

Molecular Characterization of Organically-Bound Sulfur In Crude Oils

A Feasibility Study for the Application of Raney Ni Desulfurization as a New Method to Characterize Crude Oils**

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Summary

Five crude oils with varying sulfur contents (0.1 – 4.7%) were characterized on a molecular level for organically-bound sulfur. Aromatic fractions were analyzed by GC-(MS) and asphaltene and polar fractions were analyzed by flash pyrolysis-GC-(MS). The polar fractions were also desulfurized with Raney Ni and the hydrocarbons formed were analyzed by GC-MS. Major sulfur compounds in the aromatic fractions were identified as alkylbenzo- and alkylidibenzothiophenes. The flash pyrolyzates of the asphaltene contained alkylthiophenes and alkylbenzothiophenes as major compounds, depending on the thermal maturity of the oil. Generally, the sulfur-rich crude oils contained relatively more sulfur compounds. The flash pyrolyzates of polar fractions contained a variety of sulfur compounds (alkylthiolanes, alkylthianes, terpenoid sulfides, alkylbenzothiophenes) with substantial differences between different crude oils. Raney Ni desulfurization of the polar fraction yielded hydrocarbons dominated by *n*-alkanes, but isoprenoid alkanes, *n*-alkylcyclohexanes, mid-chain methylalkanes, tricyclic terpanes, hopanes and steranes were also present. These hydrocarbons show a potential to fingerprint crude oils since their distribution patterns are more characteristic than those of the hydrocarbons present in the saturated hydrocarbon fraction.

1 Introduction

Major advances in the characterization at the molecular level of organically-bound sulfur present in fossil fuels and related materials have been reported during the last decade (for an overview see [1] and [2]). It is well established nowadays that organically-bound sulfur is formed by incorporation of reduced inorganic sulfur species (H₂S, polysulfides) into sedimentary organic matter during the earliest stages of diagenesis [3,4]. These reactions can occur either intramolecularly, giving rise to specific, low-molecular-weight (MW < 800) organic sulfur compounds or intermolecularly. In the latter case high-molecular-weight organic matter is generated from low-molecular-weight precursors ("natural vulcanization"). This results in the formation of kerogen, asphaltene and macromolecular material present in polar fractions. In some samples this latter fraction is composed (up to 40% by weight) of macromolecules consisting of a network of hydrocarbons (*n*-alkanes, isoprenoid alkanes, steranes, triterpanes) cross-linked by (poly)sulfide groups [5–14]. Desulfurization with Raney Ni or other reagents releases the hydrocarbons bound in this way. The released hydrocarbons can then be characterized by the usual methods. Similarly, asphaltene

[9,10,12] and even insoluble kerogen [10,15] can be desulfurized using these techniques. Among the hydrocarbons formed upon desulfurization are compounds which are not present as free hydrocarbons, because they are selectively incorporated into the sulfur-rich macromolecular fractions [e.g. 16]. Hence, these hydrocarbons have a great potential for the characterization of the palaeoenvironment and for fingerprinting crude oils and bitumens [1].

The results summarized above were mainly obtained from studies on immature sediment extracts (*R*₀ < 0.5%) and "low thermal stress" crude oils. The crude oils, which have been analyzed in this respect, are either extremely sulfur-rich crude oils with an "immature" signature of the saturated hydrocarbons, such as the Rozel Point oil, Utah, U.S.A. [5,13,14,17] or are heavy oils from tar sands [18–20]. The present study aimed to test new methods and concepts with respect to the characterization of organically-bound sulfur to "conventional" crude oils and to study the feasibility for crude oil characterization based on compositions of the hydrocarbons generated upon Raney Ni desulfurization of their polar fractions.

2 Materials and Methods

2.1 Samples

Five crude oils (**Table 1**) were supplied for this study by Shell Internationale Petroleum Maatschappij B.V. Crude oil A originates from N.W. Borneo. It is a land plant derived crude oil from an Upper Miocene source rock deposited in a deltaic sequence as a coaly shale. Crude oil B is a typical North Sea crude oil. It is derived from the Late Jurassic Kimmeridgian shaly source rock, deposited in a marine environment. Crude oil C is a Middle Eastern crude oil from Qatar. It was sourced from the Jurassic Hanifa carbonate source rock, deposited in an interbasinal carbonate platform. The Oman crude oil D was sourced from an Infracambrian Huqf shale, deposited in a hypersaline environment of deposition. Crude oil E is a heavy Venezuelan crude oil, sourced from the Cretaceous La Luna marls which were deposited in a marine environment. In **Table 2** some geochemical data on these five oils are given.

2.2 Separation Methods

The crude oils were fractionated as depicted in **Figure 1**. Asphaltene were obtained and purified by repeated precipitations with *n*-heptane. Maltene fractions (ca. 450 mg) were subsequently sepa-

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Table 1
Sample description.

Sample	Country	Related source rock	Depositional environment	Lithology
A	N.W. Borneo	Miocene	deltaic	coaly shale
B	North Sea (UK)	Kimmeridge (L. Jurassic)	marine	shale
C	Qatar	Hanifa (L. Jurassic)	marine	carbonate
D	Oman	Huqf (Infracambrian)	hypersaline	shale
E	Venezuela	La Luna (Cretaceous)	marine	marl

rated by column chromatography (20 cm × 18 mm; $V_0 = 35$ ml) with Al_2O_3 (activated for 2 h at 150 °C) into four fractions with hexane (45 ml) to elute the saturated hydrocarbon fraction, hexane/toluene (9:1, v/v; 100 ml) to elute aromatic hydrocarbon fraction I, toluene (100 ml) to elute aromatic hydrocarbon fraction II and methanol/ CH_2Cl_2 (1:1, v/v; 100 ml) and CH_2Cl_2 (50 ml) to elute the polar fraction.

2.3 Desulfurization

Aliquots of the polar and aromatic hydrocarbon fractions II were desulfurized using Raney Ni. Typically 20 mg were reacted with a 0.5 ml suspension (0.4 mg/ml) of Raney Ni W-6 [21] in 2 ml refluxing ethanol for 2 h under a nitrogen blanket. The desulfurization products were isolated by centrifugation and subsequent extraction with CH_2Cl_2 (×3). The combined extracts were washed with 30 ml NaCl-saturated H_2O , which was extracted thereafter with 2 ml CH_2Cl_2 (×2). The combined CH_2Cl_2 -extracts were evaporated to dryness using a rotary evaporator at 20 °C. The desulfurization products were chromatographed over a small (5 × 0.5 cm) alumina column using hexane/ CH_2Cl_2 (9:1, v/v) to elute the saturated and aromatic hydrocarbons and methanol/ CH_2Cl_2 (1:1, v/v) to elute

Table 2
Geochemical data of oil samples.

	Oil A N.W. Borneo	Oil B North Sea	Oil C Qatar	Oil D Oman	Oil E Venezuela
API	34.0	30.1	35.8	31.9	9.6
%S	0.1	1.0	1.3	1.9	4.7
Pristane/ <i>n</i> -C ₁₇	1.9	0.8	0.2	0.2	1.0
Phytane/ <i>n</i> -C ₁₈	0.2	0.6	0.3	0.7	1.8
Pristane/ phytane	8.5	1.6	0.9	0.5	0.5
$\delta^{13}C$ (‰) ^{a)}	-28.8	-29.4	-26.6	-36.0	-26.9

^{a)} Of topped oils.

