Separation of Polar Shale Oil Compounds Using High-Speed Liquid Chromatography

by
R. G. Riley

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SEPARATION OF POLAR SHALE OIL COMPOUNDS USING HIGH-SPEED LIQUID CHROMATOGRAPHY

INTRODUCTION

Previous studies of the chemical composition of shale oil have reported the identification of major compound classes of water soluble polar organic compounds present in shale oil and spent shales. Schmidt-Collerus (1974) identified polycyclic aromatic hydrocarbons (some of which are known carcinogens) from the spent shale of the Green River Formation. Cook et al. (1968) identified a variety of thiophenes and pyridines from oil obtained from retorting oil shale from the Green River Formation. Poulson et al. (1971) identified nitrogen bases from a shale oil light distillate and found most of them to be members of the following four classes: alkylpyridines, alkylquinolines, alkylpyrroles and alkylindoles. Similarly, Brown et al. (1970) identified 64 nitrogen compounds in hydrocracked shale naphtha.

Some compounds from the above classes are toxic and are present as constituents of spent shale or process waters derived naturally or through chemical conversion during the processing of shale oil. These compounds have the potential of being a waste disposal problem as well as potentially contributing to groundwater environmental problems.

If and when extraction of oil from shale becomes an economic reality, necessary guidelines will have to be established for the disposal of toxic wastes derived from the extraction process. Therefore, there is the need for developing fast and accurate analytical methods of detecting and identifying toxic or potentially toxic chemicals in spent shales and process waters. This report discusses methods for the separation of specific compounds from some of the above classes by high-speed liquid chromatography (HSLC).

The analysis of these compounds from these classes will serve a dual purpose: 1) the conditions developed for the high resolution separation of these compounds within each of the classes could be directly utilized for the separation of compounds in these same classes isolated from shale oil

and its waste products, and 2) structural information could be obtained on unknown compounds in these classes isolated from shale oil and its waste products which bear structural resemblance to the selected compounds. Specific compounds were chosen from the following three classes: aromatic and polynuclear aromatic hydrocarbons (Aromatic-PNA), thiophenes and indoles.

INSTRUMENTATION AND CHROMATOGRAPHIC CONDITIONS

For this study, a Waters Model 6000 liquid chromatograph was used with solvent programming mode and sample loop injection system (maximum injection volume, 2 ml). Compounds eluting from the liquid chromatography (LC) columns were detected employing a Schoeffel SF 770 UV monitor containing wavelength monitoring capability between 200 nanometers (nm) and 400 nm.

The following LC columns and conditions were used for the separation of the previously described classes of compounds.

The PNA's were separated by reverse phase liquid chromatography employing a μ Bondapak/C₁₈ (Waters Associates) column (1/4 in. OD x 1 ft) and the following sets of conditions:

- A. Solvent: Acetonitrile/H₂O; 60/40 (V/V)
Flow Rate: 2.0 ml/min
Chart Speed: 5 min/inch
UV Detector: 254 nm at 0.01 absorbance units (AU) sensitivity
- B. Solvent: Acetonitrile/H₂O; 60/40 to 70/30 (V/V) (Solvent program)
Flow Rate: 3.0 ml/min
Solvent Program 5: 15 min
Chart Speed: 5 min/inch
UV Detector: 254 nm at 0.01 AU sensitivity
- C. Solvent: Acetonitrile/H₂O; 40/60 to 80/20 (V/V) (Solvent program)
Flow Rate: 3.0 ml/min
Solvent Program 6: 20 min
Chart Speed: 5 min/inch
UV Detector: 254 nm at 0.01 AU sensitivity

Thiophenes were separated by liquid solid chromatography on a μ Porasil column (Waters Associates; 1/4 in. OD x 1 ft) using the following conditions:

Solvent: Hexane
Flow Rate: 1.0 ml/min
Chart Speed: 4 min/inch
UV Detector: 231 nm at 0.01 AU sensitivity

Similarly, indoles were separated by the following system on the same μ Porasil column:

Solvent: Hexane/CH₂Cl₂; 20/80 $\rightarrow$ 30/70 (V/V) (Solvent program)
Flow Rate: 2.0 ml/min
Solvent Program 6: 10 min
Chart Speed: 4 min/inch
UV Detector: 260 nm at 0.02 AU to 0.4 AU sensitivity

RESULTS AND DISCUSSION

RESOLUTION OF AROMATIC AND POLYNUCLEAR AROMATIC HYDROCARBONS BY REVERSE PHASE LIQUID CHROMATOGRAPHY

A standard containing aromatic and polynuclear aromatic hydrocarbons was prepared in acetonitrile and each component and its concentration is listed in Table 1. LC conditions were developed which maximized resolution of each component and at the same time minimized analysis time. In the first study, the standard (2.0 microliters) was analyzed employing the conditions in set A. A chromatogram of the results is shown in Figure 1. Each component was identified by comparison of retention times in the mix with individual standards. Good resolution of all components was achieved. Naphthalene, pyrene and benzo(α)pyrene were completely resolved and near base line resolution of phenanthrene and anthracene was achieved. Although resolution was good, analysis time was poor (~40 min), therefore, solvent programming was employed in an attempt to reduce analysis time, but at the same time maintain or improve resolution. The same sample (1.0 microliter) was analyzed using condition set B. A chromatogram of the results is shown in Figure 2. Analysis

TABLE 1. Concentrations of Compounds in Aromatic-PNA
Hydrocarbon Standard

COMPOUND	STRUCTURE	CONCENTRATION
		-----μg/ml-----
NAPHTHALENE		33
ANTHRACENE		33
CHRYSENE		33
PYRENE		35
PHENANTHRENE		33
TRIPHENYLENE		33
BENZO (α) PYRENE		34
1, 2, 3, 4-DIBENZANTHRACENE		13
1, 2, 5, 6-DIBENZANTHRACENE		33

FIGURE 1. Chromatogram of the Separation of Aromatic-PNA Hydrocarbon Standard by HSLC According to Condition Set A

FIGURE 2. Chromatogram of the Separation of Aromatic-PNA Hydrocarbon Standard by HSLC According to Condition Set B

time was reduced to 18 min and resolution observed in Figure 1 has been retained. For quantitation purposes, resolution of phenanthrene and anthracene was improved by utilizing condition set C. A chromatogram illustrating the results is shown in Figure 3. Phenanthrene and anthracene are almost completely resolved with analysis time maintained at a reasonable 23 min.

In conclusion, utilization of conditions in sets B and C allow for essentially base line resolution of five of the nine compounds in the aromatic mixture with the analysis time maintained in the range of 18-23 min.

QUANTITATION STUDIES

Since many of the organic compounds present in Organic-PNA class might be expected to be present in small amounts in whole shale oil, spent shale and process waters, it was necessary to determine detectability limits for these compounds.

From the standard, we selected anthracene as representative, and determined its minimum detectable concentration level at 254 nm (Anthracene ϵ max at 253 nm $\sim$ 250,000) employing conditions in set A. A calibration curve for a sample of anthracene (170 ng/ml in 60/40; $\text{CH}_3\text{CN}/\text{H}_2\text{O}$) was prepared (Figure 4) by injecting a range of sample volumes (50 μl to 1.0 ml) on the liquid chromatograph. The curve showed excellent linearity throughout the entire range (50 μl to 1.0 ml; 8.5 ng to 170 ng). Subsequently, 1 ml of an anthracene sample (6.3 ng/ml) was chromatographed and its chromatogram is shown as an inset in Figure 4. The sample gave a peak height of about 0.0003 absorbance units and the peak was about 2.5 times the height of noise level. Assuming the minimum detectable level to be twice the height of noise level, the minimum amount of anthracene that can be detected under these conditions is about 2.5 ng. Table 2 lists ϵ max and λ max for all nine compounds used in this study. A minimum concentration range can be calculated to include all nine compounds based on their extinction coefficient range. Based on this range (40,000 $\rightarrow$ 250,000) and a maximum injection volume of 2.0 ml, the minimum detectable concentration range under these conditions is estimated to be 2.5 to 15.5 ppb.

