May 1982

RKER.82.089

GEOCHEMICAL ANALYSIS OF A CRUDE OIL SAMPLE FROM WELL 206/11-1, UNITED KINGDOM

by

J.M.A. Buiskool Toxopeus and J. Posthuma

Investigation 9.12.468

KONINKLIJKE/SHELL EXPLORATIE EN PRODUKTIE LABORATORIUM

RIJSWIJK, THE NETHERLANDS

(Shell Research B.V.)

11

CONTENTS

GEOCHEMICAL ANALYSIS OF A CRUDE OIL SAMPLE FROM WELL 206/11-1, UNITED KINGDOM

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 C_{25+} 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-C_{17}, or phytane/n-C_{18} is mainly an indication of the depositional environment of the source rock. High pristane/phytane and pristane/n-C_{17} ratios are related to a swampy environement of deposition with low bacterial activity. Low ratios are expected in open aquatic conditions (marine or fresh water), where there is abundant bacterial activity.

C_7 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 C_7 hydrocarbon isomers. A triangular plot of straight-chain (normal), monobranched, and polybranched C_7 alkanes is used to distinguish slightly bacterially degraded or transformed crudes from their unaltered counterpart (Fig. B). In a plot of n-C_7 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 C_7 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:

DOM	MATURITY ZONES
<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.

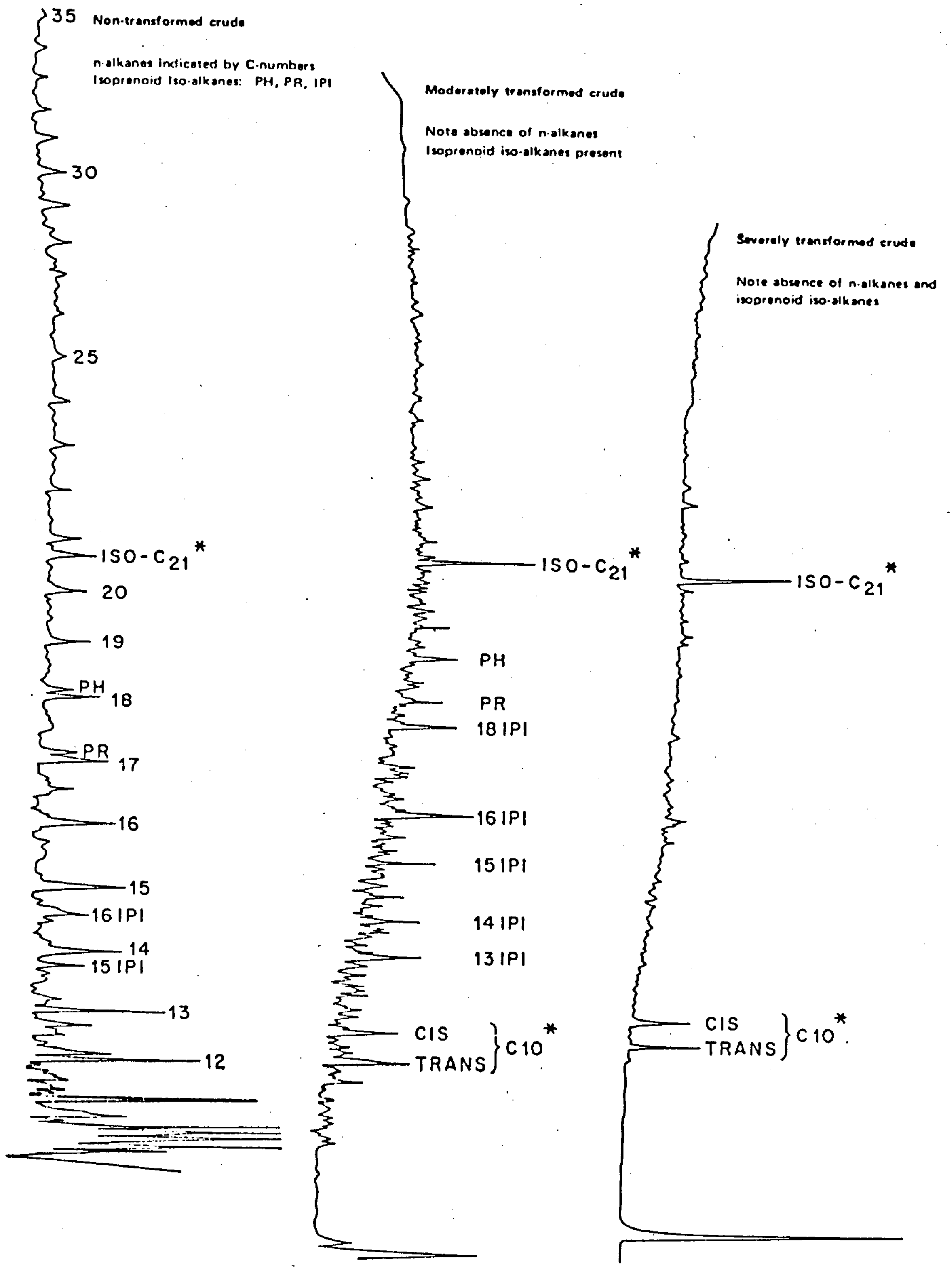
Sterane and triterpane parameters

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.

