

May 1980

RKER.80.031

GEOCHEMICAL ANALYSIS OF A CRUDE OIL SAMPLE
FROM MIDLAND LICENSES, FLORENCE COLLIERY,
UNITED KINGDOM

by

Ms. A.van der Gaag and J.Weijdema

Investigation 9.12.251

This Report has been prepared by Shell in connection with its own internal evaluations and decision-making processes. Shell, its affiliates and each of their respective officers, employees and representatives make no representation or warranty whatsoever as to the accuracy or completeness of the information contained herein, and expressly disclaim any and all liability based on or relating to any information contained in, or errors or omissions from, this Report or based on or relating to the use of this Report. Shell will not enter into any correspondence relating to the contents of this Report.

KONINKLIJKE / SHELL EXPLORATIE EN PRODUKTIE LABORATORIUM
RIJSWIJK, THE NETHERLANDS

Restricted

CONTENTS

	<u>Page</u>
Summary	III
1. Introduction	1
2. Synopsis of interpretation of geochemical parameters	
API gravity	1
Extract (Ethyl Acetate)	2
Organic carbon after extraction	2
Sulphur content	2
Porphyrins	3
Normal-alkane distribution	3
Isoprenoid isoalkanes	3
C ₇ distribution	4
Mass spectrometric analysis	4
Figure 1 Bacterial degradation displayed in gas chromatograms of saturated hydrocarbons	5
Figure 2 C ₇ distribution for characterisation of related source material	6
Figure 3 Parameters M1 and M2 to type related source material	7
3. Results and Discussion	8
4. Conclusions	8

Tables

1. Geochemical data of the oil	9
--------------------------------	---

Figures

4. Gaschromatogram of florence colliery
5. C₇ distribution of the oil
6. Parameter M1 and M2 of the oil.

SUMMARY

Geochemical analysis of an oil sample from Florence Colliery shows that the crude originates from mature source material consisting of sapropelic organic matter, with a slight algal contribution, deposited in a shaly environment.

RKER.80.031

GEOCHEMICAL ANALYSIS OF A CRUDE OIL SAMPLE FROM FLORENCE COLLIERY

1. INTRODUCTION

The purpose of geochemical typing of crude oils and rock extracts is to assess oil/oil- and oil/source rock correlation. In this context four objectives are of main interest:

1. to establish the type of source material from which certain crude oils or extracts originated.
2. to find in what type of environment a source rock has been deposited.
3. to estimate the maturity of the source material that has generated a certain oil or rock extract.
4. to determine whether or not a crude has been transformed (altered) after expulsion.

The following notes are intended as a guide to the interpretation of geochemical parameters. They are keyed to the tabulated results of the current study.

2. SYNOPSIS OF INTERPRETATION OF GEOCHEMICAL PARAMETERS

API Gravity

The API gravity scale for oils is related to its specific gravity by the following formula:

$$\text{degrees API} = \frac{141.5}{\text{S.G. at } 60^{\circ} \text{ F}} - 131.5$$

Crude oils commonly range from 10-60° API. The specific gravity is mainly determined by the maturity of the source material at the time of oil expulsion and by the extent of alteration the oil has undergone (e.g. bacterial degradation, physical or thermal transformation).

Extract (Ethyl Acetate)

Rock samples are crushed and powdered and subsequently extracted in a soxhlet apparatus using ethylacetate as a solvent. The extract, freed from solvent by evaporation, is used in further analyses.

Organic Carbon after Extraction

In the extracted rock sample the organic carbon content is determined using a LECO instrument. It is generally accepted that an organic carbon content of at least 0.5% defines the lower limit for a source rock. However, this is somewhat arbitrary, dependent on the convertibility of the organic matter type into hydrocarbons and on the expulsion capability of the source beds. In this respect only the percentage of pyrolysable organic matter is of interest.

Sulphur content

The sulphur content of a crude oil depends on:

1. the kerogen type (high or low sulphur) of the source rock, which is in turn related to its environment of deposition.
2. the level of organic metamorphism of the source rock at the time of expulsion.
3. the degree of transformation (bacterial or physical) of the crude.

The major part of the sulphur in crude oils is present in the heavy ends (higher boiling-point fractions). As bacterial degradation of a crude oil preferentially removes the light ends, the sulphur content of a crude is increased by mere concentration though usually to a not too significant extent. High-sulphur crudes are associated with sulphur-rich source material, deposited in strongly reducing environments (often rich in carbonates or cherts). Sulphur-rich crudes are often heavy, being expelled at a low maturity level. Low sulphur crudes are related to low sulphur source material, deposited either in non-marine environments or in marine siliciclastic sequences. Furthermore oils expelled at a high level of organic metamorphism of the source rock are always low in sulphur, regardless of their original source material.

