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Simultaneous preconcentration of lead and cadmium ions with methyltrioctylammonium chloride supported on microcrystalline naphthalene and determination by flame atomic absorption spectrometry

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ABSTRACT

A sensitive and selective preconcentration method has been developed for the determination of trace amounts of lead and cadmium ions by using naphthalene-methyltrioctylammonium chloride as an adsorbent. Lead and cadmium ions were retained by the adsorbent in the minicolumn as PbI_4^{2-} and CdI_4^{2-}, respectively. The column was washed by 5 mL of 2 mol L^{-1} nitric acid solution to elute the adsorbed cations. The collected eluents then were determined by flame atomic absorption spectrometry (FAAS). Potential factors affecting on the recovery of the analytes were investigated. Meanwhile optimum conditions were established. The preconcentration factor for lead (II) and cadmium (II) have been 300 and 100, respectively. The calibration curves were linear in the range of 3 to 100 ng mL^{-1} for Pb^{2+} and in the range of 1 to 100 ng mL^{-1} for Cd^{2+}, in the original water samples. The detection limits for Pb^{2+} and Cd^{2+} are 0.42 and 0.072 ng mL^{-1} respectively. On the other hand, the relative standard deviation (RSD) for 11 replicate measurements of 20 ng mL^{-1} Pb^{2+} and Cd^{2+} were 2.2% and 1.4% in the initial solution respectively (n=11). The developed method was successfully applied for the determination of trace Pb^{2+} and Cd^{2+} ions in a variety of water samples.

1. Introduction

Lead and cadmium ions have been known to have toxicological effects on human health even at very low concentrations [1]. Cadmium ion is one of the most important pollutants to be considered in terms of food chaining contamination, because it is readily taken up and translocated to different parts of plants [2,3]. Excessive cadmium ion exposure may cause damage at renal, pulmonary, hepatic, skeletal, reproductive tissue and cancer. Research findings have recently indicated that any increase of lead ion concentration in soft tissues disrupts the heme synthesis. In fact, lead ion can block some enzymes employed in heme biosynthesis [4,5]. Therefore, it has been necessary for analytical chemists to evaluate the environmental and healthy quantities based on accurate determination of Cd^{2+} and Pb^{2+} both in environmental and biological samples. For this purpose, the analytical methods including electrothermal atomic absorption spectrometry (ETAAS) [6-13], graphite furnace AAS [14-16], electroanalytical methods [17,18], inductively coupled plasma-atomic emission spectrometry (ICP-AES) [19] and inductively coupled plasma-mass spectrometry (ICP-MS) [20,21] are generally used. Most of these methods have disadvantages as far as cost and instruments used in routine analysis are concerned. Flame atomic absorption spectrometry (FAAS) with its relative low cost and good analytical performance, has been widely applied for the determination of trace metal ions. However, direct determination of metal ions at trace levels by FAAS is limited because of low analyte concentrations and matrix interferences. These problems can be resolved by the preconcentration techniques such as solid phase extraction (SPE) [22,23], solvent extraction [24], coprecipitation [25] and cloud point extraction [26,27]**.** Among these methods, solid-phase extraction (SPE) is one of the most effective preconcentration methods due to simplicity, rapidity, high preconcentration factor and high recovery. A variety of solid materials such as modified rice husk [28], acrylic acid grafted polytetrafluoroethylene fiber [29], thioureasulfonamide resin [30], polyurethane foam (PUF) loaded with 2-(6'-methyl-2'-benzothiazolylazo) chromotropic acid (Me-BTANC) [31], fullerene [32], cellulose functionalized with 8-hydroxyl quinoline [33], activated carbon [34], silica gel [35] and micro crystalline naphthalene [36] have been used for preconcentration of metals.

Solid phase extraction with microcrystalline naphthalene has recently received great attention. The advantages of this method are; simple procedure, rapid phase separation, high extraction capacity and easy combination with various highly sensitive instruments [37-45].

In this paper, a sensitive and highly selective preconcentration method for determination of lead and cadmium ions is reported. Lead and cadmium ions are simultaneously preconcentrated on the naphthalene-methyltrioctylammonium chloride as PbI_4^{2-} and CdI_4^{2-}. Then,

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the matrix is removed and the analytes are desorbed by only a little volume of nitric acid. The product is obtained in higher concentrations which can be determined by FAAS.

