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Simultaneous determination of polar and apolar compounds in environmental samples by a polyaniline/hydroxyl multi-walled carbon nanotubes composite-coated stir bar sorptive extraction coupled with high performance liquid chromatography

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ABSTRACT

Developing novel coatings for stir bar sorptive extraction (SBSE) is essential for extending the application of SBSE. Herein, a polyaniline/hydroxyl multi-walled carbon nanotubes (PANi/MWCNTs-OH) composite-coated stir bar was prepared via the adhesion technique for the simultaneous extraction of polar and apolar compounds, and a novel method of PANi/MWCNTs-OH-coated SBSE coupled with high performance liquid chromatography-ultraviolet detection (HPLC–UV) was proposed. To test the extraction performance of PANi/MWCNTs-OH-coated stir bar, phenols, non-steroidal anti-inflammatory drugs, and polychlorinated biphenyls were selected as representatives for polar, semi-polar and apolar compounds, respectively. High enrichment factors (EFs) ranged from 20.4 to 60.4-fold (theoretical EF, 100-fold) for target analytes were achieved, indicating that the proposed method is applicable in simultaneous analysis of the compounds with different polarities. The prepared PANi/MWCNTs-OH-coated stir bar has a good preparation reproducibility and can be reused for 20 times. The limits of detection (LODs, $S/N=3$) were found to be in the range of 0.09–0.81 μg/L. To validate the applicability, the proposed method was successfully applied to the analysis of eight target analytes in Yangtze River water after filtration and in the extract from sediment samples.

1. Introduction

In recent years, with the development of science and technology, the quality of human life has greatly improved. However, environmental pollution has increasingly and seriously accompanied economic development. At present, organic pollutants (OPs) are one of the most important aspects in environmental pollution, but the simultaneous determination of these OPs is difficult because they represent a variety of species (including phenols, drugs, phthalate esters, pesticides residues, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, etc.) with significantly different properties. For example, phenols are a kind of persistence hazardous pollutants [1]. The US Environmental Protection Agency (EPA) lists eleven phenols as priority pollutants, and the European Union (EU) sets a maximum concentration of 0.5 μg/L for total phenols and of 0.1 μg/L for individual phenols in drinking water [2]. Non-steroidal anti-inflammatory drugs (NSAIDs) are mainly used to alleviate the body inflammation, pain, fever and other symptoms [3], but their wide use on the global scale produce potential risks for the human body, such as heart disease and stroke [4]. Polychlorinated biphenyls (PCBs), also called chlorinated biphenyls, include 209 similarly structured compounds. As a potential pollutant, PCBs can cause great harm to the human body via hydrophobic and accumulated effects through food chains [5,6]. Therefore, the development of highly sensitive and fast methodologies for the simultaneous determination of OPs is of great significance for environmental safety assessment.

Chromatographic-based methods are commonly used for the determination of OPs, especially gas chromatography (GC) and high performance liquid chromatography (HPLC). However, in most cases, sample pretreatment steps are required before the instrumental analysis because of the very low levels of analytes and the complicated matrix in real-world samples. Conventional methods, such as liquid–liquid extraction (LLE), consume large volumes of toxic solvents and are time consuming. To avoid these drawbacks, several environmentally friendly sample pretreatment techniques,

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including liquid phase microextraction (LPME), solid phase extraction (SPE), solid phase microextraction (SPME) and stir bar sorptive extraction (SBSE), have been arisen. SBSE, developed in 1999 by Baltussen et al. [7], is a new solventless sample pretreatment technique and possesses many merits, such as high sensitivity, good reproducibility, high adsorption capacity, high recoveries and organic solvents free [7]. At present, the primary homemade SBSE coatings are organic polymers and modified polymers [8–10], and only polydimethylsiloxane (PDMS), ethylene glycol (EG)-silicone [11] and polyacrylate (PA) [12] SBSE coatings are commercialized. The commercial PDMS-coated stir bar was used for the simultaneous extraction of various OPs followed by GC–mass spectrometry (MS) detection [13–16]. However, derivatization is always necessary for the extraction of both polar and apolar compounds with PDMS-coated SBSE-GC–MS analysis. In recent years, a variety of home-made coated stir bars have been prepared for moderately polar compounds, and different approaches involving sol–gel technology and monolithic materials have been employed in the synthesis of polar coatings for SBSE [17]. Commercial EG-silicone [18] and PA [19] coatings were developed for the extraction of polar organics, but they are relative expensive and not good options for extraction of apolar compounds. Therefore, the development of new SBSE coatings for simultaneous analysis of various compounds with different polarities is highly expected.

Composite materials are composed of two or more different materials through physical or chemical methods and demonstrate new properties. The components in one composite material can complement each other in terms of their performance, resulting in the comprehensive performance being better than the original composition. Because of the good features of composite materials, they have been widely employed as adsorbents in sample pretreatment techniques, such as SPE and SPME. Du et al. [20] and Asadollahzadeh et al. [21] prepared carbon nanotubes (CNTs)/polyanilines and CNTs/polypyrrole fiber SPME with an electrochemical deposition method for the determination of phenols and phthalate esters, respectively. Composite materials show the potential in simultaneous extraction of polar and apolar compounds, however, no such application in SBSE is reported up to now.

