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Title TBP-DISTILLATION, WAX AND HYDROCARBON ANALYSIS OF CRUDE OIL FROM WELL 15/9-19SR DST 1		
Requested by Dag Petter Berg, STP PE/RES	Project	
Date 16.07.93	No. of pages 37	No. of enclosures 0

Key words TBP-distillation, wax, viscosity, asphaltenes, PNA-distribution, hydrocarbon group types, high-temperature gas chromatography

Abstract All analyses were performed on separator oil received in a pressurized 20 l Gerzat bottle. Key analytical data of crude oil from 15/9-19SR DST 1: <table> <tr> <td>Molecular weight</td> <td>: 239</td> <td>g/mole</td> </tr> <tr> <td>Density at 15 °C</td> <td>: 0.879</td> <td>g/cm³</td> </tr> <tr> <td>Weight% C₁₀₊</td> <td>: 85.21</td> <td>wt%</td> </tr> <tr> <td>Wax content</td> <td>: 13.0/4.0</td> <td>wt%</td> </tr> <tr> <td>Pentane insolubles</td> <td>: 2.1/1.6</td> <td>wt%</td> </tr> <tr> <td>Sulphur content</td> <td>: 1.66</td> <td>wt%</td> </tr> <tr> <td>Water content</td> <td>: 0.12</td> <td>wt%</td> </tr> <tr> <td>Pour point, minimum</td> <td>: -34</td> <td>°C</td> </tr> </table>	Molecular weight	: 239	g/mole	Density at 15 °C	: 0.879	g/cm ³	Weight% C ₁₀₊	: 85.21	wt%	Wax content	: 13.0/4.0	wt%	Pentane insolubles	: 2.1/1.6	wt%	Sulphur content	: 1.66	wt%	Water content	: 0.12	wt%	Pour point, minimum	: -34	°C
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INTRODUCTION

The results from a True Boiling Point (TBP) distillation and chemical and physical characterization of crude oil from well 15/9-19SR DST 1 are presented in this report.

All analyses were performed on separator oil received in a pressurized 20 l bottle. The bottle was preheated to 55 °C (separator temperature) to dissolve any precipitated wax before single flash to ambient conditions. Some data of the sample used, are given in **Table 1** below.

The distillation was performed by a combination of atmospheric and vacuum distillation up to C₂₀₊. Molecular weights and densities of fractions between C₁₀ and C₂₀ were determined by physical methods, whereas those below C₁₀ were calculated from properties of the individual components and composition from gas chromatography.

The characterisation of the oil also included the following measurements:

- Pour Point
- Wax precipitation temperature / Wax dissolution temperature
- Kinematic viscosity from 80 °C to 40 °C
- Apparent viscosity at various shear rates from 35 °C to 2 °C
- Total wax content
- Saturate - aromatic - polar distribution in C₁₀₊ and C₂₀₊ residues
- Paraffin - naphthene - aromatic distribution in carbon number fractions C₆-C₁₉
- Content of pentane insoluble asphaltenes
- Water content
- Sulphur content
- Emulsion stability test

Some data of the sample used, are summarized in **Table 1** below and a summary of essential analytical data is given in **Table 2**. A gas chromatogram of the oil is shown in **Figure 4**.

Table 1. Data of sample used in this investigation.

Well	15/9-19 SR
Test no.	DST 1
Field	Sleipner, Theta Vest
Producing zone	Hugin
Perforation interval	4316.0 - 4338.0 n MD RKB
Fluid type	Separator oil
Sampling point	Separator
Bottle no.	A-15392
Date of sampling	21.04.93
Time of sampling	00.55 - 01.05
Separator pressure	52.3 bar
Separator temperature	52.5 °C

Table 2. Summary of key analytical data of crude oil 15/9-19 SR DST 1.

		Crude oil	C ₁₀₊ fraction	C ₂₀₊ fraction
Weight % of crude oil		100.00	85.21	57.58
Molecular weight (g/mole)		239 (a)	320	506
Density (g/cc)		0.879	0.913	0.957
Water content (wt%)		0.12		
Sulphur content (wt%)		1.66		
Wax content (wt%)	Not purified	13.0		
	Purified	4.0		
Pentane insolubles (wt%)	Precipitated 1 X	2.1		
	Precipitated 2 X	1.6	1.9	2.8
Saturates (wt%)			41.0	25.1
Aromatics (wt%)			51.3	63.4
Polars (wt%)			5.8	8.7
Pristane/Phytane (b)			0.69	
Pristane /n-C ₁₇ (b)			0.69	
Phytane / n-C ₁₈ (b)			1.13	
n-C ₁₇ /n-C ₂₇ (b)			5.40	
Pour point (°C)	Minimum (c)	-34		
	Temp.cycled (d)	-6		
	"As received" (e)	-4		
Wax precipitation temperature (°C)		34		
Wax dissolution temperature (°C)		50		
Kinematic viscosity (cSt)	80 °C	4.27		
	60 °C	5.91		
	50 °C	7.81		
	40 °C	10.15		

(a) Average of calculated molecular weights using C₁₀₊ and C₂₀₊

(b) Area percent ratio from paraffin-naphthene chromatogram.

(c) After preheating to 80°C (thermal benefication)

(d) Reheated from minimum pour point to 50°C and then recooled

(e) Without thermal benefication.

RESULTS

Table 3 gives the boiling point distribution of the oil on weight, volume and mole basis as well as densities and molecular weights of each distillation fraction. The volumetric boiling point distribution to C_{20+} is illustrated in **Figure 1**.

The loss during vacuum distillation was found to be 0.05 % of the C_{10+} residue. This was corrected for by distributing the loss on the C_{10} to C_{16} fractions in a decreasing proportion to the weight of these fractions (assuming the loss to be evaporative and hence larger for the lightest fractions), giving a cumulative weight % of 100.0 in Table 3.

Table 4 compares molecular weights and densities of oil and residues obtained by direct measurements with values obtained by summation of individual fractions. The discrepancy of 2.5 % between measured and calculated molecular weights is observed for most oils, but is not clearly understood. The average of the **calculated** molecular weights is believed to be the most reliable. The discrepancy between measured and calculated densities is most likely due to the fact that the C_{10+} and C_{20+} , because of high viscosity of the residues, had to be measured at 40 °C. The densities at 15 °C was then calculated assuming a standard thermal expansion coefficient (ref.1) which may not strictly apply to residues. Hence, the **measured** density of whole oil is believed to be most reliable.

Table 5 gives the overlap between successive distillation fractions as determined by capillary gas chromatography.

Table 6 gives the detailed composition of the light end of the fluid, including n- C_9 . The weight percent of individual compounds and pseudocomponents from gas chromatography were normalised to fit the experimental C_{10+} weight percent from distillation.

Table 7 gives the complete boiling point distribution of the crude oil obtained by combining the GC-analysis of the light end with the physical distillation to C_{20+} and simulated distillation of the C_{20+} residue to C_{80+} by high temperature gas chromatography with internal standard. The atmospheric equivalent boiling point corresponding to n- C_{80} is 675 °C. The recovery of the injected sample was 98 % (w/w), which means that 2 % of the C_{20+} fraction (3.5 % of the oil) was irreversibly adsorbed on the column. This material is likely to be asphaltenes and some resins (polars). The non-recovered fraction is included in the C_{80+} fraction in **Table 7**. The boiling point distribution on weight basis is illustrated in **Figure 2**. The high temperature gas chromatogram is shown in **Figure 8**.

Table 8 gives the distribution of saturates (paraffins + naphthenes) and aromatics in all distillation fractions. For the C_{10+} and C_{20+} residues the amount of polars were estimated using an "in-house" correlation between weight fractions of polars and aromatics in C_{10+} (ref.2). The asphaltenes are defined as the material insoluble in pentane.

Table 9 gives the detailed hydrocarbon group type distributions of fractions C₁₀ to C₁₉ as determined by gas chromatography - mass spectrometry.

Table 10 gives some characteristic ratios between individual compounds, primarily of geochemical interest, based upon area percent from FID gas chromatograms of the saturate and aromatic subfractions (**Figures 5, 6 and 7**). The content of components required to calculate the MPI ratios (phenanthrenes) was too small to be measured.

Table 11 gives viscosity data of the crude oil in the temperature range from 2° to 80 °C. The oil behaved Newtonian at temperatures higher than about 35 °C. For temperatures higher than 35 °C, the dynamic viscosities μ were calculated from measured kinematic viscosities using the densities in Table 12, and fitted to the following exponential (Arrhenius) equation (standard deviation in regression line was 0.245 mPa s):

$$\mu = 10^{-5.35} e^{\frac{20.06}{RT}}$$

(μ in Pa s units)

The above equation only applies in the Newtonian range where the viscosity is independent of shear rate. Below 40 °C, the apparent (shear rate dependent) viscosity of thermally beneficiated oil is reported at four different shear rates. These viscosities were obtained by cooling the oil at a rate of 12.5 °C/hour and the specified shear rate in the viscometer. In **Figure 3**, the deviation from the Arrhenius curve as well as the shear thinning behaviour below 40 °C is illustrated.

Table 12 summarizes the kinematic viscosities in the Newtonian temperature range as measured with an Ubbelohde glass capillary viscometer tube and the densities used to convert the kinematic viscosities to the dynamic viscosities in Table 11.

