Table V. Fractional Ultracentrifugation Method May Permit Separation of Asphaltenes of Varying Vanadium Content

			Metals				
Fraction	Sp. Gr. 60/60 ° F.	Asphaltenes, wt. %	V, p.p.m.	Ni, p.p.m.	N_2, wt. %	Sulfur, wt. %	C. Res., wt. %
Feed	0.853						
IV D Top.	0.840	0.17	2.6	1.0	0.073	1.03	0.7
IV D Bot.	0.851	0.22	3.6	2.2	0.092	1.19	0.9
IV C Top.	0.852	0.34	6.2	2.2	0.114	1.22	1.2
IV C Bot.	1.863	0.61	8.6	3.5	0.134	1.49	1.8
IV B Top	0.866	1.01	4.2	1.7	0.136	1.57	1.4
IV B Bot.	0.878	2.15	15.3	4.8	0.170	1.85	2.6
Sepr. factor, Bot./Top	1.04	12.5	5.9	4.8	2.3	1.8	3.7

A fractional ultracentrifugation of West Texas crude oil (Figure 3) is summarized in Table V. Here, when data from both techniques were plotted on a common basis in Figure 4, the vanadium to asphaltenes ratio was the same in most cases. Only the heaviest portions (IV B) from the fractional technique had a metals content considerably lower than expected. This deviation could be explained either by some analytical or experimental error or by the fact that asphaltenes vary in vanadium content. If this were true, the fractional technique, in addition to speeding separations (compare data in Table I with data in Table V), could probably be used to fractionate asphaltenes.

The carbon residue of the lower centrifuge fractions are higher than those of the top layers and correlate well with asphaltenes and metals content. This is an additional indication that the colloidal particles of petroleum are of an asphaltic nature.

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Metal Content of Twenty-Four Petroleums

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VARIED INFORMATION has been published concerning the metal content of petroleums (*4, 6, 14, 17*), but the data are limited for crude oils from definitely known geographic and geologic sources. The samples analyzed in many instances have been mixtures or have been only partially identified. For this investigation 24 petroleums were collected by the Geological Survey and analyzed semiquantitatively for 27 elements and quantitatvely for vanadium, nickel, copper, and uranium. In addition, they were analyzed by the routine Bureau of Mines crude oil analysis method (*18*). These petroleums can be associated geographically with the oil field and geologically with the producing formation.

For many years the Bureau of Mines at its Laramie, Wyo., and Bartlesville, Okla., Petroleum Research Centers has been studying the properties of crude petroleums from the standpoint of utilization. The Geological Survey has studied the occurrence of petroleum from the standpoint of geochemistry and has been particulary interested in the relationships between chemical characteristics of oils and their geological assocition. The crude oil analyses discussed in this report were made by the Bureau of Mines; trace metal analyses were made by the Geological Survey.

The analytical data were examined for relationships between the four metals. Ash contents of the oils, roughly proportional to the total metal contents, were correlated with carbon residue, nitrogen, and sulfur contents. The effects of the geographical distribution and the geological age of the reservoir rocks were also considered. Although the data are too few to establish definite relationships, apparently the oils from older formations are more uniform in their proportions of contained metals.

A crude oil from Wilmington, Calif., which has been under study by Americal Petroleum Institute Research Project 52 at the Bureau of Mines Laramie Petroleum Research Center, was separated into fractions using solvent precipitation, and adsorption (*10*), and the fractions were analyzed for metals. In this way some information was gained about the association of metals with the other constituents of the crude oil, and the way in which separation processes may affect the distribution of the metals.

SIGNIFICANCE OF METALS

Interest in the metal content of petroleum arises for several reasons. Some metals are detrimental to cracking catalysts, causing reduced yields of gasolines. Some evidence suggests that the stability of petroleum products may be influenced by the metal content. Of more fundamental interest, trace metal analysis may be useful for the identification of the source of the oil and may ultimately give clues to mechanisms of formation of petroleum. The crude oils were investigated both as possible sources of uranium, and to see if trace metal analyses might be useful as geochemical indicators of uranium mineralization.

