June 1985

RKER.85.110

GEOCHEMICAL INVESTIGATION OF NINE CRUDE OILS AND TWO ROCK EXTRACTS FROM THE MIDLANDS, UNITED KINGDOM

by

J.M.A. Buiskool Toxopeus and F.M. van der Veen

Sponsor: Shell Expro London Code: 774.10.300

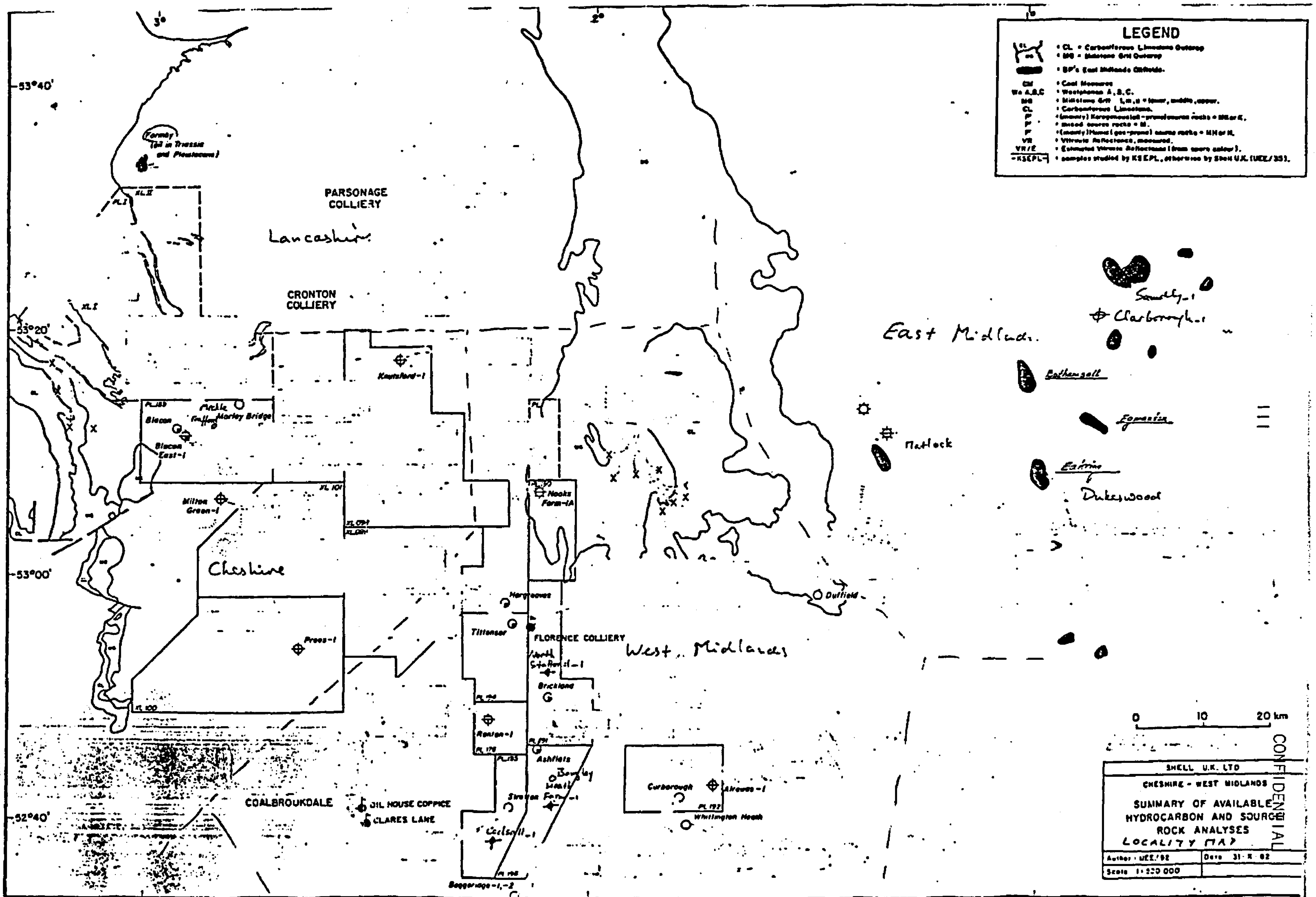
Investigation: 9.55.247

KONINKLIJKE/SHELL EXPLORATIE EN PRODUKTIE LABORATORIUM

RIJSWIJK, THE NETHERLANDS

(Shell Research B.V.)

CONTENTS



U.K. Land REFERENCE BOOK

Figure 1.c.

GEOCHEMICAL INVESTIGATION OF NINE CRUDE OILS AND TWO ROCK EXTRACTS FROM THE MIDLANDS, UNITED KINGDOM

1.0 INTRODUCTION

A geochemical investigation has been carried out on the following crude oils/extracts:

- Eakring-1 B. Sandstone ;
- Eakring-2 Rough Rock ;
- Eakring-177 Kinderscout Grit ;
- Dukeswood-45 Chadsworth Grit ;
- Dukeswood-170 Wingfield Flagstone ;
- Dukeswood-181 L. Carb. LST. ;
- Parsonage Colliery ;
- Florence Colliery ;
- Cronton Colliery ;
- Blacon (785.15-787.35 m) rock extract;
- Blacon (787.35-787.45 m) rock extract.

Most of the data presented here are analysis from 1976-1978. The objective of this study is oil typing and geochemical correlation with source rock extracts from well North Stafford-1 (RKER.85.111[1] and RKER.85.077[2]), Heath Farm (RKER.85.011[3]), and impregnations Mickle Trafford-1 (RKER.85.003[4]) and Hargreaves and Tittensor (RKER.82.104[5]). The results are shown in Tables 1-4 and in Figures 1-21. The location of the samples is shown on page III.

2.0 RESULTS

2.1 Bacterial degradation

The crudes from Eakring-1, Eakring-2, Dukeswood-45 and Dukeswood-170 have been (slightly) bacterially degraded (C_7-distributions, Fig. 12). The crudes from Eakring-177, Dukeswood-181, Florence Colliery and Parsonage Colliery have not been bacterially degraded (C_7-distribution, Fig.12). The absence of the light fraction in the Cronton Colliery crude is most probably due to evaporation rather than bacterial degradation.

2.2 Maturity

The C_{29} DOM values are not reliable (probably too high) due to the presence of waxy material. The crudes and impregnations were derived from (just-) mature source rocks. The following Table shows the results of the various parameters:

	gaschromatogram	Sterane/triterpane fragmentograms	Ph/C_{18}	% S	C_{29} DOM
Eakring-1	(just-) mature	mature	1.1	0.5	63
Eakring-2	(just-) mature	-	1.0	0.2	69
Eakring-177	(just-) mature	mature	0.6	0.3	69
Dukeswood-45	(just-) mature	mature	0.9	0.2	68
Dukeswood-170	(just-) mature	-	1.0	0.2	67
Dukeswood-181	mature	mature	0.4	0.6	69
Parsonage Colliery	(just-) mature	(just-) mature	0.3	0.2	75
Florence Colliery	mature	(just-) mature	0.2	0	75
Cronton Colliery	mature	(just-) mature	0.2	-	74
Blacon 785.15-787.35 m	mature	mature	0.4	0.5	73
Blacon 787.35-787.45 m	mature	-	0.4	0.6	71

2.3 Environment of deposition

The gaschromatograms of the bacterially not degraded crudes show intermediate to high pristane/phytane ratios for crudes Parsonage Colliery, Florence Colliery and Cronton Colliery indicating a more terrestrial (swampy) environment. The pristane/phytane ratios of Eakring-177, Dukeswood-181 and Blacon are lower and indicate a more reducing, marine environment of the source rocks. The C_7-alkane/naphthene distributions (Fig. 12) indicate shaly source rocks for Eakring-177, Florence Colliery and Parsonage Colliery, while the crude Dukeswood-181 was probably derived from a carbonate source rock.

2.4 Type of organic matter

The gaschromatograms (Figs. 1-11) indicate a variable amount of waxes. This variation indicates differences in maturity of the crudes and is also indicative for variations in the type of organic matter (facies changes in the source rock). The waxy material is most probably derived from landplant material (see environment of deposition), although especially in the more marine samples algal waxes cannot be excluded.

The C_{15}- and C_{30}-ringdistributions (Fig. 13) are indicative for crudes of mixed origin. The crude Dukeswood-181 was probably derived from a slightly different (SOM-rich) source rock (C_{30}-ringdistribution, Fig. 13).

2.5 Correlations

The sterane/triterpane fragmentograms (Figs. 14-21) suggest that roughly two groups of crudes and impregnations can be distinguished. The first group (Group I, see Table below) is characterised by a lower triterpane content compared with iso- and rearranged steranes, a low amount of C_{29}- rearranged steranes and a C_{27}- sterane predominance over C_{29}- steranes. The oils and impregnations in this group generally show low pristane/phytane ratios. The oils/impregnations in this group were derived from source rocks such as found in North Stafford-1 (4760 ft) and Heath Farm-1 with most probably a more marine character than the oils/impregnations from the second group.

The second group (group II, see Table below) is characterized by a high triterpane content over iso-and rearranged steranes, more pronounced C_{28}/C_{29}- sterane predominance and the presence of C_{29}- rearranged steranes. The oils and impregnations have higher pristane/ phytane ratios (except samples from Blacon) and are most probably derived from landplant source rocks deposited in a swampy environment such as North Stafford-1 (4090 ft). The source rock which has generated the Blacon impregnations has probably been deposited in a somewhat more marine environment.

	Wax content	Pr/Ph	C_{29}-rearranged steranes	source rock lithology	$\delta\ ^{13}C$ °/oo
Group I					
Eakring-1, -2, 177	high	1.4-1.6	low	shale	-28.0, -28.2, -29.3
Dukeswood-45, -170	high	1.3-1.5	low	shale	-28.0
Dukeswood-181	high	1.4	low	cabonate	-28.9
North Stafford-1 (4760 ft[1])	low	1.7	low	SOM/Coaly Shale	-27.6*
Heath Farm-1[3]	high	2.2,0.9	low	SOM/Coaly Shale	-26.3
Group II					
Florence Colliery	low	3.1	high	shale	-28.8
Parsonage Colliery	high	2.5	high	shale	-28.8
Cronton Colliery	low	2.9	high	shale	-28.7
Hargreaves[5]	high	3.8	high	-	-29.2
Tittensor[5]	high	3.0	high	-	-27.6
Michle Trafford[4]	-	-	high	-	-29.7
North Stafford-1 (4190 ft[1])	low	2.9	high	SOM/Coaly Shale	-27.6*
Blacon	high	1.4	high	-	-30.4

*) sample 4220 + 4730 ft determined on saturated fraction.

3.0 CONCLUSIONS

The crudes from Eakring-1 and -2 and Dukeswood-45 and -170 have been (slightly) bacterially degraded, while crudes Eakring-177, Dukeswood-181, Florence Colliery and Parsonage Colliery have not been biodegraded. The absence of the light fraction in crude oil Cronton Colliery is most probably due to evaporation rather than bacterial degradation. All crudes and impregnations were derived from (just) mature, shaly source rocks except for Dukeswood-181 which was probably generated from a carbonate source rock.

The crudes and impregnations can be roughly divided into two groups. The first group consists of the Eakring and Dukeswood crudes and was derived from source rocks such as found in North Stafford-1 (4760 ft) and Heath Farm-1 with a more marine character than the oils and impregnations from the second group. The second group consists of the Florence, Parsonage and Cronton Colliery crudes and the Blacon, Hargreaves and Tittensor impregnetions and was derived from landplant source rocks deposited in a swampy environment such as found in North Stafford-1 (4190 ft).

REFERENCES

1. Buiskool Toxopeus, J.M.A. and Veen, F.M. van der, Geochemical investigation of two rock extracts in well North Stafford-1, United Kingdom.
RKER.85.114.

2. Rodenburg, T. and Hermans, L.J.P.C.M., Evaluation of cutting samples from well North Stafford-1, United Kingdom.
RKER.85.077.

3. Veen, F.M. van der and Posthuma, J., Geochemical investigation of extracts from core samples from well Heath Farm-1 (1712.0 and 1716.8 ft, Westphalian), United Kingdom.
RKER.85.011.

4. Veen, F.M. van der and Posthuma, J., Geochemical investigation of an extract of a core sample from the Sherwood Sandstone, Mickle Trafford-1, United Kingdom.
RKER.85.003.

5. Grantham, P.J. and Posthuma, J., Geochemical analysis of impregnated hydrocarbons in cores from wells Hargreaves and Tittensor, United Kingdom.
RKER.82.104.

