

Denne rapport
tilhører



L&U DOK. SENTER

L. NR. 20088380028

KODE Well 31/2-4 nr.13

Returneres etter bruk



This **CONFIDENTIAL** report is made available subject to the condition that the recipient will use the information contained therein for his own business only and will not divulge it to third parties without the written authority of the sponsoring party.

KONINKLIJKE / SHELL EXPLORATIE EN PRODUKTIE LABORATORIUM
RIJSWIJK, THE NETHERLANDS

October 1981

RKER.81.120
GEOCHEMICAL ANALYSIS OF TWO CORE SAMPLES
FROM A GAS BEARING RESERVOIR IN WELL
31/2-4, NORWAY
by
P.J. Grantham, J. Posthuma and G.W. Lijmbach

Investigation 9.12.484

With co-operation from
R. Stuifzand and R. Lieffering

This **CONFIDENTIAL** report is made available subject to the condition that the recipient will use the information contained therein for his own business only and will not divulge it to third parties without the written authority of the sponsoring party.

Copyright is vested in Shell Research B.V.

KONINKLIJKE/SHELL EXPLORATIE EN PRODUKTIE LABORATORIUM

RIJSWIJK, THE NETHERLANDS
(Shell Research B.V.)

<u>CONTENTS</u>	<u>Page</u>
Summary	III
1. Introduction	1
2. Synopsis of interpretation of geochemical parameters	1
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 A Bacterial degradation displayed in gas chromatograms of saturated hydrocarbons	6
Figure B C ₇ distribution for characterisation of related source material	7
Figure C Parameters M ₁ and M ₂ to type related source material	8
Figure D Triterpane fragmentograms of landplant- and SOM crudes	9
Figure E Sterane fragmentogram of type IIIa and IIIb crudes	10
3. Results and Discussion	11
4. Conclusions	12
Table	
1 Geochemical data of extracts	
Figures	
1 and 2 Gas chromatograms of saturated hydrocarbons	
3 M ₁ and M ₂ distributions	
4 and 6 Sterane and triterpane fragmentograms	

SUMMARY

Geochemical analysis of micaceous (1463.35-1463.42 m) and clean (1456.65-1456-72 m) sands (core material) of a gas bearing reservoir in well 31/2-4, Norway, have been carried out.

The clean sands contain only traces of migrated oil-like material. Because of the low concentrations, no further interpretation can be given.

The micaceous sands contain oil or tar-like hydrocarbons and indigenous coaly material. The oil-like extract is bacterially degraded. It was derived from a mature source rock which contained structureless organic matter.

The extractable organic matter is very similar to crude oil in well 31/2-2 and impregnations in well 31/2-1.

These results suggest that the gas filled reservoir 31/2-4 (micaceous sand) once contained the same oil as found in well 31/2-2. The type of oil is moreover of the same type as the impregnations in well 31/2-1.

GEOCHEMICAL ANALYSIS OF TWO CORE SAMPLES FROM A GAS
BEARING RESERVOIR IN WELL 31/2-4, NORWAY

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 fraction). 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.

Porphyrins

Porphyrins are nitrogen-containing ring components often found in petroleum as nickel or vanadyl complexes. It is generally accepted that the porphyrins are derived from chlorophyll during early diagenesis. A predominance of vanadyl over nickel porphyrins is associated with a deep marine environment of deposition of the source matter, whilst nickel porphyrin 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. A).

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/pytane 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. B). 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. B). 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

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. C. Note that parameter M1 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:

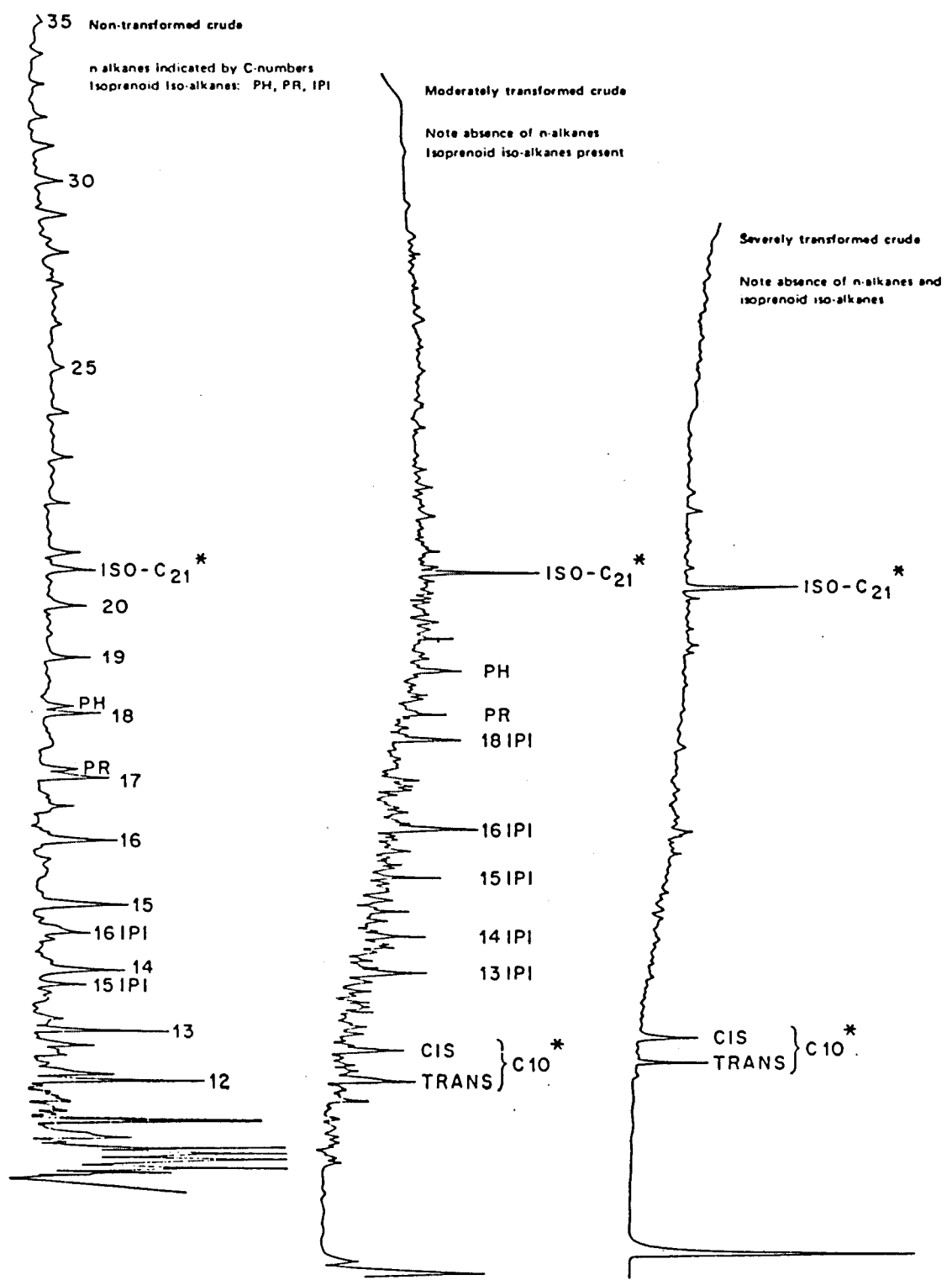
<u>DOM</u>	<u>MATURITY ZONES</u>
<60	Immature
60-75	Mature for oil generation
75-92	Mature for gas generation Post mature for oil generation
>92	Post mature for both oil and gas.

