

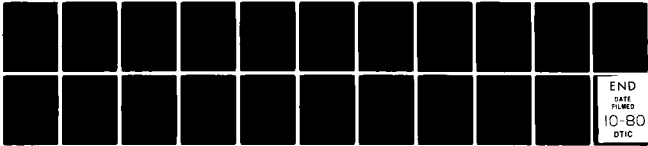
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A GEOCHEMICAL METHOD FOR DETERMINING  
HEAT HISTORY OF RETORTED SHALE OIL

BY

CAPT ELROY A. FLOM

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PROJECT 2303

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Directorate of Chemical Sciences  
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## PREFACE

This report documents work done at the Laramie Energy Technology Center (LETC) by Capt Flom between 1 June 1978 and 1 August 1978 and continued by both authors through 1 January 1979 under Work Unit Number 2303-F3-01, Energetic Materials Research. The authors wish to thank Mr. Dale Lawlor, Senior Chemist at the LETC for providing samples, equipment, and many helpful discussions. Dr. Richard Heppner of the LETC and Mr. Lloyd Pflug of the Frank J. Seiler Research Laboratory obtained the mass spectral analysis. In addition, thanks are due to Ms Gail Lotz for typing the manuscript.

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## I. INTRODUCTION

A great deal of geochemical data has been encoded in biochemical molecules which have survived to the present day. Porphyrins of various types which are found in sediments, petroleum, and bitumens have great geochemical significance.

Treibs (1) first showed that chlorophyll-bearing plants played a decisive part in the formation of bitumens and petroleum of various origins and of all geological ages. Following further work with minerals, shales, bitumens, and crudes, he postulated the now widely accepted transformation of chlorophyll into desoxophylloerythroetioporphyrin (DPEP) (2).

Chlorophyll as the precursor to today's porphyrins is chemically unique because a highly refractory aromatic nucleus supports peripheral groups of variable stability (see Figure 1). The aromatic nucleus ensures geologic survival, while the peripheral groups of its chemical descendants rather accurately reflect the environment to which the material has been exposed. One such environment is the high temperatures of the modern oil shale retorting process.

Baker, et al., have described at least four types of reactions that can occur when metalloporphyrins are subjected to severe thermal stress: (1) dealkylation; (2) isocyclic ring opening, i.e., conversion of DPEP series to etio series; (3) alkylation; and (4) thermal decomposition. The effect of increasing thermal stress on the progress of these reactions

