Anal. Chem. **2001,** *73,* 3089−3095

Silyl Derivatization of Alkylphenols, Chlorophenols, and Bisphenol A for Simultaneous GC/MS Determination

Donghao Li and Jongman Park*

Department of Chemistry, Konkuk University, 1 Hwayangdong Gwangjingu, Seoul 143-701, Korea

Jae-Ryoung Oh

Korea Ocean Research and Development Institute, Ansan P.O. Box 29, Gyounggido 425-600, Korea

A fast silyl derivatization technique for simultaneous GC/MS analysis of alkylphenols, chlorophenols, and bisphenol A was developed. The analytes were silylized with an excess amount of bis(trimethylsilyl)trifluoroacetamide (BSTFA) followed by hydrolysis of excess silyl reagent with water. Reaction rates of derivatization were studied in various solvents and found to be fastest in acetone. Derivatization reaction in acetone was completed quantitatively within 15 s at room temperature while it took more than 1 h in other solvents studied. Similar results were obtained in mixed solvents with acetone if the content of acetone was higher than 60% (v/v). Since water-immiscible solvents such as dichloromethane or hexane are frequently used in the extraction of phenolic analytes in various sample matrixes, acetone can be added to the extracts in order to accelerate the reaction rate of derivatization. Stability of the derivatives in sample for long-term storage was ensured by hydrolyzing excess derivatizing reagent, BSTFA, with a spike of water followed by dehydration using anhydrous sodium sulfate. On the basis of the above results, a derivatizing treatment kit was designed to improve the convenience of analysis. It was possible to treat sample within several minutes successfully by using the kit. So fast simultaneous determination of those anlaytes by GC/MS was possible with improved convenience as well as sensitivity and reproducibility.

Alkylphenol ethoxylates (APEs), chlorophenols (CPs), and bisphenol A (BPA) have been widely used in the preparation of detergents, wood preservatives, and polymeric materials for household and industrial applications. They have been discharged directly or indirectly to the environment and contaminated the atmosphere, water, and soil. APEs are degraded to alkylphenols (APs) during an aerobic or anaerobic waste treatment process or by microorganism[1] and photolysis[2] in nature. Although the APEs are less toxic to organisms, their metabolites[3,4] show high toxicity to organisms and fish.[5,6] So most countries have classified them as endocrine disrupter chemicals.[7−11] Numerous papers have been published about determination of APs, CPs, and BPA using various techniques. Some of the most frequently used methods for analysis of these are as follows: direct analysis using HPLC,[12−14] GC/ECD,[15−17] LC/MS,[18] GC/MS,[19,20] and other techniques[21,22] or indirect analysis of the compounds using derivatization techniques such as methylation,[23] acetylation,[24,25] and silylation.[26−28] Methylation and acetylation techniques are suitable for the analytes

* To whom correspondence should be addressed: (phone) +82-2-450-3438; (fax) +82-3436-5382; (e-mail) jmpark@kkucc.konkuk.ac.kr.

(1) Giger, W.; Brunner, P. H.; Schaffner, C. *Science* **1984**, *225*, 623−625.
(2) Destaillats, H.; Hung, H.; Hoffmann, M. R. *Environ. Sci. Technol.* **2000**, *34*, 311−317.
(3) Nimrod, A. C.; Benson, W. H. *Alkylphenols Alkylphenol Ethoxylates Rev.* **1998**, *1*, 75−101.
(4) Ahel, M.; Giger, W.; Koch, M. *Water Res.* **1994**, *28*, 1131−1142.
(5) Tabira, Y.; Nakai, M.; Asai, D.; Yakabe, Y.; Tahara, Y.; Shimyozu, T.; Noguchi, M.; Takatsuki, M.; Shimohigashi, Y. *Eur. J. Biochem.* **1999**, *262*, 240−245.
(6) Gagne, F.; Pardos, M.; Blaise, C. *Bull. Environ. Contam. Toxicol.* **1999**, *62*, 723−730.
(7) *Environmental estrogens and other hormones* [online]. Available at http://www.tmc.Tulane.edu/ECME/eehome/.
(8) *Environmental Estrogens: Consequences to human health and wildlife*; Medical Research Council: London, 1995.
(9) *World Wildlife Fund Canada* [online]. Available at http://www.wwfcanada.org/hormone-disruptors/, December 15, 1996.
(10) Hosea, N. A.; Guengerich, F. P. *Arch. Biochem. Biophys.* **1998**, *353*, 365−373.
(11) Harris, R. H.; Waring, R. H.; Kirk, C. J.; Hughes, P. J. *J. Biol. Chem.* **2000**, *275*, 159−166.
(12) Ahel, M.; Giger, W.; Schaffner, W. *Water Res.* **1994**, *28*, 1143−1152.
(13) Naylor, C. G.; Mieure, J. P.; Adams, W. J.; Weeks, J. A.; Cataldi, F. J.; Ogle, L. D.; Romano, R. R. *Alkylphenols Alkylphenol Ethoxylates Rev.* **1988**, *2*, 32−43.
(14) Rudel, R. A.; Melly, S. J.; Geno, P. W.; Sun, G.; Brody, J. G. *Environ. Sci. Technol.* **1998**, *32*, 861−869.
(15) Bartels, P.; Ebeling, E.; Kramer, B.; Kruse, H.; Osius, N.; Vowinkel, K.; Wassermann, O.; Witten, J.; Zorn, C. *Fresenius' J. Anal. Chem.* **1999**, *365*, 458−464.
(16) Buhr, A.; Genning, C.; Salthammer, C. *Fresenius' J. Anal. Chem.* **2000**, *367*, 73−78.
(17) Machera, K.; Miliadis, G. E.; Anagnostopoulos, E.; Anastassiadou, P. *Bull. Environ. Contam. Toxicol.* **1997**, *59*, 909−916.
(18) Crescenzi, C.; Corcia, A. D.; Samperi, R.; Marcomini, A. *Anal. Chem.* **1995**, *67*, 1797−1804.
(19) Bhatt, B. D.; Prasad, J. V.; Kalpana, G.; Ali, S. *J. Chromatogr. Sci.* **1992**, *30*, 203-210.
(20) Blackburn, M. A.; Waldock, M. J. *Water Res.* **1995**, *29*, 1623−1629.
(21) Zemann, A.; Volgger, D. *Anal. Chem.* **1997**, *69*, 3243−3250.
(22) Wallingford, R. A. *Anal. Chem.* **1996**, *68*, 2541−2548.
(23) Field, J. A.; Reed, R. L. *Environ. Sci. Technol.* **1996**, *30*, 3544−3550.
(24) Croley, T. R.; Lynn, B. C., Jr. *Rapid Commun. Mass Spectrom.* **1998**, *12*, 171−175.