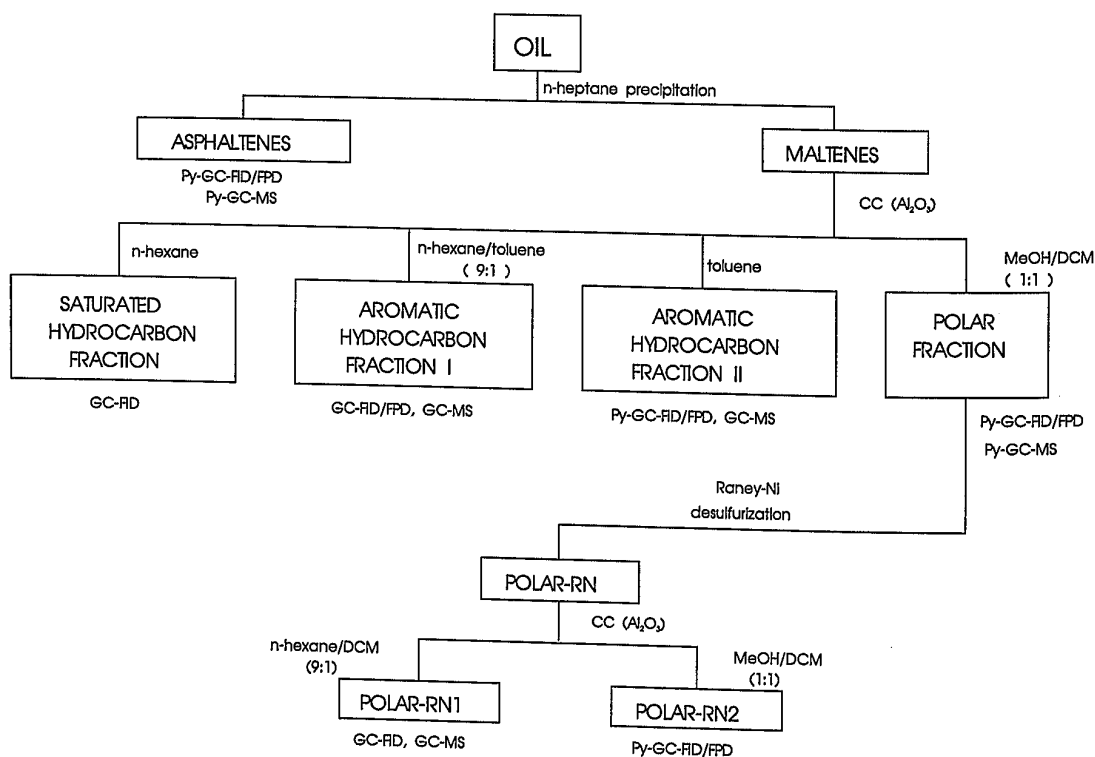
**Figure 1**
Analytical flow diagram.

Table 3
Relative amounts of the fractions obtained from the five crude oils.

	Oil A N.W. Borneo	Oil B North Sea	Oil C Qatar	Oil D Oman	Oil E Venezuela
Asphaltenes (%) ^{a)}	0.7.	2.8	0.2	0.0	12.0
Maltenes (%) ^{a)}	81	85	80	90	88
Saturated hydrocarbons (%) ^{b)}	68	49	55	41	18
Aromatic hydrocarbons I (%) ^{b)}	18	23	23	21	20
Aromatic hydrocarbons II (%) ^{b)}	8	15	17	18	28
Polars (%) ^{b)}	5	16	7	19	29
Desulfurized polars (%) ^{c)}	3(0.1)	5(0.8)	14(1.0)	7(1.3)	4(1.2)

^{a)} Normalized for the weight of total crude oil.

^{b)} Normalized for the weight of the maltene fractions.

^{c)} Normalized for the weight of the polar fractions. Values normalized for the total oil are given in parentheses.

^{d)} n.d. = not determined.

more polar compounds. The first fractions were analyzed by GC-MS. A blank experiment indicated no contribution of hydrocarbons from other sources than the treatment of the polar fractions with Raney Ni.

2.4 Gas Chromatography (GC)

GC was performed with a Carlo Erba 4160 instrument, equipped with an on-column injector. A fused silica capillary column (25 m × 0.32 mm) coated with CP Sil-5 (film thickness 0.12 mm) was used with helium as carrier gas. Detection was accomplished by a flame ionization detector (FID). GC was also performed on a Carlo Erba 5300 instrument, equipped with an on-column injector and an identical capillary column as described above. Detection was accomplished by both an FID and a sulfur-selective flame photometric detector (FPD), using a stream-splitter at the end of the column (split ratio FID:FPD = 1:2). The samples (dissolved in hexane or ethyl acetate) were injected at 70 °C and the oven was programmed to 130 °C at 10 °/min and subsequently at 4 °/min to 320 °C at which it was held for 20 min.

2.5 Flash Pyrolysis-Gas Chromatography (Py-GC)

Flash Py-GC was carried out using a pyrolysis reactor [22] which was directly mounted on the injector block of a Varian 3700 gas chromatograph. The temperature of the injector block was 250 °C. Samples were applied to ferromagnetic wires by adding 10 ml of a solution of 30 mg/ml. The wires were heated within 0.15 s to their Curie temperatures (358 or 610 °C) and were kept at this temperature for 10 s. Separation of the pyrolysis products was accomplished by a fused silica capillary column (25 m × 0.32 mm) coated with CP-Sil 5 (film thickness 0.45 mm) using helium as carrier gas. The temperature was programmed from 0 °C (5 min), by using a cryogenic unit, to 300 °C (20 min) at a rate of 3 °/min. The gas chromatograph was equipped with an FID and an FPD. The flow from the capillary column was split at the end with a stream splitter (FID:FPD = 4:1).

2.6 Gas Chromatography-Mass Spectrometry (GC-MS)

GC-MS was carried out on a Hewlett-Packard 5480 gas chromatograph connected with a VG-70s mass spectrometer operated at

70 eV with a mass range m/z 40–800 and a cycle time of 1.8 s (resolution 1000). The gas chromatograph was equipped with a fused silica capillary column (25m × 0.32 mm) coated with CP Sil-5 (film thickness 0.1 mm) and was operated with helium as carrier gas. The samples were injected at 50 °C and subsequently the oven was programmed to 130 °C at 20 °/min and then at 4 °/min to 300 °C at which it was held for 10 min.

2.7 Flash Pyrolysis-Gas Chromatography-Mass Spectrometry (Py-GC-MS)

Flash pyrolysis-GC-MS analyses were performed with a Hewlett-Packard 5480 gas chromatograph connected with a VG-70s mass spectrometer. Pyrolysis and chromatographic conditions were identical to those described above for Py-GC. Electron impact mass spectra were obtained at 70 eV with a cycle time of 1.8 s and a mass range m/z 50–800 at a resolution of 1000. Data acquisition was started 1 min after pyrolysis.

3 Results

3.1 Fractionation

The yields of the fractions obtained from the five crude oils are presented in **Table 3**. During isolation of the asphaltene fractions significant loss of material (0–20%) occurs, probably due to evaporation of volatile compounds. From crude oil D (Oman) no asphaltene could be precipitated. The subsequent fractionation of the maltene fraction shows a good recovery (95–103%).

3.2 Asphaltene

The asphaltenes were analyzed by Curie point Py-GC-FID/FPD. The FID chromatograms of these pyrolyzates are dominated by homologous series of *n*-alkanes and *n*-alk-1-enes (e.g. **Figures 2A** and **3A**). Oil A (N.W. Borneo) contains no major sulfur compounds in its asphaltene pyrolyzate apart from some very volatile ones (e.g. H₂S). Oil B (North Sea) shows a relatively large H₂S peak in its asphaltene pyrolyzate but other organic sulfur compounds (OSC) are very minor compounds.

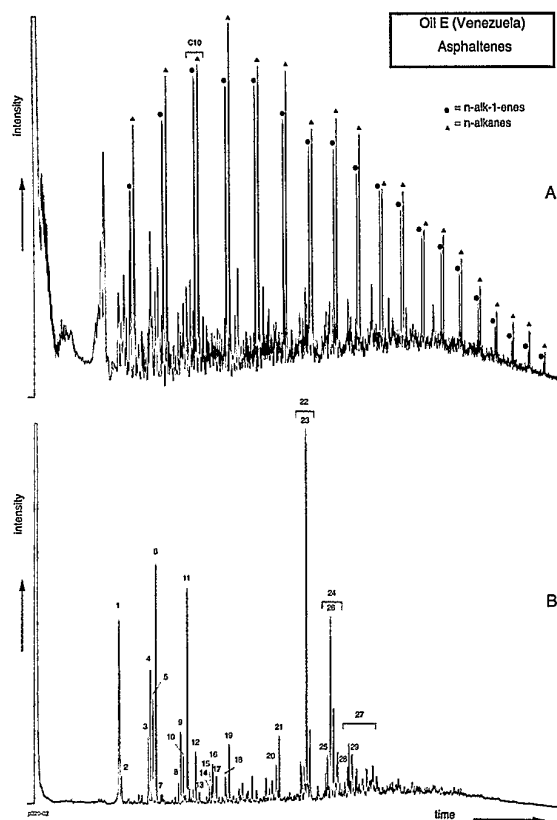


Figure 2
FID (A) and FPD (B) chromatograms of the flash pyrolyzate (610 °C) of the asphaltene fraction of crude oil E (Venezuela). Numbers in the FPD chromatogram refer to compounds listed in Table 4.

