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**GLC ANALYSIS OF N-PARAFFIN DISTRIBUTIONS IN CRUDE
OILS AND TOPPED CRUDE OILS FOR OIL IDENTIFICATION**

By

P. L. Grizzle and
H. J. Coleman

Date Published—October 1977

Bartlesville Energy Research Center
Energy Research and Development Administration
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ABSTRACT

Based upon a population of 52 crude oils and 52 corresponding artificially weathered crude oil samples, weight-percent distributions of normal paraffins obtained from gas-liquid chromatographic analyses were evaluated for their importance in oil identification. By use of statistical analysis, the weight percents for the C₁₁ through C₃₅ n-paraffins were determined to be significant variables for the differentiation of unweathered crude oil samples. Similarly, the ratios of pristane to n-heptadecane, phytane to n-octadecane, and phytane to pristane were determined to be important. By use of weight-percent distributions, two numerical methods were evaluated for reducing the variations in the analytical data between weathered crude oil samples and corresponding unweathered crude oils, resulting from environmental weathering. For a population of artificially weathered and unweathered crude oil pairs, good agreement exists between the weight-percent distributions (n-C₁₈ through n-C₃₀) when the distributions are normalized to the C₂₅ normal paraffin. Similarly, excellent agreement is observed between odd-even predominance values (above n-C₁₆). Comparative analyses of both normalized n-paraffin weight-percent distributions and odd-even predominance values of a set of artificially weathered and unweathered crude oil samples from the same general geographical region, indicate that similar unweathered crude oils can be differentiated. Although the identification of a weathered sample to the corresponding unweathered crude oil is not highly reliable by either method, such comparative data, when combined with comparable data obtained from another analytical method are shown to be very important and useful.

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INTRODUCTION

The ability to reliably identify or differentiate crude oils and related materials is of major importance to oil spill studies, geochemical studies, and crude oil pricing criteria. Improvement of this ability depends strongly upon the improvement of existing analytical methods and the development of new analytical techniques. Since no single analytical method has been developed which can uniquely characterize and, hence, identify each crude oil and related material, several analytical methods are commonly used to improve the reliability of such identification (1,3,20).³ Gas-liquid chromatographic (GLC) analysis has been used prominently in these multianalytical approaches (1-6, 8-9, 11-18, 20-21). These analyses have employed both flame-ionization and flame-photometric (2, 8-9) detectors and have used packed, capillary, and recently, open-tubular columns.

In general, interpretation of the flame-ionization gas chromatograms has been qualitative and has involved the determination of key differences between chromatograms for "fingerprinting" of oil samples. Quantitative methods of data interpretation have included comparisons of weight percents of normal paraffins between C₁₉ and C₄₀ (5), ratios of weight percents of phytane and pristane (4,21), and quantification of selected compound types such as mercaptans (thiols) and phenols (13) and triterpanes (16). The large quantity of qualitative data as compared to quantitative data in the literature reflects many of the problems inherent to GLC analysis of complex mixtures. These include a low level of reproducibility of quantitative data; a low degree of comparability of data obtained with different columns or at different times; and a need for rapid data acquisition, data manipulation, and interpretation. These problems are further compounded by the natural variations in the analytical data for spilled and suspect crude oil samples resulting from weathering. Recently, some of these problems have been circumvented. Detailed investigations in column selection, column stability, and operation conditions have improved both the reproducibility and comparability of quantitative data obtainable by GLC (21). Zafirios (21) has demonstrated that key "fingerprinting" data, such as the weight-percent ratios involving phytane, pristane, n-heptadecane, and n-octadecane, have long-term relative standard deviations of 1.8 to 4.0 percent. The use of support-coated open tubular (Scot) columns has provided excellent comparability of quantitative data both as a function of time and column (21). The use of minicomputers and microprocessors has greatly facilitated quantitative analysis and improved methods of data manipulation.

Various procedures have been incorporated into oil identification programs to simulate the effects of weathering on crude oil samples. Since the evaporation process produces the greatest short-term alteration in the characteristics of crude oils (3), these procedures include distillation of both suspect and spilled oil samples to approximately 275° C prior to analysis (1,10,14,20). Artificial weathering by distillation to this temperature greatly

³ Underlined numbers in parentheses refer to items in the list of references at the end of this report.

improved the reliability of identification by infrared analysis(10). Such artificial weathering has been incorporated into the Bartlesville Energy Research Center (BERC) program owing to the availability of physical-property data for about 9,000 foreign and domestic crude oils and corresponding distillate fractions ($>275^{\circ}\text{C}$). This open file constitutes an important bank of data on crude oils and corresponding artificially weathered crude oil samples for oil identification. Alternatively to artificial weathering, the quantitative evaluation of key components which are not strongly affected by weathering processes are being used in various oil identification programs (14,18,20).

This study statistically evaluated quantitative data obtained for crude oils and artificially weathered (distilled through 275°C) crude oil samples by GLC analysis for inclusion into oil identification programs. Various data interpretation and data comparison methods were used to reduce variations in the data associated with weathering and to ascertain the reliability of identification of both weathered and unweathered spilled samples to possible suspect oils.

EXPERIMENTAL

Fifty-two crude oil samples, representing oil-producing fields in nine states and six foreign countries, were supplied by the BERC crude oil analysis group. This same group also supplied physical-property data determined by the established Bureau of Mines routine method for crude oil analysis (19) and other data relating to the source and age of each oil sample.

To simulate the evaporation process of weathering, 10 ml of each crude oil sample was distilled under reduced pressure (10 mm Hg) and the residue, boiling above 275°C (atm), retained for subsequent analysis. Gas-liquid chromatographic analysis of each topped sample verified the initial boiling point of each sample to be approximately 275°C .

Gas-liquid chromatograms were obtained with a Hewlett-Packard model 5830A chromatograph⁴ equipped with a model 18850A integrator (microprocessor) and flame-ionization detectors. All chromatograms were obtained by use of dual stainless steel columns (10 ft by 1/8 in) containing 3 percent (w/w) OV-1 on acid-washed Chromosorb G (80/100 mesh) and helium as a carrier gas (25 ml/min). For crude oil samples analyzed, the GC oven was maintained at 50°C for 2 minutes after injection, temperature programed from 50° to 350°C at 5° per minute, and held at 350°C for 30 minutes to ensure elution of all volatile components. The topped crude oil samples were similarly analyzed by maintaining the oven at 120°C for 8 minutes after injection, temperature programing from 120° to 350°C at 5° per minute, and holding the oven at 350°C for 30 minutes. For all analyses, the injector and detector temperatures were 375°C and 380°C , respectively. All samples

⁴ Reference to specific brands of equipment is made for identification only and does not imply endorsement by the Energy Research and Development Administration (ERDA).

(approximately 0.40 to 0.80 μ l) were introduced as the undiluted oil with a 1 μ l syringe. Highly viscous samples were heated slightly to facilitate introduction.

Normalized peak areas and retention-time data were obtained from the microprocessor.

RESULTS AND DISCUSSION

Oil Samples

Table 1 presents source data for the analyzed crude oils (state or country and field) including geological formation or age and BERC identification number. These same oil samples have been previously used in this laboratory to evaluate the reliability of identifying crude oils and topped crude oil samples by infrared spectroscopy (10).

Various weathering processes are known to combine and alter both the physical and chemical characteristics of oil during exposure at sea. These include evaporation, emulsification, photo-oxidation, and biodegradation. Naturally, the degree of alteration depends upon the environmental conditions and the length of exposure. For exposures of short duration, most researchers agree that the evaporation process produces the greatest alteration in the characteristics of the spilled crude oil sample (3). As a first approximation, such alteration can be easily simulated by distillation (1, 10, 14, 20). Consequently, samples of the crude oils presented in table 1 were distilled through 275° C and the resultant residues analyzed. Distillation to this temperature represents severe evaporative weathering and is consistent with the loss of volatile components up to approximately C₁₅.

