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Determination of polychlorinated biphenyls in ocean water and bovine milk using crosslinked polymeric ionic liquid sorbent coatings by solid-phase microextraction

Manishkumar D. Joshi, Tien D. Ho, William T.S. Cole, Jared L. Anderson *

Department of Chemistry, School of Green Chemistry and Engineering, The University of Toledo, 2801 W. Bancroft Street, MS 602, Toledo, OH 43606, USA

ABSTRACT

Crosslinked polymeric ionic liquid (PIL)-based sorbent coatings were employed in the extraction of 21 polychlorinated biphenyls (PCBs) from ocean water and bovine milk using solid-phase microextraction (SPME). The extraction temperature, time, and concentration of sodium chloride added to the matrix were optimized in order to determine the best extraction conditions for the extraction of PCBs. The analytical performance of the crosslinked PIL-based SPME fibers was compared with a commercial 7 μm polydimethylsiloxane (PDMS) fiber using gas chromatography (GC) employing an electron capture detector (ECD) and mass spectrometric detection (MS). Higher sensitivities for PCBs were achieved using PIL-based fibers when compared to PDMS fiber due to the incorporation of benzyl moieties into the PIL structures. The limits of detection (LOD) for all PCBs were determined to be in the low ng L^{-1} range using the three studied coatings. Recovery studies were performed for PCBs in ocean water and bovine milk to validate the applicability of the current SPME method.

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1. Introduction

Polychlorinated biphenyls (PCBs) are a class of chlorinated hydrocarbons possessing various degrees of chlorination on a biphenyl backbone. The number of chlorine atoms present on the biphenyl backbone can vary from one to 10 resulting in the generation of different isomers. PCBs were widely used in industry as fluid for transformers and capacitors, plasticizers, adhesives, and fire retardants due to their unique properties such as chemical inertness, thermal stability, and inflammability [1].

The presence of PCBs in the environment was first observed by Risebrough and co-workers in 1968 [2]. PCBs are known to be toxic and carcinogenic to humans [3]. Elevated levels of PCBs can also alter the levels of the thyroid hormone in infants and pregnant women [4]. Due to their environmental and health hazards, the production and use of PCBs has been banned since 1977. However, due to their good thermal and chemical stability, as well as hydrophobic nature, PCBs are well-retained in the environment and can be found in trace levels within water and soil. Therefore, it is of great importance to develop analytical methods that are sensitive, rapid, and robust to quantify the trace levels of PCBs present within the environment.

The analysis of PCBs in environmental matrixes, such as soil or water, typically requires a pre-concentration or sample preparation step. Two techniques most often used for pre-concentration of PCBs are liquid–liquid extraction (LLE) and solid phase extraction (SPE) [5,6]. However, these pre-concentration methods can be tedious and time consuming. LLE typically requires the use of copious volumes of organic solvents, which makes it environmentally unfriendly. SPE usually requires less organic solvent but may need larger sample volumes and can suffer from breakthrough.

Solid-phase microextraction (SPME) is an additional sample preparation technique first described by Pawliszyn and co-workers in 1990 [7]. SPME is widely used due to the fact that it is a simple, rapid, inexpensive, and solvent-free microextraction method. In previous studies, Potter and co-workers demonstrated SPME in the pre-concentration of PCBs from water using the PDMS sorbent coating [8]. Llompart and co-workers showed the application of SPME in the extraction of PCBs from water samples using direct-immersion and headspace extraction modes [9,10]. Yang and co-workers reported the analysis of PCBs in water using SPME with gas chromatography employing an electron capture detector (GC-ECD) [11]. It was shown that headspace SPME is more sensitive than direct-immersion SPME for the analysis of PCB congeners in water [9,12]. SPME was also exploited in the analysis of PCBs from complex matrixes such as human serum, blood plasma, milk, soil, and ash [13–18]. Augusto and co-workers performed the analysis of PCBs in human milk samples [15,16]. All of the above methods involved the analysis of PCBs using the commercial PDMS fiber.

