Direct Determination of Metalloporphyrins in Boscan Crude Oil

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IN AN INVESTIGATION directed towards identification of organometallic compounds in crude petroleum, an assignment of that portion which occurs as porphyrin metal complexes was necessary. Thus, it was highly desirable to establish a rapid and reliable method of porphyrin determination. Procedures commonly utilized require lengthy and cumbersome extractions.

The principal raw material studied in this investigation was Boscan (Venezuela) crude oil, selected because of its high metal content, approximately 1200 p.p.m. of vanadium and 115 p.p.m. of nickel.

EXPERIMENTAL METHODS

Samples for metal analyses were prepared by coking with sulfuric acid, followed by complete ashing in a muffle furnace at 500° C. Nickel was determined by a modified colorimetric procedure using dimethylglyoxime (*2*). Changes in the method consisted of adjusting the pH to 1 to 2 prior to bromine addition and introducing sufficient 6*N* sodium hydroxide solution immediately after addition of the dimethylglyoxime solution to obtain a pH of 11 to 12. The latter modification prevented formation of precipitates. Vanadium was determined by modifying the colorimetric method utilizing tungstovanadic acid (*11*). The details of this procedure will appear in a separate communication.

In the direct method, a weighed sample of the petroleum fraction was dissolved in reagent grade chloroform to prepare a solution with a convenient absorbance. When the fraction had been stored in a benzene solution in the dark to minimize decomposition of metalloporphyrins, an aliquot was diluted with reagent grade chloroform. The presence of small amounts of benzene did not alter the resulting adsorption spectra. Spectra were recorded between 550 and 350 mμ with a Beckman DK-2 spectrophotometer. Background absorbance contributing to the Soret band was subtracted by drawing a base line tangentially through the valleys on either side (Figure 1). The remaining area was determined and related to metalloporphyrin concentration.

RESULTS AND DISCUSSION

The common methods (*5, 9*) of determination of porphyrins in petroleum fractions require initial digestion with hydrogen bromide in acetic acid. The resulting porphyrins freed of metals are determined directly (*5*) or purified by extraction and then determined (*9*). In the former procedure, the area under the Soret band is determined spectrophotometrically after a correction for background absorbance. These methods suggested the possibility of direct determination of porphyrins as their metal complexes as a rapid and routine analytical procedure.

In an spectrophotometric analysis, the determination of a reliable extinction coefficient is required as one of the first operations. In this instance, the principal complications arise as a consequence of the presence of many different metalloporphyrins of both vanadyl and nickel types and of molecules with different substituents in the β-positions of the pyrrole rings. Changes in peripheral attachments have much less effect on the Soret band than on the peaks in the visible range. Thus the use of the Soret band for analytical purposes was attractive (*5*). Porphyrins with carboxylic acid and other polar groups have somewhat different extinction coefficients than those without these functional groups. Thus an attempt was made to establish the relative amounts of these two types of porphyrins in Boscan crude. Chromatography of a porphyrin-rich fraction on a powdered cellulose column using 2-methoxyethanol as the eluting agent provided a rapidly moving red band containing the major portion (65%) of the metalloporphyrins. The remaining material near the top of the column released a second fraction exhibiting porphyrin absorbance (28%) when chloroform was introduced. Since the rates of movement of carboxylated and noncarboxylated porphyrins in chromatography are distinctly different (*7, 8*), data from this experiment were assumed to approximate the relative amounts of these two compound types. Another approach was based upon the greater solubility of the noncarboxylated porphyrins in ethyl ether. A porphyrin aggregate, obtained from Boscan crude by the Groennings method (*9*), was remetallated with nickel acetate. An appreciable amount (17%) of the resulting mixture of nickel porphyrins was insoluble in ethyl ether. The peaks for the spectra in the visible range of the ether-insoluble and the ether-soluble portions, both dissolved in chloroform, were at identical wave lengths. On the basis of these observations it was assumed that not less than 17% of the porphyrins with carboxylic acid and other polar groups were present. From these two experiments, the content of polar porphyrins was estimated to be 20%.

