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#### 1. INTRODUCTION

One gas and one oil sample from DST 3 in well 34/4-6 were characterised by organic geochemistry at the request of Saga Petroleum a.s. The samples were received from GECO Petroleum Laboratory as a stock tank oil sample and a separator gas sample. The following data concerning the DST fluid were also received from GECO:

Flash of reservoir fluid to Stock Tank Conditions.

Flash Conditions:	200 barg, 100.0 <sup>0</sup> C to atmosphere and 15 <sup>0</sup> C.
Gas/Oil Ratio:	$107.3 \text{ Sm}^3/\text{m}^3$ .
Bo at 200 barg:	1.419 $m^3/m^3$ .
Bo at bubble point:	1.483 $m^3/m^3$ .
Density of oil at 15 <sup>0</sup> C:	834.3 kg/m <sup>3</sup> .
Molecular weight of oil:	186.
Standard Conditions:	For gas volumes = 15 <sup>0</sup> C and 1 bar.
	For oil volumes = $15^{\circ}$ C and atmospheric
	pressure.

The DST fluid was analysed according to the analytical plan outlined by Saga Petroleum in their letter of 8 October 1985. These analyses are as follows:

#### Gas sample:

- Gas chromatography of  $C_1 - C_8$  hydrocarbons.

 $\delta^{13}$ C stable isotope ratios of C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub> components.

• D/H isotope ratio of  $C_1$ .

#### Oil sample:

API gravity.

- Sulphur, nickel and vanadium content.

- Gas chromatography of C<sub>2</sub>-C<sub>8</sub> hydrocarbons for recombination.
- Gas chromatography of whole oil.
- Liquid chromatography (MPLC) with asphaltene precipitation.
- Urea adduction of saturated hydrocarbons.
- Gas chromatography of saturated, branched/cyclic and aromatic hydrocarbons.



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GC-MS of saturated hydrocarbons (m/z 191, 217, 218).

GC-MS of aromatic hydrocarbons.

 $^{13}$ C stable isotope ratio for saturates, aromatics, NSO and asphaltenes.

The DST fluids were analysed and reported under IKU project number 22.1831. The samples were assigned the following IKU code numbers:

DST 3 gas: C-4606 oil: C-4607

One copy of a draft report is sent to Saga Petroleum a.s. for approval. On approval, ten copies of a final report are sent to Saga and ten / copies are retained at IKU.





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#### 2. DISCUSSION OF RESULTS

2.1 Recombination of DST oil and gas (C<sub>1</sub>-C<sub>8</sub> hydrocarbons)

2.1.1 Gas chromatography of  $C_1 - C_8$  hydrocarbons

Methane accounts for 28.1% of the  $C_1-C_8$  hydrocarbons analysed from the DST gas (Tables 1 and 2). The gas has a high wetness of 69.2% which is typical of oil-associated gas. An  $iC_4/nC_4$  ratio of 0.36 suggests that the gas is thermally mature.  $C_{5+}$  hydrocarbon components are almost absent from this DST gas.

2.1.2 Gas chromatography of  $C_2-C_8$  hydrocarbons (oil sample)

The  $C_2-C_8$  hydrocarbon composition of the DST oil is shown in figure 2 and table 3. The gas chromatogram suggests that the composition of the oil is dominated by n-alkanes, with the exception of occasional branched/cyclic compounds such as methylcyclohexane. The  $C_2-C_8$  fraction accounts for 19.8% of the whole oil sample. A high paraffinicity index (after Thompson, 1979) of 1.41 suggests that the oil sample is thermally mature.

2.1.3 Combination of  $C_1-C_8$  hydrocarbons for DST gas and oil

This recombination of the  $C_1-C_8$  gas composition and the  $C_2-C_8$  oil composition was carried out in an attempt to reconstruct the original  $C_1-C_8$  composition of the DST fluid. This recombination was carried out using the gas/oil ratio supplied by GECO from this DST (Table 1b).

2.1.4 Stable isotope data for the DST 3 gas sample

The carbon and deuterium ratios for the  $C_1-C_4$  gas components are shown in figure 4 and table 3. The carbon isotope ratios of the  $C_1-C_4$  components are similar to the values obtained from other 34/7 DST gases, especially 34/7-3, 34/7-6, 34/7-7 and 34/7-8. The deuterium ratio of -2110/00 is about average for the 34/7 gases.

Figures 4a and 4b suggest that the isotopic composition of the gas is fairly typical of gases associated with oils, as might be expected, although in figure 4a, the sample plots slightly into the mixed biogenic/



catagenic gas field. This is similar to the situation observed in wells 34/7-7 and 34/7-8.

#### 2.2 Crude oil characterisation

2.2.1 API gravity

The DST oil has a relatively high API gravity of  $39.4^{\circ}$  (Table 3), suggesting a thermally mature, moderately light oil. This API gravity is slightly higher than the values obtained from the 34/7 block oils. The highest API gravity for the 34/7 oils is  $37.9^{\circ}$ , obtained from the 34/7-9 FMT oil.

2.2.2 Sulphur, nickel and vanadium content

The 34/4-6 DST oil may be considered a low sulphur oil on the basis of a sulphur content of 0.27% (Table 4). The sample has a nickel content of about 8 mg/kg and a vanadium content of about 2.4 mg/kg. The sulphur content of the 34/4-6 DST sample is similar to that for the majority of the 34/7 oils. The nickel content of this oil is higher than is usually seen in the 34/7 oils, whereas the vanadium content is slightly below the average for the 34/7 oils.

2.2.3 Gross composition of the DST crude oil sample

Low molecular weight compounds in the  $<210^{\circ}$ C oil fraction account for 50.3% of the oil (Table 5). This high percentage might be expected from the relatively high API gravity of this oil.

