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### FRACTIONATION AND CHARACTERIZATION OF DEMETALLATED NON-PORPHYRINS FROM BOSCAN CRUDE OIL

Abstract: The demetallation of non-porphyrin fractions from Boscan crude oil was studied using sulfuric chloride at different reaction times. Periods longer than eight hours almost completely removed the vanadium which was determined using graphite furnace atomic absorption spectrometry (GFAAS).

Chromatographic studies (size exclusion and HPLC) indicated that demetallation led to several low molecular weight components. Mass spectrometry suggested that the vanadyl-non porphyrins have molecular weights less than 400. IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and mass spectra showed the presence of large aliphatic hydrocarbon chains.

The primary goals of the present study were to fractionate crude oil into porphyrin and non-porphyrin fractions, to demetallate non-porphyrins using sulfuric chloride, and then to separate demetallated non-porphyrin fractions by size exclusion chromatography and high performance liquid chromatography.

Chemical. The Boscan heavy crude oil was provided by INTEVEP, Caracas, Venezuela.

#### ABSTRACT

Demetallations of non-porphyrin fractions from Boscan crude oil were done using sulfuric chloride at different reaction times. Periods longer than eight hours almost completely removed the vanadium which was determined using graphite furnace atomic absorption spectrometry (GFAAS).

Chromatographic studies (size exclusion and HPLC) indicated that demetallation led to several low molecular weight components. Mass spectrometry suggested that the vanadyl-non porphyrins have molecular weights less than 400. IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and mass spectra showed the presence of large aliphatic hydrocarbon chains.

#### RESUMEN

Las fracciones de no-porfirinas del crudo de Boscan se desmetalizaron usando cloruro de sulfuro a diferentes tiempos de reacción. Periodos mayores de ocho horas removieron casi completamente el vanadio el cual se determinó usando la espectrometría de absorción atómica con horno de grafito (GFAAS).

Los estudios cromatográficos (cromatografía de exclusión y HPLC) indicaron que la desmetalización condujo a varios compuestos de bajo peso molecular. La espectrometría de masa sugirió que las vanadil-no porfirinas poseen pesos moleculares menores de 400. IR, <sup>1</sup>H RMN, <sup>13</sup>CRMN y espectrometría de masa demostraron la presencia de largas cadenas de hidrocarburos alifáticos.

#### INTRODUCTION

Crude oils from Venezuela contain unusually high amounts of vanadium and nickel [1]. Since the presence

of these metals is deleterious to cracking catalysts for petroleum, an understanding of the nature of the metals in petroleum is of importance.

Vanadium in crude oil exists predominantly as the vanadyl ion (VO<sup>2+</sup>) in chelates with porphyrins [2,3,4] and also with other largely unknown non-porphyrins [2]. The porphyrin chelates have been the most studied and have been reviewed by Baker and Palmer [5]. However, little is known about the non porphyrin fractions. An improved procedure to isolate these fractions and some of their characteristics have been published by Dickson et al. [6] and Yen et al. [2]. Spencer et al. [7] and Crouch et al. [8] reported the fractionation of vanadyl (mixed with some nickel) non-porphyrins using liquid chromatography plus UV-Visible absorbance and off-line graphite furnace atomic absorption spectroscopy (GFAAS) to detect vanadium and nickel fractions. Crouch isolated samples containing vanadium and nickel non-porphyrin complexes using size exclusion chromatography and reported a complete study of the distribution of vanadium and nickel in both porphyrins and non-porphyrin fractions using GFAAS. More recently, HPLC in combination with GFAAS has also been used by Fish et al. [9,10] to provide both a vanadium fingerprint and molecular weight categorization of the vanadyl porphyrin and non-porphyrin compounds in heavy crudes.

The primary goals of the present study were to fractionate crude oil into porphyrin and non-porphyrin fractions, to demetallate non-porphyrins using sulfuric chloride, and then to separate demetallated non-porphyrin fractions by size exclusion chromatography and high performance liquid chromatography.

#### EXPERIMENTAL SECTION

Chemical. The Boscan heavy crude oil was provided by INTEVEP, Caracas, Venezuela.

