

Preconcentration and Determination of Mercury (II) and Methylmercury in Waters by Immobilized 1,5-Diphenylcarbazone and Cold Vapor Atomic Absorption Spectrometry

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Received July 25, 2002

1,5-diphenylcarbazone was immobilized on sodium dodecyl sulfate coated alumina. The alumina particle was effectively used for collection of mercury (II) and methylmercury cations at sub-ppb level. The adsorbed mercury was eluted with 1 mol L^{-1} of hydrobromic acid solution. The mercury (II) was then directly measured by cold vapor atomic absorption spectrometry utilizing tin (II) chloride where as the total mercury was determined after the oxidation of methylmercury into the inorganic mercury. The methylmercury concentration was calculated by the difference between the value of total mercury and mercury (II). Mercury (II) and methylmercury cations were completely recovered from water with a preconcentration factor of 100 (for 1 L solution). Relative standard deviation at $Hg \text{ L } \mu\text{g L}^{-1}$ level 1.7% ($n = 8$) and the limit of detection was $0.11 \mu\text{g L}^{-1}$. The procedure was applied to spring water, well water and seawater and accuracy was assessed through recovery experiments.

Key Words : Mercury, Methylmercury, 1,5-Diphenylcarbazone, Cold vapor atomic absorption spectrometry

Introduction

In recent years, there has been an increased concern over the concentration of mercury in drinking and natural water due to its high toxicity and pollution to the environment, and especially the aquatic system.^{1,2} Mercury is leached from rocks and soil into water system by natural processes, some of which are accelerated by human activities. The World Health Organization (WHO) recommends a limit of $1 \mu\text{g L}^{-1}$ of mercury in drinking water,² which require a very accurate, selective and sensitive method of measurement. Because of its simplicity, high sensitivity and relative freedom from interference, cold vapor atomic absorption spectrometry (CVAAS) has generally been used for the determination of mercury. But on account of extremely low concentration of mercury (ng L^{-1}) in water samples, the high salinity of seawater, and the growing awareness of environmental mercury pollution, a separation and preconcentration step is required. The most frequent used method for preconcentration of mercury from natural waters is coprecipitation,³ solvent extraction,⁴ electrochemical precipitation^{5,6} and solid phase extraction.⁷⁻⁹ Solid phase extractions with immobilized organic compounds is attracting great interest because of its high enrichment capability and operation simplicity. Immobilization of organic ligands on the surface of an inorganic or organic solid support is usually aimed to modify the surface with certain target functional groups that can be exploited for further analytical uses.

Chelating sorbents can be obtained in a very simple manner by impregnation of inorganic or organic solid support with organic ligands. Several method for preconcentration of

mercury utilizing such an approach have been devised; among them are, dithizone immobilized on different base,¹⁰⁻¹⁶ sulfonic acid dithizone on anion exchanger,¹⁷ dithiocarbamate resin,¹⁸ thiomichelers keton,¹⁹ N-(2-pyridyl methyl) chitison (PMC),²⁰ 2,3-dimercapto propane-1-sulfonate (DMPS),²¹ dithiocarbamate,²² sodium diethyl dithiocarbamate,²³ dithizone derivative.²⁴ To date no such study has been directed at immobilization of 1,5-diphenylcarbazone (DPC), a well known classical chelating ligand for mercury extraction.²⁵ So it was considered appropriate to investigate whether this material would adsorb on surfactant coated support in a manner already demonstrated for some ligands.²⁶ Studies confirmed the immobilization of 1,5-diphenylcarbazone on surfactant-coated alumina and a rapid and accurate method for preconcentration, and separation of traces of mercury in surface and seawater samples based on CVAAS have been developed.

Experimental Section

Apparatus. A Buck scientific atomic absorption spectrometer Model 210 VGP was used for all measurement. A mercury hollow cathode lamp was used as the light source, and its operating current was adjusted to the value recommended by the manufacturer. The wavelength used was 253.7 nm and the bandwidth 0.7 nm.

A Buck scientific hydride vapor generator, Model 1015 was used for mercury generation. The inorganic mercury was reduced to metallic mercury with tin (II) chloride and the mercury generator was operated with nitrogen as carrier gas. The organic mercury was oxidize to inorganic mercury before to analysis by potassium permanganate, sulfuric acid and nitric acid solution as recommended by Buck scientific

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instruction.²⁷⁻²⁹

The flow of the sample through the column was adjusted with a Leybold vacuum pump model PJ7721-035.3.

