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Determination of octylphenol and nonylphenol in aqueous sample using simultaneous derivatization and dispersive liquid–liquid microextraction followed by gas chromatography–mass spectrometry

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ABSTRACT

A simple and fast sample preparation method for the determination of nonylphenol (NP) and octylphenol (OP) in aqueous samples by simultaneous derivatization and dispersive liquid–liquid microextraction (DLLME) was investigated using gas chromatography–mass spectrometry (GC/MS). In this method, a combined dispersant/derivatization catalyst (methanol/pyridine mixture) was firstly added to an aqueous sample, following which a derivatization reagent/extraction solvent (methyl chloroformate/chloroform) was rapidly injected to combine in situ derivatization and extraction in a single step. After centrifuging, the sedimented phase containing the analytes was injected into the GC port by autosampler for analysis. Several parameters, such as extraction solvent, dispersant solvent, amount of derivatization reagent, derivatization and extraction time, pH, and ionic strength were optimized to obtain higher sensitivity for the detection of NP and OP. Under the optimized conditions, good linearity was observed in the range of 0.1–1000 $\mu g\,L^{-1}$ and 0.01–100 $\mu g\,L^{-1}$ with the limits of detection (LOD) of 0.03 $\mu g\,L^{-1}$ and 0.002 $\mu g\,L^{-1}$ for NP and OP, respectively. Water samples collected from the Pearl River were analyzed with the proposed method, the concentrations of NP and OP were found to be $2.40 \pm 0.16\ \mu g\,L^{-1}$ and $0.037 \pm 0.001\ \mu g\,L^{-1}$, respectively. The relative recoveries of the water samples spiked with different concentrations of NP and OP were in the range of 88.3–106.7%. Compared with SPME and SPE, the proposed method can be successfully applied to the rapid and convenient determination of NP and OP in aqueous samples.

1. Introduction

Alkylphenols (APs) are ubiquitous pollutants in aquatic environments and mainly originated from the biodegradation of non-ionic surfactants alkylphenol ethoxylates (APEOs) which are widely used as detergents, emulsifiers and lubricants. APs are known for their estrogenic effects as endocrine disrupting chemicals (EDCs) [1,2]. Among the APs, nonylphenol (NP) which contains different isomers and 4-tert-octylphenol (OP) have attracted more attention due to their extensive use and danger towards aquatic biota [1,3]. Therefore, the determination of NP and OP in aquatic environments is of great importance for estimating their ecologic risk on the aquatic ecosystem.

Despite a number of advanced instruments have been developed for the determination of trace organic compounds in diverse samples, the determination of NP and OP in environmental samples at low concentration is still a challenge. Due to the complex matrices of environmental samples, analytical methods for the determination of NP and OP rely heavily on high performance liquid chromatography (HPLC) [4] and gas chromatography (GC) [5,6] for separation. Gas chromatography coupled with mass spectrometry (GC/MS) is frequently used due to better separation and high distinguishing power over HPLC. However, due to the poor volatility of some polar compounds, derivatization step is usually required prior to GC to produce more volatile products and to improve the sensitivity. Solid phase microextraction (SPME) with post-silylation provides a simple and solventless sample preparation and has achieved desirable results for extracting NP and OP from environment samples [5,7], but SPME is time-consuming and the fiber is expensive and is easily destroyed during the derivatization process. Compared with the SPME post-derivatization, liquid-phase microextraction (LPME) with in situ derivatization merits the benefits of both cost-effectiveness and convenience, and has been applied for the analysis of several polar chemicals by GC system [8–10]. In situ derivatization of APs by alkyl chloroformates is convenient by simply adding the derivatization reagent to the

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aqueous sample [11]. A high efficient liquid-phase microextraction (LPME) method using ethyl chloroformate (ECF) for the in situ O-alkoxycarbonylation (AOC) of OP and other APs has been reported by Fiamegos and Stalikas [12]. However, LPME with in situ derivatization still has some drawbacks such as instability of the microdrop, operational difficulties and bubble formation formed by the gas produced during the reaction.

In recent years, Assadi and co-workers presented a novel method termed dispersive liquid–liquid microextraction (DLLME) [13]. In this method, analytes in aqueous sample were extracted by a cloudy solution formed by an appropriate mixture of extraction solvent and dispersant, and then extraction solvent was separated by centrifugation and subjected to GC or LC determination. DLLME has recently been introduced for the extraction of polybrominated diphenyl ethers (PBDEs) [14], organophosphorus pesticides (OPPs) [15] and polychlorinated biphenyls (PCBs) [16] from water samples because of its high extraction efficiency, convenience and low cost. DLLME combined with in situ derivatization has also been applied for the analysis of polar compounds such as fatty acids [17], chlorophenols and anilines [18,19]. To the best of our knowledge, no publication has described the use of DLLME for the extraction of NP and OP from aqueous samples.