Porphyryns

Porphyryns are nitrogen-containing ring components often found in petroleum as nickel or vanadyl complexes. It is generally accepted that the porphyryns are derived from chlorophyll during early diagenesis. A predominance of vanadyl over nickel porphyryns is associated with a deep marine environment of deposition of the source matter, whilst nickel porphyryn predominance is linked with coastal or lagoonal waters with terrestrial influx.

Normal-Alkane Distribution

The saturated hydrocarbons of an oil (or rock extract) are separated by elution chromatography and then analysed by temperature-programmed gas chromatography. The n-alkane distribution of an oil displayed in the chromatogram provides information on its origin, maturity and possible transformation.

The shape of the n-alkane distribution reflects the original source material. The envelope of the n-alkane distributions of marine crude oils and source rock extracts are, for instance, concave, whereas landplant-related crudes and extracts usually show a convex or even bimodal n-alkane distribution.

Sometimes there is a marked predominance of odd-numbered n-alkanes over the even ones. This odd/even predominance (expressed as a 'carbon preference index') is often used as an index of maturity. However, this can be done in only a few specific cases. Indeed a distinct odd/even predominance in the C₂₅₊ region is indicative of a landplant wax contribution in the source material while oils and extracts of marine origin do not exhibit such odd/even predominance. Biodegraded oils are characteristically deficient in n-alkanes. Severe bacterial degradation will result in a complete removal of n-alkanes and finally even of the isoprenoids (see Fig. 1).

Isoprenoid isoalkanes

Many crude oils and source-rock extracts contain a series of isoalkanes with structures based on the isoprene unit. They are believed to be derived from phytol, a hydrolysis product of chlorophyll. The most common isoprenoids in crude oil are pristane and phytane. The relative abundances of these two compounds, expressed as pristane/phytane ratio, pristane/n-C₁₇, or phytane/n-C₁₈ is mainly an indication of the depositional environment of the source rock. High

pristane/phytane and pristane/n-C₁₇ ratios are related to a swampy environment of deposition with low bacterial activity. Low ratios are expected in open aquatic conditions (marine or fresh water), where there is abundant bacterial activity.

C₇ Distribution

Crude oil samples are distilled to obtain the volatile fraction boiling below 120°C. This fraction is subsequently analysed by gas chromatography to obtain a detailed distribution of all C₇ hydrocarbon isomers. A triangular plot of straight-chain (normal), monobranched, and polybranched C₇ alkanes is used to distinguish slightly bacterially degraded or transformed crudes from their unaltered counterpart (Fig. 2). In a plot of n-C₇ alkanes - branched alkanes - naphthenes oils of similar origin form clusters, while also some information is obtained from this triangular plot about the environment of deposition of the related source rocks (see Fig. 2). Note that this latter plot cannot be used for (even slightly) bacterially degraded crude oils. The relative abundances of C₇ alkanes, naphthenes and aromatics may be used to determine whether waterwashing in the reservoir has occurred.