10.1021/ac001494l CCC: $20.00 © 2001 American Chemical Society
Published on Web 05/16/2001

having high molecular weights rather than small. For the phenolic analytes concerned in this work, significant loss may occur during the sample preparation process due to the high volatility of low molecular weight methyl esters or acetates of analytes.[29]

Silyl derivatization techniques have been widely used especially in the determination of low-volatility polar compounds such as phenolic analytes. Those compounds show low sensitivity and tailing in gas chromatographic analysis. Thermally stable and highly volatile derivatives can be easily obtained by the silylation reaction. Introduction of a silyl group to highly polar analytes improves various gas chromatographic parameters such as accuracy, reproducibility, sensitivity, and resolution by suppressing tailing and enhancing thermal stability. The mass spectrometric properties of the analytes can be improved by producing not only more favorable diagnostic fragmentation patterns for structure investigation but also characteristic ions for selected ion monitoring in trace analyses. Among various silylation reagents for the derivatization of the hydroxyl group, such as nitrogen-containing silyl ethers, trimethylsilyl ether, bis(trimethylsilyl)trifluoroacetamide, bis(trimethylsilyl)acetamide, and pentafluorophenylsilyl ether, bis(trimethylsilyl)trifluoroacetamide (BSTFA) has been widely used because of its fast and quantitative reaction with various hydroxyl compounds at moderate conditions.[30]

Although previously reported derivatization techniques using BSTFA were successful for the determination of phenolic analytes in various environmental samples, the derivatization process is still time-consuming and critical in ensuring accuracy and reproducibility of analysis. It takes more than 1 h for derivatization at ambient temperature. The temperature has to be elevated to accelerate reaction rate, which might cause production of many ambiguous byproducts that interfere with the GC/MS analysis. Further simplification of the process is desired by optimizing conditions of derivatization. In this work, we studied the derivatization conditions in terms of reaction time in various solvents as well as hydrolysis conditions of excess unreacted derivatizing reagent, which greatly affects the gas chromatographic separation. In addition, a treatment kit was developed for simple and convenient silyl derivatization. The suitability of the kit for the analysis of phenolic analytes from contaminated coastal seawater was examined

EXPERIMENTAL SECTION

Alkylphenols, chlorophenols, and bisphenol A, BSTFA, gas chromatographic internal standards (naphthalene-d_8, phenanthrene-d_{10}, pyrene-d_{10}), and surrogate standard (bisphenol A-d_{14}) were purchased from Chem Service. Dichloromethane, hexane, acetone, ethyl acetate, and methanol were from Aldrich. All solvents were pesticide grade. Stock solutions of the phenolic compounds were prepared at concentration of 100 mg/L in an 8:2 mixture of hexane and acetone. The stock solutions were diluted appropriately for the preparation of spike standard, working GC internal standard, and surrogate standard.

