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A Preconcentration And Determination Of Trace Amounts Of Heavy Metals In Water Samples Using Membrane Disk By Na-PDTP And Flame Atomic Absorption Spectrometry

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ABSTRACT

A fast and simple method for preconcentration of Ni²⁺, Cd²⁺, Pb²⁺, Zn²⁺, Cu²⁺ and Co²⁺ from natural water samples was developed. The metal ions were complexed with Natriumdiethyldithiocarbaminat (Na-PDTP) then adsorbed onto octadecyl silica membrane disk, recovered and determined by FAAS. Extraction efficiency, influence of sample volume and eluent flow rates, pH, amount of Na-PDTP, nature and amount of eluent for elution of metal ions from membrane disk, break through volume and limit of detection have been evaluated. The effect of foreign ions on the percent recovery of heavy metal ions have also been studied. The limit of detection of the proposed method for Ni²⁺, Cd²⁺, Pb²⁺, Zn²⁺, Cu²⁺ and Co²⁺ was found to be 2.03, 0.47, 3.13, 0.44, 1.24 and 2.05 ng.mL⁻¹, respectively. The proposed (DDTC) method has been successfully applied to the recovery and determination of heavy metal ions in different water samples.

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KEYWORDS

Preconcentration;
Atomic absorption spectrometry;
Solid phase extraction;
Octadecyl bonded silica;
Sodiumdi-n-popyldithiophosphinate (Na-PDTP).

INTRODUCTION

Heavy metals belong to the most hazardous priority pollutants. Many methods have been developed for the preconcentration and separation of trace metals from various samples. These include liquid-liquid extraction (LLE)^[1,2,3], Co-precipitation^[4], resin

chelation^[5], electrochemical deposition^[6], and solid phase extraction (SPE)^[7,8,29]. Much interest has been shown in replacing conventional LLE for isolating environmental pollutants with SPE technique, recently^[10,22]. SPE consists of bringing a test solution in contact with a solid phase or sorbent, whereby the analyt is selectively adsorbed onto the surface

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of the solid phase.

Today SPE disks are widely and successfully used, because they reduce solvent usage and exposure, disposal costs, and extraction time for sample preparation and obtains large preconcentration factors. Thus, the SPE disks and cartridges in conjunction with determination methods have been successfully used for separation and selective determination of metal ions^[10-14]. Immobilized (adsorbed or chemically bonded) chelates on the SPE systems have found widespread application for the separation of trace metals from a variety of matrices.

Dimethylglyoxime^[15], dithiocarbamates^[16,26], hexylthioglycolates^[17], 1-(2-thiazolylazo)-2-naphthol^[18].

8-hydroxyquinoline^[19], 3-hydroxy-2-methyl-1,4-Naphthoquinone^[20,21], neocuproine^[22], 4-(2-pyridylazo)resorciol(PAR)^[24], ammonium pyrolydine dithiocarbamate (APDC)^[25], 1,10-Phenanthroline^[27], have all been immobilized on various substrates and used for separation and preconcentration of metal ions.

This paper reports a simple and rapid analytical procedure for preconcentration and determination of copper, zinc, cadmium, cobalt, nickel and lead in natural waters, using flame atomic absorption spectrometric detection, after chelation with Natrium diethyldithiocarbaminat(Na-PDTP) and sorption on SPE membrane disk composed of octadecyl bonded silica. Different experimental conditions such as the nature and amount of eluting solvent, the effects of pH, sample and eluent flow rates, the amount of Na-PDTP on the extraction efficiency and break through volume have been studied. The method is an improvement of earlier reported method^[26] and has been applied successfully for separation, preconcentration and determination of heavy metal ions in natural water samples.

EXPERIMENTAL

Reagents, standard and sample solutions

High-purity methanol, hydrochloric acid, acetic acid and nitric acid(all from Merck) were used and reagent-grade Na-PDTP(Merck) was used. Analytical grade sodium acetate, potassium chloride, sodium

nitrate, lithium nitrate, rubidium chloride, magnesium nitrate, calcium nitrate, barium nitrate, strontium nitrate(Merck) were used.

