

statoil

TBP distillation of oil
from 6407/1-3 DST no. 1

STATOIL
EXPLORATION & PRODUCTION
LABORATORY

by
Hans Petter Rønningsen

March-84

LAB 84

Den norske stats oljeselskap a.s



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Requested by

Jon Hanstveit

Subtitle

Co-workers

Arvid Osvåg, Antonious Henneman (West Lab),
Liv Tau

Title

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Prepared

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Hans Petter Rønningsen
Hans Petter Rønningsen

Approved

9/4-84

Didrik Malthe-Sørensen

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1. INTRODUCTION AND SUMMARY

This report presents the results from a true boiling point distillation, performed on a 4139 ml sample of stock tank oil from 6407/1-3 DST 1, by West LAB A/S.

The sample was fractionated from room temperature to 151.3°C at atmospheric pressure and from 175.5°C to 332.6°C at 26.6 mbar reduced pressure. The cut point temperatures according to Katz and Firoozabadi (Journ. Petr. Tech., Nov.-78, 1650) of fractions above C₁₀ had to be corrected by 0-2.9 degrees to obtain reasonably balanced n-alkane to n-alkane cuts.

Table 1. Summary of some essential data of oil
6407/1-3 DST 1

	Oil	C ₁₀ ⁺	C ₂₀ ⁺
Density (15°C, g/cm ³)	0.875	0.891	0.922
Molecular weight (g/mole)	261	314	446
% by weight of total sample	100	89.982	60.569

2. EXPERIMENTAL

2.1 Distillation

The TBP distillation was performed according to ASTM D-2892 using a Kontes Martin MK IV-B fractionator system with a 24½ inches x 25 mm i.d packed column (15 theoretical plates).

Fractions were collected according to the boiling point ranges between successive n-alkanes as given by Katz and Firoozabadi. The light end fractions ($<C_{10}$) were separated at atmospheric pressure, the $C_{10} - C_{19}^+$ 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 (gas to C9), using a Hewlett Packard 5880 gas chromatographic system.

Column for gas and cold trap fractions	:	Chrompack WCOT Cp sil 5 on fused silica, 50 m x 0.23 mm i.d. filmthickness 0.3 μ m.
Column for liquid fractions	:	Chrompack WCOT Cp sil 5 on fused silica, 25 m x 0.22 mm i.d., filmthickness 0.14 μ m.
Carrier gas	:	Helium, 23 cm/sec linear velocity at 50°C.
Detector	:	Flame ionisation, nitrogen make-up gas, temp. 320°C

- Injection : All glass splitter, with a packed "Jennings tube". Split ratio 1:100, temp. 310°C (liquid fractions) and 200°C (gas). 0.1 - 0.2 μ l liquid samples injected, 0.5 ml gas and cold trap fractions.
- Temp. programs : Gas and cold temp:
-30°C isothermal 4 min, then 8°/min to 160°C.
C₆-C₁₀: -5°C 2 min, 2°/min to 40°C, 8°/min to 300°C.
- C₁₀ - C₁₉ fractions were checked for fractions overlap, using a Perkin Elmer Sigma 300/Sigma 15 system.
- Column : Chrompack WCOT Cp sil 5 CB on fused silica, filmthickness 0.11 μ m.
- Carrier gas : Helium 22 cm/sec linear velocity at 10°C.
- Detector : FID, helium make-up gas, temp. 350°C.
- Injection : Split injection with glas liner, split ratio 1:90, temp. 350°C.
- Temp. program : 10°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 ($n\text{-C}_{14}$).

Densities were measured using a Paar DMA 46 frequency densiometer thermostated at 15°C . The C_{20+} -fraction had to be measured at 50°C because of high viscosity. The measured density at 50°C was then corrected to 15°C according to API standard 2540 (Manual of Petroleum Measurement Standards, table 53A, First edition, august 1980).

3. RESULTS

Table 2 gives all compositional data from the TBP distillation and physical data of each collected fraction. A loss of 0.657 %, as calculated by adding all fractions at the end of the distillation, has been added to the C_{20+} -fraction.

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

S = cumulative weight/cumulative volume. Total % by volume distilled is also given in this table.

Table 4 gives calculated molecular weights and densities compared to measured values.

Table 5 gives the weight distribution and calculated % overlap between collected fractions. % by weight overlap is assumed to be equal to area % overlap in gas chromatograms. Response factors are not used.

Table 6 gives a more detailed composition of the light end part. All chromatograms of gas and cold trap fractions, C₆, C₇, C₈, C₉ and partly C₁₀, have been combined to calculate "ideal" fractions without overlap. Below C₆, every single compound is reported. In C₆, C₇, C₈ and C₉ some abundant aromatics and naphtenes are reported in addition to the total cuts. In this table, "C_x rest" means "C_x total" minus the reported aromatics/naphtenes.

In addition to corrected wt %'s, corrected molecular weights and densities have been calculated, assuming these properties to be additive. Weight %'s have been calculated using theoretical, relative FID response factors.

Table 7 gives characteristic ratios involving C₁₉ and C₂₀ isoprenoid hydrocarbons.

Table 8 gives PNA-distribution of corrected fractions below C₁₀, as determined by GC, using response factors.

Table 2. Data from TBP distillation of stock tank
oil 6407/1-3 DST 1.

