



Analysis of aldehydes in human exhaled breath condensates by in-tube SPME-HPLC



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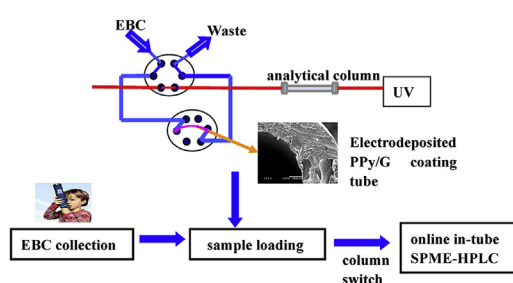
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HIGHLIGHTS

- A novel PPy/G coating was fabricated for on-line in-tube SPME.
- The coating exhibited excellent stability, lifespan, extraction capacity and selectivity.
- Good results were obtained for sensitivity, precision, accuracy, speed and matrix effect.
- The method was applied in non-invasive breath analysis.

GRAPHICAL ABSTRACT



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ABSTRACT

In this paper, polypyrrole/graphene (PPy/G) composite coating was prepared by a facile electrochemical polymerization strategy on the inner surface of a stainless steel (SS) tube. Based on the coating tube, a novel online in-tube solid-phase microextraction-high performance liquid chromatography (IT-SPME-HPLC) was developed and applied for the extraction of aldehydes in the human exhaled breath condensates (EBC). The hybrid PPy/G nanocomposite exhibits remarkable chemical and mechanical stability, high selectivity, and satisfactory extraction performance toward aldehyde compounds. Moreover, the proposed online IT-SPME-HPLC method possesses numerous superiorities, such as time and cost saving, process simplicity, high precision and sensitivity. Some parameters related to extraction efficiency were optimized systematically. Under the optimal conditions, the recoveries of the aldehyde compounds at three spiked concentration levels varied in the range of 85%–117%. Good linearity was obtained with excellent correlation coefficients (R^2) being larger than 0.994. The relative standard deviations ($n = 5$) of the method ranged from 1.8% to 11.3% and the limits of detection were between 2.3 and 3.3 nmol L⁻¹. The successful application of the proposed method in human EBC indicated that it is a promising approach for the determination of trace aldehyde metabolites in complex EBC samples.

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1. Introduction

The predominant purpose of sample pretreatment is to make

the analysis samples concentrated and purified, and to transfer the analytes of interest to the instrument for the final analysis [1]. Preconcentration methods such as solid phase extraction have been used to preconcentrate, extract and clean up the sample prior to chromatographic separation and detection, which is useful and efficient [2,3]. But these traditional off-line procedures suffer from drawbacks as they are time-consuming, labor intensive, not easy to

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automate and may consume large volumes of organic solvent and samples [4,5]. Alternatively, solid phase microextraction (SPME) has been a powerful sample preparation method since introduced by Pawliszyn in the early 1990s as its time-efficient, simplicity, field usable and linkup with detection instruments [6]. In 1997, this technique has been extended to in-tube SPME (IT-SPME) by Eisert and Pawliszyn [7]. In the method, an open tubular fused-silica capillary column with a high internal surface area is generally utilized as the extraction device [5]. To date, dozens of capillary types have been reported for IT-SPME, such as inner-wall-coated capillary [8,9], fiber-inserted capillary [10], and monolithic capillary [11–13]. Moreover, the online coupling of IT-SPME with HPLC and HPLC-MS permits the integration of extraction, concentration, desorption and injection [14], not only significant reducing analysis time and the sources of error, but increasing precision and sensitivity relative to manual off-line preparation process [15]. The online and dynamic extraction method increases the throughput of sample preparation and minimizes matrix interferences [16]. As a result, high extraction efficiency, sensitivity and precision, reduced consumption of organic solvents and samples can be obtained simultaneously.

Selection of an appropriate coating is crucial to IT-SPME. Conducting polymers such as polypyrrole (PPy) have been the most intensively studied materials due to its low cost, biocompatibility and easily synthesized by electrochemical or chemical methods [17]. Moreover, it has been reported that PPy coating has high extraction efficiency toward polar compounds [18,19] due to the joint effects of interactions based on acid-base, ion exchange, and hydrogen bonding [14,20]. However, challenges remain because the single electro-conducted coating is inclined to fall off and hence, results in a low life-cycle [21]. As we all know, graphene (G), a single atomic plane of graphite, possesses remarkable chemical stability [22] and ultra-high mechanical strength [23] as a result of the inherent configuration. Graphene has been added as doping material to improve the performance of PPy conducting polymer [24,25]. Synergistic effect can significantly enhance the mechanical strength of the resulting composite. For example, in 2011, Zou prepared polypyrrole/graphene composite-coated fiber for SPME by electrochemical polymerization. The coating possessed good anti-organic solvent ability and excellent mechanical stability [25]. However, to the best of our knowledge, there is no publication focusing on the PPy/G coating-based online in-tube SPME. Therefore, in order to better utilization of the complementary properties of PPy and graphene, in the work, we in-situ deposited PPy/G composite on the inner surface of a SS tube by a facile electrodeposition method. As opposed to other synthesis methods, electrodeposition is more convenient and provides the possibility for a large number of anions to be applied as dopants [21].

