



CONTINENTAL SHELF INSTITUTE

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REPORT TITLE/ TITTEL			
Total Organic Carbon and Kerogen Analysis of Samples from Well 34/4-3.			
CLIENT/ OPPDRAGSGIVER			
Saga Petroleum AS			
RESPONSIBLE SCIENTIST/ PROSJEKTANSVARLIG			
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AUTHORS/ FORFATTERE			
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SUMMARY/ SAMMENDRAG

A total of sixteen samples were subjected to Total Organic Carbon (TOC), Rock-Eval and Pyrolysis-gas chromatography (Py-GC) analysis.

The TOC values vary from 0.3% to 4.0%. The kerogen analysis by Py-GC is in good agreement with the Rock-Eval results, suggesting that the samples contain the following kerogen types: M-9110 (3471m) to M-9112 (3507m): immature to marginal mature type III/IV or IV; M-9113 (3527m): immature mixed type II/III; M-9114 (3528m): mature type III/IV or IV; M-9115 (3535m) to M-9119 (3768m): immature mixed type II/III; M-9120 (3807m) and M-9121 (3852m): marginal mature type III or III/IV; M-9122 (3985m): mature type III; M-9123 (4055m): marginal mature type III or III/IV; M-9124 (4345m) and M-9125 (4408m): marginal mature type III/IV or IV.

KEY WORDS/ STIKKORD Kerogen

Pyrolysis

Analysis

060/V/ah/1

EXPERIMENTAL

Total Organic Carbon (TOC)

The samples were crushed and aliquots were weighed into Leco crucibles, treated with hot 2N HCl to remove carbonate, and washed twice with distilled water to remove traces of HCl. The crucibles were then placed in a vacuum oven at 50°C and evacuated to 20mm Hg for 12 hrs. The total organic carbon (TOC) content of the dried samples was determined using a Leco EC12 carbon analyser. Results are given in Table 1.

Rock-Eval Pyrolysis

100mg crushed sample was weighed into a platinum crucible the base and cover of which are made of sintered steel, and analysed on a Rock-Eval pyrolyser. Results are given in Table 1.

Pyrolysis-Gas Chromatography (Py-GC)

Two Py-GC methods were used in this study. A temperature programmed pyrolysis technique, Py-GC (Progr.), was applied for samples with TOC values of ca. 1% and lower. Flash pyrolysis at 600°C, Py-GC (600°C), was used for samples with TOC values higher than 1%.

Thermal Extraction

20-30mg of fine ground whole rock sample was placed in a boat shaped sample probe and heated in a stream of helium at 300°C for five minutes.

Py-GC (600°C)

A chemical Data Systems (CDS) Pyroprobe 120 interfaced to a Varian 3700 gas chromatograph was used for flash pyrolysis. Fine ground thermally extracted whole rock sample was suspended in methanol and added to the platinum ribbon sample probe with a disposable Pasteur pipette. The sample was flash pyrolysed and flushed directly onto a capillary column via a laboratory built interface/splitter and analysed under the GC conditions given below.

Instrumental conditions:

Pyrolysis: 600°C for 5 sec. in nitrogen
Column: 25m OV-1 fused silica capillary; ID 0.3mm
Carrier gas: Nitrogen with inlet pressure 6 psi; Flow ca. 1.5ml/min.
Split ratio: 1:30.
Oven programme: 40°C/1 min. to 270°C at 4°C/min.

Py-GC (Progr.)

20-30mg of thermally extracted whole rock sample was pyrolysed in a stream of helium (300°C to 550°C at 35°C/min.) using a tube furnace type pyrolyzer interfaced to a Varian 3700 gas chromatograph. The outlet of the pyrolyzer was connected to a fused silica capillary column via an interface/splitter (sample/split ratio; 1:30). The pyrolysis product was trapped in a cooled (liquid nitrogen) U-shaped part at the front of the column.

The outlet of the splitter was connected to a flame ionisation detector (FID) and the course of the pyrolysis could be followed by the detector response of the bulk pyrolysis product which was recorded as a broad peak. At the end of the pyrolysis, the trapped pyrolysis product was injected by removing the liquid nitrogen bath at ambient temperature and analysed under the GC conditions given below.

Instrumental conditions:

Pyrolysis: 300°C to 550°C at 35°C/min. in helium.
Column: 25m OV-1 fused silica capillary; ID 0.3mm.
Carrier gas: Helium with inlet pressure 10 psi; Flow ca. 1.5 ml/min.
Split ratio: 1:30.
Oven program: 40°C/1 min. to 270°C at 4°C/min.

RESULTS AND DISCUSSION

A total of sixteen samples were subjected to TOC, Rock-Eval and Py-GC analysis.

Total Organic Carbon (TOC)

The TOC values are listed in Table 1 varying from 0.31% to 4.0%.

Rock-Eval Pyrolysis

M-9100 (3471m), M-9111 (3479m) and M-9112 (3507m). The T_{max} values (433 to 436) indicate that the samples are immature to marginal mature. The low hydrogen indices are typical for type III/IV and IV kerogens. Type IV kerogen is used to describe the inertinite group of macerals or reworked material with a poor potential for hydrocarbons (mainly gas).

M-9113 (3527m). The hydrogen and oxygen indices suggest a mixed type III/II kerogen. T_{max} indicate immaturity.

M-9114 (3528m). The low hydrogen index suggests a type III/IV or IV kerogen. The T_{max} value indicates maturity, however, it seems too high and might be misleading.

M-9115 (3535m), M-9116 (3541m) and M-9117 (3624m). The moderate hydrogen indices (330 to 363) and low oxygen indices suggest a type II or mixed II/III kerogens. The T_{max} values (429 to 431) indicate immaturity.

M-9118 (3700m) and M-9119 (3768m). The hydrogen indices (<200) suggest a type III kerogen. However, the oxygen indices are lower than expected for a type III kerogen. The samples contain probably a mixed type III/II kerogen. T_{max} indicate immaturity.

M-9120 (3807) and M-9121 (3852m). The hydrogen indices suggest a type III or a type III/IV or IV kerogen. T_{max} (437 and 439) indicate marginal maturity.

M-9122 (3985m). The hydrogen index and T_{max} value (445) suggest a mature type III kerogen.

M-9123 (4055m), M-9124 (4345m) and M-9125 (4408m). The low hydrogen indices suggest a type III/IV or IV kerogen. T_{\max} values indicate marginal maturity for M-9123 and M-9125. The oxygen index (441) and T_{\max} value (470) for M-9124 seem too high and are probably misleading.

Pyrolysis-Gas Chromatography (Py-GC)

The instrumental conditions are described in the experimental section. Based on retention and mass spectrometric data from other kerogens, the peaks in the pyrograms are tentatively identified: The numbered peaks are n-alkene/n-alkane doublets of the corresponding carbon number. The alkenes have the shorter retention time. T = toluene; X = m/p-xylenes, N = naphthalene; C₁N = 1- and 2- methyl naphthalenes (2-methyl naphthalene eluting first); C₂N = ethyl naphthalene and dimethyl naphthalenes; Pr = pristenes.

M-9110 (3471m), M-9111 (3479m) and M-9112 (3507m). The pyrograms of these three samples are overall very similar showing a short range, C₇ to ca. C₁₇, aliphatic homology, where the alkane peaks are much higher than the alkenes. The abundance of aromatic compounds is high. The pyrograms show a type III/IV or IV kerogen fingerprint.

M-9113 (3527m). The pyrogram shows an n-alkene/n-alkane homology ranging from C₇ to ca. C₂₇. Generally the pyrogram shows a type II kerogen fingerprint. However, the abundance of the naphthalenes in the C₁₁ to C₁₄ region is quite high indicating an input of material derived from higher plants; i.e. the sample contains a mixed type II/III kerogen.

M-9114 (3528). The pyrogram is very similar to M-9112, i.e. a type III/IV or IV kerogen fingerprint.

M-9115 (3535m), M-9116 (3541m), M-9117 (3624m), M-9118 (3700) and M-9119 (3768m). The pyrograms of these five samples are almost identical to M-9113. Again the pyrograms show a strong aliphatic homology and the abundance of naphthalene and the alkyl naphthalenes is quite high. The pyrograms suggest a mixed type II/III kerogen. The abundances of naphthalene and the 1- and 2- methyl naphthalenes are slightly higher in M-9119 than in the other samples indicating a higher input of kerogen type III material (higher plant material) in M-9119. This is in agreement with the Rock-Eval results. M-9119 has a lower hydrogen index (134) than the other samples (ca. 200 to 360).

M-1920 (3807m) and M-1921 (3852m). The pyrograms of these two samples are very similar showing a short range n-alkene/n-alkane homology (C_7 to ca. C_{19}). The abundance of aromatics is quite high. The pyrograms show a type III or a mixed type III/IV kerogen fingerprint.

