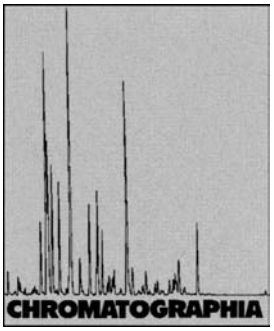
Modification of Soxhlet Extractor for Rapid and Effective Recovery of Phenolic Pollutants Adsorbed on XAD-4 Resin



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Abstract

A newly modified extractor facilitated rapid extraction (10.0 mL, 1 h) of eleven phenols from XAD-4 resin for comparable recoveries to those with conventional Soxhlet extractor (80.0 mL, 3 h). Combined with analysis by gas chromatography and gas chromatography-mass spectrometry in selected ion monitoring mode as *tert*-butyldimethylsilyl derivatives, the overall method was linear (≥ 0.9991) with satisfactory precision (≤ 9.2% RSD), accuracy (≤ 7.7% RE), detection limit (≤ 0.02 μg L^{-1}), and recovery rates (≥ 75.0%) in 0.05 to 1.0 μg L^{-1}. Six phenolic pollutants were quantitatively screened along with bisphenol A (0.028 μg L^{-1}) from river water.

Keywords

Gas chromatography-mass spectrometry
Soxhlet extraction
XAD-4 resin
Phenols in river water

Introduction

With the growing concern about water quality, trace level (sub μg L^{-1}) analysis of organic micropollutants in water has become an important task in recent years. Among the pollutants with aromatic moiety, phenols constitute an important class of ground water contaminants mainly because of their heavy uses in chemical industries [1–3]. Several alkylphenols are either known or suspected endocrine disruptors [4,5], thereby necessitating their accurate measurements in water samples. As a consequence, simultaneous detection and identification of diverse phenolic pollutants in a single analysis is frequently encountered in the monitoring of water samples for their presence and also in the controlling of their overuses.

For trace enrichment of phenols from large volume (≥ 1 L) of water samples without high consumption of organic solvents, solid-phase extraction (SPE) is currently by far the most popular in sample preparation as well reviewed in recent literature [6,7]. Among the porous polymer resins based on Amberlite XAD [1,2,5,8–16] graphitized carbon black [17,18] and siloxane-bonded silica materials [2,7,8,14,19], XAD-4 resins have gained widespread acceptance for SPE of aromatic compounds in water because of their chemical stability at a wide range of pH conditions and of their mechanical strength. The SPE of phenols utilizing polymeric resins has been exclusively performed in dynamic sorption mode.

The phenols retained on solid sorbent particles are mostly desorbed by passing through a small volume of organic solvents in dynamic mode. A longer residence time for solvent during elution step is required by slowing down eluting rate to ensure quantitative recovery. Penetration of the solvent into solid sorbent pores or sediments is essential for more efficient desorption of phenols, which is mainly achieved by Soxhlet extraction [3]. However, Soxhlet extraction requires larger volume of solvent and longer extraction time due to its inherent lengthy soaking process. As a different approach for rapid desorption, extraction performed in recycling continuous elution fashion using a given minimal volume of volatile solvent would be a better choice. This requires eliminating siphoning and soaking functions of conventional Soxhlet extractor by removing its siphon arm and bottom of soaking basin where a thimble is placed. However, this attempt to modify a Soxhlet extractor has rarely been made.

In continuation of the systematic screening for phenolic pollutants [20,21], the present study was undertaken to reduce solvent volume and extraction time as well by modifying conventional Soxhlet extractor into an open extractor that

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Table 1. Phenolic compounds studied as TBDMS derivatives by GC-SIM-MS

