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Application of a β -cyclodextrin/graphene oxide-modified fiber for solid-phase microextraction of six fragrance allergens in personal products†

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A new β -cyclodextrin/graphene oxide hybrid material prepared *via* a chemical covalent interaction and layer-to-layer assembly was developed as a sorbent for the solid-phase microextraction of fragrance allergens. As a result of its ultra-large surface area, large delocalized π -electron system and abundant hydroxyls, the β -cyclodextrin/graphene oxide-coated fiber could be used to extract particular compounds *via* strong π - π interactions, van der Waals forces and hydrogen bonding interactions. β -Cyclodextrin with a hydrophobic interior cavity and hydrophilic peripheral face was conducive in extracting the fragrances with hydrophobic and hydrophilic groups. Under the optimized extraction and desorption conditions, the β -cyclodextrin/graphene oxide-coated fiber showed acceptable extraction efficiency for hydrophilic and hydrogen-bonding-donating alcohols. Compared with other methods based on different coating fibers, the proposed fiber obtained wide linear ranges for fragrances with correlation coefficients ranging from 0.9921 to 0.9970, and low limits of detection in the range of 0.050–0.150 $\mu\text{g L}^{-1}$. The obtained results indicated that the newly developed fiber was a selective, feasible and cost-effective microextraction medium and could be successfully applied for the determination of several fragrances in personal products.

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1. Introduction

Fragrances are a group of chemical pollutants in the environment, which are present in most perfumes, cosmetics, toys and personal-care products. Due to widespread use and exposure to the fragranced products, various side effects have been reported such as skin sensitivity, respiratory illnesses, and headaches.^{1–3} Therefore, the legislation in many countries has established that all the components of cosmetic and detergent products should be mentioned on the label.^{4–6} The presence of potential fragrance allergens must be indicated in the list of ingredients when their concentrations exceed the limits of 0.001% and 0.01% (w/w) for leave-on and rinse-off products, respectively. To control possible infringements, gas chromatography (GC) can be used for the determination of fragrance chemicals, which is developed to only analyze fine fragrances

after dilution.⁷ However, sample preparation is an essential step since the direct analysis of cosmetic samples is quite problematic due to the complexity of matrix components, meaning non-volatile components will result in contamination problems.⁸ To date, several studies have been developed for the extraction of fragrances allergens, including micro-matrix-solid-phase dispersion,⁹ pressurized liquid extraction,¹⁰ ultrasound-assisted emulsification-microextraction,¹¹ ultrasound-assisted solvent extraction,¹² and dispersive liquid-liquid microextraction.^{13,14} Recently, a method based on solid-phase microextraction (SPME) coupled to gas chromatography for the determination of fragrances was also reported.^{15,16}

SPME, first introduced in the early 1990s, has established a new path for sample pretreatment owing to its solventless, simple, flexible and reliable properties.¹⁷ The key part for SPME is the fiber coating, which determines the extraction capacity and extraction selectivity. Many researches have been focused on the development of novel fibers with different coatings in accordance to various target compounds. β -Cyclodextrin (β -CD), as an oligosaccharide and macrocycle, is most widely used in a broad range of applications (electrochemical sensor,¹⁸ drug nanocarrier,¹⁹ catalyst,²⁰ and biomedical analysis²¹) due to its unique structure of a hydrophobic interior cavity and hydrophilic peripheral face.²² By taking advantage of these properties, β -CD and β -CD derivatives have been applied as adsorption materials in separation science and the

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sample pretreatment fields.^{23,24} With the widespread acceptance of SPME, a β -CD decorated nanocellulose modified SPME fiber substrate has been used for the determination of danofloxacin based on the selective molecular interaction afforded by the β -CD cavities for trapping a specific molecule from a complex matrix.²⁵ Nowadays, commercial SPME fibers have been extensively used for the determination of the above-mentioned types of fragrances. However, due to the non-specific extraction, the extraction efficiency is unsatisfactory. The fragrances with hydrophobic and hydrophilic groups could be excellently adsorbed by β -CD and there has been no report about the β -CD-coated SPME method for the determination of common fragrances yet.

Graphene (G), a perfect two dimensional carbon material found in 2004,²⁶ could be an excellent sorbent material owing to its ultra large surface area and large delocalized π -electron system.^{27–29} Moreover, graphene oxide (GO) as the precursor of graphene possesses a great number of active groups, which contribute to interact with other compounds. We previously developed a simple method for the modification of the absorbed material on a stainless steel wire based on the rich oxygen-containing groups of GO.³⁰

In the present study, a facile strategy for the preparation of a β -CD/GO hybrid material through covalent interactions was demonstrated based on our previous experiments.³⁰ The prepared fiber was used for the determination of six fragrances with the headspace (HS) SPME technique coupled with GC, and the performance with respect to linear range, limits of detection (LODs), sensitivity and precision was evaluated and discussed.

