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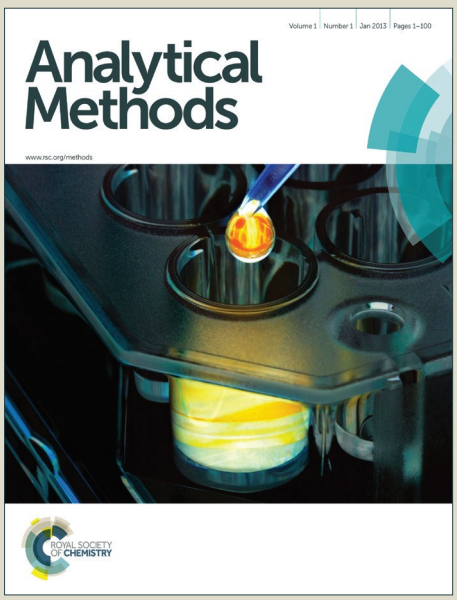

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Hollow fiber supported liquid membrane coupled with high performance liquid chromatography for highly sensitive determination of bisphenols in environmental water samples

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Abstract

Hollow fiber supported liquid membrane (HFSLM) was applied for the extraction of bisphenols (BPs) including bisphenol S, bisphenol AF, tetramethylbisphenol A, tetrachlorobisphenol A and tetrabromobisphenol A from water samples. The undecane solution of 1.0% (m/v) tri-*n*-octylphosphine oxide was supported on the pores of the polypropylene hollow fiber membranes (280 μm I.D., 50 μm wall thickness, 0.1 μm pore size, 60 cm length) to form a liquid membrane. The lumen of hollow fiber membranes was then filled with 0.3 M NaOH as acceptor to prepare the extraction device, which was placed into the 500 mL water sample (donor) adjusted to pH 4.0 with HCl. After shaking at 200 rpm for 180 min, the acceptor (~30 μL) was collected and injected into the high performance liquid chromatography system for determination of the BPs. The proposed HFSLM method provided good enrichment factors (1370-2138), low detection limits (0.1-0.2 μg/L) and good repeatability (RSD = 2.6-8.8%, n = 5). The proposed method was applied to determine the five target BPs in waste water, tap water, river water and lake water samples, with satisfactory spiked recoveries (68.6-134%) at 0.5 and 1 μg/L spiking levels, demonstrating the practicality of the proposed method for determination of BPs in environmental water samples.

Keywords: Hollow fiber supported liquid membrane; Bisphenols; Environmental waters; High performance liquid chromatography

1 Introduction

Bisphenols (BPs) including bisphenol A (BPA) and its analogues such as bisphenol S (BPS), bisphenol AF (BPAF), tetramethylbisphenol A (TMBPA), tetrachlorobisphenol A (TCBPA) and tetrabromobisphenol A (TBBPA) are a group of chemicals containing two phenol functional groups which can be substituted with other chemical groups such as methyl and halogen. Since the restricted usage of BPA in many countries for its widespread exposure to human and animals and endocrine disrupting effect [1, 2], its analogues are brought into industry for plastic production. Currently, BPs are widely used as alternative raw materials for epoxy resins, polycarbonate plastic, polyesters and fire-resistant polymers [1].

Bisphenol chemicals can easily be released into environment along with the aging of products [3]. While the widespread existence of BPA in environmental matrices has been reported, other analogue compounds such as BPAF were detected in rivers, sediments, soils, indoor dusts and well waters [1], and TCBPA and TBBPA were found in sediments and sewage sludge [4, 5]. Additionly, TBBPA has also been identified in air [6], industrial and agricultural soils [7]. As alternatives to BPA, BPS has been found in sediments [8] and indoor dusts [9]. Due to the ubiquitousness in environment, BPs have already been found in human urine and breast milk [10, 11].

While BPA and its analogues have already been proven to be endocrine disrupting chemicals [2], BPAF and its halogenated substances have certain neurotoxic properties as well [12, 13], which gives rise to significant hazard on human health. To further understand the occurrence, transport, transformation, distribution, fate and toxicity of these compounds, it is highly necessary to determine them in environmental and biological samples.

