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GEOCHEMICAL ANALYSIS OF A MIDDLE-JURASSIC CUTTINGS
SAMPLE FROM WELL 206/5-1, NORTH SEA

by

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Investigation 9.12.384

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1. Gas chromatograms of saturated hydrocarbons
2. M₁ and M₂ distributions
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SUMMARY

Geochemical analysis of the cuttings sample from well 206/5-1 (11590-11690'), North Sea, has been carried out.

The organic matter of the sample may consist partly of some migrated material although indigenous organic matter is certainly present.

The geochemical analyses are interpreted in the assumption that only indigenous organic matter is present as follows:

The extract of the sample appears to be derived mainly from structureless organic matter with contributions of waxy hydrocarbons. These hydrocarbons may be derived from either algae or land-plants and no firm conclusions as to their origin can be made.

The environment of deposition of the organic matter of the sample appears to have been reducing.

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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.

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. 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/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. 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:

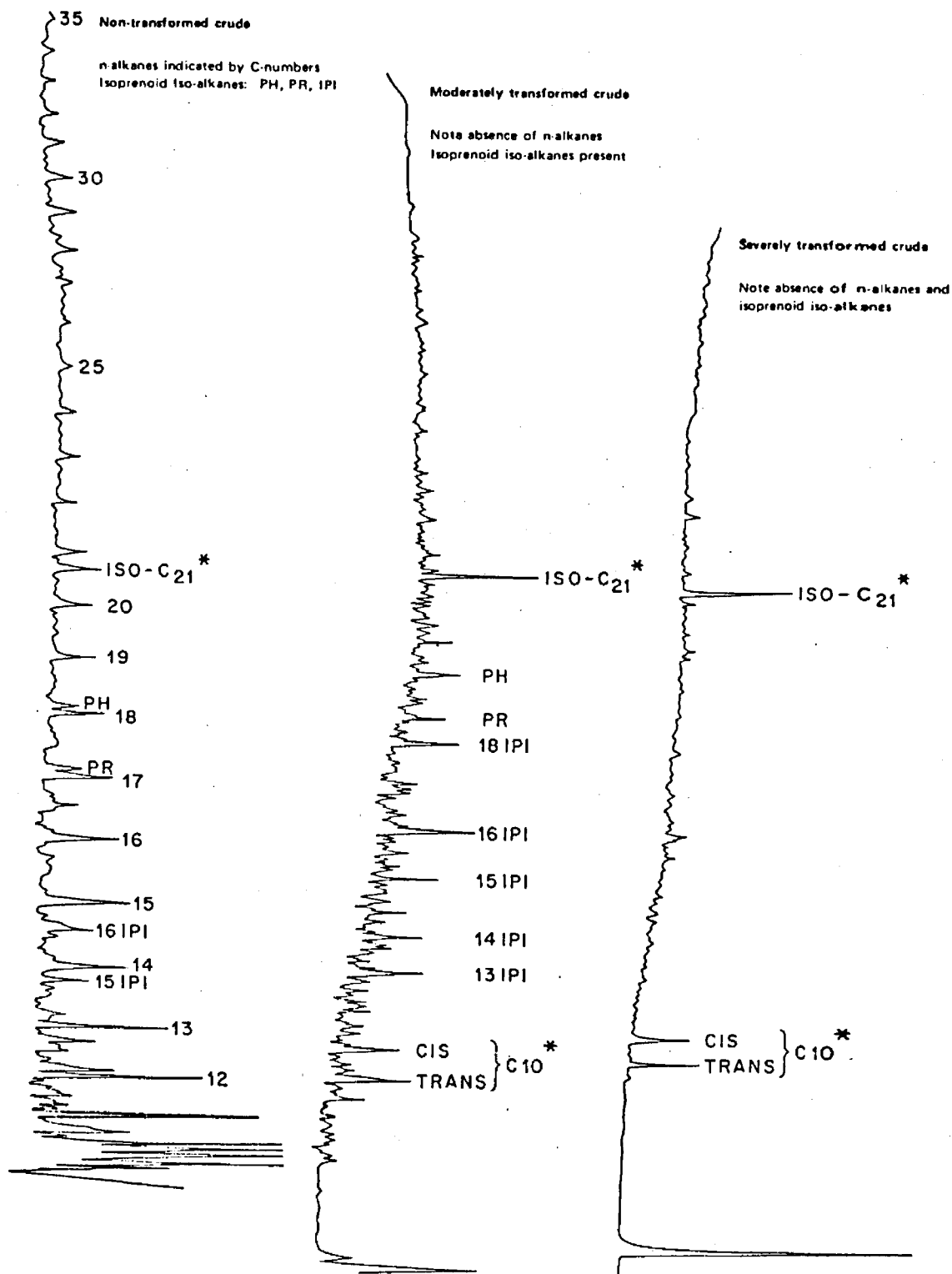
<u>DOM</u>	<u>MATURITY ZONES</u>
>60	Immature
60-75	Mature for oil generation
75-92	Mature for gas generation Post mature for oil generation
>92	Post mature for both oil and gas.

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 from 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 algae plus bacteria.