Previously, the mentioned method has been successfully employed to the preconcentration and determination of cadmium ions in some water samples [46]. Due to the high toxicity of lead and cadmium ions for human even at very low levels, in the most articles the simultaneous preconcentration of lead and cadmium have been taken into consideration. In addition, in this study, our investigations show that lead ion can be very well adsorbed on the naphthalene-methyltrioctyl ammonium chloride as PbI_4^{2-} and desorbed by a little volume of nitric acid. Therefore, we decided to separate lead and cadmium ions simultaneously by the maintained method and then eluted with nitric acid solution and determine their concentrations by FAAS. Simultaneous preconcentration of lead and cadmium reduced the time of preconcentration for both analytes.

2. Materials and methods

2.1. Instruments

A Perkin Elmer model 2380 atomic absorption spectrometer equipped with single element hollow cathode lamp and an air/acetylene burner was used for the determination of metals. The optimum conditions for FAAS were applied as follows: wavelength, 228.8 and 217.0 nm; HCL current, 4 and 7.5 mA for cadmium and lead, respectively and so were acetylene flow rate, 0.5 L min^{-1}; air flow rate, 4.0 L min^{-1}, slit width, 0.5 nm for both metals. A funnel-tipped glass tube (50 mm × 5 mm i.d.) with a fine bore packed with naphthalene-methyltrioctylammonium chloride adsorbent was used as a preconcentration column. The column loaded with above adsorbent was lightly compressed with the flat end of a glass rod. So its height could be about 3.0 cm. A Shimadzu rotary oil vacuum pump type SA18 was used for passing the high volume of sample.

2.2. Reagents

All reagents were used in analytical grade (Merck) and all solutions were prepared in double distilled water. The stock solutions (1000 mg mL^{-1}) of cadmium and lead were prepared by dissolving 0.274 g of $Cd(NO_3)_2{\cdot}4H_2O$ and 1.598 g $Pb(NO_3)_2$ in double distilled water and diluting to 100 mL in a volumetric flask. Individually they were standardized [22] and were diluted to suitable concentration. Potassium iodide solution (0.05 mol L^{-1}) was prepared by dissolving 2.075 g of potassium iodide in 250 mL of double distilled water. A 1.5 mol L^{-1} nitric acid solution was prepared by diluting 10 mL of concentrated HNO_3 (63%-Merck) to 100 mL in a volumetric flask. Solutions of alkali metal salts (1% W/V) and other various metal salts (0.1% W/V) were used to survey interferences of anions and cations, respectively. All glassware and bottles were cleaned and kept in 1 mol L^{-1} nitric acid for 24 h. The material was then rinsed three times with double distilled water. The naphthalene adsorbent solution was prepared by dissolving 10 g of naphthalene and 1 g of methyltrioctylammonium chloride in 45 mL of acetone on a hot-plate stirrer at 40°C. This solution was added drop by drop into 1000 mL of double distilled water while stirring the solution at room temperature. It was stirred for 1–2 h and allowed to stand for 30 min. The supernatant solution of naphthalene coprecipitated with methyltrioctyl ammonium chloride was drained off by decanting and washed it twice with water in the same way. This adsorbent slurry was stored in a bottle for future uses.

2.3. General procedure

A funnel-tipped glass tube used as the preconcentration column was filled with the adsorbent slurry to a height of 3.0 cm and slightly compressed with a flat glass rod. A 50 mL solution containing 0.5-50 µg of Cd^{2+}, 5-150 µg of Pb^{2+} and suitable amount of potassium iodide was prepared. The above solution was passed through the column at a flow rate of 2 mL min^{-1} for adsorbing of both complexes on the column. Then the column was washed with 3 mL of double distilled water to remove the excess iodide ion. Then PbI_4^{2-} and CdI_4^{2-} were desorbed from adsorbent by 5 mL of HNO_3 with desired concentration. The eluted solution was collected and introduced to FAAS to determine both ions. A blank solution was also prepared under similar conditions.

