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# High performance solid-phase analytical derivatization of phenols for gas chromatography–mass spectrometry

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**Abstract**

The solid-phase analytical derivatization of phenols with pentafluoropyridine is performed. Fourteen phenols including chlorophenols and alkylphenols, could be efficiently adsorbed on a strong anion-exchange solid phase, Oasis MAX. The phenols adsorbed on Oasis MAX as phenolate ions were desorbed after derivatization with pentafluoropyridine. After optimization of the adsorption and derivatization, we established a procedure for the determination of the phenols in water samples by means of GC–MS. Under the optimized conditions, calibration curves were linear in the range of 10–1000 ng/l for the alkylphenols (100–10000 ng/l for nonylphenol) and 50–1000 ng/l for the others. By processing 100 ml samples, the method detection limits (MDLs) were in the range of 0.45–2.3 ng/l for the alkylphenols (8.5 ng/l for nonylphenol) and 2.4–16 ng/l for the others. Compared with the biphasic reaction system, the signal-to-noise ratios obtained by the solid-phase analytical derivatization were significantly higher. This is ascribed to the fact that coexisting neutral and acidic compounds are efficiently removed from the sample solution by this solid-phase analytical derivatization system.


*Keywords:* Derivatization, GC; Sample preparation; Water analysis; Environmental analysis; Phenols; Pentafluoropyridine; Chlorophenols; Alkylphenols

## 1. Introduction

Solid-phase extraction (SPE) is widely used for the preconcentration of water samples. SPE has several important advantages over liquid–liquid extraction, that is, fast operation, low consumption of organic solvent, no formation of an emulsion, an easily automated procedure, and so on. In the case of the GC analysis of polar analytes, derivatization is generally carried out after extraction followed by concentration. However, the combination of SPE with derivatization generally requires complicated procedures such as purification, extraction and concentration.

One solution is to perform the derivatization on a solid phase. Many studies have been devoted to develop solid-phase analytical derivatizations (SPADs) [1]. Carboxylic acids can be derivatized on a strong anion-exchange solid phase with methyl and ethyl iodides [2–5] and *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide (MSTFA) [6]. Phenols can be derivatized on a strong anion-exchange solid phase, $C_{18}$, and styrene–divinylbenzene (PS–DVB) copolymer with acetic anhydride [7] and MSTFA [6]. Amines are also derivatized on PS–DVB with trifluoroacetic anhydride [8]. However, almost all SPADs require high temperature, a long time for the derivatization reactions, and the removal of reagents and byproducts. One excellent exception is the SPAD of carbonyl compounds on the $C_{18}$ solid phase coated with derivatizing reagents such as 2,4,6-trichlorophenylhydrazine [9] and *O*-(pentafluorobenzyl)hydroxylamine hydrochloride [10]. A fast reaction under mild conditions is indispensable for a successful SPAD. The objective of this study is to develop a simple and sensitive method for the determination of phenols by applying a derivatization on an SPE cartridge.

Very recently, we reported the derivatization of alkylphenols with pentafluoropyridine using a biphasic reaction system [11]. This derivatization efficiently proceeds to give the corresponding derivatives at room temperature within 30 min. We considered that this fast derivatization with pentafluoropyridine would enable us to perform the derivatization of phenols on SPE cartridges. In this study, we

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demonstrate the significant analytical performance for the SPAD of phenols with pentafluoropyridine.

