

## Recent Advances in Petroporphyrin Analysis\*

Saleh K. HajIbrahim

Department of Chemistry, College of Science, King Saud University,  
P.O. Box 2455 Riyadh, Saudi Arabia

---

**ABSTRACT.** A method is described for the isolation, characterization and fingerprinting of porphyrin mixtures from geological samples. The procedure, which employs various modern analytical techniques (*e.g.* high performance liquid chromatography, computerized mass spectrometry and uv/vis spectrophotometry), is simple, fast and should, thus, facilitate studies concerned with the structure elucidation of these pigments. Applied to a wide variety of oil and shale samples from the Arabian Gulf, Europe, North America, Venezuela and Indonesia, this method of crude oil fingerprinting provides a new technique for oil classification and recognition, and should prove useful in the twin areas of oil exploration and oil pollution control.

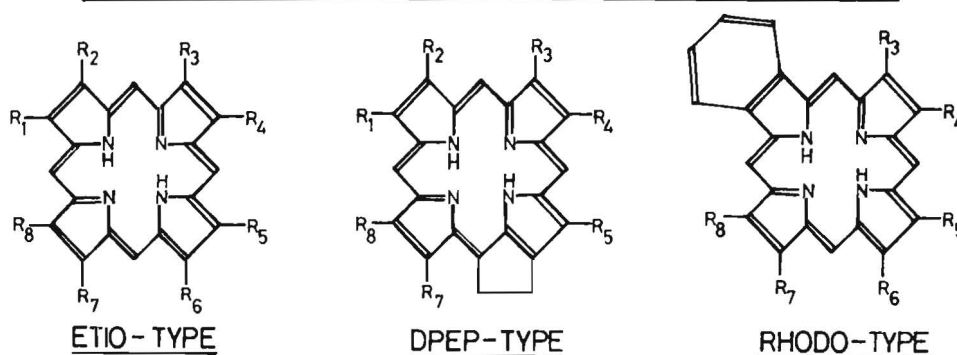
Petroporphyrins are red pigments whose chemical structure comprise four tetrapyrrole units linked together as in chlorophyll and heme nuclei. These fossil organic compounds occur in petroleum (and related materials) as metallo-complexes of mainly vanadyl and nickel (HajIbrahim 1978). Generally, they are present as a complex mixture of three main structural types (DPEP, etio and rhodo\*\*, Fig. 1) and in each type as a series extending over a carbon number ( $C_N$ ) range of  $C_{26}$  to  $C_{39}$ . Furthermore, these compounds can exist as structural isomers (HajIbrahim *et al.* 1981), thus adding to their complexity.

---

\* Presented in part at the First Asian and Pacific Chemistry Congress, Singapore, April, 1981.

\*\* These are the alkylmonobenzoporphyrins not the classical rhodo porphyrins. Their designation as a rhodo-type was based on their spectrum and prior to their structure determination. The 'rhodo' nomenclature, however, is still in use by many porphyrin geochemists.

### THE THREE MAIN STRUCTURAL TYPES OF PETROPORPHYRINS



$R_1$  to  $R_8$  = alkyl groups

**Figure 1.** General structure for the major petroporphyrin types detected in geological samples.

In the evaluation of petroporphyrins as geochemical parameters, it is essential to be able to isolate these compounds from their geological host environment quantitatively and rapidly. The classical methods (*e.g.* TLC, column chromatography) are laborious, time-consuming or nonquantitative. Direct analysis by gas-liquid chromatography is hindered by the involatility and/or thermal instability of these pigments.

This paper describes the development of a simple and quantitative procedure for the isolation and analysis of fossil porphyrin mixtures for geochemical correlations and for structure elucidation studies.

### Experimental

#### I. Isolation of Metalloporphyrin Mixture (MPP)

To 1 g of the oil sample (or the organic extract of the shale) in toluene (3 ml) was added anhydrous methanol ( $5 \times 6$  ml) and the mixture was sonicated (*ca.* 3 min); centrifugation (*ca.* 3000 rpm, 5 min) afforded an upper layer (red) containing the crude metalloporphyrin concentrate which was decanted and filtered through cotton wool. The combined extracts were concentrated (using rotary evaporator) and purified over alumina column chromatography (Woelm neutral Act. I;  $\text{CHCl}_3$ ) (sample: absorbent, 1  $\mu$ mole: 1 g). The pure MPP mixture was eluted with  $\text{CHCl}_3$  until the eluant was colorless.

## II. Separation of Nickel (NiP) from Vanadyl (VOP) Complexes

The purified metalloporphyrin mixture was chromatographed on silica gel (100-200 mesh, BDH) column (sample: absorbent, 1  $\mu$ mole: 1 g). Elution with hexane/toluene (1:1 v/v) to toluene removed the Ni-complexes, whereas  $\text{CHCl}_3$  removed the VO-complexed petroporphyrins. Each fraction was then analyzed by uv/vis spectroscopy.

## III. Isolation of Free Base Petroporphyrin Mixture (FPP)

Methane sulphonic acid (MSA) was added to the toluene solution of the purified metalloporphyrin concentrate. A sample: toluene: MSA of 1  $\mu$ mole: 1 ml: 2 ml was used. The mixture was refluxed (110°C, 1 hr). After cooling, the reaction mixture was diluted with equal volume of n-hexane: toluene (1:1 v/v) and two volumes of distilled water. The bottom layer (aqueous MSA) showed a purple color characteristic of the petroporphyrin dications. The organic layer (top) showed a black color. After separating the layers, the organic layer was repeatedly extracted with an equal volume of aq. MSA (25%) until the acid layer was colorless. The combined acidic extracts were extracted with an equal volume of  $\text{CHCl}_3$  until the latter remained colorless. The  $\text{CHCl}_3$  extracts were washed with an equal volume of  $\text{NaHCO}_3$  solution (5%) four times then twice with an equal volume of distilled water. The free base petroporphyrins concentrate, after removal of the  $\text{CHCl}_3$ , was purified by alumina (Act. II, BDH) column chromatography (sample: absorbent, 1  $\mu$ mole: 1 g). The pure petroporphyrin mixture was eluted with  $\text{CHCl}_3$  until the eluant was colorless and assayed by uv/vis spectroscopy.

## IV. High Pressure Liquid Chromatography (HPLC)

The HPLC equipment comprised Varian 5060 liquid chromatograph with Vista 401 data system and UV-50 spectrophotometer as detector. The HPLC column was Varian Micropak Si-5 (30 cm  $\times$  4.0 mm i.d.).

