

Sample preparation and preconcentration for determination of chlorophenols in water and sediment samples

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ABSTRACT

Chlorophenol compounds are used in many industries including the fabric, dye and pesticide industries. Most of the compounds are toxic to health and often contaminate wastewater and sediment. A sample preparation was investigated to optimize the extraction of phenol, 2-chlorophenol, 2,6-dichlorophenol, 2,3,6-trichlorophenol and 2,3,4,6,-tetrachlorophenol in water and sediment samples. The samples were analyzed by high performance liquid chromatograph. ENVI-18 solid-phase was suitable for extraction of chlorophenols in water samples using 5 mL of methanol:acetonitrile as an eluting solvent. Recoveries were in the range of 81.98-103.75 percent. Optimized solid-phase extraction was applied for extraction of chlorophenols in natural water and bottled drinking water. Analysis was by high performance liquid chromatography. The results showed that no chlorophenol contamination was found in all water samples.

Chlorophenols in sediment samples were achieved with solvent extraction using acetonitrile:acetone (1:1) as an extracting solvent with a 30 min extraction time. Recoveries ranged from 93.85-109.39 percent with a relative standard deviation (RSD) 0.90-3.75%. The optimum conditions were applied for extraction of chlorophenols in 6 sediment samples and determined by high performance liquid chromatography. The results showed that no contamination was found in all samples.

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KEYWORDS

Solid-phase extraction;
Liquid-liquid extraction;
High performance liquid chromatography.

INTRODUCTION

Chlorophenol compounds are used in many industries. Most of them are toxic to health and can be found in wastewater and sediment^[2,6,10]. They can also be generated from phenols during water chlorination treatment. Most of them are hydrophilic and are easily distributed in aquatic media. Since chlorophenols are toxic, the US environmental protection agency (US-EPA) and the European union set as maximum concentration of

0.5 µg/L in drinking water, while individual concentration should not exceed 0.1 µg/L^[12].

The determination of phenols is usually accomplished by the chromatographic technique, and a previous extraction step is involved. Determinations have been carried out using the standard liquid-liquid extraction methods^[14], solid-phase extraction^[5,6,13], solid-phase microextraction^[4,9], liquid-liquid microextraction^[3], liquid-liquid-liquid microextraction^[1] and liquid-membrane extraction^[8,11].

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The aim of this research was to extract and determine chlorophenols in water and sediment samples.

Material and method

Instrumentation

A high performance liquid chromatograph (Waters) with μ Bondapak C-18 column (30 x 0.39 mm), sample loop 20 μ L and photodiode array detector at 210 nm. was used. Acetonitrile: 0.1% acetic acid (1:1) with flow rate of 1 mL/min was used as mobile phase.

Chemicals

Standard chlorophenols: phenol, 2-chlorophenol, 2,6-dichlorophenol, 2,3,6-chlorophenol and 2,3,4,6-tetrachlorophenol were standard grade and obtained from Supelco (USA). The individual standard stock solutions were prepared in deionized water and stored at 4 °C. All organic solvents were HPLC grade obtained from Labscan (USA).

Sample preparation

Solid-phase extraction of chlorophenols in water samples

A 3.0 mL LC-18 (500 mg), ENVI-18 (500 mg) and 6.0 mL Florisil (1g) column were obtained from Supelco (USA). Prior to extraction, the SPE columns were conditioned with 5.0 mL methanol under vacuum followed by 5.0 mL of deionized water. Deionized water (50 mL) was spiked with the standard solution of chlorophenols (10.0 mgL⁻¹ of each) and subsequently

passed through the column at a flow rate of 1.0 mLmin⁻¹. The chlorophenols were eluted with various kinds of organic solvents and analyzed by high performance liquid chromatography. The percentage of recovery was calculated.

Liquid-liquid extraction of chlorophenols in sediment samples

The 5.00 g of sediment sample was spiked with the standard solution of phthalate ester (5.0 mgL⁻¹ of each). Ten mL of extracting solvent were added and then shaken for 10, 30 or 60 min. The solvent layer was filtered through a membrane filter (0.45 μ m) and then injected into high performance liquid chromatography. The percentage recovery was calculated.

Application to real water samples and sediment samples

Chlorophenols in tap water, natural water, waste water from a chlorination water treatment plant in Mahasarakham University, and bottled drinking water samples were analyzed using the solid-phase extraction under optimum conditions. The sediment samples, collected in the area of Mahasarakham University, were analyzed using the optimum conditions of liquid-liquid extraction.

