

GEOCHEMICAL STUDIES ON OILS AND GASES FROM NORWEGIAN NORTH SEA WELLS 2/2 - 1, 2/2 - 2, 2/1 - 3 AND 7/12 - 4.

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ROBERTSON RESEARCH INTERNATIONAL LIMITED

Saga Petroleum a.s. INFORMASJONSSENTRET

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GEOCHEMICAL STUDIES ON OILS AND GASES FROM NORWEGIAN NORTH SEA WELLS 2/2 - 1, 2/2 - 2, 2/1 - 3 AND 7/12 - 4.

by

C. DARLINGTON

PROJECT NOS. RRPS/834/D/25188 RRPS/834/D/25197

Prepared by:

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

Sega Petroleum A/S, Maries vei 20, P.O. Box 9, N - 1322 Hovik, Norway,

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ROBERTSON RESEARCH

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INTRODUCTION

Two oil samples, from the 2/1-3 and 7/12-4 wells were received for geochemical analysis on 21/12/82 and correlation to an oil sample from the 2/2-1 well, previously analysed and reported in Robertson Research International Limited Report No. 4942P/D. Subsequently a further oil sample from the 2/2-1 well and a gas sample from the 2/2-2 well were received for analysis on 9/2/83 and the results are discussed in this report. The initial oil sample from the 2/2-1 well has been labelled "Oil 1" and the later sample "Oil 2". A gas sample from the 2/2-1 well analysed previously is also discussed in this report. Data acquisition were completed and the results dispatched to the client on 31/3/83.

The analytical programme for the oils was as follows:

1. Whole Oil

*API gravity Sulphur, Nickel and Vanadium content C_1-C_4 gaseous hydrocarbon analysis C_4-C_7 gasoline hydrocarbon analysis Asphaltene precipitation Oil topped at 60°C.

2. Topped Oil

Quantitative column chromatography Gas chromatography of normal alkanes, branched/cyclic alkanes and aromatics Gas chromatography - mass spectrometry of alkanes

3. Isotope Studies

Carbon isotope ratio analysis of alkane and aromatic fractions of oils Carbon isotope and Deuterium isotope ratios of C_1-C_4 gases where gas abundances were sufficient.

Gas analyses included: Resolution of C_1-C_4 gaseous hydrocarbons. Carbon isotope and Deuterium isotope ratios of C_1-C_4 gases where gas abundances

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were sufficient.

Robertson Research staff involved in this study were:

P.C. Barnard - Chief Geochemist
C. Darlington - Project Co-ordinator

We would like to acknowledge the co-operation of Mr. T.O. Throndsen who has been our contact with Saga Petroleum A/S during this study.



RESULTS AND INTERPRETATION

A. OILS

1. Bulk Properties (Tables 1-4).

All four oils have generally similar °API gravities, ranging from 40.3 to 45.6, in the lower half of the light oil range. The two oils from the 2/2-1 well are most similar in °API gravity, 44.2 and 45.6, and are slightly lighter than the 2/1-3 and 7/12-4 oils which have °API gravities of 42.7 and 40.3 respectively. Nickel, Vanadium and Sulphur contents of all four oils are very low.

2. Gas Contents (Tables 1-4)

All four oils show very similar gas compositions but are particularly lean in methane and ethane, probably as a result of losses during sub-sampling due to high volatility. Propane, iso-butane and normal butane compositions are similar with low ratios of 0.13 to 0.30 for the iso-butane to normal butane ratio. This may be an indication of generation from the same source rock and also shows that these gases are associated with the main phase of oil generation from the source rock.

3. Gasoline Contents (Tables 1-4 and 7)

All four oils show generally similar group compositions of aromatics, normal, iso- and branched chain alkanes. Individual component abundances are also very close, except that the two 2/2-1 oils and the 2/1-3 oil show more affinities to each other than to the 7/12-4 oil (Table 7). Ratios of paired components such as iso-pentane to normal pentane and benzene to methyl cyclohexane indicate that all four oils may have been generated at similar levels of maturity, chiefly in the middle mature oil generation zone (equivalent to spore colour index range 4.5 to 6).

4. Oil Composition by Column Chromatography (Tables 1-4)

Each of the four oils was topped at 60°C prior to column chromatographic separation into alkanes, aromatics and polar compounds (asphaltenes and resense). Though the amount of oil lost by topping is rather variable, 21.0% to



33.3%, the group percentages of the three components are broadly similar. The most important variation is that the 2/2-1 oils contain rather more aromatic compounds, 13.0% and 13.4%, than the 2/1-3 oil, 8.2% and the 7/12-4 oil, 8.4%. This difference could be due to variation in source rock type given that the oils all appear to have been generated at about the same level of maturity. The asphaltene content of all four oils is low but shows some variation, ranging from 0.7% to 2.2%.

