METALLOPORPHYRINS IN EGYPTIAN OIL SHALES FROM RED SEA AREA: UV-VISIBLE SPECTROMETRY AND HPLC FINGERPRINTING

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ABSTRACT

Metalloporphyrins were extracted from asphaltene and maltene fractions of some Egyptian oil shales, which were assembled from the main producing mines (Abu-Shegeili, El-Beida, El-Nakheil and Abu-Tundub) in Red Sea area. The extraction was done using adsorption column chromatography followed by purification and separation of the metalloporphyrins from each other by means of TLC. The presence of nickel, iron, and vanadyl porphyrins was monitored by means of UV-visible spectrometry and HPLC. It was found that maltene fractions contain Ni and VO porphyrins whereas asphaltene fractions contain Fe and VO porphyrins. Metalloporphyrins were not detected in maltene or asphaltene fractions of Abu-Shegeili oil shale. UV-visible results indicated that metalloporphyrins could be a mixture of Etio and DPEP types. It was pointed out that UV-visible spectrometry can not differentiate between Ni porphyrins and Fe porphyrins. HPLC could be used as a successful tool for fingerprinting VO, Ni and Fe porphyrins since it characterized Fe porphyrins from Ni chelating complexes.

INTRODUCTION

Oil shale is defined as a rock yielding oil in a commercial amount upon pyrolysis. First, preliminary estimation of the oil shale potential in the Red Sea area indicated that a reserve of some billions bbl of oil exists in place [Truger, (1984)]. The organic fraction is mainly insoluble solid material (kerogen) and bitumen which is soluble in the most common organic solvents such as benzene and methanol [Turam et al., (1985)].

Identification of biomarkers, particularly Metalloporphyrins, has become a valuable tool in the determination of the origin and maturity of the organic matter **[Doukkali et al., (2002)]**. The most studied metal complexes associated with petroleum and its source rocks are nickel and vanadyl porphyrins. But shale oils are generally known to have much lower concentrations of Ni and V and to have potentially different metals in the porphyrins ring such as Fe **[Albert et al., (1995)]**.

Occurrence and distribution of metalloporphyrins have been studied in some Egyptian oil shale samples from Red Sea area. Five oil shale samples were assembled from the main producing mines (Abu-Shigeili, El-Beida, El-Nakheil and Abu-Tundub). The studied oil shales differ in geological age, depositional environment, source, and location **[El-Sabagh et al., (1998); El-Sabagh and Basta, (1998); El-Sabagh et al., (2000)]**. Figure 1 illustrates the location of oil shales in Upper Cretaceous sediments that are rich with organic materials **[Ganz et al., (1987)]**. Location, thickness, formation and percentage of the total organic carbon (TOC) of the samples are given in Table 1.

Table (1): Location and Identification of the Oil Shale Samples.

Sample No	Bed name	Location thickness, m	Formation	TOC%
1	Abu-Shigeili	5-10	Duwi phosphate	2.5
2	El-Beida	5-15	Duwi phosphate	5.0
3	El-Nakheil	5-15	Duwi phosphate	32.4
4	Abu-Tundub-I	10-20	Duwi phosphate	24.7
5	Abu-Tundub-II	10-20	Duwi phosphate	26.3

