A Study on the Analytical Methods Using Solid-phase Extraction for the Determination of Phenols in Water

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Based on solid phase extraction, gas chromatography and mass spectrometry procedure for determining phenol and its derivatives in natural water was presented. In solid phase extraction, three types of techniques using solid phase adsorption material were adopted, i.e. cartridge and disk extraction and solid-phase micro extraction. U.S. EPA 11 priority pollutant were treated with acid and salt, and converted second portion of acetyl derivatives. Under the these condition, extraction efficiency and detection ability dependent on extraction methods were discussed. Obtained results using optimized solid phase extraction techniques showed more convenience, simplifier and lower cost than the conventional analytical methods with holding wide dynamic range and lower detection limits.

Key words : Phenols, Solid-phase extraction(SPE), Solid-phase micro extraction(SPME),

1. Introduction

The release of phenol and its derivatives into the environmental is a great concern because of their toxicity, widespread use in industry, and roll in drinking water pollution.[1] Therefore, it is necessary to have a rapid, sensitive analytical method for the determining these compounds. Current analytical methods, such as EPA 604 and 625 are based on liquid-liquid extraction. But these methods are difficult to several phenols in water because of their high solubility. In addition to, there is analyte loss at stepwise concentration and clean up procedure, so became the potential source of low precision and bad reappearance[2].

The phenol itself is not affect harmful impact to the human and animal but chlorinated phenol derivatives generated by reaction with chlorine in the water has much toxic characteristic and represent severe taste and offensive odor. The reason of specify the phenol as regulating mater is not its toxicity but odor of its byproduct with chlorine.

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Recently, solid-phase extraction (SPE) techniques attract widespread attention as solvent-free sample preparation techniques because of regulatory pressure to reduce the use of toxic organic solvents. SPE is one of the most commonly used sorbent extraction techniques. Analytes are extracted by passing an aqueous matrix through a plastic cartridge containing sorbent or sorbent particle loaded membrane disk on a particulate support. A selective organic solvent is normally used to remove interference first. And then another solvent is chosen to wash out target analytes. SPE has a number of attractive features compared with traditional solvent extraction.

It is quite simple, is inexpensive, and uses little solvent. to conventional applied to the analytical preparation techniques. Particle loaded dlsks are developed for further improve extraction efficiency, reduce the use of solvent, and decrease plugging in SPE[3]. SPE has some limitation such as low recovery, which results from interaction between the sample matrix and analytes, and plugging of the cartridge or blocking of the pore, which results in low breakthrough volume and capacity[4]. One solution to these limitation s is to improve the geometry of the sorbent by coating it on a rod such as fused-solica fiber or wires made of appropriate materials. The sylindrical geometry of the resulting solid-phase micro extraction

(SPME) system[5] allowed rapid mass transfer during extraction and desorpton, prevent plugging, and facilitates handling and introduction into analytical instrument. The SPME results applied to the sampling phenols in water were obtained mainly using polyacrylate coating ; the detection limit, linear range, and precision are better than or equivalent to EPA method specifications.[3]

The aim of this work was to develop selective, sensitive, and solvent free methods for the analysis of phenols in water. The previous study carried on the analysis less polar, less water soluble, and relatively volatile compounds. The application solid-phase techniques to the phenols are not frequent. In this work applying solid-phase techniques to the phenols, the extraction efficiencies related to the sorbent material and the shape of solid-phase(cartridge, disk SPE, and. SPME) dependent on the effect of acid and salt treatment were investigated. It is expected that, for phenols, it will be necessary to use more polar phase or derivatization procedure to deduce their polarity and improve the chromatographic properties. Derivatization has the advantages of converting polar analytes into their less polar analogues, thus increase extraction efficiencies. Therefore, the derivatization/SPE, SPME techniques has also been applied.

