

GEOCHEMICAL SERVICE REPORT

Prepared for

SAGA PETROLEUM A.S.

GEOCHEMICAL EVALUATION OF THE DST 4 OIL FROM SAGA'S 34/4-4 WELL

March 1983

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

COMPANY PROPRIETARY

GEOCHEMICAL EVALUATION OF THE DST 4 OIL FROM SAGA'S 34/4-4 WELL

SUMMARY

This oil is a light, low sulphur crude, which is mature but not highly mature.

Analyses performed, suggest that the oil is derived from organic matter which was laid down in a relatively restricted and neducing environment.

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INTRODUCTION

This report presents the results of a geochemical evaluation of a single oil sample (DST 4) from Saga's 34/4-4 well.

The project was authorised by T.O. Throndsen, Saga Petroleum A.S., Hovik.

A. ANALYTICAL

The DST 4 oil was assigned the Geochem sample number 693-252.

Upon an analytical format specified by the client, the following analyses were performed by Geochem: API gravity, gas-oil ratio, sulphur content, nickel and vanadium content, volatile fraction content (to 210°C), light hydrocarbon analysis (C_1-C_4), carbon isotope analysis upon the methane, paraffin and aromatic fractions, gasoline range analysis (C_4-C_7), chromatographic separation of the oil into paraffin and aromatic fractions, high resolution capillary gas chromatography of the C_{15+} paraffin-naphthene, branched cyclic and aromatic fractions and capillary gas chromatography mass spectrometry of selected fragment ions.

The data are presented in tables 1 through 5 and graphically in figures 1 through 5.

B. GENERAL INFORMATION

Ten (10) copies of this report have been forwarded to T.O. Throndsen at Saga Petroleum A.S. in Hovik.

The results of this study are proprietary to Saga Petroleum A.S.

RESULTS AND INTERPRETATION

The DST 4 oil arrived at Geochem Laboratories in a pressurised steel container. Initial analyses of the oil, released from the container, revealed that the oil had an API gravity of 43°, a gas-oil ratio of 142.5 std cu. feet/barrel and a sulphur content of 0.144%. Concentrations of nickel and vanadium in the oil were close to detection limits at 1.9 ppm and less than 1 ppm respectively. Although these figures are too low to be of any value, the slightly higher concentration of nickel is as would be expected for a low sulphur crude oil.

Simulated distillation carried out on the oil, showed that approximately 60% of the total hydrocarbons were released below 210°C indicating that the oil is fairly light. A full range of hydrocarbons ranging from methane (C₁) through to nC_{34} is observed. From the paraffin distribution, the oil appears mature however, the fairly high proportion of branch chained hydrocarbons (isoprenoids) suggest that the oil is not highly mature.

Analysis of the light hydrocarbon gases $(C_1 - C_4)$ indicates that 77% of the light gases is composed of approximately equal amounts of methane, ethane and propane. The butanes account for approximately 16%, whilst the remaining 7% represents the heavier $C_5 - C_7$ fraction. An isobutane to butane ratio of 0.28 was observed.

Carbon isotope measurements, made upon the methane associated with the oil under pressure, gave a $\frac{2}{3}$ value of -46°/oo confirming a thermogenic oil associated origin for the methane.

The gasoline range hydrocarbons (C_5-C_7) appear depleted in the butanes and isoparaffins, whilst the monoaromatic and alkyl monoaromatic compounds are fairly abundant. Low isobutane/normal butane (.28) and normal hexane/methyl cyclo pentane (1.63) ratios suggest that the oil is mature.

A chromatogram of the C_{15+} paraffin-naphthene fraction shows a full range of normal alkanes ranging from nC_{15} up to nC_{35} and exhibit a slight even preference above nC_{22} . The abundance of isoprenoid hydrocarbons, e.g. pristane and phytane suggests that although mature the oil is not highly mature. The aromatic fraction contains a range of alkyl substituted naphthalenes and phenanthrenes, the sulphur bearing aromatic compounds (benzothiophenes) being present only in low concentrations.