EXPERIMENTAL

Samples

One kg of an oil shale sample was grinned in a ball mill and sieved. A portion of < 200 mesh was chosen for different analysis procedures and extraction processes after drying at 100°C. Bitumen was extracted in a Soxhelt using benzene/methanol (70:30 vol/vol) for ~ 72h. Then, the solvent was removed by means of rotary evaporation at mild conditions. Asphaltene from the extracted bitumen was precipitated according to IP 143 standard procedure. Metalloporphyrins were extracted from deasphalted (maltene) and asphaltene fractions by adsorption column chromatographic methods.
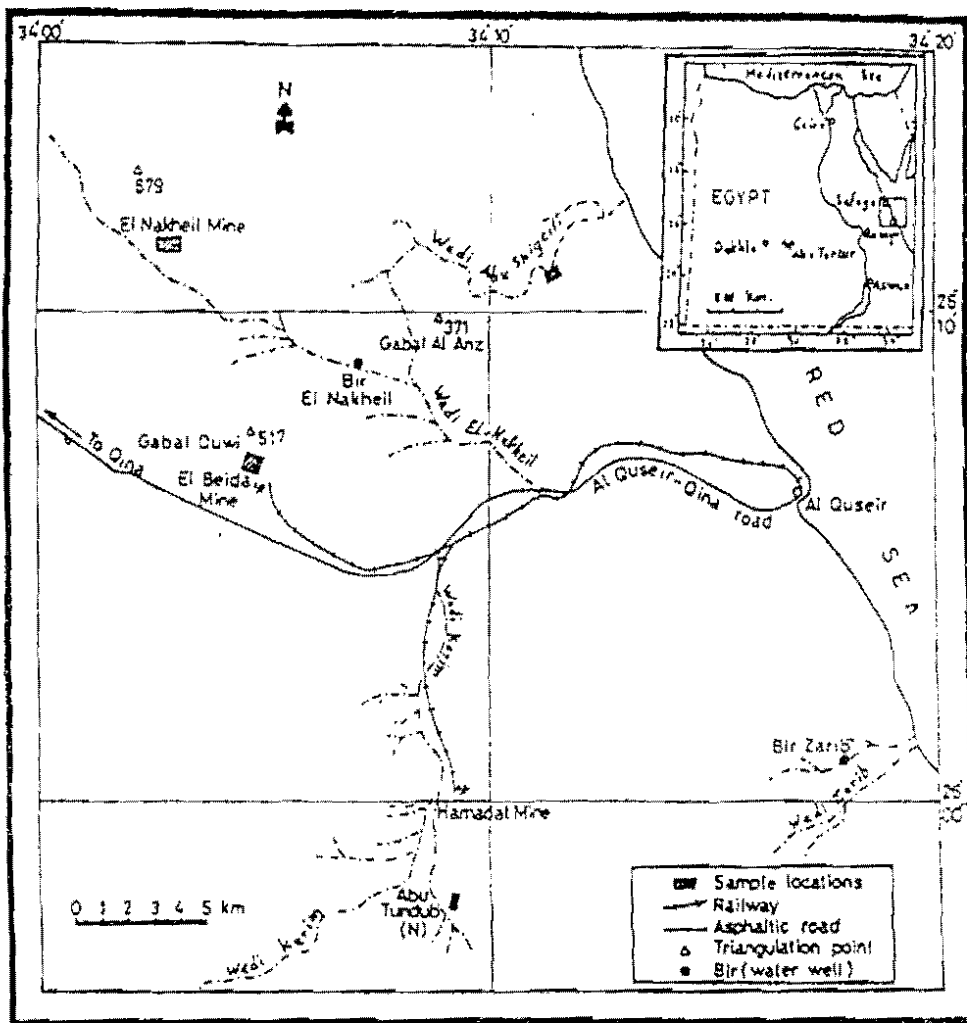
Fig. (1): The location map of the oil shale samples.

Isolation of Metalloporphyrins

Following the Scheme, shown in Fig. 2, two successive chromatographic columns were used for such extraction. One of them was packed with alumina (BDH, Brockman activity II) activated at 300 °C for 24 h and the other was packed with silica gel (Merck 80-200 mesh) activated at 200°C for 4h. Nickel, Iron and vanadyl porphyrins were isolated via elution using solvents of different polarities. These solvents were n- hexane (fraction 1), n- hexane/toluene having 1:1 vol/vol (fraction 2), and toluene (fraction 3). Then, gradient elution with methylene chloride in toluene, viz., 1:4, 2:3, 3:2, 4:1, and pure methylene chloride gave fractions 4,5,6,7 and 8, respectively. The presence of nickel, iron and vanadyl porphyrins in each fraction was monitored by means of UV-visible spectrometry.