2. Experimental

2.1 Reagents

The stainless steel wire (Φ 112.5 μm) was purchased from Yixing Shenglong Metal Wire Net. Co. (Jiangsu, China). Terpineol, citronellol, geraniol and eugenol were obtained from J&K scientific Ltd (Shanghai, China). Dodecane, dodecene, dodecanol, hexadecane, hexadecene, hexadecanol, tetraethyl orthosilicate (TEOS) and *N,N*-dimethylformamide (DMF) were purchased from Tianjin Chemical Reagent No. 2 Plant (Tianjing, China). β -CD, phenethyl alcohol, tetrahydrofurfuryl alcohol, benzyl alcohol, benzhydrol and trifluoroacetic acid (TFA) were obtained from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). 3-Aminopropyltriethoxysilane (3-APTES) was purchased from the Gaizhou Chemical Industrial Corporation. Glycidyl-oxypropyltrimethoxysilane (GPTMS, 97%) was obtained from Aladdin Chemistry Co. Ltd (Shanghai, China). All the chemicals are analytical reagents.

2.2 Apparatus

Analysis of the model compounds was performed with an Agilent 7890 GC system (Agilent Technologies, USA) equipped with a split/splitless injector. The column used for the separation was an OV1701 capillary column (30 m $\times$ 0.32 mm i.d. $\times$ 0.33 μm film thickness). The injector was used in the splitless

mode at 260 $^{\circ}\text{C}$. The detector was a flame ionic detector (FID) and the temperature was fixed at 300 $^{\circ}\text{C}$. Ultrapure nitrogen (>99.999%) was used as the carrier and makeup gas at 1 mL min^{-1} and 25 mL min^{-1} , respectively. Separation of alkanes, alkenes and fragrances was achieved using temperature programs as follows: the column temperature was initially held at 80 $^{\circ}\text{C}$ and programmed at 10 $^{\circ}\text{C min}^{-1}$ to 260 $^{\circ}\text{C}$. For the separation of other alcohols, the column temperature was initially held at 35 $^{\circ}\text{C}$ and programmed at 20 $^{\circ}\text{C min}^{-1}$ to 90 $^{\circ}\text{C}$ (maintained for 5 min), and then programmed at 15 $^{\circ}\text{C min}^{-1}$ to 160 $^{\circ}\text{C}$, and finally at the rate of 30 $^{\circ}\text{C min}^{-1}$ to 260 $^{\circ}\text{C}$ (maintained for 3 min).

Surface properties of the proposed fibers were characterized by a scanning electron microscope (SEM, JSM-6701F, JEOL Ltd, Japan). Infrared spectra were obtained on an IFS120HR Fourier transform infrared (FT-IR) spectrometer. Thermogravimetric analysis (TGA) was performed on a STA449C thermal analyzer.

2.3 Fiber preparation

2.3.1 Preparation of the GO-coated SPME fiber. The synthesis of GO and the preparation process of the GO-coated SPME fiber were in accordance with the description in our previous study.³⁰ Briefly, the precleaned and etched stainless steel wire was firstly immersed in a 10 mL glass vial with APTES for 12 h at normal temperature; after being dried, the stainless steel wire was placed into the prepared GO dispersion solution for reacting at 70 $^{\circ}\text{C}$; 30 min later, GO would form a thin layer on the surface of the substrate fiber through the amide bonding interaction between the $-\text{COOH}$, epoxy groups from GO and $-\text{NH}_2$ from APTES;³¹ and then placed in a 120 $^{\circ}\text{C}$ vacuum oven. The self-assembled monolayer was obtained to give a larger surface area and functional coating. The operations were repeated four times to give a homogeneous coating of about 20 μm in thickness.

2.3.2 Preparation of β -CD solution. In the first step, 2.5 g of β -CD was dissolved in 50 mL of anhydrous DMF,³² and the mixture was stirred at room temperature for 15 min. Then, 7.5 mL of APTES was added to the abovementioned mixture for the synthesis of APTES and β -CD. After stirring for 5 h, the prepared β -CD of amination was ready for use. The β -CD and β -CD-APTES structures are illustrated in Fig. 1a.

2.3.3 Preparation of the β -CD/GO-coated SPME fiber. The fabrication of β -CD/GO-coated stainless steel wire fiber involved the following processes (Fig. 1b): (a) the assembling of the GO monolayer was completed according to the abovementioned process; (b) the prepared β -CD-APTES solution was added to a 1.5 mL centrifuge tube; and (c) the stainless steel wire modified by single-layer GO was inserted into the centrifuge tube of (b) for 2 h at room temperature. The (a) and (c) operations described above were also repeated four times to obtain the satisfactory coating thickness.

