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## IDENTIFICATION OF HOMOLOGOUS SERIES OF ALKYLATED THIOPHENES, THIOLANES, THIANES AND BENZOTHIOPHENES PRESENT IN PYROLYSATES OF SULPHUR-RICH KEROGENS

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### SUMMARY

The ability of flash pyrolysis–gas chromatography with dual flame ionization and flame photometric detection, and flash pyrolysis–gas chromatography–mass spectrometry, to afford detailed information about the organic sulphur pyrolysis products of kerogens is exemplified through analysis of five different sulphur-rich, type II kerogens. The pyrolysates of these kerogens are extremely complex mixtures. The technique with flame photometric detection yields a chromatogram that shows the distribution of only organic sulphur products in the pyrolysates. However, a considerable loss of sensitivity in flame photometric detection was apparent for higher-molecular-weight compounds. The use of the mass spectrometer as a detector, using characteristic  $m/z$  values of organic sulphur compounds for appropriate mass chromatograms, was therefore preferable. Identification of the organic sulphur products was accomplished by sulphur-selective flame photometric detection and comparison of their mass spectral and chromatographic data with those of standard reference compounds. Chromatographic retention time data for 48 standard sulphur compounds (alkylated thiophenes, thiolanes and benzo[*b*]thiophenes) were determined. Homologous series of 2-alkylthiophenes, 2-alkyl-5-methylthiophenes, 2-alkyl-5-ethylthiophenes, 2-alkylthiolanes, 2-alkylthianes, 2-alkyl-5-methylthiolanes, 2-alkyl-4-methylbenzo[*b*]thiophenes, 4-alkyl-2-methylbenzo[*b*]thiophenes and 2-alkylbenzo[*b*]thiophenes, through a total carbon number of 22, have been identified through linear Kováts plots and comparison of mass spectral and chromatographic data of the  $C_{18}$  members of these series with those of standard compounds.

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### INTRODUCTION

Sulphur compounds are present in almost all fossil fuels, and they cause many problems. They are deleterious to the refining of petroleum and of coal liquefaction products, because they poison catalysts and cause corrosion. Furthermore, noxious sulphur dioxide is produced during combustion of sulphur-containing fuels. As such

they are toxic and some of them are suspected mutagens and/or carcinogens. Better knowledge of the forms in which sulphur occurs in fossil fuels might aid the development of methods for its removal.

A major part of the organic sulphur present in these materials occurs as thiophenic compounds, which makes this an important class of sulphur compounds to study. In petroleum the thiophene ring is mostly present as part of ring systems (primarily benzo- and dibenzothiophenes)<sup>1-3</sup> but alkylated thiophenes also occur<sup>4</sup> and are the most abundant thiophenic compounds present in shale oils<sup>5</sup>. Alkylated thiophenes are also major compounds in several sediment extracts and immature crude oils<sup>6-9</sup>. Lee and co-workers<sup>10-14</sup> and Burchill *et al.*<sup>15</sup> have identified a number of polycyclic aromatic sulphur heterocyclics in oils, synfuels, coal liquids and shale oils.

Surprisingly, no detailed chromatographic data have been published concerning alkylated thiophenes, although a number of these compounds have been synthesized for various reasons, *e.g.* mass spectrometric (MS) studies<sup>16-19</sup> and flavour evaluation<sup>20</sup>. We are especially interested in a firm identification of these alkylated thiophenes, because they are sometimes major products obtained by flash pyrolysis of kerogens, the insoluble macromolecular organic constituent of sedimentary rocks and the precursor material for petroleum.

Flash pyrolysis (Py), in combination with gas chromatography (GC) and/or mass spectrometry (MS), has been used in organic geochemistry to characterize bi- and geopolymers such as lignins<sup>21,22</sup>, humic substances<sup>23,24</sup>, coals<sup>25-27</sup>, asphaltenes<sup>28-30</sup> and kerogens<sup>25,29-35</sup> by identification of their pyrolysis products and evaluation of their relative amounts. For instance, Py-GC of the different kerogen types provides distinct fingerprints, which are useful in source rock evaluation<sup>35</sup>. We have used Py-GC and Py-GC-MS to study the structure of sulphur-rich kerogens, so-called Type II-S kerogens, which are inferred to be the source of most major high-sulphur crude oil accumulations<sup>36</sup>. This may provide an insight into the way sulphur becomes incorporated into organic matter in the geosphere and how organic sulphur compounds in crude oils have been formed. In this paper we will focus on the analytical aspects of this work; the geochemical significance of these findings will be described elsewhere<sup>37</sup>.

## EXPERIMENTAL

### *Samples*

Five samples were studied: Phosphoria Retort Shale (Montana, U.S.A.; Permian), three outcrop samples from the Monterey formation (California, U.S.A.; Miocene) and the oil shale of Jurf ed Darawish (Jordan; Cretaceous). The samples were ground in a rotary disc mill, and the powdered samples were exhaustively (40 h) Soxhlet extracted with a toluene-methanol (1:3) azeotrope.

### *Standards*

Thiophene, 2-methylthiophene, 3-methylthiophene, 2,5-dimethylthiophene and 2-ethylthiophene were commercially available. 5-Lithio derivatives of 2-methylthiophene, 3-methylthiophene, 2,3-dimethylthiophene, 2,4-dimethylthiophene and 2-ethylthiophene were obtained by reaction of these thiophenes with *n*-butyllithium. Subsequent alkylation of these lithio derivatives with ethyl bromide, 1-propyl brom-

ide and 1-butyl bromide<sup>38</sup> yielded the 5-ethyl, 5-propyl and 5-butyl derivatives of the starting thiophenes. 2-Propylthiophene, 2-butylthiophene and 2-pentylthiophene were prepared by alkylation of 2-lithiothiophene with 1-propyl bromide, 1-butyl bromide and 1-pentyl bromide. 2,4-Dimethylthiophene was obtained by methylation with dimethylsulphate of 2-lithio-4-methylthiophene. 2-Lithio-4-methylthiophene was obtained by reaction of *n*-butyllithium with 3-methylthiophene. 3,4-Dimethylthiophene, 2,3,4-trimethylthiophene, 2,3,5-trimethylthiophene and 2,3,4,5-tetramethylthiophene were prepared by metallation with *n*-butyllithium of, respectively, 3,4-dibromothiophene, 2,3,4-tribromothiophene, 2,3,5-tribromothiophene and 2,3,4,5-tetrabromothiophene, followed by subsequent methylation with dimethyl sulphate<sup>39</sup>. 2,3,5-Tribromothiophene and 2,3,4,5-tetrabromothiophene were prepared by bromination of thiophene<sup>39</sup>. 3,4-Dibromothiophene and 2,3,4-tribromothiophene were prepared by a Grignard reaction of 2,3,4,5-tetrabromothiophene with magnesium and 1,2-dibromoethane<sup>39</sup>.

Thiolane, 2-methylthiolane, 2-ethylthiolane, and the *cis* and *trans* isomers of 2,5-dimethylthiolane, 2-ethyl-5-methylthiolane, 2-methyl-5-propylthiolane and 2-butyl-5-methylthiolane were prepared by hydrogenation with triethylsilane of the corresponding thiophenes<sup>40,41</sup>.

