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NITROGEN CONTENT OF CRUDE PETROLEUMS

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Nitrogen Content of Crude Petroleums

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In order to make Bureau of Mines analyses of crude oils more useful, the value of including a determination of nitrogen content was investigated.

Nitrogen contents of 153 crude petroleums from all parts of the United States were investigated. In general, the more asphaltic crude oils contained the higher nitrogen contents and the bulk of the nitrogen was in the high molecular weight portion of the oils. Correlations were developed between the Conradson carbon residue of the oil and the nitrogen content for oils from particular geological periods.

The nitrogen content of petroleum fractions is assuming considerable importance because of its adverse effect on cracking catalysts and on stability of finished products. Consequently, generalizations as to the amount of nitrogen in the crude oil, and information as to its boiling-range distribution are important in the selection of crude stocks for particular operations. Correlations of nitrogen content with geologic age may give clues as to the origin and process of conversion of petroleum.

WHILE the presence of nitrogen in crude petroleums has been well known for many years, attention has recently been directed toward it because of its adverse effect on cracking catalysts (7, 8). Some evidence is also accumulating (6, 10) to indicate that it may contribute to formation of gum in refined

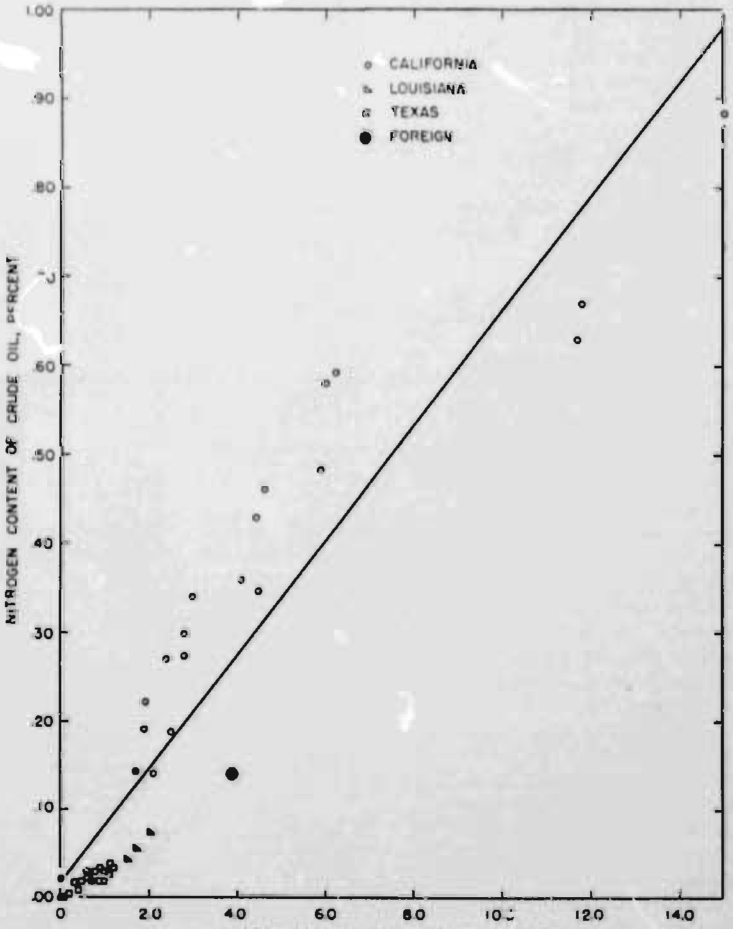

Figure 1. Crude Oils Produced from Formations of Tertiary Period

products. Consequently, the amount of nitrogen present in various crude oils is of interest.

For more than 25 years, the Bureau of Mines has been analyzing crude oils and issuing reports concerning their characteristics (3). These reports have included gravity, viscosity, sulfur content, Conradson carbon residue, and a distillation analysis giving properties of various fractions but have not included nitrogen content. The question as to whether nitrogen content should be determined as part of the analysis or whether some of the determined properties might correlate closely enough to give a good estimate of nitrogen content was investigated. The latter possibility was particularly important, considering that estimates of nitrogen contents might be possible for many analyses representing crude oils for which an additional sample would be difficult or impossible to obtain.

The samples of crude oil analyzed for nitrogen by a Kjeldahl method totaled 153 and came from 17 states and 3 foreign countries. The nitrogen distribution by boiling range was investigated for 25 of the oils. Correlation of the nitrogen content with other properties of the crude oil then was attempted.

