



Classification

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Subtitle

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Title

TBP distillation of oil
34/10-7 DST no. 3

STATOIL
EXPLORATION & PRODUCTION
LABORATORY

by

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Nov-83

LAB 83.58

Prepared

11/11-83

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16/11-83

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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 34/10-7 DST no. 3. The distillation is carried out by West Lab A/S (C_{20}) and Statoil ($C_{20} - C_{30}$).

The sample was fractionated from room temperature to 153.1 °C at atmospheric pressure, from 72.7 °C to 205.8 °C at 26.6 mbar reduced pressure and from 161.4 °C to 241.6 °C at 2.66 mbar reduced pressure.

Table 1. Summary of some essential data of oil 34/10-7 DST no.3

	Oil	C10+	C20+	C30+
Density (15°C, g x cm ⁻³)	0.826*	0.868	0.905	0.935
Molecular weight	191*	270	447	612
% by weight of total sample	100	78.822	41.221	23.661
Pour point (°C)	-24			

* Average of calculated values using C_{10+} , C_{20+} and C_{30+} densities and molecular weights.

2. EXPERIMENTAL

2.1 Distillation

The TBP distillation below C_{20} 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 cm³ protruded metal (15 theoretical plates). From C_{20} to C_{30} a Fisher HMS 500 distillation apparatus with Spaltrohr-column was used.

Fractions were collected according to corrected boiling point ranges between successive n-alkanes as given by Katz and Firoozabadi (Journ. Petr. Tech., Nov 1978,1650). The light end fractions ($< C_{10}$) were separated at atmospheric pressure, C_{10} - C_{20} fractions at 26.6 mbar and C_{20} - C_{30} -fractions at 2.66 mbar.

2.2 Gas chromatographic analysis

Single component analysis was performed on all light end fractions ($< C_{10}$). Fractions C_{10} - C_{29} 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 μ m.

Column for liquid fractions: Chrompack WCOT, C_p sil 5 on fused silica, 25 m x 0.22 mm i.d., filmthickness 0,14 μ m

Carrier gas: Helium (99.995%), 22 cm/sek linear velocity 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 - 0.4 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.
 C₆ - C₁₁ : 10°C 4 min, 4°/min to 300°C
 C₁₂ - C₂₀: 100°C 4 min, 4°/min to 300°C
 C₂₁ - C₂₅: 150°C 4 min, 4°/min to 300°C
 C₂₆ - C₂₉: 200°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 reference substance. The cryoscope was calibrated with tetradecane (n - C₁₄).

Densities were measured using a Paar DMA 46 frequency densiometer thermostatted at 15°C. The C₂₀ - C₃₀₊ -fractions were very viscous. These were therefore measured at 50°C. The measured densities were corrected to 15°C according to API standard 2540 (Manual of Petroleum Measurement standards, first edition, august 1980.)

2.4 Pour point measurement

The pour point of the oil was measured according to ASTM method D-97 (1980). The result was -24°C.

3.Results

Table 2 shows all compositional data from the TBP distillation and physical data of each fraction. Losses of 0.204% ($<C_{20}$) and 0.089% ($C_{20}-C_{30}$), as calculated by adding all fractions at the end of the distillation, have been added to the C_{20+} and C_{30+} -fractions respectively.

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

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

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

Table 4 gives 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 naphthenes are reported in addition to the total cuts. In this table, " C_x rest" means C_x total minus aromatics/naphthenes.

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 least 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 hydrocarbons.

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



U&P LAB
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SAK: KORREKSJON AV DESTILLASJONSDATA

Det er oppdaget noen feil i tidligere destillasjonsrapporter: LAB 81.25, LAB 83.58, LAB 84.205, og 84.206.

- LAB 81.25 "TBP-distillation of 34/10-11 DST 1" (det har her kommet ny rapport LAB 84.213).

Tetthet C_{13} skal være 0.817 g/cm^3 (s. 4).

- LAB 83.58 "TBP-distillation of 34/10-7 DST 3".
Nye molekylvekter (s. 7).

C_{10}	133
C_{11}	148
C_{12}	163
C_{13}	177
C_{14}	190
C_{15}	204
C_{16}	217
C_{17}	235
C_{18}	248
C_{19}	260

- LAB 84.205 "TBP-distillation of condensate 34/10-16 DST 2".
Ny molvekt C_{10}^+ : 206 (s. 1, 6 og 10)
Pour point er 0°C (s. 4)

- LAB 84.206 "TBP-distillation of oil 34/10-16 DST 1".
Pour point er $+24^{\circ}\text{C}$ (s. 4).

Table 2.
Data from TBP distillation of stock tank oil 34/10-7 DST 3.

Fraction	Cut point (°C, 760 mmHg)	Actual head- temp. at 26.6mbar	ρ_{15}^{153} (g.cm ⁻³)	MW	% by weight of total oil	% by weight distilled	Mole percent	% by volume of total oil
Gas		-	0.415	33.5	0.064	0.064	0.36	0.128
Cold trap	< 36.5	-	0.598	62.5	3.956	4.020	12.05	5.482
C ₆	69.2	-	0.685	82.0	2.016	6.036	4.68	2.437
C ₇	98.9	-	0.737	98.7	6.125	12.161	11.81	6.880
C ₈	126.1	-	0.754	109.6	4.606	16.767	8.00	5.061
C ₉	151.3	-	0.774	121.9	5.046	21.813	7.88	5.401
C ₁₀₊	> 151.3	-	0.868	270	78.822	100.635	55.19	76.610
C ₁₀	177.0	72.7	0.789	134.7 133	4.020	25.833	5.68	4.221
C ₁₁	200.1	91.6	0.794	150.3 142	3.953	29.786	5.10	4.122
C ₁₂	221.5	109.3	0.806	166.4 163	4.061	33.847	4.65	4.171
C ₁₃	240.0	125.0	0.819	181.4 177	3.800	37.647	4.00	3.841
C ₁₄	258.1	140.2	0.832	194.0 190	4.421	42.068	4.34	4.403
C ₁₅	275.5	154.6	0.834	209.4 204	3.765	45.833	3.42	3.722
C ₁₆	291.3	167.4	0.844	222.4 217	2.969	48.802	2.54	2.914
C ₁₇	306.9	181.3	0.841	240.9 235	3.800	52.602	3.00	3.742
C ₁₈	321.1	193.8	0.847	256.0 248	2.813	55.415	2.09	2.752
C ₁₉	334.9	205.7	0.860	268.2 260	3.364	58.779	2.39	2.238
C ₂₀₊	> 334.9	> 205.7	0.906	447	41.221	100.000	17.59	37.506
C ₂₀	344	161.4	0.874	269.4	1.155	59.894	0.79	1.056
C ₂₁	360	174.2	0.870	282.5	2.953	62.847	1.99	2.811
C ₂₂	371	182.7	0.872	297.7	2.061	64.908	1.32	1.957
C ₂₃	382	191.4	0.875	310.1	1.797	66.705	1.10	1.700
C ₂₄	392	199.3	0.877	321.8	1.421	68.126	0.84	1.341
C ₂₅	403	209.2	0.881	332.4	2.083	70.209	1.20	1.958
C ₂₆	415	218.9	0.886	351.1	1.781	71.990	0.96	1.664
C ₂₇	425	227.0	0.888	370.8	1.494	73.484	0.76	1.393
C ₂₈	433	234.5	0.895	381.6	1.625	75.109	0.81	1.504
C ₂₉	442	241.6	0.898	393.7	1.233	76.342	0.59	1.137
C ₃₀₊	> 442	> 241.6	0.935	612	23.661	100.003	7.28	20.950

Recovery : 99.707% (added to C₂₀₊)
Loss below C₂₀ : 0.204% (added to C₂₀₊)
Loss C₂₀-C₃₀ : 0.089% (added to C₂₀₊)

Table 3.

