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Compound-Type Separation and Characterization Studies for a 370° to 530° C Distillate of Recluse, Wyo., Crude Oil

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UNITED STATES DEPARTMENT OF THE INTERIOR

Report of Investigations 7945

Compound-Type Separation and Characterization Studies for a 370° to 530° C Distillate of Recluse, Wyo., Crude Oil

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COMPOUND-TYPE SEPARATION AND CHARACTERIZATION STUDIES FOR A 370° TO 530° C DISTILLATE OF RECLUSE, WYO., CRUDE OIL

by

D. E. Hirsch,[1] J. E. Dooley,[2] J. W. Vogh,[2] and C. J. Thompson[3]

ABSTRACT

The Bureau of Mines has developed a systematic procedure for separation, characterization, and semiquantitative analysis of high-boiling (350° to 550° C) distillates of crude oils. Isothermal and molecular distillation were used to prepare the 370° to 530° C distillate of Recluse, Wyo., crude oil. The distillate was separated into fractions by chemical treatment, silica-alumina gel adsorption, and gel permeation chromatography (GPC). The fractions were analyzed by use of GPC correlations and mass and nuclear magnetic resonance (NMR) spectrometry. The increased knowledge of petroleum composition obtained from the data will contribute to improved petroleum processing and utilization and energy conservation.

INTRODUCTION

This report is the fifth in a series of separation and characterization studies on 370° to 535° C distillates of crude oils of widely different geographic origins. Four previous investigations (2, 4-5, 10)[4] utilized a GPC correlation-mass spectral characterization procedure (11) to study the composition of 370° to 535° C distillates of Prudhoe Bay, Alaska; Gach Saran, Iran; Swan Hills (south field), Alberta, Canada; and Wilmington, Calif., crude oils.

Compositional data on these five distillates boiling in the 370° to 535° C range provide information necessary for more efficient conversion of this boiling range of petroleum into more useful energy forms (7-9). These investigations of the heavy ends of petroleum by the Bureau of Mines are performed in cooperation with the American Petroleum Institute (API) as API Research Project 60. Background information (1, 13-14) on methods, limitations (3, 6, 15), and fundamental data on selected crude oils (7-9) is available in the literature. The main objective of the project--to develop

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[1] Research chemist (now resigned).

[2] Research chemist.

[3] Acting research supervisor.

[4] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

an analytical procedure applicable to any 350° to 550° C crude oil distillate regardless of the crude oil source--has been achieved. Data obtained by the project's procedure on the fifth project crude oil (Recluse, Wyo.) are included in this report.

ACKNOWLEDGMENT

The authors are indebted to D. A. Doughty, research physicist, of the Bureau of Mines Bartlesville (Okla.) Energy Research Center for the nuclear magnetic resonance data provided in the course of this investigation. This investigation is part of the work of American Petroleum Institute Research Project 60 on "Characterization of Heavy Ends of Petroleum," which the Bureau of Mines is cooperatively conducting at the Bartlesville (Okla.) and Laramie (Wyo.) Energy Research Centers.

SAMPLE SOURCE AND PRELIMINARY ANALYSES

The Sinclair Oil Co. (now Atlantic Richfield Co.) furnished the sample from the Recluse, Wyo. oilfield. Bureau of Mines routine crude oil analyses produced the experimental data of table 1 and the derived data of tables 2 and 3.

Preparation of Distillates

The API Project 60 distillation scheme used for preparing distillates for investigation has been described (2, 4-5, 10). Figure 1 shows application of the scheme to Recluse, Wyo., crude oil to produce distillates with the following boiling ranges: 225° to 315° C, 315° to 370° C, 370° to 530° C, and 530° to 675° C.

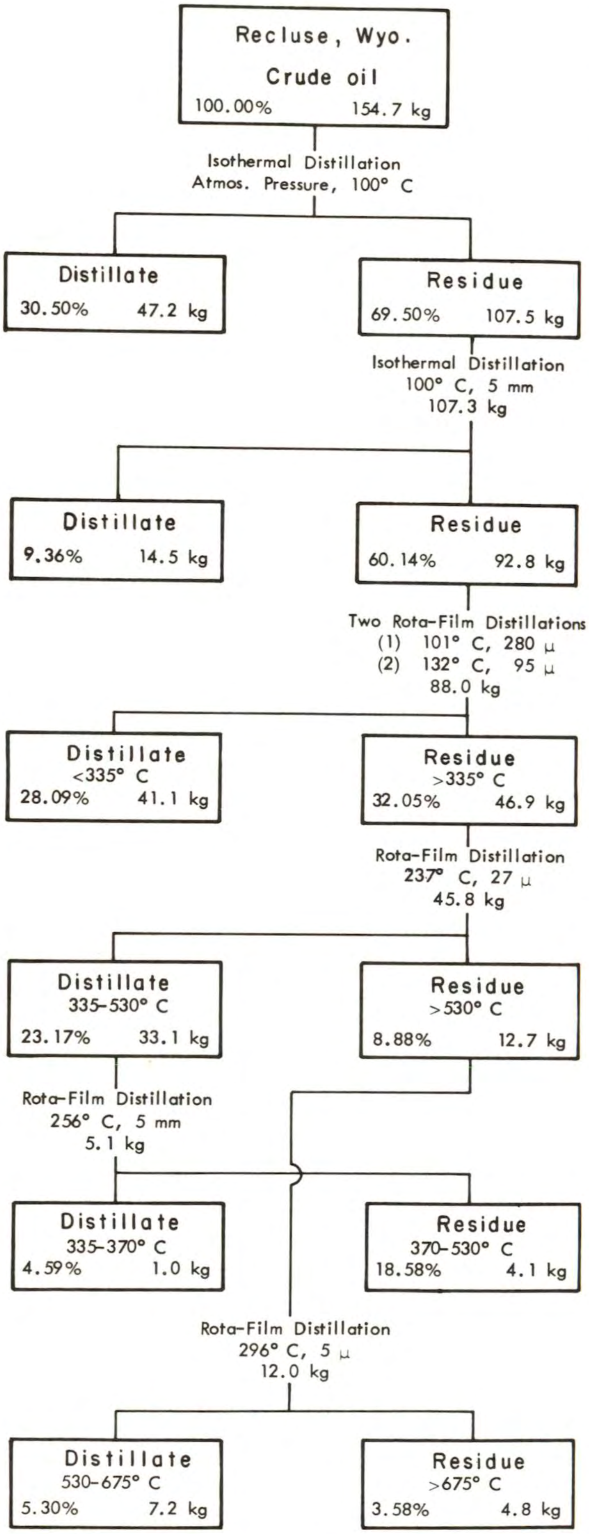


FIGURE 1. - Preparation of distillates for Recluse, Wyo., crude oil.

TABLE 1. - Data from routine analysis of Recluse, Wyo., crude oil

CRUDE PETROLEUM ANALYSIS

Bureau of Mines Bartlesville Laboratory
Sample 68169

IDENTIFICATION

Recluse field
Muddy, Dakota, Lower Cretaceous
4,700 - 5,000 feet

Wyoming
Campbell County

GENERAL CHARACTERISTICS

Gravity, specific, 0.815
Gravity, ° API, 42.1
Pour point, ° F., 60
Sulfur, percent, 0.08
Color, brownish green
Viscosity, Saybolt Universal at 77° F 42 sec ; 100° F 36 sec
Nitrogen, percent, 0.031

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

STAGE 1—Distillation at atmospheric pressure, 742 mm Hg
First drop, 77 ° F.

Fraction No.	Cut temp. ° F.	Percent	Sum, percent	Sp. gr., 60/60° F.	° API, 60° F.	C. I.	Refractive index, n_D at 20° C.	Specific dispersion	S. U. visc., 100° F.	Cloud test, ° F.
1	122	3.7	3.7	0.642	88.9					
2	167	2.7	6.4	.674	78.4	9.4	1.37815	127.8		
3	212	6.1	12.5	.718	65.6	20	1.40058	128.4		
4	257	8.2	20.7	.748	57.7	26	1.41531	135.0		
5	302	6.3	27.0	.766	53.2	26	1.42702	143.2		
6	347	5.7	32.7	.785	48.8	29	1.43595	142.9		
7	392	4.7	37.4	.797	46.0	28	1.44276	144.1		
8	437	4.8	42.2	.810	43.2	29	1.45020	145.7		
9	482	5.2	47.4	.823	40.4	30	1.45868	152.3		
10	527	4.8	52.2	.832	38.6	29	1.46523	155.2		

STAGE 2—Distillation continued at 40 mm Hg

Fraction No.	Cut temp. ° F.	Percent	Sum, percent	Sp. gr., 60/60° F.	° API, 60° F.	C. I.	Refractive index, n_D at 20° C.	Specific dispersion	S. U. visc., 100° F.	Cloud test, ° F.
11	392	4.6	56.8	0.850	35.0	34	1.47061	155.8	40	20
12	437	6.1	62.9	.858	33.4	34	1.47226	160.5	47	45
13	482	5.2	68.1	.864	32.3	33			58	70
14	527	4.9	73.0	.870	31.1	33			82	75
15	572	6.0	79.0	.885	28.4	37			142	100
Residuum		17.9	96.9	.927	21.1					

Carbon residue, Conradson: Residuum, 3.0 percent; crude, 0.6 percent.

