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Fast trace determination of nine odorant and estrogenic chloro- and bromo-phenolic compounds in real water samples through automated solid-phase extraction coupled with liquid chromatography tandem mass spectrometry

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Abstract

A fast and reliable method was developed for simultaneous trace determination of nine odorous and estrogenic chloro- and bromo-phenolic compounds (CPs and BPs) in water samples using solid-phase extraction (SPE) coupled with liquid chromatography tandem mass spectrometry (LC-MS/MS). For sample preparation, the extraction efficiencies of two widely applied cartridges Oasis HLB and Sep-Pak C18 were compared, and the Oasis HLB cartridge showed much better extraction performance; pH of water sample also plays important role on extraction, and pH = 2–3 was found to be most appropriate. For separation of the target compounds, small addition of ammonium hydroxide can obviously improve the detection sensitivity, and the optimized addition concentration was determined as 0.2%. The developed efficient method was validated and showed excellent linearity ($R^2 > 0.995$), low limit of detection (LOD, 1.9–6.2 ng/L), and good recovery efficiencies of 57–95% in surface and tap water with low relative standard deviation (RSD, 1.3–17.4%). The developed method was finally applied to one tap and one surface water samples and most of these nine targets were detected, but all of them were below their odor thresholds, and their estrogen equivalent (EEQ) were also very low.

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Introduction

Chlorophenols (CPs) and bromophenols (BPs) are one of the most important industrial raw materials, which have been extensively used in industrial manufacturing. For instance, CPs are widely used in production of pesticides, herbicides, wood preservatives, antiseptic, disinfectants, plastic, dye, and pharmaceutical industries (Ho et al. 2008). In our daily life, these products can be seen everywhere. On the other hand, BPs are one of the main constituent of flame retardants, which have been widely used in building materials, electric appliances, polyurethane foams, and textiles (Feng et al. 2016; Hassenklover et al. 2006). It is reported that 2,4,6-tribromophenol (2,4,6-TBP), 2,4-dibromophenol (2,4-DBP), and pentabromophenol (PBP) have been being increasingly used as a group of novel brominated flame retardants (BFRs) in epoxy and phenolic resins to replace the banned traditional formulations (Covaci et al. 2011). Meanwhile, BPs have also been widely used in different products such

as polymer intermediates and wood preservatives (Jiang et al. 2017). In addition, CPs and BPs can also be generated from disinfection in water treatment process (Sim et al. 2009).

Although for their wide applications mentioned above, CPs and BPs are toxic, carcinogenic, and poorly biodegradable in the natural environment, and the US EPA has classified several CPs as priority pollutants such as 2-chlorophenol (2-CP), 2,4-dichlorophenol (2,4-DCP), and 2,4,6-trichlorophenol (2,4,6-TCP, USEPA, 1980). Meanwhile, 2,4,6-TBP was reported to be neurotoxic and can be transformed into more toxic pollutants at certain exposure condition (Lyubimov et al. 1998). In addition, some industrial phenolic compounds including CPs and BPs are one group of important endocrine disrupting compounds (EDCs), and due to their potential adverse effects on humans and wildlife, EDCs have drawn much attention in the last decades (Liu et al. 2015a, 2015b, 2015c; Huang et al. 2017). The term EDCs covers a broad class of compounds, including natural/synthetic estrogens, natural/synthetic androgens, phytoestrogens, mycoestrogens, progestins, and industrial chemicals (Liu et al. 2009a, Liu et al. 2011a, 2015d). Although most industrial phenolic compounds are very weak estrogenic chemicals, but for their possible high concentration in the environment, their estrogenic effects may not be neglected. For example, 2,4-di-tert-phenol is a weak estrogenic compound, and its main source is derived from the degradation of phosphonite-based antioxidant such as antioxidant type 168 (Loschner et al. 2011, Liu et al. 2017). The migrating concentration from plastic pipe into tap water can be as high as 113 μg/L at room temperature, and the corresponding estrogen equivalent (EEQ) level has exceeded a threshold that may do harm to fish (Liu et al. 2017). In some countries, many EDCs have been in the list items of drinking water quality standards. For example, bisphenol A, diethyl phthalate, and di-butyl phthalate are three EDCs which are at present regulated in the Chinese drinking water quality standard, while 17β-estradiol (E2) and other four EDCs have been regulated in the latest Japanese drinking water quality standard (Liu et al. 2016).

