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Preconcentration by a N,N'-bis 2-hydroxy-5-bromo-benzyl 1,2 diaminopropane adsorbed on surfactant coated alumina before simultaneous determination of Pb and Cd by ETAAS

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ABSTRACT

A simple, highly sensitive, accurate and selective method for simultaneous determination of trace amounts of Pb(II) and Cd(II) in water samples is presented. The method is based on selective chelation of Pb(II) and Cd(II) on surfactant coated alumina, modified with a Schiff's base N,N'-bis 2-hydroxy-5-bromo-benzyl 1,2 diaminopropane (H_2L). The retained ions were then eluted with 4 ml of 4 M nitric acid and determined by electro thermal atomic absorption spectrometry (ETAAS) at 283.3 and 228.8 nm for Pb and Cd respectively. The influence of flow rates of sample and eluent solutions, pH, breakthrough volume, effect of foreign ions on chelation and recovery were investigated. 1.5g of surfactant coated alumina adsorbs 40mg of the Schiff's base which in turn can retain 16.0 ± 1.0 mg of each of the two ions. The limit of detection (3σ) for Pb(II) and Cd(II) were found to be 5.89 and 1.78 ng l⁻¹ respectively. The enrichment factor for both ions are 100. The mentioned method was successfully applied on determination of lead and Cd(II) in different water samples. The ions were also speciated by means of three columns system.

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KEYWORDS

Determination of lead and Cd(II);
Preconcentration;
N,N'-bis 2-hydroxy-5-bromo-benzyl 1,2-diaminopropane
ETAAS.

INTRODUCTION

Cadmium and lead, naturally occurring heavy metals, are two of the most hazardous elements to human health. Both metals causes adverse health effects in humans and their widespread presence in the human environment comes from anthropogenic activities. Cadmium is among the most dangerous of all the metal contaminants of food. Biological interest in lead has centred principally on its properties as a highly toxic cumulative poison in humans and animals. Contents of Cd and Pb in some matrices, such as foods, sediment or water can

show pollution situation of an area^[1].

In the determination of cadmium and lead in numerous real samples by atomic absorption spectrometry, there is a crucial need for a preconcentration step before their analysis due to their frequent low concentrations. Additionally, since high levels of concomitant components usually accompany analytes, a separation step is often required^[2]. Several enrichment procedures have been reported in the literature for cadmium and lead determination involving different analytical techniques, such as precipitation^[3], liquid-liquid^[4], cloud-point^[5,6] or solid-phase extraction (SPE)^[7,8]. Liquid-liq-

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liquid extractions are generally time-consuming, labor-intensive and they require strict control of extraction conditions, such as temperature, pH and ionic strength. Solid-phase extraction is an attractive alternative in preconcentration procedures because it overcomes many drawbacks of liquid-liquid extraction. Other advantages in use of SPE are disposal costs, achievement of high recoveries, broader range of applications than liquid-liquid extraction due to the large choice of solid sorbents and easy recovery of the solid phase^[9].

Trace amounts of metals are present in natural biosphere. Presence of some of these metals in very low concentrations and certain oxidation states are necessary. Higher concentrations and other oxidation states might be toxic and dangerous. Unfortunately the difference between these two levels are very small^[10,11]. Lead occurs in nature mostly as PbS. It is used in batteries, tetraethyl lead, guns, solders and X-ray instruments^[12,13]. Some of these methods suffer from poor limit of detection and harmful solvents are being used in some others. On the other hand, effect of foreign ions on the analyte is not negligible in many instances. In such cases, preconcentration of the analyte makes the determination easier and the composition of the sample less complicated. In recent years, solid phase extraction (SPE) has offered attractive possibilities in trace analysis. It has reduced the solvent and time consumption drastically^[14,31-34]. In order to increase the preconcentration or extraction power of SPE an organic or inorganic ligand is used in conjunction with the sorbent. Some of the ligands used for determination of lead and Cd(II) are: Amberlit XAD-2 with 3,4-dihydroxybenzoic acid^[15], silicagel modified with 3-aminopropyl triethoxysilane^[16], Levatit with di(2,4,4-trimethylpentyl)phosphinic acid^[17], silicagel functionalized with methyl thiosalicylate^[18], silicagel modified with zirconium phosphate^[19] and C₁₈ disks modified with a sulfur containing Schiff's base^[20].

