Simultaneous Preconcentration and Determination of Copper, Nickel, Cobalt, Lead, and Iron Content Using a Surfactant-Coated Alumina

Mehrorang Ghaedi,* Enayat Asadpour, and Azam Vafaie

Department of Chemistry, Yasouj University, Yasouj, Iran 75914-353

Received May 16, 2005; E-mail: m_ghaedi@mail.yu.ac.ir

A sensitive and simple method for the simultaneous determination of nutritionally important minerals including copper, nickel, and iron in real samples is in great demand. Atomic absorption spectrometry (AAS) coupled with a preconcentration method is shown to be an appropriate technique for this objective. The method is based on the formation of mineral complexes by α-benzyl dioxime (BDO) supported on sodium dodecyl sulfate (SDS)-coated alumina. The metal contents in the complexes are eluted using 5 mL of 6 mol L^{-1} HNO$_3$, and then detected by AAS at respective maximum wavelengths. In this procedure, minerals such as Cu, Ni, Pb, Co, and Fe can be analyzed in one run by carrying out the simultaneous separation and quantification of them. The low detection limit of these elements makes it a superior alternative to UV–vis and in several applications, also an alternative to ICP-MS techniques. The method has been successfully applied for these metal content evaluations in some real samples including waste water, river water, spring water, tap water, vegetable, and baking powder.

Important positive and negative roles of trace heavy metal ions in human health are known.[1] Considering biological research, the roles of some trace and ultra-trace elements in the body are very rich and varied. Some of them are essential to life, while others are toxic even at very low concentrations. Since these elements are taken in mostly by the human diet, the determination of their concentrations in food is very important. Simultaneous analysis of different minerals in food or biological samples is a frequent request. Several techniques such as X-ray fluorescence,[2] atomic fluorescence spectrometry,[3] polarography,[4] chromatography,[5] atomic absorption spectrophotometry,[6] and solid-phase extraction[7–10] have been used for the simultaneous determination of these ions in different samples. At the present time, the most common methods for mineral analyses are atomic absorption spectroscopy (AAS), UV–visible spectrophotometry, and inductively coupled plasma mass spectroscopy (ICP-MS). ICP-based techniques require expensive instrumentation and maintenance. However, the simultaneous determination of these ions by the use of traditional UV–visible absorption molecular spectroscopy is difficult due to the fact that overlap absorption regions and superimposed curves are not suitable for quantitative evaluation. In most complex samples, spectral overlap is often a serious problem. As a result, atomic absorption spectrometry that has only slight spectral interference was used in this study. The atomic absorption spectrometry (AAS) technique, which offers fast multi-elemental analysis, suffers from poor sensitivity in the determination of heavy elements in environmental samples like natural water and other real samples. This draw back can be overcome by the combination of a suitable preconcentration technique with subsequent AAS determination. Solid-phase extraction (SPE) has been widely used for this purpose due to advantages such as, high efficiency, simplicity, rapidity, low consumption of material (especially toxic organic solvents[11]) freedom from contamination, and the possibility of combination with ICP-AES as well as with AAS. Among the various solid phases, those obtained by immobilization of chelating agents onto support viz. alumina and silica gel have gained much attention due to high repeatability and long life time.

The molecules of anionic surfactants can effectively be sorbed on positively charged surfaces such as alumina due to formation of self-aggregates called "hemi-micelles" or "admicelles" on the solid surface; the hydrocarbon cores of these micelles have the unique ability to solubilize hydrophobic compounds that are sparsely soluble in water.[12]