RESULTS AND DISCUSSION

Figure 1 showed the chromatogram of phenol, 2-

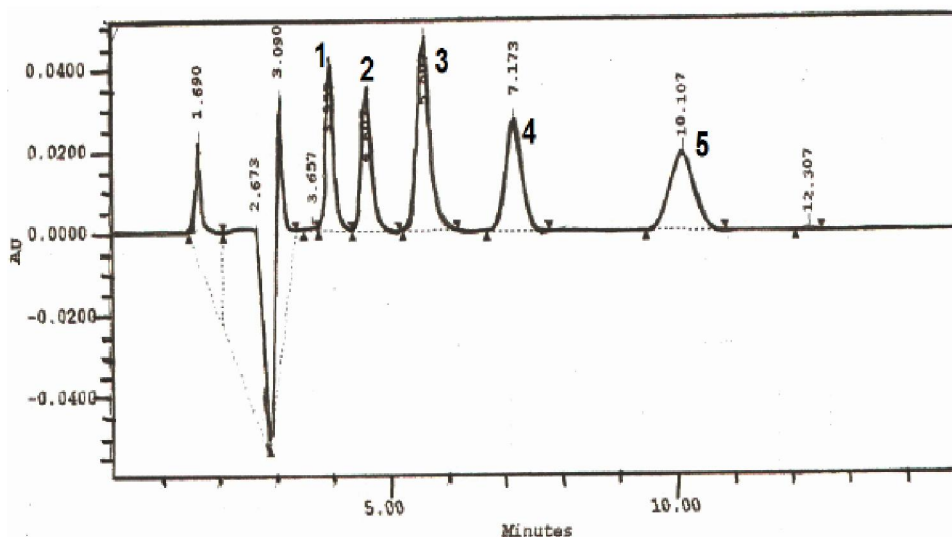


Figure 1 : Chromatogram of (1) Phenol, (2) 2-Chlorophenol, (3) 2,6-Dichlorophenol, (4) 2,3,6-Trichlorophenol and (5) 2,3,4,6-Tetrachlorophenol with the retention of 3.957, 4.607, 5.607, 7.173 and 10.107 by high performance liquid chromatography with μ Bondapak C-18, using Acetonitrile: 0.1% acetic acid (1:1) as mobile phase with the flow rate of 1 mL/min

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chlorophenol, 2,6-dichlorophenol, 2,3,6-trichlorophenol and 2,3,4,6-tetrachlorophenol times of 3.957, 4.607, 5.607, 7.173 and 10.107 min, respectively, using high performance liquid chromatograph. The linearity ranges

were 0-20, 0-20, 0-10, 0-20 and 0-20 mg/L, respectively, with a correlation coefficient in the range of 0.9974-0.9996, the detection limit of 0.10, 0.50, 0.25, 0.10 and 1.00 mg/L, respectively, as summarized in TABLE 1.

TABLE 1 : Linearity and limit of determination of chlorophenols

Analytes	Linearity range (mgL ⁻¹)	equation	R ²	Limit of detection (mgL ⁻¹)
Phenol	0 – 20	y = 80944x + 12761	0.9991	0.10
2-CP	0 – 20	y = 77949x – 2845.9	0.9980	0.50
2,6-DCP	0 - 10	y = 157649x – 11970	0.9986	0.25
2,3,6-TCP	0 – 20	y = 91947x + 35162	0.9974	0.10
2,3,4,6-TeCP	0 - 20	y = 112059x + 2702.3	0.9996	1.00

Optimization of solid-phase extraction of chlorophenols in water samples

The percentage recoveries were achieved by spiked sample (10.0 mgL⁻¹ of each) using a Florisil, LC-18 and ENVI-18 cartridge with various eluting solvents. ENVI-18 was found suitable for extraction

of chlorophenols. ENVI-18 is in form of reversed phase and the interaction is partition, the elution step is usually carried out with a polar solvent. The mixture of methanol: acetonitrile (1:1) showed good recoveries in the range of 81.98-103.75%, as shown in TABLE 2.

TABLE 2 : The percentage recoveries of chlorophenols in water samples by solid-phase extraction

Solid-phase	Eluting solvent (5 mL)	% Recovery				
		Phenol	2-CP	2,6-DCP	2,3,6-TCP	2,3,4,6,-TeCP
Florisil	Methanol:Acetonitrile (2:3)	74.34	46.87	22.12	15.12	2.51
	Acetone:Acetonitrile (2:3)	53.37	51.16	73.45	0	0
	Methanol:Acetonitrile (3:2)	11.02	62.50	34.96	72.17	92.49
LC-18	Methanol 5 mL	59.91	100.13	91.12	84.95	99.65
	Acetonitrile 5 mL	54.53	0	95.15	94.96	71.29
	Methanol:acetonitrile (1:1)	103.86	0	92.82	93.63	84.77
ENVI-18	Methanol:acetonitrile (1:1)	81.98	95.88	103.75	96.19	96.30

The precision of the method was tested by adding the standard solution in water samples at 1.0, 5.0 and 10 mgL⁻¹. The recoveries, repeatability, and

reproducibility were in the range of 81.-98-110.21%, 0.04-0.08 and 0.06-0.15% RSD, respectively, as shown in TABLE 3.

