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DETERMINATION OF NITROGEN–SULPHUR MIXED HETEROATOMIC COMPOUNDS AND SULPHUR HETEROCYCLES IN AN ANTHRACENE OIL

PAUL BURCHILL*, ALAN A. HEROD and ERNEST PRITCHARD
National Coal Board, Coal Research Establishment, Stoke Orchard, Cheltenham, Gloucestershire, GL52 4RZ (Great Britain)
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SUMMARY

Gas chromatography (GC), in conjunction with a sulphur-specific flame photometric detector (FPD), has revealed a complex mixture of nitrogen–sulphur mixed heteroatomic compounds in the basic fraction from an anthracene oil. Mass spectrometry (MS) was used to identify the major peaks in the chromatogram; using accurate mass measurement interference from other species was minimal, but the MS sensitivity was insufficient for some of the minor components. The compounds identified, which probably contain both thiophenic and pyridyl rings, were analysed quantitatively by GC–FPD. The sulphur heterocycles in the unfractionated anthracene oil were determined in the same manner.

INTRODUCTION

Recent work in this laboratory, carried out as part of a coal pyrolysis project, has involved the analysis of basic fractions from tar products by gas chromatography (GC) in conjunction with mass spectrometric (MS) and nitrogen-selective alkali flame detection[1]. The majority of the components identified were aza heterocycles, but an interesting feature of the work was the identification of several dinitrogen and mixed heteroatomic compounds (NN, NO and NS) as minor components in the bases from an anthracene oil. A few species of these types have been found previously in coal tars by MS type analysis[2], but this technique does not give information on individual isomers, and no examination of such compounds by GC appears to have been reported.

This paper describes the application of flame photometry and mass spectrometry to the GC analysis of nitrogen–sulphur (NS) mixed heteroatomic compounds in the basic fraction from an anthracene oil. For comparison, the sulphur heterocycles in the unfractionated anthracene oil were also analysed. The flame photometric detector (FPD), when operated at a wavelength of 394 nm, responds selectively to compounds containing sulphur; in another paper[3] we have described its application to the analysis of sulphur heterocycles in coal tar and pitch.

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EXPERIMENTAL AND RESULTS

Sample preparation

The anthracene oil was a standard commercial coal tar product; the basic fraction was isolated in the following manner. 5.73 g of the oil were dissolved in 40 ml dichloromethane and extracted with 2 × 20 ml of 10% sulphuric acid, then with 2 × 20 ml of 20% sulphuric acid. The aqueous acid extracts were combined, cooled and the pH adjusted to 12 by the addition of 4 *N* NaOH. The bases thus regenerated were recovered by back extraction with 40 ml dichloromethane, then with 2 × 20 ml dichloromethane, the combined organic layers being evaporated to dryness at 80°C to give 0.26 g of bases. Elemental analyses for the unfractionated anthracene oil, the bases and the residue are given in Table I.

TABLE I

ANALYTICAL DATA FOR SAMPLES

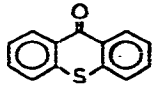
Element	*% (w/w)*		
	Unfractionated oil	*Basic fraction*	*Residue*
C	90.2	83.9	91.1
H	5.8	5.3	5.9
N (total)	1.08	9.3	0.50
N (basic)	0.53	9.3	0.03
O	2.2	1.2	2.0
S	1.25	0.7	1.25

Gas chromatography

The samples were analysed by GC using a Perkin-Elmer F-17 chromatograph fitted with a sulphur-selective FPD. 0.2-μl injections were made onto a 40-m SGE glass support-coated open tubular (SCOT) capillary column coated with SP-2250 50% methyl, 50% phenyl silicone stationary phase, using helium carrier gas with a linear velocity of 38 cm/sec. The column was programmed from 120 to 285°C at 3°/min with a 4-min initial hold. The FPD combustion gas flows were optimised for maximum sulphur response, the optimised flows being 10.0 ml/min for oxygen, and 110 ml/min for hydrogen.

The anthracene oil bases and the unfractionated oil were analysed initially as 2.25 and 1.05% (w/v) solutions respectively in dichloromethane to which 3,6-dithiaoctane (19.6 ng/μl) and di-*n*-octyl sulphide (61.9 ng/μl) had been added as internal markers. The resulting GC–FPD chromatograms are shown in Figs. 1 and 2, respectively.

The samples were then analysed quantitatively for sulphur compounds under the same chromatographic conditions using thioxanthen-9-one as internal standard.



