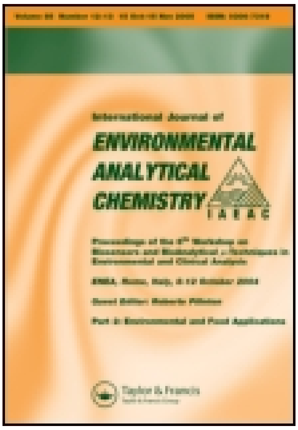

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Separation, preconcentration and speciation of chromium by solid phase extraction on immobilised ferron

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Separation, preconcentration and speciation of chromium by solid phase extraction on immobilised ferron

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A sensitive and simple method for determination of chromium species after separation and preconcentration by solid phase extraction (SPE) has been developed. For the determination of the total concentration of chromium in solution, Cr(VI) was efficiently reduced to Cr(III) by addition of hydroxylamine and Cr(III) was preconcentrated on a column of immobilised ferron on alumina. The adsorbed analyte was then eluted with 5 mL of hydrochloric acid and was determined by flame atomic absorption spectrometery. The speciation of chromium was affected by first passing the solution through an acidic alumina column which retained Cr(VI) and then Cr(III) was preconcentrated by immobilised ferron column and determined by FAAS. The concentration of Cr(VI) was determined from the difference of concentration of total chromium and Cr(III). The effect of pH, concentration of eluent, flow rate of sample and eluent solution, and foreign ions on the sorption of chromium (III) by immobilised ferron column was investigated. Under the optimised conditions the calibration curve was linear over the range of 2–400 $\mu g\,L^{-1}$ for 1000 mL preconcentration volume. The detection limit was 0.32 $\mu g\,L^{-1}$, the preconcentration factor was 400, and the relative standard deviation (%RSD) was 1.9% (at 10 $\mu g\,L^{-1}$; $n = 7$). The method was successfully applied to the determination of chromium species in water samples and total chromium in standard alloys.

Keywords: chromium (III) and (IV) species; immobilised ferron; water samples; flame atomic absorption spectrometry

1. Introduction

Chromium is found in nature in rocks, soils, plants, animals, volcanic dust, and gases. Chromium (III) and (VI) are used for making steel and other alloys, bricks, dyes, pigments, 'chrome plating', leather tanning and wood preserving [1]. Chromium species enters the air, water and soil through natural processes and anthropogenic activities. Human beings can be exposed to chromium by breathing air, drinking water, eating food containing chromium, or through the skin contact with chromium compounds. Toxicity of chromium is a function of the oxidation state and concentration of each species [2,3]. Cr(III) is considered as an essential trace element for the proper functioning of living organisms. Chromium (III) is an essential trace nutrient involved in the mechanism of the action of the

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pancreatic hormone insulin and thus influences carbohydrate, lipid and protein metabolism. On the other hand, Cr(VI) can be toxic and carcinogenetic [4]. The major toxic effects of Cr(VI) are chronic ulcers, dermatitis, corrosive reaction in nasal septum and local effects in lungs [5,6]. Based on sufficient evidence of carcinogenicity of chromium (VI) compounds in human and animals, the International Agency for Research on Cancer (IARC) and the Department of Health and Human Services have treated chromium (VI) compound as carcinogenetic compounds [7]. Due to these factors, accurate and easy determinations of chromium species in water samples are very important.

Various analytical techniques such as spectrophotometry [8,9], stripping voltammetry (SV) [10], X-ray fluorescence (XRF) [11], high performance liquid chromatography (HPLC) [12], inductively coupled plasma-optical emission spectrometry (ICP-OES) [13,14], inductivity coupled plasma-mass spectrometry (ICP-MS) [15,16] and atomic absorption spectrometry (AAS) [17–21] have been successfully used for the accurate determination of chromium in various samples.

