



Trade Science Inc.

Materials Science

An Indian Journal

Full Paper

MSAIJ, 3(3), 2007 [181-187]

Solid Phase Extraction Of Trace Co(II) Using Octadecyl Silica Membrane Disks Modified 1,5-Diphenylcarbazide

Ali Moghimi¹, Mansour Jahangiri^{2*}¹Department of Chemistry, Varamin Campus, Islamic Azad University, Varamin, (IRAN)²Department of Chemistry, Saveh Campus Islamic Azad University, Saveh, (IRAN)

Fax: (+98)-292222-5010;

E-mail: Kamran9537@yahoo.com

Received: 26th May, 2007 ; Accepted: 31st May, 2007

ABSTRACT

A simple and reproducible method for the rapid extraction and determination of trace amounts of Co(II) ions using octadecyl-bonded silica membrane disks modified by 1,5-Diphenylcarbazide and Atomic Absorption Spectrometry is presented. The method is based on complex formation on the surface of the ENVI-18 DISK™ disks followed by stripping of the retained species by minimum amounts of appropriate organic solvents. The elution is efficient and quantitative. The effect of potential interfering ions, pH, ligand amount, stripping solvent, and sample flow rate were also investigated. Under the optimal experimental conditions, the break-through volume was found to about 1000mL providing a preconcentration factor of 500. The maximum capacity of the disks was found to be $486 \pm 7 \mu\text{g}$ for Co^{2+} . The limit of detection of the proposed method is 7ng per 1000mL. The method was applied to the extraction and recovery of Co(II) in different water samples.

© 2007 Trade Science Inc. - INDIA

KEYWORDS

Co(II);
SPE;
Octadecyl silica disks;
AAS;
1,5-Diphenylcarbazide.

INTRODUCTION

Co(II) at trace concentrations acts as both a micronutrient and a toxicant in marine and fresh water systems^[1-8]. This element is needed by plants at only very low levels and is toxic at higher levels. At these levels, Co(II) can bind to the cell membrane and hinder the transport process through the cell wall. Co(II) at nearly 40 ng mL^{-1} is required for normal metabolism of many living organisms^[9,10]. On the

other hand, Co(II) is an important element in many industries. Thus, the development of new methods for selective separation, concentration and determination of it in sub-micro levels in different industrial, medicinal and environmental samples is of continuing interest. The determination of Co(II) is usually carried out by flame and graphite furnace atomic absorption spectrometry (AAS)^[11,12] as well as spectrometric methods^[13,14]. However, due to the presence of Co(II) in medicinal and environmental

Full Paper

samples at low levels, its separation from other elements presents and also the use of a preconcentration step prior to its determination is usually necessary.

Different methods, especially Liquid-Liquid extraction of Co(II) in the presence of various classical^[15-19] and macrocyclic^[20,21] co-extractant ligands has attracted considerable attention. However, the use of classical extraction methods for this purpose is usually time-consuming, labor-intensive and requires large amounts of high purity solvents for extraction. Nevertheless, several other techniques for the preconcentration and separation of Co(II) have been proposed including liquid chromatography^[22] supercritical fluid extraction^[23], flotation^[24], aggregate film formation^[25], liquid membrane^[26], column adsorption of pyrocatechol violet-Co(II) complexes on activated carbon^[27], ion pairing^[28], ion pairing^[29], preconcentration with yeast^[30], and solid phase extraction using C₁₈ cartridges and disks^[31,33].

Solid phase extraction (SPE) or liquid-solid extraction is popular and growing techniques that are used to sample preparation for analysis. It is an attractive alternative for classical liquid-liquid extraction methods that reduce solvent usage and exposure, disposal costs and extraction time for sample separation and concentration purposed^[34,36]. In recent years, the octadecyl-bonded silica SPE disks have been utilized for the extraction and separation of different organic compounds from environmental matrices^[37-40]. Moreover, the SPE disks modified by suitable ligands are successfully used for selective extraction and concentration of metal ions^[41,42].

