statoil

TBP distillation of oil from

34/10-17 DST no. 2

STATOIL
EXPLORATION & PRODUCTION
LABORATORY

by

Hans Petter Rønningsen

Nov-83 LAB83.

In addition to corrected wt%'s, corrected molecular weights and densities have been calculated, assuming these properties to be additive. Checking of calculated values against measured ones, has revealed that the assumption is valid, at test below C_9. The calculated density of the C_9 cut has an accuracy of about $\pm$1%.

Table 7 contains characteristic ratios involving C_{19} and C_{20} isoprenoid hydrokarbons.

Table 8 contains PNA-distribution of fractions below C_{10}, as determined by GC, assuming equal FID respons to the different classes of compounds.

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Classification

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Subtitle

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CONTENTS

1. INTRODUCTION AND SUMMARY

This report presents the results from a true boiling point distillation, performed on a 4000 ml sample of stock tank oil from 34/10-17 DST no. 2, by West Lab A/S.

The sample was fractionated from room temperature to 153.1 ^{o}C at atmospheric pressure, and from 71.7 ^{o}C to 206.7 ^{o}C at 26.6 mbar reduced pressure. The cut point temperatures according to Katz and Firoozabadi (1) of fractions above C_{10} had to be corrected by + 3.5 - 4.5 degrees to obtain reasonably balanced n- alkane to n-alkane cuts. This is certainly caused by the high paraffin content of this oil. Comparing this oil with earlier distilled 34/10-oils, shows that it is quite similar to 34/10-11 DST no.1 (Statfjord formation) (2). This, in turn, indicates, according to a comparison study of 34/10-oils (2), similarity to the following oils: 34/10-7 DST 1 (Cook), 34/10-13 DST 2 (Statfjord).

Table 1. Summary of some essential data of oil 34/10-17 DST no.2

	Oil	C_{10+}	C_{20+}
Density (15^{o}C, g x cm^{-3})	0.844	0.881	0.913
Molecular weight	214 *	317	489
% by weight of total sample	100	80.370	53.831
Pour point (^{o}C)	+9		

* Average of calculated values using C_{10+} and C_{20+} MW respectively

2. EXPERIMENTAL

2.1 Distillation

The TBP distillation was performed according to ASTM D-2892 using a Kontes Martin MK IV-B Fractionator with a 24½ inches x 25 mm i.d. column packed with 600 cm^3 protruded metal (15 theoretical plates).

Fractions were collected according to corrected boiling point ranges between successive n-alkanes as given by Katz and Firoozabadi (1). The light end fractions (< C_{10}) were separated at atmospheric pressure, the C_{10+} - fractions at reduced pressure (26.6 mbar = 20 mm Hg).

2.2 Gas chromatographic analysis

Single component analysis was performed on all light end fractions. C_{10+}- fractions were checked for fraction overlap. A Hewlett Packard 5880 gas chromatographic system was used.

Column for gas and cold trap fractions:	Chrompack WCOT, C_p sil 5 on fused silica, 50 m x 0.23 mm i.d., filmthickness 0.3 µm.
Column for liquid fractions:	Chrompack WCOT, Cp sil 5 on fused silica, 25 m x 0.22 mm i.d., filmthickness 0,14 µm
Carrier gas:	Helium (99.995%), 22 cm/sek linear volocity at 10°C.
Detector:	Flame ionization, nitrogen (99.6% make-up gas, temp. 320°C.

Injection: All glass splitter, with a packed "Jennings tube". Split ratio 1:80, temp. 310°C (liquid fractions) and 200°C (gas) respectively. 0.1 - 0.2 µl liquid samples injected, 0.5 ml gas and cold trap fractions injected.

Temp. programs: Gas and cold trap:
-30°C isothermal 4 min, then 8°/min to 160°C.
C_6 - C_{11}: 10°C 4 min, 4°/min to 300°C
C_{12} - C_{13}: 50°C 4 min, 4°/min to 300°C
C_{14} - C_{19}: 100°C 4 min, 4°/min to 300°C

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 - C_{14}).

Densities were measured using a Paar DMA 46 frequency densiometer thermostatted at 15°C. The C_{20+} - fraction was very viscous. It was therefor diluted with toluene, before measuring the density of the mixture. C_{20+} density was calculated using the following formula:

$$\rho 20+ = \frac{wt\%_{20+}}{\frac{100}{\rho mix} - \frac{wt\%t}{\rho t}} + 0.009$$

$\rho 20+$ = density of C_{20+} fraction
$wt\%_{20+}$ = weight % of C_{20+} fraction in mixture
ρt = density of toluene
$wt\%_{20+}$ = weight % of toluene in mixture
ρmix = density of mixture
0.009 = emipirical correction factor

2.4 Pour point measurement

The pour point of the oil was measured according to ASTM method D-97 (1980).

The pour point was measured to + 9°C (two identical parallells).

3. RESULTS

Table 2 contains all compositional data from the TBP distillation and physical data of each fraction. A loss of 0.519%, as calculated by adding all fraction at the end of the distillation, has been added to the C_{20+} - fraction.

Table 3 contains the calculated density S of recovered distillate (see also figure at the end of this chapter):

$$S = \frac{\text{cumulative weight}}{\text{cumulative volume}}$$

Total % by volume distilled is also given in this table.

Table 4 contains calculated molecular weights and densities.

Table 5 contains the weight distribution and calculated % overlap between collected fractions. % by weight overlap is assumed to be approximately equal to area % overlap in integrated GC- chromatograms.

In table 6 a more detailed composition of the light fractions is given. All chromatograms of gas and cold trap fractions, C_6, C_7, C_8, C_9 and partly C_{10}, have been combined to calculate "ideal" fractions without overlap. Below C_6, every single compound is reported. In C_6, C_7, C_8 and C_9, some abundant aromatics and naphtenes are reported in addition to the total cuts. In this table, "C_x rest" means C_x total minus aromatics/naphtenes.

REFERENCES.

1. Katz, D.L., Firoazabadi, A., Journ., Petr., Tech., Nov. 1978, 1650.

2. Statoil report LAB. 82.31.

Table 2.
Data from TBP distillasjon of stock tank oil 34/10-17 DST 2.

Fraction	Cut point (°C,760 mmHg)	Actual head-temp.at 26.6mbar	$(g.cm^{-3})^{15}$	MW	% by weight of total oil	% by weight distilled	Mole percent	% by volume of total oil
Gas		-	0.465*	37.6	0.035	0.035	0.20	0.063
Cold trap	< 36.5	-	0.605*	64.5	4.061	4.095	13.54	5.644
C_6	69.2	-	0.677*	81.2	2.357	6.452	6.24	2.927
C_7	98 9	-	0.734	97.3	4.321	10.773	9.55	4.950
C_8	126.1	-	0.756	106.2	4.570	15.342	9.25	5.083
C_9	51.3	-	0.775	119.1	4.050	19.392	7.31	4.394
C_{10}+ >	151 3	-	0.881	317	80.37		54.56	76.72
C_{10}	175.6	71.7	0.788	134.4	2.468	21.859	3.95	2.633
C_{11}	197.6	89.6	0.791	147.7	2.558	24.418	3.72	2.720
C_{12}	222.1	109.8	0.801	161.9	3.051	27.468	4.05	3.203
C_{13}	241 2	126 0	0.818	177.4	2.898	30.366	3.51	2.976
C_{14}	258.7	140.7	0.830	188.2	2.541	32.908	2.90	2.575
C_{15}	276.7	155.5	0.836	201.2	3.028	35.936	3.24	3.046
C_{16}	292.4	168.4	0.841	215.2	2.592	38.528	2.59	2.592
C_{17}	308.0	182.3	0.839	234.3	2.609	41.137	2.39	2.615
C_{18}	322.2	194.7	0.843	249.6	2.604	43.741	2.24	2.597
C_{19}	336.0	206.7	0.852	264.0	2.428	46.169	1.98	2.397
C_{20} >	336 0 >	206 7	0.913	489	53.83	100.000	23.34	49.58

Recovery : 99.48 %
Loss : 0 52 % (added to C_{20}+-fraction)
* Values calculated from GC-reports

Table 3.