Evaluation of Important Variables for Oil Identification

Without prior sample separation, the most obvious parameter obtainable from flame-ionization chromatograms for incorporation into oil identification is the normal-paraffin distributions. Figure 1 presents the flame-ionization chromatograms of crude oil 75060 and the corresponding artificially weathered (topped) sample. Assuming unit sensitivities for ionization by the flame, the quantitative comparison of weight percents obtained by GLC analysis has been shown to be useful for the differentiation of crude oil samples (5). Various other qualitative and semiquantitative approaches for differentiation by use of normal-paraffin distributions were reviewed by Wilson (20). Alternatively, quantification of the isoparaffins, phytane and pristane, has been used successfully for the differentiation of crude oil samples (4, 21). By separating the sample before analysis, quantification of selected compound types such as mercaptans (thiols) and phenols (13) and triterpanes (16) and comparison of the resultant data between crude oil samples have been used for identification. However, the time required for sample preparation and subsequent analysis has been a deterrent for expansion of the selected compound type identification approach.

TABLE 1. - Source data for analyzed crude oils

BERC identification number	State or Country	Field	Geological	
			Formation	Age
75002	Kansas	Lyons, West	Kinderhook	Lower Mississippian
75003	Ohio	Magnolia	--	Devonian
75004	Oklahoma	Perkins, East	Skinner	Pennsylvanian
75005	Wyoming	Well Draw	Teapot	Upper Cretaceous
75006	Oklahoma	Paradise	--	Mississippian
75007	Oklahoma	Paradise	Bartlesville	Pennsylvanian
75009	Wyoming	Kaye	Teapot	Upper Cretaceous
75010	Wyoming	Grieve, North	Muddy	Upper Cretaceous
75011	Wyoming	Poison Draw	Teckla	Upper Cretaceous
75012	Norway	Ekofisk	Danian	Paleocene
75014	Norway	Edda	Danian	Paleocene
75015	Mississippi	Lake Utopia	Smackover	Upper Jurassic
75018	Oklahoma	Sooner Trend	Hunton	Siluro-Devonian
75025	Oklahoma	Tonkawa, Southeast	Mississippi Chat	Mississippian
75026	Oklahoma	Tonkawa, Southeast	Red Fork	Middle Pennsylvanian
75027	Oklahoma	Delaware-Childers	Bartlesville	Pennsylvanian
75028	Louisiana	Bellevue	Blossom-Ozan	Upper Cretaceous
75030	Louisiana	Sibley	Mooringsport	Lower Cretaceous
75031	Utah	Flat Rock	Wasatch	Eocene
75032	Louisiana	Colquitt	Cotton Valley	Upper Jurassic
75041	Mississippi	Quitman	Cotton Valley	Jurassic
75042	Mississippi	Quitman	Mooringsport	Lower Cretaceous
75044	Mississippi	Nancy	Smackover	Upper Jurassic
75045	Norway	Eldfisk	Danian	Paleocene
75046	Norway	Ekofisk	Danian	Paleocene
75047	Iran	Rostam	ShuAiba	Lower Cretaceous
75049	Michigan	Columbus, North	Niagaran	Middle Silurian
75050	Michigan	Hessen	Niagaran	Middle Silurian
75051	Michigan	Burch Run	Dundee	Middle Devonian
75052	Michigan	Marine City, South	Salina, A-1	Middle Silurian
75054	Wyoming	Spearhead Ranch	Frontier	Upper Cretaceous
75057	Oklahoma	Binger, East	Marchand	Pennsylvanian
75059	Michigan	Columbus	Niagaran	Middle Silurian
75060	Michigan	Peters, East	Niagaran	Middle Silurian
75062	Michigan	Overisel	Traverse	Middle Devonian
75063	Michigan	Walker	Traverse	Middle Devonian
75064	Michigan	Hope	Traverse	Middle Devonian
75065	Michigan	Wayland	Salina	Upper Silurian
75066	Michigan	Salem	Traverse	Middle Devonian
75067	Michigan	Wayland, North	Traverse	Middle Devonian
75068	Michigan	Lawton	Traverse	Middle Devonian
75069	Michigan	Dorr	Salina	Upper Silurian
75070	Michigan	Dorr	Detroit River	Lower Devonian
75071	Michigan	Laketon	Traverse	Middle Devonian
75072	Michigan	Bloomington	Traverse	Middle Devonian
75073	Michigan	Adair	Niagaran	Middle Silurian
69069	Egypt	El Morgan	--	Miocene
69074	Indonesia	Duri	--	Tertiary
69111	Kuwait	Minagish	--	Cretaceous
70025	Venezuela	Bachaquero	--	Miocene
70113	Iran	Gach Saran	--	Miocene
71011	Alaska	Prudhoe Bay	Sadlerochit	Lower Triassic

FIGURE 1. - Flame ionization chromatograms of: crude oil 75060 and corresponding topped crude oil sample.

As previously demonstrated (10), for a measured property to be important for the differentiation of crude oils or other related samples, the variation in the measured property for a large population of samples must be significantly larger than the analytical uncertainty. This criterion has been used successfully to evaluate IR absorption bands for oil identification (10). To evaluate the importance of n-paraffin weight-percent data for differentiation, a similar analysis is presented in table 2. Assuming unit detector sensitivities for the

TABLE 2. - Evaluation of n-paraffin weight-percent data for identification of crude oils

n-paraffin	Average weight percent ¹	Percent σ pop	Percent σ pop / Percent σ anal ²
C ₁₁	9.67	41.3	11.0
C ₁₂	7.72	34.1	9.1
C ₁₃	9.40	27.6	7.4
C ₁₄	10.20	23.7	6.3
C ₁₅	8.64	21.4	5.7
C ₁₆	7.60	29.6	7.9
C ₁₇	38.75	27.0	7.2
C ₁₈	47.38	24.1	6.4
C ₁₉	4.74	24.3	6.5
C ₂₀	4.11	23.4	6.2
C ₂₁	3.27	24.2	6.5
C ₂₂	2.90	27.6	7.4
C ₂₃	2.78	32.7	8.7
C ₂₄	2.46	34.6	9.2
C ₂₅	2.22	39.2	10.4
C ₂₆	1.91	42.4	11.3
C ₂₇	1.48	56.8	15.1
C ₂₈	1.14	62.3	16.6
C ₂₉	0.89	57.3	15.3
C ₃₀	.77	75.3	20.1
C ₃₁	.55	69.1	18.4
C ₃₂	.49	108.2	28.9
C ₃₃	.31	54.8	14.6
C ₃₄	.36	55.6	14.8
C ₃₅	.26	69.2	18.5

¹ Average of 51 crude oil samples.

² Average percent σ anal = 3.75.

³ Includes contribution of pristane.

