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Floyd W. Crouch[ab]; C. S. Sommer[ac]; J. F. Galobardes[ad]; Shmuel Kraus[ae]; E. H. Schmauch[af]; Mercedes Galobardes[a]; Aqeel Fatmi[a]; Kenneth Pearsall[ag]; L. B. Rogers[a]
[a] DEPARTMENT OF CHEMISTRY, UNIVERSITY OF GEORGIA, ATHENS, GEORGIA [b] Berry College, Berry, Mt, Georgia [c] Hooker Chemicals, Research Building, Niagara Falls, New York [d] Dow Chemical Company, Midland, Michigan [e] Criminal Identification Division, Israel Police Headquarters, Jerusalem, Israel [f] Conoco Oil Company, Ponca City, Oklahoma [g] U.S. Geological Survey, Water Resources Division, Syosset, New York

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Fractionations of Nonporphyrin Complexes of Vanadium and Nickel from Boscan Crude Oil

FLOYD W. CROUCH,* C. S. SOMMER,†, J. F. GALOBARDES,‡
SHMUEL KRAUS,§ E. H. SCHMAUCH,‖
MERCEDES GALOBARDES,# AQEEL FATMI,**
KENNETH PEARSALL,† † and L. B. ROGERS

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF GEORGIA
ATHENS, GEORGIA 30602

Abstract

Samples containing vanadium and nickel nonporphyrin complexes were isolated from Boscan crude oil from Venezuela. Chromatographic studies indicated that a broad molecular weight range of components existed so that silica packings having a 300 Å average pore diameter were superior to those in the range 60 to 100 Å due to greater permeation. Solvents having widely different polarities and selectivities were needed for elution of nonporphyrins from 300 Å pore diameter silica derivatized with trimethylchlorosilane. Successive solvents eluted different percentages of the metals and of UV-visible absorbing components. Larger molecular-weight species, which contained the bulk of the metals, were eluted by chloroform, methylene chloride, and tetrahydrofuran. Results also suggested the existence of slow "equilibria" between high and low molecular weight species within a particular nonporphyrin fraction.

Present addresses:

*P.O. Box 163, Berry College, Mt. Berry, Georgia 30149.

†Hooker Chemicals, Research Building, P.O. Box 8, Niagara Falls, New York 14302.

‡Dow Chemical Company, Midland, Michigan 48640.

§Criminal Identification Division, Israel Police Headquarters, Shechem Road, Jerusalem, 97999, Israel.

‖Conoco Oil Company, P.O. Box 1267, Room 131 North Tower, Ponca City, Oklahoma 74601.

#3741 North River Road, Freeland, Michigan 48623.

**1000 Montreal Road, #49-H Plantation Apts., Clarkston, Georgia 30021.

† †U.S. Geological Survey, Water Resources Division, 5 Aeriel Way, Syosset, New York 11791.

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When asphaltenes were precipitated from a sample of crude oil by *n*-hexane, most of the vanadium and nickel was found in that higher molecular-weight fraction. Further fractionation of the soluble (maltene) fraction using neutral alumina showed that most of the maltenes could be recovered as separate hydrocarbon, porphyrin, nonporphyrin, and tetrahydrofuran fractions. In contrast, only approximately 50% of the asphaltenes (and metals) were recovered by an analogous procedure. Furthermore, when separating the asphaltenes into porphyrin and nonporphyrin fractions, an approximately one-to-one split of vanadium and nickel between the porphyrins and nonporphyrins was observed for both, whereas most of the vanadium and nickel was isolated from the maltenes as nonporphyrins. Finally, it was found that a procedure utilizing sulfuryl chloride for nonporphyrin demetallation was superior to a procedure employing methanesulfonic acid.

INTRODUCTION

Vanadium and nickel are present in unusually high amounts in crude oils from Venezuela (*1*). Vanadium is usually present as the vanadyl ion (VO^{2+}) and nickel as Ni^{2+}, the majority of each being present in the high molecular weight asphaltene fraction (*2*) complexed with both porphyrin and nonporphyrin ligands (*3*). Since these metals poison cracking catalysts used in the petroleum industry, a knowledge of their actual forms in petroleum sources is of importance. Porphyrin fractions from different petroleum sources are made up of three homologous series. However, little is known concerning the nonporphyrin complexes.

One of the primary goals of the present research was to separate nonporphyrin fractions by preparative adsorption chromatography, size-exclusion chromatography, and high performance liquid chromatography (HPLC) prior to characterizing subfractions by chomatographic and spectroscopic means. Another goal was to use the nonporphyrins as solutes to explore a general solvent optimization approach for HPLC.

In the present study, preparative adsorption chromatography was used first to fractionate crude oil into porphyrin and nonporphyrin fractions employing a procedure developed by Spencer et al. (*4*). Then, further fractionation of nonporphyrins used a procedure reported by Later et al. (*5*). HPLC separations were performed on columns packed either with polar or nonpolar adsorbents using different combinations of polar and non-polar solvents as eluents so as to determine relative solvent strengths for later use in a multisolvent optimization procedure. Size-exclusion chromatography provided molecular weight profiles based upon polystyrene standards. In addition, UV-visible and atomic absorption spectroscopy provided further information about the porphyrin subfractions.

EXPERIMENTAL

Chemicals

Boscan crude oil was provided by J. A. Lubkowitz, Instituto Venezolano de Investigaciones Cientificas, Caracas, Venezuela. Analyzed reagent grade isopropanol (IPA), diethyl ether, toluene, pyridine, concentrated hydrochloric acid, acetone, and sodium hydroxide pellets were obtained from J. T. Baker Chemical Co., (Phillipsburg, New Jersey). Chloroform, carbon tetrachloride, dimethylformamide (DMF), and benzene were Baker "photrex" grade. Methanol (MEOH), methylene chloride, and *n*-hexane were Baker HPLC grade. Methyl-t-butyl ether (MTBE) and acetonitrile (ACN) were Fisher HPLC grade (Fisher Scientific Co., Fair Lawn, New Jersey). Baker tetrahydrofuran (THF) was distilled over potassium before use. "In-house" water was deionized and distilled. Absolute ethanol was obtained from U.S. Industrial Chemicals Co. (New York, New York). Pyridine used in the derivatization procedure for porous silica was dried before use by distilling over calcium hydride. Toluene for the same procedure was dried by storage over sodium wire. Neutral alumina (Bockman activity 1, 80-200 mesh) was obtained from Fisher Scientific Co., and 100 mesh silicic acid from Mallinckrodt Chemical Works (St. Louis, Missouri).

Trimethylchlorosilane (TMCS) (PCR Research Chemicals, Gainesville, Florida), cyanopropyldimethylchlorosilane, and dimethyloctadecylchlorosilane (Petrarch Systems, Levittown, Pennsylvania) were used for derivatizations of 10 μm, 300 Å pore diameter silica (E. Merck, East Brunswick, New Jersey). Commercial cyano bonded-phase packing was obtained from Phase Separations Ltd. (Clwyd, England). Machery-Nagel nitro bonded-phase packing was obtained from Rainin Instruments Co. (Brighton, Massachusetts). Fisher 98% methanesulfonic acid, 97% sulfuryl chloride (Aldrich Chemical Co., Milwaukee, Wisconsin) and Aldrich 99+ pure phenol were used for nonporphyrin demetallations.

Polystyrene standards of 2,200, 4,000, 9,000, 17,500, 37,000, 110,000, and 233,000 molecular weight were obtained from Pressure Chemical Co. (Pittsburgh, Pennsylvania). Helium for the degassing of HPLC solvents and nitrogen for both the flameless atomic absorption procedures and the procedure for the derivatization of porous silica were obtained from Selox (Gainesville, Georgia).

Apparatus

A Model 8800 Gradient Liquid Chromatographic System (Dupont Instruments, Wilmington, Delaware) was used for all HPLC optimization studies of nonporphyrin separations. The system was equipped with a Model 7125 injection valve (Rheodyne Inc., Cotati, California) and a Dupont Model 825001.901 variable wavelength UV detector. In some cases, a Model 155-10 variable wavelength UV-visible detector was used (Altex Scientific, Berkeley, California). A potentiometric recorder (Linear Instruments, Reno, Nevada) was used to record chromatograms.

A Model 7000 Liquid Chromatographic System (Micromeritics Instrument Corp., Norcross, Georgia) was used for some size-exclusion separations and other chromatographic studies. The system was equipped with a Micromeritics 730 universal injection valve, a Varian 635 variable wavelength UV-visible detector (Varian Instruments, Palo Alto, California), and a Linear recorder.

HPLC columns were packed in 0.46 cm i.d. stainless steel column blanks (Alltech Associates, Deerfield, Illinois). Swagelok stainless steel ferrules, nuts, and reducing unions were obtained from Georgia Valve and Fitting Co. (Atlanta, Georgia). The larger ends of the 0.64 to 0.16 cm reducing unions used for HPLC columns were drilled in flat so as to minimize dead volume. Stainless steel tubing between the injector and column inlets as well as between the column outlets and detectors was 0.16 cm o.d. (0.025 cm i.d.) obtained from Alltech Associates as were the stainless steel column frits (2.0 and 0.5 μm). HPLC columns were packed using either a Micromeritics Model 705 stirred slurry packing apparatus or an "in-house" designed downflow slurry-packing apparatus in conjuction with a Varian 8500 pump.

