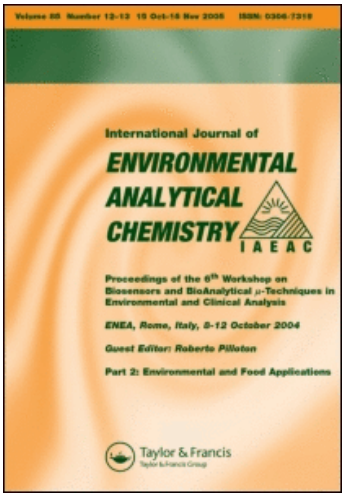

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The technique of liquid chromatography with electrochemical detection has been applied to the determination of alkylphenols in refinery effluents. Specific problems addressed were the trace enrichment of low-level phenols and the simultaneous

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detection of meta- and para-cresols which are difficult to separate chromatographically. The former problem was solved using C18 Sep Pak(TM) cartridges followed by controlled evaporation of the eluant. Separate responses for the meta and para cresols were achieved by using two different potentials. The fully developed method is sensitive and selective in the determination of alkylphenols in environmental waters.

KEY WORDS: Alkylphenols, refinery effluents, liquid chromatography, electrochemical detection.

INTRODUCTION

Phenolic compounds enter natural waters in a number of ways being directly added as herbicides, insecticides, disinfectants or as their metabolites and indirectly as byproducts of manufacturing processes of which, petroleum refining is one.

Phenols are of particular concern because of their toxicity to fish and other aquatic organisms. They also adversely affect the taste of fish and impart an odour to water. The taste and odour threshold for phenol in marine and estuarine waters has been tentatively set at 0.1–1 mg/l.[1]

Current procedures for the determination of phenolics include colorimetry, gas chromatography, mass spectrometry and liquid chromatography. The standard colorimetric procedure[2] for "total phenolics" suffers major inadequacies. In this method,[2] 4-amino-antipyrine reacts with the phenols to form a coloured derivative. No differentiation among the various phenol derivatives is possible, and certain phenols, such as those with para substituents do not react to any appreciable extent.[2]

To determine specific phenolic compounds, gas chromatographic methods utilizing flame ionization,[3] electron capture[4,5] and mass spectrometric[6,7] detection schemes have been developed. However, pretreatment is usually required to isolate and concentrate the phenols from the water followed by derivatization prior to their gas chromatographic determination. This latter step requires considerable expertise as many of the reagents used are carcinogenic, toxic or explosive. It is therefore desirable to use a method which avoids the derivatization step. Several methods using liquid chromatography (LC) with ultra-violet (UV) detection have been

reported.[8–12] Concentration of the phenolic compounds from water is necessary prior to their determination and because of the possible interference from other organic compounds that are also detected by the UV detector additional confirmatory techniques are required for positive identification.

Since most phenols are electrochemically active, the combination of reverse-phase LC with electrochemical (EC)[13–15] detection offers a very sensitive and selective alternative to the aforementioned methods.

This paper describes a method for the determination of those phenols commonly encountered in refinery effluents with reference to the efficiency and recoveries under routine operating conditions.

EXPERIMENTAL

Reagents

Acetonitrile and acetic acid were of ChromAr grade (Mallinckrodt, Aust.) specially prepared for LC. A Milli-Q (Millipore, Bedford, MA) deionizer fitted with an Organex-Q cartridge was used to prepare water free from organic contaminants. Sodium perchlorate and sodium citrate were both Analar grade (BDH).

Standards

The phenols used were part of a phenol kit purchased from Supelco Inc. (Belefonte, PA) (Part No. 4-4570) and were all 95+% pure. Stock solutions (1 mg/ml) were prepared in acetonitrile with subsequent working standards made up using mobile phase. Working standards covering the range 0.025–0.25 mg/l produced linear calibration curves ($r2 > 0.999$) for the phenols tested.

Glassware

Volumetric flasks, glass syringes and sample vials were soaked in a pyrogenically negative cleaner—PyronegTM (Diversey, Victoria, Australia) rinsed with milli-Q water and allowed to air dry. Sample blanks confirmed that this procedure was effective in eliminating free phenols and other contaminants from the glassware.