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline	12.5	0.686	74.8	
Total gasoline and naphtha	37.4	0.742	59.2	
Kerosine distillate	10.0	.817	41.7	
Gas oil	14.0	.846	35.7	
Nonviscous lubricating distillate	10.8	.860-.875	33.1-30.3	50-100
Medium lubricating distillate	6.8	.875-.893	30.3-26.9	100-200
Viscous lubricating distillate	-	-	-	Above 200
Residuum	17.9	.927	21.1	
Distillation loss	3.1			

TABLE 2. - Supplemental data on Recluse, Wyo., crude oil analysis

Fraction	Cut point		Vol-pct crude oil	Aromatics, vol-pct	Naphthenes, vol-pct	Paraffins, vol-pct	Paraffin-naphthenes, vol-pct	Sulfur wt-pct	Nitrogen, wt-pct
	° C	° F							
1	50	122	3.7	-	-	-	100.0	-	-
2	75	167	2.7	3.2	8.5	88.3	96.8	-	-
3	100	212	6.1	4.1	32.2	63.7	95.9	-	-
4	125	257	8.2	9.0	44.3	46.7	91.0	-	-
5	150	302	6.3	16.4	32.3	47.3	83.6	-	-
6	175	347	5.7	17.2	42.1	40.7	82.8	-	-
7	200	392	4.7	18.2	40.8	41.0	81.8	-	-
8	225	437	4.8	19.3	-	-	80.7	-	-
9	250	482	5.2	22.8	-	-	77.1	0.006	-
10	275	527	4.8	22.4	-	-	77.6	.015	-
11	308	587	4.6	23.0	-	-	77.0	.026	-
12	336	637	6.1	26.4	-	-	73.6	.042	-
13	364	687	5.2	-	-	-	-	.079	-
14	392	737	4.9	-	-	-	-	.108	-
15	420	787	6.0	-	-	-	-	.111	-
Residue	-	-	17.9	-	-	-	-	.193	0.134
Crude oil	-	-	-	-	-	-	-	.08	.031

TABLE 3. - Refractive index, density, and molecular weight (n-d-M) analysis of Recluse, Wyo., crude oil[1]

	Rings in paraffins-naphthenes pct	Paraffins and paraffin-chains in paraffins naphthenes, pct	Aromatic rings/ molecule	Naphthene rings/ molecule	Total rings/ molecule
Composite, fractions 6-7....	21.7	78.3	-	-	-
Composite, fractions 8-12...	23.4	76.6	-	-	-
Fraction 12.......	-	-	0.2	1.3	1.5

[1] n = refractive index; d = density; M = molecular weight.

The 370° to 530° C distillate used in this research was evaluated by simulated distillation data derived from programed high-temperature gas-liquid chromatography (16). The resultant chromatogram and accompanying data, figure 2, indicate that 92.0 percent of the distillate is within the assigned 370° to 530° C boiling range.

Separation and Preliminary Analyses of 370° to 530° C Distillate

The complexity of the 370° to 530° C distillate has been shown for four other crude oils (2, 4-5, 10). The API Project 60 separation and characterization scheme (2, 6, 8) was used, and data for the 370° to 530° C distillate of Recluse, Wyo., crude oil are given in figure 3, which shows that wax, acid, base, and neutral nitrogen fractions are removed from the distillate. Such treatment improves the distillate from the viewpoint of separations

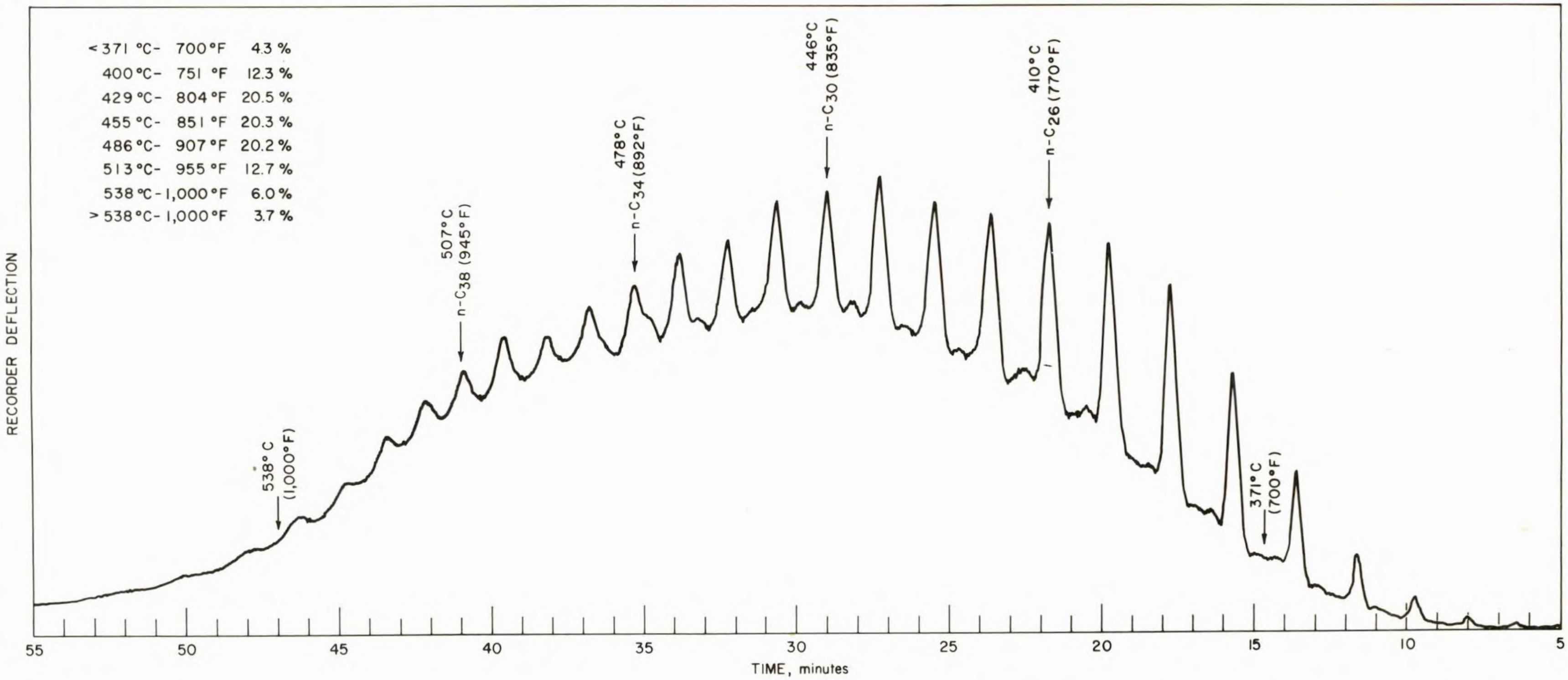
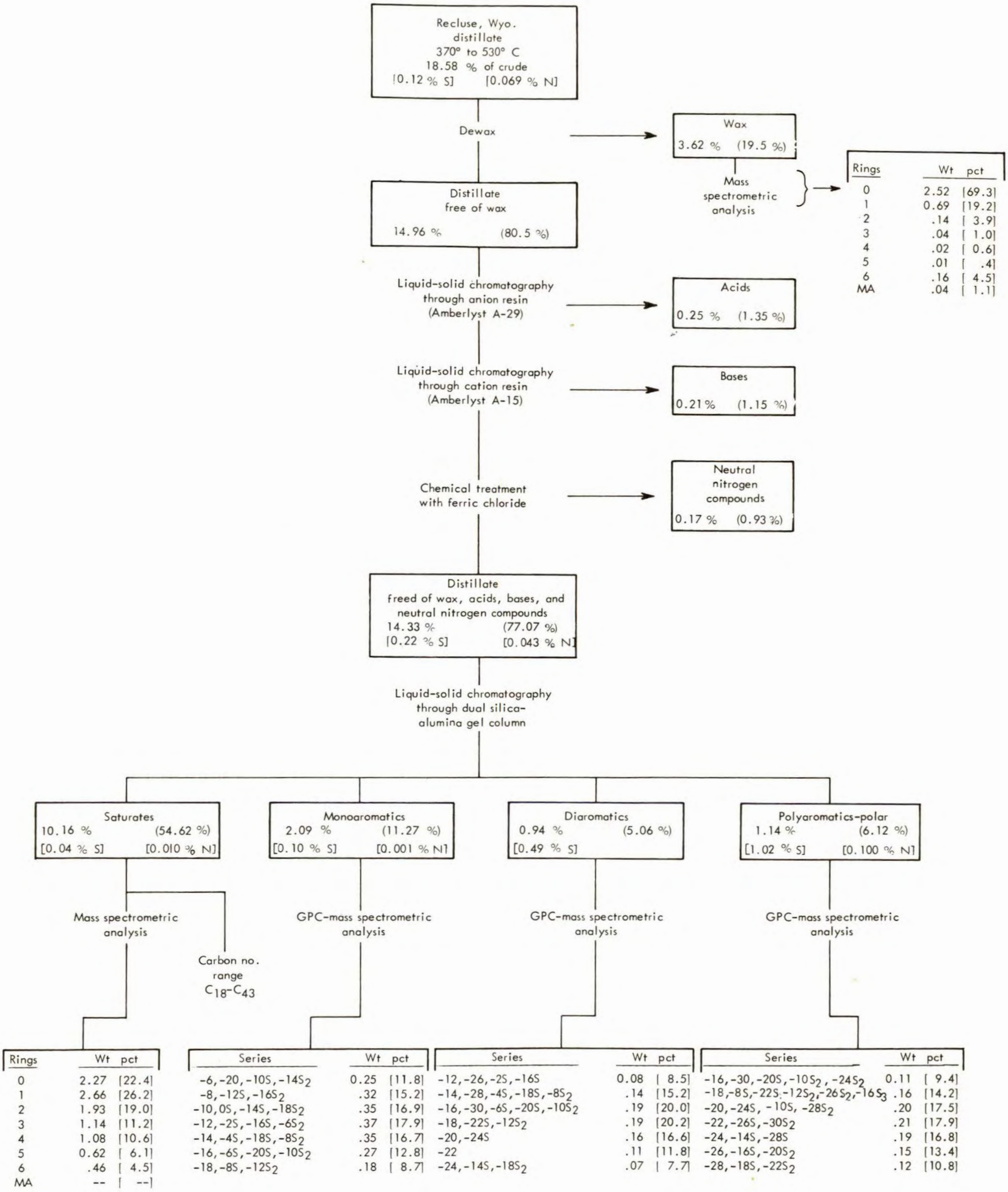


FIGURE 2. - Simulated distillation by gas-liquid chromatography of a 370° to 530° C distillate of Recluse, Wyo., crude oil.