The standard stock solution($1000\mu\text{g}\cdot\text{mL}^{-1}$)of nickel from nickel(II) chloride, zinc from zinc nitrate, cadmium from cadmium nitrate, copper from copper(II) nitrate, cobalt from cobalt(II) nitrate, lead from lead(II) nitrate were prepared by dissolving appropriate amount of each salt in water. pH in the range of 3.5-6.0 was adjusted with acetate buffers by mixing proper amounts of acetic acid and sodium acetate. pH below 3.5 was adjusted with HCl while pH above 6.0 was adjusted with NaOH solution. Doubly distilled deionized water was used throughout.

Apparatus

Extraction was performed with ENVI-DISKTM(cat.NO.57171, 47mm diameter and 0.5mm thick) containing octadecyl-bonded silica(80 μm particles, 6nm pore size)from Supelco. All the measurements were carried out by a Varian SpectrAA model 200 atomic absorption spectrometer(AAS). A Metrohm model 691 digital pH meter was used for the pH adjustments. A Millipore filtration apparatus was used for SPE of the ions. The 0.45mm nitrocellulose membrane filter used for the waste water sample filtration, was obtained from Schleicher and Schuell, Germany (REF-NO: 10404012).

Procedure

Extractions were performed with membrane disk.. The disks were washed before use by passing 10mL methanol through it. Immediately a mild vacuum was applied and the solvent was passed through the disk until the solvent surface almost reached the surface of the disk. The disk should not be allowed to soak without vacuum, and any air contact on 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 extra methanol above the disk rather than to allow air to contact the surface of the disk. Immediately thereafter 20mL deionized water was passed through it. The disk was then dried under vacuum for 5min or more if necessary. This is especially important for the disks which are used for the first time. In order

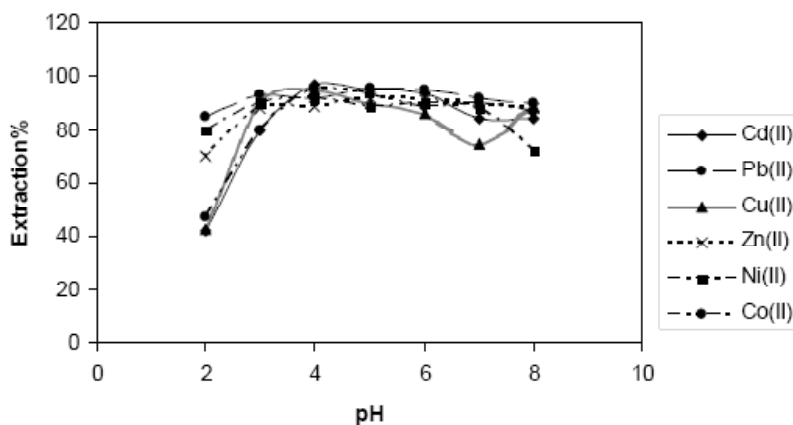


Figure 1 : Effect of pH on the recovery percentage of $0.2\mu\text{g}\cdot\text{mL}^{-1}$ of each heavy metal ions

to eliminate small suspended particles before extraction, water samples were filtered through $0.45\mu\text{m}$ pore size cellulose membrane filters.

After each filtration, the residue in the filter was washed with deionized water (10mL). The general procedure for the extraction of ions on the membrane disk was as follows. The disk was first washed with 10mL of methanol followed by 25mL of water. This step prewets the surface of the disk prior to the extraction of metal ions from water.

To each sample solution (100mL) containing $20\mu\text{g}$ of each of Cu^{2+} , Cd^{2+} , Ni^{2+} , Co^{2+} , Pb^{2+} , Zn^{2+} ions, 25mg Na-PDTP and 5mL buffer were added and its pH was adjusted at 4.5. Then it was passed through the disk by applying a mild vacuum. After the extraction, the disk was dried completely by passing air through it. A $23\text{mm}\times 200\text{mm}$ test tube was placed under the extraction funnel. The extracted complexes were eluted from the membrane disk using 5mL 0.1M of HCl dissolved in methanol. The flow rate was in the range of $5\text{-}10\text{mL}\cdot\text{min}^{-1}$. The metal ions were determined by FAAS.

