

APPLICATIONS OF LIQUID CHROMATOGRAPHY WITH ELECTROCHEMICAL DETECTION TO THE ANALYSIS OF OIL SHALE PROCESS WATERS AND LEACHATES

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ABSTRACT

The application of high performance liquid chromatography with electrochemical detection to the analysis of resin-separated fractions of oil shale retort waters and leachates is described. For compounds such as phenols and amines, having oxidizable functional groups, enhanced selectivity and sensitivity are achievable over conventional u.v. spectrophotometric detection. Phenol, 2-,3- and 4- cresol, dimethylphenols, resorcinol and 2- and 5- methylresorcinol, were detected and quantified in the hydrophobic acid fractions; the procedures for their identification are outlined. In the basic fraction, the possibility of quantifying amines, aminopyridines and heterocyclic nitrogen bases was also investigated.

INTRODUCTION

Oil shale retort waters and leachates from raw and spent shales contain a plethora of inorganic and organic compounds many of which are potentially hazardous to both aquatic and terrestrial biota. While the inorganic chemistry of retort waters has now been comprehensively studied (Fox et al., 1978), analysis of trace organics has proved to be a more challenging problem. The development of satisfactory treatment procedures for waste waters associated with oil shale production requires a thorough knowledge of their composition and identification of toxic components.

Previous studies (Fox et al., 1978) have shown that the dissolved organic carbon content of process retort waters may be as high as 5 g L^{-1} , of which the major proportion, apart from emulsified or suspended hydrocarbons, consists of aliphatic carboxylic acids (Ho et al., 1976; Torpy et al., 1981). The latter can comprise as much as 50% of the carbon content of some samples, permitting their direct analysis by gas chromatography (Ho et al., 1976), although

usually prior derivitization is performed (Fish et al., 1982). The remaining carbon content includes phenols, amines, heterocyclic bases, aromatic carboxylic acids, nitriles, alcohols, ketones and lactones, in mg L^{-1} concentrations or less. Such complex mixtures are beyond the resolution of gas or liquid chromatographic techniques.

Attempts were therefore made to separate the mixtures into smaller class fractions on the basis of either molecular size or extractability. A solvent extraction scheme to resolve acidic, basic and neutral organics has been described by Tobben et al. (1982). Leenheer (1983) recently described the use of macroreticular polymeric adsorbents for the preparative isolation of hydrophobic acidic, basic and neutral fractions of organics in waste waters, with ion exchange resins being used to resolve the hydrophilic fraction. This latter operationally-defined scheme provides useful fractions when applied to oil shale retort waters (Leenheer et al., 1982), nevertheless the authors were still able to identify only 50% of the total dissolved organic carbon content of the water.

High performance liquid chromatography (HPLC) has generally been used for analysis of the low concentrations of organics in these fractions; however the identification and quantification of eluting peaks is difficult, especially using conventional u.v. detection (Felix et al., 1977). The poor selectivity of this detector impairs resolution while, with large numbers of peaks, assignments based on the retention times of standard compounds can be misleading. Electrochemical (EC) detection affords greater selectivity, since it will respond only to compounds able to be oxidized or reduced within the potential range of the detector electrodes. It is ideally suited to oil shale retort waters since phenols and aromatic amines and some heterocyclic bases are electrochemically active.

This paper describes the application of HPLC with EC detection to the analysis of phenols and amines in oil shale retort waters and leachates. These studies form part of a program aimed at characterizing and examining the toxicity of organic compounds present in the waste waters from the processing of Australian oil shales.

EXPERIMENTAL

Shale samples from the Condor, Rundle, Julia Creek and Nagoorin deposits in Queensland, Australia were subjected to Fischer retorting to generate retort waters and spent shale for these studies. Retort water samples were also obtained from an experimental steam pyrolysis retorting rig described elsewhere in this volume (Wall, 1984).