The asphaltene pyrolyzate of oil E (Venezuela) contains a complex assemblage of OSC (**Figure 2B**). These compounds have been identified by Py-GC-MS and are listed in **Table 4**. They are dominated by C₁–C₆ alkylthiophenes and C₁–C₄ alkylbenzothiophenes and have been identified previously in flash pyrolyzates of kerogens, coals and asphaltene [2,8,23–27]. In a number of sedimentary sequences distributional changes of these compounds generated by flash pyrolysis of the kerogens with maturity were observed [26]. Upon increasing maturity an increase of the alkylbenzothiophenes relative to alkylthiophenes was noted and it was postulated that these distributional changes are caused by cyclization and subsequent aromatization of alkylthiophene units in the kerogen [26]. The maturity dependence of these transformations was supported by similar trends observed in the flash pyrolyzates of artificially matured kerogens. The ratio of alkylbenzothiophenes versus alkylthiophenes as observed in the pyrolyzate of oil E (Venezuela) asphaltene is similar to that of the residue of artificially matured Blackstone Kimmeridge kerogen for 72 h at 330 °C [26]. This sample has an average reflectance of "vitrinite-like" bitumen of $R_o = 1.0\%$ [28,29]. Py-GC-MS also revealed the presence of homologous series of 2-alkylthiophenes, 2-alkyl-5-methylthiophenes, 2-alkyl-5-ethylthiophenes, 2-alkyl-4-methylbenzothiophenes (**Figure 4A**) and 4-alkyl-2-methylbenzothiophenes (**Figure 4A**). The disproportionately large amounts of the latter two series relative to other benzothiophenes can also be explained by cyclization and aromatization of alkylthiophene units within the asphaltene structure upon increasing maturation [17,24,30].

Table 4
Sulfur compounds identified in the various crude oil fractions.

Peak	Compound
1	2-Methylthiophene
2	3-Methylthiophene
3	2-Ethylthiophene
4	2,5-Dimethylthiophene
5	2,4-Dimethylthiophene
6	2,3-Dimethylthiophene
7	3,4-Dimethylthiophene
8	2-Propylthiophene
9	2-Ethyl-5-methylthiophene
10	2-Ethyl-4-methylthiophene
11	2,3,5-Trimethylthiophene
12	2,3,4-Trimethylthiophene
13	3-Isopropyl-2-methylthiophene
14	2-Methyl-5-propylthiophene and 2,5-diethylthiophene
15	2-Butylthiophene
16	2-Ethyl-3,5-dimethylthiophene and 3-ethyl-2,5-dimethylthiophene
17	5-Ethyl-2,3-dimethylthiophene and an ethyldimethylthiophene
18	An ethyldimethylthiophene
19	2,3,4,5-Tetramethylthiophene
20	2-Methylbenzothiophene
21	4-Methyl and 3-methylbenzothiophene
22	C ₂ -Benzothiophenes
23	2,4-Dimethylbenzothiophene
24	C ₃ -Benzothiophenes
25	2-Methyl-4-ethylbenzothiophene
26	2-Ethyl-4-methylbenzothiophene and a C ₃ -benzothiophene
27	C ₄ -Benzothiophenes
28	2-Methyl-4-propylbenzothiophene
29	2-Propyl-4-methylbenzothiophene
30	Dibenzothiophene
31	4-Methyldibenzothiophene
32	2-Methyl- and 3-methyldibenzothiophene
33	1-Methyldibenzothiophene
34	Ethyldibenzothiophene
35	Dimethyldibenzothiophene
36	Dimethyldibenzothiophene
37	Dimethyldibenzothiophene
38	Dimethyldibenzothiophene
39	Dimethyldibenzothiophene
40	C ₃ -Dibenzothiophenes

In the flash pyrolyzate of the asphaltene fraction of oil C (Qatar) some OSC are present (**Figure 3B**). Alkylthiophenes are absent but alkylbenzothiophenes are still present although in low amounts relative to the hydrocarbons. Py-GC-MS revealed the presence of alkylated dibenzothiophenes in addition to the alkylbenzothiophenes. These observations indicate that this oil is probably more mature than oil E (Venezuela), which still contains alkylthiophenes. The m/z 161 mass chromatogram of the pyrolyzate of the asphaltene of oil C (Qatar) reveals a similar suite of 2-alkyl-4-methylbenzothiophenes and 4-alkyl-2-methylbenzothiophenes (**Figure 4B**) as identified in the pyrolyzate of the asphaltene of oil E (Venezuela).

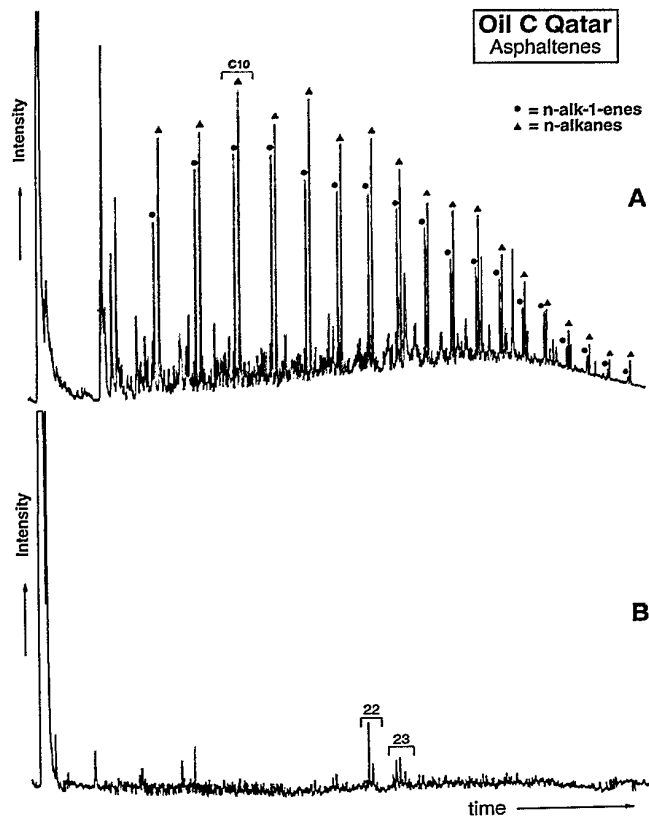


Figure 3 FID (A) and FPD (B) chromatograms of the flash pyrolyzate (610 °C) of the asphaltene fraction of crude oil C (Qatar). Numbers in the FPD chromatogram refer to compounds listed in Table 4.

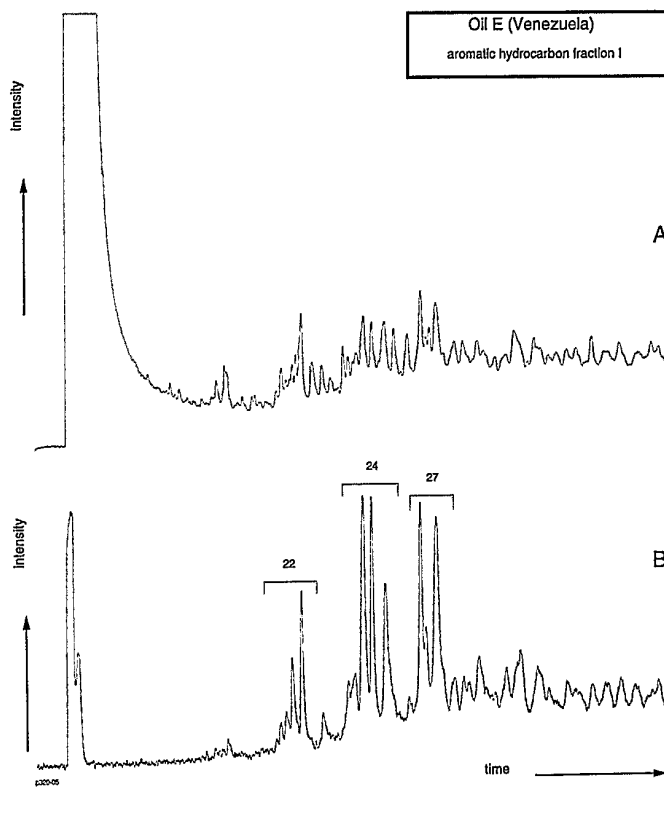


Figure 5 Partial FID (A) and FPD (B) chromatograms of the aromatic hydrocarbon I fraction of crude oil E (Venezuela). Numbers in the FPD chromatogram refer to compounds listed in Table 4.