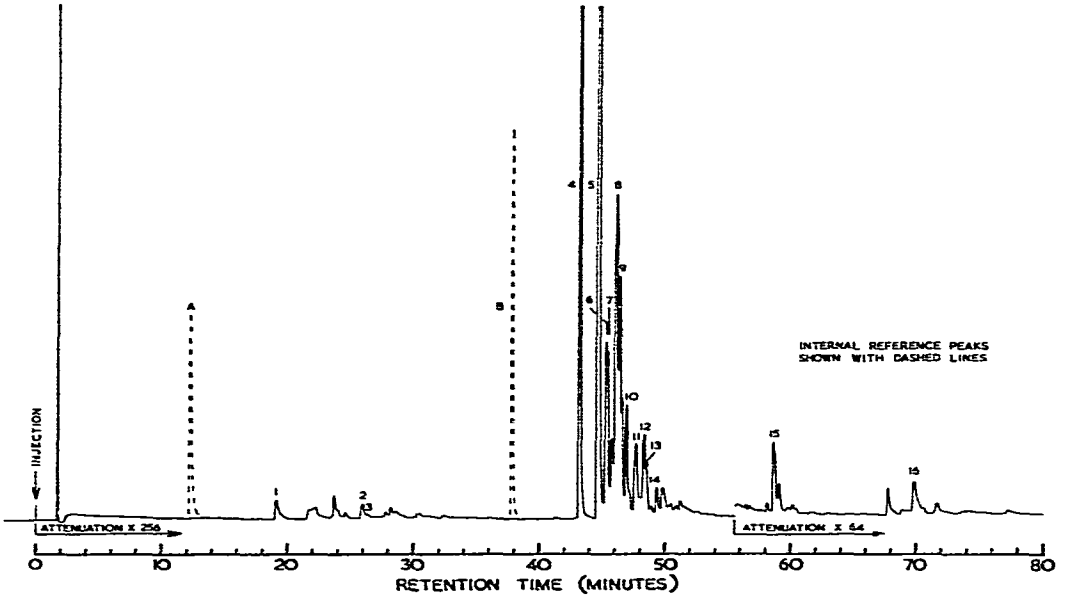


Fig. 1. GC–FPD chromatogram of anthracene oil bases showing NS mixed heteroatomic compounds. Identifications for labelled peaks given in Table II. Conditions: 40-m SP-2250 glass SCOT capillary column programmed from 120 to 285°C at 3°/min with 4-min initial hold.

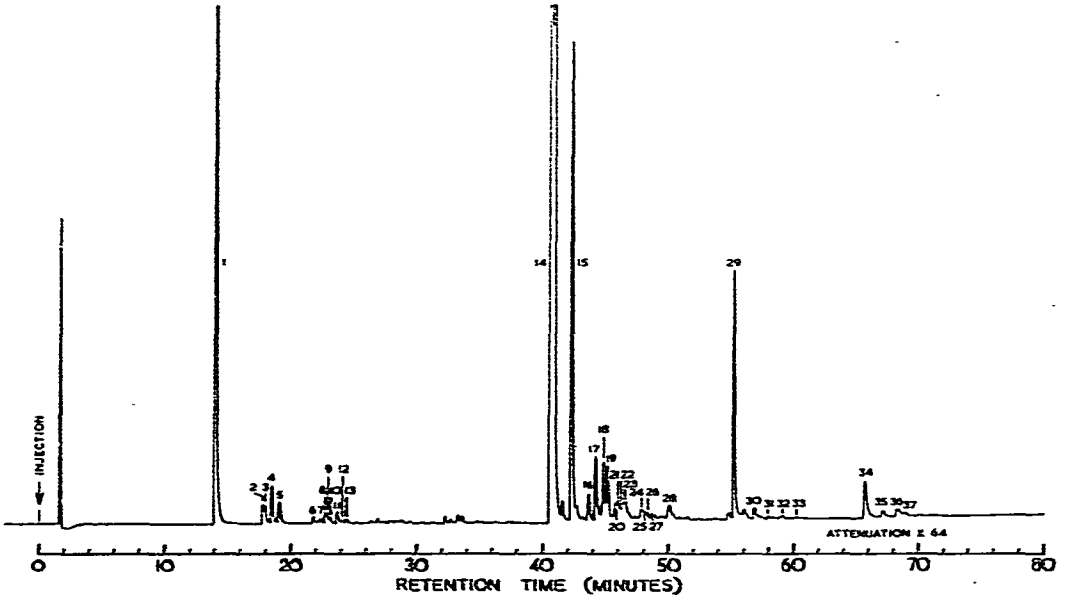


Fig. 2. GC–FPD chromatogram of unfractionated anthracene oil showing thiophenic compounds. Identifications for numbered peaks given in Table III. Conditions as in Fig. 1.

