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CHEMICAL ANALYSIS OF WATER, GAS AND OIL FROM WELL 1/9-3

STATOIL PRODUCTION LABORATORY

Den norske stats oljeselskap a.s

CHEMICAL ANALYSIS OF WATER, GAS AND OIL FROM WELL 1/9-3

STATOIL PRODUCTION LABORATORY

K.S. ÅRLAND A.M. MARTINSEN E. OSJORD A. LYKLING

Issued:			Chapter:
6.4.	79.	Chemical analysis of samples	
		from 1/9-3.	Page:
010903	/K5		1

SUMMARY.

Analysis is done on gas, water and oil samples from the production testing of 1/9-3.

Samples were collected at bubble hose and separator at ambient conditions and subjected to different types of treatment both on rig and in the lab.

Results show that

- the gas is getting richer in methane as one gets higher on the structure
- formation water total dissolved solids or salinity is about 70.000 ppm.
- 3) Oil from different depths belongs to the same types, being paraffinic with a high wax content. Most probably the oil has originated from the same source rock.
- Oil samples are correlatable even though they have been subjected to severe treatments and several months storage.

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Issued:		Chapter:
6.4.79.	Chemical analysis of samples	
	from 1/9-3.	Page:
010903 /K5		2

1. INTRODUCTION.

During the testing of 1/9-3 in Sept. 78 samples of water, gas and oil were collected from tests at four different depths.

In November samples were selected for chemical analysis by Statoil Production Laboratory. The aim was to determine the properties of the formation water and to characterize the crude oil.

This should reveal if the different zones contained the same type of fluids and whether these could be correlated with fluids from other structures in the same block.

SAMPLE DESCRIPTION. 2.

The samples were received in the lab. the 10th of November. Gas samples was collected in aluminized polyester film gas sampling bags with two valves and septum.

Water samples were collected in 25 l plastic containers.

The oil samples analysed by the lab.were collected and treated in many different ways before they arrived in the lab. Most of the oil samples had been in contact with water and vice versa for more than two months.

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Issued: 6.4.79.	Chemical analysis of samples	Chapter:
010903 /K5	from 1/9-3.	Page:

Sample description

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	Lab. code	Sample no	DST	Flow	Date	Hour	Sampling Point	Sample Cont.	
ſ									
	Gl	41	2	2	6.9.78.	21.50	Separator	Gas bag	
	G2	42	2	2	n	"	"	11	
	G3	43	2	2	11	20.07	н	11	
	G5	51	3	2	14.9.78	16.25	Bubble hose	11	
	G6	52	3	2	11	16.50	n	11	
	V10	16	1	2	2.9.78	17.40	IT	25 L plastic	
	V11	17	1	2	11	17.35	н	11	
	V12	19	2	2	6.9.78	20.42	11	11	
	V13	20	2	2	n	21.40	"	11	
	V14	21	4	4	21.9.78	08.00	Separator	R	
	04	48/47	2	2	6.9.78	21.00	Bubble hose	2xl Lglass	note]
	06	20	2	2		21.40	11	25 Lplastic	note 2
	05	46	3	2	14.9.78	10.26	11	l L glass	note 3
	014	89	4	4	21.9.78	01.30/04.00	Bubble hose	11	note 4
_	015	90	4	4		04.30/07.00		11	"
	03	8	4	4	11	08.00	Separator	20L jerry can	
		L			L	1			

Note 1.

The samples (48/47) as received in the lab. have been heated, added demulsifier and centrifuged on the rig.In the lab. the contents of the two glasses were mixed. Centrifuging gave 13% water and 0,15% sediments.

Note 2.

Oil was collected by skimming the oil slick on the water sample V13 and centrifuged.

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Issued:		Chapter:
6.4.79.	Chemical analysis of samples	
	from $1/9-3$.	Page:
010903 /K5		4

statoil

Note 3.

Collected using a plastic container as a separator for oil, gas and water.

