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Solid-phase microextraction of polychlorinated biphenyls

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Abstract

The extraction and analysis of 21 polychlorinated biphenyls (PCBs) ranging from di- to decachlorobiphenyls in ocean, wetland and leachate water samples were achieved using solid-phase microextraction (SPME) with a 100-μm poly(dimethylsiloxane) (PDMS) fiber and gas chromatography–electron-capture detection (GC–ECD). Severe carryover between samples (e.g., 20%) occurs on both stir bars and the SPME fibers demonstrating that it is important to use a new stir bar for each sample, as well as to perform SPME–GC blanks between samples to avoid quantitative errors. The equilibrium partitioning coefficients of individual PCB congeners between PDMS and water were found to be surprisingly different compared to their octanol–water partitioning coefficient (K_{ow}), demonstrating that K_{ow} cannot be used to estimate the partitioning behavior of PCBs in the SPME process. Using a 15-min SPME extraction, SPME analysis with GC–ECD was linear ($r^2 \geq 0.97$) from ~5 pg/ml to the solubility limit of each congener. Concentrations in water samples obtained by 15-min SPME extractions compared favorably with those obtained by toluene extractions, demonstrating that SPME combined with GC is a useful technique for the rapid determination of PCBs in water samples. © 1998 Elsevier Science B.V.

Keywords: Extraction methods; Water analysis; Environmental analysis; Solid-phase microextraction; Polychlorinated biphenyls

1. Introduction

Polychlorinated biphenyls (PCBs) are widely distributed in the environment, even though the production of PCBs was forbidden many years ago [1,2]. There are two main methods for the extraction of PCBs from water samples: liquid–liquid extraction and solid-phase extraction (SPE). Unfortunately, both methods suffer from several problems. Liquid–liquid extraction is time-consuming and uses large volumes of organic solvents that must be disposed of properly. While SPE reduces the amount of organic solvents used, there are still drawbacks to this method including plugging, channeling and large sample sizes used [3–5].

Solid-phase microextraction (SPME), a relatively-new extraction technique, uses a syringe-mounted fused-silica rod (fiber) coated by an absorptive organic phase (e.g., polydimethylsiloxane) with thicknesses ranging from 7 to 100 μm. Analytes are sorbed from water samples based on partitioning between the water and the organic phase. After

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SPME extraction, the analytes can be thermally desorbed inside a heated gas chromatographic injection port and analyzed directly by gas chromatography (GC) [6–14]. Because of its unique characteristics, SPME has the potential to overcome the problems associated with liquid–liquid and solid-phase extraction of organic compounds from water samples. For example, SPME completely eliminates the use of organic solvents compared to liquid–liquid extraction and, as an equilibrium technique, does not experience breakthrough, plugging and channeling that are often encountered during SPE.

To date, the application of SPME has focused mainly on relatively volatile analytes [9,11,13,15]. Although there are recent reports on the application of SPME for semivolatiles including polycyclic aromatic hydrocarbons (PAHs) [14,16,17] and two PCB congeners [17], no studies on the SPME extraction of water samples contaminated with environmentally-relevant PCB mixtures have been reported. In this work, the problems that were encountered during the SPME extraction and analysis of PCBs in water samples will be discussed, along with their solutions. Under ''problem-free'' SPME conditions, the sorption rate, desorption time, partitioning coefficients, linear range and the determination of PCBs from surface waters using SPME are reported.

2. Experimental

2.1. PCB standards

A mixture of 21 PCB congeners ranging from di- to decachlorobiphenyls in acetone (AccuStandard, New Haven, CT, USA) was used as PCB standards for this study (Table 1). The concentration of the stock solution was 100 μg/ml for each individual PCB congener. Aroclor 1254 (Chem Service, West Chester, PA, USA) was also used for the study of SPME fiber carryover and sorption rates.

2.2. Water samples

Three water samples were used in this study: ocean water, wetland water and leachate water from PCB-contaminated soil. The ocean water was collected near Cape May (NJ, USA) near the end of a public pier. The wetland water was collected in a shallow waterfowl production area near Larimore (ND, USA). The leachate water was obtained by suspending 40 g of a PCB contaminated soil (collected from an industrial site) in 1 l of water at room temperature for a week. The suspended solids were ~3% (w/w) (including salt), 0.16% and 0.06% for the ocean, wetland and leachate water, respectively.