Batch leaching of spent shales (150 g) was carried out according to the ASTM standard procedure (ASTM, 1981) using 50 g samples in 200 mL of distilled water.

Water samples were separated into acidic, basic and neutral hydrophobic fractions and a single hydrophilic fraction, using the procedure of Leenheer (1982). The fractionation of dissolved organic carbon was monitored with a Beckman TOC Analyzer (Beckman Instruments Inc.). The hydrophobic acid and base fractions were further concentrated, after the addition of base and acid respectively, by passage through Sep-PAK C₁₈ cartridges (Waters Associates), and eluted with methanol.

High performance liquid chromatographic analyses used Waters instrumentation, including a Model 450 Variable Wavelength Detector.

For electrochemical detection, a Bioanalytical Systems Inc. (BAS) TL8A glassy carbon detector cell, controlled by a Princeton Applied Research PAR Model 174 voltammeter, was used. A BAS Model MF1001 electrode was used for dual electrode studies, in conjunction with a controller constructed according to the circuit of Blank (1976). HPLC separations were carried out on a 30 cm x 3.9 mm μ -Bondapak C₁₈ column (Waters Associates).

RESULTS AND DISCUSSION

Data on the oil shales selected for study are given in Table 1. A more extensive comparison of

the chemical properties of the shales has been reported by Dale et al.

Table 1. Fischer Assay Product Details of Oil shales

Sample	Oil Yield ^a	Water ^a	Weight Loss
Julia Creek	7.62	1.60	12.0
Condor	5.38	9.73	18.7
Rundle	10.64	2.68	21.7
Nagoorin	4.95	7.98	25.7

^a g/100 g dried shale

(1984). Retort waters, obtained from the Fischer retorting of these shales, were analyzed for major components as shown in Table 2, the major differences being the higher thiosulfate, arsenic and thiocyanate concentrations in the Julia Creek sample. The total phenolic content, as estimated by the 4-aminoantipyrine spectrophotometric method (APHA 1976), approximated 2% of the total organic carbon content of the waters in all samples.

Table 2. Chemical Analysis of Retort Waters

	Julia Creek	Condor	Rundle	Nagoorin
pH	8.4	9.5	8.6	8.8
Organic C, g L ⁻¹	2.3	4.1	2.2	7.4
Ammonia, g L ⁻¹	1.3	5.0	29	8.6
Alkalinity, g L ⁻¹ (CaCO ₃)	1.6	11.5	2.6	17.1
S ₂ O ₃ ⁼ , g L ⁻¹	1.1	0.01	0.3	0.05
SO ₄ ⁼ , mg L ⁻¹	72	100	26	212
SCN ⁻ , mg L ⁻¹	97	22	29	50

Samples were fractionated using a mixed XAD-2/XAD-8 resin bed according to the scheme of Leenheer et al. (1982). In general, 30-50% organic carbon was found in the hydrophobic fraction, with the acidic and basic components contributing approximately equally, to 20% of this figure.

Since an immediate apparent application of HPLC with EC detection was to the analysis of phenols, the hydrophobic acid fraction was subjected to the most comprehensive study. Several workers have examined the separation of

phenols by HPLC (Chao and Suatoni, 1982; Leenheer et al., 1982; Shoup and Mayer, 1982) using a number of different eluent mixtures. For this study of retort water phenols, an eluent comprising 20% acetonitrile, 80% 0.005 M acetate buffer pH 5 and 0.2 M sodium perchlorate, was selected. Acetonitrile was preferred to methanol for its ability to resolve the single cresol peak into two peaks corresponding to 3- plus 4- cresol and 2-cresol respectively.

The measurement cell used in EC detection comprises a glassy carbon working electrode, a Ag/AgCl reference electrode, and a counter electrode, usually either stainless steel or glassy carbon. The potential of the working electrode is controlled by a potentiostat and a current peak will be observed if the solute as it passes the working electrode is capable of being electrochemically oxidized (or reduced) at the potential applied to this electrode.