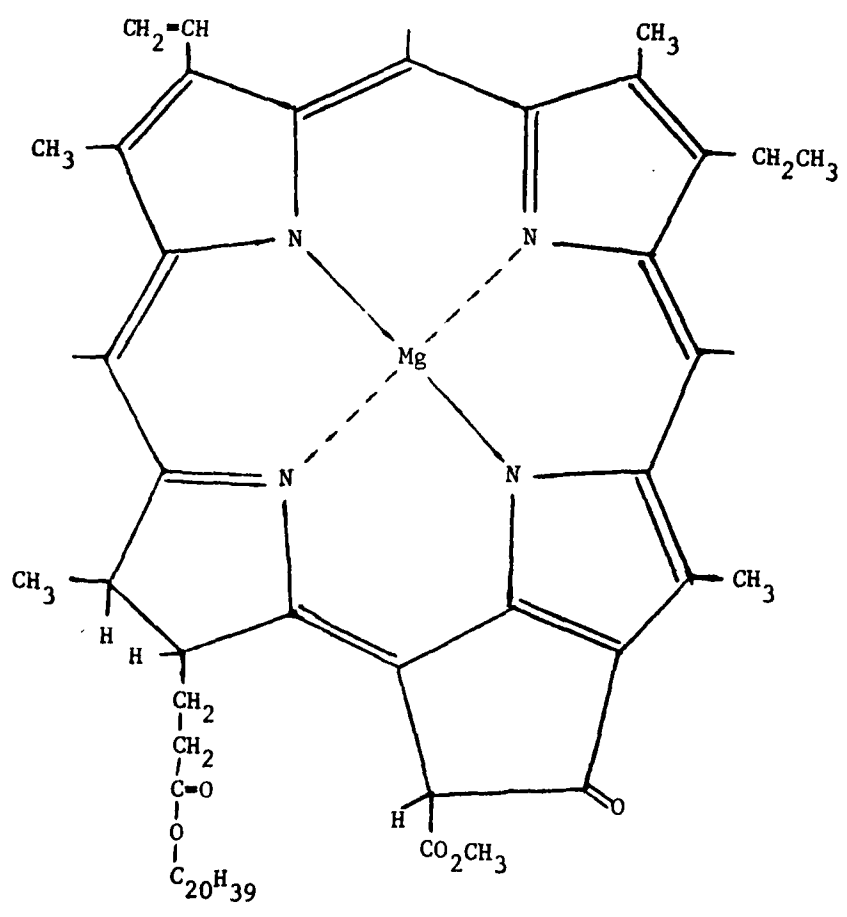


FIGURE 1 - Chlorophyll

has been established (3). The main source of etio (that is, alkyl) porphyrins is thermal opening of the DPEP isocyclic ring (4, 5) which is shown in Figure 2.

A ratio of DPEP/etio porphyrins can be calculated from mass spectrometric data by the method of Baker (3) and from integration of absorption peaks in the visible-UV region (6).

This investigation explored the possibility of determining the heat history of retorted shale oil as a function of the DPEP/etio ratio. It began with the separation of crude porphyrin fractions from the total retorted shale oil or bitumen by gel permeation chromatography (GPC) using a method described by Smith (7). The porphyrin fraction was then demetallated and fractionated further into rhodo, etio, and phyllo types. Analysis was made via mass and visible-UV spectrometry.

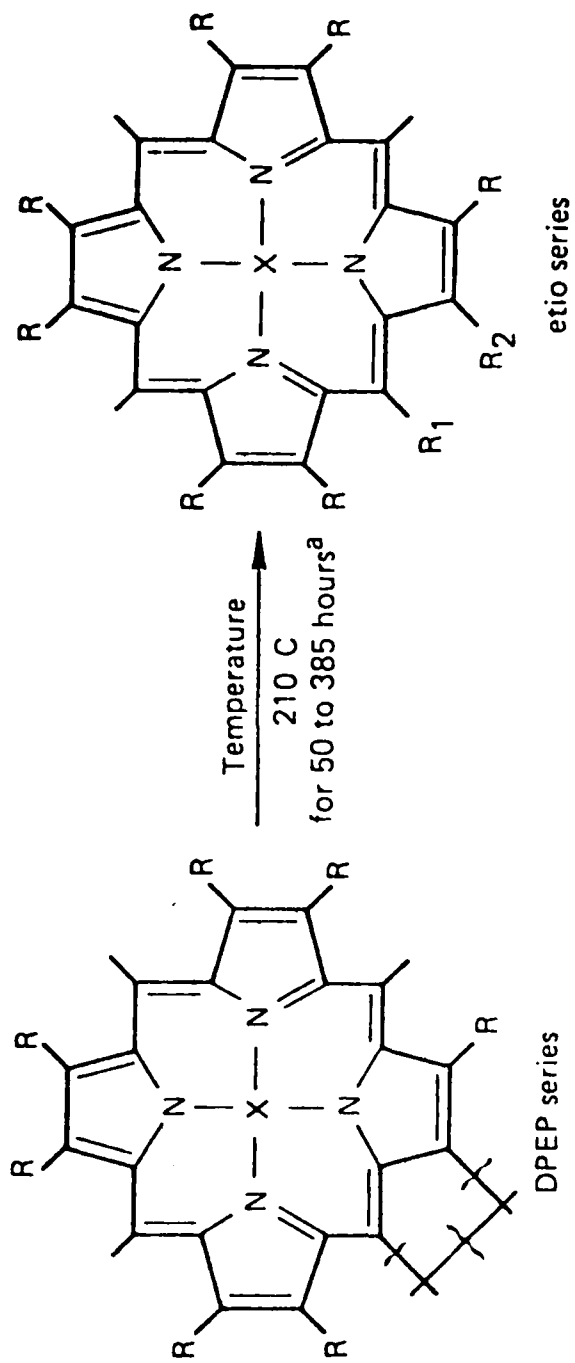
## II. EXPERIMENTAL

### Reagents and Apparatus

Benzene, methanol, and all other liquid reagents with the exception of diethyl ether were distilled in glass or used directly as Burdick and Jackson provide them. Ether was used in very small quantities and was not distilled.

Bio-Rad Laboratories Bio Beads SX-4 were used for the GPC work. Mallinckrodt SilicAR or Davison No. 923 silica gel was used to separate types of demetallated porphyrins.

Solvents were removed from samples under a stream of nitrogen or by distillation at reduced pressure.