In a recent series of papers,^[43,45] we have described the application of metal-DNA conjugates to nucleic acid sequence determination with catalytic signal amplification; the assay relies on the esterase activity of a DNA-linked Co complex. For optimization of the system and exploration of structure-activity relationships, a sensitive probe would be useful, which allows straightforward detection of esterase activity of ligated Co²⁺ in low concentration. The aim of this work was the development of a rapid, efficient and highly sensitive method for selective extraction and concentration of ultra trace amounts of Co²⁺ ions from aqueous media using octadecyl silica membrane disks modified by 1,5-Diphenylcarbazid (H₄L) and AAS determination.

EXPERIMENTAL

Reagents

All acids were of the highest purity available from Merck and were used as received. Methanol and Chloroform were of HPLC grade from Merck. Analytical grade nitrate salts of lithium, sodium, potassium, magnesium, calcium, strontium, barium, zinc, cadmium, lead, nickel, cobalt(II), and Co(II) were of the highest purity. Ultra pure organic solvents were obtained from E.Merck, Darmstadt, Germany, and High Purity double distilled deionized water was used throughout the experiments. 1,5-Diphenylcarbazid (DPC) was of analytical grade from E.Merck, D-6100 Darmstadt.F.R.Germany.

The stock standard solution of Co²⁺ was prepared by dissolving 0.1000g of the Co(II) powder in 10mL concentrated nitric acid and diluted to 1000mL with water in a calibrated flask. Working solutions were prepared by appropriate dilution of the stock solution.

Apparatus

Determination of Co²⁺ contents in working samples were carried out by a Varian spectra A.200 model atomic absorption spectrometer equipped with a high intensity hollow cathode lamp(HI-HCL) according to the recommendations of the manufacturers. These characteristics are tabulated in (TABLE 1).

Solid phase extractions were carried out by glassy membrane disks, ENVI-18DISK™ 47mm diameter ×0.6mm thickness containing octadecyl silica bonded phase (30μm particles, 70 Å pore size) obtained from Supelco in conjunction with a standard Millipore 47mm filtration apparatus equipped with a vacuum pump. The pH measurements were carried out by an ATC pH meter(EDT instruments, GP 353).

Sample extraction

TABLE 1 : The operational conditions of flame for determination of Co(II)

Slit width	0.7 nm
Operation current of HI-HCL	15 mA
Resonance fine	321.9nm
Type of background correction	Deuterium lamp
Type of flame	Air/acetylene
Air flow	9.0mL.min ⁻¹
Acetylene flow	2.4mL.min ⁻¹

Extraction were performed with glassy membrane disks, ENVI-18 DISK™ 47mm diameter×0.6 mm thickness containing octadecyl silica bonded phase(30µm particles, 70 Å pore size) from Supelco. The disks were used in conjunctions with a standard Millipore 47mm filtration apparatus connected to water aspirator^[46].

1. Sample treatment

The water samples were filtered through 45µm nylon filters. Sampling vessels were polyethylene bottles soaked in 1mol.L⁻¹ HNO₃ overnight and rinsed twice with deionized water. The analysis must be done within 2 days of sample collection to limit the risk of interconversion of Co(II). Then, 5mL of methanol was added to a 90mL portion of each before analysis. The surface of the ENVI-18 DISK™ disks is not modified with DPC and therefore could not retain Co²⁺ ions properly. Instead, 10mg of DPC was dissolved in an appropriate volume of an organic solvent(5mL) miscible with water. The most suitable solvent under the experimental conditions was acetone. The DPC solution was added to aqueous solution of Co²⁺ and the mixture was stirred gently.

