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# IDENTIFICATION OF SULPHUR HETEROCYCLES IN COAL TAR AND PITCH

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## SUMMARY

The direct application of gas chromatography with a flame photometric sulphur detector and mass spectrometry to the identification of sulphur heterocycles in coal tar and pitch without the need for prior separation of a sulphur-rich fraction is described. Accurate mass measurement has allowed the assignment of atomic compositions to the sulphur heterocycles with little ambiguity, despite their presence as minor components in a complex aromatic mixture. Single ion chromatograms and retention indices calculated relative to aromatic hydrocarbons have been used to correlate the mass spectral identifications with the sulphur-selective gas chromatograms.

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## INTRODUCTION

Sulphur occurs to some extent in all fossil fuels, and sulphur compounds are found as minor components in the pyrolysis and combustion products. Their presence in fuels is generally undesirable since they tend to poison certain catalysts used in the refining of petroleum and coal liquefaction products. The release into the atmosphere of $SO_2$ from combustion processes has led to limitation of the sulphur content of fuels in some countries. In addition, a number of sulphur heterocycles are suspected mutagens and/or carcinogens[1–3]. Sulphur heterocycles have not been characterised as fully as the parent polycyclic aromatic hydrocarbons, but the development of methods for their identification and measurement is clearly desirable for assessment of the health hazards associated with the processing of coal tars and synthetic fuels. Knowledge of the forms in which sulphur occurs in these materials should also assist in the development of improved methods for its removal.

The analytical methods which have been applied successfully to the determination of sulphur compounds have generally involved gas–liquid chromatography (GC) in conjunction with sulphur-selective detection or mass spectrometry. A few applications of microcoulometric[4–6] and electrolytic conductivity[7,8] detectors have been reported, but the most popular sulphur-selective method has involved the use of the photometric detector (FPD). However, despite its widespread use, the FPD has

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been the subject of criticism, particularly because of its non-linear response, and deviations from the theoretical square law relationship between response and concentration[9,10]. Some workers have found that co-elution of hydrocarbons may result in quenching of the sulphur response[11,12]; this may be a serious problem when the sulphur compounds are present as trace components, but it can be alleviated to some extent by the use of high resolution capillary columns[13] or modifications to the detector geometry[11,14,15]. Nevertheless, GC in conjunction with sulphur-selective detectors is extremely useful for the preliminary screening of samples and the generation of sulphur profiles[10,16,17]. In the absence of standard reference compounds it is a poor identification technique, however, and mass spectrometry (MS) has generally been used for the identification of specific compounds.

MS type analysis[18,19] and GC–MS[20–23] of unfractionated coal tars and related materials has resulted in the identification of a number of sulphur heterocycles, but these compounds are generally present as minor components in complex aromatic mixtures, and isolation of a sulphur-rich fraction prior to analysis has usually been found necessary. Most of the standard fractionation schemes for petroleum products, reviewed by Altgelt *et al.*[24], are unsatisfactory for sulphur heterocycles since these are normally eluted with the polycyclic aromatic hydrocarbons (PAHs). However, Drushel and Sommers[6] have described a method for the isolation of sulphur compounds from high boiling petroleum distillates, and a modification of their procedure has recently been applied by Lee and co-workers[1,25] to coal liquids and shale oils. The latter method involves the initial preparation of an aromatic fraction containing the sulphur heterocycles, followed by oxidation with $H_2O_2$ in acetic acid. The sulphur heterocycles are oxidised to sulphones, separated from the unreacted PAHs by column chromatography on silica gel and reduced back to sulphides with $LiAlH_4$. Although this method appears to be the most successful technique currently available, and permits the isolation of a fraction containing thiophenic compounds, it does have disadvantages. Overlap of the PAH and sulphone bands during the column chromatography step results in the presence of some PAHs with the thiophenic compounds. Oxidation of certain PAHs to quinones and subsequent reduction to hydroquinones necessitates a further silica gel column chromatography step to separate the hydroquinones from the regenerated sulphur heterocycles. The authors have suggested that oxidation of the sulphur heterocycles at positions other than the sulphur atom may result in their removal in the same way as the oxidised PAHs. Also, hydrogenation of benzothiophenes in the reduction step may occur at the double bond between the 2 and 3 positions; many of the benzothiophenes observed were partially hydrogenated, although the higher-molecular-weight benzologues appear to be stable under similar conditions.

In view of the possibility of sample degradation by the method described above, and the inefficiency and time-consuming nature of other separation schemes for sulphur heterocycles, it is felt that the investigation of unfractionated materials may be more appropriate for these compounds. The present paper reports the application of GC with a flame photometric sulphur detector and MS to the identification of sulphur compounds in unfractionated samples of coal tar and pitch.

## EXPERIMENTAL

The coke oven pitch investigated was a standard commercial product. The tar was prepared by Gray–King assay at 600°C from a German coal (Leopold, Hagen seam). Ultimate analyses for the samples were as follows, expressed as weight %: pitch C 91.4, H 4.4, N 1.3, O 1.5, S 1.07; tar C 82.9; H 7.8, N 1.0, O 6.6, S 0.65.

The samples were analysed by GC using a Perkin-Elmer F-17 chromatograph fitted with a flame ionisation detector (FID) and a sulphur-selective FPD. 0.2-$\mu$l splitless injections of 4% solutions in tetrahydrofuran were made on to SGE glass support-coated open tubular (SCOT) capillary columns coated with OV-17 or SP-2250 50% methyl, 50% phenyl silicone stationary phases, using helium carrier gas. The FPD combustion gas flows were adjusted for maximum sulphur response; the optimised flows were 10.0 ml/min for oxygen, and 110 ml/min for hydrogen. Other chromatographic conditions are given on the appropriate chromatograms.

Identification of specific compounds was achieved using GC–MS. A Perkin-Elmer F-17 chromatograph was interfaced with a Kratos MS-30 double beam mass spectrometer via a silicone rubber membrane separator maintained at 250°C. Chromatographic parameters were matched to those used for the GC–FPD and GC–FID analyses, particular attention being paid to the carrier gas linear velocity to ensure comparable elution times. Using 70-eV electron impact ionisation, up to 800 mass spectral scans were collected at 3 sec per decade of mass over the mass range 50–400 at a resolution of 3000. A Kratos DS-50 data system was used to generate total ionisation current (TIC) chromatograms, and single ion chromatograms for selected masses. Accurate mass matching allowed the assignment of atomic compositions to the sulphur compounds detected.

