Original article

Analysis of nitrobenzene compounds in water and soil samples by graphene composite-based solid-phase microextraction coupled with gas chromatography–mass spectrometry

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A B S T R A C T

In this work, solid-phase microextraction coupled with gas chromatography–mass spectrometry was developed to determine trace levels of nitrobenzene compounds in water and soil samples. Graphene was chosen as the extraction material and its composite was coated on a stainless steel wire through sol–gel technique for the solid phase microextraction. The key parameters influencing the extraction efficiency were optimized. Under the optimal conditions, the linearity for the compounds was observed in the range of 0.02–15.0 μg/L for water samples, and 0.2–60.0 μg/kg for soil samples, with the correlation coefficients (r) of 0.9966–0.9987. The limits of detection of the method were 0.0025–0.005 μg/L for water samples, and 0.02–0.04 μg/kg for soil samples. The recoveries for the spiked samples were in the range of 72.0%–113.2%, and the precision, expressed as the relative standard deviations, was less than 12.1%.

1. Introduction

Graphene [1–3], an allotrope of carbon, has engendered tremendous attention from the scientific community. As a two-dimensional single-layer sheet of sp^2-bonded carbon, graphene is the mother of all graphitic forms, including zero-dimensional fullerenes, one-dimensional carbon nanotubes, and three-dimensional graphite. Compared with other graphitic materials, graphene shows many outstanding advantages, such as remarkable thermal and chemical stability, good mechanical strength, and high surface-to-weight ratios. Moreover, with a large delocalized π-electron system, graphene can form a strong π–π stacking interaction with some organic molecules. Therefore, graphene can be expected to serve as a promising adsorbent for some analytes. Recently, graphene and graphene-based materials have been synthesized and successfully applied for sample pretreatment in solid phase extraction (SPE) [4,5], magnetic solid phase extraction (MSPE) [6,7], and solid phase microextraction (SPME) [8,9].

SPME, first developed by Pawliszyn and coworkers in the early 1990s [10], has been widely used as an effective sample pretreatment technique. It has advantages including almost no consumption of organic solvent, simplicity of operation, and easy linkup with gas chromatography. The mechanism of SPME is based on the equilibrium of the analytes between the sample and the fiber coating [11]. Thus, the adsorbent material coated onto the fiber is critical in improving the SPME performance. Although a number of SPME coatings are commercially available, their performance is not always satisfactory for the extraction of some analytes, especially from complex samples because of their instability at high temperatures and the limited selectivity of the coatings [12].

To overcome these problems, various novel SPME fiber coatings, including polymeric ionic liquid material [13–15], metal organic framework material [16,17], mesoporous material [18], and carbon nanomaterial [19,20], have been explored. Among all the coating materials, graphene can possibly become an ideal choice due to its large specific area and excellent π–π electrostatic stacking property. However, up to now, there have only been a few reports about the application of graphene on the fiber coating for SPME. In this regard, Chen et al. [21] first prepared a graphene-coated SPME fiber for the extraction of pyrethroid pesticides from water samples with satisfactory results. Then, graphene-based SPME coatings were reported to extract organochlorine pesticides [22,23], polybrominated diphenyl ethers [24], triazine herbicides [25], and polycyclic aromatic hydrocarbons [26] from water and

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soil samples. It is evident that further explorations of the potential applications of the graphene composite-based SPME fibers are necessary.

Nitrobenzene compounds are widely used in chemical industry. In recent years, the release of nitrobenzene compounds into environmental water or soil samples has drawn considerable attention due to their toxicity, persistence, and accumulation in food chains [27,28]. Therefore, developing rapid, sensitive, and effective methods for the trace analysis of nitrobenzene compounds in environmental samples is desirable.

In the current study, graphene was chosen as the extraction material and was coated on a stainless steel wire through sol–gel technique for the SPME. The applicability of the graphene composite-coated fiber for SPME was investigated through the extraction of five nitrobenzene compounds from water and soil samples followed by analysis with gas chromatography–mass spectrometry (GC–MS).

2. Experimental

2.1. Chemicals and materials

Standards of the nitrobenzene compounds (nitrobenzene, 2-nitrotoluene, 4-nitrotoluene, 4-nitrochlorobenzene and 2-nitrochlorobenzene) were purchased from Agricultural Environmental Protection Institution of Tianjin (Tianjin, China). A mixture stock solution containing each of the five nitrobenzene compounds at 50.0 mg/L was prepared in acetone and stored at 4 °C.

