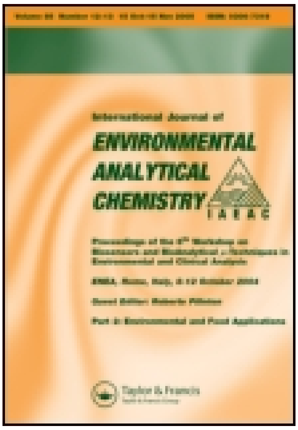

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Rapid coprecipitation-separation and flame atomic absorption spectrometric determination of lead and cadmium in water with cobalt (II) and ammonium pyrrolidine dithiocarbamate

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Rapid coprecipitation-separation and flame atomic absorption spectrometric determination of lead and cadmium in water with cobalt (II) and ammonium pyrrolidine dithiocarbamate

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A coprecipitation technique which does not require complete collection of the precipitate was proposed for the determination of trace lead and cadmium in water with flame atomic absorption spectrometry (FAAS) after preconcentration of lead and cadmium by using cobalt (II) and ammonium pyrrolidine dithiocarbamate (Co-APDC) as coprecipitant and known amount of cobalt as an internal standard. Since lead, cadmium and cobalt were well distributed in the homogeneous precipitate, the concentration ratio of lead to cobalt, and cadmium to cobalt remained unchanged in any part of the precipitate. The amount of lead and cadmium in the original sample solution can be calculated respectively from the ratio of the absorbance values of lead and cadmium to cobalt in the final sample solution that is measured by FAAS and the known amount of the lead and cadmium in the standard series solutions. The optimum pH range for quantitative coprecipitation of lead and cadmium is from 3.0 to 4.5. The 16 diverse ions tested gave no significant interferences in the lead and cadmium determination. Under optimised conditions, lead ranging from 0 to 40 µg and cadmium ranging from 0 to 8 µg were quantitatively coprecipitated with Co-APDC from 100 mL sample solution (pH ~ 3.5). This coprecipitation technique coupled with FAAS was applied to the determination of lead and cadmium in water samples with satisfactory results (recoveries in the range of 94.0–108%, relative standard deviations <6.0%).

Keywords: rapid coprecipitation; internal standard method; lead; cadmium; flame atomic absorption spectrometry

1. Introduction

At present, lead and cadmium are widespread in human environment causing adverse health effects because of anthropogenic activities [1]. Through the food chain systems, lead and cadmium are transferred into animals and human beings, causing severe contamination. Lead is readily absorbed through the alimentary tract and gastrointestinal tract [2]. Most of the lead assimilated goes into the bones, then the liver and the kidneys. It leads to vascular disease, retarding intelligence, causing nephritis, and bone injury [3–4]. Cadmium in the human body mainly accumulates in the kidneys and liver. It results in injury to bones, male urination system, reproductive system, and digestive system. Teratogenicity and

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carcinogenicity of cadmium has been proved by experiments on animals [5]. Consequently, the development of reliable methods for the determination of lead and cadmium in environmental samples is of particular significance.

Trace metals in water samples is often determined by FAAS combined with coprecipitation technique [6–11]. Many inorganic and organic coprecipitants such as diethyldithiocarbamate metal ion chelate [12–15], calcium carbonate [16], aluminum hydroxide [17–18], copper (II) mercaptobenzothiazole [19], and 1-(2-pyridylazo)-2-naphthol metal ion chelate [20–21] have been reported. But the traditional coprecipitation technique is sometimes inconvenient because it requires complete filtration of the mother liquor and complete collection of the precipitate. Furthermore, in the process of filtration and separation of the precipitate, the precipitate loss must be strictly controlled. To overcome this shortcoming, an internal standard coprecipitation technique has been proposed [22]. This coprecipitation technique coupled with FAAS was applied to the preconcentration-separation and determination of lead, iron, cadmium and copper ions in water and beer [22–24].