M-1922 (3985m). The pyrogram shows an aliphatic homology ranging from C_7 to C_{25} . The general shape of the trace; the heights of the n-alkene/n-alkane peaks are falling off sharply and the ratio of the peak heights (n-alkanes higher than n-alkenes from C_{12}), suggests a type III kerogen.

M-9123 (4055m). The pyrogram shows an n-alkene/n-alkane homology ranging from C_7 to C_{21} . The n-alkane peaks are higher than the n-alkenes and the abundance of aromatic compounds (especially the naphthalenes) are much higher than in M-1922. The pyrogram shows a type III or III/IV kerogen fingerprint.

M-9124 (4345m) and M-9125 (4408m). The pyrograms of these two samples are very similar to M-9110 to M-9112, i.e. the pyrograms show a type III/IV or IV kerogen fingerprint.

CONCLUSION

A total of sixteen samples were subjected to TOC, Rock-Eval and Pyrolysis-Gas chromatography (Py-GC) analysis.

The TOC values vary from 0.3% to 4.0%.

There is an overall good correlation between the Py-GC and Rock-Eval results. However, until more Py-GC results for type III/IV and IV kerogens are available, it is in some cases difficult to discriminate between a type III and a type III/IV or IV kerogen on the basis of Py-GC results alone.

Due to the complexity of kerogens, kerogen studies should therefore ideally include both microscopic and physico chemical methods in order to more completely understand the nature and interrelationships of the contributing material.

The Rock-Eval and Py-GC results suggest that the maturity stage and kerogen type in the samples are:

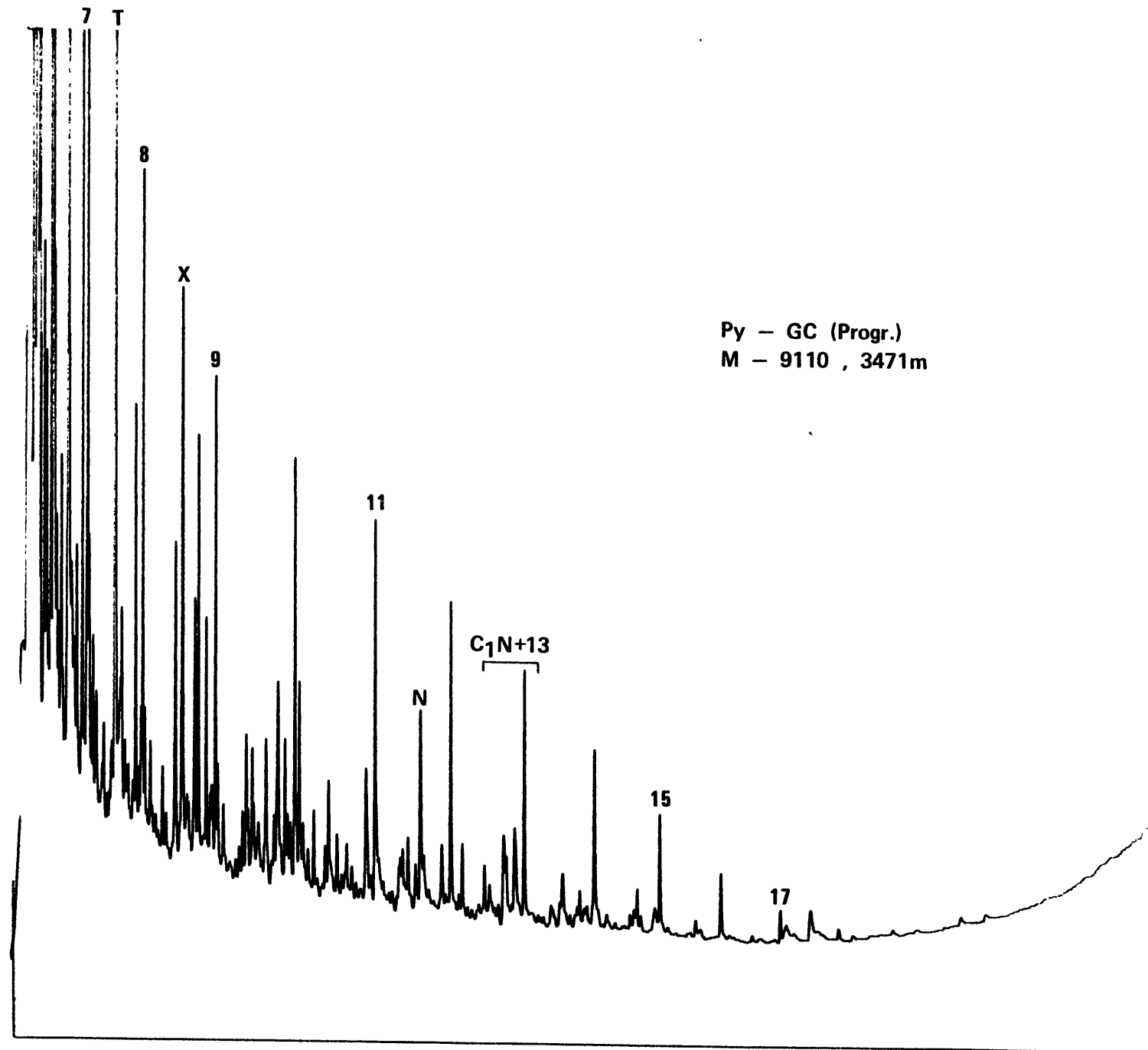
M-9110 (3471m) to M-9112 (3507m): immature to marginal mature type III/IV or IV; M-9113 (3527m): immature mixed type II/III; M-9114 (3528m): mature type III/IV or IV; M-9115 (3535m) to M-9119 (3768m): immature mixed type II/III; M-9120 (3807m) and M-9121 (3852m): marginal mature type III or III/IV; M-9122 (3985m): mature type III; M-9123 (4055m): marginal mature type III or III/IV; M-9124 (4345m) and M-9125 (4408m): marginal mature type III/IV or IV.

TABLE 1.