In the literature, a large number of chelators have been reported for trace metal enrichment. Lead, copper, cadmium, zinc, nickel, cobalt, and iron can be extracted from the water using a mixture of sodium *N*,*N*-diethyldithiocarbamate,[13] ammonium tetramethylenedithiocarbamate,[14] *N*,*N*-hexamethylenebisdithiocarbamate,[15] *o*-vanillin-immobilized silica gel,[16] sodium *N*,*N*-dibenzyldithiocarbamate,[17] methanolic 2% hexahydroazepinium hexahydroazepine-1-carbodithionate,[18] 8-quinolinol,[19] Amberlite XAD-4 resin,[20] bis(2,4,4-trimethylpentyl)-phosphinic acid, a tertiary amine,[21] thiol cotton fiber,[22] and calmagite chelates.[23]

Here, the authors report a method for the preconcentration of trace elements, viz., Co, Ni, Cu, Fe, and Pb on an SDS-coated alumina modified with α-benzyl dioxime. The sorbed elements were sequently eluted with 5 mL of 6 mol L^{-1} HNO$_3$. The effluents were further analyzed by AAS for evaluating their metals content. The schematic diagram for preconcentration is presented in Scheme 1.

Experimental

Reagents. Acids and bases were of the highest purity available from Merck and used as received. Doubly distilled deionized water was used throughout. Analytical grade nitrate salts of lead, cadmium, mercury, cobalt, nickel, copper, zinc, magnesium, calcium, barium, sodium, and potassium (all from Merck) were of

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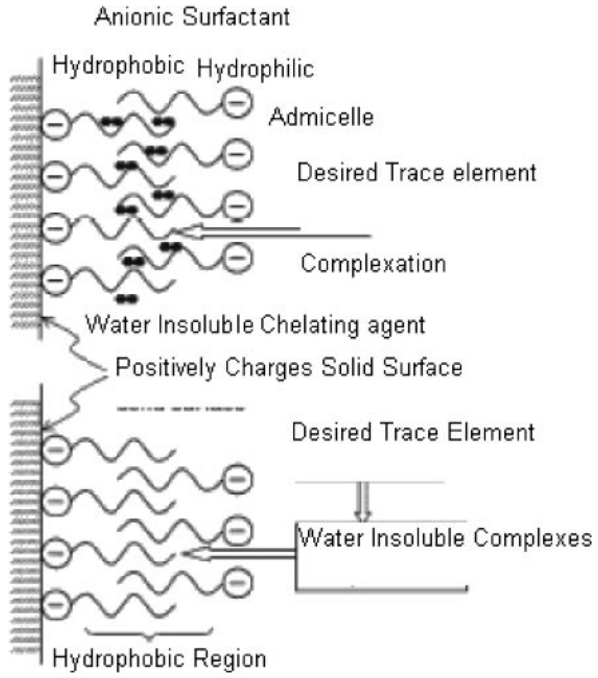

Scheme 1. Incorporation of trace elements on admicelles formed on solid surface.

the highest purity available and used without any further purification. The ligand α-benzyl dioxime (BDO) was also purchased from Merck. Buffer solutions (0.05 mol L^{-1}, pH 6.0) were prepared by adding an appropriate amount of dilute nitric acid or sodium hydroxide to phosphate solutions. The γ-Al_2O_3 10–50 mesh and sodium dodecyl sulfate (SDS) were purchased from Merck and used as received.

Instruments. The ions content determination were carried out on a Perkin-Elmer 603 atomic absorption spectrometer with a hollow cathode lamp and a deuterium background corrector at respective wavelengths (resonance line) using an air-acetylene flame. The pH was determined with a Metrohm 691 pH/Ion meter with a combined glass-calomel electrode.

Preparation of BDO-Coated Alumina. One gram of alumina was added to 50 mL of a 0.1 M ammonia solution containing 100 mg of sodium dodecyl sulfate (SDS). The solution was mixed with a magnetic stirrer, then 1.5 mL of 1% solution of BDO was added (15 mg ligand), and the pH was adjusted to approximately 2.5 by addition of 1 M HCl. The solution was shaken for 15 min, and then filtered through a Millipore filter for preparation of the column (2 cm diameter 20 cm height). The coated alumina was used for the preparation of the column. When kept in a refrigerator the sorbent is stable for at least one week.