<sup>a</sup>Didyk, *et al.*, 1975

<sup>b</sup>R = H or alkyl groups; R<sub>1</sub>, R<sub>2</sub> = H, or Et; X = Ni or V = O

<sup>c</sup>This conversion is often, but not always, associated with loss of one or two methylene units. Note that the etio series (310 + 14n) can include some members with bridge substituents which are in actuality phylloporphyrins.

FIGURE 2. - Thermal conversion of DPEP to Etio type porphyrins

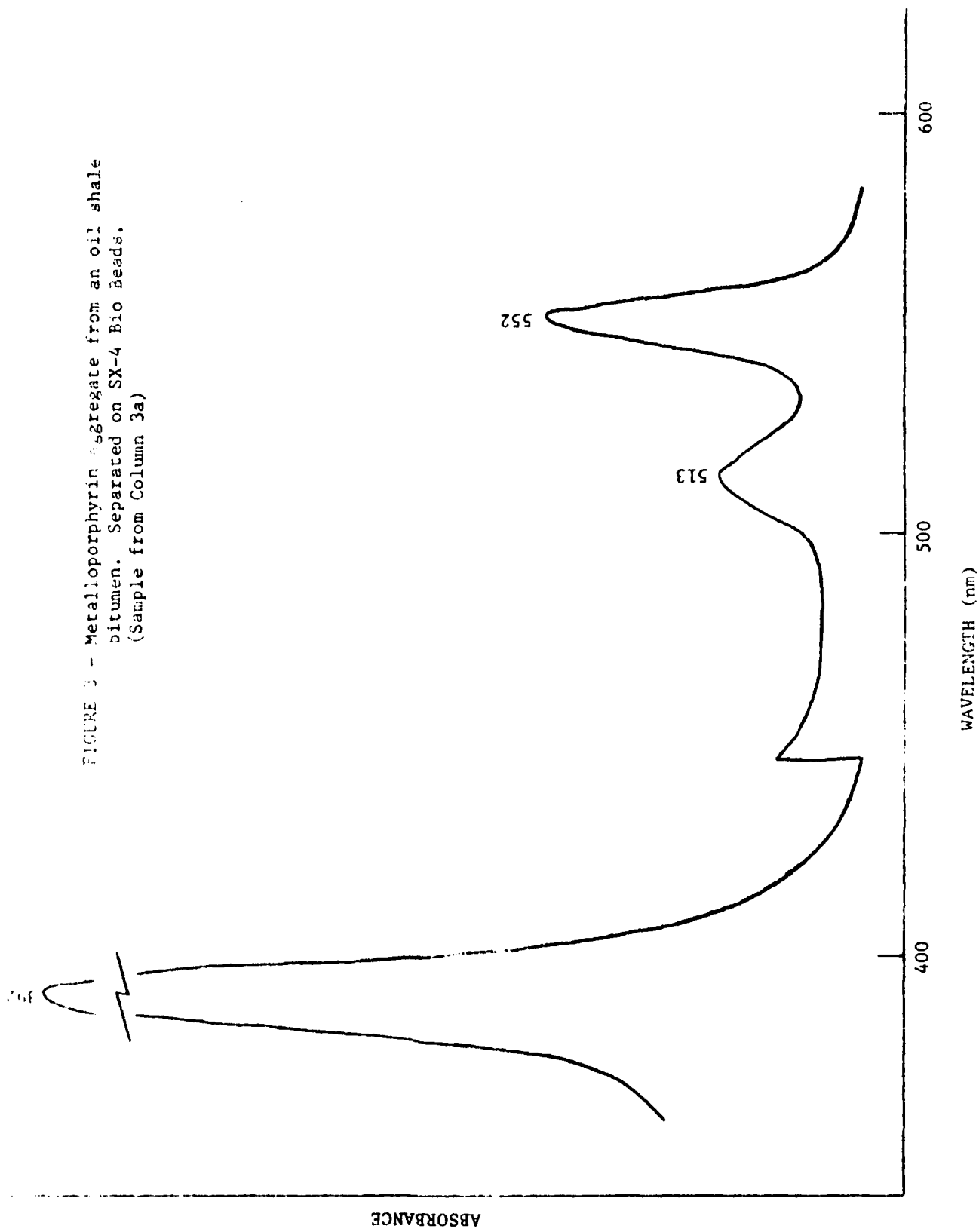
UV-visible spectra were obtained on a Beckman ACTA MIV Spectrophotometer using standard 1 cm path length quartz cells. Mass spectra were obtained with a CEC 110 high resolution instrument or a Dupont 21-491 double focusing mass spectrometer.

