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Glass-fiber reinforced poly(acrylate)-based sorptive materials for the enrichment of organic micropollutants from aqueous samples

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Abstract

A novel and simple approach to sorptive materials for the extraction of organic compounds from environmental samples is presented. It entails the use of glass fiber fabric strips coated with a customized poly(acrylate) (PA) formulation as extraction medium. Analytes were enriched by means of shaking of the PA strip in the sample and then subsequently thermally desorbed and analyzed by GC–MS. The performance of the sorptive materials was evaluated by the enrichment of compounds with different polarities (phenols, hexachlorobenzene and hexachlorocyclohexanes) from water samples. Parameters that affect the extraction process such as pH, ionic strength of the solvent, mixing mechanism, extraction time and desorption conditions were investigated. The extraction abilities of the PA extraction medium were compared with that of commercially available poly(dimethylsiloxane) (PDMS) Twisters. The results revealed that the new material shows higher affinity for phenolic compounds presumably due to the presence of polar groups. The partition coefficients for the PA strips estimated in this work were up to 15 times higher than for the PDMS Twister, resulting in higher recoveries and lower detection limits. The method was applied for the quantification of the afore mentioned compounds in contaminated surface water samples from Bitterfeld (Germany). Using both PA strips and PDMS Twisters, good agreement of the extraction data was achieved.

Keywords: Sorptive extraction; Thermodesorption GC–MS; Poly(dimethylsiloxane) Twisters; Glass-fiber reinforced poly(acrylate); Phenols; Water samples

1. Introduction

To determine organic trace compounds in aqueous matrices, a sample preparation procedure is normally required prior to chromatographic separation and detection. Since the 1990s, significant attention has been given to miniaturized and solvent-free sample preparation techniques based on sorptive extraction, e.g. solid-phase microextraction (SPME) [1–3] and stir bar sorptive extraction (SBSE) [4–6]. These techniques proved to be simple, fast and solvent-free alternatives to traditional extraction methods such as liquid–liquid extraction and solid-phase extraction (SPE) while maintaining or even improving sensitivity. The extraction efficiency for a particular analyte from a sample is determined by the partition coefficient (K_P) between the extraction phase and the sample matrix, and the phase ratio ($\beta = V_W/V_P$) between the aqueous sample and the extraction phase.

SPME, first developed by Arthur and Pawliszyn 1990 [1], entails the extraction of organic pollutants from a sample into a sorbent phase coating on a silica fiber support. A limitation of SPME is the relatively small volume of the extraction phase that results in low extraction efficiency, especially for compounds with small K_P. In 1999, a new extraction technique known as SBSE using magnetic stir bars coated with poly(dimethylsiloxane) (PDMS) was developed by Sandra and co-workers [4]. This format allowed a significant increase in the volume of the extraction phase, i.e. from approximately 0.5 μL

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for a SPME fiber up to 24–219 μL for a SBSE, ultimatively translating in higher enrichment factors and higher sample capacity. This has been experimentally demonstrated in different works that compared SBSE and SPME using both PDMS coatings for polycyclic aromatic hydrocarbons (PAHs) and organochlorine compounds [7] as well as for organophophorous insecticides [8]. Similar results have also been obtained by other sorptive alternatives that increase the amount of PDMS, namely thin-film microextraction [9] and by the use of disposable PDMS rods [10,11].

Because of their non-polar character, PDMS sorbents have been successfully applied mainly to the extraction and quantification of medium to non-polar compounds [12,13], however, failed in the extraction of more polar analytes [13,14] unless they have been subject to previously derivatization [15,16]. Despite the principal applicability of such an approach, the addition of a derivatization step complicates the overall analytical method. Using SPME, a wide range of analytes can be successfully analyzed due to the large number of different fiber coatings that are commercially available. These include non-polar PDMS, semi-polar poly(dimethylsiloxane)-divinylbenzene (PDMS-DVB), and polar poly(acrylate) (PA), carbowax-divinylbenzene (CW-DVB) liquid-like phases, and coated porous particle phases such as poly(dimethylsiloxane)-Carboxen (PDMS-Carboxen). In contrast, stir bars are only available with PDMS coatings, resulting in a quite limited enrichment capability for polar compounds. In order to overcome this limitation, a new dual phase stir bar has been commercialized by Gerstel. It consists of an empty PDMS tube (1 cm length, 0.5–1 mm thick) which can be filled with the desired sorbent. Carbonaceous materials have been tested as filling sorbents. The results obtained revealed enhanced extraction yields for polar compounds when compared with those achieved using empty PDMS tubes [17]. Recently, sol–gel technology was applied to the preparation of extraction phases based on SPME fibers [18,19], stir bars [20] and membranes [21] and applied to the extraction of polar compounds. These new phases allowed the use of polar terminations and showed advantages because of their porous structure and strong adhesion to the surface of the bare fused silica or glass.

