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## Hydrothermally tailor-made chitosan fiber for micro-solid phase extraction of petroleum acids in crude oils

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### ABSTRACT

Tailor-made chitosan fiber was prepared via hydrothermal treatment to serve as a micro-solid phase extraction (micro-SPE) sorbent for the analysis of petroleum acids (PAs) in crude oils. Chitosan fiber, which is commercial and cheap, has a diameter of about 10 μm and a length of a few centimeters. The fibrous property of the sorbent enables the micro-SPE to deal with viscous crude oil samples because of the low back-pressure during extraction, while the abundant hydroxyl groups and amino groups on the surface of chitosan fiber can provide high density of specific sites for adsorption of PAs. Moreover, it was found that hydrothermal treatment at certain conditions could tune the surface properties of chitosan fiber, leading to significant improvement of the capacity of the fiber in adsorption of PAs. Using hydrothermally treated chitosan fiber as sorbent, the micro-SPE was applied to the determination of PAs in crude oils, with the advantages of easy-operation, rapidness and high sensitivity (the limits of detection range from 0.7 ng/g to 5.4 ng/g). Furthermore, coupled with comprehensive two dimensional gas chromatography-mass spectrometry (GC×GC–MS), the treated chitosan fiber packed micro-SPE method showed a great potential for comprehensive profiling of PAs in crude oils.

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### 1. Introduction

Analysis of petroleum acids (PAs) has significant values in research of petroleum refining [1], petroleum pollution [2] and petroleum geology [3–5]. Extraction of PAs from complex crude oils is an indispensable step before instrumental analysis [6]. Up to now, base extraction [7] and nonaqueous solid phase extraction (SPE) [8] are two common methods for extraction of PAs from crude oil samples. Base extraction is a classic and selective method, but it often involves laborious processes and high consumptions of oil sample and solvent; nonaqueous SPE can save these consumptions, but the existing SPE methods [9] for extraction of PAs are still time-consuming and the development of sorbent materials with high extraction efficiency towards PAs is still less explored. Micro-SPE approaches [10], such as in-pipette-tip [11,12] or in-syringe SPE [13], have the advantages of convenience, rapidness and low

consumptions of sample and solvent. Development of a micro-SPE with specific sorbent for extraction of PAs may be a good solution to the challenges in PA analysis.

In general, the sorbent beds of home-made micro-SPE can be divided into two types. The most common type is a sandwich sorbent bed prepared by packing powder material with glass wools or cottons as stoppers on both ends [14,15]. The other type is a single-layer sorbent bed prepared by packing fiber material without any stoppers [16,17]. Among them, the sandwich type is relatively less stable and more easily separated from the micro-SPE vessel, especially when the sample solution is viscous. Crude oils, especially heavy crude oils, often possess high viscosity, and therefore a micro-SPE with fiber sorbent may be a superior candidate for dealing with crude oil samples.

Chitosan is the deacetylated derivative of chitin that is the second most abundant natural polysaccharide [18]. It is mainly composed of glucosamine and has rich amino groups and hydroxyl groups [19–21]. Chitosan fiber is a commercial and cheap biomaterial that is useful in many biomedical applications such as sutures, wound dressings and tissue engineering [22–24]. Nevertheless, the utilization of chitosan fiber as the sorbent for extraction has not

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been proposed in the literature. Considering that the amino and hydroxyl groups can provide adsorption sites for PAs and the advantages of fiber sorbent in micro-SPE, in this research, chitosan fiber was used as the sorbent for micro-SPE of PAs from crude oils. Prior to this, attempts were made to tune the surface property of chitosan fiber via hydrothermal treatment to achieve the optimal efficiency for extraction of PAs. It was found that hydrothermal treatment with pure water or aqueous solution containing low content of acid could significantly improve the extraction efficiency; this phenomenon was presented for the first time and may be an inspiration for other works that utilize other chitosan materials as sorbent for extraction. In addition, profited by the fiber sorbent bed, the proposed micro-SPE possessed low back-pressure during extraction, and could be applied to the determination of PAs in viscous samples (heavy crude oils) followed by GC–MS analysis. Encouraged by the excellent performance of the hydrothermally treated chitosan fiber, the micro-SPE was further applied to the comprehensive profiling of PAs in crude oils by coupling with GC × GC–MS.