3. Results and Discussion

Methyltrioctylammonium chloride is insoluble in water, which is widely used as a source of counter ions in solvent extraction of anionic metal complexes. The preliminary experiments have showed that methyltrioctylammonium chloride supported on naphthalene present an excellent tendency for the adsorption of cadmium as CdI_4^{2-} and lead as PbI_4^{2-} by forming their ion pairs:

$$CdI_4^{2-} + 2R_1(R_2)_3N^+ \rightarrow [CdI_4^{2-}][R_1(R_2)_3N^+]_2$$

$$PbI_4^{2-} + 2R_1(R_2)_3N^+ \rightarrow [PbI_4^{2-}][R_1(R_2)_3N^+]_2$$

Therefore, the retention of the above complexes on a column containing methyltrioctylammonium chloride–naphthalene adsorbent was chosen for simultaneous preconcentration of Cd^{2+} and Pb^{2+}. After preconcentration, the column was washed with HNO_3 to remove CdI_4^{2-} and PbI_4^{2-} by anion exchange and then Cd^{2+} and Pb^{2+} were separately determined by FAAS.

3.1. Optimization of chemical parameters

3.1.1. Effect of pH

The effect of pH on the recovery of 20 µg Pb^{2+} and 10 µg Cd^{2+} in 0.02 mol L^{-1} potassium iodide solution was studied. The mentioned ions were obtained quantitatively in the pH range of 1.5-10.0 using appropriate buffer solution as it was demonstrated in the general procedure. The results have shown that the used method is independent of extended pH range (1.5-10.0) showing its applicability to a variety of water samples.

3.1.2. Effect of potassium iodide concentration

The study of the effect of potassium iodide concentration on the quantitative preconcentration of Cd^{2+} and Pb^{2+} was performed as it was mentioned in the range of $1{\times}10^{-3}$ - $4{\times}10^{-2}$ mol L^{-1} in general procedure. The results have shown that the concentration of KI up to 0.015 mol L^{-1} (Figure 1) on the retention of Cd^{2+} and Pb^{2+} without any effects. Therefore, the low concentration of KI is very useful for the real samples with large volumes.

3.1.3. Selection and concentration of eluent for desorption of analytes

The influence of different kinds of anions such as nitrate, chloride, sulfate, tartarate and tetraphenylborate on the exchange and removal of anionic complex of analytes from the column was investigated. The results have shown that nitrate ion (NO_3^-) was the best eluent. Suitable concentration of nitrate ion was determined by tracking the highest recovery of Cd^{2+} and Pb^{2+}. So, when the nitrate concentration is 2 mol L^{-1} and/or higher, the recovery Cd^{2+} and Pb^{2+} will be quantitative (Figure 2). Therefore, a 2 mol L^{-1} concentration of nitric acid solution was selected for the following studies.

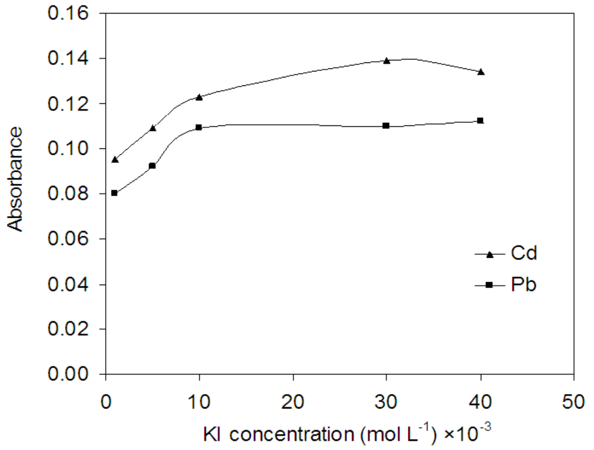

Figure 1. Effect of potassium iodide concentration on the retention of CdI_4^{2-} and PbI_4^{2-} on the naphthalene-methyltrioctylammonium chloride adsorbent (amounts of analytes: 10 µg Cd, 25 µg Pb).

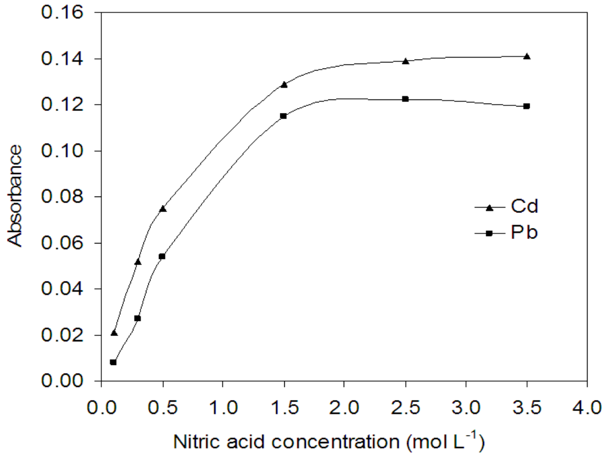

Figure 2. Effect of nitric acid concentration on the elution of CdI_4^{2-} and PbI_4^{2-} from the naphthalene-methyltrioctylammonium chloride column (amounts of analytes: 10 µg Cd, 25 µg Pb).