TABLE 1 - GEOCHEMICAL DATA OF OILS

Sample	Eakring-1	Eakring-2	Eakring-177
API	32.2	36	32.9
specific gravity	0.8645	0.842	0.8609
%w.boil. <120°C	6.1	4.5	7.8
% sulphur	0.5	0.2	0.3
ppm V as metals			
ppm Ni as metals			
Pristane/phytane	1.4	1.6	1.6
Pristane/nC_{17}	1.6	1.3	0.8
Phytane/nC_{18}	1.1	1.0	0.6
C_7-distribution			
C_7-alkane			
nC_7	35	35	45
monobranched	46	51	45
polybranched	19	14	10
C_7-alk/naphthene			
nC_7	13	16	23
naphthenes	65	58	49
branched alkanes	22	27	28
C_7-alk/naphth/arom			
nC_7	34	42	50
naphthenes	61	51	47
aromatics	5	7	3
C_{15}-distribution			
1-ring	37	37	46
2-ring	47	49	39
3-ring	16	14	15
C_{30}-distribution			
3-ring	17	23	24
4-ring	38	29	36
5-ring	45	48	40
C_{29} DOM	63	69	69
% asphaltenes			
** % saturates	66	61	
% aromatics	25	21	
% heterocompounds	10	8	
% rest			
$\delta\ ^{13}C$ °/oo	-28.0	-28.2	-29.3

N.D. = not detectable
** Determined by column chromatography

TABLE 2 - GEOCHEMICAL DATA OF OILS

Sample	Dukeswood-45	Dukeswood-170	Dukeswood-181
API	35	34	32.6
specific gravity	0.851	0.856	0.8623
%w.boil. <120°C	6.1	5.9	2.7
% sulphur	0.2	0.2	0.6
ppm V as metals	ND	0	
ppm Ni as metals	8	0	
Pristane/phytane	1.3	1.5	1.4
Pristane/nC_{17}	1.2	1.4	0.5
Phytane/nC_{18}	0.9	1.0	0.4
C_7-distribution			
C_7-alkane			
nC_7	27	35	49
monobranched	52	47	43
polybranched	21	18	7
C_7-alk/naphthene			
nC_7	12	14	36
naphthenes	54	59	28
branched alkanes	34	27	36
C_7-alk/naphth/arom			
nC_7	43	40	71
naphthenes	50	56	28
aromatics	7	4	1
C_{15}-distribution			
1-ring	31	34	50
2-ring	51	50	38
3-ring	18	16	12
C_{30}-distribution			
3-ring	26	24	40
4-ring	38	38	33
5-ring	36	38	27
C_{29} DOM	68	67	69
% asphaltenes			
** % saturates	62	58	
% aromatics	25	25	
% heterocompounds	9	8	
% rest			
$\delta\ ^{13}C$ °/oo	-28.0	-28.0	-28.9

N.D.= not detectable
** Determined by column chromatography

TABLE 3 - GEOCHEMICAL DATA OF OILS

Sample	Parsonage Colliery	Florence Colliery	Cronton Colliery
API	36.6	39.5	34.6
specific gravity	0.8420	0.8274	0.8519
%w.boil. <120°C	0.5	5.6	0
% sulphur	0.2	0	0
ppm V as metals			
ppm Ni as metals			
Pristane/phytane	2.5	3.1	2.9
Pristane/nC_{17}	0.7	0.5	0.5
Phytane/nC_{18}	0.3	0.2	0.2
C_7-distribution			
C_7-alkane			
nC_7	47	56	ND
monobranched	40	33	
polybranched	13	11	
C_7-alk/naphthene			
nC_7	25	29	
naphthenes	46	48	
branched alkanes	29	23	
C_7-alk/naphth/arom			
nC_7	52	49	
naphthenes	45	45	
aromatics	3	6	
C_{15}-distribution			
1-ring	63	61	60
2-ring	30	31	32
3-ring	7	8	8
C_{30}-distribution			
3-ring	28	19	29
4-ring	34	37	35
5-ring	38	44	36
C_{29} DOM	75	75	74
% asphaltenes			
** % saturates			
% aromatics			
% heterocompounds			
% rest			
$\delta\ ^{13}C$ °/oo	-28.8	-28.8	-28.7

N.D. = not detectable
** Determined by column chromatography

TABLE 4 - GEOCHEMICAL DATA OF EXTRACTS

Sample	Blacon 785.15-787.35 m	Blacon 787.35-787.45 m
% ethyl ecetate extract	0.4	0.3
% organic carbon after ethyl acetate extraction	0.05	0.05
extract/original carbon (after extraction)	8.0	6.0
% sulphur	0.5	0.6
ppm V as metals		
ppm Ni as metals		
Pristane/phytane	1.4	1.4
Pristane/nC_{17}	0.7	0.7
Phytane/nC_{18}	0.4	0.4
C_{15}-distribution		
1-ring	53	43
2-ring	36	43
3-ring	11	14
C_{30}-distribution		
3-ring	26	25
4-ring	38	39
5-ring	36	36
C_{29} DOM	73	71
** % saturates		
% aromatics		
% heterocompounds		
^{13}C °/oo	-30.4	-30.4

