Classes of Metallic Complexes in Petroleum

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THREE PETROLEUM crudes of low intermediate, and fairly high asphaltene content were chosen for studying the nickel and vanadium and porphyrin content. Pentane deasphaltening was a convenient method of separating each crude into asphaltenes and oils. The whole crude, the asphaltenes, and the oils left after precipitating the asphaltenes were studied separately in each case.

TREATMENT OF CRUDES

The Venezuela No. 1 crude, a high sulfur crude received November 1955, was water-washed and filtered; the other two crudes, Wyoming oils carefully sampled in glass at the well head, were centrifuged. The oils have the following properties:

Name	Source	Sp. Gr., 20°/4° C.	% Asphaltenes	A. P. I. Grav.
B. C. Prescott No. 3	Skelly Oil Co.	0.8625	3.7	29.0
Washakie O. P. C. 11, Well No. 14-T	Ohio Oil Co.	0.907	9.7	22.3
Venezuela	Creole Corp.	0.9247	16.6	19.7

PENTANE DEASPHALTENING

Reproducible weights of asphaltenes (±10%) could be produced from each crude by refluxing 100-gram samples for the same period of time (3 hours) under equal conditions of temperature (water baths maintained at 42° to 44° C. and approximately 620 mm. of mercury, barometric pressure), using 900 ml. of *n*-pentane with each 100 grams of oil (Phillips Petroleum, 95 mole % of *n*-pentane).

NICKEL AND VANADIUM ANALYSIS

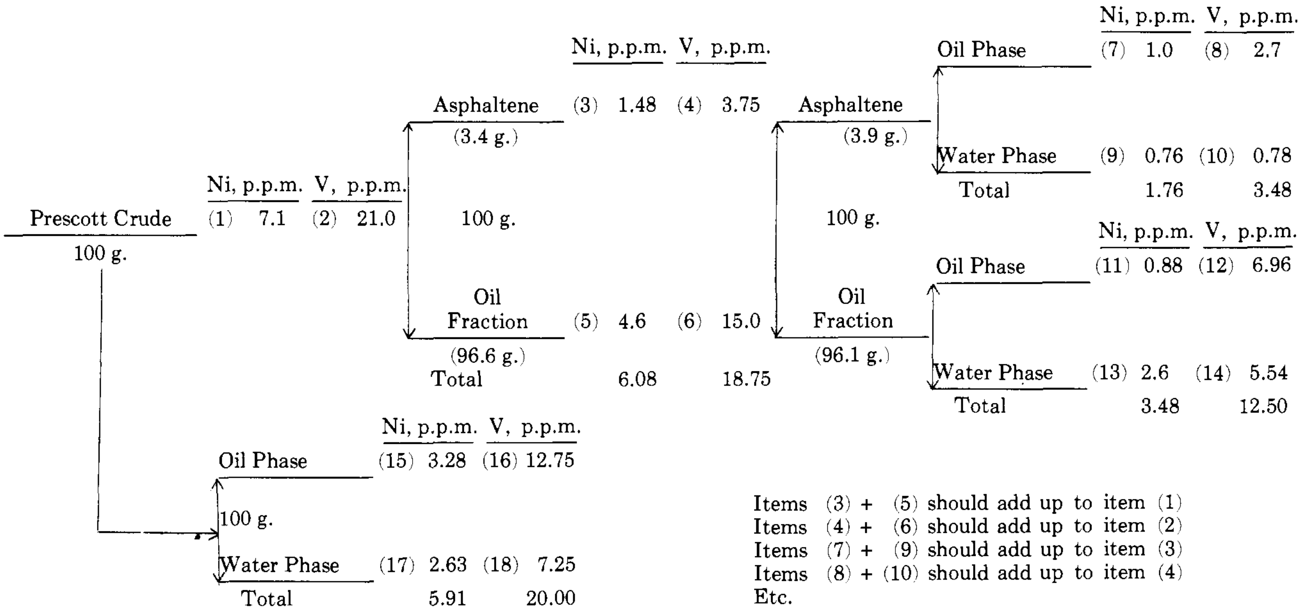
The oils were analyzed by the wet ash method, combined with the spectrophotometric procedure used by Milner and others (*4*). Fuming sulfuric acid was used because it causes much less foaming than ordinary concentrated acid. Moreover, the fuming acid can be purchased as an ACS reagent containing no trace of nickel or vanadium. Ordinary carboy acid must be tested for these metals. A loss of both nickel and vanadium as volatile compounds may occur even when fuming sulfuric acid is added to the oil unless the oil is swirled in the Vycor beaker as the acid is added.

