



## Preconcentration, speciation and determination of ultra trace amounts of mercury by modified octadecyl silica membrane disk/electron beam irradiation and cold vapor atomic absorption spectrometry

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### ABSTRACT

Mercury (II) and methyl mercury cations at the Sub-ppb level were adsorbed quantitatively from aqueous solution onto an octadecyl-bonded silica membrane disk modified by 2-[(2-mercaptophenylimino)methyl] phenol (MPMP). The trapped mercury was then eluted with 3 ml ethanol and Hg<sup>2+</sup> ion was directly measured by cold vapor atomic absorption spectrometry, utilizing tin (II) chloride. Total mercury (Hgt) was determined after conversion of MeHg<sup>+</sup> into Hg<sup>2+</sup> ion by electron beam irradiation. A sample volume of 1500 ml resulted in a preconcentration factor of 500 and the precision for a sampling volume of 500 ml at a concentration of 2.5 μg l<sup>-1</sup> (n = 7) was 3.1%. The limit of detection of the proposed method is 3.8 ng l<sup>-1</sup>. The method was successfully applied to analysis of water samples, and the accuracy was assessed via recovery experiment.

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### 1. Introduction

Mercury is a highly toxic element that is found both naturally and as an introduced contaminant in the environment. The toxic effect of mercury depends on its chemical form and the route of exposure. Methyl mercury is the most toxic form. It affects the immune system, alters genetics and enzyme systems, and damages the nervous system, including coordination and the senses of touch, taste and sight. Exposure to methyl mercury is usually by ingestion, and it is absorbed more readily and excreted more slowly than other forms of mercury. Elemental mercury causes tremor, gingivitis, and excitability when vapors are inhaled over a long period of time. Although it is less toxic than methyl mercury, elemental mercury may be found in higher concentration in environment [1]. Thus determination of species of mercury in water samples is a challenging task. Cold vapor atomic absorption spectrometry (CVAAS) is widely accepted technique for determination of mercury due to its simplicity, high sensitivity and relative freedom from interferences [2–4]. However on account of extremely low concentration of mercury (ng l<sup>-1</sup>) in water samples, the high salinity of seawater, and the growing awareness of environmental pollution, a separation and preconcentration step is required.

Although different approaches have been proposed for mercury determination at trace level by CVAAS [5–7], the recent development in the field of the preconcentration of mercury ions are focused to solid phase extraction (SPE) [4,8–12]. In compare to classical liquid–liquid extraction, SPE methods are easier to perform, less expensive from a labor and solvent consumption stand point and can help to provide an overall safer working environment. Among different SPE methods, disks modified by suitable ligands are easier to use for selective separation and preconcentration of metal ions from real samples [7]. This is due to lower back pressure encountered with these devices which enables the uses of higher flow rates and their wide bed minimizes the chance of plugging. Disks modified by hexathia-18-crown-6-tetraone [13], dibenzodiazathia-18-crown-6-dione [14], and isopropyl 2-[(isopropoxycarbothiyl)disulfanyl] ethane thioate [15] ligands have been successfully used for the separation and preconcentration of Hg (II) ion followed by its determination by CVAAS.

Electron beam irradiation had been used for purification of water [16–18], but to the best of our knowledge there is no report on the use of electron beam for the conversion of organometallic to inorganic compounds. In this study the octadecyl silica membrane disks modified by 2-[(2-mercaptophenylimino)methyl] phenol (MPMP) was used for preconcentration of Hg<sup>2+</sup> and MeHg<sup>+</sup> from water samples. The adsorbed mercury was then eluted and Hg<sup>2+</sup> ion was directly measured by CV-AAS, whereas the total mercury was determined after treatment of eluents by electron beam.

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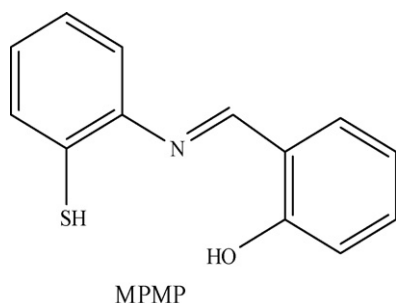


Fig. 1. Structure of MPMP ligand.

