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Crude Oil Spills Research

An Investigation and Evaluation of Analytical Techniques

UNITED STATES DEPARTMENT OF THE INTERIOR

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An Investigation and Evaluation of Analytical Techniques

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CRUDE OIL SPILLS RESEARCH

An Investigation and Evaluation of Analytical Techniques

by

C. A. Wilson,[1] E. P. Ferrero,[1] and H. J. Coleman[2]

ABSTRACT

The Bureau of Mines started a continuing program to investigate and evaluate analytical techniques to assist governmental agencies to select simple, rapid, reliable methods for crude oil spill identification. Six crude oil samples were analyzed to evaluate gas-liquid chromatography, atomic absorption spectrophotometry, infrared spectoscopy, sulfur and nitrogren determinations, mass spectrometry, nuclear magnetic resonance spectroscopy, and ultraviolet spectrophotometry. Samples were studied from the following selected fields: El Morgan, Egypt; Duri, Indonesia; Minagish, Kuwait; Bachaquero, Venezuela; Gach Saran, Iran; and Prudhoe Bay, Alaska. These samples were chosen to represent high-production fields that are likely to be involved in oceanic transport. Over 50 years of Bureau of Mines analytical research on petroleum served as the basis for evaluation of the experimental results to determine which of the methods are effective techniques to identify crude oil spills. Gas-liquid chromatographic analysis, atomic absorption spectrophotometric analysis, and sulfur-nitrogen determinations are recommended as the most useful of the techniques investigated.

INTRODUCTION

In cases of crude oil pollution of coastal waters, beaches, and inland waters, the source of pollution is often difficult to identify. Recently, successful work has been done on identification of spilled oils (1-2, 16, 19, 25, 37),[3] but much of this work has focused on identification of petroleum products. The Bureau of Mines Energy Research Center in Bartlesville, Okla., prompted by frequent inquiries from government agencies charged with responsibility for pollution control, studied the use of some identification techniques on crude oils. Current interests in applying many instrumental techniques to the oil spill problem has raised various questions about such frequently mentioned techniques as gas-liquid chromatography, atomic absorption spectrophotometry, infrared spectroscopy, mass spectrometry, and ultraviolet spectrophotometry. The Bureau of Mines evaluated these and other oil spill

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[1] Research chemist.

[2] Project leader.

[3] Underlined numbers in parentheses refer to items in the bibliography preceding the appendix.

identification techniques by analyzing crude oil samples from El Morgan, Egypt; Duri, Indonesia; Minagish, Kuwait; Bachaquero, Venezuela; Gach Saran, Iran; and Prudhoe Bay, Alaska (table 1); to assist governmental agencies in selecting simple, rapid, reliable analytical methods.

TABLE 1. - Sample source

Field	Country	Producing age	Company	Crude oil analysis tables (see appendix)
El Morgan.....	Egypt.......	Miocene......	American International Oil Co.	A-1
Duri..........	Indonesia...	Tertiary.....	California Texas Oil Corp.	A-2
Minagish......	Kuwait......	Cretaceous...	Kuwait Oil Co., Ltd.......	A-3
Bachaquero....	Venezuela...	Miocene......	Creole Petroleum Co.......	A-4
Gach Saran....	Iran........	Miocene......	California Texas Oil Corp.	A-5
Prudhoe Bay...	Alaska......	Triassic.....	Atlantic Richfield Co.....	A-6

For many years, the Bureau of Mines has analyzed crude oils from domestic and foreign fields (13-14, 30-35), and the routine crude oil distillation (41) served as a source for the two different cuts used in the study. This Bureau analytical research on crude oil composition and characteristics served as the basis for evaluation of experimental results to determine which of the methods are the most practical to aid in the identification of crude oil spills.

ACKNOWLEDGMENTS

Acknowledgment is made to the oil companies that supplied crude oil samples and sample source information. The authors are also grateful to the following personnel at the Bartlesville Energy Research Center for advice in their field: R. F. Kendall, research physicist, infrared spectroscopy; J. E. Dooley, project leader, mass spectrometry; D. A. Doughty, research physicist, nuclear magnetic resonance spectroscopy; and Dorothy T. Nichols, physical science technician, crude oil analysis. J. F. McKay, research chemist, at the Laramie Energy Research Center, Laramie, Wyo., provided advice in ultraviolet spectrophotometry.

EXPERIMENTAL STUDY

Although some analytical techniques are equally effective for identifying petroleum products and crude oils, others that are valuable for identifying petroleum product spills are less valuable for identifying crude oil spills. Also, as weathering increases, some possibly useful methods show increasingly less distinction among crude oils. Several popular techniques have been examined to determine their usefulness for identification of crude oils and topped crude oils.

Where possible, all methods were applied to the crude oil, the topped crude oil (crude oil topped at 275° C), and the residuum (crude oil topped to 420° C) in order to simulate the evaporative process of weathering. Comparisons of results from the analyses of crude oil, topped crude oil, and residuum give some indication of the effect of natural weathering on an exposed sample. These comparisons can determine the best methods to use to relate an exposed sample to a suspect sample. The following techniques have been evaluated for use for crude oil spill identification.

Analytical Techniques

Gas-Liquid Chromatography

Gas-liquid chromatography (GLC) is a popular technique for identifying spilled oils. The advantages of GLC include relatively rapid analysis on a small sample with little sample preparation. Samples in this study were analyzed without any preparation except for high-viscosity crude oils, topped crude oils, and residua that dictated some dilution with toluene prior to injection. All runs were made on an F & M Scientific Corp. Model 810 research chromatograph[4] equipped with a flame ionization detector (FID). Column and run conditions are listed in table 2.

TABLE 2. - Gas-liquid chromatography operating conditions

Columns	Dual, 1/8 in OD by 11 ft stainless steel.
Packing	3 pct OV-1 on 80/100 mesh chromosorb G, acid washed.
Carrier gas	Helium.
Flow ml/min	20
Temperatures, ° C:	
Injection port	300
Column, initial	50
Column, final	380
Detector	380
Program rate ° C/min	6
Start after injection min	2
Detector	FID

Although GLC does not completely define natural weathering effects, it does define the extent of the loss of light components due to evaporation. This loss can be compensated for by topping both the spilled oils and possible source oils to the same temperature. The comparison in figure 1 of chromatograms of the crude oil, topped crude oil, and residuum of an El Morgan, Egypt, sample demonstrates that progressive sample evaporation leaves the remaining chromatographic pattern unchanged. Although the micro-organisms that biologically degrade crude oil will preferentially attack the normal paraffins (1), the resulting loss should not substantially change the GLC pattern (8, 10)

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[4] Reference to specific brands of equipment is made for identification only and does not imply endorsement by the Bureau of Mines.

