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# Chromatographic Studies of Vanadium Compounds from Boscan Crude Oil

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**Abstract**

For the first time, vandium nonporphyrins have been fractionated. Using graphite furnace atomic absorption, the signal for vanadium was found to follow the UV absorption of the chromatogram. In addition, a simpler, faster procedure has been devised to isolate a vanadium porphyrin fraction that was more nearly free from both vanadium nonporphyrins and nickel porphyrins. Pyrolysis/GC with both the flame photometric (sulfur) detector and the flame ionization detector gave evidence for a variety of sulfur species in both the porphyrin and nonporphyrin fractions.

## INTRODUCTION

The presence of vanadium in crude oil was first studied by Triebs (*1*), who was able to isolate and identify vanadium porphyrins in crude. Since that time, many studies have been reported which have included complex separations and sophisticated instrumental techniques such as mass spectrometry and electron spin resonance spectrometry. Sebor et al. (*2*) have recently reviewed most of the studies of vanadium in crudes.

Basically, it is known that vanadyl ion, $VO^{2+}$, forms chelates with porphyrins and also with other largely unknown "nonporphyrins." The porphyrin chelates have been the most studied and have been reviewed by Baker and Palmer (*3*). Recently, a detailed HPLC separation of the demetallated porphyrin fraction was described by Hajibrahim et al. (*4*). That procedure was included in a liquid chromatographic–mass spectrometric

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system by McFadden et al. (5) for analyses of some of the individual porphyrins.

Little is known about the "nonporphyrin" fraction. An improved procedure to isolate this fraction and some of its characteristics have recently been published by Sebor et al. (8). Dickson and Petrakis (6), using electron spin resonance spectrometry, concluded that vanadium was bound as vanadyl ion just as it was in the porphyrin fraction. However, sulfur and oxygen were also bonded to the metal. Yen (7) suggested that the "nonporphyrin" chelates were "porphyrinlike" to the extent that sulfur or oxygen replaced a nitrogen in a pyrole ring of the porphyrin.

In our studies the primary goal was to isolate some new vanadium complexes using liquid chromatographic fractionation of the vanadium species and atomic absorption or flame emission detection. New or improved procedures were developed for isolating the porphyrin and nonporphyrin vanadium compounds for separating the components in those fractions. Other studies of an exploratory nature included steric exclusion runs on the vanadium fractions and pyrolysis gas chromatography of the porphyrin and nonporphyrin fractions using flame ionization and flame photometric (sulfur) detectors.



## EXPERIMENTAL

### Chemicals

Boscan crude oil and its hexane-washed asphaltenes were provided by J. A. Lubkowitz, Instituto Venezolano de Investigaciones Cientificas, Caracas, Venezuela. As shown in Table 1, this heavy crude is characterized by high vanadium, nickel, and sulfur contents.

Dimethylformamide (DMF), tetrahydrofuran (THF), methanol (MeOH), hexanes, toluene, chloroform, and methylene chloride were spectrophotometric or HPLC grade (J. T. Baker Chemical Co., Phillipsburg, New Jersey, and Fisher Scientific Co., Atlanta, Georgia). *n*-Decane was obtained from Phillips Petroleum Co. (Bartlesville, Oklahoma) and isooctane from Eastman Kodak (Rochester, New York). Activated 4 A molecular sieve (Davison Chemical co., Baltimore, Maryland) was used to dry chloroform, toluene, hexanes, and isooctane. THF was freshly distilled over sodium and obtained on a daily basis as needed. Chloroform contained 0.7% ethyl alcohol as a stabilizer. Solvents were filtered and degassed by heating and sonication when used in HPLC.

TABLE 1

Percentages of Major Elements in Boscan Crude[a]

| | Crude oil | Asphaltene[b] |
|---|---|---|
| Vanadium[c] | 1317.8 ± 9.6 ppm | 3859.7 ± 2.52 |
| Nickel[c] | 121.6 ± 18.5 ppm | 384.6 ± 3.7 |
| Carbon | 82.5% | 81.1% |
| Hydrogen | 10.4% | 8.6% |
| Nitrogen | 0.6% | 1.2% |
| Oxygen | 0.76% | 1.4% |
| Sulfur | 5.5% | 6.7% |

[a]Data provided by J. A. Lubkowitz, Instituto Venezolano de Investigaciones Cientificas, Caracas, Venezuela.

[b]Hexane precipitates.

[c]By neutron activation analyses.



Polystyrene standards for steric exclusion chromatography were 800, 2,200, 4,000, 9,000, 17,000, and 36,000 MW preparations (Pressure Chemical Co., Pittsburgh, Pennsylvania). Solutions were prepared by dissolving approximately 0.5 mg of the polystyrene in 5 mL of chloroform. If necessary, the standard was diluted using additional solvent to give a concentration that produced half-scale peaks. A drop of toluene was added to each solution to mark the total liquid volume of the column.

The chromatographic columns are listed in Table 2. Natural alumina and bulk chromatographic silica were obtained from Fisher Scientific Co. (Atlanta, Georgia). Partisil, Quanta K5F and K6F TLC plates, and the PAC (polar amino-cyano) packing were obtained from Whatman, Inc. (Clifton, New Jersey). Lichrospher 100 and 500 were obtained from E. Merck (East Brunswick, New Jersey).

Vanadium standards were made either from an aqueous, certified 1000 ppm, vanadium reference solution (Fisher Scientific Co., Atlanta, Georgia) or from vanadium oxobis-(1-phenyl-1,3-butanedionate) (Eastman Kodak Co., Rochester, New York). A "standard" solution of the latter was prepared by weighing approximately 10 mg on an analytical balance and dissolving it in 100 mL of THF or chloroform.

Gases for atomic absorption measurements were hydrogen, nitrogen, acetylene, air, and nitrous oxide. Helium and nitrogen were used with the Varian 8500 liquid chromatograph. All were obtained from Selox, Inc. (Gainesville, Georgia).

