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Facile preparation and applications of graphitic carbon nitride coating in solid-phase microextraction

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ABSTRACT

In this study, graphitic carbon nitride (g-C_3N_4) was used as a coating material for solid-phase microextraction (SPME) applications. Coupled to gas chromatography (GC), the extraction ability of the SPME fiber was investigated and compared with the commercial fibers of 100 μm PDMS and 85 μm CAR/PDMS using six target analytes including deltamethrin, nerolidol, amphetamine, dodecane, ametryn and acrylamide. The g-C_3N_4 coating revealed excellent extraction ability and durability comparing with those of the commercial fibers due to its loose structure and unique physicochemical properties. The repeatability for each single fiber was found to be 3.46% and reproducibility for fiber to fiber was 8.53%. The g-C_3N_4 SPME fiber was applied to the determination of acrylamide in potato chips, the linearity and detection limit was 0.5-250 $\mu g\,g^{-1}$ and 0.018 $\mu g\,g^{-1}$, respectively.

1. Introduction

Solid-phase microextraction (SPME), one kind of modern sample preparation technique, has gained great attention due to its advantage of simplicity, sensitivity, rapidity, solvent free and easily coupling to GC and HPLC. It has been widely applied in fields of food [1], environment [2] and medicine [3]. As known to all, the coating of SPME fiber has obvious influence on the sensitivity and selectivity of the analytical method. Up to now, there have been some materials used as coatings for commercial SPME fibers, such as polydimethylsiloxane (PDMS), polyacrylate (PA) divinylbenzene (DVB)/PDMS, carboxen (CAR)/PDMS and carbowax (CW)/DVB [4–6]. Furthermore, in order to prepare low-cost, mechanically robust, selective, sensitive and easily fabricated SPME fiber coatings, many self-made materials have been developed including molecularly imprinted polymer [7], anodized aluminum wire [8], ionic liquid [9], metal-organic framework [10–13], zinc oxide nanorods [14] and carbon materials [15–18]. Generally, carbon materials are widely used as sorbents to trap and separate inorganic or organic compounds. Among them, for example, activated carbon [19], fullerene [20], carbon nanotube [21,22] and graphene [23,24] have already been applied as SPME fiber coatings. As an analogue of graphene, g-C_3N_4 has drawn much attention in recent years. It is considered as the most promising candidate to complement carbon materials. As the most stable allotrope of carbon nitride, g-C_3N_4 is mainly composed of carbon and nitrogen [25,26]. Although the accurate structure of g-C_3N_4 is still unclear, many reports tend to infer the structure of g-C_3N_4 as a "poly (tri-s-triazine)", which is defected-rich and N-bridged. The conjugated aromatic tri-s-triazine polymer prefers to form p-conjugated planar layers, which is like graphene [27–29]. Thus, g-C_3N_4 has excellent thermal [30,31], optical [32] and photoelectrochemical [33] properties, which make it popular in many fields, such as water splitting [34,35], NO decomposition [36] and hydrogenation reactions [37]. g-C_3N_4 should be a good material as a SPME coating for the extraction of organic compounds because of its unique physicochemical properties. Furthermore, owning to the extraordinary thermal and chemical stability, the presence of g-C_3N_4 may strengthen the mechanical robustness of the SPME fiber coating.

In this paper, g-C_3N_4 was synthesized through the pyrolysis of melamine. The synthetic product was successfully characterized with X-ray diffraction (XRD), Fourier transform infrared (FT-IR) and thermogravimetric analysis (TGA). Nerolidol, amphetamine, ametryn, dodecane, deltamethrin and acrylamide were chosen as model analytes to evaluate the extraction ability of the g-C_3N_4 SPME fiber. Experimental results proved the excellent adsorptive properties of g-C_3N_4 coating. Additionally, the prepared fiber was applied to the determination of acrylamide in potato chip samples to evaluate the tolerance of g-C_3N_4 SPME fiber in complex sample matrixes.

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2. Chemicals and materials

Stainless steel wires (od. 0.15 mm) were obtained from the AnTing Micro-Injector Factory (Shanghai, China). Silicone SE-30 with chromatographic purity was purchased from Shanghai Chemical Reagent Corporation. All analytical grade reagents, potassium bromide (KBr), potassium bromate ($KBrO_3$) and melamine, were from the National Medicines Corporation (Shanghai, China). Acrylamide (99.9%) was purchased from Alfa Aesar (MA, USA). Nerolidol from Adrich (USA) was used. Deltamethrin was from the Agro-environmental Protection Institute, Ministry of Agriculture (Tianjin, China). Amphetamine was purchased from the Institute of Forensic Science of the Ministry of Public Security P.R.C. (Beijing, China). Ametryn was obtained from Fluka (USA). Dodecane was purchased from J&K Scientific Ltd. (shanghai, China). 1000 mg L^{-1} stock solutions of acrylamide, nerolidol, dodecane, amphetamine and ametryn were prepared by dissolving the above compounds in methanol. 10 mg L^{-1} stock solution of deltamethrin was prepared by diluting 100 mg L^{-1} deltamethrin n-hexane solution with acetone. All the standard solutions used for SPME extraction during the whole experiment were prepared by diluting the stock solutions to the required concentration with pure water. Pure water (18.2 MΩ) from a Millipore Autopure WR600A system (Millipore Ltd., USA) was used throughout the experiments. Potato chip samples were collected from local supermarkets in Xiamen. All the solutions mentioned above were sealed and stored at 4 °C.

