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Preconcentration of Mercury by Adsorption of its Diphenylthiocarbazone Complex on an Silica Gel-Immobilized Schiff's Base 4,4'-Dimethoxybenzil Bisthiosemicarbazone (DBTS) Column and Spectrophotometric Determination

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Abstract: A simple method has been developed for the preconcentration of mercury based on the adsorption of its Schiff's base 4,4'-Dimethoxybenzil bisthiosemicarbazone (DBTS)complex on a silica gel-immobilized Schiff's base 4,4'-Dimethoxybenzil bisthiosemicarbazone (DBTS)column. The influence of acidity, eluting agents, stability of the column, sample volume and interfering ions has been investigated in detail. The adsorbed complex could be eluted using environmentally benign polyethylene glycol (PEG 400) and the concentration of mercury was determined by visible spectrophotometry at a wavelength maximum of 535 nm. A detection limit of 5 μg L^{-1} could be achieved and the developed procedure was successfully applied for the determination of mercury in spiked water samples and city waste incineration ash (CRM176). The preconcentration factor attainable for quantitative recovery (>96%) of mercury(II) was 100 for a 1000 mL sample volume.

Key words: Mercury · Preconcentration · Silica gel-immobilized-Schiff's base 4,4'-Dimethoxybenzil bisthiosemicarbazone (DBTS)column

INTRODUCTION

In the past few decades there has been considerable emphasis on trace metal analysis. The determination of trace metals in metallurgical, agricultural and environmental samples has become increasingly important. This has led to major developments in the field of trace metal analysis, with emphasis on the development of new and greener analytical methods. As a result there has been considerable growth in the analytical chemistry of various metals. Mercury is no exception to this. A rare element in the earth's crust, mercury is found either as a native metal or in cinnabar, cordierite, livingstonite and other minerals with cinnabar being the most commonore. Methyl mercury is a toxic compound that is widely found as a pollutant in water bodies and streams. Short-term exposure to high concentrations of mercury vapor causes harmful effects on the nervous, digestive, respiratory systems and the kidneys [1]. Solid phase extraction is widely used for the removal of many toxic metal ions [2-5]. The use of environment friendly sample treatment for speciation analysis has been reviewed in detail [6,7]. Hg^{2+} is a soft acid and has good affinity towards sulfur containing ligands [8-10]. Dithizone is one such ligand, which has been used in the preconcentration of many metal ions including mercury [11,12]. A spectrophotometric method for the determination of trace level mercury using dithizone in micellar medium has been reported [13]. The calibration graphwas linear in the range 0.01-10 μg L^{-1} and the method was applied to water samples. Silica gel-immobilized-dithiocarbamate derivatives modified by dimethylsulfoxide has been used for the separation and preconcentration of mercury(II) and the method has been tested in water samples with 98% recovery [14,30-34]. Micro columns packed with chlorella vulgaris immobilized on silica gel have been studied for mercury speciation and the method has been applied in spiked tap water samples with 96% recovery [15]. Even though, a preconcentration factor of 200 could be achieved, strong acid was used for elution. Most of the solid phase extraction methods for mercury involve either strong acids or toxic organic solvents for elution. A

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survey of the literature reveals that solid phase extraction is one of the versatile methods for preconcentration. The inherent advantage of solid phase extraction is the high selectivity and preconcentration factor that could be attained. Inorganic adsorbents such as alumina and silica offer good advantages in terms of thermal, mechanical and chemical stability under various experimental conditions. Moreover, they offer good selectivity towards a particular metal ion. Chelating agents can be easily loaded on silica gel-immobilized-dithiocarbamate derivatives with good stability. Schiff's base 4,4'-Dimethoxybenzil bisthiosemicarbazone (DBTS) is one such chelating agent, which shows relatively good sensitivity and selectivity towards Hg(II) in acidic medium.

