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Stir bar sorptive extraction and trace analysis of alkylphenols in water samples by thermal desorption with *in tube* silylation and gas chromatography–mass spectrometry

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Abstract

A novel method called thermal desorption (TD) with *in tube* silylation followed by gas chromatography–mass spectrometry (GC–MS), which is used for the determination of trace amounts of alkylphenols (APs) in river water samples, is described. APs are extracted from river water samples and concentrated by the stir bar sorptive extraction (SBSE) technique. The stir bar coated with polydimethylsiloxane (PDMS) is added to 2.0 ml water sample and stirring is carried out for 60 min at room temperature (25 °C) in the vial. Then, the PDMS stir bar is subjected to TD with *in tube* silylation followed by GC–MS. The detection limit is of the sub pg ml^{-1} (ppt) level. The method shows good linearity and the correlation coefficients are higher than 0.99 for all analytes. The average recoveries of APs are higher than 90% (R.S.D.: 3.6–14.8%, $n = 6$). This simple and sensitive analytical method may be used in the determination of trace amounts of APs in river water samples.

Keywords: Alkylphenol; Water sample; Stir bar sorptive extraction (SBSE); Thermal desorption (TD); *In tube* derivatization

1. Introduction

Alkylphenols (APs) are the degradation products of such non-ionic surfactants as alkylphenolpolyethoxylates (APEOs) that exist mainly as intermediates in the manufacturing industry. APs have been detected in river water, sewage sludge and fish tissue [1–4]. In addition, the estrogenic activity of 4-*tert*-octylphenol (tOP) and 4-nonylphenol (NP), which are examples of APs, has been extensively evaluated by various assays [5–7]. Therefore, APs are considered to be endocrine disrupters (EDCs). The determination of EDCs requires highly sensitive and reliable methods for evaluating all potential risks.

Many analytical methods for the determination of APs in water samples have been reported, including liquid chromatography (LC) with mass spectrometry (MS) [8–11]. However, LC has low resolution and is frequently affected by sample matrix. On the other hand, gas chromatography–mass spectrometry (GC–MS) was initially used for the determination of phenol compounds even though derivatization was required [12–17]. The derivatization leads to sharper peaks and hence to better separation and higher sensitivity for the phenols. However, the complicated sample preparation faces the risk of contamination and hence an overestimation of AP concentration. In order to overcome this problem, in situ derivatization was developed, which involves the simple addition of a reagent to a liquid sample.

Such analytical procedures as liquid–liquid extraction (LLE) [15] and solid-phase extraction (SPE) [10–14] have been developed for the determination of APs. However, gen-

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eral LLE requires large volumes of organic solvents and additional clean-up steps, and although general SPE requires small volumes of organic solvents, the manual version, needed for the concentration of large sample volumes, still takes 8–10 h. Recently, a new sorptive extraction technique that uses a stir bar coated with polydimethylsiloxane (PDMS) was developed [18] and is known as stir bar sorptive extraction (SBSE). Its main advantage is high sensitivity and wide application range that includes volatile aromatics, halogenated solvents, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), pesticides, preservatives, odor compounds and organotin compounds [19–24]. In addition, we have reported the determination of tOP and NP in tap and river water samples [25] and human biological samples [26] by SBSE without derivatization. Moreover, SBSE with in situ acylation has been successfully used in the determination of APs in river water sample [27,28]. Many analytical methods that use SBSE with in situ acylation have been reported as well [29–32].

On the other hand, Itoh et al. have reported the utility of thermal desorption (TD) with *in tube* silylation for measuring hydroxyl polycyclic aromatic hydrocarbons (OH-PAHs) [33]. In their study, derivatization was attained by placing simultaneously glass wool to which OH-PAH standard solution was added and a glass capillary tube filled with derivatization reagent inside a glass TD tube. Then, we thought that TD with *in tube* silylation could be used in combination with the SBSE method.

