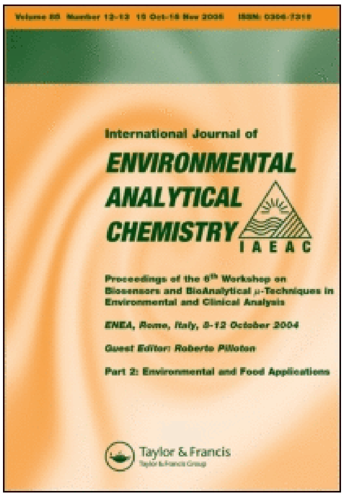

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Fingerprinting of Crude Oils for Pollution Control†

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Total, demetallated porphyrins from selected "export" and "weathered" crude oils were analyzed by high performance liquid chromatography (HPLC). The aim was to study the effect, if any, of oil weathering processes on the type and distribution of these compounds and hence, assess the applicability of their HPLC fingerprints in the area of pollution control. The results revealed that petroporphyrins are not readily susceptible to natural weathering processes and that their HPLC fingerprints may be applied to crude oil classification and could supplement other techniques of identifying oil pollutants.

KEY WORDS: Petroporphyrins; HPLC; fingerprinting of oil pollutants; pollution control.

INTRODUCTION

Nickel and vanadyl porphyrins are common trace components of crude oils, ranging in concentration from a few parts per million (ppm) in light crudes to hundreds ppm in heavy oils. Lab simulation experiments‡ and field observations§ have shown that porphyrins are less volatile, less soluble in sea water and more resistant to weathering processes (bacterial degradation, water washing and oxidation) than the hydrocarbon fraction of the oil. Thus, they should prove more useful as "passive tags" for the recognition of oil pollutants. The HPLC methods developed for petroporphyrins analysis[1] provided a new analytical technique for oil

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†Presented at the Workshop on the Chemistry and Analysis of Hydrocarbons in the Environment, Barcelona, November 1981.

‡Artificial weathering of a Kuwaiti crude oil was simulated in the laboratory (Warren Spring Laboratory, England) using sea water in a constructed tank for a duration of 100 days.

§Tar residue believed to be due to oil spills over the past five years was collected from the shore of an uninhabited island in the Arabian Gulf. Some of the specimens collected were offshore under a few feet of water, others were exposed on land.

fingerprinting. This work discusses, through representative examples, the applicability of these methods to crude oil classification and recognition for pollution control.

EXPERIMENTAL

Isolation of petroporphyrins

A known amount (*ca.* 5 g) of the crude oil, its weathered form (tar residue) or the tar sand was dissolved in minimum amount of toluene. Cellulose powder (*ca.* 5 g) was added to the oil solution (to prevent formation of a stable emulsion) followed by anhydrous methanol (100 ml). Sonication (3 min) and centrifugation (3000 rpm/5 min) afforded an upper layer containing the metalloporphyrins concentrate. The supernatant was filtered and the residue was repeatedly extracted in a similar way until the supernatant contained no porphyrins as indicated by uv/visible spectrometry. The combined supernatants were concentrated using a rotary evaporator. The residue was purified by alumina column chromatography (Woelm, Neutral Act. I). Elution with chloroform removed the purified metalloporphyrins which were assayed by uv/visible spectrometry to get their type (nickel and/or vanadyl complexes) and concentration. Methane sulphonic acid (MSA) was added to the toluene solution of the purified metalloporphyrins (acid to porphyrin ratio, 1 ml:2 μmole). The mixture was refluxed (110°C) for one hr. After cooling, the reaction mixture was diluted with equal volume of hexane/toluene (1:1 v/v) and distilled water (2 volumes). The aqueous layer (purple) contained the porphyrin dictations. After separating the layers, the organic one was repeatedly extracted with aq. MSA (25%) until the acidic layer was colourless. The combined acidic layers were extracted with methylene chloride (5 times). The organic extracts were neutralized with sodium bicarbonate solution (5%), washed with water, concentrated (rotary evaporator) and chromatographed on alumina (Act. II) column. Elution with toluene/methylene chloride (1:1 v/v) removed the purified free-base petroporphyrins used for LC fingerprinting.