Mass spectrometric analysis

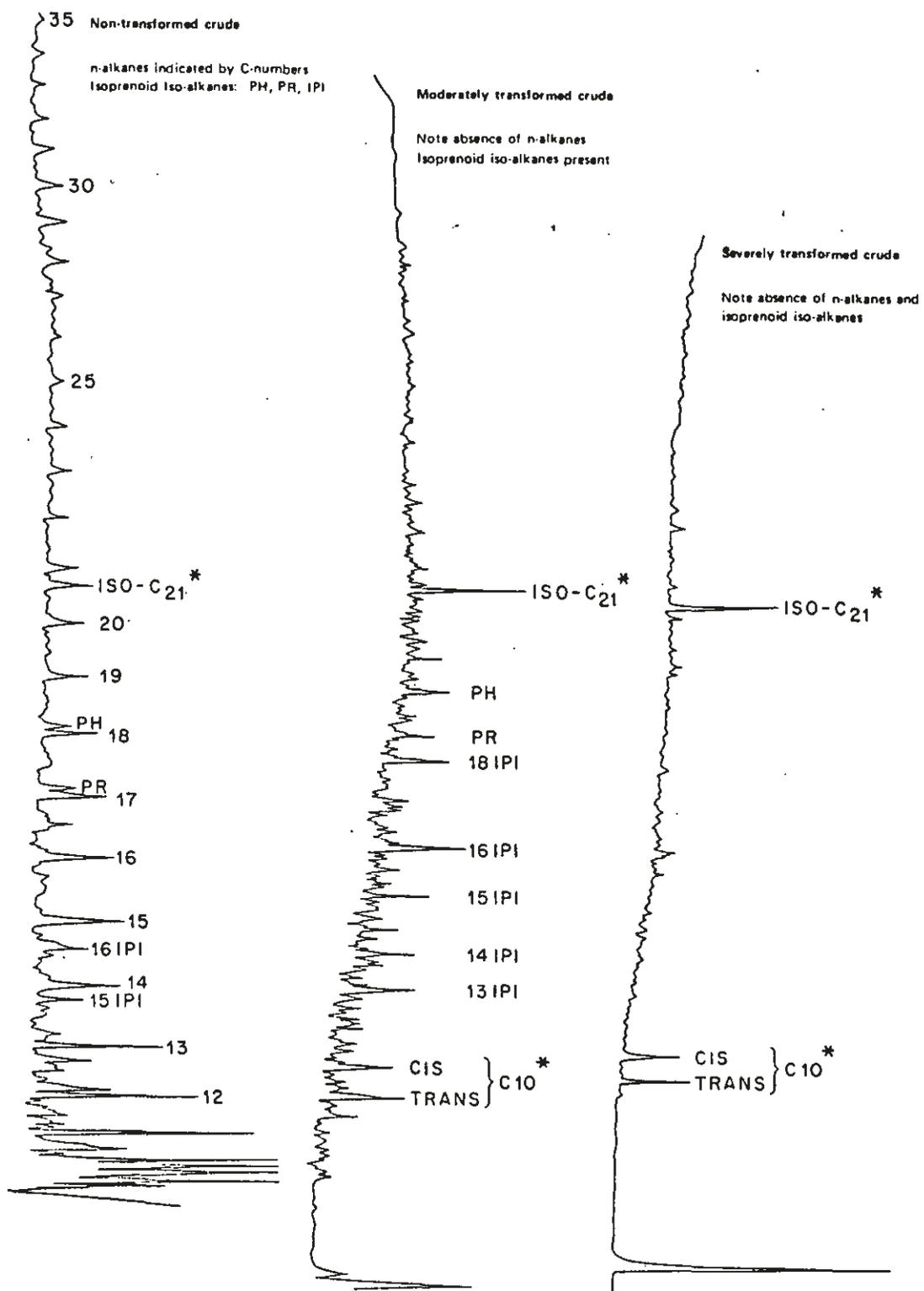
Parameters M1 and M2 (Fig. 3)

From the mass spectra of crude oils and extracts two parameters M1 and M2 can be derived, which are very useful for oil and source rock characterisation. The positions in these triangular diagrams give information about the original source material as is indicated in Fig. 3. Note that the C₁₅ diagram cannot be used for bacterially degraded crude oils.

