### **ROBERTSON RESEARCH INTERNATIONAL LIMITED**

### REPORT NO. 4644P/D

### GEOCHEMICAL STUDIES ON OIL FROM NORWEGIAN NORTH SEA WELL NOCS 35/3 - 2, DST - 2.

by

## 230KT 1981 RESISTRERY OMEDIABLICATET

A. G. COLLINS B. S. COOPER J. McEWAN

### PROJECT NO. RRPS/812/D/25015

Prepared by:

Robertson Research International Limited, Ty'n-y-Coed, Llanrhos, Llandudno, Gwynedd LL30 ISA, Wales, U.K. Prepared for:

Saga Petroleum A/S, P.O. Box 550, N - 1301 Sandvika, Norway.

September, 1981



### CONTENTS

Page No.

i

1

2

4

### SUMMARY

. اینه

1.1.1.1

.

La cara

à

Ŀ

II

III

### INTRODUCTION

### ANALYSES AND INTERPRETATION

1. Bulk properties

- 2. Gas contents
- 3. Gasoline contents
- 4. Gas chromatography of alkanes
- 5. Gas chromatography of aromatics
- 6. Gas chromatography mass spectrometry
- 7. Carbon isotope ratios

### CONCLUSIONS

### TABLES

1.	Analyses of Bulk Compositions of Oil
2.	Analyses of Light Gas Components of Oil
3.	Gasoline Hydrocarbon Analysis Data
4.	Carbon Isotope Ratios of Components of Oil

### FIGURES

1.	•	Gas Chromatogram of Alkanes
2.		Gas Chromatogram of Branched/Cyclic
		Alkanes
3.		Gas Chromatogram of Aromatic Fraction
4	•	Fragmentograms of Alkanes at m/e 191,
		217 and 259



### SUMMARY

Oil from the NOCS 35/3-2 well (DST-2) in the Norwegian sector of the Northern North Sea has been analysed. Analyses of the bulk properties are tabulated together with details of gasoline content and carbon isotope ratios. Gas chromatograms of alkane, branched and cyclic alkane and aromatic fractions are figured.

The data from the 35/3-2 well are equivocal and may be interpreted as indicative either of a near-shore or marine source or even a non-Jurassic source.



### INTRODUCTION

Ι

Oil from the Norwegian North Sea well, NOCS 35/3-2 (DST-2), has been comprehensively analysed to determine abundances of major and minor components. The oil was received in April, 1981 and analyses were completed and reported in the period up to July 1981. In total the analyses comprise determinations of:-

API gravity

Volatile (to 210°C) content Abundances of gas and gasoline components Abundances of  $C_{15+}$  hydrocarbon fractions Gas chromatography of total alkane, branched with cyclic alkane and aromatic components Gas chromatography - mass spectrometry of triterpane, sterane and rearranged sterane components Carbon isotope ratios of gaseous components,  $C_{15+}$  (alkane and aromatic) components and polar components



### ANALYSES AND INTERPRETATION

#### Bulk Properties (Table 1) 1.

The oil is a brown mobile liquid. The °API gravity is in the medium to light oil range and the volatile content of 39.7% suggests a light oil - condensate composition.

The 35/3-2 topped oil appears to have a high soluble asphaltene content and depleted alkane content.

#### 2. Gas Contents (Table 2)

The amounts of  $C_1$  to  $C_4$  gases of the 35/3-2 oil were measured prior to determination of carbon isotope ratios. The concentrations increase with molecular weight and suggest that a significant loss of volatile components, particularly gases, has occurred when the oil was sub-sampled. The marked predominance of **A**-butane over **b**-butane in the oil indicates an origin aither from the immature/mature or mature/postmature transitions of the oil generation zone, although the actual value for the ratio is high for North Sea oils. This may indicate a source rock other than the Late Jurassic. Roho is normal for north sec oils

#### 3. Gasoline Contents (Table 3)

The distinctive feature of the anlayses is the relatively high benzene to methyl cyclohexane content and indicates derivation from a late mature source rock.

#### Gas chromatography of alkanes (Figure 1) 4.

The oils shows a wide range of alkanes reaching  $n-C_{30}$  and beyond. Pristane is dominant over phytane but sterane and triterpane components are not distinct. These characteristics suggest an origin in land plant waxy debris which has reached a moderate level of maturity.

#### Gas chromatography of aromatics (Figure 3) 5.

The analysis shows that the aromatic fraction is composed of a restricted

- 2. -

II



number of dominant components and is similar to other oils of 40° to 50° API gravity and to source rocks which have reached a middle to late maturity. The content of light volatile components is high.

### 6. Gas chromatography - mass spectrometry (Figure 4)

The mass fragmentograms at m/e 191, 217 and 259 have been compared with similar data from source rocks containing various types of kerogen.

The fragmentograms for 35/3-2 show few components, particularly in the higher steranes, and yet seem to show some characteristics of a land plant origin. However, the relative amounts of these components are much less than might be expected in a typical oil derived from kerogen of land plant origin.

### 7. Carbon isotope ratios (Table 4)

The ratios of the fractions of the oil are close to  $-26^{\circ}/_{\circ \circ}$ . This value falls within the range of marine sapropel.



### CONCLUSIONS

1. The relative contents of iso-alkanes in the gasoline fraction are not typical of Northern North Sea oils.

2. Some of the analytical data for the 35/3-2 oil indicate a land plant or nearshore source (pristane/phytane and range of <u>n</u>-alkanes) but other data, from gas chromatography - mass spectrometry, are equivocal. The carbon isotope ratio data indicate a marine source or a source rock deposited during a period of generally more positive global values of carbon isotope ratio, such as may have occurred in the Carboniferous.