Rings	Wt pct
0	2.52 [69.3]
1	0.69 [19.2]
2	.14 [3.9]
3	.04 [1.0]
4	.02 [0.6]
5	.01 [.4]
6	.16 [4.5]
MA	.04 [1.1]

Rings	Wt pct
0	2.27 [22.4]
1	2.66 [26.2]
2	1.93 [19.0]
3	1.14 [11.2]
4	1.08 [10.6]
5	0.62 [6.1]
6	.46 [4.5]
MA	-- [--]

Series	Wt pct
$-6,-20,-10S,-14S_2$	0.25 [11.8]
$-8,-12S,-16S_2$	.32 [15.2]
$-10,0S,-14S,-18S_2$	.35 [16.9]
$-12,-2S,-16S,-6S_2$	.37 [17.9]
$-14,-4S,-18S,-8S_2$	.35 [16.7]
$-16,-6S,-20S,-10S_2$	.27 [12.8]
$-18,-8S,-12S_2$	.18 [8.7]

Series	Wt pct
$-12,-26,-2S,-16S$	0.08 [8.5]
$-14,-28,-4S,-18S,-8S_2$	.14 [15.2]
$-16,-30,-6S,-20S,-10S_2$	.19 [20.0]
$-18,-22S,-12S_2$	.19 [20.2]
$-20,-24S$	.16 [16.6]
-22	.11 [11.8]
$-24,-14S,-18S_2$	.07 [7.7]

Series	Wt pct
$-16,-30,-20S,-10S_2,-24S_2$	0.11 [9.4]
$-18,-8S,-22S,-12S_2,-26S_2,-16S_3$	.16 [14.2]
$-20,-24S,-10S,-28S_2$	.20 [17.5]
$-22,-26S,-30S_2$	.21 [17.9]
$-24,-14S,-28S$	.19 [16.8]
$-26,-16S,-20S_2$	.15 [13.4]
$-28,-18S,-22S_2$	.12 [10.8]

Note: Percentage figures in parentheses are on distillate basis, those in brackets are on fraction basis, and others are on crude oil basis.

FIGURE 3. - Separation procedures and related analyses for 370° to 530° C distillate of Recluse, Wyo., crude oil.

and analysis. The distillate less waxes, acids, bases, and neutral nitrogen compounds is then separated by the silica-alumina gel adsorption procedure (12) into saturate, monoaromatic, diaromatic, and polyaromatic-polar material concentrates. Preliminary mass spectral analyses of these concentrates are also shown at the bottom of figure 3. The saturate analyses were derived from high-ionizing voltage (70 eV) matrices developed by Hood and O'Neal (13). The aromatic concentrates were analyzed by low-ionizing voltage (11 eV) mass spectrometry. The mass spectral Z series designations in figure 3 are those derived from GPC-mass spectral correlations developed by the Bureau of Mines (10). The weight-percent values are given for each nominal mass Z series for each of the three aromatic concentrates. These data on each of the three aromatic concentrates will be used later for comparison with the reconstituted data from GPC-mass spectral analyses of individaul GPC subfractions of each concentrate obtained by GPC separation of each whole aromatic concentrate. This reconstitution to compare the values on the sum of the parts of a concentrate with the values obtained on the whole concentrate establishes the internal consistency of the method.

CHARACTERIZATION STUDIES

Mass spectrometry alone was used to characterize the saturate concentrate. GPC correlations, and mass and NMR spectrometry were used to analyze the three aromatic concentrates. The GPC separation technique has been described (2), and the three GPC chromatograms of figure 4 are those of the three aromatic concentrates from the 370° to 530° C distillate of Recluse, Wyo., crude oil. The chromatograms are plotted as retention volume versus percent sample recovery and are typical of those obtained from 370° to 535° C distillates of other crude oils. All of the chromatograms start at about 1,000 ml and end at about 1,450 ml for the monoaromatics, 1,575 ml for the diaromatics, and 1,850 ml for the polyaromatic-polar material. The overlap of the three chromatograms does not interfere with the analyses of the three concentrates because the very selective silica gel-alumina gel separation yields well-defined concentrates for the GPC-mass spectral characterization and analysis method.

The characterization and analysis method employs an average theoretical ring carbon number at each ring number. This average theoretical ring carbon number is based upon the total aromatic carbon number for each compound type and the theoretical average number of naphthenic carbons involved in formation of each higher ring number naphthenolog. A set of GPC correlations based on model compounds then gives the total alkyl substitution for each compound type at each ring number at a given retention volume. The theoretical average carbon number and GPC-correlation substitution values together predict a molecular weight for each compound type at each ring number for any given retention volume. Low-ionizing voltage (11 eV) mass spectral molecular-weight data are then used to establish the presence or absence of the material predicated at each ring number for a given retention volume and to obtain a semiquantitative analysis of the material present. Finally, the mass spectral and GPC-correlation data are used together to adjust the GPC values (the ring number and substitution values predicted from the theoretical ring carbon number and GPC substitution values) to give the total carbon number found by mass spectrometry. NMR trend data support the GPC-mass spectral analysis method results.

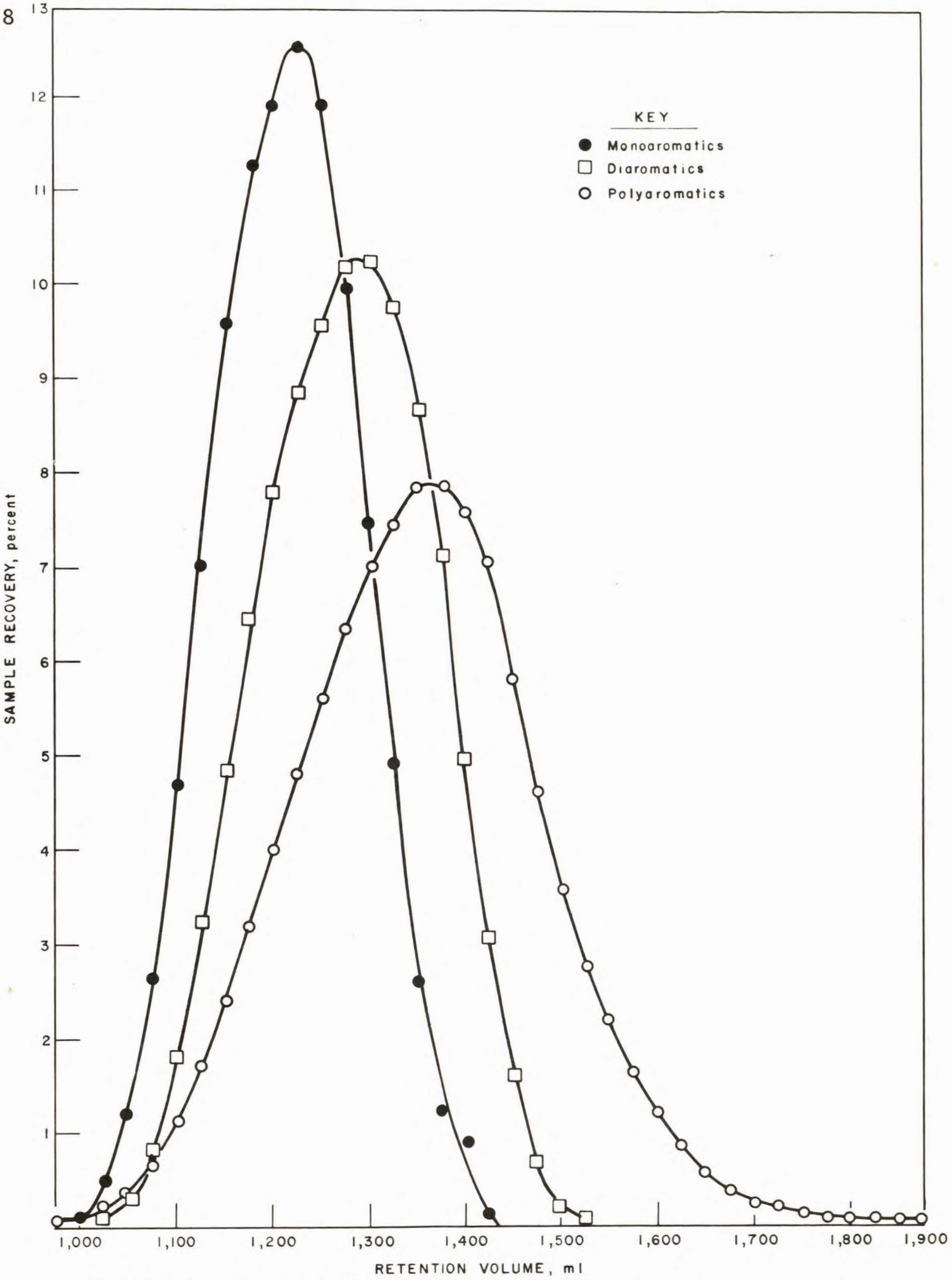


FIGURE 4. - Gel permeation chromatograms of monoaromatic, diaromatic, and polyaromatic-polar concentrates previously separated by adsorption from a 370° to 530° C distillate of Recluse, Wyo., crude oil.

Saturate Concentrate

The 370° to 530° C distillate of Recluse, Wyo., crude oil, as mentioned previously, was dewaxed with methyl isobutyl ketone to leave a fluid wax-free distillate. The saturate concentrate obtained from the adsorption step was analyzed by the high-voltage (70 eV) fragment method of Hood and O'Neal. The values in figure 3 represent an average of those obtained from the C_{24} normal alkane and isoalkane matrices. No monoaromatic types were detected, indicating that a good adsorption separation was obtained. The other saturate concentrate (the wax) was obtained prior to the adsorption step and contained approximately 1 percent of monoaromatics. The bulk (about 89 percent) of the wax was n-paraffins and mononaphthenes according to the C_{25} normal alkane matrix.

Aromatic Concentrates

The three aromatic concentrates were individually fractionated by GPC, and selected subfractions therefrom were subjected to characterization and analysis by the GPC-mass spectral analysis method previously described. High-ionizing-voltage (70 eV) spectra were also obtained to help resolve the probable compound types. For convenience in applying the GPC-mass spectral characterization and analysis method, all low-ionizing-voltage (11 eV) mass spectral data are presented as plots of mass-to-charge (m/e) ratio versus percent total ion intensity for a given parent range in each GPC subfraction. The ring number distributions for each whole concentrate analysis were quite similar to those obtained for Swan Hills (South field), Alberta, Canada, another low-sulfur crude oil (4).

Monoaromatics

Correlations developed for the GPC system and the mass spectral low-ionization-voltage profile curves of figure 5 show that long-chain alkylbenzene types elute first (-6 Z series is most prominent). As the elution progresses, monoaromatics with condensed naphthene rings emerge in order of increasing ring number (-8 through -20 Z series, respectively). Figure 5 also shows that as the elution progresses, there is a continuous decrease in average molecular weight, from about 580 in fraction 8 to about 290 in fraction 20.

Data in table 4 show that in addition to alkybenzenes and their mononaphthenologs to octanaphthenologs, cyclic sulfides and some diaromatics were found (naphthalenes and/or diphenylalkanes and their naphthenologs and benzothiophenes and their naphthenologs). Finally, a small amount (<0.1 percent) of unknown material was present. Total diaromatics amounted to 11.5 percent and cyclic sulfides to 5.1 percent.