FIGURE 3. Chromatogram of the Separation of Aromatic-PNA Hydrocarbon Standard by HPLC According to Condition Set C

FIGURE 4. Calibration Curve for Anthracene Employing Condition Set A. Inset Shows Detection of Anthracene at the Level of 6.3 Parts Per Billion

TABLE 2. Wavelength and Extinction Coefficient Maximums for Compounds in Aromatic-PNA Hydrocarbon Standard

Compound	ϵ max	λ max
Naphthalene	$\sim 100,000$	~ 220
Phenanthrene	$\sim 63,000$	~ 252
Anthracene	$\sim 250,000$	~ 253
Triphenylene	$\sim 141,000$	~ 257
Chrysene	$\sim 151,000$	~ 257
Pyrene	$\sim 85,000$	~ 241
Benzo(α)pyrene	$\sim 40,000$	~ 254
1, 2, 3, 4-dibenzanthracene	$\sim 71,000$	~ 280
1, 2, 5, 6-dibenzanthracene	$\sim 126,000$	~ 300

ANALYSIS OF SHALE OIL

In order to obtain information as to the ability of HSLC to resolve the components in complex shale oil samples, a hexane soluble shale oil sample* (50 mg/10 ml; filtered 0.45 μ millipore) was prepared and analyzed by reverse-phase liquid chromatography employing condition set B for PNA analysis. Figure 5 shows the chromatograms for crude shale oil (1) and crude shale oil containing a small amount of aromatic-PNA standard (2). Chromatogram 1 has the following interesting characteristics. The complex UV absorbing component pattern in the shale oil chromatogram is superimposed on a large envelope. This envelope is believed to be derived from light scattering and absorption derived from a large amount of overlapping UV absorbing components present in lower concentrations than those components superimposed on the envelope. Some peaks from the aromatic PNA standard

*The shale oil used in this work was obtained from a 10-ton verticle retort operation located at the Energy Research Center, Laramie, WY.

FIGURE 5. Chromatograms of UV Absorbing Components in Shale Oil (1) and Shale Oil Containing Aromatic-PNA Standard (2)

introduced into shale oil sample of chromatogram 2 match closely with peaks in natural shale oil. Further identification, for example, by gas chromatograph-mass spectrometry is needed to clarify this. In one instance, however, it was found that a peak in chromatogram 1 (unlabeled arrow) was significantly enhanced by the presence of naphthalene from the aromatic-PNA standard in chromatogram 2 suggesting the strong possibility that the component in the natural sample is naphthalene. Assuming for the moment that the component is in fact naphthalene, a calculation can be made to estimate the concentration of naphthalene in shale oil. Based on the concentration of naphthalene in the standard, the amount of naphthalene present in the shale oil would be 550 $\mu\text{g}/\text{gram}$ shale oil or 550 ppm (0.055%). A value of 0.10% has been estimated for the concentration of naphthalene in Green River Shale Oil (Cook et al., 1968).

RESOLUTION OF THIOPHENES BY HIGH-SPEED LIQUID-SOLID CHROMATOGRAPHY

A mixture containing thiophene, 2-methylthiophene, 3-methylthiophene, 2-ethylthiophene, 2, 5-dimethylthiophene and 2, 3-benzothiophene were partially separated by conditions previously described on page 3. Analysis time was approximately 11 min. Each peak was identified by comparison with known standards. The peaks in Figure 6 correspond to the following compounds:

- (A) THIOPHENE c1ccsc1
- (B) 2-METHYLTHIOPHENE + 3-METHYLTHIOPHENE Cc1ccsc1 Cc1csc(C)c1
- (C) 2-ETHYLTHIOPHENE CCc1ccsc1
- (D) 2, 5-DIMETHYLTHIOPHENE Cc1cc(C)sc1
- (E) 2, 3-BENZOTHIOPHENE c1ccc2c(c1)sc(C2)c3ccccc32