Comparing these examples with the presented method, they have either a lower enrichment factor or a higher limit of detection. On the other hand, the C₁₈ disks can be used only a few times, while the proposed sorbent could be used more than 50 times without loss of efficiency.

Surfactant coated alumina modified with chelating agents has been used for extraction and preconcentration of environmental matrixes and metals^[21-22]. Here,

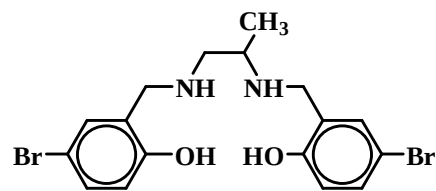


Figure 1: Structure of , N,N'-bis 2-hydroxy-5-bromo-benzyl 1,2 diaminopropane (H₂ L).

the surfactant molecules have been associated on the alumina surface forming an admicell or hemimicell. Organic molecules attach themselves on the hydrophobe part and low concentration of metallic elements also on the hydrophobe part, which includes the chelating agent^[22]. The Schiff's bases which are obtained from salicylaldehyde are known as multidentate ligands. These agents can form very stable complexes with transition metal ions^[23,24].

The main goal of the present work is development of a fast, sensitive and efficient way for simultaneous enrichment and extraction of trace amounts of Pb(II) and Cd(II) from aqueous media by means of a surfactant coated alumina modified with ligand N,N'-bis 2-hydroxy-5-bromo-benzyl 1,2 diaminopropane (H₂ L, shown in figure 1).

Such a simultaneous determination has not been reported in the literature. The structure of H₂L is shown in figure 1. The chelated ions were desorbed and determined by ETAAS. The modified solid phase could be used at least 50 times with acceptable reproducibility without any change in the composition of the sorbent, ligand or SDS. On the other hand, in terms of economy it is much cheaper than those in the market, like C₁₈ disks.

EXPERIMENTAL

Reagents and apparatus

All solutions were prepared with doubly distilled deionized water. Alumina powder γ -type for chromatography with diameter of about 50 μ m obtained from Katayama Chemicals. It was conditioned before use by suspending in 4M nitric acid for 20min, and then washed two times with water. Sodium dodecyl sulfate (SDS) obtained from Merck and used without any further purification. H₂L was prepared by refluxing

2 eq. of 5-bromo-2-hydroxybenz aldehyde(40mmol) with 1 eq. (20mmol) of 1,2 diaminopropane in 100 ml of ethanol for 4 h. The solution turned bright yellow and on cooling the yellow Schiff base solid appeared. The EtOH was removed by rotary evaporation and the solid recrystallized from hot EtOH. Approximately 10mmol of the Schiff base was dissolved in 100ml of ethanol and 2g(52mmol) of sodium borohydride added in two portions. The mixture was stirred for 2h, and approximately 40ml of double-distilled water was added to this. The product precipitated, was filtered out, and recrystallized from hot ethanol. The structure of the compound was confirmed by FT-IR and NMR spectrometry. Stock solutions of Cd^{2+} was prepared from $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and standardized titrimetrically with EDTA^[25].

Lead nitrate, Cd(II) sulfate pentahydrated, ammonium dihydrogen phosphate were of analytical reagent grade and RP- C_{18} silica(40-63 μm) obtained from Merck. The anion exchanger resin Dowex 1X-8 mesh 100-200 obtained from Fluka. The chelating resin, chelex-100, mesh 100-200 obtained from Bio Rad.

Standard stock solution of 1000 $\mu\text{g ml}^{-1}$ of Pb(II) and Cd(II) were prepared by dissolving appropriate quantity of their salts in water. A solution of 0.35M of ammonium dihydrogen phosphate in water was prepared as the matrix modifier for determination of lead. A solution of SDS- H_2L was prepared as follow: to a solution of 0.2g of H_2L in 10ml of ethanol, 5 drops of 1M NaOH and 0.5g of SDS were added, dissolved and its volume adjusted to 50ml with water.