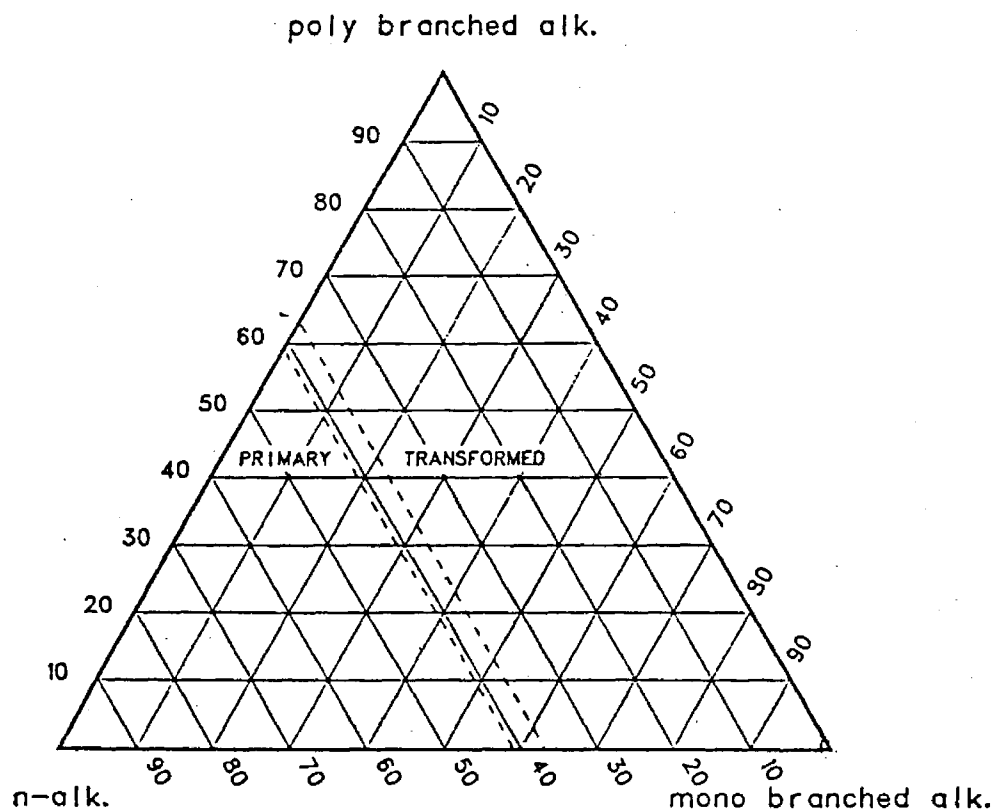


*STANDARD COMPOUNDS ADDED FOR IDENTIFICATION

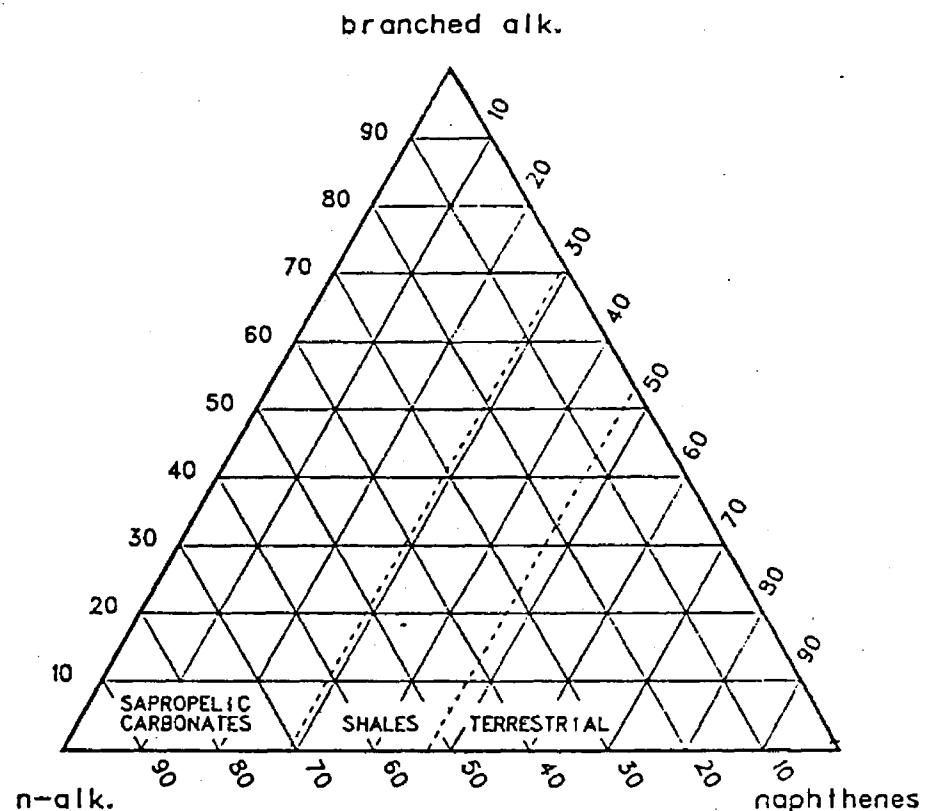
BACTERIAL DEGRADATION DISPLAYED IN GAS CHROMATOGRAMS OF SATURATED HYDROCARBONS.

