

Solid phase extraction of lead on octadecyl bonded silica membrane disk modified with Cyanex302 and determination by flame atomic absorption spectrometry

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Abstract

A simple, reliable and rapid method for preconcentration and determination of lead using octadecyl bonded silica membrane disk impregnated with Cyanex302 and flame atomic absorption spectrometry is presented. The influence of aqueous phase pH, type of eluent, flow rates of sample solution and eluent, volume of eluent and amount of extractant has been investigated. The break through volume is greater than 4.0 dm³ with an enrichment factor of more than 400 and a detection limit of 1.0 μg dm⁻³. The method developed for determination of lead is good as six replicate determinations using 100 cm³ solution containing lead in the range 1–4900 μg provides a relative standard deviation (R.S.D.) of 0.4%. The selectivity of the proposed method was confirmed from the interference studies. The developed procedure was successfully applied for the determination of lead in spiked sea water, USGS standard soil sample, sludge and industrial effluents, medicinal formulation, plant, some food products and wine.

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1. Introduction

Lead is one of the most ubiquitous elements in the environment and recognized as a major health risk to humans and animals [1,2]. Flame atomic absorption spectrometry (FAAS) is a simple technique, commonly used for determination of lead in water [3], soil [4,5] and plant samples [6]. However, the determination of traces of lead by FAAS in such complex matrices is difficult due to its low sensitivity (0.01 μg cm⁻³) and the interfering effects of matrix components. Hence, separation step is frequently necessary to improve the detection limit and sensitivity [7] which is nowadays preferably done by solid phase extraction due to the several advantages it offers [8].

Solid phase extraction procedures for lead have been reported using various solid supports such as activated carbon [9], silica gel [10], cellulose [11], Amberlite XAD series resins [12–17], Chromosorb resin [18], Amborsorb resin [19] and polyurethane

foam [20]. Two methodologies were commonly practiced for solid phase extraction of lead. One was based on chemical reactions either for synthesis of a selective ligand [14] or its covalent coupling to support material [12,15,16] and other for functionalization of the solid support itself [10–13,17]. These methods were somewhat lengthy and time-consuming.

A relatively simple alternative for preparation of the solid phase is based upon the impregnation of reagents on solid supports. Interesting studies using acidic organophosphorous extractant such as DEHPA (di-(2-ethylhexyl)phosphoric acid), Cyanex272 (bis(2,4,4-trimethyl pentyl)phosphinic acid), Cyanex302 (bis(2,4,4-trimethyl pentyl)monothio phosphinic acid), Cyanex301(bis(2,4,4-trimethyl pentyl)dithio phosphinic acid) and PC-88A or IONOQUEST 801 (2-ethylhexyl hydrogen 2-ethylhexyl phosphonate) impregnated on a solid support have been reported [21–29]. Mechanism and kinetics of the sorption of cadmium(II) with Cyanex302 [23] and Cyanex301 [24] was undertaken. The extent of impregnation of Cyanex302 [25] and PC-88A [26] on different Amberlite XAD series resins was found to influence the extractability of cadmium(II) and copper(II) [25] and ytterbium(III), terbium(III), samarium(III) and lanthanum(III) [26]. Selective separation of iron(III),

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cadmium(II) and nickel(II) was achieved using Cyanex272 and Cyanex302 impregnated on Amberlite XAD-2 by controlling aqueous phase pH [27]. While the decontamination of ground water for some heavy metals was possible due to the high sorption capacity of Cyanex302 impregnated on Amberlite IRA-96 [28]. Extraction of lead with DEHPA, Cyanex272 and IONOQUEST 801 impregnated on Amberlite XAD-7 was influenced by the pH of aqueous phase and type of extractant [29]. No attempts have been made for selective separation and concentration of lead to facilitate its determination from complex matrices using Cyanex302 impregnated on C 18 disk.

Solid phase extraction methods using columns with a narrow internal diameter limit the usable flow rates to a range of 1–10 cm³ min⁻¹ resulting in long time for enrichment from large sample volumes. While C 18 disks enable much higher flow rates [5,30].

In view of this the extraction of lead with Cyanex302 impregnated on C 18 disk and determination by FAAS was systematically studied. This type of solid phase overcomes the limitations of solvent extraction, over use of large quantities of organic solvents while high specificity and selectivity of a liquid cation exchanger can be achieved by controlling the sorption and elution parameters.