## 2. Experimental

### 2.1. Materials

4-*n*-Pentylphenol (C5), 4-*n*-hexylphenol (C6), 4-*n*-heptylphenol (C7), 2-chlorophenol (2Cl), 4-chlorophenol (4Cl), 2,4-dichlorophenol (2,4Cl), 3,4-dichlorophenol (3,4Cl), 2,3,5-trichlorophenol (2,3,5Cl), 4-bromophenol (4Br), 4-chloro-3-methylphenol (4Cl3Me), and 2,4-dichlorophenoxyacetic acid (2,4-D) were obtained from TCI (Tokyo, Japan). 4-*tert*-Butylphenol (C4), 4-*tert*-octylphenol (C8), 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), anthracene, sodium hydroxide and sodium sulfate were purchased from Wako (Osaka, Japan), and technical grade nonylphenol (C9) and 4-methoxyphenol (4OMe) were supplied from Kishida Chemical (Osaka, Japan). The stock solution of the phenols (10 mg each/l) was prepared by dissolving them in acetone and properly diluted before use. Deuterated *tert*-octylphenol (C8d) was synthesized in our laboratory and used as the surrogate compound [12]. The surrogate solution (50 mg/l) was prepared by dissolution in acetone. [$^2H_{10}$]Phenanthrene (phenanthrene-$d_{10}$; internal standard for C4, C5, C6, C8, C8d, 2Cl, 4Cl, 2,4Cl, 3,4Cl, 2,3,5Cl, 4Br, 4OMe, and 4Cl3Me) and [$^2H_{10}$]pyrene (pyrene-$d_{10}$; internal standard for C7 and C9) were obtained from Kanto Kagaku (Tokyo, Japan) and Wako, respectively. The internal standard solution (5 mg/l) was prepared by dissolving both phenanthrene-$d_{10}$ and pyrene-$d_{10}$ in hexane. All solutions were stored in the dark at 4 °C. Pentafluoropyridine and tetra-*n*-butylammonium hydrogensulfate (TBA) were purchased from TCI. All solvents of pesticide grade and other chemicals were purchased from Wako or Kishida Chemical. Sodium hydroxide solution was prepared before use. Water was purified using a Milli-Q system (Millipore, Bedford, MA, USA). The solid-phase extraction cartridges, Oasis MAX (6 ml, 500 mg, LP) and Bond Elut SAX (3 ml, 500 mg), were obtained from Waters (USA) and Varian (USA), respectively. Since the Oasis MAX was contaminated with nonylphenol, 200 mg of the solid phase was packed into a 10 ml glass SPE tube (Glass SPE cartridge kits, GL Sciences, Tokyo, Japan) and carefully washed with acetic acid/hexane solution before use. The SPE was performed on a GL-SPE vacuum manifold system (GL Sciences).

River water samples were collected from the Ina (Hyogo, Japan), Kanzaki, Yodo, and Neya rivers (Osaka, Japan), and filtered using a 0.45 μm membrane filter (Millipore) before use.

### 2.2. GC–MS conditions

Analyses were performed on a Varian 3800 gas chromatograph directly connected to a Saturn 2000 ion-trap mass spectrometer (Varian, USA). All the injections were performed in the splitless mode with the split vent closed for 1 min. The injection port temperature was 280 °C. An ID-BPX5 column (30 m × 0.25 mm i.d., 0.25 μm film thickness, SGE, Australia) was used. Helium (99.9999%) at a flow rate of 1.2 ml/min was utilized as the carrier gas. The GC oven temperature program was as follows: 60 °C for 1 min, followed by a 10 °C/min ramp to 280 °C and hold for 7 min (total analytical time: 30 min). The transfer line, manifold and ion trap temperatures were set at 280, 40, and 210 °C, respectively. The full scan electron impact ionization (EI) data were acquired under the following conditions: 100–650 *m*/*z* mass range, 0.5 s scan time, 80 μA emission current, 20,000 automatic gain control (AGC) target.

### 2.3. Derivatization on solid phase

Ten microliters of surrogate solution (50 mg/l) was added to a 100 ml water sample. An SPE cartridge, Oasis MAX, was successively conditioned with 2.5 ml of acetone, 2.5 ml of water, and 2.5 ml of 0.1 M NaOH. To the cartridge, the 100 ml water sample adjusted to ca. 1 M NaOH, was loaded at a flow rate of 5–10 ml/min. After passing acetone (2.5 ml) through the SPE cartridge, the solid phase was dried under vacuum for 15 min. The solid phase was then contacted with pentafluoropyridine solution (200 μl in 2 ml hexane). After 10 min, the derivatized phenols were eluted by draining the solution and then adding 3 ml of hexane. The eluates were collected and concentrated to 0.4 ml under a gentle stream of nitrogen. One hundred microliters of internal standard solution (5 mg/l) was added to the concentrate, and then an aliquot (2 μl) of the solution was injected into the GC–MS apparatus.