ANALYSIS FOR FREE PORPHYRINS

The Groennings procedure (*3*) was used for the porphyrin content of each fraction of the crude, with modifications suggested by Moore and Dunning (*5*). To ensure complete decomposition of metallic compounds other than the porphyrin compounds, the oil, asphaltenes, and reagents were heated in a bomb for 6 days at 50° C., and as long as 12 to 16 days in certain experiments. It was conventient to use magnesium citrate bottles closed by a Teflon gasket as the bomb holding the oil reagents. The glacial acetic acid was freshly saturated with hydrobromic acid to make up a 30 to 32% hydrobromic acid solution. The Teflon gasket was

Table I. Analysis of B. C. Prescott No. 3

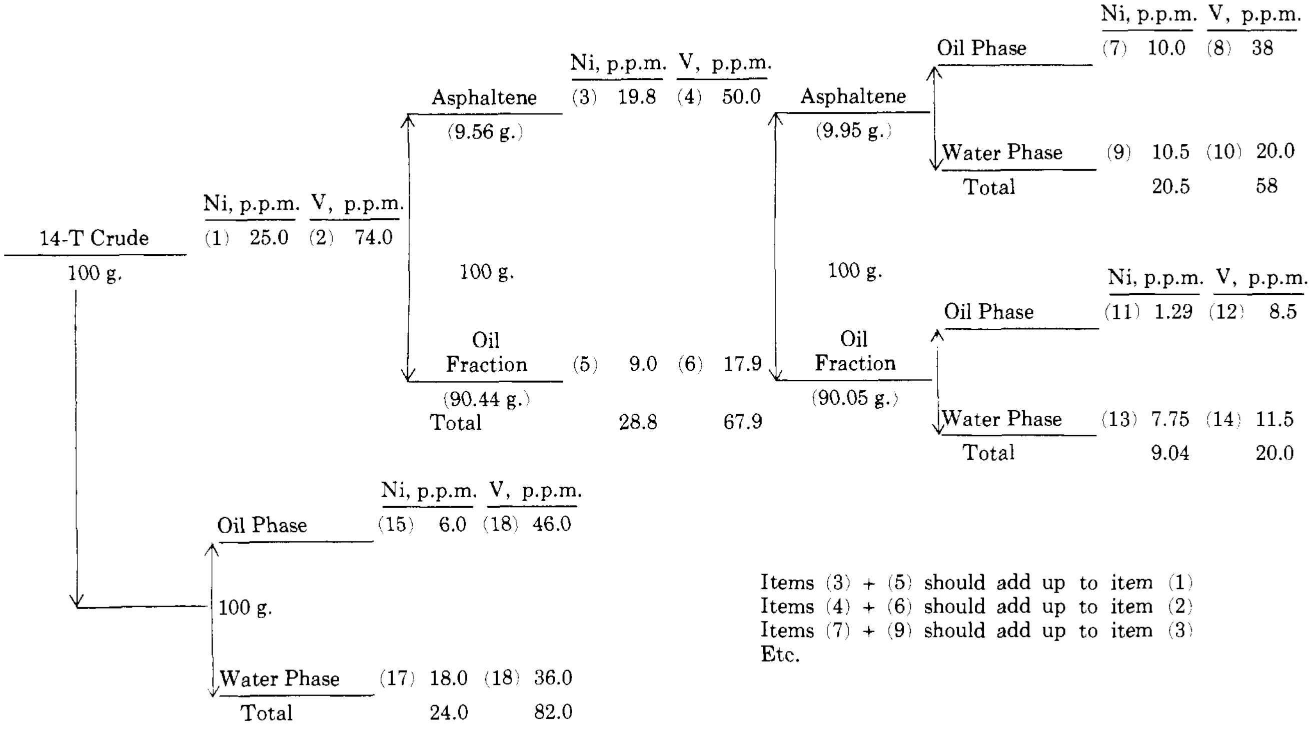
(All values based upon 100 grams of crude oil but calculated as micrograms per gram of original crude, p.p.m.)



Items (3) + (5) should add up to item (1)
Items (4) + (6) should add up to item (2)
Items (7) + (9) should add up to item (3)
Items (8) + (10) should add up to item (4)
Etc.

