HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY SEPARATION OF OLEFIN, SATURATE, AND AROMATIC HYDROCARBONS IN HIGH-BOILING DISTILLATES AND RESIDUES OF SHALE OIL

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ABSTRACT

A high-performance liquid chromatography (HPLC) method has been developed for the separation of olefin, saturate, and aromatic hydrocarbons found in high-boiling distillates and residues of shale oil and in whole shale oils. The dual-column chromatographic system uses silica gel in one column and silica gel coated with silver nitrate in a second column. Separated fractions are analyzed by infrared and carbon-13 nuclear magnetic resonance spectrometry to demonstrate the validity of the separation. The time required for a separation is about two hours. The separations are reproducible, and recovery of material after separation is generally better than 90 percent. The olefin, saturate, and aromatic fractions obtained from a separation are suitable for further analysis.

INTRODUCTION

As increased amounts of shale oil are processed together with petroleum, it becomes increasingly important to have methods available for the analyses of shale oil. A fundamental difference in the composition of shale oil and petroleum is that shale oil contains three major hydrocarbon compound types--olefins, saturates, and aromatics--while petroleum contains only saturates and aromatics. Olefins, because they are hydrogen deficient and unstable, cause problems in the processing of shale oil that are not encountered in the processing of petroleum. They are also of special interest because the amounts, and perhaps kinds, of olefins in shale oil are related to the retorting conditions that produce the shale oil. Techniques for the analysis of saturates and aromatics in petroleum are well known; however, methods for determining olefin, saturate, and aromatic hydrocarbons in the heavy distillate and residue portions of shale oil are needed.

Many techniques for the determination of olefins, saturates, and aromatics have been reported in the literature (1-11). The methods usually involve liquid chromatography with silica gel (3, 4, 10) or liquid chromatography combined with chemical reactions (1, 11, 12). The methods work well in the analytical applications for which they were designed--primarily the determination of hydrocarbon types in light distillates. Difficulties, such as incomplete separation of compound types, often arise when the methods are applied to the analyses of heavier hydrocarbon fractions. The purpose of the work discussed in this paper is to extend the analysis of olefin, saturate, and aromatic hydrocarbons to the high-boiling distillate and residue fractions of shale oil. Several requirements were established for a satisfactory analytical method: 1) the determination should be fast; 2) the results should be reproducible; 3) the samples should have minimum exposure to air, light, and heat; and 4) the separated hydrocarbon types should be chemically unaltered and therefore suitable for further analyses.

This paper describes a dual-column high-performance liquid chromatography (HPLC) method for the separation and determination of olefin, saturate, and aromatic hydrocarbons in high-boiling distillate and residue fractions of shale oil. The method can also be used to separate hydrocarbon types in whole shale oils. The dual-column technique uses silica gel to separate aromatic hydrocarbons from olefin and saturate hydrocarbons and silica gel coated with silver nitrate to separate olefin from satu-

rate hydrocarbons. Cyclohexane is used as solvent for the hydrocarbon samples. The time required for a separation is about two hours.

EXPERIMENTAL

Apparatus

Shale oil distillates and residues were obtained using an ASCO (Arthur F. Smith Co.) 2-in. Rota-Film (wiped-wall) still. Acids, bases, and neutral nitrogen compounds were removed from the samples using a gravity-flow glass column (2.5 cm x 90 cm) packed in three sections with anion resin, cation resin, and ferric chloride/Attapulgus clay. The column was wet-packed using cyclohexane.

Hydrocarbon separations were made using a dual-column system in a Waters Associates AGC/GPC-202 liquid chromatograph equipped with refractive index and ultraviolet detection units. The first column contained silica gel, and the second column contained silica gel coated with silver nitrate. Both columns were stainless steel (7.8 mm i.d. x 61 cm) and were supplied with 5-micron fritted end fittings. Infrared spectra were recorded on a Perkin-Elmer model 621 spectrophotometer, and carbon-13 NMR spectra were obtained using a Varian CFT-20 spectrometer.