NITROGEN CONTENT OF CRUDE OILS

The nitrogen contents of 153 petroleums are given in Table I. These range from 0.000 to 0.88 weight %. The table also lists the identification of the crude oil both geographically and geologically and gives the gravity, sulfur content, residuum after distillation to 300° C. at 40 mm. of mercury pressure, and carbon residue of crude. A more complete analysis of many of these oils may be found in a Bureau of Mines report (5).

Table II gives data similar to those found for the petroleums for four naturally occurring bitumens. Each of these values is high compared with petroleum. Table III gives nitrogen values for shale oils.

ANALYTICAL PROCEDURE. Nitrogen was determined on

Table I. Nitrogen Contents and Other Properties of Petroleums

Location, State and Field	Geological Formation*	Gravity, ° API	Sulfur, Weight %	Carbon Residue, Weight % of Crude	Nitrogen, Weight % of Crude
Arkansas					
Atlanta	Smackover(J)	51.1	0.37	0.3	0.093
Fouke	Paluxy(Cr)	27.9	1.47	9.1	0.071
Schuler	Jones(J)	33.2	1.54	4.0	0.063
Stevens Smart	Travis Peak(Cr)	30.2	1.99	7.3	0.080
Wesson	Hogg(Cr)	32.7	1.58	5.1	0.067
California					
Ant Hill	[illegible](T)	39.4	0.28	2.1	0.14
Bellvue	Stevens(T)	36.2	0.36	2.8	0.27
Canfield Ranch	2nd Stevens(T)	34.6	0.37	2.8	0.30
Coles Levee N.	Stevens(T)	35.0	0.50	3.0	0.34
Coyote, East	Graham-Loftus(T)	25.4	1.44	6.2	0.59
Cymric	Oceanic(T)	37.2	0.23	1.7	0.14
Elk Hills	Etchegoin(T)	23.1	0.69	4.6	0.46
Gato Ridge	Chert Shale(T)	13.8	5.21	11.8	0.67
Helm	Sand(T)	60.[illegible]	0.10		0.001
Helm	Miocene(T)	37.6	0.26	2.5	0.19
Inglewood	Fernando(T)	21.0	1.84	5.9	0.48
Jacalitos	Temblor(T)	38.6	0.34	1.9	0.22
Midway-Sunset	Etchegoin(T)	20.3	0.88	6.0	0.58
Oak Canyon	Lachler(T)	33.6	0.5[illegible]	4.1	0.36
Oxnard	Miocene(T)	7.1	7.4[illegible]	15.0	0.88
Paloma	Stevens(T)	49.2	0.08	[illegible]	0.023
Pleasant Valley	Eocene(T)	29.9	0.35	4.5	0.35
Quijarral Hills	Leda Zone(T)	36.8	0.63	2.6	0.19
Riverdale	Miocene(T)	40.0	0.22	1.9	0.19
Salt Creek	Carneros(T)	18.6	0.69	4.4	0.43
Santa Maria	Monterey Shale(T)	16.0	5.06	11.7	0.63
Temblor	Carneros(T)	25.0	0.44	2.4	0.27
Wilmington	Terminal(T)	25.6	1.24	3.3	0.58
Colorado					
Chromo	Greenhorn(Cr)	31.5	0.16	2.4	0.08