HPLC analyses were carried out using isocratic elution. The solvents used were hexane, toluene and chloroform (6 : 3 : 1 v/v) and a flow rate of 0.5 ml/min. Detection for the metalloporphyrins was at 395 nm and 572 nm for the Ni- and VO-complexes, respectively, and at 400 nm for the demetallated porphyrin mixture.

Samples (in  $\text{CHCl}_3$ ) were injected onto the column using a 10  $\mu$ l syringe and a Valco valve injector. Peaks were trapped manually for mass spectral analysis and were assigned numbers 0, 1, 2 etc. in order of their elution as indicated in Figure 4.

## V. UV-Visible Spectroscopy

All absorption spectra were recorded (in  $\text{CH}_2\text{Cl}_2$ ) with a Varian Cary 219 spectrophotometer using a set of matched cells (1 cm). The operating conditions were: scan speed, 2 nm/sec; band width, 1.0 nm; scan range, 700 to 350 nm.

## VI. Mass Spectrometry Data System (ms/c)

The electron impact (EI) analysis of petroporphyrin mixtures was performed on a Ribermag MS model R10-10 quadrapole mass spectrometer (resolution *ca.* 1000, 10% valley definition) by direct insertion *via* an independently heated/cooled stainless steel probe. The mass spectrometric conditions were: source temperature 230°C; pressure  $<10^{-6}$  torr; filament current 300  $\mu$ A; ionization energy 70 eV; scan speed 1 sec; integration 3 msec.

The petroporphyrin sample in  $\text{CH}_2\text{Cl}_2$  solution (3 to 5  $\mu$ l, 1 mg/ml) was placed in a preflamed (600°C) glass crucible. After the solvent has evaporated, the sample was inserted *via* the direct inlet probe into the ion source. The probe temperature was programmed (25 to 300°C, linear) at 10 to 20°C/min under cyclic scanning (mass range  $m/e$  1 to 850). Time and intensity data from each scan were output to a DEC PDP8/M computer *via* Riber 400 interface (Ribermag) for analogue to digital conversion. The spectra were monitored on the visual display unit (Tektronix 4010/1) of the data handling system. Petroporphyrins molecular ions appeared usually in the 190 to 250°C range. Because of the observed differences in the volatility of various petroporphyrin compounds, all petroporphyrin-containing scans were averaged (by computer) to give the spectra used in the calculation of the relative abundance of molecular petroporphyrins and of the DPEP to etio ratio.

## Results and Discussion

The analysis scheme developed in this study is depicted in Fig. 2. It is divided, for convenience, into three sections:

### I. Isolation Procedure

This included:

- a. Liquid/liquid extraction of the metallocomplexes (NiP and VOP) from their geological host environment (Step A).
- b. Separation of NiP from VOP complexes by silica column chromatography (Step B).
- c. Acid demetallation of the extracted metallo-porphyrins and purification of the product by alumina column chromatography (Step C).
- d. Fractionation and fingerprinting of the demetallated petroporphyrins by high pressure liquid chromatography (HPLC) (Step D).

### II. Instrumental Analyses

This involved the determination of the:

- a. Total petroporphyrin concentration and the NiP to VOP ratio by absorption spectrophotometry (uv/vis).



## ANALYSIS SCHEME OF PETROPORPHYRINS

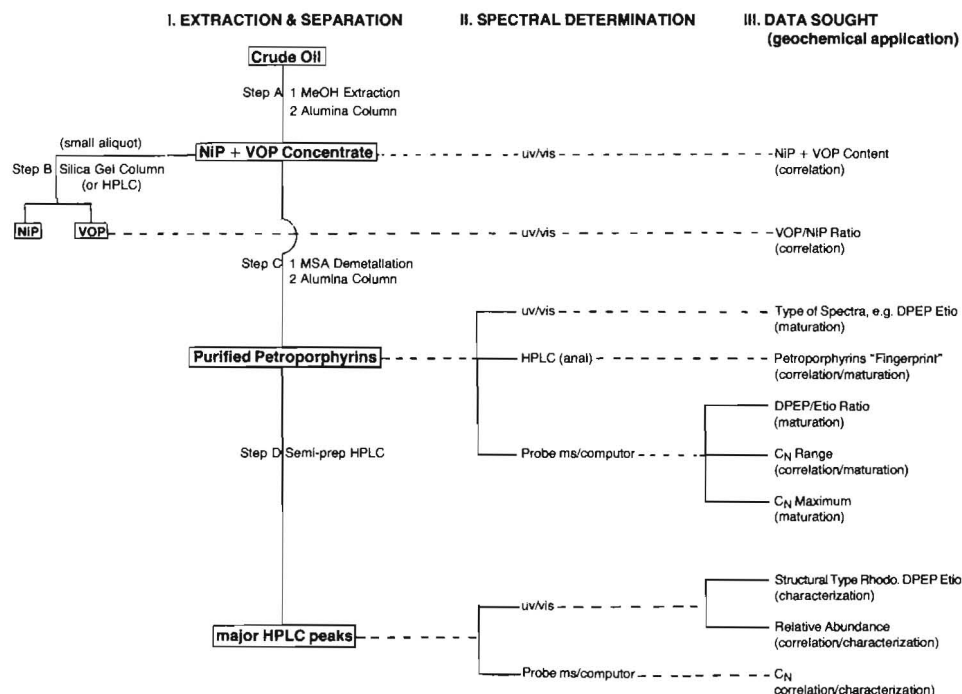


Figure 2. Schematic representation of the general procedure used for petroporphyrin analysis.

b. Relative abundance of the DPEP- and etio-type petroporphyrins by mass spectrometry/computer (ms/c).

c. C<sub>N</sub> range and maxima of each type by ms/c.

d. Relative abundance of petroporphyrin molecular ions by ms/c.

e. Relative abundance (distribution) of molecular petroporphyrins by HPLC.

### III. Data Collection

The uv/vis, ms/c and HPLC derived data were used to calculate a set of gross and molecular porphyrin characteristics, *e.g.* metalloporphyrin content; NiP/VOP ratio; DPEP/etio ratio; C<sub>N</sub> range and maxima; petroporphyrins fingerprint and the relative abundance of molecular petroporphyrins.