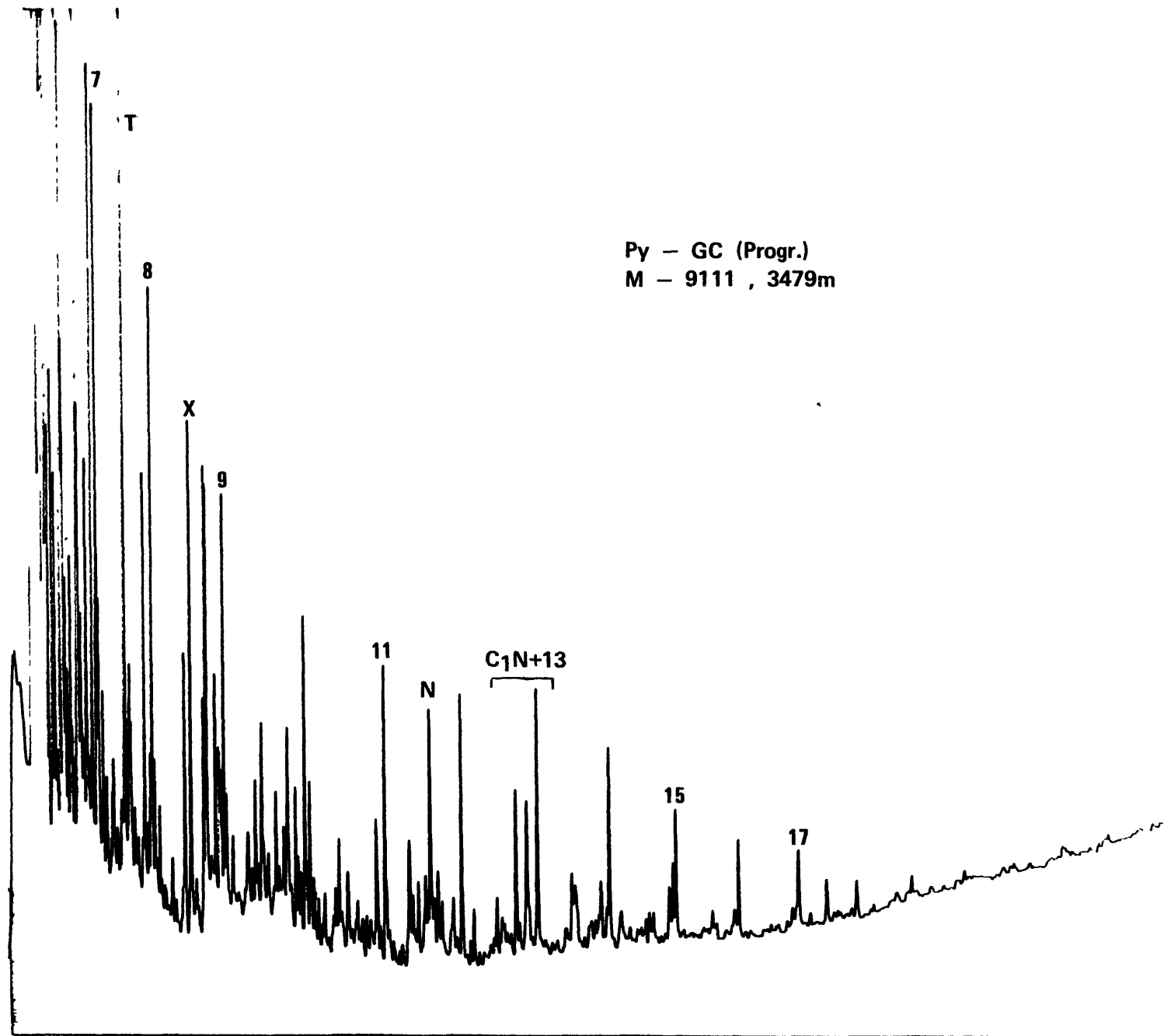
ROCK EVAL PYROLYSES

DEPTH	S1	S2	S3	TOC	HYDR. INDEX	OXYGEN INDEX	OIL OF GAS CONTENT	OF FROD. INDEX	TEMP. MAX
m	(%)						S1+S2	S1+S2	(C)
3471	0.62	0.57	0.49	0.60	46	61	0.59	0.63	433
3477	0.10	0.35	0.42	0.73	45	54	0.45	0.22	436
3507	0.10	0.15	0.32	0.59	25	54	0.25	0.40	433
3577	0.92	4.43	0.75	1.70	261	44	5.35	0.17	430
3526	0.05	0.23	0.22	0.51	45	43	0.23	0.18	444
3535	1.92	14.53	0.41	4.00	363	10	16.45	0.12	429
3541	2.28	12.23	0.40	3.71	330	11	14.51	0.16	431
3624	1.07	11.69	0.51	3.42	342	15	12.76	0.08	431
3700	0.73	7.37	0.58	3.73	198	16	8.15	0.10	429
3768	0.64	3.92	0.45	2.93	134	15	4.56	0.14	431
3807	0.24	0.65	0.89	1.09	60	82	0.89	0.27	437
3852	0.19	0.87	0.33	1.11	73	30	1.06	0.18	439
3985	0.29	2.14	0.65	1.70	126	38	2.43	0.12	445
4055	0.45	1.42	0.47	3.58	40	13	1.87	0.24	440
4345	0.05	0.12	1.50	0.34	35	441	0.17	0.29	470
4408	0.12	0.03	0.37	0.31	10	119	0.15	0.60	438

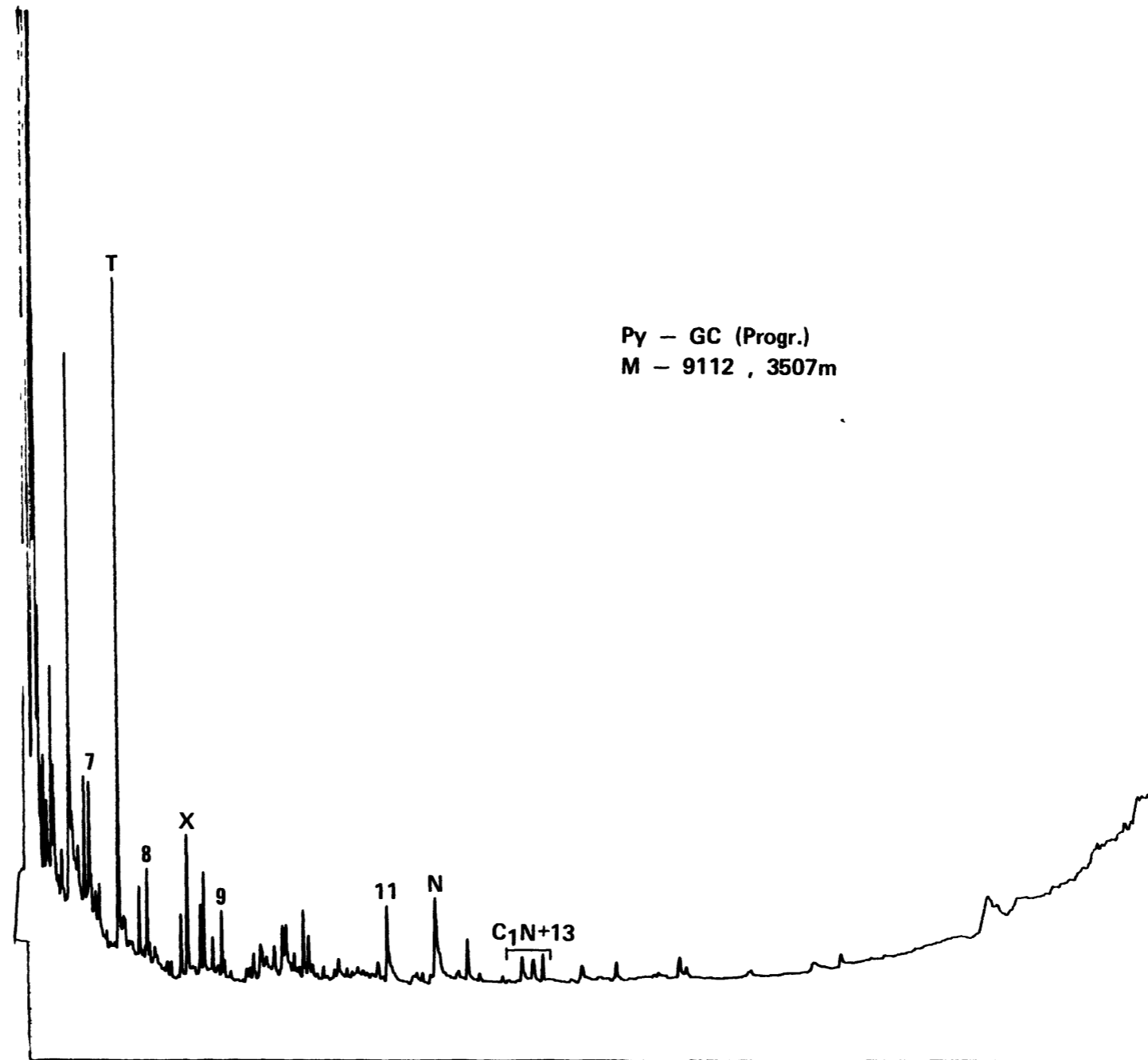
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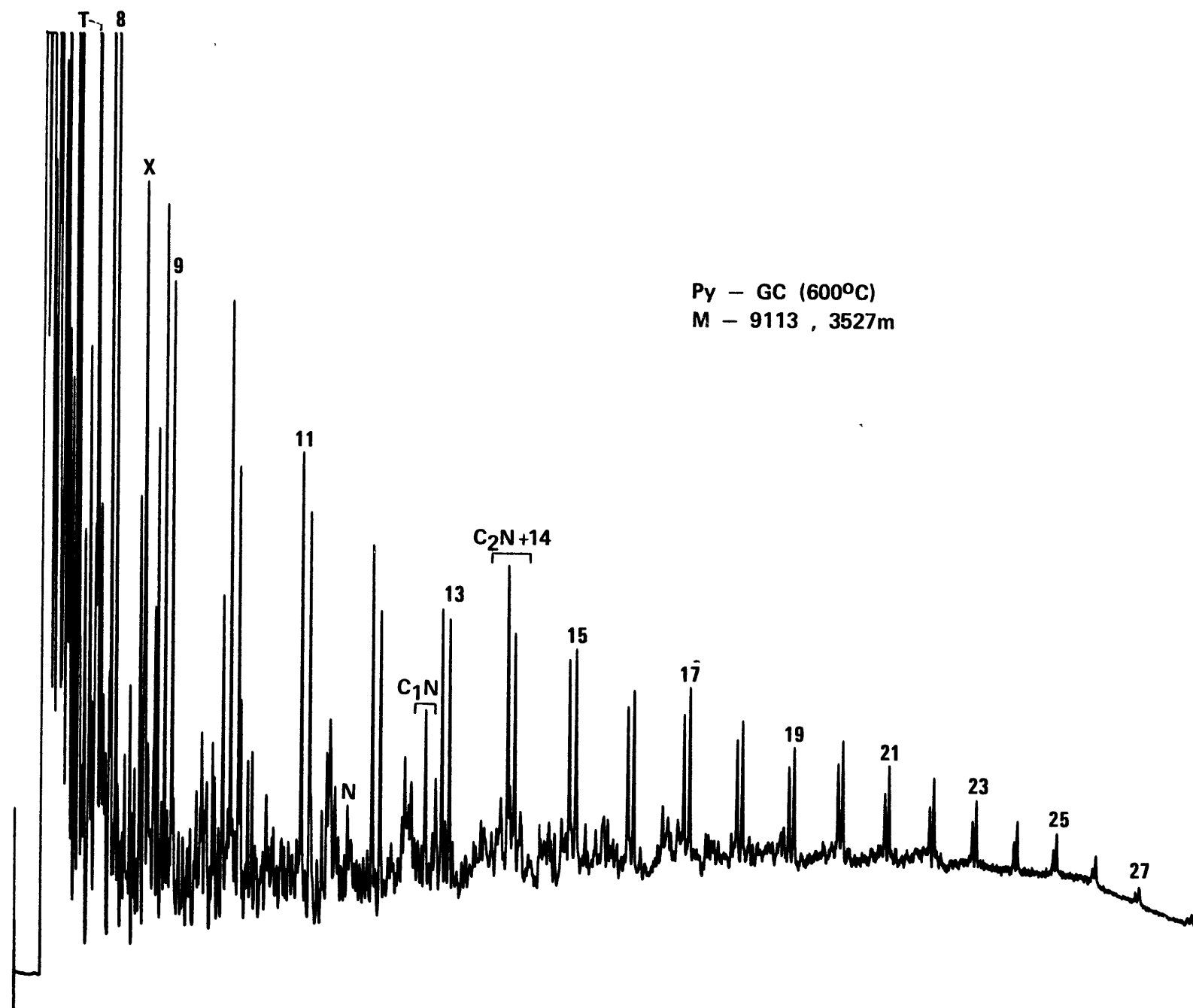
Py - GC (Progr.)
M - 9110 , 3471m