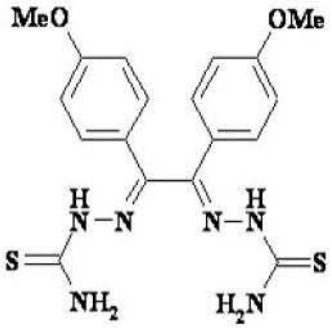
Preconcentration of mercury based on the adsorption of its. Schiff's base 4,4'-Dimethoxybenzil bisthiosemicarbazone (DBTS) complex on an silica gel-immobilized Schiff's base 4,4'-Dimethoxybenzil bisthiosemicarbazone (DBTS)column. The adsorbed complex could be eluted using environmentally benign polyethylene glycol and the concentration of mercury was determined by visible spectrophotometry. The influence of various experimental parameters such as acidity, sample volume, flow rate, diverse ions, etc. was examined in detail. The validity of the proposed method was tested in spiked water samples and city waste incineration ash (CRM176).

Experimental

Instrumentation: A Jasco V-576 (Japan) model double beam UV-Vis spectrophotometer fitted with tungsten lamp as the source was used for absorbance measurements. The 1 cm matched quartz cells were used for measuring the absorbance. The pH measurements were carried out by an ATC pH meter (EDT instruments, GP 353). Infrared spectra were recorded from KBr pellets with a Perkin-Elmer 1430 ratio recording spectrophotometer.

Chemicals and Reagents: Silica gel (70-230 mesh, 60Å pore diameter) purchased from Riedel De Haën AG, Seelze, Hannover, Germany; 3-chloropropyltrimethoxysilane, 3-aminotrimethoxysilane, ethylenediamine (EDA), diethylenetriamine (DETA) and triethylenetetramine (TETA) were purchased from Aldrich Chemical Company, USA. Carbon disulfide was purchased from Merck, Darmstadt, Germany. The solutions and Schiff's base 4,4'-Dimethoxybenzil bisthiosemicarbazone (DBTS) were of analytical reagent gradewere prepared using analytical grade reagents. Triple distilled and deionized water was used for the preparation of solutions. A stock solution of 1000 μg mL^{-1} Hg(II) was prepared by dissolving 0.1354 g of mercury(II) chloride (from Merck, Darmstadt, Germany) in 100 mL water. A working solution of 10 μg mL^{-1} was prepared by suitable dilution. About 0.0l g of Schiff's base 4,4'-Dimethoxybenzil bisthiosemicarbazone (DBTS) was dissolved in minimum amount of acetone and diluted to 100 mL. Polyethylene glycol-400 (Merck, Germany) solution was prepared in the ratio 7:3 by dissolving 7 mL of polyethylene glycol with 3 mL of deionized water. Silica gel (Merck) of particle size 150 mesh was used as the adsorbent. Sulfuric acid (Merck, Germany) of concentration 1 mol L^{-1} was prepared by diluting 55.5mLof concentrated sulfuric acid with 1 L of de-ionized water. Water samples Tap water (Tehran, taken after 10 min operation of the tap), rain water (Tehran, 26 January, 2007), were collected, acidified and stored in polythene bottles.

Synthesis and Preparation of Silica gel-immobilized Schiff'sbase4,4'-Dimethoxybenzilbisthiosemicarbazone (DBTS)column: Silica gel was first activated by refluxing in concentrated hydrochloric acid for 6 h, then filtered, washed repeatedly with DDW until acid free and dried in an oven at 160°C for 6 h. 50.0 g of the dry silica gel were suspended in 250 ml dry toluene and 100 ml of 3-chloropropyltrimethoxysilane or 3-aminopropyltrimethoxysilane in a flat-bottomed flask and refluxed for 12 h. The reaction mixture was left to cool, filtered, washed with toluene, ethanol, diethylether and finally dried at 70°C in an oven for 6 h to afford the corresponding Si-Cl or Si-NH_2, respectively. To synthesize the different silica gel-amine phases, the product Si-Cl (10.0 g) was subsequently used and mixed with 15 mmol of the selected EDA, DETA and TETA in 200 ml dry toluene, as described previously [35,36]. The reaction mixture was refluxed for 12 h, then cooled, filtered, washed with toluene, ethanol, diethylether and dried in an oven at 70°C to afford the corresponding Si-EDA, Si-DETA and Si-TETA, respectively. The newly synthesized silica gel phase-mmobilized Schiff's base 4,4'-Dimethoxybenzil bisthiosemicarbazone (DBTS) (I-IV) were prepared by refluxing 200 ml dry toluene containing 10 g of Si-NH_2 or Si-EDA or Si-DETA or Si-TETA with 20, 40, 60 and 80 ml of carbon disulfide, respectively, for 8 h. The reaction mixture was left to cool, filtered, washed with toluene, ethanol and diethylether and dried in the oven for 6 h. The structures of the newly synthesized silica gel phases (I-IV) are shown in Scheme 1.