The commonly used analytical methods for bisphenols are high performance liquid chromatography (HPLC) equipped with ultraviolet [14], fluorescence [15] and mass spectrometry [1] detectors, and gas chromatography-mass spectrometry (GC-MS) [16]. Considering that labourious derivatization is usually needed to improve the GC analysis, HPLC separation was commonly used. Given the trace levels of BPs in the environmental samples with complex matrices, it is necessary to perform preconcentration prior to HPLC analysis. In order to avoid the use of large amount of organic solvents [17], various micro-extraction methods have been developed, such as solid-phase microextraction (SPME) [18], stir bar sorptive extraction (SBSE) [19], and liquid-phase microextraction [14]. In view of the unavoidable drawbacks such as fragility of fibers, additional derivatization steps

for extracting polar compounds [20] and possibility of sample carry-over existing in SPME [21] and SBSE, HFSLM has the advantages of simplicity, good enrichment, low-price, clean-up and environmental friendship, and shows great potentials in preconcentration of weak acids and bases, as well as metal ions [22, 23]. Although there are a few reports on the extraction of BPA with SLM in environmental waters [24, 25], these methods suffered from drawbacks such as the complicated steps in preparation of the liquid membrane and laborious extraction procedure. To the best of our knowledge, no study on the simultaneous extraction of analogues of BPA with simple and convenient HFSLM has been reported.

In the present study, we developed a HFSLM method for preconcentration of BPs in environmental waters. Parameters influencing the extraction efficiency were optimized, and the optimized procedure was applied to analyze BPs in environmental waters.

2 Experimental

2.1 Reagents and materials

Bisphenol S (BPS) and bisphenol AF (BPAF) were purchased from J&K Scintific Ltd (Beijing, China). Tetramethylbisphenol A (TMBPA) and tetrachlorobisphenol A (TCBPA) were obtained from TCI co., Ltd. (Tokyo, Japan). Tetrabromobisphenol A (TBBPA) was purchased from Dr. Ehrenstorfer GmbH (Germany). Dihexyl ether was obtained from Tokyo Kasei Kogyo co., Ltd. (Kita-Ku, Tokyo, Japan). Undecane, tri-*n*-octylphosphine oxide (TOPO) was obtained from Alfa Aesar co., Ltd. (MA, USA). HPLC-grade methanol and acetonitrile were purchased from Fisher Scientific (Geel, Belgium). All the other chemicals were of analytical grade or above and were purchased from Beijing Chemicals (Beijing, China). Ultrapure water prepared by a Milli-Q Gradient system (Millipore, Bedford, MA, USA) was used throughout the experiments.

Individual standard stock solutions (1000 mg/L) of BPs were prepared by dissolving 50 mg of each standard in 50 mL of HPLC-grade methanol and stored at 4 °C. The working solutions were prepared by diluting the stock solutions with water before use.

The 50/280 Accurel PP polypropylene hollow fiber tubing (50 μm wall thickness, 280 μm inner diameter, 0.1 μm pore size) were obtained from Membrana (Wuppertal, Germany). The BD syringe (0.33 mm, 12.7 mm, 1 mL) purchased from Becton Dickinson and Company was used to fill the lumen of hollow fiber membrane with acceptor solution for extraction and to flush out the acceptor.

2.2 Extraction procedure

HFSLM extraction procedures were modified from our previous study [26]. In brief, the hollow fiber tubing (60 cm), previously flushed and fully filled with water by syringe, was completely immersed into organic liquid for a few minutes to facilitate the organic liquid successfully impregnate pores in the wall of fiber to form the organic liquid membrane. Then, into the lumen was completely filled with acceptor solution. Afterwards, the two ends of fiber were sealed together with a small piece of aluminium foil and the extraction device was immersed fully into sample solution. After shaking at 200 rpm for 180 min, the hollow fiber device was collected and the acceptor solution (~30 μL) was flushed out with a syringe filled with air and transferred into a glass vial (100 μL, Waters, Massachusetts, USA) for analysis by HPLC.

2.3 HPLC instrument and determination

The HPLC instrument (1200 Series, Agilent) equiped with auto-sampler, a quaternary pump and a VWD detector set at 214 nm was used for determination of BPs. A ZORBAX SB-Aq-C_{18} column (250 mm×4.6 mm i.d., 5 μm particle size, Agilent, USA) was used for the separation of BPs. The injection volume was 20 μL, and the column temperature was 25 °C. The mobile phase was a mixture of 20 mM acetate buffer (pH 4.5) and acetonitrile at the flow rate of 1 mL/min. The gradient elution program was as follows: keeping 60% acetonitrile in 0-3 min, and linearly increased to 80% acetonitrile during 3-10 min, then decreased to 60% acetonitrile in 10-12 min, thereafter kept the constant ratio of acetonitrile for 1 min. The retention time of each analyte was shown in Table 1.