2-Methyl-5-tridecylthiophene, 2-dodecyl-5-ethylthiophene and 2-methyl-5-tridecylthiolane were prepared previously<sup>6,9</sup>. 2-Tetradecylthiophene was prepared by coupling of thiophene with tetradecanoic acid with phosphorus pentoxide as a dehydrating agent. The obtained ketone was reduced via a modified Wolff-Kishner reaction<sup>42</sup>. 2-Tetradecylthiolane was prepared by hydrogenation with triethylsilane of 2-tetradecylthiophene<sup>40,41</sup>.

4-Nonylbenzo[*b*]thiophene, 2-decylbenzo[*b*]thiophene, 4-nonyl-2-methylbenzo[*b*]thiophene and 2-nonyl-4-methylbenzo[*b*]thiophene were made available for this study by Dr. P. Albrecht (University of Strasbourg, Strasbourg, France). The preparation of these compounds has been described by Perakis<sup>43</sup>.

#### *Curie point pyrolysis-gas chromatography*

Curie point Py-GC analysis of extracted samples was carried out using a pyrolysis reactor, previously described by Van de Meent *et al.*<sup>32</sup>, 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 pressing the dry samples on the wire<sup>44</sup>. The wires were heated within 0.1 s to their Curie temperature (in this case 610°C), and were kept at this temperature for 10 s. The pyrolysis products were separated on a fused-silica capillary column (25 m × 0.32 mm I.D.) coated with SP-Sil 5 (film thickness 0.45 µm) 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°C/min. The gas chromatograph was equipped for a flame ionization detection (FID) and flame photometric detection (FPD). The flow from the capillary column was split at the end with a splitter device (FPD:FID = 4:1), as described by Cox and Earp<sup>45</sup>.

#### *Curie point pyrolysis-gas chromatography-mass spectrometry*

Curie point Py-GC-MS analysis was performed on a Varian 3700 gas chromatograph connected to a Varian MAT 44 S quadrupole mass spectrometer by an

open atmospheric split device. Electron impact mass spectra were obtained at 80 eV under the following conditions: cycle time, 2 s; mass range,  $m/z$  20–450 up to scan 250 and  $m/z$  50–450 after scan 250;  $m/z$  28, 32, 40 and 44 were omitted from the reconstructed total ion currents. The same pyrolysis reactor, capillary column and temperature conditions were used as described for the Py–GC experiments.

#### Retention index measurements

A function was obtained by fitting a polynome of the third order through the data points (retention index, scan number) of the homologous series of *n*-alkanes present in the pyrolysates of the kerogens for each run. Subsequently, the retention indices of the organic sulphur compounds of the pyrolysates were calculated by the scan number of peaks in the reconstructed total ion current or mass chromatograms corresponding to these compounds and this regression function.

The retention indices of the standards were measured using the same methodology but by coinjection of these compounds with a standard solution of *n*-alkanes on the same capillary column and using the same temperature programme as described for the Py–GC and Py–GC–MS experiments.

#### RESULTS AND DISCUSSION

Fig. 1 is a typical example of an FID and FPD chromatogram obtained by flash Py of a sulphur-rich kerogen. The FPD chromatogram shows the distribution

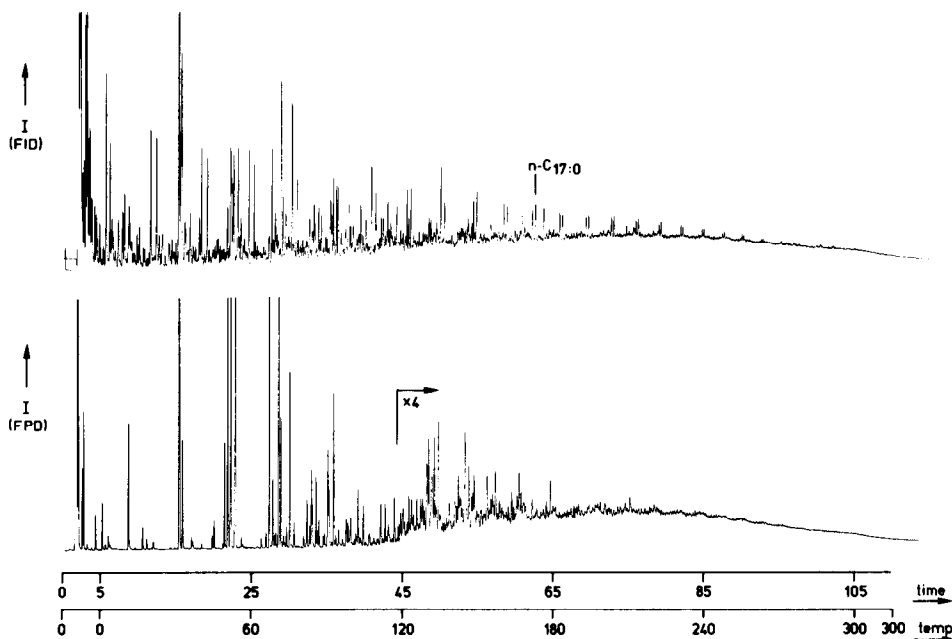


Fig. 1. FID and FPD chromatograms of the pyrolysis products generated by flash pyrolysis (Curie temperature 610°C) of the kerogen of the Phosphoria Retort Shale. Conditions: 25 m  $\times$  0.32 mm I.D. fused-silica capillary column coated with CP-Sil 5 (film thickness 0.45  $\mu$ m), temperature programmed 0–300°C at 3°C/min. n-C-17:0 indicates heptadecane.

of the organic sulphur pyrolysis products (OSPPs) generated by pyrolysis. Such a chromatogram of OSPPs may be very useful to characterize this and other types of kerogen. A disadvantage, however, is that in the range of molecular weights of OSPPs [e.g. thiophenes from 84 ( $C_4H_4S$ ) up to 336 ( $C_{22}H_{40}S$ ); see below] the sensitivity of FPD for these compounds decreases considerably as a result of the decreasing atomic sulphur fraction with increasing molecular weight (Fig. 2). This loss of sensitivity is even more severe as a result of the approximately quadratic FPD response. The mass spectrometer does not have this disadvantage and is, therefore, more suitable as a detector for this type of analysis by using appropriate mass chromatography to resolve the distributions of the OSPPs.

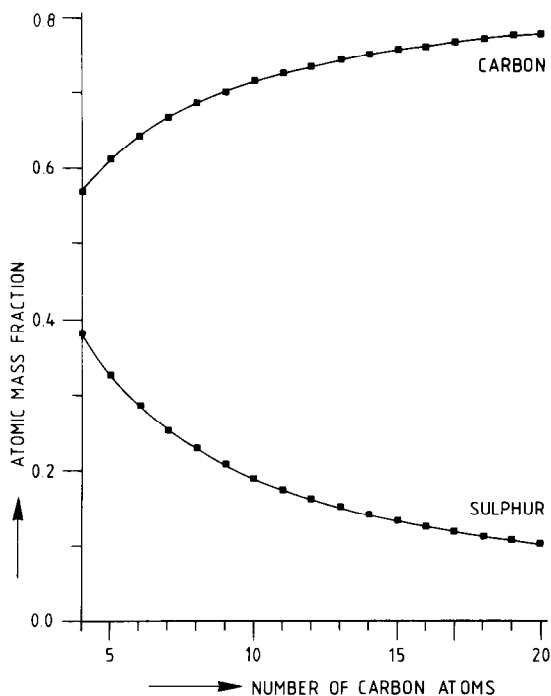


Fig. 2. Atomic sulphur and atomic carbon fraction (by weight) of alkylated thiophenes as a function of the molecular weight. Because the flame photometric detector exhibits an approximately quadratic response to the mass flow ( $ng\ S/s$ )<sup>47</sup>, these curves show the decreasing sensitivity of this detector compared with that of the flame ionization detector for detection of these thiophenes with increasing molecular weight.