Compound	Selected ion (m/z)
2-Chlorophenol	149, **185**, 187
4-Bromophenol	229, 231, **286**
4-*tert*.-Butylphenol	207, 249, **264**
2,4-Dichlorophenol	183, **219**, 221
4-*n*-Butylphenol	207, 208, **264**
3-Nitrophenol	149, 196, **253**
4-*n*-Pentylphenol	221, 222, **278**
4-*n*-Hexylphenol	235, 236, **292**
2,4-Dinitrophenol	195, 225, **241**
Pentachlorophenol	321, **323**, 325
Bisphenol A	207, **441**, 456
n-Docosane (IS_1)	113, 169, **310**
Bisphenol A-d_{16} (IS_2)	217, **452,** 470

Ultra-2 capillary column (25 m × 0.20 mm I.D., 0.11 μm d_f), from 100 °C (1 min) to 300 °C at 4 °C min^{-1} in SIM mode with 100 ms of dwell time, 2000 volts of electron multiplier and quantitation ions are in bold

provides recycling continuous solvent elution. The extraction efficiencies of the conventional- and the new- extractors were tested for the recovery of eleven phenols chosen as the model compounds that could be resolved in a single GC and GC-MS run among the diverse phenolic pollutants. The eleven phenols were pre-extracted from water samples onto XAD-4 resin by SPE in static sorption mode. The recovered phenols were converted to *tert*-butyldimethylsilyl (TBDMS) derivatives for direct analysis by GC and GC-MS in selected ion monitoring (SIM) mode.

Experimental

Materials and Reagents

Eleven phenolic standards examined in this study, *n*-docosane and deutrated bisphenol A-d_{16}, each used as internal standard (IS) were purchased from Sigma-Aldrich (Milwaukee, WI, USA), Fisher Scientific (Pittsburgh, PA, USA) and other vendors. Silylation reagent, *N*-methyl-*N*-(*tert*-butyldimethylsilyl)trifluoroacetamide (MTBSTFA) was purchased from Pierce (Rockford, IL, USA) and solvents such as toluene, acetonitrile, methanol and dichloromethane of pesticide grade from Kanto Chemical (Tokyo, Japan). All other chemicals were of analytical grade and used as received. XAD-4 resin (80–100 mesh) purchased from Supelco (Bellefonte, PA, USA) was purified by sequential extraction with methanol, acetone, and dichloromethane in a Soxhlet extractor, followed by activation (60 °C, 3 h) prior to being used as sorbent.

Preparation of Standard Solutions

Each stock solution of phenolic standards was made up at 10 μg μL^{-1} in acetonitrile and stored in a freezer. A working mixed solution containing nine phenols (0.01 μg μL^{-1} each) and two nitrophenols (0.02 μg μL^{-1} each) was prepared by combining each stock solution and diluting with acetonitrile. Bisphenol A-d_{16} used as IS_2 for imprecision of SPE and Soxhlet extraction was made at 0.1 μg μL^{-1} in acetonitrile. *n*-Docosane used as IS_1 for injection imprecision was prepared by dissolving at 0.1 μg μL^{-1} in toluene.

Gas Chromatography and Gas Chromatography-Mass Spectrometry

The GC analyses for comparison between conventional- and modified Soxhlet extractors were performed with an Hewlett-Packard HP model 5890A series II gas chromatograph (Agilent Technologies, Atlanta, GA, USA) equipped with a split/splitless capillary inlet system and a flame ionization detector. The injector was installed with an HP-5 (SE-54 bonded phase) capillary column (30 m × 0.32 mm I.D., 0.25 μm film thickness; Agilent Technologies). The injector and detector temperatures were 260 and 280 °C, respectively. The inlet pressure of helium as carrier gas was set to 130.0 kPa. Samples (ca. 1.0 μL) were injected in the splitless mode (purge delay time of 0.7 min). The oven temperature was held at 80 °C for 1 min, then programmed to 100 °C at a rate of 20 °C min^{-1}, and then to 290 °C at a rate of 3 °C min^{-1} with holding time for 20 min. All GC analyses were performed in triplicate.

