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# Solid-Phase Microextraction and Headspace Solid-Phase Microextraction for the Determination of Polychlorinated Biphenyls in Water Samples

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**A solid-phase microextraction (SPME) method has been developed for the quantification of polychlorinated biphenyls (PCBs) in water samples. Parameters such as sampling time, volume of water, volume of headspace, temperature, addition of salts, and agitation of the sample were studied. Because the time for reaching equilibrium between phases takes several hours or days, depending on the experimental conditions, it was necessary to work in nonequilibrium conditions to keep the sample analysis to a reasonable time. The possibility of sampling the headspace over the water sample (HSSPME), instead of immersing the fiber into the water (SPME), was also investigated, and despite the low partition of PCB into the headspace, HSSPME offered higher sensitivity than SPME at 100 °C. The adsorption kinetics for SPME at room temperature, SPME at 100 °C, and HSSPME at 100 °C were investigated and compared. The proposed HSSPME method exhibits excellent linearity and sensitivity. The detection limit was in the sub-ng/L level. This method has been applied to a real industrial harbor water and compared with liquid−liquid extraction. Both techniques offered similar results, but HSSPME was much more sensitive and considerably faster, by eliminating all the manual process intensive sample workup, and reduces solvent consumption entirely. The only drawback was that matrix effects were observed, but with the addition of deuterated surrogates to the sample or the use of a standard addition calibration, accurate quantification can be achieved.**

Recently, a new extraction technology called solid-phase microextraction (SPME) has been developed by Pawliszyn and co-workers.[1,2] SPME uses polymer-coated fibers to extract compounds from aqueous[3] or gaseous phase.[4] After extraction, the fiber is inserted directly into a heated GC injector, and the chemicals adsorbed on the polymer film are thermally desorbed and analyzed. This technique has also been applied to headspace sample analysis.[5,6] SPME has become popular in the past two or three years, especially in environmental analysis of volatile and semivolatile pollutants.[7−12]

In normal operation the fiber is exposed to the sample media until equilibrium is reached, but the time needed to reach the adsorption equilibrium between the sample and the polymer coating can be very long (several hours or even days). In these situations, shortening the adsorption time and working in nonequilibrium conditions are desirable, even though at the expense of sensitivity. Recently Ai[13,14] has developed a dynamic SPME model that indicates that even in nonequilibrium conditions a proportional relationship exists between the adsorbed analyte and its initial concentration in the sample matrix; this fact verifies that SPME quantitative analysis is feasible in nonequilibrium situations if the adsorption time is held constant.

Polychlorinated biphenyls (PCBs) are a class of compounds in which 1−10 chlorine atoms are attached to a biphenyl. PCBs were marketed under the tradename Aroclor from 1930 to 1977 for use in transformers, capacitors, printing inks, and other applications.[15] PCBs are classified as a probable human carcinogen, group B2, by the EPA. Currently, the two methods of choice for the extraction of this group of compounds from water are liquid−liquid extraction (LLE) or solid-phase extraction (SPE).

(1) Arthur, C. L.; Pawliszyn, J. *Anal. Chem.* **1990**, *62*, 2145−2148.
(2) Zhang, Z.; Yang, M. J.; Pawliszyn, J. *Anal. Chem.* **1994**, *66*, 844A−853A.
(3) Arthur, C. L.; Killam, L. M.; Motlagh, S.; Lim, M.; Potter, D. W.; Pawliszyn, J. *Environ. Sci. Technol.* **1992**, *26*, 979−983.
(4) Chai, M.; Pawliszyn, J. *Environ. Sci. Technol.* **1995**, *29*, 693−701.
(5) Zhang, Z.; Pawliszyn, J. *J. High Resolut. Chromatogr.* **1993**, 16, 689−692.
(6) Matich, A. J.; Rowan, D. D.; Banks, N. H. *Anal. Chem.* **1996**, *68*, 4114−4118.
(7) Buchholz, K. D.; Pawliszyn, J. *Anal. Chem.* **1994**, *66*, 160−167.
(8) Boyd-Boland, A. A.; Magdic, S.; Pawliszyn, J. *Analyst* **1996**, 121, 929−938.
(9) Lakso, H.; Ng, W. F. *Anal. Chem.* **1997**, *69*, 1866−1872.
(10) Choudhury, T. K.; Gerhardt, K. O.; Mawhinney, T. P. *Environ. Sci. Technol.* **1996**, *30*, 3259−3265.
(11) Wittkamp, B. L.; Hawthorne, S. B.; Tilotta, D. C. *Anal. Chem.* **1997**, *69*, 1204−1210.
(12) Poerschmann, J.; Zhang, Z.; Kopinke, F.-D.; Pawliszyn, J. *Anal. Chem.* **1997**, *69*, 597−600.
(13) Ai, J. *Anal. Chem.* **1997**, *69*, 1230−1236.
(14) Ai, J. *Anal. Chem.* **1997**, *69*, 3260−3266.
(15) Erickson, M. D. *Analytical Chemistry of PCBs*; Butterworths Publishers: Markham, ON, Canada, 1986; pp 15−23.