⁴ Includes contribution of phytane.

n-paraffins, the weight percents of the normal paraffins (C₁₁ to C₃₅) and associated population standard deviation (σ pop) for a statistical population of 52 crude oils have been calculated. Since the isoparaffins, pristane and phytane, are not completely resolved from n-heptadecane and n-octadecane, respectively, with the present GLC conditions and column (see figure 1), the weight percents of these isoparaffins have been summed with the weight percents of the corresponding n-paraffins in the data given in table 2. Although various liquid-phases can be used to improve this resolution, the OV-1 column was chosen owing to its long-term thermal stability. For the crude oil samples analyzed, the average analytical percent standard deviation in the n-paraffin weight-percent data was determined to be 3.75 percent, based upon repetitive determinations of n-paraffin weight-percent

distributions for selected crude oil samples. Note that this value represents the uncertainty in data obtained from a typical GC-microprocessor system and that no attempt has been made to minimize the uncertainty attributed to either GLC conditions or column types. Therefore, a value of 3.75 percent represents a typical uncertainty which can be expected in any analytical laboratory using commonly available GLC equipment. Using this value as an estimate of the analytical uncertainty in each n-paraffin weight percent, the ratio -- percent σ pop / percent σ anal was used as the criterion for determining the importance of n-paraffin weight-percent data for oil identification. For the sample population and n-paraffins (C₁₁ to C₃₅) analyzed, the average value of this ratio (table 2) is 11.6. A similar analysis of IR absorbance data at 14 selected frequencies yielded an average ratio of the corresponding uncertainties of 28.4 (10). Consequently based upon statistical considerations, weight-percent distribution data of n-paraffins in crude oils constitute a useful parameter for crude oil differentiation. However, owing to the large increase in the analytical standard deviation in the GLC data as compared to the IR absorbance data, IR analysis should be better for such differentiation. Based upon the ratio criterion, the data in table 2 suggest that the weight percent data for some n-paraffins (approximately C₂₇

through C35) may be slightly more variable for the sample population and, consequently, more useful for oil identification. However, this is not true. The increase in the population uncertainty for these n-paraffins is an experimental anomaly and reflects the baseline-correcting feature of the microprocessor (integrator) used. Since the baseline-correcting function is monitoring the change in the slope of the unresolved envelope of peaks in the chromatogram as a function of time, this increase in the ratio at approximately C27 reflects the variation in the slopes of the broad-unresolved envelope among the population. Naturally, for a given crude oil sample the data would be corrected for change in baseline at the same time, and the analytical uncertainty would not be affected.

In conjunction with the normal-paraffin weight-percent distributions, the weight percents of the isoprenoids, pristane (i-C₁₉) and phytane (i-C₂₀), and the ratios--i-C₁₉/n-C₁₇, i-C₂₀/n-C₁₈, and i-C₂₀/i-C₁₉--have been shown to be key variables for differentiation of crude oil samples (4,20). For the GLC conditions used in the study, weight percent data for pristane and phytane were obtained for 82.4 and 96.1 percent of the crude oil samples, respectively. For these samples, the ratio of weight percents for i-C₁₉/n-C₁₇, i-C₂₀/n-C₁₈, and i-C₂₀/i-C₁₉ are 62.1 ± 17.0 , 63.1 ± 34.2 , and 92.5 ± 54.5 percent, respectively. Clearly, the large variations in these ratios, as indicated by the magnitude of the associated standard deviations, demonstrate the importance of such variables for use in oil identification.

Various procedures have been incorporated into oil identification research programs in an attempt to reduce the variations in analytical data between spilled oil and probable suspect oil samples which result from weathering. For IR analysis, distillation of both the spilled and suspect oils to a common temperature (275° C) has been shown to improve greatly the reliability of "matching" the correct suspect or reference oil to the spilled sample (10). Alternatively, efforts have been made in the determination of variables which are important for oil identification and are not significantly altered upon weathering (4,14,18,20). Unfortunately, normal-paraffin weight-percent distributions are not independent of weathering phenomenon. Depending upon the environmental conditions and the duration of exposure, a significant quantity of volatile hydrocarbons are lost due to evaporation. Also, micro-organisms which biologically degrade crude oil will preferentially attack the normal paraffins (1). However, if such biodegradation is uniform, the resulting loss should not substantially alter the GLC pattern (5) and, hence, the normal-paraffin weight distribution should remain constant.

Although distillation of both the spilled and suspect samples before analysis could be used to reduce the variation in the distribution, the distillation would need to be highly repetitive and reliable. For a large population of suspect oil samples, this would greatly increase analysis time. Since the normal-paraffin weight percents are not independent variables, owing to the calculation method, a small variation in the distillation would produce significant errors in the weight-percent data. Consequently, this study investigated two approaches in numerically reducing the variations resulting from evaporation. For 15 selected Michigan crude oil samples and corresponding artificially weathered

(distilled through 275° C) crude oil samples, the n-paraffin weight percents for C₁₅ to C₃₀ were normalized to n-C₂₅, and the average percent deviations between the topped crude oil and corresponding unweathered crude oil sample calculated. Table 3 presents the

TABLE 3. - Variations in n-paraffin weight percent distributions and odd-even-predominance (OEP) values between crude oils and corresponding artificially weathered crude oil samples

n-paraffin	Average percent deviation ¹	
	Weight percent	OEP value
C ₁₅	-65.3	12.9
C ₁₆	-42.1	9.9
C ₁₇ ²	-10.9	6.9
C ₁₈ ³	-10.5	3.6
C ₁₉	- 2.7	.2
C ₂₀	- 5.9	1.0
C ₂₁	- 6.0	1.5
C ₂₂	- 2.9	.1
C ₂₃	- .1	.7
C ₂₄	.9	2.3
C ₂₅	4.0	-2.6
C ₂₆	.9	-9.2
C ₂₇	.2	-9.4
C ₂₈	2.2	-4.1
C ₂₉	3.7	1.9
C ₃₀	4.7	5.5

¹ Average for 15 selected Michigan crude oil samples.

² Includes contribution of pristane.

³ Includes contribution of phytane.

⁴ Weight-percent data normalized to C₂₅ for both crude oil and topped crude oil samples.

results. The C₂₅ normal paraffin was chosen since it would not be lost upon evaporative weathering. As seen in table 3, even though the distillation procedure used should have removed material only to n-C₁₅, significant losses of both n-C₁₅ and n-C₁₆ are noted in the data. However, above n-C₁₈ there is good agreement in the normalized weight-percent data between the topped crude oils and corresponding unweathered crude oil samples. Clearly, by normalizing the data to a component which is not affected by weathering, weathered spilled samples can be directly compared to reference crude oils. However, it should be noted that this approach strongly depends upon the accuracy of the n-C₂₅ peak area. A small error in this value will be reflected throughout the normalized distribution. A second approach, the odd-even-predominance (OEP) method, reduces this strong dependence upon the accuracy of one measured variable. For each n-paraffin, the OEP value, which is a

measurement of the deviation from an unbiased distribution of even and odd carbon numbered n-paraffins, is calculated by equation 1 (7). The variable,

$$OEP = \frac{C_i + 6 C_{i+2} + C_{i+4}}{4 C_{i+1} + 4 C_{i+3}} (-1)^{i+1} \quad (1)$$

C_i, corresponds to the weight percent of the ith carbon-numbered n-paraffin and C_{i+k} (where k = 1,2,3,4) corresponds to the weight percents of n-paraffins containing i+k number of carbon atoms. For an unbiased distribution, the OEP value as a function of carbon number is unity. Such values have been shown to be useful for geochemical correlations (7). The carbon numbers for the maxima and minima values in a plot of OEP values versus carbon number are indicative of the crude oil source rock, and the amplitudes of the maxima or minima are indicative of oil yield from the source rock (7). As shown in equation 1, the OEP value at a given carbon number depends upon five weight-percent data. Consequently, the reliability of "matching" a suspect to a spilled oil sample does not depend upon a single measurement with this approach. Table 3 presents

the average percent deviations in the OEP values as a function of n-paraffin for the 15 selected topped and unweathered crude oil samples. Above n-C₁₆ there is good agreement between the OEP values for the artificially weathered and unweathered crude oil samples. Consequently, a direct comparison of spilled and suspect oil samples can be made using OEP values without sample preparation.

