The irradiations are short thus providing for rapid determinations.

Maximum sensitivities can be obtained because the use of high beam intensities (10 μA or more) appears feasible for short irradiations. High beam intensities might have to be restricted, however, in cases involving the determination of very volatile elements (Se, Br).

Further increases in sensitivity may be obtained by repetitive irradiation-counting cycles.

The samples remain intact; even easily destroyed matrices which cannot withstand the heat dissipated in a prolonged irradiation could be considered for analysis.

The cost of analysis per sample is minimized due to the short beam time required and the elimination of radiochemical processing necessary in many cases involving longer irradiations.

Finally it is interesting to contrast the possibilities of short lived proton activation with reactor neutron activation. Most of the thirteen elements which gave little or no activity have high neutron absorption and/or activation cross sections, resulting either in severe flux depression problems or in the build-up of high levels of radioactivity. In these cases proton activation appears to be much better suited for nondestructive trace characterization.

ACKNOWLEDGMENT

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Ion-Exchange, Coordination, and Adsorption Chromatographic Separation of Heavy-End Petroleum Distillates

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Information about the composition of heavy-end petroleum distillates is needed because of the increased use of this material as an energy source. The complexity of the heavy ends requires extensive separation to give fractions amenable to compositional studies. A separation scheme is described that separates heavy-end petroleum distillates into acid, base, neutral-nitrogen, saturate, and aromatic fractions. The analytical techniques used include anion- and cation-exchange chromatography, coordination chromatography, and adsorption chromatography. The scheme has been applied to heavy-end distillates from a variety of crude oils having different compositional characteristics. Data from mass spectral analysis of the saturate and aromatic fractions are presented.

INCREASED ENERGY REQUIREMENTS together with increased environmental constraints require more efficient use of the heavy ends of petroleum. These factors will require increased processing, which to be efficiently accomplished requires a more intimate knowledge of the composition of the heavy ends of petroleum. To obtain this knowledge, a research project was established under the joint sponsorship of the Bureau of Mines and the American Petroleum Institute. One of the objectives of this project is to develop methods for the characterization of petroleum fractions boiling above 400 °C. To achieve this objective, the chemically complex, high-boiling distillate cut must be subdivided into simpler fractions that are amenable to suitable analysis. The separation scheme should meet several requirements. First, the individual separation procedures as well as the overall procedure should be analytically repeatable. Second, they must be applicable to high-molecular-weight distillates and residual fractions. Third, they should be experimentally convenient and involve a minimum investment of man hours. Finally, they should allow the recovery of the compound types present with no chemical alteration.

This paper describes a separation scheme that removes the "polar" nonhydrocarbon compounds as acid, base, and neutral-nitrogen fractions. The acid and base fractions are removed with anion- and cation-exchange resins, respectively, while the neutral-nitrogen fraction is obtained by coordination-complex formation with ferric chloride supported on Attapulgus clay. The remaining hydrocarbon and "nonpolar" nonhydrocarbon compounds are separated into saturate and aromatic fractions by adsorption chromatography using silica gel. The scheme has been applied to heavy-end distillates from several crude oils. Mass spectral analyses have been obtained on some of the saturate and aromatic fractions.

The use of ion-exchange resins to remove acids and bases from petroleum fractions was first suggested by Munday and Eaves (*1*), and several workers (*2–6*) have used the technique for that purpose. Hartung and Jewell (7) reported the use of ferric chloride to form coordination complexes with nitrogen

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[2] To whom correspondence should be addressed.

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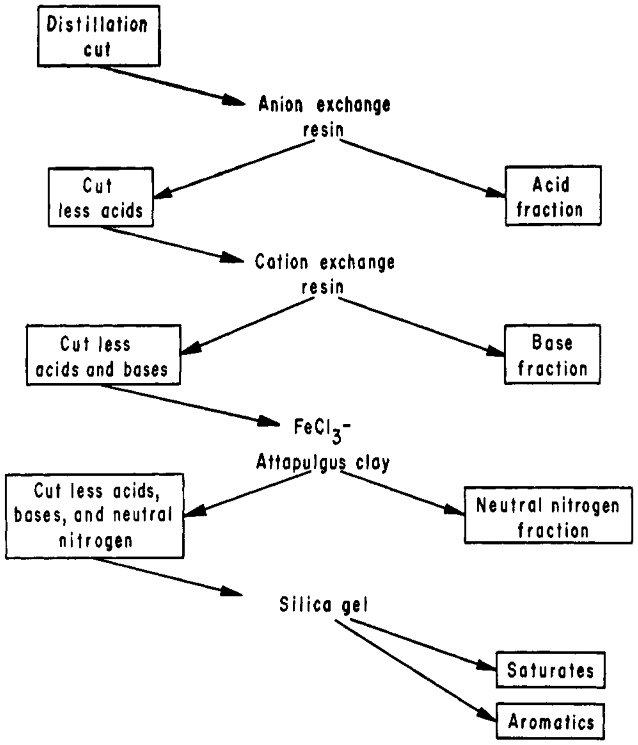

