Solid Phase Extraction of Cd(II) Traces Using Aminopolycarboxylic Acid-Type Cellulose

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Abstract: A simple and reproducible method for the rapid extraction and determination of trace amounts of Cd(II) ions using Aminopolycarboxylic acid-type cellulose (Chelest Fiber Iry) and Atomic Absorption Spectrometry is presented. Aminopolycarboxylic acid-type cellulose (Chelest Fiber Iry) has been studied for its sorption efficiencies with respect to Cd(II) from acidic solution. The influence of pH and other properties related to sorption kinetics, isotherm, maximum capacity, stability and the mechanism of sorption were discussed. Cd(II) was quantitatively retained on the proposed adsorbent in the pH range of 3.0-6 (studied pH range 1.6-6). The maximum sorption capacity was found to be 0.95 ± 0.06 mmol/g adsorbent. The decline in the efficiency of the adsorbent was not observed for repeated adsorption-desorption cycles. It was found that the preconcentration factor of 200 can be achieved. The limit of determination was found to be about 1.7µg Cd/2L. The method was applied to the determination of Cd(II) in water samples.

Key words: Solid phase extraction · Cd(II) · Aminopolycarboxylic acid-type cellulose · Tap water sample

INTRODUCTION

In the recent years, pollution of the environment by heavy metals has received considerable attention. These elements accumulate in living organisms and are of high toxic potential. Their wide technological use (fertilizers, mining, pigments), as well as their production from burning oil and coal and incineration of waste causes an extensive anthropogenic contamination of soil, air and water [1]. Several analytical techniques such as flame atomic absorption spectrometry (FAAS) [2,3], inductively coupled plasma atomic emission spectrometry (ICP-AES) [4] and inductively coupled plasma mass spectrometry (ICP-MS) [5] are available for the determination of trace metals with enough sensitivity for the most applications.

Despite good developments in the modern analytical instruments, which allow great enhancement in aspects of analysis, in many cases the available analytical instrumentation does not have enough sensitivity for the analysis of natural samples. Sample preparation is still a bottleneck for overall throughput because the involved steps often employ large volumes of hazardous organic solvents, are time consuming and/or expensive [1].

Although, the determination of trace metal ions in natural waters is difficult due to various factors, particularly their low concentrations and matrixes effects. Pre-concentration and separation can solve these problems and can lead to a higher confidence level and easy determination of the trace elements. Several procedures have been developed for the separation and preconcentration of contaminants from environmental matrixes,such as: liquid-liquid extraction (LLE) [6-8], co-precipitation [9-11], solid phase extraction (SPE) [12-36].

Although, disadvantages such as significant chemical additives, solvent losses, complex equipment, large secondary wastes, unsatisfactory enrichment factors and high time consumption, limit the application of these techniques. These problems could be addressed by the development of modular and compact processes that provide adequate separation and preconcentration without complex processes. The solvent microextraction technique effectively overcomes these difficulties by reducing the amount of organic solvent as well as allowing sample extraction and preconcentration to be done in a single step. The technique is faster and simpler than conventional methods. It is also inexpensive, sensitive and effective for the removal of interfering

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matrices. Solvent microextraction is a form of solvent extraction with phase ratio values higher than 100 [1]. Compared with the conventional solvent extraction, microextraction may provide poorer analyte recovery, instead the concentration in the organic phase greatly enhances. In addition, the amount of the used organic solvent is highly reduced and only one step of manipulation is necessary, therefore, problems of contamination and loss of analytes vanishes.

Cloud point extraction (CPE) [37-42], homogeneous liquid-liquid extraction (HLLE) [43,44] and single drop microextraction (SDME) [45-49] are fairly new methods of sample preparation which are used in separation and preconcentration of metals and can solve some of the problems encountered with the conventional pretreatment techniques.