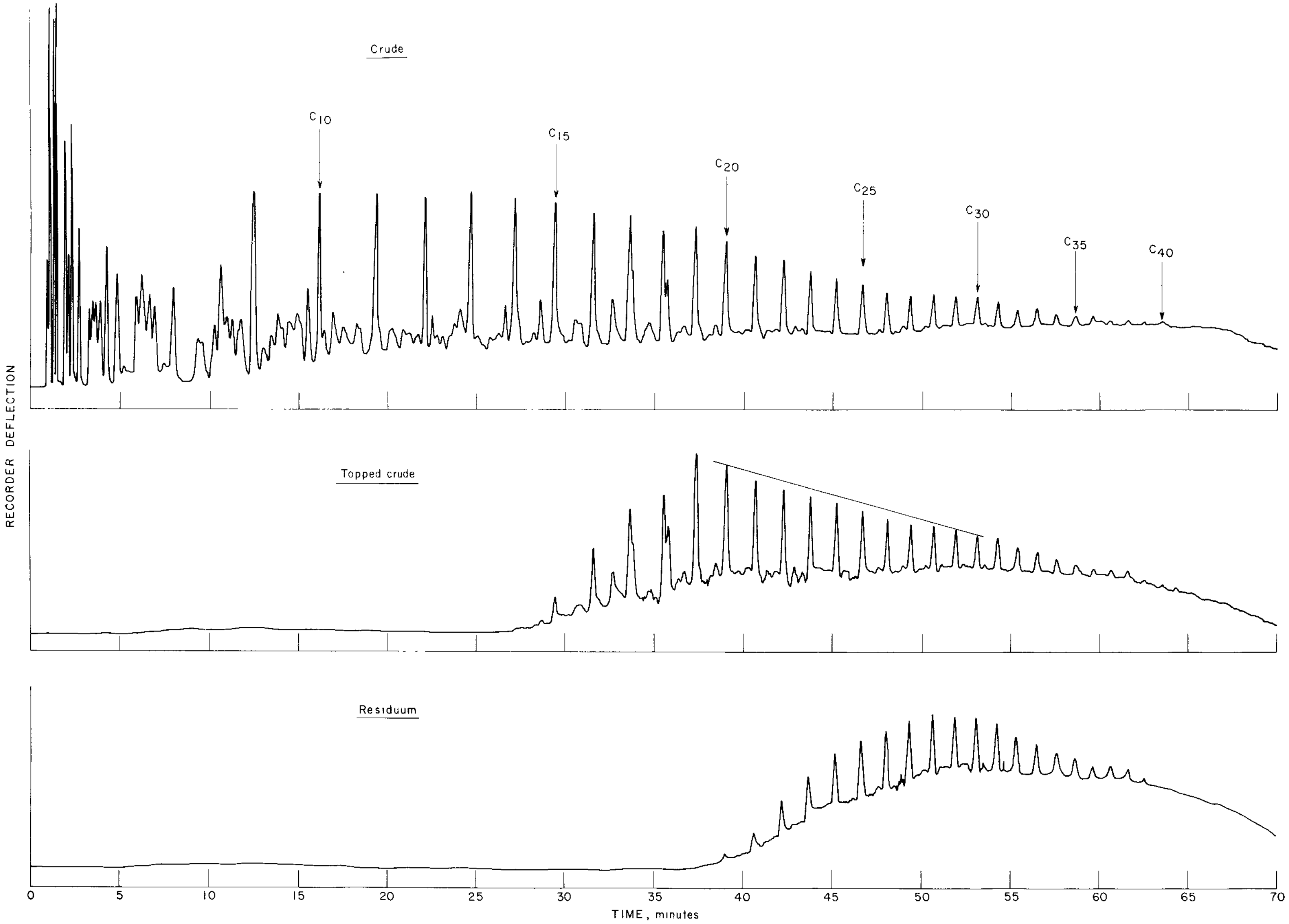

FIGURE 1. - Gas-liquid chromatograms of El Morgan, Egypt, crude, topped crude, and residuum.

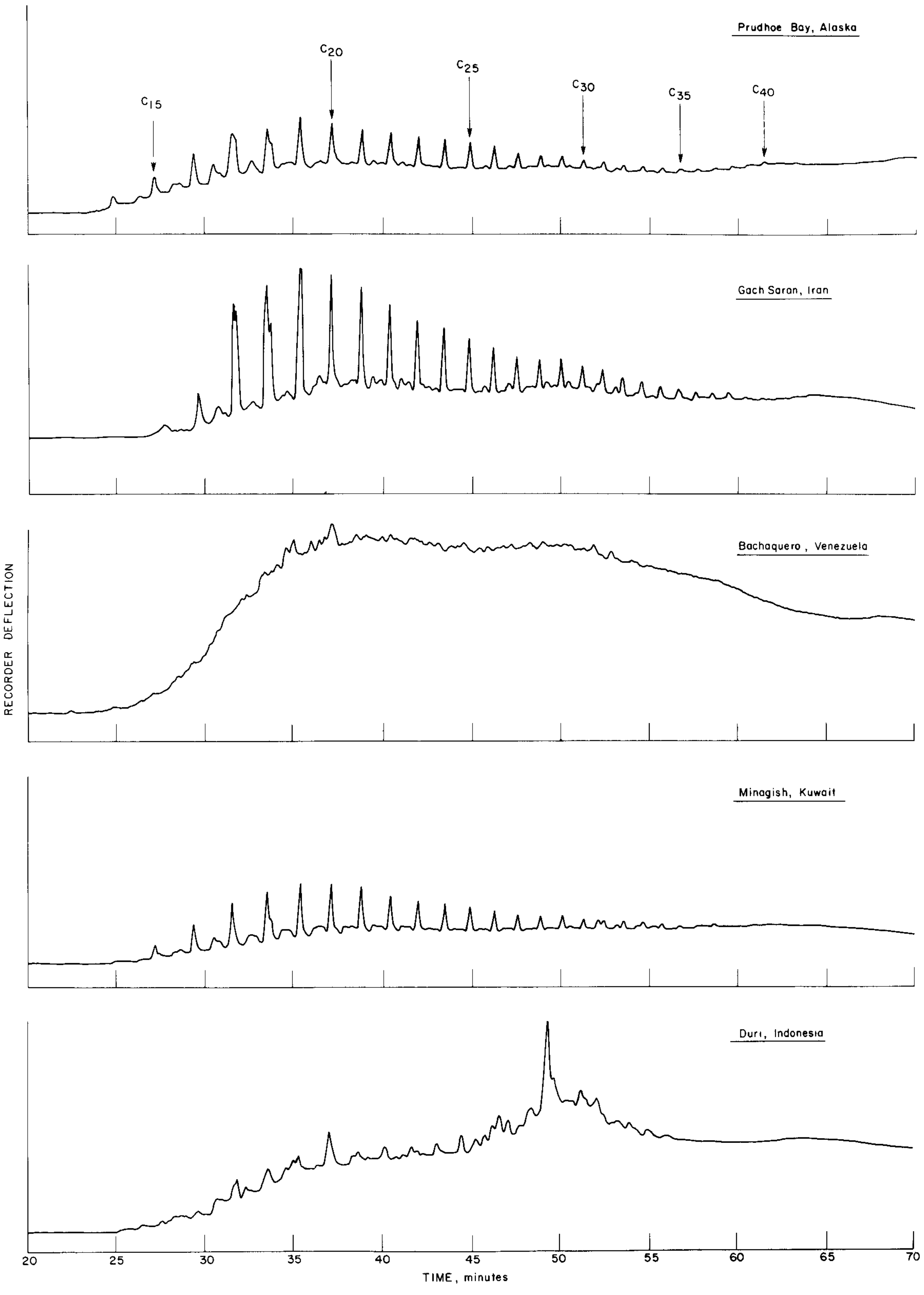

FIGURE 2. - Gas-liquid chromatograms of topped crude oils from five crude oil samples.

unless the exposure has been extreme. In fact, a chromatogram of an oil that had been on the ocean floor for several months was very similar to that of the original crude oil (12).

The major problem inherent in GLC is the interpretation of results. Inspection of chromatograms can range from visual to complex mathematical analyses. A decision on the method best suited to the particular problem should include such considerations as the number of chromatograms to be compared, the amount of time to be spent on each, and the availability of data handling devices and facilities such as on-line integrators and computerized services.

In situations involving a limited number of samples, visual comparison of chromatograms eliminates the need for time consuming determination of peak areas, normalization for sample sizes, and mathematical treatment of data. The person scanning such chromatograms need only search for (1) relative peak heights of normal paraffins as in the Minagish, Gach Saran, and Prudhoe Bay chromatograms of figure 2, (2) relative amounts of unresolved components as in the Duri and Bachaquero chromatograms of figure 2, and (3) any characteristic of a unique nature such as the peak found at about 50 minutes in the Duri chromatogram of figure 2. Unique characteristics can often be missed in a statistical treatment involving only a portion of the chromatogram.

A statistical approach can range from manual determination of peak areas of normal paraffin peaks to integration over the entire boiling range with computerized handling of data to produce any number of comparisons. The latter requires quite sophisticated electronic equipment not available at all laboratories. Evaluation of some of the simpler manual operations involved measuring and normalizing peak areas in the range from normal eicosane ($\underline{n}$-C_{20}) to normal triacontane ($\underline{n}$-C_{30}), calculating peak area ratios C_n+1/C_n , averaging the ratios, tabulating highest normal paraffin carbon numbers, plotting carbon number versus percent of total from $\underline{n}$-C_{20} through $\underline{n}$-C_{30} , and establishing a profile from $\underline{n}$-C_{20} through $\underline{n}$-C_{30} as suggested by Miller (37). The suggested profile is defined as the number of peaks that touch or extend above a line drawn from the top of peak $\underline{n}$-C_{20} to the top of peak $\underline{n}$-C_{30} as illustrated on the topped crude oil sample in figure 1. All chromatograms that did not have a $\underline{n}$-C_{20} or a $\underline{n}$-C_{30} peak were classified as "broad" (B).

Manual measurement of peak area is difficult due to the necessity of establishing a baseline; thus, the repeatability of area measurements may become as dependent on operator judgment as on variation from one crude oil to another. The adjacent normal paraffin peak ratios, calculated by the formula C_n+1/C_n and averaged as shown in table 3, revealed few distinctive characteristics for paraffinic crude oils and could not be determined for nonparaffinic crude oils. The highest normal paraffin peak resolved seemed to be as much a function of sample size and sensitivity as a characteristic of the crude oil. The plot of carbon number versus percent normal paraffin in the range $\underline{n}$-C_{20} to $\underline{n}$-C_{30} (fig. 3) exhibited little distinction among the oils and cannot be determined on nonparaffinic samples. The profile suggested by Miller seems to offer the most promise as a tool to eliminate consideration of some of the chromatograms. Profiles from the chromatograms in this study are listed in table 4. Because of the limited number of possible profiles between $\underline{n}$-C_{20} and $\underline{n}$-C_{30} (0 to 9, and B), the method cannot be used to select a specific source oil but can be used to eliminate enough chromatograms to allow visual comparison. Such visual comparison seems to be the quickest and most satisfactory way to deal with the chromatograms in the absence of a sophisticated data reduction system.