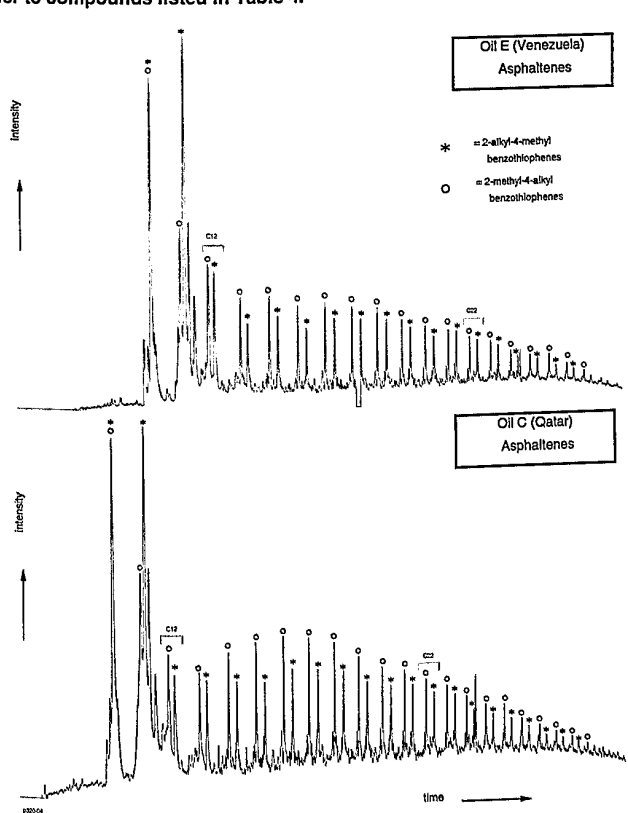


Figure 4 Partial m/z 161 mass chromatograms of the pyrolyzates (610 °C) of the asphaltene fractions of crude oils E (Venezuela) (A) and C (Qatar) (B).

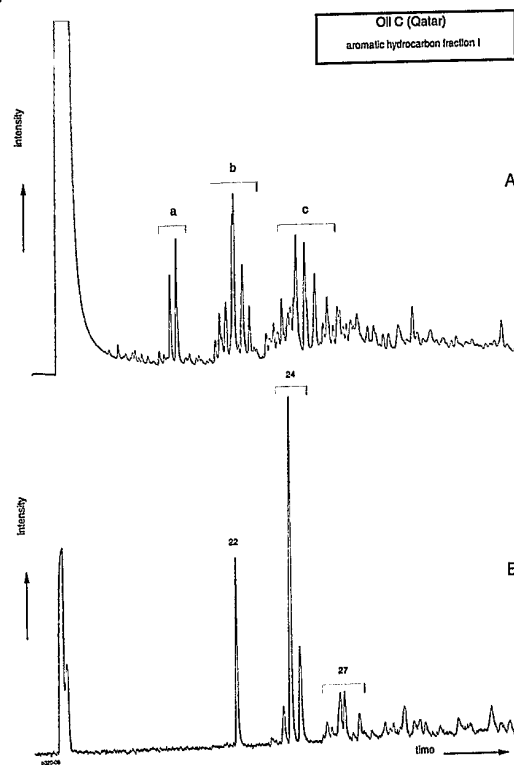


Figure 6 Partial FID (A) and FPD (B) chromatograms of the aromatic hydrocarbon I fraction of crude oil C (Qatar). Numbers in the FPD chromatogram refer to compounds listed in Table 4. Key: a = methyl naphthalenes, b = C₂-naphthalenes, c = C₃-naphthalenes.

3.3 Saturated Hydrocarbon Fractions

GC-FID/FPD analyses indicated that there are no sulfur compounds present in the saturated hydrocarbon fractions.

3.4 Aromatic Hydrocarbon Fractions I

GC-FID/FPD analyses indicated that the aromatic hydrocarbon fractions I of crude oils A (N.W. Borneo) and B (North Sea) contain no OSC and that the aromatic hydrocarbon fraction I of crude oil D (Oman) contains hardly any OSC. Aromatic hydrocarbon I fractions of crude oils E (Venezuela) and C (Qatar) contain OSC and were further analyzed by GC-MS. The major OSC in these fractions were identified as alkylbenzothiophenes. Figures 5 and 6 show partial FID and FPD chromatograms of these fractions for oils E (Venezuela) and C (Qatar), respectively. Peak numbers refer to Table 4.

3.5 Aromatic Hydrocarbon Fractions II

These fractions were initially analyzed by flash pyrolysis GC-FID/FPD using wires with a Curie temperature of 610 °C, since these fractions often contain a mixture of low-molecular-weight compounds (MW < 800) and high-molecular-weight substances. These latter substances are not "GC-amenable" and, therefore, they have to be thermally degraded by *e.g.* flash pyrolysis to characterize them

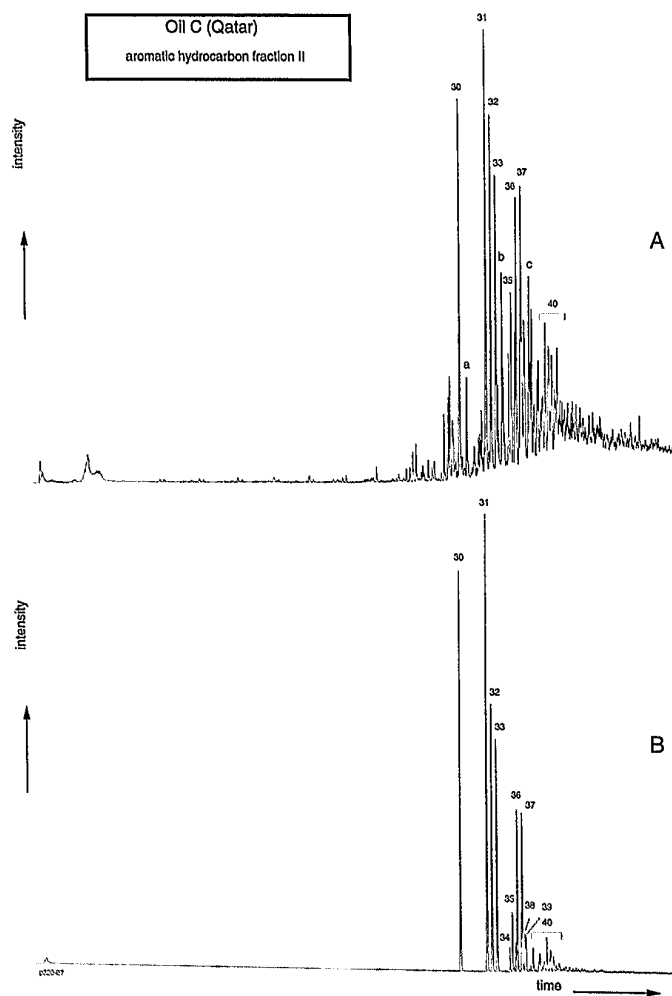


Figure 7
FID (A) and FPD (B) chromatograms of the flash pyrolyzate (610 °C) of the aromatic hydrocarbon II fraction of crude oil C (Qatar). Numbers in the FPD chromatogram refer to compounds listed in Table 4. Key: a = phenanthrene, b = methylphenanthrene, c = C₂-phenanthrenes.

with GC and GC-MS. The low-molecular-weight components simply evaporate during such analyses. As a result a mixture of evaporated compounds and pyrolysis products is obtained. By using wires with a Curie temperature of 358 °C only evaporated compounds are analyzed because, generally, the amount of energy is not sufficient for thermal breakdown of macromolecules. This method can therefore be applied to discriminate between free occurring compounds and pyrolysis products.