Pretreatment of Real Samples. Procedure for Baking Powder Sample: A sample of 100 g was dissolved in a mixture of 5 mL concentrated HNO_3 and 400 mL of distilled water. The solution was neutralized to pH 6 using 8.0 mol L^{-1} NaOH, and then the separation and preconcentration procedures given above were separately applied. The metal contents of the final solutions were determined by flame AAS.[24]

Vegetables: All vegetable samples were purchased from Gachsaran, Iran. Afterwards, they were passed through small mesh. A 40 g of vegetable sample was heated in a silica crucible for 3 h on a hot plate, and the charred material was transferred to a furnace for overnight heating at 650 °C. The residue was cooled, treated with 10.0 mL of concentrated nitric acid and 3 mL of 30% H_2O_2 and again heated in a furnace for 2 h at the same temperature so that no organic compound traces remained. The final residue was treated with 3 mL of concentrated hydrochloric acid and 2–4 mL of 70% perchloric acid and evaporated to fumes so that all the metals changed to their respective ions. The solid residue was dissolved in water, filtered and made up to 200 mL while keeping the pH at 6.0 by addition of KOH. The dissolved solution was suitably diluted and the metal concentrations were determined after suitable preconcentration using AAS.

Determination of Metal Ions in Water Samples. Waste water samples were collected from four different stations in the NGL 1200 oil refinery, Gachsaran, Iran, spring water of Cheshmeh, Mishi Sisakht, Iran, and the Beshar river, Yasouj, Iran. Before analysis, the samples were filtered through a cellulose membrane filter (Millipore) of pore size 0.45 micrometer. The organic contents of the water samples were oxidized in the presence of 1% H_2O_2 and the addition of concentrated nitric acid. The samples were filtered through filter paper. After acidification to 1% with concentrated nitric acid, they were stored in polyethylene bottles. For the preconcentration procedure, 800 mL of the water samples were heated until their volumes were 250 mL. After then, the pH of each sample was adjusted to 6 and the ligand solution was added. Then, the sample was passed through the column at a 4 mL min^{-1} flow rate. The metal chelates retained on the SDS-coated alumina were eluted with 5 mL of 6 mol L^{-1} HNO_3. The effluent was sent to FAAS for evaluation of their metal content.

Determination of Capacity of SDS-Coated Alumina Modified by BDO. A 50 mL of solution containing 500 µg of each ion at optimum conditions was added to 1.0 g of solid phase. After mixing with a magnetic stirrer for 1 h, the mixture was centrifuged and the amounts of ions in the supernatant solution was determined. The capacity of sorbent was determined by the difference of the amount of ions in the original and final solution.

Measurement of the Amount of Ligand Loaded on the SDS-Coated Alumina. One gram of γ-alumina and 100 mg of SDS were placed in a 10 mL vial, and 10 mL of 0.01 M NaOH containing 15 mg of BDO was added and shaken. After 1–2 d, a portion of the supernatant liquid was diluted to the appropriate volume and the absorbance of the solution was measured at maximum wavelength.

Preconcentration. The pH of standard water solutions containing 0.02–2.00 µg mL^{-1} of all ions was adjusted to the desired pH value (pH 6.0) by adding 10 mL of a phosphate buffer solution. The samples were passed through the column of BDO-coated alumina with the aid of a suction pump at a flow rate of 4 mL min^{-1}, to effect the deposition of analytes. The adsorbed ions were then eluted with nitric acid (5 mL of 6.0 mol L^{-1}) with a flow rate of 1 mL min^{-1}.

Results and Discussion

The effectiveness and versatility of immobilized water-insoluble chelating agents on surfactant-coated alumina has been demonstrated. The purpose of this work is to investigate the feasibility of absorption of these ions on SDS-coated alumina modified with BDO. For obtaining the maximum accuracy and precision of signals for the evaluation of these ion contents, the effective parameters viz. pH of sample, amount of ligand and solid phase, type and concentration of eluting agent, and flow rate must be optimized.

