

Simultaneous determination of C4-C9 alkylphenols and bisphenol A in environmental water at the Yellow River Estuary Area in China by gas chromatography-mass spectrometry

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Abstract

A liquid-liquid extraction combined with derivatization and gas chromatography-mass spectrometry (GC-MS) method was developed for the rapid determination of C4-C9 alkylphenols (4-tert-butylphenol, 4-n-butylphenol, 4-n-pentylphenol, 4-n-hexylphenol, 4-n-heptylphenol, 4-n-octylphenol, 4-tert-octylphenol, 4-n-nonylphenol and 4-nonylphenol) and bisphenol A in the environmental water. The extraction solvent, extraction time, solvent volume, acidity, salt content and the distillation degree were optimized. After drying and dehydration, the extract was derivatized, detected by GC-MS and quantified by internal standard method. After the dehydration, the extract was derivatized with BSTFA, detected by GC-MS and quantified by internal standard method. The results showed that the relative standard deviations of the relative response factors of the target compounds were less than 20%, the method detection limits were 0.002 µg/L-0.006 µg/L, the relative standard deviations of the three spiked levels were 0.67%-13.7%, and the average recoveries of the actual water samples were 68.0%-122%. The method precision and accuracy were good. The method is simple, rapid, accurate, stable and reliable, which is suitable for the detection of target in water. The contents of C4-C9 alkylphenols and bisphenol A in groundwater, surface water, sewage, waste water and sea water samples in Dongying City located at the Yellow River Estuary were determined by this method. The results showed that the contents of 4-nonylphenol and bisphenol A in these samples were lower than the home and abroad requirements.

Introduction

As the typical environmental endocrine disruptors, alkylphenols and bisphenol A have been the focus of attention (Wen et al. 2020; Abu-Alsoud and Bottaro 2021; Liu and Zhao 2020; Murray et al. 2017). There is no domestic standard method to monitor the alkylphenols and bisphenol A in water in China. ASTM, ISO and the Japanese government have developed the corresponding monitoring standard methods (ISO 18857-2 2009; ASTM D7065 2011; ASTM D7574 2009; JIS K 0450-10-10 2006). However, these above monitoring methods were developed early and the research objects are single, which are limited to one or several compounds of 4-tert-octylphenol, nonylphenol and bisphenol A. This is related to the early people's understanding of the use of alkylphenols. The plastic industry developed early, and the nonylphenol and octylphenol were the most widely used in the plastic industry. As a result, the proportion of nonylphenol and octylphenol in the environmental water was high, and the other alkylphenols were not detected or the detection value was very low, which did not attract people's attention. There are many detection methods of alkylphenols and bisphenol A in water, among which the liquid-liquid extraction combined GC-MS method is a more studied method, but the research objects are also concentrated on one or several compounds of 4-tert-octylphenol, nonylphenol and bisphenol A (Selvaraj et al. 2014; Shen et al. 2015; Santhi et al. 2012; Dong et al. 2015; Wang et al. 2013; Martinez and Peñuela 2013). However, with the development of new plastics and liquid crystal products, many new C4-C9 alkylphenols have been widely used. The 4-tert-butylphenol is an important raw material for the production of p-tert-butylphenol formaldehyde resin. The 4-n-pentylphenol is an effective component of disinfectant, food preservative and deodorant. The 4-n-butylphenol, 4-n-hexylphenol and 4-n-heptylphenol are often used as liquid crystal raw materials and intermediates. The wide application of C4-C9 alkylphenols leads to the continuous entry of these new alkylphenols into the environmental water. These C4-C9 alkylphenols are also the endocrine disruptors, which can also affect the performance of human endocrine system. In 1998, the Ministry of environment of Japan listed 4-pentyl phenol and other alkyl phenols as the endocrine disruptors (Ministry of the Environment of Japan 1998). However, there is no standard method for the monitoring of these C4-C9 alkylphenol and bisphenol A in water in China, and there is no standard method developed by the authoritative institutions abroad.