Sterane and triterpane parameters

Steranes and triterpanes are chemical fossils which can be used in geochemical typing. Combined gas chromatographic-mass spectrometric (GC-MS) analysis gives sterane and triterpane fragmentograms. These are gas chromatograms in which all the peaks are those of either steranes or triterpanes. Examples of the triterpane fragmentograms of a land-plant and a marine crude can be seen in Fig. D. Further differentiation between marine crudes can be obtained sterane fragmentograms (see Fig. E.).

From this analysis the organic matter can be classified into material derived from:

- I. resinous land-plant material.
- II. mixed land-plant/S.O.M. material or algae.
- IIIA reworked marine phytoplankton plus bacteria.
- IIIB reworked algal plus bacteria.

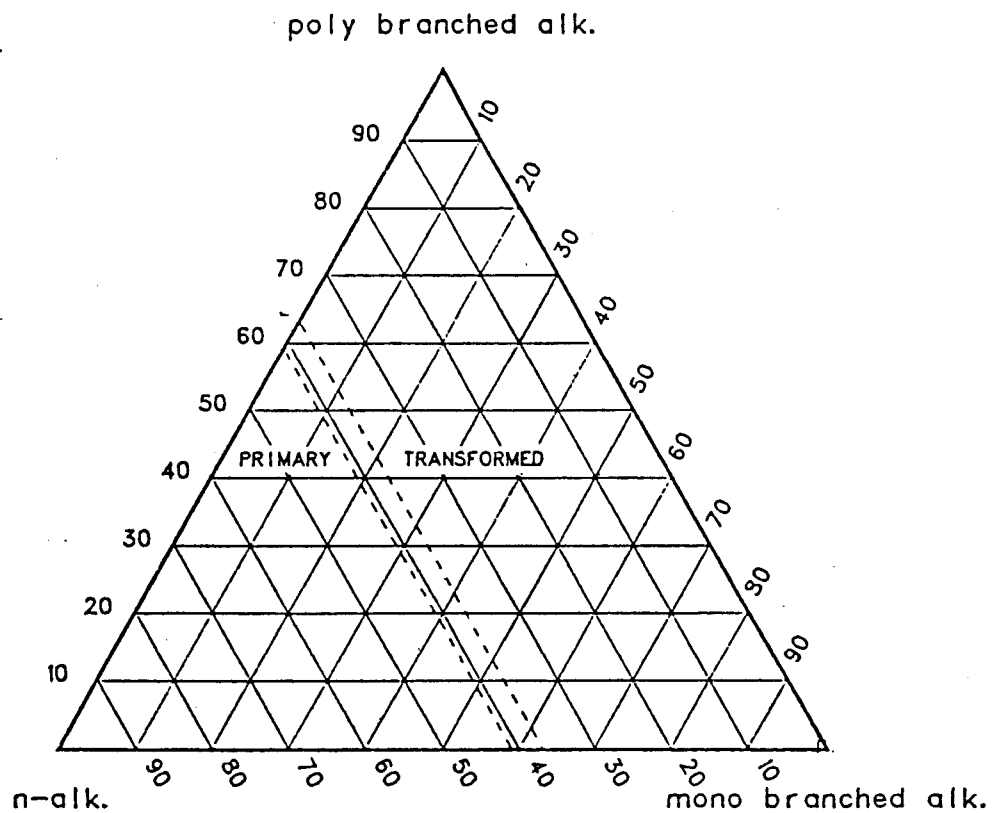


*STANDARD COMPOUNDS ADDED FOR IDENTIFICATION

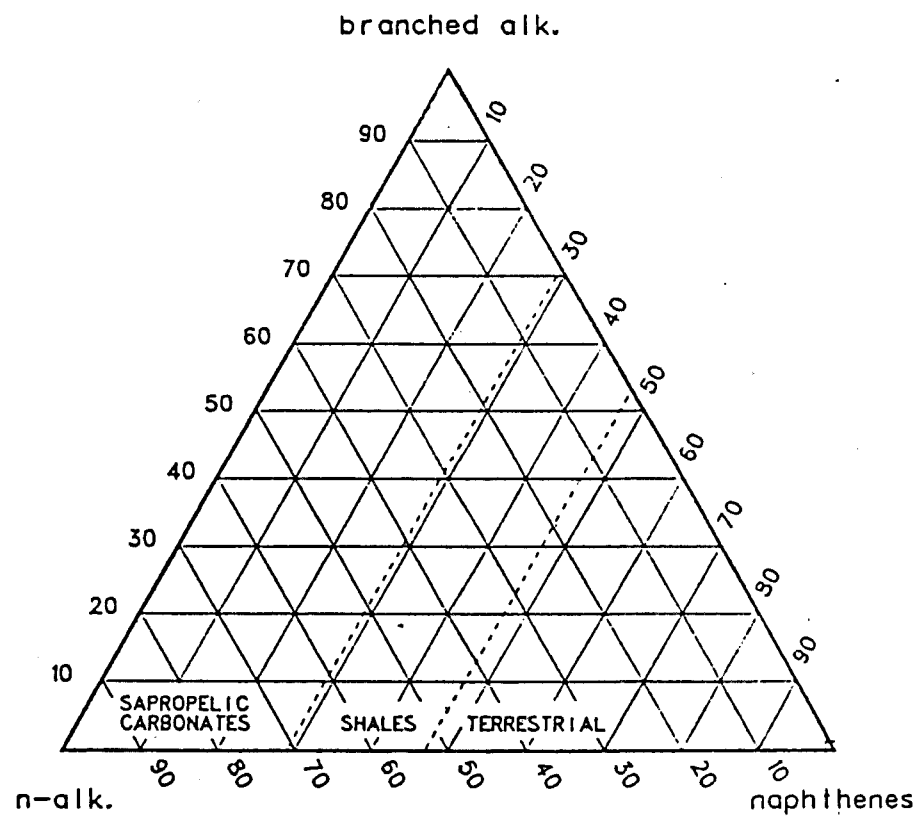
BACTERIAL DEGRADATION DISPLAYED IN GAS CHROMATOGRAMS OF SATURATED HYDROCARBONS.

