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Short communication

Simultaneous determination of alkylphenols and bisphenol A in river water by stir bar sorptive extraction with in situ acetylation and thermal desorption–gas chromatography–mass spectrometry

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Abstract

A method for the determination of seven alkylphenols and bisphenol A by stir bar sorptive extraction (SBSE) with in situ derivatization-thermal desorption (TD)–gas chromatography (GC)–mass spectrometry (MS) is described. SBSE was performed with in situ acetylation and without derivatization for comparison. For 4-*tert*-butylphenol and bisphenol A, in situ acetylation improved the responses in SBSE–TD–GC–MS. The method detection limits ranged from 0.1 to 3.2 ng/l. The recoveries of the analytes from a river water sample spiked with standards at 10 and 100 ng/l were 85.3–105.9% (R.S.D., 3.0–11.0%) and 88.3–105.8% (R.S.D., 1.6–8.3%), respectively.
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1. Introduction

Alkylphenols and bisphenol A are considered to be endocrine disrupters. The determination of the endocrine disrupters requires highly sensitive methods to evaluate all potential risks. In the proposed methods [1] of the Japan Environment Agency, alkylphenols are determined directly or as ethyl derivatives by gas chromatography–mass spectrometry (GC–MS) after 1000-fold concentration with solid-phase extraction (SPE). Bisphenol A is determined as trimethyl silyl derivative by GC–MS after SPE. The detection limits are about 10 ng/l in aqueous samples (100 ng/l for nonylphenol due to the mixture of isomers). A large number of studies have also been carried out for the analysis of alkylphenols and bisphenol A in various environmental samples by GC–MS technique [2–6]. Recently, LC–MS has also been applied to this analysis [7,8].

On the other hand, a novel approach using sorptive extraction was introduced by Baltussen et al. [9]. This technique uses a stir bar coated with polydimethylsiloxane (PDMS) and was named stir bar sorptive extraction (SBSE). The extraction mechanism is similar to that of solid-phase microextraction (SPME) based on PDMS sorption. The advantage of SBSE is the much higher mass of PDMS available, which results in high recoveries and higher sample capacity. However, apolar PDMS phase is not suitable for the extraction of polar compounds. Derivatization in aqueous phase prior to SBSE sampling improves not only chromatographic analysis but also sample enrichment in the PDMS phase. The derivatization expands the possibility of SBSE sampling for the polar compounds [10–12]. For the determination of phenols in water samples, aqueous acetylation has been used prior to SPE–GC–MS procedure [13–15].

In this study, SBSE was used for the sample enrichment of seven alkylphenols and bisphenol A in river water. Recently, SBSE was applied to the determination of 4-*tert*-octylphenol and nonylphenol in biological samples without derivatization [16]. However, especially bisphenol A and 4-*tert*-butylphenol are polar and preferably derivatized before SBSE sampling. In situ derivatizaiton in aqueous samples was performed with acetic acid anhydride as acetylation reagent.

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2. Experimental

2.1. Chemicals

4-*tert*-Butylphenol, 4-*n*-pentylphenol, 4-*n*-hexylphenol, 4-*tert*-octylphenol, 4-*n*-heptylphenol, nonylphenol, 4-*n*-octylphenol and bisphenol A were obtained from Wako (Osaka, Japan). Acetone, pesticide grade, was purchased from Wako. Stock standard solutions of the individual chemicals were prepared by diluting each compound to a concentration of 1.0 mg/ml in acetone. Anhydrous potassium carbonate (K_2CO_3) and acetic acid anhydride were obtained from Wako.

2.2. Sample preparation

Stir bars coated with PDMS (0.5 mm film thickness, 10 mm length) were commercially available from Gerstel (Mülheim a/d Ruhr, Germany) and were used for the extraction. Water sample (10 ml) was poured into a 10-ml glass vial; 0.5 g K_2CO_3 and 0.5 ml acetic acid anhydride were added. A PTFE-faced septum cap was just placed on the vial without crimping. The stir bar was stirred in the sample for 60 min at 1000 rpm at room temperature. After sampling the stir bar was removed from the vial with tweezers and briefly dried with a lint-free tissue. Subsequently, the stir bar was transferred into an empty glass thermal desorption tube and desorbed in a thermal desorption system.