## 3. Results and discussion

### 3.1. Optimization of the procedure

We selected 14 phenols including alkylphenols and chlorophenols as the analytes. Unless otherwise stated, derivatization on a solid phase was examined using a 100 ml NaOH solution spiked with alkylphenols (5 ng each except for C9 (50 ng) and surrogate (500 ng)). Several parameters such as the solid phase, the NaOH concentration, the dryness of the SPE cartridge, the amount of pentafluoropyridine and the reaction time were evaluated by comparing the peak area of the derivative to that of the internal standard.

#### 3.1.1. Solid phase

Phenols can generally be concentrated by the SPE such as $C_{18}$, PS–DVB, and graphite carbon black after acidification of the water sample [13]. In this case, the hydrophobic interaction plays a main role in the adsorption of the phenols. On the other hand, Tang et al. reported the SPE of US Environmental Protection Agency (EPA) priority phe-

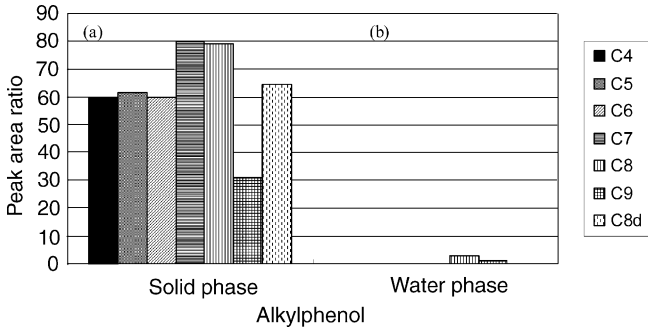


Fig. 1. Recovery of alkylphenols from (a) solid phase and (b) water phase that passed through the solid phase. The peak area ratios of C9 and C8d are reduced to 1/10 and 1/2, respectively.

nols using a strong anion-exchange solid phase [7]. To the best of our knowledge, there are no reports on the adsorption of alkylphenols onto a strong anion-exchange cartridge as their phenolates.

For the initial tests using the alkylphenols as analytes, two strong anion-exchange SPE cartridges, trimethylaminopropylsilica gel (Bond Elut SAX) and divinylbenzene-*N*-vinylpyrrolidone copolymer bearing a trimethylaminomethyl group (Oasis MAX), were investigated by the following procedures: a 1 M NaOH solution (50 ml) spiked with the alkylphenols (100 ng each except for C9 (1000 ng) and surrogate (500 ng)) was passed through the cartridge. After drying the cartridge, the solid phase was contacted with pentafluoropyridine solution (200 μl in 2 ml hexane) for 10 min. The derivatized phenols were eluted by draining the solution and then adding 3 ml of hexane. The eluates were collected, concentrated, and then injected into the GC–MS system. With the silica based solid phase (SAX), only small amounts of the alkylphenols were detected from the solid phase due to the decomposition of solid phase under the strong alkaline conditions. With the Oasis MAX (MAX), the derivatized alkylphenols were recovered from the solid phase (Fig. 1a). The trace amount of alkylphenols were recovered from the water phase that passed through the SPE cartridge (Fig. 1b), which was examined by the biphasic derivatization with pentafluoropyridine [11]. Therefore, the derivatization conditions were optimized using the Oasis MAX.

### 3.1.2. NaOH concentration in water sample

The NaOH concentration was examined using 14 phenols. The NaOH concentration in the water sample influences the dissociation of the phenols. Their p$K_a$ values examined in this study ranged from 6.4 to 10.3 (Table 1). The NaOH concentration was examined in the range from 0 to 2 M (Fig. 2). Without adding NaOH to the water sample, almost all the phenols did not adsorb onto the Oasis MAX. Constant responses were obtained at NaOH concentrations higher than 0.1 M. When the solid phase was conditioned with the NaOH solution, all the phenols also could be efficiently adsorbed without adding NaOH to the water sample.