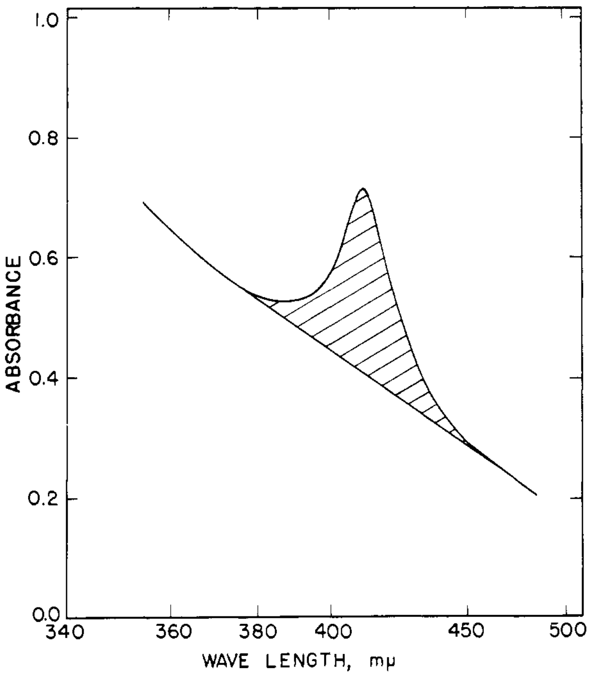

Figure 1. Integration of area under the Soret band of an extract from Boscan crude oil

Vanadyl and nickel porphyrins have distinctly different Soret extinction coefficients. Accordingly, a reasonable estimate of the ratio of the two types of porphyrins is necessary. The molar ratio of vanadium to nickel in Boscan crude and of various fractions derived therefrom, including those rich in porphyrins (Table I), is approximately 13. This metal ratio remained essentially constant, independent of metal concentration or method of isolation. In a fraction from Boscan crude, in which 79% of the metals occur as metalloporphyrins, the ratio of 14 moles of vanadium to one of nickel was determined. Thus it can be estimated

Table I. Analysis of Boscan Crude Oil

Sample	% of Crude	μMoles/Gram Crude			V + Ni,[a] %
		Ni	V	Porphyrins	
Crude	100	1.9	23.6	10.4	41
Asphaltenes (pentane)	20	1.3	17.3	6.7	36
Petrolenes	80	0.5	5.0	3.4	63
Ethyl ether extract of asphaltenes	6.4	0.32	4.44	3.78	79
Bis(2-ethoxyethyl) ether extract of asphaltenes	17.6	0.94	12.2	6.0	46

[a] As porphyrins.

with reasonable confidence that the molar ratio of vanadyl to nickel porphyrins is 13 in Boscan crude and fractions derived therefrom. However, the ratio of vanadium to nickel in other crudes need not be the same as the ratio of vanadium to nickel porphyrins, which may be established by metal analyses of a fraction essentially free of nonporphyrin metal compounds.

Although the Soret band is less dependent upon structural variations, the presence of several different molecular species in a porphyrin aggregate with absorption peaks at slightly different wave lengths would flatten this band. Thus a measurement of peak height would not provide for as meaningful a quantitative measurement of porphyrin content as integration of the area under the band. For these reasons, a new method of porphyrin analysis was developed (*5*). The same rationale would apply to the metalloporphyrins. Integration of the area under the Soret band gave the following extinction coefficients, expressed in liter mμ mole^{-1} cm.$^{-1}$, for analytical samples of vanadyl etioporphyrin I, nickel etioporphyrin I, and vanadyl mesoporphyrin IX dimethyl ester: 4.71×10^6; 3.35×10^6, and 4.52×10^6, respectively. Assuming that the molar ratio of vanadyl to nickel porphyrins is 13, that the mole fraction of polar porphyrins is $1/5$, and that the three metalloporphyrins selected as reference compounds are representative of the compounds present, an extinction coefficient of 4.5×10^6 liter mμ mole^{-1} cm.$^{-1}$ was approximated for Boscan crude and fractions derived therefrom. Considerable variances in the content of polar porphyrins would clearly have but slight effects on the magnitude of the extinction coefficient.