3.1.4. Influence of ionic strength

The effect of ionic strength of solution on the analyte adsorbent on the column was studied. For this purpose, various electrolytes such as sodium chloride, potassium chloride and sodium nitrate with concentration of 0.01- 0.1 mol L^{-1} were used. It was determined that the ionic strength solution has no effect on the complexes formation and their adsorption on the adsorbent.

3.1.5. The effect of sample and elution flow rate

The retention of CdI_4^{2-} and PbI_4^{2-} ions with methyltrioctylammonium chloride loaded on naphthalene was not affected by sample flow rate in the range of 2-8 mL min^{-1}. Thus the experiments were performed at a sample flow rate of 8 mL min^{-1} which was the maximum flow rate that could be attained with the pump used. This was the same for the elution flow rate. Elution flow rates in the range of 2-8 mL min^{-1} could be applied for small and large volumes of samples.

3.1.6. The effect of methyltrioctylammonium chloride amount

The amount of methyltrioctyl ammonium chloride loaded on naphthalene was optimized and the results are shown in Figure 3. A loading of 1 g or more amount of methyltrioctyl ammonium chloride on 10 g of naphthalene resulted in the highest adsorption for both cadmium and lead ions.

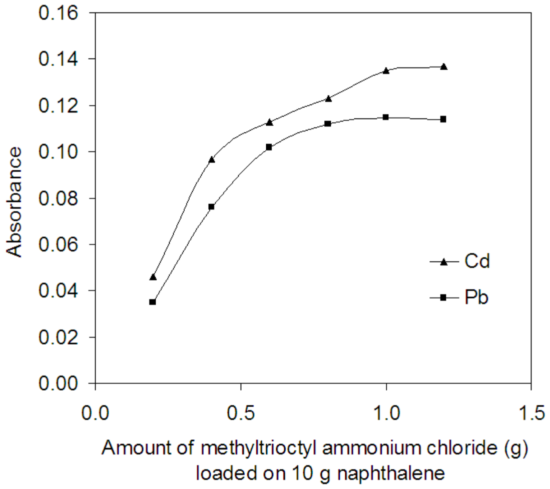

Figure 3. The effect of the amount of methyltrioctyl ammonium chloride loaded on the column conditions: volume of the sample 50 mL, KI concentration 1.5×10^{-2} (mol L^{-1}).

3.1.7. The preconcentration factor

The influence of sample volume on the retention of cadmium and lead ions on the column were studied in order to obtain the preconcenteration factor. Known volumes (200, 400, 600, 800, 1000, 1500 and 2000 mL) of double distilled water were taken in an acid-cleaned conical flask. An aliquot of metal ions (10 µg Cd^{2+} and 20 µg Pb^{2+}) solution were added to them. The general procedure for the preconcentration of the desired analytes was followed. The results showed that the recovery of lead and cadmium ions carried out with 95 % confidence level in 1500 and 500 mL respectively (Figure 4). Therefore, the preconcentration factor for lead and cadmium ions with elution the column by 5 mL HNO_3 was 300 and 100 respectively.

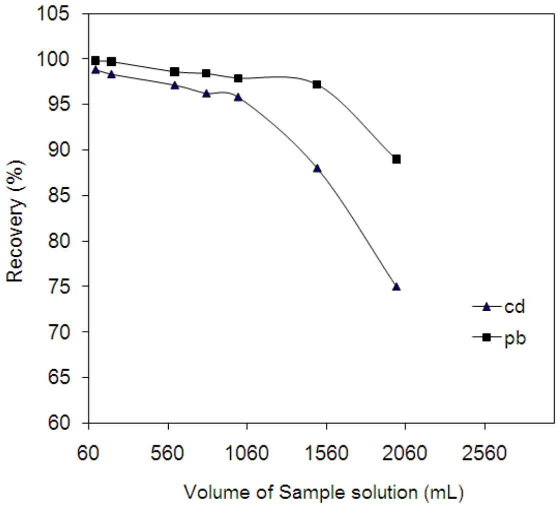

Figure 4. Effect of the sample volume on the recoveries of analyte ions (*N*=4, amounts of analytes: 10 µg Cd, 25 µg Pb).

