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THERMAL PROPERTIES & CHEMICAL REACTIVITY

L. C. Myers

DEVELOPMENT DIVISION

JULY - SEPTEMBER 1971
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MASTER

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The objective of this project is to determine the thermal and chemical stability and reactivity properties of explosives, and to continue the development and evaluation of useful thermal tests.

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Section B

THERMAL PROPERTIES & CHEMICAL REACTIVITY

ABSTRACT

The progress of the identification of the impurities in FEFO is discussed. One very high boiler has been partially isolated from a sample of concentrated impurities. Mass spectra of five of the low boiling impurities are reported.

Heats of fusion for PETN, "washed" PETN and PETN extracted from Extex are discussed. A standard deviation of less than one percent for the heat at fusion of PETN by DSC-1 is obtained.

High pressure DTA thermograms are reported for HMX, PETN, Tetryl and TNT.

DISCUSSION

FEFO IMPURITIES

Last quarter it was reported that the impurities in a sample of FEFO had been increased by a recrystallization process but this sample still contained a large percent of FEFO. The recrystallization process was tried again this quarter in an attempt to remove more of the FEFO from a sample by varying the ratio of solvent to sample during the recrystallization. If the ratio of solvent to FEFO is not correct the FEFO will not crystallize.

A chromatogram of the most concentrated sample (Sample I) of impurities obtained by this process in shown in Fig. 1. The percentage of FEFO is still several times greater than the impurities and there is a considerable amount of two high boiling impurities (Peaks G and H).

It was determined that the very high boiling impurity (Peak H) was more soluble in hexane than the other components. Since the rest of the sample does not mix with hexane, hexane was used to wash the sample and then decanted off. Fig. 2 is a chromatogram of Sample II (Sample I after three hexane washes). The concentration of the very high boiler (Peak H) was reduced significantly.

The hexane was removed from the decant by evaporation, and a chromatogram of the remains is shown in Fig. 3. The sample is better than 50% very high boiler (Peak H).

Several attempts have been made in the past to use a gas chromatograph connected in series with a mass spectrometer to obtain spectra of the impurities in samples of FEFO. These attempts were never successful because of problems with this particular GC-MS system and the small percentage of impurities in the sample. This system was successful with other types of compounds which were more volatile or thermally more stable than FEFO.

Several changes have been made to improve the GC-MS system. Initially the mass spectrometer was connected to the exhaust of the thermal conductivity detector which must be operated at a temperature greater than the maximum column oven temperature. If the column oven had to be run at 250 C to elute the high boilers, then the detector would be run above 250 C, which appeared to decompose the low boiling impurities. To correct this problem a sample collection system was added to the gas chromatograph. The temperature of the sample collection system varies with oven temperature. Therefore, the components in a sample are subjected to only the temperatures required to elute them from the column. A 40 to 1 splitter is used to divide the sample, 1 part to a flame ionization detector and 40 parts to the sample collection system.

A Nupro cross pattern fine metering valve (No. SS-2SX) is used to control the amount of flow to the mass spectrometer. The heated line connecting the gas chromatograph to this valve was reduced to a minimum. The diameter of the line to the mass spectrometer was increased from 1/4 inch to 3/8 inch so a better vacuum could be maintained in the line. This line was made from Dekoron heated tubing (Samual Moore & Co.) and the heating wire and insulation were cut so they could be used to heat the Nupro valve. All the lines from the gas chromatograph to the mass spectrometer inlet were replaced with Dekoron heated tubing to eliminate hot and cold spots.

An evaluation of these modifications was made by running a sample of FEFO and comparing a recording of the total multiplier current from the mass spectrometer to its chromatogram. If the two records are similar then there is good transfer between the instruments. If the transfer is not good then the peaks on the total multiplier current record will show much more tailing than the corresponding peaks in the chromatogram. For a sample of FEFO the total multiplier current and the chromatogram are almost identical for the low boilers; but FEFO has a very broad peak and the high boilers do not reach the mass spectrometer.

One of the problems associated with GC-MS is the varying sample concentration which the gas chromatograph supplies to the mass spectrometer. A mass spectrometer needs a constant concentration of sample. Because of the variations in sample concentration with time it is not possible to calculate the relative intensities of the mass peaks in spectra using the standard method. Without the relative intensities of the mass peaks, standard mass spectra indices such as those published by the American Society for Testing and Materials' E-14 Committee can not be used for identification.

A technique has been worked out to eliminate the problem of varying sample concentration. By recording the total multiplier current, which is proportional to sample concentration superimposed on the mass spectrum, each mass peak can be normalized to a given sample concentration by:

$$\frac{\text{Standard Sample Concentration}}{\text{Normalized Intensity for Mass Peak}} = \frac{\text{Measured Sample Concentrated from Total Multiplier Current}}{\text{Intensity for Mass Peak}}$$

and from the normalized intensities the relative intensities are determined.

A Honeywell Visicorder (Model 2106) was used to record the total multiplier current with the mass spectrum. One or two galvanometers are used to record the total multiplier current and four galvanometers (Times 1,5,20,100) are used to record the mass spectrum.

This technique is limited when the gas chromatograph peaks or total multiplier current peaks do not have the baseline separation. When a peak is located on the tail of prior peak, then the contribution from the first peak, (i.e. the background) is changing and cannot be easily corrected for and this gives the mass spectrum of the first peak superimposed on the mass spectrum of the second peak.

By using this technique with the FEFO sample having a high concentration of impurities it was possible to obtain mass spectra of five of the low boiling impurities in FEFO. The relative intensities of the m/e and a graph of the spectra for five low boiling impurities in FEFO are given in Figs. 4 through 8.

These spectra were checked against the Index of Mass Spectral Data*(1)* and the Eight Peak Index of Mass Spectra*(2)* but they did not compare with material on these indices. Therefore, an identification of these impurities has not been made.

HEAT OF FUSION OF PETN BY DSC-1

A study begun last quarter to determine if the heat of fusion of PETN could be measured with sufficent accuracy to provide data which would correlate with the performance of LX-13 or XTX-8003. Some preliminary measurements using Perkin Elmer DSC-1 were made last quarter to check out various methods of data acquision and reduction.

The operating parameters are being investigated this quarter year in an effort to improve the reproducibility of the data. Increasing the PETN sample size from 2 to 4 mg reduced the standard deviation from approximately 2 to 1% of the mean. Several 8 mg samples will be run to determine if this will reduce the standard deviation still more.

An investigation was made to determine the heat of fusion of PETN removed from uncured LX-13 or XTX-8003. A procedure which has been successfully used at Pantex to extract the PETN from uncured Extex uses toluene, ethanol and TF Freon saturated with PETN. The sample is given two washes in toluene, two washes in ethanol, one wash in TF Freon, and then dried in air at ambient temperature.

The heat of fusion for several samples of PETN and indium are given in Table I. There is some scatter in these data but the washing of a PETN sample did not appear to affect its heat of fusion. All of the PETN samples have smaller heats of fusion than the samples of PETN extracted from Extex. The PETN from lot No. 1071-391-01 was used in the formulation of Extex lot No. 2071-391-01.

Two factors were considered which might cause a change in the heat of fusion of PETN during the formulation of Extex. First, the roll milling does change the PETN particle size and this could affect the internal energy of the crystals and the heat of fusion. Second, the process used to recrystallize PETN can trap on the order of 1% acetone in the crystals, which is released when the crystals melt. But the roll milling breaks these crystals and some acetone escapes*(a)*. Assuming that lot 1071-391-01 has 1% acetone trapped in the crystals and including the heat of vaporization of the acetone (112.8 cal/gm at 100 C) in the calculation, the heat of fusion of the PETN would be 34.44 cal/g. If the heat of vaporization of the acetone is not included but the PETN sample weight is corrected for the acetone, the heat of fusion

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(1) American Society for Testing and Materials
1st Edition, July 1963

(2) Mass Spectrometry Data Center
1st Edition, 1970

(a) Estimation from effluent gas analysis indicates that less than 0.05% remains.

TABLE I. Heat of Fusion for PETN

	Lot 8263-304-01 Counts/mg ($X10^3$)	Lot 8263-304-01 "washed" Counts/mg ($X10^3$)	Lot 2071-387-01 XTX (extracted) Counts/mg ($X10^3$)	Indium Standard Counts/mg ($X10^3$)
	114.4	112.8	116.3	21.86
	112.7	115.0	114.4	21.67
	113.6	113.3	117.0	21.46
	115.6	111.4	118.2	21.86
	113.3	113.7	117.3	
	112.0		117.8	
	113.3			
Mean	113.6	113.2	116.8	21.71
σ	1.2	1.3	1.4	0.19
Heat of Fusion ± σ	35.65 ± .38	35.44 ± .37	36.53 ± .44	

	Lot 1071-386-01 Counts/mg ($2X10^3$)	Lot 1071-391-01 Counts/mg ($2X10^3$)	Lot 2071-391-01 XTX (extracted) Counts/mg ($2X10^3$)	Indium Standard Counts/mg ($2X10^3$)
	55.773	56.345	58.901	10.769
	55.375	55.894	58.171	10.856
	55.400	55.423	58.177	10.624
	54.130		58.497	10.760
	54.248		59.121	10.785
			58.634	10.859
Mean	54.985	55.887	58.417	10.775
1σ	.74	.46	.63	.086
Heat of Fusion ± 1σ	34.59 ± .47	35.22 ± .29	36.81 ± .40	

is 35.57 cal/g, as compared to 36.81 cal/g for PETN extracted from XTX. Therefore, the trapped acetone may account for some but probably not all the change in the heat of fusion of the extracted PETN samples.