FIG: A

C₇-ALKANE DISTRIBUTION

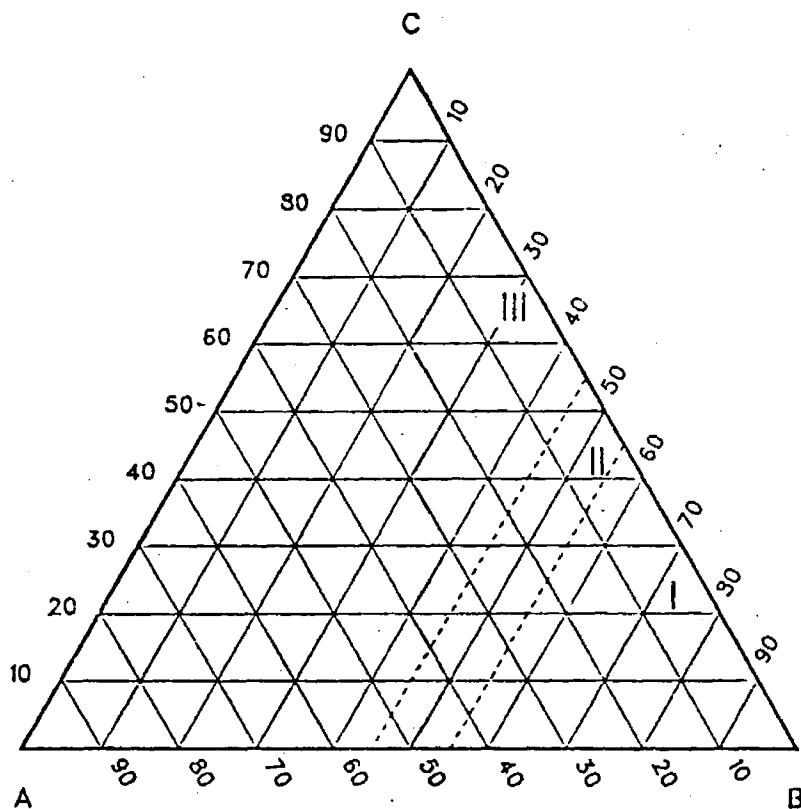


C₇-ALKANE/NAPHTHENE DISTRIBUTION

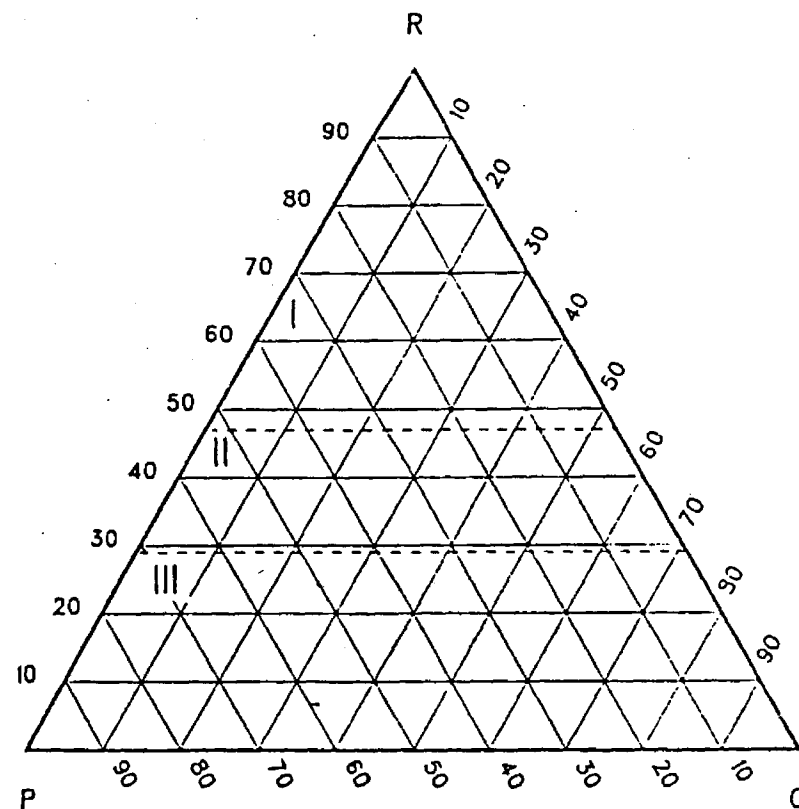


C₇ DISTRIBUTION FOR CHARACTERISATION OF RELATED SOURCE MATERIAL.