For thin layer chromatography (TLC), silica gel (20 x 20 cm) plates, pre-activated at 110 °C for 1 h, were used. The plate was developed in a conventional jar containing hexane-methylene chloride (1:1) until the solvent front was 2 cm from the top end of the plate. The four zones observed were scrapped, dissolved in methylene chloride, and analyzed by UV-visible spectrometry.

Instrumental Technique

The UV-visible spectroscopic analysis was performed on a double beam Perkin-Elmer model 558 spectrophotometer using methylene chloride as a solvent. The samples were scanned from 650 to 350 nm.

The extracted metalloporphyrins were fingerprinted by means of high performance liquid chromatography (HPLC). The instrument used was Waters Associate Milford, MA equipped with quaternary gradient pump Waters 600, auto sampler Waters 717 plus, and detector dual λ absorbance model 2487. The column used was RP C_{18} (4.6 mm x 250 mm x 5 μm). The solvent system was methanol/acetonitrile/water (45:45:10). The samples were dissolved in methylene chloride and loaded to the injection loop by means of a 10-μL syringe. Detection (UV-visible) was monitored at 405 nm.
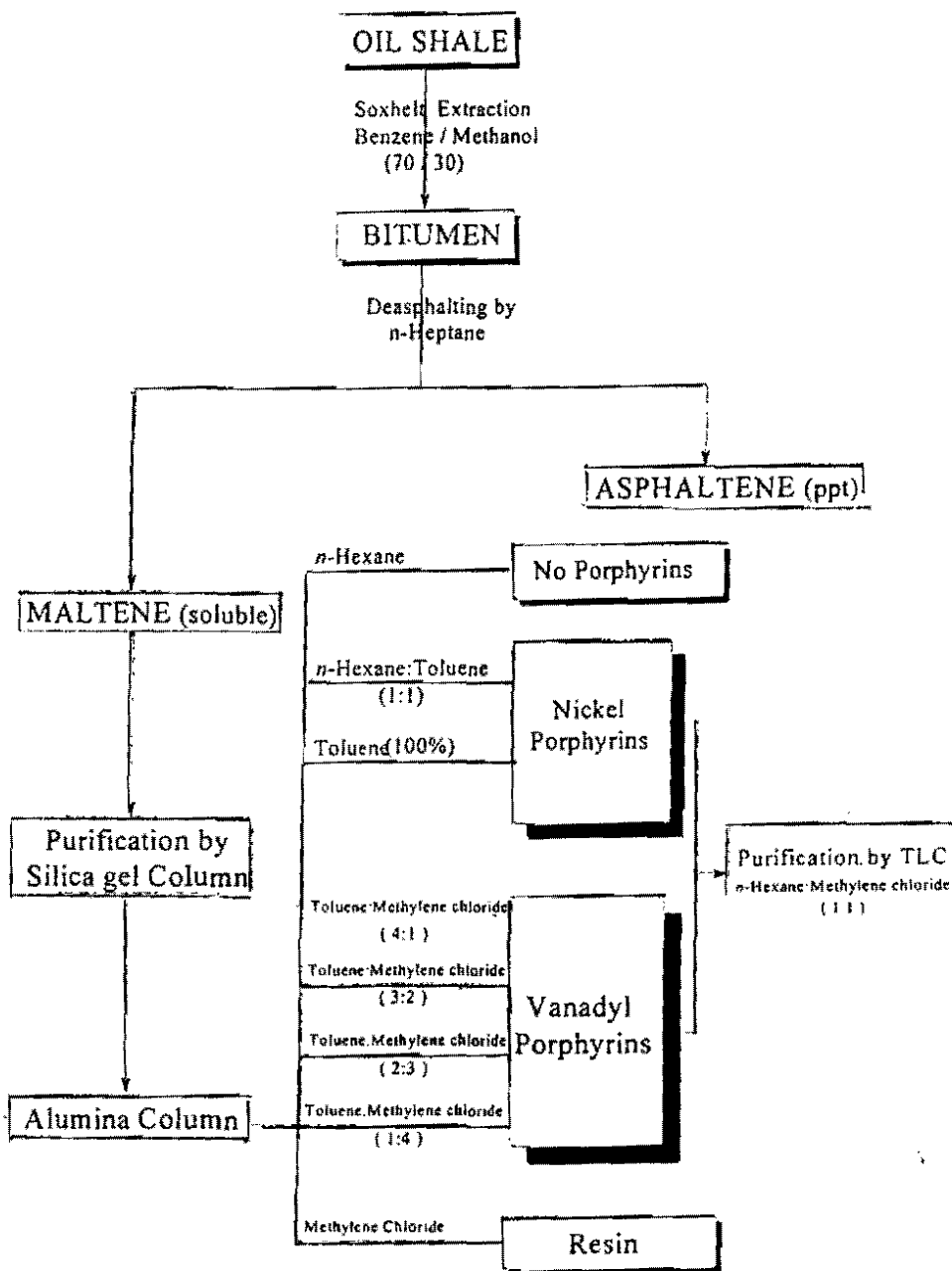
OIL SHALE

