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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 cross-linking 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

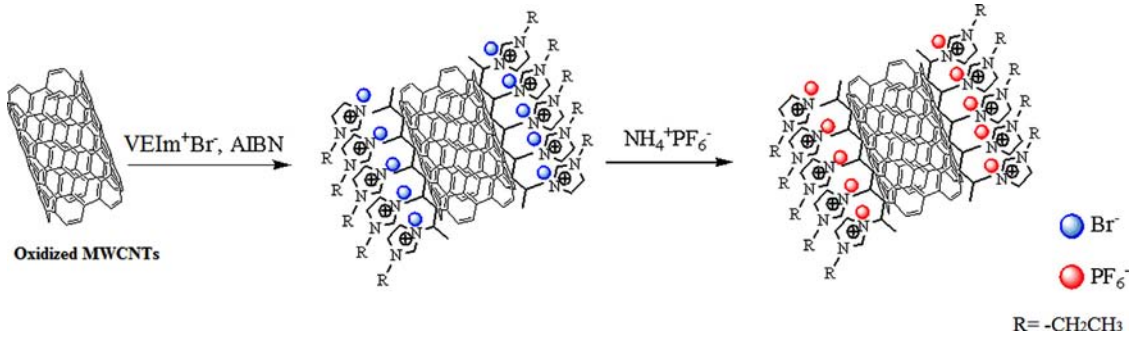

Fig. 1. Non-covalent functionalization of oxidized MWCNTs with poly($VEIm^+PF_6^-$).

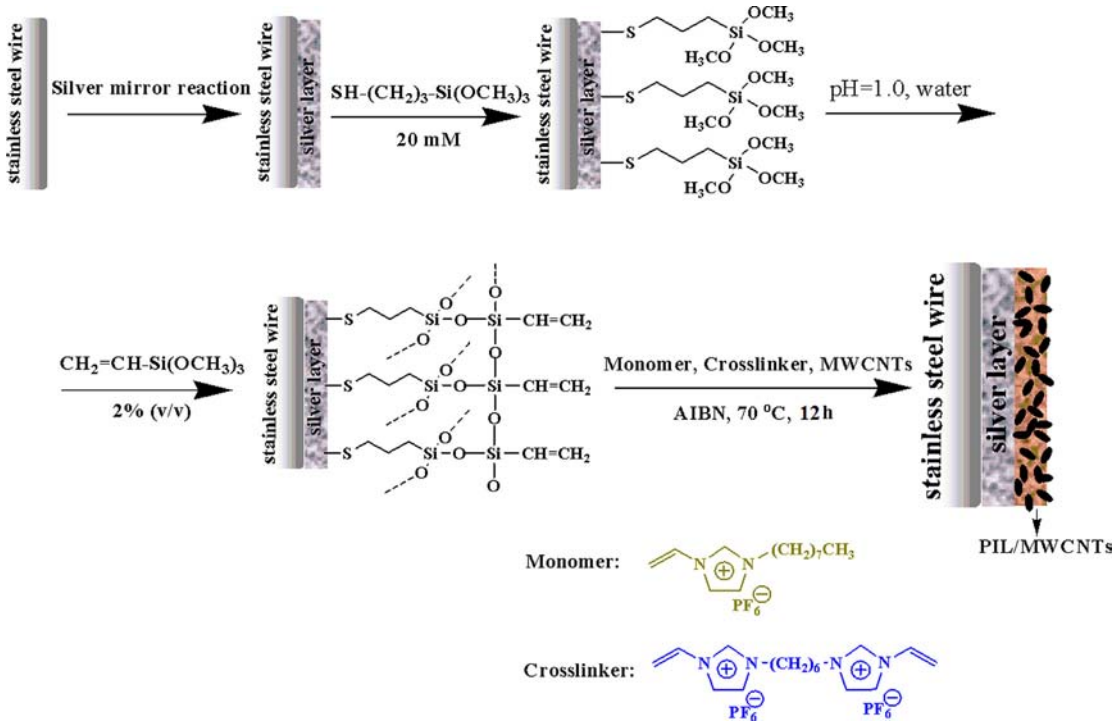

Fig. 2. Schema of preparation of MWCNTs/poly(VOIm$^+$PF$_6^-$) SPME fiber.

with water until pH 7. Finally, the oxidized MWCNTs were separated from the water by 0.45 μm filter and dried in vacuum.