Dimethylformamide (DMF), tetrahydrofuran (THF), methanol (MeOH), chloroform, carbon tetrachloride, n-hexane, benzene, and methylene chloride were spectrophotometric or HPLC grade Methyl t-butyl ether (MTBE) and acetonitrile (ACN) were Fisher HPLC grade. THF was freshly distilled over potassium and obtained on a daily basis as needed. Sulfuryl chloride (Aldrich Chemical Co.) and Aldrich 99+% pure phenol were used in the demetallation procedure.

Neutral alumina (Brockman activity 1, 80-200 mesh) was obtained from Fischer Scientific Co. Lichrosphere 60 was obtained from Alltech Associates, Inc.

Polystyrene standards of 800, 2200, 4000, 9000, 17000 and 36000 molecular weight were obtained from Pressure Chemical for use as standards in chromatography.

Vanadium standards were made from vanadium oxobis-(1-phenyl-1,3-butanedionate) (Eastman Kodak Co., Rochester, NY).

**Apparatus.** The chromatographic system consisted of and isocratic Altex pump, Model 110A (Berkeley, CA), a Valco Model ACV-6-UHP a N60 injection valve (Houston, TX) having a 10  $\mu$ L sample loop, a Perkin-Elmer Model LC 55 liquid chromatography detector (Norwalk, CT) set at 254 nm, and a Linear (Reno, NV) Model 585 chart recorder.

A model 8800 gradient liquid chromatographic system (Dupont Instruments, was used for all HPLC studies of demetallated non-porphyrins. The system was equipped with a Valco Model ACV-6-4HP a N60 injection valve having a 50  $\mu$ L sample loop. For fraction collection, a Micromeritics Automatic Injection Model 725 and a Dupont Series 8800 variable wavelength UV detector were used. An IBM Computer System Model 9000 was used to record the chromatograms and store all of the data from HPLC studies.

HPLC columns are listed in Table 1 and the gradients in Table 2. GFAAS measurements were made on a Perkin-Elmer Model 403 Atomic Absorption Spectrophotometer. IR spectra were recorded using a Perkin-Elmer Model 599B spectrometer and a Digilab FTS-20C FTIR spectrometer having a gold-coated cylindrical reflection absorption cell, over the spectral range 600-3.800  $\text{cm}^{-1}$ .

Proton nuclear magnetic resonance was performed using a Varian Model T-60 NMR spectrometer Carbon-13 nuclear magnetic resonance was done using a Joel Model FX-60 spectrometer. Electron ionization mass spectra were recorded using a Finningan Quadrupole mass spectrometer, Model 4000. The mass spectrometer was operated at 70 and 20 eV.

The isolation of porphyrin and non-porphyrin fractions from Boscan crude oil followed the procedure developed by Spencer et al [7]. The method of demetallation of non-porphyrins was derived from a procedure developed by Sugihara et. al. [11] and modified by Crouch et al. [9] in which sulfuryl chloride was used for demetallation. Finally, the vanadium in the organic fraction was determined using GFAAS and the percentage demetallation calculated.

## RESULTS

**Demetallation of Non-porphyrins.** Because sulfuryl chloride was found to be very effective under gentle reaction conditions [2,8], a series of demetallations were made at -78°C for different reaction times. Periods less than 2 h provided little reaction. However, data in Table 3 Show that a reaction time of 24 h almost completely removed the vanadium from the non-porphyrin fraction. Generally, 8 h was enough time to remove most of the metal from the non-porphyrins. The original content of vanadium and nickel was 1.300 ppm and 180 ppm respectively. UV-visible, IR and NMR spectrometries were used to monitor the demetallation procedure during the course of the reaction.

