

Speciation analysis of mercury contaminants in water samples by RP-HPLC after solid phase extraction on modified C₁₈ extraction disks with 1,3-bis(2-cyanobenzene)triazene

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Abstract

A highly sensitive and accurate method for preconcentration and determination of ultra trace amounts of inorganic mercury and organomercury compounds in different water samples is proposed. The preconcentration is achieved using octadecyl silica (C₁₈) extraction disks modified with 1,3-bis(2-cyanobenzene)triazene (CBT). The retained analytes as their triazenide complexes on the solid phase was eluted with 10 ml acetonitrile and measured by reversed-phase high-performance liquid chromatography (RP-HPLC). Type and amount of eluent, pH, amount of CBT, flow rates of sample solution and eluent have been optimized in order to obtain quantitative recovery of the analytes. The effect of interfering ions, such as Cu²⁺, Mn²⁺, Fe²⁺, Al³⁺, Zn²⁺, Cd²⁺, Ca²⁺, Mg²⁺, Ba²⁺, Pb²⁺, K⁺ and Na⁺ usually present in water samples on the recovery of the analytes has also been investigated. The enrichment factor of 100 was obtained for all mercury species and the analytical detection limits of phenylmercury, methylmercury and Hg²⁺ were found as 0.8, 1.0 and 1.3 ng l⁻¹, respectively. Stability of mercury species after extraction on the modified disks was studied and the results showed that complexes collected on the disks were stable for at least 5 days. The proposed method has been applied to the quantitative determination of mercury species in natural and synthetic water samples with recoveries more than 90%.

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1. Introduction

The study of environmental chemical contaminants and their toxicological effects has changed dramatically over the last 50 years. Initially studies concentrated on trying to identify what contaminants were actually present and to develop quantitative methods to determine the concentrations (total) present. With improving analytical techniques, studies of the speciation of contaminants began and the specific forms that were creating the major problems were gradually identified.

Mercury is a highly dangerous element because of its accumulative and persistent character in the environment and biota

[1,2]. It is well known that the toxicity, biogeochemical behavior and transportation of mercury in the environment are heavily dependent on its chemical form [3,4]. Methylmercury (MeHg) is the most commonly occurring organomercury compound in environmental and biological materials and the most toxic mercury species, which is of particular concern because of its accumulation as it passes through the food chain, whereas phenylmercury (PhHg) is quite rarely present in the environment [1–4]. In the last two decades, the development of species-selective analytical methodologies has made possible the identification and quantification of such species. The most common methods of mercury speciation are gas chromatography (GC) [4,5] and high-performance liquid chromatography (HPLC) [4–6] coupled with a mercury-specific detector. The use of HPLC has the advantage of simplified sample preparation. It is essential to form volatile, thermally stable derivatives for GC, but not for HPLC. HPLC

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allows separation of mercury compounds at ambient temperature, and easy automation [7]. The detection methods coupled with GC or HPLC for mercury speciation include atomic absorption spectrometry [4–6,8,9], atomic fluorescence spectrometry [4–7,10–12], inductively coupled plasma-mass spectrometry [11,13,14], inductively coupled plasma-atomic emission spectrometry [15,16] and microwave-induced plasma-atomic emission spectrometry [4,5,17].

Although these detection methods are attractive for mercury speciation because of their excellent detection limits and selectivity, their relatively high instrumental and/or running costs as well as complicated instrument setup make it difficult to employ these hyphenated techniques for routine speciation analysis. In this aspect, HPLC with UV detection would provide a simple and cost-effective way for speciation analysis of mercury if the detection limits could be lowered sufficiently for the detection of mercury species in real samples. Owing to matrix interferences and/or insufficient detection power, however, direct determination of mercury species in complicated matrices is difficult, and a preliminary preconcentration step is usually mandatory [18,19]. Solid phase extraction preconcentration techniques based on the sorption of their pyroldine dithiocarbamate (PDC) [12,20], diethyldithiocarbamate (DDTC) [12], dithizone [18] and dithiophosphoric acid diacyl ester [19] chelates onto a RP-C₁₈ packed microcolumn have been developed for mercury speciation analyses with HPLC. Silica with chemically bounded alkyl chains such as octadecyl bounded silica (C₁₈), modified by the use of suitable ligands has been an excellent and widely used extractor of metal ions [21–25]. The use of modified bounded silica extraction disks with a high cross-sectional area may largely prevent all the problems encountered with columns, cartridges and tubes and usually offer higher breakthrough volumes [26]. These disks with shorter bed depth allow higher flow rates for large-volume samples with low concentrations of analyte, typically encountered in environmental analysis.