FIG: A

C₇-ALKANE DISTRIBUTION

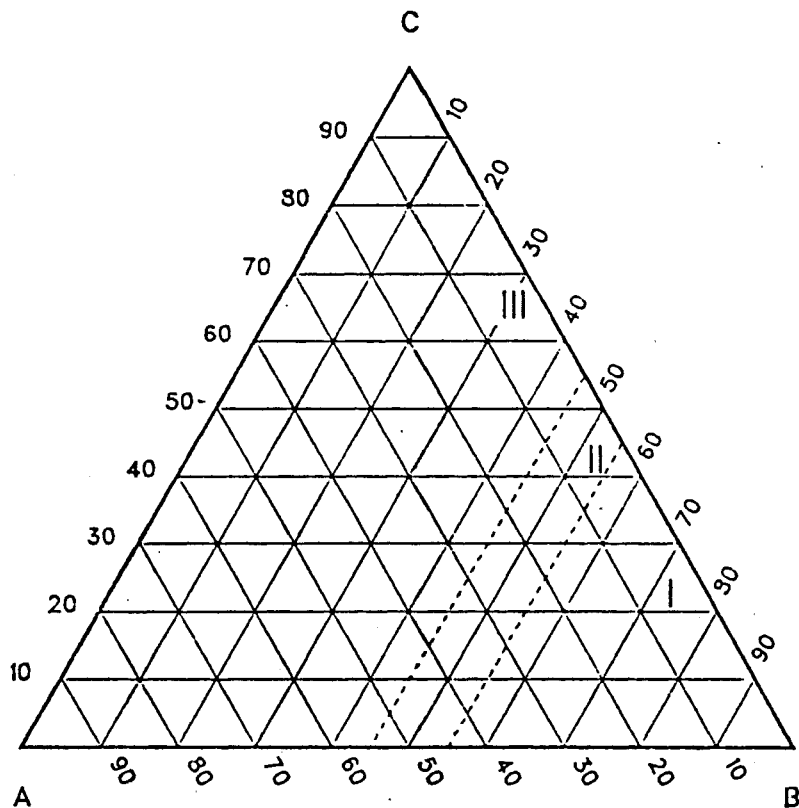


C₇-ALKANE/NAPHTHENE DISTRIBUTION

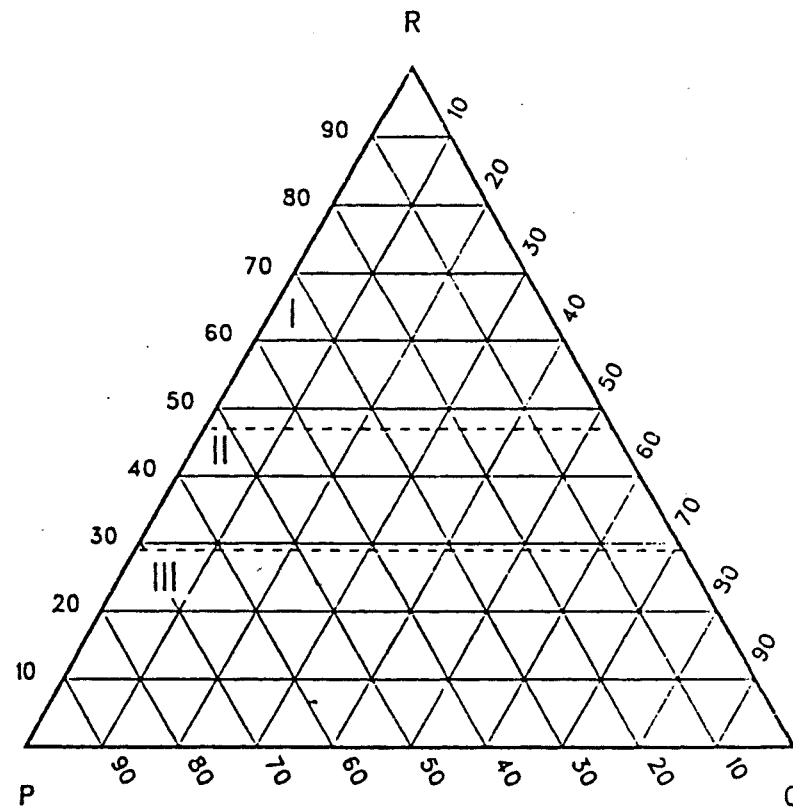


C₇ DISTRIBUTION FOR CHARACTERISATION OF RELATED SOURCE MATERIAL.

Parameter M1



Parameter M2

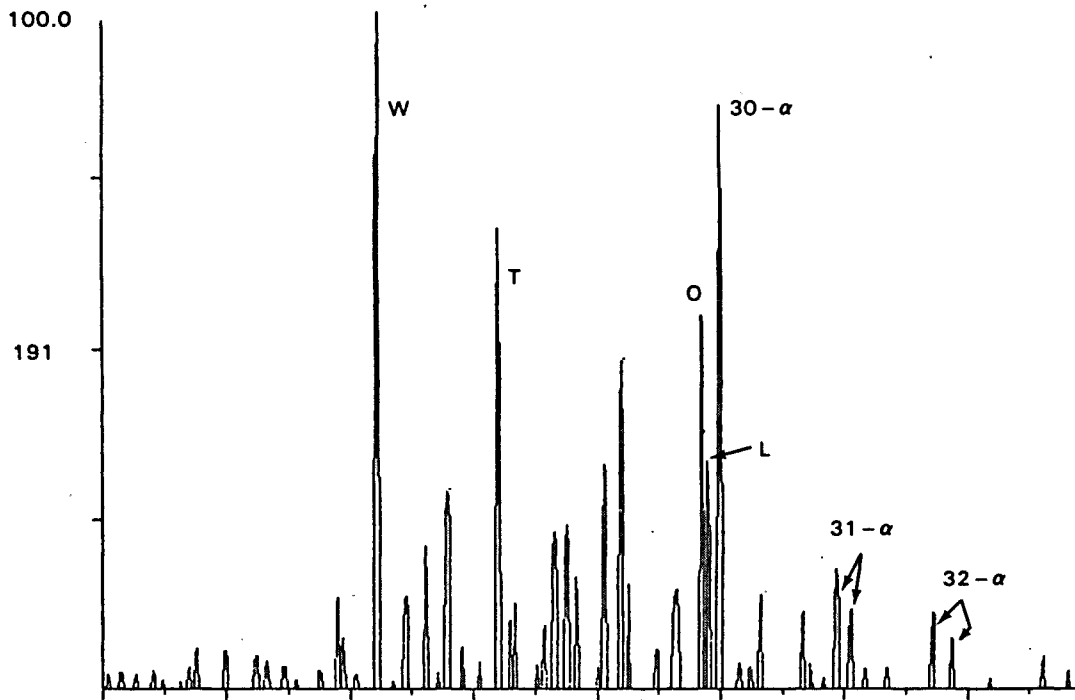


- I LANDPLANT-DERIVED CRUDES WITH SUBSTANTIAL RESIN CONTRIBUTION TO SOURCE MATTER
- II CRUDES OF MIXED ORIGIN
- III CRUDES DERIVED FROM SOM AND/OR ALGAL MATTER

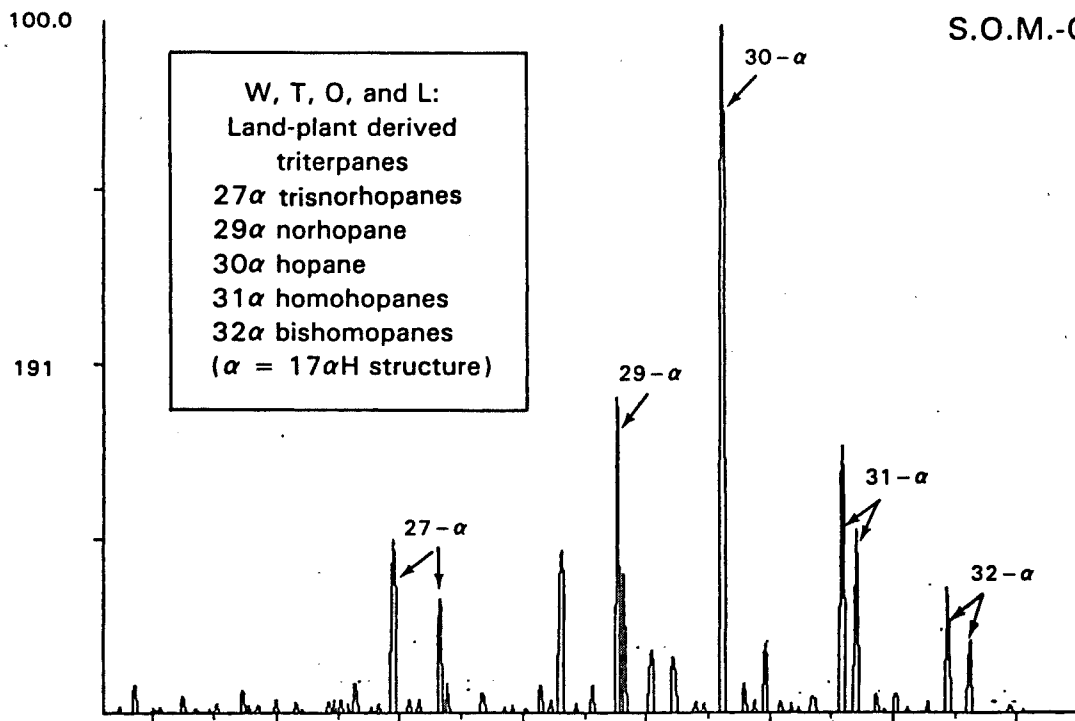
handwritten notes:
 here are
 2-2-10
 11-8-10
 8-10-10