Fraction	Cut point (C,760 mmHg)	Actual head- temp.	% by weight of total oil	% by weight distilled
Gas	-	-	0.022	0.022
Cold trap	36.5	36.5	0.795	0.817
C 6	69.2	69.2	1.595	2.413
C 7	98.9	98.9	1.645	4.058
C 8	126.1	126.1	2.918	6.977
C 9	151.3	151.3	2.835	9.812
C 10+	> 151.3	> 151.3	89.982	99.795
C 10	175.5	71.5	1.800	11.613
C 11	200.1	91.7	2.841	14.454
C 12	218.8	107.0	2.305	16.759
C 13	237.0	122.5	3.120	19.879
C 14	254.7	137.4	2.965	22.845
C 15	274.5	153.8	3.721	26.566
C 16	287.3	163.9	2.460	29.027
C 17	304.1	178.8	3.407	32.434
C 18	317.0	190.3	3.117	35.551
C 19	332.6	203.7	3.879	39.430
C 20+	> 332.6	> 203.7	60.569	100.000

Table 2 cont.

Fraction	Density (g/cm ³)	% by volume of total oil	% by volume distilled
Gas	0.536	0.036	0.036
Cold trap	0.639	1.088	1.124
C 6	0.701	1.990	3.114
C 7	0.741	1.941	5.056
C 8	0.762	3.348	8.405
C 9	0.780	3.178	11.584
C 10+	0.891	88.306	99.891
C 10	0.795	1.980	13.564
C 11	0.801	3.101	16.665
C 12	0.815	2.473	19.139
C 13	0.828	3.294	22.434
C 14	0.838	3.094	25.528
C 15	0.845	3.851	29.379
C 16	0.853	2.521	31.901
C 17	0.848	3.513	35.414
C 18	0.851	3.202	38.617
C 19	0.861	3.939	42.557
C 20+	0.922	57.442	100.000

Table 2 cont.

Fraction	Molecular weight	Mole%	Cumulative mole%
Gas	50	0.11	0.11
Cold trap	68	3.00	3.12
C 6	81	5.06	8.18
C 7	93	4.54	12.73
C 8	104	7.21	19.94
C 9	121	6.02	25.97
C 10+	314	73.67	99.65
C 10	134	3.45	29.42
C 11	149	4.90	34.33
C 12	164	3.61	37.94
C 13	176	4.55	42.50
C 14	188	4.05	46.55
C 15	203	4.71	51.27
C 16	214	2.95	54.22
C 17	232	3.77	58.00
C 18	248	3.23	61.23
C 19	259	3.85	65.08
C 20+	446	34.91	100.00

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

$$S = \text{Cum. weight/cum. volume}$$

Fraction	Cum. weight	Cum. volume	S	% by volume distilled
Gas	0.800	1.492	0.536	0.036
Cold trap	29.600	46.563	0.635	1.124
C 6	87.400	129.017	0.677	3.114
C 7	147.000	209.448	0.701	5.056
C 8	252.700	348.162	0.725	8.405
C 9	355.400	479.829	0.740	11.584
C 10	420.600	561.842	0.748	13.564
C 11	523.500	690.306	0.758	16.665
C 12	607.000	792.760	0.765	19.139
C 13	720.000	929.233	0.774	22.434
C 14	827.400	1057.400	0.782	25.528
C 15	962.200	1216.920	0.790	29.379
C 16	1051.300	1321.380	0.795	31.901
C 17	1174.700	1466.900	0.800	35.414
C 18	1287.600	1599.560	0.804	38.617
C 19	1428.100	1762.750	0.810	42.557

Table 4. Measured and calculated molecular weights and densities of oil 6407/1-3 DST 1.

	Oil	C 10+	C 20+
Measured MW	261	314	446
Calculated MW using C10+ MW	257		
Calculated MW using C20+ MW	257	313	
Measured density	0.875	0.891	0.922
Calculated density using C10+ density	0.873		
Calculated density using C20+ density	0.874	0.891	

Table 5. Weight distribution and % by weight overlap between uncorrected fractions of oil 6407/1-3 DST 1.

Fraction	% by weight of total oil	% by weight overlap between fractions *		
Gas	0.022		-	
Cold trap	0.795		-	
C 6	1.595	13	: 52	: 35
C 7	1.645	1	: 80	: 19
C 8	2.918	8	: 89	: 3
C 9	2.835	5	: 83	: 12
C 10	1.800	5	: 88	: 7
C 11	2.841	18	: 74	: 8
C 12	2.305	13	: 79	: 8
C 13	3.120	13	: 77	: 10
C 14	2.965	13	: 77	: 10
C 15	3.721	18	: 73	: 9
C 16	2.460	12	: 78	: 10
C 17	3.407	19	: 66	: 15
C 18	3.117	18	: 71	: 11
C 19	3.879	21	: 69	: 10

* Calculated on basis of area% from GC-reports
(respons factors have not been used)

Table 6. Total composition and physical properties of gas, light end fractions (< C10) and C10+, as determined by GC.