The alkylphenol is a combination of phenol and alkyl chain. Due to the different length of alkyl chain, the physical and chemical properties of these C4-C9 alkylphenols are different, such as nonpolarity, adsorption capacity on the material surface and partition coefficient between aqueous phase and organic phase. The greater the difference of alkyl chain length, the greater the difference of these properties. The quantitative determination of these C4-C9 alkylphenols and bisphenol A in groundwater, surface water, sewage and wastewater, seawater and other actual water samples is an analytical technique for trace or ultra trace mixed components in complex matrix, which is difficult to extract, enrich, separate and detect. Liquid-liquid extraction has the advantages of good separation effect, simple operation and high repeatability, which is the most widely used organic matter extraction and enrichment technology (Wang et al. 2020; Deng et al. 2018). GC-MS is the most advanced and reliable detection technology (Subuhi et al. 2020; Azzouz et al. 2020). After the derivatization, the polarity and boiling point of these alkylphenols and bisphenol A decreased, the volatility and stability increased, the anti-interference ability increased, and the samples could be stored for a long time for retest (Liu et al. 2019; Tan et al. 2019).

In this study, a liquid-liquid extraction combined with derivatization and GC-MS method with low detection limit, high recovery, good reproducibility and rapid analysis was established. Nine C4-C9 alkylphenols (4-tert-butyl phenol, 4-n-butyl phenol, 4-n-pentyl phenol, 4-n-hexyl phenol, 4-n-heptyl phenol, 4-octyl phenol, 4-tert-octyl phenol, 4-nonylphenol and 4-nonylphenol) and bisphenol A in water were analyzed. The accurate concentrations of target substances in groundwater, surface water, sewage, waste water and sea water were determined.

Materials And Methods

1.1 Materials and reagents

The standard solutions of C4-C9 alkylphenols and bisphenol A (including 4-tert-butyl phenol, 4-n-butyl phenol, 4-n-pentyl phenol, 4-n-hexyl phenol, 4-n-heptyl phenol, 4-n-octyl phenol, 4-tert-octyl phenol, 4-n-nonylphenol, 4-nonylphenol and bisphenol A, with the concentration of 1000 µg/ml), deuterated bisphenol A-d₁₆ standard solution (1000 µg/ml), deuterated naphthalene-d₈ standard solution (200 µg/ml), deuterated phenanthrene-d₁₀ standard solution (500 µg/ml), and deuterated pyrene-d₁₀ standard solution (500 µg/ml), were purchased from Dreherstorfer, Germany. Dichloromethane, acetone and n-hexane are pesticide residues, purchased from Merda company of USA. The derivatization reagent BSTFA (containing 1% TMCs) was purchased

from Drehrenstorfer, Germany. Hydrochloric acid, sodium chloride and anhydrous sodium sulfate are of high grade purity purchased from Sinopharm group of China. Sodium chloride and anhydrous sodium sulfate are roasted at 450 °C .

Alkylphenols and bisphenol A working solution (1 µg/ml), substitute solution (1 µg/ml of deuterated bisphenol A-d₁₆), and internal standard (1 µg/ml of deuterated naphthalene-d₈, deuterated phenanthrene-d₁₀, and deuterated pyrene-d₁₀, respectively) were diluted from the corresponding standard solutions with acetone.

1.2 Instruments and equipment

Agilent 7890B gas chromatograph, Agilent 5977B mass spectrometer, Heidolph rotary evaporator.

1.3 Solution preparation and standard curve

Water treatment steps: Measured 500 ml water sample into the separating funnel, added 100 µl substitute working solution and mixed well. Then added 10 g sodium chloride, shaken to complete dissolution, added 30 ml dichloromethane, shaken violently for 10 min, stood for 5-10 min, separated layers, collected organic phase, extracted again for 1-2 times, combined organic phase and dehydrated with anhydrous sodium sulfate, and concentrated organic phase to 0.5 ml. Transferred the concentrated sample to a 1 ml volumetric flask, washed the concentrated flask with a small amount of dichloromethane, and combined the washing solution into the volumetric flask. Added 100 µl of internal standard working solution and 100 µl of derivatization reagent in turn, and diluted to 1 ml with dichloromethane. The samples were obtained by derivatization at room temperature for 1 h.

Standard curve preparation: Added 100 µl internal standard working solution and 100 µl derivatization reagent respectively, and used dichloromethane to make volume to 1 ml. The low concentration calibration series are 0 µg/L, 5.0 µg/L, 10.0 µg/L, 20.0 µg/L, 40.0 µg/L, 60.0 µg/L and 80.0 µg/L, while the high concentration calibration series are 60.0 µg/L, 100 µg/L, 200 µg/L, 500 µg/L, 1000 µg/L and 2000 µg/L. After derivatization at room temperature for 1 h, the target compounds were determined from low concentration to high concentration according to the chromatographic reference conditions. The retention time and quantitative ion response values of the standard series of target compounds and corresponding internal standards were recorded. The average relative response factor was used to draw the calibration curve, and the relative standard deviation (RSD) of the relative response factor (RRF) of the standard series of target compounds should not be more than 20%.