Preparation of admicell column: to 40ml of water containing 1.5g of alumina, 10ml of the above H_2L solution was added. The pH of the suspension was adjusted to 2.0 by addition of 4M HNO_3 and stirred by mechanical stirrer for 20 min. Then the top liquid was decanted (and discarded) and the remained alumina was washed three times with water, then with 5 ml of 4 M HNO_3 and again three times with water. The prepared sorbent was transferred to a polypropylene tube (i.d 5mm, length 10mm).

The measurements were performed by a Perkin Elmer model 300 Aanalyst atomic absorption spectrometer, equipped with a graphite furnace of the type HGA-850, furnace auto sampler of the type AS-800, and a deuterium lamp for background correction. Instrumen-

TABLE 1 : Instrumental parameters for determination of Pb

Wavelength(nm)	283.3			
Slit width(nm)	0.7			
Lamp current(mA)	10			
Furnace conditions	Time(S)			
Step	Temperature (°C)	Ramp	Hold	Argon gas flow (mlmin ⁻¹)
Drying	130	20	15	250
Pyrolysis I	350	5	5	250
Pyrolysis II	450	15	5	250
Atomization	2250	0	5	0
Cleaning	2600	1	3	250
Matrix modifier0.241mg NH4H2PO4				

Matrix modifier 0.241mg $\text{NH}_4\text{H}_2\text{PO}_4$

Absorbance measurements were based on peak heights.

TABLE 2: Instrumental parameters for determination of Cd

228.8			Wavelength(nm)	
0.7			Slit width(nm)	
15			Lamp current(mA)	
Argon gas flow(ml min ⁻¹)	Time(S) ramp hold		Furnace conditions step temperature(°C)	
200	20	5	100	Drying
200	15	15	140	Pyrolysis I
200	20	10	1000	Pyrolysis II
0	5	0	2300	Atomization
250	3	1	2600	Cleaning

Absorbance measurements were based on peak heights.

tal conditions and furnace parameters for the atomizer are listed in TABLES 1 and 2. A metrohm 691 pH meter equipped with a combined glass calomel electrode was used for pH measurements.

Procedure

The pH of a solution containing 100ng of each Pb(II) and Cd(II) was adjusted to 2.0. This solution was passed through the admicell column with a flow rate of 5ml min⁻¹. The column was washed with 10ml of water and the retained ions were desorbed with 1ml of 4 M HNO_3 with a flow rate of 2ml min⁻¹. The desorption procedure was repeated 3 more times. All the acid solutions (4ml all together) were collected in a 10ml volumetric flask and diluted to the mark with water. The concentrations of lead and Cd(II) in the solution were determined by ETAAS at 283.3 and 324.8 nm respectively.

Determination of lead and Cd(II) in water samples

Polyethylene bottles, soaked in 1M HNO_3 overnight, and washed two times with water were used for sampling. The water sample was filtered through a 0.45 μm pores filter. The pH of a 1000ml portion of each sample was adjusted to 2.0(4M HNO_3) and

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passed through the column under a flow rate of 5 ml min⁻¹. The column was washed with water and the ions were desorbed and determined as the above mentioned procedure.

Speciation of lead and Cd(II) in water samples

This procedure is reported in several articles. The method has been evaluated and optimized for speciation and its application on complex mixtures^[26-29].

The chelating cation exchanger (Chelex-100) and anion exchanger, Dowex 1X-8 resins were washed with 1M HCl, water, 1 M NaOH and water respectively. 1.2g of each resin was transferred to separate polyethylene columns. Each column was washed with 10ml of 2 M HNO₃ and then 30ml of water. The C₁₈ bounded silica adsorber in a separate column was conditioned with 5ml of methanol, then 5ml of 2 M HNO₃ and at the end with 20ml of water. 5 ml of methanol was added on top of the adsorber, and passed through it until the level of methanol reached just the surface of the adsorber. Then water was added on it and connected to the other two columns. A certain volume of water sample was filtered through a 0.45µm filter and then passed through the three columns system, Dowex 1X-8, RP-C₁₈ silica adsorber and Chelex-100 respectively. The columns were then separated. The anion and cation exchanger columns were washed with 10ml of 2M HNO₃ and the C-18 column with 10ml of 1 M HCl. The flow rate of eluents was 1ml min⁻¹. The lead and Cd(II) content of each eluted solution were determined by ETAAS.