Asphaltene compounds account for 1.1% of the oil and NSO compounds account for 9.5% of the oil (Table 6). The asphaltene content of the 34/4-6 DST oil is below the average for the 34/7 oils (34/7 average = 2.0%) as is the NSO content (34/7 average = 10.2%).

Saturated hydrocarbons account for 56.7% of the  $>210^{\circ}$ C fraction of the oil, and aromatic hydrocarbons account for 30.0% (Table 7). The hydrocarbon content of the  $>210^{\circ}$ C fraction of the 34/4-6 DST oil appears to be higher than is observed in most of the 34/7 oils analysed at IKU. This might be expected from the higher API gravity of this sample.



2.2.4 Gas chromatography of the DST oil

a) Whole oil gas chromatography

The whole oil gas chromatogram of this oil is shown in figure 3 and shows a unimodal n-alkane distribution with a maximum at  $nC_5$ , decreasing smoothly to a minimum at about  $nC_{30}$ . The appearance of the gas chromatogram is similar to those for the 34/7-8 and 34/7-9 oils.

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b) Gas chromatography of saturated hydrocarbons

The saturated hydrocarbon gas chromatogram of the DST oil is shown in figure 4 and is similar in appearance to that described from 34/7-9. The n-alkanes have a smooth unimodal distribution reaching a maximum at about nC<sub>20</sub>. The rapid drop-off in peak intensity below nC<sub>20</sub> may be due to evaporation during sample preparation.

A pristane/phytane ratio of 1.6 (Table 6) suggests a mildly oxidising source-rock depositional environment, although the value may have been slightly altered during maturation. The carbon preference index value of 1.1 and pristane/nC<sub>17</sub> ratio of 0.8 suggest that the sample is thermally mature.

c) Gas chromatography of branched/cyclic hydrocarbons.

The gas chromatogram of the branched/cyclic hydrocarbons (figure 5) shows a fairly restricted development of isoprenoid hydrocarbons consisting of pristane, phytane and the  $iC_{16}$  and  $iC_{18}$  isoprenoids. The gas chromatogram also shows a 'hump' of unresolved compounds and is generally similar in appearance to gas chromatograms from 34/7-7 and 34/7-8 DST samples.

d) Gas chromatography of aromatic hydrocarbons

The aromatic hydrocarbon gas chromatogram (figure 6) is dominated by a large 'hump' of unresolved compounds. Nevertheless, there is a good development of the naphthalene and phenanthrene compounds, both groups of compounds showing nearly equal development. Methyl-phenanthrene indices of 0.96 and 0.91 (table 9) agree with other previously discussed maturation indicators and suggest that the oil is thermally mature.



The large unresolved 'hump' is seen in many of the 34/7 oils, especially in the DST's from 34/7-5, 34/7-7, 34/7-8 and 34/7-9.

2.2.5 Gas chromatography - mass spectrometry (GC-MS

#### Saturated hydrocarbons

The terpane and sterane mass chromatograms are presented in figures 9 and 10 and the molecular ratios calculated from these are given in tables 11 and 12.

The data routinely used for maturity estimation suggest a mature assemblage of hydrocarbons. Most parameters calculated from the triterpane mass chromatogram (m/z 191) have values indicative of thermal maturity. The calculated sterane parameters, however, are close to, but have not reached, final maturity values. This may suggest a more moderate thermal maturity.

A relatively high abundance of 28,30-bisnorhopane (Z in m/z 191) may indicate an Upper Jurassic source rock for this sample. This compound is common in samples from the Draupne and Heather formations.

#### Aromatic hydrocarbons

The aromatic hydrocarbon mass chromatograms are presented in figure 11 and some molecular ratios calculated from these are given in table 13.

The distribution of methylphenanthrenes and methyldibenzothiophenes, in the m/z 192 and m/z 198 mass chromatograms respectively, indicate a moderately mature hydrocarbon assemblage. The relative content of low molecular weight tri- and mono-aromatic steranes suggest an early oil window maturity of this sample, which contrasts with previously discussed maturity data for the oil sample.

2.2.6  $\delta^{13}$ C stable isotope composition of the DST oil

The carbon isotope ratios for the saturate, aromatic, NSO and asphaltene fractions of the DST 3 oil are given in figure 12 and table 14. The isotopic ratios for the four fractions have similar values of -28.50/00 to -30.60/00. These are similar to the values obtained from most of the 34/7 DST oils (excluding 34/7-8 (DST 1a) and 34/7-9).



The isotope ratio profile in figure 12 is similar to the profiles obtained from the DST 2 and DST 3 oils of well 34/7-8.



#### 3. ANALYTICAL PROCEDURES

#### Gas analyses

Natural gas (full analysis of hydrocarbons and inert gases):

Natural gas samples were analysed on an HP 5880 gas chromatograph equipped with a capillary column and an FID for hydrocarbon analysis and two packed columns and a TCD for analysis of the inert gases  $(N_2, O_2, CO_2)$ :

- 50 m x 0.2 mm i.d. fused silical column, coated with 0.5  $\mu$ m OV-101.
- 3 ft steel column packed with molecular sieve 13x, 80/100 mesh.
- 6 ft steel column packed with Porapack T x 4 ft steel column packed with Porapack Q, 80/100 mesh.

Temperature program:  $30^{\circ}C$  (12 min.) -  $8^{\circ}C/min.$  -  $150^{\circ}C$  (5 min.).

A standard gas sample containing methane, ethane, propane, n-butane, n-pentane and n-hexane was used for quantification.

#### Evaporation of the light components in fluid samples

Prior to chromatographic separation, the oil/condensate samples were heated to  $210^{\circ}$ C at atmospheric pressure until constant weight (at  $210^{\circ}$ C) was obtained.

The fraction of light components was determined as the weight difference between the original sample and the residuum left after heating.