#### Production of Free Porphyrin Aggregate

A weighed sample of bitumen or shale oil (2.8 to 6.6 gm) was dissolved in approximately 20 ml of 60:40 benzene-methanol and applied to a GPC column (2.5 x 50 cm) of Bio Beads SX-4 previously wet with the same solvent. Three large visible fractions were observed: brown, yellow, and pink; the brown being the first to be eluted. The first two fractions showed no visible-UV peaks characteristic of the tetrapyrrole pigments. The third, pink, band showed a spectrum indicating it to be rich in metalloporphyrins (see Figure 3) primarily of the nickel variety.

The porphyrin fraction was stripped of solvent and placed in a reaction vessel for demetallation after yield was determined. A few crystals of hydrazine sulfate in 15 ml methanesulfonic acid (MSA) were added to the dry fraction (approximately 0.1 g). The mixture was stirred for 1.5 hours with a magnetic stirrer at 55°C, poured onto 25 gm ice in an ice bath, and made basic with concentrated ammonium hydroxide. The free porphyrin aggregate was extracted with two - 20 ml portions of chloroform. The spectrum of this material was determined in chloroform, and the solvent was removed. It should be noted here that while chloroform is considered by some to be the universal solvent for porphyrins (6), experts also agree that chloroform should not remain in contact with the porphyrins more than one or two hours to prevent unwanted reaction products (11).

FIGURE 3 - Metalloporphyrin aggregate from an oil shale bitumen. Separated on SX-4 Bio Beads. (Sample from Column 3a)



### Separation of Porphyrin Types

The demetallated porphyrin aggregate was taken up in a minimum volume of benzene and applied to a silica gel column (1 x 40 cm) packed with Mallinkrodt SilicAR previously wetted with cyclohexane. The column was then eluted with 1:1 cyclohexane:benzene, benzene, and 50:1 benzene:diethyl ether. Rhodo, etio, and phyllo porphyrins were eluted and produced spectra similar to b and f in Figure 4, respectively (8). UV-visible spectra may be determined in these solvents, but sharper spectra were obtained in diethyl ether.

Mass spectra were obtained on the free porphyrin aggregate for calculation of the DPEP/etio ratio in a bitumen sample.

### III. RESULTS

#### Gel Permeation Chromatography

Bio Beads SX-4 provided a suitable separation medium for porphyrins from the remainder of the material in oil shale bitumen. A 60:40 ratio of benzene:methanol seemed to provide the most satisfactory solvent. Tetrahydrofuran (THF) was used but solvated the beads so extensively that flow rates dropped off to zero. THF may be used by pressurizing the solvent with a small pump (9). Yields of material in the same molecular size range as the porphyrins are shown in Table I. The shale oil sample yielded very small amounts of porphyrin-sized material. In some cases mass spectral data were difficult to obtain because of small signal response. A larger sample of shale oil must be used requiring a larger column or some type of concentration technique.

