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Multiwalled carbon nanotubes-doped polymeric ionic liquids coating for multiple headspace solid-phase microextraction

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ABSTRACT

Multiple headspace solid-phase microextraction (SPME) has proved high efficiency in analysis of volatile compounds in complex samples. Fibers used in multiple headspace SPME must provide a logarithm relationship between peak areas and extraction times. The aim of this work was to investigate the potential of a carbon nanotube doped-polymeric ionic liquid (PILs) fiber for multiple headspace SPME of 2-naphthol in fruit samples, using gas chromatography (GC) for analysis. Based on theory of multiple headspace SPME, β parameters of fruit and aqueous samples were obtained and used for quantitation. The interference effects of sample matrix on proposed multiple headspace SPME method were investigated and compared with that of headspace SPME by determination of significant differences (P) of peak areas. It showed high independence from matrix effects. The proposed multiple headspace SPME-GC method also exhibited high repeatability (relative standard deviation of 2.56%) and recoveries (81.9–110%) for the analysis of real samples.

1. Introduction

Solid-phase microextraction (SPME) was firstly introduced by Pawliszyn and co-workers in 1990s [1]. Because of its advantages over other conventional extraction methods, it has been applied widely to the analysis of environmental pollutes [2–5], food additives [6,7], biological samples [8,9], drugs [10–12], etc. SPME is an equilibration extraction technique, in which only a small portion of target analyte is removed from sample matrix and absolute recoveries are usually far from 100%. The concentration of an analyte is determined by its linear relationship with the amount of analyte extracted by the fiber coating, which can be constructed from analytical responses obtained for known amounts of analytes using standards solutions [6]. However, the calibration linearity in complex sample matrix is usually different from that obtained by standard solution because of “matrix effect”. The different components and characteristics of sample matrix cause considerable differences in the partition coefficients and releasing rates of the same analytes [13]. Moreover, for some complex samples, it is really difficult to find the same kind of matrix or blank samples for standard spiking. Traditional calibration method, such as internal standard, standard addition, and matrix matched standards are often used to compensate the matrix effect. Nevertheless, quantitative analysis of low content analytes in complex sample is still a tough task due to the difficulties in preparing spiked samples for calibration [13,14].

Multiple headspace SPME is an efficient modification of SPME developed for quantitative analysis of complex samples [6,13–18]. It involves several consecutive extractions from the same vial until the target analytes is exhaustive in sample. The sum of all of peak areas (A_T) corresponds with the total amount of analytes in sample and is therefore independent from its composition. According to the theoretical principle of multiple headspace SPME [19], A_T can be calculated by $A_1/(1-\beta)$, where A_1 is the peak area of the first extraction and β is a constant which is calculated from the linear regression of the logarithms of individual peak areas: $\ln A_i = (i-1)\ln\beta + \ln A_1$ (A_i is the corresponding peak area in the ith times extraction). However, the exponential decay of peak areas vs. the number of the extractions is difficult to obtain. It is usually related to the properties of sample matrix, extraction conditions and especially the extraction performance of SPME fibers. To obtain reliable analytical results, the β value should be in the range of 0.40 to 0.95 [19]. A suitable SPME fiber employed for the analysis was always essential to provide an appropriate coating-sample distribution coefficient, since in multiple headspace SPME it is essential to extract a significant amount of analytes to get an exponential decay of peak areas vs. the number of extractions [13].

Polymeric ionic liquids (PILs) have been widely used as coating materials in SPME. The special solvation properties provide high

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extraction efficiency for polar or non-polar analytes with different volatility [20–26]. Coating thickness of most PILs based SPME fibers prepared by in-situ polymerization process was only about 5 μm or 11 μm [21–23], and even for those prepared by physical coating that was only about 10–20 μm [24–26]. It is well known that higher coating thickness in SPME is accompanied by higher extraction efficiencies [26–29]. Currently existed PILs based SPME fibers were hard to be performed in multiple headspace SPME procedures because of the low extraction capacity. In our previous study, thickness of PIL coating was increased by an in-situ crosslinking polymerization process, and that was favorable for the increase of extraction efficiency [30].

Compared with other kinds of materials used for SPME, nanomaterials offer a significant higher surface area-to-volume ratio that promises much greater extraction capacity and efficiency [2]. Carbon nanomaterials represented by carbon nanotubes have got wide application in separation science [31–34]. In this work, the crosslinked PIL was doped by multiwalled carbon nanotubes (MWCNTs) to enhance its extraction capacity for multiple headspace SPME. The PIL/MWCNTs composite was prepared in-situ on functionalized stainless steel wire. Coupled to gas chromatography (GC), the proposed fiber was used to multiple headspace SPME of 2-naphthol. 2-Naphthol is used in the production of fungicides and preservatives, which are usually used in conservation of citrus fruits. It is harmful for blood circulation and kidney. 2-Naphthol-based preservatives are usually covered outside the peel of citrus fruits, and that is a hidden danger because long-time storage or excess use of preservatives may cause a contamination of fruit flesh. The maximum usage amount in China of 2-naphthol for citrus fruits is 0.1 g kg^{-1}, and the limits of residue is 70 mg kg^{-1} (both for the whole commodity). The reliability of the as-established multiple headspace SPME-GC method for the analysis of 2-naphthol in fruit samples was investigated in this work.