Figure 1. Separation scheme

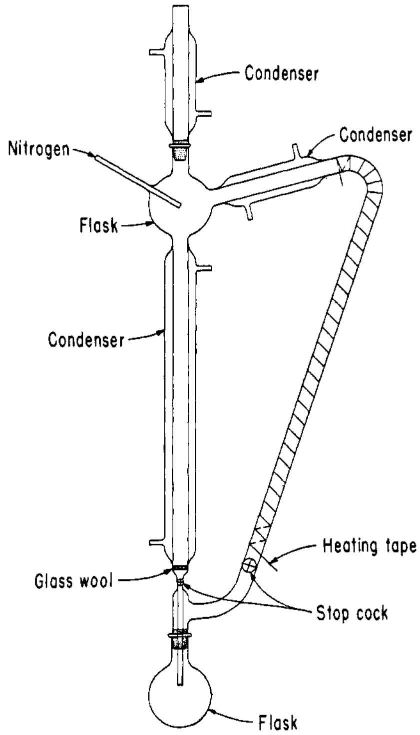

Figure 2. Recycling chromatographic column

compounds in petroleum, and Jewell and Snyder (*8*) improved the technique by supporting the metal salt on a kaolin substrate. This study reports the combination of the above techniques into a separation scheme that provided some analytical data and also produced analytical samples suitable for further characterization studies.

EXPERIMENTAL

Reagents. The anion-exchange resin was Amberlyst A-29, and the cation-exchange resin was Amberlyst 15, both supplied by Rohm and Haas. The Attapulgus clay (LVM, 50/80 mesh) was obtained from Engelhard Minerals and Chemicals Corp. and the silica gel (grade 12, 28–200 mesh) from Davidson Chemical Co. Reagent grade ferric chloride hexahydrate and potassium hydroxide were obtained from Baker and Adamson Co. *n*-Pentane (99%, Phillips Petroleum) was further purified by flash distillation and by percolation through activated silica gel; benzene, methanol, and chloroform (reagent grade, Baker and Adamson) were flash distilled; methylene chloride and 1,2-dichloroethane (reagent grade, Eastman Chemical Co.) were purified by percolation through activated silica gel. Isopropyl amine (reagent grade, Eastman) was used as received.

Preparation of Heavy-End Distillates. The distillates were prepared from five crude oils—Wilmington (Calif.), Wasson (Tex.), Gato Ridge (Calif.), Red Wash (Utah), and Recluse (Wyo.)—by a series of vacuum distillations at the Bureau of Mines Bartlesville Petroleum Research Center. The low-boiling material was removed by stripping at 10 Torr and 100 °C in an all-glass isothermal still. The gas-oil distillate was removed in a wiped-wall vacuum still operating at 1×10^{-1} Torr and 130 °C. Two heavy-end distillates were obtained by vacuum distillation in the wiped-wall still at 25×10^{-3} Torr and 237 °C, and then at 5×10^{-3} Torr and 296 °C. Thermal exposure of the oil to heated surfaces was minimized by short residence times. No detectable decomposition occurred during these distillations. Good agreement was found between the boiling points indicated by pressure–temperature relationships and simulated distillation data.

Preparation of Resins and Adsorbents. ANION-EXCHANGE RESIN. Amberlyst A-29 resin was washed four times with a methanolic HCl solution (10% volume aqueous HCl in methanol) and then rinsed with distilled water until the washings were neutral to litmus paper. The resin was activated with methanolic hydroxide solution (10% weight potassium hydroxide in methanol) and again washed with distilled water until the washings were neutral to litmus paper. Final preparation of the resin was made by 24-hour Soxhlet extractions with each of the following solvents: methanol, benzene, and pentane. The resin was then dried for 24 hours at 40 °C in a vacuum oven.

