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Determination of alkylphenols and bisphenol-A A comparative investigation of functional polymer-coated membrane microextraction and solid-phase microextraction techniques

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Abstract

A functional polymer (hydroxylated polymethacrylate) coated on porous polysulfone hollow fiber membrane (PS-HFM) was used as an adsorbent for the extraction of alkylphenols and bisphenol-A from seawater samples. Analyses of the extracts were performed using gas chromatography–mass spectrometry (GC–MS) after injection-port derivatization using bis(trimethylsilyl)trifluoroacetamide (BSTFA). We term the procedure as polymer-coated hollow fiber microextraction (PC-HFME). Owing to high porosity PS-HFM coated with hydroxylated polymer showed high extraction efficiency. Compared with solid-phase microextraction (SPME), PC-HFME showed good selectivity and sensitivity. Detection limits of alkylphenols and bisphenol-A ranged between 0.07 and 2.34 ng l^{-1}. The linearity range was from 0.01 to 15 μg l^{-1} and the correlation coefficient (r) up to 0.997. The sensitivity and selectivity of the coated HFM could be potentially tuned by changing the characteristics of the coated hydroxylated polymer. The PC-HFME procedure was applied to the detection of alkylphenols and bisphenol-A in the coastal waters of Singapore.

Keywords: Alkylphenols and bisphenol-A; Polymer-coated hollow fiber microextraction; Endocrine disruptors; Environmental analysis; Extraction methods; Solid-phase microextraction

1. Introduction

Alkylphenols (APs) and bisphenol-A (BPA) have been used for more than 40 years as detergents, emulsifiers, wetting agents and dispersing agents. They have been reported to cause a number of estrogenic effects in a variety of aquatic organisms [1].

Octylphenols and nonylphenols are used in plastic packing materials or as spermicides. The estrogenic properties of the nonylphenols and octylphenols are well documented [2]. Similarly, diethyl stilbestrol, bisphenol-A is capable of binding to DNA after metabolic activation and has estrogenic properties at low concentrations [2]. Low doses of bisphenol-A in mice could bring on early puberty in females [3]. Recently trace level contamination of alkylphenols and bisphenol-A in seafood and blood samples have been reported [4,5]. Healthy humans exposed to low level dosage of alkylphenols and bisphenol-A via daily activities may be associated with health risks [6]. Therefore, the detection and quantification of these endocrine disruptors in the aquatic environment is necessary to learn more about their biohazards.

The increased awareness of the presence of APs and BPA in the environment has led to an intensified interest in the trace

Abbreviations: AP, alkylphenol; BPA, bisphenol-A; BSTFA, bis(trimethylsilyl)trifluoroacetamide; LLE, liquid–liquid extraction; SPE, solid-phase extraction; SPME, solid-phase microextraction; SBSE, stir bar sorptive extraction; PC-HFME, polymer-coated hollow fiber extraction; PDMS, polydimethoxysilane; PDMS–DVB, polydimethoxysilane–divinylbenzene; PA, polyacrylate; PS, polysulfone; HFM, hollow fiber membrane; RSD, relative standard deviation; GC–MS, gas chromatography–mass spectrometry; HPLC, high performance liquid chromatography; CE, capillary electrophoresis; LC–MS, liquid chromatography–mass spectrometry; UV, ultraviolet

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analysis of these compounds. Determination of APs and BPA from environmental samples at low concentrations is still a challenging task. Traditional techniques for the extraction and concentration of APs and BPA from aqueous samples are liquid–liquid extraction (LLE) [7] and solid-phase extraction (SPE) [8,9]. However, in both LLE and SPE, large amount of sample and solvents are need. In recent years, solventless and solvent minimized polymer sorption techniques such as solid-phase microextraction (SPME) [10] and stir bar sorptive extraction (SBSE) [11] techniques have been employed for the extraction of APs and BPA. In SPME, polymer fibers coated with relatively polar adsorbents such as polyacrylate (PA) and polydimethoxysilane–divinylbenzene (PDMS–DVB) have been used for the extraction of APs and BPA. In the SBSE, only PDMS coated stir bars are commercially available, although, strictly speaking, the non-polar PDMS is not suitable for the extraction of APs and BPA [12]. In SBSE, thermal desorption and solvent desorption are generally used for desorption of the analytes from the PDMS coating on the stir bar [13–15].

For quantitative determination of APs and BPA, GC–MS with electron impact ionization [16], and chemical ionization [17], HPLC with UV absorbance [18], or fluorescence detection [19], LC–MS [20] and CE [21] have been used. Analysis of APs and BPA using GC–MS is more common than others [22]. Due to the polarity of APs and BPA, GC–MS requires derivatization of the analytes before analysis. A wide range of derivatization procedures have been reported in the literature, e.g. methylation [23], acetylation [24], and silylation [25]. Silylation using bis(trimethylsilyl)trifluoroacetamide (BSTFA) is a rapid and commonly used derivatization technique, even though excessive amount of BSTFA and moisture content could affect the derivatization process [22]. Three different BSTFA derivatization approaches after microextraction have been reported, which include (i) headspace derivatization [26], (ii) injection-port derivatization [27–29] and (iii) direct derivatization (extract and BSTFA were mixed and then analysed) [30].