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

$S = \text{Cumulative weight/cumulative volume}$

Fraction	Cum. weight	Cum. volume	S	% by volume distilled
Gas	2.02	4.86	0.416	0.128
Cold trap	126.2	212.7	0.593	5.610
C ₆	189.5	305.1	0.621	8.047
C ₇	381.8	565.9	0.675	14.927
C ₈	526.4	757.7	0.695	19.988
C ₉	684.8	962.5	0.711	25.389
C ₁₀	811.0	1122.5	0.722	29.610
C ₁₁	935.1	1278.8	0.731	33.732
C ₁₂	1062.6	1436.9	0.740	37.903
C ₁₃	1181.9	1582.5	0.747	41.744
C ₁₄	1320.7	1749.4	0.755	46.147
C ₁₅	1438.9	1890.5	0.761	49.869
C ₁₆	1532.1	2001.0	0.766	52.783
C ₁₇	1651.4	2142.8	0.771	56.525
C ₁₈	1739.7	2247.1	0.774	59.277
C ₁₉	1845.3	2369.9	0.779	62.515
C ₂₀	1880.3	2404.9	0.782	63.571
C ₂₁	1973.0	2516.5	0.784	66.382
C ₂₂	2037.7	2590.7	0.787	68.339
C ₂₃	2094.1	2655.1	0.789	70.039
C ₂₄	2138.7	2705.9	0.790	71.380
C ₂₅	2204.1	2780.2	0.793	73.338
C ₂₆	2260.0	2843.3	0.795	75.002
C ₂₇	2306.9	2896.1	0.797	76.395
C ₂₈	2357.9	2953.1	0.798	77.899
C ₂₉	2396.6	2996.2	0.800	79.036

Table 4.

Measured and calculated molecular weights and densities of oil
34/10-7. DST no.3.

	Oil	C ₁₀	C ₂₀ ⁺	C ₃₀ ⁺
Measured MW	203	270	447	612
Calculated MW using C ₁₀ ⁺ MW	190			
Calculated MW using C ₂₀ ⁺ MW	191	274		
Calculated MW using C ₃₀ ⁺ MW	191	274	443	
Measured density	0.831	0.868	0.905	0.935
Calculated density using C ₁₀ ⁺ density	0.823			
Calculated density using C ₂₀ ⁺ density	0.826	0.872		
Calculated density using C ₃₀ ⁺ density	0.828	0.875	0.911	

Table 5.

Weight distribution and % overlap between uncorrected fractions of 34/10-7 DST 3.

Fraction	% by weight of total oil	% by weight overlap between fractions*
Gas	0.064	
Cold trap	3.956	
C ₆	2.061	14.4 : 62.2 : 23.4
C ₇	6.125	3.6 : 65.6 : 30.8
C ₈	4.606	5.9 : 76.2 : 18.0
C ₉	5.046	10.6 : 71.0 : 18.4
C ₁₀	4.020	13 : 75 : 12
C ₁₁	3.953	15 : 75 : 10
C ₁₂	4.061	13 : 68 : 19
C ₁₃	3.800	15 : 73 : 12
C ₁₄	4.421	14 : 72 : 14
C ₁₅	3.765	14 : 71 : 15
C ₁₆	2.969	18 : 70 : 12
C ₁₇	3.800	16 : 62 : 22
C ₁₈	2.813	15 : 66 : 19
C ₁₉	3.364	16 : 69 : 15
C ₂₀	1.115	17 : 71 : 12
C ₂₁	2.953	21 : 55 : 24
C ₂₂	2.061	17 : 61 : 22
C ₂₃	1.797	24 : 59 : 17
C ₂₄	1.421	27 : 59 : 14
C ₂₅	2.083	34 : 51 : 15
C ₂₆	1.781	19 : 67 : 14
C ₂₇	1.494	15 : 59 : 26
C ₂₈	1.625	20 : 54 : 26
C ₂₉	1.233	15 : 49 : 36

* 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 (based on GC-composition). The compounds and fractions in the table constitute 21.279 % of the total oil.

	Fraction overlap	MW	Wt% of fraction	Wt% of total oil	Mole% of total oil	ρ_{15}
Methane	-	16.04	0.305	0.012	0.14	
Ethane	-	30.07	1.296	0.051	0.32	0.3580
Propane	-	44.10	11.105	0.437	1.89	0.5076
i-butane	-	58.12	8.513	0.335	1.10	0.5633
n-butane	-	58.12	28.818	1.134	3.72	0.5847
2,2-dimethylpropane	-	72.15	0.178	0.007	0.02	0.5967
i-pentane	-	72.15	20.584	1.810	2.14	0.6246
n-pentane	-	72.15	29.199	1.149	3.04	0.6309
C_6 total	0:100:0	84.8	100	2.171	4.88	0.668
C_6 rest		86.0	93.966	2.040	4.52	0.663
Cyclopentane		70.14	6.034	0.131	0.36	0.7502
C_7 total	0:100:0	91.6	100	4.429	9.21	0.735
C_7 rest		99.1	57.847	2.562	4.92	0.700
Methylcyclopentane		84.16	13.381	0.593	1.34	0.7534
Benzene		78.11	7.315	0.324	0.79	0.8842
Cyclohexane		84.16	21.449	0.950	2.15	0.7831
C_8 total	0:100:0	104.4	100	6.291	11.51	0.745
C_8 rest		110.3	59.806	3.754	6.48	0.711
Methylcyclohexane		98.19	26.068	1.648	3.20	0.7737
Ethylcyclopentane		98.19	1.345	0.085	0.17	0.7708
Toluene		92.14	12.781	0.804	1.66	0.8714
C_9 total	0:82.6:17.4	122.7	100	5.337	8.29	0.784
Included :						
Ethylcyclohexane*		112	10.268	0.548	0.93	0.7819
Ethylbenzene*		106	4.235	0.226	0.41	0.8714
m+p-xylene*		106	13.547	0.723	1.30	0.8668
o-xylene*		106	8.563	0.457	0.82	0.8844

* Additional contribution from fraction C_{10} : Ethylcyclohexane 0.034%, ethylbenzene 0.040%, m+p-xylene 0.054% and o-xylene 0.031%.

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

Table 7.