## RESULTS AND DISCUSSION

A preliminary GC–FPD investigation indicated by the appearance of negative peaks for the major hydrocarbon components that quenching of the sulphur emission by hydrocarbons was occurring. Optimisation of the FPD flame conditions by adjusting the combustion gas flows to give maximum sulphur response effectively eliminated the hydrocarbon quenching, and the negative peaks disappeared. Under these conditions a plot of $(\text{response})^{1/2}$ against weight of dibenzothiophene injected was linear over two decades (0.1–10 ng), thus confirming the theoretical square law relationship between response and concentration. The pitch and tar samples were analysed by GC–FPD under the optimised conditions, and yielded the complex chromatograms shown in Fig. 1 and 2, respectively. The samples were then analysed by GC–MS under matched chromatographic conditions.

To identify the sulphur compounds in these samples, it was necessary to locate the MS scan corresponding to teach peak in the GC–FPD chromatogram. This was achieved by calculating retention coefficients for the sulphur compounds detected in the GC–FPD chromatograms relative to naphthalene = 0 and benzo[*g*,*h*,*i*]perylene = 10.0 for the pitch, and naphthalene = 0 and chrysene = 10.0 for the tar, using retention times for the aromatic hydrocarbons obtained from GC–FID analyses under identical chromatographic conditions. Retention coefficients were calculated similarly for the GC–MS TIC chromatograms using the appropriate MS scan num-

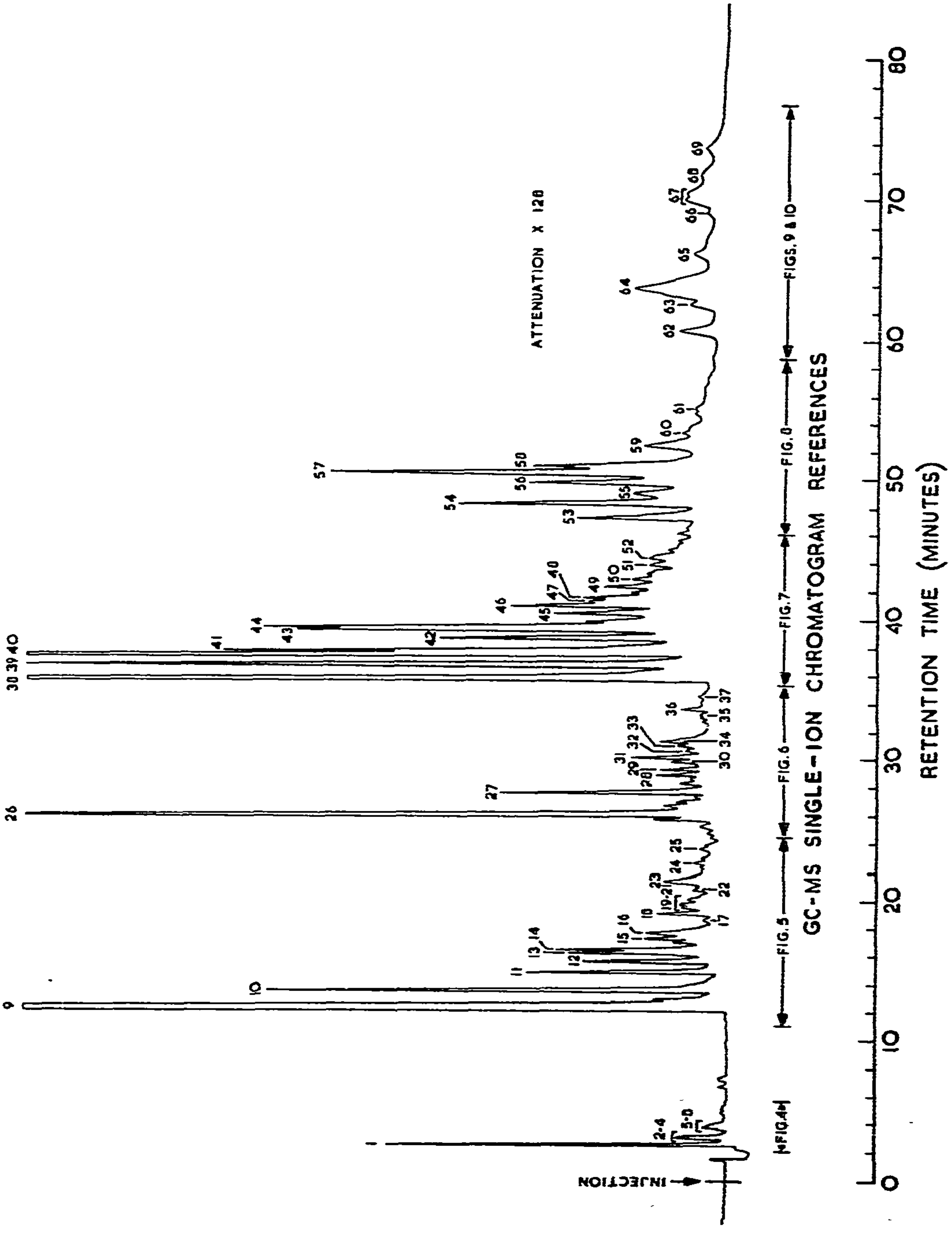


Fig. 1. GC–FPD chromatogram of coke oven pitch. Peak numbers refer to compounds listed in Table II. Conditions: 35-m OV-17 glass SCOT capillary column programmed from 180 to 285°C at 3°/min with 10-min initial hold.