2.4.2. Dispersion of oxidized MWCNTs in DMSO

To increase the dispersion of MWCNTs in pre-polymerization solution, the oxidized MWCNTs were functionalized with PIL non-covalently [36]. As shown in Fig. 1, 2.0 g of 1-vinyl-3-ethylimidazolium bromide (VEIm$^+$Br$^-$) monomer and 20 mL of ethanol were added into a round bottom flask. 20 mg of oxidized MWCNTs in 30 mL of deionized water was subjected to an ultrasonic bath for 20 min, and then added to the IL solution. After the addition of AIBN (50 mg), the flask was purged with nitrogen for 20 min and then stirred at 70 °C for 12 h under nitrogen atmosphere. After polymerization, the PIL(Br) wrapped MWCNTs (MWCNTs-PIL(Br)) were separated by centrifugation and washed with ethanol for three times. Finally, the ethanol solvent was removed in a vacuum.

The MWCNTs-PIL(Br) were dispersed in water. A 1.0 equivalent of NH_4PF_6 with original IL monomer was added into the aqueous dispersion. The mixture was stirred for 2 h at room temperature to complete the anion exchange of PIL. As a result, the MWCNTs-PIL(PF_6) were precipitated in the aqueous solution. Equal volume of dichloromethane was added into the solution and the MWCNTs-PIL(PF_6) were immediately dispersed in the organic phase. After that, the MWCNTs-PIL(PF_6) phase was washed with deionized water to remove Br^- completely. Finally, the organic solvent was removed by distillation and the MWCNTs-PIL(PF_6) were dried in vacuum. 0.1 g of MWCNTs-PIL(PF_6) were dispersed in 30 mL of DMSO for use.

2.4.3. Preparation of PIL/MWCNTs-coated SPME fiber

1,1'-(1,6-hexanediyl)bis(1-vinylimidazolium) bishexafluorophosphate was prepared and used as the crosslinking agent by procedures in our previous work [30]. 1-Vinylimidazole and 1,6-dibromohexane were dissolved in acetone with molar ratio at 2:1. The mixture was stirred for 24 h at room temperature. After the reaction, the precipitate was obtained by filtering and purified by recrystallization in acetone three times. Anions of the crosslinking agent and monomer (VOIm$^+$Br$^-$) were both exchanged with PF_6^- by anion-exchange process [21]. Target ILs were dried in a vacuum for use.

Preparation procedures of the proposed PIL/MWCNTs fiber were illustrated in Fig. 2. The functionalization of stainless steel wire was performed by the procedures in previous reports[30,37]. Briefly, the stainless steel wire was firstly coated by silver layer via silver mirror reaction [38]. The microstructured silver coated fiber was immersed in an ethanol solution of MPS (20 mM) for 12 h to form a self-assembled monolayer (SAM) of MPS on it. Then the fiber was immersed into acidic water (pH, 1.0) for hydrolysis. Finally, the SAM modified fiber was functionalized with vinyl groups by immersing it in vinyltrimethoxysilane solution in ethanol (20 mM) for 12 h.

After modification, the fiber was coated with PIL/MWCNTs composite by crosslinking copolymerization according to the following procedures: 2 mL of MWCNTs-PIL(PF_6) solution was transferred into a 15 mL vial; 60 mg of VOIm$^+$PF$_6^-$, 80 mg of crosslinking agent and 10 mg of AIBN were added into the vial and dissolved by shaking; vinyl-functionalized stainless steel wire was put into the pre-polymerization solution; the whole system was purged with nitrogen for 20 min and then reacted at 70 °C for 12 h under nitrogen atmosphere. After the reaction, the solution turned to semi-solid state like gel. The fiber was pulled out from the tube carefully. After the vapourization of solvent, the fiber was immersed again into another fresh pre-polymerization solution, and the procedure was repeated for 5 times to thicken the coating.

