

On-Line Preconcentration and Speciation of Chromium by an 8-Hydroxyquinoline Microcolumn Immobilized on Surfactant-Coated Alumina and Flow Injection Atomic Absorption Spectrometry

Seyyed Hamid AHMADI^{1*}, Ali Mohammad HAJI SHABANI^{2†},
Shayessteh DADFARNIA², Masoumeh TAEI²

¹*Chemistry and Chemical Engineering Research Center of Iran, POBox: 14335-186, Tehran-IRAN
e-mail: ahmadi@ccerci.ac.ir*

²*Department of Chemistry, Yazd University, Yazd-IRAN*

Received 19.09.2006

An on-line technique for the determination of chromium species with atomic absorption spectrometry is described. The method is based on separation and preconcentration of Cr(III) on a microcolumn of immobilized 8-hydroxyquinoline on surfactant-coated alumina. The adsorbed analyte is then eluted with 400 μL of 20% ethanolic solution of 1.5 mol L⁻¹ hydrochloric acid and is transported to a flame atomic absorption spectrometer for quantification. The effects of pH, sample and eluent flow rate, sorption capacity, and the presence of various cations and anions on the sorption of Cr(III) were investigated. The sorption was quantitative in the pH 6-8 range, and for a sample volume of 35 mL a preconcentration factor of 98 was obtained. Total chromium was determined by efficient reduction of Cr(VI) to Cr(III) with hydroxylamine. The method was applied to the determination of chromium in electroplating wastewater samples.

Key Words: Chromium speciation, on-line preconcentration, 8-hydroxyquinoline, alumina, flow injection.

Introduction

Chromium species enter the environment as a result of effluent discharge from several industries, including steel, electroplating, tanning, and chemical, as well as from oxidative dyeing and water cooling towers.¹ Chromium exists in the environment in 2 oxidation states: Cr(VI) and Cr(III). Cr(III) is a nutrient element used for control of glucose and lipid metabolism in membranes, while Cr(VI) is highly carcinogenic and mutagenic due to its high oxidative character.^{2,3} Owing to these contradicting characteristics, chromium speciation is a hot topic in modern analytical chemistry.⁴

*Corresponding author

†Corresponding author

Despite the very sensitive analytical methods available, for direct determination of low levels of chromium species in water, a separation and preconcentration step is required in order to improve their detectability and to eliminate interferences. For this purpose, various separation and preconcentration methods, such as coprecipitation,⁵ liquid-liquid extraction,⁶ cloud point extraction,⁷ ion exchange,⁸ and solid phase extraction,^{9,10} have been developed. However, these manual batch procedures are labor-, time-, and reagent-intensive, and require large volumes of sample. Flow injection (FI) on-line preconcentration and separation, coupled with flame atomic absorption spectrometry (FAAS), has been shown to be effective in terms of enhanced sensitivity, efficient removal of the matrix, possibility of speciation, high sample throughput, and high precision.^{11,12} For speciation of chromium utilizing FAAS, different on-line microcolumn enrichments have been devised, including activated alumina,^{13,14} cellulose sorbent,¹⁵ chelating ion exchanger,¹⁶ C₁₈ bonded silica,¹⁷ and polyether ether ketone.¹⁸ Enrichment factors with the above-mentioned microcolumns are typically 8- to 100-fold and the detection limit for Cr(III) is between 0.2 and 81 $\mu\text{g L}^{-1}$.

Ionic surfactants adsorb on metal oxides, such as alumina¹⁹ and iron(III) oxide,²⁰ and form aggregates known as hemimicelles and admicelles. Hydrophobic chelating agents could easily be immobilized into the micelles and can be used for the separation and preconcentration of trace metals.²¹ During the last few years the effectiveness and versatility of chelating sorbent immobilized on surfactant-coated alumina in flow injection-atomic absorption spectrometry (FI-AAS) has been demonstrated;²²⁻²⁴ however, to the best of our knowledge, there is no previous report on the use of modified alumina for chromium speciation with FI-AAS.

