statoil

TBP distillation of oil

34/10-14 DST no.1

STATOIL
EXPLORATION & PRODUCTION
LABORATORY

by

Hans Petter Rønningsen

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Classification

Requested by

Subtitle

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Title

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March-84

LAB 84.215

Approved

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N O T A T

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LAB
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SAK: TBP - RAPPORT FOR 34/10-14 DST 1 (LAB 84.215)

GULLFAKS
PRT 10. 04. 84
A.nr.: D-4.4
gass/og væskeanalyser

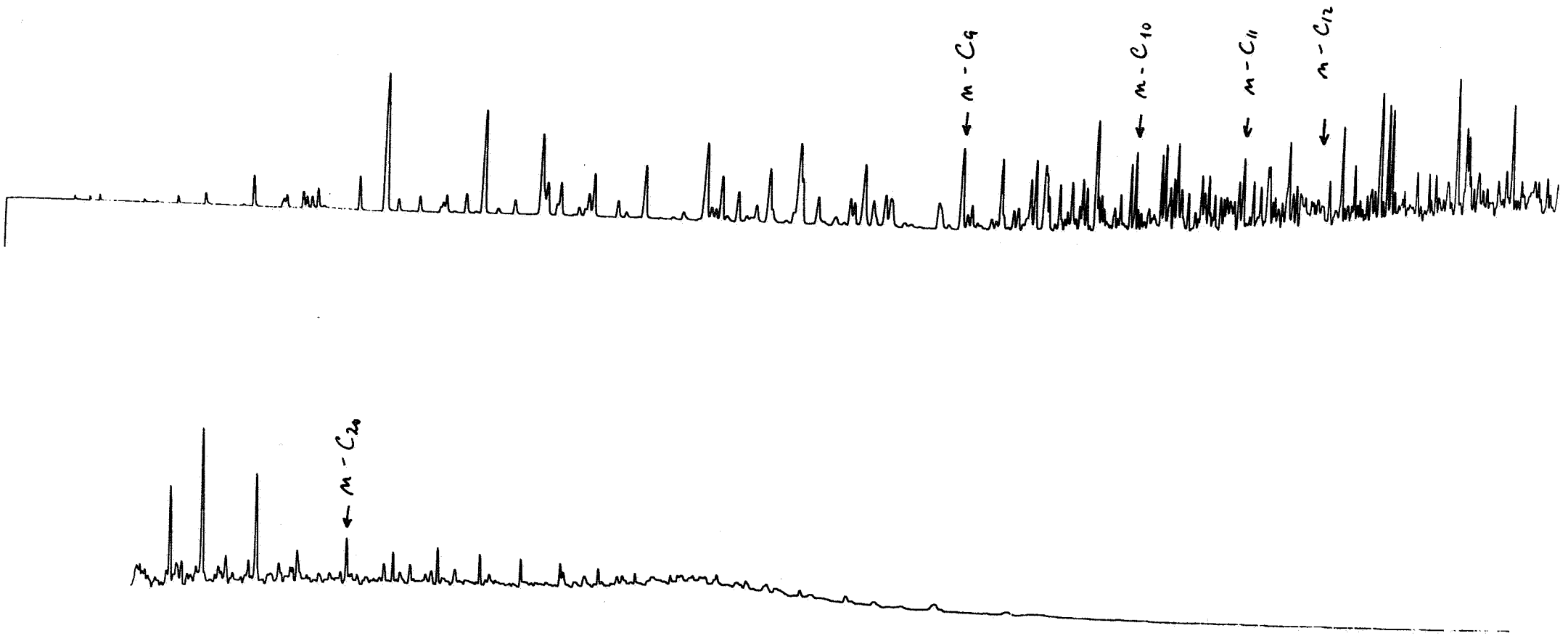
1. Det blir i notat 20.03.84 etterlyst dokumentasjon (gass-kromatogrammer) for at oljene 34/10-4 DST no.2 og 34/10-14 DST no.1 kan betraktes som svært like.