HPLC fingerprinting of free-base petroporphyrin mixtures

The development of HPLC for petroporphyrin analysis has been described elsewhere.[1]

Equipment: A Waters Associates ALC/GPC-244 liquid chromatograph including second M6000A solvent delivery system, M660 solvent programmer, M450 variable wavelength detector and U6K universal injector.

Samples: 2 μl of petroporphyrins solution in methylene chloride (*ca.* 1 mg/ml) were introduced from a 10 μl syringe.

Column: Stainless steel 24 cm × 4.6 mm i.d. packed with 5 μ silica (Partisil-5, Whatman) using a balanced density method.[2]

Mobile phase: The solvent system, using gradient elution, was toluene-hexane (1:1 v/v) as solvent B, programmed (40 min) from 20% to 100% B (curve 9) at a flow rate of 1.5 ml/min. The methylene chloride contained 1% ethanol as a modifier. Solvents were HPLC grade or glass-distilled

Detection: uv/vis at 400 nm and 0.1 AUFS.

Recorder: Bryans 28000. Response 0.1 mV, chart speed 5 min/cm.

RESULTS AND DISCUSSION

Fourteen samples were examined by the method described in the Experimental section. They came from Alberta, Canada; the North Sea; East Venezuela and the Arabian Gulf. The Alberta samples were comprised of an Athabasca tar sand and three related oils of different stages of biodegradation.[3] The Arabian Gulf samples (from Kuwait, Iran and Saudi Arabia) consisted of five production crudes, one artificially weathered oil and a tar residue from oil spills (Fig. 1). For peak

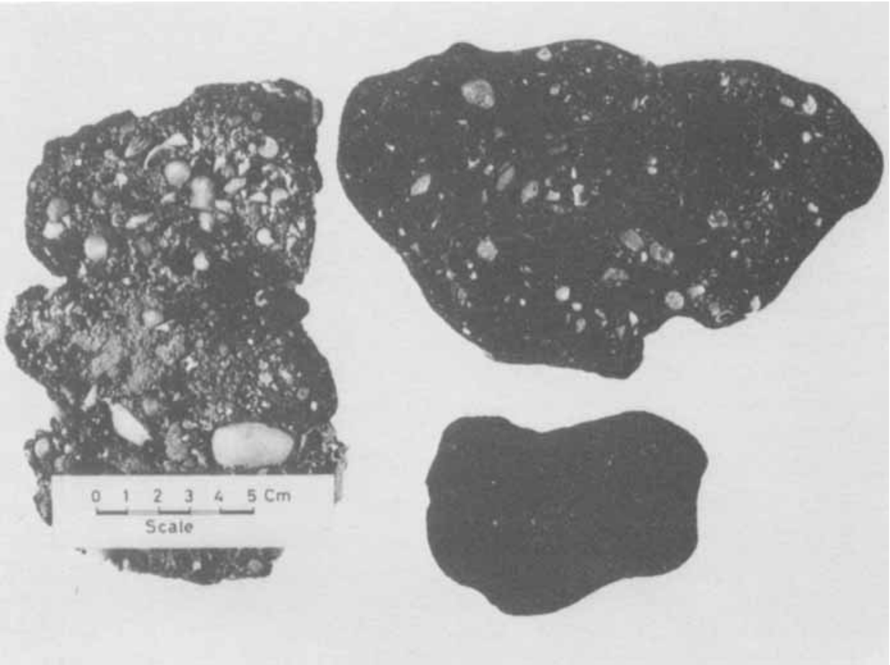

FIGURE 1 Specimens of the tar residue of oil spills in the Arabian Gulf.