CATION-EXCHANGE RESIN. Amberlyst 15 was washed four times with a methanolic hydroxide solution (10% weight potassium hydroxide in methanol) then rinsed and Soxhlet extracted with methanol. The resin was activated by adding it slowly to a stirred solution of 10% volume HCl in methanol (Caution—exothermic reaction). The resin was then washed with distilled water until the washings were neutral to litmus paper. Final preparation was made by 24-hour Soxhlet extraction of the resin with each of the following solvents: methanol, benzene, and pentane. The resin was then dried for 24 hours at 40 °C in a vacuum oven.

FERRIC CHLORIDE ON ATTAPULGUS CLAY. Ferric chloride was supported on Attapulgus clay by contacting the clay for one hour with a methanolic–ferric chloride solution (10 weight per cent ferric chloride hexahydrate in methanol). The ferric chloride–Attapulgus clay was filtered, washed several times, extracted with pentane for 48 hours in a Soxhlet to remove entrained nonadsorbed metal salt, and then dried at room temperature. The material contained 0.6–0.8% weight of iron.

SILICA-GEL ADSORBENT. The silica gel was activated by heating at a temperature of 225 °C for 24 hours in a gravity convection oven and stored in a desiccator.

Separation Procedure. A schematic diagram of the separation scheme is shown in Figure 1. All separations were carried out under nitrogen, and the columns were initially purged with nitrogen. Each column was water-jacketed and con-

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Table I. Analytical Data on Heavy-End Distillates and Residuum

Crude oil	Boiling range at 760 Torr, °C	Av mol wt^a	Heteroatom, % wt			Fraction, % wt					
			Sulfur	Nitrogen	Oxygen	Acid	Base	Neutral nitrogen	Saturate	Aromatic	Total
Wilmington	370–485	403	1.40	0.46	0.54	4.5	5.5	9.7	37.8	42.7	100.2
Wilmington	>485	848	2.28	1.36	0.86	10.7	13.3	20.4	18.4	35.1	97.9
Wasson	390–505	451	2.38	0.08	0.46	2.6	3.2	6.1	44.3	43.7	99.9
Gato Ridge	370–535	331	4.67	0.26	. . .	3.6	2.7	3.8	29.1	59.8	99.0
Gato Ridge	535–675	518	6.12	0.47	. . .	6.3	5.9	6.4	13.6	65.2	97.4
Red Wash	375–545	439	0.30	0.09	0.06	1.5	1.8	1.5	76.6	19.0	100.4
Recluse	335–530	369	0.13	0.08	0.13	1.2	0.9	1.6	75.6	21.4	100.7
Recluse	530–675	588	0.20	0.17	0.19	3.0	2.9	4.4	58.7	25.1	94.1

^{a} Vapor phase osmometry in benzene solvent.

tained a recycling arrangement that permitted the continuous elution of the sample without the need of large quantities of solvent. Figure 2 illustrates a recycling chromatographic column of the type used. All fractions were freed of solvent by vacuum stripping, followed by a nitrogen gas sweep at steam-bath temperature until a constant sample weight was obtained.

The scale of the procedures described is that used in our laboratory. Each procedure can be scaled up or down if the ratio of the sample to resin or adsorbent remains constant.

ANION-EXCHANGE CHROMATOGRAPHY. The anion-exchange resin (40 grams) was packed into a 1.4- × 119-cm column. The sample (20 grams) was dissolved in 175 to 200 cc of pentane (cyclohexane is required for oils having a high wax content) and charged to the resin. Entrained, unreactive material was washed from the resin with 200 cc of pentane for approximately 42 hours using the recycling arrangement of the column. After removal of the unreactive materials, the reactive material (acids) was recovered by successive 24-hour elutions with benzene, followed by methanol, and finally with methanol saturated with CO_2. These three solvents remove compounds of increasing acid strength, and the fractions can be analyzed separately or combined to give a total acid fraction. Data reported in this paper are on the total acid fraction.

