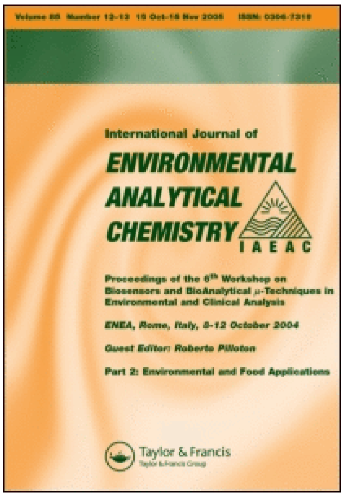

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Speciation analysis of inorganic vanadium (V(IV)/V(V)) by graphite furnace atomic absorption spectrometry following ion-exchange separation

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To cite this Article Zhao, Liang , Zhu, Xiashi , Feng, Ke and Wang, Baosheng(2006) 'Speciation analysis of inorganic vanadium (V(IV)/V(V)) by graphite furnace atomic absorption spectrometry following ion-exchange separation', International Journal of Environmental Analytical Chemistry, 86: 12, 931 — 939

To link to this Article: DOI: 10.1080/03067310600687633

URL: http://dx.doi.org/10.1080/03067310600687633

Intern. J. Environ. Anal. Chem.
Vol. 86, No. 12, 15 October 2006, 931–939

Speciation analysis of inorganic vanadium (V(IV)/V(V)) by graphite furnace atomic absorption spectrometry following ion-exchange separation

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(*Received 8 November 2005; in final form 1 March 2006*)

A sensitive and simple method of ion-exchange resin separation and graphite-furnace atomic absorption spectrometry (GFAAS) detection was proposed for the determination of inorganic vanadium species. Methylene Blue (MB) was used as a chelating agent of V(V) for ion-exchange separation. The complex of V(V) and MB could be trapped by ion-exchange resin at pH 3.0 and eluted by $1.0\,\mathrm{mol\,L^{-1}}$ NaOH. The vanadium species was determined subsequently by GFAAS. The concentration of V(IV) was calculated by subtracting the V(V) concentration from the total concentration of vanadium. Under the optimized experimental conditions, the detection limit of V(V) is $0.48\,\mu\mathrm{g\,L^{-1}}$ with RSD of 2.6% ($n = 5$, $c = 2.0\,\mu\mathrm{g\,L^{-1}}$). In order to verify the accuracy of the method, a certified reference soil sample was analyzed, and the results obtained were in good agreement with the certified values. The range of recovery for V(IV) and V(V) was 97.8–99.3% and 101.7–103.6%, respectively. The proposed method was applied to the speciation analysis of vanadium in lake-water samples.

Keywords: Speciation of inorganic vanadium; Ion-exchange resin; Methylene Blue; Graphite-furnace atomic absorption spectrometry

1. Introduction

Vanadium poisoning is an industrial hazard. High amounts of vanadium are said to be present in fossil fuels such as crude petroleum, fuel, oils, some coals, and lignite. Burning these fuels releases vanadium into the air that settles on the soil [1]. Higher vanadium concentrations are toxic for the plants, as they cause chlorosis and limit growth [2]. The distribution of vanadium among different oxidation states plays an important role in its environmental chemistry. In aqueous solutions, vanadium has various oxidation states and ionic forms; the most common two forms are IV and V, which have different toxicities, V(V) being more toxic than other species. V(V) occurs as VO_2^+ and VO_4^- in acid and alkaline media, respectively. V(IV) is present as the vanadylcation VO^{2+}, which is stable in acidic conditions and readily oxidized to the

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International Journal of Environmental and Analytical Chemistry
ISSN 0306-7319 print/ISSN 1029-0397 online © 2006 Taylor & Francis
DOI: 10.1080/03067310600687633

pentavalent state in alkaline solution. Tests carried out on yeast cells have proved that the vanadate ion is a strong inhibitor of the enzyme Na and K-ATP, while V(IV) appears to be a weaker inhibitor [3]. Therefore, it is important to obtain valance speciation of vanadium; an accurate and reliable method for the determination of inorganic vanadium species is more important than the total element measurement for a better understanding of vanadium toxicity.

Many detection techniques such as spectrophotometry [4], NAA [5], ICP-MS [6, 7] and ICP-AES [8] have been used for vanadium determination in environmental samples. GFAAS has been demonstrated to be an effective method of determination of vanadium in the presence of matrix modifier [9–11].