TABLE I
Chromatographic conditions for alkylphenol detection

Pump	LDC Constametric III, Laboratory Data Control (Riviera Beach, FL)
Injection system	WISP 710B Autosampler, Waters Associates (Milford, MA)
Column	Waters RCM-100 housing a 10 × 0.5 cm, 10 μm C18 Rad-pak operated at ambient temperature
Mobile phase	40% acetonitrile/60% 0.2 M sodium perchlorate, 0.005 M sodium citrate, 0.1% acetic acid at 2.0 ml/min
Detector	BAS LC4B/LC17 controller/flowcell with TL5A thin-layer transducer, Bioanalytical Systems Inc. (West Lafayette, IN) Potentials: Either +0.95 V or +0.85 V vs. Ag/AgCl as indicated in text Range 20 nA; offset 1–2 nA
Data collection	Appligration II Chromatography package, Dynamic Solutions Corporation (Pasadena, CA), operated on a 6502 microprocessor based computer

Instrumentation and materials

The modular liquid chromatograph and chromatographic conditions used are given in Table I. Sep PakTM C18 cartridges were purchased from Waters Associates (Milford, MA).

Sampling

Hand-drawn grab samples were collected in 1 l glass bottles and immediately preserved by the addition of 2 ml concentrated sulfuric acid and 1 g/l copper sulfate.[16] The preserved samples were then stored on ice before transportation back to the laboratory.

Procedure

Distillation of the phenolic compounds is first carried out according to the standard method.[2] Direct injection (20 μl) of the distillate is then performed under the conditions listed in Table I. If there is no significant response a concentration step is employed involving trace enrichment of the phenolic compounds onto C18 Sep PakTM cartridges. The cartridges are conditioned/activated by first washing

with 5 ml acetonitrile which serves to wet the surface of the silica and also to remove any contaminants that have been introduced onto the cartridges during manufacture or storage. This is immediately followed by 10 ml of milli-Q water making the cartridge ready for the trace enrichment step. At no time are the cartridges allowed to dry out prior to the trace enrichment step. An aliquot of sample (5.0 ml) is pipetted onto the Sep PakTM and drawn through under vacuum. The vacuum is maintained until the majority of the sample is removed and then desorption of the phenols with 1 ml of acetonitrile is carried out. The acetonitrile extract is then treated with 50 μl of 0.1 M sodium hydroxide solution and its volume reduced under a stream of nitrogen to 50 μl whereupon the volume is made up to 100 μl with 0.1 M hydrochloric acid. The final extract represents an overall enrichment of 50 fold, from which a 10 μl injection is made.

RESULTS AND DISCUSSION

Chromatographic and detector optimization

With other LC detectors, namely UV and fluorescence, a knowledge of the solute's absorption and fluorescence characteristics must first be investigated by running their respective UV or fluorescence spectra before conditions of optimum detectability can be obtained. Optimum conditions for detection with the electrochemical system are achieved by running hydrodynamic voltammograms (HDV) on the particular solute.[17] HDV's of individual phenols or mixtures of phenols are easily performed under the normal operating conditions of the LC–EC system by injecting replicate amounts of standard solutions while progressively stepping the applied potential. By plotting the normalized peak height response against applied potential, the HDV's for the test solutes are produced. The HDV's for some selected phenols are shown in Figure 1. The maximum response is observed on the limiting-current plateau (i.e.: where an increase in potential does not result in an increase in the solute peak height) of the HDV. However, when operating the glassy carbon electrode (GCE) at potentials greater than +1.0 V vs. Ag/AgCl a considerable increase in background current is observed which renders the system unusable. Acceptable conditions for the analysis

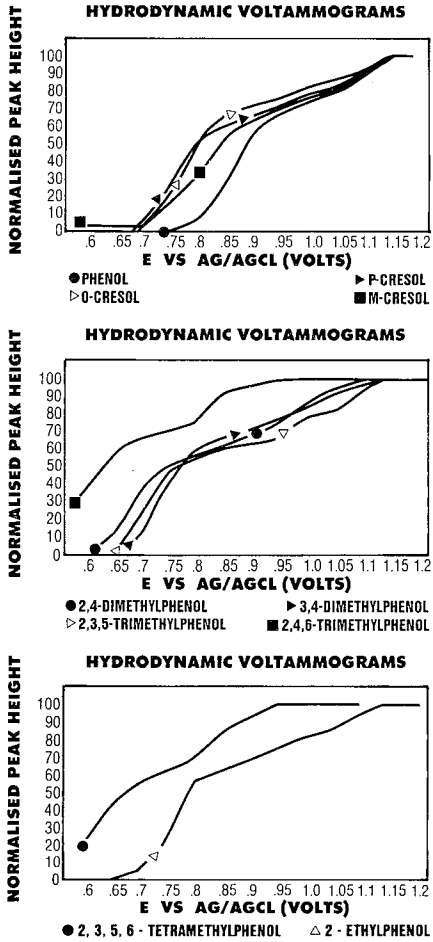

FIGURE 1 Normalised hydrodynamic voltammograms of selected alkylphenols. LC–EC conditions as stated in Table I.

can be obtained at +0.95 V and +0.85 V vs. Ag/AgCl at which potentials background current is substantially reduced. Routine HDV measurements are made in this laboratory as a means of maintaining a check on the electrochemical cell's performance.