UV-visible studies used a Perkin-Elmer Coleman Model 124 double-beam spectrophotometer (Oakbrook, Illinois) and 1 cm quartz cuvettes. Flameless atomic absorption measurements were made on a Varian AA-375 atomic absorption spectrometer equipped with a Varian CRA-90 carbon rod atomizer.

Procedures

Chromatography. All sample injections were 50 μL. HPLC columns are listed in Table 1. Optimization of HPLC separations of nonporphyrins was performed using the Dupont 8800 chromatographic system. Before each use, the four solvents were degassed approximately 15 min using helium, followed by the purging of each solvent line with approximately 30 mL of solvent. For an isocratic elution, a minimum of 30 mL of the eluent was

TABLE 1
High-Performance Liquid Chromatographic Columns

Column number	Packing	Particle diameter (μm)	Mean pore diameter (Å)	Column length[a]
1	"Cyano bonded phase" (Spherisorb)	5	80	20 + 5 cm pre column
2	"Nitro bonded phase" (Nucleosil)	10	100	25 + 5.8 cm pre column
3	Lichrosorb 60 Silica	5	60	25 cm
4	Lichrosorb 60 Silica	10	60	23.5 cm
5[b]	Lichrospher 300 derivatized using trimethylchlorosilane	10	300	25 cm
6	Lichrospher 300 derivatized using dimethyloctadecylchlorosilane	10	300	15 cm
7	Lichrospher 300 derivatized using cyanoporopyldimethylchlorosilane	10	300	20 cm

[a] 4.6 mm i.d.

[b] Column was used after the packing material had been derivatized once with TMCS and, again, after it had been derivatized a second time with TMCS.

allowed to flow through the column before sample injection; for gradient elution, a minimum of 30 mL of the initial gradient composition was passed through the column before injection of the next sample. Gradient blanks, in which only a sample solvent was injected, were performed to determine if any spurious peaks eluted. Also, prolonged elution with the final solvent composition was necessary to insure elution of all injected components, since there was approximately 7 mL of system dead-volume. The gradients are listed in Table 2.

Size-exclusion chromatography was performed using Column 3 in Table 1. With the Dupont system, a flow rate of 0.20 mL/min for the mobile phase, 100% THF, was used; with the Micromeritics system, the flow rate of THF was 0.25 mL/min. The column was calibrated at different time intervals using a solution of approximately 1×10^{-3} M benzene in chloroform, and approximately 1 mg/mL solutions of 2,200, 4,000, 9,000, and 17,500 MW polystyrene standards in chloroform. Polystyrene-equivalent molecular weights of nonporphyrin fractions were determined from linear regression data of plots of log MW vs V_r (retention volume).

TABLE 2
Linear Gradients Used in High Performance Liquid Chromatography

Gradient	Flow rate (mL/min)	Gradient description
A	0.67	98/2 hexane/IPA to 100% CH_2Cl_2 in 25 min (hold 17 min)
B	0.33	98/2 hexane/IPA to 100% CH_2Cl_2 in 25 min (hold 25 min) to 100% THF in 20 min (hold 20 min)
C	1.00	100% MEOH to 100% $CHCl_3$ in 15 min (hold 15 min)
D	1.00	100% MEOH (hold 86 min) to 100% $CHCl_3$ in 15 min (hold 15 min)
E	1.00	95/5 ACN/H_2O (hold 8 min) to 100% ACN in 1 min (hold 25 min) to 100% $CHCl_3$ in 15 min (hold 15 min)
F	1.00	90/10 ACN/H_2O (hold 8 min) to 100% ACN in 2 min (hold 90 min) to 100% $CHCl_3$ in 15 min (hold 15 min)
G	1.00	100% ACN to 100% $CHCl_3$ in 50 min (hold 20 min)
H	1.00	100% MEOH to 30/30/40 MTBE/IPA/$CHCl_3$ in 15 min (hold 15 min) to 100% $CHCl_3$ in 10 min (hold 10 min)
I	1.00	100% MEOH to 40/60 $CHCl_3$/MTBE in 15 min (hold 15 min) to 100% $CHCl_3$ in 5 min (hold 10 min)
J	1.00	100% MEOH to 20/20/60 IPA/MTBE/$CHCl_3$ in 15 min (hold 15 min) to 100% $CHCl_3$ in 8 min (hold 8 min)
K	1.00	100% MEOH to 50/30/20 MEOH/$CHCl_3$/MTBE in 10 min (hold 5 min) to 60/40 $CHCl_3$/MTBE in 10 min (hold 15 min)
L	1.00	100% MEOH to 50/30/20 MEOH/CH_2Cl_2/MTBE in 10 min (hold 5 min) to 60/40 CH_2Cl_2/MTBE in 10 min (hold 15 min)

The isolation of porphyrin and nonporphyrin fractions from Boscan crude oil followed the procedure developed by Spencer et al. (*4*). In one particular study, a 4-g crude oil sample was first separated into asphaltene and maltene fractions by precipitation of the asphaltenes with *n*-hexane. Then the asphaltenes were separated chromatographically into porphyrins, nonporphyrins, and a THF-eluted fraction. The maltenes were treated in an analogous manner except that *n*-hexane was used first to elute a hydrocarbon fraction. The nonporphyrin fractions of the asphaltenes and maltenes were then separated into "class compound" fractions using a procedure developed by Later et al. (*5*).

Derivatization of Silica. The preparation of some bonded-phase adsorbents generally followed the procedure reported by Snyder and Kirkland (*6*). First, the silica was hydrolyzed by treatment with 0.1 *M* hydrochloric acid at 90°C for 24 h. The silica was then filtered using a medium-frit sintered glass funnel, washed with several portions of distilled water, and dried under vacuum for 24 h between 150 and 200°C. The silica was then reacted with a twofold stoichiometric excess of the silane reagent in approximately 100 mL of dry toluene and 5 mL of dry pyridine under nitrogen in an apparatus which had been previously flame dried. The mixture was allowed to reflux for approximately 48 h after which MEOH was added to quench the reaction. The silica was again filtered using a sintered glass funnel and washed successively with benzene, acetone, MEOH, 1:1 MEOH/water, acetone, diethyl ether, and MEOH. Fines were removed by sonicating the silica in MEOH, adding the slurry to a 500 mL graduated cylinder containing MEOH, and decanting the fines after the coarse particles had fallen to the bottom of the cylinder. Silica which had first been reacted with cyanopropyldimethylchlorosilane or dimethyloctadecylchlorosilane was subsequently "end-capped" by reaction with TMCS before packing.

Spectroscopic Studies. For vanadium analysis by flameless atomic absorption, the wavelength of the Varian AA-375 was set at 318 nm, and the current of the hollow-cathode lamp set at 20 mA. Drying was done at 60°C for 60 s and ashing at 800°C for 40 s. For atomization, the temperature was ramped at 400°C/s to 2400°C and held for 2 s.

For nickel analysis, the wavelength was 232.5 nm and the current of the hollow-cathode lamp was 10 mA. Drying was at 60°C for 60 s and ashing at 600°C for 40 s. For atomization, the temperature was ramped at 600°C/s to 2200°C and held for 2 s.

A deuterium lamp was used for background correction for vanadium analysis, but was not needed for nickel analysis. For recovery studies of nonporphyrin fractions obtained by eluting with pure solvent, the vanadium and nickel signals were corrected by taking into account the volume of chloroform in which each sample was dissolved and the volume of solution injected into the carbon rod.

UV-visible spectra were recorded for nonporphyrin fractions after first evaporating the sample to dryness and adding 4 to 14 mL of methylene chloride. Spectra were recorded from 600 to 210 nm vs pure methylene chloride. Absorbances at approximately 410 nm (or the wavelength of maximum absorbance for the peak) and at 270 nm were corrected for differences in the volumes of methylene chloride added to the samples.

Demetallation of Nonporphyrin Samples. The first method used methanesulfonic acid for demetallation (*7*). After the nonporphyrins had reacted with methanesulfonic acid, hexane was added, and the two phases were separated using a separatory funnel. Benzene and water were then added to the acid phase, followed by separation of the phases using a separatory funnel. The vanadium contents of the hexane, benzene, and aqueous phases were determined, and the percent demetallation calculated.

Another method was derived from a procedure developed by Sugihara, Branthaver, and Willcox (*8*) in which sulfuryl chloride was used for demetallation. Approximately 4.6 mg of the nonporphyrin sample was dissolved in 50 mL of methylene chloride, and a 100-μL aliquot was analyzed for vanadium. The nonporphyrin sample was then cooled to −78°C in a 100-mL 3-neck round-bottom flask equipped with a dropping funnel, drying tube, and stopper. One milliliter of sulfuryl chloride was then added slowly, and stirring of the mixture was continued for 24 h. Then the reaction was quenched with a solution of 5% phenol in MEOH. The solution was extracted first with 5% aqueous sodium hydroxide and then with water. Finally, the aqueous and organic portions were analyzed for vanadium, and the percent demetallation was calculated.