TABLE 2

Packings and Columns

| No. | Method/use | Packing | Size | Column | Notes |
|---|---|---|---|---|---|
| 1 | LC, crudes/asphaltenes | Neutral alumina activity = 1 | 80–200 mesh | 2.5 cm × 75 cm glass | Dry-packed (sometimes sieved to 150–170 mesh) |
| 2 | LC, porphyrins | Bulk silica | 80–200 mesh | 1 cm × 40 cm glass | Dry-packed |
| 3 | LC, nonporphyrins | "Used" neutral alumina | 150–170 mesh | 5 cm × 0.41 cm i.d. stainless steel | Dry-packed-packing was coated with crude and washed with DMF and $CHCl_3$ |
| 4 | HPLC, porphyrins | Partisil | 5 or 10 $\mu$m | 25 cm × 0.41 cm i.d. stainless steel | Slurry packed, 1:1:1 MeOH, $CHCl_3$, toluene |
| 5 | HPLC, porphyrins | PAC (polar-amino-cyano) | 10 $\mu$m | 25 cm × 0.41 cm i.d. stainless steel | Slurry packed, 1:1:1 MeOH, $CHCl_3$, toluene |
| 6 | Steric exclusion | Lichrospher 100 | 10 | 15 cm × 0.46 cm i.d. stainless steel | Slurry packed, unknown method |
| | All fractions | Lichrospher 500 | 10 | | |
| 7 | TLC | Quanta K5F | 80 A silica | Precoated 5 cm × 20 cm TLC plate | Binder contains fluorescent material |
| | All fractions | Quanta K6F | 40 A silica | | |
| 8 | Pyrolysis GC, porphyrin, and nonporphyrins | 3% SE-30 on acid washed Chromosorb W | 80–100 mesh | 300 cm × 0.32 cm stainless steel | |

## Equipment

Dual Varian 8500 syringe pumps equipped with a solvent programmer module were used for gradient HPLC deparations. A Valco (Houston, Texas) Model AH-CV-6-UHPa, automatic six-port injection valve, was used for sample injection. The valve was usually equipped with a 15-$\mu$L sample loop; however, a 50-$\mu$L loop was sometimes used. The detector was a Perkin-Elmer LC-55 variable wavelength spectrometer equipped with high-pressure flow cells.

A Milton Roy Minipump was used for isochratic separations. It was equipped with a home-built pulse dampener consisting of a 250-mL stainless steel cylinder and a pressure gauge. A Valco value similar to that described above was used to inject samples. A fixed wavelength (254 and 280 nm) Duomonitor (Laboratory Data Control, Riviera Beach, Florida) was used as the detector.



Other detectors were sometimes substituted: a Variscan scanning wavelength detector (Varian Associates, Palo Alto, California) and a stabilized Spectronic 20 that held a 10-mm path length, 19 $\mu$L, ISCO (ISCO-Chemresearch, Lincoln, Nebraska) flow cell. Postdetector effluents were collected using an ISCO Model 1200 traction collector. The signals from the detectors were displayed on a Linear Instruments Model 385 recorder (Irvine, California).

All connections were made using Swagelok fittings and connected or modified so as to minimize dead volume. Connecting tubing between the column and both the injection valve and the detector were 0.5 mm i.d., 1.6 mm o.d. stainless steel. Total volume of that tubing from the injection valve to the detector was less than 80 $\mu$L.

Pyrolysis gas chromatography used a model 190 Pyroprobe (Chemical Data Systems, Oxford, Pennsylvania) fitted to a Perkin-Elmer 3920 gas chromatograph. The dried sample was placed on a ribbon filament. The gas Chromatograph employed both flame ionization and flame photometric (sulfur) detectors.

Atomic adsorption measurements of vanadium were made using a Varian AA-375 atomic absorption spectrometer equipped with a $N_2O$/acetylene flame head, a variable flow-rate nebulizer, and a deuterium lamp for background correction. Nonflame atomic absorption measurements were performed by replacing the flame head with a Varian Model 90 carbon rod analyzer graphite furnace system. This system allowed complete automatic control of the analysis including sample introduction, solvent drying, ashing, and atomization.

Flame emission measurements were made using a Heath Model EU703-02 spectrometer (Benton Harbor, Michigan) equipped with a $N_2O$/acetylene

flame head, fixed-rate nebulizer, and a gas flow controller, Model GCU-6, all from Varian. A Model 417 Keithley picoammeter converted the signal from the photomultiplier (Model EU701-30) to a voltage.

## Procedures

A schematic for the overall separation procedure is given in Fig. 1. In the initial stage, a sample of asphaltenes or, sometimes, of crude oil was separated into porphyrin and "nonporphyrin" fractions. The vanadyl porphyrins were further isolated on a second clean-up column, and the resulting "clean" porphyrins were fractionated using HPLC. The "nonporphyrins" were fractionated on a second column using a nonaqueous reverse-phase solvent system, and portions were analyzed for vanadium by nonflame atomic absorption.

For the initial separation of the porphyrin fraction, approximately 3 g of the asphaltene or crude was dissolved in 30 mL of methylene chloride.



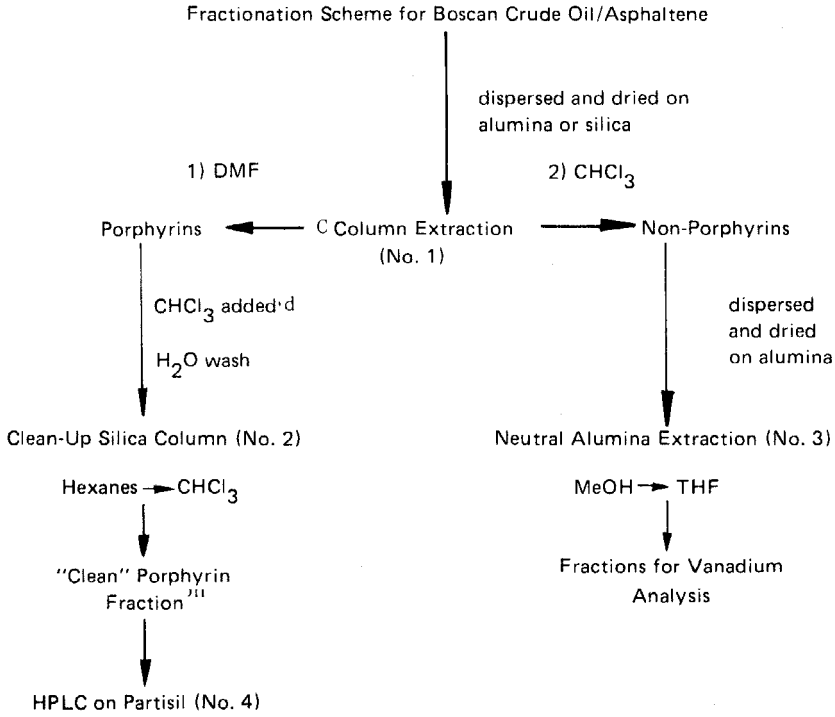


FIG. 1. Fractionation scheme for Boscan crude oil/asphaltene.