DOM of oils

The maturity of the oil and/or extract can be calculated from mass spectrometric data. The calculated maturity is expressed in DOM (degree of organic metamorphism) units, which cover the following ranges:

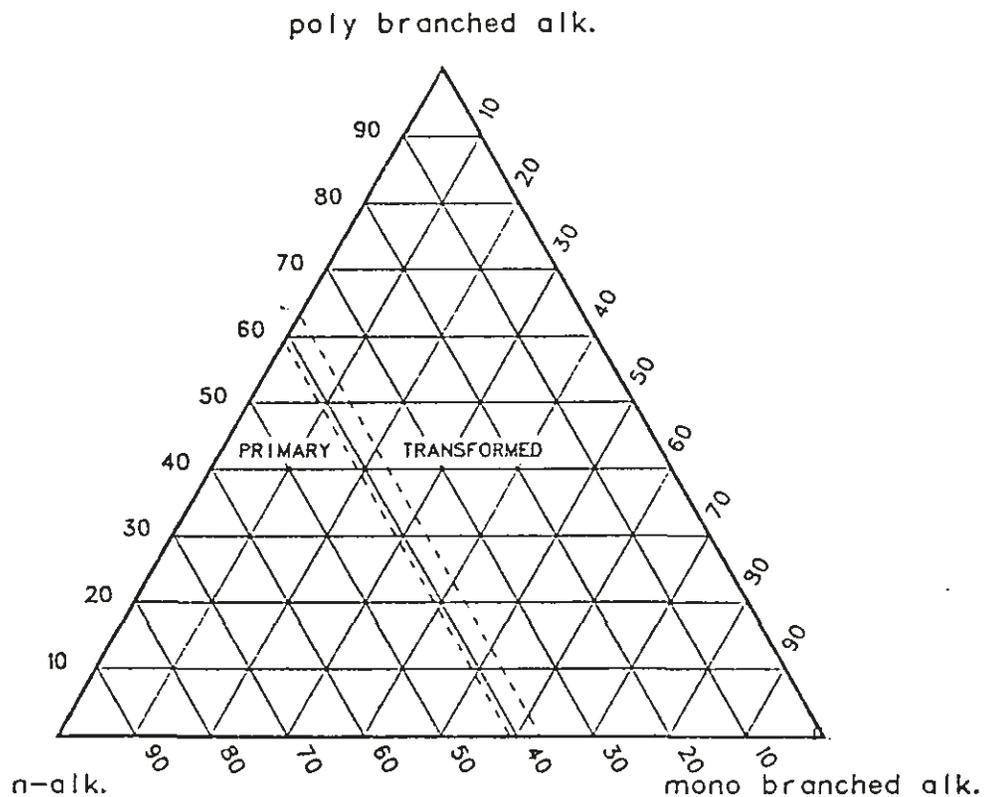
<u>DOM</u>	<u>MATURITY ZONES</u>
<60	Immature
60-75	Mature for oil generation
75-92	Mature for gas generation.
	Post mature for oil generation.
>92	Post mature for both oil and gas.



