Asian Journal of Chemistry; Vol. 23, No. 9 (2011), 4117-4121

ASIAN JOURNAL OF CHEMISTRY

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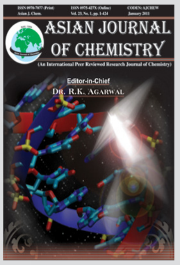

Preconcentration and Determination of Mercury(II) using Modified Silica Gel with Diphenylthiocarbazone by Cold Vapour Atomic Absorption Spectrometry

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(*Received*: 18 December 2010; *Accepted*: 20 May 2011) AJC-9980

A simple and fast method for extraction and determination of trace amounts of mercury(II) ions using silica gel bound amines phase modified with diphenylthiocarbazone (DPC). Silica gel bound amines phase modified with diphenylthiocarbazone (SG-DPC) was prepared based on chemical immobilization technique. The product (SG-DPC) was used as an adsorbent for the solid phase extraction Hg(II) prior to their determination by cold vapour atomic absorption spectrometry (CV-AAS). The uptake behaviours of SG-DPC for extracting Hg(II) ions were studied using batch and column procedures. For the batch method, the optimum pH rang for Hg(II) extraction was 2.5-7. For enrichment and determination of Hg(II) on the newly designed adsorbent, the pH value if 4.0 was selected. Hg(II) ion can be desorbed with 2 mL of 0.5 mol L^{-1} of HCl. The results indicate that SG-DPC has rapid adsorption kinetics using the batch method. The adsorption capacity for Hg(II) ion is in the 1.3 mmol g^{-1}, with a high enrichment factor of 125. The presence of commonly coexisting ions does not affect the sorption capacities. The limit of detection of the proposed method is 7 ng/mL. The relative standard deviation (RSD) of the method under optimum conditions was 4 % (n = 8) for Hg(II). The method is applied to the recovery of Hg^{2+} from different synthetic samples and water sample.

Key Words: Silica gel, Diphenylthiocarbazone, Hg(II), Solid phase extraction, CV-AAS.

INTRODUCTION

Mercury has been considered as a human health hazard because it may cause kidney toxicity, neurological damage, paralysis, chromosome breakage and birth defects[1]. Mercury and its compounds are included in all lists of priority pollutants and different regulations and guidelines have been developed limiting their levels in water and sediments[2]. But it plays an important role in science and technology and inevitably exists in the environment[3-5]. The detection of mercury has long held the attention of the analytical community and, as such, a large number of protocols have arisen[6-9]. On the other hand, the toxicity level of mercury is becoming lower and lower, the direct determination of mercury at sub-microgram per liter level is suffered from the matrix interferences. It is evident that the use of separation and preconcentration procedures is still often necessary before the determination step, despite recent advances in analytical instrumentation[10].

Recently, the solid-phase extraction is being utilized for preconcentration of heavy metals due to its flexibility, economical and environmental-friendly, absence of emulsion, speed and simplicity, sampling in the field, safety and ease of automation[11,26-30]. But the selectivity associated with solid phase extraction using solid support such as active carbon[12], ion exchange resins[13], chelating fibers[14-16] and chelating resins[17-19], *etc*. is still to be improved for specific element. Nowadays, metal ion imprinted polymers (MIIP) have been investigated as highly selective sorbents for solid phase extraction in order to concentrate and clean up samples prior to analysis. One potential application that has recently attracted widespread interest is their use for clean up and enrichment of analytes present at low concentrations in complex matrices[20-24].

In this report, silica gel-diphenylthiocarbazone (SG-DPC) was synthesized by a simple and fast reaction between silica gel phase-bound diphenylthiocarbazone through a Schiff base bond formation. It deserves mentioning that the immobilization of the compound diphenylthiocarbazone was accomplished in a one step reaction. The new adsorbent of SG-DPC has a high sorption capacity for the solid-phase extraction of Hg(II) present in the water samples by cold vapour atomic absorption spectrometry (CV-AAS).

