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Determination of Mercury and Methylmercury in Aqueous Samples by Cold Vapor Atomic Absorption Spectrometry after Pre-Concentration with Bis (2-Mercaptobenzothlazole) Immobilized on Microcrystalline Naphthalene

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A method based on cold vapor atomic absorption spectrometry was used for the determination of trace mercury (Hg^{+2}) and methylmercury ($MeHg^{+}$) in aqueous samples. The mercury in the sample was concentrated in a column packed with bis (2-mercaptobenzothiazole), immobilized on microcrystalline naphthalene. The method was optimized for different parameters affecting the pre-concentration process, in order to obtain better sensitivity. The recovery test showed that the method is quite reliable for use in the determination of trace amounts of mercury in aqueous samples. The method was applied to the speciation of mercury in river water and in the effluents of wastewater treatment plants.

INTRODUCTION

Mercury is one of the most important environmental pollutants and its toxic effects have been known for centuries [1]. Over the last 100 years, mercury has been used extensively by industries in the production of pesticides, electrical apparatus and for dental applications. Mercury is toxic at low levels to animals and humans. A considerable amount of attention has recently been directed towards the determination of ultra trace mercury in biological and environmental samples [2,3]. Upon entering the environment, mercury in any form can be converted into toxic methyl derivatives and accumulated in the tissue of fish and animals. However, organomercuric compounds, such as methylmercury, are more toxic to human beings than inorganic mercury and, therefore, speciation of the different physiochemical forms of mercury in environmental samples is necessary [4,5].

Various methods for the speciation of mercury have been reported, including gas chromatography equipped with cold vapor atomic fluorescence spectrometry (GC-CVAFS) [6], flow injection coupled with liquid chromatography and cold vapor atomic absorption spectrometry (FI-LC-CVAAS) [7], flow injection cold vapor atomic absorption spectrometry (FI-CVAAS) [8], cold vapor vapor atomic absorption spectrometry after pre-concentration with solid phase extraction (SPE-CVAAS) [9,10] and, also, gold amalgamation and cold vapor atomic absorption spectrometry [11,12]. Of the various techniques, cold vapor atomic absorption spectrometry is the most effective and popular, which is widely accepted for the determination of mercury. Although CVAAS offers a low detection limit and high sensitivity, the analysis of trace mercury still requires separation and pre-concentration.

The present work describes the use of bis (2-mercaptobenzothiazole) supported on microcrystalline naphthalene for the pre-concentration of trace mer-

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cury from aqueous samples, before determination by CVAAS.

EXPERIMENTAL

Reagents and Chemicals

All reagents used in this work were of analytical grade or better which are introduced as follows:

- Analar nitric acid, hydrochloric acid and sulfuric acid were used;
- Mercury standard solutions were diluted from 1000 mgl^{-1} of mercury standard solution for atomic absorption spectrometry (BDH Ltd.);
- Stannous chloride 3%(w/v) was prepared by dissolving the appropriate amount of tin(II)chloride dehydrate in 90 ml of 1M hydrochloric acid;
- Bis (2-mercaptobenzothiazole) was synthesized in the laboratory of organic chemistry at the University of Isfahan according to the procedure reported by Tajbakh et al. [13].

Instrumentation

The determination of mercury was carried out by cold vapor atomic absorption spectrometry. The apparatus consisted of the following parts:

1. Bubbler; a 150 ml pear-shaped flask;
2. Absorption cell; a borosilicate glass cell with quartz end windows located in place of the conventional burner of the spectrometer. The alignment of the absorption cell was such that the transmission of the hollow cathode lamp just through the cell was possible;
3. Spectrometer; the determinations were carried out on a Shimadzu atomic absorption spectrometer (Model AA-670). A shimadzu hollow cathode lamp was used as the light source. Table 1 shows the instrumental conditions used for the determination of mercury.

Table 1. Instrumental conditions for the determination of mercury by CVAAS.

Wavelength	253.7 nm
Slit	0.5 nm
Lamp Current	4 mA
Instrumental Mode	Absorption
Sample Mode	Manual
Expansion Factor	1

Preparation of Naphthalene-Bis (2-Mercaptobenzothiazole)

0.3 g of bis (2-mercaptobezothiazole) were dissolved in 40 ml of acetone by stirring. 15 g of naphthalene was then added; the mixture heated at 40°C and was stirred on a hot plate stirrer until the total volume of the mixture was reduced to 20 ml. The mixture was carefully transferred into 300 ml of distilled de-ionized water at room temperature and the naphthale co-precipitated with bis (2-mercaptobezothiazole) was separated. The naphthalene-bis (2-mercaptobezothiazole) was homogenized by stirring with a magnet stirrer for 20 min and used for packing into the column.