In addition, many CPs and BPs are known malodorous compounds in water and foods (Kim and Kim 2000; Olsen et al. 2002; Chung et al. 2003; Legler and Brouwer 2003; Blythe et al. 2006). For instance, 2-bromophenol (2-BPs), 4-bromophenol (4-BPs), 2,4-DBP, 2,6-dibromophenol (2,6-DBP), and 2,4,6-TBP are common odor compounds in sea foods and the odor thresholds of 2,6-DBP and 2,4,6-TBP in water were reported to be 85 and 3000 ng/L, respectively(Whitfield et al. 2002). 2-t-BP was identified as the odor-causing compound in a serious drinking water odor incident that occurred at Hangzhou, China, in 2013 (Liu et al. 2016). To find the odor-causing compounds as soon as possible, fast and efficient analytical method plays a very important

role. Therefore, except for the screening of their estrogenic effects that CPs and BPs may cause, odor screening of these compounds is also urgent.

For the abovementioned reasons, conventional monitoring of these CPs and BPs in water is necessary, important, and urgent. For determination of volatile odorous compounds, the gas chromatography (GC)-based analysis is the most widely applied methods (Cortada et al. 2011; Deng et al. 2011; Insa et al. 2004; Ma et al. 2012; Benanou et al. 2003; Ding et al. 2014; Kim et al. 2015). With the wide application of solid-phase microextraction (SPME) technique that is used for automation of sample preparation, the GC-based method has become to be more convenient than before. In our previous work, we have attempted to establish a method for 17 CPs and BPs with headspace solid-phase microextraction (HS-SPME) coupled with GC-MS. However, we only established an effective method for six CPs and BPs and failed to include the other 11 compounds (Yuan et al. 2016). The main reason for the failure is that BPs and CPs are polar compounds with a hydroxyl function group, and their direct analyses with GC-MS are thus insensitive. To improve the detection sensitivity, a derivatization process with BSTFA plus 1% TMCS was adopted, and a sensitive method was successfully established with online HS-SPME followed by on-fiber derivatization coupled with GC-MS (Yuan et al. 2017). However, the vapor gas of derivatization reagent could dissolve the commercial fiber coating, thus the fiber lifetime was greatly reduced, which would hinder the wide application of the above developed method. Therefore, some other efficient method is necessary to be developed. Compared to GC-based method, liquid chromatography tandem mass spectrometry (LC-MS/MS) analysis is derivatization free and showed much lower detection limits under carefully controlled conditions, which has been widely applied for non-volatile micropollutants such as estrogens, androgens, phytoestrogens, and pharmaceuticals and personal care products (Carmona et al. 2014; Liu et al. 2009b, 2010c, 2011a; Yang et al. 2017). Meanwhile, LC-MS/MS method has also been successfully applied for some volatile chemicals such as pesticides, CPs, or BPs (Vidal et al. 2004; Aguilar et al. 2017; Cai et al. 2016; Chi et al. 2017). However, to the best of our knowledge, there is no developed method for simultaneous analysis of CPs and BPs. Hence, the main objective of this work was to develop a fast and effective analytical method for simultaneous determination of CPs and BPs in surface waters by coupling SPE with LC-MS/MS.

Materials and method

Reagents and materials

Nine target compounds were selected, including 4-chlorophenol (4-CP), 4-chloro-2-methlyphenol (4-C-2-MP), 4-chloro-3-methylphenol (4-C-3-MP), 2,6-dichlorophenol

(2,6-DCP), 2-bromophenol (2-BP), 2,4,5-trichlorophenol (2,4,5-TCP), 4-BP, 2,6-DBP, and 2,4,6-TBPs. The purity of each compound was at least 99%. Some basic information of the nine target chemicals was listed in Table 1, in which some physicochemical properties, odor thresholds, and estrogenic potencies were included.

Stock solution of each individual standard at concentration of 1000 mg/L was prepared by dissolving 0.01 g standard compound into 10 mL methanol. The mixed standard stock solution of the nine target phenolic compounds was prepared in methanol at 10 mg/L, and all the stock solutions were stored in dark at −20 °C. Sodium chloride (analytical grade, China) was purified in a furnace oven at 450 °C for 2 h before use. Ultrapure water was obtained from a Milli-Q Reference water purification system (Merck Millipore, USA).