CATION-EXCHANGE CHROMATOGRAPHY. The column, amounts of resin and acid-free sample, and procedure of introducing sample and eluting unreactive material were the same as for the anion-exchange chromatography step. The reactive material (bases) was removed from the resin by successive 24-hour elutions with benzene, followed by methanol, and finally with 8% volume isopropyl amine in methanol. After the benzene elution is completed, nitrogen gas is forced up through the column until the resin bed is loose. This is a precautionary procedure to prevent column breakage due to the swelling of the resin in methanol and to the exothermic reaction of the resin with isopropyl amine. As with the acids, the bases can be removed as three fractions and analyzed separately or combined to give a total fraction.

FERRIC CHLORIDE COORDINATION CHROMATOGRAPHY. Approximately 50 grams of Amberlyst A-29 anion-exchange resin was packed into a 1.75- × 116-cm column. Then about 70 grams of the ferric chloride–Attapulgus clay was packed on top of the resin. A layer of glass wool was used to separate the two. A 10-gram sample of acid- and base-free distillate, dissolved in pentane, was slowly percolated downward through the column bed. The color changes to green or blue as the distillate passes through the column, indicating the formation of iron complexes on the surface of the clay. Entrained oil was removed by pentane elution. The colored complexes were desorbed from the clay by elution with 1,2-dichloroethane. The complexes are broken upon contact with the anion-exchange resin, the metal salt is retained on the resin, and the free compounds are recovered in the effluent.

SILICA GEL CHROMATOGRAPHY. A 1.75- × 116-cm column was packed with 200 grams of activated silica gel. A 1-gram sample of the acid-, base-, and neutral-nitrogen-free distillate was dissolved in pentane and charged to the column. The saturate fraction was eluted with pentane until the ultraviolet absorbance of the eluate at 270 nm equalled 0.05. One column volume (about 200 cc) of chloroform was then charged to the column to partially deactivate the silica gel and eliminate the problem of excessive heat created by subsequent methanol desorption. The final desorption of the aromatic fraction was made with two to four column volumes of methanol.

Mass Spectral Analyses of Saturate and Aromatic Fractions. Mass spectra were obtained for the saturate and aromatic concentrates using a Consolidated Electrodynamics Corporation (CEC) Model 21-103 mass spectrometer and a CEC Model 21-110b mass spectrometer.

SATURATE FRACTIONS. The method of Hood and O'Neal (*9*) was used to analyze the saturate concentrate. This method is a high-ionizing voltage, low-resolution method which relies on specific fragment ions to characterize the hydrocarbon types. It allows the determination of zero to six condensed-ring saturates as well as the determination of small amounts of monoaromatics resulting from incomplete separation of the distillate into saturate and aromatic concentrates.

AROMATIC FRACTIONS. High- and low-resolution spectra at high- and low-ionizing voltages were used to analyze the aromatic concentrates.

Low-voltage, or parent-peak, methods depend upon sensitivity data. The sensitivity data used in the present work were from the literature (*10*), from our laboratory, and, where necessary, from extrapolation. These data were used for analyses on both high- and low-resolution spectra.

Two high-voltage, or fragment-peak, methods were used in the analyses of the aromatic concentrates. The method of Hastings (*11*), although designed for low-resolution spectra, was applied to the high-resolution spectral data from the aromatic concentrates. This method allows the determination of nine aromatic compound types and three sulfur aromatic compound types. The second method was that of Robinson and Cook (*12*), which was designed for low-resolution mass spectral data and allows the determination of 12 aromatic compound types, 3 sulfur aromatic compound types, and 6 unidentified compound types.

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Table II. Mass Spectral Analyses of Saturate and Aromatic Fractions

Rings or "Z" number	Per cent weight Wilmington 370–485 °C	Wasson 390–505 °C	Red Wash 375–545 °C	Recluse 335–530 °C
No. of rings				
0	4.7	15.3	27.9	27.7
1	7.2	12.4	11.7	19.2
2	5.7	5.6	11.1	11.8
3	6.4	5.1	8.7	6.5
4	10.1	3.3	7.1	6.5
5	2.6	1.4	6.4	2.7
6	1.1	1.2	2.1	7.8
Total saturates	37.8	44.3	75.0[a]	75.6
"Z" number[b]				
−6	7.3	10.1	6.5	3.9
−8	6.6	5.9	3.5	3.5
−10	4.8	3.9	1.9	2.0
−12	3.5	4.0	1.7	2.2
−14	5.7	4.2	2.0	2.4
−16	7.6	5.0	2.3	3.6
−18	3.7	2.9	1.5	2.3
−22	2.3	2.0	0.8	1.1
−24	1.0	0.9	0.4	0.4
Total aromatics	42.5	38.9	20.6	21.4
−10S[c]	0.2	1.6	0.0	0.0
−16S	0.0	2.8	0.0	0.0
−22S	0.0	0.4	0.0	0.0
Total sulfur	0.2	4.8	0.0	0.0
Total	80.5	88.0	95.6	97.0

[a] Monoaromatics determined in saturate fraction were added to aromatics.