## 2. Experimental

### 2.1. Reagents

All chemicals were of highest purity available from Merck chemical company and used as received, and triply distilled water was used throughout. A stock  $1000 \mu\text{g ml}^{-1}$  of mercury (II) was prepared by dissolving  $0.1354 \text{ g HgCl}_2$  (Merck) in  $5 \text{ ml}$  concentrate nitric acid and was diluted to  $100 \text{ ml}$  with water. A stock methyl mercury solution ( $1000 \text{ mg l}^{-1}$ , Hg) was prepared by dissolving  $0.1252 \text{ g of CH}_3\text{HgCl}$  (Merck) in small amount of acetone in a  $100 \text{ ml}$  volumetric flask and was diluted to the mark with water. Working solutions were prepared daily from the stock solution by serial dilution with water.

A  $100 \text{ g l}^{-1}$  tin chloride solution was prepared by dissolving  $10 \text{ g SnCl}_2$  in  $20 \text{ ml}$  concentrate hydrochloric acid and diluting to  $100 \text{ ml}$  with water. 2-[(2-Mercaptophenylimino)methyl] phenol, Fig. 1) was synthesized and purified as described elsewhere [19,20].

The buffer of acetate (pH 5) was prepared by addition of  $35.97 \text{ g}$  of sodium acetate and  $14.3 \text{ ml}$  of concentrated acetic acid into a  $250 \text{ ml}$  flask, and diluting to the mark with water.

### 2.2. Apparatus

A Buck Scientific atomic absorption spectrometer, model 210 VGP, was used for all absorption measurements. A mercury hollow cathode lamp (Westinghouse, WL-22847) was used as the light source and its operation current was adjusted to the value recommended by the manufacturer. The wavelength and bandwidth were set at  $253.7$  and  $0.7 \text{ nm}$ , respectively.

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 methyl mercury was decomposed to inorganic mercury by electron beam irradiation ( $5 \text{ kGy}$ ). The irradiation was carried out at Yazd Radiation Processing Center using an electron beam accelerator RHOOTRON TT200. The specifications of the electron beams accelerator are given in Table 1.

Solid phase extractions were performed with  $47 \text{ mm}$  diameter  $\times 0.5 \text{ mm}$  thickness 3 M Empore™ membrane disk containing octadecyl ( $\text{C}_{18}$ ) Silica ( $8 \mu\text{m}$  particle,  $60 \text{ \AA}$  pore size) from Varian. The disk was used in conjunction with the standard Millipore  $47 \text{ mm}$  filtration apparatus.

### 2.3. Preparation of modified disk

The disk was prepared as described before [21]; i.e. in order to clean the membrane disk; it was placed in the filtration apparatus and was washed with  $10 \text{ ml}$  of methanol and  $10 \text{ ml}$  acetonitrile. The disk was dried by passing air through it for several minutes. Then,

Table 1  
RHODOTRON TT 200 electron beam accelerator parameter

Beam energy	5 and 10 MeV
Beam power at 10 MeV	~70 kW
Beam power at 5 MeV	~35 kW
Energy dispersion at 10 MeV	$\pm 300 \text{ keV}$
Scanning range	30–100 cm
Total power consumption	<300 kW
Rf	107.5 MHz
Rf power output	200 kW
Electron gun average current	0–10 mA
Resolution	$\pm 50 \mu\text{A}$

a solution of  $7 \text{ mg}$  MPMP in  $6 \text{ ml}$  chloroform was introduced onto the disk and was drawn slowly throughout by applying a slight vacuum. After complete penetration of MPMP inside the disk, the solvent was evaporated in an oven at  $50 \text{ }^\circ\text{C}$  for about  $5 \text{ min}$ . Finally, the disk was washed with  $20 \text{ ml}$  of distilled water and was dried by passing air through it. The disk is now modified with MPMP and is ready for sample extraction. It should be noted that the modified disk thus prepared can be kept at room temperature for over a week, before its use for the extraction. A single disk can be re-modified with MPMP more than 15 times.