(25) Bao, M. L.; Pantani, F.; Barbieri, K.; Burrini, D.; Griffini, O. *Chromatographia* **1996**, *42*, 227−233.
(26) Shin, N.; Donike, M. *Anal. Chem.* **1996**, *68*, 3015−3020.
(27) Brooks, C. J. W.; Cole, W. J. *J. Chromatogr.* **1990**, *514*, 305−308.
(28) Uobe, K.; Takeda, R.; Wato, M.; Nishigkawa, T.; Yamaguchi, S.; Koshimura, T.; Kawaguchi, Y.; Tsutsui, M. *J. Chromatogr.* **1981**, *514*, 177−184.
(29) Shantha, N. C.; Napolitano, G. E. *J. Chromatogr.* **1992**, *624*, 37−51.
(30) Blau, B.; Halket, J. M. *Handbook of Derivatives for Chromatography*, 2nd ed.; John Wiley & Sons: Chichester, 1993; Chapter 4.

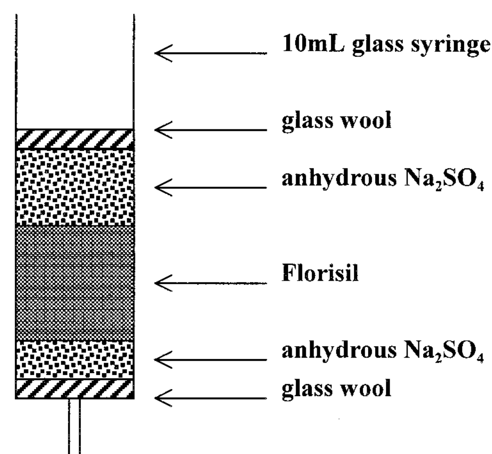

Figure 1. Schematic diagram of a silyl derivatization treatment kit.

Derivatization of phenolic analytes was performed in various solvents according to the procedure found elsewhere with slight modification.[30] A 100-μL aliquot of BSTFA (with 1% TMCS) was added to 1 mL of standard solutions or concentrated extracts of phenolic analytes in a sample vial followed by vigorous shaking with a vortex mixer for the appropriate period at room temperature. Then 100 μL of water was added to the mixture in order to hydrolyze excess unreacted BSTFA. About 1 g of anhydrous sodium sulfate was added to remove water from the sample mixture. The treated analyte solution was decanted to another vial. The residual portion of the analytes was collected by rinsing with 1 mL of dichloromethane twice and adding the rinse to the mother solution. It was concentrated to 1 mL with a gentle flow of dry N_2 followed by addition of internal standards and then subjected to GC/MS analysis. The concentrations of the phenolic analytes and internal standards were fixed to 100 ppb unless otherwise mentioned.

To improve convenience, a treatment kit was prepared as shown in Figure 1. It contains 1 g of Florisil powder (from Supelco) between an anhydrous sodium sulfate layer in a 10-mL glass syringe. The packing materials were retained with glass wool at both ends of the packing. Florisil serves as an absorbent of any polar compounds produced as a result of the treatment or existing in the sample matrix. A 10-mL aliquot of hexane was eluted first. Then hexane was filled to the top of the Florisil layer. A 0.7-mL aliquot of acetone was added to the sodium sulfate layer as solvent medium for derivatization and then followed by addition of 100 μL of BSTFA. A standard solution or extracts of phenolic analytes were added. The analytes were eluted with 3 mL of hexane twice. Water treatment of excess BSFTA was skipped here because the effectiveness of treatment was not ensured in the presence of anhydrous sodium sulfate. The analytes were eluted with 3 mL of hexane twice. The eluent was concentrated to 1 mL with a gentle flow of dry N_2 followed by addition of internal standards and then subjected to GC/MS analysis.

Separation of target compounds was performed using a Shimadzu GC-17A with a capillary column of DB-1 (0.32-mm i.d, 25-μm film, 30 m long) and helium carrier gas at 40 psi. The flow rate of the carrier gas was 2.3 mL/min. One microliter of sample was introduced by splitless mode using an autoinjector AOC-17 from Shimadzu. The temperature of the injection port and detector was 280 and 290 °C, respectively. The oven temperature was held

Table 1. Ions for Selected Ion Monitoring of Phenolic Silyl Derivatives

analyte	retention time (min)	quantification ion (abundance)	confirmation ion (abundance)
4-*tert*-butylphenol[a]	8.63	222 (12.19)	207 (100)
2,4,-dichlorophenol[a]	8.71	234 (16.51)	93 (100), 219 (51.73)
4-*n*-butylphenol[a]	9.46	222 (17.08)	179 (100)
4-*n*-pentylphenol[a]	10.60	236 (14.26)	179 (100)
4-*n*-hexylphenol[b]	11.74	250 (12.15)	179 (100)
4-*tert*-octylphenol[b]	12.01	278 (3.33)	207 (100)
4-*n*-heptylphenol[b]	12.84	264 (10.55)	179 (100)
nonylphenol[b]	13.10	221 (32.25)	207 (100), 193 (13.75)
4-*n*-octylphenol[b]	13.91	278 (20.67)	179 (100)
pentachlorophenol[b]	14.30	323 (43.42)	93 (100), 321 (24.14)
bisphenol A[c]	16.98	372 (10.53)	357 (100)
bisphenol A−d_{14}[c]	16.93	386 (9.61)	368 (100)
naphthalene-d_8	6.40	136 (100)	
phenanthrene-d_{10}	13.06	188 (100)	
pyrene-d_{10}	16.04	212 (100)	

[a] Naphthalene-d_8 was used as internal standard. [b] Phenanthrene-d_{10} was used as internal standard. [c] Pyrene-d_{10} was used as internal standard.

at 50 °C for 2 min, then elevated to 100 °C at 20 °C/min, from 100 to 200 °C at 10 °C/min, and from 200 to 290 °C at 20 °C/min, and finally held at 290 °C/min for 2 min.