TABLE II

NS MIXED HETEROATOMIC COMPOUNDS IDENTIFIED IN ANTHRACENE OIL BASES

Peak numbers refer to GC–FPD chromatogram in Fig. 1 and GC–MS single ion chromatograms in Figs. 4–7, MS scan numbers to GC–MS TIC chromatogram in Fig. 3 and GC–MS single ion chromatograms in Figs. 4–7. Retention times relative to 3,6-dithiaoctane = 0 and di-*n*-octyl sulphide = 10.0. Concentrations expressed as ppm of unfractionated anthracene oil. The *Z* No. is derived from the atomic composition according to the general formula C_nH_{2n+Z} and reflects the abundance of hydrogen relative to carbon. The more aromatic, or hydrogen-deficient, the molecule, the more negative the *Z* No. The presence or absence of alkyl side chains in an aromatic molecule does not affect the *Z* No. *Z* Nos. for heterocyclics are calculated from C and H contents only.

Peak No.	*MS scan No.*	*Retention coefficients*		*m/z*	*Atomic composition*	*Z No.*	*Name or possible type*	*Concn. (ppm)*
		GC–FPD	*GC–MS*					
A	44	0.00	0.00	150	$C_6H_{14}S_2$	+ 2.S_2	3,6-Dithiaoctane (internal marker compound)	–
1	110	2.62	2.74	135	C_7H_5NS	– 9.NS	Azabenzothiophene	45
2	173	5.37	5.35	149	C_8H_7NS	– 9.NS	Methylazabenzothiophene	37
				163	C_9H_9NS	– 9.NS	C_2-alkylazabenzothiophene	
3	183	5.70	5.77	149	C_8H_7NS	– 9.NS	Methylazabenzothiophene	22
B	285	10.00	10.00	258	$C_{16}H_{34}S$	+ 2.S	Di-*n*-octyl sulphide (internal marker compound)	–
4	332	12.01	11.95	185	$C_{11}H_7NS$	–15.NS	Azadibenzothiophene or azanaphthothiophene	200
5	346	12.57	12.53	185	$C_{11}H_7NS$	–15.NS	Azadibenzothiophene or azanaphthothiophene	250
6	351	12.84	12.74	199	$C_{12}H_9NS$	–15.NS	Methylazadibenzothiophene	98
7	354	12.90	12.86	185	$C_{11}H_7NS$	–15.NS	Azadibenzothiophene or azanaphthothiophene	80
8	359	13.18	13.07	185	$C_{11}H_7NS$	–15.NS	Azadibenzothiophene or azanaphthothiophene	150
9	362	13.30	13.20	185	$C_{11}H_7NS$	–15.NS	Azadibenzothiophene or azanaphthothiophene	110
10	367	13.49	13.40	199	$C_{12}H_9NS$	–15.NS	Methylazadibenzothiophene	92
11	373	13.78	13.65	199	$C_{12}H_9NS$	–15.NS	Methylazadibenzothiophene	73
12	380	14.04	13.95	199	$C_{12}H_9NS$	–15.NS	Methylazadibenzothiophene	77
13	382	14.11	14.03	213	$C_{13}H_{11}NS$	–15.NS	C_2-alkylazadibenzo-thiophene	48
14	389	14.44	14.32	199	$C_{12}H_9NS$	–15.NS	Methylazadibenzothiophene	39
15	478	18.05	18.01	209	$C_{13}H_7NS$	–19.NS	Azaphenanthro[*b,c,d*]-thiophene	35
16	607	23.06	23.36	235	$C_{15}H_9NS$	–21.NS	Azanaphthobenzothiophene	34

The bases and the unfractionated oil were made up as 2.60 and 1.27% (w/v) solutions respectively in dichloromethane containing thioxanthen-9-one (103.5 ng/μl). A Hewlett-Packard 3353 chromatographic data system was used to measure peak areas, and the results have been calculated assuming a square law relationship between response and concentration (response $\propto$ concentration^2), and a response factor of unity relative to the internal standard. Concentrations for the numbered peaks in Figs. 1 and 2 are given in Tables II and III respectively, expressed as ppm of the unfractionated anthracene oil.

TABLE III

THIOPHENIC COMPOUNDS IDENTIFIED IN UNFRACTIONATED ANTHRACENE OIL

Peak numbers refer to GC–FPD chromatogram in Fig. 2.