During some test runs to determine the noise level of the DSC-1 baseline and methods of obtaining the best reproducibility, it was discovered that the sample holder assembly was deteriorating. It had random noise spikes on the baseline which increased with increasing temperature. Therefore, there has been a delay in this study until a new sample holder can be purchased.

A PDP-12 data acquisition system has been installed in the thermal analysis laboratory and it will be interfaced with the DSC-1 as soon as possible. This will provide more flexibility in data collection which should help to improve the accuracy of the heat at fusion measurements.

HIGH PRESSURE DTA

The high pressure DTA runs requested by LLL were delayed because of a leaking gasket on the high pressure vessel, and the delivery of a new gasket took approximately three months. The runs for HMX, PETN, Tetryl, and TNT in nitrogen have been completed and the thermograms are shown in Figs. 9 through 20.

FUTURE WORK; COMMENTS; CONCLUSIONS

The impurities were concentrated from another sample of FEFO this quarter. Variations were made on the ratio of solvent to sample during the recrystallization in an attempt to remove more of the FEFO. The final concentrated sample still had more FEFO than any other component. A hexane wash of the concentrated sample removed most of a very high boiling impurity. The hexane was decanted and then evaporated, leaving a sample with approximately 50% of this very high boiler. Attempts will be made to identify it.

By using gas chromatography coupled with a mass spectrometer, it was possible to obtain the spectra of five of the low boiling impurities in FEFO. However, identification of these impurities has not been made.

The heat of fusion of PETN can now be measured with a standard deviation of approximately 1% and work is continuing to improve this.

Heat of fusion data were reported for PETN, PETN washed by a procedure which would remove PETN from uncured Extex, and PETN removed from Extex. The washing appears to have little or no effect on the heat at fusion, but the heat of fusion of PETN removed from Extex is higher, by more than can probably be accounted for by loss of trapped acetone.

A PDP-12 data acquisition system will be interfaced with the DSC-1 and this will improve the data acquisition and reduction.

Part of the high pressure DTA thermograms requested by LLL personnel have been completed. Those for HMX, PETN, Tetryl, and TNT at ambient, 10,000 and 30,000 psi of nitrogen are reported.