Pre-Concentration Procedure

A chromatographic glass column with a diameter of 1 cm was used as the pre-concentration column. The adsorbent was packed into the column to a height of 8 cm. The pH of the sample solution was adjusted to 6 with hydrochloric acid. 250 ml of the sample solution were passed through the column at a flow rate of 3 ml/min. The column was then washed out with 6 M, HCl to elute the adsorbed mercury. The eluent was collected into a 25 ml volumetric flask and made up to the volume by distilled de-ionized water. The latter solution was used for the determination of mercury by CVAAS.

Determination of Inorganic Mercury

The concentration of inorganic mercury in river water was determined by CVAAS, following pre-concentration. The sample solution was transferred into the bubbler of the determination system and 3 ml of 3% tin(II) chloride solution were injected into the bubbler to reduce the mercury into the absorption cell with a nitrogen current (carrier gas). The absorption signal was read and used for the determination of mercury concentration.

The determination of the concentration of inorganic mercury in the effluents of wastewater treatment plants was performed after the digestion of 50 ml of the sample with a mixture of 3 ml of 5% potassium permanganate and 8 ml of 12.5% concentrated sulfuric acid.

Determination of Total Mercury Concentration

50 ml of the sample were digested with a mixture of 0.3 g of potassium persulfate, 8 ml nitric acid and 1 ml sulfuric acid and heated at 95°C for 30 min. The digest was used for the determination of total mercury. The concentration of methylmercury was calculated by subtracting the inorganic concentration of mercury from the total mercury content.

RESULTS AND DISCUSSION

The effects of several parameters, including pH, flow rate, nature of the eluent solution etc., on the pre-concentration efficiency were investigated with a view to achieve better pre-concentration efficiency and sensitivity.

The effect of pH on the adsorption of mercury in the column is demonstrated in Figure 1. The best collection efficiency and reproducibility of the results were at pH = 6-8.

The effect of the flow rate of the sample solution through the column on the pre-concentration efficiency of mercury was studied. Figure 2 shows the results and indicates that at flow rates higher than 4 ml min^{-1} , the adsorption efficiency is reduced, due to insufficient time for effective contacting of the sample with the column packed material.

The desorption of mercury from the column containing packed material and after pre-concentration was investigated by using nitric acid, sulfuric acid, and hydrochloric acid (Figure 3). Better recovery was obtained with hydrochloric acid.

Desorption of Hg^{+2} from the column was performed using solutions of HCl with a concentration of between 1 to 7 M. Figure 4 indicates that recovery increased by increasing the concentration of HCl.

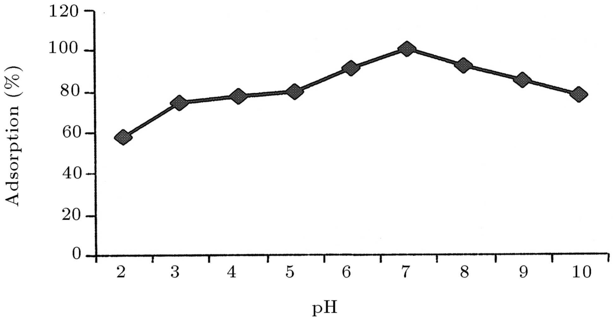

Figure 1. Effect of pH on the adsorption efficiency of the column.

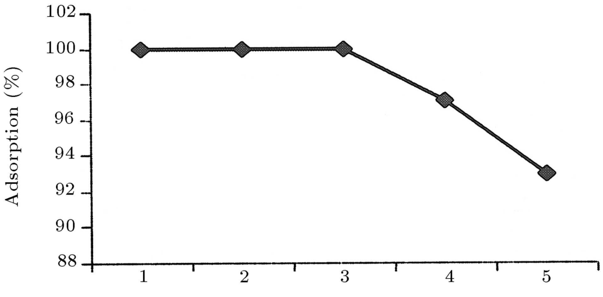

Figure 2. Effect of flow rate of sample on the pre-concentration efficiency.

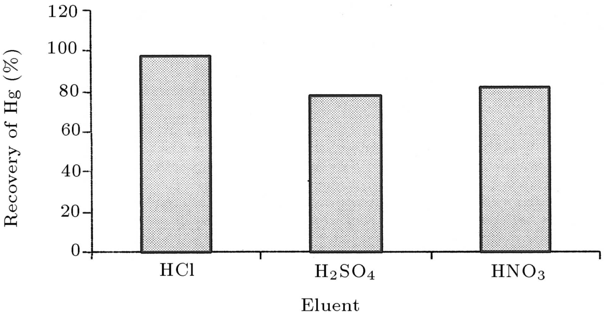

Figure 3. Effect of the selected eluents on the recovery of Hg from the column.