Table 13. The result of bottle tests at 50 °C with synthetic water-in-oil emulsion, 20% and 50% water cut, are summarized in Table 13.1 (untreated) and 13.2 (treated with 10 ppm demulsifier, NH-6011X). The test indicated that the untreated 15/9-19SR DST 1 crude forms stable emulsions at 50 °C. With 10 ppm demulsifier, 41 % free water break-out was achieved after 10 minutes for the 20 % emulsion, and 80 % for the 50 % emulsion. The water separation curves are illustrated in **Figure 9**. The composition of the formation water is given in Appendix B.

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TABLES

**Table 3. Data from distillation of stabilized oil
15/9-19SR DST 1**

Fraction	Cut temp. (°C, 760 torr)	Actual head- temp.	Weight percent	Cumulative weight percent
Gas	-	-	1.21	1.21
C 5	36.5	36.5	1.41	2.62
C 6	69.2	69.2	1.80	4.41
C 7	98.9	98.9	3.30	7.72
C 8	126.1	126.1	3.86	11.58
C 9	151.3	151.3	3.21	14.79
C 10+	>151.3		85.21	100.00
C 10	174.6	70.7	2.46	17.26
C 11	196.4	88.6	2.85	20.11
C 12	217.2	105.3	3.15	23.26
C 13	235.9	121.5	2.99	26.25
C 14	253.9	136.7	2.84	29.09
C 15	271.1	151.1	2.77	31.86
C 16	287.3	163.9	2.55	34.40
C 17	303.0	177.8	2.73	37.14
C 18	317.0	190.3	2.71	39.84
C 19	331.0	202.2	2.58	42.42
C 20+	>331.0	>202.2	57.58	100.00

cont.

Table 3 cont.

Fraction	Density (g/cm ³)	Volume percent	Cumulative volume percent
Gas	0.544	1.95	1.95
C 5	0.629	1.96	3.91
C 6	0.669	2.35	6.26
C 7	0.741	3.90	10.17
C 8	0.759	4.45	14.62
C 9	0.776	3.63	18.25
C 10+	0.913	81.75	100.00
C 10	0.792	2.73	20.98
C 11	0.793	3.15	24.13
C 12	0.810	3.41	27.54
C 13	0.821	3.18	30.72
C 14	0.831	2.99	33.71
C 15	0.839	2.89	36.60
C 16	0.849	2.63	39.23
C 17	0.852	2.81	42.04
C 18	0.855	2.77	44.82
C 19	0.863	2.61	47.43
C 20+	0.957	52.69	100.12

cont.

Table 3 cont.

Fraction	Molecular weight	Mole percent	Cumulative Mole percent
Gas	51.3	5.49	5.49
C 5	72.2	4.53	10.02
C 6	84.7	4.93	14.95
C 7	91.6	8.38	23.33
C 8	105.5	8.50	31.82
C 9	119.7	6.24	38.06
C 10+	320	61.94	100.00
C 10	132	4.33	42.39
C 11	143	4.62	47.01
C 12	156	4.70	51.71
C 13	170	4.07	55.78
C 14	183	3.60	59.38
C 15	195	3.29	62.68
C 16	209	2.84	65.52
C 17	223	2.85	68.36
C 18	239	2.63	70.99
C 19	252	2.37	73.36
C 20+	506	26.44	99.81

Table 4. Measured and calculated molecular weights and densities.

	Oil	C 10+	C 20+
Measured MW	239	320	506
Calculated MW using C 10+ MW	232		
Calculated MW using C 20+ MW	233	321	
Measured density	0.879	0.913	0.957
Calculated density using C 10+ density	0.876		
Calculated density using C 20+ density	0.875	0.912	

Table 5. Weight distribution and weight% overlap between fractions.

Fraction	Weight percent	Weight % overlap between fractions (*)		
		Cn-1	Cn	Cn+1
Gas	1.21		-	
C 5	1.41		-	
C 6	1.80	0	100	0
C 7	3.30	0	100	0
C 8	3.86	0	100	0
C 9	3.21	0	100	0
C 10	2.46	0	89	11
C 11	2.85	25	63	12
C 12	3.15	26	61	13
C 13	2.99	24	55	21
C 14	2.84	23	61	16
C 15	2.77	22	59	19
C 16	2.55	10	74	16
C 17	2.73	25	51	24
C 18	2.71	23	53	24
C 19	2.58	21	56	23

(*) Calculated using area percent from gas chromatogram

Table 6. Composition of stabilized crude oil 15/9-19SR DST 1 (gas chromatography).

Component (group)	Weight %	Molecular weight	Density
C1	0.01	16.0	0.260
C2	0.04	30.1	0.350
C3	0.33	44.1	0.508
i-C4	0.13	58.1	0.563
n-C4	0.70	58.1	0.585
2,2-DM-C3	0.00	72.2	0.597
i-C5	0.50	72.2	0.625
n-C5	0.91	72.2	0.631
Hexanes total	1.80	84.7	0.669
Hexanes paraffins	1.66	86.2	0.663
Hexanes naphthenes	0.14	70.1	0.750
Heptanes total	3.30	91.6	0.741
Heptanes paraffins	1.46	100.2	0.688
Heptanes naphthenes	1.36	88.8	0.761
Heptanes aromatics	0.48	78.1	0.884
Octanes total	3.86	105.5	0.759
Octanes paraffins	1.59	114.2	0.706
Octanes naphthenes	1.52	104.6	0.771
Octanes aromatics	0.75	92.1	0.871
Nonanes total	3.21	119.7	0.776
Nonanes paraffins	1.50	128.3	0.721
Nonanes naphthenes	0.83	121.3	0.791
Nonanes aromatics	0.88	106.2	0.873
Decanes plus	85.21 ^a	320	0.913

^a Weight percent from distillation corrected for fraction overlap between C9 and C10.

Table 7. Simulated distillation by high-temperature GC-analysis of crude oil from well 15/9-19SR DST 1.

Fraction	% of crude oil (w/w)	% Cumulative (w/w)	Boiling point (°C)
gas	1.21	1.21	
C5	1.41	2.62	36.5
C6	1.80	4.42	69.2
C7	3.30	7.72	98.9
C8	3.86	11.58	126.1
C9	3.21	14.79	151.3
C10	2.46	17.25	174.6
C11	2.85	20.10	196.4
C12	3.15	23.25	217.2
C13	2.99	26.24	235.9
C14	2.84	29.08	253.9
C15	2.77	31.85	271.1
C16	2.55	34.40	287.3
C17	2.73	37.13	303.0
C18	2.71	39.84	317.0
C19	2.58	42.42	331.0
C20	3.10	45.52	344
C21	2.09	47.61	357
C22	1.97	49.59	369
C23	2.09	51.67	381
C24	1.81	53.48	391
C25	1.86	55.34	402
C26	1.75	57.09	412
C27	2.14	59.24	423
C28	1.64	60.87	431
C29	2.03	62.90	441
C30	1.52	64.43	449
C31	1.41	65.84	457
C32	1.58	67.42	466
C33	1.41	68.83	474
C34	1.24	70.07	481
C35	1.35	71.42	489
C36	1.07	72.50	496
C37	1.02	73.51	502
C38	1.18	74.70	509
C39	1.02	75.71	516
C40	0.85	76.56	522
C41-45	4.18	80.73	551
C46-50	3.10	83.84	575
C51-55	2.65	86.49	596
C56-60	2.20	88.69	615
C61-65	1.75	90.44	632
C66-70	1.69	92.13	647
C71-75	1.58	93.71	661
C76-80	1.58	95.29	675
C80+	4.71	100.00	675+

Table 8. Hydrocarbon group type distribution (w/w) in distillation fractions and residues of crude oil 15/9-19SR DST 1.

C_n	Paraffins + naphthenes	Aromatics	Polars	Asphaltenes
6 a	100.0	0.0		
7 a	85.5	14.5		
8 a	80.5	19.5		
9 a	72.6	27.4		
10 c	72.8	27.2		
11 c	75.2	24.8		
12 c	74.7	25.3		
13 b	74.9	25.1		
14 b	74.2	25.8		
15 b	69.1	30.9		
16 b	65.5	34.5		
17 b	65.3	34.7		
18 b	65.7	34.3		
19 b	63.3	36.7		
20+ b	25.1	63.4	8.7	2.8
10+ b	41.0	51.3	5.8	1.9

(a) From GC-analysis

(b) Experimental values (preparative liquid chromatography)

(c) Calculated using correlations between density and aromatic content (ref.3), and corrected by adding the average difference between experimental values of fractions C_{13} to C_{19} .

Table 9. PNA-distribution of distillation fractions C₁₀-C₁₉ of oil 15/9-19SR DST 1, from GC-MS.