Draw. no. 25207



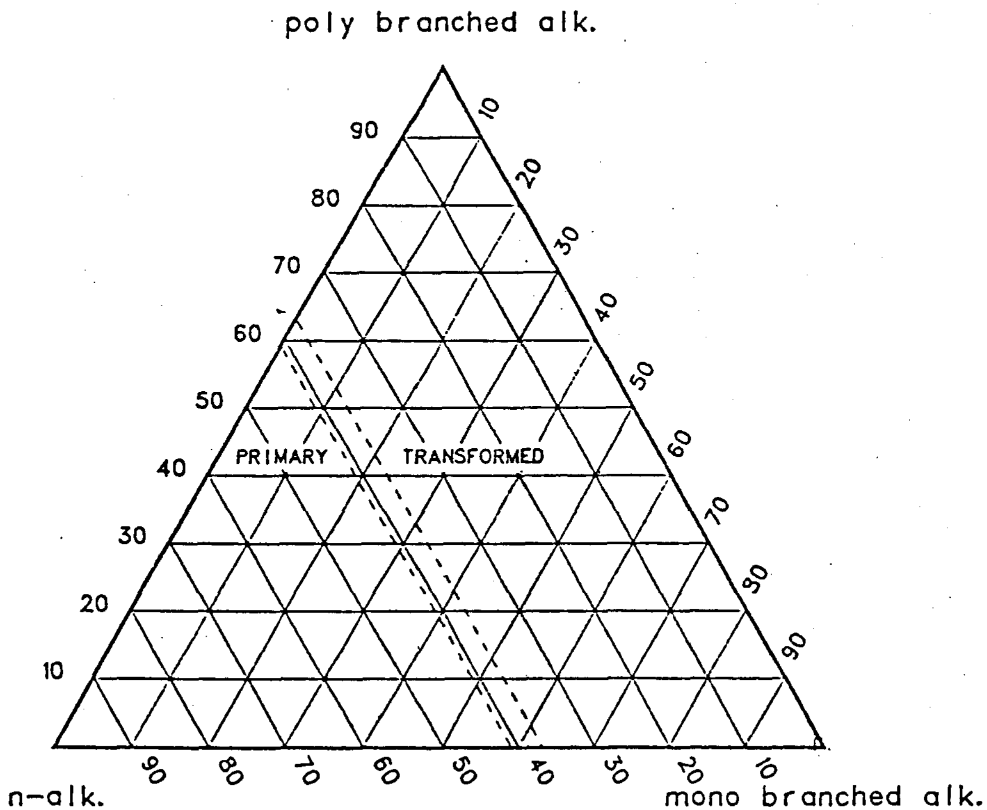
*STANDARD COMPOUNDS ADDED FOR IDENTIFICATION

BACTERIAL DEGRADATION DISPLAYED IN GAS CHROMATOGRAMS OF SATURATED HYDROCARBONS.