Parameter M1



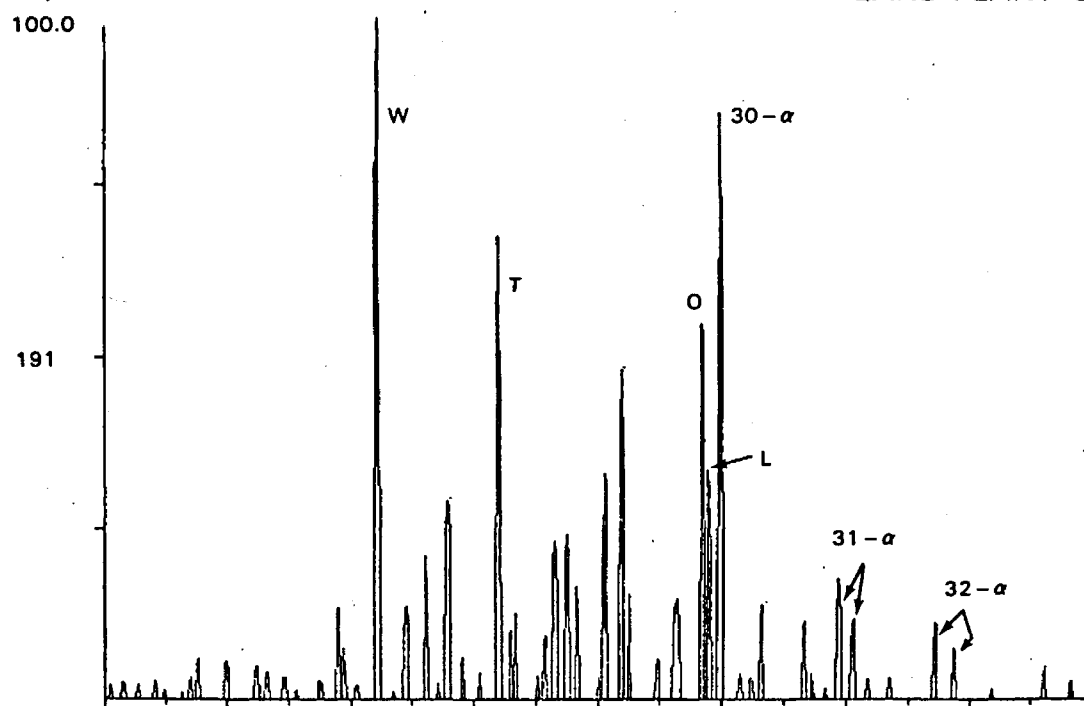
Parameter M2



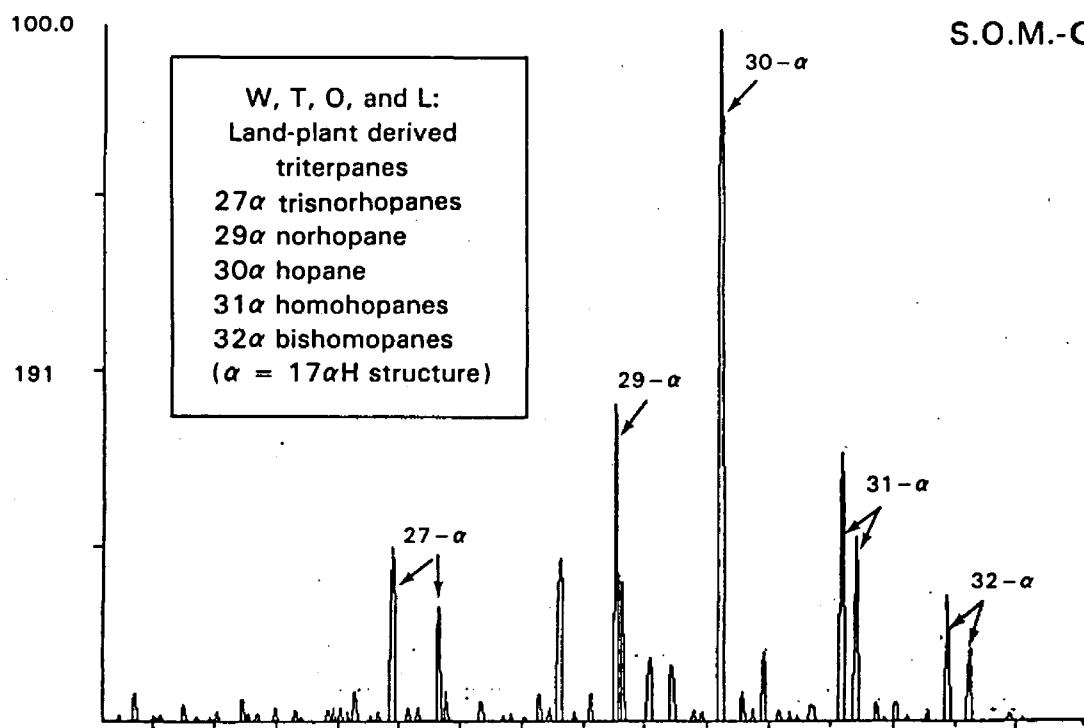
- I LANDPLANT-DERIVED CRUDES WITH SUBSTANTIAL RESIN CONTRIBUTION TO SOURCE MATTER
- II CRUDES OF MIXED ORIGIN
- III CRUDES DERIVED FROM SOM AND/OR ALGAL MATTER

PARAMETERS M1 AND M2 TO TYPE RELATED SOURCE MATERIAL.