8-Hydroxyquinoline (oxine) is a well-characterized chelating organic ligand that reacts with several metal ions under controlled pH conditions.²⁵ 8-Hydroxyquinoline and its derivatives have been physically or chemically bonded onto various supports, including Amberlite XAD-7, Fractogel, chitosan, silicagel, activated carbon, controlled pore glass, and polyacrylonitrile hollow fiber membranes, and has been used for separation and preconcentration of trace metals in on-line FI analysis.²⁶

Oxine reacts with Cr(III) more rapidly than with other chelating agents.²⁷ Oxine, or its derivatives, selectively form complexes with Cr(III), but not with Cr(VI).²⁸⁻³⁰ In this work, the possibility of immobilization of oxine on surfactant-coated alumina was considered and a rapid and accurate FI-FAAS method for preconcentration and speciation of chromium was developed.

Experimental

Apparatus

A Buck Scientific model 210 VGP flame atomic absorption spectrometer equipped with a 10-cm air-acetylene burner was used as the detector. A chromium hollow cathode lamp operated at 6.9 mA was used as the light source. The wavelength was set at a 357.9-nm resonance line and the monochromator spectral bandpass was 0.7 nm. The absorbance time response was monitored on a Linseis model L-250 x-t chart recorder. Quantitative analysis was based on the measurement of peak height of the transient signals.

The FI on-line preconcentration manifold consisted of a peristaltic pump (Ismatic, MS-REGLO/8-100 Switzerland), 2 six-way injection valves (Rheodyne, CA, USA), and a microcolumn of oxine immobilized on surfactant-coated alumina (PTFE tubing 3 cm long \times 1.5 mm i.d.), for on-line preconcentration of chromium.

Reagents

All chemicals were of analytical reagent grade (Merck, Darmstadt, Germany), and triple-distilled water was used throughout.

Stock solutions of 1000 $\mu\text{g mL}^{-1}$ of Cr(III) and Cr(VI) were prepared from chromium(III) chloride hexahydrates and potassium dichromate, respectively. Working solutions were prepared daily from stock solutions by serial dilution with water.

Alumina particles (10-50 μm , γ type, chromatographic grade) were purified by shaking with 5 mol L^{-1} nitric acid and washing 3 times with water.

Sodium dodecyl sulfate (SDS) and oxine were used without further purification. An 8-g L^{-1} oxine was prepared by dissolving oxine in methanol.

Stock solutions of interfering ions were prepared by dissolving appropriate amounts of ammonium or nitrate salts in distilled water.

Immobilization of oxine on SDS-coated alumina

To 1.5 g of alumina was added 50 mL of solution containing 100 mg of sodium dodecyl sulfate and the solution was mixed with a magnetic stirrer. The pH of the solution was adjusted to approximately 2 with 4 mol L^{-1} hydrochloric acid and was mixed for 10 min. The supernatant was decanted and the SDS-coated alumina was washed thoroughly with several portions of distilled water. Then, 50 mL of water and 4 mL of oxine solution were added, and the solution was mixed for 15 min. The mixture was then filtered through a Millipore filter, air-dried, and was kept in a closed bottle until use.

Preparation of microcolumn

Microcolumns were manufactured from PTFE (Teflon) tubing (3 cm long \times 1.5 mm i.d.) and were packed with about 70 mg of oxine immobilized on surfactant-coated alumina; the ends of the tube were fitted with glass wool to retain the sorbent in the tube.

Recommended procedure

The pH of the solution was adjusted to ~ 6.5 with 0.1 mol L^{-1} nitric acid or 0.1 mol L^{-1} NaOH. In the preconcentration stage the standard solution or sample (35 mL) was passed through the microcolumn containing oxine immobilized on surfactant-coated alumina at a flow rate 5.0 mL min^{-1} . The eluent loop was simultaneously filled with the eluent solution (400 μL of 20% ethanolic solution of 1.5 mol L^{-1} hydrochloric acid) and the baseline was set by pumping the carrier (water at 4.0 mL min^{-1}) into the instrument nebulizer.

After the preconcentration stage, the valve was switched and the elution process started. In this stage the content of the elution loop was displaced by the carrier stream to the microcolumn and, therefore, adsorbed chromium(III) was eluted and transported to the flame atomic absorption spectrometer for determination. The transient signal was monitored for quantitative analysis.