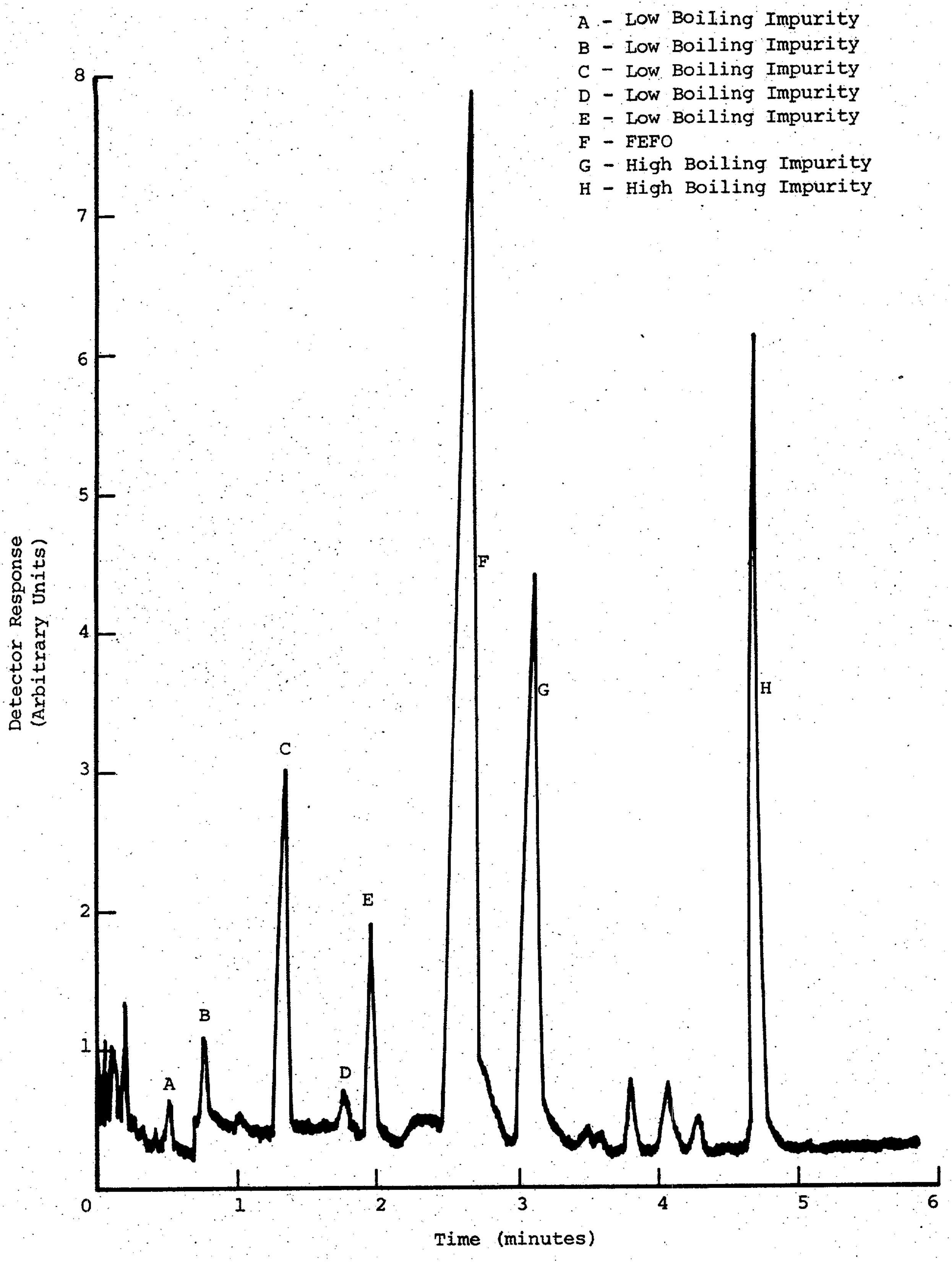


Fig. 1. Chromatogram of Impurities Concentrated in FEFO

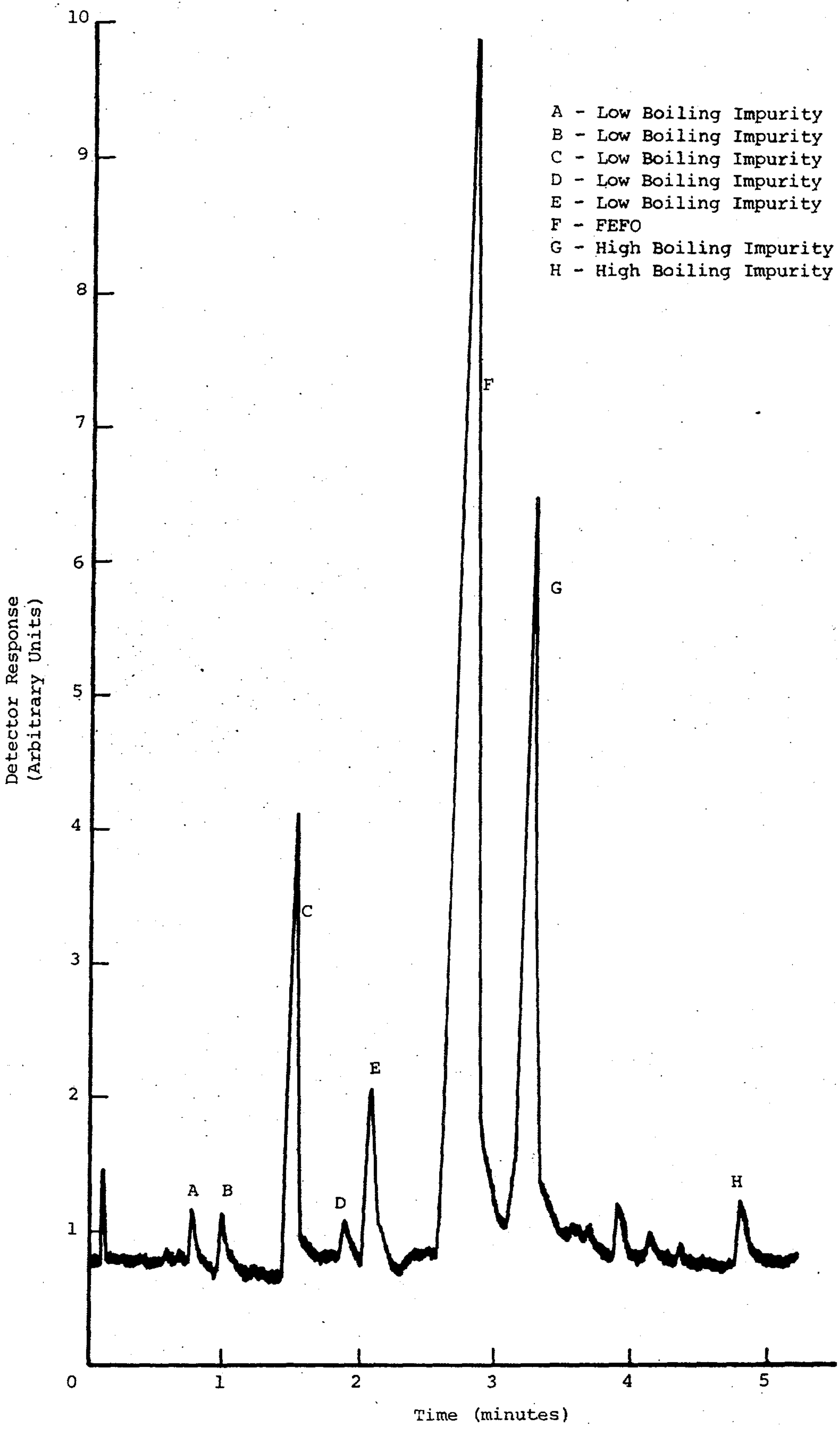


Fig. 2. Chromatogram of FEFO After Hexane Wash

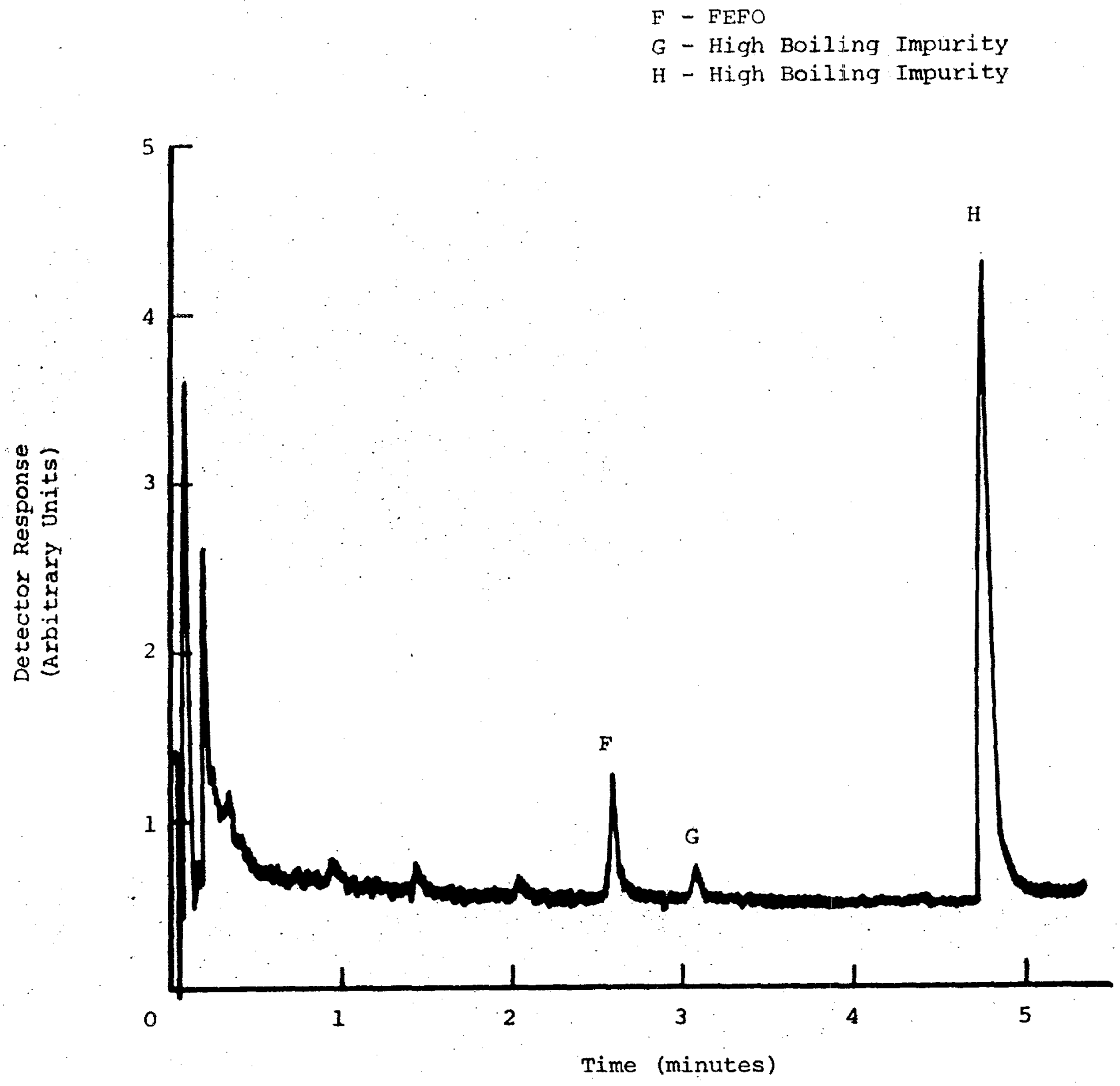
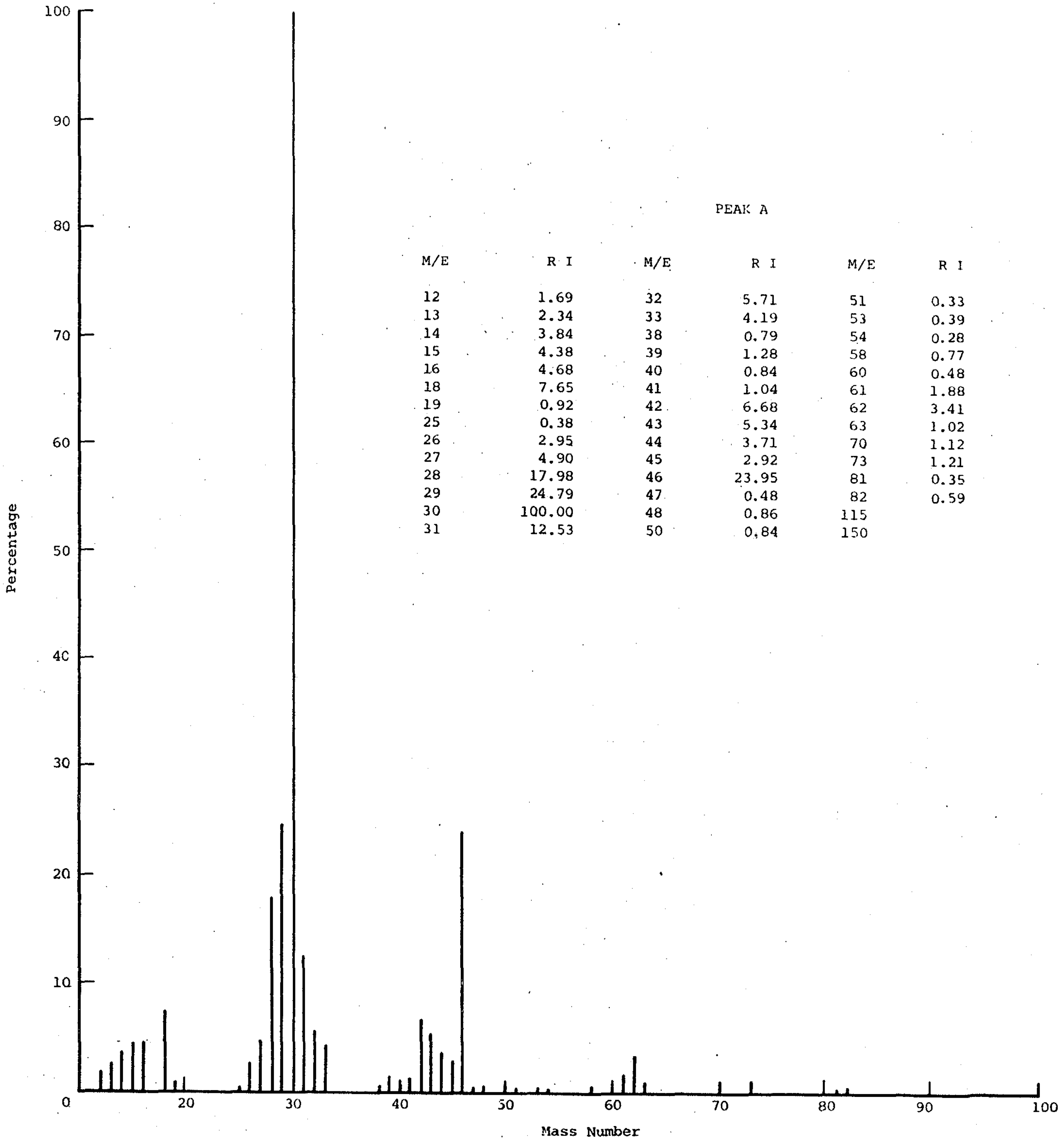


