

## 알루미나 컬럼에서 2-propylpiperidine-1-carbodithioate 착체의 흡착에 의한 수용액중에서 구리(II)의 고상추출

Ali Moghimi\* and Reza Ghiasi

Department of Chemistry, East Tehran(Ghiamdast) Campus Islamic Azad University, Tehran, Iran  
(2008. 3. 5 접수)

## Solid Phase Extraction of Copper(II) from Aqueous Solutions by Adsorption of its 2-propylpiperidine-1-carbodithioate Complex on Alumina Column

Ali Moghimi\* and Reza Ghiasi

Department of Chemistry, East Tehran(Ghiamdast) Campus Islamic Azad University, Tehran, Iran  
(Received March 5, 2008)

**요 약.** 시료용량, 간섭이온 등의 여러 인자의 효과에 대한 자세한 연구를 하였다. 흡착된 착체를 polyethylene glycol-황산 혼합물로 쉽게 용출할 수 있었고 구리의 농도를 가시선분광기로 검출하였다. 구리(II)의 검정곡선은 0-1  $\mu\text{g mL}^{-1}$ 에서 선형이었고 검출한계는 5  $\mu\text{g L}^{-1}$ 를 얻었다. 25의 가장 높은 전처리농도 인자는 알루미나 배드흡착제의 지지체로 그래스울을 사용하여 250 mL 시료양에서 얻을 수 있었다. 구리(II)를 니켈, 코발트, 황산염, 질산염 이온들로부터 효과적으로 분리할 수 있었고, 이 방법은 전기도금 폐기수와 스파크된 물시료에서 성공적으로 구리의 회수에 적용하였다.

**주제어:** 구리(II), 고상추출, 알루미나, Polyethylene glycol, 2-propylpiperidine-1-carbodithioate

**ABSTRACT.** A novel approach has been developed for the solid phase extraction of copper(II) based on the adsorption of its 2-propylpiperidine-1-carbodithioate complex on alumina column. The effect of various parameters such as acidity, sample volume, interfering ions, etc., were studied in detail. The adsorbed complex could be easily eluted using polyethylene glycol-sulfuric acid mixture and the concentration of copper has been determined using visible spectrophotometry. The calibration graph was linear in the range 0-1  $\mu\text{g mL}^{-1}$  copper(II) with a detection limit of 5  $\mu\text{g L}^{-1}$ . A highest preconcentration factor of 25 could be obtained for 250 mL sample volume using glass wool as support for the alumina bed adsorbent. Copper(II) could be effectively separated from other ions such as nickel, cobalt, zinc, chloride, sulfate, nitrate, etc., and the method has been successfully applied to study the recovery of copper in electroplating waste water and spiked water samples.

**Keywords:** Copper(II), Solid phase Extraction, Alumina, Polyethylene Glycol, 2-propylpiperidine-1-carbodithioate

### INTRODUCTION

Copper at trace concentrations acts as both a micronutrient and a toxicant in marine and fresh water systems.<sup>1-8</sup> This element is needed by plants at only very low levels and is toxic at higher levels. At these levels, copper can bind to the cell mem-

brane and hinder the transport process through the cell wall. Copper at nearly 40 ng mL<sup>-1</sup> is required for normal metabolism of many living organisms.<sup>9,10</sup> On the other hand, copper 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 copper is usually carried out by flame and graphite furnace atomic absorption spectrometry (AAS)<sup>11,12</sup> as well as spectrometric methods.<sup>13,14</sup> However, due to the presence of copper in medicinal and environmental 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 copper in the presence of various classical<sup>15-19</sup> and macrocyclic<sup>20,21</sup> 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 copper have been proposed including liquid chromatography<sup>22</sup> supercritical fluid extraction,<sup>23</sup> flotation,<sup>24</sup> aggregate film formation,<sup>25</sup> liquid membrane,<sup>26</sup> column adsorption of pyrocatechol violet-copper complexes on activated carbon,<sup>27</sup> ion pairing,<sup>28</sup> ion pairing,<sup>29</sup> preconcentration with yeast,<sup>30</sup> and solid phase extraction using C<sub>18</sub> cartridges and disks.<sup>31-33,56</sup>