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Both techniques require the concentration/extraction of several liters of water. LLE also consumes large amounts of solvent and is labor intensive.[16] SPE requires only relatively small amounts of solvent to elute the sorption media but is prone to interference from impurities leached from the plastic housing of the sorbent cartridge. SPME, on the other hand, has none of the above-mentioned drawbacks because it is a solvent-free technology and combines extraction, concentration, and sample introduction in one step.

In this work, a HSSPME method for the determination of PCBs in water samples has been developed. Parameters affecting the adsorption of analyte into the fiber, such as sampling time, sample volume, headspace volume, and temperature, have been evaluated. The adsorption kinetics for SPME at room temperature, SPME at 100 °C, and HSSPME at 100 °C were compared. The proposed HSSPME method shows excellent linearity and sensitivity. This method was applied to a real contaminated water sample and compared with liquid−liquid extraction. Both techniques offered similar results, but HSSPME was found to be much more sensitive and faster, eliminating all the tedious process (use of solvents, concentration steps, drying and clean up of the extracts) that the liquid−liquid extraction of PCB requires.

## EXPERIMENTAL SECTION

**Reagents and Materials.** Analytical reference standard solutions of Aroclor 1254 and 1260 were obtained from Ultra Scientific (Don Mills, Ontario, Canada). The isotopically labeled surrogate PCB mixture (C-13 tetrachlorobiphenyl to heptachlorobiphenyl) was purchased from Cambridge Isotope Lab (Burlington, Ontario, Canada). All the solvents (analytical grade) were purchased from Caledon (Belleville, Canada). Natural water samples were collected from Hamilton Harbor, Ontario (lat. 43° 17′, longitude 79° 48′).

**Preparation of Water Samples.** Artificial water samples containing 800 ng/L Aroclor 1260 were prepared by adding a few microliters of Aroclor standard in acetone to 2 L of Milli-Q water. The sample was stirred for 3 days before the first extraction. Other water samples were prepared by dilution of this one.

**Analysis.** Analyses were carried out on a Hewlett-Packard HP5890 series II-HP/5971 MSD operated by a HP Chemstation software (G1034). Experimental parameters were as follows: column, HP-1, 0.2 mm id, 0.3 $\mu$m film; temperature program, 120 °C for 1 min heated to a final temperature of 310 °C at 10 °C/min and held at this temperature for 10 min; injector temperature, 260 °C, capillary interface temperature, 300 °C; MSD operated in selected ion monitoring (SIM) mode using single step acquisition monitoring ions; the autotune feature was selected, and the electron multiplier was set at a nominal value of 1400 V. Quantitative analysis of PCBs in Aroclor 1260 spiked water and in Hamilton Harbour water was performed by summing nine of the most abundant congeners recognizable in the chromatogram, corresponding to PCBs with five, six, and seven chlorine atoms.

**SPME and HSSPME Extraction Procedure.** A manual SPME holder was used with a 100 $\mu$m poly(dimethylsiloxane) fiber assembly (Supelco, Missisauga, Ontario). The volume of the polymer film was $6.1 \times 10^{-4}$ cm$^3$. An aliquot of 100 mL of water containing PCB was placed in a 120 mL vial. The vial was sealed with a headspace aluminum cap with a Teflon-faced septum. The fiber was immersed into the water (SPME) or exposed to the headspace over the water (HSSPME). For the experiments carried out at high temperature, the samples were immersed in a temperature-controlled water bath during the sampling process. The aqueous samples were agitated with a magnetic stirring bar during SPME experiments; during HSSPME experiments, the samples were not agitated. The adsorption time was 30 min. The fiber was then immediately inserted into the GC injector, and analysis was carried out. The desorption time was set at 5 min, and the desorption temperature was set at 260 °C. Reinserting the SPME fiber after the run did not show any carry over. Everyday before use, the SPME fiber was conditioned for 5−10 min at 260 °C. The analyte recoveries were determinated relative to the direct injection of the standards prepared in isooctane.