2.5. Headspace solid-phase microextraction

The fiber was installed into a homemade SPME device. A certain amount of citrus sample was weighed in a 10 mL-vial, sealed and extracted at 40 °C for 50 min. The extraction of spiked aqueous samples was performed in 10 mL-vail with 0.2 mL of working solution. A magnetic agitator was used to accelerate

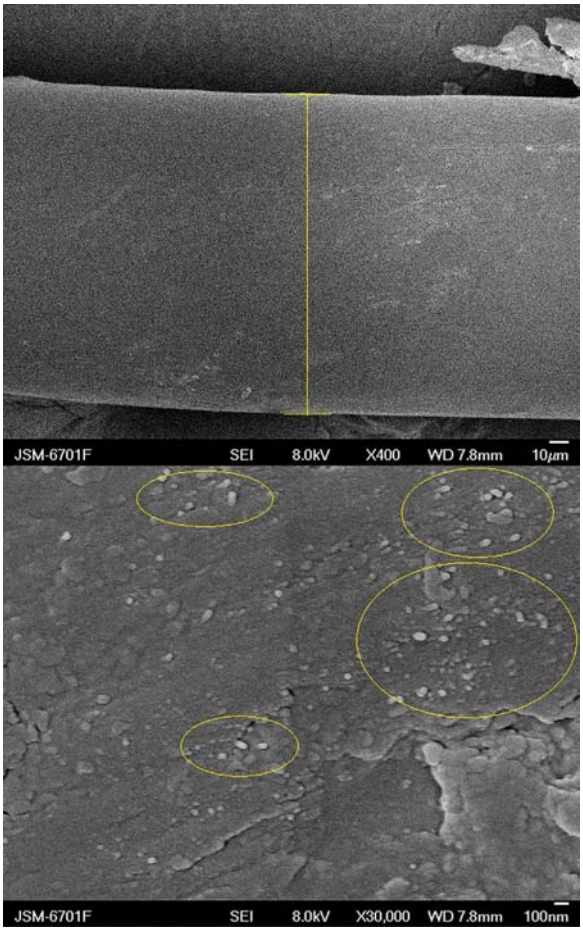

Fig. 3. SEM images of MWCNTs/poly($VOIm^+PF_6^-$) SPME fiber.

extraction. After the extraction, the fiber was immediately desorbed at 280 °C for 3 min in GC inlet. All the determinations were performed for three times except for extra explanations.

3. Results and discussion

3.1. Fiber

As 2-naphthol is naphthalene homologs of phenol with relative polarity and hydrophobicity, fiber coating which can provide polar, hydrophobic and π–π interactions was suitable for its extraction. PILs are popular with their capacity of most types of interactions with solutes (e.g., dispersive, π–π, n–π, hydrogen bonding, dipolar ionic/charge–charge), and they have been used for the analysis of polar, semipolar and nonpolar analytes. MWCNTs are capable for providing highly strengthened π–π interaction, and surface area of the fiber can be also increased through their doping in PIL. Therefore, the poly($VOIm^+PF_6^-$)/MWCNTs composite was a promising coating for efficient multiple headspace extraction of 2-naphthol.

Fig. 3 shows the scanning electron microscope (SEM) images of the prepared MWCNTs-doped PIL fiber. Thickness of the coating was about 21 μm. The coating was strewn with MWCNTs, and the MWCNTs outcrops laid all over the surface.

3.2. Optimization of extraction conditions

Extraction conditions for samples with different matrix were optimized separately by factor-by-factor method.

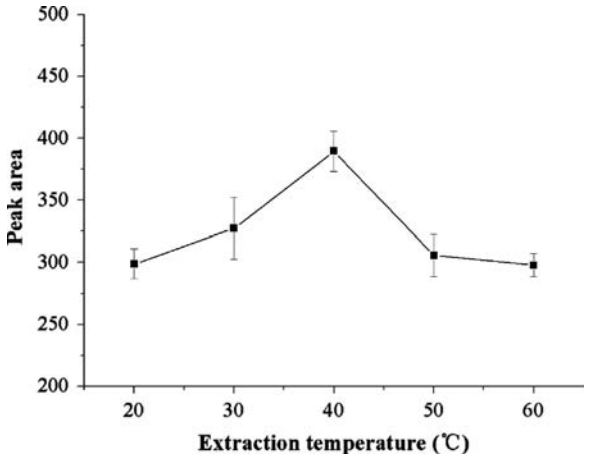

Fig. 4. Effect of extraction temperature on peak area. Conditions: extraction time, 50 min; amount of sample, 50 mg; spiking level, 2.5 μg g^{-1}.