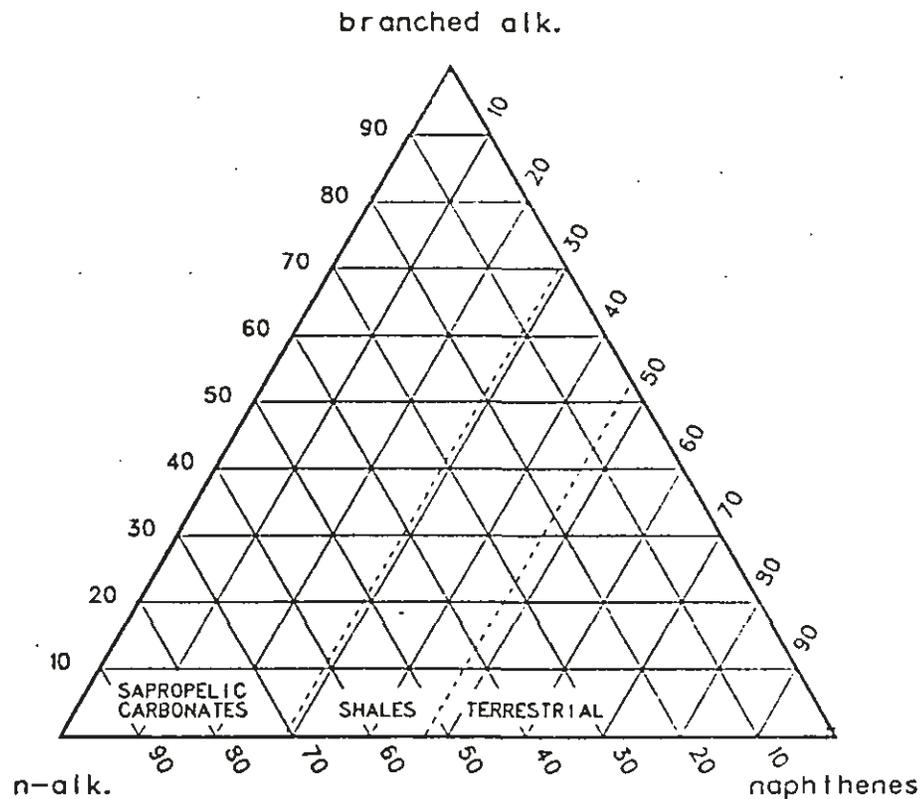
*STANDARD COMPOUNDS ADDED FOR IDENTIFICATION

BACTERIAL DEGRADATION DISPLAYED IN GAS CHROMATOGRAMS OF SATURATED HYDROCARBONS.