   At dette er tilfelle skulle framgå av vedlagte kromatogrammer. (Forskjellen i den lette delen skyldes avdampning ved lagring av prøvene). Det er likevel små forskjeller, noe som også er vist ved et sammenlikningsstudie utført ved laboratoriet i 1982 (Lab 82.31). Forskjellene er imidlertid så små at jeg mener det er forsvarlig å betrakte dem som like i denne sammenhengen, og dermed bruke 34/10-4 data der hvor 34/10-14 dataene er mangelfulle.

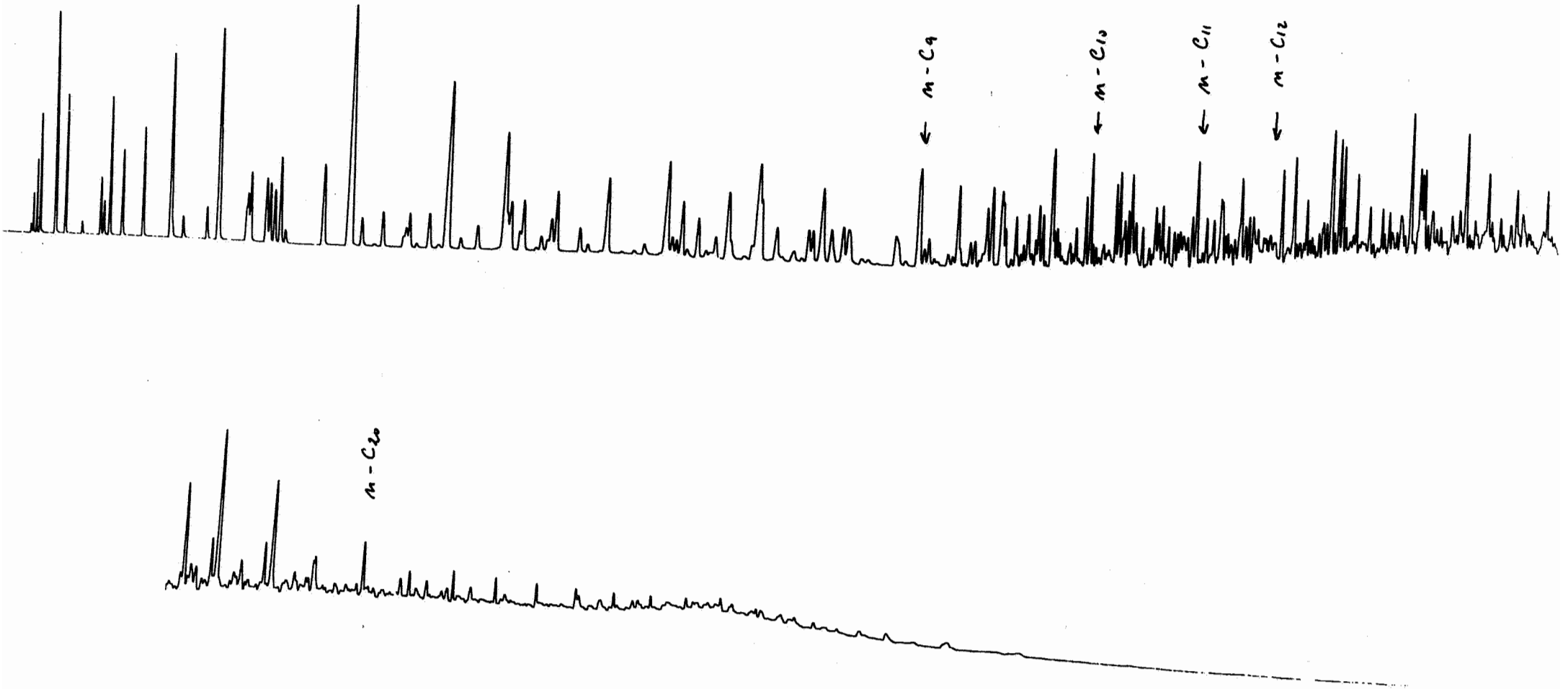
2. Molekylvektene for C_{12} og C_{19} kuttene fra 34/10-14 ble sjekket og funnet å ligge 2-3 enheter over de tilsvarende 34/10-4 kuttene. Likeledes er C_{20}-molekylvekten 3 enheter høyere for 34/10-14. Jeg gjorde da den antagelse at C_{12} - C_{19} kuttene fra 34/10-14 systematisk var litt forskjøvet i forhold til 34/10-4 kuttene, på grunn av de trykkproblemene som gjorde at 34/10-14 destillasjonen i sin tid ble betraktet som mislykket.