Total chromium was determined after the reduction of Cr(VI) to Cr(III) with hydroxylamine, according to Isshiki et al.²⁷ as follows: 2 mL of 2 mol L^{-1} hydrochloric acid was added to 80 mL of sample, followed by the addition of 1 mL of 60 g L^{-1} hydroxyl ammonium chloride. The solution was left at room temperature for at least 20 min. The pH of the solution was adjusted to ~ 6.5 with 1 mol L^{-1} NaOH and the

volume was made up to 100 mL with distilled water. The total chromium was then determined by FI-AAS. The Cr(VI) in the sample was calculated by the difference between the values of total chromium and Cr(III).

Results and Discussion

Properties of the chelating sorbent based on alumina coated surfactant

The anionic surfactant, SDS, was strongly adsorbed on positively charged γ -alumina surfaces in slightly acidic media.³¹ In preparation of the sorbent, the concentration of SDS was fixed at approximately 6.9×10^{-3} M, which is below the critical micelle concentration (8.0×10^{-3} M). Above this concentration, the excess of SDS forms micelles in the aqueous solution that are not adsorbed on alumina surfaces. Similar to chemically bonded alkylsilane moieties, the sorbed SDS molecules on alumina provide a hydrophobic environment on alumina surfaces.³² When SDS-coated alumina particles were shaken with the solution of oxine, the ligand was homogeneously trapped on the hemimicelles or admicelles, which were formed by the surfactant on alumina surfaces. The chelating sorbent was stable for several weeks and was used for preparation of the microcolumn.

Optimization of preconcentration procedure

The main factors that affected the preconcentration process were pH of the sample solution, flow rate, length of the microcolumn, type of eluent, and the volume of the loading and eluent solutions. In order to establish the best chemical and flow conditions for deposition and elution of the analyte, the procedure was optimized by univariable method.

The effect of the sample pH on the sorption of Cr(III) and Cr(VI) onto the column was studied by varying the pH between 1 and 9 (Figure 1). Cr(III) was quantitatively retained in the pH 6-8 range. At pHs < 6, the formation of the chelate of Cr(III) and the ligand were not complete and the decrease in response at higher pHs was probably due to the formation of hydroxide of the metal. It was confirmed that Cr(VI) was not retained at the pH 1-9 range.

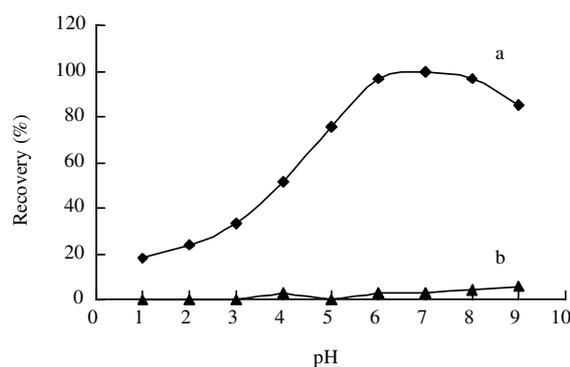


Figure 1. The effect of sample pH on the recovery of Cr(III) (a) and Cr(VI) (b). Cr(III) and Cr(VI) solution: 500 μ L, 1 μ g mL⁻¹; eluent volume: 400 μ L.

The effect of length of the microcolumn on efficiency of analyte deposition was investigated and a 3-cm microcolumn was found to be sufficient for deposition of 3.5 μ g of Cr(III) from 10 mL of solution.

Various eluents, such as nitric acid, hydrochloric acid, acetone, and acidified ethanol, were tested. It was found that 20% ethanolic solution of 1.5 mol L⁻¹ hydrochloric acid is the most suitable eluent for this purpose. The influence of the volume of this solution on the quantitative recovery of Cr(III) from the microcolumn was studied by varying the volume between 100 and 500 μ L. Total recovery of Cr(III) was achieved with 350 μ L of eluent; however, in order to ensure the quantitative recovery of the analyte, a volume of 400 μ L was chosen for subsequent work.