The GC-MS analyses in SIM mode for method validation and for screening analysis of phenolic pollutants in river water were conducted with an Agilent 6890 gas chromatograph, interfaced to an Agilent 5973 mass-selective detector (70 eV, electron impact mode) and installed with an Ultra-2 (SE-54 bonded phase; 25 m × 0.20 mm I.D., 0.11 μm film thickness) cross-linked capillary column (Agilent Technologies). Helium was used as carrier gas at a flow rate of 0.5 mL min^{-1} in constant flow mode. The injector, interface and ion source were maintained at 260, 300 and 320 °C, respectively. Samples were introduced in the split-injection mode (10:1) and the oven temperature was initially at 100 °C for 1 min and programmed to 300 °C at a rate of 4 °C min^{-1} with holding time for 10 min. The identification ions including quantification ions for each phenol, IS_1 and IS_2 were listed in Table 1. A dwell time of 100 ms and electron multiplier voltage of 2000 V were chosen for each ion monitored.

tert-Butyldimethylsilylation

To dry residues containing phenols and deutrated bisphenol A-d_{16} were added 1 μg *n*-docosane (IS_1) in 20 μL of toluene. The mixture was then reacted (60 °C for 1 h) with MTBSTFA (20 μL) to form TBDMS derivatives of phenolic group. All samples were individually prepared in triplicate and directly examined by GC and GC-SIM-MS.

Modified Soxhlet Extractor and XAD Glass Column

From a conventional Soxhlet extractor (Fig.1-A), the siphon arm was removed and the closed bottom of soaking basin was made open into solvent flask to convert to an open eluting Soxhlet extractor (Fig.1-B). The dimensions of both extractors were as follows: length, 300 mm; joint part with condenser, 34/45 mm; joint part with solvent flask (250 mL), 24/40 mm. A glass column (length, 125 mm; upper and inner diameters, 22 mm and 10 mm, respectively) secured with cleaned glass wool at its tapered end was used for collecting XAD-4 resin particles after SPE (Fig. 1-C).

Solid-Phase Extraction with Subsequent Soxhlet Extraction

Constant amount (1.0 g) of XAD-4 was added to 1 L of acidified water (pH 2, adjusted with 2.5 M H_2SO_4) spiked with eleven phenolic standards (1 μg each) and bisphenol-d_{16} A as IS_1 (1.0 μg). Each suspension was stirred using magnetic

stirring bar for 4 h at room temperature. After static SPE was completed, the resin particles were collected into an empty glass column (Fig.1-C) under gentle vacuum and residual moisture was removed under further vacuum (10 min). The dried XAD-4 column was then placed in a conventional Soxhlet extractor (Fig. 1-A) to extract retained phenolic pollutants with 80.0 mL of dichloromethane containing 10.0% acetonitrile for 3 h at 50 °C. When employing a newly modified open Soxhlet extractor, extraction was conducted with 10.0 mL for 1 h. Each extract was concentrated down to 1 mL with rotary evaporator and then reconstituted in 4 mL of dichloromethane, followed by moisture removal using $MgSO_4$. Finally, the last concentration was performed by evaporation under gentle stream of nitrogen. The dry residue was then subjected to TBDMS derivatization in the same manner as described above for direct analysis by GC. All quantitative calculations for the extraction efficiencies of phenols were based on the peak area ratios relative to that of IS_2. *F* test at 95% confidence level was performed on the two sets of standard deviations and *t* test on the two sets of data yielded by the two extractors for their significant differences.