Soxhelt Extraction
Benzene / Methanol
(70 / 30)

BITUMEN

Deasphalting by
n-Heptane

ASPHALTENE (ppt)

n-Hexane → No Porphyrins

MALTENE (soluble)

n-Hexane:Toluene
(1:1)

Toluene(100%)

Nickel
Porphyrins

Purification by
Silica gel Column

Toluene:Methylene chloride
(4:1)

Toluene:Methylene chloride
(3:2)

Toluene.Methylene chloride
(2:3)

Vanadyl
Porphyrins

Purification. by TLC
n-Hexane:Methylene chloride
(1:1)

Alumina Column

Toluene.Methylene chloride
(1:4)

Methylene Chloride → Resin

Fig. (2): Separation of Ni/Fe and VO porphyrins.

RESULTS AND DISCUSSION

Preliminary UV-visible spectrometric analysis of the bitumens and their asphaltenes showed no characteristic absorption peaks for nickel or vanadyl porphyrins. This is due to the nature of the matrix of the sample that masks the absorption of metalloporphyrins [**Ali *et al.*, (1993)**]. Therefore, separation of metalloporphyrins from the deasphalted fraction and asphaltenes should be carried out prior the adopted spectrometric investigations.

Isolation of Metalloporphyrins

Metalloporphyrins were extracted from asphaltene and deasphalted fraction of bitumen (maltene) using adsorption column chromatography according to the Scheme given in Fig. 2. Eight fractions containing nickel or iron and vanadyl porphyrins have been obtained by a gradient elution using n-hexane-toluene, methylene chloride-toluene and methylene chloride solvent systems of different polarities.

Chromatographic column, containing silica gel as packing material for the asphaltene fraction of El-Beida oil shale, exhibited brown, dark red, red and pink colored zones. The brownish zone is due to the resin materials, which accompanied with asphaltene. Based on informations stated in literature [**Maxwell et al., (1979)**], the zones of dark red and red colors are due to vanadyl porphyrins. The zone of pink color may reflect the separation of iron porphyrins. However, ICP spectrometry of bitumens showed considerable amounts of Fe as compared with those of Ni and V (Table 2). This may reflect the occurrence of Fe porphyrins in asphaltene fractions.

Table (2): Concentration of Ni, V and Fe in Bitumen Fraction of the Oil Shales.

Sample No	Bed name	Ni-Content, ppm	V-Content, ppm	Fe-Content, ppm	α/β	
					VO-Porphyrins	Ni-Porphyrins
1	Abu-Shigeili	265	19	630	--	--
2	El-Beida	455	6170	1731	1.33	2.21
3	El-Nakheil	322	1250	262	1.24	2.26
4	Abu-Tundub-I	253	111	1651	1.21	2.23
5	Abu-Tundub-II	198	1074	1199	1.22	2.21

For maltene fraction, the column showed three colored zones of brown, red and yellow. These zones are due to resins, vanadyl porphyrins and nickel porphyrins. Based on these primarily observations, it can be suggested that asphaltene fractions contain Fe and VO porphyrins whereas, maltene fractions contain Ni and VO porphyrins. This is with the exception of Abu-Shigeili oil shale where metalloporphyrins were not observed in its maltene or asphaltene fractions. The presence of nickel and vanadyl porphyrins has been monitored in each fraction by means of UV-visible spectrometry. However, it is known that the spectra of nickel and iron porphyrins are almost identical [**Moore and Dunning, (1955)**].