#### Identification of low-molecular-weight OSPPs

The OSPPs were identified from mass spectral data and comparison of retention indices (*I*) of a number of commercially available and synthetically prepared organic sulphur compounds with those of the OSPPs. Fig. 3 shows the low-molecular-weight part of a representative chromatogram of Py products as recorded by FPD. The numbers in Fig. 3 refer to compounds listed in Table I. Most of the major compounds are alkylated thiophenes.

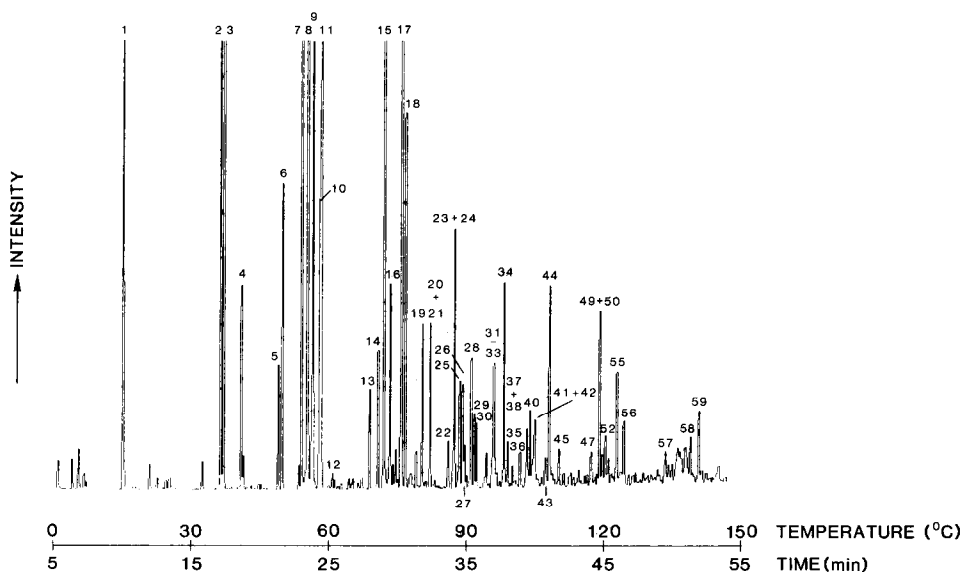


Fig. 3. Partial FPD chromatogram of the pyrolysis products generated by flash pyrolysis (Curie temperature 610°C) of the kerogen of the oil shale of Jurf ed Darawish. Conditions are given in the caption of Fig. 1. Peak numbers refer to compounds listed in Table I.

**Alkylated thiophenes.** A number of mass spectra of low-molecular-weight alkylated thiophenes have been reported<sup>16–19</sup>. The base peak for most of these thiophenes results from the breaking of a  $\beta$ -bond and expulsion of the largest alkyl residue (Table I). Exceptions to this generalization are 2,3,4- and 2,3,5-trimethylthiophene and 2,3,4,5-tetramethylthiophene, which yield base peaks at  $M^+ - CH_3$  (Fig. 4). This has been ascribed to a rearrangement involving the participation of a neighbouring methyl group<sup>46</sup>. All low-molecular-weight alkylated thiophenes show a molecular ion in their mass spectra. Therefore, mass chromatography of the  $m/z$  values of the molecular ions reveals the clusters of isomers of alkylated thiophenes in the pyrolysates (Fig. 5). Mass spectra of positional isomers often resemble each other (*e.g.* 2,3-, 2,4-, 2,5- and 3,4-dimethylthiophene; Table I), which prevents full identification. MS correlations for thiophenes have been reported by Kinney and Cook<sup>16</sup>. They can be applied to discriminate the mass spectra of positional isomers of low-molecular-weight thiophenes to a certain extent. However, most of these correlations are based on small peaks in the mass spectra of pure standards and are, therefore, difficult to apply in this study because of the considerable background in the mass spectra, which results from the complexity of the pyrolysates. Moreover, it is not possible to discriminate all positional isomers of alkylated thiophenes with  $C_{tot} > C_5$  with these MS correlations. Therefore complementary relative retention time data are a prerequisite for the full identification of structural isomers.

A number of low-molecular-weight thiophenes have been prepared and their  $I$  values were determined under the same experimental conditions as described for the Py experiments (Table II). These data were in good agreement with the  $I$  data of the OSPPs, which were obtained from the retention times of these

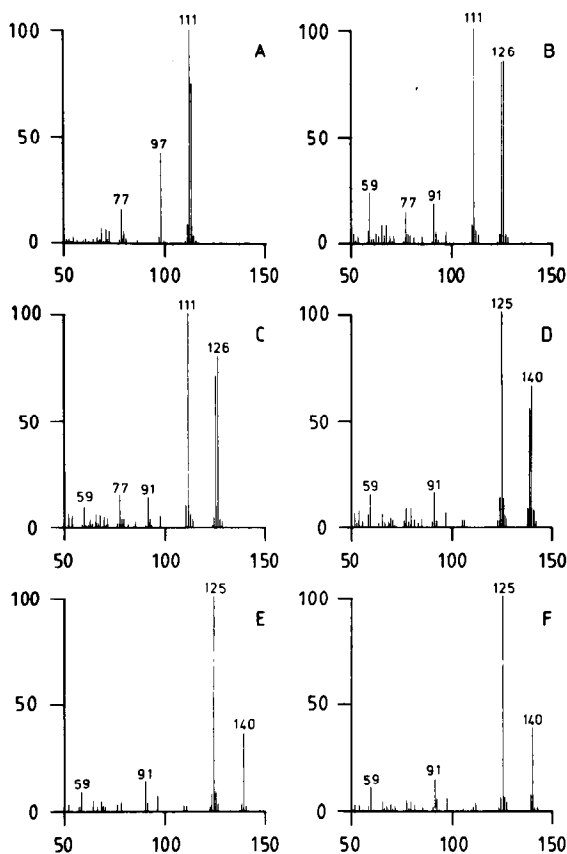


Fig. 4. Mass spectra (corrected for background) of several synthetic thiophenes: (A) 3,4-dimethylthiophene; (B) 2,3,5-trimethylthiophene; (C) 2,3,4-trimethylthiophene; (D) 2,3,4,5-tetramethylthiophene; (E) 2-ethyl-3,5-dimethylthiophene; (F) 5-ethyl-2,3-dimethylthiophene.

compounds and those of the homologous series of *n*-alkanes also generated by Py (Fig. 5). The standard deviation of the *I* data of the OSPPs (Table I) was determined by measuring the *I* values of these compounds in six different Py-GC-MS runs. A considerable reduction of the standard deviation could be obtained by using the homologous series of 2-*n*-alkylthiophenes instead of *n*-alkanes as calibration standards, as proposed previously<sup>6</sup>. This, so-called, ATI (alkyl thiophene index) was purposely defined to distinguish isoprenoid thiophenes (alkylated thiophenes with an isoprenoid carbon skeleton) from 2,5-di-*n*-alkylthiophenes. These results show that this index can also be of value as an alternative *I* system in the case of sulphur compounds.

