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PAPER

Purification and determination of bisphenol A and alkylphenol in river sediments by high performance liquid chromatography with fluorescence detection

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A sensitive method was developed for the purification and determination of bisphenol A and alkylphenols in river sediments by using 2-(9*H*-carbazol-9-yl)ethyl carbonochloridate (CEOC) as pre-column labeling reagent followed by high performance liquid chromatography (HPLC) with fluorescence detection. Solid phase extraction with Bond Elute Carbon cartridges was applied to sample purification procedure and proved to be simple and effective. The average recoveries of the three target compounds were higher than 80%, with relative standard deviation (RSD) of less than 10%. The sensitivity of the proposed method was about two orders of magnitude higher than traditional HPLC method. When 5.0 g soil sample was used for analysis, the limits of quantification of the analytes were in the range of 0.3–0.6 μg kg^{-1}. Investigation of the concentrations in sediment samples indicated that all three analytes were found at levels ranging from 1.1 to 6.1 μg kg^{-1}.

Introduction

With the rapid development of industry, numerous polycarbonate and plastic articles have been used. This provides great convenience for our everyday life. However, a lot of side effects have been exposed. Recently, a wide variety of chemicals have been confirmed to possess endocrine-disrupting properties.[1–4] Among them, 4-octylphenol (OP), 4-nonylphenol (NP), and bisphenol A (BPA) have attracted great attention because of worldwide pollution and the increasing awareness of their side effects.[5–11] BPA is a primary raw material in the production of polycarbonate (PC) plastics and epoxy resins.[12] It has been widely used in the production of food packaging materials, water bottles, baby bottles and flame retardants. While NP and OP are the precursors and the main degradation products of alkylphenol polyethoxylates (APEs), an important kind of non-ionic surfactant that is widely used in many detergent formulations and plastic products for industrial and domestic use.[13]

The annual production and assumption of BPA, OP and NP are tremendous. For example, an estimated annual production of OP was over 2000 t in the European Union in 1992. The consumption of BPA in 1993 was 347 000 t for Western Europe, and 552 000 t for the USA.[14] Therefore, they have very high incidence to be found all over the world, especially in water, soil and food samples. These compounds can mimic estrogen activity and are known as endocrine disrupting chemicals (EDCs). Exposure to very low levels of these compounds can be harmful. Transgenerational effect of BPA was also reported.[15] Great social attention has also been paid to the negative effect of these compounds. In September 2010, Canada became the first country to declare BPA a toxic substance. Baby bottles containing BPA were forbidden in many countries and the allowance of other BPA-containing materials is still under hot discussion.

Sediment samples usually contain very complex matrices and low levels of BPA and alkylphenols. It is quite challenging to remove so many matrices without an obvious loss of the target compounds. To get a good command of the contamination status of these pollutants in sediment samples, it is necessary to develop an effective and easy to operate purification method, as well as a sensitive detecting method. Various methods have been developed for the determination of BPA and alkylphenols,[2,8,12,16–20] among which gas chromatography-mass spectrometry (GC-MS) has been applied more frequently than other methods.[12,20–22] Due to the low fluorescence or ultraviolet property of these compounds, direct LC methods were rarely applied to the analysis of them unless a special pretreatment procedure was applied to concentrate the target compound to a high concentration.[23] Derivatization gradually showed its superiority in enhancing HPLC sensitivity of BPA and alkylphenols. For example, dansyl chloride, 4-(4,5-diphenyl-1*H*-imidazol-2-yl) benzoyl chloride (DIB-Cl) and *p*-nitrobenzoyl chloride have been applied to the HPLC analysis of BPA and OP with limit of detection as low as μg L^{-1}.[24–26]

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In this paper, a sensitive HPLC method with fluorescence detection has been developed for the simultaneous determination of BPA, OP and NP in river sediment samples. Sample purification procedure was also optimized and a simple and effective solid phase extraction (SPE) method was developed. The proposed method offers two excellent features. One is the high sensitivity. Derivatization with CEOC greatly enhanced the fluorescence property of the analytes, and the sensitivity was about two orders of magnitude higher than normal HPLC method. Another is the effective purification procedure. After a simple normal phase solid phase extraction (SPE) procedure, the eluted solution was clean and there was little interference in LC chromatogram. The proposed method was successfully applied to the analysis of BPA, OP and NP in river sediment samples.

