



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



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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]. Llompert 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.

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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 matrices. 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] [NTf₂] IL monomer individually with two different IL crosslinkers, namely, 1,12-di(3-vinylimidazolium)dodecane dibis[(trifluoromethyl)sulfonyl]imide ((DVMIM)₂C₁₂) 2[NTf₂]) and 1,12-di(3-vinylbenzylimidazolium)dodecane dibis[(trifluoromethyl)sulfonyl]imide ((DVBIM)₂C₁₂) 2[NTf₂]), 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 matrices.

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-methylpropiophenone (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 polytetrafluoroethylene (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] [NTf₂] IL monomer and the ((DVMIM)₂C₁₂) 2[NTf₂]) IL cross linker were performed according to previously reported procedures [21,25,26]. The synthesis of the IL crosslinker ((DVBIM)₂C₁₂) 2[NTf₂]) was achieved as described in the supplementary information.

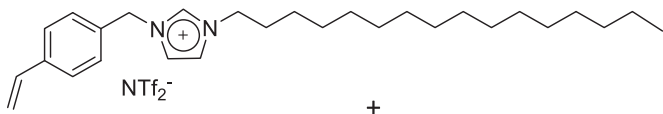
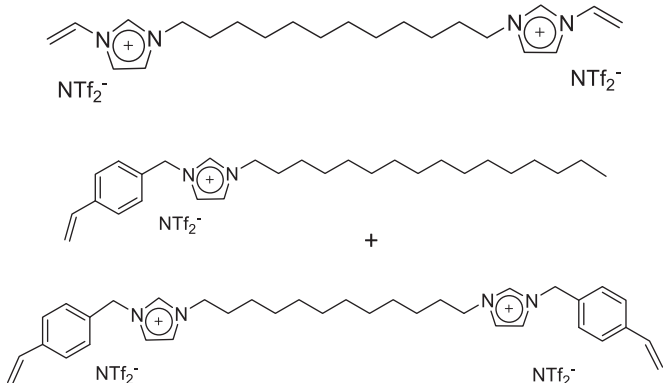
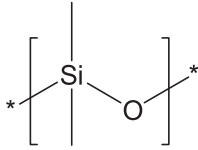
2.4. Preparation of SPME fibers

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] [NTf₂] IL monomer was used for both PILs while the IL crosslinkers ((DVMIM)₂C₁₂) 2[NTf₂]) and ((DVBIM)₂C₁₂) 2[NTf₂]) 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: initial temperature was set at 60 °C 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

Table 1
IL monomer and crosslinkers used in this study to generate PIL-based sorbent coatings.

Sorbent coating	IL monomer + IL crosslinker (2:1)	Approximate film thickness (μm)
PIL 1		5
PIL 2		2
PDMS		7

analysis are listed in Table 2. It should be noted that no agitation methods employing stir bars were used for the analysis of PCBs in the water samples. It has been shown that PCBs tend to adsorb to the Teflon-coated surface of stir bars and can severely affect the reproducibility due to analyte-to-stir bar carryover [11].

2.6. Headspace solid-phase microextraction of milk samples

To prepare milk sample solutions for analysis, 5 mL of bovine milk (stored at 4 °C) was transferred to a 20 mL amber glass vial and spiked with 400 μL of methanol. The bovine milk sample was then diluted with Milli-Q water at a 1:1 v/v ratio. The sample was then incubated for 24 h at 4 °C. After incubation, 2.0 g of sodium chloride was added to the sample and the sample was vortexed for 5 min followed by shaking for an additional 2 min. A Teflon-coated stirbar was also added to the sample vial to agitate the sample at a rate of 500 rpm during the extraction step. Although this agitation method was not employed for the extraction of PCBs in water samples, it was necessary for the analysis of milk samples in order to allow for complete homogenization and minimize coagulation of the matrix. Prior to extraction, the sample was equilibrated at 65 °C for 10 min. The fiber was exposed to the headspace for 45 min where the temperature was kept constant at 65 °C. After extraction, the fiber was exposed to the GC injector for desorption at 280 °C for 5 min. All milk samples were analyzed using GC-ECD.