Approximately 30 mL of neutral alumina was added to form a slurry which was then blown "dust" dry using nitrogen or compressed air. Failure to dry the solid sufficiently (so that it was light brown in color) resulted in poor selectivity for the porphyrins. That solid was then dry-packed into a 2.54 cm i.d. × 75 cm glass column which already contained approximately 3 cm of fresh alumina. the porphyrin fraction was extracted using DMF (200 mL was usually sufficient) until the eluent no longer had a reddish or orange color.

Either *p*-dioxane or MeOH mixed (9:1) with either benzene or toluene also permitted the isolation of a porphyrin fraction. However, the UV background at the 410-nm Soret band was larger than when DMF was used.

The prophyrin fraction was transferred to 30 mL of chloroform by shaking followed by removal of the DMF by five washings with 100-mL portions of water. Neither vanadium nor porphyrin was detected in the washings.

To develop a separation of the porphyrin fraction, thin-layer chromatography (TLC) was done. Blumer (*9*) showed that a mixture of $CHCl_3$ and a paraffinic solvent (isooctane) was advantageous for separations on paper. Our procedure substituted commercially available Quanta K5F and K6F, 5 × 20 cm, silica plates. The plates were activated at 110–120°C for 30 min prior to use and then cooled in a desiccator. Using a 50-$\mu$L syringe, a sample of the porphyrin fraction was run across the plate in a narrow band 3 cm from the bottom. After evaporating the solvent, the plate was developed using 1:1 chloroform/*n*-decane. The plates were developed in a jar holding 2 cm of solvent and lined with strips of filter paper wet with the solvent.

Plates were allowed to develop in the capped jar until the solvent front was 1 cm from the top before removal and inspection for visible red-pink porphyrin bands using a hand-held UV scanner. (The plate contained a fluorophor which was darkened by absorption of radiation by sample components.)

Based on the TLC studies, a second column procedure was developed for isolating a "clean" prophyrin fraction whose UV adsorption under the 410-nm Soret band was considerably less. A 30-mL chloroform portion of the porphyrin fraction was slurried with 5 mL of silica, dried using air or nitrogen, and dry-packed on top of 15 mL of silica in a 1 cm × 40 cm glass column. A plug of glass wool held the packing in place. Elution with 9:1 hexane/chloroform removed a yellow UV absorbing band that contained the nickel porphyrins. Elution with 7:3 hexane/chloroform removed the deep red vanadium porphyrins. Further elution with chloroform removed polar compounds having no porphyrin spectrum and little vanadium.

Prior to HPLC analysis, the "clean" porphyrin fraction was evaporated to dryness under a nitrogen stream. The procedures and solvents followed those

recommended by Hajibrahim et al. (*4*). One milliliter of 9:1 hexanes/toluene (weak solvent) was added and then the minimal amount of 1:1 chloroform/toluene (strong solvent) was used to dissolve the sample. The HPLC column was 5 or 10 $\mu$ Partisil that had been packed using an aqueous solution containing one drop of concentrated ammonium hydroxide. Columns were activated by eluting the packed column with a 5%/min gradient of a continuous elutropic series of $H_2O$, MeOH, THF, chloroform, and, finally, hexane. The strong and weak solvents were then loaded into the syringe pumps, and the solvent flow rate was adjusted to 60 mL/h of the weak solvent. The detector wavelength was set at 410 nm (Soret band) for samples having a low UV background and to the band at 572 nm when it was high.

The gradient was set to ramp from 0 to 30% strong solvent at 10%/min, from 30 to 55% at 1%/min, and from 55 to 100% at 5%/min. The actual location for the start of the 1% ramp for replicate runs was shifted between 20 and 40% strong solvent depending upon when the band was eluted. The exact location was a function of the dryness of solvents and samples. Fresh, drier solvents gave longer retentions and better separations, but the results were more difficult to duplicate. To recondition the column after a run, the gradient was ramped downward to the pure weak solvent at 5%/min.



After removal of the porphyrin fraction from the alumina column, elution with 200 mL of $CHCl_3$ removed the "nonporphyrin" fraction. This black fraction was washed three times with 200 mL portions of water to remove the small amount of DMF that remained from the original extraction.

Some material remained on the column, as evidenced by the gray-brown color of the alumina. Small amounts could be removed by THF, but most of it was impossible to elute, even with other solvents. That "used alumina" was dried and saved for use as a column packing for fractionating the nonpolyphyrin fraction.

The nonporphyrin fraction in chloroform was concentrated to approximately 30 mL using air. Approximately 10 mL of alumina was added to form a slurry which was then air-dried and used as the nonporphyrin sample.

To fractionate the nonporphyrin sample, the "used alumina" was packed in a 5 cm $\times$ 0.61 cm stainless steel column and washed with chloroform until the background at 254 nm was barely detectable. Using MeOH as the weak solvent, THF as the strong solvent, and a flow rate of 30 mL/h, methanol was pumped through the column with a back pressure of approximately 50 psi until the air had been removed. The column was then opened, and a 0.2-mL portion of the packing at the head of the column replaced by nonporphyrin sample. After MeOH had been pumped through the column to remove air bubbles, a gradient of 0–40% THF was run at 10%/min followed by 40–100% THF at 1%/min. An ISCO Model 1200 fraction collector was

set to change tubes every 4 min (2 mL). Those fractions were monitored for the Soret band in the UV-visible and for vanadium using graphite furnace atomic absorption.

Steric exclusion chromatography of the porphyrin and nonporphyrin fractions was done according to the procedure described by Hodgin et al. (*10*). Lichrospher 500 and 100 in two 15 cm columns were placed in series between a Valco injector and a Duomonitor detector set for 254 nm. Columns were joined using a 3 cm × 0.02 cm i.d., 0.16 cm o.d. stainless steel tube. THF or chloroform containing 1% MeOH was used as a solvent and pumped at 1.5 mL/min. Slower flow rates resulted in some irreversible loss of sample to the silica, indicated by discoloration of the silica and a decrease in the UV signal. Standard polystyrenes dissolved in the same carrier solvent were used for rough calibrations of the columns.

For pyrolysis gas chromatography of the dried porphyrin and nonporphyrin fractions, approximately 0.1 mg of sample was placed on the Pyroprobe ribbon, which was then placed in the injection port of the chromatograph. The sample was pyrolyzed at 400C°/s to 1000°C and held for 2 s. After pyrolyses, the program held the oven temperature at 90°C for 16 min, then increased the temperature at 8C°/min to 290°C and held it at 290°C for 64 min. The eluent from the 3% SE-30 column was split and the components detected using both an FID and flame photometric (sulfur) detector.