PARAMETERS M1 AND M2 TO TYPE RELATED SOURCE MATERIAL.

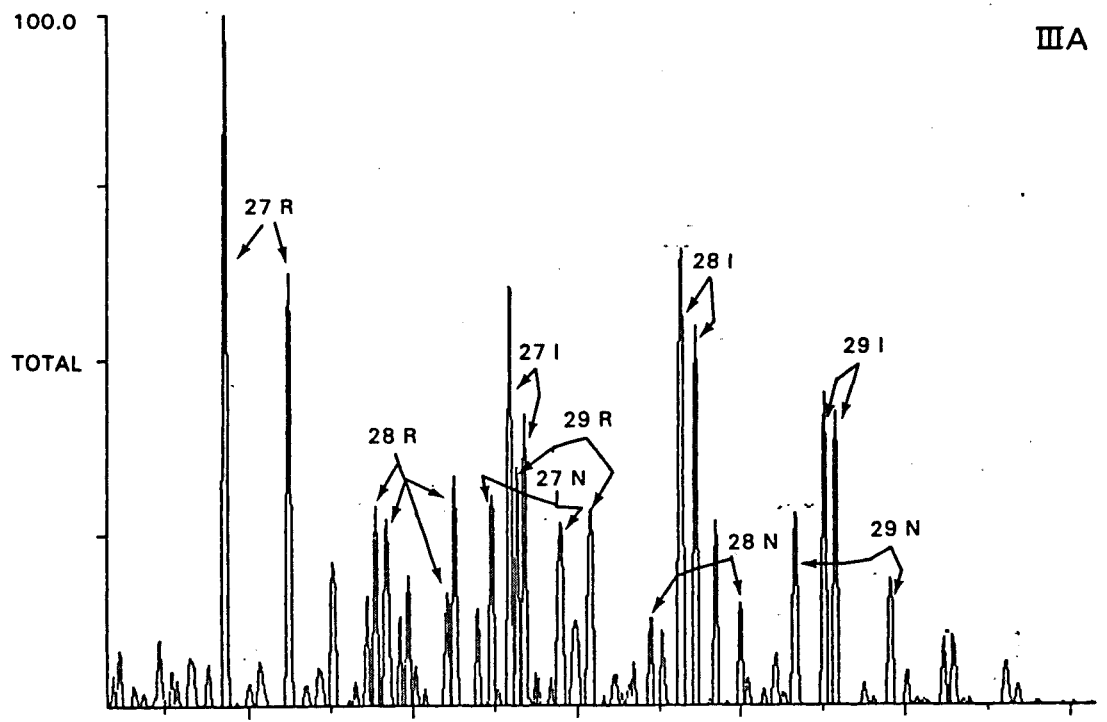
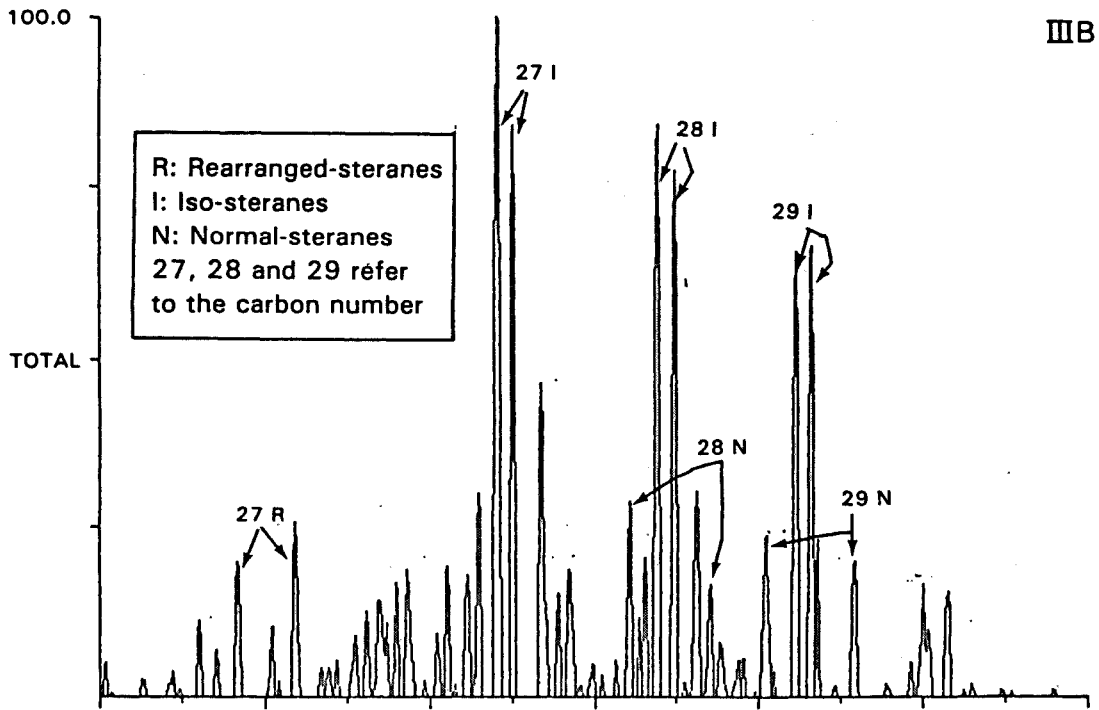
LAND-PLANT CRUDE



S.O.M.-CRUDE



TRITERPANE FRAGMENTOGRAMS OF CRUDES DERIVED FROM LAND-PLANT AND STRUCTURELESS ORGANIC MATERIAL RESPECTIVELY



STERANE FRAGMENTOGRAMS OF TYPE III A AND III B CRUDE OILS

FIG. E

3. RESULTS AND DISCUSSIONS

Geochemical analyses of micaceous (1463.35-1463.42 m) and clean (1456.65-1456.72 m) sands (core material) of a gas bearing reservoir in well 31/2-4, Norway, have been carried out. The purpose of the analysis was to determine whether residual oil or tar was present in the sand samples or not and, if present, to type the organic matter.

The results are shown in Tables 1 and 2 and Figs. 1-6.

The results of the analyses indicate the following:

- a The clean sands (1456.65-1456.72 m) contain only traces of migrated oil-like material (gas chromatogram, Fig. 2) which cannot have been derived from the very low amount of organic carbon present (0.1%). Because of its low concentration, no further interpretation of this material is given.
- b The micaceous sand (1463.35-1463.42 m) contains oil or tar-like material (extract 0.84%) and indigenous organic matter. The latter (2.8% C) has been shown by microscopic examination to contain detrital vitrinite 2, sporinite, cutinite plus some diffuse and intergranular S.O.M. which is typical of coaly material.