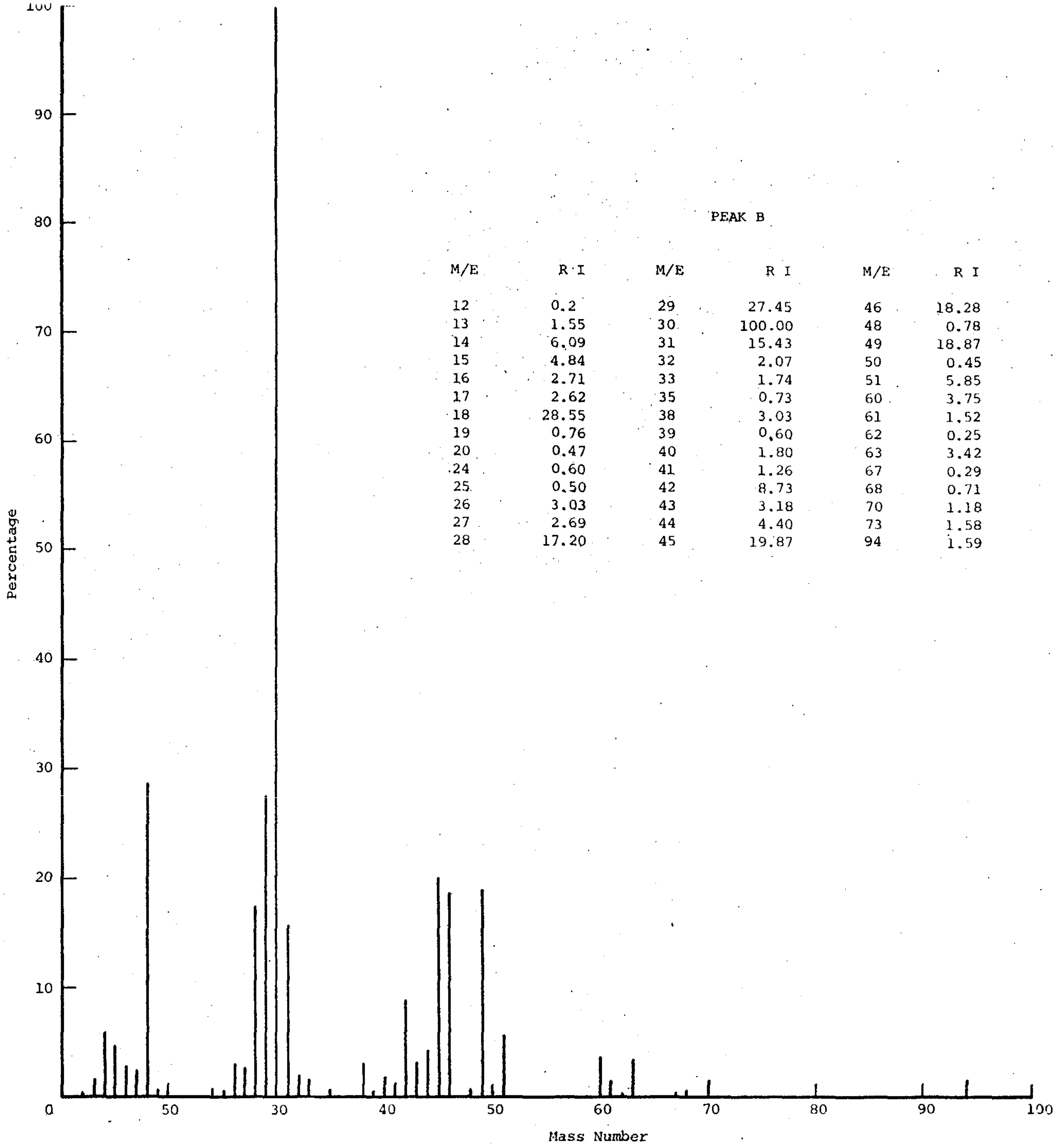
Fig. 3. Chromatogram of High Boiling Impurity Removed on Hexane Wash



PEAK A

M/E	R I	M/E	R I	M/E	R I
12	1.69	32	5.71	51	0.33
13	2.34	33	4.19	53	0.39
14	3.84	38	0.79	54	0.28
15	4.38	39	1.28	58	0.77
16	4.68	40	0.84	60	0.48
18	7.65	41	1.04	61	1.88
19	0.92	42	6.68	62	3.41
25	0.38	43	5.34	63	1.02
26	2.95	44	3.71	70	1.12
27	4.90	45	2.92	73	1.21
28	17.98	46	23.95	81	0.35
29	24.79	47	0.48	82	0.59
30	100.00	48	0.86	115	
31	12.53	50	0,84	150	

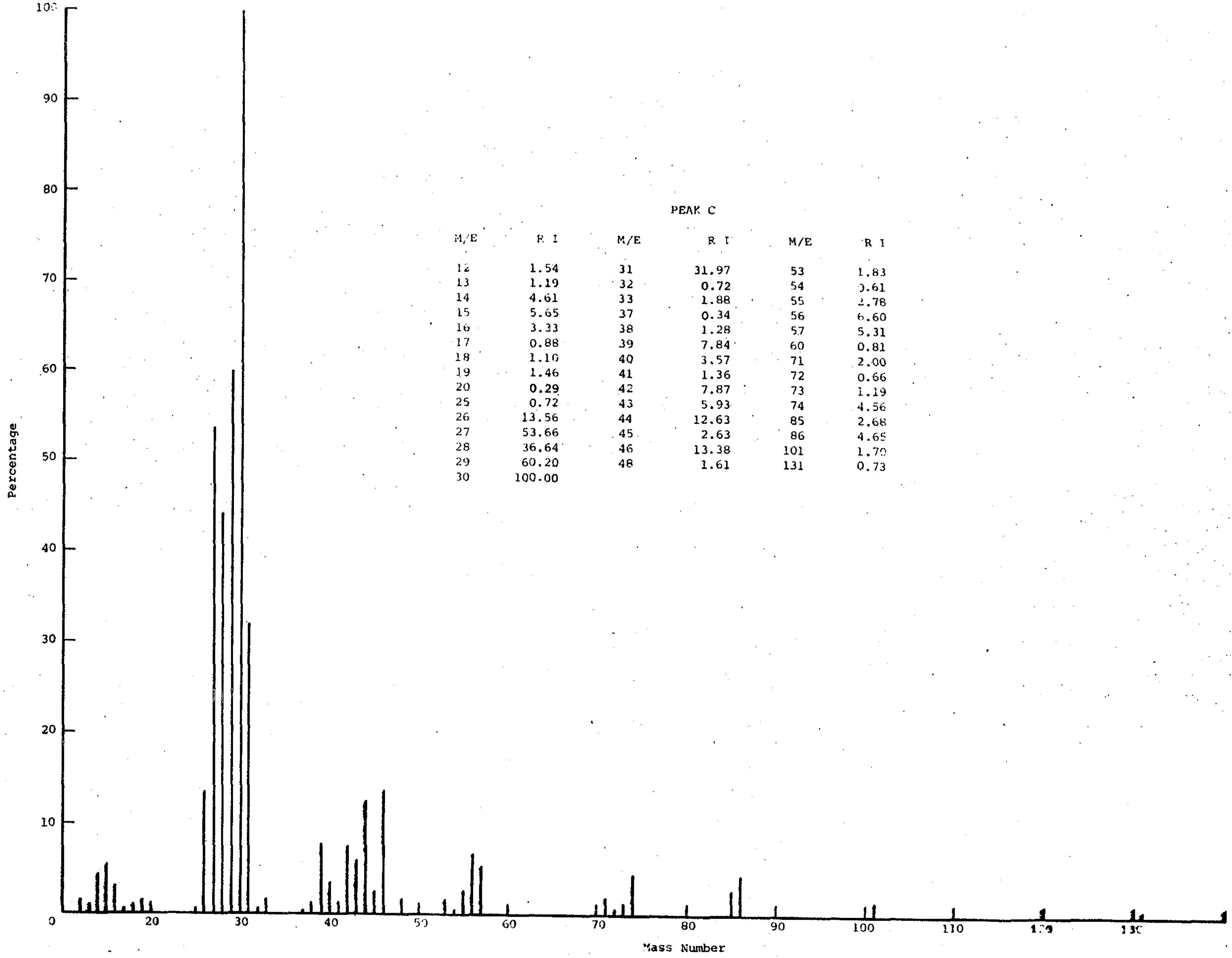
Fig. 4. Mass Spectrum at First Low Boiling Impurity Peak A on Chromatogram of



PEAK B

M/E	R·I	M/E	R I	M/E	R I
12	0.2	29	27.45	46	18.28
13	1.55	30	100.00	48	0.78
14	6.09	31	15.43	49	18.87
15	4.84	32	2.07	50	0.45
16	2.71	33	1.74	51	5.85
17	2.62	35	0.73	60	3.75
18	28.55	38	3.03	61	1.52
19	0.76	39	0.60	62	0.25
20	0.47	40	1.80	63	3.42
24	0.60	41	1.26	67	0.29
25	0.50	42	8.73	68	0.71
26	3.03	43	3.18	70	1.18
27	2.69	44	4.40	73	1.58
28	17.20	45	19.87	94	1.59