Note 4.

Sample has been centrifuged on rig.

3. METHODS.

3.1 Gas samples.

The gas was analyzed on a chromatograph with thermal conductivity detector. The instrument is calibrated and the accuracy range from 1% for C_1 to 5-7% for $C_5 - C_7$, giving 2% uncertainty of the calculated gas gravity. All samples contained a certain amount of air, due to insufficient flushing of gas bag. The amount of air is removed in the calculations by subtracting the concentration of $O_2[O_2]$ and an amount N_2 equal to $[O_2] \times 3,78$ where the factor is the ratio $[N_2]/[O_2]$ in ordinary air. In most cases this left samples free of N_2 .

3.2 Water samples.

Prior to analysis all samples was filtered through 0,45 micron filter paper. Most of the analysis were carried out according to API Recommended Practice. Exceptions are determination of iron using atomic absorption and lithium using flame emission spectroscopy.

The amount of Na⁺ is calculated by balancing equivalent weights. The analysis is "controlled" by using correlations (assuming pure NaCl solution) to estimate total dissolved solids from the measurements of specific gravity and resistivity. The concentration of Cl⁻ is multiplied by 1,65 (= $\frac{Mol.weight NaCl}{atomic weight Cl}$) to give the total dissolved solids, again assuming a pure NaCl solution.

Issued:		Chapter.
6.4.79.	Chemical analysis of samples	
	from 1/9-3.	Page:
010903 /K5		5

An equivalent NaCl concentration is calculated form the analysis using Schlumberger Log Interpretation Chart: Gen-8 (1972).

3.3 Oil analysis.

Most of the analysis was carried out according to well known ASTM and IP standards. An exception is the determination of wax content. This is done by measuring the amount of waxlike material which percipitates in two different processes:

- a) centrifuging the oil (2000 rpm in 10 min.) at several temperatures.
- b) when cooling a solution of oil in methylene chloride to $-32^{\circ}C$.

The chromatographic analysis was designed to characterize the crude so that comparisons could be made. Therefore both the oil and the gas in equilibrium with it (head space gas) was analysed using high resolution capillary column and flame ionization detector. The amount of oil eluted from the column (recovery) is typical in the order of 50%.

Compositions are compared by plotting normalized values of some naphthenic and iso prenoid molecules, since these normally will be least affected by extraction by water and bacterial action. The ratio between the amount of certain molecules in the $C_2 - C_7$ range is calculated following a suggestion by Erdman (1). The same is done for the iso prenoids pristan and phytan and the neighbouring normal paraffins. This is normal practice in organic geochemistry.

(1) Erdman, J.G : "Geochemical correlation of Petroleum". Bull. Am. Ass. Petr. Geologist. <u>58</u> pp2326 (1974)

statoil

Issued:		Chapter:
6.4.79.	Chemical analysis of samples	
	from 1/9-3.	Page:
010903 /K5		6

4. <u>RESULTS</u>.

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4.1 Gas analysis.

Concentration of gas components are given as mol %.

Lab. code	Gl	G2	G3	G5	G6
Sample no.	41	42	53	51	52
N ₂	-	-	-	0.6	-
co ₂	3.0	3.1	2.7		-
c ₁	78.0	77.7	80.8	85.4	90.3
c ₂	10.3	11.1	10.0	9.2	6.7
c ₃	5.5	5.0	4.2	3.1	2.0
ic ₄	0.70	0.85	0.65	0.36	0.25
nC4	1.56	1.47	1.14	0.84	0.52
iC ₅	0.38	0.37	0.28	0.19	0.1
nC ₅ .	0.38	0.33	0.20	0.20	0.1
с _б	0.18	0.08	0.03	0.11	0.03
Mol.% air in sample	10	36	15	6	5
Calculated gas gravity	0.740	0.738	0.707	0.660	0.623
Calculated mol. weight	21.4	21.3	20.4	19.1	18.0

statoil

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Issued:		Chapter:
6.4.79.	Chemical analysis of samples	
	from 1/9-3.	Page:
010903 /K5		7

statoil

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4.2 Water analysis

Concentration of ions are given as mg/l.

