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# Solid Phase Extraction Of Cu(II) On Octadecyl Bonded Silica Membrane Disk Modified With 4-(2-Pyridylazo)Resorcinol And Determination By Flame Atomic Absorption Spectrometry

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## ABSTRACT

A simple, reliable and rapid method for preconcentration and determination of Cu(II) using octadecyl bonded silica membrane disk impregnated with 4-(2-pyridylazo)resorcinol(PAR) and flame atomic absorption spectrometry is presented. 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 536±3μg μg for Cu(II).The limit of detection of the proposed method is 15ng per 1000mL.The method was applied to the extraction and recovery of Cu(II) in different water samples.In this method is relative standard deviation (R.S.D.) of 3%.

## KEYWORDS

Solid phase extraction;
Cu(II);
4-(2-pyridylazo) resorcinol (PAR);
Octadecyl bonded;
Silica membrane disk.

## INTRODUCTION

Cu(II) 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 Cu(II) in water[3], soil[4,5] and plant samples[6]. However, the determination of traces of Cu(II) by FAAS in such complex matrices is difficult due to its low sensitivity ($0.01\mu gcm^{-3}$) 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 Cu(II) 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], Ambersorb resin [19] and polyurethane foam[20]. Two methodologies were commonly practiced for solid phase extraction of Cu(II). 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), 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 Cu(II) 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 Cu(II) to facilitate its determination from complex matrices using 4-(2-pyridylazo)resorcinol(PAR) impregnated on C18 disk.

Solid phase extraction methods using columns with a narrow internal diameter limit the usable flow rates to a range of 1-10$cm^3min^{-1}$ resulting in long time for enrichment from large sample volumes. WhileC18 disks enable much higher flow rates[5,30,39-48].

In view of this the extraction of Cu(II) with 4-(2-pyridylazo)resorcinol impregnated on C18 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.

## EXPERIMENTAL

### Apparatus

Determination of Cu(II) contents in working samples were carried out by a Varian spectra A.200 model atomic absorption spectrometer equipped with a high intensity hallow cathode lamp(HI-HCl) according to the recommendations of the manufacturers. Solid phase extractions were carried out by glassy membrane disks, ENVI-18DISKTM 47mm diameter×0.6mm thickness containing octadecyl silica bonded phase (30 μm particles, 70 A° pore size) obtained from Supelco in conjunction with a standard Millipore 47 mm filtration apparatus equipped with a vacuum pump. The pH measurements were carried out by an ATC pH meter (EDT instruments, GP 353).

### Reagents

All acids were of the highest purity available from Merck and were used as received. Methanol and Chlorofom were of HPLC grade from Merck. Analytical grade nitrate salts of litium, sodium, potassium, magnesium, calcium, strontium, barium, zinc, cadmium, copper(II) nickel, cobalt(II), and Pb (II) and 4-(2-pyridylazo)resorcinol were of the highest purity. Ultra pure organic solvents were obtained from E.Merck, Darmstat, Germany, and High Purity double distilled deionized water was used throughout the experiments. The stock standard solution of Pb (II) was prepared by dissolving 0.1000g of the Cu(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.

### Sample extraction

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.[36]

### Sample treatment

The water samples were filtered through 45μm nylon filters. Sampling vessels were polyethylene bottles soaked in 1mol.L$^{-1}$ $HNO_3$ 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 Cu(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 PAR and therefore could not retain Cu(II) ions properly. Instead, 10 mg of PAR 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 PAR solution was added to aqueous solution of Cu(II) and the mixture was stirred gently.

### 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.

### 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).

### 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 Cu(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 PAR on the quantitative extraction of Cu(II).It was concluded that the membrane disk itself does not show any tendency for the retention of Cu(II), but introduction of 100mL portions of aqueous Cu(II) samples containing 10μg of Cu(II)and 10mg of PAR Cu(II)s to satisfactory its retention(TABLE 1). The latter case is most probably attributed to the existence of a considerable interaction between Cu(II)and the PAR. It should be mentioned that formation of stable complexes between Cu(II) and PAR at pH 5 is probably due to an ion pair formation mechanism. However, at pH higher than 5 the retention and percentage recovery of Cu(II)are negligible.