#### Medium-pressure liquid chromatography (MPLC)

The oil (>210<sup>O</sup>C) sample was diluted in DCM (1:3 mg/ $\mu$ l) and the asphaltenes were precipitated using excess n-pentane (40:1 pentane:(DCM+oil)). The asphaltene fraction was weighed after drying at 50<sup>O</sup>C for 12 hours.

The remaining maltenes were separated into saturated, aromatic and nonhydrocarbon fractions using an MPLC system with n-hexane as eluant (Radke et al., 1980). The various fractions were concentrated using a Büchi Rotavapor, transferred to glass vials and the remaining solvent removed.



#### Urea adduction

An aliquot of the saturated hydrocarbon fraction (5 mg) was diluted with n-hexane (2 ml), followed by the addition of acetone (1 ml). A saturated solution of urea in methanol (1 ml) was then added dropwise. The solvent was removed in a nitrogen stream and the adduction procedure repeated twice more. The white crystals were rinsed with hexane (3x5 ml) and the combined extract was filtered through a cotton plug covered with  $Al_2O_3$  to produce a non-adduct containing the branched and cyclic hydrocarbons. GC analyses were performed on the non-adduct using the conditions outlined in the next section.

#### Gas chromatographic analysis

A whole oil sample was analysed using an HP 5730A gas chromatograph fitted with a 15 m DB-5 fused silica column. 0.02  $\mu$ m of sample solution was injected in split mode (split ratio = 1:10). Hydrogen was used as a carrier gas with a flow rate of 2.5 ml/min, and the temperature programme used was  $-50^{\circ}$ C (2-min) -  $4^{\circ}$ C/min -  $280^{\circ}$ C.

The C<sub>2</sub>-C<sub>8</sub> hydrocarbon compounds were investigated by hydrogen stripping on a Carlo Erba Fractovap gas chromatograph fitted with a 60 m x 0.32 mm (i.d.) fused silica column coated with DB-1, 1.0  $\mu$ m. The temperature programme used was 50<sup>o</sup>C (2 min) - 4<sup>o</sup>C/min - 210<sup>o</sup>C. An internal standard was used for quantification.

The saturated and the branched/cyclic hydrocarbon fractions were each diluted with n-hexane and analysed on an HP 5730A or an HP 5710 GC. Both GCs are equipped with 15 m DB-1 fused silica columns, and hydrogen is used as carrier gas with a flow rate of about 1.5 ml/min. Injections were performed in split mode (split ratio 1:10). The temperature programme used was  $80^{\circ}C$  (2 min) -  $4^{\circ}C/min$  -  $280^{\circ}C$ .

The total aromatic fractions were diluted with n-hexane and analysed on an HP 5730A gas chromatograph, fitted with a DB-5 fused silica column (15 x 0.25 mm i.d.), using a hydrogen carrier gas with a flow rate of 2.5 ml/min. The injection split ratio was 1:10.

The temperature programme used was  $80^{\circ}$ C (2 min.) -  $4^{\circ}$ C/min -  $280^{\circ}$ C.

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Data processing for all the GC analyses was performed on a VG Multichrom lab data system.

#### Gas chromatography - mass spectrometry (GC-MS)

GC-MS analysis were performed on a VG Micromass 70-70H GC-MS-DS system. The Varian Series 3700 GC was fitted with a fused silica OV-1 capillary column (30m x 0.3 mm i.d.). Helium (1.5 ml/min) was used as carrier gas and the injections were performed in split mode (1.5  $\mu$ l, split ratio 1:15).

The GC oven was programmed from  $120^{\circ}$ C (2 min.) to  $280^{\circ}$ C at  $4^{\circ}$ C/min. for analysis of the saturated hydrocarbons, and from  $70^{\circ}$ C/min. to  $280^{\circ}$ C at  $4^{\circ}$ C/min. for analysis of the aromatic hydrocarbons.

The saturated hydrocarbons were analysed in multiple ion mode (MID) at a scan cycle time of approximately 2 secs. Full data collection was applied for the aromatic hydrocarbons at a scan time of 1 sec./decade.

The mass spectrometers operated at 70eV electron energy with an ion source temperature of  $200^{\circ}$ C. Data acquisition was performed using VG data systems.

Peaks were identified by comparison with elution patterns in certain mass chromatograms. Peak ratios were calculated from peak heights in the appropriate mass chromatograms.

# <u>δ<sup>13</sup>C isotope analysis</u>

The  $\delta^{13}$ C isotope analyses were performed by mass spectrometry at the Institute for Energy Technology (IFE) in Oslo according to their method. Their reference value for the standard NBS-22 is -29.8  $^{\rm O}$ /oo (PDB).

The samples were filled in a glass capillary and transferred into a combustion system filled with copper dioxide, heated to  $900^{\circ}$ C. A stream of ultrapure helium and oxygen flushed the reaction products through silver wool ( $450^{\circ}$ C) to remove traces of halogens and sulphur.

 $\rm H_2O$  and  $\rm CO_2$  were trapped in separate cooltraps. After removal of the carrier gas by high vacuum,  $\rm CO_2$  and  $\rm H_2O$  were sealed off separately in

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6 mm glass tubes.  $H_2^0$  was reduced to  $H_2$  by zinc at 460°C.

The  ${}^{13}\text{C}/{}^{12}\text{C}$  - isotope ratio (and D/H- isotope ratio) was measured with a high precision mass spectrometer Finnigan MAT 251.

Precision of the preparation lines and the mass spectrometer was daily controlled by measurements of standard substances and by double analyses.

The isotope ratios are given as delta-values (del):

del (%) = ((R sample - R stand.) / (R stand.)) \* 1000

13C/12C- isotope ratios are calculated versus PDB. D/H-isotope ratios are calculated versus SMOW.

The CV value is calculated after SOFER (1984) to differentiate between marine and terrestrial-sourced oils:

 $CV = (-2.53 * del^{13}C_{sat}) + (2.22 * del^{13}C_{aro}) - 11.65.$ 



### 4. CONCLUSION

An oil and a gas sample from DST 3 in well 34/4-6 were characterised using organic geochemistry. The gas has a fairly high wetness of 69% as might be expected from an oil-associated gas. An  $iC_4/nC_4$  ratio of 0.36 suggests that the gas is thermally mature.