RESULTS

Preliminary Studies

The first study compared the cyano and nitro bonded-phase polar columns (Columns 1 and 2 in Table 1) for total nonporphyrin separations using Gradients A and B, respectively. It was assumed that *n*-hexane was a weak solvent since it is used to precipitate asphaltenes, which contain the bulk of the metals, from crude oils. However, as seen in Figs. 1(A) and 2, a fairly large fraction of the sample was eluted from both columns using the initial solvent composition. It must be noted, however, that since the sample solvent (4:1 hexane/chloroform) was stronger than the initial mobile phase, the early peaks may have been distorted by a solvent effect.

One can see that the first few peaks were better resolved by the cyano column than by the nitro column. Furthermore, the pattern for the later eluting peaks on the cyano column was irreproducible from one chromatogram to another. Finally, because THF was able to elute yet another peak from the nitro column, the nitro column was more retentive than the cyano.

Since a large fraction of nonporphyrin components was eluted by the initial solvent composition from both Columns 1 and 2, it was of interest to determine if the pore diameter of the packing materials (80 Å for cyano and 100 Å for nitro) was excluding some of the larger nonporphyrin components. The first study involved Column 7 (300 Å cyano packing material). Comparison of the chromatogram obtained for the total nonporphyrin sample using this column with the chromatogram for the smaller pore diameter cyano packing (Column 1) can be seen in Figs. 1(A) and 1(B). Although

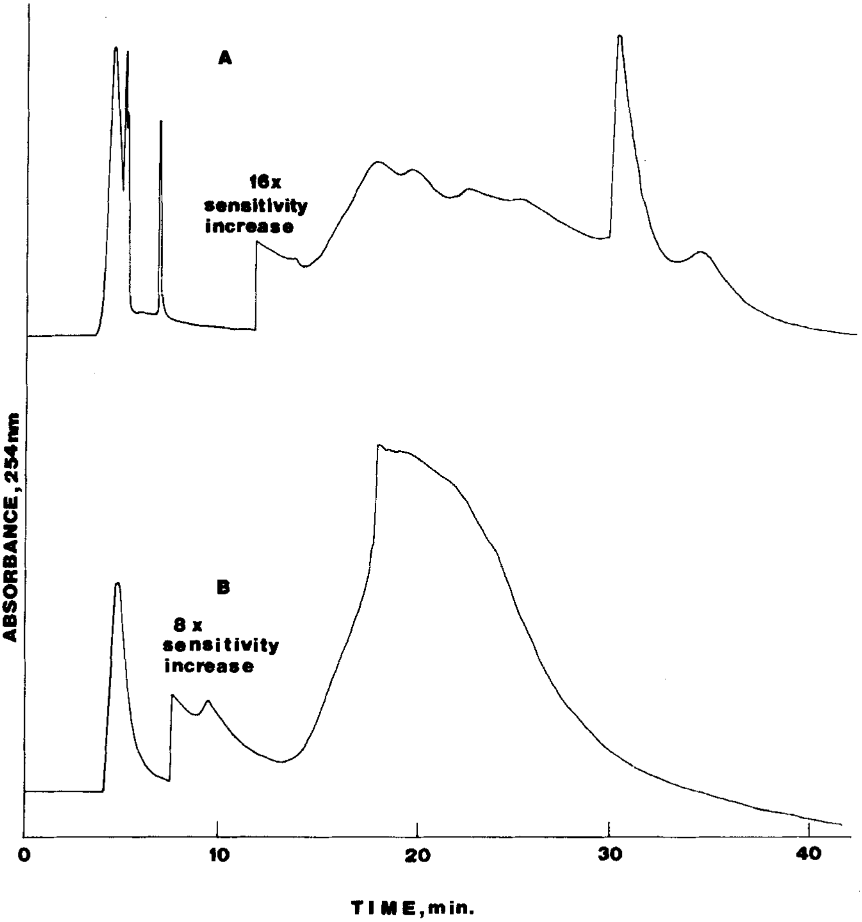


FIG. 1. Chromatograms of total nonporphyrin sample on Column 1 (A) and Column 7 (B) using Gradient A.

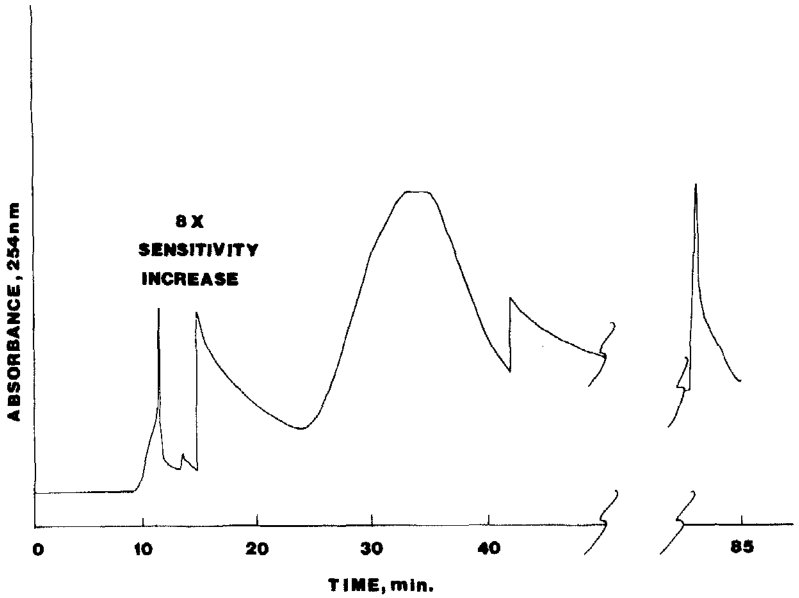


FIG. 2. Chromatogram of total nonporphyrin sample on Column 2 using Gradient B.

there was a decrease in the resolution of components when using the larger pore diameter packing, the greatest difference was in the ratio of the early to the late eluting materials. That ratio changed from approximately 2.9 for the smaller pore cyano packing to 0.60 for the larger pore packing. This indicates that greater permeation was allowed by the larger pore diameter packing.

Two other studies were performed to test the effect of pore diameter on nonporphyrin separations. The first involved size-exclusion chromatography of a portion of the total nonporphyrin sample using Column 3. Figure 3 indicates that nonporphyrin components ranged in polystyrene equivalent molecular weight from approximately 110,000 to 100. The second study involved a comparison of the pore volumes of Columns 1 and 5 by injecting onto each column a portion of the total nonporphyrin sample and a solution of benzene (which was assumed to permeate all pores). Table 3 shows that the 300-Å pore diameter packing was superior to the 80-Å pore diameter packing in terms of allowing greater permeation of the nonporphyrin components and thereby minimizing the detrimental effects of size exclusion on the fractionation by adsorption.

Another step toward optimizing the fractionation of the nonporphyrin sample was to use Column 5 with combinations of up to four solvents as the

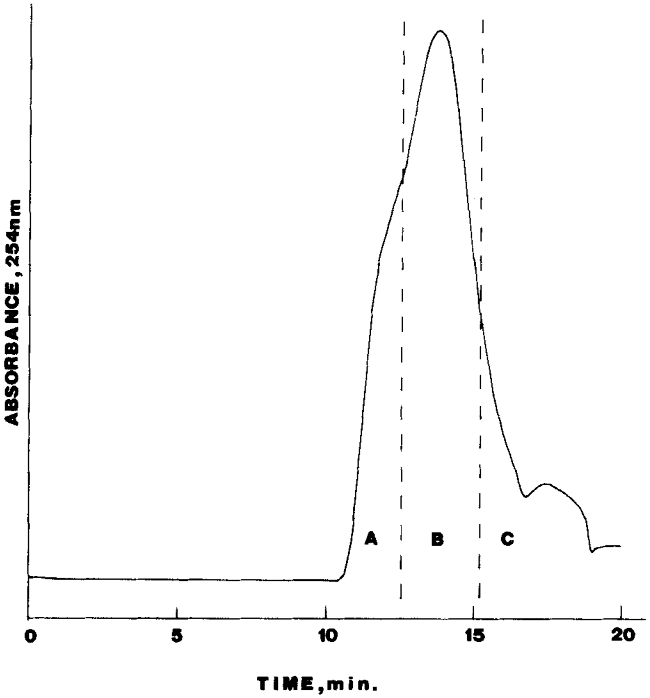


FIG. 3. Size-exclusion chromatogram of total nonporphyrin sample using Column 3 in the Dupont system at a THF flow rate of 0.20 mL/min.

TABLE 3

Comparison of the Size-Exclusion Behaviors of Columns 1 and 5

	V_r (mL)		
Column	Benzene	Nonporphyrin	Difference
1 Cyano	3.06	2.53	0.53
5 Trimethylated silica	3.55	3.36	0.19

mobile phase. A recently published reversed-phase optimization procedure (*9*) was attempted for the overall nonporphyrin fractionation. In this procedure, three strong solvents, which individually can elute all sample components and are as different as possible in selectivity properties (*10*), are chosen. In addition, a weak solvent is also chosen as a "diluent" so as to adjust the *k*′ values of the "solute" to a value near 10. The strong solvents chosen were THF (selectivity group III), ACN (selectivity group VIb), and IPA (selectivity group II). Water was chosen as the weak diluent. However, it was found that ACN and IPA were not able to elute all of the nonporphyrin components. The packing material was removed from the column and reacted once again with TMCS in order to eliminate the effect of residual hydroxyls which may have been causing incomplete elution of the nonporphyrin components. However, ACN and IPA still did not completely elute all of the nonporphyrin components. Hence, this approach was not explored further.