Table 1
p$K_a$ and log $K_{ow}$ (octanol–water partition coefficients) of phenols

| Phenol | p$K_a$ | log $K_{ow}$ |
|---|---|---|
| 2Cl | 8.53[a] | 2.29[a] |
| 4Cl | 9.38[a] | 2.39[a] |
| 4OMe | 10.21[a] | 1.34[a] |
| 4Cl3Me | 9.55[b] | 3.10[b] |
| 4Br | 9.45[c] | 2.59[c] |
| C4 | 10.23[a] | 3.31[a] |
| 2,4Cl | 7.85[c] | 3.06[c] |
| 3,4Cl | 8.87[d] | 3.37[d] |
| 2,3,5Cl | 6.43[b] | 3.85[b] |
| C5 | – | 4.09[e] |
| C6 | – | – |
| C7 | – | – |
| C8 | 10.24[f] | 5.85[f] |
| C9 | 10.25[f] | 5.76[f] |

[a] Ref. [14].
[b] Ref. [15].
[c] Ref. [16].
[d] Ref. [17].
[e] Ref. [18].
[f] Ref. [19].

### 3.1.3. Dryness of SPE cartridge

In this derivatization, we used pentafluoropyridine/hexane as the eluent. To perform the complete derivatization, drying the cartridge is important. Before the derivatization, acetone was loaded onto the SPE cartridge. By this operation, the drying step could quickly be carried out. Moreover, neutral substances adsorbed on the solid phase may probably be removed at the same time.

The amount of acetone was examined in the range of 2.5–10 ml. As a result, passing acetone had no influence on the desorption of the phenols adsorbed on the solid phase (data not shown).

### 3.1.4. Pentafluoropyridine amount

Since pentafluoropyridine has a low boiling point (83 °C), no removal step is required. Therefore, the amount of pentafluoropyridine is not limited. The amount of pentafluoropyridine was examined in the range of 10–300 μl. One hundred microliters of pentafluoropyridine was sufficient for the derivatization of the phenols (10 ng each). For the derivatization of the higher amount of the phenols (100 ng each), 200 μl of pentafluoropyridine was needed to ensure the complete derivatization. Despite of the large excess of pentafluoropyridine, a significant interference to the analysis and breakdown of GC stationary phase were not observed. We consider that it is due to both a low boiling point of the reagent and no byproduct formation during the derivatization.

### 3.1.5. Reaction time

Finally, the reaction time was examined under the conditions described above. For almost all the phenols, more than an 80% yield was obtained by only passing the pentafluoropyridine containing solution through the SPE cartridge,