Flame atomic absorption spectrometry (FAAS) has been widely used for the determination of trace metals, because of its low costs and ease of application. However, the direct determinations of metal ions by FAAS are limited due to their low concentration and matrix interferences. FAAS is also not suitable for direct determination of the chromium species including Cr(III) and Cr(IV), as it only measure total chromium. In order to solve these problems, a preconcentration and/or separation step is necessary prior to the determination of chromium species by FAAS.

The most widely used techniques for separation and preconcentration of chromium are liquid-liquid extraction (LLE) [22], could point extraction (CPE) [20,23], ion exchange separation [24,25], co-precipitation [26,27] and solid phase extraction (SPE) [6,27–30]. Among them, solid phase extraction is one of the most effective preconcentration methods because of its simplicity, rapidity and ability to attain a high preconcentration factor. A variety of solid materials such as activated alumina [31], biological sorbent [32] polytetraflouroethylene [33] modified silica gel [34] and ligand immobilised on surfactant coated alumina [29,35,36] has been used for preconcentration and speciation of chromium in water samples. Currently, one of the most important focused studies on SPE for chromium speciation and determination is the use of new solid sorbents. Recently, we reported that 8-hydroxy-7-iodoquinoline-5-sulfonic acid (ferron) directly immobilised on alumina powder can be used for iron separation and preconcentration [37]. Ferron is a well known classical ligand that form strong complexes with some metal ions [38] and had been used for the spectrophotometic determination [39] and cloud point extraction [40], but its use in the solid phase extraction is rare. In this study the possibility of extraction of the chromium by immobilised ferron was considered, and a rapid and simple method for separation/enrichment and determination of the chromium species by flame atomic absorption spectrometry was developed.

2. Experimental

2.1 *Instrumentation*

A Varian atomic absorption spectrometer (Model Spectra AA 220, Australian) was used for all absorption measurements. A chromium hollow cathode lamp and air-acetylene flame was used for all measurements. The operating conditions were as follows: wavelength 357.9 nm, slit width 0.5 nm and lamp current 7 mA. An ISTEK Model 720 P pH meter with a combined glass electrode was employed for measuring the pH of solutions.

2.2 *Reagents*

All chemicals were of highest purity available from Merck (Darmstadt, Germany) and were used as received. Deionised water was used throughout. A stock standard solution ($1000\,\mu g\,mL^{-1}$ of Cr(III) or Cr(VI)) was prepared by dissolving appropriate amount of either $CrCl_3 \cdot 6H_2O$ in $0.5\,mol\,L^{-1}$ HCl or $K_2Cr_2O_7$ in water. Working solutions were prepared daily from the stock solutions by serial dilution.

Alumina particles (γ type, 10–50 µm, chromatographic grade, Merck (Darmstadt, Germany) was purified by shaking with $5\,mol\,L^{-1}$ nitric acid and washing three times with water. Ferron (Fluka) were used without further purification.

2.3 *Immobilisation of ferron and preparation of the column*

The immobilised ferron was prepared as described before in the work by Shakerian *et al.* [37]: i.e. 50 millilitres of water and ~0.3 g of ferron was added to 3.0 g of alumina, and the solution was mixed with a magnetic stirrer for 10 min. The mixture was then filtered through a Millipore filter, washed, air-dried, and was kept in a closed bottle before use. It was stable for more than 2 months. The column was prepared by using a glass column (10 cm long and 1.0 cm in diameter) having a stopcock and a porous disc. A small amount of glass wool was placed on the disc to prevent loss of the sorbent during sample loading. Then the column was packed with immobilised ferron on alumina (to the height of 1 cm) and was covered with small amount of glass wool.

2.4 *Water samples*

The samples were filtered through a Millipore filter; the pH (~9) and potassium chloride concentration ($0.1\,mol\,L^{-1}$) were adjusted and the samples were treated according to the given procedure.