Experimental

Reagents and chemicals

Analytical standards of BPA, OP and NP were all obtained from Dr Ehrenstorfer (Ausburg, Germany) with purity higher than 99%. Methanol, dichloromethane and acetonitrile were of HPLC grade (Shandong Yuwang Industrial Co. Ltd, China). Water was purified on a Milli-Q system (Millipore, Bedford, MA, USA). All other reagents used were of HPLC grade or at least of analytical grade. ODS C18 cartridges (500 mg, 6 mL) were obtained from Chrome Expert (CA, USA), Oasis HLB cartridges (60 mg, 3 mL) were obtained from Waters (Milford, MA, USA), Bond Elute Carbon cartridges (500 mg, 6 mL) were purchased from Agilent (CA, USA), Cleanert Alumina N (AL) and Cleanert Florisil (FL) cartridges were purchased from Agela Technologies (Tianjin, China), respectively. CEOC was prepared according to the method previously described by You *et al.*[27]

Individual stock solutions of 100 mg L^{-1} for all compounds were prepared in HPLC grade acetonitrile and stored at 4 °C in the dark. Standard solutions containing all compounds were mixed and diluted with acetonitrile, and working solutions of all compounds and calibration concentrations were prepared by appropriate dilution of the stock solutions on the day of analysis.

The derivatizing reagent solution (1.0×10^{-3} mol L^{-1}) was prepared by dissolving 2.62 mg CEOC in 10 mL of anhydrous acetonitrile. When not in use, all reagent solutions were stored at 4 °C in a refrigerator.

Sample preparation

River sediment samples were collected from three different stations of Xiaoqinghe River in Jining city. The sediments were dried, ground, and passed through a 2 mm sieve prior to analysis. Spiked samples were prepared by adding 2 mL of a solution containing certain amounts of analyte standards to sediment samples. The bulk of solvent was slowly evaporated at room temperature during 12–15 h. Then the samples were dried in a heater at 40 °C for 4 h. The spiked samples were then ready for the experiments. A 5.0 g of sediment sample was weighed in a 50 mL glass centrifuge tube. The extraction was performed with 20 mL of methanol using ultra-sonication for 15 min. The samples were centrifuged at 4000 rpm for 10 min, then the supernatant was collected, and 10 mL of methanol was added into the residue for further extraction. The supernatants of the two times were united and evaporated to dryness in a rotary vacuum evaporator at 40 °C. The dry residue was redissolved in 2 mL dichloromethane and methanol (8 : 2, v/v) and transferred onto the Bond Elute Carbon cartridges previously conditioned with 5 mL of mixed solvent of dichloromethane and methanol (8 : 2, v/v). The eluate was collected as soon as the extract was transferred onto the cartridges. 10 mL of dichloromethane and methanol (8 : 2, v/v) was then used to elute the analytes. The eluate was evaporated to near 1 mL under a gentle stream of nitrogen gas at 40 °C. It was then transferred into a 2 mL vial and further evaporated to dryness for derivatization.

Derivatization procedure

Derivatization of the analytes with CEOC proceeded in alkaline medium. 80 μL $NaHCO_3$ buffer (pH 10), 100 μL acetonitrile and 50 μL CEOC acetonitrile solution were added into a 2 mL vial containing either standard or sample solution. The vial was sealed and vortexed for 1 min and then allowed to react at 40 °C for 5 min in a water bath. Then the mixture was cooled to room temperature and 20 μL 50% acetic acid solution was added to adjust pH to lower than 7.0. Finally, the derivatized sample solution was diluted to 1 mL with water : acetonitrile (3 : 7, v/v) and injected directly for HPLC analysis. The derivatization scheme is shown in Fig. 1.

HPLC analysis

The HPLC analysis was performed using an Agilent 1100 Series HPLC system, equipped with an on-line-degasser, a quaternary pump, an autosampler and a thermostatted column compartment. A fluorescence detector (model G1321A, Agilent, USA) was adjusted at wavelength 293 and 360 nm for excitation and emission. Chromatographic separation was achieved on a Hypersil BDS C8 column (200 × 4.6 mm, 5 μm i.d., Dalian Elite Analytical Instruments Co. Ltd, China). Solvent A was 5% acetonitrile in water and B was acetonitrile. The flow rate was constant at 1.0 mL min^{-1} and the column temperature was kept at 30 °C. The gradient condition of mobile phase was as follows: 70–100% B from 0 to 8 min and then held for 2 min. The column was equilibrated with the initial mobile phase for 5 min before the next injection. The injection volume was 10 μL.