### 2.4. Preparation of water samples

The samples were filtered through a Millipore filter; the pH was adjusted to  $\sim 5$  with buffer and was treated according to the given procedure.

### 2.5. Procedure

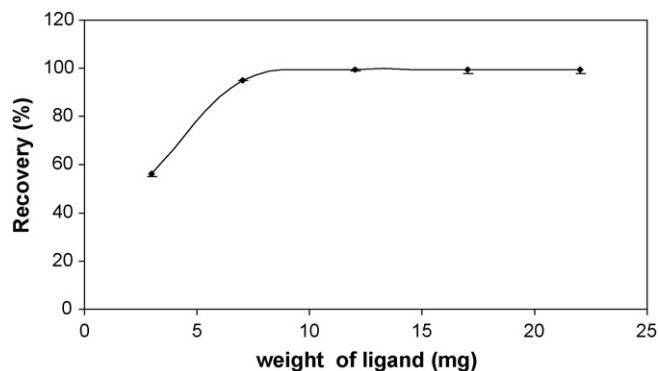
The pH of the sample solution was adjusted to  $\sim 5$  by addition of acetate buffer solution and was passed through the modified membrane disk at a flow rate of  $40 \text{ ml min}^{-1}$  with the aid of a suction pump. The disk was dried by passing air through it. A test tube was then placed under the extraction funnel and the retained mercury was eluted with  $5 \text{ ml}$  of ethanol at a flow rate of  $2 \text{ ml min}^{-1}$ . The amount of inorganic mercury in the eluent was directly measured by CV-AAS, and  $5 \text{ ml}$  of acidic solution of tin (II) chloride was used as reducing agent.

The total mercury was determined after conversion of methyl mercury into the  $\text{Hg}^{2+}$  by irradiation of the eluent with electron beam (a dose of  $5 \text{ kGy}$ ). The  $\text{MeHg}^{2+}$  concentration was then calculated by the difference between the values of total mercury and mercury (II).

Before commencement of the next cycle the disk is re-modified according to Section 2.3.

## 3. Results and discussion

Schiff bases derived from salicylaldehyde (salens) as polydentate ligands are known to form stable complexes with transition metal ions [22–25]. There have been some reports dealing with the analytical application of these ligands as ion carrier in the construction of membrane electrode [25] and as modifier in solid phase extraction [26–29]. 2-[(2-Mercaptophenylimino)methyl] phenol Schiff base with one oxygen, one sulfur and one nitrogen donating group in its structure and is insoluble in water at neutral pH. Previously we reported the use of octadecyl silica membrane disk modified by MPMP for preconcentration and separation of silver [21]. Based on the well known hard–soft acid base theory [29] it was expected that MPMP is capable of complex formation and separation of mercury from various matrices. Preliminary experiments confirmed that the modified disk with MPMP was capable of retaining mercury ions from solutions, whereas the bare mem-



**Fig. 2.** Amount of MPMP for proper modification of the octadecyl silica membrane disk for the quantitative recovery of mercury.

brane disk did not show any tendency for the retention of mercury ions.

The optimal amount of MPMP for proper modification of the octadecyl silica membrane disk for the quantitative extraction of 50  $\mu\text{g}$  mercury (II) ion from 50 ml of aqueous sample was investigated. The results of this study is shown in Fig. 2 and indicate that with 7 mg or more of the MPMP, the extraction of mercury was quantitative while the use of less amount of ligand resulted in considerable decrease in the extraction of analyte. Therefore for subsequent work the disk was modified with 7 mg of the ligand.