TABLE 4. - Statistical Evaluation of Normalized n-paraffin weight percent distributions and odd-even-predominance values for oil identification

n-paraffin	Normalized weight percent		OEP values	
	Average ¹	Percent σ pop ² Percent anal	Average ¹	Percent σ pop ² Percent anal
C ₁₅	389.2	8.6	1.099	6.0
C ₁₆	342.3	9.5	.964	5.1
C ₁₇	394.1	8.8	3.880	5.5
C ₁₈	4332.4	8.8	4.917	6.4
C ₁₉	213.5	8.8	.968	6.7
C ₂₀	185.1	8.8	1.010	7.4
C ₂₁	147.3	8.9	1.034	8.6
C ₂₂	130.6	9.2	1.022	9.6
C ₂₃	125.2	10.0	1.006	10.5
C ₂₄	110.8	10.2	.983	11.7
C ₂₅	100.0	-	.983	13.7
C ₂₆	86.0	11.2	.996	15.8
C ₂₇	66.7	12.7	.965	17.8
C ₂₈	51.4	14.6	.922	19.6
C ₂₉	40.1	14.1	.893	26.9
C ₃₀	34.7	16.0	.845	37.5

¹ Average for 51 crude oil samples.

² Error propagated assuming average percent standard deviation in individual weight percents = 3.75.

³ Includes contribution of pristane.

⁴ Includes contribution of phytane.

Table 4 presents a statistical evaluation of the normalized-to-n-C₂₅ n-paraffin weight percent distribution and the odd-even predominance method for oil identification. Using standard error propagation methods, the ratio of the population to analytical percent standard deviations have been calculated for both methods. Based upon this criterion, both appear to be generally useful for identification of crude oils. As previously discussed, the marked increase in the percent standard deviation above n-C₂₇ reflects the variation in the data resulting from the baseline-correcting function of the integrator.

Differentiation of Similar Crude Oils

The reliability of identification of a spilled sample to the true suspect crude oil depends entirely upon the uniqueness of the measured property for this oil as compared to the

suspect population. To ascertain the uniqueness of normal paraffin distributions and the method of odd-even predominance for differentiating crude oils, 15 crude oil samples and corresponding weathered samples from the same general geographical region were analyzed. Samples, representing six counties in Michigan, were obtained from three geological formations corresponding to three geological ages. Although crude oils from various locations may be quite similar, samples from the same general geographical location and geological formation or age should be very similar and, hence, difficult to differentiate.

For each unweathered and corresponding artificially weathered sample, the weight percent of each normal paraffin (C₁₅ to C₃₀) was determined, and the resultant data normalized to n-C₂₅ (see above discussion). Similarly, the OEP value for each of the normal paraffins was calculated by use of equation 1 for each sample. For rapid comparative data analysis, an approach used in the comparative analysis of IR absorbance data was used (10). Comparison of the normalized weight-percent distributions and OEP values for a given crude oil or unweathered sample (spilled sample) were rapidly compared to the comparable data for another crude oil or weathered sample (reference or possible suspect)

by use of equations 2 and 3, respectively. The variables, WP_i and OEP_i , correspond

$$\left(\frac{WP_i}{WP_i'} - 1.0 \right) 100 = \text{Percent Diff}_i \quad (2)$$

$$\left(\frac{OEP_i}{OEP_i'} - 1.0 \right) 100 = \text{Percent Diff}_i \quad (3)$$

to the weight percent and odd-even predominance value, respectively, for the i^{th} n-paraffin in the reference sample, and WP_i' and OEP_i' correspond to the weight percent and OEP value for the i^{th} n-paraffin in the spilled sample. Clearly, in the absence of analytical error, if the spilled and reference oils were the same, the Percent Diff_i calculated from both equations 2 and 3 would be zero.

Owing to the variations in the analytical data which result from weathering, two cases have been considered in the evaluation of the two GLC methods for differentiation of crude oil samples. First, in the absence of weathering, the spilled sample (unweathered crude oil) can be directly compared to a set of unweathered suspect oil samples. Alternatively if the spilled sample has been weathered substantially, the comparison of the analytical data for the spilled oil to the population of suspects must be based on those variables or measured properties which are least altered upon weathering. Assuming the unweathered crude oil sample 75066 to be the spilled suspect and the total 15 samples to constitute the suspect population, the normalized weight-percent values (n-C₁₅ through n-C₂₄ and n-C₂₆ through n-C₃₀) for the suspect oils and spilled sample have been compared by use of equation 2. Table 5 presents the number of normalized weight percents in

TABLE 5. - Comparison of normalized¹ n-paraffin weight percent distributions for crude oil 75066 to selected suspect crude oil samples

Identification number	Number of normalized weight percents differing less than				
	10 pct	20 pct	30 pct	40 pct	50 pct
75049	2	0	11	14	15
75050	3	8	11	13	15
75059	3	5	9	10	11
75060	1	4	8	8	12
75052	2	4	6	10	12
75065	2	4	6	8	11
75069	6	8	10	12	12
75062	12	15	-	-	-
75063	8	11	13	15	-
75064	13	15	-	-	-
75066	13	-	-	-	-
75067	8	14	14	14	15
75068	9	12	13	14	15
75071	9	11	13	13	14
75072	7	7	10	15	-

¹Weight percents normalized to n-C₂₅.

each suspect sample which differed by less than 10, 20, 30, 40, and 50 percent from the spilled sample. Of the 15 suspect crude oils, 3 of the samples--75062, 75064, and 75066--have extremely similar normalized weight-percent distributions. However, the most probable suspect, 75066, does correspond to the spilled sample. Previous comparative analysis of these same suspect oils to 75066 using IR absorbance data verified that oils from the same geological formation are more difficult to differentiate than samples from different formations (10). However, this observation is not as apparent from the weight-percent distribution data. Although samples 75062, 75064, and 75066 are from the same geological formation, samples 75063, 75067, 75068, 75071, and

75072 are also from the Traverse Formation. The data in table 5 do show that unweathered spilled crude oils can be differentiated from very similar suspect oils with a reasonable level of reliability.

TABLE 6. - Comparison of normalized ¹n-paraffin weight percent distributions for artificially weathered crude oil 75066 to unweathered suspect crude oil samples

Identification number	Number of normalized weight percents differing less than				
	10 pct	20 pct	30 pct	40 pct	50 pct
75049	3	6	9	10	12
75050	4	5	8	9	11
75059	3	5	8	9	10
75060	2	3	6	8	9
75052	2	3	4	8	11
75065	2	4	5	7	10
75069	4	7	9	10	12
75062	10	12	-	-	-
75063	9	12	-	-	-
75064	9	12	-	-	-
75066	10	12	-	-	-
75067	5	9	11	12	-
75068	6	10	10	10	12
75071	7	12	-	-	-
75072	6	9	11	11	12

¹Weight percents normalized to n-C₂₅.

TABLE 7. - Comparison of odd-even predominance values for crude oil 75066 to selected suspect crude oil samples

Identification number	Number of OEP values differing less than				
	10 pct	20 pct	30 pct	40 pct	50 pct
75049	9	12	14	14	16
75050	8	11	14	16	-
75059	6	12	14	15	16
75060	9	14	14	15	16
75052	9	12	14	15	16
75065	7	10	13	13	15
75069	7	11	14	16	-
75062	16	-	-	-	-
75063	10	12	14	16	-
75064	16	-	-	-	-
75066	16	-	-	-	-
75067	7	13	14	15	16
75068	15	15	16	-	-
75071	12	15	15	16	-
75072	11	13	14	15	16

Table 6 presents a similar comparative analysis assuming the artificially weathered (topped) crude oil 75066 to correspond to the spilled sample and the same 15 unweathered crude oils to correspond to the suspect set. This situation is consistent with that which generally attains in a true oil spill. The data show that four crude oil suspects--75062, 75063, 75064, and 75066--have the highest probability of being the spilled sample. Of these four samples, the "correct" suspect, 75066, and 75062 have equal higher probabilities. In this analysis, n-paraffins from C₁₈ through C₂₄ and C₂₆ through C₃₀ have been considered (see previous discussion). Considering the magnitude of the average percent deviations in the normalized weight-percent data between the unweathered and corresponding topped crude oil samples (table 3), the occurrence of two weight-percent values outside the 10 percent comparison limit is not unexpected. Reduction of the analytical error may increase the reliability of "matching" the unweathered suspect to the weathered spilled sample; however, note that the suspect population has been reduced significantly from 15 to 4 samples by use of this comparative method.