Two solid-phase extraction cartridges Oasis HLB (500 mg, 6cc) and Sep-Pak C18 (500 mg, 6cc) were purchased from Waters (Milford, MA, USA). In addition, other chemical reagents and solvents such as HPLC grade methanol and dichloromethane as well as ammonium hydroxide were all bought from ANPEL Laboratory Technologies Inc. (Shanghai, China).

Sample preparation

Concentrating of the nine phenolic compounds in water sample was carried out by automatic SPE equipment (AQUA Trace ASPE799 Assistant, Shimadzu, Japan). The extraction performances of two SPE cartridges, Oasis HLB, and Sep-Pak C18 were compared. Five hundred milliliter filtered surface or tap water with 0.47-mm Whatman glass microfilter was pH adjusted with hydrochloric acid, and solution pH was also optimized at three different ranges (pH = 7, 4–5, 2–3). For a single SPE process, the cartridge was firstly conditioned by 10 mL mixture of methanol-dichloromethane (2/8, v/v), followed by 10 mL

methanol, and then 10 mL ultrapure water at a flow rate of 20 mL/min. After that, 500 mL of surface water sample was loaded onto the SPE cartridge at a flow rate of 10 mL/min. After the sample loading, the SPE cartridge was rinsed by 10 mL of ultrapure water with a flow rate of 20 mL/min to remove some impurities. In order to remove the remaining water, the SPE cartridge was dried for 30 min under vacuum. When the drying process was finished, the targets were eluted with 5 mL mixture of methanol-dichloromethane (2/8, v/v) at a flow rate of 1 mL/min. The eluate was dried to about 200 μL under a gentle stream of nitrogen, and it was transferred into a LC injection vial. A mixed solution of methanol water (5/95, v/v) was added to the LC injection vial, and a final volume of the extracted eluate was 1 mL with a concentrating factor of 500 times.

UPLC-MS/MS analysis

The target compounds were analyzed using ultra high-performance liquid chromatography (UPLC, Waters ACQUITY, USA) coupled with tandem mass spectrometry (MS/MS, Waters TQ, USA). Separation was performed on Waters ACQuity UPLC BEH C_{18} (1.7 μm, 2.1 × 50 mm) column. HPLC water with 0.2% ammonium hydroxide (A) and methanol (B) were chosen as the two mobile phases. The gradient program was started with 5% B and kept for 0.3 min, rising to 60% B and kept for 1.7 min, then continuing to rise B to 90% and kept for 1.5 min. At the final stage of the gradient program, the mobile phase was returned to the initial condition for 0.5 min. The whole separation process was about 4 min. The mobile phase flow rate was set at 0.4 mL/min. The column temperature was kept at 30 °C, and the injected sample volume was 15 μL.

The tandem mass spectrometer was performed in negative ESI mode, and time-scheduled multiple reaction monitoring (MRM) was used. The MS/MS experimental conditions were

Table 1 Basic information of the nine target phenolic compounds

Compounds	CAS	Molecular formula	Boling point (°C)	Saturated pressure (mmHg)	Solubility (mg/L)	pKa	Odor threshold (ng/L)	Estrogenic potencies
4-CP	106-48-9	C_6H_5ClO	220	0.0783	2100	9.47	3.9E04	1.5E-6[1]
2-BP	95-56-7	C_6H_5BrO	194.5	0.315	670	8.43	24–100	–
4-C-2-MP	1570-64-5	C_7H_7ClO	223	0.0581	1000	9.87	6.2E04	2.1E-6[2]
4-C-3-MP	59-50-7	C_7H_7ClO	235	0.0335	980	9.63	6.5E03	6E-6[1]
2,6-DCP	87-65-0	$C_6H_4Cl_2O$	220	0.0828	520	7.02	5.9E03	–
2,4,5-TCP	95-95-4	$C_6H_3Cl_3O$	247	0.0106	150	7.10	6.3E04	<3E-7[1]
2,6-DBP	608-33-3	$C_6H_4Br_2O$	255	9.49E-03	1700	6.89	85	–
2,4-DBP	615-58-7	$C_6H_4Br_2O$	238.5	0.0274	730	7.86	4E03	2.8E-4[3]
2,4,6-TBP	118-79-6	$C_6H_3Br_3O$	286.8	1.50E-03	760	6.34	3E04	4.3E-6[3]