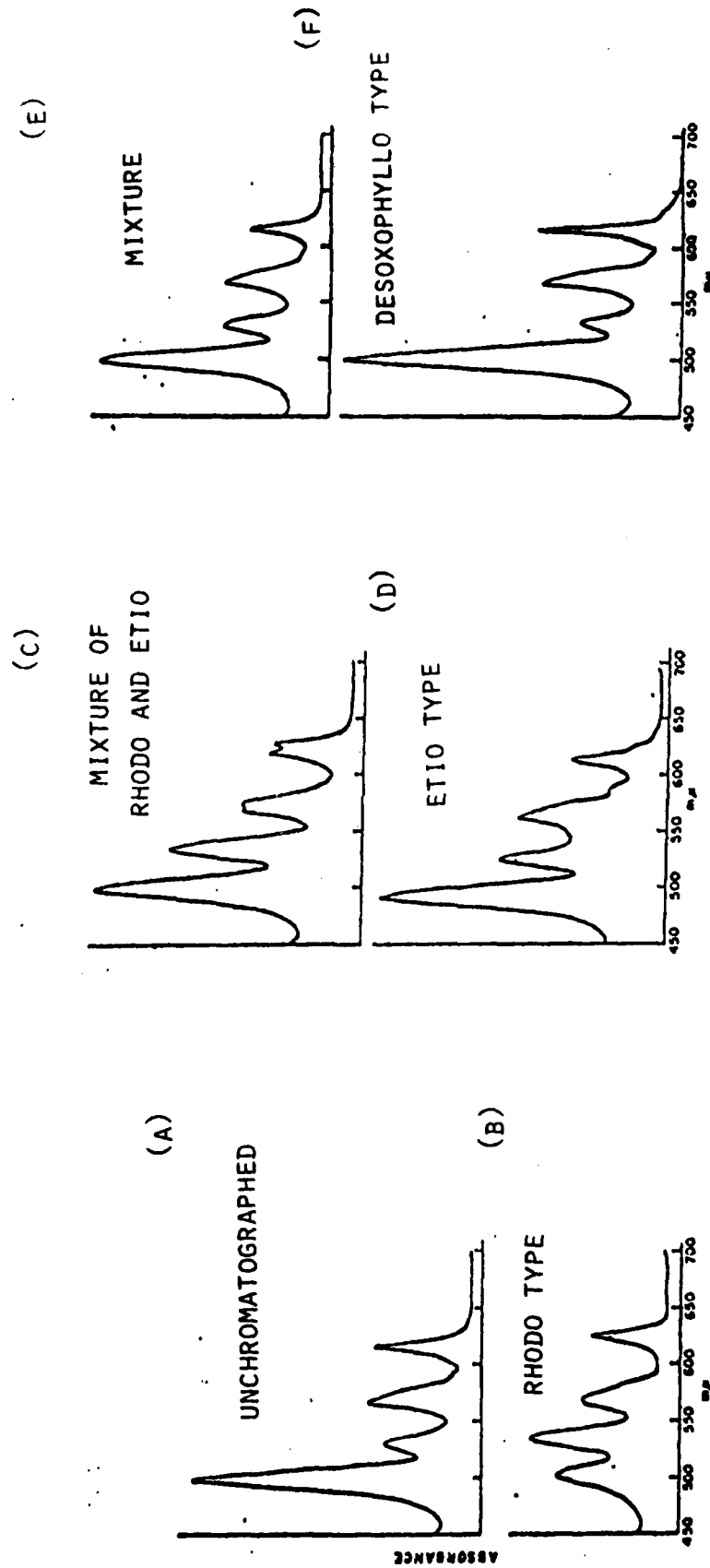


FIGURE 4. CHROMATOGRAPHIC SEPARATION OF PORPHYRINS

TABLE 1  
YIELD OF PORPHYRIN FRACTION FROM GPC

<u>Column</u>	<u>Original Material</u>	<u>Solvent</u>	<u>Yield of Porphyrin Fraction (% by weight of total sample)</u>
1	Bitumen	Benzene/Methanol	4.64
2	Bitumen	THF	----
3a	Bitumen	Benzene/Methanol	3.57
3b	Bitumen	Benzene/Methanol	1.13
4	Shale Oil	Benzene/Methanol	0.80
5	Bitumen	Benzene/Methanol	0.73

Regarding solvent choice, THF must be pumped; which constitutes a small fire hazard, but more importantly, THF leads to concentration of oxidizing peroxides in the sample as solvent is removed. Benzene/methanol appears to be more desirable from this standpoint.

#### Silica Gel Separation

Separation of the free porphyrin aggregate into three fractions each containing some porphyrinic material was accomplished using the SilicAR gel. The Davison gel caused some type of decomposition as evidenced by a color change. Further, the Davison gel produced copper porphyrins with absorption bands in the visible spectrum at 526 and 562. See work of Palmer (10).

Only very small amounts of rhodo type porphyrins, which were obviously very contaminated, were found. In the column 3a sample, an etio porphyrin spectrum was obtained in which peak ratios matched those reported by Howe (6) for special etio, although this spectrum had a poor baseline suggesting a substantial amount of impurity here also.

In comparing extinction coefficients of the various types of porphyrins in oil shale bitumen, it appears that the phyllo species is the predominant one. It gives in each case the spectrum reported by Baker for DPEP (see Figure 5).

