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Analysis of chloro- and nitrobenzenes in water by a simple polyaniline-based solid-phase microextraction coupled with gas chromatography

Xiang Li, Jianmin Chen*, Lichun Du

Department of Environmental Science & Engineering, Fudan University, Shanghai 200433, China

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Abstract

A simple solid-phase microextraction (SPME) device, coupled with gas chromatography–electron capture detection (GC–ECD) was developed to detect trace levels of chloro- and nitrobenzene compounds in environmental water samples. Polyaniline (PANI) was chosen as the extraction material for the SPME device, and was electrochemically deposited on a stainless steel wire to achieve high mechanical stability. Due to the peculiar $\pi - \pi$ conjugated structure, PANI coating shows a stable performance in high temperature (to 350 °C) and solvents (organic and inorganic). The porous structure of PANI film characterized by scanning electron microscopy (SEM) revealed high extraction efficiency. The possible extraction mechanism was explained by the study carried out using electrochemical impedance spectroscopy (EIS). Eight chloro- and nitrobenzene compounds were selected to evaluate the SPME–GC procedures. The key parameters such as extraction and desorption temperature and time, and the ionic strength were investigated and optimized. The method was applied to the detection of environmental water samples collected from Taihu Lake, representing nowadays contamination level under industrial impact. The whole PANI-SPME–GC method offers high accuracy and precision, high sensitivity and low detection limits. Thus, the method developed could be used as a new way to monitor the trace levels of chloro- and nitrobenzene compounds in real water bodies.

Keywords: Solid-phase microextraction; Polyaniline; Chlorobenzene; Nitrobenzene; Gas chromatography; Electrochemical technology

1. Introduction

Chloro- and nitrobenzene compounds are a group of chemicals commonly used in the chemical industry. The release of chloro- and nitrobenzene compounds into the environment has caused great concern because of their toxicity, persistence and accumulation in the food chain [1,2]. A typical example is some chlorobenzene derivatives have been identified as priority pollutants by the US Environmental Protection Agency (EPA) [3]. Thus monitoring of chloro- and nitrobenzene compounds residues in the environment is of high importance [4]. It can also provide valuable information for the further remediation in the environment.

In general, liquid–liquid extraction (LLE) [5,6] and solid-phase extraction (SPE) [7,8] are the most commonly used sample pretreatment methods for the isolation and/or enrichment of chloro- and nitrobenzene compounds. But these methods require extensive clean-up and evaporative concentration procedures, which may cause loss of the volatile compounds and are time-consuming. Moreover, these extraction methods need expensive and hazardous solvents, which are undesirable for health and disposal reasons [9].

Solid-phase microextraction (SPME), developed by Pawliszyn and coworkers [10–12], is an alternative to the above techniques. It is a rapid, simple, solvent-free and easily automated technique for the isolation of organic compounds from gaseous and liquid samples. There have been some publications reporting the use of SPME with polyacrylate- or poly(dimethiylsiloxane)-coated fibres to the analysis of chloro- and nitrobenzene compounds in water [13,14], soil [15,16] and air samples [17]. However, despite several advantages of SPME [18], some practical drawbacks for the method such as lower thermal and chemical stabilities have already been emerged [19,20]. This is due to most of commercially available fibers

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* Corresponding author. Tel.: +86 21 65642521; fax: +86 21 65642080.
E-mail address: lixiang@fudan.edu.cn (J. Chen).

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are generally prepared by mere physical deposition of the polymer coating on the surface of the fused-silica fiber. This process requires very expensive equipment, which accounts for the high price of SPME fibers. Furthermore, silica fibers are fragile and must be handled with great care. So, firm SPME fibers with a long life are highly desired [21].

To overcome these problems, an electrochemical approach was attempted by Wu and Pawliszyn [22,23]. The technology effectively combines surface treatment, deactivation, coating and stationary phase immobilization into a single step. It offers a simple and convenient way to synthesize the conductive polymer for the SPME fiber. Owing to the chemical bonding of the porous polymer to the metal wire surface, electrochemically coated fiber enhances the stability properties as compared to conventionally coated fibers. Few custom-made polyaniline (PANI)-SPME fibers have been used in the extraction of aromatic amines and phenols from the gaseous phase of water samples [24,25]. However, the use of PANI-SPME fiber to extract chloro- and nitrobenzene compounds directly in environmental water samples has not been reported so far.