## 2. Materials and methods

### 2.1. Chemicals and materials

Acetic acid (HAc) was purchased from Shanghai General Chemical Reagent Factory (Shanghai, China). Cyclohexanecarboxylic acid (CHA), nonanoic acid, decanoic acid (DA), lauric acid (LA), myristic acid, palmitic acid, stearic acid, 1-adamantanecarboxylic acid (ACA), 1-adamantaneacetic acid (AAA), trans-4-(trifluoromethyl)cinnamic acid (TCA), N-tert-butyltrimethylsilyl-N-methyltrifluoroacetamide (MTBSTFA) and trifluoroacetic acid (TFA) were purchased from Aladdin Chemical Reagent (Shanghai, China). Bicyclo [2,2,1] heptane-2-carboxylic acid (BCHCA) and 3-noradamantanecarboxylic acid (NACA) were supplied by Thermo Fisher Scientific (MA, USA). Trans-4-ethylcyclohexanecarboxylic acid (t-ECHA), trans-4-isopropylcyclohexanecarboxylic acid (t-iPCHA), trans-4-butylcyclohexanecarboxylic acid (t-BCHA) and trans-4-pentylcyclohexanecarboxylic acid (t-PCHA) were purchased from Adamas-beta (Shanghai, China). HPLC grade n-hexane, dichloromethane (DCM), ethyl acetate (EtAc), methanol (MeOH) and acetone were obtained from Fisher Scientific (PA, USA). Chitosan fiber (the deacetylation degree is 90%) was supplied by Haili Biological Product Factory (Laizhou, China). Crude oil samples were supported from our cooperative oil company. Glass pipettes with a length of 15 cm, an inner diameter from 2 mm to 8 mm and a capacity of 1.5 mL were purchased from Aopu Huabo (Wuhan, China).

### 2.2. Hydrothermal treatment of chitosan fiber

Typically, 0.5 g of chitosan fiber was added to 50 mL of aqueous solution containing acetic acid with content ranging from 0 to 0.5% (v/v) (Table 1). Then, the hydrothermal reaction was carried out in a Teflon-lined autoclave at 120 °C for 6 h. Finally, the product was washed by ethanol and deionized water for several times, and then dried at 60 °C for 6 h.

**Table 1**  
Weight losses of chitosan fibers after hydrothermal treatment under different conditions.

Product	CF-0	CF-0.05	CF-0.1	CF-0.15	CF-0.2	CF-0.5
HAc/H <sub>2</sub> O (v/v)	0/100	0.05/99.95	0.1/99.9	0.15/99.85	0.2/99.8	0.5/99.5
Weight loss (%)	12	21	37	40	67	100

### 2.3. Characterization of chitosan fiber

Scanning electron microscopy (SEM) images were taken by using a Quanta-200 scanning electron microscope (FEI, Holland). The infrared spectra were obtained on a Nicolet iS50 Fourier transformed infrared spectroscopy (FTIR) equipped with attenuated total reflection (ATR) accessory (Thermo Fisher Scientific, USA). The contact angle was measured on a SL200KB optical contact angle and interface tension meter (KINO, GA, USA) with water droplets of 2 μL for 1 min and repeated three times on three different random areas on the samples. To investigate the capacities of adsorption of petroleum acids with chitosan fibers before and after hydrothermal treatment, 20 mg of fibers was put into 1 mL of hexane spiked with 11 PA standards at a concentration of 1 μg/mL. The mixture was shaken vigorously at 25 °C for 15 min, and then 100 μL of the supernatant was derivatized with 10 μL of MTBSTFA under vortex at room temperature for 5 min prior to analysis by GC–MS. The adsorption efficiencies can be calculated via the difference between the analytical results of the supernatant and the standard solution.

### 2.4. Extraction of PAs with chitosan fiber packed micro-SPE

The preparation of the micro-SPE device and the procedures of the micro-SPE were adapted from our previous work [15] with some modifications. Chitosan fiber (15 mg) was tightly packed in the middle of a glass pipette (the top of the thinner tube). The chitosan fiber packed micro-SPE was directly used for extraction experiments. Crude oils were diluted 5 times with hexane. TCA was added at a concentration of 200 ng/mL to the diluted samples to serve as the internal standard (IS) for quantification. The diluted oil sample (0.5 mL) was aspirated and dispensed repeatedly to allow PAs to be trapped on the sorbent. After washing twice with 0.5 mL of hexane/DCM (1/1, v/v), the adsorbed PAs were eluted with 100 μL of TFA/EtAc (1/99, v/v). The eluate was derivatized with 10 μL of MTBSTFA under vortex at room temperature for 5 min prior to analysis by GC–MS.

For optimization of extraction conditions, diluted oil sample was spiked with 11 PA standards (Table 2) at a certain concentration (200 ng/mL), and the IS (TCA) was added in the eluate rather than the sampling solution.

To obtain a blank sample for calibration purpose, a crude oil was fractionated into saturates, aromatics, resins and asphaltenes (SARA fractionation method) [25], and then the saturates, the aromatics and the asphaltenes fractions were remixed together as the matrix free of PAs.

### 2.5. GC–MS analysis

Analysis of PAs was carried out on a GC–MS system consisting of an Agilent 7890 GC, an Agilent 7683B autosampler and an Agilent 5975C mass spectrometer (CA, USA). The GC separation was performed on a DB-5MS capillary column, 30 m (length) × 0.25 mm (i.d.) × 0.25 μm (film thickness), purchased from Agilent (CA, USA). High purity helium (99.9995%) was used as carrier gas at a flow rate of 1.0 mL/min. The injector temperature was 300 °C. The injection volume was 1.0 μL in splitless mode. The oven temperature was programmed from 100 °C to 210 °C at 6 °C/min, then to 300 °C at 12 °C/min and held for 5 min. The solvent delay was 8.5 min. The mass spectrometer was operated in the electron impact mode

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