3. Results and discussion

3.1. Effect of extraction temperature and time

In HS-SPME, elevated temperatures can significantly increase the amount of analytes that partition to the headspace and can increase the overall extraction efficiency of the system. However,

an increase in temperature may also decrease the partition coefficient of analytes sorbed to the fiber coating while also increasing the likelihood of analytes leaking from the vial cap, leading to a loss of analyte [27]. Thus, optimizing the extraction temperature is critical for obtaining high analyte extraction efficiency and low LODs. In this study, the PIL 1 fiber was used to evaluate the effect of temperature on the extraction efficiency of PCBs in water by HS-SPME. Three different extraction temperatures, namely, 45 °C, 65 °C, and 85 °C were evaluated. An extraction time of 45 min and salt concentration of 30% (w/v) were employed. As shown in Fig. 1, the extraction efficiency of PCBs increased significantly as the extraction temperature was increased from 45 °C to 65 °C. However, as the temperature was increased from 65 °C to 85 °C, the extraction efficiency of all 21 PCBs decreased. This may be due to a combination of a decrease in the coating-to-analyte partition coefficient from high temperatures and leaking of analyte from the sample vial. It is important to note that the variation in the extraction efficiencies of PCB congeners 8, 18, 118, 153, 138, 201 was found to be negligible when the temperature was varied from 45 °C to 65 °C. An optimized extraction temperature of 65 °C was used throughout this study.

The optimization of extraction time can have profound effects on the extraction efficiency of an analyte. With an increase in extraction time, higher amounts of analytes can be sorbed to the fiber coating until a steady-state is reached. The effect of extraction time on the extraction performance of 21 PCBs was evaluated by examining four different extraction times (i.e., 15, 30, 45, and 60 min). As shown in Fig. 2, the extraction efficiencies of all PCBs increased significantly as the extraction time increased from 15 to 45 min. An extraction time longer than 45 min resulted in a slight decrease in the extraction efficiencies, a likely result of analyte adsorption to the sample vial surface [28]. Hence, 45 min was used as an optimized extraction time for subsequent HS-SPME measurements.

Table 2
Names, structures, and SIM ions chosen for all studied PCBs.

PCB	Name	Structure	SIM ions
8	2,4'-dichlorobiphenyl		75,152, 222
18	2,2',5-trichlorobiphenyl		186, 221, 256
28	2,4,4'-trichlorobiphenyl		150, 186, 258
52	2,2',5,5'-tetrachlorobiphenyl		150, 220, 292
44	2,2',3,5'-tetrachlorobiphenyl		220, 257, 292
66	2,3',4,4'-tetrachlorobiphenyl		150, 220, 292
101	2,2',4,5,5'-pentachlorobiphenyl		254, 291, 326
77	3,3',4,4'-tetrachlorobiphenyl		150, 220, 292
118	2,3',4,4',5-pentachlorobiphenyl		184, 256, 326
153	2,2',4,4',5,5'-hexachlorobiphenyl		184, 256, 326
108	2,3,3',4,4'-pentachlorobiphenyl		218, 290, 360
138	2,2',3,4,4',5'-hexachlorobiphenyl		218, 290, 360
126	3,3',4,4',5-pentachlorobiphenyl		184, 256, 326
187	2,2',3,4',5,5',6-heptachlorobiphenyl		324, 360, 396
128	2,2',3,3',4,4',-hexachlorobiphenyl		145, 290, 360
201	2,2',3,3',4,5',6,6'-octachlorobiphenyl		179, 360, 430
180	2,2',3,4,4',5,5'-heptachlorobiphenyl		324, 360, 394
170	2,2',3,3',4,4',5-heptachlorobiphenyl		324, 360, 394
195	2,2',3,3',4,4',5,6-octachlorobiphenyl		179, 360, 430
206	2,2',3,3',4,4',5,5',6-nonachlorobiphenyl		392, 430, 464
209	2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl		179, 214, 498

3.2. Effect of salt concentration

It is well-known that the addition of kosmotropic salts to an aqueous sample solution can decrease the solubility of organic

analytes, especially non-polar compounds, and increase the partitioning of these compounds to the sample headspace [29]. Using the commercial PDMS fiber, the effect of salt concentration on the extraction efficiency of various PCBs has been controversially

discussed within the literature. Llompart and co-workers saturated an aqueous PCB sample with potassium chloride and observed no effect on the extraction efficiency while using a 100 μm PDMS fiber [9]. A decrease in the extraction efficiency of PCBs from water samples was observed by Shu and co-workers

when sodium chloride was added and the extraction performed using a 100 μm PDMS fiber [30]. Contrarily, Wang and co-workers observed an increase in the extraction efficiency of PCBs with an increase in sodium chloride concentration when using the fluorinated PANI-based sorbent coating [12]. Since a number of mixed

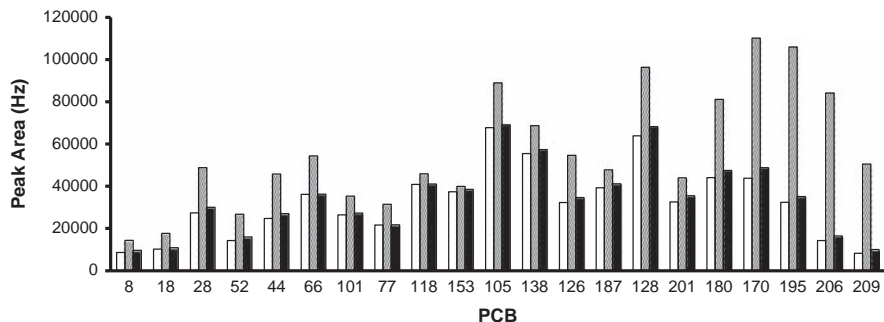


Fig. 1. Comparison of the extraction efficiency obtained for all studied PCBs at (□) 45 °C, (▨) 65 °C, and (■) 85 °C.