TABLE 3. - Average adjacent n-paraffin peak ratios, C_{20} to C_{30}

Sample	Crude	Topped crude	Residuum
El Morgan	0.90	0.89	1.28
Duri	NA	NA	NA
Minagish	.86	.94	1.38
Bachaquero	NA	NA	NA
Gach Saran	.86	.86	1.12
Prudhoe Bay	.85	.89	1.26

NA--Not available for nonparaffinic oils.

TABLE 4. - Profile classification of GLC data from n-C_{20} to n-C_{30}

Sample	Crude	Topped crude	Residuum
El Morgan	0	1	9
Duri	B	B	B
Minagish	2	2	7
Bachaquero	B	B	B
Gach Saran	0	0	9
Prudhoe Bay	2	6	B

B--Broad

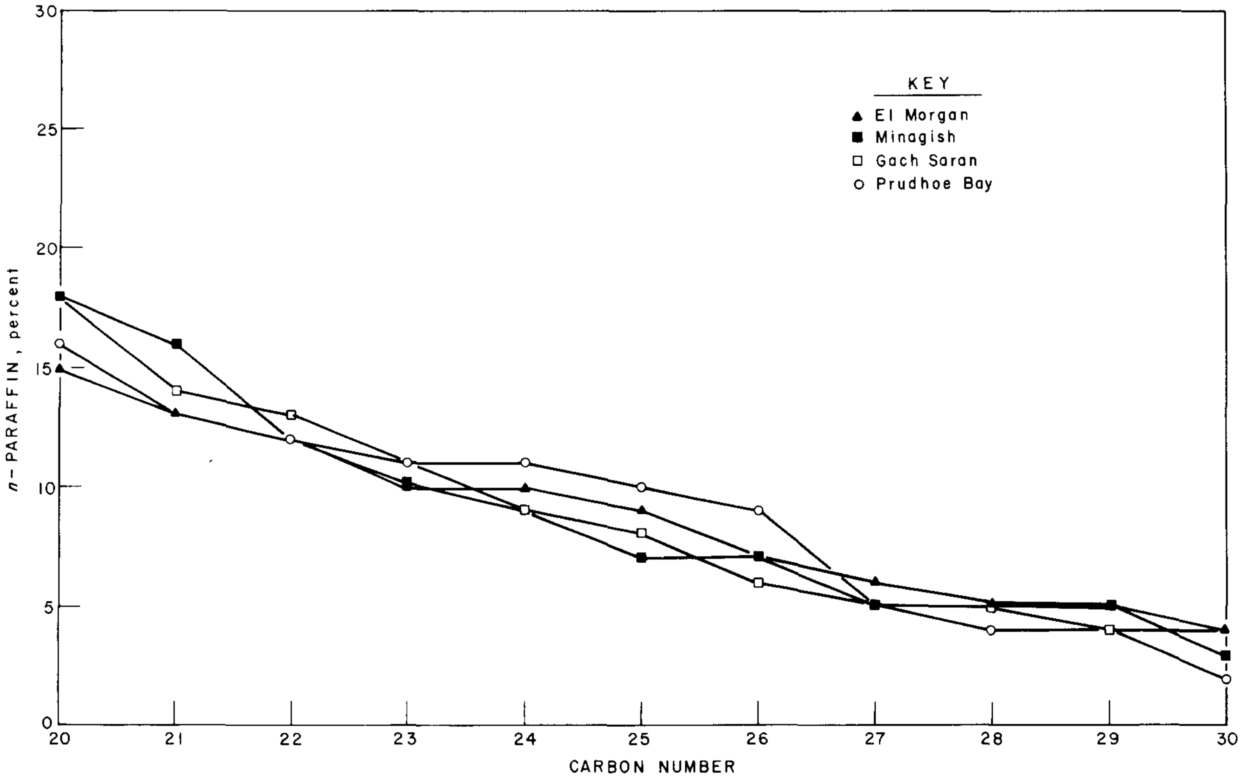

FIGURE 3. - Comparison of percent n-paraffin to carbon numbers from C_{20} to C_{30} as determined from GLC data on topped crude oil samples.

Atomic Absorption Spectrophotometry and Colorimetry--Vanadium and Nickel

Often recommended for oil characterization, vanadium and nickel are among the most abundant trace metals. In addition to being present in readily measurable quantities, the vanadium and nickel contents vary widely among crude oils and are generally thought to be little affected by weathering, making them ideal for identification purposes. Most current vanadium and nickel determinations are made by atomic absorption (AA) spectrophotometry.

Samples for atomic absorption analysis were ashed by the benzene-sulfonic acid method (4, 40) and dissolved in a hydrochloric acid-water matrix. Standard solutions were prepared to cover the expected range, and vanadium and nickel were determined with a Perkin Elmer Model 403 atomic absorption spectrophotometer. For highly paraffinic or viscous samples, the ashing technique was found to show better repeatability than simple dilution of the sample for direct burning. Once the ashing was accomplished, many samples could be run at one time so that the method was not as time-consuming as it might appear.

Atomic absorption repeatability was frequently in the 10 to 20 percent range, and great care was necessary in both the sampling and ashing of oils in order to obtain results differing by less than 20 percent. Although repeatability can be less than desirable, vanadium and nickel concentrations were found to vary enough from crude oil to crude oil to make this parameter a useful identification tool (table 5).

TABLE 5. - Vanadium and nickel concentration data[1]

Sample	Vanadium, ppm			Nickel, ppm			Vanadium-to-nickel ratio		
	Crude	Topped crude	Residuum	Crude	Topped crude	Residuum	Crude	Topped crude	Residuum
El Morgan........	43.7	75.6	98.6	24.0	43.2	51.2	1.8	1.8	1.9
Duri.............	0	0	4.0	33.7	35.1	49.0	0	0	.1
Minagish.........	10.5	26.8	47.8	6.0	11.3	19.2	1.8	2.4	2.5
Bachaquero.......	442.2	512.8	695.7	58.2	71.4	86.6	7.6	7.2	8.0
Gach Saran.......	89.0	189.8	233.7	30.5	55.9	62.2	2.9	3.4	3.8
Prudhoe Bay......	28.2	33.2	59.1	8.8	16.4	25.4	3.2	2.0	2.3

[1] Determined by atomic absorption spectrophotometry.

The use of the vanadium-to-nickel ratio has often been recommended, the argument being that exposure will have an identical effect on both metals, and therefore the ratio will remain constant. For the samples in this study, the ratios varied as much from crude oil to topped crude oil to residuum as from sample to sample, as can be seen in table 5, possibly due to the lack of repeatability or to the different relative volatilities of vanadium and nickel compounds. Although there is some validity to the argument for using a ratio, the absolute values cover a much wider range than do the ratios and can be compared directly with the values of other samples topped to the same temperature. In table 5, the absolute values of El Morgan compared with those of Minagish and Gach Saran compared with those of Prudhoe Bay are distinguishable, but the ratios of the same samples are similar enough to be troublesome. If ratios are used, they should not be reported without citing absolute values (24, 37).

In addition to atomic absorption, vanadium and nickel were determined colorimetrically (table 6). Samples were ashed with sulfuric acid. Vanadium was determined by the sodium tungstate method (42), and nickel was determined by the dimethylglyoxime method (9). In both cases, readings were made with a Bausch and Lomb Spectronic 20 visible spectrophotometer.

TABLE 6. - Trace metals results--comparison of two methods

Sample, crude	Vanadium, ppm		Nickel, ppm	
	Atomic absorption	Colorimetric	Atomic absorption	Colorimetric
El Morgan...........	43.7	39.2	24.0	22.2
Prudhoe Bay..........	28.2	16.5	8.8	8.9

Although the colorimetric method can yield better repeatability than atomic absorption (36), the procedures, particularly the one for nickel, are complex and time consuming, and therefore not desirable for routine use (3). Only a few samples can be run at one time owing to the excessive manipulation required for each sample, and without extreme care, repeatability is reduced to a level comparable with that of atomic absorption. Painstaking colorimetric results can be more repeatable than atomic absorption results, but the improved repeatability does not seem important enough to justify the extra time involved.

Infrared Spectroscopy

Infrared spectra for use in oil spills identification seem to offer several advantages. First, the required instrumentation is relatively inexpensive and simple to operate; second, little or no sample preparation is required; and finally, the analysis can be completed in less time than is needed for any other method evaluated. Unfortunately the value of the information obtained may be limited.

Samples were run on a Perkin Elmer Model 467 infrared spectrophotometer with a sodium chloride sample cell. Sample preparation was necessary only when samples would not spread uniformly; tacky samples were first diluted with a suitable solvent (carbon disulfide) that had no absorbance bands in the regions of interest. Absorbance was measured for bands at 720, 810, 1,375, and 1,600 cm^{-1}, and the ratios (tables 7 and 8) were calculated. The use of the ratios as an identification tool has been recommended as a mathematical solution to evaluate infrared spectra (20, 22).