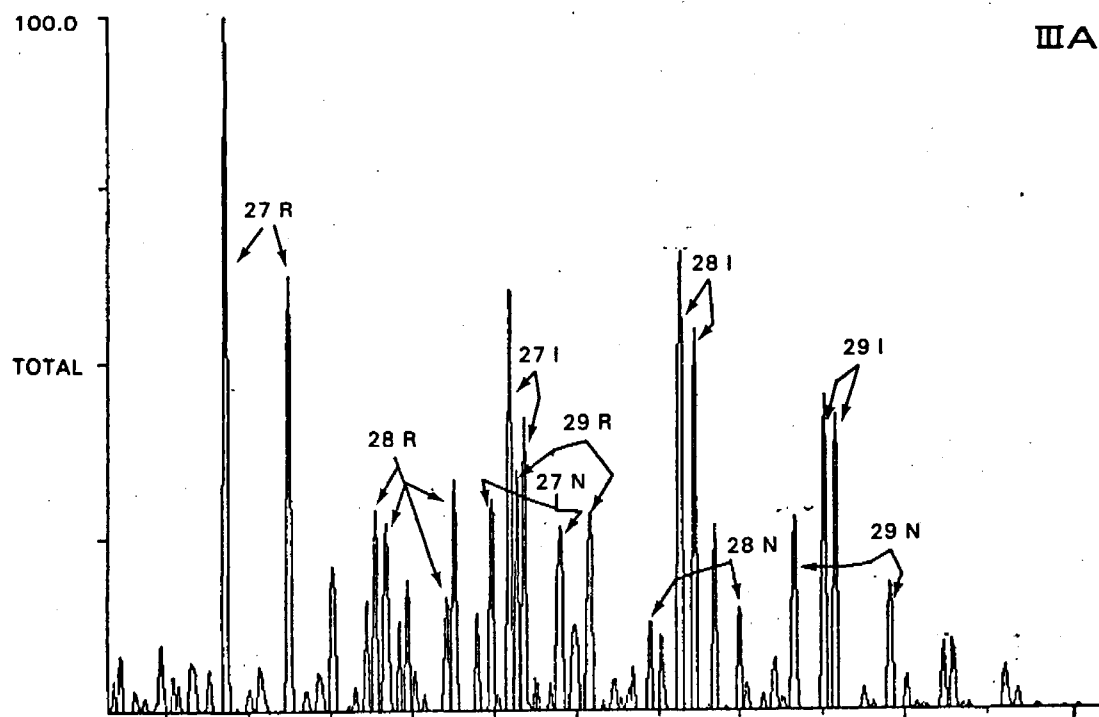
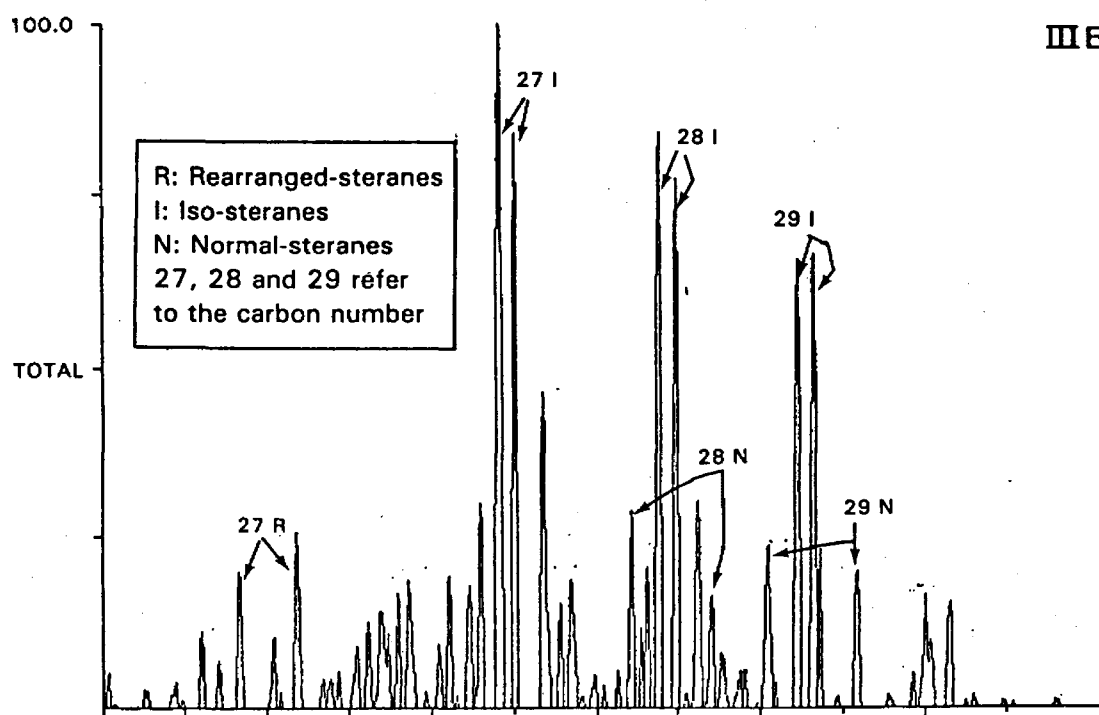
LAND-PLANT CRUDE



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

2. RESULTS AND DISCUSSION

Geochemical analysis of the Middle-Jurassic cuttings sample from well 206/5-1 (11590-11690'), North Sea, has been carried out. The results are shown in Table 1 and Figures 1-3.

The extract/carbon ratio (0.26) and the amount of saturates in the extract (60%), which are both rather high for a source rock, may indicate that migrated hydrocarbons are present in the cuttings. However, indigenous organic matter is certainly present as revealed by the organic carbon content of 2.5% after extraction.

The following geochemical interpretation is given assuming that only indigenous material is present in the sample.