Table II. Analysis of 14-T

(All values are based upon 100 grams of crude oil but calculated as micrograms per gram of crude oil, p.p.m.)



Items (3) + (5) should add up to item (1)
Items (4) + (6) should add up to item (2)
Items (7) + (9) should add up to item (3)
Etc.

securely clamped over the lip of the bottle by a metal clamp especially devised for the purpose, and tightened with wing nuts. The pressure in the bomb was not high; no losses or accidents occured in using these bottles.

SEPARATION OF METALS FROM OIL AND ITS FRACTIONS

The Groennings procedure results in an oil phase and a water phase. When the contents of the bomb were poured over ice, two layers oridinarily formed in the separatory funnel. The porphyrins are present as salts in the water layer, giving it a familiar porphyrin red color. The nickel and vanadium separated from the porphyrins and any other metal present in the oil should appear in the water phase as acetates or bromides.

The experiments show that, stoichometrically, there are more moles of nickel and vanadium present in the water phase than moles of porphyrin (see Table IV). Indeed, there exists only from 10 to 40% enough porphyrin in the oil or its fractions to satisfy the nickel and vanadium, not counting all other metals present (one exception—the B.C.P. asphaltenes). The discrepancy between porphyrin and metal content has been pointed out by Moore and Dunning (5), who compared the total metal content of the oils with the total porphyrin content. The present article compares the amount of metals which go into solution in the water phase with the porphyrin content of the oils.

A careful qualitative spectroscopic examination was made on the ash from the three crude oils. A photographic record was made of the spectra using a Baird 3-meter grating spectrograph. Nickel and vanadium were by far the most prominent metals occuring in these three crudes. They all contained some iron and some copper, but at a lower level than that of nickel and vanadium.

The experiments show that some nickel and vanadium are not separated from the oil or its fractions by the Groennings procedure (Tables I to III). The asphaltene fraction contains the greatest proportion of the metallic complexes, not decomposed by the acetic-hydrobromic acid mixture. These stable complexes occur in the oil fraction to a lesser extent.

DIFFICULTY IN TREATING ASPHALTENE FRACTION

In this procedure the oil layer is separated and washed with successive portions of 20% hydrochloric acid. When the asphaltene mixture is poured from the bomb onto ice in the separatory funnel, separation of phases might not come about. In such a case—most cases involving the asphaltenes—it is best to centrifuge the mixture, where upon a black gel is deposited in the bottom of the centrifuge beaker. This black gel is fifficult to handle, but it may be treated successfully as follows: Centrifuge. Pour the benzene (upper) layer into a separatory funnel. Pour visible drops of water into a second separatory funnel. Stir 20% hydrochloric acid into the gel in 25-ml. portions, pouring the acid which separates into the second separatory funnel. After repeated acid washing, the gel shrinks, and finally, a water-repellent "wad" of asphaltenes remains, and each acid washing shows less of a pink color due to free porphyrins. Presumably the asphaltene fraction has now been washed free of the metal acetates or metal bromides.

It is difficult to handle the asphaltene fraction because it produces so many emulsifying agents. Several less favored procedures were tried, such as refluxing with alcohol or neutralizing with ammonia.

CALCULATION OF RESULTS

The nickel, vanadium, and free porphyrin content of the various fractions is listed on the basis of the weight of the original crude from which these fractions were obtained. There are several reasons for choosing this basis instead of the weight of the individual fractions.

Table III. Analysis of Venezuela No. 1

(All values based upon 100 grams of crude oil but calculated as micrograms per gram of original crude, p.p.m.)

		Ni, p.p.m.	V, p.p.m.
Venezuela Crude	100 g.	(1) 99.0	(2) 157.0
Asphaltene	(16.7 g.)	(3) 65.0	(4) 124.0
Oil Fraction	(83.3 g.)	(5) 30.8	(6) 50.0
Total		95.8	174.0

		Ni, p.p.m.	V, p.p.m.
Asphaltene	(17.7 g.)		
Oil Phase		(7) 13.6	(8) 57.0
Water Phase		(9) 42.6	(10) 66.0
Total		56.2	123.0
	100 g.		
Oil Fraction	(82.3 g.)		
Oil Phase		(11) 1.0	(12) 8.0
Water Phase		(13) 30.0	(14) 36.0
Total		31.0	44.0

		Ni, p.p.m.	V, p.p.m.
Oil Phase		(15) 14.5	(16) 58.0
	100 g.		
Water Phase		(17) 77.0	(18) 92.0
Total		91.5	150.0

Items (3) + (5) should add up to item (1)
Items (4) + (6) should add up to item (2)
Items (7) + (9) should add up to item (3)
Items (8) + (10) should add up to item (4)
Etc.