The extractable material of the micaceous sand appears to have been bacterially degraded (gas chromatogram, Fig. 1). It is derived from a mature source rock (sterane fragmentogram, Fig. 4) which contained reworked phytoplankton (structureless organic matter- M_1 and M_2 ring distributions, Fig. 3, C_{27} - C_{29} range of sterane fragmentogram, Fig. 4).

The extractable organic matter is very similar to the crude oil from well 31/2-2 at 1586.5-1588.5 m (see RKER.81.099 and Table 1) and the core impregnations from well 31/2-1 (see RKER.80.074 and Table 1). This is indicated by the similarity in gas chromatograms (see reports) and fragmentograms (compare Figs. 4 and 6). There are however differences in M_2 distributions (Fig. 3) and carbon isotope values (Table 1) which are most probably caused by contributions from the coaly material present in the micaceous sand.

These results suggest that the now gas filled reservoir 31/2-4 (micaceous sand) once contained the same oil as found in 31/2-2 and that the (residual) oil in 31/2-4 is also of the same type of organic matter as found in the impregnations in well 31/2-1.

2. CONCLUSIONS

The clean sands at 1456.65-1456.72 m contain only traces of migrated oil-like material. Because of the low concentrations, no further interpretation can be given.

The micaceous sands at 1463.35-1463.41 m contain oil or tar-like hydrocarbons and indigenous coaly material. The oil-like extract is bacterially degraded. It was derived from a mature source rock which contained structureless organic matter.

The extractable organic matter is very similar to crude oil in well 31/2-2 and impregnations in well 31/2-1.

These results suggest that the gas filled reservoir 31/2-4 (micaceous sand) once contained the same oil as found in well 31/2-2. The type of oil is moreover of the same type as the impregnations in well 31/2-1.

Table 1 Geochemical data of extracts

sample	31/2-4 1463.35-1463.42 m 'micaceous sands'	31/2-4 1456.65-1456.72 m 'clean sand'	31/2-2 1586.5-1588.5 oil	31/2-1 core 11 1573.2 m impregnation
% ethylacetate extract				1.8
% chloroform/ ethanol extract	0.84	0.06		
% organic carbon after extraction	2.8	0.1		1.1
% sulphur	3.3	n.e.	0.5	0.7
ppm V ^o porphyrins	b.l.	n.e.	b.l.	b.l.
ppm Ni porphyrins	b.l.		b.l.	b.l.
pristane/phytane	1.8	1.4	1.8	2.1
pristane/nC ₁₇	2.7	1.7	1.9	2.5
phytane/nC ₁₈	1.5	1.7	1.2	1.2
Parameter M ₁				
A	41	37	55	35
B	39	42	31	47
C	20	21	14	18
Parameter M ₂				
P	27	30	30	26
Q	31	45	44	49
R	42	25	26	25
DOM of oil	62	65	63	64
extract/carbon	0.3	0.6		
% saturates	32	n.e.	45	49
% aromatics	32		34	37
% heterocompounds	36		21	14
δ 13C ^o /oo	-27.1	-	-28.3	-28.1