### Choice of eluent

In order to select the most appropriate eluent for the quantitative stripping of the retained Cu(II)on the disks, 5mL of various non organic solvents were tested. The results in figure 3. As can be seen, the best eluting solvents were found to be 5mL of $HNO_3$, 1M, resulting in quantitative elution of Cu(II)from the disk.

### The effect of the pH

The pH of the sample solutions were adjusted

**TABLE 1 : The effect of presence of PAR on extraction percent of Cu(II)**[a]

| PAR | pH | Extraction percent of Cu(II)(II) |
|---|---|---|
| Absence | 2-7 | 1.2(6.0)[b] |
| Presence | 2-6.5 | 98.4(2.2) to 67(2.8) |

[a]Initial samples contained 10μg of Cu(II) in 100mL of water.

[b]Values in parentheses are $RSD_S$ based on five individual replicate analyses.

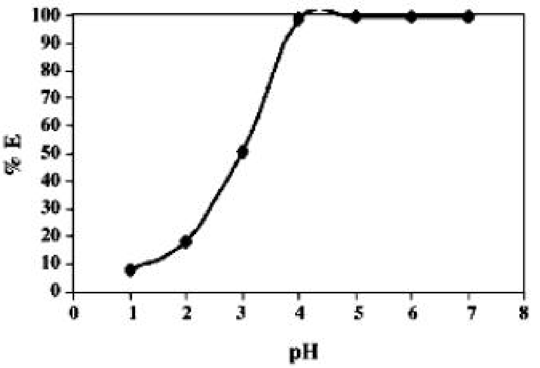

**Figure 1 : Influence of sample pH and dissolving solvent of PAR on the percentage recovery of Cu(II)**

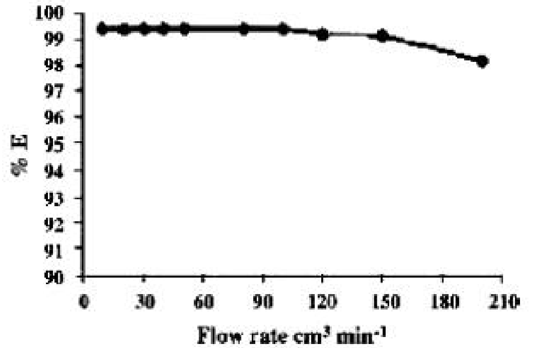

**Figure 2 : The effect of the flow-rate on extraction percent of Cu(II)**

to different values between 2-8 by addition of hydrochloric acid or a suitable buffer such as sodium acceate-acetic acid or sodium dihydrogen phosphate-disodium hydrogen phosphate, and then solutions passed through the disks.

Eventually, the metal ions were stripped by 5mL of $HNO_3$, 1M followed by flame atomic absorption determination of the eluted Cu(II).Then, percentage recovery at various pH values was determined (Figure 1). According to the results shown in Figure1 up to pH 4.5-5, 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 PAR occurs and there is a weak tendency for retention between Cu(II)and PAR, whereas at higher values(pH>5.5), Cu(II)reacts with hydroxide ions to produce $Pb(OH)_2$. Therefore, sodium acceate-acetic acid buffer with pH=5 was used for the preconcentration step. Other solvents used for dissolving PAR were 5mL of $HNO_3$, 1M. The influences of these solvents on the recoveries as a function of pH are compared and shown in figure 1. 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[37].

## Effect amount of counter anion

In order to investigate the effect of counter ion on the recovery Cu(II) ions by the modified disks, different counter anions were tested Table 2, it is immediately obvious that the nature of the counter anion strongly influences the retention of Cu(II) ions by the disk. The results revealed that the PAR behaves as a neutral ionophore in the pH range 4.5-5.0[38-40] so that the Cu(II) 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 Cu(II)ions. The influence of the concentration of sodium acetate ion on Cu(II) recovery was investigated, and the results are shown in TABLE 2. As seen, the percent recovery of Cu(II) increased with the acetate concentration until a reagent concentration of about 0.1M is reached, beyond which the recovery remained quantitative.