2.5 *Procedure*

To determine total concentration of chromium in solution, Cr(VI) was efficiently reduced to Cr(III) upon addition of 5 mL of $0.1\,mol\,L^{-1}$ of hydroxylamine (per each 100 mL of sample solution). Then the pH and the concentration of KCl solution were adjusted to ~9 and $0.01\,mol\,L^{-1}$, respectively, and the sample was passed through the column at a flow rate of $40\,mL\,min^{-1}$ with the aid of a suction pump. In this stage the Cr(III) was retained on the column. After the passage of the sample, the retained chromium (III) was eluted with 5 mL of $5\,mol\,L^{-1}$ hydrochloric acid at a flow rate of $1\,mL\,min^{-1}$. The concentration of total chromium was then determined by flame atomic absorption spectrometry using an appropriate calibration graph.

The speciation of chromium was affected by first passing the solution through an acidic alumina (pH ~ 1) column which retained only Cr(VI). The pH and KCl concentration of solution were then adjusted to ~9 and $0.01\,mol\,L^{-1}$, respectively. Cr(III) was preconcentrated and determined by immobilised ferron column and FAAS.

Table 1. Effect of nature of salt on recovery: concentrated volume 25 mL, Cr(III) concentration 500 μg L^{-1} ($n = 3$).

Salt (1.0×10^{-2})	Recovery (%)
LiCl	91.6 ± 0.5
NaCl	92.1 ± 0.7
NH_4Cl	93.5 ± 0.9
KCl	104 ± 1.3
TBA*Br	105 ± 1.9
TBACl	98 ± 0.8

The concentration of the Cr(VI) was determined from the difference of concentration of total chromium and Cr(III).

3. Results and discussion

3.1 *Optimisation of the procedure*

In the preliminary study it was observed that the immobilised ferron is capable of sorption of about 74% of Cr(III); however, the retention was increased when KCl was added to the solution. Then, the effect of different salts such as LiCl, NaCl, NH_4Cl, KCl and tetra-*n*-butylammonium chloride (TBACl) at a concentration of 1.0×10^{-2} mol L^{-1} on retention of Cr(III) on the immobilised ferron column was considered. It was found (Table 1) that the size of cation has a significant effect on the extraction efficiency and the recovery of chromium from aqueous phase increases with an increase in the size of cation and was maximised with tetra-*n*-butylammonium cation (TBA) and potassium chloride. A possible explanation for this observation is that, immobilised ferron form partially negatively charged complexes with Cr(III), and the larger cation form stronger ion pair with the complex which increased its retention on the column. Further experiment showed that potassium chloride solution of 5.0×10^{-3}–0.1 mol L^{-1} was sufficient for quantitative extraction of chromium. Subsequent studies were therefore performed with samples prepared in 0.01 mol L^{-1} of potassium chloride.

As was stated in studies concerned with SPE, the recovery of the metal ions in SPE process preconcentration are influenced by different factors such as the sample pH, the concentration of eluent, the flow rate of sample and eluent, etc. Systematic studies were aimed at optimisation of deposition/elution stages and identification of the analytical useful operation conditions.

Deposition of the analyte was depended on the sample pH. As shown in Figure 1, the recovery of chromium (III) increase with an increase in the pH and reaches its maximum at pH of 9 and remained constant at higher pH. The decrease in the extraction at pH less than 6 is probably due to the protonation of the ligand. A pH of ~9 was therefore selected for subsequent work.

The effect of the flow rate of the sample through the column on deposition of Cr(III) was considered by varying the flow rate within 1 to 60 mL min^{-1}; while, keeping the amount of pre-concentrated Cr(III) at 12.5 μg. It was found (Figure 2) that the kinetic of sorption of the analyte was very fast and was independent of the flow rate in the

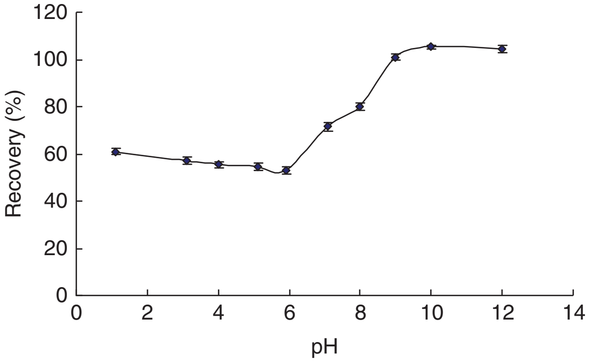

Figure 1. Effect of sample pH on recovery of Cr(III); concentrated volume 25 mL, Cr(III) concentration 500 μg L^{-1}.