In order to choose a proper eluent for the retained mercury ions, after the extraction of 250 ng of inorganic mercury from 25 ml sample solution by modified disks, the mercury ions were stripped with 10 ml of varying concentration of various stripping agents and the results are summarized in Table 2. The results of this study (Table 2) revealed that, of the different stripping agents examined, ethanol provide quantitative elution of mercury as MPMP–mercury complex from the disk. Furthermore the effect of ethanol volume on elution of retained mercury was examined and it was found that 3 ml of ethanol is sufficient for quantitative stripping of retained mercury.

The effect of pH on the retention of 250 ng of mercury from 50 ml of solution onto modified disk was studied. The pH was adjusted by either diluted nitric acid or ammonium hydroxide solution. The results of this investigation (Fig. 3) revealed that mercury was quantitatively adsorbed over the pH range of 4–6. Thus an optimum pH of  $\sim 5$  was selected for subsequent work, and the pH was adjusted by acetic acid/sodium acetate buffer. At pH greater than 6, preconcentration of mercury extremely decreased probably due to precipitation of mercury as mercury hydroxide. A pH greater than 8.5 were not tested because of the possibility of hydrolysis of membrane disk.

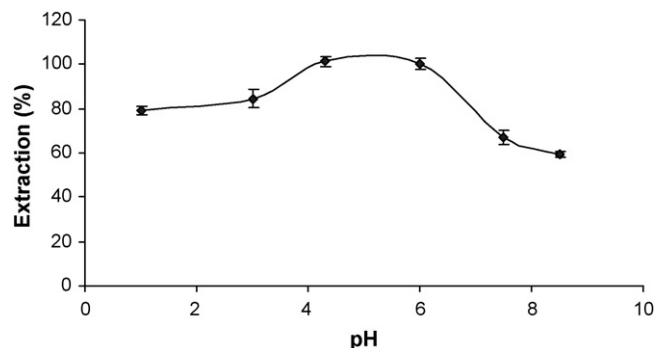
The effect of sample flow rate on the extraction of mercury by the modified disk was investigated in the flow rate range of

**Table 2**

Recovery of mercury from the modified membrane disk using different stripping agent:  $[\text{Hg}^{2+}] = 10 \mu\text{g l}^{-1}$ ; sample volume 25 ml pH  $\sim 5.5$  eluent volume 10 ml

Stripping solution	Recovery (%)
HBr (0.1 mol l <sup>-1</sup> )	45.3 $\pm$ 1.4
HBr (3 mol l <sup>-1</sup> )	66.6 $\pm$ 1.4
HNO <sub>3</sub> (1 mol l <sup>-1</sup> )	71.5 $\pm$ 2.7
HNO <sub>3</sub> (3 mol l <sup>-1</sup> )	80.6 $\pm$ 1.4
NH <sub>2</sub> CSNH <sub>2</sub> (2 mol l <sup>-1</sup> )	67.8 $\pm$ 2.7
HCl (2 mol l <sup>-1</sup> )	55.4 $\pm$ 1.6
NH <sub>4</sub> SCN (2 mol l <sup>-1</sup> )	73.2 $\pm$ 2.5
Histidine (0.1 mol l <sup>-1</sup> )	32.3 $\pm$ 2.7
Ethanol <sup>a</sup>	100.1 $\pm$ 1.4

<sup>a</sup> Even with 3 ml of ethanol, the recovery was quantitative.



**Fig. 3.** Effect of sample pH on extraction of inorganic mercury.  $[\text{Hg}^{2+}] = 5 \mu\text{g l}^{-1}$ ; sample volume = 50 ml; eluent 3 ml of ethanol.

20–75 ml min<sup>-1</sup>. The retention of mercury was independent of flow rate up to 45 ml min<sup>-1</sup>. On the other hand, quantitative stripping of mercury ions from the disk was achieved in a flow rate of 1–25 ml min<sup>-1</sup>.