** Determined by thin-layer chromatography

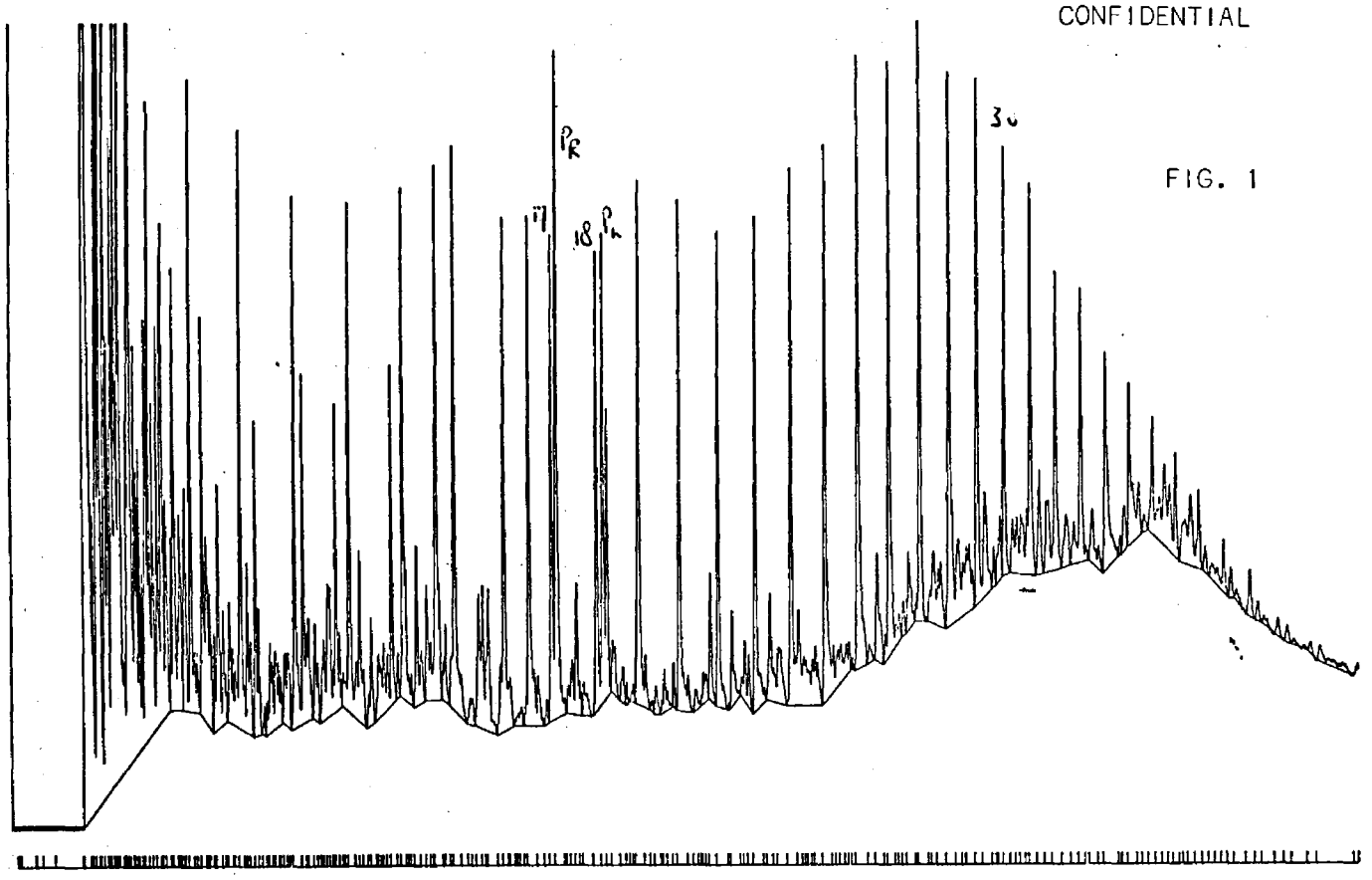


FIG. 1

NAME U.K. EAKRING-1

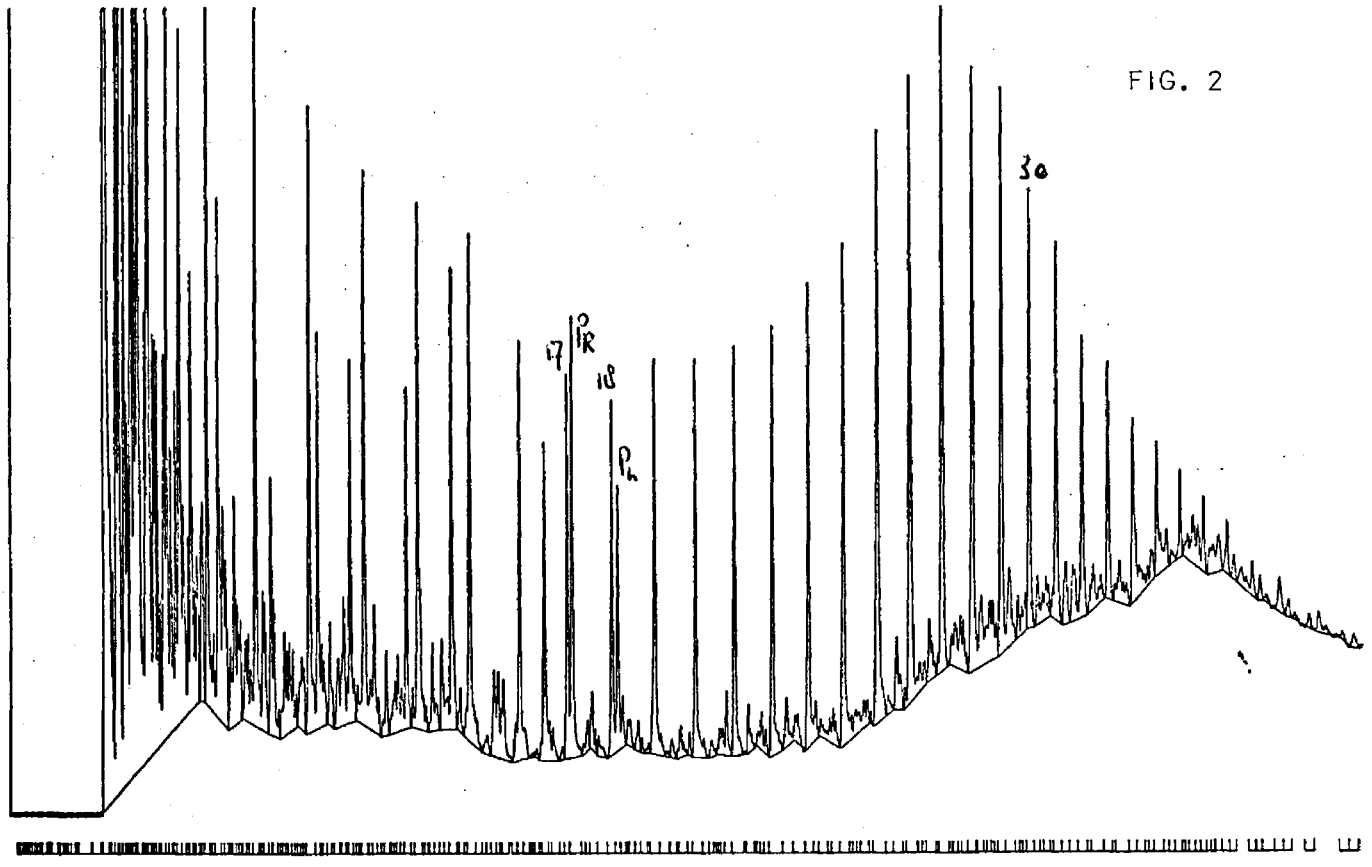
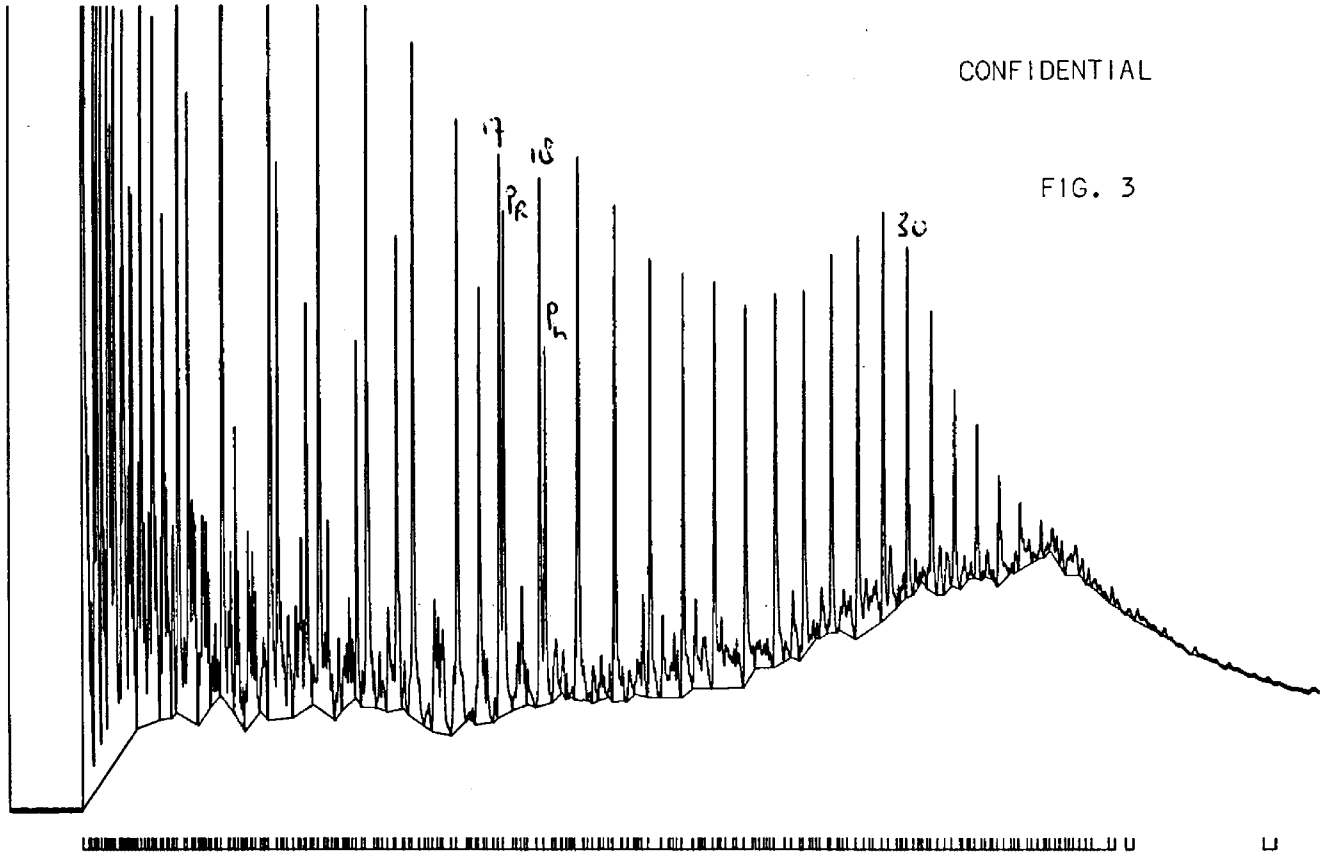


