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

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SUMMARY

The application of liquid chromatography with electrochemical detection for the selective analysis of organics in complex mixtures is described. Experimental conditions are given for the quantification of phenols, aromatic amines and certain heterocyclic bases related to piperidine and pyrrolidine, after preliminary separation into acidic, basic and neutral fractions. The technique is applied to the analysis of oil shale retort waters.

INTRODUCTION

The analysis of oil shale process waters presents a challenging analytical problem because of the plethora of compounds present at parts-per-billion (μg/l) concentrations or above[1,2]. The unknown compounds are principally organics. Direct analysis by gas chromatography–mass spectrometry (GC–MS) does not identify unambigously any but the major organic components[3]; this limitation can be overcome to some extent if preliminary separations are used to limit the number of compounds present in the injected aliquot. Nevertheless, peak overlaps, and the possibility that mass fragmentation patterns are assignable with similar confidence to more than one compound in the spectral library, present major difficulties. There is a need therefore for analytical methods which are selective, within the whole or fractionated sample, for specific compounds or compound classes.

High-performance liquid chromatography (HPLC) provides an alternative separation technique to GC, and reversed-phase HPLC separations are particularly attractive for the separation of polar water-soluble molecules. Conventional HPLC detection systems using UV or fluorescence absorption provide little selectivity, unless spectral scans are possible such as with diode array detectors. Electrochemical detection (ED) offers a more attractive option for certain compound classes although MS remains the only technique for ultimate confirmation of compound identity.

To be capable of electrochemical detection, compounds must have functional groups which are oxidizable or reducible within the potential window of the mea-

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suring electrode. This extends from about +1.5 V *versus* Ag/AgCl, the anodic limit of glassy carbon electrodes, to −1.3 V *versus* Ag/AgCl, the cathodic limit for a mercury electrode. Mercury is not suitable as an electrode for oxidative detection, whereas glassy carbon is of limited use for reductive detection. Detectable compounds include those having phenolic, amino or nitro functional groups. Phenols and amines are known components of oil shale retort waters[2].

This paper describes the applications of HPLC with ED to analyze selectively these and other oxidizable compounds in oil shale process waters.

EXPERIMENTAL

Voltammetric studies were carried out using a Princeton Applied Research (PAR) model 174 polarographic analyzer, connected to a Hewlett-Packard Model 7130 *x–y* recorder. A glassy carbon working electrode was used.

Instrumentation for HPLC comprised a Waters Assoc. Model M6000 pump and a 30 cm × 3.9 mm μBondapak C_{18} column. Post-column mixing via a low dead-volume tee union was controlled by a second type M6000 pump. For UV detection a Waters Model 450 variable-wavelength detector was used, and for ED, a Bioanalytical Systems (BAS) Model TL8A single-electrode cell or Model MF1001 dual glassy carbon electrode cell was used in conjunction with a bi-potentiostat constructed according to the circuit of Blank[4].

Reagents

Substituted phenols were obtained from Merck (Darmstadt, F.R.G.) and Fluka (Buchs, Switzerland). Piperidine, N-ethylpiperidine and pyrrole were BDH (Poole, U.K.) reagents. Other organic bases were obtained from Fluka. Discoloured bases were redistilled under vacuum before use. All inorganic chemicals were from Merck.

RESULTS AND DISCUSSION

Retort water composition

Retort waters were generated by Fischer assay from samples of four Australian oil shale deposits at Julia Creek, Condor, Rundle and Nagoorin in Queensland. These waters were basic, and both the Condor and Nagoorin retort waters exhibited a high carbonate alkalinity (Table I). The total phenolic content of the four waters, estimated by the 4-aminoantipyrene method[5], was approximately 0.5–2.5% of the total organic carbon content.

Before analysis, retort water samples were fractionated according to the scheme of Leenheer *et al.*[1], using a mixed XAD-2/XAD-8 resin bed. In general, 30–50% of the organic carbon content partitioned in the hydrophobic fractions, about 20% of which was from approximately equal contributions by the acidic and basic components. The acidic fraction was comprehensively examined by HPLC for phenolic compounds, and the basic and neutral fractions were investigated for other electroactive species.

ED of phenols

The separation of phenols by HPLC has been reported elsewhere[1], and for ED

TABLE I

CHEMICAL ANALYSIS OF RETORT WATERS

	Condor	*Rundle*	*Julia Creek*	*Nagoorin*
pH	9.5	8.6	8.4	8.8
Organic C (g l^{-1})	4.1	2.2	2.3	7.4
Ammonia (g l^{-1})	5.0	29	1.3	8.6
Alkalinity (g l^{-1})	11.5	2.6	1.6	17.1
$S_2O_3^{2-}$ (g l^{-1})	0.01	0.3	1.1	0.05
Total phenolics (mg l^{-1})	29	41	58	37

several eluent mixtures were used[6,7]. For this study, an eluent comprising acetonitrile–0.005 *M* acetate 0.2 *M* sodium perchlorate buffer, pH 5 (20:80) was used. Acetonitrile was preferred to methanol for its ability to resolve the single cresol peak into two peaks corresponding to *m*- plus *p*-cresol and *o*-cresol, respectively.

