase Extraction.

INTRODUCTION

Lead is considered as one of the metals of prime environmental concern and is tabulated among 129 priority pollutants and one of the 25 hazardous species for human health and has been classified as a class B2 pollutant by environmental protection agency (EPA)¹. It has long been recognized that presence of lead in various forms leads to complicated problems and disturbances in living organisms. The major drawback of lead on human health is its cumulative toxicity and damaging influences on brain, kidney and central nervous system².

Meanwhile, the toxicological treatment of lead may be attributed to its ability for uncoupling oxidative phosphorylation, modification of ion transport in mitochondria, and inhibition of the metabolisms of enzymes containing thiol (-SH) group in hem synthesis and mitochondria energetic processes³.

In literature numerous procedures and techniques have been reported for lead determination. These methods and techniques are predominately including spectrophotometry,⁴ flame

atomic absorption spectrometry⁵, electrothermal atomic absorption spectrometry (ETAAS)⁶, inductively coupled plasma atomic emission spectrometry (ICP-AES)⁷, inductively coupled plasma optical emission spectrometry (ICP-OES)⁸, and inductively coupled plasma - mass spectrometry (ICP-MS)⁹.

However, these procedures do not possess sufficient enrichment factor, desirable relative standard deviation (RSD), sensitivity and selectivity. On the other hand, to ensure the efficiency of the analysis, especially when high sample throughput is required, on-line separation and concentration techniques are employed¹⁰. These techniques circumvent most of the latter problems and feasible the monitoring of a wide variety of elements and their related species by fully automated manifolds. However, they suffer from poor reproducibility¹¹.

Due to occurrence of lead in different matrices at low levels, introduction and development of novel approaches for pre-concentration, matrix elimination and determination of lead is indispensable and has a prime importance.

Liquid-liquid extraction of various metal ions has been widely utilized in literature¹². However, traditional classical methods are frequently time consuming, labor intensive, require too large volumes of ultrapure hazardous solvents, comprising excess experimental steps, encounter with emulsion formation, and suffer from elaborative automation, practically. An additional concern is the disposal cost of the used solvents which creates severe environmental problems. In order to eliminate some of the above mentioned difficulties, solid phase extraction (SPE) is considered as the best attractive alternative method. SPE features are mainly based on the utilization of a major constituent component as sorbent (bonded stationary phase) impregnated with suitable chelating or immobilized by functional groups. Practically, the selectivity of each loaded sorbent would be assigned via its donating groups.

The use of chelating resins has been referred in literature, frequently¹³⁻¹⁴. The main restriction associated with ion-exchange resins is related to matrixes containing high electrolyte concentrations, which limits both adsorption capacity and selectivity. Other proper and effective sorbents are co-crystallized naphthalene⁸, Chitosan¹⁵, amino carboxylic acid-type cellulose known as Chelest fiber Iry¹⁶, functionalized activated carbon¹⁷⁻¹⁸, poly tetra fluoro ethylene (PTFE) turnings¹⁹, immobilized C₁₈ on silica, activated carbon and polyurethane foam¹⁶, cellulose nitrate²⁰, rice bran²¹, and chemically bonded 4-aminoantipyrine to silica gel²², and alumina²³.

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 follows: shorter sample processing time and decreased plugging by suspended materials and matrix components due to the large cross-sectional area of the disk, higher 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; selective 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 pre-concentration factor over similar adsorbents^{2, 24- 25}.

Dithiocarbamates as a suitable generation of multi-purpose chelating groups have been used more than other agents during the recent decades in combination with other powerful analytical techniques such as graphite furnace atomic absorption spectrometry (GFAAS)²⁶, ICP-AES²⁷, neutron activation analysis (NAA)²⁸, anodic stripping voltammetry (ASV)²⁹, gas-liquid chromatography (GLC)³⁰, and high performance liquid chromatography (HPLC)³¹. Soylak and his co-worker have reported a membrane filtration treatment for simultaneous multielement analysis of some heavy metal ions, recently³².

In our previous reports, we employed octadecyl silica membrane disks for enrichment and monitoring the trace amounts of chromium³³⁻³⁴, and lead³⁵⁻³⁶, effectively.

The present report is an attempt to develop a facile and quantitative method for concentrative separation and subsequent assessment of the ppb and sub-ppb levels of lead in some water samples collected in different regions of Tehran. To generalize the efficiency of the method, some relevant factors on retention and elution of lead ions were tested. To the best of our knowledge, octadecyl silica membrane disks modified by ammonium pyrrolidine dithiocarbamate (APDC) (Fig. -1) have not been used for isolation, pre-concentration and monitoring of the lead traces, previously.