2. Experimental

2.1. Materials and reagents

The stainless steel wire (∅ 112.5 μm) was purchased from the Yixing Shenglong Metal Wire Net. Co. (Jiangsu, China). Aqueous ammonia ($NH_3 \cdot H_2O$, 28 wt%) was purchased from the Laiyang Fine Chemical Factory (Laiyang, China); 1,6-dibromohexane, 1-vinylimidazole, 3-mercaptopropyltrimethoxysilane (MPS), vinyltrimethoxysilane and glucose were purchased from the Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Azodiisobutyronitrile (AIBN) was obtained from Shanpu Chemical Co. (Shanghai, China) and purified through recrystallization before use. 1-Vinyl-3-ethylimidazolium bromide ($VEIm^+Br^-$) and 1-vinyl-3-octylimidazolium bromide ($VOIm^+Br^-$) were purchased from Shanghai Chengjie Chemical Co. (Shanghai, China). Ammonium hexafluorophosphate (NH_4PF_6) was purchased from the J&K Scientific Ltd. The MWCNTs was purchased from the Chengdu Organic Chemicals, Chinese Academy of Science (Chengdu, China). 2-Naphthol was purchased from Tianjing Chemical Reagent Plant (Tianjin, China). Stock solution of 2-naphthol was prepared in ethanol at 1 mg mL^{-1} and stored at 4 °C for use.

2.2. Samples for multiple headspace SPME

Three kinds of citrus sample were purchased from local market in Jinan of China. The peel part and the flesh part of orange (sample 1) were used in condition optimization and method validation procedures. They were triturated by a blender at room temperature respectively and then placed in vials without any headspace and stored at −4 °C until analysis. In the spiking procedure, a certain amount of 2-naphthol stock solution was added into 50 g of flesh sample to reach concentration levels at 20, 40, 50, 80, 100, 150, 200 and 400 μg g^{-1}, respectively. The flesh parts of pomelo and orange (sample 2 and sample 3) were used for evaluation of matrix effect on headspace SPME and multiple headspace SPME, which were also triturated by a blender at room temperature respectively. Both of the two samples were spiked at 2 and 6 μg g^{-1}. The spiked samples were homogenized by stirring, and finally kept in darkness for 24 h before it was used for analysis.

Aqueous working solutions with concentration of 2-naphthol at 10, 15, 30, 50, 80, and 100 μg L^{-1} were prepared by diluting the stock solution with distilled water.

2.3. Apparatus

Analysis of the model compounds was performed with an Agilent 7890A GC system (Agilent Technologies, USA) equipped with a flame ionization detector (FID) and a split/splitless injector. The column for the determination was an HP-5 capillary column (Agilent Technologies, USA) (30 m × 0.32 mm id. × 0.25 μm film thickness).

Ultrapure nitrogen ($>99.999\%$) was used as the carrier and make-up gas at 1.0 mL min^{-1} and 25 mL min^{-1}, respectively. The injector was used in splitless mode at 280 °C. The detector temperature was fixed at 300 °C. Temperature programs for analysis was as follows: initial temperature was held at 120 °C and programmed at 15 °C min^{-1} to 300 °C.

Surface properties of the proposed fiber were characterized by a scanning electron microscope (SEM, JSM-6701F, JEOL Ltd., Japan).

2.4. Preparation of PIL/MWCNTs-coated SPME fiber

2.4.1. Oxidation of MWCTNs

Oxidized MWCNTs was prepared according to procedures described in Ref. [35]. 0.5 g of MWCNTs and 100 mL of mixed acid ($H_2SO_4/HNO_3=3/1$, v/v) were added into a beaker and then subjected to an ultrasonic bath for 30 min. Then the mixed acid solution was removed, and the oxidized MWCNTs were washed

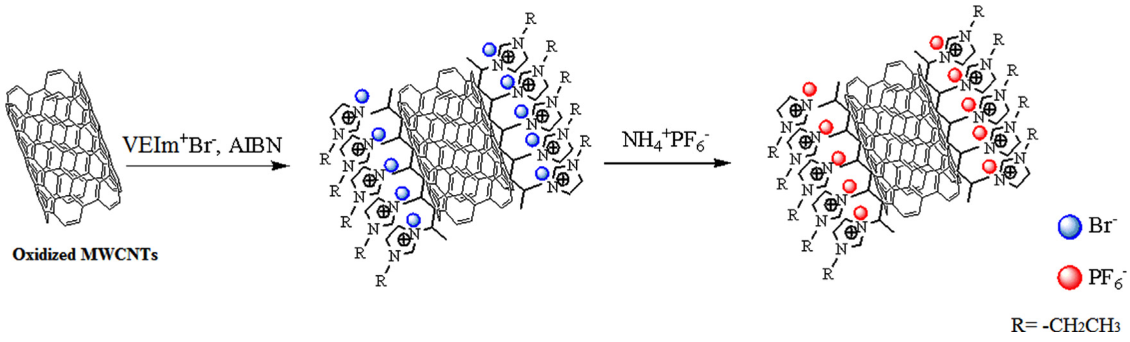

Fig. 1. Non-covalent functionalization of oxidized MWCNTs with poly($VEIm^+PF_6^-$).