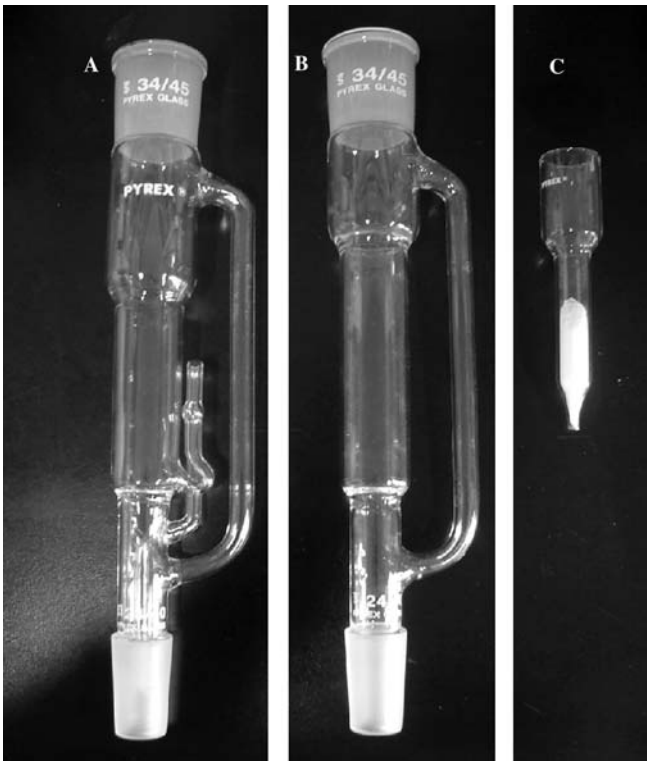

Fig. 1. Conventional Soxhlet extractor (A), modified Soxhlet extractor (B) and XAD glass column

Validation of Modified Soxhlet Extraction for Assay of Phenolic Pollutants

Three water samples containing nine phenols at 0.05, 0.1 or 0.5 μg L^{-1}, two nitrophenols at 0.1, 0.2 or 1.0 μg L^{-1}, and IS_2 at fixed amount (1.0 μg L^{-1}) were prepared by adding the working mixed solution and IS_2 solution into 1.0 L of acidified water (pH 2). Each calibration sample was then subjected to the SPE in static sorption mode with subsequent solvent extraction employing a modified Soxhlet extractor according to the preceding procedures, followed by TBDMS derivatization for direct analysis by GC-SIM-MS. All quantitative calculations for the extraction efficiencies of phenols were based on the peak area ratios relative to that of IS_2. Linearity was tested by least-squares regression analysis on the peak area ratios against increasing concentration ratios to plot calibration curves. The LOD (limit of detection) of each analyte was estimated based on the lowest concentration giving a signal taken as the sum of the mean blank signal plus three times the standard deviation of the blank signal obtained via three blank measurements. Precision expressed as percentage of relative standard deviation (% RSD) and accuracy as percentage of relative error (% RE) of the method was determined from calibration samples at two different concentrations (0.05 to 1.0 μg L^{-1}) in triplicate. The recovery rates were assessed by comparing the percentages of peak area ratios of extracted samples to those of non-extracted counterparts (representing 100% recovery) prepared by direct TBDMS derivatization in dry neat form at the same nominal concentrations.

Sample Preparation for Phenolic Pollutants in River Water

Standard addition method was employed for quantitative analysis of eleven phenolic pollutants in water sample: Aliquots (1 L) of river water adjusted to pH 2.0 and were added with constant amount (1.0 μg L^{-1}) of IS_2, 0.0, 0.1 or 0.5 μg L^{-1} for each phenol except for the two nitrophenols (0.0, 0.2 or 1.0 μg L^{-1}). Each sample was then subjected to the SPE with subsequent Soxhlet extraction and derivatization in the same manner as described in the validation section for direct analysis by GC-SIM-MS. River samples were individually prepared in triplicate.

Results and Discussion

In the course of screening analysis of aromatic micropollutants in large volume of water samples, the conventional Soxhlet extraction step was found to be the bottle neck by making the overall sample preparation extremely lengthy. The present work was thus focused on the modification of the conventional Soxhlet extractor in an attempt to reduce the solvent volume and extraction time employing eleven phenols as the target compounds that could be completely resolved in a single GC and GC-MS run among the diverse phenolic pollutants.