The oil is a moderately light, thermally mature, low sulphur oil. The 34/4-6 oil is similar in composition to a number of DST oils analysed from block 34/7, and is thought to be derived from a similar Upper Jurassic source rock.



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Previous IKU reports concerned with block 34/7 fluids:

05.1725.00/02/84: Fluid characterisation of well 34/7-1. 05.1728.00/02/85: Hydrocarbon characterisation of well 34/7-3. 22.1767.00/03/85: Hydrocarbon characterisation of well 34/7-4. 22.1771.00/03/85: Analysis of fluid and gas samples from well 34/7-5. 22.1779.00/03/85: Analysis of fluid and gas samples from well 34/7-6 (DST 2 and DST 3b). 22.1805.00/01/86: Analysis of fluid and gas samples from well 34/7-7.



<u>Table 1a</u> : Rat	ios obtain	ed from C	1 <sup>-C</sup> 8 gas/oil c	ompositions.	
IKU no.	DST no.	%CH <sub>4</sub>	%Wetness	iC <sub>4</sub> /nC <sub>4</sub>	P.I. 1
C-4606/4607	3	28.1	69.2	0.36	1.38
%Wetness = (Σ	c <sub>2</sub> -c <sub>5</sub> /Σc <sub>1</sub> -	C <sub>5</sub> ) x 100			

P.I. 1 (after Thompson, 1978) =  $2MeC_6 + 3MeC_6 / diMeCyC_5$  (3 isomers).



Tab	le	1b:
		the second s

C1-C8 YIELD WELL NO: 34/4-6 IKU NO,GAS:C4606 IKU NO,OIL:C4607 GOR = 107.3 SM3/M3

Recombination of DST gas and oil ( $C_1 - C_8$ hydrocarbons): DST 3.

	GAS	GAS	OIL	TOTAL HC IN MG/ML OF
COMPOUND	MG/ML	MG/107.3ML	MG/ML	RESERVOIR FLUID
Methane	0.262	28.113	0.000	28.113
Ethane	0.176	18.885	0.000	18.885
Propane	0.250	26.825	0.000	21.825
i-Butane	0.047	5.043	0.000	5.043
n-Butane	0.131	14.056	1.812	15.868
i-Pentane	0.031	3.326	5.087	8.413
n-Pentane	0.031	3.326	9.452	12.778
Cyclo-C5+				
2,3-diMeC4	0.002	0.210	1.900	2.110
2-MeC5	0.001	0.107	5.371	5.478
3-MeC5	0.000	0.000	3.392	3.392
n-Hexane	0.000	0.000	11.101	11.101
MeCyC5	0.000	0.000	6.526	6:526
Benzene	0.000	0.000	1.881	1.881
CycloC6	0.000	0.000	6.982	6.982
2-MeC6	0.000	0.000	3.244	3.244
2,3-diMeC5	0.000	0.000	1.127	1.127
3-MeC6	0.000	0.000	4.831	4.831
diMeCyC5	0.000	0.000	6.125	6.125
n-Heptane	0.000	0.000	11.126	11.126
MeCyC6	0.000	0.000	14.111	14.111
EtCyC5+				.•
2,5-diMeC6	0.000	0.000	1.671	1.671
2,4-diMeC6	0.000	0.000	1.104	1.104
triMeCyC5	0.000	0.000	1.045	1.045
Toluene	0.000	0.000	6.507	6.507
2-MeC7+				
4-MeC7	0.000	0.000	5.416	5.416
3-MeC7	0.000	0.000	2.687	2.687
diMeCyC6	0.000	0.000	5.329	5.329
n-Octane	0.000	0.000	11.003	11.003
2,4-diMeC7+				
diMeCyC6	0.000	0.000	2.064	2.064
EtCyC6	0.000	0.000	4.479	4.479
EtBenzene	0.000	0.000	1.987	1.987
m+p-xylene	0.000	0.000	5.671	5.671
2-MeC8+				
4-MeC8	0.000	0.000	2.704	2.704
0-Xylene	0.000	0.000	2.297	2.297
SUM	0.931	99.891	148.192	248.083



 $C_2-C_8$  hydrocarbon composition of DST 3 oil.

C 4607	area	ug	mg/ml	% of t.oil
nC3	O	.000	.000	.000
150-C4	0	.000	.000	.000
nC4	84085	.543	1.812	.218
iso-C5	236012	1.526	5.087	.614
nC5	438511	2.835	9.452	1.141
CyC5+2,3diMeC4	88163	.570	1.900	.229
2MeC5	249202	1.611	5.371	.648
3MeC5	157384	1.017	3.392	.409
nC6	515024	3.330	11.101	1.340
MeCyC5	302762	1.957	6.526	.788
benzene	87269	.564	1.881	.227
CyC6	323942	2.094	6.982	.843
2MeC6	150522	.973	3.244	.391
2,3diMeC5	52329	.338	1.127	.136
3MeC6	224150	1.449	4.831	.583
DiMeCyC5	284183	1.837	6.125	.739
nC7	516171	3.337	11.126	1.343
MeCyC6	654699	4.233	14.111	1.704
EtCyC5+2,5diMeC6	77564	.501	1.671	.201
′2,4diMeC6	51236	.331	1.104	.133
triMeCyC5	48523	.313	1.045	.126
toluene	301915	1.952	6.507	.785
2+4MeC7	251273	1.624	5.416	.654
3MeC7	124667	.806	2.687	.324
DiMeCyC6	247266	1.598	5.329	.643
nC8	510471	3.300	11.003	1.328
2,4diMeC7+diMeCyC6	95766	.619	2.064	.249
EtCyC6	207823	1.343	4.479	.540
EtBenzene	92215	.596	1.987	.240
m,p-Xylene	263141	1.701	5.671	.684
2+4MeC8	125477	.811	2.704	.326
o-xylene	106590	.689	2.297	.277