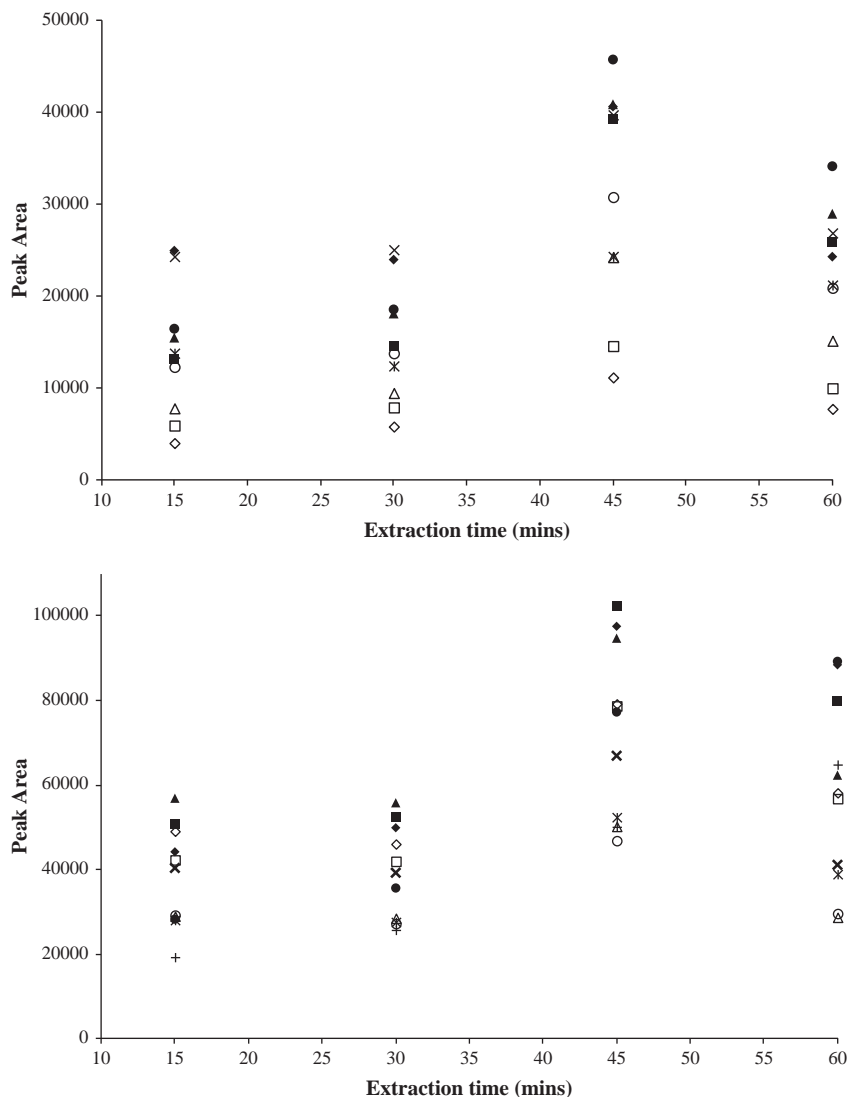


Fig. 2. Effect of extraction times on the extraction efficiency of different PCBs using the PIL 1 sorbent coating. (A) 8 (◆), 18 (□), 28 (▲), 52 (△), 44 (■), 66 (●), 101 (○), 77 (*), 118 (◆), 153 (◇) and (B) 105 (◇), 138 (◆), 126 (*), 187(▲), 128 (▲), 201 (○), 180 (□), 170 (■), 195 (◇), 206 (●), 209 (+). A PCB concentration of 1 $\mu\text{g L}^{-1}$ in 30% (w/v) aqueous sodium chloride solution was chosen for the extraction. The extraction was performed at 65 °C.