Table 7 presents data for a similar analysis based upon odd-even predominance values for n-paraffins C₁₅ through C₃₀. In this analysis, the unweathered crude oil 75066 was assumed to be the spilled sample, and unweathered crude oils constituted the suspect population. For crude oil samples 75062, 75064, and 75066, all OEP values differ by less than 10 percent from the spilled sample. Consequently, these oils

are not differentiated using this procedure; the suspect population has only been reduced from 15 to 4 samples. However, the failure to differentiate these crude oils is not totally unexpected. OEP values have been used to identify crude oils from a common source rock (7). Therefore, the data verify that these similar crude oil samples are from the same source rock. For diverse samples from various source rocks, the reliability of identifying the "correct" suspect oil should be much better. The data in table 8 which purpose-

TABLE 8. - Comparison of odd-even predominance values for crude oil 75052 to selected suspect crude oil samples

Identification number	Number of OEP values differing less than				
	10 pct	20 pct	30 pct	40 pct	50 pct
75049	10	12	13	16	-
75050	10	14	14	15	16
75059	7	8	13	14	15
75060	14	15	16	-	-
75052	16	-	-	-	-
75065	8	12	15	16	-
75069	6	15	16	-	-
75062	9	10	13	14	15
75063	8	13	13	14	14
75064	8	10	13	-	-
75066	9	10	12	14	14
75067	8	10	10	11	12
75068	8	10	11	13	13
75071	6	9	12	13	13
75072	8	10	13	14	14

TABLE 9. - Comparison of odd-even predominance values for artificially weathered crude oil 75066 to unweathered suspect crude oil samples

Identification number	Number of OEP values differing less than				
	10 pct	20 pct	30 pct	40 pct	50 pct
75049	5	10	12	13	-
75050	7	10	13	-	-
75059	5	10	13	-	-
75060	9	12	13	-	-
75052	8	11	12	13	-
75065	4	8	9	13	-
75069	4	10	13	-	-
75062	10	12	13	-	-
75063	10	13	-	-	-
75064	10	12	13	-	-
75066	10	11	13	-	-
75067	6	10	10	11	11
75068	9	11	12	13	-
75071	10	13	-	-	-
75072	8	12	13	-	-

fully involves the comparative analysis of a crude oil from another source, demonstrate this increased probability. In this analysis, the unweathered sample 75052 is the spilled sample and the suspect set consists of unweathered crude oil samples. For this case, the "correct" suspect oil is uniquely characterized as being the most probable.

Table 9 presents another OEP comparative analysis assuming the artificially weathered crude oil sample 75066 to be the spilled sample and the same 15 unweathered crude oils listed in table 8 to be the suspect set. Again, this situation is consistent with that generally encountered in a true oil spill. Comparison of the data in table 9 with the comparable analysis in table 6, which used normalized weight-percent distributions, indicates that the suspect population is reduced more by use of the weight-percent procedure. However, the OEP values for suspect oils from various world-wide locations would probably be much nearer unique for the individual oils than are these values for the suspect set used in this study. Note that the comparative data presented in tables 5 through 9 represent the most difficult set of circumstances which could be encountered which involve differentiation of samples from the same general geographical and often times same geological formation.

Multianalytical Approach to Oil Identification

Since no single analytical method has been developed which can uniquely characterize

and, hence, identify each crude oil or related material, a multianalytical approach is required. This is adequately demonstrated by the results presented in both tables 6 and 9. The data in these tables can be used primarily only to reduce the suspect population. However, such data, when combined with similar analysis obtained by another analytical method, become extremely important. Table 10 gives data for a comparative analysis

TABLE 10. - Comparison of IR absorbances for artificially weathered crude oil 75066 to similarly weathered suspect crude oil samples

Identification number	Number of absorbance bands differing less than				
	5 pct	10 pct	15 pct	20 pct	25 pct
75049	7	9	10	11	12
75050	5	7	11	12	-
75059	4	9	12	-	-
75060	6	8	10	12	-
75052	6	7	9	12	-
75065	2	4	5	8	11
75069	5	8	9	11	12
75062	6	11	12	-	-
75063	4	11	12	-	-
75064	9	11	12	-	-
75066	12	-	-	-	-
75067	6	12	-	-	-
75068	3	12	-	-	-
75071	9	12	-	-	-
75072	12	-	-	-	-

technique which used IR absorbance data at 12 selected frequencies (10). In this analysis, the artificially weathered crude oil, 75066, was compared to the 15 selected artificially weathered crude oils. Within a 5-percent limit, sample 75066, the actual spilled oil, and 75072 are not distinguishable. However, by use of the GLC data for these samples and subsequent analyses, as presented in tables 6 and 9, in combination with the IR data, these samples are distinguishable. Consequently, a measured property, which may not be singularly unique for a population of very similar samples, can be a significantly useful key in the reliable differentiation of the samples when combined with another analytically measured property.

SUMMARY

Based upon a population of 52 crude oils and 52 corresponding artificially weathered crude oil samples, weight-percent distributions of normal paraffins obtained from GLC analyses were evaluated for their importance in oil identification. Using the ratio, percent σ_{pop} /percent σ_{anal} , as the criterion for this evaluation, the weight percents for the C₁₁ through C₃₅ n-paraffins were determined to be significant variables for the differentiation of unweathered crude oil samples. Similarly, the ratios of pristane to n-heptadecane, phytane to n-octadecane and phytane to pristane were determined to be important. Note that these conclusions were determined from data obtained from a typical GLC-integrator system and that no attempt was made to minimize the analytical uncertainty by maximizing GLC operating conditions or column selection. Consequently, these distributions should be of importance to all oil identification research programs without regard to available equipment or expertise.

Two numerical methods, using weight-percent distributions, were evaluated for reducing the variations in the analytical data between a weathered crude oil sample (spilled oil) and the corresponding unweathered suspect crude oil sample which results from weathering. For 15 selected Michigan crude oils and corresponding artificially weathered (distilled through 275° C) crude oil samples, good agreement exists between the weight-percent distributions (n-C₁₈ through n-C₃₀) for the weathered and unweathered pairs when

the distributions are normalized to the C₂₅ normal paraffin. This has pragmatic consequences since, in general, a weathered spilled sample must be compared to a set of unweathered reference samples. Note, however, that this approach strongly depends upon the accuracy of only one variable: the C₂₅ n-paraffin peak area. The second numerical approach, the odd-even-predominance method, reduces this strong dependence upon the accuracy of one measured variable. Above n-C₁₆, there is excellent agreement between the OEP values for artificially weathered and corresponding unweathered crude oil samples. Consequently, both OEP values and normalized weight-percent distributions can be used to compare directly weathered spilled samples to unweathered suspects.

To ascertain the uniqueness of normal paraffin weight-percent distributions and the method of OEP for differentiating crude oils, 15 crude oils and corresponding artificially weathered samples from the same general geographical location were comparatively analyzed. For the differentiation of similar unweathered crude oil samples, the normalized weight-percent distributions yield a more reliable identification than does the OEP approach. However, this is expected because OEP values are characteristic of source rocks. For crude oil samples from various source rocks, this study showed a marked increase in the reliability of differentiation with the use of OEP values. Neither method uniquely identifies a weathered spilled sample from a suspect population of these very similar crude oils. However, significant reduction in the size of the suspect population is noted. Such data, when combined with comparative data obtained from another analytical method, become extremely important for the reliable identification of spilled crude oil samples.