A typical chromatogram, shown in Figure 1, indicates the selectivity and resultant improved resolution of electrochemical detection compared

with the less specific u.v. detection. The assignment of specific peaks in these chromatograms requires the use of standard compounds with which retention times and electrochemical behaviour can be compared.

Retention time is the parameter in HPLC which is characteristic of an eluting solute. In reversed phase liquid chromatography, retention time is governed by the interaction of the solute with both the non-polar stationary phase of the column and the eluting solvent, and will depend on factors such as the surface area and dipole moment of the solute and the surface tension of the solvent. The solvent system selected for this study, produced the elution order for substituted phenols shown in Table 3. Previous studies of retort waters (Leenheer et al., 1982, Torpy et al., 1982) have indicated the presence of phenol, cresols and dimethylphenol isomers. These were readily identified in our samples, on the basis of retention times using EC detection. There were, however, a number of unidentified peaks, and their electrochemical behaviour was also examined.

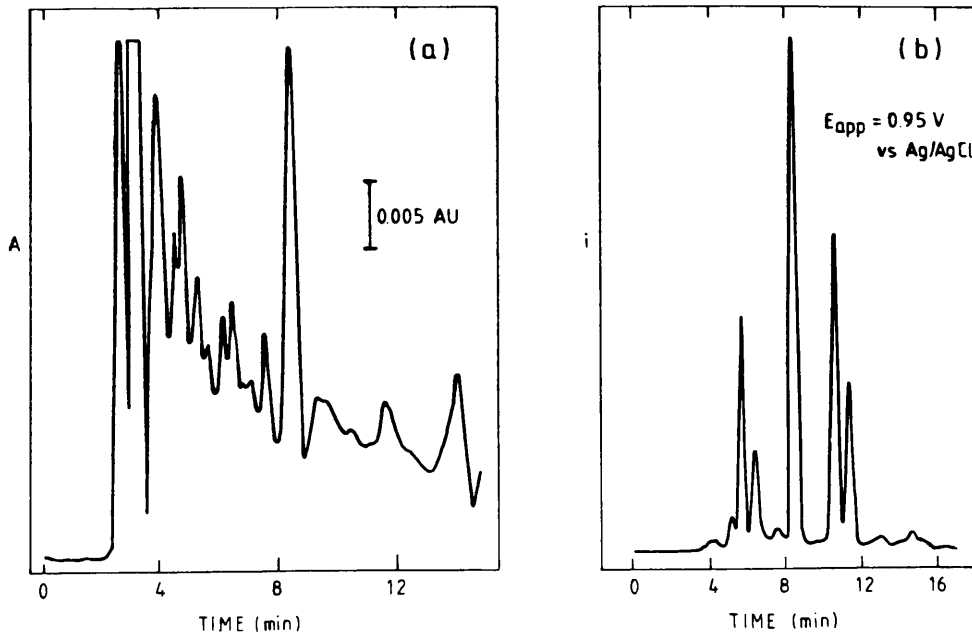


FIGURE 1. Analysis of phenols in the hydrophobic acid extract of an oil shale retort water by HPLC showing the enhanced selectivity of electrochemical detection (b) compared to conventional u.v. spectrophotometric detection (a)

Table 3. Retention and Voltammetric Data for Phenolic Compounds in 20% acetonitrile/80% 0.2 M NaClO₄, 0.005 M acetate buffer pH 5