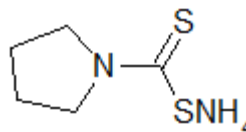


Fig. 1. Molecular structure of APDC

EXPERIMENTAL

Reagents

All chemicals were of analytical grade and used as received without any further purification. Ultra pure organic solvents were of the highest purity and obtained from E. Merck, Darmstadt, Germany. 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 Nanopure ultrapure water system from Barnstead Company (USA) and was used throughout the experiments.

Reversed phase C₁₈-silica membrane disks

Solid phase extractions were carried out by glassy membrane disks, ENVI-18DSK™ 47 mm diameter × 0.6 mm thickness containing octadecyl silica bonded phase (as irregular 30 µm particles with 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 flat disks supply high cross sectional area and are capable of separating bulky ion-pairs and neutral organic and organometallic molecules. 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.

Apparatus

The pH measurements were carried out by an ATC pH meter equipped with a combined glass calomel electrode (EDT instruments, GP 353). Determination of lead contents of working samples was performed by a Varian spectra A.200 model atomic absorption spectrometer equipped with a high intensity hollow cathode lamp (HI-HCL) and instrumental parameters were adjusted according to the recommendations of the manufacturers. These characteristics are tabulated in Table -1. The pH measurements were carried out by an ATC pH meter equipped with a combined glass calomel electrode (EDT instruments, GP 353).

Table -1 : 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 fine	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

Preparation of stock and standard solutions

The stock solution of lead (II) was prepared by dissolving a proper quantity of analytical grade lead (II) nitrate (159.8 mg) of deionized water in a 100 mL volumetric flask. 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.

Sample extraction

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

1) First Step: Sample treatment: In order to eliminate suspended materials, water samples were filtered through 45 µm nylon filters before extraction. After each filtration, the residue remained on the filter was washed with 10 mL of deionized water. Sampling vessels were polyethylene bottles soaked in 1 mol.L⁻¹ HNO₃ overnight, rinsed twice with deionized water, and dried in a dust-free environment.

2) Second Step: 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 accomplished 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) Third Step: Disk modification: This step could be performed by either of the following manners:

a) A solution of 3 mg of APDC in 1 mL of CHCl₃

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 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 no turbidity is observed anymore and remains clear. The disk was then washed with 25 mL of water and dried by passing air through it.

- b) A solution of 3 mg of APDC 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 (change of appearance of the disk). 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) **Fourth Step: Analyte extraction:** 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 20 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 1-10 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 performed.

RESULTS AND DISCUSSION

Evaluation the nature and role of APDC

APDC is a non-selective chelating agent and reacts with a wide variety of metal ions, properly. This reagent is slightly soluble in water at neutral pH, and quite stable in acidic media. This ligand behaves as a bidentate univalent anionic ligand via its two S donor atoms and tends to form complexes with those metal ions containing partially filled d orbitals, filled d orbitals but low positive charge and ions with 18+2 electronic structure. Despite this fact, under the best optimal experimental conditions, it was observed that only Pb^{2+} -APDC complexes could be retained on the surface of octadecyl silica membrane disks, drastically, while other metal complexes are sorbed

Table - 2 : Effect of eluent type and volume on percent recovery of metal-APDC complexes^a

Eluting solution	Recovery (%) ^b			
	3	5	8	10
HNO ₃ (0.5M)	8.2	12.4	21.2	16.7
HNO ₃ (1M)	12.4	15.0	18.3	14.2
HNO ₃ (3M)	9.5	23.3	28.9	16.9
HCl (1M)	3.3	11.2	14.1	14.3
HCl (3M)	7.4	10.5	13.8	19.3
CH ₃ COOH (1M)	10.5	27.4	31.5	33.2
CH ₃ COOH (3M)	14.5	38.9	43.4	37.5
H ₃ PO ₄ (1M)	5.6	13.8	11.2	9.8
H ₃ PO ₄ (3M)	12.1	18.6	21.3	26.6
CH ₃ OH (6M)	63.5	99.1	95.3	97.3
CH ₃ CH ₂ OH (6M)	60.2	98.9	98.2	96.5
CH ₂ OHCH ₂ CH ₃ (6M)	40.4	74.3	81.5	80.5

^a Initial samples contained 20 µg of Pb^{2+} in a 500 mL of sample.

^b RSDs based on three individual replicate analyses were within 0.5-3.2.

partially. To evaluate the quantitative retention of Pb^{2+} ions by C_{18} -membrane disks, some preliminary experiments were carried out in the absence and presence of ligand. It was observed that while the disk itself shows low tendency for Pb^{2+} ions (as about 8%) each disk modified with APDC is capable to retain lead ions, virtually.