The aim of this study was to determine trace amounts of APs in river water samples by SBSE and TD with *in tube* silylation followed by GC–MS. A comparison of three methods, namely, SBSE–TD–GC–MS without derivatization, SBSE with in situ acylation and TD–GC–MS, and SBSE and TD with *in tube* silylation followed by GC–MS, was performed. The usefulness of SBSE and TD with *in tube* silylation followed by GC–MS was examined. Then, this method was applied to river water samples.

2. Experimental

2.1. Materials and reagents

4-*tert*-Butylphenol (tBP), 4-*n*-pentylphenol (nPP), 4-*n*-hexylphenol (nHexP), 4-*n*-heptylphenol (nHepP), 4-*tert*-octylphenol (tOP), 4-*n*-octylphenol (nOP), 4-nonylphenol (NP) and 4-*n*-nonylphenol (nNP) of environmental analytical grade and acetic acid anhydride for trace analysis were purchased from Kanto Chemical Inc. (Tokyo, Japan). 4-*n*-Butylphenol (nBP) and 4-*tert*-pentylphenol (tPP) were purchased from Tokyo Kasei Inc. (Tokyo, Japan). Anhydrous potassium carbonate (K_2CO_3) of analytical grade was purchased from Wako Pure Chemical, Inc. (Osaka, Japan). *N*,*O*-Bis(trimethylsilyl)acetamide (BSTFA) was purchased form Supelco (Bellefonte, PA, USA). The water purification system used was a Milli-Q gradient A 10 with an EDS polisher (Millipore, Bedford, MA, USA). Stir bars coated with a 0.5 mm thick PDMS layer (24 μl) were obtained from Gerstel (Mülheim an der Ruhr, Germany). The stir bars could be used more than 50 times with appropriate re-conditioning (the stir bars were conditioned for 2 h at 300 °C in a flow of helium). The reconditioning is the same as the cited conditioning cycle. For the extraction, a 10 ml headspace vial from Agilent Technologies (Palo Alto, CA, USA) was used. For the silylation, the internal hold-up volume of 0.5, 1.0, and 2.0 μl glass capillary tubes were obtained from Drummond Scientific Company (Broomall, PA, USA).

2.2. Standard solutions

Concentrated solutions (1.0 mg ml^{-1}) of APs were prepared by the addition of methanol. More than six-point calibrations (1, 2, 5, 10, 20, 50, 100, 200, 500 and 1000 pg/ml) were prepared by the addition of purified water and performed daily for all samples with surrogate standards.

2.3. Instrumentation

TD was performed with a Gerstel TDS 2 thermodesorption system equipped with a Gerstel TDS A autosampler and a Gerstel Cooled Injection System (CIS) 4 programmable temperature vaporization (PTV) inlet. GC–MS was performed with an Agilent 6890 N gas chromatograph equipped with a 5973 N mass-selective detector with an ultra ion source (Agilent Technologies).

2.4. TD–GC–MS conditions

The TDS 2 temperature was programmed to increase from 20 °C (held for 1 min) to 280 °C (held for 5 min) at 60 °C min^{-1}. The desorbed compounds were cryofocused in the CIS 4 at −150 °C. After the desorption, the CIS 4 temperature was programmed to increase from −150 to 300 °C (held for 10 min) at 12 °C s^{-1} to inject the trapped compounds into the analytical column. The CIS 4 is a kind of PTV. Once an analyte is trapped by means of temperature control, the total focused amount is subjected to GC–MS. Injection was performed in the solvent vent mode. The separations were conducted on a DB-5MS fused silica column (30 m × 0.25 mm i.d., 0.5 μm film thickness, Agilent Technologies). The oven temperature was programmed to increase from 60 to 300 °C (held for 4 min) at 15 °C min^{-1}. Helium was used as the carrier gas at a flow rate of 1.2 ml min^{-1}. The mass spectrometer was operated in the selected ion-monitoring (SIM) mode with electron ionization (ionization voltage: 70 eV). A blank run of the stir bar was performed after an analysis, although memory effects were never detected.

