

## Solid phase extraction and determination of sub-ppb levels of hazardous $\text{Hg}^{2+}$ ions

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### Abstract

A simple, rapid and reliable method has been developed to selectively separate and concentrate ultra trace amounts of mercury(II) ions from aqueous samples for its highly sensitive measurement by cold vapor atomic absorption spectrometry (CV-AAS). The  $\text{Hg}^{2+}$  ions were adsorbed selectively and quantitatively during the passage of aqueous samples through octadecyl silica membrane disks modified by isopropyl 2-[(isopropoxycarbothioly)disulfanyl]ethane thioate (IIDE). The retained  $\text{Hg}^{2+}$  ions were then stripped from the disk with minimal amounts of 0.5 M hydrobromic acid (two 8 ml portions) as eluent, and determined by CV-AAS. The break-through volume of the method is greater than 3000 ml, which results in enrichment factors >150. Maximum capacity of the membrane disks modified with 10 mg of the ligand was found to be  $350 \pm 30 \mu\text{g}$  of mercury(II), and the limit of detection is  $0.005 \text{ ng ml}^{-1}$ . The effect of various cationic interferences on the recovery of mercury in binary mixtures was studied. The method was applied to the recovery of  $\text{Hg}^{2+}$  ions from different synthetic and tap water samples, as well as the determination of mercury in human hair samples.

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### 1. Introduction

The toxic effects of mercury are well known. Mercury may enter a human body by inhalation of mercury vapor (mainly in the form of  $\text{Hg}^0$ ), drinking water (mainly as inorganic mercury,  $\text{Hg}^{2+}$ ), and/or by the consumption of fish and fish products (mainly as methylmercury,  $\text{CH}_3\text{Hg}^+$ ) in the diet [1]. The contents of mercury species in hair may represent the cumulative exposure from the occupational environment and/or daily diet [2]. Although the levels of total mercury in hair for a normal person are in the range of  $0.4\text{--}6.0 \mu\text{g g}^{-1}$ , a concentration greater than  $50 \mu\text{g g}^{-1}$  is considered to be poisonous [3]. The level of total mercury in hair is about 300-times larger than that in blood and a hair sample is easier to acquire

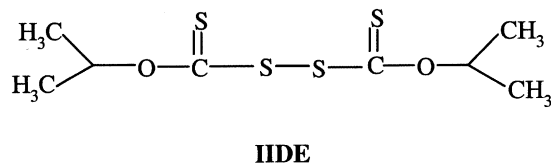
and store than one of blood [2]. Hence, the concentration of mercury species in hair would be convenient as a biological marker [2]. However, the direct determination of (ultra) trace amounts of mercury in hair, water and the other complicated matrices is usually difficult owing to matrix interferences and/or insufficient detection power. Consequently, a preliminary pre-concentration and/or separation is usually required.

Several methods commonly used for the pre-concentration of mercury include concentration in a palladium-coated graphite tube [4], pre-concentration on a gold amalgamator prior to using CV-AAS [5], pre-concentration in a liquid nitrogen trap and solid phase extraction [6,7]. Moreover, the solid phase extraction (SPE) cartridges and disks modified by suitable ligands have been successfully used for the selective separation and determination of metal ions [8–11].

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Solid phase extraction (SPE) techniques are now routinely applied in different analytical [12], chromatographic [13], clinical [14], pharmaceutical [15], environmental [16], industrial [17] and agricultural [18] fields. SPE is always used and followed by a direct analytical method for separation and detection of the solid phase extracted organic or inorganic species for the final qualitative and quantitative evaluation procedures. The method provides several major advantages over the classical liquid extraction technique. These include (i) the fast, simple and direct sample application in small size without any sample loss, (ii) no waste generation as practiced in liquid extraction method, (iii) the possibility of interfacing with major chromatographic techniques either in on-line or off-line modes and, finally, (iv) time and cost saving. The analysis of complex samples (e.g., environmental and biological samples) generally involves a pre-treatment step aimed at the reduction of the matrix content and the enrichment of the analyte. This is often performed by solid phase extraction [19].

The aim of this work was the development of a rapid and efficient method for the selective extraction, concentration and CV-AAS determination of  $\mu\text{g l}^{-1}$  levels of  $\text{Hg}^{2+}$  ion in aqueous solutions and digested hair samples by sorption on octadecyl silica membrane disks modified by isopropyl 2-[(isopropoxycarbothioyl)disulfanyl]ethane thioate (IIDE).