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

S = Cum. weight/cum.volume

Fraction	Cum. weight	Cum. volume	S	% by volume distilled
Gas	0.630	1.355	0.465	0.063
Cold trap	74.030	122.677	0.603	5.707
C_6	116.630	185.602	0.628	8.634
C_7	194.730	292.005	0.667	13.584
C_8	277.330	401.264	0.691	18.667
C_9	350.530	495.716	0.707	23.061
C_{10}	395.137	552.324	0.715	25.695
C_{11}	441.381	610.787	0.723	28.415
C_{12}	496.526	679.632	0.731	31.617
C_{13}	548.909	743.670	0.738	34.596
C_{14}	594.846	799.016	0.744	37.171
C_{15}	649.582	864.490	0.751	40.217
C_{16}	696.440	920.207	0.757	42.809
C_{17}	743.605	976.422	0.762	45.424
C_{18}	790.668	1032.250	0.766	48.021
C_{19}	834.559	1083.765	0.770	50.418

Table 4.

Measured and calculated molecular weights and densities of oil 34/10-17. DST 2.

	Oil	C_{10}	C_{20}+
Measured MW		317	489
Calculated MW using C_{10}+ MW	213		
Calculated MW using C_{20}+ MW	214	319	
Measured density	0.844	0.881	0.913
Calculated density using C_{10}+ density	0.841		
Calculated density using C_{20}+ density	0.841	0.881	

Table 5.

Weight distribution and % overlap between uncorrected fractions of 34/10-17 DST 2 oil.

Fraction	% by weight of total oil	% by weight overlap between fractions*
Gas	0.035	
Cold trap	4.061	
C_6	2.357	20.2 : 59.4 : 20.4
C_7	4.321	9.9 : 65.1 : 25.0
C_8	4.570	11.1 : 77.6 : 11.3
C_9	4.050	16.3 : 71.8 : 11.9
C_{10}	2.468	10 : 76 : 14
C_{11}	2.558	24 : 66 : 10
C_{12}	3.051	22 : 62 : 16
C_{13}	2.898	13 : 71 : 16
C_{14}	2.541	15 : 70 : 15
C_{15}	3.028	19 : 68 : 13
C_{16}	2.592	18 : 66 : 16
C_{17}	2.609	18 : 65 : 17
C_{18}	2.604	18 : 64 : 18
C_{19}	2.428	17 : 66 : 17

* Calculated on basis of area % from GC-reports.

Table 6.
Total composition and physical properties of gas and light end fractions ($<C_{10}$), corrected to 0% overlap, as determined by GC The compounds and fractions in the table constitute 19 63 % of the total oil.

	Fraction overlap	MW	Wt% of fraction	Wt% of total oil	Mole% of total oil	δ_{15}
Methane		16.04	-	0.001	0.01	
Ethane		30.07	-	0.016	0.12	0.3580
Propane		44.10	-	0.331	1.60	0.5076
i-butane		58.12	-	0.387	1.42	0.5633
n-butane		58.12	-	1.108	4.07	0.5847
2.2-dimethyl-propane		72.15	-	0.008	0.02	0.5967
i-pentane		72.15	-	1.034	3.06	0.6246
n-pentane		72.15	-	1.207	3.56	0.6309
C_6 total	0:100:0	85.2	100	3.903	5.49	0.732
C_6 rest		86.2	94.890	2.078	5.14	0.663
Cyclopentane		70.14	5.110	0.112	0.34	0.7502
C_7 total	0·100·0	91 9	100	3.903	9.06	0.732
C_7 rest		99.4	57.341	2.238	4.81	0.699
Methylcyclo-pentane		84.16	15.245	0.545	1.51	0.7534
Benzene		78.11	4.637	0.181	0.49	0.8842
Cyclohexane		84.16	22.777	0.889	2.25	0.7831
C_8 total	0·100·0	104.4	100	5.277	10.78	0.762
C_8 rest		113.6	51.678	2.727	5.13	0.745
Methylcyclo-hexane		98.19	31.779	1.677	3.62	0.7737
Ethylcyclo-pentane		98.19	1.402	0.074	0.12	0.7708
Toluene		92.14	15.141	0.799	1.85	0.8714
C_9 total	0:87.7·12.3	119.7	100	3.923	6.98	0.785
Included :						
Ethylcyclo-hexane*		112 22	9.839	0.386	0.74	0.7819
Ethylbenzene*		106.17	4 639	0.182	0.37	0.8714
m+p-xylene*		106.17	19.500	0.765	1.56	0.8668
o-xylene*		106.17	9.075	0.356	0.75	0.8844

* Additional contribution from C_{10}-fraction : Ethylcyclohexane 0.004%, ethylbenzene 0.004%, m+p-xylene 0.014% and o-xylene 0.017%.

** Average density of m- and p-xylene.

Table 7.

Characteristic isoprenoid hydrocarbon ratios of oil 34/10-17 DST 2*

	Ratio
C_{17}/pristane	1.93
C_{18}/phytane	3.46
Pristane/phytane	1.95

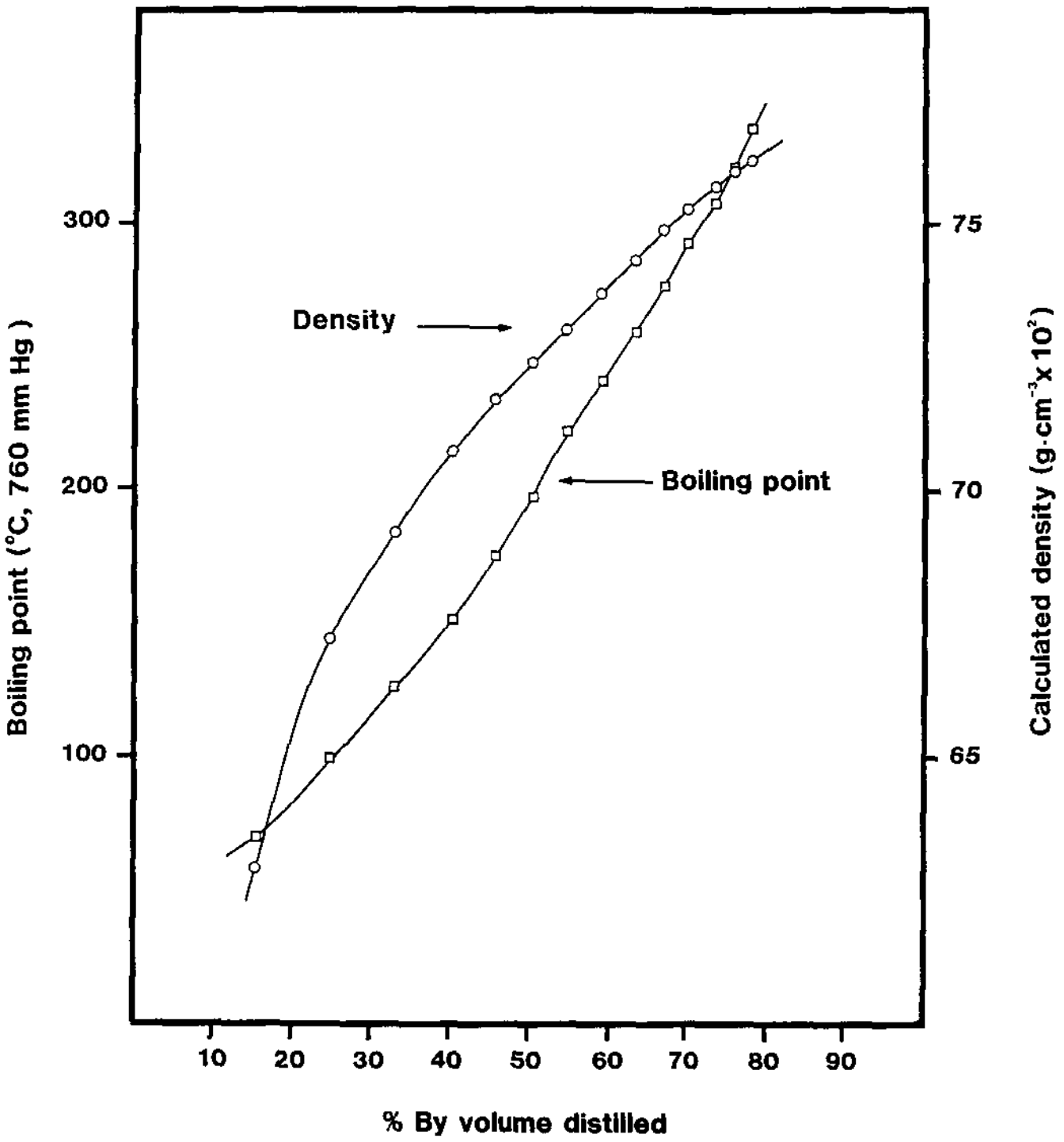
* Peak height ratio from GC.

