Uranium and Other Metals In Crude Oils

GEOLOGICAL SURVEY BULLETIN 1100

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U.S. DEPARTMENT OF THE INTERIOR
March 3, 1849

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A. Methods of Analysis for Uranium and Other Metals in Crude Oils, With Data on Reliability

By C. A. HORR, A. T. MYERS, *and* P. J. DUNTON

B. Distribution of Uranium and Other Metals in Crude Oils

By HAROLD J. HYDEN

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By C. A. HORR, A. T. MYERS, *and* P. J. DUNTON

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METHODS OF ANALYSIS FOR URANIUM AND OTHER METALS IN CRUDE OILS, WITH DATA ON RELIABILITY

By C. A. Horr, A. T. Myers, and P. J. Dunton

ABSTRACT

The content of uranium and other metals in crude oils ranges from a few tenths to several hundred parts per million. To concentrate these metals, crude-oil samples were prepared for analysis and reduced to ash by two methods: (a) a modified A.S.T.M. method of dry ignition, and (b) a wet oxidation followed by ashing. These two methods were compared by ashing duplicate samples of the same oil and determining the concentration of 15 trace elements in the ash by quantitative spectrochemical procedures. Results obtained by the two methods do not differ appreciably. The concentration of copper, vanadium, and nickel in the ash of 37 oils was determined by both the quantitative and semiquantitative spectrochemical procedures. A comparison of the results showed that more than 60 percent of the semiquantitative results for these three elements are in the same one-third order of magnitude as the quantitative results. Uranium in the ash was determined fluorimetrically and comparative results on several samples showed satisfactory agreement.

Based on the results of the above tests, the methods used for the study of 117 samples of crude oil and 16 samples of refinery residue as described in chapter B were the modified A.S.T.M. method of dry ashing the oil, the fluorimetric determination of uranium, and the semiquantitative spectrochemical determination of the other metals in the ash of these oils.

INTRODUCTION

Although many geologists recognize the widespread association of uranium with organic material in sedimentary rocks, the data on uranium in crude oil, natural asphalt, and in other petrolific materials are scant (Erickson and others, 1954). In 1953 the U.S. Geological Survey undertook an investigation of many different types of oils from the Western United States to study the occurrences of metal in the oils in relation to their geologic environment. The oil fields were so selected that they include a wide range in the composition of the crude oils, in the age of the reservoir rocks, and in geologic conditions.

Other fields were selected because of their proximity to uranium-ore deposits or to uranium-bearing formations. The final selection of type and location of crude oils to be studied was made by N. W. Bass and H. J. Hyden with the advice of W. H. Smith and J. S. Ball of the Bureau of Mines. As a result 117 samples of crude oil and 16 samples of refinery residue were collected by H. J. Hyden and submitted for analysis.

Chapter A of this report describes the methods of analysis used and provides data to indicate their reliability. These methods comprise means for ashing the samples without significant loss of metals, for the fluorimetric determination of uranium in the ash, and for the spectrochemical determination of metals in the ash by semiquantitative and quantitative procedures. Nickel, vanadium, and copper were determined by this quantitative method in 37 crude-oil ashes because these elements are consistently found in petroleum. Witherspoon and Nagashima (1957) discussed the use of nickel to vanadium ratios for estimating the age of crude oil. Copper was also determined quantitatively because of its relatively high concentration in the oil and because of the possibility of finding signficant variations of this element in oils of different types.

The concentration of the trace elements in the ash of the samples collected are presented in chapter B of this report. With the exception of the quantitative spectrochemical determinations of copper, nickel, and vanadium in 37 of the samples, the semiquantitative or visual comparison method was used for the estimation of the trace materials to obtain the large quantity of needed data at low cost. Hyden (1956) has given a preliminary report on uranium, vanadium, and nickel content of some of these samples.

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ANALYTICAL METHODS

PREPARATION OF THE SAMPLES

The samples as received contained materials other than oil, such as brine and sand, which had to be removed before the oil was analyzed.

The raw crude oil was first washed several times in a separatory funnel with distilled water to remove the brine, each time draining off and discarding the water layer. To remove the last traces of wash water and any suspended sand or clay particles, the oil was filtered through a dry medium-fine fluted filter paper. The API gravity of the sample was then determined and the sample stored in a clean container.

PREPARATION OF ASH

Most crude oils contain a few tenths to several hundred parts per million of trace elements, including uranium. In order to concentrate these trace elements to make them readily measurable, the prepared crude oil was burned to ash by the A.S.T.M. D482–46 procedure (American Society for Testing Materials, 1947). This procedure was modified by igniting separate small amounts of the sample at a time and by using an oxygen atmosphere in the final reduction to ash in the muffle. To determine whether metals are volatilized as metal organic compounds during ignition, several crude-oil samples were treated by a wet oxidation technique to destroy the organic matter before final ignition to ash. These two methods of ashing the sample will be hereafter referred to as the "dry ash" and "wet oxidation" methods.

Morgan and Turner (1951) showed by radioactive tracer technique that no significant losses occur if the ashing is carried out below 550° C. Milner and others (1952), Karchmer and Gunn (1952), and Gamble and Jones (1955) have shown that losses of metals in the dry ash method for crude oils and residual stocks are not appreciable; however, in charge stocks and overhead fractions obtained by vacuum distillation, losses of metals, particularly iron, vanadium, and nickel may be considerable.

Milner and others (1952) described a wet oxidation method for crude oils, residual, and overhead stocks, whereby the sample is coked with sulfuric acid and the carbonaceous residue ashed in a muffle furnace at 500° C without loss of metals. This procedure was used to compare recoveries of metals with those obtained by the dry ashing technique.

DRY ASHING METHOD

A convenient volume, usually a liter, of the prepared sample was carefully weighed to the nearest 0.01 gram. Small volumes (about 25 ml) of the weighed sample were transferred to a 250–ml tared platinum dish, and each increment ignited and allowed to burn freely in the open dish until reduced to a dry char before the next increment was added. The sample was added in small portions to minimize possible losses caused by too rapid combustion, spattering, or mechanical entrainment. With some heavy oils the platinum dish and contents were gently heated from below to promote burning.

The charred mass was then heated in an electric muffle furnace at 500° C until all carbon was removed. By passing a slow stream of oxygen through the muffle furnace, carbon was removed in about one-third the time usually required. Occasional stirring of the ash aided in removing all traces of carbon. The platinum dish and ash were allowed to cool, then weighed, and the percentage of ash calculated. Use of a desiccator was found to be unnecessary because the ash was not hygroscopic. The ash was thoroughly ground in an agate mortar before analysis.

WET OXIDATION METHOD

For wet oxidation the platinum dish containing the oil sample was placed on a silica triangle on a hot place and surrounded by an aluminum shield 4 inches high and 8 inches in diameter to protect the sample from air currents. Infrared lamps were placed directly over the samples. For each 10 g of oil 2.5 ml of reagent grade concentrated sulfuric acid was added. The dish and contents were heated gently by the hot plate and infrared lamps until frothing of the sample ceased. The heat from both sources was increased until fumes of sulfur trioxide were evolved, and continued until a dry cokelike mass was produced. The dish and contents were then heated in an electric muffle at 500° C until all the carbon was removed. The ash was then thoroughly ground before analysis.

DETERMINATION OF URANIUM IN THE CRUDE-OIL ASH

Uranium in the ash was determined by the fluorimetric method similar to that described by Grimaldi and others (1952, 1954). Because this ash usually contains only small amounts of uranium, special care was necessary to keep the laboratory and all glassware clean and free of possible contaminants. Reagents used were the purest available or purified to give low and uniform blank determinations.

Usually 10 mg of the ash was weighed, placed in a small platinum dish, and moistened with a few drops of distilled water. When the ash content of the oil was too low to provide sufficient material for the analyses an ash sample diluted with quartz powder was used. The dish was placed on a steam bath and 3 to 5 ml of concentrated nitric acid and 1 to 2 ml of 48 percent hydrofluoric acid added. The solution was evaporated to dryness and the same amount of acids again added. The hydrofluoric acid helps decompose refractory oxides in the ash.

The residue in the platinum dish was then dissolved in 5 ml of 7 percent nitric acid by gentle warming, and the solution transferred quantitatively to a glass-stoppered test tube containing 9.5 g of previously purified aluminum nitrate. The tube was warmed and shaken to dissolve the aluminum nitrate, and then cooled to room temperature. Ten milliliters of anhydrous ethyl acetate was added, and the tube was stoppered and shaken for about 3 minutes. The layers were allowed to separate, and the upper ethyl acetate layer was filtered through a dry filter paper into another tube. A portion, usually 2 or 5 ml, was measured with a pipette, placed in a 7 ml flat-bottomed platinum dish (Grimaldi and others, 1952) ignited with a lighted splinter, and the ethyl acetate allowed to burn completely. The dish was gently heated, below redness, to destroy the organic residue. Two grams of mixed fluoride-carbonate flux mixture (45.5 parts by weight Na_2CO_3, 45.5 parts K_2CO_3, and 9 parts NaF) was weighed and transferred to the platinum dish; the phosphor was prepared in an apparatus described by Stevens and others (1959).

The fluorescence of the phosphor was then measured with a transmission fluorimeter similar to those described by Kinser (1954) and Parshall and Rader (1957). The uranium content of the phosphors was measured by comparing the fluorimeter readings with those obtained with phosphors containing known concentrations of uranium. The uranium content of the ash was then calculated.

SPECTROCHEMICAL ANALYSIS

Reference is made in this paper to two kinds of spectrochemical analysis, quantitative and semiquantitative. Equipment and much of the procedure for the two are identical. Both procedures are conventional direct-current arc methods using powdered samples in graphite electrodes. The quantitative procedures, which is much more time consuming, differs from the semiquantitative in the attention given to preparing the samples, the standards used, the method of reading the spectra and the method of expressing the results.

A brief description of the operating conditions and spectrographic equipment used follows:

Spectrograph: Wadsworth-mounted grating spectrograph equipped with a 15,000 lines-per-inch grating, a reciprocal linear dispersion of 5.24 A per mm in the first order.

Electrodes: Lower electrode, preformed "¼ inch," high purity graphite having a crater with inside diameter 0.195 inch and a maximum depth of 0.180 inch, wall thickness 0.015 inch. Upper electrode, ¼-inch diameter, hemispherically tipped, made of high purity graphite rods.

Sample and standards: 10 mg of sample or standard plus 20 mg of graphite powder. Samples and standards weighed and arced under identical conditions.

Analytical gap: 5 to 6 mm maintained throughout excitation period.

Excitation source: Direct-current arc operated at 12–13 amperes, open circuit potential 300 volts.

Length of exposure: Samples and standards arced for 120 seconds.

Emulsion: Eastman III-0, X thin plates, developed at 20° C in D-19 for 3½ minutes with continuous agitation.

Wavelength region: 2250–4900 A, first order.

Densitometer: Direct-reading projection comparator microphotometer, split viewing screen with a 20-diameter magnification.

Emulsion calibration: Use of iron lines whose relative intensities have been determined. Based on selected iron lines present in spectra of a quartz feldspar mixture containing 1 percent Fe_2O_3.

Light intensity: Controlled by neutral filters.

Optics: Arc image was focused on the collimator, using a mask to select the central 2–3 mm portion of the arc. Cylindrical quartz lens used in front of slit.

The spectral lines used are given in table 1.

QUANTITATIVE SPECTROCHEMICAL PROCEDURE

In the quantitative procedure weighed amounts of samples and standards were mixed with graphite and placed in cupped electrodes of precisely controlled dimensions and burned to completion in a 13 ampere d–c arc. The total energy method of Slavin (1938, 1939) was used with external standards whose compositions were approximately those of the samples. As described below concentrations of the elements are calculated from microphotometer readings of selected lines, plate calibration, and analytical curves according to standard accepted procedures.

To estimate the sample dilution needed to obtain optimum analytical line intensities for the quantitative procedure, several dilutions of each sample were made using a standard coarse matrix blank in ratios of 1 to 9, 1 to 19, and 1 to 49. The diluted samples were ground and were then analyzed as outlined below.

For the actual quantitative determinations, 10 mg of the diluted ash was mixed by further grinding in an agate mortar with 20 mg of pure graphite powder and arced for 120 seconds under conditions identical with those for prepared standard powders containing appropriate amounts of copper, nickel, and vanadium. Analytical working curves were established for the standards by plotting concentrations against relative intensities of the lines. Plates were calibrated using a set of homologous iron lines for which relative intensities have been determined by Crosswhite (1950). Spectral lines used for quantitative results are identified in table 1 by an asterisk (*).

Quantitative results for Cu, Ni, and V are given for 37 samples in both chapters of this bulletin. In this part, quantitative results for 15 elements, Cu, Ni, Co, V, Cr, Pb, Mo, Mn, Zn, Y, As, U, Fe, Zr, and

Sr, were obtained on 3 samples of crude oil and 1 sample of asphaltite ashed in duplicate by both ashing methods.

SEMIQUANTITATIVE SPECTROCHEMICAL PROCEDURE

Instead of repeated exposures of standards closely matching the samples the semiquantitative procedures make use of a set of standard plates exposed under conditions matching as closely as practical a larger variety of samples than would be used for the quantitative procedure. Consistent with the precision of the method, plates are

TABLE 1.—*Spectral lines used in the semiquantitative and quantitative methods*

[* indicates lines used for quantitative results]

Element	Wavelength (A)
Ag	3382.9
	3280.7
Al	3092.7
	3082.2
	2660.4
	2652.5
As	2898.7
	2860.4
	*2780.2
	2492.9
	2349.8
	2288.1
Au	3122.8
	2676.0
	2428.0
B	2497.7
	2496.8
Ba	4554.0
	3071.6
Be	3321.3
	3131.1
	3130.4
	2348.6
Bi	3067.7
	2897.9
Ca	4226.7
	3179.3
	3158.9
	2398.6
Cd	3466.2
	3261.5
	2763.9
	2288.0
Ce	4296.7
	4248.7
	4222.6
	3243.4
	3201.7
Co	*3462.8
	*3453.5
	*3449.6
	3412.6
	3412.3
	3405.1
Cr	4289.7
	4274.8
	*4254.4
	*3021.6
	2769.9
Cu	*3274.0
	3247.5
	2824.4
	2293.8
Dy	3454.3
	3407.8
	3393.6
	3319.8
Er	3385.1
	3372.8
	3220.7
	3230.6
Fe	3441.0
	3440.6
	3225.8
	*3222.1
	3100.6
	3100.3
	3099.97
	3099.90
	3020.6
	3020.5
	*3021.1
Ga	2943.6
	2874.2
Gd	4262.1
	3423.9
	3422.5
	3362.2
Ge	3039.1
	2691.3
	2651.6
	2651.2
Hf	3134.7
	3109.1
	2904.7
	2904.4
	2861.7
Hg	4358.4
	3125.7
	2536.5
In	4511.3
	3256.1
	3039.4
Ir	3220.8
	3133.3
	2849.7
	2543.9
K	4047.2
	4044.1
	3446.7
La	4429.9
	4333.7
	3337.5
	3245.1
Li	4602.9
	3232.6
Mg	2852.1
	2795.5
	2779.8
	2776.7
Mn	*2949.2
	2939.3
	*2801.1
	2794.8
Mo	3194.0
	*3170.4
	2816.2
Na	3303.0
	3302.3
Nb	3195.0
	3191.9
	3163.4
	3130.8
	3094.4
Nd	4358.2
	4304.6
	3328.3
Ni	3493.0
	3433.6
	*3414.8
	3101.9
	3101.6
	*3050.8
	2943.9
Os	3301.6
	3058.7
P	2554.9
	2553.3
	2535.7
	2534.0
Pb	2873.3
	*2833.1
	2802.0
	2663.2
Pd	3421.2
	3404.6
	3242.7
Pt	3064.7
	3042.6
	2659.4
Re	3464.7
	3460.5
	3424.6
	3405.9
Rh	3434.9
	3396.8
Ru	3436.7
	3428.3
Sb	3267.5
	2877.9
	2598.1
Sc	4246.8
	3353.7
	3019.4
Si	2881.6
	2528.5
	2524.1
	2516.1
	2435.2
Sm	4434.3
	4433.9
	4424.3
	4329.0
	4244.7
Sn	3262.3
	3175.0
	3034.1
	2863.3
	2840.0
Sr	*4607.3
	3464.6
	3351.2
Ta	3311.2
	2714.8
	2653.3
Te	4771.6
	2385.8
	2383.2
Th	4381.9
	4019.1
	2942.9
	2870.4
	2837.3
Ti	3372.8
	3248.6
	3242.0
	3234.5
	3224.2
	3168.5
	3152.3
	3088.0
Tl	3229.8
	2767.9
U	4244.4
	4241.7
	3270.1
	*2865.7
V	3185.4
	3184.0
	*3183.4
	3122.9
	3102.3
	2714.2
	*2688.7
W	4302.1
	4294.6
	4008.8
	2947.0
	2896.4
Y	4374.9
	*3327.9
	3242.3
Yb	3289.4
	3107.9
	2891.4
Zn	3345.6
	*3345.0
	*3302.9
	3302.6
Zr	3430.5
	3392.0
	*3279.3
	*3273.1

not calibrated. Concentrations of the elements are estimated by visually comparing lines of sample spectra with reference spectra. This method was described in part by Myers and Barnett (1953) and more details are given below.

The spectral lines used are the same for both procedures, semiquantitative and quantitative, and are given in table 1.

The crude-oil ash was diluted with pure quartz in the ratio of 1:3.64, so that the sample analyzed contained excess silica and was comparable to the matrix used for standards; this dilution factor is related to the method of reporting given below. Ten milligrams of this diluted crude oil ash was mixed with 20 mg of graphite powder, burned on a controlled direct-current arc and its spectrum recorded on a photographic plate. Selected analytical lines on the resulting plate were visually compared with those of standard plates. These standard plates were exposed and developed in precisely the same manner as were the plates for the unknowns, except that standard powders were used instead of samples. These standard powders contained a group of elements (as oxides) in a matrix consisting of 60 parts of quartz, 40 parts of feldspar, and 1 part of Fe_2O_3. The concentrations of the elements were so chosen that they decreased from 10 to about 0.0001 percent by a factor of the reciprocal of the cube root of ten to give the series approximating 10, 4.6, 2.2, 1.0, 0.46, . . . 0.00046, 0.00022, 0.0001 percent. This factor thus provides a

TABLE 2.—*Approximate visual detection limits for the elements determined by the semiquantitative spectrochemical method*

[Some combinations of elements affect the detectabilities. Approximate values are given. In unusually favorable materials, concentrations somewhat lower than the values given may be detected. In unfavorable materials the given detectabilities may not be attained for some of the elements. A different exposure is required for the detectabilities shown in parentheses]

Element	Percent	Element	Percent	Element	Percent
Ag	0.0001	Hf	0.1	Rh	0.005
Al	.001	Hg	1.0	Ru	.005
As	.1	In	.001	Sb	.05
Au	.005	Ir	.005	Sc	.001
B	.005	K	1.0 (0.005)	Si	.001
Ba	.0001	La	.005	Sm	.01
Be	.0001	Li	.01 (0.0001)	Sn	.001
Bi	.001	Mg	.005	Sr	.0001
Ca	.001	Mn	.0005	Ta	.05
Cd	.005	Mo	.001	Te	.5
Ce	.05	Na	.05 (0.001)	Th	.05
Co	.0005	Nb	.001	Ti	.001
Cr	.0005	Nd	.01	Tl	.05
Cu	.0001	Ni	.0005	U	.05
Dy	.05	Os	.005	V	.001
Er	.005	P	.5	W	.01
Fe	.001	Pb	.001	Y	.001
Ga	.001	Pd	.0005	Yb	.0005
Gd	.05	Pt	.005	Zn	.05
Ge	.0005	Re	.005	Zr	.001

series having three subdivisions for each order of magnitude which is consistent with the relation between blackness of a spectral line and amount of an element present. By means of a comparator showing "twenty power" adjacent images of the sample spectra and the standard spectra, visual estimates were made of concentrations of the elements in the sample that were then reported by numbers as being between two standards in the following manner: 3 indicating the middle subdivision (4.6 to 2.2) of an order of magnitude, 7 the high subdivision (10 to 4.6), and 1.5 the lower subdivision (2.2 to 1); M indicated major constituent greater than 10 percent. Comparisons of this type of semiquantitative results with data obtained by quantitative methods, either chemical or spectrochemical, show that the assigned group includes the quantitative result about 60 percent of the time. Table 2 indicates the lowest concentration reported with this method.

PRECISION AND ACCURACY OF THE METHODS OF ANALYSIS

TYPES OF OILS USED IN COMPARISON OF METHODS OF ASHING

One sample of an asphaltite and three samples of crude oil were chosen as representative of the various types of petroliferous material being routinely analyzed in the laboratory. Sample 215821 is of an asphaltite from the Seven Rivers formation, Carlsbad, N. Mex. The material was carefully handpicked to remove the host rock. Sample 251822 is of an asphaltic crude oil from the Santa Maria Valley, Calif. Sample 251823 is of a light, paraffinic type crude oil from Texas. Sample 251824 is of a tarry, asphaltic crude oil from the Herrick oil pool, Albany County, Wyo.

Some of the above samples for testing the methods of ashing are not included in chapter B, but were considered representative of the different types of oils studied.

COMPARISON OF RESULTS BY DRY ASHING WITH THOSE BY WET OXIDATION

The results of the two methods of ashing are given in table 3. Each method gives good precision for the ash content; results within either method agreeing to about one digit in the second significant figure. Results for ash content by the wet oxidation method are generally about 16 percent higher than those by dry ashing; hence results between methods are not directly comparable, mainly because of retention of sulfate ions by the ash after the wet oxidation with sulfuric acid. The metal content in each ash, determined by the quantitative spectrographic method, is shown in table 3. In table 4, the metal

TABLE 3.—*Comparison of results for metals in the ash obtained by dry ashing and wet oxidation of crude-oil samples*

[Quantitative spectrochemical results in percent. 0, looked for but not found; leaders indicate not looked for. Analysts: P. J. Dunton and C. A. Horr]

Sample		Method of ashing	Percent ash	Percent in ash														
No.	Description			Cu	Ni	Co	V	Cr	Pb	Mo	Mn	Zn	Y	As	U	Fe	Zr	Sr
251821 A	Asphaltite, handpicked from Seven Rivers formation, Carlsbad N. Mex.	Dry	8.65	0.094	0.80	0.13	0.020	0.021	0.17	0.24	-------	0	0.12	8.5	40	3.0	0.062	0.012
B		Dry	8.56	.082	.80	.14	.020	.020	.16	.26	-------	0	.12	9.0	43	3.0	.082	.012
C		Wet	9.67	.064	.74	.11	.017	.022	.17	.23	-------	0	.11	8.5	34	2.3	.050	.0095
D		Wet	9.73	.062	.74	.12	.018	.023	.16	.23	-------	0	.12	8.5	33	2.5	.057	.0095
251822 A	API(COAR) 53–1593 Santa Maria Valley, Calif.	Dry	.0856	.019	9.5	.026	29	.067	.011	.17	0.003	0	0	0	0	.56	-------	.014
B		Dry	.0868	.013	11	.025	34	.077	.026	.21	.004	0	0	0	0	.56	-------	.016
C		Wet	.0929	.044	9.2	.022	30	.066	.048	.18	.004	0	0	0	0	.50	-------	.014
D		Wet	.0931	.035	10	.025	29	.076	.035	.19	.004	0	0	0	0	.50	-------	.014
251823 A	Phillips Mudget No. 1, sec. 85, block 46, H and TC Survey Hutchinson County, Tex.	Dry	.0221	.056	1.3	-------	1.4	.022	.19	[1].0073	.013	28	0	0	0	.66	0	.013
B		Dry	.0209	.056	1.3	-------	1.6	.022	.19	.0016	.014	28	0	0	0	.66	0	.013
C		Wet	.0295	.094	1.3	-------	1.3	.021	.38	.0017	.019	19	0	0	0	.66	0	.020
D		Wet	.0328	.062	1.3	-------	1.2	.018	.15	.0015	.022	19	0	0		.66	0	.037
251824 A	Herrick oil pool, Albany County, Wyo.	Dry	.0315	.033	7.2	.018	37	.077	.042	.028	.005	-------	0	0	0	.66	0	.010
B		Dry	.0300	.060	6.7	.018	40	.072	.067	.027	.005	-------	0	0	0	.66	0	.010
C		Wet	.0360	.12	6.7	.016	34	.074	.11	.025	.01	-------	0	0	0	1.0	0	.012
D		Wet	.0345	.10	6.3	.017	31	.069	.084	.025	.01	-------	0	0	0	.96	0	.012

Probably contaminated.

TABLE 4.—*Comparison of results for metals in crude-oil samples obtained by dry ashing and wet oxidation of the oil*

[Calculated from percent ash and quantitative spectrochemical analyses of ash (table 3). Results in parts per million. 0, looked for but not found; leaders indicate not looked for. Analysts: P. J. Dunton and C. A. Horr]

Sample		Method of ashing	Percent ash	Parts per million in crude oil														
No.	Description			Cu	Ni	Co	V	Cr	Pb	Mo	Mn	Zn	Y	As	U	Fe	Zr	Sr
251821 A	Asphaltite, handpicked from Seven Rivers formation, Carlsbad, N. Mex.	Dry	8.65	81	690	110	17	18	150	240	-------	0	100	7,400	35,000	2,600	54	10
B		Dry	8.56	70	690	120	17	17	140	220	-------	0	100	7,700	37,000	2,600	70	10
C		Wet	9.67	62	720	110	16	21	160	220	-------	0	110	8,200	33,000	2,200	48	9.2
D		Wet	9.73	60	720	120	18	22	160	220	-------	0	120	8,300	32,000	2,400	55	9.2
251822 A	API(COAR) 53-1593 Santa Maria Valley, Calif.	Dry	.0856	.16	81	.22	250	.57	.094	1.5	0.026	0	0	0	0	4.8	------	.12
B		Dry	.0868	.11	95	.22	300	.67	.23	1.8	.035	0	0	0	0	4.9	------	.14
C		Wet	.0929	.41	85	.20	280	.61	.44	1.7	.037	0	0	0	0	4.6	------	.13
D		Wet	.0931	.33	93	.23	270	.71	.33	1.8	.037	0	0	0	0	4.6	------	.13
251823 A	Phillips Mudget No. 1, sec. 85, block 46, H and TC Survey, Hutchinson County, Tex.	Dry	.0221	.12	2.9	--------	3.1	.049	.42	[1].016	.029	62	0	0	0	1.5	0	.029
B		Dry	.0209	.12	2.7	--------	3.3	.046	.40	.0033	.029	58	0	0	0	1.4	0	.027
C		Wet	.0295	.28	3.8	--------	3.8	.062	1.1	.0050	.056	56	0	0	0	2.0	0	.059
D		Wet	.0328	.20	4.3	--------	3.9	.059	.49	.0049	.072	62	0	0	0	2.2	0	.12
251824 A	Herrick oil pool, Albany County, Wyo.	Dry	.0315	.10	23	.057	120	.24	.13	.088	.016	------	0	0	0	2.1	0	.032
B		Dry	.0300	.18	20	.054	120	.22	.20	.081	.015	------	0	0	0	2.0	0	.030
C		Wet	.0360	.43	24	.058	120	.27	.40	.090	.036	------	0	0	0	3.6	0	.043
C		Wet	.0345	.34	22	.059	110	.24	.29	.086	.034	------	0	0	0	3.3	0	.041

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[1] Probably contaminated.

content is calculated as parts per million of metal in the oil. The two methods of ashing show generally close agreement for the metals contained in the oil. The metal content of the ash obtained by dry ashing of the sample should be slightly higher than that obtained by wet oxidation in which sulfate is retained in the ash; in most cases this is apparently true. However, where results for metals by dry ashing gave a slightly lower figure than by wet oxidation (for example, Cu in samples 251822, 251823, and 251824 and Mn in samples 251823), there may be some minor loss of metals during the ignition of the oil samples. Results by the two methods of ashing were considered to be in sufficiently close agreement to justify the routine use of the described dry ashing method in the analysis of crude oils for investigations of the kind considered here.

COMPARISON OF QUANTITATIVE AND SEMIQUANTITATIVE SPECTROCHEMICAL RESULTS

A comparison of the results of quantitative and semiquantitative spectrochemical determinations of copper, vanadium, and nickel are given in table 5. The general agreement of these results for 37 samples by the two spectrochemical methods can be summarized as follows:

	Same ⅓ order		Miss by ⅓ order	
	Number	*Percent*	*Number*	*Percent*
Copper	28	76	9	24
Vanadium	26	70	11	30
Nickel	23	62	14	38

Thus, 76 percent of the semiquantitative results for copper, 70 percent of those for vanadium, and 62 percent of those for nickel show agreement to one-third order of magnitude (geometric) with results by the quantitative procedure. This percentage of agreement is consistent with results of analyses obtained by this method over a period of several years on many types of materials.

No special study was made of the precision and accuracy of the quantitative spectrochemical results obtained on ashes from crude oil. However, experience with this method has shown that at least an overall accuracy of ±20 percent may be expected.

The general agreement of the results by the semiquantitative or visual comparison method with quantitative results permitted confidence in using the semiquantitative method as a routine in analyzing the oils.