Moreover, acetate ion acts as a suitable buffering agent, while it effectively contributes to the ions-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 effi-

**TABLE 2 : Percent recovery of Cu(II) from the modified membrane disk in the presence of 0.01M of different counter anions[a]**

| counter anion | %Recovery |
|---|---|
| $Cl^-$ | 27.0 |
| $Br^-$ | 24.7 |
| $ClO_4^-$ | 37.0 |
| $SCN^-$ | 46.8 |
| Picrate | 77.5 |
| Acetate | 97.3 |

[a]Initial samples contained 10μg of Cu(II) in 100mL of water

**TABLE 3 : Influence of the PAR amount on the recovery of Cu(II) ions[a]**

| PAR amount (mg) | Recovery(%) of Cu(II) |
|---|---|
| 2 | 35(2.1)[b] |
| 6 | 44(2.9) |
| 8 | 86(2.8) |
| 10 | 98.8(2.5) |
| 15 | 98.9(2.3) |
| 20 | 98.8(2.6) |

[a] Initial samples contained 10μg of each Cu(II) in 100mL water
[b] Values in parentheses are RSDs based on five individual replicate analysis

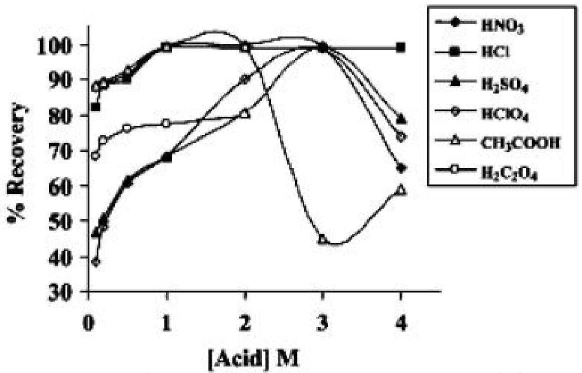

**Figure 3 : Influence of eluents on recovery of Cu(II)**
Aqueous phase=100cm$^3$, pH=5, flow rate=30-40cm$^3$min$^{-1}$, eluent volume=5cm$^3$, flow rate=10cm$^3$min$^{-1}$.

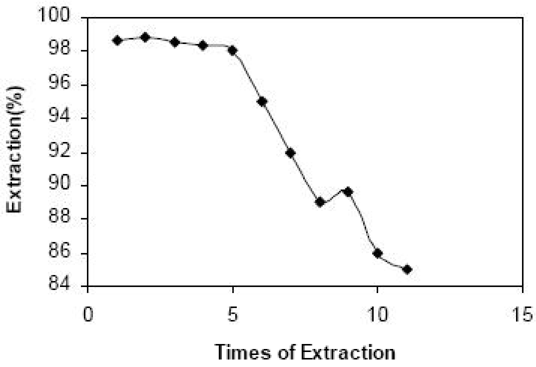

**Figure 4 : Influence of eluent type on disk efficiency**

ciencies was investigated. It was found that in the range of 10-150mL.min$^{-1}$, the retention of Cu(II)was not considerably affected by the sample solutions flow-rates and Cu(II)s to reproducible and satisfactory results (Figure 2). Thus, the flow-rate was maintained at 89mL.min$^{-1}$ throughout the experiment.

### Quantity of the PAR

The optimum amount of PAR for the quantitative extraction of Cu(II) was also investigated by adding various amounts of it to solution(between 2-20mg). The results are listed in TABLE 3. The experimental results revealed that the extraction of Cu(II)was quantitative using a sample solution containing more than 10mg PAR. Hence, subsequent extractions were performed with 15mg of PAR.

### 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 14 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 10replicates. These observations are represented in figure 4.