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TABLE A-1. - Relative n-Paraffin Weight-Percent Data for Crude Oils Analyzed

Crude Oil Number	Relative Weight Percent by Carbon Number											
	C ₁₁	C ₁₂	C ₁₃	C ₁₄	C ₁₅	C ₁₆	C ₁₇ ¹	C ₁₈ ²	C ₁₉	C ₂₀	C ₂₁	C ₂₂
75002	10.28	7.99	12.31	11.74	9.86	7.14	9.61	6.59	5.26	3.88	2.60	2.22
75003	11.92	11.85	11.99	15.81	5.98	5.58	7.09	5.69	3.96	3.52	2.93	2.32
75004	9.88	8.14	10.32	12.90	10.25	6.38	8.57	6.97	4.52	4.32	3.02	2.61
75005	10.83	9.08	10.63	12.27	7.51	7.22	9.61	6.53	4.68	4.18	3.36	2.64
75006	15.13	9.47	8.41	10.59	7.41	7.01	9.08	7.41	4.71	4.21	2.93	2.31
75007	13.65	9.45	9.25	13.24	9.45	6.33	8.74	6.82	4.24	3.78	2.62	2.09
75009	9.43	6.95	7.67	9.71	9.24	6.98	10.21	7.12	5.42	4.77	3.92	3.04
75010	6.95	5.09	8.23	9.71	7.56	7.39	8.29	6.94	4.84	4.98	4.09	3.86
75011	12.44	7.15	6.94	9.61	7.62	7.80	10.58	7.28	5.27	4.96	3.87	3.04
75012	9.07	9.02	15.02	9.17	6.37	6.52	9.05	6.92	4.91	3.69	3.19	2.78
75014	9.78	8.96	8.85	9.86	7.18	7.40	9.02	7.31	5.79	5.45	3.57	3.30
75015	8.15	6.09	7.68	8.85	9.86	13.08	11.63	6.14	4.29	4.21	3.57	4.24
75018	12.46	11.17	11.61	12.36	5.37	5.81	7.57	6.27	4.84	4.14	3.18	2.47
75025	8.00	6.34	11.64	9.32	8.75	11.21	10.68	10.37	8.82	2.62	2.26	1.83
75026	10.81	8.08	11.33	11.13	10.51	11.07	9.99	4.45	3.96	3.40	2.72	2.19
75027	13.24	10.02	14.82	14.55	14.22	4.81	6.65	5.68	4.53	2.68	1.36	1.07
75028	8.30	6.52	9.16	9.30	7.99	10.06	11.25	10.55	3.18	3.32	2.75	2.83
75030	10.02	8.63	9.05	10.65	11.93	7.75	8.47	7.61	4.68	4.44	3.01	2.47
75031	4.85	4.35	7.48	6.55	6.44	8.79	10.19	7.92	3.89	3.86	3.81	3.91
75032	6.67	5.80	10.35	7.57	10.93	5.24	6.44	7.12	5.64	5.46	4.67	4.14
75041	12.68	8.86	10.90	8.34	6.81	6.77	6.74	7.66	4.89	4.28	3.75	2.85
75042	10.76	8.20	8.90	9.55	9.24	8.90	8.78	8.67	5.05	4.58	3.42	2.84
75044	9.40	7.69	8.79	9.68	9.75	12.35	12.77	10.94	3.49	3.04	2.29	1.90
75045	7.08	6.14	8.87	8.64	8.00	9.04	11.09	9.72	7.59	3.90	3.10	2.70
75046	7.83	6.57	10.01	10.03	9.22	10.79	12.16	5.82	4.49	4.05	2.95	2.45
75047	9.11	7.54	12.58	9.99	10.50	12.75	11.33	5.09	3.55	3.57	2.40	2.02
75049	6.52	5.11	6.15	7.20	7.76	9.06	10.29	8.25	4.59	4.01	3.93	3.62
75050	7.98	6.20	7.40	8.09	8.83	10.13	6.30	8.63	4.64	3.71	3.18	3.17
75051	9.24	7.24	11.11	14.44	12.39	10.36	12.27	8.65	3.84	2.60	1.45	1.48
75052	6.20	4.50	5.33	6.41	6.79	6.77	6.42	9.13	5.20	4.65	4.12	4.15
75054	9.22	7.09	12.31	13.54	11.18	10.78	7.60	5.84	4.33	3.73	2.68	2.17
75057	9.56	7.88	10.08	12.79	10.74	6.62	8.41	7.19	4.63	4.24	2.99	2.70
75059	8.68	7.48	4.39	5.98	6.21	4.71	6.44	9.67	5.02	4.33	4.50	4.12
75060	5.95	5.44	5.89	6.31	6.92	4.86	7.51	9.00	5.17	4.40	4.39	4.19
75062	9.33	6.40	9.82	10.72	8.98	8.37	8.07	6.73	4.33	4.66	3.74	3.31
75063	10.47	7.00	10.70	12.57	9.91	6.73	9.40	6.60	3.94	3.89	2.90	2.85
75064	8.71	6.40	9.97	10.34	8.12	8.94	8.59	6.84	4.45	4.53	3.73	3.33
75065	5.60	4.96	4.34	5.94	6.43	5.59	6.21	7.50	4.50	4.61	3.88	3.88
75066	10.91	7.05	8.04	11.71	8.54	8.80	7.81	6.49	4.11	4.33	3.52	3.19
75067	9.69	7.49	10.37	12.90	10.14	4.68	7.74	6.26	4.05	3.17	3.45	2.78
75068	10.51	7.05	12.77	13.02	9.55	4.58	6.45	5.76	3.83	4.03	3.34	2.97
75069	7.78	6.12	6.31	9.02	6.74	5.17	5.61	8.08	5.31	4.54	5.04	4.42
75070	27.96	10.25	11.65	11.56	8.27	3.99	3.65	2.56	1.69	1.41	1.35	1.32
75071	16.64	9.57	9.46	14.02	10.07	6.13	7.87	5.42	3.44	2.95	2.42	1.99
75072	17.64	12.15	9.16	9.26	8.28	6.11	8.29	6.15	4.01	3.45	2.87	2.54
75073	0.32	1.75	5.44	10.30	10.37	7.26	11.37	11.90	7.41	5.05	4.18	3.83
69069	5.63	6.36	6.93	7.86	6.42	6.62	9.34	8.29	5.47	5.00	4.34	4.01
69111	9.16	10.43	10.28	9.97	8.94	6.97	7.06	6.41	4.85	4.09	3.50	2.97
70113	9.60	9.64	7.51	10.00	8.07	6.56	9.45	8.20	4.86	4.14	3.54	3.03
71011	5.13	13.21	15.19	9.09	6.65	5.69	8.78	6.06	4.48	3.68	3.27	2.97

¹ Includes contribution of pristane.

² Includes contribution of phytane.

TABLE A-1. - Relative n-Paraffin Weight-Percent Data for Crude Oils Analyzed--
continued