Selection of stripping solution

In order to choose the proper eluting solution for quantitative clean-up of the retained lead ions, after the extraction of 20 μg of Pb^{2+} from a 500 mL of a water sample by means of the modified membrane disk, the retained Pb^{2+} complexes were stripped with various volumes of different non-organic and organic solutions. The subsequent results are presented in Table -2. Obviously, according to these data, among the 12 employed removing solutions, only organic eluents are capable for effective recovery of the sorbed Pb^{2+} ions. However, mineral eluents could not elute the analyte completely and consequently are not regarded as effective stripping agents. It should be emphasized that addition of methanol to each of the mineral eluting solutions leads to more reliable results. This may be because of the better contact of eluent with hydrophobic surface of the disk. According to the data given in Table -3, it can be seen that the most effective mineral eluents are the ones containing 5 % v.v⁻¹ of methanol.

Undoubtedly, one of the interesting respects of SPE procedures is the percentage recovery of eluted Pb^{2+} species in sequential volumes of quantitative stripping agents. The numerical

percentage recovery of each efficient eluent has been demonstrated in Table - 4.

Effect of pH

By notifying the fact that most chelating ligands behave as conjugate bases of weak acids, they show a very strong affinity for H^+ ions. Therefore, the pH will be a crucial and critical parameter in separation of metal ions by chelation. To evaluate the effect of pH on the SPE of lead ions, the pH of each aqueous solution containing 20 μg of Pb^{2+} was adjusted to appropriate pH values over 1-8 by addition of proper amounts of diluted nitric acid or ammonia solutions. The percent recovery plot versus pH is shown in Fig. -2.

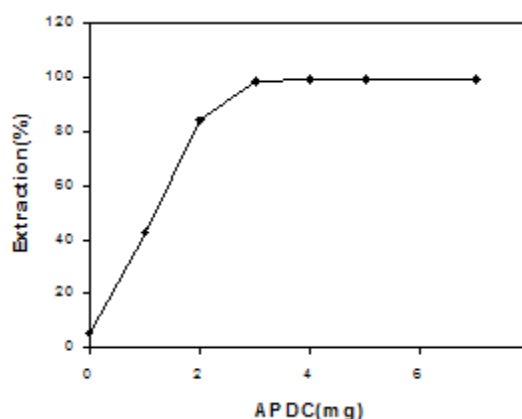


Fig. 2. Effect of amount of APDC on extraction efficiency of lead ions

Table - 3 : Influence of methanol on the extraction efficiency of mineral eluents^a

Eluent	Recovery (%) ^b			
	0.5	V.V ⁻¹ % of methanol		
		1	3	5
HNO ₃ (0.5M)	18.9	23.3	48.2	50.1
HNO ₃ (1M)	17.8	21.9	42.3	53.4
HNO ₃ (3M)	19.2	32.3	42.2	60.3
HCl (1M)	13.2	18.6	24	49.4
HCl (3M)	14.4	17.1	18.3	22.9
CH ₃ COOH (1M)	21.3	32.3	47.6	58.7
CH ₃ COOH (3M)	20.1	31.6	48.2	56.3
H ₃ PO ₄ (1M)	11.8	19.3	29.2	33.8
H ₃ PO ₄ (3M)	15.1	20.8	22.9	30.3

^aInitial samples contained 20 μg of Pb^{2+} in a 500 mL of sample.

^bRSDs based on three individual replicate analyses were within 0.8-4.5.

Accordingly, at the pH=2 extractions are complete and quantitative. At lower pH values (<2), there is the probability of protonation of sulfur atoms (donating atoms) which will reduce the stability of APDC and Pb^{2+} ions complexes and subsequently, diminish the recoveries efficiencies. 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 disks³⁷. To achieve higher selectivity and better results, it was decided to adjust the pH of the lead solution to 2.0 throughout the experiments.

Effect of the amount of APDC and flow-rate

To investigate the optimized amount of APDC on the percentage recovery of lead by membrane disks, the extraction was conducted by varying the amount of APDC over the range of 0-7 mg (Fig. -3). As can be seen, the extraction would be complete by using of at least 3 mg of the ligand. Therefore, subsequent extraction experiments were performed with 3 mg of it.