Peak No.	*m/z*	*Atomic composition*	*Z No.*	*Name or possible type*	*Concn. (ppm)*
1	134	C_8H_6S	−10.S	Benzothiophene	6100
2	148	C_9H_8S	−10.S	Methylbenzothiophene	1200
3	148	C_9H_8S	−10.S	Methylbenzothiophene	1000
4	148	C_9H_8S	−10.S	Methylbenzothiophene	1500
5	148	C_9H_8S	−10.S	Methylbenzothiophene	1300
6	162	$C_{10}H_{10}S$	−10.S	C_2-alkylbenzothiophene	660
7	162	$C_{10}H_{10}S$	−10.S	C_2-alkylbenzothiophene	590
8	162	$C_{10}H_{10}S$	−10.S	C_2-alkylbenzothiophene	800
9	162	$C_{10}H_{10}S$	−10.S	C_2-alkylbenzothiophene	780
10	162	$C_{10}H_{10}S$	−10.S	C_2-alkylbenzothiophene	670
11	162	$C_{10}H_{10}S$	−10.S	C_2-alkylbenzothiophene	1000
12	162	$C_{10}H_{10}S$	−10.S	C_2-alkylbenzothiophene	490
13	162	$C_{10}H_{10}S$	−10.S	C_2-alkylbenzothiophene	720
14	184	$C_{12}H_8S$	−16.S	Dibenzothiophene	12,200
15	184	$C_{12}H_8S$	−16.S	Dibenzothiophene	5400
16	184	$C_{12}H_8S$	−16.S	Dibenzothiophene	1400
17	198	$C_{13}H_{10}S$	−16.S	Methyldibenzothiophene	2300
18	198	$C_{13}H_{10}S$	−16.S	Methyldibenzothiophene	2200
19	198	$C_{13}H_{10}S$	−16.S	Methyldibenzothiophene	2300
20	198	$C_{13}H_{10}S$	−16.S	Methyldibenzothiophene	1200
21	198	$C_{13}H_{10}S$	−16.S	Methyldibenzothiophene	1500
22	198	$C_{13}H_{10}S$	−16.S	Methyldibenzothiophene	1200
23	198	$C_{13}H_{10}S$	−16.S	Methyldibenzothiophene	2300
24	212	$C_{14}H_{12}S$	−16.S	C_2-alkyldibenzothiophene	850
25	212	$C_{14}H_{12}S$	−16.S	C_2-alkyldibenzothiophene	960
26	212	$C_{14}H_{12}S$	−16.S	C_2-alkyldibenzothiophene	810
27	212	$C_{14}H_{12}S$	−16.S	C_2-alkyldibenzothiophene	1000
28	212	$C_{14}H_{12}S$	−16.S	C_2-alkyldibenzothiophene	1300
29	208	$C_{14}H_8S$	−20.S	Phenanthro[*b,c,d*]thiophene	3500
30	208	$C_{14}H_8S$	−20.S	Phenanthro[*b,c,d*]thiophene	940
31	222	$C_{15}H_{10}S$	−20.S	Methylphenanthro[*b,c,d*]thiophene	440
32	222	$C_{15}H_{10}S$	−20.S	Methylphenanthro[*b,c,d*]thiophene	530
33	222	$C_{15}H_{10}S$	−20.S	Methylphenanthro[*b,c,d*]thiophene	450
34	234	$C_{16}H_{10}S$	−22.S	Naphthobenzothiophene	1600
35	234	$C_{16}H_{10}S$	−22.S	Naphthobenzothiophene	710
36	234	$C_{16}H_{10}S$	−22.S	Naphthobenzothiophene	900
37	234	$C_{16}H_{10}S$	−22.S	Naphthobenzothiophene	600

Mass spectrometry

Identification of specific compounds in the anthracene oil bases was achieved using GC–MS. A Perkin-Elmer F-17 chromatograph was interfaced with a Kratos MS-30 double-beam mass spectrometer–DS-50 data system via a glass jet separator maintained at 250°C. The sample was made up as a 2.77% (w/v) solution in dichloromethane containing 3,6-dithiaoctane (505 ng/μl), di-*n*-octyl sulphide (461 ng/μl) and di-*n*-dodecyl sulphide (532 ng/μl) as internal markers. 1.3 μl were injected onto a 55-m SGE glass SCOT capillary column coated with SP-2250 under chromatographic conditions matched to those used for the GC–FPD analyses. Particular attention was paid to the helium carrier gas linear velocity to ensure comparable retention times. Using 70-eV electron impact ionisation, 630 mass spectral scans were collected at 3 sec per decade of mass over the mass range 50–400 at a resolution of 3000. The data system was used to generate the total ionisation current (TIC) chromatogram, and single ion chromatograms for selected masses. Accurate mass measurement using the double-beam technique allowed the assignment of atomic compositions to the compounds present.