5. Gas Chromatography

a. Normal Alkanes and Isoprenoids (Figures 1A-D)

The normal alkanes for all four oils show broad overall ranges with maxima and highest individual component abundances in the shorter chain length <u>n</u>-alkanes range particularly below <u>n</u>-Cl7. The two 2/2-1 oils gave very similar chromatograms with fairly uniform abundances of <u>n</u>-alkanes in the <u>n</u>-C₁₇ to <u>n</u>-C₂₅ region and a slight odd-over-even chain length preference.

The 2/1-3 and 7/12-4 oils show a more rapid drop off in <u>n</u>-alkanes abundance between <u>n</u>-C₁₇ and <u>n</u>-C₂₅ and virtually no odd-over-even carbon chain length preference. The isoprenoids appear more abundant in the 2/1-3 and 7/12-4 oils relative to the normal alkanes. Pristane to phytane and isoprenoid to normal alkane ratios are given below for these four oils and for oils from this region of the Norwegian North Sea (Southern Offshore Norway: Phase Two Study: Robertson Research International Limited 1981).

<u>Oil/Field</u>	Pristane/Phytane	Pristane/ <u>n</u> -C ₁₇	Phytane/ <u>n</u> -C ₁₈
2/2-1 011 1	2.36	0.35	0.17
2/2-1 Oil 2	2.22	0.44	0.20
2/1-3 Oil	1.23	0.49	0.51?
Valhall	1.40	0.53	0.50
Hod	1.38	0.57	0.47
Ekofisk	1.23	0.41	0.36
7/12-4 Oil	1.30	0.34	0.31
Ula	1.35	0.39	0.35
S.E. Tor	1.43	0.35	0.29
Edda	1.57	0.37	0.29

Comparison of these ratios suggests that the 2/2-1 oils are distinctly different



from either the 2/1-3 or 7/12-4 oils or any other oils in the vicinity, principally due to the particularly low abundance of phytane. On the basis of normal alkane/isoprenoid content the 7/12-4 oil is typical of that of the Ula and the Tor and Edda Fields. The 2/1-3 oil shows some similarities to Valhall, Hod and possibly Ekofisk.

b. Branched and Cyclic Alkanes (Figures 2A-D)

The chromatograms of the 2/2-1 oils are very similar except for slight variations in the relative abundance of some of the lower molecular weight components as cyclo-octane and farnesane. The 2/1-3 and 7/12-4 oils have much higher abundances of the lower molecular weight compounds, up to iso- C_{16} compared to the higher isoprenoids than in the 2/2-1 oils.

c. Aromatics (Figures 3A-D)

The 2/2-1 oils are seen to contain similar abundances of aromatic compounds with alkylated naphthalenes much more abundant than alkylated phenanthrenes. Conversely the 2/1-3 and 7/12-4 oils, though containing very similar abundances of the aromatic compounds, show alkylated phenanthrenes to be more abundant than alkylated naphthalenes. The differences in the relative amounts of these compounds may be due to their generation from organic matter with different steroid or terpenoid composition.

6. Carbon and Deuterium Isotope Ratio Data (Tables 1-4)

Generally insufficient amounts of gases could be isolated from the oils for isotope analysis though some data of interest were obtained. Almost identical ethane and propane δ^{13} C values relative to PDB (PDB = Pee Dee Belemnite Standard) of $-34.7^{\circ}/\circ o$ and $-32.1^{\circ}/\circ o$ were recorded from the 2/1-3 oil and $-35.8^{\circ}/\circ o$ and $-31.7^{\circ}/\circ o$ for the 2/2-1 Oil 2. These values are typical of gases generated thermogenically from a mature source rock. The 2/2-1 Oil 2 also gave a δ^{13} C value of $-46.2^{\circ}/\circ o$ for methane, quite unlike that for the gas sample from the 2/2-1 well of $-64.8^{\circ}/\circ o$. These and other isotope data for the oils are discussed in more detail together with the gas data in part B of this report.

Carbon isotope ratio analysis was also conducted on the column chromatographically separated alkane and aromatic fractions and the data are presented below together with comparable data for other oils from this area



(Southern Offshore Norway: Phase Two Study: Robertson Research International Limited 1981).

Oil/Field	§ ¹³ C Alkanes ^O /oo(PDB)	5 ¹³ C Aromatics ⁰ /00(PDB)
2/2-1 Oil 1	-27.4	-26.1
2/2-1 Oil 2	-27.7	-26.4
Valhall	-27.6	-27.0
Hod	-27.7	-27.5
2/1-3 Oil	-28.5	-28.2
Ekofisk	-28.5	-27.4
7/12-4 011	-29.4	-28.6
Edda	-29.4	-28.4
S.E. Tor	-29.9	-28.4

The 2/2-1 oils are isotopically less negative than any of the other oils from the area, except maybe Valhall and Hod. The 7/12-4 oil (Ula) has 13 C ratios which are close to those of Edda and S.E. Tor oils. The alkane fraction of the 2/1-3 oil gave values almost identical to Ekofisk oil though the aromatic fraction gave a considerably more negative value, more in line with that of Edda or S.E. Tor oils. The \$¹³C data suggest that the 2/2-1 oils are derived from a mixture either of waxy sapropel and lagoonal sapropel (2:1) or waxy sapropel and marine algal sapropel (1:4) (Robertson Research International Limited Report No. 4942P/D). The 2/2-1 oils contain a significant marine organic matter derived component. The 2/1-3 oil is less strongly influenced by marine organic matter and may be derived from near equal proportions of waxy sapropel of terrestrial origin and marine algal sapropel. The 7/12-4 oil appears even more subject to the influence of a terrestrial organic matter source.

