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Electrospun polystyrene/graphene nanofiber film as a novel adsorbent of thin film microextraction for extraction of aldehydes in human exhaled breath condensates

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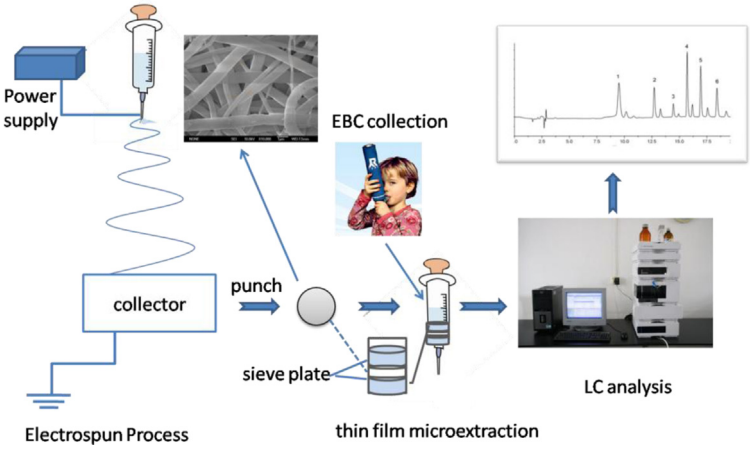
HIGHLIGHTS

- Novel porous PS/G composite nanofibers were prepared as the extraction phase of TFME.
- Excellent extraction efficiency and fast extraction speed are remarkable advantages of the method.
- The simple, fast, sensitive and non-invasive method was successfully applied to breath analysis.

GRAPHICAL ABSTRACT



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ABSTRACT

In the current study, we introduced a novel polystyrene/graphene (PS/G) composite nanofiber film for thin film microextraction (TFME) for the first time. The PS/G nanofiber film was fabricated on the surface of filter paper by a facile electrospinning method. The morphology and extraction performance of the resultant composite film were investigated systematically. The PS/G nanofiber film exhibited porous fibrous structure, large surface area and strong hydrophobicity. A new thin film microextraction-high performance liquid chromatography (TFME-HPLC) method was developed for the determination of six aldehydes in human exhaled breath condensates. The method showed high enrichment efficiency and fast analysis speed. Under the optimal conditions, the linear ranges of the analytes were in the range of 0.02–30 μmol L^{-1} with correlation coefficients above 0.9938, and the recoveries were between 79.8% and 105.6% with the relative standard deviation values lower than 16.3% ($n = 5$). The limits of quantification of six aldehydes ranged from 13.8 to 64.6 nmol L^{-1}. The established method was successfully applied for the quantification of aldehyde metabolites in exhaled breath condensates of lung cancer patients and healthy people. Taken together, the TFME-HPLC method provides a simple, rapid, sensitive, cost-effective, non-invasion approach for the analysis of linear aliphatic aldehydes in human exhaled breath condensates.

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1. Introduction

Sample preparation, such as extraction, concentration, and isolation of analytes, is an essential step prior to analysis, greatly influencing the reliability and accuracy of the analysis. Solid phase extraction (SPE) is one of the most extensively used sample preparation methods and can be used for extraction of different classes of compounds [1]. Conventional SPE suffers from some limitations, including being tedious, requiring large volumes of samples and solvents [2], and easily jammed when dealing with complex samples. Solid phase microextraction (SPME), introduced by Pawliszyn in the early 1990s, is considered one of the great ideas in analytical chemistry [3]. In the method, a small amount of extraction phase is immobilized on the outside of a fused-silica fiber, analytes are extracted from an aqueous, gaseous or headspace above the samples onto the stationary phase. It is attractive owing to its simplicity, and its being solvent-free, time-efficient, easy-to-automate, and field usable [4]. However, the extraction capacity of the non-exhaustive sample preparation method is limited because of the small surface area-to-volume ratio and the thickness of coating, simply increasing the thickness of the coating results in long equilibrium times [5]. Addressing this issue, thin-film micro-extraction (TFME) was developed using a sheet of flat film with high surface area-to-volume ratio as extraction phase. This exhaustive extraction method can quickly reach extraction equilibrium and provide a large adsorption capacity [6]. It has been used for the extraction of PAHs [7] and pesticides [8] in water samples. Nowadays, an important direction for TFME development is exploration of new coatings and new thin-film formats for a wide variety of applications [5].

Electrospinning is currently the most promising technique to produce continuous nanofibers on a large scale with tunable fiber diameter from nanometers to microns [9]. Due to the three-dimensional morphology, large surface area-to-volume ratio, and similar size-scale to the natural extracellular matrix [10], electrospun nanofibers have been studied extensively in many fields, including bone tissue engineering [11], wound dressing [12] and proton exchange membranes [13]. Besides, they have great potential as novel extracting mediums in sample preparation [14], and the relevant applications in SPE [15–19] and SPME [20–22] have been reported recently. For example, He et al. prepared polystyrene/oxidized carbon nanotubes film by electrospinning [23], and applied this film as an adsorbent of thin film microextraction and a matrix of matrix-assisted laser desorption/ionization time-of-flight mass spectrometry for the determination of benzo[a]pyrene and 1-hydroxypyrene.