Triazene compounds, characterized by having a diazoamino group (–N=N–N–), have been studied for over 130 years concerning their interesting structural, anticancer and reactivity properties. They have been used in medicinal, combinatorial chemistry and as organometallic ligands [27]. However, despite extensive scientific reports on the synthesis, characterization and crystalline structure of the transition metal triazenide complexes, reports on analytical application of these ligands are quite sparse. Triazene

derivatives have been used as selective and sensitive chromogenic reagents for spectrophotometric determination of trace amounts of mercury(II) [28]. Recently we have reported the crystal structure of a triazene ligand, 1,3-bis(2-methoxybenzene)triazene with mercury(II) [29]. In this work, a new triazene derivative, 1,3-bis(2-cyanobenzene)triazene (CBT), illustrated in Scheme 1, is synthesized and used to modify the C₁₈ extraction disks. Using these disks, a highly efficient and simple method for the preconcentration of ultra trace amounts of organic and inorganic mercury species in natural water samples is developed and the separation of triazenide complexes of them is achieved using RP-HPLC.

2. Experimental

2.1. Apparatus

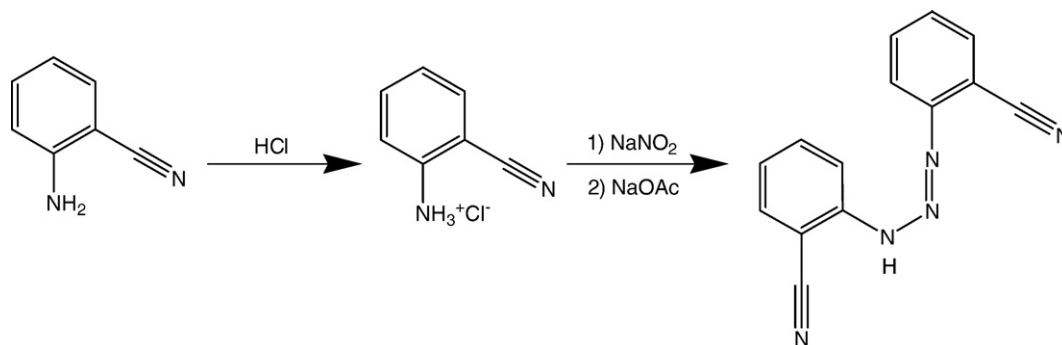
A chromatographic system (Perkin-Elmer, USA) consisting of binary pump Model 200, Rheodyne injector with a 20 µl loop and UV-VIS detector Model 200 was used. All separations were achieved using an analytical reversed-phase column (Spherisorb ODS, 5 µm, 4.6 mm i.d. × 22 cm length, Perkin-Elmer, USA) at room temperature under isocratic conditions. The TotalChrom software was used to acquire and process spectral and chromatographic data from the detector. The detector was operated between 210 and 350 nm, setting 281 nm for peak area measurements.

The modified C₁₈ extraction disks were used in conjunction with a standard 47 mm filtration apparatus (Schleicher and Schüell, Dassel, Germany) connected to a vacuum.

2.2. Reagents

Stock standard solutions of Hg²⁺, PhHg and MeHg were prepared by dissolving appropriate amounts of mercury(II) nitrate monohydrate, Phenyl mercury (Merck, Darmstadt, Germany) and methyl mercury chloride (99%), (Sigma–Aldrich, Germany) in methanol, respectively. All standards were stored in PTFE bottles at 4 °C. All metal salts, acids and solvents used were purchased from Merck (Darmstadt, Germany) and were of analytical reagent grade. Deionized double distilled water was used throughout.

The mobile phase was methanol:acetonitrile:0.1 M sodium acetate–acetic acid (pH=4) (40:38:22). The eluent was filtered through a 0.45 µm filter (Millipore), degassed in ultrasonic bath before use and delivered isocratically at a flow rate of 1 ml



Scheme 1. Synthesis of CBT.

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