RESULTS AND DISCUSSION

H₂L is a Schiff's base. It is a four dentate ligand. It is insoluble in water, but soluble in slightly alkaline ethanol. Primary investigations revealed that surfactant coated alumina could not retain Pb(II) and Cd(II) cations, but when modified with H₂L, retains these cations selectively. It was then decided to investigate the capability of H₂L as a ligand for simultaneous preconcentration and determination of lead and Cd(II) on admicell.

The alumina surface in acidic media (1 < pH < 6) attracts protons and becomes positively charged. The hydrophyl part of SDS (-SO₃⁻), is attached strongly to these protons. On the other hand, the ligand molecules

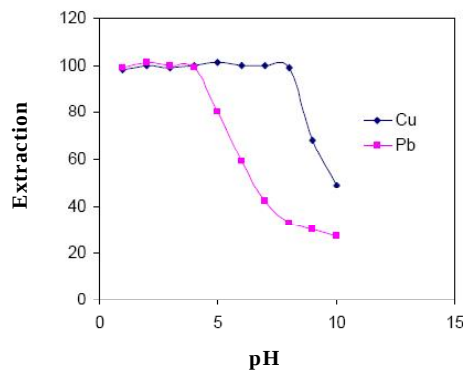


Figure 2 : Extraction percentage of Pb(II) and Cd(II) against pH

are attached to hydrophobe part of SDS and retain small quantities of metallic cations^[22].

Effect of pH

The effect of pH of the aqueous solution on the extraction of 100ng of each of the cations Pb(II) and Cd(II) was studied in the pH rang of 1-10. The pH of the solution was adjusted by means of either 0.01M HNO₃ or 0.01M NaOH. The results indicate that complete chelation and recovery of Pb(II) occurs in pH range of 2-4 and that of Cd(II) in 2-8 and are shown in figure 2. It is probable that at higher pH values, the cations might be hydrolysed and complete desorption does not occur. Hence, in order to prevent hydrolysis of the cations and also keeping SDS on the alumina, pH=2.5 was chosen for further studies.

Effect of flow rates of solutions

Effect of flow rate of the solutions of the cations on chelation of them on the substrate was also studied. It was indicated that flow rates of 1-5ml min⁻¹ would not affect the retention efficiency of the substrate. Higher flow rates cause incomplete chelation of the cations on the sorbent. The similar range of flow rate for chelation of cations on modified alumina with SDS and a ligand has been reported in literature^[21,22]. Flow rate of 1-2ml min⁻¹ for desorption of the cations with 4 ml of 4 M HNO₃ has been found suitable. Higher flow rates need larger volume of acid. Hence, flow rates of 5ml min⁻¹ and 2ml min⁻¹ were used for sample solution and eluting solvent throughout respectively.

Effect of H₂L quantity

To study optimum quantity of H₂L on quantitative

extraction of lead and Cd(II), 50ml portions of solutions containing 100ng of each cation were passed through different columns the sorbent of which were modified with various amounts, between 10-50mg of the ligand. The best result was obtained on the sorbent which was modified with 40mg of the ligand.