2.4 Water sample collection and treatment

Waste water was collected from effluents of the Gaobeidian municipal wastewater treatment plant (Beijing, China). River water was collected from the Songhua River (Jilin, China). Lake water was collected from a campus (Beijing, China), and the tap water was collected in our laboratory after running for 5 min. Prior to the HFSLM, the samples were adjusted to pH 4.0 with HCl and purged with N_2 for 15 min to eliminate dissolved carbon dioxide and carbonate which could significantly reduce the acceptor pH and thus the recovery of analytes by their co-extraction from sample solution into acceptor [27]. For the tap water, it was pretreated with 0.1% $Na_2S_2O_3$ to eliminate hypochlorite before adjusted to pH 4.0 with HCl [28].

2.5 Calibration and data processing

All the experimental results were shown as mean values of at least three replicates, and the extraction performance was evaluated by enrichment factor, which is defined as the ratio of final concentration of an analyte in the acceptor to its initial concentration in the donor solution. Sample analysis was calibrated with external standard calibration by conducting the same extraction procedure for both the standard solutions and the real water samples. The calibration curves were prepared by injecting 20 μL of various concentrations of standards into the HPLC system, and plotting the obtained peak areas against the analyte concentrations.

3 Results and discussion

3.1 Optimization of HFSLM extraction conditions

3.1.1 Selection of liquid membrane

The species of liquid membrane is one of the most important factors influencing the HFSLM efficiency. Undecane and dihexyl ether, the two commonly used membrane solvents, were tested as liquid membrane. Results shown in Fig. 1 indicated that while dihexyl ether can only extract 3 analytes (BPAF, TMBPA and TBBPA), undecane facilitated the extraction of 4 analytes (BPAF, TMBPA, TCBPA and TBBPA). Since the addition of TOPO into membrane liquid could usually enhance the extraction efficiency of weak organic acids [29], undecane and dihexyl ether dissolved with 5% (m/v) TOPO were further tested as liquid membrane, respectively. As shown in Fig. 1, while 5% (m/v) TOPO in dihexyl ether can only extract 4 analytes, all the target analytes were extracted by 5% (m/v) TOPO in undecane. The addition of TOPO into the liquid membrane facilitates the extraction of BPs into the liquid membrane, but hinders the back extraction of BPs into the acceptor phase. Thus, the overall enrichment factor was the compromise result of these two extraction procedure. For BPS with the lowest K_{OW}, TOPO significantly enhanced its extraction into the liquid membrane but had negligible effect on its back extraction, thus improved the enrichment factor. On the contrary, TOPO significantly hindered the back extraction of TMBPA for its high pK_a value, thus reduced the enrichment factor of TMBPA. In addition, due to the relatively short extraction time (1 h), the addition of TOPO reduced enrichment factor of all the target analytes except for BPS. This can be overcome by prolonging the extraction time.

3.1.2 Effect of donor pH

Donor pH is also a crucial parameter in the extraction of BPs, which can control the form of compounds in the sample phase and therefore influence their enrichment in the acceptor. According to the pK_a value of five compounds shown in Table 1, the donor pH was optimized in the range of 1-6, which was set a little bit lower than the pK_a value in order to facilitate the present of compounds as non-ionized forms [22], and therefore their extraction into the liquid membrane. Results demonstrated that for most target analytes, the highest enrichment factor was obtained at pH 4. This is because these analytes have pK_a values over 6, and a sample (donor) pH of 2 units below the pK_a value facilitates their presence mainly in neutralized form for extraction into the liquid membrane. Therefore, pH 4.0 was selected as optimum in the following optimization.

3.1.3 Effect of NaOH concentration

In the HFSLM, the BPs transported through liquid membrane in neutralized form and were trapped in the basic acceptor (NaOH) in the ionized form. In this experiment, the NaOH concentration was optimized in the range of 0.1 - 0.5 M and the results were shown in Fig. 2. As expected, TMBPA required the highest NaOH concentration to obtain the maxium enrichment factor due to its highest pK_a (10.3) among the five target analytes. However, although BPS has the second large pK_a value, its maximum apparent enrichment factor occurred at relatively lower NaOH concentration compared to other four analytes. This can be attributed to the first elution of BPS in HPLC analysis, in which part of the ionized BPS was eluted out before protonized by buffer in the mobile phase when the NaOH concentration in the acceptor was too high. The reduction of apparent enrichment factor of the other four BPs at over 0.4 M NaOH can also be ascribed to the insufficient protonization in the HPLC determination system. In the following optimization, 0.3 M NaOH was adopted as compromise.