HPLC Studies of Relative Solvent Strengths

Since ACN and IPA were not able to elute all nonporphyrin components from Column 5, a study of the strengths of different solvents was undertaken using two-, three-, and four-solvent systems. First, Gradients C and D were employed following two separate nonporphyrin injections on Column 5. Note that, with Gradient D, methanol was allowed to elute nonporphyrin components for 86 min before starting the ramp to chloroform. Chloroform was assumed to be a strong solvent since it was used to elute nonporphyrins from neutral alumina during the process of nonporphyrin isolation (*4*). It can be seen in Fig. 4 that the area of the last eluting peak was reduced by prolonged elution with MEOH. In an analogous study performed with ACN, prolonged elution did not have as great an effect as that with MEOH. (See Figs. 5A and 5B where Gradients E and F were used.) In a separate study, however, in which ACN was allowed to elute some nonporphyrin components followed by a ramp to 100% MEOH, it was determined that ACN and MEOH have nearly equivalent eluting strengths for nonporphyins.

The effect of using a slower change in the gradient from ACN to chloroform was studied using Gradient G. Figure 5(C) indicates that the slow ramp served only to broaden the later peaks. Comparing Figs. 4 and 5, one can see that somewhat better resolution of the later peaks was obtained when the starting solvent was ACN rather than MEOH.

The effect of mixing 5% (Fig. 5A) and 10% (Fig. 5B) water with the ACN used to generate the initial eluent was also studied. The resolution of the first peak was not enhanced, compared to Fig. 5(C), but more material was left

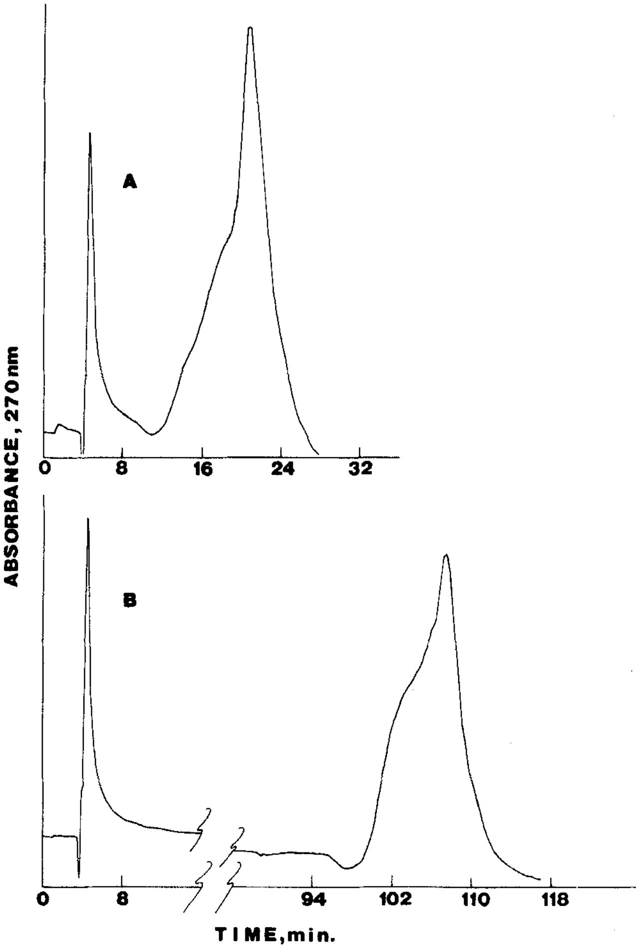


FIG. 4. Chromatograms of total nonporphyrin sample on Column 5 using Gradient C (A) and Gradient D (B).

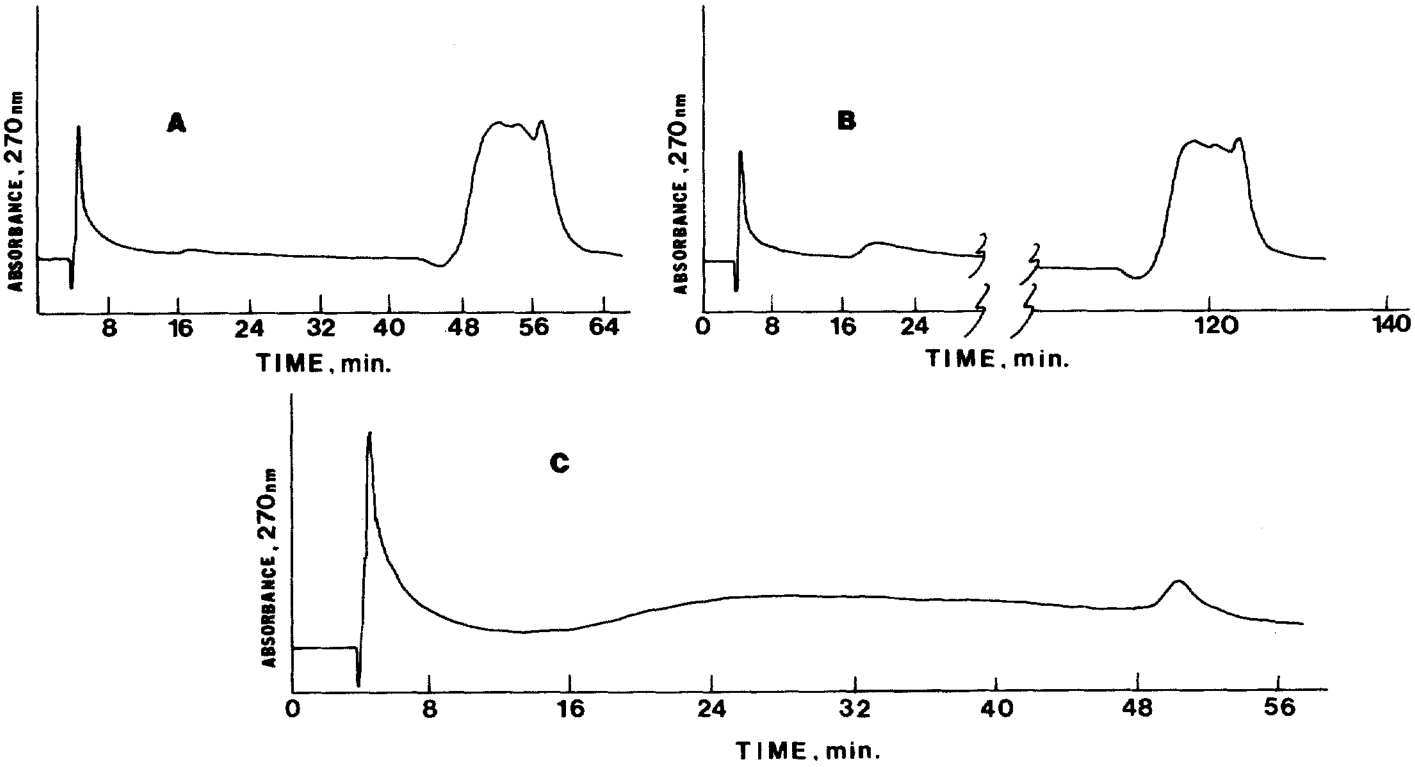


FIG. 5. Chromatograms of total nonporphyrin sample on Column 5 using Gradient E(A), Gradient F (B), and Gradient G (C).

for 100% ACN to elute. Other experiments showed that the same was true when water was mixed with MEOH and with 1:1 MEOH:ACN. Hence, neither slower gradients nor weaker solvents increased the resolution of components within the major peaks.

Several other solvents were also examined. The capabilities of IPA and *n*-hexane for elution of nonporphyrin components from Column 5 were first tested. Then, since methyl-*t*-butyl ether (MTBE) is finding increased applicability as a solvent in "normal-phase" separations, its applicability was also explored. Finally, the solvent strengths of methylene chloride and carbon tetrachloride relative to chloroform for nonporphyrin elution were determined.

In separate experiments, IPA was found to elute some nonporphyrin components that MEOH did not and, although MTBE eluted some nonporphyrin components, others were left for chloroform to elute. Therefore, an experiment was devised to compare the strengths of IPA and MTBE. Gradients H, I, and J were run on separate nonporphyrin injections onto Column 5, and the results shown in Figs. 6(A), 6(B), and 6(C), respectively. In Gradient I, where MTBE was substituted for the IPA used in Gradient H, the peaks in Fig. 6(B) had shorter retention times than those in Figure 6(A). Therefore, MTBE was a stronger solvent than IPA. Figure 6(C) indicated that the intermediate solvent composition represented by Gradient J was sufficient to elute all nonporphyrin components that could be eluted by 100% chloroform.