## 2. Experimental

### 2.1. Reagents

All acids and salts used were of the highest purity available from Merck chemical company and used as received. All organic solvents used were of HPLC grade from Merck. Analytical grade tin chloride, sodium hydroxide and EDTA were purchased from Merck and used as received. Reagent grade mercuric chloride and the nitrate salts of the other cations used (all from Merck) were of the highest purity available and used without any further purification except for vacuum drying. Isopropyl 2-[(isopropoxycarbothioyl)disulfanyl]ethane thioate was synthesized and purified in our laboratories. Doubly distilled, deionized water was used throughout. The standard solution of mercury(II) was prepared by dissolving an appropriate amount of mercuric chloride in 1% (v/v) nitric acid solution. Working solutions were prepared by appropriate dilution of the stock solution with water.

### 2.2. Synthesis of IIDE

Iodine (1 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 ml) was added to a stirred solution of potassium *o*-isopropyl(dithiocarbamate)

(1 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 ml) and stirred for 1 h. The reaction mixture was washed with 10% aqueous  $\text{Na}_2\text{S}_2\text{O}_3$  (2 ml  $\times$  10 ml) and  $\text{H}_2\text{O}$  (2 ml  $\times$  10 ml). The organic layer was dried over  $\text{MgSO}_4$  and evaporated under reduced pressure. More purification was achieved by re-crystallization in hexane, so that pale yellow crystals of IIDE were obtained in 90% yield (0.24 g). The structure and purity of IIDE was confirmed by elemental analysis, NMR and IR spectroscopy.  $^1\text{H}$  NMR ( $\text{CCl}_4$ ).  $\delta$  (ppm): 1.43 (t, 12H,  $\text{CH}_3$ ), 5.63 (m, 2H, CH). IR (KBr).  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ): 2979.8 (s), 2869.9 (w), 1463.9 (s), 1442.7 (s), 1373.0 (s), 1271.1 (s, b), 1145.6 (s), 1082.2 (s), 1048.0 (s, b) 898.8 (s), 796.5 (s), 690.5 (m).

### 2.3. Apparatus

The determination of mercury was carried out with a Shimadzu AA-670 atomic absorption spectrometer equipped with a Hg-hollow cathode lamp (HCL) and an on-line cold vapor generation system using  $\text{SnCl}_2$ . The absorbance wavelength was set at 253.7 nm (resonance line) and the spectral bandwidth at 0.5 nm. A long path quartz cell (2-cm i.d., 10-cm long) connected to the spectrometer was used as a detection system. The determination of all other cations were carried out with a Shimadzu AA-670 atomic absorption spectrometer under recommended conditions for each metal ion. A digital pH meter, Metrohm model 632, equipped with a combined glass calomel electrode was used for the pH adjustments. Extractions were performed with 47 mm diameter  $\times$  0.5 mm thickness 3 M Empore<sup>TM</sup> membrane disks containing octadecyl-bonded silica (8  $\mu\text{m}$  particle size, 60  $\text{\AA}$  pore size) distributed by Varian with a standard Millipore 47-mm filtration apparatus.

### 2.4. Sample extraction

To remove all contaminants arising from the manufacturing process and environment and to ensure optimal extraction of the analyte of interest, disk cleaning and conditioning should carry out before its use. Thus, after placing the membrane disk in the filtration apparatus, 10 ml of methanol were poured onto the disk and immediately drawn through the disk by applying a slight vacuum. The disk conditioning then began by pouring 10 ml acetonitrile onto the disk. Immediately, a low vacuum was applied and the solvent was drawn through the disk. The disk was then dried under vacuum for few minutes. Then, a solution of 10 mg of IIDE ligand dissolved in 4 ml of acetonitrile was introduced onto the disk so that the solution was spread on the whole disk surface, and was drawn slowly through the disk by applying a slight vacuum. This solution was collected in a test tube. A few drops of water were added to the test tube (until just before appearance of a colloidal suspension) and the resulting mixture was again introduced to the reservoir and passed slowly through the disk. The filtration was repeated (if necessary) several times. Finally, the disk was washed with 15 ml water and dried under vacuum for several minutes. The membrane

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