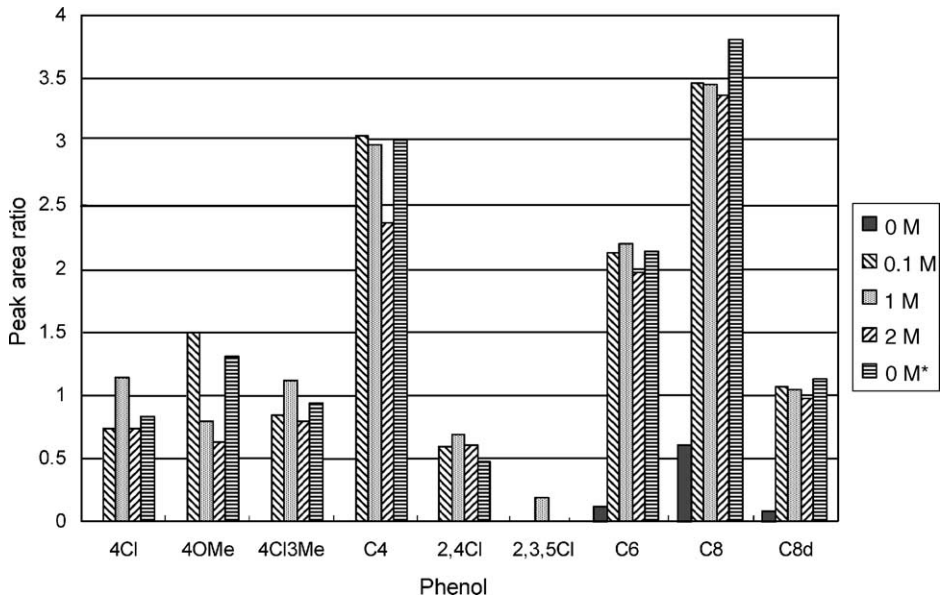


Fig. 2. Effect of NaOH concentration on adsorption of phenols. The peak area ratio of C8d is reduced to 1/100. *Solid phase was conditioned with 0.1 M NaOH (2.5 ml).

showing that the derivatization is fast. Since no significant changes were observed after 10 min, the reaction time was fixed at 10 min.

### 3.2. Effect of coexisting substances on adsorption and derivatization

There is a significant possibility that coexisting compounds in the river water may interfere with the adsorption and derivatization of the phenols. Before performing a quantitative calibration, we tested the recovery of the phenols from the river water instead of pure water. In this case, all the phenols were very poorly recovered (Table 2). The recoveries decreased to 19–56% probably due to the interference of the coexisting compounds with the adsorption of the phenols. In order to effectively adsorb the phenols from the river water, the adjustment of water sample to higher than 1 M NaOH was required.

The recoveries from pure water were examined in the presence of the coexisting substances, i.e., inorganic ions and organic compounds. These results are shown in Table 2. The addition of the inorganic ions has a significant influence on the recovery of the phenols. When chloride ion (300 mg) and sulfate ion (30 mg) were added to pure water containing the phenols, the adsorption efficiency of the phenols decreased. This is attributed to their breakthrough rather than to lack of the derivatization. This result shows that a hydroxyl anion on the exchange site of the solid phase is easily substituted by chloride and sulfate anions. When the water sample containing inorganic anions was adjusted to 1 M alkaline solution by adding NaOH, the recoveries of the phenols were improved except for 4-methoxyphenol. The low

Table 2
Effect of coexisting substances on adsorption and derivatization of phenols

| Phenol | River water[a] | | Pure water containing inorganic ions[b] | | Pure water containing organic compounds[c] | |
|---|---|---|---|---|---|---|
| | Without NaOH | 1 M NaOH | Without NaOH | 1 M NaOH | Without NaOH | 1 M NaOH |
| 4Cl | 42 | 88 | 14 | 81 | 73 | 113 |
| 4OMe | 55 | 43 | 11 | 0 | 113 | 87 |
| 4Cl3Me | 39 | 102 | 15 | 85 | 98 | 103 |
| C4 | 21 | 85 | 9 | 87 | 106 | 112 |
| 2,4Cl | 56 | 102 | 39 | 71 | 94 | 105 |
| 2,3,5Cl | 33 | 85 | 25 | 116 | 76 | 87 |
| C6 | 21 | 96 | 14 | 77 | 115 | 105 |
| C8 | 31 | 101 | 18 | 89 | 114 | 99 |
| C8d | 19 | 91 | 16 | 86 | 115 | 95 |

All entries indicate the recovery (%).
[a] Taken from Kanzaki river.
[b] Chloride ion (300 mg) and sulfate ion (30 mg) were added as their sodium salts.
[c] 2,4-D, 2,4,5-T, and anthracene (1 μg each) were added.