The TIC chromatogram of the anthracene oil bases is shown in Fig. 3. Identifications for the labelled peaks, which comprise the major aza nitrogen compounds, together with the added internal markers, are given in Table IV. The peaks in this chromatogram were searched for the presence of compounds containing both N and S atoms. Single ion chromatograms for nominal *m/z* values corresponding to possible NS mixed heteroatomic compounds were also drawn, and the accurate masses of the molecular ions in the resulting peaks were checked to confirm the presence of these compounds. Single ion chromatograms for isomers of azabenzothiophene (*m/z* 135),

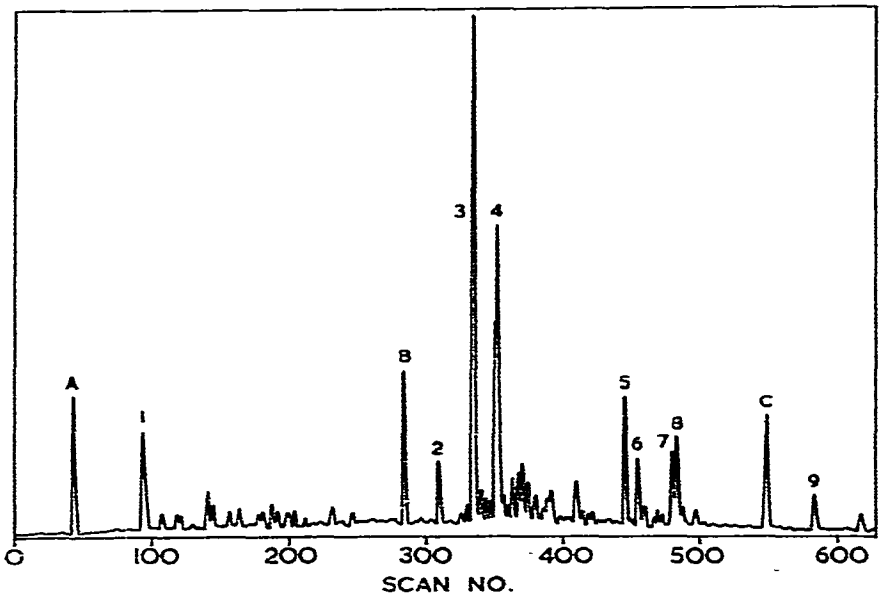


Fig. 3. GC–MS TIC chromatogram of anthracene oil bases. Identifications for labelled peaks given in Table IV. Conditions: 55-m SP-2250 glass SCOT capillary column programmed from 120 to 285°C at 3°/min with 4-min initial hold.

TABLE IV

IDENTIFICATIONS FOR LABELLED PEAKS IN GC–MS TIC CHROMATOGRAM OF ANTHRACENE OIL BASES (FIG. 3)

MS scan numbers refer to GC–MS TIC chromatogram in Fig. 3, and GC–MS single ion chromatograms in Figs. 4–7.

Peak No.	*MS scan No.*	*m/z*	*Atomic composition*	*Compound*
A	44	150	$C_6H_{14}S_2$	3,6-Dithiaoctane (added internal marker)
1	95	129	C_9H_7N	Quinoline
B	285	258	$C_{16}H_{34}S$	Di-*n*-octyl sulphide (added internal marker)
2	310	181	$C_{12}H_7NO$	Azafluorenone
3	336	179	$C_{13}H_9N$	7,8-Benzoquinoline
4	354	179	$C_{13}H_9N$	3,4- and 5,6-benzoquinolines
5	446	203	$C_{15}H_9N$	Azafluoranthene
6	456	203	$C_{15}H_9N$	Azafluoranthene
7	481	203	$C_{15}H_9N$	Azapyrene
8	484	203	$C_{15}H_9N$	Azapyrene
C	550	370	$C_{24}H_{50}S$	Di-*n*-dodecyl sulphide (added internal marker)
9	585	229	$C_{17}H_{11}N$	Dibenzoquinoline