On the other hand, the influence of flow-rates of the sample and removal solutions from the membrane disk on the retention and recovery of Pb^{2+} ions was also evaluated. Under the optimized conditions, it was found out that in the range of 10-75 mL.min⁻¹, the retention and sorption of the lead complexes through each membrane disk was not considerably affected by the sample solution flow-rate. Meanwhile, quantitative stripping of the lead complexes from the disk was achieved in a flow-rate of 1-10 mL.min⁻¹ of proper eluents. For our studies, the selected flow-rates were 60 and 5 mL.min⁻¹ for sample solution and eluent, respectively. At higher flow-rates, complete recovery of lead required larger volumes of eluents. It is also notable that as the amount of loaded ligand on the membrane disk increases, the flow-rate of solutions through the modified disk decreases.

Inspection of the disk efficiencies

To examine the feasibility of each membrane disk for complete clean-up and extraction, a series

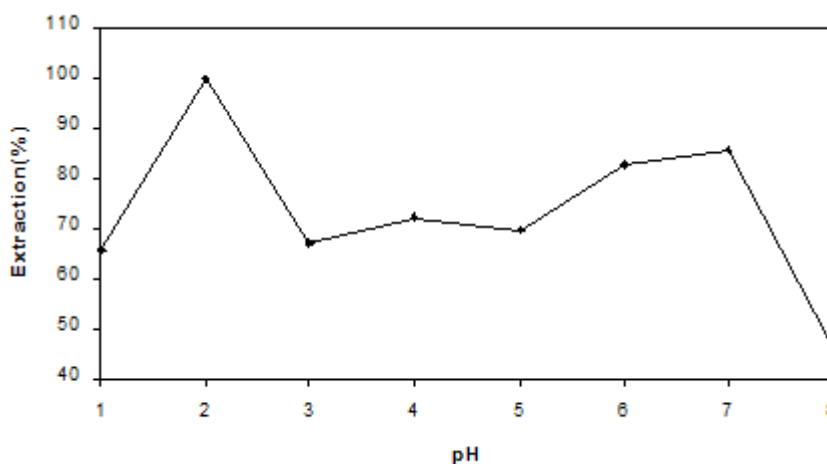


Fig. - 3 : The influence of pH on retention of Pb^{2+} - APDC complexes

of organic and mineral eluents were chosen and the recommended method was followed. Under the optimized conditions, it was found out that each ENVI-18DSK™ disk could afford at least 24 replicate analyses when organic eluents are utilized, while acidic and alkaline eluents restrict the times of accurate recoveries to a maximum of 17 and 4 replicates, respectively. The excessive abatement of disk efficiencies in alkaline solutions is most probably attributed to the probability of the hydrolysis of octadecyl silica bonded phase in these conditions.

Analytical performance

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 2.5-30 $\mu\text{g.mL}^{-1}$.

The capacity of the modified membrane disks was determined by pouring of 500 mL portions of sample solutions involving 1000 μg of lead at pH=2.0 followed by the monitoring of the retained Pb^{2+} ions in the eluates by FAAS using an

Table - 4 : Percent extraction of lead through modified C₁₈ disks by using the sequential volumes of stripping solutions^a

Eluent agent	Volume (mL)					Total
	First 1 mL	Second 1mL	Third 1mL	Forth 1mL	Fifth 1mL	
Methanol (6M)	28.6	22.1	20.7	16.2	13.5	99.1
Ethanol (6M)	29.1	21.3	19.3	16.8	12.4	98.9

^a Initial samples contained 20 µg of Pb²⁺ in a 500 mL of sample.

Table - 5 : Performance characteristics of the proposed method for pre-concentration of lead

L.R.E ^a	A=0.015C + 0.0032
L.D.R (µg.mL ⁻¹) ^b	2.5-30
Disk capacity (µg)	453 ± 5 ^c
Break-through volume (mL)	1000
Enrichment factor	200
LOD (ng.mL ⁻¹)	0.93

^a Linear regression equation

^b Linear dynamic range

^c Standard deviation based on three individual replicate analysis

Table - 6 : Effect of matrix ions on recovery of Pb²⁺ ions^a

Ion	Added as	Concentration (mg.L ⁻¹)	Recovery (%)
Li ⁺	LiCl	50	98.2
Na ⁺	NaCl	50	97.4
K ⁺	KNO ₃	45	100.1
Cs ⁺	CsCl	50	99.2
Mg ²⁺	Mg(NO ₃) ₂	55	99.1
Ca ²⁺	CaCl ₂	35	98.6
Ba ²⁺	Ba(NO ₃) ₂	35	97.8
Al ³⁺	Al(NO ₃) ₃	8	100.5
Cr ³⁺	Cr(NO ₃) ₃ ,hydrated	5	99.4
Cr ⁶⁺	K ₂ Cr ₂ O ₇	2.5	99.3
Fe ²⁺	FeCl ₂	0.05	98.5
Fe ³⁺	FeCl ₃	0.01	96.7
SO ₄ ²⁻	Na ₂ SO ₄	150	100.1
PO ₄ ³⁻	Na ₃ PO ₄	200	101.4
VO ₃ ⁻	NaVO ₃	80	99.3
Cl ⁻	NH ₄ Cl	250	99.8