Parameters that can affect the adsorption and elution efficiency of the metal ions were studied in batch and column modes. Then, the method was validated by analyzing the applied to the analysis of water samples with satisfactory results. This element was selected for evaluation of the procedure because Hg(II) is one of the principal heavy metals of analytical interest due to its extreme toxicity even at relatively low concentrations[26,27].

EXPERIMENTAL

Reagents of analytical and spectral purity were used for all experiments and double distilled water was used throughout. Standard laboratory wares and glasswares used were repeatedly cleaned with HNO_3 and rinsed with double distilled water[31].

Standard stock solutions of Hg(II) (1 mg mL^{-1}) was prepared by dissolving a spectral pure grade chemicals mercury(II) nitrate in double distilled water with the addition of hydrochloric acid and further diluted daily prior to use. Silica gel (80-120 mesh, from Aldrich Chemical Company) and diphenylthiocarbazone (all from Merck) were used in this work. 3-Chloropropyltrimethoxysilane was purchased from from Aldrich Chemical Company. Analytical-grade nitrate salts of sodium, magnesium, calcium, strontium, barium, cobalt, nickel, lead, zinc, cadmium and mercury (all from Merck) were of the highest purity available and used without any further purification except for vacuum drying over P_2O_5.

A Varian spectra A.200 model atomic absorption spectrometer in conjunction with a Perkin-Elmer FIAS-400 flow injection system and an AS-90 autosampler was used in this study. The mercury was determined by flow injection cold vapour atomic absorption spectrometry (CV-AAS) modified from the published method[25]. 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 the bandwidth 0.7 nm. The mercury compounds were reduced to metallic mercury with sodium tetrahydroborate and the mercury generator was operated with argon as carrier gas.The pH measurements were carried out by an ATC pH meter (EDT instruments, GP 353). Infrared spectra (4000-400 cm^{-1}) in KBr were recorded on a Varian FT-IR apparatus. peristaltic pump was used in the separation/ preconcentration process. A self-made glass column (20 cm × 4 mm i.d.) was used in column solid phase extraction procedure.

Sample preparation: Tap water (Tehran, taken after 10 min operation of the tap), rain water (Tehran, 23 January, 2007), Snow water (Saveh, 8 February, 2007) and Sea water (taken from Caspian sea, near the Mahmoud-Abad shore) water was collected. To oxidize organic matter such as humic acid, the samples were digested by oxidizing UV photolysis in the presence of 1 % H_2O_2 using a low-pressure Hg lamp which was integrated in a closed quartz vessel[32,33].

Preparation of silica gel-bound diphenylthiocarbazone (SG-DPC): Activation of silica gel surface was first accomplished by refluxing in a conc. HCl for 4 h to remove any adsorbed metal ions, then filtered and repeatedly washed with water until the filtrate is neutral and dried in an oven at 160 °C for 8 h to remove surface-adsorbed water. Then 10 g of dry silica gel was suspended in 150 mL dry toluene containing 10 mL of 3-chloropropyltrimethoxysilane and refluxed overnight. The product silica gel phase was filtered off, washed with toluene, ethanol and diethyl ether and dried in an oven at 60 °C for 6 h. The product was silica gel-bound 3-chloropropyl phase (SG-BCP). For the synthesis of silica gel-bound amines phase, a 10.0 g amount of SG-BCP was suspended in 75 mL of dry toluene and 10 mL of ethylenediamine were added to the suspension and refluxed for 12 h. The product (SG-BEDA) was filtered off, washed with toluene, ethanol and diethyl ether and dried in an oven at 60 °C for 6 h.

For preparation of SG-DPC: Chemically immobilized silica gel-bound diphenylthiocarbazone (SG-DPC). 1.7 g of diphenylthiocarbazone was dissolved in 300 mL dry and hot toluene. The reaction mixture was refluxed for 10 h, then the resulting phase was filtered, washed with toluene, ethanol and dried in an oven at 80 °C for 6 h. The product was silica gel-bound diphenylthiocarbazone.