The relative solvent strength of *n*-hexane was examined by eluting first with IPA and then ramping to *n*-hexane. A large amount of material eluted with *n*-hexane, as determined by monitoring the effluent at 270 nm. A further ramp to MTBE revealed the presence of additional components. In a separate experiment, elution with MTBE followed by a ramp to *n*-hexane indicated that no additional components were eluted. Therefore, *n*-hexane appeared to be a stronger solvent for nonporphyrin elution than IPA, but weaker than MTBE. However, the complexity of the relationships between solvents was shown when, in a separate experiment in which a nonporphyrin sample was eluted first with *n*-hexane followed by a ramp to IPA, material remained to be eluted by IPA. This evidence suggests that the order of solvent strengths was not absolute. Instead, each solvent appeared to have the capability of eluting classes of compounds whose order might differ with the solvent.

At this point, the effects of replacing IPA with MTBE in Gradient J and of splitting the gradient by introducing a "hold" at an intermediate solvent composition were examined with respect to resolution of the last three peaks. Gradient K was developed, and by comparing either chromatogram in Fig. 7 with the chromatogram illustrated in Fig. 6(C), it is obvious that the split

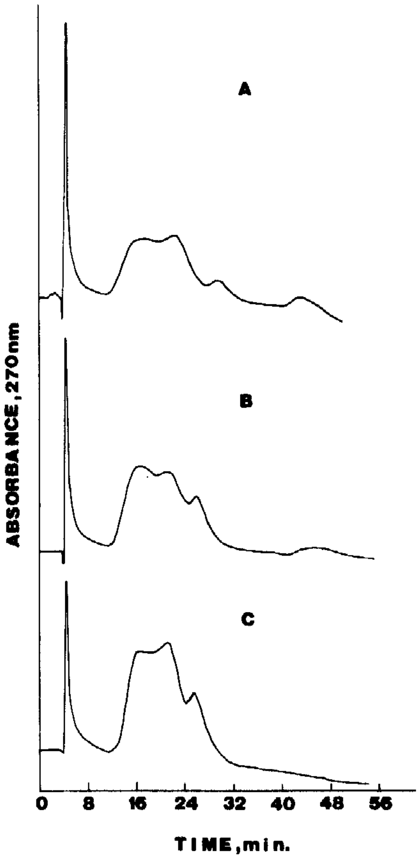


FIG. 6. Chromatograms of total nonporphyrin sample on Column 5 using Gradient H (A), Gradient I (B), and Gradient J (C).

gradient improved the resolution of the last three peaks. Futhermore, vanadium was found to be contained only in those last three peaks. Polystyrene-equivalent molecular weights (Table 4) increased significantly with the retention. In addition, there was fairly good agreement between molecular weights of the fractions between older and newer samples. However, a comparison of Fig. 7(A), a chromatogram obtained from injection of a nonporphyrin sample approximately 6 months old, with Fig. 7(B), a chromatogram obtained from a nonporphyrin sample only several days after isolation, shows that the first peak was much more prominent with

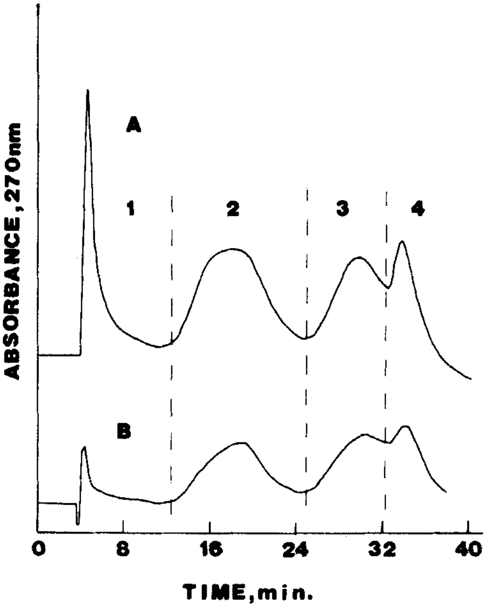


FIG. 7. Chromatograms of 6-months old total nonporphyrin sample (A) and new nonporphyrin sample (B) on Column 5 using Gradient K.

TABLE 4
Polystyrene Equivalent Molecular Weights of Nonporphyrin Chromatographic Fractions

	Molecular Weights	
Fraction	Sample 1 (older)	Sample 2 (newer)
1	1753	1370
2	5068	4970
3	7219	7390

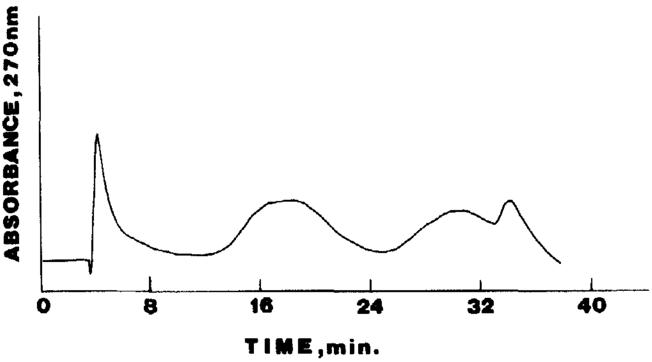


FIG. 8. Chromatogram of total nonporphyrin sample on Column 5 using Gradient L.

the older sample. Aging, therefore, appeared to affect the relative amounts of the species.

To test the strength of methylene chloride for nonporphyrin elution, it was substituted for chloroform in Gradient K to generate Gradient L. Since the elution times of the peaks in Fig. 8 were roughly equivalent to those in Fig. 7(A), methylene chloride is approximately the same strength as chloroform. In a separate experiment, carbon tetrachloride gave virtually the same results. Therefore, the chlorinated hydrocarbon solvents methylene chloride, chloroform, and carbon tetrachloride possessed equivalent eluting powers for nonporphyrins from Column 5. This was an interesting finding, since these three solvents have widely different polarities and generally exhibit noticeably different selectivities. One wonders if the selectivity effects were "eliminated" as a result of the large molecular weights of the solutes.

Since a tentative solvent strength order had been established for Column 5 (e.g., H_2O < ACN ≅ MEOH < IPA < hexane < methylene chloride ≅ chloroform ≅ carbon tetrachloride < THF), an effort was made to confirm this solvent-strength order and to examine any spectral differences in the fractions eluted by these solvents. Therefore, three "pure solvent" gradients were chosen, as listed in Table 5. THF was included since it was found to be the only solvent able to elute all nonporphyrin components from Column 5. Three 50-μL injections of a concentrated nonporphyrin sample were made onto Column 5 for each of the three gradients, and fractions corresponding to each solvent in each gradient were collected.

When 270 nm detection was used, each succeeding solvent in each series did indeed elute another nonporphyrin fraction. The fact that MTBE was found to be a weaker solvent for nonporphyrin elution than chloroform was also confirmed on Column 6, which was packed with an "in-house"-prepared

TABLE 5
Series of Pure Solvents

Series	Solvents								
	1[a]		2		3		4		5
1	MEOH	to	IPA	to	MTBE	to	Chloroform	to	THF
	1′		2′		3′		4′		5′
2	ACN	to	IPA	to	MTBE	to	Methylene chloride	to	THF
	1″		2″		3″				
3	IPA	to	Hexane	to	THF				

[a] Numbers identify solvents reported in Tables 6 and 7.

300 Å pore diameter C-18 bonded-phase adsorbent. However, as indicated earlier, because MEOH, IPA, and MTBE individually eluted a portion of the fraction originally eluted only by chloroform, care must be taken not to assume that a stronger solvent will elute all of the components that a weaker solvent does or that the solvent strength order is absolute.

Partial Characterizations of Fractions

The complexity of the nonporphyrin sample was also shown in other experiments. Studies were made on chromatographic fractions obtained first as illustrated in Fig. 7(B), second as size-exclusion fractions as illustrated in Fig. 3, and finally as fractions obtained by elution using a pure solvent. The first study examined the effect of collecting a fraction of a nonporphyrin sample, reinjecting it, and then collecting and reinjecting it again. Figure 9 shows the chromatograms obtained by the injection of Fractions 4 (Fig. 9A) and 2 (Fig. 9B) obtained as illustrated in Fig. 7(B) using Column 5 and Gradient K. Both fractions, upon reinjection, contained components of other fractions. The result is even more striking for the reinjection of Fraction 3, as illustrated in Fig. 10(A), and Fig. 10(B) where, again, all fractions were present. The results indicate that a slow interconversion must occur that permits the component(s) of a single large peak to convert to those that made up other major peaks.

Further fractionations of these chromatographic species were also attempted by injection onto Column 6 and use of isocratic mobile phases consisting of chloroform, methylene chloride, THF, and the weak diluent, MEOH. No resolution of the components within a fraction was seen when mobile phases assumed to be strong enough to elute all components in a

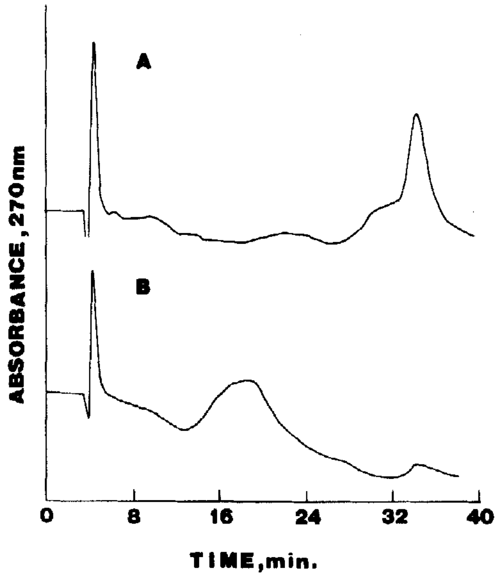


FIG. 9. Chromatograms of Fraction 4 (A) and Fraction 2 (B) from Fig. 7B using Gradient K.

fraction were used. Also, gradient separations, in which MEOH was the starting solvent together with a ramp to a combination of either THF/ACN/methylene chloride or to THF/ACN/chloroform (so as to elute more strongly adsorbed components), failed to elute multiple peaks for the fraction.