Graphene (G), a two-dimensional carbon-based nanomaterial, has sparked great interest of scientists due to its excellent mechanical, electrical, thermal and optical properties, and ultra-high specific surface area [24]. These unique properties make graphene very attractive for various applications including sample preparation (SPE [25–29] and SPME [30,31]). However, leakage and blocking may occur when direct use of nano-sized graphene as sorbent in SPE [32]. In addition, graphene is ready to aggregate, which leads to the decrease of the accessible active surfaces.

The aim of the work is to fabricate new polystyrene/graphene (PS/G) composite nanofibers with the electrospinning method, and investigate the potential application of the nanofibers as the extraction phase of TFME. Linear aliphatic aldehydes (butanal, pentanal, hexanal, heptanal, octanal and nonanal) were selected as model compounds. Exhaled breath analysis has been considered to be a potential and auxiliary diagnostic approach to recognize lung cancer and infectious diseases in early stage [33,34]. A series of parameters affecting the electrospinning and the extraction efficiency were optimized, the method validation was investigated systematically. And this method was applied to determine six aldehydes in human exhaled breath condensate (EBC) of lung cancer patients and healthy volunteers by coupling to high performance liquid chromatography (HPLC).

2. Materials and methods

2.1. Chemicals and materials

Nonanal (97%) was purchased from Alfa Aesar. Hexanal (98%) and heptanal (97%) were supplied from ABCR GmbH & Co., KG. Pentanal (98.5%) was purchased from Amethyst Chemicals, J&K Scientific Ltd. Butanal (98%) and octanal (98%) were offered from TCI Development Co., Ltd. 1-Hydroxypyrene (98%, internal standard, IS) was obtained from Dr. Ehrenstorfer (Germany). 2,4-Dinitrophenyl hydrazine (DNPH, 99.6%) was obtained from Chem Service, and recrystallized once in acetonitrile–water (1:5, v/v) solution before use. Graphite powder (325 mesh, 99.95%) was purchased from Jinrilai graphite Co., Ltd. (Qingdao, China). Polystyrene (PS, average MW∼192,000) was purchased from Sigma–Aldrich (USA). Formic acid (96%) was purchased from Tedia (Tedia Company, USA). Hydrogen peroxide (H_2O_2), sodium borohydride ($NaBH_4$), sodiumnitrate ($NaNO_3$), potassium permanganate ($KMnO_4$) and concentrated sulfuric acid (98%) were all of analytical grade and purchased from Shanghai Chemical Reagents Company (Shanghai, China). HPLC-grade methanol was purchased from Tedia Company (USA), and filtered by microporous filter membrane (0.45 μm). HPLC-grade acetonitrile, isopropanol, and ethanol were obtained from Merck (Darmstadt, Germany). Ultrapure water was obtained from a WaterPro Water Purification System (Sartorius, Germany).

2.2. Instrumentation

HPLC analysis was carried out with Agilent 1100 HPLC system (Agilent Technologies, Palo Alto, CA, USA). The instrument was equipped with a variable wavelength detector (VWD) with the detection wavelength of 360 nm, and the injection volume was 10 μL. The chromatographic separations were achieved on a Venusil XBP-C18 column (250 mm × 4.6 mm, 5 μm, Agela Technologies Inc., Beijing, China) at the flow rate of 1.0 mL min^{-1}(40 °C). A gradient elution was carried out using a binary mobile phase composed of eluent A (methanol) and eluent B (water). The linear gradient program was as follows: 0–10 min, 75% A; 10–17 min, 75–93% A; 17–23 min, 93% A; 23–26 min, 93–75% B; 26–31 min, 75% A.

Exhaled breath condensate (EBC) samples were collected by a commercially available condenser (RTube™, Respiratory Research, Inc., USA). Morphology of the synthesized nanofibers was observed using a LEO 1450VP scanning electron microscope (Germany) and a JEM-2100 (HR) transmission electron microscope (JEOL, Japan). The contact angles of the nanofiber film for water and oil were measured using OCA20 contact angle meter (Dataphysics, Germany). The surface area was determined by nitrogen adsorption/desorption using the Brunauer–Emmett–Teller method (BEL SORP-mini BEL Japan Inc., Japan). The sample was degassed under inert nitrogen (N_2) at 60 °C for 2 h prior to BET measurements. Infrared spectra were measured on a Nicolet Avatar 360 Fourier transform infrared (FT-IR) system. The electrospinning experiments were performed using a regulated power supply (DW-P303-1ACF0 electrostatic spinning high DC voltage power, Tianjin, China). A WZ-50C6 micro-infusion pump (Smiths Medical Instrument, Zhejiang, China) was used to deliver polymer solution in the electrospinning process. A laboratorial syringe infusion pump (Baoding Longer Precision Pump Co., Ltd., Hebei, China) was