Extraction Efficiency of a Modified Soxhlet Extractor

From a number of preliminary experiments, extractions with 80.0 mL of dichloromethane containing 10% of acetonitrile for 3 h, and with 10.0 mL for 1 h were chosen as the optimal conditions for the conventional Soxhlet extractor and

Table 2. Comparison between conventional Soxhlet extractor and modified extractor for extraction recovery of 11 phenols

Compound	Soxhlet extraction		Statistical analysis			
	Mean peak area ratio ± SD (%RSD, n = 3)[a]		*F* test value		*t* test value	
	Conventional[b]	Modified[c]	Calculated[d]	Table[e]	Calculated[f]	Table[h]
2-Chlorophenol	0.61 ± 0.05 (8.2)	0.54 ± 0.05 (9.3)	1.0	19.0	1.715	2.776
4-Bromophenol	0.47 ± 0.03 (6.4)	0.50 ± 0.02 (4.0)	2.3	19.0	1.441	2.776
4-*tert*.-Butylphenol	0.66 ± 0.03 (4.5)	0.57 ± 0.05 (8.8)	2.8	19.0	2.673	2.776
2,4-Dichlorophenol	0.40 ± 0.03 (7.5)	0.32 ± 0.02 (6.3)	2.3	19.0	3.843	2.776
4-*n*-Butylphenol	1.47 ± 0.07 (4.8)	1.06 ± 0.01 (0.9)	49.0	19.0	10.043[g]	4.30∼3.182[i]
3-Nitrophenol	1.09 ± 0.06 (5.5)	1.20 ± 0.06 (5.0)	1.0	19.0	2.245	2.776
4-*n*-Pentylphenol	0.74 ± 0.03 (4.1)	0.69 ± 0.04 (5.8)	1.8	19.0	1.732	2.776
4-*n*-Hexylphenol	1.68 ± 0.03 (1.8)	1.63 ± 0.06 (3.7)	4.0	19.0	1.291	2.776
2,4-Dinitrophenol	0.25 ± 0.01 (4.0)	0.39 ± 0.03 (7.7)	9.0	19.0	7.668	2.776
Pentachlorophenol	0.80 ± 0.02 (2.5)	0.91 ± 0.01 (1.1)	4.0	19.0	8.521	2.776
Bisphenol A	1.04 ± 0.01 (1.0)	1.10 ± 0.01 (0.9)	1.0	19.0	7.348	2.776

HP-5 capillary column (30 m × 0.32 mm I.D., 0.25 μm d_f), from 80 °C (1 min) to 100 °C (1 min) at 20 °C min^{-1}, then to 290 °C (3 min) at 4 °C min^{-1} by GC-FID. Aliquots (1.0 L) of water samples (pH 2) containing phenols (1 or 2 μg each) and bisphenol A-d_{16} as IS_2 (1 μg) were subjected to SPE with subsequent Soxhlet extraction and TBDMS derivatization as described in the text

[a] Mean peak area ratio relative to IS_2 and standard deviation for triplicate runs

[b] Conventional Soxhlet extraction (80.0 mL for 3 h)

[c] Modified Soxhlet extraction (10.0 mL for 1 h)

[d] SD_1^2/SD_2^2, or SD_2^2/SD_1^2

[e] Critical value at 95% confidence level

[f] $SD_{pooled} = [\{SD_1^2 (n_1-1) + SD_2^2 (n_2-1)\}/ n_1 + n_2-2]^{1/2}$, $t_{calculated} = |Mean_1-Mean_2| / SD_{pooled} \times (n_1 n_2 / n_1 + n_2)^{1/2}$

[g] Degrees of freedom $= [(SD_1^2/n_1 + SD_2^2/n_2)^2 / \{(SD_1^2/n_1)^2 / n_1 + 1\} + \{(SD_2^2/n_2)^2 / n_2 + 1\}]-2$, $t_{calculated} = |Mean_1-Mean_2| / (SD_1^2/n_1 + SD_2^2/n_2)^{1/2}$

[h] Critical value of Student's *t* at 95% confidence level 4 degrees of freedom

[i] Critical value of Student's *t* at 95% confidence level for 2.2 degrees of freedom

