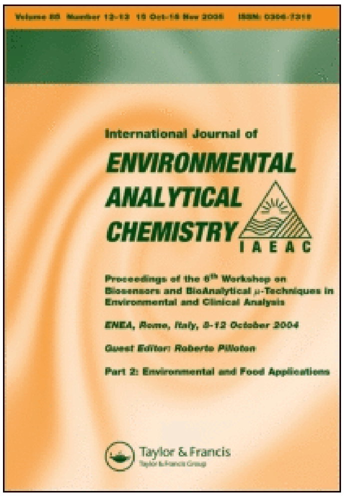

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Silica gel modified with diaminothiourea as selective solid-phase extractant for determination of Hg(II) in biological and natural water samples

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In this paper, a new method that utilizes diaminothiourea-modified silica gel as solid-phase extractant has been developed for preconcentration of trace Hg(II) prior to the measurement by cold-vapour atomic absorption spectrometry. The separation/preconcentration conditions of the analyte, which include the effects of the pH, sample flow rate and volume, elution conditions, shaking time, and interfering ions on the recovery of the analyte were investigated. At pH 2, the adsorption capacity of modified silica gel for Hg(II) was found to be 36.3 mg/g. According to the definition of IUPAC, the detection limits (3σ) of this method for Hg(II) was 0.28 ng/mL. The proposed method yielded satisfactory results when it was applied to the determination of trace Hg(II) in biological and natural water samples.

Keywords: Diaminothiourea; Hg(II); Preconcentration; CVAAS

1. Introduction

Mercury(II) and its organometallic species have been considered as a human health hazard because they may cause kidney toxicity, neurological damage, paralysis, chromosome breakage, and birth defects [1]. The formation of organometallic species in water systems is mainly initiated by the presence of free mercury(II) ions as well as bacteria producing methane and methylcobalamin, leading to the generation of highly toxic organomercury species [2]. Thus, the determination of mercury(II) in biological and natural water samples is of vital importance. Mercury(II) in these samples is usually present at low concentration levels. Despite recent progress in instrumental techniques and increases in the selectivity and sensitivity of analytical techniques, direct determination of trace elements in some samples is still difficult. Therefore, preconcentration and selective separation of trace elements from biological and natural water samples are very important and need much more attention.

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Recently, solid-phase extraction (SPE) has been utilized for preconcentration of heavy metals due to its flexibility, simplicity, safety, and ease of automation [3–8]. Among the different solid-phase extractants, modified silica gel has received considerable attention. On the basis of hard–soft acid–base theory, mercury(II), palladium(II), platinium(II) and (IV), silver(I) and cadmium(II), etc. as soft acids favour strong and selective binding between sulfur-containing compounds. This characteristic behaviour has prompted many researchers to immobilize the silica gel surface with sulfur-containing chelate compounds for preconcentration and separation of these metal ions. Examples of such phases are as follows: silica gel immobilized by dithioacetal derivative [9], dithizone phases [10], dithiocarbamate derivatives [11], aminopropylbenzoylazo-2-mercaptobenzothiazole [12], and 2-mercaptobenzimidazol [13] as potential solid-phase extractors for mercury(II) from environmental samples, Cd(II)-imprinted thol-functionalized silica gel sorbent for selective solid phase of Cd (II) [14], silica gel modified by isodiphenylthiourea [15], and amidinothioureido [16] for preconcentration of trace silver, gold, palladium, and platinum in geological and metallurgical samples.

However, the utilization of diaminothiourea (DATU)-modified silica gel as a solid-phase extractant for preconcentration of trace amounts of mercury(II) from biological and natural water samples has not yet been reported. This work is devoted to synthesis, characterization, and evaluation of the sorption properties of silica gel modified with DATU. The proposed method was applied to the determination of trace mercury(II) in biological and natural water samples by cold-vapour atomic absorption spectrometry (CVAAS). The analytical precision and accuracy of the proposed method were satisfactory.