**Liquid−Liquid Extraction.** Extractions using a liquid−liquid extraction method were performed on a 1 L Hamilton Harbour water sample. A mixture of isotopically labeled surrogates (C-13 tetrachlorobiphenyl to heptachlorobiphenyl) was added to the sample just before the extraction. Extraction was carried out with a 50 mL aliquot of dichloromethane in a 1 L separatory funnel, and the process was repeated two more times with fresh solvent. The extracts were combined and, after the addition of 1 mL of isooctane, were evaporated to ∼1 mL using a rotavapor system. The extracts were filtered and dried over $Na_2SO_4$, and the solvent was changed to hexane. The extracts were again concentrated in the rotavapor system, and a florisil column chromatography cleanup was carried out. Finally the extracts were again concentrated using a rotavapor and nitrogen blow down to dryness. The extract was made up with 50 $\mu$L of isooctane. One microliter of the final extract was injected in the GC/MSD for analysis.

## RESULTS AND DISCUSSION

In the following discussion, Aroclor 1260 is treated as a single entity having nominal physical paramenters such as solubility, Henry's law constant, partition coefficients, etc. (This assumption is necessary for the sake of simplicity.) In reality, of course, Aroclor is made up of at least four isomers, each made up of many congeners.

**Extraction Time Profile.** The extraction time profile for Aroclor 1260 was established by plotting the detector response versus the extraction time. The sample volume was 2000 mL. The equilibrium is reached when a further increase of the extraction time does not result in a significant increase in the detector response. As can be seen in Figure 1 the adsorption of PCBs from the water into the fiber is a very slow process, and a sampling time of several days is necessary in order to reach the equilibrium. To be a viable analytical method and keep a reasonable sampling time, operation under nonequilibrium conditions is necessary. Recently, Ai[13] has proposed a dynamic model for the SPME adsorption process. One of the conclusions of this model is that the amount of analyte adsorbed into the fiber is proportional to the initial concentration in the sample matrix, once the agitation conditions and the sampling time are held constant, and hence, SPME quantization is feasible before adsorption equilibrium is reached. The data presented in Ai's paper were in good agreement with the model he proposes. In all of the rest of our studies, the sampling time was fixed at 30 min. The GC analysis is 25 min in duration, so a 30 min extraction time provides

(16) Maguire, R. J.; Tkacz, R. J. *Chemosphere* **1989**, 19, 1277−1287.

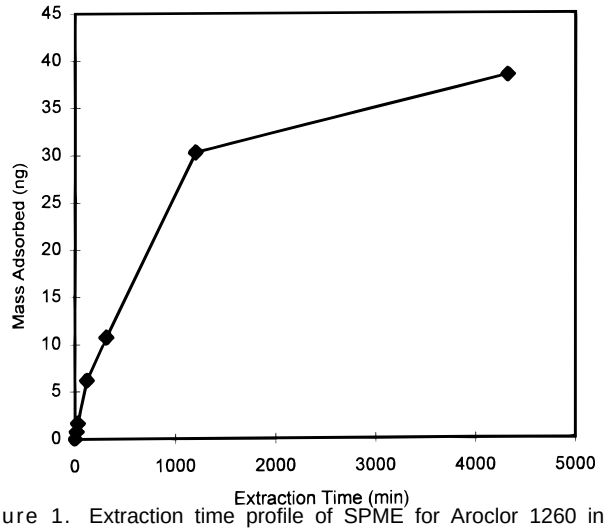


Figure 1. Extraction time profile of SPME for Aroclor 1260 in aqueous solution at room temperature (volume of water, 2000 mL; initial concentration, $C_o$, 800 ng/L).

optimum time utilization for the SPME method by ensuring that once the GC run is completed and the oven has cooled to the initial temperature, the next sample is ready for injection.

**Effect of Sample Volume.** We investigated the effect of the sample volume on the amount of analyte extracted from the sample into the SPME fiber. Sample volume is an important parameter affecting quantitative results, and contrary to a common belief, it is negligible only in few cases.