The extracted metalloporphyrins were subjected to purification and further separation of the chelating porphyrins from each other by means of thin layer chromatography (TLC). In the case of asphaltene fraction, three bands were observed on a silica gel plate at R_f values of 0.27-0.60, 0.15-0.27, and 0.00-0.15. The first bands at (R_f) values of 0.27-0.60 showed a pink color, which is characteristic of iron porphyrins. The red band of vanadyl porphyrins appears at R_f 0.15-0.27. Iron and vanadyl porphyrins zones were removed, extracted with methylene chloride, and stored for further investigations. For the maltene fraction, the isolated metalloporphyrins were found to be nickel and vanadyl porphyrins.

Metalloporphyrins were not observed in maltene or asphaltene fractions of Abu-Shegeili oil shale. This could be linked directly with the higher maturation level of the deposited organic matter (kerogen) as compared with that of the other oil shales. In the previous work [**El-Sabagh et al., (2000)**], it was reported that the maturation of the kerogen decreases in the order of Abu-Shigeili > El-Beida > El-Nakheil > Abu-Tundub.

UV-Visible Spectrometry of Metalloporphyrins

Representative models UV-visible spectra of the extracted nickel, iron and vanadyl porphyrins are shown in Fig.3. For nickel or Fe porphyrins, the spectrum revealed a sort band at 390 nm and two characteristics absorption peaks, assigned as α and β, at 545 nm and 515 nm. The spectrum of vanadyl porphyrins, shown in Fig. 3a, revealed a sort band at 405 nm and two characteristics peaks (α and β) at 565nm and 525 nm. In some cases of vanadyl porphyrins, an absorption peak at 590 nm appeared in a low relative intensity as compared to the

characteristic peaks. These results are in agreement with those reported in literature **[Baker and Palmer, (1978) and Quirke *et al.*, (1980)]**.

The heights of α and β peaks (h_1 and h_2), taken as the difference between peak maximum and the two peak minima, are used for the calculation of α/β ratio. The α/β is a ratio between the heights of the two characteristics absorption peaks α and β (h_1 and h_2). Different types of metalloporphyrins, which may occur in geo-sphere, are illustrated in Fig. 4. The main two types are etioporphyrins and deoxophylloerthroetioporphyrin (DPEP). It was stated in literature **[Baker and Palmer, (1978)]** that nickel etio porphyrins reveal the two bands (α and β) with a α/β ratio of about 3 whereas nickel DPEP has a lower α/β ratio of 2. Results of α/β ratio of nickel porphyrins revealed the intermediate values (2.21-2.26), which are very close to that of Ni DPEP. The values of α/β ratio of Fe porphyrins ranged between 2.40 and 2.79.

Baker and Palmer (1978) stated that α/β ratios of vanadyl etio porphyrins and vanadyl DPEP were 2.0 and 1.3, respectively. The values of α/β ratio are in the range of 1.22-1.58. Vanadyl porphyrins extracted from maltene fraction exhibit lower values (1.21-1.33) as compared to those separated from asphaltene. This may be due to the predominance of vanadyl DPEP type in maltene fractions. It may be concluded that the vanadyl porphyrins present in the asphaltenes could be composed of different types of etio and DPEP.