2. Disk cleaning and conditioning

A disk was placed in the apparatus and was washed with 10mL of methanol to remove all contaminants arising from the manufacturing process and the environment. Then, the disk was dried by passing air through it for several minutes. To insure optimal extraction of the analytes of interest, the disk was again washed with 10mL of methanol, immediately followed by 10mL of water, without letting the surface of the disk dry. This step pre-wets the disk surface prior to extraction. Improper performance of this step causes slow flow-rate and poor analyte recoveries. It is important to avoid any air contact with the surface of the disk before the addition of the sample.

3. Sample addition

After complete homogenization, accurate volumes of the sample solutions (100mL portions) were transferred to the top reservoir of the disk apparatus. At the same time, the solution was drawn through the disk by applying a mild vacuum. Application of vacuum was continued until the disk was completely

dry (about 5 minute).

4. Analyte elution

In order to elute the analyte selectively, exactly 5mL of acidified solvents 0.1M-HCl in methanol was passed through the disk and collected into a 5.0mL volumetric flask under the extraction funnel. It was found that ultra pure alcoholic organic solvents were the best eluting agents. The concentration of Co(II) in the eluates were then determined by FAAS using an external calibration graph.

RESULTS AND DISCUSSION

Evaluation of the role of the ligand

Some preliminary experiments were performed for investigation of absence or presence of DPC on the quantitative extraction of Co(II). It was concluded that the membrane disk itself does not show any tendency for the retention of Co(II), but introduction of 100mL portions of aqueous Co(II) samples containing 10µg of Co(II) and 10mg of DPC leads to satisfactory its retention (TABLE 2). The latter case is most probably attributed to the existence of a considerable interaction between Co(II) and the DPC. It should be mentioned that formation of stable complexes between Co(II) and DPC at pH=2 is probably due to an ion pair formation mechanism. However, at pH higher than 2 the retention and percentage recovery of Co(II) are negligible.

Choice of eluent

In order to select the most appropriate eluent for the quantitative stripping of the retained Co(II) on the disks, 5mL of various non organic (each containing 10%V.V⁻¹ methanol) and different organic solvents were tested. The results tabulated in TABLE 2. As can be seen, the best eluting solvents were found to be 5mL of methanol or ethanol, resulting in quantitative elution of Co(II) from the disk. It should be em-

TABLE 2 : The effect of presence of DPC on extraction percent of Co(II)^a

DPC	pH	Extraction percent of Co(II)
Absence	2-6	0.00(7.1) ^b
Presence	2-6	99.8(1.9) to 85(3.10)

^aInitial samples contained 10µg of Co(II) in 100mL of water.

^bValues in parentheses are RSD_s based on five individual replicate analyses.

Full Paper

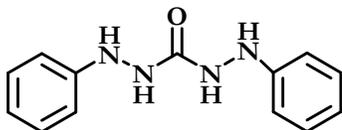
1,5-Diphenylcarbazid(H₄L)

Figure 1 : Molecular structure of 1,5-diphenylcarbazid (DPC)

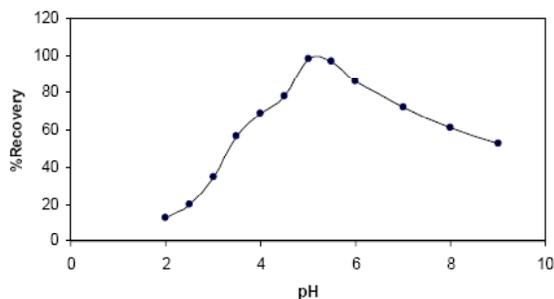


Figure 2 : Influence of sample pH and dissolving solvent of DPC on the percentage recovery of Co(II)

TABLE 3 : Effect of different eluting solvents on Percentage recovery of Co(II) adsorbed on the disk^a