FIG. 2

NAME U.K.EAKRING-2

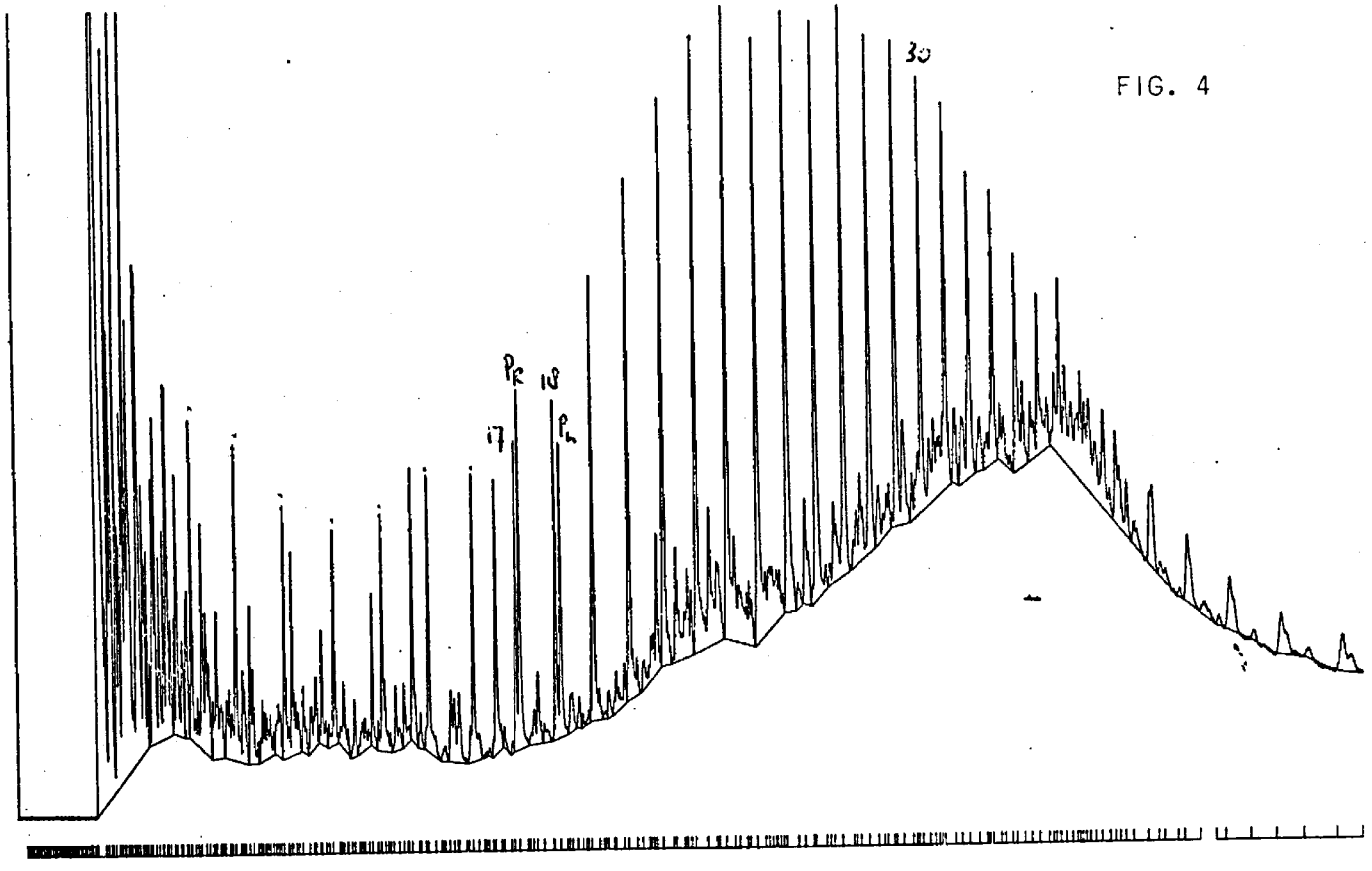
CONFIDENTIAL

FIG. 3



NAME U.K. EAKRING-177

FIG. 4



NAME U.K. DUKESWOOD-45

CONFIDENTIAL

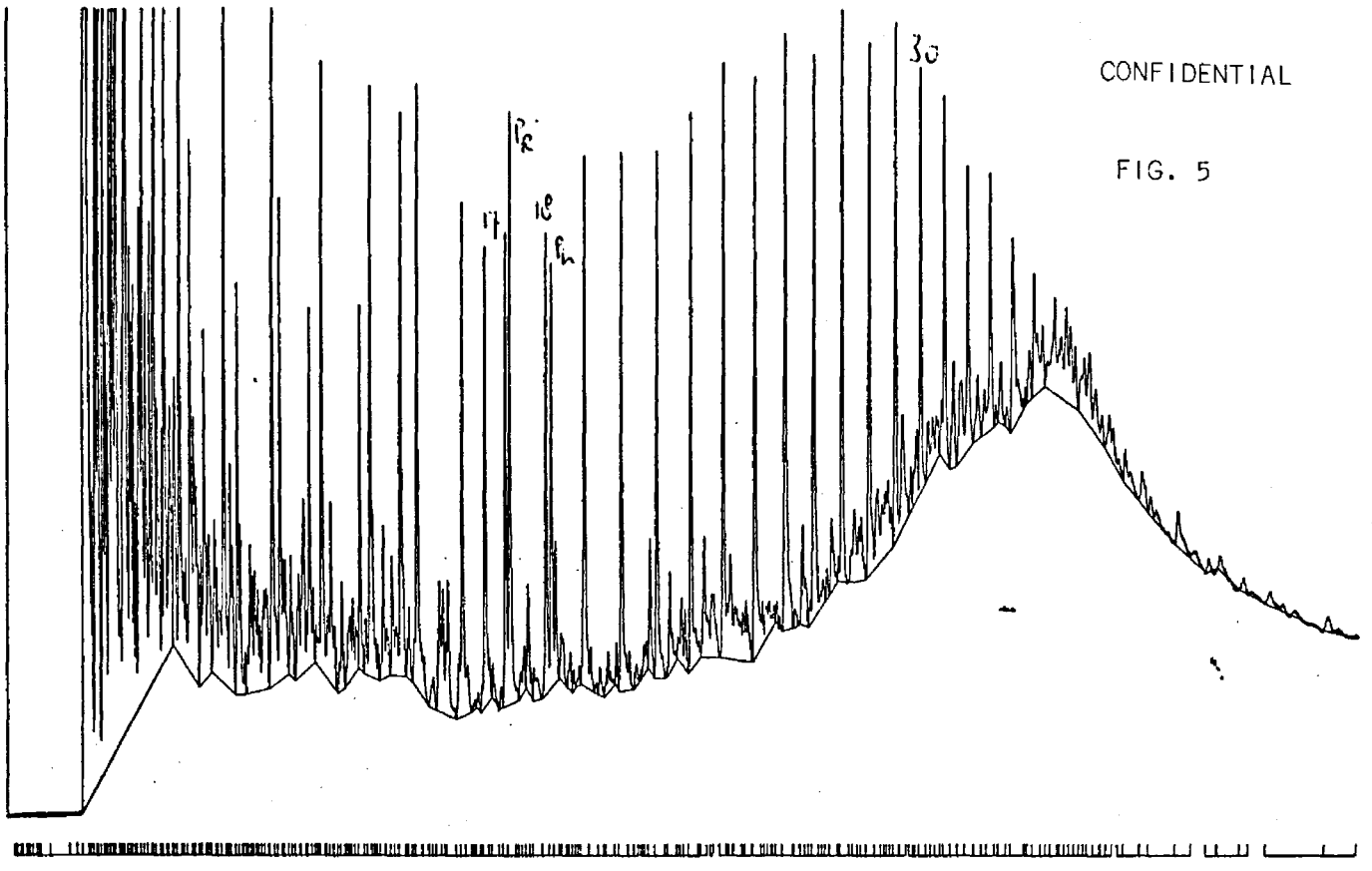


FIG. 5

NAME U.K. DUKESWOOD-170

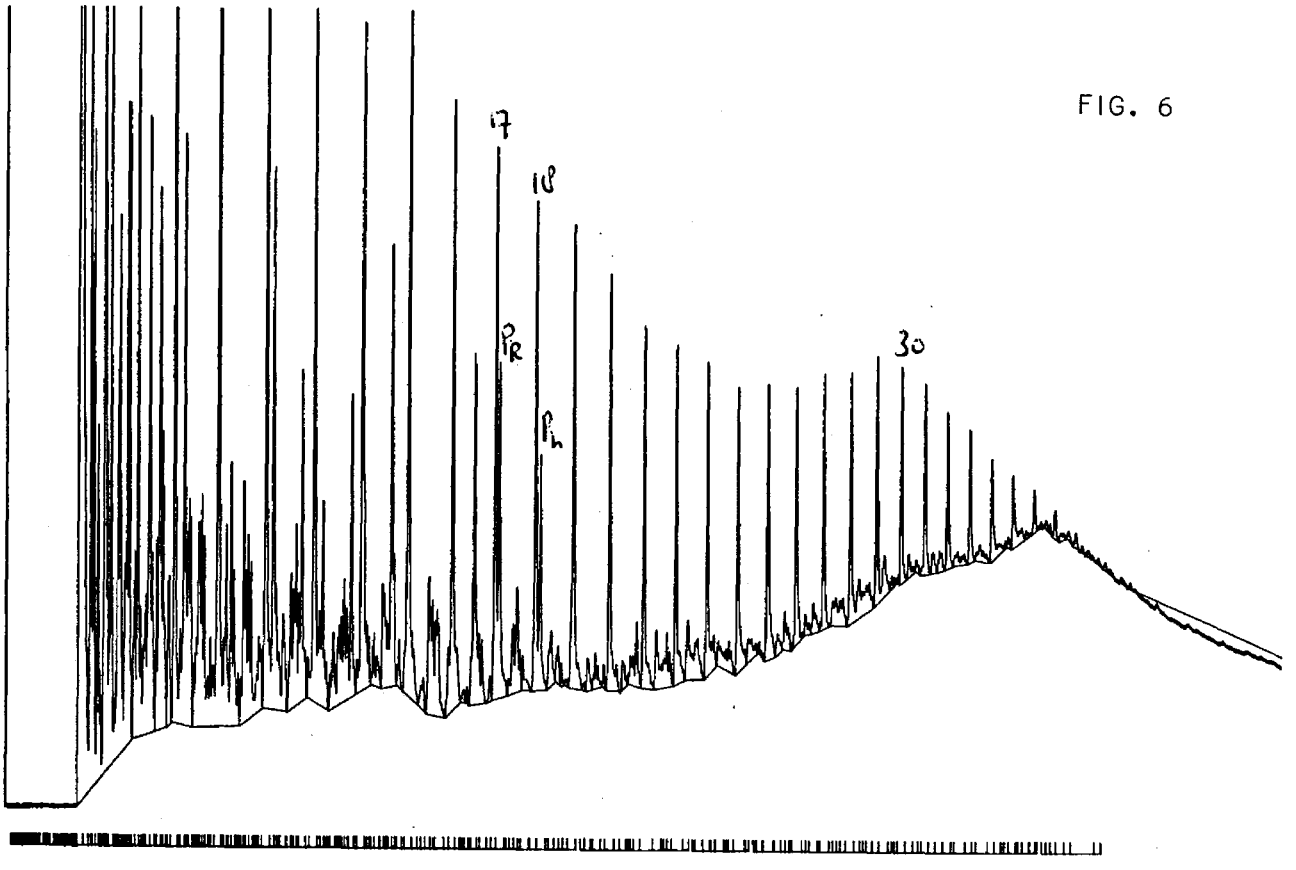
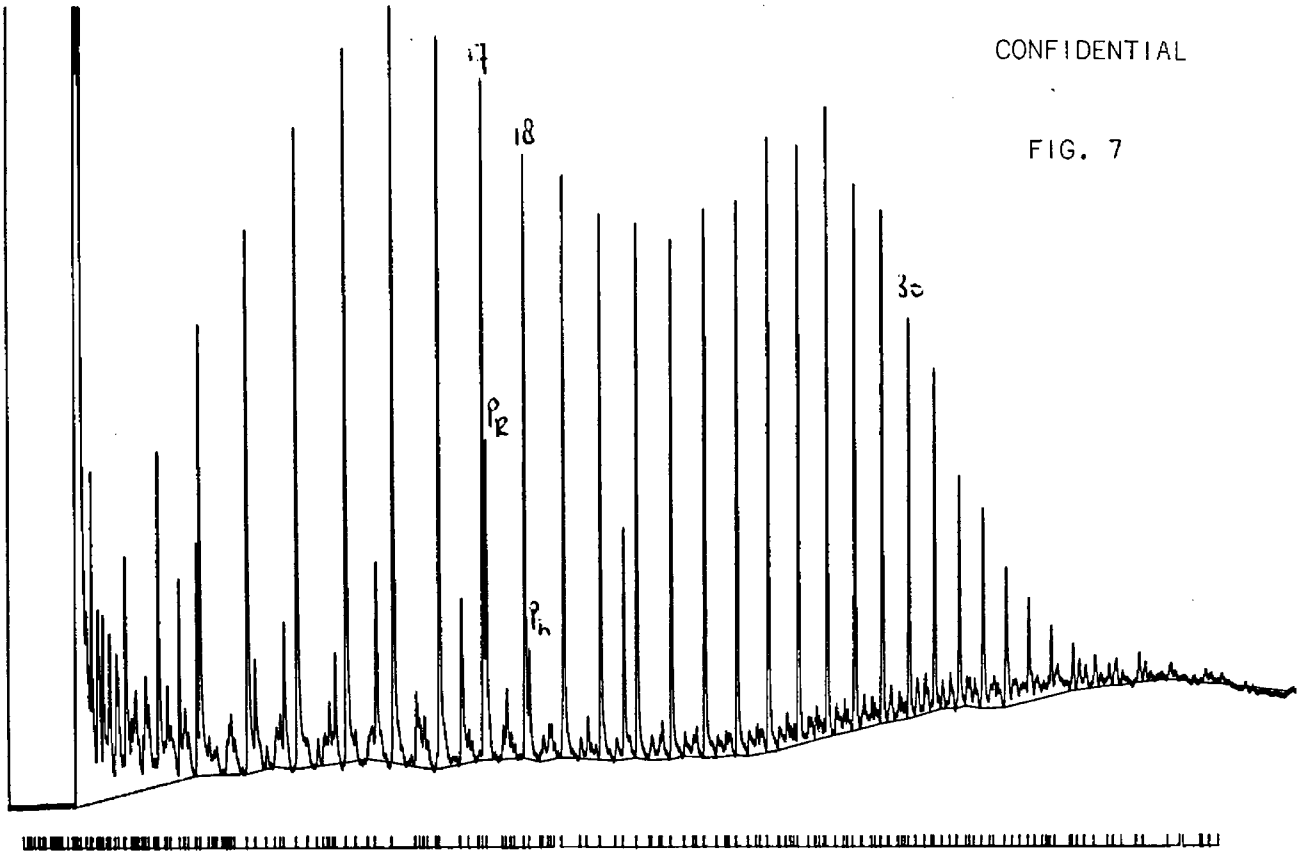


FIG. 6

NAME U.K. DUKESWOOD-181

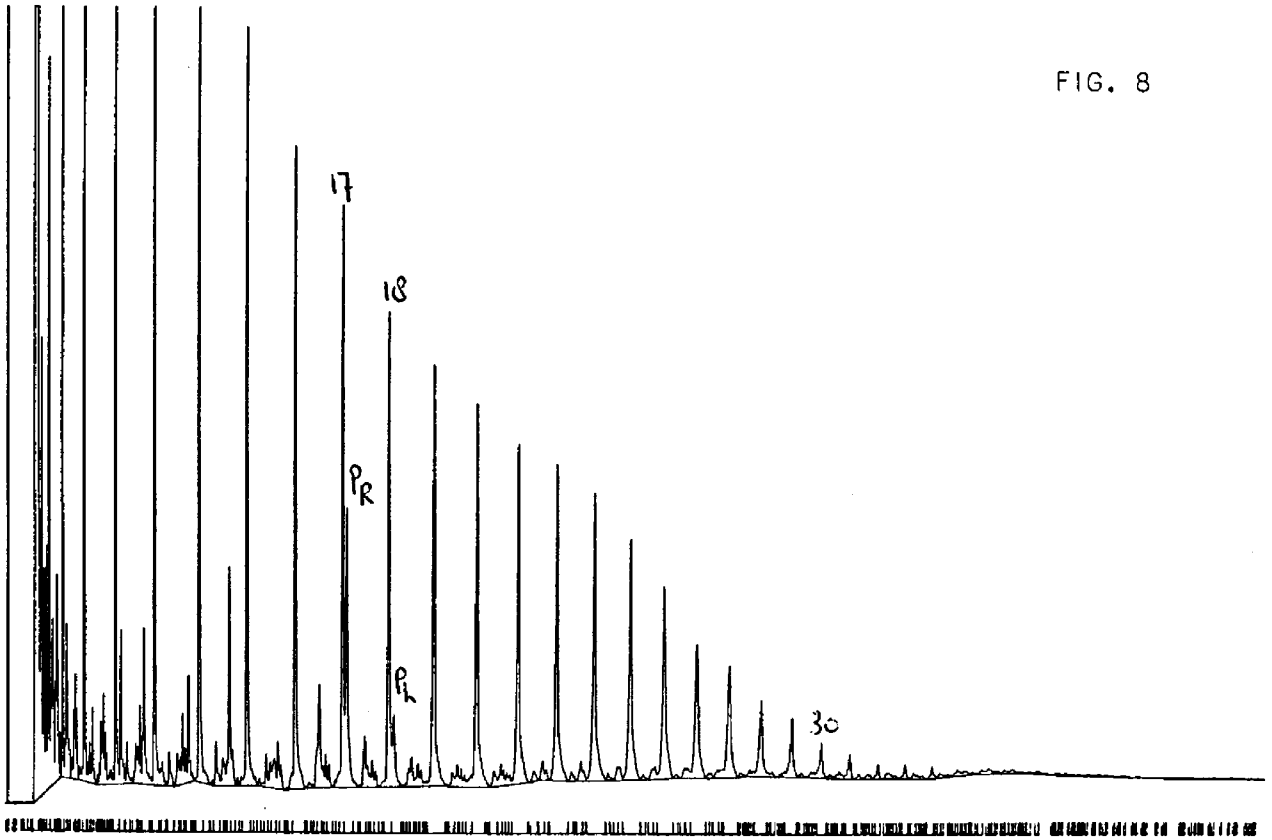
CONFIDENTIAL

FIG. 7



NAME PARSONAGE COLLIERY UK

FIG. 8



UK FLORENCE COLLIERY-2

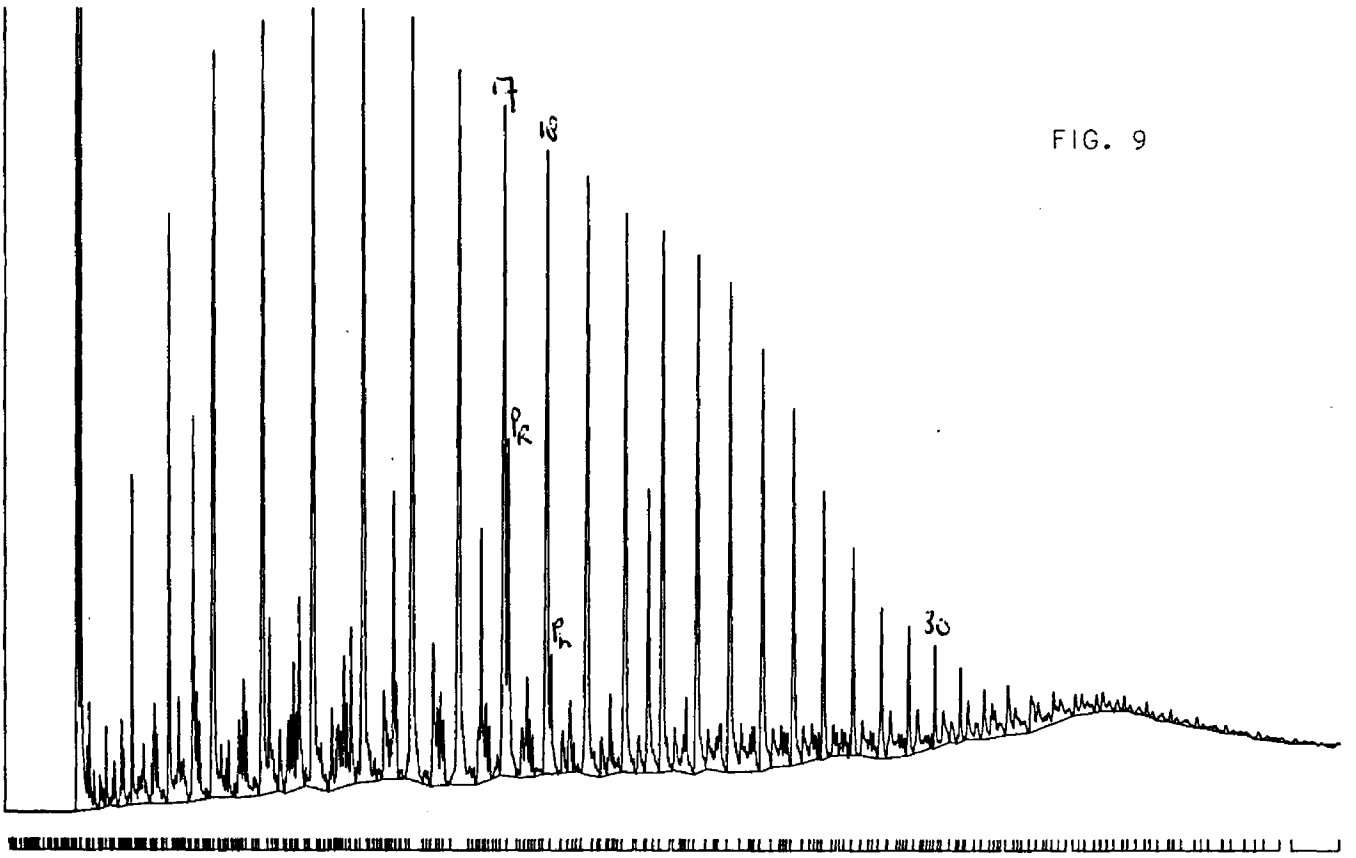


FIG. 9

NAME U.K. CRONTON COLLIERY .