For detection of vanadium using flame emission, a Heath system was used with an $N_2O$/acetylene flame which had been optimized for the solvent used. The nebulizer had a fixed uptake rate of 4.1 mL/min. The 4379 Å emission line was monitored, and background was subtracted by scanning off the line.

Atomic absorption measurements of vanadium were made using the Varian AA-375 with its carbon rod analyzer. The 3184 Å absorption line was used with a spectrometer slit width of 0.1 nm. Using that automated system, a 20-μL aliquote of a 2-mL sample was placed in the graphite tube. The solvent was dried at 50°C for 30 s, ashed at 1000°C for 15 s, and finally ramped at 400C°/s to 2500°C and held for 1.5 s. During atomization, a gas sheath composed of 0.5 L/min of hydrogen and 5 L/min of nitrogen surrounded the graphite tube. Total analysis time was approximately 2 min/sample. The signal was measured using a deuterium lamp for background correction. For weak signals, additional aliquots of the sample were placed in the tube before ashing and atomization. In all cases, signals were compared to those from vanadium oxobis-(1-phenyl-1,3-butanedionate) in THF.

To monitor the porphyrin fraction during the separation stages, UV-visible spectra from 350–650 nm were obtained against chloroform using a Cary 14. Lower wavelengths were not scanned because those fractions usually

contained toluene. The Soret band was used to estimate the amount of porphyrin by using the reported 300,000 molar extinction coefficient, a l-cm cell path length, and the sample volume or dilution factor used to bring the Soret band on scale. Peak size was corrected by subtracting the average UV background.

Separation of the nonporphyrin fraction was monitored using the 254–260 nm region. The nonporphyrin fraction was also scanned from 240–450 nm against a distilled THF or chloroform reference. Sharp peaks were not observed; maximum adsorption occurred in the 250–300 nm region.

Demetallation of the porphyrin fraction followed the procedure described by Baker (*11*). A 25-mL portion of "clean" porphyrin concentrate (~3 μmol) was dried under nitrogen. A 9-mL portion of methane sulfonic acid and a few crystals of hydrazine sulfate were added to a 150-mL three-neck flask that contained the sample. The flask was placed in a 60°C oil bath, and dry nitrogen flushed the flask. After 1 h the dry flask was allowed to cool, and 100 mL of water and 20 mL of methylene chloride added. The mixture was transferred to an extraction flask where the salts were removed by draining off the water. The methylene chloride was washed two more times with water. Infrared spectra were obtained using a Perkin-Elmer 599B. A sample was dried under vacuum on sodium chloride blocks for measurement.



## RESULTS

### Preliminary Studies

The initial studies evaluated the effects of solvents on the crude and asphaltenes. Solvents in the polarity range from carbon tetrachloride to the THF dissolved both samples. As polarity of the solvent decreased below that for carbon tetrachloride, some components precipitated from the crude. The more volatile hydrocarbons in crudes were easily separated from the heavier fractions using a hydrocarbon solvent such as pentane, hexane, or cyclohexane. However, those fractions did not show porphyrin spectra, and the vanadium concentrations were low. This was in accord with Table 1, which shows that vanadium remains in the asphaltene fraction. Hence the asphaltenes were generally preferred for further studies.

As polarity of the solvent increased above that of pure THF, e.g., MeOH, less sample dissolved. It was interesting to find that DMF had a particular ability to solubilize easily the porphyrin compounds whereas dimethylsulfoxide did not. Aromatic solvents such as xylene, toluene, and benzene were also very effective in solubilizing the crude and asphaltenes but were less desirable because they absorbed in the UV.

Exploratory separations were done on commercial TLC silica plates which readily separated the red vanadyl porphyrins from the crude. Although mixtures of chloroform and hexanes or MeOH/benzene worked as did DMF alone, the best separation was obtained using 1:1 *n*-decane/chloroform on the 80 A K5F silica plate. There the porphyrin fraction separated into four distinct pink bands, consistent with the studies of Blumer (*9*) who used chloroform/isooctane to separate porphyrins on paper.

TLC studies also showed that considerable nonporphyrin material was permanently bound to the silica. Chloroform removed some components but left a dark band. Reapplication of the chloroform-removed species caused a new permanent band to form on the silica plate at the point of application.

## Isolations of Porphyrin and Nonporphyrin Fractions



Column chromatography was done on alumina using DMF as the first solvent and chloroform as the second. Because of the strong absorption of the Soret band, the monitoring of the separation of the metalloporphyrin fraction was straightforward. Figure 2 shows UV-visible scans of the Soret region for the porphyrin fraction (DMF) and the nonporphyrin fractions (chloroform). The main differences in these two fractions were the colors of the porphyrin (wine red) and nonporphyrin (black) fractions, the relative intensity of their Soret bands, and the size of the UV background from 350–450 nm. The nonporphyrin fraction shown in Fig. 2 was diluted five times as much as the porphyrin fraction in obtaining those spectra.

Isolation of the porphyrin fraction using DMF was similar to a procedure described by Serebrennikova et al. (*12*) who used solvent extraction with DMF of crude dispersed on keiselguhr to remove 95–98% of the porphyrins. Our recoveries were not as high, usually approximately 90%. That figure was highly dependent upon how the background was subtracted and how the porphyrin was measured in the crude and in the nonporphyrin sample where a large UV background masked the Soret band.