In this method, an accurately known amount of coprecipitant is added to the sample solution. The concentrations of both the coprecipitated trace metals and the coprecipitant in the final sample solution are measured. Since the coprecipitated trace metal and the coprecipitant were well distributed in the homogeneous precipitation, the ratio of the coprecipitated trace metal to the coprecipitant in any part of the precipitation is completely the same, and the metal content in the original sample solution can be calculated from the amount of coprecipitant added to the initial sample solution, the amount of the coprecipitated trace metal and the coprecipitant in the final sample solution which was the dissolved part precipitate. Therefore, the precipitate can be easily separated from most of the mother liquor by decantation without any filtration, and then be conveniently centrifuged for its separation from the remaining mother liquor. By using this coprecipitation technique, the operation of preconcentration is particularly convenient.

Co-APDC has been reported to be a useful coprecipitant for some metals, and it has been utilised for the concentration of lead and cadmium prior to a FAAS determination; the added cobalt has been precipitated almost completely [25]. In this work, cobalt is used as an internal standard element; since the concentration of lead or cadmium in the original sample solution was calculated from the ratio of the lead or cadmium to the cobalt in the final solution, the amount of cobalt that existed in the original sample solution before sampling must be negligibly small. In this case, relatively more cobalt was added to the original sample solution, and subsensitive line at 352.7 nm was applied to the determination of cobalt without further dilution. This method proposed here is simple, rapid and useful for the determination of lead and cadmium in water.

2. Experimental

2.1 *Apparatus*

A model WFX-210 atomic absorption spectrometer with model lead, cadmium or cobalt hollow-cathode lamp (Rayleigh, China) was used for the measurement of the flame atomic absorbance of lead, cadmium or cobalt. The operating conditions were as follows: wavelength, 283.3, 228.8 and 352.7 nm for Pb, Cd and Co respectively; bandwidth, 0.4 nm; lamp current, 8.0 mA; acetylene and air flow rates, 2.0 and 10.0 L min^{-1}; background correction, D_2 lamp method. For the separation of the precipitate from the remained mother liquor, a centrifuge of model 80-1 was utilised. The pH measurements were carried out with a model pHS-25 pH meter equipped with a model E-201 combined pH electrode.

2.2 *Reagents*

All chemicals except nitric acid (guaranteed reagent grade) were of analytical reagent grade. Distilled water was used in all experiments. All the glassware and plastic vessels were treated by dilute (1 : 1) HNO_3 acid for 24 h and then rinsed with distilled water before the use. Pb(II), Cd(II) and carrier element Co(II) stock solutions ($1000\,mg\,L^{-1}$) were bought from the Chinese National Research Center for Certified Reference Material. The working solutions of metals were obtained by diluting these stock solutions prior to use. The calibration curve was prepared using the standard solutions diluted from the working solutions. APDC solution 2% (w/v) was prepared by dissolving 2.00 g of ammonium pyrrolidinedithiocarbamate (Shanghai, China) in 100 mL of distilled water. The HNO_3 ($1\,mol\,L^{-1}$) and the ammonium acetate solution ($2\,mol\,L^{-1}$) were utilised to adjust the pH of the precipitation reaction.

2.3 *Recommended procedure*

To seven 250 mL beakers, 100 mL distilled water and 3.0 mL cobalt (II) standard solution ($100\,\mu g\,mL^{-1}$) were added respectively, then 0.0, 0.5, 1.0, 1.5, 2.0, 3.0, 4.0 mL Pb(II) standard solution ($10\,\mu g\,mL^{-1}$) and 0.0, 0.1, 0.2, 0.3, 0.4, 0.6, 0.8 mL Cd(II) standard solution ($10\,\mu g\,mL^{-1}$) were added respectively, and finally 12.0 mL APDC (2%) solutions were added, respectively. The pH values of the solutions were adjusted to about 3.5 with the HNO_3 and the NH_4AC solution by using the pH meter. After the formation of the precipitate, the precipitate was allowed to sit for five minutes. Most of the mother liquor was decanted, and then the remaining solutions were centrifuged at 3000 rpm for 1 min. The supernatant was decanted, then the precipitate was dissolved with heated $3\,mol\,L^{-1}$ HNO_3, and diluted with distilled water to 5 mL. The absorbance of lead (A_{Pb}), cadmium (A_{Cd}) and cobalt (A_{Co}) in the final solutions were consecutively measured by FAAS at 283.3, 228.3 and 352.7 nm, respectively. The calibration curve of lead was obtained with the ratio of the absorbance value of lead to cobalt in the final solutions (A_{Pb}/A_{Co}) as ordinate and the amount of lead added to the standard solutions (W_{Pb}) as abscissa. Similarly, the calibration curve of cadmium was also obtained with the ratio of the absorbance value of cadmium to cobalt in the final solutions (A_{Cd}/A_{Co}) as ordinate and the amount of cadmium added to the standard solutions (W_{Cd}) as abscissa.