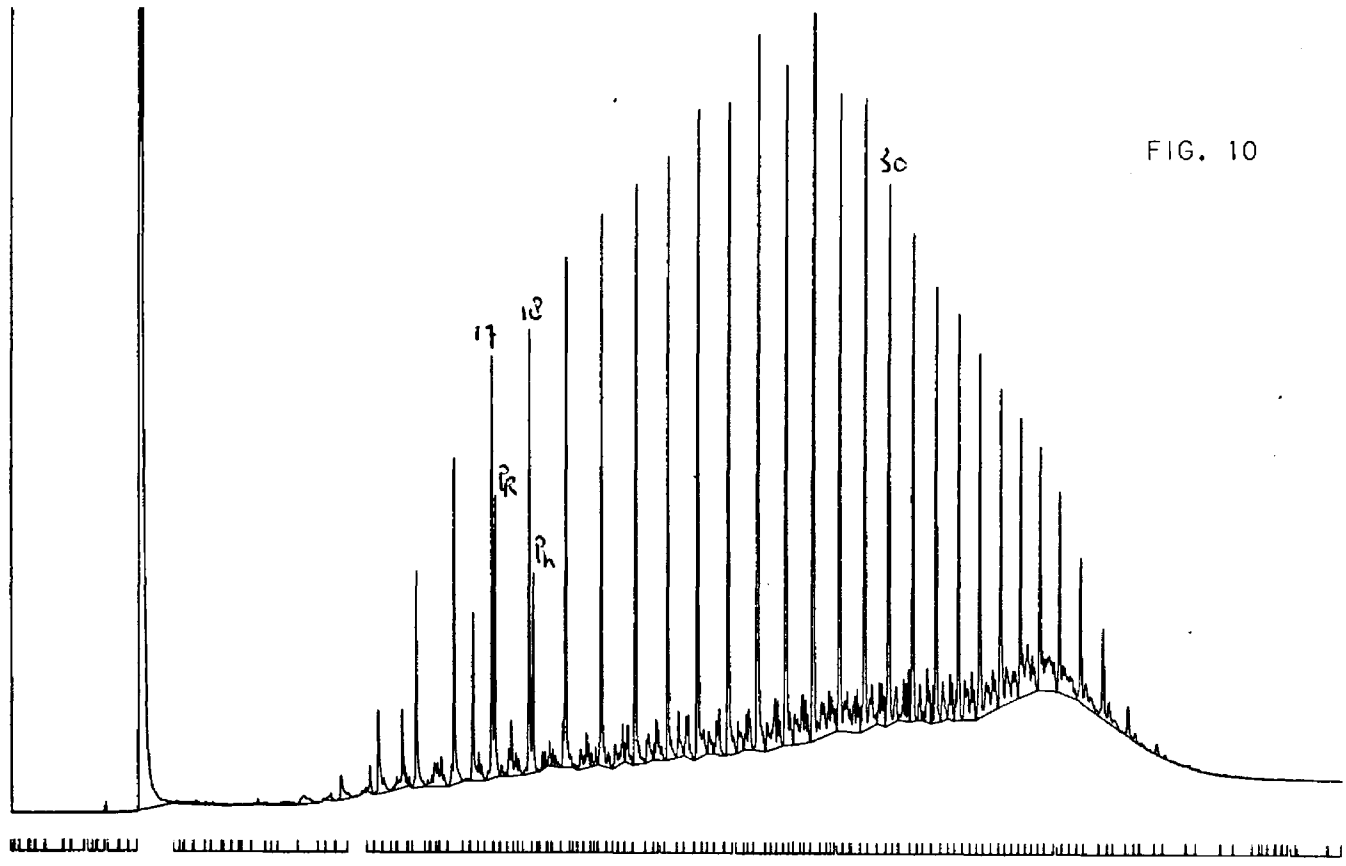


FIG. 10

NAME PENT.EL.,NCB BLACON,787.15-7.35 M.

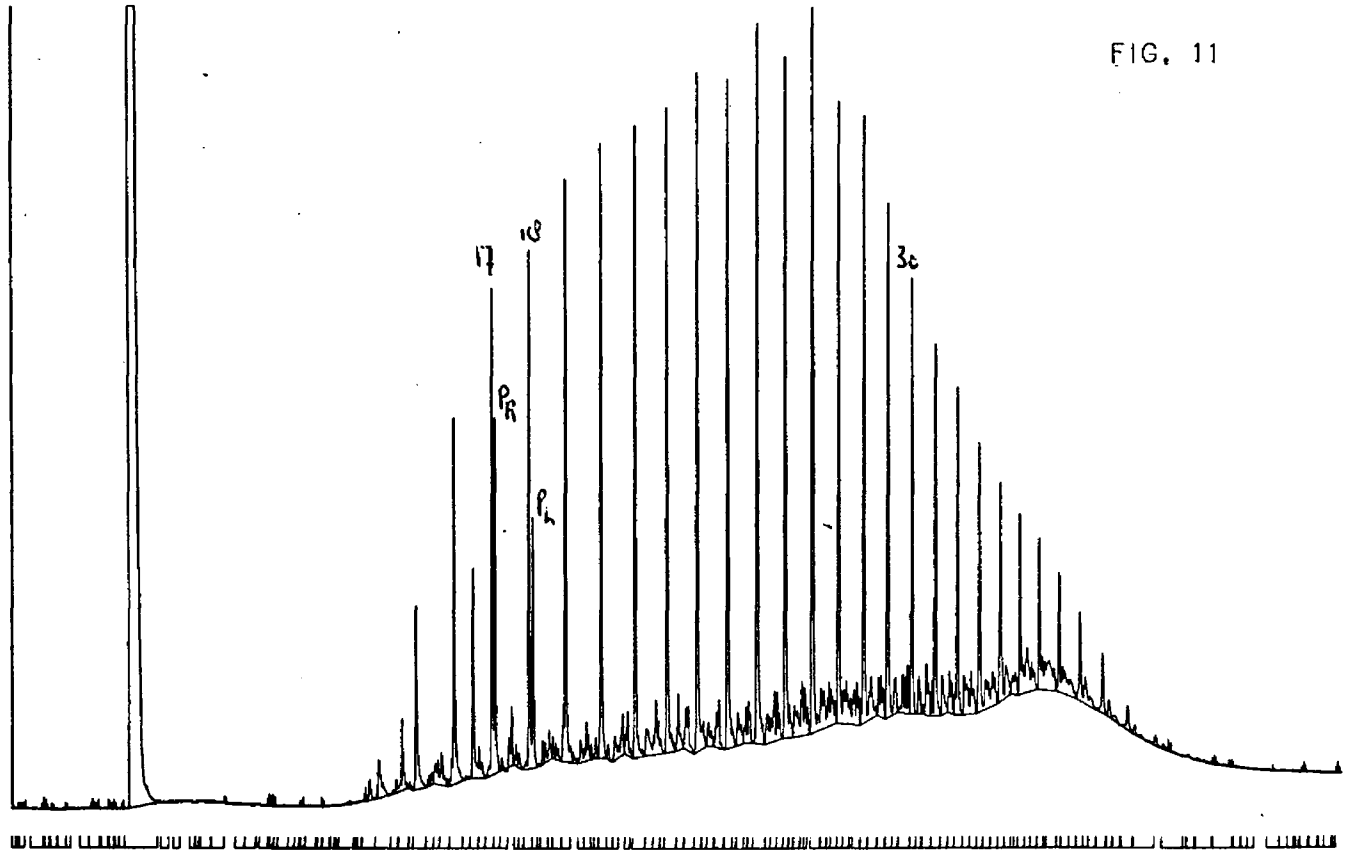
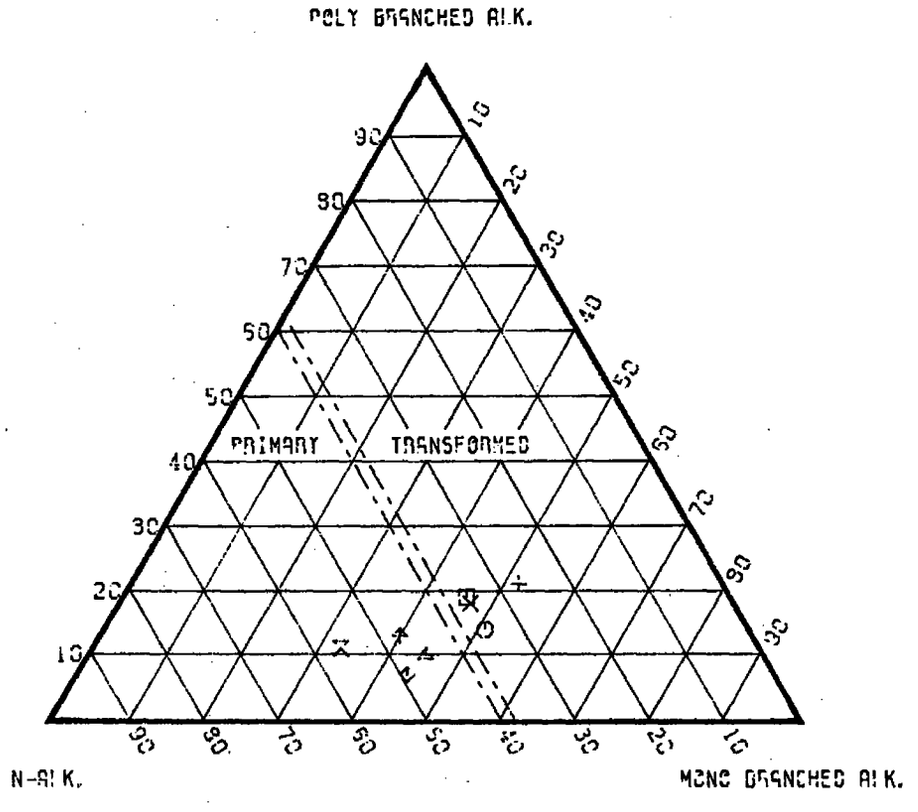


