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Application of XAD-4 Solid Sorbent and HPLC with Electrochemical Detection to the Analysis of Phenols in Water

Final Report

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Supported by

U.S. ARMY TOXIC AND HAZARDOUS MATERIALS AGENCY
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Project Officer: Mary Ann Ryan

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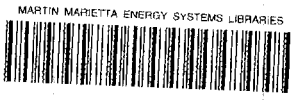

EXECUTIVE SUMMARY

The military is supporting collection and analytical methods development as a part of the DOD Installation Restoration Program. In this report, the collection and determination of phenol; o-, m-, and p-cresols; 2,4,5- and 2,4,6-trichlorophenols; 2,3,4,5- and 2,3,5,6-tetrachlorophenols; and pentachlorophenol are described.

The phenols are collected from water samples by adsorption on XAD-4 cartridges. After elution with diethyl ether and returning to an aqueous media, the phenols are determined by high performance liquid chromatography with electrochemical detection (HPLC/EC).

Initial studies demonstrated that a C_{18} reverse phase column could not resolve all of these phenols. However, a cyclobond 1β column composed of a cyclodextrin bonded to a high purity silica, was able to separate the phenols. An electrochemical detector with a glassy carbon electrode held at +1 V vs an Ag/AgCl reference electrode allowed detection limits of 1 μg/L for phenol and 5 μg/L for the chlorophenols at a signal to noise ratio of 3.

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INTRODUCTION

Phenolic compounds are of concern in environmental waters due to their widespread usage. Chlorophenols, because of their use in the manufacture of herbicides and pesticides, are of particular interest in waters in view of their toxicity to fish and other aquatic life.

In support of the DOD Installation Restoration Program, we report on the collection and measurement of phenol, o-, m-, and p-cresols; 2,4,5- and 2,3,5,6-tetrachlorophenols and pentachlorophenol in water. The phenols are collected on XAD-4 cartridges and determined by HPLC with electrochemical detection following separation on a Cyclobond 1β (5 μm) column.

EXPERIMENTAL

Liquid Chromatography-Electrochemical Detection

The HPLC system consisted of a Perkin-Elmer Series 2 liquid chromatograph. A Bioanalytical Systems (BAS) Model MF 4000 flow-through pulse damper was installed between the pump and injection valve. A Model 7120 Rheodyne valve fitted with a 20 μL samples loop was used for sample injection. Mobile phases [acetonitride: 0.002 M sodium acetate (PH 5) 0.02 M KNO_3 (25:75) and (10:90)] were added to solvent reservoirs for pump A and pump B, respectively. All solvents and sample solutions were filtered through 0.45 μm nylon-66 filters.

A BAS LC-4B amperometric detector was used in conjunction with a TL-5A glassy carbon electrode assembly. All potentials were referred to an REl Ag/AgCl reference electrode. A Hewlett-Packard Model 7045A X-Y recorder and a Hewlett-Packard Model 3390A integrator were employed for data collection. The LC column was a 25 x 0.46 cm Cyclobond 1β column (5 μm particle size) from Advanced Separation Technologies, Inc., Whippany, New Jersey.

Procedure for XAD-4 Preparation and Collection of Phenols

The XAD-4 resin to be used is precleaned by Soxhlet extraction with acetone for 48 hours. The Soxhlet extractor is operated in the normal manner. At the conclusion of the Soxhlet extraction, the acetone is drained from the resin and replaced with methanol. After the Soxhlet extraction, the resin is never allowed to dry out. The cleaned resin is stored in an Erlenmeyer flask under methanol until the collection cartridges are filled.

The cartridges (1/4" x 10" glass tubes) are cleaned by rinsing with methanol. A glass wool plug is inserted in one end of the tube and a capped union is attached. The tube is filled with methanol and all air

bubbles removed. A slurry of XAD-4 in methanol is then added, and the methanol is allowed to drain slowly from the cartridge by loosening the union cap. When sufficient resin has been added to bring the level within 1/4" of the top of the tube, a second glass wool plug is inserted and the ends are capped. The capping can be accomplished using capped unions or, more economically, by submerging the tube in methanol.

An agreement was made with SKC, Inc. (Eighty-Four, PA) on the production of disposable XAD-4 cartridges of the appropriate geometry for this purpose. The cartridges contain 1.2 g resin and are nominally 0.8 mm o.d. This is a reasonable compromise between capacity and speed of extraction. The columns are purchased in lots of 100 for $2.00 each.