1.4 Actual water sample collection

According to the relevant environmental protection standards (HJ 91.1 2019; HJ/T 164 2020; HJ/T 493 2009), the sewage, river water, the drainage of wastewater treatment plant and Bohai Sea water were collected in Dongying City. The hydrochloric acid solution was added to adjust the pH of the water sample to be less than or equal to 2. The water sample should be filled with the sample bottle and sealed. It should be stored under 4 °C in dark and refrigerated. The extraction and derivation should be completed within 10 days, and the analysis should be completed within 5 days after the extraction.

1.5 Establishment of analytical method

(1) Gas chromatographic conditions

Injection port temperature: 300 °C, no split injection. He gas pressure: 40 kPa for 5 min, 2 kPa/min to 70 kPa, 5 min; column temperature: 50 °C, 2 min, 20 °C/min to 100 °C, 10 °C/min to 200 °C, 20 °C/min to 300 °C, 5 min; injection volume: 1 µl. The chromatographic column was hp-5ms capillary column, 30 m long, 0.25 mm inner diameter and 0.25 µm film thickness.

(2) Mass spectrometry conditions

Transmission line temperature: 280 °C. Quadrupole temperature: 150 °C. Ion source temperature: 230 °C. Electron energy of ion source: 70 ev. Mass range: 35-400 amu. Data acquisition mode: SIM. The quantitative and qualitative ions are shown in Table 1.

Table 1 Quantitative ion and qualitative ion of target compounds

Compound Name	CAS number	Quantitative ion	Qualitative ion	Note
deuterated naphthalene-d ₈ IS 1	1146-65-2	136	—	—
4-tert-butyl phenol	98-54-4	207	222	IS 1
4-n-butyl phenol	1638-22-8	179	222	IS 1
4-n-pentyl phenol	14938-35-3	179	236	IS 1
4-n-hexyl phenol	2446-69-7	179	250	IS 1
4-tert-octyl phenol	140-66-9	207	278	IS 1
4-n-heptyl phenol	1987-50-4	179	264	IS 2
4-nonylphenol	84852-15-3	207	221, 193	IS 2
deuterated phenanthrene-d ₁₀ IS 2	1517-22-2	188	—	—
4-n-octyl phenol	1806-26-4	179	278	IS 2
4-n-nonylphenol	104-40-5	179	292	IS 2
deuterated pyrene-d ₁₀ IS 3	1718-52-1	212	—	—
deuterated bisphenol A-d ₁₆ Surrogate	96210-87-6	368	386	IS 3
bisphenol A	80-05-7	357	372	IS 3

Results And Discussion

2.1 Influence of extraction solvent

500 ml of laboratory water was added into the separating funnel, and then alkylphenol and bisphenol A working solution were added to make the concentration of target substance in the water sample 0.20 µg/L. The effects of different extraction solvents on the recovery of target compounds are shown in Table 2. According to the data in the table, dichloromethane has the best extraction effect.

Table 2 Average extraction efficiency of C4-C9 alkylphenols and bisphenol A for different extraction solvents

Extraction solvent	Recovery rate %									
4-tert-butyl phenol	4-n-butyl phenol	4-n-pentyl phenol	4-n-hexyl phenol	4-tert-octyl phenol	4-n-heptyl phenol	4-nonylphenol	4-n-octyl phenol	4-n-nonylphenol	bisphenol A	
Dichloromethane	104	101	115	101	98.7	110	95.4	109	120	98.8
Hexane	118	13.5	83.	94.1	108	97.6	96.5	107	87.5	106
Ethyl acetate	91.2	84.2	83.7	65.8	72.1	80.6	65.4	82.9	66.5	76.2
Toluene	65.3	88.9	65.0	78.5	72.0	83.6	79.4	88.1	75.4	55.1

2.2 Influence of extraction times

The effects of different extraction times of dichloromethane on the recovery of target compounds are shown in Table 3. It can be seen from the table that C4-C9 alkylphenols can be extracted completely after one extraction, and bisphenol A can be extracted mainly after two extraction. When dichloromethane is selected as the extraction solvent, the second extraction can meet the requirements.