HYDROCARBON CLASS	CLASS NO.
Paraffins (n -+ i-)	1
Monocyclic naphthenes	2
Alkylbenzenes	3
Indanes + Tetralines	4
Indenes + Dihydronaphtalene	5
Naphtalenes	6
Alkylnaphtalenes	7
Acenaphthenes + Diphenyls	8
Acenaphtylenes + Fluorenes	9
Tricyclic aromatics	10

Unit : WEIGHT %

Fraction Class:	C ₁₀	C ₁₁	C ₁₂	C ₁₃	C ₁₄
1	32.3	44.8	44.2	46.3	49.1
2	40.5	30.4	30.5	28.6	25.1
3	27.0	23.2	16.4	12.3	11.4
4	0.0	1.5	4.0	5.6	7.1
5	0.0	0.0	0.0	0.0	0.0
6	0.2	0.0	4.7	0.5	0.0
7	0.0	0.0	0.0	6.7	7.1
8	0.0	0.1	0.0	0.0	0.3
9	0.0	0.0	0.2	0.0	0.0
10	0.0	0.0	0.0	0.0	0.0
Fraction Class :	C ₁₅	C ₁₆	C ₁₇	C ₁₈	C ₁₉
1	47.9	44.1	45.6	48.5	45.8
2	21.2	21.4	19.7	17.2	17.5
3	11.9	14.9	15.2	14.3	16.2
4	6.2	3.8	2.7	3.0	3.5
5	0.0	0.1	1.3	1.0	0.0
6	0.6	0.6	0.3	0.3	0.4
7	10.9	12.5	9.4	7.2	6.4
8	1.3	2.7	5.6	7.3	8.7
9	0.0	0.0	0.1	1.1	0.2
10	0.0	0.0	0.0	0.1	1.3

Table 10. Characteristics ratios of some individual saturated and aromatic compounds in oil 15/9-19SR DST 1.

Saturated compounds:	Area percent ratio
Cyclohexane/ methylcyclopentane	0.67
Toluene/n-heptane	0.86
n-heptane/methylcyclohexane	1.46
Pristane/phytane	0.69
Pristane/n-C17	0.69
Phytane/n-C18	1.13
n-C17/n-C27	5.40
CPI 1	0.94
CPI 2	0.94

Aromatics:	Area percent ratio
2MN/1MN	1.16
2.6+2.7-/1.4+1.5+2.3 DMN	0.45
Biphenyl/1+2 EN	0.36
Biphenyl/3M-biphenyl	0.59
MPI 1	----
MPI 2	----

N = naphtalene
M = methyl-
DM = dimethyl-

Table 11. Dynamic and apparent viscosity of thermal beneficiated crude oil 15/9-19SR DST 1.

Temp. (°C)	Dynamic viscosity ^a			
80°	3.56		Fit of Newtonian viscosities to Arrhenius equation : $\mu = A e^{E_a/RT}$ $\log A = -5.35$ $E_a = 20.06 \text{ kJ mole}^{-1}$ $R = 0.0083144 \text{ kJ k}^{-1} \text{ mole}^{-1}$	
70°	4.22			
60°	5.01			
50°	6.67			
40°	8.47 7.4			
	Viscosity ^b (mPa s) at shear rate			
	30 s ⁻¹	100 s ⁻¹	300 s ⁻¹	500 s ⁻¹
35°	12.4	12.0	12.0	11.6
32°	24.7	16.4	14.6	13.5
30°	31.2	18.1	16.0	15.1
28°	34.3	20.9	18.1	17.0
26°	39.2	24.6	20.5	19.5
24°	42.9	26.6	23.1	22.3
22°	46.7	31.0	25.8	25.7
20°	53.6	33.9	29.1	29.6
18°	60.1	40.4	33.2	34.9
16°	68.0	45.9	38.8	42.9
14°	80.6	53.4	45.7	52.6
12°	92.8	65.7	55.0	66.1
10°	117	80.8	66.7	82.7
8°	124	98.7	81.4	101
6°	155	121	97.1	121
4°	184	150	117.5	146
2°	223	184	140.7	176

^aCalculated from kinematic viscosities and densities in Table 12.

^bViscometer cooled at a rate of 12.5 °C/hour from 35 ° to 2 °C at various constant shear rates

Table 12. Kinematic viscosity and density of crude oil 15/9-19SR DST 1 at various temperatures.

Temperature	Kinematic viscosity (cSt)	Density^a (kg/m³)
80	4.27	833.0
70	5.02	840.2
60	5.91	847.3
50	7.81	854.4
40	10.15	861.5

^a Measured at 15 °C. Calculated at other temperatures using API standard 2540 (august 1980)

Table 13.1 **Water separation (%) from synthetic water-in-oil emulsions with crude oil 15/9-19SR DST 1 at 50 °C. No emulsion breaker.**

Watercut (%)	Water separation (%)						
	1 min	3 min	6 min	10 min	15 min	20 min	30 min
20	0	0	0	0	0	0	0
50	0	0	0	15	18	0	0

Table 13.2 **Water separation (%) from synthetic water-in-oil emulsions with crude oil 15/9-19SR DST 1 at 50 oC. 10 ppm emulsion breaker[#].**

Watercut (%)	Water separation (%)						
	1 min	3 min	6 min	10 min	15 min	20 min	30 min
20	0	0	27	41	73	73	73
50	0	0	13	80	82	82	82

[#] NH-6011X (Scandinavian Oilfield Chemicals)

