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ESTIMATION OF BASIC NITROGEN COMPOUNDS IN SOME COAL LIQUEFACTION PRODUCTS

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SUMMARY

Gas chromatography–mass spectrometry (GC–MS) has been used to identify nitrogen compounds in basic fractions from three coal liquefaction products. Selective chemical derivatisation was used to assist in distinguishing between the various possible isomeric compounds types. The compounds thus identified were quantified by GC in conjunction with flame-ionisation detection (FID); they were largely aza heterocycles and anilines, no higher aromatic primary amines being identified. The use of a nitrogen-selective alkali-flame detector for the direct GC determination of nitrogen compounds in unfractionated coal liquefaction samples was evaluated, and the results agreed satisfactorily with those obtained by GC–FID analysis of the basic fractions.

INTRODUCTION

With the depletion of crude petroleum and natural gas supplies, increased attention is being given to the exploitation of oil shale and coal reserves. In particular, processes for coal liquefaction are being investigated both in Britain and the U.S.A. Nitrogen is present to some extent in all fossil fuels, but although its level is generally $<0.5\%$ in crude petroleum, significantly higher levels (1–2%) may be present in shale oils and coal. Nitrogen compounds are found as minor components in the distillation, extraction and combustion products. Heterocyclic pyrrolic and pyridinic (aza) compounds appear to be the major nitrogen-containing species, even in the largely aliphatic petroleum products, but aromatic primary and secondary amines, nitriles, amides and porphyrins have also been identified, together with some dinitrogen and mixed (NO and NS) heterocyclic systems. Although these compounds have not been characterised as fully as the predominant hydrocarbon components, they are important because they may cause problems in the stability and further refining of the products. These problems, which include catalyst poisoning, viscosity increase on storage, gum formation and discolouration, are due to the reactivity of the nitrogen compounds and other polar heteroatomic species. A number of the basic nitrogen compounds are toxic, several of the aza heterocycles and higher aromatic primary amines being known, or suspected carcinogens[1–3].

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A detailed knowledge of the types and concentrations of nitrogen compounds present in the newer coal-derived materials is clearly desirable in order to optimise methods for their removal and to specify procedures for the safe handling of such materials. Several gas chromatographic–mass spectrometric (GC–MS) studies of basic nitrogen compounds in products from American coal liquefaction processes have been published[1,4–9], and investigations of similar compounds in coal tars[10,11], cannabis and tobacco smoke condensates[10,12] and environmental samples[13–15] have also been reported. Although nitrogen-selective detectors have been used to generate GC profiles of nitrogen compounds in atmospheric pollution samples[16] and engine oils[17], their use for quantitative analyses has been much more restricted. However, Albert[18] has used an alkali-flame detector (AFD) to determine the nitrogen compound distribution in petroleum, Becher[19] has used a similar detector to determine aromatic amines in workplace atmospheres, and in two earlier papers[20,21] we have described the application of GC in conjunction with MS and AFD for the determination of nitrogen compounds in coal tar products. In this paper we report the application of similar techniques to the determination of basic nitrogen compounds in three samples from a British coal liquefaction process. Selective chemical derivatisation has been used to assist in distinguishing between the various possible isomeric nitrogen compound types identified by GC–MS. Although derivatisation is widely used to improve the chromatographic behaviour of polar compounds such as amines, very few applications of selective derivatisation for distinguishing between isomers have been reported hitherto. However, Guerin *et al.*[1] and Tomkins and Ho[8] have recently described the use of trifluoroacetylation to distinguish between free amines and their methylaza-arene isomers in bases from natural and synthetic crude oils, and Lee *et al.*[7] have used similar derivatives to enhance the electron-capture detector response to amino polycyclic aromatic compounds in solvent refined coal. In the present work we have used the commercial methylating reagent "Methyl-8" for the selective derivatisation of primary amines in basic fractions from coal liquefaction samples; as far as we are aware the reagent has not been used before for this purpose, and it may possess advantages over the trifluoroacetylating reagents.

EXPERIMENTAL AND RESULTS

Sample preparation

The samples were prepared at this Establishment from a British bituminous coal (Coal Rank Code 702; ash 2.9%; moisture 6.0%; volatile matter 37.2%, dry ash free; ultimate analysis C 84.0%, H 5.4%, N 1.9%, O 8.0%, S 0.7% (w/w), dry mineral matter free) by a liquid solvent extraction process[22]. They comprised a coal extract solution in recycle solvent, a light ends distillation product and a digester condensate. Nitrogen analyses are given in Table I. Basic nitrogen was determined by potentiometric titration with perchloric acid in a glacial acetic acid medium using a procedure similar to that described by Moore *et al.*[23]. Basic fractions were then prepared in the following manner. Approximately 5 g of each sample was weighed and dissolved in 40 ml dichloromethane. The solutions were extracted with 2 × 20 ml 10% sulphuric acid then with 2 × 20 ml 20% sulphuric acid. The aqueous acid extracts were combined, filtered to remove traces of oily residue, cooled and the pH adjusted to 12 with 4 *N* sodium hydroxide solution. The bases thus regenerated were recovered

by back extraction with 40 ml dichloromethane then with 2 × 20 ml dichloromethane. The combined extracts were reduced to a volume of approximately 1 ml under nitrogen at room temperature for analysis.

TABLE I

NITROGEN CONCENTRATIONS IN UNFRACTIONATED SAMPLES

	Concentration (ppm)		
	Coal extract in recycle solvent	*Light ends product*	*Digester condensate*
N (total)	4050	1200	1350
N (basic)	3400	1000	800
Basic as % of total N	84	83	59

Gas chromatography

The samples were analysed by GC using a Perkin-Elmer F-17 chromatograph fitted with a flame-ionisation detector (FID) and a nitrogen-selective AFD. The design of the AFD was essentially that of Kolb and Bischoff[24], employing an electrically-heated rubidium glass bead as the source of alkali metal ions. The statistical method of Rubin and Bayne[25] was used to adjust the AFD combustion gas flows and bead heating current for maximum response and selectivity towards nitrogen compounds; the optimised flow-rates were 3.0 ml/min for hydrogen and 19 ml/min for air, a bead heating current of 5.5 on the arbitrary control box scale being used. Under these conditions the selectivity factor for acridine–phenanthrene was 700. 0.2-μl splitless 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 hydrogen carrier gas (93 cm/sec linear velocity) for the FID analyses, and helium (38 cm/sec linear velocity) for the AFD analyses. Other chromatographic conditions are given on the appropriate chromatograms.

The basic fractions were analysed by GC–FID using dibenzyl as an internal standard. A 1-ml volume of a solution containing 400 ng/μl of dibenzyl in dichloromethane was added to each fraction which was then concentrated to 1 ml prior to analysis. GC–FID chromatograms for the coal extract solution, light ends product and digester condensate are given as the upper traces in Figs. 1–3, respectively. A Hewlett-Packard 3353 chromatographic data system was used to measure peak areas and calculate the results. Responses relative to dibenzyl were determined under identical chromatographic conditions for those compounds for which reference materials were available, and the results corrected accordingly. In cases where an unambiguous identification of a component could not be achieved, or reference materials were unavailable, a response factor of unity relative to the internal standard was assumed; the same assumption was made for multi-component peaks. Concentrations for the numbered peaks in Figs. 1–3 are given in Tables II–IV, respectively, expressed as ppm of the original, unfractionated samples.

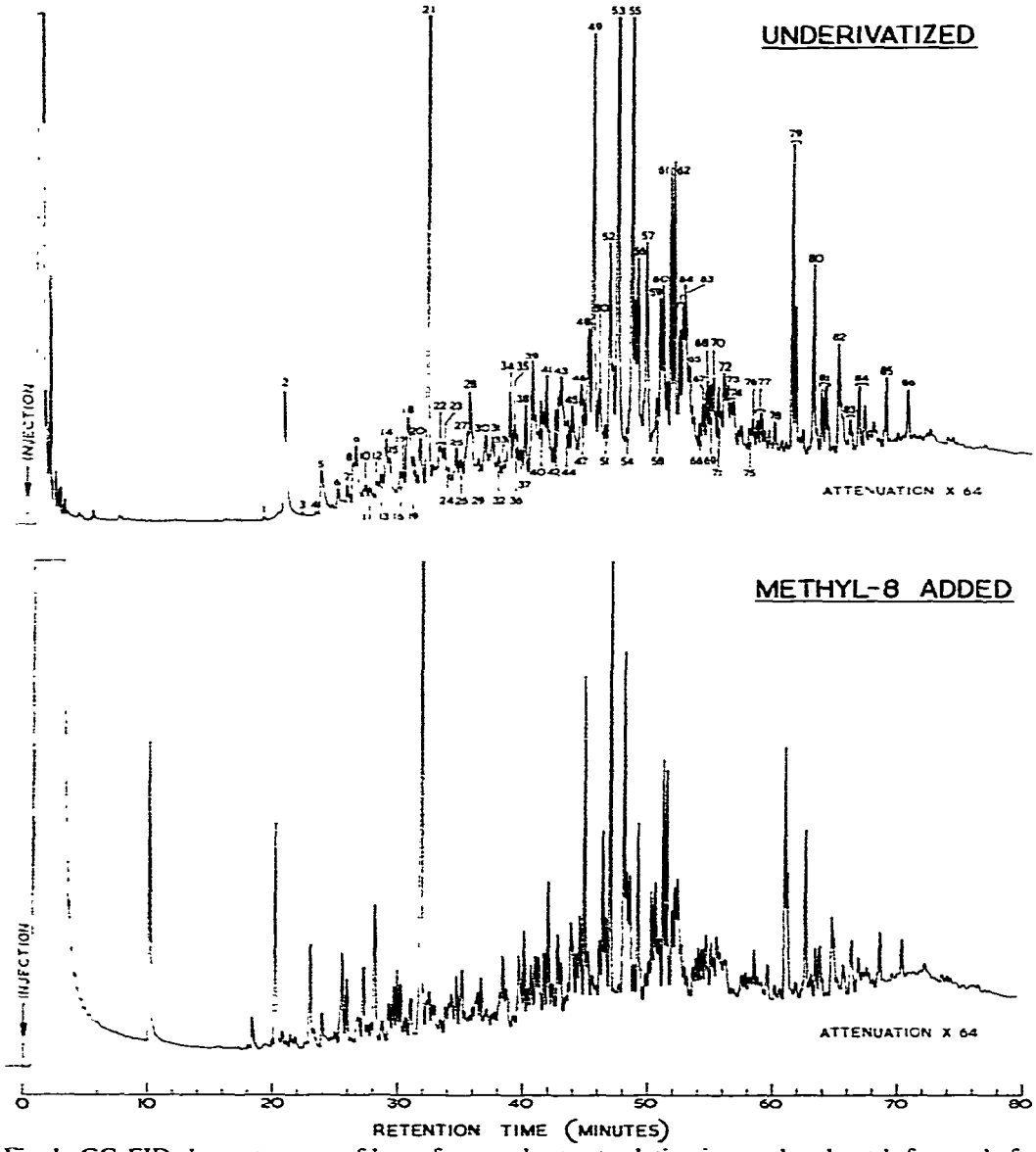


Fig. 1. GC–FID chromatograms of bases from coal extract solution in recycle solvent before and after derivatisation with Methyl-8. Identities of numbered peaks given in Table II. Conditions: 40 m, SP-2250 glass SCOT capillary column programmed from 85–285°C at 3°/min with 4-min initial hold.