TABLE 7. - Comparison of duplicate infrared absorbance ratios

Sample, topped crude[1]	Wave number ratio				
	720/1,375	1,600/1,375	1,600/720	810/1,375	810/720
El Morgan, A...........	0.227	0.182	0.801	0.127	0.559
El Morgan, B...........	.205	.196	.958	.124	.605
Minagish, A............	.227	.151	.664	.146	.642
Minagish, B............	.223	.166	.746	.145	.650
Duri, I................	.293	.249	.848	.139	.474
Duri, II...............	.294	.256	.873	.144	.492
Prudhoe Bay, I.........	.161	.236	1.467	.152	.944
Prudhoe Bay, II........	.141	.229	1.627	.150	1.064

[1] B is A sampled in a new cell 2 months later. II is a second distillation cut at the same temperature as I.

TABLE 8. - Infrared absorbance ratios of topped oils from crude oil samples

Sample, topped crude	Wave number ratio				
	720/1,375	1,600/1,375	1,600/720	810/1,375	810/720
El Morgan..............	0.227	0.182	0.801	0.127	0.559
Duri...................	.293	.249	.848	.139	.474
Minagish...............	.227	.151	.664	.146	.642
Bachaquero.............	.099	.274	2.771	.166	1.679
Gach Saran.............	.175	.226	1.288	.138	.786
Prudhoe Bay............	.161	.236	1.467	.152	.944

More than one-fourth of the absorbance ratios (table 7) differed by as much as 17 percent within the same ratio when comparisons were made of duplicate runs of the same topped sample or of determinations on different topped samples from two separate distillations of the same crude oil. Ratios from repeated distillations were comparable with ratios from duplicate runs of the same sample (table 7), indicating that the distillation process was not accountable for the repeatability differences. Instrument repeatability was good. Discrepancies in peak measurement by the analyst seemed to be the significant factor responsible for deviations (28). Less than one-fourth of the results from the six different topped crude oils (table 8) showed greater variation than duplicate runs. Because duplicate runs often show as much variation as found with different samples, the use of these infrared ratios--$\frac{720}{1,375}$, $\frac{1,600}{1,375}$, $\frac{1,600}{720}$, $\frac{810}{1,375}$, and $\frac{810}{720}$--is not a satisfactory answer to identifying crude oil spills.

Computer analysis of infrared ratios of 21 bands in the 650 to 1,200 cm^{-1} region has been used to identify oil spills (26). Not only does this method require computer capabilities, but as the sample becomes more severely weathered, the spectrum becomes less distinctive as in the 600 to 900 cm^{-1} region of the Prudhoe Bay sample in figure 4. Oxidation of weathered samples can cause changes in some portions of the spectrum (1, 25). For a crude oil, these factors make it difficult as weathering increases to match a spilled oil with a suspect source on the basis of only the infrared spectrum. Used as a confirmatory technique, an infrared spectrum could be of value,

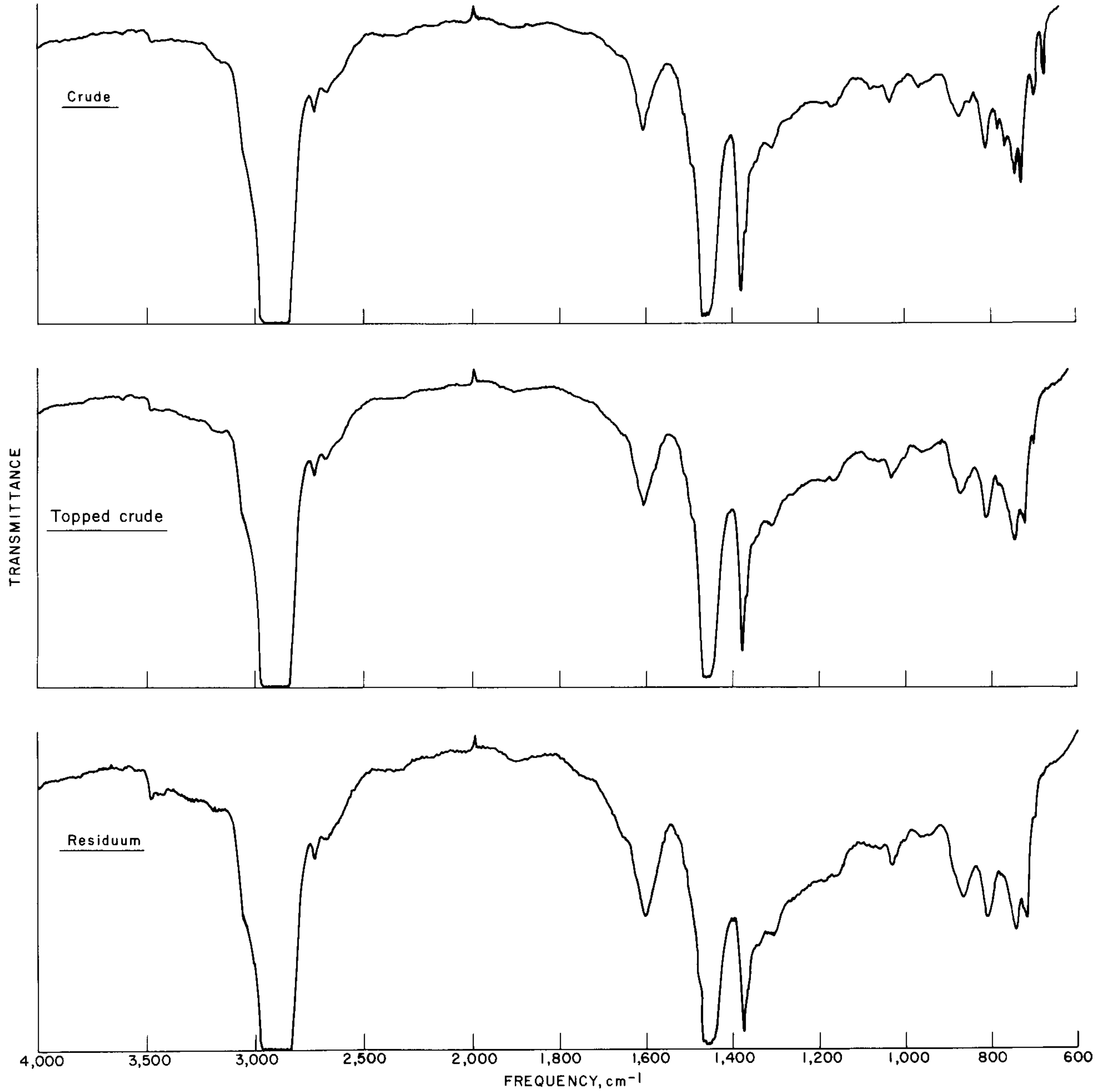

FIGURE 4. - Infrared spectra of Prudhoe Bay, Alaska, crude, topped crude, and residuum.

particularly if it was scanned for any unique portion that might be missed by measurement of a few individual absorbance bands (11). Examples of contrasting portions of the spectra can be found in the 700 to 900 cm^{-1} region of the topped crude oil samples. Bachaquero (fig. 5), Gach Saran (fig. 5), and Prudhoe Bay (fig. 4) topped crude oils are the most distinctive, whereas El Morgan, Duri, and Minagish topped crude oils (fig. 5) are relatively similar. As the exposure time for a spilled oil increases, the likelihood of the infrared spectrum being distinctive decreases. Therefore, the usefulness of the method is extremely dependent on the extent of weathering.

