Phenols In Shale Oil

The search for alternate energy sources to meet increasing demand has created a challenging analytical problem. Individual compounds in a complex matrix must be accurately quantitated in order to determine their effect on the environment. Many of these compounds pose a health threat so monitoring becomes increasingly more important. Presently, involved extractions or HPLC fractionation is employed for separation of compounds prior to other means of instrumental analysis. Identification and quantitation is accomplished by gas chromatography, gas chromatography/mass spectrometry, or liquid chromatography(1). In this Note, a highly selective liquid chromatography/electrochemistry method takes advantage of the facile oxidation of phenolic compounds at a glassy carbon electrode.

This assay, for phenol and cresols in shale oil, is comprised of a rapid, single-step liquid-liquid extraction prior to the LC analysis. A step-gradient from 25% to 50% acetonitrile in 0.2 M sodium perchlorate/0.005 M trisodium citrate (pH 5.00) was utilized to elute the more strongly retained compounds approximately 16 minutes after the injection via a 3-way slider valve. The system requires a minimum of 15 minutes equilibration after returning to the original mobile phase.

Materials

Reagents

0.1 M NaOH. Dissolve 4.0 g sodium hydroxide in 1 L of deionized, distilled water.

0.2 M Sodium perchlorate/0.005 M trisodium citrate buffer. Dissolve 28.1 g sodium perchlorate and 1.47 g trisodium citrate in 1 L deionized, distilled water. Adjust to pH 5.0.

Acetonitrile. Baker "Resi-Analyzed"

Hexane. Analytical reagent grade.

Phenol stock solution. Dissolve 500 mg phenol in 100 mL of 10% acetonitrile/90% 0.2 M sodium

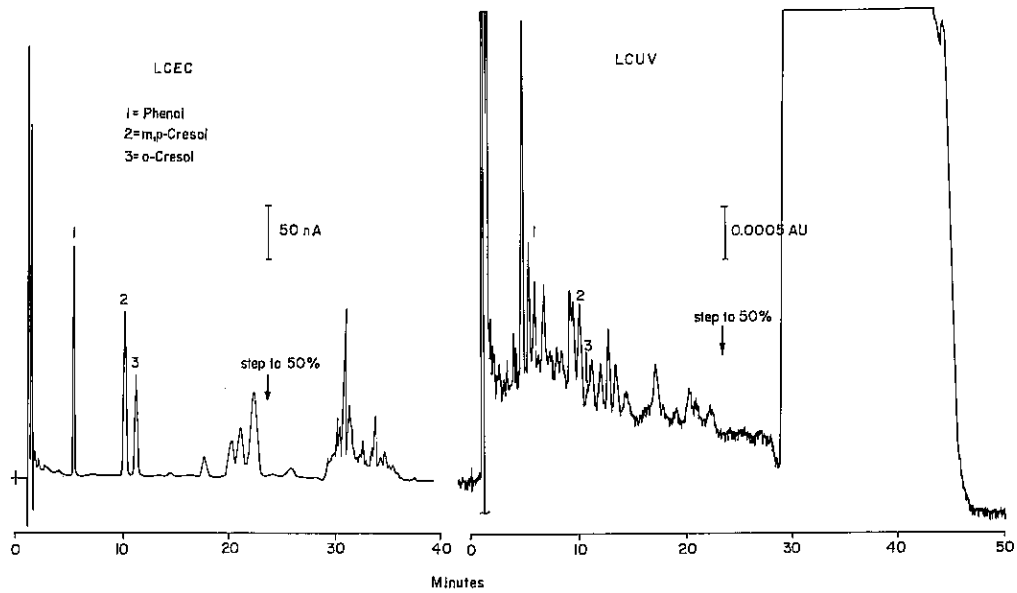

Figure 1. A comparsion of electrochemical detection at +0.90 V and ultraviolet detection at 254 nm for shale oil.

Table 1. Shale Oil Concentrations (µg/gm)

	BAS Single step extraction	NBS HPLC extraction, quantitation by			NBS acid/base extraction, quantitation by
	LCEC	LC	GC	GC/MS	GC/MS
Phenol	400 ± 26	383 ± 50	387 ± 26	416 ± 28	334 ± 63
o-Cresol	345 ± 38	330 ± 34	334 ± 86	350 ± 16	322 ± 45

perchlorate/0.005 M trisodium citrate buffer. Refrigerate.

o-Cresol stock solution. Dissolve 500 mg o-cresol in 100 mL of 10% acetonitrile/90% 0.2 M sodium perchlorate/0.005 M trisodium citrate buffer. Refrigerate.

Shale oil. Samples were donated by Dr. W.E. May of the National Bureau of Standards.

Conditions

Liquid Chromatograph: LC-304 (Bioanalytical Systems Inc.)
Mobile Phase: 25% acetonitrile/75% 0.2 M sodium perchlorate/0.005 M sodium citrate buffer pH 5.00 and 50% CH3CN/50% buffer.
Flow Rate: 2 mL/min.
Stationary Phase: Biophase ODS 5 µm (p/n MF6017, BAS) 250 mm x 4.6 mm
Temperature: ambient
Amount Injected: 10 µL
Detector: LC-4B amperometric detector with a TL-5A glassy carbon working electrode (Bioanalytical Systems Inc.)
Detector Potential: +0.95 volts (vs. Ag/AgCl)
Detector Sensitivity: 100 nAfs

Apparatus

Liquid Chromatograph. Bioanalytical Systems LC-304 (or BAS 200 or 400) with a TL-5A glassy carbon working electrode.

A manual 3-way slider valve (Altex) was used to select the mobile phase and control the step-gradient. The BAS 200 Problem Solver has these capabilities built-in.

Procedure

1. Dissolve 100 mg of shale oil in 10 mL hexane.

2. Extract 1 mL aliquots of the shale oil/hexane solution with 5 mL 0.1 M NaOH.

3. Remove 0.8 mL of the aqueous layer by passing through the organic layer and acidify this aliquot to pH 1.0 with 20 µL concentrated HCl.

4. Inject 10 µL into the chromatograph. A standard addition technique was used for quantitation of phenol and o-cresol. "Spiked" samples underwent the same extraction procedure.

Results

The superior selectivity and sensitivity of this LCEC method is demonstrated in F1. The absence of electrochemically active compounds enables the use of a simple extraction procedure rather than the laborious acid/base extractions which are frequently used. The concentration of phenol and o-cresol correspond well with the determinations of several NBS methods as shown in T2.

Reference

1. H.S. Hertz, J.M. Brown, S.M. Chesler, F.R. Guenther, L.R. Hilpert, W.E. May, R.M. Parris, and S.A. Wise, Anal. Chem., 52(1980) 1650-1657.