2. Experimental section

2.1 Materials

Methanol, Dichloromethane(99.8%, HPLC grade), Phenols standards(SupelCo.; phenol, 2-chlorophenol, 2-nitrophenol, 2,4-dimethylphenol, 2,4-dichlorophenol, 4-chloro-3-methylphenol, 2,4,6-trichloro phenol, 2,4-dinitrophenol, 4-nitro phenol, 2-methyl-4,6-dinitrophenol, pentachloro phenol, 2000 ppm each), NaCl, $NaHCO_3$ (99.9%, Hayashi) , SPE cartridge, disk(SupelCo. C-18 and polystylene divinylbenzene) SPME fiber(SupelCo. polyacrylate coated), acetyl chloride(Alltech. 18053A)

2.2 Instrument and apparatus

Gas Chromatograph(HP 5890 II), MSD(HP 5971), GC column(DB-5, J&W, 5% phenyl methyl silicon crosslinking moiety, 0.25mm id. x 30m), SPE cartridge holder(SupelCo. SPE large volume sampler, Cat.No. 57275), SPE disk holder(3 M, 6 station port), SPME fiber holder plunger(SupelCo. 5-7330), SPME fiber(100 ㎛ poly-dimethyl siloxane coated, 85 ㎛, poly acrylate coated, SupelCo. 5-7300 and 5-7304).

2.3 Analysis

SPE sorbent was pre-washed with methanol and not allowed to dry out. Blank water drained through the SPE sorbent to remove excess wetting solvent. A slight vacuum of 13 cm of mercury was used during all operation. Flushed each cartridge and disk with 10 mL aliquots of dichloromethane, follwed by two 10 mL aliquots of methanol, letting the sorbent drain dry after each flush. The Water sample pretreated acid and/or salt was poured to the reservoil and then passed through the SPE sorbent.

Maintained the sorbent material immersed in water at all times. After all, the sample passed through the SPE sorbent, and dried with drawing air. Eluted two 5 mL of dichloromethane and then passed through the drying column packed with anhydrous sodium sulfate and into the collection vial. In SPME, 1- cm length of polyacylate sorbent coated silica fiber assembled to manual fiber holder plunger. When a vial is sampled, the plunger is pulled back, drawing the fiber into the needle. Once the needle has pierced the septum, the plunger is pushed down to expose the fiber to the sample. Magnetic stirring was used for the SPME extraction to ensure proper mixing of the sample.

All the analysis has done with 40-mL EPA vials contained 0.5-in. stir bar. Once an equilibrium is reached between the analyte concentration in the solution and fiber sorbent, the plunger is drawn back up and the needle is removed from the septum. The needle is then used to pierce the septum of the GC injector., where the analytes are desorbed off from the sorbent coating and enter the GC column for separation and analysis. Initial work was done with poly-dimethyl siloxane coated fiber and the poly-acrylate coated fiber were conditioned under helium at 350 °C.

3. Results and Discussion

Table 1. shows extraction trends of phenols in different adsorption sorbent material(C-18, and poly-stylene divylbenzene) and shape(cartridge and disk). Obtained results using poly-stylene

divinylbenzene disk represent moderate extraction efficiencies and advisable reappearance to the all phenols.

Table 1. Percent recovery and relative standard Deviation of phenols by different SPE and GC/MS.

Compounds	% Mean recovery [a] (% RSD [b])			
	CC[c]	CD[d]	DC[e]	DD[f]
Phenol	45(14.5)	28(16.5)	25(27.6)	68(8.7)
2-Chlorophenol	88(11.3)	65(13.7)	33(23.9)	95(7.9)
2-Nitrophenol	73(12.8)	68(16.9)	22(32.1)	98(12.1)
2,4-Dimethylphenol	97(6.5)	73(8.7)	85(11.8)	95(6.3)
2,4-Dichlorophenol	94(7.7)	78(9.4)	75(15.5)	94(11.2)
4-Chloro-3-methyl phenol	99(6.7)	83(6.5)	67(13.4)	90(5.4)
2,4,6-Trichlorophenol	96(5.8)	81(6.8)	60(8.8)	93(4.7)
2,4-Dinitrophenol	45(17.5)	99(12.3)	55(21.7)	66(18.7)
4-Nitrophenol	52(22.3)	88(11.5)	15(37.5)	87(14.8)
2-Methyl-4,6-dinitro phenol	61(19.2)	75(13.4)	12(33.6)	88(7.7)
Pentachlorophenol	98(5.4)	97(5.2)	89(7.3)	99(5.0)