To the 100 mL sample solution in a 250 mL beaker, accurately 3.0 mL of the Co(II) standard solution ($100\,\mu g\,mL^{-1}$) was added, followed by the addition of 12.0 mL of the APDC (2%) solution, and the proposed coprecipitation and measure procedure was applied to the sample. The absorbance values of lead (A_{pb1}), cadmium (A_{Cd1}) and cobalt (A_{Co1}) in the final solution were measured by FAAS. The amount of lead and the cadmium in the original sample solution (W_{Pb1} μg and W_{Cd1} μg) can be calculated respectively from the slopes of the calibration curves and the ratio of the absorbance values of lead and cadmium to cobalt in the final solution by using the following equations: $W_{Pb1} = (A_{Pb1}/A_{Co1}) \times W_{Pb}/(A_{Pb}/A_{Co})$; $W_{Cd1} = (A_{Cd1}/A_{Co1}) \times W_{Cd}/(A_{Cd}/A_{Co})$.

3. Results and discussion

3.1 *Optimum conditions for coprecipitation of lead and cadmium*

The optimum conditions for the coprecipitation of lead and cadmium with Co-APDC were investigated. The pH of model solutions was adjusted to pH value requested by using the HNO_3 water solutions ($1\,mol\,L^{-1}$) and the NH_4AC water solutions ($2\,mol\,L^{-1}$). Then the coprecipitation procedure described in the *Recommended Procedure* section above was applied. Quantitative recoveries (>90%) were found at the pH 3.0–4.5 for the both analytes (Figure 1). Above pH 5, the percentage recovery values of Pb and Cd decrease; therefore, the working pH was chosen as 3.5 for the following experiments.

The influence of carrier ion Co(II) amount needed for coprecipitation of Pb(II) and Cd(II) was also investigated with model solutions including Co(II) changed from 100 to 300 µg. The pH value of the solution was adjusted to about 3.5. The results obtained indicate that the recoveries of lead and cadmium are quantitative and stable in the range 180–300 µg Co(II) (Figure 2). The Co(II) amount of 300 µg was taken in further experiments.

The effect of APDC amount on the coprecipitation of Pb(II) and Cd(II) was examined using the model solutions of 100 mL containing 300 µg Co(II) at pH 3.5. The volume of APDC (2%) added to the model solutions changed from 5 to 30 mL. The absorbency of the Pb and Cd in the model solutions was maximal and stable when the volume of APDC (2%) was above 10 mL. The 12 mL of APDC was used in subsequent studies.

The chosen experimental optimum conditions for coprecipitation of lead and cadmium in the original sample water were pH, 3.5; APDC (2%), 12 mL; and Cobalt (II), 300 µg, respectively.