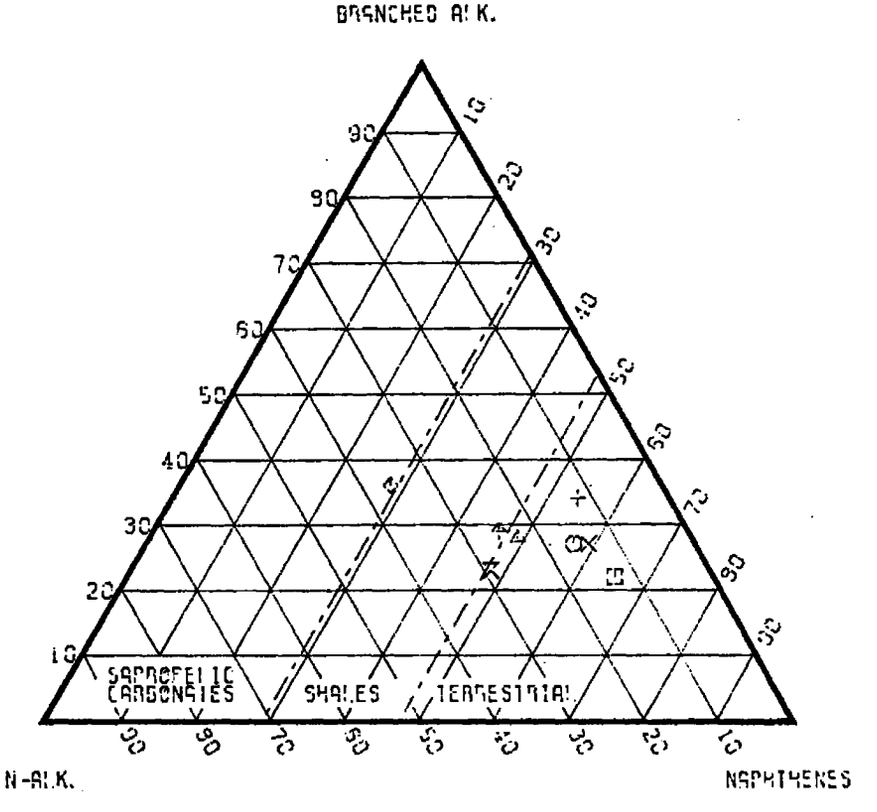
FIG. 11

NAME PENT.EL.,NCB BLACON,787.35-7.45 M

C7-ALKANE DISTRIBUTION



C7-ALKANE/NAPHTHENE DISTRIBUTION



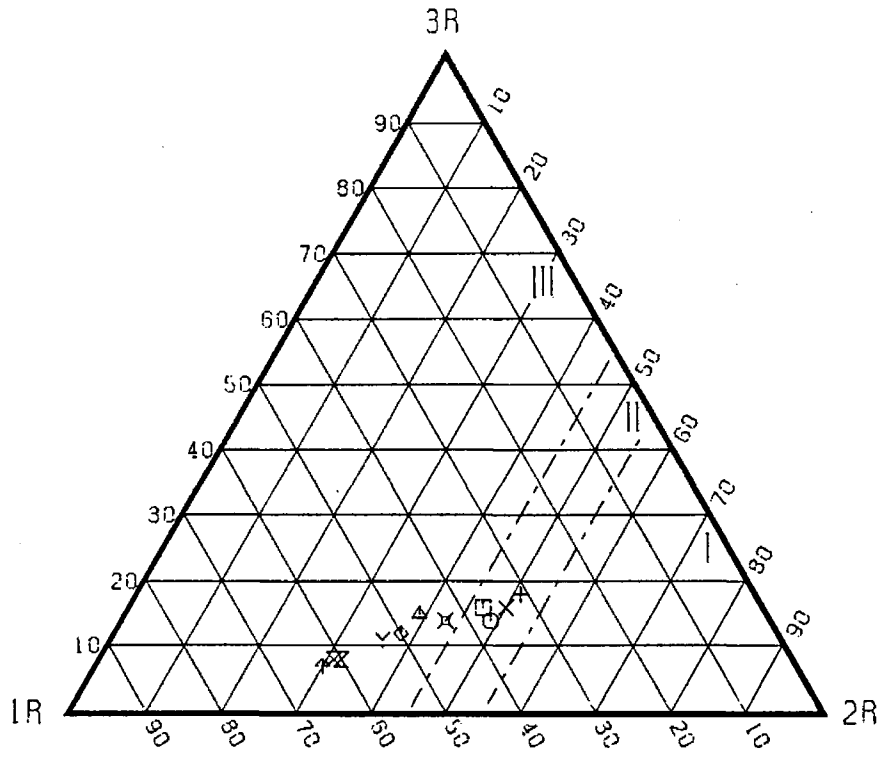
LEGEND
⊡ - FAKRING-1
⊙ - FAKRING-2
⊿ - FAKRING-177
+ - DUKESWOOD-45
× - DUKESWOOD-170
◇ - DUKESWOOD-191
✦ - PARSONAGE COLLIERY
✕ - FLORENCE COLLIERY

RKER 85.110

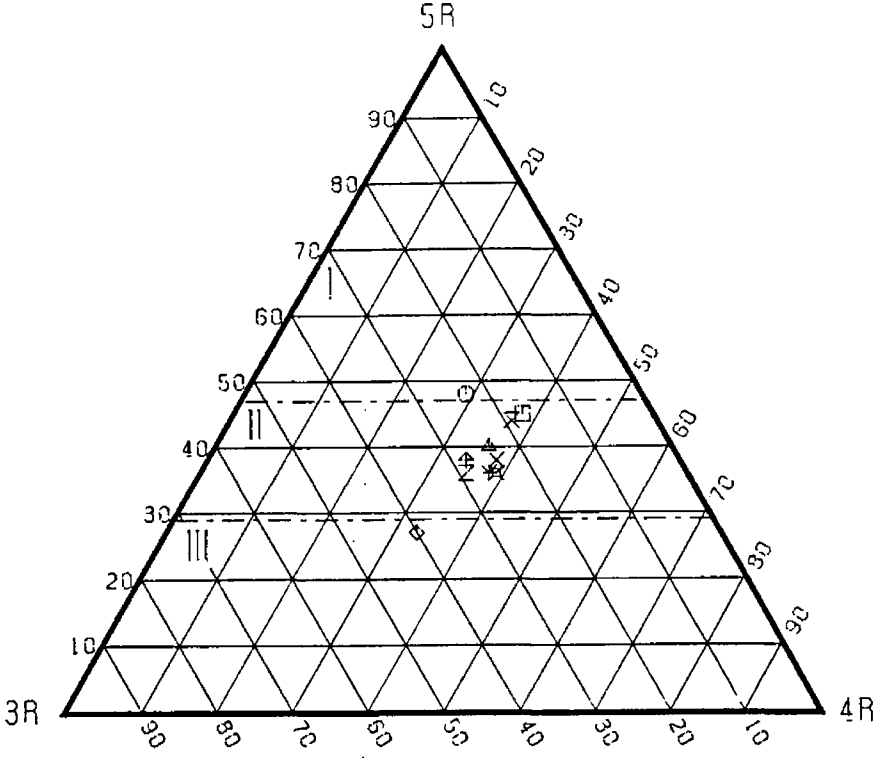
FIG. 12

CONFIDENTIAL

C_{15}-RINGDISTRIBUTION



C_{30}-RINGDISTRIBUTION



I LANDPLANT-DERIVED CRUDES WITH SUBSTANTIAL RESIN CONTRIBUTION TO SOURCE MATTER

II CRUDES OF MIXED ORIGIN

III CRUDES DERIVED FROM SOM AND/OR ALGAL MATTER

LEGEND	
⊡ - EAKRING-1	↑ - PARSONAGE COLLIERY
⊙ - EAKRING-2	⊠ - FLORENCE COLLIERY
△ - EAKRING-177	Z - CRONTON COLLIERY
+ - DUKESWOOD-45	Y - BLACON 785.15-787.35 M
× - DUKESWOOD-170	⊠ - BLACON 787.35-787.45 M
◇ - DUKESWOOD-181	