A typical chromatogram obtained using ED for the hydrophobic acid extract of an oil shale retort water is shown in Fig. 1b. The equivalent UV absorbance detection trace is shown for comparison (Fig. 1a), to highlight the improved selectivity of the electrochemical detector. The solvent system selected for this study produced the elution order for substituted phenols shown in Table II. Previous studies of retort waters[1,2] have indicated the presence of phenol, cresols and dimethylphenol isomers. These were readily identified on the basis of retention times using ED. There was, however, a number of unidentified peaks whose electrochemical characteristics were also examined.

With our instrumentation, three procedures are available to assist in the iden-

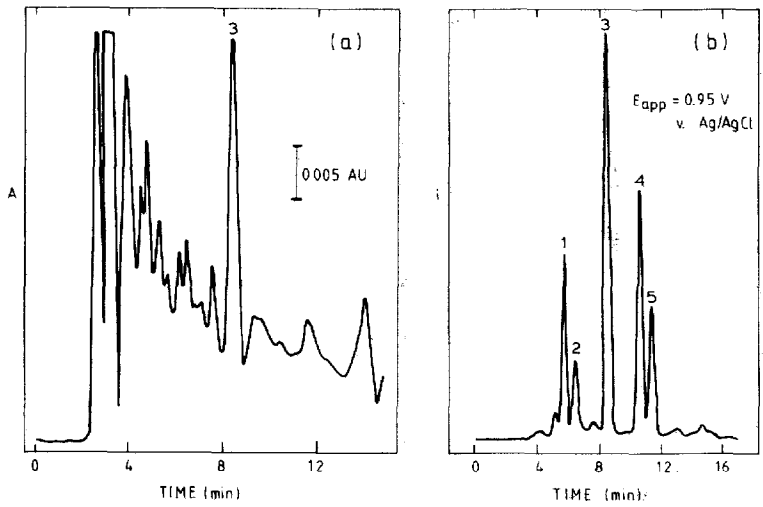

Fig. 1. Analysis of phenols in the hydrophobic acid extract of an oil shale retort water by HPLC showing the enhanced selectivity of electrochemical detection (b) compared to conventional UV spectrophotometric detection (a). Peaks: 1 = 2-methylresorcinol; 2 = 5-methylresorcinol; 3 = phenol; 4 = *m*- and *p*-cresol, and 5 = *o*-cresol.

TABLE II

RETENTION AND VOLTAMMETRIC DATA FOR PHENOLIC COMPOUNDS

Eluent: acetonitrile–0.2 *M* sodium perchlorate (20:80), containing 0.0005 *M* acetate buffer, pH 5.

Compound	*Retention time (min)*	$E_{p/2}$ *(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
m-Cresol	13.50	0.635
p-Cresol	13.50	0.575
o-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

* μBondapak C_{18}: flow-rate 1 ml min^{-1}.

** For $1 \cdot 10^{-4}$ *M* phenols at glassy carbon electrode, scan rate 50 mV s^{-1}.

tification of unknown peaks. First, a hydrodynamic voltammogram can be constructed by measuring the peak current response for different detector potentials. This requires a separate injection for each data point on the voltammogram. Second, a stopped-flow accessory (Millipore-Waters) can be employed to hold the eluting compound in the detector cell while a voltammogram is being recorded. Third, a dual glassy carbon electrode system is used in either series or parallel configuration. In the series combination, the oxidation product formed at the first electrode is reducible at the second downstream electrode, whereas in the parallel configuration, the differing detector potentials may be selected to discriminate groups of compounds. For both combinations, ratios of currents at each electrode yield values characteristic of each compound in a manner similar to absorbance ratioing with UV detection. Stopped-flow voltammetry is useful only when the solution concentration of the phenol is greater than about $1 \cdot 10^{-4}$ *M*.

Peak potentials (E_p), or the more readily measured half-peak potentials ($E_{p/2}$), from linear sweep voltammograms are altered by substituent groups in a manner which for aromatic phenols may be predicted on the basis of Hammett substituent constants[8]. Retention and voltammetric data for a range of phenols are given in Table II. Voltammograms recorded for several unidentified peaks enabled their assignment to substituted resorcinols based on the data in Table II; these assignments were confirmed using known compounds. Further confirmation was obtained using dual-electrode detection. Table III shows that the peak current ratios for both series

TABLE III

DUAL-ELECTRODE DETECTION OF PHENOLS

Eluent: acetonitrile–0.2 *M* sodium perchlorate (20:80), containing 0.005 *M* acetate buffer, pH 5.