The effect of the sample flow rate during the loading step was studied. The results shown in Figure 2 indicate that at a flow rate > 6.0 mL min⁻¹ the signal response is independent of flow rate. This confirmed a rapid and efficient uptake of Cr(III) by the microcolumn. Subsequent sample loading was performed at a flow rate of 5.0 mL min⁻¹.

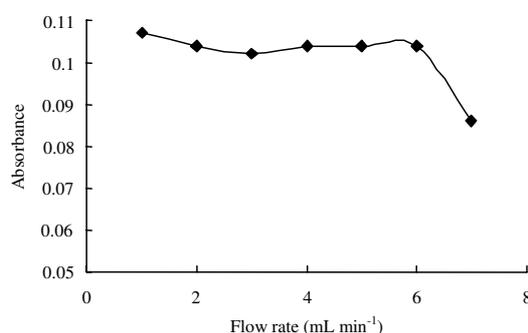


Figure 2. The effect of sample flow rate on retention of Cr(III). Cr(III) solution: 10 mL, 0.1 μ g mL⁻¹; pH : ~6.5 ; eluent volume: 400 μ L.

The performance of the flow system was investigated using 30 ng mL⁻¹ of Cr(III) solution at a sample flow rate of 5.0 mL min⁻¹, and preconcentration time varied from 2-20 min. The analytical signal increased proportionally with the preconcentration time, up to 20 min, and then leveled off at longer preconcentration times.

The effect of the eluent flow rate in the range of 1.0-7.0 mL min⁻¹ was studied. A virtually linear increase in peak height was observed, which leveled off at a flow rate > 3.5 mL min⁻¹. The decrease in peak height at flow rates < 3.5 mL min⁻¹ is due to peak broadening observed at low flow rates. The relative independence of response from the solution flow rate in the range of 3.5-5.0 mL min⁻¹ indicates the fast kinetics of exchange of the elution process. A flow rate of 4.0 mL min⁻¹ was selected for further studies.

The capacity of oxine-coated alumina was determined by the batch method. Thus, 1.0 g of oxine-coated alumina was added to 50 mL of solution (pH ~6.5) containing 2.5 mg of Cr(III). The mixture was shaken with a mechanical shaker for 30 min and then filtered through a sintered glass funnel. The amount of chromium left in the filtrate was determined by FASS. The capacity of the sorbent was 1.23 mg g⁻¹.

Study of interferences

The effect of common coexisting ions on the determination of 20 ng mL⁻¹ of Cr(III) was investigated by the recommended procedure. The results are summarized in Table 1. A relative error < 5% was considered to be within the range of experimental error. At the given concentration, most cations and anions did not interfere in the determination of Cr(III) at trace level.

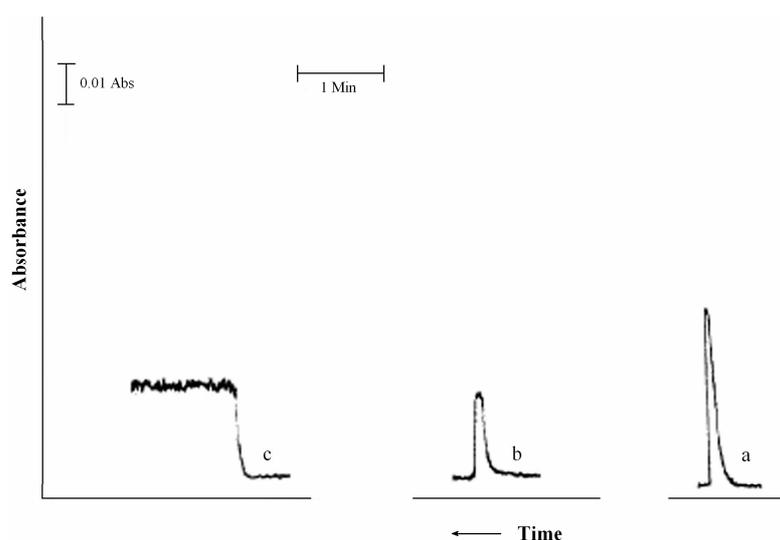
Table 1. The effect of diverse ions in the determination of Cr(III). Cr(III) concentration $20 \mu\text{g L}^{-1}$; concentrated volume 10 mL; pH 6-8; flow rate 5 mL min^{-1} .