Characteristic isoprenoid hydrocarbon ratios of oil 34/10-7 DST 3

	Ratio*
C ₁₇ /pristane	0.19
C ₁₈ /phytane	0.21
Pristane/phytane	1.41

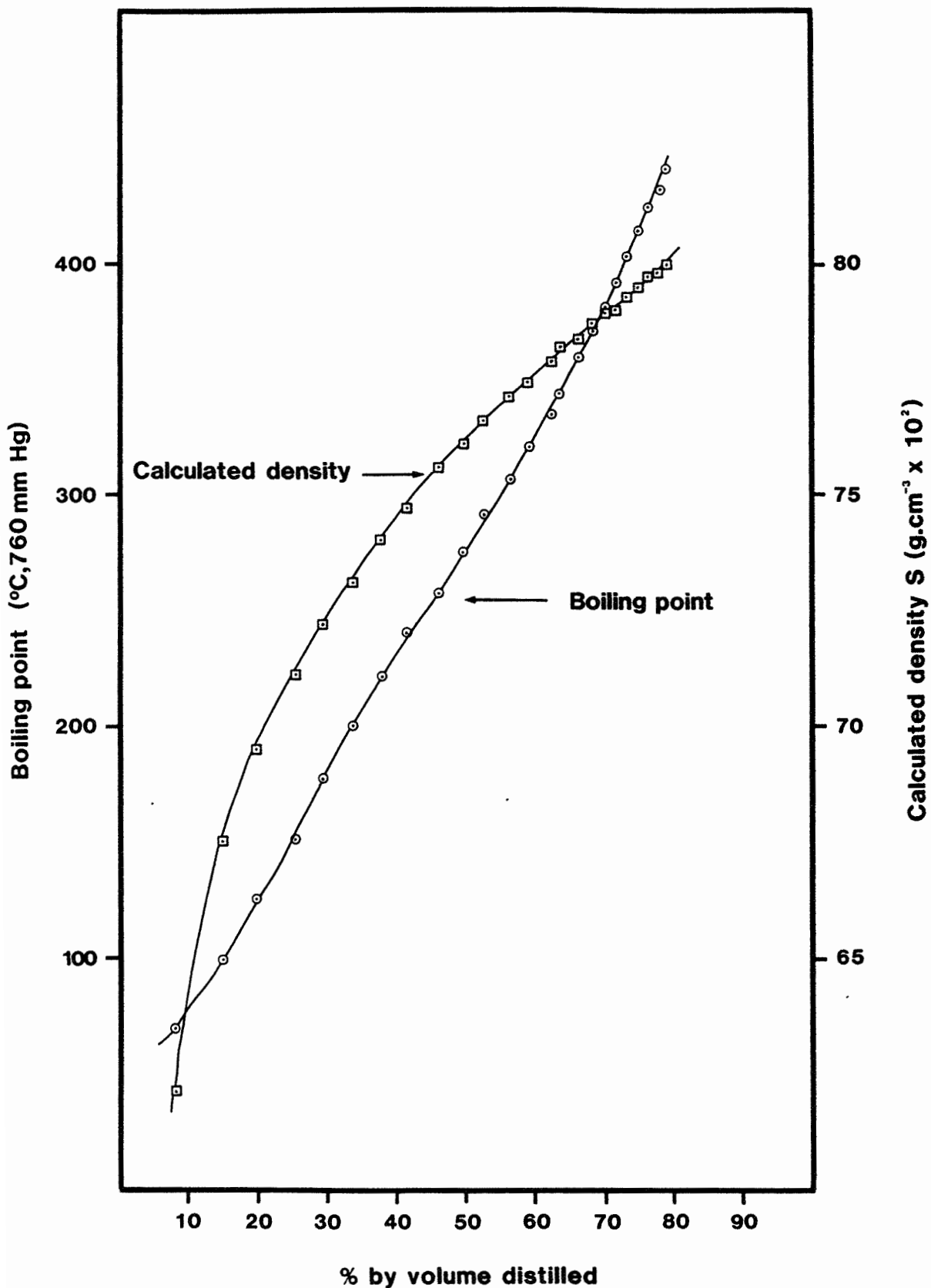
* Peak height ratio from GC.

Table 8.

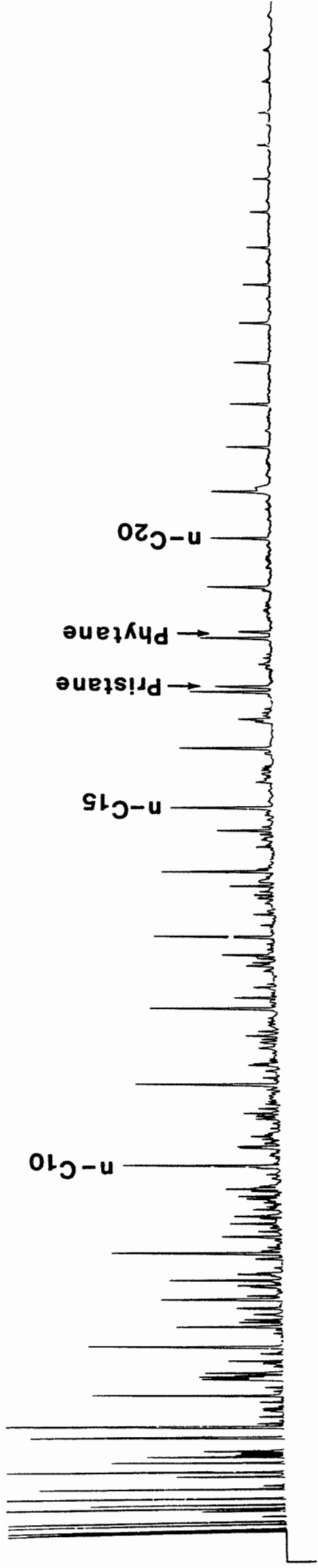
PNA-distribution of light end fractions (% by weight).

Fraction	Paraffines	Naphtenes	Aromatics
C ₆	94.0	6.0	0
C ₇	46.1	46.6	7.3
C ₈	40.3	46.9	12.8
C ₉	43.0	25.9	31.1