Batch procedure: The data are given on the simple mean of three replicates, whereas those of the applications were repeated eight times from which the statistical evaluation is pertained. A total of 30 mg of SG-DPC sorbent was suspended with constant stirring for 0.5 h in 10 mL of 1.0 μg mL^{-1} of Hg(II) at the desired pH value. Then the mixture was shaken vigorously for 0.5 h to facilitate adsorption of the metal ions onto the SG-DPC. After extraction, the concentrations of the Hg(II) in solution were directly determined by CV-AAS. The adsorbent was then eluted with HCl of optimum concentration and the desorbed metal ions were measured by CV-AAS.

Column solid phase extraction procedure: About 50 mg of functionalized silica gel adsorbent was packed in a glass column (20 cm × 4 mm i.d.) plugged with a small portion of glass wool at both ends. Before use, the column was treated with 0.5 mol L^{-1} HCl and washed with double distilled water until free from acid. A suitable aliquot of the sample solution containing 1.0 μg mL^{-1} of Hg(II) in a volume of 50 mL was passed through the column after adjusting its pH to 4.0, at a flow rate of 1.5 mL min^{-1} controlled with a peristaltic pump. The bound metal ions were stripped off from the gel column with 0.5 mol L^{-1} HCl. The concentration of the metal ions in the eluate was determined by CV-AAS.

RESULTS AND DISCUSSION

Evaluation of the role of the adsorbent (SG-DPC): Some preliminary experiments were performed for investigation of absence or presence of SG- DPC on the quantitative extraction of Hg(II) (Table-1). The latter case is most probably attributed to the existence of a considerable interaction between Hg(II)and the SG-DPC. It should be mentioned that formation of stable complexes between Hg(II) and SG-DPC at pH = 4. After extraction, the concentrations of the Hg(II) in solution were directly determined by cold vapour atomic absorption spectrometry (CV-AAS).

TABLE-1
EFFECT OF PRESENCE OF MERCURY(II) ON THE SG-DPC[a]

SG-DPC	Extraction per cent of Mercury(II)
Absence	0.08 (3.6)[b]
Presence	97.3 (3.8) to 83 (3.5)

[a]Conditions, pH 4.0; temperature 25 ºC; [b]Values in parentheses are RSDs based on five individual replicate analyses.

Effect of pH: The pH of the sample solutions were adjusted to different values between 2-9 by addition of HCl or a suitable buffer such as sodium acetate-acetic acid or sodium dihydrogen phosphate-disodium hydrogen phosphate and then solutions passed through the adsorbent (SG-DPC). Eventually, the metal ions were stripped by pure methanol or ethanol solutions followed by cold vapour atomic absorption spectrometry of the eluted mercury(II). The acidity of a solution has two effects on metal adsorption. First, protons in an acidic solution can protonate the binding sites of the chelating molecules. Secondly, the hydroxide in a basic solution may complex and precipitate many metals. Therefore, the pH of a solution is the first parameter to be optimized. The reaction between Hg(II) and the adsorbent (SG- DPC) can be influenced by changes of the pH value. In order to determine this parameter, the effect of the pH on Hg(II) sorption onto SG-DPC was investigated over the range of 1 to 7 using the batch procedure. The adsorption experiments were in triplicates. According to the results shown in Fig. 1 up to pH 2.5-7.5, complete recoveries are obtained. However, at higher pH values, percentage recovery decreases. The optimum pH values for maximum Hg(II) have occurred at pH = 4. This can be explained by the different binding affinity of the binding sites for Hg(II) of the adsorbent. In order to avoid hydrolyzing at higher pH values, the pH 4 was chosen as the optimum pH for further studies.

