



# Electrospun polystyrene/oxidized carbon nanotubes film as both sorbent for thin film microextraction and matrix for matrix-assisted laser desorption/ionization time-of-flight mass spectrometry



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## ABSTRACT

In the current study, polystyrene/oxidized carbon nanotubes (PS/OCNTs) film was prepared and applied as both an adsorbent of thin film microextraction (TFME) and matrix for matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI–TOF–MS) for the first time. The uniform size of PS/OCNTs film with OCNTs evenly and firmly immobilized in PS was obtained by electrospinning. And a novel TFME device was developed using the prepared PS/OCNTs film to enrich benzo[a]pyrene (BaP) from water, and also BaP and 1-hydroxypyrene (1-OHP) from urine sample. Then the extracted analytes on the PS/OCNTs film were directly applied to MALDI–MS analysis with PS/OCNTs film as the MALDI matrix. Our results show that PS/OCNTs film is a good TFME adsorbent toward the analytes and an excellent matrix for the sensitive determination of BaP and 1-OHP using MALDI–TOF–MS. The employment of PS/OCNTs as the matrix for MALDI can effectively avoid the large variation of signal intensity normally resulting from heterogeneous distribution of the adsorbed analyte on matrix layer, which therefore significantly improve spot-to-spot reproducibility. The introduction of PS in the film can prevent OCNTs from flying out of MALDI plate to damage the equipment. In addition, PS/OCNTs film also largely extended the duration of ion signal of target analyte compared to OCNTs matrix. The developed method was further successfully used to quantitatively determine BaP in environmental water and 1-OHP in urine samples. The results show that BaP and 1-OHP could be easily detected at concentrations of 50 pg mL<sup>-1</sup> and 500 pg mL<sup>-1</sup>, respectively, indicating the high detection sensitivity of this method. For BaP analysis, the linear range was 0.1–20 ng mL<sup>-1</sup> with a correlation coefficient of 0.9970 and the recoveries were in the range of 81.3 to 123.4% with the RSD ≤ 8.5% (n = 3); for urinary 1-OHP analysis, the linear range was 0.5–20 ng mL<sup>-1</sup> with a correlation coefficient of 0.9937 and the recoveries were in the range of 79.2 to 103.4% with the RSD ≤ 7.6% (n = 3). Taken together, the developed method provides a simple, rapid, cost-effective and high-throughput approach for the analysis of BaP in environmental water and endogenous 1-OHP in urine samples.

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## 1. Introduction

Thin film microextraction (TFME), one of solid-phase microextraction (SPME) techniques, has drawn an ever-increasing attention in the recent years. Although sample preparation methods such as solid-phase extraction (SPE) [1,2] and solid-phase microextraction (SPME) [3–5] have already been widely used in the past decades, TFME was considered as a good alternative to SPE due to its fast processing speed, labor-saving and environmental friendly

properties. Moreover, TFME can achieve higher extraction efficiency and shorter equilibration time than other SPME techniques owing to its large surface area and low thickness of membranous extraction phase [6,7].

Up to now, TFME has been used for sample preparation in various formats. Pawliszyn et al. coiled the film on a stainless-steel wire and then packed it into a glass tube, which was applied for polycyclic aromatic hydrocarbons (PAHs) sampling in aquatic environment and can fit well with gas chromatography (GC) injection port [8,9]. Gobas et al. coated the thin film on glass surface as a solid-phase sampler to measure the fugacity of some organic chemicals [10,11]. However, most of the developed TFME techniques are hard to scale up and cannot meet the needs of modern

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high-throughput analysis. In this regard, Vuckovic et al. developed an automated TFME device in a 96 robotic station for high-throughput analysis using liquid chromatography–electrospray tandem mass spectrometry [12], which, to some extent, indicates the great need of high throughput sample-pretreatment method.

As we know, MALDI–MS has its own advantages, such as simplicity of operation, high sensitivity and high throughput [13–16]. However, traditional organic matrices of MALDI, such as  $\alpha$ -cyano-4-hydroxycinnamic acid (CHCA), 2,5-dihydroxybenzoic acid (2,5-DHB) and sinapic acid (SA) are prone to produce high background interference in the low-molecule-mass region (<500 Da), which restricts the analysis of low-molecular-weight compounds. To solve this problem, various matrices have been proposed, including surfactant-suppressed matrix [17,18], nanostructure-based matrix-free substrates [19–22], carbon-based materials including C60 [23], carbon nanotubes (CNTs) [24–26], oxidized carbon nanotubes (OCNTs) [27,28], graphene (G) [29,30] and graphene oxide (GO) [31,32], as well as some new organic matrices such as 9-aminoacridine [33] and ion-less matrix [34]. Taking advantages of the efficient desorption/ionization ability, high surface area and  $\pi$ – $\pi$  electrostatic stacking property, CNTs-based materials have been regarded as one of the most powerful and promising matrices for the MALDI–MS analysis of small molecules and excellent adsorbent for the enrichment of aromatic analytes [35]. In our previous work, OCNTs were applied as both an adsorbent and MALDI matrix for the determination of benzo[a]pyrene (BaP) [27]. However, OCNTs are easy to aggregate together and make the matrix distribution heterogeneous, leading to poor reproducibility [28]. On the other hand, unimmobilized-OCNTs cannot attach firmly on the MALDI plate and may easily fly off from the plate under vacuum, resulting in contamination of the instrument and time-limited signals [17,24].