Method validation

Calibration curves consisted of 5 calibration points covering from 1.5 to 100 ng mL^{-1} for BPA, 3.0 to 100 ng mL^{-1} for OP and NP. The linearity of each calibration curve was determined by plotting peak area *versus* concentration. Limit of detection (LOD) and quantification (LOQ) were defined as the concentrations that gave a signal to noise ratio of 3 and 10, respectively. Recovery was measured by analyzing five spiked samples at three levels (1.0, 5.0 and 10 μg kg^{-1}). Repeatability and reproducibility

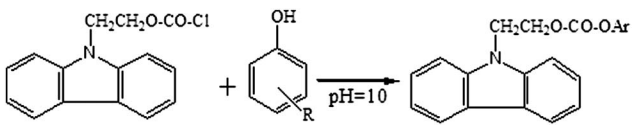

Fig. 1 The derivatization scheme of CEOC with BPA, OP and NP.

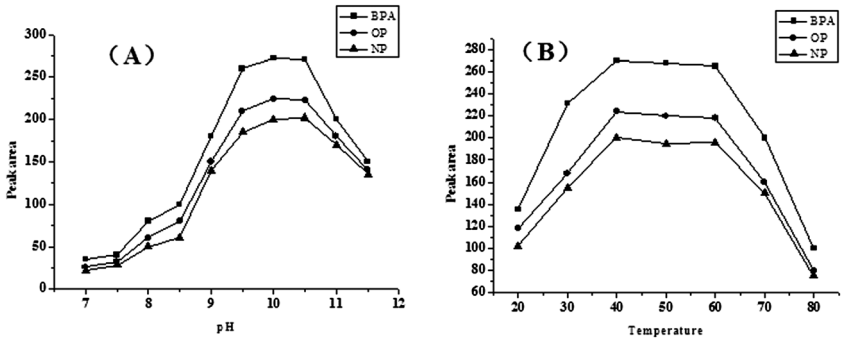

Fig. 2 (A) Effect of pH on derivatization; (B) effect of temperature on derivatization.

was evaluated by spiking sediment samples at a concentration of 5.0 μg kg^{-1} in five replicates within 1 day and over the course of three consecutive days, respectively.

Results and discussion

Sample extraction and purification

Sediment samples usually possess large quantities of matrices, and therefore intricate purification procedure is indispensable. Solid phase extraction is often used in the purification of EDCs due to its low organic solvent-consumption and the character of easy to operate. Different types of SPE cartridges were evaluated in order to obtain good recoveries and less interferences. The recoveries of OP and NP obtained by HLB cartridges were lower than 60%, and similar results were also reported by other authors.[2,28,29] FL cartridges were usually applied in the purification of organochlorine in soil samples and they were also tested in our method for the purification of BPA, OP and NP. Though a clean chromatogram was obtained, the recovery of BPA was lower than 40%. C18 and AL cartridges were also tested, but none of them could provide a clean chromatogram with high recovery.

Graphitized carbon black cartridges (GCB) have proved to be a valuable adsorbing material for the SPE of pesticides in water sample.[30,31] However, little research was tried on sediment sample purification. Bond Elute Carbon cartridges (packed with graphitized carbon particles) were applied in our method considering their powerful adsorptivity of interferences. The recovery of BPA could be higher than 90% by sole elution of methanol. However, almost no recovery was observed for OP and NP by this method. Ethyl acetate, *n*-hexane, acetone, dichloromethane and their mixture were then compared for their elution efficiency, and neither could provide a satisfying result. An ideal elution of the three target compounds was obtained by using a mixture of dichloromethane and methanol as eluent. The final purification procedure was as follows: the extracts were passed through the cartridges previously conditioned with 5 mL of mixed solvent of dichloromethane and methanol (8/2, v/v) at a flow rate of 2–3 mL min^{-1}, then the analytes were eluted with 10 mL of mixed solvent of dichloromethane and methanol (8/2, v/v). It should be noted that the eluate was collected the moment the extract was transferred on to the cartridges. The procedure was simple, but the recoveries were higher than 80% for all three compounds, and excellent recovery (>90%) of BPA could be obtained by using an additional 5 mL of methanol. The elution was colorless and no obvious interference was observed during LC analysis.