Optimization of Variables. The effect of pH on the preconcentration of metals on SDS loaded with BDO was studied

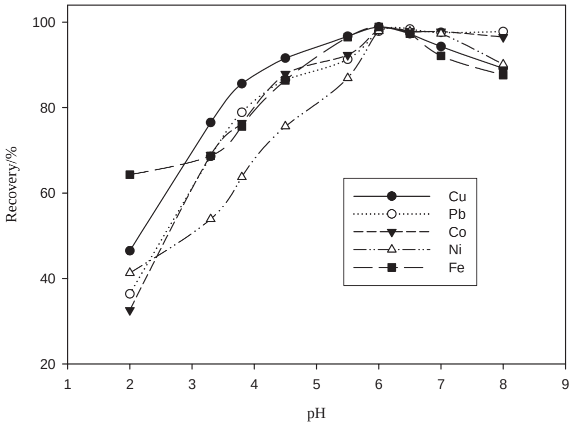

Fig. 1. Effect of pH on recovery of metal ions at optimum conditions according Table 1.

by the determination of 50 µg of individual elements (250 mL 0.2 µg mL^{-1}) in the pH range of 2.0–8.0 by introducing 15 mg of BDO on the SDS-coated alumina. The elution was performed with 5 mL of 6 mol L^{-1} HNO_3. The data corresponding to each element is shown in Fig. 1. At pH 6.0, maximum recoveries were obtained for all of the elements. Therefore, the pH 6.0 ± 0.1 has been selected for the determination of metals content. The decrease in signal at pH $>$ 6.0 is probably due to the precipitation of ions in the form of their related hydroxide, and at pH $<$ 6 may be due to competition from the hydronium ion toward ions for complexation with BDO, which led to the decrease in recovery. To achieve high efficiency and good selectivity, a pH of ≈6.0 was selected for subsequent work.

The nature and concentration of eluting agents were found to have a significant effect on the desorption process of the adsorbed ions from the column. The choosing of the eluent was a difficult problem because of the limitation of the AAS to tolerate organic solvents. In addition, the eluent should not destroy the SDS-coated alumina.

Hence, for the simultaneous determination of the preconcentrated elements by AAS, the elution was performed with 2.5–7.0 mol L^{-1} HNO_3 or HCl. The elution is dependent on the concentration of HNO_3. Quantitative multi-element elution was achieved for 5 mL of 6 mol L^{-1} HNO_3. Hence, 5 mL of 6 mol L^{-1} HNO_3 was chosen as the optimum eluent for the multi-element determination. The recoveries were about 99%.

The metal ion recoveries have a strong dependency on the amount of modifier. Therefore, a solid phase comprised of various amounts of ligand at a constant amount of alumina and SDS were prepared, and enrichment experiments for 250 mL of 0.2 µg mL^{-1} of all ions were carried out; the results are shown in Fig. 2. As can be seen, with increasing the amount of ligand up to 15 mg an increase in recoveries can be achieved and further increase does not mentionable change the efficiency. Various amounts of solid phase have been used for preconcentration of these ions, and the results display up to a 1.0 g of solid-phase efficiency of extractions increase and that further addition of BDO has no significant effect on recoveries. The optimum condition of the method for these metal content evaluations in subsequent works are set in Table 1.

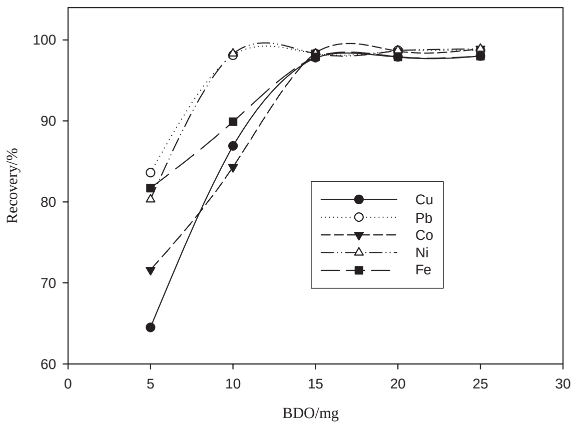

Fig. 2. Effect of amount of BDO on recovery of metal ions at optimum conditions according Table 1.