[a] : Average of triplicates, [b] : percent relative standard deviation of 7 replicayes, [c] : cartride C-18, [d] : cartridge poly0stylenedivinylbenzene, [e] : disk C-18, [f] : disk poly-stylenedivinyl benzene.

Table 2. Method detection limits of the phenols in different SPE and GC/MS. unit : ug/L

Compounds	IDL[a]	MDL[b]			
		CC[c]	CD[d]	DC[e]	DD[f]
Phenol	0.7	2.5	1.7	3.5	1.8
2-Chlorophenol	0.8	1.2	1.6	3.2	0.8
2-Nitrophenol	1.0	4.3	5.2	14.8	3.6
2,4-Dimethylphenol	1.0	0.6	0.9	0.8	0.7
2,4-Dichlorophenol	1.0	0.8	1.0	1.0	0.8
4-Chloro-3-methyl phenol	1.5	0.5	0.7	0.8	0.5
2,4,6-Trichlorophenol	1.5	0.4	0.5	0.9	0.4
2,4-Dinitrophenol	1.5	12.7	5.5	10.2	8.3
4-Nitrophenol	1.7	2.4	1.6	10.7	1.8
2-Methyl-4,6-dinitro phenol	1.8	1.5	1.2	8.6	0.5
Pentachlorophenol	2.0	0.4	0.4	0.5	0.4

[a] : Instrumental detection limit, concentration equivalent to signal to noise ratio 2.5, [b] : Method detection limit, KS_b/m(K=3, S_b : standard deviation of average noise level, m : slope of calibration line), [c] : cartridge C-18, [d] : cartridge polytylenedivinylbenzene, [e] : disk C-18, [f] : disk poly-stylenedivinylbenzene.

Table 3. Extracted amount of phenols dependent on acid and salt effect using SPME-GC/MSD.

Compounds	pKa	I_i to I_0 [a]	
		pH=2 [b]	pH=2, NaCl
Phenol	9.89	2.2	4.5
2-Chlorophenol	8.48	1.7	3.7
2-Nitrophenol	7.23	1.8	3.5
2,4-Dimethylphenol	10.63	1.6	5.8
2,4-Dichlorophenol	7.85	1.2	2.3
4-Chloro-3-methyl phenol	9.55	1.2	1.8
2,4,6-Trichlorophenol	7.42	1.4	2.0
2,4-Dinitrophenol	4.09	4.5	10.3
4-Nitrophenol	7.15	2.8	5.5
2-Methyl-4,6-dinitro phenol	4.35	10.2	18.7
Pentachlorophenol	4.74	1.5	2.0

[a] : Obtained GC count ratio of phenols(I_i : intensities from the acidified and/or salt treated water, I_0 : intensities from the untreated tab water. [b] : Acidified with 6N HCl, made pH 2 solution, [c] : acidified to pH 2 and salt saturated solution.
All the results are obtained using poly-acrylate fiber SPME and GC/MSD

Table 4. Method detection limits of the phenols in different SPE and GC/MS. unit : ug/L

Compounds	EPA		SPME	
	604[a]	625[b]	FID	MSD
Phenol	0.14	1.5	1.2	1.0
2-Chlorophenol	0. 31	3.3	0.6	0.8
2-Nitrophenol	0.45	3.6	1.4	1.7
2,4-Dimethylphenol	0.32	2.7	0.2	0.3
2,4-Dichlorophenol	0.39	2.7	0.2	0.3
4-Chloro-3-methyl phenol	0.36	3.0	0.25	0.4
2,4,6-Trichlorophenol	0.64	2.7	0.15	0.2
2,4-Dinitrophenol	13.0	42.0	3.0	7.5
4-Nitrophenol	2.8	2.4	1.8	2.0
2-Methyl-4,6-dinitro phenol	16.0	24.0	1.2	4.0
Pentachlorophenol	7.4	3.6	0.3	0.6

[a] : EPA 604 method, liquid-liquid extraction GC/FID, [b]: EPA 625 method, general method for the determination semivolatiles in waster water by GC/MS.