TABLE I

Mass spectral characteristics of the major peaks in the liquid chromatogram of demetallated porphyrin mixture (*ex.* boscan oil)

		Petroporphyrin molecular ions[b]		
Peak no.	t_R^a (min)	Major component	Minor component(s)	(%)[c]
4	11.00	$C_{30}E$	$C_{28}E$(26)	
5	12.5	$C_{32}E$	—	
6	14.25	$C_{29}E$	—	
7	16.00	$C_{31}E$	—	
8	18.00	$C_{28}E$	—	
9	20.75	$C_{30}E$	—	
11	26.25	$C_{29}E$	—	
14	33.00	$C_{32}D$	—	
16	37.00	$C_{31}D$	—	
17	39.00	$C_{30}D$	—	

[a] Absolute retention time on Partisil-5 silica column using gradient elution. Reproducibility, ±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.

characterization see Table I. The North Sea (well 2/1–1) and East Venezuela (wells Ostra and Merey, Muturin Basin) crudes represented single-oil wells.

Fig. 2 depicts the petroporphyrin fingerprints for the Kuwaiti export oil and its artificially weathered form, whereas Fig. 3 presents the fingerprints for the Athabasca tar sand and a conventional crude oil (Bellshill Lake) from the same region. Inspection of Figs. 2 and 3 shows that artificial weathering and in-reservoir water washing and biodegradation[4]† had little effect, if any, on the distribution of petroporphyrin compounds. Furthermore, petroporphyrins were not readily affected by natural weathering processes acting on oil spills as indicated by the close pattern similarity in the fingerprints (Figures not shown) of the oil spills and few oils from fields in the vicinity.

On the other hand, the comparison of Figs. 2 with 3 reveals, as expected, that oils from different geographical locations have different petroporphyrin fingerprints, whereas those from one location show similar

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†According to G. T. Demaison,[4] water washing and biodegradation of crude oil in reservoirs have taken place in most supergiant tar sand or heavy oil deposits from Western Canada (Athabasca) and Eastern Venezuela (Orinoco heavy oil belt).

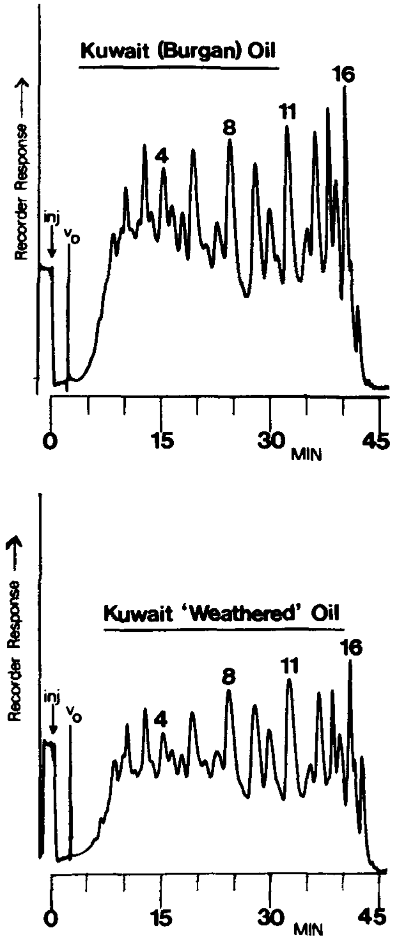

FIGURE 2 HPLC fingerptints of the petroporphyrins obtained from a Kuwaiti export oil and its weathered form. (The numbering of certain peaks in Figs. 2–5 is meant to facilitate correlation between fingerprints. For the identity of numbered peaks see Table I, Reference 1.)