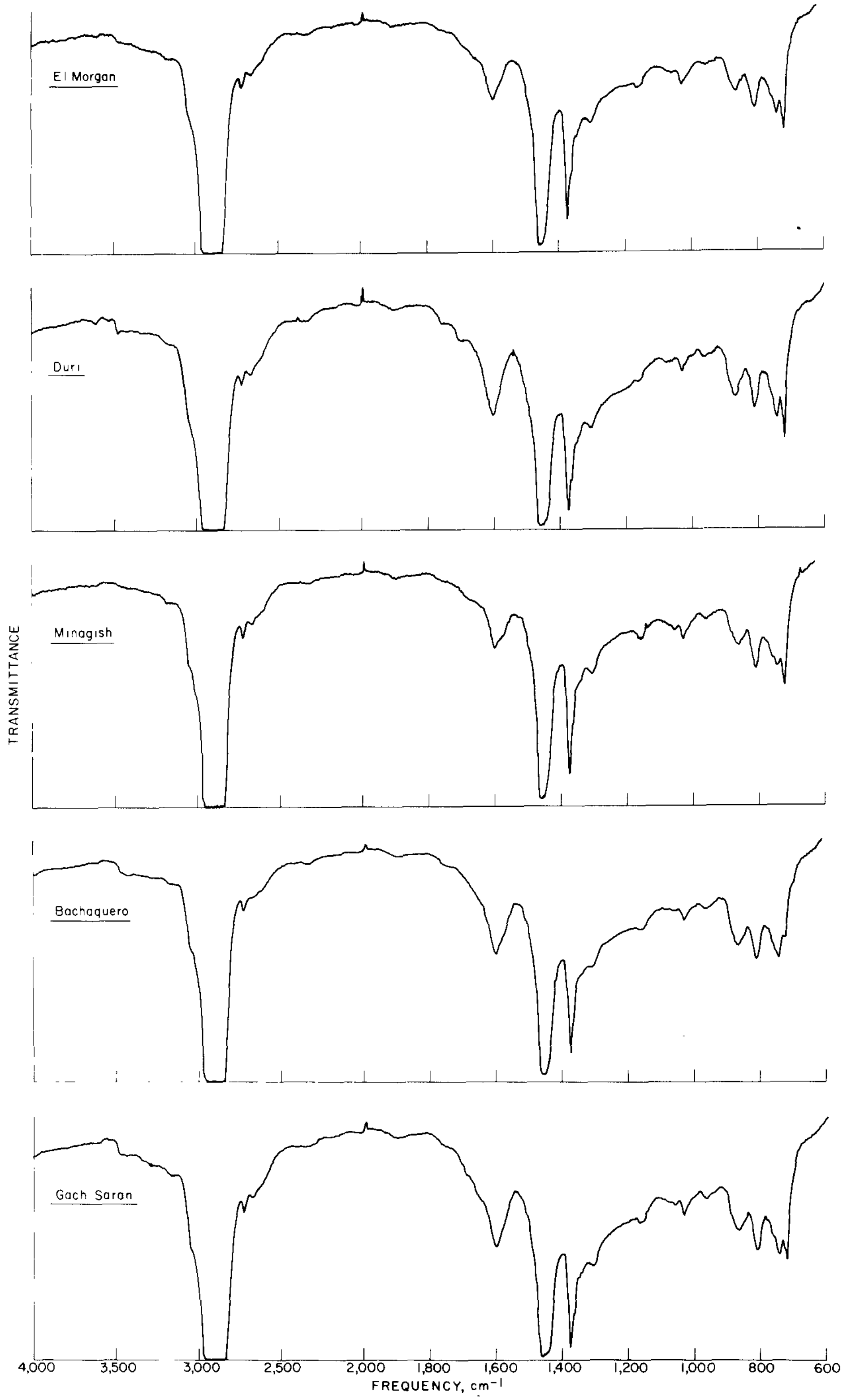

FIGURE 5. - Infrared spectra of five topped crude oil samples.

Mass Spectrometry

Mass spectra on the topped crude oil samples were obtained with a CEC (Consolidated Electrodynamics Corp.) Model 21-102 mass spectrometer, which has been modified to be equivalent to the Model 21-103. All runs were made at 15 electron volts, and samples were introduced through a 300° C all-glass inlet.

The data were initially plotted as percent of total ionization versus nominal mass Z series number. The nominal mass Z series number is taken from the general hydrocarbon formula $C_n H_{2n+Z}$ and represents a homologous series with each successive homologue being increased by the addition of a methylene group, CH_2 (14 mass units). The initial graph (fig. 6) showed little distinction between samples. Consequently, graphs of percent of total ion intensity versus the individual mass numbers for the

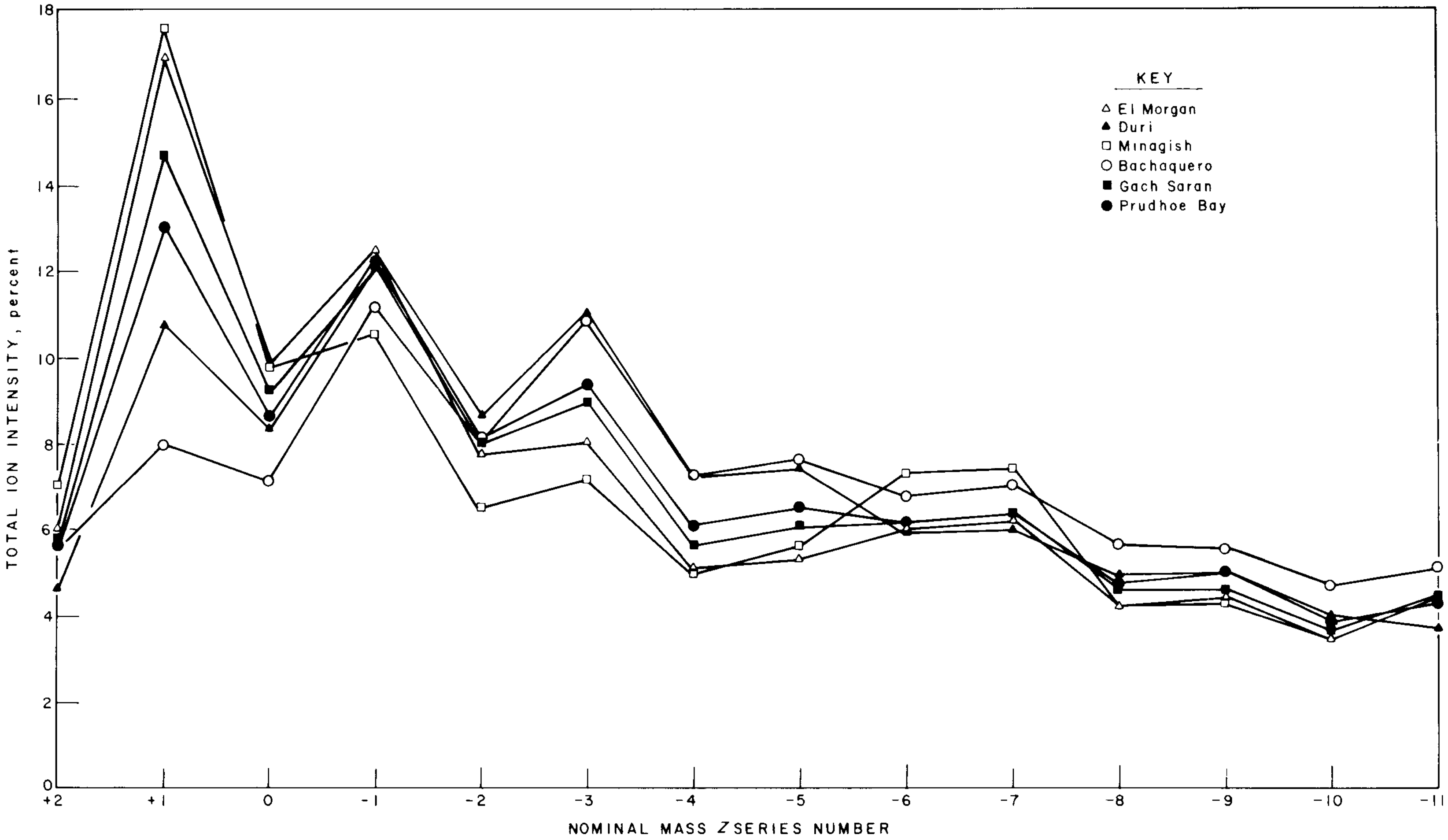

FIGURE 6. - Comparison of percent total ion intensity to nominal mass Z series number for topped crude oil samples.