2.3.4 Preparation of the β -CD-coated SPME fiber. The sol-gel method was used for the preparation of the β -CD fiber coating.³⁰ 100 mg of β -CD was initially dissolved in 1 mL of dichloromethane, and then 200 μL of TEOS, 200 μL of GPTMS and 1 mL of TFA were added into the obtained mixture. The

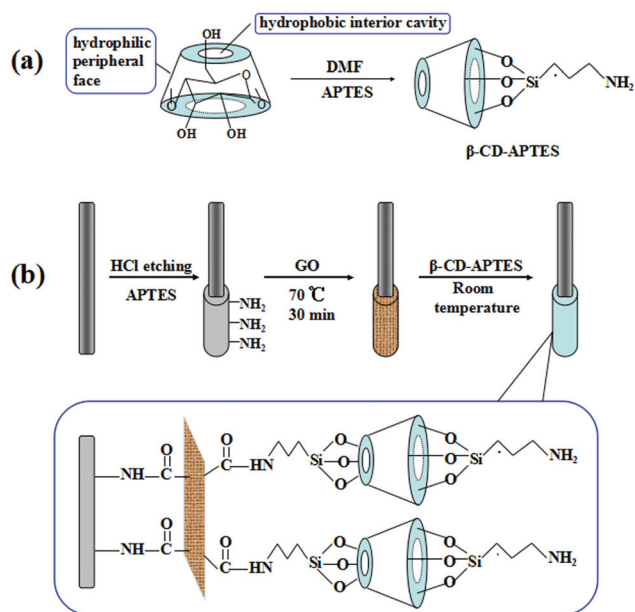


Fig. 1 Synthesis process for β -CD-APTES (a) and fabrication process of the β -CD/GO SPME fiber (b).

etched stainless steel wire was vertically immersed into the sol solution at room temperature for 12 h in a fume hood.

2.4 Procedure for solid-phase microextraction

Stock solutions of analytes were prepared in *n*-hexane at concentrations of 1.0 mg mL^{-1} and maintained at 4°C . Working solutions were prepared daily by diluting the stock solution with distilled water. The fiber was installed into a homemade SPME device, which was a modification of a $5 \mu\text{L}$ syringe, as described in ref. 33. Prior to use, the fiber was conditioned in the GC injector under nitrogen at $80\text{--}260^\circ\text{C}$ with a gradual increase in the temperature ratio at $10^\circ\text{C min}^{-1}$ and held at 260°C for 5 h. For model compound analysis, all extraction experiments were carried out in a 20 mL working solution, which was introduced to a 25 mL vial. The standards were extracted through the immersion SPME for tetrahydrofurfuryl alcohol, benzyl alcohol, phenethyl alcohol, benzhydrol, and headspace mode for other compounds in the solution with a constant depth under the optimal extraction conditions. A magnetic stirrer was used to agitate the solution at 600 rpm . After the extraction, the fiber was withdrawn into the syringe needle and immediately inserted into GC inlet for thermal desorption. All the extractions were triplicated, and the average values were selected for optimization and method validation.

3. Results and discussion

3.1 Characterization of the GO-coated and the β -CD/GO-coated SPME fiber

Surface morphology of the GO-coated and β -CD/GO-coated SPME fibers were characterized by SEM. Fig. 2 reveals that the

prepared materials were successfully immobilized on the fibers, and the coatings were all very uneven and fluctuant. Compared with the GO coating, there were many ridges on the β -CD/GO coating (Fig. 2d), which demonstrated that the latter coating would exhibit more excellent extraction efficiency. The thickness of each different layer (β -CD, GO, β -CD/GO) has been measured by SEM (Fig. S-1†). The sol-gel β -CD coating was approximately $16 \mu\text{m}$ and the GO, β -CD/GO coatings were all about $20 \mu\text{m}$. FT-IR spectrometry was used to verify the existence of the β -CD/GO composite (Fig. S-2†). 3410 cm^{-1} was the O-H stretching vibration from GO, and due to the formation of hydrogen bonding after the addition of β -CD, the adsorption peak moved to a low wavenumber at 3365 cm^{-1} . 2925 cm^{-1} and 1245 cm^{-1} were the signal peaks of C-H and C-C stretching vibration from β -CD, respectively, all of which demonstrated that the β -CD/GO composite was successfully synthesized. TGA of the β -CD/GO composite was performed to observe the thermal stability of the prepared coating (Fig. S-3†). The study was carried out in a N_2 atmosphere within the temperature range from room temperature to 800°C . The mass loss of β -CD/GO in the range of $60\text{--}90^\circ\text{C}$ was due to the evaporation of water and other solvents. Due to the thermal decomposition of β -CD, the mass suddenly decreased at 347°C . However, this temperature was far higher than the injector temperature of 260°C .

3.2 Comparison of GC chromatograms of APTES, β -CD, GO and β -CD/GO-coated SPME fibers

GC chromatograms of APTES, β -CD, GO and β -CD/GO-coated SPME fibers for extraction of six fragrances are shown in Fig. 3. From the chromatograms, the APTES-coated fiber exhibited scarcely any extraction capacity for analytes, which testified that APTES, as a coupling reagent, would not influence the performance validation of other extraction materials. Through the comparison of β -CD, GO and β -CD/GO-coated SPME fibers, the β -CD/GO-coated fiber showed higher signal peaks. Therefore, the β -CD/GO-coated fiber, combining the advantages of β -CD with the hydrophobic interior cavity and hydrophilic peripheral face and GO with large surface area, was used for extraction of fragrances.