In this study, we introduce polymer-coated hollow fiber extraction (PC-HFME) of AP and BPA in which hydroxylated polymethacrylate is coated on porous polysulfone (PS) hollow fiber membrane (HFM) and used as adsorbent. Compared with SPME sorbent coating materials, our novel polymer has high number of functional groups and increased swelling tendency in water. Such features are expected to enhance the extraction efficiency. Results from PC-HFME are compared with SPME experiment to evaluate the procedure.

2. Experimental

2.1. Chemicals and reagents

The following chemical standards (purity ≥97%) were obtained from Wako Chemicals (Tokyo, Japan): 4-*n*-butylphenol, 4-*tert*-butylphenol, 4-*n*-pentylphenol, 4-*n*-hexylphenol, 4-*n*-octylphenol, 4-*tert*-octylphenol, 4-*n*-heptylphenol, 4-nonylphenol, and bisphenol-A. The derivatization agent bis(trimethylsilyl)trifluoroacetamide (BSTFA) (purity >98%) and all HPLC-grade organic solvents, hydrochloric acid, sodium hydroxide and sodium chloride were purchased from Merck (Darmstadt, Germany). Ultrapure water was prepared on a Milli-Q (Milford, MA, USA) system. A standard stock solution of 50 μg ml^{-1} of each analyte was prepared in acetone. A working standard solution (1 μg ml^{-1} of each analyte) was used for low concentration spiking (<1000 ng l^{-1}) and for higher concentrations the 50 μg ml^{-1} stock solution was used.

2.2. Materials

MicroPES® 0.3/2 polysulfone hollow fiber membrane (PS-HFM) was purchased from Membrana (Wuppertal, Germany). The HFM with an inner diameter of 300 μm and a pore size of 0.2 μm was used for polymer-coating. The SPME fiber holder and fibers (PDMS 7 μm, 100 μm, PDMS–DVB and polyacrylate (PA) 85 μm) and extraction vials, septa and aluminium caps were purchased from Supelco (Bellefonte, PA, USA) and used without modification. Before extraction the fibers were conditioned in the GC injection port based on the manufacturer's recommended procedure. Ultrasonicator was purchased from Midmark (Versailles, Ohio, USA) and

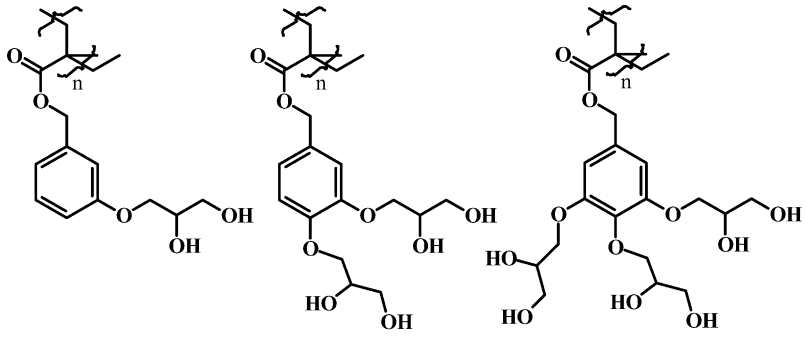

Fig. 1. Molecular structure of the polymers (**1**–**3**) used in our investigation.

the magnetic stirrer/hot plate was obtained from Heidolph (Cinnaminson, NJ, USA).

2.3. Synthesis of hydrogel and coating on polysulfone membrane

A stable hydrogel was prepared from poly hydroxylated poly(methacrylic acid) (Fig. 1). The poly(methacrylic acid) used for synthesis did not show any swelling tendency. However, the hydroxylated poly(methacrylate) showed increased swelling in water with increasing number of hydroxyl groups within the repeating unit. Synthetic scheme of hydroylated polymethacrylates is shown in Fig. 2.

To coat the porous PS-HFM, it was cut into 1.2 cm lengths and immersed in a 0.5 g ml^{-1} of hydrogel for a day. The functional polymer formed a thin layer on the HFM. Physical characterization of the polymer-coated HFM was carried out; scanning electron micrographs, and attenuated total reflection Fourier transform infrared spectra indicate the presence of hydroxylated groups on the fiber surface.