Compound	Retention time	E _{p/2}
	min	V vs Ag/AgCl
2-Hydroxybenzoic acid	3.08	0.830
4-Hydroxybenzoic acid	3.08	0.745
2-Hydroxy-3-methylbenzoic acid	3.88	0.800
2-Hydroxy-4-methylbenzoic Acid	4.03	0.850
Resorcinol	4.50	0.645
2-Naphthol	4.91	0.530
Catechol	5.10	0.255
2-Methylresorcinol	5.70	0.560
5-Methylresorcinol	6.26	0.605
4-Methoxyphenol	7.43	0.445
Phenol	8.48	0.755
3-Cresol	13.50	0.635
4-Cresol	13.50	0.575
2-Cresol	14.45	0.585
3,4-Dimethylphenol	22.36	0.540
2,3-Dimethylphenol	25.31	0.615
2,4-Dimethylphenol	26.68	0.485
2,5-Dimethylphenol	26.97	0.530
3,5-Dimethylphenol	25.86	0.545

^a μ -Bondapak C18; flow rate 1 mL min⁻¹
^b For 1x10⁻⁴ M phenols at glassy carbon electrode, scan rate 50 mV s⁻¹

Examination of the voltammetric characteristics of electrochemically-active compounds enables selection of an applied potential, suitable for their electrochemical detection. For aromatic compounds such as phenols, peak potentials (E_p), or the more accurately determined half-peak potentials (E_{p/2}), as measured by linear sweep voltammetry, will be altered by substituent groups, in a manner which may be predicted on the basis of Hammett substituent constants (Suatoni et al., 1961). Peak potentials measured for a range of substituted phenols are given in Table 3, which shows, for substituted phenols are more readily oxidized. Peak potentials for compounds giving unidentified peaks can be determined by recording a hydrodynamic voltammogram obtained by measuring the current response for different detector potentials; they requires a separate injection for a large number of

of detector potentials. Alternatively, the stopped-flow capability in the Waters HPLC instrument can be utilized and the voltammogram recorded with the eluting compound held in the detector. This approach is rapid but can be unsuccessful if the solution concentration of the phenol is lower than about 1 x 10⁻⁴ M. Use of this procedure enabled identification of several unknown peaks as substituted resorcinols.

A dual-electrode detector, having two working electrodes, was used to simultaneously monitor the current at two applied potentials (Shoup and Mayer, 1982). With the electrodes in parallel, the equivalent of absorbance ratioing with a u.v. detector can be carried out by comparing currents at each electrode. Electrodes in series may permit the oxidized products found at the first electrode to be reduced at the second downstream electrode. Typical current ratios for phenolic compounds at series and parallel electrodes are given in Table 4. This procedure also confirmed the presence of substituted resorcinols.

Table 4. Dual-Electrode Detection of Phenols in 20% acetonitrile, 80% 0.2 M NaClO₄, 0.005 M acetate buffer pH 5

Compound	Parallel Electrodes	Series Electrodes
	iE ₁ /iE ₂	iE ₁ /10 iE ₂
	E ₁ = +1.00 V ^a	E ₁ = +1.00 V ^a
	E ₂ = +0.65 V ^a	E ₂ = -0.20 V ^a
4-Hydroxybenzoic acid	1.0	1.0
4-Methoxyphenol	1.0	0.3
Resorcinol	3.5	8.6
2-Methylresorcinol	0.9	19.5
5-Methylresorcinol	1.8	12.1
Phenol	12.8	1.3
4-Cresol	1.6	4.8
3-Cresol	2.9	2.0
2-Cresol	1.8	1.6

^a vs Ag/AgCl

The distribution of phenols identified in the retort waters is given in Table 5. Unlike the results of previous studies of (Leenheer et al., 1982; Bell et al., 1983), the percentage of these compounds present in the samples as the

Table 5. Distribution of Phenolic Compounds in Fischer Retort Waters (%)

	<u>Rundle</u>	<u>Julia Creek</u>	<u>Condor</u>	<u>Nagoorin</u>
Phenol	79.3	75.1	66.5	85.2
3- and 4- Cresol	9.7	13.4	16.5	9.6
2-Cresol	3.3	4.6	4.8	2.8
Resorcinol	0.4	0.1	0.2	0.2
2-Methylresorcinol	0.2	0.1	<0.2	0.3
5-Methylresorcinol	0.4	<0.1	<0.2	0.8
Dimethylphenols	0.4	1.5	1.2	0.2
Other phenolics	6.3	5.1	10.6	0.9