3.1.4 Effect of TOPO contents in the liquid membrane

The lone electron pair on oxygen atom of TOPO tends to form hydrogen bonding with compounds containing hydroxyl or carboxyl [34], which is helpful for serving as extractant for the five target analytes with two phenolic hydroxyls (Table 1) and therefore enhancing the enrichment factor. The TOPO concentration in undecane was optimized in the range of 0-5% (m/v), as TOPO separated out at room temperature at concentrations over 5% (m/v). As can be seen in Fig. 3, the enrichment

factor of the most compounds increased in the range of 0-1% (m/v) TOPO, and then slightly decreased with the futher increase of TOPO concentration except for BPS. As a result, 1% (m/v) TOPO was adopted in the following studies.

3.1.5 Effect of sample volume

It is well known that high enrichment factor can be obtained by increasing the sample volume under a constant acceptor volume [35]. In this present study, the effects of sample volume on enrichment factor was studied by using a series of volume ranging from 50 ml to 1000 ml. Results revealed that the enrichment factors of all the analytes increased with the sample volume up to 500 ml, and then decreased with the further increase of sample volume. Therefore, 500 ml sample volume was adopted.

3.1.6 Effect of NaCl content

In general, addition of salt into sample solution is inclined to increase the ionic strength and thus enhance the partition coefficient of analytes in organic phase, facilitating the compounds from water phase into organic phase. However, effect of ionic strength on extraction was rather complicated taken into account of electrostatic interactions, ion exchange, water adsorption, the salting out effect, and the nature of the adsorbate and the salt concentration [36]. As shown in Fig. 4, the maximum enrichment factors of almost all the analytes were obatianed in the range of 0-1% (m/v) NaCl concentration. Since the salinity is < 1% in most environmental waters, no salt was added in sample solution.

3.1.7 Effect of shaking rates and extraction time

Generally, a suitable shaking rate makes the diffusion layer thin in the interface between the donor and acceptor phases and could enhance the mass transfer rate of analytes, which can shorten the extraction time and enhance the enrichment factor. In this study, it was found that the enrichment factor increased gradually with the increase of shaking rate. However, at shaking rates over 200 rpm, the fibers were tangled up and many air bubbles were formed and attached to the surface of hollow fiber, which reduced the mass transfer efficiency. Hence, a shaking rate of 200 rpm was adopted. At this fixed shaking rate, the effect of extraction time on enrichment factor was examined in the range of 15-720 min. Results shown in Fig. 5 showed that the enrichment factor increased sharply within

180 min, then the enrichment factor of most analytes increased slowly with prolonged extraction time until 300 min, and finally decreased with further increased extraction time, which might result from the partial destruction of the liquid membrane. Therefore, 180 min was selected as optimized extraction time.

3.2 Evaluation of method performance

Under the optimized conditions, the analytical performance characteristics of the proposed method were determined with six standard solutions with different analyte concentrations. Results shown in Table 2 demonstrated that this proposed method exhibited low detection limits (LODs) of 0.1-0.2 μg/L (*S/N* = 3), acceptable precision (2.6 - 8.8%, n = 5), and good linearity with the correlation coefficients (r > 0.99). The enrichment factors, ranged from 1370 to 2138, were much higher than that of solid-phase extraction which is usually below 500. The LODs of the present method were much lower than that of solid-phase microextraction and solid-phase extraction [15], indicating that the proposed method is very efficient for the enrichment of BPs.

3.3 Analysis of real water samples

The proposed method was successfully applied to determine the five target BPs in waste water, tap water, river water and lake water. The recoveries for the analytes were determined at 0.5 and 1 μg/L spiking levels. As shown in Table 3, BPs in these samples were below the detection limits, while the spiked recoveries were in the range of 80-120% except for the relatively low recovery of TCBPA (68.6%) in river water and the relatively high recovery of BPS (134%) and TMBPA (127%) in tap water at 0.5 μg/L spiked level, demonstrating the feasibility of the proposed method for determination of BPs in environmental water samples.