High Performance Liquid Chromatography (HPLC)

The HPLC chromatograms of VO, Ni and Fe porphyrins, extracted from TLC plates, are shown in Fig.5. For instance, the three chromatograms are completely different. Vanadyl porphyrins (Fig. 5-a) reveal peaks at a retention time (RT) ranging between 13 min. and 74 min. The chromatogram shows the maximum at 54 min. Figure 5-b shows peaks in range from 40 min. to 111 min. of retention time. The chromatogram exhibits strongest peak at 84 min. With respect to Fe porphyrins (Fig. 5-c), the peaks are eluted at higher retention times as compared with the chromatograms of vanadyl and nickel porphyrins. The chromatogram of Fe porphyrins shows peaks at (RT) range of 79-138 min. The maximum concentration of Fe porphyrins appears at RT = 133 min.
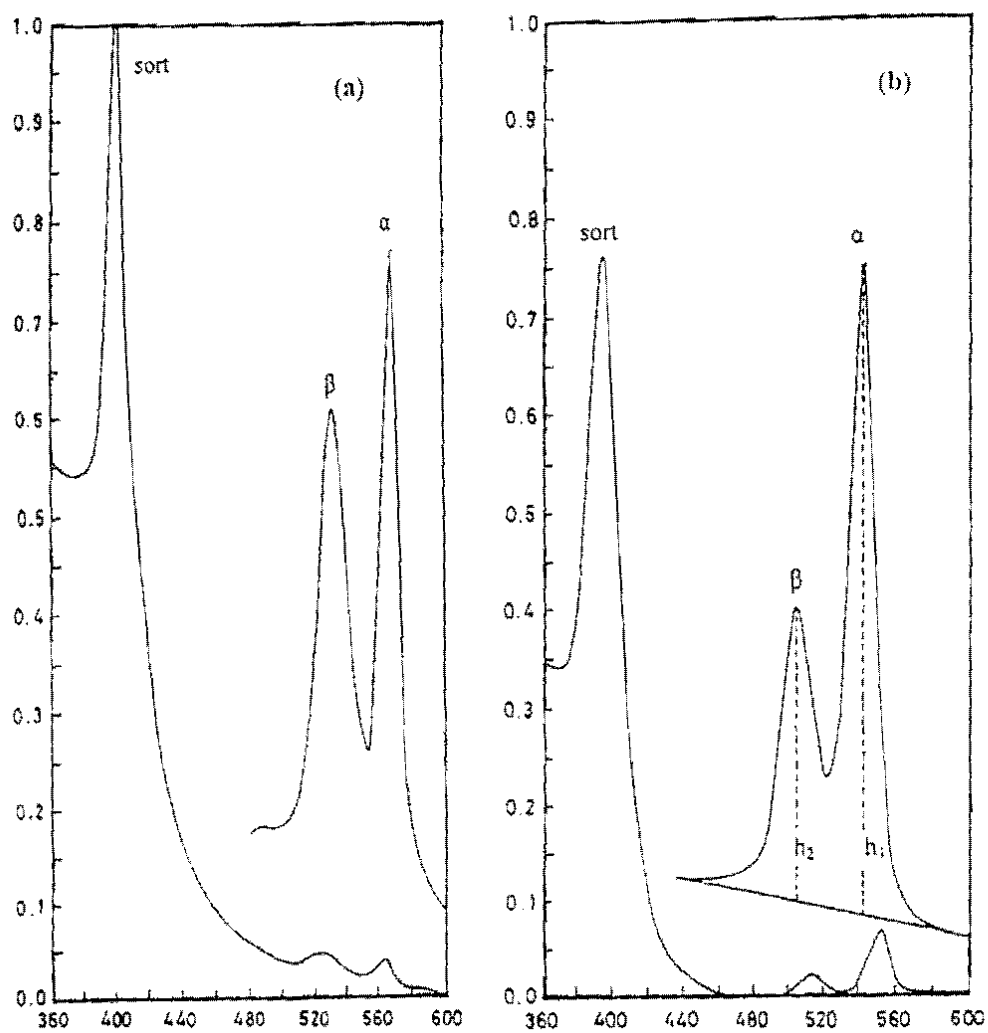
Fig. (3): UV-visible spectra of (a) VO porphyrins extracted from asphaltene of El-Nakheil oil shale (b) NI porphyrins extracted from maltene of El-Beida oil shale.

