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Eliminating the matrix effects of dissolved carbon dioxide and carbonate in extraction of triclosan and chlorophenols in environmental waters by hollow fiber supported liquid membrane

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Hollow fiber supported liquid membrane (HFSLM) extraction often suffers from matrix effects in extracting weak organic acids in environmental waters, but the reasons for which are unclear. This work systematically studied the influence of dissolved carbon dioxide and carbonate on the HFSLM extraction of analytes in environmental waters, by using triclosan and its two typical degradation products, 2,4-dichlorophenol and 2,4,6-trichlorophenol, as model compounds. HFSLM was conducted by immersing a HFSLM extraction device into a 200 mL water sample modified with 0.01 M HCl and 10% (m/v) NaCl, and shaking at 250 rpm for 90 min. The extraction device was prepared by immobilizing dihexyl ether on the polypropylene hollow fiber membrane wall (60 cm length, 50 μm wall thickness, 280 μm inner diameter), filling the fiber lumen with 0.4 M NaOH as acceptor, and closing the two ends of the fiber with aluminum foil. It was demonstrated that the dissolved carbon dioxide and carbonate present in environmental samples reduces the acceptor pH and thus the recovery of target analytes, and purging the acidified sample with $\sim 50 \text{ mL min}^{-1} \text{ N}_2$ for 15 min is a very efficient approach to eliminate this matrix effect. With this purging pretreatment, the recoveries of the analytes in environmental samples increased substantially from below 40% to between 63% and 121%. For the three analytes, the proposed HFSLM method provided enrichment factors in the range of 1090–1322, and detection limits in the range of 0.1–0.2 $\mu\text{g L}^{-1}$ by coupling with an ultra-performance liquid chromatography-mass spectrometry system.

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1 Introduction

Supported liquid membrane extraction (SLM) is a highly efficient and selective sample pretreatment technique for the enrichment of weak organic acids/bases and metal ions.^{1–3} In principle, the extraction process in SLM involves the partitioning of the neutral form of analytes from the sample into the organic liquid supported on the membrane, and the back-extraction of analytes from the membrane liquid into the acceptor where the analytes were ionized. While flat membranes were adopted for supporting the membrane liquid in the early days of SLM, hollow fiber supported liquid membrane (HFSLM) is commonly used in sample preparation nowadays for its simplicity and low cost.^{4–6}

Most HFSLM extraction for environmental samples was conducted in the regime of incomplete extraction and with a very large sample-to-acceptor ratio, *i.e.*, a small part of the

target analytes were extracted from a large volume of sample into a small volume of acceptor to obtain a high enrichment factor in a short extraction time.^{7–9} In this approach, some matrix substances can be co-extracted into the acceptor which reduces the extraction efficiency of target analytes. Although the matrix effects can be reduced by performing HFSLM in a complete extraction mode, it requires a long time to achieve complete extraction.^{10,11} Therefore, it remains a great challenge to eliminate the matrix effects in HFSLM.

Many organic pollutants are weak organic acids that are suitable for extraction by HFSLM. During the HFSLM extraction of target weak organic acids, the dissolved carbon dioxide and carbonate that are widely present in environmental waters are co-extracted by partitioning in the form of CO_2 or H_2CO_3 into the liquid membrane and then trapping into the acceptor as carbonate.¹² Given the high concentration of dissolved carbon dioxide and carbonate (at mM level)¹³ in comparison to the target analytes (at nM level), the trapping of dissolved carbon dioxide and carbonate in the basic acceptor might significantly reduce the acceptor pH and therefore the extraction efficiency of the target analytes. As the dissolved

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carbon dioxide and carbonate in reagent water used to prepare standard solutions are negligible, the reduced extraction efficiency of target analytes resulted from the relatively high contents of dissolved carbon dioxide and carbonate in real environmental samples, giving rise to low recovery of analytes. Our previous study indicates that, in both continuous-flow liquid membrane extraction^{14,15} and HFSLM,¹⁶ the use of $\text{NaHCO}_3\text{--Na}_2\text{CO}_3$ buffer as acceptor alleviates the influence of dissolved carbon dioxide and carbonate, as the CO_2 has lower solubility in $\text{NaHCO}_3\text{--Na}_2\text{CO}_3$ buffer in comparison with other buffers. Very recently, it was reported that the carbonate in sample solutions reduced the extraction efficiency of substituted phenols in HFSLM pretreatment of environmental samples.¹⁷ Nevertheless, there is no systematic study on the influence of dissolved carbon dioxide and carbonate on the HFSLM extraction of analytes in environmental waters.