Tab	1e	1
-----	----	---

 $\mathbf{E} \in \mathbb{R} \setminus \mathbb{R}$ 

10000

1 .....

## Analayses of Bulk Compositions of Oil

		35/3-2
API Gravity (20°C), degrees Fraction boiling below 210°C. %		42.2 39.7
Sulphur content, %		-
Nickel content		-
Alkane content of topped oil, % Aromatic content of topped oil, %	·	61.4 10.0
Resene content of topped oil, % Soluble asphaltene content of topped oil, % Asphaltene content by precipitation %		2.6 26.0 0.0



Here a state way in the second state of the second state of the second state of the second state of the second



### Analyses of Light Gas Components of Oil

### Concentration in ppm

<u>35/3-2</u>

Methane Ethane Propane La-Butane Ni-Butane

1. N. N. N.

1.121.0

i-Butane n-Butane

J.s 0.45

ROBERTSON

COMPANY: SAGA

10 C 20 M

1000000

EU 10.6.6

 $\mathbf{U} = \{\mathbf{u}_i, \mathbf{u}_i, \mathbf{u}$ 

2

LOCATION: NORWEGIAN NORTH SEA

DEPTH:	OIL							
GASOLINE HYDROCARBON Components	RELA	TIVE GASO	LINE	HYDRI	DCARBON	COMPONENT	ABUNDANCE	s. (%)
<u>i</u> -butane	1.5							
<u>n</u> -BUTANE	3.3							
<u>i</u> -PENTANE	4.3							
<u>n</u> -PENTANE	6.4							
2, 2 - DIMETHYL BUTANE	0.4							
CYCLOPENTANE	0.8							
2, 3 - DIMETHYL BUTANE	0.6							
2 - METHYL PENTANE	2.6							
3- METHYL PENTANE	1.9							
<u>₽</u> -HEXANE	5.8							
2, 2 - DIMETHYL PENTANE / METHYL CYCLOPENTANE	4.2							
2,4-DIMETHYL PENTANE	0.5							
BENZENE	4.8							-
3, 3 - DIMETHYL PENTANE	0.2							
CYCLOHEXANE	10.8							
2 - METHYL HEXANE	2.5			-				
1, 1 - DIMETHYL CYCLOPENTANE	0.5							
3-METHYL HEXANE	2.0							
1, cis – 3 – DIMETHYL CYCLOPENTANE	0.6							
1, trans – 3 – DIMETHYL CYCLOPENTÂNE	0.8							
1. trans – 2 – DIMETHYL CYCLOPENTANE	1.4							
3 - ETHYL PENTANE	-							
	6.4							
1, <i>cis</i> - 2 - DIMETHYL CYCLOPENTANE / METHYL CYCLOHEXANE	18.3							
ETHYL CYCLOPENTANE	0.9							
TOLUENE	16.0							
TOTAL ABUNDANCE (ppm)	121640							
ORGANIC CARBON (%)								
GASOLINE ABUNDANCE AT 1% ORGANIC CARBON								

Note: Total gasoline abundance values are expressed as weight of gas relative to weight of wat rock.

TABLE 3 Gasoline Hydrocarbon Analysis Data

Methane 280 ppm (0.2%), Ethane 520 ppm (0.4%), Propane 2180 ppm (1.8%)

### Table 4

E.S. A. A.

EALLS.

1742-02-02

1 - V - D

 $1 \leq n \leq n \leq n$ 

### Carbon Isotope Ratios of Components of Oil

35/3-2
-45 5
~4J.J
39.0
-30.4
-28.4
-26.7
-25.7
<del>-</del> 25.1

Values are quoted in parts per mil measured against PDB standard.



<u>Figure 1</u> Gas Chromatogram of Alkanes

1.500





1991 - 1994 - 1994 - 1994 - 1994 - 1994 - 1994 - 1994 - 1994 - 1994 - 1994 - 1994 - 1994 - 1994 - 1994 - 1994 -

 $\left( \left[ \begin{array}{c} c \\ c \end{array} \right] \right)$ 

AND ARE

RUVU

the set of the set of

P.523.0

(

Figure 2

D. N. N.

unitaria transferanti transferantia. . (200

6

Gas Chromatogram of Branched/Cyclic Alkanes



FIGURE 2 Branched/Cyclic Alkanes 35/3-2

m. M.M. M. M. M. M. M. Marken M.

Ph Pr

Rear Strategy (St.

· M.M.M.M.M.M.

1 7252.17

1.752.04

Figure 3

1.2.2.6.3

 $P^{(n)}(x,y,y) = 0$ 

t stilled

1.156.1

Gas Chromatogram of Aromatic Fraction





Figure 4

63.47.2

1.144.1

Var alla

Fragmentograms of Alkanes at m/e 191, 217 and 259

ROBERTSON

FIGURE 4

WY 6.2 CM







SCAN #



# **GEOCHEMICAL SERVICE REPORT**

Prepared for

SAGA PETROLEUM A.S.

GEOCHEMICAL CHARACTERISATION OF THE 35/3-2 CONDENSATE

1 0 AUG. 1981 REGISTRERT OLJEDIREKTORATET

June 1981

- CHESTER STREET · CHESTER CH4 8RD · ENGLAND ----

COMPANY PROPRIETARY

;

### GEOCHEMICAL CHARACTERISATION OF THE 35/3-2 CONDENSATE

### SUMMARY

The 35/3-2 condensate sample has an API gravity of  $42.7^{\circ}$  and a sulphur content of 0.053%.

.

Although depleted in gaseous hydrocarbons, due most probably to losses in transit and storage, the gasoline range and heavier hydrocarbons are normal in their distribution. These data suggest that the fluid is unaffected by water washing or biodegradation in the reservoir.

Analyses of the heavy hydrocarbon fractions indicate that the fluid is moderately mature and that it was sourced by sediments rich in land plant organic matter.