It can be seen at a glance what portion of the metal in the original crude is found in each fraction. For example, in Table I for the B. C. Prescott crude, 3.75 p.p.m. of vanadium based on weight of original crude, appears in the asphaltene fraction, while 15.0 p.p.m. appears in the oil fraction. On the other hand, based on the weight of the fraction (3.4 grams) the asphaltenes contain 110 p.p.m. and the oil fraction (96.6 grams) 15.5 p.p.m. Without examining the weights of the fractions, listing of the latter figures may lead to the erroneous assumption that the major portion of the vanadium in the crude appears in the asphaltene fraction.

On the basis of the weight of the original crude, the accuracy of the data can be judged simply by adding up the figures for the various fractions.

The authors have noted that for the asphaltene fractions that vary by 10% in weight, the parts per million of vanadium based on the weight of the original crude, agreed much better than the parts per million based on the weight of the asphaltene fraction.

Sample Calculation. The ash from 3.4 grams of asphaltene (derived from 100 grams of B. C. Prescott crude) gave a reading of 6.0 p.p.m. from the standard curve. The ash was in 25 ml. A 10-ml. aliquot was diluted to 25 ml. Calculation:

$$6.0 \times 25 \times \frac{25}{10} \times \frac{1}{100} = 3.75 \text{ p.p.m. V.}$$

(micrograms per gram of crude).

THREE CLASSES OF METALLIC COMPLEXES

Two Classes Decomposed by Glacial Acetic–Hydrobromic Acid Mixtures. The absorption spectra of the porphyrins were determined on the Beckman DU spectrophotometer. When plotting absorbance *vs.* wave length, these spectra show four characteristic peaks of absorbance in the range of 450 to 650 mμ. The crude and both fractions of the B. C. Prescott No. 3 crude and the fractions of 14-T crude showed the etio type of porphyrin spectrum (*1*) in which peak II is lower than peak III. The Venezuela crude and its fractions showed the phyllo type of porphyrin spectrum in which peak II is higher than peak III.

The concentration of the porphyrins (micromoles per gram of original crude) is shown for each crude and its fractions in Table IV. At the same time the concentration of nickel and vanadium (micromoles per gram of original crude) are shown. The values in Table IV are based on an absorption spectrum for a pure porphyrin (meso-porphyrin IX dimethyl ester) as published by Dunning and Moore (*2*) using chloroform as solvent (*2*, Figure 2, page 2002). The average absorbance at the four peaks calculates to be 0.360. The concentration shown in Figure 2 is 6.15 x $10^{-5}M$, which would be 4.16 x 10^{-5} molal or 41.6 micromolal. Hence:

concentration = average absorbance × constant
or 41.6 = (absorbance) average × constant = 0.36 × constant
Constant = 116 for concentration micromolal

This procedure of averaging out the absorbance corrects for background in an impure sample. The Groennings curve (*3*) was also used; the results from it are slightly higher, in general, than the results using Moore and Dunning's standard. Also analyzed was a purified porphyrin aggregate extracted from 2000 grams of a Wyoming crude, No. 79C, taken from the same field, the Grass Creek Field, of the Ohio Oil Co. as was sample 14-T, referred to in the tables. The purity of the porphyrin aggregate obtained from Wyoming crude 79C is unsatisfactory. However, it did give analyses higher than that using Moore and Dunning's curve and lower than that using Groennings' curve. The authors consider any of the procedures for purifying a porphyrin aggregate reported in the literature unsatisfactory [Groennings (*3*) and Sanik (*6*)], but feel that the method used for correcting for background proposed by Moore and Dunning

Table IV. Concentration in the Water Phase Produced by Groennings Procedure

(All values expressed as micromoles per gram of original crude)