Table 1
Full names of the PCB standards used in this study

IUPAC No.	Congener
PCB-8	2,4′-dichlorobiphenyl
PCB-18	2,2′,5-trichlorobiphenyl
PCB-28	2,4,4′-trichlorobiphenyl
PCB-52	2,2′,5,5′-tetrachlorobiphenyl
PCB-44	2,2′,3,5′-tetrachlorobiphenyl
PCB-66	2,3′,4,4′-tetrachlorobiphenyl
PCB-101	2,2′,4,5,5′-pentachlorobiphenyl
PCB-77	3,3′,4,4′-tetrachlorobiphenyl
PCB-118	2,3′,4,4′,5-pentachlorobiphenyl
PCB-153	2,2′,4,4′,5,5′-hexachlorobiphenyl
PCB-105	2,3,3′,4,4′-pentachlorobiphenyl
PCB-138	2,2′,3,4,4′,5′-hexachlorobiphenyl
PCB-126	3,3′,4,4′,5-pentachlorobiphenyl
PCB-187	2,2′,3,4′,5,5′,6-heptachlorobiphenyl
PCB-128	2,2′,3,3′,4,4′,-hexachlorobiphenyl
PCB-201	2,2′,3,3′,4,5′,6,6′-octachlorobiphenyl
PCB-180	2,2′,3,4,4′,5,5′-heptachlorobiphenyl
PCB-170	2,2′,3,3′,4,4′,5-heptachlorobiphenyl
PCB-195	2,2′,3,3′,4,4′,5,6-octachlorobiphenyl
PCB-206	2,2′,3,3′,4,4′,5,5′,6-nonachlorobiphenyl
PCB-209	2,2′,3,3′,4,4′,5,5′,6,6′-decachlorobiphenyl

2.3. SPME and GC–electron-capture detection (ECD) analysis

Each water sample was loaded into a 2-ml silanized GC autosampler vial with a PTFE-lined septum cap. As reported in the literature [16,17], glass vessels can adsorb hydrophobic organic compounds from water samples. Therefore, all of the SPME extractions were performed using silanized vials in this study [16,17]. The glassware was silanized by soaking the glassware overnight in a 15% (v/v) mixture of dichlorodimethylsilane (Aldrich) in toluene. The silanized glassware was rinsed in toluene and methanol and oven-dried for 1 h at 150°C [12].

Commercially available 100- and 7-μm film thickness poly(dimethylsiloxane) (PDMS) fibers housed in manual holders (Supelco, Bellefonte, PA, USA) were used for the SPME extractions. The fiber was withdrawn inside the needle of the holder and the septum of the sample vial was pierced with the needle. Once the needle had penetrated the septum of the vial, the plunger on the fiber holder was depressed to expose the fiber to the water sample during the entire extraction time. The water sample was continuously agitated with a PTFE-coated magnetic stir bar (8 mm length×1.5 mm diameter) revolving at ~1000 rpm on a stir plate. Once the extraction period was completed, the fiber was retracted back inside the fiber holder, removed from the water sample, and analyzed immediately.

The extracted PCBs on the fiber were analyzed using a Hewlett-Packard 5890 Series II gas chromatograph equipped with a ^{63}Ni electron-capture detector. The column was a 25-m HP-5 with an internal diameter of 0.32 mm and a stationary phase thickness of 0.17 μm (Hewlett-Packard). Immediately after the SPME extraction, the fiber that was retracted inside the needle of the SPME holder was injected into the GC injection port. The plunger on the SPME holder was depressed to expose the fiber inside the 300°C split/splitless injection port in the splitless mode. A narrow-bore liner (2 mm I.D.) was used to improve peak shapes as previously described [12]. The extracted PCBs were thermally desorbed inside the injection port for 1 min (5 min for the studies of fiber carryover) and swept into the column by the carrier gas. The desorbed PCBs were trapped and focused at the column inlet by maintaining the oven at 60°C during the desorption. After the desorption, the fiber was withdrawn back into its holder and removed from the GC injection port. Once the desorption was completed, the split vent was opened and the GC run was started in the normal manner. The initial temperature (60°C) was ramped at 25°C/min to 130°C and then at 8°C/min to 320°C.

Details of the method used to determine SPME fiber–water partitioning coefficients (K_d) are given in Ref. [16]. In short, the GC–ECD response was calibrated by solvent injections of PCB standards into a cool on-column injector (to determine peak area per mass of each PCB congener injected). Based on these calibrations, the mass of each congener in the SPME fiber was determined from the ECD peak area. Since the mass of each congener in the spiked water samples used to determine K_d values are known, K_d values (i.e., the concentration of each congener in the SPME phase divided by its concentration in the water after equilibrium) are calculated from the mass of each PCB in the fiber (based on the ECD area), the mass of spiked PCB congener in the water standard (at equilibrium), and the fiber volume (0.612 and 0.026 μl for the 100- and 7-μm fibers, respectively).