The NMR data of figure 6 substantiate the observations made from the mass spectral and GPC data. In the NMR spectra H_a refers to hydrogen in methyl groups gamma and farther from the ring system; H_b refers to methylene and methine hydrogen, beta and farther from the ring system, and also refers to methyl groups beta to the ring system; H_c refers to methyl, methylene, and methine hydrogen alpha to the ring system; and H_d refers to aromatic hydrogen

TABLE 4. - Maximum of distribution for each mass Z series of monoaromatic GPC fractions from 370° to 530° C distillate of Recluse, Wyo., crude oil

Mass Z series	GPC fraction number					Probable type
	8	11	14	17	20	
-6	540	414	344,358	302	-	Alkylbenzenes.
-8	552	440	356,370	314	258	Naphthenobenzenes.
-10	578	466	368,382	326,340	270	Dinaphthenobenzenes.
-12	604	492	394,408	352	282	Trinaphthenobenzenes.
-14	616	504	406,420	364	294	Tetranaphthenobenzenes.
-16	628	530	432	376	306	Pentanaphthenobenzenes.
-18	-	542	458	388	318	Hexanaphthenobenzenes.
-20	-	540	470	400	344	Heptanaphthenobenzenes.
-22	-	-	-	412	370	Octanaphthenobenzenes.
-12	-	-	380	324	282	Alkylnaphthalenes.
-14	-	-	392	336	308	Naphthenonaphthalenes/biphenyls.
-16	-	-	404	362	334	Dinaphthenonaphthalenes/naphthenodiphenylalkanes.
-18	-	-	-	374,388	346	Trinaphthenonaphthalenes/dinaphthenodiphenylalkanes.
-10S	-	-	414	-	-	Benzothiophenes.
-12S	-	-	426	-	-	Naphthenobenzothiophenes.
-14S	-	-	440	-	-	Dinaphthenobenzothiophenes.
0S	-	550		-	-	Cyclic sulfides.
-2S	-	548		-	-	Dicyclic sulfides.
-4S	-	546		-	-	Tricyclic sulfides.
-6S	-	544		-	-	Tetracyclic sulfides.
	582	456	-	-	-	Unknown.
	596	470	-	-	-	Unknown.

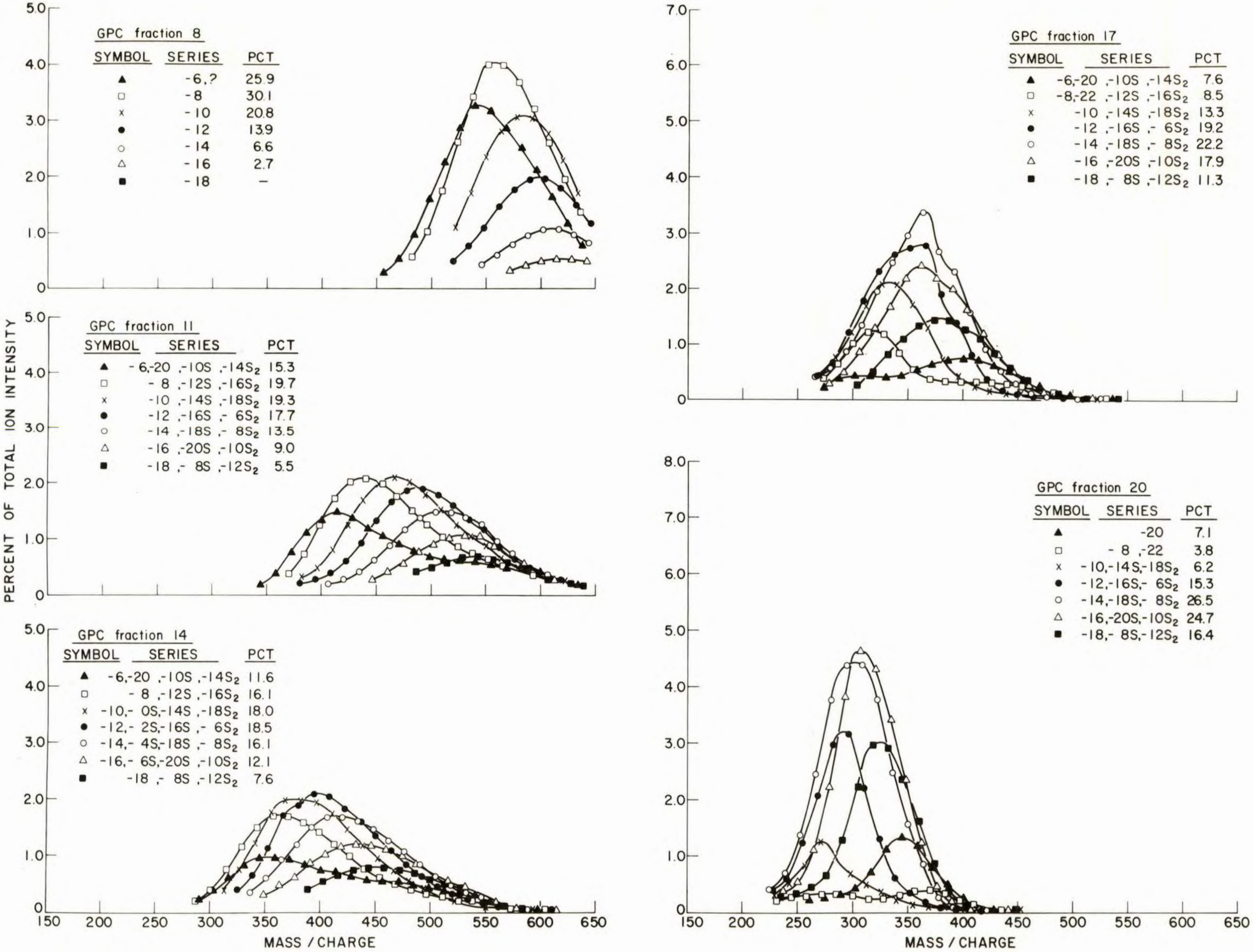


FIGURE 5. - Low-voltage mass spectral data for selected GPC-separated fractions of a monoaromatic concentrate from a 370° to 530° C distillate of Recluse, Wyo., crude oil.

attached directly to the ring. The following trends are seen to occur across the GPC chromatogram:

1. There is a general decrease in percentage of integral of H_a and H_b from fraction 9 to fraction 21 and an accompanying increase of percentage of integral of the H_c and H_d peaks. This indicates a decreasing length of side chains and/or decreasing degree of substitution about the ring systems.

2. The sharpness and amplitude of the H_b peak decreases markedly from GPC fraction 9 to fraction 21 and indicates that the length of side chains is decreasing.

3. The total integral of spectral peaks generally decreases from fraction to fraction as the elution progresses. This indicates a decrease in the percentage of hydrogen in the fractions as elution progresses.

The location of the H_d peak (6.8 ppm below TMS[4]) and the division of the H_c peak (an alpha methyl peak near 2.2 ppm, and an alpha methylene peak near 2.5 ppm) confirm the monoaromatic designation of these fractions. The H_d peak in fractions 19 and 21 broadens out downfield (below 7.0 ppm), confirming the mass spectral findings of diaromatic types in these fractions. Some sulfur types

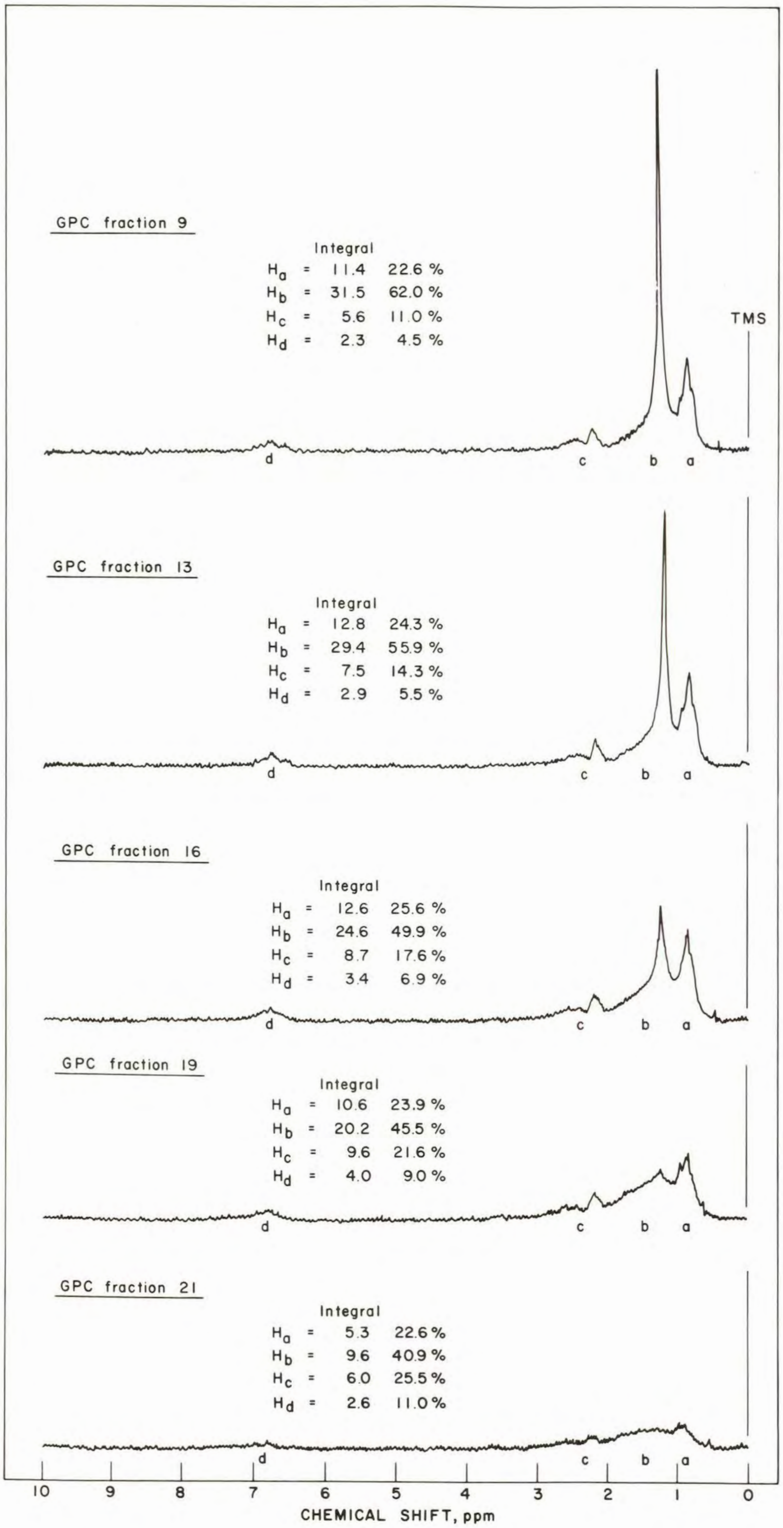


FIGURE 6. - 60-MHz NMR spectra of selected GPC-separated fractions of a monoaromatic concentrate from a 370° to 530° C distillate of Recluse, Wyo., crude oil.