**Size Exclusion Chromatography.** The chromatogram of the demetallated non-porphyrins in Figure 1 shows that the components ranged in polystyrene equivalent molecular weight from 17000 to 100 with the major peaks at 1700 and 1500. Figures 1 also indicates that demetallation resulted in the formation of low molecular weight components having maxima at 600 and 200. There is the possibility that these peaks were caused by a break-up of micelles of the non-porphyrins [10-12]. If the non-porphyrins were present as micelles formed by compounds of relatively lower molecular weight (as a result of strong intermolecular associations), it could account for the low volatility and limited solubility of the non-porphyrins fractions. SEC fractions were collected from multiple aliquots of samples so as to obtain enough material for subsequent reinjection and fractionation. Figure 2 shows the four fractions from SEC of demetallated non-porphyrins and the chromatograms for the individual fraction upon reinjection under the same chromatographic conditions. Chromatograms of each fraction showed components for all of the other fractions. The results indicated once again that slow interconversions must have occurred [8,13]. Another interesting finding was the improved resolution for the last two peaks, specially for fractions 1 and 2. HPLC studies. According to Crouch et al. [8] the best column for fractionating the non-porphyrin samples was 300 Å trimethylated silica (TMS); the best gradient was gradient A. (See Table 1 and 2). When Column 2 and gradient A were used to fractionate the demetallated non-porphyrin samples, Figure 3 show that, unlike the case with the porphyrins [14], demetallated non-porphyrins showed only four or five peaks instead of many peaks. As seen in Figure 3, the area of the first broad peak for vanadyl non-porphyrins is larger than that for the demetallated non-porphyrins. Conversely, the area of the second broad peak was smaller for the demetallated non-porphyrins.

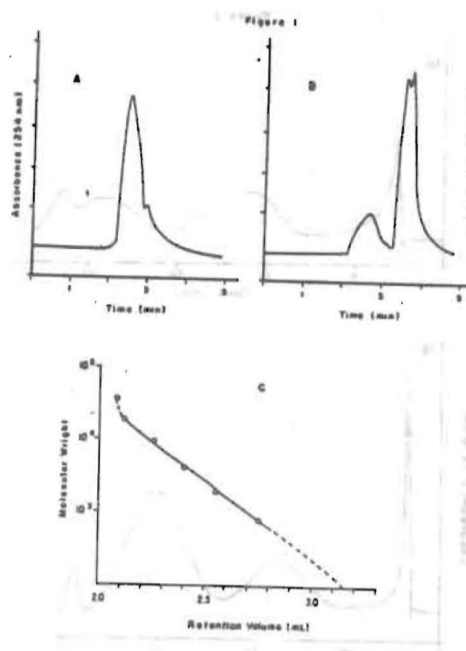
HPLC fractions of demetallated non-porphyrins were collected from many samples so that chromatographic and spectral differences could be examined. Figure 4 shows the six fractions collected from the HPLC chromatogram and the results fo reinjecting fractions 1-6. We confirmed the finding of Crouch et al.[8] that each fraction contained some of each of the other fractions. The results, like the earlier SEC results, indicate that slow interconversion must occur between the components of the different fractions.

Spectrometric studies. Each of the SEC fractions was

TABLE 1

## HIGH PERFORMANCE LIQUID CHROMATOGRAPHIC COLUMNS

Column Number	Packing	Particle Diam., $\mu\text{m}$	Mean Pore Diam., $\text{\AA}$	Column Length
1	Lichrosorb 60 Silica	5	60	25 cm
2	C <sub>18</sub> on Lichrosphere 300	10	300	25 cm
3	Lichrosorb Diol	10	300	5 cm
4	Phenyl on Lichrosorb 300	10	300	25 cm

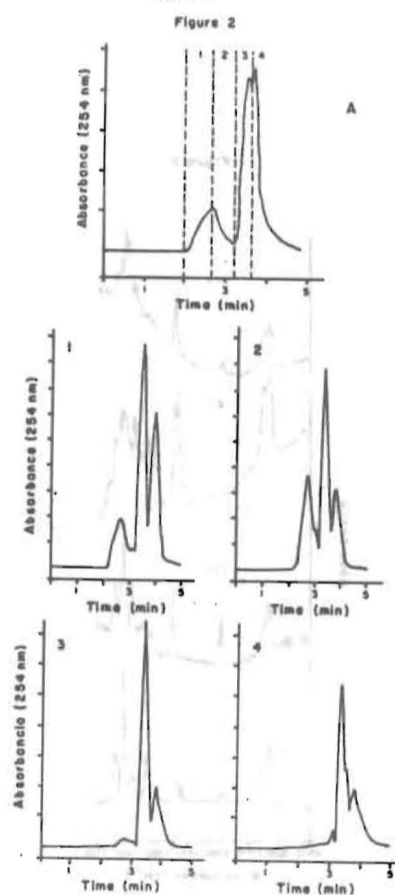
TABLE 2  
LINEAR GRADIENTS USED IN HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