Fig.1 TBP - and density-profiles for oil 34/10-7 DST no. 3

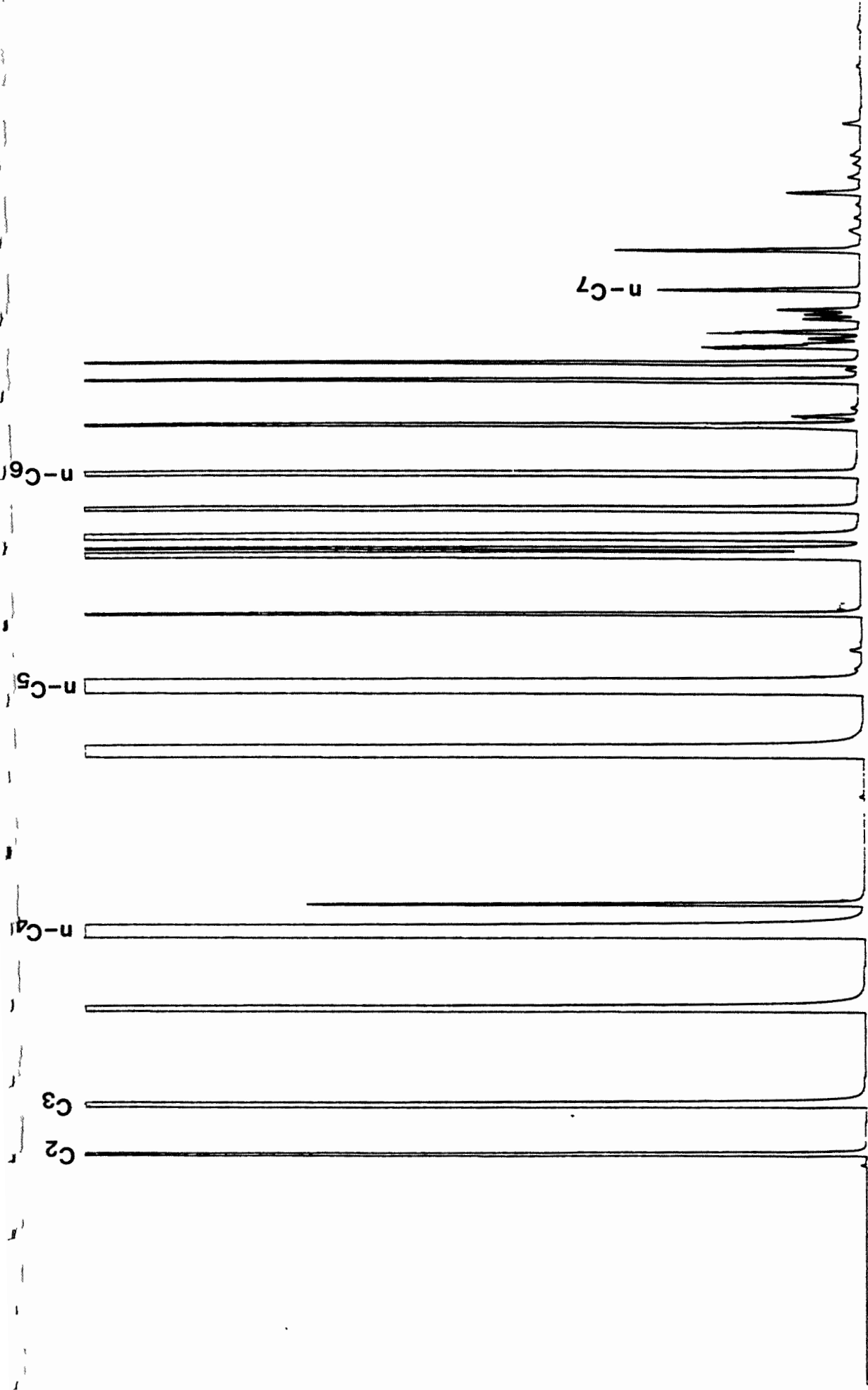


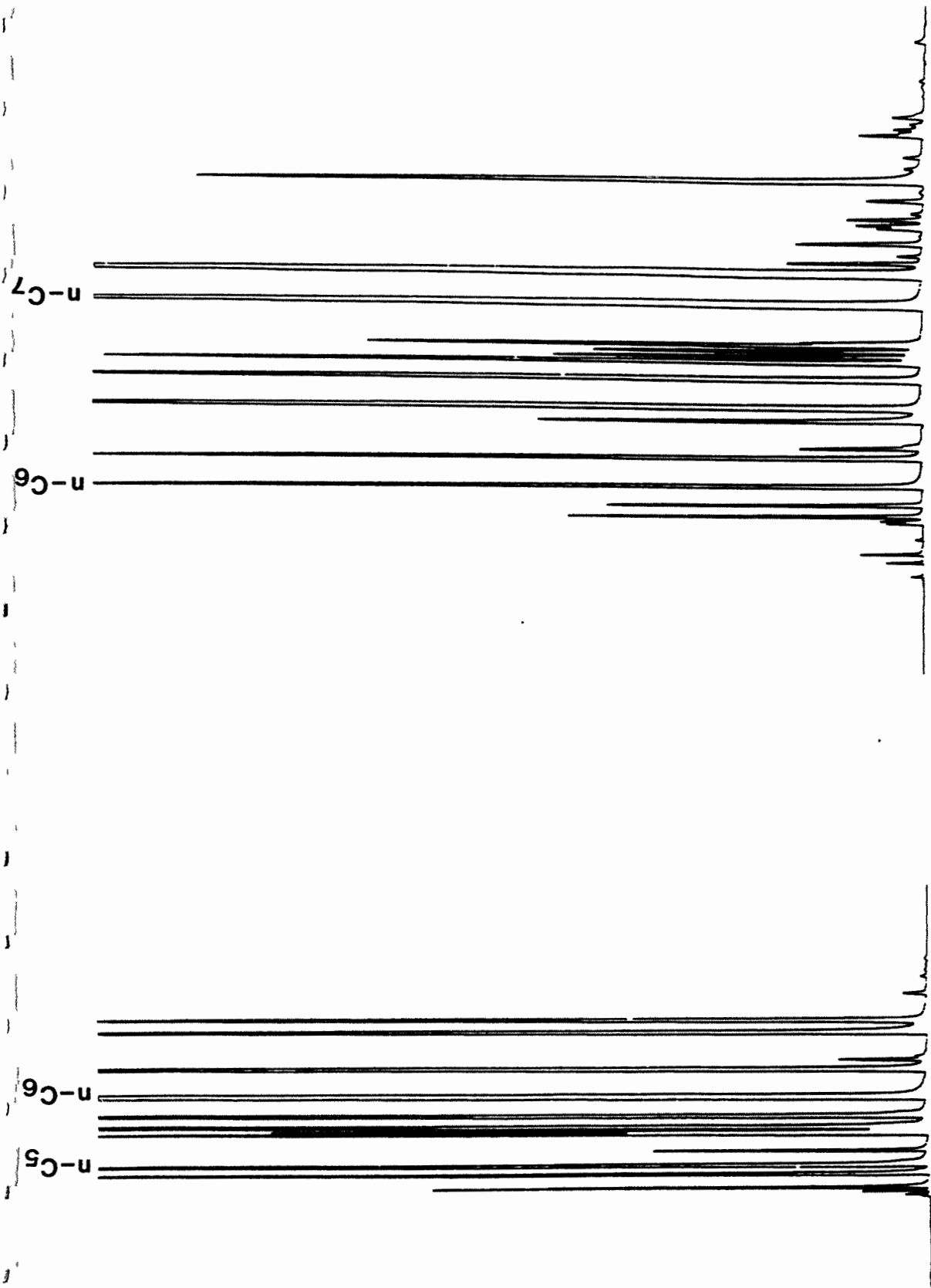
**APPENDIX
GAS CHROMATOGRAMS**



OIL 34/10-7 DST 3

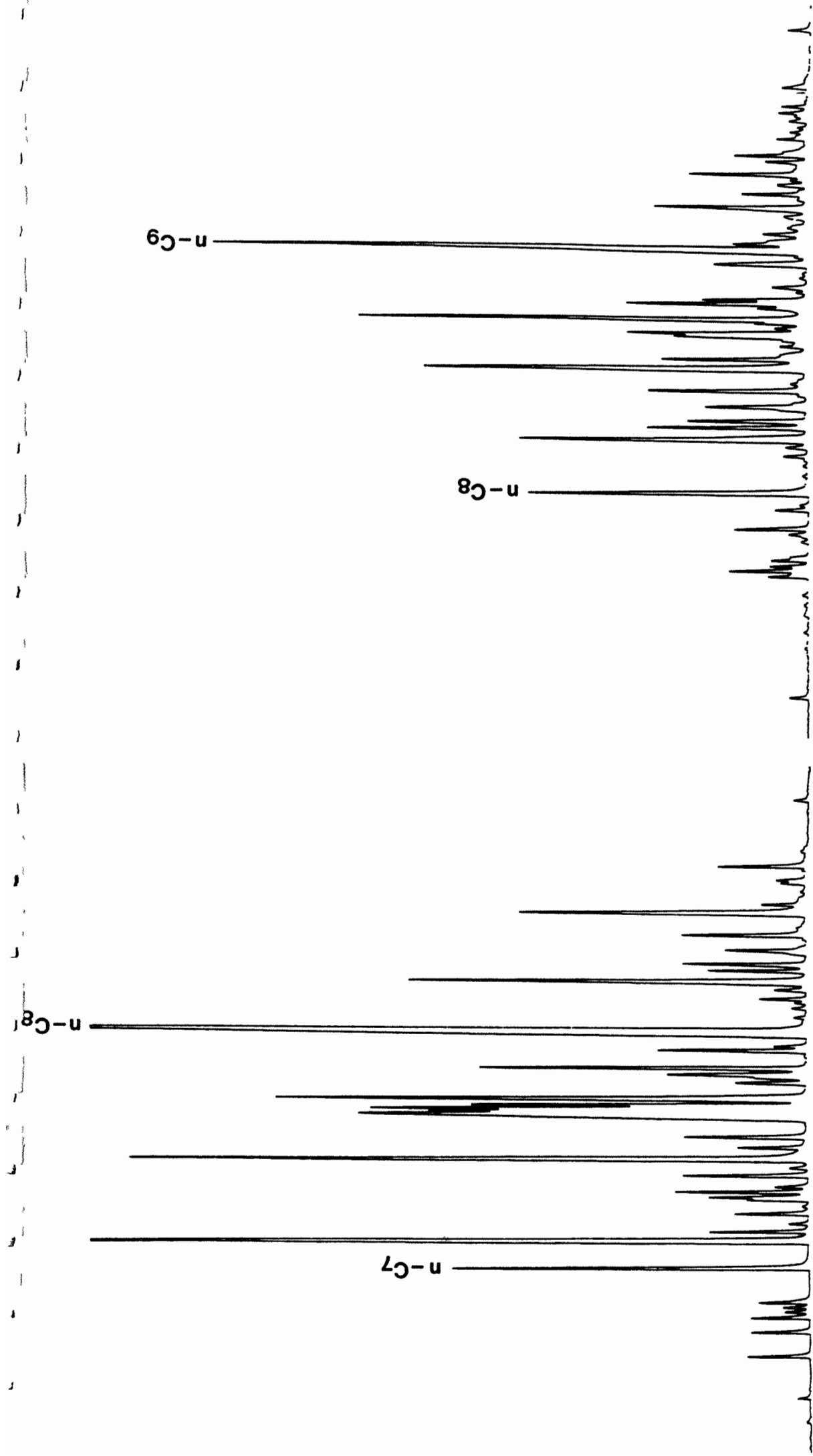