### Analytical performance

When solutions of 10μg Cu(II) in 10, 50, 100, 500, 1000, 2000, 2500 and 3000mL solutions under optimal experimental conditions were passed through the disks, the Cu(II) was quantitatively retained in all cases. Thus, the breakthrough volume for the method must be greater than 2500mL, providing a concentration factor of >500. The limit of detection(LOD) of the method for the determination of Cu(II)was studied under the optimal experimental conditions. The LOD based on 3σ of the blank is 15ng per 1000mL.

The capacity of modified disks(5mg PAR) was determined by passing 50mL portions of sample solutions containing 8mg of Cu(II) and 0.1M sodium acceate-acetic acid buffer with pH 4.5-5.0, followed 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 536±3μg of Cu(II) on the disk.

In order to investigate the selective separation and determination of Cu(II) ions from its binary mixtures with various metal ions, an aliquot of aqueous solutions (50mL) containing 10μg Cu(II) and mg amounts of other cations was taken and the recom-

**TABLE 4: Separation of Cu(II) from binary mixtures[a]**

| Diverse ion | Amounts taken(mg) | % Found | %Recoveryof Cu(II) ion |
|---|---|---|---|
| $Na^+$ | 95.4 | 1.15(2.9)[b] | 98.7(1.8) |
| $K^+$ | 92.5 | 1.32(2.1) | 98.8(2.2) |
| $Mg^{2+}$ | 14.6 | 0.7(1.8) | 98.7(1.7) |
| $Ca^{2+}$ | 28.3 | 1.29(2.0) | 98.7(1.8) |
| $Sr^{2+}$ | 3.45 | 2.85(2.2) | 98.2(2.0) |
| $Ba^{2+}$ | 2.47 | 3.16(2.4) | 98.3(2.5) |
| $Mn^{2+}$ | 2.68 | 1.75(2.3) | 96.4(1.8) |
| $Co^{2+}$ | 2.67 | 1.4(2.3) | 99.7(2.9) |
| $Ni^{2+}$ | 2.67 | 2.0(2.4) | 98.5(2.4) |
| $Zn^{2+}$ | 2.34 | 1.97(2.1) | 97.5(2.2) |
| $Cd^{2+}$ | 2.57 | 1.92.0) | 98.7(2.8) |
| Cu(II) | 2.54 | 2.7(1.9) | 98.5(2.7) |
| $Hg^{2+}$ | 2.43 | 2.81(2.1) | 98.7(2.8) |
| $Ag^+$ | 2.67 | 3.45(2.9) | 96.8(2.2) |
| $Cr^{3+}$ | 1.37 | 2.92(2.30 | 97.3(2.4) |
| $UO^{2+}$ | 2.83 | 2.8(2.5) | 98.3(2.6) |

[a]Initial samples contained 10µg Cu(II) and different amounts of various ions in 100mL water(0.1 M acetate ion)

[b]Values in parentheses are RSDs based on five individual replicate analysis

**TABLE 5 : Recovery of Cu(II) added to 1000mL of different water samples(contaning 0.1M acetate at pH=4.5-5.0)**

| Sample | Cu(II) added(µg) | Cu(II) determined(ng.mL$^{-1}$) |
|---|---|---|
| Tap water | 0.0, 10.0 | 4.90(2.0)[a], 14.61(2.2) |
| Snow water | 0.0, 10.0 | 9.58(2.7), 19.97(2.6) |
| Rain water | 0.0, 10.0 | 5.45(2.0), 15.96(2.5) |
| Sea Water | 0.0, 10.0 | 19.62(2.0), 29.93(2.8) |

[a]Values in parentheses are RSDs based on five individual replicate analysis

mended procedure was followed. The results are summarized in TABLE 5. The results show that the Cu(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 Cu(II)ion. Its is interesting to note that, in other experiments, we found that in the presence of high enough concentrations $NH_2OH.HCl$ as a suitable reducing agent (>0.5M)[38].