TABLE 5.—*Comparison of quantitative and semiquantitative spectrochemical determinations on the ash of 37 crude-oil samples*

[The figures for quantitative determinations are averages of duplicate analyses. Analyst, P. J. Dunton]

Denver Laboratory No.	Copper (percent)		Vanadium (percent)		Nickel (percent)	
	Quantitative	Semiquantitative	Quantitative	Semiquantitative	Quantitative	Semiquantitative
91693	1.6	1.5	13	M	8.3	3
91696	.84	.7	12	7	7.0	3
91698	3.4	3	7.9	3	5.2	3
91701	1.3	1.5	20	M	7.6	M
91707	.31	.3	.3	.3	.22	.15
91710	.48	.7	34	M	7.6	M
91712	.15	.07	8.8	7	2.4	3
91715	.04	.03	22	M	6.2	7
91716	.002	.0015	.86	.7	.19	.15
91721	.007	.007	1.2	.7	.69	.3
92402	.13	.07	.41	.3	7.6	M
92403	.03	.03	.07	.07	1.7	1.5
96070	.40	.7	.80	.7	.66	.7
96075	.10	.07	20	M	11	M
96077	.16	.3	38	M	9.2	M
96083	.10	.15	22	M	5.9	7
96084	.26	.3	17	M	4.8	7
96085	.22	.3	40	M	8.2	7
96086	.03	.03	40	M	7.6	7
96087	.03	.03	22	M	6.4	7
96092	.07	.15	28	M	7.0	7
96093	.16	.3	46	M	7.6	7
96094	.10	.15	28	M	6.4	7
96097	.10	.07	28	M	7.6	M
96110	.60	.7	3.9	1.5	9.2	7
96112	.07	.15	6.2	3	6.4	7
96115	.26	.3	5.6	3	7.2	M
96116	1.6	1.5	5.5	3	1.6	1.5
96122	.26	.3	9.6	7	16	M
96123	.26	.3	4.2	3	7.6	M
96127	5.6	3	.007	.007	.09	.07
200793	.22	.15	16	7	5.0	7
200799	.35	.15	3.7	1.5	2.5	1.5
200805	.84	.7	4.4	1.5	5.4	7
200808	.08	.07	20	M	9.2	M
200810	.13	M	8.4	7	2.2	1.5
200813	2.5	3	3.2	1.5	2.5	1.5

FLUORIMETRIC DETERMINATION OF URANIUM

The spectrograph is not sensitive enough for the determination of the small percentages of uranium normally present in the ash of crude oils. Therefore, uranium in the ash was determined by the more sensitive fluorimetric method. The precision and accuracy of this method for uranium in rocks has been studied by Grimaldi and others (1952, 1954) ; there was no apparent reason why the method would not apply as well to the determination of uranium in the ash of crude oil. The precision of the method obtained within the Denver laboratory is illustrated in the replicate results for uranium in table 6. A comparison of results obtained between the Washington, D.C., and Denver laboratories on duplicate samples is shown in table 7.

TABLE 6.—*Reproducibility of determinations of ash and of uranium in the ash of crude oils*

[Analysts: M. C. Curtis, D. L. Ferguson, and C. A. Horr]

Denver Laboratory No.	Ash (percent)		Uranium in ash (percent)	
	A	B	A	B
67430	0. 068	0. 065	0. 31	0. 30
67431	3. 46	3. 51	. 10	. 091
67431A	. 083	. 086	. 47	. 48
67432	1. 47	1. 26	. 41	. 37
67433	1. 31	1. 49	. 20	. 18
86656	. 0365	[1] . 0457	. 0008	[2] . 0010
90301	(3)		. 0003	. 0004
90307	(3)		. 0020	. 0019
90308	(3)		. 0004	. 0004
96037	(3)		. 0025	. 0028
96038	(3)		. 0036	. 0035
96039	(3)		. 004	. 004
96040	(3)		. 0016	. 0016
96041	(3)		. 0014	. 0014
96042	(3)		. 005	. 005
96043	(3)		. 0032	. 0029
96077	. 0094	. 0108	(3)	
96104	. 0099	. 0101	(3)	
96105	. 0155	. 0160	(3)	
96107	. 0167	. 0168	. 0005	. 0003
96108	. 0166	. 0169	. 0002	. 0002
96110	. 00287	. 00286	. 0009	. 0008
96112	. 0034	. 0034	. 0003	. 0004
96120	. 0003	. 0005	. 0097	. 0050
96122	. 00055	. 0005	. 0060	. 0042
96123	. 00099	. 0009	. 0017	. 0016
200815	. 117	. 116	. 0016	. 0018

[1] A third determination yielded 0.0442.
[2] A third determination also yielded 0.0010.
[3] Single determination.

TABLE 7.—*Comparison of results obtained at 2 laboratories for uranium in the ash of crude oils*

Denver Laboratory No.	Uranium in ash (percent)			
	Washington [1]		Denver [2]	
96037	0. 0030	0. 0030	0. 0025	0. 0028
96038	. 0034	. 0033	. 0036	. 0035
96039	. 0039	. 0040	. 0045	. 0040
96040	. 0019	. 0019	. 0016	. 0016
96041	. 0015	. 0014	. 0014	. 0014
96042	. 0055	. 0058	. 0050	. 0054
96043	. 0036	. 0034	. 0032	. 0029

[1] Analyses made under the supervision of F. S. Grimaldi.
[2] Analysts: M. C. Curtis and C. A. Horr.

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Distribution of Uranium and Other Metals in Crude Oils

By HAROLD J. HYDEN

URANIUM AND OTHER METALS IN CRUDE OILS

GEOLOGICAL SURVEY BULLETIN 1100-B

U.S. DEPARTMENT OF THE INTERIOR
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DISTRIBUTION OF URANIUM AND OTHER METALS IN CRUDE OILS

By Harold J. Hyden

ABSTRACT

A total of 120 samples of crude oil and 16 samples of refinery residue were collected from oil fields and refineries located in the western half of the United States. The oil and residue samples were reduced to ash; the uranium content of the ash was determined by fluorometric analysis, and the content of other metals by emission spectrograph.

The uranium content in the ash of a majority of the samples is included in the range 0.0002 to 0.001 percent. The reported average uranium content in the crust of the earth is within this percentage range. In contrast, vanadium and nickel contents in the ash of most of the samples are included in the range of 10 to 50 percent, which is several orders of magnitude greater than the reported vanadium and nickel contents in the crust of the earth. The amounts of other metals in the ash of oil are similar to those in the crust of the earth; among these latter metals, molybdenum shows the greatest relative enrichment in the ash of crude oil.

Twenty classes of oil are designated on the basis of U.S. Bureau of Mines crude-oil analyses. The classes are numbered so that the smaller numbers indicate light paraffinic oils and the larger numbers indicate heavy naphthenic or aromatic oils. The vanadium, nickel, gallium, and molybdenum contents of the ash of the several crude-oil classes are significantly different and tend to increase in the heavier, more naphthenic or aromatic crude oils. Among the metals the uranium content varied least from oil class to oil class.

In further comparisons the vanadium and nickel contents are found to be associated with nitrogen content, residual carbon content, and other items measured in crude-oil analysis. Gallium and cobalt contents show a lesser association; titanium, chromium, and molybdenum seem to be slightly associated; and uranium and copper seem to be unassociated.

The ratios of vanadium to nickel of the oil samples are restricted to a small range of values, but tend to increase with increasing age of reservoir rock. Vanadium and nickel are thought to be present in crude oil mainly as porphyrins, which are organo-metallic complexes. Gallium, cobalt, and molybdenum also are inferred to be present as organo-metallic complexes.

Tests indicate that crude oil can leach uranium from sandstone containing uranium minerals such as uraninite and carnotite, although the chemical process is unknown. The uranium content of crude oils, therefore, can be indicative of the uranium content in sandstone oil reservoirs.

INTRODUCTION

The occurrence of small amounts of metals, particularly vanadium and nickel, in petroleum and other natural hydrocarbons has been reported by many authors, for example Hewett (1910), Shirey (1931), Orlov (1932), Vinogradov and Bergman (1935), Fester and Cruellas (1936), Katchenkov (1949), Southwick,[1] Jones and Hardy (1952), and Erickson and others (1954).

The association of uranium with carbonaceous material in sedimentary rocks was frequently noted during the intensive development of uranium resources after World War II. High concentrations of uranium among the ore deposits of the Colorado Plateau commonly are associated intimately with fossil logs or other carbonaceous debris. Uranium has been found in association wth coal, particularly in the lignites from South Dakota (Denson and Gill, 1956). The high radioactivity and high uranium content of organic-rich shale, such as the Chattanooga shale, in the southeastern part of the United States have been the subject of numerous studies. Davidson and Bowie (1951) described occurrences of "thucolite," a hydrocarbon-uranium mixture. A wide range in uranium content of natural asphalts and oil seeps was noted by Hail (1957). Erickson and others (1954) were the first to report a comprehensive survey of uranium and other metals in natural asphalts and oils.

The metal content, particularly the uranium content, of the crude oil is so minute that crude oil cannot be considered a possible commercial source of these metals. The vanadium and nickel contents of crude oils, however, are important to petroleum refiners, because of their adverse affect on cracking catalysts. The primary objectives of this study are to ascertain the concentration and distribution of uranium and other metals in oil, and to evalaute the resulting data in order to determine the geologic and geochemical factors that control their distribution.

ACKNOWLEDGMENTS

Basic data used in this report were provided by the laboratories of the U.S. Geological Survey and the U.S. Bureau of Mines. Harold M. Smith and John S. Ball directed the work by the Bureau of Mines, and provided important counsel. W. J. Wenger and C. M. McKinney of the Bureau of Mines analyzed crude-oil samples collected for this investigation. The oil companies were most cooperative and helpful in the collection of oil samples. N. Wood Bass, formerly of the Geological Survey, provided invaluable advice and guidance. A. T.

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[1] Southwick, S. H., 1951, Inorganic constituents of crude oil: Massachusetts Institute of Technology, Ph. D. thesis, 93 p.

Myers and C. A. Horr directed the laboratory work done by the Geological Survey. Pauline Dunton made all spectrographic determinations; Mary Curtis, Dorothy Ferguson, and Sylvia Furman made uranium analyses and performed other duties preparatory to analysis. The investigation was sponsored in part by the Division of Raw Materials of the U.S. Atomic Energy Commission and in part by the Geological Survey.

METHODS OF INVESTIGATION

SELECTION OF SAMPLE LOCALITIES

Oil fields in the western part of the United States were selected for sample collection to include a wide range in composition of crude oil, in age of reservoir rock, and in geologic conditions (fig. 1). Certain fields were selected because of their proximity to uranium-ore deposits or to uranium-bearing formations, such as the Morrison formation and Shinarump member of the Chinle formation of Colorado and Utah.

With the exception of one oil field, samples were not collected where secondary recovery methods were used, because such methods may introduce metals into the crude oil. Sixteen samples of refinery residue were collected from ten petroleum refineries.

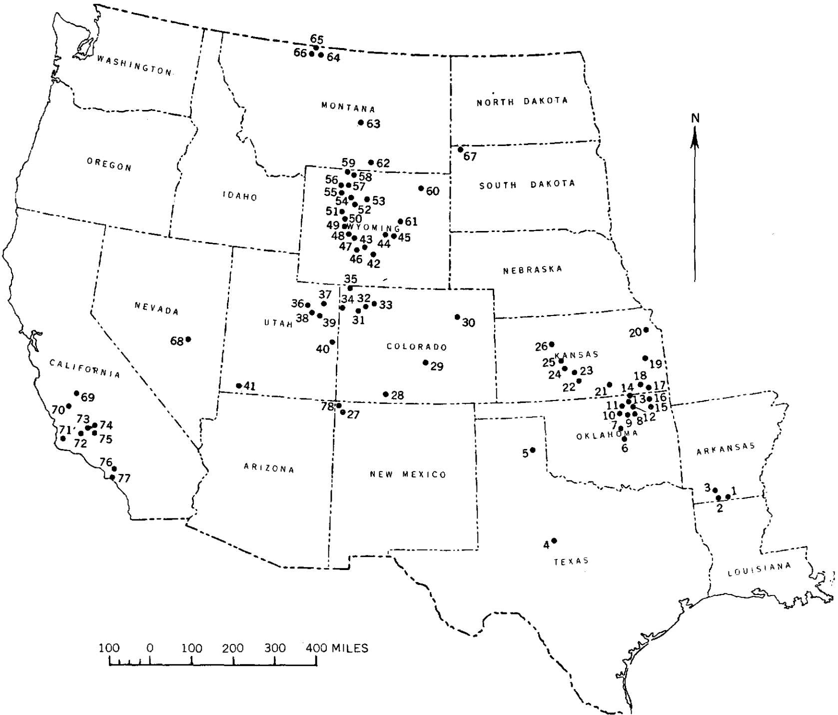
SAMPLING TECHNIQUES

Two-gallon oil samples were usually collected in glass containers at the well head, where most of the produced water was separated by decantation. In a few fields the oil samples were collected from pipelines or storage tanks where the produced water had been previously eliminated. Three samples of residues from tank bottoms were collected by use of cylindrical sampling devices known as "thieves."

LABORATORY METHODS

The laboratory methods are described in detail in chapter A of this bulletin, where comparisons of different techniques are reported. The following is a brief description of the processes involved in the metal analyses.

In the laboratory any water remaining with the oil was removed, and the oils were filtered. Increments of the filtered crude-oil samples or of the refinery residues were placed in platinum dishes, ignited in the air, and allowed to burn freely to produce a dry carbon mass in each dish. The carbon was then removed in an electric muffle at 500° C. The ash of each sample, so derived, was diluted with a pure quartz powder, and then divided into two parts: one part for fluoro-



LIST OF OIL-FIELD LOCALITIES

1. Schuler
2. West Atlanta
3. Stephens-Smart
4. Dora
5. Finley (Panhandle)
6. Laffoon
7. Kendrick
8. Flat Rock
9. Osage City
10. Middle Gilliland
11. Naval Reserve
12. Wildhorse
13. Wynona, New England
14. Pond Creek
15. Chelsea (Nowata)
16. Alluwe (Nowata)
17. Coffeyville
18. Brewster
19. Iola
20. McLouth
21. Hittle
22. Cunningham
23. Brock
24. Pawnee Rock
25. Otis-Albert
26. Solomon
27. Table Mesa
28. Gramps
29. Florence
30. Badger Creek
31. White River
32. Wilson Creek
33. Moffat Dome
34. Rangley
35. Hiawatha
36. Duchesne County
37. Roosevelt
38. Duchesne
39. West Pleasant Valley
40. Seiber Nose
41. Virgin
42. Lost Soldier
43. Crooks Gap
44. South Casper Creek
45. Oil Mountain
46. Bison Basin
47. Derby
48. Dallas
49. Winkleman Dome
50. Pilot Butte, Steamboat Butte
51. Circle Ridge
52. Hamilton Dome
53. South Fork
54. Grass Creek
55. South Spring Creek
56. Half Moon
57. North Oregon Basin
58. Garland
59. Elk Basin
60. Mitchell Creek
61. Salt Creek
62. Soap Creek
63. Big Wall
64. Bears Den
65. Flat Coulee
66. Whitlash
67. Custer area
68. Eagle Springs
69. Helm
70. Coalinga
71. Santa Maria Valley
72. Midway (Oxford pool)
73. Elk Hills
74. Coles Levee
75. Ant Hill
76. Inglewood
77. Wilmington
78. Rattlesnake

Figure 1.—Map of the western part of the United States showing localities where samples of crude oil were collected for analysis of uranium and other trace-metal content.

metric determination of uranium content and the other part for spectrographic analysis. However, the volume of ash of some samples was insufficient for both types of analyses, and only one type was made.

A routine semiquantitative spectrographic analysis was performed on the ash of each sample. In addition, a quantitive spectrographic analysis was made for vanadium, nickel, and copper contents in 37 samples.

APPLICABILITY OF DATA

In order to test gross relations between metals and hydrocarbons, samples of crude oil were collected from many oil fields representing a large geographical area producing many different types of crude oil. Data from analyses of oil samples from different wells in the same field indicate that metals in crude oil are not uniformly distributed in each oil field; however, no attempt was made to collect sufficient samples to define a representative sample for each field.

Tests of metal content in samples from an oil storage tank indicate stratification of metal content of the oil stored in the tank, and support the possibility that metals in crude oil are stratified within each oil reservoir. The filling of a tank at Nowata field was interrupted to allow minimal time for settling, and samples of crude oil were collected at 2-foot intervals. As the fluorometric test for uranium is the most sensitive metal analysis used in this investigation, uranium content was tested in these samples. The following analyses show a general increase of ash and uranium content with increase in depth.

Depth from surface (feet)	Laboratory No.	Ash in oil (percent)	Uranium in ash (percent)	Uranium in oil (ppb)
0 (top surface of oil)	242341	0. 0049	0. 010	5. 0
2	242346	. 0053	. 016	8. 7
4	242339	. 0058	. 016	9. 3
6 (bottom of tank)	242338	. 0059	. 016	9. 5

Inasmuch as this report is concerned primarily with general relations of metal content to other crude-oil characteristics, no attempt was made to obtain samples that would provide determination of horizontal and vertical variations of metal content in the crude oil of any pool.

DISTRIBUTION OF METALS IN ASH OF OIL

The distribution of metals in the ash of crude oil is summarized in figure 2. The metals are arranged from left to right in order of decreasing abundance in the crust of the earth (Goldschmidt, 1954; Krauskopf, 1956) to illustrate relative concentrations. The data presented in figure 2 are based on 117 fluorometric analyses for uranium and 102 quantitative or semiquantitative analyses for the other metals. For some samples the amount of ash was not sufficient for both uranium and spectographic analyses, and only one analysis was performed.

Metal quantities as determined by the semiquantitative method for this study are reported within a range of values, and the ranges

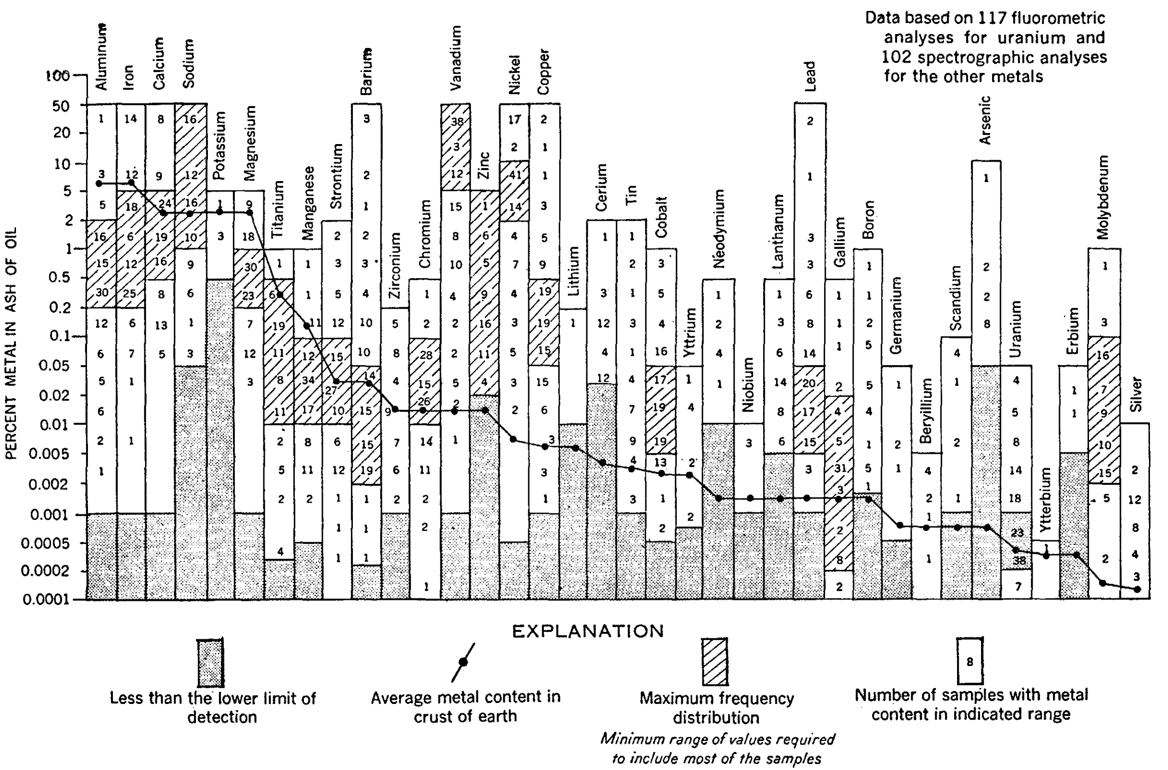


FIGURE 2.—Distribution of metals in the ash of crude oil arranged in order of average metal content in crust of earth.

reported are a threefold division of each decimal place. The division points are the digits 1, 2, and 5 and these division values define the vertical units of the histogram in figure 2. Quantitative spectrographic analyses for this study were reported to two significant figures. The results of quantitative analyses for vanadium, nickel, and copper content of 37 crude oil samples are included within the proper semiquantitative divisions in figure 2. Sixty percent agreement has been estimated between the threefold semiquantitative method and the quantitative method (Flanagan, 1957, p. 317).

The diagonally lined area of each bar is the area of maximum frequency distribution and is used as the standard for comparison. This area represents the minimum range of values required to include most of the samples tested. Figure 2 shows that the order of abundance of metals in the ash of crude oils, with some exceptions, is similar to that in the crust of the earth. Vanadium and nickel are the notable exceptions; these metals are the most abundant in the ash of crude oil.

Aluminum and iron are major constituents both in the crust of the earth and in the ash of crude oils; and because of their ubiquity they are very probable contaminants in the oil samples. Silicon, also a major constituent in the crust of the earth, has been noted in crude oils (Erickson and others, 1954), and was undoubtedly present in the crude-oil samples collected for this investigation. However, pure quartz was used as a matrix in preparation of the ash sample for the spectrograph, and therefore the silicon content was not tested. Platinum content was not tested because of the probability of contamination from the platinum crucibles in which the oil samples were ignited. Some metals were not detected in more than half the samples. This may be due either to the actual scarcity of the metals in the ash, or to the limitation of the spectrograph in detecting metals. Potassium was detected in only 4 out of 102 samples, probably owing to its high limit of detection (fig. 2).

The vanadium and nickel contents each constitute more than 10 percent of most of the ash samples, and are distinctly high compared with their average content in the crust of the earth. Molybdenum also appears to be abundant in the ash of oil relative to its average content in the crust of the earth. The uranium content, on the contrary, is minor both in oil ash and in the crust of the earth. The relation of uranium content in the ash of most samples to the average uranium content in the crust of the earth seems to be typical of the relation of the content of most of the metals shown in figure 2 with their average content in the earth's crust; the order of abundance of these metals is very similar in the ash of crude oil and in the crust of the earth.

DISTRIBUTION OF METALS IN CLASSES OF OIL

CRUDE-OIL CLASSES

In order to provide a framework for studying metal content of oil in conjunction with crude-oil composition, the author devised 20 crude-oil classes based on Bureau of Mines routine crude-oil analyses. Crude oils consist of mixtures of numerous types of hydrocarbons. Any particular sample of crude oil usually includes both aliphatic and aromatic compounds. The complexity of the mixtures and the diversity of hydrocarbons involved are major difficulties in devising a practical system of comparing crude oils.

The Bureau of Mines routine crude-oil analysis is widely used among oil producers and refiners as a standard description of any given crude oil, and numerous analyses of this type have been published. Laboratories of the Bureau of Mines analyzed some of the samples of crude oil collected for this report, especially those from the fields where analyses were not available; their analyses are used in this report as a means of classification of the samples of crude oil for comparison of metal content.

The Bureau of Mines crude-oil analysis includes a fractional distillation, by which distillation fractions or "cuts" are made at intervals of 25° C (Smith, 1940; Smith and others, 1951). Correlation index numbers are reported by the Bureau for each distillation cut. The correlation index is calculated from the specific gravity and the reciprocal of the average boiling point (Smith, 1940, p. 3). The empirically developed equation for calculating the correlation index is—

$$C.I.=\frac{48640}{K}+473.7G-456.8$$

where $C.I.$ is the correlation index for each cut,

K is the average boiling point of that fraction in degrees Kelvin,

and G is the specific gravity of that fraction at 60° F./60° F.

The correlation indices for the analyses were plotted against the cut numbers and the curves so obtained furnish the basis for the classification of oils used in this report.

The terms "paraffin-base" crude oil and "asphalt-base" crude oil have been long in popular use. Lane and Garton (1935) suggest that the term "paraffin-base" originated in reference to the waxy material that settles out when some oils are chilled. The same authors report that the term "base" connoted to many oil producers and refiners a nonvolatile material, analogous to the inert materials that act as carriers for active material in pharmaceuticals, such as salves and ointments.

In addition to this connotation, the popular "base" system of classification includes crude oils of highly diverse composition in the same classification, and the classifications are not well defined. The terms "paraffin-base," "asphalt-base," or "intermediate-base," although well known, were considered unsuitable for use in this investigation.

H. M. Smith (1940, p. 5–13) has shown how the correlation index numbers, computed from data derived from the distillation of pure hydrocarbons, are related to the type of hydrocarbons involved. The correlation index of a pure hydrocarbon may be predicted to fall within a range of values; thus the correlation index of a distillation fraction generally indicates the composition of that fraction: straight-chain paraffins have the index of 0, branching-chain paraffins have values of 1 to 12, naphthenes have values of 12 to 50, and aromatics have values of 26 to 100. Thus, the larger the correlation index, the heavier the fraction and the more naphthenic or aromatic the composition.

Graphical plots of correlation indices provide a means of comparing crude oils and evaluating similarity of composition. The author devised 20 crude-oil classes on the basis of correlation plots for the purpose of studying metal content in conjunction with crude-oil composition. In general, oils having larger correlation index numbers are in oil classes of larger number (fig. 3); consequently the larger class number generally indicates larger correlation indices and heavier, more naphthenic or aromatic oils. Figures 11–39 show graphical plots for the 20 oil classes.

The definition of crude-oil classes was derived from visual comparison. Oils with similar correlation indices were deemed most similar in composition and were placed in the same class. This crude-oil classification is therefore specific and not general; the classification applies only to the oil samples included in this study and to no other oil samples. The member crude oils of each class can be said to define that class, and therefore, if additional oils were to be studied, a complete reclassification would be necessary.

A subjective aspect was necessarily involved in this definition of classes; this aspect was diminished by having others repeat the process and come to a final agreement. Some of the classes so determined were further subdivided into groups. (See figures 11–39.) The 20 classes consist of 87 different oils. The number of oils in each class differs, and it ranges from 1 oil in classes I and XIX to 12 oils in class XII. Class IV has been divided into the largest number of

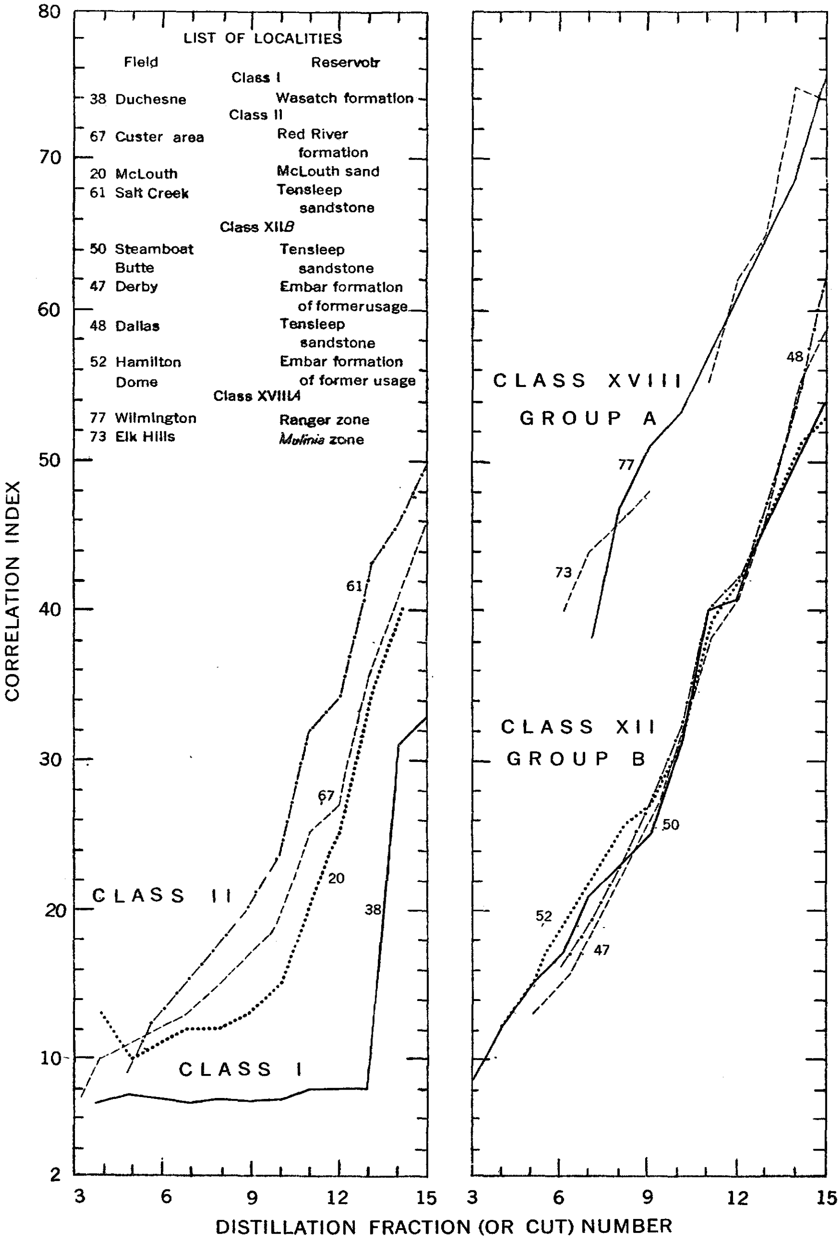


FIGURE 3.—Correlation index plots of four selected classes of oil.

groups—4. Classes I through IX include oils from the central midcontinent and Rocky Mountain areas, class X through class XII oils are from Wyoming, and Montana class XIV oils are from Oklahoma and Kansas, and the heavy asphaltic oils of classes XVI through XIX are from Wyoming and California.

The assignment of numbers to the oil classes was also partly subjective. Averages of the correlation indices were used to arrange the classes in order; however, many decisions as to the assignment of particular class numbers were arbitrary because of the differing shapes and slopes of the curves. Thus, for two classes, one may have higher correlation index numbers for the lower boiling point fractions, and the other may have higher correlation index numbers for the higher boiling point fractions. However, the higher oil-class numbers generally indicate higher correlation index numbers.

The correlation indices of four of the oils analyzed do not fit in classes I–XIX, and are placed in a special class called class *S* (fig. 39). The plots in this class are not restricted to a beltlike area as characterizes the other classes. These plots are distinctive in that their slopes vary from positive to negative and the correlation index values do not show a marked increase to the right.

COMMON METALS

The crude-oil classification devised for this report provides a framework for a survey of metal-hydrocarbon association. Similarity of composition as well as significant difference of composition of crude-oil samples are indicated by the class numbers, and significant association of a metal with a particular type of hydrocarbon could be revealed by the distribution patterns of metal content in oil classes.

The distribution of the metals that were detected in more than half the oil samples is shown on plate 2. Histograms are used for the comparison of metal contents in oil classes. The histograms show the gross characteristics of the distribution and mask some of the minor irregularities.

The horizontal units of the histograms are quantities of metals expressed in parts per million (ppm), except for uranium which is in parts per billion (ppb [10^9]). The metal content in the oil was computed according to the formula: parts per million metal in oil= percent metal in ash × percent ash × 100.

For some metals the unit on the left end of the horizontal scale includes not only samples with less than 0.0001 ppm, but also samples in which the metals were not detected. The undetected amounts of any metal may have actually exceeded 0.0001 ppm in the oil. Owing to the limits of the analytical instruments, this unit, therefore, is not as accurately determined as the other units.