The "clean" vanadyl porphyrin fraction was obtained by an additional separation of the porphyrin fraction using a silica column. First, elution with hexanes removed UV absorbing components, a step that was especially important when working with crudes. The fraction was bright yellow. Second, 10% chloroform in the hexane removed a nearly colorless fraction that held the nickel porphyrins and some additional UV absorbing material. A UV-visible scan of the nickel porphyrin fraction is shown in Fig. 3 where the Soret, $\beta$, and $\alpha$ bands were noticeable at the expected 390, 525, and 560 nm wavelengths. The nickel porphyrins were much less than the vanadium porphyrins as expected from their relative concentrations in the crude. Because of the small amounts and the difficulty in isolating the nickel

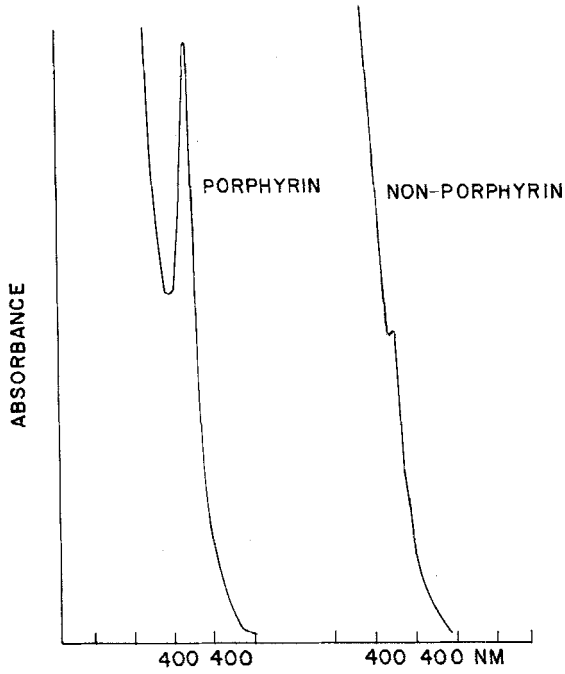


FIG. 2. Soret bands at 410 nm for porphyrin and nonporphyrin fractions.



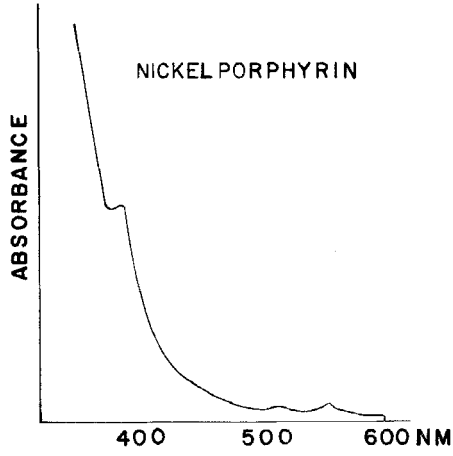


FIG. 3. UV-visible spectrum of the nickel porphyrin fraction.

porphyrins from the UV background, that fraction was not studied further.

Third, the "clean" vanadium porphyrin fraction was obtained from the silica column using 7:3 hexanes/chloroform. A UV-visible scan of that fraction is shown in Fig. 4. The fraction has the Soret band at 412 nm, the $\beta$ band at 535 nm, and the $\alpha$ band at 572 nm, as expected. A slight shoulder on the Soret band in the 390–400 nm region indicated that a slight amount of nickel or other metal porphyrin was most likely present in the vanadium fraction. The additional shoulder at 590 nm was also found in spectra published by Berti et al. (*13*) and by Serebrennikova et al. (*14*).

## Fractionation of the "Clean" Porphyrins

HPLC removal of the "clean" vanadyl porphyrin fraction from 10 $\mu$m Partisil (Column 4) followed the procedure recommended by Hajibrahim et al. (*4*). In the present study, however, changes were made in the gradient so as to improve the separation; in addition, separation of the metalloporphyrins rather than the demetallated species was stressed.

Figure 5 shows a typical chromatogram of the vanadyl porphyrins. A series of partially resolved overlapping peaks was observed. A similar chromatogram was obtained for a porphyrin fraction isolated according to the procedure of Hajibrahim et al. (*4*).

Based upon their work with demetallated porphyrins and that of McFadden et al. (5) with LC/MS, we have suggested that the etio porphyrins

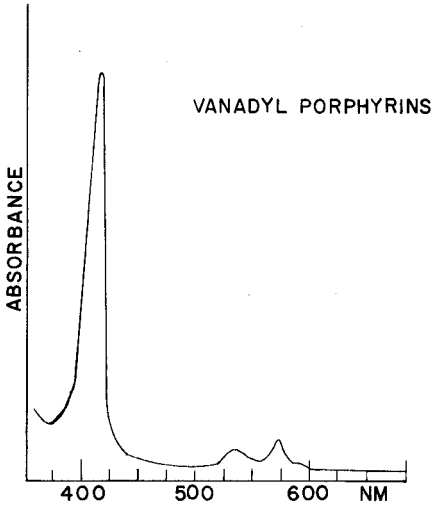


FIG. 4. UV-visible spectrum of the "clean" vanadyl porphyrin fraction.

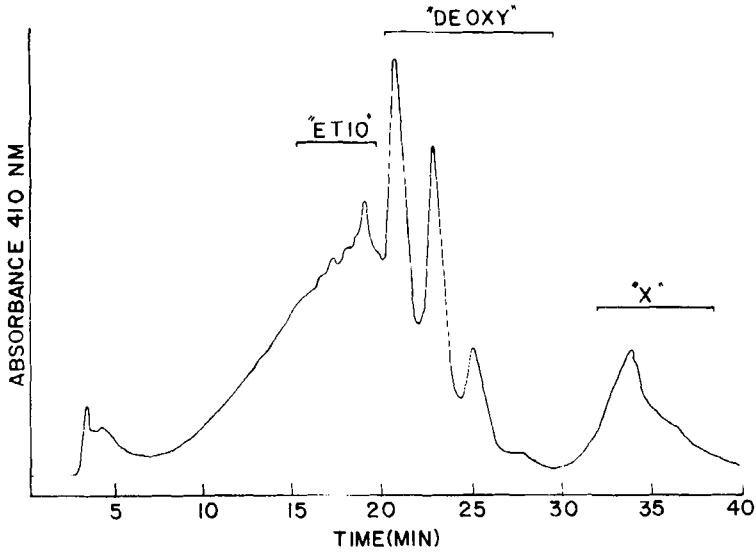


FIG. 5. 10 μm Partisil chromatogram of the "clean" vanadyl porphyrin fraction using Column No. 4. Possible etioporphyrins and deoxyphylloerthroetioporphyrins are marked, as is an irreproducible peak, "X", which was probably an artifact of the separation procedure.



eluted first and the deoxyphylloerthroetioporphyrin series later. The figure shows first that the etio species gradually increased in concentration on going from nonpolar to polar eluents, suggesting that the shorter chain species were more prevalent. Altrirki et al. (*15*), who looked at the maliimides obtained by oxidation of the porphyrin rings, reached the same conclusion. Second, the deoxyphylloerthroetioporphyrins occurred in several distinct types as indicated by the series of major peaks. Finally, the peak marked "X" in the chromatogram might be an artifact because it did not appear in every separation, and when it did occur, it shifted position on successive runs.