The contrary, the results using c-18 disk show wrong extraction efficiencies and reappearance in spite of the one improved some problem in cartridge. Especially those having nitro group

show very poor results in all the methods. In cartridge C-18, except for the phenol, the results of the remainder similar to that of cartridge poly-stylene divinylbenzene. Generally, the one obtained from poly stylene divinylbenzne shows more excellent to the one from the C-18. These results are directly compared spiked amount of phenols in tab water to same amount injected to GC.

Another method using solid-phase as means of extracting tool, SPME represents more convenience and superior detecting ability. But use like pretreatment tool in environmental tool is restricted to cleaned sample because of limitation of adsorption capability.

Table 2. represents detection limits phenols using SPE-GC/MS. those one obtained from poly-stylene divinylbenzene disk has the lower detection than the other. Those compounds having the nitro group shows lower detecting abilities. Table 3. shows improvement of extraction efficiencies by acidifying and salt saturation. These results are obtained from comparing that of untreated sample.

Table 5. Linear range and relative standard deviation for the determine phenols by using poly-acylate SPME and GC/FID, MSD

Compounds	RSD[a] (%)	Linear range(mg/L)	
		GC/FID	GC/MSD
Phenol	4.5	0.1-2.0	0.005-1.0
2-Chlorophenol	3.8	0.01-2.0	0.005-1.0
2-Nitrophenol	4.8	0.02-2.0	0.005-1.0
2,4-Dimethylphenol	4.0	0.01-2.0	0.005-1.0
2,4-Dichlorophenol	5.0	0.005-2.0	0.003-1.0
4-Chloro-3-methyl phenol	4.6	0.01-10.0	0.005-1.0
2,4,6-Trichlorophenol	5.0	0.05-5.0	0.002-1.0
2,4-Dinitrophenol	10.0	0.2-7.0	0.05-1.0
4-Nitrophenol	12.5	0.05-10.0	0.01-1.0
2-Methyl-4,6-dinitro phenol	6.5	0.05-10.0	0.01-1.0
Pentachlorophenol	14.5	0.01-10.0	0.01-1.0

[a] : percent RSD of 7 replicates obtained using GC/FID

The reason for improved results of acidifying is the effect of weakened interaction between phenols and water molecular. In addition to, remained polar interaction is mostly removed by salt saturation. As the result, the ability of adsorption between fiber and phenols are increased. Especially, such trends are dominant in the compounds containing nitro group. EPA methods for analyzing phenols are No. 604 and 625. EPA 604 is conventional liquid-liquid extraction method using GC/FID and EPA 625 is general method for the determining semivolatiles. The detection limits for the phenols obtained from SPME compared to the one from the methods as shown below.

SPME results show similar or lower detection level compared to that of 604, 625. The results of nitro phenols are predominant. Table 5. represents linear dynamic range of phenols in SPME GC/FID, MSD. MSD results are obtained from using SIM acquired method. All the results show that proper range for quantitation is several ppb to ppm.

4. Conclusions

The application of solid-phase techniques to phenols in water is not so much. The conventional analytical methods for determine phenols are very time consuming and require expensive, toxic organic solvent . In these works, the application techniques to the solid-phase as extracting tool for determine phenols has been implemented. Obtained results showed that applied methods are more simple and accurate in spite of not or small amount using of organic solvent. Generally, obtained results from SPME method represented more better than the ones from the others. But SPME has the narrow quantitation range and restriction of sample having complex matrix. So proper use of SPE and SPME suitable to sample type is desirable.

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