### 3.1. Conversion of methyl mercury to inorganic mercury

The effect of electron beam irradiation on the conversion of methyl mercury to inorganic mercury was studied. To 10 ml of ethanolic solution containing 250 ng of  $\text{CH}_3\text{Hg}^+$ , varying doses of electron beam was applied and the sample was then analyzed by the given cold vapor procedure. The recovery was expressed as  $[\text{peak absorbance of MeHg}^+]/[\text{peak absorbance of Hg}^{2+}] \times 100$ . The results of this investigation are given in Table 3 and it was found that 5 kGy electron beam is sufficient for complete conversion of methyl mercury to inorganic mercury. Furthermore, 100 ml of a solution containing 250 ng of  $\text{CH}_3\text{HgCl}$  was passed through the membrane disk and after elution with 5 ml of ethanol; the eluent was irradiated with electron beam (5 kGy) and was analyzed according to the given procedure. For comparison, the methyl mercury in another eluents was oxidized to inorganic mercury by the accepted procedure of potassium permanganate and potassium persulfate in acidic media [30–32], and at 95% confidence limit the results of both study was the same.

### 3.2. Analytical performance

The breakthrough volume of sample solution was tested by processing 1  $\mu\text{g}$  of inorganic mercury in different volumes of aqueous solution (200–2000) according to the recommended procedure under optimal conditions. The results showed that up to 1500 ml, the extraction was quantitative. Consequently, a concentration factor of 500 was determined based on consideration of the final elution volume (3 ml) and the breakthrough volume (1500 ml).

The limit of detection (LOD) of the proposed method for the determination of mercury (II) was studied under the optimal experimental conditions. The LOD of the method defined as three times the standard deviation of the blank (3S) was 3.8 ng l<sup>-1</sup>. The relative standard deviation ( $n = 7$ ) at 2.5  $\mu\text{g l}^{-1}$  of mercury (II) was 3.1%.

**Table 3**

Effect of irradiation doses on conversion of  $\text{CH}_3\text{HgCl}$  to inorganic mercury: sample contained 250 ng of  $\text{CH}_3\text{HgCl}$  in 10 ml

Irradiation dose (kGy)	Recovery (%)
1	47.1 $\pm$ 3.3
3	70.9 $\pm$ 3.1
5	98.2 $\pm$ 2.0
10	98.1 $\pm$ 2.5

**Table 4**

Effect of diverse ions (in binary mixtures) on extraction of 250 ng of mercury from 100 ml sample

Diverse ion	Molar ratio (ion/mercury)	Extraction <sup>a</sup> (%)
Co <sup>2+</sup>	1000	97.6 ± 2.4
Ag <sup>+</sup>	1000	95.5 ± 2.3
Cd <sup>2+</sup>	1000	95.6 ± 2.0
Cu <sup>2+</sup>	1000	98.9 ± 1.9
Zn <sup>2+</sup>	1000	95.0 ± 2.9
Fe <sup>3+</sup>	1000	97.9 ± 2.7
Ni <sup>2+</sup>	1000	95.5 ± 1.9
Ca <sup>2+</sup>	1000	100.7 ± 2.6
Na <sup>+</sup>	1000	98.6 ± 2.9
CrO <sub>4</sub> <sup>2-</sup>	1000	100.0 ± 1.9
SO <sub>4</sub> <sup>2-</sup>	1000	98.6 ± 2.4
IO <sub>3</sub> <sup>-</sup>	1000	99.3 ± 1.9
Br <sup>-</sup>	1000	96.4 ± 3.0
Cl <sup>-</sup>	2000	100.7 ± 2.9
NO <sub>3</sub> <sup>-</sup>	2000	95.3 ± 2.4

<sup>a</sup> Each number is the average and standard deviation of three experiments.