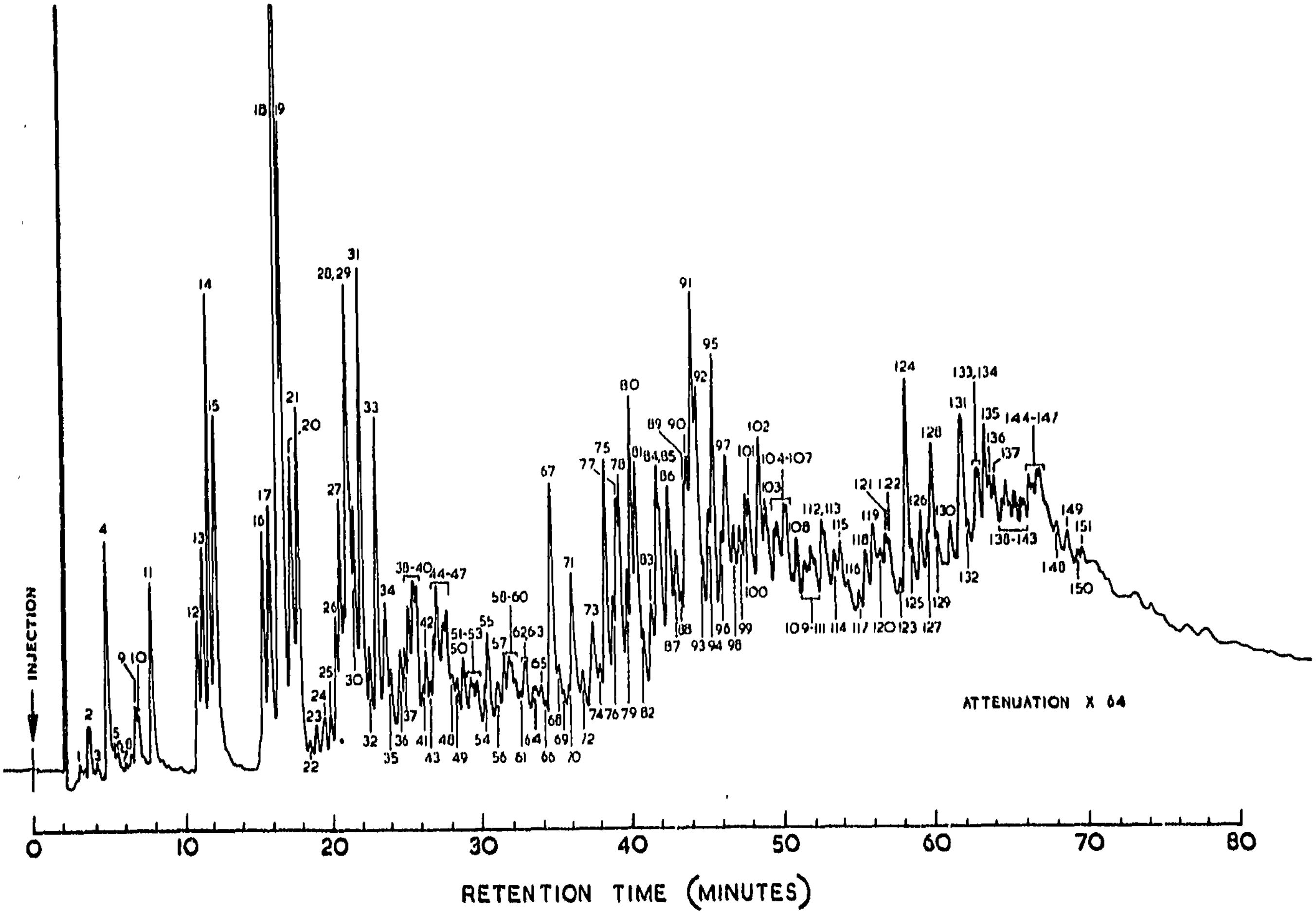


Fig. 2. GC-FPD chromatogram of Gray–King tar. Peak numbers refer to compounds listed in Table III. Conditions: 39-m SP-2250 glass SCOT capillary column programmed from 120 to 285°C at 3°/min with 10-min initial hold.

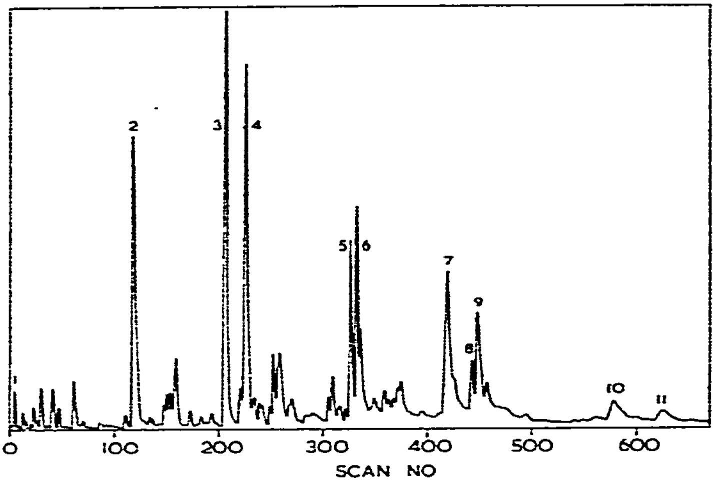


Fig. 3. GC–MS TIC chromatogram of coke oven pitch. Peak numbers refer to compounds listed in Table I. Conditions: 50-m OV-17 glass SCOT capillary column programmed from 180 to 285°C at 3°/min with 10-min initial hold.

bers for naphthalene, chrysene and benzo[*g*,*h*,*i*]perylene, which were present in the samples. The GC–MS TIC chromatogram of the coke oven pitch is shown in Fig. 3; identifications for the numbered peaks, which represent the major aromatic hydrocarbons, are given in Table I. In this way the MS scan number corresponding to each peak in the GC–FPD chromatograms could be calculated.

Accurate mass measurement to within ±0.005 a.m.u. using the double beam technique enabled the assignment of atomic compositions to all the components de-

TABLE I

MAJOR AROMATIC HYDROCARBON COMPONENTS IDENTIFIED IN COKE OVEN PITCH

Peak numbers refer to GC–MS TIC chromatogram in Fig. 3. MS scan numbers to GC–MS TIC chromatogram in Fig. 3 and GC–MS single ion chromatograms in Figs. 4–10. Retention times relative to naphthalene = 0 and benzo[*g*,*h*,*i*]perylene = 10.0. For definition of "Z No." see ref. 27, Table II.

| *Peak No.* | *MS scan No.* | *m/z* | *Atomic composition* | *Z No.* | *Compound* | *Retention coefficients* | |
|---|---|---|---|---|---|---|---|
| | | | | | | *GC–FID* | *GC–MS* |
| 1 | 6 | 128 | $C_{10}H_8$ | −12 | Naphthalene | 0.00 | 0.00 |
| 2 | 119 | 178 | $C_{14}H_{10}$ | −18 | Phenanthrene/Anthracene | 1.77 | 1.82 |
| 3 | 208 | 202 | $C_{16}H_{10}$ | −22 | Fluoranthene | 3.20 | 3.26 |
| 4 | 227 | 202 | $C_{16}H_{10}$ | −22 | Pyrene | 3.52 | 3.57 |
| 5 | 328 | 228 | $C_{18}H_{12}$ | −24 | Benz[*a*]anthracene | 5.16 | 5.20 |
| 6 | 333 | 228 | $C_{18}H_{12}$ | −24 | Chrysene | 5.23 | 5.28 |
| 7 | 420 | 252 | $C_{20}H_{12}$ | −28 | Benzo[*b* + *j* + *k*]fluoranthenes | 6.59–6.66 | 6.69 |
| 8 | 443 | 252 | $C_{20}H_{12}$ | −28 | Benzo[*e*]pyrene | 7.07 | 7.06 |
| 9 | 448 | 252 | $C_{20}H_{12}$ | −28 | Benzo[*a*]pyrene | 7.15 | 7.14 |
| 10 | 580 | 276 | $C_{22}H_{12}$ | −32 | Indeno[1,2,3-*c*,*d*]pyrene | 9.41 | 9.27 |
| 11 | 625 | 276 | $C_{22}H_{12}$ | −32 | Benzo[*g*,*h*,*i*]perylene | 10.00 | 10.00 |