4 Conclusions

HFSLM extraction was combined with HPLC-UV for the first time to simultaneously determine five BPs in environmental waters. The developed HFSLM procedure provides high enrichment factor, good precision and reproducibility for the studied BPs. Although the extraction time is relatively long, it integrates extraction, clean-up and enrichment into one step, and consumes negligible organic solvents. Such application could be extended for determination of other trace pollutants in environmental samples.

Acknowledgements

This work was supported by the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB14020101), the National Natural Science Foundation of China (21025729, 21321004), and the Chinese Academy of Sciences (YSW2013B01) .

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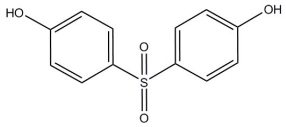
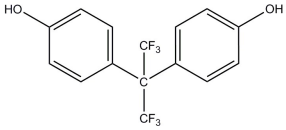
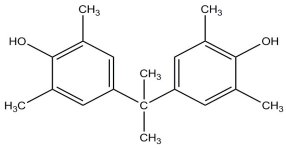
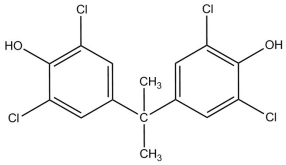
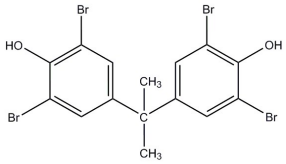
309

310 **Table 1.** Properties of the five studied bisphenol compounds

Chemical Name	Abbreviated Formula	Structual Formula	logK_{ow} [a]	pK_a [b]	Retention Time (min)
Bisphenol S	BPS		3.19	8.47	3.3
Bisphenol AF	BPAF		4.47	8.31	5.5
Tetramethylbisphenol A	TMBPA		5.27	10.3	6.9
Tetrachlorobisphenol A	TCBPA		5.68	6.42	7.7
Tetrabromobisphenol A	TBBPA		7.29	6.33	8.6

311 [a] the logarithm of 1-octanol/water partition coefficient (see Ref. [30] for BPS, value of BPAF estimated using PBT
312 Profiler see [31], the values of TMBPA, TCBPA and TBBPA calculated using Advanced Chemistry Development
313 (ACD/Labs) software referred to [32]).

314 [b] the negative logarithm form of the acidity dissociation constants (see Ref. [30] for BPS, Ref. [33] for BPAF, the
315 values of TMBPA, TCBPA and TBBPA referred to [32] as well).

316

Table 2. Analytical performance of the proposed extraction method.

Analytes	Enrichment factors	Detection limits (μg/L)	Precision[a] (RSD %, n = 5)	Linear range (μg/L)	Correlation coefficients (r)
BPS	2138	0.2	3.9	0.5-100	0.9935
BPAF	1731	0.1	6.3	0.2-100	0.9989
TMBPA	1464	0.2	2.6	0.5-100	0.9972
TCBPA	1405	0.1	5.6	0.2-100	0.9965
TBBPA	1370	0.1	8.8	0.2-100	0.9984

[a] Determined at 5 μg/L of each target analytes.

Table 3. Analytes concentration and spike recovery (mean ± SD, %, n = 3) in natural water samples by the proposed method.

Water samples	Spkied (μg/L)	BPS		BPAF		TMBPA		TCBPA		TBBPA	
		Detected (μg/L)	Recovery (%)	Detected (μg/L)	Recovery (%)	Detected (μg/L)	Recovery (%)	Detected (μg/L)	Recovery (%)	Detected (μg/L)	Recovery (%)
Wastewater	0	nd[a]	nd	nd	nd	nd	nd	nd	nd	nd	nd
	0.5	0.549 ± 0.010	110 ± 2	0.522 ± 0.047	104 ± 9	0.481 ± 0.088	96.2 ± 17.5	0.501 ± 0.059	100 ± 12	0.414 ± 0.006	82.8 ± 1.2
	1.0	0.885 ± 0.018	88.5 ± 1.8	0.808 ± 0.006	80.8 ± 0.6	1.02 ± 0.16	102 ± 16	0.903 ± 0.005	90.3 ± 0.5	1.05 ± 0.07	105 ± 7
Tap water	0	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	0.5	0.672 ± 0.052	134 ± 10	0.497 ± 0.124	99.4 ± 24.7	0.638 ± 0.075	127 ± 15	0.546 ± 0.076	109 ± 15	0.493 ± 0.133	98.6 ± 26.7
	1.0	0.839 ± 0.041	83.9 ± 4.1	1.09 ± 0.02	109 ± 2	0.972 ± 0.055	97.2 ± 5.5	0.964 ± 0.029	96.4 ± 2.9	1.09 ± 0.16	109 ± 16
River water	0	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	0.5	0.512 ± 0.025	102 ± 5	0.553 ± 0.034	111 ± 7	0.498 ± 0.036	100 ± 7	0.343 ± 0.010	68.6 ± 2.0	0.443 ± 0.005	88.5 ± 1.1
	1.0	1.05 ± 0.06	105 ± 6	0.933 ± 0.137	93.3 ± 13.7	1.10 ± 0.12	110 ± 12	1.15 ± 0.11	115 ± 11	0.902 ± 0.022	90.2 ± 2.2
Lake water	0	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	0.5	0.555 ± 0.018	111 ± 4	0.472 ± 0.046	94.3 ± 9.1	0.534 ± 0.030	107 ± 6	0.569 ± 0.046	114 ± 9	0.493 ± 0.014	98.5 ± 2.9
	1.0	0.909 ± 0.069	90.9 ± 6.9	0.879 ± 0.085	87.9 ± 8.5	1.00 ± 0.07	100 ± 7	0.946 ± 0.016	94.6 ± 1.6	1.01 ± 0.07	101 ± 7