The unfractionated light ends product was also analysed by GC–AFD as an approximately 20% (w/v) solution in tetrahydrofuran containing 4-phenylpyridine (979 ng/μl) as an internal standard. The resulting chromatogram is shown in Fig. 4. It is very similar to the GC–FID chromatogram of the bases from the same sample shown in Fig. 2 and the peaks have been numbered in the same manner, identifications being given in Table III. Concentrations for the numbered peaks in Fig. 4

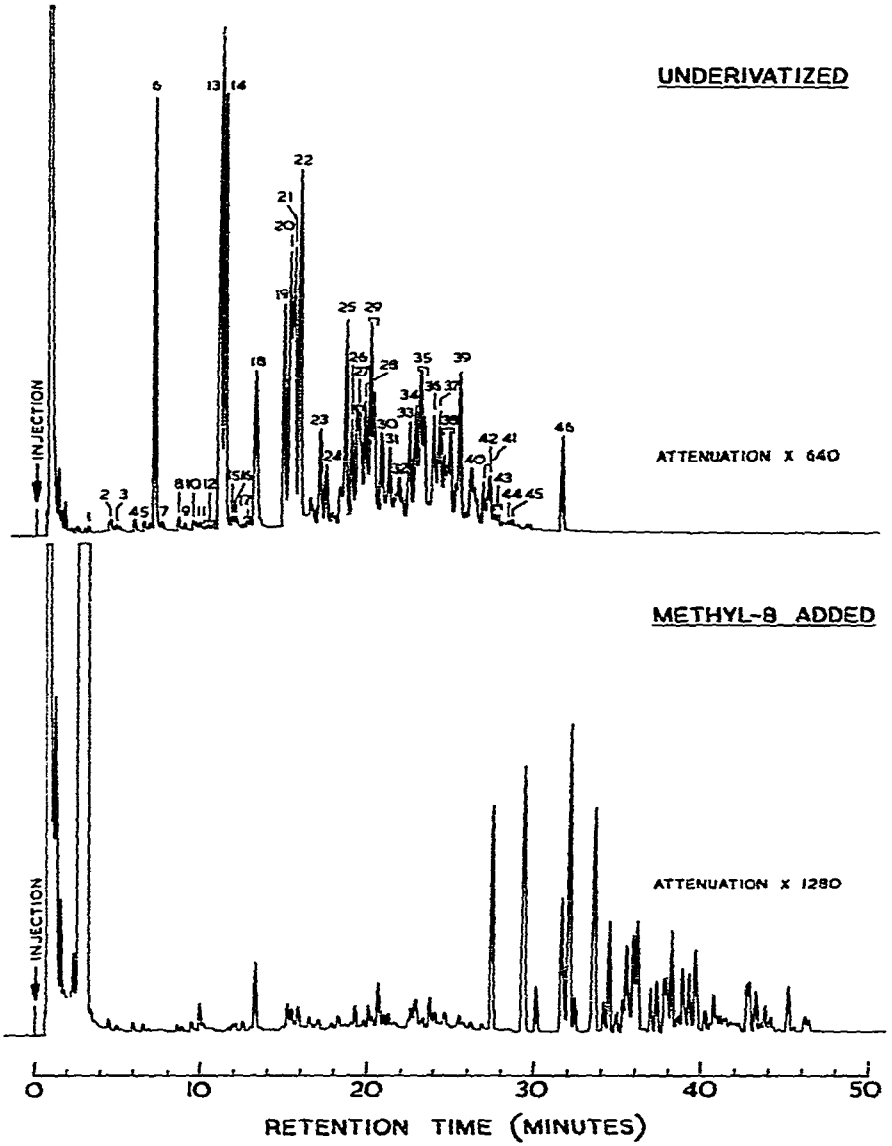


Fig. 2. GC–FID chromatograms of bases from light ends product before and after derivatisation with Methyl-8. Identities of numbered peaks given in Table III. Conditions as in Fig. 1.

have been calculated assuming a response factor of unity relative to 4-phenylpyridine, and are also given in Table III.

Mass spectrometry

GC–MS was used for the identification of specific compounds in the basic fractions. 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. Approximately 2.5-μl splitless injections were made onto a 50-m

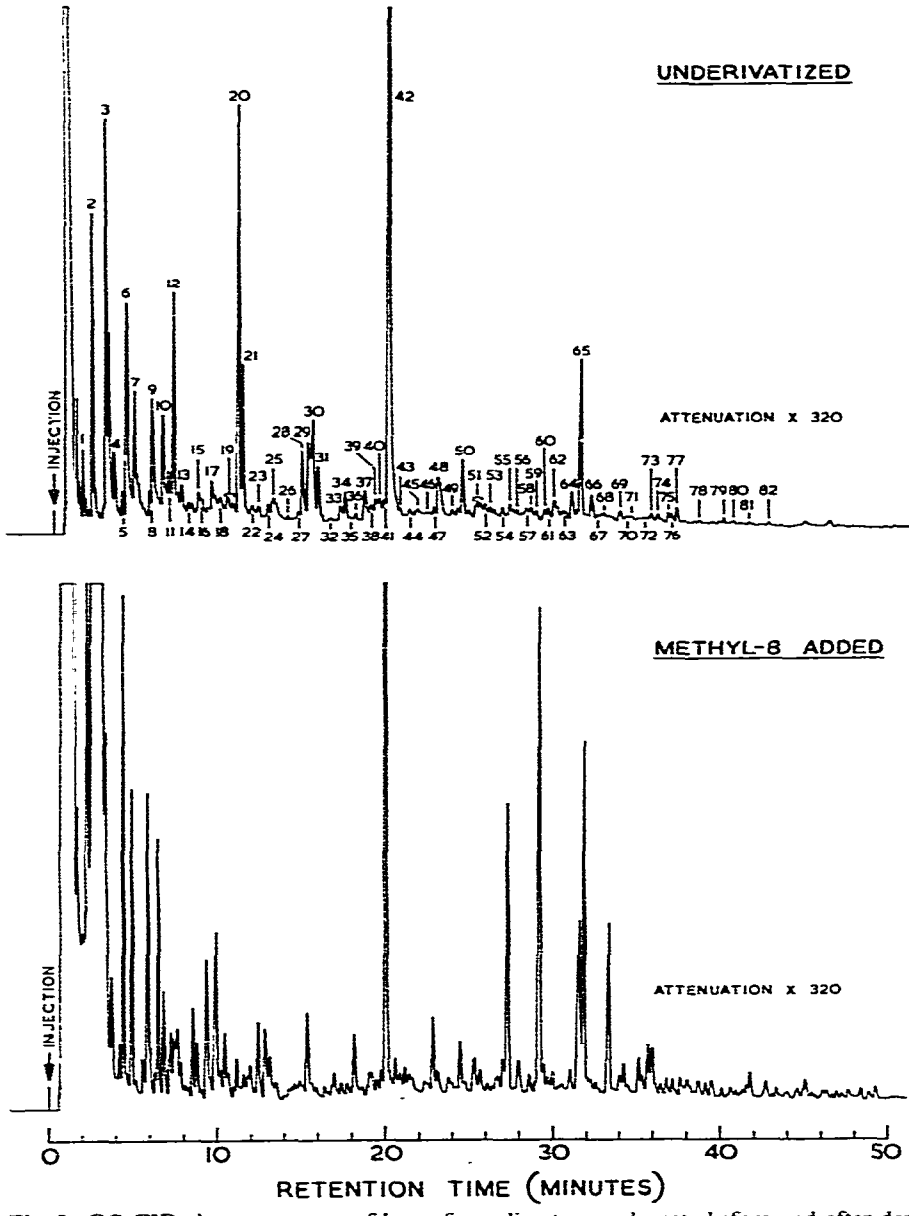


Fig. 3. GC–FID chromatograms of bases from digester condensate before and after derivatisation with Methyl-8. Identities of numbered peaks given in Table IV. Conditions as in Fig. 1.

SGE SP-2250 glass SCOT capillary column under similar chromatographic conditions to those used for the GC–FID and GC–AFD analyses. Mass spectral scans were collected at 3 sec per decade of mass over the mass range 50–400 at a resolution of 3000 using 70 eV electron-impact ionisation. The data system was used to generate the total ionisation current (TIC) chromatograms, and single ion chromatograms for

TABLE II

COMPOUNDS IDENTIFIED IN BASIC FRACTION OF COAL EXTRACT IN RECYCLE SOLVENT

Peak numbers refer to GC–FID chromatogram in Fig. 1. Concentrations determined by GC–FID and expressed as ppm of original, unfractionated sample.

Peak No.	*m/z*	*Atomic composition*	*Z No.*	*Conc. (ppm)*	*Name or possible type*
1	133	$C_9H_{11}N$	− 7.N	<1	Tetrahydroquinoline
2	129	C_9H_7N	−11.N	15	Quinoline
2	147	$C_{10}H_{13}N$	− 7.N		Methyltetrahydroquinoline
3	147	$C_{10}H_{13}N$	− 7.N	<1	Methyltetrahydroquinoline
4	129	C_9H_7N	−11.N	<1	Isoquinoline
4	147	$C_{10}H_{13}N$	− 7.N		Methyltetrahydroquinoline
5	143	$C_{10}H_9N$	−11.N	8	2-Methylquinoline
6	143	$C_{10}H_9N$	−11.N	3	Methylquinoline
7	147	$C_{10}H_{13}N$	− 7.N	4	Methyltetrahydroquinoline
7	161	$C_{11}H_{15}N$	− 7.N		C_2-Alkyltetrahydroquinoline
8	143	$C_{10}H_9N$	−11.N	4	Methylquinoline
9	143	$C_{10}H_9N$	−11.N	11	Methylquinoline
9	161	$C_{11}H_{15}N$	− 7.N		C_2-Alkyltetrahydroquinoline
9	175	$C_{12}H_{17}N$	− 7.N		C_3-Alkyltetrahydroquinoline
10	157	$C_{11}H_{11}N$	−11.N	3	C_2-Alkylquinoline
10	161	$C_{11}H_{15}N$	− 7.N		C_2-Alkyltetrahydroquinoline
11	143	$C_{10}H_9N$	−11.N	5	4-Methylquinoline
12	143	$C_{10}H_9N$	−11.N	5	Methylquinoline
12	157	$C_{11}H_{11}N$	−11.N		C_2-Alkylquinoline
12	161	$C_{11}H_{15}N$	− 7.N		C_2-Alkyltetrahydroquinoline
13	157	$C_{11}H_{11}N$	−11.N	4	C_2-Alkylquinoline
13	161	$C_{11}H_{15}N$	− 7.N		C_2Alkyltetrahydroquinoline
14	157	$C_{11}H_{11}N$	−11.N	13	2,6 + 2,7-Dimethylquinolines
15	157	$C_{11}H_{11}N$	−11.N	7	C_2-Alkylquinoline
15	175	$C_{12}H_{17}N$	− 7.N		C_3-Alkyltetrahydroquinoline
16	157	$C_{11}H_{11}N$	−11.N	6	C_2-Alkylquinoline
16	175	$C_{12}H_{17}N$	− 7.N		C_3-Alkyltetrahydroquinoline
17	157	$C_{11}H_{11}N$	−11.N	4	C_2-Alkylquinoline
17	161	$C_{11}H_{15}N$	− 7.N		C_2-Alkyltetrahydroquinoline
18	157	$C_{11}H_{11}N$	−11.N	18	C_2-Alkylquinoline
18	171	$C_{12}H_{13}N$	−11.N		C_3-Alkylquinoline
19	157	$C_{11}H_{11}N$	−11.N	8	C_2-Alkylquinoline
19	171	$C_{12}H_{13}N$	−11.N		C_3-Alkylquinoline
19	175	$C_{12}H_{17}N$	− 7.N		C_3-Alkyltetrahydroquinoline
20	157	$C_{11}H_{11}N$	−11.N	12	C_2-Alkylquinoline
20	171	$C_{12}H_{13}N$	−11.N		C_3-Alkylquinoline
20	175	$C_{12}H_{17}N$	− 7.N		C_3-Alkyltetrahydroquinoline
21	182	$C_{14}H_{14}$	−14	–	Dibenzyl (internal standard)
22	157	$C_{11}H_{11}N$	−11.N	13	C_2-Alkylquinoline
22	171	$C_{12}H_{13}N$	−11.N		C_3-Alkylquinoline
23	171	$C_{12}H_{13}N$	−11.N	8	C_3-Alkylquinoline
24	171	$C_{12}H_{13}N$	−11.N	6	C_3-Alkylquinoline
25	171	$C_{12}H_{13}N$	−11.N	11	C_3-Alkylquinoline
26	171	$C_{12}H_{13}N$	−11.N	7	C_3-Alkylquinoline
26	185	$C_{13}H_{15}N$	−11.N		C_4-Alkylquinoline