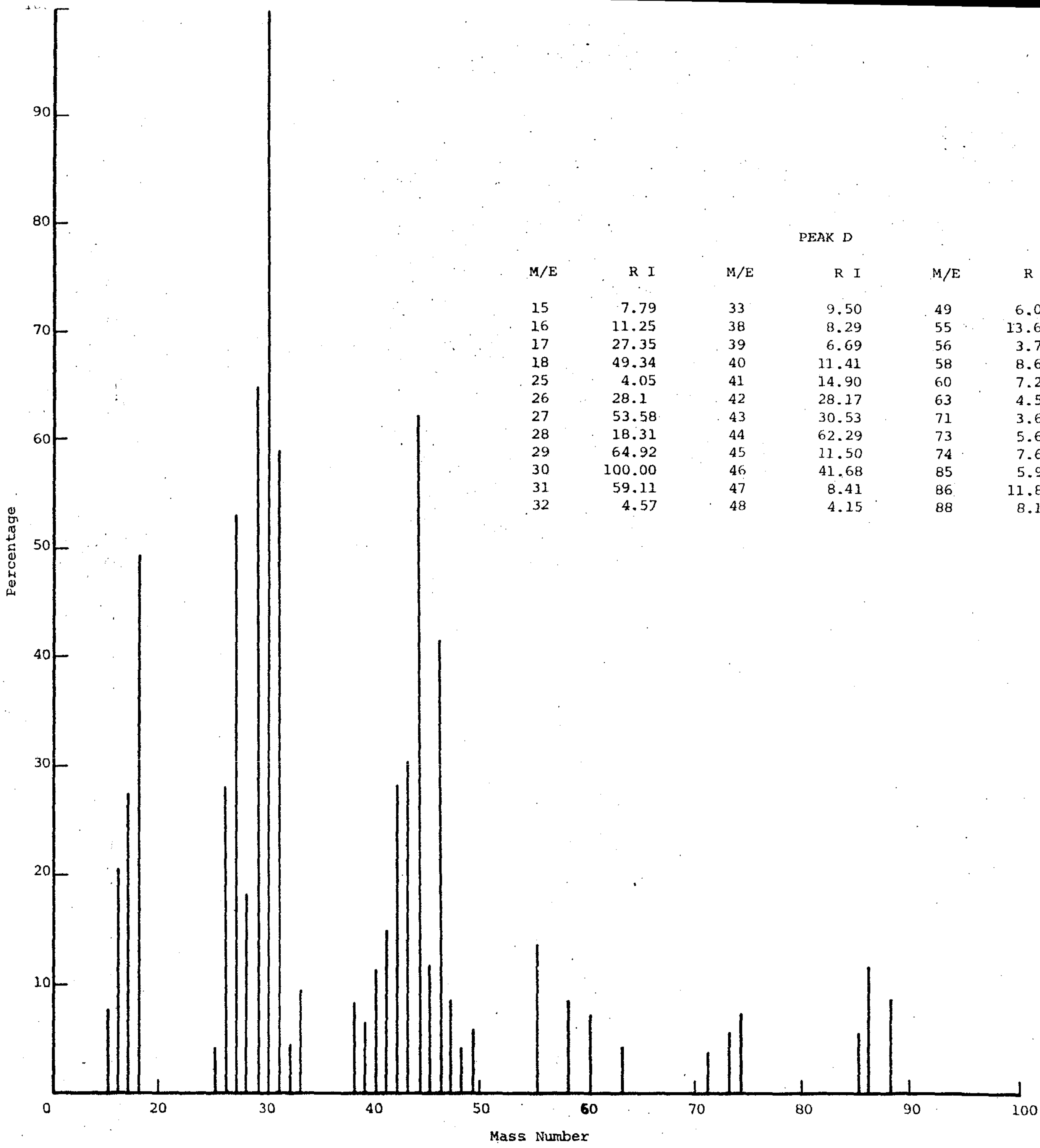
Fig. 5. Mass Spectrum of Second Low Boiling Impurity Peak B in Chromatogram of FEFO



PEAK C

M/E	R I	M/E	R I	M/E	R I
12	1.54	31	31.97	53	1.83
13	1.19	32	0.72	54	0.61
14	4.61	33	1.88	55	2.78
15	5.65	37	0.34	56	6.60
16	3.33	38	1.28	57	5.31
17	0.88	39	7.84	60	0.81
18	1.10	40	3.57	71	2.00
19	1.46	41	1.36	72	0.66
20	0.29	42	7.87	73	1.19
25	0.72	43	5.93	74	4.56
26	13.56	44	12.63	85	2.68
27	53.66	45	2.63	86	4.65
28	36.64	46	13.38	101	1.70
29	60.20	48	1.61	131	0.73
30	100.00				

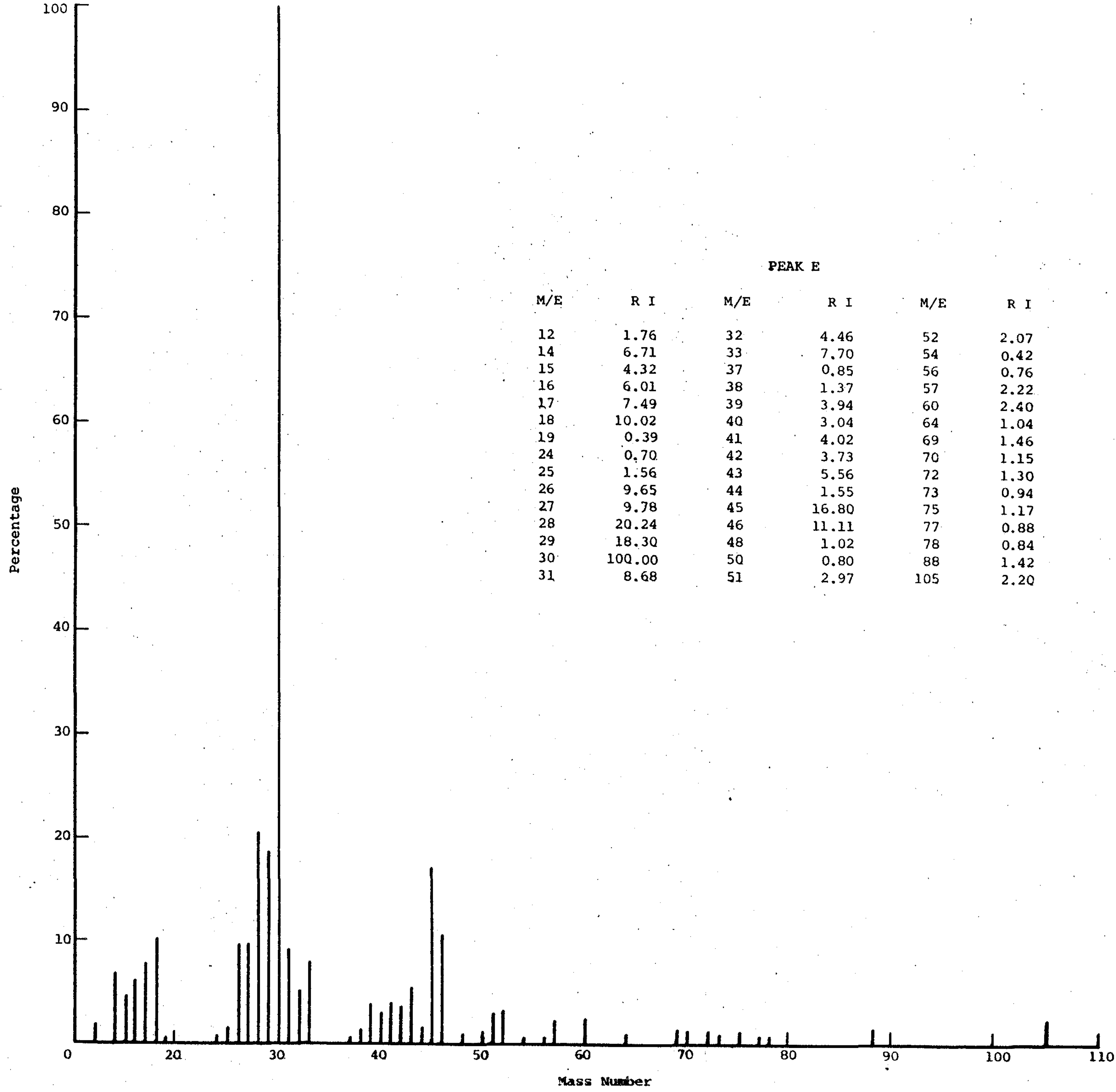
Fig. 6. Mass Spectrum of Low Boiling Impurity Peak C in Chromatogram of FEFO



PEAK D

M/E	R I	M/E	R I	M/E	R I
15	7.79	33	9.50	49	6.04
16	11.25	38	8.29	55	13.65
17	27.35	39	6.69	56	3.79
18	49.34	40	11.41	58	8.65
25	4.05	41	14.90	60	7.24
26	28.1	42	28.17	63	4.55
27	53.58	43	30.53	71	3.60
28	18.31	44	62.29	73	5.66
29	64.92	45	11.50	74	7.66
30	100.00	46	41.68	85	5.96
31	59.11	47	8.41	86	11.88
32	4.57	48	4.15	88	8.11

Fig. 7. Mass Spectrum of Low Boiling Impurities Peak D in Chromatogram of FEFO



PEAK E

M/E	R I	M/E	R I	M/E	R I
12	1.76	32	4.46	52	2.07
14	6.71	33	7.70	54	0.42
15	4.32	37	0.85	56	0.76
16	6.01	38	1.37	57	2.22
17	7.49	39	3.94	60	2.40
18	10.02	40	3.04	64	1.04
19	0.39	41	4.02	69	1.46
24	0.70	42	3.73	70	1.15
25	1.56	43	5.56	72	1.30
26	9.65	44	1.55	73	0.94
27	9.78	45	16.80	75	1.17
28	20.24	46	11.11	77	0.88
29	18.30	48	1.02	78	0.84
30	100.00	50	0.80	88	1.42
31	8.68	51	2.97	105	2.20