OCCURRENCE OF METALS

A semiquantitative spectrographic examination by the Geological Survey of the 24 crude oils revealed the presence of 27 elements. In addition, uranium was determined chemically. Figure 1 shows the number of oils containing various levels of concentration of each of the 28 elements indicated by the numbers inserted on the bars. Most of the oils contain vanadium as the major metallic constituent with Nickel second and copper third. The levels of concentration are measured as weight per cent metal in the ash from the oils.

The type of combination by which a metal is held in the oil is somewhat obscure. The presence of porphyrins and their metal complexes in petroleums has been shown (*2, 5*), but the amount of porphyrins measured has been small as related to the total metal content of the oil. This indicates either that only part of the porphyrin content has been measured or that other types of combination occur.

The presence of metal salts of petroleum acids may account for the metal content, but thus far no compounds of this type have been identified. The presence of inorganic salts in solution in emulsified water in petroleum is common, and these salts should be eliminated before analysis.

Garner (*8*) has stated that iron and sodium are present as inorganic salts and can be removed by water extraction. He has also shown that nickel and vanadium can be concentrated in the propane-isoluble fraction of the oil.

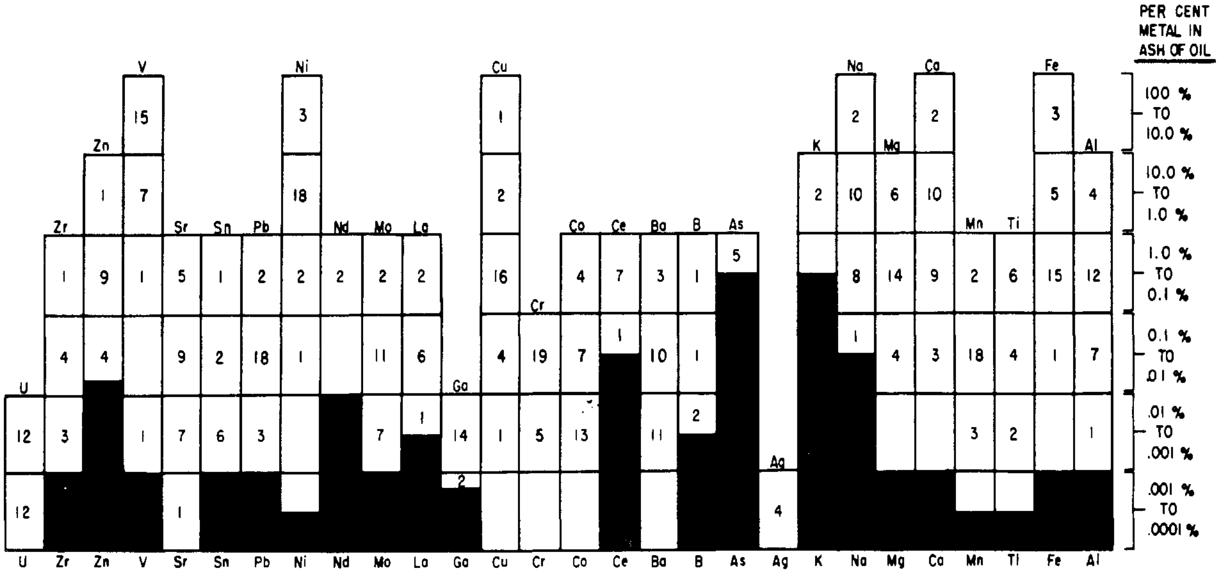
PROCEDURE

Crude-oil samples were collected from Midcontinent, Rocky Mountain, and West Coast fields. Many of the oils were selected on the basis of nitrogen contents to test the assumption that metals and nitrogen were associated. Portions of each oil were analyzed by the routine method of the Bureau of Mines and for trace metals by the Geological Survey. The sample of Wilmington (Calif.) crude oil and four fractions obtained by solvent extraction and adsorption also were included in the work. The method of preparing these fractions has been described by API Research Project 52 (*10*), shown graphically in Figure 2.