Recoveries

The electrochemical detector is highly sensitive and direct injection of the sample (after distillation), into the LC–EC system affords detection limits in the low mg/l range. The obvious advantages of direct injection make this the logical starting point in the analysis of environmental samples. If lower detection limits are required then trace enrichment and a subsequent concentration step is carried out allowing detection limits in the μg/l range to be achieved. The trace enrichment step using C18 Sep PakTM cartridges is limited by the polar nature of the phenols which allows only a small volume of sample to be enriched before breakthrough occurs, as can be seen in Figure 2. Hence a volume of 5.0 ml is used in order to obtain recoveries (for phenol especially) greater than 90%. Further concentration of the acetonitrile extract using a stream of dry nitrogen was evaluated, however significant losses, particularly for phenol, were observed. The introduction of a base to the acetonitrile extract by the addition of 50 μl solution of a 0.1 M sodium hydroxide converted the phenolic species to their respective phenolate anions thereby reducing their volatility sufficiently to allow concentration of the extract with a stream of dry nitrogen without significant losses occurring. Neutralization is then performed with the addition of 50 μl of 0.1 M HCl giving a final volume of 100 μl, thereby realising

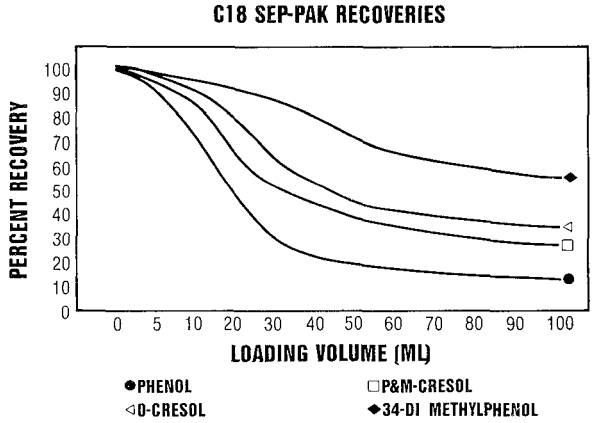

FIGURE 2 Percent recovery from C18 Sep PakTM cartridges as a function of the loading volume for phenol, *p*-cresol, *m*-cresol, *o*-cresol and 3,4-dimethylphenol.

an enrichment factor of 50 times. The overall recoveries were better than 85% for the phenols tested (phenol-85 ± 9%, *p*-cresol-88 ± 5%, *o*-cresol-88 ± 4%, and 3,4-dimethylphenol-94 ± 6%). These recoveries were determined using replicate analyses ($n=9$) of a solution containing these phenols each at a concentration of 0.25 mg/l.

Chromatographic separation

Isocratic separation of standard phenols (5 ng each) is presented in Figure 3. Good separation for the commonly encountered phenols is achieved except for para- and meta-cresols. This problem has been encountered by many other researchers using similar conditions with some ignoring it completely and others quoting a combined figure calculated on an equal response of a mixture (1:1) of the two isomers. As each isomer has its own individual hydrodynamic properties (see Figure 1), the responses at different potentials can not only serve as a fingerprinting tool but may also be used to calculate the amount of each in a mixture. Examination of the respective HDV's (Figure 1) for para- and meta-cresols at +0.95 V reveals that their electrochemical responses are similar, however at +0.85 V the difference is quite marked. By injecting the individual para- and meta-cresols and the sample containing the unresolved mixture at the two potentials (+0.95 V/+0.85 V) sufficient information can be obtained to solve two simultaneous equations (1) and (2) and therefore algebraically derive the concentrations of the individual isomers in the mixture.

$$ax + by = z1 \tag{1}$$

$$cx + dy = z2 \tag{2}$$

where

x = mass in ng of *p*-cresol present in mixture,
y = mass in ng of *m*-cresol present in the mixture,
a = response factor of *p*-cresol at Eappl. +0.95 V,
b = response factor of *m*-cresol at Eappl. +0.95 V,
c = response factor of *p*-cresol at Eappl. +0.85 V,
d = response factor of *m*-cresol at Eappl. +0.85 V,
$z1$ = peak area of *p*- and *m*-cresol peak at Eappl. +0.95 V,
$z2$ = peak area of *p*- and *m*-cresol peak at Eappl. +0.85 V.