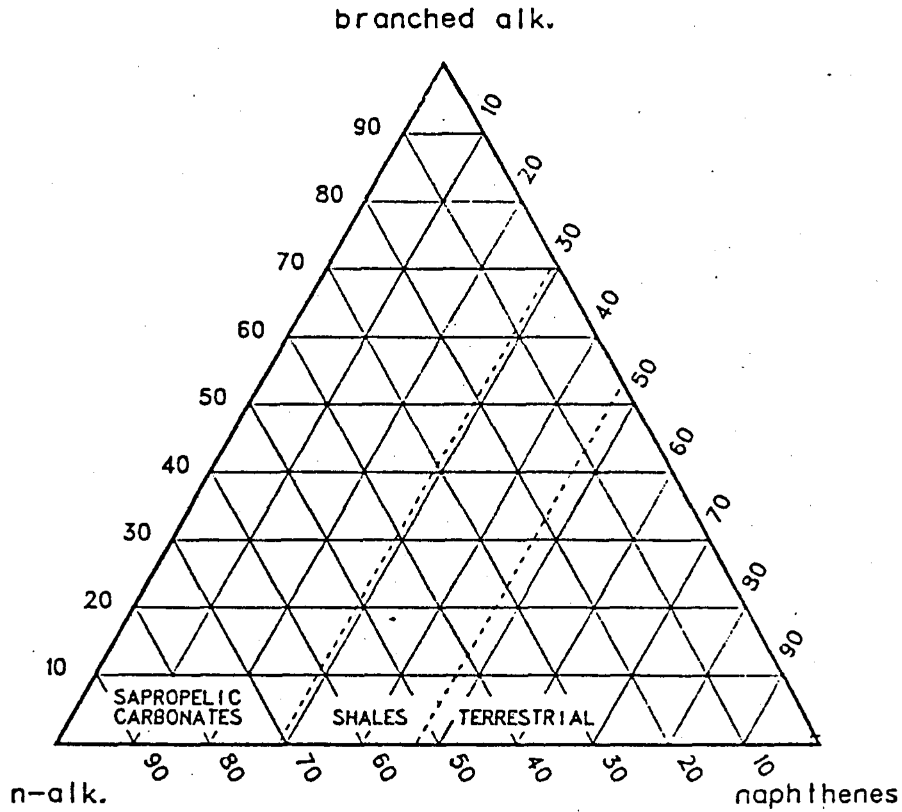
FIG: A

Draw. no. 25208

C_7–ALKANE DISTRIBUTION



C_7–ALKANE/NAPHTHENE DISTRIBUTION

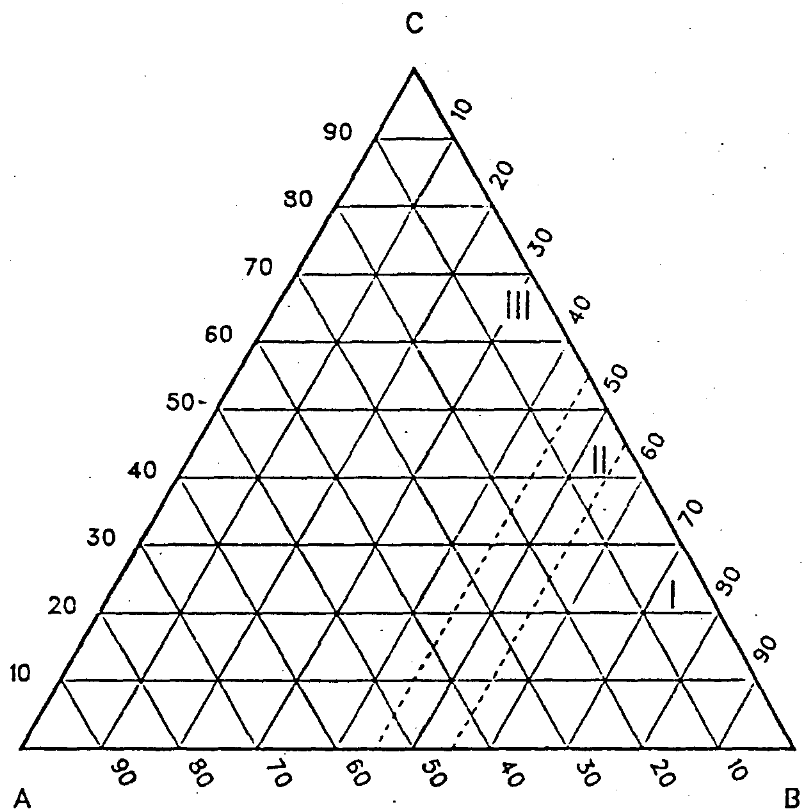


C_7 DISTRIBUTION FOR CHARACTERISATION OF RELATED SOURCE MATERIAL.