If the partition coefficient, $K$, is known, the effect of the sample volume in the partitioning of an analyte between the sample and the polymeric film on the fiber in the equilibrium can be predicted using the equation[17]

$$K = \frac{C_f}{C_s} = \frac{(n/V_f)}{C_o - (n/V_s)} \quad (1)$$

where $C_f$ is the concentration of the analyte in the SPME polymer film, $C_s$ concentration of the analyte in the sample matrix, $n$ is the amount of the analyte adsorbed by the SPME polymer film, $V_f$ is the volume of the SPME polymer film, $C_o$ is the initial concentration of the analyte in the sample matrix before SPME sampling, and $V_s$ is the volume of the sample matrix. Solving this equation for $n$,

$$n = \frac{KV_fV_s}{V_s + KV_f}C_o \quad (2)$$

This equation gives the relation between the amount of analyte adsorbed by the fiber and the volume of sample.

Figure 2a shows the influence of the sample volume on the amount of analyte adsorbed by a 100 $\mu$m fiber according to eq 2, assuming $K = 10^5$ ($C_o$ was considered to be 800 ng/L). The real value of $K$ for Aroclor 1260 is not known, but from the results obtained in the extraction time profile study (Figure 1), it appears to be very close to the assumed value. The response increases

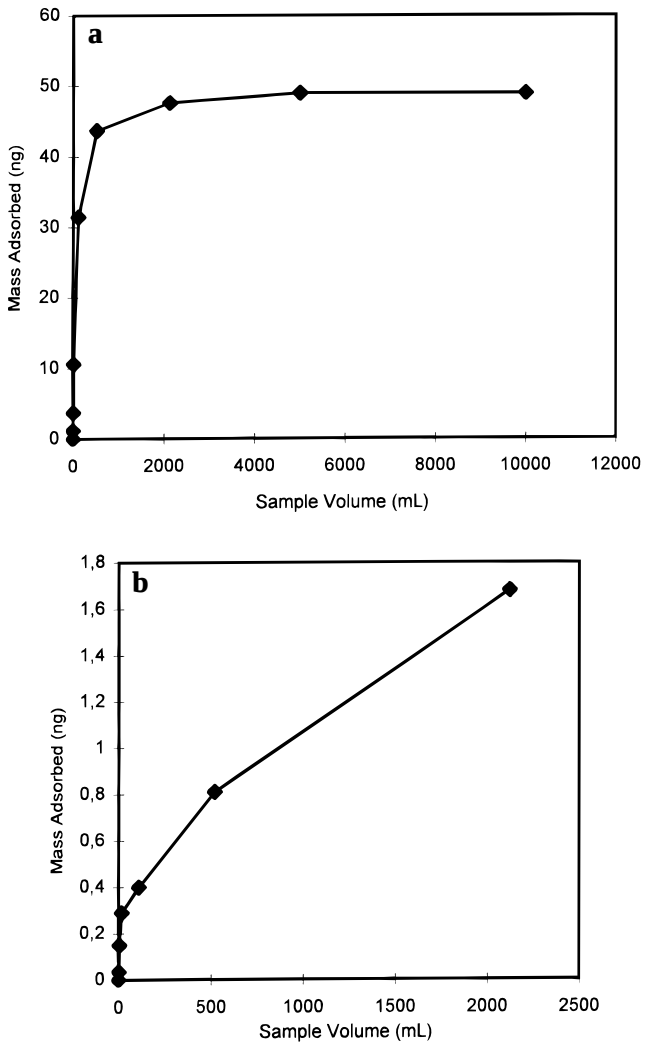


Figure 2. (a) Predicted effect of the water sample volume in the amount of analyte adsorbed by eq 2, assuming $K = 10^5$ (Initial concentration, $C_o$, 800 ng/L). (b) Experimental effect of the water sample volume in the amount of analyte adsorbed (initial concentration, $C_o$, 800 ng/L).

with the volume up to 5000 mL, and larger sample volumes than this do not produce any increase in the response. We carried out a series of experiments for a volume of sample between 1.5 and 2120 mL. The concentration of the water samples was 800 ng/L and the sampling time 30 min. All of the different volumes were investigated by analyzing duplicates. Despite our system being far from equilibrium, and despite sample volume effects on the kinetics of the process, the general behavior of the system (shown in Figure 2b) appears to be the same as the one predicted from eq 2, as shown in Figure 2a. The amount of analyte adsorbed into the fiber increased with sample volume in the range studied, although the effect of the volume was more significant for small sample volumes. If this study were extended to larger volumes, a point would be reached in which increasing the volume would not produce any increase in response.

**SPME and HSSPME. Temperature and Agitation Effect.** We investigated the possibility of sampling the headspace over the water sample (HSSPME) instead of immersing the fiber in the water (SPME). Also, the temperature effect was studied. In these experiments the volume of water ($V_s$) was 100 mL and the

(17) Louch, D.; Motlagh, S.; and Pawliszyn, J. *Anal. Chem.* **1992**, *64*, 1187–1199.