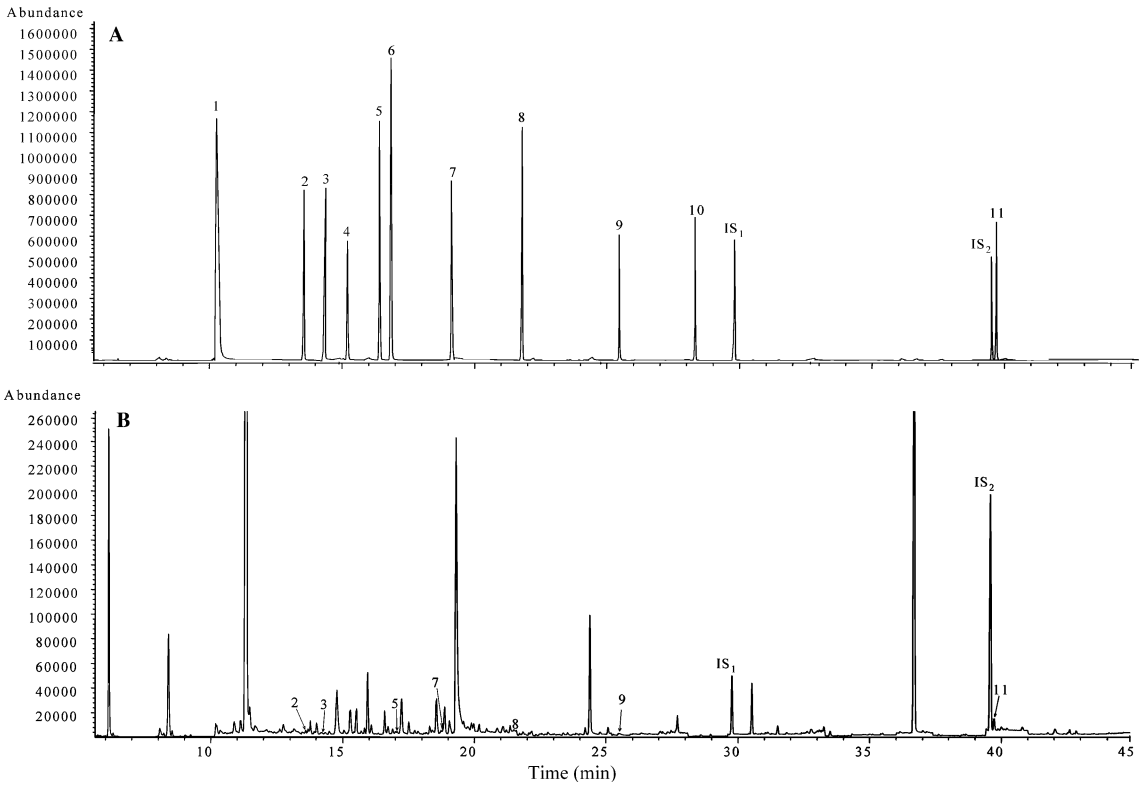

Fig. 2. GC-SIM-MS phenolic profiles in a standard sample (A) and in a river water (B) as *tert*-butyldimethylsilyl derivatives separated on Ultra-2 column (SE-54 bonded phase; 25 m × 0.20 mm I.D., 0.11 μm film thickness) under helium at 0.5 mL min^{-1} in constant flow mode. Samples were injected in the split-injection mode (10:1) and the oven temperature was initially at 100 °C for 1 min and programmed to 300 °C at a rate of 4 °C min^{-1} with holding time for 10 min. Peaks: **1** = 2-chlorophenol, **2** = 4-bromophenol, **3** = 4-*tert*-buthylphenol, **4** = 2,4-dichlorophenol, **5** = 4-*n*-butylphenol, **6** = 3-nitrophenol, **7** = 4-*n*-pentylphenol, **8** = 4-*n*-hexylphenol, **9** = 2,4-dinitrophenol, **10** = pentachlorophenol, **11** = bisphenol A, IS_1 = *n*-docosane, IS_2 = bisphenol A-d_{16}