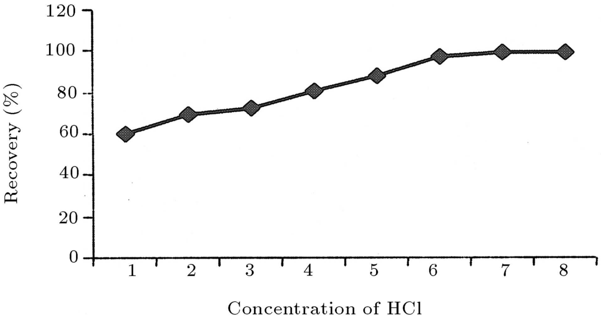

Figure 4. Effect of HCl concentration on recovery of Hg^{+2} from the column.

The effect of the flow rate of HCl on the separation of mercury from the column (after pre-concentration) was examined. Table 2 shows the results.

In order to study the ability of the column for pre-concentration of mercury, 200 ml portions of Hg^{2+} solutions containing 5 μg/l of mercury were passed through the column and the concentration of mercury in the effluent was then determined. It was found that the mercury was adsorbed completely from the solution up to 2000 ml.

The accuracy and selectivity of the pre-concentration procedure for Hg^{2+} in the presence of different cations and anions were examined. A synthetic water containing Na^+ (30 mg/l), Mn^{2+} (30 mg/l), Ca^{2+} (120 mg/l), Ni^{2+} (30 mg/l), Zn^{2+} (30 mg/l), Fe^{2+} (30 mg/l), $SO_4{}^{2-}$ (150 mg/l) and Cl^- (150 mg/l) was prepared and spiked with the different amounts of Hg^{+2} and passed through the pre-concentration column. The results, which are summarized in Table 3, indicate that there is no interference from cations and anions in the pre-concentration of the mercury. It can be concluded that bis (2-mercapobenzothiazole) immobilized on naphthalene is highly selective to Hg^{+2}.

Table 2. Effect of the flow rate of HCl on the recovery of Hg^+ from the column.

Flow Rate of HCl (ml/min)	0.5	0.7	0.9	1.1	1.3
Recovery (%)	100	100	97	92	84

Table 3. Efficiency of pre-concentration of Hg^{+2} from synthetic water. (Number of analyses is 4.)

Hg^{+2} Added (ng/l)	Found (ng/l)	Recovery%	RSD%
250	241.4	98.5	1.5
500	491.5	98.3	1.5
750	733.9	97.8	1.6

Table 4. Recovery of Hg^{+2} and $MeHg^+$ from river water and effluents of wastewater treatment plants.

Sample	Inorganic Mercury (μg/l)		Recovery (%)	Methylmercury (μg/l)		Recovery (%)
	Added	Found		Added	Found	
River Water	0.00	0.68	-	0.00	-	-
	2.00	2.63	98.0	2.00	1.95	97.5
Effluent 1	0.00	3.72	-	0.00	1.85	-
	2.00	5.62	98.0	2.00	3.74	97.1
Effluent 2	0.0	6.42	-	0.00	3.67	-
	2.00	8.21	97.5	2.00	5.49	96.8

The reliability of the method was evaluated by performing a recovery test. The recovery test was performed on river water and also on the effluents of two wastewater treatment plants. The results are summarized in Table 4 and show that the method is quite capable and reliable for the determination of trace amounts of mercury in aqueous samples with different matrices.

The concentration of total mercury was determined in the waters of the Zayanderood river (the most important river in central Iran). The samples were collected from different sampling sites and the results are shown in Figure 5. It is shown that the concentration of mercury continuously increased along the river.

The reason for such an increase in mercury content is the discharge of effluents of wastewater treatment plants and a reduction in the flow rate of the river at end areas. Considering the fact that inorganic mercury can be converted into more toxic species, such as methylmercury, and that Zayanderood river water is finally discharged into the Gav-Khouni, an internationally registered wetland with valuable animal diversity, control of the mercury concentration in the river water is of first priority.

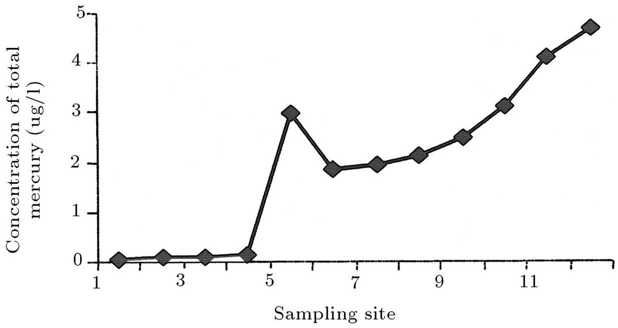

Figure 5. Concentration of mercury along the Zayanderood river.

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