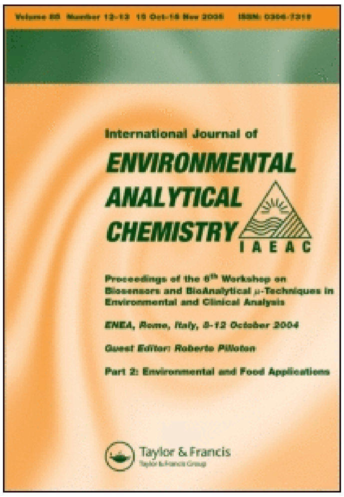

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Determination of 2-Phenylphenol and 4-Chloro-3-Methylphenol in Water and Sediments by Liquid Chromatography Using Electrochemical Detection

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Liquid chromatography with amperometric detection was used to determine 4-chloro-3-methylphenol and 2-phenylphenol released into the environment after a chemical

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fire. Recovery studies on estuarine water, water and sediment matrices were undertaken.

KEY WORDS: Amperometric detection, liquid chromatography, 4-chloro-3-methylphenol, 2-phenylphenol, water, sediment.

INTRODUCTION

As a result of a major chemical fire in Melbourne on 12 April, 1985, two phenols were released into a wild-life reserve and threatened to contaminate a major river system. Because the river has important commercial and recreational value, it was necessary to develop a rapid and sensitive technique to monitor macro and trace levels of the two phenols and to facilitate the clean-up operation.

The relatively high water solubility of the two phenols and the large volume of water used during the fire-fighting process quickly transported them from the site of the fire through the stormwater drainage system leading into the wild-life reserve (Figure 1). By using the phenols as markers the extent of the pollution could be assessed and the degree of environmental clean-up required addressed accordingly.

A variety of chromatographic techniques has been used to determine individual phenols.[1-6] We have found reverse-phase liquid chromatography using electrochemical detection to be the method of choice for a wide range of substituted phenols as it is rapid, very sensitive and selective.[7]

This paper describes the application of this method to the determination of 4-chloro-3-methylphenol and 2-phenylphenol in fresh water, estuarine water and sediments under routine operating conditions.

EXPERIMENTAL

Reagents

Acetonitrile and acetic acid were of ChromAr™ grade (Mallinckrodt, Aust.) specially prepared for liquid chromatography. Distilled water passed through a Milli-Q™ purification system (Millipore, Bedford,

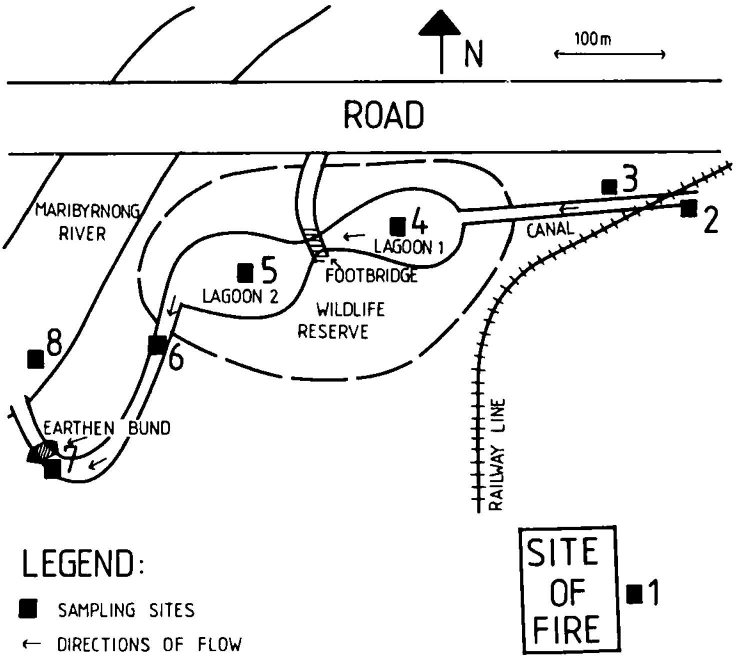

Figure 1 Map of the canal system affected by the fire indicating numbered sampling sites and location of wild-life reserve.