Schematic 1: The DBTS structure

A glass column 1.5 cm in diameter and 15 cm in length was used for the preconcentration of mercury. About 0.8 g of neutral silica gel-immobilized Schiff's base 4,4'-Dimethoxybenzil bisthiosemicarbazone (DBTS)was mixed with 25mL of triple distilled water to form slurry and then loaded on to the column. Cotton was placed at the bottom for allowing silica gel-immobilized Schiff's base 4,4'-Dimethoxybenzil bisthiosemicarbazone (DBTS)to settle properly. The column was packed up to a height of 3 cm.

Procedure for Preconcentration: A 1 mL volume of 10 μg mL^{-1} Hg(II) solution was mixed with 5mL of 0.5 mol L^{-1} sulfuric acid followed by the addition of 5 mL of Schiff's base 4,4'-Dimethoxybenzil bisthiosemicarbazone (DBTS) solution and the resulting volume was maintained at 100 mL. The sample solution was loaded on to the column of silica gel-immobilized Schiff's base 4,4'-Dimethoxybenzil bisthiosemicarbazone (DBTS) maintaining a flow rate of 2 mL min^{-1}. The complex was adsorbed as a narrow band on the top of the column. The adsorbed complex was elutedusing 10 mL of polyethylene glycol at a flow rate of 2 mL min^{-1} and the concentration of mercury was determined by visible spectrophotometry at 535 nm Fig. 3.

RESULTS AND DISCUSSION

Determination of Surface Coverage: Several approaches are commonly used to evaluate the modification of silica gel with the organic compounds. Among these is the use of the elemental analysis data for carbon and nitrogen [37]. The second approach is known as metal probe testing [35] and in this, the determination of the mmol g^{-1} coverage of organic chelate is calculated from the maximum metal ion taken up between all the tested metal ions. Third, is the use of potentiometric titration to evaluate and determine such values [37]. We chose to determine the surface coverage of the newly synthesized phases with Schiff's base 4,4'-Dimethoxybenzil bisthiosemicarbazone (DBTS) moiety by measuring the sulfur content of sulfur containing phases. The mmol g^{-1} values found on this basis were 0.642, 0.833, 1.200 and 1.850 for phases I, II, III and IV, respectively. Infrared studies of the phases (I-IV) showed a significant peak centered at 1465 cm^{-1} which is assigned to the n.NCS_2/ along with the region below 1400 cm^{-1} which is completely obscured by the strong absorption of silica gel matrix. The structures of the newly synthesized silica gel modified phases (I-IV) are given in Scheme 1.

Effect of Acidity: The effect of acidity plays a significant role in the preconcentration studies. The volume of 0.5 mol L^{-1} sulfuric acid was varied from 1 to 6 mL in 100 mL sample volume. The results are presented in Fig. 1. Quantitative recovery (>96%) was obtained in the range 3.5-6.0mL of 0.5 mol L^{-1} sulfuric acid. Beyond 6 mL, there was no change in the recovery of mercury.