Stripping solution	%Recovery		
	2ml	5ml	10ml
Methanol	87(1.6) ^b	99.1(1.9)	99.7(1.8)
Acidified methanol ^c	67(2.0)	88.2(2.2)	87.9(1.7)
Ammoniacal methanol ^d	54 (2.1)	85.7(1.7)	86.9(2.2)
Ethanol	85.1(1.7)	97.8(1.5)	98.8(1.3)
1-Propanol	23(2.8)	45(5.7)	48(4.6)
Formic acid(1M)10% V.V ⁻¹ mthanol	55(1.2)	62(1.0)	71(1.2)
Hydrochloric acid(3M) 10% V.V ⁻¹ mthanol	69(1.8)	91(2.1)	90(1.9)
Hydrochloric acid(1M) 10% V.V ⁻¹ mthanol	66(2.0)	89(1.6)	91(1.7)
Nitric acid(3M)10% V.V ⁻¹ mthanol	60(1.9)	82(2.2)	88(2.0)
Nitric acid(1M)10% V.V ⁻¹ mthanol	62(2.1)	80(1.6)	83(1.7)
Ethanol	85(1.8)	98.6(2.0)	98.4(1.9)

^aInitial samples contained 10 μ g of each Co(II) in 100mL water ; ^bValues in parentheses are RSDs based on five individual replicate analysis ; ^cAcidified solvents obtained by addition of 0.1M-HCl ; ^dAmmoniacal solvents obtained by addition of 0.1M-NH₃

TABLE 4 : Percent recovery of Co(II) from the modified membrane disk in the presence of 0.01 M of different counter anions^a

Counter anion	%Recovery
Cl ⁻	12.7
Br ⁻	18.9
ClO ₄ ⁻	18.4
SCN ⁻	20.9
Picrate	82.5
Acetate	98.2

phasized that presence of methanol in any kind of employed solvents helps to better the contact of eluent with hydrophobic surface of the disk.

The effect of the pH

The pH of the sample solutions were adjusted to different values between 2-9 by addition of hydrochloric acid or a suitable buffer such as sodium acetate-acetic acid or sodium dihydrogen phosphate-disodium hydrogen phosphate, and then solutions passed through the disks.

Eventually, the metal ions were stripped by pure methanol or ethanol solutions followed by flame atomic absorption determination of the eluted Co(II). Then, percentage recovery at various pH values was determined (Figure 2). According to the results shown in figure 2 up to pH 5.0-5.5, complete recoveries are obtained. However, at higher pH values, percentage recovery decreases. This is due to fact that in an acidic solution the protonation of DPC occurs and there is a weak tendency for retention between Co(II) and DPC, whereas at higher values (pH>5), Co(II) reacts with hydroxide ions to produce Co(OH)₂. Therefore, sodium acetate-acetic acid buffer with pH=5 was used for the preconcentration step. Other solvents used for dissolving DPC were methanol and ethanol. The influences of these solvents on the recoveries as a function of pH are compared and shown in figure 2. Mean while, other organic solvents were not tested because of their restricted solubility and formation of two phases with aqueous solutions and incompatibility with flame. Higher pH values (>7) were not tested because of the possibility of the hydrolysis of octadecyl silica in the disks^[47].

Effect amount of counter anion

In order to investigate the effect of counter ion on the recovery Co²⁺ ions by the modified disks, different counter anions were tested TABLE 4, it is immediately obvious that the nature of the counter anion strongly influences the retention of Co ions by the disk. The results revealed that the DPC behaves as a neutral ionophore in the pH range 5.5-6.0^[49,50] so that the Co ions are retained as ion pair complexes by the membrane disks. As seen, acetate ion is the most efficient counter anion for the SPE

of Co(II) ions. The influence of the concentration of sodium acetate ion on Co recovery was investigated, and the results are shown in TABLE 4. As seen, the percent recovery of Co^{2+} increased with the acetate concentration until a reagent concentration of about 0.1 M is reached, beyond which the recovery remained quantitative.

Moreover, acetate ion acts as a suitable buffering agent, while it effectively contributes to the ion-pair formation; thus, in the SPE experiments, there was no need for the addition of any buffer solution.