Crude Oil Analysis. The Bureau of Mines routine crude oil analysis method (*18*) has been applied to more than 8000 samples of crude oil, providing a background for comparison with newly discovered oils. The method includes determination of properties such as gravity, viscosity, sulfur content, color, and pour point. The oil then is distilled at atmospheric pressure to 275° C., and at a reduced pressure of 40 mm. of mercury to 300° C., taking fractions at 25° intervals. Such properties as gravity, viscosity, aniline point, and cloud point are determined on certain fractions, and carbon residue and gravity are determined on the residuum. From these measurements, various values are calculated. In addition to the routine crude oil analysis, values were obtained for nitrogen content of the oils.

Trace Metal Analysis. Difficulties in determining trace metals are readily apparent. The low content of metals makes a concentration step necessary. The possibility exists of losses of volatile metallo-complexes during the dry ashing of the oil (*7*). The use of wet-ashing procedures may introduce, from the reagents, greater amounts of metals than were originally present. Highly sensitive methods must be used for measurement of the metals, and spectrographic methods appear the most convenient.

The method of analysis used by the Geological Survey is as follows: The oil is washed with distilled water and filtered to remove soluble salts. The oil is then reduced to an ash by a dry-ashing technique (*6*). The ash is divided; one portion is analyzed fluorimetrically (*9*) for uranium content, and the other portion is analyzed spectrographically (*15*) for vanadium, nickel, and copper.



KEY

NUMBERS IN SQUARES INDICATE NUMBER OF OILS HAVING THAT MAGNITUDE OF THE METAL PRESENT IN THE ASH

■ LIMIT OF DETECTION

Figures 1. Distribution of trace metals in the ashes of 24 Crude oils

Table I. Metal Content of 24 Petroleums

No.	Location: State	Location: Field	Metal Content, P.P.M.: V	Ni	Cu	U
1	Ark.	Schuler	15	10	0.34	0.0025
2		Stevens-Smart	1.8	2.1	1.4	0.00048
3	Calif.	Wilmington	35	35	0.22	0.00088
4	Colo.	Gramps (Dakota)	0.42	0.76	0.03	0.00017
5		Gramps (Morrison)	0.96	1.6	0.03	0.00050
6	Kan.	Brewster	2.6	1.7	0.32	0.00028
7		Coffeyville	3.2	1.0	0.04	0.00024
8		Iola	16	9.0	0.09	0.00260
9	Mont.	Big Wall	24	13	0.12	0.00012
10	N.M.	Table Mesa	0.002	0.03	1.7	0.00054
11	Okla.	Kendrick	0.84	0.22	1.3	0.00032
12		Laffoon	44	20	0.18	0.0020
13	Utah.	Roosevelt	0.16	3.0	0.05	0.00004
14	Wyo.	Elk Basin	38	9.2	0.16	0.00030
15		Grass Creek	106	21	0.38	0.00076
16		Halfmoon (Embar)	99	28	1.5	0.0017
17		Halfmoon (Tensleep)	51	0.23	0.23	0.00069
18		Hamilton Done (Curtis)	106	24	0.38	0.0015
19		Hamilton Dome (Embar)	55	9.1	0.19	0.00036
20		Hamilton Dome (Madison)	106	27	0.27	0.0011
21		Lost Soldier	0.56	0.72	0.03	0.00024
22		Oregon Basib, N. (Embar)	60	11	0.05	0.0065
23		Oregon Basin, N. (Tensleep)	72	15	0.40	0.013
24		Oregon Basin, N. (Madison)	77	22	0.11	0.0077