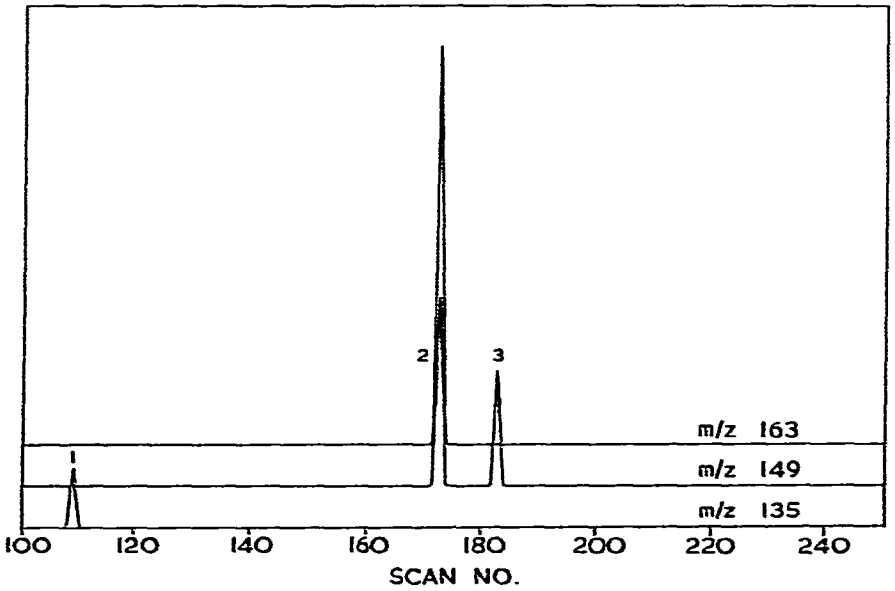


Fig. 4. GC–MS single ion chromatograms of anthracene oil bases showing azabenzothiophene (*m/z* 135) and C_1- and C_2-alkyl derivatives (*m/z* 149 and 163). Identifications for numbered peaks given in Table II. Conditions as in Fig. 3.

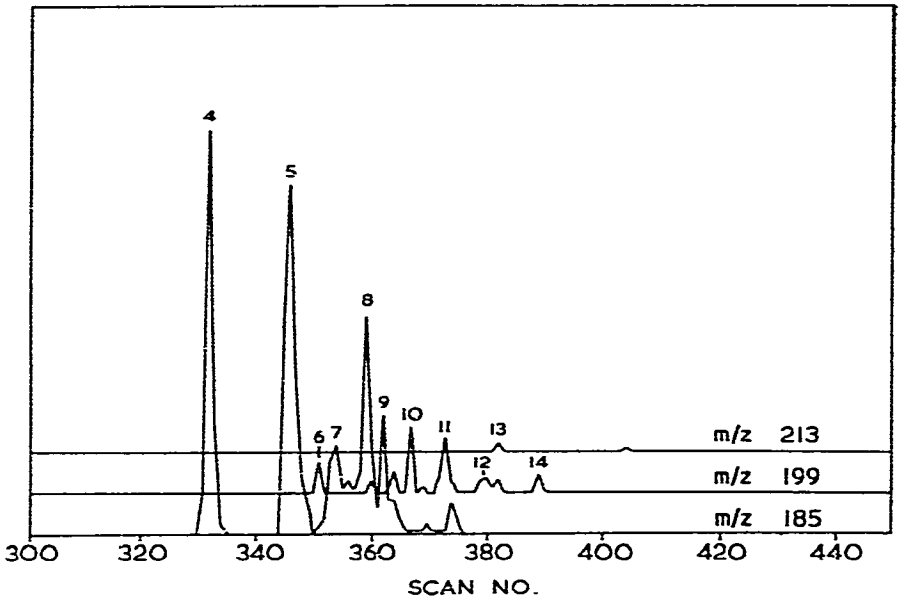


Fig. 5. GC–MS single ion chromatograms of anthracene oil bases showing azadibenzothiophenes and azanaphthothiophenes (*m/z* 185) and C_1- and C_2-alkyl derivatives (*m/z* 199 and 213). Identifications for numbered peaks given in Table II. Conditions as in Fig. 3.

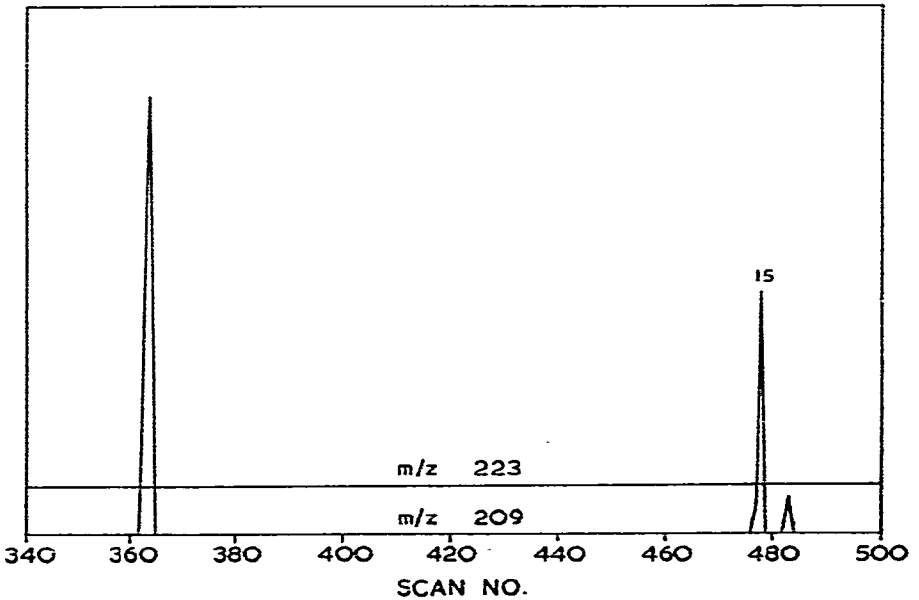


Fig. 6. GC–MS single ion chromatograms of anthracene oil bases for azaphenanthro[4,5-*b*,*c*,*d*]thiophenes (*m/z* 209) and methyl derivatives (*m/z* 223). Identification for numbered peak given in Table II. Conditions as in Fig. 3.