The objective of this study is to understand the mechanism of the reduction of extraction efficiency by dissolved carbon dioxide and carbonate, and develop efficient methods to eliminate their influence in HFSLM of weak acids. To this end, triclosan (5-chloro-2-(2,4-dichlorophenoxy)phenol, TCS) and its two typical breakdown products of reaction with free chlorine, 2,4-dichlorophenol (DCP) and 2,4,6-trichlorophenol (TCP),¹⁸ were adopted as model compounds. These three compounds are widely present in environmental waters and are weak organic acids with pK_a and K_{ow} values (Table 1) that are suitable for extraction by SLM.¹⁹ TCS is extensively used as a broad-spectrum antibacterial agent in many personal care products.²⁰ The wide application of TCS has led to its extensive release into the environment, and TCS has become a ubiquitous pollutant in waste and surface water.^{21–26} We first optimized the key parameters affecting the extraction efficiency of HFSLM, including the membrane liquid for HFSLM, pH and salinity of the samples, and acceptor buffer pH. Then, the interference of dissolved carbon dioxide and carbonate was evaluated and an approach for efficient elimination of this interference was developed. Finally, this proposed procedure was applied to determine aqueous concentrations of TCS and related chlorophenols (CPs) in environmental water samples.

Fig. 1 Effect of sample (donor) pH on the enrichment factor. Donor: 15 mL of aqueous solution with 20% (m/v) NaCl, $10\ \mu\text{g L}^{-1}$ each of the analytes and varied pH; acceptor: 0.1 M NaOH; extraction time: 30 min.

2 Experimental

2.1 Reagents and materials

A standard solution of triclosan (TCS, $1000\ \text{mg L}^{-1}$) was prepared by dissolving appropriate amounts of TCS (99.5%), purchased from Dr Ehrenstorfer (Augsburg, Germany), in HPLC-grade methanol. Individual standards ($1000\ \text{mg L}^{-1}$) of 2,4-dichlorophenol (DCP) and 2,4,6-trichlorophenol (TCP) were purchased from the National Research Center for Reference Material (Beijing, China). Standard stock solutions ($100\ \text{mg L}^{-1}$) were prepared by diluting the above individual standards with HPLC-grade methanol and stored at $4\ ^\circ\text{C}$. Working solutions were obtained daily by appropriate dilution of the stock solutions with water. HPLC-grade methanol and acetonitrile were obtained from J.T. Baker (Phillipsburg, NJ, USA). Dihexyl ether (DHE) was purchased from Tokyo Chemical Industry Co. Ltd (Tokyo, Japan). All other chemicals were of analytical grade or above and purchased from Beijing Chemicals Corporation (Beijing, China). Ultrapure water prepared by a Milli-Q SP reagent water system from Millipore (Milford, MA, USA) was used throughout the experiments. The 50/280 Accurel polypropylene hollow fiber membrane (50 μm wall thickness, 280 μm inner diameter, 0.1 μm pore size, 60% porosity) was purchased from Membrana GmbH (Wuppertal, Germany). A BD Micro-Fine syringe (with a needle of 0.30 mm outer diameter

Table 1 The molecular weight (MW), acid dissociation constant (pK_a), partition coefficient ($\log K_{ow}$) and LC-ESI-MS/MS detection parameters of the studied analytes

Analytes	M_w	pK_a^a	$\log K_{ow}^a$	Retention time (min)	Transitions	Collision energy (eV)
DCP	163.0	7.90	2.98	4.96	161.0 $\rightarrow$ 125.2	19
					163.0 $\rightarrow$ 125.2	18
					163.0 $\rightarrow$ 127.2	18
TCP	197.4	6.10	3.56	5.35	195.0 $\rightarrow$ 159.1	23
					97.0 $\rightarrow$ 161.1	25
					286.8 $\rightarrow$ 35.5	10
TCS	289.5	7.8	4.8	5.72	287.0 $\rightarrow$ 35.4	11
					288.8 $\rightarrow$ 35.6	12
					289.0 $\rightarrow$ 35.4	11
					289.0 $\rightarrow$ 35.4	12

^a Data cited from ref. 27.

and 8 mm length, 0.5 mL) obtained from BD Consumer Healthcare (Franklin Lakes, NJ, USA) was used to fill the acceptor into the lumen of the hollow fiber for extraction and to flush out the acceptor.