In order to facilitate a visual evaluation of metal distribution in oil classes, the bar in each histogram of plate 2 that indicates the largest number of samples is patterned and is called the modal bar.

The condition in which the modal bar concentration for any metal increases or decreases regularly with progression of oil classes is considered to be favorable evidence of a relation between metal content and oil class. The vanadium content fulfills this condition fairly well. The modal bars for vanadium appear in five concentration ranges and show a general increase of vanadium content with increase in number of the oil class. The vanadium content seems to be related to the oil classes. Nickel, like vanadium, also shows a general increase with increase in oil class number. Gallium, chromium, and molybdenum also show this tendency but to a lesser degree than vanadium and nickel. In contrast, the modal bars for uranium in all the oil classes are restricted to the 0.1 to 1, and 1 to 10 ppb ranges, and thus seem to be clearly independent of the oil class.

For the other metals shown on plate 2, no clear regular pattern of concentration of the modal bars relative to oil classes is discernible.

It is interesting to compare vanadium, nickel, and uranium contents of the oils in class *S* (pl. 2). Class *S* is not an effective classification for these metals. Vanadium and nickel are present in class *S* in a wide range of values (0.001 to 10 ppm), and thus this class of oil has no apparent selective affinity for these metals. The uranium content in class *S* contrasts to the vanadium and nickel contents and is restricted in class *S* to the 0.1 to 1 ppb range. Uranium appears to be present in oil in a restricted range of quantities regardless of oil class.

The content of metals in the ash of the oil samples is shown by plate 3. The vanadium and nickel histograms show a distribution pattern less well defined but similar to the pattern shown on plate 2. The modal bars for uranium content in ash are restricted to a two decimal place range as are the modal bars for the uranium content of oil.

Vanadium and nickel are the metals most concentrated in the ash of oil as compared with their concentration in the crust of the earth (fig. 2). These two metals also show the strongest correlation with the class of oil. For these reasons, along with others to be discussed later, vanadium and nickel are considered most representative of metals showing organic chemical control.

The ash content of the oil, shown on plate 3, tends to increase in progressively higher numbered oil classes. The change in position of the modal bar with oil class for ash content is similar to that change for the vanadium modal bar. Indeed, vanadium and nickel each commonly constitute more than 10 percent of the ash of the higher oil classes.

UNCOMMON METALS

Among the 36 metals detected in the crude-oil samples (fig. 2), 17 metals were detected in less than half of the samples. Of these 17 metals the most frequently detected were tin, silver, boron, arsenic, zirconium, neodymium, lanthanum, cerium, and yttrium.

The percentage of samples in which each of these metals was detected in each oil class is shown by the histograms in figure 4. These metals seem to fall into two groups. The metals of the first group—tin, silver, boron, and possibly arsenic and zirconium—are common in the lower numbered oil classes and less common in the higher numbered oil classes. The diminishing lengths of the bars in the direction of the large oil class numbers suggest this relation. Silver, for example, was not detected in any oil with a class number larger than X, although it was present in every sample of this class. The distribution of the metals of the second group—neodymium, lanthanum, cerium, and yttrium—seem to bear no consistent relation to the oil classes.

The relative scarcity of tin, silver, boron, arsenic, and zirconium in the higher numbered oil classes could be due to a scarcity of hydrocarbons that have affinities for these metals; or these metals may be present equally in very small amounts in any or all oils, but their presence in the higher numbered oil classes may be masked by the dilution effect of high content of vanadium and nickel. The rare-earth metals lanthanum and cerium were detected in many samples represented in figure 4 by yttrium and neodymium were detected in very few. No relation to oil class is apparent for these rare-earth metals.

RATIO OF VANADIUM TO OTHER METALS

The vanadium-to-nickel ratio in crude oils seems to be restricted to a small range of values, and it seems to be related to the age of the reservoir rock. This has been noted by Katchenkov (1949), Gulyaeva (1952), Scott and others (1954), and Hodgson (1954). The ratios of vanadium to nickel derived from quantitative spectrographic analyses of 37 crude-oil samples are shown in table 1. In addition, the ratios of vanadium to gallium, cobalt, titanium, molybdenum, and uranium are shown. The relation of these metals to crude-oil characteristics is discussed later.

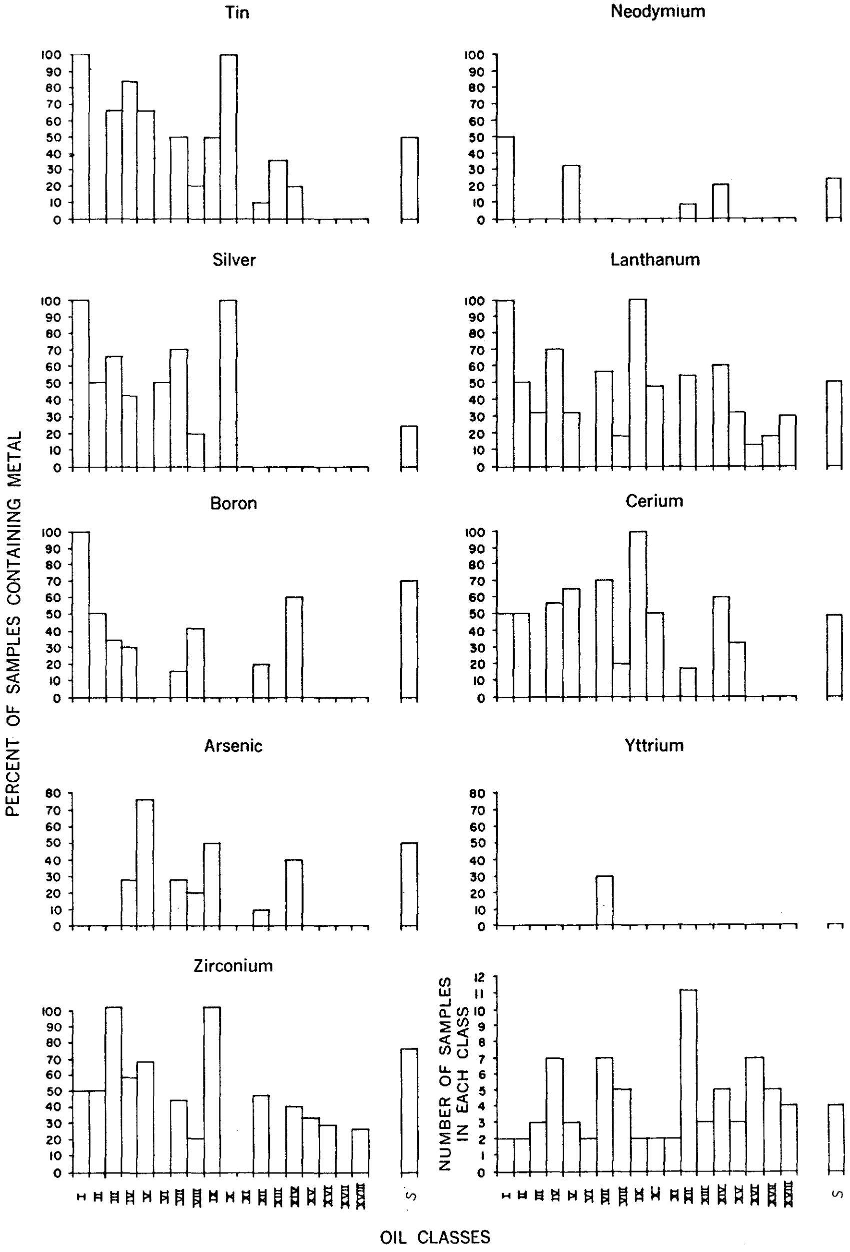


FIGURE 4.—Distribution of oil samples according to the presence of nine less commonly detected metals. (See figures 11–39 for oil classes.)

TABLE 1.—*Ratios of vanadium to other metals in order of age and type of reservoir rock*

[Vanadium and nickel contents are from quantitative spectrographic analyses. Uranium content was determined by fluorometric analyses. The remaining metal contents are from semiquantitative spectrographic analyses. Ratios and averages are shown as computed to two significant figures for nickel and uranium and one significant figure for other ratios. The infinity sign (∞) indicates that vanadium was detected but that the other metal was not detected.]

Reservoir rock	Oil sample laboratory No.	Ratio of vanadium to—					
		Nickel	Gallium	Cobalt	Titanium	Molybdenum	Uranium
Reservoirs in rocks of Paleozoic age							
Cambrian sandstone	D91715	3.5	70,000	1,000	1,000	3,000	73,000
Cambrian and Ordovician limestone	D91693	1.5	90,000	2,000	1,000	∞	9,300
	D91712	3.7	30,000	300	5,000	∞	22,000
	D91716	4.5	30,000	300	30	∞	960
	200793	3.2	10,000	1,000	100	2,000	13,000
Ordovician sandstone	D91707	1.3	∞	100	1,000	∞	180
	200808	2.2	∞	700	100	∞	22,000
Mississippian limestone	D96087	3.4	7,000	7,000	∞	300	10,000
	D96092	4.0	9,000	9,000	∞	400	93,000
Pennsylvanian sandstone	D91696	1.8	∞	400	800	∞	7,600
	D91698	1.5	∞	100	500	∞	----------
	D91701	2.6	∞	700	1,000	∞	4,400
	D91721	1.7	∞	200	400	∞	6,000
	D96075	1.8	7,000	300	∞	3,000	13,000
	D96077	4.1	10,000	10,000	∞	10,000	3,800
	D96083	220	7,000	3,000	∞	100	73,000
	D96085	4.9	10,000	10,000	∞	600	5,300
	200813	1.3	∞	200	∞	200	1,000
Pennsylvanian limestone	D91710	4.5	100,000	1,000	11,000	----------	42,000
	200810	3.8	∞	1,000	300	60,000	2,600
Permian interbedded limestone and sandstone	D96084	3.5	5,000	6,000	∞	100	56.000
	D96086	5.3	10,000	6,000	∞	600	9,300
	D96093	6.0	10,000	1,000	∞	1,000	150,000
Reservoirs in rocks of Mesozoic age							
Triassic sandstone	D96094	4.4	9,000	4,000	∞	400	70,000
	D96097	3.7	9,000	4,000	∞	400	140,000
Jurassic sandstone	D96070	1.2	300	10	∞	300	∞
	D96122	.62	600	30	60	600	1,600
	200799	1.5	2,000	100	200	∞	6,200
Cretaceous sandstone	D96110	0.42	600	10	60	600	4,600
	D96112	.97	900	∞	∞	2,000	31,000
	D96115	.78	900	80	40	2,000	2,300
	D96123	.55	300	6	60	600	2,500
	D96127	.08	20	1	∞	1	3.9
	200805	.82	600	100	30	100	3,700
Reservoirs in rocks of Tertiary age							
Eocene sandstone and marlstone	D92402	0.05	∞	1	100	10	4,100
	D92403	.04	∞	1	200	20	<700
	D96116	3.4	∞	∞	4	∞	----------

The following observations concerning the vanadium-to-nickel ratios may be drawn from table 1.

1. For Paleozoic rocks the ratios range from 1.3 to 6.0 (except for one anomalous value of 220).
2. For Mesozoic rocks the ratios range from 0.08 to 4.4.
3. For Tertiary rocks the ratios range from 0.04 to 3.4.
4. Ratios of less than 1.0 occur only in oils from Jurassic and younger rocks.

With the exception of one anomalously high value of 220, the vanadium-to-nickel ratios are confined to a small range of values and show a general increase with increase in age of reservoir rock. This relation is consistent with values reported by Katchenkov (1949) and Gulyaeva (1952).

The ratios of vanadium to gallium have a much wider range of values than the ratios of vanadium to nickel. A general, although poorly defined, increase in ratio with age of reservoir rocks may be noted; for example, ratios less than 1,000 are only in oils from Jurassic and younger rocks.

The ratios of vanadium to cobalt, titanium, molybdenum, and uranium all have wide ranges of values in contrast to the small range of values for vanadium-to-nickel ratios. The increase in ratio with increase in age is only faintly suggested for the ratios of vanadium to cobalt, titanium, and molybdenum. Not even a suggestion of a relation of age with the vanadium-to-uranium ratio appears in table 1.

CORRELATION COEFFICIENTS

The distillation analysis of crude oils, previously described, is considered to be the main part of the Bureau of Mines crude-oil analysis. In addition, however, the determination of certain other characteristics is included as a part of the crude-oil analysis (Smith and others, 1951, p. 2–4). Among these are the numerical vaules for the gravity of the oil, the sulfur content, the content of residue from the distillation, the gravity of the residue, and the carbon content. The determination of nitrogen content was recently added as part of the crude-oil analyses (Ball and others, 1951). These characteristics, as well as the correlation index of the fifteenth distillation fraction, which is the last distillation fraction, are compared with metal contents in table 2.

The rank correlation coefficients shown in table 2 are statistical quantities and should not be confused with the previously discussed correlation indices, which are determined in the Bureau of Mines analyses. The numerical values of the correlation coefficients are much more amenable to ordinal comparison than are scatter diagrams. The crude oils are of complex and largely undetermined chemical

TABLE 2.—*Rank correlation coefficients for vanadium, nickel, and uranium contents according to seven crude-oil characteristics*

[Coefficients are from Kendall, 1955, p. 1–48]

Metal	Crude-oil analyses						
	Nitrogen content (percent) (28 samples)	Gravity of residue (29 samples)	Correlation index of cut 15 (29 samples)	Residual carbon content (percent) (29 samples)	Residue content (percent) (29 samples)	Sulfur content (percent) (29 samples)	Gravity of oil [1] (°API) (29 samples)
Nickel	0.69	0.78	0.52	0.64	0.48	0.57	0.54
Vanadium	.60	.64	.52	.57	.49	.57	.54
Uranium	.07	.13	.03	<.01	.17	.10	.09

[1] Values ranked in inverse order of degrees API.

composition; each characteristic determined in a crude-oil analysis represents a multiplicity of organic compounds or complexes, rather than just one. The purpose of this comparison of correlation coefficients, therefore, is not to measure exact chemical relations. Thus this is not an attempt to measure how closely two variables approach a linear relation, but instead, an attempt to compare the ranking of different metals.

Data in table 2 are from the analyses of 29 oils for both metal content and crude-oil characteristics. Twenty-eight of these oils were analyzed both for metals and for nitrogen content. Nine quantitative and 20 semiquantitative spectrographic analyses are the sources of data on vanadium and nickel content. All the uranium values are from fluorometric analysis. Vanadium, nickel, and uranium were detected in all 29 samples.

Normal distributions could not be proved for every metal; hence, the product-moment correlation coefficient was considered unsuitable, and a nonparametric correlation was needed. Kendall's (1955) rank correlation coefficient was selected as the most suitable for this investigation. This rank correlation coefficient theoretically varies from one, for perfect correlation of rank, through zero for no correlation of rank whatsoever, to minus one for perfect inverse correlation of rank. As the correlation coefficients approach zero from either direction, their statistical significance decreases and the probability increases that such results may be due to chance. Contrariwise, the large correlation coefficients, positive or negative, are the more significant.

In table 2 the vanadium and nickel correlation coefficients are relatively large and are the more significant values; they range from 0.48 to 0.78. For any of the seven crude-oil characteristics the correlation coefficients of the two metals are roughly the same. The uranium correlation coefficients are very small; all seven are less than 0.2, and four of the seven are less than 0.1. The rank correlation coefficients show a similar relation between each of the crude-oil characteristics and the three metals: the nickel correlation is the best, the vanadium correlation is either the same or slightly less, and the uranium correlation is extremely small. The data shown in table 2 indicate that vanadium and nickel content are related to the hydrocarbon composition of the crude oil and that uranium content is not related, at least as closely as vanadium and nickel.

Three of the items in table 2—nitrogen, gravity of residue, and residual carbon—show the highest positive correlations for vanadium and nickel, and hence seem to be the more significant items indicating a relation of these metals to the hydrocarbons in crude oils. Fourteen metals, which were identified only by semiquantitative spectrographic analysis and which proved to be commonly present in crude oils, are ranked in table 3 according to these three items. Vanadium, nickel, and uranium correlation coefficients, already shown in table 2, are repeated in table 3 for the purpose of comparison.

TABLE 3.—*Rank correlation coefficients for 14 metals according to 3 crude-oil characteristics*

[Coefficients are from Kendall, 1955, pp. 1-48]

Metals	Crude-oil characteristics		
	Nitrogen content (percent) (28 samples)	Gravity of residue [1] (29 samples)	Residual carbon content (percent) (29 samples)
Nickel	0.69	0.78	0.64
Vanadium	.60	.64	.57
Gallium	.64	.74	.67
Cobalt	.64	.61	.54
Titanium	.41	.46	.46
Chromium	.38	.47	.34
Molybdenum	.37	.46	.28
Barium	.17	.15	.13
Strontium	.15	.16	.10
Copper	.02	.15	.11
Uranium	.07	.13	<.01
Manganese	−.10	−.02	−.03
Lead	−.37	−.24	−.15
Zinc	−.59	−.30	−.34

[1] Values were ranked in inverse order of degrees API.

Vanadium, nickel, and uranium were detected in all 29 samples; however, gallium and zinc were undetected in 9 samples, manganese in 5, lead in 4, and cobalt, titanium, and chromium in 1 each. All reports of undetected metals were ranked together, and hence this rank can include a much larger range of values than the other ranks. Statistical adjustments were made for these and other ties, according to the method suggested by Kendall (1955, p. 49-66). Nonetheless, insofar as a large number of samples are included in the undetermined rank, the correlation is poorly tested. For this reason the correlation coefficients for gallium, zinc, manganese, and lead are probably less reliable than for the others.

The correlation coefficients for gallium and cobalt, shown in table

3, are the same order of magnitude as those for nickel and vanadium. The correlation coefficients for the remaining metals are smaller and less significant; the correlation coefficients for copper, uranium, and manganese are the smallest.

Like vanadium and nickel, gallium and cobalt contents seem to be related to the crude-oil characteristics, although to a lesser degree. The titanium, chromium, and molybdenum contents seem to be slightly related. Barium, strontium, copper, uranium, and manganese show little relation. Lead and zinc seem to prefer oils with less nitrogen, lighter residue, and less residual carbon.

The correlation coefficients of barium and strontium are remarkably alike, as are those of chromium and molybdenum. These similarities further support the inference of control of metal content by oil characteristics, for barium and strontium are in group IIA in the periodic table and chromium and molybdenum are in group VIA. Thus, atomic structure appears to be a factor in the correlation of at least four metals with crude-oil charateristics.

DISTRIBUTION OF METALS IN FRACTIONS OF OIL

REFINERY RESIDUES

The evidence gathered in this investigation indicates that a large part of all the metals in crude oil are associated with the residue from distillation processes. In figure 5 a summary of the metal analyses of 16 samples of refinery residues is compared with a summary of the metal contents in the crude-oil samples shown in figure 2. The diagonally lined area of each bar shows the area of maximum frequency concentration of the metals in the ash of the refinery residues; the elongated circles on each bar show the area of maximum frequency concentration for the crude-oil samples. These areas represent the minimum range of values required to include a majority of the samples tested.

The general distribution of metals in the oils and the residues is very similar. The circles and the diagonal patterns share areas in whole, or in part, for all but four metals: zirconium, cerium, scandium, and gallium. These four apparent exceptions may be due to an insufficient number of samples, especially of refinery residue samples, rather than to significant differences of distribution of these metals.

THREE DISTILLATION FRACTIONS

The metal content of distillation fractions and the residue of the distillation were compared. Table 4 shows metal analyses for three distillation fractions and a residue of a 40-gallon oil sample from the Bartlesville sand in the Alluwe pool of the Nowata field, Oklahoma.

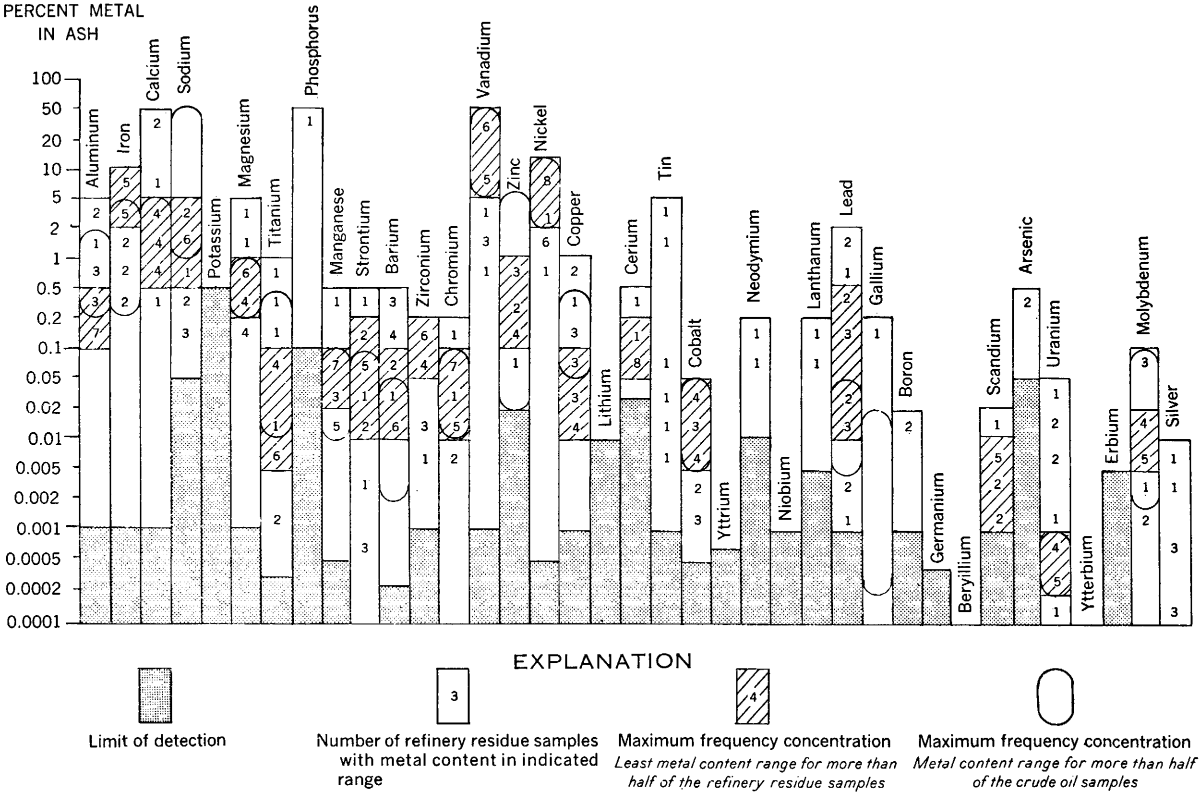


FIGURE 5.—Distribution of metals in the ash of 16 samples of petroleum refinery residues compared with distribution of metals in the ash of crude-oil samples.

The following conclusions can be drawn from the data presented in this table: The ash of the residue constitutes approximately 93 percent of the total ash of this oil sample, and the residue contains more than 98 percent of any of the metals—vanadium, nickel, or uranium.

TABLE 4.—*Vanadium, nickel, and uranium contents of three distillation fractions and the residue of crude oil from the Alluwe pool of the Nowata field, Oklahoma*

[Distillation fractions furnished by Frank B. Schwartz, U.S. Bureau of Mines, Bartlesville, Okla.]

Laboratory No.	Distillation fraction		Ash		Vanadium			Nickel			Uranium		
	Temperature (° F)	Pressure (mm of mercury)	Percent of fraction	Percent of whole	Percent in ash	ppm in oil	Percent of whole	Percent in ash	ppm in oil	Percent of whole	Percent in ash	ppb in oil	Percent of whole
242342	392	746	0.0002	1.2	0.15	0.003	0.1	0.3	0.006	0.2	0.0045	0.09	0.5
242343	392	40	.0002	1.2	0	0	0	.07	.0014	≲.1	.0045	.09	.6
242344	392	5	.0008	4.8	0	0	0	.015	.0012	≲.1	.008	.06	.4
242345	Residuum		.015	92.8	3	4.6	99.9+	1.5	2.4	99.6	.010	15.96	98.5
Total			0.0162	100.0	3.15	4.6+	100.0+	1.885	2.41	99.8+	0.020	16.20	100.0

All the other metals detected were similarly concentrated in the residue. The metals potassium, beryllium, cerium, gallium, germanium, lanthanum, scandium, yttrium, ytterbium, and zirconium were detected only in the residue. Cobalt, sodium, strontium, and zinc were undetected in the first fraction (pressure of 746 mm); vanadium and molybdenum were undetected in the second and third fractions (pressures of 40 mm and 5 mm).

The concentration of metals in the residue of the 40-gallon oil sample is consistent with the similarity of metal content in crude oil and refinery residues (fig. 5). Data presented in table 4 show that less than 1 percent of the total vanadium, nickel, or uranium content of the oil is included in any distillation fraction, and that less than 1 percent of the total vanadium and nickel content was included in all the distillation fractions combined. These minute amounts of metal may be included in the distillation fractions as a result of mechanical entrainment rather than chemical combination.

POSSIBLE MANNER OF OCCURRENCE OF METALS IN OIL

Vanadium and nickel are common major constituents of the ash of crude oils (fig. 2 and pl. 3). Because of their relative abundance in crude oils and asphalts, the vanadium and nickel of naturally occurring hydrocarbons have been the most frequently studied metals (Baragwanath, 1921; Bergman, 1940; Bird and Calcott, 1914; DeGolyer, 1924; Fester and Bertuzzi, 1925; Fester and Cruellas, 1936;

Fester and others, 1939; Gulyaeva, 1952; Hodgson, 1954; Katchenkov, 1949; Scott and others, 1954; Skinner, 1952; Vinogradov and Bergman, 1935). The discovery of vanadium and nickel porphyrins in crude oils by Treibs (1934, 1935) provides significant knowledge on the manner of occurrence of metals in crude oil. Porphyrins are chelates, and have a closed planar ring structure. The chelated metal is held in the central area of the ring. Treibs (1934) identified both hemoglobin and chlorophyll derivatives among the porphyrins in crude oil. Since Treibs' discovery many other investigators have identified vanadium and nickel porphyrins in crude oils (Dunning and others, 1953; Glebovskaya and Vol'kenshtein, 1948; Skinner, 1952; and Southwick[2]).

Southwick[3] carefully analyzed the metal contents of four crude-oil samples, and also determined metal contents in several fractions (separated chromatographically and by solubility) of one oil sample. He concluded that vanadium and nickel probably were present in the oil samples as porphyrins, but that the chromium present in the oils was not "combined organically." The fact that chromium was not found in an organic complex in one oil sample does not preclude the possibility that chromium complexes are present in some oils, as is suggested by the data shown in figure 4 and in table 3.

The correlations of vanadium and nickel with types of crude oil, and with crude-oil characteristics noted in this investigation, are inferred to show the existence of vanadium and nickel porphyrins in the crude-oil samples. The small range of values for the ratio of vanadium to nickel (table 2) supports this inference, and the suggested increase in this ratio with age may indicate that the vanadium porphyrin has greater stability than the nickel porphyrin.

If the inference is valid—that vanadium and nickel are present in crude oils as porphyrins—then the comparison of relations of other metals with vanadium and nickel may point to the possible existence of porphyrins or other types of complexes of the other metals in crude oil.

Martell and Calvin (1952, p. 181–183) propose that the transition elements—titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, and zinc—have the strongest tendency toward the formation of chelates, but that substantially all positive metal ions of the periodic system are chelate forming. The same authors (1952, p. 183) state that the relative strength of such tendencies is influenced by "(1) the ionic forces which are related to both charge and radius of the metal ion, and (2) the relative tendencies of various metals to form homopolar bonds with electron donors." This statement recalls the previously cited similarity (p. 35, in reference to table 3) of correlation coefficients for barium and strontium, two alkaline earth

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[2] Op. cit.

[3] Op. cit.

metals of the same group of the periodic table. The ionic potentials are 1.40 for Ba^{2+}, and 1.57 for Sr^{2+}. There is some suggestion here that small amounts of barium and strontium chelates or complexes may be present in crude oil. The correlation coefficients for barium and strontium shown in table 3, however, are all within the range of 0.10 to 0.17 and hence not very significant. This evidence is very speculative.

In summary of the several comparisons of metals with vanadium and nickel, made in an attempt to point indirectly to common affinities with hydrocarbons, the evidence of similarity to vanadium and nickel was strongest for gallium; it was favorable to a lesser degree for molybdenum; and to a much lesser degree for cobalt, titanium, and chromium. The evidence was unfavorable for uranium, copper, managanese, and the other metals. The possibility remains that some of the vanadium and nickel and by far the greater part of the remaining metals are present in crude oil in some form other than a chelate. Many metals may be combined in salts of organic acids, but none such have yet been discovered.

OIL-LEACHING TEST

The metals found in crude oil may have been indigenous, either incorporated in the original organic material during metabolism, or adsorbed by the organic material during burial and transformation to petroleum. All the metals detected in crude oil in this investigation have been detected in the ash of modern marine organisms (Vinogradov. 1953), and these metals may very well have been present in the ancient organisms that formed the source matter of crude oil.

The possibility that vanadium and nickel may have been involved in the metabolism of the organisms, which were source material, may be inferred. Treibs (1934) found porphyrin derivatives of both hemoglobin and chlorophyll in the crude oils he examined, and identified vanadium salts in these porphyrins. Although vanadium porphyrins have not been detected in modern organisms, vanadin, a vanadium-bearing pigment, has been identified in the blood of some species of Ascidiae (Vinogradov, 1953, p. 422–429), a very primitive vertebrate, which is considered to have undergone retrogressive, instead of progressive, evolution (Van Name, 1954).

Vanadium has also been found to be an important ingredient in the life processes of some lower plants (Bertrand, 1950, p. 431–432). Bertrand's view (1950, p. 444, 446) that the mean elementary composition of living organisms has varied in geologic time, and that vanadium was probably a more common constituent of organisms in past geologic time, seems sound. Thus vanadium may have been present in the ancient organic matter from which crude oil was formed in much greater quantity than in modern organisms.

Krauskopf (1956) reported laboratory experiments wherein significant quantities of zinc, lead, silver, and molybdenum were adsorbed by organisms in sea water. Ewing and others (1955) found that biological sludges would take up uranium from saline solutions. These data support the hypothesis that some of the metal content in crude oil results from adsorption on organic material during burial and transformation to crude oil.

Even though some metal content in crude oil may be indigenous, a part of the total metal content of any given oil sample may have entered the oil postgenetically. If some metals entered the crude oil postgenetically, the quantity of such metals in a given oil sample might reflect the quantities of these metals available in source rocks of the oil, rocks through which the oil migrated, or the reservoir rock. Here lies the promise of clues as to the source and movement of crude oil, as well as information applicable to other geologic problems.