COLD TRAP-FRACTION





C6-FRACTION

C7-FRACTION



C9-FRACTION

C8-FRACTION

n-C₁₁

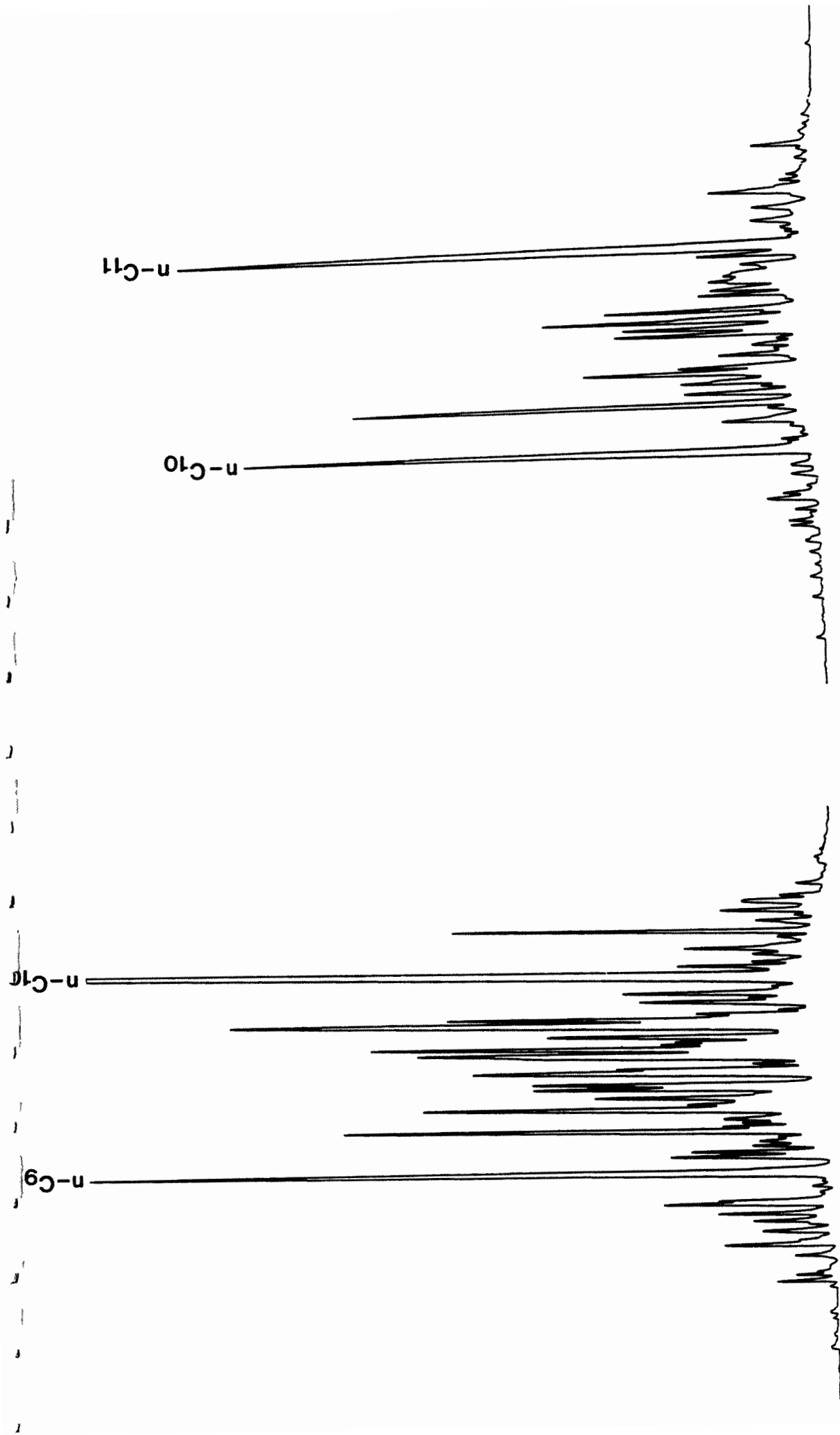
n-C₁₀

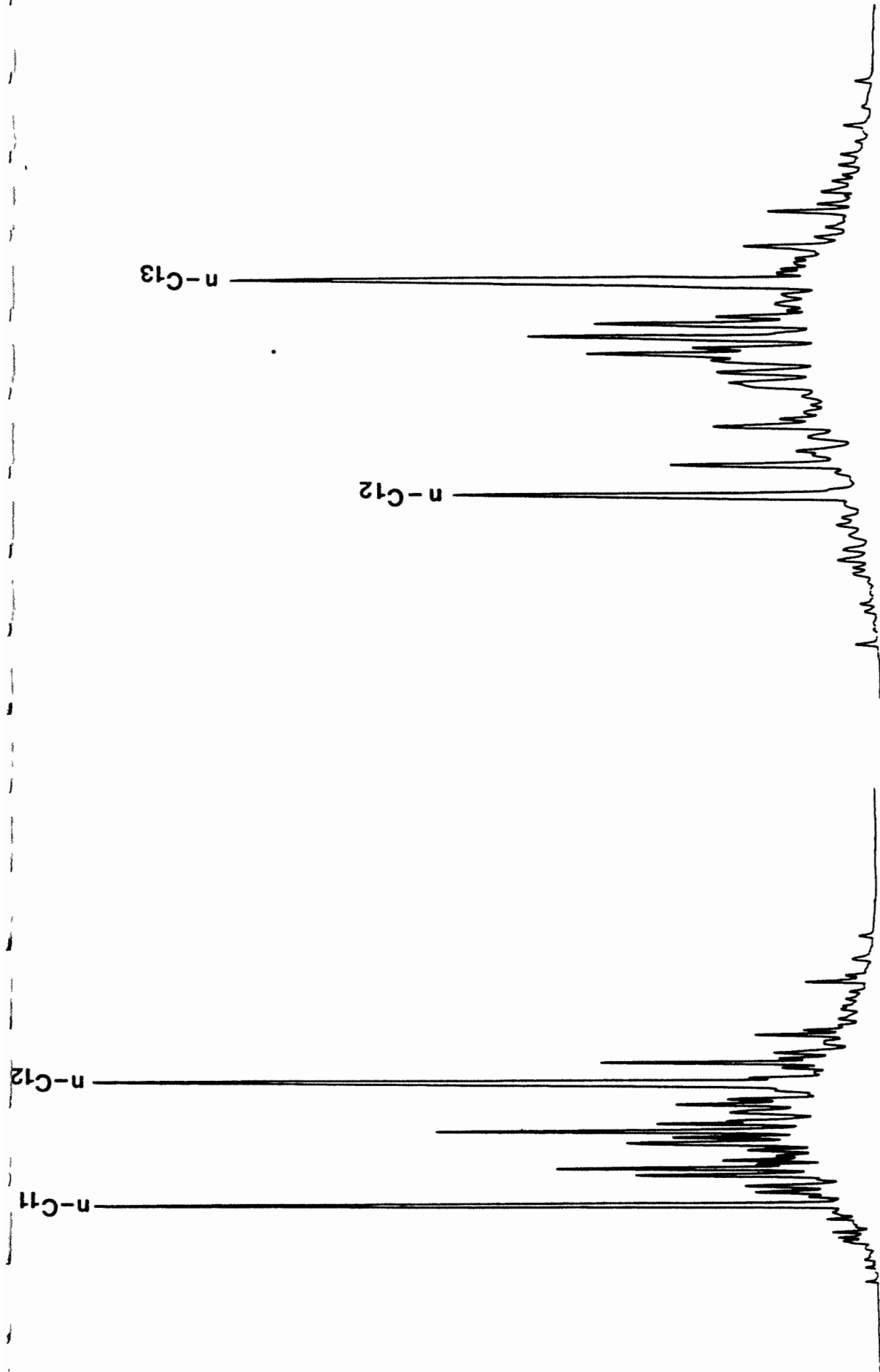
n-C₁₀

n-C₉

C11-FRACTION