2.4. Organic solvent extraction

The leachate water (35 ml) and toluene (5 ml) were loaded into a 40-ml vial, the internal standards (PCB-103 and PCB-169) were added to the vial, and the vial was mixed by a rotator for 30 min to extract the PCBs from the water into the toluene phase. After the extraction, the toluene phase was removed and the leachate water was extracted an additional two times using fresh toluene (without adding internal standards). All of the three toluene extracts were combined and were then concentrated by evaporating the toluene to ~300 μl. Analysis was done by GC–ECD with cool on-column injection.

3. Results and discussion

3.1. Carryover problems occurring with SPME of PCBs

During initial development of the SPME method for PCBs, two major sources of sample cross-contamination were encountered, i.e., carryover of PCBs on the stir bar, and incomplete desorption of the PCBs from used SPME fibers.

3.1.1. Stir bar contamination

Magnetic stir bars have mainly been used for sample agitation in manual SPME. However, stir bar contamination has not generally been investigated in the literature. In our initial studies, the stir bar was routinely cleaned by stirring in acetone inside an autosampler vial for 5 min before each SPME extraction. Unfortunately, we still experienced significant carryover of PCBs to subsequent blank water

samples. Apparently, the PCBs can be sorbed by the PTFE coating of the stir bar. Fig. 1 shows the GC–ECD chromatogram of a blank SPME (new water and vial) using a stir bar that had previously been used for the SPME extraction of a water sample spiked with 5 ng/ml of each PCB congener (PCB AccuStandard). Despite the 5 min acetone cleaning, up to 5% of the original PCBs were found in subsequent blanks. The stir bar contamination becomes serious when the PCB concentration varies from sample to sample. For example, if the PCB concentration is 100-times higher in sample 1 than that in sample 2, and the same stir bar is used for both samples, 5% carryover of stir bar contamination from sample 1 can result in a false result ~5 times higher than the actual concentration for sample 2.

Attempts to clean the contaminated stir bar included soaking the bar in acetone (using a stir plate) or sonicating the bar (in acetone) overnight. Neither of the methods was efficient enough to clean the contaminated stir bar, i.e., subsequent water blanks using these stir bars showed significant PCB contamination. Therefore, a new stir bar should be used for each water sample.

3.1.2. Incomplete desorption of PCBs from SPME fibers

A second problem in SPME extraction of PCBs is incomplete desorption during the GC injection. Both new and used fibers (used more than 30 times) were tested to determine the PCB carryover. After the 15-min SPME extraction of a water sample spiked