tected, including the sulphur compounds. This was possible despite the presence of the sulphur compounds as minor components in a complex aromatic mixture because they give relatively intense molecular ions. Identifications for the numbered peaks in the GC–FPD chromatograms are given in Tables II and III for the pitch and tar, respectively.

GC–MS identification was assisted by drawing single ion chromatograms for masses corresponding to sulphur heterocyclic compounds. This was carried out for isomers of benzothiophene (*m/z* 134), dibenzothiophene (*m/z* 184), phenanthro[4,5-*b,c,d*]thiophene (*m/z* 208), benzonaphthothiophene (*m/z* 234), benzophenanthro[4,5-*b,c,d*]thiophene (*m/z* 258), dinaphthothiophene (*m/z* 284), perylo[1,12-*b,c,d*]thiophene (*m/z* 282) and their successive alkyl derivatives. Single ion chromatograms for these

TABLE II

SULPHUR HETEROCYCLES IDENTIFIED IN COKE OVEN PITCH

Peak numbers refer to GC–FPD chromatogram in Fig. 1, and GC–MS single ion chromatograms in Figs. 4–10. MS scan numbers to GC–MS TIC chromatogram in Fig. 3 and GC–MS single ion chromatograms in Figs. 4–10. Retention times relative to naphthalene = 0 and benzo[*g,h,i*]perylene = 10.0.

| *Peak No.* | *MS scan No.* | *m/z* | *Atomic composition* | *Z No.* | *Compound* | *Retention coefficients* | |
|---|---|---|---|---|---|---|---|
| | | | | | | *GC–FPD* | *GC–MS* |
| 1 | 7 | 134 | $C_8H_6S$ | −10.S | Benzo[*b*]thiophene | 0.09 | 0.01 |
| 2 | 14 | 148 | $C_9H_8S$ | −10.S | Methylbenzo[*b*]thiophene | 0.14 | 0.13 |
| 3 | 15 | 148 | $C_9H_8S$ | −10.S | Methylbenzo[*b*]thiophene | 0.17 | 0.15 |
| 4 | 17 | 148 | $C_9H_8S$ | −10.S | Methylbenzo[*b*]thiophene | 0.18 | 0.18 |
| 5 | 23 | 162 | $C_{10}H_{10}S$ | −10.S | $C_2$-alkylbenzo[*b*]thiophene | 0.24 | 0.27 |
| 6 | 26 | 162 | $C_{10}H_{10}S$ | −10.S | $C_2$-alkylbenzo[*b*]thiophene | 0.28 | 0.32 |
| 7 | 26 | 162 | $C_{10}H_{10}S$ | −10.S | $C_2$-alkylbenzo[*b*]thiophene | 0.30 | 0.32 |
| 8 | 30 | 162 | $C_{10}H_{10}S$ | −10.S | $C_2$-alkylbenzo[*b*]thiophene | 0.32 | 0.38 |
| 9 | 112 | 184 | $C_{12}H_8S$ | −16.S | Dibenzothiophene/naphthothiophene isomer | 1.61 | 1.71 |
| 10 | 123 | 184 | $C_{12}H_8S$ | −16.S | Dibenzothiophene/naphthothiophene isomer | 1.74 | 1.89 |
| 11 | 133 | 184 | $C_{12}H_8S$ | −16.S | Dibenzothiophene/naphthothiophene isomer | 1.90 | 2.05 |
| 12 | 137 | 198 | $C_{13}H_{10}S$ | −16.S | Methyldibenzothiophene | 1.99 | 2.11 |
| 13 | 144 | 198 | $C_{13}H_{10}S$ | −16.S | Methyldibenzothiophene | 2.08 | 2.23 |
| 14 | 144 | 198 | $C_{13}H_{10}S$ | −16.S | Methyldibenzothiophene | 2.12 | 2.23 |
| 15 | 150 | 198 | $C_{13}H_{10}S$ | −16.S | Methyldibenzothiophene | 2.22 | 2.33 |
| 16 | 150 | 198 | $C_{13}H_{10}S$ | −16.S | Methyldibenzothiophene | 2.29 | 2.33 |
| 17 | 163 | 212 | $C_{14}H_{12}S$ | −16.S | $C_2$-alkyldibenzothiophene | 2.40 | 2.53 |
| 18 | 164 | 198 | $C_{13}H_{10}S$ | −16.S | Methyldibenzothiophene | 2.48 | 2.55 |
| 19 | 168 | 212 | $C_{14}H_{12}S$ | −16.S | $C_2$-alkyldibenzothiophene | 2.54 | 2.62 |
| 20 | 170 | 212 | $C_{14}H_{12}S$ | −16.S | $C_2$-alkyldibenzothiophene | 2.57 | 2.64 |
| 21 | 171 | 212 | $C_{14}H_{12}S$ | −16.S | $C_2$-alkyldibenzothiophene | 2.62 | 2.67 |
| 22 | 176 | 212 | $C_{14}H_{12}S$ | −16.S | $C_2$-alkyldibenzothiophene | 2.71 | 2.74 |
| 23 | 181 | 212 | $C_{14}H_{12}S$ | −16.S | $C_2$-alkyldibenzothiophene | 2.82 | 2.82 |
| 24 | 193 | 212 | $C_{14}H_{12}S$ | −16.S | $C_2$-alkyldibenzothiophene | 3.00 | 3.02 |
| 25 | 199 | 212 | $C_{14}H_{12}S$ | −16.S | $C_2$-alkyldibenzothiophene | 3.13 | 3.12 |
| 26 | 221 | 208 | $C_{14}H_8S$ | −20.S | Phenanthro[4,5-*b,c,d*]thiophene | 3.49 | 3.48 |
| 27 | 235 | 208 | $C_{14}H_8S$ | −20.S | Isomer of phenanthro[4,5-*b,c,d*]thiophene | 3.72 | 3.70 |
| 28 | 245 | 222 | $C_{15}H_{10}S$ | −20.S | Methylphenanthro[4,5-*b,c,d*]thiophene | 3.90 | 3.86 |