Electrospinning is a simple, versatile and high-throughput technique to prepare fibrous materials with controllable diameters, compositions and morphologies [36]. The principle of electrospinning is similar to electrospray, by which the spinnable sol is applied with a high voltage and drew into nanofibers. As the spun fibers can uniformly deposit on a flat substrate to form the thin film, electrospinning technique has been gradually introduced to prepare thin film extraction materials in recent years [6,37]. Electrospun thin film extraction materials such as nylon 6 nanofiber membrane [38–40], polyacrylonitrile/polyaniline core/shell nanofiber mat [41] and polypyrrole–polyamide nanofiber sheet [42,43] have been reported in the recent years. However, little effort has been taken to combine high-throughput electrospinning preparation technique with high-throughput MALDI–MS analysis technique through TFME technique.

In the current study, we incorporated OCNTs to electrospun PS fibers to form stable PS/OCNTs film. We then developed a novel TFME device coupled with MALDI–TOF–MS analysis using PS/OCNTs film as both an adsorbent of TFME and MALDI matrix for the determination of BaP in water and 1-OHP in urine. Here, PS/OCNTs electrospun film was applied as an extraction material for the first time, and this new coupling analysis approach combining TFME with MALDI–MS was also proposed for the first time. For this new TFME device, the PS/OCNTs film was fixed on the inner wall of the cap of sample vial for the extraction of analytes. After sample loading, the PS/OCNTs film was directly applied to MALDI plate for analysis without any additional desorption process or adding matrix. The proposed analytical procedure is quite simple and can avoid the loss of analytes due to no desorption process. Since OCNTs were evenly and firmly immobilized in the electrospun PS, it avoids the large variation of signal intensity across different positions on the MALDI plate well resulting from heterogeneous distribution of matrix–analyte layer. The

developed method was then further successfully applied to quantitative analysis of BaP in environmental water and 1-OHP in urine with good performance.

## 2. Experimental

### 2.1. Reagents and materials

Polystyrene (PS, average MW 250,000) and benzo[a]pyrene (BaP) ( $4 \text{ mg mL}^{-1}$  in  $\text{CH}_2\text{Cl}_2$ ) were purchased from J&K Chemical Ltd. (Tianjin, China). Benzo[a]pyrene- $d^{12}$  (BaP $^{12}$ , 98%) was purchased from Sigma-Aldrich (St. Louis, MO, USA). 1-Hydroxypyrene (1-OHP) stock solution ( $100 \text{ mg L}^{-1}$  in methanol) was provided by Prof. Huanwen Chen (East China Institute of Technology, Nanchang, China). 2,5-Dihydroxybenzoic acid (2,5-DHB),  $\alpha$ -cyano-4-hydroxycinnamic (CHCA), sinapic acid (SA), trifluoroacetic (TFA) and phosphoric acid ( $\text{H}_3\text{PO}_4$ ) and  $\beta$ -glucuronidase/arylsulfatase (type H2 from *Helix pomatia*) were purchased from Sigma-Aldrich (St. Louis, Missouri, USA). Dimethyl formamide (DMF), isopropyl alcohol, acetonitrile (ACN) and methanol were HPLC grade. Purified water was obtained with a Milli-Q apparatus (Millipore, Bedford, Massachusetts, USA). Multi-walled carbon nanotubes (MWCNTs, length 5.0–15  $\mu\text{m}$ , diameter 10–20 nm) modified with carboxyl (carboxyl ratio 2.31 wt%) were purchased from Nanotech Port Co. (Shenzhen, China). Before use, MWCNTs were washed with toluene by Soxhlet extraction for 48 h at  $120^\circ\text{C}$ , then the resultant MWCNTs were dried under reduced pressure at  $80^\circ\text{C}$  for 24 h.

### 2.2. Preparation of standard solutions

BaP and BaP $^{12}$  were dissolved in isopropyl alcohol at concentrations of  $10 \mu\text{g mL}^{-1}$  and  $1.0 \mu\text{g mL}^{-1}$ , respectively, as stock solutions. BaP, BaP $^{12}$  and 1-OHP were diluted to different concentrations and stored at  $4^\circ\text{C}$  before use. The volume of each diluted solution for MALDI–TOF–MS analysis was  $0.8 \mu\text{L}$ .

### 2.3. Preparation of water samples

Five types of water samples were selected for investigation. Water sample 1 was tap water and taken from the laboratory after flowing for 10 min. Water samples 2 and 3 were taken from the East Lake and the South Lake (Wuhan, China), respectively. Water samples 4 and 5 were taken from a factory of Wuhan (China). All water samples were filtered through  $0.45 \mu\text{m}$  micropore membranes and stored in brown glass bottles at  $4^\circ\text{C}$ .

### 2.4. Preparation of urine sample

Urine samples were collected from Zhongnan Hospital (Wuhan, China). Written informed consent was obtained from the study subjects, and an approval was granted by the Zhongnan Hospital Ethics Committee and met the declaration of Helsinki. The collected urine samples were kept frozen at  $-20^\circ\text{C}$  before use.

A  $0.5 \text{ mL}$  aliquot of urine sample was diluted with  $0.5 \text{ mL}$  acetate buffer (pH 5.2,  $10 \text{ mM}$ ), and then  $10 \mu\text{L}$  of  $\beta$ -glucuronidase/arylsulfatase ( $\geq 85,000 \text{ unit mL}^{-1}$   $\beta$ -glucuronidase and  $\geq 7500 \text{ units mL}^{-1}$  sulfatase) was added to the above solution. The mixture was incubated in a shaker at  $37^\circ\text{C}$  for 3 h. The resulting samples were further diluted 2 times with ACN and centrifugation. The supernatant was collected and diluted 2.5 times with sodium acetate solution (pH 5.2,  $10 \text{ mM}$ ) for the extraction process.

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