Table 8.

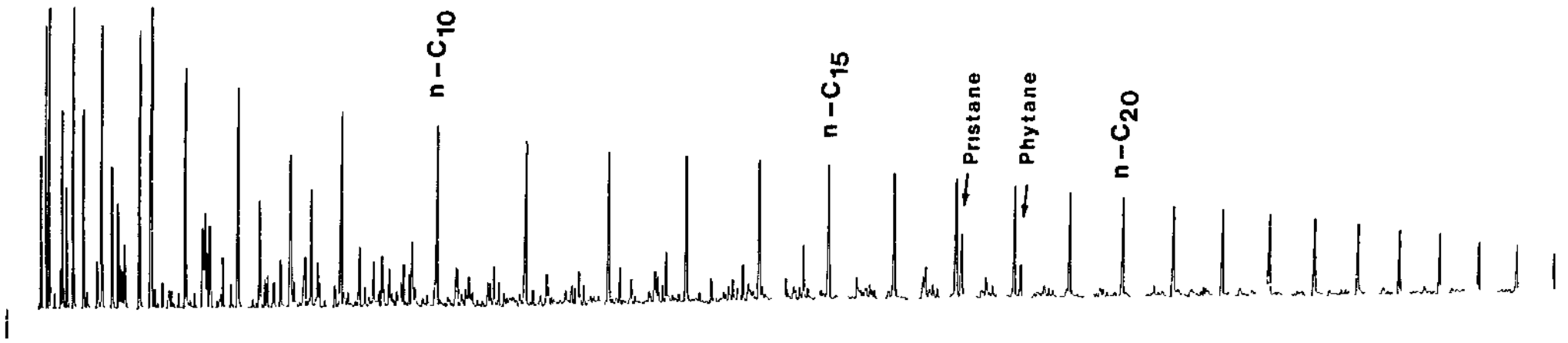
PNA-distribution of light end fractions (% by weight).

Fraction	Paraffines	Naphtenes	Aromatics
C_6	94.9	5.1	0
C_7	46.0	49.4	4.6
C_8	33.6	51.3	15.1
C_9	39.9	23.2	36.9

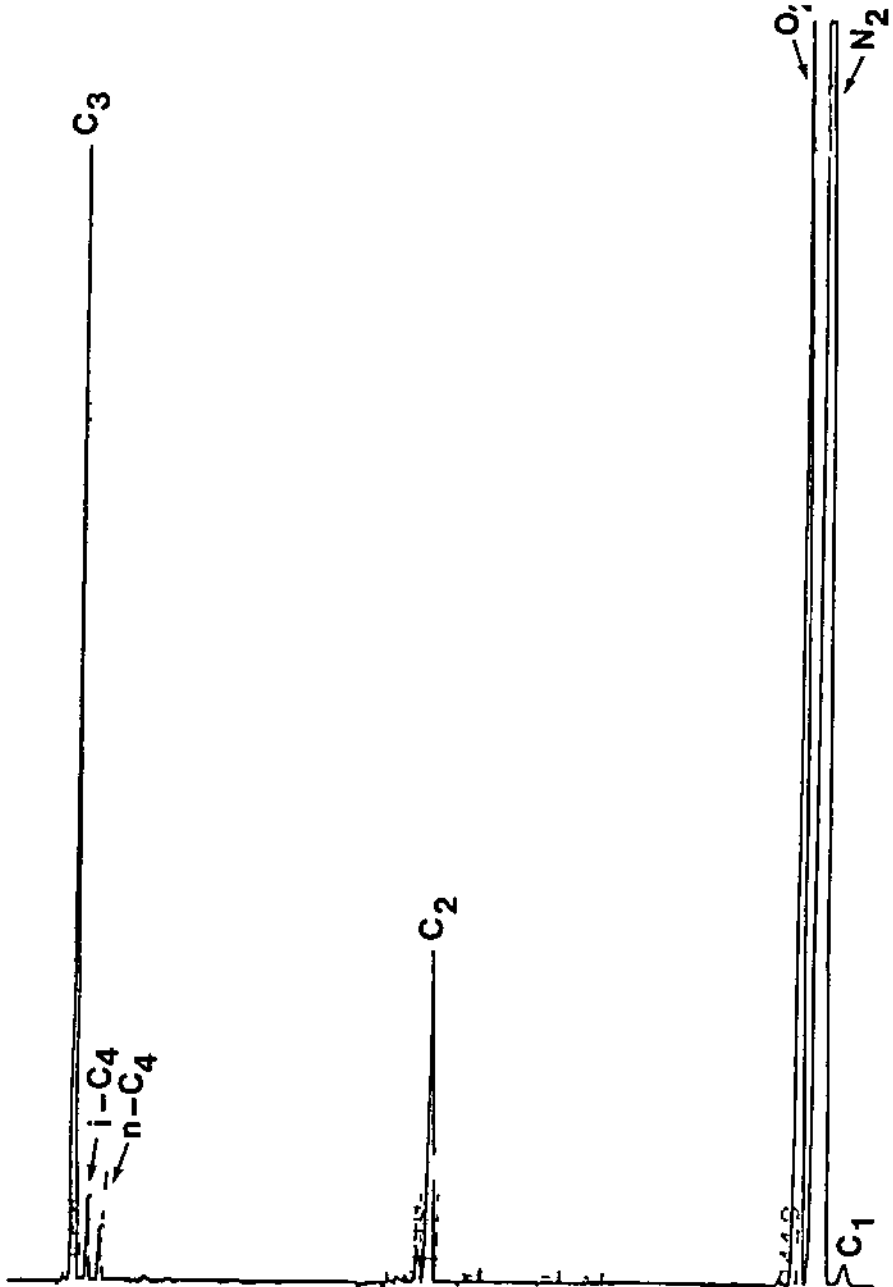
TBP-and density profiles for oil 34/10-17 DST no.2