Compound/ fraction	Wt% of total oil	Wt% of fraction	MW	Mole% of total oil	Density
Methane	0.000	-	16.0	0.000	-
Ethane	0.001	-	30.1	0.013	0.358
Propane	0.028	-	44.4	0.149	0.508
i-butane	0.051	-	58.1	0.205	0.563
n-butane	0.217	-	58.1	0.865	0.585
2,2-dimethyl- propane	0.001	-	72.2	0.006	0.597
i-pentane	0.242	-	72.2	0.777	0.625
n-pentane	0.424	-	72.2	1.358	0.631
C6 total	0.945	100.000	84.6	2.582	0.669
C6 rest	0.870	92.063	86.1	2.333	0.720
Cyclopentane	0.075	7.937	70.1	0.248	0.750
C7 total	2.115	100.000	90.5	5.403	0.745
C7 rest	1.085	51.300	99.7	2.514	0.701
Methylcyclo- pentane	0.306	14.468	84.2	0.841	0.753
Benzene	0.274	12.955	78.1	0.813	0.884
Cyclohexane	0.449	21.229	84.2	1.233	0.783
C8 total	2.815	100.000	104.4	6.231	0.760
C8 rest	1.511	53.677	113.7	3.071	0.720
Methylcyclo- hexane	0.669	23.766	98.2	1.575	0.774
Ethylcyclo- pentane	0.059	2.096	98.2	0.140	0.771
Toluene	0.575	20.426	92.1	1.443	0.871
C9 total	2.585	100.000	119.4	5.003	0.772
C9 rest	1.652	63.907	127.4	2.997	0.735
Ethylcyclo- hexane	0.214	8.279	112.2	0.442	0.782
Ethylbenzene	0.217	8.395	106.2	0.474	0.871
m+p-xylene	0.354	13.694	106.2	0.771	0.867
o-xylene	0.145	5.609	106.2	0.316	0.884
C10	2.420	100.000	131.3	4.259	0.800
C10+	90.602	100.000	310.7	67.394	0.890

Table 7. Characteristic isoprenoid hydrocarbon ratios
of oil 6407/1-3 DST 1. *

	Ratio
n-C 17/pristane	1.27
n-C 18/phytane	1.34
Pristane/phytane	1.16

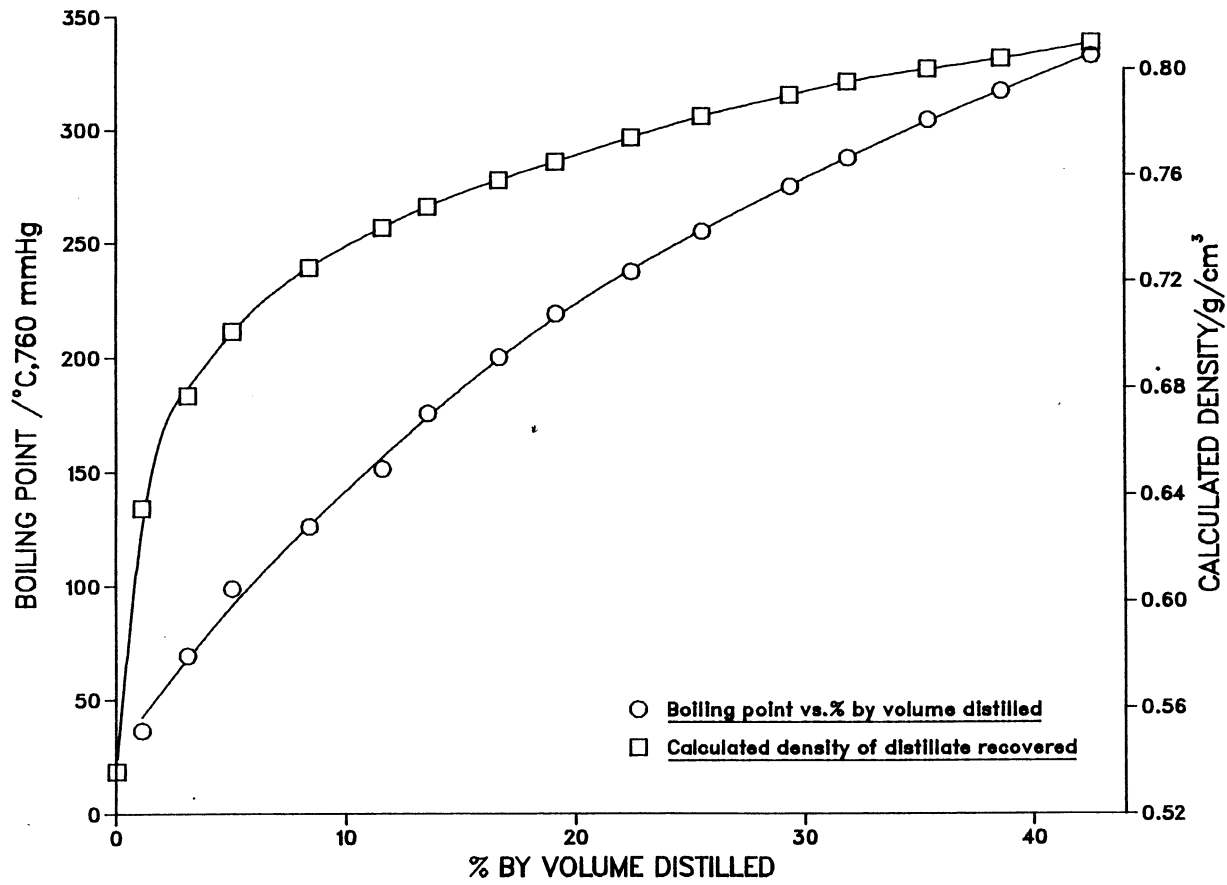
* Peak height ratio from GC.