The aim of the present work was to establish an in situ derivatization DLLME procedure using methyl chloroformate (MCF) as derivatization reagent for the derivatization and extraction of NP and OP. This study focused on taking advantage of the water miscible organic solvents both as derivatization catalyst and dispersant. Some key factors such as MCF amount, extraction solvent, pH and ionic strength were also studied. The proposed method was successfully applied for the determination of NP and OP contents in the Pearl River (Guangzhou, China).

2. Experimental

2.1. Standards and reagents

Nonylphenol (technical NP, t-NP), 4-tert-octylphenol (OP, 97%) and methyl chloroformate (MCF, 99%) were purchased from Sigma–Aldrich (St. Louis, MO, USA). HPLC-grade methanol, acetone, chloroform, tetrachloroethlene, carbon tetrachloride and pyridine were purchased from Merck (Darmstadt, Germany). Tetradeuterated labeled 4-n-nonylphenol(NP-d4) was from C/D/N isotope Inc. (Quebec, Canada) and used as internal standard. Ultra pure water was produced using Milli-Q Advantage A10 system (Bedford, MA, USA). Sodium hydroxide (NaOH), sodium chloride (NaCl), hydrochloric acid (HCl), and other reagents are of analytical grade supplied by Guangzhou chemical reagent factory.

The individual stock solutions of NP, OP and NP-d4 at 1.00 g L^{-1} were prepared by dissolving 50 mg of each standard compound in 50 mL acetone with volumetric flask. A mixed stock solution of 10 mg L^{-1} NP and 1 mg L^{-1} OP was obtained by appropriate dilution of each stock solution with acetone. Working solution was freshly prepared by appropriate dilution of the mixed stock solution with ultra pure water. NP-d4, used as internal standard, was spiked at the concentration of 0.5 μg L^{-1} for calibration.

River water was collected from the Pearl River for method validation. The water samples were filtered through 0.45 μm membrane and stored in 500 mL amber glass bottles at 4 °C prior to use. All water samples were analyzed in less than a week.

2.2. Simultaneous derivatization and DLLME procedure

For the simultaneous derivatization and DLLME, an aliquot of 5.0 mL working solution containing 100 μg L^{-1} NP and 10 μg L^{-1} OP was placed in a 10 mL conical-bottom glass centrifuge tube with a PTFE-lined screw cap and 0.5 mL methanol:pyridine (4:1, v/v) solution was added as dispersant solvent and catalyst. A mixture of 150 μL MCF (derivatization reagent) and 50 μL $CHCl_3$ (extraction solvent) was rapidly injected into the aqueous solution by a 200 μL syringe. The tube was tightly capped and shaken vigorously for about 10 s to mix the phases, then the tube was placed in an ultrasonic bath for derivatization and extraction for 5 min. $CHCl_3$ was then dispersed into fine droplets by ultrasonication. In this step, the NP and OP derivatives were extracted from the aqueous phases into the fine droplets of $CHCl_3$. After centrifuging at 5000 rpm for 5 min, the fine droplets of extraction solvent were sedimented at the bottom of the centrifuge tube. The sedimented phase (20 ± 2 μL) was withdrawn and calculated by a 100 μL syringe and subsequently stored in a 2 mL GC vial with a 100 μL insert for automated injection. Finally, 1 μL sample was injected to the GC port for GC–MS analysis. All samples were performed in triplicate. Due to noxious gas formation during the derivatization step, the entire procedure was conducted in a fume-hood, with gloves and mask.

2.3. GC–MS analysis

Sample analysis was performed with an Agilent 6890A-5973N GC–MS (Agilent technologies, USA) equipped with a Gerstel MPS2 multipurpose autosampler (Munich, Germany). A DB-5MS fused silica capillary column was used (30 m × 0.25 mm × 0.25 μm). Helium was used as carrier gas, and the flow rate was set constantly at 1.0 mL min^{-1}. Inlet temperature was set at 280 °C with the splitless mode selected. The oven temperature was programmed as follows: initially at 80 °C, raised to 180 °C at 20 °C min^{-1} and to 240 °C at 5 °C min^{-1}, finally raised to 300 °C at 20 °C min^{-1}. Mass spectrometry was performed with the electron impact mode (EI) at 70 eV.