Choice of the Eluent: A variety of reagents were tested in order to elute the adsorbed complex from the column. In order to choose the most effective eluent for the quantitative recovery of mercury, methylisobutylketone, chloroform, acetone, sodium hydroxide, polyethylene glycol and ethanol were studied. The adsorption studies were carried out maintaining an overall Hg(II) concentration of 10 μg in 100 mL sample volume. The recovery of mercury was found to be quantitative with ethanol and polyethylene glycol as eluting agents. However, polyethylene glycol was preferred owing to its non-inflammability and less toxicity [16,17]. It was observed that when the ratio of polyethylene glycol-water mixture is 7:3, a recovery of 99.7% could be attained Table 5.

Effect of Sample Volume: The effect of sample volume on the recovery of the analyte was investigated in the range 100-1500 mL maintaining an overall concentration of 0.025 mol L^{-1} sulfuric acid. The resulting complex was eluted using 10mL of polyethylene glycol. The results are presented in Fig. 2. As can be seen from the figure, it is evident that the recovery of mercury is quantitative (>96%) up to 1000 mL sample volume. A preconcentration factor of 100 could be attained for quantitative recovery (>96%) of Hg(II) when the sample volume was 1000 mL.

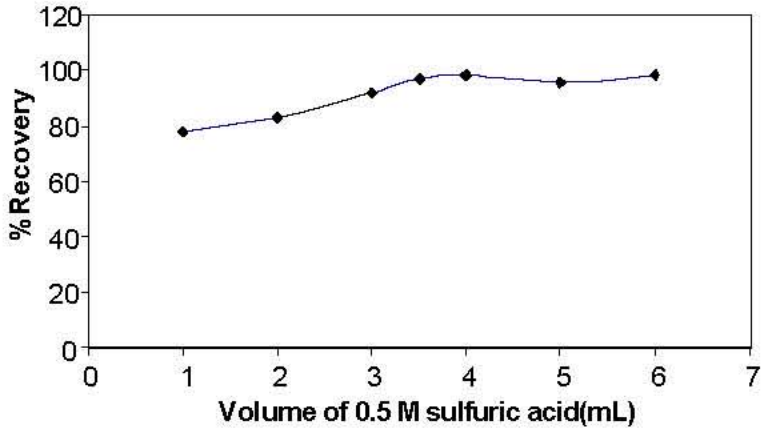


Fig. 1: Effect of variation of volume of 0.5 mol L^{-1} sulfuric acid on the recovery of mercury