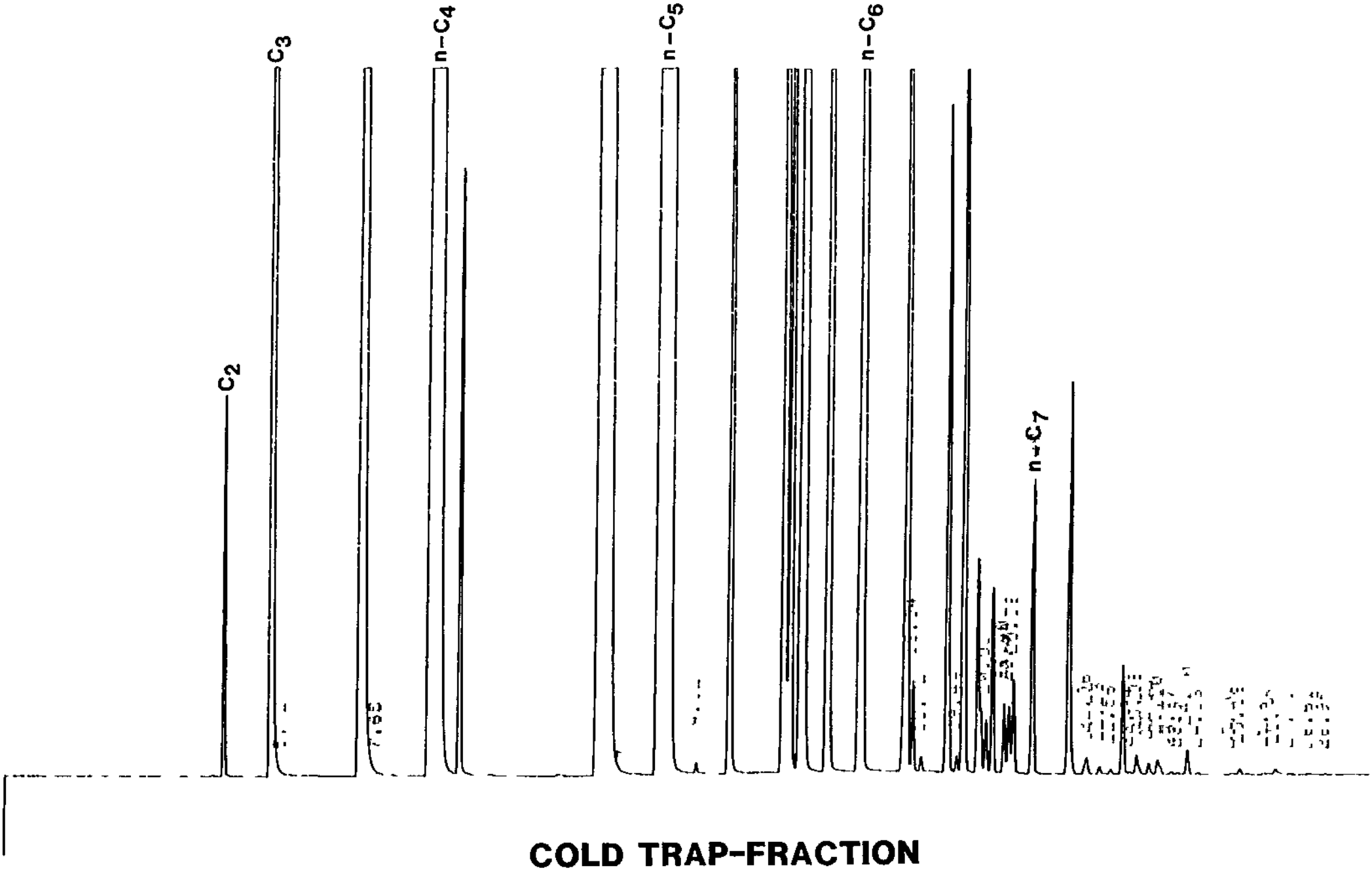
APPENDIX
GAS CHROMATOGRAMS

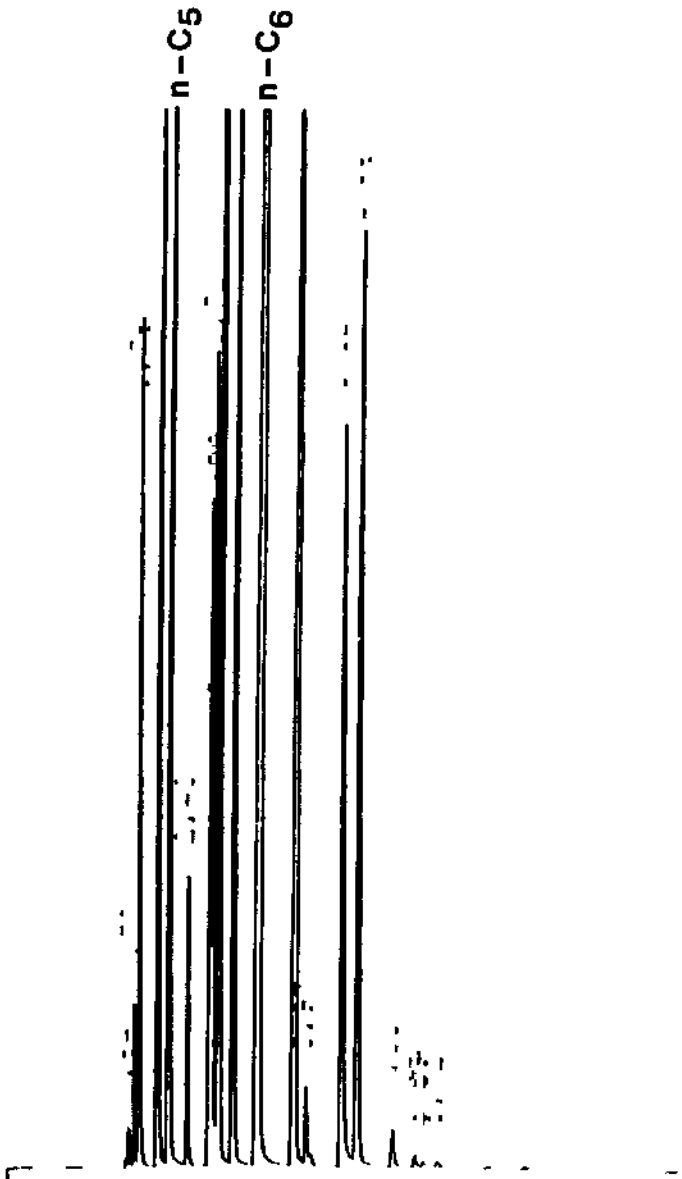


Oil 34/10-17 DST2

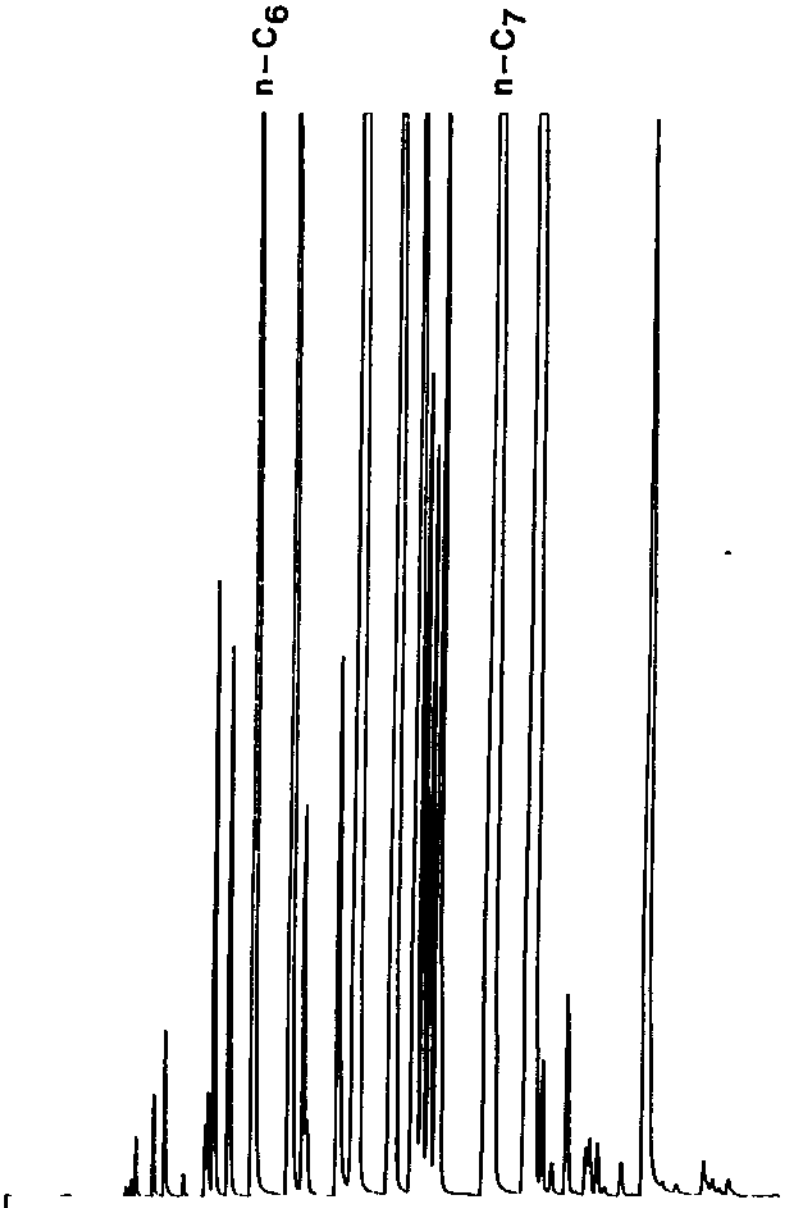


GAS-FRACTION