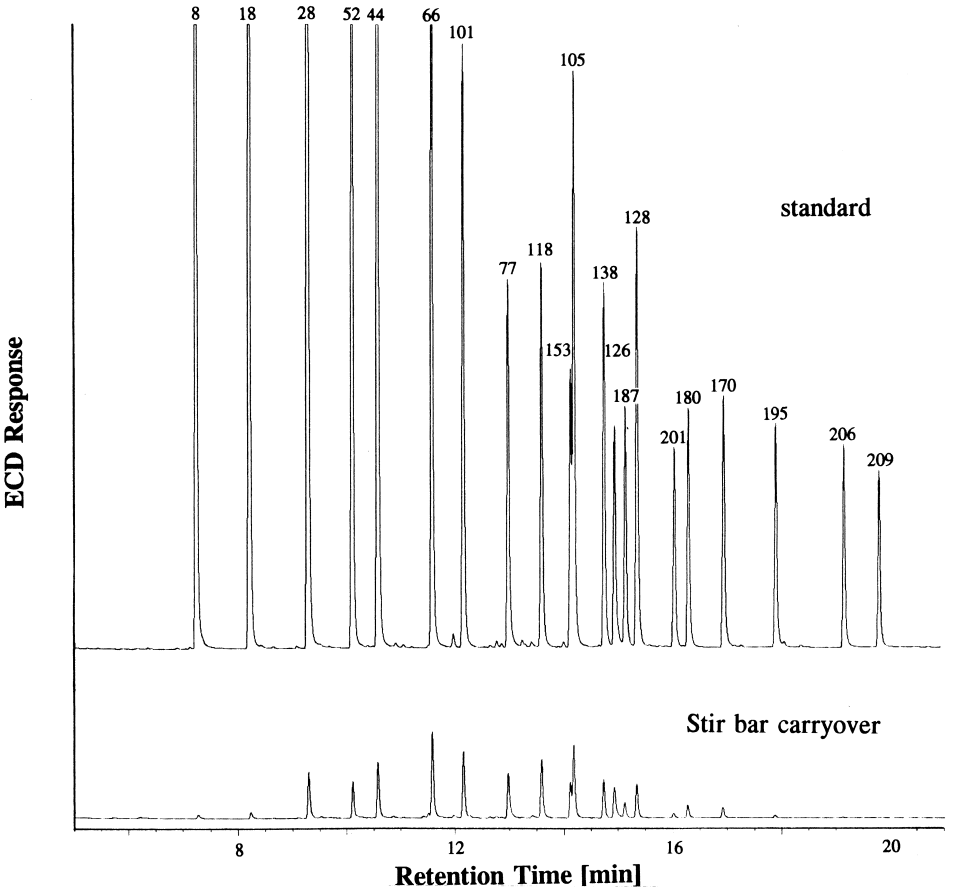

Fig. 1. GC–ECD chromatogram of a blank SPME extraction (bottom) using a stir bar contaminated by a previous SPME extraction of a PCB-spiked water sample (5 ng/ml, top). Peaks are identified by the PCB congener number.

with Aroclor 1254 (total PCBs: 3.75 ng/ml), the sorbed PCBs on a 100-μm fiber were thermally desorbed in the GC injection port for 1 min at 300°C and then analyzed by GC–ECD. After the GC run was completed, the same fiber was then heated again in the injection port for an additional 5 min to desorb the remaining PCBs in the fiber and the desorbed PCBs were analyzed by GC to determine carryover. As shown in Table 2, the fiber carryover is typically ≤3% for new 100-μm fibers demonstrating that a 1-min desorption is reasonably efficient to desorb PCBs from the new fiber. In contrast, the carryover is significantly higher (around 20%) for old fibers (used more 30 times) after the 1-min desorption. Even after a third 5-min desorption, there were still as much as 2–6% of the PCBs (versus the original concentration) desorbed from the old fibers. Although this degree of carryover seems quite high, these results are similar to a previous report where 9–23% of the sorbed PCBs still remained on a laboratory-made 15-μm thick PDMS fiber after the 1-min desorption time at 300°C [17].

Because the 100-μm fibers showed severe carryover problems as just discussed above, new and old 7-μm fibers were also used to determine the fiber carryover. The phase volume of the 100-μm fiber is much larger (23.5 times) than that of the 7-μm fiber, so the thermal desorption was expected to be more efficient for 7-μm than 100-μm fibers. However, the carryover was similar with 7-μm fibers compared to 100-μm fibers as shown in Table 2. The carryover is very low (typically ≤3%) for new 7-μm fibers and high (generally around 20%) for old 7-μm fibers (Table 2). Since 7-μm fibers do not have a lower carryover than 100-μm fibers and the capacity of the 100-μm is higher than that of the 7-μm fiber, the 100-μm fiber was used for the remainder of this study.

Table 2
Carryover of PCBs using new and used PDMS fibers

	% Carryover[a]			
	New fiber		Used fiber[b]	
	7 μm	100 μm	7 μm	100 μm
PCB-52	3±1	2±1	25±7	19±5
PCB-44	4±2	3±1	15±3	21±4
PCB-66	2±1	3±1	17±3	21±5
PCB-101	2±1	2±1	17±5	18±2
PCB-82	3±1	3±1	13±4	13±3
PCB-176	2±1	2±1	17±4	20±4
PCB-153	2±1	2±1	21±5	27±6
PCB-138	3±2	5±2	12±4	29±6

[a] Standard deviations are based on triplicate SPME–GC analyses.
[b] Used more than 30 times.

For new fibers, the low percentage of PCBs left on the fiber after the 1-min desorption could be removed by heating the fiber in the GC injection port for 10 min at 300°C before each SPME extraction. However, the same approach did not work well for old fibers. Therefore, once a fiber shows a significant PCB carryover (i.e., quantities of PCBs that would affect their determination in subsequent water samples) after the 1-min desorption, this fiber should not be used for SPME extractions of PCBs; otherwise, the carryover can result in serious error if the SPME extraction of a high-concentration sample is followed by the extraction of a low-concentration sample. This is especially critical in an automated SPME system if no blank extractions are performed between each sample to check the performance of the used fibers. Therefore, all of the fibers for the remainder of this study were cleaned for 10 min (in addition to the 1-min analytical desorption) at 300°C before each SPME extraction to eliminate fiber carryover. The 10-min cleaning step was performed in a separate GC injection port so that any additional PCBs or SPME degradation products would not go into the analytical column. Furthermore, SPME–GC blanks were performed between samples, especially with old fibers.