3. Results and discussion

Generally, alkyl chloroformates are lipophilic chemicals with limited solubility in water. When used for the O-alkoxycarbonylation (AOC) of phenolic hydroxyl group in aqueous sample, water miscible organic solvents such as alcohol, acetone, acetonitrile and pyridine are required to modify the organic content and also to catalyze the reaction. But these water miscible solvents in the aqueous sample may cause adverse effects on the extraction procedure, especially when SPME is performed [20]. DLLME can resolve this problem by taking advantage of these water miscible solvents as dispersant for assisting extraction. In our experiments, the mixture of methanol and pyridine (4:1, v/v) as modifier and catalyst also act as dispersant in DLLME. The full-scan chromatogram of the APs after derivatization by MCF is shown in Fig. 1. The molecular ions $[M]^+$ at *m/z* 264, *m/z* 278 and *m/z* 282 are identified to be the O-methoxycarbonyl of OP, t-NP and NP-d4, respectively. Since both OP and the most abundant group of NP isomers had a tertiary-α-carbon in the alkyl moiety, which exhibited a similar mass fraction pattern [21] and gave the most intensive ion at *m/z* 193 after *o*-methoxycarbonylation (MOC), this ion was selected for quantitation of OP and NP. This fragment underwent further detachment (elimination of $–OCOCH_3$ and $–CH_2$ groups) to give an ion at *m/z* 121. For the NP-d4, as it contains a linear alkyl moiety, the cleavage at the primary-α-carbon of the alkyl moiety from the derivative produced an ion at *m/z* 169, however, the cleavage at the primary-β-carbon and further detachment of $–OCOCH_3$ gave the most intensive fragment at *m/z* 125. The mass fraction patterns of OP and NP-d4 are illustrated in Fig. 2. The retention time and ions monitored for each analytes are listed in Table 1.

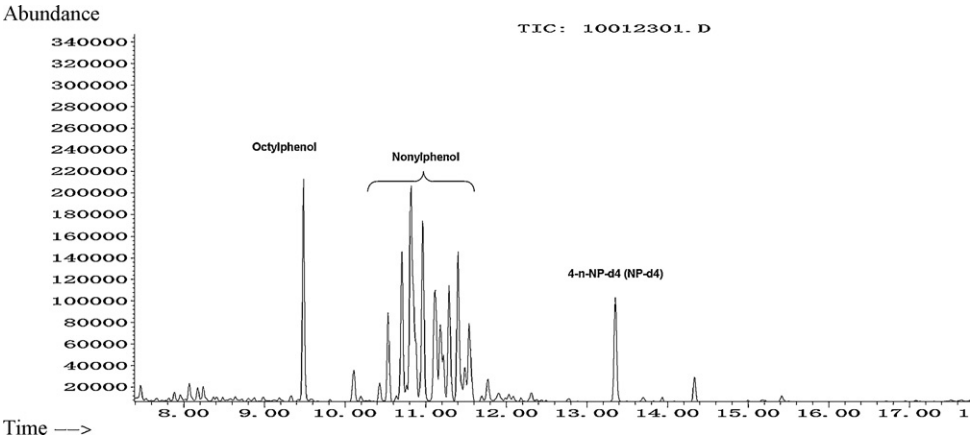

Fig. 1. Total ion chromatogram (TIC) of NP, OP and internal standard (NP-d4) in aqueous samples after in situ derivatization DLLME. NP was spiked at the concentration of 100 μg L^{-1}, OP and NP-d4 was spiked at 10 μg L^{-1}.