Optimization of derivatization parameters

Effect of sodium bicarbonate buffer on derivatization. Buffer solutions play an important role in pre-column derivatization. Several kinds of buffers were tested in this study for derivatization, including sodium bicarbonate buffers, phosphate buffers

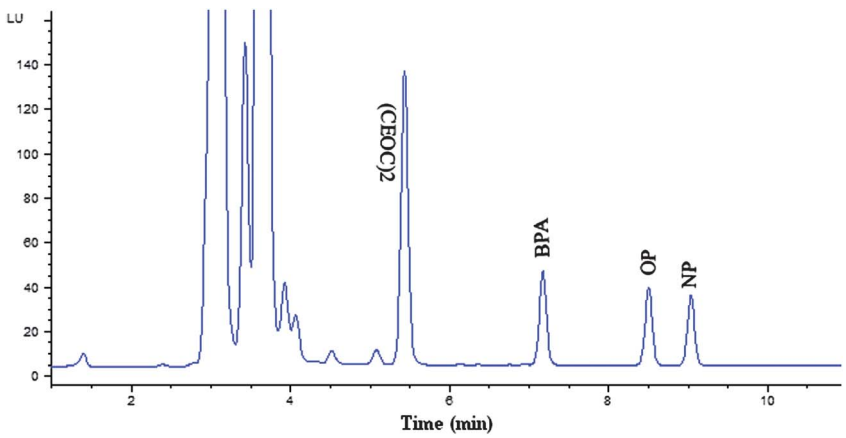

Fig. 3 Chromatogram of BPA, OP and NP derivatives (15, 30 and 30 μg L^{-1} for BPA, OP and NP, respectively).

Table 1 Linearity, LOD, LOQ, repeatability and reproducibility obtained with the proposed method

Analyte	Linearity (R)	LOD (μg kg^{-1})	LOQ (μg kg^{-1})	Repeatability (RSD %, $n = 5$)	Reproducibility (RSD %, $n = 5$)
BPA	0.996	0.1	0.3	6.8	9.5
OP	0.996	0.2	0.6	4.9	7.8
NP	0.996	0.2	0.6	5.6	8.9

Table 2 Recoveries and relative standard deviation of target compounds in soil ($n = 5$)

Analyte	Spiked level (μg kg^{-1})	Recovery (%)	RSD (%)
BPA	1	80.2	9.8
	5	81.6	7.6
	10	83.4	8.0
OP	1	84.1	6.8
	5	90.5	5.5
	10	87.5	6.2
NP	1	83.2	7.2
	5	85.4	6.5
	10	86.7	5.4

and borate buffers. Sodium bicarbonate buffer was selected for latter experiments because of its high derivatization yields for the target compounds. Effect of sodium bicarbonate buffer pH on the derivatization reaction was then evaluated in the pH range of 7–11.5. As can be seen from Fig. 2A, the maximum derivatization yields were stable in the pH range of 10.0–10.5. Therefore, 0.1 M sodium bicarbonate buffer with pH 10 was applied for all subsequent derivatizations.

Effect of CEOC concentration on derivatization. BPA has two phenolic hydroxyl groups to easily react with CEOC under the proposed conditions. Therefore, the amount of CEOC should be sufficient enough to obtain solely disubstituted derivatives. The effects of CEOC concentrations in the range of 1.0×10^{-4} to 1.0×10^{-3} mol L^{-1} were investigated. When the amount of CEOC was not sufficient enough, both mono- and disubstituted derivatives of BPA were observed and mono-substituted derivatives eluted earlier than the disubstituted one since it was less hydrophobic. Only disubstituted derivatives could be obtained when the CEOC concentration was 1.0×10^{-3} mol L^{-1}. Further increasing the excess of CEOC beyond this level had no improvement on the yield of disubstituted derivatives of BPA.