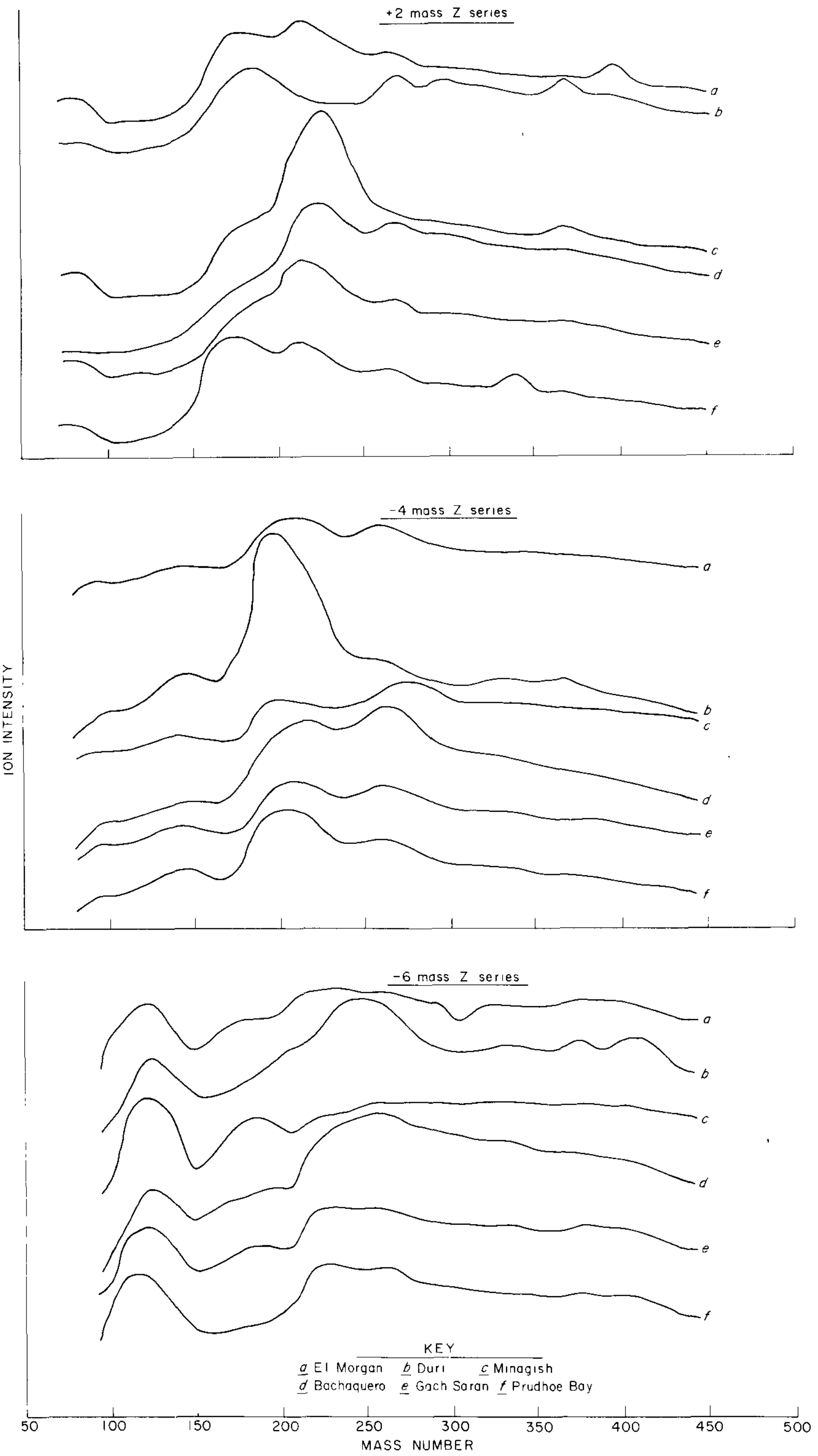

FIGURE 7. - Comparison of percent total ion intensity to mass number for selected nominal mass Z series of topped crude oil samples.

even numbered series were plotted. A comparison of the graphs of selected series, representing the most abundant types of compounds found in crude oils, did reveal some obvious contrasts. The nominal series selected were the $^{+}2$ series, which represents the paraffin- and naphthalene-type compounds, the -4 series, which represents the phenanthrene- and anthracene-type compounds, and the -6 series, which represents the benzene-type compounds.

Some distinctive characteristics shown in figure 7 are obvious, such as Minagish at about 225 mass units in the $^{+}2$ series and Duri at about 200 mass units in the -4 series, but many differences that are not as obvious, such as that of El Morgan at about 400 mass units in the $^{+}2$ series, are significant to experienced personnel.

As an overall identification tool, the use of mass spectra has several limitations. The initial expense for instrument purchase is generally prohibitive for the smaller laboratory. In addition, without computerized data handling facilities, the time involved in data reduction is excessive in comparison with the time needed for the other methods tested. To be fully utilized, mass data should be interpreted by highly experienced personnel using an elaborate data-reduction system. The expense, time, and personnel requirements represent the major drawbacks to this method, which otherwise can yield useful characteristics for oil spills research.

Bomb Sulfur and Kjeldahl Nitrogen

Sulfur and nitrogen contents of crude oils, and more recently crude oil residua, have long been a part of the Bureau of Mines routine crude oil analysis. The standard methods used have been the bomb method (5) for sulfur and Kjeldahl method for nitrogen. In connection with oil spill research, the use of these sulfur and nitrogen values has been advocated as a valuable identification characteristic (24-25, 27).

There are several reasons why sulfur and nitrogen values are attractive for oil spill use. Values can be determined by simple procedures involving relatively inexpensive equipment. The repeatability of the methods is good (24, 27), and the values cover a wide range (table 9) and are unique because they are available for most of the world's crude oils.

TABLE 9. - Sulfur and nitrogen data

Sample	Sulfur, percent			Nitrogen, percent			Sulfur-to-nitrogen ratio		
	Crude	Topped crude	Residuum	Crude	Topped crude	Residuum	Crude	Topped crude	Residuum
El Morgan........	1.67	2.26	2.77	0.201	0.313	0.468	8.3	7.2	5.9
Duri.............	.17	.20	.20	.336	.400	.432	.5	.5	.5
Minagish.........	2.12	3.47	4.00	.115	.185	.318	18.4	18.8	12.6
Bachaquero.......	2.68	2.98	3.21	.402	.483	.618	6.7	6.2	5.2
Gach Saran.......	1.57	2.22	2.74	.267	.418	.583	5.9	5.3	4.7
Prudhoe Bay......	.82	1.45	1.87	.209	.283	.468	3.9	5.1	4.0

The only factor interfering with the use of sulfur and nitrogen content is disagreement on net quantitative effects of weathering. Sulfur has specifically been reported to be subject to loss as high as 15 percent in exposed samples (10, 17). Others report that only a small percent of sulfur compounds boil below tridecane (C_{13}), as determined with a flame photometric detector on gas-liquid chromatographic effluents, and also that sulfur is less subject to biological attack than the normal paraffins (1-2, 15). The effect of exposure on nitrogen compounds has received little mention but is generally assumed to be negligible (1).

To overcome any weathering effects, the use of a sulfur-to-nitrogen ratio has been proposed (25, 37) based on the assumption that both will be similarly affected. As previously mentioned and as shown by other Bureau of Mines research (6), this is not the case. The use of the ratio instead of absolute values can actually minimize differences between oils. The topped crude oil samples of Gach Saran and Prudhoe Bay have similar sulfur-to-nitrogen ratios, but these topped samples have readily distinguishable absolute sulfur and nitrogen values (table 9). If the same boiling-range cut of spilled oil and suspect oil are used, there is no justification for use of the ratio in preference to absolute values.

Nuclear Magnetic Resonance Spectroscopy

The nuclear magnetic resonance (NMR) spectra of the six topped crude oil samples were run on a Varian Associates DP-60 nuclear magnetic resonance spectrometer. A limited examination showed little spectral variation particularly among oils of similar gravity and composition (table 10). All NMR spectra were quite similar; however, some diversity was found in the H_b peak (a measure of paraffinicity and paraffinic side chain length) and in the H_d peak (a measure of the degreee of aromaticity). Except in cases of relatively unique crude oils, such as Duri and Bachaquero, variations were minor and of little value for crude oil spill research.

TABLE 10. - Hydrogen types by nuclear magnetic resonance

Sample, topped crude	Hydrogen type, percent[1]			
	H_a	H_b	H_c	H_d
El Morgan..................	20.0	59.8	13.8	6.4
Duri.......................	20.3	64.6	10.9	4.2
Minagish...................	18.6	59.2	15.4	6.8
Bachaquero.................	24.1	49.2	18.3	8.4
Gach Saran.................	21.4	57.0	15.0	6.6
Prudhoe Bay................	20.5	57.1	16.3	6.1

[1] H_a--methyl groups γ and further from aromatic rings or paraffinic methyl groups.
H_b--methyl groups β to aromatic rings, methylene or methine groups β and further from aromatic rings, or paraffinic methylene groups.
H_c--methyl, methylene, and methine groups α to aromatic ring.
H_d--aromatic hydrogen attached to aromatic rings.

Ultraviolet, Fluorescence Excitation, and Fluorescence Emission Spectrophotometry

Ultraviolet runs were made on a Beckman DBG ultraviolet spectrophotometer, and fluorescence runs were made on a Perkin Elmer MPF-2A spectrophotometer. A total of seven fluorescence spectra were recorded for each sample at different wavelengths with benzene as the solvent, and an ultraviolet spectrum was recorded for each sample with cyclohexane as the solvent. Within each method, spectra were similar or even identical. Although ultraviolet absorption spectra have been reported to be useful in differentiating various oils (1), initial examination showed such little promise for crude oil spill identification that no further work (such as the use of a different or a more sensitive instrument) was undertaken.

Natural Weathering Effects

Although in recent years much attention has been given to the problems presented by spilled crude oil and to its identification, the literature available on the effect of natural weathering of samples is limited. Some sources have reported undertaking simulated weathering (23, 25, 37), but no comparison to natural weathering has been established. Much disagreement exists among available sources as to the exact effect that exposure has on each parameter proposed for identification, and the situation is further complicated by the fact that exposure effects also depend on the nature of the sample (23). Another critical factor is the exposure time. If the exposure time is very short, a direct comparison of the spill to the suspect source may be feasible, otherwise use of a topped suspect sample will be more comparable and eliminate evaporation differences.