### Analysis of water samples

To assess the applicability of the method to real samples, it was applied to the extraction and determination of Cu(II) from different water samples. Tap water(Tehran, taken after 10min operation of the tap),rain water(Tehran, 22 January, 2007), Snow water (Saveh , 20 February ,2007)and Sea water(taken from Caspian sea, near the Mahmoud-Abad shore) samples were analyzed(TABLE 5). As can be seen from TABLE 4 the added Cu(II) ions can be quantitatively recovered from the water samples used.

## CONCLUSION

A simple, precise and accurate method was developed for selective separation, preconcentration and determination of Cu(II) 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 4-(2-pyridylazo)resorcinol. 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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## REFERENCES

[1] ATSDR-Standards and Regulations, Lead Toxicity Case Study,

[2] Current Status of Lead in India, Released on World Environment Day, **(2001)**

[3] K.Suvardhan, K.Suresh Kumar, D.Rekha, B.Jayaraj, G.Krishnamurthy Naidu, P.Chiranjeevi; Talanta, **68**, 735-740 **(2006)**.

[4] S.Tokalioglu, S.Kartal; J. Trace Microprobe Tech., **20**, 127-140 **(2002)**.

[5] M.Shamsipur, F.Raoufi, H.Sharghi; Talanta, **52**, 637-643 **(2000)**.

[6] A.Moghimi; Material Science Research India In press **(2006)**.

[7] K.Prasad, P.Gopikrishna, R.Kala, T.Prasada Rao, G.R.K.Naidu; Talanta, **69**, 938- 945 **(2006)**.

[8] M.das Gracas, A.Korn, J.B.Andrade, D.S.de Jesus,V.A.Lemos, M.L.S.F.Bandeira, W.N.L. Santos, M.A.Bezerra, F.A.C.Amorim, A.S.Souza, S.L.C. Ferreira; Talanta, **69**, 16-24 **(2006)**.

[9] H.Cesur; Turk.J.Chem., **27**, 307-314 **(2003)**.

**[10]** J.P.Bernal, E.Rodriguez, D.S.Miguel, J.C.Aguilar, G.Salazar, J.De Gyves; Sep.Sci.Technol., **35**, 1661-1679 **(2000)**.

**[11]** V.Gurnani, A.K.Singh; Ind.Eng.Chem.Res., **43**, 2302-2309 **(2004)**.

**[12]** D.Prabhakaran, M.S.Subramanian; Talanta, **59**, 1227-1236 **(2003)**.

**[13]** I.Narin, M.Soylak, K.Kayakirilmaz, L.Elci, M.Dogan; Anal.Lett., **36**, 641-658 **(2003)**.

**[14]** D.Prabhakaran, M.S.Subramanian; React.Funct. Polym., **57**, 147-155 **(2003)**.

**[15]** M.Kumar, D.P.S.Rathore, A.K.Singh; Talanta, **51**, 1187-1196 **(2000)**.

**[16]** M.Kumar, D.P.S.Rathore, A.K.Singh; Analyst, **125**, 1221-1225 **(2000)**.

**[17]** R.Pathak, G.N.Rao; Talanta, **44**, 1447-1453 **(1997)**.

**[18]** M.Tuzen, K.Parlar, M.Soylak; J.Hazard.Mater., **121**, 79-87 **(2005)**.

**[19]** S.Baytak, A.R.Turker; J.Hazard.Mater., **129**, 137-142 **(2006)**.

**[20]** V.A.Lemos, M.de la Guardia, S.L.C.Ferreira; Talanta, **58**, 475-480 **(2002)**.

**[21]** R.S.Juang; Proc.Natl.Sci.Counc.ROC, **A23**, 353-364 **(1999)**.

**[22]** J.L.Cortina, N.Miralles, A.Sastre, M.Aguilar, A.Profumo, M.Pesavento; React.Polym., **21**, 89-101 **(1993**).

**[23]** N.Kabay, N.Gizli, M.Demircioglu, M.Yuksel, M.Saglam, M.Arda, U.Yuksel, B.Saha, M.Streat; Chem.Eng.Commun., **190**, 936-947 **(2003)**.