RESULTS AND DISCUSSION

Some preliminary experiments were carried out in order to investigate quantitative retention of metal ions by membrane disk in the absence and presence of Na-PDTP. It was found that bare membrane disk doesn't show any affinity for Cu^{2+} , Cd^{2+} , Zn^{2+} , Ni^{2+} , Co^{2+} and Pb^{2+} ions, but it is capable of retaining metal ion-DDTC complexes from the sample solutions quan-

titatively. The test solution used contained $20\mu\text{g}$ of each ion and 25mg of Na-PDTP in 100mL water. Na-PDTP reacts with many metals to give strongly colored chelate compounds. In the reaction of Na-PDTP with metal ions (M^{n+}), chelates with the uncommon four membered ring are formed^[30].

The DDTC complexes are sparingly soluble in water, but dissolve readily in organic solvents such as chloroform, methanol, carbontetrachloride, diethylether and acetone^[31]. In the present work, the complexes of Cu^{2+} , Zn^{2+} , Cd^{2+} , Ni^{2+} , Co^{2+} and Pb^{2+} with Na-PDTP were initially extracted from water media onto membrane disk then stripped off using appropriate amounts of suitable organic solvents.

Results showed that the extraction of metal ions is quantitative when 25mg or more Na-DDTC is used.

The influence of pH on the extraction of metal ions was studied in the range of 2-8 using acetic acid/sodium acetate buffer and 1MHCl or 1MNaOH for pH adjustment. Higher pH values were not tested because there was the possibility of hydrolyzing octadecyl silica in the membrane disks^[30]. Cu^{2+} , Cd^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} and Pb^{2+} are quantitatively extracted above $\text{pH}=4.5$ (Figure 1).

The $\text{pH}=4.5$ is suitable for extraction because stable complexes are formed in this Ph^[30]. In order to choose a proper eluent for the retained ions, after the extraction of $20\mu\text{g}$ of Cu^{2+} , Zn^{2+} , Cd^{2+} , Ni^{2+} , Co^{2+} , Pb^{2+} form 100mL of water by the sorbent, the mentioned ions were stripped off with different eluents. From the data listed in (TABLE 1) it is obvious that the best eluent is 10mL, 0.1M of HCl in methanol.

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TABLE 1 : Effect of different eluting solvents on percentage recovery of heavy metal ions

Eluting solvents	% Recovery					
	Cu ²⁺	Cd ²⁺	Ni ²⁺	Co ²⁺	Pb ²⁺	Zn ²⁺
Methanol	63.2(2.5) ^b	55.2(2.9)	71.3(2.4)	76.3(1.5)	65.0(1.8)	57.4(3.4)
Acidified methanol ^c	95.1(1.5)	96.2(3.5)	98.2(1.4)	94.3(2.8)	98.9(1.8)	99.5(2.7)
Ammoniacal methanol ^d	90.2(2.5)	91.2(3.5)	90.2(3.3)	89.7(1.7)	87.4(2.2)	90.3(3.6)
Ethanol	90.5(1.5)	91.6(3.0)	89.5(3.5)	91.2(2.5)	90.5(3.1)	92.2(2.6)
1-Propanol	89.5(2.1)	88.5(3.0)	88.4(2.5)	89.2(1.5)	85.6(2.5)	86.3(1.5)
Formic acid(1M)	52.0(2.3)	51.1(2.0)	55.2(3.0)	51.1(1.7)	57.2(3.5)	50.5(2.2)
Hydrochloric acid(3M)	81.4(2.1)	84.2(1.7)	86.5(2.9)	88.2(3.0)	85.5(1.5)	86.2(1.5)
Hydrochloric acid(1M)	70.5(3.2)	77.2(2.1)	76.2(1.8)	72.5(2.1)	73.7(2.1)	78.3(2.8)
Nitric acid(3M)	72.6(1.5)	70.1(2.9)	79.2(1.2)	77.7(3.2)	77.6(3.0)	79.2(0.5)
Nitric acid(1M)	70.2(2.5)	69.6(1.5)	75.5(2.4)	72.2(1.5)	77.1(3.0)	72.2(0.7)

