Journal of Hazardous Materials 161 (2009) 276–280

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

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

Hamid Ashkenani[a], Shayessteh Dadfarnia[a,*], Ali Mohammad Haji Shabani[a], Abbas Ali Jaffari[a], Abbas Behjat[b]

[a] Department of Chemistry, Yazd University, Yazd, Iran
[b] Department of physics, Yazd University, Yazd, Iran

ARTICLE INFO

Article history:
Received 18 November 2007
Received in revised form 15 March 2008
Accepted 19 March 2008
Available online 15 April 2008

Keywords:
Mercury determination
Electron beam
Preconcentration/separation
Cold vapor atomic absorption spectrometry

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-mercaptophyenylimino)methyl] phenol (MPMP). The trapped mercury was then eluted with 3 ml ethanol and Hg^{2+} ion was directly measured by cold vapor atomic absorption spectrometry, utilizing tin (II) chloride. Total mercury (Hgt) was determined after conversion of $MeHg^{+}$ into Hg^{2+} 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 $\mu g\,l^{-1}$ ($n=7$) was 3.1%. The limit of detection of the proposed method is 3.8 $ng\,l^{-1}$. The method was successfully applied to analysis of water samples, and the accuracy was assessed via recovery experiment.

1. Introduction

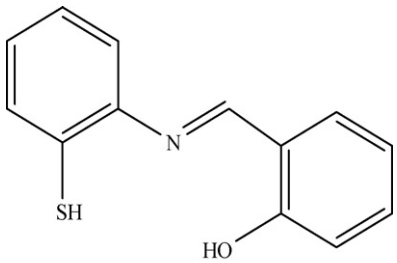
Mercury is a highly toxic element that is found both naturally and as an introduced contaminant in the environment. The toxic effect of mercury depends on its chemical form and the route of exposure. Methyl mercury is the most toxic form. It affects the immune system, alters genetics and enzyme systems, 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, gingiviti, 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 ($ng\,l^{-1}$) 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 filed 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-[(isopropoxycarbothiolyl)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-mercaptophyenylimino)methyl] phenol (MPMP) was used for preconcentration of Hg^{2+} and $MeHg^{+}$ from water samples. The adsorbed mercury was then eluted and Hg^{2+} ion was directly measured by CV-AAS, whereas the total mercury was determined after treatment of eluents by electron beam.

* Corresponding author. Tel.: +98 351 8244901; fax: +98 351 8210690.
E-mail address: sdadfarnia@yazduni.ac.ir (S. Dadfarnia).

0304-3894/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2008.03.139



MPMP

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 μg ml^{-1} of mercury (II) was prepared by dissolving 0.1354 g $HgCl_2$ (Merck) in 5 ml concentrate nitric acid and was diluted to 100 ml with water. A stock methyl mercury solution (1000 mg l^{-1}, Hg) was prepared by dissolving 0.1252 g of CH_3HgCl (Merck) in small amount of acetone in a 100 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 g l^{-1} tin chloride solution was prepared by dissolving 10 g $SnCl_2$ in 20 ml concentrate hydrochloric acid and diluting to 100 ml with water. 2-[(2-Mercaptophyenylimino)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 g of sodium acetate and 14.3 ml of concentrated acetic acid into a 250 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 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 kGy). The irradiation was carried out at Yazd Radiation Processing Center using an electron beam accelerator ROHDOTRON TT200. The specifications of the electron beams accelerator are given in Table 1.

Solid phase extractions were performed with 47 mm diameter × 0.5 mm thickness 3 M Empore^{TM} membrane disk containing octadecyl (C_{18}) Silica (8 μm particle, 60 Å pore size) from Varian. The disk was used in conjunction with the standard Millipore 47 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 ml of methanol and 10 ml acetonitrile. The disk was dried by passing air through it for several minutes. Then, a solution of 7 mg MPMP in 6 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 on oven at 50 °C for about 5 min. Finally, the disk was washed with 20 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.

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	±300 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	±50 μA

2.4. Preparation of water samples

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

2.5. Procedure

The pH of the sample solution was adjusted to ~5 by addition of acetate buffer solution and was passed through the modified membrane disk at a flow rate of 40 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 ml of ethanol at a flow rate of 2 ml min^{-1}. The amount of inorganic mercury in the eluent was directly measured by CV-AAS, and 5 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 Hg^{2+} by irradiation of the eluent with electron beam (a dose of 5 kGy). The $MeHg^{2+}$ 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-Mercaptophyenylimino)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-