A general picture of exposure effects on the techniques evaluated can be put together from available literature. All sources agree that the major effect on gas-liquid chromatography is the evaporative loss of lighter components. Although some researchers contend that there will be little change in normal paraffins above pentadecane ($\underline{n}$-C_{15}) (10, 12), most recent sources agree that more severe weathering will result in some decrease of normal paraffins and a corresponding increase of asphaltenes (25, 37). Slight losses of nickel and vanadium may occur due to water solubility or volatility, but prevalent opinion is that trace metals are little affected by exposure (1, 10, 25, 37). Oxidation effects can change certain infrared absorption bands, but no comprehensive study of such changes has been made (1, 25). Although some loss of sulfur has been reported, including one actual spill (10, 17), many authors still contend that weathering has no affect on values of sulfur and nitrogen (25, 37). Note that these views on weathering represent a literature composite, not a single comprehensive study.

CONCLUSIONS

The difficulties presented by the crude oil spill identification problem are not merely confined to development of techniques to characterize oils. The complexities of crude oil that allow so many identification techniques to exist also prevent any one technique from providing the ultimate answer. For this reason, several techniques were investigated to evaluate their applicability to the problem. In addition to the complexities of the oil, obstacles to selection of a single source in case of a spill include that the suspect sources frequently may be of similar origin, may be shipped from the same port, and may be bound for the same destination. Finally, the lack of exact definition of natural weathering effect on individual characteristics proposed for oil identification hinders any investigation.

Of the seven methods evaluated for oil spill identification, three--gas-liquid chromatography, vanadium and nickel by atomic absorption, and sulfur and nitrogen analysis--manifest the simplicity, reliability, and rapidity desired as well as involving moderate costs. Once the proper column has been prepared, gas-liquid chromatography involves a short analysis time and a minimal sample and provides some assessment of the extent of weathering. More time would be needed to handle the gas-liquid chromatographic data quantitatively, and a detailed quantitative examination does not seem warranted unless there are too many samples to inspect visually. Determination of vanadium and nickel by atomic absorption is slightly more time consuming, requires more sample, and is not very precise, but the wide concentration range of the two metals make the method desirable for oil spill characterization. Routine sulfur and nitrogen determinations exhibit good precision, relatively simple techniques are involved, and concentrations cover a wide enough range to be useful in crude oil spills research.

Although mass spectra and infrared spectra have limitations, each offers some unique qualities that can be useful for identification. Mass spectra in particular show distinctive characteristics, but instrumentation is expensive and spectral interpretation is difficult and time consuming. On the other hand, infrared spectra are simple and rapid to obtain, and though there are usually few distinctive bands, unique portions can appear in the spectra. If available, these spectra can be used as auxiliaries to substantiate other data.

The limited study of nuclear magnetic resonance and ultraviolet absorption demonstrated few characteristics useful for identification of spilled crude oils.

In the identification of pollutant crude oils, negative results are often more conclusive than positive ones, but if negative results are to be used, a complete set of suspect sources must be obtained along with the pollutant oil. Even the most complex identification schemes, involving elaborate mathematical and computerized data processing, will not always provide positive identification (25, 37). To be able to positively identify an oil spill without any knowledge of the possible sources involved would be extremely difficult with data currently available on the world's oils. The Bureau of Mines evaluated the previously discussed techniques for use with a spilled crude oil compared with suspect oils and found that gas-liquid chromatography and vanadium, nickel, sulfur, and nitrogen determinations were the most useful of the techniques investigated to aid in crude oil spill identification.

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APPENDIX. - CRUDE OIL ANALYSES

TABLE A-1. - Data from routine analysis of El Morgan, Egypt, crude oil

Bureau of Mines Bartlesville Laboratory
Sample 69069

IDENTIFICATION

El Morgan field — Africa
Miocene — Egypt

GENERAL CHARACTERISTICS

Gravity, specific, 0.865 Gravity, ° API, 32.1 Pour point, ° F., 40
Sulfur, percent, 1.67 Color, brownish black
Viscosity, Saybolt Universal at 77° F, 77 sec; 100° F, 60 sec Nitrogen, percent, 0.201

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

STAGE 1—Distillation at atmospheric pressure, 743 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	2.6	2.6	0.646	87.5					
2	167	2.3	4.9	.662	82.2	3.7	1.38759	129.7		
3	212	3.7	8.6	.706	68.9	15	1.39538	134.5		
4	257	4.3	12.9	.735	61.0	19	1.40905	137.2		
5	302	4.7	17.6	.756	55.7	22	1.42093	140.3		
6	347	4.1	21.7	.776	50.8	24	1.43124	140.9		
7	392	3.9	25.6	.791	47.4	25	1.43933	142.3		
8	437	4.1	29.7	.804	44.5	26	1.44745	144.4		
9	482	4.1	33.8	.819	41.3	28	1.45582	150.9		
10	527	4.5	38.3	.835	38.0	31	1.46420	151.7		

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	4.1	42.4	0.856	33.8	36	1.47408	163.6	39	20
12	437	5.1	47.5	.864	32.3	36	1.47837	159.2	47	40
13	482	5.2	52.7	.875	30.2	38	1.48527	168.1	60	70
14	527	4.9	57.6	.888	27.8	41	. . .		92	120
15	572	5.7	63.3	.898	26.1	43			173	140
Residuum.	. . . . . .	34.5	97.8	.984	12.3					

Carbon residue, Conradson: Residuum, 9.8 percent; crude, 3.8 percent.

Residuum:
Sulfur, percent, 2.77
Nitrogen, percent, 0.468

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline	8.6	0.676	77.8	
Total gasoline and naphtha	25.6	0.734	61.2	
Kerosine distillate	8.2	.812	42.9	
Gas oil	12.3	.850	34.9	
Nonviscous lubricating distillate	9.5	.867-.889	31.8-27.7	50-100
Medium lubricating distillate	6.6	.889-.901	27.7-25.5	100-200
Viscous lubricating distillate	1.1	.901-.903	25.5-25.1	Above 200
Residuum	34.5	.984	12.3	
Distillation loss	2.2			

TABLE A-2. - Data from routine analysis of Duri, Indonesia, crude oil

Bureau of Mines Bartlesville Laboratory
Sample 69074

IDENTIFICATION

Duri field
Tertiary

Asia
Indonesia
Sumatra

GENERAL CHARACTERISTICS

Gravity, specific, 0.936
Gravity, ° API, 19.7
Pour point, ° F., 50
Sulfur, percent, 0.17
Color, brownish black
Viscosity, Saybolt Universal at 100° F, 1,661 sec; 130° F, 618 sec
Nitrogen, percent, 0.336

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

STAGE 1—Distillation at atmospheric pressure, 742 mm. Hg
First drop, 136 ° 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									
2	167									
3	212									
4	257	0.8	0.8	0.765	53.5	-	1.41593	130.5		
5	302	1.2	2.0	.774	51.3	30	1.42690	132.7		
6	347	1.1	3.1	.792	47.2	32	1.43958	135.7		
7	392	1.4	4.5	.818	41.5	38	1.44894	140.2		
8	437	2.0	6.5	.835	38.0	41	1.45903	141.9		
9	482	3.1	9.6	.853	34.4	44	1.47027	148.9		
10	527	4.3	13.9	.869	31.3	47	1.48085	162.8		

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	3.8	17.7	0.889	27.7	52	1.49433	176.7	45	Below 5
12	437	4.8	22.5	.906	24.7	56	1.50149	185.4	60	10
13	482	4.4	26.9	.915	23.1	57			93	40
14	527	4.5	31.4	.925	21.5	59			158	55
1/15	572	5.5	36.9	.933	20.2	60			255	75
Residuum	......	62.6	99.5	.968	14.7					

Carbon residue, Conradson: Residuum, 5.7 percent; crude, 3.7 percent.

Residuum:
Sulfur, percent, 0.20
Nitrogen, percent, 0.432

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline				
Total gasoline and naphtha	4.5	0.790	47.5	
Kerosine distillate	-	-	-	
Gas oil	12.7	.865	32.1	
Nonviscous lubricating distillate	8.0	.895-.916	26.7-23.0	50-100
Medium lubricating distillate	6.1	.916-.928	23.0-20.9	100-200
Viscous lubricating distillate	5.6	.928-.937	20.9-19.4	Above 200
Residuum	62.6	.968	14.7	
Distillation loss	.5			

1/ Distillation discontinued at 545° F.

TABLE A-3. - Data from routine analysis of Minagish, Kuwait, crude oil

Bureau of Mines Bartlesville Laboratory
Sample 69111

IDENTIFICATION

Minagish field	Asia
Cretaceous	Kuwait

GENERAL CHARACTERISTICS

Gravity, specific, 0.859 Gravity, ° API, 33.2 Pour point, ° F., below 5
Sulfur, percent, 2.12 Color, brownish black
Viscosity, Saybolt Universal at 77° F, 62 sec; 100° F, 52 sec Nitrogen, percent, 0.115

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

STAGE 1—Distillation at atmospheric pressure, 744 mm. Hg
First drop, 79 ° 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	2.1	2.1	0.634	91.7					
2	167	2.9	5.0	.656	84.2	0.8	1.37164	130.1		
3	212	3.7	8.7	.693	72.7	8.5	1.39299	132.1		
4	257	4.3	13.0	.719	65.3	12	1.40372	133.6		
5	302	4.6	17.6	.745	58.4	17	1.41823	145.8		
6	347	5.3	22.9	.768	52.7	21	1.43085	146.1		
7	392	4.3	27.2	.787	48.3	23	1.43922	147.3		
8	437	4.5	31.7	.796	46.3	22	1.44454	154.0		
9	482	4.5	36.2	.809	43.4	23	1.45135	147.2		
10	527	4.6	40.8	.825	40.0	26	1.46030	154.9		

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	4.5	45.3	0.850	35.0	34	1.47207	163.7	40	20
12	437	4.7	50.0	.864	32.0	36	1.47827	165.6	45	55
13	482	6.3	56.3	.883	28.7	42	1.48811	168.7	71	60
14	527	5.8	62.1	.896	26.4	45			95	75
15	572	8.3	70.4	.913	23.5	50			185	90
Residuum	......	27.7	98.1	1.008	8.9					

Carbon residue, Conradson: Residuum, 12.1 percent; crude, 3.9 percent.