(Continued on p. 278)

TABLE II *(continued)*

Peak No.	*m/z*	*Atomic composition*	*Z No.*	*Conc. (ppm)*	*Name or possible type*
27	171	$C_{12}H_{13}N$	−11.N		C_3-Alkylquinoline
27	185	$C_{13}H_{15}N$	−11.N	30	C_4-Alkylquinoline
28	171	$C_{12}H_{13}N$	−11.N		C_3-Alkylquinoline
29	171	$C_{12}H_{13}N$	−11.N	8	C_3-Alkylquinoline
29	185	$C_{13}H_{15}N$	−11.N		C_4-Alkylquinoline
30	185	$C_{13}H_{15}N$	−11.N	14	C_4-Alkylquinoline
31	189	$C_{13}H_{19}N$	− 7.N	12	C_4-Alkyltetrahydroquinoline
32	185	$C_{13}H_{15}N$	−11.N	9	C_4-Alkylquinoline
33	185	$C_{13}H_{15}N$	−11.N	4	C_4-Alkylquinoline
34	185	$C_{13}H_{15}N$	−11.N	14	C_4-Alkylquinoline
34	187	$C_{13}H_{17}N$	− 9.N		Octahydrobenzoquinoline
35	185	$C_{13}H_{15}N$	−11.N	9	C_4-Alkylquinoline
36	185	$C_{13}H_{15}N$	−11.N	10	C_4-Alkylquinoline
36	199	$C_{14}H_{17}N$	−11.N		C_5-Alkylquinoline
37	183	$C_{13}H_{13}N$	−13.N	6	Tetrahydrobenzoquinoline or methyldiphenylamine
37	185	$C_{13}H_{15}N$	−11.N		C_4-Alkylquinoline
38	169	$C_{12}H_{11}N$	−13.N	12	Diphenylamine or aminobiphenyl
38	185	$C_{13}H_{15}N$	−11.N		C_4-Alkylquinoline
39	169	$C_{12}H_{11}N$	−13.N	16	Diphenylamine or aminobiphenyl
39	183	$C_{13}H_{13}N$	−13.N		Methyldiphenylamine
39	199	$C_{14}H_{17}N$	−11.N		C_5-Alkylquinoline
40	169	$C_{12}H_{11}N$	−13.N	11	Diphenylamine or aminobiphenyl
40	183	$C_{13}H_{13}N$	−13.N		Methyldiphenylamine
40	199	$C_{14}H_{17}N$	−11.N		C_5-Alkylquinoline
41	183	$C_{13}H_{13}N$	−13.N	19	Methyldiphenylamine
41	197	$C_{14}H_{15}N$	−13.N		C_2-Alkyldiphenylamine
41	185	$C_{13}H_{15}N$	−11.N		C_4-Alkylquinoline
42	183	$C_{13}H_{13}N$	−13.N	10	Methyldiphenylamine
42	187	$C_{13}H_{17}N$	− 9.N		Octahydrobenzoquinoline
42	199	$C_{14}H_{17}N$	−11.N		C_5-Alkylquinoline
43	187	$C_{13}H_{17}N$	− 9.N	28	Octahydrobenzoquinoline
44	183	$C_{13}H_{13}N$	−13.N	13	Methyldiphenylamine
44	197	$C_{14}H_{15}N$	−13.N		C_2-Alkyldiphenylamine
44	199	$C_{14}H_{17}N$	−11.N		C_5-Alkylquinoline
45	183	$C_{13}H_{13}N$	−13.N	21	Methyldiphenylamine
45	197	$C_{14}H_{15}N$	−13.N		C_2-Alkyldiphenylamine
45	199	$C_{14}H_{17}N$	−11.N		C_5-Alkylquinoline
45	201	$C_{14}H_{19}N$	− 9.N		Methyloctahydrobenzoquinoline
45	213	$C_{15}H_{19}N$	−11.N		C_6-Alkylquinoline
46	183	$C_{13}H_{13}N$	−13.N		Methyldiphenylamine
46	197	$C_{14}H_{15}N$	−13.N	21	C_2-Alkyldiphenylamine
47	183	$C_{13}H_{13}N$	−13.N		Methyldiphenylamine
47	197	$C_{14}H_{15}N$	−13.N		C_2-Alkyldiphenylamine
48	183	$C_{13}H_{13}N$	−13.N	23	Methyldiphenylamine
48	197	$C_{14}H_{15}N$	−13.N		C_2-Alkyldiphenylamine
49	183	$C_{13}H_{13}N$	−13.N	44	Methyldiphenylamine
49	197	$C_{14}H_{15}N$	−13.N		C_2-Alkyldiphenylamine
50	197	$C_{14}H_{15}N$	−13.N	20	C_2-Alkyldiphenylamine
50	183	$C_{13}H_{13}N$	−13.N		Methyldiphenylamine
51	197	$C_{14}H_{15}N$	−13.N	7	C_2-Alkyldiphenylamine
51	183	$C_{13}H_{13}N$	−13.N		Methyldiphenylamine

TABLE II *(continued)*

Peak No.	*m/z*	*Atomic composition*	*Z No.*	*Conc. (ppm)*	*Name or possible type*
52	179	$C_{13}H_9N$	−17.N	36	7,8-Benzoquinoline
52	197	$C_{14}H_{15}N$	−13.N		C_2-Alkyldiphenylamine
53	179	$C_{13}H_9N$	−17.N	63	2,3-Benzoquinoline
53	197	$C_{14}H_{15}N$	−13.N		C_2-Alkyldiphenylamine
54	211	$C_{15}H_{17}N$	−13.N	4	C_3-Alkyldiphenylamine
55	179	$C_{13}H_9N$	−17.N	56	3,4 + 5,6-Benzoquinolines
55	193	$C_{14}H_{11}N$	−17.N		Methylbenzoquinoline
55	211	$C_{15}H_{17}N$	−13.N		C_3-Alkyldiphenylamine
56	193	$C_{14}H_{11}N$	−17.N	30	Methylbenzoquinoline
56	197	$C_{14}H_{15}N$	−13.N		C_2-Alkyldiphenylamine
57	197	$C_{14}H_{15}N$	−13.N	33	C_2-Alkyldiphenylamine
57	211	$C_{15}H_{17}N$	−13.N		C_3-Alkyldiphenylamine
58	197	$C_{14}H_{15}N$	−13.N	9	C_2-Alkyldiphenylamine
58	211	$C_{15}H_{17}N$	−13.N		C_3-Alkyldiphenylamine
59	193	$C_{14}H_{11}N$	−17.N	15	Methylbenzoquinoline
59	211	$C_{15}H_{17}N$	−13.N		C_3-Alkyldiphenylamine
60	193	$C_{14}H_{11}N$	−17.N	21	Methylbenzoquinoline
60	211	$C_{15}H_{17}N$	−13.N		C_3-Alkyldiphenylamine
60	207	$C_{15}H_{13}N$	−17.N		C_2-Alkylbenzoquinoline
61	193	$C_{14}H_{11}N$	−17.N	24	Methylbenzoquinoline
61	211	$C_{15}H_{17}N$	−13.N		C_3-Alkyldiphenylamine
62	193	$C_{14}H_{11}N$	−17.N	30	Methylbenzoquinoline
62	211	$C_{15}H_{17}N$	−13.N		C_3-Alkyldiphenylamine
62	209	$C_{15}H_{15}N$	−15.N		C_3-Alkylazafluorene
63	193	$C_{14}H_{11}N$	−17.N	28	Methylbenzoquinoline
63	211	$C_{15}H_{17}N$	−13.N		C_3-Alkyldiphenylamine
63	207	$C_{15}H_{13}N$	−17.N		C_2-Alkylbenzoquinoline
63	209	$C_{15}H_{15}N$	−15.N		C_3-Alkylazafluorene
64	193	$C_{14}H_{11}N$	−17.N	23	Methylbenzoquinoline
64	211	$C_{15}H_{17}N$	−13.N		C_3-Alkyldiphenylamine
64	207	$C_{15}H_{13}N$	−17.N		C_2-Alkylbenzoquinoline
64	225	$C_{16}H_{19}N$	−13.N		C_4-Alkyldiphenylamine
65	207	$C_{15}H_{13}N$	−17.N	10	C_2-Alkylbenzoquinoline
65	209	$C_{15}H_{15}N$	−15.N		C_3-Alkylazafluorene
65	211	$C_{15}H_{17}N$	−13.N		C_3-Alkyldiphenylamine
65	223	$C_{16}H_{17}N$	−15.N		C_4-Alkylazafluorene
66	207	$C_{15}H_{13}N$	−17.N	6	C_2-Alkylbenzoquinoline
66	211	$C_{15}H_{17}N$	−13.N		C_3-Alkyldiphenylamine
66	225	$C_{16}H_{19}N$	−13.N		C_4-Alkyldiphenylamine
67	207	$C_{15}H_{13}N$	−17.N	11	C_2-Alkylbenzoquinoline
67	211	$C_{15}H_{17}N$	−13.N		C_3-Alkyldiphenylamine
68	207	$C_{15}H_{13}N$	−17.N	10	C_2-Alkylbenzoquinoline
69	207	$C_{15}H_{13}N$	−17.N	9	C_2-Alkylbenzoquinoline
70	207	$C_{15}H_{13}N$	−17.N	15	C_2-Alkylbenzoquinoline
70	221	$C_{16}H_{15}N$	−17.N		C_3-Alkylbenzoquinoline
71	207	$C_{15}H_{13}N$	−17.N	9	C_2-Alkylbenzoquinoline
71	211	$C_{15}H_{17}N$	−13.N		C_3-Alkyldiphenylamine
71	225	$C_{16}H_{19}N$	−13.N		C_4-Alkyldiphenylamine
72	207	$C_{15}H_{13}N$	−17.N	13	C_2-Alkylbenzoquinoline
72	221	$C_{16}H_{15}N$	−17.N		C_3-Alkylbenzoquinoline

(Continued on p. 280)