The objective of the present work is to investigate for the first time, the possibility of using a simple SPME device with electrochemically coated polyaniline fibers for the analysis of eight chloro- and nitrobenzene compounds in water samples. Experimental parameters affecting the extraction of the studied chloro- and nitrobenzene compounds, such as extraction and desorption temperature and time, and the ionic strength were studied and optimized. Under the optimized experimental conditions, the detection limit and the dynamic linear range of the proposed method were then evaluated. By coupling the GC technology, the developed protocol was applied to detect chloro- and nitrobenzene compounds in water samples collected from Taihu lake water bodies in Southern China, and the results were compared to that of other extraction methods.

2. Experimental

2.1. Reagents and chemicals

1,2,4-Trichlorobenzene, 1,2,3,4-tetrachlorobenzene, 1,2,3,5-tetrachlorobenzene, *p*-dinitrobenzene, *m*-dinitrobenzene were supplied by Supelco (Bellefonte, USA), *o*-dinitrobenzene and 4-chloronitrobenzene were purchased from Aldrich (Milwaukee, USA). Nitrobenzene and aniline were obtained from Shanghai Reagent Plant (Shanghai, China). To ensure >99.9% purity, aniline was further purified by vacuum distillation before use. All organic solvents (methanol, acetone and hexane) were of HPLC grade and were obtained from Supelco (Bellefonte, USA). Analytical grade hydrochloric acid, potassium hydroxide and potassium chloride were used to adjust the pH and ionic strength of water samples during the optimization of experimental parameters. These chemicals were purchased from the Reagent Factory of Shanghai (Shanghai, China). Double-distilled water was used for preparing working standard solutions.

The stock standard solutions of chloro- and nitrobenzenes (1000 mg/L) were prepared in methanol and were stored and refrigerated at 4 °C. These stock standard solutions were diluted with methanol to prepare a mixed stock of analytes in such a way that the concentration of mixture was 0.5 mg/L 1,2,3,4-tetrachlorobenzene and 1,2,3,5-tetrachlorobenzene, 1 mg/L 4-chloronitrobenzene, 1.5 mg/L *p*-dinitrobenzene, 2 mg/L 1,2,4-trichlorobenzene, 4.5 mg/L *o*-dinitrobenzene, 7 mg/L *m*-dinitrobenzene and 20 mg/L nitrobenzene. Then, working standard solutions were freshly prepared by diluting the mixed standard solution with doubly distilled water to the required concentrations. Stock and working standards were stored at 4 °C in the dark before use.

2.2. Collection of water samples

Environmental water samples were collected from the Meiliang Bay region of Taihu Lake in May 2005. The studied area spread between 120°12′ and 120°13′ in east longitude and 31°28′ and 31°30′ in north latitude, just in Wuxi region of the Jiangsu, China. It is known that these areas have intense agricultural and industrial activity. Thus, they can result in possible contamination of the drinking water resource. The map with the 11 sampling stations is given in Fig. 1.

The water samples for chloro- and nitrobenzenes measurement were collected from each sampling location in amber glass containers (1 L). The containers were carefully filled just to overflowing, without passing air bubbles through sample or trapping air bubbles in sealed bottles. Preparation of containers included washing with detergent, rinsing with tap water, double-distilled water, acetone and placing in an oven at 150 °C for 2 h. After sampling, samples were acidified to pH 2.0 with hydrochloric acid to inhibit biological activity and were filtered through 0.45 μm filter membranes to remove sand and debris. Then, samples were stored in the dark at temperatures between 0 and 4 °C prior extraction, normally within 48 h.

2.3. Apparatus

Surface characteristic studies of the prepared polyaniline fibers were performed by scanning electron microscopy (SEM, model XL30-ESEM, FEI, USA). A homemade SPME device was used. A 0.20-mm-diameter × 7.5-cm-long prepared stainless steel wire was mounted into the SPME device, and the exposed fiber was trimmed to 1 cm. A CHI 650A electrochemical workstation (CH Instrument Corp., USA) was used to electrodeposit PANI on stainless steel wire, and came into being a SPME extraction fiber. Monitoring of the analytes was performed with a Gas chromatograph (model GC-HP-6890N, Agilent, USA), equipped with an electron capture detector (ECD) and a data processor model Agilent Chemstation System NT4.0.

2.4. Gas chromatography conditions

The column was a DB-17 capillary, 30 m × 0.25 mm × 0.25 μm film thickness (J&W Scientific, Folsom, CA, USA). Helium with a flow-rate of 23.8 mL/min was used as the carrier gas. High purity nitrogen (>99.99%) was the make-up gas for the ECD and had a flow-rate of 48 mL/min. Injection port and detector temperatures were 250 and 300 °C, respectively. The