3.3 Optimization of extraction and desorption conditions

Terpineol, citronellol, geraniol, eugenol, dodecanol and hexadecanol were selected as target compounds based on their hydrophobic and hydrophilic groups. Experimental parameters, including extraction temperature, extraction time, ionic strength, desorption temperature and desorption time were investigated and optimized by factor-by-factor optimizations for analytes. Prior to optimization, 600 rpm was fixed as the stirring rate during extraction.

3.3.1 Extraction time. SPME is an equilibrium-based technique, and the best extraction time should be the equilibrium time. The effect of extraction time on extraction efficiency was investigated in a range between 10 and 60 min. The peak area to time profiles for fragrances extracted by the β -CD/GO-coated SPME fiber are shown in Fig. 4a. Extraction equilibrium for all

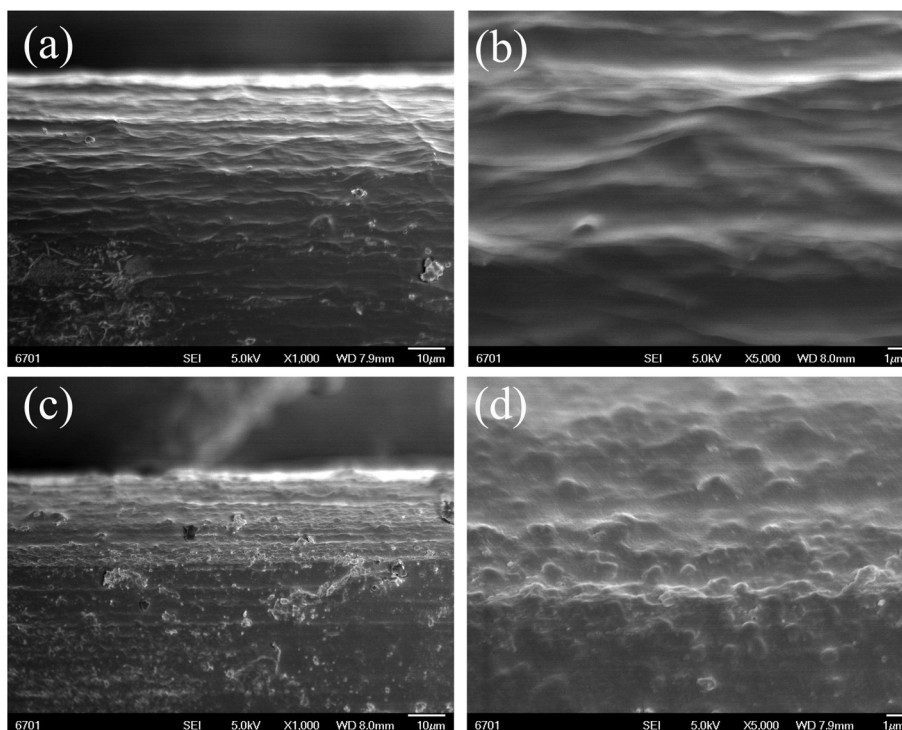


Fig. 2 Scanning electron microscopy images of GO (a and b) and β -CD/GO (c and d): (a and c) $\times 1000$, (b and d) $\times 5000$.

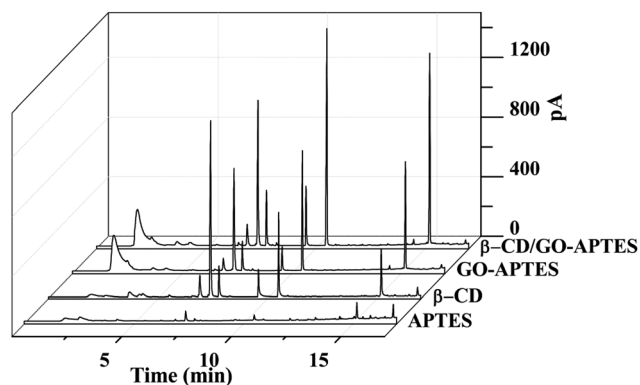


Fig. 3 Comparison of GC chromatograms of APTES, β -CD, GO and β -CD/GO-coated SPME fibers for the extraction of six fragrances.

the analytes was obtained at about 40 min. After reaching equilibrium, as the extraction time increased from 40 to 60 min, the adsorption percentage and efficiency hardly changed. Considering most of the analytes and the total operation time, the extraction time of 40 min was chosen as the optimized extraction time.

3.3.2 Extraction temperature. HS-SPME is a two-step equilibrium process, in which analytes are distributed among the aqueous sample, the headspace and the coating extraction phase. Temperature has an important influence on mass transfer during extraction, as temperature determines the diffusion coefficient and partition coefficient for target compounds in

the three phases. Because the sample matrix was water, the impacts of extraction temperature on extraction efficiencies were investigated in the range of 30–80 °C, which were below the water boiling point. As shown in Fig. 4b, all the analytes had the highest peak area when the temperature was 70 °C. The result may be due to the increase of Henry's constant and diffusion coefficients of analytes in the headspace at a high temperature. However, the distribution constants of analytes in the coating extraction phase decreased with the increase of temperature. Therefore, 70 °C was selected as the extraction temperature.