M.J. Sauer GEOCHEM LABORATORIES (UK) LIMITED

### INTRODUCTION

This report presents a geochemical evaluation of a condensate sample from the 35/3-2 well, drilled in the Norwegian sector of the North Sea.

The purpose of this study was to characterise the fluid and if possible to determine the nature and maturity of the parent source rock.

The study was authorised by Mr. T.O. Throndsen, Saga Petroleum A.S., Sandvika, Norway.

### ANALYTICAL

Α.

The condensate, sample 29 from DST 2, was assigned the Geochem job number 532-001.

Visually the fluid is a pale coloured mobile liquid.

The sample, with the exception of the gas oil ratio, was analysed in accordance with an analytical programme proposed by the client.

To characterise the condensate, one API gravity determination, one sulphur determination, one vanadium and one nickel determination, one distillation, one light hydrocarbons analysis, one gasoline range analysis, two chromatographic fractionations, one high resolution paraffin-naphthene analysis, one high resolution aromatics analysis, one high resolution branched cyclics analysis, one three ion mass fragmentogram and two carbon isotope determinations were performed.

### B. GENERAL INFORMATION

Three copies of this report have been forwarded to Mr. T.O. Throndsen, Sage Petroleum A.S., Sandvika. A copy has been retained by Geochem for future consultation with authorised Saga personnel.

All of the results and interpretations contained in this report are regarded as highly confidential and are proprietary to Saga Petroleum A.S.

### RESULTS AND DISCUSSION

A programme of analysis, specified by the client, has been carried out in order to characterise a condensate sample from the 35/3-2 well.

The condensate is a, mobile, pale yellow coloured liquid. It has an API gravity of 42.7° and a sulphur content of 0.053%. Nickel and vanadium contents are both less than 1ppm and their ratio, therefore has little significance.

A sample of the headspace gases above the condensate were analysed for the individual  $C_1-C_4$  and combined  $C_5-C_7$  hydrocarbons. Because of their volatility methane (48 ppm) and ethane (811 ppm) are depleted relative to the  $C_3$  and  $C_4$  hydrocarbons. The absolute concentrations, however, have little significance but, since the two analyses overlap, may be used to extend the gasoline range data. If the  $C_1-C_4$  and  $C_5-C_7$  results are combined and renormalised then methane, ethane and propane are 0.03%, 0.48% and 3.15% of the total  $C_1-C_7$  fraction.

The 20-210°C fraction (58.6% of the total fluid) contains approximately equal proportions of n-paraffins (20.3%) isoparaffins (15.9%), naphthenes (37.7%) and aromatics (26.2%). No single group of hydrocarbons in this fraction is depleted - suggesting that the condensate is relatively unaltered by water washing or biodegradation. In more detail a chromatogram of the 20-210°C fraction reveals a complete range of hydrocarbons in which the C4-C7, and higher, species are identified. Particularly intense peaks are toluene (27.7%) and methyl cyclohexame(20.0%).

The distillation residue  $(210+^{\circ}C \text{ fraction})$  contains 68.5% paraffinnaphthene and 24.4% aromatic hydrocarbons, asphaltenes amount to 0.3% and NSO compounds 6.8%. Minor differences are apparent when these data are compared to the corresponding C15+ fraction values.

Î

A more detailed analysis of the  $C_{15+}$  fraction, by capillary GC, indicates that the n-paraffins are dominant, that they extend out to nC<sub>35</sub> and have a slight odd carbon preference. This odd carbon preference suggests moderate maturity and, in conjunction with the low pristane and phytane abundances, is sometimes associated with a land plant type source organic matter.

Pristane and phytane are dominant in the  $C_{15+}$  branched/cyclics chromatogram but are virtually non existant (showing almost complete exclusion of non normal paraffins) in the corresponding n-paraffins trace. Residual n-paraffins, limited to the  $C_{15}$  to  $C_{20}$  range, are minimal in the branched/cyclics fraction.

The  $C_{15+}$  aromatic hydrocarbons have been analysed by capillary gas chromatography. This fraction is largely composed of the

dimethyl naphthalenes, with decreasing quantities of the di- and tri methyl naphthalenes, longer chain alkyl naphthalenes, and the triaromatic hydrocarbons such as phenanthrene and the methyl phenanthrenes.

Mass fragmentograms are principally used for correlation purposes. Nonetheless, a certain amount of information concerning the type of source organic matter involved may also be derived from them. Triterpanes, including the 17 $\checkmark$  and 17 $\beta$  C<sub>27</sub> trisnorhopanes (A), 17 $\checkmark$  C<sub>29</sub> norhopane (B), 17 $\checkmark$  H C<sub>30</sub> hopane (C) and the C<sub>31</sub>\_C<sub>34</sub> hopanes are identified on the <sup>m</sup>/e 191 fragmentogram. The <sup>m</sup>/e 217 and <sup>m</sup>/e 259 fragmentograms display the steranes and rearranged steranes, notably 5 $\checkmark$  and 5 $\beta$  C<sub>27</sub> cholestane (E), C<sub>28</sub> ergostane (F) and the C<sub>29</sub> stigmastanes (G). The hopanes (particularly the higher hopanes), ergostane and the stigmastanes are generally associated with land plant type organic matter.

Carbon isotope  $\delta$  values are -28.9% oo for the C<sub>15+</sub> paraffinnaphthene fraction and -27.6% of for the corresponding aromatic hydrocarbons. They fall within the range normally associated with hydrocarbons derived from source rocks rich in land plant debris.

### CONCLUSIONS

A sample of condensate from the 35/3-2 well has been analysed in accordance with a scheme proposed by the client. The type of data generated by these analyses, although most effectively used for correlation studies, provides useful information on the characteristics of a condensate or oil.