Table 6. Distribution of Phenolic Compounds in Steam Pyrolysis Retort Waters (%)

	<u>Rundle</u>	<u>Julia Creek</u>	<u>Condor</u>
Phenol	51.7	53.1	57.3
3- and 4- Cresol	19.8	28.1	22.4
2-Cresol	10.7	12.4	8.2
Resorcinol	6.0	0.3	3.0
2-Methylresorcinol	0.5	0.1	0.2
5-Methylresorcinol	2.3	0.3	1.2
Dimethylphenols	4.7	2.4	1.3
Other phenolics	4.3	3.3	6.4

Table 7. Retention and Voltammetric Data for Hydrophobic Bases in 10% acetonitrile/90% 0.2 M NaClO₄, 0.005 M phosphate buffer pH 7

<u>Compound</u>	Retention time ^a <u>min</u>	E _{p/2} ^b V vs Ag/AgCl
2-Aminobenzoic acid	1.77	0.675
2-Phenylenediamine	3.35	0.225
4-Phenylenediamine	2.45	0.075
2-Aminopyridine	4.05	0.940
3-Aminopyridine	2.60	0.475
4-Aminopyridine	3.22	n.e. ^c
Aniline	5.32	0.640
4-Anisidine	5.57	0.380
3,4-Diaminotoluene	5.32	0.115
2-Toluidine	10.05	0.335
4-Toluidine	10.42	0.395
2,5 Dimethylaniline	19.50	0.430
2,6-Dimethylaniline	18.20	0.435
2,3-Diaminopyridine	2.90	0.450
2,6-Diaminopyridine	3.00	0.435

a μ -Bondapak C18; flow rate 2 mL min⁻¹

b For 1x10⁻⁴ M bases at glassy carbon electrode; scan rate 50 mV s⁻¹

c n.e. = not electroactive

parent phenol was high. This could be a function of retorting conditions where both temperature and the water content of the shales could be expected to influence the distribution of steam volatile products. This is further illustrated with the samples produced by steam pyrolysis retorting (Table 6). Both the Rundle and Julia Creek shales, which under Fischer retorting yield small amounts of water, showed increased concentrations of substituted phenols in steam pyrolysis retort waters.

The presence of dihydroxyphenols has not previously been reported in retort waters, although 5-alkylresorcinols, presumed to result from poly β -carbonyl structures derived from polyunsaturated acids in the precursor marine organisms. Resorcinol and 2-methyl resorcinol have also been found, but not other dihydroxy isomers (Purre and Lille, 1973).

The limit of EC detection on the sample as injected was 2 ng, compared with the practical limit using u.v. detection of 10 ng. This is significantly lower than can be achieved by gas chromatography-mass spectrometry (GC-MS) unless extensive preconcentration procedures are employed. A highly sensitive technique was essential, however, for the analysis of leachates. Using EC detection, the range of phenols observed in retort waters was also found in the resin-separated leachate fractions. The maximum concentration of phenol detected was 1×10^{-5} M in the leachate from Julia Creek retorted shale.

Equally suited to EC detection are the aromatic amines likely to be present in the hydrophobic base fraction of retort waters. Electrochemical and elution characteristics of a range of potential components are given in Table 7.

As already discussed, retention times in HPLC do not provide unambiguous identification and, in the case of aniline, similar GC-MS behaviour to methylpyridines has been reported (Barbour and Guffy, 1981). Electrochemical detection should resolve these compounds since only aniline will be electroactive. Preliminary studies of hydrophobic base extracts did reveal aniline in low concentrations. In addition, it was found that certain piperidine bases detected by GC-MS also

exhibited electrochemical activity.

Quantification of the full range of these compounds is currently being undertaken.

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