TABLE II *(continued)*

Peak No.	*m/z*	*Atomic composition*	*Z No.*	*Conc. (ppm)*	*Name or possible type*
73	207	$C_{15}H_{13}N$	−17.N	10	C_2-Alkylbenzoquinoline
73	221	$C_{16}H_{15}N$	−17.N		C_3-Alkylbenzoquinoline
74	207	$C_{15}H_{13}N$	−17.N	19	C_2-Alkylbenzoquinoline
74	221	$C_{16}H_{15}N$	−17.N		C_3-Alkylbenzoquinoline
75	207	$C_{15}H_{13}N$	−17.N	7	C_2-Alkylbenzoquinoline
75	221	$C_{16}H_{15}N$	−17.N		C_3-Alkylbenzoquinoline
76	207	$C_{15}H_{13}N$	−17.N	7	C_2-Alkylbenzoquinoline
76	221	$C_{16}H_{15}N$	−17.N		C_3-Alkylbenzoquinoline
76	223	$C_{16}H_{17}N$	−15.N		C_4-Alkylazafluorene
77	202	$C_{16}H_{10}$	−22	14	Fluoranthene or pyrene
77	221	$C_{16}H_{15}N$	−17.N		C_3-Alkylbenzoquinoline
77	223	$C_{16}H_{17}N$	−15.N		C_4-Alkylazafluorene
78	221	$C_{16}H_{15}N$	−17.N	6	C_3-Alkylbenzoquinoline
78	223	$C_{16}H_{17}N$	−15.N		C_4-Alkylazafluorene
79	203	$C_{15}H_9N$	−21.N	36	Azafluoranthene/pyrene
80	217	$C_{16}H_{11}N$	−21.N	19	Methylazafluoranthene/pyrene or azabenzofluorene
80	233	C_1-$H_{15}N$	−19.N		C_3-Alkylazacyclopenteno[*def*]-phenanthrene or tetrahydrodibenzoquinoline
81	219	$C_{16}H_{13}N$	−19.N	19	C_2-Alkylazacyclopenteno[*def*]-phenanthrene
81	217	$C_{16}H_{11}N$	−21.N		Methylazafluoranthene/pyrene or azabenzofluorene
81	231	$C_{17}H_{13}N$	−21.N		C_2-Alkylazafluoranthene/pyrene or methylazabenzofluorene
82	217	$C_{16}H_{11}N$	−21.N	21	Methylazafluoranthene/pyrene or azabenzofluorene
82	231	$C_{17}H_{13}N$	−21.N		C_2-Alkylazafluoranthene/pyrene or methylazabenzofluorene
82	233	$C_{17}H_{15}N$	−19.N		C_3-Alkylazacyclopenteno[*def*]-phenanthrene or tetrahydrodibenzoquinoline
83	233	$C_{17}H_{15}N$	−19.N	9	C_3-Alkylazacyclopenteno[*def*]-phenanthrene or tetrahydrodibenzoquinoline
83	217	$C_{16}H_{11}N$	−21.N		Methylazafluoranthene/pyrene or azabenzofluorene
84	233	$C_{17}H_{15}N$	−19.N	16	C_3-Alkylazacyclopenteno[*def*]-phenanthrene or tetrahydrodibenzoquinoline
85	229	$C_{17}H_{11}N$	−23.N	10	3,4-Benzacridine
85	233	$C_{17}H_{15}N$	−19.N		C_3-Alkylazacyclopenteno[*def*]-phenanthrene or tetrahydrodibenzoquinoline
86	229	$C_{17}H_{11}N$	−23.N	10	Dibenzoquinoline.

selected masses. Accurate mass measurement, generally to within ±5 mmu using the double-beam technique, permitted the assignment of atomic compositions.

GC–MS identification was assisted by using the data system to draw single ion chromatograms for nominal *m/z* values corresponding to possible nitrogen com-

TABLE III

COMPOUNDS IDENTIFIED IN BASIC FRACTION OF LIGHT ENDS PRODUCT

Peak numbers refer to GC–FID chromatogram in Fig. 2, and also GC–AFD chromatogram of unfractionated sample in Fig. 4. Concentrations determined by GC–FID and GC–AFD and expressed as ppm of original, unfractionated sample.

Peak No.	*m/z*	*Atomic composition*	*Z No.*	*Conc. (ppm)*		*Name or possible type*
				GC–FID	*GC–AFD*	
1	107	C_7H_9N	– 5.N	4	5	C_2-Alkylpyridine
2	107	C_7H_9N	– 5.N	21	14	C_2-Alkylpyridine
3	121	$C_8H_{11}N$	– 5.N	6	5	C_3-Alkylpyridine
4	121	$C_8H_{11}N$	– 5.N	12	11	C_3-Alkylpyridine
5	121	$C_8H_{11}N$	– 5.N	12	9	C_3-Alkylpyridine
6	93	C_6H_7N	– 5.N	320	360	Aniline
6	135	$C_9H_{13}N$	– 5.N			C_4-Alkylpyridine
7	107	C_7H_9N	– 5.N	3	28	C_2-Alkylpyridine
7	121	$C_8H_{11}N$	– 5.N			C_3-Alkylpyridine
8	135	$C_9H_{13}N$	– 5.N	10	20	C_4-Alkylpyridine
9	121	$C_8H_{11}N$	– 5.N	4	1	C_3-Alkylpyridine
10	121	$C_8H_{11}N$	– 5.N	8	6	C_3-Alkylpyridine
10	135	$C_9H_{13}N$	– 5.N			C_4-Alkylpyridine
10	149	$C_{10}H_{15}N$	– 5.N			C_5-Alkylpyridine
11	135	$C_9H_{13}N$	– 5.N	11	2	C_4-Alkylpyridine
12	–	–	–	13	28	Not identified
13	107	C_7H_9N	– 5.N	520	490	*o*-Toluidine
13	135	$C_9H_{13}N$	– 5.N			C_4-Alkylpyridine
14	107	C_7H_9N	– 5.N	400	410	*m*-Toluidine
14	135	$C_9H_{13}N$	– 5.N			C_4-Alkylpyridine
15	121	$C_8H_{11}N$	– 5.N	2	–	C_3-Alkylpyridine
15	135	$C_9H_{13}N$	– 5.N			C_4-Alkylpiridine
15	149	$C_{10}H_{15}N$	– 5.N			C_5-Alkylpyridine
16	135	$C_9H_{13}N$	– 5.N	15	15	C_4-Alkylpyridine
17	121	$C_8H_{11}N$	– 5.N	3	10	C_3-Alkylpyridine
17	135	$C_9H_{13}N$	– 5.N			C_4-Alkylpyridine
17	149	$C_{10}H_{15}N$	– 5.N			C_5-Alkylpyridine
18	165	$C_{11}H_{19}N$	– 3.N	160	150	Azaperhydroacenaphthene
19	121	$C_8H_{11}N$	– 5.N	180	190	*o*-Ethylaniline
20	121	$C_8H_{11}N$	– 5.N	280	330	2,4- + 2,6-Dimethylanilines
21	121	$C_8H_{11}N$	– 5.N	320	220	2,5-Dimethyl- + *p*-ethylanilines
22	121	$C_8H_{11}N$	– 5.N	340	370	3,5-Dimethyl- + *m*-ethylanilines
23	121	$C_8H_{11}N$	– 5.N	74	68	3,4-Dimethylaniline
23	179	$C_{12}H_{21}N$	– 3.N			Methylazaperhydro-acenaphthene
24	121	$C_8H_{11}N$	– 5.N	47	59	2,3-Dimethylaniline
24	179	$C_{12}H_{21}N$	– 3.N			Methylazaperhydro-acenaphthene
25	135	$C_9H_{13}N$	– 5.N	180	160	C_3-Alkylaniline
25	149	$C_{10}H_{15}N$	– 5.N			C_5-Alkylpyridine
26	135	$C_9H_{13}N$	– 5.N	67	55	C_3-Alkylaniline
26	149	$C_{10}H_{15}N$	– 5.N			C_5-Alkylpyridine
26	163	$C_{11}H_{17}N$	– 5.N			C_6-Alkylpyridine

(Continued on p. 282)

TABLE III *(continued)*

Peak No.	*m/z*	*Atomic composition*	*Z No.*	*Conc. (ppm)*		*Name or possible type*
				GC–FID	*GC–AFD*	
26	177	$C_{12}H_{19}N$	– 5.N			C_7-Alkylpyridine
27	135	$C_9H_{13}N$	– 5.N	160	150	C_3-Alkylaniline
27	163	$C_{11}H_{17}N$	– 5.N			C_6-Alkylpyridine
27	177	$C_{12}H_{19}N$	– 5.N			C_7-Alkylpyridine
28	135	$C_9H_{13}N$	– 5.N	82	150	C_3-Alkylaniline
28	149	$C_{10}H_{15}N$	– 5.N			C_5-Alkylpyridine
29	135	$C_9H_{13}N$	– 5.N	170	190	C_3-Alkylaniline
29	149	$C_{10}H_{15}N$	– 5.N			C_5-Alkylpyridine
29	177	$C_{12}H_{19}N$	– 5.N			C_7-Alkylpyridine
30	147	$C_{10}H_{13}N$	– 7.N	420	270	Methyltetrahydroquinoline
30	161	$C_{11}H_{15}N$	– 7.N			C_2-Alkyltetrahydroquinoline
31	135	$C_9H_{13}N$	– 5.N	94	41	C_3-Alkylaniline
31	163	$C_{11}H_{17}N$	– 5.N			C_6-Alkylpyridine
32	135	$C_9H_{13}N$	– 5.N	48	41	C_3-Alkylaniline
32	163	$C_{11}H_{17}N$	– 5.N			C_6-Alkylpyridine
32	147	$C_{10}H_{13}N$	– 7.N			Methyltetrahydroquinoline
33	149	$C_{10}H_{15}N$	– 5.N	100	85	C_4-Alkylaniline
33	163	$C_{11}H_{17}N$	– 5.N			C_6-Alkylpyridine
33	177	$C_{12}H_{19}N$	– 5.N			C_7-Alkylpyridine
34	149	$C_{10}H_{15}N$	– 5.N	90	68	C_4-Alkylaniline
34	161	$C_{11}H_{15}N$	– 7.N			C_2-Alkyltetrahydroquinoline
34	177	$C_{12}H_{19}N$	– 5.N			C_7-Alkylpyridine
35	149	$C_{10}H_{15}N$	– 5.N	290	200	C_4-Alkylaniline
35	163	$C_{11}H_{17}N$	– 5.N			C_6-Alkylpyridine
35	161	$C_{11}H_{15}N$	– 7.N			C_2-Alkyltetrahydroquinoline
35	177	$C_{12}H_{19}N$	– 5.N			C_7-Alkylpyridine
36	149	$C_{10}H_{15}N$	– 5.N	72	140	C_4-Alkylaniline
36	161	$C_{11}H_{15}N$	– 7.N			C_2-Alkyltetrahydroquinoline
36	175	$C_{12}H_{17}N$	– 7.N			C_3-Alkyltetrahydroquinoline
37	149	$C_{10}H_{15}N$	– 5.N	95	140	C_4-Alkylaniline
37	161	$C_{11}H_{15}N$	– 7.N			C_2-Alkyltetrahydroquinoline
37	177	$C_{12}H_{19}N$	– 5.N			C_7-Alkylpyridine
38	149	$C_{10}H_{15}N$	– 5.N	190	210	C_4-Alkylaniline
38	163	$C_{11}H_{17}N$	– 5.N			C_6-Alkylpyridine
38	177	$C_{12}H_{19}N$	– 5.N			C_7-Alkylpyridine
38	175	$C_{12}H_{17}N$	– 7.N			C_3-Alkyltetrahydroquinoline
39	175	$C_{12}H_{17}N$	– 7.N	140	110	C_3-Alkyltetrahydroquinoline
39	161	$C_{11}H_{15}N$	– 7.N			C_2-Alkyltetrahydroquinoline
39	149	$C_{10}H_{15}N$	– 5.N			C_4-Alkylaniline
39	157	$C_{11}H_{11}N$	–11.N			C_2-Alkylquinoline
40	163	$C_{11}H_{17}N$	– 5.N	84	69	C_5-Alkylaniline
40	175	$C_{12}H_{17}N$	– 7.N			C_3-Alkyltetrahydroquinoline
41	163	$C_{11}H_{17}N$	– 5.N	32	42	C_5-Alkylaniline
41	175	$C_{12}H_{17}N$	– 5.N			C_3-Alkyltetrahydroquinoline
42	163	$C_{11}H_{17}N$	– 5.N	62	110	C_5-Alkylaniline
42	161	$C_{11}H_{15}N$	– 7.N			C_2-Alkyltetrahydroquinoline
43	163	$C_{11}H_{17}N$	– 5.N	18	38	C_5-Alkylaniline
43	161	$C_{11}H_{15}N$	– 7.N			C_2-Alkyltetrahydroquinoline
44	163	$C_{11}H_{17}N$	– 5.N	16	–	C_5-Alkylaniline
44	161	$C_{11}H_{15}N$	– 7.N			C_2-Alkyltetrahydroquinoline
45	163	$C_{11}H_{17}N$	– 5.N	8	5	C_5-Alkylaniline
46	182	$C_{14}H_{14}$	–14	–	–	Dibenzyl (internal standard)

TABLE IV

COMPOUNDS IDENTIFIED IN BASIC FRACTION OF LSE DIGESTER CONDENSATE

Peak numbers refer to GC–FID chromatogram in Fig. 3. Concentrations determined by GC–FID and expressed as ppm of original, unfractionated sample.