The gas chromatogram of the saturated hydrocarbons (Fig. 1), the DOM of oil of 65 and the sterane fragmentogram (Fig. 3) indicate that the extracted organic matter is mature.

The M_1 and M_2 distributions (Fig. 2) indicate the presence of mainly structureless organic matter. This has been confirmed by maceral analysis which reveals the presence of (common) diffuse and intergranular SOM.

The gas chromatogram (Fig. 1) shows the presence of some waxy hydrocarbons (odd-numbered predominant n -alkanes between C_{23} and C_{29} are present). This waxy material may be derived from algae; the presence of laminated (algal) S.O.M. as shown by maceral analysis seems to support this hypothesis.

However, the waxy hydrocarbons could also be derived from land-plants: maceral analysis has shown that vitrinite-II, sporinite and fusinite, although not common, are still present in the sample.

No firm conclusions as to the origin of the waxy hydrocarbons can therefore be made.

The pristane/ n - C_{17} ratio (0.4) and the sulphur content (2.6%) indicate that the environment of deposition of the source rock was reducing.

2. CONCLUSIONS

The organic matter of the cuttings sample from well 206/5-1 (11590-11690') may consist partly of some migrated material although indigenous organic matter is certainly present.

The geochemical analyses are interpreted in the assumption that only indigenous organic matter is present as follows:

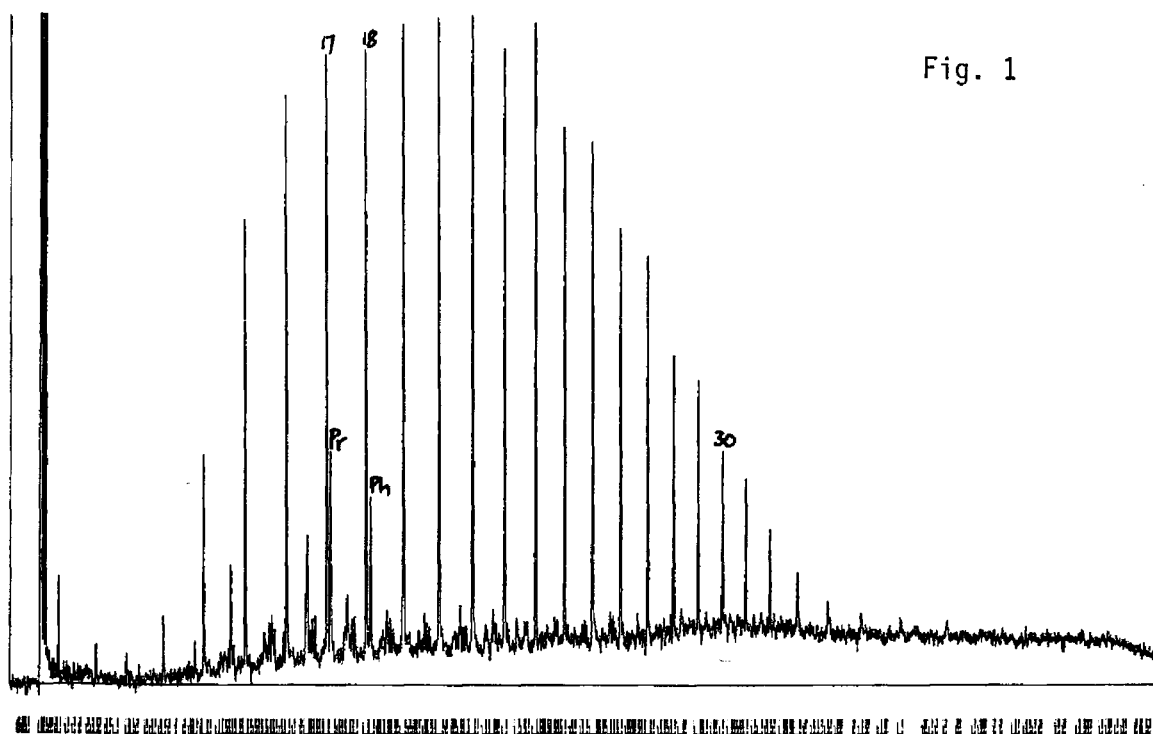
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The environment of deposition of the organic matter of the sample appears to have been reducing.

Table 1 - Geochemical data of extract

	Well 206/5-1 11590-11690' cuttings
% ethylacetate extract	0.65
% organic carbon after extraction	2.5
% sulphur	2.6
ppm V ^O porphyrins	b.l.
ppm Ni porphyrins	b.l.
pristane/phytane	1.4
pristane/nC17	0.4
phytane/nC18	0.4
Parameter M ₁	
A	46
B	35
C	19
Parameter M ₂	
P	18
Q	45
R	37
DOM of oil	65
% saturates	60
% aromatics	15
% heterocompounds	25
extract/carbon	0.26