The influence of flow-rate

One of the most important parameters affecting solid phase extraction is the speed of the process. Hence, the effect of flow-rates on extraction efficiencies was investigated. It was found that in the range of 10-100 mL.min⁻¹, the retention of Co(II) was not considerably affected by the sample solutions flow-rates and leads to reproducible and satisfactory results (Figure 3). Thus, the flow-rate was maintained at 57 mL.min⁻¹ throughout the experiment.

Quantity of the DPC

The optimum amount of DPC for the quantitative extraction of Co(II) was also investigated by adding various amounts of it to solution (between 2-20 mg). The results are listed in TABLE 5. The experimental results revealed that the extraction of Co(II) was quantitative using a sample solution containing more than 10 mg DPC. Hence, subsequent extractions were performed with 12 mg of DPC.

Disk efficiency

Undoubtedly, one of the major parameters affecting in the SPE determinations is the efficiency of the used membrane disks. However, to the best of our knowledge this case has not been discussed elsewhere in similar reports. Under the optimum experimental conditions, it was found out that each ENV-18 DISK™ disk could perform at least 15 replicate analyses if organic eluting solvents are used. On the other hand, acidic, eluents practically decrease the number of time a disk could be used to 10 replicates. These observations are represented in figure 4.

Analytical performance

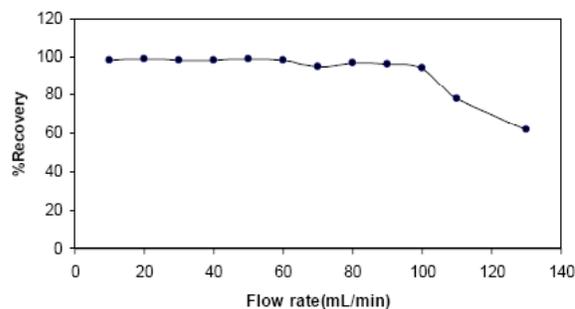


Figure 3 : The effect of the flow-rate on extraction percent of Co(II)

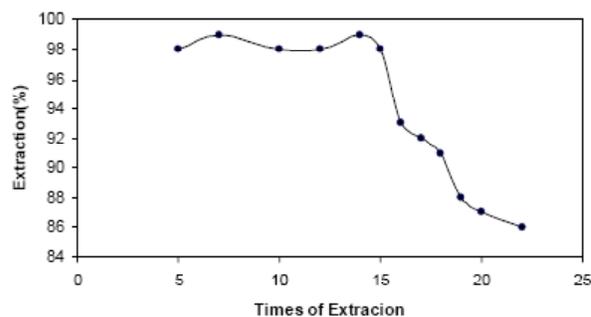


Figure 4 : Influence of eluent type on disk efficiency

TABLE 5 : Influence of the DPC amount on the recovery of Co(II) ions^a

DPC amount (mg)	Recovery(%) of Co(II)
2	45(1.8) ^b
5	68(1.9)
8	84(1.9)
10	96.6(1.8)
15	96.2(2.2)
20	97.9(2.3)

^aInitial samples contained 10 μg of each Co(II) in 100 mL water

^bValues in parentheses are RSDs based on five individual replicate analysis

When solutions of 10 μg Co(II) in 10, 50, 100, 500, 1000, 2000 and 2500 mL solutions under optimal experimental conditions were passed through the disks, the Co(II) was quantitatively retained in all cases. Thus, the breakthrough volume for the method must be greater than 2000 mL, providing a concentration factor of >400. The limit of detection (LOD) of the method for the determination of Co(II) was studied under the optimal experimental conditions. The LOD based on 3σ of the blank is 7 ng per 1000 mL.