C₇-ALKANE DISTRIBUTION

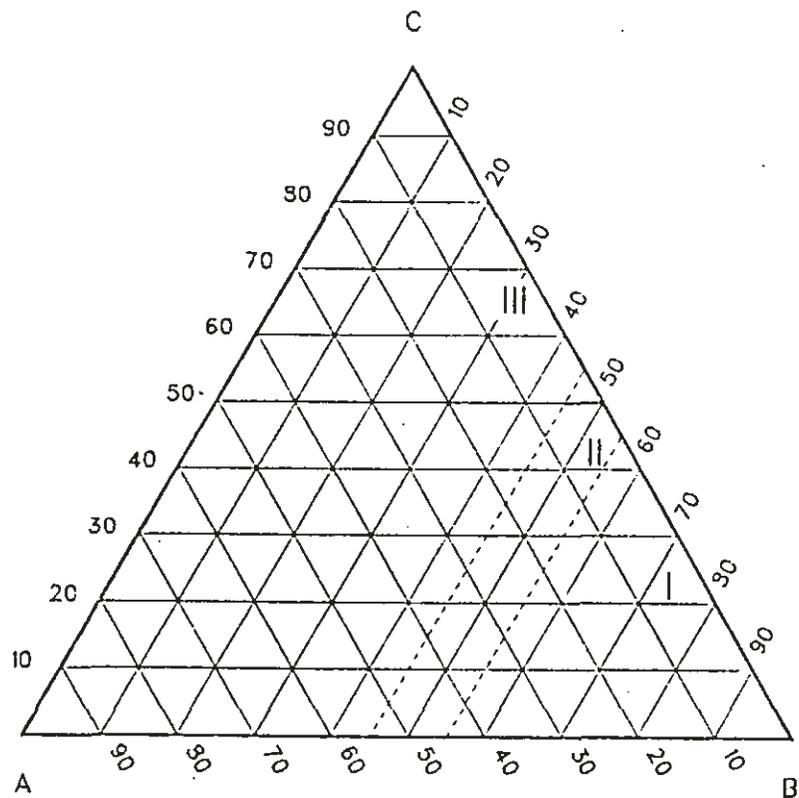


C₇-ALKANE/NAPHTHENE DISTRIBUTION

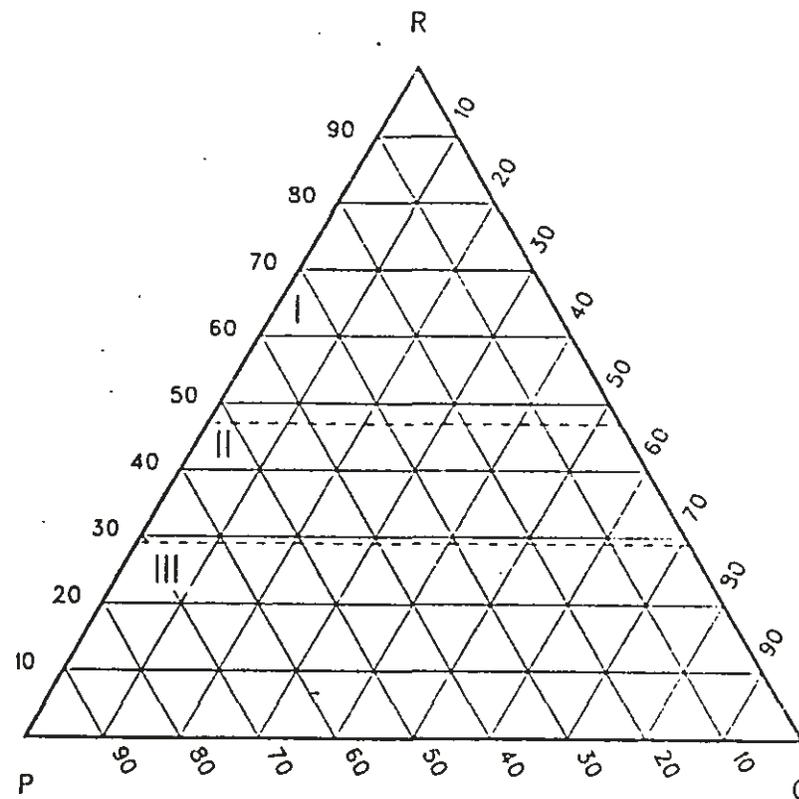


C₇ DISTRIBUTION FOR CHARACTERISATION OF RELATED SOURCE MATERIAL.

Parameter M1



Parameter M2



- 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

PARAMETERS M1 AND M2 TO TYPE RELATED SOURCE MATERIAL.

3. RESULTS AND DISCUSSION

Results of the geochemical analysis are given in Table 1 and Figures 4-6. The gas chromatogram of the saturated hydrocarbons (Fig. 4) and the C₇-alkane distribution (Fig. 5) indicate that the oil is not bacterially degraded.

The "DOM of oil" value of 75 shows that the sample represents a mature expulsion product. This concurs with the low intensities of the non-normal alkanes in the C₃₀ range of the gas chromatogram.

The gas chromatogram of the saturated hydrocarbons (Fig. 4) and the M1 and M2 parameters (Fig. 6) point to source material consisting of sapropelic organic matter with a slight contribution of algae.

The C₇ alkane/naphthene distribution (Fig. 5) and the pristane/nC₁₇ ratio indicate a reducing shaly environment of deposition of the source material.

4. CONCLUSIONS

The sample represents a crude expelled from a mature source rock.

The parent source material consists of sapropelic organic matter with a slight algal contribution and has been deposited in a reducing shaly environment.