The vanadium and nickel contents of crude oil have been shown to correlate with and hence reflect the type of crude oil. The quantities of these metals found in a crude oil are believed more likely to be related to the original composition of the oil than to the metal content of the reservoir rock. In contrast, the uranium content of oil appears to be least related to type of crude oil, and so is believed more likely to reflect the uranium content of reservoir rocks or source rocks of petroleum.

To test the possibility that crude oils might leach uranium from permeable rocks, samples of uraniferous sandstone were permitted to soak in crude oil for 14 months. Samples of three types of uraniferous sandstone, containing high-grade uraninite, autunite, and schroeckingerite, were disaggregated and placed in four different samples of oil. The sandstone samples were disaggregated in order to give maximum surface contact of uranium minerals to the oil, and so to compensate somewhat for the probable difference in time involved between laboratory test and natural conditions. The period of the first soaking test began in July 1956 and terminated in September 1957. At the end of this soaking period the oil samples were first filtered through no. 12 Whatman paper filters, and then diluted with carbon disulfide at a 1:4 ratio by volume. The mixtures were centrifuged, and the supernatant fluid drawn off. The carbon disulfide was then evaporated, the oil samples were reduced to ash, and the uranium content determined by fluorometric analysis.

Definite enrichment of uranium content in the four oil samples is indicated by the data from this test (table 5). The uranium content of each oil sample was enriched many hundred or thousand times; and the ash content of the oil was enriched as much as 17 times. Although the oil samples of the soaking test were definitely enriched in uranium, the manner in which the leaching occurred and the metal was retained in the oil is very much in doubt.

The evidence gathered in this investigation, as previously stated, is unfavorable for postulating the existence of uranium porphyrins or uranium complexes. The possibilities either that uranium is oil soluble or that uranium oxide or salt crystals may be present in colloidal suspension are favored as alternatives. An investigation of the colloidal material in the soaking samples is one method of attacking this problem.

The Tyndall effect, or scattering of light from colloidal particles, has been frequently noted in crude oils and is considered a characteristic property of crude oils. Nellensteyn (1928) suggested that natural asphalts are colloidal systems, and that "asphaltenes" are colloidal carbon particles surrounded by protective bodies. Changes in the colloidal content of the oils in which the uraniferous sands were placed are therefore of interest.

The making of quantitative measurements of the Tyndall effect was considered. The heavy black oils, however, transmitted very little light, and the addition of a dilutent would introduce possible changes in the colloidal content (Prekshot and others, 1943; Katz and Beu, 1945). For these reasons the measurement of light intensities was considered impractical, and instead the oils were examined by Dr. V. L. VanBreemen of the University of Colorado Medical School under an electron microscope.

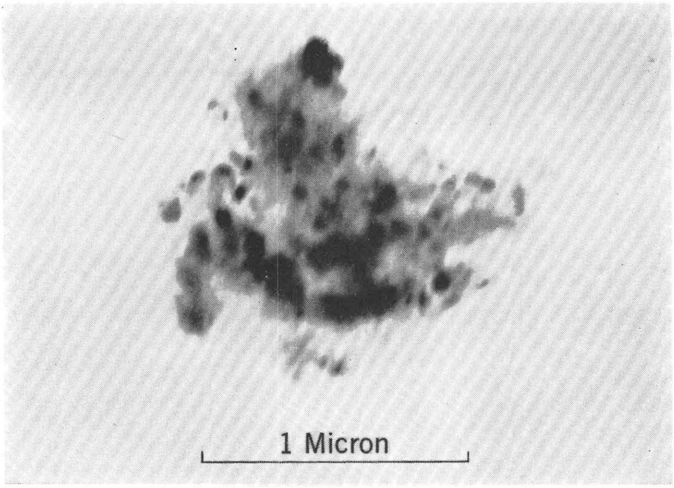
A large number of clusters of particles with maximum diameter of 1 to 3 microns were noted in the oil samples that had soaked the uraniferous sands. Such clusters were very rare in control samples, which had not been in contact with the sands. These clusters on close examination seemed to consist of opaque dots, approximately one-tenth of a micron in diameter, embedded in a less opaque, nebular mass that was surrounded by a medium transparent to the electron rays. (See pl. 1*A*.)

The small dots within the nebular material seem to be crystalline, and the total mass seems to be one of crystalline solids aggregated in a cloud of dense liquid material. Since these aggregates were so rare in the control samples, it is probable that crystalline particles of the order of magnitude of one-tenth micron were present with the sand, and became aggregated in groups still small enough to pass through the filter, and remain in suspension during centrifuging.

A second soaking test was made to eliminate the fine particles produced in disaggregation of sandstone samples, and so to better parallel natural conditions. A sample of the uraninite-bearing sand

TABLE 5.—*Change in uranium content of oils that had soaked uraniferous sand and sandstone for 14 and 5 months*

Oil sample			Soaked material			Uranium in ash (percent)		Ash of oil (percent)		Uranium in oil (ppb)	
Laboratory No.	Oil class	Gravity (°API)	Description	Weight (pounds)	Uranium (percent)	Presoaking	Postsoaking	Presoaking	Postsoaking	Presoaking	Postsoaking
			Disaggregated sandstone—14-month soaking period								
246435	IV	43.2	Schroeckingerite-bearing	10¾	1.98	0.0002	4.26	0.0055	0.018	0.11	7,600
246436	VII	39.4	Autunite-bearing	17	.34	.024	3.69	.002	.013	4.8	4,700
246437	X	34.6	Uraninite-bearing	22	.41	.0005	.87	.0013	.023	.065	2,000
246438	XV	23.1	do	19	.41	.0009	.50	.022	.030	1.98	1,800
			Sand and sandstone—5-month soaking period								
246433	X	34.6	Disaggregated uraninite-bearing sandstone, from which particles less than 0.351 mm had been eliminated.		0.51	0.0005	1.53	0.0005	0.0013	0.065	200
246434	VII	34.0	Large chunk of carnotite-bearing sandstone.		4.55	.023	.86	.015	.02	35.7	1,700



A. FIRST SOAKING TEST

B. SECOND SOAKING TEST

ELECTRON MICROGRAPHS OF CLUSTERS OF PARTICLES FROM OIL-SOAKED URANIFEROUS SAND AND SANDSTONE

was washed repeatedly on a seive that passed particles 0.351 mm in diameter and smaller. When such washing failed further to remove particles, the sample was immersed in oil. A large chunk of carnotite-bearing sandstone was immersed in another container of crude oil, and the two samples were permitted to soak for five months.

After five months the oil was extracted from the solid sandstone with organic solvents. The oils from both samples were filtered, centrifuged, ashed, and analyzed as before. The analytical results are given in the lower part of table 5; the data from the second soaking test also show a significant gain in uranium content.

The sample of the oil that had soaked the uraninite sand from which fine particles had been removed was observed in the electron microscope, as was a control sample of the oil that had not been in contact with the sand. The clusters of particles, so common in oils of the first soaking test, were very rare in this oil of the second test; even fewer clusters were counted in the tested oil sample than in the control sample. Apparently the sieving had effectively removed fine material, and uranium had been dissolved in the oil.

One of the few clusters noted in the oil of the second soaking test was in a globular mass of dense oil, which refracted the electron rays. (See pl. 1*B*.)

In summary, the leaching tests favor the hypothesis that uranium minerals are soluble in crude oil, but additional refined tests should be made to determine the actual chemical controls.

REGIONAL AND LOCAL DISTRIBUTIONS OF METALS IN OIL SAMPLES

The trace-metal content of crude oils may serve as an important geologic tool when knowledge of the subject is more complete. It is hoped that the information gathered during this investigation will provide useful data for future studies. For this reason, all of the analyses discussed in this report are presented in table 6 according to geographic areas and the geologic age of reservoir rock.

The names of the rock reservoirs, used in this table, are those used by the oil-field operators. No attempt was made to verify correlations of oil reservoirs with surface units, and hence no correlations are endorsed in this informal usage.

The locality numbers used in table 6 are the same as those on the index map (fig. 1); thus the oil field, reservoir rock, oil type, and metal content are keyed to the locality. In the following discussion the distribution of metals shown in figure 2 is the reference standard, and quantities of metal in oil from particular areas are described as relatively great or small by comparison with the maximum frequency distribution shown on this chart.

TABLE 6.—*Metal content of crude-oil samples listed according to geographic distribution of oil fields and age and type of reservoir rock*

[See figures 11–39 for oil classes; nd, not determined]

Locality No.	State	Laboratory No.	Oil field	Oil reservoir	Oil class and group	Ash (percent)	Uranium[1] in ash (percent)	Uranium in oil (ppb)	Metals[2] in ash of oil (percent)							
									Al[3]	Fe[3]	Ca[3]	Na[3]	K	Mg[3]	Ti[3]	Mn[3]
				MIDCONTINENT REGION												
				Sandstone of Cambrian age												
25	Kansas	D91715	Otis-Albert	Reagan sandstone	VIII	0.0097	0.0003	0.3	0.3	0.3	0.7	3	0	0.7	0.015	0.007
25	do	D91723[4]	do	do	VIII	.013	.0004	.5	.3	7	.7	7	0	3	.15	.03
4	Texas	207297[5]	Dora	Cambrian sandstone	IV*A*	.0006	.0007	<.1	------	------	------	------	------	------	------	------
				Sandstone of Ordovician age												
10	Oklahoma	D91707	Middle Gilliland	Hominy sand	nd	0.0050	0.0017	0.9	0.3	0.07	7	30	0	0.7	0.0003	0.003
6	do	200808	Laffoon	Wilcox sand	XV	.022	.0009	2	.3	.7	1.5	1.5	0	.7	.15	.015
				Limestone of Cambrian and Ordovician age												
14	Oklahoma	D90308[5]	Pond Creek	Arbuckle group	XIV*B*[6]	0.0014	0.0004	<0.1	------	------	------	------	------	------	------	------
24	Kansas	D91712	Pawnee Rock	do	nd	.014	.0004	.6	0.3	0.3	3	30	0	0.7	0.0015	0.007
24	do	D91713	do	do	nd	.067	.002	1.4	.3	.07	3	30	0	.7	.015	.003
18	do	D91693	Brewster	do	XIV*A*	.0016	.0014	.2	.15	.3	3	3	0	1.5	.015	.003
18	do	D91695	do	do	XIV*A*	.0013	.021	2.7	.7	.7	1.5	3	0	1.5	.03	.15
26	do	D91716[7]	Solomon	do	nd	nd	nd	nd	.015	.007	3	30	0	3	.03	.003
26	do	D91718	do	do	nd	.10	.002	2	.07	.03	3	30	0	.7	.03	.003
23	do	D91720	Brock	do	VIII	.0034	.0013	.4	.3	30	.7	30	0	.15	.015	.03
17	do	200793	Coffeyville	do	XIV*B*	.0024	.0012	.3	1.5	30	3	1.5	0	.7	.15	.15
21	do	D90303[5]	Hittle	do	VII*A*[8]	.0005	.0014	<.1	------	------	------	------	------	------	------	------
21	do	D90306[5]	do	do	VII*A*[8]	.0010	.0003	<.1	------	------	------	------	------	------	------	------

Locality No.	Metals 2 in ash of oil (percent)—Continued																										
	Sr 3	Ba 3	Zr	Cr 3	V 3	Zn 3	Ni 3	Cu 3	Li	Ce	Sn	Co 3	Y	Nd	Nb	La	Pb 3	Ga 3	B	Ge	Be	Sc	As	Yb	Er	Mo 3	Ag
	MIDCONTINENT REGION—Continued																										
	Sandstone of Cambrian age																										
25	0.07	0.03	0	0.015	22	0	6.2	0.04	0	0.03	0	0.03	0	0	0	0	0.007	0.0003	0	0	0	0	0	0	0	0.007	0
25	.3	.7	0	.003	30	0	7	.07	0	.03	.007	.03	0	0	0	0	.03	.0003	.003	0	0	0	0	0	0	.003	-------
4	--------	-------	------	-------	------	-----	------	------	-----	-----	------	------	------	-----	------	------	------	-------	------	-----	------	------	-----	------	-----	------	-------
	Sandstone of Ordovician age																										
10	0.15	0.015	0	0.003	0.30	0	0.22	0.31	0	0	0	0.003	0	0	0	0.015	0.007	0	0.003	0	0	0	0	0	0	0	0
6	.07	.015	.15	.007	20	.15	9.2	.08	0	.15	0	.03	0	0	0	0	.07	0	0	0	0	0	0	0	0	0	0
	Limestone of Cambrian and Ordovician age																										
14	--------	-------	------	-------	------	-----	------	------	-----	-----	------	------	------	-----	------	------	------	-------	------	-----	------	------	-----	------	-----	------	-------
24	0.07	0.007	0	0.015	8.8	0	2.4	0.15	0	0	0	0.03	0	0	0	0	0.007	0.0003	0	0	0	0	0	0	0	0	0
24	.07	.003	0	.0007	1.5	0	.3	.03	0	0	0	.007	0	0	0	0	.003	0	0	0	0	0	0	0	0	0	0
18	.15	.015	0	.007	13	0	8.4	1.6	0	.03	0	.007	0	0	0	.03	.03	.00015	0	0	0	0	0	0	0	0	0
18	.07	.03	.003	.015	7	0	30	.07	0	.15	0	.007	0	.07	0	.07	.03	.003	.015	0	0	0	.3	0	0	0	0
26	.15	.0003	0	.00015	.86	0	.19	.002	0	0	0	.003	0	0	0	0	0	0	.07	0	0	0	0	0	0	0	0
26	.03	.003	0	.003	3	0	.7	.007	0	.03	0	.015	0	0	0	0	0	0	0	0	0	0	0	0	0	.0015	0
23	.007	.015	0	.03	3	.7	7	.07	0	.03	0	.015	0	0	0	.007	.07	.0003	.003	0	0	0	7	0	0	.003	.0003
17	.15	.15	.07	.007	16	.15	5	.22	6	0	.015	.015	0	0	0	0	.07	.0015	0	0	0	0	.15	0	0	.007	0
21	--------	-------	------	-------	------	-----	------	------	-----	-----	------	------	------	-----	------	------	------	-------	------	-----	------	------	-----	------	-----	------	-------
21	--------	-------	------	-------	------	-----	------	------	-----	-----	------	------	------	-----	------	------	------	-------	------	-----	------	------	-----	------	-----	------	-------

See footnotes at end of table.

TABLE 6.—*Metal content of crude-oil samples listed according to geographic distribution of oil fields and age and type of reservoir rock*—Continued

[See figures 11–39 for oil classes; nd, not determined]

Locality No.	State	Laboratory No.	Oil field	Oil reservoir	Oil class and group	Ash (percent)	Uranium[1] in ash (percent)	Uranium in oil (ppb)	Metals[2] in ash of oil (percent)							
									Al[3]	Fe[3]	Ca[3]	Na[3]	K	Mg[3]	Ti[3]	Mn[3]
MIDCONTINENT REGION—Continued																
Sandstone of Pennsylvanian age																
8	Oklahoma	D90301[5]	Flat Rock	Lower Bartlesville sand	*S*[8]	0.015	0.0004	0.6	------	------	------	------	------	------	------	------
13	do	D91698[7]	Wynona	Bartlesville sand	VII*B*	.0006	------	------	1.5	30	30	1.5	0	0.7	0.015	0.15
13	do	D91700	do	do	VII*B*	.0007	.0050	.3	1.5	1.5	3	.3	0	1.5	.003	.015
12	do	D91701	Wildhorse	Cleveland sand	S	.0013	.0045	.6	1.5	1.5	1.5	1.5	0	.3	.015	.03
11	do	200796	Naval Reserve	Burbank sand	IV*B*	.020	.0004	.8	.15	.15	.7	7	0	1.5	.007	.007
13	do	D91705	New England	Burgess sand	VIII	.0074	.0010	.7	.3	.07	7	30	0	3	.003	.003
9	do	D91696	Osage City	Buzzard sand	V*C*[6]	.0023	.0017	.4	.15	30	3	3	0	1.5	.015	.03
16	do	224895[9]	Alluwe (Nowata)	Bartlesville sand	VII*B*	.002	.045	9	.7	7	3	3	0	.7	.15	.07
16	do	224896[9]	do	do	VII*B*	.017	.017	29	.7	30	30	3	0	.7	.03	.15
16	do	224897[9]	do	do	VII*B*	.002	.018	3.6	1.5	7	30	3	0	.7	.3	.15
15	do	224899[9]	Chelsea (Nowata)	do	VII*B*	.009	.027	24	1.5	30	30	3	0	1.5	.07	.15
15	do	224900[9]	do	do	VII*B*	.002	.013	2.6	1.5	30	7	7	0	1.5	.15	.15
15	do	224898[10]	do	do	VII*B*	.001	.040	4	.7	7	3	3	0	.7	.15	.07
5	Texas	200813	Finley	Granite wash	IV*A*	.0082	.0031	2.5	.7	7	3	7	0	.7	.007	.07
21	Kansas	D90307[5]	Hittle	Peru sand	------	.0014	.002	.3	------	------	------	------	------	------	------	------
20	do	D91708	McLouth	McLouth sand	II[11]	.0021	.0051	1.1	.3	.7	.7	3	0	.3	.0003	.003
19	do	D91721	Iola	Lower Bartlesville sand	XIV*C*[11]	.13	.0002	2.6	.15	.3	1.5	30	0	.7	.003	.003
19	do	D91722	do	do	XIV*C*[11]	.015	.0001	.1	.15	.07	.3	3	0	.3	.015	.003
Limestone of Pennsylvanian age																
7	Oklahoma	200810	Kendrick	Fort Scott limestone	IV*B*	0.001	0.0032	0.3	0.7	1.5	1.5	1.5	0	0.3	0.03	0.015
22	Kansas	D91710	Cunningham	Lansing group	VII*A*[11]	0.013	0.0008	1.0	.07	.15	.3	.7	0	.15	.003	.007
22	do	D91711	do	do	VII*A*[11]	.008	.0005	.4	.07	.7	.7	.7	0	.3	.015	.007
Sandstone of Jurassic age																
1	Arkansas	200799	Schuler	Jones sand	IX*A*	0.041	0.0006	2.5	0.15	0.3	30	7	0	1.5	0.015	0.015

Metals[2] in ash of oil (percent)—Continued

MIDCONTINENT REGION—Continued

Sandstone of Pennsylvanian age

Locality No.	Sr[3]	Ba[3]	Zr	Cr[3]	V[3]	Zn[3]	Ni[3]	Cu[3]	Li	Ce	Sn	Co[3]	Y	Nd	Nb	La	Pb[3]	Ga[3]	B	Ge	Be	Sc	As	Yb	Er	Mo[3]	Ag
8	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----
13	0.15	0.03	0.015	0.015	7.9	0.7	5.2	3.4	0	0.15	0.3	0.07	0.015	0	0	0.07	30	0	0.03	0.03	0.003	0.007	0	0	0	0	0
13	.15	.03	0	.003	1.5	.3	1.5	30	0	0	.07	.007	0	0	0	.03	.15	0	.015	0	0	0	0	0	0	0	.0015
12	.015	0	0	.0015	20	.3	7.6	1.3	0	0	0	.03	0	0	0	0	.15	0	0	0	0	0	0	0	0	0	0
11	.15	.015	0	.0007	.15	0	.07	.15	0	0	.015	0	0	0	0	0	.015	0	0	0	0	0	0	0	0	0	0
13	.3	.015	0	.003	.3	0	.07	.15	0	0	0	.0007	0	0	0	0	.007	0	.03	0	0	0	0	0	0	0	0
9	.03	0	0	.015	12.5	.15	7.0	.84	0	0	0	.03	0	0	0	0	.15	0	0	0	0	0	0	0	0	0	0
16	.7	30	.07	.07	3	.03	3	.07	0	.07	.007	.07	.015	0	0	.03	.07	.00015	0	0	.003	.07	.15	0	.015	.003	.0015
16	1.5	7	.15	.015	.7	.15	.7	.7	0	0	.015	.07	.015	0	0	0	.15	0	0	0	.0015	.07	0	0	0	0	0
16	.7	30	.15	.07	3	.15	30	.15	0	0	.015	.07	.015	0	0	0	.07	0	0	.007	.003	.07	.3	0	0	.003	.0007
15	1.5	7	.15	.015	1.5	.15	1.5	.7	0	0	0	.07	.03	0	.007	0	.3	0	0	0	.0015	.07	0	0	0	0	.0015
15	.3	.7	.07	.015	3	3	3	1.5	0	0	.15	.07	0	0	.007	0	.3	0	.015	.007	0	.007	0	0	0	.007	.0015
15	.7	30	.07	.07	3	.03	3	.07	0	.03	.007	.07	.015	0	0	.007	.07	.0003	0	.003	.003	.03	.15	0	.03	.003	.0015
5	.15	.07	.015	.015	3.2	.15	2.5	2.5	0	.07	.007	.015	0	0	0	.015	.07	0	0	0	0	0	.15	0	0	.015	0
21	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----
20	.03	.03	.003	.015	.7	.15	30	.07	0	.03	0	.015	0	0	0	.015	.015	0	.003	0	.0003	0	0	0	0	.003	0
19	.15	.15	0	.003	1.2	0	.69	.007	0	0	0	.007	0	0	0	0	0	0	.003	0	0	0	0	0	0	0	0
19	.07	.03	0	.007	3	0	3	.07	0	.03	0	.015	0	0	0	0	.007	0	.0015	0	0	0	0	0	0	0	0

Limestone of Pennsylvanian age

Locality No.	Sr[3]	Ba[3]	Zr	Cr[3]	V[3]	Zn[3]	Ni[3]	Cu[3]	Li	Ce	Sn	Co[3]	Y	Nd	Nb	La	Pb[3]	Ga[3]	B	Ge	Be	Sc	As	Yb	Er	Mo[3]	Ag
7	0.03	0.015	0.015	0.015	8.4	1.5	2.2	13.2	0	0.15	0	0.007	0	0	0	0.07	0.3	0	0	0	0	0	0.15	0	0	0.0015	0.0007
22	.03	.003	0	.007	34	.07	7.6	.48	0	.03	0	.03	0	0	0	0	.007	.0003	0	0	0	0	0	0	0	0	0
22	.03	.007	0	.015	30	.03	30	.015	0	.03	0	.03	0	0	0	0	.007	.0003	0	0	0	0	0	0	0	0	0

Sandstone of Jurassic age

Locality No.	Sr[3]	Ba[3]	Zr	Cr[3]	V[3]	Zn[3]	Ni[3]	Cu[3]	Li	Ce	Sn	Co[3]	Y	Nd	Nb	La	Pb[3]	Ga[3]	B	Ge	Be	Sc	As	Yb	Er	Mo[3]	Ag
1	0.3	0.015	0.015	0.015	3.7	0.15	2.5	0.35	0	0.15	0	0.03	0	0	0	0	0.015	0.0015	0	0	0	0	0	0	0	0	0

See footnotes at end of table.

TABLE 6.—*Metal content of crude-oil samples listed according to geographic distribution of oil fields and age and type of reservoir rock*—Continued

[See figures 11–39 for oil classes; nd, not determined]

Locality No.	State	Laboratory No.	Oil field	Oil reservoir	Oil class and group	Ash (percent)	Uranium[1] in ash (percent)	Uranium in oil (ppb)	Metals[2] in ash of oil (percent)							
									Al[3]	Fe[3]	Ca[3]	Na[3]	K	Mg[3]	Ti[3]	Mn[3]
MIDCONTINENT REGION—Continued																
Limestone of Jurassic age																
2	Arkansas	200802	West Atlanta	Smackover formation	*S*	0.0005	0.0065	0.3	3	0.3	0.15	1.5	0	1.5	0.15	0.07
Sandstone of Cretaceous age																
3	Arkansas	200805	Stephens-Smart	Travis Peak Sand	IX*A*	0.042	0.0012	5.0	1.5	1.5	7	7	0	1.5	0.15	0.07
ROCKY MOUNTAIN REGION																
Sandstone of Cambrian age																
42	Wyoming	D96113	Lost Soldier	Flathead sandstone	XII*A*	0.0007	0.0031	0.2	7	0.7	1.5	1.5	0	0.7	0.15	0.03
Limestone of Ordovician age																
67	South Dakota	205773[5]	Custer area	Red River formation	II	0.0008	0.0006	<0.1	------	------	------	------	------	------	------	------
Limestone of Mississippian age																
52	Wyoming	D96092	Hamilton Dome	Madison limestone	XVI*B*	0.038	0.0003	1.1	0.003	0.07	0.07	0	0	0.03	0	0.03
57	do	D96087	North Oregon Basin	do	XII*C*	.035	.0022	7.6	.015	.3	3	0	1.5	3	0	.015
51	do	D96108	Circle Ridge	do	XII*C*	.016	.0003	.5	.15	.3	.15	0	0	.03	0	.03
55	do	D96091	South Spring Creek	do	XVI*B*	.034	.0009	3.1	.007	.3	.07	0	0	.07	0	.03

Locality No.	Metals[2] in ash of oil (percent)—Continued																									
	Sr[3]	Ba[3]	Zr	Cr[3]	V[3]	Zn[3]	Ni[3]	Cu[3]	Li	Ce	Sn	Co[3]	Y	Nd	Nb	La	Pb[3]	Ga[3]	B	Ge	Be	Sc	As	Yb	Er	Mo[3]	Ag
MIDCONTINENT REGION—Continued																											
Limestone of Jurassic age																											
2	0.07	0.15	0.007	0.03	0.07	0.15	0.03	0.15	0	0	0	0.03	0	0	0	0	0.07	0	0.07	0	0	0	0.15	0	0	0	0.0015
Sandstone of Cretaceous age																											
3	0.03	0.15	0.07	0.015	4.4	0.7	5.4	0.84	0	0.15	0.03	0.03	0	0	0	0.015	0.7	0.007	0	0	0	0	0.15	0	0	0.03	0
ROCKY MOUNTAIN REGION																											
Sandstone of Cambrian age																											
42	0.15	0.03	0.015	0.07	7	0.7	3	0.15	0	0.15	0.0015	0.0015	0	0	0	0.03	0.15	0	0.015	0	------	0	0	0	0	0.0015	0
Limestone of Ordovician age																											
67	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------
Limestone of Mississippian age																											
52	0	0.003	0	0.07	28	0	7.0	0.07	0	0	0	0.003	0	0	0	0	0.003	0.003	0	0	------	0	0	0	0	0.07	0
57	.07	.003	0	.07	22	0	6.4	.03	0	0	0	.003	0	0	0	.03	.015	.003	0	0	------	0	0	0	0	.07	0
51	.003	.007	.0015	.07	30	.07	7	.7	0	0	0	.003	0	0	0	.007	.07	.003	0	0	------	0	0	0	0	.07	0
55	0	.003	.03	.07	30	0	30	.3	0	0	0	.03	0	0	0	0	.007	.003	0	0	------	0	0	0	0	.07	0

See footnotes at end of table.

TABLE 6.—*Metal content of crude-oil samples listed according to geographic distribution of oil fields and age and type of reservoir rock*—Continued

[See figures 11–39 for oil classes; nd, not determined]

Locality No.	State	Laboratory No.	Oil field	Oil reservoir	Oil class and group	Ash (percent)	Uranium [1] in ash (percent)	Uranium in oil (ppb)	Metals [2] in ash of oil (percent)							
									Al [3]	Fe [3]	Ca [3]	Na [3]	K	Mg [3]	Ti [3]	Mn [3]
ROCKY MOUNTAIN REGION—Continued																
Sandstone of Mississippian and Pennsylvanian age																
63	Montana	D96075	Big Wall	Amsden formation	VIII	0.012	0.0002	0.2	0.3	0.3	0.7	7	0	0.3	0	0.007
Sandstone of Pennsylvanian and Permian age																
45	Wyoming	D96071	Oil Mountain	Tensleep sandstone	XVII*A*	0.048	0.0003	1.4	0.03	0.07	1.5	0.7	0	0.7	0	0.015
44	do	D96072	South Casper Creek	do	XVII*A*	.0043	.004	1.7	.3	.3	1.5	.7	0	.7	0	.03
59	do	D96077	Elk Basin	do	XV [12]	.010	.0003	.3	.7	.7	.15	.07	0	.15	0	.03
59	do	D96078	do	do	XV [12]	.0028	.0003	.1	.3	.3	.7	.3	0	.3	0	.03
58	do	D96079	Garland	do	XII*C*	.012	.0013	1.6	.3	3	.15	0	0	.07	0	.03
58	do	D96080 [5]	do	do	XII*C*	.012	.0003	.3	------	------	------	------	------	------	------	------
56	do	D96083	Half Moon	do	XVI*A*	.023	.0003	.7	.3	.3	3	3	0	1.5	0	.03
57	do	D96085	North Oregon Basin	do	XVI*A* [13]	.018	.0075	13.5	.03	.3	.07	0	0	.07	0	.03
55	do	D96090	South Spring Creek	do	XVI*A*	.039	.0006	2.3	.015	.07	1.5	.7	0	.7	0	.015
48	do	D96099	Dallas	do	XII*B*	.022	.0004	.8	.015	.3	.3	.07	0	.3	0	.03
50	do	D96104	Steamboat Butte	do	XII*B*	.0097	.0003	.3	.3	.3	.15	0	0	.07	0	.03
50	do	D96105	Pilot Butte	do	XII*C*	.015	.0001	.2	.07	.15	.15	0	0	.07	0	.03
61	do	227741	Salt Creek	do	II	.028	.0002	.6	.3	.15	7	7	0	1.5	.15	.03
Sandstone of Pennsylvanian age																
60	Wyoming	205772	Mitchell Creek	Minnelusa sandstone	XII*C*	0.024	0.0004	1	1.5	3	7	0	0	1.5	0.3	0.07
34	Colorado	217875	Rangely	Weber sandstone	VII*A*	.0009	.0032	.3	.15	.3	3	1.5	0	.7	.015	.015
34	do	205778	do	Unknown reservoir (presumed Weber sandstone).	VII*A*	.0022	.0015	.3	1.5	30	1.5	0	0	.3	.3	.07

Locality No.	Metals [2] in ash of oil (percent)—Continued																										
	Sr [3]	Ba [3]	Zr	Cr [3]	V [3]	Zn [3]	Ni [3]	Cu [3]	Li	Ce	Sn	Co [3]	Y	Nd	Nb	La	Pb [3]	Ga [3]	B	Ge	Be	Sc	As	Yb	Er	Mo [3]	Ag
ROCKY MOUNTAIN REGION—Continued																											
Sandstone of Mississippian and Pennsylvanian age																											
63	0.03	0.003	0.07	0.015	20	0	11	0.10	0	0	0	0.07	0	0	0	0	0.015	0.003	0	0	------	0	0	0	0	0.007	0
Sandstone of Pennsylvanian and Permian age																											
45	0.03	0.003	0	0.07	30	0	7	0.03	0	0	0	0.015	0	0	0	0	0.015	0.003	0	0	------	0	0	0	0	0.03	0
44	.03	.007	0	.07	30	0	7	.03	0	0	0	.007	0	0	0	.03	.03	.003	0	0	------	0	0	0	0	.015	0
59	.003	.007	0	.07	38	.07	9.2	.16	0	0	0	.003	0	0	0	0	.03	.003	0	0	------	0	0	0	0	.003	0
59	.003	.015	0	.07	30	.07	7	.3	0	0	0	.003	0	0	0	.03	.03	.003	0	0	------	0	0	0	0	.003	0
58	.003	.007	0	.07	30	.07	20	.15	0	0	0	.007	0	0	0	.03	.03	.003	0	0	------	0	0	0	0	.03	.0015
58	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------
56	.07	.007	0	.07	22	0	.10	.10	0	0	0	.007	0	0	0	0	.007	.003	0	0	------	0	0	0	0	.15	0
57	.003	.003	0	.07	40	.07	8.2	.22	0	0	0	.003	0	0	0	0	.03	.003	0	0	------	0	0	0	0	.07	0
55	.03	.003	.03	.07	30	0	7	.07	0	0	0	.015	0	0	0	0	.015	.003	0	0	------	0	0	0	0	.07	0
48	.003	.003	0	.07	30	.07	7	.3	0	0	0	.015	0	0	0	.03	.007	.003	0	0	------	0	0	0	0	.07	0
50	0	.007	0	.07	30	.07	7	.07	0	0	0	.003	0	0	0	0	.007	.003	0	0	------	0	0	0	0	.0015	------
50	0	.003	0	.07	30	0	7	.03	0	0	0	.003	0	0	0	0	.007	.003	0	0	------	0	0	0	0	.03	0
61	.15	.003	0	.03	30	0	3	.015	0	0	0	0	0	0	0	0	.015	0	0	0	------	0	0	0	0	0	.0015
Sandstone of Pennsylvanian age																											
60	0.015	0.3	0	0.15	30	1.5	30	0.3	0	0	0	0.015	0	0	0	0	0.07	0.003	0	0	------	0	0	0	0	0.15	0
34	.03	.007	.007	.03	30	.3	7	3	0	0	0	.015	0	0	0	0	.7	0	0	0	0	0	0	0	0	0	.0007
34	.015	1.5	0	.03	.7	1.5	.7	.3	0	.15	.15	.015	0	0	0	.03	7	0	0	0	0	0	0	0	0	.015	.0015

See footnotes at end of table.