2. Experimental

2.1. Instrumentation

A Perkin-Elmer atomic absorption spectrophotometer AAnalyst200 and a Digispec 110-D visible spectrophotometer, Feedback India Ltd. were employed for determining metal ion concentration. An Elico LI-120 digital pH meter Elico India Ltd., was used for pH adjustments. A millipore vacuum pump was used to maintain the sample flow rates through disk. An inductively coupled plasma atomic emission spectrophotometer (ICP-AES JY JOBIN YVON HORIBA ULTIMA 2) was also used.

2.2. Chemicals and reagents

A stock solution of lead 1 mg cm⁻³ was prepared by dissolving appropriate quantity of lead metal powder (Sisco Chemicals Ltd.) in slightly acidified distilled water. The solution was standardized volumetrically [31], and a working solution containing 10 μg cm⁻³ lead was prepared by appropriate dilution. 3 M Empore membrane disks (47 mm diameter and 0.5 mm thick, 10% PTFE fibrillated) containing octadecyl bonded silica (8 mm particle, 60-Å pore size), distributed by Varian India Ltd. were used in conjunction with standard 47 mm filtration apparatus. Cyanex302 obtained as a gift sample from Cytec Canada was used as such without further purification. All chemicals and reagents used were of A.R. grade.

2.3. Preparation of impregnated octadecyl bonded silica membrane disk

The Cyanex302 impregnated octadecyl bonded silica membrane disk was prepared as follows. After placing the membrane

disk in the filtration apparatus, the disk was washed with 10 cm³ of HPLC grade methanol and double distilled water repeatedly by applying a slight vacuum. After all of the solvent had passed through the disk, it was dried by passing air through it for 2 min. The disk was then conditioned with 10 cm³ of HPLC grade methanol under a low vacuum. The disk was not allowed to soak without vacuum and air was not allowed to make contact with the surface of the disk. The disk was then dried under vacuum for 5 min. Finally, a solution containing 30 mg of Cyanex302 in 2 cm³ 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 and methanol was collected and repeatedly passed through the disk to ensure complete impregnation of Cyanex302 on the disk. During this entire process no vacuum was applied. Time required for impregnation of Cyanex302 on C 18 disk was not more than 25 min.

The amount of Cyanex302 adsorbed was evaluated by passing methanol (20–30 cm³) at high vacuum. The eluate was then titrated against standard NaOH using phenolphthalein indicator.

2.4. Solid phase extraction, general procedure

Impregnated C 18 disk was preconditioned with 20–50 cm³ of double distilled water adjusted to pH 5.0 with 1.0 M HNO₃ or 1:1 NH₃. A 100 cm³ sample solution containing 10 μg lead, adjusted to a pH 5.0 using 1.0 M HNO₃ or 1:1 NH₃ was passed through the disk under vacuum to maintain a flow rate of 30–40 cm³ min⁻¹. Lead extracted on disk was then eluted with 1.0 M HNO₃ at a flow rate of 10 cm³ min⁻¹. The amount of lead extracted was determined by flame atomic absorption spectrophotometer (air–acetylene flame, 283.3 nm, 0.7 nm slit width) using a calibration curve. The reproducibility of the method evaluated for lead determination in six replicate experiments using the general procedure had a R.S.D. of 0.4%.

3. Results and discussion

3.1. Effect of aqueous phase pH and flow rate

The extraction of lead in sample solution was studied in the pH range 1.0–7.0 by adjusting pH with 1.0 M HNO₃ or 1:1 NH₃. A plot of percentage of lead extracted (%E) versus pH (Fig. 1) indicated its quantitative extraction from pH 4.0 to 7.0 due to the formation of cationic species of lead [32]. Higher pH values (>7) were not tested due to the possibility of hydrolysis of octadecyl silica in the disk. The optimum pH 5.0 was selected for further studies

The effect of sample flow rate on the uptake of lead at pH 5.0 by the modified disk was studied. It was found that extraction of the metal ion was quantitative (99.4 ± 0.4%) and reproducible up to a sample flow rate of 20–150 cm³ min⁻¹ (Fig. 2). The flow rate selected for all studies was 30–40 cm³ min⁻¹. Extraction of lead using this flow rate was rapid as compared to other reports [15,16,18,19].