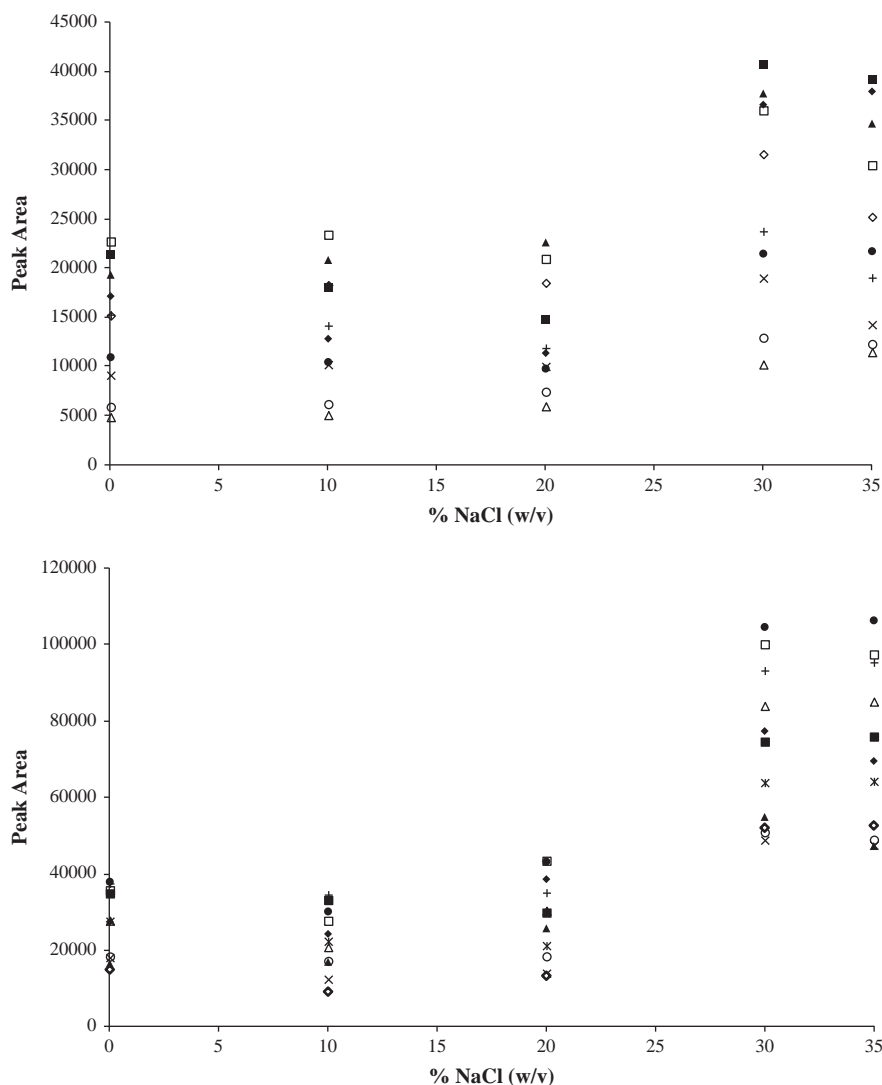


Fig. 3. Effect of sodium chloride concentration on the extraction efficiency of all PCBs using the PIL 1 sorbent coating. (A) 8 (\blacktriangle), 18 (\bullet), 28 (\blacktriangle), 52 (\blacklozenge), 44 (\blacklozenge), 66 (\square), 101 ($+$), 77 (\bullet), 118 (\blacksquare), 153 (\blacklozenge) and (B) 105 (\blacksquare), 138 (\times), 126 (\circ), 187 (\blacklozenge), 128 ($+$), 201 (\blacklozenge), 180 (\blacktriangle), 170 (\bullet), 195 (\square), 206 (\blacklozenge), 209 (\blacktriangle). A PCB concentration of $1 \mu\text{g L}^{-1}$ in 30% (w/v) aqueous sodium chloride solution was chosen for the study. The extraction time and temperature were maintained at 45 min and 65°C , respectively.

results have been reported from the addition of salt to the matrix, the effect of salt concentration using the crosslinked PIL-based coatings was investigated.

As shown in Fig. 3, sodium chloride was added to the aqueous samples at various concentrations (0–35% w/v) to evaluate the effect on the PCB extraction efficiency using the PIL 1 fiber. When the concentration of sodium chloride was increased from 0 to 20% (w/v), no significant increase in the extraction of PCBs was observed. This is in agreement with the observations of Shu and co-workers [30]. However, the extraction efficiencies increased significantly for all PCBs when the salt concentration was increased from 20 to 30% (w/v). The extraction efficiency of most PCBs leveled off and remained constant when the salt concentration was increased from 30 to 35% (w/v). Therefore, a 30% (w/v) salt concentration was applied for all subsequent studies involving SPME analysis of water samples.