Dove Creek	Paradox(C)	43.8	<0.10	0.2	0.01
Rangely	Weber(C)	35.2	0.73	2.8	0.063
Illinois					
Bible Grove	McClosky(C)	40.0	0.17	2.0	0.094
Boyd	Benoist(C)	39.4	0.14	2.[illegible]	0.095
Centralia	Chester(C)	37.2	0.19	3.1	0.11
Louden	Bethel(C)	38.8	0.26	2.6	0.094
Indiana					
Griffin	Cypress(C)	36.0	0.19	3.0	0.12
Kansas					
Bornholdt	Mississippi(C)	34.8	0.62	5.6	0.15
Kraft-Prusa	Basal(O)	43.0	0.27	2.6	0.17
Kentucky					
Poole Consol.	Jett(C)	36.6	0.26	3.5	0.17
Smith Mills Consol.	Cypress(C)	32.7	0.39	3.7	0.20
Louisiana					
Delta Farms	Miocene(T)	33.8	0.22	1.7	0.055
Rodessa	Dees(Cr)	39.8	0.30	1.2	0.022
Vinton	Miocene(T)	32.5	0.19	1.4	0.044
West Bay	Miocene(T)	33.0	0.26	2.0	0.073
Michigan					
Adams	Dundee(D)	33.2	0.66	5.1	0.10
Deep River	Dundee(D)	34.2	0.60	4.3	0.12
Mississippi					
Baxterville	Massive(Cr)	15.0	3.07	15.2	0.19
Brookhaven	Tuscaloosa(Cr)	26.6	0.86	6.5	0.066
Eucutta	Eutaw(Cr)	23.1	3.89	9.7	0.13
Heidelberg	Eutaw(Cr)	25.7	3.03	7.8	0.11
Tinsley	Woodruff(Cr)	34.6	0.77	3.9	0.048
Montana					
Cut Bank	Moulton (Lander)(Cr)	46.5	0.38	0.9	0.018
Cut Bank	Cut Bank(Cr)	37.6	0.84	1.7	0.056
Elk Basin	Madison(C)	28.4	1.98	6.1	0.023
Elk Basin	Dakota(Cr)	51.1	<0.10	0.3	0.009
New Mexico					
Brunson	Ellenberger(O)	40.2	0.30	1.8	0.047
Drinkard	Drinkard(C)	41.1	0.33	1.3	0.063
Dublin	Ellenberger(O)	51.8	0.11	0.2	0.002
Fenton	Delaware(C)	41.3	0.24	0.7	0.058
Hogback	Dakota(Cr)	60.2	<0.10	0.0	0.000
Langlie	Permian(C)	34.8	1.33	2.0	0.066
Rattlesnake	Dakota(Cr)	56.7	<0.10	0.0	0.000
Russell	Yates(C)	18.4	1.95	7.4	0.24
Table Mesa	Dakota(Cr)	56.2	<0.10	0.1	0.01
New York					
Allegany	Penny(D)	41.5	0.17	0.5	0.006
Oklahoma					
Allen Dist.	Gilcrease and Cromwell(C)	29.9	0.24	3.2	0.16
Antioch	Deese(C)	42.3	0.14	0.6	0.047
Apache	Wilcox(O)	38.8	0.38	1.5	0.087
Burbank	Burbank(C)	35.8	0.21	1.3	0.050
Cement	Marchard(C)	31.0	0.21	1.3	0.095
Cumberland	Simpson Zone(O)	34.8	0.46	2.5	0.19
Edmond	Hunton(D)	41.5	0.14	0.6	0.045
Healdton	Pennsylvania(C)	33.6	0.77	2.7	0.16
Tussy	Deese(C)	26.3	1.44	5.8	0.34
Velma	Red Beds(C)	28.2	0.81	3.1	0.27
Texas					
Agua Dulce	Frio(T)	37.0	<0.10	0.3	0.017
Bay City	Frio(T)	34.6	0.12	0.6	0.022
Big Lake	Ellenberger(O)	41.3	0.14	0.7	0.028
Colorado	Colorado(T)	44.5	0.04	<0.1	0.001