– not available; [1] Olsen et al. 2002; [2] Nishihara et al. 2000; [3] Schummer et al. 2009

Table 2 Optimized parameters of the nine phenolic compounds

Analytes	Retention time (min)	MRM transitions	Cone volt (eV)	Collision energy (eV)
2-BP	0.71	170.9 > 78.9	38	18
2,6-DCP	0.82	160.8 > 35	38	18
2,4-DBP	1.24	248.9 > 78.9	36	25
4-CP	1.69	126.9 > 35	34	20
2,6-DBP	1.81	248.9 > 78.9	36	24
2,4,5-TCP	2.06	194.8 > 159	30	18
2,4,6-TBP	2.22	326.7 > 78.9	42	26
4-C-2-MP	2.63	140.9 > 35	38	14
4-C-3-MP	2.81	140.9 > 35	38	14

optimized by injection of both individual standard solution and a mixed solution of all the target compounds, and the optimized parameters are shown in Table 2. Nitrogen gas was used as the desolvation and collision gas, the desolvation temperature was set at 400 °C, the desolvation gas flow rate was 800 L/h, and the collision gas flow rate was 0.17 L/min.

Results and discussion

Optimization of the mobile phase

The mobile phase has significant influence in separation of target compounds, peak shape, and ionization efficiencies (Gomez et al. 2006; Tran et al. 2013, 2016). In this study, the effect of small amount of ammonium hydroxide (NH$_4$OH) into mobile phase A (water) at four different concentrations was investigated. As shown in Fig. 1, the signals of all the target compounds were enhanced with the addition

of small amount of NH$_4$OH, and the enhanced signals for most targets increased with the increasing of the NH$_4$OH addition in the range of 0–0.5%. However, the signal increasing extents with addition of 0.5% NH$_4$OH were not notable when compared to those at 0.2% NH$_4$OH. Considering higher concentration of NH$_4$OH might give bigger damage to the separation column, the addition level of NH$_4$OH was determined at 0.2%. In Chi et al. (2017), determination of 2, 6-BP was failed for its very low signal intensity, while its corresponding signal intensity was satisfactory in this study. As their two mobile phases were the same as we did in this study except they did not add a small amount of NH$_4$OH. The fact suggested that small amount addition of buffer solution is very helpful for analysis of CPs and BPs. With the optimized mobile phase condition, separation chromatographs of the nine target phenolic compounds are shown in Fig. 2.

For ionizable and weak acidic analytes, application of buffered mobile phase is normally preferable, and both acidic and basic conditions are available. However, under