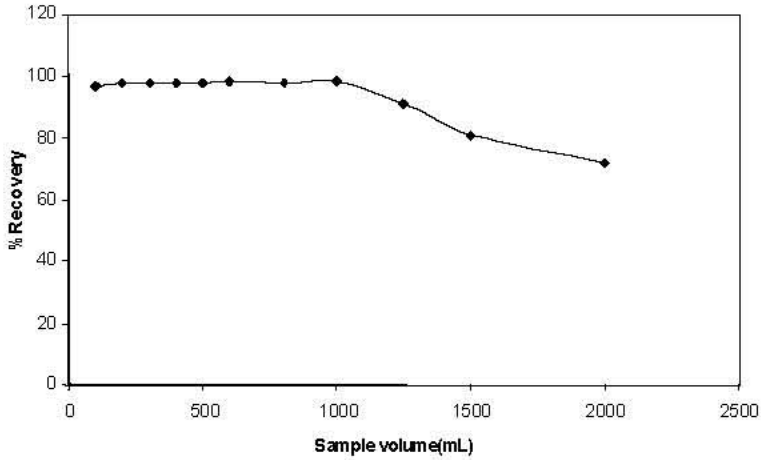


Fig. 2: Effect of sample volume on the recovery of mercury

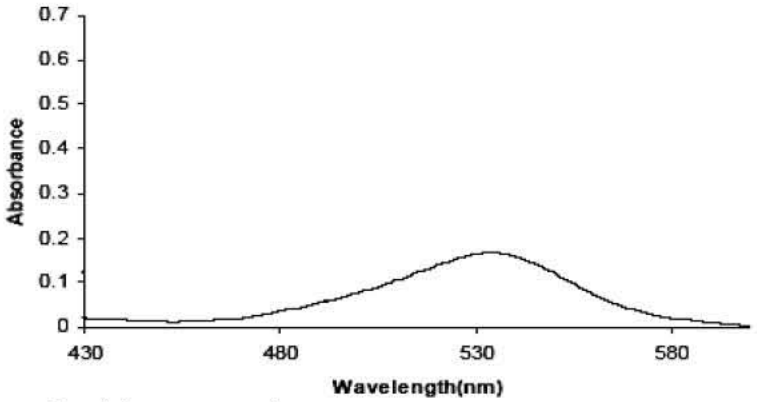


Fig. 3: Absorption spectra of Hg(II)-DDTC complex

Effect of Flow Rate: The flow rate of 1-5 mL min^{-1} was found to be suitable for optimum loading of Hg(II) DDTC complex on the silica gel-immobilized-Schiff's base 4,4'-Dimethoxybenzil bisthiosemicarbazone (DBTS) derivatives column. At higher flow rates, there was a reduction in the percentage adsorption of mercury. This could be probably due to the insufficient contact time between the sample solution and silica gel-immobilized Schiff's base 4,4'-Dimethoxybenzil bisthiosemicarbazone (DBTS). A flow rate of 2 mL min^{-1} was maintained for the elution of mercury.

Effect of the amount of silica gel-immobilized-Schiff's base 4,4'-Dimethoxybenzil bisthiosemicarbazone (DBTS): The amount of silica gel-immobilized 4,4'-Dimethoxybenzil bisthiosemicarbazone (DBTS)loaded was varied from 0.25 to 2.0 g and the preconcentration studies were carried as before. Quantitative recovery of Hg(II) could be attained in the range 0.75-2.0 g of silica gel-immobilized 4,4'-Dimethoxybenzil bisthiosemicarbazone (DBTS). For amounts less than 0.75 g there was a significant reduction in the recovery beyond a sample volume of 100 mL.

Precision Studies and Limit of Detection: The precision studies were carried out at 10 μg level of mercury(II) by carrying out 10 separate determinations using the above-mentioned procedure. The sample volume was maintained at 100 mL. The relative standard deviation of the method was found to be 3%. The sensitivity of the developed method is reflected by the limit of detection studies, defined as the lowest concentration of Hg(II) below which quantitative recovery of the metal ion by silica gel-immobilized-4,4'-Dimethoxybenzil bisthiosemicarbazone (DBTS) is not perceptibly seen. The limit of detection was found to be 5 μg L^{-1}.

Stability of the Column: The stability of the column was tested using 10 μg Hg(II) maintaining a sample volume of 100 mL. The adsorbed Hg(II)-DDTC complex was eluted using 10 mL of polyethylene glycol-water mixture. The column could be used with good precision and quantitative recovery (>96%) for at least 10 cycles. Beyond 10 cycles, there was a significant reduction in the recovery of mercury.

Effect of Other Ions: The interfering effect of diverse ions was studied at varying concentrations. The preconcentration studies were carried out as mentioned above using 10 μg Hg(II) maintaining a sample volume of 100 mL. The studies indicated that Na^+, Mg^{2+}, Ca^{2+}, Cu^{2+}, $SO4^{2-}$, Cl^-, NO_3^-, Zn^{2+}, Co^{2+}, Fe^{2+} did not cause any significant reduction in the recovery of mercury. The results are presented in Table 1 showing the recovery of Hg(II) with varying concentrations of metal ions. The recovery was found to be quantitative in the concentration range of the metal ions that was investigated. Since, the ions that are commonly present in water samples did not interfere significantly, the method was applied to study the recovery of mercury in water samples.