Table II. Metal Content and Other Properties of 24 Petroleums

Sample No.	Reservoir Rocks a	Ash %	Metals, % of Ash: V	Ni	Cu	U	Carbon Residue,[b] %	Sulfur, %	Nitrogen, %
3	Terminal sand (T)	0.022	16	16	0.1	0.0004	6.5	1.59	0.65
13	Green River fm. (T)	0.004	0.41	7.6	0.13	0.0001	2.7	0.14	0.169
21	Wall Creek ss. (C)	0.001	5.6	7.2	0.26	0.0024	1.1	0.14	0.054
4	Dakota ss. (C)	0.001	4.2	7.6	0.26	0.0017	2.4	0.22	0.130
10	Dakota ss. (C)	0.003	0.007	0.09	5.6	0.0018	0.1	0.10	0.01
2	Travis Peak ss. (C)	0.004	4.4	5.4	0.84	0.0012	6.4	2.05	0.077
1	Jones sand (J)	0.041	3.7	2.5	0.35	0.0006	4.1	1.58	0.075
5	Morrison fm. (J)	0.001	9.6	16	0.26	0.005	2.6	0.23	0.113
15	Curtis ss (Tr)	0.038	28	7.6	0.10	0.0002	8.2	2.59	0.30
18	Curtis ss. (Tr)	0.038	28	6.4	0.10	0.0004	10.3	3.07	0.33
16	Embar Is. (Pe and Tr)	0.058	17	4.8	0.26	0.0003	10.9	4.11	0.43
19	Embar Is. (Pe and Tr)	0.012	46	7.6	0.16	0.0003	7.8	2.68	0.32
22	Embar Is. (Pe and Tr)	0.015	40	7.6	0.03	0.0043	7.3	3.03	0.31
11	Fort Scott Is. (P)	0.001	8.4	2.2	13	0.0032	0.8	0.17	0.046
8	Upper Bartlesville ss. (P)	0.130	1.2	0.69	0.007	0.0002	6.9	0.74	0.279
14	Tensleep ss. (P)	0.010	38	9.2	0.16	0.0003	3.7	1.89	0.14
17	Tensleep ss. (P)	0.023	22	0.10	0.10	0.0003	11.2	4.08	0.43
24	Tensleep ss. (P)	0.018	40	8.2	0.22	0.0075	7.2	3.20	0.30
9	Heath fm. (M)	0.012	20	11	0.10	0.0001	5.0	0.77	0.146
20	Madision Is. (M)	0.038	28	7.0	0.07	0.0003	11.4	3.93	0.41
23	Madision Is. (M)	0.035	22	6.4	0.03	0.0022	9.0	3.18	0.35
12	Wilcox sand (O)	0.022	20	9.2	0.08	0.0009	8.6	1.05	0.38
6	Arbuckle Is. (Ca and O)	0.002	13	8.4	1.6	0.0014	4.7	0.59	0.117
7	Arbuckle Is. (Ca and O)	0.002	16	5.0	0.22	0.0012	2.4	0.61	0.125

[a] Period or system indicated in parentheses: T, Teriary; C, Cretaceous; J, Jurassic; Tr, Triassic; Pe and Tr, Permian and Triassic; P, Pennsylvanian; M, Mississippian; O, Ordovician; Ca and O, Cambrian and Ordovician. These names were used by the producers at the time the oil samples were collected; many of them are drillers' terms, and none are necessarily endorsed as geologic names by the U.S. Geological Survey. [b] All carbon residue values are reported as Conradson values.

RESULTS

Quantitative spectrographic determinations for vanadium, nickel, and copper, and chemical determinations of uranium, are given in Table I. The ranges of values for the content of these elements in oil as computed from their content in the ash are: vanadium, 0.002 to 106 p.p.m.; nickel, 0.03 to 35 p.p.m.; copper, 0.03 to 1.7 p.p.m.; and uranium, 0.00004 to 0.013 p.p.m. The vanadium and nickel contents of the ash are generally greater than the copper content, although the ranges of values for these three elements overlap considerably.