Table 1. Effect of interfering ions on the recovery of 20 and 150 ng mL^{-1} of Cd and Pb.

Interfering ion	Concentration of interfering (mg L^{-1})
Na^+, K^+, Cl^-, Ca^{2+}, Li^+	10000
Mg^{2+}, SO_4^{2-}, NO_3^-	5000
Fe^{2+}, Al^{3+}, Cr^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+}, Br^-, Ag^+, Ba^{2+}, SO_4^{2-}, $C_2O_4^{2-}$, $Cr_2O_7^{2-}$, F^-, Br^-, CO_3^{2-}, SCN^-	250

Table 2. Determination of Cd and Pb in water samples.

Sample	Cd^{2+} (ng mL^{-1})			Pb^{2+} (ng mL^{-1})		
	Added	Found [a]	Recovery (%)	Added	Found [a]	Recovery (%)
Zayandeh roud river water	-	2.3 ± 0.04	-	-	7.6 ± 0.11	-
	5.0	7.4 ± 0.07	102.0	5.0	12.5 ± 0.24	98.0
	10.0	12.1± 0.11	98.0	10.0	17.8 ± 0.25	102.0
	15.0	17.4 ± 0.16	100.6	15.0	22.4 ± 0.23	98.5
Fin region of Kashan	-	3.4 ± 0.12	-	-	8.9 ± 0.13	-
	5.0	8.3 ± 0.14	102.0	5.0	14.1 ± 0.22	104.0
	10.0	13.2 ± 0.15	98.0	10.0	18.6 ± 0.19	97.0
	15.0	18.2 ± 0.21	98.6	15.0	24.3 ± 0.24	103.0
Tap water	-	<LOD	-	-	5.3 ± 0.07	-
	5.0	5.1 ± 0.16	102.0	5.0	10.1 ± 0.28	96.0
	10.0	9.9 ± 0.09	99.0	10.0	15.8 ± 0.11	105.0
	15.0	15.3 ± 0.22	102.0	15.0	20.6 ± 0.22	102.0

[a] Average of five determinations ± standard deviation.

3.1.8. The effect of interfering ions

The influence of matrix ions in water samples on the separation and recovery of Cd^{2+} and Pb^{2+} ions were investigated by passing of different amounts of potential interfering ions as well as 150 ng mL^{-1} of Pb^{2+} and 20 ng mL^{-1} of Cd^{2+}. Tolerable amounts of interference ions, whose tolerance limit was less than 5% error in the cadmium and lead determination, were evaluated. The results are shown in Table 1. The ions naturally existed in water samples had no interference under the experimental conditions. Meanwhile, some of the transition metals at mg L^{-1} levels have no interference with analyte ions recoveries. These results confirmed that the proposed preconcentration method could be applied for samples which contain high amounts of other ions and some transition metals at mg L^{-1} levels.

3.2. Retention capacity of the adsorbent

The retention capacity of the adsorbent was determined by a funnel-tipped glass tube. The funnel was filled with the adsorbent slurry to the height of 5 cm and pressed down slightly with a flat glass rod. A series of solution containing lead and cadmium ions in each one in the range of 500-2000 µg was prepared. These solutions were passed through the column starting with low concentration. This process continued until mentioned cations eluted from the column. It indicated the adsorbent's capacity was full. For weight determination of adsorbent, the contents of the column was filtered on a filter paper and dried in ambient temperature. The ratio of the amount of cadmium or lead ion adsorbed to the amount of adsorbent was used in order to calculate the retention capacity of the adsorbent for each cation. The results showed that the maximum amount of retention capacities were 3.2 mg and 4.9 mg for Cd^{2+} and Pb^{2+} respectively, per g of adsorbent.

3.3. Analytical Characteristics

Under the optimized conditions, calibration curves were constructed for each metal ion at their own atomic absorption wavelength. Linearity in the calibration plots were seen in the concentration range of 0.5-50 µg Cd^{2+} and 5-150 µg of Pb^{2+} in the 5 mL of the final eluent solution (linear graphs were obtained in the range of 1-100 ng mL^{-1} for Cd^{2+} and 3-100 ng mL^{-1} for Pb^{2+} in the initial solution.). The equations for the lines were $A = 1.2 \times 10^{-2} C + 9.8 \times 10^{-4}$, with $r = 0.9994$ for Cd^{2+} and $A = 3.9 \times 10^{-3} C + 7.0 \times 10^{-4}$, with $r = 0.998$ for Pb^{2+}. The detection limits were calculated, as three times of the standard deviation of nine replicates of blanks prepared using 50 mL of double distilled water, to be 0.072 ng mL^{-1} for Cd^{2+} and 0.42 ng mL^{-1} for Pb^{2+}. The relative standard deviations (RSD) for 11 replicate measurements of 20 ng mL^{-1} were 1.4 % and 2.2% for Cd^{2+} and Pb^{2+} respectively.