2.3. Instrumentation

GC–MS was carried out with an Agilent 6890/5973 system (Agilent Technologies, Palo Alto, CA, USA) equipped with a Gerstel TDS-2 thermodesorption system. A CIS-4 PTV injector (Gerstel) was used for cryofocusing the analytes prior to transfer onto the analytical column. The CIS-4 was equipped with a deactivated empty glass liner with baffles. Liquid nitrogen was used to cool the CIS-4 down to −100 °C during thermal desorption. SBSE desorption was performed at 20 °C for 0.5 min, then programmed at 60 °C/min to 250 °C, which was held for 5 min under a flow of 50 ml/min helium. The injector temperature was held at −100 °C for 0.5 min, then programmed at 12 °C/s to 300 °C, which was held for 10 min. A HP-5MS capillary column (30 m × 0.25 mm i.d. 0.25 μm film thickness) was used. The column temperature was held at 40 °C for 3 min, then programmed at 10 °C/min to 280 °C, which was held for 5 min. Helium was used as the carrier gas with a column flow rate of 1.2 ml/min in constant flow mode. The ion source was kept at 230 °C. MS was operated in the electron impact ionization (EI) mode and with a scan range of *m*/*z* 29–400 at 3.88 scans/s. For determination, the selected ion monitoring (SIM) mode was used. The monitoring ions are *m*/*z* 192 and 135 for 4-*tert*-butylphenol; *m*/*z* 164 and 107 for 4-*n*-pentylphenol; *m*/*z* 220 and 107 for 4-*n*-hexylphenol; *m*/*z* 248 and 135 for 4-*tert*-octylphenol; *m*/*z* 234 and 107 for 4-*n*-heptylphenol; *m*/*z* 135 and 262 for nonylphenol; *m*/*z* 107 and 248 for 4-*n*-octylphenol; *m*/*z* 312 and 213 for bisphenol A.

3. Results and discussion

3.1. Comparison of the responses of SBSE sampling without derivatization and SBSE sampling with acetylation

The comparison of the responses (peak areas of total ion chromatograms in the scan mode) of SBSE sampling without derivatization under pH 3.5 and SBSE sampling with acetylation is shown in Table 1. Both samplings were carried out for 60 min at room temperature. The responses of nonylphenol were calculated on the basis of a representative peak among its isomers. For SBSE sampling after acetylation, the responses of 4-*tert*-butylphenol and bisphenol A were dramatically increased due to the introduction of the acetyl groups to the phenolic hydroxyl groups.

3.2. Validation of the method and application to river water

The linearity was evaluated at seven levels of concentration ranging from 1 to 1000 ng/l in natural water. The calibration curves for all the analytes as acetyl derivatives were linear at 1, 5, 10, 50, 100, 500 and 1000 ng/l in natural water with correlation coefficients between 0.9981 and 0.9999. The method detection limits (MDLs) were calculated from three times the standard deviation ($n = 6$) of natural water fortified at 0.2–10 ng/l. The MDLs ranged from 0.1 to 3.2 ng/l. The results are listed in Table 2. SIM chromatograms of the acetyl derivatives of alkylphenols and bisphenol A extracted from the fortified water at 50 ng/l are shown in Fig. 1. Standards (100 and 1000 pg: 10 and 100 ng/l, respectively, as concentration in river water) were added to 10 ml of a river water sample. The recoveries of the method were tested by replicate analysis ($n = 6$) of the spiked sample and the results are listed in Table 3. Good re-

Table 1
Comparison of responses of SBSE sampling without derivatization and SBSE sampling with acetylation

Analyte	SBSE sampling without derivatization	SBSE sampling with acetylation
4-*tert*-Butylphenol	1 899 038	22 328 804
4-*n*-Pentylphenol	13 407 426	23 493 332
4-*n*-Hexylphenol	24 872 745	27 807 443
4-*tert*-Octylphenol	23 474 733	20 760 161
4-*n*-Heptylphenol	33 787 968	30 229 474
Nonylphenol	3 556 959[a]	2 764 445[a]
4-*n*-Octylphenol	22 308 813	12 196 731
Bisphenol A	368 853	38 954 272

[a] Responses of nonylphenol were calculated on the basis of a representative peak among its isomers.

Table 2
Correlation coefficients of calibration curves and method detection limits

Analyte	*m/z*	Correlation coefficient[a]	Method detection limit (ng/l)
4-*tert*-Butylphenol	192	1.0000	0.7
4-*n*-Pentylphenol	164	0.9937	1.3
4-*n*-Hexylphenol	220	0.9991	0.3
4-*tert*-Octylphenol	248	0.9889	1.2
4-*n*-Heptylphenol	234	0.9912	0.5
Nonylphenol	135	0.9948	3.2
4-*n*-Octylphenol	107	0.9955	0.1
Bisphenol A	312	0.9961	0.6

[a] Concentration range: 1–1000 ng/l.

Table 3
Recoveries of alkylphenols and bisphenol A from river water and precision ($n = 6$)

Analyte	Recovery, % (R.S.D., %) spiked 100 pg in 10 ml river water	Recovery, % (R.S.D., %) spiked 1000 pg in 10 ml river water
4-*tert*-Butylphenol	90.0 (4.5)	97.3 (1.6)
4-*n*-Pentylphenol	102.4 (3.0)	94.0 (2.0)
4-*n*-Hexylphenol	85.3 (3.2)	90.9 (3.5)
4-*tert*-Octylphenol	96.8 (3.0)	92.6 (3.8)
4-*n*-Heptylphenol	105.9 (5.6)	88.3 (5.8)
Nonylphenol	95.0 (5.8)	100.9 (6.1)
4-*n*-Octylphenol	94.1 (11.0)	91.4 (8.3)
Bisphenol A	90.9 (4.7)	105.8 (4.1)

coveries were obtained for all the analytes between 85.3 and 105.9% with RSD values between 3.0 and 11.0% at 10 ng/l and between 88.3 and 105.8% with RSD values between 1.6 and 8.3% at 100 ng/l. The method was applied to the determination of alkylphenols and bisphenol A in river water. 4-*tert*-Octylphenol, nonylphenol and bisphenol A were detected at 2.5, 14.9 and 11.3 ng/l, respectively, in the Tama River (Tokyo, Japan). Fig. 2 shows SIM chromatograms of the acetyl derivatives of alkylphenols and bisphenol A extracted from the river water. In the Tone river (Chiba, Japan),