Table III. Weight of Metals in Fractions from Wilmington Crude Oil

	Weights, Parts Per Million: V	Ni	Cu	U	Ash
Crude oil	36	36	0.2	0.0009	220
Deasphaltened oil	18	18	0.4	0.002	120
Asphaltenes	330	300	41	0.008	2800
Hydrocarbon eluate	0.04	0.04	0.11	0.0002	22
Nitrogen concentrate	46	58	26	. . .[a]	1600

[a] Not determined.

Table II, arranged in order of increasing age of the producing formation, gives additional information on the 24 oils. The ash contents range from 0.001 to 0.130%. As the metal content appears to be associated with the asphaltic portions of the oil, the carbon residue, sulfur, and nitrogen contents are thought to be the most pertinent determinations in the crude-oil analysis. Accordingly, these values are listed in the table.

Figure 2 shows the distribution of the vanadium and nickel in the fractions resulting from the process of solvent precipitation with *n*-pentane and adsorption on florisil. The figures in parentheses indicate the percentage by weight of the crude oil that each fraction represents, and the weight per cent of ash in each fraction also is given. Table III gives the weights of four metals and the ash in each of the fractions. The weight balances are poor, probably because of contamination in the processing of the sample. However, the data indicate the general pattern of distribution of metals and ash resulting from the separation procedures.

A semiquantitative analysis for many of the metal components of the same crude oil and its fractions is shown in Figure 3.

DISCUSSION

An important question is whether the quantity of metals present can be estimated from other characteristics of the oil. The total metal content is roughly proportional to the weight of ash, so that one approach is to look for a correlation between the amount of ash and other measured characteristics. If the metals are associated largely with the asphaltic portions of the oil, carbon residue and sulfur are properties that might correlate with metal content. The establishment of the porphyrin-metal-complex occurrence suggests that nitrogen content might correlate with the ash. Three of these ratios, carbon residue to ash, nitrogen to ash, and sulfur to ash, as well as the vanadium to nickel ratio, are shown in Table IV, where the oils are arranged in order of increasing age of reservoir rocks. The carbon residue ash ratios for 14 of the 24 oils fall between 200 and 1,000. The nitrogen-ash ratios for 13 oils lie between 1 and 20. The sulfur-ash ratios for 13 of the oils range from 50 to 200. Although these ratios fall within relatively narrow limits, the oils represent various geographic locations and geologic formations. Nine of the oils fall in the above-mentioned restricted groups for each of the three ratios. This might be expected from the correlation that has been reported (*1*) between carbon residue and nitrogen. If most of the metals occur in a porphyrin-metal complex, the nitrogen content might correlate with the ash. Whether this nitrogen is in other types of combination or there is a large amount of uncombined porphyrin is highly significant. If the latter is true, it might indicate that the metals present were derived from the original source material of the oil rather than from the reservoir rocks or the rocks through which the oil may have migrated.

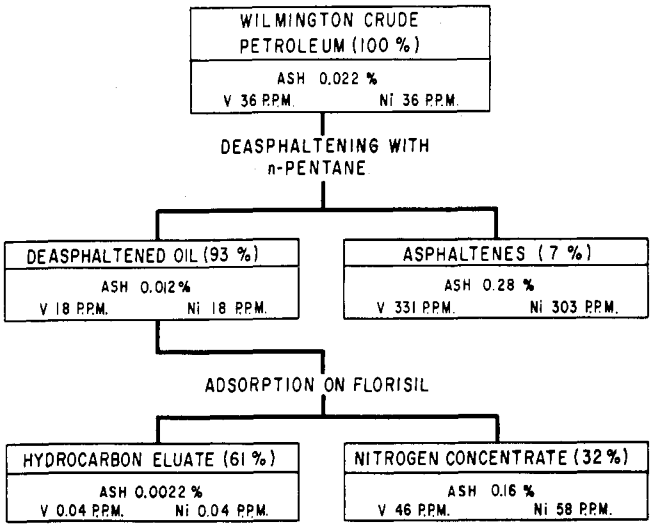


Figure 2. Schematic representation of metal distribution in separation processes

For the oils younger than Triassic, less than 30% fall within the limits described above, but for the oils from Triassic or older formations almost 70% are included. Thus the older oils studied fit the correlations better, possibly indicating a closer approach to equilibrium conditions.