In the previous studies, we demonstrated a novel microextraction technique, named dispersive liquid-liquid microextraction (DLLME), which was successfully used, for the extraction and determination of polycyclic aromatic hydrocarbons (PAHs), organphosphorus pesticides (OPPs) and chlorobenzenes in water samples [50-52] DLLME is a modified solvent extraction method and its acceptor-to-donor phase ratio is greatly reduced compared to the other methods. In DLLME, the appropriate mixture of the extraction and disperser solvents is rapidly injected by syringe into aqueous samples containing analytes. Thereby, cloudy solution forms. In fact, the cloudy state results from the formation of fine droplets of the extraction solvent, which disperse in the sample solution. Then, this cloudy solution shall be centrifuged and the fine droplets sediment at the bottom of the conical test tube. The determination of anlaytes in sedimented phase can be performed by instrumental analysis. In this extraction method any component in the solution, directly or indirectly after previous (or simultaneous) derivatization reaction, interacts with the fine droplets of the extraction solvent and consequently gets extracted from the initial solution and concentrates in the small volume of the sedimented phase. Simplicity of the operation, rapidity, low sample volume, low cost, high recovery and high enrichment factor are some advantages of DLLME.

In this paper, we describe the application of a iminodiacetate-type cellulose (Chelest Fiber Iry, Fig. 1), which has flexible functional groups on the cellulose support to the batch and column adsorptions of Cd(II) from the aqueous solution. The cost of this adsorbent is much lower than the chelating resin.
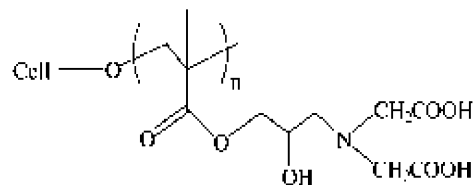

Fig. 1: Structure of Chelest Fiber Iry.

Experimental

Reagents: Working solutions of Cd(II) were prepared by diluting a 1 mg/L Cd(II) solution (Merck) with a 0.1 mol/L nitric acid solution. Commercial Chelest Fiber Iry (size: 0.5mm length, 30-40 μm i.d.) was purchased from Chinese and was used as the adsorbent for Cd(II). Chelest Fiber Iry was prepared by the reaction of iminodiacetate in aqueous solution with cellulose which had been graft polymerized with glycidyl methacrylate. The material possesses the glycidyl methacrylate as the crosslinking agent which makes the increasing conformational flexibility of functional groups. Further, the adsorbent maintains mechanical and chemical stabilities and filtering properties after the modification. Thus, it permits the quantitative extraction of metal ion in a low concentration range. Buffer solutions were prepared by mixing 1 mol/l acetic acid and 1 mol/l sodium acetate solution and adjusting to the desired pH. All other reagents were of analytical reagent grade.

Apparatus: Determination of Cd^{2+} content 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.

An EYELA Model MP-3N Micro Tube Pump (Tokyo Rikakikai) was to control the flow rate of sample solution passing through the column. The column was an Isolute SPE column (polypropylene syringe, 78mm×16mm i.d. International Sorbent Tech.). Polyethylene disk filter (16mm i.d. 2mm thick and 2 μm pore size) was placed at the bottom of the column and adequate amount of Chelest Fiber Iry was packed. IR spectra were recorded over the range 4000-400 cm^{-1} with a Shimadzu FT-IR 8300 spectrophotometer using KBr pellets. The pH measurements were carried out by an ATC pH meter (EDT instruments, GP 353).

Batch and Column Experiments: In a 200 ml Erlenmeyer flask, 100 ml distilled water was taken and 3ml of standard solution containing 3.0 mg of Cd(II), 5ml of buffer solution

(pH 4.0) and 0.3 g of Chelest Fiber Iry were subsequently added. The mixture was stirred for 110 min with a magnetic stirrer and then filtered with a 0.45 μm membrane filter. After measurement of pH, Cd(II) in the filtrate was determined by flame atomic absorption spectrometry (AAS). The percentage extraction of Cd(II) was calculated from the difference between the Cd(II) Concentrations of aqueous solution before and after the equilibration.

The Isolute SPE column equipped with polyethylene disk filter and a stopcock was used to pack about 1.0 g of the Chelest Fiber Iry. A 100 ml sample solution containing appropriate amount of Cd(II), after adjustment to pH 3.5-4.0 with acetate buffer solution, was passed through the column at flow rate of 35 ml/min. After washing with distilled water, the adsorbed Cd(II) was stripped from the adsorbent using 20 ml of 0.4 mol/L HNO_3 at a flow rate of 4.0 mL /min. The Cd(II) content was then determined by flame AAS.