This fluid has an API gravity of  $42.7^{\circ}$  and a sulphur content of 0.053%. Only traces (less than 1 ppm) of vanadium and nickel were detected. The condensate sample is depleted (during transit and storage ?) in the gaseous hydrocarbons although the gasoline range analysis appears to be normal. An abundance of aromatic hydrocarbons (21.7% toluene) and a full range of the C4-C7 iso and normal paraffins suggests that the condensate has not been altered (e.g. by water washing or biodegradation) in the reservoir.

The heavier C15+ paraffin-naphthene fraction hydrocarbons have characteristics (e.g. slight odd carbon preference and low abundances of pristane and phytane) which suggest that the fluid is moderately mature and that it is, most probably, derived from a source rich in land plant debris. This conclusion is also supported by the triterpane and sterane mass fragmentograms, and by the carbon isotope  $\delta$  values.

### TABLE 1

### BULK PROPERTIES OF CONDENSATE

٢

Ô

GEOCHEM	API	SULPHUR	20-210 <sup>0</sup> C	- ]	PPM	
NUMBER	GRAVITY	CONTENT	FRACTION	NICKEL	VANADIUM	•
532-001	42.7 <sup>0</sup>	0.053%	58.6% w/w	<1	<1	

. .

. .

-

			· · ·		TAB	LE 2					
<b>P</b>		CON	CENTRATION	V (VOL. PPM	) OF	C1 - C7 HYDR	OCARBONS	IN AIR SPACE	GAS	·	· · ·
GEOCHEM SAMPLE NUMBER	DEPTH	C1 Methane	C2 Ethane	Cg Propane	iC4 Isobutane	nC4 Butane	тотаL С <sub>1</sub> - С4	TOTAL C <sub>2</sub> - C <sub>4</sub>	% GAS WETNESS	TOTAL C5 - C7	iC4 nC4
532-001	35/3-2	48	811	5351	2280	5911	14401	14353	99.7	24247	0.39

Ø

. .

## TABLE 3 DETAILED GASOLINE RANGE (C<sub>4</sub> – C<sub>7</sub>) ANALYSIS

NUMBER	532-001
DEPTH	35/3-2 Condensate
isobutane	1.18
n - butane (nB)	3.48
isopentane	3.84
n - pentane (nP)	4.38
2,2 - dimethylB	0.33
cyclopentane (CP)	0.98 ~
2,3 - dimethylB	
2 - methylP	2.75
3 - metnyir	1.67
n - bexane (nH)	4.02
methyICP (MCP)	4.92
2,2 - dimethyIP	0.44
benzene	<i>A A</i> 5
2,4 - dimethylP	0.08
2,2,3 - trimethylB	
cyclohexane (CH)	10.07 ~
3,3 - dimethylP	
1,1 - dimethyICP	
2 - methylH	3.27
2,3 - dimethylP	
1,c,3 - dimethyICP	0.77
3- methylH	2.27
142 dimension	
1,1,3 - dimethylCP	0.72
3. ethylP	1.54
	0.05
n - heotane	7 50
1.c.2 - dimethvICP	
methyICH (MCH)	19.98
toluene	21.70
ABUNDANCE (ppm)	- · · · · · · · · · · · · · · · · · · ·
MCP/benzene	0.81
MCP/MCH	0.18
CULAND	2.79
CH/MCP	
iP/nP	0.88
%n - PARAFFINS	20.29
% ISOPARAFFINS	15.89
	· · · · · · · · · · · · · · · · · · ·
% NAPHTHENES	3/00/
% AROMATICS	26.16
	DEPTH DEPTH isobutane n - butane (nB) isopentane n - pentane (nP) 2,2 - dimethylB cyclopentane (CP) 2,3 - dimethylB 2 - methylP n - hexane (nH) methylCP (MCP) 2,2 - dimethylP 2,2 - dimethylP 2,2,3 - trimethylB cyclohexane (CH) 3,3 - dimethylP 1,1 - dimethylCP 2 - methylH 2,3 - dimethylP 1,c,3 - dimethylP 1,c,3 - dimethylCP 3 - methylH 1,t,2 - dimethylCP 3 - ethylP n - heptane 1,c,2 - dimethylCP methylCH {MCH} toluene MCP/MCH CH/MCP iP/nP %n - PARAFFINS % NAPHTHENES % AROMATICS

• .

 TABLE 4A

 WEIGHT (GRAMMES) OF C15+ EXTRACTS AND CHROMATOGRAPHIC FRACTIONS

())

					TOTAL E	XTRACT	······································	nC5 S		<b>FION</b>	
	GEOCHEM SAMPLE NUMBER	INTERVAL	INITIAL SAMPLE	TOTAL EXTRACT OBTAINED	Preciptd. Asphaltenes	nC5 soluble	Paraffin — Naphthenes	Aromatics	Eluted NSO's	Non-eluted NSO's	Sulphur
•	532 <b>-</b> 001 532-001	210°C <sub>+</sub> , C <sub>1</sub> 210°C <sub>+</sub> , C <sub>1</sub>	5+ 0.1898 5+ 0.0413	0.14107 0.02348	0.00041 0.00022	0.14066 0.02326	0.09664 0.01522	0.03442	0.00595 0.00124	0.00365	0.00000

GEOCHEM SAMPLE NUMBER		HYDROCARBONS			NON HYDROCARBONS					
	INTERVAL	Paraffin — Naphthenes	Aromatics	<u>P – N</u> AROM	Preciptd. Asphaltenes	Eluted NSO's	Non eluted NSO's	Sulphur	ASPH NSO	HC NON HC
532-001 532-001	210°C+ C <sub>15+</sub> 210°C+ C <sub>15+</sub>	68.51 64.82	24.40 24.96	2.81 2.60	0.29 0.94	4.22 5.28	2.59 4.00	0.00	0.04 0.10	13.09 8.78