Table 8. PNA-distribution of corrected light end
fractions (% by weight).

Fraction	Paraffines	Naphtenes	Aromatics
C 6	92.0	7.9	0.0
C 7	40.1	46.8	12.9
C 8	39.8	39.7	20.4
C 9	49.2	22.9	27.7

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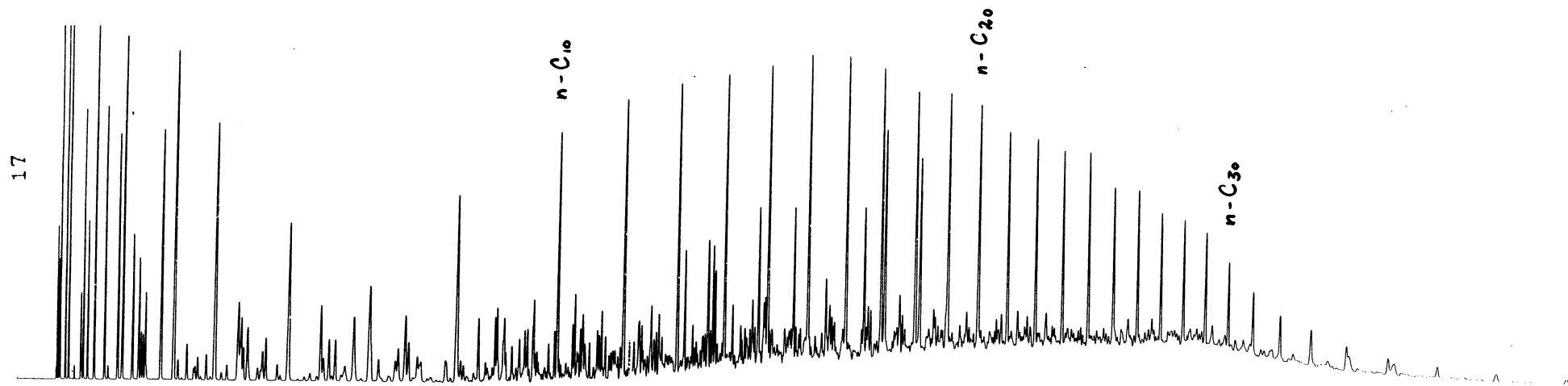
Fig 1. TBP- and density-profiles:
Oil 6407/1-3,DST 1.