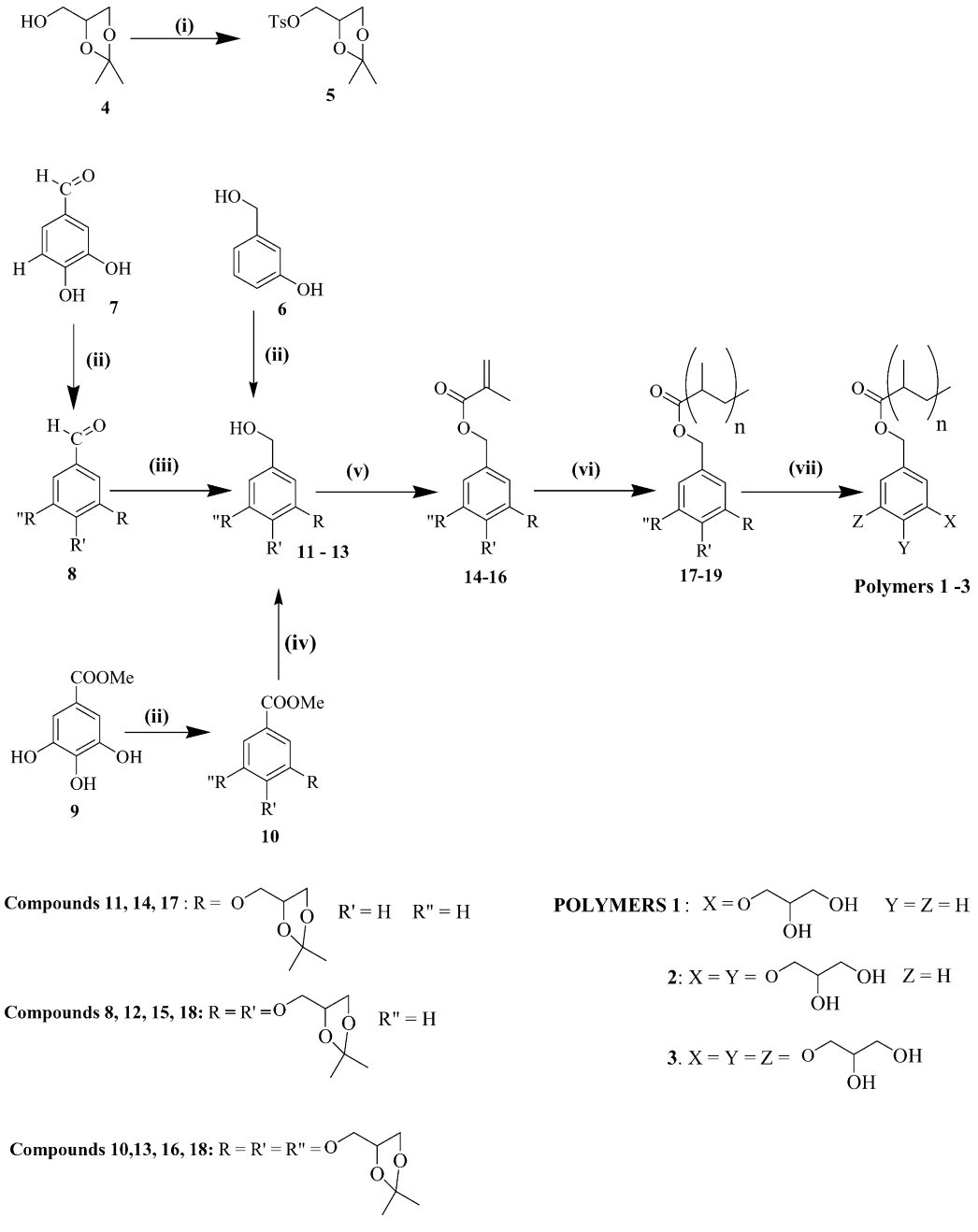

Fig. 2. Synthesis of polymers **1**–**3**: (i) tosyl chloride, 5 N NaOH, tetrahydrofuran (THF), 0 °C-rt, 12 h, 99%; (ii) 5/dimethylformamide, potassium carbonate, 18-crown[6], 75 °C, 5 days, 65%; (iii) sodium cyanoborohydride, THF/ethanol, acetic acid, 0 °C-rt, 12 h, 92%; (iv) lithium aluminumhydride, THF, sodium sulphate, 0 °C-rt, 12 h, 96%; (v) methacryloyl chloride, triethylamine, THF, 0 °C-rt, 6 h,76%; (vi) azobisisobutyronitrile, toluene, 48 h, 80% and (vii) 10% HCl, THF, 70 °C, 1.5 h, 70%.

2.4. PC-HFME procedure

Ten milliliters of ultrapure water containing 50 ng l^{-1} of each AP and BPA was placed in a 10 ml screw-cap glass vial containing a 10 mm × 5 mm PTFE-coated stir bar. The sample pH was adjusted to 2 and salt concentration to 30% (w/v). A polymer-coated HFM was placed in the sample solution, and extraction was performed for 30 min. The solution was stirred at 105 rad s^{-1} (1000 rpm; 1 rpm = 0.1047 rad s^{-1}). After equilibrium was established, the fiber was removed with a pair of tweezers and dried in a lint free tissue. The analyte containing HFM was desorbed ultrasonically in methanol (1 ml) for 20 min. After complete desorption of analytes, 2 μl of extract and 2 μl of BSTFA were injected into the GC injector-port simultaneously with two different syringes.