Table 1 - Geochemical data of the oil

Samp.	Depth	API	Spec. grav.	% w. boil. <120C	% sulph.	pr ph	pr nC ₁₇	ph nC ₁₈	C ₇ -distribution						Mass spectrometry						DOM of oil			
									C ₇ -alkane			C ₇ -alk/naph.		C ₇ -alk/naph/arom			Parameter M1			Parameter M2				
									nC ₇	mono br.	poly br.	nC ₇	naph. br.	nC ₇	naph.	arom	A	B	C	P		Q	R	
Florence Colliery		39.5	0.827	5.6	0.0	3.1	0.5	0.2	56	33	11	29	48	23	49	45	6	61	31	8	19	37	44	75

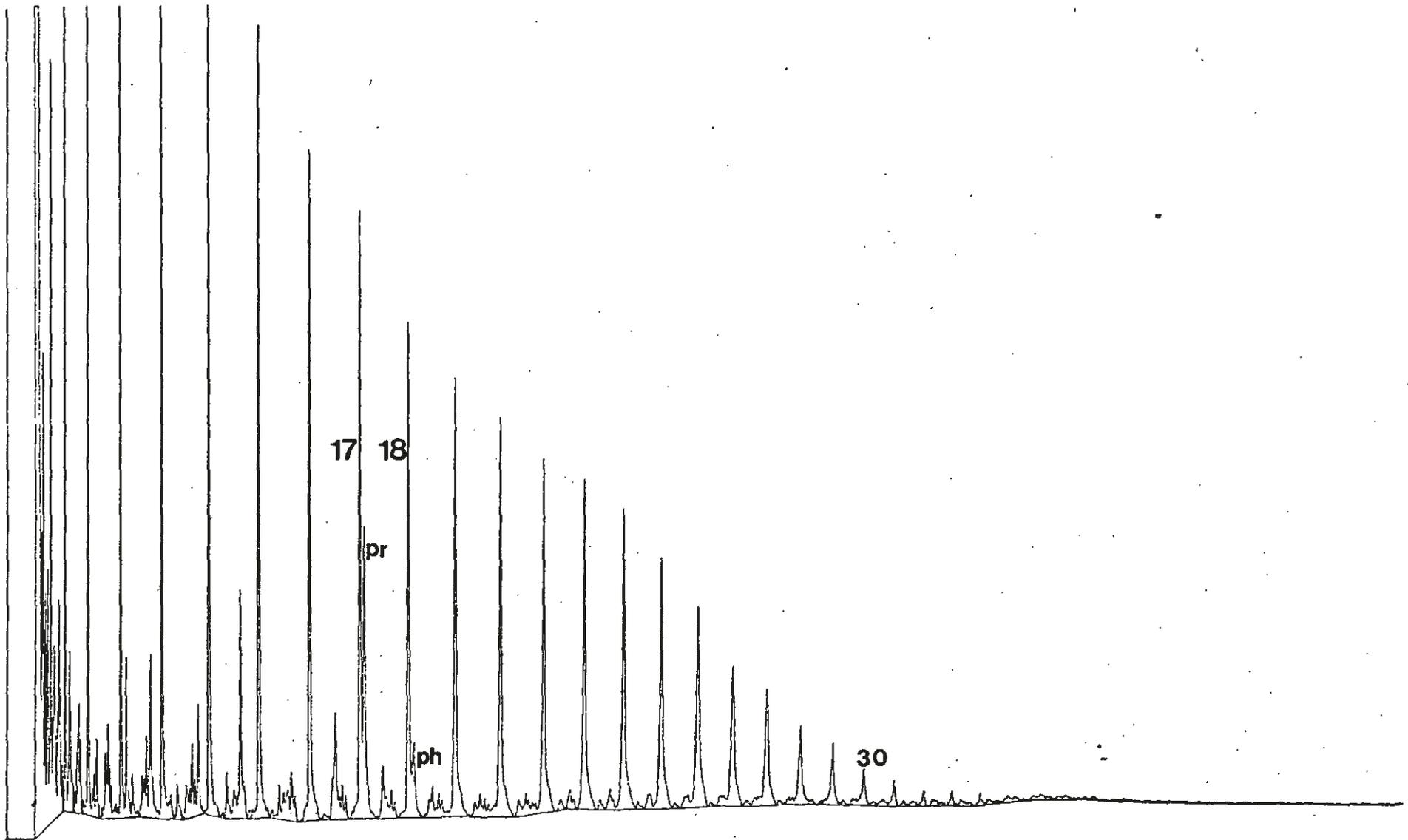
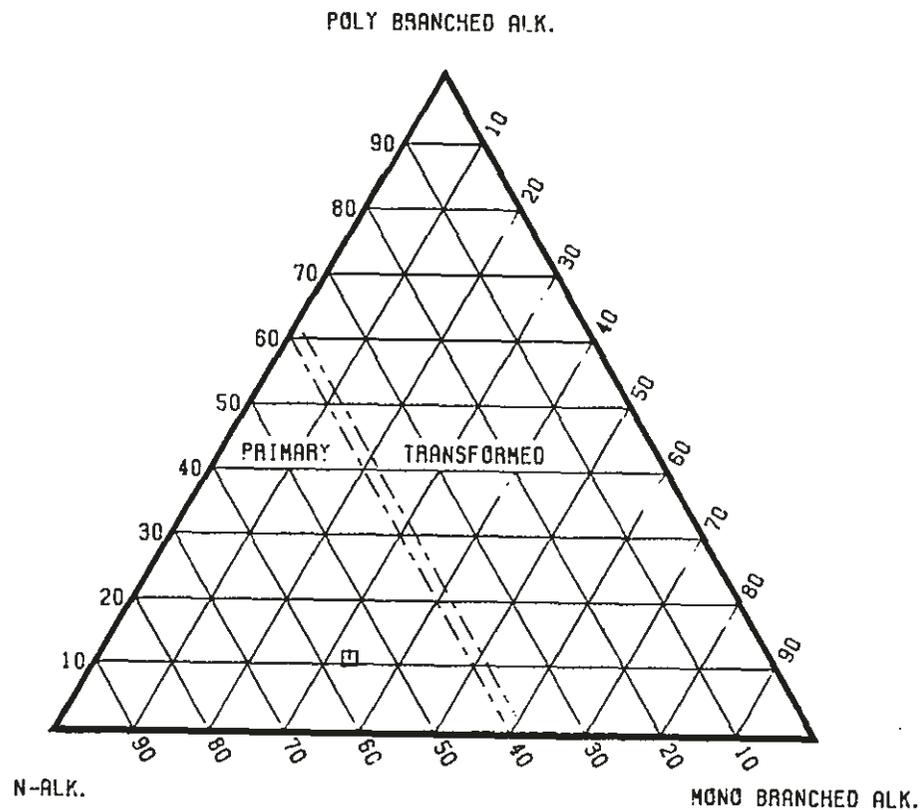