An effort was made with the column 3b sample to remove impurities of an organic nature from the demetallated material. This was accomplished by loading the SilicAR column with hexane, introducing the sample in benzene, and further eluting with hexane. The benzene aliquot in hexane elutes small amounts of nickel porphyrins. The hexane elutes small

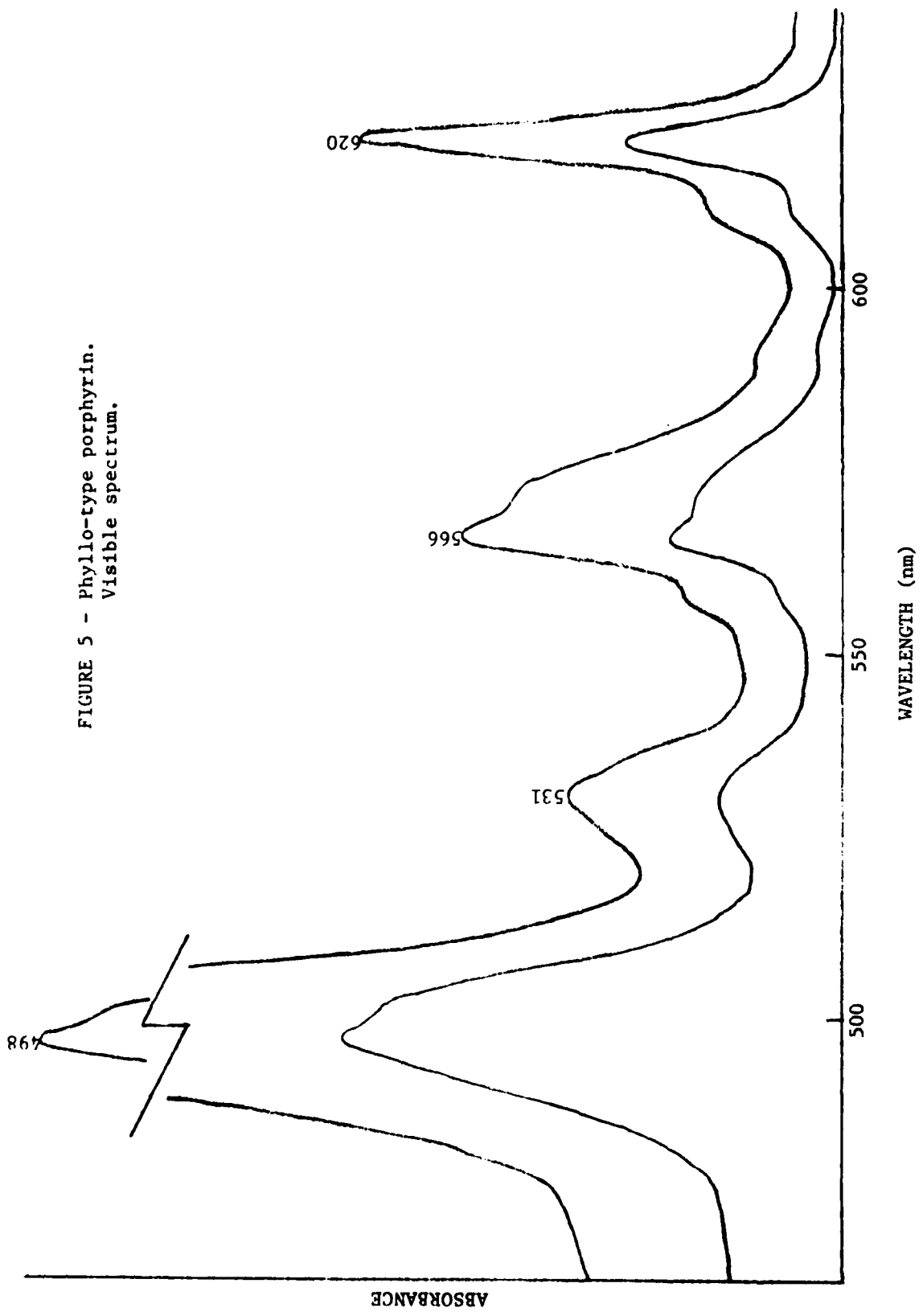


FIGURE 5 - Phyllo-type porphyrin.  
Visible spectrum.

amounts of organic material as evidenced by a decreasing baseline in the UV-visible region.

#### Absorption Coefficient Quantitative Analysis

The technique of Howe may be used to get an approximation of the DPEP/etio series. A larger sample must be employed to get appreciable quantities of the etio porphyrins.

#### Mass Spectral Data

Using Baker's method, five homologous series of porphyrin materials were observed in a sample of shale-derived bitumen (see Table II). The B and C series with copper represent contaminated samples in which the copper has been reintroduced probably from the silica gels used to separate the demetallated porphyrins. The A, B, and C series correspond to phyllo-type porphyrins in their masses whereas the D series  $C_n H_{2n-28} N_5 O_2$  gives a mass of the etio type. The number of rings + double bonds in the respective porphyrin series are consistent with these findings.