Flash pyrolysis (610 °C) of the aromatic hydrocarbon fractions II obtained from the five crude oils yielded mainly evaporated compounds as was proven by flash pyrolysis experiments at 358 °C. **Figure 7** shows an example of the obtained FID and FPD chromatograms for oil C (Qatar). The major compounds of this fraction are sulfur-containing compounds and were identified by GC-MS (peak numbers refer to Table 4). They are dibenzothiophene and alkylated derivatives of dibenzothiophene, often encountered in crude oils as major sulfur compounds [31–34].

In other samples this suite of sulfur compounds is also present but the amounts relative to other constituents of these fractions (probably tri- and tetra-aromatic hydrocarbons) are significantly less.

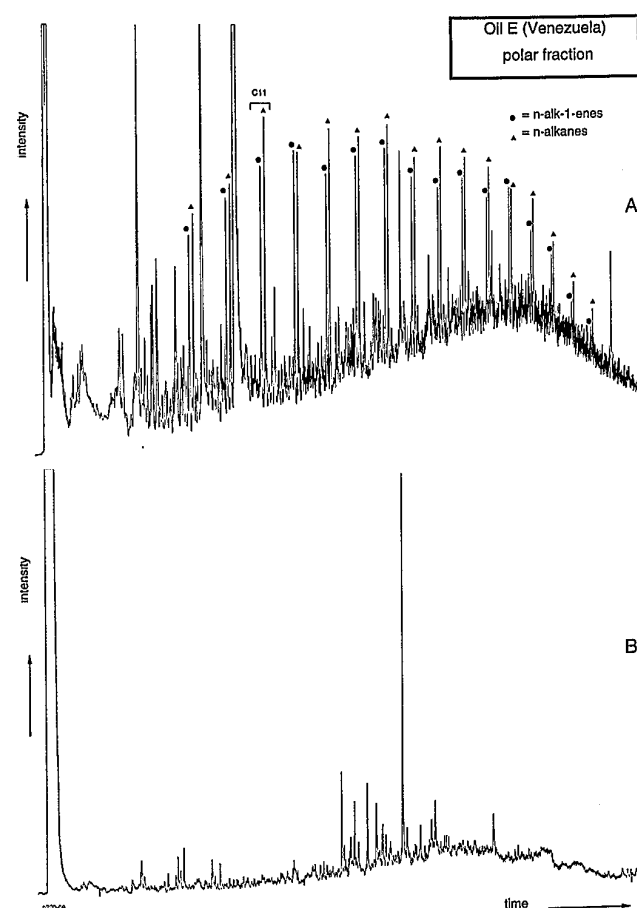


Figure 8
FID (A) and FPD (B) chromatograms of the flash pyrolyzate (610 °C) of the polar fraction of crude oil E (Venezuela).

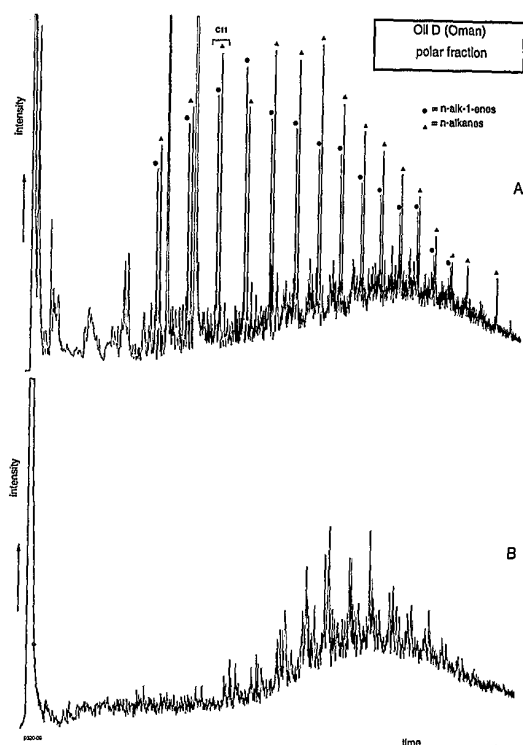


Figure 9 FID (A) and FPD (B) chromatograms of the flash pyrolyzate (610 °C) of the polar fraction of crude oil D (Oman).

Table 5 Relative abundances and carbon number distribution of classes of saturated hydrocarbons formed on desulfurization of the polar fractions of five oils.

	Oil A N.W. Borneo	Oil B North Sea	Oil C Qatar	Oil D Oman	Oil E Venezuela
n-Alkanes	+++ ^{a)} 15-47 (24, 40) ^{b)}	+++ 14-44 (16, 42)	+++ 14-43 (16)	+++ 15-42 (17)	+++ 15-40 (18, 28)
Isoprenoid alkanes	++ 18-20 (19) Pr/Ph = 2.7 ^{c)}	+ 18-20 (20) Pr/Ph = 0.9	+ 18-20 (20) Pr/Ph = 1.0	+ 18-20 (20) Pr/Ph = 0.6	++ 18-20 (20) Pr/Ph = 0.6
Mid-chain methylalkanes	-	-	-	+ 16-32(17)	-
n-Alkylcyclohexanes	+ 16-31 (20)	+ 15-31 (17)	+ 15-31 (17, 26)	+ 15-31 (17, 21)	+ 15-31 (17, 28)
Steranes	-	-	-	+ 28-29 (29)	+ 27-29
Hopanes	+ 27-35 (29)	-	-	-	+ 27-35 (31)
Bicyclic terpanes	-	-	+ 15-18 (15)	-	+ 15-18 (18)
Tricyclic terpanes	-	+ 23	+ 21-23 (23)	+ 20-25 (23)	++ 20-25 (23)

a) +++ = member of this compound class is the most abundant component in the TIC, ++ = a member of this compound class is 50-100% of the most abundant component in the TIC, + = a member of this compound class is 0-50% of the most abundant component in the TIC, - = below detection limit. ^{b)} Numbers indicate range of occurrence, numbers in parentheses indicate (sub)maxima. ^{c)} As determined from peak height data in the m/z 57 mass chromatograms.

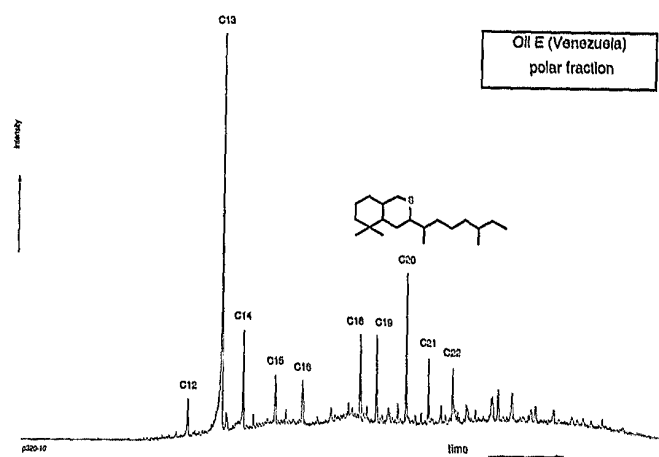


Figure 10 Partial m/z 183 mass chromatograms of the pyrolyzates (610 °C) of the polar fraction of crude oil E (Venezuela).