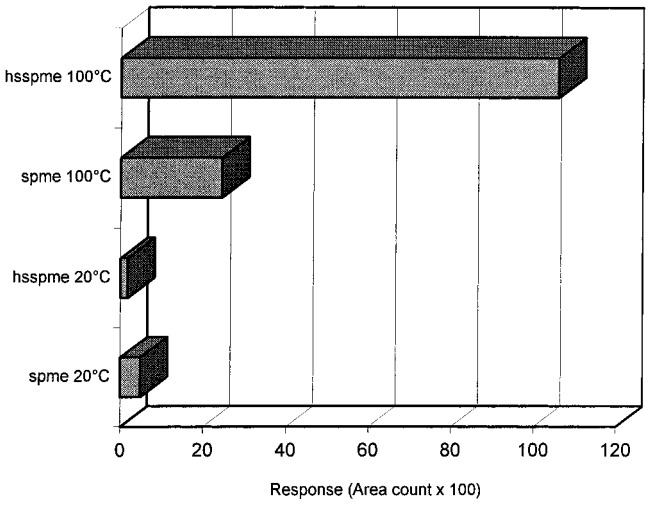


Figure 3. Comparison of responses, after 30 min extraction, for SPME and HSSPME at 20 and 100 °C ($C_o$ = 80 ng/L, $V_s$ = 100 mL, $V_g$ = 20 mL).

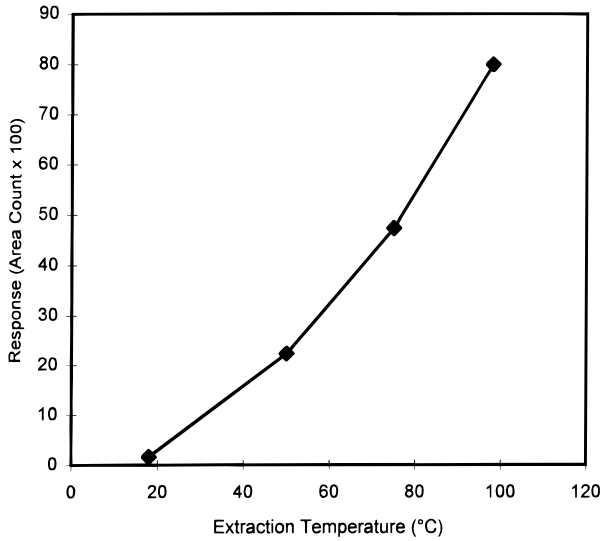


Figure 4. Effect of the temperature in the response obtained by HSSPME ($C_o$ = 80 ng/L, $V_s$ = 100 mL, $V_g$ = 20 mL).

volume of headspace ($V_g$) was 20 mL. The initial concentration of the water ($C_o$) was 80 ng/L. The results obtained are summarized in Figure 3. Despite the low vapor pressure of Aroclor 1260 ($4.0 \times 10^{-5}$ Torr at 25 °C),[18] HSSPME was shown to be a viable technique for the determination of PCBs in water, even at room temperature (~20 °C), although the response obtained with SPME was 3 times higher. At 100 °C the responses obtained with SPME and HSSPME were higher than those at room temperature by a factor of 5 for SPME and by a factor of 60 for HSSPME. At 100 °C HSSPME response was considerably higher than SPME response. Working with HSSPME provides important advantages: not only does it give sensitivity 5 times higher than SPME but also, because the fiber is not in contact with the sampling medium, the background is much cleaner and the useful life of the fiber is prolonged.

It must be pointed out again that the system in all of these experiments is not in equilibrium. Increasing the temperature provides the system with more kinetic energy, speeding up mass transport so that the response obtained is higher. If the system were in equilibrium, higher temperatures would not give higher responses since adsorption is an exothermic process. Thus higher temperatures increase the response only in nonequilibrium situations. For HSSPME the effect of the temperature is more complex. At higher temperatures diffusion and mass transfer are accelerated, but probably the main reason for the increase in response is the increase in the concentration of analyte into the headspace. Increasing the temperature increases the Henry constant of Aroclor 1260, resulting in a higher analyte partial vapor pressure in the headspace. In summary, for HSSPME a higher temperature not only speeds up the kinetics of the process but also affects thermodynamics. Figure 4 shows the effect of the temperature in the HSSPME response. The increase in the response due to the temperature increase appears to be exponential.