Fig. 8. Mass Spectrum of Low Boiling Impurities Peak E in Chromatogram of FEFO

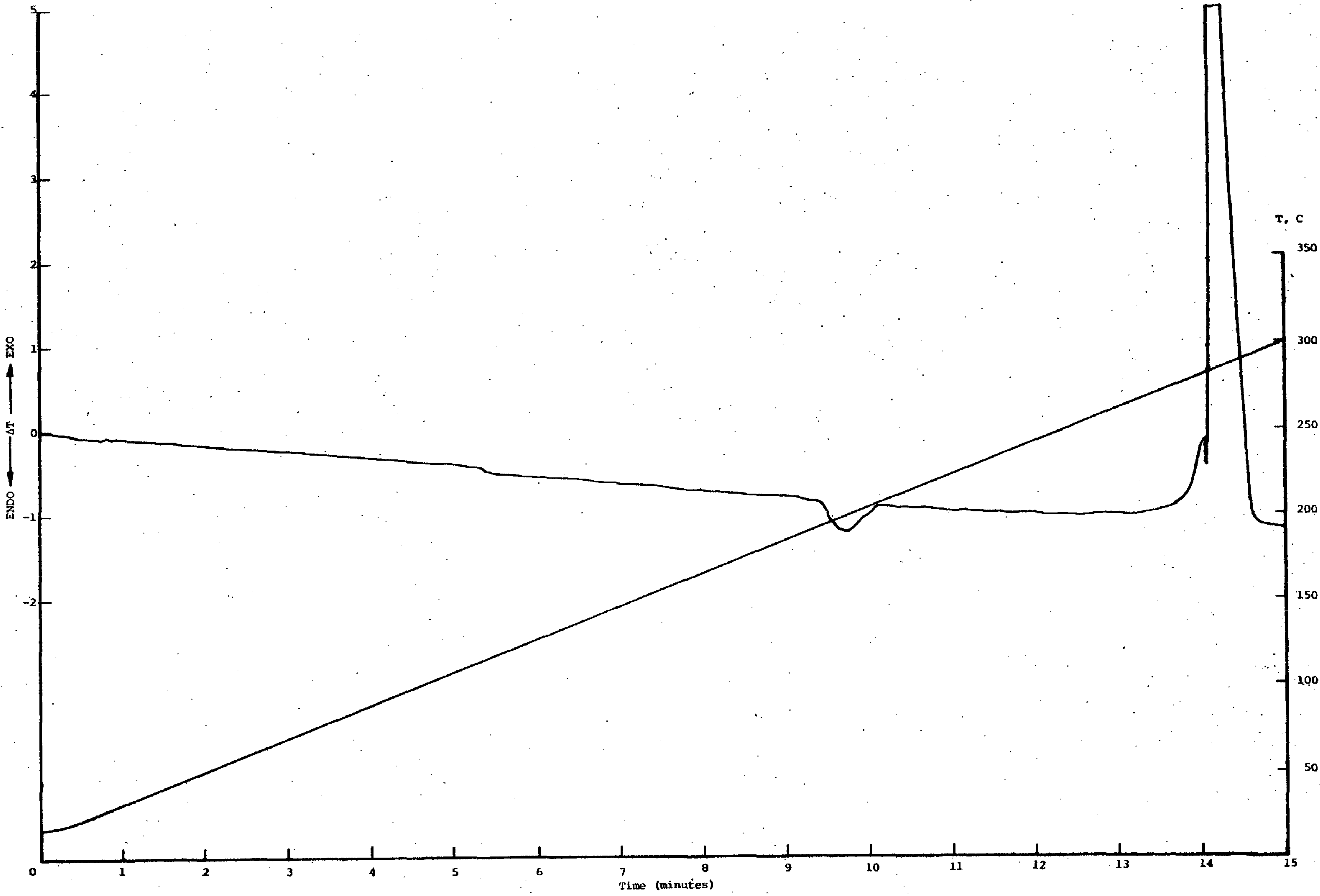


Fig. 9. DTA of HMX at 15 psi of N_2 Heating Rate 10 C/min

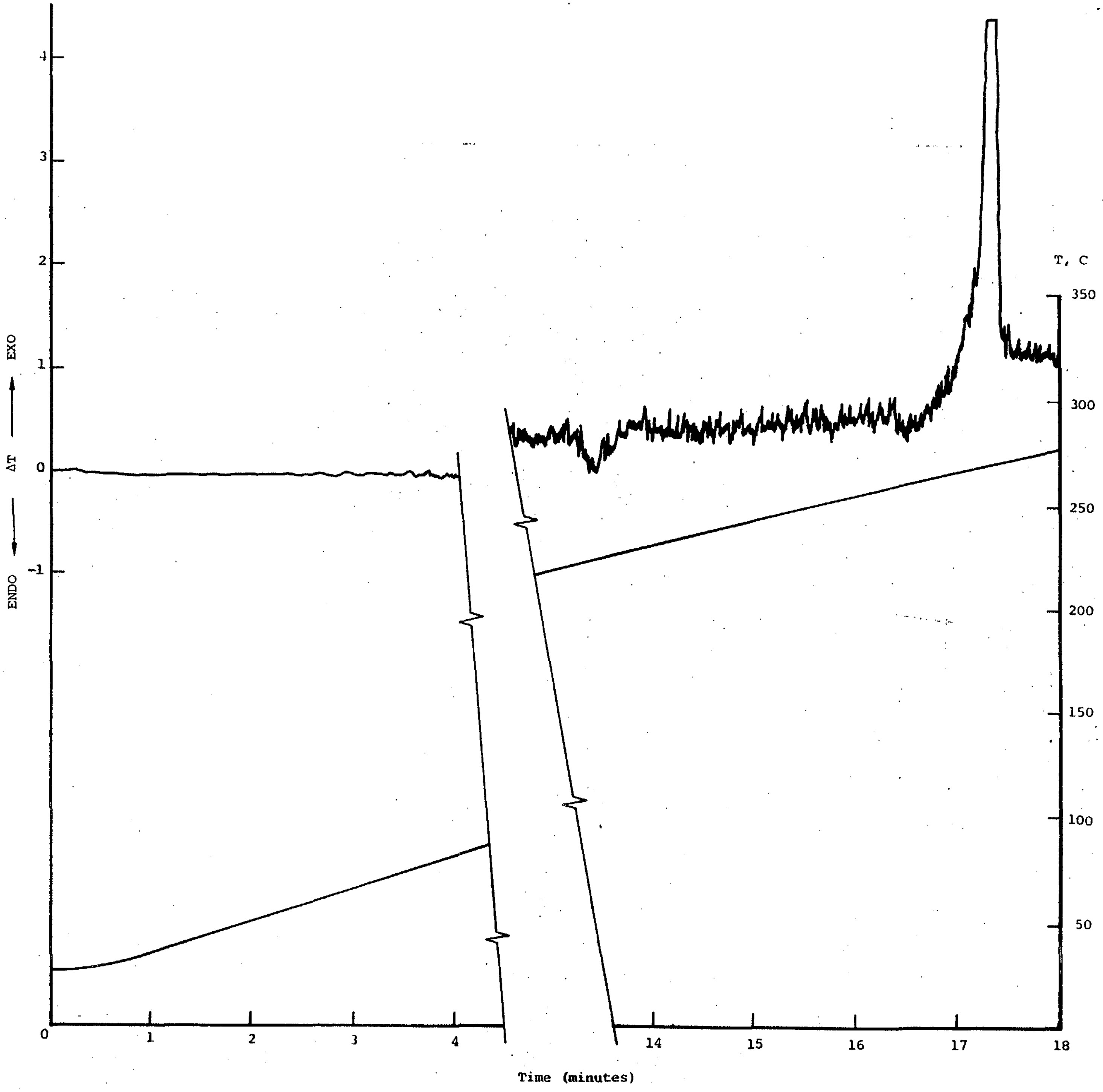


Fig. 10. DTA of HMX at 10,000 psi of N_2 Heating Rate 100 C/min