In this paper, a novel approach to sorptive extraction based on a glass fiber strip coating with PA and evaluation for the extraction of polar and non-polar compounds with $\log(K_{\mathrm{ow}})$ between 1.46 for phenol and 5.73 for hexachlorobenzene is reported. PA coatings have already been applied successfully to the extraction of polar compounds by SPME [22–24]. The PA coating displays high affinity for both polar and non-polar compounds since its structure consists of a hydrocarbon chain backbone with ester side chains of adjustable polarity. However, this sorbent only slightly favors the polar compounds over the non-polar one. The novel format allows a significant increase in the volume of the extraction phase compared with PA-based SPME fibers. The extraction ability of the new PA material was compared with that of commercially available PDMS Twisters. Finally, PA materials were applied to determine the pollutant concentration in surface water samples.

2. Experimental

2.1. Reagents and materials

An EPA phenolic standard, consisting of seven phenols (phenol, 2-chlorophenol, 2,4,-dimethylphenol, 2,4-dichlorophenol, 4-chloro-3-methylphenol, 2,4,6-trichlorophenol, pentachlorophenol) with a concentration of 500 mg/L of each phenol as well as α-hexachlorocyclohexane, δ-hexachlorocyclohexane and hexachlorobenzene standards were obtained from Supelco (Bellefonte, PA, USA). Standard stock solutions of hexachlorocyclohexanes and hexachlorobenzene (1000 μg/mL) were prepared in methanol. Spiking solutions of all the studied compounds (50 μg/mL and 5 μg/mL of each) were prepared by diluting suitable volumes of each standard solution with methanol. Methanol, acetone and sodium chloride were purchased from Merck (Darmstadt, Germany). Hydrochloric acid was purchased from Riedel-de Haën (Seelze, Germany). Commercial stir bars Twisters (herein referred to as "Twisters") for sorptive extraction were obtained from Gerstel (Mülheim an der Ruhr, Germany). It consists of a glass-encapsulated magnetic stir bar, 10 mm in length, externally coated with 22 mg of PDMS. This layer is 0.5 mm thick, which corresponds to a volume of 25 μL of PDMS. Prior to first use, the stir bar was conditioned 16 h at 250 °C with a nitrogen stream of 30 mL/min. For foil coating, the commercial urethane acrylates EB 294/25, EB 5129, both from Cytec (Drogenbos, Belgium), CN 922, and SR 368, both from Sartomer (Paris, France), were used. For glass fiber strip preparation, laurylacrylate (SR 335), trimethylolpropanetriacrylate (TMPTA), and cyclic trimethylolpropane formal acrylate (SR 531) were obtained from Sartomer, hydroxyethylacrylate (HEA), from Dow Chemicals (Edegem, Belgium), and 2-hydroxy-2-methyl-1-phenyl-propan-1-one (DC 1173), from Ciba Specialty Chemicals (Basel, Switzerland), were used without further purification. Glass fiber fabrics (25 g/m^2 and 49 g/m^2, finish FK800, canvas) were obtained from Conrad Elektronik (Hirschau, Germany).

2.2. Preparation of glass fiber strips coated with PA

A formulation consisting of 3.500 g SR 335, 3.025 g HEA, 3.011 g TMPTA, 0.429 g SR 531 and 0.160 g DC 1173 was prepared and thoroughly mixed. A piece of glass fiber fabric was placed on top of a sheet of poly(ethylene) foil (25 μm) and fixed by application of vacuum on an applicator table (Simex, Haan, Germany). The fabric was soaked with the formulation and a second sheet of poly(ethylene) foil placed on top. Excessive liquid was pressed out by using a steel rod. The sandwich was cured under inert conditions (<50 ppm O_2) in a UV-curing conveyor tunnel (IST Strahlentechnik Metz, Nuertigen, Germany) using multiple passes (1.3 kJ/m^2 Hg-high pressure UV) on both sides to ensure complete depletion of the photoinitiator. Finally, the covering poly(ethylene) foils were peeled off the cured glass fiber composite. Coating weights were determined gravimetrically after cutting pieces of 10 cm × 10 cm from the cured sandwich and subtracting the fabric weight provided by the manufacturer. The finer fabric (25 g/m^2) was thus found to require