(*Continued on p. 58*)

TABLE II *(continued)*

| *Peak No.* | *MS scan No.* | *m/z* | *Atomic composition* | *Z No.* | *Compound* | *Retention coefficients* | |
|---|---|---|---|---|---|---|---|
| | | | | | | *GC–FPD* | *GC–MS* |
| 29 | 250 | 222 | $C_{15}H_{10}S$ | −20.S | Methylphenanthro[4,5-*b,c,d*]thiophene | 3.95 | 3.94 |
| 30 | 256 | 222 | $C_{15}H_{10}S$ | −20.S | Methylphenanthro[4,5-*b,c,d*]thiophene | 4.04 | 4.03 |
| 31 | 256 | 222 | $C_{15}H_{10}S$ | −20.S | Methylphenanthro[4,5-*b,c,d*]thiophene | 4.08 | 4.03 |
| 32 | 263 | 222 | $C_{15}H_{10}S$ | −20.S | Methylphenanthro[4,5-*b,c,d*]thiophene | 4.14 | 4.16 |
| 33 | 263 | 222 | $C_{15}H_{10}S$ | −20.S | Methylphenanthro[4,5-*b,c,d*]thiophene | 4.20 | 4.16 |
| 34 | 266 | 222 | $C_{15}H_{10}S$ | −20.S | Methylphenanthro[4,5-*b,c,d*]thiophene | 4.24 | 4.20 |
| 35 | 280 | 236 | $C_{16}H_{12}S$ | −20.S | $C_2$-alkylphenanthro[4,5-*b,c,d*]thiophene | 4.50 | 4.42 |
| 36 | 286 | 236 | $C_{16}H_{12}S$ | −20.S | $C_2$-alkylphenanthro[4,5-*b,c,d*]thiophene | 4.57 | 4.52 |
| 37 | 294 | 236 | $C_{16}H_{12}S$ | −20.S | $C_2$-alkylphenanthro[4,5-*b,c,d*]thiophene | 4.70 | 4.66 |
| 38 | 306 | 234 | $C_{16}H_{10}S$ | −22.S | Benzonaphthothiophene isomer | 4.90 | 4.84 |
| 39 | 315 | 234 | $C_{16}H_{10}S$ | −22.S | Benzonaphthothiophene isomer | 5.04 | 4.99 |
| 40 | 323 | 234 | $C_{16}H_{10}S$ | −22.S | Benzonaphthothiophene isomer | 5.15 | 5.12 |
| 41 | 326 | 234 | $C_{16}H_{10}S$ | −22.S | Benzonaphthothiophene isomer | 5.20 | 5.17 |
| 42 | 333 | 234 | $C_{16}H_{10}S$ | −22.S | Benzonaphthothiophene isomer | 5.31 | 5.28 |
| 42 | 333 | 248 | $C_{17}H_{12}S$ | −22.S | Methylbenzonaphthothiophene | 5.31 | 5.28 |
| 43 | 338 | 248 | $C_{17}H_{12}S$ | −22.S | Methylbenzonaphthothiophene | 5.40 | 5.37 |
| 44 | 340 | 234 | $C_{16}H_{10}S$ | −22.S | Benzonaphthothiophene isomer | 5.43 | 5.40 |
| 45 | 348 | 248 | $C_{17}H_{12}S$ | −22.S | Methylbenzonaphthothiophene | 5.58 | 5.52 |
| 46 | 353 | 248 | $C_{17}H_{12}S$ | −22.S | Methylbenzonaphthothiophene | 5.65 | 5.61 |
| 47 | 358 | 248 | $C_{17}H_{12}S$ | −22.S | Methylbenzonaphthothiophene | 5.70 | 5.69 |
| 48 | 358 | 248 | $C_{17}H_{12}S$ | −22.S | Methylbenzonaphthothiophene | 5.73 | 5.69 |
| 49 | 364 | 248 | $C_{17}H_{12}S$ | −22.S | Methylbenzonaphthothiophene | 5.84 | 5.79 |
| 49 | 364 | 262 | $C_{18}H_{14}S$ | −22.S | $C_2$-alkylbenzonaphthothiophene | 5.84 | 5.79 |
| 50 | 373 | 262 | $C_{18}H_{14}S$ | −22.S | $C_2$-alkylbenzonaphthothiophene | 5.91 | 5.93 |
| 51 | 379 | 262 | $C_{18}H_{14}S$ | −22.S | $C_2$-alkylbenzonaphthothiophene | 6.07 | 6.03 |
| 52 | 384 | 262 | $C_{18}H_{14}S$ | −22.S | $C_2$-alkylbenzonaphthothiophene | 6.13 | 6.11 |
| 53 | 412 | 258 | $C_{18}H_{10}S$ | −26.S | Benzophenanthro[4,5-*b,c,d*]thiophene isomer | 6.57 | 6.56 |
| 54 | 422 | 258 | $C_{18}H_{10}S$ | −26.S | Benzophenanthro[4,5-*b,c,d*]thiophene isomer | 6.71 | 6.72 |
| 55 | 425 | 258 | $C_{18}H_{10}S$ | −26.S | Benzophenanthro[4,5-*b,c,d*]thiophene isomer | 6.82 | 6.82 |
| 56 | 434 | 258 | $C_{18}H_{10}S$ | −26.S | Benzophenanthro[4,5-*b,c,d*]thiophene isomer | 6.94 | 6.91 |
| 57 | 441 | 258 | $C_{18}H_{10}S$ | −26.S | Benzophenanthro[4,5-*b,c,d*]thiophene isomer | 7.03 | 7.02 |
| 58 | 445 | 258 | $C_{18}H_{10}S$ | −26.S | Benzophenanthro[4,5-*b,c,d*]thiophene isomer | 7.10 | 7.09 |
| 59 | 458 | 258 | $C_{18}H_{10}S$ | −26.S | Benzophenanthro[4,5-*b,c,d*]thiophene isomer | 7.32 | 7.30 |
| 59 | 458 | 272 | $C_{19}H_{12}S$ | −26.S | Methylbenzophenanthro[4,5-*b,c,d*]thiophene | 7.32 | 7.30 |
| 60 | 465 | 272 | $C_{19}H_{12}S$ | −26.S | Methylbenzophenanthro[4,5-*b,c,d*]thiophene | 7.44 | 7.41 |
| 61 | 480 | 272 | $C_{19}H_{12}S$ | −26.S | Methylbenzophenanthro[4,5-*b,c,d*]thiophene | 7.70 | 7.66 |
| 62 | 526 | 284 | $C_{20}H_{12}S$ | −28.S | Dinaphthothiophene isomer | 8.51 | 8.40 |
| 63 | 540 | 284 | $C_{20}H_{12}S$ | −28.S | Dinaphthothiophene isomer | 8.80 | 8.69 |
| 64 | 554 | 284 | $C_{20}H_{12}S$ | −28.S | Dinaphthothiophene isomer | 8.98 | 8.86 |
| 65 | 570 | 284 | $C_{20}H_{12}S$ | −28.S | Dinaphthothiophene isomer | 9.20 | 9.11 |
| 66 | 605 | 282 | $C_{20}H_{10}S$ | −30.S | Perylo[1,12-*b,c,d*]thiophene isomer | 9.73 | 9.68 |
| 67 | 620 | 282 | $C_{20}H_{10}S$ | −30.S | Perylo[1,12-*b,c,d*]thiophene isomer | 9.88 | 9.92 |
| 68 | 630 | 282 | $C_{20}H_{10}S$ | −30.S | Perylo[1,12-*b,c,d*]thiophene isomer | 10.15 | 10.09 |
| 69 | 644 | 282 | $C_{20}H_{10}S$ | −30.S | Perylo[1,12-*b,c,d*]thiophene isomer | 10.41 | 10.31 |