Materials

Amberlyst IRA-904 anion-exchange resin (Rohm and Haas) was used for removal of acids, and Amberlyst A-15 cation-exchange resin (Rohm and Haas) was used for removal of bases. Attapulgus clay, 50/80 mesh (Engelhard Minerals and Chemical Corp.) coated with ferric chloride (Baker and Adamson) removed neutral nitrogen compounds from the samples. The preparation of resins and ferric chloride/Attapulgus clay has been described (13).

Silica gel 60G (E. Merck) for thin-layer chromatography was used as received to separate aromatics from saturates and olefins. The same silica gel coated with 20 percent silver nitrate (Baker and Adamson) separated saturates from olefins. The silver nitrate-coated gel was prepared by dissolving the silver nitrate in water, mixing the solution with silica gel, and removing the water on a rotary evaporator. The gel was activated at 110°C for 12 hours. Cyclohexane, benzene, and methanol were commercial HPLC-grade solvents from various suppliers and were used as received.

Shale Oil Samples

The shale oils used in this study were produced by in situ and aboveground retorting processes (14). The Site 9 oil was obtained from the Laramie Energy Technology Center (LETC) in situ experiment near Rock Springs, Wyo. The 150-ton retort oil is from the LETC simulated in situ 150-ton retort near Laramie, Wyo. Paraho and Superior oils are from aboveground retorts located at Anvil Points, Colo., Cleveland, Ohio, respectively.

Distillation of Shale Oils

Crude shale oils that had been centrifuged to remove particulate matter and water were distilled using a wiped-wall still. The still was operated at 20 torr to remove oil boiling below 210°C (corrected to atmospheric pressure). Distillate fractions boiling from corrected temperatures of 210 to 370°C and 370 to 535°C were obtained at lower pressures and increased temperatures. The residue was recovered material that did not distill at 250°C (corrected) and 0.2 torr. The residue was actually exposed to a temperature of 250°C for only a few seconds so that thermal degradation was minimal.

Preparation of Hydrocarbon Samples

A sample (1 g) of distillate, residue, or whole shale oil was dissolved in cyclohexane (100 ml) and passed through a gravity-flow glass column containing successive beds of anion (80 g) and cation (80 g) resins and ferric chloride/ Attapulgus clay (100 g). The column was washed with cyclohexane (500 ml) to recover the hydrocarbons. The cyclohexane was removed from the hydrocarbons using a rotary evaporator.

Preparation and Assembly of HPLC Columns

A reservoir column was attached to an empty HPLC column, and both columns were filled with dry silica gel or silver nitrate/silica gel (about 20 g). Cyclohexane was then pumped through the system to wet and compress the packing material into the HPLC column. The reservoir column was then detached. Columns packed using this technique contained 15 g of gel wetted with cyclohexane, and the gel was uniformly distributed in the column. After a separation, the silver nitrate/silica gel column could be reactivated by washing with cyclohexane (100 ml). The silica gel column was not reusable. Figure 1 shows the dual-column assembly, chromatograph, and detectors.

Column Calibration

During routine analyses, the cut point for the separation of saturates and olefins from aromatics on the silica column was made according to elution volume. The proper elution volume was established prior to the separations by passing samples through the silica gel column and monitoring the separation with ultraviolet and refractive index detectors. Once the proper elution volume had been established, the detectors were removed from the chromatographic system.

Separation Procedure

A routine separation was made in the following manner. A shale oil hydrocarbon sample (200 mg), dissolved in cyclohexane (1 ml), was placed on the silica gel column, and cyclohexane was pumped through the two columns for 40 minutes at a rate of 1 ml/min and a pressure of about 350 psig. Under these elution conditions aromatics are retained on column 1, while saturates and olefins pass through to column 2. Valves between the columns and a second solvent reservoir allowed continued pumping cyclohexane through the second column where olefins and saturates were separated. Saturates were eluted with cyclohexane from the silver nitrate column with continued pumping for 30 minutes at 1 ml/min. Olefins were then eluted from the silver nitrate column by pumping benzene/cyclohexane, 20/80 percent, through the column for 30 minutes at 1 ml/min. Simultaneously, benzene/methanol, 40/60 percent, was pumped through the first column for 60 minutes to elute aromatics. The total separation time was about 2 hours.