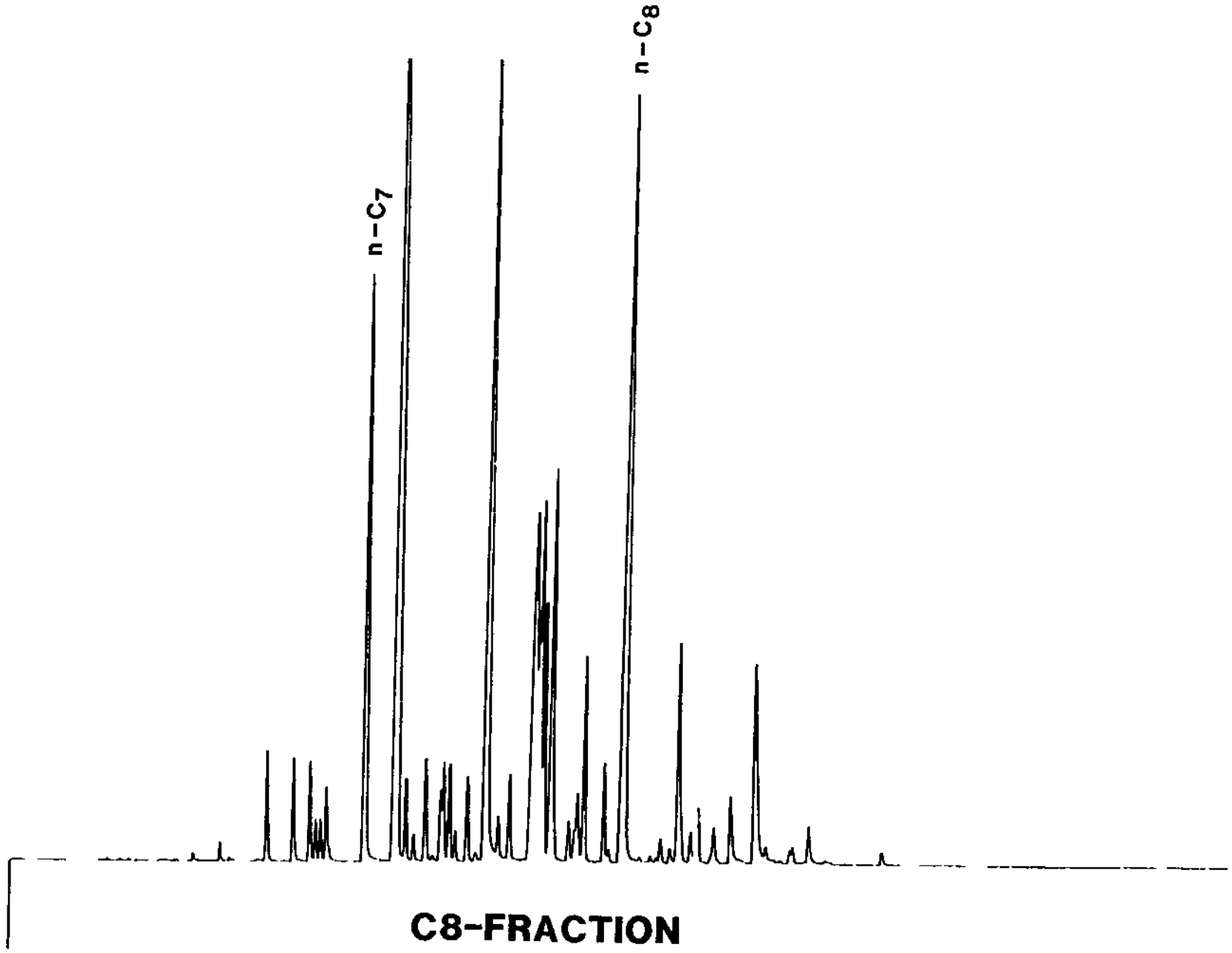

C2
C3
n-C4
n-C5
n-C6
n-C7
COLD TRAP-FRACTION

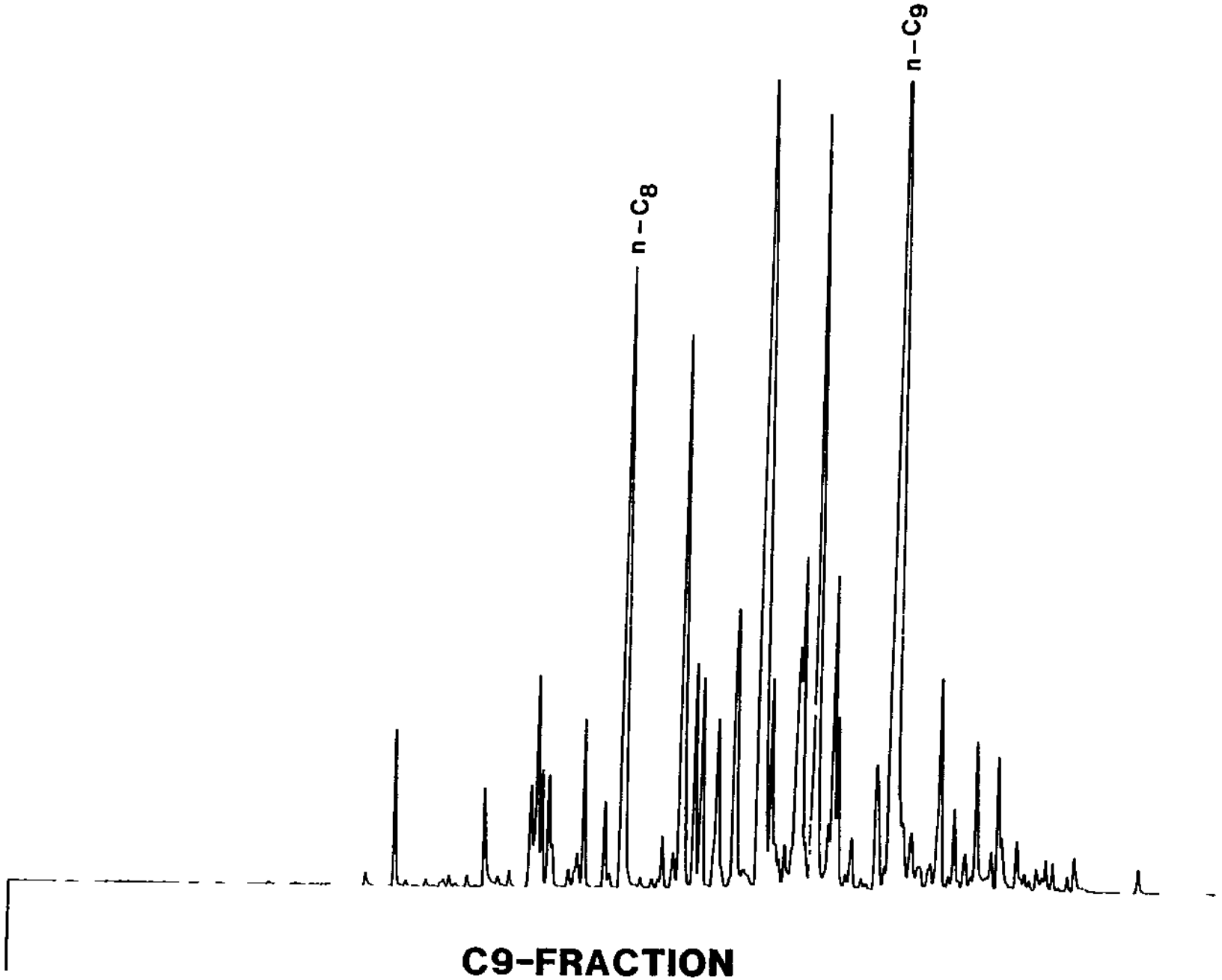


C6-FRACTION

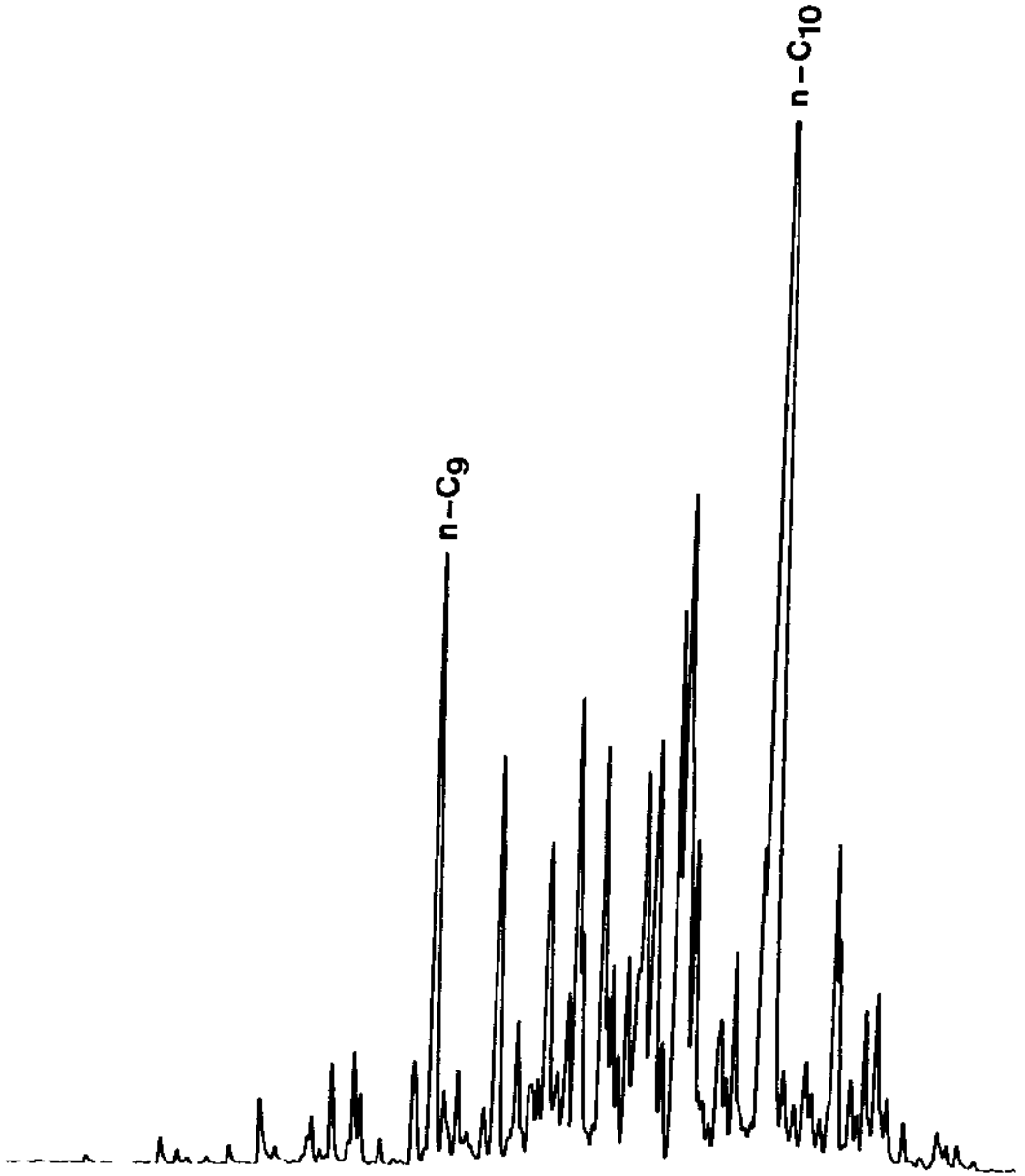