*Alkylated thiolanes and thianes.* Alkylated thiolanes and thianes were present in considerably smaller amounts than the alkylated thiophenes. They were identified from their MS and relative retention time data (Table III) and, in case of the alkylated thiolanes, from comparison with data for standards prepared by ionic hydrogenation<sup>40,41</sup> of corresponding thiophenes. Mass spectra of several low-molecular-weight cyclic sulphides have been reported<sup>19,48-51</sup>. Fig. 6 shows the distribution of these

TABLE I

MAJOR LOW-MOLECULAR-WEIGHT ORGANIC SULPHUR COMPOUNDS IDENTIFIED IN PYROLYSATES OF SULPHUR-RICH KEROGENS

No.*	Compound	Mol. wt.	I	S.D. (n=6)	ATI <sub>97</sub> **	S.D. (n=6)	CL***	Characteristic ions
1	Thiophene	84	643.7	1.1	—	—	SC	84(100), 83(15), 58(55)
2	2-Methylthiophene	98	750.5	2.0	500.0	—	SC	98(55), 97(100)
3	3-Methylthiophene	98	756.2	2.5	505.6	0.7	SC	98(55), 97(100)
4	Thiolane	88	774.9	2.4	525.8	1.2	SC	88(60), 87(20), 60(100)
5	Methyldihydrothiophene	100	815.6	1.0 <sup>§</sup>	571.9	0.3 <sup>§</sup>	C	100(90), 99(100), 85(90)
6	2-Methylthiolane	102	821.8	2.0	575.9	0.8	SC	102(55), 87(100)
7	2-Ethylthiophene	112	845.0	1.7	600.0	—	SC	112(40), 97(100)
8	2,5-Dimethylthiophene	112	852.4	1.8	608.2	1.1	SC	112(90), 111(100), 97(60), 59(20)
9	2,4-Dimethylthiophene	112	858.7	1.8	614.9	0.7	SC	112(75), 111(100), 97(40)
10	2-Vinylthiophene	110	866.9	1.6	623.0	0.4	C	110(100), 109(85), 84(25), 66(35)
11	2,3-Dimethylthiophene	112	868.2	2.4	625.2	0.6	SC	112(100), 111(90), 97(95)
12	3,4-Dimethylthiophene	112	881.5	2.0	638.9	0.3	SC	112(75), 111(100), 97(40)
13	2-Ethylthiolane	116	926.5	2.0	685.3	0.5	SC	116(25), 87(100)
14	2-Propylthiophene	126	937.0	1.6	700.0	—	SC	126(20), 97(100)
15	2-Ethyl-5-methylthiophene	126	945.3	1.5	704.5	0.6	SC	126(40), 111(100)
16	2-Ethyl-4-methylthiophene	126	952.7	1.6	712.1	0.3	SC	126(35), 111(100)
17	2,3,5-Trimethylthiophene	126	966.9	1.6	726.6	0.6	SC	126(85), 125(85), 111(100), 59(20)
18	2-Methyl-5-vinylthiophene	124	971.4	1.7	731.2	0.2	T	124(85), 123(100), 97(25)
19	2,3,4-Trimethylthiophene	126	993.4	2.1	733.4	0.8	SC	126(80), 125(70), 111(100)
20	Isopropylmethylthiophene	140	1003.5	1.8	763.7	0.6	C	140(25), 125(100), 97(25)
21	C <sub>3,1</sub> -Thiophene	124	1003.7	1.6	763.9	0.5	T	124(100), 123(50)
22	2-Propylthiolane	130	1027.5	2.0	787.8	0.7	C	130(20), 87(100)
23	2-Methyl-5-propylthiophene	140	1034.8	1.6	795.1	0.4	SC	140(25), 111(100)
24	2,5-Diethylthiophene	140	1034.8	1.6	795.1	0.4	SC	140(40), 125(100), 111(10), 110(10)
25	2-Butylthiophene	140	1041.1	1.7	800.0	—	SC	140(20), 97(100)
26	2-Ethyl-3,5-dimethylthiophene	140	1045.3	1.6	805.6	0.4	SC	140(40), 125(100), 59(10)
27	Ethylidimethylthiophene	140	1047.1	1.5	807.5	0.5	T	140(45), 125(100)
28	5-Ethyl-2,3-dimethylthiophene	140	1056.4	1.5	816.7	0.6	SC	140(40), 125(100), 59(10)
29	Ethylidimethylthiophene	140	1060.6	1.9	820.9	0.8	T	140(40), 125(100)
30	C <sub>4,1</sub> -Thiophene	138	1063.8	1.7	824.1	0.5	T	138(100), 137(60), 123(90)
31	C <sub>4,1</sub> -Thiophene	138	1085.8	1.5	845.8	0.3	T	138(100), 137(90), 123(30)



32	Ethyl dimethylthiophene	140	1087.0	1.6	847.0	0.5	T	140(25), 125(100)
33	C <sub>4:1</sub> -Thiophene	138	1089.1	1.9	849.1	0.7	T	138(100), 137(80), 123(55)
34	2,3,4,5-Tetramethylthiophene	140	1101.4	1.8	861.3	0.8	SC	140(70), 139(60), 125(100)
35	C <sub>4:1</sub> -Thiophene	138	1106.2	1.8	866.0	0.7	T	138(95), 137(60), 123(100)
36	2-Ethyl-5-propylthiophene	154	1122.5	1.3	882.0	0.5	SC	154(30), 125(100), 139(10), 110(10)
37	3,5-Dimethyl-2-propylthiophene	154	1131.3	1.6	890.7	0.5	SC	154(30), 125(100)
38	C <sub>5</sub> -Thiophene	154	1132.9	1.3	892.6	0.5	T	154(30), 139(100)
39	2-Butylthiolane	144	1133.2	2.0	892.3	0.9	C	144(10), 87(100)
40	2-Butyl-5-methylthiophene	154	1136.5	1.3	895.7	0.4	SC	154(20), 111(100)
41	2-Pentylthiophene	154	1142.5	1.4	900.1	—	SC	154(15), 97(100)
42	2,3-Dimethyl-5-propylthiophene	154	1144.0	1.4	903.1	0.4	SC	154(30), 125(100)
43	2-Propyl-5-vinylthiophene	152	1153.7	1.5	912.6	0.5	T	152(20), 123(100)
44	C <sub>5</sub> -Thiophene	154	1163.4	1.4	922.1	0.6	T	154(40), 139(100)
45	C <sub>5</sub> -Thiophene	154	1177.7	1.7	935.9	0.8	T	154(35), 139(100)
46	C <sub>6</sub> -Thiophene	168	1192.0	1.4	949.8	0.7	T	168(20), 125(100)
47	2-Butyl-5-ethylthiophene	168	1223.6	1.2	980.3	0.6	SC	168(25), 153(10), 125(100), 110(5)
48	2-Butyl-3,5-dimethylthiophene	168	1228.7	1.2	986.5	0.5	SC	168(20), 125(100)
49	2-Methyl-5-pentylthiophene	168	1236.6	1.2	993.0	0.4	C	168(20), 111(100)
50	2-Pentylthiolane	158	1237.8	2.1	994.2	0.8	C	158(10), 87(100)
51	C <sub>5</sub> -Thiophene	168	1240.8	1.7	997.0	0.5	T	168(35), 153(100)
52	2-Hexylthiophene	168	1245.1	1.5	1000.0	—	C	168(20), 97(100)
53	5-Butyl-2,3-dimethylthiophene	168	1245.1	1.5	1000.0	—	SC	168(20), 125(100)
54	2-Butyl-5-vinylthiophene	166	1256.4	1.7	1012.0	0.5	T	166(20), 123(100)
55	Methylbenzo[b]thiophene	148	1264.8	3.6	1020.1	2.2	C	148(65), 147(100)
56	Methylbenzo[b]thiophene	148	1276.9	3.9	1031.7	2.5	C	148(65), 147(100)
57	2-Hexyl-5-methylthiophene	182	1336.8	1.3	1089.1	0.3	C	182(15), 111(100)
58	Dimethylbenzo[b]thiophene	162	1381.5	4.3	1131.6	2.6	C	162(85), 161(100), 147(125)
59	Dimethylbenzo[b]thiophene	162	1395.0	4.7	1144.5	2.9	C	162(95), 161(65), 147(100)