3.2. Sorption rate

The amount of PCBs sorbed by the fiber is a function of the absorption time. Once the fiber–water system reaches equilibrium, the absorbed amount will not increase by increasing the sorption time. To determine the sorption behavior, different extraction times (15 min, 5 h and 24 h) were used for SPME extractions of water samples spiked with 50 pg/ml of each congener (PCB AccuStandard). As shown in Fig. 2, the peak areas of PCBs are enhanced up to ~2.5-times by increasing the sorption time from 15 min to 5 h. Further increasing the sorption time from 5 to 24 h did not increase the peak areas of the absorbed PCBs, which demonstrates that the

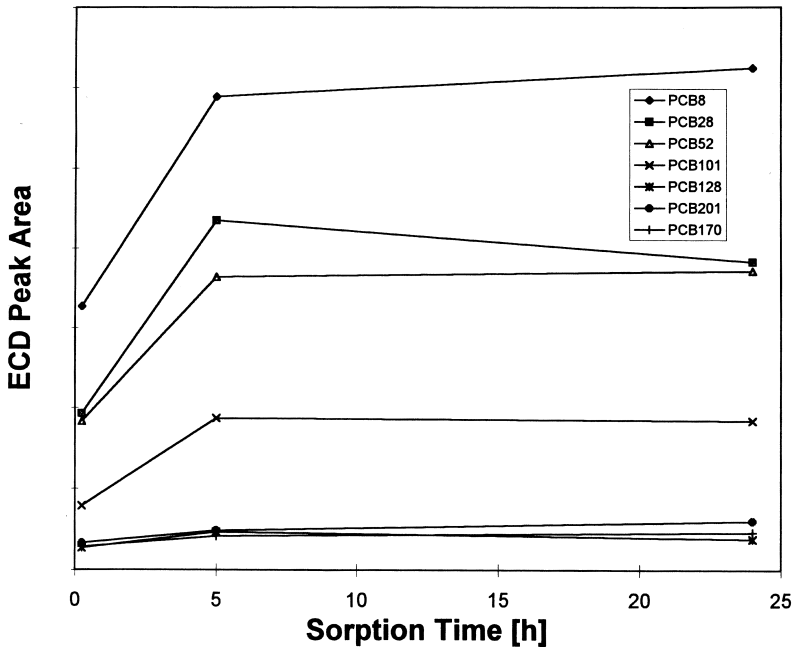

Fig. 2. Equilibration time profiles of PCBs from spiked water samples using a 100-μm PDMS fiber.

equilibration was achieved within 5 h for all of the 21 PCB congeners.

3.3. Equilibrium partitioning coefficients

Water samples spiked with the AccuStandard containing PCBs with three to 10 chlorines were used for the determination of SPME–water partitioning coefficients (K_d values). As discussed below, a concentration of 50 pg/ml for each individual PCB congener is well within the SPME linear range for all of the 21 congeners. Therefore, this concentration was used to determine the K_d values. Since the equilibrium between the PDMS and water was established within 5 h for all of the PCBs tested (Fig. 2), a SPME sampling time of 5 h was used for the determination of partitioning coefficients.

Table 3 shows the comparison of experimentally determined K_d values with literature values of octanol–water partitioning coefficients (K_{ow} values). Surprisingly, the K_d and K_{ow} values showed large disagreement (discussed below). The K_d values determined in this study were further confirmed by performing sequential SPME extractions and analyses on a single water sample. Table 4 shows the

Table 3
Experimentally determined SPME partitioning coefficients in comparison with reported values of K_{ow}

	K_d^a ($\cdot 10^{-3}$)	K_{ow} ($\cdot 10^{-3}$) [1,20]
PCB-8	11	210
PCB-18	10	440
PCB-28	8.7	550
PCB-52	7.3	1800
PCB-44	7.7	4700
PCB-66	8.5	4700
PCB-101	3.7	7100
PCB-77	8.3	3300
PCB-118	3.3	2500
PCB-153	2.5	28 000
PCB-105	3.1	
PCB-138	2.3	10 000
PCB-126	1.8	
PCB-187	1.5	
PCB-128	0.93	28 000
PCB-201	0.97	
PCB-180	0.87	
PCB-170	0.82	
PCB-195	0.51	
PCB-206	0.30	1 400 000
PCB-209	0.25	4 000 000

[a] The R.S.D.s of triplicate determination are typically 20%.