7. <u>Gas Chromatography - Mass Spectrometry</u> (Figures 4A-D, 5A-D, 6A-D, 7A-D) Examination of the mass fragmentograms of the 2/2-1 oil shows almost identical distributions of triterpanes at M/e 191 and very similar patterns of steranes and re-arranged steranes, M/e 217 and M/e 259, respectively. The distribution of triterpanes and steranes in the 2/1-3 oil is quite different to that of the 2/2-1 oils but is similar to that of the 7/12-4 oil even though these components are less abundant. The ratio of triterpanes to steranes and re-arranged steranes in the 2/1-3 and 7/12-4 oils is similar.



For other fragment ions a similar situation is seen with the two 2/2-1 oils similar to each other but quite different from the 2/1-3 and 7/12-4 oils.

Comparison of these spectra to those of other oils from this area indicates the similarity between the 7/12-4 oil (Ula) and the Edda and Tor oils (Southern Offshore Norway: Phase Two Study: Robertson Research International Limited 1981). The 2/1-3 oil may also be included in this group. The 2/2-1 oil triterpane pattern is very similar to that of the Hod and Valhall oils though the sterane and re-arranged sterane patterns show minor differences.

B. GASES (Tables 5 and 6)

1. Gas Composition

The compositions of the gases from the 2/2-1 and 2/2-2 wells are virtually identical both being almost dry with over 98% methane. Iso-butane to normal butane ratios are also very similar at 2.4 for the 2/2-1 well and 2.8 for the 2/2-2 well, ratios usually attributed to gas associated with petroleum generation from mature source rocks.

2. Isotope Studies

The strongest point of departure between the 2/2-1 and 2/2-2 gases is in the difference in the ${}^{13}C$ and D values of the methane component. The ${}^{13}C$ value of $-64.8^{\circ}/\circ\circ$ for methane from the 2/2-1 well indicates a biogenic source while that of $-38.2^{\circ}/\circ\circ$ for the 2/2-2 gas suggests that methane is thermogenic. Deuterium isotope values show comparable differences. Sufficient amounts of ethane and propane for isotope examination could only be prepared from the 2/2-1 gas. These results indicated that the gas from this well is likely to be a mixture of biogenic methane and thermogenically derived ethane, propane and butane generated either from an early mature gas source or mature oil source.

It is of interest to compare these data with those obtained on the gaseous components of the 2/2-1 Oil 2 and 2/1-3 oil. The data for methane, ethane and propane of both oils are similar and close to the values for the 2/2-2 gas and the ethane and propane components of the 2/2-1 gas. Only the methane component of the 2/2-1 gas appears to have originated through biogenic processes rather than a process of thermal generation from a mature source rock.



CONCLUSIONS

III

The following conclusions have been reached from a study of oils and gases from the 2/2-1, 2/2-2, 2/1-3 and 7/12-4 wells.

- 1. All four oils examined are non-biodegraded, generated from well matured source rocks and show many general similarities.
- Differences in the detailed composition of the oils have been found mainly contrasting the 2/2-1 oils with the 2/1-3 and 7/12-4 oils.
- 3. The 2/1-3 and 7/12-4 oils show similarities to most other oils in this region of the southern part of the Norwegian North Sea such as Ula, Tor and Edda.
- 4. The 2/2-1 oils show differences in detailed composition to most oils from this area but some affinities to Valhall and Hod oils.
- 5. The original organic source material of the 2/2-1 oils contains a substantial component of marine algal, or lagoonal material while that of the 2/1-3 and particularly the 7/12-4 is influenced more strongly by terrestrial derived waxy organic matter.
- 6. The wet gas components of the 2/2-1 and 2/2-2 gases and the wet gas components of the 2/2-1 and 2/1-3 oils show similarities in that all were thermally generated probably in association with petroleum generation.
- 7. The methane component of the 2/2-1 oil and the 2/2-2 gas are predominantly thermogenic in origin but the methane component of the 2/2-1 gas appears to be biogenic in origin.