Lab code	V 10	V 11	V 12	V 13	V 14
Sample no.	16	17	19	20	21
Cloride, Cl	41800	42400	40800	32800	54500
Sulfate, $SO_4^{}$	970	815	730	480	1200
Carbonate, $CO_3^{}$	0	0	0	0	0
Bicarbonate, HCO_3^{-}	610	480	670	490	390
Hydrooxyd, OH	0	0	0	0	0
Calcium, Ca ⁺⁺	4550	4670	3900	3125	25640
Magnesium, Mg ⁺⁺	212	207	1530	390	2190
Iron, Fe (total)	1.85	1.75	4.2	6.8	390
Lithium, Li ⁺	11.2	11.3	11.2	9.1	4.4
рн	7.4	7.2	7.4	7.3	4.65
Specific grav.(15 ⁰ C)	1.0508	1.0509	1.0500	1.0404	1.083
Resistivity (nm) at 23 C	0.107	0.108	0.110	0.132	0.091
Calculated values:					
Sodium, Na ⁺ Equivalent NaCl(g/]	22135 67.94	22089 68.51	19624 64.94	17330 53.24	2267 -
solids(g/l) by l) adding	70.28	70.66	67.27	54.62	86.52
2) gravity corr.	68.0	68.0	67.0	54.0	112.0
3) resist. corr.	69.3	69.3	67.5	54.3	89.9
4) Cl ⁻ concentr.	68.9	70.0	67.3	54.1	83.6

Add. measurements made on V14: Na: 10.500 mg/1. Solids: 108.250 mg/1.

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4.3 OIL ANALYSIS.

A summary of the properties of the 6 oil samples is presented below. The chromatographic data are given as weight %. For the liquid phase the composition is normalized to 100% for the fraction eluting up to and including nC_{22} .

Lab. code	04		06		C) 5	5 01		0 15		03	
Sample no.	48 8	47	20 46		89		9	0	8			
Density, 15 ⁰ C	0.85	525	0.84	199	0.8	0.8516		039	0.7962		0.7702	
Approx. ^O API	34	1.3	34	1.8		34.5	4	4.5	4	6.2	5	2.0
kin. vis c osity at 40 ⁰ C (cst)	8	3.3	8	3.1		7.0		1.98		1.65		1.13
K (OUP)	12	2.1	12	2.1]	L2.05	1	.2.10]]	2.05	1	2.1
- 10°C centri- + 5°C fuging + 10°C *	nc visi	ot Lble	nc visi	ot ble	nc visi	ot ible	5	50 80 .0 5		50 20 2	2 1	5 0 2 1
Methylene chloride methode	10).5	-	7.0	I	8.5				7		4.5
Cloudpoint (^O C)		– NOT	MEASU	RABLE			+2	2	+2	22	+	6
Pourpoint (^O C)	+7		+6	5		-5	-]	L5	÷]	L5	-2	24
Asphalt %	C	0.46	c).19		0.81		0.052		0.065		0.052
Salt mg/l					12		13	80	1]	LO	35	
Chromatography	gas 0 140	<u>11q</u> .	gas	<u> </u>	gas	11 q .	gas	11q.	gas	11q.	gas	<u></u>
	0.148	-	0.294	-	0.047	-	0.296	-	2.94	0.002	-	-
^C 2	2.30	-	2.91	0.003	0.036	-	1.88	0.009	8.41	0.014	5.02	0.036
² 3	12.8	0.057	16.2	0.08	16.4	0.24	7.84	0.057	15.1	0.078	30.6	0.805
^{1C} 4	/./0	0.071	8.69	0.101	13.4	0.33	15.1	0.063	6.26	0.078	11.2	0.70
nC ₄	1/./	0.26	20.6	0.35	28.3	0.842	15.5	0.246	15.7	0.291	23.3	2.24
^{iC} 5	9	0.380	9.83	0.449	10.6	0.612	11.2	0.413	8.94	0.447	8.01	1.96
nC ₅	16.9	0.935	11.5	0.694	11.8	0.838	15.1	0.735	11.4	0.770	8.58	2.90
^{2MC} 5	4.90	0.653	3.45	0.502	2.87	0.431	5.69	0.682	4.02	0.724	1.94	1.57
3 MC ₅	2.28	0.357	1.89	0.335	1.50	0.268	3.20	0.451	2.24	0.478	1.02	0.958
nC ₆	5.39	1.08	5.46	1.20	4.21	0.916	9.29	1.76	6.53	1.80	2.77	3.32
MCC ₅	1.57	0.422	1.59	0.466	1.03	0.294	2.39	0.589	1.67	0.597	0.68	0.99
^{nC} 7	2.32	1.63	2.25	1.81	1.44	1.05	2.93	2.83	2.19	2.92	0.795	3.42
MCC ECC6 Farnesane	1.93	1.61 0.779 1.01	1.88	1.74 0.819 1.05	1.09	0.917 0.440 1.29	2.21	2.30 1.068 0.948	1.59	2.33 1.103 0.925	0.602	2.61 1.016 0.700
nC ₁₇		1.52		1.48		1.75		1.18		1.05		0.806
Pristane		1.24	}	1.64		2.07		1.06		0.964		0.749
nC ₁₈		1.45	1	1.62		1.63		1.14	ļ	1.02		0.728
Phytane		1.24		1.25		1.61		0.807		0.745	L	0.568