\* Numbers refer to Figs. 3 and 5.

\*\* AT<sub>197</sub> = Alkyl thiophene index with the homologous series of 2-alkylthiophenes (which show base peaks at *m/z* 97 in their mass spectra) as calibration standards (ref. 6).

\*\*\* CL = confidence level of structural assignment; SC = standard confirmed, retention time and MS data agree with those of a standard; C = confident, mass spectrum is identical with a reference mass spectrum from the literature or MS database or the compound is a higher homologue of a synthetic standard as determined by a linear Kováts plot and a similar mass spectral fragmentation; T = tentative.

§ Two determinations.

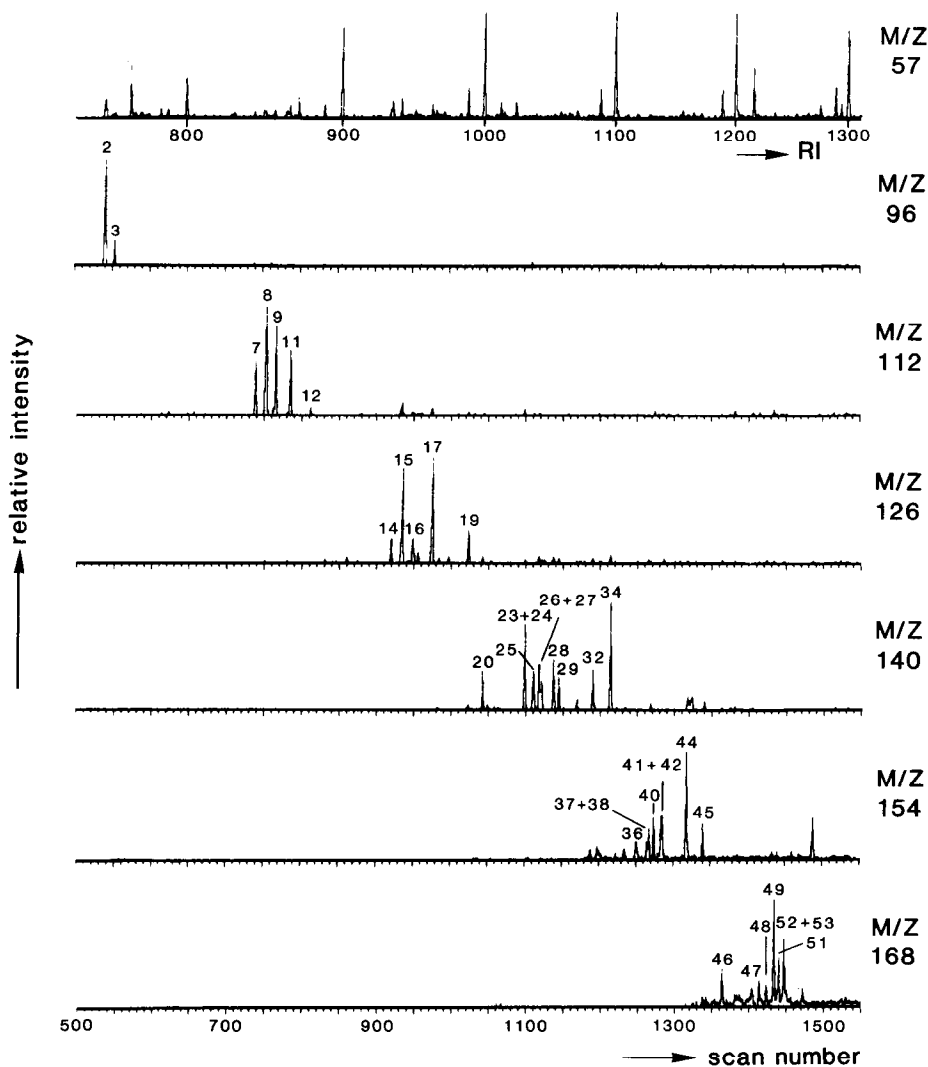


Fig. 5. Partial mass chromatograms showing the  $C_8$ – $C_{13}$  *n*-alkanes ( $m/z$  57) and the  $C_1$ – $C_6$  alkyl derivatives of thiophene ( $m/z$  96, 112, 126, 140, 154 and 168) present in the pyrolysate (Curie temperature  $610^\circ\text{C}$ ) of the kerogen of the oil shale of Jurf ed Darawish. Peak numbers refer to compounds listed in Table I. Conditions are given in the caption of Fig. 1.

compounds by means of mass chromatograms of  $m/z$  87 and 101. The peak numbers in Fig. 6 refer to compounds listed in Table III. The most abundant series is the 2-alkylthiolane series. The mass spectra of the members of this series are characterized by a base peak at  $m/z$  87 as a result of  $\alpha$ -cleavage. The mass chromatogram of  $m/z$  101 is much more complicated. Two series have been identified: the 2-alkyl-5-methylthiolane series and the 2-alkylthiane series. The mass spectra of these compounds are more or less similar, showing a base peak at  $m/z$  101 due to  $\alpha$ -cleavage. Synthesis