MA) fitted with an Organex-Q^{TM} cartridge was used to prepare water free from organic contaminants and was used throughout this study. Sodium perchlorate and trisodium citrate were both Analar grade (BDH, Aust.).

Standards

The 4-chloro-3-methylphenol was part of a phenol kit (Part No. 4-4570) purchased from Supelco Inc. (Belefonte, PA) and was 95+% pure. Technical 2-phenylphenol (Dowicide 1) obtained from Dow Chemicals was recrystallised from water prior to use (m.p. 56°C, lit. value[8] 55.5–57.5°C). Stock solutions (1 g/L) were prepared in acetonitrile with subsequent working standards made up using mobile phase. Working standards covering the range 0.05–10 mg/L produced linear calibration curves ($r^2 > 0.999$) using peak area for both phenols.

Glassware

Volumetric flasks, distillation apparatus, glass syringes and sample vials were soaked in a pyrogenically negative cleaner—Pyroneg™ (Diversey, Aust.), rinsed with water and allowed to air dry. Sample blanks confirmed that this procedure was effective in eliminating free phenols and other contaminants from the glassware.

Instrumentation and materials

Details of the modular liquid chromatograph used are previously described,[7] except that the column in this study is a Waters (Millipore, Bedford, MA) Nova-PAK C_{18} (10 cm × 0.5 cm, 4 μm). The mobile phase consisted of 40% acetonitrile/59% 0.2 M sodium perchlorate, 0.005 M trisodium citrate/1% acetic acid with the flow rate adjusted to 1.5 mL/min.

Sampling

Waters: Hand-drawn grab samples were collected in 1 L glass bottles and immediately preserved with the addition of 2 mL concentrated sulphuric acid/L and 1 g copper sulphate/L.[9] The preserved samples were stored on ice during transportation back to the laboratory. Sample analysis was begun as soon as practicable (within 24 hours) after sample collection.

Sediments: Samples of approximaaately 0.5–1 kg were taken using a stainless steel spatula and placed into wide-mouthed glass reagent bottles. No preservation of these samples other than storage at −18°C was undertaken with analysis normally undertaken within 7 days.

Sample preparation

Waters: Distillation of the phenolic compounds was performed on 100 mL of sample in a round-bottom flask connected to a still-head and condenser (Graham-type). The first 90 mL of distillate was collected in a 100 mL volumetric flask. At this stage the distillation was stopped, the apparatus allowed to cool and a further 10 mL water added to the distillation flask. The distillation was then recommenced and continued until the total volume of distillate collected was 100.0 mL. Direct injection (20 μL) of the distillate was then performed. Sample dilution was carried out using mobile phase as required.

Sediments: The thick pasty sample (approx. 500 g) was homogenised by hand using a spatula and subsequently divided into smaller batches. This procedure was repeated to reduce the sample to a workable size. Normally 50 g of the well mixed sample was taken and 100 mL water added. Copper sulphate (1 g/10 g sample) and concentrated sulphuric acid (to pH < 2) were added prior to distillation. The distillation procedure differed from that described for the water samples because severe bumping was experienced as the water content in the sediment distillation flask decreased. As a result, the distillation was stopped after only 50 mL of the distillate had been collected. A further 50 mL of water was added after allowing the apparatus to cool and the distillation continued until 100.0 mL of distillate had been collected.