RESULTS AND DISCUSSION

PH Dependence of Adsorption: The influence of pH on the adsorption of 3mg Cd(II) on the Chelest Fiber Iry from 100 ml solution was studied over the pH range 1.6-6 by the batch process described above. The pH of the solution was adjusted with either acetate buffer (pH 3-6) or hydrochloric acid (pH <3). Higher pH values were not tested because of the possibility of the hydrolysis of Cd(II) ion in the solution. The Cd(II) was quantitatively adsorbed onto the Chelest Fiber Iry at pH >3.0. Fig. 2 shows the percentage removal of Cd(II) by the adsorbent as a function of pH. The complex formation in relatively low pH region can be used to separate Cd(II) from common metal ions. In the following experiments, around pH 3.5 was chosen for the adsorption of Cd(II).

The plots of log$D$ versus pH gave straight line of slope near 2 (Fig. 3), indicating that the adsorption of 1 mol of Cd(II) ion is accompanied by the release of two moles of hydrogen ions. Thus, the extraction process may be represented by the equation

$$Cd^{2+} + H_mIry \rightarrow H_{m-2}Iry\text{-}Cd + 2H^+$$

$$K = \frac{\left[Cd^{2+}\right]_S \left[H^+\right]_a^2}{\left[Cd^{2+}\right]_a \left[H^+\right]_S^2}, \quad D = \frac{\left[Cd^{2+}\right]_S}{\left[Cd^{2+}\right]_a}$$

hence,

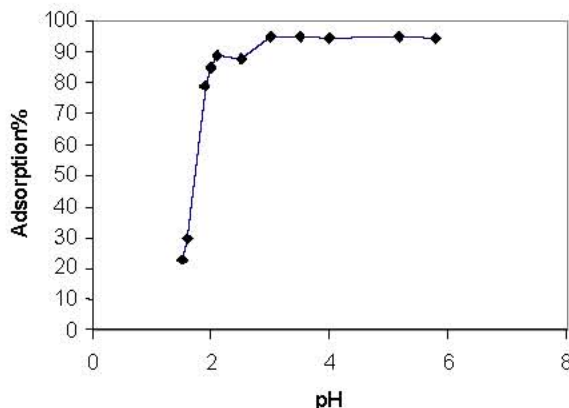$$\log D = 2pH + \log K - \log [H^+]_S$$

Fig. 2: Influence of pH on the adsorption on Cd ion. Cd, 3.0 mg; amount of adsorbent, 0.3 g; sample volume, 108 mL; stirring time, 110 min.
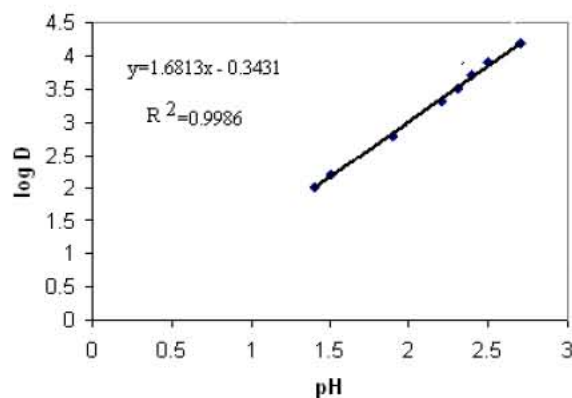
Fig. 3: Distribution ratio for Cd ion as a function of the pH. Cd, 3.0 mg; amount of adsorbent, 0.3 g; sample volume, 108 ml; stirring time, 110 min.

where HmIry represents the chelating fiber, D the distribution ratio of Cd(II) ion between the solid phase and the aqueous phase. The indices 's' and 'a' denote solid phase and aqueous phase, respectively. In the IR spectra of the prepared Cd complex with Chelest Fiber Iry there appear strong absorption bands of asymmetric vibration of COO^- (v_{as}) at 1593 cm^{-1} and symmetric one (v_s) at 1400 cm^{-1}, also the band at 1725 cm^{-1} arising from the vibration of COOH group became weaker than that of the Chelest Fiber Iry alone. This indicates that the COOH group takes part in the Cd(II) removal.

