

LIQUID CHROMATOGRAPHIC CLASS SEPARATION AND HIGH RESOLUTION GAS CHROMATOGRAPHY
OF SHALE OIL POLAR COMPOUNDS

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The largest reserves of fossil fuels in the United States lie in coal and oil shale. Yen (1) has estimated the United States petroleum reserves from shale in the Green River Formation (located in Colorado, Utah and Wyoming) to be some 600 billion barrels. This figure is based on an oil yield of 25-100 gallons of oil per ton of raw shale. Oil shale has been broadly defined as any shallow rock yielding oil in commercial amounts upon pyrolysis. The major organic component of shale is known as 'Kerogen' which is a high molecular weight macromolecular material that is insoluble in most organic solvents. Shale oil is generated when raw shale is heated to temperatures ca. 500°C in a process known as 'retorting.' The high temperatures cause breakdown of the macromolecular kerogen into smaller organic molecules, producing oil.

The organic content of oil shales, and the subsequent amount of oil produced, is dependent upon the source of the original organic precursor species (2). If it is from a terrestrial source the kerogen formed will be closely related to coal and will yield very little oil upon pyrolysis. An example of this type of deposit is in the Chattanooga shales of the Tennessee-Georgia area which yield only about 10 gallons per ton upon pyrolysis. If, however, the kerogen was formed from organic matter in a marine or lacustrine environment, the shale will yield substantial amounts of oil. Shale of this origin is typical of the Green River shales which may yield 25-100 gallons of oil per ton. A second source of organic substances in shale are the bitumens. These are defined as the extractable organic material originally present in the rock. One-three percent of the organic content of Green River shale is present as bitumens. Important differences in chemical composition exist between crude shale oils and typical petroleum crudes; for example in the high olefin content of middle distillates for the former (30 - 50%) with nitrogen content in the 1.8 - 2.1% range, in contrast to the 0.3 - 0.4% range of natural crudes.

To date, no large scale retort has been built in the United States; the only production has been from small pilot plants. However, with the world's dwindling petroleum reserves the prospects for development of this resource now seem favorable. Development must take place in the areas of mining of the raw shale, production of the oil, disposal of the spent shale, and refining of the crude shale oil. The development of new analytical techniques to characterize and evaluate each step in the production of the oil is also needed. In terms of refining operations a careful monitoring of the nitrogen and oxygen containing compounds is needed. In general, shale oil must be modified by hydrotreating or some other process to make it suitable for refining. Without detailed characterization of the hydrocarbons and heterocompounds at each step of the process it is not possible to determine the probable origin of hydrocarbons in the final product. Also, from an environmental standpoint monitoring of organic and inorganic components in both the raw crude and the spent shale is vital. Shale oil also has potential as a petrochemical source due to the diversity of compound types and functionalities present. As a result there is a need to develop new analytical techniques which quantitate shale oil by chemical compound class and in terms of each compound individually.

Crude oils generally comprise four chemical compound classes: (i) asphaltenes (hexane insolubles); (ii) alkanes/alkenes; (iii) aromatics; and (iv) polars (N- and O-containing compounds). Extensive separation schemes for petroleum have been

reported in the literature (3,4). These separations generally deal with distillate fractions which are important to product characterization. The scheme that is most widely employed for the class separation of crudes is the ASTM Clay-Gel Adsorption Chromatographic Method (5). However, the majority of the methods reported for the analysis of petroleum are unsatisfactory for samples containing olefinic unsaturation or non-hydrocarbon material (N- and O-containing compounds), and since shale oil has a high concentration of both these classes either modifications or existing techniques or the development of new techniques is required.