[b] Refers to the formula C_nH_{2n+z}.

[c] Refers to the formula $C_nH_{2n+z}S$.

RESULTS AND DISCUSSION

One of the advantages of the separation scheme is the good reproducibility and recovery. Each separation technique was found to have a reproducibility of ±4% of the value reported. As an example, the following data were obtained from five runs on the heavy-end distillate from Wilmington crude oil: Acids, 4.46 ± 0.14% wt; bases, 5.51 ± 0.18% wt; neutral-nitrogen, 9.65 ± 0.37% wt; saturates, 37.82 ± 0.76% wt; and aromatics, 42.7 ± 1.0 % wt. Material recovery from the four separation procedures was 96% weight or better.

Table I shows the results of the separation of seven heavy-end distillates and a residuum. The average molecular weight, boiling range, per cent weight sulfur, per cent weight nitrogen, and per cent weight oxygen of each distillate are also presented to show the general applicability of the scheme. Two distillates from the Recluse and Gato Ridge oils were analyzed to show the compositional trends with increased boiling point. A heavy residuum (bp > 485 °C) from Wilmington crude oil was separated to show that the procedure is applicable to residual materials as well as to distillates.

The separation procedure provides some valuable information about the composition of the distillates. As shown in Table I, the Wilmington, Wasson, and Gato Ridge distillates are high in nonhydrocarbon compounds (acids, bases, and neutral nitrogen). These oils are also high in heteroatom content. The hydrocarbons in the Wilmington and Wasson distillates are about equally divided between saturates and aromatics, Recluse and Red Wash are high in saturates, and Gato Ridge is high in aromatics. The oils highest in saturate content are the lowest in nonhydrocarbons. The higher boiling distillates of Recluse and Gato Ridge have approximately twice the nonhydrocarbon content of the lower boiling distillates, but the ratio of the acid fraction to the base fraction to the neutral-nitrogen fraction remains about the same. The aromatic-to-saturate ratio decreases with an increase in boiling point. The Wilmington residue shows the same trend to a higher degree.

The mass spectral results from the application of Hood and O'Neal's method to the saturate fractions from the low-boiling Wilmington, Wasson, Recluse, and Red Wash distillates are presented in Table II. For all oils except the Wilmington, the concentration of compound types decreases from zero-ring compounds to six-ring compounds. In the Wilmington, the predominance of tetracyclanes is most noticeable. Previously reported work (*13*) as well as extensive NMR studies performed in our laboratory on the Wilmington saturates, is in agreement with the pronounced amount of four-condensed-ring saturates reported. Currently we are investigating subfractions of the Wilmington saturate by GC–MS so that we might obtain new calibration data to update Hood and O'Neal's method.

To check if artifacts were formed in the saturates as a result of the steps used to remove the polar materials from the distillates, two Wilmington saturate fractions were prepared and analyzed. The first was obtained by the procedure described in this investigation; the other was obtained by subjecting the distillate to the saturate-aromatic separation step only. The saturate analyses were the same within experimental error, showing that changes in the saturate portion of the oil were negligible.

Quantitative mass spectral methods used in characterizing aromatic compounds consist of high-voltage methods (fragment peak) and low-voltage methods (parent-peak). The lack of suitable standards in the high-molecular-weight range of the oils studied makes it impossible to determine the accuracy of any one method. Consequently, one must rely on agreement among several methods as a criterion of accuracy. The aromatic fractions from the distillates were analyzed by the following methods: (1) Hastings' method—high voltage, modified high resolution; (2) Robinson and Cook's method—high voltage, low resolution; and (3) parent-peak method—low voltage, high resolution. The data shown in Table II were obtained by averaging the results from the three methods. The deviations encountered were within 20% for most of the hydrocarbon components present. One notices immediately that the aromatic portions of the oil offer a means for distinguishing between oils. For example, the high concentration of alkyl benzenes in the Red Wash oil easily distinguishes this oil from the Recluse oil.