Table 3 Average extraction efficiency of C4-C9 alkylphenols and bisphenol A for different extraction times

Extraction times	Recovery rate %										
4-tert-butyl phenol	4-n-butyl phenol	4-n-pentyl phenol	4-n-hexyl phenol	4-tert-octyl phenol	4-n-heptyl phenol	4-nonylphenol	4-n-octyl phenol	4-n-nonylphenol	bisphenol A	Surrogate	
1	97.8	102	113	109	119	117	96.9	117	103	76.3	62.6
2	1.9	2.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.0	24.9	27.4
3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	4.6	5.2
4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

2.3 Influence of extraction time

The influence of different extraction time on the recovery rate of target compounds is shown in Table 4. It can be seen that the extraction time has a slight effect on the extraction efficiency. With the extension of the extraction time, the recovery rate of the target substance increases slightly. It can be seen from the table that the extraction time of 5 minutes is enough to fully recover the target substance in the water sample.

Table 4 Average extraction efficiency of C4-C9 alkylphenols and bisphenol A for different extraction time

Extraction time [min]	Recovery rate %										
4-tert-butyl phenol	4-n-butyl phenol	4-n-pentyl phenol	4-n-hexyl phenol	4-tert-octyl phenol	4-n-heptyl phenol	4-nonylphenol	4-n-octyl phenol	4-n-nonylphenol	bisphenol A	Surrogate	
5	98.9	101	109	101	118	112	95.6	115	106	98.7	91.0
10	99.7	104	113	109	119	117	96.9	117	104	101	90.0
15	104	109	118	117	122	127	98.1	123	106	101	92.3

2.4 Influence of acidity in water

The effect of acidity in water on the recovery rate of target compounds is shown in Table 5. It can be seen from the table that when the pH value is higher than 6, the recoveries of 4-nonylphenol and 4-n-octyl phenol decrease, but the recoveries of other target compounds are not affected. Considering that acidic conditions are conducive to inhibiting bacteria in water and preventing bacteria from consuming alkylphenol organics, the pH value of water sample is usually less than 2.

Table 5 Average extraction efficiency of C4-C9 alkylphenols and bisphenol A for different pH value

pH	<1	1-2	2-3	3-4	4-5	6-7
4-tert-butyl phenol	107	98.6	107	102	99.0	100
4-n-butyl phenol	110	99	104	101	99.4	96.8
4-n-pentyl phenol	117	111	113	110	109	106
4-n-hexyl phenol	117	109	112	108	106	102
4-tert-octyl phenol	122	106	115	110	109	110
4-n-heptyl phenol	125	115	120	114	113	105
4-nonylphenol	105	97.3	105	101	97.4	91.3
4-n-octyl phenol	116	106	112	107	107	97.7
4-n-nonylphenol	121	110	121	115	120	108
bisphenol A	110	115	116	108	114	113
Surrogate	117	110	121	115	114	113

2.5 Influence of extraction solvent volume

The effects of different extraction solvent volumes on the recovery of target compounds are shown in Table 6. It can be seen from the table that 20 ml of dichloromethane can meet the extraction requirements.

Table 6 Average extraction efficiency of C4-C9 alkylphenols and bisphenol A for different extraction solvent volume

Extraction solvent volume/ml	Recovery rate %										
4-tert-butyl phenol	4-n-butyl phenol	4-n-pentyl phenol	4-n-hexyl phenol	4-tert-octyl phenol	4-n-heptyl phenol	4-nonylphenol	4-n-octyl phenol	4-n-nonylphenol	bisphenol A	Surrogate	
20	95.2	99.7	111	97.0	104	116	95.2	96.7	99.0	98.4	100
30	104	109	116	100	104	118	95.2	96.3	97.6	101	103
40	107	111	118	101	103	117	98.3	97.9	97.1	103	104
50	108	113	121	104	106	122	100	101	103	104	104

2.6 Influence of salt content

Phenols are water-soluble and need salting out to improve extraction efficiency. The effect of different salt amount on the recovery rate of target substance is shown in Table 7. It can be seen from the table that adding sodium chloride can indeed improve the recovery rate of the target substance, but the improvement effect is not significant. The main reason is that the recovery rate data is high enough without adding salt. After comprehensive consideration, 5g sodium chloride can be added in water sample extraction.