**[24]** L.H.Reyes, I.S.Medina, R.N.Mendoza, J.R.Vazquez, M.A.Rodryguez, E.Guibal; Ind.Eng.Chem.Res., **40**, 1422-1433 **(2001)**.

**[25]** N.Kabay, M.Demircioglu, H.Ekinci, M.Yuksel, M.Saglam, M.Streat; React.Funct. Polym., **38**, 219-226 **(1998)**.

**[26]** H.Matsunaga, A.A.Ismail, Y.Wakui, T.Yokoyama; React.Funct.Polym., **49**, 189-195 **(2001)**.

**[27]** M.P.Gonzalez, I.Saucedo, R.Navarro, M.Avila, E.Guibal; Ind.Eng.Chem.Res., **40**, 6004-6013 **(2001)**.

**[28]** M.Y.Vilensky, B.B.Witz, A.Warshawsky; Environ.Sci. Technol., **36**, 1851-1855 **(2002)**.

**[29]** M.T.Draa, T.Belaid, M.Benamor; Sep.Purif. Technol., **40**, 77-86 **(2004)**.

**[30]** M.Shamsipur, A.R.Ghiasvand, Y.Yamini; Anal. Chem., **71**, 4892-4895 **(1999)**.

**[31]** A.I.Vogel; 'A Textbook of Quantitative Inorganic Analysis', 5th ed., Longmans Green, London, 443 **(1968)**.

**[32]** A.P.Argekar, A.K.Shetty; Talanta, **45**, 909-915 **(1998)**.

**[33]** O.R.Hashemi, M.R.Kargar, F.Raoufi, A.Moghimi, H.Aghabozorg, M.R.Ganjali; J.Microchem., **69**, 1-6 **(2001)**.

**[34]** O.R.Hashemi, F.Raoufi, M.R.Ganjali, A.Moghimi, M.Karagar-Razi, H.Aghabozorg, M.Shamsipur; Anal.Sci., **16**, 1221-1223 **(2000)**.

**[35]** F.Raoufi, Y.Yamini, H.Sharghi, M.Shamsipur; Microchem.J., **63**, 311-316 **(1999)**.

**[36]** D.F.Hagen, C.G.Mrkell, G.A.Schmitt, D.D.Blevins; Anal.Chim.Acta, **236**, 157 **(1990)**.

**[37]** Y.Yamini, N.Alizadeh, M.Shamsipur; Anal.Chim.Acta, **69**, 355 **(1997)**.

**[38]** Y.Petit de Pena, M.Gallego, M.Valcarcel; Anal.Chem., **67**, 2524 **(1995)**.

**[39]** N.Alizadeh, H.Naeimi, H.Sharghi, Samsipur, M.Polish; J.Chem., **73**, 915 **(1999)**.

**[40]** N.Alizadeh, H.Naeimi, H.Sharghi, Samsipur, M.Polish, Fresennius; J.Ana.Chem., In press.

**[41]** Y.S.Choi, H.S.Choi; Bull.Korean Chem.Soc., **24**, 222 **(2003)**.

**[42]** E.Matoso, L.T.Kubota, S.Cadore; Talanta, **60**, 1105 **(2003)**.

**[43]** B.Purachat, S.Liawruangrath, P.Sooksamiti, S.Rattanaphani, Buddhasukh; Anal.Sci., **17**, 443 **(2001)**.

**[44]** A.A.Ensafi, S.Abbasi, H.Rahimi Mansour, Mohammad pour Baltork; I.Anal.Sci., **17**, 609 **(2001)**.

**[45]** M.Saber Tehrani, F.Rastegar, A.Parchehbaf, Z.Rezvani; Chinese Journal of Chemistry, **23**, 1437 **(2005)**.

**[46]** A.Moghimi, Material Science Research India, In press **(2006)**.

**[47]** P.Nayebi, A.Moghimi; Oriental Journal of Chemistry, **22(3),** 507 **(2006)**.

**[48]** A.Moghimi; Oriental Journal of Chemistry, **22(3),** 507 **(2006)**.