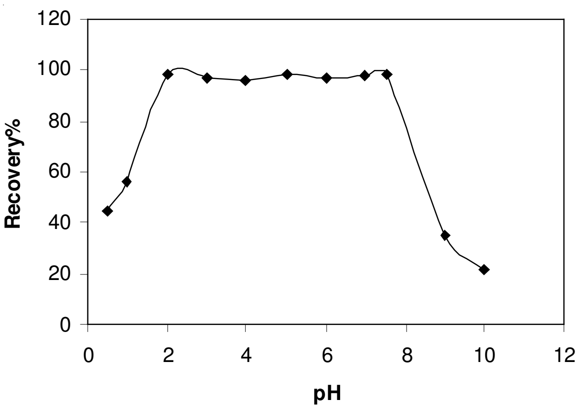

Fig. 1. Effect of pH on sorption of 1.0 μg mL^{-1} Hg(II) on SG-DPC. Other conditions: shaking time 0.5 h, temperature 25 °C

Effect of shaking time: The effect of shaking time is another important factor in evaluating the affinity of SG-DPC to Hg(II). To determine the rate of loading of Hg(II) on the SG-DPC, the recommended batch procedure was carried out. The contact time varied from 5 to 30 min and the results are shown in Fig. 2. The shaking time of 15 min for Hg(II) were found to be sufficient to saturation at pH 4. The results indicate that SG-DPC has rapid adsorption kinetics. Hence, 15 min of stirring was enough to reach maximum values of Hg(II). Therefore, it is suitable for application in flow system or using in the preconcentration of trace Hg(II).

Effect of flow rate: The flow rate of sample solutions through the packed volume is an important parameter because the retention of elements on the adsorbent depends upon the flow rate of the sample solutions. In this study, different flow rates (0.25-2 mL min^{-1}) were investigated using the column procedure. As shown in Fig. 3, the results indicated that the flow rate has a strong influence on the adsorption of Hg(II). The adsorption of Hg(II) decreased with an increase in flow rate. Quantitative recoveries of Hg(II) were obtained with 0.3-0.75 mL min^{-1}. Above 2.0 mL min^{-1}, the recovery of Hg(II) of less than 95 % and flow rates of 0.75 mL min^{-1} were not employed to avoid the long extraction time. Thus, a flow rate of 0.5 mL min^{-1} was selected for column procedure.

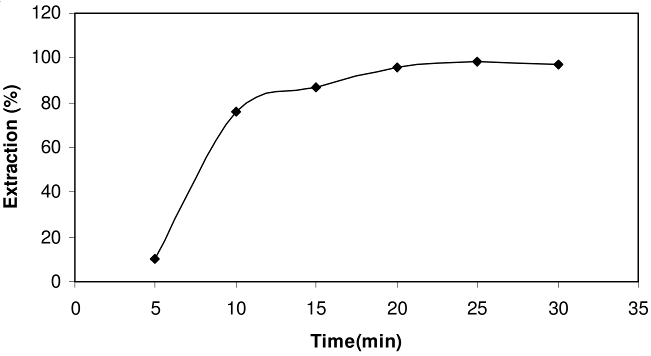

Fig. 2. Effect of shaking time of Hg(II) on SG-DPC. Other conditions: pH 4.0, temperature 25 °C

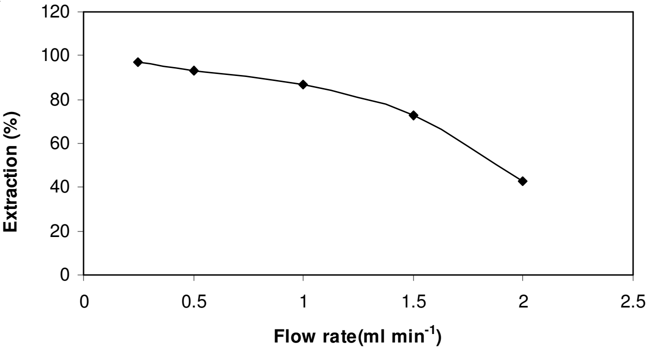

Fig. 3. Effect of solution flow rates on the sorption of Hg(II). Other conditions: 50 mg of SG-DPC, volume 50 mL, pH 4.0, temperature 25 °C