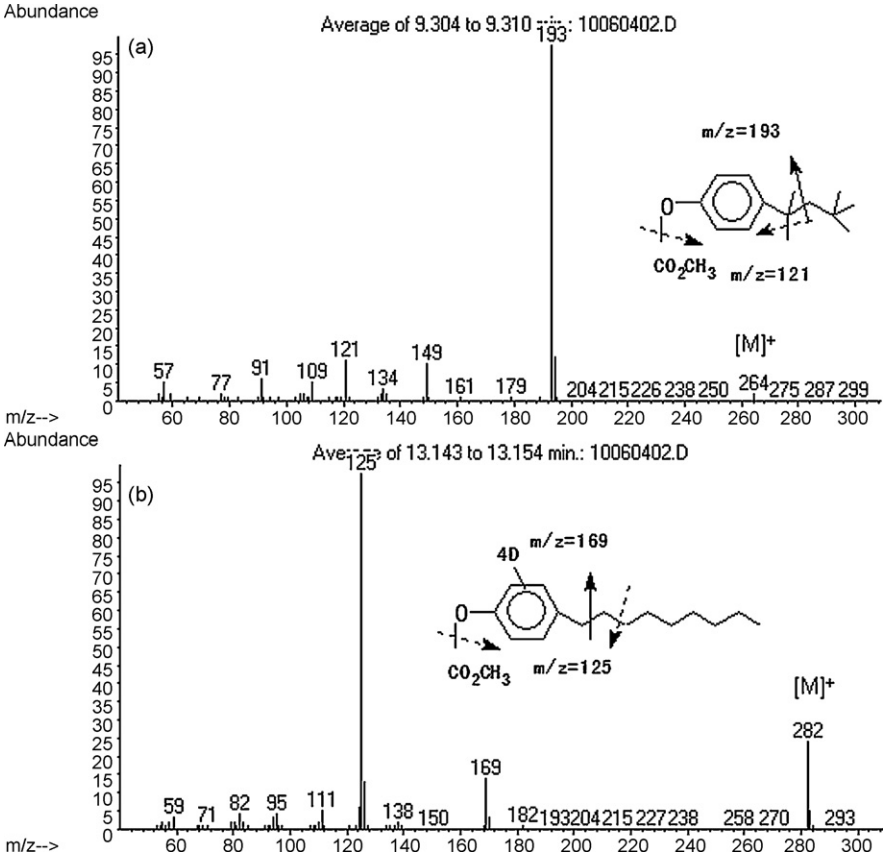

Fig. 2. EI (70 eV) mass spectrum of (a) O-methoxycarbonyl-OP and (b) O-methoxycarbonyl-tetradeuterate-4-n-NP.

3.1. Effects of prior derivatization and simultaneous derivatization and extraction

Two series of experiments were performed to study the effects of prior derivatization and simultaneous derivatization and extraction on the performance of DLLME for NP and OP. For the prior derivatization, 100 μL MCF was injected into a centrifuge tube containing 5.0 mL working solution and 0.5 mL methanol:pyridine (4:1, v/v) solution, after 5 min ultrasonic derivatization, 100 μL $CHCl_3$ was added followed by 5 min ultrasonic extraction. In the

Table 1
Molecular weights, CAS numbers, retention time and mass spectra fragments of the O-methoxycarbonylation of NP, OP and internal standard (NP-d4) obtained in the electron impact mode (70 eV).

Compounds	CAS No.	MW	RT (min)	Quantitative ions	Qualitative ions
OP	1806-26-4	264	9.45	193	121, 264
NP	84852-15-3	278	10.5–11.65	193	121, 278
NP-d4	359730-95-7	282	13.30	125	169, 282

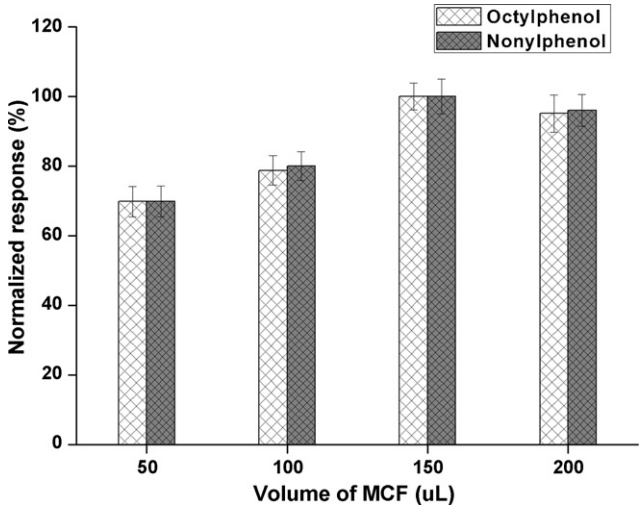

Fig. 3. Effect of the amount of MCF on the detector responses of NP and OP. *Experiment conditions*: Sample volume, 5.0 mL; dispersant solvent, 0.5 mL methanol:pyridine (4:1, v/v); extraction solvent, 100 μL $CHCl_3$; derivatization and extraction time, 5 min.

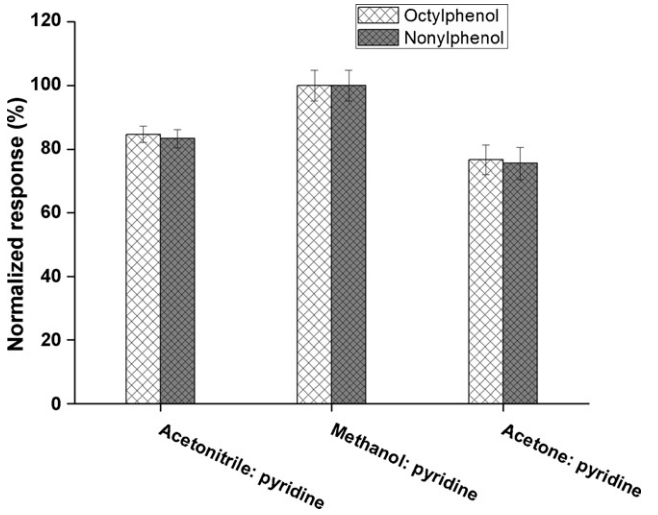

Fig. 4. Effect of dispersant solvent on the detector responses of NP and OP. *Experiment conditions*: Sample volume, 5.0 mL; dispersant solvent volume, 0.5 mL; derivatization reagent, 150 μL MCF; extraction solvent, 100 μL $CHCl_3$; derivatization and extraction time, 5 min.