3.3.3 Ionic strength. The ionic strength of the working solution was adjusted by adding NaCl. Addition of salt into an aqueous sample can reduce the solubility of analytes in solution, due to the formation of hydration spheres around the ionic salt molecules,³⁴ and enhance the partition of analytes into the coating adsorbent. Compared with the immersion mode, headspace extraction could avoid the competitive effect from salt adsorption. The effect of ionic strength on extraction efficiency was investigated by adding 0%–30% (w/v) of NaCl to the working solution. 30% is close to the saturation degree of NaCl in water. As shown in Fig. 4c, peak areas of all analytes increased with the increase of NaCl content. Therefore, the content of NaCl in the working solution and samples was held at 30% in all the extraction processes.

3.3.4 Desorption temperature and time. The effects of desorption temperature and time on the peak area of each fragrance are displayed in Fig. S-4 and S-5.† From Fig. S-4† and under the consideration of the β -CD thermal stability and fiber

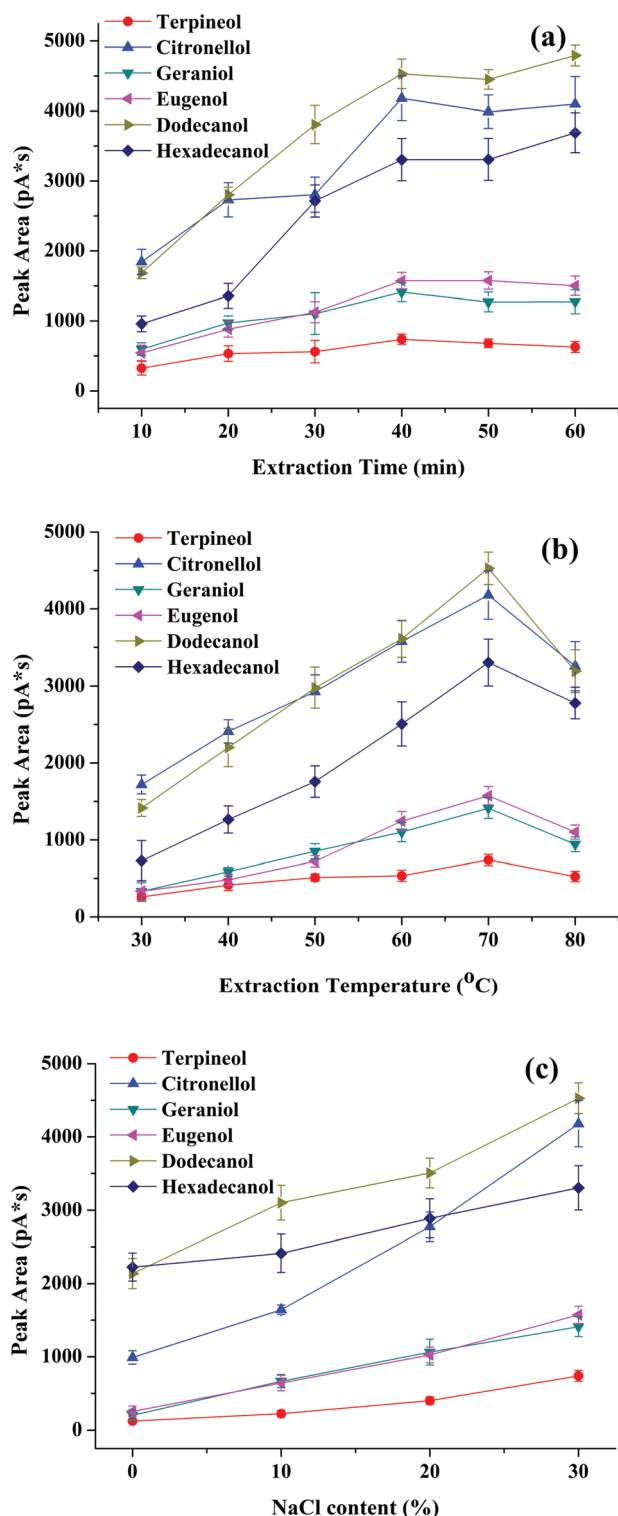


Fig. 4 Effect of extraction conditions on extraction efficiency of β -CD/GO-coated fiber for the extraction of six fragrances. Conditions: extraction time, 40 min; extraction temperature, 70 $^{\circ}$ C; NaCl content, 30% (w/v); desorption time, 9 min; desorption temperature, 260 $^{\circ}$ C.

lifetime, the desorption temperature was fixed at 260 $^{\circ}$ C. The effects of desorption time on the peak area of each fragrance were evaluated from 1 to 11 min at intervals of 2 min. The

results showed that 9 min was enough for all the analytes to be desorbed from the fiber and to avoid the occurrence of the carryover effect. The longer desorption time may be related to the β -CD structure and adsorption mechanism, for which the analytes would enter into the cavity interior of β -CD during the extraction process so that the adsorption needed longer time. Finally, the desorption conditions were chosen as 260 $^{\circ}$ C for 9 min.