Table 1: Effect of diverse ions on the recovery of 10 μg Hg(II) in a sample volume of 100 mL

Recovery of mercury (%)	Amount (μg)	Ions
99.0	100	Ca^{2+}
98.6	1000	
98.7	500	
98.4	100	Mg^{2+}
98.2	500	
98.1	1000	
99.1	5	Zn^{2+}
98.6	10	
98.5	25	
98.8	100	Cl-
98.1	500	
98.0	1000	
98.6	100	NO_3^-
99.0	50	
98.3	1000	
98.7	100	SO_4^{2-}
98.0	500	
98.1	1000	
98.9	5	Co^{2+}
98.5	10	
98.3	25	
98.9	5	Cu^{2+}
98.2	10	
97.9	25	
98.8	100	Fe^{2+}
98.0	250	

Eluent 7:3 PEG-water mixture, flow rate 2 mL min^{-1}

Table 2: Analytical results for the recovery of Hg(II) in water samples

Recovery (%)	Sample volume (mL)	Hg(II) found (μg)	Hg(II) added (μg)	Sample
98.0	100	99.5	100	
98.7	250	99.5	100	Rain
97.5	1000	9.92	10	water
98.3	100	9.93	10	
98.6	100	9.90	10	
98.7	200	9.94	10	Tap
98.4	500	9.93	10	
97.3	750	9.91	10	water
98.9	1000	9.92	10	

Recovery Studies in Tap Water and Well Water Samples: The validity of the proposed method was tested by spiking known concentrations of mercury to tap water and well water samples. The water samples were filtered and stored in polythene bottles. The recovery of mercury was found to be satisfactory with a relative standard deviation of 2% for five replicate measurements and the results are shown in Table 2.

Table 3: Analysis of mercury content in city waste incineration ash sample

ICP-AES	Recovery (%)	Relative standard deviation (%)	Amount of Hg(II) found (μg)	Amount of Hg(II) added (μg)	Analysis of mercury content in city waste incineration ash sample
31.3	-	2.3	31.1	0	City waste incineration ash (CRM176)
36.8	98.4	2.6	36.3	5.0	1 g/100 mL
41.2	98.6	2.8	41.4	10.0	

Table 4: Comparison with other solid phase adsorbents

References	Eluent	Preconcentration factor	Method	Chelating agent/solid phase adsorbent
[18]	7 mol L^{-1} HCl	200	CV-AAS	Dithizone/microcrystalline naphthalene
[19]	0.1 mol L^{-1} HNO3	50	Atomic absorption spec-trophotometry	β-Naphthol/polyurethane foam
[20]	10 mol L^{-1} HCl	200	CV-AAS	Dithizone/silica gel
[21]	Tetraphenyl-borate	80	Anodic stripping voltammetry	HgI_4^{2-}-Aliquat-336/naphthalene
[22]	H_2SO_4-H_2O_2 mixture	40	ICP-AES	DuoliteGT-73 resin
[23]	Water	5	CV-AAS	Dithioacetal/SiO2
[24]	1 mol L^{-1} HBr	50	CV-AAS	Hexathia18 crown-6 tetraone/Empore disk
[25]	1 mol L^{-1} HBr	100	CV-AAS	1,5-Diphenylcarbazone/SDS coated alumina
[26]	HNO_3	-	ICP-AES	1,5-Bis(2-pyridyl)-3-sulfophenylmethylene) thiocarbonohydrazide/Dowex anion exchange resin
[27]	6 mol L^{-1} HCl	50	CV-AAS	4-(2-Pyridyl azo)resorcinol/nano-sized SiO_2
[28]	2 mol L^{-1} HNO_3 in acetone	300	CV-AAS	2-Mercaptobenzoxazole/chromosorb
[29]	Acetone	50	Spectrophotometry	Bis(2-rcaptophenyl)ethanediamide/silica gel-Present work
	Polyethylene glycol	100	Spectrophotometry	4,4'-Dimethoxybenzil Bisthiosemicarbazone (DBTS)/ silica gel-immobilized 4,4'-Dimethoxybenzil Bisthiosemicarbazone (DBTS) ocarbamate derivatives