Gradient	Flow-rate ml/min	Gradient Description
A	1	100% MeOH to 50/50/20 MeOH/CHCl <sub>3</sub> /MTBE in 10 min (hold 5 min) to 60/40 CHCl <sub>3</sub> /MTBE in 10 min (hold 5 min) to CHCl <sub>3</sub> in 10 min (hold 5 min) to MeOH in 5 min (hold 5 min).
B	1	100% MeOH to 90/4 MTBE/MeOH in 15 min (hold 5 min) to 70/30 CHCl <sub>3</sub> /MTBE in 15 min (hold 5 min) to MeOH in 5 min (hold 10 min).
C	1	100% MTBE to 4/96 MeOH/MeOH in 10 min (hold 5 min) to 30/70 MeOH/CHCl <sub>3</sub> in 10 min (hold 5 min) to MTBE in 5 min (hold 10 min).

TABLE 3

## DEMETHALLATION OF NON-PORPHYRIN SAMPLES

Time, h	Demetalation, %
2	10
4	73
8	76
16	84
24	95



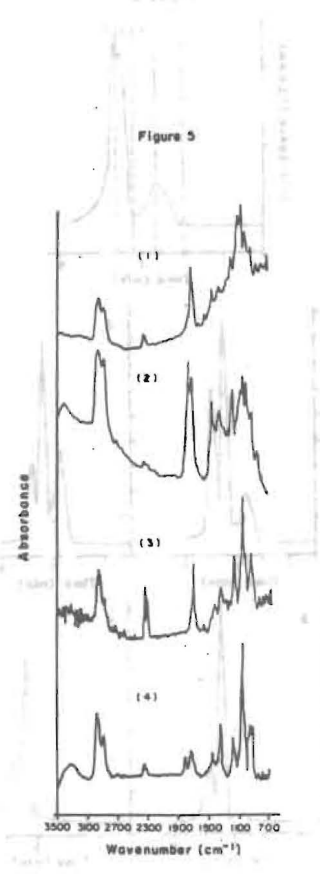
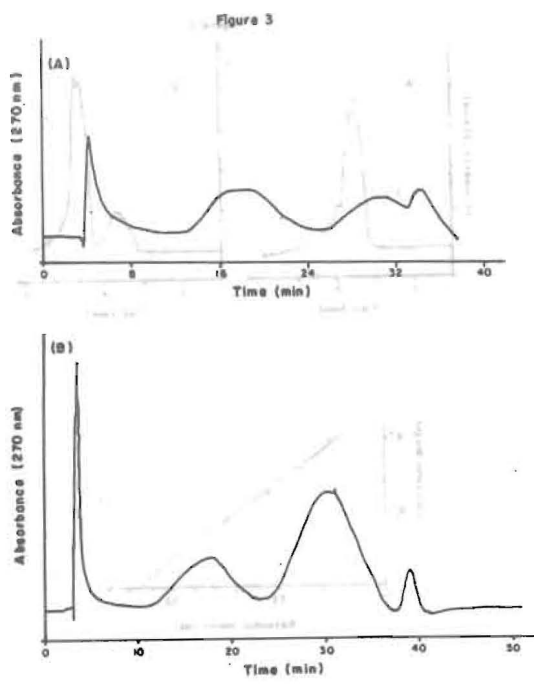
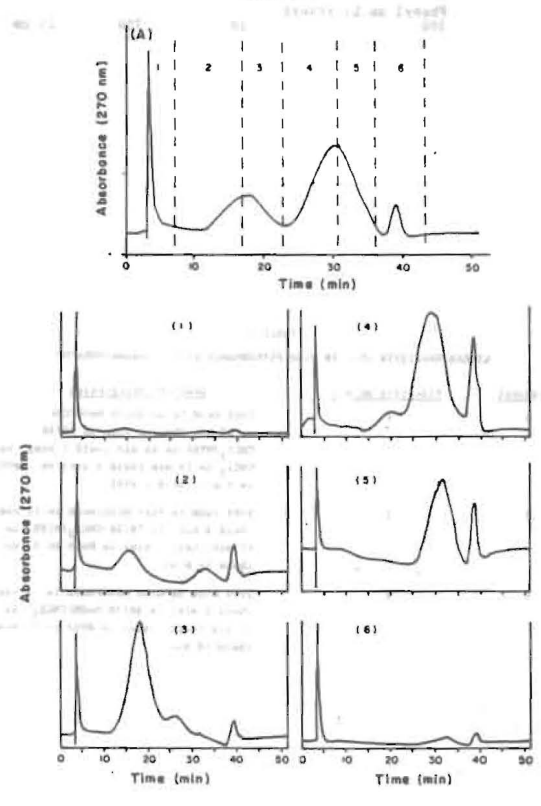