2.5. Water samples

River water was sampled from three sites (upstream (A), midstream (B) and downstream (C)) at Tama River,

Tokyo, Japan. All samples were stored at 4 °C prior to use.

2.6. Sample preparation

2.6.1. SBSE–TD–GC–MS without derivatization

A 2 ml river water sample was added into a 10 ml headspace vial. A stir bar was added and the vial was crimped with a Teflon-coated silicone septum cap. SBSE was performed at room temperature for 60 min while stirring at 500 rpm. This equilibrium extraction time was set by referring to our previous work [25]. After the extraction, the stir bar was easily removed with forceps (due to the magnetic attraction effect), rinsed with purified water, dried with lint-free tissue and placed inside a glass TD tube. The TD tube was placed inside the TD system where the stir bar was thermally desorbed and subjected to GC–MS thereafter. For SIM, the following ions were monitored (*m/z* 135, 107 for tBP, tPP, tOP and NP; *m/z* 107, 150 for nBP; *m/z* 107, 164 for nPP; *m/z* 107, 178 for nHexP; *m/z* 107, 192 for nHepP; *m/z* 107, 206 for nOP and *m/z* 107, 220 for nNP. The underlined number is the *m/z* of the ion used for the quantification.).

2.6.2. SBSE with in situ acylation and TD–GC–MS

A 2 ml river water sample was added into a 10 ml headspace vial. To the sample were added 1 M potassium carbonate (200 μl) as the pH adjustment agent (pH 11.5) and acetic acid anhydride (20 μl) as the derivatization reagent. A stir bar was added and a Teflon-coated silicone septum cap was placed on the vial without crimping. SBSE was performed at room temperature for 60 min while stirring at 500 rpm. These derivatization and extraction conditions were set by referring to our previous paper [27]. The TD–GC–MS conditions were the same as those of SBSE–TD–GC–MS without derivatization.

2.6.3. SBSE and TD with in tube silylation followed by GC–MS

The SBSE conditions were the same as those of SBSE–TD–GC–MS without derivatization. After extraction, the stir bar was easily removed with forceps, rinsed with purified water, dried with lint-free issue and placed inside a glass TD tube. Then, a glass capillary tube filled with BSTFA (0.5 μl) was inserted into the back portion of the glass TD tube (Fig. 1). The TD tube was placed inside the TD system where the stir bar was thermally desorbed and subjected to GC–MS thereafter. For SIM, the following ions were monitored (*m/z* 207, 222 for tBP-TMS; *m/z* 179222 for nBP-TMS; 207, 236 for tPP-TMS; *m/z* 179, 236 for nPP-TMS; *m/z* 179, 250 for nHexP-TMS; *m/z* 179, 264 for nHepP-TMS; 207, 278 for tOP-TMS; *m/z* 179, 278 for nOP-TMS; 207, 292 for NP-TMS and *m/z* 179, 292 for nNP-TMS. The underlined number is the *m/z* of the ion used for the quantification.).

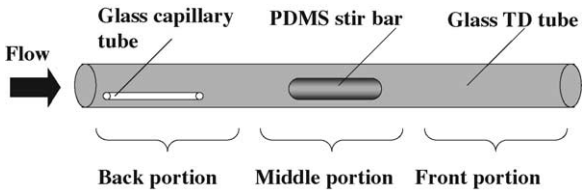

Fig. 1. Schematic of glass TD tube.