A Shimadzu MS QP-5000 system was interfaced with the chromatographic system. The interface temperature was same as the temperature of the GC detector. The electron multiplier voltage was 1500 V, and the energy of ionizing electron was 70 eV. The selected ion monitoring (SIM) mode was used with a sampling rate of 0.2 s. Quantification was done by an internal standard method. Naphthalene-d_8, phenanthrene-d_{10}, and pyrene-d_{10} were used as GC internal standards for the analytes studied as shown in Table 1 through all the experiments. Bisphenol A-d_{14} was used as a surrogate standard in the analysis of the seawater sample to trace the reliability of analysis. The selected ion groups for phenolic silyl derivatives are given in Table 1.

Seawater samples were prepared and analyzed as follows: seawater was sampled in glass bottles and pH was adjusted to 2 with 6 N HCl. One liter of sample was taken into a 2-L separatory funnel, and then 100 μL of 1 ppm surrogate standard or 100 μL of 1 ppm standards was spiked. The analytes were extracted three times with 60 mL of dichloromethane. The extracts were treated with 15 g of anhydrous sodium sulfate and then concentrated to 0.8 mL with a rotary evaporator and gentle flow of dry N_2. The extracts were subjected to derivatization using treatment kits as described above and then subjected to GC/MS analysis.

RESULTS AND DISCUSSION

In this study, silyl derivatizations of phenolic analytes were performed at room temperature rather than elevated temperature because a moderate condition was desirable for analytical convenience. The silylation rates of the analytes were studied in various solvents, and the condition of the derivatization reaction was optimized.

To make sure the silylation yields in dichloromethane were comparable, enough reaction time was allowed, i.e., 1 h at 80 °C and 3 h at room temperature. The silylation yields for both conditions were very close (data not shown). Similar results were obtained for other solvents studied in this work. Sufficient reaction time afforded quantitative derivatization even at room temperature.

Since organic reaction rate is very dependent on the polarity or strength of the solvent, silylation kinetics were studied in various solvents such as dichloromethane, ethyl acetate, hexane, and acetone. The silylation yields were monitored as a function of reaction time for these solvents. Silylation was quenched by hydrolyzing excess BSTFA with a spike of water at the end of reaction. The silylation reaction rates for phenolic analytes were very dependent on solvent characteristics as shown in Figure 2. It took at least 1 h in dichloromethane and ethyl acetate and more than 3 h in hexane for the completion of reaction (Figure 2B−D). However, derivatization was completed quantitatively in acetone as soon as BSTFA was added (Figure 2A). It implies that acetone is very suitable for silyl derivatization of alkyl phenols, chlorophenols and bisphenol A. The feasibility of the silyl derivatization in these solvents was the following order: acetone $\gg$ ethyl acetate > dichloromethane > hexane. It is likely related to the polarity of the solvents. The more polar the solvent, the faster the reaction rate was for all phenolic analytes. Presumably the formation of an intermediate is favored due to the stabilization of the oxonium ion in polar solvents, resulting faster reaction rates.

Practically water-immiscible solvents such as dichloromethane or hexane have been widely used for the extraction of phenolic analytes from environmental or biological samples, but the silyl reaction rates are slow in such solvents as shown above. On the basis of the result of above experiment, one might expect the possibility of reaction rate acceleration by adding acetone to reaction medium. We tested the dependence of reaction rate on the acetone content in the reaction medium. Dichloromethane and hexane media were chosen for the test. Silylation yield after reaction for 30 s was monitored with variation of acetone content in reaction medium and is shown in Figure 3. The reaction rates of chlorophenols were so fast that any remarkable change in rate was not noticed with variation of acetone content in the reaction medium. However, the reaction rates for the other phenolic analytes were dependent on the content of acetone in the reaction medium. Above 60% (v/v) acetone content, the silylation were completed quantitatively within 30 s in both cases. This result suggests that one might add acetone to dichloromethane or