TABLE 6.—*Metal content of crude-oil samples listed according to geographic distribution of oil fields and age and type of reservoir rock*—Continued

[See figures 11–39 for oil classes; nd, not determined]

Locality No.	State	Laboratory No.	Oil field	Oil reservoir	Oil class and group	Ash (percent)	Uranium[1] in ash (percent)	Uranium in oil (ppb)	Metals[2] in ash of oil (percent)							
									Al[3]	Fe[3]	Ca[3]	Na[3]	K	Mg[3]	Ti[3]	Mn[3]
				ROCKY MOUNTAIN REGION—Continued												
				Limestone or dolomite of Pennsylvanian age												
62	Montana	D96073	Soap Creek	Amsden formation	XII*C*	0.044	0.0018	7.9	0.03	0.15	0.15	0	0	0.07	0	0.003
				Limestone of Permian age												
56	Wyoming	D96084	Half Moon	Embar formation of former usage.	XVI*B*	0.058	0.0003	1.7	0.03	0.3	30	1.5	1.5	3	0	0.015
57	do.	D96086	North Oregon Basin	do.	XVI*A*[13]	.015	.0043	6.4	.03	.3	.07	0	0	.07	0	.03
52	do.	D96093	Hamilton Dome	do.	XII*B*	.012	.0003	.4	.07	.7	.15	.3	0	.3	0	.03
53	do.	D96096	South Fork	do.	nd	.0073	.0002	.1	.015	.7	.15	.7	0	.3	0	.03
48	do.	D96100	Dallas	do.	XII*B*	.022	.0003	.7	.015	.7	.7	.07	0	.3	0	.03
47	do.	D96102	Derby	do.	XII*B*	.013	.0024	3.1	.3	.7	.3	.7	0	.7	0	.03
50	do.	D96103	Pilot Butte	do.	nd	.008	.0001	.1	.007	.3	.15	.7	0	.07	0	.015
50	do.	D96106[5]	Steamboat Butte	do.	XII*A*	.0079	.0006	.5	------	------	------	------	------	------	------	------
49	do.	D96107	Winkleman Dome	do.	XII*C*	.016	.0005	.8	.15	.3	.15	0	0	.07	0	.03
				Sandstone of Triassic age												
52	Wyoming	D96094	Hamilton Dome	Chugwater formation	XI	0.038	0.0004	1.5	0.3	0.7	0.3	7	0	0.3	0	0.03
52	do.	D96095[5]	do.	do.	XI	.048	.0006	2.9	------	------	------	------	------	------	------	------
54	do.	D96097	Grass Creek	do.	XI	.038	.0002	.8	.07	.3	.3	3	0	.3	0	.015
34	Colorado	D92406[5]	Rangely	Shinarump member of the Chinle formation.	V*A*	.0002	.0005	<.1	------	------	------	------	------	------	------	------
33	do.	203735	Moffat Dome	do.	III	.0013	.0007	.1	7	3	3	------	3	1.5	.3	.03
				Limestone of Jurassic age												
41	Utah	220441	Virgin	Moenkopi formation	VIII	0.0048	0.0004	0.2	0.3	7	3	------	0	1.5	0.15	0.15
41	do.	220442	do.	do.	XIII	.0027	.0003	.1	.3	7	1.5	------	0	.7	.15	.15

Locality No.	Metals[2] in ash of oil (percent)—Continued																										
	Sr[3]	Ba[3]	Zr	Cr[3]	V[3]	Zn[3]	Ni[3]	Cu[3]	Li	Ce	Sn	Co[3]	Y	Nd	Nb	La	Pb[3]	Ga[3]	B	Ge	Be	Sc	As	Yb	Er	Mo[3]	Ag
ROCKY MOUNTAIN REGION—Continued																											
Limestone or dolomite of Pennsylvanian age																											
62	0.0007	0.003	0	0.03	30	0	3	0.03	0	0	0	0.015	0	0	0	0	0.007	0.003	0	0	------	0	0	0	0	0.07	0
Limestone of Permian age																											
56	0.15	0.003	0	0.07	17	0.03	4.8	0.26	0	0	0	0.003	0	0	0	0	0.03	0.003	0	0	0	0	0	0	0	0.15	0
57	.003	.007	0	.07	40	0	7.6	.03	0	0	0	.007	0	0	0	.015	.007	.003	0	0	0	0	0	0	0	.07	0
52	.003	.003	.015	.07	46	0	7.6	.16	0	0	0	.03	0	0	0	0	.015	.003	.07	0	0	0	0	0	0	.03	0
53	0	.003	0	.07	30	0	30	.03	0	0	0	.007	0	0	0	.015	.015	.003	0	0	0	0	0	0	0	.07	0
48	.007	.007	0	.07	30	.3	30	.7	0	.15	0	.007	0	.07	0	.07	.015	.003	0	0	0	0	0	0	0	.07	.0007
47	.03	.007	0	.07	30	0	30	.15	0	.15	0	.007	0	.07	0	.07	.03	.003	0	0	0	0	0	0	0	.07	0
50	.003	.003	0	.03	30	0	7	.15	0	0	0	.003	0	0	0	0	.015	.003	0	0	0	0	0	0	0	.03	0
50	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------
49	.003	.003	.0015	.07	30	.07	7	.15	0	0	0	.003	0	0	0	0	.007	.003	0	0	0	0	.7	0	0	.07	0
Sandstone of Triassic age																											
52	0.03	0.007	0	0.07	28	0	6.4	0.10	0	0	0	0.007	0	0	0	0	0.03	0.003	0	0	0	0	0	0	0	0.07	0
52	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------
54	.007	.007	0	.07	28	0	7.6	.10	0	0	0	.007	0	0	0	0	.03	.003	0	0	0	0	0	0	0	.07	0
34	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------
33	.015	.07	.007	.007	.15	.3	.03	.015	0	0	.015	.0007	.003	0	0	.007	.7	.0007	.03	0	0	0	0	.0003	0	.003	.0003
Limestone of Jurassic age																											
41	0.03	0.015	0	0.03	30	0.3	30	0.15	0	0	0.15	0.03	0	0	0	0	1.5	0.3	0	0	0	0	0	0	0	0.015	0
41	.015	.15	0	.015	30	0	30	.3	0	0	.7	.07	0	0	0	0	30	.0015	0	0	0	0	0	0	0	.015	0

See footnotes at end of table.

TABLE 6.—*Metal content of crude-oil samples listed according to geographic distribution of oil fields and age and type of reservoir rock*—Continued

[See figures 11–39 for oil classes; nd, not determined]

Locality No.	State	Laboratory No.	Oil field	Oil reservoir	Oil class and group	Ash (percent)	Uranium [1] in ash (percent)	Uranium in oil (ppb)	Metals [2] in ash of oil (percent)							
									Al [3]	Fe [3]	Ca [3]	Na [3]	K	Mg [3]	Ti [3]	Mn [3]
								ROCKY MOUNTAIN REGION—Continued								
								Sandstone of Jurassic age								
32	Colorado	D92409 [5]	Wilson Creek	Entrada sandstone	IV *B*[12]	0.0048	0.007	3.3	----	----	----	----	----	----	----	----
28	do	D96122	Gramps	Morrison formation	V*C*	.0005	.006	.3	0.7	3	0.7	0.3	0	0.3	0.15	0.03
40	Utah	229659 [5]	Seiber Nose	do	V*B*	.0028	.0008	.2	----	----	----	----	----	----	----	----
61	Wyoming	227739	Salt Creek	Sundance formation 3d	VI	.020	.0003	.6	.3	.15	3	----	0	.7	0	.015
61	do	227740	do	Sundance formation	VI	.0078	.0004	.3	.3	30	30	----	0	.7	.0015	.07
42	do	D96070	Lost Soldier	Morrison formation	----	----	----	----	.3	30	.7	30	0	.3	0	.03
42	do	D96114	do	Sundance formation	*S*	.002	.0009	.2	.7	3	.7	7	0	.3	0	.007
66	Montana	201524	Whitlash	Swift formation	IX*B*	.0006	.0019	.1	----	----	----	----	----	----	----	----
								Sandstone of Cretaceous age								
30	Colorado	D96119	Badger Creek	Dakota sandstone—D sand	IV*D*	0.0003	0.0117	0.3	0.7	3	1.5	3	0	0.3	0	0.03
30	do	D96120	do	Dakota sandstone—J sand	IV*D*	.0003	.0097	.3	1.5	3	1.5	3	0	.7	.15	.03
28	do	D96123	Gramps	Dakota sandstone	V*C*	.0010	.0017	.2	1.5	1.5	.7	7	0	.7	.07	.03
42	Wyoming	D96115	Lost Soldier	Wall Creek sandstone member of Frontier formation.	S	.0007	.0024	.2	3	1.5	.7	.15	0	.15	.15	.015
43	do	D96112	Crooks Gap	Muddy sandstone member of Thermapolis shale.	X	.0034	.0002	.1	.15	3	.3	30	0	3	0	.015
46	do	D96110	Bison Basin	Frontier formation	XIX	.0029	.0008	.2	.7	3	3	3	0	.7	.07	.07
61	do	227737	Salt Creek	2d Wall Creek sand	X	.0013	.0005	.1	3	30	1.5	----	0	.3	.15	.15
27	New Mexico	D96127 [4]	Table Mesa	Dakota sandstone	nd	.0033	.0018	.6	.15	30	.15	.3	0	.03	0	.15
78	do	D96128	Rattlesnake	Dakota sandstone—3d sand	III	.0003	.006	.2	3	3	3	.7	0	1.5	.3	.15
78	do	D96129	do	Dakota sandstone—1st sand	III	.001	.0032	.3	.7	7	1.5	.3	0	.15	.07	.07
64	Montana	200525 [5]	Bears Den	Sunburst sand	IX*A*	.0011	.01	1.1	----	----	----	----	----	----	----	----
65	do	200523 [5]	Flat Coulee	do	IX*B*	.0013	.0023	.3	----	----	----	----	----	----	----	----

Locality No.	Metals[2] in ash of oil (percent)—Continued																										
	Sr[3]	Ba[3]	Zr	Cr[3]	V[3]	Zn[3]	Ni[3]	Cu[3]	Li	Ce	Sn	Co[3]	Y	Nd	Nb	La	Pb[3]	Ga[3]	B	Ge	Be	Sc	As	Yb	Er	Mo[3]	Ag
	ROCKY MOUNTAIN REGION—Continued																										
	Sandstone of Jurassic age																										
32	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------
28	<0.0001	0.03	0.015	0.015	9.6	0.3	16	0.26	0	0.15	0.003	0.3	0	0	0	0	0.03	0.015	0	0	0	0	0.7	0	0	0.015	0
40	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------
61	.03	.0015	0	.003	.7	0	.7	.07	0	0	0	.07	0	0	0	0	.015	0	0	0	0	0	0	0	0	0	.0015
61	.3	.07	0	.003	.7	0	.7	.07	0	0	0	.03	0	0	0	0	.03	0	0	0	0	0	0	0	0	0	0
42	.03	.15	.07	.03	.80	.15	.66	.40	0	.07	.03	.07	0	.03	0	.03	.3	.003	.07	0	0	0	0	0	0	.003	.0015
42	.07	.3	.07	.007	.7	.15	3	.7	0	.03	.03	.07	0	0	0	.03	.15	.0007	.3	0	0	0	0	0	0	.003	.0007
66	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------
	Sandstone of Cretaceous age																										
30	0.03	0.07	0	0.03	1.5	1.5	7	0.3	0	1.5	0.015	0.15	0	0.3	0	0.3	0.15	0	0	0	0	0	0	0	0	0	0.003
30	.003	.03	.015	.015	.7	.3	7	1.5	0	.3	.015	.15	0	.15	0	.15	.3	0	0	0	0	0	0	0	0	0	0
28	.015	.015	.15	.015	4.2	.15	7.6	.26	0	.3	.0015	.7	0	.15	0	.15	.07	.015	0	0	0	0	.15	0	0	.007	.0007
42	.003	.03	.07	.015	5.6	.15	7.2	.26	0	.3	.007	.07	0	0	0	.15	.07	0	.15	0	0	0	0	0	0	.003	0
43	.03	.3	0	.015	6.2	.15	6.4	.07	0	.03	.003	0	0	0	0	.015	.07	.007	0	0	0	0	0	0	0	.003	.0007
46	.03	.07	.003	.015	3.9	.15	9.2	.60	0	.07	.007	.3	0	0	0	.03	1.5	.007	0	0	0	0	0	0	0	.007	.003
61	.015	.15	0	.03	1.5	0	30	.7	0	0	.03	.03	0	0	0	0	.3	0	0	0	0	0	0	0	0	.003	.0015
27	.007	.07	.007	.03	.007	.7	.09	5.6	0	0	.007	.007	.0007	0	0	0	.015	.0003	0	0	0	0	0	0	0	.007	.0003
78	.03	.15	.03	.007	.03	0	.07	.3	0	0	0	.015	.003	0	0	0	.015	0	0	0	0	0	0	0	0	0	0
78	.007	.03	0	.007	.015	1.5	.07	30	0	0	0	.015	0	0	0	.015	.03	0	0	0	0	0	0	0	0	0	.0007
64	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------
65	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------

See footnotes at end of table.

TABLE 6.—*Metal content of crude-oil samples listed according to geographic distribution of oil fields and age and type of reservoir rock*—Continued

[See figures 11–39 for oil classes; nd, not determined]

Locality No.	State	Laboratory No.	Oil field	Oil reservoir	Oil class and group	Ash (percent)	Uranium[1] in ash (percent)	Uranium in oil (ppb)	Metals[2] in ash of oil (percent)							
									Al[3]	Fe[3]	Ca[3]	Na[3]	K	Mg[3]	Ti[3]	Mn[3]
ROCKY MOUNTAIN REGION—Continued																
Shale of Cretaceous age																
29	Colorado	207300[5]	Florence	Pierre shale	VI	0.0003	0.0008	<0.1	------	------	------	------	------	------	------	------
34	do	217873[10]	Rangely	Mancos shale	III	.0009	.0032	.3	1.5	30	7	1.5	0	0.7	0.07	0.3
Sandstone and claystone of Tertiary age																
39	Utah	D91724	West Pleasant Valley	Green River formation	------	3.8	0.0013	400	7	3	7	7	1.5	3	0.15	0.03
38	do	D92399	Duchesne	Wasatch formation	I	.013	.0005	.7	.7	3	3	30	0	.7	.03	.03
38	do	D92400	do	do	I	.0047	.0016	.8	.7	3	3	30	0	.3	.03	.015
37	do	D92402	Roosevelt	Green River formation	IV*C*	.0042	.0001	<.1	.3	.3	3	30	0	.3	.003	.007
37	do	D92403	do	do	IV*C*	.032	<.0001	<.3	.3	.3	.7	30	0	.3	.0003	.0015
36	do	D92405	Duchesne County	do	------	.41	.0001	4.1	.3	.3	.15	30	0	.07	.0003	.0015
35	Colorado	223234	Hiawatha	Wasatch formation	nd	.0007	.0014	.1	.3	7	1.5	30	0	.7	.07	.015
31	do	205775[14]	White River area	do	nd	.032	.0005	1.6	3	30	30	------	0	.7	.07	.7

Locality No.	Metals[2] in ash of oil (percent)—Continued																										
	Sr[3]	Ba[3]	Zr	Cr[3]	V[3]	Zn[3]	Ni[3]	Cu[3]	Li	Ce	Sn	Co[3]	Y	Nd	Nb	La	Pb[3]	Ga[3]	B	Ge	Be	Sc	As	Yb	Er	Mo[3]	Ag
ROCKY MOUNTAIN REGION—Continued																											
Shale of Cretaceous age																											
29	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----
34	0.03	0.7	0.007	0.015	0.7	0.3	1.5	0.3	0	0	0.007	0.015	0	0	0	0	1.5	0	0	0	0	0	0	0	0	0.0015	0.0003
Sandstone and claystone of Tertiary age																											
39	0.03	0.07	0.007	0.003	0.03	0	0.15	0.007	0	0	0	0.015	0.0007	0	0	0	0.03	0	0.15	0	0	0.0015	0	0	0	0.007	0
38	.15	3	.003	.007	.03	.07	.015	.07	0	0	.003	.007	0	0	0	.007	.03	0	.03	0	0	0	0	0	0	.0003	.00015
38	.07	1.5	0	.007	.03	.07	.015	.03	0	.15	.0015	.007	0	.07	0	.07	.03	0	.03	0	0	0	0	0	0	.0003	.00015
37	.03	.07	.003	.007	.41	0	7.6	.13	0	0	.003	.3	0	0	0	.007	.03	0	.007	0	0	0	0	0	0	.03	.00015
37	.07	.03	0	.003	.07	0	1.7	.03	.15	0	0	.07	0	0	0	0	.003	0	.07	0	0	0	0	0	0	.003	0
36	.0003	.07	.003	.0015	.015	0	.3	.003	0	0	0	.015	0	0	0	0	0	0	.7	0	0	0	0	0	0	0	0
35	.07	.03	.007	.03	.3	0	.3	.15	0	0	.007	0	0	0	.007	0	.03	0	0	0	.0007	0	0	0	0	0	0
31	.07	.15	0	.015	.03	1.5	.03	.15	0	0	.7	.007	0	0	0	0	.15	0	0	0	0	0	0	0	0	0	0

See footnotes at end of table.

TABLE 6.—*Metal content of crude-oil samples listed according to geographic distribution of oil fields and age and type of reservoir rock*—Continued

[See figures 11–39 for oil classes; nd, not determined]

Locality No.	State	Laboratory No.	Oil field	Oil reservoir	Oil class and group	Ash (percent)	Uranium [1] in ash (percent)	Uranium in oil (ppb)	Metals [2] in ash of oil (percent)							
									Al [3]	Fe [3]	Ca [3]	Na [3]	K	Mg [3]	Ti [3]	Mn [3]
WEST COAST REGION																
Sandstone of Tertiary age																
68	Nevada	224843 [5]	Eagle Springs	Humboldt formation	IV*A*	0.002	0.0006	<0.1	------	------	------	------	------	------	------	------
69	California	224842	Helm	Weyant sand	XIII	0.0035	0.0002	<0.1	1.5	7	0.15	------	0	0.07	0.07	0
70	do	224841	Coalinga	Temblor formation	XVIII*B*	.0073	.0003	.2	.7	7	1.5	------	0	.15	.07	.03
72	do	224836	Midway	Potter sand	XVIII*B*	.118	.0012	14	30	7	3	------	0	3	.7	.07
73	do	224834	Elk Hills	*Mulinia* zone	XVIII*A*	.055	.0003	1.6	.15	7	7	------	0	1.5	.07	.07
74	do	224833	Coles Levee	Miocene sand	XIII	.0072	.0001	<.1	.3	3	.3	------	0	.15	.03	0
75	do	224837	Ant Hill	Olcese sand	XVII	.095	.0004	3.8	1.5	3	.7	------	0	.3	.15	0
77	do	224838	Wilmington	Ranger zone	XVIII*A*	.120	.0002	2.4	.3	3	1.5	------	0	1.5	.07	0
76	do	224839	Inglewood	Vickers-Machado zone	XVII*B*	.419	.0009	38	.3	3	1.5	------	0	3	.15	0
Shale of Tertiary age																
71	California	224840	Santa Maria Valley	Monterey shale	XVII*B*	0.058	0.0006	3.5	1.5	0.3	0.07	------	0	0.07	.3	0.003

Locality No.	Metals[2] in ash of oil (percent)—Continued																										
	Sr[3]	Ba[3]	Zr	Cr[3]	V[3]	Zn[3]	Ni[3]	Cu[3]	Li	Ce	Sn	Co[3]	Y	Nd	Nb	La	Pb[3]	Ga[3]	B	Ge	Be	Sc	As	Yb	Er	Mo[3]	Ag
WEST COAST REGION																											
Sandstone of Tertiary age																											
68	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----
69	0.0015	0.015	0	0.015	7	0	30	0.015	0	0	1.5	0.7	0	0	0	0	0.03	0.003	0	0	0	0	0	0	0	0	0
70	.015	.015	0	.03	7	0	30	.015	0	0	0	.3	0	0	0	.03	.015	.03	0	0	0	0	0	0	0	.015	0
72	.03	.15	.03	.15	7	0	7	.03	0	0	0	.15	0	0	0	0	0	.07	0	0	0	0	0	0	0	.07	0
73	.015	.007	0	.007	1.5	0	7	.03	0	0	0	.7	0	0	0	0	.07	.03	0	0	0	0	0	0	0	.007	0
74	.07	.03	0	.003	3	0	30	.015	0	0	0	.3	0	0	0	0	0	.015	0	0	0	0	0	0	0	.007	0
75	.007	.015	0	.007	1.5	0	7	.03	0	0	0	.15	0	0	0	0	.015	.007	0	0	0	0	0	0	0	0	0
77	.03	.3	0	.015	3	0	7	.003	0	0	0	.07	0	0	0	0	0	.015	0	0	0	0	0	0	0	.015	0
76	.03	.015	0	.03	3	0	3	.03	0	0	0	.07	0	0	0	0	0	.007	0	0	0	0	0	0	0	.015	0
Shale of Tertiary age																											
71	0	0.0007	0	0.3	30	0	30	0.0015	0	0	0	0.03	0	0	0	0	0	0.15	0	0	0	0	0	0	0	0.7	0

[1] Uranium content was determined by fluorometric analysis; analysts, Mary Curtis, Dorothy Ferguson, and Sylvia Furman.

[2] The figures 1.5, 3, and 7 result from semiquantitative spectrographic analyses and are approximate midvalues of the ranges 1–2.0, 2.0–5.0, and 5.0–10.0; these midpoints represent the appropriate ranges, that is, 0.015 represents 0.01–0.02. The results of quantitative spectrographic analyses are reported to two significant figures. An element not looked for is indicated by leaders (----). An element looked for but not detected is indicated by 0. Analyst, Pauline Dunton.

[3] Element detected in more than half the oil samples.

[4] Sample of oil-tank bottoms.

[5] No spectrographic analysis.

[6] Crude-oil analysis from Blade, 1948.

[7] No uranium analysis.

[8] Crude-oil analysis from Tulsa Geological Society Research Committee (1947).

[9] Sample collected by N. W. Bass and N. M. Denson.

[10] Sample collected by Kenneth G. Bell.

[11] Crude-oil analysis from Lane and Garton (1943).

[12] Crude-oil analysis from McKinney and Blade (1948).

[13] Crude-oil analysis from Crawford and Larsen (1943).

[14] Drill-stem test.

The lack of sufficient data to determine representative samples for each field was mentioned on page 21. The qualitative aspect of the data presented here is here stressed, and the representations of local abundance are offered only as suggestions to be validated by further sampling. The lack of homogeneity of crude oil within an oil tank or an oil reservoir, pointed out on page 21, must be considered in making interpretations. Sludge is known to accumulate at the bottom of storage tanks. Local and temporal accumulations of sludge are suspected to exist in oil reservoirs, and samples of relatively high ash content are considered the more questionable.

MIDCONTINENT REGION

Most of the oils collected from the midcontinent region are in oil classes IV through IX. A few heavy oils of class XIV, one usually light oil of class II, and three oils in class *S* were collected. The ash samples, as would be expected from the oil classifications, were generally deficient in vanadium, nickel, gallium, and molybdenum. Cerium and several other metals were locally present in abnormally large amounts. The greatest abundance of the less common metals, as well as unusually high concentrations of uranium, occurred in the ash of oil samples from the Bartlesville sand in northeastern Oklahoma.

Arkansas.—Sample localities 1, 2, and 3 are in southernmost Arkansas. This area lies between two major structural features: the Sabine uplift in northern Louisiana and the Ouachita folded belt in Arkansas. The three localities are of the three oil fields, Schuler, West Atlanta, and Stephens-Smart. The oil in each of these fields has accumulated in a structural dome; a migration of the oil at least a short distance must be inferred.

The oil reservoirs at Stephens-Smart and Schuler are sandstones of Jurassic and Cretaceous age (fig. 6) and the oils are quite similar in composition and are placed in class IX. The oil from the Smackover formation of Jurassic age at West Atlanta is very different from the other two oils, and has been placed in class *S;* the suite of metals, however, in all three oils is much the same.

The vanadium, nickel, gallium, and molybdenum contents in the Arkansas oils are relatively small. The amounts of these metals in the ash of oil have been shown to be related to the type of oil, and relatively low percentages are expected in class IX oils and in the lightest class *S* oils. The Arkansas oils are relatively rich in calcium, magnesium, barium, and lead. The detection of minor metals such as cerium and arsenic may be due to the fact that they are not diluted by abundant vanadium and nickel.

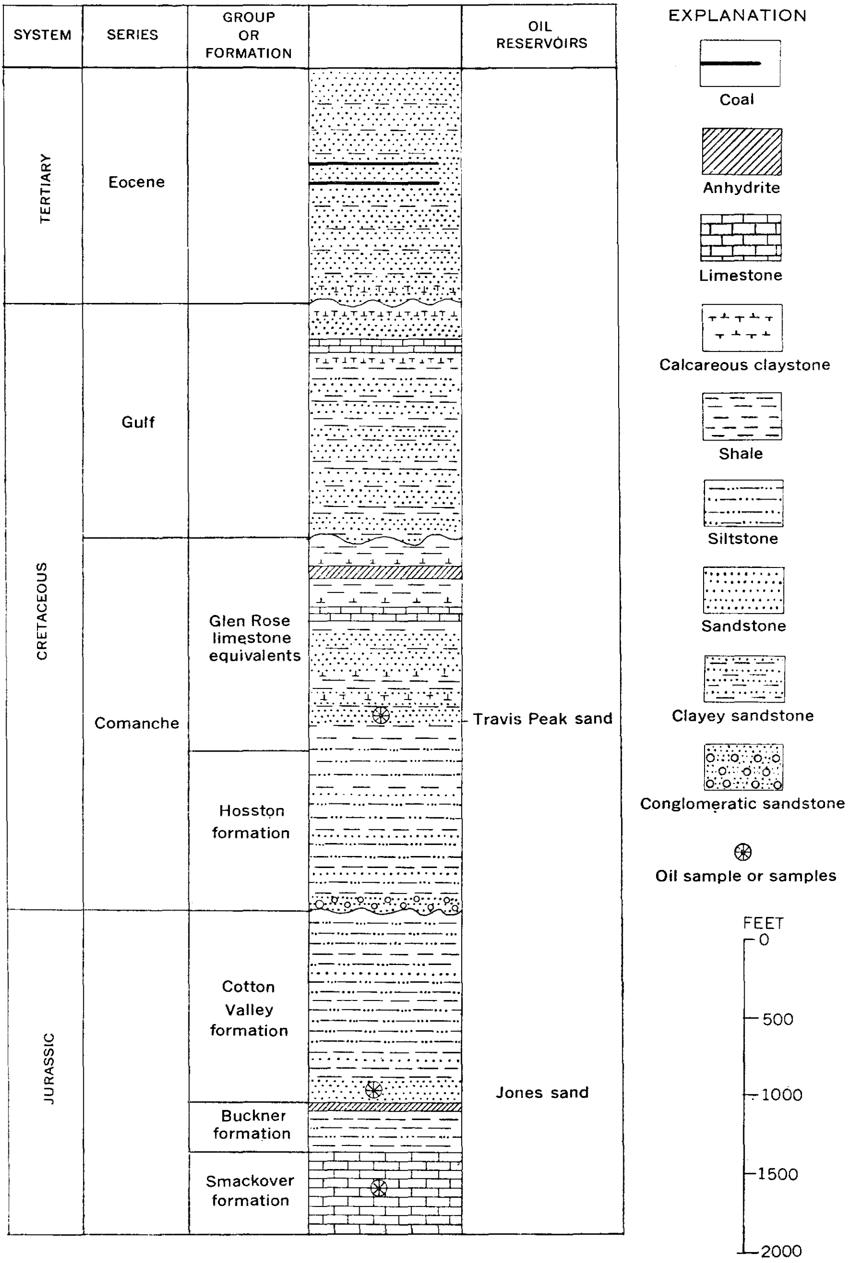


FIGURE 6.—Generalized columnar section for Stephens-Smart, West Atlanta, and Schuler fields, Arkansas (modified after Imlay, 1950).