A brief experiment was tried in which a polar-amino-cyano (PAC) packing (Column 5) was substituted for Partisil. Using hexane as the weak solvent and chloroform as the strong solvent, and a 5%/min gradient from weak to strong solvent, the porphyrins eluted as a single band at 90% strong solvent. Some UV absorbing compounds, which were nonporphyrin, eluted before the porphyrins at 40% strong solvent.

## Fractionation of the Nonporphyrins

A "used" neutral alumina gave the best separation. Silica packings irreversibly adsorbed the species, while acidic and basic alumina not only

failed to resolve as many compounds as neutral alumina, but they also irreversibly adsorbed more compounds, as indicated by the black color of the packing after elution with chloroform.

Separation of the nonporphyrin fraction, shown in Fig. 6, used a nonaqueous system of MeOH as the weak solvent and THF as the strong solvent. Some additional compounds were eluted by following the MeOH/THF system with a 1% THF/chloroform gradient. A decrease in solvent flow from 60 to 30 mL/h improved the separation, probably due to slow desorption from the surface of the sample. Increasing the column length from 5 to 25 cm did not change the separation appreciably, thereby indicating that the separation was controlled by desorption of the sample from the alumina. Interestingly, elution with a system of hexane to chloroform eluted an overall mixture having the same total UV absorption as that from the MeOH/THF system, but resolution was not as good.

The nonporphyrin separation was very difficult to duplicate even though the overall shape was approximately the same as shown in Figs. 6 and 7. Part of the nonreproducibility can be explained by assuming that the packing material was different for successive separations as a result of components



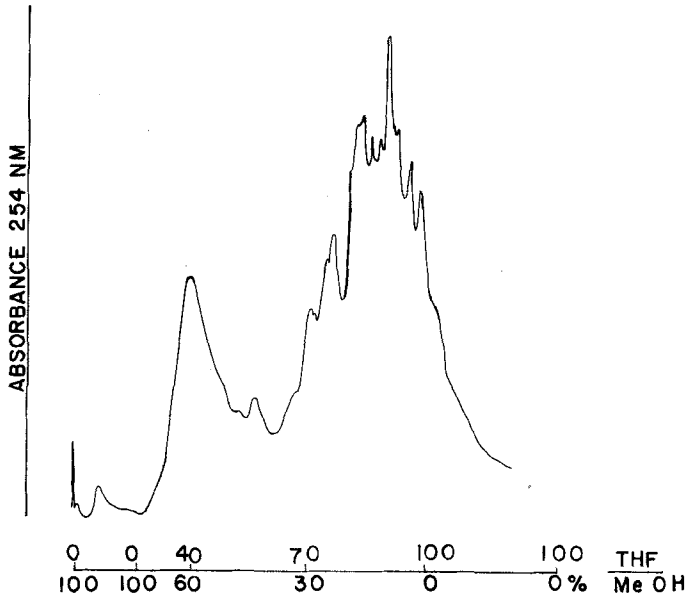


FIG. 6. Liquid chromatographic extraction of the nonporphyrin compounds from alumina (Column No. 3) using methanol/tetrahydrofuran gradient.

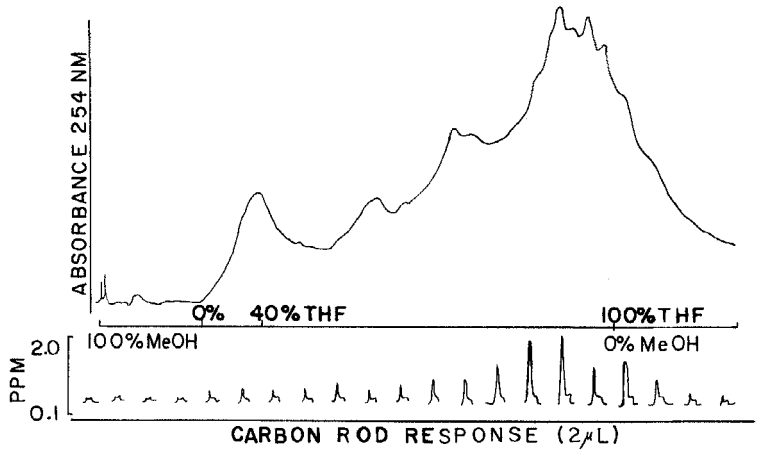


FIG. 7. Liquid chromatographic extraction of the nonporphyrin compounds from alumina (Column No. 3) using a methanol/tetrahydrofuran gradient showing vanadium responses from graphite-furnace atomic adsorption measurements of 21 fractions.



which eluted only after several runs or not at all. Hence, in one sense, an uncontrolled reverse-phase system was operative.

Injection of the nonporphyrin solution using a valve was unsatisfactory. A solvent that was strong enough (MeOH) to dissolve all the sample was too strong to permit fractionation of most of the components; a weaker solvent (hexane) caused the sample to precipitate. Sample dissolved in a strong solvent, when injected into a much weaker mobile phase, caused a precipitate that plugged the column frits.

## Detection of Vanadium

The porphyrin fraction contained approximately 30% of the total vanadium, assuming that the vanadium response was the same in both the porphyrin and nonporphyrin fractions. That ratio was consistent with the figures reported by Berti et al. (*13*) and Sebor et al. (*16*) for Boscan crude.

Direct detection of vanadium in crude was difficult at low concentrations when using flame emission because of refractory oxides and the high background of the burning crude. A minimum practical amount was found to be 40 ppm even though standards were detectable to 10 ppm.

Bacause the actual samples were much more dilute, a nonflame method, which worked well down to the 0.1 ppm level, was used. The ashed sample gave consistent and repeatable results with little background. The bottom

portion of Fig. 7 shows the vanadium signals obtained from 2 mL fractions of the nonporphyrin sample. The UV absorption of this separation is shown in the top half of Fig. 7 where the levels of vanadium can be observed to parallel rather well the UV absorption. This indicated that vanadium was dispersed throughout the nonporphyrin fraction.

## Other Experiments

The IR spectra of the porphyrin and nonporphyrin fractions provided only limited information. Based on the work of Selbin and Holmes (*17*) and Erdman et al. (*18*), a strong absorption band assigned to the V-O stretching frequency should have been detectable at 990–1000 $cm^{-1}$. Instead, only a broad band was observed for the porphyrin fraction. As shown in Fig. 8, the porphyrin fraction indicated some carbonyl species. This band was broad and suggested that acidic, ketone, and aldehyde groups were present. The IR of the nonporphyrin fraction showed only a small C-H stretch on an otherwise level background.