^aInitial samples contained 20µg of each heavy metal ions in 100mL water ; ^bValues in parentheses are RSDs based on five individual replicate analysis ; ^cAcidified solvents 0.1M-HCl in methanol ; ^dAmmoniacal solvents 0.1M- NH₃ in methanol

Mixture of methanol and 0.1M of HCl favors the contact between the liquid sample and the octadecyl silica disk .Similar results for elution of Cu²⁺, Zn²⁺, Cd²⁺, Ni²⁺, Co²⁺, Pb²⁺ in a preconcentration procedure have already been reported^[31,32].

100mL of sample solution containing 0.2mg.L⁻¹ of each cation was passed through the disk. Then

the disk was washed by different volumes. It was found that 10mL of eluting solvent was sufficient for complete desorption of metal ions.

The effect of different flow rates of sample solutions through the membrane disk on the adsorption of metal ions was also investigated. The flow rates were varied from 1 to 10mL.min⁻¹. Results indicated that only at flow rate of 10mL min⁻¹ or less the retention of all metal ions were complete. However, at flow rates higher than 10mL.min⁻¹ there is a decrease in recoveries of Zn²⁺ and Co²⁺.

On the other hand, complete elution of metal ions from the membrane disk was achieved when the flow rate was in the range of 1-5mL.min⁻¹. Thus, for further studies, the flow rates of 10ml min⁻¹ and 5mL.min⁻¹ for sample solution and eluting solvents were used.

The breakthrough volume of sample solution was tested by dissolving 20µg of metal ions in 50, 100, 150, 200, 250, 500, 1000, 2000 and 2500mL water .It was found that the extraction of Cu²⁺, Cd²⁺, Ni²⁺, Co²⁺, Pb²⁺, and Zn²⁺ by membrane disk up to 1000mL was complete. Use of higher volumes shows a decrease in retention of ions. Thus, the breakthrough volume of the method for these ions should be about