2.2 Extraction procedure

The HFSLM was performed as described in our previous study with some modifications.¹⁶ In short, the lumen of the hollow fiber tubing (~60 cm length) was flushed and filled with acceptor solution (0.4 M NaOH) using a BD Micro-Fine Syringe. Then, the pores of the hollow fiber wall were impregnated with the liquid membrane by immersing the fiber in the organic solvent for 2 min. After that, the lumen of the fiber was flushed carefully and fully filled with the acceptor solution, and the two ends of the fiber were folded and enveloped with a strip of aluminum foil. After washing away the surplus membrane liquid on the surface of the fiber with reagent water, the prepared extraction device was placed and immersed completely into the 200 mL sample containing 0.01 M HCl and held in a 250 mL flask. The sample with the extraction device was shaken on an orbital shaker (IKA KS 4000i control, Staufen im Breisgau, Germany) at 250 rpm to perform the extraction and enrichment. After extraction for 90 min, the hollow fiber extraction device was collected and one sealed end of the fiber was cut and connected to the needle of a BD Micro-Fine syringe filled with air. After cutting the other sealed end of the fiber, the acceptor containing the extracted analytes (~40 μ L) was flushed from the fiber lumen into a clean and dry glass insert of a sample vial (100 μ L, Alltech, Deerfield, IL, USA).

2.3 LC-MS/MS determination

Separation of TCS, DCP and TCP was accomplished using an ultra-performance liquid chromatography (UPLC) system (ACQUITY UPLC, Waters, USA) equipped with a Waters BEH C₈ column (2.1 $\times$ 50 mm, 1.7 μ m). The injection volume was 10 μ L. For the gradient elution, a binary mobile phase of an aqueous solution of 0.1% formic acid (A) and methanol containing 0.1% formic acid (B) at a flow rate of 0.2 mL min⁻¹ was utilized. The gradient elution program was as follows: 20% B during 0–1 min, then increasing to 100% B from 1–5 min and keeping constant from 5–6 min, decreasing to 20% B from 6–6.1 min and keeping constant for 2 min. The retention time of each analyte was shown in Table 1.

A TSQ Quantum Access (Thermo Scientific, USA) triple quadrupole mass spectrometer was interfaced to the UPLC for determination of the analytes. The electrospray ionization (ESI) was run in the negative ion mode, and the best conditions were set as follows: peak width resolution 0.7 m/z , spray voltage 4500 V, sheath gas pressure 30 units, aux gas pressure 20 units, and capillary temperature 350 °C. The selected reaction monitoring (SRM) transitions were listed in Table 1.

The calibration curves were obtained by injecting 10 μ L of standards with various concentrations of analytes into the UPLC-MS/MS system, and plotting the obtained peak area against the analyte concentration. The nine standards contain 0, 0.5, 1, 2, 5, 10, 20, 50 and 100 μ g L⁻¹ each of the analyte. Real

sample analysis was calibrated with external standard calibration by conducting the same extraction procedure for both the standard solutions and the real samples.

2.4 Sample collection and preparation

Lake water samples were collected from the Shisanling Lake (Beijing, China), river water samples were collected from Chaobai River (Beijing, China), and the wastewater samples were from effluents of the Gaobeidian municipal wastewater treatment plant (Beijing, China). Mineral drinking water was purchased from a local supermarket in Beijing. Prior to the HFSLM, the samples were adjusted to pH 2.0 with HCl and purged with N₂ for 15 min to eliminate dissolved carbon dioxide and carbonate.