To quantify the mass spectral data obtained on a sample of bitumen, Baker's statistical analysis was applied. The results are presented in Table III. The highest peak intensity in the etio series centered around 450 mass units while the phyllo series centered about 476. The weighted average mass (arithmetic mean) for the etio and phyllo series were 466.9 and 467.7 mass units respectively. The band widths of the porphyrin envelope for both the etio and phyllo are as shown. If the envelope of mass peaks corresponding to each of the series is sketched, a skewness in the distribution of intensities is noted. It may be calculated by the

TABLE II  
HIGH RESOLUTION MASS SPECTROSCOPIC RESULTS FOR OIL SHALE BITUMEN  
 $CH_2 = 14.0000$

Homologous series	Empirical formulae	Measured decimal	Decimal difference	Ring + double bonds	Carbon number range
A	$C_n H_{2n-28} N_4$	0.762	0.000	17.0	30-32
B	$C_n H_{2n-30} N_4 C_u^{63}$	0.604	-0.004	18.0	30-32
C	$C_n H_{2n-30} N_4 C_u^{65}$	0.607	-0.004	18.0	30-32
D	$C_n H_{2n-38} N_3$	0.701	-0.007	21.5	43-48
	$C_n H_{2n-38} N_4$	0.701	0.005	22.0	42-47
	$C_n H_{2n-40} O$	0.701	-0.008	21.0	45-50
	$C_n H_{2n-40} NO$	0.701	0.004	21.5	44-49
	$C_n H_{2n-28} N_5 O_2$	0.701	-0.003	17.5	38-43
	$C_n H_{2n-28} N_6 O_2$	0.701	0.009	18.0	37-42
	$C_n H_{2n-30} N_2 O_3$	0.701	-0.004	17.0	49-45
	$C_n H_{2n-30} N_3 O_3$	0.701	0.008	17.5	39-44
	$C_n H_{2n-32} O_4$	0.701	0.006	17.0	41-46
	E	$C_n H_{2n-39} N_3$	0.698	-0.003	22.0
$C_n H_{2n-39} N_4$		0.698	0.009	22.5	42-47
$C_n H_{2n-41} O$		0.698	-0.004	21.5	45-50
$C_n H_{2n-41} NO$		0.698	0.008	22.0	44-49
$C_n H_{2n-29} N_5 O_2$		0.698	0.001	18.0	38-43
$C_n H_{2n-31} N_2 O_3$		0.698	-0.001	17.5	40-45
$C_n H_{2n-19} N_6 O_4$		0.698	-0.007	13.5	34-39

TABLE III  
 MASS SPECTROSCOPIC DATA FOR SHALE OIL BITUMEN

<u>ETIO MASS UNIT</u>	<u>ETIO PEAK INTENSITY</u>	<u>PHYLLO MASS UNIT</u>	<u>PHYLLO PEAK INTENSITY</u>
506.0	6.1	504.0	6.8
492.0	8.3	490.0	10.0
478.0	12.2	476.0	53.0
464.0	12.1	462.0	35.3
450.0	14.5	448.0	21.4
436.0	9.8	434.0	8.4

WEIGHTED AVERAGE MASS OF ETIO - 466.9  
 WEIGHTED AVERAGE MASS OF PHYLLO - 467.7  
 BAND WIDTH OF ETIO - 21.7  
 BAND WIDTH OF PHYLLO - 16.5  
 SKEWNESS OF ETIO - 0.1  
 SKEWNESS OF PHYLLO - 0.2  
 PHYLLO/ETIO RATIO - 2.141

formula  $Sk = (\bar{X} - Mo)/\sigma$ , where  $\bar{X}$  is the statistical mean mass,  $Mo$  the mode, and  $\sigma$  the band width. The skewness for both series in this illustrative bitumen sample is positive because the mean exceeds the mode.

The series ratio of phyllo to etio peaks as defined by Baker, et al (3), is 2.141 indicating that the majority of these bitumen porphyrins are still in the phyllo form.

#### IV. CONCLUSIONS AND RECOMMENDATIONS

Baker first suggested that differences in type and distribution of the petroporphyrins present in bitumens be utilized as a geochemical tool. While an exhaustive study of retorting and extraction conditions versus the ratio of phyllo/etio present is warranted and would likely produce interesting results, the present work illustrates certain principles. Gel permeation chromatography was successfully utilized to separate a crude porphyrin fraction from oil shale bitumen and the total retorted shale oil. The demetallated porphyrins were separated into etio and phyllo series by silica gel. Traces of copper and iron and possibly other metals which may have given rise to a metalloporphyrin contaminant in the elution of the silica gel columns might be extracted by acid in future work. UV/visible and mass spectrometry are useful in analyzing the characteristics of the separated series. It is recommended that follow-on work use a flow diagram like that shown in Figure 6. Shale oils from various sources and differing thermal histories should be analyzed to determine if the phyllo/etio ratio is temperature dependent. The length of time that a sample is exposed to a given temperature may also be a significant factor.