Table 3
Quantitative calibration and method detection limits

| Phenol | Ions for determination and identification (*m*/*z*) | Regression equation[a] | Correlation coefficient (*R*) | Method detection limit (ng/l)[b] |
|---|---|---|---|---|
| 2Cl | 277/279 | $y = 0.0227x - 0.585$ | 0.9986 | 4.7 |
| 4Cl | 271/256 | $y = 0.0256x - 0.388$ | 0.9990 | 4.3 |
| 4OMe | 273/258 | $y = 0.0156x - 0.353$ | 0.9980 | 5.4 |
| 4Cl3Me | 291/293, 256 | $y = 0.0291x - 0.317$ | 0.9989 | 2.4 |
| 4Br | 323/321 | $y = 0.0203x - 0.653$ | 0.9989 | 7.5 |
| C4 | 284/256 | $y = 0.0697x + 0.125$ | 0.9997 | 0.95 |
| 2,4Cl | 311/313 | $y = 0.0178x - 0.416$ | 0.9951 | 3.1 |
| 3,4Cl | 311/313 | $y = 0.0182x + 0.106$ | 0.9998 | 4.9 |
| 2,3,5Cl | 347/310 | $y = 0.00845x + 0.520$ | 0.9914 | 16 |
| C5 | 256/313 | $y = 0.0715x - 0.0465$ | 0.9982 | 0.88 |
| C6 | 256/327 | $y = 0.0630x + 0.186$ | 0.9997 | 2.1 |
| C7 | 256/341 | $y = 0.0900x - 0.407$ | 0.9998 | 0.45 |
| C8 | 284/256 | $y = 0.0853x + 1.08$ | 0.9990 | 2.3 |
| C9 | 284/256 | $y = 0.0340x - 0.0147$ | 0.9993 | 8.5 |

Concentration range; 10–1000 ng/l (C4–C8), 100–10000 ng/l (C9), 50–1000 ng/l (other phenols).
[a] $y$ = peak area ratio, $x$ = concentration of analyte (ng/l).
[b] Calculated as standard deviation × $t$, where $t = 1.895$ from one-sided $t$-distribution at 95% confidence level ($n = 8$, at 50 ng/l except for C9: 500 ng/l).

recovery of 4OMe may be convincingly explained by its high hydrophilicity (Table 1).

We next examined the influence of the organic coexisting substanses including the neutral and acidic substances on the adsorption and derivatization. We used 2,4-dichlorophenoxyacetic acid and 2,4,5-trichlorophenoxyacetic acid as carboxylic acids, and anthracene as the neutral substance. In contrast to inorganic compounds, the organic compounds (1 μg each) showed little effect on the adsorption and derivatization of the phenols (Table 2).

Finally, we examined the contamination of organic compounds to the sample injected into the GC–MS system. Thus, pure water containing 2,4-D, 2,4,5-T, anthracene (1 μg each), and the phenols (10 ng each) was adjusted to 1 M NaOH, and then loaded onto an SPE cartridge. After drying the cartridge with acetone, the phenols were eluted by adding the pentafluoropyridine solution. The GC–MS analysis showed that the injected sample contained a small amount of anthracene (ca. 5% of spiked amount) and quantitative amount of the derivatized phenols. We also analyzed the water phase that passed through the solid phase, the acetone solution, and the solid phase after elution with the pentafluoropyridine solution. Almost all of the anthracene was detected in the acetone solution. Since the carboxylic acids are not derivatized in this derivatization, all the carboxylic acids were quantitatively recovered from the solid phase by in-vial methylation with MeI [4]. These results indicate that the present solid-phase analytical derivatization has also a significant cleanup effect.

### 3.3. Quantitative calibration and reproducibilities

Under the optimized conditions, calibration curves were constructed by applying 100 ml pure water containing the phenols to the Oasis MAX (Table 3). All the calibration curves were linear in the range of 10–1000 ng/l for the alkylphenols (100–10000 ng/l for nonylphenol) and 50–1000 ng/l for the others. The method detection limits (MDLs) were in the range of 0.45–2.3 ng/l for the alkylphenols (8.5 ng/l for nonylphenol) and 2.4–16 ng/l for the others. Compared with the biphasic reaction system [11], the MDLs for the alkylphenols were several times lower. This is ascribed to the selective elution of the solid-phase derivatization system.