3.3. Analytical performance of selected coatings in the extraction of PCBs using headspace SPME

The analytical performance was studied for all coatings in order to explore their differences in selectivity for the PCBs. Calibration curves of the PCBs, obtained by GC-ECD, in an aqueous sample

solution containing 30% (w/v) sodium chloride were constructed for the PIL 1, PIL 2, and PDMS coatings. As shown in Table 1, the approximate film thicknesses of PIL 1 ($5 \mu\text{m}$) and PIL 2 ($2 \mu\text{m}$) are smaller than that of the $7 \mu\text{m}$ PDMS coating. As listed in Tables S1–S3, the linear range of all fibers varied from 2.5 ng L^{-1} to 100 ng L^{-1} . The LODs were determined by decreasing the analyte concentration until a 3:1 signal: noise (S:N) ratio was achieved. In the case of the PDMS coating, the LOD ranged from 1 to 20 ng L^{-1} when using ECD and 2.5 ng L^{-1} when using MS detection. The precision of the method using the PDMS coating was slightly higher than the PIL-based coatings and ranged from 1.6 to 21.5% and 4.9 to 22.4% using ECD and MS detection, respectively. Similar to the PDMS coating, the crosslinked PIL-based coatings were highly applicable in the determination of trace-level PCBs from a simple water matrix. The LODs of all PCBs using PIL 1 ranged from 1 to 2.5 ng L^{-1} and 2.5 to 25 ng L^{-1} while the precision ranged from 2.0 to 19.1% and 0.3 to 19.5% for ECD and MS detection, respectively. The analytical performance of PIL 2 fiber for the extraction of PCBs in terms of LOD ranged 1 – 7.5 ng L^{-1} using ECD detection while a LOD of 2.5 ng L^{-1} was achieved using MS detection. The precision for the PIL 2 fiber in the extraction of PCBs ranged from 0.7 to 20.7% and 4.1 to 18.8% using ECD and MS detection, respectively.

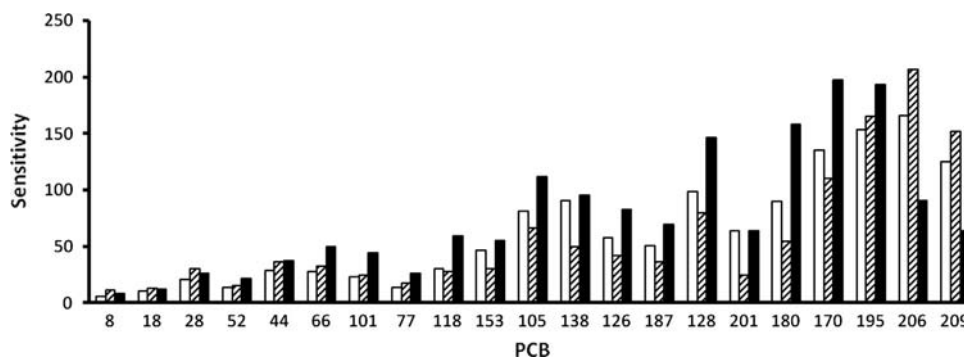


Fig. 4. Comparison of the sensitivities (slope of the calibration curve) obtained for all studied PCBs using the (□) PDMS, (▨) PIL 1, and (■) PIL 2 sorbent coatings.

A bar graph describing the sensitivities obtained for all coatings is represented in Fig. 4. The sensitivity, defined as the slope of the calibration curve, varied significantly when different coatings were used. Compared to the crosslinked PIL-based coatings, lower sensitivities were obtained using the PDMS coating for congeners with lower degrees of chlorine substitution. As the degree of substitution increased to more than four chlorine atoms, the PDMS coating exhibited noticeably higher sensitivities compared to PIL 1. The PIL 1 coating possessed the highest sensitivity for PCBs containing the highest and lowest degrees of substitution, namely PCBs 8, 18, 28, 206, and 209. However, the sensitivities of many other congeners, such as those containing four to six chlorine atoms, were relatively lower to those obtained with the PDMS and PIL 2 coatings. The PIL 2 coating exhibited up to a two-fold increase in sensitivity for congeners containing four to eight chlorine atoms when compared to the other coatings. This may be due to the aromatic moieties specifically tailored within the structure of the dicationic IL crosslinker in addition to the benzyl moiety present in the monocationic IL monomer. Analogous to previous studies employing PILs composed of aromatic substituents for the extraction of aromatic analytes [28,31], the benzyl moieties tailored to both the monomer and crosslinker can enhance π - π interactions with the PCBs, leading to higher analyte sensitivity and selectivity. Although PIL 2 exhibited superior sensitivities for most PCBs, this coating showed relatively lower sensitivity for congeners containing the highest degrees of chlorine substitution, namely PCBs 206 and 209. Overall, both PIL 1 and PIL 2 coatings exhibit unique selectivity and often similar or better sensitivity for all PCB congeners compared to the PDMS coating, even though they possess smaller film thicknesses.