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.<sup>34-36</sup> In recent years, the octadecyl-bonded silica SPE disks have been utilized for the extraction and separation of different organic compounds from environmental matrices.<sup>37-40,46-47</sup> Moreover, the SPE disks modified by suitable ligands are successfully used for selective extraction and concentration of metal ions.<sup>41-42</sup>

In a recent series of papers,<sup>43-45</sup> 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 Cu 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 Cu<sup>2+</sup> in low concentration. In this paper, we report a simple and novel approach for the preconcentration of copper based on the adsorption of its 2-propylpiperidine-1-carbodithioate complex onto adsorbent alumina column. 2-propylpiperidine-1-carbodithioate is a ligand that gives a very sensitive color reaction with copper(II). The adsorbed complex could be easily eluted using polyethylene glycol-sulfuric acid mixture and the recovery of copper was established using visible spectrophotometry. The effects of various experimental parameters such as sample volume, flow rate, effect of diverse ions, etc., were studied in detail. The validity of the proposed method was checked by applying it to the determination of copper in electroplating wastewater and spiked water samples.

## EXPERIMENTAL

### Reagents

#### Synthesis of sodium 2-propylpiperidine-1-carbodithioate reagent

Carbondisulphide (1.05 mol) was slowly added to a solution of 2-propyl-piperidine (1.43 mol) in 25 ml of water at 5°C with constant stirring, followed by 1.0 mol of sodium hydroxide dissolved in 20 ml of water to form sodium 2-propylpiperidine-1- carbodithioate as shown in Fig. 1(a). The product was warmed to room temperature and washed 2~3 times with purified acetone. The reaction product was recrystallized from warm acetone. The purified compound has a melting point of 303~308°C at 740mm pressure. Crystallization of water is less in 2-propylpiperidine-1- carbodithioate when compared with other carbodithioate, therefore, the extractability of the complex become easier. The metal salt of this reagent is a resonance hybrid of the structures, which contributed to the stability of metal complexes as shown in Fig. 1(b).

Analytical grade reagents were used in the preparation of all solutions. Triple distilled water was used for the preparation of solutions. The 1000 µg mL<sup>-1</sup> Cu(II) were prepared.

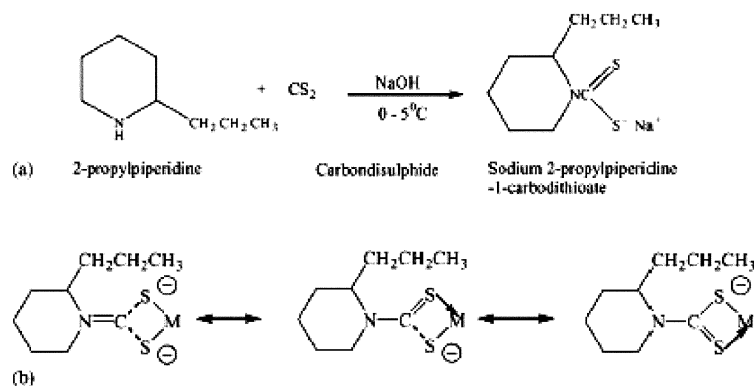


Fig. 1. (a) Synthesis of sodium 2-propylpiperidine-1-carbodithioate reagent. (b) Resonance hybrid of the 2-propyl piperidine-1-carbodithioate with metal.

A working solution of  $10\ \mu\text{g mL}^{-1}$  Cu(II) was prepared by appropriate dilution. Polyethylene glycol and neutral alumina were from Merck. A 0.25 g of sodium 2-propylpiperidine-1-carbodithioate was taken in a volumetric flask and diluted to 100 mL using acetone. Sulfuric acid of the required concentrations was prepared from concentrated sulfuric acid by appropriate dilution. The alumina was prepared by treatment  $2.5\ \text{mol L}^{-1}$  sulfuric acid for 12 h at  $50^{\circ}\text{C}$ . After the completion of the acid activation process, the reaction mixture was transferred to 1000 mL of ice-cold water to quench the activation process.