Table 1. Optimum Value of Method

Parameter	Optimum Value
pH	6.0
Amount of BDO/mg	15
Amount of SDS/mg	100
Amount of alumina/g	1.0
Amount of solid phase/g	1.1
Eluting agent	6 mol L^{-1} HNO_3
Flow rate/mL min^{-1}	4
Volume of sample 0.2 µg mL^{-1}/mL	250

Investigation of Method Performances. By passing a 250 mL solution of 0.02–2.00 µg mL^{-1} of all of the mentioned ions at the optimum conditions according to Table 1, the calibration curves, repeatability and reproducibility were obtained. The effluent was sent to AAS for ions content evaluation. The characteristic performances of the method that are presented in Table 2 show good linear range, low detection limits, high reproducibility, and low relative standard deviation for all elements. The detection limits of each element are expressed as the amount of analytes in ng mL^{-1} giving a signal to noise ratio of 3.

Matrix Effects. Analytical preconcentration/separation procedures for trace elements in the high salt content samples

Table 2. Specification of Method at Optimum Conditions for Each Element According Table 1

	Value for each ion				
Parameters	Co	Ni	Pb	Cu	Fe
Linear range/µg mL^{-1}	0.03–1.5	0.03–1.6	0.05–1.3	0.04–1.2	0.03–1.7
Detection limit/ng mL^{-1}	1.0	0.9	1.6	1.8	0.7
Loading capacity/mg g^{-1}	0.45	0.52	0.46	0.50	0.61
RSD/%	2.1	2.0	1.8	2.2	1.7
Recovery/%	98.7	98.6	98.5	98.8	98.9

can be strongly affected by the matrix constituents of the sample. This is known as the matrix effect. Before the application of the preconcentration method for the determination of analyte ions in baking soda samples, the influences of some alkaline and alkaline-earth ions on the recoveries of the analyte ions were also investigated. The results are given in Table 3. The tolerance limit is defined as the ion concentration causing a relative error smaller than ±5% related to the preconcentration and determination of analytes. Metal ions were quantitatively recovered at large amounts for alkaline and alkaline-earth ions, and some anions. The matrix ion contents in the eluent solutions were found to be significantly lower and suitable for atomic absorption spectrometric determinations. The concentrations of the investigated matrix ions in the baking soda were within tolerable limits.

Accuracy and Applications. We have explored the feasibility of a methodology using preconcentration with BDO immobilized on surfactant-coated alumina for the determination of these ions in different matrices such as baking soda, vegetable, and natural water (spring, river, tap, and waste water). Reliabilities were checked by spiking experiments and independent analysis using the standard addition method. The percent of recoveries and relative standard deviation for each element in spiked the vegetable sample, baking soda sample, and water samples (tap, spring, river, and waste water) are given in

Table 3. Effects of the Matrix Ions on the Recoveries of the Examined Metal Ions ($N = 3$)

Ion	Added as	Tolerance limit ion /mg L^{-1}
Na^+	NaCl	50000
K^+	KCl	2500
Ca^{2+}	$CaCl_2$	2500
Cl^-	NaCl	75000
$SO_4{}^{2-}$	$(NH_4)_2SO_4$	2500
Mg^{2+}	$MgCl_2$	5000
$HCO_3{}^-$	$NaHCO_3$	7500
$PO_4{}^{3-}$	Na_3PO_4	3000
Zn^{2+}, Cd^{2+}, Hg^{2+}, Ag^+, Al^{3+}, Cr^{3+}, Ba^{2+},	Nitrate salt	500