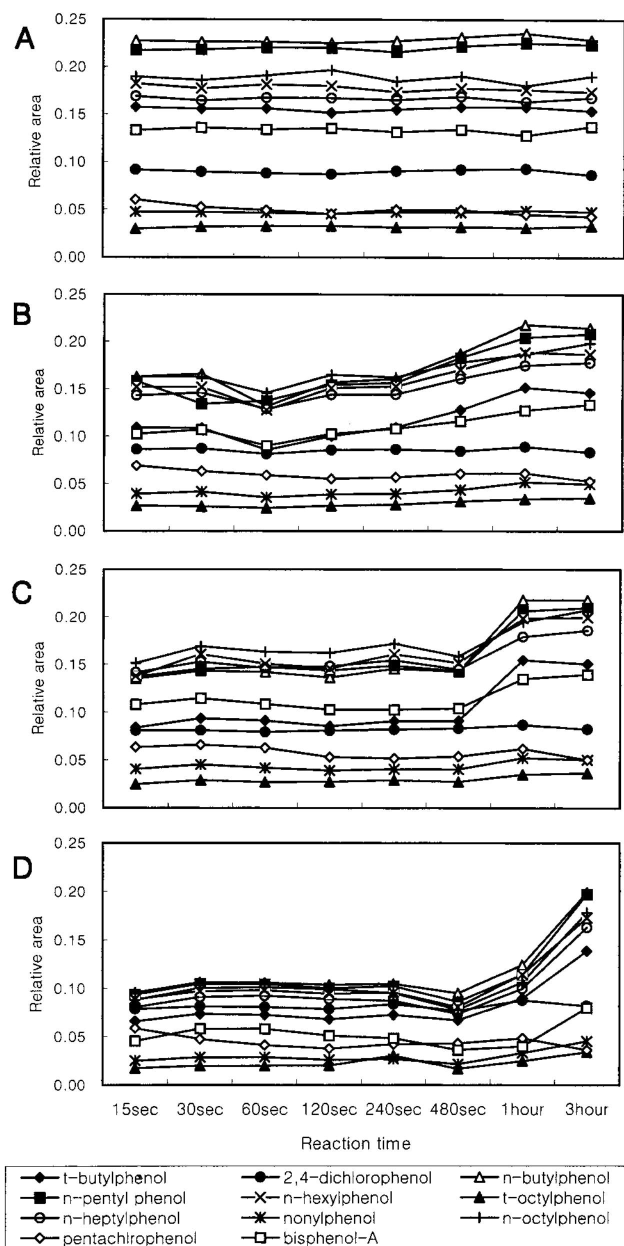

Figure 2. Time dependence of silylation reactions of various phenolate analytes in different solvents. (A) acetone, (B) ethyl acetate, (C) dichloromethane, and (D) hexane.

hexane extracts of phenolic analytes to shorten the silyl derivatization procedure. On the basis of this result, we designed a new on-column silyl derivatization technique for phenolic analytes, which will be discussed later. This technique is fast, simple, and convenient.

BSTFA is a highly volatile and reactive derivatizing reagent. Although it is suitable for silylation of target phenolic compounds, it is not good for the storage of derivatized samples in vials for a long period. If the derivatized sample is taken once from the sample vial for analysis, unreacted excess BSTFA may be exposed to the silicone rubber septum of the sample vial through the hole formed by the injector needle, resulting in contamination of the derivatized samples. Although well-defined sharp peaks resulted because of the low polarity and high volatility of the derivatized analytes, frequently unexpected interference peaks in the chromatograms between peaks of analytes or at the end of the elution were observed when the derivatized samples was analyzed again later. (See arrows in the chromatogram in Figure 4B.) A mass spectrometric library search indicated those were silyl derivatives of septum material. So removal of unreacted excess derivatizing reagent is desired. It was reported that propanol can be used for the removal of unreacted excess silyl reagent in steroid and bile acid analysis.[31] However, this technique cannot be applied to phenolic analytes because most phenolic silyl derivatives rapidly transform backward to phenolic compounds. Figure 5 shows the stability of the silyl derivatives upon the addition of propanol. Chromatographic analyses were performed 30 min after addition of propanol. Increasing the ratio of propanol to BSTFA resulted in a decrease of the peak area of the silyl derivatives, while the peak area of underivatized phenol compounds increased. Instead of propanol, 100 μL of deionized water was added to hydrolyze unreacted excess BSTFA in this work, and then anhydrous sodium sulfate was added to remove water from the derivatized extracts. After excess BSTFA treated with water, the phenolic analytes were discovered quantitatively. Even after 55 days of derivatization treatment, the silylized phenolic analytes were found without remarkable change. The result implies that the stability of the phenolic analytes can be maintained during long-term storage by treating excess derivatizing reagent with water. Although treat-