#### Instrumentation

A Jasco V-576 (Japan) model UV-visible spectrophotometer was used for absorbance measurements. One centimeter matched quartz cells were used to record the absorbances. The pH measurements were carried out by an ATC pH meter (EDT instruments, GP 353). Determination of  $\text{Cu}^{2+}$  contents in working samples were carried out by a Varian spectra.

#### Column preparation

A glass column 9.5 mm in diameter and 15 cm in length was used for preconcentration. A 3 g of alumina to form slurry with 25 mL water. The alumina adsorbent was poured into the column and packed to a height of 5 cm. Glass wool was placed at the bottom and at the top of the column for allowing the adsorbent to settle properly. The column was washed using triple distilled water fol-

lowed by conditioning it using  $0.1\ \text{mol L}^{-1}$  sulfuric acid.

#### General procedure for adsorption

A 1 mL volume of  $10\ \mu\text{g mL}^{-1}$  solution of Cu(II) was alumina with 2 mL of  $0.5\ \text{mol L}^{-1}$  sulfuric acid followed by the addition of 2 mL of 2-propylpiperidine-1-carbodithioate and the resulting volume was maintained at 100 mL. The sample solution was loaded on to the column containing alumina adsorbent maintaining a flow rate of  $2\ \text{mL min}^{-1}$ . The reddish violet complex was adsorbed on to the column, which was evident from the absorbance of the resulting solution that emerged out of the column. The adsorbed complex was then eluted using 10 mL of polyethylene glycol- $4.5\ \text{mol L}^{-1}$  sulfuric acid mixture and the concentration of copper was determined by visible spectrophotometry at 598 nm.

## RESULTS AND DISCUSSION

#### Extraction of copper(II) from aqueous solutions Effect of acidity

The effect of acidity plays a significant role in the preconcentration studies. The complex once prepared is stable even at moderately low pH. The volume of  $0.5\ \text{mol L}^{-1}$  sulfuric acid was varied from 1 to 3 mL for preparing different concentrations of the complex in 100 mL sample volume. The adsorbed complex was eluted using 10 mL of polyethylene glycol-sulfuric acid mixture. The results are presented in Fig. 2. As can be seen from the figure, it

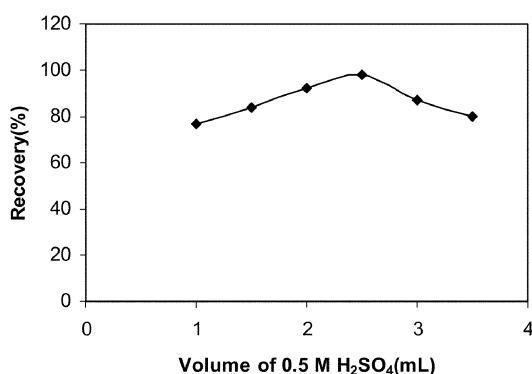


Fig. 2. Effect of variation of volume of 0.5 mol L<sup>-1</sup> sulfuric acid on the recovery of copper(II).

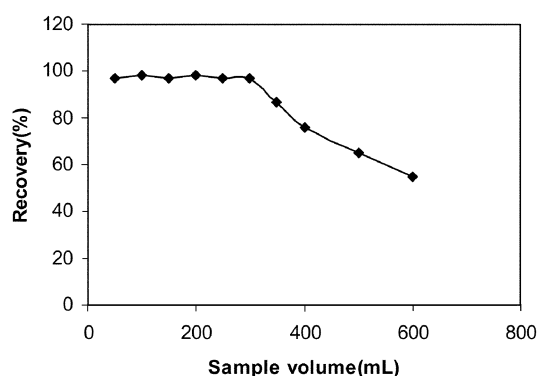


Fig. 3. Effect of variation of sample volume on the recovery of copper(II).

is evident that 2.5 mL of 0.5 mol L<sup>-1</sup> sulfuric acid is required to achieve quantitative recovery of the copper-2-propylpiperidine-1-carbodithioate complex. Beyond 2 mL, there was a decrease in the recovery of copper.