Furthermore, the concentration of vanadium in environmental samples is very low, of the order of a few micrograms per litre, and a separation/preconcentration step is often necessary prior to analysis [12]. Many separation/preconcentration techniques for the determination of vanadium species have been proposed, including solvent extraction [13], co-precipitation [14], high-performance liquid chromatography [15], and capillary electrophoresis [16]. However, conventional solvent extraction and co-precipitation are laborious and can carry a risk of contamination. These chromatography techniques often have disadvantages such as incomplete derivatization, being time-consuming, and entailing complicated operating procedures.

The ion-exchange resin is superior for preconcentration of trace metals in respect of minimum solvent waste generation and sorption of the target species on the resin surface in a more stable chemical form [17]. The selectivity of the resin is usually enhanced by loading with the organic ligand [18–22]. Reference [23] reports the simultaneous preconcentration and separation of trace amounts of vanadium species with palmitoyl quinolin-8-ol bonded amberlite XAD 2 copolymer resin column prior to simultaneous speciation analysis. However, the pretreatment of the resin is complicated, and the procedure is time-consuming. Another simple and rapid two-step method for the separation and determination of V(IV) and V(V) was used. In the first step, one of vanadium species (V(V) or V(V)) was retained on the resin as a complex. Subsequently, in the second stage, another vanadium species was calculated by subtracting the concentration of V(V) or V(IV) from the total concentration of vanadium. Thus, the complicated procedure of loading the resin was avoided. In the earlier reference, Eriochrome Cyanide R (ECR) [24], 8-hydroxyquinoline (8-HQ) [25], 2-(5-bromo-2- pyridylazo)-5-diethylaminophenol (5-Br-PADAP) [26] had been used as the chelating agent. In this article, Methylene Blue (MB) was used as a chelating agent for V(V) species separation. This sensitive and simple method was studied for speciation analysis of vanadium by GFAAS after separation/proconcentration with an ion-exchange resin. The proposed method was applied to determination of vanadium species in standard soil samples and water samples, and satisfactory results were obtained.

2. Experimental

2.1 *Apparatus and reagents*

$717^{\#}$ anion-exchange resin (Cl-type; 80–100 mesh; Shanghai Chemical Reagent Corporation, Shanghai, China) was used.

Table 1. Operating conditions for GFAAS.

Parameters
Element: V
Wavelength: 318.4 nm
Slit: 1.3 nm
HCl. Current: 5 mA
Graphite furnace
Dry temperature: 100°C (ramp 15 s, hold 15 s)
Ashing temperature: 400°C (ramp 10 s, hold 10 s)
Atomization temperature: 2800°C (ramp 0 s, hold 6 s)
Cleaning temperature: 2850°C (ramp 2 s, hold 3 s)
Flow rate (Ar): 200 mL min^{-1}

The stock standard solutions of 1.0 mg L^{-1} V(V) were prepared by dissolving 1.7852 g of V_2O_5 (>99.9%; Tianjin Chemical Reagent Co., Inc. Tianjin, China) in 100 mL of 12.0 mol L^{-1} HCl; a 1.0 mg L^{-1} V(IV) stock solution was prepared by dissolving 0.4968 g of $VOSO_4 \cdot 5H_2O$ (99.99%; Shanghai Chemical Reagent Corporation) in 100 mL of 0.01 mol L^{-1} HCl. The buffer solution used was usually 0.20 mol L^{-1} of HCl–NaAc.

A 0.05% MB (Shanghai Chemical Reagent Corporation) solution was prepared by dissolving 0.050 g of methyl thionine chloride in 100 mL of deionized water. A 1.0 mol L^{-1} solution of $Mg(NO_3)_2$ (Shanghai Chemical Reagent Corporation) was prepared by dissolving 14.8 g $Mg(NO_3)_2$ in 100 mL of deionised water.

All other reagents used in this work were of the highest available purity, free from traces of V and dissolved in the deionised water. Unless stated otherwise, all the reagents used were of analytical grade.

A WFX-100 graphite furnace atomic absorption spectrometer (Beijing RuiLi Instrument Company, China) with a deuterium background correction was employed. The hollow-cathode lamp for V (Beijing RuiLi Instrument Company, China) was used. The operating conditions for GFAAS are given in table 1. A UV-Vis-2550 ultraviolet spectrophotometer (Shimadzu, Japan), pHS-25 pH-meter (Shanghai, China), timing multifunctional oscillator (Guohua Limited Company, China), and digital constant-temperature water-bath (Guohua Limited Company, China) were used.