| Ions | Tolerance limit Mole ratio |
|---|-------------------------------|
| Mg^{2+} , Ca^{2+} , K^+ , Na^+ | 1000 ^a |
| Br^- , NO_3^- , SO_4^{2-} , PO_4^{3-} | 1000 ^a |
| Ba^{2+} , Zn^{2+} , Cl^- , CO_3^{2-} | 500 |
| Cd^{2+} , Mn^{2+} , Ni^{2+} | 200 |
| Al^{3+} , Pb^{2+} , Co^{2+} | 40 |
| Cu^{2+} | 20 |
| Fe^{3+} | 10 |

^aMaximum value tested

Analytical performance

A typical absorbance-time response for the sequential injection of a standard solution [$400 \mu\text{L}$ of $1 \mu\text{g mL}^{-1}$ Cr(III)] and eluent ($400 \mu\text{L}$) is given in Figure 3a. For comparison, the equivalent transient signals for direct injection and pneumatic nebulization of the sample [$1 \mu\text{g mL}^{-1}$ Cr(III)] are also included (Figure 3b and c). The relatively narrow and intense elution response (Figure 3a) relative to the signal for direct injection (Figure 3b) indicates a degree of preconcentration for the microcolumn sample processing, even though the same volume ($400 \mu\text{L}$) of solution was used in the deposition-elution steps. In terms of peak height of conventional nebulization and peak height of sequential injection with the microcolumn, a dispersion coefficient of 0.5 was calculated. By comparing the area of the signals of the microcolumn elution peak (Figure 3a) and direct injection (Figure 3b), a recovery of more than 97% was obtained with a single injection of eluent.

**Figure 3.** Absorbance-time response for (a) through-column injections of Cr(III) solution ($400 \mu\text{L}$, $1 \mu\text{g mL}^{-1}$; pH = 6.5) and eluent ($400 \mu\text{L}$), (b) direct injection of Cr solution ($400 \mu\text{L}$, $1 \mu\text{g mL}^{-1}$), and (c) conventional nebulization of Cr solution ($1 \mu\text{g mL}^{-1}$).

The system showed linearity within the concentration range of 1-100 $\mu\text{g L}^{-1}$ of Cr(III) and a sampling volume of 35 mL. The calibration graph under the optimum chemical and flow conditions has the equation $A = 0.00372 C + 0.0011$ ($C =$ chromium concentration, $\mu\text{g L}^{-1}$), and a correlation coefficient of 0.9998.

By using direct aspiration in FAAS, without preconcentration, the linear range for Cr(III) determination took place between 100 and 5000 $\mu\text{g L}^{-1}$ ($A = 0.000038 C + 0.00016$). The experimental preconcentration factor,^{33,34} calculated as the ratio of the slopes of the calibration curves obtained with and without preconcentration, was 98 for a 35-mL sample. The theoretical preconcentration factor was 88, which further confirmed that a degree of response enhancement occurs during the microcolumn sample processing.

The relative standard deviation (RSD) of 8 replicate measurements for 40 ng mL^{-1} of Cr(III) with a sample volume of 35 mL was 3.3%.

The limit of detection, defined as the concentration of Cr(III) that gives a response equivalent to 3 times the standard deviation of the blank, was 0.16 ng mL^{-1} for processing 35 mL of distilled water.

Application

The applicability of the proposed procedure for quantitative determination of chromium species was first checked in aqueous solutions by analyzing various mixtures of Cr(III) and Cr(VI). Table 2 shows that nearly all Cr(III) and Cr(VI) are recovered from the mixture, and the procedure could be used for speciation of chromium.