For collection of the sample, the tubes are uncapped and 25 mL of organic-free water are pumped through the column in order to remove the methanol. The sample is adjusted to pH 2 with nitric acid and placed in a volumetric flask of 500 mL volume (smaller volumes can be used if the levels of phenols are expected to be high). Teflon tubing (1/8") is used to siphon the water sample through the resin cartridge by gravity flow. The flow rate should be adjusted to 3-6 mL/min. The entire sample is allowed to drain through the cartridge. Again, the cartridge is not allowed to go dry. Five mL of organic-free water is added to the tube after the sample has been collected; the tube is capped and refrigerated at 4°C prior to analysis.

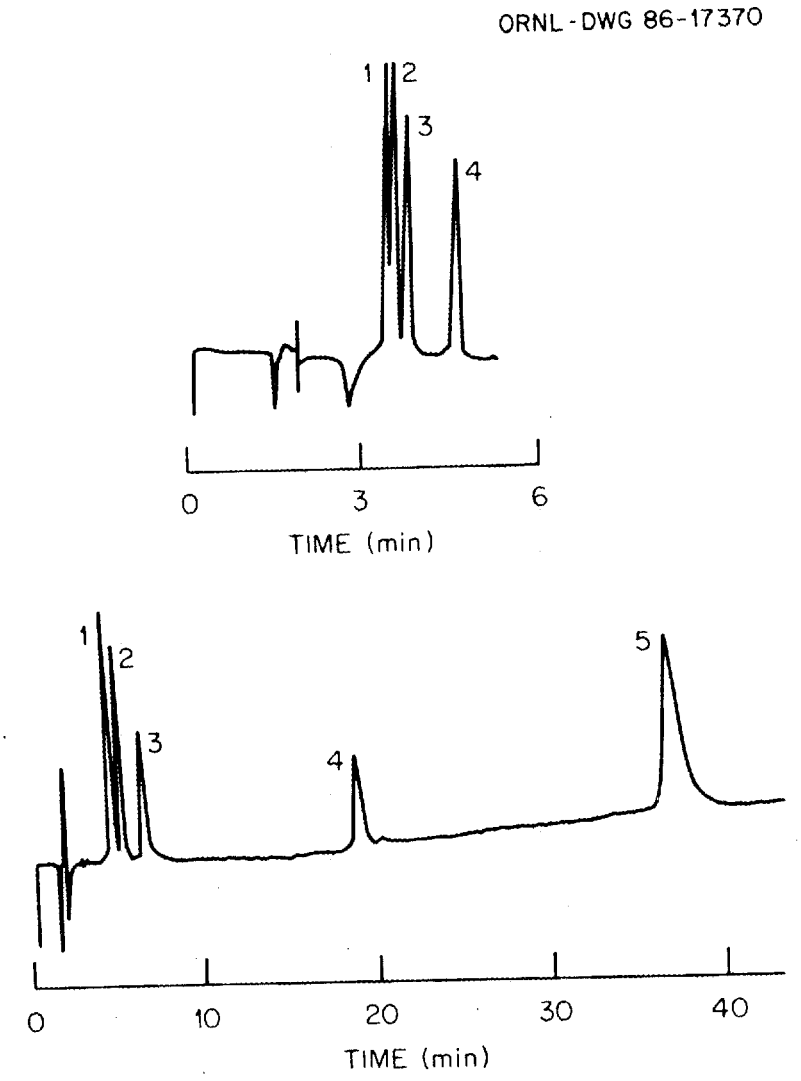
For phenols and cresols, the tubes are desorbed by first passing dry nitrogen (10 lbs. pressure) through the tubes for ten minutes to remove the excess water. The tubes are inverted and the phenols are desorbed by passing 5 mL diethyl ether through the column (gravity flow) in the opposite direction as the aqueous sample flow. The ether eluate is collected in 15 mL beaker which contains 1 mL water. The ether is allowed to evaporate and the resulting water layer adjusted to 1 mL. This is the final volume for the HPLC measurement.

For the chlorophenols, collect the ether eluate in a 15 mL beaker that contains 1 mL of 0.02 N NaOH. Mix the phases thoroughly. The ether is then allowed to evaporate and the resulting solution is neutralized with 0.1 N HNO_3 (~100 μL) and adjusted to 2 mL. This is the final volume for the HPLC measurement.