2.2 *Recommended procedure*

2.2.1 Pretreatment of 717# anion-exchange resin (Cl^--type). The resin was immersed in the saturated NaCl solution and then rinsed with deionized water. The resin was washed with HCl (5.0%), deionized water, NaOH (2.0–4.0%), and deionized water in sequence, and stirred in each case for 15 min. Finally, the resin was immersed again in the saturated NaCl solution, and then the resin was finally rinsed with deionized water and air-dried [27].

2.2.2 Preparation of soil sample. One-gram air-dried homogenized samples were treated with 30 mL of aqua regia in a 100 mL beaker for 18–20 h. Then, the vessels were heated on a hot plate at 80°C for 3–4 h and gently boiled almost to dryness. A further

5 mL (60%) of $HClO_4$ was added, and the solutions were again boiled almost to dryness. The digests were diluted with 10 mL HCl (1 : 1) and filtered in a 100 mL calibrated flask.

2.2.3 Static adsorption and desorption of V(IV)/V(V). At a temperature of 45°C, 10.0 mL analytical solution containing 20.0 µg V(IV) (and/or V(V)), 0.05% MB and 0.30 g $717^{\#}$ anion exchange resin was mixed, controlling the appropriate acidity. The mixture was shaken on the timing multifunctional oscillator for 15 min and then filtered. The resin was eluted by NaOH solution. V(V) in effluent solution was detected by GFAAS. V(IV) was calculated by total V and V(V).

3. Results and discussion

3.1 *Effect of pH on adsorption of V(IV)/V(V)*

The acidity of the solution is one of the important factors affecting the complexation between MB and V(IV)/V(V) and the adsorption of V(IV)–MB. At 45°C, the effect of pH on the sorption efficiency of vanadium on the $717^{\#}$ anion exchange resin was evaluated at pH values varying between 2.0 and 5.0 (figure 1).

From figure 1, it can be seen that the maximum adsorption of V(V)–MB is at pH 3.0, whereas V(IV) could not be adsorbed on the resin. The results indicated that the speciation analysis of vanadium was achieved by carrying out the following procedures: the temperature and acidity of the sample solution were adjusted to 45°C (in a digital constant-temperature water-bath) and pH 3.0, respectively. Then, the solution was passed through the resin to separated V(IV) from V(V). The concentration of V(IV) was calculated by subtracting the V(V) concentration from the total concentration of vanadium.

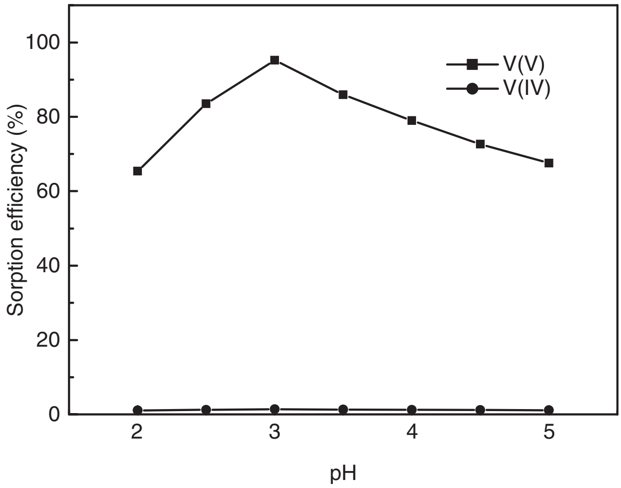

Figure 1. Effect of pH on adsorption. V(V): 2.0 µg mL^{-1}; V(IV): 2.0 µg mL^{-1}; MB: 0.05%; $T = 45$°C.

To verify the formation of the V(V)–(MB), the spectrum of the system containing V(IV) or V(IV) and MB was measured using a UV-Vis spectrophotometer (figure 2). The experimental results indicate that the complex of V(V)–(MB) was rapidly formed at pH 3.0, and the maximum wavelength was 545 nm, whereas the complex of V(IV)–(MB) could not be formed.

3.2 *Effect of temperature on adsorption of V(IV)/V(V)*

Temperature is another important factor affecting the adsorption of V(V)–MB on resin. From the experiment, the best adsorption efficiency of V(V)–MB with the resin was at $T = 45°\mathrm{C}$. This result was similar to that in a previous study [28].