#### Effect of volume of the eluent

The volume of polyethylene glycol-sulfuric acid mixture as the eluting agent was varied using glass wool as support for the adsorbent. Maximum quantitative recovery of copper(II) was observed with 4:6 ratio of polyethylene glycol-4.5 mol L<sup>-1</sup> sulfuric acid mixture. The results are presented in Table 1. The use of polyethylene glycol alone or sulfuric acid of lower concentrations was not effective in the elution of the complex.

#### Effect of sample volume

The sample volume was varied from 50 to 500 mL maintaining an overall acidity of 0.01 mol L<sup>-1</sup> sulfuric acid. The resulting complex was eluted using 10 mL of polyethylene glycol-sulfuric acid mixture. The effect of the sample volume and the corresponding preconcentration factors are given in Figs.

Table 1. Variation of volume of PEG-sulfuric acid mixture

Recovery of copper (%)	Volume of PEG (mL)	Volume of 4.5 mol L <sup>-1</sup> sulfuric acid (mL)
94.2	2.0	8.0
97.6	3.0	7.0
98.9	4.0	6.0
91.9	5.0	5.0
82.7	6.0	4.0
70.9	8.0	2.0

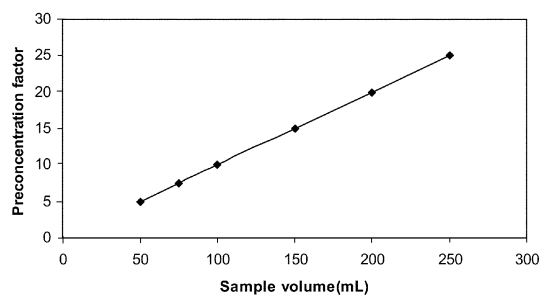


Fig. 4. Effect of sample volume on the preconcentration factor.

3 and 4. As can be seen from the figures, it is evident that the recovery of copper is quantitative (>95%) up to 250 mL sample volume. A preconcentration factor of 25 could be attained for quantitative recovery (>95%) of Cu(II) when the sample volume was 250 mL.

#### Effect of the ratio of alumina loaded on the column

The amount of alumina was varied from 1.0 to 4.0 g. The concentration of copper(II) was maintained at 10 µg in a 100 mL sample volume. The results are shown in Fig. 5. Quantitative recovery of copper(II) could be attained in the range 2.5-4.0 g of alumina. For amounts less than 2.5 g there was a significant reduction in the recovery of copper.

#### Effect of flow rate

The flow rate of 1-4 mLmin<sup>-1</sup> was found to be suitable for optimum loading of the Cu(II)-propylpiperidine-1-carbodithioate complex on the alumina adsorbent column. At higher flow rates, there was a

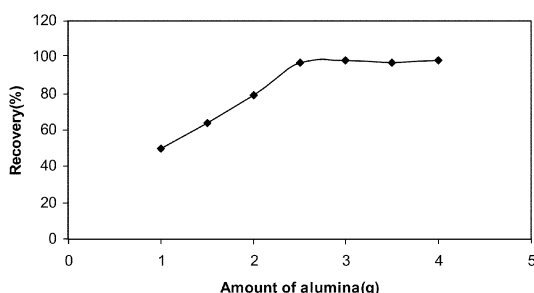


Fig. 5. Effect of amount of alumina on the recovery of copper (alumina, 10  $\mu\text{g}$  copper(II) in a sample volume of 100 mL).

reduction in the percentage adsorption of copper. This could be probably due to the insufficient contact time between the sample solution and the adsorbent. A flow rate of  $2 \text{ mL min}^{-1}$  was maintained for the elution of the complex.