Etio   DPEP
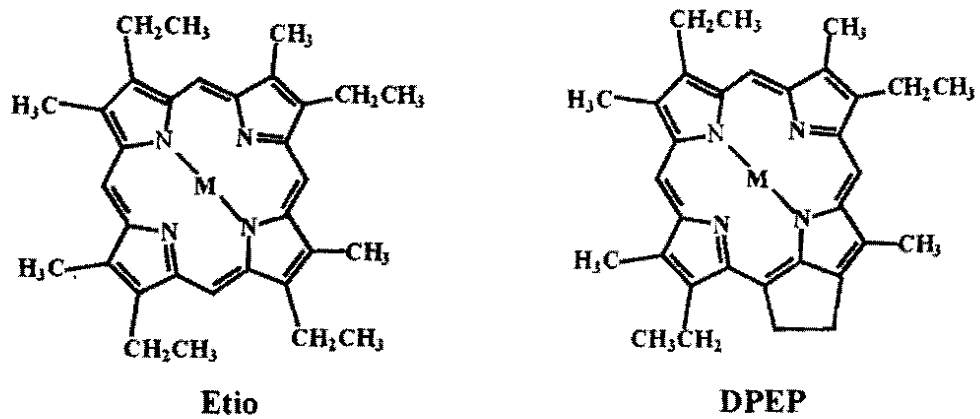
Fig. 4: Structures of Different Types of Metalloporphyrins
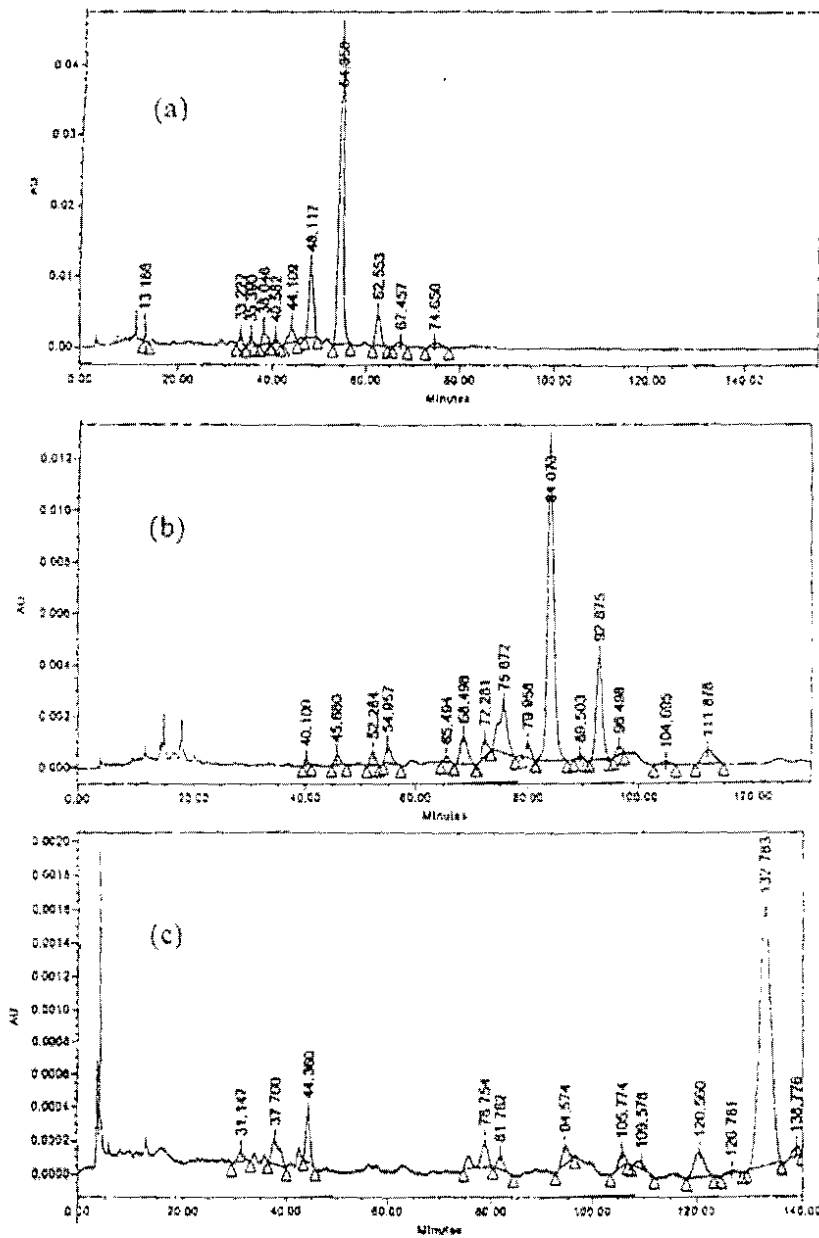
Fig. (5): HPLC chromatograms of (a) VO porphyrins, (b) Ni porphyrins, (c) Fe porphyrins.