3 Results and discussion

3.1 Optimization of the HFSLM parameters

The type of membrane liquid is a crucial parameter that affects the extraction efficiency. Undecane, dihexyl ether, and 1-octyl-3-methylimidazolium hexafluorophosphate ionic liquid were tested as membrane liquids in this study. By using 15 mL sample solution prepared by spiking 100 μ g L⁻¹ each of the analytes into a solution containing 0.01 M HCl and 20% (m/v) NaCl as the donor, and 0.1 M NaOH as acceptor, the extraction was performed at 250 rpm for 30 min. Experiments showed that dihexyl ether gave rise to the highest enrichment factor for all the three analytes. Therefore, dihexyl ether was used as the membrane liquid in the following studies.

The extraction efficiency in SLM of organic weak acids/bases is strongly dependent on the pH of sample (donor) and acceptor, as well as the species of acceptor. Since the three analytes are weak acids with pK_a values in the range of 6.10–7.90, the pH value should be less than 3 for the sample (donor) and above 11 for the acceptor to trap these analytes efficiently.²⁸ By using 0.1 M NaOH as the acceptor, the sample pH was optimized in the range of pH 1.0–6.0. Results shown in Fig. 1 indicate that the highest enrichment factor was at pH 2.0, thus all the samples were acidified by adding 0.01 M HCl in the following studies.

Our previous study showed that in comparison with other buffers such as phosphate, glycine and sodium tetraborate, higher extraction rates and better repeatability were obtained by using NaOH as the acceptor.¹¹ However, NaHCO₃–Na₂CO₃ buffer as acceptor provided the highest buffer capacity for the dissolved carbon dioxide and carbonate present in surface water.^{14–16} Given the buffer capacity of NaHCO₃–Na₂CO₃ is relatively low at pH 11, which is the lowest pH for efficient trapping of the analytes, NaOH was adopted as the acceptor in this study. The NaOH acceptor concentration was optimized in the range of 0.05–0.5 M, by using a 15 mL sample spiked with 100 μ g L⁻¹ each of the analytes, 0.01 M HCl and 20% (m/v) NaCl. Results showed that the highest enrichment factor was obtained at 0.3 M NaOH for all the analytes. Considering that real samples may contain matrix substances that can be

co-extracted and consume NaOH, 0.4 M NaOH was adopted as acceptor in the following studies.

It is well known that the addition of salt into the donor enhances the extraction efficiency of some organic compounds in SLM. This salt-out effect was studied by adding various concentrations of NaCl (0–25%, m/v) into the sample solution. Results shown in Fig. 2 illustrate that higher enrichment factors were obtained at zero and 10% NaCl for all three analytes. It is well known that real environmental water samples have salinity in the range of 0–3.5% NaCl. By adding 10% NaCl into the samples, the salinity in extraction samples was in the range of 10–13.5%. As shown in Fig. 2, the variation of extraction efficiency in the range of 10–13.5% NaCl is lower than that in the range of 0–3.5% NaCl. In the following studies, 10% NaCl was added into the sample solution.

The influence of sample volume was studied using a donor containing $100\ \mu\text{g L}^{-1}$ each of the analytes, 0.01 M HCl and 10% NaCl, and an acceptor of 0.4 M NaOH. The results showed that the enrichment factor increased with the donor (sample) volume up to 200 mL and then leveled off. Therefore, 200 mL of sample was preferred for obtaining low detection limits.

Experiments showed that the enrichment factor increased markedly with shaking rate in the range of 0–250 rpm, suggesting that the diffusion of analytes through the aqueous diffusion layer is the rate limiting process. By using 250 rpm as an optimum shaking rate, the effect of extraction time was studied in the range of 15–150 min. Results showed that the enrichment factor increased markedly with time up to 90 min for all three analytes. With the further increase of extraction time from 90 min to 150 min, the extraction efficiency slightly increased for TCS but decreased for DCP and TCP. In the following studies, samples were extracted at 250 rpm for 90 min.