DISCUSSION

Identification of Hydrocarbon Types

Infrared and carbon-13 NMR spectrometry were used to analyze the hydrocarbon fractions prepared by the dual-column chromatographic system. The analyses demonstrate the validity of the separations. Both spectrometric techniques have special analytical advantages and limitations; when used together they permit a satisfactory analysis of the hydrocarbon fractions.

The fractions of saturates, olefins, and aromatics were first examined using infrared spectrometry. Two absorption bands were used to analyze the fractions: 1) the monoolefin stretching band at 1630 cm^{-1} to identify olefins and 2) the aromatic ring carbon-carbon stretching band at 1600 cm^{-1} to identify aromatics. Saturates have no absorption bands in the infrared that distinguish them from other hydrocarbon types.

An example of the use of infrared spectrometry in analyzing hydrocarbon fractions presented in Figure 2, which shows the partial infrared spectrum of the total hydrocarbons from a 210-370°C distillate together with the partial infrared spectra of separated fractions. In Figure 2a, both mono-olefin and aromatic absorption may be seen in the spectrum of the total hydrocarbons. Figures 2b, 2c, and 2d show that a separation of aromatics, olefins, and saturates has been achieved. Only trace amounts of aromatics absorbing at 1600 cm^{-1} can be observed in the spectrum of the saturates (Fig. 2d) and olefins (Fig. 2c). Olefins are observed in only the olefin fraction (Fig. 2c).

In general, infrared spectrometry is a very useful method for analyzing the hydrocarbon fractions because it is fast and sensitive. It does, however, have limitations. First, in a mixture of hydrocarbon types, saturates cannot be distinguished from olefins or aromatics. Second, use of the 1630 cm^{-1} band does not allow the detection of conjugated di- and tri- olefins. Third, infrared analyses of complex mixtures of olefins cannot be quantitative because the molar absorptivities of individual olefinic compounds are quite variable. The correct value of molar absorptivity to use in an infrared calculation involving Beer's law is not known.

Carbon-13 NMR spectrometry was used to complement infrared spectrometry in the analyses of separated fractions. These data confirmed infrared data and provided additional information about the hydrocarbon types, especially the olefins.

Figure 3 shows carbon-13 NMR spectra of saturates (Fig. 3a), olefins (Fig. 3b), and aromatics (Fig. 3c) from a 370-535°C hydrocarbon concentrate. For quantitative determination of olefins, the spectral region of interest is between 110 and 140 ppm relative to tetramethylsilane (TMS). Saturates show no carbon-13 absorption in this region. Olefins show absorption bands between 114 and 138 ppm (15, 16); the position of absorption is dependent upon the type of olefin. Alpha olefin bands are observed at 114 and 138 ppm, while internal olefins have absorption bands between 114 and 138 ppm. Aromatic carbons are seen as a broad, symmetrical absorption envelope centered at about 128 ppm. Figure 3a shows that, in this particular separation run, the saturates contain 1 or 2 percent of another hydrocarbon type, probably aromatics. Olefins are observed only in the olefin fraction, not in the saturate or aromatic fractions. Trace amounts of aromatics appear to be in the olefin fraction, confirming the infrared data.

Carbon-13 NMR is useful not only because it aids in judging the quality of separation that has been achieved but also because it provides detailed information about molecular structure. For example, in an olefin mixture, the number of double bonds of an average olefin molecule can be calculated if the average molecular weight of the olefin mixture is known and if the ratio of aliphatic/olefinic carbons can be measured by carbon-13 NMR. However, carbon-13 NMR also has limitations. First, in a mixture of hydrocarbons, saturates cannot be distinguished from olefins and aromatics. Second, olefins may not be observable in a concentrate of saturates or aromatics if the amount of olefins is lower than about 3 or 4 percent. Third, with carbon-13 spectrometry alone, it may be difficult to distinguish between internal olefins and aromatics; in such a case ultraviolet analyses are useful.

Infrared and NMR analyses established that saturate, olefin, and aromatic compound classes were separated into three discrete fractions by the dual-column system. This allowed the quantitative determination of each class to be made gravimetrically.