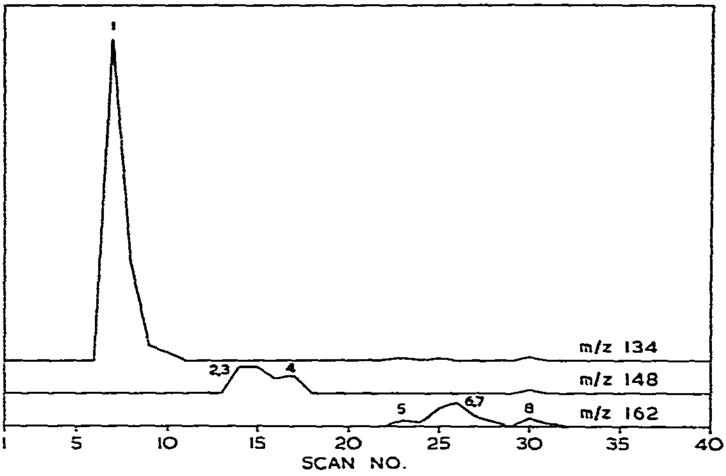


Fig. 4. GC–MS single ion chromatograms of coke oven pitch showing benzo[*b*]thiophene (*m/z* 134) and $C_1$- and $C_2$-alkyl derivatives (*m/z* 148 and 162). Peak numbers refer to compounds listed in Table II. Conditions as in Fig. 3.

masses are shown in Figs. 4–10 respectively for the pitch. Visual comparison of the GC–MS single ion chromatograms with the appropriate portions of the GC–FPD chromatograms shows a good correlation; the regions covered by the single ion chromatograms in Figs. 4–10 are marked on the GC–FPD chromatogram shown in Fig. 1. In comparing the relative peak heights it should be noted that the FPD response is proportional to the square of the concentration, whereas the MS response in the single ion chromatograms is linear with concentration.

Since the single ion chromatograms are drawn using nominal masses, the accurate mass at each peak was checked to confirm the presence of a sulphur compound. Doublets which might occur at the same nominal mass as the sulphur com-

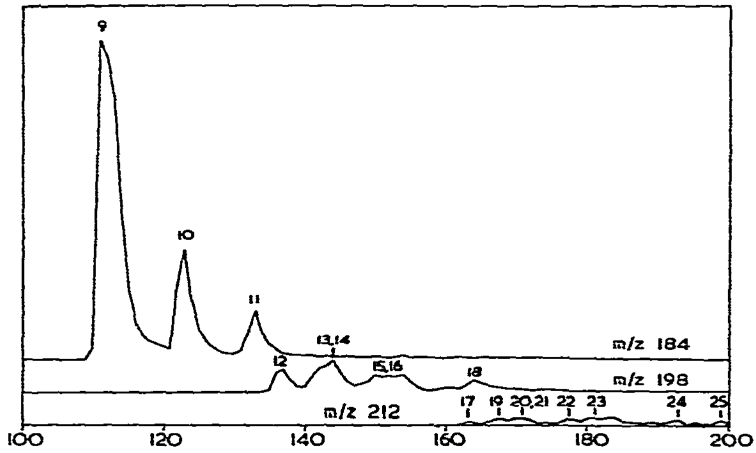


Fig. 5. GC–MS single ion chromatograms of coke oven pitch showing dibenzothiophene and naphthothiophenes (*m/z* 184) and $C_1$- and $C_2$-alkyl derivatives (*m/z* 198 and 212). Peak numbers refer to compounds listed in Table II. Conditions as in Fig. 3.

TABLE III

SULPHUR HETEROCYCLES IDENTIFIED IN GRAY-KING TAR

Peak numbers refer to GC-FPD chromatogram in Fig. 2. Retention times relative to naphthalene = 0 and chrysene = 10.0.