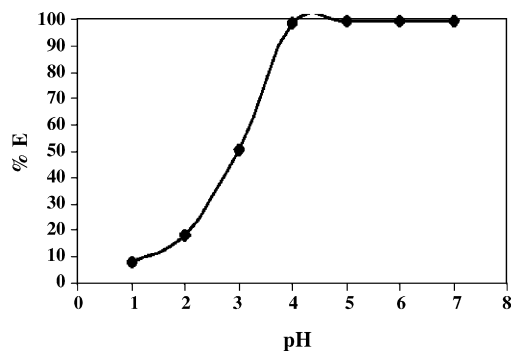


Fig. 1. Effect of aqueous phase pH on extraction of lead. Lead = 10 μg , aqueous phase volume = 100 cm^3 , flow rate = 30–40 $\text{cm}^3 \text{min}^{-1}$.

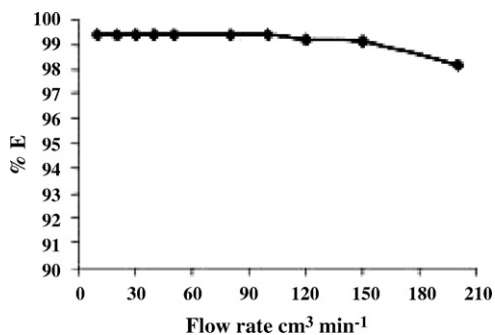


Fig. 2. Effect of aqueous phase flow rate on extraction of lead. Aqueous phase volume = 100 cm^3 , lead = 10 μg , pH 5.

3.2. Effect of amount of Cyanex302

Enrichment of 10 μg of lead on C 18 disk, modified with varying amounts of Cyanex302 (Fig. 3) was systematically studied. For preparation of C 18 disk with different amounts of Cyanex302, a known amount of Cyanex302 in 2 cm^3 methanol was passed through disk as described in Section 2.3 for impregnation. The extraction of 10 μg of lead in 100 cm^3 of aqueous phase at pH 5.0 was studied with each of these C 18 disks modified with different quantities of Cyanex302. The minimum quantity of Cyanex302 required for quantitative extraction of lead was 30 mg. Hence for subsequent studies 30 mg Cyanex302 sorbed on C 18 disk was used.

3.3. Choice of eluent

In order to choose the most effective eluent for the quantitative stripping of the lead retained by the disk, different concentra-

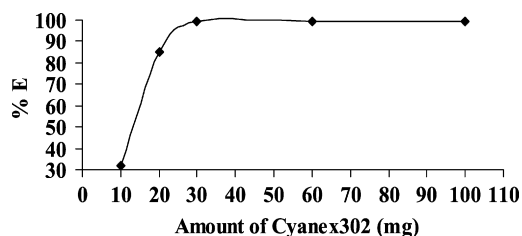


Fig. 3. Effect of amount of Cyanex302 on extraction of lead. Lead = 10 μg , aqueous phase = 100 cm^3 , pH 5, flow rate = 30–40 $\text{cm}^3 \text{min}^{-1}$, eluent = 10 cm^3 , 1.0 M HNO_3 , flow rate = 10 $\text{cm}^3 \text{min}^{-1}$.

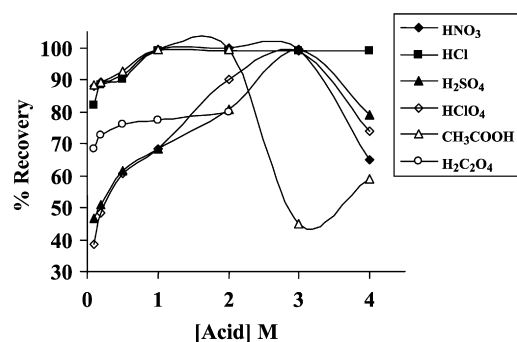


Fig. 4. Influence of eluents on recovery of lead. Aqueous phase = 100 cm^3 , pH 5, flow rate = 30–40 $\text{cm}^3 \text{min}^{-1}$, eluent volume = 10 cm^3 , flow rate = 10 $\text{cm}^3 \text{min}^{-1}$.

Table 1
Effect of eluent volume

S. no.	Volume of 1.0 M HNO_3 (cm^3)	Recovery (%) ^a
1	5	87.2
2	10	99.4
3	15	99.4
4	20	99.5

Aqueous phase: 10 μg lead in 100 cm^3 , pH 5, flow rate = 30–40 $\text{cm}^3 \text{min}^{-1}$, amount of Cyanex302 = 30 mg, eluent flow rate = 10 $\text{cm}^3 \text{min}^{-1}$.