3.4. Method application in real samples

The proposed method was used for lead and cadmium determination in water samples. Water samples were taken from the Zayandeh Roud River in Isfahan, Fin region and tap water in Kashan. The river water sample was filtered by using filter paper Whatman No. 1. The proposed method was applied to measure the Cd^{2+} and Pb^{2+} contents with the standard addition method. The obtained results are shown in Table 2. The analytical recovery was also calculated by measuring the above mentioned water samples as far as the standard addition method was concerned. Recovery values were obtained in the range of 96.0–105.0%, which demonstrated the applicability of the method and indicated the proposed method is essentially useful in analyzing water samples without any interference from the other ions.

4. Conclusions

The determination of cadmium and lead ions at trace level is very important in the context of environmental protection, food and agricultural chemistry. The proposed method is simple, sensitive and highly selective for determination of low level Cd^{2+} and Pb^{2+} in water samples. The various cations and anions were tested as possible interferent ions and it was shown that the determination of analytes could be achieved without any interference of these. Preconcentration factor of 300 and 100 are obtained in 5 mL final solution. Meanwhile, to get a better preconcentration factor, it is possible to use less volume eluent. The method, due to its easy application and the simple instrument it requires, can be successfully applied to the preconcentration and determination of analyte ions in water samples.

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References

[1]. Rose, J. Trace Elements in Health, London, 1983.
[2]. Al-Alawi, M. M.; Mandiwana, K. L. *J. Hazard. Mater.* **2007**, *148*, 43–46.
[3]. Rikans, L. E.; Yamano, T. *J. Biochem. Mol. Toxicol.* **2000**, *14*, 110–117.

[4]. Seiler, H. G., Sigel, H., Sigel, A., Handbook on Toxicity of Inorganic Compounds, Marcel Dekker, New York, 1988.

[5]. Beck, B. D. *Fundam. Appl. Toxicol.* **1992**, *18*, 1–16.

[6]. Acar, O. *Anal. Chim. Acta* **2005**, *542*, 280-286.

[7]. Freschi, G. P. G.; Dakuzaku, C. S.; Moraes, M.; Nobrega, J. A.; Neto, J. A. G. *Spectrochim. Acta B* **2001,** *56*, 1987-1993.

[8]. Bruhn, C. G.; San Francisco, N. A.; Neira, J. Y.; Noberga, J. A. *Talanta* **1999**, *50*, 967-975.

[9]. Grinshtein, I. L.; Vilpan, Y. A.; Saraev, A. V.; Vasilieva, L. A. *Spectrochim. Acta B* **2001**, *56*, 261-274.

[10]. Correia, P. R. M., Oliviera, E., Oliviera, P. V. *Anal. Chim. Acta* **2000**, *405*, 205-211.

[11]. Tsaliv, D. L.; Lampugnani, L.; Georgieva, R.; Chakarova, K. K.; Petrov, Jr. I. I. *Talanta* **2002**, *58*, 331-340.

[12]. Ruiz-Jimenez, J.; Luque-Garcia, J. L.; Luque de, Castro, M. D. *Anal. Chim. Acta* **2003**, *480*, 231-237.

[13]. Acar, O. *Talanta* **2001**, *55*, 613-622.

[14]. Colognesi, M.; Abollino, O.; Aceto, M.; Sarzanini, C.; Mentasti, E. *Talanta* **1997**, *44*, 867-875.

[15]. Cabon, J. Y. *Spectrochim Acta B* **2002**, *57*, 513-524.

[16]. Muse, J. O.; Carducci, C. N.; Stripeikis, J. D.; Tudino, M. B.; Fernandez, F. M. *Environ. Pollut.* **2006**, *141*, 126-130.

[17]. Yantasee, W.; Lin, Y.; Fryxell, G. E.; Busche, B. J. *Anal. Chim. Acta* **2004**, *502*, 207-212.