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lssued: 6.4.79		Chemical analysis of samples	Chapter:
010903	/KS	from 1/9-3	Page: 9

statoil

Results calculated from the chromatographic data for the crude oil (liq.).

Lab. code	04	06	05	0 14	0 15	03
Sample no.	48&47	20	46	89	90	8
Ratio between sel- ected molecules:						
c ₂ /c ₃	-	0.038	-	0.16	0.18	0.045
iC ₄ /nC ₄	0.27	0.28	0.39	0.26	0.27	0.31
iC ₅ /nC ₅	0.41	0.65	0.73	0.56	0.58	0.67
2мс ₅ /3мс ₅	1.83	1.50	1.61	1.51	1.52	1.64
^{nC} 6 ^{/M} с 5	2.56	2.58	3.11	2.98	3.02	3.36
^{nC} 7 ^{/M.Ć} 6	1.01	1.04	1.15	1.23	1.25	1.31
nC ₁₇ /Pristan	1.23	0.91	0.84	1.12	1.09	1.08
nC ₁₈ /Phytan	1.18	1.30	1.02	1.42	1.38	1.28
Pristan/Phytan	1.00	1.31	1.29	1.31	1.30	1.32
Compositional data for some naphthe- nic & isoprenoid molecules:						
MCC5	0.26	0.27	0.32	0.26	0.26	0.38
MCC ₆ ECC ₆ Farnesane	1 0.48 0.63	1 0.47 0.60	1 0.48 1.40	1 0.46 0.41	1 0.47 0.40	1 0.39 0.27
Pristan	0.77	0.94	2.26	0.46	0.41	0.29
Phytan	0.77	0.72	1.76	0.35	0.32	0.22

The data is plotted in appendix 1 and 2.

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Issued:		Chapter:		
6.4.79.	Chemical analysis of samples			
	from 1/9-3.	Page:		
010903 /K5		10		

5. DISCUSSION.

5.1 Gas analysis.

Samples Gl and 2 are parallel samples and the differences found are due to the sampling, leaving 36% air in the gas bag in sample no. G2. Samples G5 and G6 have no CO₂ content and shows an increasing amount of methan and decreasing specific gravity with time.