3.3 *Effect of time on adsorption of V(V)*

The effect of time on the rate of adsorption was investigated. The complex of V(V)–(MB) was quantitatively adsorbed by the resin after 10 min. Meanwhile, V(IV) was not adsorbed. Thus, the adsorption time was 15 min.

3.4 *Effect of NaOH concentration on desorption of V(V)*

With NaOH as the eluant, the desorption behaviour of V(V) was studied. V(V) could be eluated from the resin completely when the concentration of NaOH was 0.5–3.0 mol $\mathrm{L^{-1}}$ (figure 3). Thus, an eluted NaOH concentration of 1.0 mol $\mathrm{L^{-1}}$ was selected.

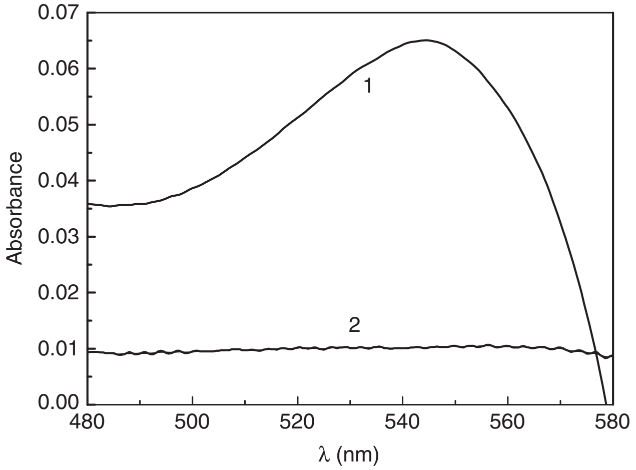

Figure 2. UV-Vis spectrometry of V and Methylene Blue. 1: V(V) + MB; 2: V(IV) + MB; agent blank: MB. V(V): 2.0 µg $\mathrm{mL^{-1}}$; V(IV): 2.0 µg $\mathrm{mL^{-1}}$; MB: 0.05%; $T = 45°\mathrm{C}$, pH = 3.0.

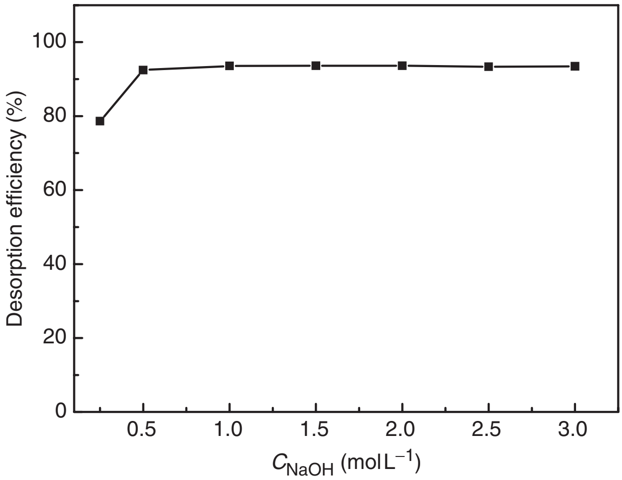

Figure 3. Effect of the NaOH concentration on desorption of V(V). V(V): 2.0 μg mL^{-1}; MB: 0.05%; $T = 25$°C.

3.5 *Effect of amount of NaOH on desorption of V(V)*

Various amounts of NaOH solution were added to investigate the effects on the rate of desorption of V(V) from 0.5 mL to 3.0 mL. The desorption rate of V(V) increased with increasing volume of NaOH. The optimum volume of NaOH solution chosen for this work was 3.0 mL.

3.6 *Effect of amount of resin on adsorption of V(V)*

The effect of the amount of resin on the adsorption of 150.0 μg of V(V) in the range of 0.05–0.35 g was investigated (figure 4). It was found that the rate of adsorption of V(V) increased with the amount of resin between 0.05 and 0.25 g, and the mass of ion-exchange resin selected in the experiment was 0.30 g.

3.7 *Matrix modifier*

At high temperature, vanadium tended to react with carbon and form the carbide, which had a high melting point. As a result, vanadium could not be atomized completely at low temperatures. However, the carbon tube could be destroyed rapidly if the temperature was increased [29]. In this article, $Mg(NO_3)_2$ was used as the matrix modifier to determine V(V) [30]. Research indicated that the ashing curve was not influenced by the modifier, but the signal intensity clearly increased in the atomic curve, and the atomization temperature was selected at 2800°C.