TABLE 4C COMPOSITION (NORMALISED %) OF C15+ MATERIAL EXTRACTED

### TABLE 5

## CARBON ISOTOPES (%00, PDB)

GEOCHEM SAMPLE NUMBER	LOCATION	PARAFFIN- NAPHTHENE	AROMATIC
532-001	35/3-2	-28.9	-27.6

الم المانية محمد المارية المارية المارية المحمد المارية المحمد المارية محمد المارية المارية المارية المارية الماري

 ${}$ 

TABLE 6

COMPOSITION (NODMALISED 0/)	ACC. DADACCINI	
COMPOSITION (NURMALISED %)	UF UIGH FANAFFIN	- MAPHINE HIDNUCANDUNS

GEOCHEM SAMPLE NUMBER	532-001	
DEPTH	35/3-2	
SAMPLE TYPE	CONDENSATE	
nC <sub>15</sub>	10.50	
<sup>nC</sup> 16	9.99	
<sup>nC</sup> 17	8.97	
<sup>nC</sup> 18	9.16	
<sup>nC</sup> 19	7.82	
<sup>nC</sup> 20	6.93	
<sup>nC</sup> 21	6.68	
6 <sup>7C</sup> 22	6.17	
<sup>nC</sup> 23	5.73	
<sup>nC</sup> 24	4.52	
<sup>nC</sup> 25	4.77	
<sup>nC</sup> 26	4.20	
nC <sub>27</sub>	3.94	
<sup>nC</sup> 28	3.05	
<sup>nC</sup> 29	2.54	
<sup>nC</sup> 30	1.91	
<sup>nC</sup> 31	1.40	
<sup>nC</sup> 32	0.76	
<sup>nC</sup> 33	0.57	
( <sup>nC34</sup>	0.25	
<sup>nC</sup> 35	0.13	
PARAFFIN	82.65	
ISOPRENOID	2.73	
NAPHTHENE	14.62	
CPI INDEX A	1.07	
CPI INDEX B	1.10	
	0.74	
PRISTANE/PHYTANE	2./1	
PRISTANE/nC17	0.27	

#### BRIEF DESCRIPTION OF THE ANALYSES PERFORMED BY GEOCHEM

"Screen Analyses" are described in sections A, C and D, "Sample Preparation" in section B, "Follow-up Analyses" in sections E through K and "Correlation Studies" in section L. The analyses can be run on either core or cuttings material with the proviso that samples must be canned for the  $C_1$ - $C_7$  analysis and should be canned (or at least wet) for the  $C_4$ - $C_7$  analysis. The other analyses can be run on both canned and bagged samples.

### A) C1-C7 LIGHT HYDROCARBON ANALYSIS

The abundance and composition of the  $C_1-C_7$  hydrocarbons in sediments reflects their source richness, maturity and the character of the hydrocarbons they can yield. Most importantly, it is extremely sensitive to the presence of migrated hydrocarbons and is an excellent method for their detection. As it provides the information on most of the critical parameters and is also economical, this analysis is excellent for screening samples to decide which of them merit further analysis.

During the time which elapses between the collection of the sample at the wellsite and its analysis in the laboratory, a fraction of the total gas passes from the rock to the air space at the top of the can. For this reason, both the air space and the cuttings are analysed.

The analysis involves the gas chromatographic separation of the individual  $C_1-C_4$  gaseous hydrocarbons (methane, ethane, propane, isobutane and normal butane) and a partial resolution of the C5-C7 gasoline-range hydrocarbons (for their complete resolution see Section E). The ppm abundance of the five gases and of the total  $C_5-C_7$  hydrocarbons are calculated from their electronically integrated peak areas (not from peak height) by comparison with a standard.

In the report, the following data are tabulated: the abundance and composition of the air space gas, of the cuttings gas and of the combined air space and cuttings gases. The combined results are also presented graphically.

### B) SAMPLE WASHING AND HAND PICKING

All of the analyses described in subsequent sections are run on washed and hand picked samples.

Cuttings are washed to remove the drilling mud, care being taken not to remove soft clays and fine sand during the washing procedure. Using the  $C_1$ - $C_7$  hydrocarbon data profile of the well, or the organic carbon profile (if this analysis is used for screening), electric logs (if supplied) and the appearance of the cuttings under the binocular microscope, samples are selected to represent the lithological and geochemical zones penetrated by the well. These samples are then carefully hand picked and the lithology of the uncaved material is described. It is these samples which are submitted for further analysis.

Sample material remaining after analysis is retained for six months. Unless instructions are received to the contrary, Geochem Laboratories may then destroy the samples.

Our reports incorporate a gross lithological description of <u>all</u> the samples which have been analysed and litho percentage logs. As screen analyses are recommended at narrow intervals, a complete lithological profile is obtained.

#### C) ORGANIC CARBON ANALYSIS

The organic carbon content of a rock is a measure of its total organic richness. Combined with the visual kerogen,  $C_1$ - $C_7$ ,  $C_4$ - $C_7$ , pyrolysis and  $C_{15+}$  analyses, the organic carbon content is used to evaluate the potential (not necessarily actual) hydrocarbon source richness of the sediment. This analysis is an integral part of a total evaluation and it can also be used as an economical screen analysis for dry samples (when the  $C_1$ - $C_7$  analysis cannot be used).

Hand picked samples are dried, crushed and then acidised to remove the inorganic calcium and magnesium carbonates. The actual analysis involves combustion in a Leco carbon analyser. Blanks, standards and duplicates are run routinely for purposes of quality control at no extra cost to the client.

The data are tabulated and presented diagramatically in our reports in a manner which facilitates comparison with the gross lithology (see Section B) of the samples.