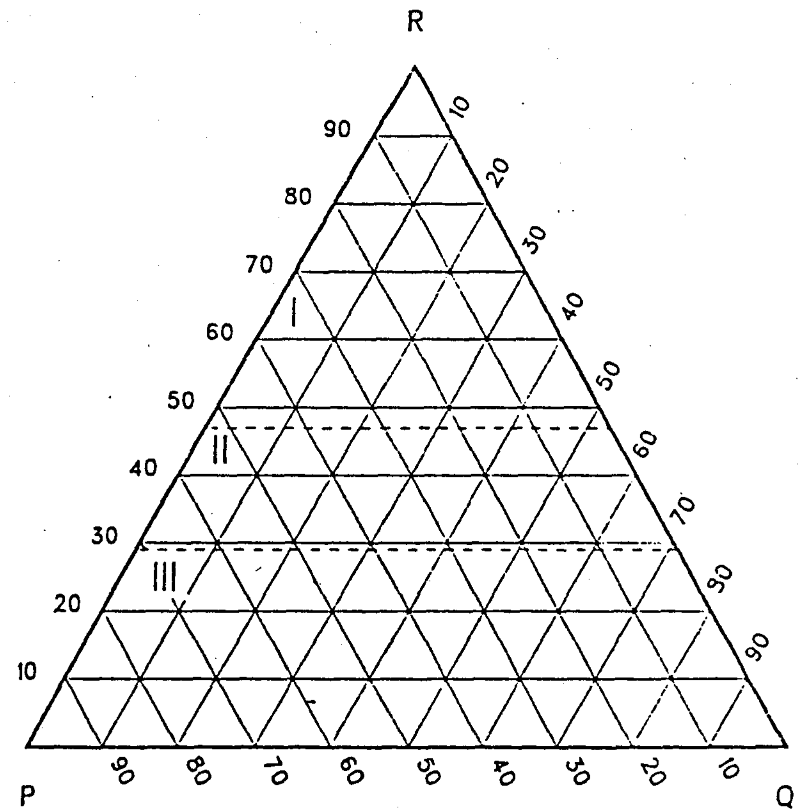
FIG: B

Draw. no. 25209

Parameter M1



Parameter M2



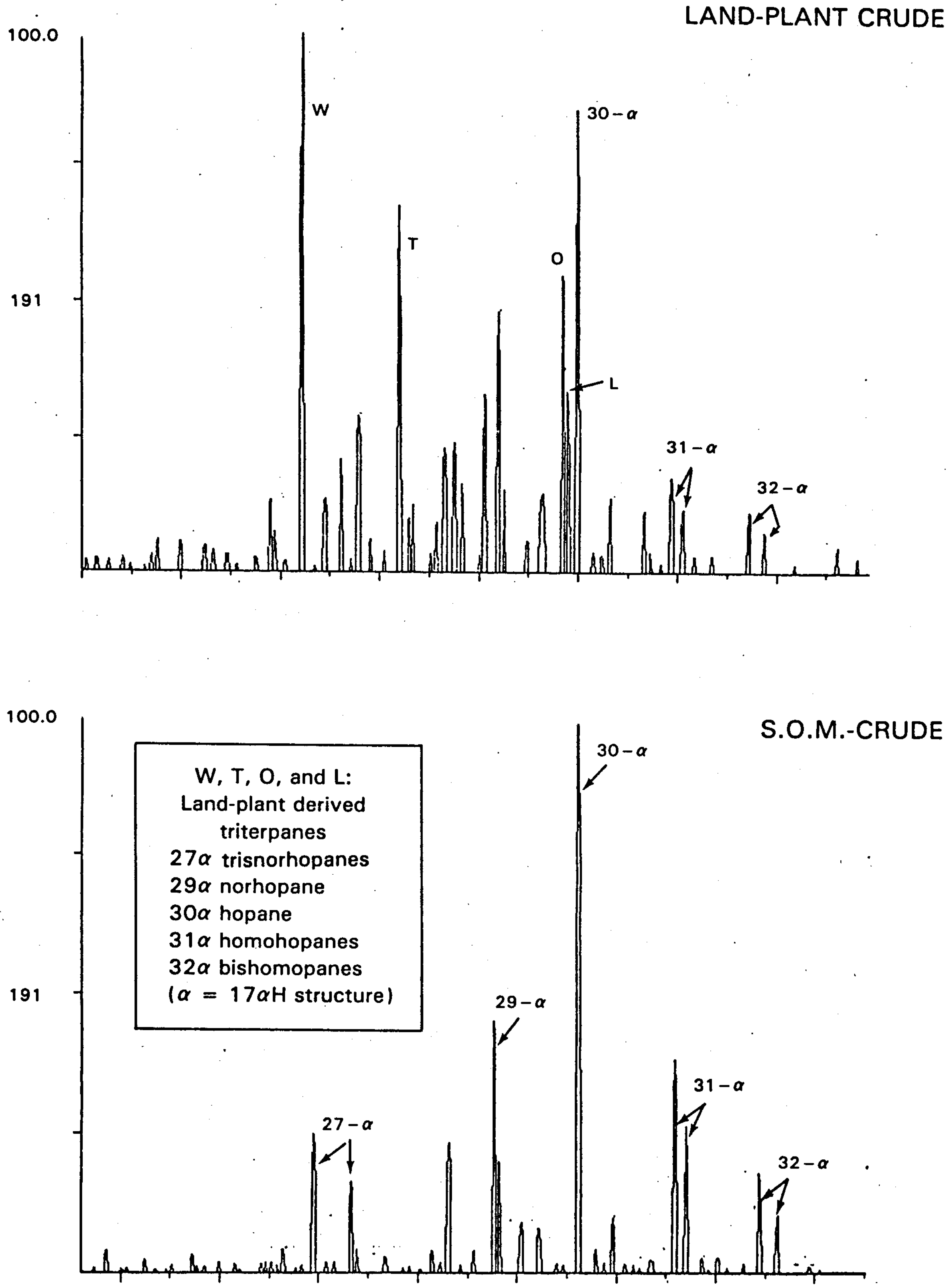
I LANDPLANT-DERIVED CRUDES WITH SUBSTANTIAL RESIN CONTRIBUTION TO SOURCE MATTER

II CRUDES OF MIXED ORIGIN

III CRUDES DERIVED FROM SOM AND/OR ALGAL MATTER

PARAMETERS M1 AND M2 TO TYPE RELATED SOURCE MATERIAL.