TABLE 2 : Effect of foreign ions on extraction efficiency^a

Foreign ion	Amount taken (mg)	%Recovery					
		Cu ²⁺	Co ²⁺	Cd ²⁺	Ni ²⁺	Zn ²⁺	Pb ²⁺
Na ⁺	386.7	91.8(2.8) ^b	93.4(2.9)	90.1(3.1)	91.2(3.5)	92.5(1.7)	94.7(2.7)
K ⁺	195.6	92.5(2.8)	92.7(2.5)	91.2(1.9)	89.2(1.7)	93.1(1.9)	95.1(1.9)
Mg ²⁺	1162.7	92.8(3.1)	94.1(2.3)	92.9(3.7)	90.7(2.5)	93.2(2.2)	95.0(2.8)
Ca ²⁺	602.2	93.5(2.4)	94.0(2.8)	92.8(3.1)	92.0(3.6)	92.5(2.6)	94.7(3.0)
Bi(III)	0.080	92.8(2.8)	93.7(2.6)	92.0(2.7)	92.5(3.0)	91.9(2.9)	94.2(2.4)
Mn(II)	0.080	93.7(2.7)	94.3(2.8)	92.5(2.1)	91.9(2.6)	93.5(2.8)	95.4(2.9)
Fe(III)	0.050	92.9(2.2)	94.0(2.9)	91.8(3.0)	92.5(2.9)	92.7(3.1)	95.7(2.7)
Hg(II)	0.50	93.9(2.9)	92.6(2.2)	92.3(2.8)	93.0(2.8)	93.0(2.4)	95.3(3.0)
Sn(IV)	0.50	94.0(3.0)	93.8(3.1)	92.4(3.0)	92.6(1.9)	93.5(2.8)	95.6(2.7)
Ag(I)	0.50	93.2(2.7)	93.6(2.7)	92.5(2.7)	91.9(2.5)	92.8(2.4)	94.3(2.2)
As(III)	0.50	92.9(2.5)	94.6(3.0)	91.9(2.9)	92.6(2.4)	92.5(3.0)	95.0(2.8)
Sb(III)	0.50	93.1(2.4)	93.6(2.7)	92.5(2.8)	92.4(3.0)	93.4(2.7)	94.7(3.0)
Fe ²⁺ &Fe ³⁺	0.050, 0.050	92.1(2.9)	93.1(3.0)	92.1(2.7)	92.5(2.5)	92.1(2.4)	93.9(3.1)
Fe ²⁺	0.050	93.1(3.0)	94.3(2.7)	92.5(2.9)	92.4(1.9)	92.6(2.6)	94.7(1.6)
Rb ⁺	162.5	92.9(2.8)	92.9(1.9)	91.8(2.0)	91.8(2.9)	92.9(2.1)	94.7(3.0)
Ba ²⁺	200.5	94.0(2.5)	93.6(2.0)	92.7(2.9)	90.7(3.0)	94.0(3.0)	95.1(2.5)
Sr ²⁺	256.6	92.8(2.0)	92.9(2.1)	91.6(2.8)	91.0(2.6)	92.5(2.2)	94.2(3.1)
Li ⁺	1002.5	93.5(2.5)	93.7(2.0)	92.8(3.0)	92.0 (3.0)	93.2(2.9)	94.6(2.8)
SO ₄ ²⁻	245.3	93.2(3.0)	93.5(3.0)	91.9(2.7)	99.2(2.1)	93.7(2.6)	95.1(2.7)
Cl ⁻	400.5	93.3(2.7)	93.7(2.7)	91.9(2.5)	92.0(2.2)	92.9(2.0)	94.6(2.7)
NO ₃ ⁻	1805.7	93.1(2.3)	92.7(1.9)	91.9(2.8)	99.4(1.7)	92.7(2.7)	95.0(2.8)

^aInitial samples contained 20µg of each heavy metal ions in 100mL of water ; ^bValues in parentheses are RSDs based on five individual replicate analysis

TABLE 3 : The equations of calibration graphs of determined cations

cation	Equations of calibration graphs	R ²
Ni ²⁺	y=0.0177x+0.0022	0.9981
Co ²⁺	y=0.0177x+ 0.0009	0.9983
Pb ²⁺	y=0.0076x+0.00005	0.9987
Zn ²⁺	y=0.0967x+0.0015	0.9988
Cu ²⁺	y=0.0271x+0.0001	0.9997
Cd ²⁺	y=0.072x+ 0.0008	0.9997

1000mL. Therefore, enrichment factor for(Cu²⁺, Cd²⁺, Ni²⁺, Co²⁺, Pb²⁺, Zn²⁺) are 100.

The preconcentration factor of the method was superior to those previously reported^[32,36]. The limit of detection (LOD)of metal ions by this method disk was studied under optimal experimental conditions, calculated as $C_{LOD} = K_b \cdot S_b / m^{[28]}$ where K_b is a numerical factor of 3, S_b is the standard deviation of ten replicates blank measurements and m is the slop of calibration curve. The LOD obtained for Cu²⁺, Cd²⁺, Ni²⁺, Co²⁺, Pb²⁺ and Zn²⁺ were 1.24, 0.47, 2.03, 2.05, 3.13 and 0.44ng.mL⁻¹ respectively. The LOD values of previous methods were higher than those of our work, thus better LOD has been achieved by the developed method^[33,34].

In order to investigate the effect of foreign ions on the determination of metal ions, an aliquot of aqueous solutions(100mL) containing 20µg of each metal ions and a given amounts of other ions as indicated in the(TABLE 2) were taken and the recommended procedure was applied. The results are summarized in TABLE 2. It was revealed that quantitative extraction of the ions could be performed in presence of the foreign ions.