OIL ANALYSIS DATA

COMPANY: SAGA WELL: 2/2-1 OIL1 LOCATION: NORWEGIAN NORTH SEA 1. Percentages of gaseous components in $C_1 - C_4$ fraction **METHANE** 0.5% ETHANE 0.7% 21.9% PROPANE i-BUTANE 12.7% 64.7% n-BUTANE Total Abundance 25600ppm i-butane : n-butane ratio 0.20 2. Group percentages of components of gasoline fraction AROMATICS 6.8% NORMAL ALKANES 35.4% ISO-ALKANES 24.4% CYCLO ALKANES 33.5% 3. Amount of oil lost after topping = 21.6% Group percentages of oil fraction by column chromatography after topping 4. 65.3% ALKANE S AROMATICS 13.4% 4.0% POLARS TOTAL RECOVERED 82.7% 5. Asphaltene content by precipitation = 1.1% Carbon isotope ratio. data for oils (δ^{13} C °/°° PDB) 6. Alkane Fraction -27.4°/00 Aromatic Fraction-26.1º/.. 7. Density 0.8055 Kg/litre at 15C = 44.2 API Sulphur in oil = 0.15%8. 9. Nickel and Vanadium Contents Ni = < lmg/litre V = < lmg/litre (Note PDB = Pee Dee Belemite Standard)

COMPANY: SAGA WELL: 2/2-1 OIL 2 LOCATION: NORWEGIAN NORTH SEA 1. Percentages of gaseous components in $C_1 - C_4$ fraction ME THANE 0.2% ETHANE 1.7% 24.1% PROPANE 17.3% i-BUTANE i-BUTANE 56.5% Total Abundance 36200ppm i-butane : n-butane ratio 0.30 2. Group percentages of components of gasoline fraction AROMATICS 4.6% NORMAL ALKANES 41.8% ISO-ALKANES 27.0% CYCLO ALKANES 26.7% 3. Amount of oil lost after topping= 33.3% 4. Group percentages of oil fraction by column chromatography after topping ALKANE S 63.9% AROMATICS 13.0% 7.3% POLARS TOTAL RECOVERED 84.2% 5. Asphaltene content by precipitation = 2.2% 6. Density 0.799 kg/litre at $60^{\circ}F = 45.6^{\circ}API$ 7. Sulphur in oil = 0.12%8. Nickel and Vanadium Contents Ni = 2mg/litre v = <lmg/litre</pre> 9. Carbon isotope ratio data for oils (δ^{13} C °/ $_{\circ\circ}$ PDB) -27.7 °/.. (PDB)* Alkane Fraction Aromatic Fraction -26.4 °/ .. (PDB)* 10. Carbon and Deuterium isotope ratio data for gaseous components of oil Methane $\begin{cases} 13 \\ 13C -46.2 \\ 13C -35.8 \\ 10C -35.8 \\ 10C -31.7 \\ 1$ Propane δ D-151°/ $_{\circ\circ}$ (SMOW) * very small samples Note SMOW = Standard Mean Ocean Water Standard)

COMPANY: SAGA WELL: 2/1-3LOCATION: NORWEGIAN NORTH SEA 1. Percentages of gaseous components in $C_1 - C_{L}$ fraction ME THANE 0.8% **E**THANE 1.5% PROPANE 23.8% 13.0% i-BUTANE n-BUTANE 60.8% Total Abundance 13200 ppm i-butane : n-butane ratio 0.21 2. Group percentages of components of gasoline fraction AROMATICS 4.3% NORMAL ALKANES 41.1% **ISO-ALKANES** 28.5% CYCLO ALKANES 26.2% 3. Amount of oil lost after topping = 28.0% 4. Group percentages of oil fraction by column chromatography after topping 66.7% ALKANES AROMATICS 8.2% POLARS 6.4% TOTAL RECOVERED 81.3% 5. Asphaltene content by precipitation = 0.7% 6. Density 0.812 Kg/litre at 60°F = 42.7 °API 7. Sulphur in oil = 0.13% 8. Nickle and Vanadium Contents Ni = 3mg/litre V = < lmg/litre 9. Carbon isotope ratio data for oils $(\delta^{13}C^{\circ}/_{\circ\circ}PDB)$ -28.5 °/.. Alkane Fraction Aromatic Fraction -28.2 °/... 10. Carbon isotope ratio data for gaseous components of oil (δ^{13} C °/_{••}PDB) -34.7°/... Ethane Propane -32.1°/..

TABLE 3

WELL: 7/12-4 COMPANY: SAGA LOCATION: NORWEGIAN NORTH SEA 1. Percentages of gaseous components in C_1-C_4 fraction METHANE Trace ETHANE Trace PROPANE Trace i-BUTANE 11.4% 88.6% n-BUTANE Total Abundance 3650 ppm i-butane : n-butane ratio 0.13 2. Group percentages of components of gasoline fraction AROMATICS 6.5% NORMAL ALKANES 35.3% ISO-ALKANES 26.0% CYCLO ALKANES 32.2% 3. Amount of oil lost after topping = 21.0% 4. Group percentages of oil fraction by column chromatography after topping ALKANE S 68.6% 8.4% AROMATICS POLARS 6.3% TOTAL RECOVERED 83.3% 5. Asphaltene content by precipitation = 1.30% Carbon isotope ratio data for oil $(S^{13}C^{\circ}/_{\circ\circ})$ (PDB) 6. Alkane Fraction - 29.4 °/ ... Aromatic Fraction - 28.6 °/ ... 7. Density 0.823 Kg/litre at 60°F = 40.3 °API 8. Sulphur in oil = 0.09%9. Nickel and Vanadium Contents 4mg/litre Ni = = < lmg/litre V