Separation Results

a. Hydrocarbons in High-Boiling Distillates and Residues. - The dual-column method was used to separate hydrocarbons from three different boiling ranges of four shale oils. The results of the separations are shown in Table 1. All data were obtained gravimetrically. Duplicate determinations were made to show the reproducibility that

can be expected with the separation technique. In most cases the reproducibility is similar to that experienced in the silica gel separation of saturate and aromatic hydrocarbons in petroleum. The cause of the poor reproducibility experienced in some runs is not known. The recovery of separated hydrocarbon types was generally better than 90 percent.

From a characterization point of view, the data in Table 1 show some interesting trends. First, distillates and residues from the Site 9 in situ oil and the 150-ton retort oil contain smaller amounts of olefins and larger amounts of saturates than the other oils. Thus, it appears that the Site 9 and 150-ton retort oils were produced under milder retorting conditions than the Paraho and Superior oils. Second, the distributions of hydrocarbon compound types as related to distillation temperature can be seen. For example, in the Site 9 oil, the aromatics increase as the distillation temperature increases. The olefins are constant in the distillates and increase in the residue. These changes are at the expense of saturates which decrease as the distillation temperature increases.

b. Hydrocarbons from Whole Shale Oils. - The dual-column method permitted the fast determination of saturates, olefins, and aromatics in whole shale oils. The results of the separations are shown in Table 2. Both reproducibility and recovery values are similar to those seen in the separation of distillates and residues. Unknown amounts of light hydrocarbons from the whole shale oils were lost during the solvent-removal procedure.

SUMMARY AND CONCLUSIONS

An HPLC method has been developed for the separation of saturates, olefins, and aromatics in high-boiling distillates and residues of shale oil and in whole shale oils. The dual-column chromatographic system uses silica gel in one column and silica gel coated with 20 percent silver nitrate in a second column. The time required for a separation is about two hours. The separations are reproducible; recovery of material after separation is generally better than 90 percent. The saturate, olefin, and aromatic fractions obtained from a separation are suitable for further analyses.

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DISCLAIMER

Mention of specific models or brand names of equipment is made for information only and does not imply endorsement by the Department of Energy.

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TABLE 1. - Hydrocarbon separation results of distillates and residues

Sample		Wt. percent of total hydrocarbon fraction			Percent recovery
		Saturate	Olefin	Aromatic	
150-ton,	210-370°C dist.	64	5	19	88
	"	63	7	20	90
	370-535°C dist.	61	6	29	96
	"	59	7	34	100
	>535°C residue	45	11	43	99
	"	45	11	38	94
Site 9,	210-370°C dist.	70	5	17	92
	"	72	6	23	101
	370-535°C dist.	64	6	24	94
	"	59	5	29	93
	>535°C residue	48	8	40	96
	"	40	10	47	97
Paraho,	210-370°C dist.	25	27	30	82
	"	36	23	26	85
	370-535°C dist.	38	24	34	96
	"	31	23	35	89
	>535°C residue	19	10	48	77
	"	23	13	44	80
Superior,	210-370°C dist.	25	29	30	84
	"	27	36	28	91
	370-535°C dist.	32	21	42	95
	"	32	22	42	96
	>535°C residue	27	22	47	96
	"	31	19	48	98

TABLE 2. - Hydrocarbon separation results of whole shale oils

Shale oil sample	Wt. percent of hydrocarbons from total oil			Percent recovery
	Saturate	Olefin	Aromatic	
150-ton retort	53	17	22	92
"	40	21	22	83
Site 9 retort	46	18	18	82
"	55	15	20	90
Paraho retort	41	27	24	92
Superior retort	41	26	32	99
"	36	31	28	95