3. Grunnen til at data for C_{10} og C_{11} er utelatt i hydrokarbon gruppe-analysen, er at en stor del av prøven i disse to tilfellene ble mistet med avdamping av løsningsmiddel. Resultatene ble dermed betraktet som svært upålitelige. Dette er et generelt problem med C_{10} - C_{12} kuttene, hvis ikke inndampingen skjer ytterst forsiktig. C_{19}-kuttet ble utelatt p.g.a. at dette destillasjonskuttet ved en feil ble forurenset med et annet kutt.

GASSKROMATOGRAM AV 34/10 - 4 DST no. 2



GASSKROMATOGRAM AV 34/10 - 14 DST no. 1



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1. INTRODUCTION AND SUMMARY

This report presents the results from three true boiling point distillations, performed on oil 34/10-14 DST no.1 (Brent formation). For gas to C11, data from a distillation performed in july -81 are used. From C12 to C20+, data from a distillation in july -82 are used. The last distillation from C20 to C30+ was performed in july -83.

Because different equipment has been used and different people have been involved in the distillations, one will emphasize that the data might not be as reliable as they should. But comparison to oil 34/10-4 DST 2 (Brent, Rannoch 2 formation), which by fingerprint and hydrocarbon group type analysis has been found quite similar to 34/10-14 DST 1, indicates that the data are of acceptable quality.

Like 34/10-4 DST 2, 34/10-14 DST 1 is a very aromatic crude oil. The content of aliphatic and aromatic compounds has been determined for all fractions C12 - C29 by liquid chromatographic separation and gravimetric quantification.

Table 1. Summary of some essential data of oil 34/10-14 DST no.1 (Brent formation, interval 1933.5 - 1937.5 m RKB).

	Oil	C10+	C20+	C30+
% by weight of oil	100	88.904	55.285	34.416
Density (15 ^{o}C, g/cm3)	0.879	0.898	0.932	0.952
Molecular weight	236	292	461	628
Pour point (^{o}C)	-33			
Kinematic viscosity (50 ^{o}C, sSt)	6.9			
Hexane insolubles (wt%)	0.7			

2. EXPERIMENTAL

2.1 Distillation

TBP distillations were performed according to ASTM D-2892 using a HYPER-CAL "Podbielniac" distillation apparatus (to C11) and a Fischer HMS 500 apparatus (C12 - C30+). Fractions were collected according to the boiling point ranges between successive n-alkanes, as given by Katz and Firoozabadi (Journ. Petr. Tech., nov. 1978, 1650). The sample was fractionated from room temperature to 151.3 ^{o}C at atmospheric pressure, from 38.3 to 185 ^{o}C at 13.3 mbar (10 mm Hg) and from 150.6 to 242.3 ^{o}C at 2.66 mbar (2 mm Hg) reduced pressure.

2.2 Hydrocarbon group type analysis.

Separation of collected distillate fractions into saturates (paraffines+ naphtenes) and aromatics was performed using a Waters Prep LC SYSTEM 500 A with a 30 cm x 58 mm i.d. radial compression silica column. 3 -5 g samples were dissolved to about 10 ml with hexane before injection and eluted with hexane as mobile phase at a flowrate of 250 ml/min. The column was backflushed after elution of the saturates in order to elute the aromatics as a single peak.

Most of the hexane was removed using a rotary evaporator. The rest was removed with purified nitrogen, and the sample weighed. Using 2,2,4-trimethyl-pentane as internal standard, the residual amount of hexane was determined by gas chromatography, to obtain corrected gravimetric data.

The density of each subfraction was measured at 15 ^{o}C. The measured densities of sample + residual hexane were corrected according to the following equation:

$$d\ i = \frac{wt\%\ i}{\frac{100}{d\ tot} - \frac{wt\%\ C6}{d\ C6}}$$

d i = corrected density of sufraction
d tot = measured density of sample + hexane
d C6 = density of hexane
wt% i = weight percent of subfraction in total sample
wt% C6 = weight percent of hexane in total sample

2.3 Other measurements

Molecular weights were determined by freezing point depression using a Cryette cryoscope with benzene as referance substance. The cryoscope was calibrated with tetradecane (n-C14).