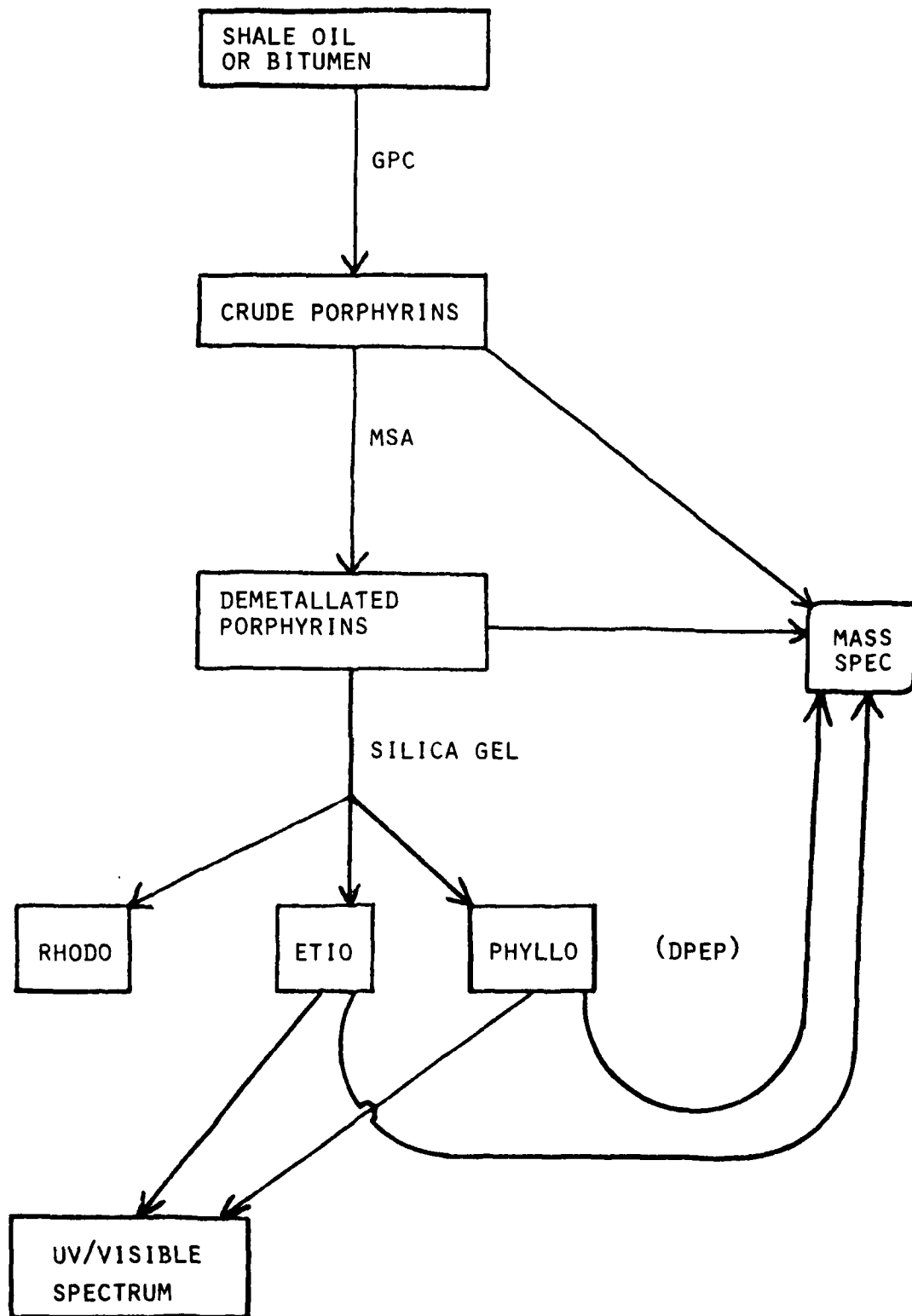


FIGURE 6. Flow Diagram for Separation and Analysis

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