3.2 *Evaluation of cobalt as internal standard element for this coprecipitation technique*

In this method, the amount of cobalt in the original sample solutions must be negligibly small, and the added cobalt must be precipitated almost completely because the content of lead and cadmium in the original sample solution is calculated based on the uniform

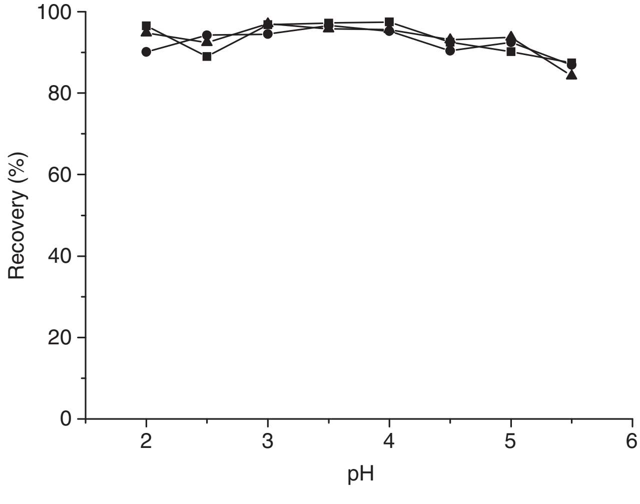

Figure 1. Effect of the pH on the recovery of lead (■), cadmium (●) and cobalt (▲). Model sample volume, 100 mL; cobalt, 300 µg; lead, 40 µg; cadmium, 8 µg; APDC (2%), 12.0 mL.

amount of cobalt added to the standard series solutions and samples. In order to increase the amount of cobalt added to the sample solution as carrier and internal standard element, subsensitive line 352.7 nm was applied to measure cobalt in the final sample solution by FAAS without further dilution. Thus, the content of cobalt in the original water sample is relatively small and negligible. In the original water sample solutions used in our experiments, cobalt was not detected by FAAS at 352.7 nm. Cobalt can be used as the carrier and internal standard element for this coprecipitation technique on the FAAS.

In order to prove that the ratio of the amount of lead or cadmium to the amount of the carrier element cobalt in any part of the precipitate remains unchanged, the amount of lead, cadmium and cobalt were measured in different parts of the precipitate according to the recommended optimum conditions. The results obtained showed that lead, cadmium and cobalt were well distributed in the whole precipitate and the concentration ratio of lead to cobalt or cadmium to cobalt in any part of the precipitate remained unchanged (Figure 3).

3.3 *Calibration curves*

Calibration curves of lead and cadmium were prepared according to the recommended procedure. The relation between the amount of lead added to the standard series solutions (W_{Pb} μg) and the ratio of the absorbance value of lead to cobalt in the final solutions (A_{Pb}/A_{Co}) is shown in Figure 4. The relation between the amount of cadmium added to the standard series solutions (W_{Cd} μg) and the ratio of the absorbance value of cadmium to cobalt in the final solutions (A_{Cd}/A_{Co}) is shown in Figure 5. Good linear relationship passing through the origin was obtained ranging from 0 to 40 μg for lead and 0 to 8.0 μg for cadmium. The linear correlation coefficient was 0.9997 for both lead and cadmium.

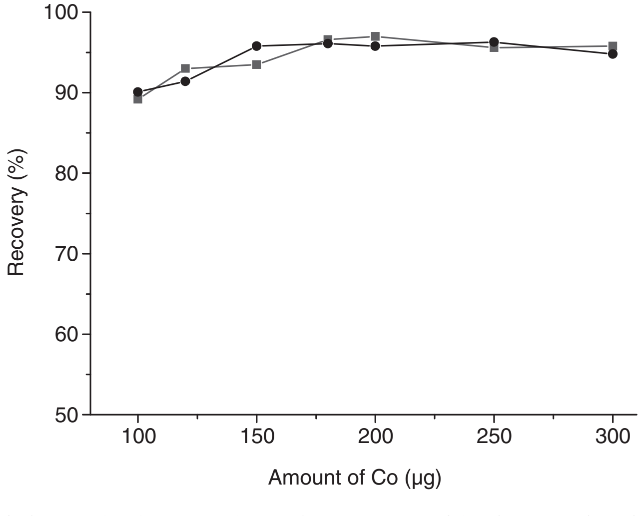

Figure 2. Effect of the carrier ion Co(II) on the recovery of lead (■) and cadmium (•). Model sample volume, 100 mL; pH, 3.5; lead, 40 μg; cadmium, 8 μg; APDC (2%), 12.0 mL.