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[4] Tetramethylsilane.

may also contribute to the downfield shift of the H_d peak in the later eluting fractions.

Diaromatics

Figure 7 shows the low-voltage mass spectral profile curves for selected GPC fractions of the diaromatic concentrate. Trends similar to those found for the monoaromatic GPC fractions are observed. That is, long-chain diaromatic types elute first, followed by types with an increasing number of condensed naphthene rings and shorter chains. Again, a sharp decrease in molecular weight is observed as the elution progresses.

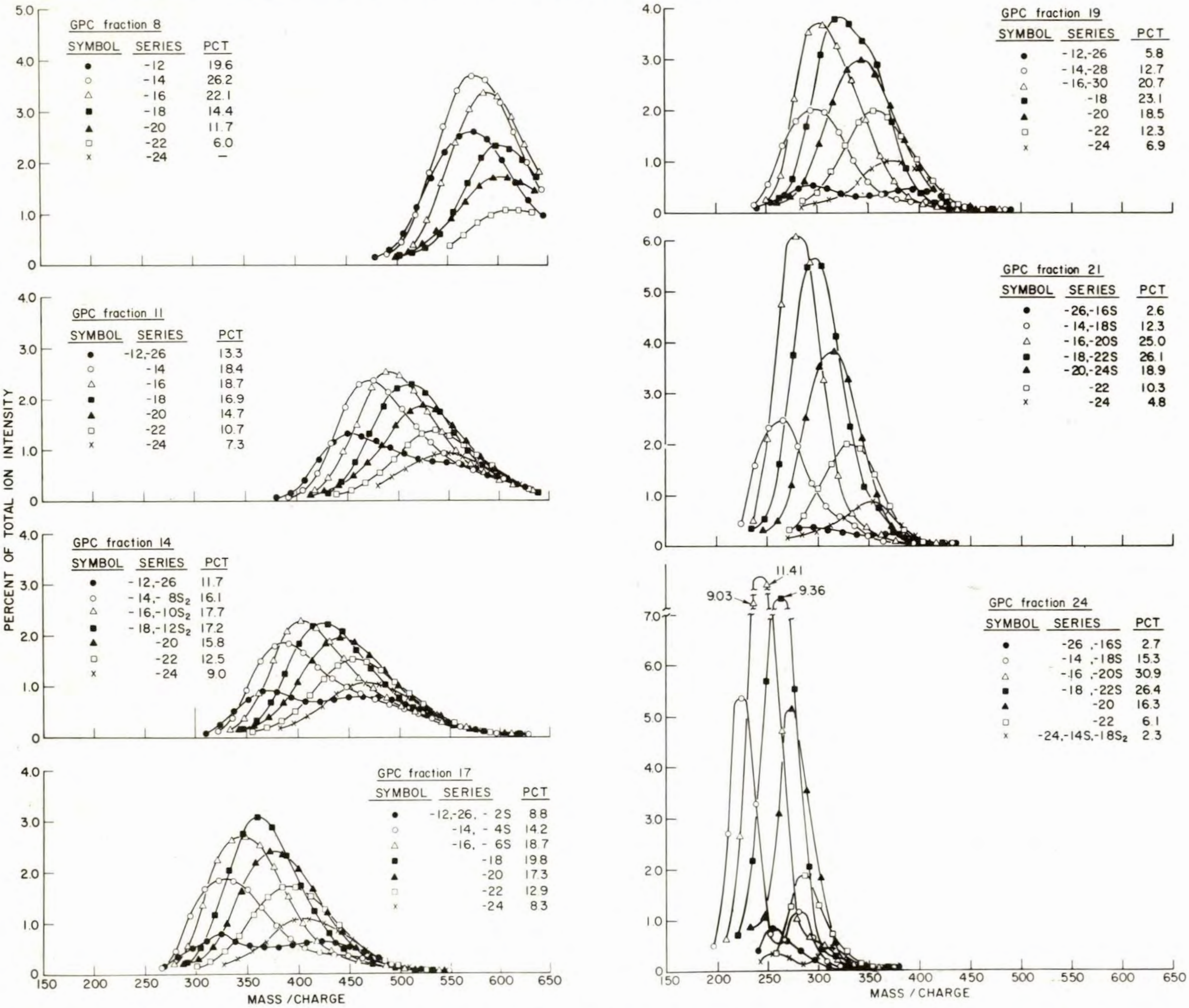

FIGURE 7. - Low-voltage mass spectral data for selected GPC-separated fractions of a diaromatic concentrate from a 370° to 530° C distillate of Recluse, Wyo., crude oil.

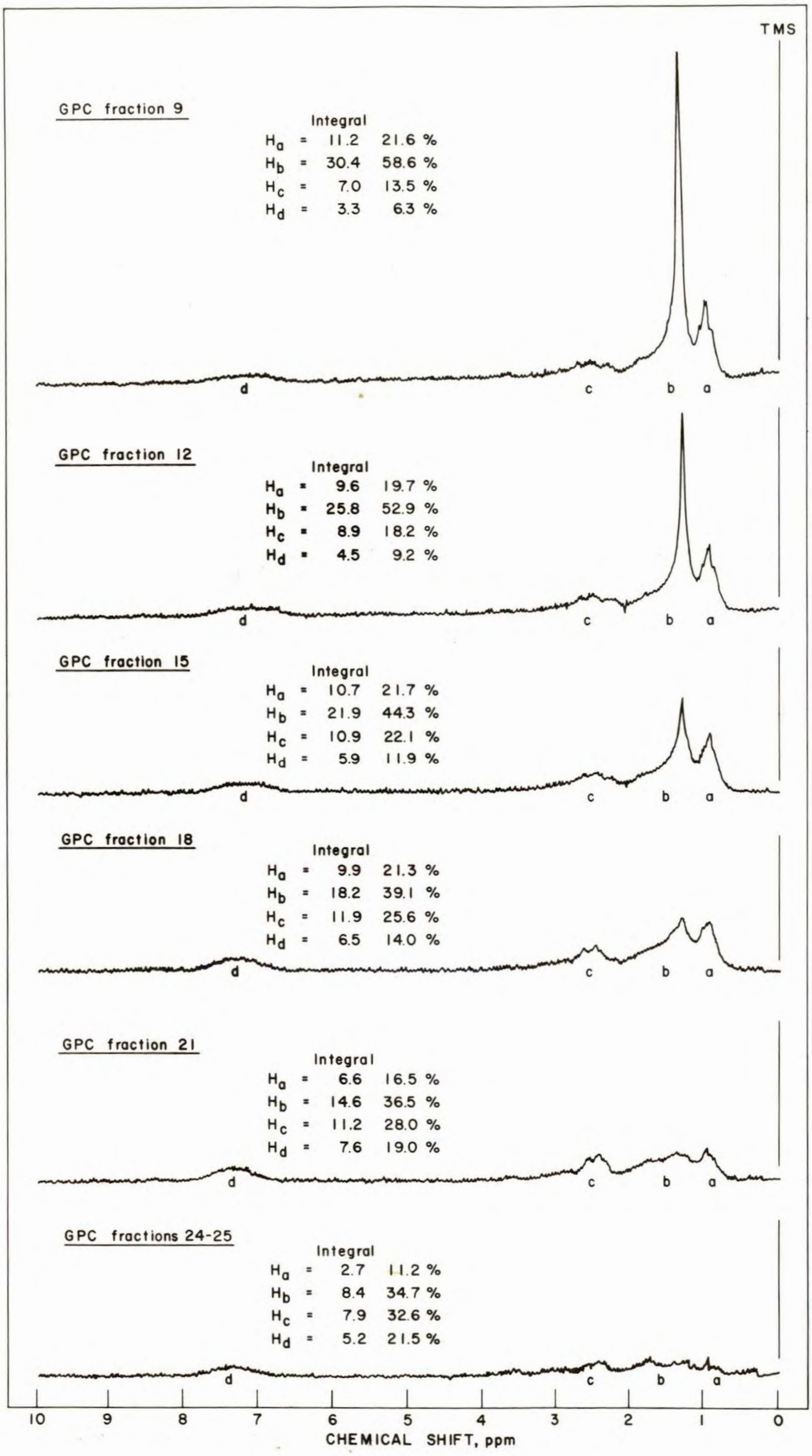

FIGURE 8. - 60-MHz NMR spectra of selected GPC-separated fractions of a diaromatic concentrate from a 370° to 530° C distillate of Recluse, Wyo., crude oil.

Table 5 lists the maximum for each mode of each mass Z series distribution in each diaromatic GPC fraction. Probable types responsible for these maxima accompany the listing. These data indicate that naphthalenes and biphenyl or diphenylalkane types and their naphthenologs predominate. Benzothiophenes and their naphthenologs are present in small quantities and some polyaromatic types are also observed. Monoaromatic contaminants amount to <0.1 percent, polyaromatic types to 5.1 percent, and sulfide types to 4.2 percent.

The NMR data of figure 8 verify the GPC-mass spectral findings. The diaromatics are distinguished from the monoaromatics by the broader H_d peak and by its location (7.1 to 7.3 ppm below TMS). In addition, the H_c peak does not have the characteristics of the monoaromatic H_c peak (as given in the discussion of figure 6). Finally in the last two fractions (21 and 24-25), the presence of small amounts of polyaromatics with three or more rings is confirmed by a small peak at 8.3 ppm below TMS.