50 mg of flesh sample was weighed in a 10 mL-vial and used as working sample for optimization procedures. As shown in Fig. 4, the extracted amount of 2-naphthol increased as the temperature increased from 20 to 40 °C and decreased with a further temperature increase. It was also found that at lower extraction temperature (20 and 30 °C), peak areas for the first and the second extraction were approximately the same. This could be explained by the slow diffusion of analytes from sample to headspace at low temperature. Peak areas decreased at high temperature (60 °C). It possibly can be ascribed to the displacement of equilibrium between the fiber coating and headspace to the vapor phase, which decreased compounds retention on sorbent material [39]. Changes of peak areas extracted for 10, 20, 30, 40, 50 and 60 min were shown in Fig. 5. The extraction reached stable and high extraction efficiency at 50 min, and so the extraction time was fixed at 50 min.

Besides, optimum conditions for the peel part were studied by similar procedures. It was the same with that of the fresh sample (optimum extraction time was 50 min and extraction temperature was 40 °C).

Optimum extraction conditions for aqueous samples were studied with 0.2 mL of aqueous sample with addition level at 50 μg L^{-1}. Based on the experimental results, the extraction time was 40 min, and the extraction temperature was 40 °C. Ionic strength of the aqueous sample was adjusted by KCl (30%, w/v, g mL^{-1}) to obtain highest extraction efficiency.

3.3. Sample and standard amounts

The amount of sample placed in the vial must be appropriate to observe an exponential decay of the peak area with the number of extractions [6]. Because there was no 2-naphthol detected in flesh part, the flesh sample was spiked at 2.5 μg g^{-1} for use. The peel part was directly used after triturate and homogenization. According to experimental results as shown in Table 1, when the amounts of flesh was higher than 100 mg, there were no significant changes on peak area for successive extractions and the linearity of ln A_i vs. $(i-1)$ was not acceptable. The maximum mass for the peel part with acceptable linearity was 150 mg. Large mass of samples brought highly concentrated analytes in headspace phase, which made the effect of the amount extracted onto the fiber became negligible [39], and that may be the reason for bad linearity when high sample amount was used. A small load of sample was favorable for good linearity. But if the mass was too low, sensitivity and reproducibility were often limited, especially when the sample was not very homogeneous. In this work, the standard

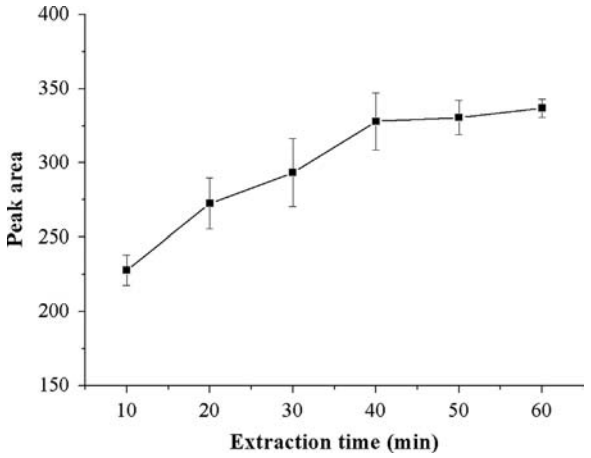

Fig. 5. Effect of extraction time on peak area. Conditions: extraction temperature, 40 °C, amount of sample, 50 mg; spiking level, 2.5 μg g^{-1}.

Table 1
Correlation coefficients (R^2) of $\ln A_i$ vs. $(i-1)$ for 2-naphthol with different mass of fresh (R_1^2) and peel (R_2^2) parts.

Sample mass/mg	20	40	50	80	100	150	200	400
R_1^2	0.996	0.992	0.994	0.998	0.984	0.965	0.902	0.934
R_2^2	0.993	0.991	0.995	0.995	0.990	0.998	0.945	0.967

Calibration level: $N=3$.

amount of flesh sample was 50 mg and the peel sample was 150 mg. For the extraction of aqueous sample, exponential decay of the peak area with the number of extractions can be obtained with 0.2 mL of sample with addition level at 50 μg L^{-1}.

3.4. β parameter

After the determination of optimum extraction conditions and suitable sample amount, β value was obtained by extraction of 50 mg spiked flesh and 150 mg of the peel sample. It was calculated from the slope of the linear plot of $\ln A_i$ vs. $(i-1)$, where i is the number of consecutive extractions, and A_i is the peak area of ith extraction. Plot used to determine β value is shown in Fig. 6(A) and (B). β value of flesh and peel samples was 0.812 and 0.733.

β values of 2-naphthol in aqueous solution was 0.788 with correlation coefficient (R^2) of 0.999 (Fig.6(C)).

Once β was determined, A_T can be calculated by $A_1/(1-\beta)$, where A_1 is the peak area of the first extraction.