2. Experimental

2.1 *Reagents and solutions*

All reagents were of analytical grade. Metal ion (1 mg/mL) solutions were prepared by dissolving analytical-grade salts in double-distilled water (DDW) with the addition of hydrochloric acid and further diluted daily prior to use.

Carbon disulfide and hydrazine hydrate were used in this work (The Third Reagent Factory, Shanghai, China). Silica gel (200–300 mesh, Qingdao Hailang Chemical Factory, Qingdao, China, http://www.qdsilica-gel.com/mainen.htm) and 3-chloropropyltrimethoxysilane (CPS) (Ocean University Chemical Company, Qingdao, China) were used in this work. All solutions were prepared from DDW. Standard labware and glassware were acid-washed and rinsed with DDW.

2.2 *Apparatus*

Mercury was determined by CVAAS with a Perkin-Elmer AA-6800 atomic absorption spectrometer. A Perkin-Elmer mercury electrodeless discharge lamp operated at 180 mA was used as the light source. The mercury absorbance was measured at 253.6 nm with a bandwidth of 0.7 nm. The mercury generator was operated with argon as carrier gas. All measurements were carried out in the cold state under the conditions: signal processing, integrated hold with integration time 10 s, argon carrier gas flow rate, 70 mL/min, 5 mol/L HCl flow rate, 2.5 mL/min, 0.5% $NaBH_4$ flow rate, 2.2 mL/min. The pH value was controlled with a pHs-10C digital pH meter (Xiaoshan Instrument Factory, China). Infrared spectra were recorded on a Nicolet NEXUS 670 FT-IR apparatus (Nicolet, Madison, WI). Elementar Analysis Vario-EL (Hanau, Germany) was used to determine enhancement factor. A YL-110 peristaltic pump (The General Research Academe of Coloured Metal, Beijing, China) was used in the separation/preconcentration process, and a PTFE column (45 mm × 9.0 mm i.d.) was used also.

2.3 *Sample preparation*

Yellow River water was collected from Yellow River, Lanzhou, China. The water sample was filtered through a 0.45-μm membrane filter (Tianjin, Jinteng Instrument Factory, Tianjin, China), and acidified to a pH of about 1 with concentrated HCl prior to storage for use. The usual general precautions were taken to avoid contamination.

The standard references (GBW 07601: human hair power and GBW09101: tea leaf) were provided by National Research Center for Certified Reference Materials (Beijing, China). Lotus leaf was collected from Yueyang, China. Pig liver was purchased from Binhe market, Lanzhou, China. A quantity of 0.500 g of fresh lotus leaf and fresh pig liver were weighed and transferred to a digestion tube, and then 5 mL of concentrated HNO_3 was added to the mixture. The tube was left at room temperature for one night. Then, it was placed in a digester block and heated slowly until the temperature was up to 165°C. This temperature was maintained until the evolution of brown fumes ceased. After the tube was cooled down, 1.3 mL of perchloric acid was added into it. Then, the temperature was raised to 210°C until the evolution of white fumes began. The volume was adjusted to 100 mL with DDW when the tube had cooled down [17]. At the same time, 0.500 g of the above fresh samples was dried in an oven at 80°C to constant weight. The weight of the dried samples was recorded, and calculations with respect to dried sample were made.

2.4 *Modification of DATU onto silica gel*

2.4.1 Synthesis of DATU [18]. Hydrazine hydrate (50 mL) and water (150 mL) were placed into a three-necked flask, and then carbon disulfide was dropped into the mixture with slow stirring. The reaction mixture was refluxed for an hour, left to cool, and filtered off. The crude product was then recrystallized with water and finally dried for use.

2.4.2 Preparation of silica gel-DATU phase. Silica gel was first activated by refluxing in concentrated hydrochloric acid for 4 h to move any adsorbed metal ions, then filtered, washed repeatedly with DDW to neutral filtrate, and dried in an oven at 160°C for 8 h.