^a Average of six replicate analysis, R.S.D. < 0.4%.

Table 2
Effect of eluent flow rate

S. no.	Flow rate ($\text{cm}^3 \text{min}^{-1}$)	Recovery (%) ^a
1	5	99.6
2	10	99.4
3	15	96.3
4	20	86.9

Aqueous phase: 10 μg lead in 100 cm^3 , pH 5, flow rate = 30–40 $\text{cm}^3 \text{min}^{-1}$, amount of Cyanex302 = 30 mg, eluent = 10 cm^3 , 1.0 M HNO_3 .

^a Average of six replicate analysis, R.S.D. < 0.4%.

tions of HNO_3 , HCl , HClO_4 , H_2SO_4 , CH_3COOH and $\text{H}_2\text{C}_2\text{O}_4$ were studied (Fig. 4). About 1.0 M HNO_3 was selected as an eluent for further studies. The elution studies with different volumes of 1.0 M HNO_3 with different flow rates were also carried out. The results are summarized in Tables 1 and 2. From the results, it is clear that quantitative recovery of lead was possible with 10 cm^3 , 1.0 M HNO_3 , hence 10 cm^3 , 1.0 M HNO_3 at flow rate of 10 $\text{cm}^3 \text{min}^{-1}$ was used for further studies.

4. Analytical performance

4.1. Reusability of the disk

The stability and potential reusability of the disk was assessed by monitoring the change in recovery of lead through several extraction–elution cycles (Fig. 5). For each cycle, the impregnated C 18 disk was preconditioned with 20–50 cm^3 of double distilled water adjusted to pH 5.0. A 100 cm^3 sample solution containing 10 μg lead, adjusted to a pH 5.0 was then passed through disk at a flow rate of 30–40 $\text{cm}^3 \text{min}^{-1}$. Lead

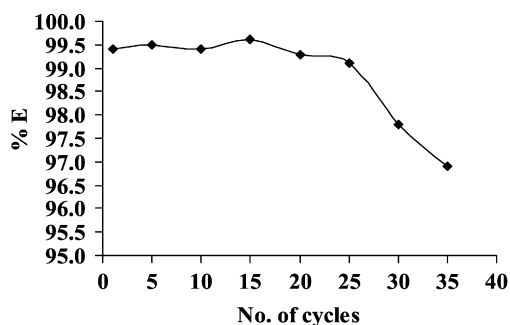


Fig. 5. Reusability of modified solid support. Aqueous phase = 100 cm^3 , pH 5, flow rate = $30\text{--}40\text{ cm}^3\text{ min}^{-1}$, eluent = 10 cm^3 , 1.0 M HNO_3 , flow rate = $10\text{ cm}^3\text{ min}^{-1}$.

extracted on disk was eluted with 1.0 M HNO_3 at a flow rate of $10\text{ cm}^3\text{ min}^{-1}$. Recovery of lead was quantitative with reproducible results (lead recovery $99.4 \pm 0.4\%$) up to 25 cycles using the same disk. This indicates a very high reusability and reliability of the solid phase for continuous usage.

4.2. Sorption capacity

The sorption capacity of the C 18 adsorbed Cyanex302 was determined by passing a 100 cm^3 of sample solution containing $1\text{--}10\text{ mg}$ lead at a flow rate of $30\text{--}40\text{ cm}^3\text{ min}^{-1}$ through disk loaded with Cyanex302. The amount of lead in the aqueous phase was determined by FAAS. The difference in the initial amount of lead in sample solution and the amount found in the aqueous phase after passing the sample solution through the disk was the amount of lead extracted on the disk. The sample solutions containing ($1\text{--}4.9\text{ mg}$) lead were quantitatively extracted by the modified disk. The amount of lead extracted on the modified disk was constant (4.9 mg) from sample solutions containing more than 5.0 mg of lead. Thus the maximum sorption capacity of this modified solid support for lead was 4.9 mg (Fig. 6), which was much higher than modified solid supports [5,33–35].