APPENDIX

GAS CHROMATOGRAMS

6407/1-3 DST 1

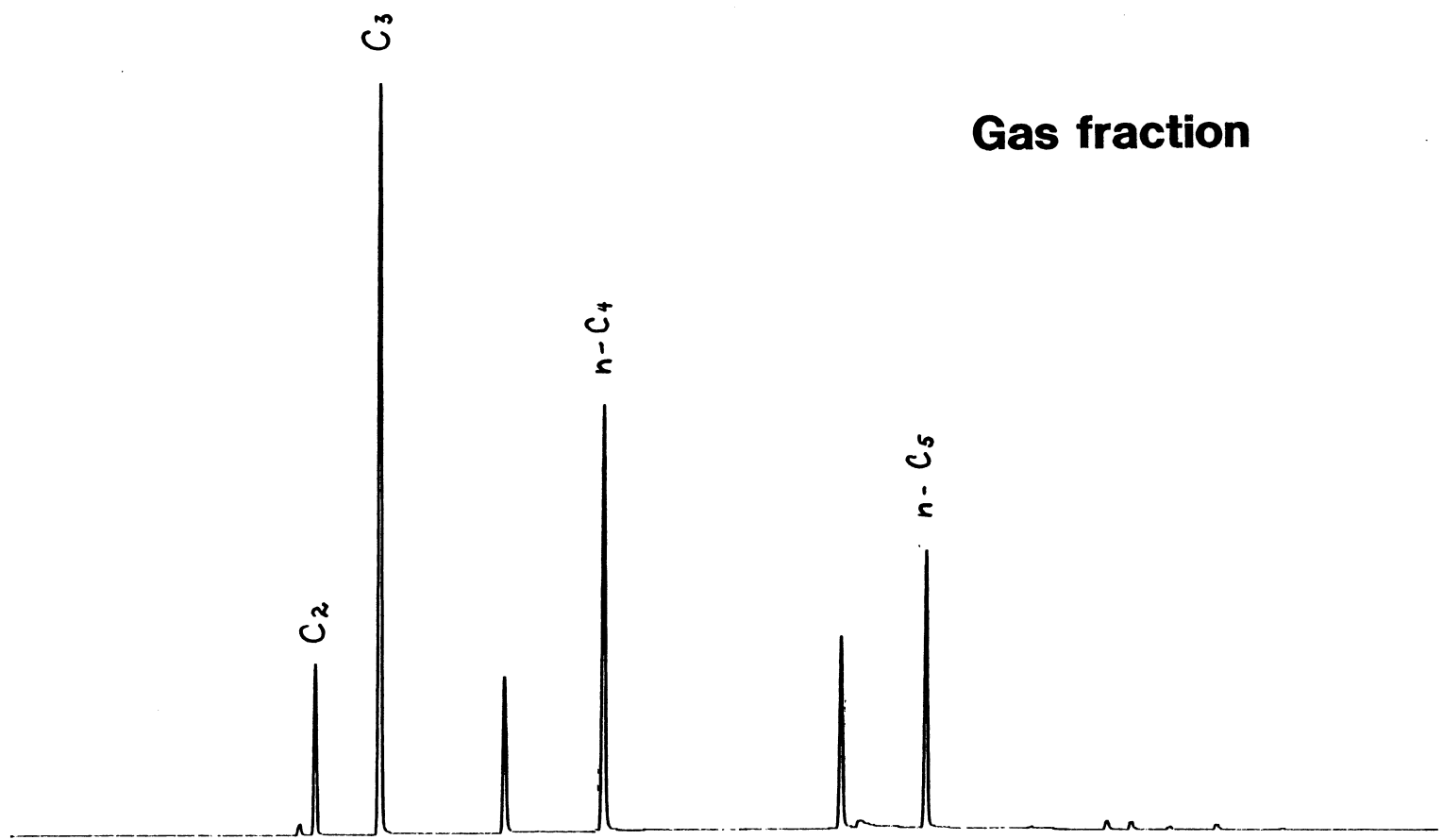


17