Activated silica gel (6 g) was suspended in 100 mL of dry toluene mixed with 6 mL of CPS and refluxed for 20 h. The products (silica-Cl) was filtered off, washed with toluene, alcohol, and diethylether, and dried in an oven at 70°C for 6 h.

Silica-gel-immobilized DATU was prepared by the addition of 5 g of silica-Cl phase to 2.5 g of DATU already dissolved in 100 mL (1 + 1) hot ethylene glycol water solution, and refluxed for 10 h. The resulting phase was filtered, repeatedly washed with hot DDW, and then dried at 70°C for 7 h.

2.5 *Procedure*

2.5.1 Static method. Silica-gel-DATU (50 mg) was added to 20 mL of Hg(II) solution after adjusting to the desired pH value. Then, the mixture was shaken vigorously for 30 min to facilitate adsorption of the metal ion onto the adsorbent at 25°C. After the solution was centrifuged, the concentrations of the Hg(II) in the solution were directly determined by CVAAS.

2.5.2 Dynamic method. A total of 300 mg silica gel-DATU was filled into a PTFE column (50 mm × 9.0 mm i.d.). The ends of the column were plugged with a small portion of glass wool to retain the adsorbent in the column. After cleaning by passing through ethanol, 0.1 mol L^{-1} HCl solution and doubly distilled deionized water once more, the column was conditioned with HNO_3 solution (pH2). Each solution was passed through the column at a flow rate of 4 mL/min using a peristaltic pump. Afterwards, Hg(II) retained on column was eluted with 2.0 mL of 2 mol/L HCl in 2% thiourea. Finally, Hg(II) in the elution was determined by CVAAS.

3. Results and discussion

3.1 *FTIR spectra and elemental analysis*

As shown in figure 1, Fourier-transform infrared (FTIR) spectra were obtained from DATU, activated silica gel, modified silica gel–DATU, and Hg(II) sorbed on silica gel–DATU. According to the literature [19, 20], the main characteristic peaks of DATU are assigned as follows: υ NH or υ NH_2 (3204.33/cm), δ NH (1530.68/cm, 933.80/cm), υ C=S (1489.32/cm, 1285.96/cm,1141.22/cm, 755.56/cm). The main characteristic peaks of activated silica gel are assigned as follows: υ OH (3434.85/cm, 1641.57/cm), υ Si–O–Si (1102.32/cm), υ Si–O–H (952.01/cm), υ Si–O (807.52/cm), δ Si–O–Si (469.89/cm). The main characteristic peaks of modified silica gel–DATU are assigned as follows: υ CH_2 (2927.43/cm), δ CH (1430.95/cm, 1408.91/cm), δ NH (1554.84/cm, 1526.49/cm), υ C=S (745.92/cm). The main bands of Hg (II) sorbed on silica gel–DATU are δ NH (1571.33/cm, 1552.83/cm, 1519.97/cm), υ C=S (739.32/cm). FTIR spectra reveal that some peaks shift slightly, and the intensity of the peaks changes after chelating between silica gel–DATU and Hg(II). The percentage of element 'N' in silica gel-DATU was 2.69% by elemental analysis. After calculation, the quantity of DATU attached on the surface was 5.09 mg per gram of silica gel.

The above experimental results suggest that interaction exists at the interface of silica gel and DATU, and silica gel is successfully modified by DATU. The structure of the newly synthesized silica gel-DATU is shown in figure 2.