simultaneous derivatization and extraction, a binary mixture of 100 μL MCF and 100 μL $CHCl_3$ was rapidly injected into the tube, then followed by 5 min simultaneous ultrasonic derivatization and extraction. No significant difference was shown between the results obtained by the two sets of experiments. This finding designated that the derivatization was not affected by the coexisting $CHCl_3$. Thus, simultaneous derivatization and extraction was selected.

3.1.1. Effect of MCF amount

When used for in situ derivatization, the major consumption of alkyl chloroformates is that its hydrolysis in water. In order to find a moderate amount of MCF needed for the in situ derivatization of NP and OP, different volumes of MCF were tested ranging from 50 μL to 200 μL at intervals of 50 μL. 100 μL $CHCl_3$ and MCF were added for derivatization and extraction. The results (Fig. 3) revealed that the responses of NP and OP increased with the increment of MCF content in the range of 50–150 μL and then approached a plateau. This indicated that the derivatization efficiency was not affected by the MCF amount when it was higher than 150 μL. This amount of MCF was thus used for the following experiments.

3.1.2. Effect of dispersant solvent

Generally, miscibility of dispersant solvent in organic phase and aqueous phase is the most important factor in selecting dispersant solvent. The water miscible solvents such as acetone, acetonitrile, and methanol were compared in this study. Experimental results showed that any of these selected solvents when used alone as dispersant, derivatization could not be completed (data not shown). Since pyridine is an essential catalyst for the alkoxycarbonylation in aqueous sample and always supplemented at fixed ratios to the reaction medium [22], a mixture of the selected solvent (acetone, acetonitrile or methanol) and pyridine at the ratio of 4:1 (v/v) was used as catalyst and dispersant. The results in Fig. 4 showed that highest responses of NP and OP were obtained when a mixture of methanol and pyridine (4:1, v/v) was used. As this ratio was found to be a more proper ratio for assisting derivatization in most studies [17,23], the ratio of methanol:pyridine at 4:1 (v/v) was chosen as catalyst and dispersant for the following experiments without further study.

The effects of dispersant volume on the derivatization and extraction were also studied by varying its volume from 0 mL to 1.0 mL. Fig. 5 shows that the responses of NP and OP increased with increasing dispersant volume and reached 80% at 0.5 mL. However, it was observed that the volume of sedimented phase significantly decreased from 94 μL to 50 μL and that higher sensitivity was attained in smaller volume of sedimented phase. But the cloudy phase was not formed when the dispersant volume was large than 1.5 mL, especially when using smaller amounts of extraction solvent to increase the sensitivity (as can be seen in the next section). Therefore, 0.5 mL of a mixture of methanol and pyridine (4:1, v/v) was selected in the following experiments.

3.1.3. Effect of extraction solvent

Selection of a proper extraction solvent is important for DLLME. The density of the extraction solvent should be higher than that of water with limited solubility in water. For this reason, the extraction efficiencies of chloroform ($CHCl_3$), chlorobenzene (C_6H_5Cl), carbon tetrachloride (CCl_4), and tetrachloroethylene (C_2Cl_4) were compared. A binary mixture of 150 μL MCF and 100 μL abovementioned solvent was used for derivatization and extraction using the procedure described above. The highest responses of NP and

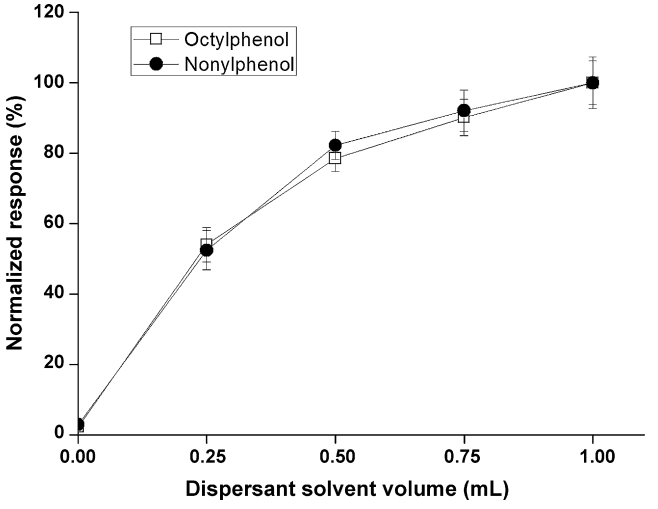

Fig. 5. Effect of amount of dispersant solvent on the detector responses of NP and OP. *Experiment conditions*: Sample volume, 5.0 mL; dispersant solvent, methanol:pyridine (4:1, v/v); derivatization reagent, 150 μL MCF; extraction solvent, 100 μL $CHCl_3$; derivatization and extraction time, 5 min.