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

Table - 7 : Percent recovery of 20 µg of lead added to 500 mL of synthetic solutions at pH=2

Synthetic Sample	Ingredients	Recovery (%)
1	K ⁺ , Mg ²⁺ , Al ³⁺ (5mg) ^a	96.5(2.1) ^b
2	Zn ²⁺ , Co ²⁺ , Fe ²⁺ (50µg)	99.1(3.5)
3	Cr ³⁺ , Cr(VI) and Fe ³⁺ (5mg)	97.2(0.5)

^a Values in parentheses are mg and µg amounts of each mentioned cation.

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

Table - 8 : Percent recovery of 20 µg of lead added to a 500 mL solution of real water samples

Sample	Pb ²⁺ content (µg)	Recovered amount (µg)
Waste water 1 ^a	8	27.2(2.4) ^e
Waste water 2 ^b	75	92.3(0.3)
Waste water 3 ^c	72	91.6(1.9)
Waste water 4 ^d	62	80.3(2.2)

^a Located in Jajrood

^b Located in Bumehen-up

^c Located in Bumehen-down

^d Located in Roodehen

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

Table - 9 : 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⁺		Pb ²⁺	Cu ²⁺	
Pb ²⁺	120	-	20	16.7	-	40
Pb ²⁺	100	-	1-30	0.075	-	41
Pb ²⁺ , Cu ²⁺	200	200	1-20	0.9	0.2	42
Pb ²⁺	75	-	1-60	5	-	43
Pb ²⁺	200	-	60	0.93	-	proposed method

external calibration curve. The maximal capacity of the disk obtained from three replicate measurements was 453 ± 5 μg of lead on the disk.

By passing of solutions containing 20 μg of Pb^{2+} in 50, 100, 250, 500, 750 and 1000 mL of water under the optimal conditions, the Pb^{2+} was retained in all cases, quantitatively. Thus, the break-through volume of the method must be greater than 1000 mL. Consequently, by considering the final elution volume of 5.0 mL of each suitable eluent and the break-through volume of 1000 mL, an enrichment factor of 200 is easily achievable. The limit of detection (LOD) is defined operationally as the analyte concentration yielding an analytical signal equal to some confidence factor (K_b) times the standard deviation of the blank measurements (S_b) divided by the slope of linear calibration curve (m). The related equation is presented as: $\text{LOD} = K_b S_b m^{-1}$ where K_b is a numerical factor³⁸⁻³⁹. For a numerical factor of $K_b=3$ and pre-concentration factor of 200, a LOD of about 0.93 ng.mL^{-1} is achievable. In Table - 5, the analytical parameters and figures of merit of the present work have been presented.

Effect of interfering ions

The utility and selectivity of the proposed procedure was examined in the presence of various ions. For this purpose, the influence of ions at milligram and microgram levels on the extraction efficiency of 20 μg of lead in a 500 mL of an aqueous sample solution was tested and the related results are summarized in Table 6. As it is seen, none of the metals interferes the lead recovery. The tolerance limit was set as the ion concentration needed to cause at most $\pm 4\%$ error in the recovery values of 20 μg of Pb^{2+} in 500 mL of water. As it is seen, the suggested method is free from

interferences from a large number of ions even at high concentrations. The tolerable levels of some interferic ions seem adequate for our investigations because the levels of these ions in real samples are lower than their tolerance amount.

Determination of lead in synthetic and real water samples

In order to assess the applicability of the proposed method to synthetic and real water samples with different matrices containing varying amounts of a variety of diverse ions, it was applied to the isolation and recovery of lead ions from three synthetic samples as well as four different samples (obtained from east of Tehran). According to the results presented in Tables 7 and 8, the lead recovery is almost quantitative and satisfactory.

Conclusion

The overall proposed method is economic, convenient, reliable, and permits an enrichment factor of 200 under minimal experimental requirements. Therefore, the LOD could be improved as 200 times. It does not need to any elaborative and time consuming sample pre-treatment steps. The RSD of the method is at the most 2 % and hence is satisfactorily reproducible. In Table 9, the comparability or even superiority of the described method over similar methods has been discussed. The maximum time taken for extraction, concentration and assessment of 20 μg of Pb^{2+} in 500 mL of a water sample is at the most 15 min.

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