GAS ANALYSIS DATA

COMPANY: SAGA

WELL: 2/2-1 LOCATION: NORWEGIAN NORTH SEA

Gas Sample Composition, Carbon and Deuterium Isotope Ratios

Gaseous Component δ^{13}_{C} °/. (PDB) $\delta D(^{\circ}/^{\circ})(SMOW)$

METHANE	98.2%	-64.8	-214
ETHANE	1.0%	-38.3	*
PROPANE	0.5%	-30.4-	*
i-BUTANE	0.2%	-	-
n-BUTANE	0.1%	-	-
n-BUTANE	0.1%	-	-

<u>i</u>-butane : <u>n</u>-butane ratio 2.4 measured separately

* insufficient ethane and propane concentrations for measurement of $\delta\,D$

COMPANY: SAGA

WELL: 2/2-2

LOCATION: NORWEGIAN NORTH SEA

Gas Sample Composition, Carbon and Deuterium Isotope Ratios

Gaseous Component		δ^{13} C°/ $_{\circ\circ}$ (PDB)	δD °/ 。。(Smow)
METHANE	98.2%	-38.2	-153	
ETHANE	0.9%	-	-	
PROPANE	0.6%	-	-	
i-BUTANE	0.2%	-	-	
n-BUTANE	0.1%	-	-	

<u>i</u>-butane : <u>n</u>-butane ratio 2.8 measured separately

COMPANY: SAGA

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DEPTH: OIL SAMPLES	OIL 1 2/2-1	OIL 2 2/2-1	2/1-3	7/12-4			
GASOLINE HYDROCARBON Components	RELA	TIVE GASO	LINE HYDR	OCARBON C	OMPONENT	ABUNDANCES	; (%)
<u>i</u> -BUTANE	1.4	4.5	3.3	0.5			
<u>n</u> -BUTANE	7.0	14.7	15.3	4.1			
<u>_i</u> – PENTANE	8.6	9.4	10.1	6.6			
<u>n</u> -PENTANE	10.4	11.0	11.3	9.0			
2, 2 – DIMETHYL BUTANE	0.1	0.1	0.2	0.2		1	
CYCLOPENTANE	1.9	1.7	2.0	1.5			
2, 3 – DIMETHYL BUTANE	0.5	0.6	0.6	0.7			
2 – METHYL PENTANE	4.6	4.5	4.8	5.4		1	
3 – METHYL PENTANE	2.8	2.6	3.4	3.5			
<u>n</u> – HEXANE	9.5	9.2	8.8	11.8		1 1	
2, 2 - DIMETHYL PENTANE / METHYL CYCLOPENTANE	6.7	5.9	6.0	6.5			
2, 4 - DIMETHYL PENTANE	0.3	0.5	0.4	0.7			
BENZENE	2.2	1.9	1.6	2.5			
3, 3 - DIMETHYL PENTANE	0.0	*	*	0.1			
CYCLOHEXANE	7.0	5.9	5.2	6.4			
2 – METHYL HEXANE	2.7	2.7	3.1+	4.6+			
1, 1 - DIMETHYL CYCLOPENTANE	0.6	0.5	0.5	0.6			
3-METHYL HEXANE	2.6	2.1	2.6	3.7			
1, cis – 3 – DIMETHYL CYCLOPENTANE	1.3	1.0	1.1	1.3			
1, trans – 3 – DIMETHYL CYCLOPENTANE	1.1	0.9	1.0	1.3	1		
1, <i>trans</i> — 2 — DIMETHYL CYCLOPENTANE	2.2	1.5	1.9	2.1			
3 – ETHYL PENTANE	0.0	*	*	*			
<u>л</u> -нертале	8.5	6.9	5.7	10.4			·····
1, <i>cis</i> – 2 – DIMETHYL CYCLOPENTANE / METHYL CYCLOHEXANE	12.3	9.0	7.9	11.9			
ETHYL CYCLOPENTANE	0.5	0.3	0.6	0.6			
TOLUENE	4.6	2.7	2.7	4.0			
TOTAL ABUNDANCE (ppb)	364000	139300	52700	79600			
ORGANIC CARBON (%)							
GASOLINE ABUNDANCE AT 1% ORGANIC CARBON			<u> </u>				