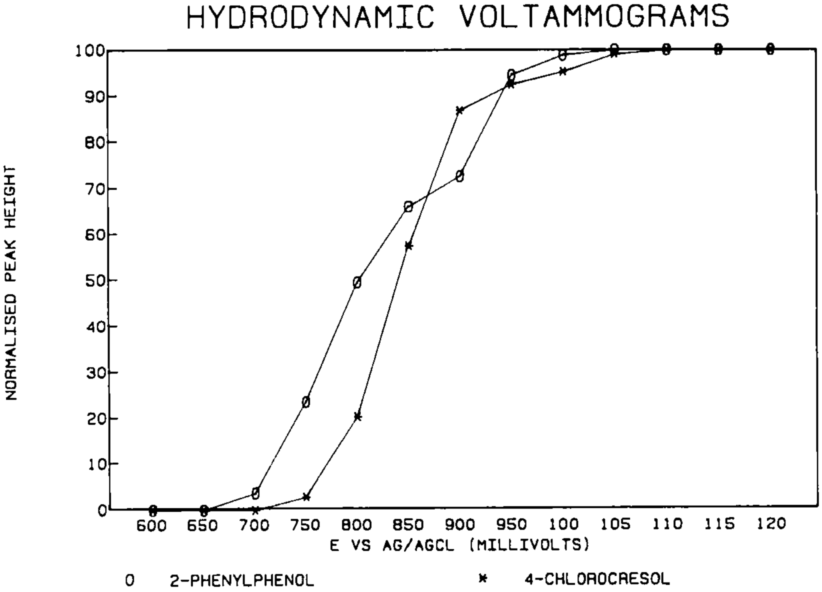

Figure 2 Normalized hydrodynamic voltammograms for 4-chloro-3-methylphenol and 2-phenylphenol. LC-EC conditions: column—Nova-PAK™ C_{18} (10 cm × 0.5 cm, 4 μm); mobile phase—40% acetonitrile/59% 0.2 M sodium perchlorate, 0.005 M trisodium citrate/1% acetic acid; flow rate—1.5 mL/min.

RESULTS AND DISCUSSION

To obtain maximum response for each phenol, hydrodynamic voltammograms (HDV's) were performed under routine operating conditions as previously described[10] and are shown in Figure 2. Electrode potentials of +0.95 and +0.85 volts vs Ag/AgCl reference electrode (3 M NaCl) were selected on the basis of best signal to noise ratios for both the phenols tested.

Recovery study

Samples of estuarine water upstream of the canal discharge point (Site 8) and Milli-Q™ water were spiked at the 1.0 mg/L and 10.0 mg/L levels by adding 500 μL and 5.0 mL of 1000 mg/L stock solutions to 500 mL of the respective water samples. Aliquots of 100.0 ml were distilled as previously described.

Sediment samples collected from an area adjacent to the earthen bund which showed no levels of contamination were used as control samples and also for the recovery study. The uncontaminated sediments (50 g) were spiked at the 1.0 mg/kg and 10.0 mg/kg levels by adding 50 μL and 500 μL of the respective 1000 mg/L stock solutions prior to distillation. The results of the recovery study for both phenols on each of the water and sediment samples are presented in Table 1.

Excellent recoveries were obtained for the water samples but recoveries for the sediment samples were low because of an inefficient distillation procedure. Similar variability in the recovery of phenols from sludges has been reported previously.[11]

Table 1 Percentage recovery ($\% \pm \sigma$) of 2-phenylphenol and 4-chloro-3-methylphenol after distillation.

	Water	*Estuarine water*[a]	*Sediment*[b]
2-phenylphenol			
10 mg/L ($n=5$)	97±4	98±5	74±11
1 mg/L ($n=5$)	91±5	94±5	69±12
4-chloro-3-methylphenol			
10 mg/L ($n=5$)	99±3	99±4	79±11
1 mg/L ($n=5$)	96±4	95±4	74±13

[a] Salinity 19 parts per thousand.
[b] Sediment results expressed as mg/kg.