Oklahoma.—Oil-sample localities 6 through 16 are located in northeastern and central Oklahoma. The dominant regional structural feature in this area is a homocline dipping gently to the southwest.

Most of the oil in this area is produced from Pennsylvanian sandstones deposited in the shelf area of the McAlester Basin. Three samples of oil were collected from pre-Pennsylvanian reservoir rocks, and 14 samples were collected from Pennsylvanian reservoir rocks (fig. 7). Because of insufficient ash for both fluorometric and spectrographic analyses, only the uranium content was determined for the oil sample from the Arbuckle lime at Pond Creek field; and uranium content, 0.0004 percent of the ash, is within the range of values for most samples.

Two samples of oil were collected from sandstones that immediately overlie the Arbuckle group—the Hominy sand at Middle Gilliland field and the Wilcox sand at Laffoon field. These two oil samples were comparatively deficient in gallium, molybdenum, and chromium, even though the Laffoon oil is of class XV, a heavy asphaltic oil.

The oil samples collected from Pennsylvanian sandstone reservoirs in Oklahoma consist of class IV, V, VII, VIII, and *S* oils. As would be expected, the vanadium, nickel, gallium, and molybdenum contents of these lower class oils were relatively low. On the other hand they were relatively rich in uranium as well as the following metals: aluminum, iron, manganese, strontium, barium, cobalt, and lead. Zirconium, tin, lanthanum, germanium, beryllium, scandium, arsenic, silver, yttrium, and erbium, which are less common, also were detected in these oil samples.

The group of oil pools, including Alluwe and Chelsea pools, near the town of Nowata, are collectively termed Nowata field. The oil produced from these pools comes essentially from the Bartlesville sand, a single large elongate sandstone lens in marine shale. The six oil samples collected from Nowata field contained generally the largest amount of uranium in the ash of any of the samples included in this investigation, the amounts ranging from 0.013 to 0.045 percent. The smallest uranium content in the ash of any of the samples, 0.013, is exceeded by only one sample from another area (0.021 percent uranium in ash of oil from Brewster field in Kansas.) The value 0.045 percent uranium in the ash of an oil sample from Alluwe pool is the highest uranium value reported.

Nowata field is the only field among those included in this investigation in which water had been introduced into the reservoir rock from the surface as a secondary recovery operation. The water so introduced may cause additions of some metals to the crude oil and losses of other metals.

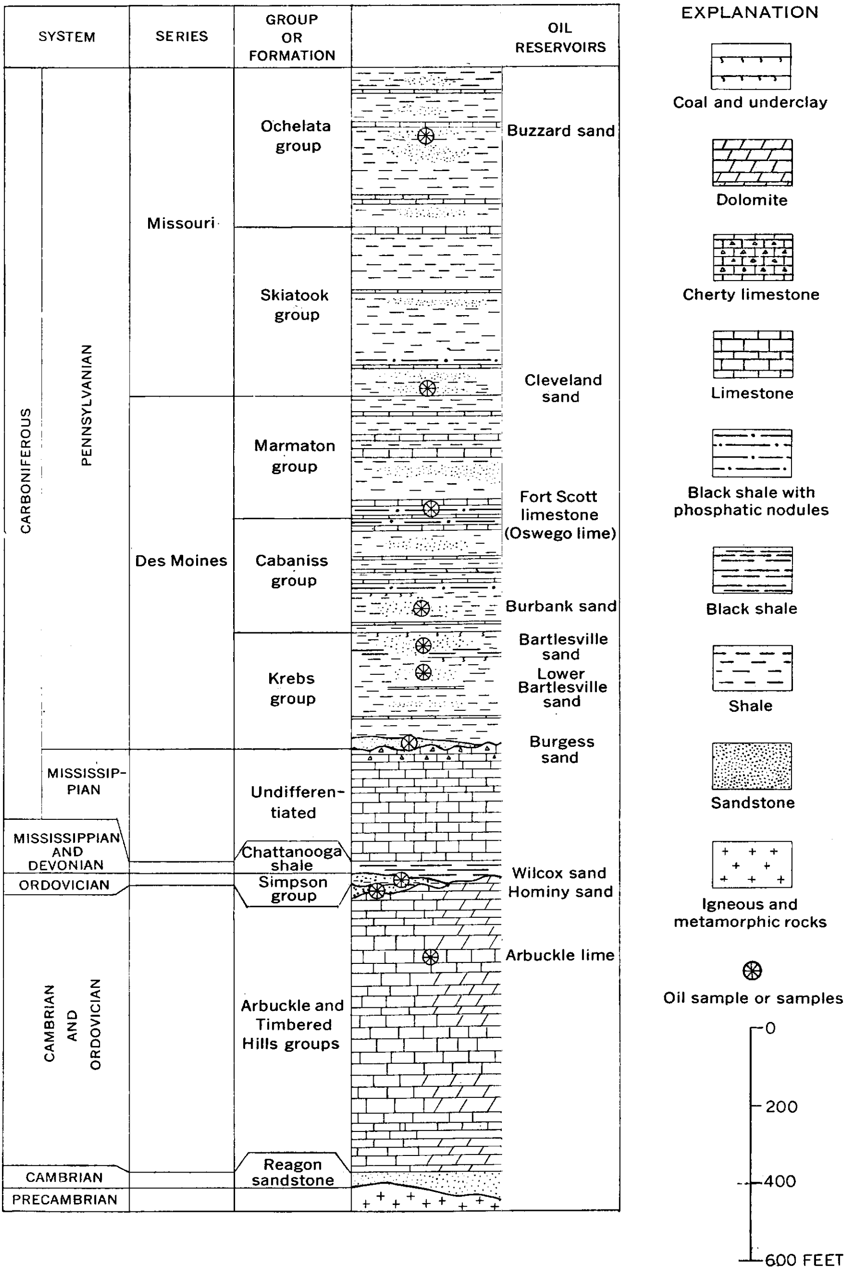


FIGURE 7.—Generalized stratigraphic column for fields where oil samples were collected in Oklahoma.

In another investigation of uranium occurrences in Pennsylvanian rocks in Oklahoma (Danilchik and Hyden, written communication, 1958) oil was extracted from two cores from water-injection wells in the Nowata field. The uranium content of these oils was determined to test the possibility that the portion of oil remaining in the ground after primary production may contain more uranium than the produced oil. The cores were not fresh, and the crude oil in them had been subject to volatilization in air; the ash content was much higher than the ash content of the crude oil being produced at Nowata, but the amount of uranium was no higher in the ash of the oil extracted from the core than that in ash of the produced oil. The range in values for the Nowata crude oils is 0.013 to 0.045 percent uranium in ash. Apparently the oil from the cores was no richer in uranium than the produced oil.

Analyses of extracted oil

Laboratory No.	Ash (percent)	Uranium in ash (percent)
240500	0. 0959	0. 016
237166	1. 29	. 0084

The Nowata oil samples, samples from the Bartlesville sand in other fields not water flooded, and samples from other Pennsylvanian sandstones in Oklahoma, are relatively rich in lead, zirconium, strontium, tin, yttrium, beryllium, copper, and silver. This fact seems to indicate that such enrichment is not entirely due to contamination by water flooding.

The Pennsylvanian system in the midcontinent region is characterized by vertical repetition of similar lithologic units including marine black shales and coals. Some sandstones, for example, the Bartlesville sand, are beach or offshore-bar deposits(Bass and others, 1937; Tanner, 1956) that represent environments transitional between marine sediments and such terrestrial units as coals.

The minor metals that are relatively abundant in crude oil from the Bartlesville sand are common to the coals and black shales of neighboring rocks, and an association of crude oil with coal and shale is indicated. These metals may have migrated from coal or shale beds to the crude-oil reservoir either in coal oil or shale oil or in ground water. The metals erbium, yttrium, scandium, beryllium, and germanium were found in more of the 13 oil samples from Pennsylvanian sandstones in Oklahoma than among the remaining 92 oil samples analyzed spectrographically; silver and strontium also were identified in the oil samples from the Bartlesville sand more consistently than in other oils. These metals, generally rare in crude oils, are common in Pennsylvanian coal and black shale in Oklahoma. Danilchik and Hyden (written communication, 1958) collected 9 Pennsylvanian coal samples from northeastern Oklahoma and southeastern Kansas. Germanium, scandium, yttrium, silver, and strontium were detected in 8 of the 9 samples, and beryllium was detected in all 9 samples. Erbium was not detected in the coal samples but was detected in many of the phosphatic nodules, which are common in the associated black bituminous marine shale. Yttrium, scandium, beryllium, silver, and strontium are also common to the black shales as well as to the coals. The nodule-bearing black shale is also relatively rich in uranium.

Sections of core of the Bartlesville sand from Nowata field contained many detrital flakes of coal ranging in maximum dimension from less than ¼ inch to 4 inches. These detrital flakes within the oil reservoir itself are the likely source of germanium and some other metals in the oil. These metals may have been taken into solution in the crude oil from the solid coal, or the metals may have been constituents of a coal oil, which was squeezed out of the coal with increasing pressure of overburden to become a part of the crude oils.

The cores of Bartlesville sand also contained black shale laminae and flakes. This black shale detritus may have been a source for uranium which was transferred either by entering solution, or by squeezing as postulated above. However, as uranium is much more soluble in aqueous solution in the oxidized, hexavalent form than in the reduced quadrivalent from (Goldschmidt, 1954, p. 565), another mechanism for transfer is possible. Weathering and oxidation of uraniferous black shales may have mobilized the uranium and made uranyl ions available for solution. The uranyl ions in aqueous solution could have been transferred to crude oil in the reducing environment of the crude oil. The leaching and squeezing mechanisms, however, seem the more plausible explanations.

Kansas.—Sample localities 17 through 26 are in eastern and central Kansas. In eastern Kansas much oil is produced from shallow Pennsylvanian sandstones, as in northeastern Oklahoma. Sample localities 21 through 26 are in fields associated with major anticlinal structures, the Central Kansas uplift, the Pratt anticline, and the Nemaha anticline.

Figure 8 is a very generalized stratigraphic representation showing lithologic units that may be present at the localities where crude-oil samples were collected. The units shown are, of course, not present at every locality. Rocks of Mississippian through late Ordovician age are absent over much of the Central Kansas uplift. Sample localities 23 through 26 are in this area, where Mississippian and

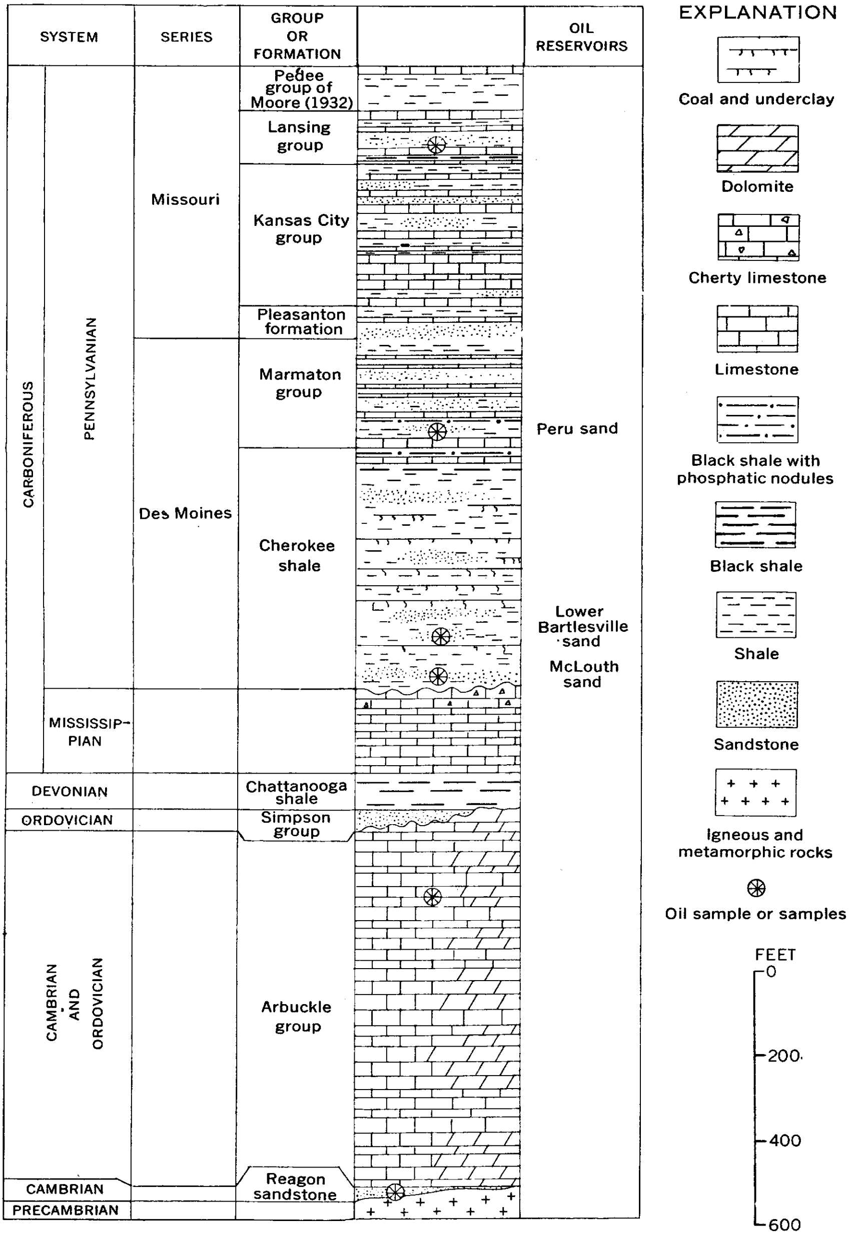


FIGURE 8.—Generalized stratigraphic column for fields where oil samples were collected in Kansas.

older beds are absent. The remaining sample localities are in basin areas, where Mississippian and older beds are present.

The two samples of oil collected at locality 25, Otis-Albert field, were produced from the Reagan sandstone of Cambrian age (fig. 8); both are class VIII oils. Except for the presence of cerium and a relatively small amount of manganese and the absence of zirconium, the metal analysis (D91715, table 6) is typical (fig. 2). The second analysis for locality 25 (D91723, table 6) is of a sample of "storage-tank bottoms." These "bottoms" are moderately higher in iron, magnesium, strontium, barium, tin, and boron. Water collects at the bottom of the tank, and an emulsion forms. Separation of oil and water is difficult and the enrichment in metals may result from incomplete separation of these two liquids.

Ten samples of oil were collected from the Arbuckle lime of Cambrian and Ordovician age at six fields in Kansas (locality nos. 17, 18, 21, 23, 24, and 26). Bass and others of the Tulsa Geological Society Research Committee (1947, p. 144–148) have pointed out that a great variety of oils are produced from the upper Arbuckle, and that these oils probably migrated from rocks lying unconformably above the Arbuckle. Evidence bearing on this possibility may be shown by a comparison of oil samples from the Arbuckle lime and Reagan sandstone (of Cambrian age) with oil samples from Pennsylvanian rocks. The oil sample from the Arbuckle lime at Hittle field, Kansas, is in oil class VII, and is similar to the class VII sample from the Lansing group of Pennsylvanian age at Cunningham field, Kansas, and to the three class VII samples from the Bartlesville sand of Pennsylvanian age at Nowata and Wynona fields, Oklahoma. The sample from the Arbuckle lime at Brock field, Kansas, and the sample from the Reagan sandstone at Otis-Albert field, Kansas, are both class VIII oils, and thus are similar to the class VIII oil sample from the Burgess sand of Pennsylvanian age at New England field, Oklahoma. The similarity of the Cambrian and Ordovician oil samples to the Pennsylvanian oil samples supports the possibility that the oils may have a common source.

Oil samples from the Arbuckle lime at Brewster, and Coffeyville fields fall into oil class XIV. The earliest boiling fractions of these oils were not present, possibly owing to loss by volatilization. The sample from Brewster is an oil unusually heavy for the midcontinent region.

The metal contents of the oil samples from the Arbuckle lime in Kansas are similar. Cerium and boron are relatively abundant; zinc and molybdenum are relatively deficient. One oil sample from Brewster contained 0.021 percent uranium in the ash, the highest uranium content of any Kansas sample.

Four samples of oil from Pennsylvanian sandstone were collected at Hittle, McLouth, and Iola fields, Kansas. The oil sample from McLouth field is in oil class II, a light oil; one of the oil samples from Iola field in oil class XIV is the heaviest sample collected in Kansas. Despite the difference in oil class, the metal contents of these two samples are similar. In a comparison with figure 2 they seem to be relatively high in cerium and boron, and low in vanadium, gallium, molybdenum, zinc, titanium, manganese, and chromium. Oil classes and metal content of oil samples from Pennsylvanian sandstones in Kansas contrast sharply with oil classes and metal content of oil samples from Pennsylvanian sandstones in Oklahoma, and suggest the possibility of a different diagenetic or postdiagenetic history of the two groups.

Two oil samples from Pennsylvanian limestone were collected at Cunningham field, Kansas. Both samples are in oil class VII, which also includes oil samples from Pennsylvanian sandstone in Oklahoma and the Arbuckle lime of Cambrian and Ordovician age in Kansas. The metal content of the samples from Cunningham field is similar to the other class VII samples, and generally to all other samples from Kansas and Oklahoma, except that they have a higher content of vanadium, nickel, and gallium.

An oil sample from granite wash, collected at Finley field in the Texas Panhandle, is in oil class IV and has a metal content similar to the Kansas oils.

ROCKY MOUNTAIN REGION

Colorado, Utah, and New Mexico.—Two oil samples from the Weber sandstone of Pennsylvanian age (table 7) were collected at Rangely field, Colorado. One of the samples came from an unknown depth but its correlation index curve is class VII*A*, the same as the known Weber sample, and so is considered to have come from Weber. Samples of oil produced from the Shinarump member of the Chinle formation of Triassic age were collected at Rangely field and at Moffat Dome field, Colorado. These oils are in class V and III, respectively.

Samples of oil from Jurassic and Cretaceous reservoirs were collected at Wilson Creek, Badger Creek, Gramps, and Rangely fields in Colorado, as well as from Table Mesa and Rattlesnake fields in New Mexico. The oil produced from the Dakota sandstone at Table Mesa and Rattlesnake is light colored and very light weight, and although the correlation index plot of the sample from Rattlesnake is placed in class III, there were no distillation fractions after cut

TABLE 7.—*Generalized stratigraphy for fields where oil samples were collected in western Colorado, eastern Utah, and northwestern New Mexico*

Era	System	Series	Group	Stratigraphic unit	Description	Oil fields and States where oil samples were collected
Cenozoic	Tertiary	Eocene		Green River formation	Gray dolomitic marlstone (oil shale), sandstone, siltstone and tuff, and thin limestone beds; lacustrine.	Roosevelt, Duchesne County, and West Pleasant Valley, Utah.
				Wasatch formation	Red, yellow, and gray mudstone and sandstone, and interbedded red and gray shale; fluviatile and lacustrine.	Hiawatha and White River, Colorado. Duchesne, Utah.
		Paleocene		Fort Union formation	Sandstone, shale, and coal beds.	
Mesozoic	Cretaceous			Lance formation	Shale, sandstone, and coal beds.	
				Lewis shale	Dark-gray marine shale.	
			Mesaverde		Light-brown sandstone, gray shale, sandy shale, and coal beds.	
				Mancos shale	Dark-gray marine shale, and thin sandstone and limestone beds.	Rangely, Colorado.
				Dakota sandstone	Light-yellow sandstone, and interbedded shale and coal.	Table Mesa and Rattlesnake, New Mexico. Gramps, Colorado.
	Jurassic			Morrison formation	Green, gray, and maroon shale, and sandstone.	Gramps, Colorado. Seiber Nose, Utah.
			San Rafael	Curtis formation	Sandstone, shale, and thin limestone beds; marine.	
				Entrada sandstone	Massively bedded sandstone.	Wilson Creek, Colorado.
				Carmel formation	Red sandstone, siltstone, and shale.	
			Glen Canyon	Navajo sandstone	Red to buff cross-bedded eolian sandstone.	
	Triassic			Chinle formation	Calcareous shale, mudstone, and sandstone.	
				Shinarump member of Chinle formation	Conglomerate and sandstone.	Rangely and Moffat Dome, Colorado.
				Moenkopi formation	Shale, siltstone, and thin limestone beds in lower part.	Virgin, Utah.
Paleozoic	Permian				Sandy shale, sandstone, and limestone.	
	Pennsylvanian			Weber sandstone	Massively bedded sandstone.	Rangely, Colorado.
				Morgan formation	Sandstone, shale, and limestone.	

number 10. A sample of oil from the Mancos shale at Rangely field also is in class III. The remaining samples from Jurassic and Cretaceous reservoirs are included in oil classes IV through VI.

The vanadium and nickel content of the light oils from Jurassic and Cretaceous reservoirs are low, and the nickel content exceeds the vanadium content. The amount of uranium in the ash of these oil samples is high, and some of the oils are high in cobalt, cerium, and tin (table 6).

The oil samples collected from Mesozoic reservoirs in Utah, an area of many uranium-ore deposits, were not rich in uranium, as might have been expected (table 6). The uranium content of the ash of an oil from the Seiber Nose field, in an area of uranium production, contained only 0.0008 percent uranium.

The oil production at the Virgin field is from wells drilled entirely in the Moenkopi formation. Two oil samples were collected from this field: the sample listed in figure 21 among the class VIII oils was similar in appearance to oil produced from all other wells in the field, except one; the sample listed in figure 29 among the class XIII oils was distinctive in appearance from all other oil produced in the field and must have come from a different source rock. Neither sample from the Virgin field contained much uranium, but the class XIII oil had a very high content of lead in the ash. Limestone of the Moenkopi formation commonly contains galena, and may have been the source of the lead detected in the oil sample.

Oil samples, from Eocene reservoirs, rocks of terrestrial origin, were collected from fields in northwestern Colorado and northeastern Utah (table 7). These oils are light in color and weight, and the samples are in oil classes I and IV (table 6). The oils produced from the Green River and Wasatch formations in the Uinta basin are unusual because of their high melting points; they are solid in the ordinary temperatures of the region.

The uranium content in the ash of the oils produced at Roosevelt and Duchesne County fields is not relatively high. The calculated uranium content of the total oil sample from West Pleasant Valley, Utah, was the highest found. The high calculated uranium content of this sample is due to the relatively high ash content. This sample from West Pleasant Valley is an unusual oil; its gravity was 7° API (heavier than water), and it was very viscous, resembling grease. Although the Green River and Wasatch formations contain tuffaceous sediments, the crude oils apparently have not been enriched by uranium from these sediments.

Generally the oils from the Rocky Mountain region Eocene reservoirs, as compared with all the oil samples, are deficient in vanadium, nickel, gallium, molybdenum, zinc, and chromium, and relatively rich in barium, zirconium, tin, and boron (table 6 and fig. 2).

Wyoming.—The oldest reservoir rock from which an oil sample was taken is a sandstone of Cambrian age at Lost Soldier field (table 6 and fig. 9). The oil from this sandstone is in class XII*A* together with an oil from the Embar reservoir of Permian age at Steamboat Butte.

The oil produced from the Tensleep sandstone of Pennsylvanian and early Permian age at Salt Creek is a very light oil (class II); the remaining samples of oil from Paleozoic reservoirs are heavy black oils and are included in oil classes XII, XV, XVI, and XVII. The same class of oil came from both sandstone and limestone reservoirs of differing ages.

The oils from the Paleozoic reservoirs are generally not enriched in any of the more common metals (table 6 and fig. 2); among the minor metals, however, lanthanum is more common in Wyoming oils than in all the other oils. Many of these oils from Paleozoic reservoirs are relatively deficient in titanium, strontium, and zinc.

Oils produced from a Triassic sandstone reservoir at Grass Creek and Hamilton Dome fields (table 6) were sampled. This reservoir is informally called the Curtis sand (fig. 9); however, the Curtis sand is considered the equivalent of the Crow Mountain sandstone member of the Chugwater formation (McGrew, 1955). A radioactive zone within the Crow Mountain sandstone member has been noted on gamma ray logs by J. D. Love (written communication, 1953); however, oil samples from the Crow Mountain sandstone member at Grass Creek and Hamilton Dome do not contain unusually large amounts of uranium.

The oil samples from Jurassic and Cretaceous reservoirs (fig. 9) consist of lighter oils (classes VI, IX, and *S*) than the samples from Paleozoic reservoirs, except for the very heavy (class XIX) oil from the Frontier formation of Cretaceous age at Bison Basin field. The oils from Jurassic and Cretaceous reservoirs are relatively rich in barium, lead, cobalt, silver, and lanthanum (table 6 and fig. 2). The nickel content of these oils is generally greater than the vanadium content.

Montana.—The oil samples collected from Montana are from five fields alined in a north-northwest direction across the central part of the State (fig. 1). The generalized stratigraphy along this line is shown in figure 10. Soap Creek field in southern Montana lies in the Bighorn Basin. The oil sample from the Amsden formation of Pennsylvanian age at Soap Creek is a heavy black oil and is similar

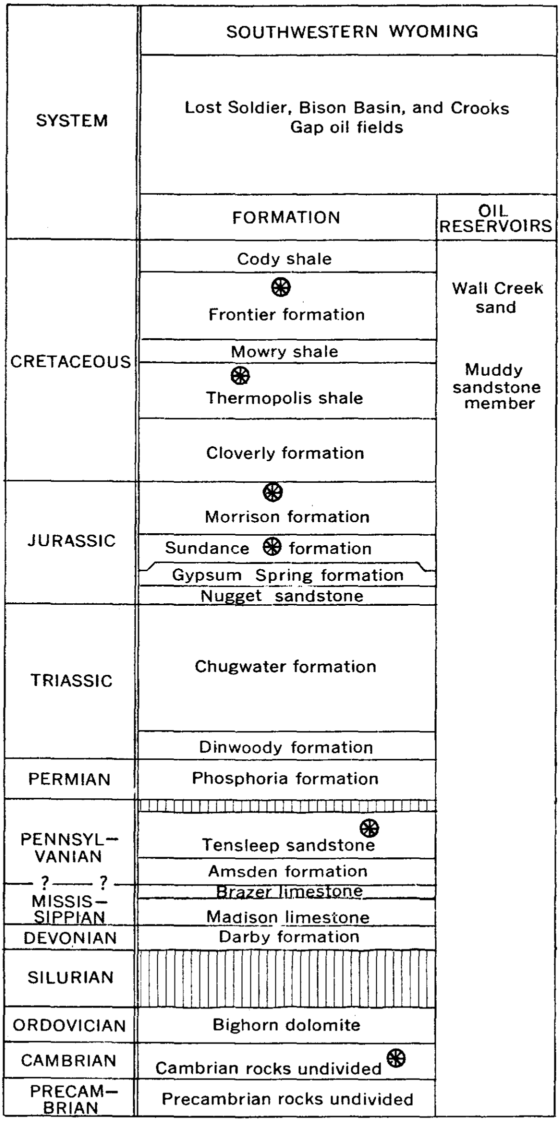
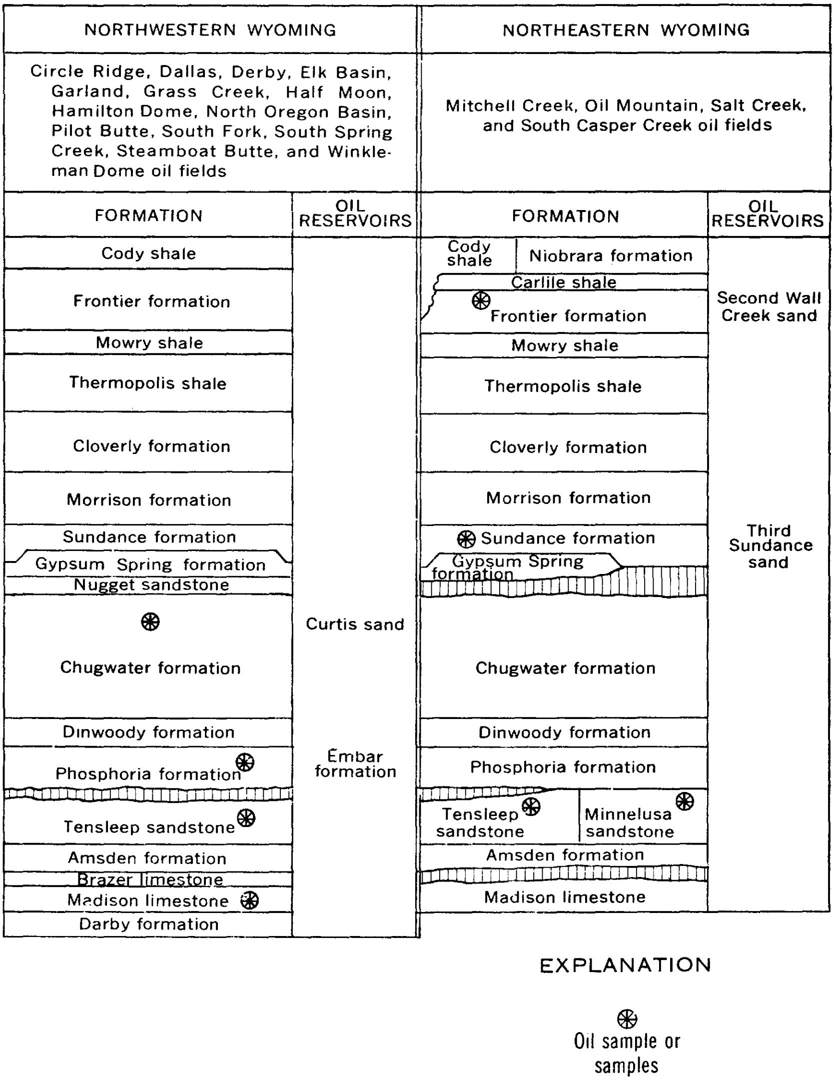


FIGURE 9.—Correlation chart for oil

to other oil samples from Paleozoic formations (class XII*C*) in the Wyoming part of the Bighorn Basin.