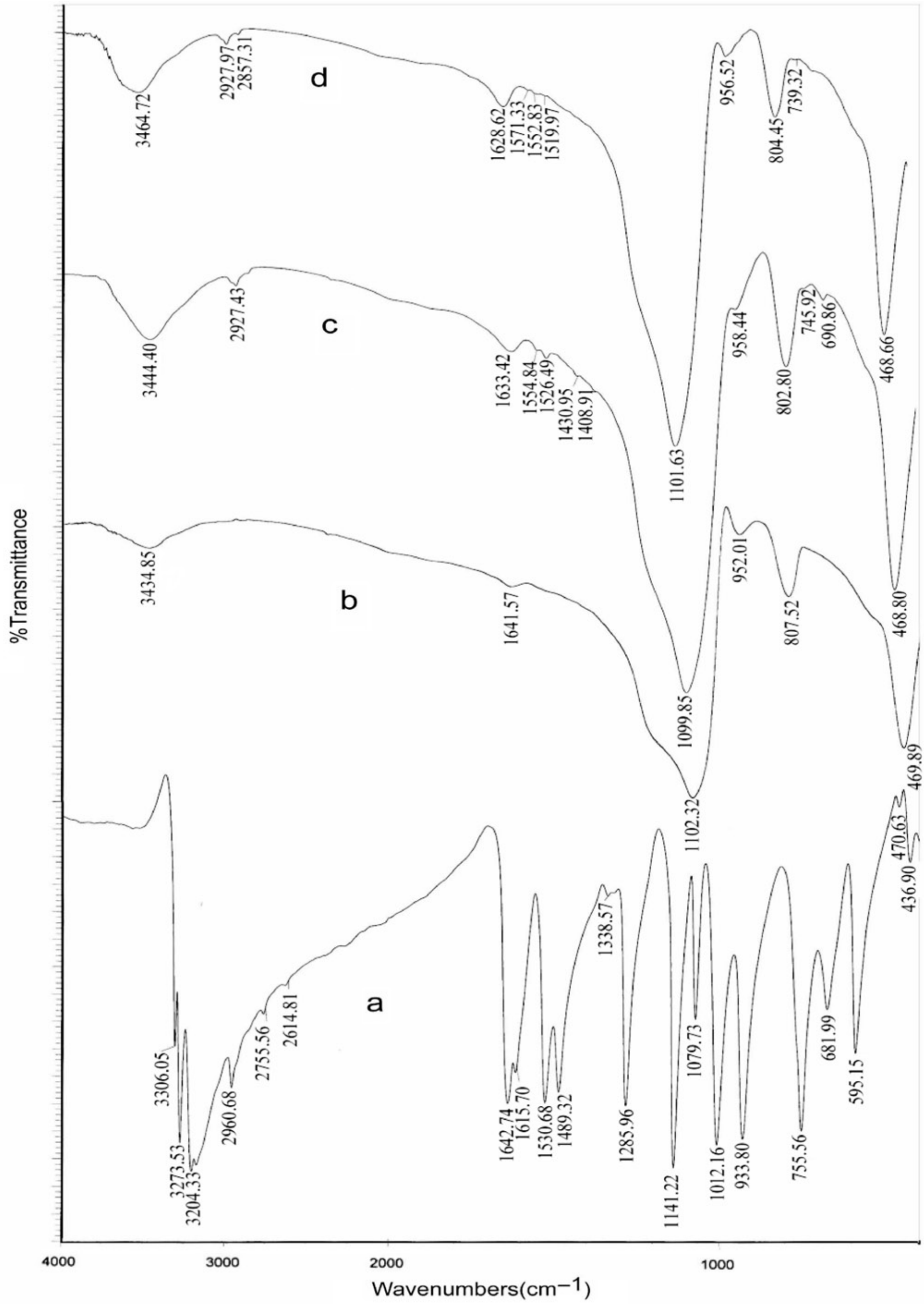

Figure 1. IR spectra of (a) DATU, (b) activated silica gel, (c) silica gel-DATU, and (d) Hg(II) sorbed on silica gel.

3.2 *Effect of pH*

The adsorption of Hg(II) on silica gel-DATU was studied at different pH values (pH 1–7) following the recommended procedure. Quantitative extraction (>95%) of Hg (II) is found in the pH range of 2–7. pH 2 was selected as the enrichment acidity for subsequent experiments.

3.3 *Effect of elution condition on recovery*

Elution of Hg(II) from the column containing the sorbent was investigated using 2.0 mL of various concentrations of HCl in 2% thiourea solution following the general procedure (dynamic method). The obtained results showed that 2.0 mL of 2 mol/L HCl in 2% thiourea was sufficient for 99% recovery for Hg(II). Therefore, 2.0 mL of 2 mol/L HCl in 2% thiourea was used as eluent in further experiments.