Application to environmental samples

Samples of water and sediment were collected from locations about the site of the fire and canal environs as shown in Figure 1. Examples of the chromatography achieved on these samples are given in the following figures. Figure 3 illustrates the analysis of 4-chloro-3-methylphenol and 2-phenylphenol in the distillate from a water sample. Figure 4 illustrates the corresponding chromatograms for a sediment sample after 1:4 dilution with mobile phase. Figure 5 is the chromatogram obtained for a mixture of 5 ng of each of the phenol standards. Phenol was present in varying amounts in all of the water and sediment samples analysed and is probably due to the breakdown of the two substituted phenols, which may have occurred in the environment or during the course of the fire. It can be seen

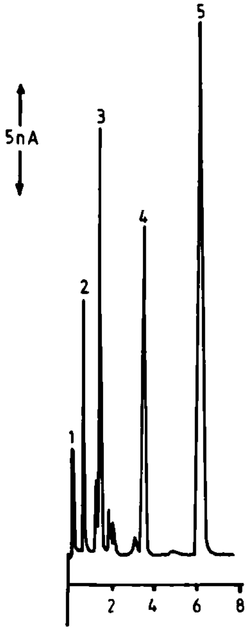

Figure 3 Chromatogram for direct injection (20 μL) of a water sample distillate recorded at 0.95 volts vs Ag/AgCl reference electrode (3 M NaCl). LC-EC conditions as in Figure 2. Peak identities: (1) injection artifact, (2) solvent, (3) phenol, (4) 4-chloro-3-methylphenol and (5) 2-phenylphenol.

from Figures 3 and 4 that the two phenols of analytical interest are well separated from other components in the samples and that the clean-up procedure used in both cases gave clean extracts. The components represented by peaks 1 and 2 in the figures are an injection artifact and solvent respectively as they are both observed when pure solvent is injected. Other minor peaks in the two figures have not been positively identified.

Peak identifications were made on the basis of retention time and current response ratio matches (0.95/0.85 volt) with authentic standards.

Results of the LC-EC analyses at various sampling locations are listed in Table 2.

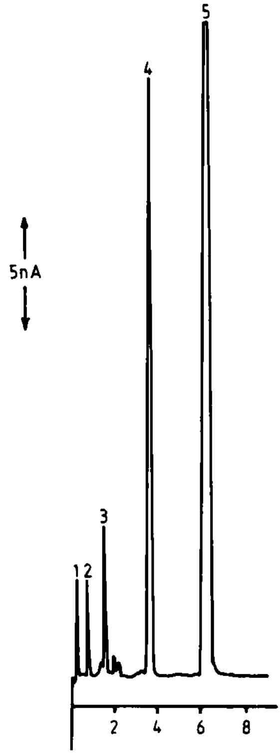

Figure 4 Chromatogram for direct injection (20 μL) of a sediment sample distillate after a 1:4 dilution with mobile phase. Peak identities as in Figure 3.

Examination of the above results from the different sites depict a situation as follows:

Site 1—Not surprisingly, as this was the closest sampling site to the fire, samples of water and sediment exhibited the highest levels of contamination.

Site 2—Situated approximately 10 m upstream of the main discharge point into the canal, this site shows no contamination and therefore indicates that there are no additional upstream inputs of these phenols into the canal system.

Site 3—This is the main storm-water drainage input into the canal system and exhibits moderately high levels of phenols in the water and sediments. This drain was capped after initial sampling and the storm-water system isolated. The contents of this system were educted and transported away for treatment/disposal.

Sites 4 & 5—These two sites are lagoons, designed to act as a buffer zone to handle peak flows from the storm-water drainage

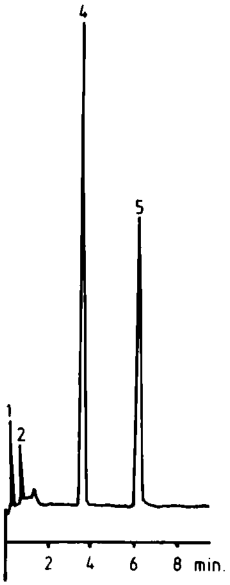

Figure 5 Chromatogram for a mixture of 5 ng of each of the standards, 4-chloro-3-methylphenol and 2-phenylphenol. Peak identities as in Figure 3.