Table 4
Predicted and experimental PCB removal after two sequential 5-h extractions from a single HPLC-grade water standard

	% Removal of PCBs	
	Predicted[a]	Experimental[b]
PCB-8	95	92±14
PCB-18	94	88±11
PCB-28	92	88±19
PCB-52	90	84±17
PCB-44	91	84±14
PCB-66	92	88±16
PCB-101	78	71±11
PCB-77	92	84±14
PCB-118	75	70±17
PCB-153	68	66±15
PCB-105	74	66±14
PCB-138	65	66±15
PCB-126	59	64±11
PCB-187	54	52±11
PCB-128	40	42±12
PCB-201	40	43±3
PCB-180	38	43±8
PCB-170	36	38±1
PCB-195	25	27±7
PCB-206	16	16±4
PCB-209	14	12±2

[a] Predicted values were calculated using Eq. (1) and experimentally-determined values of K_d shown in Table 3.
[b] Standard deviations are based on triplicate SPME–GC determinations.

cumulative percent extracted after two sequential extractions from 2-ml water standards containing 50 pg/ml of each test PCB congener (each extraction was performed for 5 h), as well as the predicted values based on the equation below [16,17]:

$$n_f = K_d V_f V_{aq} C^0 / (K_d V_f + V_{aq}) \quad (1)$$

where n_f is the mass of analyte absorbed by the fiber, K_d is the fiber–water partitioning coefficient, V_f is the volume of the fiber coating, V_{aq} is the aqueous phase volume, and C^0 is the initial analyte concentration in the aqueous phase. In general, good agreement was obtained between the experimental and theoretical removal of each individual PCB congener demonstrating that the K_d values in Table 3 are valid.

Earlier investigators have reported strong correlation between K_{ow} and K_d values with PDMS sorbents [7,11,14,17,18]. These reports have used K_{ow} to predict K_d values for SPME–water equilibria [18]. However, Table 3 shows that the partitioning coefficients of PCBs between PDMS and water do not even remotely correlate with K_{ow} values. For the lowest molecular mass PCBs, K_{ow} and K_d values agree within an order of magnitude. However, the differences increase with the molecular mass to where K_{ow} and K_d disagree by eight orders of magnitude. As discussed above, increasing the sorption time from 5 to 24 h did not increase the PCB amount absorbed by the fiber, demonstrating that these K_d values were determined at equilibrium.

While the correlation between K_{ow} and K_d has often been reported for analytes such as benzene, toluene and xylenes [7,11,14,17,18], the phenomena of decreased K_d with increasing molecular mass of the analytes was also reported in the literature for both PAHs and PCBs, even though this issue was not discussed in these reports [16,17]. For example, the K_d of pyrene ($M_r = 202$) was reported to be 3.9-times higher than that of benzo[*a*]pyrene ($M_r = 252$) using a 100-μm PDMS fiber [16], despite the fact that the K_{ow} of pyrene is 58-times lower than that of benzo[*a*]pyrene [17,19]. Similarly, the K_d of PCB-18 ($M_r = 258$) was reported to be 1.1-times higher than that of the PCB-87 ($M_r = 326$) using a 15-μm PDMS fiber, although the K_{ow} of PCB-87 is 16-times higher than that of PCB-18 [17]. The contradictory relationship of K_{ow} with K_d seems to be associated with the molecular mass of the analytes. While good correlations between K_{ow} and K_d may exist for analytes with low molecular mass (e.g., <200 u) such as benzene, toluene and xylenes, there are either poor or no correlations between K_{ow} and K_d for the analytes with molecular masses greater than 200. Therefore, it appears that K_{ow} cannot be used to anticipate trends in SPME K_d values for analytes with higher molecular masses.

3.4. Quantitation of PCBs in water samples

Although the determination of K_d values requires long enough sorption time to establish equilibrium, quantitation can be performed with shorter sorption times as long as water calibration standards are analyzed using identical conditions. Since one GC run lasts ~26 min and SPME of a new sample can be performed simultaneously with GC analysis of a previous sample, a shorter SPME sampling time can

decrease the total time of the SPME–GC process. Therefore, a 15-min sampling time was used for all of the remaining SPME extractions.