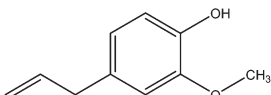
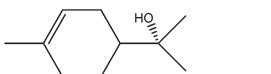
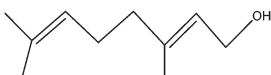
3.4 Method validation

Analytical parameters, including enrichment factors (EFs), linear range, correlation coefficient (R), LODs, single-fiber repeatability and fiber-to-fiber reproducibility, are listed in Tables 1, 2 and 3. The analytical performance of the β -CD/GO-coated fiber and GO-coated fiber was examined for various analytes under the optimized extraction conditions.

3.4.1 Enrichment factor and extraction selectivity. EF, an indicator for the evaluation of the extraction capacity of the proposed SPME fiber for the model compounds, is calculated according to the following equation: $EF = C_f/C_s$, where C_f is the concentration of analyte presented in the fiber coating after extraction and C_s is the concentration of analyte originally present in the sample solution. The chromatographic peak area was obtained by direct injection of 1 μ L of standard solution from 5 μ g mL $^{-1}$ to 1 mg mL $^{-1}$ of fragrances. In this experiment, the impact of sample volume on the value of EF was also investigated. As shown in Fig. S-6,[†] there was almost no influence because the sample volume was sufficiently larger than the coating.³⁵

To explore the extraction capacity and selectivity of the β -CD/GO SPME fiber coating, a series of organic compounds with different physical-chemical properties (hydrophobicity, hydrophilicity, and π electron system) were selected as analytes. The adsorption affinity of the GO coating and the β -CD/GO coating to different compounds was evaluated by the EFs for the extraction and the results are stated in Tables 1 and 2. In comparison with the EFs of the GO-coated fiber, the β -CD/GO-coated fiber with specific properties of two materials presented higher enrichment capacity for all the analytes. The results of extraction for six fragrances showed that the EF values increased with the increase of the $\log K_{ow}$ values with the hydrophilic group for most analytes, which demonstrated that the hydrophilicity of compounds had a significant effect on the extraction efficiency. Furthermore, the extraction efficiencies for two compounds of eugenol and terpineol with similar structure were different, and the EF of the former one with more double bonds and a lower $\log K_{ow}$ value (2.27) was higher than that of the other ($\log K_{ow}$, 3.28). This abnormal result was ascribed to the π electron cloud of GO, which can form π - π conjugation with the analytes. The abovementioned explanation was also identically appropriate for citronellol and geraniol. From the results, it was also clearly found that the EF value of hexadecanol ($\log K_{ow}$, 6.73) was slightly lower than that of dodecanol ($\log K_{ow}$, 5.13). Hexadecanol with a larger molecular-weight was not easy to transfer from the aqueous solution to the coating, which decreased the EF of hexadecanol

Table 1 Physical chemical properties of six fragrances and enrichment factors for fragrances obtained with the cyclodextrin/GO-coated SPME fiber

Compound	Structure	Molecular weight	Log K_{ow} ^a	Log K_{aw} ^b	EFs ^c	
					β -CD/GO-coated fiber	GO-coated fiber
Eugenol		164.2	2.27	-4.09	164.0	67.7
Terpineol		154.3	3.28	-3.30	127.9	35.3
Citronellol		156.3	3.91	-2.63	274.9	52.8
Geraniol		154.3	3.47	-3.33	301.9	112.7
Dodecanol		186.3	5.13	-3.04	881.2	187.1
Hexadecanol		242.5	6.73	-2.72	714.3	134.9

^a K_{ow} : Octanol–water partitioning coefficients. ^b K_{aw} : Air-to-water partitioning coefficients. ^c EFs: Enrichment factors.

Table 2 Comparison of the enrichment factors of alkanes, alkenes, and alcohols

Compound	Log K_{ow}	EFs	
		β -CD/GO-coated fiber	GO-coated fiber
Dodecane	6.10	50.5	21.0
Dodecene	6.10	69.4	34.5
Dodecanol	5.13	881.2	437.2
Hexadecane	8.20	275.6	149.1
Hexadecene	8.06	321.5	266.7
Hexadecanol	6.73	714.3	463.1
Tetrahydrofurfuryl alcohol	-0.11	5.8	5.6
Benzyl alcohol	1.10	42.2	16.1
Phenethyl alcohol	1.36	34.4	16.7
Benzhydrol	2.67	148.2	63.8

on the SPME fiber. Moreover, the EFs of alkanes, alkenes and alcohols with the same carbon chain were also compared. The hydrophilic aliphatic compounds (dodecanol and hexadecanol) with even lower log K_{ow} values were adsorbed more strongly than the hydrophobic alkanes and alkenes, supporting the presence of the hydrogen-bonding interaction between the hydroxyl groups of alcohols and β -CD/GO. The extraction efficiencies of the β -CD/GO-coated fiber for other alcohols were lower than those of the aliphatic compounds, as these alcohols with a strong hydrophilic nature (low log K_{ow} value) were more difficult to remove from the aqueous solution.

