Preliminary construction of integral analysis for characteristic components in complex matrices by in-house fabricated solid-phase microextraction fibers combined with gas chromatography–mass spectrometry

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ABSTRACT

Integral analysis plays an important role in study and quality control of substances with complex matrices in our daily life. As the preliminary construction of integral analysis of substances with complex matrices, developing a relatively comprehensive and sensitive methodology might offer more informative and reliable characteristic components. Flavoring mixtures belonging to the representatives of substances with complex matrices have now been widely used in various fields. To better study and control the quality of flavoring mixtures as additives in food industry, an in-house fabricated solid-phase microextraction (SPME) fiber was prepared based on sol-gel technology in this work. The active organic component of the fiber coating was multi-walled carbon nanotubes (MWCNTs) functionalized with hydroxyl-terminated polydimethyldiphenylsiloxane, which integrate the non-polar and polar chains of both materials. In this way, more sensitive extraction capability for a wider range of compounds can be obtained in comparison with commercial SPME fibers. Preliminarily integral analysis of three similar types of samples were realized by the optimized SPME-GC–MS method. With the obtained GC–MS data, a valid and well-fit model was established by partial least square discriminant analysis (PLS-DA) for classification of these samples (R2X = 0.661, R2Y = 0.996, Q2 = 0.986). The validity of the model (R2 = 0.266, Q2 = −0.465) has also approved the potential to predict the "belongingness" of new samples. With the PLS-DA and SPSS method, further screening out the markers among three similar batches of samples may be helpful for monitoring and controlling the quality of the flavoring mixtures as additives in food industry. Conversely, the reliability and effectiveness of the GC–MS data has verified the comprehensive and efficient extraction performance of the in-house fabricated fiber.

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1. Introduction

As a lot of substances in our daily life have complex matrices, such as herbal medicines and essential oils, chromatographic fingerprint plays an important role in study and quality control of these substances [1]. A chromatographic fingerprint is in practice based on the integral analysis of targets investigated, resulting with the features of "integrity" and "fuzziness" or "sameness" and "difference". To construct integral analysis of complex substances with good performance, more comprehensive and sensitive extraction of chemical ingredients might offer more informative and reliable characteristic components. Therefore, developing a method, which can realize the comprehensive and sensitive extraction of characteristic components in complex substances, is the preliminary construction of integral analysis of these substances.

Flavoring mixtures as additives in food industry has been widely used nowadays. They are artificial mixtures of various kinds of essential oils and additives to improve the taste of food. Essential oils are extracted from a wide variety of plants and herbs, resulting as complex mixtures of various compounds. The flavoring mixtures

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in turn belongs to the representatives of substances with complex matrices. As they can be used in various fields, especially the food industry, the effective quality control of flavoring mixtures is particularly necessary. Currently, the generally used methods including physicochemical parameter testing and sensory evaluation [2] have obvious limitations like time-consuming, costly and low efficiency. The need for developing a fast and efficient method is in urgent need. Generally, volatile organic compounds (VOCs) which constitute the major part of flavoring mixtures are important for integral analysis of the samples, since they are responsible for the characteristic natural odor and flavor. As a result, how to extract more VOCs as characteristic components is a prerequisite to realize the study and quality control of flavoring mixtures.

Solid-phase microextraction (SPME) has been used successfully to develop chromatographic fingerprints [3,4]. It is a pre-concentration technology which integrate sampling, extraction and sample introduction into a single solvent-free step [5,6]. Being considered as a more promising pre-treatment method, SPME has been widely used in various fields, such as food chemistry [7–9], biological matrices [10–13], and environmental applications [14–17]. As one of the most important part of SPME technology, the development of fiber coating is believed to greatly influence the further extension of SPME technique. Carbon nanotubes (CNTs), which was firstly found in 1991 [18], have been extremely attractive in the field of SPME due to their distinctive characters [19]. To overcome its limitation of insolubility in various solvents, functionalization of CNTs has captured great interest in the development of sensitive and robust methodologies of enrichment. Moreover, CNTs can also be functionalized with various chemical groups to make them designable for selective extraction of target analytes [20]. In this work, we realized the functionalization of CNTs via covalent reaction between hydroxyl-terminated polydimethyldiphenylsiloxane (PDMDPS) and multi-walled carbon nanotubes (MWCNTs). The PDMDPS has been reported to offer the advantage of efficiently extracting moderately polar aromatic analytes [21,22]. The PDMDPS-g-MWCNTs polymer has been used as a surface-bonded stationary phase coating by sol-gel technology.