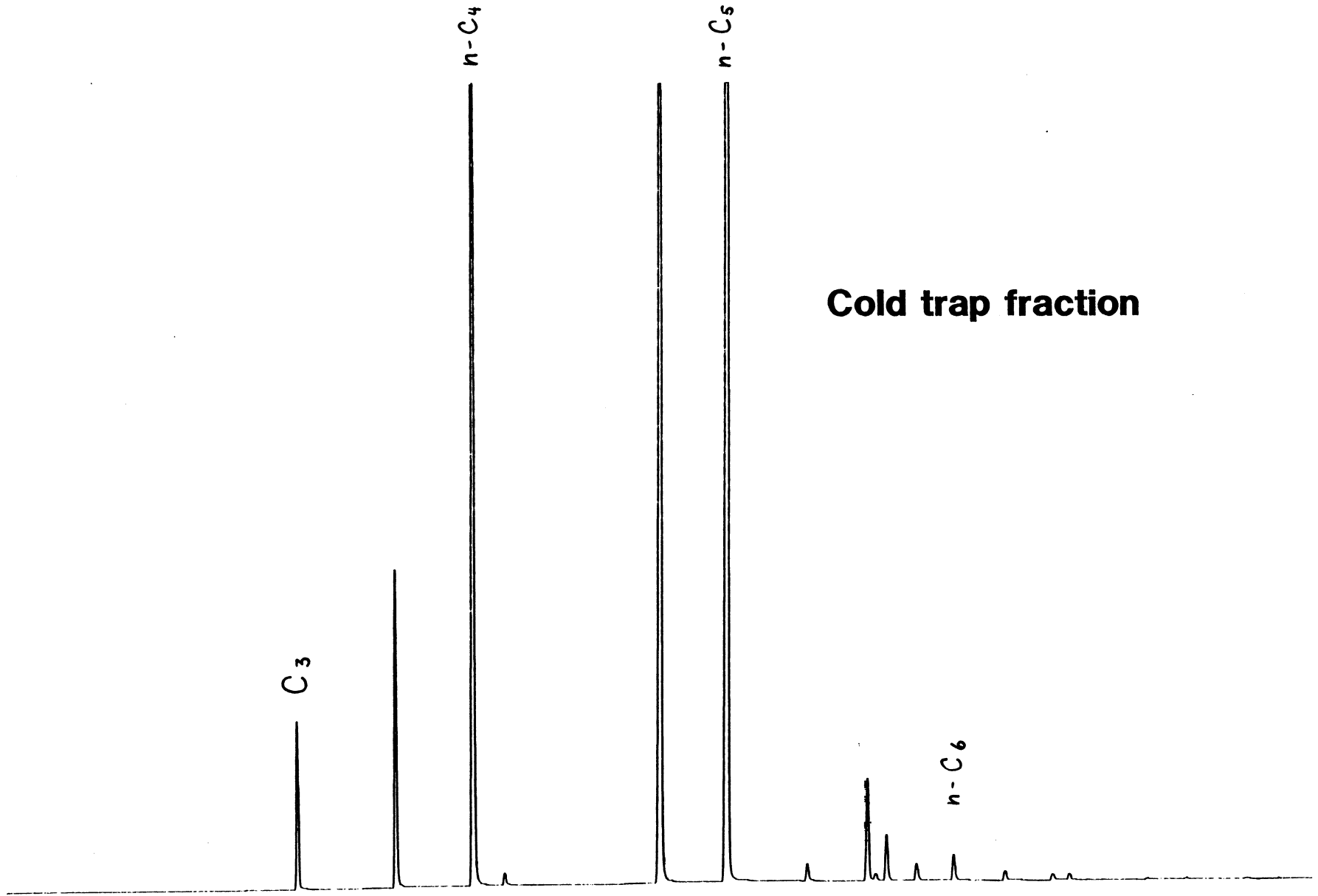
n-C₁₀

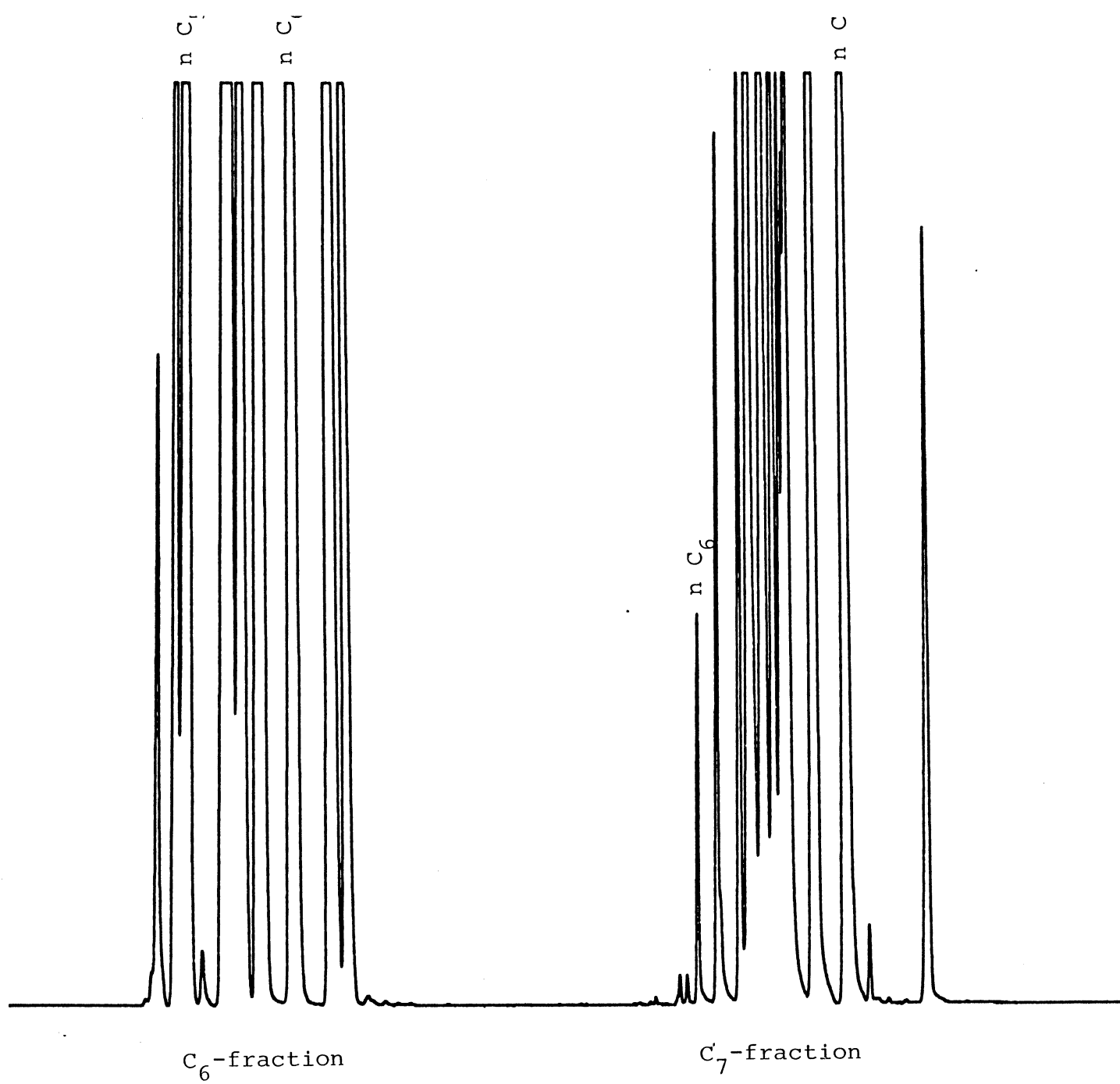