Effect of reaction temperature on derivatization. The effect of reaction temperature on the fluorescence spectra of the derivatives was tested over the temperature range from 20 °C to 80 °C. The results are shown in Fig. 2B. It is obvious that the complete derivatization could be achieved at 40 °C for 5 min. With reaction temperature <30 °C, a long derivatization time was needed to obtain a constant response. Increasing temperature to 60 °C, no improvement or decrease in response was observed. However, when the temperature was higher than 70 °C, an obvious decrease in response was observed. This should be attributed to the fact that high temperature results in the hydrolysis of the derivatives in basic media. Based on these results, derivatization was performed at 40 °C for 5 min with pH 10.

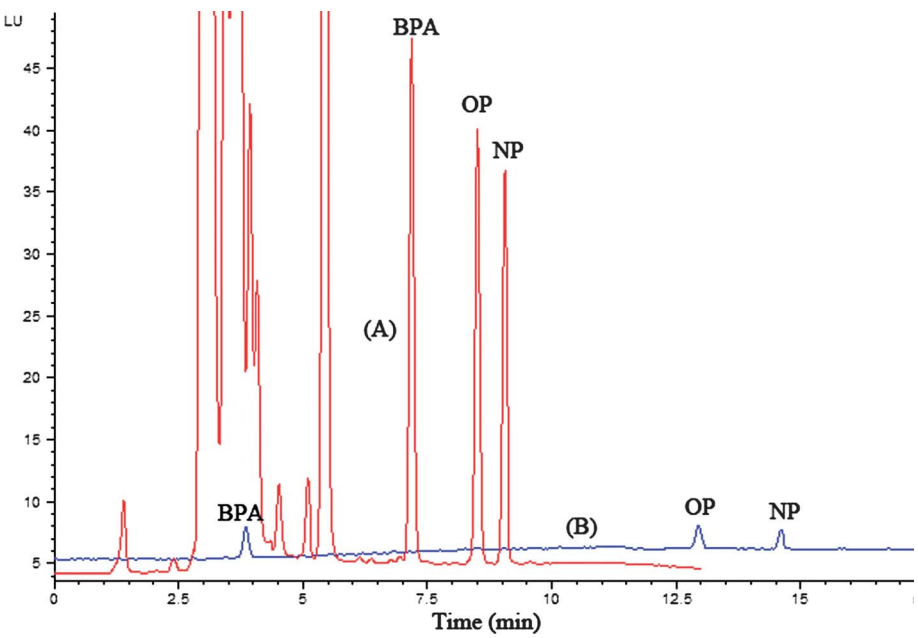

Fig. 4 Comparison of HPLC chromatograms of the analytes. (A) Chromatogram of CEOC derivatives of the analytes (15, 30 and 30 μg L^{-1} for BPA, OP and NP, respectively); (B) chromatogram of the analytes without derivatization (1000 μg L^{-1}).

Table 3 Comparison of the methods used before to the proposed method

Reference	Analytes	Method	Derivatizing reagent	LOD (μg kg^{-1})		
				OP	NP	BPA
21	Soil	GC-MS	Acetic anhydride	—[a]	0.2	1.7
22	Soil	GC-MS	BSTFA[b]	9	9	—
32	Soil	LC-MS	—	1.0	1.0	—
24	Sewage sludge	HPLC	Dansyl chloride	1[c]	5	5
25	Urine	HPLC	*p*-Nitrobenzoyl chloride	—	2.9	2.7
26	Plastic	HPLC	DIB-Cl[d]	—	1.3	0.67
This article	Sediment	HPLC	CEOC	0.2	0.2	0.1

[a] Not included in the method. [b] *N*,*O*-Bis(trimethylsilyl)trifluoro acetamide (BSTFA). [c] The values in the reference are shown in ng (per 100 μL injection volume). [d] DIB-Cl: 4-(4,5-diphenyl-1*H*-imidazol-2-yl)benzoyl chloride.

HPLC separation

The complete HPLC separation of the derivatives could be easily accomplished using a Hypersil BDS C8 column in combination with a gradient elution with water and acetonitrile as mobile phase composition (see Fig. 3). The derivatives were separated within 10 min with a good baseline resolution. A noticeable improvement was observed for BPA. Derivatization increased the hydrophobicity and retention time of BPA, therefore it was shifted out of the often noise in LC analysis.