### D) MINI-PYROLYSIS

An ideal screen analysis which provides a definitive measure of potential source richness upon those samples whose organic carbon contents suggest fair or good source potential. This is described in detail in section K.

### E) DETAILED C4-C7 HYDROCARBON ANALYSIS

The abundance and composition of the  $C_4-C_7$  gasoline-range hydrocarbons in sediments reflects their source quality, level of thermal maturation and organic facies. In addition, the data also reveal the presence of migrated hydrocarbons and can be used for crude oil-parent source rock correlation studies.

This powerful analysis, performed upon hand picked lithologies, is employed as a follow-up to confirm the potential of samples which have been selected using the initial screen analysis. It is used in conjunction with the organic carbon, visual kerogen and  $C_{15+}$  analyses.

The individual normal paraffins, isoparaffins, naphthenes and aromatics with between four and seven carbon atoms in the molecule (but also including toluene) are resolved by capillary gas chromatography and their peak areas electronically integrated.

Normalised compositions, selected ratios and the ppm abundance of the total gasoline-range fraction are tabulated in the report and also presented graphically.

#### F) KEROGEN TYPE AND MATURATION

Kerogen is the insoluble organic matter in rocks. Visual examination of the kerogen gives a direct measure of thermal maturity and of the composition of the organic matter (organic facies) and indicates the source quality of the sediment - which is confirmed using the organic carbon, light hydrocarbon, pyrolysis and  $C_{15+}$  analyses.

The type of hydrocarbon (oil or gas) generated by a source rock is a function of the types and level of thermal maturation of the organic matter which are present. Both of these parameters are measured directly by this method.

Kerogen is separated from the inorganic rock matrix by acid digestion and flotation methods which avoid oxidation of the organic matter. It is then mounted on a glass slide and examined at high and low magnifications with a Leitz microscope. Chemical methods measure the total kerogen population but, with this technique, individual particles can be selected for examination and spurious material identified. This is particularly valuable in reworked, contaminated and turbodrilled sediments.

The following data are generated: the types of organic matter present and their relative abundances, an estimate of the proportion of reworked material, preservation state, the thermal maturity of the non-reworked organic matter using the spore colouration technique.

Our maturation scale has been developed to digitise small but recognisable changes in organic matter colouration resulting from increasing maturity and to place particular emphasis upon the immature to mature transition. In the absence of a universal colouration scale, the most significant points on our scale have been calibrated against equivalent vitrinite reflectance values. The following maturation stages are recognised at the low end of the scale:-

- a) immature; thermal index less than 2- (0.45% Ro)
- b) marginally mature; indices between 2- and 2.
   Minor hydrocarbon generation from amorphous and herbaceous (<sup>±</sup> algal) organic matter
- c) mature; indices between 2 (0.53% Ro) and 2 to 2+ (0.72% Ro), significant generation from amorphous, algal and herbaceous organic matter but wood only marginally mature
- d) oil window; indices of 2 to 2+ (0.72% Ro) through to 3 (1.2% Ro). Peak hydrocarbon generation.

The condensate zone starts at a thermal index of 3 whilst indices of 3+ (2.0% Ro) and higher indicate the eometamorphic dry gas stage.

A total of fourteen types of organic matter are sought based upon the major categories of algal, amorphous, herbaceous (spore, pollen, cuticle), wood, inertinite and resin. This detail is essential for a proper understanding of hydrocarbon source potential as the different sub-groups within each category have different properties.

Upon completion of the study, the kerogen slides are sent to the client.

#### G) VITRINITE REFLECTANCE

Vitrinite reflectance is an alternative/confirmatory method for evaluating thermal maturation which is used in conjection with the <u>visual kerogen</u> analysis. The reflectivity of vitrinite macerals increases in response to thermal alteration and is used to define maturation levels and, by projection, to predict maturity at depth or the thicknesses of section removed by erosion.

Measurements are made upon kerogen separations in conjunction with polished whole rock samples. In general, this analysis is performed upon the same samples as the visual kerogen analysis, thus facilitating a direct comparison of the two sets of results.

If possible, forty to fifty measurements are taken per sample - unless the sediments are organically lean, vitrinite is sparse or only a single uniform population is present. The data are plotted in a histogram which distinguishes the indigenous vitrinite from possible reworked or caved material. Averages are calculated for each population. Comments upon exinite fluorescence and upon the character of the phytoclasts are noted on the histograms. The reports contain the tabulated data, histograms and the reflectivities plotted against depth.

The vitrinite and visual kerogen techniques provide mutually complementary information upon maturity, organic matter type and diagenesis.

### H) C15+ EXTRACTION, DEASPHALTENING AND CHROMATOGRAPHIC SEPARATION

Sections "A" and "E" dealt with analyses covering the light end of the hydrocarbon spectrum. This section is concerned with the solvent extractable organic material in the rock with more than fourteen carbon atoms in the molecule (i.e. the heavy end). The amount and composition of this extract indicates source richness and type, the level of thermal maturation and the possible presence of migrated hydrocarbons.

These results are integrated with those derived from the pyrolysis, visual kerogen, organic carbon and light hydrocarbon analyses.

The techniques involved in this analysis employ pure solvents and have been designed to give reproducible results. Hand picked samples are ground and then solvent extracted in a soxhlet apparatus, or by blending, with dichloromethane (the solvent system can be adapted to client's specifications). After asphaltene precipitation, the total extract is separated by column chromatography or high pressure liquid chromatography into the following fractions: paraffin-naphthene hydrocarbons, aromatic hydrocarbons, eluted NSO's (nitrogen-, sulphur-, and oxygen- containing non-hydrocarbons) and non-eluted NSO's. Note that the non-hydrocarbons are split into three fractions and not reported as a gross value. These fractions can be submitted for further analyses (carbon isotopes, gas chromatography, high mass spectroscopy) including correlation studies.