Numerous separation schemes have been reported in the literature for the alkane/alkene, aromatic, and polar fractions of shale oil which rely on conventional gravity columns packed with silica or alumina or on solvent/solvent extractions but these methods are both time consuming and inefficient. An ideal separation scheme should have the following properties: (i) it should be rapid and highly efficient; (ii) it should require minimal sample preparation; (iii) it should consist of a minimal number of steps; and (iv) it should be reproducible. Preparative high pressure liquid chromatography on microparticulate bonded stationary phases meets the criteria noted above. Suantoni et al. (6) performed hydrocarbon group type analysis on petroleum distillate fractions by HPLC on μ -Porasil. Saturate and aromatic fractions were eluted with hexane while the polar fraction was eluted with methylene chloride. Dark et al. (7) employed preparative HPLC to evaluate a hydro-treated coal liquefaction aromatic fraction by ring number. In our study, shale oil from different retorting processes has been resolved into individual chemical compound classes by HPLC using preparative columns packed with i) cyano-bonded and ii) amino-bonded stationary phases. Following the separations, each fraction was further characterized by high resolution gas chromatography and by analytical HPLC. GC detection was by nitrogen specificity, UV absorption and mass spectrometry.

Experimental

Analytical and preparative HPLC was carried out with a gradient system (Laboratory Data Control - Constametric I and II G pumps and 1601 gradient former), with preparative (20 μ m) and analytical (10 μ m) bonded cyano (LC-8) and bonded amino (LC-9) (Johns Manville Corp.). UV detection was employed. Gas chromatography was carried out on Varian Model 3700 and 2760 instruments using fused silica or glass wall-coated capillary columns. GC-MS was performed on a Hewlett-Packard 5985A mass spectrometer system. Shale oil samples were obtained from The Oil Shale Corporation (TOSCO II above ground retort), the Paraho project and a modified In Situ process (DOE, Laramie, Wyoming). Samples were pre-treated before liquid chromatography by dissolution in hexane, filtration of asphaltenes and removal of hexane prior to injection.

Results and Discussion

The chromatographic conditions for the shale oil class separation utilizing the cyano-bonded LC-8 column have been reported (8). In general isocratic hexane elution was followed by an exponential gradient to 100% n-butanol. The overall class elution sequence was i) alkanes/alkenes, ii) aromatics, and iii) polar compounds. A 20 μ m preparative column could be readily re-equilibrated with hexane after elution of oil samples.

Gas chromatography of alkane/alkene fractions, carried out on a 25 meter SP-2100 200 μ m bore fused silica column (Hewlett Packard), clearly exhibited characteristic homologous hydrocarbon series from C₁₀ - C₂₉ (8). Prominent doublets seen at each carbon number sequenced 1-alkenes and n-alkanes, alkene content for TOSCO II oil being much greater than in Paraho or In Situ oils.

Aromatic fractions were chromatographed on the same fused silica column and also on a glass Carbowax 20 M wall coated capillary column (8). Figure 1 shows

a comparison of the aromatic fraction of TOSCO II oil from the cyano-bonded column with a number of aromatic standards, obtained on the SP 2100 fused silica column from which systems of up to 5 rings may be eluted. No alkane/alkene pattern is discernible on this fraction and a minimum of 95% resolution of the aromatic fraction is apparent.

Carbowax 20M was the preferred phase for the general characterization of the polar HPLC fraction. A nitrogen specific non-flame thermionic detector (TSD) proves helpful in determining the nitrogen content of this fraction and a typical dual detector chromatogram is shown in Figure 2 for Paraho shale oil. The nitrogen species are primarily heterocyclic compounds with a maximal concentration in the 3-4 ring area, at a somewhat higher molecular weight range than TOSCO II or In Situ. The nitrogen content of the three oils decreases in the order Paraho > TOSCO II > In Situ, as shown both by microanalysis and TSD peak envelope areas. The In Situ oil has the lowest nitrogen content of the oils, attributable to the high degree of coking losses present in this retort process. The larger shale blocks heat slowly, causing low effective retorting temperatures and as a result extensive liquid phase polymerization occurs. Since the N-compounds selectively condense and polymerize they are in effect removed from the oil.

Identification of compounds by GC alone relies on the resolution of the columns and the ability to match retention times against standards. For full identification and characterization GC-mass spectrometer interfacing has great advantages particularly in a field as complex as petroleum analysis where it has been heavily used (9,10). To illustrate the utility of capillary gas chromatography/mass spectrometry with selective ion monitoring in characterization of shale oil classes resolved by the preparative HPLC procedures, two typical analyses are presented. Capillary GC was performed on an OV-101 WCOT fused silica column (19 meter x 200 micron i.d., Quadrex), the capillary being connected directly to the ion source of the mass spectrometer via a Pt/Ir transfer line. Sample introduction was by splitless injection with 1 mL/minute helium carrier gas flow. Mass spectral scans were at 70 eV electron impact ionization voltage, being recorded between 50-350 AMU at a scan rate of 128.6 AMU/sec.