Table 3. Linearity for assay of 11 phenols employing modified Soxhlet extractor

Compound	Calibration range (μg L^{-1})	Regression line		r^2 [a]	LOD (μg L^{-1}) [b]
		Slope	Intercept		
2-Chlorophenol	0.05–0.5	1.848 ± 0.002	−0.0594 ± 0.0006	0.9999	0.01
4-Bromophenol	0.05–0.5	0.514 ± 0.007	−0.009 ± 0.002	0.9998	0.001
4-*tert*.-Butylphenol	0.05–0.5	1.09 ± 0.03	−0.023 ± 0.008	0.9994	0.004
2,4-Dichlorophenol	0.05–0.5	1.46 ± 0.02	0.012 ± 0.005	0.9999	0.01
4-*n*-Butylphenol	0.05–0.5	1.11 ± 0.03	−0.02 ± 0.01	0.9991	0.002
3-Nitrophenol	0.1–1.0	0.386 ± 0.002	0.056 ± 0.001	0.9999	0.02
4-*n*-Pentylphenol	0.05–0.5	1.171 ± 0.027	0.020 ± 0.008	0.9995	0.001
4-*n*-Hexylphenol	0.05–0.5	2.43 ± 0.02	−0.001 ± 0.005	0.9999	0.001
2,4-Dinitrophenol	0.1–1.0	1.378 ± 0.002	0.030 ± 0.001	0.9999	0.002
Pentachlorophenol	0.05–0.5	3.21 ± 0.07	0.12 ± 0.02	0.9995	0.004
Bisphenol A	0.05–0.5	3.06 ± 0.05	−0.06 ± 0.01	0.9997	0.001

All quantitative calculations were based on peak ratios relative to IS (bisphenol A-d_{16}) measured under GC-SIM-MS conditions as described in Table 1. Calibration samples were prepared with aliquots (1.0 L) of water samples (pH 2) spiked with nine phenols (0.05, 0.1, or 0.5 μg each), two nitrophenols (0.1, 0.2, or 1.0 μg each), and bisphenol A-d_{16} as IS (1 μg) (n = 3) using modified extractor as described in text

[a] Correlation coefficient

[b] Limit of detection calculated according to (3 standard deviation of blank response/slope)

modified extractor, respectively. Under these conditions, the modified extractor yielded similar extraction efficiencies and precisions to those obtained by conventional extractor except for 4-*n*-butylphenol (Table 2).

Except for 4-*n*-butylphenol, the smaller $F_{calculated}$ values (= 1.0 ∼ 9.0) than F_{table} (=19.0 at 95%) for the phenols studied prove that the two standard deviations for each phenol are not significantly different from each other above the 95% confidence level (Table 2). And the *t* test indicates that the difference of the two methods is significant for the five phenols within 95% confidence level ($t_{table} = 2.776$) and the significant difference is more pronounced for 4-*n*-butylphenol. However, the modified extractor yielded higher precision (% RSD = 0.9) compared to the conventional extractor (% RSD = 4.8) for 4-*n*-butylphenol. The present modified extractor proves to be more cost-efficient compared to the conventional Soxhlet extractor considering its lower solvent consumption and shorter extraction time.

Method Validation for Assay of Phenolic Pollutants

The present modified extractor was validated to demonstrate its suitability for quantitative analysis of eleven phenolic pollutants at trace amounts in water samples. Under the present GC-SIM-MS conditions (Table 1), the phenolic compounds as TBDMS derivatives were well resolved within 40 min (Fig. 2-A). The calibration curves for the phenols measured at different ranges (0.05∼1.0 μg L^{-1}) were linear (r^2= 0.9991∼0.9999), and the LODs were varied from 0.004 to 0.02 μg L^{-1} (Table 3). The good overall linearity proved suitability of the present method for quantitative measurements of phenolic pollutants in unknown samples. The ranges of precision (% RSD) and accuracy (% RE) of the overall procedure for each phenol measured at two different added amounts varied from 1.4 to 9.2 and from −5.9 to 7.7, respectively (Table 4). These values of the present method indicated that the levels of phenolic pollutants could be measured with acceptable precision and accuracy. The average recovery rates examined on the nine phenols at 0.5 μg L^{-1} and two nitrophenols at 1.0 μg L^{-1} were ranged from 75.0 to 98.5% with good precision (% RSD ≤ 8.2) (Table 4).