### *Extraction of Metalloporphyrins*

The general approach used for the isolation of metalloporphyrins from crude oils is to extract these compounds with a solvent in which the bulk of the matrix is not soluble. Thus, methanol, aqueous pyridine, aniline and other similar polar co-ordinating solvents have been used (Dean and Whitehead 1963, Hodgson *et al.* 1963). In the course of this investigation, it became obvious that the extraction methods reported in the literature were time-consuming, required large quantities of the extracting solvents or semi-quantitative. In other words, these methods were impractical for geochemical correlation studies which require analysis of a large number of oil/shale samples and so they had to be modified. The findings from experiments designed to overcome these difficulties showed that the efficiency of the extraction process was greatly improved by using:

- (i) anhydrous methanol as the extracting solvent;
- (ii) a methanol to oil ratio of 5 : 1 (v/w);
- (iii) sonication (*ca.* 5 min) and centrifugation (3000 rpm, 5 min) of the oil mixture prior to filtration.

These simple modifications resulted in reducing the number of extractions needed (and thus reducing the analysis time and the amount of solvent used) to quantitatively isolate the metalloporphyrin concentrate.

### *Purification & Separation of Ni- from VO-Porphyrin Complexes*

Adsorption column chromatography (on silica) is the method commonly used to separate the NiP from their VOP counterparts in the metalloporphyrin concentrate (Dunning and Moore 1957, Hodgson *et al.* 1963, Treibs 1934). However, thin layer chromatography can also be used for small separation (HajIbrahim 1978). Because this concentrate contained considerable amount (up to 50%) of polar substances which co-extracted with the metalloporphyrins, it was found advantageous to purify the metalloporphyrins prior to fractionation. In fact, purification became a necessity when studying oils with low petroporphyrin content. The purification process saved on the time, the amount of absorbent and solvents needed for the separation process, and on the amount of methane sulphonic acid used for the demetallation process (see below), thus rendering the isolation procedure more practical and less costly. The purification method developed in this study is outlined in Table 1. Alumina was selected over silica for the purification of metalloporphyrins concentrate because it gave better results. Of the various commercially available grades, Woelm alumina (Neutral, Act. I) gave the best results. On the other hand, silica gave better separation of NiP from VOP fractions. Several silica grades and solvent systems were tested for this separation. None performed better than the combination given in Table 1 except Davison silica gel No. 923. However, this silica is too expensive.

**Table 1.** Chromatographic Procedures for Petroporphyrin Separations.

Sample	Type of Separation	Chromatographic Column	Mobile Phase <sup>a</sup>	Results <sup>b</sup>
MPP-concentrate (Fig. 2, Step A)	Purification of MPP fraction	Woelm Alumina Neutral Act. I	Toluene CHCl <sub>3</sub> MeOH	i. Toluene removed yellow non-porphyrin material. ii. CHCl <sub>3</sub> removed red material containing the MPP. iii. MeOH removed dark non-porphyrin substances.
Purified MPP	Separation of NiP and VOP	Silica gel, 100-200 mesh	Hexane Toluene CHCl <sub>3</sub>	i. 30% toluene in hexane removed more of the yellow material. ii. NiP appeared in the hex-tol (1:1) eluent. iii. Tol/CHCl <sub>3</sub> (1:1) eluted the VOP fraction. iv. Dark impurities moved out with CHCl <sub>3</sub> /MeOH (1:1).
Crude demetallated petroporphyrins (Fig. 2, Step B)	Purification of FPP	Al <sub>2</sub> O <sub>3</sub> Act. II	Toluene CHCl <sub>3</sub>	i. Toluene (solvent front) removed yellow-green impurities. ii. The FPP (red band) was removed by subsequent elution with CHCl <sub>3</sub> . iii. MeOH removed green impurities remaining on top of the column.

- a. The polarity of the mobile phase was increased gradually (*ca.* by 10%) after component had eluted (as indicated by the color change of the eluant).
- b. Elution was monitored by uv/vis-spectroscopy. Fractions which had the same type spectra were then combined.

#### *Isolation of Free Base Petroporphyrins*

The inclusion of demetallation in the developed procedure was prompted by the experimental findings that:

- (i) the metal ions tend to contaminate the ion source in the mass spectrometer.

This complicated the analysis by mass spectrometry of a large number of samples, as it required frequent dismantling of the ion source for cleaning.

(ii) the metalloporphyrins were less amenable to HPLC separation than their demetallated analogues (see below).

Accordingly, HPLC analysis of the free base porphyrins provided better separation of the components for structure elucidation studies and more informative fingerprints for geochemical correlations.

The demetallation procedure adopted in the present work was modified from the method developed by Erdman (1965) using methane sulphonic acid. The main modification involved the application of the acid to the purified metalloporphyrin fraction rather than to the total crude oil. This helped reduce the quantity of acid (an expensive reagent) needed by up to 10-fold. It also simplified the recovery of the demetallated petroporphyrin, thereby making the method more quantitative. The demetallated porphyrins were further purified on the alumina column (Table 1) prior to MS and HPLC analyses.

#### *HPLC Separation and Analysis*

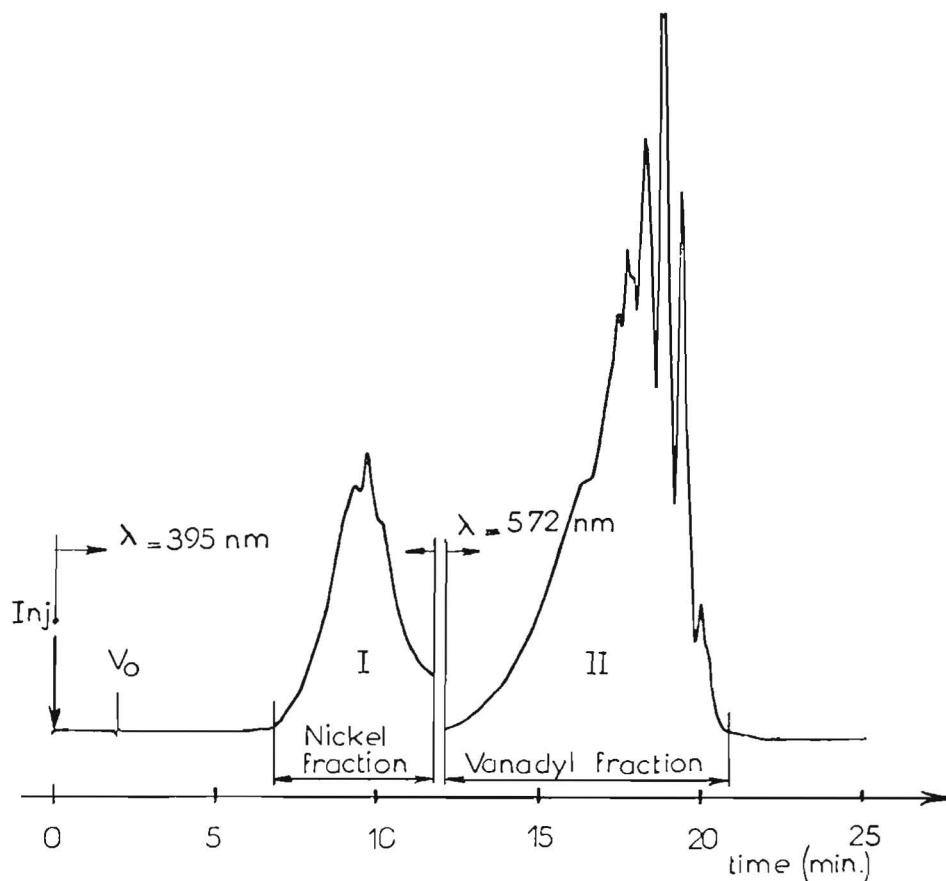
With its ability to combine chromatographic separation with detection and quantitation, its resolution and sensitivity, its speed and convenience, HPLC promises to be one of the most powerful techniques for petroporphyrin analysis. The development of HPLC for the analysis of fossil porphyrins has been reported previously (HajIbrahim 1981, HajIbrahim *et al.* 1978). The developed method can be applied to four areas of petroporphyrin studies:

- (i) separation of Ni- from VO-complexes,
- (ii) purification and/or checking the purity of synthetic porphyrins for spectral characterization by nmr, mass spectrometry, etc.,
- (iii) fractionation of petroporphyrin mixtures for structural studies, and
- (iv) fingerprinting of petroporphyrin distributions for geochemical correlation studies.

Figure 3 depicts the HPLC separation of Ni- from VO-complexed porphyrins isolated from a Venezuelan oil (Boscan field, Maracaibo Basin). The whole separation takes 20 min as compared to 1 to 2 hr when carried out on TLC or classical column chromatography. Furthermore, the HPLC method is more convenient and more sensitive.

Figure 4 shows an example of an HPLC trace (fingerprint) for the total demetallated porphyrin mixture from the same Boscan oil. The comparison of Fig. 3 with Fig. 4 clearly indicates the influence of the complexing metals (Ni and VO) on the chromatographic behaviour of the petroporphyrin compounds, hence the need to

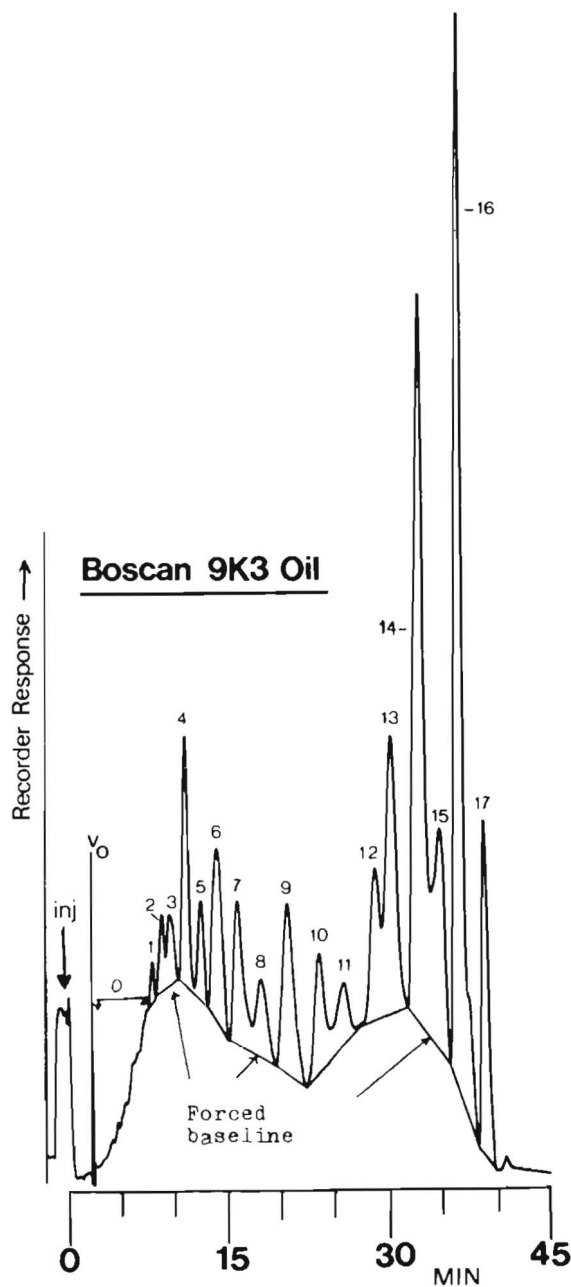




**Figure 3.** HPLC separation of Ni-complexed from VO-complexed porphyrins extracted from Boscan crude oil. For operating conditions, see Experimental.

demetallate prior to HPLC fingerprinting. The trapping of numbered peaks in Fig. 4 followed by mass spectral analysis revealed the following (Table 2):

1. Complete separation of the etio-type from the DPEP-type porphyrins, except for peak 11 (a  $C_{29}$  etio) which overlapped the DPEP-type region.
2. The presence of porphyrin isomers in petroleum. Thus, peaks 3 and 7 contained a  $C_{31}$  etio compound, peaks 4 and 9 contained a  $C_{30}$  etio, peaks 6 and 11 contained a  $C_{29}$  etio, peaks 10 and 17 contained a  $C_{30}$  DPEP, and so on (Table 2).
3. Poor resolution of the less polar etio-type compounds as indicated by the presence of a 'hump' in the first part of Fig. 4. However, this difficulty has been overcome by using reverse phase HPLC columns (HajIbrahim 1981).



**Figure 4.** HPLC record of the free base porphyrin mixture obtained from the Boscan oil. Numbered peaks were trapped then characterized by ms/c (see Table 2). For chromatographic conditions, see Experimental.

**Table 2.** Mass Spectral Characteristics of the Major Peaks in the Liquid Chromatogram of Demetallated Porphyrin Mixture (ex. Boscan Oil).