FIG. 4

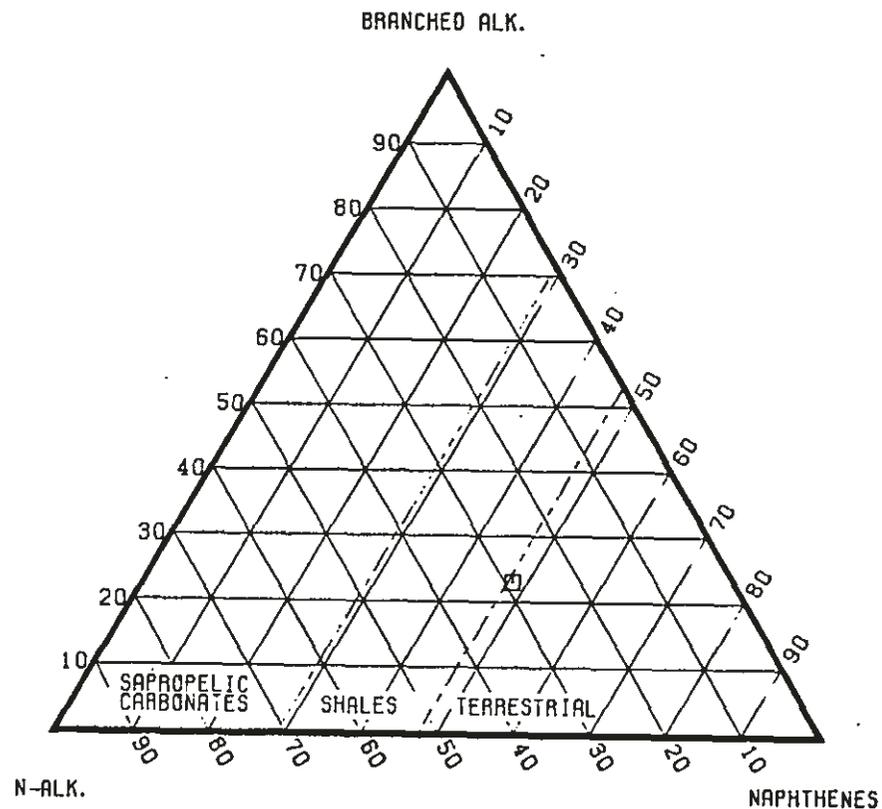
UK FLORENCE COLLIERY-2

Restricted

C7-ALKANE DISTRIBUTION



C7-ALKANE/NAPHTHENE DISTRIBUTION



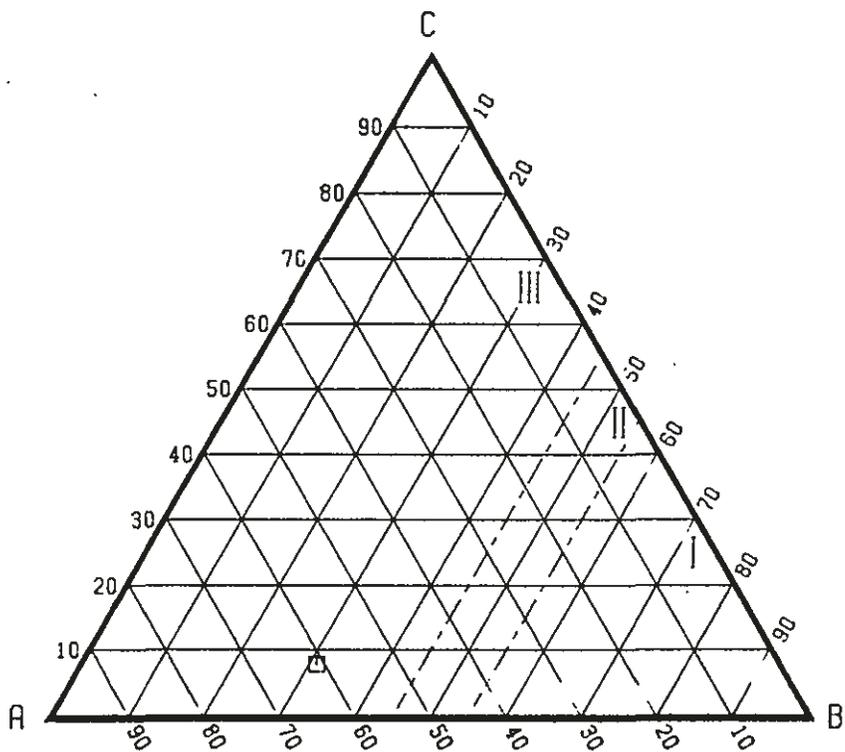
LEGEND

□ - FLOR. COLL.

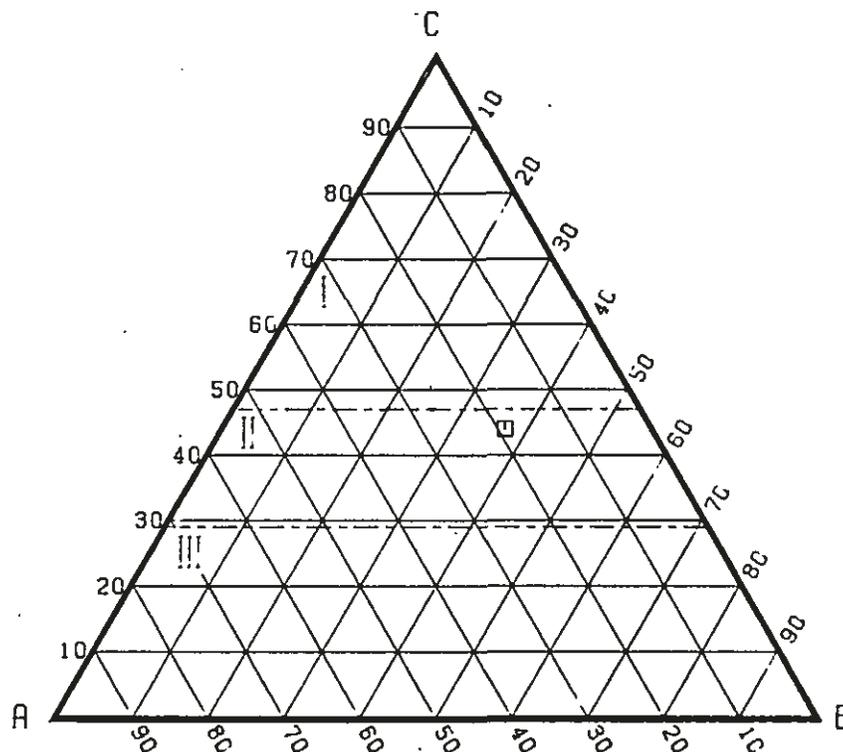
FIG. 5

Restricted

PARAMETER M1



PARAMETER M2



- 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

□ - FLOR. COLL

INITIAL DISTRIBUTION

3 Copies

SIPM-EP/12/13

RKER.80.031

Restricted