Peak No.	*m/z*	*Atomic composition*	*Z No.*	*Conc. (ppm)*	*Name or possible type*
1	164	C_2Cl_4	0	–	Tetrachloroethylene (solvent impurity)
2	93	C_6H_7N	– 5.N	61	2-Picoline
3	107	C_7H_9N	– 5.N	120	2,6-Lutidine
3	93	C_6H_7N	– 5.N		3- + 4-Picolines
4	107	C_7H_9N	– 5.N	27	2-Ethylpyridine
5	98	$C_6H_{10}O$	– 2.O	10	Cyclohexanone
6	107	C_7H_9N	– 5.N	81	2,4 + 2,5-Lutidines
7	121	$C_8H_{11}N$	– 5.N	73	C_3-Alkylpyridine
7	107	C_7H_9N	– 5.N		2,3-Lutidine
8	107	C_7H_9N	– 5.N	6	4-Ethylpyridine
9	121	$C_8H_{11}N$	– 5.N	54	C_3-Alkylpyridine
10	121	$C_8H_{11}N$	– 5.N	58	C_3-Alkylpyridine
11	121	$C_8H_{11}N$	– 5.N	–	C_3-Alkylpyridine
12	93	C_6H_7N	– 5.N	91	Aniline
13	121	$C_8H_{11}N$	– 5.N	22	C_3-Alkylpyridine
13	107	C_7H_9N	– 5.N		3,4-Lutidine
14	121	$C_8H_{11}N$	– 5.N	7	C_3-Alkylpyridine
14	107	C_7H_9N	– 5.N		C_2-Alkylpyridine
15	135	$C_9H_{13}N$	– 5.N	20	C_4-Alkylpyridine
16	121	$C_8H_{11}N$	– 5.N	25	C_3-Alkylpyridine
16	135	$C_9H_{13}N$	– 5.N		C_4-Alkylpyridine
17	121	$C_8H_{11}N$	– 5.N	22	C_3-Alkylpyridine
17	135	$C_9H_{13}N$	– 5.N		C_4-Alkylpyridine
18	135	$C_9H_{13}N$	– 5.N	22	C_4-Alkylpyridine
18	121	$C_8H_{11}N$	– 5.N		C_3-Alkylpyridine
19	135	$C_9H_{13}N$	– 5.N	25	C_4-Alkylpyridine
19	121	$C_8H_{11}N$	– 5.N		C_3-Alkylpyridine
19	149	$C_{10}H_{15}N$	– 5.N		C_5-Alkylpyridine
20	107	C_7H_9N	– 5.N	140	*o*-Toluidine
21	107	C_7H_9N	– 5.N	53	*m*-Toluidine
22	107	C_7H_9N	– 5.N	22	Methylaniline
22	135	$C_9H_{13}N$	– 5.N		C_4-Alkylpyridine
22	149	$C_{10}H_{15}N$	– 5.N		C_5-Alkylpyridine
23	135	$C_9H_{13}N$	– 5.N	9	C_4-Alkylpyridine
24	119	C_8H_9N	– 7.N		Dihydroindole or azaindane
24	135	$C_9H_{13}N$	– 5.N		C_4-Alkylpyridine
25	119	C_8H_9N	– 7.N	26	Dihydroindole or azaindane
25	135	$C_9H_{13}N$	– 5.N		C_4-Alkylpyridine
25	149	$C_{10}H_{15}N$	– 5.N		C_5-Alkylpyridine
26	135	$C_9H_{13}N$	– 5.N	6	C_4-Alkylpyridine
26	149	$C_{10}H_{15}N$	– 5.N		C_5-Alkylpyridine
27	149	$C_{10}H_{15}N$	– 5.N	–	C_5-Alkylpyridine
28	121	$C_8H_{11}N$	– 5.N	28	*o*-Ethylaniline
29	121	$C_8H_{11}N$	– 5.N	41	2,4- + 2,6-Dimethylanilines
29	133	$C_9H_{11}N$	– 7.N		Tetrahydroquinoline or methyldihydroindole or methylazaindane

(Continued on p. 284)

TABLE IV *(continued)*

Peak No.	*m/z*	*Atomic composition*	*Z No.*	*Conc. (ppm)*	*Name or possible type*
30	121	$C_8H_{11}N$	− 5.N	39	2,5-Dimethyl + *p*-ethylanilines
31	121	$C_8H_{11}N$	− 5.N	22	3,5-Dimethyl + *m*-ethylanilines
31	149	$C_{10}H_{15}N$	− 5.N		C_5-Alkylpyridine
32	149	$C_{10}H_{15}N$	− 5.N	1	C_5-Alkylpyridine
32	135	$C_9H_{13}N$	− 5.N		C_4-Alkylpyridine
33	147	$C_{10}H_{13}N$	− 7.N	6	Methyltetrahydroquinoline or C_2-alkyldihydroindole or C_2-alkylazaindane
33	149	$C_{10}H_{15}N$	− 5.N		C_5-Alkylpyridine
34	121	$C_8H_{11}N$	− 5.N	12	2,3-Dimethylaniline
35	121	$C_8H_{11}N$	− 5.N	5	C_2-Alkylaniline
35	133	$C_9H_{11}N$	− 7.N		Tetrahydroquinoline or methyldihydroindole or methylazaindane
36	147	$C_{10}H_{13}N$	− 7.N	5	Methyltetrahydroquinoline or C_2-alkyldihydroindole or C_2-alkylazaindane
37	133	$C_9H_{11}N$	− 7.N	13	Tetrahydroquinoline or methyldihydroindole or methylazaindane
38	135	$C_9H_{13}N$	− 5.N	6	C_3-Alkylaniline
38	147	$C_{10}H_{13}N$	− 7.N		Methyltetrahydroquinoline or C_2-alkyldihydroindole or C_2-alkylazaindane
38	161	$C_{11}H_{15}N$	− 7.N		C_3-Alkyldihydroindole or C_3-alkylazaindane
39	135	$C_9H_{13}N$	− 5.N	18	C_3-Alkylaniline
39	147	$C_{10}H_{13}N$	− 7.N		Methyltetrahydroquinoline
40	135	$C_9H_{13}N$	− 5.N	13	2,4,6-Trimethylaniline
40	147	$C_{10}H_{13}N$	− 7.N		Methyltetrahydroquinoline
41	135	$C_9H_{13}N$	− 5.N	15	C_3-Alkylaniline
41	147	$C_{10}H_{13}N$	− 7.N		Methyltetrahydroquinoline
42	129	C_9H_7N	−11.N	260	Quinoline
43	147	$C_{10}H_{13}N$	− 7.N	13	Methyltetrahydroquinoline
43	161	$C_{11}H_{15}N$	− 7.N		C_2-Alkyltetrahydroquinoline
44	147	$C_{10}H_{13}N$	− 7.N	6	Methyltetrahydroquinoline
44	161	$C_{11}H_{15}N$	− 7.N		C_2-Alkyltetrahydroquinoline
45	147	$C_{10}H_{13}N$	− 7.N	8	Methyltetrahydroquinoline
46	129	C_9H_7N	−11.N	13	Isoquinoline
46	147	$C_{10}H_{13}N$	− 7.N		Methyltetrahydroquinoline
46	161	$C_{11}H_{15}N$	− 7.N		C_2-Alkyltetrahydroquinoline
47	149	$C_{10}H_{15}N$	− 5.N	9	C_4-Alkylaniline
47	175	$C_{12}H_{17}N$	− 7.N		C_3-Alkyltetrahydroquinoline
48	143	$C_{10}H_9N$	−11.N	44	2-Methylquinoline
48	149	$C_{10}H_{15}N$	− 5.N		C_4-Alkylaniline
49	143	$C_{10}H_9N$	−11.N	11	Methylquinoline
49	175	$C_{12}H_{17}N$	− 7.N		C_3-Alkyltetrahydroquinoline
50	133	$C_9H_{11}N$	− 7.N	28	1,2,3,4-Tetrahydroquinoline
51	143	$C_{10}H_9N$	−11.N	19	Methylquinoline
51	161	$C_{11}H_{15}N$	− 7.N		C_2-Alkyltetrahydroquinoline
52	143	$C_{10}H_9N$	−11.N	29	Methylquinoline
52	161	$C_{11}H_{15}N$	− 7.N		C_2-Alkyltetrahydroquinoline
53	163	$C_{11}H_{17}N$	− 5.N	12	C_5-Alkylaniline
54	143	$C_{10}H_9N$	−11.N	12	Methylquinoline

TABLE IV *(continued)*

Peak No.	*m/z*	*Atomic composition*	*Z No.*	*Conc. (ppm)*	*Name or possible type*
54	161	$C_{11}H_{15}N$	− 7.N		C_2-Alkyltetrahydroquinoline
54	163	$C_{11}H_{17}N$	− 5.N		C_5-Alkylaniline
55	143	$C_{10}H_9N$	−11.N	8	4-Methylquinoline
55	161	$C_{11}H_{15}N$	− 7.N		C_2-Alkyltetrahydroquinoline
55	163	$C_{11}H_{17}N$	− 5.N		C_5-Alkylaniline
55	157	$C_{11}H_{11}N$	−11.N		C_2-Alkylquinoline
56	161	$C_{11}H_{15}N$	− 7.N	9	C_2-Alkyltetrahydroquinoline
57	157	$C_{11}H_{11}N$	−11.N	19	2,6- + 2,7-Dimethylquinolines
57	161	$C_{11}H_{15}N$	− 7.N		C_2-Alkyltetrahydroquinoline
58	161	$C_{11}H_{15}N$	− 7.N	19	C_2-Alkyltetrahydroquinoline
59	175	$C_{12}H_{17}N$	− 7.N	10	C_3-Alkyltetrahydroquinoline
59	157	$C_{11}H_{11}N$	−11.N		C_2-Alkylquinoline
60	157	$C_{11}H_{11}N$	−11.N	19	C_2-Alkylquinoline
60	175	$C_{12}H_{17}N$	− 7.N		C_3-Alkyltetrahydroquinoline
60	204	$C_{15}H_{24}$	− 6		Alkylbenzene
61	157	$C_{11}H_{11}N$	−11.N		C_2-Alkylquinoline
61	175	$C_{12}H_{17}N$	− 7.N	22	C_3-Alkyltetrahydroquinoline
62	157	$C_{11}H_{11}N$	−11.N		C_2-Alkyl quinoline
62	175	$C_{12}H_{17}N$	− 7.N		C_3-Alkyltetrahydroquinoline
63	161	$C_{11}H_{15}N$	− 7.N	14	C_2-Alkyltetrahydroquinoline
63	175	$C_{12}H_{17}N$	− 7.N		C_3-Alkyltetrahydroquinoline
64	157	$C_{11}H_{11}N$	−11.N	21	C_2-Alkylquinoline
64	189	$C_{13}H_{19}N$	− 7.N		C_4-Alkyltetrahydroquinoline
65	182	$C_{14}H_{14}$	−14	–	Dibenzyl (internal standard)
66	177	$C_{12}H_{19}N$	− 5.N	18	C_6-Alkylaniline
67	189	$C_{13}H_{19}N$	− 7.N	12	C_4-Alkyltetrahydroquinoline
68	161	$C_{11}H_{15}N$	− 7.N	12	C_2-Alkyltetrahydroquinoline
68	171	$C_{12}H_{13}N$	−11.N		C_3-Alkylquinoline
69	171	$C_{12}H_{13}N$	−11.N	10	C_3-Alkylquinoline
69	161	$C_{11}H_{15}N$	− 7.N		C_2-Alkyltetrahydroquinoline
70	171	$C_{12}H_{13}N$	−11.N	5	C_3-Alkylquinoline
71	171	$C_{12}H_{13}N$	−11.N	7	C_3-Alkylquinoline
72	171	$C_{12}H_{13}N$	−11.N	6	C_3-Alkylquinoline
72	175	$C_{12}H_{17}N$	− 7.N		C_3-Alkyltetrahydroquinoline
73	185	$C_{13}H_{15}N$	−11.N	7	C_4-Alkylquinoline
74	175	$C_{12}H_{17}N$	− 7.N		C_3-Alkyltetrahydroquinoline
74	161	$C_{11}H_{15}N$	− 7.N		C_2-Alkyltetrahydroquinoline
75	175	$C_{12}H_{17}N$	− 7.N	10	C_3-Alkyltetrahydroquinoline
75	161	$C_{11}H_{15}N$	− 7.N		C_2-Alkyltetrahydroquinoline
75	185	$C_{13}H_{15}N$	−11.N		C_4-Alkylquinoline
76	175	$C_{12}H_{17}N$	− 7.N	11	C_3-Alkyltetrahydroquinoline
76	189	$C_{13}H_{19}N$	− 7.N		C_4-Alkyltetrahydroquinoline
77	169	$C_{12}H_{11}N$	−13.N	10	Diphenylamine or aminobiphenyl or aminoacenaphthene
78	161	$C_{11}H_{15}N$	− 7.N	5	C_2-Alkyltetrahydroquinoline
78	203	$C_{14}H_{21}N$	− 7.N		C_5-Alkyltetrahydroquinoline
79	–	–	–	3	No molecular ion detected; probably from $Z = -7.N$ series
80	–	–	–	3	No molecular ion detected; probably from $Z = -7.N$ series
81	187	$C_{13}H_{17}N$	− 9.N	2	Octahydrobenzoquinoline
82	–	–	–	1	No molecular ion detected; probably phthalate