Effects of Amount of Adsorbent and Volume of Sample Solution: The quantitative adsorption of 3mg Cd(II) from 100 ml aqueous solution under the optimal experimental conditions was obtained at more than 0.03 g of adsorbent as shown in Fig. 4. Subsequent batch operations were carried out with 0.3 g of the adsorbent.The extraction of
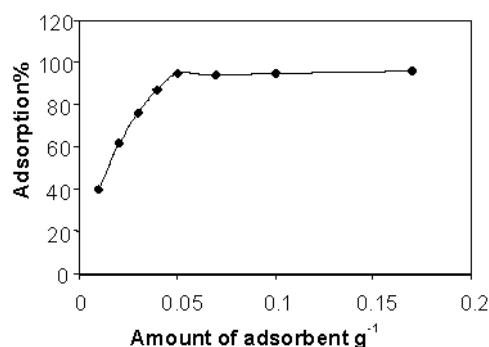
Fig. 4: Effect of amount of adsorbent on the Cd adsorption. Cd, 0.3 mg; sample volume, 108 mL; stirring time, 110 min; pH 4.

Fig. 5: Freundlich plots for Cd on a Chelest Fiber Iry. Q_e, adsorption amount; C_e, equilibrium concentration; pH 4.0 ± 0.2.

Table 1: Effect of diverse ions on the adsorption of 3mg of Cd

Ion	Amount of ion added (mg)	Cd found (μg/ml)	Adsorption (%)
Ca	50	0.33	99.2
Co	8	0.30	99.7
Zn(II)	8	0.24	97.6
Fe(III)	10	0.34	99.5
Mg	30	0.25	98.4
Mn(II)	10	0.25	98.3
Ni	10	0.24	97.4
K	60	0.25	98.5

Cd, 3.0 mg/100 mL; adsorbent, 0.3 g.

3mg Cd(II) under the optimal experimental conditions was done with the batch method by varying the sample volume from 100 to 2000 ml. In all cases, the Cd(II) could be retained quantitatively by the adsorbent.

Effect of Diverse Ions: The effect of cations on the retention of Cd was studied individually by adding the common metal ions in the batch procedure. The experimental results are shown in Table 1. The results show that 3.0 mg of Cd in the solution was retained significantly by the adsorbent, in the presence of 8 and 10 mg of various ions. Ca in the presence up to 50 mg did not interfere with the adsorption of 3.0 mg of Cd.

Rate of Sorption: The sorption rate is a very important parameter for the evaluation of adsorbent. The quantitative sorption of chemical species should be completed as fast as possible. Cd(II) was quantitatively adsorbed onto the adsorbent by stirring for more than 2 min with a magnetic stirrer under optimal experimental conditions. The sorption rate of metal ion is more rapid than C18/SG [53] and C18/SP207 [54] adsorbents. If quantitative retention had not been performed due to the
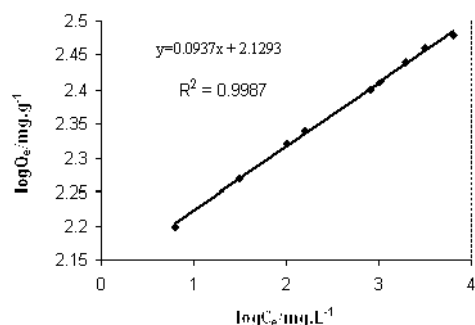
large sample volume, the sample solution would have been stirred for long time until the sorption was quantitative. Subsequent solid phase extraction experiments were carried out with stirring time of 110 min. The observed rapid sorption of Cd(II) on the Chelest Fiber Iry is most probably due to the hydrophilic property of the adsorbent.