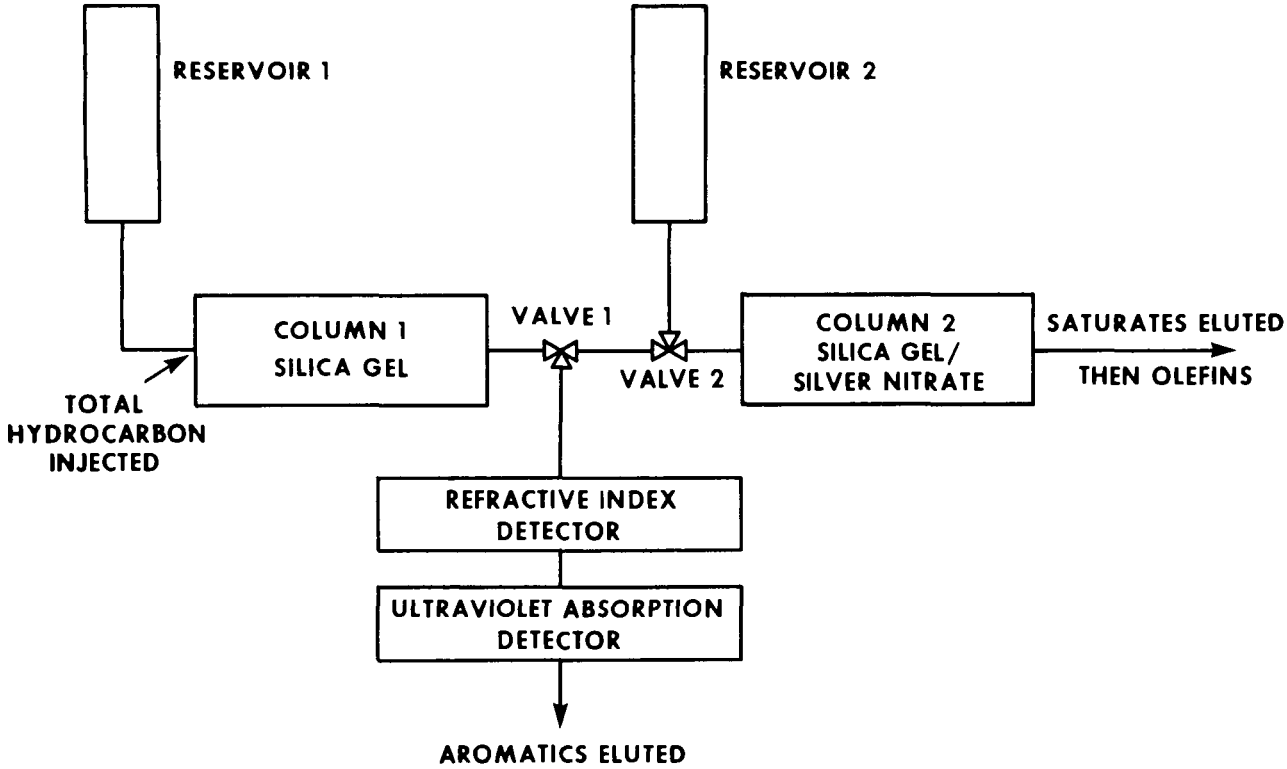

FIGURE 1. HPLC apparatus

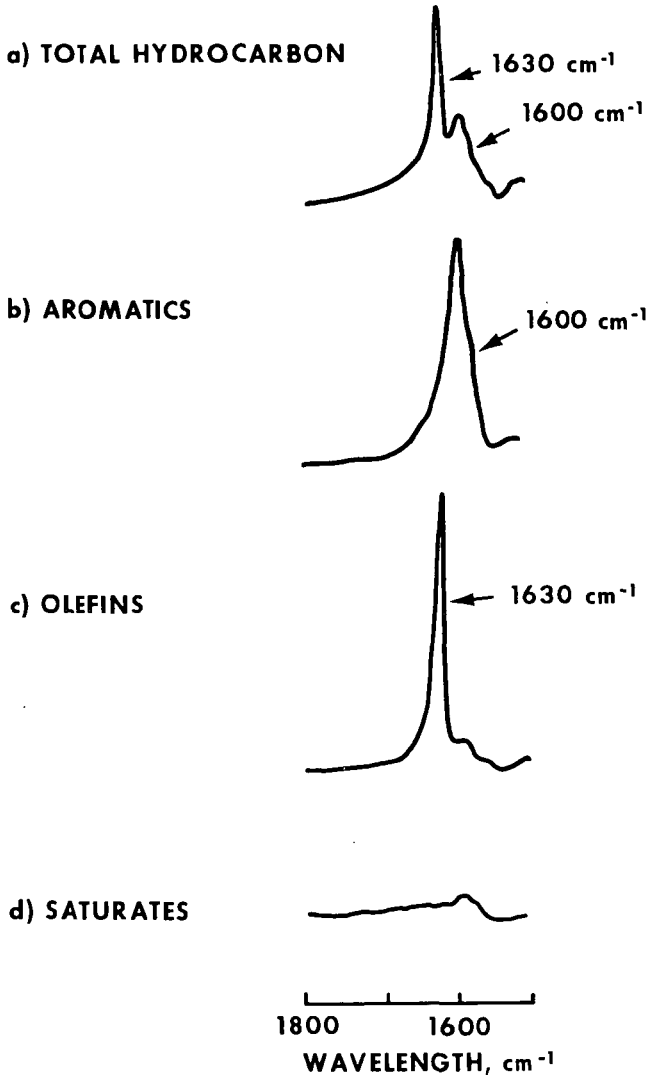

FIGURE 2. Partial infrared spectra of shale oil 210-370°C