Table 2. Determination of Cr(III) and Cr(VI) in synthetic mixtures.

| Added ($\mu\text{g L}^{-1}$) | | Found ($\mu\text{g L}^{-1}$) ^a | |
|--------------------------------|---------|---|----------------|
| Cr(VI) | Cr(III) | Cr(VI) | Cr(III) |
| 0 | 10 | 0 | 10.2 \pm 0.3 |
| 10 | 0 | 9.8 \pm 0.2 | 0 |
| 10 | 10 | 10.1 \pm 0.5 | 10.4 \pm 0.4 |
| 20 | 10 | 19.8 \pm 0.4 | 10.3 \pm 0.3 |
| 10 | 20 | 9.8 \pm 0.2 | 19.8 \pm 0.2 |
| 20 | 20 | 20.1 \pm 0.4 | 19.4 \pm 0.7 |

Sample volume: 35 mL

^aAverage and standard deviation of 3 determinations

Thus, the proposed method was validated using certified reference material BCR 544 (lyophilized solution) for both species. The results of this investigation, together with certified values, are given in Table 3. It is obvious that there is good agreement between the results and accepted values.

Table 3. Determination of Cr(III) and Cr(VI) in certified reference material BCR 544^a.

| | Cr(III) | Cr(VI) |
|---|----------------|----------------|
| Certified value ($\mu\text{g L}^{-1}$) | 26.8 \pm 1.0 | 22.8 \pm 1.0 |
| Found ^b ($\mu\text{g L}^{-1}$) | 26.3 \pm 0.7 | 23.2 \pm 0.6 |

^aLyophilized chromium solution [Cr(III), Cr(VI)]

^bAverage and standard deviation of 3 determinations

Furthermore, the procedure was applied to the determination of Cr(III) and Cr(VI) in wastewater samples. The reliability of the method was checked by recovery experiments. The obtained results are given

in Table 4. Recovery values are in the range of 97%-102%, which demonstrates the applicability of the method to the determination of chromium in water and wastewater samples.

Table 4. Determination of Cr(III) and Cr(VI) in wastewater samples^a.

| Sample | Added ($\mu\text{g L}^{-1}$) | | Found ^b ($\mu\text{g L}^{-1}$) | | Recovery (%) | |
|--------|--------------------------------|--------|---|----------------|--------------|--------|
| | Cr(III) | Cr(VI) | Cr(III) | Cr(VI) | Cr(III) | Cr(VI) |
| 1 | 0 | 0 | 8.0 ± 0.2 | 11.4 ± 0.3 | | |
| | 10 | 10 | 17.7 ± 0.5 | 21.5 ± 0.6 | 97 | 101 |
| 2 | 0 | 0 | 39.2 ± 0.6 | 67.4 ± 0.8 | | |
| | 10 | 10 | 49.1 ± 1.3 | 77.2 ± 1.2 | 99 | 98 |
| 3 | 0 | 0 | 12.9 ± 0.4 | 24.1 ± 0.8 | | |
| | 10 | 10 | 23.1 ± 0.6 | 33.9 ± 1.3 | 102 | 98 |

Sample volume: 35 mL

^aSamples were taken from electroplating facilities located east of Tehran

^bAverage and standard deviation of 3 determinations

Conclusion

Oxine immobilized on a surfactant-coated alumina microcolumn presents a new alternative for trace determination of chromium(III) and total chromium in an FI-AAS system. The preconcentration factor of 98 achieved in this method makes it a very sensitive procedure for the determination of chromium in natural and wastewater samples. The proposed method proved to be simple, rapid, and reliable for chromium determination in wastewater samples. Future work will be directed toward assessment of the multi-element enrichment capability of oxine immobilized on a surfactant-coated alumina sorbent.

Acknowledgments

The authors wish to thank the graduate school of Yazd University for their support.