[a] Not detected.

Figure captions

Figure 1. Effect of liquid membrane on enrichment of BPs. Donor, 200 mL of 0.01 M HCl spiked with 100 μg/L each of BPs; Acceptor, 0.1 M NaOH filled in the lumen of a 60 cm hollow fiber membrane; Shaking rate, 200 rpm; Extraction time: 1 h. Membrane liquids, pure dihexyl ether, pure undecane, dihexyl ether with 5% (m/v) TOPO, and undecane with 5% (m/v) TOPO.

Figure 2. Effect of NaOH concentration in acceptor on enrichment of BPs. Donor, 200 mL of reagent water spiked with 100 μg/L each of BPs and adjust to pH 4.0 with HCl; Acceptor, into the lumen of a 60 cm hollow fiber membrane was filled with NaOH with different concentrstions; Shaking rate, 200 rpm; Extraction time: 1 h. Membrane liquids, undecane with 5% (m/v) TOPO.

Figure 3. Effect of TOPO contents in the liquid membrane on enrichment of BPs. Donor, 200 mL of reagent water spiked with 100 μg/L each of BPs and adjust to pH 4.0 with HCl; Acceptor, 0.3 M NaOH filled in the lumen of a 60 cm hollow fiber membrane; Shaking rate, 200 rpm; Extraction time: 1 h. Membrane liquids, undecane with TOPO with different contents.

Figure 4. Effect of NaCl content in sample solution on enrichment of BPs. Donor, 500 mL reagent water spiked with 20 μg/L each of BPs and adjust to pH 4.0 with HCl, and added with NaCl with different contents; Acceptor, 0.3 M NaOH filled in the lumen of a 60 cm hollow fiber membrane; Shaking rate, 200 rpm; Extraction time: 1 h. Membrane liquids, undecane with 1.0% (m/v) TOPO.

Figure 5. Effect of extraction time on enrichment of BPs. Donor, 500 mL reagent water spiked with 20 μg/L each of BPs and adjust to pH 4.0 with HCl; Acceptor, 0.3 M NaOH filled in the lumen of a 60 cm hollow fiber membrane; Shaking rate, 200 rpm; Membrane liquids, undecane with 1.0% (m/v) TOPO.