FIGURES

TBP- AND DENSITY-PROFILES

Crude oil 15/9-19SR DST 1

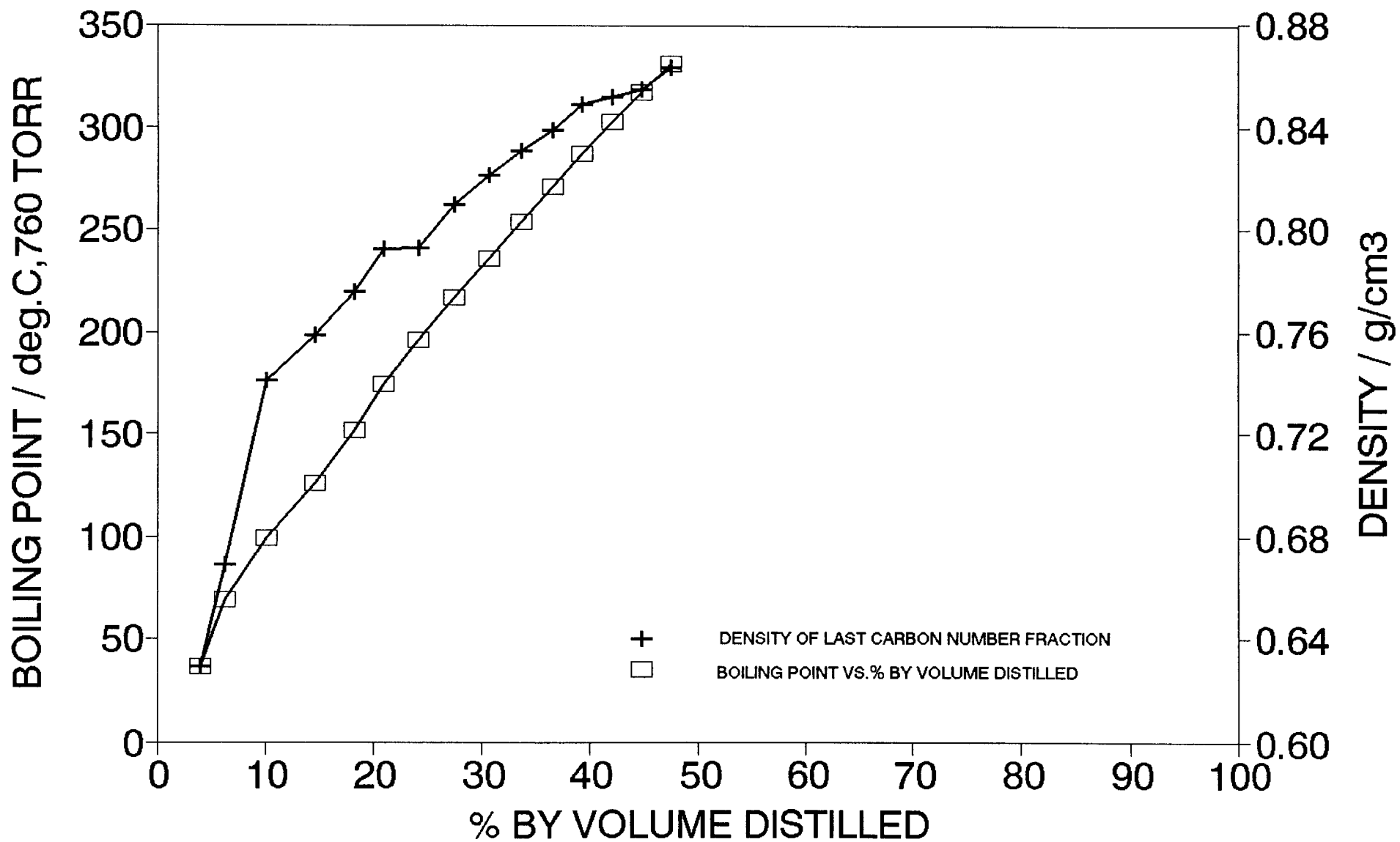


Fig. 1

BOILING POINT DISTRIBUTION

Crude oil 15/9-19SR DST 1

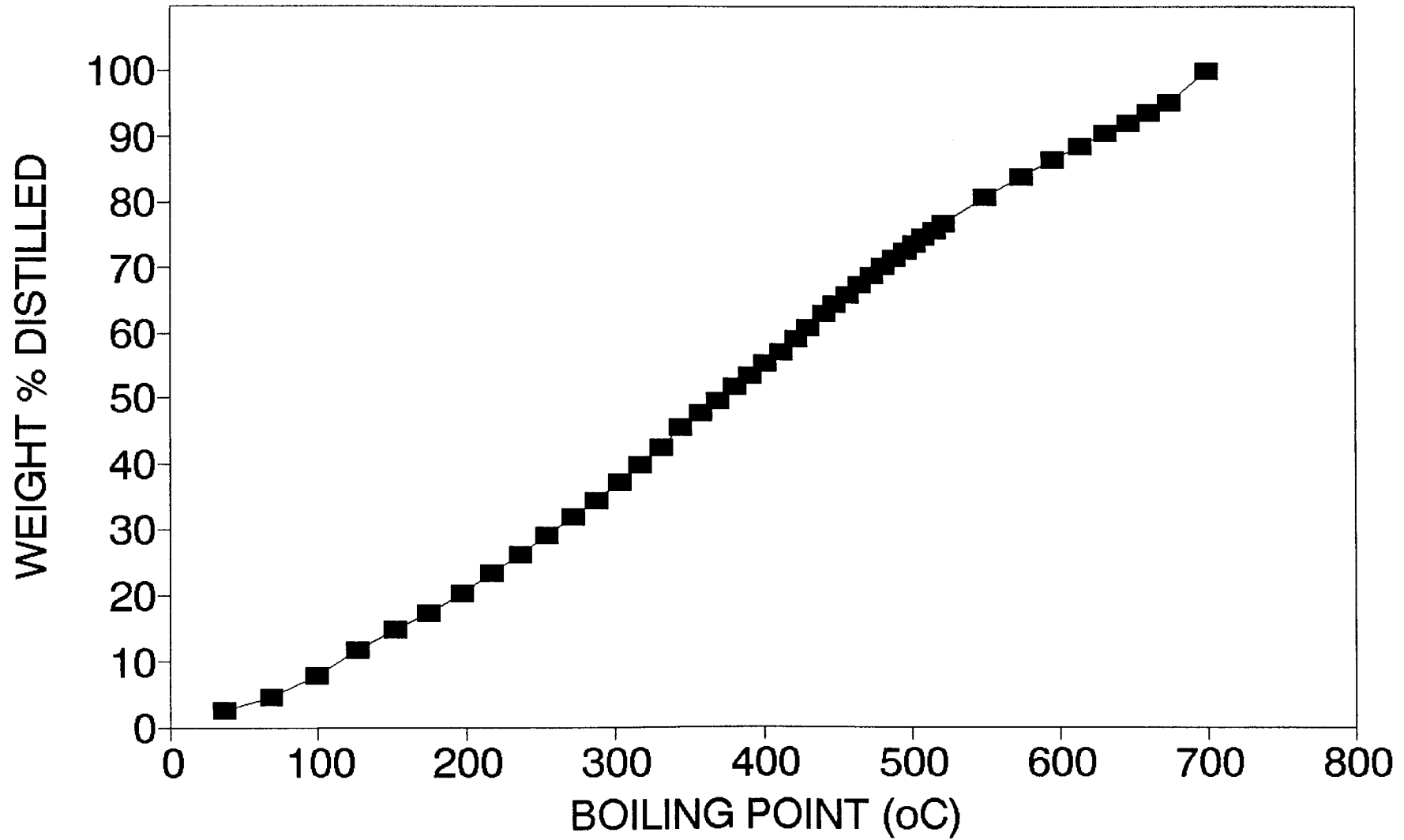


Fig.2

VISCOSITY VS. TEMPERATURE CRUDE OIL 15/9-19SR DST 1

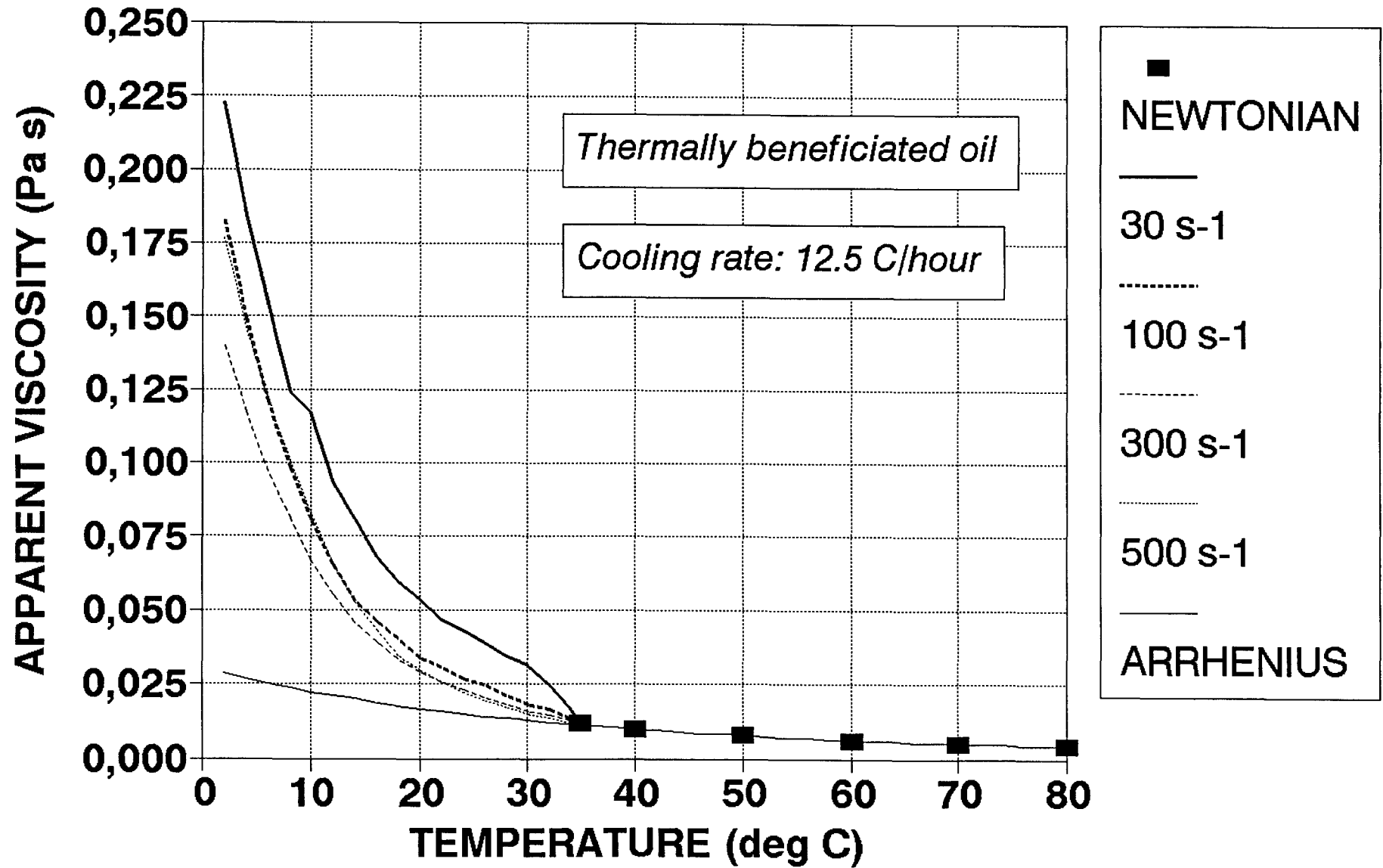