The absorption spectra of Boscan crude and its fractions contain a variable amount of background absorption in the general area of the Soret band. A correction for the presence of compounds other than metalloporphyrins absorbing in this range was made (Figure 1) in the same manner as described previously (*5*) for porphyrins freed of metals. The base-line method of correcting for background absorption was previously applied (*1, 10*). Some experiments were made to determine whether drawing a base line to subtract incidental absorption would provide consistent analytical data. In one experiment, pure vanadyl mesoporphyrin IX dimethyl ester, in an amount expected to double the area under the Soret band, was dissolved in a given extract with high background absorbance. Analysis of the resulting solution by the direct integration technique demonstrated that the measured concentration differed from the calculated by only 2.2%. Another indication of the consistency of the method was obtained by the observation that material balance for porphyrins could be demonstrated. The sum of the porphyrin content of several fractions was essentially equal to the amount in the precursor, even when certain separation procedures might be expected to disturb a given colloidal system. The porphyrin content in Boscan crude was equal to the sum of the amounts found in asphaltenes and petrolenes (Table I). Upon extracting Boscan asphaltenes with a mixture of tetrahydrofuran and acetone, the sum of porphyrins contained in 11 successive extracts (22.4 μmoles per gram of asphaltenes) was found to be equal to the content found in the combined solution (22.8 μmoles per gram of asphaltenes).

In all cases, amounts of metalloporphyrins found by the direct integration method were substantially larger than amounts of porphyrins determined by the Groennings method (*9*) or by the modification proposed by Costantinides (*5*). Studies were directed towards a better understanding of these variances (Table II). An ethyl ether extract of Boscan asphaltenes, enriched in metalloporphyrins, was used as reference sample. About 0.7 gram containing 17.6 μmoles of metalloporphyrins by the direct method of analysis was demetallated with hydrogen bromide in acetic acid by the usual procedure (*9*). Analysis of the acid extract following the method of Costantinides (*5*) demonstrated the presence of 7.62 μmoles (43% of 17.6) of porphyrins. Another sample carried through the same procedure, but purified by extractions (*9*) and then analyzed by the area integration method was found to contain 5.03 μmoles (29% of 17.6) of porphyrins. The same extract to which 5.6 μmoles of vanadyl mesoporphyrin IX dimethyl ester was added was also treated with hydrogen bromide in acetic acid. Direct analysis of the acid extract revealed 12.6 μmoles (54% of 23.2) of porphyrins. When 5.6 μmoles of pure vanadyl mesoporphyrin IX dimethyl ester were subjected to the same treatment with hydrogen bromide in acetic acid, the resulting acid solution contained 4.7 μmoles (84% of 5.6) of porphyrins as determined by the method of Costantinides (*5*). The experiment with the pure porphyrin demonstrated clearly that the demetallation procedure caused decomposition of porphyrins. Such observations have been made by others (*3*).

Residues from the acid extractions of the three samples

Table II. Porphyrin Recovery Following Demetallation

Sample	Metalloporphyrins, μMoles	Demetallation Procedure	Porphyrins, %		
			Extracted	Unextracted	Unaccountable
Ether extract	17.6	Groennings (*9*)	29	25	46
	17.6	Costantinides (*5*)	43	21	36
Ether extract + pure vanadyl porphyrin	23.2	Costantinides	54	...	...
Pure vanadyl porphyrin	5.6	Costantinides	84	...	...

containing the ether extract had absorption spectra indicative of large amounts of porphyrins. The visible spectrum in each case contained five peaks and a shoulder. The Soret band was broader than that of the parent material or of the acid extract, and the maximum was located at 402.5 mµ, which is intermediate in position between the metallated (410 mµ) and the nonmetallated (399 mµ) porphyrins from Boscan crude. These spectral characteristics were assumed to arise from the presence of both metalloporphyrins and free porphyrins. Accordingly, an approximate extinction coefficient was calculated based upon the location of the Soret peak. Using this figure, residues from the acid extractions were found to contain 20 to 25% of the original porphyrins. Since a major portion of the porphyrins remaining occurred in the demetallated form, insolubility in the acid solutions would hardly be expected for usual porphyrin compounds found in petroleum. Porphyrins with large and complex substituents or polymeric porphyrins (*4*) may, however, not be extractable by the polar, acidic media applied.