The capacity of modified disks (5 mg DPC) was determined by passing 50 mL portions of sample solutions containing 8 mg of Co(II) and 0.1 M sodium acetate-acetic acid buffer with pH 5.5-6.0, followed

Full Paper

TABLE 6 : Separation of Co(II) from binary mixtures^a

Diverseion	Amounts taken(mg)	% Found	%Recovery of Co ²⁺ ion
Na ⁺	80.5	1.25(1.9) ^b	98.0(1.8)
K ⁺	85.5	1.42(1.1)	96.5(1.2)
Mg ²⁺	15.7	0.7(1.8)	98.7(1.7)
Ca ²⁺	28.6	1.27(1.0)	99.6(2.1)
Sr ²⁺	3.18	2.25(1.2)	98.2(1.1)
Ba ²⁺	2.26	3.11(1.4)	98.3(1.3)
Mn ²⁺	2.78	1.55(1.3)	98.7(2.9)
Co ²⁺	2.10	1.8(2.3)	98.0(0.9)
Ni ²⁺	2.46	2.0(1.4)	98.4(1.4)
Zn ²⁺	2.21	1.87(2.1)	98.8(2.2)
Cd ²⁺	2.15	1.93(2.1)	98.2(2.8)
Pb ²⁺	2.22	2.22(2.0)	98.5(1.7)
Hg ²⁺	2.53	4.81(2.1)	97.5(1.8)
Ag ⁺	2.15	2.45(1.9)	96.6(1.9)
Cr ³⁺	1.96	2.92(2.30)	97.3(1.4)
UO ²⁺	2.06	1.8(1.10)	98.3(1.7)

^aInitial samples contained 10 μ g Co²⁺ and different amounts of various ions in 100mL water(0.1 M acetate ion).

^bValues in parentheses are RSDs based on five individual replicate analysis

TABLE 7 : Recovery of Co(II) added to 1000mL of different water samples(contaning 0.1M acetate at pH=5.5-6.0)

Sample	Co ²⁺ added(μ g)	Co ²⁺ determined(ng .mL ⁻¹)
Tap water	0.0	1.82(2.9) ^a
	10.0	12.22(2.2)
Snow water	0.0	4.86(1.8)
	10.0	14.94(2.9)
Rain water	0.0	2.56(2.1)
	10.0	12.38(2.8)
Sea Water	0.0	13.54(2.7)
	10.0	23.95(1.2)

^aValues in parentheses are RSDs based on five individual replicate analysis

by the determination of the retained metal ions in the eluting solution using AAS. The maximal capacity of the disk obtained from three replicate measurements was 486 \pm 7 μ g of Co²⁺ on the disk.

In order to investigate the selective separation and determination of Co²⁺ ions from its binary mixtures with various metal ions, an aliquot of aqueous solutions(50mL) containing 105 μ g Co²⁺ and mg amounts of other cations was taken and the recommended procedure was followed. The results are summarized in TABLE 6. The results show that the Co(II) ions in binary mixtures are retained almost completely by the modified disk, even in the presence of up to about 100mg of various ions. Meanwhile, retention of other cations by the disk is very

low and they can separated effectively from the Co²⁺ ion. Its is interesting to note that, in other experiments, we found that in the presence of high enough concentrations NH₂OH.HCl as a suitable reducing agent(>0.3M) [48].

Analysis of water samples

To assess the applicability of the method to real samples, it was applied to the extraction and determination of Co(II) from different water samples. Tap water(Tehran, taken after 10min operation of the tap), rain water(Tehran, 26th January, 2006), Snow water (Saveh, 6th February, 2006)and Sea water(taken from Caspian sea, near the Mahmoud-Abad shore) samples were analyzed(TABLE 7). As can be seen from TABLE 4 the added Co(II) ions can be quantitatively recovered from the water samples used.

CONCLUSION

Results presented in this work demonstrate well the tremendous possibilities offered by the solid phase extraction of trace amounts of Co(II) in water samples using Octadecyl Silica membrane disks modified by 1,5-Diphenylcarbazid and its determination by FAAS. The method developed was simple, reliable, and precise for determining Co(II) in water. Also, the proposed method was free of interference compared to conventional procedures to determine Co(II)^[51-55]. The methode can be successfully applied to the separation and determination of Co(II) in binary mixtures.