5.2 Water analysis.

5.2.1 Technical comments.

For samples V 10 - 13, calculated total dissolved solids showed good agreement with solid content inferred from correlations with resistivity and specific gravity. This means that the major ions are identified and that the calculated amount of Na⁺ probably is "correct". Na⁺ and total dissolved solids should have been determined by direct measurements to give a control of the analysis.

Lithium is determined to get an idea of the order of magnitude present. This should also have been done for K^+ and Ba^{2+} .

It is seen that the "equivalent NaCl" concept tends to give higher resistivities than actually measured.

The calculated Na⁺ concentration in V 14 was much too low to be believed and the total dissolved solids did not correlate with the specific gravity. Therefore Na⁺ and the solid was determined independently. This shows that an anion is missing.

5.2.2 Interpretation of results.

V 10 and V 11 are almost parallel samples and the results

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Issued: 6.4

010903

Chemical analysis of samples from 1/9-3.

Chapter:

Page: 11

are very similar. V 13 is sampled one hour later than V 12 and shows a much lower Cl⁻ content. The Cl⁻ concentration in the samples V 10 - V 12 is significantly higher than in the mud (Cl⁻ in mud is approx. 15.000 ppm), the pH is close to neutral, and the well was flowed for several hours after clean up. Therefore one can assume that these samples are representative for the formation water.

No explanation can be given for the low Cl⁻ concentration in sample V 13.

V 14 is collected after acidizing and shows a high Cl and Ca⁺⁺ and a low pH as expected. The missing anion could be due to other acids in the stimulation fluid. This hypothesis can not be tested since the sample is discarded.

5.3 Oil analysis.

Density and viscosity varies considerably but the UOP characterization factor is the same for all samples indicating same type of oil (paraffinic). This correlation is, however, not very sensitive.

The chromatographic analysis, as seen in appendix 1 and 2, shows that most probably the oils stems from the same source rock. The agreement is closer than what could be expected when considering the rough treatment given to several of the samples.

The wax content, however, varies quite a lot. This is also seen from the pour and cloud point. The variation seems to follow the variation in density and molecular weight. The wax content is high and the asphaltene is low, which again indicates paraffinic oil.



÷#† Π i h 11 ----HULL AP -7-PE ;;;[[Ē Π <u>til i E</u> Ш÷р :1111:11 泪井 111 Dis LEO Б 01 FFHH) Φ 0 4 0 5 0 14 . 毌 -Hi SIS CULE E 8.0 MDI G. LE E n Fi H H NORMAL Ħ HCC 2E 0 015 ÷. ЦЦ. THE A Ē 5.11 HE. 1.71 11 HH4 ЩĒ 1.1 11 15 11 1111 **HÖ** 11111 HEIII . ЦЦ HŦ :::1 1414 HH. 94 i 144 Litter: 19934 ΗĦ 4.14 TT: H ÉШ ļ. Ĥ - Hite -Fł 0.8 HT rit 幵牛 田田 ## 111 H Ħ Ti **THE** 副に 11<u>-1</u>+1+ -----HH 111 ir: 111 n1 Uffi 11 11111 Fi H ÷, 471 U - 11 П. ЦПТ 141111 444 0.5 :11 Ĥ TEELE ιii H r H T ΞΠII 11-11-1.1 445 511 HIL FILL. Ш ЦĖ ЦŦ 1111 0,4 H 111 ļ: <u>1</u>[.] ЦŢ :::::::T: []] : HŦ H 1 I F. 111 锢 11 0,3 Hi 24 調告 Щ 141-11 . [. . 調告 3010 н 0.2 Elli i. ΗŦ . 詽 TH: ШĒ n III T, F TT 11 Шij 11111 111 611.1 ΠŦ 語 時 田臣 Η HH H Ŧ HA **i**ttei 4444 iЩ ----illin 匪 曲田 111 144 MC. BCC. FARNESAUR C¢s A 45 E ELSTATION ------ Hili ĦΗ 曲日 4::41.11 489.51 HH.

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