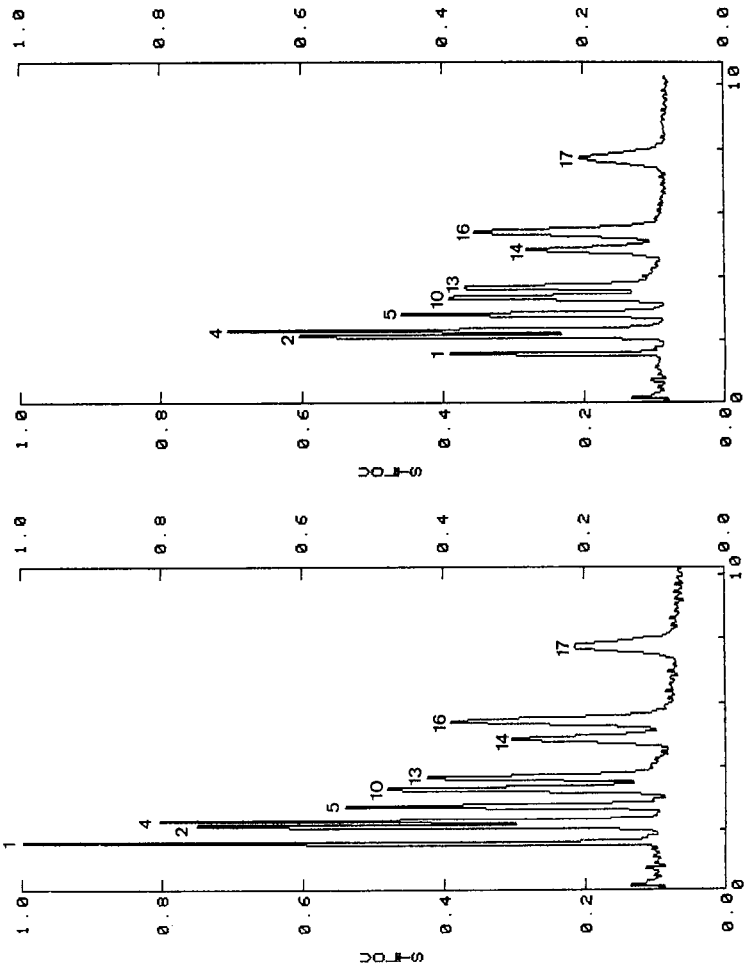

FIGURE 3 Chromatogram of phenol standards, (a) applied potential +0.95 V vs. Ag/AgCl reference; (b) applied potential +0.85 V vs. Ag/AgCl reference. LC–EC conditions as stated in Table I.

TABLE II

Results for the masses of *p*- and *m*-cresols in mixtures of varying concentrations calculated using Eqs. (1) and (2)

p-cresol added to mixture (ng/20 μl)	*p*-cresol calculated (ng/20 μl)	*m*-cresol added to mixture (ng/20 μl)	*m*-cresol calculated (ng/20 μl)
20.00	19.78	0.00	0.17
19.05	18.68	0.95	1.02
19.51	19.52	0.49	0.11
17.14	17.12	2.86	2.57
15.00	15.00	5.00	5.01
10.00	9.93	10.00	9.92
5.00	5.29	15.00	14.41
5.00	4.83	5.00	4.88
2.86	3.27	17.14	16.12
0.95	1.49	19.05	17.70
0.49	0.87	19.51	18.11
0.00	0.30	20.00	18.95

Verification of the above procedure was carried out over a wide range of para- to meta-cresol concentrations with acceptable agreement between the expected and calculated values as shown in Table II.

The phenols investigated are listed in Table III along with their capacity factors and electrochemical response ratios at the two operating potentials.

Application to real samples

The method was applied to samples from treated refinery effluent before its discharge into Corio Bay (Geelong, Victoria, Australia). Direct injection (20 μl) of a sample (taken 20.2.85) after preliminary steam-distillation gave the chromatogram shown in Figure 4, containing 0.35 mg/l phenol, 0.2 mg/l† *m*-cresol, 0.02 mg/l† *p*-cresol, 0.08 mg/l *o*-cresol and 0.02 mg/l 3,4-dimethylphenol. The majority of samples analysed contained only the five phenols as outlined above with adequate sensitivity being realised with direct injection.