It was pointed out that UV-visible spectrometry cannot differentiate between Ni porphyrins and Fe porphyrins. Based on these findings, HPLC technique could be used as a successful tool to characterize Fe porphyrins from Ni chelating complexes.

CONCLUSIONS

From the obtained results one may conclude that the adopted chromatographic techniques, used for the extraction and separation of metalloporphyrins, have the following advantages:

- Metalloporphyrins were obtained in a higher purity as compared with those obtained in the previous work **[El-Sabagh, (1998); Ali et al., (1993); and Haj-Ibrahim, (1982)]**.
- Thin layer chromatography has not only been used for purification of metalloporphyrins but also in separation of nickel, iron porphyrins and vanadyl porphyrins. This is due to the solvent system (methylene chloride / n-hexane) used for such separation.
- HPLC technique could be used as a successful tool for fingerprinting the metalloporphyrins.

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البورفيرينات الفلزية في الصخور الزيتية من منطقة البحر الاحمر: مطيافية الاشعة الفوق بنفسجية - المرئية - كروماتوجرافيا السائل عالى الاداء

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تـم استخلاص البورفيرينات من اجزاء المالتين والاسفلتين لبعض الصخور الزيتية المصـرية ، الـتى تـم تجميعها من المناجم الرئيسية المنتجة (ابو شجيلة - البيضا - النخيل وابوتـندب) فـى منطقة البحر الاحمر. تم الاستخلاص والتنقية باستخدام عمود الادمصاص الكروماتوجـرافى وكذلك تم فصل البورفيرينات الفلزية عن بعضها باستخدام كروماتوجرافيا الطبقة الرقيقة تم تحديد وجود كل من بورفيرينات النيكل ،الحديد ،الفاناديل بواسطة مطيافيه الاشـعة الفوق بنفسجية - المرئية وكروماتوجرافيا السائل عالى الاداء. ووجد ان اجزاء المالتين تحتوى على ورفيرينات النيكل والفاناديل بينما الاجزاء الاسفلتينية كانت تحتوى على بورفيريـنات الحديـد والفاناديل . لم تظهر صخور ابو شجيلة وجود البورفيرينات الفلزية فى اى من اجزاء المالتين أو الاسفلتين . بينت نتائج مطيافيه الاشعة الفوق بنفسجية - المرئية أن البورفيريـنات الفلـزية توجـد فى صورة مخلوط من انواع DPEP, Etio . وقد اشير ان مطيافـية الاشـعة الفـوق بنفسجية - المرئية لم تفرق بين بورفيرينات الحديد وبورفيرينات النـيكل . وكذلك استخدمت تقنية كروماتوجرافيا السائل عالى الاداء بنجاح فى تحديد كل من بورفيرينات الفاناديل والحديد ولنيكل حيث ميزت بورفيرينات الحديد من متراكبات النيكل .