The effect of sample agitation was also investigated for both techniques. In all of the previous experiments, the water was stirred in SPME and was not in HSSPME. Agitation has important repercussions on the kinetics. In these experiments $V_s$ was 100 mL, $V_g$ 20 mL, $C_o$ 80 ng/L, and the temperature 100 °C. The results, shown in Table 1, are the main of two replicates. For SPME work, diffusion through the water is usually the rate-controlling step in the SPME adsorption process. Stirring the system speeds up the equilibrium process, so the response obtained after 30 min sampling was higher (see Table 1). For HSSPME, stirring may be beneficial because it facilitates the mass transfer from the liquid to the gaseous phase. However, we have not observed that stirring affects significantly the response. Stirring did not produce any benefit, which suggests that the controlling step in this case is the diffusion of the analyte in the PDMS liquid coating of the SPME fiber.

Table 1. Effect of Agitation on the Response Obtained by SPME and HSSPME at 100 °C ($C_o$ = 80 ng/L, $V_s$ = 100 mL, $V_g$ = 20 mL)

| | response (area cts) | |
|---|---|---|
| | SPME | HSSPME |
| no stirring | 261 | 8515 |
| stirring | 2413 | 9724 |

**SPME and HSSPME. Extraction Time Profile.** We also studied the extraction time profile between 10 min and 7 h for SPME at room temperature, SPME at 100 °C, and HSSPME at 100 °C. The volume of water sample was 100 mL, and the volume of HS was 20 mL. Figure 5 shows the results obtained. SPME and HSSPME at 100 °C reached equilibrium in about 4 h. Even in equilibrium conditions the sensitivity obtained with HSSPME was superior to the sensitivity of SPME by a factor of 2, despite the concentration in the gas phase being much lower than that in the water. This indicates that $K$ is much higher between the vapor phase and the fiber than between the liquid phase and the fiber. SPME at room temperature was still far from equilibrium after 7 h of sampling. For SPME at room temperature we studied the extraction process up to 3 days (Figure 6). After 3 days of sampling, SPME at 20 °C reached the maximum response

(18) ATSDR. *Toxicological Profile for Selected PCBs* (Aroclor 1260, 1254, 1248, 1242, 1232, 1221, and 1216); Agency of Toxicological Substances and Disease Registry: Atlanta, GA, 1989 (ATSDR/TP-88/21).

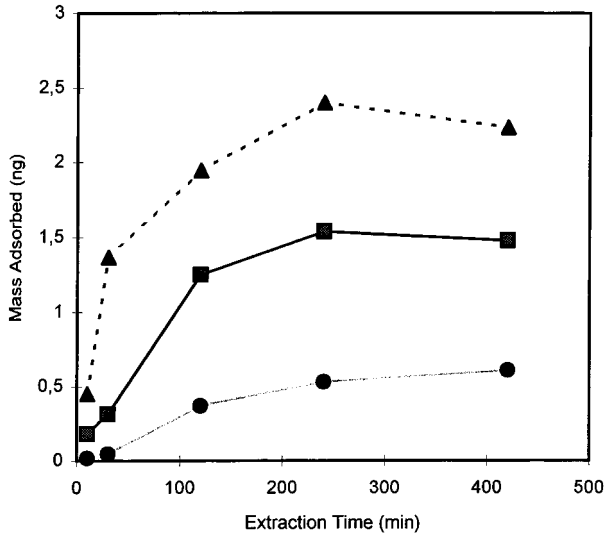


Figure 5. Extraction time profile: (●) SPME at room temperature, (■) SPME at 100 °C, and (▲) HSSPME at 100 °C ($C_o$ = 80 ng/L, $V_s$ = 100 mL, $V_g$ = 20 mL).

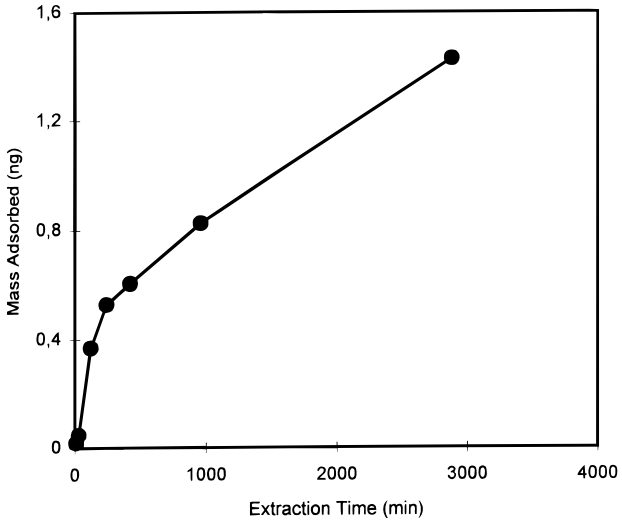


Figure 6. Extraction time profile for SPME at room temperature ($C_o$ = 80 ng/L, $V_s$ = 100 mL, $V_g$ = 20 mL).