For convenience and thoroughness, the data are reported in three formats: the weights of the fractions, ppm abundances and normalised percentage compositions. The data are also presented diagramatically.

### J) GC ANALYSIS OF C15+ PARAFFIN-NAPHTHENE HYDROCARBONS

6

The gas chromatographic configurations of the heavy  $C_{15+}$  paraffinnaphthene hydrocarbons reflect source type, the degree of thermal maturation and the presence and character of migrated hydrocarbons or contamination.

Not only is this analysis an integral part of any source rock study but it also provides a fingerprint for correlation purposes and helps to define the geochemical/palynological environmental character of the source rocks from which crude oils were derived.

The paraffin-naphthene hydrocarbons obtained by column chromatography are separated by high resolution capillary chromatography. Excellent resolution of the individual normal paraffins, isoprenoids and significant individual isoparaffins and naphthenes is achieved. Runs are normally terminated at nC35. A powerful in-house microprocessor system is being introduced to correct for the change in response factor with chain length.

The normal paraffin carbon preference indices (C.P.I.) indicate if odd (values in excess of 1) or even (values less than 1) normal paraffins are dominant. Strong odd preferences (± strong pristane peaks) are characteristic of immature land plant organic matter whilst even preferences (± strong phytane peaks) suggest a reducing environment of deposition. With increasing maturity, values approach 1.0 and oils are typically close to 1.0. The indices are calculated using the following formulae:

C.P.I<sub>A</sub> = 
$$\frac{c_{21} + c_{23} + c_{25} + c_{27}}{c_{20} + c_{22} + c_{24} + c_{26}}$$
 +  $\frac{c_{21} + c_{23} + c_{25} + c_{27}}{c_{22} + c_{24} + c_{26} + c_{28}}$   
C.P.I<sub>B</sub> =  $\frac{c_{25} + c_{27} + c_{29} + c_{31}}{c_{24} + c_{26} + c_{28} + c_{30}}$  +  $\frac{c_{25} + c_{27} + c_{29} + c_{31}}{c_{26} + c_{28} + c_{30} + c_{32}}$ 

Chromatograms are reproduced in the report for use as visual fingerprints and in addition, the following data are tabulated: normalised normal paraffin distributions; proportions of paraffins, isoprenoids and naphthenes in the total paraffin-naphthene fraction; C.P.I<sub>A</sub> and C.P.I<sub>B</sub>; pristane to phytane ratio; pristane to  $nC_{17}$  ratio.

### K) PYROLYSIS

The process of thermal maturation can be simulated in the laboratory by pyrolysis, which involves heating the sample under specified conditions and measuring the oil-like material which is freed/generated from the rock. With this analysis, the potential richness of immature sediments can be determined and, by coupling the pyrolysis unit to a gas chromatograph, the liberated material can be characterised. These results are correlated with those obtained from the organic carbon, kerogen and  $C_{15+}$  analyses.

Small amounts of powdered sample are heated in helium to release the thermal bitumen (up to 340°C) and pyrolysate (340-550°C). The thermal bitumen correlates with the solvent extractable material (see above) whilst the pyrolysate fraction does not exist in a "free" state but is generated from the kerogen, thus simulating maturation in the subsurface. Abundances (weight ppm of rock) are measured with a flame ionisation detector against a standard. Thermal bitumen includes source indigenous, contaminant and migrated hydrocarbons but the pyrolysate abundance is a measure of ultimate source richness. The capillary gas chromatogram of the pyrolysate is used to evaluate the character of the parent organic matter and whether it is oil or gas prone. Peak temperature(s) of pyrolysate evolution is recorded. Carbon dioxide can be measured if requested but is normally ignored as the separation of the organic and inorganic species has been found to be artificial and unreliable.

Pyrolysate yields provide a definitive measure of potential source richness which avoids the ambiguities of the organic carbon data and the problem of contamination. This analysis is also used to evaluate the quality and character of the organic matter and the degree to which it has realised its ultimate hydrocarbon potential. Geochem does not employ the pyrolysis technique to evaluate maturation, preferring the kerogen and vitrinite reflectance analyses which avoid the problem of reworking and hence, are more reliable.

Capillary chromatograms produced for the pyrolysate hydrocarbons range from C1 (methane) out towards C35 but exhibit considerable variations. They are used to define whether a source rock will yield oil, condensate or gas. With this new technique, it is now possible to complete the evaluation of a source rock.

The data are tabulated and presented graphically. MINI-PYROLYSIS includes ppm thermal bitumen and ppm pyrolsate. PYROLYSIS also provides the above together with the temperature of peak pyrolysate evolution. The capillary chromatograms of the pyrolysate obtained by PYROLYSIS-GC are reproduced in the report. The Mini-Pyrolysis analysis is recommended as a screening technique.

### L) CORRELATION STUDY ANALYSES

Oil to oil and oil to parent source rock correlation studies require high resolution analytical techniques. This requirement is satisfied by some of the analyses discussed above but others have been selected specifically for correlation work. Many of these analyses also provide information upon the character of the environment of deposition of the parent source rocks.