Table 6. Recovery of Trace Elements from Spiked Spring Water Sample after Preconcentration on SDS-Coated Alumina Modified with BDO

Element[a)]	Spring water			
	Added	Found	RSD/%	Recovery/%
Fe	0	43.6	2.3	—
	50	94.9	1.8	102.6
Co	0	B. L.[b)]	—	—
	50	67.8	2.1	—
	100	165.6	1.5	97.8
Ni	0	B. L.[b)]	—	—
	50	73.4	1.9	—
	100	172.8	1.3	99.4
Cu	0	B. L.[b)]	—	—
	50	87.6	1.7	—
	100	189.7	1.2	102.1
Pb	0	B. L.[b)]	2.5	—
	50	73.9	2.0	—
	100	175.6	1.6	101.7

a) All values are μg L^{-1}. b) B. L.: below linear range.

Table 4. Recovery Studies of Trace Metal Ions in Baking Powder Sample and Vegetable Sample

Element[a)]	Vegetable				Baking powder[b)]			
	Added	Found	RSD/%	Recovery/%	Added	Found	RSD/%	Recovery/%
Fe	0	87.6	2.3	—	0	4.3	3.6	—
	75	164.3	1.8	102.2	5	9.4	2.7	102.0
Co	0	67.4	2.5	—	0	N.D.[c)]	—	—
	75	143.7	2.1	101.7	5	4.9	2.1	98.0
Ni	0	71.3	2.3	—	0	3.6	2.7	—
	75	148.6	1.9	103.1	5	8.4	2.1	96.0
Cu	0	86.4	2.0	—	0	4.4	2.6	—
	75	163.2	1.7	102.4	5	9.2	2.0	96.0
Pb	0	65.4	2.5	—	0	N.D.	—	—
	75	142.5	2.0	102.8	5	5.1	2.2	102.0

a) All values are μg L^{-1}. b) All values are μg. c) N.D.: Not Detected.

Table 5. Recovery of Trace Elements from Spiked Tap Water Sample after Preconcentration on SDS-Coated Alumina Modified with BDO

Element[a)]	Amount of each ion added 90 μg L^{-1}			Amount of each ion added 800 μg L^{-1}		
	Found/μg L^{-1}	Recovery/%	RSD/%	Found/μg L^{-1}	Recovery/%	RSD/%
Cu	87.6	97.3	3.0	808.9	101.1	1.4
Fe	89.4	99.3	2.3	796.4	99.6	1.2
Pb	88.2	98.0	2.8	804.9	100.6	1.7
Ni	87.3	97.0	3.0	807.8	101.0	1.6
Co	87.9	97.7	2.7	805.7	100.7	1.5

a) For 3 measurement.

Table 7. Recovery of Trace Elements from Spiked Waste and River Water Samples after Preconcentration on SDS-Coated Alumina Modified with BDO

Element[a)]	Waste water[b)]				River water[c)]			
	Added	Found	RSD/%	Recovery/%	Added	Found	RSD/%	Recovery/%
Fe	0	94.6	2.4	—	0	164.3	1.8	—
	50	145.8	1.9	102.4	100	267.4	1.4	103.1
Co	0	55.9	2.3	—	0	46.8	2.6	—
	50	104.2	2.0	97.8	100	145.3	2.0	98.5
Ni	0	56.9	2.5	—	0	37.7	2.4	—
	50	105.6	1.9	97.4	100	136.5	1.8	98.8
Cu	0	86.4	2.1	—	0	83.9	2.2	—
	50	137.6	1.7	102.4	100	185.6	1.7	101.7
Pb	0	65.4	2.3	—	0	64.3	2.0	—
	50	116.5	1.9	102.2	100	165.8	1.7	101.5

a) All values are for 3 measurements vs $\mu g\,L^{-1}$. b) All samples are $\mu g\,L^{-1}$. c) All samples are $\mu g\,L^{-1}$.