Table 4. Precision, accuracy and recovery for assay of 11 phenols employing modified Soxhlet extractor

Compound	Amount added (μg)	Precision (% RSD)	Accuracy (% RE)	Recovery (%) (mean ± S.D.)[a]
2-Chlorophenol	0.1	7.4	−0.3	
	0.5	8.4	0.01	83.1 ±6.1
4-Bromophenol	0.1	7.3	3.8	
	0.5	3.8	−0.1	81.0 ±4.9
4-*tert*.-Butylphenol	0.1	5.4	6.4	
	0.5	7.0	−0.1	95.9 ±5.4
2,4-Dichlorophenol	0.1	4.6	−2.9	
	0.5	5.3	0.1	84.0 ±3.9
4-*n*-Butylphenol	0.1	7.8	7.7	
	0.5	1.4	−0.2	90.7 ±5.9
3-Nitrophenol	0.2	9.2	1.6	
	1.0	6.1	−0.03	75.0 ±6.5
4-*n*-Pentylphenol	0.1	7.5	−5.9	
	0.5	2.0	−0.2	90.5 ±5.7
4-*n*-Hexylphenol	0.1	7.0	−2.0	
	0.5	4.7	0.03	95.0 ±7.1
2,4-Dinitrophenol	0.2	4.1	−0.4	
	1.0	6.4	0.04	80.3 ±3.7
Pentachlorophenol	0.1	6.5	6.0	
	0.5	3.9	0.1	86.5 ±3.0
Bisphenol A	0.1	4.2	−4.2	
	0.5	2.5	−0.1	98.5 ±8.2

[a] Recovery rate, calculated at 0.5 μg for nine phenols and for two nitrophenols at 1.0 μg with *n*-docosane as IS_1 (1.0 μg), according to (extracted peak area ratio/non-extracted peak area ratio) × 100. Sample preparation and GC-SIM-MS conditions are as in Table 3

Screening for Phenolic Pollutants in River Water

When applied to a river water sample to screen for the eleven phenolic pollutants, six phenols were positively detected along with bisphenol A (Fig. 2-B). Standard addition for the quantitative analysis was very appropriate since the composition of

Table 5. Phenolic pollutants screened in a river water sample

Compound	Concentration ($\mu g\ L^{-1}$)
2-Chlorophenol	NQ [a]
4-Bromophenol	0.008 ± < 0.001
4-*tert*.-Butylphenol	0.014 ± < 0.001
2,4-Dichlorophenol	NQ
4-*n*-Butylphenol	0.008 ± < 0.001
3-Nitrophenol	NQ
4-*n*-Pentylphenol	0.007 ± < 0.001
4-*n*-Hexylphenol	0.007 ± < 0.001
2,4-Dinitrophenol	0.058 ± 0.018
Pentachlorophenol	NQ
Bisphenol A	0.028 ± < 0.001

[a] Not quantified

the river water examined was unknown. The amounts of seven phenolic pollutants measured were ranged from 0.007 to 0.058 $\mu g\ L^{-1}$ (Table 5).

Conclusion

The present modified extractor was found more cost-efficient from smaller solvent volume and shorter time (10.0 mL for 1 h) for the extraction of eleven phenols retained on XAD-4 resin particles compared with the conventional Soxhlet extractor (80.0 mL for 3 h). The overall method for phenol measurement by GC-SIM-MS as TBDMS derivatives in the range of 0.05 to 1.0 $\mu g\ L^{-1}$ were linear ($r^2 \geq 0.9991$) with satisfactory precision, accuracy, and recovery rates. Further optimization of the present extractor is under way for extension to other phenolic- and neutral aromatic-micropollutants as well.

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