3.4. Method validation and recovery in real-world samples

Ocean water and bovine milk were chosen as real-world matrixes for the extraction of the PCBs in order to demonstrate the applicability of the proposed method. Ocean water samples were prepared by spiking 30 ng L^{-1} of PCBs into a 20 mL sample vial containing 15 mL ocean water with the addition of 30% (w/v) NaCl. Extractions were performed at 65°C via headspace SPME-GC/MS. Prior to the analysis, blank extractions were performed to ensure no analyte was present in the sample matrix. As shown in Table 3, the relative recoveries of the PCBs from ocean water ranged from 89.7 to 136.1%, 61.2 to 115.6%, and 76.0 to 135.7% for the PDMS, PIL 1, and PIL 2 fibers, respectively. The proposed method proves to be highly applicable in real-water matrixes as the concentration of PCBs chosen (in parts-per-trillion range) approaches the actual concentrations of PCBs found in various water sources [32].

Various experimental parameters were modified in the extraction of bovine milk samples. Unlike ocean water, bovine milk contains proteins, carbohydrates, and lipids which can severely

Table 3

Relative recoveries of all PCBs from ocean water using selected SPME sorbent coatings. An analyte concentration of 30 ng L^{-1} was chosen for the analysis using HS-SPME GC/MS. (–) Data not available.

PCB	PIL 1	PIL 2	PDMS
8	–	109 ± 14	120 ± 16
18	61.9 ± 9.5	117 ± 6.6	99.0 ± 22
28	72.9 ± 21	113 ± 6.5	93.2 ± 13
52	61.2 ± 27	116 ± 11	101 ± 17
44	79.1 ± 13	110 ± 11	105 ± 10
66	74.1 ± 17	99.1 ± 14	97.8 ± 8.5
101	80.2 ± 16	98.1 ± 15	93.8 ± 11
77	68.1 ± 22	76.0 ± 15	113 ± 10
118	76.5 ± 21	78.7 ± 15	98.3 ± 14
153	81.1 ± 16	80.1 ± 14	103 ± 14
108	77.4 ± 9.3	87.7 ± 14	89.7 ± 19
138	84.5 ± 12	81.8 ± 15	102 ± 18
126	95.7 ± 6.7	78.9 ± 13	136 ± 19
187	82.9 ± 15	136 ± 12	113 ± 17
128	87.8 ± 7.8	125 ± 16	121 ± 17
201	–	124 ± 11	111 ± 20
180	–	114 ± 18	117 ± 20
170	97.3 ± 17	115 ± 9.0	119 ± 19
195	106 ± 2.3	114 ± 19	120 ± 21
206	106 ± 18	109 ± 15	125 ± 19
209	116 ± 14.9	112 ± 14	125 ± 18

interfere with analysis. In an effort to decrease the effects of matrix interference [33] as well as increase the extraction efficiency of the PCBs, milk samples were diluted with de-ionized water at a 1:1 (v:v) ratio. Furthermore, agitation using a Teflon-coated stir bar was employed to ensure thorough mixing of the sample components during extraction and to also prevent coagulation of the milk samples. Finally, 4% methanol (v/v) was added to sample solution to minimize any non-specific analyte adsorption to the sampling vial wall [18]. Samples were prepared by spiking 15 or $60 \mu\text{g L}^{-1}$ of PCBs into a 20 mL sample vial containing 10 mL of the milk/water mixture with the addition of 20% (w/v) NaCl. It should be noted that 20% (w/v) NaCl was added instead of the optimized concentration of 30% (w/v) in order to ensure complete solubility of the salt in the milk/water matrix. Headspace SPME was performed under agitation at 65°C with ECD detection. As shown in Table 4, the relative recoveries of most PCBs from the milk/water mixture were in acceptable ranges for all three coatings at a spiking concentration of $60 \mu\text{g L}^{-1}$. The recovery of all PCBs at this concentration ranged from 81.9 to 110.4%, 96.7 to 132.5%, and 89.3 to 120.2% for the PDMS, PIL 1, and PIL 2 coatings, respectively. It is also interesting to note that recoveries could not be determined for congeners 201–209 using the PDMS coating since this spiking concentration exceeded the linear range of this fiber. At the lower spiking concentration ($15 \mu\text{g L}^{-1}$), the PDMS coating produced much better recoveries. The recoveries ranged

Table 4

Relative recoveries of all PCBs from bovine milk using selected SPME sorbent coatings. Analyte concentrations of 15 and 60 $\mu\text{g L}^{-1}$ were chosen for the analysis using HS-SPME GC/ECD. (–) Data not available.

