# Facile modification of multi-walled carbon nanotubes–polymeric ionic liquids-coated solid-phase microextraction fibers by on-fiber anion exchange

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A B S T R A C T

In situ anion exchange has been proved to be an efficient method for facile modification of polymeric ionic liquids (PILs)-based stationary phases. In this work, an on-fiber anion exchange process was utilized to tune the extraction performance of a multi-walled carbon nanotubes (MWCNTs)-poly(1-vinyl-3-octylimidazolium bromide) (poly(VOIm⁺Br⁻))-coated solid-phase microextraction (SPME) fiber. MWCNTs were first coated onto the stainless steel wire through a layer-by-layer fabrication method and then the PILs were coated onto the MWCNTs physically. Anion of the MWCNTs–poly(VOIm⁺Br⁻) fiber was changed into bis(triflroromethanesulfonyl)imide (NTf₂⁻) and 2-naphthalene-sulfonate (NapSO₃⁻) by on-fiber anion exchange. Coupled to gas chromatography, the MWCNTs–poly(VOIm⁺Br⁻) fiber showed acceptable extraction efficiency for hydrophilic and hydrogen-bonding-donating alcohols, with limits of detection (LODs) in the range of 0.005–0.05 $\mu$g mL$^{-1}$; after the anion exchange with NTf₂⁻, the obtained MWCNTs–poly(VOIm⁺NTf₂⁻) fiber brought wide linear ranges for hydrophobic *n*-alkanes with correlation coefficient ($R$) ranging from 0.994 to 0.997; aromatic property of the fiber was enhanced by aromatic NapSO₃⁻ anions to get sufficient extraction capacity for phthalate esters and halogenated aromatic hydrocarbons. The MWCNTs–poly(VOIm⁺NapSO₃⁻) fiber was finally applied to determine several halogenated aromatic hydrocarbons in groundwater of industrial park.

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## 1. Introduction

Solid-phase microextraction (SPME) has received wide applications since its first introduction in the 1990s [1]. One of the most important factors of this method is the extraction property of fiber sorbent coatings. Hydrophobic coating materials are usually used for non-polar and medium polar analytes [2–8]. Polar and hydrophilic compounds often keep strong affinity with aqueous sample matrix. To obtain satisfactory extraction efficiency, sorbent coating materials for these analytes should have appropriate polar functional groups to strengthen the interactions between the coating and the analytes [9].

Compared with other kinds of materials applied for SPME, carbon nanotubes have attracted much more attention because of their high surface-to-volume ratio, the possibility of surface

functionalization and favorable thermal features, etc. [10]. The characteristic structures and electronic properties allow them to interact strongly with some organic molecules through non-covalent forces, such as hydrogen bonding, $\pi$–$\pi$ stacking, electrostatic forces, van der Waals forces and hydrophobic interactions [11–13]. These interactions and the hollow nano-sized structure make them a good candidate for sorbent materials of sample preparation methods.

Ionic liquids (ILs) are another kind of popular sorbent material for sample preparation. They are capable of providing most types of interactions with solutes (e.g., dispersive, $\pi$–$\pi$, $n$–$\pi$, hydrogen bonding, dipolar, ionic/charge–charge) [14]. Polymeric ionic liquids (PILs) have got more applications than ILs in SPME because of the improved thermal stability and viscosity. Recent reports showed that PILs-based SPME sorbents exhibited excellent tunability for different analytical tasks. PILs with halogen anions had high extraction efficiency for analytes with hydrogen bond donating property, such as alcohols and some organic acids [15,16]; PILs with PF₆⁻ and bis(triflroromethanesulfonyl)imide (NTf₂⁻) anions were hydrophobic, and they were suitable for the extraction of