In order to investigate the selective separation and determination of Hg<sup>2+</sup> ion from its binary mixtures with diverse metal ion, an aliquot of aqueous solutions (100 ml) containing 250 ng Hg<sup>2+</sup> and other cations at the mole ratio of at least 1000 was taken and the recommended procedure were followed. A relative error of less than 5% was considered to be within the range of experimental error. The results are summarized in Table 4. These data show that the mercury ions in the binary mixtures are retained completely by the modified membrane disk, even in the presence of high concentration of different ions. Furthermore, the validity and accuracy of the technique for selective extraction of mercury in water matrices was examined. Recovery of Hg<sup>2+</sup> and MeHg<sup>+</sup> present at various levels from a synthetic water solution with concentration (mg l<sup>-1</sup>) Na<sup>+</sup> 30, k<sup>+</sup> 8, Mg<sup>2+</sup> 40, Ca<sup>2+</sup> 110, Cl<sup>-</sup> 248, SO<sub>4</sub><sup>2-</sup> 158, conforming to acceptable limits for drinking water, was studied. A 250 ml portion of the synthetic water spiked with different concentration of Hg<sup>2+</sup> and MeHg<sup>+</sup> was processed according to the given procedure (Table 5). As the results indicate, there is a preferential uptake of mercury relative to matrix ions, and it is projected that in the analysis of the samples the extraction efficiency would not be affected by the presence of a high concentration of matrix ions.

### 3.3. Application

The proposed procedure was applied to the determination of Hg<sup>2+</sup> and MeHg<sup>+</sup> in tap water, spring water and sea water. The reliability of the method was checked by recovery experiments. The results (Table 6) show that, in all samples, the mercury recovery is almost quantitative (97–99%), which demonstrates the applicability of the method to the determination of mercury in samples with very high salinity (Persian Gulf, with conductivity of 48.4 ms cm<sup>-1</sup>), without any pretreatment.

**Table 5**Extraction of Hg<sup>2+</sup> and MeHg<sup>+</sup> cations from synthetic water: pH ~ 5: sample volume = 250 ml flow rate 40 ml min<sup>-1</sup>; irradiation dose = 5 kGy

Added (ng)		Found <sup>a</sup> (ng)		Hgt <sup>b</sup> (%)
Hg <sup>2+</sup>	MeHg <sup>+</sup>	Before irradiation	After irradiation	
250	0	245.2 ± 2.5	–	98.1 ± 2.5
500	0	496.3 ± 1.9	–	99.3 ± 1.9
0	250	–	247.0 ± 3.3	98.8 ± 3.3
0	500	–	470.8 ± 3.1	94.1 ± 3.1
250	250	248.0 ± 2.5	481.2 ± 2.4	96.2 ± 2.4

<sup>a</sup> Mean and standard deviation of three experiments.<sup>b</sup> Total mercury.**Table 6**Determination of mercury in water samples: pH ~ 5: sample volume = 800 ml flow rate 40 ml min<sup>-1</sup>; irradiation dose = 5 kGy

Sample	Added (ng l <sup>-1</sup> )		Found <sup>a</sup> (ng l <sup>-1</sup> )		Recovery (%)	
	Hg <sup>2+</sup>	MeHg <sup>+</sup>	Hg <sup>2+</sup>	MeHg <sup>+</sup>	Hg <sup>2+</sup>	MeHg <sup>+</sup>
Sea water (Persian Gulf water)	–	–	139.5 ± 2.1	27.2 ± 1.7	–	–
River water	156	156	290.4 ± 2.3	175.8 ± 3.1	96.7	95.2
Well water	–	–	102.9 ± 2.3	17.3 ± 1.5	–	–
	156	156	256.6 ± 3.3	170.1 ± 2.2	98.5	97.9
	–	–	171.9 ± 4.2	–	–	–
	156	156	324.6 ± 1.8	152.0 ± 2.9	97.9	97.4

<sup>a</sup> Mean and standard deviation of three experiments.

## 4. Conclusions

It has been demonstrated that SPE procedure based on octadecyl membrane disk modified by MPMP is a simple, rapid, highly selective and reproducible method for the separation, concentration and determination of mercury ion. Comparing with the previously reported modified disk SPE methods [13–15], this method has been applied for preconcentration and determination of Hg<sup>2+</sup> and MeHg<sup>+</sup> cations. Furthermore, this paper reports the applicability of electron beam for conversion of MeHg<sup>+</sup> to inorganic mercury.

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