PCB	PIL 1		PIL 2		PDMS	
	15 $\mu\text{g/L}$	60 $\mu\text{g/L}$	15 $\mu\text{g/L}$	60 $\mu\text{g/L}$	15 $\mu\text{g/L}$	60 $\mu\text{g/L}$
8	87.3 ± 1.1	103 ± 10	121 ± 15	97.3 ± 8.2	106 ± 8.6	95.7 ± 6.9
18	95.6 ± 2.6	102 ± 6.7	138 ± 18	94.8 ± 7.2	104 ± 8.6	85.0 ± 4.7
28	102 ± 13	100 ± 2.9	135 ± 24	92.5 ± 3.6	105 ± 13	101 ± 21
52	113 ± 12	100 ± 12	123 ± 23	94.5 ± 1.5	107 ± 6.8	93.2 ± 8.7
44	101 ± 10	101 ± 10	133 ± 4.6	91.5 ± 1.6	101 ± 8.6	99.9 ± 17
66	118 ± 17	99.9 ± 13	117 ± 27	91.4 ± 5.5	114 ± 11	110 ± 21
101	99.7 ± 13	102 ± 11	114 ± 26	89.3 ± 5.6	110 ± 8.1	99.6 ± 9.3
77	125 ± 22	96.7 ± 12	107 ± 22	106 ± 4.8	111 ± 16	97.2 ± 18
118	68.9 ± 13	100 ± 16	121 ± 13	101 ± 2.7	114 ± 18	96.0 ± 14
153	115 ± 25	99.9 ± 23	94.6 ± 16	99.5 ± 2.6	105 ± 21	83.0 ± 17
108	108 ± 21	99.2 ± 19	87.6 ± 11	105 ± 3.5	109 ± 17	85.9 ± 15
138	115 ± 23	99.1 ± 19	84.1 ± 13	95.8 ± 4.6	119 ± 22	81.9 ± 17
126	131 ± 18	97.4 ± 11	73.6 ± 6.3	115 ± 11	107 ± 13	101 ± 18
187	111 ± 25	115 ± 13	99.9 ± 11	101 ± 4.6	94.3 ± 17	78.8 ± 19
128	124 ± 20	99.0 ± 16	60.4 ± 5.0	101 ± 8.6	110 ± 11	85.1 ± 16
201	117 ± 8.8	98.8 ± 22	91.6 ± 8.7	120 ± 10	118 ± 9.0	–
180	121 ± 7.5	112 ± 15	91.9 ± 13	97.9 ± 8.1	119 ± 10	–
170	105 ± 6.6	116 ± 15	78.9 ± 7.4	96.9 ± 8.8	121 ± 6.4	–
195	105 ± 11	133 ± 11	89.7 ± 4.8	99.2 ± 11	122 ± 7.1	–
206	91.7 ± 7.6	104 ± 13	101 ± 3.8	93.4 ± 9.7	117 ± 16	–
209	92.5 ± 4.0	115 ± 8.8	–	104 ± 7.4	109 ± 15	–

from 94.3 to 121.6%, 68.9 to 131.1%, and 60.4 to 138.4% for the PDMS, PIL 1, and PIL 2 coatings, respectively.

4. Conclusions

The successful application of HS-SPME using crosslinked PIL-based sorbent coatings was demonstrated for the extraction of PCBs from water and bovine milk samples. The crosslinking of the IL monomer significantly increased the structural integrity and thermal stability of the PIL-based sorbent coating making it applicable to more complex matrixes. The crosslinked PIL-based SPME fibers proved to be superior in terms of sensitivity and exhibited comparable LODs to the commercial PDMS fiber, despite possessing lower film thicknesses. The enhanced selectivity towards PCBs exhibited by the PIL-based coatings can be partly attributed to π - π interactions due to the introduction of aromatic moieties to the IL monomer and IL crosslinker. The LODs for PCBs in aqueous samples were found to be in the ng L^{-1} range using ECD and MS detection. Recovery studies in both environmental and complex biological matrixes were in acceptable ranges. Based on this work, the benzyl-functionalized crosslinked PIL-based SPME coatings have proven to be useful sorbent coatings in the analysis of higher boiling compounds. Future investigations into the robustness of the SPME sorbent coatings will be explored by examining the extraction performance within biological samples to aim for a broader range of analytical applications.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.talanta.2013.10.014>.