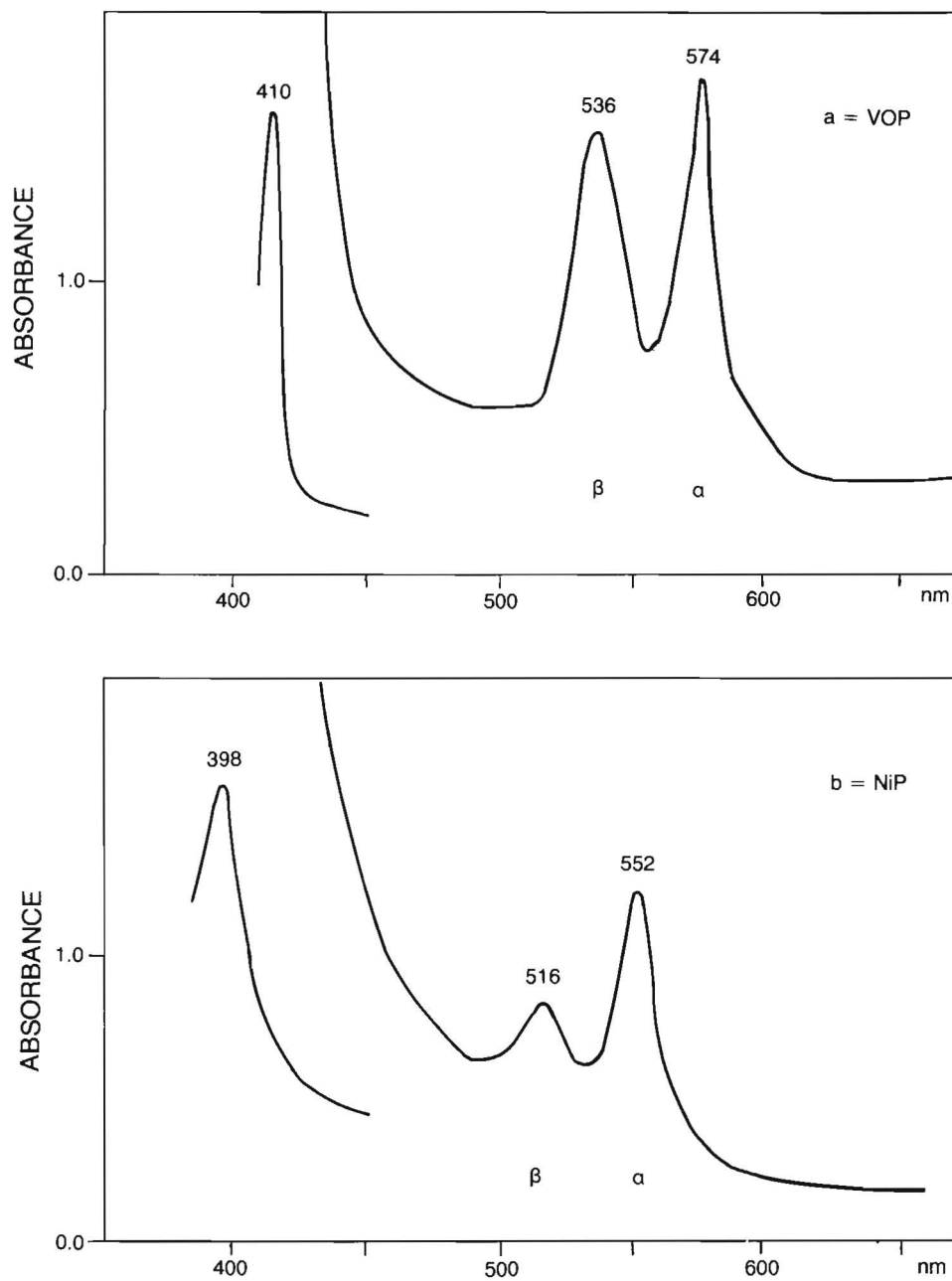
Peak No.	$t_R^a$ (min)	Petroporphyrin Molecular Ions <sup>b</sup>	
		Major component	Minor component(s) (%) <sup>c</sup>
0	2.5-7.5	C <sub>32</sub> E	C <sub>31</sub> E(89); C <sub>33</sub> E(53); C <sub>30</sub> E(51); C <sub>34</sub> E(22)
1	8.00	C <sub>32</sub> E	C <sub>30</sub> E(65); C <sub>29</sub> E(55); C <sub>33</sub> E(40)
2	9.00	C <sub>29</sub> E	C <sub>31</sub> E(79); C <sub>32</sub> E(72)
3	9.50	C <sub>31</sub> E	—
4	11.00	C <sub>30</sub> E	C <sub>28</sub> E(26)
5	12.50	C <sub>32</sub> E	—
6	14.25	C <sub>29</sub> E	—
7	16.00	C <sub>31</sub> E	—
8	18.00	C <sub>28</sub> E	—
9	20.75	C <sub>30</sub> E	—
10	23.75	C <sub>30</sub> D	—
11	26.25	C <sub>29</sub> E	—
12	29.00	C <sub>31</sub> D	C <sub>34</sub> D(74)
13	30.50	C <sub>29</sub> D	C <sub>33</sub> D(71); C <sub>30</sub> D(53)
14	33.00	C <sub>32</sub> D	—
15	35.00	C <sub>32</sub> D	C <sub>30</sub> D(60)
16	37.00	C <sub>31</sub> D	—
17	39.00	C <sub>30</sub> D	—

- a. Absolute retention time on Partisil-5 silica column using gradient elution. Reproducibility,  $\pm 1$  min.
- b. From the EI mass spectra of the trapped peaks expressed as carbon number; E = etio-type; D = DPEP-type.
- c. Relative to the major ion = 100. The presence of the same porphyrins in the mass spectra of adjacent peaks is likely due to overlapping of the peaks rather than different isomers.

### *Spectral Characterization of Petroporphyrins*

#### *I. Adsorption Spectrophotometry (uv/vis)*

Because of their aromaticity due to the conjugated system of their nuclei, porphyrin pigments possess a characteristic adsorption of the uv/vis region (*e.g.* 390-650 nm) of the spectrum. Absorption spectroscopy is, thus, a simple and fast method for the recognition of porphyrins in geological samples. The metallo-complexes are characterized by a two-banded visible spectrum between 510 and 580 nm, and a very strong peak (Soret band) in the near uv region, 390-410 nm (Fig. 5). The demetallated pigments show a four-banded visible spectrum between 490 and 650 nm in addition to the Soret band at about 400 nm (Fig. 6).