TABLE 5. - Maximum of distribution for each mass Z series of diaromatic GPC fractions from 370° to 530° C distillate of Recluse, Wyo., crude oil

Mass Z series	GPC fraction number							Probable type
	8	11	14	17	19	21	24	
-12	576	450	366	296,310	282-296	254	-	Alkylnapthalenes.
-14	574	476	392	322	1/294 2/308	266	224	Napthenonaphthalenes/biphenyls.
-16	586	488	404	348	1/306 2/320,334	278	250	Dinaphthenonaphthalenes/ naphthenodiphenylalkanes.
-18	598	514	430	360	1/318 2/346,360	290,304	262	Trinaphthenonaphthalenes/ dinaphthenodiphenylalkanes.
-20	610	526	442	372	344	316	274	Tetranaphtenonaphthalenes/ trinaphthenodiphenylalkanes.
-22	622	538	454	398	356	328	286	Pentanaphthenonaphthalenes/ tetranaphthenodiphenylalkanes.
-24	-	550	466	410	368,382	354	302	Hexanaphthenonaphthalenes/ pentanaphthenodiphenylalkanes.
-26	-	562	478	422	394	366,380	-	Heptanaphthenonaphthalenes/ hexanaphthenodiphenylalkanes.
-28	-	574	492	434	406	-	-	Octanaphthenonaphthalenes/ heptanaphthenodiphenylalkanes.
-30	-	-	-	-	418	-	-	Octanaphthenodiphenylalkanes.
-16,-6S	-	-	-	348	306	278	250	Phenylalkyl sulfides or acenaphthalenes.
-18,-8S	-	-	-	360	332	290,304	262	Naphthenophenylalkyl sulfides or mononaphthenoacenaphthalenes.
-20,-10S	-	-	-	-	-	316	274	Dinaphthenophenylalkyl sulfides or dinaphthenoacenaphthalenes.
-16S	-	-	-	-	-	296	254	Dibenzothiophenes.
-18S	-	-	-	-	-	322	280	Naphthenodibenzothiophenes.
-20S	-	-	-	-	-	334	306	Dinaphthenodibenzothiophenes.
-22S	-	-	-	-	-	360	318	Trinaphthenodibenzothiophenes.
-24S	-	-	-	-	-	372	330	Tetranaphthenodibenzothiophenes.
-14S	-	-	-	-	-	-	256	Thienoindenes.
$-18S_2$	-	-	-	-	-	-	312	Dithienoindenes.

1/ The lower mass-to-charge ratio is probably the diphenylalkane type.

2/ The higher mass-to-charge ratio is probably the naphthalene type.

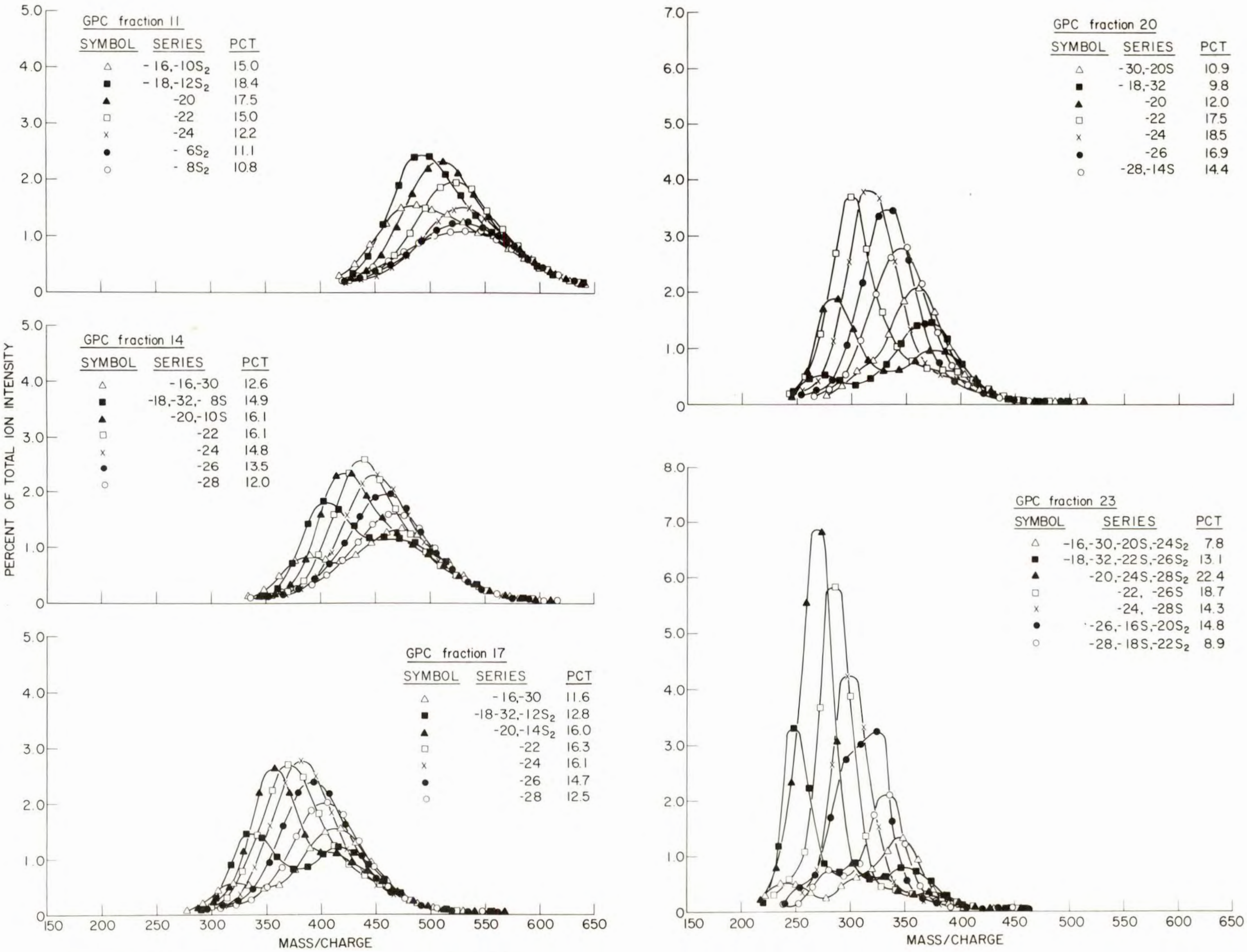

FIGURE 9. - Low-voltage mass spectral data for selected GPC-separated fractions of a polyaromatic-polar concentrate from a 370° to 530° C distillate of Recluse, Wyo., crude oil.

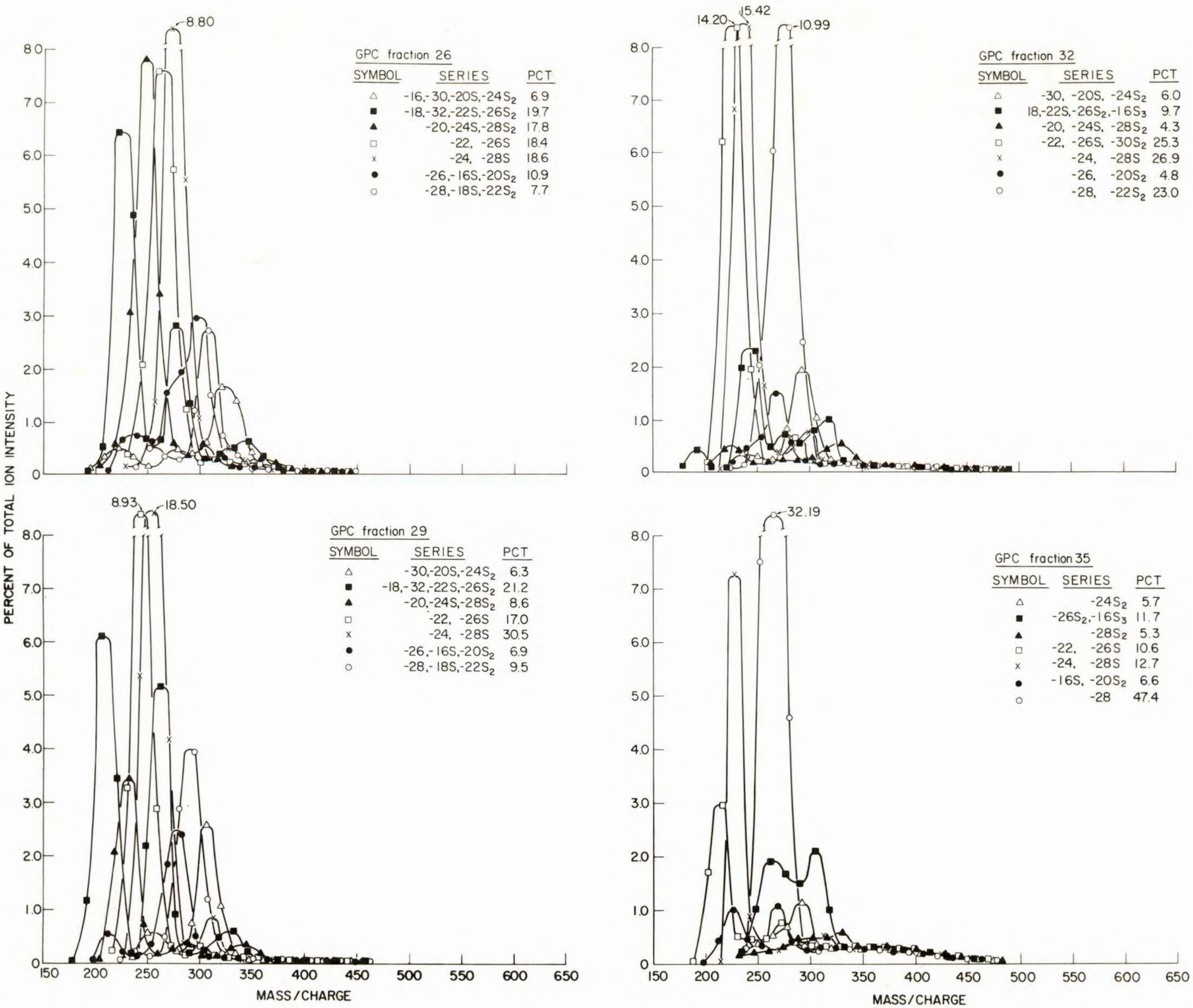

FIGURE 9. - Low-voltage mass spectral data for selected GPC-separated fractions of a polyaromatic-polar concentrate from a 370° to 530° C distillate of Recluse, Wyo., crude oil.—Continued