Figures of merit

The breakthrough volume is of prime importance for solid phase extractions. Hence, the effect of sample volume on the recovery of the cations was studied. 100ng of each cation was dissolved in 50, 100, 500 and 1000ml of water. It was indicated that in all the cases, chelation and desorption of the cations were quantitative. It was then concluded that the breakthrough volume could be even more than 1000ml. Because the sample volume was 1000ml and the cations were eluted into 10ml solution, the enrichment factor for both cations are 100, which is easily achievable. The maximum capacity of 1.5g of the substrate was determined as follow; 500ml of a solution containing 50mg of each cation was passed through the column. The chelated ions were eluted and determined by ETAAS. The maximum capacity of the sorbent for three individual replicates was found to be $16.0 \pm 1.0 \mu\text{g}$ of each cation. The limit of detection (3σ) for the cations^[30] were found to be 5.89 and 1.78 ng l^{-1} for lead and Cd(II) ions respectively. Reproducibility of the method for extraction and determination of 100ng of each cation in a 50 ml solution was examined. As the results of seven individual replicate measurements indicated, they were 2.89% and 2.68% for Pb(II) and Cd(II) respectively.

Effect of foreign ions

Effect of foreign ions were also investigated on the measurements of lead and Cd(II). Here a certain amount of foreign ion was added to 50ml of sample solution containing 100ng of each Pb(II) and Cd(II) with a pH of 2.5. The amounts of the foreign ions and the percentages of the recovery of lead and Cd(II) are listed in TABLE 3. As it is seen, it is possible to determine lead and Cd(II) without being affected by the mentioned ions.

Analysis of the water samples

The prepared sorbent was used for analysis of real samples. To do this, the amounts of lead and Cd(II)

TABLE 3 : Effect of foreign ions on the recovery of 100ng of Pb or Cd

Diverse ion	Amounts taken (mg) added to 50mL	% Found	% Recovery of Cd ²⁺ ion	% Recovery of Pb ²⁺ ion
Na ⁺	92.5	1.15(2.9) ^a	98.7(1.8)	97.3(2.8)
K ⁺	92.5	1.32(2.1)	98.5(2.2)	98.2(2.2)
Mg ²⁺	14.4	0.7(1.8)	98.7(1.7)	98.5(3.0)
Ca ²⁺	28.3	1.25(2.5)	99.0(1.8)	99.0(2.3)
Sr ²⁺	3.45	2.85(2.2)	98.8(2.9)	98.5(2.6)
Ba ²⁺	2.66	3.16(2.4)	98.3(2.5)	98.8(2.5)
Mn ²⁺	2.66	1.75(2.3)	98.3(1.8)	98.6(3.3)
Co ²⁺	2.17	2.4(2.3)	97.3(2.9)	99.9(2.9)
Ni ²⁺	2.44	2.0(2.4)	98.5(2.4)	99.5(2.4)
Zn ²⁺	2.78	2.97(2.1)	97.5(3.2)	98.5(2.2)
Cd ²⁺	2.58	1.93(2.0)	98.2(2.8)	99.2(2.7)
Bi ³⁺	2.23	2.7(1.9)	98.5(2.7)	98.5(2.4)
Al ³⁺	2.43	2.81(2.1)	98.3(2.4)	98.7(2.3)
Fe ³⁺	2.60	3.43(2.4)	96.6(2.8)	96.6(2.2)
Cr ³⁺	1.74	2.92(2.5)	97.5(2.6)	97.7(2.8)
UO ²⁺	2.86	1.3(2.9)	97.4(2.9)	98.6(2.7)
NO ₃ ⁻	5.0	3.3 (2.3)	96.3(2.8)	99.6(3.4)
CH ₃ COO ⁻	5.0	2.2(2.6)	98.4(2.0)	97.3(2.6)
SO ₄ ²⁻	5.0	2.9(3.1)	98.7(2.1)	99.4(3.5)
CO ₃ ²⁻	5.0	1.8(2.4)	93.3(2.4)	99.3(3.0)
PO ₄ ³⁻	2.0	2.1(2.2)	98.4(2.4)	100.3(3.2)

^aValues in parenthesis are CVs based on three individual replicate measurements.

were determined in different water samples namely: distilled water, tap water of Tehran (Tehran, taken after 10 min operation of the tap), rain water (Tehran, 26 January, 2006), snow water (Saveh, 6 February, 2006), and two synthetic samples containing different cations. The results are tabulated in TABLE 4. As it is seen, the amounts of lead or Cd(II) added to the water samples are extracted and determined quantitatively which indicates accuracy and precision of the present method.