Adsorption capacity: The capacity of the adsorbent is an important factor because it determines how much adsorbent is required to quantitatively remove a specific amount of metal ions from the solutions[34]. The adsorption capacity was tested following the batch procedure. 30 mg of SG-DPC was equilibrated with 50 mL of Hg(II) for 1 h. In order to reach the "saturation", the initial Hg(II) ion concentrations were increased till the plateau values (adsorption capacity values) were obtained. The results showed that adsorption capacity of various metal ions probably differdue to their size, degree of hydration and the value of their binding constant with the adsorbent. The maximum adsorption capacity has been found to be 1.30 mmol g^{-1} for Hg(II).

Choose a proper eluent, maximum sample volume, enrichment factor and elution condition: To choose a proper eluent for the retained 1.0 μg mL^{-1} Hg^{2+} on the SG-DPC, after extraction mercury from 50mL water, the mercury ions were stripped with varying amounts of 1 M concentrations of different acids and the results are summarized in Table-2. It is seen that the elution of mercury from the SG- DPC was quantitative with 1 mL of 0.5 mol L^{-1}.The enrichment factor was studied by the recommended column procedure using increasing volume of investigated Hg(II) solution. The maximum sample volume can be up to 250 mL with 95 % recovery. Several preconcentration papers employing modified silica gel use either nitric acid as eluent[35] or hydrochloric acid[36]. In this work, the elution condition was studied in the column procedure using various concentrations and volumes of HCl for the desorption of retained Hg(II). As shown in Table-2, 1 mL of 0.5 mol L^{-1} HCl was sufficient for 95 % recovery for Hg(II). Quantitative recoveries of all Hg(II)were obtained with 2 mL of 0.5 mol L^{-1} HCl. Therefore, the high enrichment factor of 125 was obtained.

TABLE-2
PERCENTAGE RECOVERY OF Hg(II)ADSORBED ON SG-DPC USING DIFFERENT VOLUMES OF 0.5 M SOLUTIONS OF DIFFERENT ACIDS

Volume (mL)	Recovery (%)			
	Acetic acid	Hydrochloric acid	Hydrobromic acid	Nitric acid
1	65.8 ± 2	95.6 ± 5	38.5 ± 4	40.4 ± 3[a]
2	86.3 ± 4	99.2 ± 2	44.2 ± 5	66.5 ± 3
3	98.8 ± 3	100.2 ± 4	63.2 ± 3	80.6 ± 3
4	99.5 ± 4	100.2 ± 2	83.5 ± 2	92.7 ± 4
5	100 ± 3	101.2 ± 4	92.2 ± 4	93.6 ± 3

[a] $\bar{x} \pm s$ (n = 3). $\bar{x}$ average value for three determinations, s standard deviation.

Effect of coexisting ions: The effect of different cations and anions on the adsorption of Hg(II) on SG-DPC were studied using the batch procedure. The results showed that in excess of 2000 μg mL^{-1} of K^+, Na^+, NO_3^-, Cl^-, NH_4^+; 1000 μg mL^{-1} of Ca^{2+}, Mg^{2+}, SO_4^{2-}; 50 μg mL^{-1} of Cd^{2+}, Mn^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+} and 20 μg mL^{-1} of Fe^{3+} ions did not affect the separation process. The results showed that high concentrations of the ions tested did not interfere with the separation and determination of the analytes. This was due to the low adsorption capacity or rates for interfering ions.

Accuracy and precision of the method: The applicability of the method to real samples with different matrices containing different amounts of a variety of diverse ions was assessed by using it to separate and recover mercury ions from different synthetic and water samples. The results are given in Table-3. The results of three analyses of each sample show that, in all cases, mercury recovery is almost quantitative.