### 3.4. Application to river water samples

The recovery test was carried out using two river waters, the Ina river (low polluted river) and the Neya river (highly polluted river). Table 4 summarizes the average recovery of all the phenols in the fortified river waters. The

Table 4
Recoveries of phenols from river waters

| Phenol | Ina river | | Neya river | |
|---|---|---|---|---|
| | Recovery (%)[a] | R.S.D. (%)[b] | Recovery (%)[a] | R.S.D. (%)[b] |
| 2Cl | 86 | 6.2 | 95 | 15 |
| 4Cl | 88 | 6.9 | 95 | 17 |
| 4OMe | 43 | 12 | 42 | 21 |
| 4Cl3Me | 102 | 4.9 | 96 | 10 |
| 4Br | 94 | 2.5 | 121 | 5.9 |
| C4 | 86 | 7.4 | 99 | 5.4 |
| 2,4Cl | 102 | 15 | 116 | 16 |
| 3,4Cl | 86 | 11 | 104 | 15 |
| 2,3,5Cl | 85 | 15 | 81 | 14 |
| C5 | 91 | 6.9 | 124 | 18 |
| C6 | 96 | 5.2 | 99 | 5.9 |
| C7 | 95 | 7.0 | 120 | 6.4 |
| C8 | 101 | 14 | 107 | 5.5 |
| C9 | 107 | 7.0 | 142 | 9.4 |
| C8d | 101 | 6.0 | 97 | 3.6 |

[a] Average recovery ($n = 5$) at 100 ng/l (C9: 1000 ng/l, C8d: 5000 ng/l).
[b] Relative standard deviation ($n = 5$).

Table 5
Concentrations of phenols detected in river waters

| Phenol | Ina river | | Neya river | | Yodo river | | Kanzaki river | |
|---|---|---|---|---|---|---|---|---|
| | Concentration | R.S.D. | Concentration | R.S.D. | Concentration | R.S.D. | Concentration | R.S.D. |
| C4 | nd | – | 30 | 11 | 2.9[a] | 7.1 | 4.5[a] | 4.8 |
| C8 | 38 | 31 | 204 | 6.4 | nd | – | 23 | 20 |
| C9 | 16[a] | 14 | 1030 | 7.2 | 120 | 5.4 | 290 | 8.8 |
| C8d | 87[b] | 17 | 94[b] | 5.3 | 104[b] | 4.4 | 92[b] | 1.6 |

Average concentration (ng/l) and relative standard deviation (%, $n = 5$).
[a] Estimated value by extrapolating the calibration curve.
[b] Average recovery (%) at 5000 ng/l.

average recoveries from the low polluted river at a concentration of 100 ng/l were in the range of 85–107% with good reproducibilities (R.S.D. = 2.5–15%) except for 4-methoxyphenol. Similar or slightly higher recoveries were obtained from the highly polluted river with slightly lower reproducibilities. There is a possibility that humic and fulvic acids in the environmental water interfere with an analysis of phenols. However, the high recoveries of the phenols from river water show that humic and fulvic acids have little effect on the present method. Moreover the use of deuterated octylphenol as a surrogate compound ensures the precise analysis.

This method was applied to the analysis of the phenols in river water samples collected from two rivers running through Osaka city (the Yodo and Kanzaki rivers) besides the Ina and Neya rivers. The analytical results are shown in Table 5. Three branched alkylphenols, 4-*tert*-butylphenol, 4-*tert*-octylphenol and 4-nonylphenol were detected. The