Densities were measured using a Paar 602 frequency densiometer, thermostatted at 15 ^{o}C.

Pour point was measured according to ASTM D-97 (1980) and kinematic viscosity according to ASTM D-445.

3. COMMENTS

Gas and cold trap molecular weights were calculated from gas chromatograms. For C6 - C11 34/10-4 DST 2 molecular weights were used directly. For C12 - C19 34/10-4 DST 2 molecular weights were adjusted by + 2-3 units. C20 - C30+ and C10+ molecular weights are measured on 34/10-14 fractions. (For 34/10-4 DST 2 molecular weights, see report LAB 83.55).

4. RESULTS

(next pages)

Table 2. Data from TBP distillation of stock tank oil 34/10-14 DST 1.

Fraction	Cut point (°C,760 mmHg)	Actual head-temp.	% by weight of total oil	% by weight distilled
Gas	-	-	0.335	0.335
Cold trap	36.5	36.5	0.588	0.923
C 6	69.2	69.2	0.575	1.499
C 7	98.9	98.9	1.972	3.471
C 8	126.1	126.1	3.706	7.178
C 9	151.3	151.3	3.918	11.097
C 10+	> 151.3	> 151.3	88.904	100.001
C 10	174.6	56.9	3.079	14.176
C 11	196.4	74.3	2.918	17.095
C 12	216.8	90.7	3.121	20.217
C 13	235.9	106.5	3.404	23.621
C 14	253.9	121.2	3.493	27.114
C 15	271.1	135.0	3.502	30.617
C 16	287.3	147.5	2.863	33.481
C 17	303.0	161.1	3.778	37.259
C 18	317.0	173.3	3.493	40.752
C 19	331.0	185.0	3.961	44.714
C 20+	> 331.0	> 185.0	55.285	100.000
C 20	344.0	161.1	2.641	47.356
C 21	357.0	171.7	2.373	49.729
C 22	369.0	181.1	2.410	52.140
C 23	381.0	190.6	2.105	54.245
C 24	392.0	199.4	1.941	56.187
C 25	402.0	208.3	1.956	58.144
C 26	413.0	216.9	1.803	59.947
C 27	424.1	226.0	2.136	62.083
C 28	433.6	234.5	1.533	63.617
C 29	443.1	242.3	1.966	65.583
C 30+	> 443.1	> 242.3	34.416	100.000

Table 2 cont.

Fraction	Density (g/cm3)	% by volume of total oil	% by volume distilled
Gas	0.425	0.692	0.692
Cold trap	0.625	0.827	1.520
C 6	0.667	0.758	2.278
C 7	0.731	2.369	4.648
C 8	0.762	4.272	8.920
C 9	0.783	4.396	13.317
C 10+	0.898	86.965	100.282
C 10	0.798	3.390	16.707
C 11	0.808	3.173	19.880
C 12	0.830	3.303	23.184
C 13	0.849	3.521	26.706
C 14	0.858	3.577	30.283
C 15	0.867	3.549	33.832
C 16	0.875	2.874	36.706
C 17	0.870	3.814	40.521
C 18	0.872	3.519	44.040
C 19	0.885	3.932	47.973
C 20+	0.932	52.107	100.080
C 20	0.894	2.595	50.568
C 21	0.896	2.326	52.895
C 22	0.899	2.354	55.250
C 23	0.900	2.055	57.305
C 24	0.901	1.893	59.198
C 25	0.905	1.899	61.097
C 26	0.908	1.744	62.842
C 27	0.910	2.062	64.904
C 28	0.919	1.466	66.370
C 29	0.922	1.873	68.244
C 30+	0.952	31.756	100.000

Table 2 cont.