	µmole Ni / G. Crude	µmole V / G. Crude	µmole Porphyrin / G. Crude	Mole Porph. / Mole (Ni + V) × 100
B. C. Prescott #3				
Crude	0.045	0.142	0.074	39.6
Asphaltenes	0.013	0.015	0.029	103.5
Oil fraction	0.044	0.109	0.041	26.8
14-T crude				
Crude	0.306	0.710	0.212	20.8
Asphaltenes	0.179	0.391	0.041	7.2
Oil fraction	0.131	0.266	0.149	41.7
Venezuela No. 1				
Crude	1.30	1.80	0.435	14.0
Asphaltenes	0.72	1.30	0.282	14.0
Oil fraction	0.51	0.71	0.204	16.7

Separate 100-gram samples of oil were used to develop each fraction, and separate samples were used first, to analyze for Ni and V, and second, for the porphyrin content.

(*4*) must be fundamentally correct. Their curve is based on a pure porphyrin, meso-porphyrin IX dimethyl ester; the analysis of a porphyrin aggregate by using it must therefore be somewhat in error. Until a better procedure for purifying a porphyrin aggregate is worked out, the authors will use Moore and Dunning's curve.

The interpretation of the results—namely, that the metals extracted and going into the water phase show a concentration much in excess of the porphyrin content of the oils—would not be altered even if the analyses in Table IV were in error by 100%.

The results shown in Table IV show that the porphyrin analyses are consistent among themselves. For each crude, the porphyrin content in the crude equals the sum of the porphyrin contents of the asphaltene plus the oil fractions (±10% deviation). The porphyrin content of the various fractions satisfy only 10 to 40% of the nickel and vanadium content (one exception, B. C. P. asphaltene fraction). This means that in addition to the metallic porphyrins in the oil, there are other nickel and vanadium compounds which are decomposed in the Groennings procedure.

Third Class of Metallic Complexes. Tables I to III demonstrate that there are nickel and vanadium compounds in the oils not decomposed by acetic–hydrobromic acid mixtures. For the most part, these compounds are concentrated in the asphaltene fractions. However, evidence soon appeared that often the results could not be checked when dealing with the water phase and oil phase of any fraction. These discrepancies were caused by the difficulty involved in washing glacial acetic acid out of the oil layer. It is believed that the glacial acetic acid acts as a solubilizer to hold part of the metal acetates and bromides in the oil. The difficulties were overcome, and the results shown in Tables I to III do show the proper correlation. To ensure that metallic compounds not decomposable by glacial acetic–hydrobromic acid mixture were present, two of the asphaltene fractions were subjected to two or more successive treatments by the Groennings procedure (Table V). The fraction was given a 6-day treatment, then formed into oil and water layers. The oil layer was washed until all the pink color due to porphyrins was removed. The fraction was then distilled to a temperature of 85° C. to remove benzene, water, and acetic acid which came over as azeotropic mixtures. The oil fraction was then put in a bomb with benzene and glacial acetic–hydrobromic acid, and given 6 more days' treatment. After the second treatment the asphaltene fraction showed no pink coloration in its water phase. After this strenuous treatment the asphaltene fraction still showed metal compounds not decomposed by glacial acetic–hydrobromic acid.

The evidence in Table VI points to a fairly rigid division of the metallic complexes into three classes.

If washing is complete, the solubles collected from the asphaltene fraction plus the solubles collected from the oil fraction should equal the solubles obtained from the whole crude. This being true, one would expect the residue of metals in the treated asphaltene fraction plus the residues from the oil fraction would add up to the residues in the treated whole crude. Table VI shows this (within the limits of experimental error). This correlation of data points definitely to a fixed amount of metals not soluble in glacial acetic–hydrobromic acid mixtures.

Table V. Successive Treatment by the Groennings Procedure

(Values calculated as micrograms per gram of original crude, p.p.m.)

14-T Crude, Asphaltene Fraction

	Ni, P.P.M.	V, P.P.M.
1st Groennings treatment (6 days)		
1st water phase	6.8	10.0
2nd successive Groennings treatment (6 days)		
2nd water phase	0.063	0.88
Oil phase	7.4	36.4

(Here 6.8 + 7.4 + 0.06 = 14.3; should equal 19.8 for nickel. 10.0 + 0.88 + 36.4 = 47.28; should equal 50.0 for vanadium. See Table II)

Venezuela Crude, Asphaltene Fraction

	Ni, P.P.M.	V, P.P.M.
1st Groennings treatment (6 days)		
1st water phase	36.6	58.0
2nd successive Groennings treatment (6 days)		
2nd water phase	8.0	4.0
3rd successive Groennings treatment (6 days)		
3rd water phase	0.0	1.25
Oil phase	11.2	46.0

(36.6 + 8.0 + 0.0 + 11.2 = 55.8; should equal 65.0 for nickel. 58.0 + 4.0 + 1.25 + 46.0 = 109.25; should equal 124 for vanadium. See Table III)

Table VI. Data to Show that Same Degree of Extraction is Obtained for Each Treated Crude and Its Treated Fractions

(Using Groennings procedure calculated as micrograms per gram of original crude, p.p.m.)