[18]. Yuan, S.; Chen, W.; Hu, S. *Talanta* **2004**, *64*, 922-928.

[19]. Sabarudin, A.; Lenghor, N.; Oshimaa, M.; Hakima, L.; Takayanagi, T.; Gaob, Y. H.; Motomizu, S. *Talanta* **2007**, *72*, 1609–1617.

[20]. Rahmi, D.; Zhu, Y.; Fujimori, E.; Umemura, T; Haraguchi, H. *Talanta* **2007**, *72*, 600–606.

[21]. Matsumiya, H.; Yatsuya, Y.; Hiraide, M. *Anal. Chim. Acta* **2007**, *588*, 82–87.

[22]. Tuzen, M.; Parlar, K.; Soylak, M. *J. Hazard. Mater.* **2005**, *121*, 79-87.

[23]. Prasad, K.; Gopikrishna, P.; Kala, R.; Prasada, R. T.; Naidu, G. R. K. *Talanta* **2006**, *69*, 938-945.

[24]. Shukla, R.; Rao, G. N. *Talanta* **2002**, *57*, 633–639.

[25]. Peker, D. S. K.; Turkoglu, O.; Soylak, M. *J. Hazard. Mater.* **2007**, *143*, 555–560.

[26]. Manzoori, J. L.; Bavili-Tabrizi, A. *Anal. Chim. Acta* **2002**, *470*, 215-221.

[27]. Maranhao, T. A.; Borges, D. L. G.; Veiga, M. A. M. S.; Curtius, A. J. *Spectrochim. Acta B* **2005**, *60*, 667-672.

[28]. Tarley, C. R. T.; Ferreira, S. L. C.; M. Arruda, A. Z. *Microchem. J.* **2004**, *77*, 163-175.

[29]. Wang, Z. H.; Zhang, Z. P.; Wang, Z. P.; Liu, L. W.; Yan, X. P. *Anal. Chim. Acta* **2004**, *514*, 151–157.

[30]. Senkal, B. F.; Ince, M.; Yavuz, E.; Yaman, M. *Talanta* **2007**, *72*, 962–967.

[31]. Gama, E. M.; Lima, A. S.; Lemos, V. A. *J. Hazard. Mater.* **2006**, *136*, 757-762.

[32]. Pereira, M. G.; Pereira-Filho, E. R.; Berndt, H.; Arruda, M. A. Z. *Spectrochim. Acta B* **2004**, *59*, 515–521.

[33]. Gurnani, V.; Singh, A. K.; Venkataramani, B. *Anal. Chim. Acta* **2003**, *485*, 221–232.

[34]. Xingguang, S.; Meijia, W.; Yihua, Z.; Jiahua, Z.; Hanqi, Z.; Qinhan, J. *Talanta* **2003**, *59*, 989-/997.

[35]. Goswami, A.; Singh, A. K. *Talanta* **2002**, *58*, 669-678.

[36]. Taher, M. A.; Puri, B. K.; Bansal, R.K. *Microchem. J.* **1998**, *58*, 21-30.

[37]. Pancras, J. P.; Puri, B. K. *Anal. Bioanal. Chem.* **2002**, *374*, 1306-1311.

[38]. Taher, M. A. *Microchim. Acta* **2003**, *141*, 101-106.

[39]. Behpour, M.; Attaran, A. M.; Ghoreishi, S. M.; Soltani, N. *Anal. Bioanal. Chem.* **2005**, *382*, 444-447.

[40]. Haji, S. A. M.; Dadfarnia, S. *Anal. Bioanal. Chem.* **2004**, *378*, 1388-1391.

[41]. Fan, Z.; Hu, B.; Jiang, Z. *Spectrochim. Acta B* **2005**, *60*, 65–71.

[42]. Pourreza, N.; Zavvar, M. H. *Talanta* **2004**, *64*, 264-267.

[43]. Wang, G. F.; Satake, M.; Horita, K. *Talanta* **1998**, *46*, 671–678.

[44]. Xiong, C.; Jiang, Z.; Hu, B. *Anal. Chim. Acta* **2006**, *559*, 113–119.

[45]. Behpour, M.; Ghoreishi, S. M.; Salehi, S. Acta Chim. Slov. **2005**, *52*, 323–327.

[46]. Pourreza, N.; Zavvar, M.H. *Anal. Chim. Acta* **2004**, *503*, 279–282.