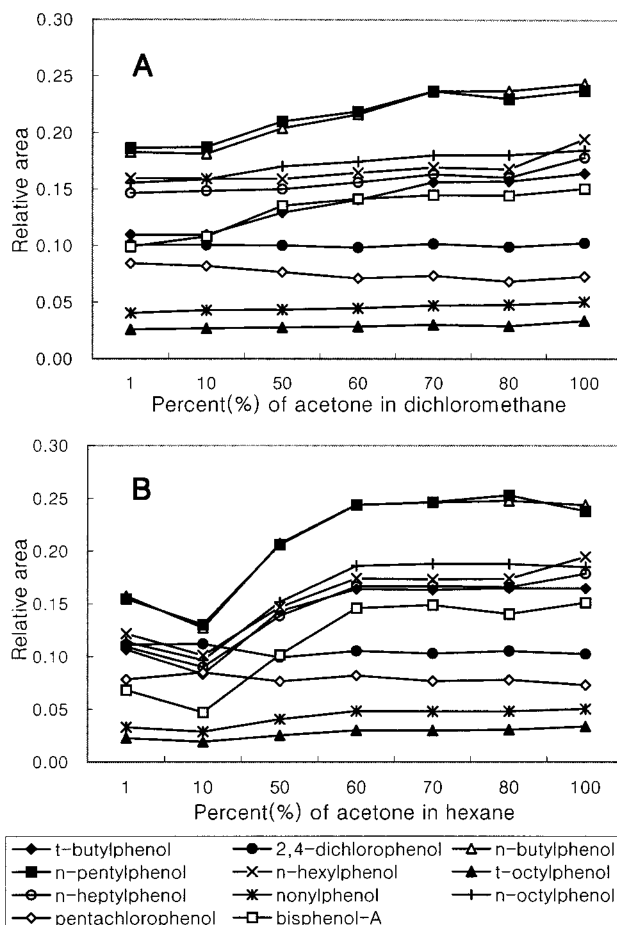

Figure 3. Effect of acetone content on silylation reaction rates. (A) dichloromethane and acetone mixture; (B) hexane and acetone mixture.

(31) Andersson, S. H. G.; Sjövall, J. *J. Chromatogr.* **1984**, *289*, 195−206.

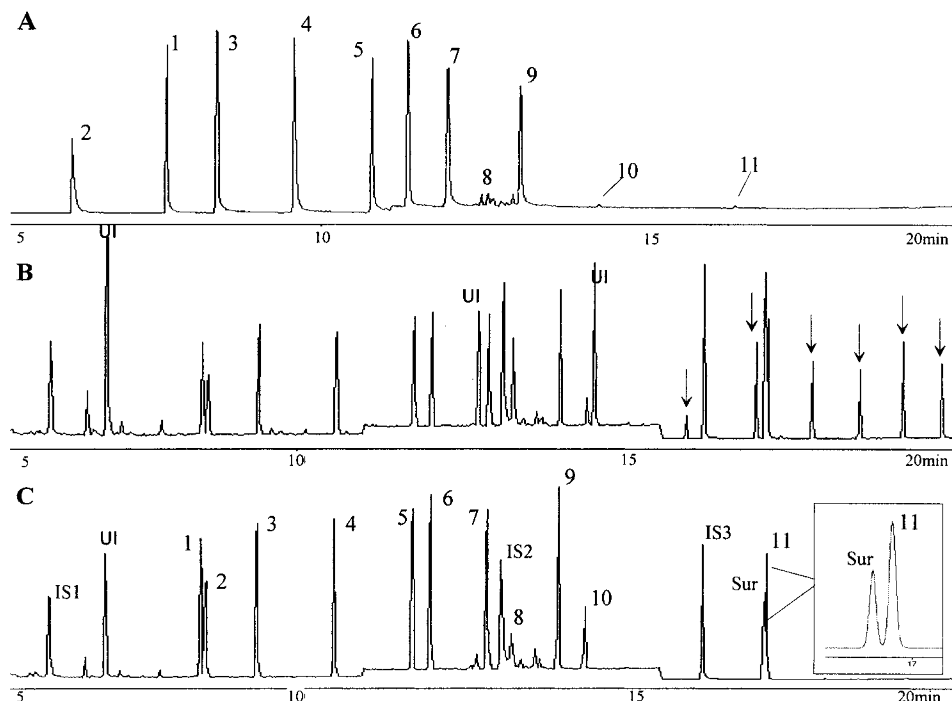

Figure 4. Chromatograms of phenolic analytes. (A) without derivatization, (B) with derivatization only, after 3-days exposure to septum material through a hole formed by injection needle, and (C) with derivatization followed by hydrolysis with water, after 3 days. (1) *tert*-butylphenol, (2) 2,4-dichlorophenol, (3) *n*-butylphenol, (4) *n*-pentylphenol, (5) *n*-hexylphenol, (6) *tert*-octylphenol, (7) *n*-heptylphenol, (8) nonylphenol, (9) *n*-octylphenol, (10) pentachlorophenol, (11) bisphenol A. IS, Sur, and UI, internal standard peak, surrogate standard peak, and unidentified peak, respectively.