Fig. 1 Influence of ammonium hydroxide into the mobile phase in the peak intensities of the nine target compounds
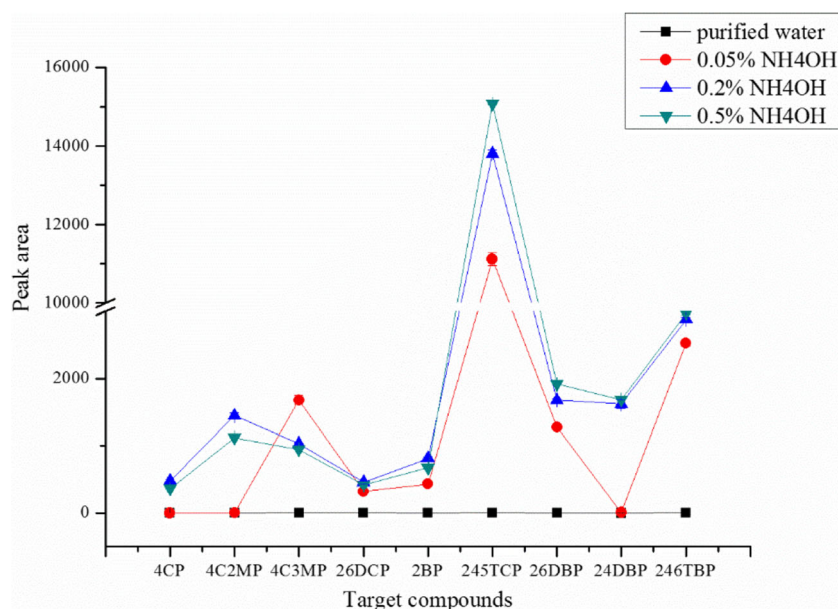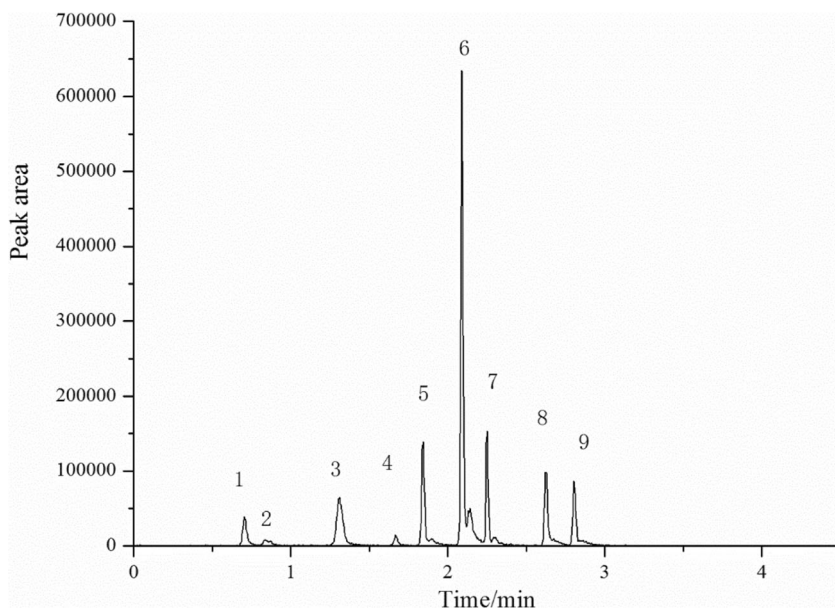
Fig. 2 Chromatograms of the nine analytes at a concentration of 400 μg/L (1: 2-BP, 2: 2,6-DCP, 3: 2,4-DBP, 4: 4-CP, 5: 2,6-DBP, 6: 2,4,5-TCP, 7: 2,4,6-TBP, 8: 4-C-2-MP, 9: 4-C-3-MP)


ion suppression condition with low pH, the analyte is neutral and much more hydrophobic, and the retention time of the analyte would be much longer, which is undesirable for fast determination. For example, in Loos et al. (2003), the retention times of 4-C-3-MP, 2,4,6-TBP, and 2-BP ranged from 16.9 to 24.3 min with acetonitrile and 0.1% acetic acid water (pH = 3.5) as the two mobile phases, while their retention times at alkaline condition in this study were greatly decreased to less than 3 min (Fig. 2). Our results agreed with other studies, in which ammonium acetate was used as the buffer (Cai et al. 2016; Pan et al. 2014).

Selection of SPE cartridges

The extraction performances of two widely used SPE cartridges, Oasis HLB, and Sep-Pak C18 on the nine target phenolic compounds were compared in this study. To find which one can give better recoveries, a spiked concentration at 40 ng/L in 500 mL of purified water was used. After the SPE procedure with a concentrating factor of 500 times, the extracted solution was subjected to the UPLC-MS/MS. As shown in the Fig. 3, C18 showed much poorer extraction performances. Our results agreed with those of other studies (Bagheri and