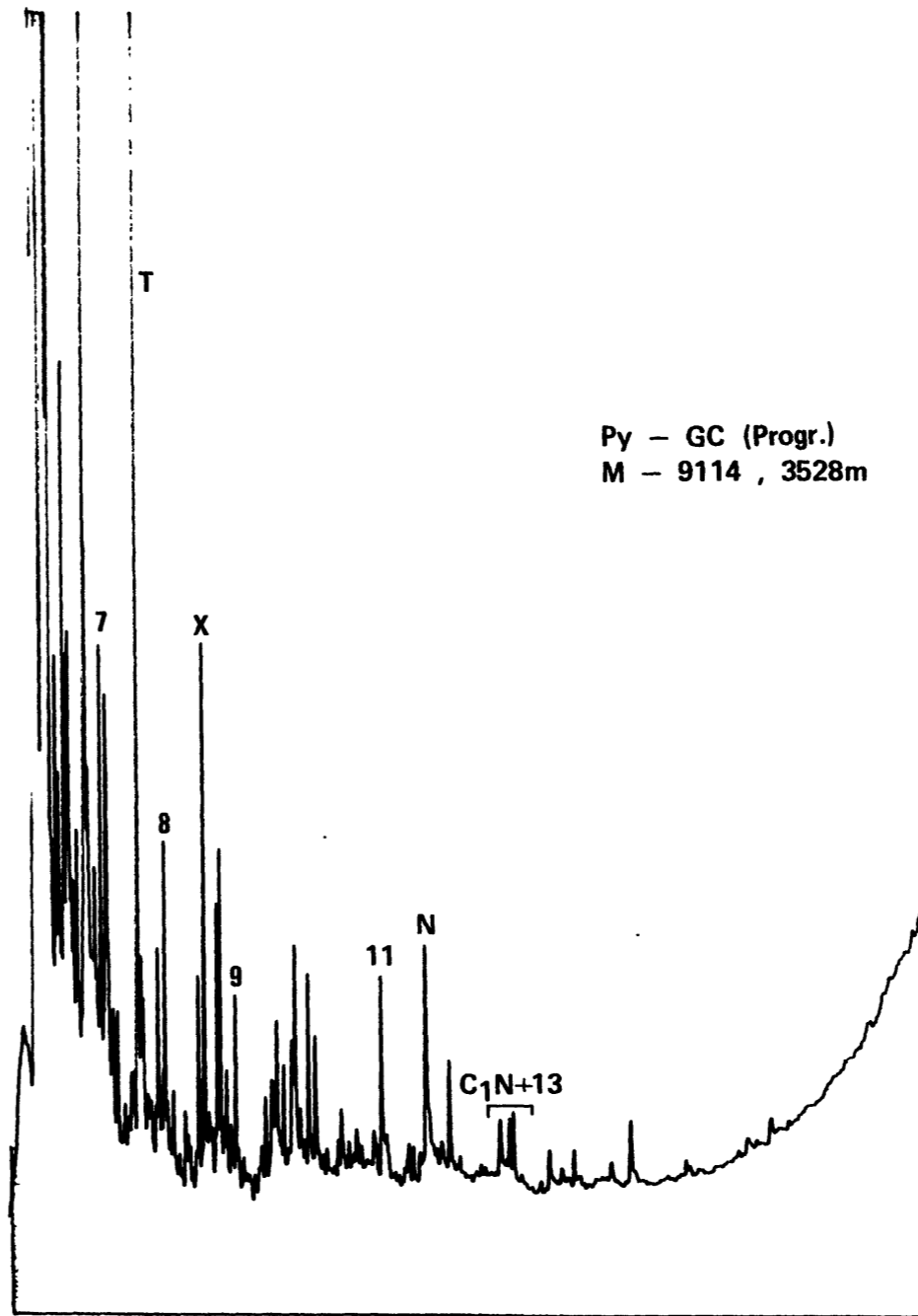
Py - GC (Progr.)
M - 9111 , 3479m



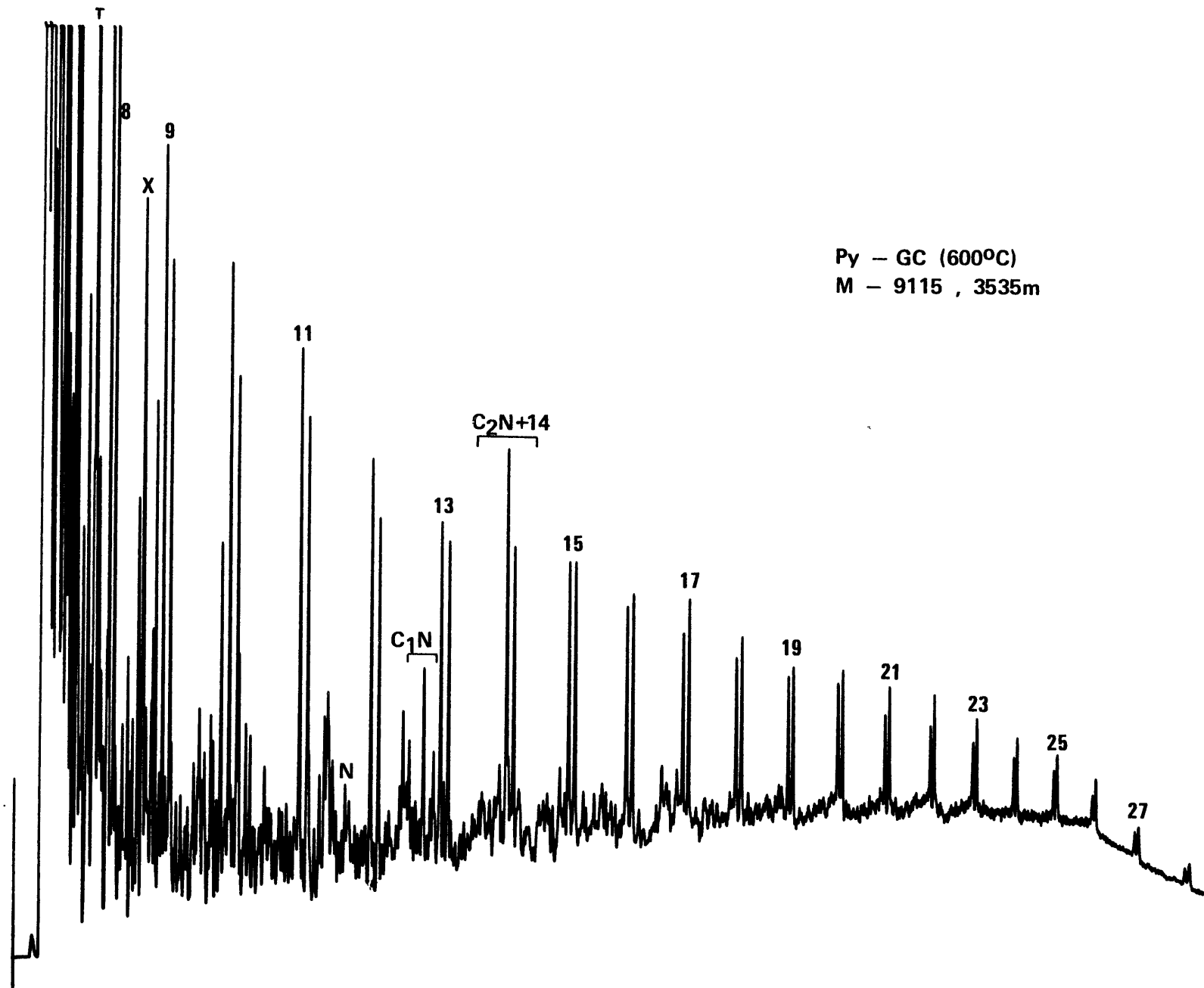
Py - GC (Progr.)
M - 9112 , 3507m



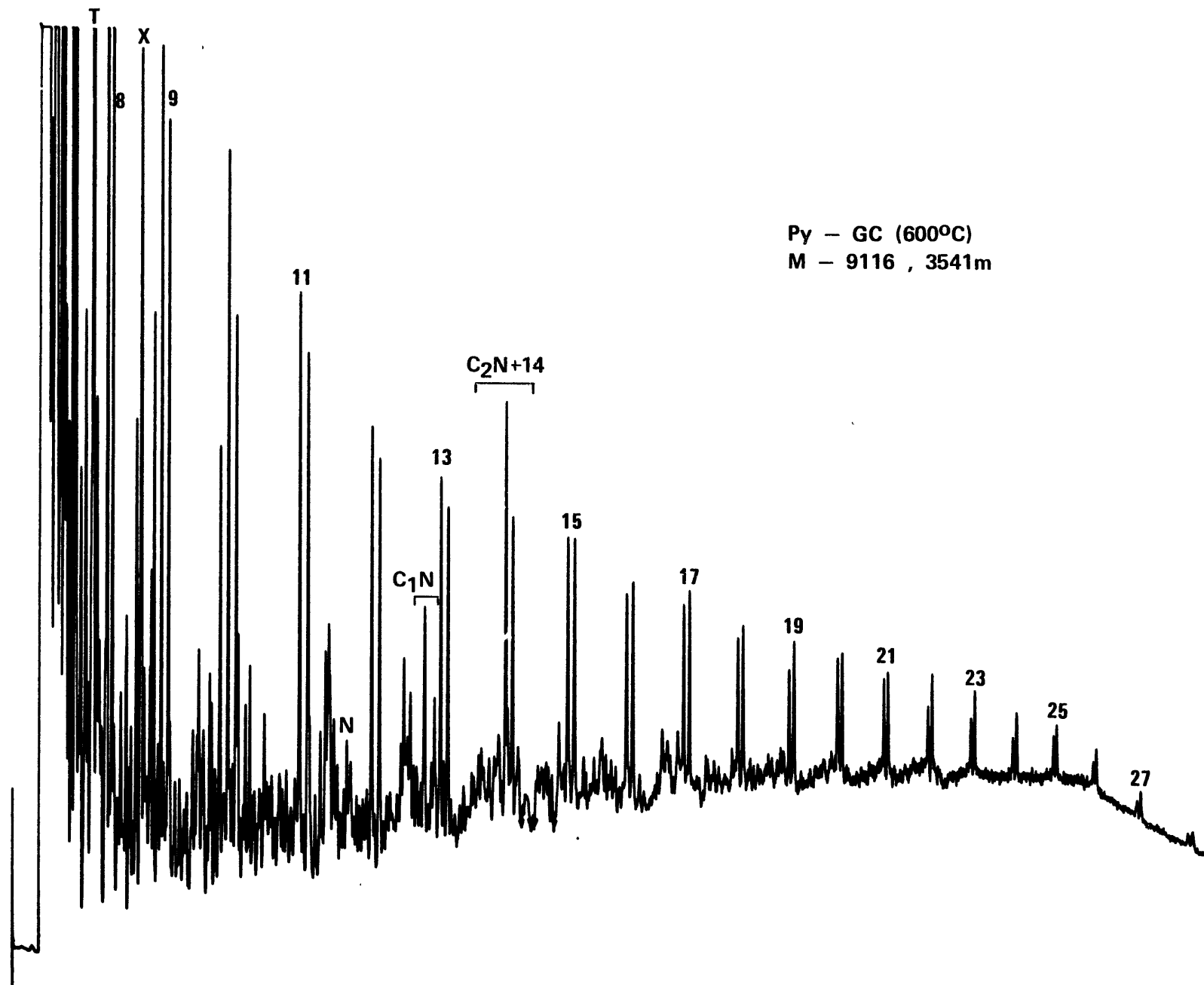
Py - GC (600°C)
M - 9113 , 3527m