TABLE II  
RETENTION INDICES OF STANDARDS

Compound	<i>I</i>	<i>S.D.</i> ( <i>n</i> = 4)
<i>Alkylated thiophenes</i>		
Thiophene	644.9	0.1
2-Methylthiophene	749.8	0.1
3-Methylthiophene	757.2	0.2
2-Ethylthiophene	845.9	0.1
2,5-Dimethylthiophene	852.3	0.1
2,4-Dimethylthiophene	859.1	0.1
2,3-Dimethylthiophene	868.9	0.2
3,4-Dimethylthiophene	883.0	0.1
2-Propylthiophene	937.4	0.1
2-Ethyl-5-methylthiophene	944.1	0.1
2-Ethyl-4-methylthiophene	952.3	0.1
2,3,5-Trimethylthiophene	965.7	0.1
2,3,4-Trimethylthiophene	993.4	0.1
2-Methyl-5-propylthiophene	1033.3	0.2
2,5-Diethylthiophene	1033.3	0.2
2-Butylthiophene	1039.9	0.1
2-Propyl-4-methylthiophene	1040.6	0.1
2-Ethyl-3,5-dimethylthiophene	1043.6	0.1
5-Ethyl-2,3-dimethylthiophene	1055.0	0.4
2,3,4,5-Tetramethylthiophene	1100*	—
2-Ethyl-5-propylthiophene	1120.4	0.1
3,5-Dimethyl-2-propylthiophene	1128.9	0.2
2-Butyl-5-methylthiophene	1135.0	0.1
2-Pentylthiophene	1141.2	0.1
2-Butyl-4-methylthiophene	1141.9	0.1
2,3-Dimethyl-5-propylthiophene	1142.4	0.2
2-Butyl-5-ethylthiophene	1222.5	0.3
2-Butyl-3,5-dimethylthiophene	1228.7	0.3
5-Butyl-2,3-dimethylthiophene	1245.5	0.3
<i>Alkylated thiolanes</i>		
Thiolane	777.9	0.7
2-Methylthiolane	824.7	0.1
<i>cis</i> -2,5-Dimethylthiolane	862.7	0.0
<i>trans</i> -2,5-Dimethylthiolane	866.2	0.1
2-Ethylthiolane	928.3	0.1
<i>cis</i> -2-Ethyl-5-methylthiolane	962.5	0.1
<i>trans</i> -2-Ethyl-5-methylthiolane	966.4	0.2
<i>cis</i> -2-Methyl-5-propylthiolane	1059.7	0.2
<i>trans</i> -2-Methyl-5-propylthiolane	1062.3	0.2
2-Butyl-5-methylthiolane	1163.7	0.1
<i>Higher-molecular-weight organic sulphur compounds**</i>		
2-Tetradecylthiophene	2085.2	0.8***
2-Methyl-5-tridecylthiophene	2066.2	0.5***
2-Ethyl-5-dodecylthiophene	2046.1	0.9***
2-Tetradecylthiolane	2200 <sup>§</sup>	—
2-Methyl-5-tridecylthiolane (mixture of <i>cis</i> and <i>trans</i> )	2112.9	0.8***
4-Nonylbenzo[ <i>b</i> ]thiophene	2089.1	0.8***
2-Methyl-4-nonylbenzo[ <i>b</i> ]thiophene	2169.5	0.4***
4-Methyl-2-nonylbenzo[ <i>b</i> ]thiophene	2206.9	1.1***
2-Decylbenzo[ <i>b</i> ]thiophene	2212.3	1.4***

\* Coelution with undecane.

\*\* Measured with the following temperature programme: 50°C, 3°/min, 300°C.

\*\*\* Three determinations.

§ Coelution with docosane.

TABLE III

LOW-MOLECULAR-WEIGHT CYCLIC SULPHIDES IDENTIFIED IN PYROLYSATES OF SULPHUR-RICH KEROGENS

No.*	Compound	Mol.wt.	I	S.D.**	CL***
1	Thiolane	88	774.9	2.4	SC
2	2-Methylthiolane	102	821.8	2.0	SC
3	Thiane	102	841.8	2.4	C
4	<i>cis</i> -2,5-Dimethylthiolane	116	861.7	2.1	SC
5	<i>trans</i> -2,5-Dimethylthiolane	116	864.7	2.1	SC
6	2-Methylthiane	116	902.2	2.6	C
7	2-Ethylthiolane	116	926.5	2.0	SC
8	<i>cis</i> -2-Ethyl-5-methylthiolane	130	962.5	1.8	SC
9	<i>trans</i> -2-Ethyl-5-methylthiolane	130	966.5	1.9	SC
10	2-Ethylthiane	130	1010.6	2.5	C
11	2-Propylthiolane	130	1027.5	2.0	C
12	<i>cis</i> -2-Methyl-5-propylthiolane	144	1061.4	1.7	SC
13	<i>trans</i> -2-Methyl-5-propylthiolane	144	1064.2	1.8	SC
14	2-Propylthiane	144	1108.4	2.3	C
15	2-Butylthiolane	144	1133.2	2.0	C
16	2-Butyl-5-methylthiolane	158	1165.9	1.5	SC
17	2-Butylthiane	158	1212.1	2.6	C
18	2-Pentylthiolane	158	1237.8	2.1	C

\* Compound numbers refer to Fig. 6.

\*\* Five determinations (in different samples).

\*\*\* CL = Confidence level of structural assignment; see footnote to Table I.

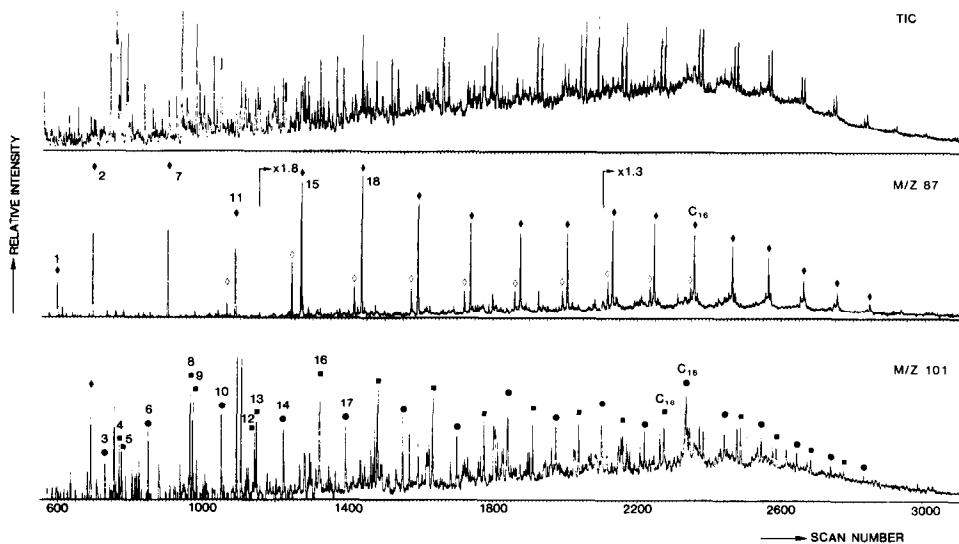


Fig. 6. Mass chromatograms of  $m/z$  87 and 101, showing the homologous series of 2-alkylthiolanes (black diamonds), 2-alkylthianes (black circles) and 2-alkyl-5-methylthiolanes (black squares), and part of the total ion chromatogram (TIC) (upper trace) of the pyrolysate (Curie temperature 610°C) of the kerogen of the oil shale of Jurf ed Darawish. Peak numbers refer to compounds listed in Table III.  $C_{16}$  indicates the member of the homologous series with 16 carbon atoms. The other homologous series present in the mass chromatogram of  $m/z$  87 (open diamonds) is that of 2-(alkenyl)thiolanes, probably 2-( $\omega$ -alkenyl)thiolanes. Conditions are given in the caption of Fig. 1.

of *cis* and *trans* isomers of 2,5-dimethylthiolane, 2-ethyl-5-methylthiolane, 2-methyl-5-propylthiolane and 2-butyl-5-methylthiolane showed that the isomers of the first three were separated under the GC conditions applied. The first eluting components were designated as the *cis* isomers, as was proved for the *cis* and *trans* isomers of 2,5-diheptylthiolane<sup>9</sup>. *I* data of the synthetic 2-alkyl-5-methylthiolanes was used to identify these compounds in the pyrolysates.