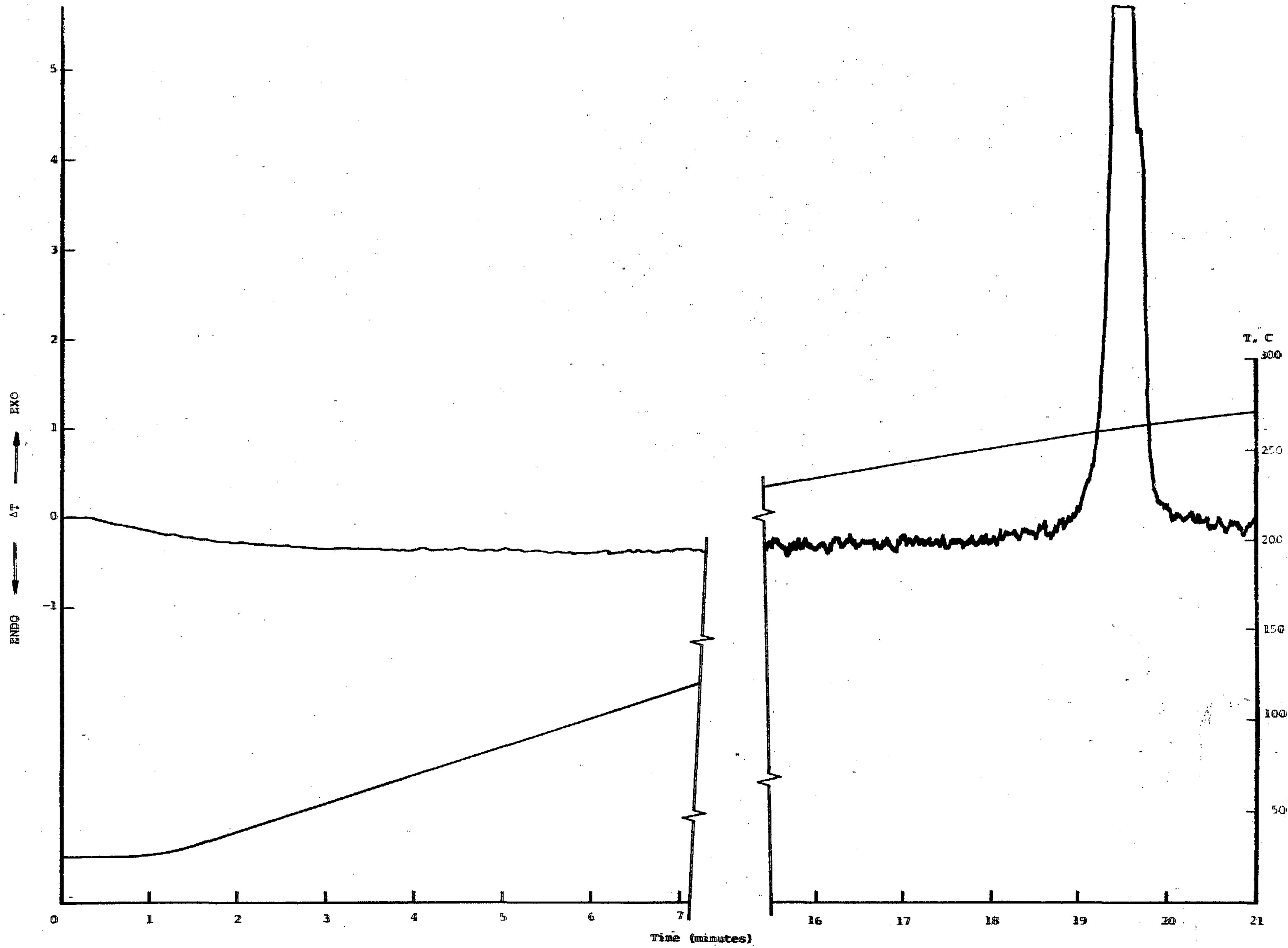


Fig. 11. DTA of HMX at 30,000 psi of N_2 Heating Rate 100 C/min

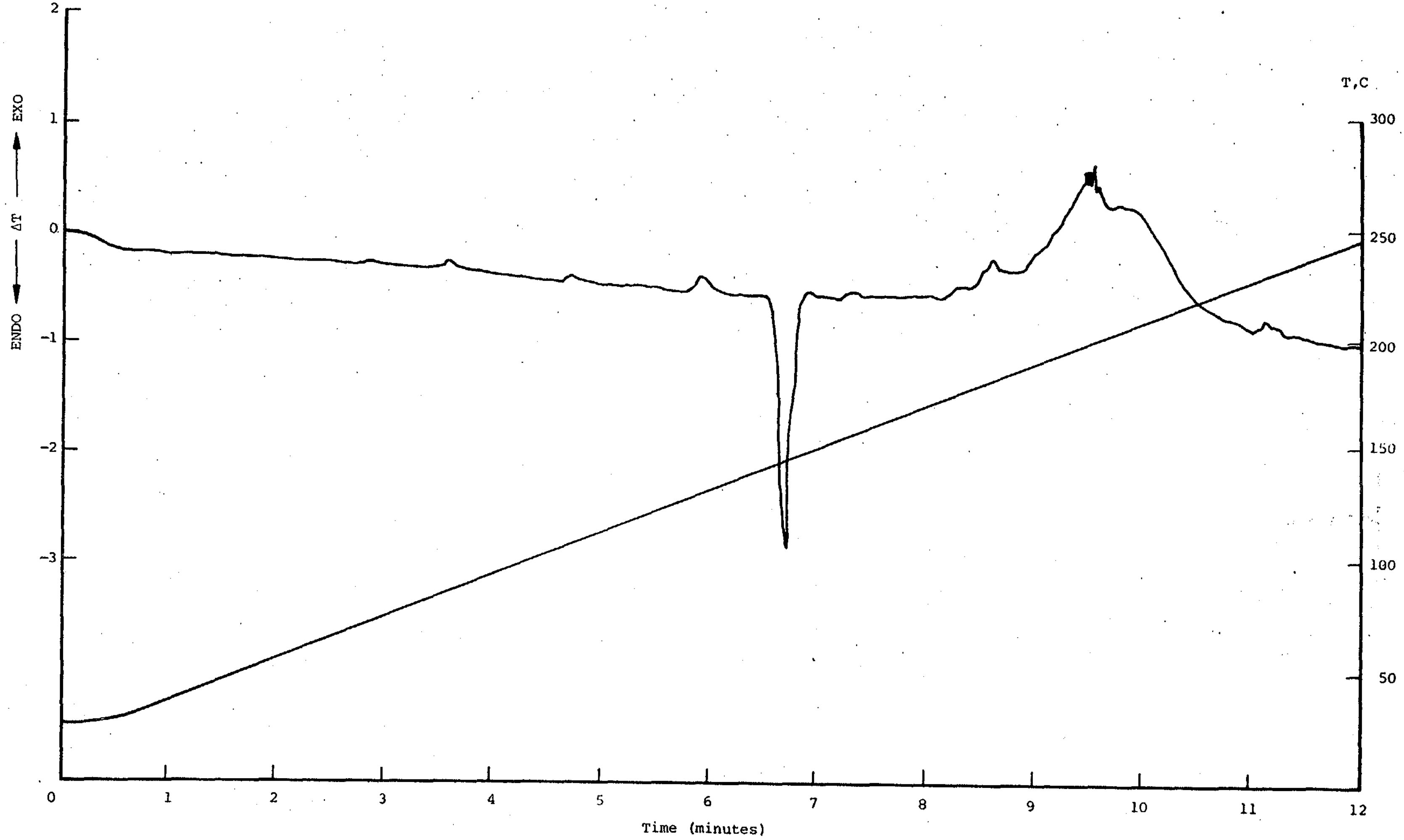


Fig. 12. DTA of PETN at 15 psi of N_2 Heating Rate 10 C/min

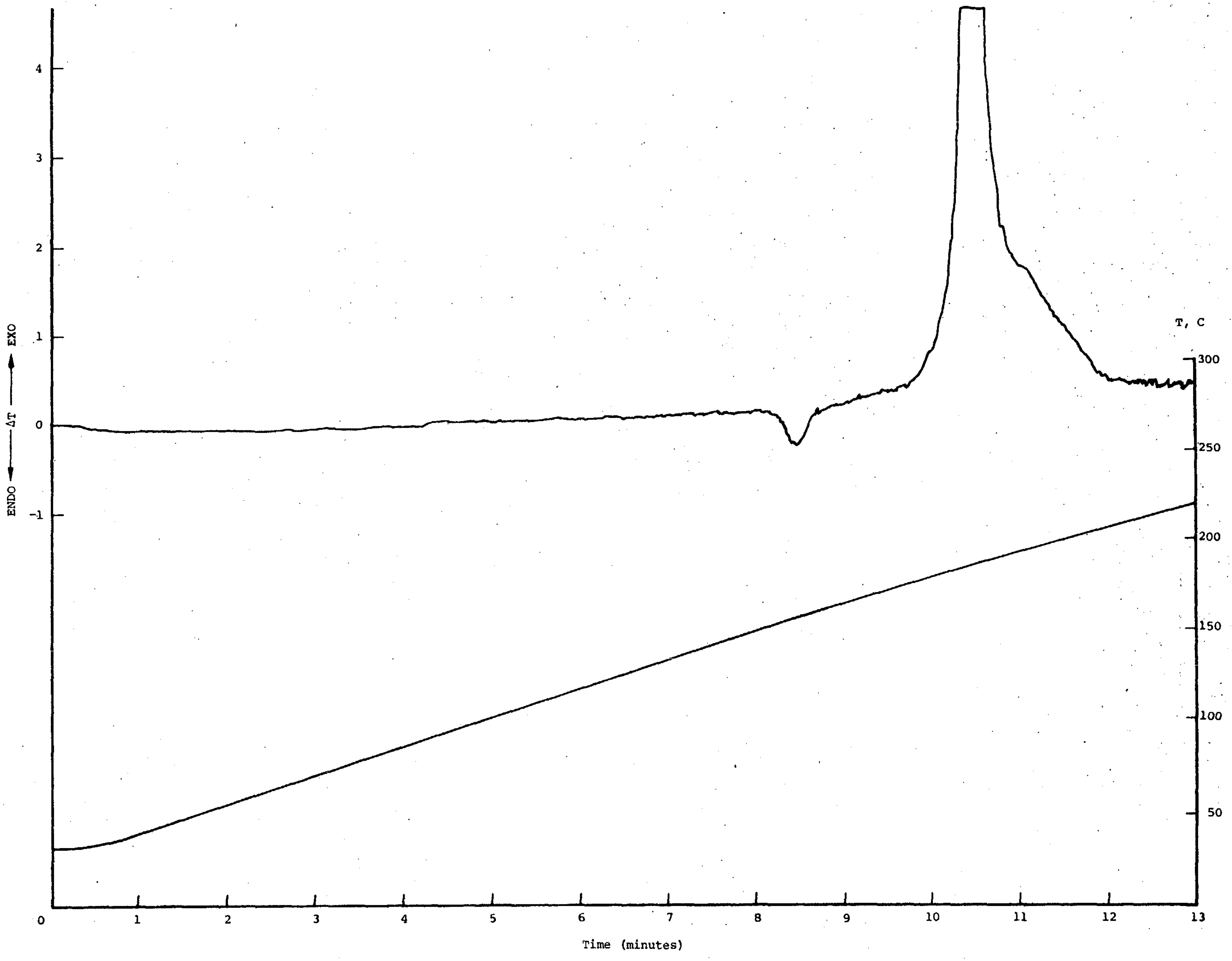