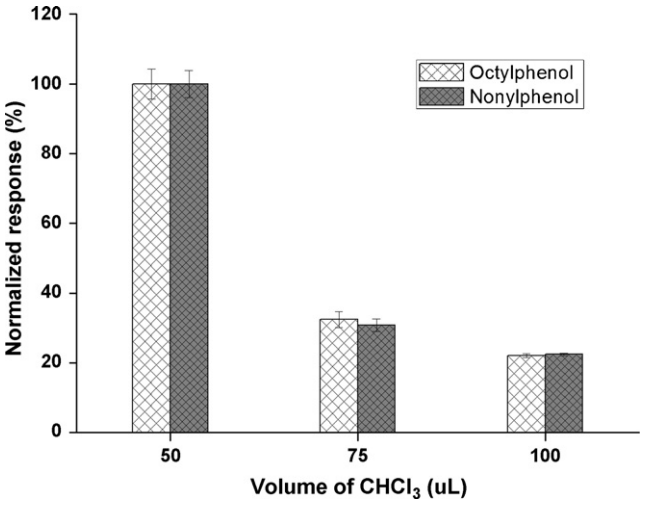

Fig. 6. Effect of extraction solvent ($CHCl_3$) amount on the detector responses of NP and OP. *Experiment conditions*: Sample volume, 5.0 mL; dispersant solvent, 0.5 mL methanol: pyridine (4:1, v/v); derivatization reagent, 150 μL MCF; derivatization and extraction time, 5 min.

OP were obtained by using $CHCl_3$. Hence, $CHCl_3$ was used as the extraction solvent.

Different volumes (25 μL, 50 μL, 75 μL and 100 μL) of $CHCl_3$ were also investigated. Results showed that the responses of NP and OP increased with the decrease in the volume of extraction solvent. But cloudy phase was not formed when using 25 μL $CHCl_3$, thus no sedimented phase was obtained. The highest response was obtained when 50 μL $CHCl_3$ was used (Fig. 6). Therefore, 50 μL $CHCl_3$ was selected in the following studies.

3.1.4. Effect of simultaneous derivatization and extraction time

In simultaneous derivatization and DLLME, the derivatization and extraction time is defined as the time between injection of the mixture of MCF and $CHCl_3$ and subjecting it to centrifugation. The effect of derivatization and extraction time was examined at 1 min, 3 min and 5 min by ultrasonication, respectively. No significant differences in the responses of NP and OP were observed, indicating that 1 min of ultrasonication was adequate for derivatization and extraction. However, when derivatization was performed in less than 5 min, air bubbles from the sedimented $CHCl_3$ affected the withdrawal procedure. Therefore, the derivatization and extraction time was selected at 5 min.

3.1.5. Effect of pH value

The effects of the pH of the sample solution were examined at pH 3, 5, 7 and 9 (adjusted by HCl and NaOH), respectively. Other experimental conditions were kept constant as mentioned above. According to the results, the effects of various pH values on responses of NP and OP were insignificant. The reason may be attributed to the production of HCl during the AOC process, thus the pH values in aqueous phase dropped to below 2 after derivatization. Re-adjusting the pH value of each individual samples to their original values by the addition of 1 M NaOH after the derivatization step (before the DLLME process) did not affect the extraction efficiency. This indicated that both the derivatization and extraction were not affected by the variation in pH values.

3.1.6. Effect of ionic strength

The ionic strength was studied by spiking a series of NaCl contents ranging from 0 g L^{-1} to 200 g L^{-1} into the sample solution. The sedimented phase was enlarged from 20 ± 2.1 μL to 24 ± 1.5 μL with increment in ionic strength, and thus the responses of NP and OP decreased by dilution effect. In addition, salt addition could increase the density of aqueous sample, thus the sedimented phase could be easily suspended in the aqueous phase and difficult to be withdrawn. Therefore, salt was not added in the following experiments.