TABLE 3 : Analytical performance of solid-phase extraction (ENVI -18) using 5 mL Methanol:acetonitrile (1:1) as eluting solvent

Analytes	%Recovery			LOD (mgL ⁻¹)	Repeatability (RSD)	Reproducibility (RSD, n =5)
	1.0 mgL ⁻¹	5.0 mgL ⁻¹	10 mgL ⁻¹			
Phenol	82.48	94.79	81.98	0.02	0.04	0.10
2-CP	83.88	84.49	95388	0.30	0.04	0.09
2,6-DCP	105.28	96.80	103.75	0.05	0.04	0.06
2,3,6-TCP	109.51	88.35	96.19	0.10	0.07	0.15
2,3,4,6-TeCP	110.21	99.22	96.30	0.05	0.08	0.08

Optimization of liquid-liquid extraction of chlorophenols in sediment samples

The percentage recoveries were achieved by

spiked sample (5.0 mgL⁻¹ of each) and extracted with various extracting solvents. The 10 mL of Acetonitrile:acetone (1:1) showed high percentage recoveries in the range of 93.85-109.39 and 0.90-3.75

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%RSD, with 30 min extraction time, as shown in TABLE 4-5. The precision, by adding the standard solution in sediment sample at 5.0 and 10.0 mgL⁻¹, is shown in TABLE 6 with the repeatability ranging between 0.90-3.86 % RSD.

Application in drinking water and sediment samples

To achieve the optimum SPE procedure, this technique was used to determine the amount of chlorophenols in tap water and natural water collected

TABLE 4 : The percentage recoveries of chlorophenols in sediment samples by liquid-liquid extraction (10 mL)

Chlorophenols	%Recovery				
	Phenol	2-CP	2,3,6-TCP	2,6-DCP	2,3,4,6-TeCP
acetonitrile :water(1:1)	87.33	96.61	82.99	80.30	74.80
acetonitrile :methanol(1:1)	81.50	89.12	82.32	82.67	81.50
acetonitrile : acetone (1:1)	93.85	109.39	97.47	100.04	105.05
acetonitrile:0.1%acetic acid (1:1)	55.40	47.14	47.53	52.16	56.05
methanol : water (1:1)	37.34	37.59	42.64	39.34	94.63

TABLE 5 : Analytical performance liquid-liquid extraction using 10 mL acetonitrile : acetone (1:1) as extracting solvent

Chlorophenols	% Recovery		
	15 min	30 min	60 min
Phenol	60.83	93.85	83.80
2-chlorophenol	81.87	109.39	93.78
2,3,6-chlorophenol	71.23	97.47	88.11
2,6-chlorophenol	66.37	100.04	88.89
2,3,4,6-chlorophenol	88.83	105.05	361.81

in Maharashtra province and from three drinking water samples purchased from a supermarket in Maha-Sarakham Province, Thailand. The results indicated that no chlorophenols were found in all water samples.

CONCLUSION

ENVI-18 Solid-phase showed good recoveries and a low limit of detection for extraction of chlorophenols in water samples using with the mixture of methanol:acetonitrile (1:1) as the eluting solvent. Extraction of chlorophenols in sediment samples was achieved with liquid-liquid extraction using acetonitrile:acetone (1:1) as the extracting solvent with 30 min extraction time. Application of the optimum method was successful to analysis of chlorophenols in water samples and sediment samples. The results found no chlorophenol contamination in all samples.

TABLE 6 : The percentage recovery and repeatability for extraction of chlorophenols in sediment sample using 10 mL acetonitrile : acetone (1:1) as extracting solvent and 30 min extraction time

Chlorophenols	%Recovery ± RSD	
	5.0 mgL ⁻¹	10.0 mgL ⁻¹
Phenol	93.85 ± 3.41	78.90 ± 2.58
2-Chlorophenol	109.39 ± 3.75	87.27 ± 1.15
2,6-Dichlorophenol	97.47 ± 1.85	82.18 ± 3.29
2,3,6-Trichlorophenol	100.04 ± 0.90	84.44 ± 1.90
2,3,4,6-Tetrachlorophenol	105.05 ± 1.81	105.25 ± 3.86

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