**Figure 5.** UV/VIS Spectra of nickel (Ni) and vanadyl (VO)-complexed porphyrin.



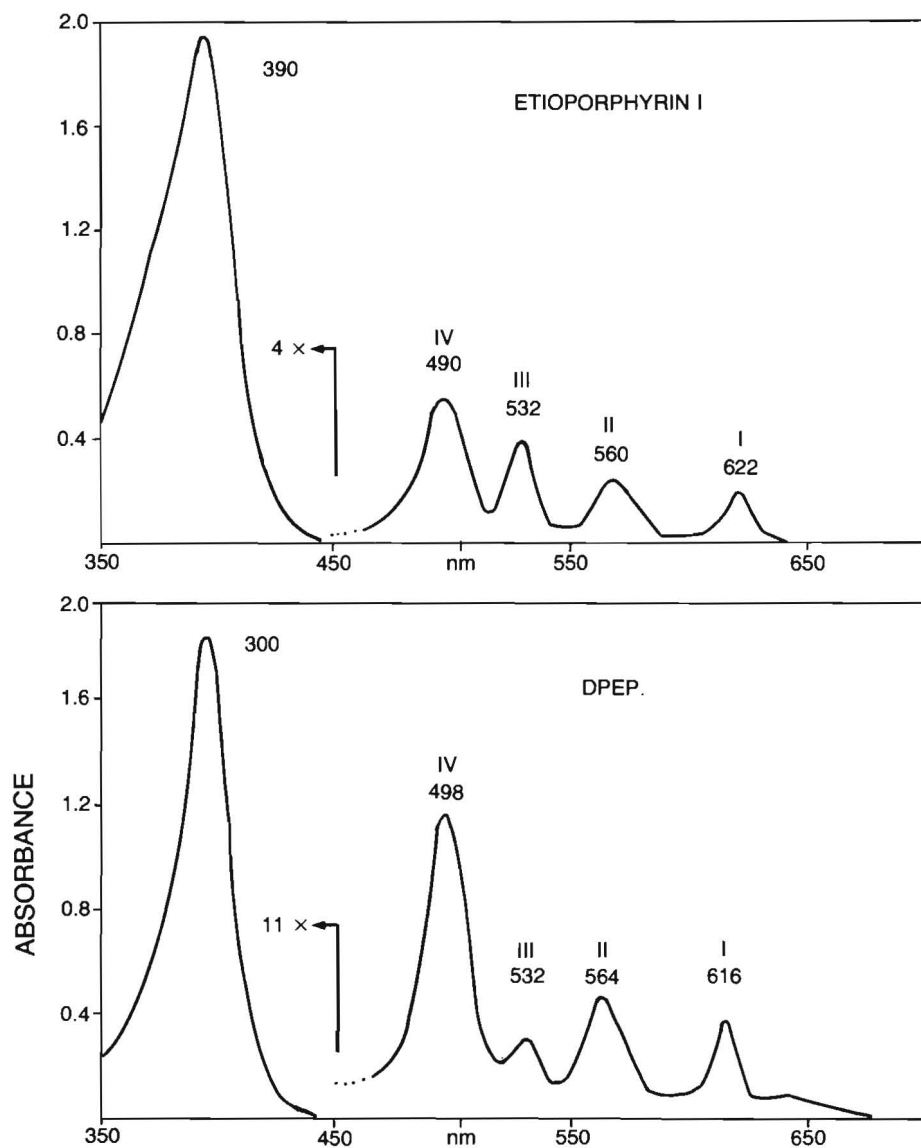


Figure 6. UV/VIS Spectra of free base (metal free) porphyrins.

VO-complexes can be distinguished from Ni-complexes by the position (wavelength) of their bands, whereas the DPEP-type and etio-type differ in the relative intensity of bands II and III.

The uv/vis spectrum is also used to estimate the porphyrins content of a given

oil/shale sample. This is commonly achieved by measuring the absorbance of the Soret band then applying Beer-Lambert's Law using an extinction coefficient  $\epsilon$  value for a standard porphyrin. However, there were two inherent approximations in the methods reported in the literature. First, different petroporphyrin classes (NiP, VOP, DPEP, etio) have different  $\epsilon$  values. Second, different geological samples (and thus the porphyrin mixtures isolated from them) have different compositions of these classes (HajIbrahim 1978). Thus, using the same  $\epsilon$  value for the determination of porphyrin contents for different oil/shale samples can produce erroneous results. In the present study, this problem was solved by using a weight average  $\epsilon$  value for each sample analyzed, based on its DPEP/etio ratio. The DPEP/ratio is determined from the mass spectrum (see below). The ratio is then used to calculate the weighed average  $\epsilon$  value, as shown,

$$\epsilon_{\text{average}} = \frac{\epsilon_{\text{DPEP}} \times \sum \frac{\text{DPEP}}{\text{etio}} + \epsilon_{\text{etio}}}{\sum \frac{\text{DPEP}}{\text{etio}} + 1}$$

$\epsilon_{\text{DPEP}}$  for authentic  $\text{C}_{32}$  compound and equals  $296 \times 10^3$ ,  $\epsilon_{\text{etio}}$  for authentic  $\text{C}_{32}$  etio compound and equals  $167 \times 10^3$  (HajIbrahim 1978). The calculated  $\epsilon$  value is then used to calculate the concentration of NiP and VOP using Beer-Lambert's law. The total porphyrin content ( $\mu\text{mole}$ ) is the summation of NiP and VOP concentration. In calculating the content in ppm, the yield in  $\mu\text{moles}$  is multiplied by the average molecular weight for the mixture in question, which was computed from  $\Sigma \text{MI}/\Sigma \text{I}$ , where M = mass and I = intensity of the molecular ions. Using the average weight gave more accurate results than using the molecular weight of the most abundant ion in the mass spectrum.

## II. Mass Spectrometry (ms)

The important features of a porphyrin electron impact (EI, 70 eV) spectrum are:

- (i) The molecular ion is always the base peak,
- (ii) Fragmentation of side-chains usually are of a benzylic nature,
- (iii) The presence of doubly charged ions.

The application of mass spectrometry to quantitative analysis of petroporphyrins as reported in the literature (Baker *et al.* 1967) has certain limitations. In these methods, the mass spectrum for a petroporphyrin mixture was recorded at a given probe temperature. However, it was found that the DPEP-type compounds are less volatile than the etio-type under the ion source conditions, *i.e.* etio-type molecular ions maximize at lower probe temperatures. Furthermore, the homologues within each type seemed to maximize at different probe temperatures.

As a results, the DPEP/etio ratio and the  $C_N$  maximum for a given petroporphyrin mixture recorded at a given probe temperature (Baker *et al.* 1967) are not likely to represent the 'true' value of these parameters and, thus, are of little use for geochemical correlation studies. An example of the dependence of the calculated DPEP/etio ratio on probe temperature is presented in Fig. 7, whereas Fig. 8 shows the variation of the relative intensity of petroporphyrin molecular ion (of the same type) with probe temperature. Thus, it was necessary to analyze the petroporphyrin mixtures using probe temperature programming. The spectra were then recorded by averaging (by computer) all the scans showing petroporphyrin molecular ions.