3.4 *Effect of shaking time*

The effect of shaking time is another important factor in the evaluation process of the affinity of silica gel-DATU to Hg(II). To determine the rate of loading of Hg(II) on the silica gel-DATU, the static procedure was carried out. Quantitative adsorption (>98%) of Hg(II) was obtained at pH 2 during the first 5 min, which reflects the high affinity and selectivity of the silica gel-DATU for Hg(II).

3.5 *Effect of the flow rate of the sample solution*

As the retention of elements on adsorbent depends upon the flow rate of the sample solution, its effect was examined under the optimum conditions (pH, eluent, etc.) by passing sample solution through the PTFE column with a peristaltic pump. The flow rates were adjusted in the range of 1.0–6.0 mL/min. Quantitative recoveries (>95%) of Hg(II) were achieved when the flow rate was ≤4.0 mL/min. Thus, a flow rate of 4.0 mL/min was selected in this work.

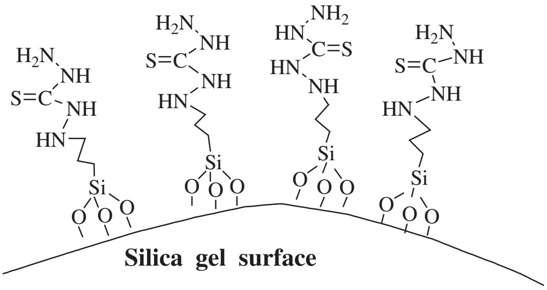

Figure 2. Suggested structure of silica-gel DATU.

3.6 *Effect of sample volume and enrichment factor*

To explore the possibility of enriching low concentrations of Hg(II) from a large volume, the effect of sample volume on the retention of metal ions was also investigated. For this purpose, 50, 100, 150, 200, 300, and 400 mL of sample solutions containing 1 µg of Hg(II) were passed through the PTFE column with the optimum flow rate. Quantitative recoveries of Hg(II) (>95%) were obtained when the sample volume was $\leq$300 mL. Therefore, 300 mL of sample solution was adopted for the preconcentration of Hg(II) from sample solutions. As the amount of Hg(II) in 300 mL was measured after elution of adsorbed Hg(II) with 2.0 mL of 2 mol/L HCl in 2% thiourea solution, the solution was concentrated by a factor of 150. A preconcentration factor of 150 makes the method very promising for use at the sub-ng/mL Hg(II) level in combination with a more sensitive technique such as CVAAS.

3.7 *Adsorption capacities and enhancement factor*

The adsorption capacity is an important factor because it determines how much adsorbent is required to quantitatively concentrate the analytes from a given solution. Ten-millilitre aliquots of a series of concentrations (10–500 mg/L) were adjusted to the appropriate pH, and the recommended procedure (static method) described above was applied. A breakthrough curve was obtained by plotting the concentration (mg/L) vs. the micrograms of Hg(II) adsorbed per gram. From the breakthrough curve (figure 3), the adsorption of modified silica gel-DATU for Hg(II) was found to be 36.3 mg/g at pH2. However, Hg(II) was barely adsorbed on untreated silica gel at pH 2, and the enhancement factor was found to be 774 at pH 2 compared with commercial silica gel. The results showed that the adsorption capacity of modified silica gel for Hg(II) was significantly high.