Table 5: Effect of different eluting solvents on percentage recovery of Hg(II) ions[a]

	Recovery (%)		
eluent	2 ml	5 ml	10 ml
Methylisobuty lketone	29.6(2.6)[b]	48.5(3.1)[b]	58.5(3.0)[b]
chloroform,	39.2(2.8)	47.2(2.7)	68.5(2.8)
acetone	19.7(2.1)	29.9(2.9)	49.4(2.4)
sodium hydroxide	42.8(1.5)	62.0(2.9)	72.0(2.8)
polyethylene glycol	48.8(2.5)	68.5(2.8)	93.5(3.0)
polyethylene glycol + water[c]	67.4(2.6)	79.8(2.5)	99.6(2.6)
ethanol	34.9(2.2)	54.2(2.5)	69.6(3.2)

[a] Initial samples contained 10 μg of Hg(II) ions in 50 mL water; [b] Values in parentheses are RSDs based on five individual replicate analysis.
[c] ratio of polyethylene glycol-water mixture is 7:3

Analysis of Mercury Content in Real Sample: To assess the applicability of the method to real samples, it was applied to the extraction and determination of mercury from different water samples. Tap water (Tehran, taken after 10 min operation of the tap), rain water (Tehran, 26 January, 2007), samples were analyzed (Table 3). As can be seen from Table 4 the added mercury ions can be quantitatively recovered from the water samples used.

A known amount of the sample was digested with $KMnO_4$-H_2SO_4-H_2O_2 mixture and diluted to a particular volume. Known aliquots were taken and subjected to the preconcentration procedure as mentioned above. The recovery of mercury was found to be quantitative and the results are presented in. As can be seen from the results, the added Hg(II) ions can be quantitatively recovered from the mercury content in city waste incineration ash sample used and satisfactory agreements exist between the results obtained by proposed method and the results reported by ICP-AES (Qazvin University, Department of Chemistry) Table 3.

Comparison with Other Solid Phase Adsorbents: The proposed methodology was compared to a variety of solid adsorbents reported recently in the literature.

The distinct features are summarized in Table 4. As can be seen from the table, it is evident that the preconcentration factor obtained with silica gel-immobilized 4,4'-Dimethoxybenzil bisthiosemicarbazone (DBTS)is comparable to or even better than most of the other chelating matrices. The other significant feature of the proposed method is the use of environmentally benign polyethylene glycol for the elution of the complex.

CONCLUSION

The proposed spectrophotometric method for mercury is simple, sensitive and exhibits good selectivity. The elution of the complex does not involve strong acids or toxic organic solvents. The advantage of using polyethylene glycol as the eluent lies in the fact that it is non-inflammable, inexpensive and non-toxic. The conventional solvent extraction procedure associated with metal 4,4'-Dimethoxybenzil bisthiosemicarbazone (DBTS)is avoided in this methodology. The highest preconcentration factor attainable was 100 for a 1000 mL sample volume. The method showed minimum interferences with commonly found ions in water sample and the recovery of mercury was quantitative. The important features of the proposed methodare its higher adsorption capacity with good preconcentration factor. The developed method is sensitive in detecting Hg(II) at ppb levels. The column could be used with good precision and quantitative recovery for at least 10 cycles. The quantitative recovery of mercury(II) with a low relative standard deviation of 3% reflects the validity and accuracy of the proposed method when applied to real samples.