Analyze the sample as soon as possible. An early eluting peak is observed which is due to peroxides from the ether. This peak increases with time and may interfere with the analysis.

RESULTS AND DISCUSSION

The separation of phenol, cresols, and chlorophenols on a Cyclobond 1β (5 μ) column is shown in Figure 1. As indicated, this type column,



Mobile phase: acetonitrile: 0.002 M sodium acetate (pH 5)
0.02 M potassium nitrate

Upper: (10:90) flow rate 1 mL/min.
Lower: (25:75) flow rate 1.5 mL/min.

Injection volume: 20 μL.

Detector: glassy carbon electrode @ +1 V vs. Ag/AgCl.

Figure 1. HPLC/EC chromatograms showing the separation on a Cyclobond 1 β (5 μ) column of (upper) (1) phenol, (2) o-cresol, (3) m-cresol, (4) p-cresol; (lower) (1) 2,4,6-trichlorophenol, (2) 2,4,5,-trichlorophenol, (3) 2,3,4,5-tetrachlorophenol, (4) 2,3,5,6-tetrachlorophenol, (5) pentachlorophenol.

which is composed of cyclodextrin bonded to high purity silica, was able to separate all of the phenols. In this respect, the Cyclobond column out-performed a C_{18} reverse phase type column which, as we observed, could not resolve all of these compounds. The Cyclobond column has been shown to be effective for the separation of many closely-related stereo-isomers (1-5).

The electrochemical detector with a glassy carbon electrode held at +1 V vs. an Ag/AgCl reference electrode allowed detection limits of about 10 μg/L for phenols and 40 μg/L for the chlorophenols at an S/N = 3.

Results from a four-day replication study for the collection of phenols and chlorophenols from fortified laboratory water on XAD-4 cartridges are shown in Tables 1 and 2, respectively. A typical HPLC/EC chromatogram showing the separation of chlorophenols following collection on XAD-4 and elution with diethyl ether is shown in Figure 2. The early eluting peak is due to peroxides from the ether.

The recoveries of the compounds tested are reasonable, generally in the range of 40-60%. For the range tested, 0.5-10 μg/L phenols and 5-100 μg/L chlorophenols, this is quite good in view of the fact that phenols are not recovered well in solvent partition (EPA 625) or previous resin systems (6) at low concentrations (< 500 ppb). The range tested here is probably below any regulatory threshold and represents a worst-case scenario for the application of the methodology. We also wish to point out that the recoveries reported are absolute. Therefore, the data can be compared to that provided by USEPA in Method 1625 for acceptability of internal standard recovery. The resin data would appear adequate when viewed against these criteria.

It has been demonstrated that HPLC/EC is well-suited for the analysis of low concentrations of phenolic substances (7-9). The electrochemical detector, because of its excellent sensitivity, was definitely the detector of choice for this work. However, phenols, and particularly chlorophenols, are notorious for electrode fouling. Therefore, it is good practice to keep the amount injected onto the LC column as small as practical. After several days, depending on usage, a significant loss in sensitivity will likely occur. Upon viewing the glassy carbon electrode with a hand magnifier, a "reddish" film is evident. Usually, a brisk rubbing with Kleenex tissue will restore the electrode. If not, the electrode must be repolished.

For future work, we plan to choose a phenol closely related to the phenols of interest for use as an internal standard. This should help to minimize changes in electrode characteristics.

Table 1. Analysis of phenol and cresols in water by HPLC/EC following collection on XAD-4 and elution with diethyl ether.

REPLICATE 1 DATA

Compound	Added (μg/L)	Found (μg/L)	Recovery (%)
Phenol	0.5	0.41	82
	1	0.93	93
	2	1.44	72
	5	2.80	56
	10	6.7	67
o-cresol	0.5	0.28	55
	1	0.84	84
	2	0.88	44
	5	2.05	41
	10	6.1	61
p-cresol	0.5	0.31	61
	1	0.60	60
	2	0.74	60
	5	2.20	44
	10	5.70	57
m-cresol	0.5	0.33	66
	1	0.62	62
	2	1.22	61
	5	2.25	45
	10	6.60	66