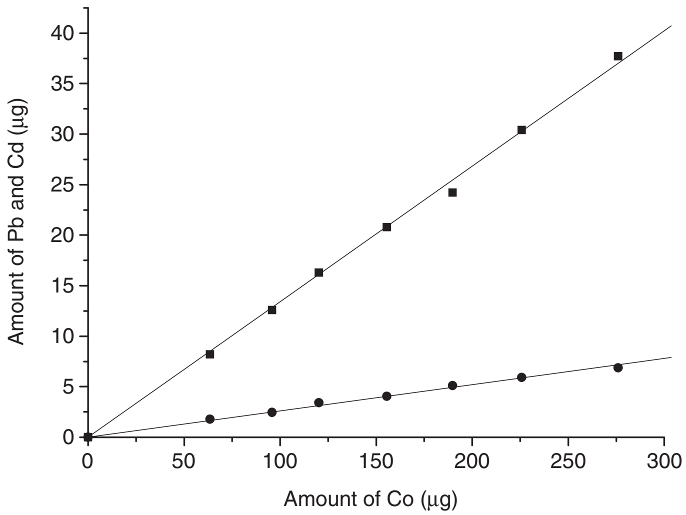

Figure 3. Relation between the amount of lead (■), cadmium (●) and cobalt in the precipitate. Model sample volume, 100 mL; pH, 3.5; cobalt, 300 μg; lead, 40 μg; cadmium, 8 μg; APDC (2%), 12.0 mL.

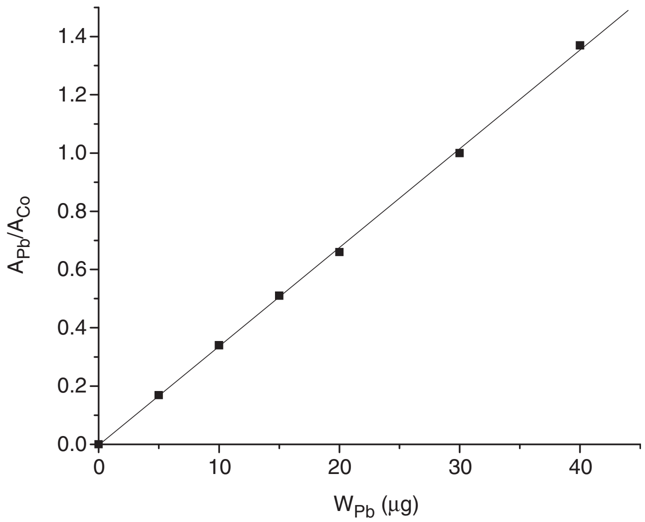

Figure 4. The calibration curve of lead. Standard series solution volume, 100 mL; pH, 3.5; cobalt, 300 μg; APDC (2%), 12.0 mL.

3.4 *Interferences*

The influence of 16 diverse ions on the determination of 40 μg of lead and 8 μg cadmium was examined using 100 mL sample solution according to the recommended procedure. As shown in Table 1, the recoveries of lead and cadmium were both in between 92.0% and 110% in the presence of large amounts of sodium, potassium, magnesium, calcium, chloride, phosphate or sulphate. Large amounts of the matrix components have no serious interfering effect on the recovery of the examined elements.

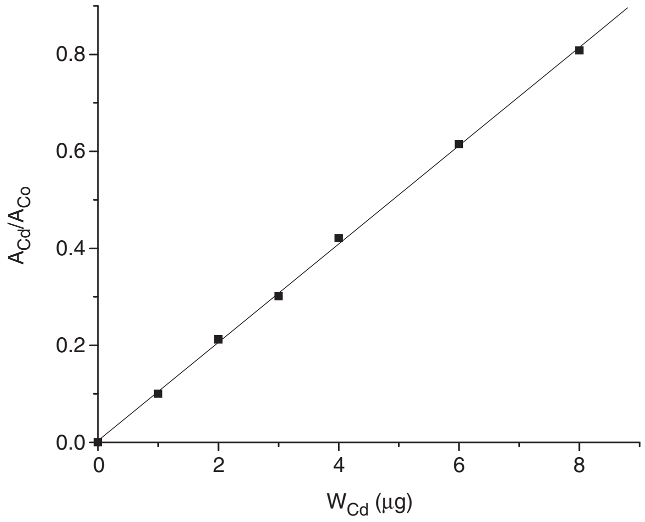

Figure 5. The calibration curve of cadmium. Standard series solution volume, 100 mL; pH, 3.5; cobalt, 300 μg; APDC (2%), 12.0 mL.