TABLE-3
RECOVERY OF 7 μg MERCURY ADDED TO 1000 mL SOLUTIONS OF THE SYNTHETIC AND WATER SAMPLES

Recovery (%) of Hg^{2+}	Sample
96.5 (2.0)	Synthetic sample 1 (Na^+, Mg^{2+}, Ca^{2+}, Co^{2+}, Pb^{2+}, Cu^{2+}, 2 mg of each cation)
98.2 (1.7)	Synthetic sample 2 (Na^+, Mg^{2+}, Sr^{2+}, Ba^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}, 2 mg of each cation)
99.0 (1.5)	Synthetic sample 3 (Na^+, Mg^{2+}, Zn^{2+}, Cd^{2+}, Cu^{2+}, Mn^{2+}, Fe^{3+} 2 mg of each cation)

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, 23 January, 2007), Snow water (Saveh, 8 February, 2007) and Sea water (taken from Caspian sea, near the Mahmoud-Abad shore) samples were analyzed (Table-4). As can be seen from Table-4 the added mercury ions can be quantitatively recovered from the water samples used.

TABLE-4
ANALYTICAL RESULTS FOR THE DETERMINATION OF Hg(II) IN WATER SAMPLES (CONTAINING 0.1 M ACETATE AT pH = 4.0)

Sample	Hg^{2+} added (μg)	Hg^{2+} determined (ng mL^{-1})
Tap water	0.0	NAPD
	10.0	10.10 (1.5)[a]
Snow water	0.0	NAPD[b]
	10.0	10.54 (2.4)
Rain water	0.0	NAPD
	10.0	10.70 (2.5)
Sea water	0.0	11.53 (1.6)
	10.0	21.98 (1.7)

[a]Values in parentheses are RSDs based on five individual replicate analysis; [b]No adsorption, passes through adsorbent.

The limit of detection (LOD) of the proposed method for the determination of mercury(II) was studied under optimal experimental conditions. The LOD obtained from $C_{LOD} = K_bS_b m^{-1}$ is 7 ng mL^{-1}. The results obtained on 10 replicate measurements revealed a RSD of < 4 %.

According to the results shown in Table-3, good agreement was obtained between the estimated content by the proposed method and the certified values of Hg(II). The results also indicated that the developed preconcentration method for Hg(II) was not affected by potential interferences from the major matrix elements of the analyzed standard material.

Application of the method: The proposed method was then applied for the determination of Hg(II) in sample water samples by CV-AAS. For the analysis of the water samples, The results are given in Table-3. The results of three analyses of each sample show that, in all cases, mercury recovery is almost quantitative.As shown in Table-4, the recoveries of analytes were in the range of 96.5-99 %. It demonstrated the suitability of the SG-DPC for the preconcentration of Hg(II)from water samples prior to CV-AAS analysis.

Conclusion

The proposed method is simple, highly selective and reproducible. The reproducibility of the procedure is at RSD of < 4 %. We had successfully synthesized a novel chemically modified silica gel containing diphenylthiocarbazone and applied to solid-phase extraction and preconcentration of Hg(II) by CV-AAS. This matrix shows better or comparable capacity values and enrichment factor (125) to most of the other matrices used for enrichment of Hg(II) The short loading time of the present matrix makes the analytical procedure reasonably fast. The proposed method was simple and of low cost. The preconcentration of Hg(II) showed the versatility of the system, increasing the analytical frequency. The determination of Hg(II) in the certified simple synthesize showed good accuracy. The proposed procedure can be successfully applied for the determination of Hg(II) in water samples without any effect from the interfering ions.

ACKNOWLEDGEMENTS

The authour wish to thank the Chemistery Department of Varamin Campus Islamic Azad University and Saveh Campus Islamic Azad University for financial support.

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