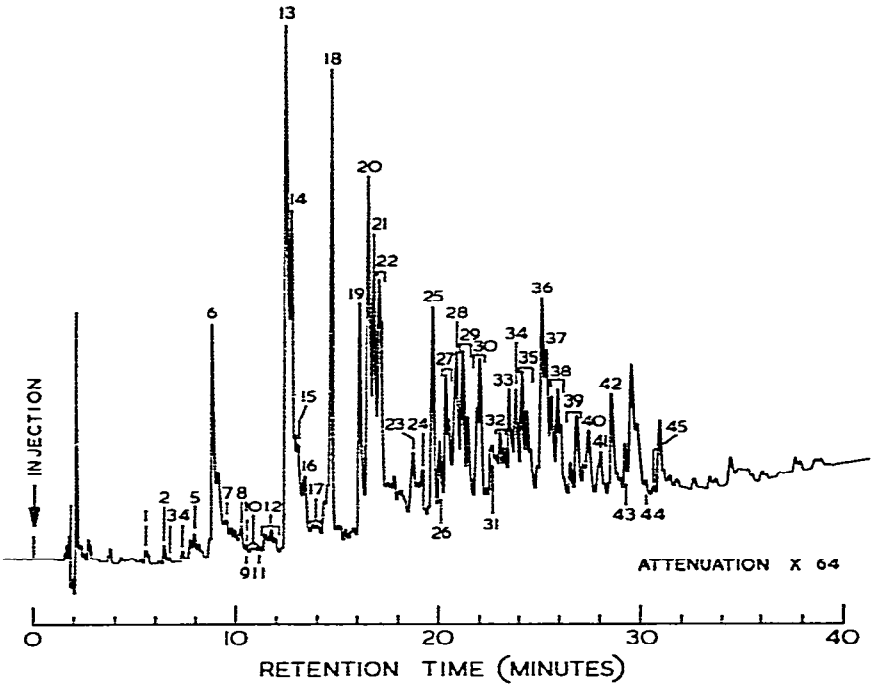


Fig. 4. GC–AFD chromatogram of unfractionated light ends product. Identities of numbered peaks given in Table III. Conditions: 40 m, SP-2250 glass SCOT capillary column programmed from 105–285°C at 3 min with 4-min initial hold.

pounds. Examples are shown for the $Z = -5$.N series (pyridines and anilines) and the $Z = -11$.N series (quinolines) in the digester condensate bases in Figs. 5 and 6, respectively. The relevant portion of the TIC chromatogram is included, and may be compared with the GC–FID chromatogram shown as the upper trace in Fig. 3. The peaks revealed in the single ion chromatograms were checked by accurate mass measurement to confirm the presence of nitrogen compounds. GC–MS identifications for the numbered peaks in the GC–FID chromatograms shown in Figs. 1–3 are given in Tables II–IV for the coal extract solution, light ends product and digester condensate bases, respectively. Many of the peaks contain more than one component, and in these cases the components are listed in decreasing order of concentration. In some cases, a number of compound types are possible for a given atomic composition, and chemical derivatisation has been used to distinguish between these.

Chemical derivatisation

The use of several reagents for the selective derivatisation of basic nitrogen compounds was investigated. The most successful reagent was found to be the alkylating agent dimethylformamidedimethylacetal (Methyl-8), supplied by Pierce and Warriner (Great Britain). The specific reaction of Methyl-8 with aromatic primary amines is shown below for 2-naphthylamine.

Methyl-8

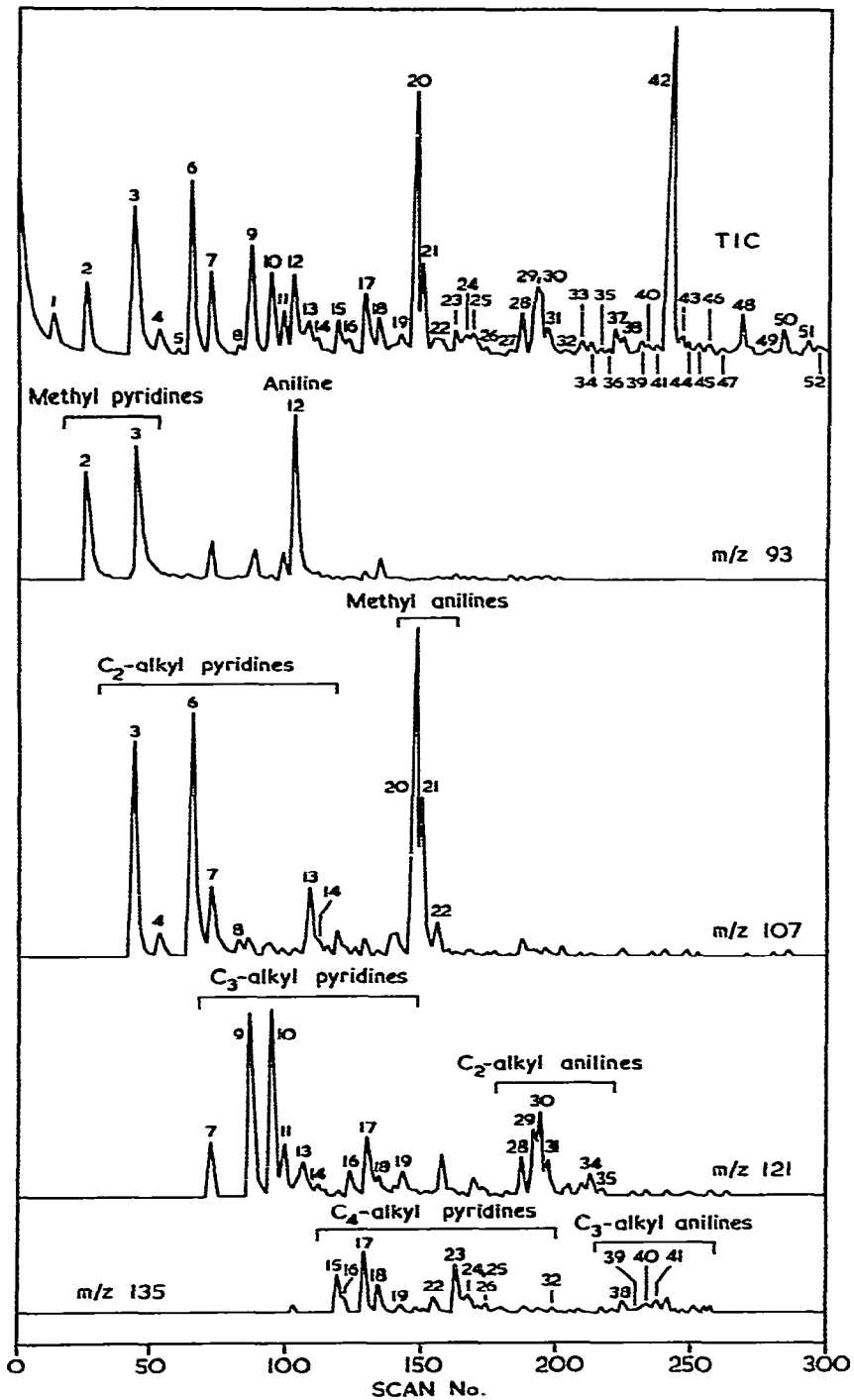


Fig. 5. GC–MS single ion chromatograms of anilines and pyridines ($Z = -5$.N series) in digester condensate bases. Identities of numbered peaks given in Table IV. Conditions: 50 m, SP-2250 glass SCOT capillary column programmed from 85–285°C at 3°/min with 4-min initial hold.