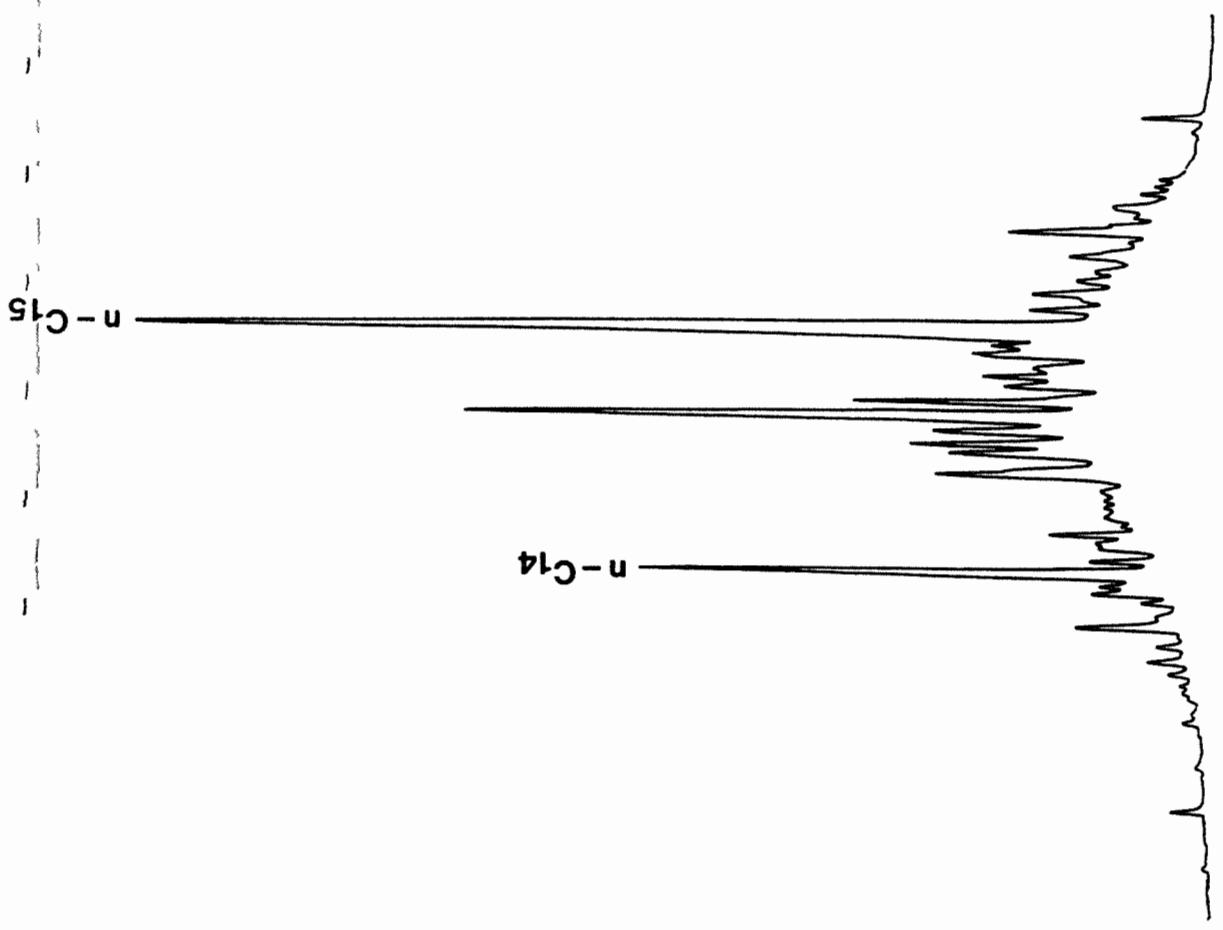
C10-FRACTION



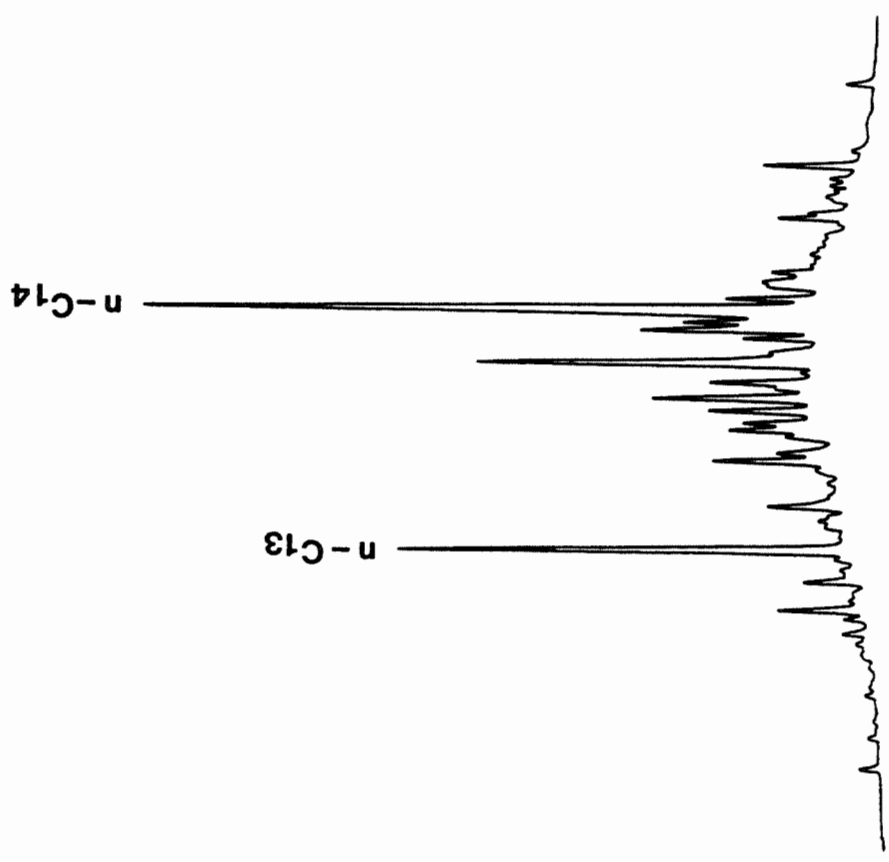


C13-FRACTION

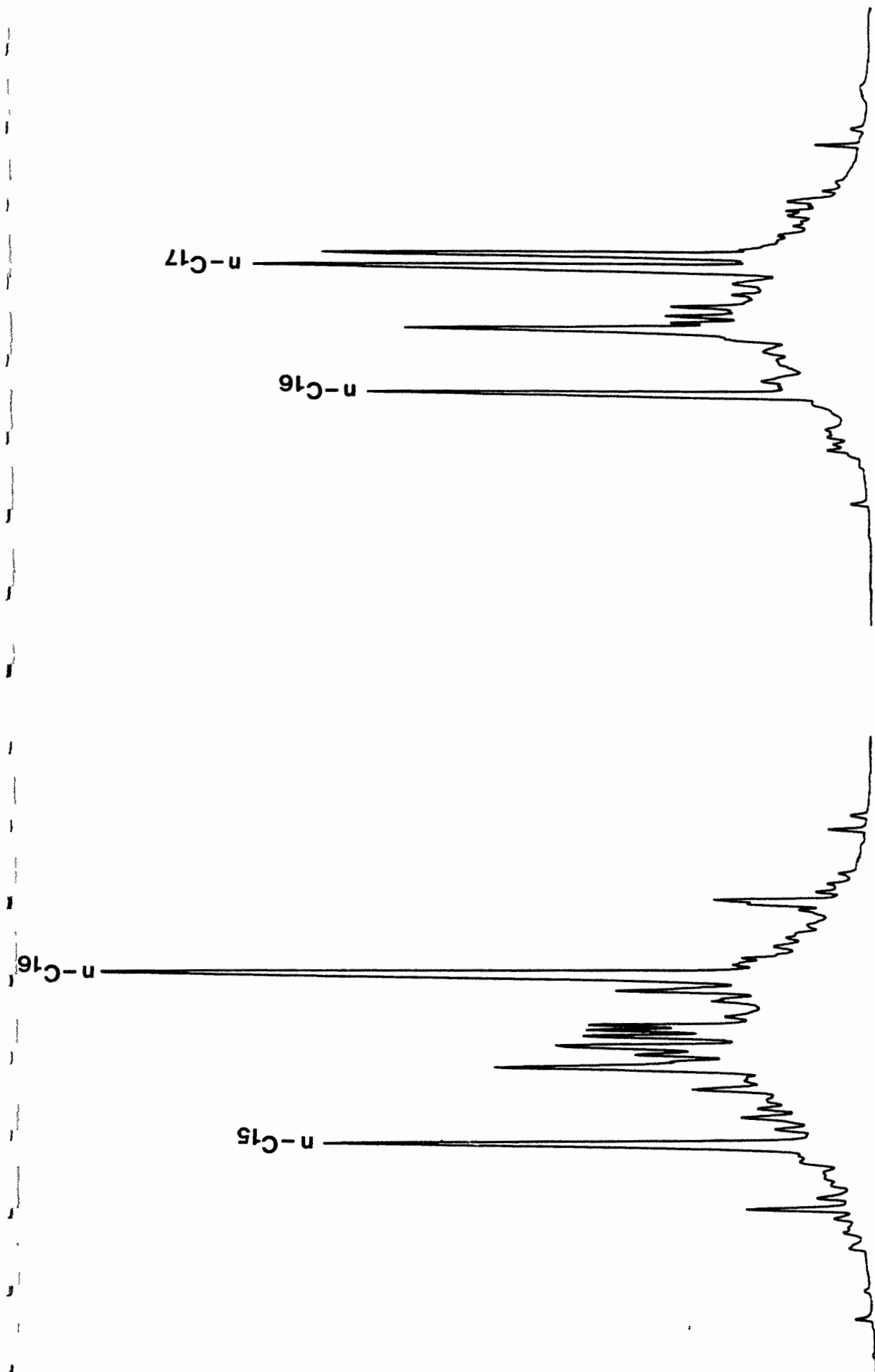
C12-FRACTION



C15-FRACTION

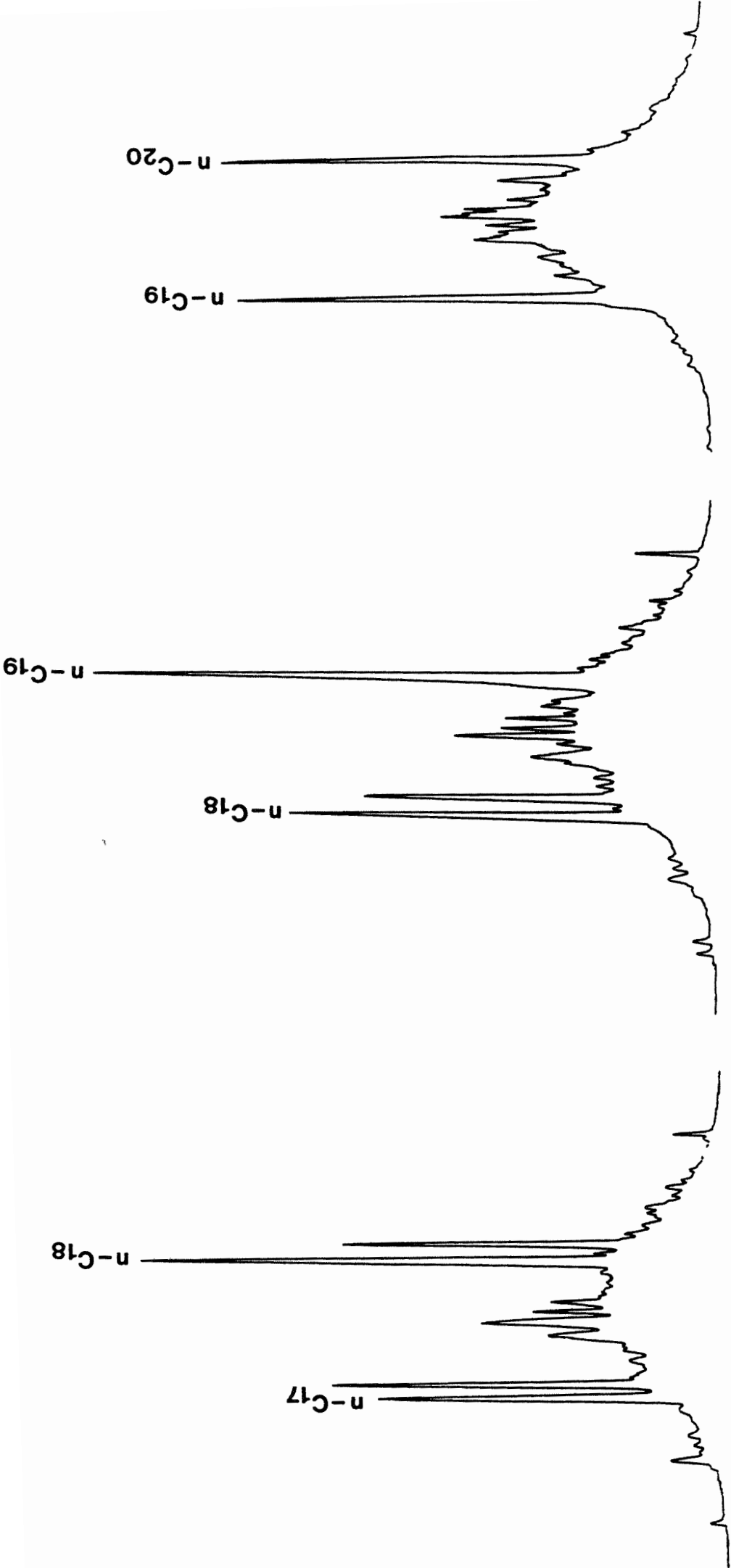