References

- [1] S. Harrad, E. Goosey, J. Desborough, M.A.-E. Abdallah, L. Roosens, A. Covaci, *Environ. Sci. Technol.* 44 (2010) 4198–4202.
- [2] R. Risebrough, P. Rieche, *Nature* 220 (1968) 1098–1102.
- [3] S. Safe, *Environ. Health Perspect.* 100 (1993) 259–268.
- [4] C. Koopman-Esseboom, D.C. Morse, N. Weisglas-Kuperus, L. LutkeSchipholt, C.V. Paauw, L. Tuinstra, A. Brouwer, P.J. Sauer, *Pediatr. Res.* 36 (1994) 468–473.
- [5] B. Ahling, S. Jensen, *Anal. Chem.* 42 (1970) 1483–1486.
- [6] P. Musty, G. Nickless, *J. Chromatogr. A* 89 (1974) 185–190.
- [7] C.L. Arthur, J. Pawliszyn, *Anal. Chem.* 62 (1990) 2145–2148.
- [8] D.W. Potter, J. Pawliszyn, *Environ. Sci. Technol.* 28 (1994) 298–305.
- [9] M. Llompart, K. Li, M. Fingas, *Anal. Chem.* 70 (1998) 2510–2515.
- [10] M. Polo, G. Gómez-Noya, J. Quintana, M. Llompart, C. Garcia-Jares, R. Cela, *Anal. Chem.* 76 (2004) 1054–1062.
- [11] Y. Yang, D.J. Miller, S.B. Hawthorne, *J. Chromatogr. A* 800 (1998) 257–266.
- [12] Y. Wang, Y. Li, J. Zhang, S. Xu, S. Yang, C. Sun, *Anal. Chim. Acta* 646 (2009) 78–84.
- [13] R. López, F. Goñi, A. Etxandia, E. Millán, *J. Chromatogr., B: Anal. Technol. Biomed. Life Sci.* 846 (2007) 298–305.
- [14] C. Basheer, H.K. Lee, J.P. Obbard, *J. Chromatogr. A* 1022 (2004) 161–169.
- [15] C.H. Kowalski, J.G. Costa, H.T. Godoya, F. Augusto, *J. Braz. Chem. Soc.* 21 (2010) 502–509.
- [16] C.H. Kowalski, G.A. Silva, R.J. Poppi, H.T. Godoy, F. Augusto, *Anal. Chim. Acta* 585 (2007) 66–75.
- [17] S.B. Hawthorne, C.B. Grabanski, K.J. Hageman, D.J. Miller, *J. Chromatogr. A* 814 (1998) 151–160.
- [18] M.R. Criado, I.R. Pereiro, R.C. Torrijos, *Talanta* 63 (2004) 533–540.
- [19] M.D. Joshi, J.L. Anderson, *RSC Adv.* 2 (2012) 5470–5484.
- [20] X. Han, D.W. Armstrong, *Acc. Chem. Res.* 40 (2007) 1079–1086.
- [21] F. Zhao, Y. Meng, J.L. Anderson, *J. Chromatogr. A* 1208 (2008) 1–9.
- [22] Y. Meng, V. Pino, J.L. Anderson, *Anal. Chim. Acta* 687 (2011) 141–149.
- [23] T.D. Ho, A.J. Canestraro, J.L. Anderson, *Anal. Chim. Acta* 695 (2011) 18–43.
- [24] T.D. Ho, H. Yu, W.T. Cole, J.L. Anderson, *Anal. Chem.* 84 (2012) 9520–9528.
- [25] J.L. Anderson, R. Ding, A. Ellern, D.W. Armstrong, *J. Am. Chem. Soc.* 127 (2005) 593–604.
- [26] J.L. Anderson, D.W. Armstrong, *Anal. Chem.* 77 (2005) 6453–6462.
- [27] H. Lord, J. Pawliszyn, *J. Chromatogr. A* 885 (2000) 153–193.
- [28] Y. Meng, J.L. Anderson, *J. Chromatogr. A* 1217 (2010) 6143–6152.
- [29] A. Steffen, J. Pawliszyn, *J. Agric. Food Chem.* 44 (1996) 2187–2193.
- [30] Y.Y. Shu, S.S. Wang, M. Tardif, Y. Huang, *J. Chromatogr. A* 1008 (2003) 1–12.
- [31] J. López-Darias, V. Pino, M. Yunjing, J.L. Anderson, A.M. Afonso, *J. Chromatogr. A* 1217 (2010) 7189–7197.
- [32] N.L. Howell, M.P. Suarez, H.S. Rifai, L. Koenig, *Chemosphere* 70 (2008) 593–606.
- [33] M. Fernandez-Alvarez, M. Llompart, J.P. Lamas, M. Lores, C. Garcia-Jares, R. Cela, T. Dagnac, *Anal. Chim. Acta* 617 (2008) 37–50.