Figure 4

Figure 4 is a chromatogram showing Absorbance at 270 nm versus Time in minutes. Six specific peaks are identified and numbered 1 through 6, with vertical dashed lines indicating their retention times. The peaks occur at approximately 5, 15, 25, 30, 40, and 45 minutes.



individually collected and concentrated to form a carbon tetrachloride sample for the FT-IR. Figure 5 shows that fractions 1 and 2 showed a large amount of aliphatic C-H stretching ( $3000-2800\text{ cm}^{-1}$ ). On going to fractions 3 and 4, this peak decreased and at the same time became progressively broader. Fractions 2 and 4 revealed NH and OH at  $3200-3400\text{ cm}^{-1}$ , respectively, which did not appear in fractions 1 and 3.

Fractions 1 and 2 also showed a sharp carbonyl peak at  $1750\text{ cm}^{-1}$ . For fraction 2 this peak appeared as a doublet and at a higher wave number that corresponds to that for carboxylic acids. In fractions 4, this peak became very small. The CO absorption region at  $1.000\text{ cm}^{-1}$  was smallest in fraction 1, but increased in fractions 3 and 4.

Mass spectrometry of demetallated non-porphyrins. Figure 7 shows small strong peaks at  $m/e$  205 and 207 attributable to non porphyrins. This agrees with the last two peaks in our SEC and is support for the recent study made by Fish et al. [10]. They concluded that vanadyl non-porphyrins with apparent molecular weights greater than 2000 by SEC actually had molecular weights of less than 400 by mass spectrometry. That implies that the vanadyl non-porphyrins either form aggregates or are complexed with the large molecular weight asphaltenic components of heavy crude petroleum. This is supported also by the work of Dicky and Yen [12], who suggested that the microstructure of asphaltic materials consists of three entities: micelles, particles, and unit sheets. Micelles were described as being composed of smaller associated entities called particles which in turn are said to be made up of yet smaller unit sheets thought to be held together by intermolecular forces.

The metal content in the non-porphyrin fraction was high enough so that  $^1\text{H}$ NMR and  $^{13}\text{C}$ NMR spectra were not obtainable [15]. However, an  $^1\text{H}$ NMR spectrum of the demetallated non-porphyrins is shown in Figure 6. This spectrum contained one major region of signals around  $\delta = 1.0-3.0\text{ ppm}$  which indicates a large amount of aliphatic protons. Also, the  $^{13}\text{C}$ NMR spectrum of the demetallated non-porphyrins in Figure 7 shows absorption in the  $\delta = 14-37\text{ ppm}$  region which is indicative of aliphatic carbons. The strong singlet at 30 ppm is suggestive of tertiary methyl carbons ( $\text{C}(\text{CH}_3)_3$ ) [16].