Table 2. Analytical Characteristics of GC/MS Analysis of Phenolic Analytes

	reproducibility of retention time		recovery[a]		dynamic concn range[b]	
analytes	average (min)	RSD (%)	average (%)	RSD (%)	range (ng/mL)	R^{2c}
4-*tert*-butylphenol	8.60	0.02	94.2	3.4	1−3000	1.000
2,4,-dichlorophenol	8.67	0.04	104.7	2.4	1−3000	0.998
4-*n*-butylphenol	9.43	0.03	91.5	7.1	1−2500	0.999
4-*n*-pentylphenol	10.57	0.02	93.7	5.6	1−2500	0.999
4-*n*-hexylphenol	11.72	0.01	94.5	2.0	1−2500	0.999
4-*tert*-octylphenol	11.98	0.02	91.2	6.7	1−2500	0.999
4-*n*-heptylphenol	12.82	0.01	92.6	1.6	1−2500	0.998
nonylphenol	13.07	0.04	100.0	1.5	1−2500	0.999
4-*n*-octylphenol	13.88	0.01	93.8	5.3	1−2000	0.999
pentachlorophenol	14.27	0.04	82.2	7.9	1−1500	0.993
bisphenol A	16.95	0.01	98.2	4.1	1−3500	0.997

[a] For the recovery test, four replicate artificial seawater samples of 100 ppb in phenolic analyte concentration were used. [b] Dynamic concentration ranges were evaluated with criteria of ±10% of average response factor. [c] R^2 represents the square of correlation coefficient of linear regression analysis.

ment with acidic or basic aqueous solution was attempted, no significant difference was noted. Typical chromatograms of phenolic analytes are shown in Figure 4. Chromatogram A is for analytes without derivatization. Highly polar untreated phenolic analytes showed wide and tailing peaks due to the strong interaction with column materials, which cause low resolution and sensitivity. Chromatogram C was obtained with derivatization followed by hydrolysis of excess reagent. The interference peaks in chromatogram B disappeared in chromatogram C, which implies the effectiveness of hydrolysis of the derivatizing reagent. The analytical characteristics of GC/MS analysis of phenolic analytes treated by the above procedure were very similar to those of previously reported work by others as shown in Table 2.[32]

On the basis of the above results, a fast silyl treatment kit was designed as described in Figure 1. Table 3 shows the comparison of the standard derivatization procedure and treatment kit procedure in terms of analytical signals and relative standard deviations of analyses. The variability of the analysis in the treatment kit procedure was about twice that of the standard derivatization procedure except for pentachlorophenol, but it was still satisfactory. And the analytical signals of analytes in the treatment kit procedure also ranged above 95% relative to the standard procedure except for pentachlorophenol. Pentachlorophenol is highly polar compound compared to the others. It is

(32) Hong, J.; Kim, H.; Baek, I.; Kim, D.; Seo, J.; Seo, J.; Chung, B.; Pyo, H.; Kim, K.; Kim, Y. *Anal. Sci. Technol.* **2000**, *4*, 484−493.

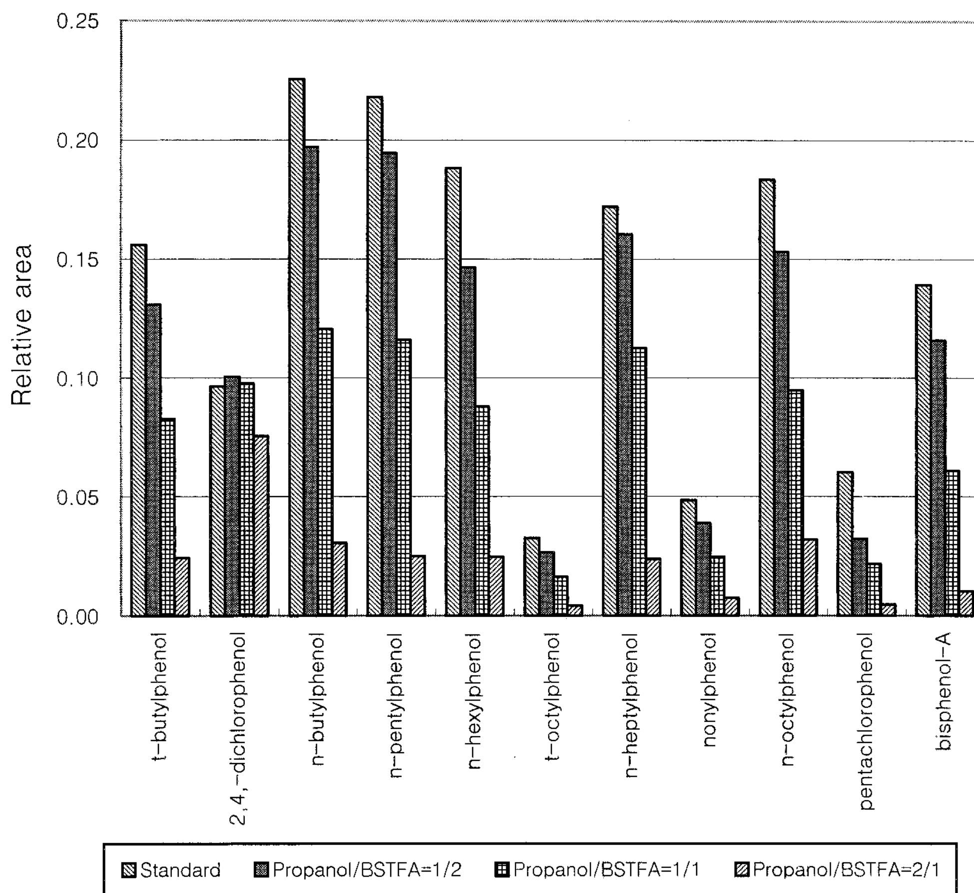

Figure 5. Effect of propanol content on the stability of derivatives of phenolic analytes.