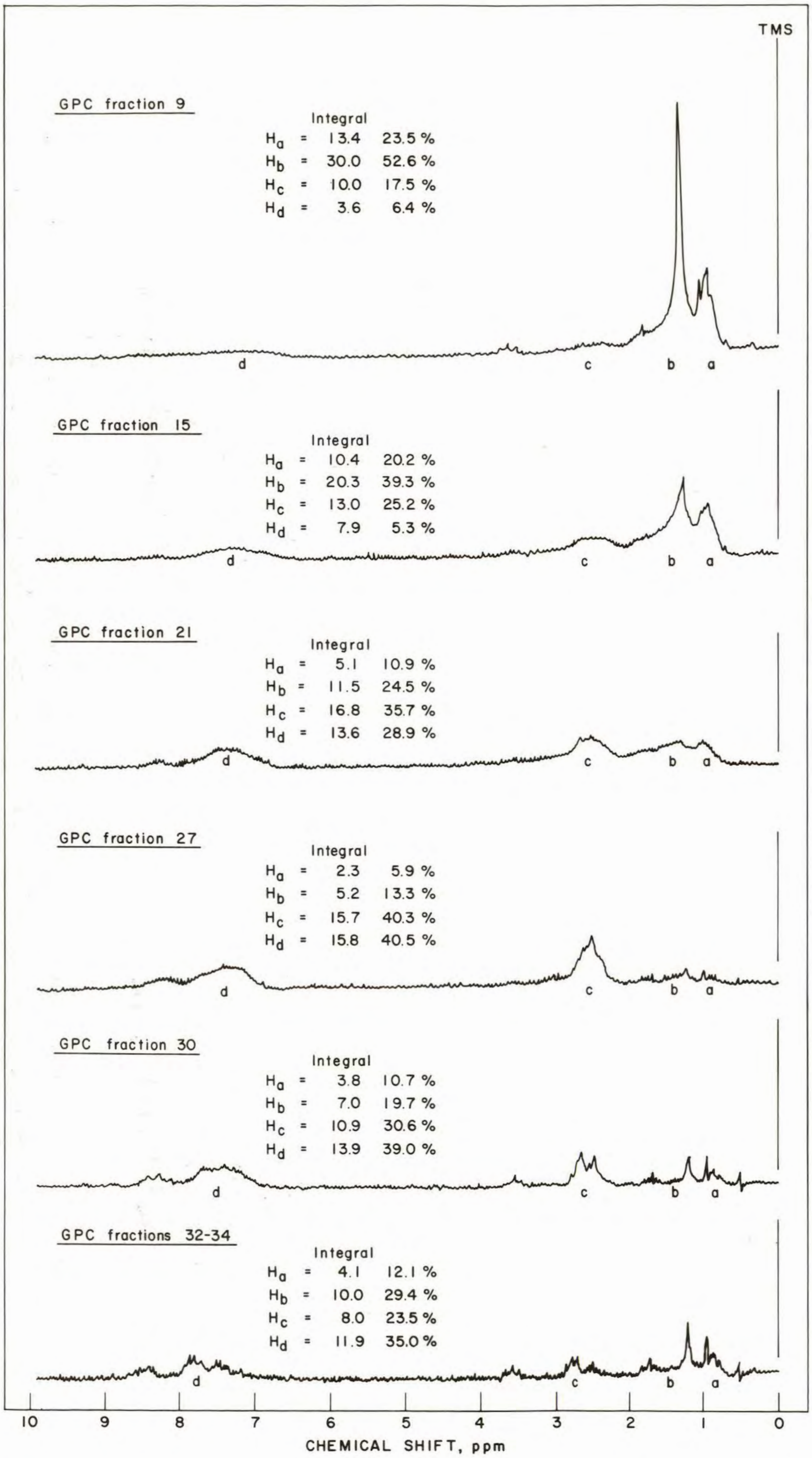

FIGURE 10. - 60-MHz NMR spectra of selected GPC-separated fractions of a polyaromatic-polar concentrate from a 370° to 530° C distillate of Recluse, Wyo., crude oil.

Polyaromatic-Polar Material

Figure 9 shows low-voltage mass spectral profile curves for selected GPC fractions from the polyaromatic-polar concentrate. Trends similar to those for monoaromatic and diaromatic GPC separations are found. That is, the typical decrease in molecular weight as the elution progresses is observed as well as an increase in condensation with accompanying decrease in chain length and degree of substitution as the elution progresses. Diaromatic types amount to 0.3 percent and sulfides to 2.5 percent.

Table 6 shows the maximum of distribution for each mass Z series in selected GPC fractions and the compound types probably responsible for these distribution maxima. Three-aromatic-ring types and their naphtheno derivatives elute first in order of increasing ring number. Condensed four-, five-, and six-aromatic-ring types are eluted subsequently. These data also show that compounds having up to nine total rings (three to six of these being aromatic) are present.

TABLE 6. - Maximum of distribution for each mass Z series of polyaromatic-polar GPC fractions from 370° to 530° C distillate of Recluse, Wyo., crude oil

Mass Z series	GPC fraction number									Probable type
	11	14	17	20	23	26	29	32	35	
-16	488	390	320	-	-	-	-	-	-	Alkylacenaphthalenes.
-18	500	402	332	276	248	-	-	-	-	Naphthenoacenaphthalenes.
-20	512	428	358	288	274	246	-	-	-	Dinaphthenoacenaphthalenes.
-22	524	440	370	300	286	258	244	-	-	Trinaphthenoacenaphthalenes or dibenzoindenes.
-24	536	452	382	312	298	270	256	-	-	Tetranaphthenoacenaphthalenes or mononaphthenodibenzoindenes.
-26	-	464	394	338	310	296	268, 282	-	-	Pentanaphthenoacenaphthalenes or dinaphthenodibenzoindenes.
-28	-	462, 476	406	350	336	308	280, 294	-	-	Hexanaphthenoacenaphthalenes or trinaphthenodibenzoindenes.
-30	-	474	418	362	348	320	306	-	-	Heptanaphthenoacenaphthalenes or tetranaphthenodibenzoindenes.
-32	-	486	430	374	360	332, 346	332	-	-	Octanaphthenoacenaphthalenes or pentanaphthenodibenzoindenes.
-34	-	-	-	386	372	-	-	-	-	Hexanaphthenodibenzoindenes.
-36	-	-	-	398	-	-	-	-	-	Heptanaphthenodibenzoindenes.
-18	-	-	-	276	248	220	206	192	-	Alkylanthracenes/phenanthrenes.
-20	-	-	-	288	274	246	232	218, 232	-	Naphtheno(anthracenes/phenanthrenes).
-22	-	-	-	300	286	258	244	230	-	Dinaphtheno(anthracenes/phenanthrenes).
-24	-	-	-	312	298	270	256	242	-	Trinaphtheno(anthracenes/phenanthrenes).
-26	-	-	-	338	310	296	268, 282	268	-	Tetranaphtheno(anthracenes/phenanthrenes).
-28	-	-	-	-	336	308	280, 294	280	-	Pentanaphtheno(anthracenes/phenanthrenes).
-30	-	-	-	-	-	-	306	292	-	Hexanaphtheno(anthracenes/phenanthrenes).
-16S	-	-	-	-	254	240	212	-	-	Alkyldibenzothiophenes.
-18S	-	-	-	-	280	252	238	-	-	Naphthenodibenzothiophenes.
-20S	-	-	-	-	292	264, 278	250	236	-	Dinaphthenodibenzothiophenes.
-22S	-	-	-	-	304	276	262	248	-	Trinaphthenodibenzothiophenes or thieno(anthracenes/phenanthrenes).
-24S	-	-	-	-	330	302	288	274	-	Tetranaphthenodibenzothiophenes or naphthenothieno(anthracenes/phenanthrenes).
-26S	-	-	-	-	342	314	300	-	-	Pentanaphthenodibenzothiophenes or dinaphthenothieno(anthracenes/phenanthrenes).
-28S	-	-	-	-	354	326	312	-	-	Hexanaphthenodibenzothiophenes or trinaphthenothieno(anthracenes/phenanthrenes).
$-20S_2$	-	-	-	-	324	296	268, 282	240	-	Thienodibenzothiophenes.
$-22S_2$	-	-	-	-	336	308	294	252, 266	-	Naphthenothienodibenzothiophenes.
$-24S_2$	-	-	-	-	348	320	306	292	292	Dinaphthenothienodibenzothiophenes.
$-26S_2$	-	-	-	-	360	346	332	304, 318	304	Trinaphthenothienodibenzothiophenes or dithieno(anthracenes/phenanthrenes).
$-28S_2$	-	-	-	-	386	358	344	330	330	Tetranaphthenothienodibenzothiophenes or dithienonaphtheno(anthracenes/phenanthrenes).
-16	-	-	-	-	236, 250	222	-	-	-	Dinaphthenonaphthalenes.
$-6S_2$	534	-	-	-	-	-	-	-	-	Thienocyclic sulfide.
$-8S_2$	532	-	-	-	-	-	-	-	-	Thienodicyclic sulfide.
$-10S_2$	530	-	-	-	-	-	-	-	-	Thienotricyclic sulfide.
$-12S_2$	528	-	-	-	-	-	-	-	-	Thienotetracyclic sulfide.
-14S	-	-	-	-	-	-	-	-	298	Dibenzocyclic sulfides.
-16S	-	-	-	-	-	-	-	-	268	Naphthenodibenzocyclic sulfide.
-18S	-	-	-	-	-	-	-	-	266	Dinaphthenodibenzocyclic sulfide.
-20S	-	-	-	-	-	-	-	-	264	Trinaphthenodibenzocyclic sulfide.
-22S	-	-	-	-	-	-	-	276	276	Tetranaphthenodibenzocyclic sulfide.
-24S	-	-	-	-	-	-	-	-	302	Pentanaphthenodibenzocyclic sulfide.
-8S	-	472	416	-	-	-	-	-	-	Benzocyclic sulfide.
-10S	-	470	414	-	-	-	-	-	-	Naphthenobenzocyclic sulfide.
-28	-	-	-	-	-	-	-	280, 294	266	Alkylbenzopyrenes/perylenes.
-26S	-	-	-	-	-	-	-	286	272	Thienopyrenes.
-28S	-	-	-	-	-	-	-	298	284	Thienochrysenes.
$-30S_2$	-	-	-	-	-	-	-	342	-	Dithienopyrenes.
-22	-	-	-	-	-	-	-	-	216	Alkylpyrenes.
-24	-	-	-	-	-	-	-	-	228	Chrysene.
$-28S_2$	-	-	-	-	-	-	-	-	288, 302	Dithienodiacenaphthalene.
$-16S_3$	-	-	-	-	-	-	-	276	262	Dithienobenzocyclicsulfides.
-20S	-	-	-	320	-	-	-	-		Thienoacenaphthalenes.
$-20S_2$	-	-	-	-	-	-	-	-	268	Thienodibenzocyclic sulfides.