Fraction	Molecular weight	Mole%	Cumulative mole%
Gas	38	2.13	2.13
Cold trap	58	2.45	4.58
C 6	80	1.74	6.32
C 7	93	5.12	11.45
C 8	107	8.37	19.83
C 9	120	7.89	27.72
C 10+	292	73.61	101.34
C 10	132	5.64	33.36
C 11	148	4.76	38.13
C 12	162	4.65	42.79
C 13	175	4.70	47.49
C 14	188	4.49	51.99
C 15	200	4.23	56.22
C 16	212	3.26	59.49
C 17	229	3.98	63.48
C 18	245	3.44	66.93
C 19	256	3.74	70.67
C 20+	461	28.99	99.67
C 20	265	2.41	73.08
C 21	277	2.07	75.15
C 22	290	2.00	77.16
C 23	303	1.68	78.84
C 24	318	1.47	80.32
C 25	329	1.43	81.75
C 26	342	1.27	83.03
C 27	358	1.44	84.47
C 28	367	1.01	85.48
C 29	377	1.26	86.74
C 30+	628	13.25	100.00

Table 3. Cumulative weight and volume, % by volume distilled and calculated density S of recovered material

S = Cum. weight/cum. volume

Fraction	Cum. weight	Cum. volume	S	% by volume distilled
Gas	1.375	3.235	0.425	0.692
Cold trap	3.792	7.102	0.533	1.520
C 6	6.156	10.646	0.578	2.278
C 7	14.250	21.719	0.656	4.648
C 8	29.461	41.681	0.706	8.920
C 9	45.545	62.222	0.731	13.317
C 10	58.186	78.063	0.745	16.707
C 11	70.166	92.890	0.755	19.880
C 12	82.976	108.324	0.765	23.184
C 13	96.947	124.780	0.776	26.706
C 14	111.287	141.493	0.786	30.283
C 15	125.664	158.076	0.794	33.832
C 16	137.415	171.505	0.801	36.706
C 17	152.921	189.328	0.807	40.521
C 18	167.261	205.773	0.812	44.040
C 19	183.522	224.147	0.818	47.973
C 20	194.365	236.276	0.822	50.568
C 21	204.105	247.146	0.825	52.895
C 22	213.997	258.150	0.828	55.250
C 23	222.639	267.752	0.831	57.305
C 24	230.609	276.598	0.833	59.198
C 25	238.639	285.470	0.835	61.097
C 26	246.039	293.620	0.837	62.842
C 27	254.807	303.255	0.840	64.904
C 28	261.102	310.105	0.841	66.370
C 29	269.174	318.860	0.844	68.244

Table 4. Measured and calculated molecular weights and densities of oil 34/10-14 DST 1.

	Oil	C 10+	C 20+	C 30+
Measured MW	236	292	461	628
Calculated MW using C10+ MW	238			
Calculated MW using C20+ MW	242	298		
Calculated MW using C30+ MW	241	297	455	
Measured density	0,879	0.898	0.932	0.952
Calculated density using C10+ density	0.875			
Calculated density using C20+ density	0.877	0.900		
Calculated density using C30+ density	0.878	0.900	0.933	

Table 5 . Hydrocarbon group type analysis of oil 34/10-14 DST 1.

Fraction	Composition, wt%		% by wt of total oil		Density (15°C)	
	P+N	A	P+N	A	P+N	A
C 12	75.6	24.4	2.359	0.762	0.805	0.858
C 13	67.1	32.9	2.284	1.120	0.814	0.882
C 14	65.0	35.0	2.271	1.223	0.821	0.890
C 15	63.1	36.9	2.210	1.293	0.829	0.905
C 16	60.9	39.1	1.744	1.119	0.821	0.902
C 17	64.0	36.0	2.418	1.360	0.832	0.924
C 18	64.0	36.0	2.236	1.258	0.833	0.902
C 19	0.0	0.0	0.000	0.000	0.000	0.000
C 20	60.5	39.5	1.598	1.043	0.848	0.963
C 21	59.5	40.5	2.007	1.366	0.849	0.971
C 22	59.4	40.6	1.427	0.978	0.852	0.965
C 23	59.4	40.6	1.250	0.855	0.854	0.966
C 24	61.6	38.4	1.199	0.745	0.852	0.950
C 25	57.7	42.3	1.129	0.827	0.856	0.970
C 26	56.3	43.7	1.015	0.788	0.859	0.962
C 27	56.9	43.7	1.215	0.921	0.863	0.950
C 28	57.4	42.6	0.880	0.653	0.869	0.954
C 29	62.6	37.4	1.231	0.735	0.881	0.953