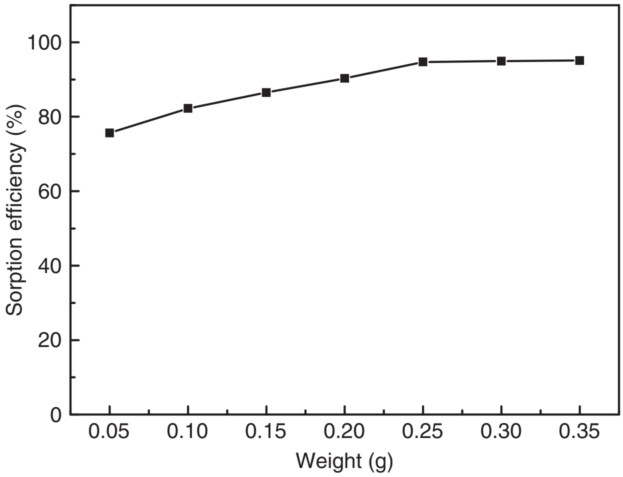

Figure 4. Effect of the amount of resin on adsorption of V(V). V(V): 2.0 μg mL^{-1}; MB: 0.05%; $T = 45$°C, pH = 3.0.

Table 2. Influence of coexisting ion on determination of V(IV) and V(V).

Ions	^{M}Tolerance/Vanadium (w/w)	Ions	^{M}Tolerance/Vanadium (w/w)
Na^+	2000	Ni^{2+}	100
K^+	2000	Mg^{2+}	500
Ca^{2+}	1500	Cr^{6+}	250
Cr^{3+}	500	Cd^{2+}	500
Co^{2+}	500	Fe^{3+}[a]	500

[a] Spiked 0.5 mL of 1% NaF solution.

3.8 *Interferences*

The effects of diverse ions on the determination of analytes were investigated. Solutions of 2.0 μg mL^{-1} of V(V) and V(IV) containing the added interfering ions were treated according to the recommended procedure. The results are summarized in table 2. It was clear that the permissible amounts for most elements listed were high enough, and the developed method is largely free of any interference from diverse ions commonly found in natural water.

3.9 *Analytical performance*

By using the proposed method, the calibration graph for the GFAAS determination of V(V) was linear over 0–120.0 μg L^{-1}. The corresponding coefficient of correlation was $r = 0.9978$. The relative standard deviation was 2.6% ($n = 5$, $c = 2.0$ μg L^{-1}). The limit of detection with this procedure was 0.48 μg L^{-1}, and the preconcentration factor was 50.

Table 3. Analysis results for the standard soil sample.

Sample	Standard value ($\mu g\, g^{-1}$)	Determination value ($\mu g\, g^{-1}$) ($n=3$)
V(IV)[a]	100.0	98.4 ± 1.0
V(V)[b]	77.5 ± 8.0	78.8 ± 0.6

[a] Spiked environmental reference sample.

[b] National reference materials (Standard Tibet Soil 83401, Research Center for Eco-Environmental Sciences, The Chinese Academy of Sciences).

Table 4. Determination results of inorganic V in water sample ($n=3$).

	Added ($\mu g\, L^{-1}$)		Found V ($\mu g\, L^{-1}$)		Recovery (%)	
Samples	V(IV)	V(V)	V(IV)	V(V)	V(IV)	V(V)
Lake water[a]	0	0	ND[b]	4.36 ± 0.14	–	–
	5.0	5.0	4.89 ± 0.12	9.55 ± 0.23	97.8	103.6
	10.0	10.0	9.93 ± 0.07	15.09 ± 0.34	99.3	101.7

[a] Surface lake water was collected from Slender West Lake, Yangzhou, China (pH = 7.2).

[b] Not detectable.

3.10 *Determination of sample*

The standard sample was determined according to the static adsorption and desorption of V(IV)/V(V) procedures. The results are shown in table 3. The analytical contents of V(IV) and V(V) in environmental reference materials are in good agreement with the certified value.

The proposed method was applied to determine speciation of vanadium in Slender West Lake water samples. The results are shown in table 4. The recovery range for V(IV) and V(V) was 97.8–99.3% and 101.7–103.6%, respectively.