Table 7 Average extraction efficiency of C4-C9 alkylphenols and bisphenol A for different salt content

NaCl Dosage (g)	0	5	10	20	30
4-tert-butyl phenol	97.5	100	103	103	102
4-n-butyl phenol	97.3	102	103	106	107
4-n-pentyl phenol	107	110	112	115	114
4-n-hexyl phenol	100	106	108	111	112
4-tert-octyl phenol	107	110	110	114	110
4-n-heptyl phenol	102	110	112	115	115
4-nonylphenol	93.9	104	103	105	105
4-n-octyl phenol	95.6	103	109	107	108
4-n-nonylphenol	99.1	107	113	112	111
bisphenol A	107	108	115	110	114
Surrogate	97.8	101	106	109	108

2.7 Effect of drying time during concentration process

In the standard of organic matter determination in water, when liquid-liquid extraction is used, it is related to whether the extraction liquid is dried during the concentration process. For C4-C9 alkylphenols, some of the target compounds are liquid with vapor pressure, and volatilization occurs when the vacuum is appropriate. Some of the solid targets are powder or velvet with low density, and they also have drift loss when the vacuum is appropriate. The influence of organic phase concentration to 0.5 ml or concentration to dryness and continuous rotary evaporation for different time on the recovery of target substance is shown in Table 8. It can be seen from the table that drying can significantly reduce the detection results, especially for some alkylphenols (4-tert-butylphenyl, etc.) which are liquid at room temperature. The experimental results are consistent with the above analysis. Finally, in the process of concentration, the treatment mode without drying was selected.

Table 8 Average extraction efficiency of C4-C9 alkylphenols and bisphenol A for different drying process

Drying time/min	Condense to 0.5 ml	1	5	10
4-tert-butyl phenol	102	40.1	21.5	20.9
4-n-butyl phenol	100	54.0	22.3	18.8
4-n-pentyl phenol	104	73.2	32.3	23.2
4-n-hexyl phenol	102	84.6	56.1	44.4
4-tert-octyl phenol	103	88.1	60.7	53.7
4-n-heptyl phenol	104	90.9	79.4	74.4
4-nonylphenol	100	92.3	82.5	74.9
4-n-octyl phenol	99.6	90.5	87.8	84.7
4-n-nonylphenol	104	95.4	94.1	92.6
bisphenol A	102	93.6	94.6	92.1
Surrogate	101	95.1	96.0	92.9

2.8 Spectrogram

The chromatogram of the standard sample of the target analytes is shown in Fig 1. It can be seen from the figure that under the conditions of reference gas chromatography-mass spectrometry, the peaks of each compound are independent and clear. Due to the use of derivatization treatment, there is basically no tailing phenomenon of phenolic compounds. 4-nonylphenol is a mixed peak of one group of isomers, and other compounds are single peaks.

2.9 Standard curve

The linear correlation coefficient of the standard curve of the object to be measured is shown in Table 9. It can be seen from the table that the standard curves of the target compounds are linear.

Table 9 Linear correlation coefficient, detection limit and lower limit of determination of C4-C9 alkylphenols and bisphenol A

RSD of RRF	4-tert-butyl phenol	4-n-butyl phenol	4-n-pentyl phenol	4-n-hexyl phenol	4-tert-octyl phenol	4-n-heptyl phenol	4-nonylphenol	4-n-octyl phenol	4-n-nonylphenol	bisphenol A
Low concentration curve	12.2%	6.02%	6.21%	6.30%	5.85%	6.71%	8.00%	4.04%	4.31%	3.05%
High concentration curve	1.71%	3.42%	4.87%	7.03%	5.36%	10.7%	3.18%	9.64%	9.64%	6.47%
detection limit($\mu\text{g/L}$)	0.002	0.002	0.002	0.002	0.002	0.002	0.006	0.002	0.003	0.003
Lower limit of determination($\mu\text{g/L}$)	0.008	0.008	0.008	0.008	0.008	0.008	0.024	0.008	0.012	0.012

2.10 Method detection limit

The detection limit of the method was confirmed according to the relevant environmental protection standard method (HJ 168 2020), and seven laboratory blank samples with or without the target objects working solution were analyzed continuously. Because 4-tert-butylphenyl, 4-tert-octylphenyl, 4-nonylphenol and bisphenol A were detected in the laboratory blank, the detection limits of these target substances were determined by the method of laboratory blank without standard addition and the detection limits of the remaining analytes were determined by the method of laboratory blank with standard addition. The concentration of these remaining analytes in the laboratory blank sample with standard addition is all 0.010 $\mu\text{g/L}$. The lower limit of determination is 4 times of the detection limit and both of which are listed in Table 9. These detection limits of the target compounds changes from 0.002 $\mu\text{g/L}$ to 0.006 $\mu\text{g/L}$ and the lower limit of determination from 0.008 $\mu\text{g/L}$ to 0.024 $\mu\text{g/L}$.