The identification of the 2-alkylthiane series was not based on synthesis of appropriate standards. However, the retention behaviour of these compounds indicated their identity. From data presented here it is known that 2-alkylthiolanes elute much later than the corresponding *cis*- and *trans*-2-alkyl-5-methylthiolane isomers (which coelute if  $C_{tot} > C_7$ ). Earlier work<sup>9</sup> showed that the other (both *cis* and *trans*) 2,5-di-*n*-alkylthiolane isomers elute just before the *cis*- and *trans*-2-alkyl-5-methylthiolanes. It was also shown that 2,5-di-*n*-alkylthianes elute just before the corresponding isomeric thiolanes<sup>9</sup>. Because the thiane series encountered here elute before the 2-alkylthiolane series but considerably later than the 2-alkyl-5-methylthiolane series, it is deemed likely to be the 2-alkylthiane series.

**Other compounds.** Apart from the alkylated thiophenes, thiolanes and thianes, several other low-molecular-weight OSPPs were identified on the basis of their MS data: unsaturated alkylated thiophenes (compounds 10, 18, 21, 30, 31, 33, 35, 43 and 54 in Table I), alkylated dihydrothiophenes (compound 5) and alkylated benzo[*b*]thiophenes (compounds 55, 56, 58 and 59).

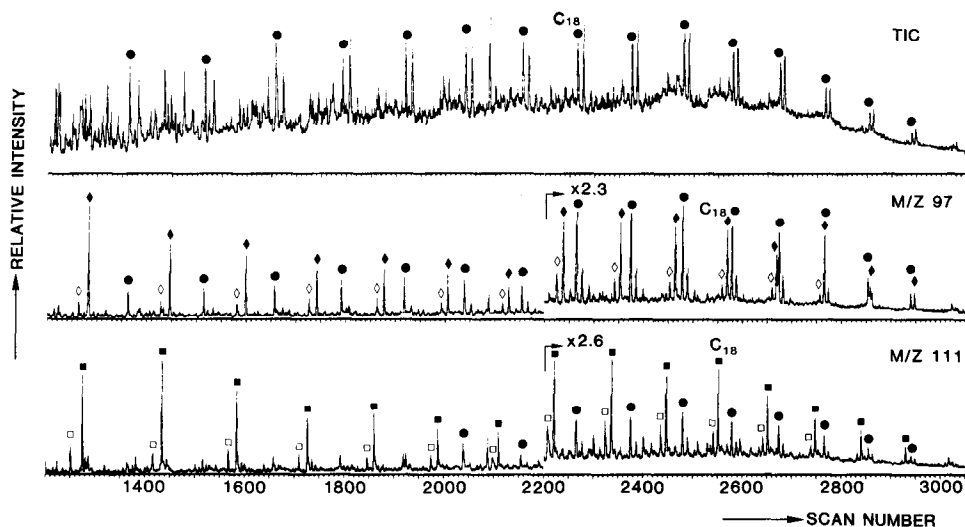


Fig. 7. Mass chromatograms of  $m/z$  97 and 111, showing the homologous series of 2-alkylthiophenes (black diamonds), 2-alkyl-5-methylthiophenes (black squares) and *n*-alk-1-enes (black circles), and part of the TIC (upper trace) of the pyrolysate (Curie temperature 610°C) of the kerogen of the oil shale of Jurf ed Darawish.  $C_{18}$  indicates the member of the homologous series with 18 carbon atoms. The other homologous series present in the mass chromatograms are those of 2-(alkenyl)thiophenes, probably 2-( $\omega$ -alkenyl)thiophenes (open diamonds) and 2-(alkenyl)-5-methylthiophenes, probably 2-( $\omega$ -alkenyl)-5-methylthiophenes (open squares). Conditions are given in the caption of Fig. 1.

### Identification of higher-molecular-weight OSPPs

In the higher-molecular-weight part of the pyrograms, mass chromatography of  $m/z$  97, 111, 125, 139, 87, 101, 147, 148, 161 and 162 revealed the presence of several homologous series. The mass chromatograms of  $m/z$  87 and 101,  $m/z$  97 and 111, and  $m/z$  147, 161 and 162 of typical Py-GC-MS runs are shown in Figs. 6–8. The compounds were identified from their MS and relative retention time data. The mass spectra of the higher-molecular-weight OSPPs were characterized by the base peaks indicated in Fig. 9 and a molecular ion. When the  $I$  values of these homologous series were plotted as a function of their carbon number, straight lines were obtained (Figs. 10 and 11). The constant methylene increment of  $I$  observed for these series strongly suggests that all the compounds are indeed members of the indicated homologous series. In the cases of 2-alkylthiophene (I), 2-alkyl-5-methylthiophene (II), 2-alkyl-5-ethylthiophene (III), 2-alkylthiolane (V), 2-alkyl-5-methylthiolane (VI) (both *cis* and *trans*), 2-alkyl-4-methylbenzo[*b*]thiophene (VII), 4-alkyl-2-methylben-

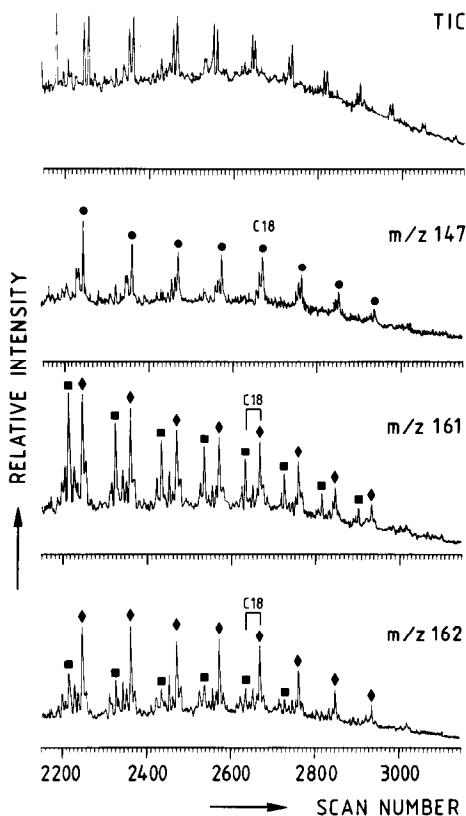


Fig. 8. Mass chromatograms of  $m/z$  147, 161 and 162, showing the homologous series of 2-alkylbenzo[*b*]thiophenes (black circles), 2-alkyl-4-methylbenzo[*b*]thiophenes (black squares) and 4-alkyl-2-methylbenzo[*b*]thiophenes (black diamonds), and part of the TIC (upper trace) of the pyrolysate (Curie temperature 610°C) of the kerogen of the Phosphoria Retort Shale. C<sub>18</sub> indicates the member of the homologous series with 18 carbon atoms. Conditions are given in the caption of Fig. 1.