Crude	Oil Phase		Water Phase	
B. C. Prescott	Ni	V	Ni	V
Asphaltenes	1.0	2.7	0.76	0.78
Oil fraction	0.88	6.96	2.60	5.54
Total	1.88	9.66	3.36	6.32
Crude	3.28	12.75	2.63	7.25
14-T				
Asphaltenes	10.0	38	10.5	20.0
Oil fraction	1.29	8.5	7.75	11.5
Total	11.29	46.5	18.25	31.5
Crude	6.0	46.0	18.0	36.0
Venezula				
Asphaltenes	13.6	57.0	42.6	66.0
Oil fraction	1.0	8.0	30.0	36.0
Total	14.6	65.0	72.6	102.0
Crude	14.5	58.0	77.0	92.0

The deviation for the sum of the metal content in the asphaltenes and the oils compared to the metal content of the whole crude was from 0.3 to 14%. Duplicate results on a single sample varied from 0.2 to 5.4% and parallel results on similiar samples varied from 0.2 to 10%, the B. C. Prescott oil excepted. Many of the values for this oil ran below 10 p.p.m. Standard curves yielded an accuracy of about 25% in this range.

For these reasons, the experimenters feel sure that there are at least three classes of metallic complexes in crude petroleum: (1) the metallic porphyrins, (2) metallic compounds—nonporphyrins which are easily decomposable by glacial acetic-hydrobromic acid mixtures, and (3) metallic compounds—nonporphyrins which are not readily decomposed by glacial acetic-hydrobromic acid mixtures.

ACKNOWLEDGMENT

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Some Physical Properties of Certain C_9 and C_{10} Aliphatic Acids and Their Methyl Esters

2-Ethylheptanoic and Pelargonic Acids, and Methyl Esters of 2-Ethylpentanoic, Pelargonic, 2, 5-Diethyladipic, 2-Ethylsuberic, and Sebacic Acids.

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THE COMMERCIAL process for the manufacture of Isosebacic acid produces a mixture of 2,5-diethyladipic acid (12 to 18%), 2-ethylsuberic acid (72 to 80%), sebacic acid (6 to 10%), and small amounts of pelargonic and 2-ethylheptanoic acids. The data recorded herein are concerned with two of these five acids and the methyl esters of all five acids.

Scattered data are available in the literature on pelargonic acid, 2-ethylheptanoic acid, methyl pelargonate, and dimethyl sebacate. The most recent data on pelargonic acid are those given by Mumford and Phillips (*6*). They recorded the freezing point as 12.0° C., boiling point as 254° C. at 760 mm. of mercury, specific gravity as 0.9052 at 20° C. referred to water at 0° C., and refractive index as 1.4322 at 20° C. with sodium *D* line. Eggenberger and others (*3*) give a value of 12.52° C. as the melting point of pelargonic acid. Dorinson, McCorkle, and Ralston (*2*) report the refractive index of pelargonic acid at temperatures from 20° to 80° C. and the density as 0.8570 gram per ml. at 80° C. Pool and Ralston (*7*) give the boiling point of pelargonic acid at different temperatures from a vapor pressure of 1 mm. of mercury to the boiling point at 1 atm. The values cited by Pool and Ralston for vapor pressure are generally lower than those given in this article over the temperature range studied. The purity of the compounds was established by chromatography, so the values reported here may be considered as taken on compounds of known composition.

Methyl pelargonate was prepared by the Gartenmeister method (*5*), and its boiling point established as 213.5° C. at 760 mm. of mercury. Walbaum and Rosenthal (*11*) reported the specific gravity as 0.8799 at 15° C. *vs.* water at 4° C. and the refractive index as 1.42135 at 20° C. using the sodium *D* line.

Royals and Covington (*9*) describe the preparation of