Figure 1

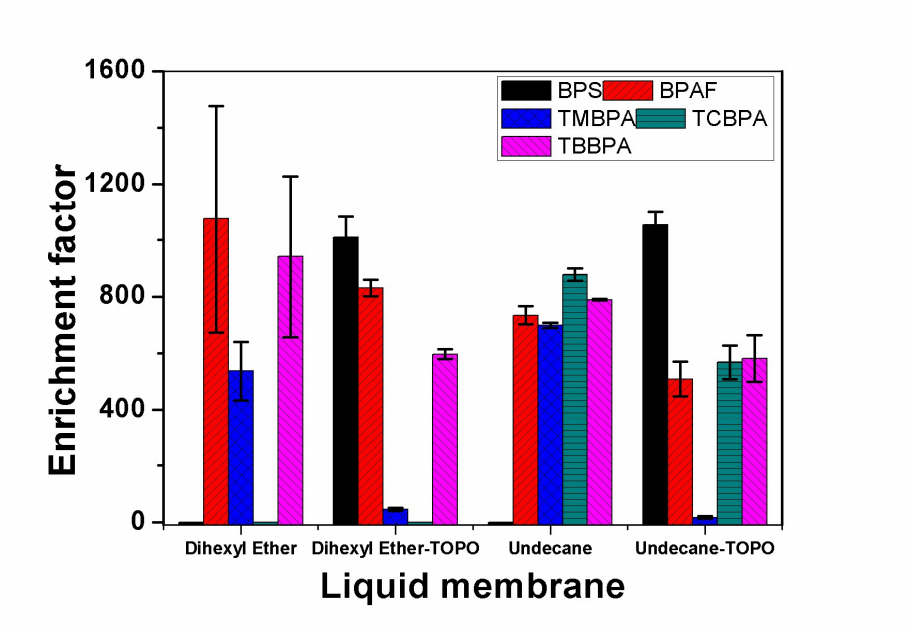


Figure 2

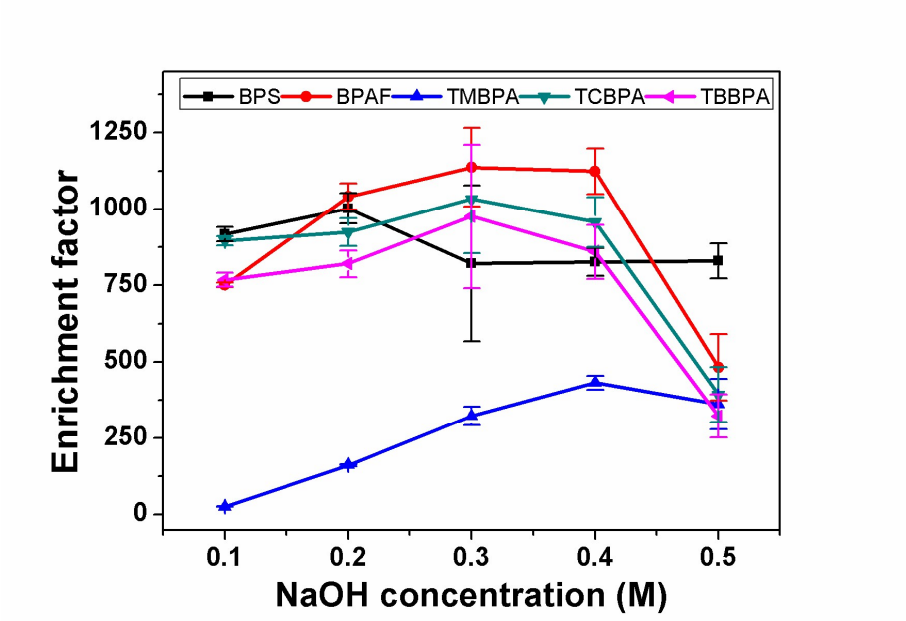


Figure 3

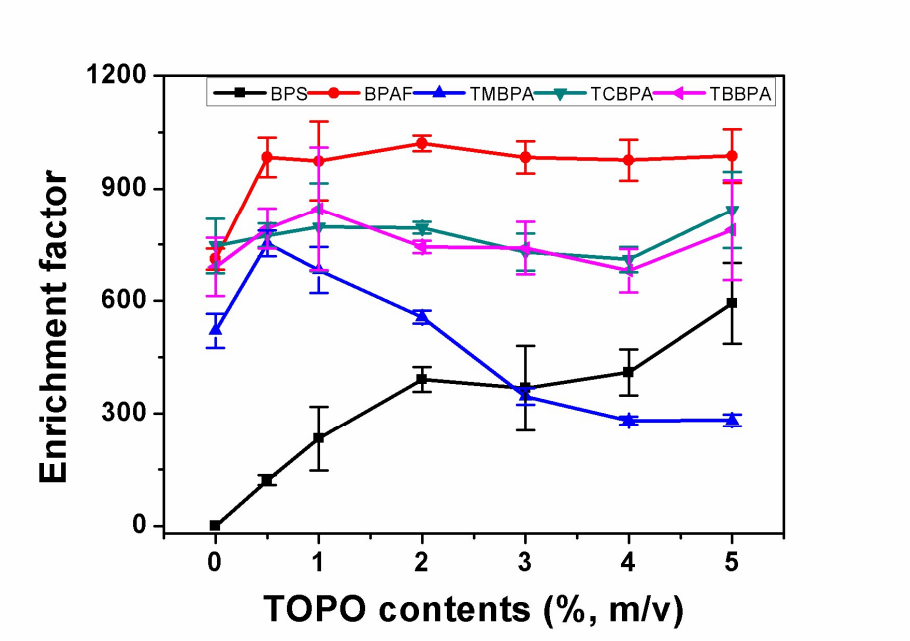


Figure 4

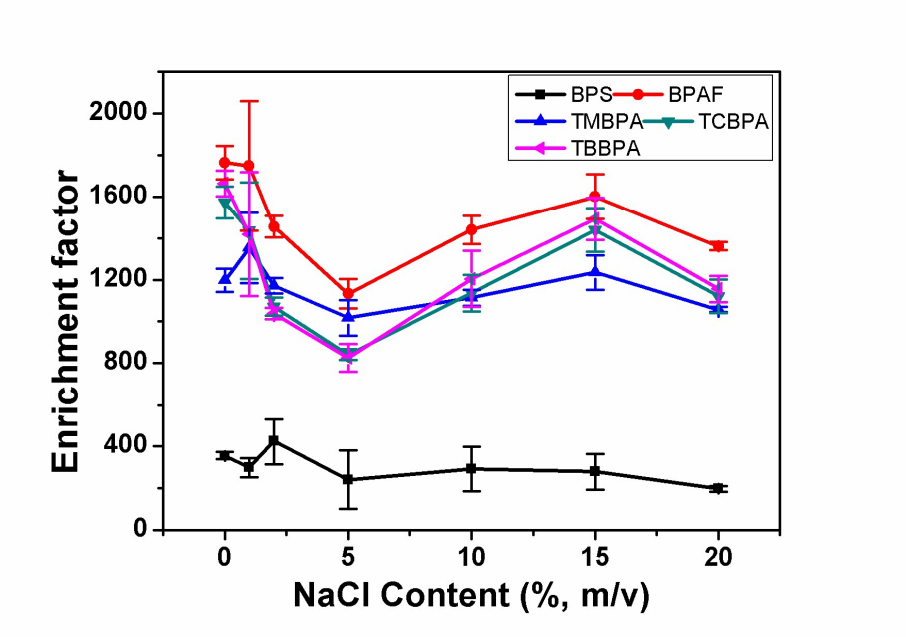