Compound	*Parallel electrodes, iE_1/iE_2 (E_1 = +1.00 V; E_2 = +0.65 V)**	*Series electrodes, $iE_1/10iE_2$ (E_1 = +1.00 V; E_2 = −0.20 V)**
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
p-Cresol	1.6	4.8
m-Cresol	2.9	2.0
o-Cresol	1.8	1.6

* *vs.* Ag/AgCl.

and parallel electrode modes differ greatly for related compounds as expected from their differing voltammetric behaviour. From a single injection it is therefore possible to more specifically identify the eluting peaks from these ratios rather than undertaking the more lengthy procedure of obtaining full voltammograms for each eluting compound.

Results for Fischer retort waters for Australian shales are given in Table IV. Phenol was present in lower concentrations than reported previously for retort waters[1,9]. 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 was seen with retort waters produced during steam pyrolysis[10] which contained almost 50% substituted phenols compared with nearer 20% for the Fischer assay waters (Table IV).

The presence of dihydroxyphenols has not previously been reported in retort waters although, on the basis of studies of some shale oils, their presence might be

TABLE IV

DISTRIBUTION OF PHENOLIC COMPOUNDS IN FISCHER RETORT WATERS (%)

Compound	*Rundle*	*Condor*	*Nagoorin*	*Julia Creek*	*Julia Creek steam pyrolysis*
Phenol	79.3	66.5	85.2	75.1	53.1
m- and *p*-Cresol	9.7	16.5	9.6	13.4	28.1
o-Cresol	3.3	4.8	2.8	4.6	12.4
Resorcinol	0.4	0.2	0.2	0.1	0.3
2-Methylresorcinol	0.2	<0.2	0.3	0.1	0.1
5-Methylresorcinol	0.4	<0.2	0.8	<0.1	0.3
Dimethylphenols	0.4	1.2	0.2	1.5	2.4
Other phenolics	6.3	10.6	0.9	5.1	3.3

TABLE V

RETENTION AND VOLTAMMETRIC DATA FOR HYDROPHOBIC BASES

Eluent: acetonitrile–0.2 *M* sodium perchlorate (10:90), containing 0.005 *M* phosphate buffer, pH 7.

Compound	pK_a	*Retention time** *(min)*	$E_{p/2}$** *(V vs. Ag/AgCl)*
2-Aminobenzoic acid	2,0, 4.8	1.77	0.675
2-Phenylenediamine	1.3, 4.5	3.35	0.225
4-Phenylenediamine	2.7, 6.2	2.45	0.075
2-Aminopyridine	6.8	4.05	0.940
3-Aminopyridine	5.9	2.60	0.475
4-Aminopyridine	9.5	3.22	n.e.***
Aniline	4.6	5.32	0.640
4-Anisidine	5.3	5.57	0.380
3,4-Diaminotoluene	–	5.32	0.115
2-Toluidine	4.5	10.42	0.395
4-Toluidine	5.1	10.42	0.395
2,5-Dimethylaniline	4.5	19.50	0.430
2,6-Dimethylaniline	3.9	18.20	0.435
2,3-Diaminopyridine	–	2.90	0.450
2,6-Diaminopyridine	–	3.00	0.435

* μBondapak C_{18}; flow-rate 2 ml min^{-1}.
** For $1 \cdot 10^{-4}$ *M* bases at glassy carbon electrode; scan rate 50 mV s^{-1}.
*** n.e. = Not electroactive.

anticipated. Studies of Estonian oil shale[11] specifically identified 5-alkylresorcinols, presumably caused by poly β-carboxyl structures derived from polyunsaturated acids in the precursor organisms. Recorcinol and 2-methylresorcinol have also been found in shale oils, but no other dihydroxy isomers[12].

The detection limit of ED on the injected samples was 2 ng for all except the dimethylphenols where the limit was 4 ng, compared with the practical limit using UV detection of 10 ng, and 20 ng for dimethylphenols. This is significantly lower than can be achieved by GC–MS unless extensive preconcentration procedures are employed. Fouling of the detector electrodes due to polymeric film formation, as previously reported[7], only occurred after prolonged usage and with high concentrations of phenol in particular. This was evident from an apparent decrease in sensitivity and could be rectified by repolishing the electrodes.