Fig.3

15/9-19SR DST 1 CRUDE OIL

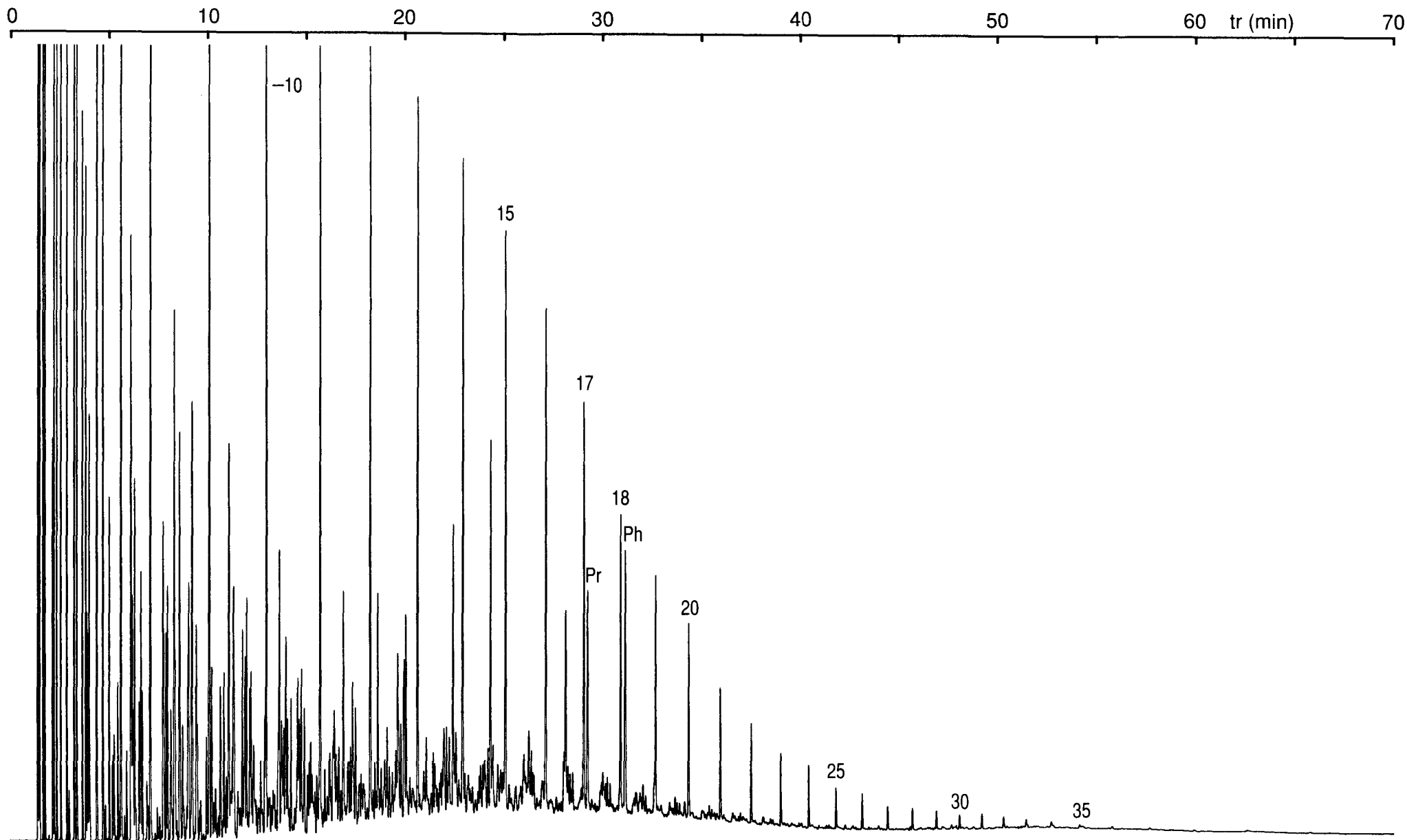


FIG. 4

15/9-19SR DST 1 C10+ PARAFFIN+NAPHTHENE FRACTION

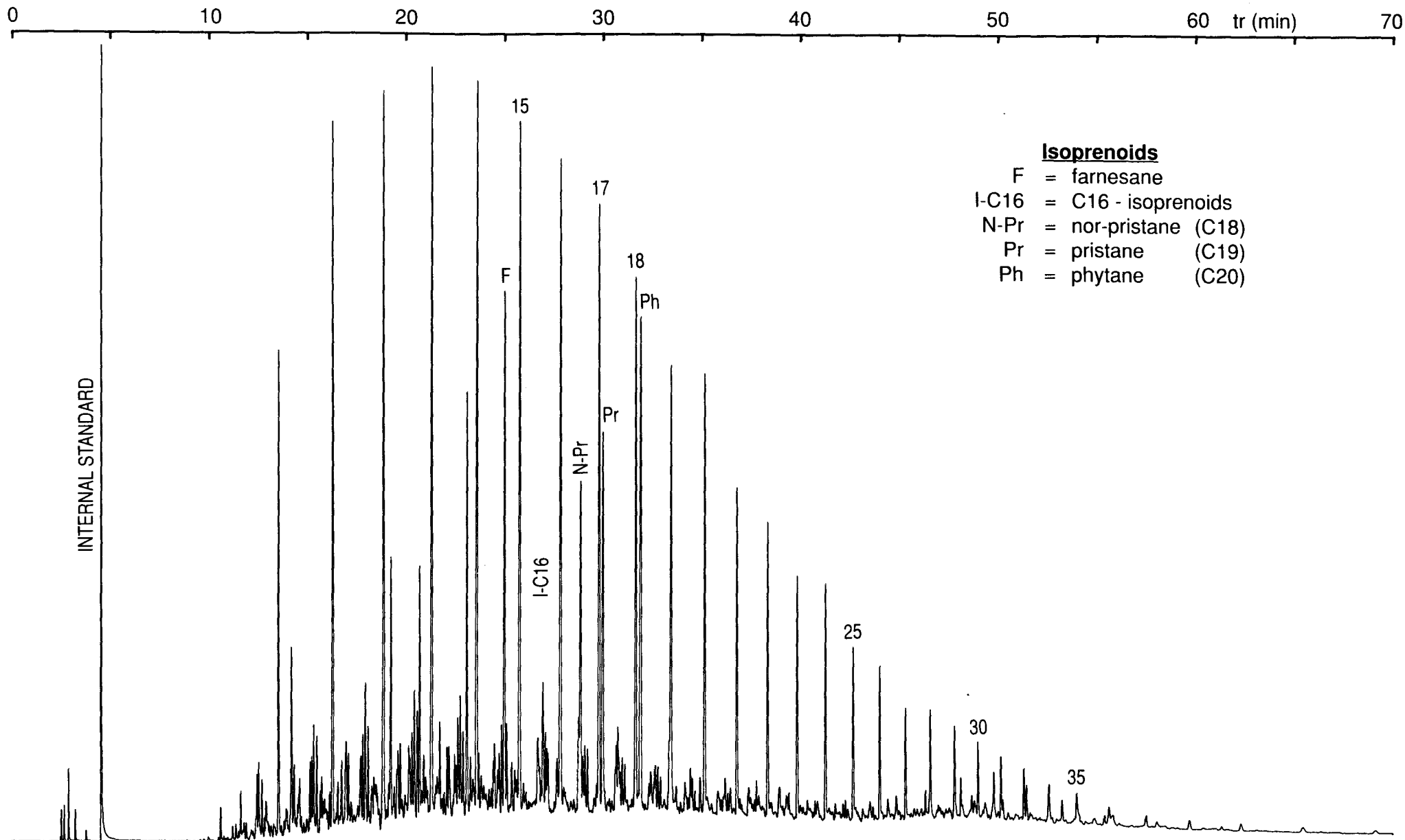


FIG. 5

m19sr1 20 mv

15/9-19SR DST 1 C10+ AROMATIC FRACTION

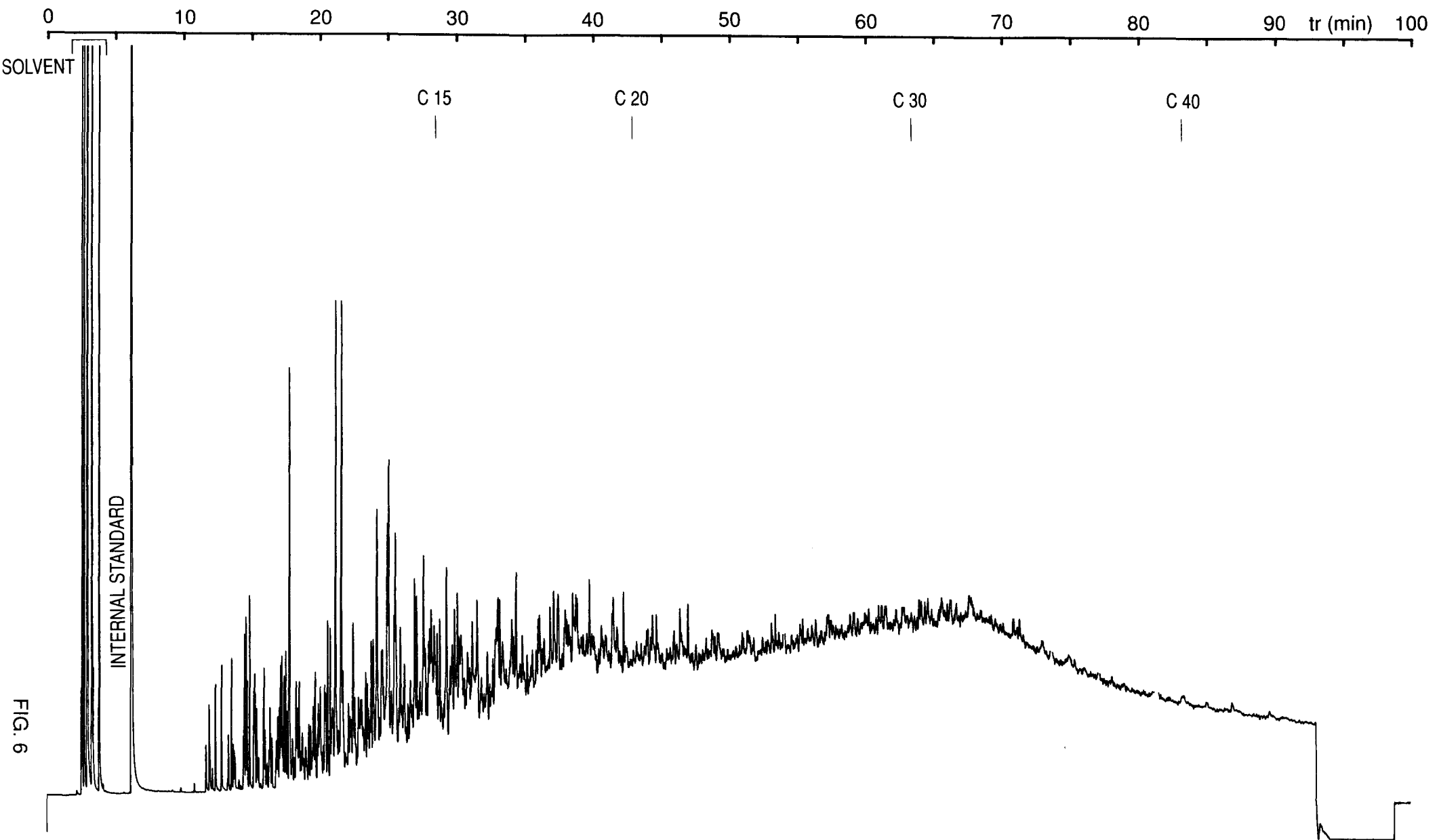