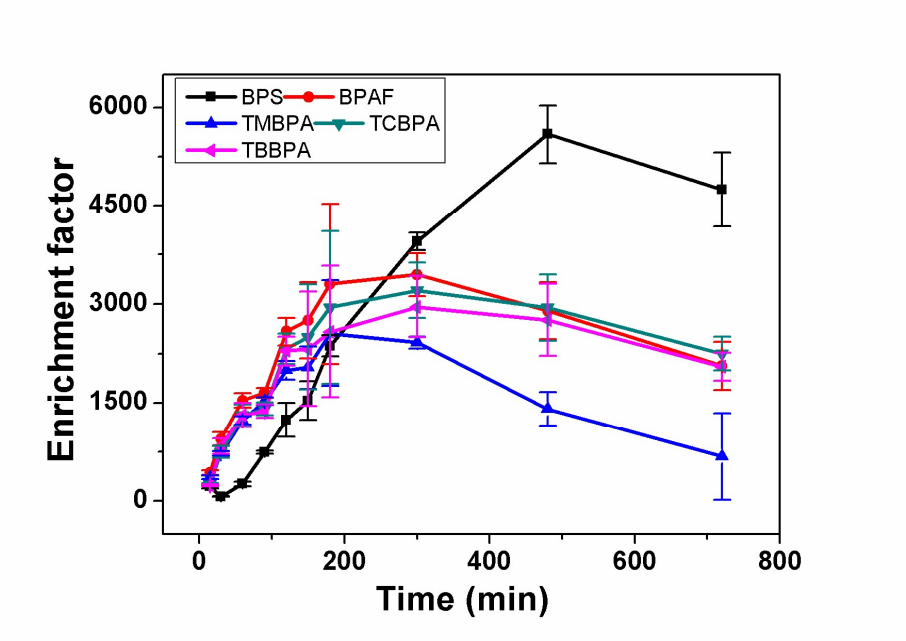


Figure 5



Graphical abstract

Hollow fiber supported liquid membrane (HFSLM) extraction provides high enrichment factor and sample clean-up for bisphenols in environmental waters.