Relative Weight Percent by Carbon Number												
C ₂₃	C ₂₄	C ₂₅	C ₂₆	C ₂₇	C ₂₈	C ₂₉	C ₃₀	C ₃₁	C ₃₂	C ₃₃	C ₃₄	C ₃₅
2.07	1.64	1.52	1.26	0.94	0.58	0.60	0.49	0.34	0.33	0.27	0.27	0.19
2.16	1.80	1.67	1.33	1.01	.85	.72	.51	.46	.31	.22	.19	.11
2.48	1.93	1.76	1.51	1.02	.68	.63	.49	.38	.34	.29	.30	.22
2.73	2.26	1.80	1.31	.86	.66	.48	.26	.31	.23	.23	.22	.12
2.20	1.85	1.79	1.32	.89	.88	.59	.42	.46	.26	.25	.33	.08
1.97	1.74	1.62	1.17	.78	.80	.57	.40	.44	.25	.23	.30	.07
3.15	2.77	2.20	1.83	1.17	.93	.82	.54	.65	.39	.41	.39	.26
3.72	3.28	2.83	2.32	2.12	1.53	1.26	1.18	1.00	.84	.71	.74	.55
3.05	2.61	2.11	1.53	1.03	.79	.60	.29	.43	.27	.28	.28	.18
2.88	2.48	2.08	1.72	1.16	.86	.65	.62	.46	.38	.42	.40	.19
3.07	2.62	2.25	1.70	.95	.68	.48	.42	.38	.21	.31	.29	.16
2.16	1.99	1.69	1.90	1.25	1.08	.80	.78	.59	.63	.40	.41	.32
2.45	2.12	1.86	1.46	1.00	.81	.73	.45	.53	.39	.36	.37	.23
1.61	1.42	1.19	0.99	.65	.50	.44	.32	.29	.23	.20	.19	.13
1.91	1.70	1.42	1.21	.80	.61	.52	.39	.35	.28	.25	.23	.15
1.01	1.07	0.94	.81	.57	.36	.32	.27	.22	.19	.21	.25	.16
3.05	2.75	2.40	1.78	1.21	.88	.71	.54	.46	.35	.28	.24	.15
2.17	2.05	1.65	1.37	.91	.59	.53	.55	.44	.31	.24	.28	.18
3.86	3.72	3.55	3.31	3.20	2.71	2.40	1.82	1.56	.73	.60	.33	.19
3.73	3.42	2.85	2.67	1.96	1.53	.89	.74	.64	.55	.38	.34	.27
2.51	2.27	1.92	2.08	1.28	1.08	.86	.93	.57	.69	.42	.48	.35
2.38	2.16	1.69	1.58	.90	.65	.43	.51	.15	.24	.10	.18	.12
1.61	1.60	1.26	1.17	.67	.47	.31	.27	.13	.15	.09	.12	.07
2.72	2.22	1.87	1.50	1.16	.76	.68	.69	.76	.62	.46	.44	.25
2.51	2.29	1.87	1.50	1.13	.74	.63	.72	.61	.46	.45	.45	.27
1.71	1.62	1.26	1.11	.89	.62	.52	.56	.32	.35	.22	.24	.17
3.87	3.59	3.41	3.07	2.64	1.56	1.45	1.25	.61	.79	.26	.55	.44
3.29	3.08	3.07	2.75	2.40	1.38	1.45	1.15	.67	.84	.39	.69	.57
0.89	0.76	.73	.57	.43	.29	.32	.30	.15	.16	.12	.13	.09
4.47	4.30	4.23	3.96	3.55	3.18	1.90	1.53	.77	.97	.29	.60	.59
2.19	1.74	1.44	1.05	.73	.52	.44	.31	.31	.23	.22	.20	.15
2.58	2.08	1.83	1.42	.99	.67	.61	.44	.42	.33	.31	.29	.21
4.32	3.91	3.87	3.59	3.24	2.00	2.00	1.65	.94	1.10	.42	.76	.70
4.39	3.91	3.90	3.71	3.41	3.09	2.11	1.64	.93	1.13	.39	.80	.53
2.97	2.42	2.38	1.97	1.42	1.08	.88	.64	.49	.38	.31	.27	.20
2.28	2.23	1.98	1.60	1.26	.94	.59	.40	.16	.16	.12	.21	.17
3.03	2.39	2.48	2.12	1.54	1.12	.90	.66	.52	.42	.34	.31	.25
4.59	4.23	4.33	3.19	3.55	2.23	2.02	3.64	2.41	3.63	.92	.99	.84
2.87	2.38	2.25	1.97	1.53	1.19	.60	.80	.54	.40	.31	.34	.25
2.82	2.30	2.35	2.21	1.72	1.26	1.06	.73	.86	.42	.34	.35	.24
2.72	2.25	2.19	2.06	1.54	1.23	1.08	.80	.68	.49	.43	.39	.29
4.84	3.77	3.79	3.09	2.70	2.00	1.53	1.38	.76	.79	.32	.54	.34
1.24	1.11	1.01	.71	.57	.58	.31	.36	.13	.32	--	--	--
1.84	1.44	1.55	1.25	.97	.72	.59	.45	.32	.28	.23	.22	.16
2.34	1.86	1.85	1.48	.99	.63	.46	.26	.12	.09	--	--	--
4.13	3.70	3.51	2.92	2.38	1.27	1.08	.68	.38	.32	.06	.18	.21
3.74	3.58	3.00	2.69	2.25	1.96	1.49	1.33	1.00	.83	.62	.60	.67
2.60	2.43	1.97	1.60	1.18	1.11	.75	1.28	.72	.62	.32	.33	.25
2.88	2.71	2.02	1.99	1.32	.88	.72	.75	.48	.52	.39	.39	.35
2.84	2.79	2.41	2.32	1.46	.82	.70	.59	.43	.39	.36	.41	.31

TABLE A-2. - Relative n-Paraffin Weight-Percent Data for Topped Crude Oils Analyzed

Topped Crude Oil Number	Relative Weight Percent by Carbon Number									
	C ₁₅	C ₁₆	C ₁₇ ¹	C ₁₈ ²	C ₁₉	C ₂₀	C ₂₁	C ₂₂	C ₂₃	C ₂₄
75002	5.08	9.89	18.07	12.69	10.82	8.73	5.57	5.37	4.70	3.63
75003	4.42	9.38	15.21	10.95	8.72	7.23	6.56	6.12	5.72	5.02
75004	3.69	8.34	17.43	13.52	8.58	8.66	6.35	6.09	5.38	4.24
75005	2.06	6.69	17.17	12.49	8.72	8.19	7.20	6.74	6.32	5.36
75006	2.48	6.81	17.46	11.48	9.43	7.62	6.97	6.76	6.56	5.54
75007	8.41	9.32	17.89	15.49	7.53	7.14	5.12	4.77	4.69	3.67
75009	5.69	8.98	15.87	11.30	10.77	6.49	6.03	5.83	5.56	5.09
75010	5.38	7.14	13.81	11.24	7.30	7.40	6.32	5.98	5.66	5.05
75011	8.15	9.75	17.16	11.65	8.27	7.28	6.22	5.73	5.31	4.60
75012	7.29	8.90	12.80	13.06	7.75	8.23	6.10	5.66	5.59	4.56
75014	7.53	9.69	15.29	15.02	8.31	8.10	5.87	5.55	5.26	4.46
75015	5.45	9.82	11.74	11.90	8.88	9.65	6.34	5.42	4.72	4.61
75018	4.08	7.62	16.30	15.82	7.71	7.99	6.42	5.42	5.16	4.15
75025	7.14	8.02	13.57	11.43	10.07	10.58	7.68	6.76	6.03	4.97
75026	7.36	8.87	17.08	15.56	7.78	7.99	6.10	5.36	4.77	3.75
75027	6.59	9.67	26.81	14.50	9.07	8.19	3.61	3.79	2.75	2.58
75028	2.38	4.37	8.10	10.76	10.70	10.71	8.23	8.05	7.95	6.90
75030	0.44	6.39	13.77	15.30	11.14	9.33	6.74	6.26	5.98	5.16
75031	5.18	6.00	11.45	8.83	8.09	6.62	6.50	6.39	6.13	5.77
75032	2.25	6.44	12.84	16.24	9.44	8.63	7.59	6.54	5.72	5.22
75041	1.42	5.63	9.98	14.07	10.41	8.54	6.82	6.40	5.86	5.79
75042	2.57	7.70	11.46	13.50	10.16	9.01	7.78	6.68	6.05	5.80
75044	4.73	7.53	7.62	10.59	9.77	9.27	8.77	7.50	6.64	6.32
75045	0.85	4.74	13.63	12.29	12.81	7.72	6.45	6.06	6.09	4.98
75046	4.25	7.42	16.13	12.94	9.02	8.19	6.25	5.80	5.68	4.85
75047	6.55	9.88	10.69	13.24	12.58	7.57	5.80	5.58	4.78	4.30
75049	2.69	4.57	7.80	12.95	8.26	5.83	6.69	6.29	6.84	6.41
75050	5.30	5.21	9.88	13.44	7.69	5.97	5.45	5.61	6.03	5.44
75051	6.52	13.03	23.98	10.63	12.96	8.15	4.62	3.62	3.11	2.51
75052	3.96	5.00	7.95	12.67	7.15	5.58	6.42	6.11	6.77	6.49
75054	1.14	5.90	13.80	12.44	10.68	10.11	8.20	7.36	6.73	5.48
75057	4.10	9.16	17.72	12.28	10.19	7.42	6.12	5.81	5.59	4.60
75059	2.14	3.45	8.61	11.12	7.53	5.05	5.84	5.57	6.14	5.95
75060	2.33	4.16	7.46	10.92	8.11	6.67	6.88	6.59	7.09	6.88
75062	2.53	4.64	11.66	10.44	11.31	12.17	9.53	9.12	8.54	7.59
75063	3.19	5.94	12.70	8.62	9.91	10.69	8.64	7.26	0.70	7.70
75064	3.14	7.61	18.86	11.53	8.60	8.81	6.20	6.02	5.64	4.72
75065	2.16	4.27	5.68	10.78	6.72	6.17	5.87	5.86	7.23	5.39
75066	12.86	10.52	16.70	10.59	7.57	7.67	5.52	5.12	4.59	3.82
75067	7.54	8.04	17.27	11.46	7.52	7.38	6.60	6.12	5.75	4.07
75068	4.11	7.61	16.41	11.06	8.91	8.81	6.11	5.65	6.03	4.56
75069	4.17	6.01	7.68	10.76	7.79	6.48	6.99	6.31	7.06	6.04
75070	21.06	12.46	10.52	10.63	6.30	5.42	5.06	5.55	4.00	4.10
75071	10.80	11.06	18.16	13.63	7.11	6.72	5.05	4.64	4.44	3.84
75072	9.15	9.58	17.30	14.79	7.79	8.09	5.71	5.38	4.89	4.05
75073	5.64	7.58	16.03	13.40	10.41	8.09	5.41	5.44	5.39	4.74
69069	4.99	6.47	12.55	9.46	7.73	6.55	6.34	6.48	5.96	5.63
69111	5.06	8.83	11.49	11.96	9.21	7.86	6.87	5.81	5.30	4.94
70113	3.67	6.07	14.88	13.25	8.81	7.31	7.04	6.29	5.70	5.41
71011	3.84	6.27	17.87	11.24	8.12	7.34	6.80	6.10	5.66	5.21