Sorption Isotherm: The sorption isotherm of Cd(II) onto the Chelest Fiber Iry adsorbent from an aqueous solution was studied. The linear isotherm indicates a partitioning process of the solute onto the adsorbent. According to the Langmuir model, there is no interaction between the adsorbate molecules and the adsorption takes place in a monolayer. Thereafter, no further sorption is observed. The Freundlich equation is an empirical relationship describing the sorption of solutes from a liquid to a solid surface. This equation has widely been used [55,56] for the mathematical description of adsorption. The equation can be expressed as $Q_e = KC^{1/n}$ e and $\log Q_e = \log K + (1/n) \log C_e$, where Q_e is the adsorption amount (mg/g) and C the metal concentration (mg/l) at the final equilibrium, respectively. The $1/n$ and K are arbitrary parameters. The isotherm obeyed the Freundlich equation as shown in Fig. 5. with Freundlich's constants

Effect of Flow Rate: The effects of varying the flow rate of the sample solution through column were studied over the range 4-26 mL/min. The adsorption of Cd(II) found to be quantitative regardless of any changes in the flow rate. Hence, subsequent column operations were carried out at a flow rate of 35 ml/min. On the other hand, quantitative stripping of Cd(II) ion from the adsorbent was achieved at flow rate of 4 ml/min, using more than 10 ml of 0.4mol/L HNO_3, as shown in Fig. 6. Subsequent desorption experiments were carried out with 20 ml of 0.4 mol/L HNO_3.

Table 2: Analytical results of Cd(II) in tap water and waste water samples.

Sample	Sample taken (L)	Added(mg)	Found (mg)	Cd(mg/L)	Recovery(%)
Tap water	2	0.0	4.2±0.9	2.1	
	2	4.0	9.1±0.6		98.6
Waste water	0.1	0.0	46.2±0.4	467	
	0.1	10	56.5±0.8	567	94

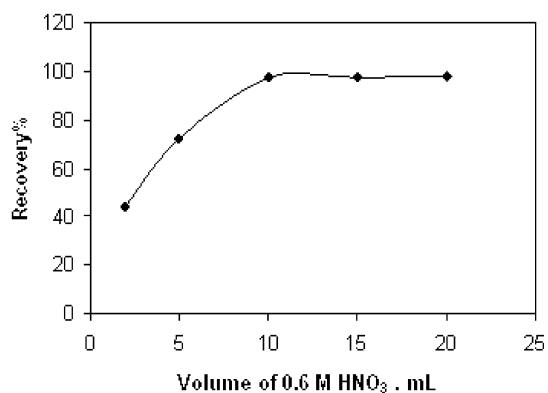All results are mean value of three determinations.

Fig. 6: Stripping of Cd(II) ion from adsorbent. Adsorbent, 1.0 g; Cd, 50 μg; flow rate of stripping acid, 3.8 mL/min; stripping acid, 0.4 mol/L nitric acid.

In order to study the adsorptive capacity of the adsorbent for the Cd(II), the column method was used. The maximum sorption capacity was determined by passing 100 ml portion of sample solution containing 300 mg of Cd(II) to the column (adsorbent 0.24 g) at flow rate of 35 ml/min and pH 4.0. After washing the column with distilled water, the retained Cd(II) was eluted with 0.4 mol/l HNO_3 and the eluate was diluted to appropriate volume for the determination of Cd(II) by flame AAS. The highest sorption capacity for Cd(II) obtained from three replicate measurements was found to be 0.95 ± 0.06 mmol/g adsorbent.

The adsorption-elution cycle of Chelest Fiber Iry for Cd was repeated 20 times by the column experiment described in Section 2.3 and no decline in the adsorption was found.

Determination of Cd(II) in Tap Water and Waste Water Samples: In order to demonstrate the applicability of the proposed method to environmental water sample, the Chelest Fiber Iry was applied to the extraction and determination of trace Cd(II) from tap water and waste water samples. Tap water (Tehran, taken after 10 min operation of the tap), waste water (Naz Gool manufacture, 26 January, 2007), samples were analyzed (Table 2). Two thousand milliliters of tap water sample (waste water

sample;100 ml) was passed through the Chelest Fiber Iry column at 35 ml/min flow rate. The retained Cd(II) was eluted with 20 ml of 0.4 mol/l HNO_3 at 4.0 ml/min flow rate. To estimate the accuracy of the procedure, adequate amount of Cd(II) was added to each sample and the resulting solution were submitted to the preconcentration procedure. The results are summarized in Table 2. The added Cd(II) can be quantitatively recovered from the sample solution. The proposed column is enough to preconcentrate traces Cd(II) from 2000 mL sample solution and provides the possibility of Cd(II) extraction with a concentration factor of 200. By the present method, about 1.7.0μg of Cd can be determined using 2 l of water sample. (The instrumental determination limit is about 0.1 μg/mL.)