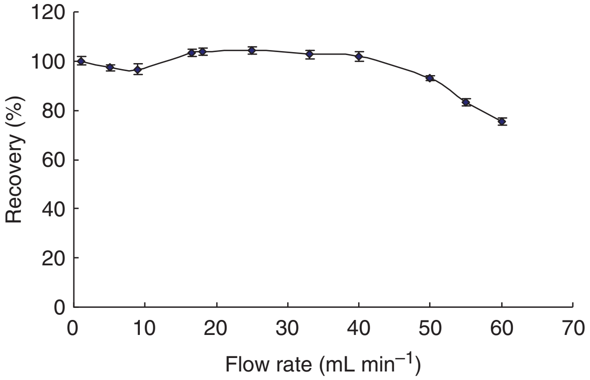

Figure 2. Effect of sample flow rate on retention of Cr(III); concentrated volume 250 mL, Cr(III) concentration 50 μg L^{-1}.

range of 1–40 mL min^{-1}. Quantitative elution of the chromium ions from the column was achieved at the flow rate of 1 mL min^{-1} using 5 mL of 5 mol L^{-1} hydrochloric acid. At higher flow rate, larger eluent volume was necessary for quantitative elution of Cr(III) ions.

Furthermore, it was found that under optimised conditions the bare basic alumina is capable of retention of only 57 ± 4% Cr (III), which indicate the higher capability of immobilised ferron column for retention of chromium.

3.2 *Evaluation of sorbent properties*

In order to quantify chromium at a low level (μg L^{-1}), the preconcentration capability of the solid-phase extraction system was investigated by measurement of the breakthrough volume. The breakthrough volume represents the sample volume that can be preconcentrated without loss of the analyte during deposition step. The breakthrough volume of the column was tested by processing 12.5 μg of Cr(III) in different volume of water (25–2500 mL) according to the recommended procedure. The results showed that up

Table 2. Determination of Cr(III) and Cr(VI) in spiked sample solution: concentrated volume 500 mL ($n = 3$).

Added (μg L^{-1})		Found (μg L^{-1})		Recovery (%)	
Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)
200.0	50.0	199.0 ± 2.1	47.8 ± 0.3	99.5	95.6
50.0	200.0	48.2 ± 0.7	197.3 ± 1.7	96.4	98.6
100.0	200.0	98.5 ± 0.6	202.3 ± 1.2	98.5	101.1
200.0	100.0	201.4 ± 1.2	99.5 ± 0.6	100.7	99.5
0.0	400.0	ND	403.5 ± 2.1	–	100.9
0.0	250.0	ND	249.9 ± 1.7	–	100.0
200.0	200.0	198.7 ± 2.3	203.1 ± 1.1	99.4	101.5
400.0	0.0	397.6 ± 2.4	ND	99.4	–
250.0	0.0	252.0 ± 1.9	ND	100.8	–

Note: ND, not detected.

to 2000 mL, the extraction was quantitative. Thus the breakthrough volume for the method is 2000 mL.

The capability of the column for the retention of Cr(VI) under the optimum condition was considered by processing 100 mL of Cr(VI) sample solution. The results revealed that about 43% of Cr(VI) is retained by the immobilised ferron column. This indicated that for the determination of total chromium in the sample, it is necessary to reduce Cr(VI) to Cr(III) prior to the passage through the immobilised ferron column. Hydroxylamine was selected as the reducing agent and its concentration for the effective reduction of Cr(VI) to Cr(III) was optimised, by processing 100 mL of Cr(VI) at the concentration of 125 μg L^{-1} in the presence of the varying volume of 0.1 mol L^{-1} hydroxylamine. It was found that, with 5 mL of 0.1 mol L^{-1} of hydroxylamine, the recovery of the chromium is quantitative. Furthermore, the capability of the method for speciation of chromium was investigated by processing synthetic solution of Cr(III) and Cr(VI) according to the given procedure. Results of Table 2 reveal that the recovery of both species of chromium is quantitative, thus the system is capable of speciation of chromium.