Separation and speciation of cations by three columns system. It is possible to preconcentrate and at the same time separate the neutral metal complexes of organic ligands, anionic complexes and free ions from each other by this method^[27]. Water samples were passed through the three connected columns: anion exchanger, C₁₈-silica adsorber and chelating cation exchanger. Each species of lead or Cd(II) is retained in one of the columns; anionic complexes in the first column, neutral complexes of organic ligands in the second, and the free ions in the third. The results of passing certain volumes of different water samples through the columns are listed in TABLE 5. According to the re-

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TABLE 4 : Recovery of Pb and Cd contents of water samples

		Amount added(μg)	Found(μg)	% Recovery
Sample distilled water (100mL)	Pb	-	-	-
		0.050	0.048(3.55)	96
	Cd	0.100	0.098(2.55)	98
		-	-	-
Tap water(100mL)	Pb	-	0.013(4.51)	-
		0.050	0.063(3.42)	97
	Cd	-	0.054(3.71)	-
		0.050	0.103(2.31)	99
Snow water(50mL)	Pb	-	0.048(3.25)	-
		0.100	0.153(2.65)	98.5
	Cd	-	0.060(3.65)	-
		0.050	0.121(2.55)	99
Rain water(100mL)	Pb	-	0.042(3.23)	-
		0.100	0.148(2.43)	97.5
	Cd	-	0.044(3.53)	-
		0.100	0.143(2.43)	98
Synthetic, sample 1 Ca^{2+} , Fe^{3+} , Na^{+} , Co^{2+} , Cr^{3+} , Hg^{2+} , 1mg l^{-1} of each cation	Pb	-	-	-
		0.100	0.101(3.43)	98.0
	Cd	-	-	-
		0.100	0.101(3.31)	98.0
Synthetic sample 2 K^{+} , Ba^{2+} , Mn^{2+} , Cd^{2+} , Ni^{2+} , Zn^{2+} , 1mg l^{-1} of each cation	Pb	-	-	-
		0.100	0.101(2.71)	98.6
	Cd	-	-	-
		0.100	0.101(3.11)	98.6

^aValues in parenthesis are CVs based on three individual replicate measurements.

sults, it is indicated that lead and Cd(II) present only as cations. On the other hand the t-test comparing the obtained mean values of the present work with those published indicate no significant difference between them.

TABLE 5 : Results of speciation of Pb and Cd in different samples by three columns system

	River water (50ml)		water sample (1000ml) ^a		Tap water (1000ml)	
Column	Pb(μg)	Cd(μg)	Pb(μg)	Cd(μg)	Pb(μg)	Cd(μg)
Dowex 1X8	-	-	-	-	-	-
Silica C-18	-	-	-	-	-	-
Chelex-100	0.014 (4.7) ^b	0.021 (3.8)	0.102 (3.1)	0.014 (3.1)	0.101 (3.1)	0.037 (3.5)

a: This was a solution containing 0.1 μg of each cation in 1000 ml of distilled water; b: Values in parenthesis are CVs based on three replicate analysis. The samples are the same as those mentioned in Table 4

CONCLUSIONS

We have proposed a method for simultaneous determination and preconcentration of Pb and Cd in water samples using surfactant coated alumina impregnated with a Sciff's base. The proposed method offers simple, highly sensitive, accurate and selective method for simultaneous determination of trace amounts of Pb(II) and Cd(II) in water samples.