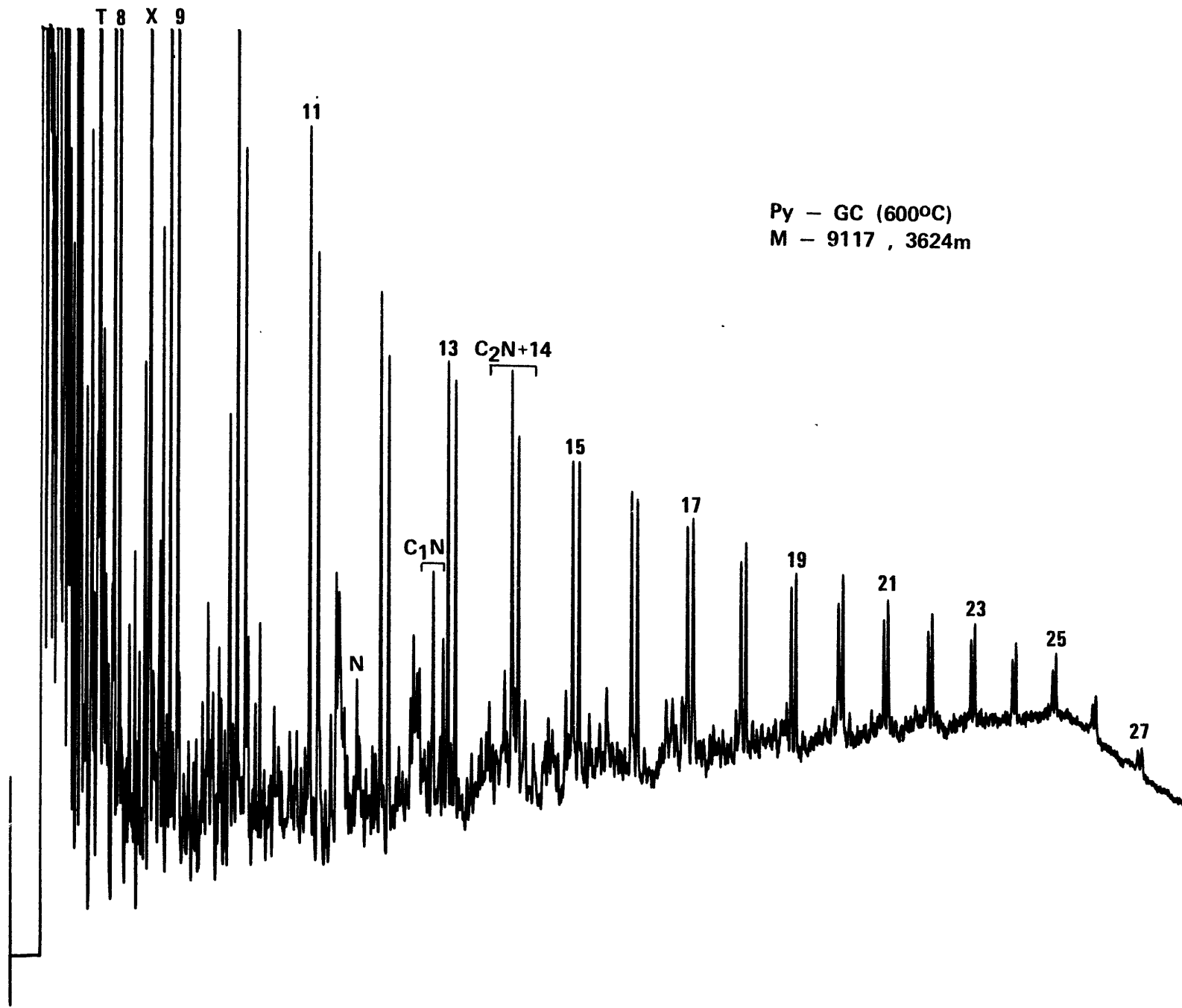
Py - GC (Progr.)
M - 9114 , 3528m



Py - GC (600°C)
M - 9115 , 3535m

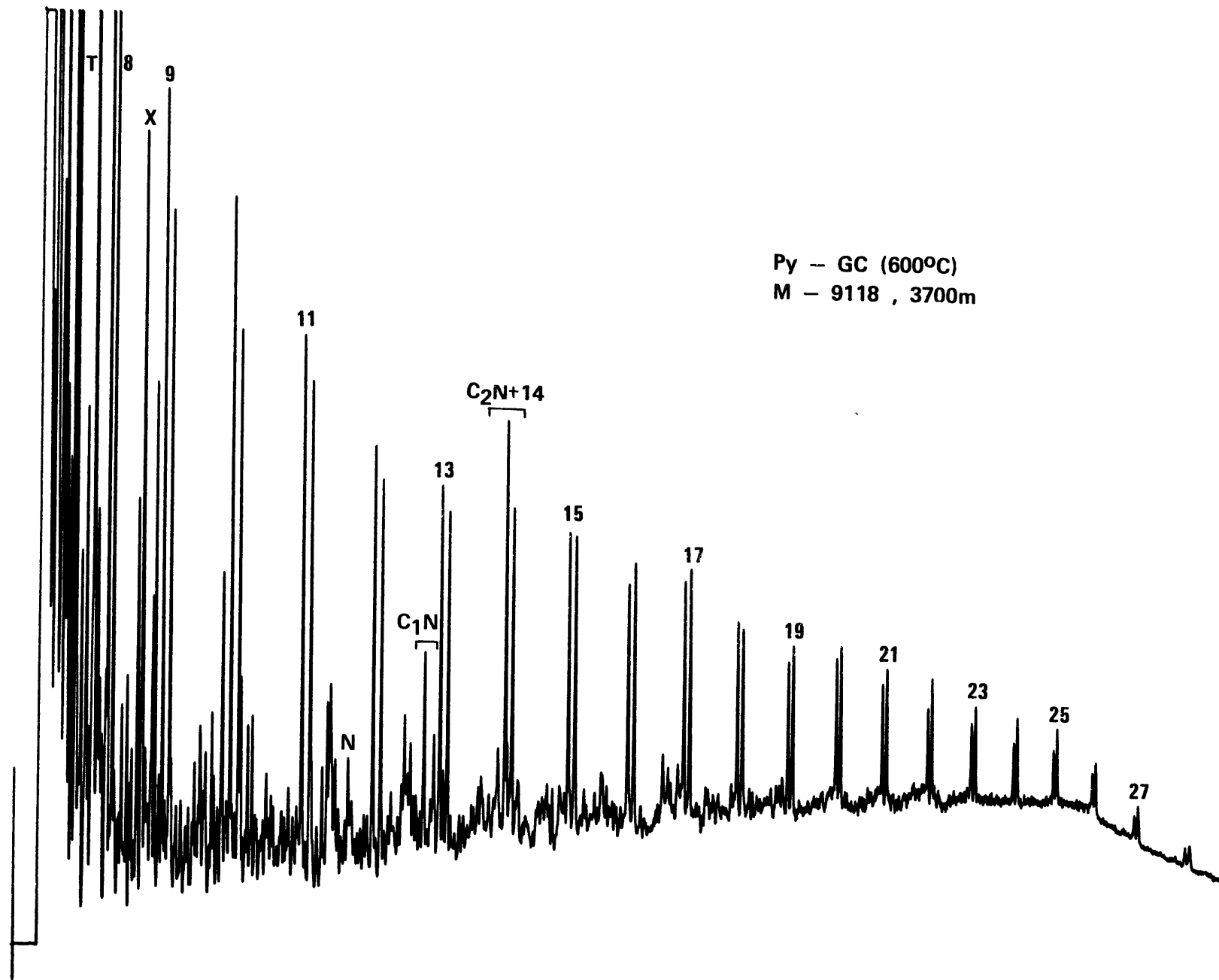


Py - GC (600°C)
M - 9116 , 3541m



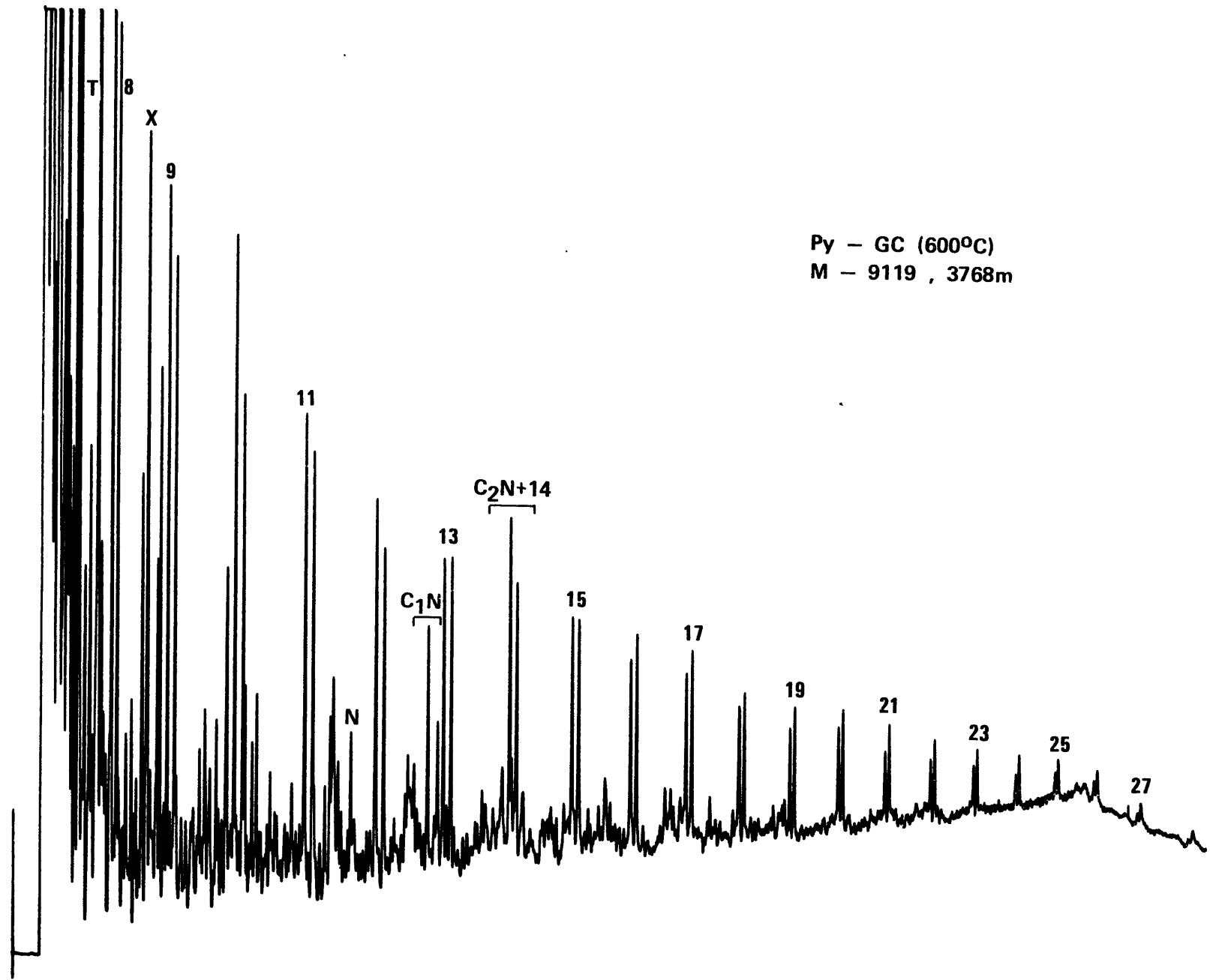
Py - GC (600°C)