C14-FRACTION



C17-FRACTION

C16-FRACTION



C20-FRACTION

C19-FRACTION

C18-FRACTION

n-C₂₃

n-C₂₂

n-C₂₂

n-C₂₁

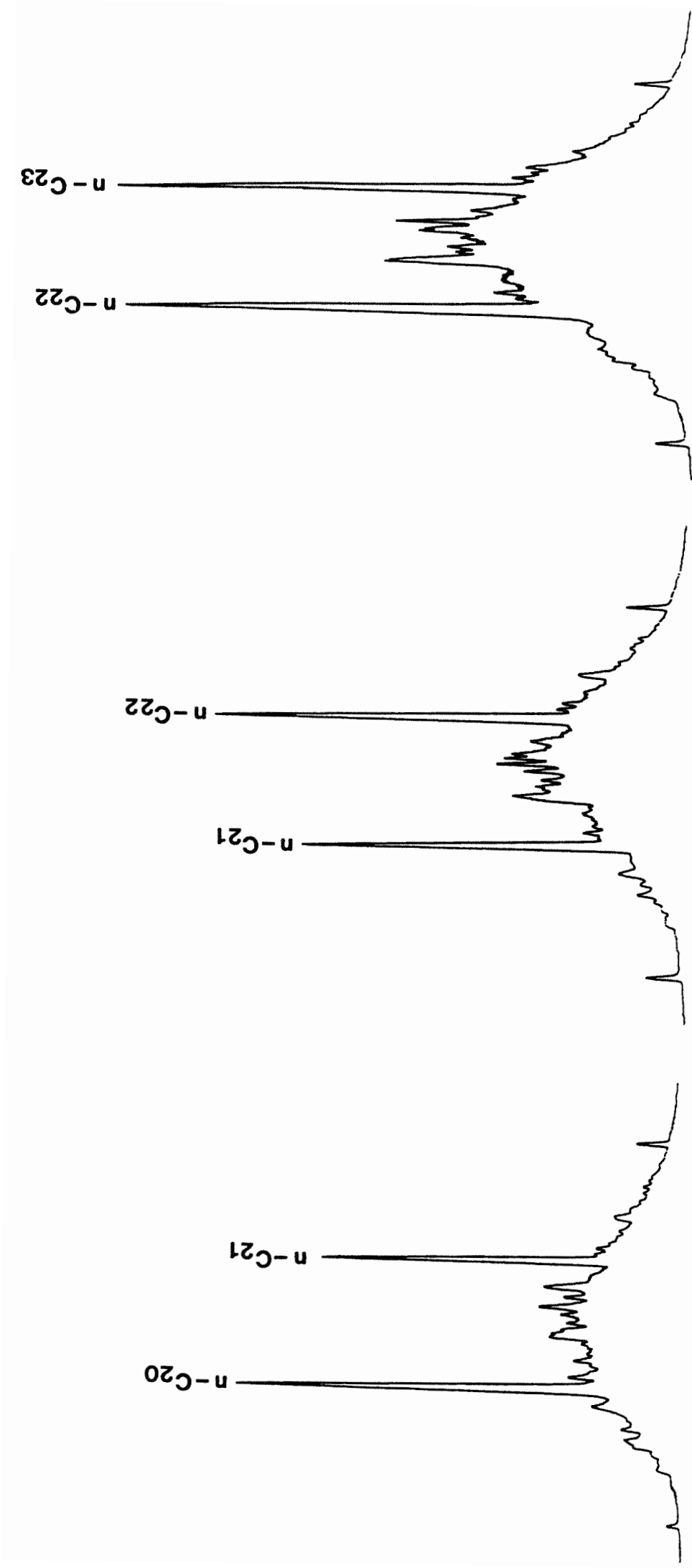
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