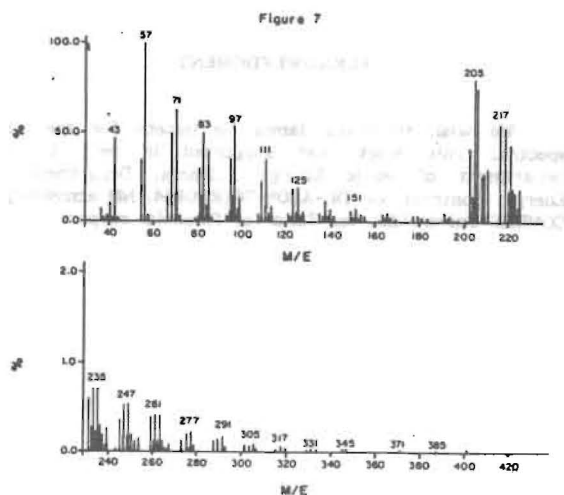
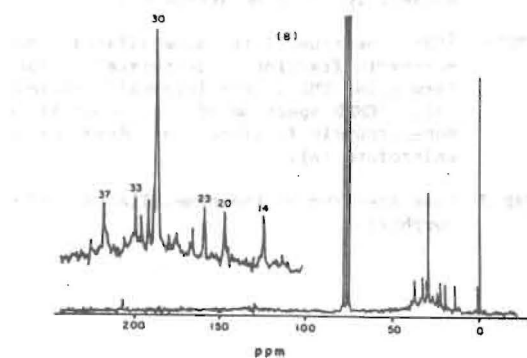
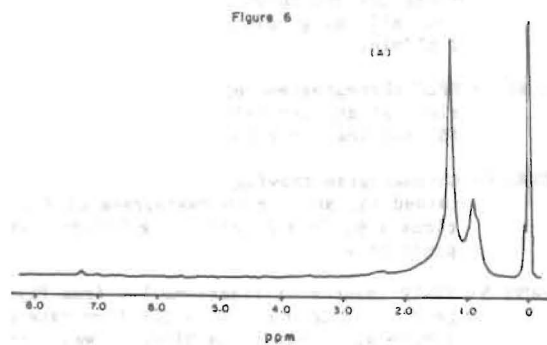
The other peaks in this range correspond to methylene carbons belonging to long aliphatic chains. The small absorption at 207 ppm is weakly indicative of low concentrations of aldehydes and/or ketones in this fraction.

## CONCLUSIONS

Demetallation of the non-porphyrins using sulfuric chloride was very effective under gentle reaction conditions.

The demetallated non-porphyrin fractions obtained from SEC exhibited complex behavior in that, upon reinjection of a single peak, peaks characteristic of other fractions also eluted. This finding suggested that a slow interconversion was possible between components of the different fractions.

The mass spectrometry studies suggested that non porphyrins having apparent molecular weights greater than 800 may actually have molecular weights less than 400. This may imply that vanadyl non-porphyrins either form aggregates of complexes with the large molecular weight components of heavy crude petroleum by  $\pi-\pi$  interaction or by hydrogen bonding [7,8]. IR,  $^1\text{H}$ NMR,  $^{13}\text{C}$ NMR and mass spectrometry showed that these non-porphyrins have large aliphatic hydrocarbon chains attached.



## LIST OF FIGURES

- FIGURE 1: Size-exclusion chromatograms of original (A) and demetallated (B) non-porphyrin samples using a 60 Å pore size column at a THF flow rate of 1 mL/min. Size exclusion chromatography calibration curve (C).
- FIGURE 2: Chromatogram showing size-exclusion fractions (A) and chromatograms of fractions 1-4, all using column 1, at a THF rate of 1 mL/min.
- FIGURE 3: HPLC chromatograms of vanadyl non-porphyrins (A) and demetallated non-porphyrins (B) samples using column 2 and gradient A.
- FIGURE 4: Chromatogram showing HPLC fractions obtained (A) and the chromatograms of fractions 1-6, from A, all using Column 2 and gradient A.
- FIGURE 5: FT-IR spectra of fractions 1-4 from Figure 2 using Column 1 at a THF flow rate of 1 mL/min. Carbon tetrachloride was the solvent for FTIR measurements.
- FIGURE 6: <sup>1</sup>H NMR spectrum of the demetallated non-porphyrin fraction in deuterated chloroform using TMS as the internal reference (A), <sup>13</sup>C NMR spectrum of the demetallated non-porphyrin fraction in deuterated chloroform (B).
- FIGURE 7: Mass spectrum of the demetallated non-porphyrin.

## ACKNOWLEDGMENT

We wish to thank James De Haseth for the FTIR spectra. This work was supported in part by the Department of Basic Energy Sciences, Department of Energy, Contract No. DE-AS09-76ER00854. NM acknowledges CONDES-Universidad del Zulia for financial support.

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