* Corresponding author. Tel.: +1 41 9530 1508; fax: +1 41 9530 4033.
 E-mail address: Jared.Anderson@UToledo.edu (J.L. Anderson).

However, the development of new SPME sorbent materials as coatings is necessary to enhance the sensitivity and selectivity of the method, particularly when performing analysis from complex matrixes. Recently, Wang and co-workers developed fluorinated polyaniline-based (PANI) SPME sorbent coatings for the analysis of various PCB congeners [12]. The limit of detection (LOD) obtained for various PCBs using the PANI-based fibers was in the sub ng L^{-1} range and relatively lower than the 100 μm PDMS fiber (ng L^{-1}).

Recently, ionic liquids (ILs) have emerged as novel sorbent materials in various microextraction methods including single drop microextraction, liquid phase microextraction, dispersive liquid–liquid microextraction and SPME [19,20]. The tunable nature of ILs provided the capability to enhance the extraction efficiency and selectivity for various analytes of interest. Our group has been particularly interested in designing polymeric ionic liquid (PIL)-based sorbent coatings for SPME [21–23]. The recent introduction of an "on-fiber" photo-initiated polymerization approach enables the generation of crosslinked PIL-based sorbent coatings [24]. Crosslinked PIL-based sorbent coatings possess enhanced mechanical and thermal stability in addition to being highly robust due to the cross-linking and covalent bonding of IL monomers to the silica support.

In this work, two structurally diverse PIL-based crosslinked SPME sorbent coatings were generated for the analysis of PCBs. The PIL-based crosslinked sorbent coatings were fabricated by mixing the 1-vinylbenzyl-3-hexadecylimidazolium bis[(trifluoromethyl)sulfonyl]imide [VBHDIM] [NTf$_2$] IL monomer individually with two different IL crosslinkers, namely, 1,12-di(3-vinylimidazolium)dodecane dibis[(trifluoromethyl)sulfonyl]imide ([(DVIM)$_2$C$_{12}$] 2[NTf$_2$]) and 1,12-di(3-vinylbenzylimidazolium)dodecane dibis[(trifluoromethyl)sulfonyl]imide ([(DVBIM)$_2$C$_{12}$] 2[NTf$_2$]), respectively. The analytical performance of the novel PIL-based crosslinked coatings was compared to a PDMS coating by using two different detectors, namely, ECD and mass spectrometer (MS) in conjunction with GC. Method validation was performed via recovery experiments in an environmental seawater and a biological bovine milk matrix. This is the first report to exploit crosslinked PIL-based SPME sorbent coatings for the analysis of PCBs in two complex sample matrixes.

2. Experimental

2.1. Instrumentation

A RPR-100 UV reactor containing 16 lamps and a spinning carousel was obtained from Southern New England Ultraviolet Company (Bradford, Connecticut, USA). UV polymerization was performed at a wavelength of 360 nm. An Agilent Technologies 7890 gas chromatograph (Santa Clara, CA, USA) equipped with an electron capture detector as well as a 5975C inert XL MSD with a Triple Axis detector (GC–MS) was used. The separation of 21 PCB congeners by GC-ECD was achieved using a HP-5 capillary column (30 m × 0.25 mm I.D., 0.25 μm film thickness) obtained from Agilent Technologies (Santa Clara, CA, USA). The separation of analytes by GC–MS was performed using a HP-1 column (30 m × 0.25 mm I.D., 0.25 μm film thickness).

2.2. Materials

1-Vinylimidazole, 1,12-dibromododecane, vinyltrimethoxysilane (VTMS), ammonium hydrogen difluoride, and 2-hydroxy-2-methyl-propiophenone (DAROCUR 1173) were purchased from Sigma-Aldrich (Milwaukee, WI, USA). The PCB mixture containing 100 μg mL^{-1} of 21 different congeners in acetone was purchased from Accustandard (New Haven, CT, USA). Acetonitrile, acetone, chloroform, methanol, isopropanol, dichloromethane, ethyl acetate, and sodium chloride were purchased from Fisher Scientific (Fair Lawn, NJ, USA). A 10 μL syringe

was obtained from Hamilton (Reno, NV, USA). A 7 μm PDMS fiber was obtained from Supelco (Bellefonte, PA, USA). Untreated fused silica capillary tubing (0.5 mm I.D), amber glass vials (20 mL), and poly-tetrafluoroethylene (PTFE) septa caps were purchased from Supelco. Milli-Q water (18.2 MΩ cm) was obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA). Bovine milk containing 1% fat was purchased from a local market (Toledo, OH, USA). Seawater was obtained from Charleston Bay (Charleston, SC, USA).