sum

4111

148.046

44.413

17.877

tot.oil ant ug inj.: 248.430ug

%C2-C8(tot.area)in tot.oil: 19.773%



# Table 3: Stable isotope data for DST 3 gas.

	C <sub>1</sub>		с <sub>2</sub>	с <sub>3</sub>	1-C <sub>4</sub>	n-C <sub>4</sub>
IKU nr.	δ <sup>13</sup> C PDB	ôD SMOW	δ <sup>13</sup> C PDB	δ <sup>13</sup> C PDB	δ <sup>13</sup> C PDB	δ <sup>13</sup> C PDB
C-4606	-49.7	-211	-34.5	-31.8	-32.8	-30.7

162/gg/an1/14



Project No.: 22.1831 Date : 27-6-86

# Table 4:

## API GRAVITY OF OIL SAMPLE

== I I	IKU-No	co	==== )E	:	API	GRAVI	=== TY	(DENSI		=== I I
1 1 ==	: ها بنه بنه بنه <u>م</u> حد جد :	n ni all 70 i	====	: : ==	Crude (	⊃il =======	:	>21	.0'C	1 I ====
I I I ==	34/4-6 C-4607	DST	3		39.4 (0	.8281)		24.7	(0.9057)	I I I I



Project No.: 22.1831 Date : 27-6-86

# Table 5:

CONTENT OF SULPHUR, NICKEL AND VANADIUM IN OIL >210'C-

_===		=====	=====	========	aziziz	=====			==
I		2		1					Ι
I	IKU-No	:	CODE	<b>:</b> .	S	·# .	Ni	: V	I
I		1		4		:		•	I
I		:		;	%	: (m	g/kg)	: (mg/kg)	I
Ξ				=======	======		========	======	==
==	2 92 92 <del>92 92 92 93</del> 92 92 92 92 92 92 92 92 92 92 92 92 92			: <u></u>		11) 200 200 200 200 2	<u>12 12 12 12 12 12 1</u>	= <u>= = = = =</u> : :	== I
I I I	.34/4-6			:======= : :		*====	12 15 m 25 m 31 T	= = :;; ::: ::: ::: ::: ::: ::: ::: ; ;	== I I
== I I I	34/4-6 C-4607		DST 3		0.27	===== : : :8.2	====== 1-7.72	======================================	== I I 2I
I I I I	.34/4-6 C-4607		DST 3		0.27	::::::::::::::::::::::::::::::::::::::	<b>1-7.7</b> 2	2.46-2.2	I I I 2I I I



Project No.: 22.1831 Date : 22 - 7 - 86

## Table 6:

### FRACTION BOILING BELOW 210 C

	IKU No	:	CODE		Crude Oil (mg)		EOM >210 C (mg)	:	Low f Weight (mg)	101e Com :	cular pounds (%)	I I I I I
I I 3 I I	4/4-6 C 4607		DST 3	: : : : :	709.9	:	352.8	:	357.1		50.3	I I I I



Project no.: 22.1831 DATE : 9 - 7 - 86

# Table 7:

AMOUNT OF ASPHALTENES AND NSO'S IN OIL

===		===	ی سے جب جب مع		یک بند جند دی چی چی چ	===		====		≠≈≈	=====	====		==
I I I	IKU No	1	DST N	: lo :	Crude Oil	:	Aspha	lter	ies	4 2 2 2		NSO		I I I
I I			20 00 10 vir ve a	:	(mg)	:	(mg)	1	(%)	:	(mg)	: -:	(%)	I I
I I I I	34/4-6 C-4607		3	: : :	709.9		7.5	:	1.1		67.2	:	9.5	I I I I



Project No.: 22.1831 Well : 34/4-6 Date : 22 - 7 - 86

# Table 8a:

### CONCENTRATION OF OIL CHROMATOGRAPHIC FRACTIONS

	IKU No		CODE	Crude Oil (mg)		EOM >210C (mg)		Sat. (mg)		Aro. (mg)		HC (mg)	Non HC (mg)	I I I I I
I I I	C 4607	:	DST 3	 709.9	:	352.8	1	154.0	1	80.5	:	234.5	 47.1	I I I



Project No.: 22.1831 Well : 34/4-6 Date : 22 - 7 - 86

## Table 8b:

## COMPOSITION OF OIL

	IKU No	:=====	CODE		Sat. EOM %		Aro. EOM %		HC EOM %	:	Sat.  Aro. × 100		Non HC EOM %		HC Non HC x 100	I I I I I
I I I ====	C 4607	:	DST 3	1	56.7	:	30.0	:	86.7	:	191.3	1	13.4	1	649.0	I I I

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## Table 9:

TABULATION OF DATA FROM THE GASCHROMATOGRAMS

I I I	IKU No.	CODE	PRISTANE PHYTANE	A =	PRISTANE n-C17	===== B =	PHYTANE n-C18	A 	n-C17 n-C27	CPI	== I I I
I I I I	C 4607	DST 3	1.6		D.8		0.5	1.7	1.7	1.1	I I I ==

DATE : 4 - 7 - 86.



# <u>Table 10:</u>

Ratios from aromatic gas chromatograms.

IKU no.	DST no.	MPI-1	MPI-2
C-4607	3	0.96	0.91

MPI-1 = 1.5(2-MP+3-MP)/P+1-MP+9-MP

MPI-2 = 3(2-MP)/P+1-MP+9-MP

## 159/bb/jb1/3



Table 11: Molecular ratios from sterane and terpane mass chromatograms. Maturity ratios.