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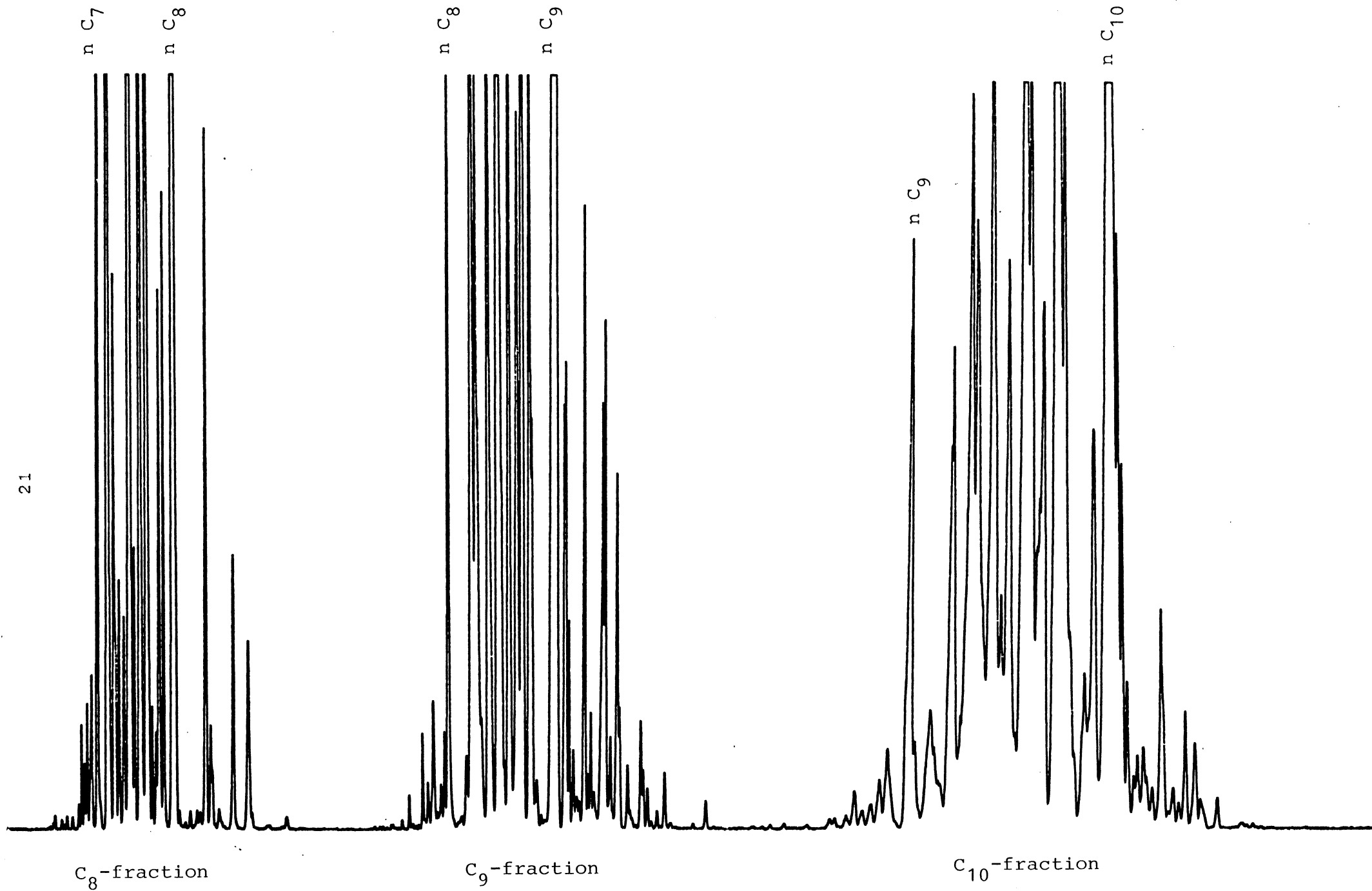
n-C₃₀