C7-FRACTION


n-C7
n-C8
C8-FRACTION



C9-FRACTION



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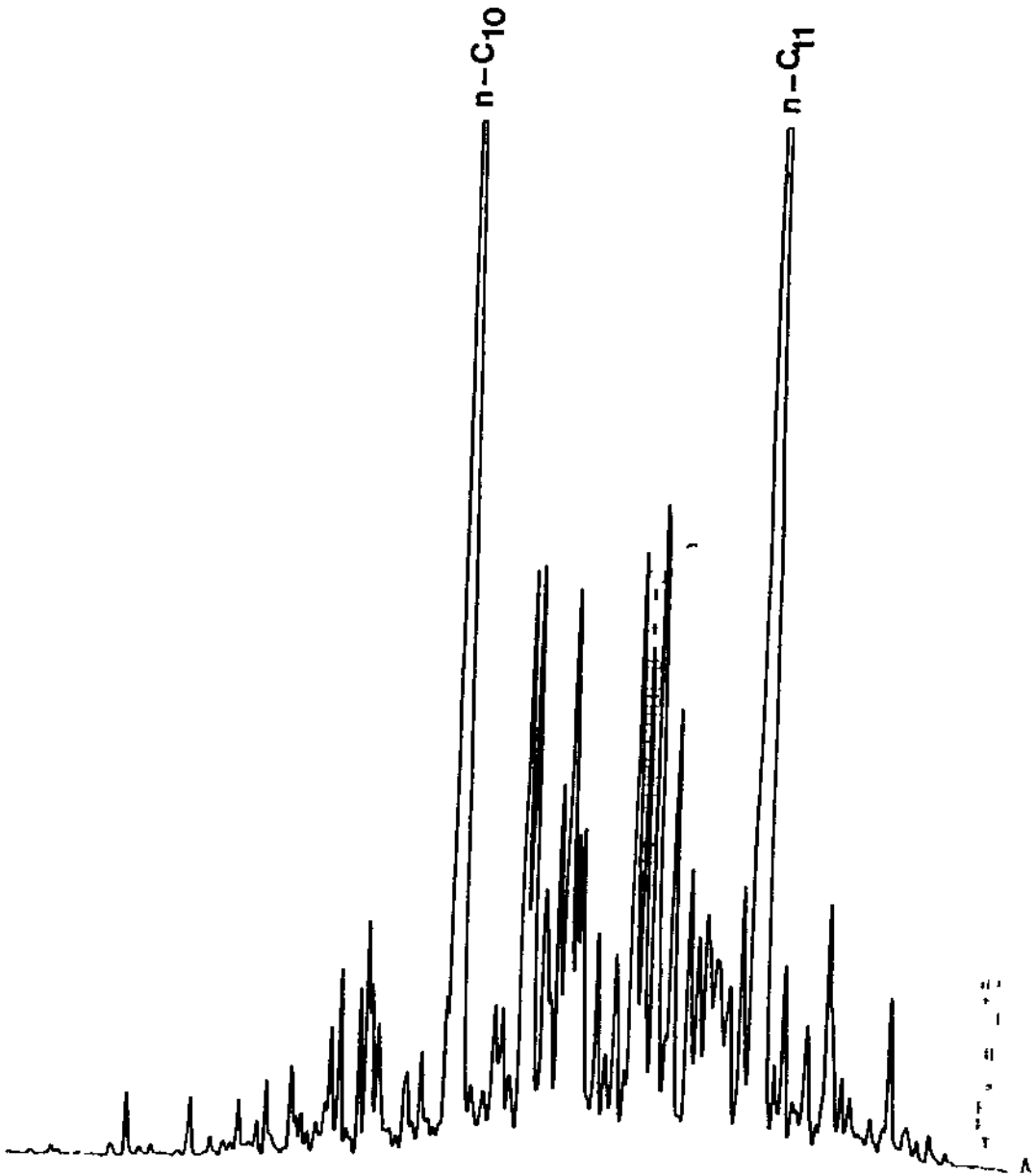
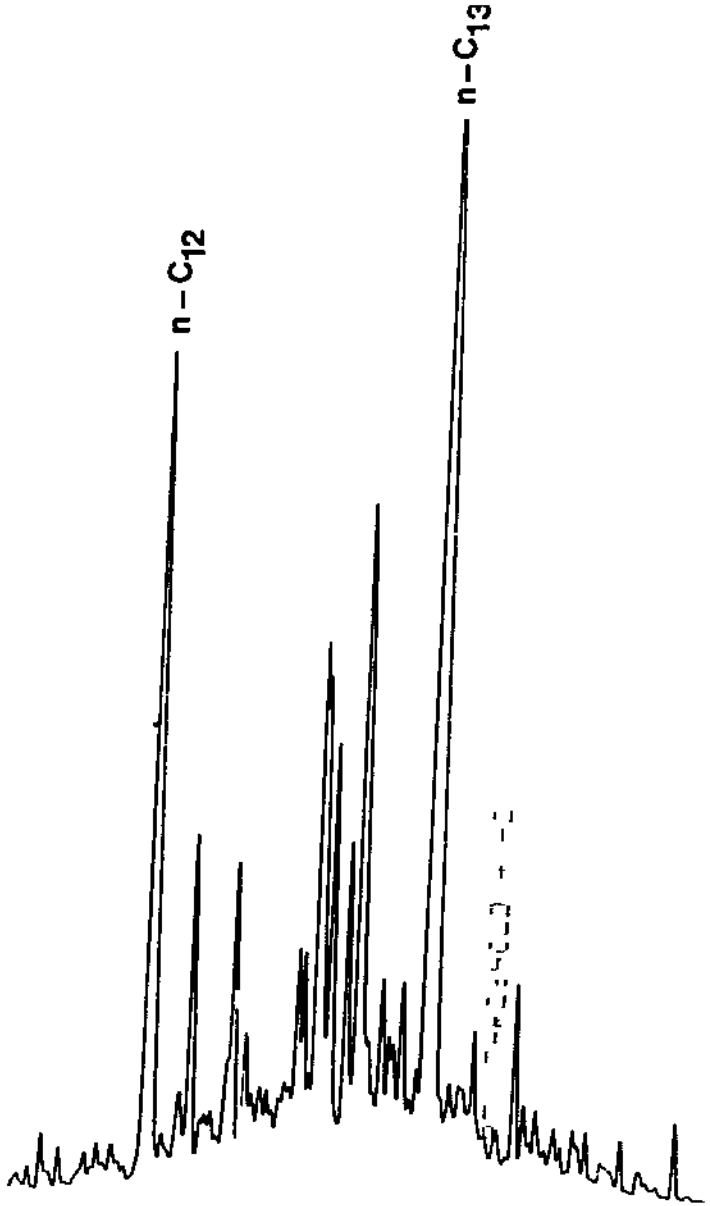


