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Preparation of phenyl group-functionalized magnetic mesoporous silica microspheres for fast extraction and analysis of acetaldehyde in mainstream cigarette smoke by gas chromatography–mass spectrometry



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ABSTRACT

Acetaldehyde is regarded as a toxic mainstream cigarette smoke constituent, and measurement of acetaldehyde in complex real samples is difficult owing to its high volatility and reactivity. In this work, phenyl group-functionalized magnetic mesoporous microspheres were developed as the solid-phase extraction sorbents for enrichment and analysis of acetaldehyde in mainstream cigarette smoke. The functional magnetic microspheres were first synthesized through a facile one-pot co-condensation approach. The prepared nanomaterials possessed abundant silanol groups in the exterior surface and numerous phenyl groups in the interior pore-walls, as well as a large surface area (273.5 m²/g), strong superparamagnetism and uniform mesopores (3.3 nm). Acetaldehyde in mainstream cigarette smoke was collected in water and derivatized with O-2,3,4,5,6-(pentafluorobenzyl)hydroxylamine. The formed acetaldehyde oximes were extracted and enriched by the prepared adsorbents via π – π interactions and subsequently analyzed using GC–MS. Extraction conditions such as amounts of sorbents, eluting solvent, adsorption and desorption time were investigated and optimized to achieve the best efficiency. Method validations including linearity, recovery, repeatability, and limit of detection were also studied. It was found that the suggested methodology provided low detection limit of 0.04 mg/mL, good recovery of 88–92%, intra-day and inter-day RSD values of 4.5% and 10.1%, and linear range of 0.25–4 mg/mL ($R^2=0.999$). The results indicated that the proposed method based on phenyl-functionalized magnetic mesoporous microspheres was rapid, efficient and convenient for the enrichment and analysis of acetaldehyde in tobacco.

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1. Introduction

Acetaldehyde has been identified as a mainstream cigarette smoke constituent of concern. It is mainly derived from sugars and flavors added in tobacco processing [1,2]. In addition, acetaldehyde has been classified as a main toxic component of large amounts in mainstream smoke with significant potential biological activity [3,4]. Being a reactive carbonyl compound, acetaldehyde is associated with many cigarette smoking diseases including chronic pulmonary disorder and cancer [5,6]. Acetaldehyde is highly cytotoxic and genotoxic. It can directly react with proteins

and bind covalently to nucleic acids, consequently causing biological complications [7]. Furthermore, acetaldehyde from tobacco smoke is also an important source of carbonyls to indoor air, where it may cause various diseases not only in smokers but also in non-smokers [8,9]. Therefore, the monitor of the amount of acetaldehyde in mainstream cigarette smoke is essential to estimate environmental exposure, and guide the development of potential risk-reduced tobacco products.

The determination of acetaldehyde in cigarette smoke sample has been carried out by high performance liquid chromatography (HPLC) as their 2,4-dinitrophenylhydrazine (DNPH) derivatives and gas chromatography (GC) as their benzyloxime or thiazolidine derivatives [10]. However, in highly complex cigarette smoke, the potential of interferences always appears. Moreover, certain carbonyl compounds are always present at trace levels. The direct measurement of acetaldehyde in cigarette smoke is very difficult [11]. To solve the above problems, it is quite desirable to develop a fast and efficient sample extraction and enrichment technique for the analysis of acetaldehyde in mainstream cigarette smoke.

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In this regard, magnetic mesoporous silica microspheres may be the key to this issue. Magnetic silica-based materials consisting of a magnetic core surrounded by a mesoporous silica shell have attracted considerable interests for drug delivery, controlled release, and bioseparation over the past decades [12,13]. They possess the excellent characteristics of strong magnetization, high surface areas, uniform mesopore distribution, tunable pore sizes, large pore volumes, thermal and mechanical stabilities, and extra adsorption capacity [14–20]. Considering the special advantages of high adsorption capacity of mesoporous silica and separation convenience of magnetic nanoparticles, the functionalized magnetic mesoporous silica materials are considered as promising adsorbents for enrichment and preconcentration of target pollutants from environmental samples [21–23]. By employing those as solid-phase extraction (SPE) sorbents, simplified extraction procedure and high anti-interference ability can be readily achieved. The anti-interference ability of functionalized magnetic mesoporous microspheres first lies in that the functional groups on the sorbents contribute to selective extraction of targeted analytes due to specific forces and interactions. Another factor is that the exterior shell of mesoporous silica can prevent macromolecules (e.g. humic acid, BSA) in matrices from entering into the interior pore-walls, thus aiming at enrichment of specific small molecules [24]. In our previous work, C18 groups functionalized magnetic mesoporous silica spheres had been successfully synthesized and then applied to the extraction and analysis of phthalates in water [25]. The satisfactory results inspired us to take further researches on the application of functionalized magnetic mesoporous materials to a complicated matrix.

In the present work, phenyl group-functionalized magnetic mesoporous ($\text{Fe}_3\text{O}_4@m\text{SiO}_2$) microspheres were prepared by a simple co-condensation approach. Acetaldehyde in mainstream cigarette smoke was collected and derivatized in water, and then extracted by the synthesized sorbents followed by the analysis of gas chromatography–mass spectrograph (GC–MS). Quantitative analyses of acetaldehyde were performed by measurement of its oximes. SPE extraction conditions and the method validations were also studied.