3.3 *Interference studies*

A study of the potential interferences in the determination of chromium was performed. A relative error of less than 5% was considered to be within the range of experimental error. A quantity of 500 mL of sample solution containing 12.5 μg of Cr(III) and various amounts of different ions were analysed according to the recommended procedure. The results of this study shown in Table 3 indicated that at the given level there is no significant interference with the extraction and determination of chromium. Thus, the system has high selectivity for chromium ions.

3.4 *Analytical performance*

Performance characteristics of this technique were obtained by processing standard solution of Cr(III). For a sample solution of 1000 mL the calibration graph exhibits linearity over the range of 2–400 μg L^{-1} with a correlation coefficient of 0.9999.

Table 3. Effect of foreign ions on the recovery of chromium (III): concentrated volume 500 mL, Cr(III) concentration 25 μg L^{-1} ($n = 3$).

Foreign ion	Molar ratio (ion/Cr(III))	Chromium recovery (%)	Foreign ion	Molar ratio (ion/Cr(III))	Chromium recovery (%)
Mg^{2+}	1000	98.1 ± 0.6	Sn^{2+}	300	104.8 ± 0.2
Ca^{2+}	1000	101.8 ± 0.7	Zn^{2+}	200	94.6 ± 1.4
Ba^{2}	1000	96.5 ± 0.4	CH_3COO^-	200	105.5 ± 0.7
Cu^{2+}	1000	96.8 ± 1.1	Co^{2+}	150	105.2 ± 1.2
Pb^{2+}	1000	105.3 ± 0.5	Mn^{2+}	100	105.1 ± 0.1
Al^{3+}	1000	99.5 ± 1.2	Cd^{2+}	100	96.7 ± 0.7
Hg^{2+}	1000	95.6 ± 1.1	Ni^{2+}	100	96.1 ± 0.5
Li^+	1000	95.7 ± 0.3	CN^-	100	103.4 ± 0.5
NO_2^-	1000	103.2 ± 0.5	Ag^+	100	96.7 ± 0.7
Br^-	1000	103.1 ± 0.3	F^-	100	97.2 ± 0.2

Table 4. Analytical characteristics of the method.

Linear range (μg L^{-1})	2–400
Slope	1.8×10^{-3}
Correlation coefficient (r)	0.9999
RSD at 10 μg L^{-1} (%) ($n = 7$)	1.9
Detection limit (μg L^{-1})	0.32
Quantification limit (μg L^{-1})	1.1
Enhancement factor*	400

*Calculated as the slope ratio of the calibration graphs obtained with preconentration of 2000 mL solution and without preconcentration.

The calibration function was $Y = 0.0018\,C + 0.0196$, where Y is the absorbance and C is the concentration of chromium in μg L^{-1}. The precision of the method was studied by processing seven replicate solutions at the same day. The relative standard deviation at 10 μg L^{-1} (sample volume 1000 mL) was 1.9%. The limit of detection and quantification defined as a concentration which gives a signal equivalent to the $3S_b$ and $10S_b$ (where S_b is standard deviation of the blank signals) were 0.32 μg L^{-1} and 1.1 μg L^{-1} respectively.

In order to quantify chromium at low level (μg L^{-1}), the preconcentration capability of the system was investigated. By considering the final elution volume (5 mL) and the breakthrough volume of the sample solution (2000 mL), a concentration factor of 400 was determined. Furthermore, the enhancement factor determined on the basis of the ratio of the slope of calibration standard curve with SPE and without preconcentration, was found to be 400; thus, retention and elution process is quantitative. The analytical characteristics of the method are summarised in Table 4.