Reagents. All the reagents were of analytical-grade, and triply distilled; de-ionized water was used throughout.

A stock 1000 $\mu\text{g mL}^{-1}$ of mercury (II) was prepared by dissolving 0.1354 g of HgCl_2 (Merck) in 5 mL of concentrate nitric acid and was diluted to 100 mL.

A stock methylmercury solution (1000 $\mu\text{g mL}^{-1}$ Hg) was prepared by dissolving 0.1252 g of CH_3HgCl (Merck) in a small amount of acetone in a 100 mL volumetric flask and was diluted to the mark with water.

A 10% (m/V) tin chloride solution was prepared by dissolving 10 g SnCl_2 in 20 mL concentrate hydrochloric acid and diluting to 100 mL with water. A 0.2% solution of 1,5-diphenylcarbazone (Merck) was prepared by dissolving 0.2 g of it in 100 mL ethanol.

Sodium dodecyle sulfate (SDS) (Merck), and 1,5-diphenylcarbazone were used without further purification.

Alumina (10, 50 μm , α , γ type, chromatographic grade, Merck) was purified by shaking with 5 mol L^{-1} nitric acid and washing three times with water, alumina fiber was activated by heating at 500 $^\circ\text{C}$ for 3 hrs as recommended by S.Dadfarnia.³⁰ Sulfhydryl cotton was prepared according to Lee and Mowter procedure.³¹

Preparation of 1,5-diphenylcarbazone coated alumina. 1.5 g of alumina was added to 50 mL of a solution containing 100 mg of sodium dodecyl sulfate (SDS). The solution was mixed with a magnetic stirrer, then 4 mL of 0.2% solution of 1,5-diphenylcarbazone was added, and the pH was adjusted approximately to 7. The solution was shaken for 15 min, and was filtered through Millipore filter for preparation of the column (10 mm diameter and 18 mm height). A color change of alumina from white to reddish-orange was used as the indication of immobilization of 1,5-diphenylcarbazone on alumina. The coated alumina was used for preparation of the column. When kept in a refrigerator the sorbent is stable at least for one week.

Determination of capacity of immobilized H_2DPC on surfactant coated alumina. 50 mL of a solution containing 500 μg of Hg (II) at optimum pH was added to 1.5 g of alumina coated with 1,5 diphenyl carbazone. The solution was mixed with magnetic stirrer for 1 hr, the mixture was then centrifuged and the amount of mercury in supernatant solution was determined. The capacity of sorbent was determined by the difference of the amount of mercury in the original and final solution.

Recommended procedure. The pH of sample (500-2000 mL) was adjusted to ~ 7 by addition of ammonia solution (0.1 mol L^{-1}). The samples were passed through the column of 1,5-diphenylcarbazone coated alumina with the aid of a suction pump, at a flow rate 20-60 mL min^{-1} , to effect the deposition of analyte. The adsorbed mercury was then eluted with hydrobromic acid (10 mL, 1 mol L^{-1}) with a flow rate of 1.5 mL min^{-1} . The inorganic mercury in the eluent was directly measured by CVAAS. The total mercury was determined after the oxidation of methylmercury into the inorganic

mercury with potassium permanganate, sulfuric/nitric acid solution according to the accepted procedure²⁷⁻²⁹ as follows: 2.5 mL of concentrate sulfuric acid, 1.5 mL of concentrate nitric acid and 7.5 mL of 5% potassium permanganate solution were added to the eluent. After 15 min, 5 mL of 5% peroxydisulfate was added and the solution was heated for 2 hrs at 90 $^\circ\text{C}$ over a water bath. The solution was then let to cool, and in order to reduce the extra permanganate, 3 mL of 6% hydroxyl ammonium chloride solution was added. The total mercury was then determined by CVAAS. The methyl mercury concentration was calculated by the difference between the values of the total mercury and mercury (II).