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

 TABLE
 7
 Gasoline Hydrocarbon Analysis Data

FIGURES 1,2 AND 3 GAS CHROMATOGRAMS OF OILS

FIGURE	WELL	CHROMATOGRAM TYPE
1A	2/2-1 OIL 1	Normal Alkanes
18	2/2-1 OIL 2	11
1C	2/1-3	tt
1D	7/12-4	"
2 A	2/2-1 OIL 1	Branched/Cyclic Alkanes
2B	2/2-1 OIL 2	"
2C	2/1-3	11
2D	7/12-4	11
3 A	2/2-1 OIL 1	Aromatics
3B	2/2-1 OIL 2	11
3C	2/1-3	11
3D	7/12-4	tt

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KEY TO NOTATION ON AROMATIC AND

BRANCHED/CYCLIC GAS CHROMATOGRAMS

1. AROMATIC COMPOUNDS

- METHYL NAPHTHALENES Α.
- B. DI METHYL NAPHTHALENES
- с. TRI METHYL NAPHTHALENES
- METHYL FLUORENES D.
- PHENANTHRENES Ε.
- F. METHYL PHENANTHRENES
- G. DI METHYL PHENANTHRENES

2. BRANCHED/CYCLIC COMPOUNDS

- Pr. PRISTANE
- Ph. PHYTANE
- Α. ISO C14
- ISO C₁₅ (FARNESANE) Β.
- C.
- ISO C¹⁶ ISO C¹⁶₁₈ (NORPRISTANE) D.

CYCLIC DERIVATIVES

7 = CYCLO-HEPTANE

8 = CYCLO-OCTANE etc.



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(Scale values refer to normal alkane carbon chain lengths)







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FIGURES 7A-7D

MASS FRAGMENTOGRAMS AT M/e 183; (ISOPRENOIDS/BRANCHED ALKANES), M/e 203; (STERANES)AND M/e 253; (AROMATISED STERANES).

2.

COMPANY:	SAGA		LOCATION:	NORWEGIAN	NORTH	SEA
FIGURE		WELL		SAMPLE TYP	PE .	
7 A		2/2-1		OIL 1		
7B		2/2-1		OIL 2		
7C		2/1-3		OIL		
7D		7/12-4		OIL		

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This appendix summarises the main steps in the analyses carried out in the Robertson Research geochemistry laboratories. Conditions for chemical analyses are given and interpretation guidelines are defined. Techniques may in certain circumstances be adapted to suit particular samples or conditions.

1. Sample Preparation

Following airspace gas analysis of the canned samples, the cuttings are washed. After setting aside a wet sub-sample for gasoline analysis, the remainder i oven-dried at 50°C and described. Obvious cavings and particulate contaminants are removed and the significant lithologies hand-picked for organic carbon screening analysis. Coals if present are picked for vitrinite reflectivity measurement and splits of the total cuttings are made for the preparation of kerogen concentrates. Subsequently the bulk samples except those containing much loose sand or coal are crushed to pass through a 250 micron (60 - mesh) sieve and submitted for organic carbon screening analysis.

2. Maturity Evaluation

Maturation is assessed by measurement of spore colour and vitrinite reflectivity and the analysis of airspace gas and gasolines. Keregen concentrates for microscopic analysis are prepared using standard palynological procedures (i.e. acid maceration) but without oxidation and acetolysis. Mineral residues, particularly pyrite, are separated from the kerogen by a combination of ultrasonic vibration and zinc bromide flotation. For spore colour measurement and kerogen typing, mounts are prepared of both the total kerogen and the coarserthan-20-micron size fraction. Sample blocks for measurement of vitrinite reflectivity are prepared by mounting the coarser-than-20-micron kerogen fraction in an epoxy resin, followed by polishing with carborundum and alumina.

Airspace Gas Analysis

If samples of wet cuttings are collected at the well-site and sealed in an airtight can, the headspace gases can be analysed in the laboratory to provide a rapid assessment of maturity. The gas is extracted from the sealed can using a can piercer fitted with a septum and analysed by gas liquid chromatography. The proportions of methane, ethane, propane and butane are calculated by comparison with a standard mixture of these gases. Methane is usually the dominant gas and comprises 90-100% from immature sediments and 30-70% from mature sediments. Abrupt departures from composition/depth trends may indicate faults with migrant gases or reservoir rocks.

Gasoline Analysis

Cuttings samples received wet, preferably in sealed containers, are suitable for gasoline analysis. A portion of the washed cuttings sample is retained wet, pulverised in a sealed shaker and warmed to expel the gasoline components into the shaker airspace. A sample of this airspace gas is then removed and analysed by gas chromatography. 28 hydrocarbon species are identified in the C_4 to C_7 range and their relative proportions calculated with reference to standard mixtures. Immature source rocks yield mixtures dominated by a small

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number of components but mature source rocks usually contain a full range of identified hydrocarbons in similar orders of concentration. The onset of maturity may also be indicated by an increase in total gasolines relative to the organic carbon content of the host rock (+200 ppm hydrocarbons per 1% organic carbon). Occasionally, oil stain will be recognised by the presence of anomalous amounts and it may be possible to identify its source rock by a similarity in distribution of components.