CONCLUSION

The Chelest Fiber Iry adsorbent was applied to the separation and concentration of Cd(II) by batch and column methods. The adsorbent shows excellent adsorption ability for Cd(II) even at low pH. The adsorptive equilibration rate is high; the time taken for the adsorption of Cd(II) in 100 ml sample solution is within 2 min. The adsorbent is chemically stable and adsorption-desorption cycles could be repeated. The Chelest Fiber Iry could be successfully applied to the separation and determination of trace Cd(II) in real samples.

ACKNOWLEDGEMENTS

REFERENCES

1. Carasek, E., J.W. Tonjes and M. Scharf, 2002. Talanta, 56: 185.
2. Moghimi Ali, 2008. J. Chin. Chem. Soc., 55(2): 369.
3. Anthemidis, A.N., G.A. Zachariadis, C.G. Farastelis and J.A. Stratis, 2004. Talanta, 62 :437.
4. Boevski, I.V., N. Daskalova and I. Havezov, 2000. Spectrochim. Acta. Part. B., 55: 1643.

5. Xia, L., B. Hu, Z. Jiang, Y. Wu, L. Li and R. Chen, J. Anal. At. Spectrom. 20: 441.

6. Welz, B., 1985. *Atomic Absorption Spectrometry*, VCH, Amsterdam,

7. Marczenko, Z., 1986. *Separation and Spectrophotometric Determination of Elements*, Ellis Hardwood, London,

8. Anthemidis, A.N., G.A. Zachariadis and J.A. Stratis, 2003. J. Anal. At. Spectrom. 18: 1400.

9. Atsumi, K., Minami and T. Uada, 2005. J. Anal. Sci., 21: 647.

10. Saracoglu, S., M. Soylak and L. Elci, 2003. Talanta, 59: 287.

11. Doner, G. and A. Ege, 2005. Anal. Chim. Acta., 547: 14.

12. Yamini, Y., L. Hejazi and D.E. Mohammadi, 2003. Microchim. Acta., 142: 21.

13. Burham, N., S.M. Abdel-Azeem, M.F. El-Shahat, 2006. Anal. Chim. Acta., 579: 193.

14. Moghimi, A., 2007. "Chinese J. Chemistry" 25: 640.

15. Jamali, M.R., Y. Assadi, F Shemirani, M.R. Milani Hosseini, R. Rahnama M. Kozani, Masteri-Farahani and M. Salavati-Niasari, 2006. Anal. Chim. Acta., 579: 68.