REPLICATE 2 DATA

Compound	Added (μg/L)	Found (μg/L)	Recovery (%)
Phenol	0.5	0.41	82
	1	0.48	48
	2	0.78	39
	5	1.90	38
	10	8.2	82
o-cresol	0.5	0.30	60
	1	0.42	42
	2	0.62	31
	5	1.50	30
	10	6.3	63
p-cresol	0.5	0.23	45
	1	0.24	24
	2	0.62	31
	5	1.95	39
	10	6.2	62
m-cresol	0.5	0.31	62
	1	0.25	25
	2	0.56	28
	5	1.50	30
	10	6.50	65

REPLICATE 3 DATA

Compound	Added (μg/L)	Found (μg/L)	Recovery (%)
Phenol	0.5	0.34	67
	1	0.53	53
	2	1.26	64
	5	1.75	35
	10	7.1	71
o-cresol	0.5	0.23	50
	1	0.47	47
	2	0.54	27
	5	1.25	27
	10	6.3	63
p-cresol	0.5	0.19	37
	1	0.34	34
	2	1.04	52
	5	1.50	30
	10	5.7	57
m-cresol	0.5	0.27	54
	1	0.39	39
	2	0.84	42
	5	1.55	31
	10	6.8	68

REPLICATE 4 DATA

Compound	Added (μg/L)	Found (μg/L)	Recovery (%)
Phenol	0.5	0.40	80
	1	1.00	100
	2	0.50	25
	5	1.90	38
	10	7.7	77
o-cresol	0.5	0.33	65
	1	0.94	94
	2	0.40	20
	5	1.90	38
	10	6.8	68
p-cresol	0.5	0.30	60
	1	0.65	65
	2	0.50	25
	5	1.90	38
	10	6.0	60
m-cresol	0.5	0.41	41
	1	0.65	65
	2	0.40	20
	5	1.45	29

Table 2. Analysis of chlorophenols in water by HPLC/EC following collection on XAD-4 and elution with diethyl ether

REPLICATE 1 DATA

Compound	Added (μg/L)	Found (μg/L)	Recovery (%)
2,4,6,-trichlorophenol	2.5	2.2	88
	5	4.4	88
	10	7.6	76
	25	16.5	66
	50	38.0	76
2,4,5-trichlorophenol	2.5	2.0	80
	5	4.2	84
	10	7.4	74
	25	13.5	54
	50	44.0	88
2,3,4,5-tetrachlorophenol	2.5	2.2	89
	5	4.4	88
	10	7.8	78
	25	17.3	69
	50	30.5	61
2,3,5,6-tetrachlorophenol	2.5	2.0	80
	5	2.3	50
	10	6.1	61
	25	16.7	67
	50	38.0	76
Pentachlorophenol	5	3.8	75
	10	4.8	48
	20	9.6	48
	50	37.5	75
	100	80	80