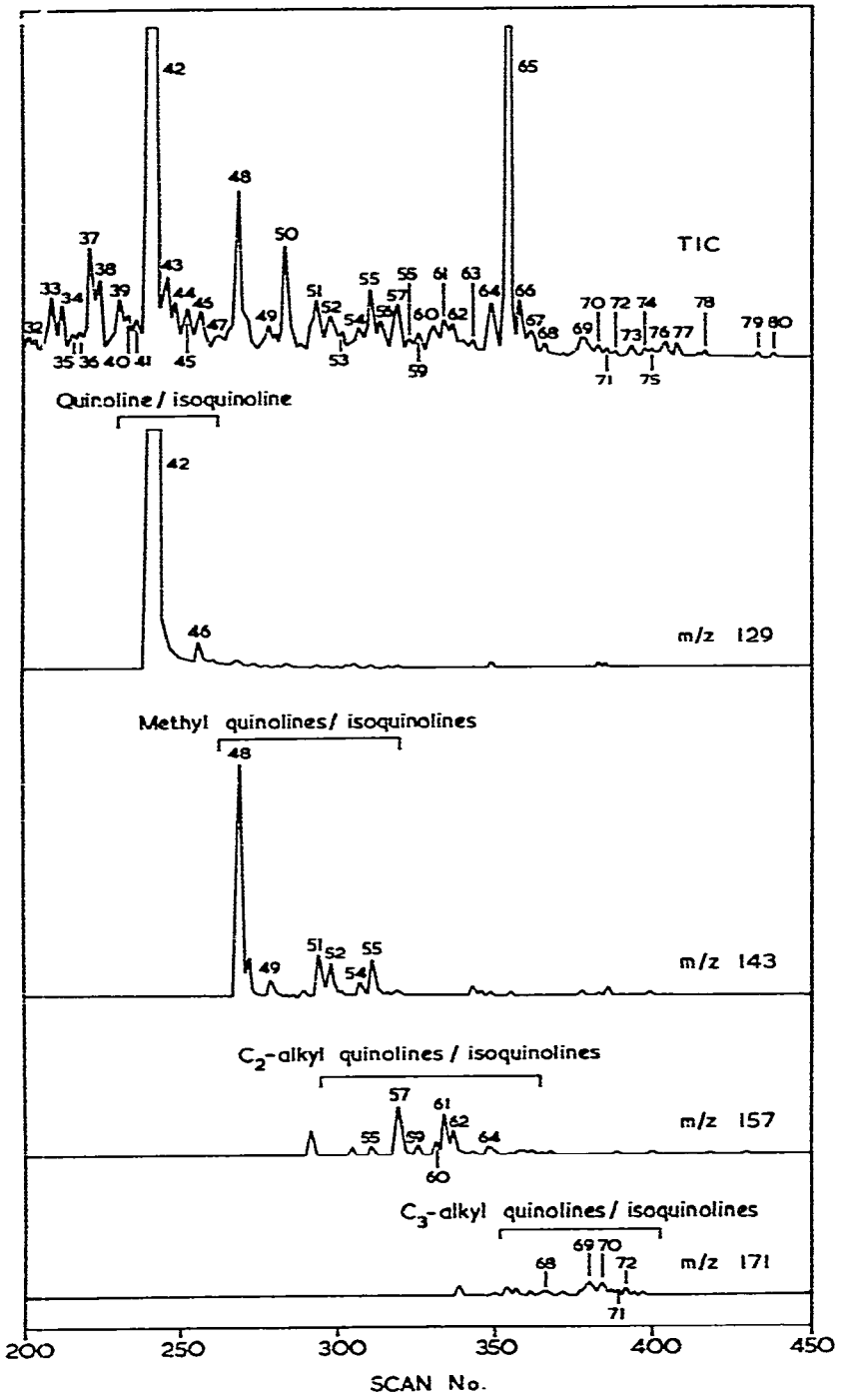


Fig. 6. GC–MS single ion chromatograms of quinolines ($Z = -11$.N series) in digester condensate bases. Identities of numbered peaks given in Table IV. Conditions as in Fig. 5.

Although Methyl-8 should not react with aza compounds, indeed pyridine is recommended as a suitable solvent for its reactions, the derivatisation procedure was checked using synthetic mixtures of amines and aza compounds. An amine mixture containing 1 % (v/v) each of aniline, *m*-toluidine, 2,5-dimethylaniline and 2,4,6-trimethylaniline in tetrahydrofuran was prepared, together with an aza compound mixture containing similar levels of pyridine, 2-picoline, 2,4-lutidine, 2,4,6-collidine and quinoline. A 0.5-ml volume of neat Methyl-8 was added to 0.5 ml of each solution in PTFE-faced septum cap phials. The reaction mixtures and the underivatised solutions were ana-

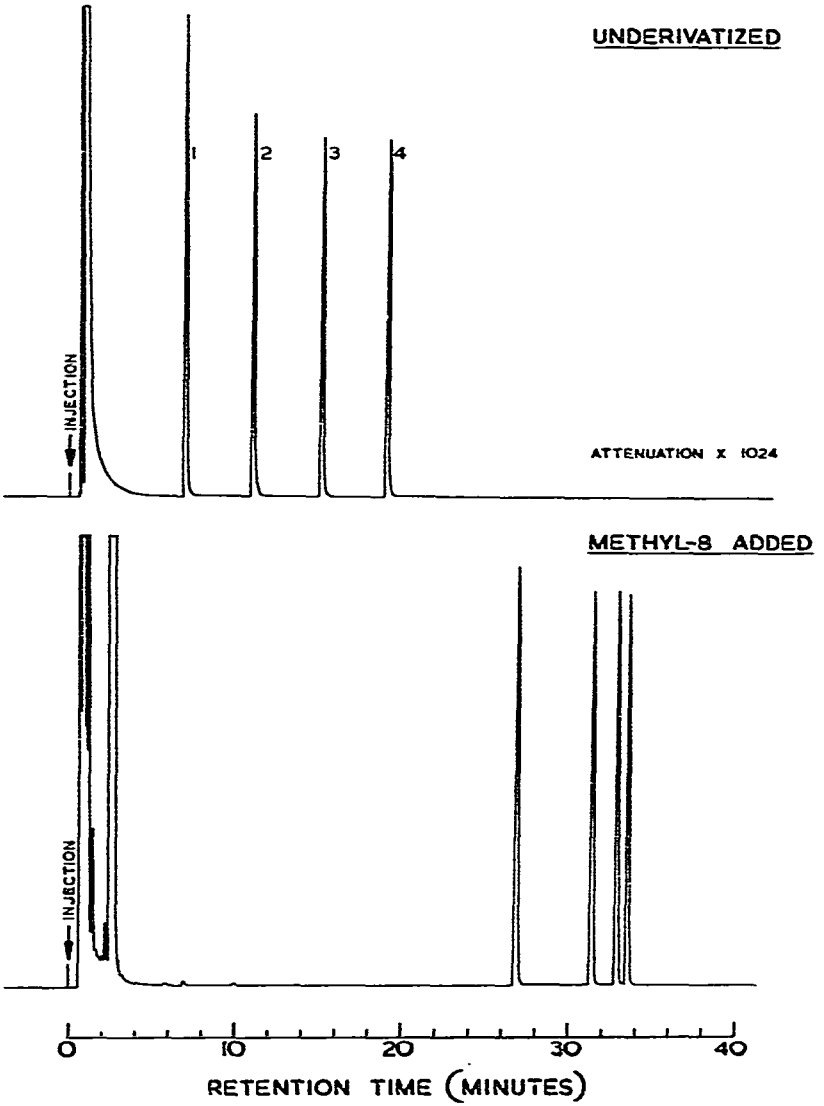


Fig. 7. GC–FID chromatograms of standard amines before and after derivatisation with Methyl-8. Identities of numbered peaks: 1 = aniline; 2 = *m*-toluidine; 3 = 2,5-dimethylaniline; 4 = 2,4,6-trimethylaniline. Conditions as in Fig. 1.

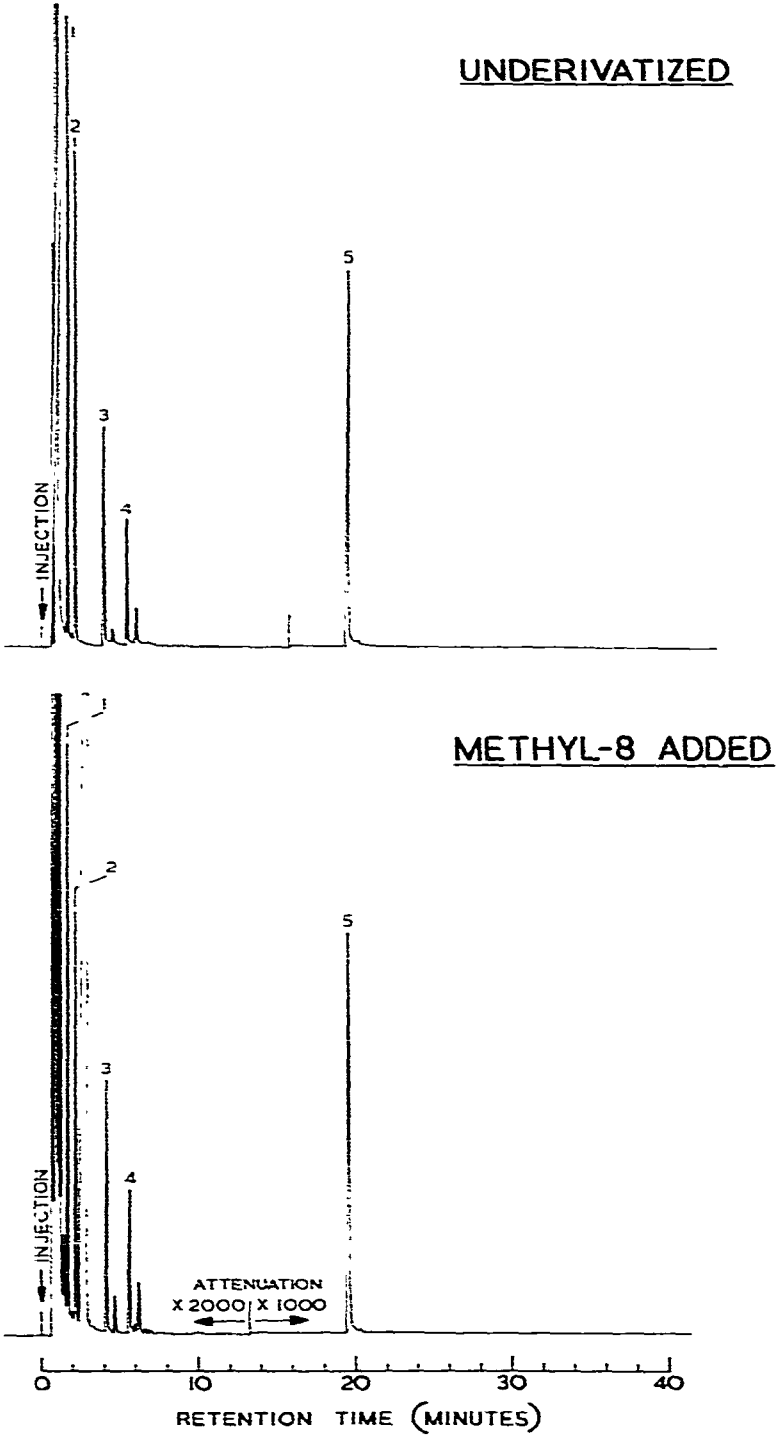


Fig. 8. GC–FID chromatograms of standard aza compounds before and after derivatisation with Methyl-8. Identities of numbered peaks: 1 = pyridine; 2 = 2-picoline; 3 = 2,4-lutidine; 4 = 2,4,6-collidine; 5 = quinoline. Conditions as in Fig. 1.

lysed by GC–FID under the conditions described earlier. The resulting chromatograms for the amines are shown in Fig. 7, and those for the aza compounds in Fig. 8. It can be seen that the Methyl-8 reacts quantitatively with the primary aromatic amines, although heating for up to 2 h at 100°C was required for the complete reaction of sterically-hindered species such as 2,4,6-trimethylaniline. The aza compounds showed no reaction, even after heating for 2 h at 100°C. Fig. 7 shows that the Methyl-8 derivatives have considerably longer retention times than the unreacted amines. Although alternative derivatising reagents, such as the acetylating agent N-methyl-bis(trifluoroacetamide) (MBTFA), also supplied by Pierce and Warriner, were found to react more rapidly with sterically-hindered amines, the retention times of the derivatives were too close to those of the unreacted compounds.

Following their analysis by GC–FID and GC–MS, the basic fractions from the three coal liquefaction samples were diluted to 1.5 ml with dichloromethane. Approximately 0.5 ml of each was placed in a 1-ml phial, and 0.4 ml of neat Methyl-8 added. The phials were sealed and heated for 1 h at 100°C, and the reaction mixtures were then reduced to approximately 0.3 ml under nitrogen at room temperature to give solutions of approximately the same concentrations as those used for the quantitative GC–FID analyses. The derivatised bases were then analysed by GC–FID under the conditions described earlier, chromatograms for the coal extract solution, light ends product and digester condensate being shown as the lower traces in Figs. 1–3, respectively.

DISCUSSION

Nitrogen analyses

Nitrogen analyses for the unfractionated samples are presented in Table I. In comparison with the coal tar products investigated in our earlier work[20], which had total nitrogen contents in the range 1.0–1.3% (w/w), the nitrogen levels in the light ends product and digester condensate were very low. A higher value was obtained for the coal extract solution, but in view of the low levels of nitrogen compounds measured by GC in this sample (Table II), it is assumed that the major nitrogen-containing components were concentrated at higher molecular weights beyond the range of GC.