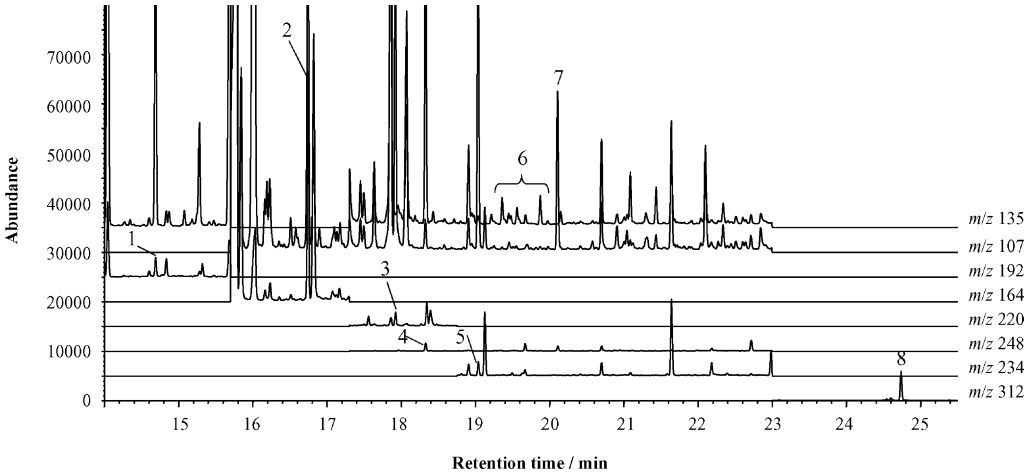

Fig. 1. SIM chromatograms of the acetyl derivatives of alkylphenols and bisphenol A extracted from the fortified water at 50 ng/l: (1) 4-*tert*-butylphenol; (2) 4-*n*-pentylphenol; (3) 4-*n*-hexylphenol; (4) 4-*tert*-octylphenol; (5) 4-*n*-heptylphenol; (6) isomers of nonylphenol; (7) 4-*n*-octylphenol; (8) bisphenol A.

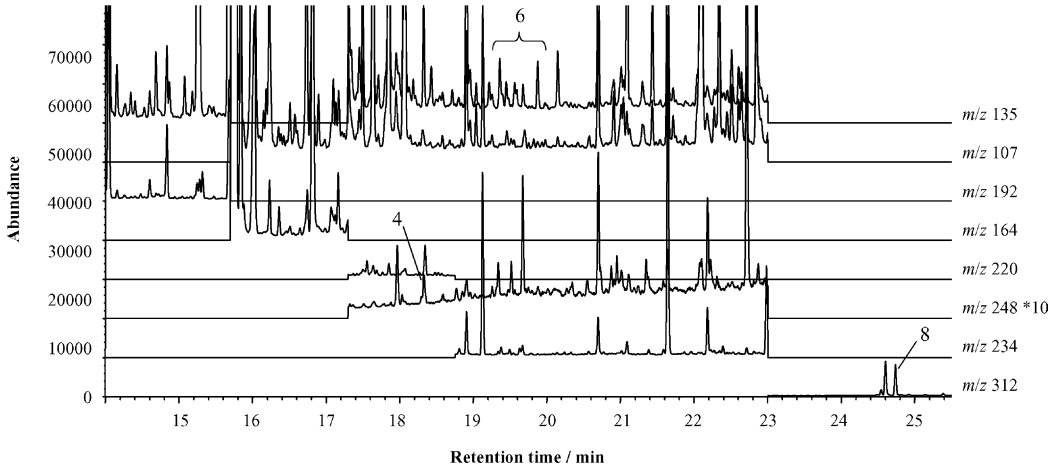

Fig. 2. SIM chromatograms of the acetyl derivatives of alkylphenols and bisphenol A extracted from the river water: (4) 4-*tert*-octylphenol; (6) isomers of nonylphenol; (8) bisphenol A.

bisphenol A was detected at 1.4 ng/l. All the analytes could be determined without interference from the river matrix.

4. Conclusions

An SBSE–TD–GC–MS with in situ derivatization method for the determination of seven alkylphenol and bisphenol A in river water was developed. Significant advantages of the proposed method are that the in situ derivatization improved the responses of 4-*tert*-butylphenol and bisphenol A; SBSE-TD provided high sensitivity and rapid sample preparation. The method allows the detection of levels in the range 0.1–3.2 ng/l of the analytes. The method also provided a wide range of linearity, satisfactory recovery and acceptable precision.

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