FIGURE 6. Chromatogram of the Separation of Substituted Thiophenes by HSLC on μ Porasil Column

RESOLUTION OF INDOLES BY HIGH-SPEED LIQUID-SOLID CHROMATOGRAPHY

The following mixture containing indole, 2-methylindole, 3-methylindole, 1, 2-dimethylindole, 2, 3-dimethylindole and 2, 5-dimethylindole were partially separated by conditions described on page 3. Analysis time for the mixture was approximately 10 min. Each peak was identified by comparison with known standards. The peaks in Figure 7 correspond to the following compounds:

(A) 1, 2-DIMETHYLINDOLE

(B) 3-METHYLINDOLE

(C) 2, 3-DIMETHYLINDOLE

(D) INDOLE

(E) 2-METHYLINDOLE

+

2, 5-DIMETHYLINDOLE

FIGURE 7. Chromatogram of the Separation of Substituted Indoles by HPLC on μ Porasil

CONCLUSIONS

Successful separation of a mixture of aromatic and polynuclear aromatic hydrocarbons by reverse-phase liquid chromatography has been achieved. Utilization of conditions in sets B and C allow for essentially base line separation of five of the nine compounds in the aromatic mixture in the minimum range of time of 18-23 min. The resolved compounds were naphthalene, phenanthrene, anthracene, pyrene and benzo(α)pyrene.

The minimum amount of anthracene that could be detected employing the conditions in the study was 2.5 ng. Based on the extinction coefficient range for the nine aromatic compounds studied, a minimum detectable concentration range of all nine compounds was estimated to be 2.5 to 15.5 ppb.

Analysis of hexane soluble shale oil by reverse-phase liquid chromatography produced a chromatogram containing a complex of UV absorbing compounds superimposed on a large envelope. Some peaks from an aromatic-PNA internal standard matched closely with peaks in natural shale oil suggesting the presence of some of these components in the oil. One component in shale oil is strongly suggested to be naphthalene because its peak is enhanced by the presence of an internal standard of naphthalene. Based on the assumption that the unknown component in shale oil is naphthalene, its concentration was calculated to be 550 μ g/gram shale oil or 550 ppm.

A mixture of six thiophenes were partially separated by high-speed liquid-solid chromatography. Analysis time was approximately 11 min. Thiophene, 2, 5-dimethylthiophene and 2, 3-benzothiophene were base line resolved whereas 2-methylthiophene and 3-methylthiophene were not resolvable and 2-ethylthiophene only slightly separated from the two methylthiophenes. Increased resolution of 2-ethylthiophene from the methylthiophenes could be achieved by using two μ porasil columns in series. It is doubtful that such a measure would produce any degree of separation between the methylthiophenes.

Similarly, a mixture of six alkylindoles were partially separated by high-speed liquid chromatography. Analysis time was approximately 10 min. 1, 2-dimethylindole was clearly separated from the other alkylindoles. 3-methylindole and 2, 3-dimethylindole were partially resolved from each other and indole was nearly completely separated from 2-methylindole and 2, 5-dimethylindole which were nonresolvable. As was suggested for the mixture of thiophenes, placing two columns in series would improve their resolution.

Before the separation procedures described in this report can be fully utilized, other separation schemes have to be developed which separate shale oil or its waste products into fractions containing the individual compound classes previously described.** Because of this, no attempt has been made to identify or quantitate compounds from the above classes in shale oil, especially in the case of thiophenes and indoles. Nevertheless, we have demonstrated that high-pressure liquid chromatography can be a rapid and sensitive method for the separation of polar compounds from classes recognized to be present in shale oil and its waste products.

**Crude fractionation of shale oil or its waste products could be achieved in the following manner: Aqueous acidic extraction of shale oil would remove indoles and other nitrogen bases from the crude oil. This polar fraction could be analyzed further by the procedure described in this report or by other means, for example, ion-exchange chromatography. Furthermore, the neutral organic fraction (aromatics, PNA's thiophenes, etc.) could be further fractionated by thin-layer chromatography or preparative high-pressure liquid chromatography prior to utilization of the schemes described in this report.

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