The new fiber coating was prepared aiming to provide a more comprehensive and sensitive extraction capability which can effectively work in study and quality control of flavoring mixtures with complex matrices. To verify the extraction performance of the fiber, comparison with commercial fibers was carried out. In this study, SPME procedure has been optimized based on the information content (Φ) of a continuous chromatographic signal, according to the fact that the information theory can be applied to obtain well-behaved chromatographic fingerprints with more active and chemically characteristic components [1].

2. Experiment

2.1. Chemicals and reagents

The functionalized MWCNTs (-COOH) were purchased from Chengdu Organic Chemicals Company Limited (Chengdu, China). Methyltrimethoxysilane (MTMOS), poly(methylhydrosiloxane) (PMHS), polydimethyldiphenylsiloxane (PDMDPS) and trifluoroacetic acid (TFA, 99%) were purchased from Sigma Aldrich. Stainless steel wires were from Shenzhen Santk Metal Material Company Limited (Shenzhen, China). Three similar types of flavoring mixtures were supplied by China Tobacco Yunnan Industrial Corporation. Four kinds of commercial SPME fibers (PA, CAR-PDMS, PDMS-DVB, DVB-CAR-PDMS) were from Supelco. Sulfoxide chloride, toluene, tetrahydrofuran (THF), and trimethylamine were purchased from Chengdu Hengxin Chemical Industry.
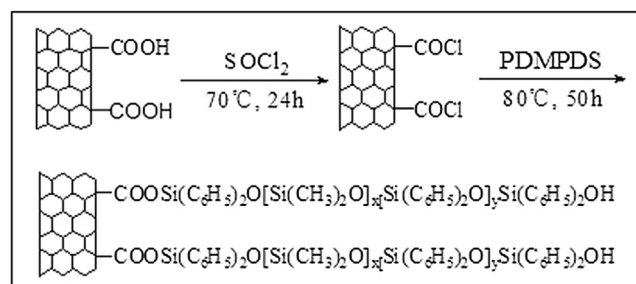

Fig. 1. The procedure for fabrication of PDMDPS functionalized MWCNTs.

2.2. Instruments

Analysis was carried out with an Agilent 7890A GC system fitted with a 220 ion trap mass spectrometer. Helium was used as the carrier gas at a constant flow rate of 1.0 ml/min. Chromatographic separations were realized with a 30 m × 0.25 mm diameter × 0.25 μm film VF-5 fused-silica capillary column (J&W Scientific Inc., USA). The GC injection port was set at 270 °C for fiber desorption. Desorption of analytes from SPME fiber was conducted in split ratio of 30:1. The optimized column temperature program was as follows: 3 min in 50 °C and then increased to 80 °C at the rate of 5 °C/min, then to 120 °C at the rate of 3 °C/min and held at this temperature for 5 min, then to 180 °C at the rate of 3 °C/min, finally increased to 270 °C at the rate of 10 °C/min and held at this temperature for another 10 min. The MS analysis was carried out in full scan mode. Mass spectra were acquired in electron impact mode with mass range of 30–500 m/z. The interface, manifold and ion trap temperature were set at 250 °C, 45 °C and 150 °C, respectively.

The device of microwave induced plasma used to modify the stainless steel wires was described in our last work [19]. Fourier transform infrared spectroscopy (FT-IR) was used to study the chemical structures of MWCNTs-COOH, pure PDMDPS and the functionalized MWCNTs-COOH. Scanning electron microscope (SEM) was employed to investigate the morphology of the in-house fabricated fiber.

2.3. Preparation of PDMDPS-g-MWCNTs

Firstly, synthesis of MWNTs-COCl was referred to Refs. [23,24]. 0.5 g of MWCNTs-COOH was stirred in 60 ml of sulfoxide chloride for 24 h at 70 °C to convert the surface-bound carboxyl groups into acyl chloride groups. After centrifugation, the solid was rinsed repeatedly with anhydrous tetrahydrofuran (THF) and then dried at room temperature under vacuum.

The prepared MWNTs-COCl was then mixed with 5 g PDMDPS in 20 ml solvent of toluene and THF (v/v = 3/1). The mixture was stirred for 50 h at 80 °C under nitrogen atmosphere with 2 ml trimethylamine as catalyzer. The resultant solid was filtered, repeatedly washed with deionized water and dried under vacuum.

The synthesis procedure is shown in Fig. 1.

2.4. Fiber preparation

In this study, a similar reaction was used for the preparation of sol solution except taking PDMDPS-g-MWCNTs and MWCNTs-COOH as sol–gel active organic components [19]. The sol solution was prepared as follows: 20 mg PDMDPS functionalized MWCNTs, 6 mg MWCNTs-COOH, 50 μl ultrapure water and 400 μl MTMOS were added in a centrifugal tube. The mixture was vibrated for 2 min and agitated thoroughly by ultrasonic water bath for 30 min, successively. 100 μl TFA and 50 μl PMHS were then added with