Results and Discussion

It was somewhat surprising to discover that 1,5-diphenylcarbazone, the classical analytical reagent, has not so far been incorporated in a resin matrix. This may be due to theoretical considerations, which suggest that 1,5-diphenylcarbazone should show little tendency to be coupled with species generally used to synthesize chelating resins. However Hiradie *et al.*³² proposed that water-insoluble chelating sorbents could be trapped into the aggregate of sodium dodecyl sulfate (SDS) on alumina particles. The molecules of anionic surfactants can effectively be sorbed on the positively charged surface. Therefore, the capability of α , γ fibrous alumina and sulfhydryl cotton on sorption of SDS was examined.

To 50 mL of water, 1.5 g of the base and 100 mg of surfactant were added, and the pH was adjusted to different values with hydrochloric acid or aqueous ammonia solution. The suspension was shaken for 5 min, and after centrifugation the amount of SDS left in solution was determined by toluidine blue method.¹⁴ The result of this study is shown in Figure 1 and clearly indicates the higher power of γ -alumina on sorption of SDS over a wide pH range (1-6) in compared

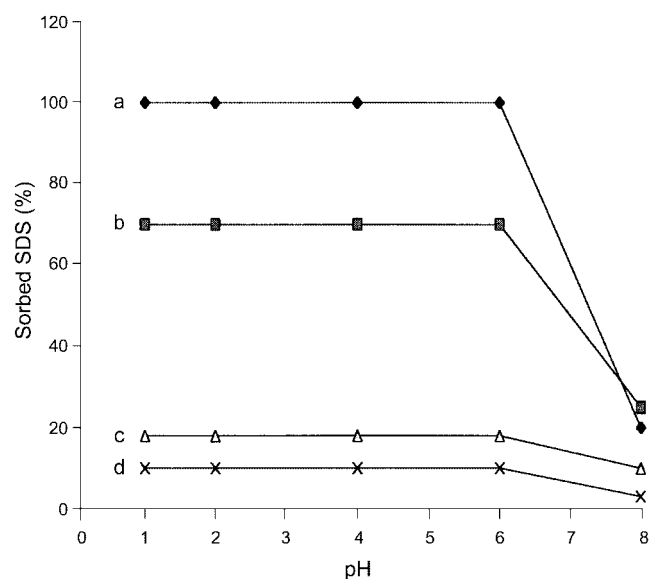


Figure 1. Effect of pH on absorption of SDS on different bases: a; γ -alumina b; sulfhydryl cotton c; α -alumina d; alumina fiber.

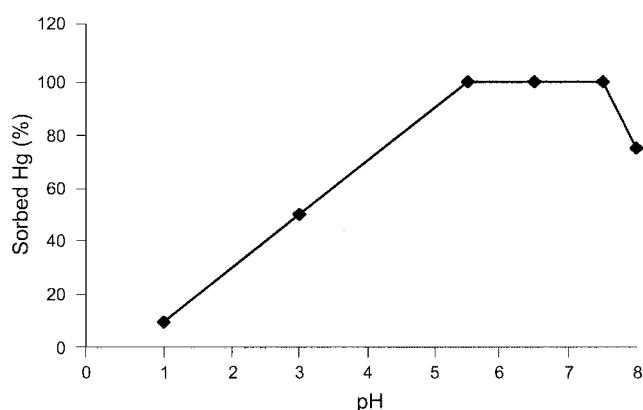
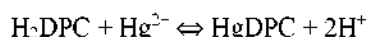


Figure 2. Effect of pH on mercury deposition: mercury concentration 10 ng mL^{-1} ; concentrated volume 50 mL ; flow rate 20 mL min^{-1} .

with other bases used. The scant adsorption of SDS on α and fibrous alumina may be related to their chemically inert surface, while the lower capability of sulfhydryl cotton is probably due to the difference in structure and active groups (S in sulfhydryl cotton and O in γ -alumina) of the two bases. Therefore the use of γ -alumina was found to be essential for the preparation of chelating sorbent. Mixing the 0.2% alcoholic solution of 1,5-diphenylcarbazone with the solution of SDS and alumina caused the 1,5-diphenylcarbazone to be trapped homogeneously on the hemi-micells or ad-micells formed by SDS on alumina surface and the color of alumina was changed from white to reddish-orange.