Fig. 3 Extraction performances of the Oasis HLB and Sep-pak C18 cartridges on the nine target compounds
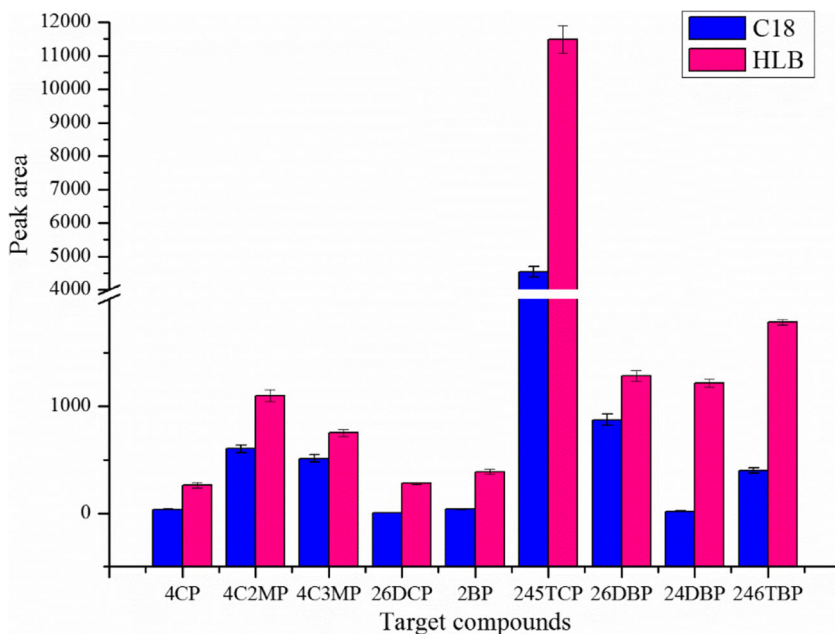
Saraji 2003; Chi et al. 2017). Therefore, Oasis HLB cartridge was selected as the SPE cartridges in the subsequent study.

Acidity of water samples

pH of water sample is a key parameter that may affect the extraction efficiencies of phenolic compounds (Rodriguez et al. 2000; Li et al. 2012). In this study, three pH ranges (pH = 7, pH = 4–5, pH = 2–3) of sample solution adjusted with hydrochloric acid were investigated. As shown in Fig. 4, it is clear that the extraction at pH = 4–5 gave the worst extract efficiencies, and the extraction efficiencies of four out of the nine target compounds were below 60%. Although the extraction efficiencies of seven out of the nine target compounds at pH = 7 were the highest, the extraction efficiencies of 4-CP and 2,4,6-TBP were poor and both were around 50%. Moreover, it was reported that BPs in water samples were instable, and they could be disappeared after 24-h storage in lab at 4 °C, and to avoid possible degradation before extraction, storage of water sample at pH below 2.5 is necessary (Chi et al. 2017). Considering the two important points above, water acidity of pH = 2–3 before extraction was determined. Other researchers also selected the same pH range when they extracted phenolic compounds in water samples (Fattahi et al. 2007; Li et al. 2012).

Performance of the developed method

The developed method was validated in terms of linearity, sensitivity, recovery, and precision under the above optimized conditions, which were listed in Table 3. Calibration curves of the nine target phenolic compounds were established based on external standard method, and good linearity ($R^2 \geq 0.995$) was obtained for each target compound at six different concentration levels ranged from 10 to 500 μg/L in methanol solvent. LOD and LOQ were calculated based on three times and ten times of the standard deviation (SD), in which the SD was calculated from seven repeated surface water sample (500 mL) spiked with the lowest concentration for the standard calibration curve. The LOD and LOQ of all the phenolic compounds were 2.0–6.2 and 6.4–20.6 ng/L, respectively, and all of them were below their odor thresholds as shown in Table 1; hence, the sensitivity of this developed method for the nine target phenolic compounds is satisfactory for odor problem screening in water. Recovery experiments were performed by spiking each target with three known concentrations at 80, 200, and 500 ng/L into surface water and tap water, and the recovery efficiencies of all the targets ranged from 57 to 95% for surface water and 66–95% for tap water. The precision of this developed method expressed as their relative standard deviations (RSD, $n = 6$) were all below 17.4%. The recovery efficiencies satisfied the requirements of the