2.11 Recovery and precision

Taking the laboratory water without the target analytes as the blank matrix, C4-C9 alkylphenols and bisphenol A standard solutions with three different concentration levels were added respectively. The pretreatment and test were carried out according to the method steps. Each concentration level was determined for six times in parallel. The relative standard deviation results are shown in table 10. Take surface water, sewage and wastewater as sample matrix, add C4-C9 alkylphenols and bisphenol A standard solution with matrix concentration level of 0.5-3 times, repeat the above laboratory test, and the average recovery results are shown in Table 11. The relative standard deviations of the target samples ranged from 0.67% to 13.7%, and the average recovery ranged from 68.0% to 122%, which indicates that the precision and accuracy of the experiment are good.

Table 10 Precision datas

Spiked concentration (µg/L)	Relative standard deviation%									
4-tert-butyl phenol	4-n-butyl phenol	4-n-pentyl phenol	4-n-hexyl phenol	4-tert-octyl phenol	4-n-heptyl phenol	4-nonylphenol	4-n-octyl phenol	4-n-nonylphenol	bisphenol A	
0.02	9.52	4.62	3.93	2.90	2.68	4.69	10.1	10.2	12.3	7.08
0.50	3.20	2.15	1.88	1.92	1.96	1.79	2.49	2.29	3.12	2.44
2.0	2.05	2.42	2.12	2.19	1.51	1.74	5.32	7.20	13.7	0.67

Table 11 Recovery datas

Water sample	Spiked concentration(µg/L)	Recovery rate of standard addition %									
4-tert-butyl phenol	4-n-butyl phenol	4-n-pentyl phenol	4-n-hexyl phenol	4-tert-octyl phenol	4-n-heptyl phenol	4-nonylphenol	4-n-octyl phenol	4-n-nonylphenol	bisphenol A		
Sewage	0.05	106	96.0	111	104	102	101	90.7	112	99.1 107	
Surface water	0.50	99.5	102	110	116	121	122	72.4	79.1	88.2 68.0	
Wastewater	2.0	95.9	102	104	107	104	111	97.9	102	98.6 91.4	

2.12 Determination of typical representative water samples

The contents of target analytes in groundwater, surface water, sewage, wastewater and seawater samples are shown in Table 12. It can be seen from the table that the contents of 4-nonylphenol and bisphenol A in the environmental water in Dongying City are below the requirements of relevant directives at home and abroad (GB 31572 2015; GB 31571 2015; U.S. EPA 2005; [European Commission EC 2003](#)), and the contents of target substances in groundwater, surface water and seawater are very low.

Table 12 The measured value of target analytes in actual water sample µg/L

4-tert-butyl phenol	4-n-butyl phenol	4-n-pentyl phenol	4-n-hexyl phenol	4-tert-octyl phenol	4-n-heptyl phenol	4-nonylphenol	4-n-octyl phenol	4-n-nonylphenol	bisphenol A	Surrogate Recovery	
Groundwater	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.016	124%
Surface water 1	n.d.	n.d.	n.d.	n.d.	0.003	n.d.	0.049	n.d.	n.d.	0.023	125%
Surface water 2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.026	n.d.	n.d.	0.032	78.6%
Surface water 3	0.031	0.007	n.d.	n.d.	0.008	0.002	0.139	0.002	0.003	0.068	92.3%
Surface water 4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.228	n.d.	n.d.	0.226	77.4%
Sewage 1	0.004	0.008	n.d.	n.d.	0.019	0.003	0.965	0.003	n.d.	0.024	110%
Sewage 2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.344	n.d.	n.d.	0.156	88.5%
Wastewater 1	0.002	n.d.	n.d.	n.d.	0.007	n.d.	1.37	n.d.	0.001	0.200	115%
Wastewater 2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.207	n.d.	n.d.	0.029	81.9%
Wastewater 3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.81	n.d.	n.d.	2.30	70.5%
Wastewater 4	0.006	0.004	0.005	0.007	0.016	0.017	0.218	0.064	0.094	0.870	97.9%
Wastewater 5	0.004	n.d.	n.d.	n.d.	0.009	n.d.	0.114	0.026	0.035	32.8	87.3%
Seawater	n.d.	0.003	0.001	n.d.	n.d.	0.002	0.077	0.008	n.d.	0.011	104%