Method validation

Linearity, repeatability, and reproducibility. The linear regression of the peak areas *versus* concentrations were fitted over the concentration range of 1.5–100.0 ng mL^{-1} for BPA, 3.0–100.0 ng mL^{-1} for OP and NP. Each standard calibration curve consisted of 5 points and was done on the same day of soil sample analysis. The linearity obtained for all analytes were good with correlation coefficients of 0.996 (Table 1). For repeatability, five replicates at a concentration of 5.0 μg kg^{-1} were analyzed on the same day ($n = 5$) and by the same analyst. For reproducibility, five replicates of 5.0 μg kg^{-1} were analyzed on three different days by different analysts. Results for repeatability reveal good precision of the method with mean relative standard deviation (RSD) values less than 7.0% for all compounds. The results for reproducibility indicate the robustness of the method with mean RSD values less than 10%.

Table 4 Concentrations of BPA, OP and NP in river sediment samples ($n = 3$)

Sample number	BPA (μg kg^{-1})	OP (μg kg^{-1})	NP (μg kg^{-1})
1	1.9	3.8	3.7
2	1.1	5.7	5.2
3	2.2	4.4	6.1

Sensitivity, accuracy and stability. As can be seen from Table 1, when 5.0 g sample was analyzed, the LODs ranged from 0.1 to 0.2 μg kg^{-1}, while the LOQs were in the range of 0.3–0.6 μg kg^{-1}, respectively. When sediment samples were spiked at LOQ levels with three replicates, the average recoveries of the target compounds were higher than 80%. Accuracy (evaluated by recovery) was then measured by analyzing five spiked samples at three levels (1.0 μg kg^{-1}, 5.0 μg kg^{-1} and 10 μg kg^{-1}). A good degree of accuracy was achieved for the analytes with recoveries ranging from 80.2% to 90.5% (Table 2).

The stability of CEOC and sample derivatives was also tested. Anhydrous acetonitrile solution of CEOC could be stored at 4 °C for one week without obvious decrease in derivatization yields

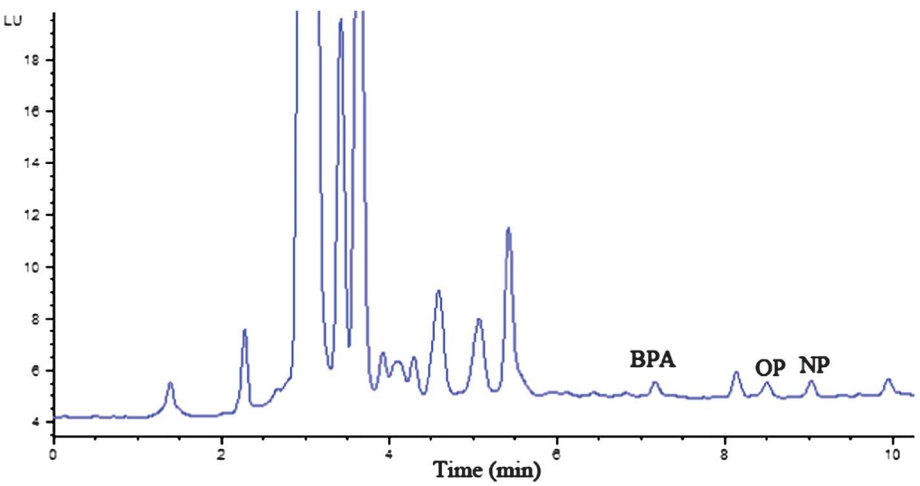

Fig. 5 A representative chromatogram of sediment sample no.1 listed in Table 4.

for the target compounds compared to those newly prepared CEOC solutions. The stabilities of the corresponding derivatives were also investigated. Standard solution of 5 μg L^{-1} and sediment sample spiked at 5 μg L^{-1} were derivatized by CEOC. The derivatized solutions were then neutralized to pH < 7.0. These solutions were repeatedly analyzed by HPLC after being placed at room temperature for 0, 4, 8, 12, 24, 48, 72 and 96 h, respectively. The corresponding derivatives were stable with peak area deviations (RSDs) of less than 3.2%.