C11-FRACTION

C12-FRACTION



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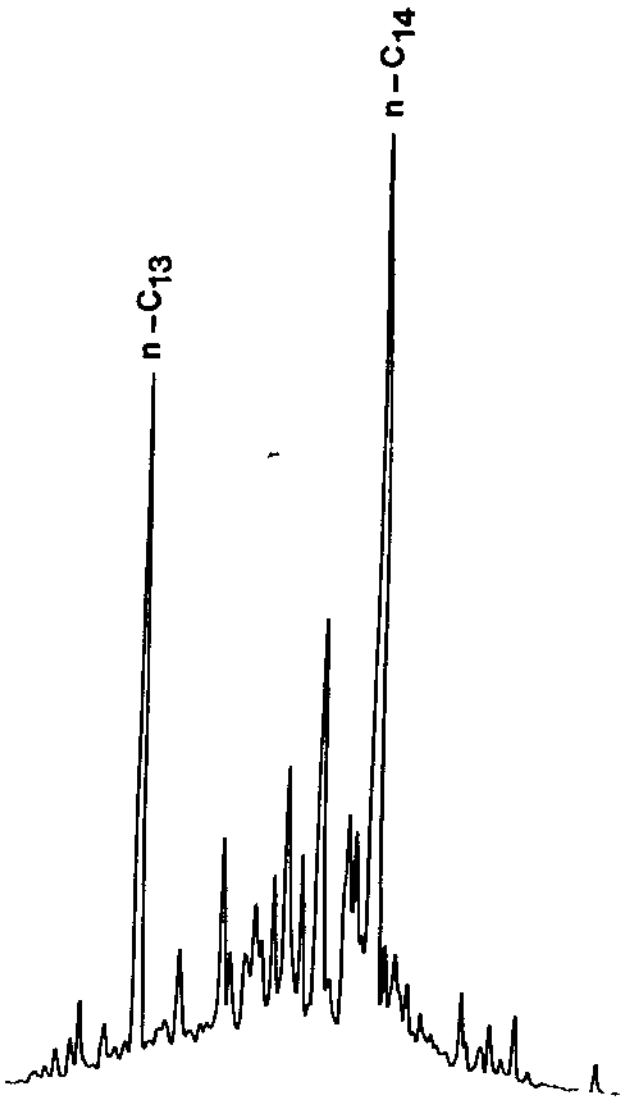

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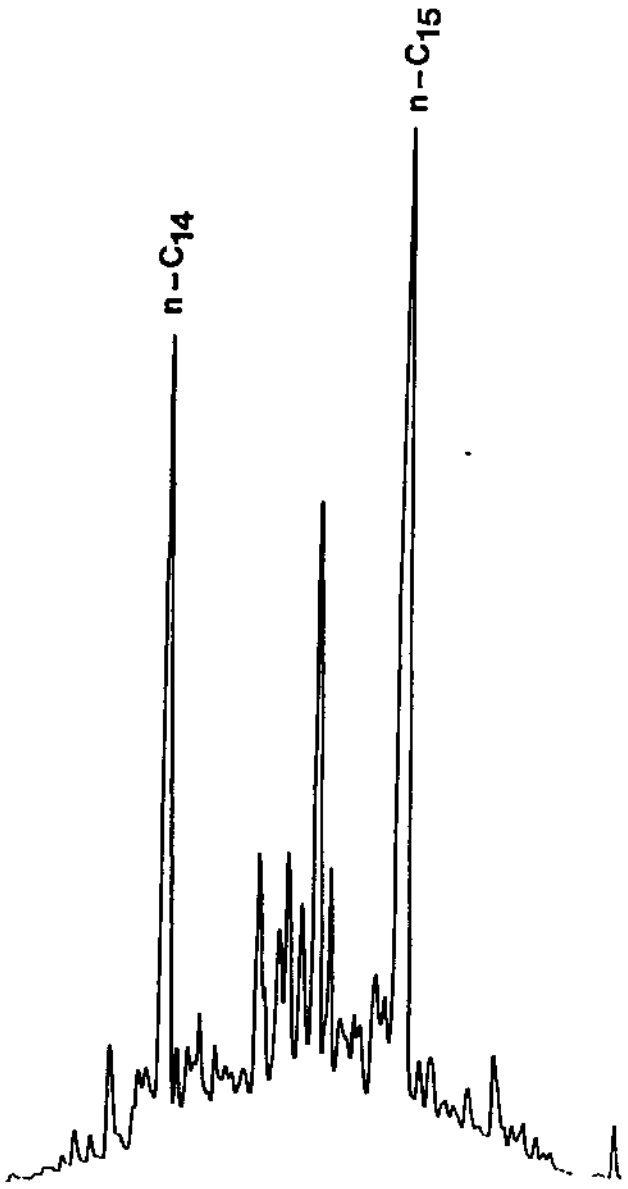

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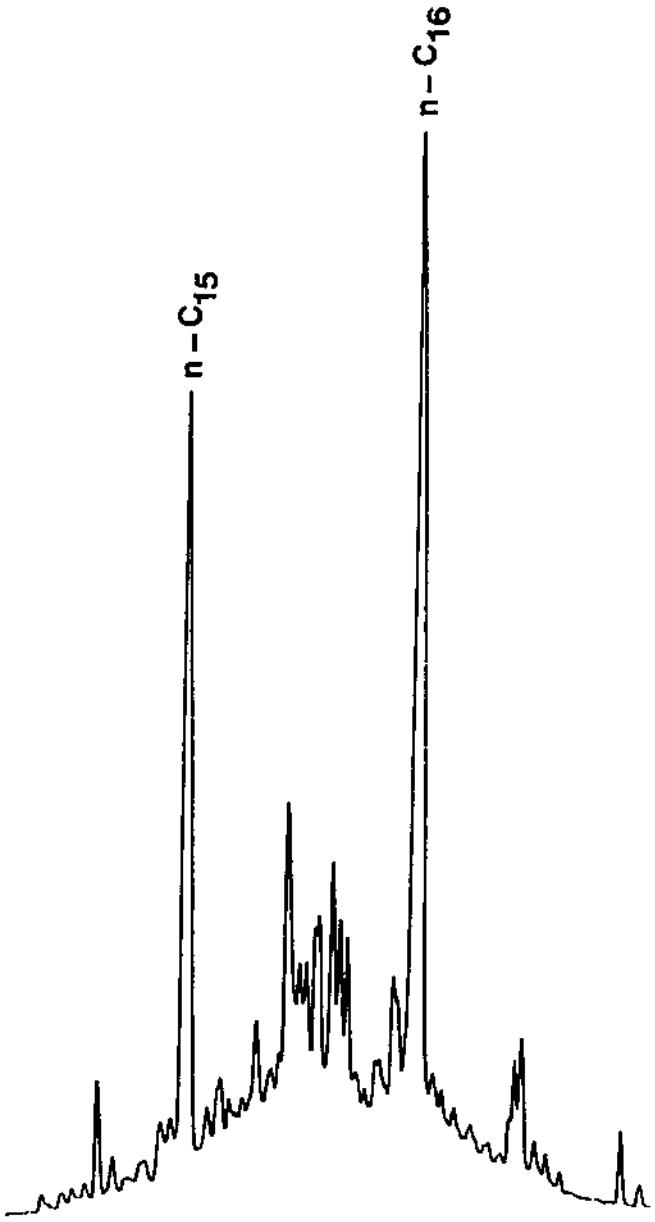