¹ Includes contribution of pristane.² Includes contribution of phytane.

TABLE A-2. - Relative n-Paraffin Weight-Percent Data for Topped Crude Oils
Analyzed--continued

Relative Weight Percent by Carbon Number										
C ₂₅	C ₂₆	C ₂₇	C ₂₈	C ₂₉	C ₃₀	C ₃₁	C ₃₂	C ₃₃	C ₃₄	C ₃₅
3.43	2.89	2.12	1.54	1.33	1.04	0.78	0.71	0.59	0.56	0.44
4.81	3.60	2.83	2.32	1.99	1.48	1.20	.86	.60	.56	.44
3.94	3.37	2.33	1.50	1.48	1.12	.95	.86	.79	.77	.59
4.35	3.67	2.51	1.95	1.33	1.04	1.00	.76	.78	.72	.69
4.37	3.67	2.50	1.81	1.46	1.14	.94	.80	.75	.83	.61
3.65	3.04	2.17	1.36	1.27	0.96	.80	.72	.68	.73	.56
4.22	3.87	2.57	1.77	1.11	.91	1.17	.69	.67	.79	.63
4.28	3.76	3.45	3.43	1.83	1.66	1.33	1.12	1.00	1.03	.77
3.88	3.32	2.23	1.76	1.06	.77	.72	.55	.54	.53	.49
3.94	3.31	2.57	1.71	1.28	1.74	1.60	1.38	.92	.90	.70
3.96	3.32	2.53	1.20	0.77	.67	.47	.41	.48	.58	.54
3.94	3.88	2.48	2.42	1.73	1.69	1.33	1.42	.95	.94	.69
3.93	3.28	2.68	1.79	1.50	1.29	1.17	.98	.93	1.03	.78
4.71	2.21	1.52	1.22	.95	.76	.64	.52	.47	.43	.33
3.43	2.94	2.08	1.62	1.24	.99	.85	.68	.61	.56	.39
3.01	2.55	1.59	0.89	.84	.58	.63	.56	.59	.72	.50
6.03	4.70	3.44	1.82	1.44	1.09	.97	.74	.62	.56	.43
4.31	3.58	2.49	1.69	1.49	1.47	1.30	.98	.79	.80	.59
5.45	4.98	4.90	3.96	3.26	2.28	1.94	.92	.77	.42	.26
4.07	3.78	2.55	1.92	1.53	1.27	1.17	1.01	.69	.62	.47
4.58	4.73	3.58	2.50	1.88	2.21	1.59	1.63	.91	.98	.76
4.46	4.13	2.96	2.61	1.14	1.27	.66	.88	.38	.46	.36
5.60	5.41	4.19	3.73	.65	.55	.27	.29	.16	.20	.19
4.75	4.25	3.79	3.68	1.50	1.39	1.31	1.29	.96	.92	.56
4.06	3.44	2.62	1.87	1.32	1.38	1.32	.90	.93	.94	.68
3.47	3.26	2.36	1.98	1.45	1.93	1.24	1.16	.80	.79	.60
6.06	5.44	4.80	5.27	3.65	2.06	1.16	1.20	.35	.91	.78
5.46	4.95	4.41	4.09	2.60	2.43	1.25	1.54	.89	1.29	1.07
2.17	1.84	1.51	1.23	1.08	.90	.57	.57	.37	.39	.24
6.37	5.85	5.30	5.59	2.48	2.25	1.22	1.21	.34	.79	.47
4.59	3.29	2.28	1.84	1.49	1.09	.98	.71	.70	.63	.57
4.08	3.12	2.31	1.84	1.47	.98	.88	.69	.65	.59	.39
5.81	5.47	5.00	5.52	5.28	4.34	2.85	1.55	.65	1.23	.88
6.64	6.20	5.62	6.09	2.30	2.03	.99	1.31	.42	.80	.51
2.97	2.46	1.78	1.33	1.01	.74	.58	.42	.33	.30	.20
8.23	2.51	1.99	1.44	.68	.51	.36	.28	.17	.23	.18
4.89	3.77	2.76	1.88	1.51	1.27	.82	.61	.52	.47	.36
5.88	4.65	4.98	2.92	2.76	5.92	4.68	4.65	1.42	1.11	.88
3.61	3.16	2.33	1.75	1.21	.99	.54	.51	.35	.40	.29
4.17	3.67	3.13	2.04	1.65	1.11	.85	.59	.46	.44	.33
4.69	3.93	2.81	2.42	2.14	1.55	1.21	.67	.54	.46	.32
6.03	5.10	4.60	3.98	3.33	2.34	1.14	1.99	.62	.80	.61
3.37	2.87	2.08	1.99	1.03	1.59	.49	.59	.13	.42	.32
3.13	2.67	2.09	1.71	1.26	.97	.69	.63	.51	.51	.41
3.94	3.03	2.12	1.50	.92	.65	.29	.28	.14	.23	.18
4.52	3.90	3.23	1.77	1.42	1.13	.52	.54	.07	.39	.38
5.12	3.88	3.21	3.68	2.17	2.40	1.85	1.30	.96	1.09	1.18
3.85	3.55	3.17	2.20	1.70	3.06	1.74	1.45	.71	.72	.52
4.48	4.02	2.78	1.91	1.59	1.72	1.07	1.11	.91	1.05	.92
4.56	4.50	3.17	2.04	1.45	1.19	1.37	.88	.76	.89	.75