3.4.1. Linear range and detection limit

The linearity of the SPME extraction was determined using water samples spiked with the AccuStandard. Individual congener concentrations in the water samples ranged from 5 pg/ml to 50 ng/ml. The SPME extraction time was 15 min for all determinations. Fig. 3 shows a SPME–GC–ECD chromatogram of a 2-ml water sample containing 5 pg/ml of each PCB congener. As shown in Fig. 3, the detection limit is easily less than 5 pg/ml for all of the tested congeners with a S/N ratio $>\sim 10/1$. Linearity ranged from 5 pg/ml up to the solubility limits of each individual PCB congener. For example, the linear ranges are 5 to 50 000 pg/ml for PCB-28 (water solubility of 85 000 pg/ml, Ref. [1]) with a r^2 of 0.99 and 5 to 500 pg/ml for PCB-209 (water solubility of 490 pg/ml, Ref. [1]) with a r^2 of 0.97. Therefore, the linear ranges of less chlorinated biphenyls is wider than those of highly chlorinated biphenyls since the highly chlorinated biphenyls have much lower water solubilities.

3.4.2. Analysis of PCBs in wetland and ocean water

Initial SPME analyses of the wetland and ocean water showed no detectable concentrations of PCBs, demonstrating that they were suitable for spike recovery studies. Both samples were spiked with the Accustandard to a concentration of 50 pg/ml of each congener. Quantitative calibrations were performed by SPME analysis of PCB-spiked HPLC-grade water. For the spiked water samples that were analyzed immediately after spiking, SPME determinations gave good agreement with the known values for both wetland and ocean waters, as shown in

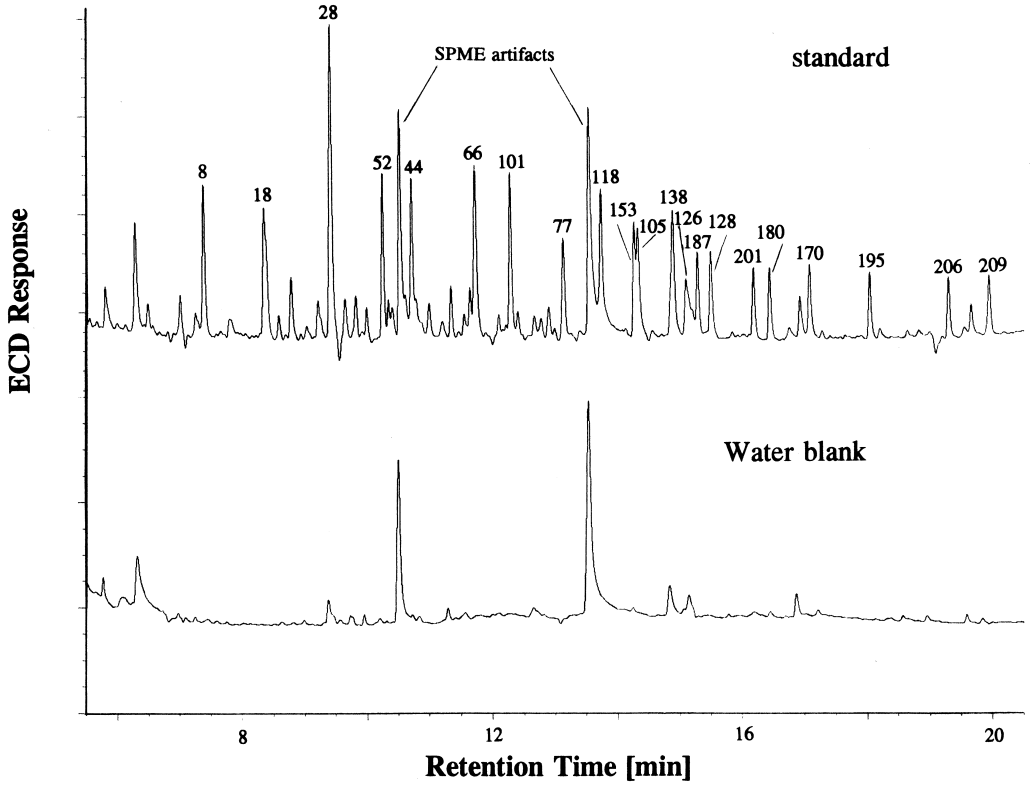

Fig. 3. SPME–GC–ECD chromatogram of a water sample containing 5 pg/ml for each individual PCB congener.