(Continued on page 2579)

each of the crude oils by a Kjeldahl method similar to that used by Poth, Armstrong, Cogburn, and Bailey (9). Modifications of this method were made to reduce the time of the analysis. The conditions necessary for complete conversion of the nitrogen were later shown (4) to depend largely on the temperature of digestion. The procedure specified assures attainment of that temperature. The modifications made were:

Samples consisting of less than 1 gram to 2 grams were used instead of the 1- to 5-gram samples.

Thirty milliliters of concentrated sulfuric acid were used for each determination instead of 150 ml. For some determinations in which 2-gram samples of oil were used, 30 ml. of acid were insufficient, so 40 ml. were used.

Twenty grams of digestion mixture, consisting of 15 grams of potassium sulfate, 3 grams of mercuric oxide, and 2 grams of copper sulfate, were used for each determination instead of a mixture containing 50 grams of potassium sulfate, 2.5 grams of mercuric oxide, and 2.5 grams of copper sulfate.

The total digestion time was 2 hours instead of 7.5.

One and one-half grams of mossy zinc, instead of 1 gram of granulated zinc, were added to the caustic mixture during the ammonia distillation. This modified method is similar to that of the Universal Oil Products procedure (11) except for the proportions in the catalyst mixture and a closer specification as to quantities and times involved.