3.4.2 Linearity and limit of detection. Calibration curves were plotted using a series of spiked levels of eugenol in the range of 0.5–500 $\mu\text{g L}^{-1}$ and citronellol, geraniol, terpineol, dodecanol, hexadecanol in the range of 0.2–500 $\mu\text{g L}^{-1}$ with good correlation coefficients ($R \geq 0.9921$). LODs, calculated as 3 times the standard deviation of the obtained peak area at the

Table 3 Analytical parameters for six fragrances measured with the β -CD/GO-coated and GO-coated fibers based on the HS-SPME-GC method

Compound	β -CD/GO-coated fiber					GO-coated fiber				
	Linear range ($\mu\text{g L}^{-1}$)	R^a	LOD ^b ($\mu\text{g L}^{-1}$)	Repeatability ($n = 5$, %)	Reproducibility ($n = 5$, %)	Linear range ($\mu\text{g L}^{-1}$)	R^a	LOD ^b ($\mu\text{g L}^{-1}$)	Repeatability ($n = 5$, %)	Reproducibility ($n = 5$, %)
Terpineol	0.2–500	0.9970	0.050	9.9	10.4	1.0–500	0.9921	0.300	8.3	11.7
Citronellol	0.2–500	0.9960	0.075	7.6	9.3	1.0–500	0.9943	0.250	9.2	7.8
Geraniol	0.2–500	0.9957	0.050	9.6	10.8	1.0–500	0.9947	0.300	6.6	12.4
Eugenol	0.5–500	0.9969	0.150	7.8	11.4	2.0–500	0.9910	0.750	8.1	9.3
Dodecanol	0.2–500	0.9943	0.050	4.7	7.3	1.0–500	0.9914	0.250	7.5	8.5
Hexadecanol	0.2–500	0.9921	0.050	9.2	9.7	1.0–500	0.9921	0.250	9.6	10.3

^a Correlation coefficient. ^b LOD, limit of detection for S/N = 3.

Table 4 Determination results of mode fragrances in samples and recoveries spiked at 15 $\mu\text{g L}^{-1}$ and 30 $\mu\text{g L}^{-1}$ by the β -CD/GO-SPME-GC method

Compound	Shampoo			Skin care water		
	Concentration (%, w/w)	Recovery (%, 15 $\mu\text{g L}^{-1}$)	Recovery (%, 30 $\mu\text{g L}^{-1}$)	Concentration (%, w/w)	Recovery (%, 15 $\mu\text{g L}^{-1}$)	Recovery (%, 30 $\mu\text{g L}^{-1}$)
Eugenol	N.D. ^a	81.0 $\pm$ 9.4	90.4 $\pm$ 7.3	N.D.	80.2 $\pm$ 7.3	88.3 $\pm$ 8.2
Terpineol	0.00046	85.2 $\pm$ 8.3	91.6 $\pm$ 10.6	0.00021	87.4 $\pm$ 9.5	92.6 $\pm$ 7.4
Citronellol	N.D.	91.3 $\pm$ 8.5	85.4 $\pm$ 9.2	N.D.	89.5 $\pm$ 9.3	83.1 $\pm$ 10.1
Geraniol	0.00031	92.7 $\pm$ 9.3	87.2 $\pm$ 8.3	N.D.	94.1 $\pm$ 8.1	89.0 $\pm$ 6.2
Dodecanol	N.D.	90.1 $\pm$ 9.4	93.5 $\pm$ 10.1	0.00010	90.3 $\pm$ 9.3	92.5 $\pm$ 7.2
Hexadecanol	0.00035	79.5 $\pm$ 11.2	84.7 $\pm$ 11.7	0.00092	70.1 $\pm$ 12.4	76.9 $\pm$ 11.7

^a N.D., not detection.

lowest sample concentration divided by the slope of the calibration curve, were in the interval between 0.050 and 0.150 $\mu\text{g L}^{-1}$. Performance of the GO-coated fiber for the extraction of fragrances is also shown in Table 3. Compared with the GO-coated fiber, the β -CD/GO-coated fiber obtained wider linear ranges, lower limits of quantitation and LODs. However, the repeatability and reproducibility of the two SPME fibers have no obvious differences. Moreover, the proposed method was compared with the previously published ones, including extraction materials, LODs, and recoveries, which showed apparent merits of the β -CD/GO composite for the extraction of fragrances and is presented in Table S-1.†