distillate total hydrocarbon and fractions

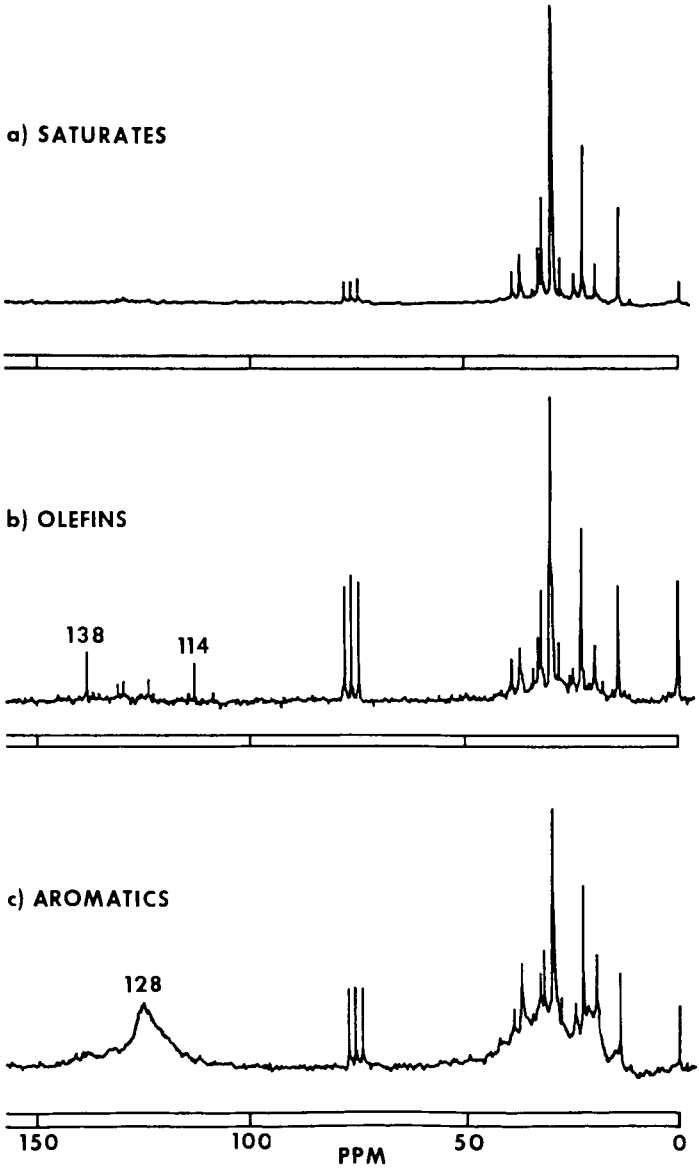

FIGURE 3. Carbon-13 NMR spectra of hydrocarbon fractions from Paraho 370-535°C distillate