4. Conclusion

In this work, an effective method for separation and determination of V(IV) and V(V) has been developed. Compared with existing methods, the main advantages of this method are its simplicity and rapidity. The proposed method has been applied to speciation analysis of vanadium in standard soil samples and water samples, and satisfactory results have been obtained.

References

[1] A.S. Amin. *Spectrochim. Acta A*, **59**, 1025 (2003).
[2] J. Poledniok, F. Buhl. *Talanta*, **59**, 1 (2003).
[3] K. Pyrzyńska, T. Wierzbicki. *Talanta*, **64**, 823 (2004).
[4] K. Pyrzyńska. *Microchim. Acta*, **149**, 159 (2005).
[5] J. Kucera, V. Sychra, J. Koubek. *Fresenius' J. Anal. Chem.*, **360**, 402 (1998).
[6] C. Latkochy, T. Prohaska, G. Stingeder, W. Wenzel. *Fresenius' J. Anal. Chem.*, **368**, 256 (2000).

[7] H. Liu, S.-J. Jiang. *J. Anal. Atom. Spectrom.*, **17**, 556 (2002).

[8] R.G. Wuilloud, J.A. Salonia, J.A. Gasquez, R.A. Olsina, L.D. Martinez. *Anal. Chim. Acta*, **420**, 73 (2000).

[9] K.R. Sperling, B. Bahr, J. Ott. *Fresenius J. Anal. Chem.*, **366**, 132 (2000).

[10] P. Bermejo-Barrera, T. Pardiñas-Alvite, M.C. Barciela-Alonso, A. Bermejo-Barrera, J.A. Cocho de Juan, J.M. Fraga-Bermúdez. *J. Anal. Atom. Spectrom.*, **15**, 435 (2000).

[11] N.S. Thomaidis, E.A. Piperaki. *Analyst*, **121**, 111 (1996).

[12] Z. Fan, B. Hu, Z. Jiang. *Spectrochim. Acta B*, **60**, 65 (2005).

[13] I. Nukatsuka, Y. Shimizu, K. Onzeki. *Anal. Sci.*, **18**, 1009 (2002).

[14] S. Nakano, S. Kinoshita, M. Ikuta, T. Kawashima. *Anal. Sci.*, **6**, 435 (1990).

[15] M. Sugiyama, T. Tamadab, T. Hori. *Anal. Chim. Acta*, **431**, 141 (2001).

[16] Z.L. Chen, R. Naidu. *Anal. Bioanal. Chem.*, **374**, 502 (2002).

[17] K. Pyrzyńska, T. Wierzbicki. *Microchim. Acta*, **147**, 59 (2004).

[18] L. Minelli, E. Veschetti, S. Giammanco, G. Mancini, M. Ottaviani. *Microchem. J.*, **67**, 83 (2000).

[19] K. Okamura, M. Sugiyama, H. Obata, M. Maruo, E. Nakayama, H. Karatani. *Anal. Chim. Acta*, **443**, 143 (2001).

[20] D. Banerjee, B.C. Mondal, D. Das, A.K. Das. *Microchim. Acta*, **141**, 107 (2003).

[21] K. Pyrzyńska, T. Wierzbicki. *Anal. Chim. Acta*, **540**, 91 (2005).

[22] Y. Wu, Z. Jiang, B. Hu. *Talanta*, **67**, 854 (2005).

[23] H. Filik, K.I. Berker, N. Balkis, R. Apak. *Anal. Chim. Acta*, **518**, 173 (2004).

[24] J. Bosque-Sendra, M.C. Valencia, S. Boundra. *Fresenius J. Anal. Chem.*, **360**, 31 (1998).

[25] G. Abbasse, B. Ouddane, J.C. Fischer. *Anal. Bioanal. Chem.*, **374**, 873 (2002).

[26] R.G. Wuilloud, J.C. Wuilloud, R.A. Olsina, L.D. Martinez. *Analyst*, **126**, 715 (2001).

[27] T.Y. Zhang. *Assay Work Applied Manual*, pp. 505–508, Chemical Industry Press, Beijing (2003).

[28] T.W. Zeng, W.C. Dai, Z. Zhang, Q.J. Zhu. *Chin. Ion Exch. Adsorp.*, **18**, 453 (2002).

[29] T.X. Zha, L.S. Cai. *Chin. J. Anal. Sci.*, **19**, 355 (2003).

[30] L.R. Xiang, X. Wang, S.C. Liu. *Chin. Anal. Lab.*, **14**, 26 (1995).