16. Bowles, K.C., S.C. Apte, G.E. Batley, L.T. Hales and N.J. Rogers, 2006. Anal. Chim. Acta., 558: 237.

17. Melek, E., M. Tuzen and M. Soylak, 2006. Anal. Chim. Acta., 578: 213.

18. Dos Santos, E.J., A.B. Herrmann, A.S. Ribeiro and A.J. Curtius, 2005. Talanta, 65: 593.

19. Lemos, V.A. and P.X. Baliza, 2005. Talanta, 67: 564.

20. Wang, J. and E.H. Hansen, 2002. J. Anal. At. Spectrom. 17: 248.

21. Robards, K. and P. Worsfold, 1991. Analyst, 116: 549.

22. Kaewsarn, P. and Q. Yu, 2001. Environ. Pollut., 112: 209.

23. Taylor, K.Z., D.S. Waddell and E.J. Reiner, 1995. Anal. Chem., 67: 1186.

24. Yamini, Y. and M. Ashraf-Khorassani, 1994. J. High Resolut. Chromatogr., 17: 634.

25. Shamsipur, M., A.R. Ghiasvand, Y. Yamini, 1999. Anal. Chem., 71: 4892.

26. Shamsipur, M., A.R. Ghiasvand and H. Sharghi, 2001. Int. J. Environ. Anal.Chem., 82: 23.

27. Brunner, J., A. Mokhir and R.J Kramer,. 2003. Am. Chem. Soc., 125: 12410.

28. Zelder, F.H., J. Brunner and R. Kramer, 2004. Chem. Commun., pp: 902.

29. Boll, I., R. Kramer, J. Brunner and A. Mokhir, 2005. J. Am. Chem. Soc., 27: 7849.

30. Moghimi, A., 2006. Oriental J. Chemistry 22(3): 527.

31. Nayebi, P. and A. Moghimi, 2006. Oriental J. Chemistry, 22(3): 507.

32. Moghimi, A., 2007. "Chinese J. Chemistry, 25(12): 1842.

33. Moghimi, A., 2007. Chinese J. Chemistry, 25(10): 1536.

34. Moghimi, A. and S. Ghammamy, 2007. "Environmental chemistry an Indian J., 2: (3).

35. Choi, Y.S. and H.S. Choi, 2003. Bull. Korean, Chem. Soc., 24: 222 .

36. Saber Tehrani, M., F. Rastegar, A. Parchehbaf and Z. Rezvani, 2005. Chinese J. Chemistry, 23: 1437.

37. Hinze, W.L., E. Pramaur and Rev. Crit, 1993. Anal. Chem., 24: 133.

38. Stalikas, C.D., 2002. Trends. Anal. Chem., 21: 343.

39. Paleogos, E.K., D.L. Giokas and M.I. Karayannis, 2005. Trends. Anal. Chem., 24: 426.

40. Borges, D.L.G., M.A.M.S. DaVeiga, V.L.A. Frescura, B. Welz and A.J. Curtius, J. Anal. At. Spectrom. 18: 501.

41. Moghimi, Ali, Poursharifi and Mohammad Javad, 2005. Asian J. Chemistry, 20(7): 5071.

42. . Zhu, X., X. Zhu and B. Wang, 2006. Microchim. Acta., 154: 95.

43. Ghiasvand, A.R., S. Shadabi, E. Mohagheghzadeh ands P. Hashemi, 2005. Talanta, 66: 912.

44. Igarashi, S., N. Ide and Y. Takagai, 2000. Anal. Chim. Acta., 424: 263.

45. Fan, Z. and W. Zhou, 2006. Spectrochim. Acta. Part B., 61: 870.

46. Li, L., B. Hu, L. Xia and Z. Jiang, 2006. Talanta, 70: 468.

47. Chamsaz, M., M.H. Arabab-Zavar and S. Nazari, 2003. J. Anal. At. Spectrom. 18: 1279.

48. Fragueiro, S., I. Lavilla and C. Bendicho, 2004. Spectrochim. Acta. Part. B., 59: 851.

49. Fragueiro, S., I. Lavilla and C. Bendicho, 2006. Talanta, 68: 1096.

50. Rezaee, M., Y. Assadi, M.R. Milani Hosseini, E. Aghaee, F. Ahmadi and S. Berijani, 2005. J. Chromatogr. A., 1116: 1.

51. Berijani, S., Y. Assadi, M. Anbia, M.R. Milani Hosseini and E Aghaee, 2006. J. Chromatogr. A., 1123: 1.

52. Rahnama Kozani, R., Y. Assadi, F. Shemirani, M.R. Milani Hosseini and M.R. Jamali, 2007. Talanta, Talanta, 79: 498.

53. Tong, A., Y. Akama, S. Tanaka, 1990. Analyst, 115: 947.

54. Anzai, Y., M. Mori, K. Sato and Y. Akama, Bull. Soc. Sea. Water. Sci. Jpn., 56: 241.

55. Saeed, M.M., S.M. Hasany and M. Ahmed, Talanta, 50: 625.

56. Hasany, S.M., M.M. Saeed and M. Ahmed, Talanta, 54: 89.