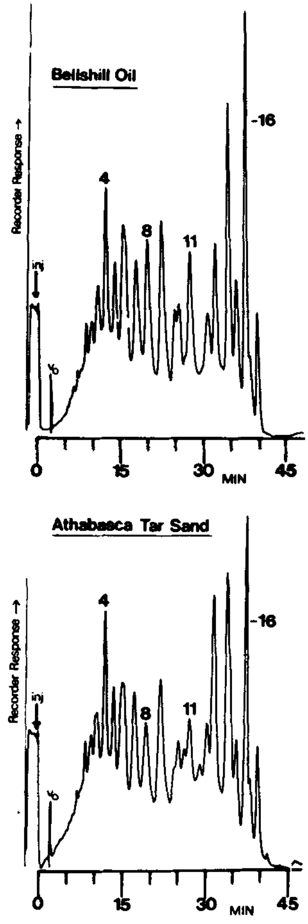

FIGURE 3 HPLC fingerprints of the petroporphyrins obtained from Athabasca tar sand and Bellshill Lake oil, Alberta.

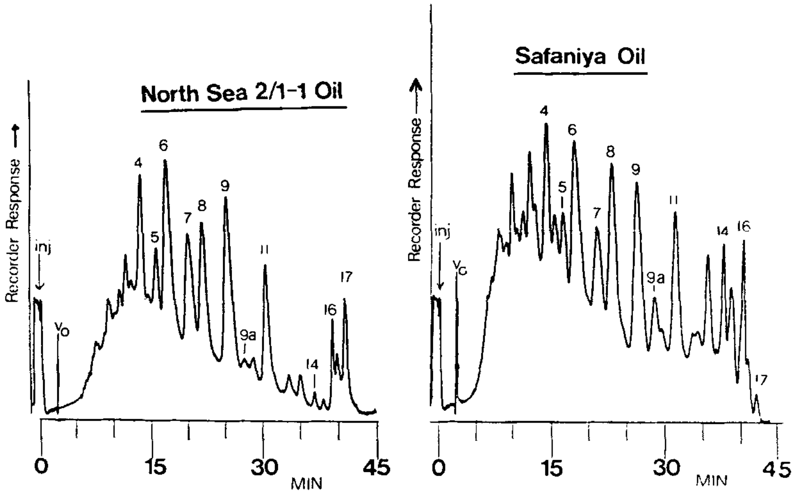

FIGURE 4 HPLC fingerprints of the petroporphyrins obtained from a North Sea and a Saudi Arabian (Safaniya) oil.

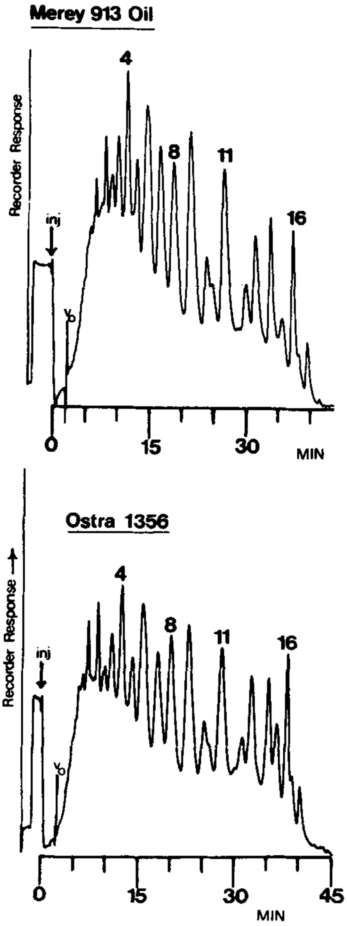

FIGURE 5 HPLC fingerprints of the petroporphyrins obtained from two East Venezuelan crudes.

petroporphyrin distributions. This finding, which was consistent throughout this study, is further illustrated in Figs. 4 and 5. Fig. 4 contrasts the fingerprints for the North Sea and a Saudi Arabian (Safaniya) production oils, whereas Fig. 5 compares the petroporphyrin distributions in the two East Venezuelan oils.

The results of this study ascertain the usefulness of petroporphyrins fingerprinting by HPLC as an analytical technique for oil classification. However, the real potential of this technique in pollution control will be established when fingerprints of a much wider collection of crude oils have been catalogued.

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