#### Stability of the column

The stability of the column was tested using 10  $\mu\text{g}$  Cu(II) maintaining a sample volume of 100 mL. The adsorbed Cu(II)-2-propylpiperidine-1-carbodithioate complex was eluted using 10 mL of polyethylene glycol-4.5 mol  $\text{L}^{-1}$  sulfuric acid mixture. The column could be used with good precision and quantitative recovery (>95%) for 10 cycles. Beyond 10 cycles, there was a considerable reduction in the recovery of copper.

#### Precision and detection limit

The precision studies were carried out at 0.2  $\mu\text{g mL}^{-1}$  level of copper by carrying out 10 separate determinations using the above-mentioned procedure. The sample volume was maintained at 100 mL. The relative standard deviation of the method was found to be 4.0%. The sensitivity of the developed method is reflected by the limit of detection (LOD) studies, defined as the lowest concentration of copper(II) below which quantitative sorption of the metal ion by the adsorbent is not perceptibly seen. The LOD for Cu(II) was found to be  $5 \mu\text{g L}^{-1}$ .

#### Effect of diverse ions

The effect of diverse ions was studied at varying concentrations. The solid phase extraction studies were carried out as mentioned above using 10  $\mu\text{g}$  Cu(II) maintaining a sample volume of 100 mL.

Table 2. Effect of diverse ions on the recovery of 10  $\mu\text{g}$  copper(II) in a volume of 100 mL

Recovery of copper (%)	Amount ( $\mu\text{g}$ )	Ions
98.4	500	$\text{Mg}^{2+}$
98.3	1000	
98.5	250	
98.6	500	$\text{Ca}^{2+}$
98.5	1000	
98.3	250	
98.5	1000	$\text{Ni}^{2+}$
98.3	500	
98.2	50	
98.7	1000	$\text{Cl}$
98.2	500	
98.0	250	
98.6	1000	$\text{NO}_3$
98.5	500	
98.3	250	
98.3	1000	$\text{SO}_4^{2-}$
98.5	500	
98.1	250	
98.6	1000	$\text{Co}^{2+}$
98.7	500	
98.4	250	
95.3	150	$\text{Fe}^{3+}$
78.8	500	
75.3	1000	

The studies indicated that  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}$ ,  $\text{NO}_3$ ,  $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  did not cause any significant reduction in the recovery of copper. The results are presented in Table 2 showing the recovery of copper with varying concentrations of metal ions. Except  $\text{Fe}^{3+}$ , the recovery was found to be quantitative in the concentration range of the metal ions that was investigated. Since, the ions that are commonly present in water samples did not affect significantly the recovery of copper the method was applied to study the recovery of copper in electroplating wastewater and spiked tap water and well water samples.

#### Analysis of copper(II) in electroplating wastewater and spiked water samples

The proposed method was applied to study the recovery of copper(II) in electroplating wastewater sample. The electroplating wastewater sample had the following characteristics-pH 2.8, calcium: 65  $\text{mg L}^{-1}$ , magnesium: 40.5  $\text{mg L}^{-1}$ , chloride: 970  $\text{mg L}^{-1}$ ,

Table 3. Analysis of copper(II) in electroplating wastewater

Recovery (%)	Relative standard deviation (%)	Concentration of copper(II) found (mg L <sup>-1</sup> )	Concentration of copper(II) added (mg L <sup>-1</sup> )	Sample
-	3.2	83.0	0	Electroplating wastewater
98.97	3.8	87.1	5.0	
98.70	3.5	91.8	10.0	

Table 4. Recovery study in water samples

Sample	Cu(II) added (μg)	Cu(II) found (μg)	Sample volume (mL)	Recovery of copper (%)
Well water	5.0	4.83	100	97.6
	2.0	1.96	250	98.6
	10	9.6	100	98.6
	10	9.87	250	98.5
Tap water	10	9.85	100	98.7
	10	9.84	200	98.5
	5.0	4.86	150	97.4
	4.0	3.94	250	98.2
	2.0	1.94	250	97

sulfate: 780 mg L<sup>-1</sup>. The wastewater sample was diluted to the required concentration and the pre-concentration procedure was applied as mentioned above. The recovery of copper was found to be quantitative and the results are presented in Table 3. The proposed method was also applied to tap water (Tehran, 20 January, 2007) and well water (Saveh, 8 February, 2007) samples by spiking known concentrations of copper in varying sample volumes. The recovery of copper was found to be quantitative with an average relative standard deviation of 3.5% on triplicate measurements and the results are shown in Table 4.