2.3. Synthesis of ionic liquid monomer and cross-linkers

The structures of the three ILs used to synthesize the PIL-based sorbent coatings are shown in Table 1. The synthesis of the [VBHDIM] [NTf$_2$] IL monomer and the ([(DVIM)$_2$C$_{12}$] 2[NTf$_2$]) IL cross linker were performed according to previously reported procedures [21,25,26]. The synthesis of the IL crosslinker ([(DVBIM)$_2$C$_{12}$] 2[NTf$_2$]) was achieved as described in the supplementary information.

2.4. Preparation of SPME fibers

The PIL-based sorbent coating was prepared by an on-fiber photoinitiated copolymerization approach recently developed by our group [24]. Briefly, 1 cm of the fiber's polyimide coating was removed. This was followed by immersing the bare fiber in a 5% (w/v) methanolic solution of ammonium hydrogen difluoride for 30 min, dried in air for 30 min, and conditioned in the GC injector port for 1 h at 250 °C. The etched fiber surface was derivatized by immersing the etched portion of the fiber into 10 mL of VTMS solution for 30 min. The derivatized fiber was conditioned by exposing the fiber in the GC injection port at 200 °C for 5 min. The etched and derivatized fiber was dip-coated with a mixture containing the IL monomer, cross-linker (50% of monomer weight) and the photoinitiator DAROCUR 1173 (3% by weight). This was followed by exposing the fiber to 360 nm UV light for 30 min. The fiber was then conditioned several times at 280 °C for 5 min each. Two different PIL-based sorbent coatings were generated, namely, PIL 1 and PIL 2. As shown in Table 1, the [VBHDIM] [NTf$_2$] IL monomer was used for both PILs while the IL crosslinkers ([(DVIM)$_2$C$_{12}$] 2[NTf$_2$]) and ([(DVBIM)$_2$C$_{12}$] 2[NTf$_2$]) were employed in PIL 1 and PIL 2, respectively.

2.5. Headspace solid-phase microextraction of water samples

It has been shown previously that HS-SPME provides higher extraction efficiencies compared to DI-SPME at elevated extraction temperatures [9]. Therefore, HS-SPME was chosen as a preferred method for the extraction of PCBs. The mixture of 21 different PCB congeners containing 100 μg mL^{-1} of each PCB congener was diluted using acetone to prepare a series of stock solutions at concentrations of 10 ng mL^{-1}, 100 ng mL^{-1} and 1000 ng mL^{-1}. A 20 mL amber glass vial was filled with 15 mL of an aqueous sodium chloride solution (30% w/v). A certain volume of the PCB stock solution was spiked into the vial and the vial immediately immersed in an oil bath thermostated at 65 °C. After 10 min, the fiber was exposed to the headspace of the sampling vial for 45 min. The fiber was then withdrawn and exposed to the GC injection port for 5 min at 280 °C. The temperature program used for GC-ECD was as follows: initial temperature was set at 60 °C and ramped to 130 °C at 25 °C/min. The temperature was then increased to 300 °C at 8 °C/min and held for 2 min. The μ-ECD detector temperature was set to 300 °C and the argon/methane make-up flow was set to 60 mL/min. The temperature program used for GC–MS was as follows: intial temperature was set at 60 °C hold and ramped to 130 °C at 15 °C/min. The temperature was then increased to 200 °C at a rate of 5 °C/min and held for 15 min. Finally, the temperature was increased to 280 °C at 8 °C/min and held for 5 min. The SIM ions chosen for each PCB during GC–MS