Spore Colouration

The maturity of oil-prone organic matter present in kerogen concentrates is assessed by visual examination of the indigenous sporomorphs. With increasing thermal maturity, spore colours change from pale yellow, through orange and brown, to black. Measurement is made using a standard reference set of sporomorphs. Spore colouration indices measured are on the Robertson Research scale of 1 to 10. Our experience shows that values of 3.0 to 3.5 are representative of the transition zone between immaturity and maturity. The range 3.5 to 8.0 is arbitrarily divided into zones of organic maturity: 3.5 to 5.0, early maturity; 5.0 to 7.0, middle maturity; 7.0 to 8.0 late maturity. Direct comparison with source rock data indicates that, given the presence of oil-prone organic matter, low gravity oils are likely to be generated in the zone of early maturity, medium gravity oils in the zone of middle maturity and high gravity oils in the zone of late maturity. The onset of generation of condensate, wet gas and, ultimately, dry gas is characterised by spore colour indices above 8.0.

Vitrinite Reflectivity

Vitrinite, a humic degradation product largely derived from the anaerobic decomposition of the lignin, cellulose and nitrogen-containing compounds of woody tissues, is the chief component of coals and is also common in fine-grained clastic rocks. The reflectivity of an optically flat surface is defined as the percentage of normally incident light reflected from the surface. Reflectivity can be used to define the level of thermal maturity of sedimentary organic matter since it increases from approximately 0.2% to 5.0% at a relatively uniform rate through the coal rank series. Zones of oil and gas generation can be related to the coal rank series and therefore defined in terms of vitrinite reflectivity, even though vitrinite is not an oil source but generates gas. The onset of oil generation has been placed at between 0.35% and 0.6% reflectivity, depending on the type of sedimentary basin; 0.5% is a widely accepted threshold value. The floor for oil generation is characterised by a vitrinite reflectivity of approximately 1.2%. Wet gas generation peaks at a reflectivity of about 1.0% and ceases at the 2.0% level. Dry gas generation peaks at a reflectivity of about 1.5% and ceases at the 3% level. However, to define the appropriate limits for a particular basin, vitrinite reflectivity must be correlated with other thermal maturation parameters.

3. Source Rock Evaluation

Organic Carbon Content

On average, between 1% and 2% of argillaceous sediments consist of organic carbon. Since major hydrocarbon accumulations are the exception rather than the rule it is likely that their sources are of above average organic carbon content. Sediments containing less than 0.3% organic carbon are regarded as having no source potential, and those containing between 0.3% and 1.0% are



marginal sources. Obviously the kerogen type is also of fundamental importance in determining the source potential of a rock.

Organic carbon values are obtained as follows. A 0.1 or 0.5 g sample, depending on lithotype, of crushed rock is treated with concentrated hydrochloric acid to remove carbonates and the residue filtered onto a glass fibre paper prior to ignition in a 'Leco' carbon analyser.

Extract Analysis

The soluble organic materials present in rocks can be extracted with organic solvents, fractionated and analysed. The type and amount of material extracted depends largely upon the nature of the contained organic matter and its maturity.

A maximum of 40 g of crushed sample is extracted for a minimum of 12 hours in a 'Soxhlet' apparatus by a 2 : 1 mixture of laboratory redistilled dichloromethane and methanol. The weight of the 'total extract' after final evaporation is expressed as ppm of the total rock. The more volatile components (up to C-15) are lost during extraction. The total extract is dissolved in hexane and a known volume separated by high pressure liquid chromatography into saturate hydrocarbon (alkanes), aromatic hydrocarbon and resene-asphaltene fractions.

Extract analysis provides a measure of source-rock richness in the oilgeneration maturity zone. In addition to organic carbon contents, five parameters are calculated; total extract, extract/organic carbon x 100 i.e. extractability or EPOC, hydrocarbons as ppm of rock, hydrocarbons as percent of extract and alkanes as percent of hydrocarbons.

The extractability of oil-prone sapropelic organic matter increases rapidly in the oil generation zone and diminishes to very low values in postmature sediments. Overall the extractability of sapropelic organic matter is greater than that of gas-prone humic organic matter for similar levels of maturity. Samples with extractabilities of greater than 20% generally contain migrated oil or are contaminated with mud additives.

The hydrocarbon content of a rock is the sum of the alkane and aromatic fractions of the total extract. As maturation proceeds in the oil generation zone the proportion of hydrocarbons in the total extract increases from less than 20% to a maximum in the most productive horizons of around 60%. This trend is reversed as the oil-condensate zone is entered. The relative proportions of alkanes to aromatics can be used as a check for low levels of contamination.

Pyrolysis

Pyrolysis data are obtained using the IFP-Fina "ROCK-EVAL" apparatus. The method involves the heating of samples from 250° to 550°C at 25°C/minute in a stream of inert gas. During this time, three pulses of gases are released and recorded as weights of gas. The first of these pulses relates to hydrocarbons present in the sediment which could normally be extracted by organic solvents; these are either the adsorbed hydrocarbons indicating present source potential, or reservoired hydrocarbons. The second gas pulse is of hydrocarbons released by the thermal breakdown of kerogen (optimum source potential), and simultaneously the temperature of maximum rate of evolution is measured. The third pulse comprises carbon dioxide.