Since loss of porphyrin could be demonstrated by using the pure sample of vanadyl mesoporphyrin IX dimethyl ester, decomposition of the natural porphyrins would also be expected. On the basis of porphyrins contained in the acid extract and in the residue, the extent of this loss was estimated to be approximately 35% of the original. The greater sensitivity to decomposition of the petroporphyrins as compared to the single pure compound included in this study might be expected. The poorer recovery of porphyrins by the Groennings method involving a series of extractions was undoubtedly attributable, at least in part, to mechanical losses.

Another experiment was performed to determine whether proceeding in the opposite direction, that is, conversion of the free porphyrins into metalloporphyrins, could provide materials giving essentially the same values for porphyrin content. This procedure has the advantage of not requiring an extraction. A porphyrin aggregate containing 11.0 µmoles of free porphyrins, as determined by the area integration method, was remetallated with nickel acetate. The resulting nickel porphyrins were analyzed, using the extinction coefficient for nickel etioporphyrin I as the reference figure, and found to amount to 10.5 µmoles. As an independent confirmation of porphyrin content, an analysis revealed the presence of 10.0 µmoles of nickel. These data provide strong evidence that the direct analysis of porphyrins as their metal complexes gives substantially the same figure as obtained in the determination of the free porphyrins.

This direct determination of metalloporphyrins and analyses for vanadium and nickel gave the data (Table I); 41% of all of the vanadium and nickel in Boscan crude oil occur as porphyrin complexes. This figure is approximately two and one third times as large as that previously reported (*6*).

This method of analysis was extended to Wilmington crude oil, which has a much smaller porphyrin content. Since the Soret absorption was small as compared to the background, a modification in subtracting background absorption was necessary. A straight base line would clearly remove absorption attributable to porphyrins and so a curved line approximating the absorption of the background was drawn (Figure 2). An extinction coefficient of 4.0×10^6 liter mµ mole^{-1} cm^{-1} was approximated for this oil in which the vanadium to nickel ratio is close to unity in fractions rich in metalloporphyrins. Since the area under the Soret band was small, five separate recordings were made on the spectrophotometer and averaged for each sample. The porphyrin concentration in Wilmingto crude was found to be 1.35 µmoles per gram as opposed to 0.42 µmoles per gram found by the Groennings method (*6*).

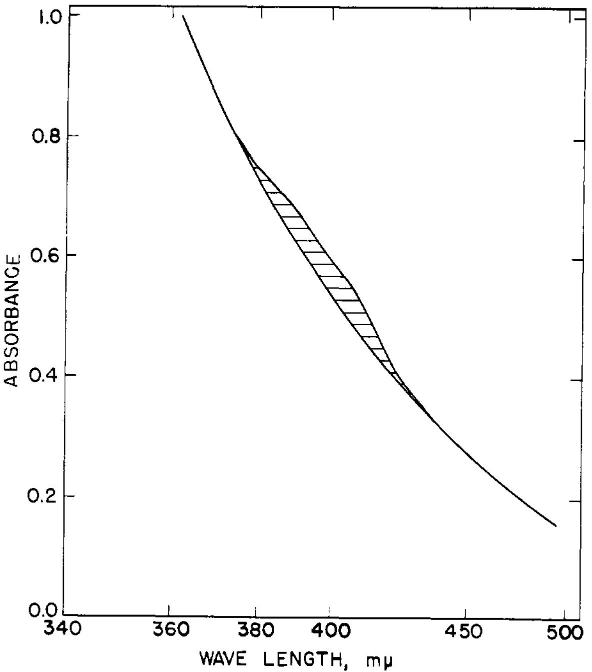

Figure 2. Integration of area under the Soret band of Wilmington crude oil

CONCLUSION

The direct method of determination of metalloporphyrins is a simple and rapid procedure, in which losses of porphyrins occurring by incomplete demetallation, by decomposition, and by incomplete extraction are eliminated. The procedure exhibits good precision for samples with relatively high ratio of porphyrin to background absorbances. Good material balance of porphyrins is found for materials derived from a given source. Determination of an extinction coefficient for a given material requires a knowledge of the relative amounts of metals present in the porphyrin complexes. The method may not be generally applicable to materials with low concentrations of porphyrins.

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