3.6 Polar Fractions

The polar fractions, often referred to as resin fractions, vary from 5 up to 29 weight % of the maltene fractions (Table 3). They contain both low-molecular-weight components as well as high-molecular-weight material. The polar fractions were analyzed by flash pyrolysis-GC and -GC-MS and by Raney Ni desulfurization. The scope and limitations of flash pyrolysis have been explained in the pre-

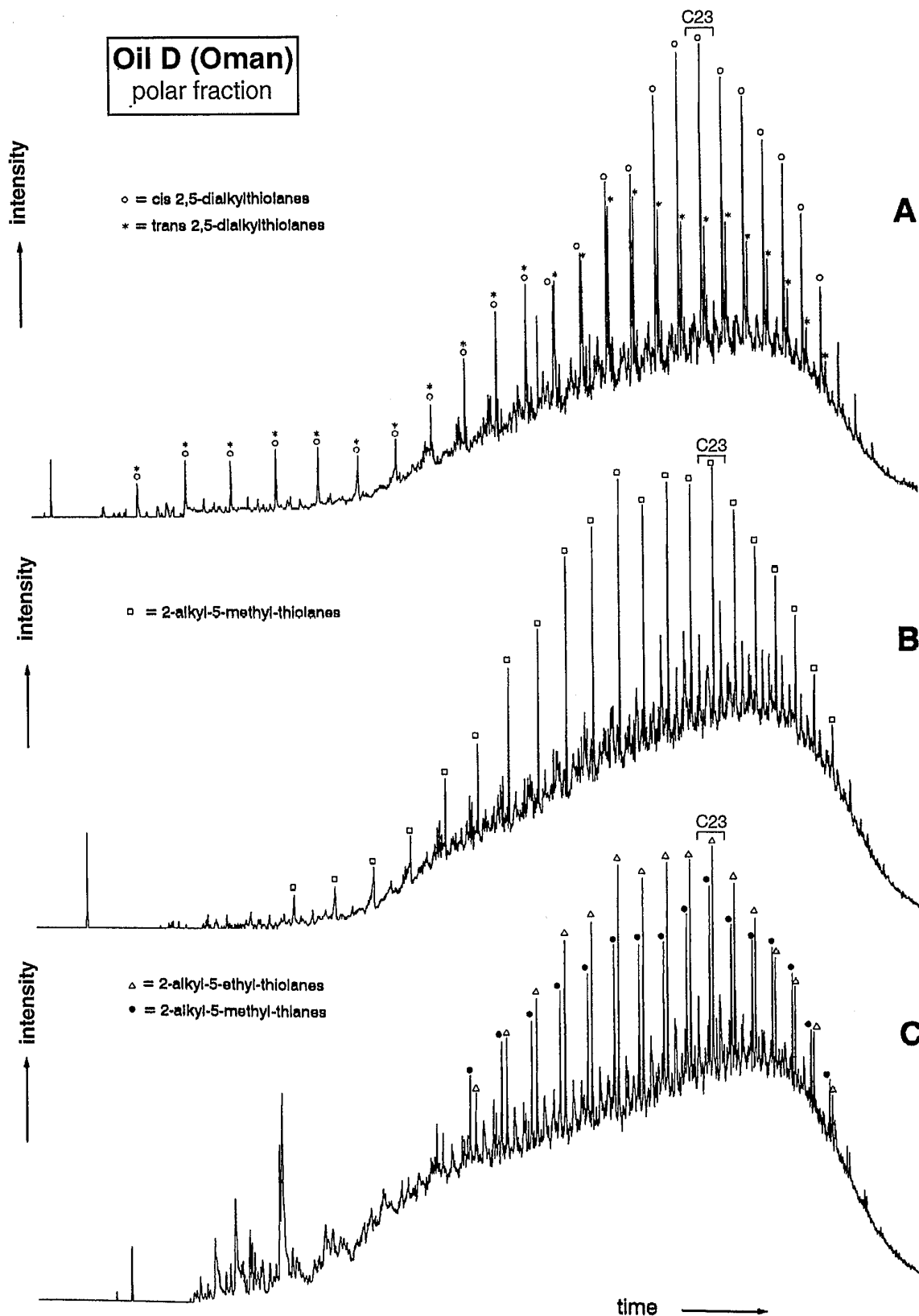


Figure 11
Partial m/z 87 (A), 101 (B) and 115 (C) mass chromatograms of the pyrolyzates (610 °C) of the polar fraction of crude oil D (Oman).

vious section. Raney Ni desulfurization is a chemical degradation method which reductively cleaves carbon-sulfur bonds selectively. The products obtained are hydrocarbons which can be analyzed by GC and GC-MS.

GC-FID/FPD analyses revealed the relative abundances of sulfur compounds in the flash pyrolyzates (e.g. **Figures 8 and 9**) of the polar fractions of the oils. In the polar fractions of crude oils A (N.W. Borneo) and B (North Sea) these compounds are very low or absent, whereas in the polar fractions of crude oils C (Qatar), D (Oman) and, especially, E (Venezuela) these compounds are more abundant. In oils E (Venezuela) and D (Oman) the sulfur compounds have been identified by GC-MS. In the pyrolyzate of the polar fraction of oil E (Venezuela) bicyclic terpenoid sulfides are the most abundant sulfur compounds. These compounds have been identified previously in crude oils and bitumens [18–20] and in a pyrolyzate of an asphaltene fraction of the Athabasca bitumen [30]. Their distribution is exemplified by a mass chromatogram of m/z 183 (**Figure 10**). In addition, alkylbenzothiophenes, tetracyclic terpenoid sulfides and linear alkylthiolanes were also identified in the pyrolyzate. In the pyrolyzate of the polar fraction of oil D (Oman) the sulfur compounds are lower in abundance with respect to the dominant n -alkanes and n -alk-1-enes generated upon pyrolysis (**Figure 9**). They are dominated by homologous series of 2-alkyl-5-methylthiolanes, 2-alkyl-5-ethylthiolanes and both *cis* and *trans* 2,5-dialkylthiolanes as shown

by the mass chromatograms of m/z 101, 115 and 87, respectively (**Figure 11**). These compounds have been identified previously in bitumens and crude oils [17,35–38] and in flash pyrolyzates of asphaltene [30] and kerogens and coals [2,11,23,39,40].

Raney Ni desulfurization of the polar fractions yielded in all cases small amounts of saturated hydrocarbons (3–14 wt.% of the polar fraction; 0.1–1.3 wt.% of the total crude oil, Table 3). Some of the polar fractions obtained after column chromatography of the desulfurized polar fractions were submitted to flash pyrolysis GC-FID/FPD. These analyses revealed that the desulfurization was complete since sulfur compounds were no longer detected in the pyrolyzates. The obtained apolar compounds were analyzed by GC-MS. The major compounds formed are n -alkanes, isoprenoid alkanes (phytane, pristane and norpristane) and tricyclic terpanes. n -Alkylcyclohexanes, mid-chain methylalkanes, bicyclic terpanes, steranes and hopanes are present in lower and varying concentrations. An overview of the relative abundance of the hydrocarbons formed upon desulfurization and their carbon number distributions is given in **Table 5**. **Figure 12** depicts the mass chromatograms of m/z 57 showing the distributions of n -alkanes, isoprenoid alkanes and mid-chain methylalkanes. In **Figure 13** the mass chromatograms of m/z 82 reveal the distribution patterns of the n -alkylcyclohexanes. Since n -alkanes are the major components of the desulfurization products (Table 5) these compounds are also en-