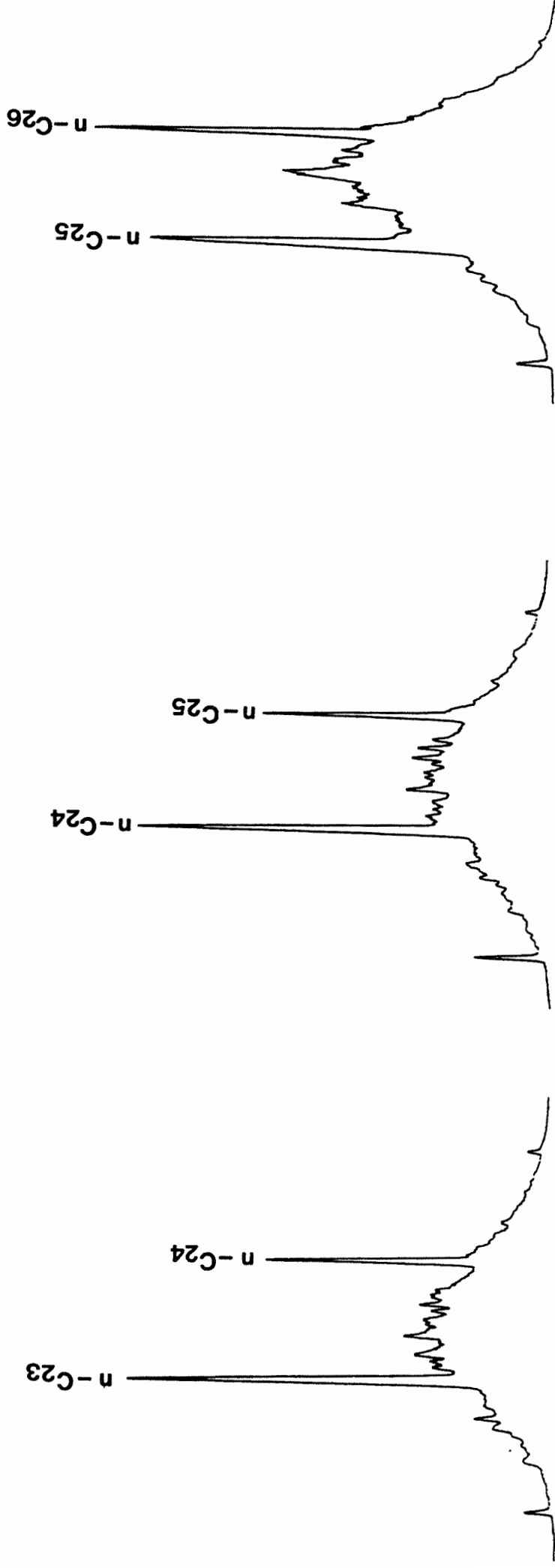
n-C₂₀

C21-FRACTION

C22-FRACTION

C23-FRACTION

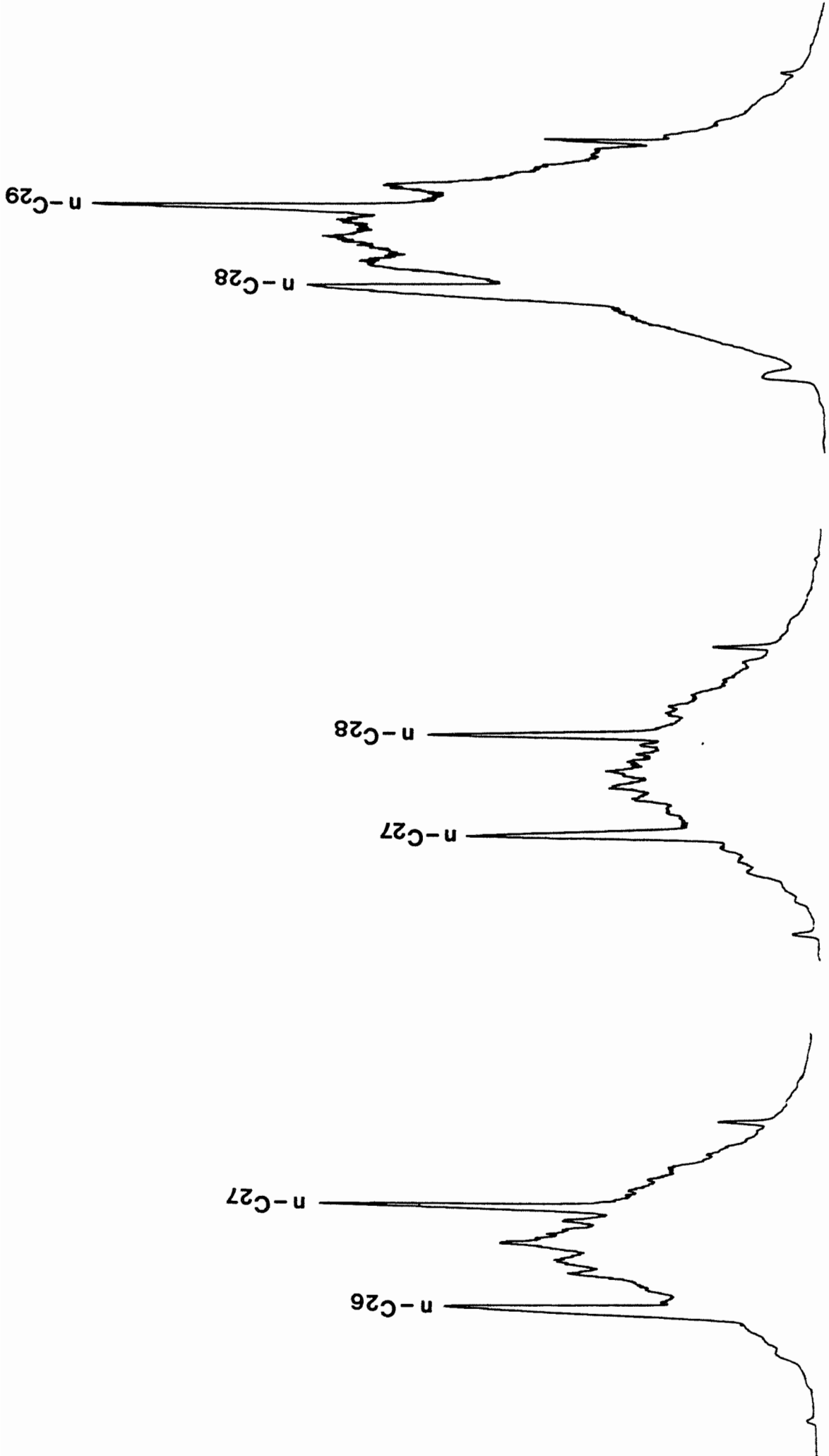




C24-FRACTION

C25-FRACTION

C26-FRACTION



C27-FRACTION

C28-FRACTION

C29-FRACTION