2.5. SPME procedure

AP and BPA (20 ng l^{-1} of each analyte) in a 10 ml sample solution (pH and salt concentration were adjusted to 2 and 30% (w/v), respectively) were extracted by direct immersion of SPME fiber with stirring (at 105 rad s^{-1}). Equilibrium was established after 90 min. After completing the extraction step, the SPME fiber was placed in the headspace of a 3 ml GC autosampler vial containing 50 μl of BSTFA in 1 ml of acetone at 60 °C, for 20 min. Finally, the fiber was desorbed in the injection-port of the GC for 3 min at 250 °C. Possible carry-over was minimized by keeping the fiber in the injector for an additional 10 min. Blanks were run periodically to confirm the absence of contaminants.

In SPME, derivatization of analytes on the fiber by exposing them to a derivatization agent at the headspace has been reported by others [31–33]. Using this procedure, rapid derivatization with low precision was observed with pure BSTFA. When a solution of BSTFA in acetone was used, derivatization was slower but better precision was attained. To optimize this procedure further, a range of (5–100 μl) of BSTFA was added to 1 ml of acetone placed in a 3 ml vial. Headspace derivatization was then performed at 60 °C for 20 min on the analytes adsorbed on the fiber immediately after SPME. When <50 μl of BSTFA in 1 ml of acetone was used, the desorption data showed mixtures of both derivatized and underivatized compounds. Fifty microliters BSTFA gave complete derivatization of analytes in subsequent experiments.

Fig. 3 shows chromatograms of extracts after PC-HFME and SPME, with spiked sample at the same concentration. It indicates significant differences between PC-HFME and SPME extracts. Extraction is faster in PC-HFME (30 min) than for SPME (90 min). PC-HFME analyte enrichment was between 50 and 100 times higher than those obtained by SPME. This could be due to the hydrogel having functional groups which have higher electrostatic interaction with APs and BPA, and its swelling increases the surface area of the coating.

2.6. GC–MS analysis

Analysis was carried out using a Shimadzu (Tokyo, Japan) QP2010 GC–MS system equipped with a Shimadzu AOC-20i autosampler and a DB-5 fused silica capillary column (30 m × 0.32 mm I.D., film thickness 0.25 μm, from J & W Scientific, Folsom, CA, USA). Helium was used as the carrier gas at a flow rate of 2.1 ml min^{-1}. Two microliters of sample was injected into the GC–MS with a splitless injection-port under splitless mode after a sampling time (holding time) of 2 min (i.e. sample and derivatization agent were retained in the injection-port for 2 min). The injection temperature was set at 300 °C, and the interface temperature at 270 °C. The GC temperature programme was as follows: 50 °C (2 min); 20 °C min^{-1} to 100 °C; 10 °C min^{-1} to 200 °C; 20 °C min^{-1} to 300 °C (7 min). The pressure pro-

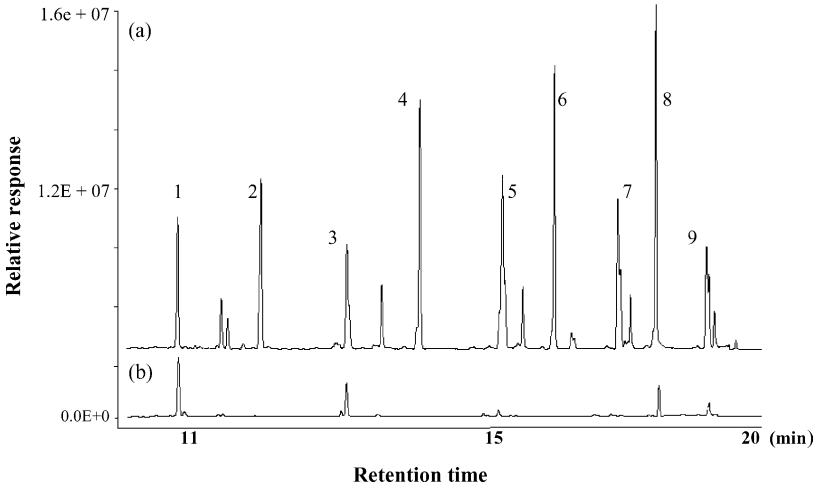

Fig. 3. Total ion chromatogram of the BSTFA derivatives of APs and BPA, seawater spiked at the same concentration (a) after PC-HFME, and (b) SPME. Peak identification [1] 4-*tert*-butylphenol, [2] 4-*n*-butylphenol, [3] 4-*n*-pentylphenol, [4] 4-*n*-hexylphenol, [5] 4-*tert*-octylphenol, [6] 4-*n*-heptylphenol, [7] 4-nonylphenol, [8] 4-*n*-octylphenol, [9] bisphenol-A. Extraction conditions are given in the text.

gramme was as follows: carrier gas pressure 40 kPa (for 5 min), then increased by 2 kPa/min to 70 kPa, held for 7 min. All standards and samples were analysed in selective ion monitoring (SIM) mode with a detector voltage of 1.5 kV and a mass scan range of *m/z* 50 to *m/z* 500. The most abundant ion present was selected as the quantitative ion, while a further two ions were used for confirmation of individual compounds [29].