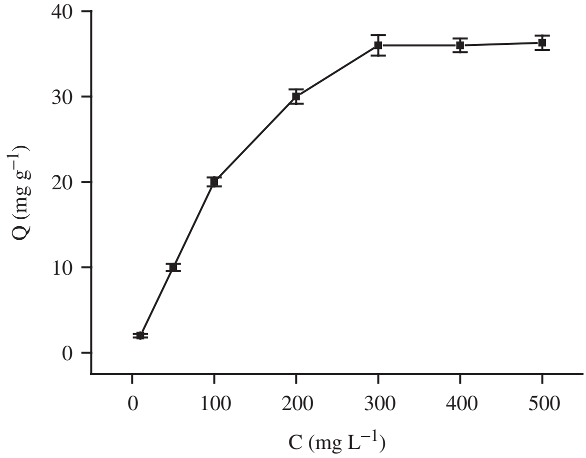

Figure 3. Effect of Hg(II) initial concentration on the adsorption quantity of silica-gel DATU, pH2.

3.8 *Stability tests*

To test the stability, the cycle of extraction–recovery–regeneration was repeated seven times for one batch of sorbents according to the column operation. The uptake performance of regenerated sorbent was found to be very similar to that of the freshly prepared adsorbents, which indicates that silica gel-DATU can be regenerated and reused repeatedly at least seven times.

3.9 *Effects of coexisting ions*

The effects of common coexisting ions on the adsorption of Hg(II) in silica gel-DATU were investigated. In these experiments, solutions of 1.0 µg/mL of Hg(II) that contain the added interfering ion were analysed according to the recommended column procedure. The tolerance of the coexisting ions was given in table 1. It can be seen that the presence of major cations had no obvious influence on the determination under the selected conditions.

3.10 *Analytical precision and detection limits*

Under the selected conditions, 11 portions of standard solutions were enriched and analysed simultaneously following the recommended procedure. According to the definition of IUPAC, the detection limit (3σ) of this method for Hg(II) was 0.28 ng/mL, the relative standard deviation (RSD) was 1.16% ($n = 11$, $C = 10$ ng/mL), which indicated that the method had a good precision for the analysis of trace Hg(II) in solution samples.

3.11 *Application of the method*

The proposed method was applied to the analysis of mercury in two certified reference materials (GBW 07601 and GBW09101), biological and natural water samples.

Table 1. Effect of foreign ions on recovery of Hg(II) (1.0 µg/mL).

Ions	Concentration (µg/mL)	Recovery of Hg(II) (%)
Cl^-	2000	99.30
NO_3^-	1000	100.36
SO_4^{2-}	1000	98.08
PO_4^{3-}	100	96.74
NH_4^+	2000	99.55
Na^+	2000	101.17
Ca^{2+}	1000	99.80
Cd^{2+}	100	98.68
Cr^{3+}	100	97.84
Mn^{2+}	100	98.42
Ni^{2+}	100	98.40
Co^{2+}	100	99.09
Fe^{3+}	100	99.43
Pb^{2+}	100	98.38
Cu^{2+}	50	95.32
Zn^{2+}	100	99.65

The results are listed in table 2. The analytical results for the standard material were in good agreement with the certified values. For the analysis of biological and natural water samples, the standard addition method was used, and the recoveries of Hg(II) were in the range of 96–102%. The results demonstrate the suitability of the silica gel-DATU for preconcentration of Hg(II) from biological and natural water samples.

4. Conclusions

In this study, a simple, rapid, accurate, selective, and reliable method for the determination of trace level of Hg(II) was developed using silica gel-DATU as a solid-phase extractant. The adsorption capacity for Hg(II) is 36.3 mg/g at pH2. As shown in table 3, the enrichment acidity and the adsorption capacity for Hg(II) are much higher than those of sorbents for Hg(II) in the literatures. This newly developed method has been successfully applied to analyse trace Hg(II) in biological and natural water samples. The precision and accuracy of the method are satisfactory.

Table 2. Analytical results for the determination of Hg(II) in standard reference materials and natural samples.

Samples	Added Hg(II) (μg/L)	Measured[a] (μg/g)		Certified (μg/g)	Recovery (%)
		Standard materials	Natural samples		
GBW 07601		0.35 ± 0.09		0.36 ± 0.08	
GBW 09101		2.20 ± 0.11		2.16 ± 0.21	
Pig liver	0		0.54 ± 0.11		
	0.5		1.02 ± 0.17		96
	1		1.55 ± 0.20		101
Lotus leaf	0		nd		
	0.5		0.51 ± 0.16		102
	1		0.99 ± 0.25		99
Yellow River water[b]	0		0.31 ± 0.03		
	0.5		0.80 ± 0.08		98
	1		1.28 ± 0.14		97

[a] μg/L.
[b] Average values for three determinations.