## CONCLUSIONS

The proposed method for copper is simple, novel and could be effectively used for the solid phase extraction of copper. The preconcentration factor was 25 for a 250 mL sample volume. The method showed minimum interferences with commonly found ions in real samples and the recovery of copper was quantitative. The quantitative recovery of copper(II) in electroplating wastewater and spiked water samples with a relative standard deviation of 3.5% reflects the validity and accuracy of the method when applied to real samples. The adsor-

bent alumina exhibits better or comparable capacity values in comparison to most of the chelating matrices reported in the literature.<sup>48-53</sup> The adsorbent exhibited good stability under the experimental conditions. The important features of the proposed method are its high sorption capacity with good enrichment factor. The developed method is sensitive in detecting copper(II) at ppb levels. The alumina column was stable with the data reproducibility up to 10 cycles of continuous usage. Hence, it can be concluded that the proposed method can be used for the effective solid phase extraction of copper(II).

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

- nol. Oceanogr.* **1991**, 36, 1742.
5. Gordan, A.S. *Mar. Chem.* **1992**, 38, 1.
  6. Moffett, J. W.; Brand, L. E.; Croot, P. L.; Barbeau, K. A. *Limnol. Oceanogr.* **1997**, 42, 789.
  7. Croot, P. L.; Moffett, J. W.; Brand, L. E. *Limnol. Oceanogr.* **2000**, 45, 619.
  8. Wood, M.; Wang, H. K. *Environ. Sci. Technol.* **1983**, 17, 582A.
  9. Greenwood, N. N.; Eamshow, A. *Chemistry of Elements*, Pergamon Press, New York, 1984.
  10. Burtis, C. A.; Ashwood, E. R. *Tietz Textbook of Clinical Chemistry*, third ed., Macmillan, New York, 1999.
  11. Wetz, B. *Atomic Absorption Spectroscopy*, VCH, Amsterdam, 1985.
  12. Eaton, A. D.; Clesceri, L. S.; Greenberg, A. E. *Standard Methods for the examination of water and waste water*, 19th ed, American Public Health Association, Washington, DC, 1995.
  13. Welcher, F. J.; Boschmann, E. *Organic Reagents for Copper*, Krieger Huntington, New York, 1979.
  14. Marczenko, Z. *Separation and Spectrophotometric Determination of Elements*, Ellis Horwood, London, 1986.
  15. Bharagava, O. P. *Talanta* **1969**, 16, 743.
  16. Schilt, A. A.; Hoyle, W. C. *Anal. Chem.* **1964**, 41, 344.
  17. Borchart, L. G.; Butler, J. P. *Anal. Chem.* **1957**, 29, 414.
  18. Chaisuksant, R.; Ayuthaya, W. P.; Grudpan, K. *Talanta* **2000**, 53, 579.
  19. Kara, D.; Alkan, M. *Microchem. J.* **2002**, 71, 29.
  20. Saito, K.; Murakami, S.; Muromatsu, A.; Sekido, E. *Anal. Chim. Acta* **1994**, 294, 329.
  21. Ikeda, K.; Abe, S. *Anal. Chim. Acta* **1998**, 363, 165.