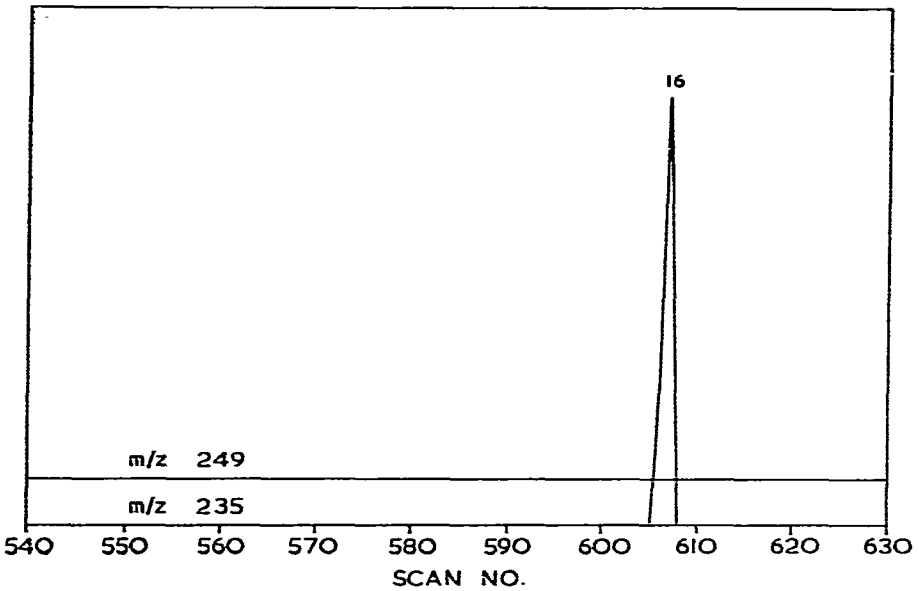
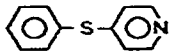


Fig. 7. GC–MS single ion chromatograms of anthracene oil bases for azanaphthobenzothiophenes (*m/z* 235) and methyl derivatives (*m/z* 249). Identification for numbered peak given in Table II. Conditions as in Fig. 3.

azadibenzothiophene (*m/z* 185), azaphenanthro[*b*,*c*,*d*]thiophene (*m/z* 209), azanaphthobenzothiophene (*m/z* 235) and their successive alkyl derivatives are shown in Figs. 4–7, respectively. The compound azadiphenyl sulphide was searched for, but not found.



m/z 187

The retention coefficients of the NS mixed heteroatomic compounds identified by GC–MS were calculated relative to 3,6-dithiaoctane = 0 and di-*n*-octyl sulphide = 10.0, and are listed in Table II. The retention coefficients of the peaks in the GC–FPD chromatogram of the bases shown in Fig. 1 have been calculated on the same basis and are also listed in Table II. Correlation of the retention coefficients was good, and GC–MS assignments for the numbered peaks in the GC–FPD chromatogram are given in Table II.

The numbered peaks in the GC–FPD chromatogram of the unfractionated anthracene oil shown in Fig. 2 have been identified on the basis of an earlier GC–MS analysis of a coke oven pitch[3], and assignments are given in Table III.

DISCUSSION

Identification of NS mixed heteroatomic compounds

The elemental analyses given in Table I show that most of the sulphur in the

anthracene oil remains in the residue after isolation of the basic fraction. These sulphur compounds are the non-basic thiophenic species seen in Fig. 2, which were identified in earlier work on coal tars and pitches[3]. However, a limited amount of sulphur is extracted into the basic fraction. The GC–MS analysis of this fraction indicated that all molecules contained a nitrogen atom, and the compounds appeared to be almost exclusively of the aza (pyridinic) type. It may, therefore, be inferred that any sulphur-containing compounds present in the basic fraction are likely to be NS mixed heteroatomic species. It is these compounds which have been revealed by the sulphur-specific FPD in the present work.