Residuum:
Sulfur, percent, 4.00
Nitrogen, percent, 0.318

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline	8.7	0.666	80.8	
Total gasoline and naphtha	27.2	0.727	63.2	
Kerosine distillate	13.6	.810	43.2	
Gas oil	7.9	.855	34.0	
Nonviscous lubricating distillate	10.9	.868-.897	31.6-26.3	50-100
Medium lubricating distillate	7.8	.897-.916	26.3-23.0	100-200
Viscous lubricating distillate	3.0	.916-.923	23.0-21.8	Above 200
Residuum	27.7	1.008	8.9	
Distillation loss	1.9			

TABLE A-4. - Data from routine analysis of Bachaquero, Venezuela, crude oil

Bureau of Mines Bartlesville Laboratory
Sample 70025

IDENTIFICATION

Bachaquero field	South America
Miocene	Venezuela

GENERAL CHARACTERISTICS

Gravity, specific, 0.965
Gravity, ° API, 15.1
Pour point, ° F., 35
Sulfur, percent, 2.68
Color, brownish black
Viscosity, Saybolt Universal at 100° F, 4,441 sec; 130° F, 1,198 sec
Nitrogen, percent, 0.402

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

Stage 1—Distillation at atmospheric pressure, 744 mm. Hg
First drop, 140 ° 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									
2	167									
3	212									
4	257	1.5	1.5	0.729	62.6	-	1.40431	127.3		
5	302	.9	2.4	.763	54.0	25	1.42215	133.5		
6	347	1.2	3.6	.781	49.7	27	1.43380	133.6		
7	392	1.4	5.0	.812	42.8	35	1.44654	140.2		
8	437	2.2	7.2	.833	38.4	40	1.45784	141.0		
9	482	3.5	10.7	.854	34.2	44	1.46877	145.8		
10	527	4.7	15.4	.873	30.6	49	1.47976	154.6		

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	2.1	17.5	0.901	25.5	58	1.49226	166.9	44	Below 5
12	437	4.9	22.4	.909	24.2	58	1.49902	167.8	55	do.
13	482	5.3	27.7	.921	22.1	60	-		81	do.
14	527	9.5	37.2	.938	19.4	65			183	do.
15	572	10.2	47.4	.947	17.9	66			455	do.
Residuum		51.6	99.0	1.031	5.7					

Carbon residue, Conradson: Residuum, 11.7 percent; crude, 6.5 percent.

Residuum:
Sulfur, percent, 3.21
Nitrogen, percent, 0.618

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline				
Total gasoline and naphtha	5.0	0.771	52.1	
Kerosine distillate	-	-	-	
Gas oil	13.4	.868	31.5	
Nonviscous lubricating distillate	8.1	.905-.924	24.8-21.6	50-100
Medium lubricating distillate	6.6	.924-.939	21.6-19.3	100-200
Viscous lubricating distillate	14.3	.939-.952	19.3-17.2	Above 200
Residuum	51.6	1.031	5.7	
Distillation loss	1.0			

TABLE A-5. - Data from routine analysis of Gach Saran, Iran, crude oil

Bureau of Mines Bartlesville Laboratory
Sample 70113

IDENTIFICATION

Gach Saran field	Asia
Miocene	Iran

GENERAL CHARACTERISTICS

Gravity, specific, 0.880 Gravity, ° API, 29.3 Pour point, ° F., below 5
Sulfur, percent, 1.57 Color, brownish black
Viscosity, Saybolt Universal at 77° F., 91 sec; 100° F., 72 sec Nitrogen, percent, 0.267

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

STAGE 1—Distillation at atmospheric pressure, 759 mm. Hg
First drop, 84 ° 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									
2	167	2.5	2.5	0.660	82.9	-	1.37285	122.3		
3	212	3.3	5.8	.705	69.2	14	1.39538	122.4		
4	257	4.9	10.7	.737	60.5	20	1.41056	137.1		
5	302	4.6	15.3	.760	54.7	24	1.42299	137.3		
6	347	4.9	20.2	.778	50.4	25	1.43315	140.6		
7	392	4.5	24.7	.793	46.9	26	1.44067	144.1		
8	437	4.5	29.2	.805	44.3	26	1.44801	150.2		
9	482	5.1	34.3	.822	40.6	29	1.45711	152.2		
10	527	5.7	40.0	.837	37.6	31	1.46611	157.0		
STAGE 2—Distillation continued at 40 mm. Hg										
11	392	3.0	43.0	0.861	32.8	39	1.47540	160.6	41	20
12	437	5.5	48.5	.870	31.1	39	1.47880	164.0	46	30
13	482	4.9	53.4	.884	28.6	43	1.48776	178.3	58	55
14	527	5.5	58.9	.895	26.6	45			88	75
15	572	5.6	64.5	.909	24.2	48			161	95
Residuum		34.2	98.7	.999	10.1					

Carbon residue, Conradson: Residuum, 11.9 percent; crude, 4.6 percent.

Residuum:
Sulfur, percent, 2.74
Nitrogen, percent, 0.583

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline	5.8	0.686	74.9	
Total gasoline and naphtha	24.7	0.748	57.8	
Kerosine distillate	9.6	.814	42.3	
Gas oil	13.2	.853	34.3	
Nonviscous lubricating distillate	9.6	.875-.897	30.3-26.2	50-100
Medium lubricating distillate	7.4	.897-.916	26.2-23.0	100-200
Viscous lubricating distillate	-	-	-	Above 200
Residuum	34.2	.999	10.1	
Distillation loss	1.3			

TABLE A-6. - Data from routine analysis of Prudhoe Bay, Alaska, crude oil

Bureau of Mines Bartlesville Laboratory
Sample 71011

IDENTIFICATION

Prudhoe Bay field
Sadlerochit, Permian and Lower Triassic

North America
Alaska

GENERAL CHARACTERISTICS

Gravity, specific, 0.893
Gravity, ° API, 27.0
Pour point, ° F., 15
Sulfur, percent, 0.82
Color, brownish black
Viscosity, Saybolt Universal at 77° F, 111 sec; 100° F, 84 sec
Nitrogen, percent, 0.209

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

Stage 1—Distillation at atmospheric pressure, 741 mm. Hg
First drop, 81 ° 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									
2	167	2.1	2.1	0.693	72.7	-	1.38591	127.9		
3	212	2.6	4.7	.723	64.2	23	1.40312	139.0		
4	257	3.5	8.2	.752	56.7	27	1.41922	141.9		
5	302	3.6	11.8	.773	51.6	30	1.43082	147.0		
6	347	3.7	15.5	.790	47.6	31	1.43922	149.6		
7	392	3.5	19.0	.801	45.2	30	1.44626	152.1		
8	437	4.3	23.3	.818	41.5	33	1.45528	154.7		
9	482	4.8	28.1	.836	37.8	36	1.46565	157.0		
10	527	5.0	33.1	.851	34.8	38	1.47467	160.5		

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	2.8	35.9	0.873	30.6	45	1.48218	161.5	40	10
12	437	6.5	42.4	.881	29.1	45	1.48650	168.6	45	30
13	482	6.8	49.2	.897	26.2	49	1.49477	169.4	58	50
14	527	6.0	55.2	.910	24.0	52			93	70
15	572	7.4	62.6	.919	22.5	53			176	90
Residuum		36.3	98.9	.990	11.4					

Carbon residue, Conradson: Residuum, 11.6 percent; crude, 4.7 percent.

Residuum:
Sulfur, percent, 1.87
Nitrogen, percent, 0.468

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline	4.7	0.710	67.9	
Total gasoline and naphtha	19.0	0.762	54.2	
Kerosine distillate	4.3	.818	41.5	
Gas oil	18.4	.860	33.1	
Nonviscous lubricating distillate	11.0	.887-.911	28.0-23.9	50-100
Medium lubricating distillate	8.1	.911-.922	23.9-22.0	100-200
Viscous lubricating distillate	1.8	.922-.924	22.0-21.6	Above 200
Residuum	36.3	.990	11.4	
Distillation loss	1.1			

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