Tables 4–7, respectively. The results show sufficiently high recoveries (>97%) for the Co, Cu, Ni, Pb, and Fe with a low RSD. The recoveries of the spiked samples are satisfactory and were confirmed using standard addition method, which indicates the capability of the system in the determination of trace amounts of these elements in different samples.

Conclusion

BDO loaded on SDS-coated alumina is a sensitive and accurate method for the determination of trace elements in low concentrations. The results presented in this paper have confirmed its applicability to the separation and preconcentration of metals. This method is simple and there is no need for an elaborate cleanup procedure, since the adsorbed metals are simply eluted with 5 mL of 6 mol L^{-1} HNO_3 and were analyzed by AAS. Each column can be used for at least 10 successive analyses without a considerable change in metal ion recoveries.

References

1 H. W. Nurnberg, *Pollutants and Their Ecotoxicological Significance*, John Wiley & Sons, Ltd., Chichester, **1985**.

2 O. Lau, S. Ho, *Anal. Chim. Acta* **1993**, *280*, 269.

3 V. Rigin, *Anal. Chim. Acta* **1993**, *283*, 895.

4 Z. She, Z. Wang, *Fenxi Huaxue* **1993**, *21*, 1313.

5 N. Xie, C. Huang, H. Fu, *Sepu* **1990**, *8*, 114.

6 Z. She, F. Nie, Y. Chen, *Fenxi Huaxue* **1991**, *19*, 1272.

7 S. Saracoglu, M. Soylak, L. Elci, *Acta Chim. Slov.* **2003**, *50*, 807.

8 T. Tanaka, Y. Ando, T. Saitoh, M. Hiraide, *J. Anal. At. Spectrom.* **2002**, *17*, 1556.

9 Z. Todorovi, P. Poli, T. Sabo, M. Caki, *J. Serb. Chem. Soc.* **2002**, *67*, 879.

10 L. A. de M. Gomesa, P. de M. Padilha, J. C. Moreiraa, N. L. D. Filhoc, Y. Gushikemd, *J. Braz. Chem. Soc.* **1998**, *9*, 494.

11 C. K. Sekhar, S. N. Chary, K. C. Tirumala, V. Aparna, *Acta Chim. Slov.* **2003**, *50*, 409.

12 M. Hiraide, W. Shibata, *Anal. Sci.* **1998**, *14*, 1085.

13 D. Chakraborti, F. Adams, W. Van-Mol, K. J. Irgolic, *Anal. Chim. Acta* **1987**, *196*, 23.

14 J. D. Lee, J. M. Lo, *Anal. Chim. Acta* **1994**, *287*, 259.

15 T. P. Hsieh, L. K. Liu, *Anal. Chim. Acta* **1993**, *282*, 221.

16 B. S. Garg, R. K. Sharma, J. S. Bist, N. Bhojak, S. Mittal, *Talanta* **1999**, *48*, 49.

17 A. Prange, W. Knoechel, M. Michaelis, *Anal. Chim. Acta* **1985**, *172*, 79.

18 H. Tao, A. Miyazaki, K. Bansho, Y. Umezaki, *Anal. Chim. Acta* **1984**, *156*, 159.

19 B. Wen, X. Shan, S. Xu, *Analyst* **1999**, *124*, 621.

20 A. Uzun, M. Soylak, L. Elci, *Talanta* **2001**, *54*, 197.

21 J. S. Kim, S. Chah, J. Yi, *Korean J. Chem. Eng.* **2000**, *17*, 118.

22 M. Yu, W. Tian, D. Sun, W. Shen, G. Wang, N. Xu, *Anal. Chim. Acta* **2001**, *428*, 209.

23 M. Soylak, U. Divrikli, L. Elci, M. Dogan, *Talanta* **2000**, *56*, 565.

24 S. Saracoglu, U. Divrikli, M. Soylak, L. Elci, *J. Food Drug Anal.* **2002**, *10*, 188.