ACKNOWLEDGEMENTS

The authour wish to thank the Chemistery Department of Varamin Campus Islamic Azad University and SavehCampus Islamic Azad University for financial support.

REFERENCES

- [1] H.J.M.Bowen; 'Enviromental Chemistery of the Elements', Academic Press, New York, 132-135 (1979).
- [2] L.E.Brand, W.G.Sunda, R.R.L.Guillard; J.Exp.Mar. Biol.Ecol., 96, 225 (1986).
- [3] H.H.Taylor, J.M.Anstiss; Mar.Freshwat.Res., 50, 907 (1999).
- [4] F.M.M.Morel, R.J.M.Hudson, N.M.Price; Limnol.

- Oceanogr., **36**, 1742 (1991).
- [5] A.S.Gordan; *Mar.Chem.*, **38**, 1 (1992).
- [6] J.W.Moffett, L.E.Brand, P.L.Croot, K.A.Barbeau; *Limnol.Oceanogr.*, **42**, 789 (1997).
- [7] P.L.Croot, J.W.Moffett, L.E.Brand; *Limnol. Oceanogr.*, **45**, 619 (2000).
- [8] M.Wood, H.K.Wang; *Environ.Sci.Technol.*, **17**, 582A (1983).
- [9] N.N.Greenwood, A.Eamshow; 'Chemistry of Elements', Pergamon Press, New York, (1984).
- [10] C.A.Burtis, E.R.Ashwood; 'Textbook of Clinical Chemistry', third ed., Macmillan, New York, (1999).
- [11] B.Wetz; 'Atomic Absorption Spectroscopy', VCH, Amsterdam, (1985).
- [12] A.D.Eaton, L.S.Clesceri, A.E.Greenberg; 'Standard Methods for the examination of water and waste water', 19th ed, American Public Health Association, Washington, DC, (1995).
- [13] F.J.Welcher, E.Boschmann; 'Organic Reagents for Co(II)', Krieger Huntington, New York, (1979).
- [14] Z.Marczenko; 'Separation and Spectrophotometric Determination of Elements', Ellis Horwood, London, (1986).
- [15] O.P.Bharagava; *Talanta*, **16**, 743 (1969).
- [16] A.A.Schilt, W.C.Hoyle; *Anal.Chem.*, **41**, 344 (1964).
- [17] L.G.Borchart, J.P.Butler; *Anal.Chem.*, **29**, 414 (1957).
- [18] R.Chaisuksant, W.P.Ayuthaya, K.Grudpan; *Talanta*, **53**, 579 (2000).
- [19] D.Kara, M.Alkan; *J.Microchem.*, **71**, 29 (2002).
- [20] K.Saito, S.Murakami, A.Muromatsu, E.Sekido; *Anal.Chim.Acta*, **294**, 329 (1994).
- [21] K.Ikeda, S.Abe; *Anal.Chim.Acta*, **363**, 165 (1998).
- [22] S.Igarashi, N.Ide, Y.Takagai; *Anal.Chim.Acta*, **424**, 263 (2000).
- [23] J.Liu, W.Wang, G.Li; *Talanta*, **53**, 1149 (2001).
- [24] A.N.Anthemidis, G.A.Zachariadis, J.A.Stratis; *Talanta*, **54**, 935 (2001).
- [25] D.Zenedelovska, G.Pavlovska, K.Cundeva, T.Stafilov; *Talanta*, **54**, 139 (2001).
- [26] M.Endo, K.Suzuki, S.Abe; *Anal.Chim.Acta*, **364**, 13 (1998).
- [27] M.E.Campderros, A.Acosta, J.Marchese; *Talanta*, **47**, 19 (1998).