ED of bases

Recent studies[2,6,13] of the base/neutral fraction of retort waters have identified piperidinones as the major components. The fraction separated by ammonia stripping of Oxy-6 retort waters contained 45 wt.% of piperidinones, 16 wt.% of pyrrolidinones together with cyclopentanopiperidinones and cyclohexanopyrrolidinones[2]. Bell *et al.*[9] found that N-methyl-2-pyrrolidinone greatly exceeded the concentration of any other organic compound in the basic fraction of a Rundle oil shale retort water, whereas Fox *et al.*[13] qualitatively identified N-methyl-2-piperidinone, N-methyl-2-pyrrolidinone and related compounds in Paraho oil shale gas condensate and spent shale leachate. Other studies have reported the presence of aromatic amines and pyridine derivatives[1,9].

The anodic voltammetric behaviour of aromatic amines and aminopyridines is well-known[13,14] and these compounds should be readily detectable electrochemically. Reports of the ability of certain substituted piperidinone and tertiary amines to undergo electrochemical oxidation at a glassy carbon electrode[15,16] prompted an investigation of these bases also. A summary of the bases examined is given in Tables V and VI. Where known, pK_{5a} values are also indicated.

The aromatic amines and aminopyridines studied are relatively weak bases and were readily detected as the free bases in a phosphate buffer of pH 7. The N-alkylated piperidines and pyrrolidines are much stronger bases (pK_a = 10.4–11.1) with the piperidinones and pyrrolidinones having pK_a values near 8.

The voltammetric behaviour of the latter group of compounds was examined over a range of pH values using a glassy carbon working electrode. All oxidations were found to be highly irreversible and only the free bases and not their conjugate acids were electroactive. A plot of peak current *versus* pH had an inflection point equivalent to the pK_a of the base. Coulometric studies confirmed a 2-electron reaction for this compound, however, attempts to identify oxidation products were unsuccessful. The more likely reaction is the formation of the N-oxide, as was proposed by Barradas *et al.*[17] for piperidine oxidation. The presence of an α-keto substituent adjacent to the heterocyclic nitrogen gave added stability and, these compounds, unlike the γ-keto analogues, could not be oxidised electrochemically in the pH range studied.

Because of their pK_a values, most of the heterocyclic bases listed in Table VI will only appear as bases in the XAD resin separation scheme, if the pH is first adjusted to above 10 with sodium hydroxide; otherwise, they will appear in the hy-

TABLE VI

RETENTION AND VOLTAMMETRIC DATA FOR PIPERIDINE, PYRROLE AND RELATED COMPOUNDS

Eluent: acetonitrile–0.005 *M* phosphate buffer, pH 6 (5:95), containing 0.01 *M* 1-heptanesulfonic acid.

	pK_a	*Retention time* (min)*	$E_{p/2}$** *(V vs. Ag/AgCl)*
Pyrrole	–	8.9	0.750
N-Methylpyrrolidine	10.4	9.4	0.780
2-Pyrrolidine	7.8	–	n.e.***
4-Hydroxypiperidine	–	11.3	1.040
N-Methyl-4-piperidinone	7.9	11.9	1.120
N-Methyl-2-piperidinone	7.9	–	n.e.
2-Piperidinone	8.0	–	n.e.
N-Methyl-4-hydroxypiperidine	–	15.6	1.000
3-Hydroxypiperidine	–	16.5	1.050
Piperidine	11.1	13.0§	1.100
N-Ethylpiperidine	10.5	19.0§	0.800

* On μBondapak C_{18} column, flow-rate 1 ml min^{-1}, post-column addition of 0.2 *M* sodium perchlorate, 0.01 *M* dibasic sodiumphosphate pH 11.2 at 0.7 ml min^{-1}.

** For $1 \cdot 10^{-4}$ *M* bases at pH 9 at a glassy carbon electrode.

*** n.e. = Not electroactive under these conditions.

§ Retention time using 10% acetonitrile.

drophilic base fraction. Furthermore, for electrochemical detection, an eluent pH above 10 was required to ensure maximum electrode response for all compounds. As such conditions are detrimental to silica-based HPLC columns, the separation of the protonated bases had to be carried out at pH 6, with post-column addition of bases to raise the pH before detection. Under these conditions, the compounds eluted close to the solvent front; however, it was possible to increase retention times and satisfactorily resolve the bases by the addition to the eluent of an ion-pairing reagent 1-heptanesulfonic acid.

Analysis of the hydrophobic base fraction of the four retort waters revealed the presence only of N-ethylpiperidine, with traces of aniline. The detection limits for these compounds are estimated to be 5 and 0.2 ng, respectively. Their measured concentrations were 0.7 mg l^{-1} and 0.2 mg l^{-1}, respectively, in the Condor retort water.

CONCLUSIONS

Electrochemical detection is a highly selective method for quantification using HPLC of specific compound classes in complex mixtures, such as oil shale retort waters. Among the compounds exhibiting electrochemical reactivity are phenols, aromatic amines and heterocyclic bases such as piperidine and pyrrolidine and their derivatives. Particular separation and detection conditions have been developed.

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