IKU code	Well no.	αβ/αβ+βα <sup>1</sup> )	%22S <sup>2)</sup>	<sub>%ββ</sub> 3)	%20S <sup>4)</sup>
C-4607	34/4-6	0.93	59.7	76.1	50.8

- 1) E/E+F in m/z 191
- Average % distribution between first and second eluting isomers of extended hopanes (G-M in m/z 191)
- 3) 2(r+s)/(q+t+2(r+s)) in m/z 217
- 4) q/q+t in m/z 217



Table 12: Molecular ratios from terpane and sterane mass chromatograms. Maturity and source characteristic ratios.

IKU no. Well no.			Q/E <sup>1)</sup>	Tm/Ts <sup>2)</sup>	X/E <sup>3)</sup>	Z/E <sup>4)</sup>	a/a+j <sup>5)</sup>
C-4607	34/4-6	· .	0.08	0.50	0.12	0.40	0.75

1) Relative abundance of tricyclic terpanes (Q/E in m/z 191)

2) B/A in m/z 191

- 3) Relative abundance of unknown (X/E in m/z 191)
- 4) Relative abundance of bisnorhopane (Z/E in m/z 191)
- 5) Relative abundance of  $C_{27}$  rearranged steranes (a/a+j in m/z 217)

$\bigcirc$	IKU
	SINTEF-GRUPPEN

Table 13: Molecular ratios from mass chromatograms of aromatic fractions.

C-4607 34/4-6 35.4 32.5 Stock tank oil no.3

- <sup>1)</sup> Relative abundance of low molecular weight triaromatic steranes (M/M+P in m/z 231).
- <sup>2)</sup> Relative abundance of low molecular weight monoaromatic steranes (a/a+h in m/z 253).



<u>Table 14:</u>  $\delta^{13}$ C isotope data for DST oil fractions.

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IKU no. DST no. SAT AROM NSO ASF

C-4607 3 -30.6 -28.5 -28.5 -30.2

Figure 2. RT: VALVE 2 + ON  $C_1 - C_8$  Hydrocarbons DST 3 OV: START PRGM RATE 1 C - 4606 3: 99 nC1 nC<sub>2</sub> 3.90 nC3 5.13 isoC4 6.18 nC4 5.52 neo-C<sub>5</sub> 8.59 isoC5 9.54 nC<sub>5</sub> 10.16 19.74 2,2DMC4 2,3DMC<sub>4</sub> CyC<sub>5</sub> 11:73 2MC5 3MC<sub>5</sub> 12.49 12.97 13.19 nC<sub>6</sub> MCyC<sub>5</sub> 14.00 14.29 2,4DMC5 \_\_\_\_2MC<sub>6</sub> 15.13 CyC<sub>6</sub> - 3MC<sub>6</sub> DMCyC5 <u>17.26</u> 17.19 МСуС<mark>6</mark> 17:38 OV: START FINAL TIME 1

- 34 -

52



FIGURE 3

C2-C8 HYDROCARBON GAS CHROMATOGRAMS



-t 



Figure 4a: The DST gas sample has a  $\delta^{13}$ C isotope value which plots close to the zone of gases associated with oils condensates, but lying just inside the zone normally associated with mixed catagenic/biogenic gases. (After Schoell 1983).



Figure 4b: The DST 3 gas plots within the field for oil-associated gases as might be expected. (After Schoell, 1983).

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# FIGURE 5

## WHOLE OIL GAS CHROMATOGRAMS

C <sub>10</sub> etc.	-	n-alkanes
Cy-C <sub>6</sub>	÷	cyclohexane
MeCy-C <sub>6</sub>	-	methylcyclohexane
Pr	-	pristane
Ph	÷	phytane



1 39 4



# FIGURE 6

## SATURATED HYDROCARBON GAS CHROMATOGRAMS

n-C <sub>15</sub> etc.	-	n-alkanes
Pr	÷	pristane
Ph	<b>6</b> 23	phytane
*	Mark	other acyclic
		isoprenoids



ı.



# FIGURE 7

# BRANCHED/CYCLIC HYDROCARBON GAS CHROMATOGRAMS

Pr	- pristane
Ph ,	- phytane
isopr.C <sub>18</sub> etc.	- isoprenoids
*	- n-alkanes remaining after
	adduction





# FIGURE 8

## AROMATIC HYDROCARBON GAS CHROMATOGRAMS FID DETECTION

N,MN,DMN,TMN P,MP,DMP naphthalene and alkylated homologsphenanthrene and alkylated homologs



Ĩ.

Figure 9.

KU.

Mass chromatograms representing terpanes (m/z 191)