| *Peak Nos.* | *m/z* | *Atomic composition* | *Z No.* | *Compound* | *Retention coefficients* | |
|---|---|---|---|---|---|---|
| | | | | | *GC-FPD* | *GC-MS* |
| 1–10 | | Not identified | −4.S | Probably alkylthiophenes | −0.53–0.16 | |
| 11 | 134 | $C_8H_6S$ | −10.S | Benzo[*b*]thiophene | 0.31 | 0.27 |
| 12–15 | 148 | $C_9H_8S$ | −10.S | Methylbenzo[*b*]thiophenes | 0.91–1.14 | 0.99–1.36 |
| 16–24 | 162 | $C_{10}H_{10}S$ | −10.S | $C_2$-alkylbenzo[*b*]thiophenes | 1.72–2.43 | 1.81–2.35 |
| 25–35 | 176 | $C_{11}H_{12}S$ | −10.S | $C_3$-alkylbenzo[*b*]thiophenes | 2.52–3.28 | 2.62–3.35 |
| 36–49 | 190 | $C_{12}H_{14}S$ | −10.S | $C_4$-alkylbenzo[*b*]thiophenes | 3.38–4.09 | 3.60–3.89 |
| 50–66 | 204 | $C_{13}H_{16}S$ and higher alkyl derivatives | −10.S | $C_5$ and higher alkylbenzo[*b*]-thiophenes | 4.17–5.14 | 3.98–5.20 |
| 67–73 | 184 | $C_{12}H_8S$ | −16.S | Dibenzothiophene/naphthothiophene isomers | 5.21–5.74 | 5.24–5.75 |
| 74–85 | 198 | $C_{13}H_{10}S$ | −16.S | Methyldibenzothiophenes | 5.83–6.58 | 5.79–6.42 |
| 86–95 | 212 | $C_{14}H_{12}S$ | −16.S | $C_2$-alkyldibenzothiophenes | 6.69–7.22 | 6.51–7.14 |
| 96–101 | 226 | $C_{15}H_{14}S$ | −16.S | $C_3$-alkyldibenzothiophenes | 7.32–7.66 | 7.31–7.61 |
| 102 | 208 | $C_{14}H_8S$ | −20.S | Phenanthro[4,5-*b,c,d*]thiophene | 7.79 | 7.69 |
| 103 | 210 | $C_{14}H_{10}S$ | −18.S | Phenanthrothiol or dihydrophenanthro[4,5-*b,c,d*]thiophene | 7.86 | 7.81 |
| 104–111 | 240 | $C_{16}H_{16}S$ | −16.S | $C_4$-alkyldibenzothiophenes | 7.99–8.46 | 7.87–8.45 |
| 112–116 | 222 | $C_{15}H_{10}S$ | −20.S | Methylphenanthro[4,5-*b,c,d*]thiophene | 8.56–8.87 | 8.50–8.81 |
| 117–123 | 236 | $C_{16}H_{12}S$ and higher alkyl derivatives | −20.S | $C_2$ and higher alkylphenanthro-[4,5-*b,c,d*]thiophenes | 8.99–9.50 | 8.86–9.13 |
| 124–129 | 234 | $C_{16}H_{10}S$ | −22.S | Benzonaphthothiophene isomers | 9.56–9.94 | 9.31–9.67 |
| 130–141 | 248 | $C_{17}H_{12}S$ | −22.S | Methylbenzonaphthothiophenes | 10.11–10.89 | 10.0–10.6 |
| 142–151 | 262 | $C_{18}H_{14}S$ | −22.S | $C_2$-alkylbenzonaphthothiophenes | 10.96–11.69 | 11.1–11.7 |

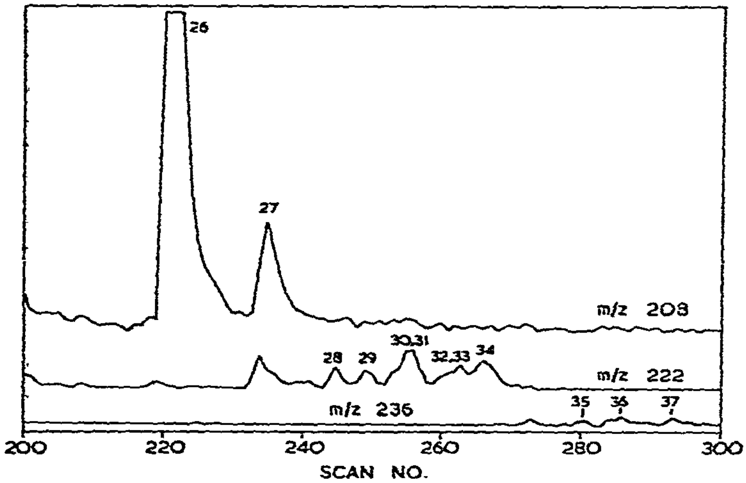


Fig. 6. GC–MS single ion chromatograms of coke oven pitch showing isomers of phenanthro[4,5-*b,c,d*]thiophene (*m/z* 208) and $C_1$- and $C_2$-alkyl derivatives (*m/z* 222 and 236). Peak numbers refer to compounds listed in Table II. Conditions as in Fig. 3.

pound $RSH_4$ are $RC_3$, $RC_2H_{12}$ and $RCOH_8$, as well as the $^{13}C$ isotopic peak from a fragment ion at the next lower mass number. Although the $SH_4$–$C_3$ doublet could not be resolved in this work, the $C_3$ element of the doublet is generally too hydrogen-deficient to exist. The other doublets from which interference might be experienced could be resolved adequately at the MS resolution of 3000, but this was generally unnecessary since the compound types to which they correspond were separated chromatographically.

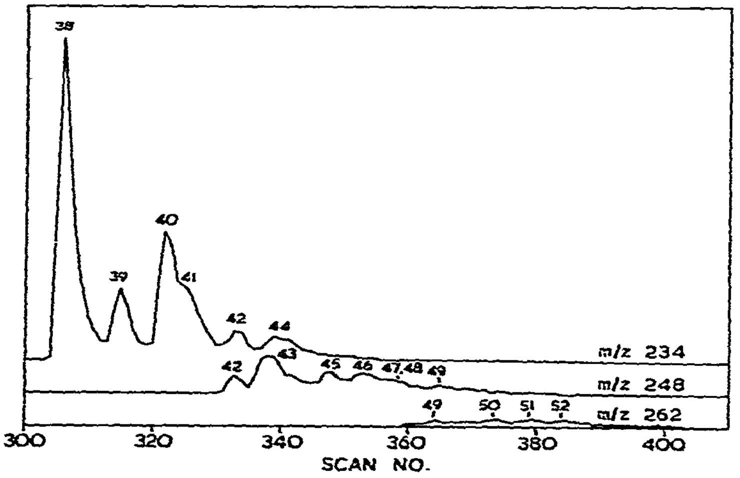
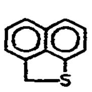
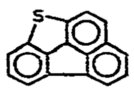
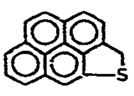


Fig. 7. GC–MS single ion chromatograms of coke oven pitch showing isomers of benzonaphthothiophene (*m/z* 234) and $C_1$- and $C_2$-alkyl derivatives (*m/z* 248 and 262). Peak numbers refer to compounds listed in Table II. Conditions as in Fig. 3.