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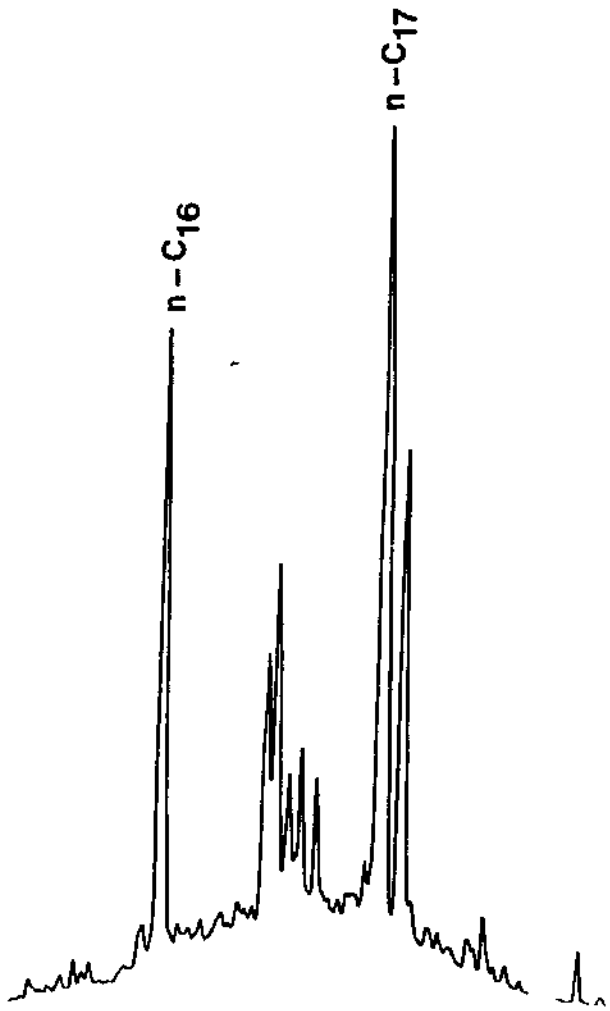

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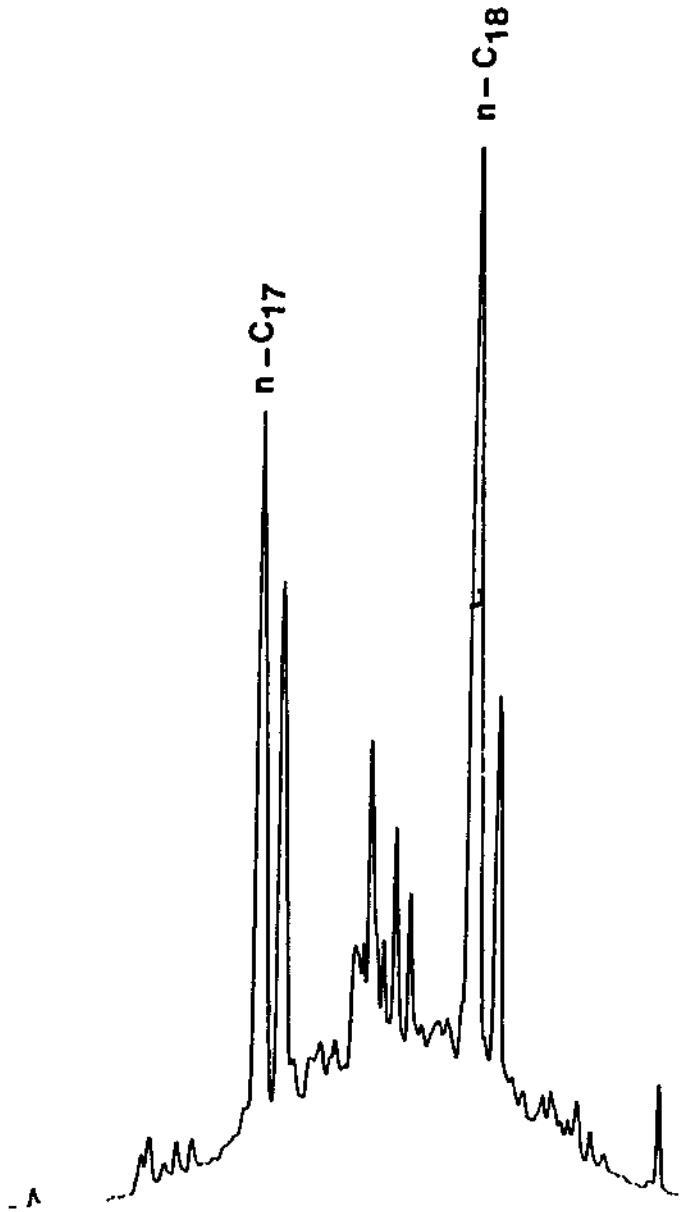

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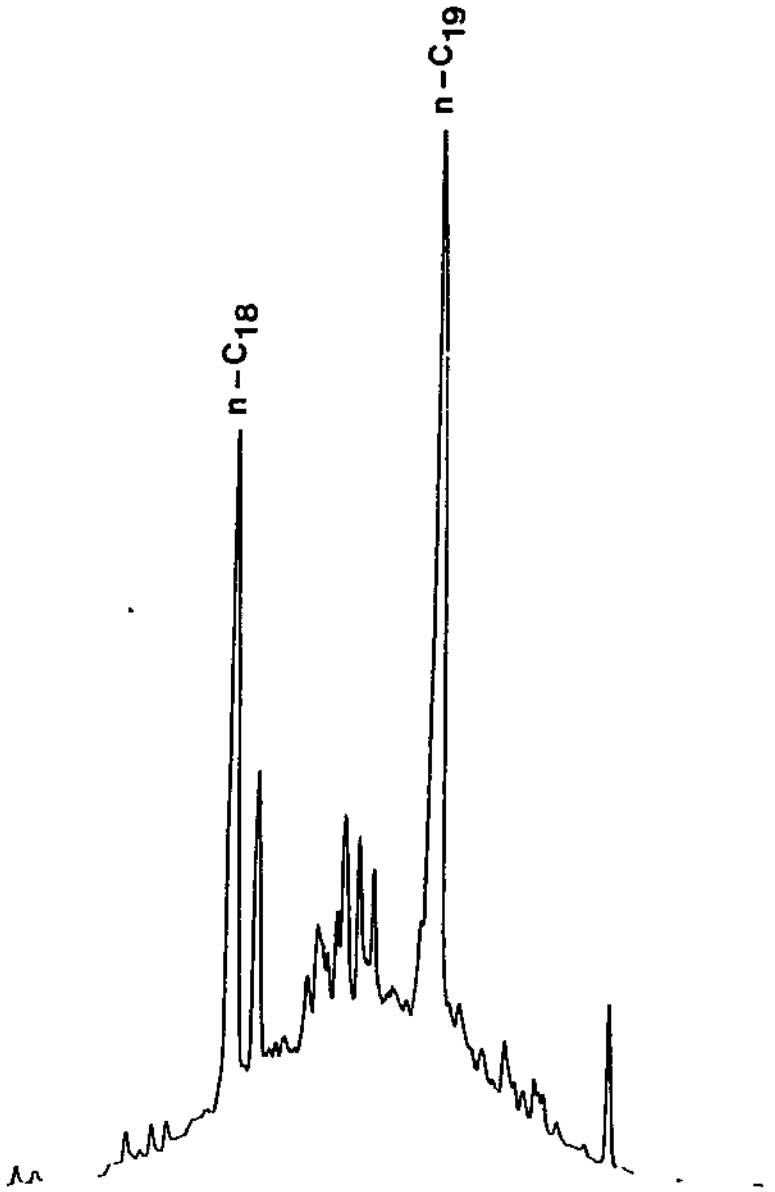

C19-FRACTION