Note: surface water 1 is drinking water, surface water 2 is yellow river water, surface water 3 is Guangli River water, surface water 4 is Xiaqing River water, sewage 1 is outlet water of a sewage treatment plant in Dongying City, sewage 2 is outlet water of a sewage treatment plant in Guangrao County, Dongying City, wastewater 1 is outlet water of an industrial wastewater treatment plant in Dongying City, and wastewater 2 is outlet water of an oil processing enterprise in Dongying City, wastewater 3 is from the workshop of an oil processing enterprise in Dongying City, wastewater 4 is from the workshop of a bisphenol A production enterprise in Dongying City, and wastewater 5 is from the workshop of a bisphenol A production enterprise in Dongying City.

Conclusions

(1) Aiming to monitor of C4-C9 alkylphenols and bisphenol A in water, A liquid-liquid extraction combined with derivatization and gas chromatography-mass spectrometry (GC-MS) method was used to optimize the extraction solvent, extraction times, extraction time, extraction solvent volume, acidity, salt content, rotary distillation concentration degree and other conditions. After optimization, dichloromethane was used as the extraction solvent, the extraction time was 5 min, the extraction solvent was 30 ml, the pH value was less than 2, and the amount of salt was 5 g.

(2) The method has the advantages of high sensitivity, low detection limit, accurate quantification and good precision, which can meet the needs of the determination of C4-C9 alkylphenols and bisphenol A in water.

(3) The method was used to detect the groundwater, surface water, sewage, wastewater and sea water samples in Dongying City located at the Yellow River Estuary. The results showed that the contents of 4-nonylphenol and bisphenol A in the samples were lower than the requirements of relevant directives at home and abroad.

Declarations

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Authors' contributions Ziqi Guo, Xinliang Liu and Jian Zhao carried out the experiment. Hailiang Yin and Tongna Zhou put forward the idea. All authors have read and approved the final manuscript.

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Compliance with ethical standards

Ethics approval and consent to participate Not applicable.

Consent for publication Not applicable.

Competing interests The authors declare that they have no competing interests.

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Figures

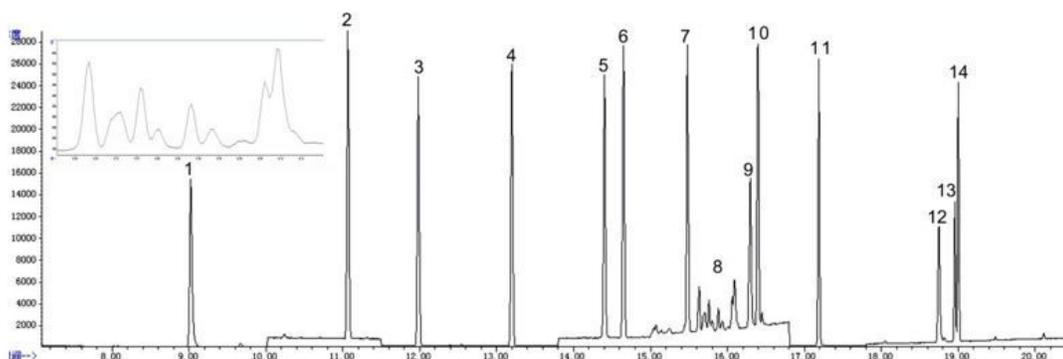


Figure 1

Total ion flow diagram of C4-C9 alkylphenols and bisphenol A (SIM) 1-1S1 2-4-tert-butyl phenol 3-4-n-butyl phenol 4-4-n-pentyl phenol 5-4-n-hexyl phenol 6-4-tert-octyl phenol 7-4-n-heptyl phenol 8-4-nonylphenol 9-IS2 10-4-n-octyl phenol 11-4-n-nonylphenol 12-IS3 13-Surrogate 14-bisphenol A

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