(equilibrium response) obtained for SPME at 100 °C. The adsorption process at room temperature is very slow.

From these findings, we conclude the optimal procedure is to employ HSSPME at 100 °C without stirring the sample. The sampling time was constant at 30 min.

**HSSPME Volume Study.** The effect of headspace volume as well as the effect of the water sample volume was investigated. A set of experiments were done using 10 mL of water in different vials: a 22 mL vial with 2.0 cm diameter, a 40 mL vial with 2.6 cm diameter, and a 120 mL vial with 5.0 cm diameter. The HS volume was 12, 30, and 110 mL, respectively. The response obtained was similar in all of these situations.

Another set of experiments were done using a constant vial volume (120 mL) and increasing the volume of water between 10 and 110 mL. The volume of headspace over the water sample decreases with the increase of the water sample size. Results are shown in Figure 7. The response obtained increased with the water sample size.

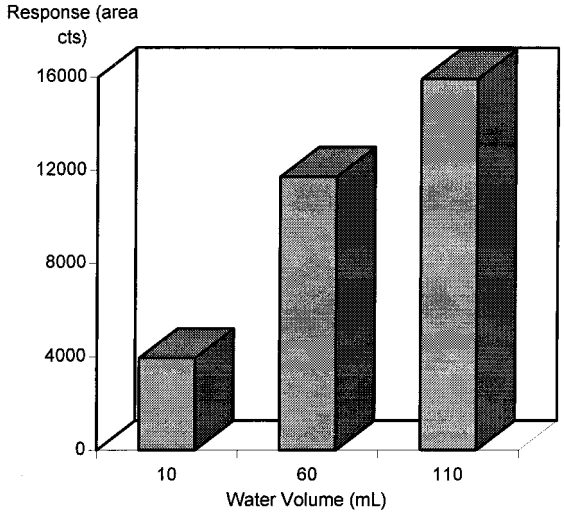


Figure 7. Effect of the volume of water in the response obtained by HSSPME at 100 °C ($C_o$ = 80 ng/L, $V_s$ = 100 mL, $V_g$ = 20 mL).

The effect of the phase volumes in a three-phase equilibrium system is very complex and is strongly dependent on the partition constants between the phases. If the system is not in equilibrium, this effect is even more complex because the kinetics of the process are also affected by the volumes of the phases. For a HSSPME partition equilibrium between sample headspace and polymeric film, the amount of analyte adsorbed is given by this equation[19]

$$n = \frac{K_1 K_2 V_f V_s}{K_1 K_2 V_f + K_1 V_g + V_s} C_o \qquad (3)$$

where $K_1$ is the equilibrium partition constant of the analyte between the headspace and the sample, $K_2$ the equilibrium partition constant of the analyte between the SPME polymer phase and the headspace, $V_f$ the volume of the SPME polymer film, $C_o$ the initial concentration of the analyte in the sample matrix before SPME sampling, $V_s$ the volume of the water sample, and $V_g$ the volume of the headspace.

In all of our experiments $V_f$, $C_o$, $K_1$, and $K_2$ were constant, and the difference in the responses obtained were due to the different headspace and water volumes. In the first set of experiments $V_s$ was constant (10 mL) and $V_g$ was between 10 and 110 mL. The values of $K_1$ and $K_2$ are not known, but $K_1$ must be very low due to the low vapor pressure of Aroclor 1260. Assuming $K_1 = 10^{-3}$ and solving eq 3 for HSSPME with the amount of the analyte adsorbed by the fiber in the equilibrium ($n$ = 2.4 ng for $C_o$ = 80 ng/L, $V_s$ = 100 mL, and $V_g$ = 20 mL, see Figure 5), the $K_2$ obtained is 5.4 × $10^7$. Solving the eq 3 for these values of $K_1$ and $K_2$, considering the experimental conditions of our first set of experiments, the response obtained does not change apreciably with the headspace volume between 10 and 110 mL. If $K_1$ were different from $10^{-3}$ but $\leq 10^{-2}$ the conclusion would be the same. These theoretical results agree with the experimental results. The experimental results point out again that the rate-controlling step in the kinetics of the HSSPME process is the diffusion of the analyte into the fiber and not the evaporation of the analytes from

