

Selective Concentration and Determination of Phenol and Chlorophenols by Solid Phase Extraction

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Abstract : This study employs the variety of mixtures of XAD resin and active carbons as concentration base for solid phase extraction (SPE) which has been widely used to preconcentrate and purify phenol and chlorophenols in determination of environmental water samples. In this study, we employed variety of mixtures of copolymer based XAD-4 resin with active carbons. This cartridges shows advantages of both materials, such as better affinity to phenol by active carbon and better mechanical stabilities from XAD resin. The better enrichment factor, pretreatment time, recoveries and limit of detection (LOD) were achieved by the attempts to pack precolumns with both materials for preconcentration.

Introduction.

Phenol occurs in the aquatic environment due to their wide spread usage. Some phenols are products of natural origin such as thyme oil and methyl salicylate, an insect attractant, in oil of wintergreen. Others are generated as by products in manufacturing processes such as coke production in the steel industry, paper and pulp processing, and so on.

Phenols are also manufactured for use as fungicides, antimicrobials, wood preservatives, and as reactants or intermediates for many synthetic products such as pharmaceuticals, dyes, and pesticides.^[1]

Phenols has a broad spectrum of toxicity due to their varied uses and the nature of the substituents in environmentally important phenols. Some of phenolic compounds are known to impact objectionable odor and taste to water at the ppb level. Others such as

2,4-dichlorophenol, 2,4,6-trichlorophenol, and pentachlorophenol are classified as suspected carcinogenic compounds in drinking water.^[2]

The monitoring of industrial effluents and natural waters for trace concentration of phenols is also carried out because these compounds can adversely affect the potability of water at low concentration. Chlorinated phenols are also determined in air, water, sediment and biota to assess their environmental impact on the aquatic ecosystem.

Solid phase extraction (SPE) is now widely used for the preconcentration and clean up of analytical samples, for the purification of various chemicals and for applications such as the removal of toxic or valuable substances from a variety of predominantly aqueous solutions. The most used and convenient sorbents are reverse phase, because the analytes should be retained by the sorbent and

not eluted by water, such as widely used octadecyl-bonded silicas (C₁₈), some divinylbenzene-styrene copolymers and carbon based sorbents. Especially, carbon based materials and copolymer-based sorbents were found to have an enhanced affinity for medium-polarity compounds such as mono and dichlorophenols.^{[3]-[6]}

However, copolymer based sorbents were shown poor affinity to phenol, because its polarity.^[7] That property prevent to enhance enrichment factor, when we analyze phenol and chlorophenols simultaneously.

Graphitized carbon black has proved to be as an excellent gas chromatographic adsorbent in a wide variety of applications^[8], but practical application in high performance liquid chromatography (HPLC) is prevented by its poor mechanical properties.^[9]

In this study, we employed variety of mixtures of copolymer based XAD resin and active carbons. This cartridges shows advantages of both materials, such as better affinity to phenol by active carbon and better mechanical stabilities from XAD resins.

The better enrichment factor, pretreatment time, recoveries and limit of detection (LOD) were achieved by the attempts to pack precolumns with both materials for preconcentration.

Experimental.

Reagents : Phenol and chlorophenols (2-; 4-; 2,4-; 2,4,6-; 2,3,4,5,6-) were obtained from Fluka Chemical Co. HPLC-grade acetonitrile (ACN) was commercially obtained from Boxtor Healthcare Co., and methanol (MeOH) was obtained from Mallinckrodt Chemical, Inc.

Analytical reagent grade solvents were used without purification. Water was deionized by

Zenopure (Zenon) water purification system.

Amberlite XAD-4 resin was purchased from Janssen Chimica Co. It was obtained as 20 - 60 mesh and this was used for the distribution coefficient studies. Columns (2 mm i.d × 50 mm) were manufactured with microparticles (100 - 150 mesh) prepared by crushing in a mortar and sieving, by dry packing method.

Active carbons were purchased from Norit Ind. XAD-4 and active carbon were cleaned by extraction in a Soxhlet extractor with acetone and MeOH for 24 hours each.

Instrumentation : HPLC system with HPLC pump from Rainin (dynamax SD-200) equipped with a Rheodyne 7125 injector having a 20 μL loop and with a model S-3710 variable UV-VIS detector (Soma, Tokyo, Japan) was used. Rainin Microsorb-MV C₁₈ column (4.6 × 250 mm, 5 μm) was used.

Mobile phase was mixed solvent of MeOH and water (3:1). Its pH was adjusted to 3 with H₃PO₄. Flow rate was fixed at 1 mL/min and analytical procedure was performed at room temperature.

Procedures

Distribution coefficient : The procedure for determining batch distribution coefficient, K_D, was described elsewhere^[10] and calculated according to :

$$K_D = \frac{(\text{Volume solution})(\text{weight of solute on solid phase})}{(\text{Weight of solid phase})(\text{weight of solute in solution})}$$

Initial concentration level for each phenol spiked was 10 ppm. All solvent mixtures are percent by volume. Solid phase (total 0.09g) was mixture of XAD-4 and active carbon (3%, wt/wt).