A notable feature of the elemental analyses was the variation in the amount of basic nitrogen expressed as a percentage of total nitrogen. For the coal tar products investigated previously[20], the parameter varied only from 49–51%, but in the present work the values ranged from 59–84%. Confirmation of the relatively high basic nitrogen content of the light ends product is provided by the GC–AFD chromatogram shown in Fig. 4. This chromatogram, which also shows any neutral nitrogen components, is very similar to that of the basic fraction (Fig. 2), and indicates that the greater part of the nitrogen in the sample is present as basic compounds.

Isolation of basic fractions

Basic fractions were isolated using an aqueous acid extraction technique. This method was shown in our earlier work[21] to be effective for coal tars in the molecular weight range 80–300, and yielded fractions containing exclusively basic nitrogen compounds. The method is dependent upon the solubility of the protonated base in the

aqueous acid. It has been noted[26] that such solubilities decrease markedly with increasing molecular weight, and the method is unlikely to be quantitative for material of high molecular weight. Alternative procedures, such as the precipitation of the bases with gaseous hydrogen chloride, may be necessary for such samples. Nevertheless, the aqueous acid extraction technique should be satisfactory for those compounds which lie within the normal range of GC (molecular weight <300).

Two of the samples investigated contained low-boiling material, and the basic fractions were maintained in dichloromethane solution to avoid evaporation losses.

Techniques used for the identification of basic nitrogen compounds

GC–MS was used for the identification of compounds in the basic fractions. In common with the aromatic hydrocarbons, which predominate in most coal-derived materials, the nitrogen heteroatomic compounds tend to give intense molecular ions with little fragmentation. Aromatic compounds with short alkyl substituents, which may be major components of low-temperature tars, also give intense molecular ions. However, coal liquefaction products often contain substantial amounts of partially hydrogenated material, and such compounds may be characterised by the presence of an intense fragment ion 28 mass units lower than the molecular ion; this corresponds to the elimination of an uncharged C_2H_4 fragment from a cyclohexylbenzene unit. Once the molecular ion had been located, accurate mass measurement was used to give an atomic composition.

An atomic composition determined in this way may correspond to several different isomeric compound types, for each of which a number of individual isomers may be possible. The electron-impact mass spectra of aromatic nitrogen compounds generally show relatively intense molecular ions and few significant fragment ions, and thus little structural information of relevance in identifying specific isomers was available. The problem may be illustrated by reference to two isomeric compound types, the aza heterocycles and the corresponding aromatic primary amines, examples of which are given below.

C_6H_7N

m/z 93 Z=-5.N

The GC–MS single ion chromatograms for pyridines and anilines in the $Z = -5.N$ series are shown in Fig. 5 for the digester condensate bases. For each of the selected masses, corresponding to successive alkyl derivatives, there are two distinct series of isomers. Both compound types give intense molecular ions and similar, limited fragmentation patterns, and it is not possible to distinguish between them on the basis of mass spectrometry alone. Other methods must, therefore, be used for their identification.

If standard compounds are available, it is possible to use their GC retention times to distinguish between isomers assuming that they are sufficiently well separated. Standard compounds were available for some of the anilines and pyridines in the $Z = -5.N$ series, and examples are shown in the GC–FID chromatograms in Figs. 7 and 8, respectively. It can be seen that the pyridines are eluted well before the isomeric anilines, thus confirming the identities of the two series of isomeric com-

pound types observed in the GC–MS single ion chromatograms of the digester condensate bases (Fig. 5).

Chemical properties may also be used to distinguish between isomeric compound types. The preparation of basic fractions has eliminated the neutral nitrogen compounds, so species such as pyrroles, amides and nitriles do not need to be considered as possible isomers for compounds identified in terms of an atomic composition by GC–MS. The use of chemical derivatisation has also been evaluated. If the digester condensate bases (Fig. 3) are taken as an example, on derivatisation with Methyl-8 the peaks tentatively identified by GC–MS as anilines (Table IV) are shifted to longer retention times, whereas those due to pyridines and quinolines, which were shown in the derivatisation experiments not to react with Methyl-8, were unchanged. The elution times of the anilines in the digester condensate bases before and after derivatisation (Fig. 3) correspond closely to those for the standard compounds shown in Fig. 7, thus confirming their presence in this sample. Their presence was similarly confirmed in the bases from the light ends product.

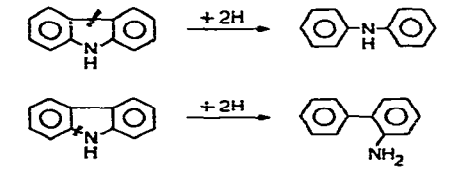
The derivatisation procedure may be especially useful for distinguishing between isomeric compound types when reference materials are not available. For example, peaks 56, 61 and 62 in the GC–FID chromatogram of the basic fraction from the coal extract solution (Fig. 1) have been shown by GC–MS to have the molecular formula $C_{14}H_{11}N$, and may be either methylbenzoquinolines or aminophenanthrenes/anthracenes, as shown below.

$C_{14}H_{11}N$ m/z 193

Standard compounds were not available. However, these peaks were unaffected by derivatisation of the sample with Methyl-8, and were therefore shown to be methylbenzoquinolines rather than the aromatic primary amines.

Basic nitrogen compounds identified in coal liquefaction products

Anilines were the major basic nitrogen components of the light ends product, and substantial components of the digester condensate. Otherwise the major basic nitrogen compounds were generally aza species, although in many cases these were heavily alkylated and hydrogenated. With the exception of some aminobiphenyls, no higher aromatic primary amines were identified. Significant amounts of diphenylamines and aminobiphenyls were found in the coal extract solution; their origin is uncertain, but it is felt that they may result from the ring opening of carbazole type structures during extraction.



$C_{12}H_9N$ m/z 167 Neutral

$C_{12}H_{11}N$ m/z 169 Basic

Pyrrolic compounds such as carbazoles are generally the major neutral nitrogen species in coal-derived materials, and it is considered that the conversion of neutral compounds to basic compounds such as diphenylamines during extraction and hydrogenation may, in part, explain the high figures for basic nitrogen expressed as a percentage of total nitrogen found for the coal liquefaction samples.

Direct GC–AFD determination of nitrogen compounds

The use of the nitrogen-selective AFD for the quantitative GC determination of nitrogen compounds in unfractionated coal liquefaction materials was evaluated using the sample of light ends product. We have previously reported the application of this technique to the analysis of coal tar products[20]. The GC–AFD chromatogram of the unfractionated light ends product, shown in Fig. 4, is very similar to the GC–FID chromatogram of the basic fraction shown in Fig. 2. This is consistent with the very high (83%) figure for basic nitrogen expressed as a percentage of total nitrogen in the sample. The minor differences between the two chromatograms are attributed to the additional neutral nitrogen compounds detected by the AFD. 4-Phenylpyridine was added as an internal standard for the GC–AFD quantification, and the results given in Table III agree satisfactorily with those obtained by GC–FID analysis of the basic fraction, which are also given in Table III.

Assuming a 0.2-μl injection of a 20% solution, the absolute GC–AFD detection limit of 0.07 ng established previously for nitrogen compounds[20] corresponds to a concentration of approximately 2 ppm in the unfractionated samples. For the GC–FID analyses, 5 g samples were extracted, and the resulting basic fractions concentrated to 1 ml. If the minimum detection limit is taken as a data system area count of 1000 μV sec, this corresponds to a concentration of approximately 0.1 ppm in the unfractionated material. Thus, although the AFD and FID have similar absolute detection limits, under the conditions used the direct GC–AFD method is less sensitive by a factor of 20 than the GC–FID analysis of the basic fractions.

The direct GC–AFD analysis can be carried out in about 60 min, and avoids the necessity for time-consuming separation procedures, with the attendant risk of poor recoveries. It also possesses the major advantage of allowing quantification of the neutral nitrogen species as well as the basic compounds. However, it is a poor identification technique, and unless the resulting pattern of peaks in the GC–AFD profile can be recognised, GC–MS will be necessary and will probably require the preparation of hydrocarbon-free fractions. Nevertheless, once a typical nitrogen profile has been characterised, the GC–AFD method should allow a rapid quantification of all the nitrogen compounds present.

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REFERENCES

1 M. R. Guerin, C. H. Ho, T. K. Rao, B. R. Clark and J. L. Epler, *Environm. Res.*, 23 (1980) 42–53.
2 C. H. Ho, B. R. Clark, M. R. Guerin, B. D. Barkenbus, T. K. Rao and J. L. Epler, *Mutat. Res.*, 85 (1981) 335–345.

3 B. W. Wilson, M. R. Petersen, R. A. Pelroy and J. T. Cresto. *Biomedical Studies on Solvent Refined Coal (SRC-II) Liquefaction Materials: A Status Report, PNL-3189, Pacific Northwest Laboratory*, US DOE Contract EY-76-C-06-1830, October 1979; also published, in part, in *Fuel*, 60 (1981) 289-294.
4 C. M. White, F. K. Schweighardt and J. L. Shultz, *Fuel Processing Technology*, 1 (1977/1978) 209–215.
5 W. W. Paudler and M. Cheplen, *Fuel*, 58 (1979) 775–778.
6 M. Novotny, R. Kump, F. Merli and L. J. Todd, *Anal. Chem.*, 52 (1980) 401–406.
7 D. W. Later, M. L. Lee and B. W. Wilson, *Anal. Chem.*, 54 (1982) 117–123.
8 B. A. Tomkins and C. H. Ho, *Anal. Chem.*, 54 (1982) 91–96.
9 D. A. Haugen, M. J. Peak, K. M. Suhrbler and V. C. Stamoudis, *Anal. Chem.*, 54 (1982) 32–37.
10 F. Merli, M. Novotny and M. L. Lee, *J. Chromatogr.*, 199 (1980) 371–378.
11 J. Macak, V. M. Nabivach, P. Buryan and J. S. Berlizov, *J. Chromatogr.*, 209 (1981) 472–475.
12 I. Schmeltz and D. Hoffmann, *AIChE Symp. Ser.*, No. 196 (1980) 312–322.
13 E. Sawicki, T. W. Stanley and W. C. Elbert, *J. Chromatogr.*, 18 (1965) 512–519.
14 M. W. Dong, D. C. Locke and D. Hoffmann, *Environm. Sci. Techn.*, 11 (1977) 612–618.
15 D. L. Vassilaros, P. W. Stoker, G. M. Booth and M. L. Lee, *Anal. Chem.*, 54 (1982) 106–112.
16 M. J. Hartigan, J. E. Purcell, M. Novotny, M. L. McConnell and M. L. Lee, *J. Chromatogr.*, 99 (1974) 339–348.
17 M. L. Lee, K. D. Bartle and M. V. Novotny, *Anal. Chem.*, 47 (1975) 540–543.
18 D. K. Albert, *Anal. Chem.*, 50 (1978) 1822–1829.
19 G. Becher, *J. Chromatogr.*, 211 (1981) 103–110.
20 P. Burchill, A. A. Herod and E. Pritchard, *Fuel*, submitted for publication.
21 P. Burchill, A. A. Herod and E. Pritchard, *Fuel*, submitted for publication.
22 G. O. Davies, *Chem. Ind.*, (1978) 560–566.
23 R. T. Moore, P. McCutchan and D. A. Young, *Anal. Chem.*, 23 (1951) 1639–1641.
24 B. Kolb and J. Bischoff, *J. Chromatogr. Sci.*, 12 (1974) 625–629.
25 I. B. Rubin and C. K. Bayne, *Anal. Chem.*, 51 (1979) 541–546.
26 K. H. Altgelt, D. M. Jewell, D. R. Latham and M. L. Selucky, in K. H. Altgelt and T. H. Gouw (Editors), *Chromatography in Petroleum Analysis*, Marcel Dekker, New York, 1979, Ch. 9, p. 186.