- detailed  $C_4-C_7$  hydrocarbon (gasoline range) analysis. See Section E. Although these hydrocarbons can be affected by migrational/alteration processes, they commonly provide a very useful correlation parameter.
- capillary gas chromatography of the C15+ paraffin-naphthenes.
   See section J. The branched<sup>±</sup>normal paraffin distributions are used to "fingerprint" the samples.
- capillary chromatograms of whole oils and of the  $\rm C_{\rm 8+}$  fraction of source rocks.
- capillary gas chromatography of  $C_{15+}$  aromatic hydrocarbons. Separate chromatograms of the hydrocarbons and of the sulphurbearing species are reproduced.
- high pressure liquid chromatograms.
- mass spectrometric carbon isotope analyses of crude oil and rock extract fractions and of kerogen separations. A powerful tool for comparing hydrocarbons and correlating hydrocarbons to organic matter. With this technique the problem of source rock contamination can be avoided. The data are recorded on x-y or Galimov plots.
- mass fragmentograms (mass chromatograms) of fragment ions characteristic of selected hydrocarbon groups such as the steranes and terpanes. The fragmentograms provide a convenient and simple means of presenting detailed mass spectrometric data and are used as a sophisticated fingerprinting technique. This provides the ultimate resolution for correlating hydrocarbons and facilitates the examination of hydrocarbon classes.
- vanadium and nickel contents.

Suites of (rather than single) analyses are employed in correlation studies, the actual selection depending upon the complexity of the problem. See also section N.

### M) ANALYSES FOR SPECIAL CASES

#### M-1) ELEMENTAL KEROGEN ANALYSIS

This analysis evaluates source quality, whether the sediments are oil or gas prone, the character of the organic matter and its level of thermal maturation. It is the chemical equivalent of the visual kerogen analysis. The pyrolysis analysis is generally preferred to this technique, both methods providing similar information.

#### M-2) SULPHUR ANALYSIS

The abundance of sulphur in source rocks and crude oils.

### M-3) CARBONATE CONTENT

The mineral carbonate content of sediments is determined by acid treatment. These data are particularly useful when used in conjunction with organic carbon contents as a screening technique.

### M-4) NORMAL PARAFFIN ANALYSIS

Following the removal of the branched paraffins and naphthenes from the total paraffin-naphthene fraction, a chromatogram of the normal paraffins is obtained. The resulting less complicated chromatogram facilitates the examination of normal paraffin distributions.

### M-5) SOLID BITUMEN EVALUATION

Residual solid bitumen after crude oil is generated by three prime processes: the action of waters, gas deasphalting, thermal alteration. Thus it provides a means of determing the reservoir history of a crude and of evaluating whether adjacent traps will or will not be prospective for oil. In carbonate sections, where organic matter is sometimes sparse, this technique is also used to evaluate thermal maturation levels.

The analysis involves the determination of the solubility (in  $CS_2$ ) of the solid bitumen and of the atomic hydrogen to carbon ratio of the insoluble fraction.

N) CRUDE OIL ANALYSIS

N-1) API GRAVITY

E.

This can be performed upon large (hydrometer) and small (SG bottle, pycnometer) samples and even upon stains extracted from sediments (refractive index).

N-2) SULPHUR CONTENTS (ASTM E30-47)

N-3) POUR POINT (ASTM D97-66, IP15/67)

N-4) VISCOSITY (ASTM D445-72, IP71/75)

N-5) FRACTIONAL DISTILLATION

Graph of cumulative distillation yield against temperature. Five percent cuts taken for further analysis. Mass spectrometric studies of these fractions provide a detailed picture of the distribution of paraffins and of the various naphthene and aromatic groups within a crude, which is useful both for correlation and for refinery evaluation purposes.

### KEY TO PRINCIPAL COMPONENTS IN

### CRUDE OIL 20-210°C FRACTIONS

- 1. iso-butane
- 2. n-butane
- 3. iso-pentane
- 4. n-pentane
- 5. 2,2-dimethylbutane
- 6. cyclopentane
- 7. 2,3-dimethylbutane
- 8. 2-methylpentane
- 9. 3-methylpentane
- 10. n hexane

()

( :)

- 11. methylcyclopentane
- 14. benzene
- 16. cyclohexane
- 17. 2-methylhexane
- 19. 3.methylhexane
- 20. 1,C,3-dimethylcyclopentane
- 21. 1,t,3-dimethylcyclopentane
- 22. 1,t,2-dimethylcyclopentane
- 24. n heptane
- 26. methylcyclohexane
- 27. trimethylcyclopentane
- 28. ethylcyclopentane
- 29. dimethylhexane
- 30. dimethylhexane
- 31. trimethylpentane

- 33. trimethylcyclopentane
- 35. toluene
- 39. 2-methylheptane
- 40. 4-methylheptane
- 42. 3-methylheptane
- 43. ethylhexane
- 44. cycloheptane
- 47. dimethylcyclohexane
- 49. dimethylcyclohexane
- 50. n-octane
- 55. methylheptane
- 56. dimethylcyclohexane
- 61. ethylbenzene
- 63. p-xylene
- 64. m-xylene
- 68. alkylcyclohexene
- 69. O-xylene
- 73. n-nonane
- 77. cumene
- 78. alkylcyclohexane
- 79. isoparaffin
- 88. n-decane
- 89. p-cymene
- 94. n-undecane



 $( \ )$ 

ř,





#### WELL 35/3-2

# SAMPLE 29 DST 2

RIMETHYL NAPHTHALENES

ALKYL NAPHTHALENES

HENANTHRENE AND METHYL PHENANTHRENES

## C15+ BRANCHED CYCLICS



WELL 35/3-2

# SAMPLE 29

# DST 2

# m/e 191

## m/e 217

## m/e 259

·

(·1025

Mand. 0.78 (50.5.70). - 2000 0.619 Jun - 2000 0.619 Jun 

Fr E/SE

 $\hat{}$ 

35/3-2 hendensel



.

Parolline 68.5 { 89.7 partini 2.7 isopravad +martin Aromaler. 24.4. NSO 64.7.

the real state of the state of the

· #.

adding a constant of the first · 两个"新闻" · 两部 · 思议 (1、 古林)上来了 · 正讲第一 · · 著

1.

1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 -· · · · · 4 4 8