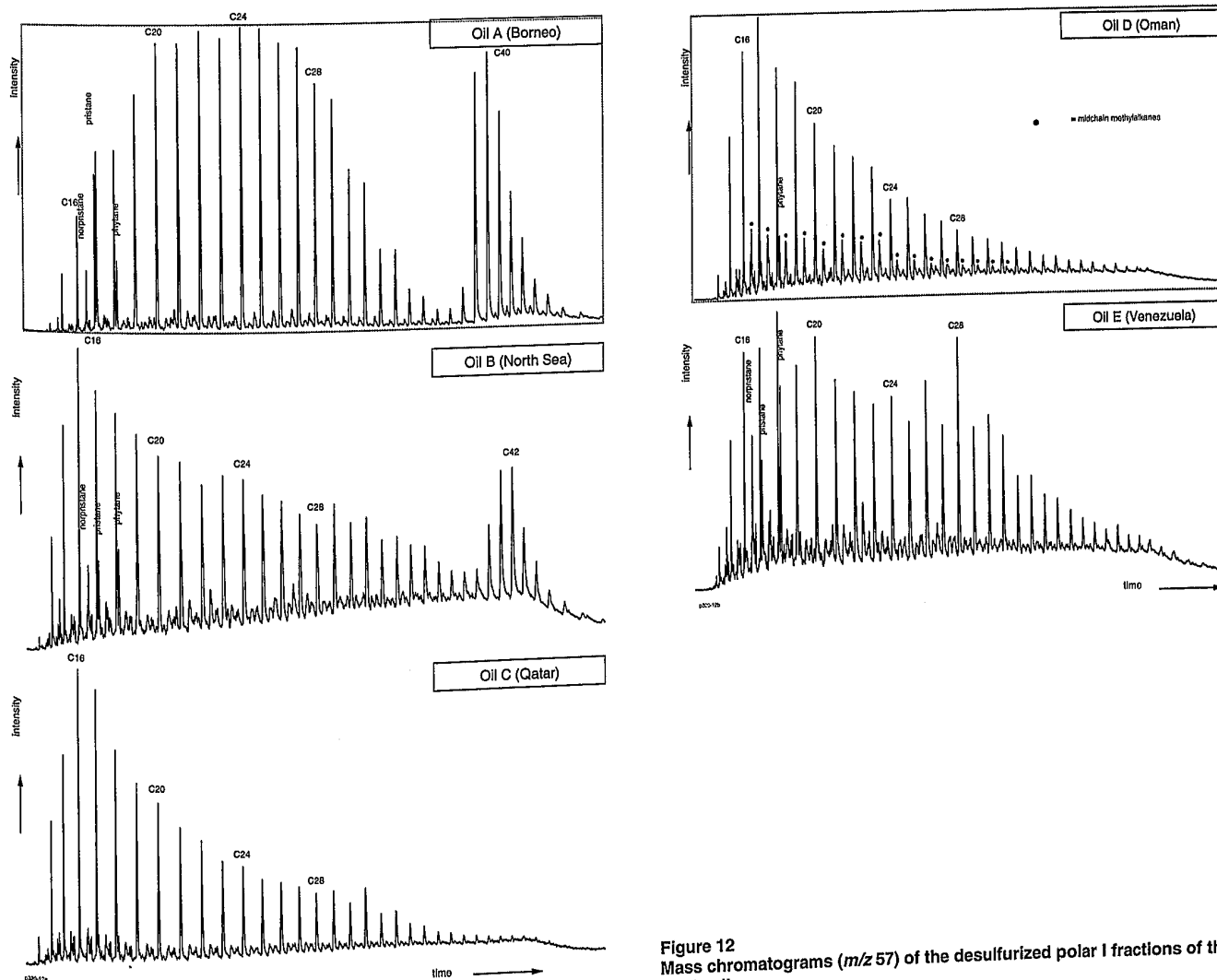


Figure 12
Mass chromatograms (m/z 57) of the desulfurized polar I fractions of the five crude oils.

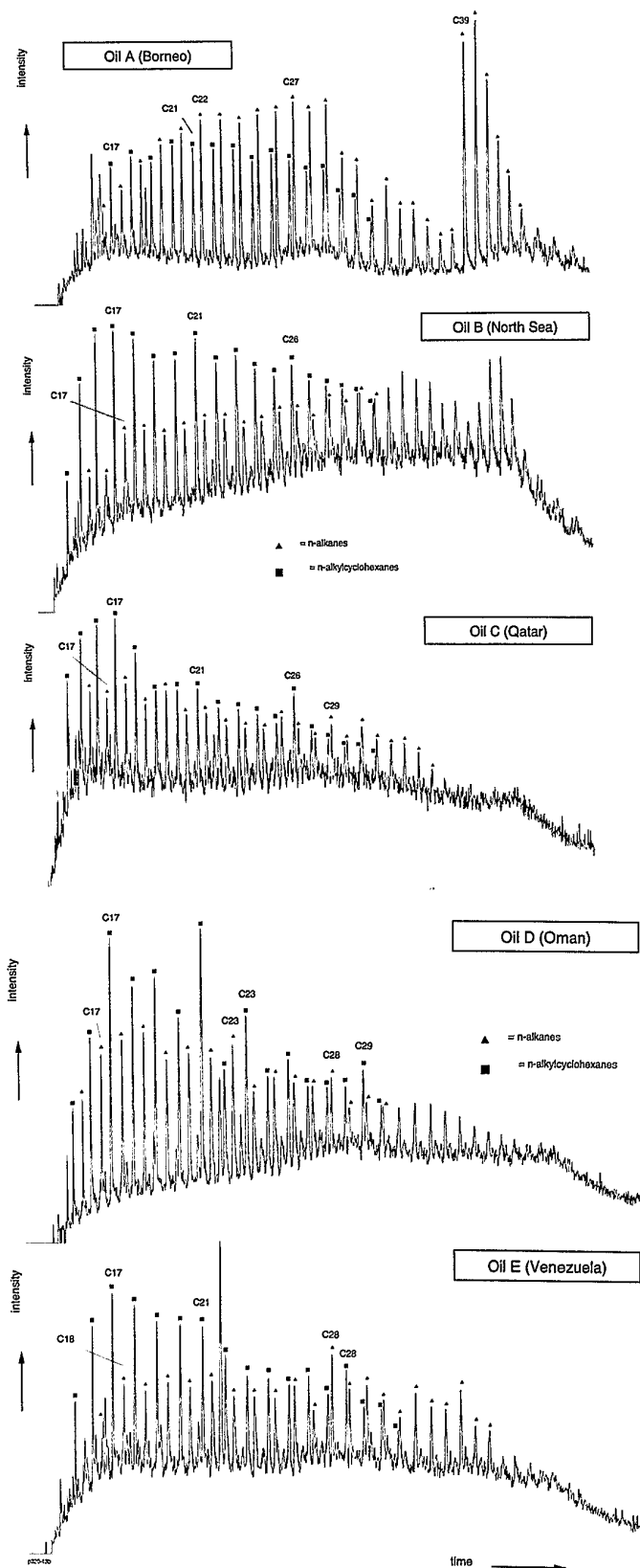


Figure 13
Mass chromatograms (m/z 82) of the desulfurized polar I fractions of the five crude oils.

countered in the m/z 82 mass chromatograms. No monocyclic terpanes could be identified in the desulfurization mixtures. This is somewhat surprising since bicyclic terpenoid sulfides are major sulfur compounds in the pyrolyzate of the polar fraction of crude oil E (Venezuela). This may be due to losses of the volatile monocyclic hydrocarbons formed upon desulfurization of these bicyclic terpenoid sulfides during work-up. **Figure 14** shows a mass chroma-

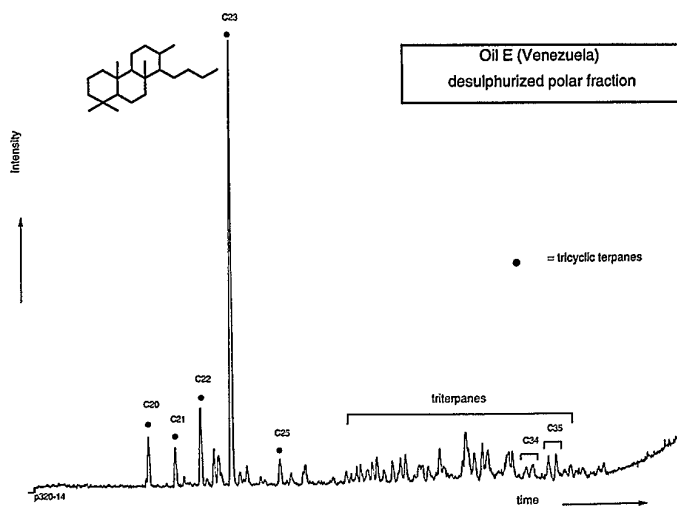


Figure 14
Mass chromatogram (m/z 191) of the desulfurized polar I fraction of crude oil E (Venezuela).

togram of m/z 191 for oil E (Venezuela). This reveals the distribution of the tricyclic terpanes formed upon desulfurization.