The relationship between size-exclusion behavior and adsorption behavior was then explored. The three fractions of the size-exclusion chromatograms (Fig. 3) were collected and injected onto Column 5 using Gradient K. Figure 11 indicates that the larger molecular weight fractions eluted as the later HPLC fractions. This confirmed earlier findings that the later HPLC fractions, illustrated in Fig. 7, were of higher molecular weights. Vanadium was found in all three size-exclusion fractions.

Finally, fractions obtained by using a succession of pure solvents were studied so as to determine the types of nonporphyrin components eluted by each solvent. The polystyrene-equivalent molecular weight of each fraction was determined as well as the V/Ni ratio and 270 nm/410 nm absorbance ratio. Also, the percentages of V, Ni, 270 nm absorbance, and 410 nm absorbance eluted by each solvent in each series were determined as were the V and Ni recoveries for each of the three series.

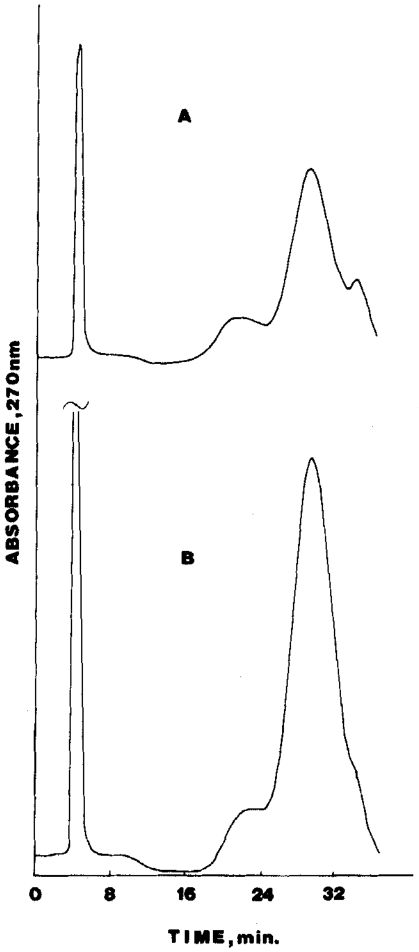


FIG. 10. Effect of successive reinjections using first a portion of Fraction 3 from Figure 7B (A) followed by reinjection of the new Fraction 3 (B). Column 5 and Gradient K were used.

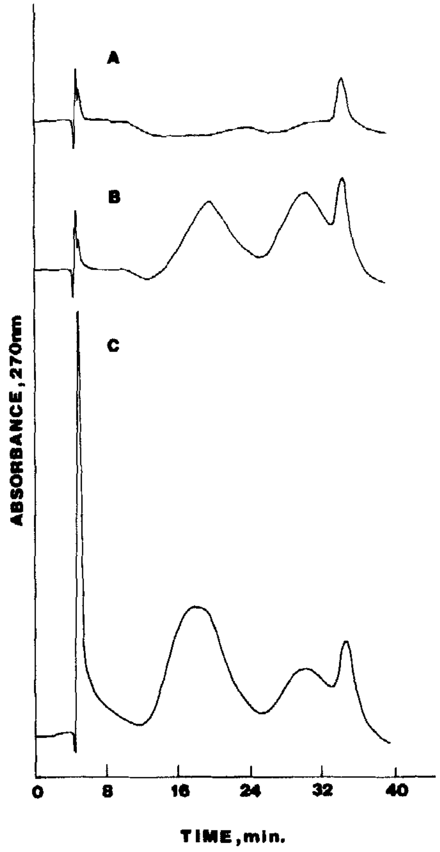


FIG. 11. Chromatograms of size-exclusion Fractions A (A), B (B), and C (C) using Column 5 and Gradient K.

The results of these studies can be seen in Tables 6 and 7. For Series 1, it was found that the V/Ni ratio increased with the molecular weight, except for Fraction 5. Also, the 270 nm/410 nm absorbance ratio was lower for Fractions 3, 4, and 5 than for the first two fractions. Nickel recovery was greater than vanadium recovery (which was also true for solvent Series 2 and 3). In a parallel study, semiquantitative measurements of the vanadium held irreversibly by neutral alumina were made after dissolving the alumina following its use in the procedure of Spencer et al. (*4*) to fractionate a crude oil sample into porphyrins and nonporphyrins. The presence of a substantial fraction of the original vanadium content of the crude oil was found in that solution.

TABLE 6
Analyses of Nonporphyrin Fractions Eluted by Pure Solvents

Solvent[a]	V/Ni	270 nm/410 nm	Recovery (%) V	Recovery (%) Ni	Polystyrene equivalent MW	Log MW
1	0.423	9			847 (913)[b]	2.93 (2.96)
2	0.743	10			1416 (1443)	3.15 (3.16)
3	2.54	3.07			2855 (3005)	3.46 (3.48)
4	3.29	2.6			5756 (4336)	3.76 (3.64)
5	1.49	3.6	76[c]	118[c]		
1′	1.70	5.3			401 (400)	2.60 (2.60)
2′	1.26	6.5			1351 (1443)	3.13 (3.16)
3′	4.08	3.07			2725 (3610)	3.44 (3.56)
4′	3.79	2.7			4348 (4752)	3.64 (3.68)
5′	0.646	3.4	82[d]	128[d]	2855	3.46
1″	0.679	14			1416	3.15
2″	2.50	2.4			2481	3.39
3″	3.51	1.4	76[e]	94[e]	3779	3.58

[a] See Table 5 for identification of solvent.
[b] Value for an earlier sample that had been separated and analyzed in the same way.
[c] Total recovered from solvents 1–5.
[d] Total recovered from solvents 1′–5′.
[e] Total recovered from solvents 1″–3″.

In Series 2, the increase in the V/Ni ratio did not correlate as well with an increase in molecular weight as it did in the first solvent series. The 270 nm/410 nm absorbance ratio was larger for the first two fractions than the last three fractions, as in Series 1. However, THF eluted approximately twice the percentage of vanadium, four times the percentage of nickel, and three times the percentages of 270 and 410 nm absorbances in Series 2 compared to Series 1.

In solvent Series 3, as in Series 1, the V/Ni ratio increased and the 270 nm/410 nm absorbance ratio decreased with an increase in molecular weight. Table 8 shows the proportions of the percentages of vanadium, nickel, 270 nm absorbance, and 410 nm absorbance eluted by each solvent except THF. No further differentiation of solvents was attempted since only one spectrum and one V and Ni determination was made for each fraction. Also, since weak solvent elution was followed by intermediate solvent elution and then by stronger solvent elution, one could not assess the effect of each solvent individually. However, one sees that the abilities of ACN,

TABLE 7

Percentages of Metals and UV-Visible Absorbing Material Eluted by Different Solvents

Solvent[a]	V (%)	Ni (%)	270 nm absorbance (%)	410 nm absorbance (%)
1	1.1	6.3	3.4	1.3
2	2.93	9.38	14.3	4.6
3	43.6	40.9	52.6	57.3
4	45.9	33.2	26.1	33
5	6.44	10.3	3.6	3.4
1′	1.2	1.7	2.7	1.7
2′	3.31	6.29	17.2	8.8
3′	41.5	24.4	47.7	51.7
4′	43.2	27.4	22.1	28
5′	10.8	40.2	10	10
1″	2.1	9.12	26.9	47
2″	19.5	23.6	47.5	48
3″	78.5	67.5	25.7	4.8

[a] See Table 5 for identification of solvent.

TABLE 8

Relative Amounts of Metals and UV-Visible Absorbing Components Eluted by Solvents

Solvent	Series	Absorbance		Metals	
		270 nm	410 nm	V	Ni
ACN	2	1	0.63	0.44	0.63
MEOH	1	0.60	0.20	0.20	1
IPA	1	1	0.32	0.21	0.65
IPA	2	1	0.50	0.19	0.45
IPA	3	1	1	0.41	0.49
n-Hexane	3	1	1	0.40	0.50
MTBE	1	0.92	1	0.76	0.71
MTBE	2	0.95	1	0.62	0.48
Chloroform	1	0.57	0.71	1	0.71
Methylene chloride	2	0.50	0.63	1	0.63

TABLE 9
Vanadium Demetallation Studies of Nonporphyrin Samples from Boscan Crude Oil

Reagent	Time (h)	Demetallation (%)
Methanesulfonic acid	12	0
Methanesulfonic acid	18	0
Methanesulfonic acid	120	30
Sulfuryl chloride	24	96

MEOH, IPA, and hexane to elute vanadium are limited, whereas those of MTBE and the chlorinated hydrocarbons are greater. Also, methylene chloride and chloroform were almost identical in the proportion of each nonporphyrin fraction eluted. Finally, one can see that MEOH exhibited a striking ability to elute nickel.