2. Material and methods

2.1. Chemicals and reagents

The standards of O-(2,3,4,5,6-pentafluorophenyl)hydroxylamine hydrochloride (PFBHA) and phenyl-triethoxysilane (PTES, Purity > 95%) were purchased from Alfa Aesar (Tianjin, China). Acetaldehyde, iron chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), ethylene glycol (EG), poly (ethylene glycol)-20000 (PEG-20000), hydrochloric acid, sodium hydroxide, trisodium citrate and sodium acetate anhydrous were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Tetraethyl orthosilicate (TEOS) and cetyltrimethyl ammonium bromide (CTAB) were acquired from Qiangshun Chemical Reagent Co., Ltd. (Shanghai, China). Deionized water was purified by a Milli-Qsystem (Milford, MA, USA). Cigarette samples used as in the study were purchased from Shanghai Tobacco Monopoly store.

The standard stock solution of PFBHA was prepared by dissolving the required amounts in deionized water to acquire an initial concentration of 20 mg/mL. Standard stock solutions of acetaldehyde-PFBHA derivatives ranged 20–5000 $\mu\text{g}/\text{ml}$ were prepared in deionized water. The chemical formula of the derivatization reaction was shown in Fig. S1. The derivatization of carbonyls with PFBHA can be performed under mild reaction conditions (ambient temperature and aqueous solution). The reaction is very fast and the corresponding oximes form in seconds [1]. The

working standard solutions were stored under 4 °C and were found to be stable for three months.

2.2. Preparation of phenyl group-functionalized $\text{Fe}_3\text{O}_4@m\text{SiO}_2$ microspheres

Magnetic Fe_3O_4 microspheres with a mean diameter of 250 nm were synthesized according to a previously reported method [26]. The phenyl group-functionalized $\text{Fe}_3\text{O}_4@m\text{SiO}_2$ microspheres were prepared through a surfactant involved sol–gel process referring to the previous method with some modifications [27–29]. The prepared Fe_3O_4 magnetic particles and CTAB with a ratio of 50 mg/500 mg were dispersed in 50 mL deionized water and sonicated for 30 min. The resultant dispersion was mixed with 450 mL diluted NaOH aqueous solution and further sonicated for 5 min to form a stable mixture. The dispersion was then heated at 60 °C for 30 min. Afterwards, 2.5 mL TEOS/ethanol (v/v: 1/4) solution was added drop by drop under mechanical stirring, followed by heating at 60 °C for 30 min with stirring. Subsequently, 150 μL TEOS/PTES (v/v: 2/1) mixture was injected into the dispersion which was further heated at 60 °C for 12 h. The resulting products were collected by magnetic separation and refluxed in acetone at 60 °C to remove the CTAB templates thoroughly. Finally, the obtained phenyl-functionalized $\text{Fe}_3\text{O}_4@m\text{SiO}_2$ microspheres were dried at 50 °C for 24 h in vacuum for future use.

2.3. Instrument and chromatographic conditions

Scanning electronic microscopy (SEM) images were recorded on a Philips XL30 electron microscope (Netherlands) operated at 20 kV. Transmission electron microscopy (TEM) images were taken on a JEOL 2011 microscope (Japan) performed at 200 kV. Fourier transform infrared (FT-IR) spectra were collected on Nicolet Nexus 470 Fourier spectrophotometer (USA) using KBr pellets. Nitrogen sorption isotherms, pore size distribution and BET surface area were measured at 77 K with a Micromeritics Tristar 3000 analyzer (USA). Vibration in extraction procedure was performed by a Qilinbeier XW-80A vortex (Jiangsu, China) at 2800 rpm/min. The cigarette samples were smoked by a simple smoking machine that fulfilled the requirements recommended by the International Organization for Standardization (ISO), i.e. puffing parameters of 35 mL volume, 2 s duration and 60 s interval between puffs [1].

The GC–MS analyses were performed with a PerkinElmer Clarus 680 gas chromatograph (Waltham, MA, USA) connected to a Perkin Elmer Clarus SQ8T mass spectrometer (Waltham, MA, USA). Compounds were separated on an Elite-5 MS capillary column (30 m \times 0.25 mm, 0.25 μm), and the samples were injected in splitless mode. The column oven temperature was programmed with an initial temperature of 40 °C for 2 min, raised to 80 °C with a ramping rate of 30 °C/min and held for 2 min, and then heated at 30 °C/min to 180 °C and kept for 9 min. Helium (99.999%) was used as the carrier gas at a flow rate of 1 mL/min. All samples were analyzed in scan mode in the range of 50–300 amu. The electron energy of MS is 70 eV, and the source temperature is set at 150 °C. The m/z ratio of quantitative ion for acetaldehyde oximes is 181, and m/z ratios of qualitative ions are 83, 209 and 85. TurboMass Ver 6.0.0 software was used for data acquisition.

2.4. The micro solid-phase extraction procedure by phenyl group-functionalized $\text{Fe}_3\text{O}_4@m\text{SiO}_2$ microspheres

The schematic procedure of sample collection and enrichment process was shown in Scheme 1. For the optimization studies, the mainstream cigarette smoke was collected in 100 mL water containing 150 μL of 20 mg/mL PFBHA solution. Then, 10 mL sample

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