3.5. Method validation

Since the multiple headspace SPME provides a total peak area independent of sample matrix, the linear calibration was obtained by external solvent calibration which was performed by injecting 1 μL of standard ethanol solution at several different concentration levels [6,39]. It was in the range of 0.5–5000 ng with linear coefficient of 0.9996 (R^2). Limit of detection ($S/N=3$) was 0.15 ng. Linear relationship between peak area (A) and sample mass (m/ng) was: $A=15.3\ m-0.559$.

To evaluate the feasibility of quantitation by aforesaid external solvent calibration, recoveries for 2-naphthol in both aqueous solution and citrus samples were determined at corresponding optimum conditions.

Three different water samples spiked at 15, 50 and 80 μg L^{-1} were quantified with multiple headspace SPME method. The A_T for each sample was calculated by $A_1/(1-\beta)$, and then the mass of

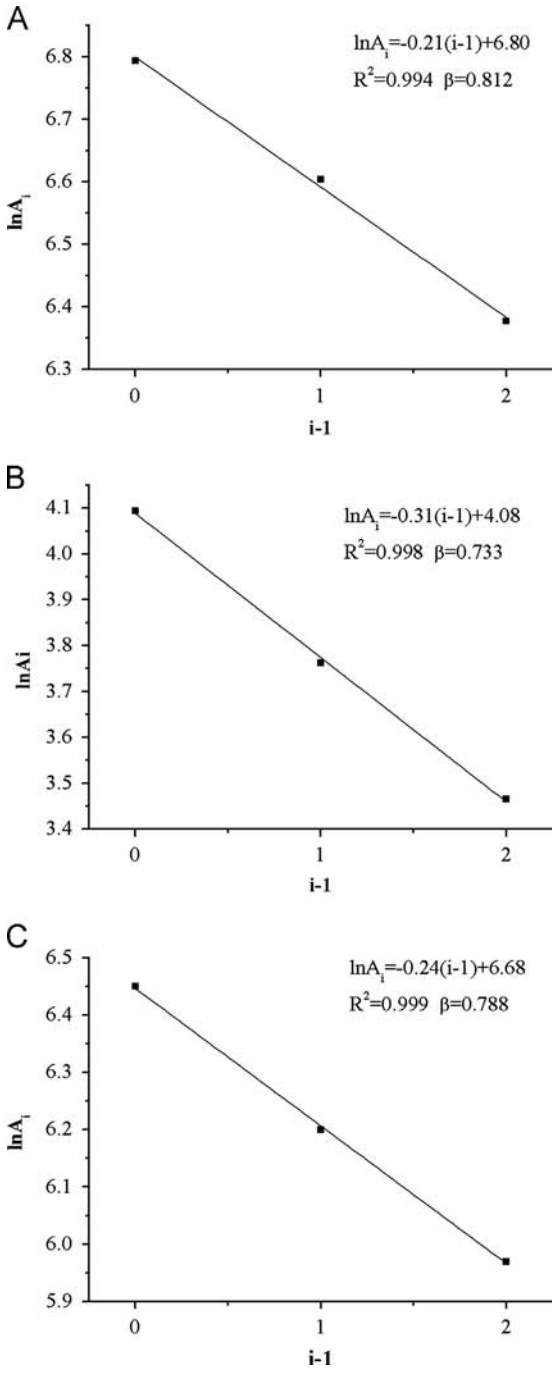

Fig. 6. Plots of $\ln A_i$ vs. $(i-1)$ used to determine β values of flesh (A), peel (B) and aqueous (C) samples.

2-naphthol in each sample was obtained with the external solvent calibration. Experimental concentration (C_e) was the ratio between mass of 2-naphthol and sample volume. Recoveries were defined as the ratio of C_e and the original spiking level (C_o). As shown in Table 2, recovery values were in the range of 86.8–98.6%. Citrus flesh samples spiked at 1.0, 2.0 and 2.5 μg g^{-1} were determined with similar procedures. Recoveries were from 81.9 to 110%. External solvent calibration was feasible for the determination of 2-naphthol by the proposed multiple headspace SPME-GC method in this work. Relative standard deviation for three replicates of citrus sample spiked at 2.5 μg g^{-1} was 2.56%. That indicated the good repeatability of this method.

Table 2
Recoveries of the proposed multiple headspace SPME-GC method for determination of 2-naphthnol in aqueous and fruit samples.