3.2 Effect of dissolved carbon dioxide and carbonate

Environmental waters usually contain dissolved carbon dioxide and carbonate at levels much higher than that of the target analytes. During the HFSLM processes, the dissolved carbon dioxide and carbonate in water samples can be trapped in the basic acceptor, which reduces the acceptor pH and thereafter the recovery of target analytes. To evaluate the effect of dissolved carbon dioxide and carbonate in the samples, standard

solutions prepared with reagent water and two real surface water samples (river water and mineral drinking water) were tested under the above optimized HFSLM conditions. It was demonstrated that while the acceptor pH maintained its initial value (13.5) for the standard sample solution, the acceptor pH decreased from 13.5 to 9.5 for river water and to 12.5 for mineral drinking water. When the two real surface water samples were acidified by spiking with 0.01 M HCl and purged with N_2 at about $50\ \text{mL min}^{-1}$ for 30 min, however, the acceptor pH kept its initial value (13.5) after conducting the proposed HFSLM. This result suggests that the dissolved carbon dioxide and carbonate in real water samples can significantly reduce the basic acceptor pH, and this effect can be eliminated by acidifying the sample to transform carbonate to CO_2 and purging the sample solution with N_2 .

The negative effect of dissolved carbon dioxide and carbonate on the HFSLM extraction was further evidenced by measuring the spiked recoveries of TCS and CPs. It was found that the recoveries at a $5\ \mu\text{g L}^{-1}$ spiking level were below 20% for all the three analytes in the two real samples. This result agreed well with that of a very recent study which reported the reduction of extraction efficiency of substituted phenols by carbonate in HFSLM pretreatment of environmental samples.¹⁷

3.3 Elimination of the matrix effects of dissolved carbon dioxide and carbonate

To eliminate the negative effect of dissolved carbon dioxide and carbonate, into respective samples of reagent water, river water, and river water spiked with 5 mM Na_2CO_3 , was added 0.01 M HCl and 10% (m/v) NaCl, they were then spiked with $100\ \mu\text{g L}^{-1}$ each of the analytes and purged with N_2 at $\sim 50\ \text{mL min}^{-1}$ for various times before subjecting to HFSLM. Results shown in Fig. 3 indicate that for the reagent water, the acceptor maintained its initial pH (13.5) regardless of the purging time. For the river water with and without the addition of 5 mM Na_2CO_3 , the acceptor pH increased with the purging time, suggesting the dissolved carbon dioxide and carbonate were purged out of the sample. When the purging time was prolonged up to 15 min, the acceptor kept its initial pH (13.5) after HFSLM extraction.

To further verify the effectiveness of purging in elimination of the matrix effects of dissolved carbon dioxide and carbonate, three real environmental samples (river water, lake water and wastewater) were spiked with $5\ \mu\text{g L}^{-1}$ each of the three analytes, and subject to HFSLM directly and after purging with N_2 at $\sim 50\ \text{mL min}^{-1}$ for 15 min, respectively. As shown in Fig. 4, the recoveries of the analytes increased substantially from below 40% to above 84%, demonstrating purging with N_2 is a very efficient approach to eliminate the matrix effects of dissolved carbon dioxide and carbonate. In the following studies, real samples were purged with N_2 at $\sim 50\ \text{mL min}^{-1}$ for 15 min before conducting the HFSLM extraction.

3.4 Evaluation of the method performance

The analytical performance characteristics of the proposed method were determined with nine synthetic standard

Fig. 2 Effect of salinity (NaCl) on the enrichment factor. Donor: 15 mL of aqueous solutions containing 0.01 M HCl and $10\ \mu\text{g L}^{-1}$ each of the analytes; acceptor: 0.4 M NaOH; extraction time, 30 min.

Fig. 3 Effect of purging time on the acceptor pH after extraction. Donor: 200 mL of samples containing 0.01 M HCl, 10% (m/v) NaCl, and $10 \mu\text{g L}^{-1}$ each of the analytes; acceptor: 0.4 M NaOH.