BOILING RANGE DISTRIBUTION OF NITROGEN

The Bureau of Mines crude oil analysis method includes distillation to give fractions consisting of each 25° C. boiling range up to 275° C. at

Table I. Nitrogen Contents and Other Properties of Petroleums (*Concluded*)

Location, State and Field	Geological Formation[a]	Gravity, ° API	Sulfur, Weight %	Carbon Residue, Weight % of Crude	Nitrogen, Weight % of Crude
Texas (*Contd.*)					
Conroe	———(T)	37.8	0.12	0.3	0.009
Dyersdale	Frio(T)	22.8	0.18	1.2	0.033
East Texas	Woodbine(Cr)	37.8	0.36	2.3	0.085
Embar	Ellenberger(O)	42.6	0.24	0.6	0.035
Fig Ridge	Frio(T)	34.4	0.16	0.7	0.018
Foster	Grayburg(C)	36.4	1.07	1.9	0.078
Ganado	Marginulina(T)	25.7	0.20	0.4	0.033
Ganado Deep	Frio(T)	34.2	0.13	0.9	0.021
Goldsmith	San Andres(C)	34.2	1.90	2.5	0.086
Hardin	Frio(T)	35.2	0.14	1.0	0.028
Hastings	Frio(T)	31.3	0.24	0.9	0.034
Hawkins	Woodbine(Cr)	25.7	2.45	8.3	0.13
Howard-Glasscock	Permian(C)	29.1	1.64	3.6	0.12
La Gloria	Frio(T)	43.6	<0.10	0.4	0.009
Markham, N.	Frio(T)	37.0	0.11	0.5	0.015
McElroy	Grayburg(C)	31.3	2.39	3.1	0.097
Oyster Bayou	Frio(T)	36.6	0.18	1.0	0.029
Ramsey	Wilcox(O)	54.0	0.10		0.004
Rincon	Frio(T)	43.8	<0.10	0.1	0.005
Seeligson	Frio(T)	40.9	<0.10	0.2	0.004
Sour Lake	Eocene(T)	40.6	0.14	0.5	0.016
Stewart	Frio(T)	25.4	0.18	0.6	0.030
Stowell	Intermediate(T)	33.4	0.17	1.1	0.026
Sugar Valley	Frio(T)	33.6	0.16	1.0	0.022
Thompson N.	Vicksburg(T)	36.4	0.11	0.8	0.030
Thompson S.	Miocene(T)	25.7	0.20	1.1	0.037
Tijerina Canales	Tijerina(T)	39.9	0.11	0.2	0.017
Tijerina Canales	Canales(T)	40.2	0.07	0.2	0.014
Tijerina Canales	Stray(T)	51.1	0.04	<0.1	0.004
Tijerina Canales	7000 feet(T)	40.9	0.06	0.8	0.016
Wasson	Permian(C)	34.2	1.90	1.5	0.10
Willamar	Willamar(T)	31.7	0.43	2.4	0.038
Yates	Permian(C)	29.1	1.59	3.3	0.16
Utah					
Boundary Butte	Coconino(C)	42.5	0.11	1.0	0.000
Wyoming					
Adon	Minnelusa(C)	30.6	1.20	4.5	0.12
Beaver Creek	Cloverly(Cr)	56.7	<0.10	0.0	0.000
Beaver Creek	Frontier(Cr)	57.9	<0.10	0.0	0.000
Beaver Creek	Muddy(Cr)	54.4	<0.10	0.0	0.000
Beaver Creek	Tensleep(C)	44.3	0.58	0.7	0.01
Big Sand Draw	Phosphoria(C)	62.1	0.32	0.0	0.000
Circle Ridge	Madison(C)	23.5	2.84	6.5	0.23
Dallas	Tensleep(C)	19.0	3.06	9.4	0.28
Derby	Embar(C)	22.1	2.60	7.0	0.25
Dubois	Phosphoria(C)	20.6	2.45	9.8	0.29
Elk Basin	Tensleep(C)	31.5	1.72	4.1	0.14
Garland	Tensleep(C)	23.0	2.77	8.3	0.22
Hatfield	Tensleep(C)	43.6	0.44	0.4	0.01
Hatfield	Sundance(J)	34.4	0.72	1.9	0.015
Lance Creek	*Sundance(J)*	*44.5*	*0.65*	*0.5*	*0.027*
Lost Soldier	Madison(C)	35.6	1.22	3.0	0.082
Lost Soldier	Cambrian(Ca)	34.6	1.27	3.3	0.097
Mush Creek	Newcastle(Cr)	42.8	0.10	0.4	0.039
Neiber	Embar(C)	40.6	1.88	0.8	0.010
Oregon Basin	Embar and Tensleep(C)	22.0	3.27	8.1	0.35
Pilot Butte	Muddy(Cr)	46.5	<0.10	0.3	0.000
Pilot Butte	Phosphoria(C)	26.2	2.30	7.1	0.22
Pilot Butte	Tensleep(C)	25.0	2.68	7.2	0.20
River Dome	Embar(C)	34.2	1.91	1.8	0.053
Riverton Dome	Tensleep(C)	40.8	0.83	0.6	0.000
Sage Creek	Embar (Phosphoria)(C)	20.3	3.54	7.7	0.28
Sand Creek	Frontier(Cr)	43.4	<0.10	0.2	0.022
Sand Draw	Tensleep(C)	34.2	1.35	3.1	0.093
Sheldon Dome	Tensleep(C)	34.6	1.06	2.5	0.093
South Fork	Embar(C)	28.2	1.91	6.1	0.17
Steamboat Butte	Phosphoria(C)	31.1	1.83	4.6	0.16
Steamboat Butte	Tensleep(C)	28.2	2.18	6.0	0.18
Sussex	Dakota(Cr)	39.2	0.35	1.7	0.068
Wertz	Amsden(C)	35.0	1.25	2.6	0.089
Wertz	Madison(C)	35.0	1.34	2.8	0.083
West Poison Spider	Frontier(Cr)	41.5	<0.10	0.4	0.025
Winkelman Dome	Phosphoria(C)	25.7	2.59	7.0	0.23
Foreign					
Agha-Jeri (Iran)	Asmari(T)	36.0	1.36	3.9	0.14
Keri (Greece)	....	7.9	5.76	12.0	0.17
Kirkuk (Iraq)	....	36.6	1.93	4.0	0.094