b.l. = below limit of detectability

n.e. = not enough sample available for the determination

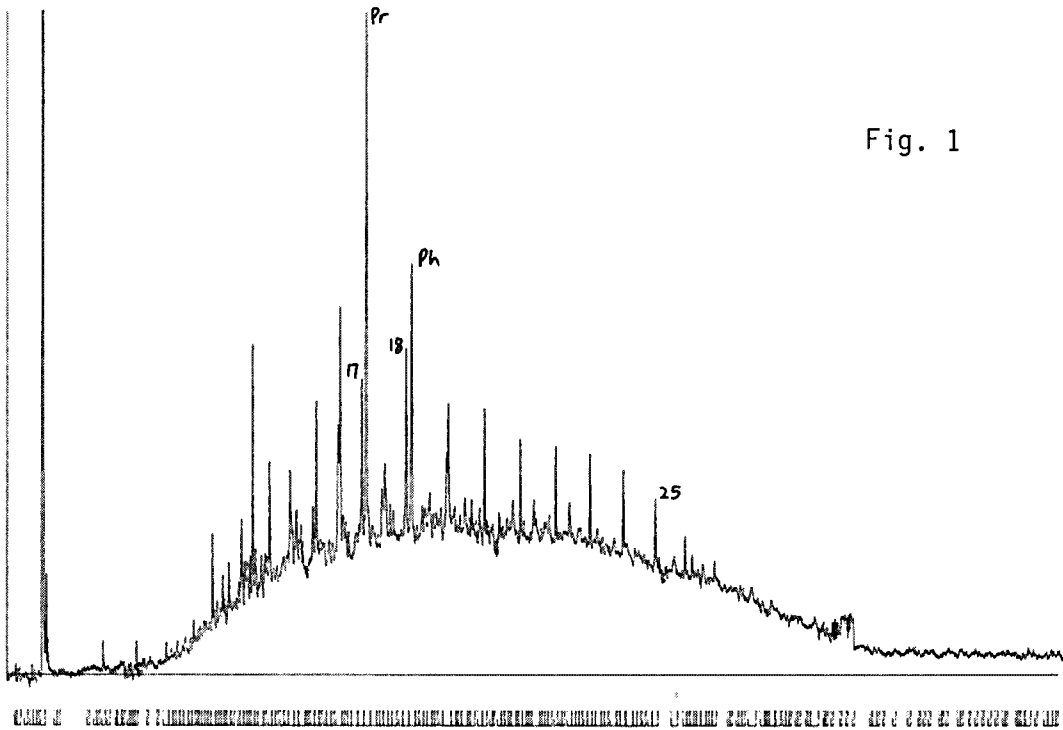


Fig. 1

GAS CHROMATOGRAM OF SATURATED HYDROCARBONS
 NORWAY 31/2-4 1463.35-1463.42 M

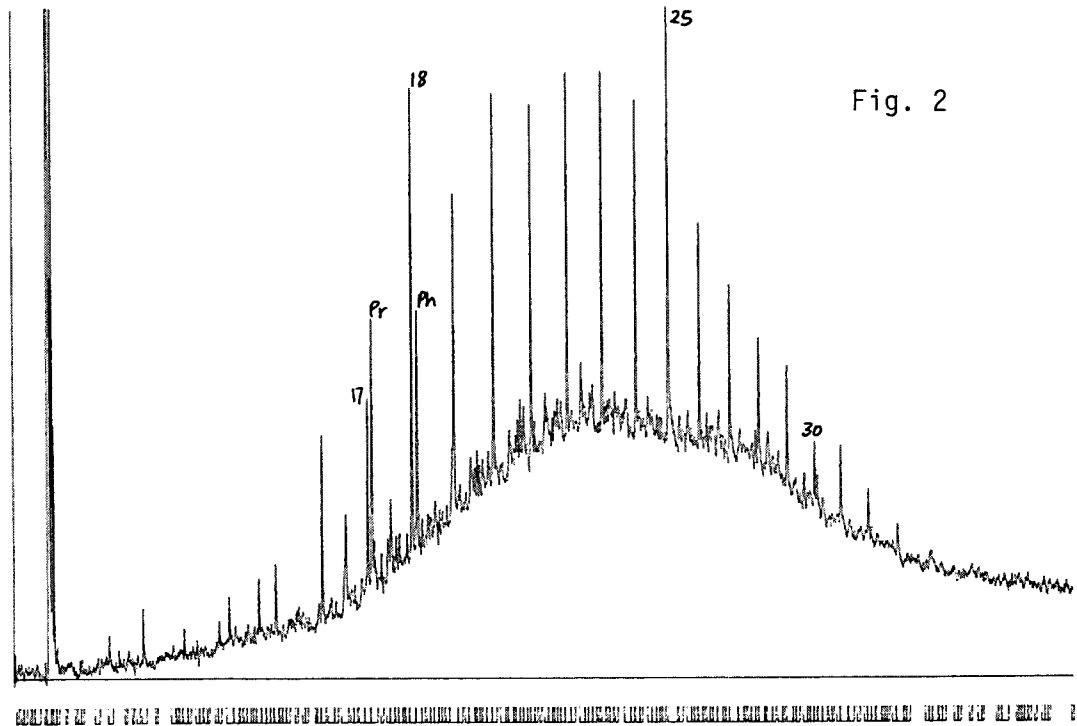
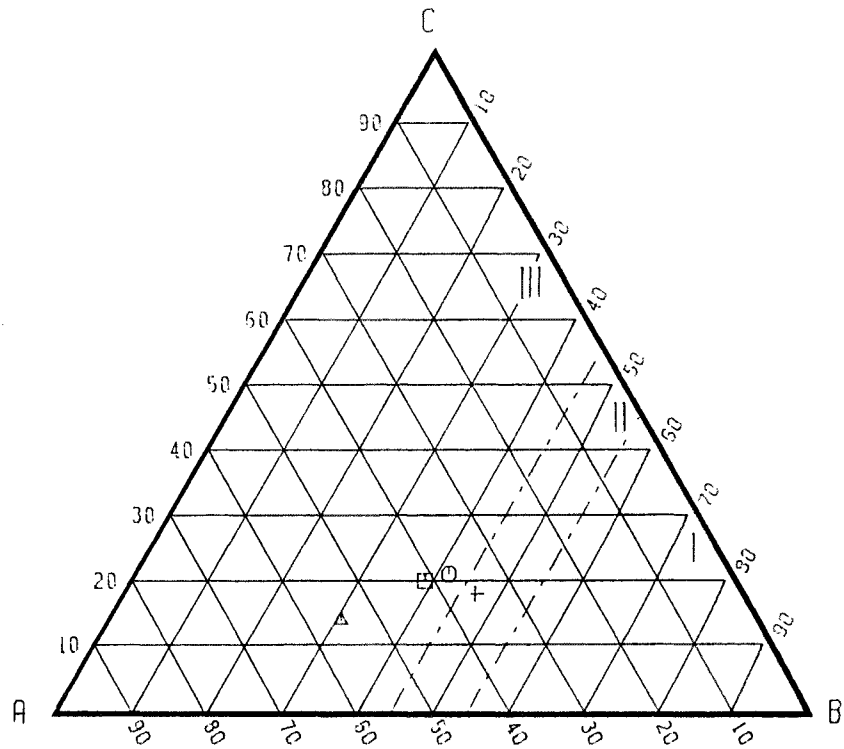