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REFERENCES

- [1] D.L.Tslev, Z.K.Zaprianov; 'Atomic Absorption Spectrometry in Occupational and Environmental Health Practice', CRC Press, Boca Raton, USA, (1984).
- [2] B.Welz, M.Sperling; 'Atomic Absorption Spectrometry', Wiley-VCH, Weinheim, Germany, (1999).
- [3] S.Saracoglu, M.Soylak, L.Elci; Talanta, **59**, 287 (2003).
- [4] M.C.T.Diniz, O.F.Filho, J.J.R.Rohwedder; Anal.Chim.Acta, **525**, 281 (2004).
- [5] M.A.Bezerra, M.A.Z.Arruda, S.L.C.Ferreira; Appl.Spectrosc.Rev., **40**, 1-31 (2005).
- [6] V.A.Lemos, P.X.Baliza, J.S.Santos; J.Braz.Chem.Soc., **17**, 30 (2006).
- [7] M.Tuzen, K.Parlar, M.Soylak; J.Hazard.Mater., **121**, 79 (2005).
- [8] Y.Liu, Y.Guo, X.Chang, S.Meng, D.Yang, B.Din;

- Microchim.Acta, **149**, 95 (2005).
- [9] V.Camel; Acta, Part B, **58**, 1177 (2003).
- [10] S.N.Luoma; Sci.Total Environ., **28**, 1 (1983).
- [11] U.Forstner, G.T.W.William; Spring, Verlag, Berlin, (1983).
- [12] R.E.Kirk, D.F.Othmer; 'Encyclopedia of Chemical Technology', 3rd Ed., John Wiley and sons, New York, **14**, (1979).
- [13] L.Parmeggiani; 'Encyclopedia of Occupational Health and Safety', 3rd International Labor Organization, Geneva, **1**, (1983).
- [14] D.F.Hagen, C.G.Markell, G.A.Schmitt, D.D.Blevins; Anal.Chim.Acta, **236**, 157 (1990).
- [15] V.A.Lemos, P.X.Baliza, R.T.Yamaki, M.E.Rocha, A.P.O.Alves; Talanta, **61**, 675 (2003).
- [16] N.Tokman, S.Akman, M.Ozcan; Talanta, **59**, 201 (2003).
- [17] E.Castillo, J.L.Cortina, J.L.Beltran, M.D.Pratt, M.Granados; Analyst, **126**, 1149 (2001).
- [18] M.Zougagh, A.G.D.Torres, E.V.Alonso, J.M.C.Povon; Talanta, **62**, 503 (2004).
- [19] E.Matoso, L.T.Kubota, S.Cadore; Talanta, **60**, 1105 (2003).
- [20] O.R.Hashemi, M.Razi Kargar, F.Raoufi, A.Moghimi, H.Aghabozorg, M.R.Ganjali; Microchem.J., **62**, 1 (2001).
- [21] J.L.Manzoori, M.H.Sorouraddin, A.M.Haji Shabani; J.Anal.At.Spectrom., **13**, 305 (1998).
- [22] M.Hiraide, J.Hori; Anal.Sci., **15**, 1055 (1999).
- [23] M.Calligaris, R.Randaccio; G.Wilkinson, R.D.Gillard Mc Cleverty (Eds.); 'Comprehensive Coordination Chemistry', Oxford, London, Chap.20, **2**, (1987).
- [24] D.A.Alwood; Coord.Chem.Rev., **195**, 267 (1997).
- [25] G.H.Jeffery, J.Bassett, J.Mendham, R.C.Denney; 'Vogels Textbook of Quantitative Chemical Analysis', 5th ed., John Wiley & Sons, Inc., New York, (1991).
- [26] O.Abollino, M.Aceto, C.Sarzanini, E.Mentasti; Anal.Chim.Acta, **411**, 233 (2000).
- [27] Y.Liu, J.D.Ingle; Anal.Chem., **61**, 525 (1989).
- [28] M.Groschner, P.Appriou; Anal.Chim.Acta, **297**, 369 (1994).
- [29] B.L.Lewis, W.M.Landing; Mar.Chem., **40**, 105 (1992).
- [30] D.A.Skoog, F.J.Holler, T.A.Nieman; 'Principles of Instrumental Analysis', 5th ed., Saunders College publishing, (1998).
- [31] A.Moghimi; Material Science Research India, impress, (2006).
- [32] A.Moghimi; Material Science Research India, impress, (2006).
- [33] P.Nayebi, A.Moghimi; Oriental Journal of Chemistry, **22(3)**, 507 (2006).
- A.Moghimi; Oriental Journal of Chemistry, **22(3)**, 527 (2006).