Table 2 Concentrations of 4-chloro-3-methylphenol and 2-phenylphenol compounds in samples collected during and after the clean-up operations.

Site no.	*Sample type*	*Date collected*	*Compound*		*Salinity (ppt)*[a]
			4-chloro-3-methyl phenol	*2-phenylphenol*	
1.	W	19.04.85	0.95	1.45	8
	W	26.04.85	0.60	0.85	6
	S	30.04.85	20	50	
	W	9.05.85	0.40	0.62	6
	S	20.06.85	1.62	2.75	
2.	W	24.04.85	<0.05	<0.05	2
	S	24.04.85	<0.1	<0.1	
3.	W	24.04.85	0.17	0.25	8
	S	24.04.85	1.2	2.7	
4.	W	24.04.85	0.12	0.18	9
	S	24.04.85	0.9	1.9	
	W	1.05.85	0.11	0.16	10
	W	3.05.85	0.05	0.09	9
	W	6.05.85	0.06	0.09	10
	S	6.05.85	0.6	1.4	
	S	8.05.85	0.3	0.9	
5.	W	24.04.85	0.10	0.16	13
	S	24.04.85	0.3	0.8	
	W	1.05.85	0.12	0.16	10
	W	3.05.85	0.08	0.12	10
	W	6.05.85	0.06	0.10	10
	S	6.05.85	0.3	0.5	
	S	8.05.85	0.1	0.4	
6.	W	24.04.85	0.05	0.08	13
	W	1.05.85	<0.05	0.05	14
	W	6.05.85	<0.05	0.05	14
7.	W	24.04.85	<0.05	0.06	18
8.	W	24.04.85	<0.05	<0.05	19

W—water; S—sediments, soil.

All results for water expressed as mg/L and sediments as mg/kg wet weight basis and have been corrected from recovery data.

[a] ppt—parts per thousand.

system entering the canal from the industrial estate before the storm-water enters the Maribyrnong River. To further complicate matters, the lagoons and surrounding areas have been turned into a wild-life reserve open to the public and it is a popular habitat for water birds. Hence, this represents a particularly sensitive environmental area and one in which a more comprehensive study was carried out. Results indicate moderate levels of contamination in the water and sediment samples with slightly lesser amounts in the downstream lagoon (site 5).

Site 6—Located approximately 20 m downstream from the second lagoon and consisting of a narrow canal, results indicate a trace level of the two phenols in water only.

Site 7—Adjacent to the earthen bund, which was constructed on the night of the fire to block any flow of contaminated water into the Maribyrnong River, this site represents the furthest point from the source of the contamination. Traces of 2-phenylphenol were detected in water samples.

Site 8—Sample taken from the Maribyrnong River nearby the canal entrance exhibited levels of the two phenols below the detection limit of the technique.

Overall, the highest levels of contamination by the two phenols were recorded in the sediments indicating a partitioning effect from the water into the sediment, with levels of 2-phenylphenol exceeding 4-chloro-3-methylphenol in all samples.

Although only a small number of samples were collected from each site, it is fairly clear from the data in Table 2 that a decrease in the levels of the phenols was observed with time at all of the sites.

Low levels of the two phenols in the water samples at sampling points 6 & 7 indicates that their transport through the canal system to the lagoons was rapid but that the construction of the bund was effective in preventing further transport beyond the canal system to the river. The extremely high sensitivity of the LC-EC technique further demonstrates the usefulness in monitoring these phenols at trace levels.

Conclusion

This work shows the ability of the LC-EC technique in the determination of 4-chloro-3-methylphenol and 2-phenylphenol at sub mg/L levels and demonstrates its applicability in the analysis of both sediment and water samples. The level of these or similar phenols could be used as a measure of the extent of the distribution of these and other organic pollutants in urban waterways arising from similar industrial accidents. The analytical data from this study demonstrates the effectiveness of the steps taken in the environmental clean-up which prevented more widespread contamination of a major river system.

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