	Aqueous sample ($\mu g\ L^{-1}$)			Fruit sample ($\mu g\ g^{-1}$)		
Spiked level	15	50	80	1.0	2.0	2.5
[a]C_e	13.0	46.1	78.9	0.819	1.945	2.753
Recovery (%)	86.8	92.2	98.6	81.9	97.2	110

[a] Experimental concentration.

Table 3
Peak areas of 2-naphthol obtained by multiple headspace SPME and headspace SPME in two types of flesh samples, and *P*-values of peak areas.

Sample matrix	Peak area ($2\ \mu g\ g^{-1}$)		Peak area ($6\ \mu g\ g^{-1}$)	
	[a]Multiple headspace SPME	[b]Headspace SPME	Multiple headspace SPME	Headspace SPME
Pomelo	[c]1438 ± 102	601 ± 74	2493 ± 377	1397 ± 108
Orange	1330 ± 143	461 ± 69	2384 ± 264	881 ± 104
[d]P	0.3000	0.0207	0.5808	0.0118

[a] Obtained by sums of peak areas of five consecutive extractions.
[b] Peak areas of the first extraction.
[c] Calibration level: $N=3$.
[d] Critical value, 0.05.

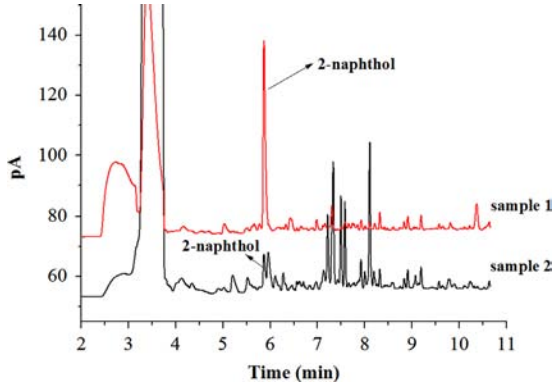

Fig. 7. Multiple headspace SPME-GC chromatograms for the first extraction of peel parts of two citrus fruits. Conditions: extraction temperature, 40 °C; extraction time, 50 min; amount of sample, 150 mg.

3.6. Evaluation of sample matrix effect on multiple headspace SPME and headspace SPME

In order to investigate the independence of the proposed multiple headspace SPME-GC method from matrix effect, peak areas obtained by multiple headspace SPME and headspace SPME for samples with different matrix were studied and compared with values of significant differences (*P*) [6]. Peak areas of multiple headspace SPME were obtained by sums of peak areas of five consecutive extractions (where peak areas of the sixth extraction and the latter were neglectable). The headspace SPME was measured by peak areas of the first extraction. As can be seen in Table 3, peak areas of headspace SPME showed differences ($P<0.05$), while the five total peak areas obtained by multiple headspace SPME showed statistically identical ($P>0.05$). It can be concluded that difference of sample matrix had great influence on headspace SPME, and the multiple headspace SPME exhibited great independence from matrix effect. The proposed multiple headspace SPME kept high applicability for determination of 2-naphthol in different fruits samples.

3.7. Determination of 2-naphthol in whole citrus fruits

Preservatives usually coated on the peel surface of citrus fruits to act the antiseptic function. Because of the limited storage time or the low concentration level of preservatives, there was no 2-naphthol detected in the flesh part. Among the ten types of selected citrus samples, two of them was analyzed with existence of 2-naphthol in their peel parts. Fig. 7 shows the multiple headspace SPME-GC-FID chromatograms for the first extraction of peel parts. Concentration of 2-naphthol in sample 1 and sample 2 were 0.94 and 0.20 $\mu g\ g^{-1}$, respectively. Great difference of concentration directly related to the usage amount of preservatives. Furthermore, because of the multiple preservative types, 2/10th of the selected samples were detected with 2-naphthol.

4. Conclusions

A MWCNTs doped-PIL fiber was prepared by in-situ polymerization with stainless steel wire as support. With the joint effect of MWCNTs and poly($VOIm^+PF_6^-$), the proposed fiber provided sufficient extraction capacity for its use for multiple headspace SPME. Recoveries of 2-naphthol in aqueous and citrus samples were in the range of 81.9–110%, which were obtained based on the external solvent calibration. The proposed MWCNTs/PIL-SPME-GC method also showed great independence from sample matrix compared with headspace SPME method, and it was reliable enough for practical analysis.

Acknowledgments

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