To check whether artifacts were introduced into the aromatic fraction by the "polar" separation steps, two aromatic fractions were prepared from the Wilmington distillate and analyzed by low-voltage mass spectrometry. The first sample was obtained by the procedure described in this investigation; the other was obtained by subjecting the distillate to the saturate-aromatic separation only. The most notable change in the spectra was the absence of the odd mass-to-charge ratio peaks, typical of nitrogen compounds, in the sample with the "polars" removed. This is expected because of the high nitrogen content of the polar material which has been removed. The close similarity of the even mass-to-charge ratios implied that no significant alteration has occurred in the aromatic portion of the sample as a result of the steps used to remove the polar materials and that the heteroatom compounds removed

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are evenly distributed through the hydrocarbon Z series. The latter demonstrates the importance of and the need for removal of the polar compounds to obtain a good analysis of the aromatic fraction.

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Nuclear Magnetic Resonance Spectrometry of Petroleum Fractions

Carbon-13 and Proton Nuclear Magnetic Resonance Characterizations in Terms of Average Molecule Parameters

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A novel development in compositional characterization techniques of petroleum fractions has been made based upon carbon-13 and proton nuclear magnetic resonance spectrometry. The techniques developed have two very attractive features: First, they provide a direct and accurate value of "aromaticity" or aromatic carbon as a fraction of the total carbon. Second, they provide a series of parameters or indices of an "average molecule" based entirely upon the nuclear magnetic resonance spectrum, and thus they afford an excellent characterization of complex, multicomponent petroleum fractions. The previously developed treatments of the data are reexamined and a new, improved procedure is described that provides "fingerprinting" information. It is demonstrated that high quality ^{13}C NMR data can be used to calibrate the ^{1}H NMR, and thus make it possible to obtain the required information from the ^{1}H spectra. Relatively inexpensive modifications to a conventional Varian HA-60IL spectrometer that allow us to do CW carbon-13 NMR with proton noise decoupling in the internal lock mode as well as operate with an external proton lock without decoupling are described. The techniques are illustrated in terms of some FCC charge stocks, but their applicability is wider, and they can be extended to a great variety of petroleum fractions.

Table I. Average Parameters Calculable for Petroleum Fractions

n = average number of carbon atoms per alkyl substituent.
f = average carbon-hydrogen weight ratio of the alkyl groups.
%AS = per cent substitution of alkyl groups on non-bridge aromatic ring carbons.
$\#C_A$ = average number of aromatic ring carbon atoms per average molecule.
$\#C_1$ = average number of non-bridge aromatic ring carbon atoms per average molecule.
R_A = average number of aromatic rings per average molecule.
R_S = average number of alkyl substituents per average molecule.
R_N = average number of naphthenic rings per average molecule.
f_a = molar ratio of aromatic carbon to total carbon in sample.
BI = branchiness index.
MW = average molecular weight.
$\%C_S$ = fraction saturate carbon.
$\%C_N$ = fraction naphthenic carbon.
r = number of naphthene rings per substituent
$\%C_1$ = fraction non-bridge aromatic ring carbons.
Average Molecular Formula

DETAILED COMPOSITIONAL CHARACTERIZATION of petroleum fractions is extremely important, but has proved both quite difficult and time consuming. For this reason, among the various analytical schemes that have been devised, procedures have also been proposed which attempt to describe a particular petroleum fraction in terms of a hypothetical average molecule (*1–4*). Proton nuclear magnetic resonance spectrometry can be used to provide a detailed characterization of aromatic fractions provided the proper correlation between hydrogen and skeletal carbons is used. Through the use of the integrated intensities of the various types of protons in the sample, the parameters associated with an average molecule can be ascertained. Carbon-13 nuclear magnetic resonance on the other hand is capable of directly observing the skeletal carbons, and thus by utilizing the integrated intensities of the various carbon types a good picture of the average molecule can be visualized.

Table I lists the average parameters and a brief description of each which can be determined for petroleum fractions. Various approaches can be taken to determine these parameters with some methods requiring additional information such as elemental analysis and an average molecular weight of the sample. These averages parameters are the weighted average for certain properties of the sample and upon putting these average parameters together, an average molecule can be constructed for a given sample. In most instances the values determined are non-integral.

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