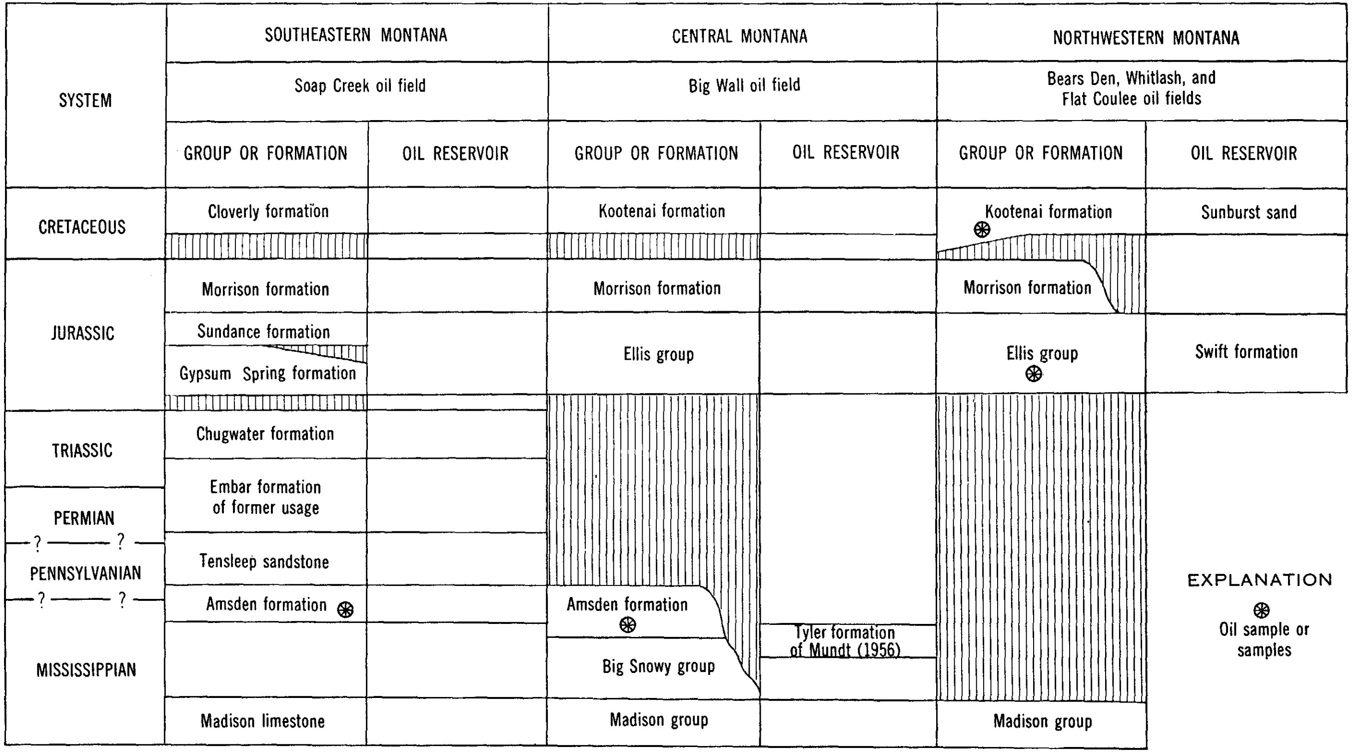
Big Wall field in central Montana is located on a small dome on the southern flank of the Big Snowy anticlinorium. An oil sample was collected at Big Wall field from a producing zone designated at the time as the lower part of the Amsden formation, and this is the designation used in this report. Other names have been used



fields in Wyoming (after McGrew, 1955).

for this same zone; they include Heath, Heath-Amsden transition zone, and Tyler formation (Mundt, 1956). No particular nomenclature or stratigraphic correlation is endorsed in this report. The oil sample from Big Wall is in class VIII and hence is similar to some oil samples from Paleozoic reservoirs in Kansas.

The metal contents of the samples from Big Wall and from Soap Creek are similar to those of the majority of oils as shown in figure



SYSTEM	SOUTHEASTERN MONTANA		CENTRAL MONTANA		NORTHWESTERN MONTANA	
	Soap Creek oil field		Big Wall oil field		Bears Den, Whitlash, and Flat Coulee oil fields	
	GROUP OR FORMATION	OIL RESERVOIR	GROUP OR FORMATION	OIL RESERVOIR	GROUP OR FORMATION	OIL RESERVOIR
CRETACEOUS	Cloverly formation		Kootenai formation		Kootenai formation ⊛	Sunburst sand
JURASSIC	Morrison formation		Morrison formation		Morrison formation	
	Sundance formation Gypsum Spring formation		Ellis group		Ellis group ⊛	Swift formation
TRIASSIC	Chugwater formation					
PERMIAN	Embar formation of former usage					
—? —— ?—						
PENNSYLVANIAN	Tensleep sandstone					
—? —— ?—	Amsden formation ⊛		Amsden formation ⊛			
MISSISSIPPIAN			Big Snowy group	Tyler formation of Mundt (1956)		
	Madison limestone		Madison group		Madison group	

EXPLANATION

⊛ Oil sample or samples

FIGURE 10.—Correlation chart for oil fields in Montana (modified after Billings Geological Society Nomenclature Committee, 1957).

2; however, they are relatively deficient in titanium, strontium, and zinc.

Bears Den and Flat Coulee fields are on the Sweetgrass Hills structure, and are near small intrusive bodies (C. E. Erdmann, written communication, 1953). The oil samples were produced from sandstones of Cretaceous age at these fields (table 6 and fig. 10). The oil samples are class IX, with oils from Cretaceous sandstone reservoirs in southern Arkansas.

The oil samples from Bears Den and Flat Coulee had only slightly greater uranium content in the ash than the majority of oils, and there is no reason to believe that the nearby intrusive bodies contributed uranium to the oil.

WEST COAST REGION

Nevada.—A sample of oil was collected from the first discovery well in Nevada at the Eagle Springs field. The oil is produced from a reservoir of volcanic clastic rocks of Tertiary age. The uranium content of the ash of this oil (table 6) is well within the range of values for the majority of samples. The oil sample is of class IV*A*.

California.—Heavy black oils of classes XIII, XVII, and XVIII were collected from Tertiary reservoirs in California (table 8). These samples are from the San Joaquin Valley, the Los Angeles basin, and the Santa Maria basin.

Three of the oil samples in class XVIII from the San Joaquin Valley contain relatively large amounts of gallium in the ash. No zinc was detected in any of the California oil samples, and manganese and vanadium were relatively deficient in the ash of most of these samples. Cobalt is present in relatively large amounts in the ash of all but one oil sample.

TABLE 8.—*Generalized descriptions of rocks from which oil samples were taken in three sedimentary basins in California*

Age	Description of lithology	Thickness (feet)	Remarks
Los Angeles Basin[1]			
Quaternary	Nonmarine sand, gravel, and clay	0- 1,000	
Pliocene	Sandstone, siltstone, and gray, green, and brown shale.	800- 1,700	Oil sample from Vickers-Machado zone (lower part of Pico formation and upper part of Repetto formation of former usage) at Inglewood field; Oil sample from Ranger zone in Repetto formation of former usage at Wilmington field.
Miocene	Hard brown shale, sandstone, and conglomerate; layers of diatomaceous shale in top part.	4,000- 6,000	

See footnotes at end of table.

TABLE 8.—*Generalized descriptions of rocks from which oil samples were taken in three sedimentary basins in California*—Continued

Age	Description of lithology	Thickness (feet)	Remarks
San Joaquin Valley [2]			
Quaternary	Clay, sand, and conglomerate; buff to gray and greenish-gray, poorly cemented and poorly sorted. Almost entirely alluvial-fan and lacustrine material.	8,000-10,000	
Pliocene	Soft greenish-gray claystone and interbedded permeable sand; upper third nonmarine and marine; lower two-thirds marine, particularly in central basin areas.	8,000- 9,000	Oil sample from *Mulinia* zone (lower Pliocene) of Etchegoin formation at Elk Hills field.
Miocene	Brown and gray clay shale and hard siliceous shale, with numerous permeable sandstone and conglomeratic sandstone members; marine with Foraminifera, diatoms, and megafossils, except uppermost and basal nonmarine members along eastern and southeastern borders. Basaltic and andesitic flows and intrusions in lower part along southeastern border.	12,000-13,000	Oil sample from Potter sand (upper Miocene) at Midway field; Oil sample from upper Miocene sand at Coles Levee field; Oil sample from sandstone of the Temblor formation (middle Miocene) at Coalinga field; Oil sample from Olcese sand (lower and middle Miocene) at Ant Hill field.
Oligocene and late Eocene.	Gray and brown shale and hard siliceous shale with some permeable sand in local border areas; marine with Foraminifera and megafossils, except for red and green nonmarine beds in Oligocene of eastern and southeastern borders.	8,000- 9,000	
Early Eocene and Paleocene.	Gray shale with some sand beds that are locally thick and very permeable, particularly in Coalinga and southern border areas. Marine, with Foraminifers and megafossils.	5,000- 6,000	Oil sample from Weyant sand (Paleocene?) at Helm field.
Late Cretaceous	Upper part is dark-gray siliceous and calcareous foraminiferal shale and clay shale with local sand; middle and lower parts massive concretionary sandstone, conglomerate, and dark shale with intercalated sandstone. Marine.	25,000+	
Santa Maria Basin [3]			
Quaternary	Sand, gravel and silt; alluvial and dune deposits.	330	
Pleistocene	Sand and gravel; marine and nonmarine terrace deposits.	1,000	
Late Pliocene and early Pleistocene.	Sand, gravel, clay, and limestone	4,500	
Middle(?) and late Pliocene.	Sandstone, conglomerate, siltstone, and mudstone.	5,000	
Late Miocene to middle Pliocene.	Sandstone, conglomerate, siltstone, mudstone, diatomaceous mudstone, and porcelaneous mudstone, claystone, and shale.	8,000	
Middle and late Miocene.	Porcelaneous shale, laminated diatomite, chert, cherty shale, phosphatic shale, and silty shale.	5,000	Oil sample from Monterey shale at Santa Maria Valley field.
Early and middle Miocene.	Mudstone, siltstone, sandstone, and conglomerate.	5,600	

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[1] Data from Driver, 1943, p. 306-309; Bartosh, 1938, p. 1048-1079; Murray-Aaron and Pfeil, 1948.

[2] Data from Hoots and others, 1954, p. 113.

[3] Data from Woodring and Bramlette, 1950, p. 10-11.

The ash of the oil sample from the Monterey shale at Santa Maria Valley field contains more nickel, gallium, molybdenum, chromium, and titanium than do other California samples. All of these metals have been specified in this investigation to be the metals most likely present in crude oils in porphyrins or organic complexes, and therefore this oil from Monterey shale may be unusually rich in such complexes.

The very heavy, black, asphaltic oils from California have relatively high ash contents. The oil sample from Inglewood field contains the largest amount of ash of any California sample, which accounts for the relatively large (38 ppb) calculated uranium content of the oil. The uranium content in the ash of the other California samples is within the range for most of the samples analyzed.

GENERAL SUMMARY

In the comparison of metals in oil samples from the various regions, previously reported correlations of vanadium, nickel, gallium, and molybdenum with type of oil and age of host rock are confirmed. However, no significant association of metals with any of the lithologic types of reservoir rock is noted.

Relatively high proportions of uranium and other metals in the ash of crude oil produced from the Bartlesville sand in northeastern Oklahoma are noted and carbonaceous material is suggested as a possible source; however, the uranium content in general seems to be independent of the type of reservoir rock.

LOCALIZATION OF URANIUM BY ORGANIC MATERIAL

The intensive search for uranium in the recent years after World War II has revealed the widespread association of uranium with hydrocarbons of natural origin. High concentrations of uranium have been found in association with carbonaceous debris in sandstone, lignitic coals, and asphaltite pellets; the uranium content of organic-rich shales has been noted and studied by many investigators. In this investigation uranium was not found in crude oil in significant quantities.

In reconnaissance for high concentrations of uranium, oil samples were collected from western Colorado, eastern Utah, and Wyoming, areas which include many uranium mines; wherever possible oil samples were collected from lithologic units known to contain ore. Oil samples were collected from reservoirs in Wyoming, Utah, Nevada, and California that are rich in volcanic constituents. These samples were collected in order to test the possibility that crude oil might concentrate uranium from volcanic sediments, just as the lignite beds in South Dakota are believed to have concentrated uranium leached from tuff beds (Denson, Bachman, and Zeller, 1959; Denson and Gill, 1956). No high concentrations of uranium were found in the crude-oil samples nor is there indication that crude oils from rocks in uraniferous regions or from rocks rich in volcanic materials are enriched in uranium in comparison with other crude oils.

These data indicate a significant difference in the uranium-collecting properties of crude oils and those of lignitic or carbonaceous materials. Szalay (1952) not only demonstrated that lignites and other woody materials can extract uranium from aqueous solution, but also found that humic acids are the agents responsible for this extraction. Thus a constituent common only in carbonaceous material can cause enrichment in uranium content; no enrichment of uranium in crude oil would be expected by this mechanism.

Although it seems that petroleum is not an effective agent for the extraction and concentration of uranium from aqueous solution, as are lignites and other carbonaceous material, the results of soaking uranium ore in crude oil indicate that crude oil can leach uranium directly from sandstone. The possibility of finding high concentrations of uranium in crude oil, however, is probably limited by the fact that radiation can alter liquid hydrocarbons.

Lind and Bardwell (1926) first experimented with the effects of radiation on hydrocarbons and reported alteration of compounds with the liberation of hydrogen. Whitehead (1954) confirmed these results. The net effect of irradiation of liquid hydrocarbons, therefore, is to decrease the hydrogen-carbon ratio and to tend toward solid carbon. Petroleum, if subject to radiation from uranium in the crust of the earth for a sufficient period of time, should be altered to a plastic or solid form. Such an origin has been suggested for the uranium-hydrocarbon mixture called thucholite (Davidson and Bowie, 1951).

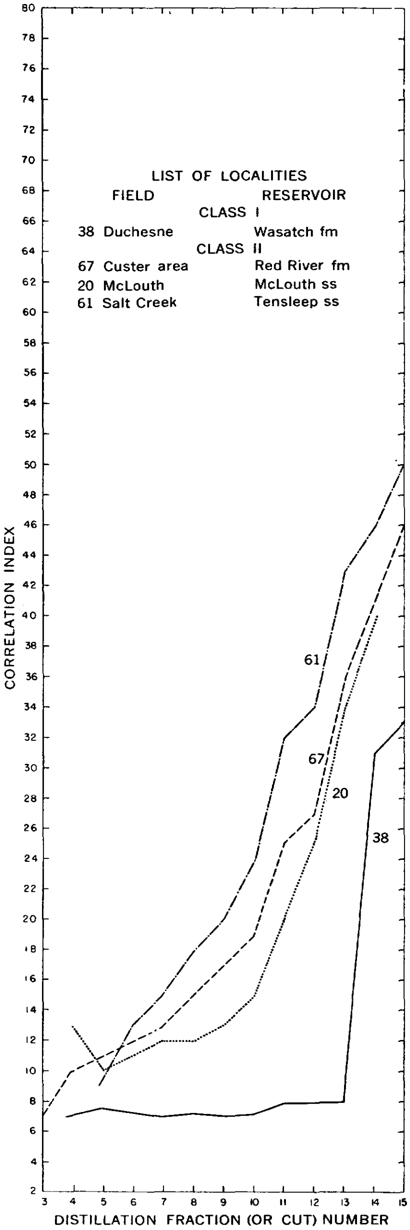

FIGURE 11.—Oil classes I and II.

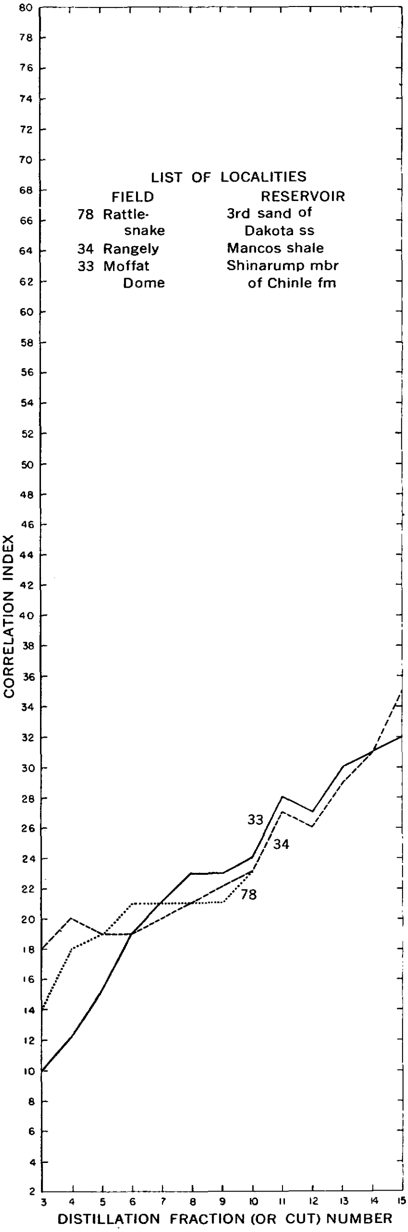

FIGURE 12.—Oil class III.

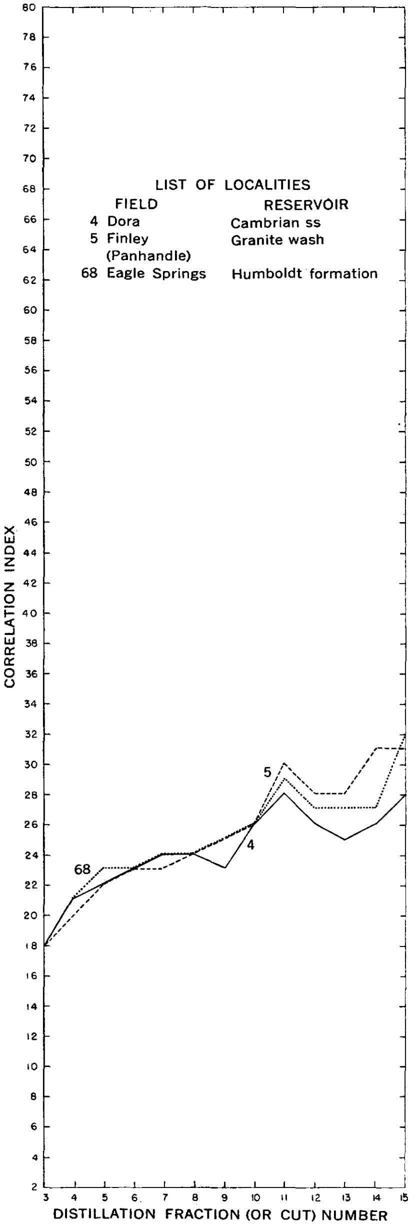

Figure 13.—Oil class IV*A*.

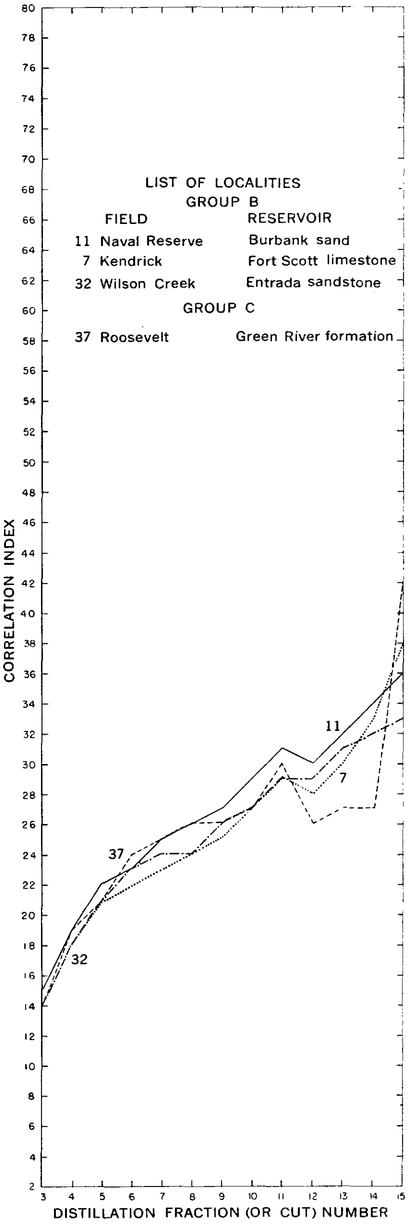

Figure 14.—Oil class IV*B* and *C*.

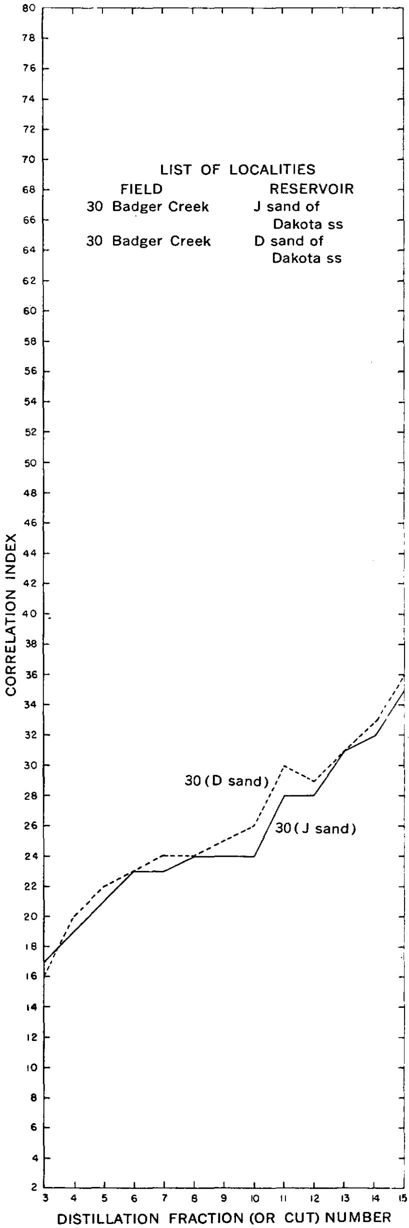

Figure 15.—Oil class IV*D*.

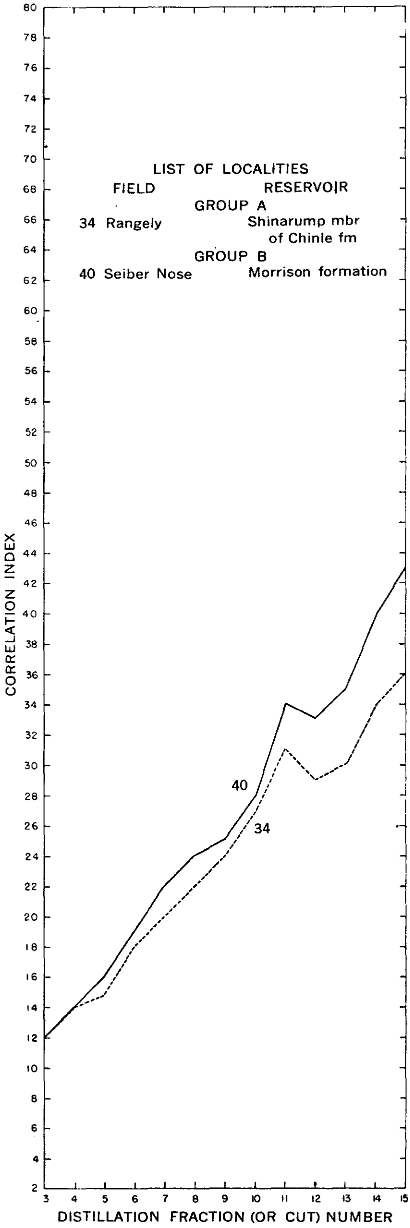

Figure 16.—Oil class V*A* and *B*.

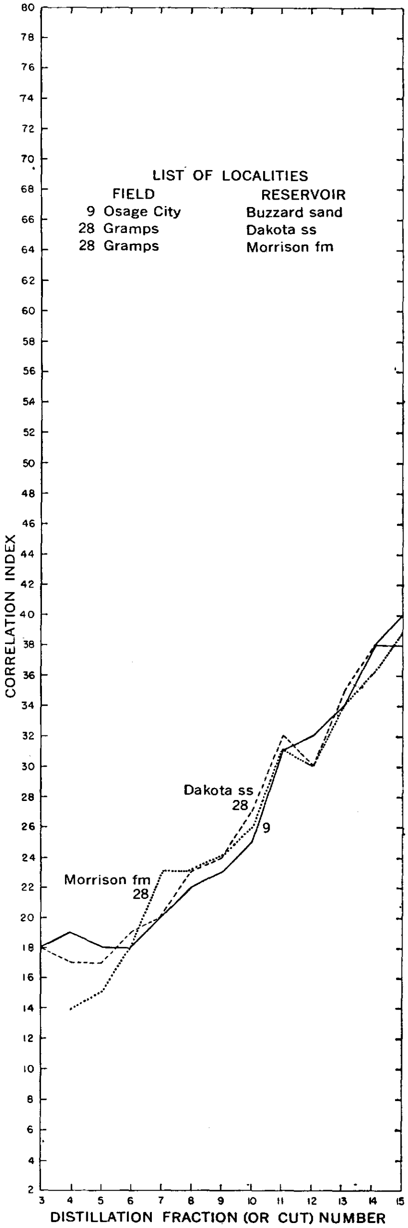

FIGURE 17.—Oil class *VC*.

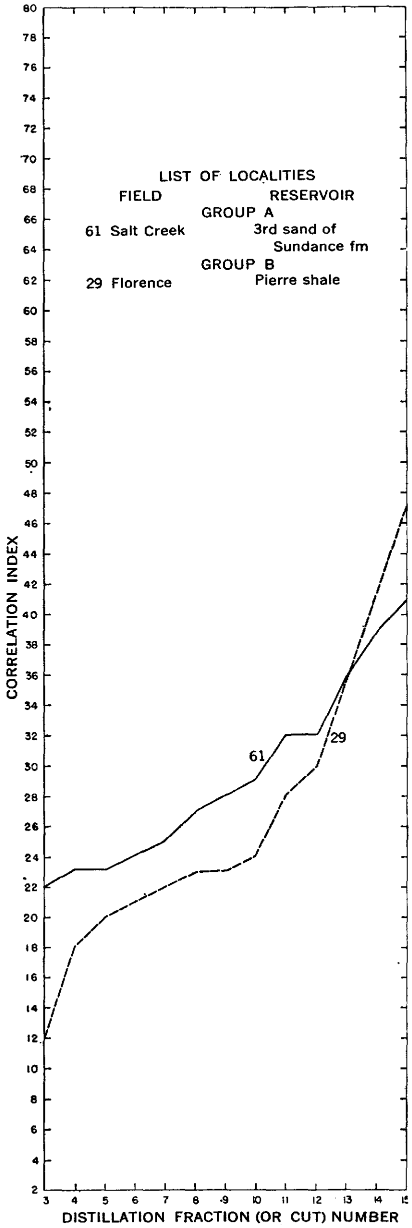

FIGURE 18.—Oil class *VIA* and *B*.

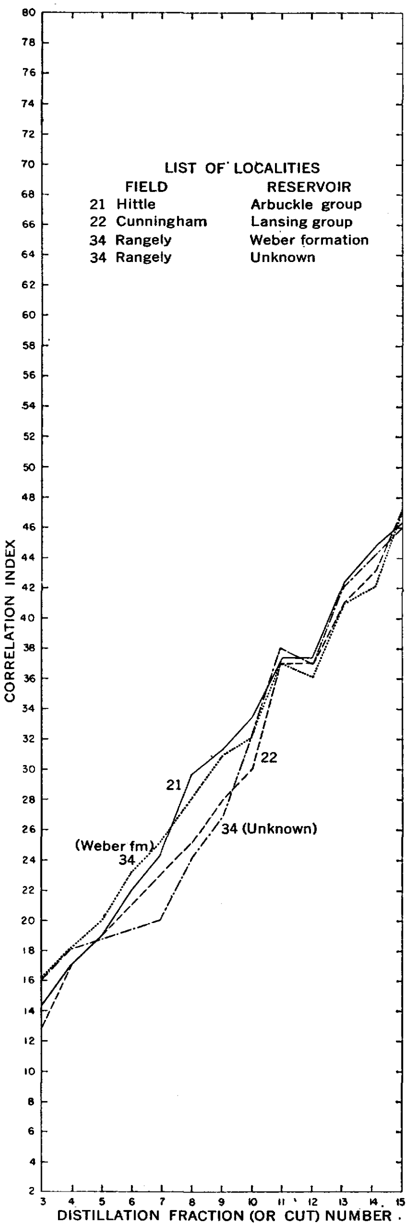

FIGURE 19.—Oil class VII*A*.

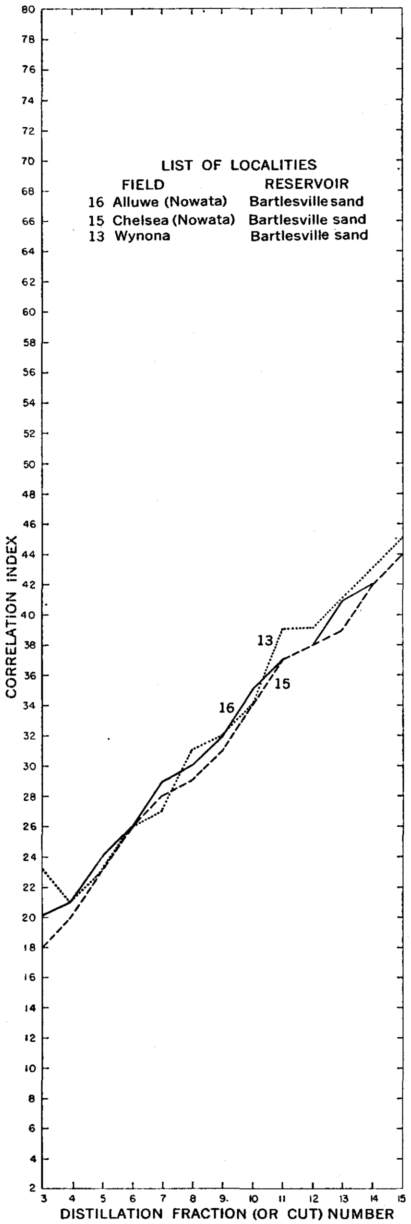

FIGURE 20.—Oil class VII*B*.