The DST 4 oil was analysed by GC-MS (after urea adduction of the paraffin fraction) using selective ion monitoring to detect the triterpane (m/e 191) and sterane (m/e 217) fractions. A series of steranes and triterpanes have been identified.

TRITERPANES

Tricyclic terpanes are present only in very low concentrations, the bulk of the terpanes identified range from C_{27} (trisnorhopane) to C_{35} (pentahopanes) and peak with the C_{30} hopane. The most striking feature is the relative abundance of an unusual triterpane; namely a C_{28} triterpane identified as Bisnorhopane (6).

STERANES

A complex mixture of steranes have been identified and show a C_{27}/C_{29} ratio slightly in favour of the C_{27} components. The relative abundance of /3/3 steranes (m/e 218) confirm the relative maturity of the oil, a conclusion also supported by the ratios of the 20R and 20S isomers (approximately 50:50 mixture). Monoaromatic steranes (m/e 253, 239) are not abundant and again this reflects the maturity of the oil.

Determinations of the stable carbon isotope ratios, were undertaken upon the C_{15+} hydrocarbon fractions of the oil. Values of $-30.5^{\circ}/oo$ and $-29.6^{\circ}/oo$ were obtained for the saturated and aromatic hydrocarbon fractions respectively and are suggestive of organic matter which was deposited in a relatively restricted environment.

CONCLUSIONS

Analyses performed upon the DST 4 oil show that it is a light (API 43°), low sulphur (0.144%) relatively mature oil. The results indicate that the oil was derived from organic matter laid down in a relatively restricted, and reducing environment.

DETAILED GASOLINE (C4-C7) ANALYSIS

GEOCHEM SAMPLE	0.5.0	5.			
NUMBER	202		 o on ini ni ni ni ni ni ni ni ni	n ene me ver ver en aar aar a	
DEPTH	DST-4		 e lan geran ne ar ar ar ar a		
isobutane	0.85				<i>1</i> 0
n-butane	5.81				
isopentane	4.57				
n-pentane	8.67				
2.2-dimethvlB	0.09	м. С			
ovelonantana(CP)	1 01				
2 3-dimethylR	0.07		2		
2mmothv1P	1. 67				
3-methylP	2,95				
	i dagi da ji kati kati ji				
n-hexane	9.98				
methylCP(MCP)	6.13				
2,2-dimethylP	0.42				
2,4-dimethy1P	0.06				
2,2,3-trimethylB	0.00				
benzene	2.22				
cvclohexane(CH)	6.76				
3.3-dimethvlP	0.80				
1.1-dimethvlCP	0.00				
2-methy1H	3.96				
2,3-dimethylP	0.81				
3-methylH	3.66				
l,c,3-dimethylCP	1.53				
1,t.3-dimethylCP	1.47				
1.t.2-dimethvlCP	3,26				
3-ethylP	0.00				
n Joont and	20. 40				
mothyl CH(MCH)	10.72				
1 o 7mdimothy100	0.00				
toluene	6 84				
eosterne.					
ABUNDANCE					
nC7/C7nap x100	54.96				
MCP/Bz	2.76				
MH/DMCP	1.22				
nC6/MCP	1.63				
Y~~DADAFFING	3/ 0%				
MILLINGELLING Signation DADADDING	27 () 2 22 18				
also "farmf f 193 7 Na Durupyd p	33 88				
* MELETILERADIAD * ADAMATICE	0 A7				
A RENUBLY LOD	2*01	15			

	*****		1.01.5						
GEOCHEM SAMPLE NUMBER		HYDROC	ARBONS	NON HYDROCARBONS					
	DEPTH	Paraffin Naphthenes	Aromatics	Precipid. Asphaitenes	Eluted NSO's	Non aluted NSO's	Sulphur		
693-252	DST-4	35.74	29.29	5.37	553	3.25	0.81		