Shale oil aromatic fractions in general show predominantly alkyl substituted benzenes, naphthalenes, indans and tetralins. Alkylbenzenes are characterized by a series of ions corresponding to masses with an empirical formula $C_6H_5C_nH_{2n+1}$ (77, 91, 105, 119, 133, 147, 161, etc.). The most characteristic ions in these spectra correspond to the rupture of the benzylic bond of the largest alkyl group. This cleavage produces the characteristic $C_7H_7^+$ tropylium ion in the case of phenylalkyls or ions of higher mass/charge ratios in the case of polyalkylbenzenes. Total ion current and specific ion detection chromatograms are shown in Figure 3 where C_4 , C_5 and C_6 substituted alkyl benzenes are characterized at m/e 133, 147, and 161 respectively. An important class of compounds which co-elute with the aromatic fraction are thiophenes, which are characterized by a series of ions corresponding to masses of empirical formula $C_4H_3SC_nH_{2n}$ (83, 97, 111, 125, etc.). The total ion and selective ion chromatogram for this class is shown in Figure 4.

The total polar HPLC fraction is too complex for direct analysis by GC-MS. The polars are normally further separated by ion exchange chromatography or acid/base extraction which, however partially degrades the sample by, for example, polymerization of the pyrroles. Resolution of the polars into acidic, neutral and basic fractions by HPLC has not been reported. Using a modified amino bonded stationary phase shale oil has been separated into four chemical classes. An analytical and preparative amino-bonded LC-9 column were washed once with two column volumes of 1% phosphoric acid in water and then reequilibrated to hexane. The chromatographic conditions were isocratic elution with hexane, a step gradient to 5% acetic acid in

hexane followed by an exponential gradient to 100% isopropanol. The overall class elution sequence was i) alkanes/alkenes/l-ring aromatics, ii) polynuclear aromatics, iii) acidics/neutral nitrogen compounds, iv) basic nitrogen compounds.

Figure 5 shows a chromatogram of In Situ shale oil on an analytical amino-bonded column. Figure 6 depicts a comparison of In-Situ shale oil bases chromatographed on a 10 meter SE-30 wide bore (300 micron i.d.) fused silica column (A - obtained by acid extraction, B - obtained by preparative HPLC. Below 140°C the chromatograms show the same pattern except for some initially lower relative peak heights in A due to evaporation losses. Above 140°C curve A shows much lower relative amounts of compounds due presumably to inefficiency of acid extraction of the higher molecular weight basic nitrogen compounds.

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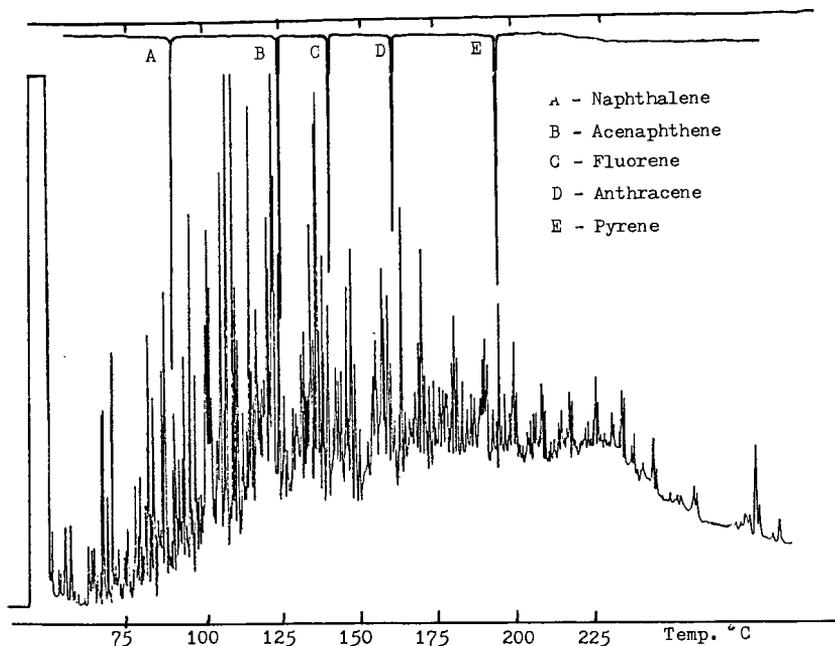