[a] Period or system is indicated in parenthesis: J, Jurassic; Cr, Cretaceous; T, Tertiary; C, Carboniferous; D, Devonian; O, Ordovician; Ca, Cambrian.

Table II. Nitrogen Contents and Other Properties of Bitumens

Location, State, Field, and (County)	Geological Data: Formation	Geological Data: Period	Gravity, ° API	Sulfur, Weight %	Residuum, Volume % of Crude	Carbon Residue of Crude, Weight %	Nitrogen, Weight %
California							
Edna bitumen (San Louis Obispo)	Edna bitumen ss.	Tertiary	4.3	3.20	77.9	17.7	1.23
Utah							
Sunnyside bitumen (Carbon)	Wasatch, Green River	Tertiary	6.7	0.51	56.4	13.7	0.96
Vernal bitumen (Uintah)	Wasatch, Green River	Tertiary	8.6	0.50	86.7	15.1	1.18
Canada							
Horse River Reserve (Alberta)	Athabaska	Cretaceous	13.0	5.15	54.4	13.3	0.43

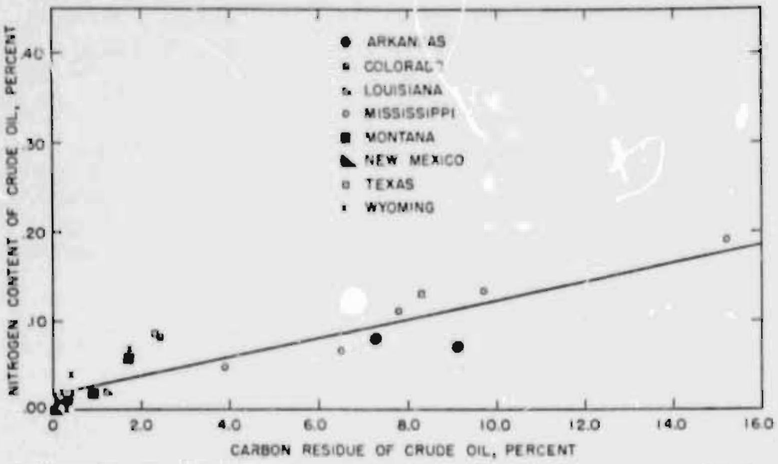

Figure 2. Crude Oils Produced from Formations of Cretaceous Period

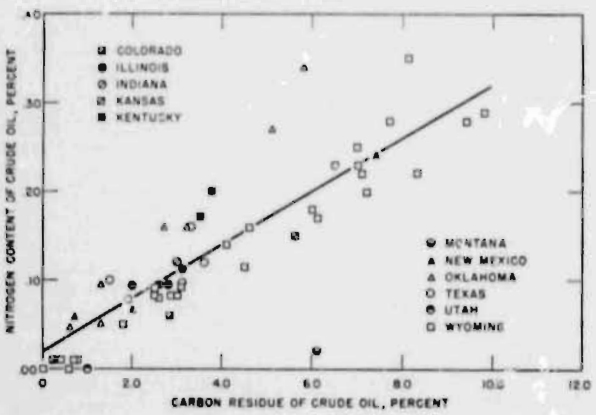

Figure 3. Crude Oils Produced from Formations of Carboniferous Period

atmospheric pressure, and then up to 300° C. at 40 mm. of mercury pressure. This results in 10 atmospheric and 5 vacuum fractions and a residuum. These fractions were examined for nitrogen content on three crude oils and the results are shown in Table IV. The major part of the nitrogen is found in the residuum, and the nitrogen content decreases sharply in fractions of lower boiling point. As shown in Table V, the percentage of the total nitrogen occurring in the residuum varies from 85 to 100%.

Inasmuch as the nitrogen content seems to be concentrated in the high molecular weight portion of the crude oil, its distribution as to the type of asphaltic constituents was of interest. Accordingly, the oils, resins, and asphaltenes as separated by the method of Hubbard and Stanfield (2) from asphalts made from Oregon Basin and Tampico crude oils were analyzed for nitrogen. The results are shown in Table VI.

CORRELATIONS

Table I shows that the high nitrogen contents seem always to be associated with high residuum values and Tables IV and V show that the nitrogen seems to be chiefly in the residuum. Therefore, a property associated with the residuum should give the best correlation. Such a property is the Conradson carbon residue (1) which is determined on the residuum and calculated to the crude basis. Plotting nitrogen content versus carbon residue resulted in a graph containing several groupings. The California oils—noted for their high nitrogen contents—gave a steep curve, the oils from Mississippi gave a flat curve, and the remainder were intermediate. This suggested that a geological correlation might be possible, as the California oils were predominantly from Tertiary formations, while the Mississippi oils were from Cretaceous formations.

The oils from Tertiary, Cretaceous, and Carboniferous formations are plotted in Figures 1, 2, and 3. A straight line was drawn, using the method of least squares. The constants for the equations of these curves are given in Table VII, together with similar data for other geological periods. Because of the small number of oils investigated, the data for the Jurassic, Devonian, and Ordovician periods may not be significant.

Use of this correlation to calculate per cent nitrogen, knowing the carbon residue and the geological period or system, results in an average deviation of 0.039% nitrogen. The deviations in various ranges of nitrogen content are shown in Table VIII. The average deviation represents about 20% of the total nitrogen present.

A correlation between sulfur content and nitrogen content might be suspected. Upon plotting, somewhat similar relationships as with carbon

TABLE III. NITROGEN CONTENTS AND OTHER PROPERTIES OF SHALE OILS

Country	Retort	Gravity, ° API	Sulfur, Weight %	Residuum, Volume %	Carbon Residue, Weight %	Nitrogen, Weight %
Australia	Pumpherston	26.9	0.56	27.2	1.1	0.52
France	Petit	25.0	3.40	19.4	6.4	0.65
	Marecaux	24.5	3.00	18.9	2.4	0.53
	G.P.	24.3	0.61	21.5	1.8	0.54
	Pumpherston	20.5	0.51	28.4	1.9	0.90
Scotland	Pumpherston	30.4	0.35	25.1	1.1	0.77
South Africa	Salermo	24.7	0.64	31.8	2.2	0.85
Spain	Pumpherston	27.9	0.40	18.0	0.8	0.68
Sweden	Rockesholm	13.3	1.65	22.8	2.7	0.68
	Lungstrom	43.4	0.71	0.3		0.11
United States	N-T-U	19.8	0.69	45.8	3.4	1.85
	Pumpherston	25.7	0.77	12.7	1.5	1.57
	Union Oil Co.	18.2	0.71	48.0	3.7	1.89