M - 9117 , 3624m



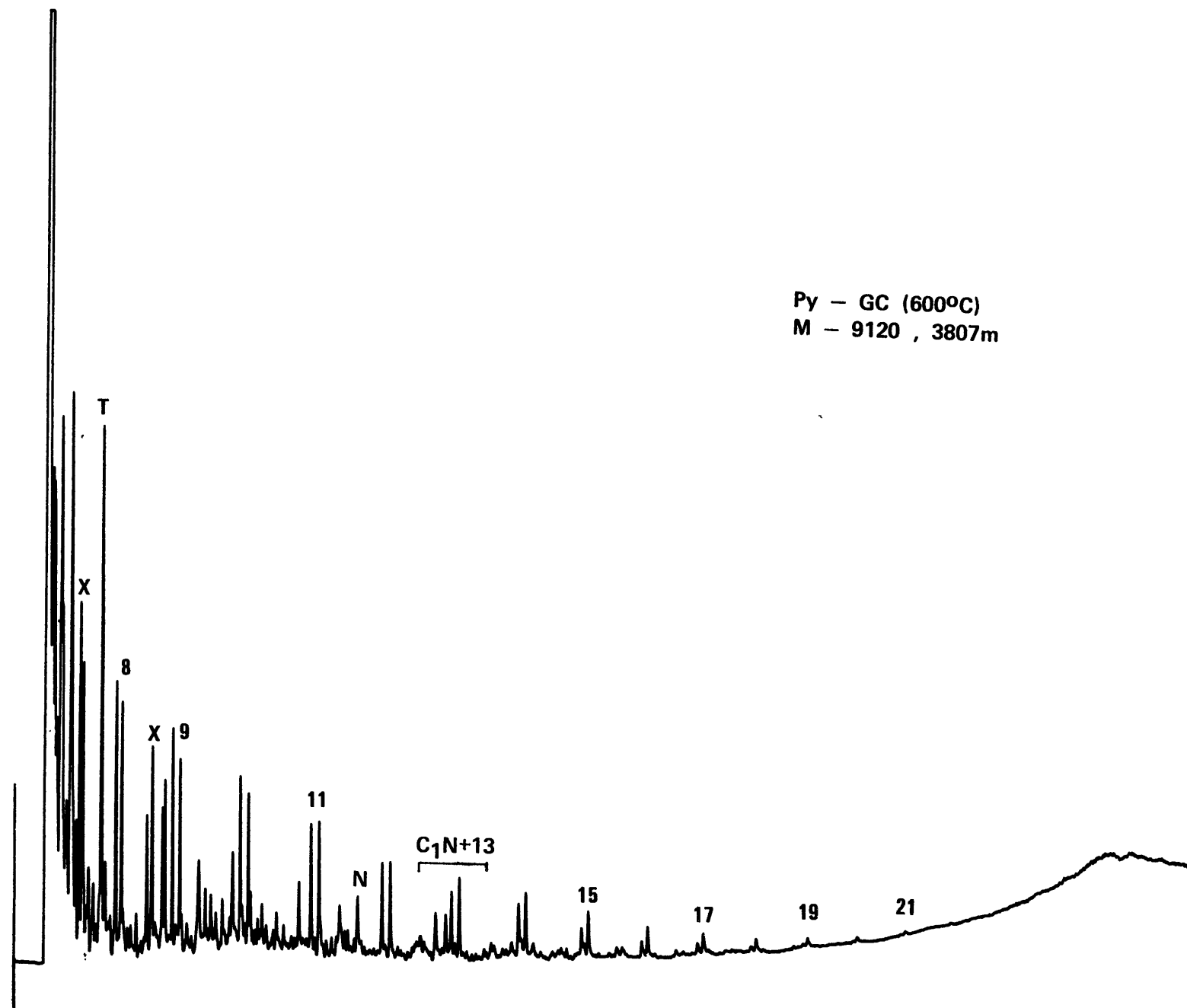
Py - GC (600°C)