3. Results and discussion

3.1. TD with in tube silylation

First, the BSTFA addition method was considered. When BSTFA (0.5 μl) was directly added by means of syringe to the PDMS stir bar to which APs standard solution was extracted by SBSE method, the peak form was dull. Itoh et al. reported that silylation was attained by placing simultaneously glass wool to which OH-PAH standard solution was added and a glass capillary tube filled with BSTFA inside a glass TD tube [33]. Then, we tried to apply SBSE and TD with *in tube* silylation by using a glass capillary tube filled with BSTFA. We inserted a glass capillary tube filled with BSTFA into the front, middle or back portion of the glass TD tube (Fig. 1). Consequently, when a glass capillary tube filled with BSTFA was inserted into the back portion of the glass TD tube, the peak form became sharp. As BSTFA was quite volatile, it was surmised that the result would be obtained.

Second, the volume of BSTFA added was examined. Various volumes of BSTFA, namely, 0.5, 1.0, and 2.0 μl, were examined and it was found that when 0.5 μl of BSTFA was added, the highest peak response and sharpest peak form were obtained. This was therefore considered to be the optimal volume of BSTFA added. The mass spectra and structure of fragment ion of analyte were shows in Fig. 2. The SIM chromatograms (*m/z*: 179 and 207) of water sample spiked with AP standard solutions (1.0 ng ml^{-1}) are shown in Fig. 3.

3.2. Comparison of sample preparation

The responses (peak area of SIM chromatograms) of SBSE and TD–GC–MS without derivatization, SBSE with in situ acylation and TD–GC–MS, and SBSE and TD with *in tube* silylation followed by GC–MS are shown in Table 1. The $K_{o/w}$ values were calculated from the log *P* predictor that is available from the KowWin program (Syracuse Research Corporation, USA). The response of NP (mixture type) was calculated as the sum of all peak areas. When SBSE and TD with *in tube* silylation followed by GC–MS was compared with SBSE–TD–GC–MS without derivatization, the former exhibited 2.0- to 3.3-fold higher sensitivity for all analytes than the latter. On the other hand, the *in tube* silylation method was compared with the in situ acylation method. In nPP, nHexP, nHepP, tOP, nOP, NP and nNP, the sensitivity of the former was 1.2- to 1.8-fold higher than