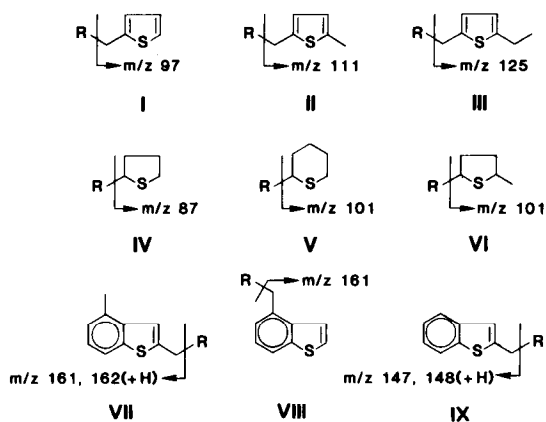


Fig. 9. Mass spectral fragmentation of nine homologous series of OSPPs encountered in pyrolysates of sulphur-rich kerogens.

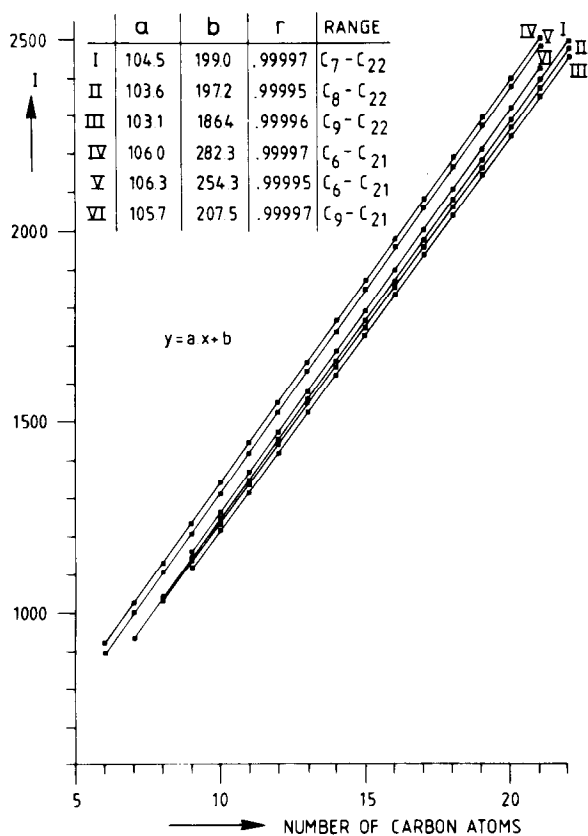


Fig. 10. Kováts plots for the homologous series of 2-alkylthiophenes (I), 2-alkyl-5-methylthiophenes (II), 2-alkyl-5-ethylthiophenes (III), 2-alkylthiolanes (V), and 2-alkyl-5-methylthiolanes (VI).

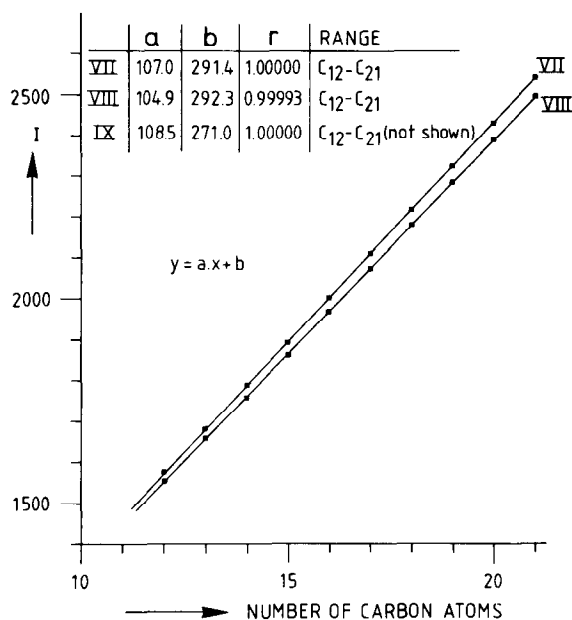


Fig. 11. Kováts plots for the homologous series of 2-alkyl-4-methylbenzo[b]thiophenes (VII) and 4-alkyl-2-methylbenzo[b]thiophenes (VIII).

zo[b]thiophene (VIII) and 2-alkylbenzo[b]thiophene (IX) series, these identifications were based on comparison of the MS and *I* (Table IV) data with those of synthetic C<sub>18</sub> standards of these homologous series (Table II).

TABLE IV

C<sub>18</sub> ORGANIC SULPHUR COMPOUNDS IDENTIFIED IN PYROLYSATES OF SULPHUR-RICH KEROGENS

Compound	Mol.wt.	<i>I</i>	S.D.*	CL**
<i>Thiophenes</i>				
2-Tetradecylthiophene	280	2087.3	2.9	SC
2-Methyl-5-tridecylthiophene	280	2069.1	3.0	SC
2-Dodecyl-5-ethylthiophene	280	2048.0	3.1	SC
<i>Thiolanes</i>				
2-Tetradecylthiolane	284	2199.4	3.3	SC
2-Methyl-5-tridecylthiolane	284	2115.9	2.9***	SC
<i>Benzothiophenes</i>				
2-Decylbenzo[b]thiophene	274	2222.6	1.1§	SC
4-Methyl-2-nonylbenzo[b]thiophene	274	2217.2	0.7§	SC
2-Methyl-4-nonylbenzo[b]thiophene	274	2178.6	1.0§	SC

\* Five determinations (in different samples).

\*\* CL = Confidence Level of structural assignment; see footnote to Table I.

\*\*\* Four determinations.

§ Two determinations of the same sample.



## CONCLUSIONS

Py-GC-FID/FPD and Py-GC-MS analysis of five different sulphur-rich, type II-S kerogens revealed the presence of large numbers of OSPPs. Detection of these compounds by MS is preferable over sulphur-selective FPD because of the considerable loss of sensitivity of the latter for higher-molecular-weight components. MS and relative retention time data of a number of synthetic standards were of vital importance for identifying most of the low-molecular-weight OSPPs. In the higher-molecular-weight range, homologous series of 2-alkylthiophenes, 2-alkyl-5-methylthiophenes, 2-alkyl-5-ethylthiophenes, 2-alkylthiolanes, 2-alkylthianes, 2-alkyl-5-methylthiolanes, 2-alkyl-4-methylbenzo[*b*]thiophenes, 4-alkyl-2-methylbenzo[*b*]thiophenes and 2-alkylbenzo[*b*]thiophenes were identified by the straight lines obtained in their Kováts plots and by comparison of MS and relative retention time data of the C<sub>18</sub> members of these series with those of synthetic standards (except for the 2-alkylthiane series).

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