Steric exclusion chromatography using a Lichrospher column gave rough estimates of the molecular size distribution of the separation fractions. The



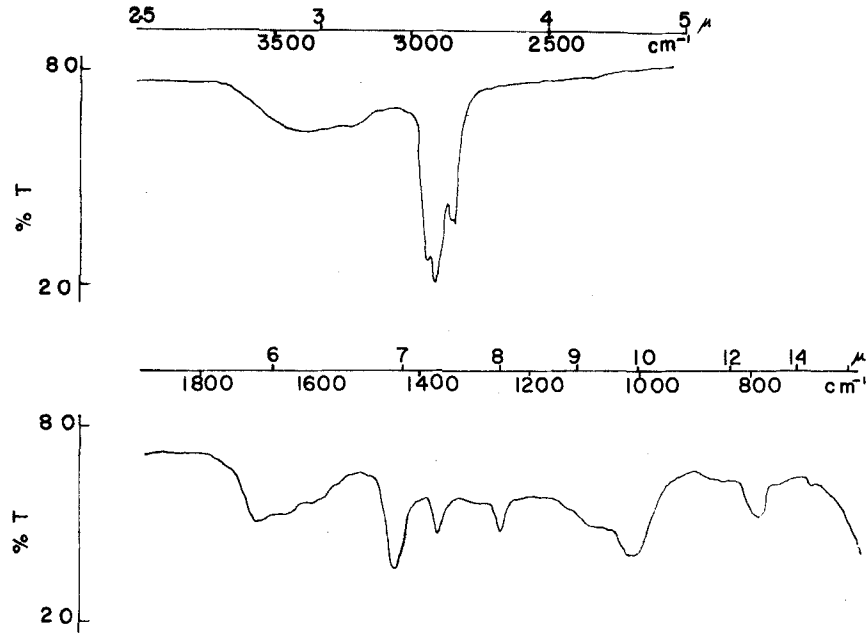


FIG. 8. Infrared spectra of the "clean" vanadium porphyrin fraction.

Boscan crude and asphaltenes had been previously analyzed by Hodgin et al. (*10*), who showed that the retention was approximately the same as that for the 2000–3000 molecular weight polystyrene; the asphaltene fraction was similar to the crude but skewed to a higher molecular size with a decrease in the lower molecular sizes. Our studies found similar results.

The DMF/porphyrin fractions obtained from the asphaltenes had an average molecular size approximately the same as that of the 800 MW polystyrene. However, that fraction also included a larger molecular size which began about 17,000 and extended above 37,000. That fraction was roughly 5% of the prophyrins based upon the absorption at 254 nm. It did not have a Soret absorption band. The "clean" porphyrin fraction had an average molecular size approximately the same as 800 MW polystyrene and a small shoulder at approximately the 1500 molecular size. The higher molecular weights were not present in that fraction.

The nonporphyrin fraction had a molecular size distribution which matched that of the crudes themselves. The average size eluted where the 2000–3000 MW polystyrene did.

The chromatogram obtained from pyrolysis of the "clean" porphyrin fraction was surprising in that only a few peaks were observed in the flame detector. However, the sulfur response was large (Fig. 9A) and indicated many compounds dispersed throughout the chromatogram, with the higher boiling components being more prominent. The chromatogram obtained from pyrolysis of the nonporphyrin fraction (Fig. 9B) showed an expected, high content of sulfur peaks that tended to match the flame response. Lower boilers were more prominent and tended to occur in a regular progression.

The UV-visible spectrum of a demetallated porphyrin fraction, shown in Fig. 10, is similar to that given by Baker (*11*). It indicated the presence of the deoxyphylloerthroetioporphyrins and the etioporphyrin types, as expected. The porphyrin bands IV–I are clearly observed at 490, 570, and 534, and 617 nm, respectively. The Soret band was no longer evident and the UV background in the 400–450 region had increased.

## DISCUSSION

The present separations of asphaltenes and crudes into porphyrin and nonporphyrin fractions were simple compared to others that have been developed (*4, 11, 13, 18*). Isolation of the porphyrins in two separation stages required less than 4 h and minimal effort. The chromatographic columns did not need to be specially treated or packed, being essentially a medium from which the porphyrins were differentially desorbed rather than one which the solutes repeatedly adsorbed as they progressed along the

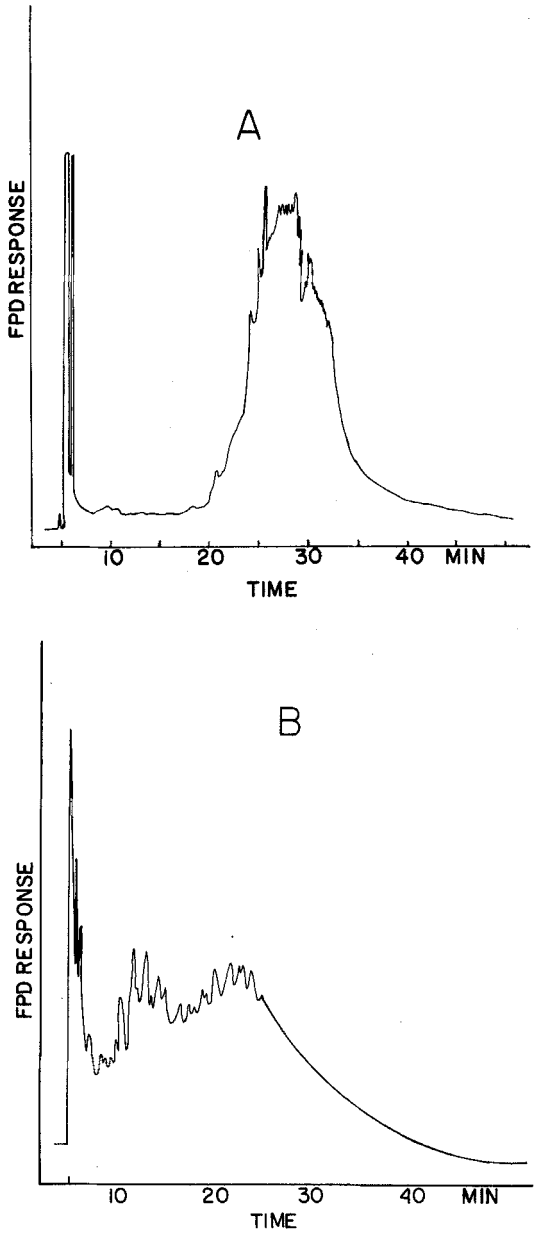


FIG. 9. Flame photometric (sulfur) detector responses of the gas chromatographic eluent from pyrolyzed (A) "clean" porphyrin fraction, and (B) nonporphyrin fraction.