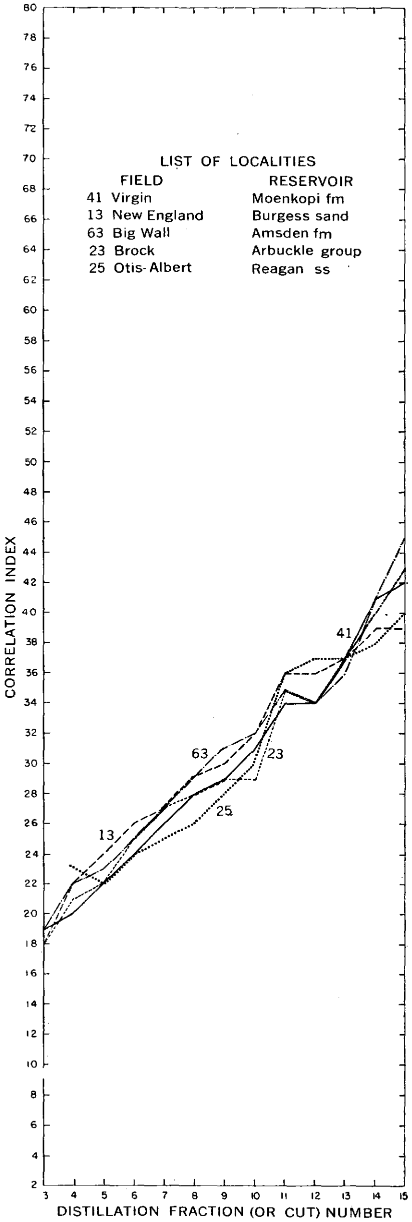

FIGURE 21.—Oil class VIII.

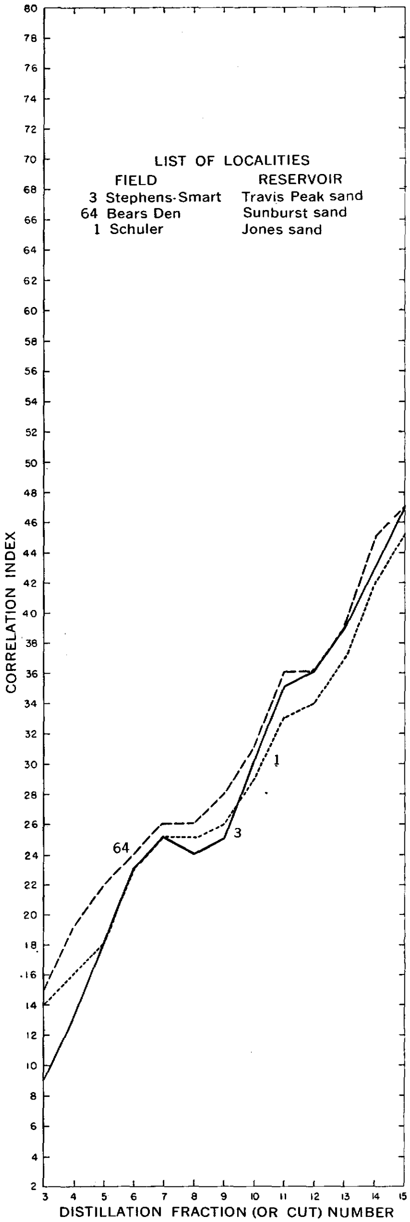

FIGURE 22.—Oil class IXA.

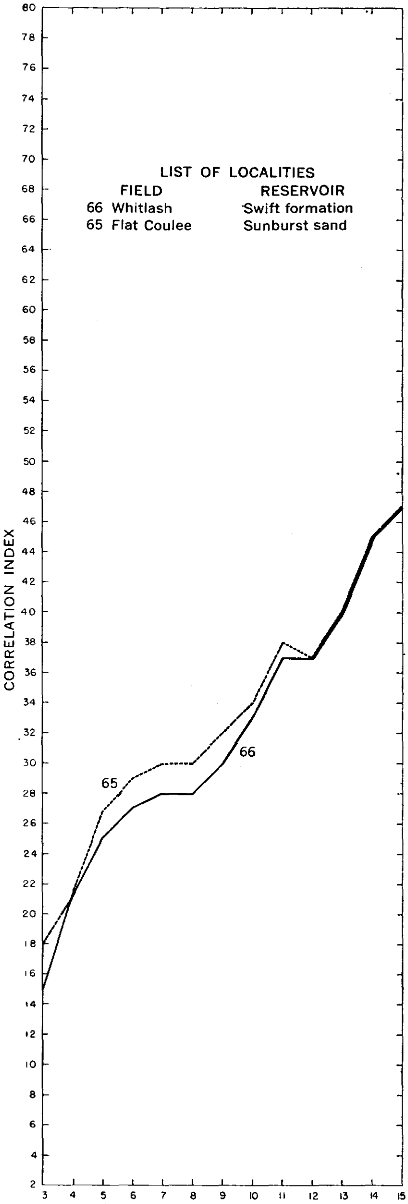

Figure 23.—Oil class IX*B*.

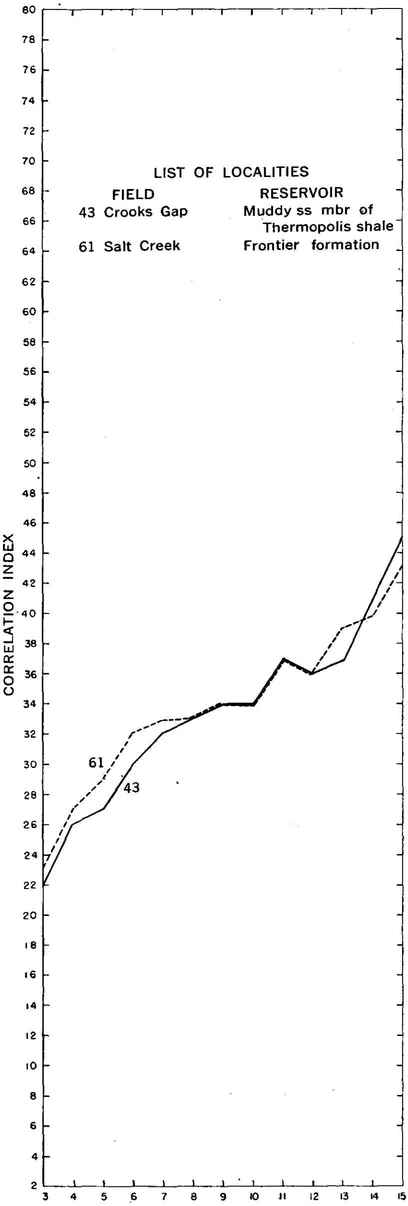

Figure 24.—Oil class X.

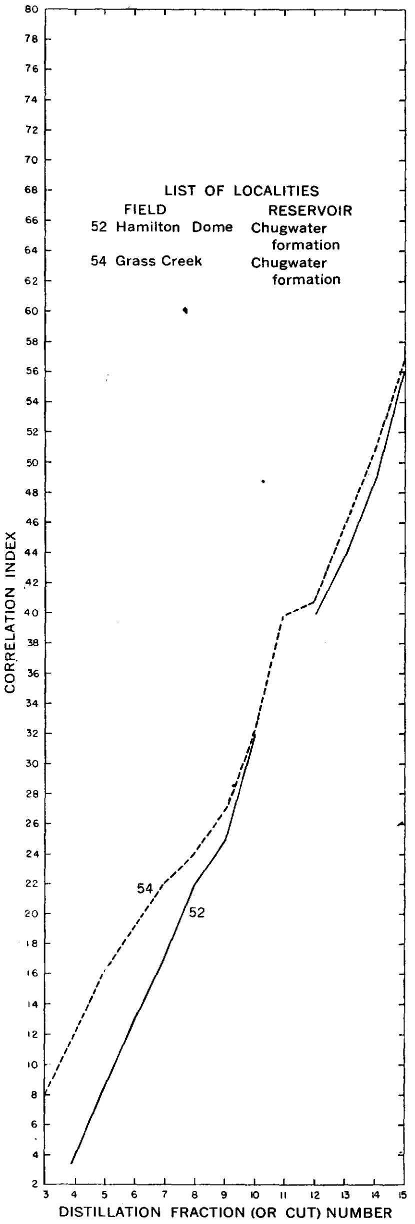

Figure 25.—Oil class XI.

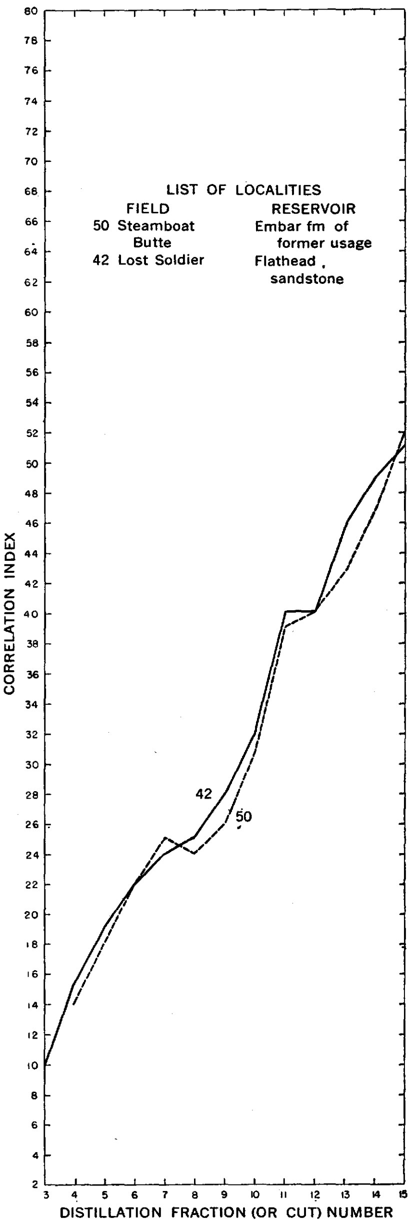

Figure 26.—Oil class XIIA.

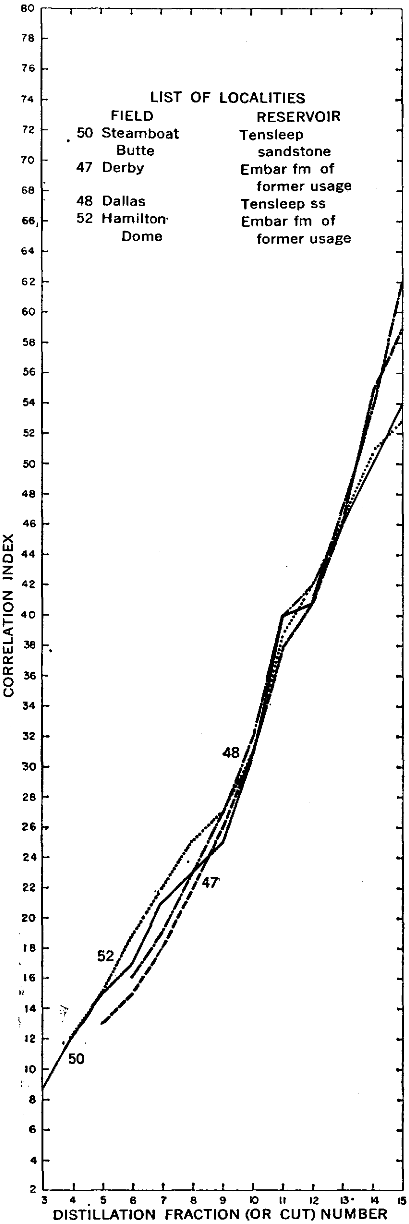

Figure 27.—Oil class XII*B*.

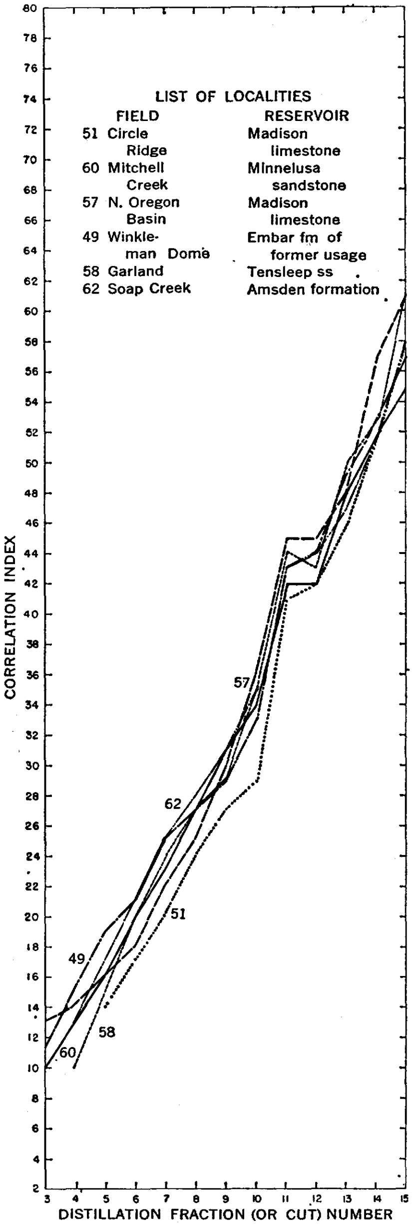

Figure 28.—Oil class XII*C*.

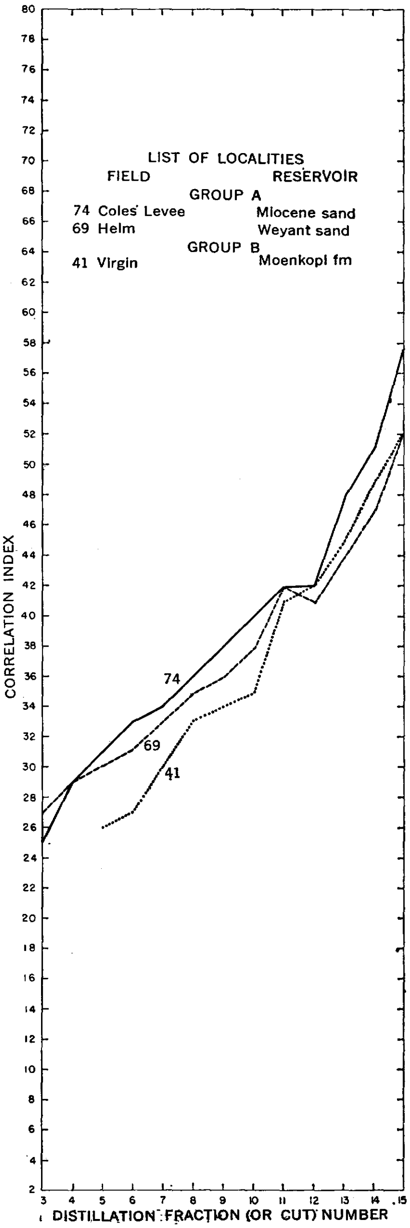

FIGURE 29.—Oil class XIII.

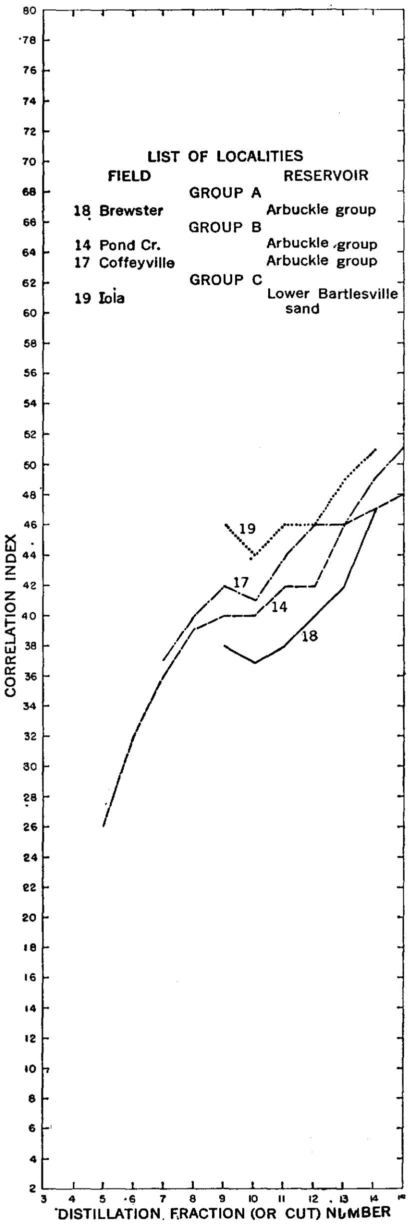

FIGURE 30.—Oil class XIV.

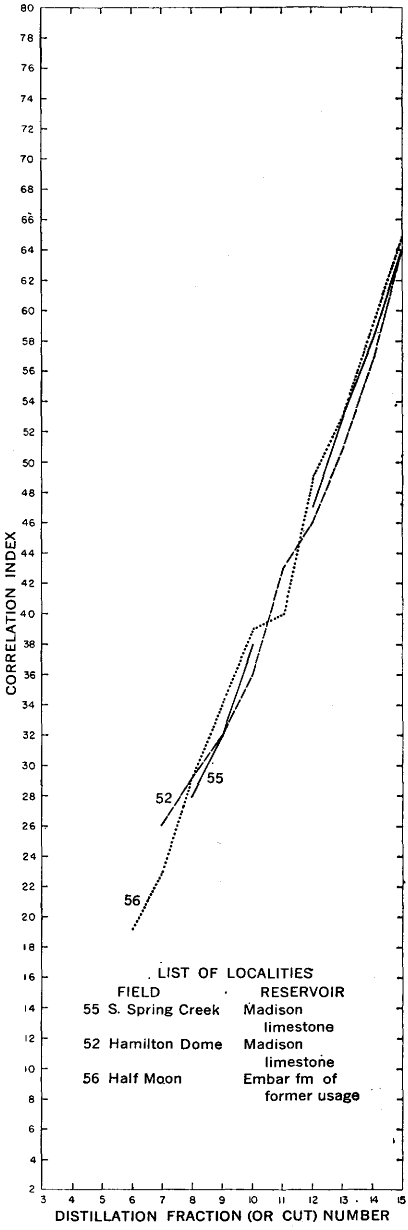

FIGURE 31.—Oil class XV.

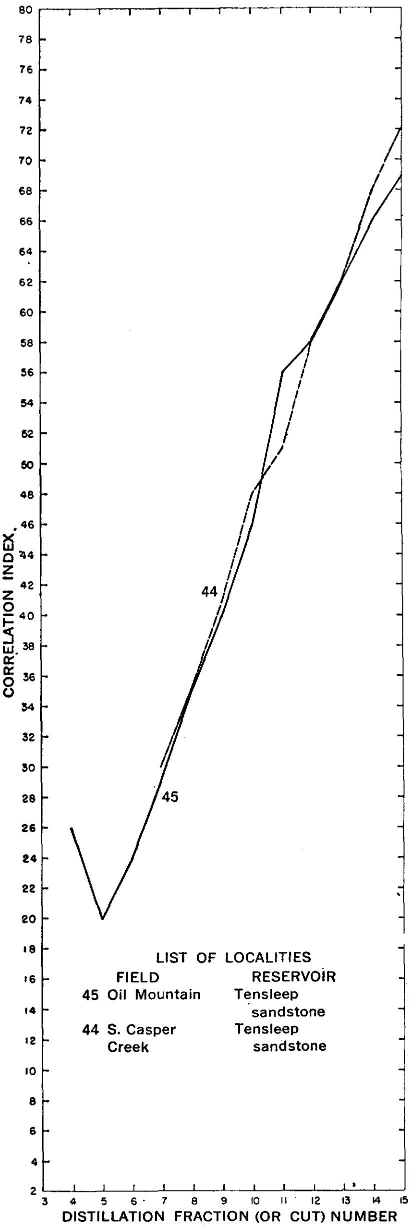

FIGURE 32.—Oil class XVIA.

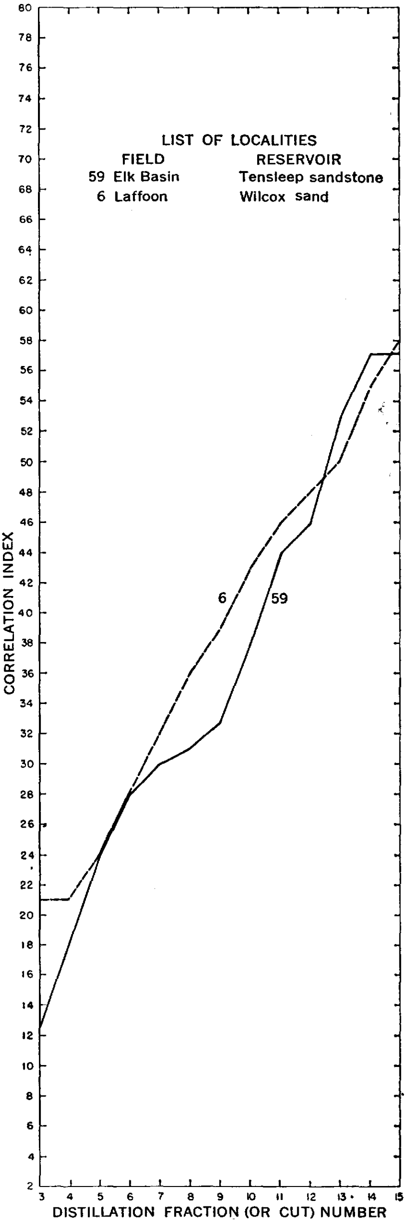

FIGURE 33.—Oil class XVIB.

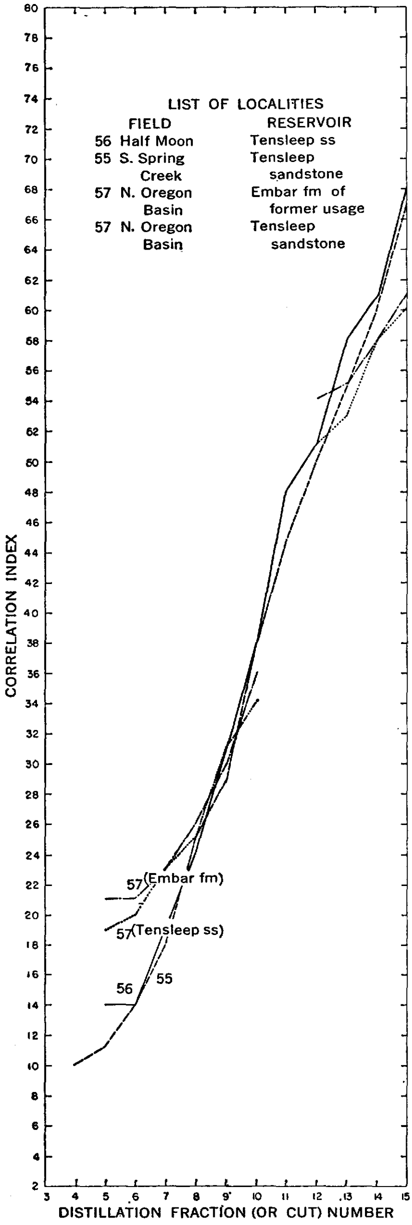

FIGURE 34.—Oil class XVIIA.

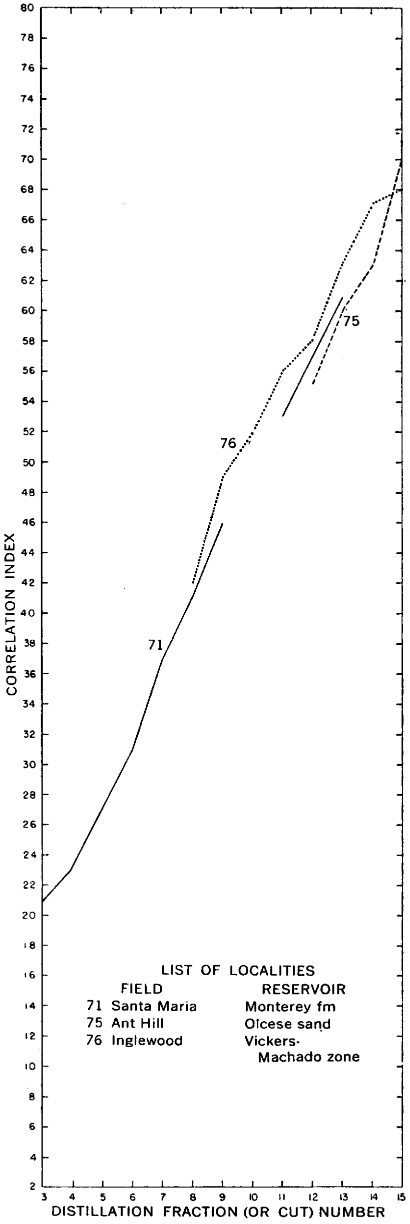

FIGURE 35.—Oil class XVII*B*.

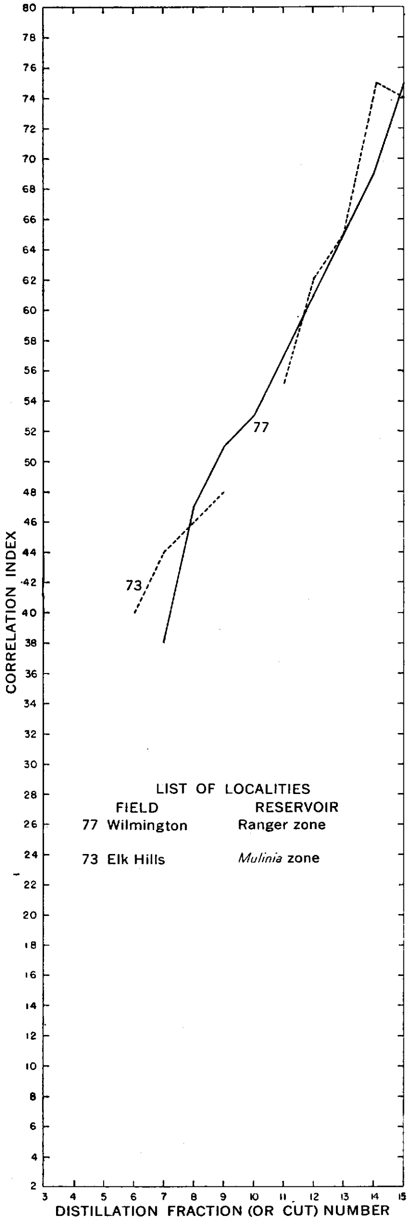

FIGURE 36.—Oil class XVIII*A*.

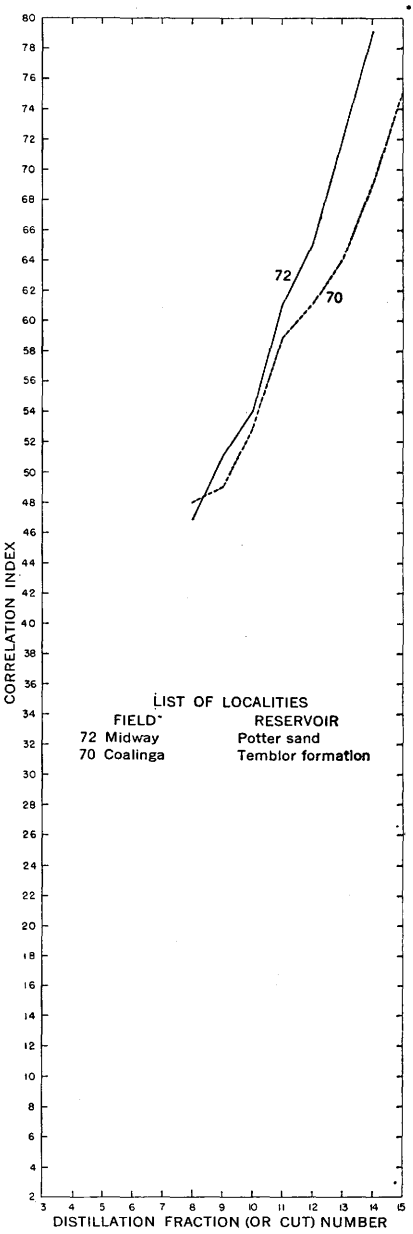

FIGURE 37.—Oil class XVIII*B*.

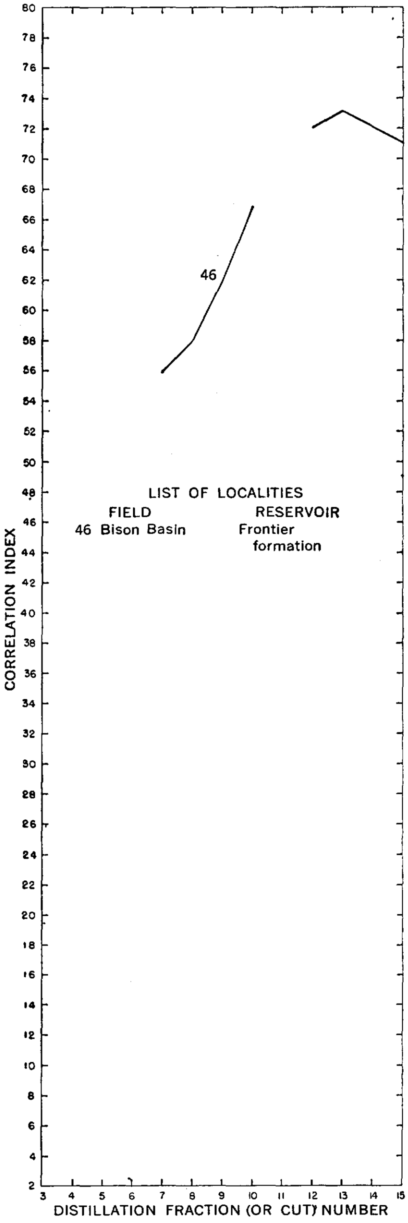

FIGURE 38.—Oil class XIX.

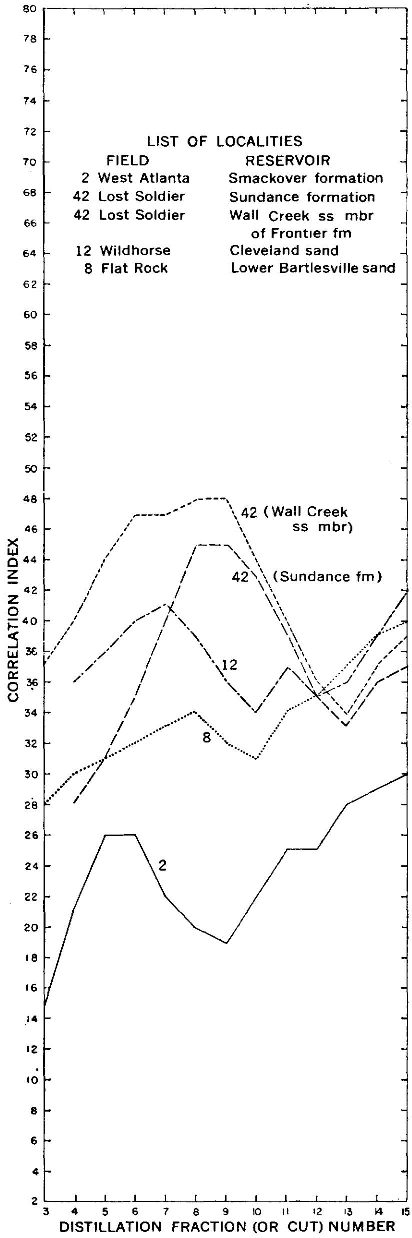

FIGURE 39.—Oil class *S*.

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