hydrophobic compounds [17]; aromatically functionalized cation or anion can bring high extraction efficiency for aromatic analytes [18–20]; crown ether functionalized ILs fiber showed high selectivity for medium polar to polar compounds [21,22]. The above modifications of PILs were performed on IL monomers before fiber preparation. It was noted that properties of ILs-modified materials can be easily tuned by in situ anion exchange process. Qiu et al. [23] used an in situ anion exchange procedure to enhance the chromatographic selectivity of a PILs-based stationary phase. We also improved the chromatographic separation of an imidazolium IL functionalized silica column by in situ anion-exchange with dodecyl sulfonate and dodecylbenzene sulfonate anions [24]. IL-modified carbon nanotubes can be tuned by anion exchange to obtain reversible and switchable solubility between aqueous and organic solvents [25]. All these attractive results were instructive for preparing functionalized PILs-SPME fibers by in situ anion exchange. Anderson and co-workers [26] recently prepared a novel cross-linked PIL bucky gel SPME coating by free-radical polymerization of PILs gelled with multi-walled carbon nanotubes (MWCNTs). The MWCNTs–PILs composite coating showed higher extraction efficiency for model analytes.

In this work, the "in situ anion exchange" was applied as an "on-fiber" process to tune the extraction performances of a MWCNTs–poly(1-vinyl-3-octylimidazolium bromide) SPME fiber. The MWCNTs, used to support the PILs, were first coated onto the stainless steel wire by a layer-by-layer chemical-bonding process. The poly(1-vinyl-3-octylimidazolium bromide) (poly(VOIm$^+$Br$^-$)) was physically coated onto the MWCNTs. The on-fiber anion exchange strategy was then applied to change the anion of poly(VOIm$^+$Br$^-$) into NTf$_2^-$ and 2-naphthalene-sulfonate (NapSO$_3^-$), respectively. Extraction performances of fibers with Br$^-$, NTf$_2^-$, and NapSO$_3^-$ anions were investigated using four kinds of model analytes, including alcohols, $n$-alkanes, phthalate esters and halogenated aromatic hydrocarbons. The proposed MWCNTs–poly(VOIm$^+$NapSO$_3^-$)-SPME method combined with GC was also used to determine several halogenated aromatic hydrocarbons in groundwater of industrial park.

## 2. Experimental

### 2.1. Chemicals and materials

The stainless steel wire was purchased from Yixing Shenglong Metal Wire Net. Co. (Jiangsu, China). Aqueous ammonia (NH$_3$·H$_2$O, 28 wt.%) was purchased from Laiyang Fine Chemical Factory (Laiyang, China). Glucose was purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). 3-Mercaptopropyltrimethoxysilane (98%) and 3-aminopropyltrimethoxysilane (98%) were obtained from Qufu Chenguang Fine Chemical Co. (Shandong, China) and purified by vacuum distillation before use. The MWCNTs–COOH (o.d. 8–15 nm) were purchased from Chengdu Organic Chemicals, Chinese Academy of Science (Chengdu, China). $n$-Octane (C$_8$), $n$-decane (C$_{10}$), $n$-dodecane (C$_{12}$), $n$-tetradecane (C$_{14}$), $n$-hexadecane (C$_{16}$), 1,3-dichlorobenzene (1,3-DCB), 1,2-dichlorobenzene (1,2-DCB), 1,4-dichlorobenzene (1,4-DCB), 1,3-dibromobenzene (1,3-DBB), 1-chloronaphthalene (1-CN) and 1-bromonaphthalene (1-BN) were obtained from Shanghai Chemical Reagent Factory (Shanghai, China). Methanol, ethanol, $sec$-butanol, $n$-propanol, $iso$-butanol, $iso$-pentanol, $n$-pentanol, and $n$-hexanol were purchased from Beijing Fuxing Chemical Reagent Plant (Beijing, China). Lithium bis(trifluoromethanesulfonyl)imide (Li$^+$NTf$_2^-$) was obtained from Alfa Aesar (Ward Hill, MA, USA). Sodium 2-naphthalene-sulfonate (Na$^+$NapSO$_3^-$) was obtained from Aladdin reagent (Shanghai, China). Azobisisobutyronitrile (AIBN) was obtained from Shanpu

Chemical Co. (Shanghai, China) and purified through recrystallization before use. 1-Vinyl-3-octylimidazolium bromide (VOIm$^+$Br$^-$) was purchased from Shanghai Chengjie Chemical Co. (Shanghai, China). Di-$n$-butyl phthalate (DBP), dicyclohexyl phthalate (DCHP), di-$n$-amyl phthalate (DAP), di-$n$-octyl phthalate (DOP), butyl benzyl phthalate (BBP), and di-(2-ethylhexyl) phthalate (DEHP) were purchased from Shanghai Jingchun Industry Co. (Shanghai, China).