M - 9118 , 3700m

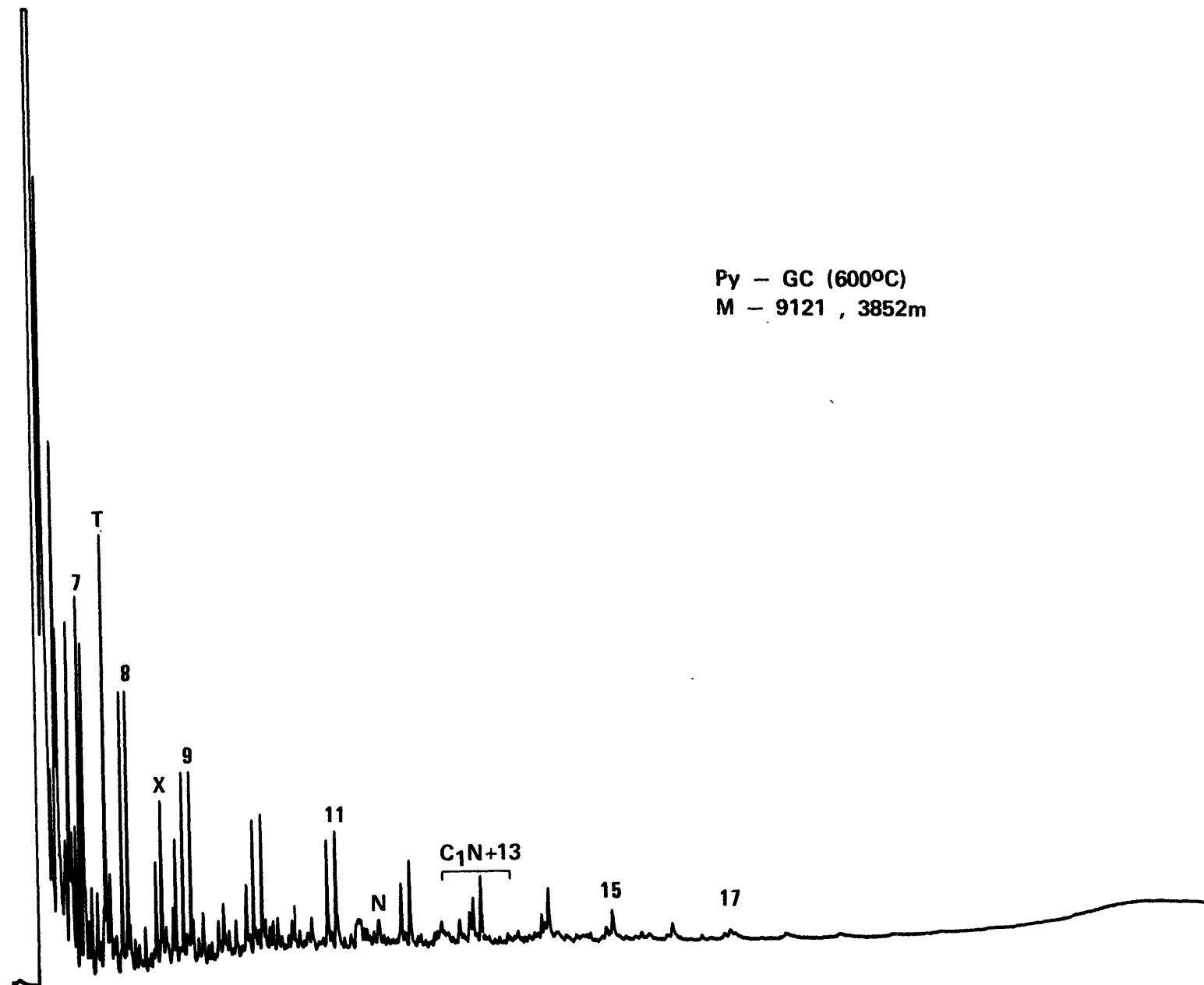


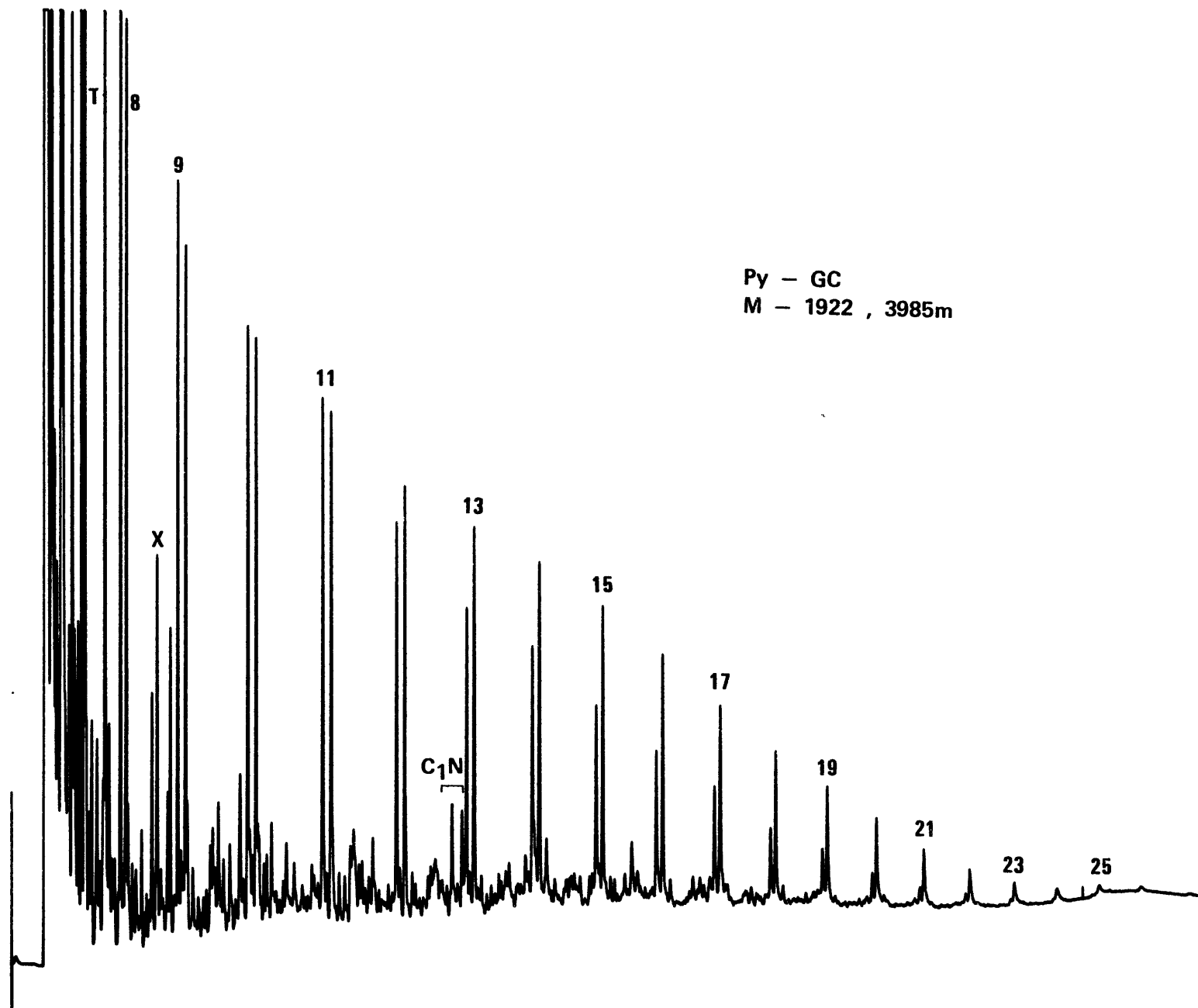
Py - GC (600°C)
M - 9119 , 3768m

Py - GC (600°C)
M - 9120 , 3807m

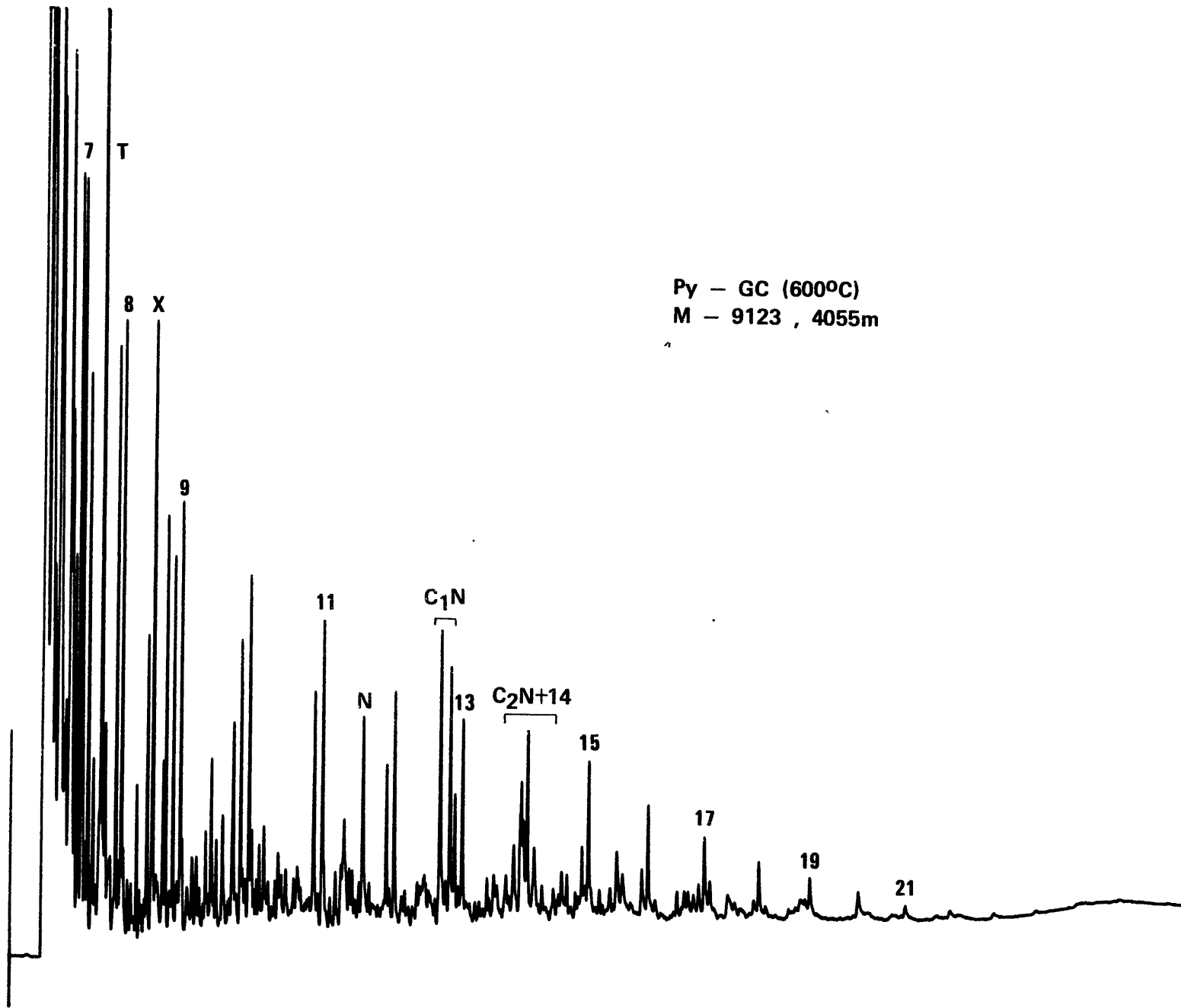