2.1. Instruments

A commercial manual sampling SPME device and two commercial SPME fibers, 100 μm PDMS and 85 μm CAR/PDMS, were purchased from Supelco (Bellefonte, PA, USA). The determination of nerolidol, amphetamine, ametryn and dodecane were carried on a Shimadazu GC-2010 gas chromatograph (GC) system coupled with a flame ionization detector (FID). In the determination of deltamethrin, an electron capture detector (ECD) was selected and used. Nerolidol, amphetamine, ametryn, dodecane and deltamethrin were separated by a 30 m × 0.25 mm I.D. DB-5 capillary column. Derivated acrylamide was separated by a Rtx-Wax capillary column (30 m × 0.32 mm I.D., 0.25 μm) and detected by an ECD. The column temperature program used for the separation of nerolidol, amphetamine, ametryn and dodecane was set as follows: an initial temperature of 80 °C, and stayed 3 min, then increased to 120 °C at 20 °C min^{-1}, and held 2 min, then raised to 240 °C at 10 °C min^{-1} and maintained 2 min, finally ramped to 280 °C at 30 °C min^{-1} and maintained 2 min. The detector temperature was held at 300 °C and the temperature of the injector was set at 240 °C. In the separation of deltamethrin, the column temperature program was set as: an initial temperature of 60 °C, stayed 5 min, then increased to 170 °C at 30 °C min^{-1}, and held 2 min, then increased to 260 °C at 30 °C min^{-1}, and held 1 min, and finally ramped to 280 °C at 5 °C min^{-1} and maintained 4.5 min. The detector temperature was at 300 °C and the temperature of the injector was set at 240 °C. As for the separation of derivated acrylamide, the column temperature program was: an initial temperature of 80 °C, stayed 2 min, then increased to 240 °C at 10 °C min^{-1}, held 2 min. The detector temperature was at 280 °C and the temperature of the injector was set at 230 °C. The phase identification of g-C_3N_4 power was obtained by X-ray diffraction (XRD) on a Rigaku Ultima IV XRD with Cu Kα radiation (35 kV, 15 mA, λ = 1.54051 Å). Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on a Nicolet 380 spectrophotometer. Thermogravimetric analysis (TGA) of g-C_3N_4 was performed on a SDT Q600 TG/DTA thermogravimetric analyzer, the morphology of the fiber coating was observed by an S4800 scanning electron microscope (SEM, Hitachi, Tokyo, Japan).

2.2. Synthesis of g-C_3N_4

The bulk g-C_3N_4 was synthesized by pyrolysis of melamine molecules under high temperature. In the synthesis, 20 g melamine was heated at 550 °C for 4 h in air. The obtained yellow product was the g-C_3N_4, then the bulk g-C_3N_4 was grinded into powder, which was used for the g-C_3N_4 fiber coating [34].

2.3. Preparation of g-C_3N_4 SPME Fiber

Before the coating fabrication, the stainless steel (17.5 cm) was sequentially washed with acetone and pure water for 10 min with ultrasonication, and then dried in an oven at 60 °C. A length of 1.5 cm from the end part of stainless steel wire was immersed into a ca 0.3 g mL^{-1} silicone SE-30 hexane solution for 30 s, and then g-C_3N_4 was stuck to the stainless steel. Finally, the g-C_3N_4 coated fiber was heated in an oven at 90 °C overnight.

2.4. SPME procedure

The g-C_3N_4 coated fiber was installed into a 5 μL microsyringe. Before use, the fiber was aged at 230 °C for 30 min under nitrogen to avoid any contamination or carryover of analytes. The extraction was conducted in a 20 mL amber glass vial with a PTFE-lined septum cap. During the extraction, the coated fiber was exposed and directly dipped into middle of the sample solution, and the working solution was agitated by a magnetic stirring bar with a constant stirring rate (800 rpm) at room temperature. After the extraction, the fiber was withdrawn back and immediately inserted into the GC injector for the thermal desorption and analysis.

2.5. Sample preparation

Potato chip samples were grinded into powder, and 1.000 g of sample was added into a 50 mL centrifuge tube. After addition of 10 mL n-hexane, the sample was homogenized with ultrasonication for 10 min, then the supernatant n-hexane was removed. The degreasing process was repeated as the above mentioned procedure. 10 mL methanol/H_2O (1/1, v/v) solution was added into the residue to exact acrylamide from the sample through ultrasonication for 10 min. In order to get clarified aqueous layer, the tube was centrifuged at 10,000 rpm for 10 min. The residue was extracted once more. The liquor was merged and transferred into a 50 mL quantitative flask for further use. In the derivation of acrylamide, 1.0 mL H_2SO_4 (10%, v/v) was added into the flask. The mixture was then placed in a refrigerator at 4 °C for 10 min. 1 mL 0.1 mol L^{-1} $KBrO_3$ and 1.0 g KBr power were sequentially added into the precooled solution. The mixture was mixed homogeneously and taken into a refrigerator at 4 °C for 1 h. 0.1 mol L^{-1} $Na_2S_2O_3$ was added into the mixture until the solution color turned to colorless. Lastly, the mixture was diluted with water to a constant volume (50 mL) for SPME experiments.

3. Results and discussion

3.1. Characterization of g-C_3N_4

As shown in Fig. 1a, the phase identification of g-C_3N_4 revealed that two characteristic peaks in the sample could be identified clearly. The strong diffraction peak at 27.5° (0 0 2) was an interlayer stacking peak of aromatic systems (d_{002} = 0.324 nm) of g-C_3N_4. The small peak at 13.0° (1 0 0) was an in-planar peak (d_{100} = 0.676 nm) [38]. The FT-IR spectrum of g-C_3N_4 as shown in Fig. 1b displayed