Katchenkov (*13*) observed a relative constancy of the ratio of vanadium to nickel in crude oils in Russia. This ratio was about 3 to 1 for crude oil from Paleozoic rocks and less than 1 for crude oil from Cenozoic rocks. Scott and others (*16*) observed a constancy of the ratio of vanadium to nickel in crude oils from Cretaceous rocks in Canada. Hodgson and Baker (*11*) in a study of oil from some Canadian fields report systematic variations in vanadium, nickel, and other constituents; however, the vanadium-nickel ratios are not presented in sufficient detail for a good comparison with the data in Table IV. The two samples of oil from Cenozoic (Tertiary) rocks in Table IV agree with the observation of Katchenkov; however, the ratios for oils from Paleozoic rocks (Permian, Pennsylvanian, Mississippian, and Ordovician), except for sample 17, range from 1.6 to 6.1 The oils from Mesozoic rocks (Cretaceous, Jurassic, and Triassic) have values ranging from 0.08 to 4.4. Thus the ratio of vanadium to nickel is greater in the oil from older (Triassic system and Paleozoic era) rocks than in the oil from the younger (Jurassic system and younger) rocks. One possibility is that the vanadium organo-complex is more stable than the nickel organo-complex.

The most common order of abundance (true for 15 of the oils) of the four elements determined on the ash is V, Ni, Cu, U. For five of the oils the order is Ni, V, Cu, U. For two of the remaining four oils, copper is predominant. All the 15 oils with the common pattern are from reservoir rocks of Jurassic age or older, whereas the five in which nickel predominates are from reservoir rocks of Jurassic age or younger. The Wilmington oil might

Table IV. Ratios of Some Contituents of 24 Petroleums

Geological Age of Reservoir Rocks	Sample No.	Carbon Residue Ash	Nitrogen Ash	Sulfur Ash	Vanadium Nickel
Tertiary	13	675	42.3	....	0.05
	3	295	29.5	72.3	1.0
Cretaceous	2	1600	0.04	20.9	0.8
	4	2400	130	220	0.6
	10	333	3.3	....	0.08
	21	1100	54.0	140	0.8
Jurassic	1	100	1.8	38.5	1.5
	5	2600	113	230	0.6
Triassic	15	216	7.9	68.2	3.7
	18	271	8.7	80.8	4.4
Permian	16	188	7.4	70.9	3.5
	19	650	26.7	223	6.1
	22	487	20.7	202	5.3
Pennsylvanian	8	53	2.1	5.7	1.7
	9	417	12.2	64.2	1.9
	11	8000	46.0	170	3.8
	14	370	14.0	194	4.1
	17	487	18.7	125	220
	24	400	19.4	178	4.9
Mississippian	20	300	10.8	103	4.0
	23	257	10.0	90.9	3.4
Ordovician	6	2350	58.5	295	1.6
	7	1200	62.5	305	3.2
	12	390	17.3	50.0	2.2

fit with these five, even though the nickel and vanadium are equal. The copper content of the ash apparently is unrelated to the age of the reservoir rocks.

The uranium content of the ash of the crude oil ranges from 0.0001 to 0.0075%, suggesting that recovery of uranium from oil is uneconomical.