Signal enhancement. Most of the methods applied to the determination of BPA, OP and NP are GC-MS.[21,22] Liquid chromatography-mass spectrometry (LC-MS)[28,32] methods have also been applied to sample analysis frequently, though the ionization efficiency of these compounds was limited.[33] Since the fluorescence or ultraviolet absorption property of these compounds was weak, LC methods without derivatization were rarely applied to the determination of BPA, OP and NP. In this method, the HPLC sensitivity of BPA, OP and NP was greatly enhanced through the introduction of CEOC with excellent property into the analyte molecules. Signal enhancement was depicted by comparing the chromatogram of BPA, OP and NP derivatives with that of direct LC analysis (see Fig. 4). To ensure the chromatograms used for comparison were obtained at their best conditions, the wavelengths of the target compounds in direct LC analysis were optimized and set at 227 and 313 nm for excitation and emission wavelengths, respectively. While the wavelengths of the proposed method were set at λ_{ex} 293 and λ_{em} 360 nm as previously described.[27] It is obvious that the sensitivity was enhanced by almost two orders of magnitude. In addition, the sensitivity of this proposed method was also compared to some sensitive GC-MS, LC-MS and HPLC methods published before, and the results are summarized in Table 3. Though the proposed method is much easier and cheaper, its sensitivity is equivalent or superior to those of GC-MS or LC-MS methods. Though the sensitivities obtained by previously reported HPLC methods with derivatization were very sensitive, the proposed method still showed some superiority to them not only in sensitivity, but also in the quick labeling property. For example, the derivatization of BPA, OP and NP with dansyl chloride should proceed in the dark for 16 h. DIB-Cl needed the least reaction time, but 20 min was still necessary. In contrast, only 5 min was necessary in this method.

Application

The developed method was successfully applied to the determination of BPA, OP and NP in river sediment samples. Fig. 5 shows a representative chromatogram of the target compounds in river sediment sample. BPA, OP and NP were found in all the samples analyzed, ranging from 1.12 to 6.09 μg kg^{-1} and their concentrations are summarized in Table 4. The pollution status is not as severe as rivers such as Pearl River Delta, China,[34] probably because there are fewer factories along the river.

Conclusions

A new sensitive method was developed for the determination of BPA, OP and NP in river sediment samples. The sensitivity was greatly enhanced due to the introduction of CEOC with excellent fluorescence property into the molecules of the analytes. Since the synthesis procedure of CEOC is simple and the materials are commercially available, it can be well applied to the analysis of BPA, OP and NP in normal laboratories with slight experience. Bond Elute Carbon cartridges were successfully applied to the purification of BPA, OP and NP in sediment samples with simple procedures. No obvious interference was observed in the LC chromatogram, and the recoveries were higher than 80% for all the target compounds. The purification procedure can be well applied to the pretreatment of BPA, OP and NP in soil or sediment samples. This method also makes the sensitive determination of BPA, OP and NP feasible in laboratories without the use of expensive MS spectrometers.