Dichloromethane (CH_2Cl_2), hydrofluoric acid (HF, 40%, w/w), methyltrimethoxysilane (MTMOS), trifluoroacetic acid (TFA, 99%) and hydroxy terminated polydimethylsiloxane (HO-PDMS) were obtained from Boaixin Chemical Reagents Company (Baoding, China). Sodium chloride (NaCl) was purchased from Tianjin Fuchen Chemical Reagent Factory (Tianjin, China). Stainless steel wires (o.d. 150 μm) were purchased from Anting Micro-Injector Factory (Shanghai, China). The commercial SPME fibers coated with polydimethylsiloxane (PDMS, 100 μm), carbowax/divinylbenzene (CW/DVB, 70 μm), and polyacrylate (PA, 85 μm) were purchased from Supelco (Bellefonte, PA, USA). Graphene was synthesized according to the method reported in our previous work [29].

2.2. Preparation of graphene composite-coated SPME fiber

Based on the literature method [24] with some modifications, the fabrication of the graphene composite-coated fiber involved the following steps. Firstly, the sol solution of graphene composite coating material was prepared as follows: Graphene (50 mg), CH_2Cl_2 (100 μL), MTMOS (100 μL), and HO-PDMS (100 μL) were added to an Eppendorf tube (1.0 mL) and mixed by vortexing for 5 min. Then, 80 μL of TFA (95% water solution) was added and mixed thoroughly for 2 min. Secondly, a stainless steel wire, which was first etched with HF solution for 15 min, was dipped into the above sol solution to a depth of 1.0 cm for 2 min. Then, it was pulled out and dried at room temperature for 10 min so that the gel coating was formed on the etched surface. This procedure was repeated about 12 times so as to obtain a desired thickness of the coating (about 50 μm). The fiber was then assembled into a 5 μL GC microsyringe by replacing the plunger with a homemade SPME device, and finally it was conditioned in the GC injector under nitrogen at 200 °C for 2 h.

2.3. Instrumental and analytical conditions

The DF-101S temperature-controlled magnetic stirrer was purchased from Baoding High-tech Zone Sunshine Science Instrument Company (Baoding, China). The WH-861 vortex shaker

Table 1
Retention time and SIM parameters for each analyte.

Compounds	Retention time (min)	MS SIM parameters	
		Quantitation icon (m/z)	Qualifying icons (m/z)
Nitrobenzene	6.32	123	77, 51
2-Nitrotoluene	7.38	120	137, 91
4-Nitrotoluene	8.14	137	91, 65
4-Nitrochlorobenzene	8.46	157	111, 75
2-Nitrochlorobenzene	8.66	157	111, 75

was from Shanghai Jinggong Industrial Limited Liability Company (Shanghai, China).

A Shimadzu (Kyoto, Japan) GCMS-QP2010 SE system equipped with a TG-5MS fused silica capillary column (30 m × 0.25 mm × 0.25 μm) (Scientific, Thermo, www.thermo.com/columns) was used for analysis. The injector was operated in the splitless mode, and the injection port temperature was maintained at 270 °C. Chromatographic separations were performed with an initial oven temperature of 60 °C, followed by heating at 10 °C/min to 150 °C (held for 2 min), and finally programmed at 30 °C/min to 210 °C. The mass spectrometer was operated in the electron ionization (EI) mode with the temperature of the transfer line and the ion source being kept at 250 °C and 200 °C, respectively. Data collection was carried out in the selected ion monitoring (SIM) mode. Ion peaks including one for quantification and two for qualification were monitored for each nitrobenzene compound based on the full-scan results. The retention time and SIM parameters for each analyte are listed in Table 1. The quantification was performed by calculating the absolute peak areas in SIM mode. Helium at a flow rate of 37.5 cm/s in the constant linear velocity mode was employed as the carrier gas.

2.4. Sample preparation

Lake water was collected from our campus (Baoding, China); river water was collected from Jiucheng (Huanghua, China). For headspace SPME, 15.0 mL of water sample and 5.5 g of NaCl were added into a 30 mL glass vial and then mixed until the NaCl was completely dissolved.

Soil samples were collected both from our campus (Baoding, China) and from a farmland (Zhongjie, China), respectively, which were pulverized and passed through 450 μm sieves. 5.0 g soil sample was weighted into a 30.0 mL glass vial. Then, 15.0 mL saturated NaCl solution (about 37%, w/v) was added and mixed thoroughly to form a homogeneous soil suspension for headspace SPME.

2.5. Headspace SPME procedure

The 30.0 mL glass vial containing 15.0 mL of the above sample solution with a Teflon-lined cap was immersed in a water bath at 50 °C. The extraction was performed by the exposure of the graphene composite fiber to the headspace above the sample under stirring at 600 rpm for 30 min. After extraction, the SPME fiber was inserted into the GC injector to desorb the analytes at 270 °C for 1.5 min for GC–MS analysis.

3. Results and discussion

3.1. Surface structure of the graphene composite-coated SPME fiber

Fig. 1A shows the low-magnification surface morphological structure of the graphene composite-coated fiber observed by scanning electron microscope (SEM), from which it can be seen