  22. Igarashi, S.; Ide, N.; Takagai, Y. *Anal. Chim. Acta* **2000**, 424, 263.
  23. Liu, J.; Wang, W.; Li, G. *Talanta* **2001**, 53, 1149.
  24. Anthemidis, A. N.; Zachariadis, G. A.; Stratis, J. A. *Talanta* **2001**, 54, 935.
  25. Zenedelovska, D.; Pavlovska, G.; Cundeva, K.; Stafilov, T. *Talanta* **2001**, 54, 139.
  26. Endo, M.; Suzuki, K.; Abe, S. *Anal. Chim. Acta* **1998**, 364, 13.
  27. Campderros, M. E.; Acosta, A. Marchese, J. *Talanta* **1998**, 47, 19.
  28. Narin, I.; Soylak, M.; Elic, L.; Dogan, M. *Talanta* **2000**, 52, 1041.
  29. Akama, Y.; Ito, M.; Tanaka, S. *Talanta* **2000**, 52, 645.
  30. Ohta, K.; Tanahasi, H.; Suzuki, T.; Kaneco, S. *Talanta* **2001**, 53, 715.
  31. Cuculic, V.; Mlakar, M.; Branica, M. *Anal. Chim. Acta* **1997**, 339, 181.
  32. Moghimi, A.; Tehrani, M. S.; Husain, S. W. *Material Science Research India* **2006**, 3(1a), 27.
  33. Tehrani, M. S.; Moghimi, A.; Husain, S. W. *Material Science Research India* **2005**, 3(2), 135.
  34. Thurman, E. M.; Mills, M. S. *Solid-Phase Extraction, Principles and Practice*, Wiley, New York, 1998.
  35. Pawliszyn, J. *Solid-Phase Microextraction, Theory and Practice*, Wiley-VCH, New York, 1997.
  36. Izatt, R. M.; Bradshaw, J. S.; Bruening, R. L. *Pure Appl. Chem.* **1996**, 68, 1237.
  37. Moghimi, A. *Oriental Journal of Chemistry* **2006**, 22(3), 527.
  38. Moghimi, A. *Chinese Journal of Chemistry* **2007**, 25, 640.
  39. Taylor, K. Z.; Waddell, D. S.; Reiner, E. J. *Anal. Chem.* **1995**, 67, 1186.
  40. Moghimi, A.; Ghammamy, S. "Environmental chemistry an Indian journal" **2007**, 2, 3.
  41. Shamsipur, M.; Ghiasvand, A. R.; Yamini, Y. *Anal. Chem.* **1999**, 71, 4892.
  42. Shamsipur, M.; Ghiasvand, A. R.; Sharghi, H. *Int. J. Environ. Anal. Chem.* **2001**, 82, 23.
  43. Brunner, J.; Mokhir, A.; Kramer, R. J. *Am. Chem. Soc.* **2003**, 125, 12410.
  44. Zelder, F. H.; Brunner, J.; Kramer, R. *Chem. Commun.* **2004**, 902.
  45. Boll, I.; Kramer, R.; Brunner, J.; Mokhir, A. *J. Am. Chem. Soc.* **2005**, 127, 7849.
  46. Moghimi, A. *Chinese Journal of Chemistry* **2007**, 25(10), 1536.
  47. Nayeibi, P.; Moghimi, A. *Oriental Journal of Chemistry* **2006**, 22(3), 507.
  48. Choi, Y. S.; Choi, H. S. *Bull. Korean Chem. Soc.* **2003**, 24, 222.
  49. Matoso, E.; Kubota, L. T.; Cadore, S. *Talanta* **2003**, 60, 1105.
  50. Purachat, B.; Liawruangrath, S.; Sooksamiti, P.; Ratanaphani, S.; Buddhasukh, D. *Anal. Sci.* **2001**, 17, 443.
  51. Ensafi, A. A.; Abbasi, S.; Rahimi Mansour, H.; Mohammad pour Baltork, I. *Anal. Sci.* **2001**, 17, 609.
  52. Saber Tehrani, M.; Rastegar, F.; Parchehbaf, A.; Rezvani, Z.; *Chinese Journal of Chemistry* **2005**, 23, 1437.
  53. Moghimi, A. *Material Science Research India* impress **2006**, 22(3).