3. Results and discussion

3.1. Optimization of PC-HFME and SPME

The PC-HFME and SPME parameters that were optimized include extraction time, sorbent material, sample ionic strength, pH, desorption solvent, desorption time, and various aspects of the derivatization procedure.

The extraction time profile for the target analytes was studied between 5 and 40 min for PC-HFME. The solution was stirred at 105 rad s^{-1} (ca. 1000 rpm). The peak areas did not increase significantly after 20 min except for 4-*n*-hexylphenol. The peak area for 4-*n*-hexylphenol decreased after 30 min. Therefore, 30 min was selected as the optimum extraction time. The SPME equilibrium time was established with 2 μg l^{-1} spiked analytes from 10 to 100 min extraction time using the PA fiber. Fig. 4a and b shows that extraction equilibria of most of the analytes were achieved after 30 min for PC-HFME, and 80 min for SPME.

The extraction efficiency of PC-HFME based on various polyhydroxylated polymers **1**–**3** (Fig. 1, two, four and six hydroxyl groups incorporated on every repeating units on the polymer backbone) for APs and BPA over 30 min, was compared with the values obtained for PA-SPME fibers for over 90 min. As expected in SPME, PA fibers gave good response than the rest of the fibers [27,29,34]. However, when comparing with PC-HFME, the response was highest for the polymer **3** coated fibers (Fig. 5). The polymers **1** and **2** have lower extraction efficiency than PA fiber, except for 4-nonlyphenol and 4-*n*-octylphenol. Therefore, polymer **3** coated hollow fibers and PA-SPME fibers were chosen for further studies (Fig. 5).

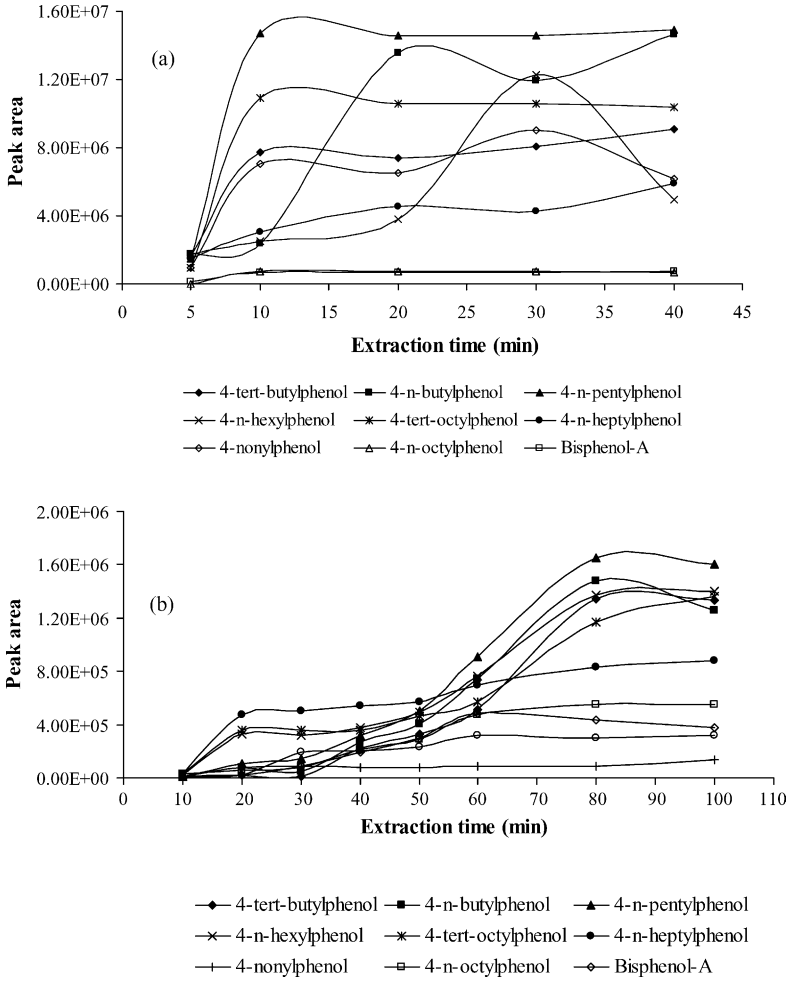

Fig. 4. Effect of extraction time on (a) PC-HFME. Methanol was used as desorption solvent, stirring speed was 105 rad s^{-1}. Sample pH was 2 and ionic strength was 30% with injection port-derivatization. (b) SPME. Sample conditions are similar with PC-HFME and headspace on-fiber derivatization was used in SPME.