- [28] I.Narin, M.Soylak, L.Elic, M.Dogan; *Talanta*, **52**, 1041 (2000).
- [29] Y.Akama, M.Ito, S.Tanaka; *Talanta*, **52**, 645 (2000).
- [30] K.Ohta, H.Tanahasi, T.Suzuki, S.Kaneco; *Talanta*, **53**, 715 (2001).
- [31] V.Cuculic, M.Mlakar, M.Branica; *Anal.Chim.Acta*, **339**, 181 (1997).
- [32] A.Moghimi, M.S.Tehrani, S.Waqif Husain; Chinese Journal of Chemistry in press.
- [33] M.S.Tehrani, A.Moghimi, S.Waqif Husain; Chinese Journal of Chemistry in press.
- [34] E.M.Thurman, M.S.Mills; *Solid-Phase Extraction, Principles and Practice*, Wiley, New York, (1998).
- [35] J.Pawliszyn; 'Solid-Phase Microextraction, Theory and Practice', Wiley-VCH, New York, (1997).
- [36] R.M.Izatt, J.S.Bradshaw, R.L.Brueening; *Pure Appl. Chem.*, **68**, 1237 (1996).
- [37] D.F.Hagen, C.G.Markell, G.A.Schmitt; *Anal.Chim. Acta*, **236**, 157 (1990).
- [38] C.J.Krueger, J.A.Fild; *Anal.Chem.*, **67**, 3363 (1995).
- [39] K.Z.Taylor, D.S.Waddell, E.J.Reiner; *Anal.Chem.*, **67**, 1186 (1995).
- [40] Y.Yamini, M.Ashraf-Khorassani; *J.High Resolut. Chromatogr.*, **17**, 634 (1994).
- [41] M.Shamsipur, A.R.Ghiasvand, Y.Yamini; *Anal. Chem.*, **71**, 4892 (1999).
- [42] M.Shamsipur, A.R.Ghiasvand, H.Sharghi; *Int.J. Environ.Anal.Chem.*, **82**, 23 (2001).
- [43] J.Brunner, A.Mokhir, R.Kramer; *J.Am.Chem.Soc.*, **125**, 12410 (2003).
- [44] F.H.Zelder, J.Brunner, R.Kramer; *Chem.Commun.*, 902 (2004).
- [45] I.Boll, R.Kramer, J.Brunner, A.Mokhir; *J.Am.Chem. Soc.*, **27**, 7849 (2005).
- [46] D.F.Hagen, C.G.Mrkell, G.A.Schmitt, D.D.Blevins; *Anal.Chim.Acta*, **236**, 157 (1990).
- [47] Y.Yamini, N.Alizadeh, M.Shamsipur; *Anal.Chim.Acta*, **69**, 355 (1997).
- [48] Y.Petit de Pena, M.Gallego, M.Valcarcel; *Anal.Chem.*, **67**, 2524 (1995).
- [49] N.Alizadeh, H.Naeimi, H.Sharghi, Samsipur, M.Polish; *J.Chem.*, **73**, 915 (1999).
- [50] N.Alizadeh, H.Naeimi, H.Sharghi, Samsipur, M.Polish, Fresenius; *J.Anal.Chem.*, In press.
- [51] Y.S.hoi, H.S.Choi; *Bull.Korean Chem.Soc.*, **24**, 222 (2003).
- [52] E.Matoso, L.T.Kubota, S.Cadore; *Talanta*, **60**, 1105 (2003).
- [53] B.Purachat, S.Liawruangrath, P.Sooksamiti, S.Rattanaphani, Buddhasukh; *D.Anal.Sci.*, **17**, 443 (2001).
- [54] A.A.Ensafi, S.Abbasi, H.Rahimi Mansour, Mohammad pour Baltork; *I.Anal.Sci.*, **17**, 609 (2001).
- [55] M.Saber Tehrani, F.Rastegar, A.Parchehbaf, Z.Rezvani; *Chinese Journal of Chemistry*, **23**, 1437 (2005).