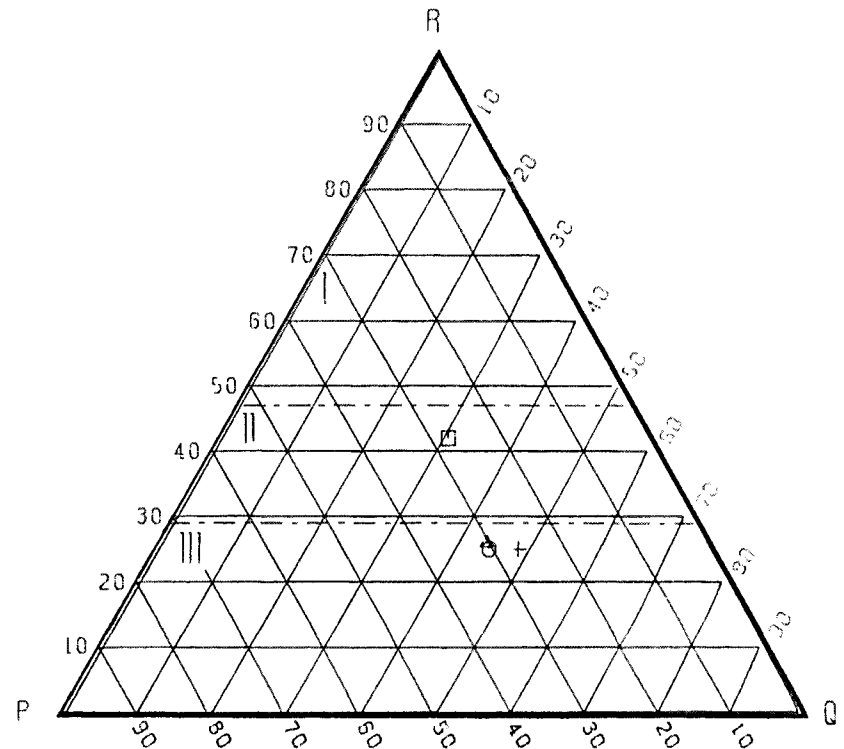
Fig. 2

GAS CHROMATOGRAM OF SATURATED HYDROCARBONS
 NORWAY 31/2-41456.65-1456.72 M

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

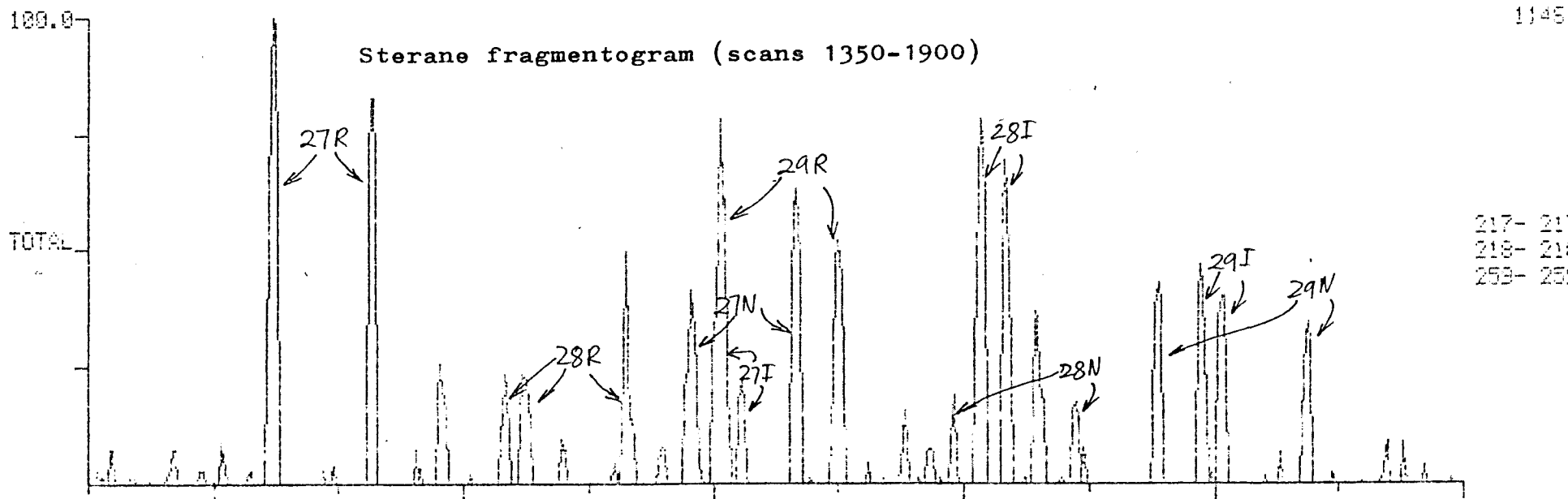
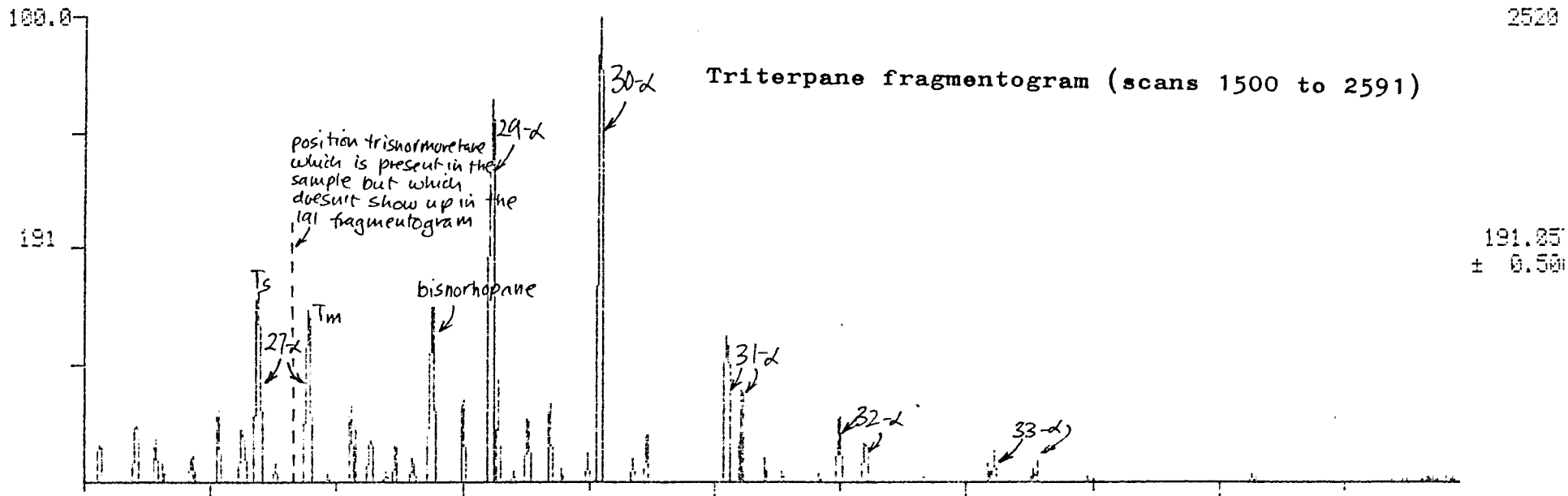
LEGEND	
□	3i/2-4 MICACEOUS SAND
○	3i/2-4 CLEAN SAND
△	3i/2-2 OIL
+	3i/2-1 CORE II IMPREGNATION