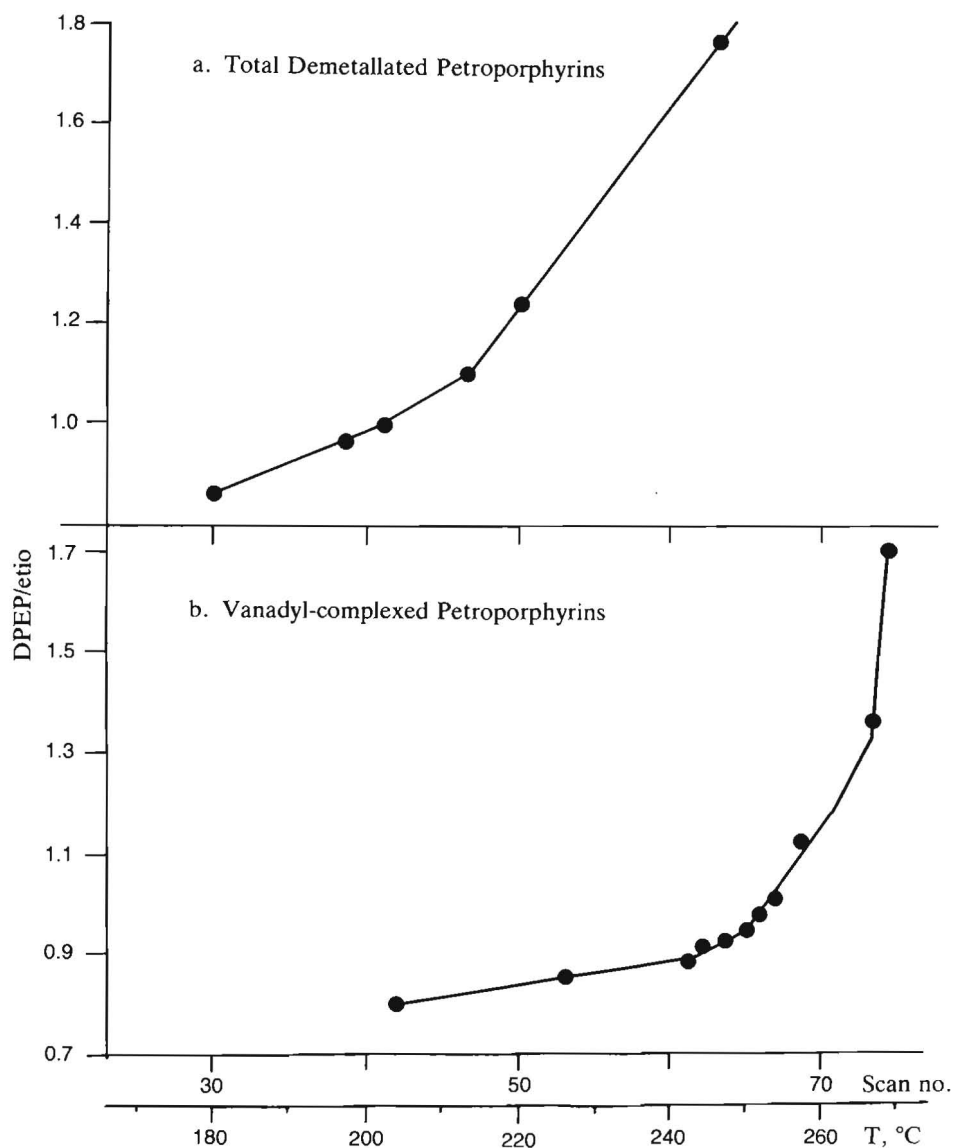
#### *Applied Aspects of the Developed Analytical Techniques*

In the development of a new analytical technique for correlation studies, in which a large number of samples are to be analyzed, it is essential that these techniques be simple, quantitative and reproducible. That the methods developed in this study are simple and quantitative was discussed above.

The reproducibility of the extraction and fractionation procedures (Steps A and B, respectively, Fig. 2) was demonstrated by the almost identical values of the MPP content and NiP/VOP ratio obtained from repeated extractions for a selected number of oil/shale samples. The reproducibility of the demetallation procedure (Step C, Fig. 2) and mass spectrometric analysis was indicated by the similarity of mass spectrally derived data (DPEP/etio ratio,  $C_N$  range and maxima) obtained from duplicate demetallations of either aliquots of the same MPP concentrate or MPP from separate extractions. Undoubtedly, the best evidence in support of the reproducibility of the overall procedure as well as its applicability to geochemical correlation problems was observed from the consistency and coherence of the conclusions based on the petroporphyrin data and those based on other well established geochemical data for a wide variety of geological samples analyzed by this procedure. Case studies illustrating the application of the developed analytical techniques in areas of structure elucidation of petroporphyrin, oil-source rock correlations and identification of oil pollutants were discussed elsewhere (Eglinton *et al.* 1980, HajIbrahim 1980; HajIbrahim 1982a; HajIbrahim 1982b; HajIbrahim 1982c; HajIbrahim *et al.* 1983).

#### **Conclusion**

The methods reported here for petroporphyrins analyses enable the determination of several porphyrin characteristics which could be used as geochemical indicators. The HPLC technique also allows for the separation of single porphyrins, and thus should facilitate studies concerned with determining the structure of these compounds. The entire analysis procedure is practical, quantitative and reproducible. It is equally applicable to studying oil or shale samples containing as little as a few ppm or as high as thousands ppm porphyrins.