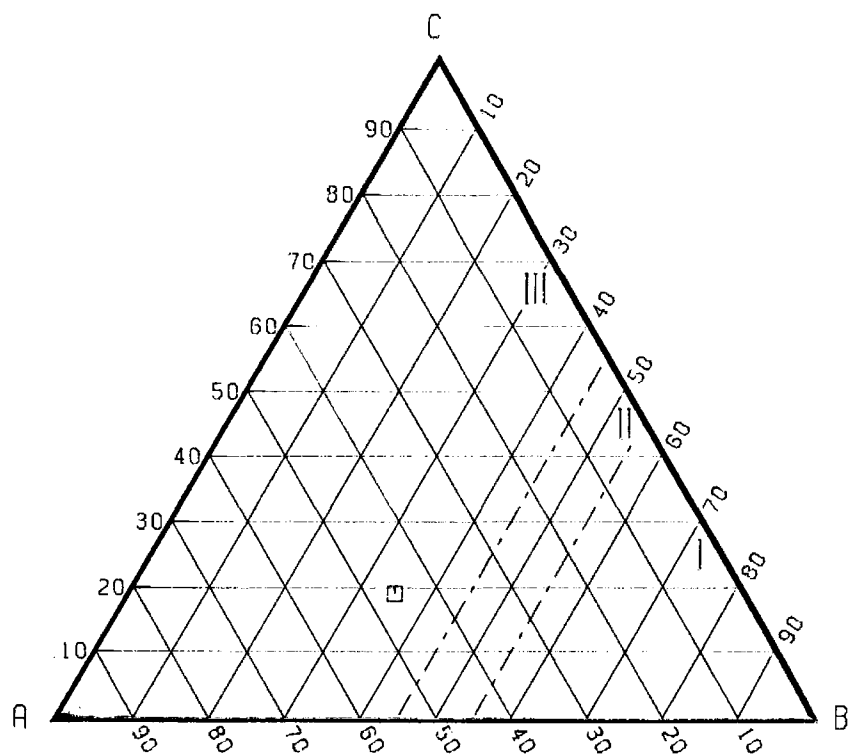
b.l. = below limit of detectability



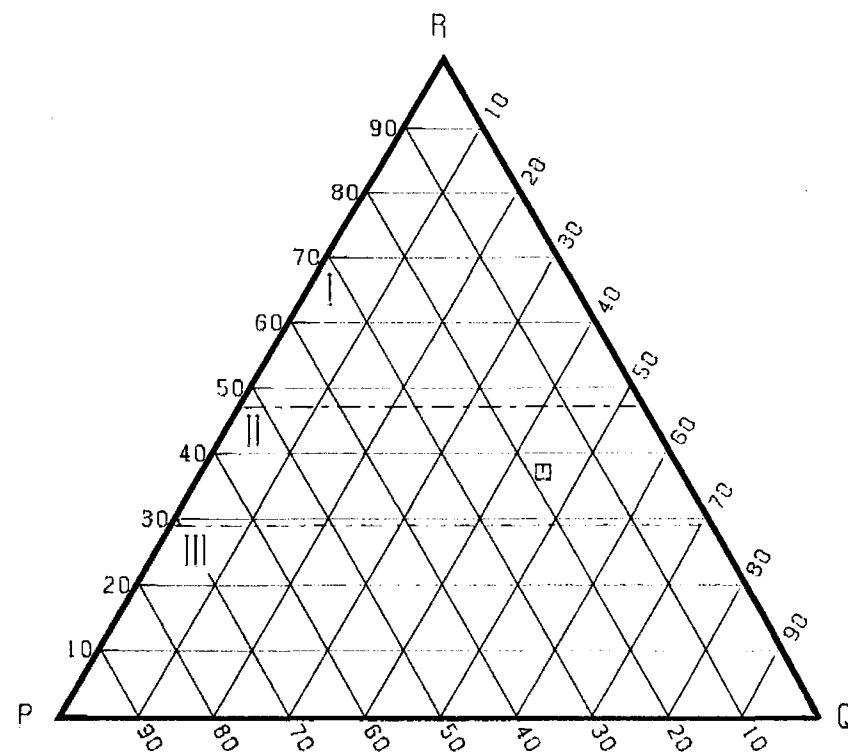
GAS CHROMATOGRAM OF SATURATED HYDROCARBONS

206/5-1 11590-11690 F1

PARAMETER M1



PARAMETER M2



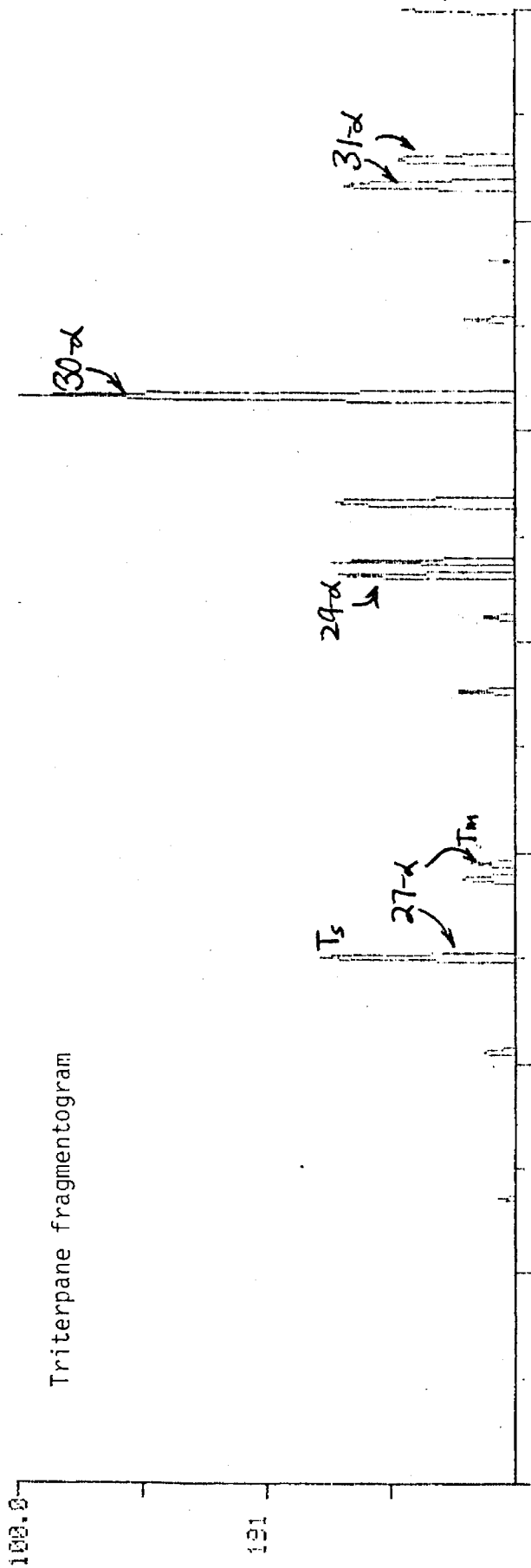
- I LANDPLANT-DERIVED CRUDES WITH SUBSTANTIAL RESIN CONTRIBUTION TO SOURCE MATTER
- II CRUDES OF MIXED ORIGIN
- III CRUDES DERIVED FROM SOM AND/OR ALGAL MATTER

LEGEND

□ - 206/5-1 11590-11690 F1

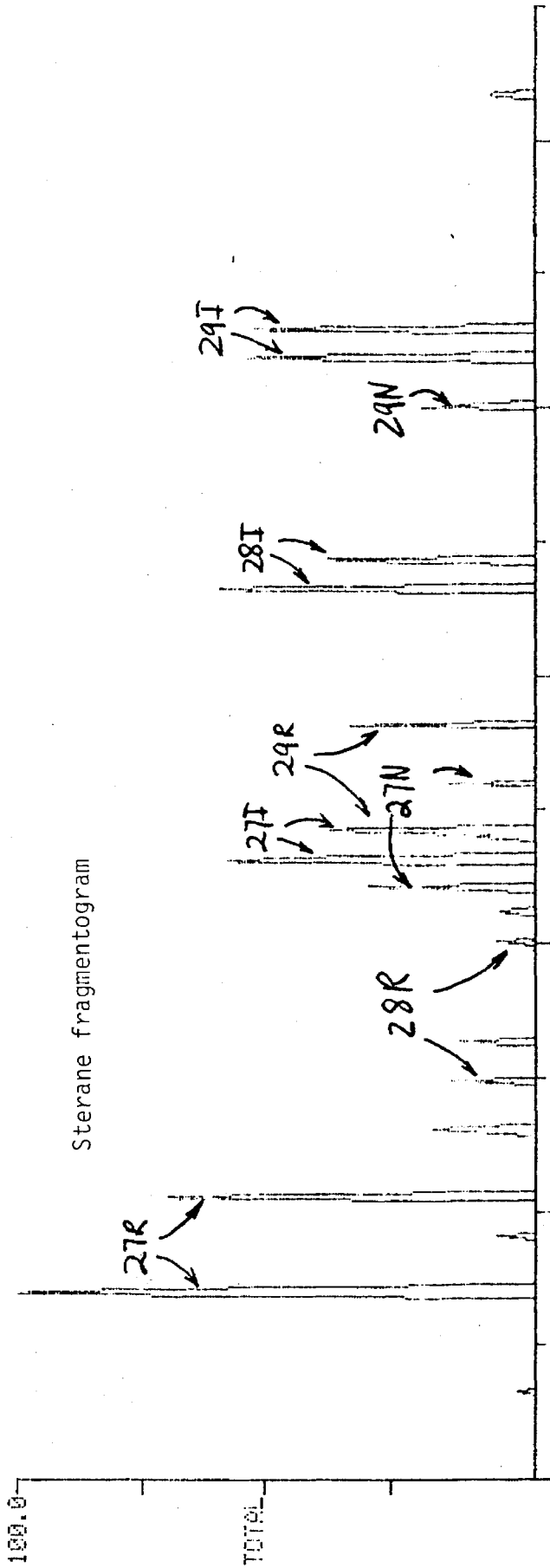
6192

191.35
± 0.50



1352

217-21
218-21
259-25



GC-MS analysis 206/5-1 11590-11690 ft

Fig. 3

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ADDITIONS			LOCATION MAP TABLE 1 FIG. A-E (orig. by KALKMAN) FIG. 1-3
DISTRIBUTION			3 MET KAFT (RINGBAND) = AUSTRALIA NORWAY 3 Vee 13/35/9/91 3 SIPM EP 11/13 1 VGG 1 GRA 1 PHA 1 LYM 1 circuleren: ^{SNRJ} DGO, EHT, GUT, BAAK/ KST, BTX, HRM/H14 Hsz, Vir, SFZ/ FAB/ LBC/ LIEFF., VEE 1 FILE HTG 1 BIBLIOTHEEK x13 KAFT 2
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