A	T <sub>s</sub> , 18¤(H)-trisnorneohopane	C <sub>27</sub> H <sub>46</sub>	(111)
В	T <sub>m</sub> , 17α(H)-trisnorhopane	C <sub>27</sub> H <sub>46</sub>	(I,R=H)
<b>C</b> -	17¤(H)-norhopane	C <sub>29</sub> H <sub>50</sub>	(I,R=C <sub>2</sub> H <sub>5</sub> )
D	17β(H)-normoretane	C <sub>29</sub> H <sub>50</sub>	$(II, R = \bar{C}_2 H_5)$
Ε	17∝(H)-hopane	C <sub>30</sub> H <sub>52</sub>	(I,R=C <sub>3</sub> H <sub>7</sub> )
F	17ß(H)-moretane	C <sub>30</sub> H <sub>52</sub>	$(II, R=C_3H_7)$
G	17∝(H)-homohopane (22S)	C <sub>31</sub> H <sub>54</sub>	(I,R=C <sub>4</sub> H <sub>9</sub> )
Н	17∝(H)-homohopane (22R)	C <sub>31</sub> H <sub>54</sub>	$(I,R=C_{4}H_{9})$
	+ unknown triterpane (gammacerane?)		
Ι	17B(H)-homomoretane	C <sub>31</sub> H <sub>54</sub>	$(II,R=C_4H_9)$
J	17¤(H)-bishomohopane (22S,22R)	C <sub>32</sub> H <sub>56</sub>	$(I,R=C_5H_{11})$
К	17α(H)-trishomohopane (22S,22R)	C <sub>33</sub> H <sub>58</sub>	$(I, R=C_6H_{13})$
L	17∝(H)-tetrakishomohopane (22S,22R)	C <sub>34</sub> H <sub>60</sub>	$(I, R=C_7H_{15})$
Μ	17¤(H)-pentakishomohopane (22S,22R)	C <sub>35</sub> H <sub>62</sub>	$(I,R=C_8H_{17})$
Z	bisnorhopane	C <sub>28</sub> H <sub>48</sub>	
Х	unknown triterpane	C <sub>30</sub> H <sub>52</sub>	
Ρ	tricyclic terpane	C <sub>23</sub> H <sub>42</sub>	(IV,R=C <sub>4</sub> H <sub>9</sub> )
Q	tricyclic terpane	C24H44	$(IV, R=C_5H_{11})$
R	tricyclic terpane (17R,17S)	C <sub>25</sub> H <sub>46</sub>	$(IV, R=C_6H_{13})$
S	tetracyclic terpane	C <sub>24</sub> H <sub>42</sub>	(V)
T	tricyclic terpane (17R,17S)	C <sub>26</sub> H <sub>48</sub>	$(IV, R=C_7H_{15})$







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Figure 10.

Mass chromatograms representing steranes (m/z 217 and 218)

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			•
a	$13\beta(H), 17\alpha(H)$ -diasterane (20S)	C <sub>27</sub> H <sub>48</sub>	(III,R=H)
b 、	$13\beta(H), 17\alpha(H)$ -diasterane (20R)	C27H48	(III,R=H)
с	$13_{\alpha}(H), 17_{\beta}(H)$ -diasterane (20S)	C27H48	(IV,R=H)
ď	$13\alpha(H), 17\beta(H)-diasterane (20R)$	C <sub>27</sub> H <sub>A8</sub>	(IV,R=H)
е	$13\beta(H), 17\alpha(H)$ -diasterane (20S)	C <sub>28</sub> H <sub>50</sub>	$(III, R=CH_2)$
f	$13\beta(H), 17\alpha(H)$ -diasterane (20R)	C28H50	(III,R=CH <sub>2</sub> )
g	$13_{\alpha}(H), 17_{\beta}(H)$ -diasterane (20S)	C20H50	(IV,R=CH <sub>2</sub> )
	+ $14\alpha(H)$ , $17\alpha(H)$ -sterane (20S)	$C_{27}H_{AP}$	(I,R=H)
h	$13\beta(H), 17\alpha(H)$ -diasterane (20S)	$C_{20}H_{E2}$	(III,R=C <sub>2</sub> H <sub>E</sub> )
	+ $14\beta(H), 17\beta(H)$ -sterane (20R)	$C_{27}H_{AB}$	(II,R=H)
i	$14\beta(H), 17\beta(H)$ -sterane (20S)	C <sub>27</sub> H <sub>40</sub>	(II,R=H)
	+ $13_{\alpha}(H)$ , $17_{\beta}(H)$ -diasterane (20R)	27 48 Cao <sup>H</sup> ro	(IV,R=CH <sub>2</sub> )
j	$14_{\alpha}(H), 17_{\alpha}(H)$ -sterane (20R)	28 50 CarH40	(I,R=H)
k	$13_{B}(H), 17_{\alpha}(H)$ -diasterane (20R)	27 48 CaoHra	(III,R=C <sub>o</sub> H <sub>c</sub> )
1	$13_{\alpha}(H), 17_{\beta}(H)$ -diasterane (20S)	29 52 CooHro	(III,R=C <sub>o</sub> H <sub>r</sub> )
m	$14\alpha(H), 17\alpha(H)$ -sterane (20S)	29 52 Coolleo	(I.R=CH_)
n	$13_{\alpha}(H)$ , $17_{\beta}(H)$ -diasterane (20R)	28 50 Coolleo	(III.R=C_H_)
	+ 148(H).178(H)-sterane (20R)	~29~52 CooHee	(II.R=CH_)
ò	148(H), 178(H)-sterane (20S)	-28 50 Cooll-c	(II.R=CH_)
n	$14_{\alpha}(H)$ , $17_{\alpha}(H)$ -sterane (20R)	*28 50 CH	(I.R=CH_)
۲ n	$14_{\alpha}(H), 17_{\alpha}(H)$ -sterane (205)	°28''50 CH	(I_R=C_H_)
ч *	14a(H), 17a(H) = storano (20R)	°29 <sup></sup> 52 с н	(11, 02, 5)
	$\pm$ unknown storano	29''52	(11,1,2,2,5)
~	1/a(H) $17a(H)$ -storang (205)	сн	(II P=C H )
э +	14p(1), 17p(1) - 5 terane (200)	C 29''52	(T P-C H )
ւ 	14a(n), $1/a(n)$ -Stemane (20K)	ັ29 <sup>°</sup> 52	$(v_{p-c} \mu)$
u 		<sup>6</sup> 21 <sup>7</sup> 36	(1) P = C + 1
V	5a(H)-Sterane	<sup>C</sup> 22 <sup>H</sup> 38	(1 <b>v</b> , K=C3 <sup>H</sup> 7)

I

II



v







## FIGURE 11

## MASS CHROMATOGRAMS REPRESENTING AROMATIC HYDROCARBONS

TIC	- total ion current chromatogram
m/z 92,106	- alkylbenzenes
m/z 142,156,170	- alkylnaphthalenes
m/z 178,192,206	- phenanthrene and alkylphenanthrenes
m/z 184,198,212	- dibenzothiophene and alkyldibenzo-
	thiophenes
m/z 231	- triaromatic steranes
m/z 253	- monoaromatic steranes



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Mass chromatograms representing monoaromatic (m/z 239 and 253) and triaromatic (m/z 231) steranes.