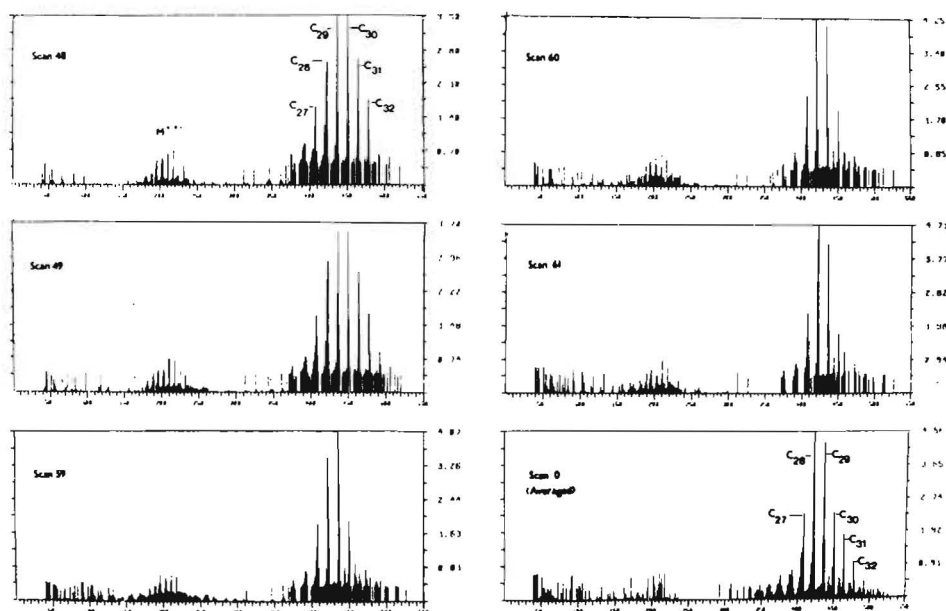


**Figure 7.** Variation of the DPEP/etio ratio of the Boscan porphyrins with the probe temperature: A) demetallated mixture; B) vanadyl-complexed fraction. DPEP/etio ratio was calculated from:

$$\frac{\sum I_{\text{DPEP}}}{\sum I_{\text{etio}}}, I = \text{molecular ion intensity.}$$

Probe temperature was recorded by visual reading of the thermocouple meter ( $\pm 3^\circ\text{C}$ ).





**Figure 8.** Variation of the relative intensity of demetallated petroporphyrins molecular ions with scan number (probe temperature). The porphyrins were obtained from a Jurassic crude oil (Saudi Arabia).

### References

- Baker, E.W., Yen, T.F., Dickie, J.P., Rhodes, R.E., and Clark, L.F.** (1967) Mass Spectrometry of Porphyrins. II. Characterization of Petroporphyrins, *J. Am. chem. Soc.* **89** : 3631.
- Dean, R.A. and Whitehead, E.V.** (1963) The Composition of High Boiling Petroleum Distillates and Residues, *Proc. 6th World Petroleum Congress, Frankfurt*, Section V, 261.
- Dunning, H.M. and Moore, J.W.** (1957) Porphyrin Research and Origin of Petroleum, *Bull. Am. Ass. Petrol. Geol.* **41** : 2403-2412.
- Eglinton, G., HajIbrahim, S.K., Maxwell, J.R. and Quirke, J.M.E.** (1980) Petroporphyrins: Structural Elucidation and the Application of HPLC Fingerprinting to Geochemical Problems, *Adv. Org. Geochem.*, **Maxwell, J.R. and Douglas, A.G. (eds)** Pergamon, Oxford, pp. 193-203.
- Erdman, J.G.** (1965) Process for Removing Porphyrin Metallocomplexes from Heavy Oils, *U.S. Patent* 3, 190, 829.
- HajIbrahim S.K.** (1978) *Application of Petroporphyrins to the Maturation, Migration and Origin of Crude Oils*, Ph.D. Thesis, University of Bristol, 276 p.
- HajIbrahim, S.K.** (1980) Geochemical Aspects of Metalloporphyrins in Petroleum, *Proc. 3rd Arab Chemical Research Seminar, Organized by UNESCO*, March 24-27, Jeddah, p. 21.

- HajIbrahim, S.K.** (1981) Development of HPLC for Fractionation and Fingerprinting of Petroleum Porphyrins, *J. Liq. Chrom.* **4** : 749-764. (Presented in part at the 13th International Symposium on Chromatography, June 30-July 4, Cannes.)
- HajIbrahim, S.K.** (1982a) Fingerprinting of Crude Oils for Pollution Control, *Int. J. environ. anal. Chem.* **12** : 123-130. (Presented at the 2nd International Congress on Analytical Techniques in Environmental Chemistry, Nov. 23-25, 1981, Barcelona.)
- HajIbrahim, S.K.** (1982b) An Organic Geochemical Approach to Oil Exploration and Environmental Pollution Studies, *Proceedings, Nature to Man's Rescue Seminar*, Jan. 10-15, Riyadh.
- HajIbrahim, S.K.** (1982c) The Geochemistry of Coal vs Shale Porphyrins, *Preprints*, Division of Geochemistry, American Chemical Society, Las Vegas, March 28-April 2.
- HajIbrahim, S.K., Quirke, J.M.E. and Eglinton, G.** (1981) Structurally Related Porphyrin Series in Bitumens, Shales and Petroleums, *Chem. Geol.* **32** : 173-188.
- HajIbrahim, S.K. and Okla, S.** (1983) Oil-Oil and Oil-Source Rock Correlations in the Gulf of Suez, Egypt, Accepted for presentation at the *AAPG 68th Annual Convention*, April 17-20, Dallas.
- HajIbrahim, S.K., Tibbetts, P.J.C., Watts, C.D., Maxwell, J.R., Eglinton, G., Colin, H. and Guiochon, G.** (1978) Analysis of Carotenoids and Porphyrins of Geochemical Interest by High Performance Liquid Chromatography (HPLC), *Analyt. Chem.* **50** : 549.
- Hodgson, G.W., Baker, B.L. and Peak, E.** (1963) The Origin of Petroleum Porphyrins, *Athabasca Oil Sands* (ed. K.A. Clark), Res. Council, Alberta, Inform. Series, **45**, 75.
- Treibs, A.** (1936) Chlorophyll and Haminderivate in Organisschen Mineralstoffen, *Angew. Chem.* **49** : 682-686.

(Received 28/07/1982;  
in revised form 09/02/1983)

## التطورات الحديثة في تحليل مركبات البورفيرين

صالح خليل الحاج إبراهيم  
قسم الكيمياء - كلية العلوم - جامعة الملك سعود  
الرياض - المملكة العربية السعودية

يختص هذا البحث بوصف طريقة حديثة لفصل وتحليل مركبات البورفيرين المستخلصة من عينات جيولوجية . وتستخدم في هذه الطريقة عدة وسائل تحليل آلي منها التحليل اللوني السائل والتحليل الكتلي المبرمج والتحليل الطيفي ، والطريقة غير معقدة وسريعة وعليه فإنها سوف تسهل دراسة التركيب البنائي لمركبات البورفيرين .

وقد تم تطبيق هذه الطريقة لدراسة مركبات البورفيرين المستخلصة من عينات بترول وصخور مختلفة من منطقة الخليج العربي وأوروبا وأمريكا الشمالية وفنزويلا وإندونيسيا . وأظهرت النتائج أهمية هذه الطريقة في تصنيف البترول حسب مصدره بحيث يمكن الاستفادة منها كوسيلة جديدة في التنقيب عن البترول وفي التعرف على مصدر تلوث البيئة بالنفط .