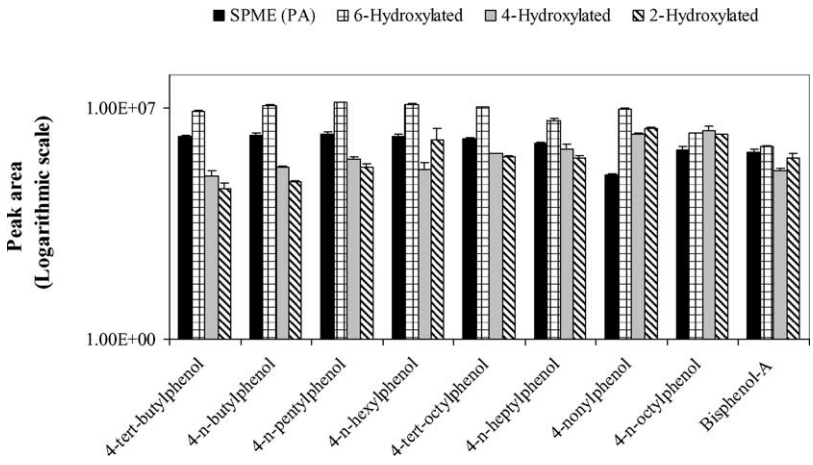

Fig. 5. Comparison on the extraction efficiency of SPME with PA fiber and PC-HFME with all three polymers.

The effects of sample pH, over a range of 2–10, on extraction were investigated. It is well known that APs and BPA can be effectively extracted at a sample pH of 2 [27,29]. At low pH, hydroxyl groups in the polymer were easily protonated and extraction efficiency was also increased due to the electrostatic interaction between the polymer and analyte. Addition of salt to the aqueous sample can enhance the availability of analytes for extraction. Accordingly, the ionic strength of the solution was varied between 10 and 30% (w/v) by adding NaCl. This generally increased the extraction efficiency of both microextraction techniques (data not shown), a result that has been observed previously [27,29].

The dependence of the efficacy of PC-HFME and SPME on sample size was evaluated. The lower the sample volume the higher the analyte enrichment for SPME, whereas for PC-HFME, the efficiency increased from 5 to 10 ml and then decreased. Although the extraction concepts are similar, substantial differences between both methods were observed. PC-HFME enrichment (based on GC–MS peak area) ranged from nearly100% using 10 ml of sample to 70% using 20 ml. However, SPME enrichment responses were 35% when the sample size 20 ml was used. The analyte enrichment decreases considerably for sample volumes higher than 10 ml (PC-HFME) and 5 ml for SPME. Therefore, sample sizes of 10 ml (PC-HFME) and 5 ml (SPME) were selected for further experiments as a compromise to attain appropriate enrichment.

Similar to SBSE [13–15,35] procedure, the analytes were desorbed using an organic solvent from the hollow fiber after extraction. Selection of a suitable solvent is one of the prerequisites of PC-HFME. There are many factors affecting the desorption behavior of the analytes, such as the solubility of the analytes, solvent polarity and solubility of the hydrogel and PS membrane. The functional hydrogel was not soluble in common solvents whereas PS membranes dissolve in polar solvents such as acetone, dichloromethane and tetrahydrofuran but not in methanol, hexane, isooctane and *n*-nonane. Fig. 6 shows the desorption profiles of APs and BPA using different solvents. Based on the results, methanol was used as the eluting solvent for analyte desorption for all our analyses owing to the insolubility of hydrogel and PS membrane in

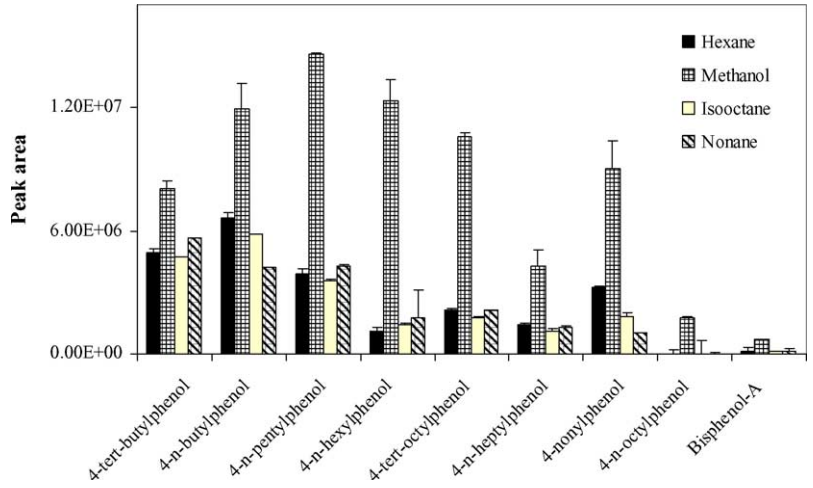

Fig. 6. Desorption profile of APs and BPA using different solvents.

methanol and it gave better extraction results as compared to other solvents.