FIG. 3

GC-MS analysis 31/2-4

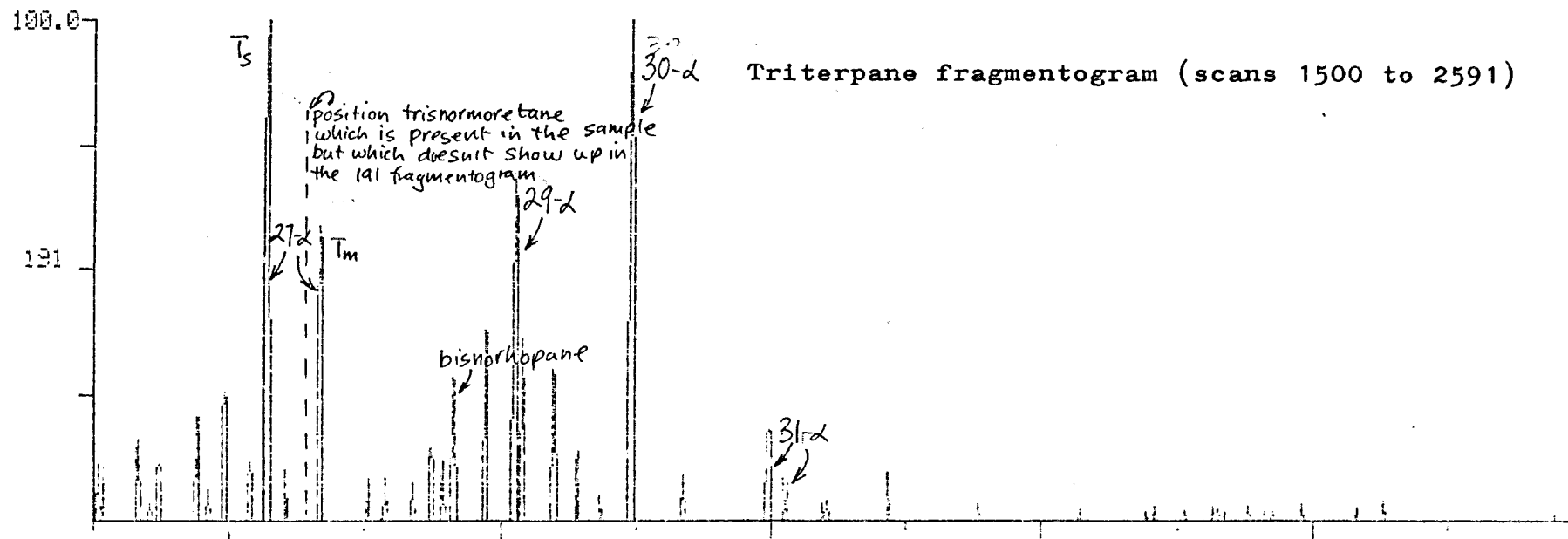
1456.65-1456.72 m

FIG. 4



GC-MS analysis 31/2-4 1463.35-1463.42 m

745



1225

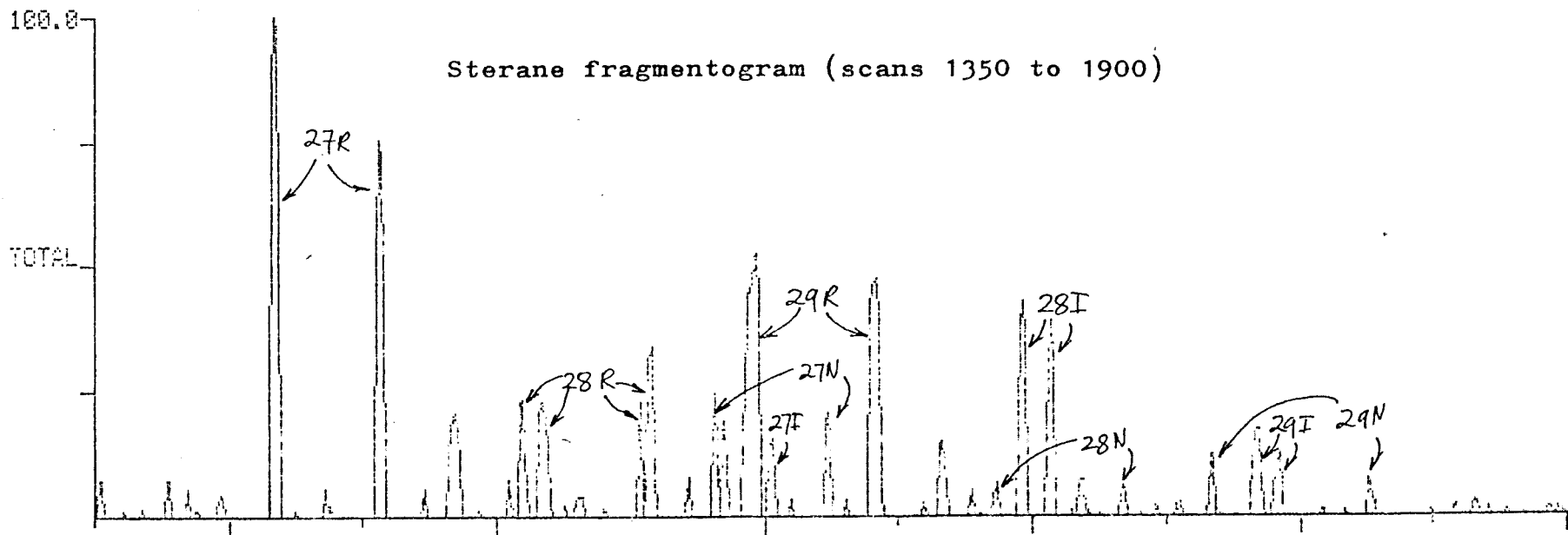


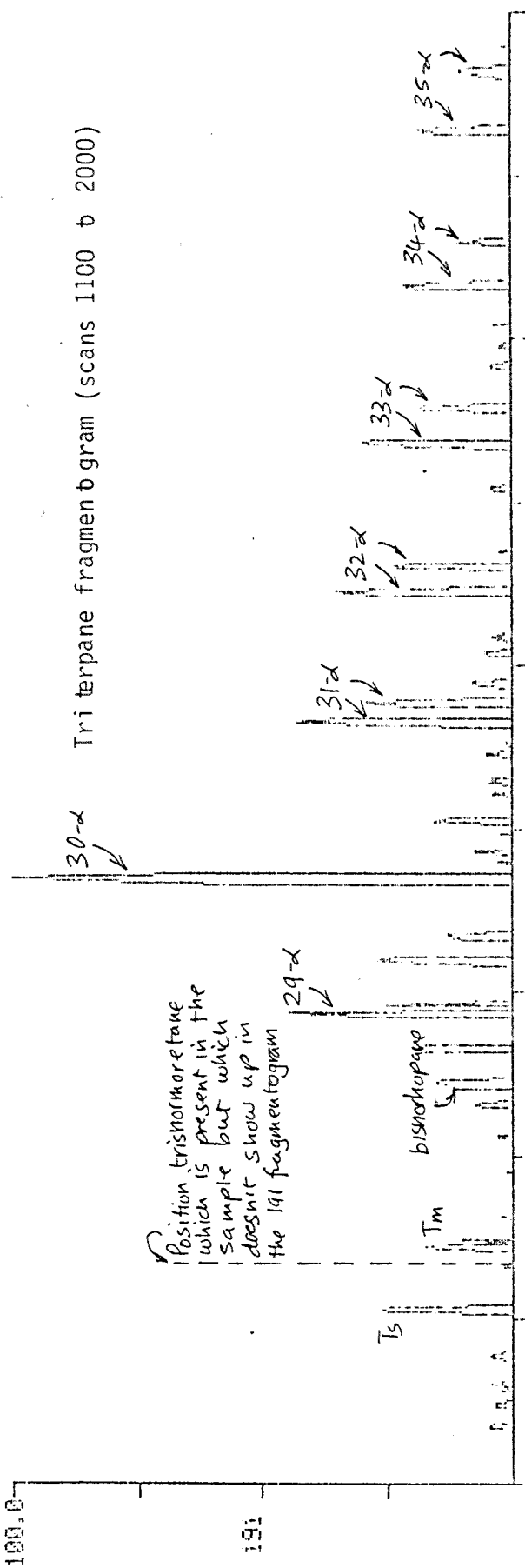
FIG. 5

100.0 12120

Tri terpane fragmen b gram (scans 1100 to 2000)

Position trisnormorethane which is present in the sample but which doesn't show up in the 141 fragmentogram

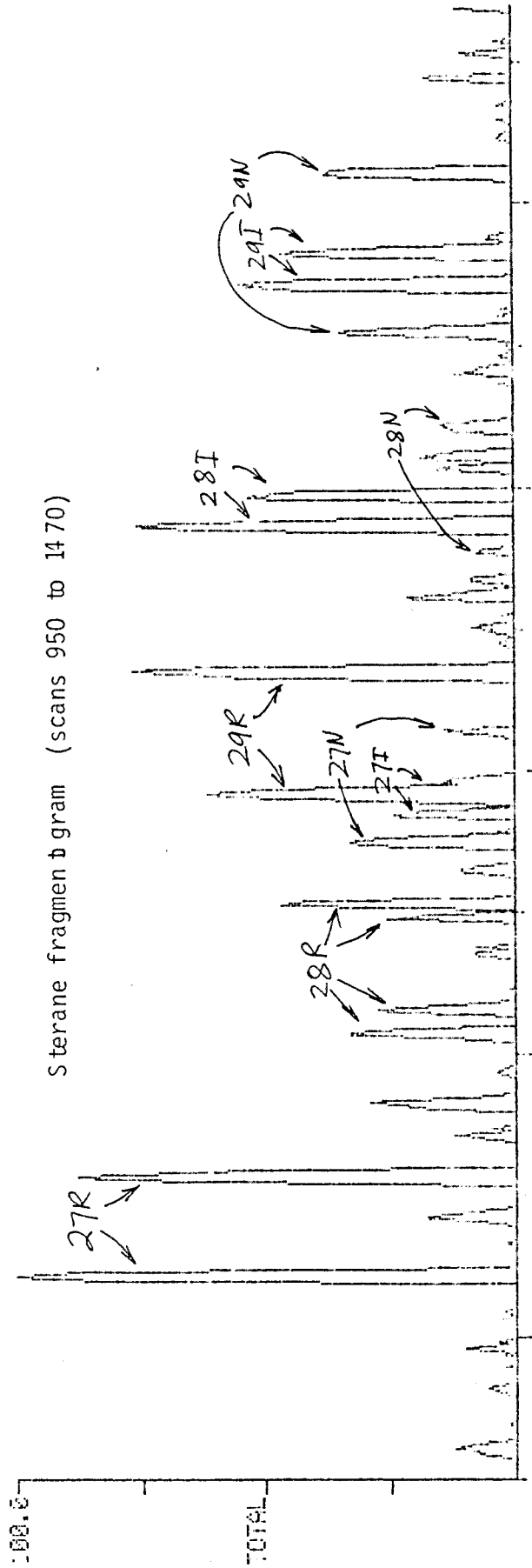
191.25 ± 0.50



100.0 6040

Sterane fragmen b gram (scans 950 to 1470)

217-21
218-21
253-25



GC-MS analysis 31/2-2 crude oil

Fig. 6

INITIAL DISTRIBUTION

3 Copies

3 Copies

Shell Forus ep epxt/1 (epxepp epxt)
SIPM-EP/11/13