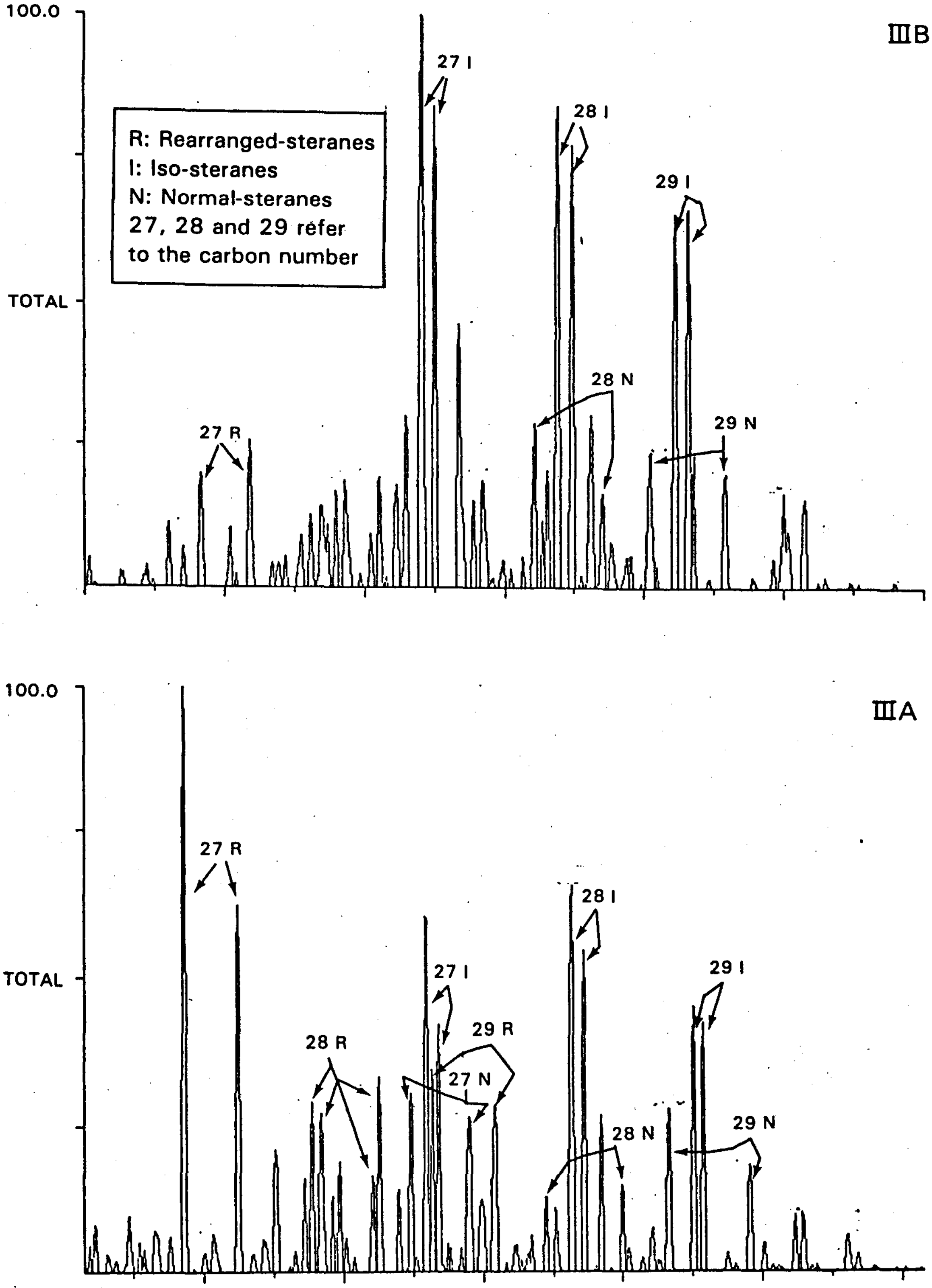
FIG C



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

FIG. D

DI 49619



STERANE FRAGMENTOGRAMS OF TYPE IIIA AND IIIB CRUDE OILS

FIG. E

3. RESULTS AND DISCUSSION

A crude oil sample from well 206/11-1, United Kingdom, was geochemically investigated. The results are shown in Table 1 and in Figures 1-4. The results indicate the following:

3.1 The crude 206/11-1 is bacterially non-degraded (gas chromatogram, Fig. 1; C_7 alkane distribution, Fig. 2).

3.2 The crude was expelled from a mature source rock (gas chromatogram, Fig. 1; sterane/triterpane fragmentogram, Fig. 4; API gravity; gross composition).

3.3 The environment of deposition of the source rock from which the crude was generated was shaly (C_7-alkane/naphthene distribution, Fig. 2).

3.4 The shape of the gas chromatogram (Fig. 1) and the parameters M_1 and M_2 (Fig. 3) indicate that the organic matter from which the crude was generated, was structureless organic matter (SOM). The sterane/triterpane fragmentograms (Fig. 4) are in agreement with this observation and show that the variety of SOM is of bacterially-reworked-phytoplanktonic origin.

3.5 The geochemical parameters of this crude are very similar to an average North Sea crude.

4. CONCLUSIONS

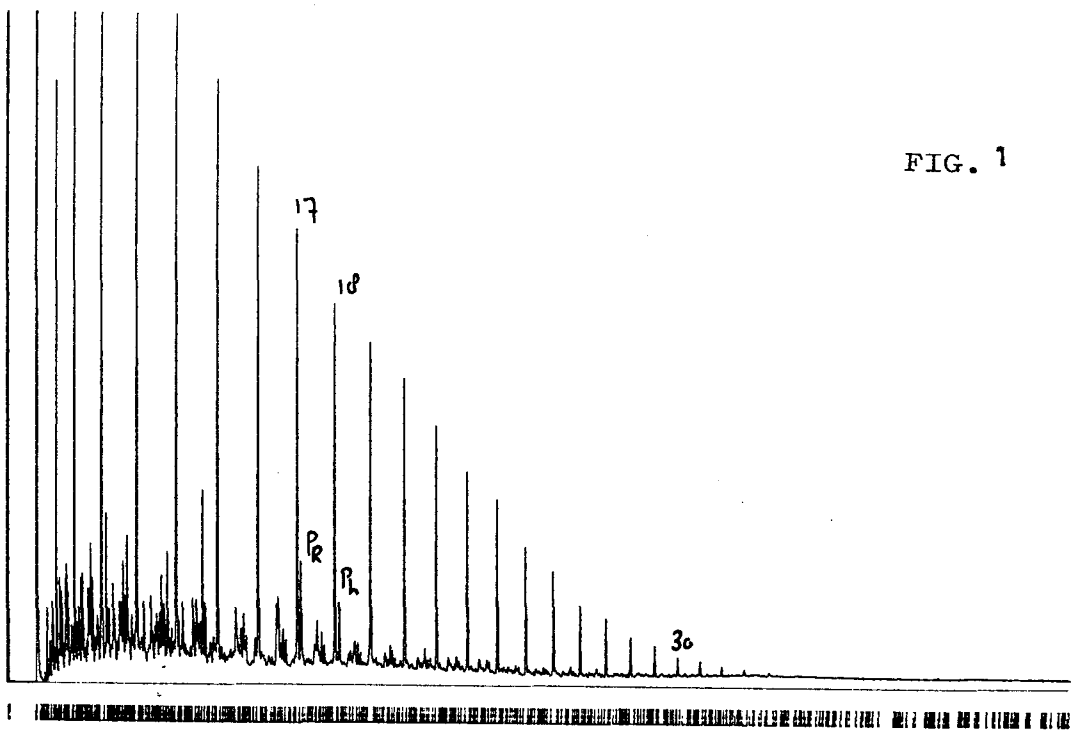
A crude oil from well 206/11-1, United Kingdom, is bacterially non-degraded. The crude was expelled from a mature source rock. The source rock from which the crude was generated contained predominantly organic matter of bacterially-reworked-phytoplanktonic origin. The geochemical parameters of 206/11-1 are very similar to an average North Sea crude.