4.3. Breakthrough volume

The break through volume of disk was tested using different volumes ($10\text{--}4000\text{ cm}^3$) of aqueous phase containing $10\text{ }\mu\text{g}$ of

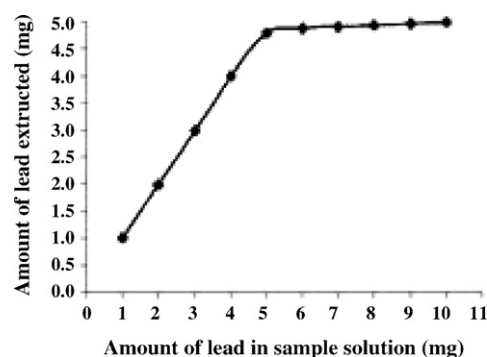


Fig. 6. Sorption capacity of C 18 disk impregnated with Cyanex302. Aqueous phase = 100 cm^3 , pH 5, flow rate = $30\text{--}40\text{ cm}^3\text{ min}^{-1}$, eluent = 1.0 M HNO_3 , volume = 10 cm^3 , flow rate = $10\text{ cm}^3\text{ min}^{-1}$.

lead. The recovery of lead was tested by the recommended procedure. It was observed that the extraction of lead was quantitative even up to 4000 cm^3 of sample solution. Hence the breakthrough volume for the method should be greater than 4000 cm^3 and a preconcentration factor of 400 was attainable when 10 cm^3 eluent is used for recovery of lead.

4.4. Limit of detection

The limit of detection (LOD) of the proposed method for the determination of lead was studied under the optimal extraction conditions. The LOD was obtained from $C_{\text{LOD}} = 3\sigma/m$ [19] where σ is the standard deviation of the blank measurements ($N=20$) and m is the slope of the linear calibration graph. The LOD of the method was found to be $1.0\text{ }\mu\text{g dm}^{-3}$.

4.5. Effect of diverse ions on sorption of lead

In order to check the selectivity of the method for extraction and determination of lead, interference of various ions on recovery of lead was investigated (Table 3). A 100 cm^3 of sample solution containing $10\text{ }\mu\text{g}$ lead and different concentrations of the other ions was passed through the modified solid support under the optimum extraction conditions. The tolerated amount of the other ion was the amount up to which the recovery of lead was $99.4 \pm 2\%$. Alkali, alkaline earth metals and some of

Table 3
Effect of diverse ions

Ion	Concentration of ion ($\mu\text{g cm}^{-3}$)	Recovery (%) of lead ^a	Ion	Concentration of ion ($\mu\text{g cm}^{-3}$)	Recovery (%) of lead ^a
Na ⁺	15×10^3	100	Mo ⁶⁺	0.5	99.4
K ⁺	400	99.6	Th ⁴⁺	0.3	99.2
Ca ²⁺	400	99.9	U ⁶⁺	0.3	98.4
Mg ²⁺	150	99.6	Cl ⁻	20×10^3	99.2
Sr ²⁺	50	98.8	NO ₃ ⁻	300	99.0
Co ²⁺	10	99.8	SO ₄ ²⁻	350	98.6
Ni ²⁺	10	99.8	PO ₄ ³⁻	100	98.1
Mn ²⁺	10	99.6	CH ₃ COO ⁻	100	98.1
Cr ³⁺	1	98.9	C ₂ O ₄ ²⁻	100	97.8
Cr ⁶⁺	10	99.6	Citrate	100	98.7
V ⁵⁺	5	99.7	Tartarate	100	98.3
Cd ²⁺	0.5	98.6	Ascorbate	500	99.0

^a Average of triplicate analysis, R.S.D. < 0.4%.

the transition metal ions were tolerated in higher concentration during extraction of lead compared to other methods [3,12,16] indicating suitability of method for determination of lead in sea water.

5. Analytical applications

5.1. Determination of lead in sea water and standard (USGS GXR-2) soil sample

A 1 dm³ sea water sample was spiked with different amounts of lead (1, 5 and 10.0 µg) and analyzed for determination of lead using the proposed method (Table 4).

About 0.5 g of USGS standard soil sample, GXR-2 was treated with HF and HNO₃ in 5:1 ratio in a Teflon beaker at 150 °C [7]. After complete digestion, the residue was extracted with double distilled water and an aliquot from this diluted solution was used for determination of lead using the general procedure. The amount of lead was found to be 686.5 ± 0.8 µg g⁻¹ by the proposed method as against 690 µg g⁻¹ of certified value. Thus the recovery of lead was 99.5 ± 0.8 by the proposed method.