†Derived algebraically from Eqs. (1) and (2).

TABLE III

Capacity factors, k', and electrochemical response ratios (RR) for 17 alkylphenols

Peak no.	Compound	k'	RR
1	phenol	1.93	6.24
2	*p*-cresol	3.07	1.55
3	*m*-cresol	3.09	5.90
4	*o*-cresol	3.52	1.82
5	3,4,-dimethylphenol	4.52	3.79
6	3,5-dimethylphenol	5.04	2.61
7	3-ethylphenol	5.33	3.24
8	4-ethylphenol	5.39	2.12
9	2,3-dimethylphenol	5.52	3.19
10	2,4-dimethylphenol	5.74	2.03
11	2,5-dimethylphenol	5.74	1.55
12	2,6-dimethylphenol	6.24	4.54
13	2-ethylphenol	6.50	1.21
14	2,3,5-trimethylphenol	9.06	1.86
15	2,3,6-trimethylphenol	9.87	1.66
16	2,4,6-trimethylphenol	10.37	1.25
17	2,3,5,6-tetramethylphenol	15.52	1.58

$k' = tr - to/to$, where tr is the retention time of the solute and to is the retention time of an unretained solute estimated from the appearance of the solvent from the injection.

RR = response at +0.95 V/response at +0.85 V.

Peak identifications were made on the basis of retention time and current response ratio matches with authentic standards. Quantitation of the individual phenols was carried out at the two operating potentials and averages reported. Over an operating period of a day the two estimates differed by no more than 4%.

CONCLUSION

This work shows the ability of the LC–EC technique in the determination of alkylphenols and demonstrates its applicability in the analysis of refinery effluent samples. As well as this the trace enrichment procedure provides a sensitivity which has been long sought after in this type of analysis. The information obtained from

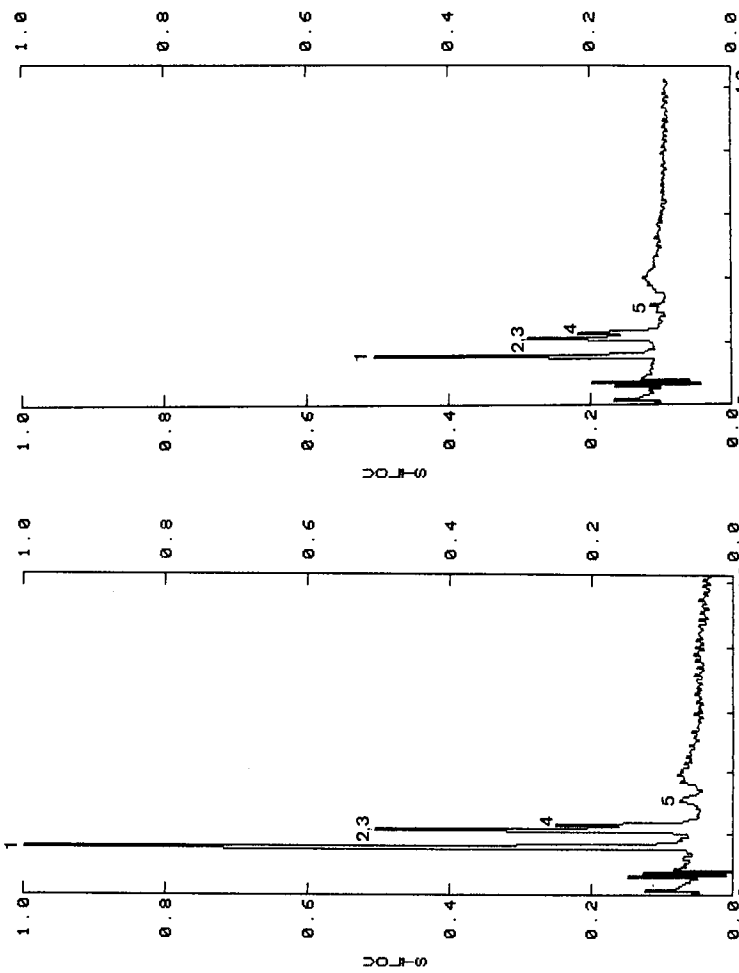

FIGURE 4 Chromatogram of final refinery effluent (sampled 20.2.85), (a) applied potential +0.95 V vs. Ag/AgCl reference; (b) applied potential +0.85 V vs. Ag/AgCl reference. LC–EC conditions as stated in Table I.

the HDV's of para- and meta-cresols has provided a means of quantifying these two components simultaneously even though chromatographic separation is generally not achieved.

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