The reproducibility of the proposed method for the extraction and determination of 20µg of Cu²⁺, Cd²⁺, Ni²⁺, Co²⁺, Pb²⁺, and Zn²⁺ in 100mL of water was also studied. The results of 10 replicate measurements revealed RSD_s of 1.5%, 2.0%, 1.7%, 2.5%, 3.0% and 1.4% for Cu²⁺, Cd²⁺, Ni²⁺, Co²⁺, Pb²⁺, and Zn²⁺ respectively. The reproducibility of this method surpassed those of the previous reports^{33, 34, 35, 36}. The calibration graph equations of cations are given in TABLE 3.

The applicability of the proposed method was evaluated by the determination of metal ions in 20µg of metals added to 500ml of the demineralized

TABLE 4 : Determination of metal ions in natural water(µg.L⁻¹)

Water samples	Cu ²⁺	Ni ²⁺	Cd ²⁺	Zn ²⁺	Pb ²⁺	Co ²⁺
Ground waterCharmshar	10.1(1.9) ^a	4.3(2.3)	9.0(2.0)	84.0(18)	71.1(3.2)	ND ^b
Karage spring	3.1(2.2)	3.3(2.3)	4.2(2.1)	12.0(2.9)	10.0(2.3)	ND
Ground waterVaramin	4.3 (1.2)	3.0(2.2)	6.0(2.2)	75.0(2.7)	13.1(2.9)	ND

^aStandard deviation based on three individual replicate measurement.

^bNot detected

water(see experimental section). Recovery percent of 20µg ions Cu²⁺, Cd²⁺, Ni²⁺, Co²⁺, Pb²⁺ and Zn²⁺ added to 500ml of the deions water were 95.0(1.8), 94.0(2.0), 94.2(2.5), 96.3(2.2), 95.1(2.1) and 97.0(2.0) respectively.

All elements of interest could be quantitatively from natural water samples with good precision. To assess the applicability of the method to real samples, it was applied to the extraction and determination of metal ions from 100mL of different water samples TABLE 4. The results showed that trace amounts of metal ions can be determined by proposed method.

CONCLUSION

Results presented in this work demonstrate well the good possibilities offered by the solid phase extraction of DDTC complexes of trace amounts of Cu²⁺, Cd²⁺, Ni²⁺, Co²⁺, Pb²⁺, and Zn²⁺ in water samples using octadecyl silica disk, and its determination by FAAS. The method developed is simple, reliable and precise for determining Cu²⁺, Cd²⁺, Ni²⁺, Co²⁺, Pb²⁺, and Zn²⁺ in water, also, the proposed method was free of interference compared to conventional procedures^[33,36,37]. The method could be successfully applied for the determination of Cu²⁺, Cd²⁺, Ni²⁺, Co²⁺, Pb²⁺, and Zn²⁺ in water samples.

REFERENCES

- [1] S.C.Sarkar, P.M.Dhadke; Sep.Purif.Technol, **15**, 131 (1999).
- [2] S.A.Popva, S.P.Bratinova, C.R.Ivanona; Analyst, **116**, 525 (1991).
- [3] N.Chimpalee, D.Chimpalee, S.Lohwithee, L.Nakwatchara; Anal.Chim.Acta, **329**, 315 (1996).
- [4] W.Yoshimura, Z.Uzawa, Bunseki Kagaku; **36**, 367 (1987).