3.2. Method evaluation and sample analysis

3.2.1. Evaluation of method

Under the selected conditions, the proposed method was evaluated in terms of linear range, correlation coefficient (R^2), precision (RSD), limit of detection (LOD) and limit of quantification (LOQ). Ultrapured water spiked with different concentrations of NP and OP (0.1–1000 μg L^{-1} for NP, 0.01–100 μg L^{-1} for OP, respectively) were used. The LOD and LOQ values were calculated based on signal-to-noise ratio (S/N) of 3 and 10.

It could be seen from Table 2 that the linear range of calibration curves of NP and OP using DLLME ranged from 0.1 μg L^{-1} to 1000 μg L^{-1} and 0.01 μg L^{-1} to 100 μg L^{-1}, respectively. The LOD and LOQ were 0.03 μg L^{-1} and 0.08 μg L^{-1} for NP, 0.002 μg L^{-1} and 0.007 μg L^{-1} for OP, respectively. Higher LOD (LOQ) obtained for NP than OP might have been caused by the differences in mass fraction pattern of NP isomers [21], of which some were not selected for quantification in this study. Overall, the detection and quantification limits of DLLME were the same magnitude as those of SPME and SPE methods [5]. However, DLLME was less time-consuming and not as laborious. Moreover, concerning the costly SPME fiber and SPE cartridge, DLLME could be considered as a replacement for SPME and SPE for NP and OP determination.

3.2.2. Real sample analysis

The present method was also applied to analyze environmental samples collected from the Pearl River in South China to investigate the efficiency of the developed method. Ultrapure water spiked with 0.5 μg L^{-1} of NP-d4 (internal standard) was used for serial dilution of the mixed stock solution, from which seven calibration standards spanning over four orders of magnitude were prepared (0.1–1000 μg L^{-1} for NP, 0.01–100 μg L^{-1} for OP, respectively). Calibration curves were obtained by plotting the ratios of each analytes to internal standard in detector responses versus their concentrations. The internal standard NP-d4 was added into the river water samples at a final concentration of 0.5 μg L^{-1} for quantitative analysis. The concentrations of NP and OP in river water samples were found to be 2.40 ± 0.16 μg L^{-1} and 0.037 ± 0.001 μg L^{-1}, respectively. Samples spiked with 1.0 μg L^{-1}, 10 μg L^{-1} and 100 μg L^{-1} of NP (for OP, the concentrations were 0.1 μg L^{-1}, 1.0 μg L^{-1} and 10.0 μg L^{-1}, respectively) were used to evaluate the recoveries of NP and OP from sample matrix. The recoveries were calculated by subtracting the results for the

Table 2
Analytical characteristics of the established method.

Compounds	Calibration range (μg L^{-1})	Correlation coefficient (R^2)	LOD (μg L^{-1})[a]	LOQ (μg L^{-1})	Precision (%RSD, n = 3)[b]
NP	0.1–1000	0.9982	0.03	0.08	6
OP	0.01–100	0.9995	0.002	0.007	9

[a] The LOD and LOQ values were estimated based on the lowest detectable peak that had signal/noise = 3 and 10.
[b] NP (OP) concentration was 1.0 (0.1) μg L^{-1} for which RSD was obtained.