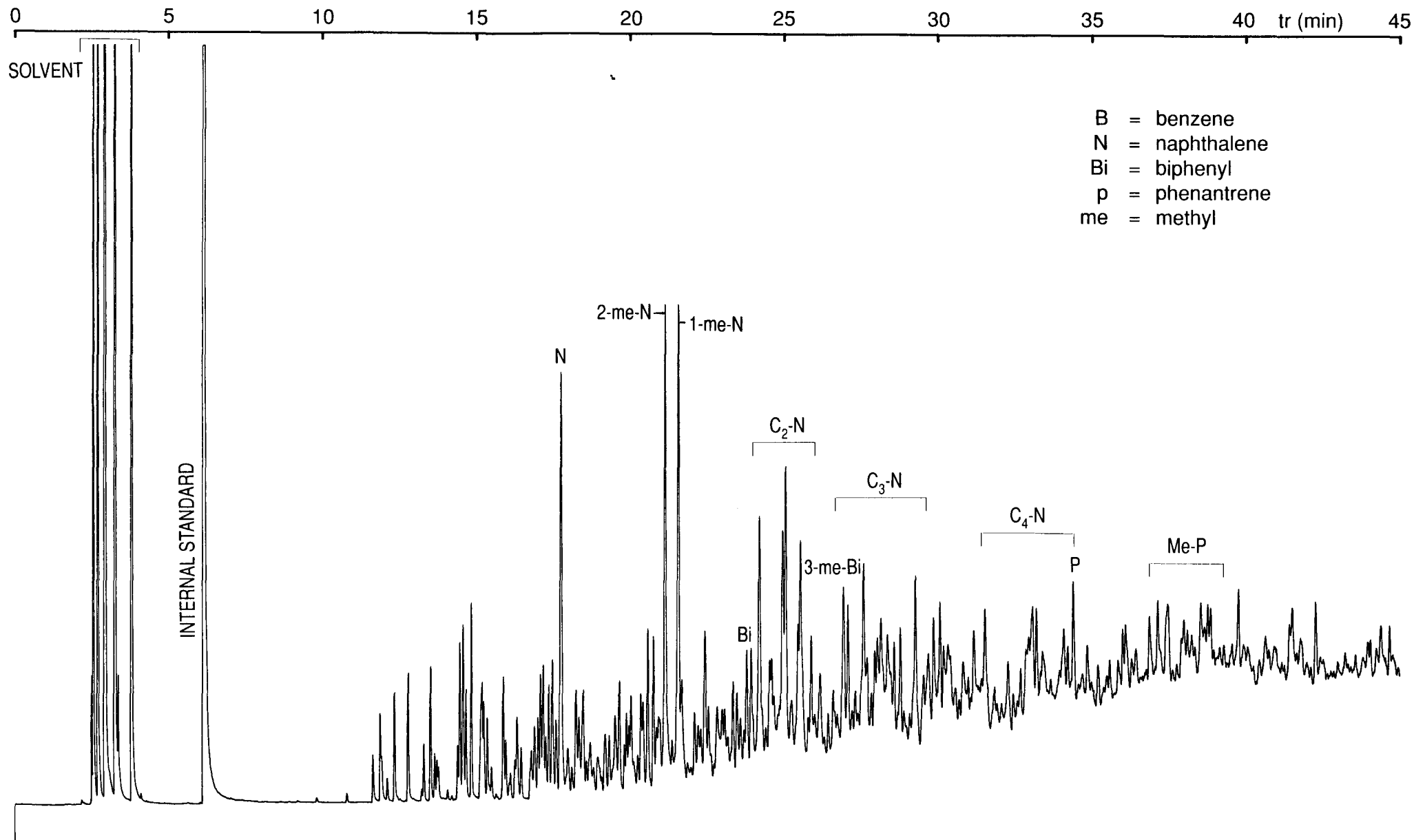


FIG. 6

15/9-19SR DST 1 C10+ AROMATIC FRACTION



B = benzene
N = naphthalene
Bi = biphenyl
p = phenanthrene
me = methyl

FIG. 7

DATA FILE=0106_13D FROM 0.00 MIN. TO 82.00 MIN. LOW SCALE= 0.000 Mv. HIGH SCALE= 120.000 Mv.
SIM.DIST.BY HT-GC 15/9-19SR DST1 C20+ w/Istd