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References

1 R. H. Waring and R. M. Harris, *Maturitas*, 2011, **68**, 111–115.
2 R. Jeannot, H. Sabik, E. Sauvard, T. Dagnac and K. Dohrendorf, *J. Chromatogr., A*, 2002, **974**, 143–159.
3 T. T. Schug, A. Janesick, B. Blumberg and J. J. Heindel, *J. Steroid Biochem. Mol. Biol.*, 2011, **127**, 204–215.
4 J. Lintelmann, A. Katayama, N. Kurihara, L. Shore and A. Wenzel, *Pure Appl. Chem.*, 2003, **75**, 631–681.
5 A. David, H. Fenet and E. Gomez, *Mar. Pollut. Bull.*, 2009, **58**, 953–960.
6 R. A. Keri, S. M. Ho, P. A. Hunt, K. E. Knudsen, A. M. Soto and G. S. Prins, *Reprod. Toxicol.*, 2007, **24**, 240–252.
7 J. Oehlmann, M. Oetken and U. Schulte-Oehlmann, *Environ. Res.*, 2008, **108**, 140–149.
8 A. Soares, B. Guieysse, B. Jefferson, E. Cartmell and J. Lester, *Environ. Int.*, 2008, **34**, 1033–1049.
9 C. A. Staples, P. B. Dome, G. M. Klecka, S. T. Oblock and L. R. Harris, *Chemosphere*, 1998, **36**, 2149–2173.
10 G. G. Ying, B. Williams and R. Kookana, *Environ. Int.*, 2002, **28**, 215–226.
11 J. T. Wolstenholme, E. F. Rissman and J. J. Connelly, *Horm. Behav.*, 2011, **59**, 296–305.
12 M. Kawaguchi, K. Inoue, M. Yoshimura, R. Ito, N. Sakui, N. Okanouchi and H. Nakazawa, *J. Chromatogr., B: Anal. Technol. Biomed. Life Sci.*, 2004, **805**, 41–48.
13 Y. Niu, J. Zhang, Y. Wu and B. Shao, *J. Chromatogr., A*, 2011, **1218**, 5248–5253.
14 M. Duft, U. Schulte-Oehlmann, L. Weltje, M. Tillmann and J. Oehlmann, *Aquat. Toxicol.*, 2003, **64**, 437–449.
15 B. Yi, C. Kim and M. Yang, *J. Chromatogr., B: Anal. Technol. Biomed. Life Sci.*, 2010, **878**, 2606–2610.
16 M. Rezaee, Y. Yamini, S. Shariati, A. Esrafili and M. Shamsipur, *J. Chromatogr., A*, 2009, **1216**, 1511–1514.
17 X. Chen, C. Wang, X. Tan and J. Wang, *Anal. Chim. Acta*, 2011, **689**, 92–96.
18 X. Wang, H. Zeng, L. Zhao and J. Lin, *Anal. Chim. Acta*, 2006, **556**, 313–318.
19 D. G. Mita, A. Attanasio, F. Arduini, N. Diano, V. Grano, U. Bencivenga, S. Rossi, A. Amine and D. Moscone, *Biosens. Bioelectron.*, 2007, **23**, 60–65.
20 Y. Jiao, L. Ding, S. Fu, S. Zhu, H. Li and L. Wang, *Anal. Methods*, 2012, **4**, 291.
21 J. Llorca-Pórcel, M. Martínez-Parreño, E. Martínez-Soriano and I. Valor, *J. Chromatogr., A*, 2009, **1216**, 5955–5961.
22 I. Jiménez-Díaz, O. Ballesteros, A. Zafra-Gómez, G. Crovetto, J. L. Vílchez, A. Navalón, C. Verge and J. A. de Ferrer, *Chemosphere*, 2010, **80**, 248–255.

23 X. Liu, X. Zhang, H. Zhang and M. Liu, *J. Chromatogr. Sci.*, 2008, **46**, 596–600.
24 M. Naassner, M. Mergler, K. Wolf and I. Schuphan, *J. Chromatogr., A*, 2002, **945**, 133–138.
25 L. Mao, C. Sun, H. Zhang, Y. Li and D. Wu, *Anal. Chim. Acta*, 2004, **522**, 241–246.
26 Y. Sun, M. Wada, N. Kuroda, K. Hirayama, H. Nakazawa and K. Nakashima, *Anal. Sci.*, 2001, **17**, 697–702.
27 J. You, Y. Shan, L. Zhen, L. Zhang and Y. Zhang, *Anal. Biochem.*, 2003, **313**, 17–27.
28 I. C. Beck, R. Bruhn, J. Gandrass and W. Ruck, *J. Chromatogr., A*, 2005, **1090**, 98–106.
29 R. Carabias-Martinez, E. Rodriguez-Gonzalo and P. Revilla-Ruiz, *J. Chromatogr., A*, 2004, **1056**, 131–138.
30 A. Di Corcia and M. Marchetti, *Anal. Chem.*, 1991, **63**, 580–585.
31 A. Di Corcia, A. Bellioni, M. D. Madbouly and S. Marchese, *J. Chromatogr., A*, 1996, **733**, 383–393.
32 J. Wang, H. Pan, Z. Liu and F. Ge, *J. Chromatogr., A*, 2009, **1216**, 2499–2503.
33 T. Higashi and K. Shimada, *Anal. Bioanal. Chem.*, 2004, **378**, 875–882.
34 J. Gong, Y. Ran, D.-Y. Chen and Y. Yang, *Mar. Pollut. Bull.*, 2011, **63**, 556–563.