In this work, a novel polyaniline/hydroxyl multi-walled carbon nanotubes (PANi/MWCNTs-OH) composite-coated stir bar was prepared and coupled with HPLC–UV for the simultaneous determination of polar, semi-polar and apolar compounds (phenols, NSAIDs and PCBs as representatives, respectively). The prepared composite coating was characterized, and the effect of experimental parameters on the extraction of target analytes, such as extraction time, extraction temperature, pH and ionic strength, was also investigated. The performance of the proposed PANi/MWCNTs-OH-SBSE-HPLC–UV method was validated. The method was successfully applied to the simultaneous analysis of target analytes in environmental water after filtration and in the extract from sediment samples.

2. Experimental

2.1. Reagents and standards

Sodium dihydrogen phosphate (NaH_2PO_4), sodium chloride (NaCl), hydrochloric acid (HCl), sodium hydroxide (NaOH), methanol, ethanol, acetonitrile, dichloromethane (CH_2Cl_2), ammonium persulfate ($(NH_4)_2S_2O_8$) and aniline were purchased from China Medicine (Group) Chemical Reagent Corporation (Shanghai, China). MWCNTs-OH were purchased from Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Science (Chengdu, China). The used capillary glass bars were obtained from the Apparatus Factory of West China University of Medical Sciences (Chengdu, China). The PDMS sol solution that was used for adhering the PANi and MWCNTs-OH particles consisted of a mixture of oligomers (component A) and crosslinking agents (component B) (GE RTV 615, Momentive performance materials, NY, USA) at a ratio of 10/1. Component A was a poly(dimethyl-methylvinylsiloxane) prepolymer with small amount of platinum (Pt) catalyst. The curing agent of B was a mixture of vinyl-endcapped PDMS precursors and poly(dimethyl-methylhydrogenosiloxane) precursors as crosslinkers. All of the solid reagents and solvents used in this study were of analytical grade. High-purity water obtained from a Milli-Q

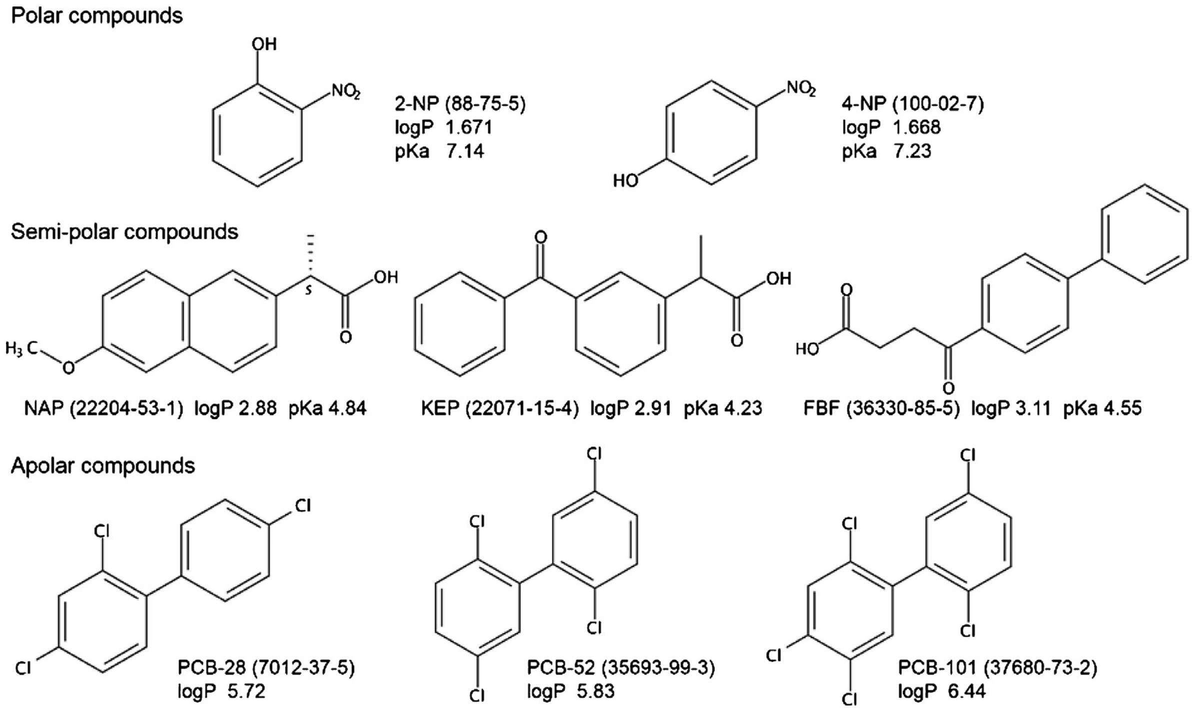

Fig. 1. Structures and CAS no. of eight target analytes and their log *P* and pKa values.