The comparison of retention times calculated relative to two internal marker compounds (3,6-dithiaoctane and di-*n*-octyl sulphide) has proved a satisfactory method of correlating peaks in the GC–FPD chromatogram of the anthracene oil bases (Fig. 1) with the NS mixed heteroatomic compounds identified by GC–MS. Sixteen of the major peaks in the chromatogram have been identified in this way in terms of atomic compositions. These compounds, which as far as we are aware have not been reported previously in anthracene oils, all appear to contain both thiophenic and pyridyl rings. Earlier work on coal tar products has shown these to be the most common structures for sulphur[3] and basic nitrogen[1] compounds, respectively, and it is therefore unnecessary to invoke alternative structures for the NS mixed heteroatomic compounds. Examples of the compound types identified are shown in Fig. 8; several isomers are possible for each structure, and many of these have been observed in the chromatogram.

A number of the minor peaks in the GC–FPD chromatogram of the anthracene oil bases (Fig. 1) could not be identified by GC–MS. Sulphur is a mass-deficient element, and accurate mass measurement will normally allow the assignment

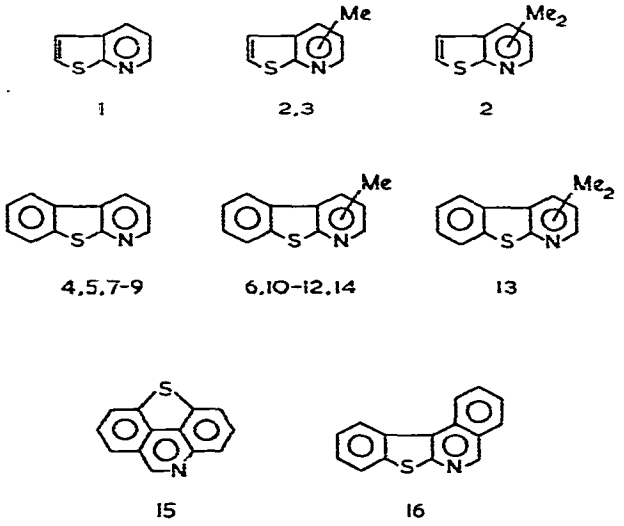
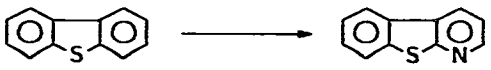


Fig. 8. Possible structures for NS mixed heteroatomic compounds identified in anthracene oil bases. Numbers refer to peaks in GC–FPD chromatogram in Fig. 1 and compounds listed in Table II. Me = Methyl. Me_2 represents two methyl groups or a C_2-alkyl group, the substitution positions of these cannot be specified.

of atomic compositions to the NS mixed heteroatomic compounds without ambiguity in the mixture of aza compounds. The hydrocarbon portion of the C_3–SH_4 doublet, which, with a mass separation of 0.003 a.m.u. is the most likely source of interference, is generally too hydrogen-deficient to exist. The problem is therefore likely to be one of sensitivity rather than interference. Many of the minor chromatographic peaks are of low intensity, and their narrowness, due to the high resolution of the capillary column, has resulted in a number appearing in one MS scan only. It is possible that some of the minor GC peaks may have been eluted between MS scans, and will not have been recorded by the mass spectrometer.

Comparison of the MS identifications indicates that the NS mixed heteroatomic compounds listed in Table II are closely related to the thiophenic compounds listed in Table III, and appear to be derived schematically by the replacement of one aromatic ring by a pyridyl ring, thus:



m/z 184 dibenzothiophene

m/z 185 azadibenzothiophene

The NS mixed heteroatomic compounds are one mass unit higher than the corresponding thiophenic compounds as a result of the mass difference N–CH.

Quantitative analyses

The approximate concentrations of the NS mixed heteroatomic compounds and the parent thiophenic compounds in the anthracene oil are given in Tables II and III, respectively. They have been calculated assuming a square law relationship between response and concentration, and a response factor of unity relative to the thioxanthen-9-one internal standard.

The choice of a suitable compound as internal standard is restricted; it is desirable that the compound should have a similar structure and sulphur content to the compounds being analysed, and it should also be eluted in a suitable retention time window on the chromatogram. The compound should also not contain groups which could give rise to additional emission at the sulphur detection wavelength. Although thioxanthen-9-one satisfies these requirements, the compounds being analysed will inevitably give relative responses which differ slightly from that for the internal standard. Deviations from a pure square law relationship between response and concentration may also occur[4,5]; these will be most marked for those components which differ significantly in concentration from the internal standard. Assumptions of this nature will always have to be made to quantify compounds for which no reference materials are available.

The quantitative results indicate that levels of the NS mixed heteroatomic compounds are very low, the largest single component, an azadibenzothiophene, representing only 250 ppm of the unfractionated anthracene oil. These compounds are less abundant by a factor of approximately 20 than their parent thiophenic and aza nitrogen compounds. A similar relationship has been observed between the latter compounds and their parent aromatic hydrocarbons.

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