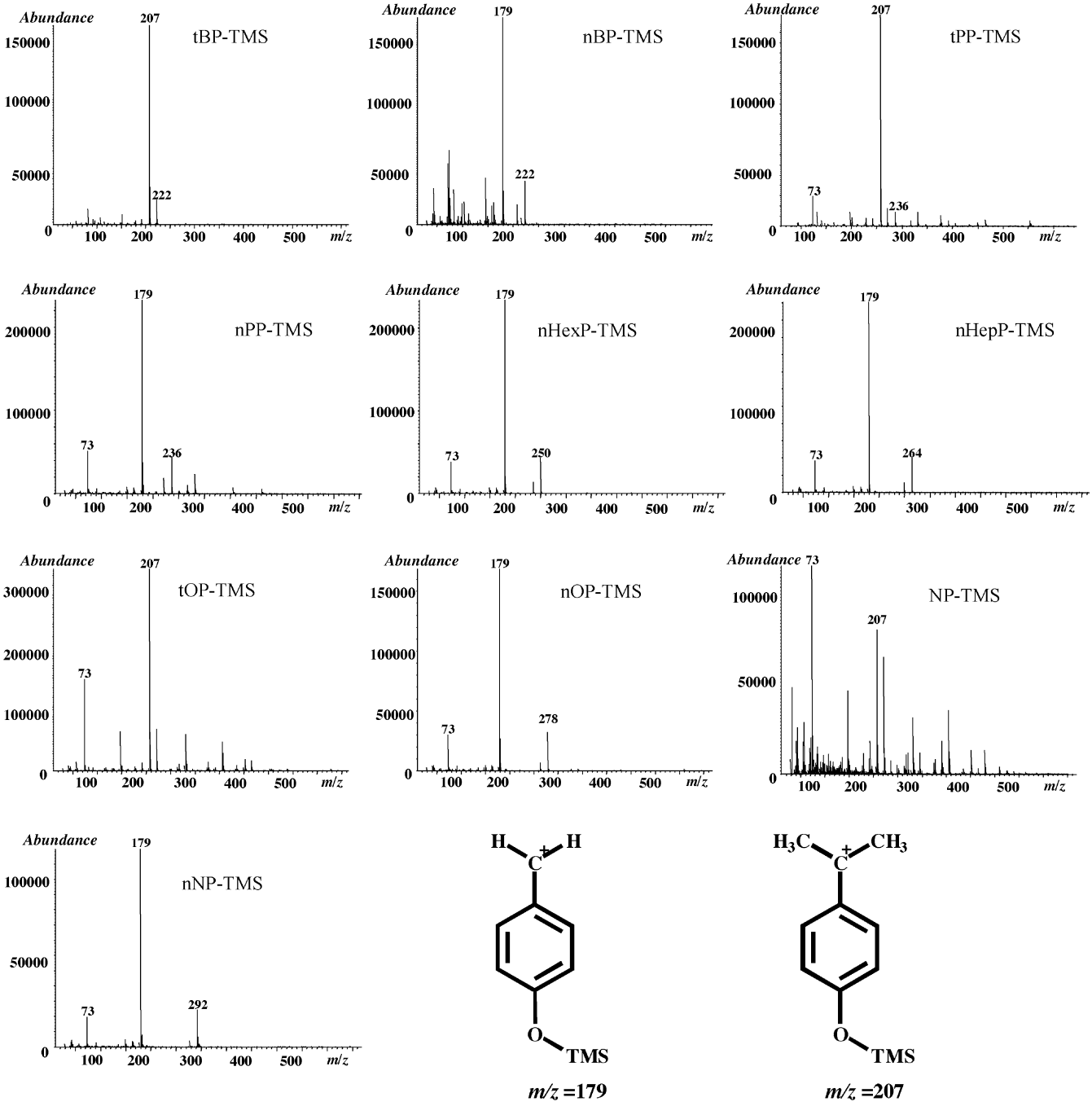

Fig. 2. Mass spectra and structure of fragment ion of silylation of analyte.

that of the latter. However, in tBP, nBP and tPP, the sensitivity of in situ acylation was higher than that of *in tube* silylation. In our previous study, we found that the recovery of the analyte was improved by using the in situ acylation method. In particular, an increase in recovery from the PDMS stir bar was reported for analytes with small $\log K_{o/w}$. Therefore, the in situ acylation method may be useful for analytes with hydrophilic property and the *in tube* silylation method may be useful for analytes with hydrophobic property.

3.3. Figures of merit of SBSE and TD with in tube silylation followed by GC–MS for determination of AP

The calculated detection limits (LODs) of APs were 0.2–10 pg ml^{-1} for SBSE and TD with *in tube* silylation followed by GC–MS, with the ratio of the compound's signal to the background signal (S/N) being 3. In addition, the limits of quantification (LOQs) when S/N > 10 were 1–50 pg ml^{-1} for APs. The method shows good linearity and the correlation coefficients (r) are higher than 0.99 for all analytes ($n = 1$).

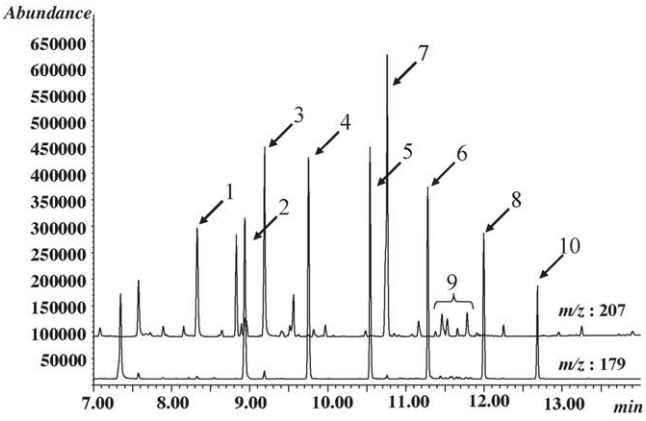

Fig. 3. SIM chromatograms of water sample spiked with 1.0 ng ml^{-1} standard solutions. (1) tBP-TMS, (2) nBP-TMS, (3) tPP-TMS, (4) nPP-TMS, (5) nHexP-TMS, (6) nHepP-TMS, (7) tOP-TMS, (8) nOP-TMS, (9) NP-TMS, (10) nNP-TMS.