Figure 1. SP 2100 fused silica capillary chromatograms; TOSCO aromatic fraction.

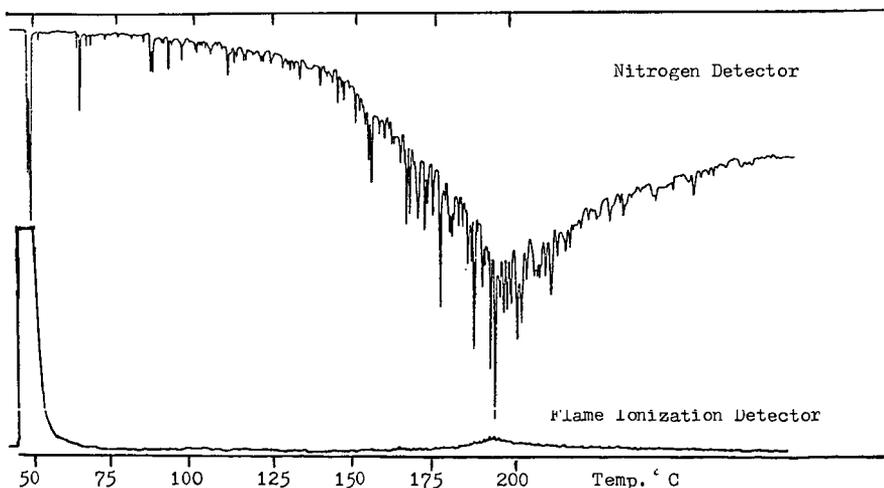


Figure 2. Simultaneous flame ionization and nitrogen specific detection of Paraho Polar fraction on Carbowax 20M glass WCOT column.

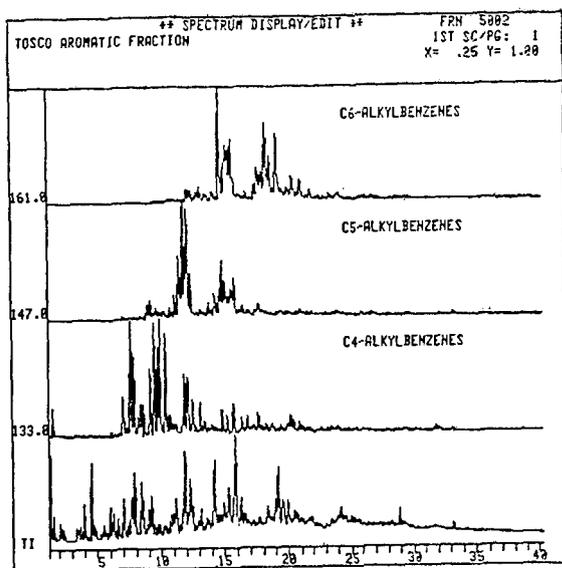


Figure 3. Tosco aromatic fraction; total ion current and selective ion chromatograms. C_4 , C_5 and C_6 alkyl benzenes at m/e 133, 147 and 161.