### m/z 253

- a  $C_{21}$  monoaromatic sterane
- $b C_{22}$  monoaromatic sterane
- c unidentified
- d  $C_{27}$  monoaromatic sterane
- e  $C_{27}$  monoaromatic sterane
- f  $C_{28}$  monoaromatic sterane
- g  $C_{27}$  monoaromatic sterane
- $h C_{28} + C_{29}$  monoaromatic sterane
- i  $C_{29}$  monoaromatic sterane
- $j C_{29}$  monoaromatic sterane
- k unidentified
- 1 unidentified

m/z 231

- $M C_{20}$  triaromatic sterane
- $N C_{21}$  triaromatic sterane
- $0 C_{26}^{--}$  triaromatic sterane
- $P C_{26} + C_{27}$  triaromatic sterane
- Q  $C_{28}$  triaromatic sterane
- $R C_{27}$  triaromatic sterane
- S  $C_{28}^{-1}$  triaromatic sterane







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an tahun su



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Well: SAGA 34/4-6 Sample: DST 3

Figure 12: Plot of  $\delta^{13}$ C values for various oil fractions.(After Stahl, 1977).



#### APPENDIX 1.

## <u>Molecular ratios from terpane and sterane mass chromatograms applied</u> as maturity and source characteristic parameters

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Geochemical fossil/biological marker compounds are characteristic of the type of organic matter present at the time the sediments were deposited. The biological isomers of these compounds are converted to the geochemical isomers with increasing maturity until a stable mixture of the isomers is attained. Migration and weathering processes also alter the distribution of biomarker compounds in a sample.

Hopanes, moretanes and tricyclic terpanes are the most common compounds in the m/z 191 mass chromatograms of most extracts and oils. Of the hopanes, the  $C_{27}$  and  $C_{29}$ - $C_{35}$  homologs are ubiquitous, while 28,30-bisnorhopane is believed to be typical of certain types of source rocks. This is also thought to be true for a component, probably gammacerane, which sometimes coelutes with the 22S isomer of the  $C_{31}$  17 $\alpha$ (H)-hopanes. The relative distribution of the  $C_{27}$  trisnorhopanes is thought to be both sourceand maturity-dependant.

In the m/z 217 and 218 sterane mass chromatograms, the molecular weight distribution of the  $C_{27}$ - $C_{30}$  regular steranes is thought to be representative of the original organic matter input. The  $C_{29}$  steranes are generally indicative of input from higher land plants, but, more recently, similar compounds have been reported from marine micro-organisms. Moldowan (1984) has also recently published data on  $C_{30}$  steranes that are thought to be characteristic of input from marine organisms. This is one of the few marine markers reported, and previously the indication of marine origin for mature geolipids was assessed on the basis of absence of nonmarine marker compounds.

The biological hopane isomers, the  $17\beta(H), 21\beta(H)$ -hopanes, undergo structural changes during maturation. These isomerisation reactions are believed to proceed through the  $17\beta(H), 21\alpha(H)$ -hopane structure (moretanes) to the stable  $17\alpha(H), 21\beta\alpha(H)$ -hopane structure. With thermal maturity,  $17\alpha(H)$ -hopanes account for 90-100% of the hopanes present. The ratio  $\alpha\beta/\alpha\beta+\beta\alpha$  is used to describe this reaction. In the extended hopanes  $(\geq C_{31})$ , the thermally stable S configurations at C-22 become increasingly more abundant compared to the biologically preferred R configu-



rations with increased maturity. The ratio of the 22S:22R isomers stabilises at about 60:40 at thermal maturity. The Tm/Ts  $C_{27}$  hopane ratio (Seifert et al, 1978) also varies with thermal maturity such that, with increasing maturity,  $17\alpha(H)$ -trisnorhopane (Tm) is reduced in intensity relative to the more stable  $18\alpha(H)$ -trisnorhopane (Ts), causing the Tm/Ts ratio to decrease. However, this ratio is also thought to be source-dependant, and this should be allowed for when using the ratio as a maturation indicator. The tricylic terpanes vary in abundance with maturity (Schou et al., 1984a), as does 28,30-bisnorhopane (Cornford et al.,1983; Schou et al., 1984b).

Two sterane isomerisation reactions are commonly used for maturity determination based on data from the m/z 217 mass chromatogram. The biologically preferred  $14\alpha(H)$ ,  $17\alpha(H)$  regular sterane isomers are gradually replaced by the more thermally stable  $14\beta(H)$ ,  $17\beta(H)$ -sterane isomers. At thermal maturity,  $\beta\beta$  isomers may account for 75-85% of the  $\alpha\alpha/\beta\beta$  mixture. Mackenzie et al (1980) have observed a change from a dominance of the biological sterane epimer in recent sediments to the more stable S-configuration at C<sub>20</sub>, such that this configuration accounts for 50% of the epimers at thermal maturity. The abundance of rearranged steranes relative to regular steranes has also been reported to increase with thermal maturity.

One of the reactions taking place at an early stage of diagenesis is the aromatisation of steranes, leading to the formation of mono- and triaromatic analogs. This process is measured by the abundance of triaromatic compounds relative to mono-aromatic compounds (% tri/tri+mono) from the m/z 231 and 253 mass chromatograms, respectively. Cracking processes also take place during early diagenesis, and may be used for maturity determination together with the %tri/tri+mono ratio (Mackenzie et al., 1980; 1981; 1982).

The effect of migration and weathering on the distribution of biological markers is less well understood than maturity-induced changes. Migration may be observed to cause an increase in the relative amounts of rearranged and  $14\beta(H),17\beta(H)$  regular steranes (Seifert and Moldowan, 1978). Severe biological alteration leads to the formation of desmethyl-hopanes (Seifert and Moldowan, 1979).