Demetallation Studies of Nonporphyrins

Since HPLC studies of demetallated porphyrin samples revealed increased resolution compared to those of the original porphyrin samples (*11–13*), demetallations of nonporphyrin samples were attempted. Two different procedures, one utilizing methanesulfonic acid and the other utilizing sulfuryl chloride, were used. Table 9 indicates that the sulfuryl chloride method was much superior to the methanesulfonic acid method in terms of demetallation yield and the time needed to attain a major percentage of demetallation. Size-exclusion chromatograms of the demetallated and nonreacted nonporphyrins, compared in Fig. 12, suggested that demetallation resulted in the formation of several low molecular weight components. These peaks may have been due to chlorinated ligands or other chlorinated species ("impurities") formed during the demetallation as well as to the original ligands themselves.

Exploratory Studies on Asphaltenes and Maltenes

Asphaltene and maltene fractions were produced by precipitating the asphaltenes from crude oil by *n*-hexane. A comparison was made of the chromatographic behavior of the fractions by first separating each fraction by Spencer et al.'s procedure (*4*) and then separating the nonporphyrin fractions generated by the procedure of Later et al. (*5*). Figure 13 shows that, although approximately 80% by weight of the crude oil sample was maltenes, the

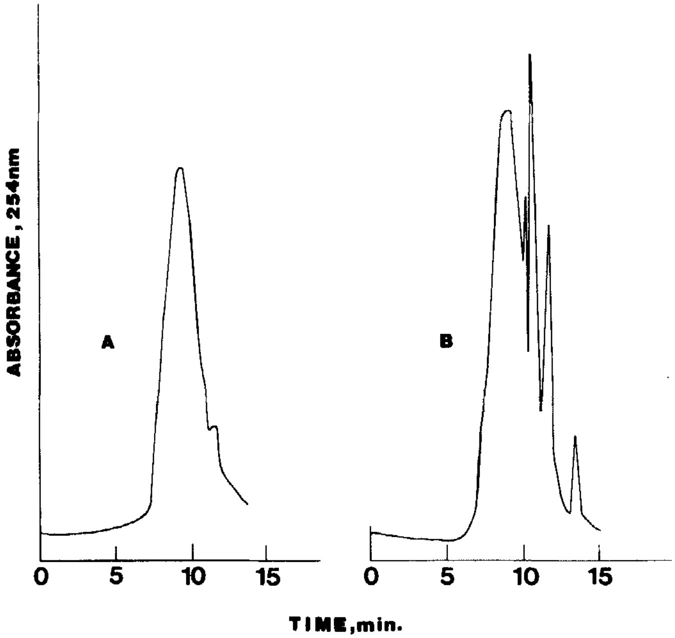


FIG. 12. Size-exclusion chromatograms of original (A) and demetallated (B) nonporphyrin samples using Column 3 in the Micromeritics system at a THF flow rate of 0.25 mL/min.

majority of the metals was in the asphaltene fraction. When each of these fractions was further separated by Spencer et al.'s procedure (*4*), only about 50% of the asphaltenes by weight was recovered from neutral alumina, whereas approximately 100% of the maltenes was recovered. A loss of high molecular weight asphaltene components on neutral alumina was observed by comparing the molecular weights of the asphaltenes with those of the fractions obtained by use of Spencer et al.'s procedure (*4*). The polystyrene-equivalent molecular weight changed from about 37,000 to about 13,000. The distribution of vanadium and nickel in the asphaltene fraction was fairly even between porphyrins and nonporphyrins, but most of the metals in the maltene fraction were isolated as nonporphyrins.

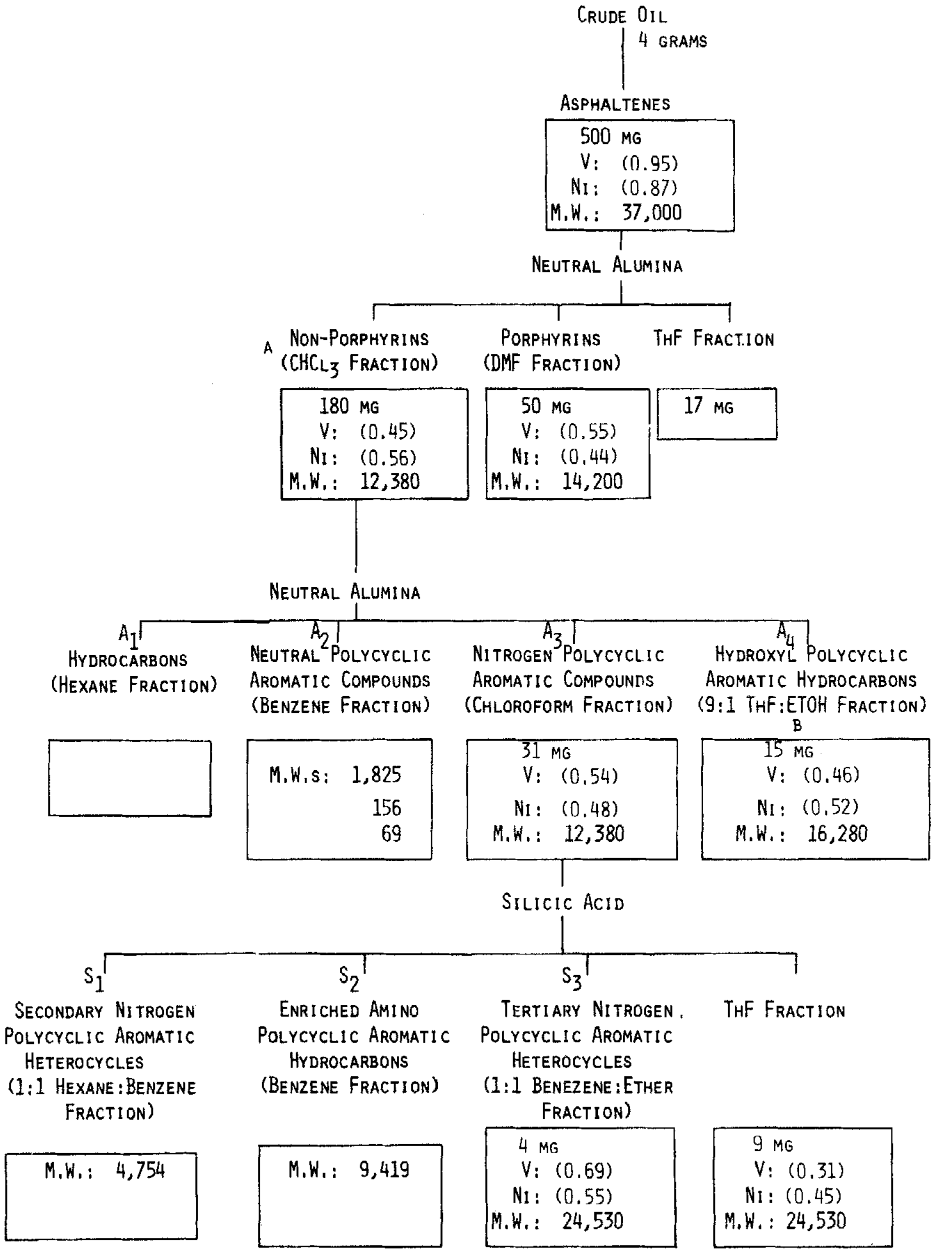
The behavior of the nonporphyrins in the procedure of Later et al. (5) was examined to see if any further fractionation of the nonporphyrins could be accomplished by preparative adsorption chromatograpy on alumina and silicic acid. More specifically, the goal was to examine the nature of the compounds with which the metals were associated. As seen in Fig. 13, only about 42% of the asphaltene nonporphyrins were recovered from the alumina column during the first part of the procedure, whereas about 68% of the maltene nonporphyrins were recovered. The fact that about half of the asphaltene nonporphyrin metals eluted as hydroxyl polycyclic aromatic asphaltene nonporpyrins eluted as such, may indicate the ability of THF to elute metal-containing species. Otherwise, most of the metals in the maltene and asphaltene fractions were found in the nitrogen polycyclic aromatic compound fraction (eluted with chloroform). However, the next greatest fraction of the maltene metals was found in the neutral polycyclic aromatic compounds (eluted with benzene). A parallel between the eluting order found here (i.e., chloroform then THF) and the eluting order for nonporphyrin separations on Column 5 is consistent because the starting material for the latter study was crude oil (i.e., asphaltenes plus maltenes). From Fig. 13 it appears that a majority of each of the metals was found with nitrogen-containing compounds (eluted with chloroform or 1:1 benzene/ether) or with THF-eluted fractions.

In the separation of nitrogenous compounds on silicic acid, about half of the asphaltene nonporphyrin nitrogenous compounds were recovered whereas there was (somewhat greater than) 100% recovery for the analogous maltene fraction. There was also an approximately twofold increase from 12,000 to 24,500 MW in the polystyrene-equivalent molecular weights of the nitrogenous compounds from the asphaltene nonporphyrins after a separation on silicic acid.

A brief, final study involved the separation of a sample of asphaltenes dissolved in THF using Column 4 in the Micromeritics system and on-line detection at 400 nm. The components on the column were eluted successively using *n*-hexane, DMF, chloroform, and THF. The results, seen in Fig. 14, indicate that this may be a good method for monitoring the separation of complexes of porphyrins and nonporphyrins from crude oil with minimal interference from uncomplexed compounds.