Analyte deposition was dependent on sample pH and as shown in Figure 2, high deposition efficiency was achieved over a pH range of 5.5-7.5. Mercury form a complex with 1,5-diphenylcarbazone (H_2DPC) according to the following equation:



Therefore, the progressive decrease in the retention of mercury at low pH is due to competition between the hydrogen ion and mercury for adsorption on DPC. While the decrease in adsorption at $pH > 7.5$ is probably due to factors such as the precipitation of mercury as mercury hydroxide and the formation of negative charge on the alumina surface, which

Table 1. Effect of flow rate on mercury deposition: mercury concentration 10 ng mL^{-1} ; concentrated volume 50 mL ; $pH = 7$

Flow rate (mL/min)	Adsorbed Mercury (%)
2	97 ± 1
5	98 ± 2
10	100 ± 1
12	99 ± 1
15	100 ± 2
20	100 ± 1
30	98 ± 1
40	100 ± 1
50	97 ± 1
60	98 ± 2

result in the reduction of SDS adsorption. To achieve high efficiency a pH of ~ 7 was selected for subsequent studies.

The results of Table 1 indicate that the kinetic of exchange on the deposition step is very fast and signal response is independent on the flow rate up to 60 mL min^{-1} , which is one of the advantages of this method over the other solid phase extraction of mercury.^{13,14,16,24} In subsequent study a flow rate of 20 mL min^{-1} was chosen as was more convenient. However, the kinetic of desorption of mercury from the column was slow, with 10 mL eluent the complete elution of analyte was possible at a flow rate of 1.5 mL min^{-1} .

The nature of eluents were found to have a significant effect on the desorption process of mercury from the column and its subsequent measurement by CVAAS. 10 mL of different eluents such as hydrochloric, hydrobromic, hydroiodic acids, acetone and thiourea were examined, and we found that hydrobromic acid was the most suitable eluent for this purpose. With $9M$ hydrochloric acid and $4M$ nitric acid the complete recovery of mercury was possible, but some of the SDS was also desorbed and caused foam formation during measurement, which blocked the T cell vapor generator. When $1 M$ hydroiodic acid was used as eluent, a yellow precipitate, probably HgI_2 was formed in the cold vapor generator. The mercury was completely recovered by acetone, but the background of the measurement was very noisy. The thiourea (pH range 1-5) as eluent was incapable of complete recovery of adsorbed mercury. Therefore, HBr was selected as the eluent, and the effect of its concentration was considered. It was found that 10 mL of $1 M$ HBr solution is sufficient for quantitative recovery of adsorbed mercury.

The capacity of immobilized H_2DPC on surfactant coated alumina was examined and was found to be $330 \mu\text{g g}^{-1}$ as Hg^{2+} , which indicates that the column is suitable for pre-concentration of traces of mercury.

Basic analytical performance. Performance characteristics of the technique were obtained by processing standard solutions of mercury. For a sample of 500 mL , the calibration graph exhibited linearity over the range of $0.6\text{-}5 \mu\text{g L}^{-1}$, with a correlation coefficient of 0.9999 ($A = 1.7724C + 0.1031$, where A is the area of peak and C is the concentration). The relative standard deviation ($n = 8$) at $1 \mu\text{g L}^{-1}$ (sample volume 500 mL) was 1.7% and the detection limit, based on three times the standard deviation of the blank signal for processing 500 mL of solution, was $0.11 \mu\text{g L}^{-1}$. Extending the sample processing volume, however, results in improved method sensitivity. In the present study sampling volume up to 1000 mL for a solution of $2 \mu\text{g L}^{-1}$ mercury were investigated and response was found to increase linearly with volume ($r^2 = 0.9996$).

The capability of the system to quantify the methylmercury at low level ($\mu\text{g L}^{-1}$) was investigated. Consideration of the relative peak area of responses of 250 mL of standard solutions of methylmercury ($2 \mu\text{g L}^{-1}$ with respect to mercury), mixture of mercury and methylmercury ($2 \mu\text{g L}^{-1}$ with respect to Hg) after oxidation, and inorganic mercury ($2 \mu\text{g L}^{-1}$) without oxidation revealed the suitability of the method

Table 2. Effect of diverse anion on recovery of mercury: mercury concentration 10 ng mL⁻¹; concentrated volume 50 mL; pH = 7; flow rate 20 mL min⁻¹

Anions	mole ratio of X ⁿ⁻ /Hg ²⁺	Recovery (%)
ClO ₄ ⁻	1000	99.4
Cl ⁻	1000	99.5
NO ₃ ⁻	1000	96.5
SO ₄ ²⁻	1000	97.8
CH ₃ COO ⁻	650	97.6
C ₂ O ₄ ²⁻	500	98.5
I ⁻	500	99.7
CO ₃ ²⁻	500	98.5
Br ⁻	500	99.8