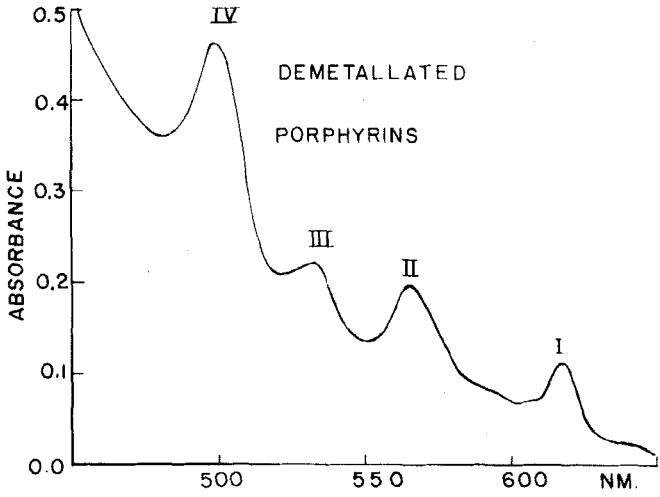


FIG. 10. UV-visible spectrum of the "clean" porphyrin fraction after removal of vanadium by methane sulfonic acid.



column. Because DMF was selective for the porphyrins, relatively few nonporphyrin compounds remained to be removed by the second stage of separation.

The coating of the crude or asphaltene on a surface allowed the quick extraction of the porphyrins. However, direct extraction of porphyrins from the solid asphaltenes using DMF did not work well due to slow removal of the porphyrins. A similar problem was encountered by Hajibrahim et al. (*4*) who reported that the asphaltenes needed to be extracted six times with MeOH/benzene solvent. That process required centrifugation to separate the particles from he extracting solvent, whereas our procedure did not. In contrast, use of the coated sample provided a simple method for obtaining a nonporphyrin fraction from which the most polar compounds had been removed as a result of their being permanently bound to the chromatographic adsorbent.

HPLC separation of the "clean" porphyrin fraction into a multitude of partially resolved components was similar to that reported by Hajibrahim et al. (*4*). Vanadium was easily monitored by scanning the UV-visible spectrum in the immediate vicinity of the Soret band at 410 nm. Detection of sulfur in that fraction was surprising because the UV-visible spectra had indicated sharp porphyrin spectra having only a small UV background. However, the incorporation of sulfur into "porphyrinlike" compounds has been mentioned by Yen (*7*) and Dickson and Petrakis (*6*).

A brief experiment using another polar phase, PAC, did not work out as well as silica for separating a "clean" vanadium fraction because the porphyrins eluted as a single band. However, some nonporphyrin bands did separate from the sample, so further studies should be done. Reverse phase separations were not explored because Hajibrahim et al. (*4*) had concluded that they did not work as well as those on silica. Gas chromatography of the demetallated and then silylated complexes likewise were not done since Boylan et al. (*20*) had shown that considerable sample preparation was required, and the resulting chromotographic separations were poor.

Future studies might be done in which ternary solvents are used, apparent pH is varied, and ion pairing or derivatizing agents are added. The pyrolysis GC/mass spectra of this porphyrin fraction might also give clues as to the nature of the sulfur compounds in that fraction.

Separation of the nonporphyrin fraction showed that the mixture was highly complex on the basis of its UV adsorption. Because vanadium content tended to parallel UV absorption, separation of a distinctly nonporphyrin vanadium complex from other UV absorbing compounds was not accomplished.



The porphyrin and nonporphyrin fractions clearly differed in their relative molecular size distributions. The nonporphyrin fraction was similar to the asphaltene fraction in that it consisted mainly of large molecules (2000–3000 MW). That plus the fact that the carbon-to-hydrogen ratio was large suggests that the nonporphyrin fraction consisted mainly of highly branched carbon rings that incorporated some sulfur and, probably, nitrogen. The porphyrin fraction, on the other hand, was composed mainly of smaller molecules (~600–800 MW) which would be expected for single porphyrin rings having different groups attached to the tetrapyrole rings.

Literature values for molecular sizes of Boscan asphaltenes differ considerably, and the values range from ~1000 to 6000 MW for the average size. That variation has been mainly attributed to the uncertainties of the analysis methods and the fact that the molecular size was solvent dependent (*21, 22*). The fact that the molecular size was based on polystyrene standards rather than on compounds similar to those in the crude is another source of possible error.

On-line specific detection of vanadium using flame emission as the basis for an LC detector proved to be impractical for several reasons. First, the detection limit of 40 ppm was too high for the levels in the desired samples. Second, a solvent gradient during elution required that the composition of the flame gas be continually adjusted so as to optimize flame emission. When gradients of chloroform and hexane were used, very slight changes in composition caused significant changes in the flame. Third, the nebulizer was most efficient at a volume uptake much faster than the desired LC flow rate.

Fourth, although chloroform was a desirable LC solvent, its use in the $N_2O$/acetylene flame was not recommended due to possible formation of toxic gas. Finally, when the organic compounds were destroyed in the flame, the background increased. Furthermore, ligands bound to vanadium affected its signal by changing desolvation and atomization rates (*16*). Altogether, quantitative measurements were difficult to make.

Nonflame atomic absorption measurement of vanadium appeared to solve the problem of detecting it in dilute HPLC effluents. However, there were some limitations to the graphite furnace method. The number of analyses per graphite tube was limited to approximately 50 analyses due to the high temperature required for atomization. In addition, dry ashing of the sample at 1000°C may have caused losses of volatile vanadium complexes.

In summary, this study has separated the vanadium-containing compounds into two fractions, porphyrin and nonporphyrin. The latter has been partially separated using gradient liquid chromatographic techniques, but additional studies are needed to provide cleaner subfractions. The overall nonporphyrin fraction is a highly complex sample having vanadium compounds dispersed throughout.

Additional studies using pyrolysis gas chromatography/mass spectrometry should help to clarify the forms in which sulfur are found in both the porphyrin and nonporphyrin fractions. In addition, resonance Raman and Fourier transform infrared of both the original species and their pyrolysis products should prove to be useful, even for the small amounts produced by HPLC.



## Acknowledgments

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