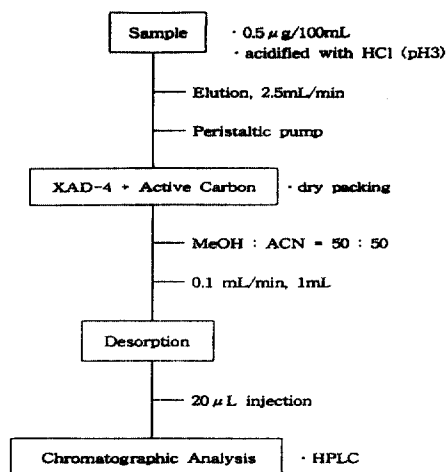


Fig. 1 Analytical Procedure

Column purification : All analytical procedure was summarized in Fig. 1.

XAD-4 and active carbon was premixed and dry packed. Concentration columns were eluted by peristaltic pump from Gilson (Minipuls 3). Sorbent was activated by eluting with 10 mL of MeOH, which was subsequently rinsed with 20 mL of water.

The standard solution (5 ppb, acidified with 0.1M HCl to pH 3), 100 mL was eluted at a flow rate of 2.5 mL/min. Adsorbed samples were reeluted by 1 mL mixed solvent (MeOH : ACN = 1 : 1) at a flow rate of 0.1 mL/min. 20 µL of reeluted solution was injected to HPLC.

Breakthrough point determination : The breakthrough characteristics of phenol were measured for a solution in deionized water (pH 3). Concentration column was directly connected to the fluorescence detector.

Excitation and emission wavelength were 270 nm and 330 nm each. To measure a breakthrough curve, a 10 ppm solution of the analyte was pumped through the column at a flow rate of 2.5 mL/min and fluorescence

absorbance was recorded at an interval of two minutes.

Evaluation of analytical data : Calibration curves for phenol and chlorophenols were obtained by processing analytical procedure of standard solutions with known concentration of samples (2 - 10 ppm, each phenols).

The analytical recoveries for each compound were determined by comparing the peak area of chromatogram of standard to that of reeluted solution from column.

Result and discussion

The choice of reeluting solvent is one of the most important factor in success of experiment. If solvent is too strong, all impurities are eluted with analyte. If too weak, then recovery value should be sacrificed.

Table I is summary of distribution coefficient experiment data. From the K_D value, methanol solution with 50% ACN showed the best result. We performed similar experiments with other solvents such as tetrahydrofuran and carbon tetrachloride, but we didn't find better combination of solvents for reeluting solution.

Table I. Distribution Coefficient (K_D) of Phenol and Chlorophenols

Compound	% MeOH with ACN					
	0	10	20	30	40	50
phenol	0.43	0.22	0.23	0.22	0.055	0.008
2-chlorophenol	0.20	0.19	0.22	0.20	0.15	0.11
4-chlorophenol	0.20	0.23	0.21	0.16	0.14	0.04
2,4-dichlorophenol	0.15	0.13	0.19	0.15	0.17	0.15
2,4,6-trichlorophenol	0.16	0.13	0.20	0.16	0.24	0.17
pentachlorophenol	0.28	0.20	0.25	0.38	0.28	0.24

Solid Phase : (XAD-4 + 3%(wt/wt) Active Carbon) 0.09g

Carbon based sorbents and copolymer based sorbents were found to have an enhanced affinity for medium-polarity compounds such as mono and dichlorophenols.³⁻⁶ However, copolymer based sorbents were shown poor affinity to phenol because their polarity.⁷

Therefore breakthrough points were measured to investigate the pertinence of solid phase for retaining phenol.

Table II listed the data obtained with cencetration column made with solid phase mixture of XAD-4 and CN-1 type active carbon. As amounts of active carbon were increased, breakthrough points were also increased, which means that the more phenols are retained in solid phase and would not be easily washed by aqueous sample solution. And the enrichment factors can be enhanced.

However, when amounts of active carbon were increased, the more pressure of pump was needed to eluting solvent, because powder of active carbon was aggregated in the column.

The recoveries, limit of detections (LOD) for each phenols were obtained and listed in Table III. The data obtained with 3 % active carbon mixed solid phase were compared with the data with XAD-4.

Recoveries of mixed solid phase are very good with more than 90 % for all phenols, and considerably improved for pentachlorophenol.

Table II. The Breakthrough Volumn of Phenol in Mixed Solid Phase

	XAD-4	3%	6%	10%
Breakthrough Volume	18.1ml	22.8ml	20.4ml	31.6ml
Capacity Volume	36.9ml	44.7ml	49.6ml	58.4ml

* Concentration of phenol spiked in distilled water : 10 ppm, Detector : Fluorescence detector, Excitation wavelength : 270nm, Emission wavelength : 330nm, Flow rate : 2.5 mL/min

Table III. Analytical Data of Phenols with Mixed Solid Phase

Compound	% recovery ^a		limit of detection ^b	
	XAD-4	3%	XAD-4	3%
phenol	91.4	93.4	5.3	322
2-chlorophenol	95.1	96.7	417	455
4-chlorophenol	93.4	101	925	1100
2,4-dichlorophenol	92.5	95.0	953	799
2,4,6-trichlorophenol	87.2	90.1	430	413
pentachlorophenol	84.3	92.9	40	918

^a Concentration of compound spiked in distilled water : 0.5 µg/100 mL, ^b Unit : part per trillion (ng/L)

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