Table 3. Figures of merit of comparable methods for determination of Hg(II) by modified silica gel.

Functional group	pH	Capacity (μg/g)	LOD (ng/mL)	Precision ($n = 11$) (%RSD)	PF	Ref.
2-Mercaptobenzimidazol	7	0.7	0.07	8.8		[13]
1,5 Diphenylcarbazide	6	5.6				[21]
Diphenylcarbazone	7	8	0.9	<3	500	[22]
DATU	2	36.3	0.28	1.16	150	Present work

References

[1] S.E. Manahan. *Environmental Chemistry*, 6th edn, p. 185, Lewis, Boca Raton, FL (1994).
[2] S.E. Manahan. *Environmental Chemistry*, p. 342, Willard Grant Press, Boston (1972).
[3] E.M. Thurman, M.S. Mills. *Solid-Phase Extraction: Principles and Practice*, p. 132, Wiley, New York (1998).
[4] S. Arpadjan, L. Vuchkova, E. Kostadinova. *Analyst*, **122**, 243 (1997).
[5] V. Flotron, J. Houessou, A. Bosio, C. Delteil, A. Bermond, V. Camel. *Spectrochim. Acta B*, **58**, 1177 (2003).
[6] E. Vereda Alonso, A. García de Torres, J.M. Cano Pavón. *Talanta*, **55**, 219 (2001).
[7] Y. Liu, X. Chang, D. Yang, Y. Guo, S. Meng. *Anal. Chim. Acta*, **538**, 85 (2005).
[8] Y. Zhai, X. Chang, Y. Cui, N. Lian, S. Lai, H. Zhen, Q. He. *Microchim. Acta*, **154**, 253 (2006).
[9] M.E. Mahmoud, G.A. Gohar. *Talanta*, **51**, 77 (2000).
[10] M.E. Mahmoud, M.M. Osman, M.E. Amer. *Anal. Chim. Acta*, **415**, 33 (2000).
[11] M.E. Mahmoud. *Anal. Chim. Acta*, **398**, 297 (1999).
[12] W. Ma, F. Liu, K. Li, W. Chen, S. Tong. *Anal. Chim. Acta*, **416**, 191 (2000).
[13] H. Bagheri, A. Gholami. *Talanta*, **55**, 1141 (2001).
[14] G. Fang, J. Tan, X. Yan. *Anal. Chem.*, **77**, 1734 (2005).
[15] P. Liu, Q. Pu, Z. Su. *Analyst*, **125**, 147 (2000).
[16] S. Zhang, Q. Pu, P. Liu, Q. Sun, Z. Su. *Anal. Chim. Acta*, **452**, 223 (2002).
[17] E.S. Miranda Carlos, B.F. Reis, N. Baccan, A.P. Packer, M.F. Gine. *Anal. Chim. Acta*, **453**, 301 (2002).
[18] G.R. Burns. *Inorg. Chem.*, **7**, 277 (1968).
[19] R.A. Nyquist, R.O. Kagel. *Infrared Spectra of Inorganic Compounds*, p. 94, Academic Press, New York (1971).
[20] S.S. Kirupavathy, S.S. Marya, P. Srinivasana, N. Vijayand, G. Bhagavannarayanad, R. Gopalakrishnana. *J. Crystal Growth*, **306**, 102 (2007).
[21] A. Khan, F. Mahmood, M.Y. Khokhar, S. Ahmed. *React. Funct. Polym.*, **66**, 1014 (2006).
[22] J. Fan, Y. Qin, C. Ye, P. Peng, C. Wu. *J. Hazard Mater* in press (doi: 10.1016/j.jhazmat.2007.04.111).