Table 2 Analytical performance of the proposed procedure

	TCS	DCP	TCP
Linear range ($\mu\text{g L}^{-1}$)	1–100	0.5–100	0.5–100
Correlation coefficient (<i>R</i>)	0.9982	0.9998	0.9987
Enrichment factor	1095	1090	1322
Limit of detection (LOD, $\mu\text{g L}^{-1}$)	0.2	0.2	0.1
Precision ^a (RSD, %)	4.8	3.8	9.3

^a Determined at $5 \mu\text{g L}^{-1}$ level.

solutions with various concentrations of the analytes. Results shown in Table 2 indicate that this proposed method has good linearity ($R = 0.9982\text{--}0.9998$), excellent precisions ($\text{RSD} < 9.3\%$, $n = 5$) at $5 \mu\text{g L}^{-1}$ level, and low detection limits ($\sim 0.1\text{--}0.2 \mu\text{g L}^{-1}$, $S/N = 3$). The enrichment factors, calculated from the ratio of the final analyte concentration in the acceptor to the initial analyte concentration in the sample, were in the range of 1090–1322. In comparison with the enrichment in SPE, which is usually below 500, the higher enrichment factor of this HFSLM procedure indicates that the proposed method is very efficient for the enrichment of the target analytes.

Fig. 4 Spike recovery of the three target analytes (TCS, DCP, and TCP) in real water samples without and with pretreatment of N_2 -purging (RW, river water; LW, lake water; WW, wastewater).

3.5 Application in the analysis of real water samples

The proposed method was applied to analyze four real water samples including mineral drinking water, river water, lake water, and wastewater from the effluent of a municipal wastewater treatment plant. The recoveries for the analytes were determined at 2.5 and $5 \mu\text{g L}^{-1}$ spiking levels. From the results shown in Table 3, the recoveries ranged from 80.4% to 121%, except for the relatively low recovery of TCS (63.4%) in the mineral drinking water at $5 \mu\text{g L}^{-1}$, indicating that the proposed method is reliable for the determination of trace TCS and CPs in surface waters.

4 Conclusions

This study demonstrated that, in the HFSLM of weak acids with basic acceptor, the relatively large amount of dissolved carbon dioxide and carbonate in environmental samples can severely reduce the acceptor pH and thus the recovery of target analytes, and purging the sample with N_2 after acidification is a very

Table 3 Analyte concentration and spike recovery (mean $\pm$ SD, $n = 3$) of real samples determined by the proposed method

Sample	Spiked ($\mu\text{g L}^{-1}$)	TCS		DCP		TCP	
		Determined ($\mu\text{g L}^{-1}$)	Recovery (%)	Determined ($\mu\text{g L}^{-1}$)	Recovery (%)	Determined ($\mu\text{g L}^{-1}$)	Recovery (%)
Mineral drinking water	0	0.20 ± 0.04	—	ND ^a	—	ND	—
	2.5	2.21 ± 0.41	80.4 ± 16.2	2.41 ± 0.15	96.4 ± 5.9	2.67 ± 0.21	106 ± 8
	5	3.37 ± 0.20	63.4 ± 4.0	5.24 ± 0.57	105 ± 11	4.99 ± 0.07	99.8 ± 1.4
River water	0	ND	—	0.33 ± 0.02	—	0.13 ± 0.05	—
	2.5	2.91 ± 0.31	116 ± 13	3.13 ± 0.40	112 ± 16	2.92 ± 0.50	112 ± 20
	5	5.53 ± 0.35	111 ± 7	6.40 ± 0.24	121 ± 5	4.93 ± 0.12	95.9 ± 2.5
Lake water	0	ND	—	ND	—	ND	—
	2.5	2.21 ± 0.01	88.4 ± 0.1	2.16 ± 0.07	86.4 ± 2.8	2.6 ± 0.30	104 ± 12
	5	4.89 ± 0.68	97.8 ± 13.6	4.99 ± 0.08	99.8 ± 1.5	4.71 ± 0.21	94.2 ± 4.2
Wastewater	0	0.24 ± 0.08	—	ND	—	ND	—
	2.5	2.51 ± 0.11	90.8 ± 9.0	2.42 ± 0.13	96.8 ± 5.1	2.30 ± 0.08	92.2 ± 3.2
	5	4.63 ± 0.24	87.8 ± 4.7	4.79 ± 0.08	95.8 ± 1.6	4.79 ± 0.44	95.8 ± 8.7

^a ND: not detected.

efficient approach to eliminate their interference. In addition, a novel method based on HFSLM coupled with UPLC-MS/MS was developed for the simultaneous determination of trace TCS and CPs in surface waters. The proposed HFSLM method integrates extraction, clean-up and enrichment into one step, and provides high enrichment factor, good precision, and reproducibility for the studied analytes.

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