To assess the applicability of the proposed method to real samples, the procedure was applied to determination of Cr(III) and Cr(VI) species in domestic tap water, well water, spring water and sea water (taken from Caspian Sea). Reliability was checked by the spiking experiment. The results of Table 5 show that the recoveries are within the range of 95–105% indicating that the proposed method can be successfully applied to the determination of the chromium species in different water samples.

Table 5. Recovery of Cr(III) and Cr(VI) from water samples.

	Added ($\mu g\,L^{-1}$)		Recovery (%)	
Sample	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)
Well water	20.0	20.0	98.5 ± 1.5	97.5 ± 1.9
	20.0	–	103 ± 2.0	–
	–	20.0	–	100.5 ± 0.9
Tap water	20.0	20.0	105.5 ± 1.7	104.5 ± 1.6
	20.0	–	101.0 ± 2.0	–
	–	20.0	–	105.0 ± 2.1
Spring water	20.0	20.0	103.0 ± 1.8	101.5 ± 0.9
	20.0	–	104.0 ± 2.2	–
	–	20.0	–	101.5 ± 1.5
Sea water	20.0	20.0	98.5 ± 0.9	96.5 ± 2.0
	20.0	–	103.5 ± 1.8	–
	–	20.0	–	95.0 ± 2.1

The procedure was also applied to the determination of total chromium in a standard reference copper concentrate CCU-1b. The concentration of the chromium in the sample was found to be $7.7 \pm 0.4\,\mu g\,g^{-1}$, which is in good agreement with the accepted value of $8.0 \pm 0.6\,\mu g\,g^{-1}$. This further confirmed the reliability of the method for analysis of a wide range of sample.

4. Conclusions

In this study a new application of immobilised ferron on alumina as the sorbent was described for the determination of chromium species in water samples. It has also been demonstrated that the solid-phase extraction-FAAS system using immobilised ferron column offers an alternative procedure to techniques such as GFAAS and ICP-AES for the determination of chromium at $\mu g\,L^{-1}$ level in the complex matrices, such as sea water. The sample manipulation is very simple and the procedure show high tolerance to interference from the matrix ions in different samples. Performance characteristics such as preconcentration factor, flow rate and detection limit are better or comparable to the earlier solid-phase extraction [6,29–34], and it is judged that the procedure have considerable potential for determination of chromium species in water samples.

References

[1] D.G. Barceloux, J. Toxicol. Clin. Toxicol. **37**, 173 (1999).
[2] P.M. Outridge and A.M. Scheuhammer, Rev. Environ. Contam. Toxicol. **130**, 31 (1993).
[3] M.J. Marques, A. Salvador, A. Morales Rubio, and M. de la Guardia, J. Anal. Chem. **367**, 601 (2000).
[4] P. Liang and J. Li, At. Spectrosc. **26**, 89 (2005).
[5] P.G. Krishna, J.M. Gladis, U. Rambabu, T.P. Rao, and G.R.K. Naida, Talanta **63**, 541 (2004).
[6] I. Narin, A. Kars, and M. Soylak, J. Hazard. Mater. **150**, 453 (2008).
[7] A. Baral and R.D. Engelken, Environ. Sci. Policy **5**, 121 (2002).
[8] N. Rajesh, B.G. Mishra, and P.K. Pareek, Spectrochim. Acta A **69**, 612 (2008).

[9] I. Narin, Y. Surme, M. Soylak, and M. Dogan, J. Hazard. Mater. **136**, 579 (2006).

[10] M. Grabarczyk, K. Tyszczuk, and M. Korolczuk, Electroanalysis **18**, 1223 (2006).

[11] M. Korolczuk and M. Grabarczyk, Microchem. J. **72**, 103 (2002).

[12] A. Padarauskas, A. Judzentiene, E. Naujalis, and V. Paliulionyte, J. Chromatogr. A **808**, 193 (1998).