TABLE 1 - GEOCHEMICAL DATA OF OILS

Sample	206/11-1*, dst-2
API	45.9
specific gravity	0.7973
%w. boil. <120°C	30.0
% sulphur	0.03
ppm V as metals	0
ppm Ni as metals	2
pristane/phytane	1.6
pristane/nC17	0.3
phytane/nC18	0.2
C_7-distribution	
C_7-alkane	
nC7	51
monobranched	36
polybranched	13
C_7-alk/naphthene	
nC7	27
naphthenes	47
branched alkanes	26
C_7-alk/naphth/arom	
nC7	37
naphthenes	33
aromatics	30
Parameter M_1	
A	42
B	44
C	14
Parameter M_2	
P	26
Q	43
R	31
DOM of oil	66
% asphaltenes	<0.05
** % saturates	48
% aromatics	1
% heterocompounds	0
% rest	51
$\delta^{13}C$ °/oo	-28.7

** Determined by column chromatography.

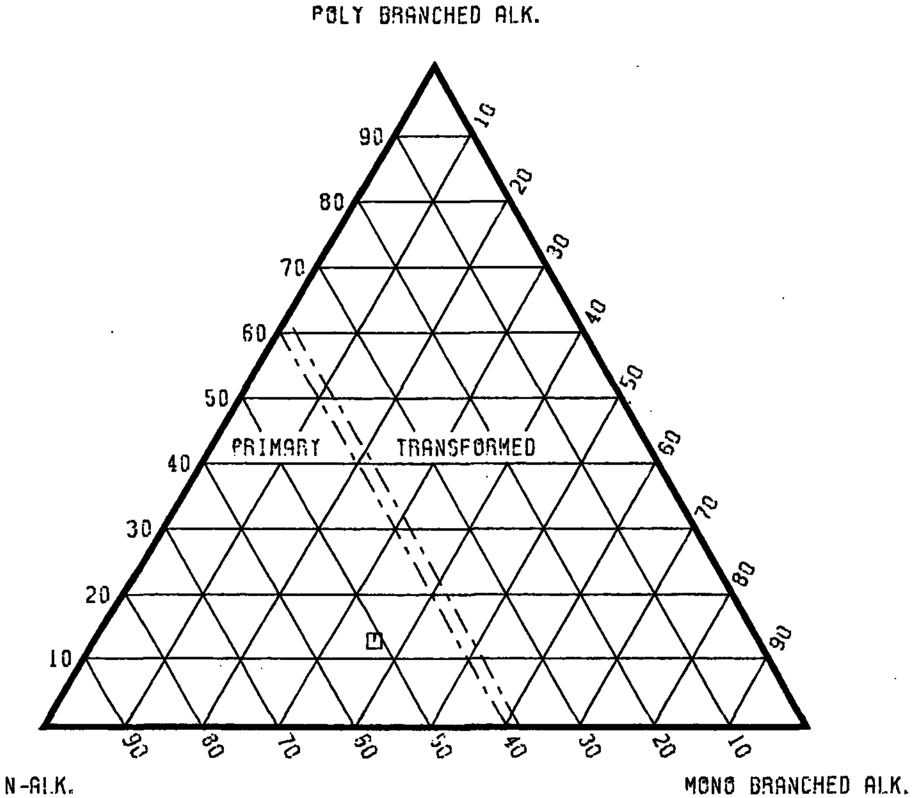
FIG. 1



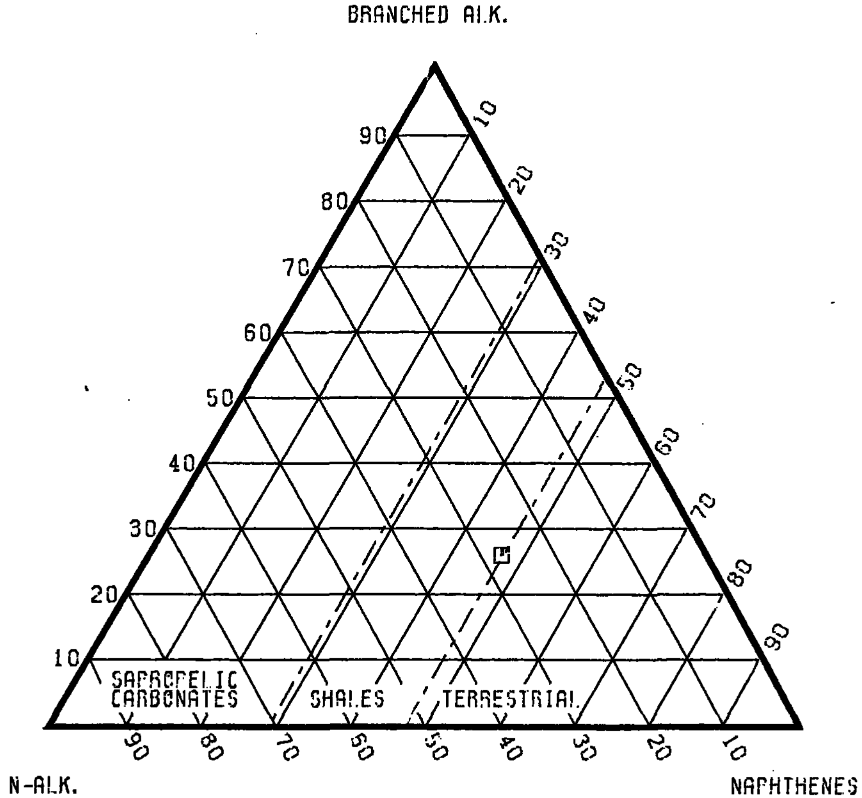
GAS CHROMATOGRAM OF SATURATED HYDROCARBONS

UNITED KINGDOM 206/11-1

C7-ALKANE DISTRIBUTION

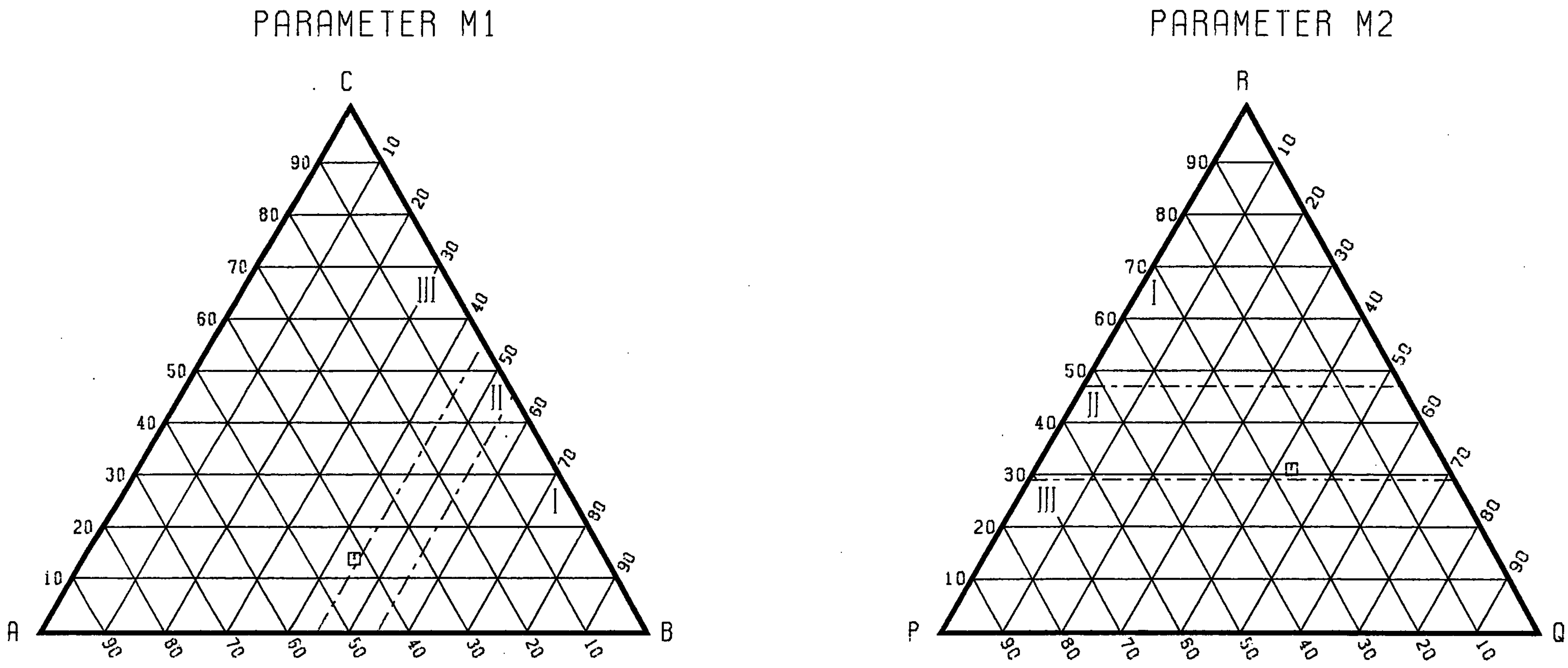


C7-ALKANE/NAPHTHENE DISTRIBUTION



LEGEND
◻ - 206/11-1

FIG. 2



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
⊡ - 206/11-1

FIG. 3

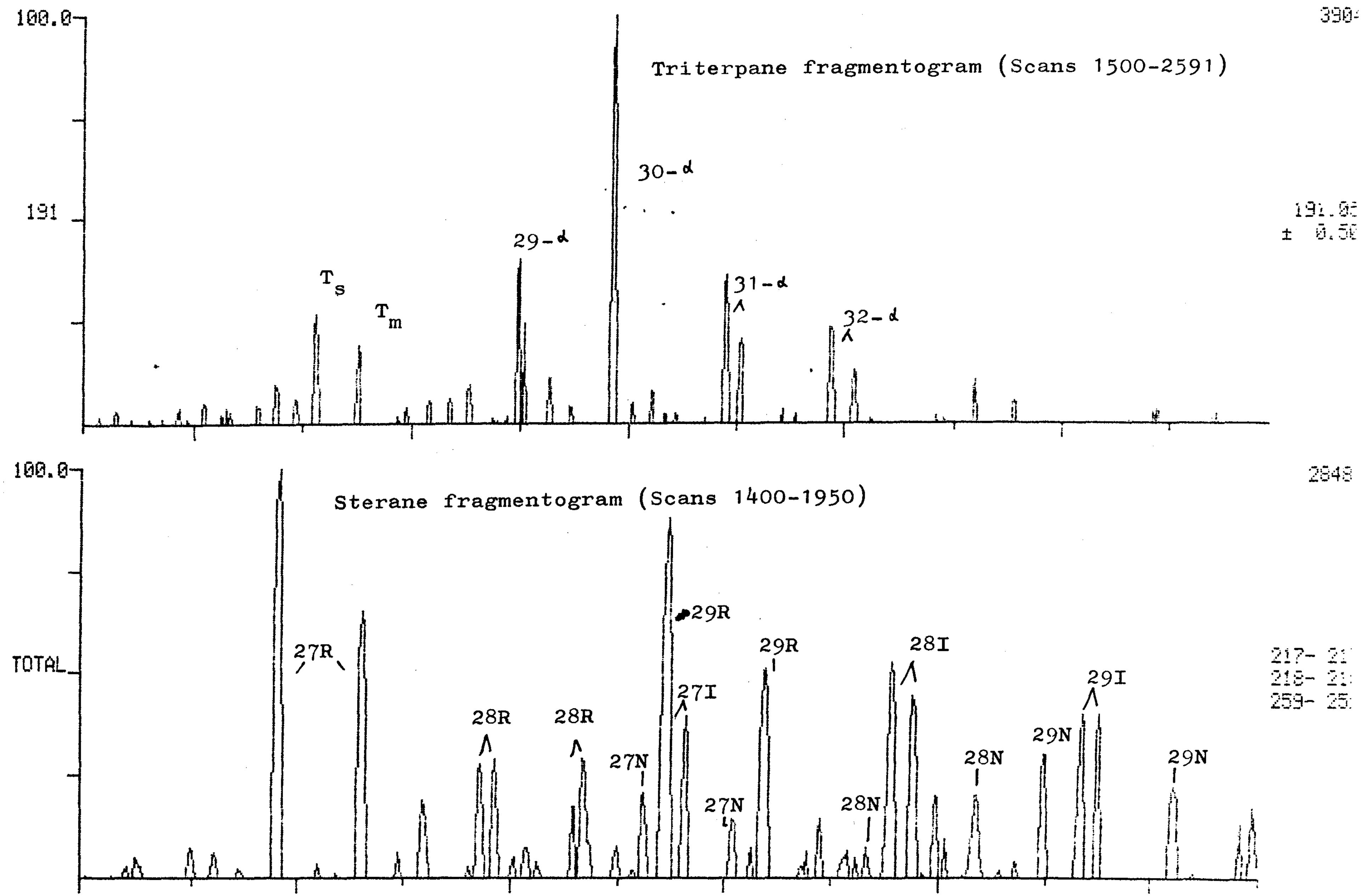


FIG. 4. GC-MS analysis 206/11-1

Confidential

INITIAL DISTRIBUTION

3 copies	Shell Expro London, UEE/35/3/9/91/12
3 copies	SIPM The Hague, EP/11/13

SPECIFICATIELIJST van: RKER 82 089

Ex.	Bij/door	Datum	Aan (te)
ADDITIONS			~~LOCATION MAP~~
			TABLE 1
			FIG. A-E (Orig. by KALKMAN)
			FIG. 1-4
DISTRIBUTION			3 Shell Expro London UEE/35/3/9/91/12
			3 SIPM EP 11/13
			1 VGG
			1 GRA
			1 LYM
			~~1 circuleren: DUA, DIX, DGO, SNR, EHT, GOT, HSZ, HRM,~~
			~~HIC, VIR, BAA, SEZ, KST, FAB, LIE, EBC,~~
			~~VEE~~
			1 file secretariaat Exploratie
			1 landfile
			1 Bibliotheek
			~~11/13~~
			X12
			KAFT 2
			INV. 912468

FL 52