5.2. Determination of lead in industrial effluents and sludge samples

Appropriate aliquots from the industrial effluents (collected near CBD, Belapur, Mumbai) were taken and extracted with ethyl acetate to remove excess of iron [36]. The aqueous phase containing lead was then adjusted to pH 5.0, diluted to 100 cm³ to recover lead as per the general procedure.

About 0.5 g each of sludge samples (collected from CBD, Belapur, Mumbai) were treated in similar manner as mentioned in earlier section for standard soil sample [7].

The results obtained from these analyses presented in Table 5 indicate the suitability of developed method to control discharge of lead by the proposed method.

5.3. Determination of lead from food, medicinal plant and formulation and wine sample

- (a) Sample solution for black tea and black pepper were obtained by treating 0.1 g of each sample with 7 cm³ HNO₃ and keeping over night followed by treatment with 8 cm³ HClO₄. The resultant solution was evaporated to dryness

Table 4
Sea water analysis

Sample	Amount of lead added (µg dm ⁻³)	Amount of lead found (µg dm ⁻³) ^a	Recovery (%) of lead ^a
	–	ND	–
Sea water	1.0	0.996	99.6
	5.0	4.996	99.9
	10.0	9.980	99.8

Aqueous phase = 1 dm³ sea water, flow rate = 30–40 cm³ min⁻¹, eluent = 10 cm³, 1.0 M HNO₃, flow rate = 10 cm³ min⁻¹.

^a Average of triplicate analysis, R.S.D. < 0.4%.

Table 5
Determination of lead in sludge samples and industrial effluents

Sample	Concentration of lead ppm ^a (by present method)	Concentration of lead ppm (certified value)	Recovery (%) ^a
Sludge 1	817.4 ± 0.01	826	98.9 ± 0.01
Sludge 2	445.3 ± 2.1	458	97.2 ± 2.1
Industrial effluent 1	10.1 ± 1.0	10.15	99.0 ± 1.0
Industrial effluent 2	12.3 ± 2.0	12.77	96.5 ± 2.0
Industrial effluent 3	1.22 ± 4.1	1.21	101.1 ± 4.1
Industrial effluent 4	100.3 ± 0.6	100	100.3 ± 0.6

Aqueous phase = 100 cm³ sample solution, pH 5.0, flow rate = 30–40 cm³ min⁻¹, eluent = 10 cm³, 1.0 M HNO₃, flow rate = 10 cm³ min⁻¹.

^a Average of triplicate analysis with R.S.D.

Table 6
Determination of lead in various samples

Sample	Concentration of lead ppm ^a (by present method)	Concentration of lead ppm (by ICP-AES)	Recovery (%) ^a
Black tea	48.8	49.3	99.0
Black pepper	22.7	22.8	99.7
Plant	25.77	25.8	99.9
Medicinal formulation	11.8	11.85	99.8
Cocoa powder	12.8	12.85	99.8
Wine	13.4	13.5	99.3

Aqueous phase = 100 cm³ sample solution, pH 5.0, flow rate = 30–40 cm³ min⁻¹, eluent = 10 cm³, 1.0 M HNO₃, flow rate = 10 cm³ min⁻¹.

^a Average of triplicate analysis, R.S.D. < 0.4%.

and the residue obtained was extracted with double distilled water [37].

- (b) Sample solutions of plant sample (0.5 g), medicinal formulation (1 g), and cocoa powder (0.5 g) were prepared by dry ashing at 500 °C in a muffle furnace for 6 h [38] and extracting with dilute HNO₃.
- (c) A wine sample (25 cm³) was treated with H₂O₂ and HNO₃ in 1:1 ratio on steam bath for digestion [20].

Appropriate aliquots from all these samples were then taken for lead determination as per the general procedure. The amount of lead was detected in aqueous phase as well as in the eluent. All these results obtained are presented in Table 6. The values obtained by the developed method compare well with the results obtained using ICP-AES.

6. Conclusion

A simple, precise and accurate method was developed for selective separation, preconcentration and determination of lead from various complex matrices. In comparison to other solid phases [15,16,18,19], high flow rates and large preconcentration factor was achieved using C 18 disk modified with Cyanex 302. While other advantages over reported methods are the high tolerances for matrix components [3,12,16], superior sorption capacity and good reusability [5,33–35].

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