FIG. 13

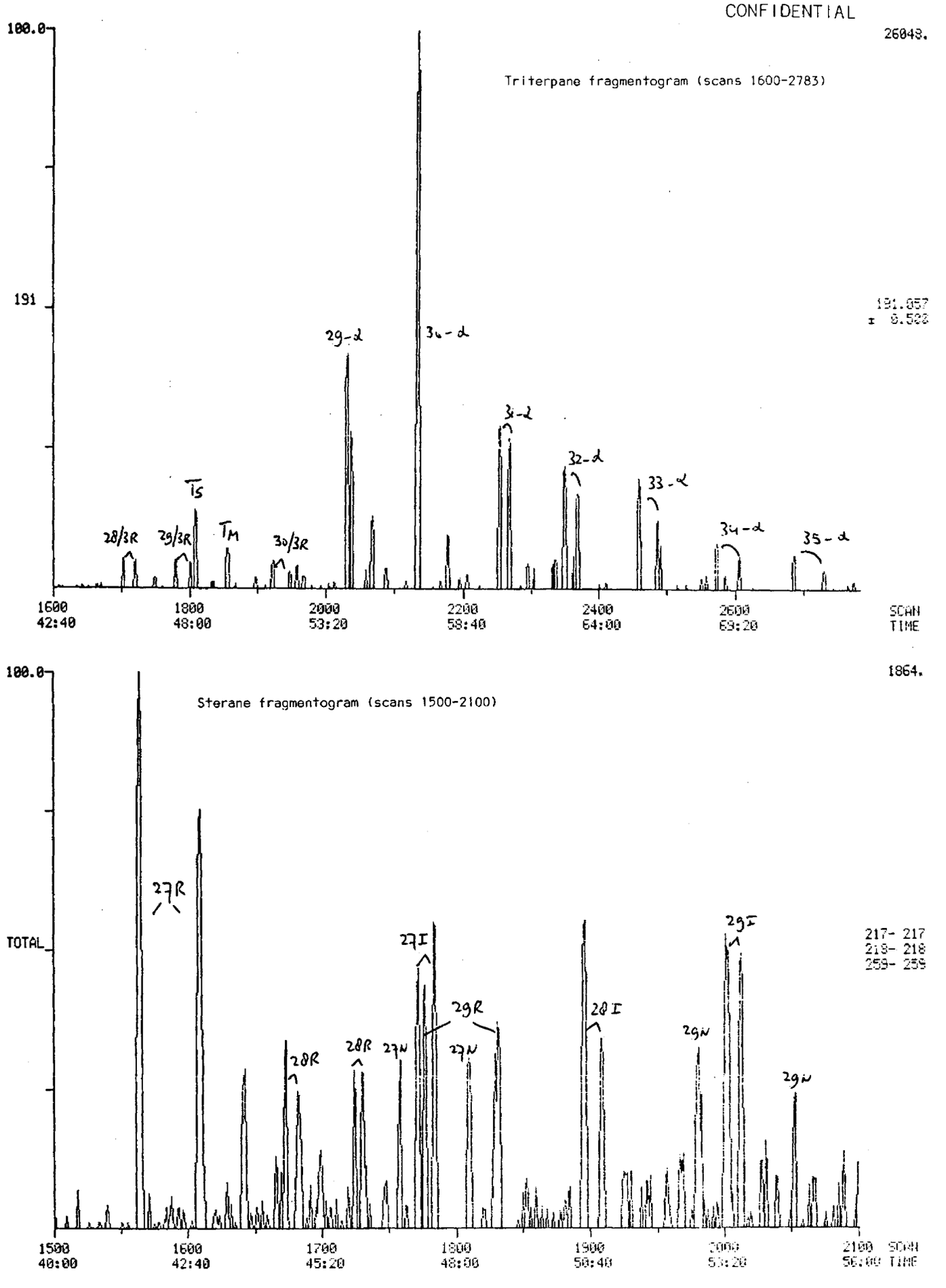


FIG. 14. GC-MS analysis Eakring-1

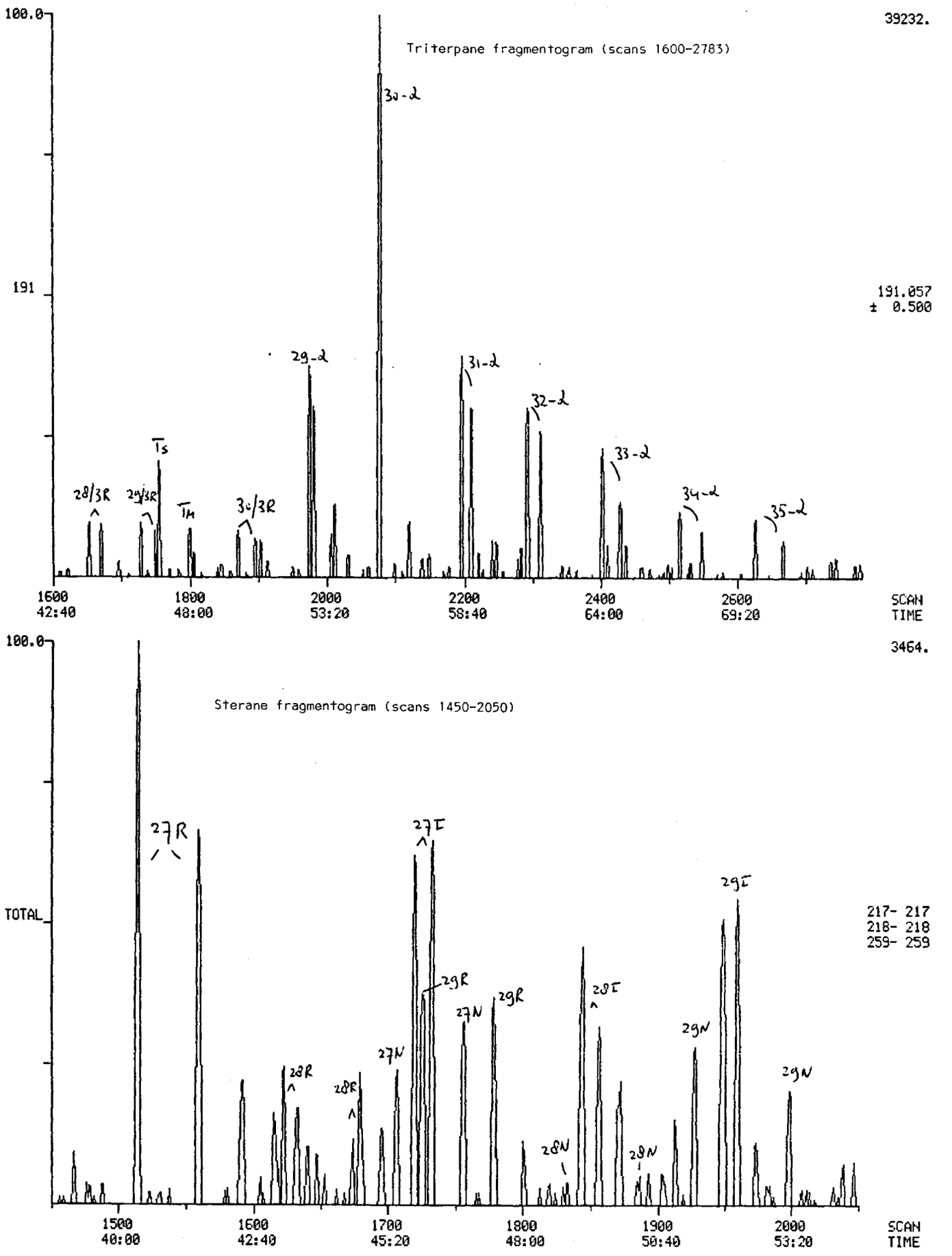


FIG. 15. GC-MS analysis Eakring-177

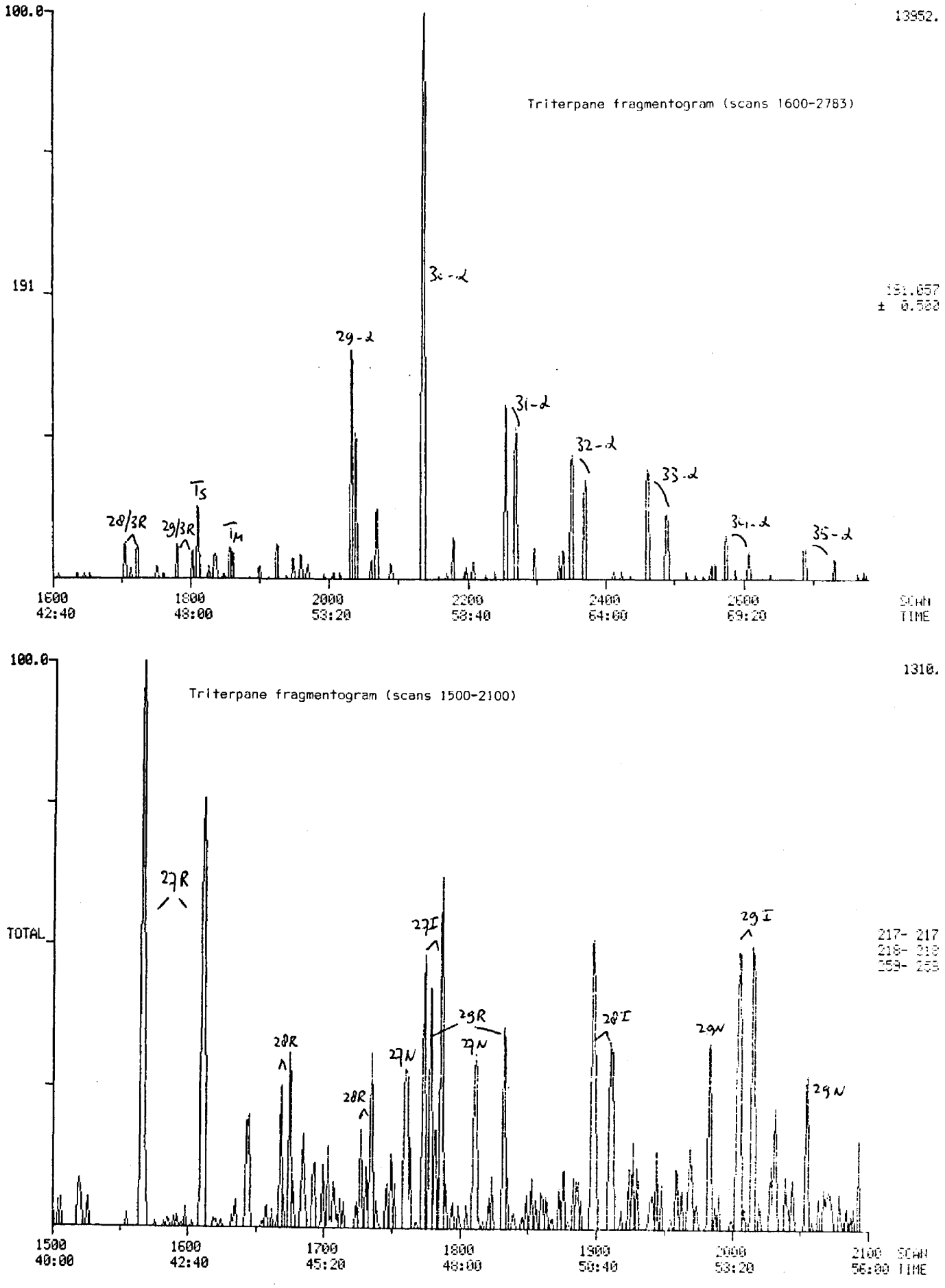


FIG. 16. GC-MS analysis Dukeswood-45

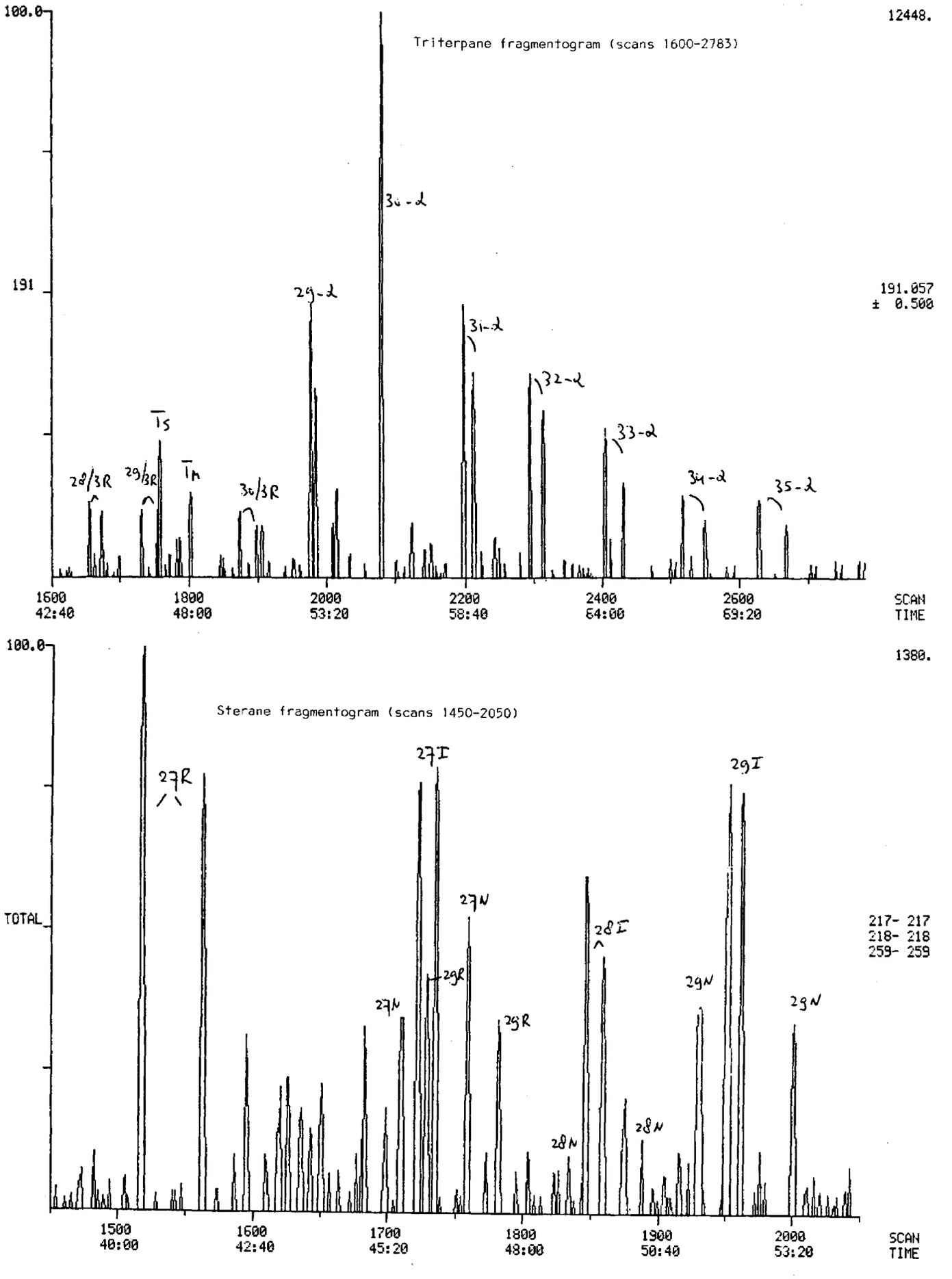


FIG. 17. GC-MS analysis Dukeswood-181

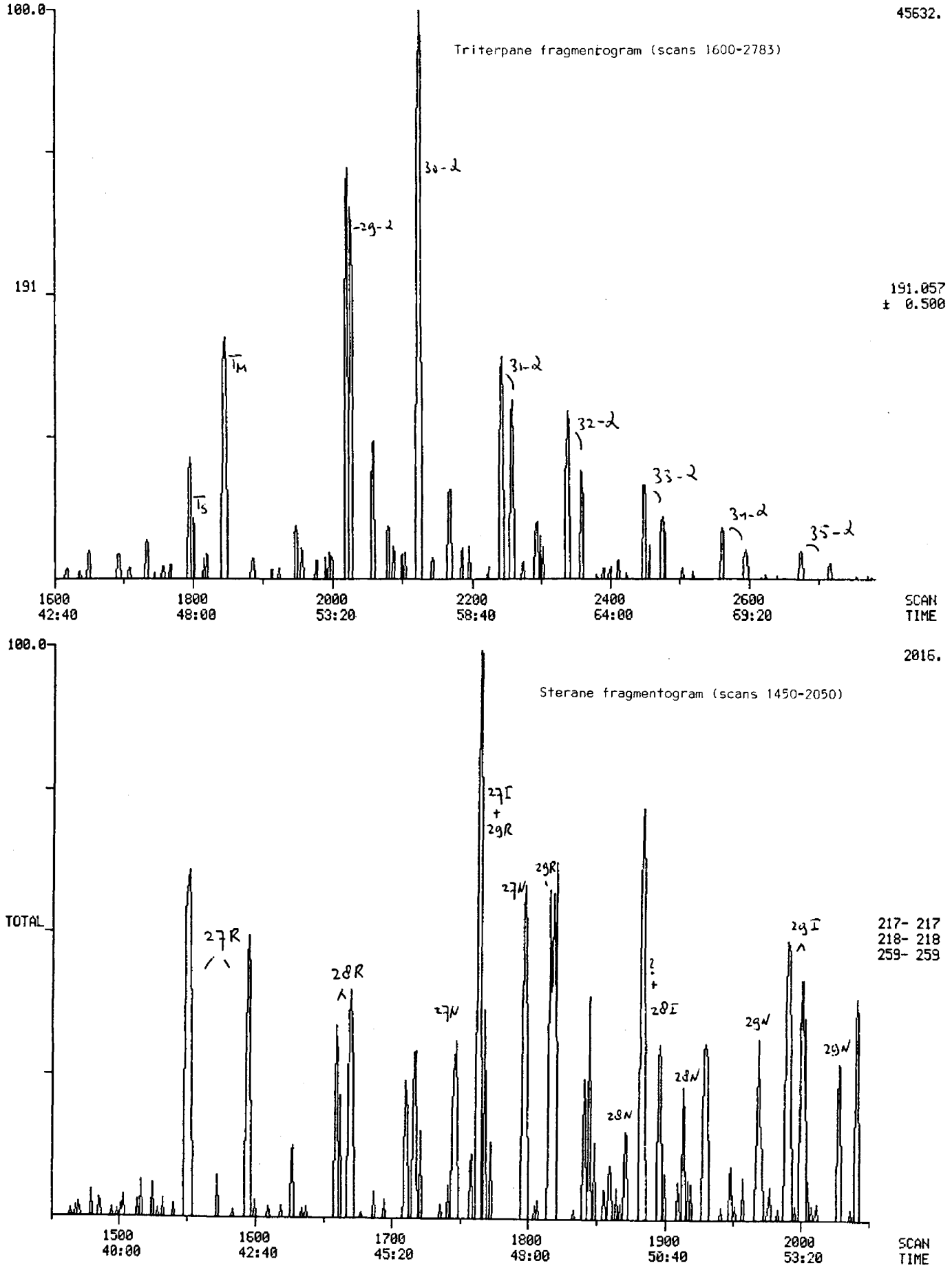