P+N = paraffines + naphtenes
A = aromatics

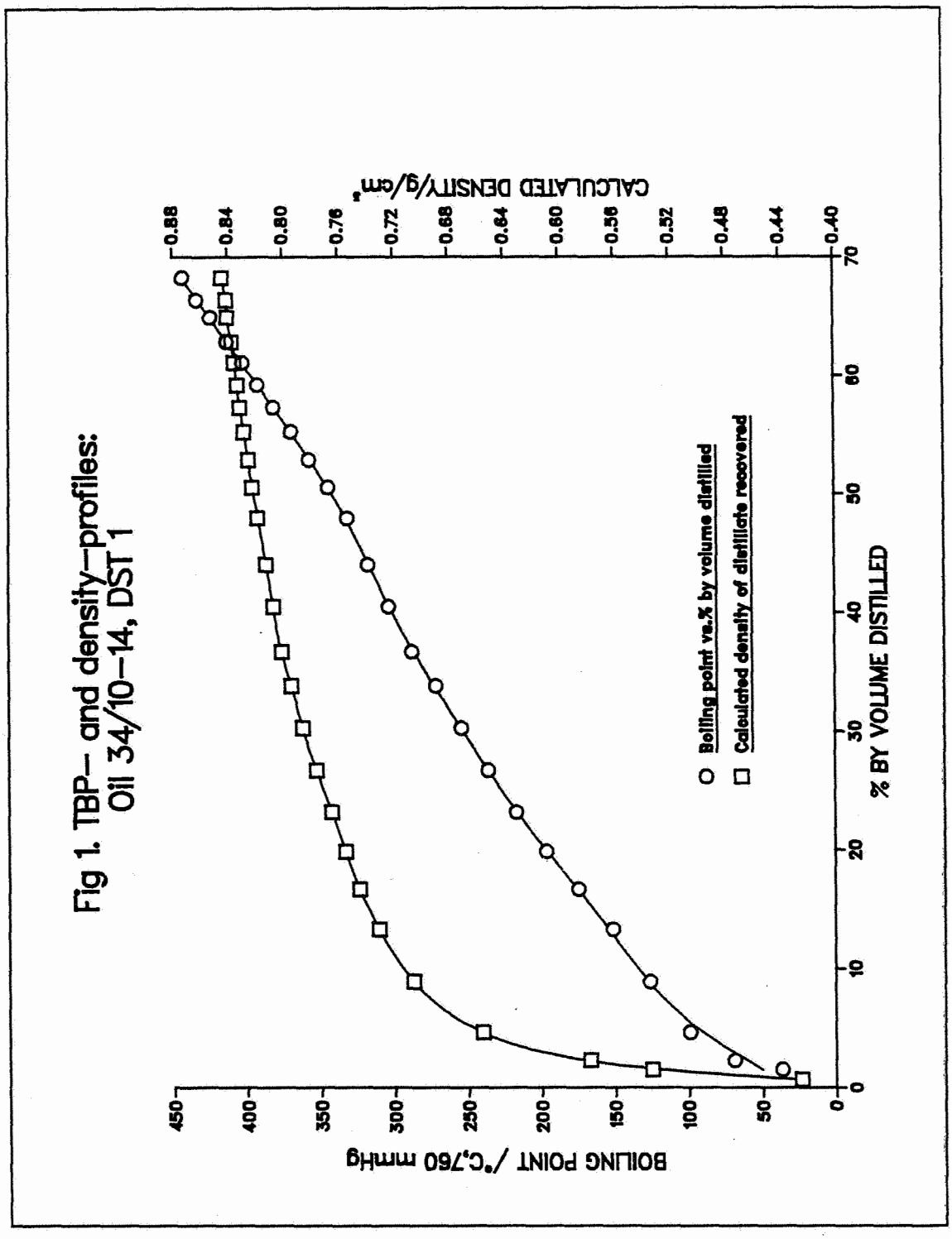
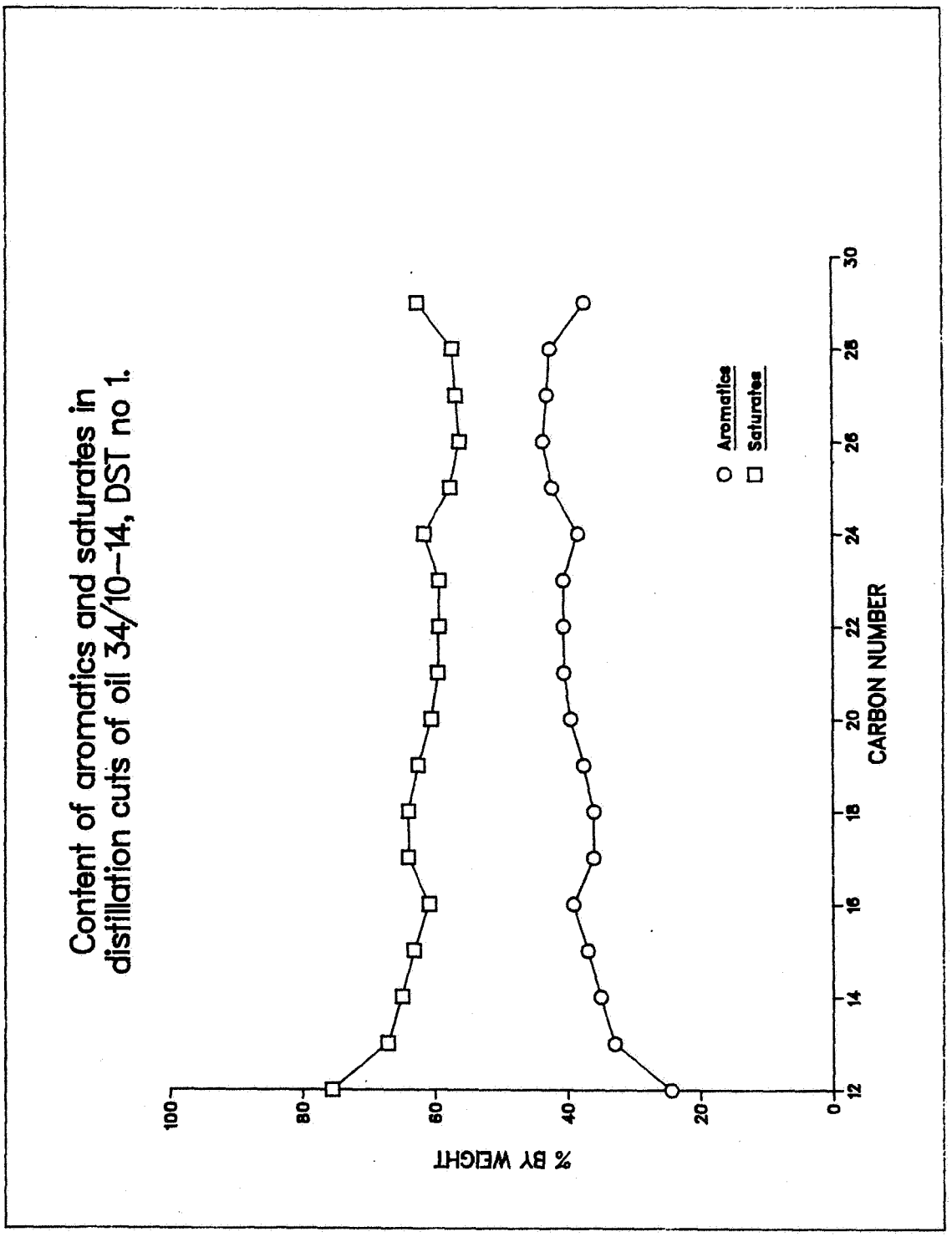
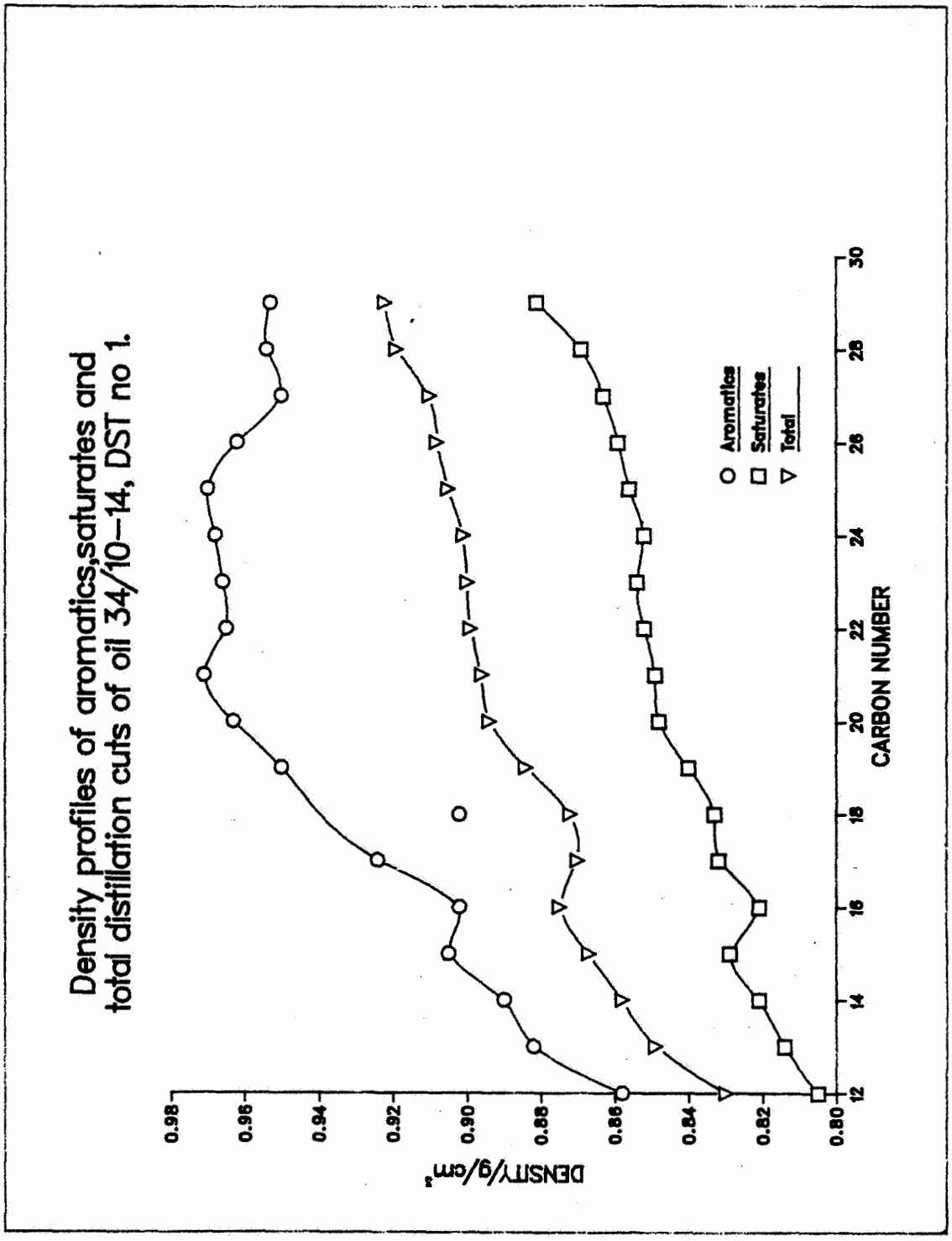


Fig 1. TBP– and density–profiles:
Oil 34/10–14, DST 1
BOILING POINT /°C,760 mmHg
CALCULATED DENSITY/g/cm³
% BY VOLUME DISTILLED
Boiling point vs.% by volume distilled
Calculated density of distillate recovered
450
400
350
300
250
200
150
100
50
0.88
0.84
0.80
0.76
0.72
0.68
0.64
0.60
0.56
0.52
0.48
0.44
0.40
0
10
20
30
40
50
60
70


Content of aromatics and saturates in distillation cuts of oil 34/10–14, DST no 1.
% BY WEIGHT
100
80
60
40
20
0
12
14
16
18
20
22
24
26
28
30
CARBON NUMBER
Aromatics
Saturates


Density profiles of aromatics,saturates and total distillation cuts of oil 34/10-14, DST no 1.
DENSITY/g/cm³
0.98
0.96
0.94
0.92
0.90
0.88
0.86
0.84
0.82
0.80
12
14
16
18
20
22
24
26
28
30
CARBON NUMBER
Aromatics
Saturates
Total