Py - GC (600°C)
M - 9121 , 3852m

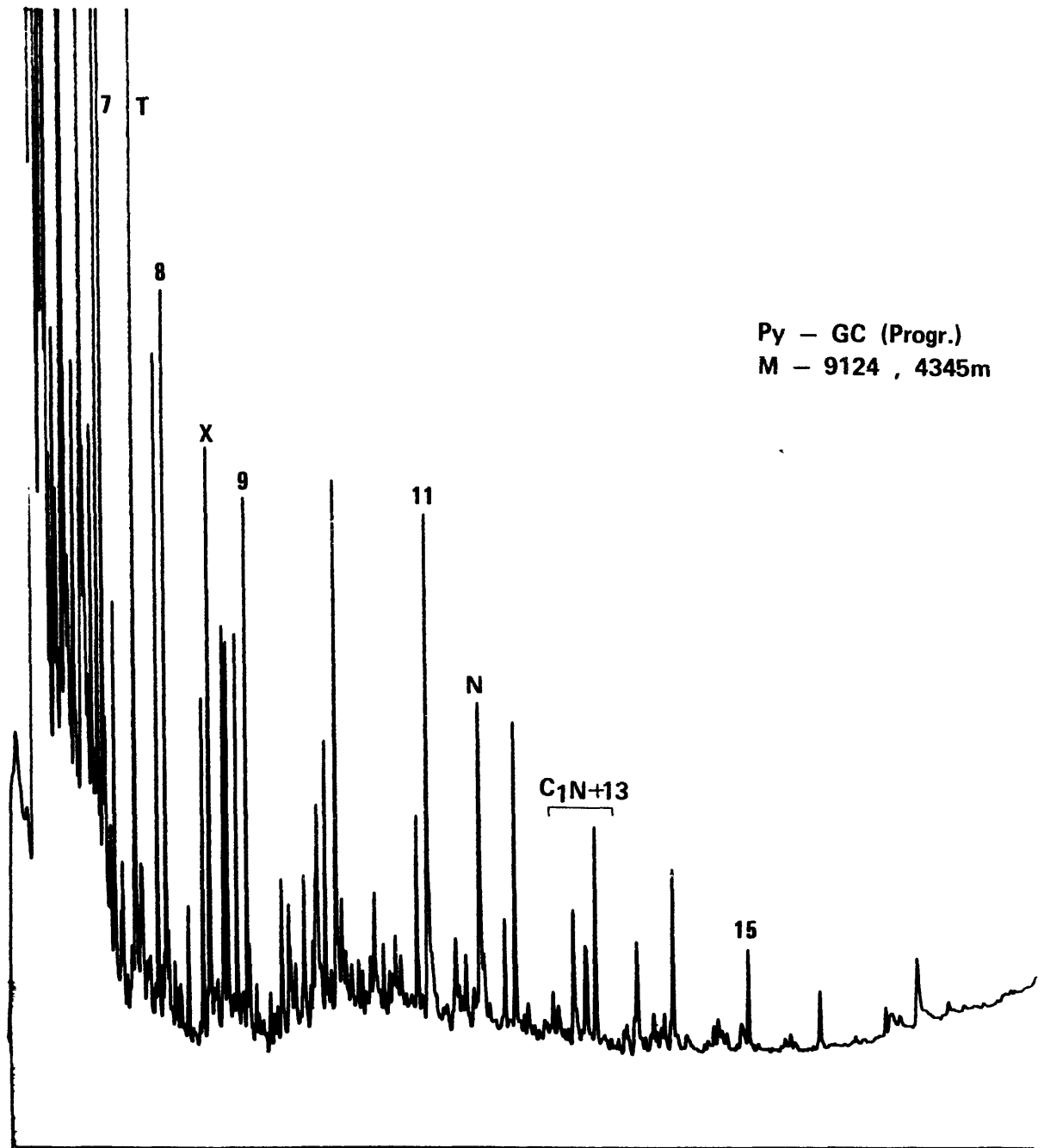




Py - GC
M - 1922 , 3985m



Py - GC (600°C)
M - 9123 , 4055m



Py - GC (Progr.)
M - 9124 , 4345m

Py - GC (Progr.)
M - 9125 , 4408m