During recent years, a vast of researchers focused on the non-invasive detection of lung cancer by analysis of exhaled breath, blood and urine samples from patients [26]. Meanwhile, human exhaled breath condensate (EBC), which can be collected in a short time interval, has recently been considered to be a desired candidate for non-invasive analysis of lung cancer [27]. Volatile organic compounds (VOCs) refer to a set of small organic molecules [28], which have been recognized as potential biomarkers [29]. Among them, aldehydes generated in the human body during the metabolic process have gained obviously increasing interests [30].

The aim of the article is intended to develop a novel PPy/G coated tube and evaluate its application in on-line IT-SPME-HPLC. In this study, PPy/G composite was electrodeposited on the inner surface of a SS tube (20 cm × 0.80 mm) as IT-SPME coating. A novel IT-SPME method was developed and on-line coupled with HPLC for the determination of six aldehyde metabolites in human exhaled breath condensates. Some features (morphology, extraction ability,

durability and resistance capacity to the matrix effect) of the coating were investigated. Extraction conditions, including the thickness of coating, sample volume and the flow rate of sample were optimized systematically in order to get the best extraction efficiency. The developed online IT-SPME-HPLC method was compared with the previously reported literature and its suitability for breath analysis was also studied.

2. Materials and methods

2.1. Chemicals and materials

Butanal (98%) and octanal (98%) were supplied by TCI Development Co. LTD. (Shanghai, China). Pentanal (98.5%) was obtained from Amethyst Chemicals, J&K Scientific LTD. (Beijing, China). Hexanal (98%) and heptanal (97%) were purchased from ABCR GmbH & Co. KG (Germany). Nonanal (97%) and pyrrole (99%) were obtained from Alfa Aesar (Tianjin, China). 2,4-Dinitrophenylhydrazine (DNPH, 99.6%) was purchased from CHEM SERVICE (West Chester, PA, USA) and it was recrystallized once in acetonitrile–water (1:5) solution before use. HPLC-grade methanol and formic acid (96%) were provided by TEDIA Company Inc. (Fairfield, OH, USA). Graphite powder (325 mesh, 99.95%) was obtained from Jinrilai graphite (Qingdao, China). Sodium dodecyl sulfonate (SDS) was purchased from Biosharp (Anhui, China). Bovine serum albumin (BSA) and α -salivary amylase were obtained from Rujie Biotech. Co., (Shanghai, China). Ultrapure water used in all experiments was produced with a WaterPro Water Purification System (Sartorius, Germany).

2.2. Equipment and chromatographic conditions

HPLC analysis was performed with an Agilent 1100 HPLC system (Agilent Technologies, Palo Alto, CA, USA) equipped with a vacuum degasser, a quaternary pump, a thermostatted column compartment, a manual injector (Rheodyne 7725i) and a variable wavelength detector (VWD). The separations were operated on a Venusil XBP-C18 column (250 mm × 4.6 mm, 5 μ m, Agela Technologies Inc., Beijing, China) at the mobile flow rate of 1.0 mL min⁻¹. The linear gradient elution was set as follows: 70% methanol and 30% water linear to 93% methanol from 0 to 9 min and maintained 7 min, then returned to 70:30 methanol/water (v/v) within 2 min and held this composition for 2 min. The optimal detection wavelength was 360 nm and the column temperature used in the study was 40 °C.

EBC samples were acquired by a commercially available condenser (RTube™, Respiratory Research, Inc. USA). A laboratorial syringe infusion pump (Lsp02-1B) was supplied by Baoding Longer Precision Pump Co., Ltd. (Hebei, China). The resistance capacity of the coating to matrix effect was studied by ultraviolet spectrophotometry (UV, HIFACHI, U-3310, Japan).

2.3. Sample preparation and collection

2.3.1. Preparation of standard solutions

Standard stock solutions of 5 mmol L⁻¹ aldehydes (butanal, pentanal, hexanal, heptanal, octanal and nonanal) were prepared separately in methanol, stored at -20 °C. All the daily standard working solutions were prepared by appropriate dilution of the standard stock solution with ultra-pure water according to demand. A series of calibration solutions were prepared by spiking the standard stock solution in real EBC samples.

2.3.2. Preparation of EBC samples

Breath sampling was performed according to a validated procedure, which has previously been reported [31]. Briefly, EBC

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