Next, desorption time over the range of 2–25 min was investigated. Analyte desorption peak areas were not significantly increased after 10 min. However, there was a slight increase in desorption of 4-*n*-octylphenol and 4-*tert*-octylphenol. Therefore, an optimized desorption time of 20 min was selected. After the first desorption, fibers were further desorbed to test carryover effects. Only 4-nonylphenol remained on the fiber in most cases. However, since the fibers are relatively cheap and only small amount of the active polymer is needed for coating, sample carryover effects were eliminated by the simple expedient of using the coated fiber once only.

Since SPME fibers are designed to be reusable, it is important to monitor carryover effects. Carryover is more serious when analyzing low levels of concentration [30]. Desorption temperature was varied between 200 and 280 °C, the later gave complete desorption with no carryover with a 10 min desorption, indicating that analytes were readily desorbed from the fiber. For five successive analyses, a desorbed fiber was respectively tested for the presence of analytes by reinserting it immediately into the GC injector. No carryover effect was observed.

3.2. Derivatization of APs and BPA

After PC-HFME, two mode of derivatization, i.e. on-fiber derivatization and injection-port derivatization were tested. During the on-fiber derivatization, the analyte-containing HFM was desorbed in a solution of the derivatization agent (10 μl) and methanol (90 μl). In this approach, the extract was diluted, as expected and low peak areas were obtained. In a injector-port derivatization, higher peak areas were observed due to the analytes being directly derivatized in the injection-port. Derivatization using BSTFA is fast only 15 s is enough to complete the procedure [22]. In the present work, both extract and BSTFA were retained in the injection port at 280 °C for 2 min before being channeled into the GC column. This led to complete volatilization and derivatization of the analytes. Different derivatization ratios of extract and BSTFA volumes were evaluated and a 1:1 ratio gave better results than other (Fig. 7). Lower volume of analytes and less concentrated BSTFA solution gave comparatively poor results, as did on-fiber derivatization. The higher volume ratio or excessive BSTFA was also gave poor peak resolution and low precision of the analysis. In routine analyses, trace amounts of 4-nonylphenol and 4-*n*-octylphenol were found to be retained in the injection-port/column. Therefore, the possibility of the carryover effect and BSTFA contamination by "soiled" septa were carefully monitored after a few injections.

3.3. Quantitative results of PC-HFME and SPME

To evaluate the applicability of the proposed PC-HFME and SPME procedures, the repeatability, linearity and limits of detection (LOD) were investigated using the optimum extraction conditions. The concentration of APs and BPA detected in the most of the real samples lie in the range of 0.01–15 μg l^{-1}. To evaluate the linearity of the calibration plots, samples were spiked with APs and BPA to give final sample concentrations of 0.01, 0.10, 1, 10 and 15 μg l^{-1} and then extracted. The GC peak area counts were plotted against the respective analyte concentrations to generate calibration curves. The calibration plots were linear over the range of 0.01–15 μg l^{-1} with correlation coefficient (r) between 0.9859 and 0.9973 for PC-HFME. For SPME, the linear range was from 0.5 to 50 μg l^{-1} with linearity between 0.9693 and 0.9960. The linearity of the calibration curves, constructed from the analysis of spiked samples was satisfactory in both methods.

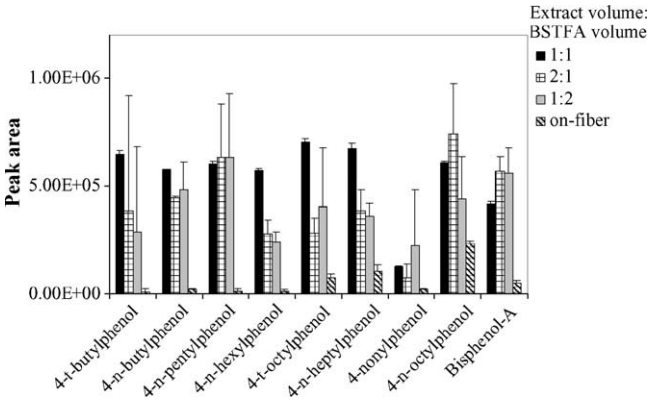

Fig. 7. Influence of extract volume and BSTFA volume ratio on injection-port derivatization after PC-HFME. Data for on-fiber derivatization are also given.

The limits of detection for all target analytes were determined by progressively decreasing the concentrations of analytes until signals were just detected at a signal-to-noise ratio of 3 (S/N = 3) using PC-HFME and SPME. The LODs ranged from 0.07 to 2.34 ng l^{-1} and 2 to 14 ng l^{-1} for PC-HFME and SPME, respectively (Table 1). While determining the LOD, blanks were carried out to confirm that no sample carryover occurred. Three replicates were used to calculate LODs. The relative standard deviation (RSD) was performed by extracting ultrapure water spiked at 250 ng l^{-1} of each compound (three replicates).