References

1. J. Kotaz and Z. Stasicka, **Environment. Pollut.** **107**, 263-283 (2000).
2. R.A Andersen, **Sci. Total Environ.** **86**, 75-81 (1989).
3. C.S. Gad, **Sci. Total Environ.** **86**, 149-157 (1989).
4. M.J. Marques, A. Salvador, A. Morales-Rubio and M. de la Guardia, **Fresenius J. Anal. Chem.** **367**, 601-613 (2000).
5. Q. Zhang, H. Minami, S. Inoue and I. Atsuya, **Anal. Chim. Acta** **401**, 277-82 (1999).
6. K.S. Subramanian, **Anal. Chem.** **60**, 11-15 (1988).
7. E.K. Paleologos, C.D. Stalikas, S.M. Tzouwara-Karayanni and M.I. Karayannis, **Anal. Chim. Acta** **436**, 49-57 (2001).
8. C.A. Johnson, **Anal Chim Acta** **238**, 273-278 (1990).
9. R.E. Sturgeon, S.S. Berman and S.N. Willie, **Talanta** **29**, 167-171 (1982).

10. E. Vassileva and N. Furuta, **Fresenius J. Anal. Chem.** **370**, 52-59 (2001).
11. Z. Fang, "**Flow Injection Atomic Absorption Spectrometry**", Wiley, Chichester, 1995.
12. J.F. Tyson, "**FIA Techniques and Strategies Expand the Potential of Atomic Spectrometry**", in *Flow Analysis with Atomic Spectrometric Detectors*, ed. A. Sanz-Medel, Elsevier Science Ltd, Amsterdam, 1999.
13. M. J. Marques, A. Morales-rubio, A. Salvador and M. de la Guardia, **Talanta** **35**, 1229-1239 (2001).
14. M. Sperling, S. Xu and B. Welz, **Anal. Chem.** **64**, 3101-3108 (1992).
15. A.M. Naghmush, K. Pyrzynska and M. Trojanowicz, **Anal. Chim. Acta** **288**, 247-257 (1994).
16. R.M. Cespon-Romero, M.C. Yebra-Biurrun and M.P. Bermejo-Barrera, **Anal. Chim. Acta** **327**, 37-45 (1996).
17. A. Gaspar, C. Sogor and J. Posta, **Microchem. J.** **58**, 251-255 (1999).
18. A. Gaspar and J. Posta, **Anal. Chim. Acta** **354**, 151-158 (1997).
19. K.T. Valsaraj, **Sep. Sci. Technol.** **27**, 1633-1642 (1992).
20. T.M. Holsen, E.R. Taylor, Y.C. Seo and P.R. Anderson, **Environ. Sci. Technol.** **25**, 1585-1589 (1991).
21. M. Hiraide, M.H. Sorouraddin and H. Kawaguchi, **Anal. Sci.** **10**, 125-127 (1994).
22. A.M. Haji Shabani, S. Dadfarnia and K. Dehghan, **Talanta** **59**, 719-725 (2003).
23. S. Dadfarnia, A.M. Salmazadeh and A.M. Haji Shabani, **J. Anal. At. Spectrom.** **17**, 1434-1438 (2002).
24. S. Dadfarnia, A.M. Haji Shabani, F. Tamaddon and M. Rezaei, **Anal. Chim. Acta** **539**, 69-75 (2005).
25. R.A. Nickson, S.J. Hill and P.J. Worsfold, **Anal. Proc.** **32**, 387-395 (1995).
26. T. Prasada Rao and J. Mary Gladis, **Anal. Sci.** **18**, 517-524 (2002).
27. K. Isshiki, Y. Sohrin, H. Karatani and E. Nakayama, **Anal. Chim. Acta**, **224**, 55-64 (1989).
28. H. Filik, **Microchim. Acta** **140**, 205-210 (2002).
29. H. Filik, M. Dogutan and R. Apak, **Anal. Bioanal. Chem.** **376**, 928-933 (2003).
30. B. Wen, X. Shan and J. Lian, **Talanta** **56**, 681-687 (2002).
31. M. Hiraide, J. Iwasawa, S. Hiramatsu and H. Kawaguchi, **Anal. Sci.** **11**, 611-615 (1995).
32. F. Merino, R. Soledad and D. Perez-Bendito, **Anal. Chem.** **75**, 6799-6806 (2003).
33. Z. Fang, "**Flow Injection Separation and Preconcentration**", VCH, Weinheim, 1993.
34. V.A. Lemos, W.N.L. dos Santos, J.S. Santos and M.B. de Carvalho, **Anal. Chim. Acta** **481**, 283-290 (2003).