TABLE 2 COMPOSITION (NORMALISED %) OF C15+ MATERIAL EXTRACTED FROM ROCK

COMPOSITION (NORMALISED %) OF C15+ PARAFFIN - NAPHTHENE HYDROCARBONS

GEOCHEM SAMPLE NUMBER	~252						
DEPTH	DST-4						
SAMPLE TYPE		~~~~~~		 		·····	
nC ₁₅	12.18						
nC ₁₆	10.45		4		e.		
nC ₁₇	9.27						
nc ₁₈	8.36						
nC ₁₉	7.82						
nC ₂₀	7.45						
nC ₂₁	6,18						
nC ₂₂	6.09						
^{nC} 23	5.45						
nc ₂₄	5.09						
nC ₂₅	4.27						
^{nC} 26	3.82						
nc ₂₇	2.91						
^{nC} 28	2.82						
^{nC} 29	2.45		÷				
^{nc} 30	1.82						
^{nC} 31	1.27						
¹¹⁰ 32	0.02 0.64						
	0.55						
34 	0.27		×				
> 33 PARAFFTN	59.49			 			
ISOPRENOID	6,98						
NAPHTHENE	33.53						
CPI INDEX A	0.95						
CPI INDEX B	0.99						
DDTSTANE /DEVTANE	1, 10			.îr			
PRISTANE/nC	0,74						
17				 			

CARBON ISOTOPE DATA (PDB 0/00)

GEOCHEM SAMPLE NUMBER	IDENTIFICATION	PARAFFIN- NAPHTHENE	AROMATICS	METHANE
693-252	DST-4	~30,5	-29.6	-46%00

BULK PROPERTIES OF DST4 OIL

SULPHUR CONTENT	0.144%	
API GRAVITY	430	
GAS OIL RATIO	142.5 std. cu. feet/barre	Ĩ.
NICKEL CONTENT	1.9 ppm	
VANADIUM CONTENT	l ppm	

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e.



DST 4

FIGURE 2 C15+ PARAFFIN-NAPHTHENES WELL 34/4-4







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C₁₅₊





FIGURE 4

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AROMATIC CHROMATOGRAMS

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TERPANES & STERANES









MASSFRAGMENTOGRAMS W

MONOAROMATIC STERANES

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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 betwwen 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-C4 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 (<u>not</u> 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 -C7, C_4 -C7, 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 -C7 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 C4-C7 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.

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

F) REROGEN 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 factes) and indicates the source quality of the sediment - which is confirmed using the organic carbon, light hydrocarbon, pyrolysis and C_{154} 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 <u>directly</u> 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.

Cur 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 (* 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 cometamorphic 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, inertifie 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 visual kerogen 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) Clet EXTRACTION, DEASPHALTENING AND CHROMATOGRAPHIC SEPARATION

Sections "A" and "Z" 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-NAPHTHEME HYDROCARBONS

The gas chromatographic configurations of the heavy C₁₅, 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/palyhological 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:

**	C21	* Cg	3 *	C25	4	027	-	C ₂₁	÷.	653	*	<u>°25</u>	्रक्षेः २०००००	C27
	C20	+ C;	2 *	C24	+	C26		C22	+	C24	بېد	C26	*	C28
	~~~~~						2							
æ	025	* C7	7 4	C29	4	C31	4	C25	*	C27	-	C29	*	C31
	C24	+ 0;	6 +	- C28	*	C30		C26	÷.	¢28	*	C 30	*	<u>032</u>
	**	$= \frac{C_{21}}{C_{20}}$ $= \frac{C_{25}}{C_{24}}$	$= \frac{C_{21} + C_2}{C_{20} + C_2}$ $= \frac{C_{25} + C_2}{C_{24} + C_2}$	$= \frac{C_{21} + C_{23} + C_{20} + C_{22} + C_{20} + C_{22} + C_{21} + C_{25} + C_{25}$	$= \frac{C_{21} + C_{23} + C_{25}}{C_{20} + C_{22} + C_{24}}$ $= \frac{C_{25} + C_{27} + C_{29}}{C_{24} + C_{26} + C_{28}}$	$= \frac{c_{21} + c_{23} + c_{25} + c_{25}}{c_{20} + c_{22} + c_{24} + c_{25}}$ $= \frac{c_{25} + c_{27} + c_{29} + c_{24} + c_{26} + c_{28} + c_{$	$= \frac{c_{21} + c_{23} + c_{25} + c_{27}}{c_{20} + c_{22} + c_{24} + c_{26}}$ $= \frac{c_{25} + c_{27} + c_{29} + c_{31}}{c_{24} + c_{26} + c_{28} + c_{30}}$	$= \frac{c_{21} + c_{23} + c_{25} + c_{27} + c_{26}}{c_{20} + c_{22} + c_{24} + c_{26}}$ $= \frac{c_{25} + c_{27} + c_{29} + c_{31}}{c_{24} + c_{26} + c_{28} + c_{30}}$	$= \frac{c_{21} + c_{23} + c_{25} + c_{27} + c_{21}}{c_{20} + c_{22} + c_{24} + c_{26}} \frac{c_{22}}{c_{22}}$ $= \frac{c_{25} + c_{27} + c_{29} + c_{31}}{c_{24} + c_{26} + c_{28} + c_{30}} \frac{c_{26}}{c_{26}}$	$= \frac{c_{21} + c_{23} + c_{25} + c_{27} + c_{21} + c_{21} + c_{20} + c_{22} + c_{24} + c_{26} + c_{22} + c_{22} + c_{23} + c_{25} + c_{25} + c_{25} + c_{25} + c_{25} + c_{26} + c_{28} + c_{30} + c_{26} + c_{26} + c_{26} + c_{26} + c_{30} + c_{26} + c_{26} + c_{30} + c_{30}$	$= \frac{c_{21} + c_{23} + c_{25} + c_{27} + c_{21} + c_{23}}{c_{20} + c_{22} + c_{24} + c_{26}} + \frac{c_{21} + c_{23}}{c_{22} + c_{24}}$ $= \frac{c_{25} + c_{27} + c_{29} + c_{31}}{c_{24} + c_{26} + c_{28} + c_{30}} + \frac{c_{25} + c_{27}}{c_{26} + c_{28}}$	$= \frac{c_{21} + c_{23} + c_{25} + c_{27}}{c_{20} + c_{22} + c_{24} + c_{26}} + \frac{c_{21} + c_{23} + c_{23}}{c_{22} + c_{24} + c_{26}}$ $= \frac{c_{25} + c_{27} + c_{29} + c_{31}}{c_{24} + c_{26} + c_{28} + c_{30}} + \frac{c_{25} + c_{27} + c_{27} + c_{26}}{c_{26} + c_{28} + c_{30}}$	$= \frac{c_{21} + c_{23} + c_{25} + c_{27} + c_{21} + c_{23} + c_{25}}{c_{20} + c_{22} + c_{24} + c_{26}}$ $= \frac{c_{25} + c_{27} + c_{29} + c_{31}}{c_{24} + c_{26} + c_{28} + c_{30}}$ $= \frac{c_{25} + c_{27} + c_{29} + c_{31}}{c_{24} + c_{26} + c_{28} + c_{30}}$	$= \frac{c_{21} + c_{23} + c_{25} + c_{27} + c_{21} + c_{23} + c_{25} + c_{25} + c_{25} + c_{26} + c_{26}$

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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_A and C.P.I_B; 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 (340-350°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 C4-C7 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*normal paraffin distributions are used to "fingerprint" the samples.
- capillary chromatograms of whole oils and of the Cg+ fraction of source rocks.
- capillary gas chromatography of C15+ 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.

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#### M-S) 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

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) <u>VISCOSITY</u> (ASTM D445-72, IP71/75)
- N-S) 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. .

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8 - PRISTANE 6 - PHYTANE



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FIGURE 4

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## AROMATIC CHROMATOGRAMS











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FIGURE 5b

## MASSFRAGMENTOGRAMS

## MONOAROMATIC STERANES