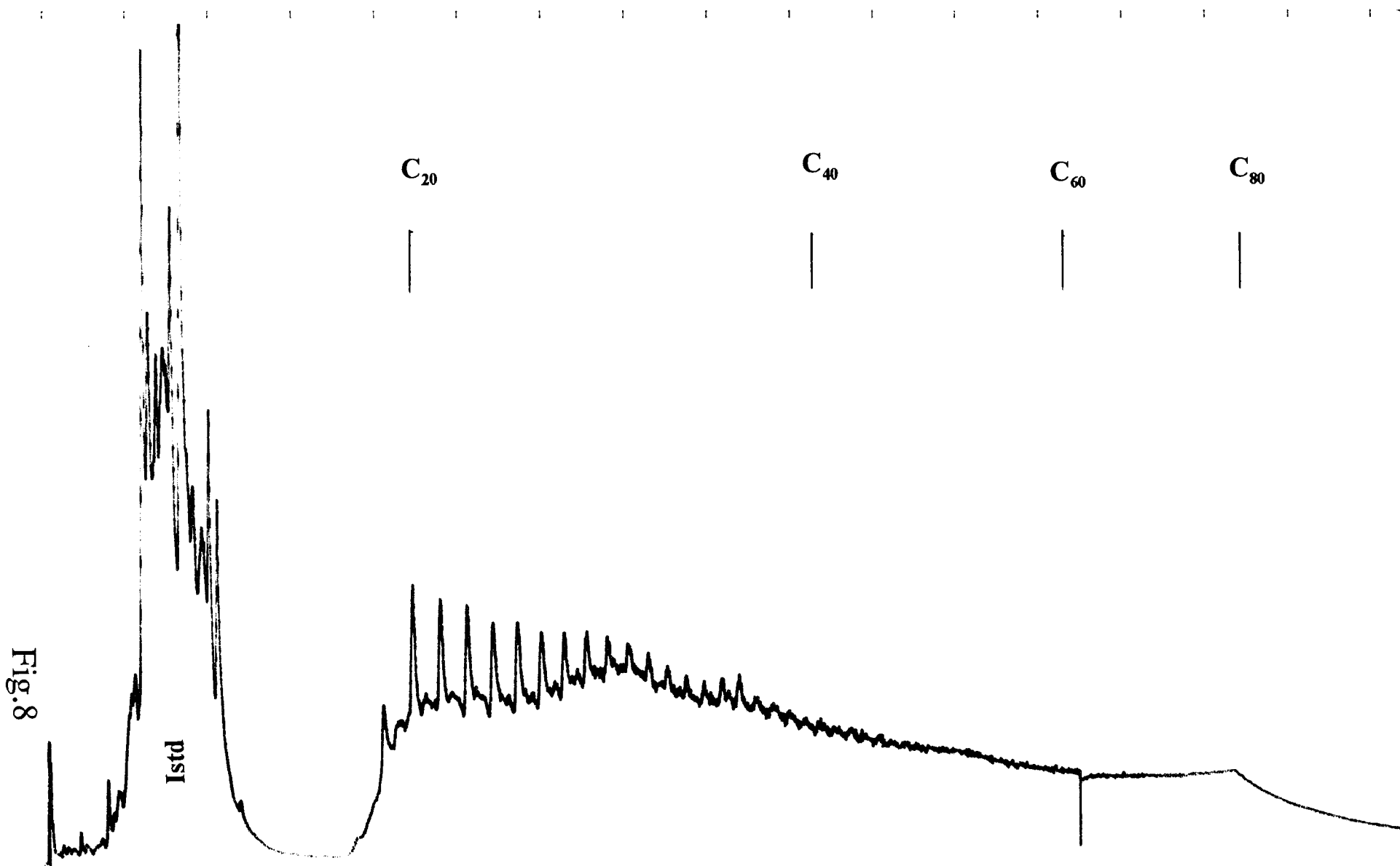


Fig. 8

CRUDE OIL 15/9-19SR DST 1 TEMPERATURE 50 °C

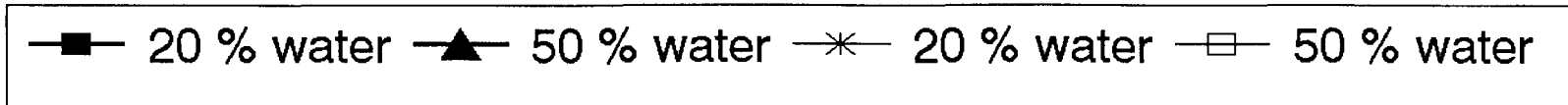
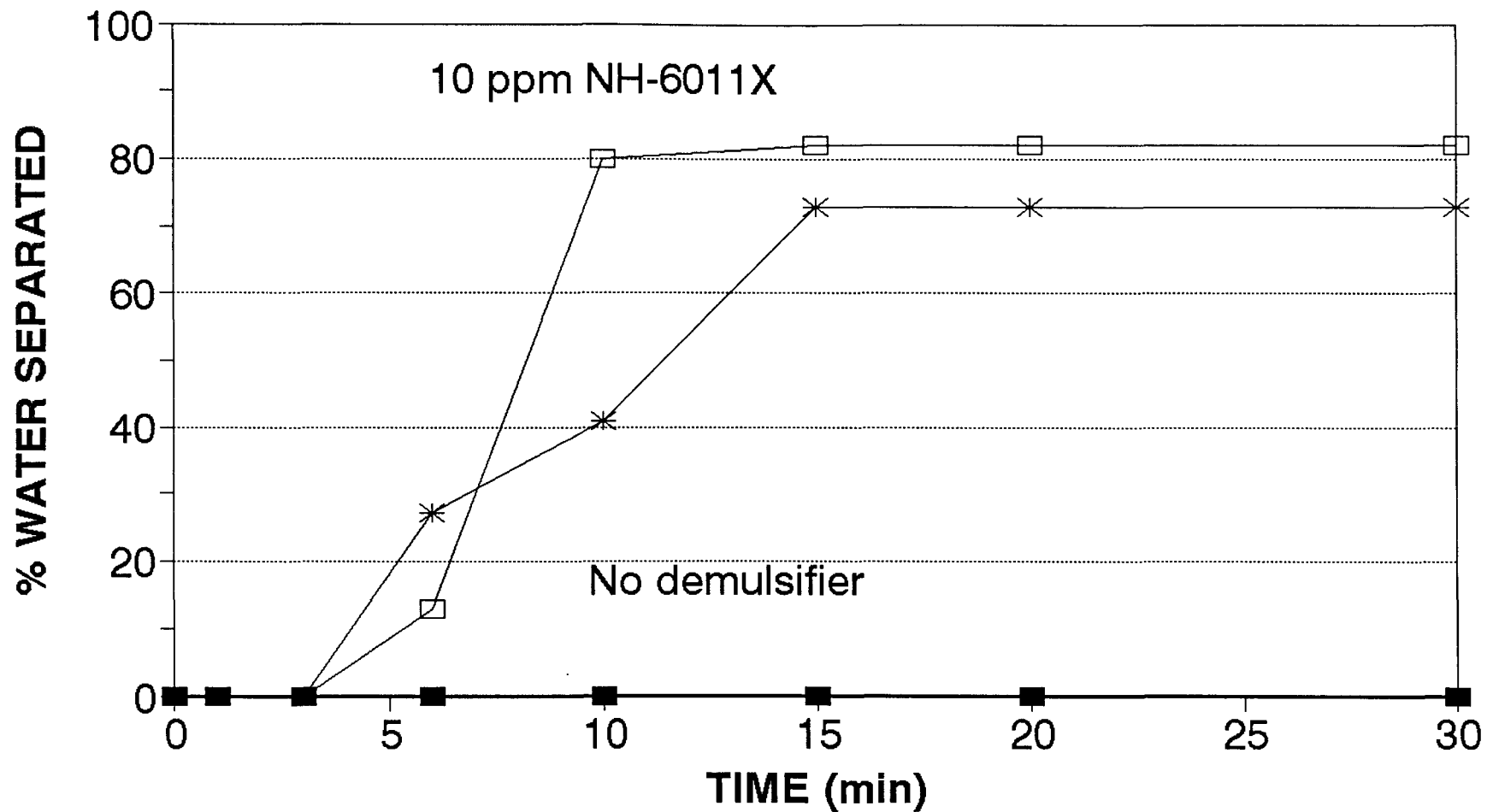


Fig.9

APPENDICES

APPENDIX A

Table A.1. Detailed composition of light end of stabilized crude oil 15/9-19SR DST 1.

Component	Weight %	Molecular weight	Density
C1	0.01	16.0	0.260
C2	0.04	30.1	0.358
C3	0.33	44.1	0.508
i-C4	0.13	58.1	0.563
n-C4	0.70	58.1	0.585
2,2-DM-C3	0.00	72.2	0.597
i-C5	0.50	72.2	0.625
n-C5	0.91	72.2	0.631
2,2-DM-C4	0.00	86.2	0.654
Cy-C5	0.14	70.1	0.750
2,3-DM-C4	0.04	86.2	0.666
2-M-C5	0.43	86.2	0.657
3-M-C5	0.28	86.2	0.669
n-C6	0.91	86.2	0.664
M-Cy-C5	0.52	84.2	0.753
2,4-DM-C5	0.02	100.2	0.677
2,2,3-TM-C4	0.00	100.2	0.659
Benzene	0.50	78.1	0.884
3,3-DM-C5	0.00	100.2	0.698
Cy-C6	0.34	84.2	0.783
2-M-C6	0.26	100.2	0.683
2,3-DM-Cy-C5	0.06	98.2	0.755
1,1-DM-Cy-C5	0.01	98.2	0.759
3-M-C6	0.30	100.2	0.692
1-cis,3-DM-Cy-C5	0.10	98.2	0.749
1-trans,3-DM-Cy-C5	0.09	98.2	0.753
1-trans,2-DM-Cy-C5	0.22	98.2	0.756
n-C7	0.88	100.2	0.688
Unspecified C7	0.00	100.2	0.688
M-Cy-C6	0.60	98.2	0.774
1,1,3-TM-Cy-C5	0.02	112.2	0.753
E-Cy-C5	0.17	98.2	0.771
2,5-DM-C6	0.03	114.2	0.698
2,4-DM-C6	0.04	114.2	0.704
1-tr,2-cis,4-TM-Cy-C5	0.06	112.2	0.752
1-tr,2-cis,3-TM-Cy-C5	0.08	112.2	0.758
2,3,4-TM-C5	0.02	114.2	0.723

Table A.1. cont.

Component	Weight %	Molecular weight	Density
Toluene	0.75	92.1	0.871
1,1,2-TM-Cy-C5	0.04	112.2	0.777
2,3-DM-C6	0.02	114.2	0.716
2-M-C7	0.32	114.2	0.702
4-M-C7	0.09	114.2	0.709
3,4-DM-C6	0.01	114.2	0.724
3-M-C7	0.18	114.2	0.710
1-cis,3-DM-Cy-C6	0.17	112.2	0.770
1-trans,4-DM-Cy-C6	0.06	112.2	0.767
1,1-DM-Cy-C6	0.02	112.2	0.785
Unspecified naphthene	0.06	112.2	0.770
1-M-tr,2-E-Cy-C5	0.15	112.2	0.773
Unspecified naphthene	0.00	112.2	0.770
1-trans,2-DM-Cy-C6	0.08	112.2	0.780
n-C8	0.83	114.2	0.707
Unspecified C8	0.06	114.2	0.700
1-cis,2-DM-Cy-C6	0.05	112.2	0.800
E-Cy-C6	0.39	118.0	0.790
1,1,3-TM-Cy-C6	0.12	126.2	0.783
Ethylbenzene	0.35	106.2	0.871
Unspecified naphthene	0.03	126.2	0.790
Unspecified naphthene	0.02	126.2	0.790
Meta+Para-Xylene	0.32	106.2	0.868
4-M-C8	0.11	128.3	0.724
2-M-C8	0.14	128.3	0.717
Unspecified naphthene	0.02	126.2	0.790
Unspecified naphthene	0.01	126.2	0.790
3-M-C8	0.19	128.3	0.724
Ortho-Xylene	0.20	106.2	0.884
1-M,3-E-Cy-C6	0.09	126.2	0.800
1-M,4-E-Cy-C6	0.05	126.2	0.790
Unspecified naphthene	0.02	126.2	0.790
Unspecified naphthene	0.03	126.2	0.790
n-C9	0.72	128.3	0.721
Unspecified C9	0.35	128.3	0.721

Explanation of the abbreviations :

Cy- = Cyclo-

D- =Di-

E- = Ethyl-

M- = Methyl-

T- = Tri-

APPENDIX B : Composition of synthetic formation water used in the emulsion stability test of crude oil 15/9-19SR DST 1.

Salt	Concentration g/l
NaCl	112.90
KCl	3.55
CaCl ₂ ·2H ₂ O	63.77
MgCl ₂ ·6H ₂ O	20.20
BaCl ₂ ·2H ₂ O	0.237
SrCl ₂ ·2H ₂ O	2.54

APPENDIX C

A brief description of analytical methods.

1. Distillation.

True boiling point (TBP)-distillation is performed using an automatic HMS 500 AC unit from Fischer, Meckenheim (West Germany). An AC 001 control system, modified by Statoil lab, controls temperatures, reflux, pressure and fraction discharge. At operating conditions the number of theoretical plates are in the range 50 to 60.

The distillation is done in two steps. In step one a C₁₀₊ fraction is prepared at atmospheric pressure by boiling off all components up to, and including n-C₉. Corrections are made for water content, static hold-up material (wetting) and possible overlaps.