Vanadium-porphyrin complexes and nickel-porphyrin complexes have been identified in crude oil, but no uranium-porphyrin complexes have been identified. Although uranium is probably not present in a porphyrin complex, there are many reported combinations of uranium with carbonaceous materials. One of these is thucolite, which is supposed (*3*) to have been formed by polymerization of hydrocarbons subject to radioactive emanations.

A concentration of vanadium and nickel in various fractions was obtained by deasphaltening (solvent precipitation with *n*-pentane) and adsorption on Florisil. This is shown in Figure 2 and Table III. More than one half of the vanadium and nickel is precipitated with the 7% of asphaltenes. Adsorption of the raffinate on Florisil results in further concentration of the remaining vanadium and nickel in the nitrogen concentrate. An association of vanadium and nickel with asphaltenes and with nitrogen is indicated.

Copper contamination from apparatus used in the deasphaltening was so great that no conclusions regarding copper can be made. Contamination also became a more critical problem for the metals present in very small quantity. Uranium is such a metal, although it appears to be concentrated in the asphaltene fraction. Hyden (*12*) has shown that uranium contents of crude oils do not correlate with nitrogen contents as do vanadium and nickel contents.

Figure 3 shows the concentration of other metals in the four fractions. This figure shows the amount of ash, as well as the relative amount of each metal in the ash. There is no apparent selectivity between metals in the deasphaltening, for the analyses of the ashes from the asphaltenes, and the deasphaltened oil are very similar. However, the adsorption step, in addition to concentrating all the metals, appears to show selectivity for nickel and vanadium and perhaps for copper and zinc.

CONCLUSIONS

The results of trace metal analyses on 24 petroleums have been compared with properties of the organic portion of the crude oils. The limited data suggest that predictable relationships exist between the metal content and the nature of the organic constituents in petroleum. These relationships may prove to be significant with respect to a mechanism of formation of the oil. Results on oils from older formations are more consistent. Uranium is not present in any of the 24 oils in quantities suitable for commercial exploitation as a source of the metal.

In the process of deasphaltening, the major portion of the metals is concentrated in the asphaltenes. However, appreciable amounts remain in the deasphaltened oil. Adsorption of the deasphaltened oil on florisil results in a hydrocarbon eluate of very low metal content and a desorbed fraction containing most of the metals. The latter fraction is a concentrate of the nitrogen compounds, and this suggests that much of the metal content is bound to the nitrogen constituents of the oil.

ACKNOWLEDGMENT

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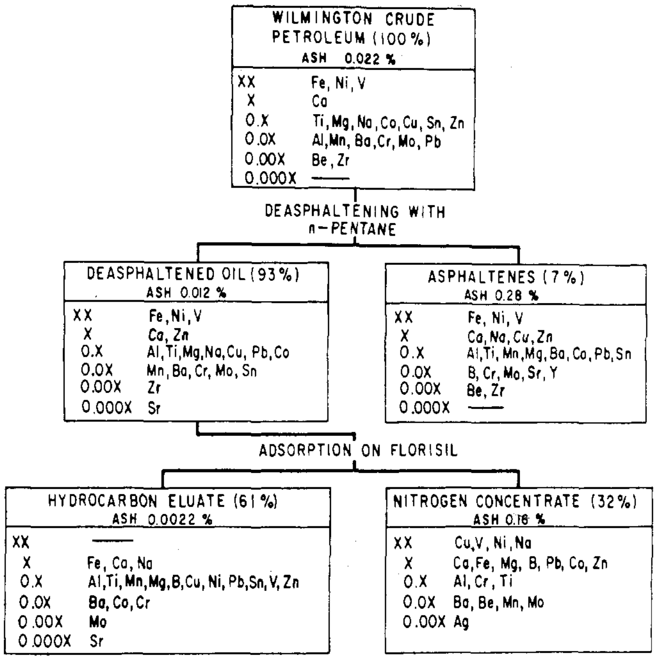

Figure 3. Semiquantitative analyses for metals on ash of Wilmington crude petroleum and fractions

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