Table 3. Effect of divers cation on recovery of mercury: mercury concentration 10 ng mL⁻¹; concentrated volume 50 mL; pH = 7; flow rate 20 mL min⁻¹

Cation	mole ratio of M ⁿ⁺ /Hg ²⁺	Recovery (%)
Ca ²⁺	100000	99.2
Mg ²⁺	16400	99.3
Na ⁺	2000	99.8
K ⁺	1030	99.7
Ag ⁺	185	98.7
Cd ²⁺	180	98.6
Pb ²⁺	100	98.5
Ni ²⁺	18	98.5
Cu ²⁺	17	99.7
Zn ²⁺	16	98.6

for quantitative measurement of methylmercury.

Effect of diverse ions. The selectivity and utility of the method were examined in the presence of various ions (Table 2 and 3). An error of ± 3% in recovery was considered tolerable.

As the results indicated the cations and anions at the given mole ratio in the table, were tolerated. This suggest a preferential uptake of mercury relative to matrix ions, and it is projected that in the analysis of samples, the deposition efficiency would not be affected by the presence of a high concentration of matrix ions.

Application. The feasibility of the technique for the determination of mercury in different matrices was examined. Recovery of mercury (II) and methylmercury from a synthetic water sample having the composition (mg L⁻¹) Na⁺ 30, K⁺ 8, Mg²⁺ 40, Ca²⁺ 110, Cl⁻ 248, SO₄²⁻ 158, and conforming to acceptable limits for drinking water, was studied. The results (Table 4) show that the presence of salts do not affect the degree of sorption of these cations.

The procedure was also applied to the determination of inorganic and total mercury in well water, spring water and seawater. Reliability was checked by spiking experiments. The results of this investigation are given in Table 5 and 6. It can be seen that the recovery of spiked samples is good, which indicates the capability of the system in determination of mercury for water samples.

Table 4. Recovery of mercury and methylmercury cations from synthetic water:: concentrated volume 500 mL; pH = 7; flow rate 20 mL min⁻¹

Species	Added (ng)	Determined*	Recovery (%)	RSD (%)
Hg ²⁺	300	301.8 ± 8.2	100.6	2.7
	500	499.6 ± 7.1	99.9	1.4
CH ₃ Hg ⁺	300	302.5 ± 4.5	100.8	1.5
	500	494.7 ± 12.6	98.9	2.5

*Mean ± standard deviation (n = 3).

Table 5. Determine of inorganic mercury in natural water: concentrated volume 500 mL; pH = 7; flow rate 20 mL min⁻¹

	Mercury (ng L ⁻¹)		Recovery (%)	RSD (%)
	Added	Determined*		
Well water	0	138.5 ± 4.3		3.1
	300	444.4 ± 5.6	101.3	1.3
Spring water	0	not detected		
	300	301.5 ± 7.5	100.5	2.5
Sea water	0	125.3 ± 2.8		2.2
	300	428.4 ± 4.3	100.7	1

*Mean ± standard deviation (n = 3).

Table 6. Determine of total mercury in natural water: concentrated volume 500 mL; pH = 7; flow rate 20 mL min⁻¹

	Mercury (ng L ⁻¹)		Recovery (%)	RSD (%)
	added	Determined*		
Well water	0	140.4 ± 4.3		3.1
	300	437.8 ± 4.3	99.4	1
Spring water	0	not detected		
	300	299.4 ± 3.8	99.8	1.3
Sea water	0	131.9 ± 4.3		3.3
	300	430.3 ± 2.8	99.6	0.7

*Mean ± standard deviation (n = 3).

Conclusion

It has been demonstrated that the H₂DPC immobilized on surfactant coated alumina provides a novel, fast route for determination of inorganic and total mercury in several categories of natural waters. The main benefits of solid phase extraction methodology, were enhanced sensitivity, attainability of large preconcentration factor and facility of separation.

Future work will be directed at biological samples and assessment of the multielement enrichment capability of column for determination of ultratrace mercury in seawater.

Acknowledgment. The authors wish to thank the graduate school of Yazd university for its support.

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