REPLICATE 2 DATA

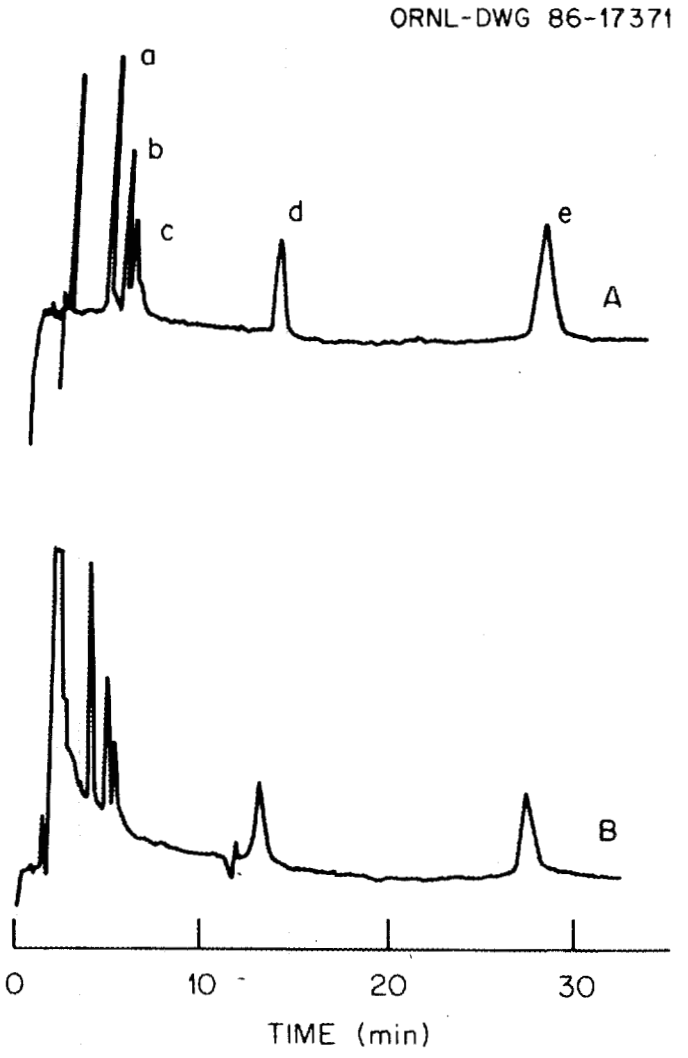
Compound	Added (μg/L)	Found (μg/L)	Recovery (%)
2,4,6,-trichlorophenol	2.5	1.6	65
	5	3.7	73
	10	8.3	83
	25	18.8	75
	50	40.5	81
2,4,5-trichlorophenol	2.5	1.5	60
	5	3.5	69
	10	8.3	83
	25	10.3	41
	50	31.0	62
2,3,4,5-tetrachlorophenol	2.5	1.6	63
	5	4.2	83
	10	8.3	83
	25	14.5	58
	50	21.5	43
2,3,5,6-tetrachlorophenol	2.5	1.4	55
	5	3.8	76
	10	7.3	73
	25	15.0	60
	50	34.0	68
Pentachlorophenol	5	3.2	64
	10	6.4	64
	20	7.6	38
	50	29.0	58
	100	71.0	71

REPLICATE 3 DATA

Compound	Added (μg/L)	Found (μg/L)	Recovery (%)
2,4,6,-trichlorophenol	2.5	2.2	87
	5	4.4	87
	10	7.2	72
	25	16.8	67
	50	38.5	77
2,4,5-trichlorophenol	2.5	1.4	57
	5	4.4	86
	10	8.6	86
	25	16.5	66
	50	35.0	70
2,3,4,5-tetrachlorophenol	2.5	1.9	75
	5	4.3	85
	10	7.0	70
	25	16.0	65
	50	27.5	55
2,3,5,6-tetrachlorophenol	2.5	2.1	85
	5	4.1	82
	10	4.6	46
	25	19.3	77
	50	26.5	53
Pentachlorophenol	5	4.0	80
	10	7.7	77
	20	13.0	65
	50	41.0	82
	100	63.0	63

REPLICATE 4 DATA

Compound	Added (μg/L)	Found (μg/L)	Recovery (%)
2,4,6,-trichlorophenol	2.5	1.5	61
	5	3.6	72
	10	8.0	80
	25	17.8	71
	50	37.5	75
2,4,5-trichlorophenol	2.5	1.8	70
	5	4.3	85
	10	7.5	75
	25	18.3	73
	50	39.5	79
2,3,4,5-tetrachlorophenol	2.5	2.0	80
	5	3.8	75
	10	8.3	83
	25	16.8	67
	50	26.0	52
2,3,5,6-tetrachlorophenol	2.5	1.9	78
	5	4.0	80
	10	6.8	68
	25	17.8	71
	50	32.5	65
Pentachlorophenol	5	3.4	67
	10	7.2	72
	20	10	50
	50	32.0	64
	100	55.0	55



(A) Calibration standard, 250 μg/L.
(B) Sample, 5 μg/L, 100 mL original volume, 2 mL final volume.

Column: Cyclobond 1 β, 5 μ.
Mobile phase: acetonitrile: 0.002 M sodium acetate (pH 5)
0.02 M KNO_3 (25:75) 1.5 mL/min
Electrode: Glassy carbon, +1 V vs Ag/AgCl, 10 nAFs
Compounds:
(a) 2,4,6-trichlorophenol
(b) 2,4,5-trichlorophenol
(c) 2,3,4,5-tetrachlorophenol
(d) 2,3,5,6-tetrachlorophenol
(e) pentachlorophenol

Figure 2. HPLC/EC analysis of chlorophenols following collection on XAD-4 and elution with diethylether.

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