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- [5] P.Burba Fresenius; *J.Anal.Chem.*, **341**, 709 (1991).
- [6] E.Batley, G.Matousek; *J.P.Anal.Chem.*, **52**, 1570 (1980).
- [7] R.Major; *LC-GC*, **4**, 972 (1986).
- [8] A.Siriraks, H.A.Kington, J.M.Riviello; *Anal.Chem.*, **62**, 1185 (1990).
- [9] C.Markell, D.F.Hagen, V.A.Bunnelle; *LC-GG International*, **4**, 10 (1991).
- [10] M.Saber Tehrani, A.Afshar Ebrahimi, F.Rastegar, *Annali di Chimica*, **94**, 429 (2004).
- [11] E.Vassileva, B.Varimezova, K.Hadjivanov; *Ana.J.Chim.Acta.*, **336**, 141 (1996).
- [12] V.Cuculic, M.Mlakar, M.Branica; *Anal.Chim.Acta*, **339**, 181 (1997).
- [13] A.Alexandrova, S.Arpadjan; *Anal.Chim.Acta*, **307**, 71 (1995).
- [14] I.Karado Jova, *Mikrochim.Acta.*, **130**, 185 (1999).
- [15] D.W.Lee, M.Halman; *Anal.Chem.*, **48**, 2214 (1976).
- [16] E.M.Moyers, J.S.Fritz; *Anal.Chem.*, **49**, 418 (1977).
- [17] E.M.Moyers, S.J.Fritz; *Anal.Chem.*, **48**, 1117 (1976).
- [18] O.Zaporozhets, N.Petruiock, O.Bessarabova, V.Sukhan; *Talanta*, **49**, 899 (1999).
- [19] R.E.Sturgeon, S.Berrman, S.N.Willie; *Talanta*, **29**, 167 (1982).
- [20] S.Hutchinson, G.A.Kearney, E.Horne, B.Lynch, J.D.Gennon, M.A.Mckerverey, S.J.Harris; *Anal.Chem. Acat.*, **291**, 296 (1994).
- [21] B.S.Garg, J.S.Bist, R.K.Sharma, N.Bhojak; *Talanta*, **43**, 2093 (1996).
- [22] Y.Yamini, A.Tamaddon; *Talanta*, **49**, 119 (1999).
- [23] H.G.Malakova, Z.M.Mateva; *Talanta*, **43**, 55 (1996).
- [24] V.Leepipatpiboon; *J.Chromatogr.A.*, **697**, 137 (1995).
- [25] Z.Aneva, S.Stamov, I.Kalaydjieva; *Anal.Lab.*, **6**, 67 (1997).
- [26] D.Atanasova, V.Stefanova, E.Russeva; *Talanta*, **45**, 857 (1998).
- [27] O.Zaporoz Hets, O.Gawer, V.Sukhun; *Talanta*, **46**, 1387 (1998).
- [28] D.J.Ingle, S.R.Crouch; *Spectrochemical analysis*, Hall Engle Wood Cliff.N.J, (1987).
- [29] S.Taguchi, K.Morisaku, Y.Sengoku, I.Kasahara; *The Analyst*, **124**, 1489 (1999).
- [30] Z.B.Alfassi, C.M.Wai; *Preconcentration techniques for trace elements*, CRC Press.B.Ca, Raton Ann Arbor London, 113 (1990).
- [31] M.C.Yebra, N.Carro, M.F.Enriquez, A.Moreno-cid, A.Garcia; *Analyst*, **126**, 933 (2001).
- [32] M.Saber Tehrani, F.Rastegar, A.Parchebaf, Z.Rezvani; *Chinese Journal of Chemistry*, **23**, 1 (2005).
- [33] E.Tagliati, G.Righetti, C.Locatelli; *Annali di Chimica* **93**, 659 (2003).
- [34] J.S.Fritz, M.P.Arena, S.A.Steiner, M.D.Porter; *Journal of Chromatography*, **A997**, 41 (2003).
- [35] S.N.Ignatova, A.B.Volynskii; *Journal of Analytical Chemistry*, **56(11)**, 1015 (2001).
- [36] E.Castillo, J.L.Cortina, J.L.Beltran, M.D.Pratt, M.Granados; *Analyst*, **126**, 1149 (2001).
- [37] V.P.Dedkova, O.P.Shoeva, S.B.Savvin; *Journal of Analytical Chemistry*, **56(8)**, 758 (2001).