The figures of merit of the present method are summarized in Table 2.

The recovery and precision of the method were assessed by replicate analysis ($n = 6$) of river water samples fortified at 100 and 1000 pg ml^{-1} levels. The non-spiked and spiked samples were subjected to SBSE and TD with *in tube* silylation followed by GC–MS. The recovery was calculated by subtracting the results for the non-spiked samples from those for the spiked samples. The results were obtained by using calibration curves obtained from standard solutions. The recovery and precision were 93.1–98.6% (R.S.D.: 3.6–14.8%) for river water samples (Table 3). Therefore, the method enables the precise determination of standards and may be applicable to the determination of trace amounts of APs in river water samples.

3.4. Determination of APs in river water samples

A total of three river water samples were analyzed for APs using the present method and the results are shown in Table 4. In the Tama River water samples, 12.6–18.2 pg ml^{-1} tOP and 55.1–59.7 pg ml^{-1} NP were detected by the present method. A typical chromatogram of river water sample (Point C) is shown in Fig. 4. SBSE and TD with *in tube* silylation followed by GC–MS enabled the successful determination of trace amounts of APs in river water sample.

Table 2
Figures of merit of SBSE and TD with *in tube* silylation followed by GC–MS

Analyte	LOD[a] (pg ml^{-1})	LOQ[b] (pg ml^{-1})	Correlation coefficient (r)
tBP	5	20	0.99 (20–1000)[c]
nBP	1	5	0.99 (5–1000)
tPP	5	20	0.99 (20–1000)
nPP	1	5	0.99 (5–1000)
nHexP	1	5	0.99 (5–1000)
nHepP	1	5	0.99 (5–1000)
tOP	2	10	0.99 (10–1000)
nOP	0.2	1	0.99 (1–1000)
NP	10	50	0.99 (50–1000)
nNP	0.5	2	0.99 (2–1000)

[a] LOD: limit of detection (S/N = 3).
[b] LOQ: limit of quantification (S/N > 10).
[c] Values in parentheses are the linear ranges of the calibration curves (pg ml^{-1}).

Table 3
Recoveries of APs in spiked river water samples

Analyte	Amount spiked (pg ml^{-1})			
	100		1000	
	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)[a]
tBP	94.0	12.9	94.9	5.4
nBP	93.1	5.2	97.8	3.6
tPP	94.7	13.4	93.2	7.0
nPP	96.1	5.3	94.5	3.7
nHexP	97.2	5.9	98.6	3.9
nHepP	95.6	5.1	96.6	3.8
tOP	93.3	11.3	96.4	7.7
nOP	96.0	4.9	97.4	4.4
NP	94.7	14.8	93.3	11.0
nNP	95.1	5.7	98.5	3.9

[a] The recovery and precision were examined by replicate analysis ($n = 6$) of river water samples.

Table 1
Comparison of responses of SBSE–TD–GC–MS without derivatization, SBSE with in situ acylation and TD–GC–MS, and SBSE and TD with *in tube* silylation followed by GC–MS