(19) Zhang, Z.; Pawliszyn, J. *Anal. Chem.* **1993**, *65*, 1843−1850.

the water, because if the controlling step were the evaporation of the analyte, the results for our three experiments would be different, even if at equilibrium the three would give the same result. The experiment with larger contact surface between the water and the headspace would be the fastest experiment (faster evaporation rate) and the one that would give the highest response after 30 min. Solving eq 3 for $K_1 = 10^{-3}$ and $K_2 = 5.4 \times 10^7$, considering the volumes of headspace and water of our second set of experiments, we also obtained behavior similar to our real case.

**Effect of the Addition of Salts.** The effect of the addition of KCl to the sample was studied. Water samples were saturated with KCl before extraction. Also, artificial seawater was prepared by adding a salt seawater mix in adequate proportion. The response obtained was the same in all these experiments; the addition of salts did not produced any change in the response obtained in HSSPME.

**Linearity, Precision, and Sensitivity Study.** To evaluate the linearity of the HSSPME method a calibration study was performed by spiking deionized water with Aroclor 1260 to give 1.6, 8, 24, 80, and 240 ng/L. The five-point calibration curve was found to have good linearity characterized by a correlation coefficient of 0.999.

The precision of the experimental procedure was also evaluated at two different concentration levels (1.6 and 80 ng/L) and was found to give a relative standard deviation (RSD) of about 5%, even for concentration levels as low as 1.6 ng/L. The number of replicates for each level was 5. To check uniformity in response of different fibers, three fibers from different lots were conditioned and the experiment was repeated. The RSD between fibers was on the same order as the ones obtained using the same fiber for all the extractions.

The detection and quantification limits (signal-to-noise ratio = 3 and 10) were 0.3 and 1.0 ng/L, respectively.

**Application of the Method to a Real Sample. HSSPME versus Liquid−Liquid Extraction.** Since there is no reference PCB-contaminated water commercially available, we have sought to locate a naturally contaminated water sample that has been well characterized so that a comparison could be made. The location we have chosen was from Hamilton Harbour, Hamilton, Ontario. The harbor receives industrial discharge from the heavy industry (steel-making) in Hamilton, and supports active shipping. This water body has also been studied extensively in other research.[20]

Preliminary analysis of this water revealed matrix interferences: response of surrogates was considerably lower than in Milli-Q water. For this reason, the method of standard additions was used to quantify the sample. A four-point calibration was performed by adding Aroclor 1254 between 0 and 8 ng/L. The resulting calibration curve was linear with a correlation coefficient of 0.999. The final PCB concentration obtained was 4.6 ng/L with a 10.2% RSD ($n = 3$). This value is within the range 2−24 ng/L PCB reported by other researchers between 1988 and 1994.[20] Considering the seasonal variation and differences of the sampling location, the agreement was considered remarkable.

In addition, we have also carried out a liquid−liquid extraction in triplicate and found 4.1 ng/L PCB with a 9.1% RSD ($n = 3$).

During the course of this study, the sample, in a 4 L amber solvent bottle, was continuosly stirred at room temperature. Measurement using HSSPME over a 1 week period did not show any variation despite the fact that no preservative was added to the water, and the reproducibility of the method was characterized at 10% RSD.

## CONCLUSIONS

SPME and HSSPME have proven to be very suitable techniques for the determination of PCBs in water samples. Because the equilibrium between phases takes up to several hours, one needs to work in nonequilibrium conditions to keep sampling time reasonably short. Due to the high affinity of PCBs for the PDMS fiber, which exhibits very high sensitivity, the loss in response is not a problem. With a 100 °C working temperature and a 30 min sampling time, HSSPME provides significant enhacement in sensitivity versus SPME. The HSSPME method has good linearity in a wide range of concentrations and also good precision, between 5 and 10%. The detection limit is in the sub nanogram per liter range, using water samples of 100 mL. With larger water volumes or sampling times longer than 30 min the detection limit is even lower. This extraction method is a viable and convenient alternative to liquid−liquid extraction, since it allows working with much smaller sample size and eliminates the manual labor intensive liquid−liquid extraction and the use of solvent altogether.

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(20) Onuska, F. I.; Terry, K. A. *J. High Resolut. Chromatogr.* **1995**, *18*, 417−421.