4. Application of method for seawater analysis

To demonstrate the feasibility of the PC-HFME method, genuine seawater samples were analyzed. Coastal water from locations in the vicinity of recreational sites of Singapore, were collected and analyzed to assess the contamination of APs and BPA. APs and BPA were detected in all seawater samples. Therefore, a standard addition method was used to assess the matrix effect and calculate the recovery efficiency of PC-HFME. APs and BPA standards (100 and 1000 ng l^{-1} as concentration in seawater) were added to 10 ml of one

Table 1
Quantitative data: linearity, precision and LODs (S/N = 3) of PC-HFME and SPME

Analytes	PC-HFME[a]			SPME[b]		
	Correlation coefficient (r)	RSD (n = 3) (%)	LODs (ng l^{-1})	Correlation coefficient (r)	RSD (n = 3) (%)	LODs (ng l^{-1})
4-*tert*-Butylphenol	0.9918	5.1	0.07	0.9960	7.0	4.1
4-*n*-Butylphenol	0.9859	6.9	0.14	0.9927	1.7	2.3
4-*n*-Pentylphenol	0.9917	6.6	0.14	0.9935	5.8	3.0
4-*n*-Hexylphenol	0.9971	9.3	0.42	0.9943	6.1	2.2
4-*tert*-Octylphenol	0.9950	10.4	1.36	0.9920	11.3	2.4
4-*n*-Heptylphenol	0.9973	7.6	2.34	0.9951	1.7	6.3
4-Nonylphenol	0.9860	11.0	1.43	0.9923	12.0	14.1
4-*n*-Octylphenol	0.9922	8.5	1.66	0.9900	11.8	8.2
Bisphenol-A	0.9897	6.2	1.04	0.9693	12.7	3.3

[a] Linear range for PC-HFME 0.1–15 μg l^{-1}.
[b] Linear range for SPME 0.5–50 μg l^{-1}.

Table 2
Recoveries of alkylphenols and bisphenol-A from real seawater by PC-HFME combined with injection-port derivatization (n = 3)

Analytes	PC-HFME			
	Relative recovery, % spiked at 100 ng l^{-1}	RSD (n = 3)	Relative recovery, % spiked at 1000 ng l^{-1}	RSD (n = 3)
4-*tert*-Butylphenol	84.0	7.9	94.4	4.2
4-*n*-Butylphenol	113.8	8.6	99.9	7.5
4-*n*-Pentylphenol	91.2	9.9	91.1	5.3
4-*n*-Hexylphenol	76.2	6.5	99.4	12.2
4-*tert*-Octylphenol	82.6	9.4	94.1	4.4
4-*n*-Heptylphenol	86.2	10.7	90.9	5.0
4-Nonylphenol	83.5	8.2	83.1	5.5
4-*n*-Octylphenol	92.5	13.1	85.6	7.5
Bisphenol-A	98.0	10.7	117.7	10.8

seawater sample. The recoveries of the method were tested by triplicate analysis (n = 3) of the spiked sample and the results are listed in Table 2. Good recoveries were obtained for all the analytes (between 83.5 and 113.8% with RSD values between 6.5 and 13.1% at the 100 ng l^{-1} spiking level. Recoveries of 83.1 and 117.7% with RSD values between 4.2 and 12.2% were obtained for sample spiked at a concentration of 1000 ng l^{-1}. These results clearly demonstrate that seawater matrices had little effect on the efficiency of PC-HFME, which is therefore suitable for analysis of trace level of APs and BPA from environmental samples.

The optimized PC-HFME conditions were applied to the seawater samples. The concentrations of 4-nonylphenol (ca. 0.02–0.07 μg l^{-1}) detected in this preliminary survey from recreational sites were lower than those reported from these locations in year 2000 [4], also lower than the value reported from Canada (Laurentian Great Lakes basin), (7.8 μg l^{-1}) [36]; upper New York Harbor (up to 70 μg l^{-1}) [37], etc. BPA levels were lower than those reported for the Elbe river, Germany (0.221 μg l^{-1}) [38].

5. Conclusion

This paper demonstrates the successful application of PC-HFME in combination with GC–MS, for the analysis of APs and BPA from seawater samples. To the best of our knowledge, this is the first time a functional (hydrogel) polymer-coated polysulfone hollow fiber membrane is used for the extraction of organic pollutants from aqueous samples. Compared with SPME, higher enrichment factors were obtained at optimized extraction conditions. The detection limits for APs and BPA were from 0.07 to 2.34 ng l^{-1}, exceeding the United State Environmental Protection Agency requirement for APs and BPA analysis in aqueous samples.

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