CONCLUSIONS

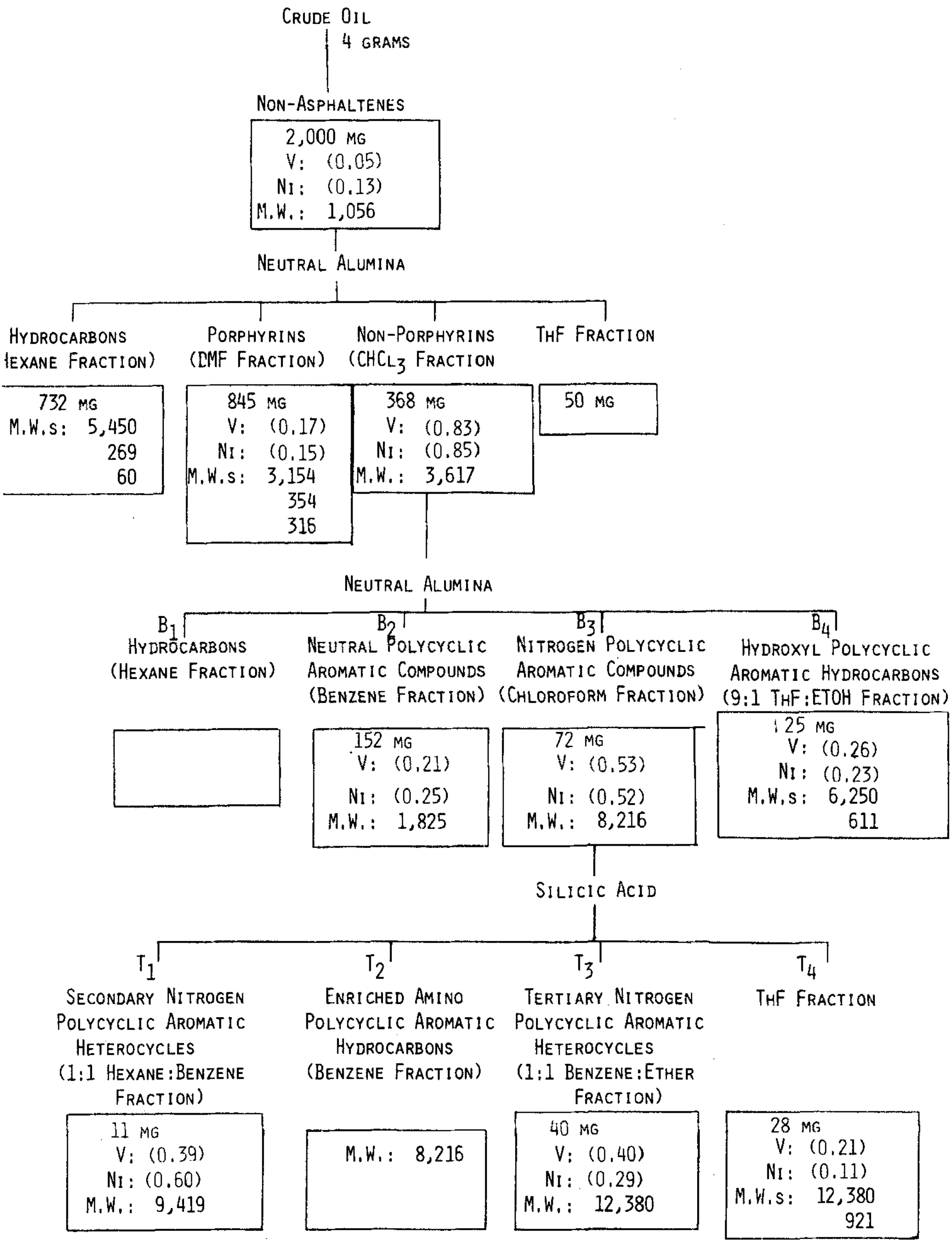
Nonporphyrin samples exhibited broad molecular weight ranges, so HPLC packings having at least 300Å average pore diameter were needed to allow more nearly complete permeation by nonporphyrin components. Instead of individual compounds, only four to five classes of compounds eluted from the column packed with 300 Å pore diameter trimethylated



[A] $CHCl_3$ = chloroform

[B] ETOH = ethanol

FIG. 13. Scheme used for exploratory study of a crude oil sample. Values in boxes (from top to bottom, if given) denote weights of particular fractions, relative amounts of total vanadium and nickel signal for a specific group of fractions, and the molecular weight(s) of chromatographic



fraction(s) as determined by size-exclusion chromatography. Above dashed line denotes the use of the procedure of Spencer et al. (*4*), and below denotes the use of the procedure of Later et al. (5). (Nonasphaltenes are defined as maltenes.)

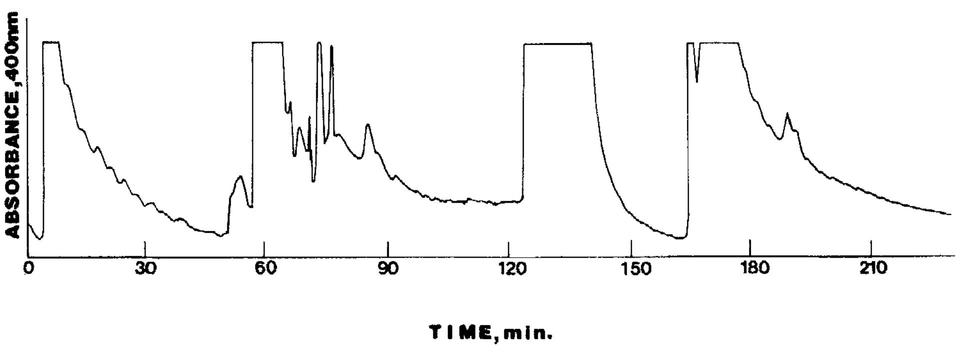


FIG. 14. Elution profile for an asphaltene sample separated using Column 4 by successive elutions with *n*-hexane, DMF, chloroform, and THF, using the Micromeritics system and a flow rate of 1.1 mL/min.

silica. The large molecular weight fractions, which eluted using methylene chloride, chloroform, or THF, contained a larger percentage of vanadium and nickel as well as a higher V/Ni ratio than the lower molecular weight fractions. Also, the nonporphyrin fractions obtained from the 300 Å trimethylated silica column exhibited complex behavior in that, upon reinjection of a single peak, peaks characteristic of other fractions also eluted. This finding suggested a slow interconversion between components in different fractions, and it is consistent with the report of Selucky et al. (*14*) that asphaltene fractions exhibited time-dependent degradation into lower molcular weight species upon dilution.

Solvents for elutions of nonporphyrins from the 300 Å trimethylated silica column differed widely in polarity and selectivity properties. Hexane was first assumed to be a weak solvent since it was used to precipitate asphaltenes from crude oils. In addition, hexane is of low polarity and enters into only dispersion-type interaction with solutes. Nevertheless, it was found to be an intermediate strength solvent that eluted a fairly large nonporphyrin fraction.

Since IPA and ACN, both of which are usually strong reversed-phase solvents, failed to elute all nonporphyrin components, a four-solvent study of the type proposed by Glajch et al. (*9*) could not be performed. Instead, a solvent-strength study was undertaken. The relative abilities of the solvents to elute nonporphyrins was $H_2O <$ ACN $\cong$ MEOH $<$ IPA *n*-hexane $<$ MTBE $<$ methylene chloride $\cong$ chloroform $\cong$ carbon tetrachloride $<$ THF. Each solvent in the final "solvent-strength order" was found to have different capabilities for eluting some nonporphyrin components, so the order cannot be assumed to be absolute. Also, the fact that the chlorinated hydrocarbons are apparently of equivalent eluting power and selectivity is unexpected since these solvents usually exhibit widely different selectivity properties. Finally, the fact that little vanadium or nickel is eluted by the first five solvents in the "strength" series may indicate that these solvents are only partially breaking up the micelles that have been proposed to be large aggregates of metal-containing asphaltenes (*15*). Later solvents in the series may have a greater tendency to break up the asphaltene micelles.

Exploratory studies of nonporphyrin demetallation using methanesulfonic acid (used previously for porphyrin demetallations) were not promising. A more successful method utilized sulfuryl chloride as a reagent, and it produced several low molecular weight nonporphyrin components. None of the compounds in the fractions have as yet been identified. It will be of interest to determine if a fraction consists of a homologous series of ligands or a mixture of different species. It will also be of interest to see if any of the fractions represent chlorinated species produced by the demetallation reaction.

Exploratory studies on crude oil indicated that most of the metals were found in the higher molecular weight asphaltene fraction, which comprised only approximately 20% by weight of the crude oil. Using Later et al.'s procedure (*5*), it was found that most of the nonporphyrin metals eluted as nitrogen-containing compounds (using chloroform) or THF. This, in a sense, confirmed the findings for nonporphyrin fractionation using Column 5. Finally, these studies also indicated that silica may be superior to alumina for isolations of nonporphyrins based upon the smaller loss of higher molecular weight components.

Acknowledgments

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