[13] M.S. Karacan and N. Aslantas, J. Hazard. Mater. **155**, 551 (2008).

[14] M.A. Bezerra, S.M.N. Maeda, E.P. Oliveira, M.F.B. Carralho, and R.E. Santelli, Spectrochim. Acta B **62**, 985 (2007).

[15] B. Wen, X.Q. Shan, and J. Lian, Talanta **56**, 681 (2002).

[16] N. Zhang, J.S. Suleiman, M. He, and B. Hu, Talanta **75**, 536 (2008).

[17] H.F. Maltez and E. Carasek, Talanta **65**, 53 (2005).

[18] R.A. Gil., S. Cerutti, J.A. Gasquez, R.A. Olsina, and L.D. Martinez, Talanta **68**, 1065 (2006).

[19] P. Liang and H. Sang, J. Hazard. Mater. **154**, 1115 (2008).

[20] G.D. Matos, E.B. dos Reis, C.S. Costa, and S.L.C. Ferreira, Michrochem. J. **92**, 135 (2009).

[21] J.U.R. Memon, S.Q. Memon, M.I. Bhanger, and M.Y. Khuhawar, J. Hazard. Mater. **163**, 511 (2009).

[22] A. Beni, R. Karosi, and J. Posta, Microchem. J. **85**, 103 (2007).

[23] Z. Sun and P. Liang, Microchim. Acta **1620**, 121 (2008).

[24] D.M. Adria-Cerezo, M. Llobat-Estelles, and A.R. Mauri-Aucejo, Talanta **51**, 531 (2000).

[25] M.S. El-Shahawi, S.S.M. Hassan, A.M. Othman, M.A. Zyada, and M.A. El-Sonbati, Anal. Chim. Acta **534**, 319 (2005).

[26] V.N. Bulut, D. Ozdes, O. Bekircan, A. Gundogdu, C. Duran, and M. Soylak, Anal. Chim. Acta **632**, 35 (2009).

[27] D.M. Adria-Cerezo, M. Llobat-Estelles, and A.R. Mauri-Aucejo, Talanta **51**, 531 (2000).

[28] A.M. Zow, X.Y. Tang, M.L. Chen, and J.H. Wang, Spectrochim. Acta B **63**, 607 (2008).

[29] S.H. Ahmadi, A.M. Haji Shabani, S. Dadfarnia, and M. Taei, Turk. J. Chem. **31**, 191 (2007).

[30] M. Tuzen and M. Soylak, J. Hazard. Mater. **129**, 266 (2006).

[31] M.Y. Marques, A. Morales-Rubio, A. Salvador, and M. Guardia, Talanta **53**, 1229 (2001).

[32] H. Bag, A.R. Turker, M. Lale, and A. Tunceli, Talanta **51**, 895 (2000).

[33] A.N. Anthemidis, G.A. Zachariadis, J.S. Kougoulis, and J.A. Stratis, Talanta **57**, 15 (2002).

[34] E. Martendal, H.F. Maltez, and E. Carasek, J. Hazard. Mater. **161**, 450 (2009).

[35] M.E. Mahmoud, A.A. Yakout, S.B. Ahmad, and M.M. Osman, Int. J. Environ. Anal. Chem. **88**, 1017 (2008).

[36] K. Farhadi, N. Abdollahnezhad, and R. Maleki, Int. J. Enivron. Anal. Chem. **88**, 725 (2008).

[37] F. Shakerian, S. Dadfarnia, A.M. Haji Shabani, and M. Rohani, Talanta **77**, 551 (2008).

[38] W.G. Hanna and M.M. Moawad, J. Coord. Chem. **55**, 43 (2002).

[39] S. Przeszlakowski and E. Habrat, Analyst **107**, 1320 (1982).

[40] F. Shakerian, S. Dadfarnia, and A.M. Haji Shabani, J. Iran. Chem. Soc. **6**, 594 (2009).