Table 5
SPME determinations of PCBs in different water samples

	Percent of known values[a] (% R.S.D.)[b]			
	Wetland water		Ocean water	
	Fresh spiked	Aging for 24 h after spiking	Fresh spiked	Aging for 24 h after spiking
PCB-8	106 (16)	86 (24)	113 (11)	98 (5)
PCB-18	102 (17)	72 (14)	116 (17)	99 (17)
PCB-28	117 (16)	80 (23)	110 (21)	95 (13)
PCB-52	107 (16)	62 (13)	115 (23)	65 (17)
PCB-44	99 (24)	63 (12)	99 (17)	71 (20)
PCB-66	89 (14)	48 (30)	87 (18)	68 (15)
PCB-101	101 (19)	45 (7)	101 (21)	64 (13)
PCB-77	114 (24)	42 (29)	102 (25)	70 (18)
PCB-118	96 (18)	66 (20)	113 (18)	69 (21)
PCB-153	103 (23)	78 (28)	97 (23)	85 (18)
PCB-105	113 (26)	57 (31)	117 (12)	62 (23)
PCB-138	109 (20)	55 (26)	104 (22)	67 (18)
PCB-126	115 (16)	80 (17)	87 (11)	97 (21)
PCB-187	111 (25)	76 (23)	107 (9)	83 (13)
PCB-128	111 (14)	60 (11)	99 (10)	85 (18)
PCB-201	101 (18)	57 (11)	103 (20)	80 (12)
PCB-180	97 (26)	83 (20)	101 (18)	79 (3)
PCB-170	102 (14)	77 (14)	94 (19)	89 (19)
PCB-195	98 (18)	47 (12)	95 (7)	74 (15)
PCB-206	86 (24)	59 (9)	95 (16)	77 (22)
PCB-209	89 (23)	68 (10)	101 (9)	76 (13)

[a] Concentration versus pure water standards prepared and stored in an identical manner.
[b] R.S.D.s based on triplicate SPME–GC analyses.

Table 5. However, when the spiked wetland and ocean water samples were stored for 24 h prior to analysis, PCB losses were substantial (up to ~50%, Table 5) from both surface waters, demonstrating that the existence of the suspended solids (ranging from 0.16 to 3%, respectively) can significantly influence the free PCB concentrations in water. Similar effects of suspended solids on PAH concentrations in surface waters have also been reported [16].

3.4.3. Analysis of PCBs in the leachate water of a contaminated soil

The PCBs in the leachate water of a contaminated soil were extracted using SPME for 15 min and the results were compared with those of multiple toluene extractions of replicate water samples. A calibration curve generated by 15-min SPME extractions of PCB-spiked (AccuStandard) HPLC-grade water with different concentrations was used for the quantitation of PCBs for the SPME determinations. The toluene extracts were analyzed by on-column injection and the quantitation of the PCBs was done by using a calibration curve made by on-column injections of the AccuStandard with different concentrations of

Table 6
PCB concentrations in a leachate water sample determined by SPME versus toluene extraction

	PCB concentration (ng/ml)[a]	
	SPME	Toluene extraction
PCB-66	1.03±0.13	1.06±0.18
PCB-101	0.75±0.04	0.80±0.11
PCB-77	1.37±0.16	1.34±0.21
PCB-118	0.98±0.12	0.83±0.03
PCB-153	2.26±0.25	2.73±0.36
PCB-138	1.69±0.22	1.44±0.17
PCB-126	0.43±0.04	0.54±0.08
PCB-201	0.74±0.07	0.92±0.18

[a] Standard deviations are based on the extraction and analysis of triplicate water samples for both SPME and toluene extractions.

target PCBs. As shown in Table 6, the PCB concentrations in the leachate water sample obtained by SPME extractions agree well with that obtained by toluene solvent extraction, demonstrating that 15-min SPME extractions are capable of obtaining good agreement with conventional organic solvent extractions.

4. Conclusions

SPME can yield good quantitative results for PCBs from surface water samples. However, significant cross-contamination between samples can occur, both from PTFE-coated stir bars and incomplete removal of PCBs from used fibers during thermal desorption. The use of new stir bars and frequent SPME blanks are required if multiple samples are analyzed. In contrast to previous reports of good agreement between K_{ow} and K_d for PDMS fibers with low-molecular-mass analytes, K_{ow} does not predict K_d behavior for PCBs, especially for high-molecular-mass congeners.

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