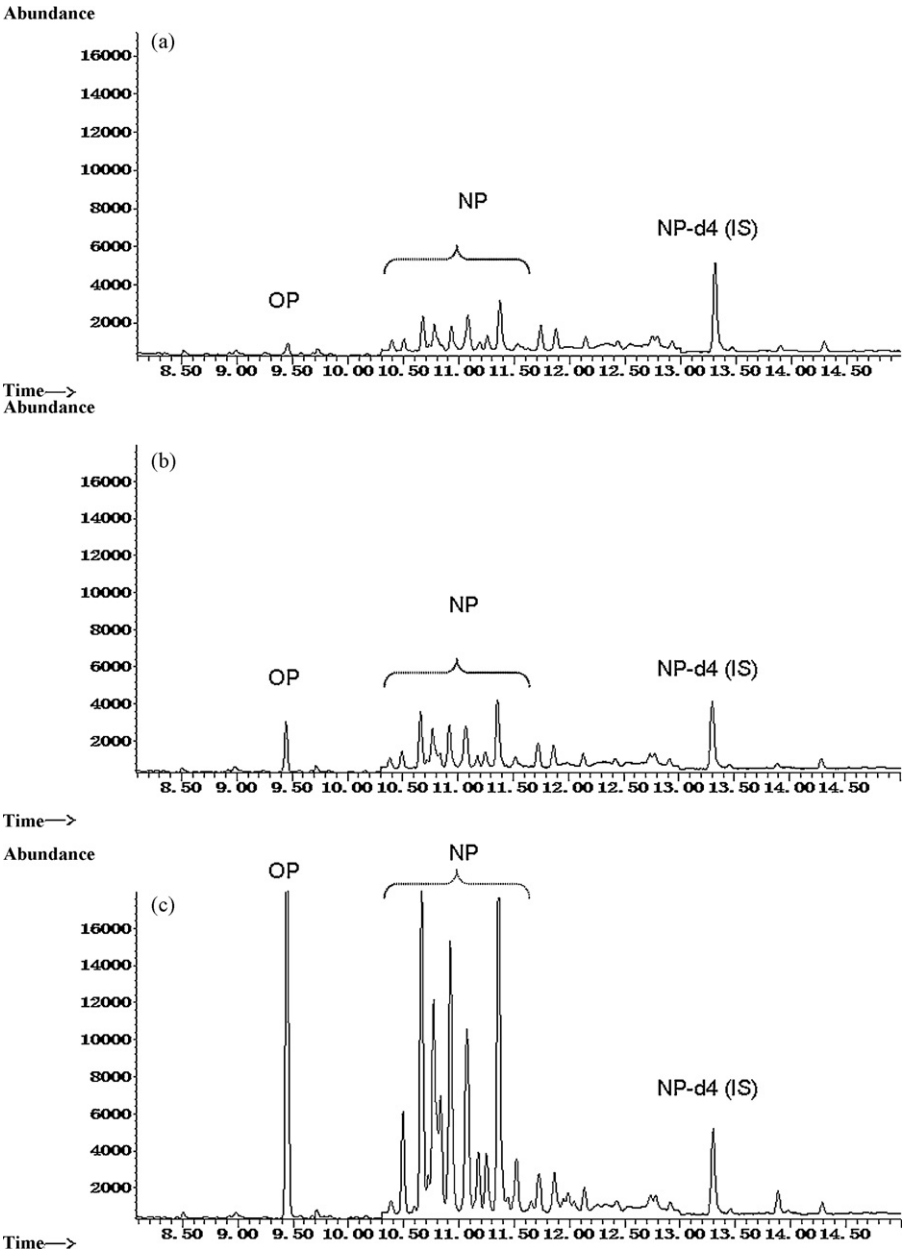

Fig. 7. Total ion chromatogram (TIC) of NP and OP in (a) river water before spiking, (b) river water spiked with 1.0 (0.1) $\mu g\,L^{-1}$ of NP(OP) and (c) river water spiked with 10 (1.0) $\mu g\,L^{-1}$ of NP (OP) using in situ derivatization DLLME method under optimum condition.

Table 3
Concentration and recoveries of NP and OP in the Pearl River water samples at different spiked levels.

Compounds	Concentration ($\mu g\,L^{-1}$)	Spiked ($\mu g\,L^{-1}$)	Found ($\mu g\,L^{-1}$)	Recovery (%)
NP	2.40 ± 0.16	1	3.47 ± 0.25	106.7
		10	11.23 ± 0.50	88.3
		100	98.90 ± 4.33	96.5
OP	0.037 ± 0.001	0.1	0.129 ± 0.003	92.1
		1	0.970 ± 0.053	93.3
		10	9.607 ± 0.160	95.7

non-spiked samples from those for the spiked samples. The chromatograms of the river water and river water spiked with 1.0 (0.1) $\mu g\,L^{-1}$, 10 (1.0) $\mu g\,L^{-1}$ for NP (OP) are showed in Fig. 7. The recoveries of NP and OP ranged from 88.3% to 106.7% (Table 3), which indicated that the proposed method coupled with GC/MS could be used to analyze NP and OP in river water samples quantitatively.

4. Conclusion

In this study, a fast sample pretreatment using simultaneous in situ derivatization and DLLME was established for the determination of trace amounts of NP and OP in aqueous samples. The linear range of the calibration curves of NP and OP using DLLME ranged from 0.1 $\mu g\,L^{-1}$ to 1000 $\mu g\,L^{-1}$ and 0.01 $\mu g\,L^{-1}$ to

100 μg L^{-1}, respectively. The LOD and the LOQ were 0.03 μg L^{-1} and 0.08 μg L^{-1} for NP, 0.002 μg L^{-1} and 0.007 μg L^{-1} for OP, respectively. The recoveries of spiked NP and OP in real samples ranged from 88.3% to 106.7%. Compared with the conventional SPE and other extraction methods, the proposed method is more rapid (about 5 min), cost-effective and more easier to perform. Since chloroformates are also capable of derivatization of carboxylic and amino groups in aqueous phase [22,24], it could provide a simple, convenient and cost-effective method for the analysis of phenolic, carboxylic and amino compounds in aqueous samples using in situ derivatization and DLLME procedure.

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