Stock solution of alcohols was prepared in acetone with the concentration at 10.0 mg mL$^{-1}$. Stock solutions of $n$-alkanes, phthalate esters and halogenated aromatic hydrocarbons were prepared in ethanol with the concentration at 1.0 mg mL$^{-1}$. Working solutions for extraction were freshly prepared by diluting the stock solutions with distilled water. Groundwater samples were obtained from Shouguang Bohai Chemical Industrial Park.

### 2.2. Chromatographic method

Separation and detection of analytes were performed by an Agilent 7890A gas chromatograph equipped with a flame ionization detector system and a split/splitless injector (Agilent Technologies, USA). The column used for the separations of $n$-alkanes, phthalate esters and halogenated aromatic hydrocarbons was HP-5 capillary column (30 m × 0.32 mm i.d. × 0.25 μm film thickness) (Agilent Technologies, USA). The column used for the separation of alcohols was AT-FFAP capillary column (30 m × 0.32 mm i.d. × 0.33 μm film thickness) (AT, Lanzhou).

Ultrapure nitrogen (>99.999%) was used as the carrier gas at 1 mL min$^{-1}$ for alcohols, $n$-alkanes and halogenated aromatic hydrocarbons, and 1.5 mL min$^{-1}$ for phthalate esters. The make-up gas was fixed at 25 mL min$^{-1}$. The injector was used in splitless mode at 200 °C for alcohols, 250 °C for $n$-alkanes and halogenated aromatic hydrocarbons, and 280 °C for phthalate esters. The temperature programs for separations were as follows: for the separation of phthalate esters, the column temperature was initially held at 100 °C, and programmed at 10 °C min$^{-1}$ to 300 °C; for the separation of $n$-alkanes, the column temperature was initially held at 50 °C, and programmed at 5 °C min$^{-1}$ to 75 °C, and then programmed at 15 °C min$^{-1}$ to 300 °C; for the separation of alcohols, initial temperature was held at 45 °C for 6 min and programmed at 2 °C min$^{-1}$ to 46 °C, and finally at 8 °C min$^{-1}$ to 160 °C; for the separation of halogenated aromatic hydrocarbons, the column temperature was initially held at 40 °C for 5 min, and programmed at 12 °C min$^{-1}$ to 70 °C, and then at the rate of 20 °C min$^{-1}$ to 220 °C. A series of standard solutions with different concentration levels were prepared and used to obtain analytical parameters in method validation and quantification data of real samples.

### 2.3. Characterization

Fourier transform infrared spectra (4000–500 cm$^{-1}$) in KBr were recorded with an Infrared spectrum instrument (Thermo Nicolet Nexus 870, ALS, CA). Surface morphological studies were performed by a scanning electron microscope (SEM, JSM-6701F, JEOL Ltd., Japan) at 5.0 kV.

### 2.4. Fiber preparation

#### 2.4.1. Surface functionalization of stainless steel wire
The fabrication of the MWCNTs–PILs fiber was illustrated in Fig. 1. The stainless steel wire was first cut into 18 cm in length. One tip of the wire (2 cm) was washed with NaOH aqueous solution (1.0 mol L$^{-1}$) and then dipped in mixed acid (H$_2$SO$_4$:HNO$_3$ = 3:1, v/v) at 70 °C for 1 min to remove the oxide layer. After being washed with distilled water, it was immersed into the mixture of glucose solution and [Ag(NH$_3$)$_2$]$^+$ solution to form a microstructured silver