Gas fraction



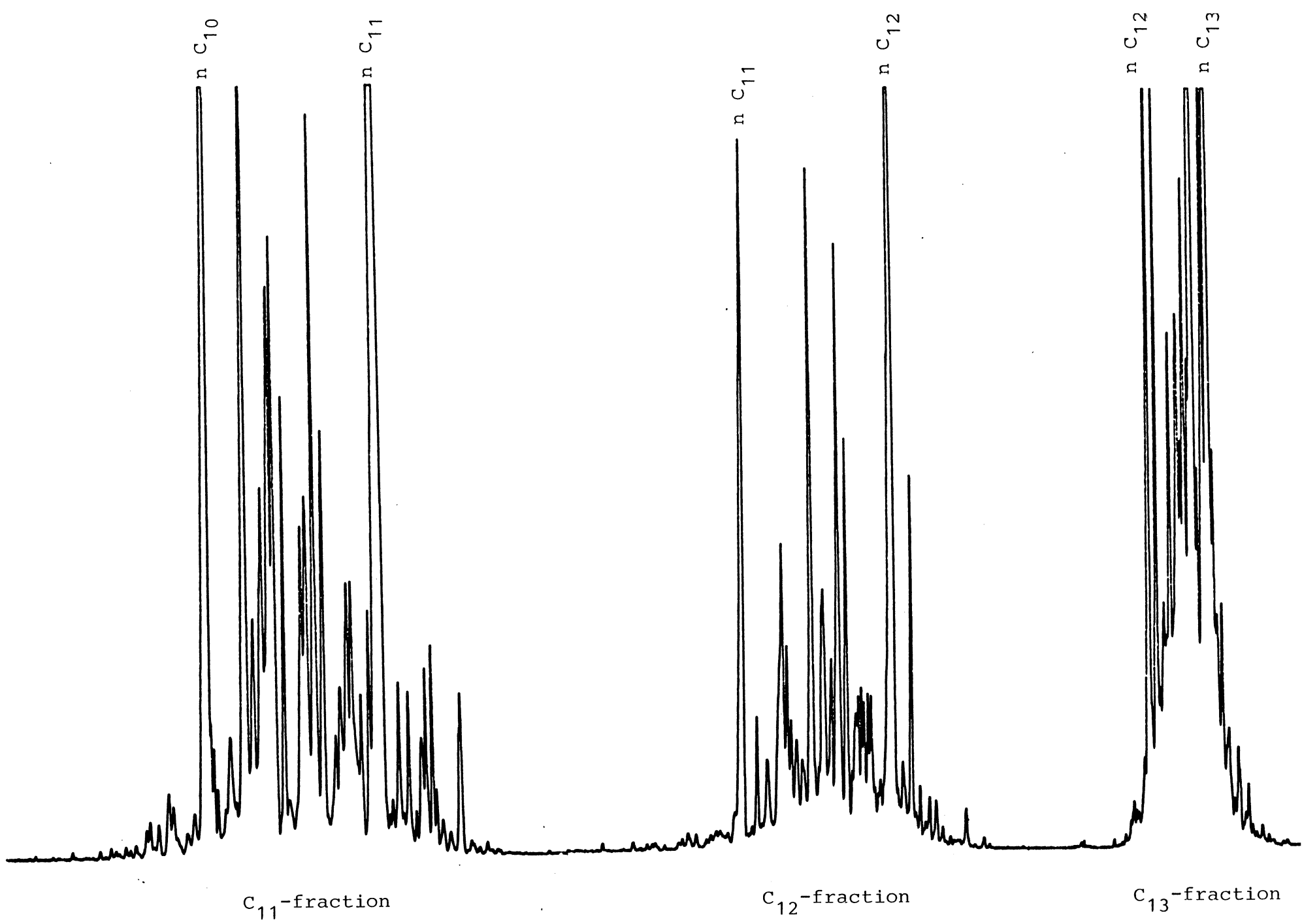




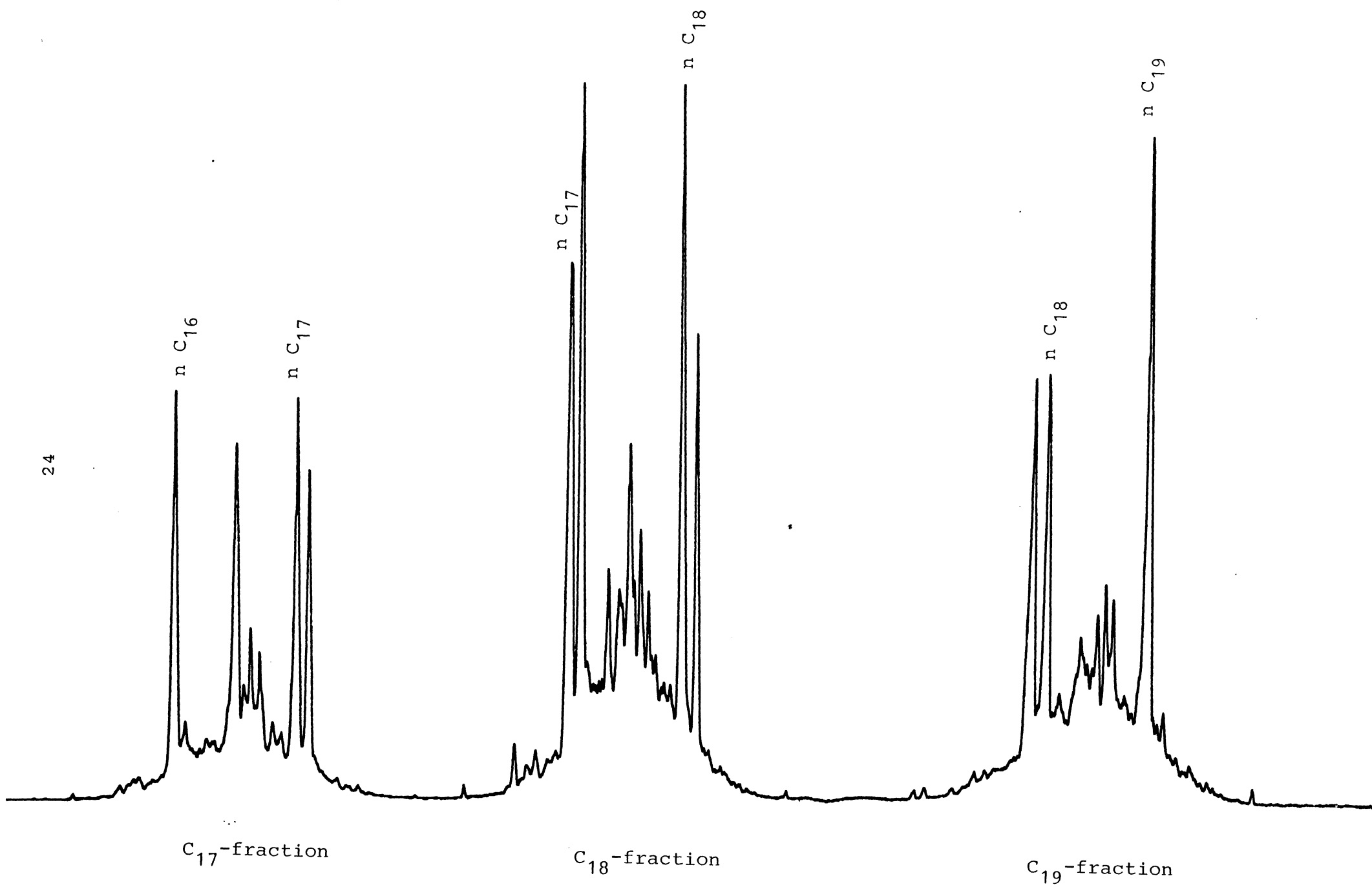
C₈-fraction

C₉-fraction

C₁₀-fraction



24



C₁₇-fraction

C₁₈-fraction

C₁₉-fraction

n C₁₆

n C₁₇

n C₁₇

n C₁₈

n C₁₈

n C₁₉