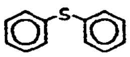
Unsuccessful searches of the mass spectral data for the tar and pitch were made for the following compounds

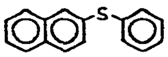

m/z 172

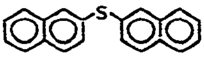

m/z 232


m/z 246

and the sulphides

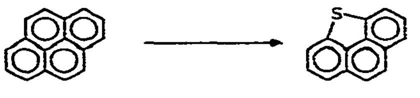

m/z 186


m/z 236


m/z 286

Some of these may have been swamped by oxygenated compounds such as $C_{17}H_{12}O$, *m/z* 232, and $C_{18}H_{14}O$, *m/z* 246, or the $^{34}S$ isotope peak from a more abundant sulphur-containing compound two mass units lower.

All the sulphur compounds identified in both the pitch and the tar appear to be benzologues of thiophene. Unsubstituted compounds predominate in the pitch, a product of high-temperature carbonisation, but alkyl derivatives are more prominent in the low-temperature tar. These heterocyclic compounds reflect closely the nature of the hydrocarbon components in the samples. For example, the major sulphur compounds in the tar are $C_2$–$C_4$ alkylbenzothiophenes, whereas the major hydrocarbons are $C_2$–$C_4$ alkylnaphthalenes, 6 mass units lower. This relationship between sulphur compounds and the hydrocarbons has been noted by Karcher *et al.*[26] who found that PAH materials prepared from coal or petroleum products often contain a thiophene derivative resulting schematically from the replacement of one aromatic ring by a thiophene ring, thus:


m/z 202 pyrene

m/z 208 phenanthro[4,5-b,c,d]thiophene

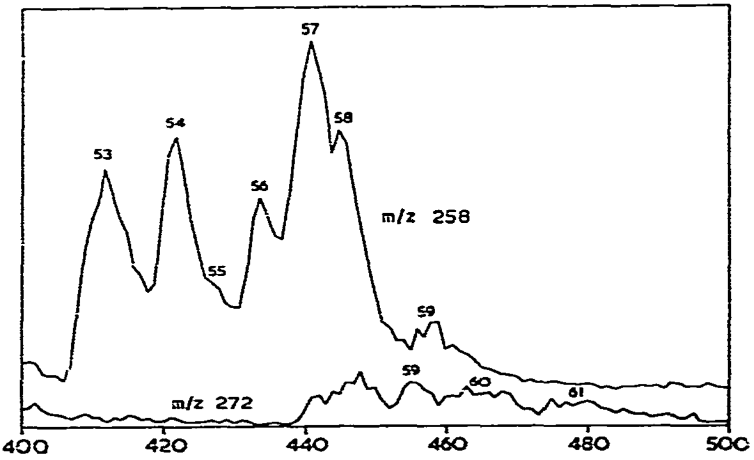


Fig. 8. GC–MS single ion chromatograms of coke oven pitch showing isomers of benzophenanthro[4,5-*b,c,d*]thiophene (*m/z* 258) and methyl derivatives (*m/z* 272). Peak numbers refer to compounds listed in Table II. Conditions as in Fig. 3.

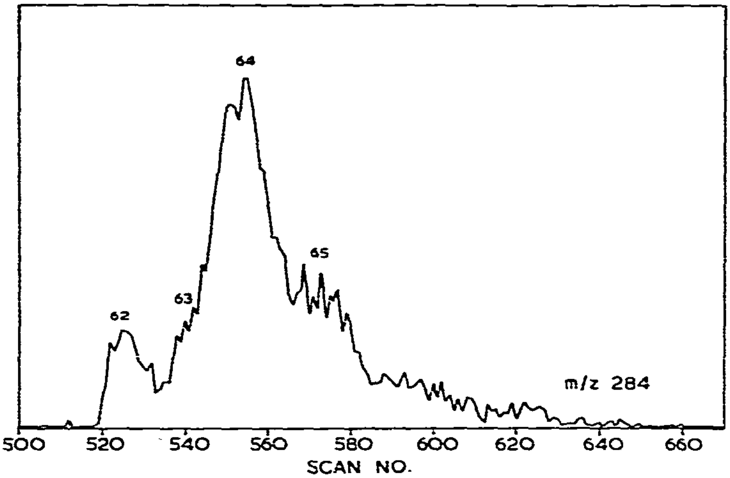


Fig. 9. GC–MS single ion chromatogram of coke oven pitch showing isomers of dinaphthothiophene (*m/z* 284). Peak numbers refer to compounds listed in Table II. Conditions as in Fig. 3.

Such sulphur compounds are 6 mass units higher that the corresponding aromatic hydrocarbon as a result of the mass difference S–$C_2H_2$.

Several isomers have been observed for each of the sulphur compounds identified in terms of their atomic compositions. Each structural isomer was eluted as part of a composite GC peak, identified by the molecular ion rather than by a fragmentation pattern, and consequently it was not possible to derive any structural information. The electron impact mass spectra of sulphur heterocycles generally show relatively intense molecular ions and few significant fragment ions, and thus little structural information of relevance in identifying specific isomers would be available, even for a concentrated sulphur heterocycle fraction. Positive identification of isomeric

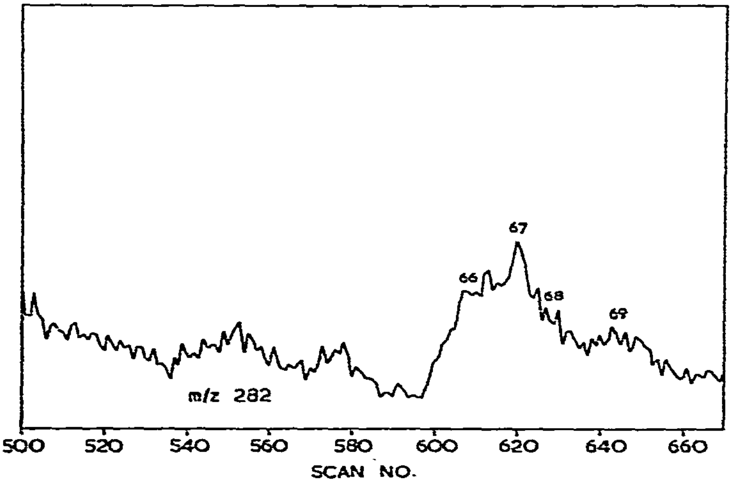


Fig. 10. GC–MS single ion chromatogram of coke oven pitch showing isomers of perylo[1,12-*b,c,d*]thiophene (*m/z* 282). Peak numbers refer to compounds listed in Table II. Conditions as in Fig. 3.

components will probably rely substantially on the use of chromatographic retention indices for standard reference compounds, but few of these are available at present.

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