A gas chromatographic analysis of the raw sample material, according to ref.4, is then performed to obtain a detailed composition, as well as physical properties, of the C₄-C₉ fractions. GC results are adjusted to conform with the C₁₀₊ weight % from distillation.

In step two the distillation is continued on the C10+ material at 25.4 mbar (19.1 mm Hg) with a reflux of 3:1. Fractions (C10 to C19) are cut at temperatures given in Table 3 in this report, aiming at atmospheric equivalent temperature AET) cutpoints as given by Katz and Firoozabadi (ref.5). After the elution of n-C19, the process is stopped and direct measurements of density and molecular weight of fractions and residue are done. C10+ density and molecular weight is used to get total volume and total number of moles (and hence volume-and mole percents), (see Table 3).

Temperature-pressure conversion, Table 3 and 4 in ASTM D 2892 (ref.6) gives systematically too low cut point with the reference of n-alkane elution in our distillation system. One possible explanation for this is the difference in number of theoretical plates (ASTM D 2892 describes 14 to 18 theoretical plates). Another possible explanation is that the conversion table in D 2892 assume the oil characterization factor K=12, which may be systematically different for North Sea oils.

he gas chromatic analysis to get detailed composition of the light end, is done on a Chrompac Sil column (50 m X 0.23 mm i.d., 0.4 µm filmthickness). The oven temperature programme is :

10°C 2 min.
3 °/min to 115 °C
10 °C/min to 300 °C
300 °C 60 min
Injector (split) :300 °C
Detector (FID) : 350 °C

2. Gas Chromatogram of whole oil is recorded using a Cp Sil 5 CB column (25 m x 0.23 mm i.d., 0.13µm filmthickness) and FI-detector.

The following temperature programme is used:

10 °C 2 min
6 °C/min to 300 °C

Injector (split) : 320 °C
 Detector 350 °C

3. High-temperature gas chromatographic analysis of C₂₀₊ is carried out on a Carlo Erba Mega Series Chromatograph with a 5m x0.53mm i.d. non-polar Chrompac column (film thickness 0.10 µm).
 Temperature program:
 35 °C 2 min
 5 °/min to 390 °C
 390 °C 10 min
 Injector :On column 35 °C
 Detector :FID 400 °C
 The C₂₀₊ samples are analyzed using combined C₁₃-C₁₄ fraction as internal standard.
4. Molecular weights are determined by freezing point depression of benzene (Cryette, Precision Instr.), except for C₄-C₉ which are calculated from GC composition. Precision of the method is about 1.5 % (RSD) for residues and about 1 % for lower fractions.
5. Densities of liquid fractions are measured using a Paar DMA 62 frequency densitometer, thermostated at 15 °C. Precision of the method is +/- 0.0002 g/cc. Densities of the C₄-C₉ fractions are calculated from the GC composition. Density of the C₂₀₊ residue is measured at 50 °C and converted to the reference temperature 15 °C by API table 53A, ref.1
6. Water content (wt %) is determined by Karl Fischer titration.
7. Sulphur content is determined by X-ray fluorescence (Lab-X 2000, Oxford Analytical).
8. Wax Content is determined by a modified UOP method 46-64, (ref. 3 and 7), the acetone precipitation technique. The wax is precipitated with acetone at -25 °C and filtrated. The precipitate is purified by elusion through a short silica cartridge.
9. Thermal pretreatment (benefication) of crude oil. Separator oil collected in 20 litre Gerzat-bottle is depressurizes in one step to atmospheric pressure and room temperature after beeing heated to about 60 °C in the bottle. The stabilized crude oil is transferred to a 1 litre gas-tight stainless steel pretreatment cell. It is emphasized to conduct the transfer quickly in order to minimize exposure to air and light which may cause oxidation processes to occur with formation of surface active species. The crude is topped with nitrogen and heated to 80 °C for 2 hours in order to dissolve wax and thus erase the memory of previous wax formation. Finally, the oil is cooled at a rate of 9 °C/hour to the actual test temperature before transfer to the various instruments (pour point, viscosity).
10. Pour point: The method to determine the Pour point is a modified version (ref.3) of ASTM D97 (ref.8):
 - The Pour point "as received" is the Pour point measured on the untreated oil.
 - The Minimum Pour point is the Pour point measured after controlled cooling from 80 °C.
 - The Maximum Pour point is the Pour point measured after reheating the oil to 50 °C followed by controlled recooling.
11. a.Wax precipitation temperature (WPT) is determined by polarization microscopy (due to optical anisotropy wax crystals have the ability to rotate polarizes light). The sample is cooled at a rate of 0.5 °C/min. after first being heated to 70 °C. For detailes, see ref.3.

b.Wax dissolution temperature is determined in the same way as WPT. When WPT has been established, the sample is left at room temperature for at least 30 minutes, and then reheated at a rate of 0.5 °C/min.

12. Kinematic viscosity is measured in the Newtonian temperature range using an Ubbelohde glass capillary viscometer with an appropriate capillary constant. The viscometer tubes are kept in a thermostated bath for 15 minutes at each temperature prior to measurements, which are run in triplicate. The kinematic viscosity is related to dynamic viscosities as follows :
 Dyn. visc. (mPa s) = Kin.visc.(cSt)*Density (g/cm³).
 cSt = 10⁻² mm²/s.
13. Apparent viscosity of beneficiated oil is measured with a Haake RV 12 rotational viscometer. Temperature curves (viscosity vs. temperature) at various shear rates are run in the non-Newtonian temperature range of the oil.
14. Pentane insolubles (asphaltenes) are precipitated with pentane at room temperature (1:40 vol:vol) and filtrated through a 0.45 µm filter. The precipitated material is dissolved in toluene, followed by precipitation with pentane and a new filtration through a 0.45 µm filter.
15. a. Hydrocarbon group type analysis of C₁₀₊, C₂₀₊ and distillation-fractions are performed by preparative liquid chromatography using a silica column to separate aromatics from saturates (paraffins/naphthenes). The polar fraction is estimated from the correlation between the aromatic and the polar fraction (ref.2).
 The solvent is removed by vacuum evaporation, and the fractions quantified by weighing. Residual hexane is determined by GC with internal standard.

b. Hydrocarbon group type PNA analysis of distillation fractions C₁₀ to C₁₉ is performed by gas chromatography-mass spectrometry. A slightly modified ASTM D-2425 method is applied (ref. 7 and 8). The distribution of paraffins and naphthenes as well as a series of aromatic subclasses are determined. The results are normalized to fit the weight percent aromatics from liquid chromatography or a density-aromatic correlation (ref.3).

Experimental conditions :

Mass spectrometer	: VG TS-250
Inlet system	: GC (HP 5890)with splitless injection 300 °C
Temp.prog.GC	: 60 °C 2 min.,5 °C/min. to 300 °C- 300 °C 70 min.
Interface temp.	: 280 °C
Acceleration voltage	: 4 kV
Ionization	: 0.2 mA
Ionization potential	: 70 eV
Resolution	: 500
Scan rate	: 50-450
Ion source temperature	:220 °C
Scanning	: 1 sec./scan

16. Emulsion stability test :

Equipment:

Homogenizer	Propeller type - Buhler HO4 incl.Heto temp.controller and circulator.
Circulator bath	:Heto Lab. Equipment

Experimental procedures:

The crude oil was given a thermal pretreatment at 80 °C for 2 hours in a gas-tight stainless

steel cell, to erase any memory of previous wax formation. The oil was then cooled to 50 °C in the cell.

A representative sample of beneficiated oil was added to an appropriate volume of synthetic formation water in the homogenizer and kept at the specified temperature.

Standard emulsification conditions are :

Propeller speed	: 8000 rpm
Mixing time	: 1 min.
Mixing volume	: 11 cm ³
Temperature	: 50 °C
Water cut	: 20 % and 50 %

After homogenizing, the emulsion was transferred to a preheated, screw capped, graded glass vial (10 cm³). The demulsifier was added immediately after emulsification by shaking for 30 seconds and placed in a thermostated bath kept at the specified temperature (50 °C). The separation of free water was recorded as a function of time for 30 minutes.

The demulsifier was diluted with xylene. 10µl xylene solution was added, giving the wanted concentration of demulsifier (3 or 10 ppm).

Synthetic formation water was mixed according to the recipe given in Appendix B.

APPENDIX D**Definition of Carbon Preference Indices :**

$$\text{CPI 1} = \frac{1}{2} \left(\frac{\text{C25} + \text{C27} + \text{C29} + \text{C31}}{\text{C24} + \text{C26} + \text{C28} + \text{C30}} + \frac{\text{C25} + \text{C27} + \text{C29} + \text{C31}}{\text{C26} + \text{C28} + \text{C30} + \text{C32}} \right)$$

$$\text{CPI 2} = \frac{2 \text{ C27}}{\text{C26} + \text{C28}}$$

Definition of Methyl Phenantrene Indices :

$$\text{MPI 1} = \frac{1.5 (2\text{-MP} + 3\text{-MP})}{\text{P} + 9\text{-MP} + 1\text{-MP}}$$

$$\text{MPI 2} = \frac{3(2\text{-MP})}{\text{P} + 9\text{-MP} + 1\text{-MP}}$$