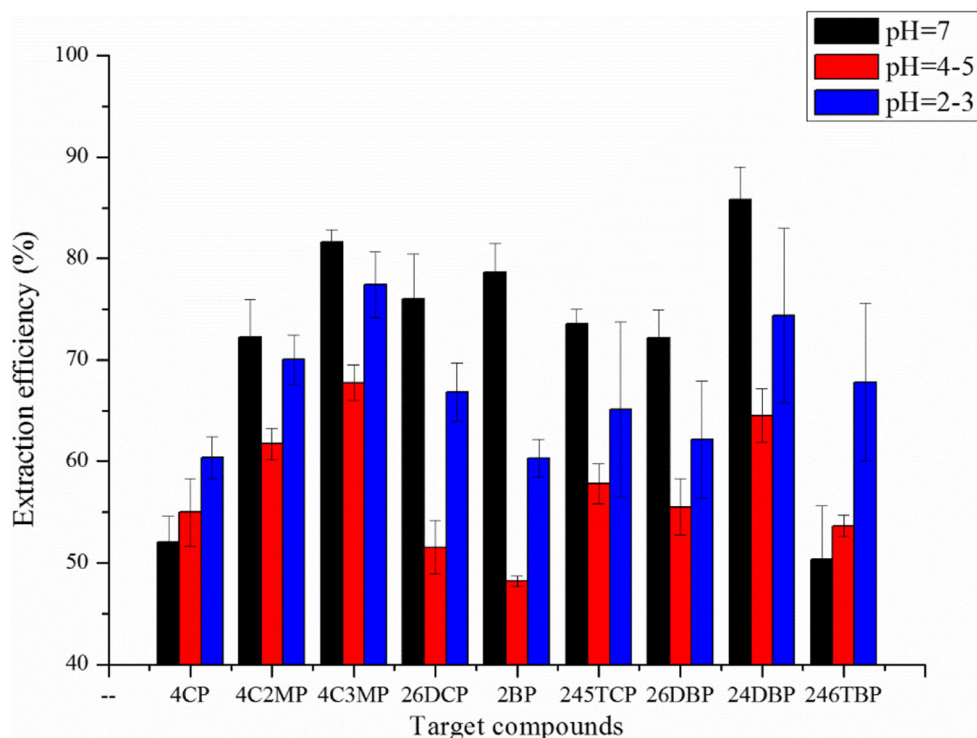**Fig. 4** Effects of water sample acidity on extraction efficiencies of the nine target compounds

Table 3 Analytical performances of the developed method

Compounds	Coefficient of determination (R^2)	LOD (ng/L)	LOQ (ng/L)	Surface water spiking recovery ± RSD (%, $n = 6$)			Tap water spiking recovery ± RSD (%, $n = 6$)		
				80 ng/L	200 ng/L	500 ng/L	80 ng/L	200 ng/L	500 ng/L
4-CP	0.995	5.0	16.5	58 ± 8.3	58 ± 1.7	57 ± 3.7	74 ± 10.5	66 ± 6.8	67 ± 5.4
4-C-2-MP	0.999	5.1	16.9	76 ± 3.4	75 ± 3.1	72 ± 4.7	72 ± 3.8	75 ± 2.2	79 ± 2.8
4-C-3-MP	0.999	2.4	8.0	95 ± 3.4	90 ± 4.7	93 ± 2.4	71 ± 6.3	80 ± 4.3	85 ± 1.9
2,6-DCP	0.999	4.9	16.4	88 ± 10.5	80 ± 3.6	82 ± 12.6	92 ± 4.6	83 ± 8.1	92 ± 5.2
2-BP	1.000	6.2	20.6	80 ± 4.8	73 ± 5.3	69 ± 14.3	68 ± 17.4	87 ± 13.6	89 ± 4.1
2,4,5-TCP	1.000	4.2	13.9	80 ± 2.7	74 ± 2.7	70 ± 6.3	73 ± 8.2	79 ± 2.6	80 ± 2.7
2,6-DBP	0.998	2.8	16.0	74 ± 3.2	63 ± 4.3	57 ± 4.0	66 ± 4.8	68 ± 4.3	69 ± 1.3
2,4-DBP	0.999	3.2	10.6	83 ± 6.9	83 ± 3.2	78 ± 10.0	95 ± 2.4	85 ± 3.5	88 ± 3.7
2,4,6-TBP	0.999	1.9	6.4	89 ± 5.3	81 ± 4.2	75 ± 10.8	81 ± 5.1	83 ± 3.3	79 ± 4.3

The concentration gradients for standard calibration of the nine phenolic compounds were 10, 20, 50, 100, 200, and 500 μg/L

analytical manual of Japanese Ministry of Land, Infrastructure, Transport, and Tourism for EDCs, in which recovery efficiency between 50 and 120% with RSD below 20% is regards as acceptable (Liu et al. 2010a, 2010b, 2011b). All parameters including linearity, sensitivity, recovery, and precision of the method suggest that this method is reliable and appropriate for simultaneous analysis of CPs and BPs. Compared to our previous work through online HS-SPME with on-fiber derivatization coupled with GC-MS method, the analytical time was greatly reduced; meanwhile, the sensitivity of this developed method was enhanced 1.79–22.6 times (Table 4). Based on the database of Web of Science, there are three references relating LC-MS/(MS) analytical methods for one or more same targets. As shown in Table 4, the sensitivities are similar, but the analysis time of our work was greatly decreased.