In general, the NMR spectra of figure 10 show the same trends that were observed for monoaromatic and diaromatic GPC fractions. In addition, the early eluting fractions, 9 and 12, resemble the diaromatic spectra, particularly in the shape and location of the H_d peak. This supports the findings of some diaromatic types by GPC-mass spectral analysis and is probably also partly due to the presence of some polyaromatics that are phenyl derivatives of monoaromatic and diaromatic types. After fractions 9 and 12, the characteristic polyaromatic-polar H_d peak is observed (the main part at 7.3 to 7.4 ppm below TMS and a smaller division around 8.3 ppm). Also, the finer detail present in the H_d peak of fractions 32 to 34 indicates that a mixture of only a few similar types of polyaromatic molecules are present. Finally, a small peak at about 3.7 ppm is indicative of bridge hydrogens of condensed naphthene rings on condensed aromatic rings.

The polyaromatic-polar material contains about 3.0 percent of unidentified nitrogen compounds, which were barely detectable in the mass spectra.

Semiquantitative Analyses of Concentrates

The semiquantitative analysis of the saturate fraction was given in figure 3, and no further study of this material was undertaken.

Semiquantitative data for all three aromatic concentrates are summarized in table 7. The data were derived from the mass spectral distributions in figures 5, 7, and 9 following application of known GPC correlations. Compound type classification is made by mass Z series, and the series totals are compared to the same nominal Z series values of figure 3 for each whole aromatic concentrate (prior to GPC separation). The two sets of data agree well, thus indicating the internal consistency of the method.

The quantity of sulfur compounds indicated by GPC-mass spectrometry compares favorably with the quantity calculated from the total sulfur value for each aromatic concentrate. The calculated values are based on one sulfur atom per molecule and an average molecular weight of about 400. Monoaromatics, for example, containing 0.100 percent sulfur, calculate to about 1.3 percent sulfur compounds on the basis just mentioned. The GPC-mass spectral data indicate about 5.1 percent sulfur compounds containing one sulfur atom and none containing two sulfur atoms per molecule. The cause of the discrepancy will be discussed in a later section. The diaromatics, based on a sulfur content of 0.49 percent, calculate to about 6.1 percent sulfur compounds. This compares with the GPC-mass spectral determined values of 5.1 percent sulfur compounds containing one sulfur atom and 0.1 percent containing two sulfur atoms for a total of 5.3 percent sulfur compounds on a one sulfur atom basis. Data on the polyaromatic-polar concentrate suggest 12.5 percent sulfur compounds by sulfur analysis versus 15.1 percent by GPC-mass spectral evaluation.

TABLE 7. - Semiquantitative mass Z series distribution from GPC-mass spectral data of three aromatic adsorption fractions of 370° to 530° C distillate of Recluse, Wyo., crude oil

Z series	Wt-pct as derived from GPC-mass spectral data	Wt-pct as derived from whole aromatic concentrate
MONOAROMATIC CONCENTRATE		
-6 (MA)[1]	9.1	-
-20 (MA)	3.2	-
-10S (DA)	.6	-
Series total	12.9	11.8
-8 (MA)	15.0	-
-22 (MA)	.3	-
-12S (DA)	.9	-
Series total	16.2	15.2
-10 (MA)	15.5	-
0S (Cy S)	.9	-
Series total	16.4	16.9
-12 (MA)	13.5	-
-12 (DA)	3.7	-
-2S (Cy S)	.9	-
Series total	18.1	17.9
-14 (MA)	12.3	-
-14 (MA)	3.2	-
-4S (Cy S)	1.0	-
Series total	16.5	16.7
-16 (MA)	9.2	-
-16 (DA)	2.3	-
-6S (Cy S)	.8	-
Series total	12.3	12.8
-18 (MA)	6.8	-
-18 (DA)	.8	-
Series total	7.6	8.7
DIAROMATIC CONCENTRATE		
-12 (DA)	4.7	-
-26 (DA)	3.8	-
-16s (PAP)	.2	-
Series total	8.7	8.5
-14 (DA)	13.5	-
-28 (DA)	1.0	-
-18S (PAP)	.3	-
Series total	14.8	15.2
-16 (DA)	15.9	-
-16 (PAP)	1.9	-
-6S (PhAS)	2.0	-
-20S (PAP)	.2	-
Series total	20.0	20.0
-18 (DA)	16.5	-
-18 (PAP)	1.9	-
-8S (PhAS)	1.9	-
-22S (PAP)	.1	-
Series total	20.4	20.2
-20 (DA)	16.1	-
-20 (PAP)	.4	-
-10S (PhAS)	.4	-
-24S (PAP)	.1	-
Series total	17.0	16.6
-22 (DA)	11.8	-
-26S (PAP)	tr	-
Series total	11.8	11.8
-24 (DA)	7.3	-
-14 S (PAP)	tr	-
-18S$_2$ (PAP)	tr	-
Series total	7.3	7.7
POLYAROMATIC-POLAR CONCENTRATE		
-16 (DA)	0.3	-
-16 (PAP)	2.0	-
-30 (PAP)	6.5	-
-20S (PAP)	.5	-
-20S (PAP)	.3	-
-20S (N Cy S)	tr	-
-10S$_2$ (Th Cy S)	.2	
-24S$_2$ (PAP)	.8	-
Series total	10.6	9.4
-18 (PAP)	6.2	-
-32 (PAP)	5.2	-
-8S (B Cy S)	.5	-
-22S (PAP)	1.2	-
-22S (N Cy S)	tr	-
-12S$_2$ (Th Cy S)	.2	-
-26S$_2$ (PAP)	.5	-
-16S$_3$ (D Th Cy S)	tr	-
Series total	13.8	14.2
-20 (PAP)	12.9	-
-34 (PAP)	1.2	-
-10S (B Cy S)	1.2	-
-24S (PAP)	.5	-
-24S (N Cy S)	tr	-
-28S$_2$ (PAP)	.3	-
Series total	16.1	17.5
-22 (PAP)	[2] 16.0	-
-22 (PAP)	.2	-
-36 (PAP)	.2	-
-26S (PAP)	.4	-
-26S (PAP)	tr	-
Series total	16.8	17.9
-24 (PAP)	15.8	-
-24 (PAP)	.2	-
-14S (N Cy S)	tr	-
-28S (PAP)	.5	-
-28S (PAP)	tr	-
Series total	16.5	16.8
-26 (PAP)	12.5	-
-16S (PAP)	.4	-
-16S (N Cy S)	tr	-
-6S$_2$ (Th Cy S)	.2	-
-20S$_2$ (PAP)	1.0	-
Series total	14.1	13.4
-28 (PAP)	9.7	-
-28 (PAP)	.5	-
-18S (PAP)	.5	-
-18S (N Cy S)	tr	-
-8S$_2$ (Th Cy S)	.2	-
-22S$_2$ (PAP)	1.1	-
Series total	12.0	10.8

[1] Abbreviations shown in parentheses in the table denote as follows: MA = monoaromatic, DA = diaromatic; PAP = polyaromatic polar, Cy S = cyclic sulfide, PhAS = phenylalkyl sulfide, B Cy S = benzocyclic sulfide, Th Cy S = thienocyclic sulfide, N Cy S = naphthalenocyclic (dibenzocyclic) sulfides, D Th Cy S = dithienocyclic sulfide.

[2] This number, the largest single total, is lowered by 0.1 because the total of all trace components is 0.1. Total is then 99.9 percent.

Discussion of Limitations Inherent in the Analyses

In the analyses, there are some limitations that result from the workup of the data. These limitations result from analyzing only one fraction in three, the splitting of modes on the mass spectral plots, the lack of appropriate reference compounds for mass spectral sensitivity and GPC correlation data, and errors in the total sulfur and total nitrogen analyses.

The errors in the analyses generally involve types that are low in concentration and that often contain polyheteroatoms. Again, the excellent agreement between the analysis of each whole aromatic concentrate and the analysis obtained by reconstituting the analyses of every third GPC subfraction and the general agreement between the sulfur values by total sulfur and the GPC-mass spectral methods further establish that the limitations are of little practical importance.

With the presence of small amounts of compounds containing two sulfur atoms, it is noted that the sulfur compounds determined by GPC-mass spectral analysis show less agreement with the values determined from the total sulfur analysis than if only compounds containing one sulfur atom were present.

Thus, for the monoaromatic concentrate, 11.5 percent of the compounds are more sensitive diaromatic contaminants, and 3.6 percent of the compounds contain sulfide or disulfide sulfur which leads to sensitivities much greater than those of the monoaromatic hydrocarbons. For the diaromatic concentrate, there are 4.2 percent sulfides and 5.1 percent polyaromatics that have greater sensitivity than the diaromatics. In addition, 0.9 percent of greater sensitivity triaromatics (dibenzothiophenes) are present. In view of the limitations discussed above, the discrepancy between the total sulfur value and GPC-mass spectral sulfur value given earlier (6.1 versus 5.3 percent) is still not unreasonable. For the polyaromatic-polar concentrate, there are 2.5 percent cyclic sulfide sulfur of assorted types and 8.0 percent of one and two sulfur atom aromatics which are more sensitive than the analogous polyaromatic hydrocarbons to account for the discrepancy. In table 7, the excellent agreement between the whole concentrate analyses and reconstituted analyses of the GPC fractions (for all mass Z series) shows the internal consistency of the method, and although there are several limitations in the method, as previously discussed, they pertain to only a small part of the total sample.

SUMMARY

Isothermal and molecular distillation produced a 370° to 530° C distillate of Recluse, Wyo., crude oil. This distillate was dewaxed and then rendered more amenable to instrumental analysis by removal of acids and bases by ion-exchange chromatography, removal of neutral nitrogen compounds by $FeCl_3$ on cellulose, separation by silica gel-alumina gel adsorption chromatography into compound-type concentrates, and separation of these concentrates by molecular size by gel permeation chromatography. Characterization was accomplished by gel permeation chromatography--molecular structure correlations and mass and nuclear magnetic resonance spectrometry.

General characteristics of Recluse, Wyo., crude oil were also determined by the Bureau of Mines routine crude oil analysis method.

These data are useful in optimizing petroleum processing methods for improved utilization of petroleum, and in gaining a more thorough understanding of crude oil composition which should be of value to researchers interested in increased energy production and conservation.

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