Table 1. Effect of matrix ions on the determination of Pb and Cd (40 μg of Pb and 8 μg of Cd; $n = 3$).

Ion	Added as	Amount added (mg)	Recovery (%)	
			Pb	Cd
Na^+	NaCl	1000	94.2	105.0
K^+	KNO_3	400	96.2	95.8
Ca^{2+}	$CaCl_2$	400	95.1	97.2
Ba^{2+}	$BaCl_2$	1	95.0	99.0
Mg^{2+}	$Mg(NO_3)_2$	100	102.0	110.0
Li^+	$LiNO_3$	1	98.1	97.2
Al^{3+}	$Al(NO_3)_3$	1	94.5	95.0
Cu^{2+}	$Cu(SO_4)_2$	1	99.4	96.5
Fe^{2+}	$Fe(NO_3)_2$	1	98.1	100
Ni^{2+}	$Ni(NO_3)_2$	1	98.5	95.6
Mn^{2+}	$Mn(NO_3)_2$	1	96.3	95.0
Cr^{3+}	$Cr(NO_3)_3$	1	99.6	104
Zn^{2+}	$Zn(NO_3)_2$	1	95.9	100.0
Cl^-	NaCl	1000	99.8	103.0
SO_4^{2-}	Na_2SO_4	500	105.0	98.5
PO_4^{3-}	KH_2PO_4	10	92.0	95.8

3.5 *Detection limit*

The detection limits (DLs) of the proposed coprecipitation method for the determination of lead and cadmium were studied under optimal experimental conditions by applying the procedure for 100 mL blank solutions ($n = 10$). The detection limit was calculated as the ratio of the three standard deviations of the blank absorbance signals to the slope of the

Table 2. Results of the determination of lead and cadmium in water samples (sample volume: 100 mL, $n = 6$).

Sample*	Element	Average content (μg mL^{-1})	RSD% ($n = 6$)	Amount added (μg mL^{-1})	Found of total amount (μg mL^{-1})	Recovery (%)
River water A	Pb	0.051	5.8	0.10	0.153	102
	Cd	0.016	5.2	0.05	0.064	96
River water B	Pb	0.048	4.5	0.10	0.152	104
	Cd	0.012	3.2	0.05	0.066	108
Tap water	Pb	0.038	6.0	0.10	0.137	99
	Cd	0.014	6.0	0.05	0.061	94
Lake water	Pb	0.061	3.8	0.10	0.162	101
	Cd	0.021	5.4	0.05	0.072	102

* River water A and river water B were sampled in different reaches of one river.

calibration curve (3 s/b). DLs were found as 0.022 for Pb and 0.006 μg mL^{-1} for Cd using the preconcentration factor of 20.

3.6 *Analysis of water samples*

Tap water in our lab was analysed using the recommended procedure without any pretreatment. The river water from Daxi River and lake water from Taihu Lake was immediately filtered through a Millipore cellulose membrane filter (0.45 mm pore size, Millipore, USA), acidified to pH 2 with HNO_3, and stored in precleaned polyethylene bottles. The recoveries of lead and cadmium from some water samples spiked with lead and cadmium were examined. As shown in Table 2, recoveries in the range of 94.0–108% were obtained from the water samples. The relative standard deviations for the results obtained from six replicate determinations were no more than 6.0% for lead and cadmium in 100 mL of the sample solution. From these results, the proposed method seems to be applicable to analyses of these samples.