TABLE IV. BOILING RANGE DISTRIBUTION OF NITROGEN ON THREE PETROLEUMS

	Winkleman Dome, Wyo.		Sage Creek, Wyo.		Steamboat Butte, Wyo.	
	Nitrogen, weight %	Total nitrogen, %	Nitrogen, weight %	Total nitrogen, %	Nitrogen, weight %	Total nitrogen, %
Crude	0.23	100.0	0.28	100.0	0.16	100.0
Residuum	0.50	91.3	0.53	92.9	0.44	87.5
Fraction 15	0.144	4.0	0.13	2.9	0.136	6.3
Fraction 14	0.105	2.5	0.09	1.8	0.096	3.1
Fraction 13	0.058	1.4	0.05	1.1	0.059	1.9
Fraction 12	0.036	1.0	0.02	0.4	0.030	1.1
Fraction 11	0.026	0.4	0.01	0.4	0.024	0.6
Fraction 10	0.005	0.1			0.003	0.1
		100.7		99.5		100.6

Table V. Per Cent of Nitrogen Present in Residuum

Petroleum	Nitrogen, Weight %	Nitrogen in Residuum, Weight %	Nitrogen in Residuum, Weight % of Total Nitrogen
Schuler, Ark.	0.06	0.16	88.3
Heidelberg, Miss.	0.11	0.24	106.0
Deep River, Mich.	0.12	0.32	90.8
Midway-Sunset, Calif.	0.58	1.15	84.5
Velma, Okla.	0.27	0.60	88.9
Yates, Tex.	0.16	0.34	87.5
Chromo, Colo.	0.08	0.20	100.0
Dallas, Wyo.	0.28	0.54	96.4
Derby, Wyo.	0.25	0.53	96.0
Pilot Butte, Wyo.	0.22	0.52	95.4
Keri, Greece	0.17	0.25	94.1
Circle Ridge, Wyo.	0.23	0.50	95.7

Table VII. Equation Constants for Curves Relating Carbon Residue and Nitrogen Content

Geological Period	Intercept % Nitrogen	Slope, % Nitrogen: % Carbon Residue
Carboniferous	+0.019	0.030
Cretaceous	+0.015	0.011
Devonian	+0.019	0.019
Jurassic	+0.006	0.012
Ordovician	−0.019	0.068
Tertiary	+0.016	0.065

residue were exhibited but these were not so close to straight-line relationships and more exceptions were apparent.

DISCUSSION

The use of nitrogen content as a means of identifying source beds in which petroleum originated seems to show some promise. The ratio of per cent nitrogen to per cent carbon residue appears to be an indication of the geological origin.

These ratios for petroleum from various geological periods are Tertiary, 0.065; Cretaceous, 0.011; Jurassic, 0.012; Carboniferous, 0.030; Ordovician, 0.068; and Devonian, 0.019. The naturally occurring bitumens correspond somewhat to these ratios, the three of Tertiary origin having ratios of 0.076, 0.070, and 0.078, while that from the Cretaceous has a ratio of 0.032.

Table VI. Nitrogen Contents of Asphaltic Constituents from Oregon Basin, Wyo., and Mexican Asphalts

	Nitrogen, Weight %	
	Oregon Basin	Tampico
Crude oil	0.35	
100-penetration asphalt	0.64	0.50
Oils	0.13	0.05
Resins	0.89	0.78
Asphaltenes	1.18	1.06

The shale oils give values for the ratio ranging from 0.102 to 1.047, definitely indicating their different character.

Sulfur content fails to show as close a relationship with nitrogen content as carbon residue. This may be because it is derived from two sources—organic starting material and reduction of inorganic sulfates. Nitrogen, on the other hand, is derived chiefly from the organic source material.

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Table VIII. Average Deviations in Calculation of Nitrogen Content

Geological Period	No. of Samples	Average Deviation, All Samples	Average Deviation, Samples Having Nitrogen Contents Up to 0.099	0.1 to 0.19	0.2 to 0.29	0.3 to 0.49	0.5 and over
Carboniferous	54	0.032	0.026	0.027	0.036	0.108	
Cretaceous	25	0.011	0.018	0.012			
Devonian	4	0.020	0.021	0.018			
Jurassic	4	0.013	0.013				
Ordovician	6	0.019	0.015	0.035			
Tertiary	41	0.069	0.044	0.044	0.086	0.103	0.141
All	134	0.039	0.027	0.028	0.046	0.104	0.141

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