Method application to real water samples

The developed efficient and fast analytical method was successfully applied to trace determination of the nine target phenolic compounds in one tap water collected from the laboratory and one surface water in Shenzhen, China. The tap water sample was collected after a 2-min pre-flow, and the surface water sample was collected in spot-sampling. As shown in the Table 5, there were several target compounds were detected in both tap and surface water, but most of them were below their LOQ. The concentration of 2,4-DBP was 13.6 ng/L in the tap water and 14.1 ng/L in the surface water. The concentration of 2,6-DCP in the tap water was detected at 17.8 ng/L. Their concentrations of the nine target compounds in surface and tap water were all below their odor thresholds. With the detected concentrations of the nine targets and their

Table 4 Comparison of this developed method to the online HS-SPME with on-fiber derivatization coupled with GC-MS method and other studies

Target compounds	LOD (ng/L)					Retention time (min)				
	This study	On-fiber derivatization	Marchese et al. 2004	Chi et al. 2017	Loos et al. 2003	This study	On-fiber derivatization	Marchese et al. 2004	Chi et al. 2017	Loos et al. 2003
4-CP	4.9	8.8	–	–	–	1.69	10.1	–	–	–
4-C-2-MP	5.1	12.6	–	–	–	2.63	11.3	–	–	–
4-C-3-MP	2.4	14.6	2	–	2	2.81	11.3	Around 8	–	16.9
2,6-DCP	4.9	12.9	–	–	–	0.82	11.7	–	–	–
2-BP	6.2	13.6	–	–	2	0.71	10.8	–	–	24.3
2,4,5-TCP	4.2	9.8	–	–	–	2.06	12.7	–	–	–
2,6-DBP	2.8	14.6	–	–	–	1.81	13.8	–	–	–
2,4-DBP	3.2	12.6	–	17.5	–	1.24	14.0	–	Around 10	–
2,4,6-TBP	1.9	42.9	–	2.8	2	2.22	16.9	–	Around 16	21.6

Table 5 Concentration levels of the nine phenolic compounds in tap and surface water (ng/L)

Compounds	Tap water	Surface water
4-CP	<LOQ	<LOQ
4-C-2-MP	<LOD	<LOD
4-C-3-MP	n.d	n.d
2,6-DCP	17.8	<LOQ
2-BP	n.d	n.d
2,4,5-TCP	<LOD	<LOQ
2,6-DBP	<LOQ	<LOQ
2,4-DBP	13.6	14.1
2,4,6-TBP	<LOQ	<LOQ

n.d not detected

corresponding estrogenic potencies, EEQ can be easily calculated as equation below (Liu et al. 2009b, 2009c, 2010c).

$$EEQ = \sum EP_i \times c_i \qquad (1)$$

where EP and c denote the estrogenic potency of one specific target compound and the corresponding detected concentration, respectively. The unit of EEQ is ngE2/L. EEQ in the surface and tap water were below 0.0039 and 0.0041 ngE2/L, respectively. The result showed that the EEQ levels in both the surface and tap water were very low.

Conclusions

A reliable and efficient analytical method based on SPE-UPLC-MS/MS was developed and validated for simultaneous trace determination of nine estrogenic odorant phenolic compounds. This method obtained satisfactory linearity ($R^2 > 0.995$) and good recoveries of 57–95% for spiking to surface water and 66–95% for tap water with satisfactory RSD. The LOD and LOQ of this developed method were 2.0–6.5 and 8.0–25.9 ng/L, respectively. This method was successfully applied to one tap water and surface water for trace determination of the nine target phenolic compounds. The developed method is appropriate for trace determination of CPs and BPs in tap and surface water samples for routine odor screening and risk evaluation of their estrogenic effects.

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