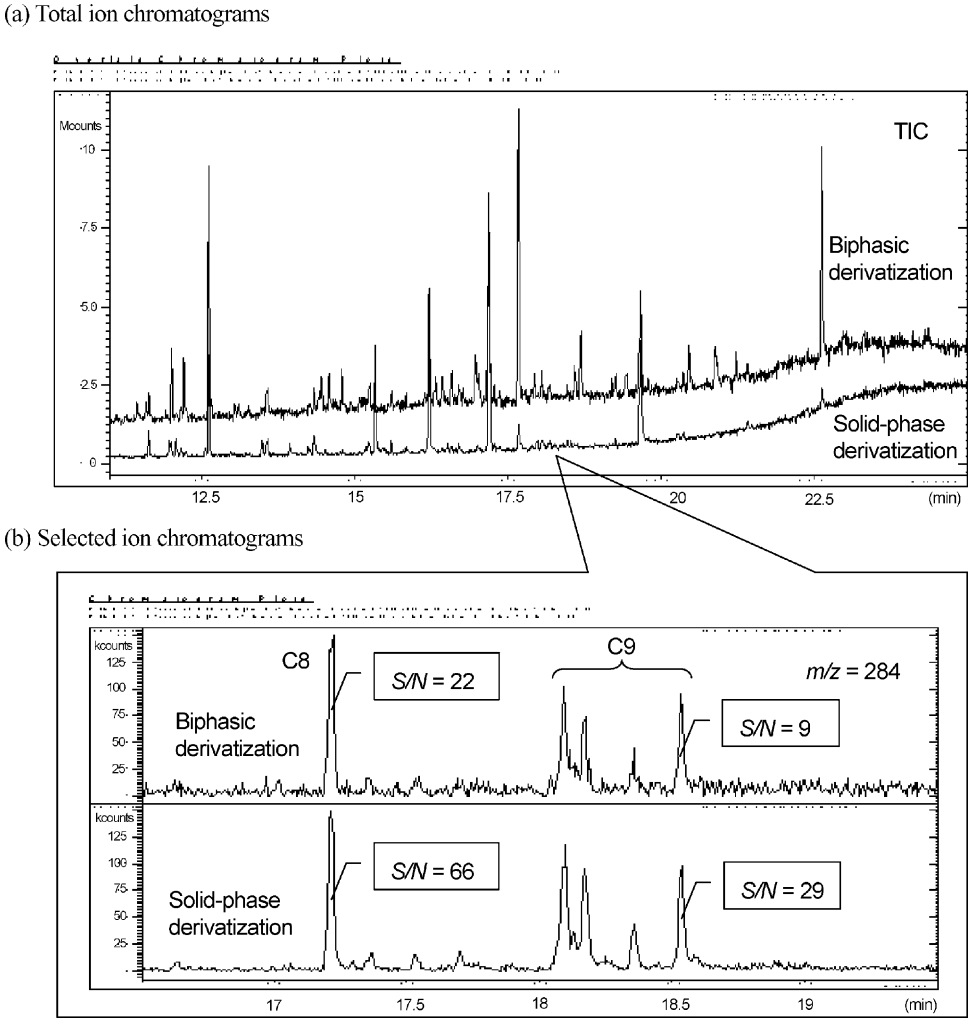


Fig. 3. Total and selected ion chromatograms for analytes in river water.

R.S.D. values were in the range of 4.8–31%. All the other phenols were less than the detection limits. For all cases, the recoveries of the surrogate were more than 87% with good reproducibilities.

Two methods, the solid-phase derivatization and the biphasic derivatization with pentafluoropyridine, were compared by analyzing the same river water sample. The total and selected ion chromatograms obtained by the solid-phase derivatization system are shown in Fig. 3 together with those obtained by the biphasic derivatization system. TIC of the biphasic derivatization showed a higher background level than that of the solid-phase derivatization (Fig. 3a). Furthermore, in the selected ion chromatograms at $m/z = 284$, a smaller noise was observed in the solid-phase derivatization (Fig. 3b). The signal-to-noise ratios of octylphenol and nonylphenol detected in the river water were about three times higher in the case of the solid-phase derivatization. These results clearly show the high performance of this solid-phase derivatization system.

## 4. Conclusion

The efficient solid-phase analytical derivatization of the phenols has been established by using pentafluoropyridine as a derivatizing reagent under mild conditions. The Oasis MAX showed good adsorption ability for the phenols. This method has many advantages. The phenols adsorbed onto the Oasis MAX were derivatized with pentafluoropyridine in the SPE cartridge under mild conditions (room temperature, 10 min). By applying this method, no special cleanup step was required for the following reasons: (i) neutral compounds can be removed by passing acetone through the SPE cartridge before the derivatization, (ii) only the derivatized phenols could be eluted from the solid phase, (iii) carboxylic acid still remains on the solid phase after the derivatization, (iv) no byproduct is formed during the derivatization, and (v) pentafluoropyridine is highly volatile (boiling point: 83 °C). The total analytical procedure for this method is quite simple. This method allows a relatively high sample throughput for the determination of the phenols.

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