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REFERENCES

1. Fergusson, J.E., 1990. The Heavy Elements: Chemistry, Environmental Impact and Health Effects, Pergamon.
2. Camel, V., 2003. Spectrochim. Acta B, 58: 1177.
3. Venkatesh, G. And A.K. Singh, 2007. Talanta, 71: 282.
4. Tuzen, M., K. Parlar and M. Soylak, 2005. J. Hazard. Mater., 121: 79.
5. Moghimi, A. And M.J. Poursharifi, 2009. Asian J. Chem., 21(3): 1657-1666.
6. Wrobel, K., S. Kannamkumarth, K. Wrobel and J.A. Caruso, 2003. Green Chem., 5: 250.
7. Spivakov, B.Ya. And G.I. Malofeeva, O.M. Petrukhin, 2006. Anal. Sci., 22: 503.
8. Walcarius, A. And C. Delcote, 2005. Anal. Chim. Acta, 547: 3.
9. Fontas, C., M. Hidalgo, V. Salvado and E. Antico, 2005. Anal. Chim. Acta, 547: 255.
10. Starvin, A.M. and T. Prasada Rao, 2004. J. Hazard. Mater, 113: 75.
11. Moghimi, A., M.S. Tehrani and S. Waqif Husain, 2006. Material Sci. Res. India, 3(1a): 27.
12. Tehrani, M.S., A. Moghimi and S. Waqif Husain, 2005. Material Science Research India, 3(2):135.
13. Khan, H., M.J. Ahmed and M.I. Bhanger, 2005. Anal. Sci., 21: 207.
14. Soliman, E.M., M.B. Shah and S.A. Ahmed, 2006. Talanta, 69: 55.
15. Tajes-Martinez, P., E. Beceiro-Gonzalez, S. Muniategui-Lorenzo and D. PradaRodriguez, 2006. Talanta, 68: 1489.
16. Roundhill, D.M., 2004. J. Chem. Ed., 81: 275.
17. Smith, C.B., C.L. Raston and A.N. Sobolev, 2005. Green Chem., 7: 650.
18. Haji Shabani, A.M., S.N. Dadfarnia and N. Nasirizadeh, 2004. Anal. Bioanal. Chem., 37: 1388.
19. Moawed, E.A., M.A.A. Zaid and M.F. El-Shahat, 2005. Acta Chromatogr., 15: 220.
20. Mahmoud, M.E., M.M. Osman and M.E. Amer, 2000. Anal. Chim. Acta, 415: 33.
21. Pourrezza, N. And M. Behpour, 2003. Anal. Chim. Acta, 481: 23.
22. Pohl, P. And B. Pruiszz, 2004. Anal. Sci., 20: 1367.
23. Mahmoud, M.E. and G.A. Gohar, 2000. Talanta, 51: 77.
24. Yamini, Y., N. Alizadeh and M. Shamsipur, 1997. Anal. Chim. Acta, 355: 69.
25. Dadfarnia, S., A.M. Salmanzadeh and A.M. Haji Shabani, 2002. Bull. Korean Chem. Soc., 239: 1719.
26. Rudner, P.C., A. Garcia de Torres, J.M. Cano Pavon and F. Sanchez Rojas, 1998. Talanta, 46: 1095.
27. Zhai, U., X. Chang, Y. Cui, N. Lian, S. Lai, H. Zhen and Q. He, 2006. Microchim. Acta, 154: 253.
28. Ghaedi, M., M.R. Fathi, A. Shokrollahi and F. Shajarat, 2006. Anal. Lett., 39: 1171.
29. Kera, D. And N. Tekin, 2005. Microchim. Acta, 149: 193.

30. Moghimi, A., 2006. Oriental J. Chem., 22(3): 527.
31. Nayebi, P. And A. Moghimi, 2006. Oriental J. Chem., 2(3): 507.
32. Moghimi, A., 2007. Chinese J. Chem., 25: 640.
33. Moghimi, A., 2007. Chinese J. Chem., 25(10): 1536.
34. Moghimi, A. And S. Ghammamy, 2007. Environ. Chem. an Indian J., 2(3): 256.
35. Poursharifi, M.J. and A. Moghimi, 2009. Asian J. Chem., 21(4): 2549.
36. Tajodini, N. And A. Moghimi, 2010. Asian J. Chem., 22(7): 4994-5000.
37. Jezorek, J.R., J. Tang, W.L. Cook, R. Obie, D. Ji and J.M. Rowe, 1994. Anal. Chim. Acta, 290: 303.