FIG. 18. GC-MS analysis Florence Colliery

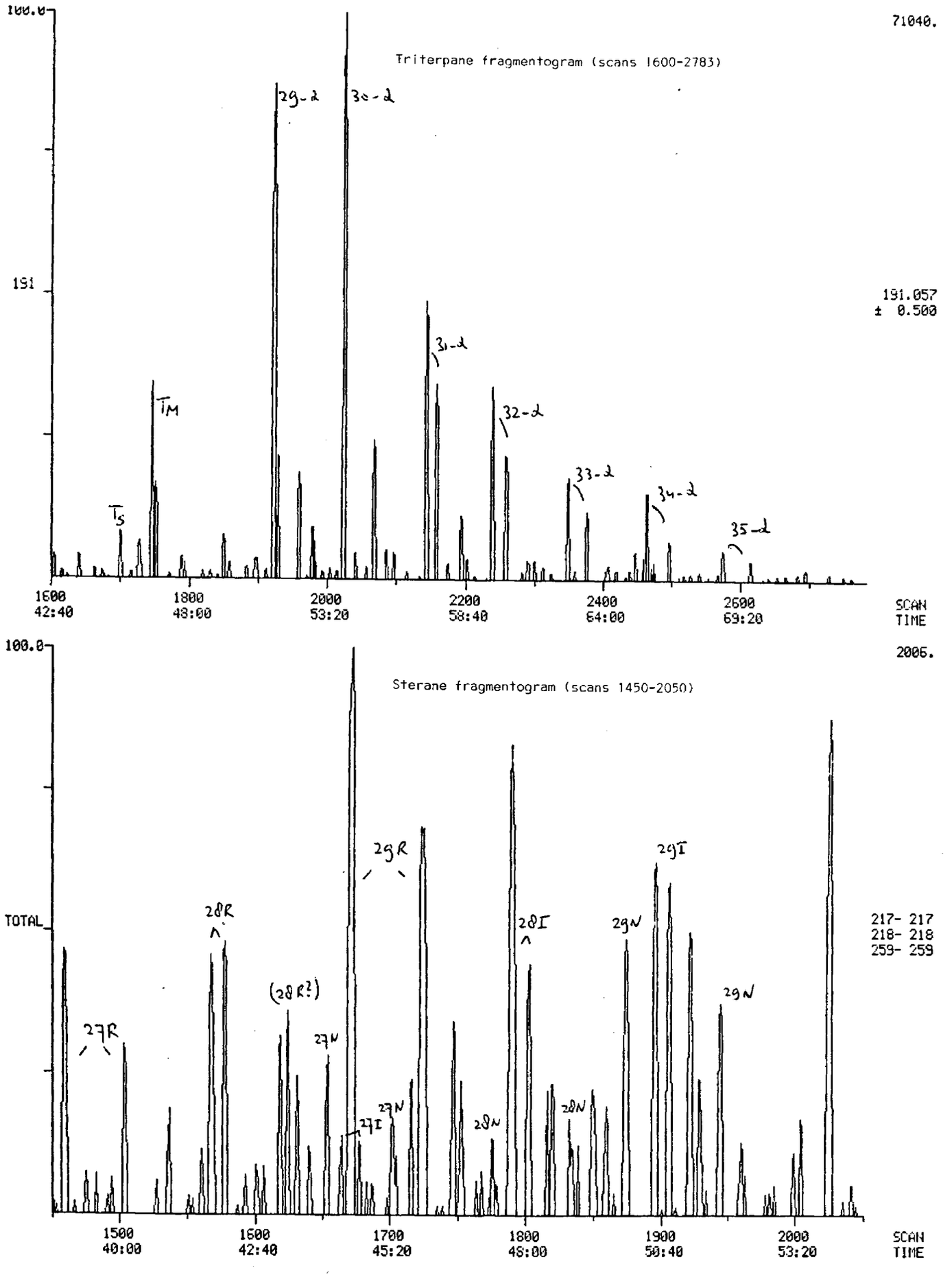


FIG. 19. GC-MS analysis Parsonage Colliery

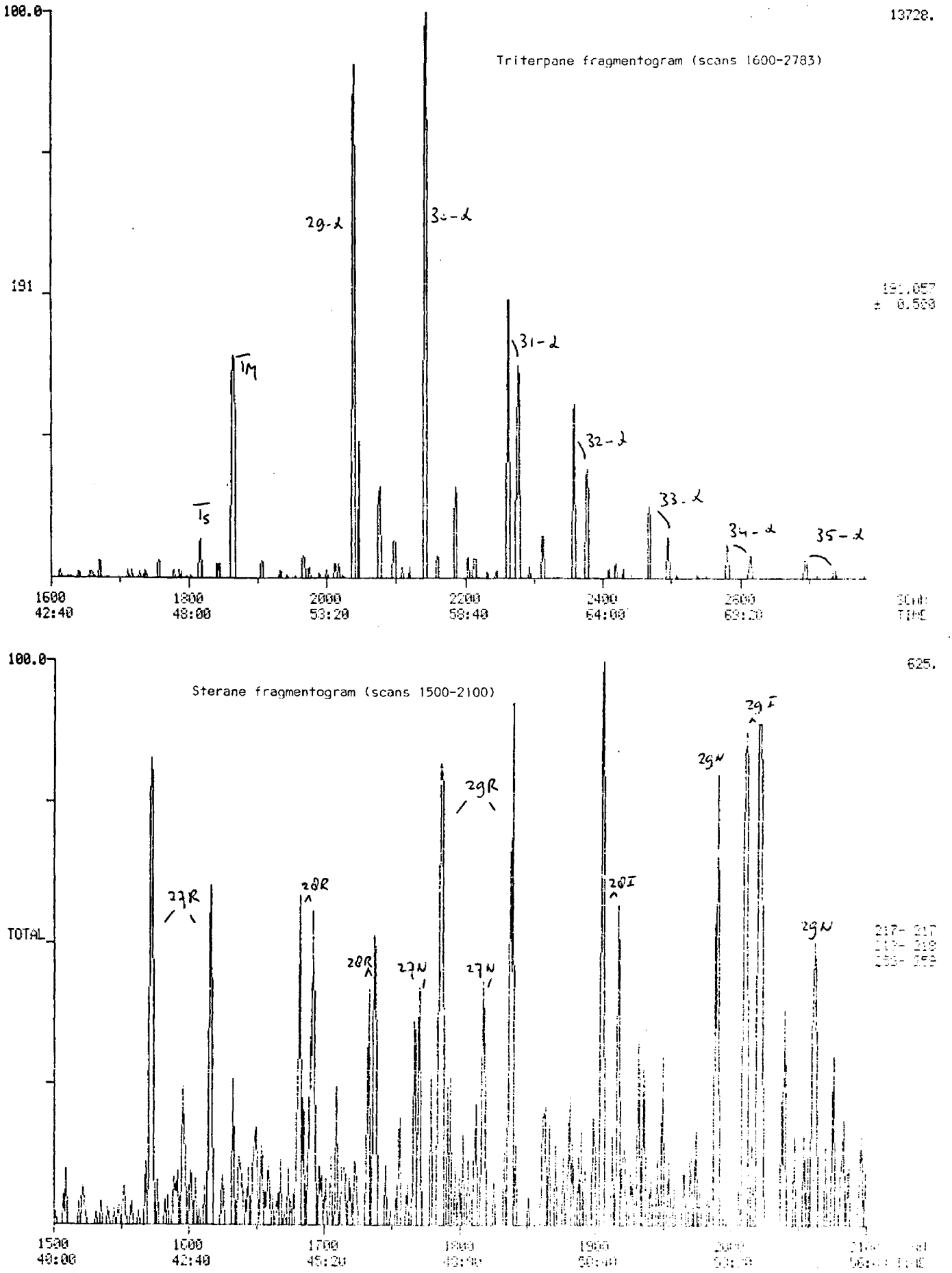


FIG. 20. GC-MS analysis Cronton Colliery

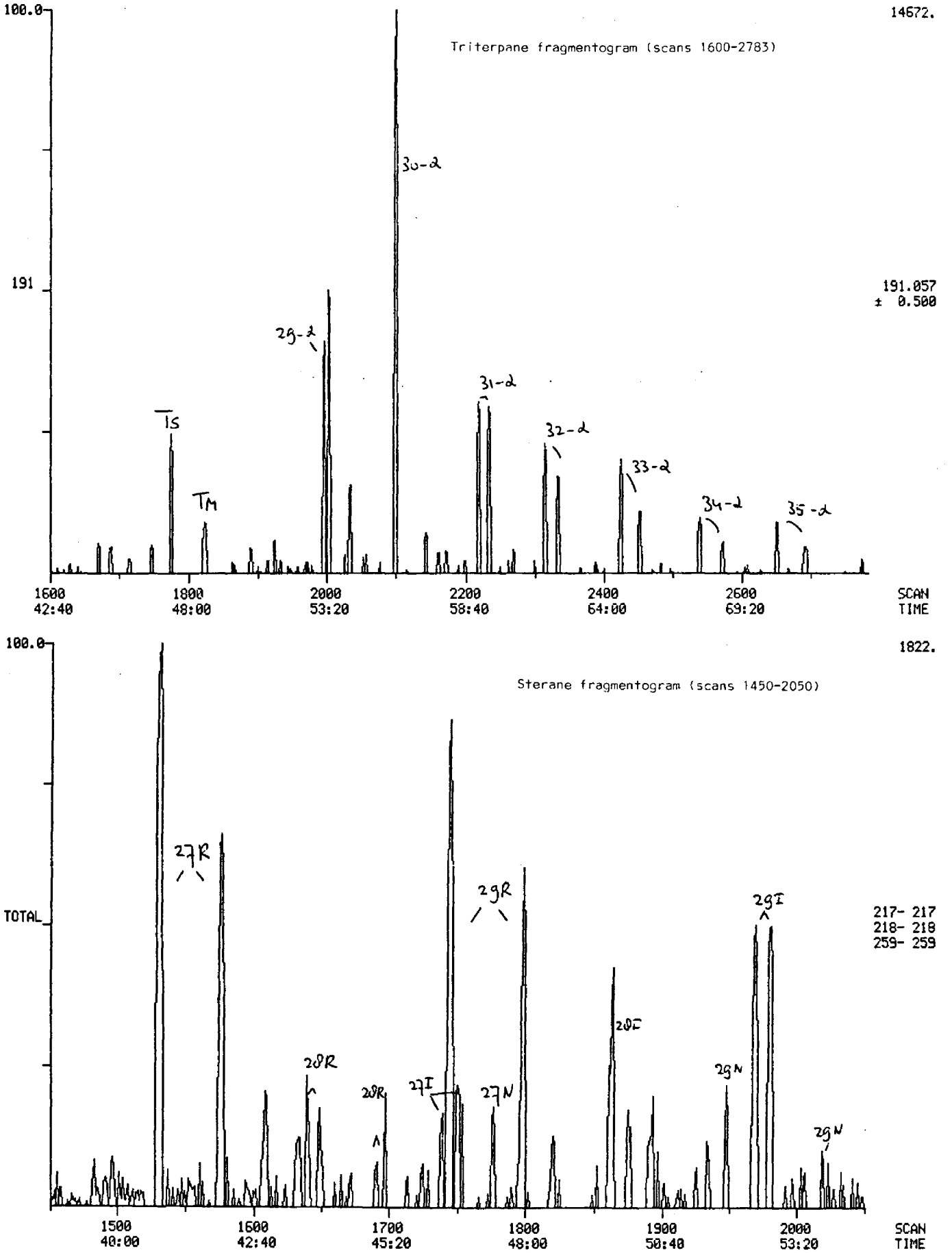


FIG. 21. GC-MS analysis Blacon 785.15-787.35 m extract

INITIAL DISTRIBUTION

3 Copies	Shell Expro London UEE/32/3
3 Copies	SIPM The Hague EP/11/13