Analyte	log $K_{o/w}$[a]	Abundance (A)	Abundance (B)	Abundance (C)	C/A	C/B
4-*tert*-Butylphenol (tBP)	3.42	1188604	4910034	3120515	2.6	0.6
4-*n*-Butylphenol (nBP)	3.53	1958425	4453351	3943610	2.0	0.9
4-*tert*-Pentylphenol (tPP)	3.91	2073843	5286874	5086471	2.5	1.0
4-*n*-Pentylphenol (nPP)	4.02	2476154	4216730	5079081	2.1	1.2
4-*n*-Hexylphenol (nHexP)	4.52	2323977	4036215	5435980	2.3	1.3
4-*n*-Heptylphenol (nHepP)	5.01	1843653	3447760	5208606	2.8	1.5
4-*tert*-Octylphenol (tOP)	5.28	2997896	4469942	6200012	2.1	1.4
4-*n*-Octylphenol (nOP)	5.50	1263004	2501857	3984755	3.2	1.6
Nonylphenol (mix type) (NP)	5.77	875618	1422048	2503427	2.9	1.8
4-*n*-Nonylphenol (nNP)	5.99	775120	1461752	2527533	3.3	1.7

A: SBSE–TD–GC–MS without derivatization; B: SBSE with *in situ* acylation and TD–GC–MS; C: SBSE and TD with *in tube* silylation followed by GC–MS.
[a] log $K_{o/w}$ value for APs as predicted from "SRC KowWin".

Table 4
Concentrations of APs in river water samples

Analyte	Tama river (pg ml^{-1})		
	A	B	C
tBP	N.D.[a]	N.D.	N.D.
nBP	N.D.	N.D.	N.D.
tPP	N.D.	N.D.	N.D.
nPP	N.D.	N.D.	N.D.
nHexP	N.D.	N.D.	N.D.
nHepP	N.D.	N.D.	N.D.
tOP	12.6	14.8	18.2
nOP	N.D.	N.D.	N.D.
NP	57.3	55.1	59.7
nNP	N.D.	N.D.	N.D.

[a] N.D.: not detected.

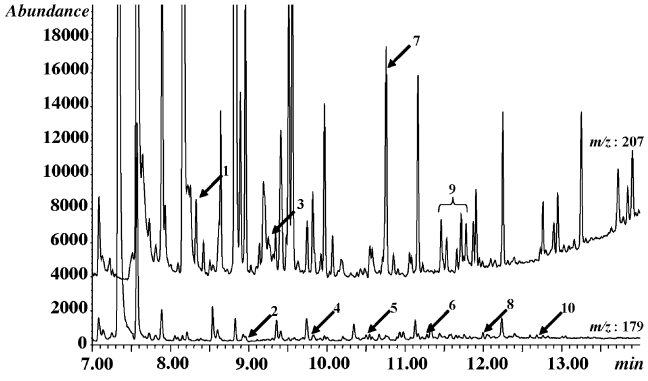

Fig. 4. Chromatogram of tOP-TMS and NP-TMS in river water sample (Point C). (1) tBP-TMS (not detected, N.D.), (2) nBP-TMS (N.D.), (3) tPP-TMS (N.D.), (4) nPP-TMS (N.D.), (5) nHexP-TMS (N.D.), (6) nHepP-TMS (N.D.), (7) tOP-TMS (18.2 pg ml^{-1}), (8) nOP-TMS (N.D.), (9) NP-TMS (59.7 pg ml^{-1}), (10) nNP-TMS (N.D.).

4. Conclusions

The determination of trace amounts of APs in river water samples using SBSE and TD with *in tube* silylation followed by GC–MS was described. The proposed method has many practical advantages, such as a small sample volume (2 ml) and simplicity of extraction; it is also solvent-free and has high sensitivity. The detection limits for APs were of sub pg ml^{-1} level. In addition, the present method showed good linearity and high correlation coefficients using surrogate standards. The recovery was high (93.1–98.6%) and the precision was good (R.S.D.: 3.6–14.8%) for river water samples fortified at the 100 and 1000 pg ml^{-1} levels. The SBSE and TD with *in tube* silylation method is expected to be applicable to not only phenols but also amines, carboxylic acids, and alcohols. This simple, accurate and highly sensitive method is expected to have potential applications in various analytes.

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