3.4.3 Precision, accuracy and durability. The precision and accuracy of the β -CD/GO-GC-FID method were confirmed by replicate extractions of single fibers and different fibers for repeatability. The single-fiber repeatability was calculated using five parallel extractions of an aqueous sample containing 500 $\mu\text{g L}^{-1}$ with the same fiber under the optimum conditions. The relative standard deviation (RSD) values of the peak area varied from 4.7% to 9.9%. Five different fibers prepared by the same procedure were used to evaluate the fiber-to-fiber reproducibility of β -CD/GO preparation. The RSD values were in the range of 7.3%–11.4% for analytes, which confirmed that the preparation method was quite stable. GO had an inherent high thermal stability and chemical durability, and these properties were favorable for the analysis of complex-matrix samples and high boiling compounds. The β -CD/GO layer was coated onto the stainless steel wire through a layer-by-layer chemical-bonding process, and β -CD was attached onto the GO also through non-covalent forces, including hydrogen bonding, van der Waals force and hydrophilic interactions. For just this reason, although β -CD had lower thermal resistance than GO, the β -CD/GO composite material still showed satisfactory durability during the performance evaluation. According to the life-time of the fibers, the adsorption temperature was fixed at 260 $^{\circ}\text{C}$, which was favorable to meet the adsorption of analytes. The whole optimization and method evaluation for each type of analytes can be performed by one single fiber.

3.5 Determination of fragrances in personal products

The proposed SPME-GC-FID method established by β -CD/GO fiber was applied to determine the six mode fragrances men-

tioned above in personal products. In some cases, the extracts were properly diluted due to the high concentration of the analytes in samples. 0.05 g of shampoo of Shulei and 0.1 g of skin care water of Jiumeizi were dissolved into a 100 mL volumetric flask to prepare for the extraction and analysis processes. Determination results are listed in Table 4 and GC chromatograms of two samples are presented in Fig. 5. From the table,

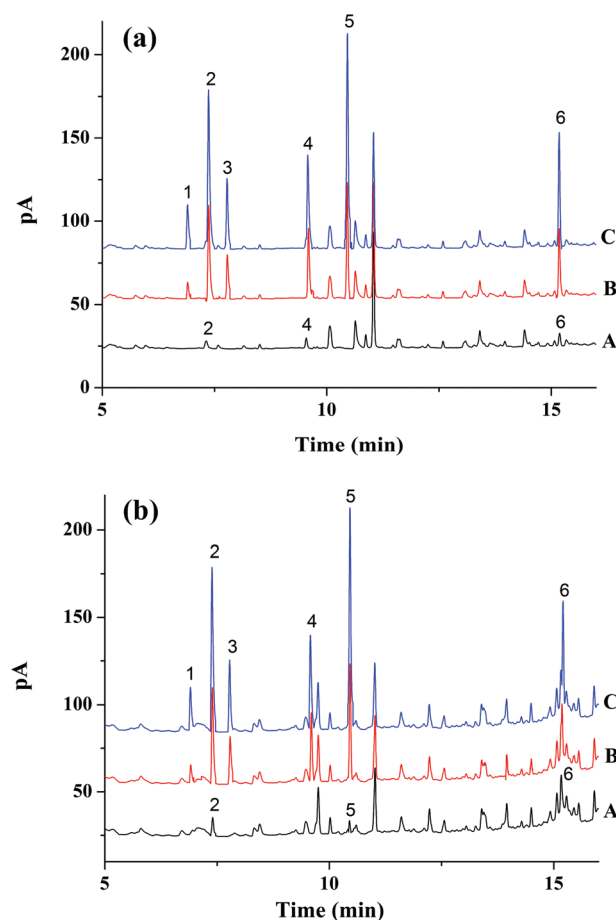


Fig. 5 GC-FID chromatograms of real samples (A) and the samples spiked at 15 $\mu\text{g L}^{-1}$ (B), 30 $\mu\text{g L}^{-1}$ (C): shampoo (a) and skin care water (b); (1) terpineol, (2) citronellol, (3) geraniol, (4) eugenol, (5) dodecanol, (6) hexadecanol.

we can see that the concentrations of detected compounds did not exceed the limited values. To further demonstrate the practicality of the proposed method, the recovery test was studied by adding different amounts (15 and 30 $\mu\text{g L}^{-1}$) of analytes into two samples and recoveries of the method were in the range of 70.1%–94.1%. The abovementioned results indicated that the proposed method was highly accurate, precise and reproducible.

4. Conclusions

In this study, a particular β -CD/GO-HS-SPME-GC approach for the detection and quantification of six fragrance allergens in personal products was established and verified. β -CD/GO with a large surface area and rich hydroxyls was successfully synthesized by chemical covalent interactions and hydrogen bonding and used as a sorbent for the preconcentration and separation. The introduction of β -CD into the GO matrix significantly increased the numbers of hydroxyls and extensively maintained the effective surface area of GO so that the composite material had an excellent extraction capacity for alcohols, which was testified through the EFs comparison of various mode compounds. Performance and reliability of the present approach were demonstrated in terms of linearity and repeatability. The sensitivity was also convincingly demonstrated in view of LODs below 0.050 $\mu\text{g L}^{-1}$. The data collected with real samples demonstrated that undesirable fragrance allergens were present in personal products but not more than the limited concentrations. The excellent extraction results achieved by the β -CD/GO-SPME method for the six fragrances indicated that this method would be a promising candidate for the determination of the fragrances in real samples.

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