The parameters used in interpretation are the hydrogen index (ratio of released hydrocarbons to organic carbon content), the oxygen index (ratio of released carbon dioxide to organic carbon content), the temperature of maximum rate of pyrolysis, and the production index (ratio of the amount of hydrocarbons released in the first stage of heating to the total amount of released hydrocarbons). Kerogens rich in sapropelic matter exhibit a high hydrogen index and a low oxygen index while those in which humic debris predominates will display a low hydrogen index and a high oxygen index. Hydrogen and oxygen indices for a particular type of kerogen are also susceptible to a reduction in their values during the course of thermal maturation.

The hydrogen index is a measure of the hydrocarbon generating potential of the kerogen. Immature, organically rich source rocks and oil shales give values above 500, mature oil source rocks give values between 200 and 550.

The temperature of maximum rate of pyrolysis depends on the nature of the organic matter, but the transition from immature to mature organic matter is marked by temperatures between 415° and 435°C. The maturity transition from oil and wet gas generation to dry gas generation is marked by temperatures between 455° and 460°C. In practice, greater variation than these ideal temperature ranges may be seen, but they are nevertheless useful as general guides to the level of maturity attained by the sediment.

The production index increases with maturity from values near zero for immature organic matter to maximum values of 0.15 during the late stages of oil generation. Anomalously high values indicate the presence of free oil. The hydrocarbon yield is an indication of the potential yield of hydrocarbons from the source rock at optimum maturity and is a measure of the quality of the source rock. A value of 0 to 2000 of hydrocarbon in ppm of rock characterises a poor source rock, 2000 to 6000 ppm fair, 6000 to 20,000 ppm good and above 20,000 ppm very good.

Visual Examination of Kerogen Concentrates

All palynological preparations are examined in transmitted white and ultraviolet light and the relative abundances of vitrinite, inertinite and sapropel (essentially a fine-grained, apparently amorphous mixture of liptinite and exinite) estimated. The coarser-than-20-micron fractions are also examined in reflected white and ultraviolet light.

Gas Chromatography of C-15+ Alkanes

A portion of the "total extract" obtained from Soxhlet extraction is eluted with pentane through a short silica column to yield the saturate hydrocarbon fraction. This fraction is evaporated to dryness in a stream of dry nitrogen at room temperature. A small portion of the fraction is then taken up in methylene dichloride and injected on to a 25 metre, wall-coated, open-tubular, glass capillary column coated with OV-1 mounted in a Perkin Elmer F-17 gas chromatograph and programmed from 80°C to 260°C at 4° C/minute.

Distributions of n-alkanes and the relative abundances of steranes and triterpanes are noted and the ratios pristane/n-C₁₇ and phytane/n-C₁₈ are measured. The CPI may also be measured. Inspection of the chromatograms may reveal information about the kerogen type of the source rock, its maturity and conditions of deposition and, if migrant oil is present, whether this has been water-flushed or biodegraded. Drilling mud additives may be identified.



Gas chromatography-mass spectrometry

Mass spectrometry is a technique in which molecules are bombarded with high energy electrons causing ionisation and fragmentation of the molecules into ions of varying mass and charge. The way in which a molecule fragments into ions of various m/z values known as its fragmentation pattern, or mass spectrum, is unique. When linked to a gas chromatograph the mass spectrometer can be used in two different modes:-

- 1. Full Scan Mode: A mass spectrum is obtained of each peak eluting from the gas chromatograph and a structural identification of the compound causing that peak can be made.
- Multiple or Single Ion Monitoring Mode: The mass spectrometer is tuned 2. to certain m/z values to detect whether a peak, eluting from the gas chromatograph, fragments to give an ion at that value. Certain fragmentations are indicative of specific compound types and the most commonly monitored fragment ions used in petroleum geochemistry are those with m/z values of 191,217 and 259 which are the principal fragment ions obtained from groups of alkanes known as triterpanes, regular steranes and rearranged steranes respectively. These are compounds containing 27 to 35 carbon atoms arranged in a polycyclic, normally 4 or 5 ring, structure. They occur in the $n-C_{26}$ to $n-C_{35}$ region of a gas chromatogram but since the total amount of such polycyclic compounds is usually quite low, their presence is often not easily perceived in the presence of the strongly dominant straight chain alkanes. The basic molecular skeletons of these compounds are very similar to those of the original organic matter deposited in the sediment and so these 191, 217 and 239 distribution plots, known as mass fragmentograms or mass chromatograms, form a pattern characteristic of the source material. This technique of "fingerprinting" is thus very useful, and one of the more exact methods of correlating an oil to its source, or to another oil.