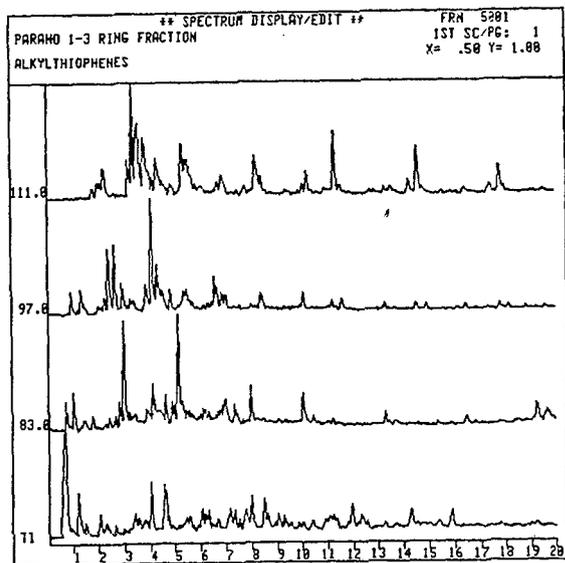


Figure 4. Paraho 1-3 ring fraction; total ion and selective ion chromatograms Alkylthiophenes $C_4H_3SC_nH_{2n}$.

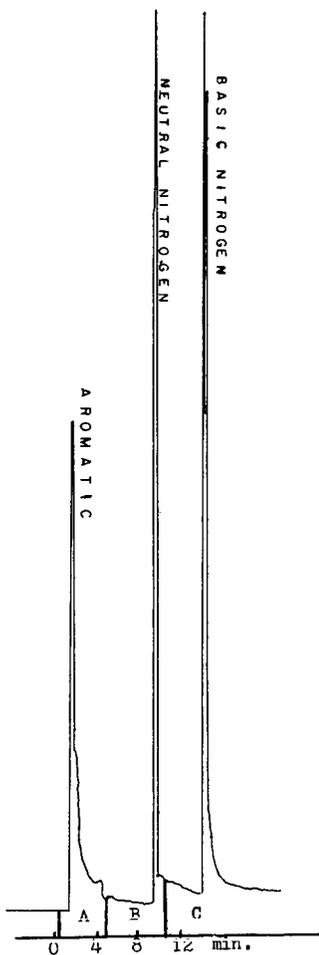


Figure 5. Chromatogram of 4 µl of In Situ shale oil (50% in n-hexane) on 10 micron LC-9 amino-bonded HPLC column. Solvents: A - n-hexane; B - 5% acetic acid/n-hexane C - isopropanol.

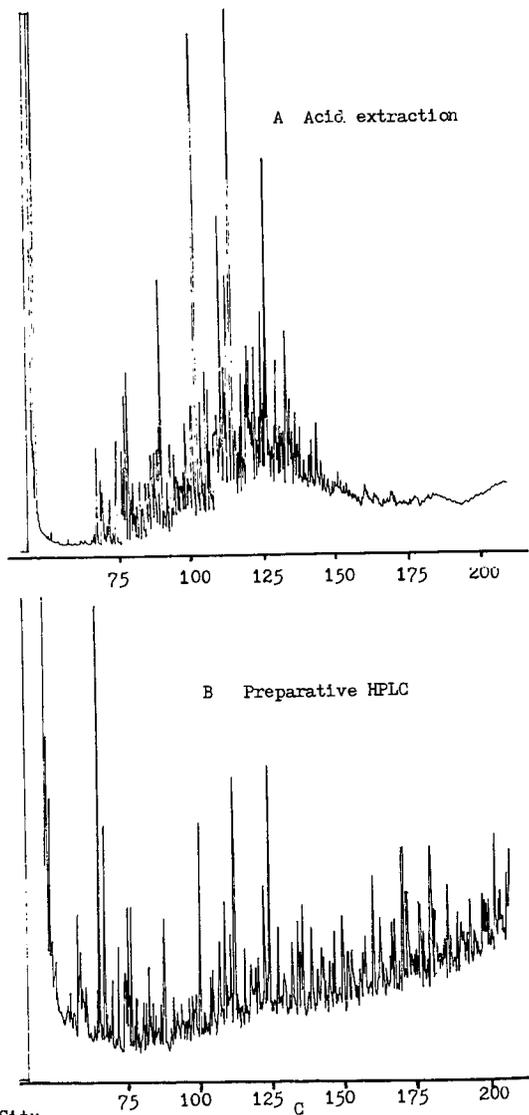


Figure 6. In Situ shale oil bases on a 10 meter SE 30 fused silica column (300 micron i.d.) A - acid extraction; B - preparative HPLC.