4. Conclusions

This coprecipitation method with Co-APDC can be applied to the determination of lead and cadmium in water. This method is reliable, simple, economic, rapid and precise. The time required for the determination of lead and cadmium is much less than the time required by the method using a filtration technique for the separation of all the precipitate from the mother liquor and for the complete collection of the precipitate. In this method, the recoveries of the two elements in the presence of the most common matrix elements containing the alkaline and alkaline earth metals and transition metals were fairly good. The relative standard deviations for the results obtained from six replicate determinations are no more than 6.0% in 100 mL of the sample solution.

References

[1] J. Xu and L.H. Xu, J. Environ. Occup. Med. **22**, 271 (2005).

[2] D.R. Juberg, C.F. Kleiman, and S.C. Kwon, Ecotox. Environ. Safety. **38**, 162 (1997).

[3] M. Suwalsky, F. Villena, B. Norris, F. Cuevas, C.P. Sotomayor, and P. Zatta, J. Inorg. Biochem. **97**, 308 (2003).

[4] M.G. Mayer and D.N. Wilson, J. Power Source **73**, 17 (1998).
[5] Y.J. Cui, Y.Z. Huang, and Y.G. Zhu, J. Hygiene Res. **35**, 656 (2006).
[6] C.S. Zhou, *Chemical Separation-Concentration and Their Application* (Central South University of Technology Press, Changsha, 2001), p. 185.
[7] C. Vandecasteele and C.B. Block, *Modern Methods for Trace Element Determination* (Wiley, Chichester, 1993), p. 171.
[8] L. Elci, Ü. Divrikli, and M. Soylak, Int. J. Environ. Anal. Chem. **88**, 711 (2008).
[9] L. Wang, B. Hu, Z. Jiang, and Z. Li, Int. J. Environ. Anal. Chem. **82**, 387 (2002).
[10] M. Tuzen and M. Soylak, J. Hazard. Mater. **162**, 724 (2009).
[11] M.A. Korn, J.B. Andrade, D.S. Jesus, V.A. Lemos, M.L.S.F. Bandeira, W.N.L. Santos, M.A. Bezerra, F.A.C. Amorim, A.S. Souza, and S.L.C. Ferreira, Talanta **69**, 16 (2006).
[12] H. Chen, J. Jin, and Y. Wang, Anal. Chim. Acta. **353**, 181 (1997).
[13] J. Liu, H. Chen, X. Mao, and X. Jin, Int. J. Environ. Anal. Chem. **76**, 267 (2000).
[14] G.H. Tan, W.H. Huang, and C.X. Diao, Stud. Trace Elem. Health **20**, 37 (2003).
[15] L. Elçi, U. Şahin, and S. Öztaş, Talanta **44**, 1017 (1997).
[16] J.H. Zhong and H.B. Wang, Rock Mineral Anal. **25**, 89 (2006).
[17] F.L. Xue, H.M. Li, and J. Chin, Spectrom. Lab. **23**, 807 (2006).
[18] G. Döner and A. Ege, Anal. Chim. Acta. **547**, 14 (2005).
[19] Ş. Tokalıġlu, T. Oymak, and Ş. Kartal, Microchim Acta **159**, 133 (2007).
[20] Q. Xia, Y.D. Su, H.F. Ran, and Y.M. Ni, J. Tongji Univ. **28**, 368 (2000).
[21] Ş. Tokalıoğlu, H. Büyükbaş, and Ş. Kartal, J. Braz. Chem. Soc. **17**, 98 (2006).
[22] S. Kagaya, Y. Araki, and K. Hasegawa, Fresenius J. Anal. Chem. **366**, 842 (2000).
[23] S. Kagaya, Y. Araki, and K. Hasegawa, Ana. Sci. **18**, 923 (2002).
[24] Y.D. Su, B.B. Hao, L.J. Qin, and L.H. Gan, Spectrosc. Spectral Anal. **27**, 589 (2007).
[25] Y.J. Xu and H.J. Yuan, J. Shanghai Univ. (Nat. Sci.) **4**, 4 (1998).