4 Discussion

4.1 Abundance of Organically-Bound Sulfur in the Various Fractions

Table 6 gives an overview of the estimated relative amounts of organically-bound sulfur in the various crude oil fractions obtained. In general, these amounts correlate well with the total sulfur contents of the crude oils; the oil with the lowest amount of sulfur [Oil A (N.W. Borneo)] has the lowest relative amounts of organically-bound sulfur in its fractions whilst the most sulfur-rich oil [Oil E (Venezuela)] shows the highest relative amounts of organically-bound sulfur in its fractions. The trend is, to some extent, disturbed by crude oil D (Oman) since its fractions contain less organically-bound sulfur than expected from its relatively high sulfur content (**Table 6**). To further substantiate these findings the sulfur content of each individual fraction has to be assessed by elemental analysis.

4.2 Origin of Sulfur Compounds and Macromolecularly-Bound Sulfur

The low-molecular-weight sulfur compounds identified in the aromatic hydrocarbon I and II fractions are alkylated benzo- and dibenzothiophenes. This composition differs markedly from that of immature bitumens and "low thermal stress" crude oils [1]. In such samples ($R_0 = ca. 0.25 - 0.4\%$) the sulfur compounds are dominated by alkylthiolanes, -thianes and -thiophenes although in some cases alkylbenzothiophenes have been identified as well. This difference in composition is probably due to the different degrees of thermal

Table 6
Sulfur content and estimated relative amounts of sulfur present in the fractions obtained from the five crude oils.

	Oil A N.W. Borneo	Oil B North Sea	Oil C Qatar	Oil D Oman	Oil E Venezuela
Sulfur (%)	0.1	1.0	1.3	1.9	4.7
Asphaltenes	_a)	-	+	n.d. b)	++
Aromatic hydrocarbons I	-	-	+++	+	+++
Aromatic hydrocarbons II	+	+	+++	+	+
Polars	+	+	+	++	++

a) +++ = abundant, ++ = moderate, + = minor, - = very minor or absent.

b) No asphaltene fraction present.

maturity. The five crude oils studied are obviously more mature, which explains the lower relative amounts of sulfur and differences in the composition of sulfur compounds [1]. *Sinninghe Damsté* and *de Leeuw* [1] have proposed a scheme for the diagenetic pathways of sulfur compounds and sulfur-containing high-molecular-weight substances, which is reproduced in **Figure 15**. Alkylated benzo- and dibenzothiophenes are generated from both cyclization and aromatization reactions of low-molecular-weight sulfur compounds as well as from thermal breakdown of sulfur-containing high-molecular-weight substances (*i.e.* kerogen and asphaltene). Both forms

of organically-bound sulfur are formed by incorporation of reduced inorganic sulfur species into a linear precursor (as an example) during early diagenesis. The last step in this diagenetical scheme is as yet hypothetical. Methyl transfer reactions are proposed to explain isomerization of aromatic hydrocarbons and sulfur compounds [33]. Complete identification of C₁-C₄ alkylbenzothiophenes is a prerequisite for the confirmation of this pathway.

The results from this study fit well into the proposed diagenetical scheme. The alkylated benzo- and dibenzothiophenes are products from diagenetic reactions as described above. Flash pyrolysis of the asphaltene revealed that in two samples some sulfur-containing moieties presumed to be precursors of low-molecular-weight alkylbenzothiophenes are still present. Moieties with linear carbon skeletons [24] dominate over other types of sulfur-containing structural units as shown by the abundance of 2-alkyl-4-methyl- and 2-methyl-4-alkylbenzothiophenes (Figs. 4A and 4B). Only the co-occurrence of both alkylthiolanes and alkylbenzothiophenes in the pyrolyzates of the polar fractions is somewhat puzzling in this respect.

4.3 Organically-Bound Sulfur in the Polar Fractions

Flash pyrolysis of the polar fractions indicated that the amount of sulfur compounds produced is generally relatively low. This is in sharp contrast with polar fractions of immature samples since sulfur compounds are often the most abundant components in their pyrolyzates [8]. The composition of the flash pyrolyzates of the polar fractions with respect to the sulfur compounds is completely different from those of the corresponding asphaltene fractions. This has been noted before in immature samples [8]. The relatively low abundance of sulfur compounds in the flash pyrolyzates is consistent with the low amounts of hydrocarbons released by Raney Ni desulfurization. This is, again, in contrast with immature samples since Raney Ni desulfurization of the polar fraction often yields hydrocarbons in relatively high yield (20% [5-14]). This is probably due to differences in degree of thermal maturity. (Poly)sulfide bonds are relatively weak and are, therefore, the first bonds in macromolecules to break upon thermal stress. The amounts of hydrocarbons released on Raney Ni desulfurization from the polar fractions on a total oil basis (Table 3) show a general trend with the total sulfur content with the sulfur-rich oils generating the highest amounts of saturated hydrocarbons upon desulfurization of the polar fraction.

The molecular compositions of the desulfurized polar I fractions reveal that this technique is useful in the characterization of crude oils. Although these fractions contain less abundant biomarkers (*i.e.* steranes, hopanes) than the corresponding fractions from immature

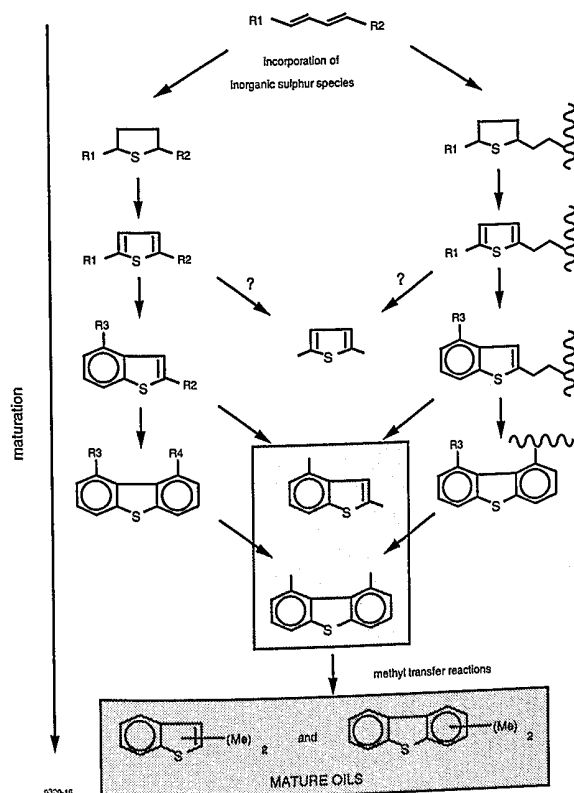


Figure 15
Possible diagenetic pathways for sulfur compounds and sulfur-containing high-molecular-weight substances (Reproduced with permission from *Organic Geochemistry*, 16, *J.S. Sinninghe Damsté* and *J.W. de Leeuw*, Analysis, the structure and geochemical significance of organically bound sulfur in the geosphere: State of the art and future research, © 1990 Pergamon Press plc.).

samples [5–14] and the amounts obtained (on a total oil basis) are low, the distributions of the hydrocarbon classes are different from those observed in the saturated hydrocarbon fractions and the relative abundances of compound classes are, sometimes, completely different. For example, the *n*-alkane distribution of the desulfurized polar I fraction of crude oil E (Venezuela) shows an even carbon number predominance whereas this is not the case for the *n*-alkanes present in the saturated hydrocarbon fraction of this oil. Furthermore, tricyclic terpanes are abundant components in the desulfurized polar I fraction of this oil and are much lower in the saturated hydrocarbon fraction. The obtained fingerprints are useful for correlation purposes.

In the case of immature samples, desulfurized polar fractions were obtained which contained biomarkers (e.g. C₃₅ hopanes, diaryl isoprenoids, C₃₇ and C₃₈ *n*-alkanes), which could be used to assess sources of organic matter [5–14]. In this respect, the desulfurized polar I fractions of the five oils studied contain significantly less information. However, a comparison of the compositions of the saturated hydrocarbon fractions of the five crude oils and those of the desulfurized polar I fractions indicates that the variations between the samples are greater for the latter fraction. Therefore, Raney Ni desulfurization is a useful fingerprinting technique for the characterization of crude oils.

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