Table 3. Comparison of the Standard Silyl Derivatization Procedure and Treatment Kit Procedure[a]

	by standard procedure		by treatment kit		
analytes	relative area[b] (A)	RSD (%)	relative area[b] (B)	RSD (%)	ratio (B/A)
4-*tert*-butylphenol	0.98	2.2	0.93	5.2	0.96
2,4,-dichlorophenol	0.65	2.3	0.62	5.3	0.95
4-*n*-butylphenol	1.54	2.6	1.49	4.9	0.96
4-*n*-pentylphenol	1.53	2.4	1.47	4.7	0.96
4-*n*-hexylphenol	1.13	2.2	1.10	3.7	0.98
4-*tert*-octylphenol	0.18	3.2	0.17	4.3	0.98
4-*n*-heptylphenol	0.99	2.9	0.97	4.0	0.98
nonylphenol	0.32	2.2	0.32	3.3	0.98
4-*n*-octylphenol	1.04	3.2	1.02	3.9	0.98
pentachlorophenol	0.73	6.5	0.59	20.7	0.81
bisphenol A	0.87	2.8	0.86	4.7	0.99

[a] One ppm of phenolic analytes and 200 ppb of internal standards were used. [b] Relative area is the average relative area of each compound to the area of corresponding internal standard ($n = 4$).

likely that polar Florisil retained the silyl derivative of pentachlorophenol quite strongly, giving the low recovery compared to the others. If the sequence of the addition of BSTFA and solution of analytes was reversed, the recoveries of analytes were much lowered. Presumably strong adsorption of polar phenolic analytes on the surface of the Florisil reduced the reaction rate of silylation.

Finally, the derivatization techniques were applied to the analysis of a contaminated coastal seawater sample. The sample was treated using a treatment kit after extraction with dichloromethane. For quality control of the analysis, standard spiked sample was treated using a treatment kit as well as the standard derivatization process. The analytical results are shown in Table 4. The recoveries of the spiked phenolic analytes to the sample ranged from 81 to 102% in the standard procedure and 79 to 97% in the treatment kit procedure. The relative standard deviations of spiked sample analyses were quite close to each other in both derivatization procedures. The recoveries of the surrogate standard, bisphenol A-d_{14} appeared to be higher than 90% in all cases. These results indicate that alkylphenols, chlorophenols, and

Table 4. Analytical Results of a Contaminated Coastal Seawater Sample

analytes	sample, ppt (% RSD, $n = 4$)	spiked sample (ppt)[a] by standard procedure (% RSD, $n = 4$)	spiked sample (ppt)[a] by treatment kit (% RSD, $n = 4$)
4-*tert*-butylphenol	10(9)	112(5)	107(5)
2,4,-dichlorophenol	0	89(9)	88(7)
4-*n*-butylphenol	0	99(7)	92(2)
4-*n*-pentylphenol	0	102(4)	93(4)
4-*n*-hexylphenol	0	96(4)	94(3)
4-*tert*-octylphenol	8(17)	111(4)	100(9)
4-*n*-heptylphenol	0	93(5)	90(3)
nonylphenol	99(6)	190(1.4)	190(6)
4-*n*-octylphenol	0.9(21)	93.9(8)	88.9(4)
pentachlorophenol	0	81(13)	76(12)
bisphenol A	46(4)	138(6)	138(4)
bisphenol A−d_{14}[b]	90(6)	96(10)	94(7)

[a] Standards were spiked to the samples to 100 ppt level. [b] Bisphenol A-d_{14} was spiked to the samples to 100 ppt level as a surrogate standard.

bisphenol A can be simultaneously determined from an environmental sample using the treatment kit technique with satisfactory recovery and reproducibility.

In summary, by using acetone as the reaction medium, fast silyl derivatization of phenolic analytes at room temperature was possible quantitatively. Similar results were obtained in a mixed solvent of dichloromethane or hexane with acetone unless the content of acetone was lower than 60% (v/v). It affords reliable simultaneous GC/MS analysis of alkylphenols, chlorophenols, and bisphenol A with greatly improved convenience. Hydrolysis of unreacted excess derivatizing reagent enhanced the stability of derivatized analytes for long-term storage. The use of an on-column derivatization kit was also demonstrated successfully. It was possible to treat sample within several minutes by using the kit. The analytical utility of this technique for various samples is under investigation in our laboratory.

ACKNOWLEDGMENT

The authors are grateful to Shimadzu Corp. for the donation of a GC/MS system and reagents.

Received for review December 19, 2000. Accepted March 8, 2001.

AC001494L