Fig. 13. DTA of PETN at 10,000 psi of N_2 Heating Rate 10 C/min

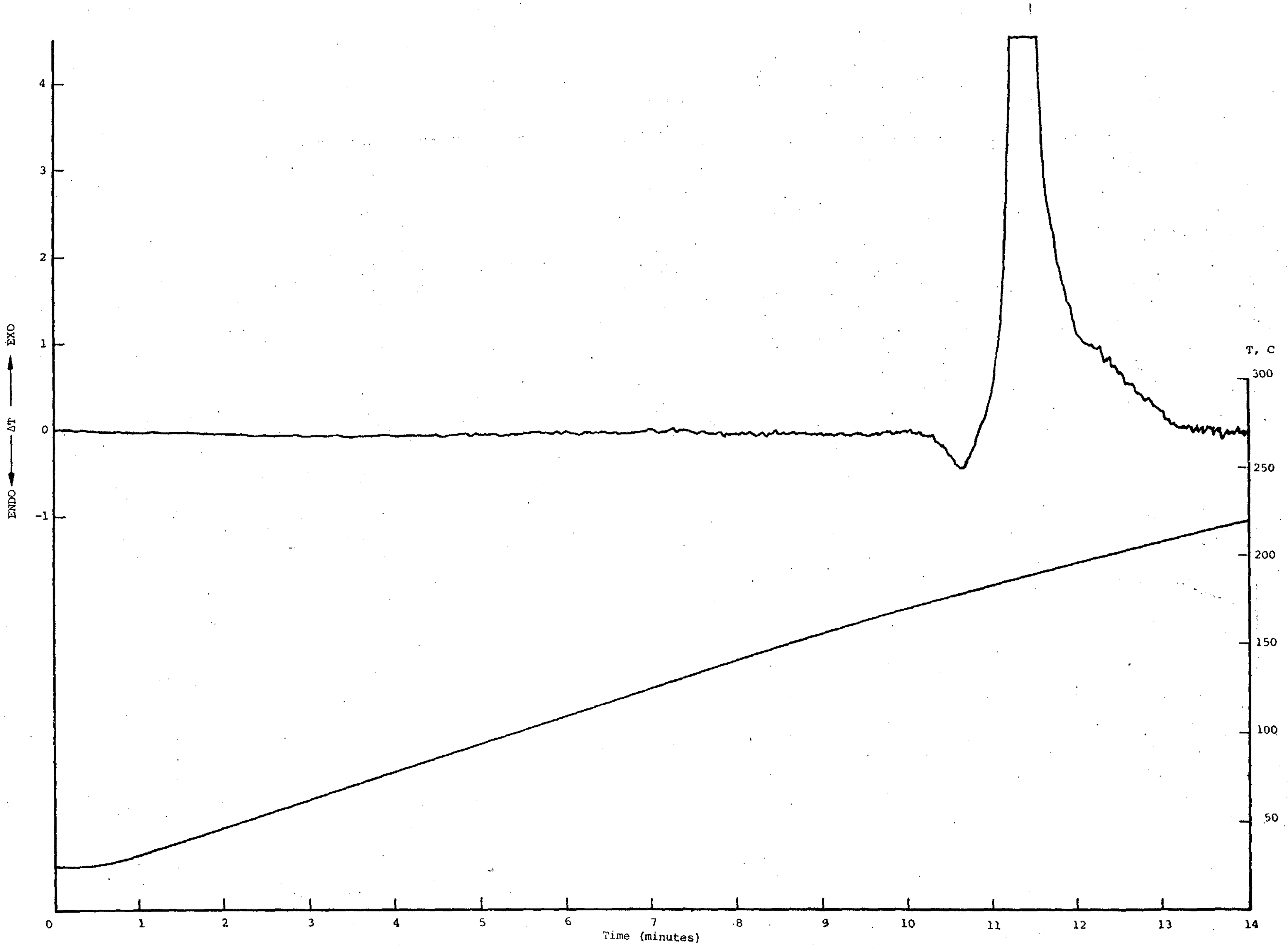


Fig. 14. DTA of PETN at 30,000 psi of N_2 Heating Rate 10 C/min

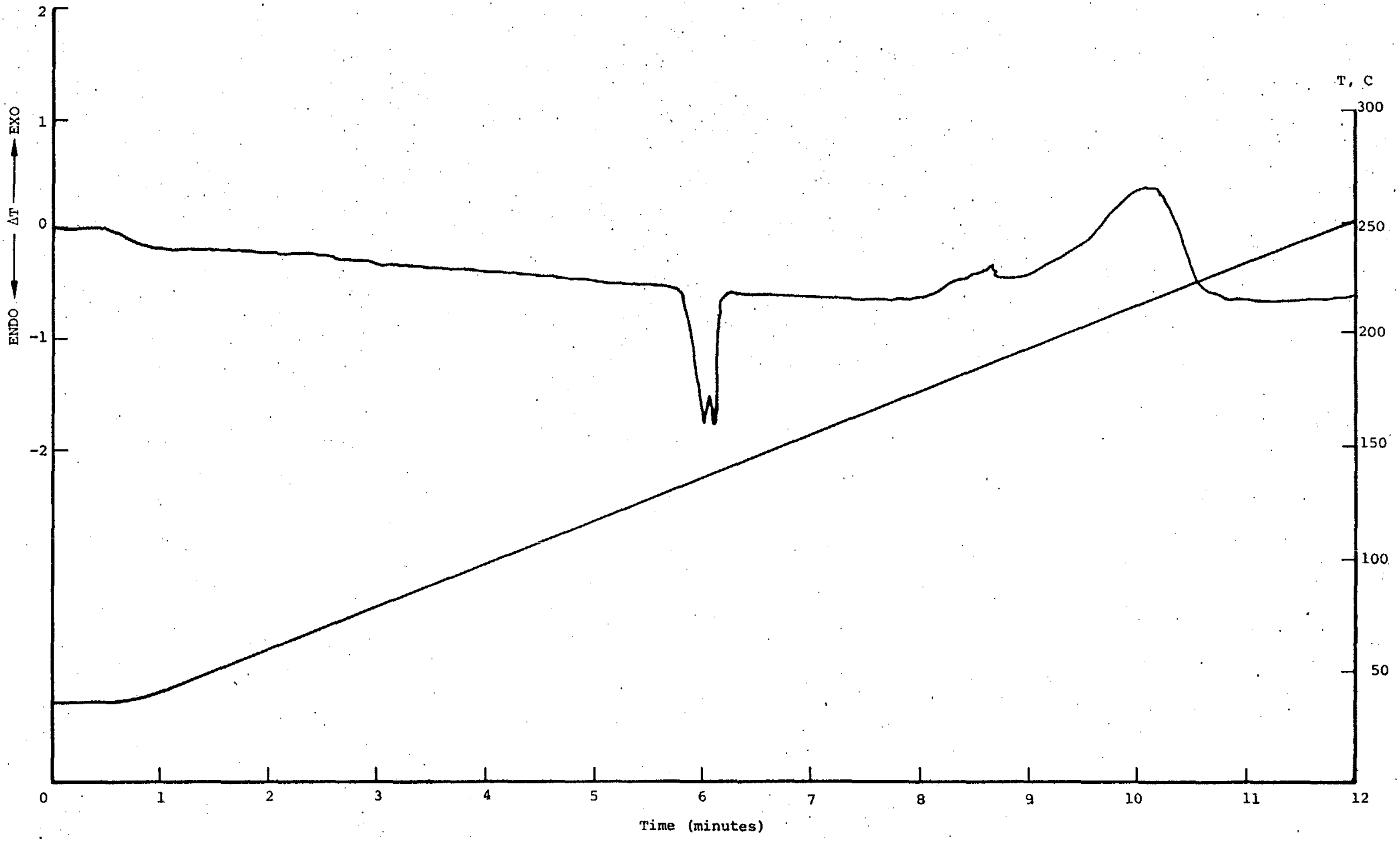


Fig. 15. DTA of Tetryl at 15 psi of N_2 Heating Rate 10 C/min

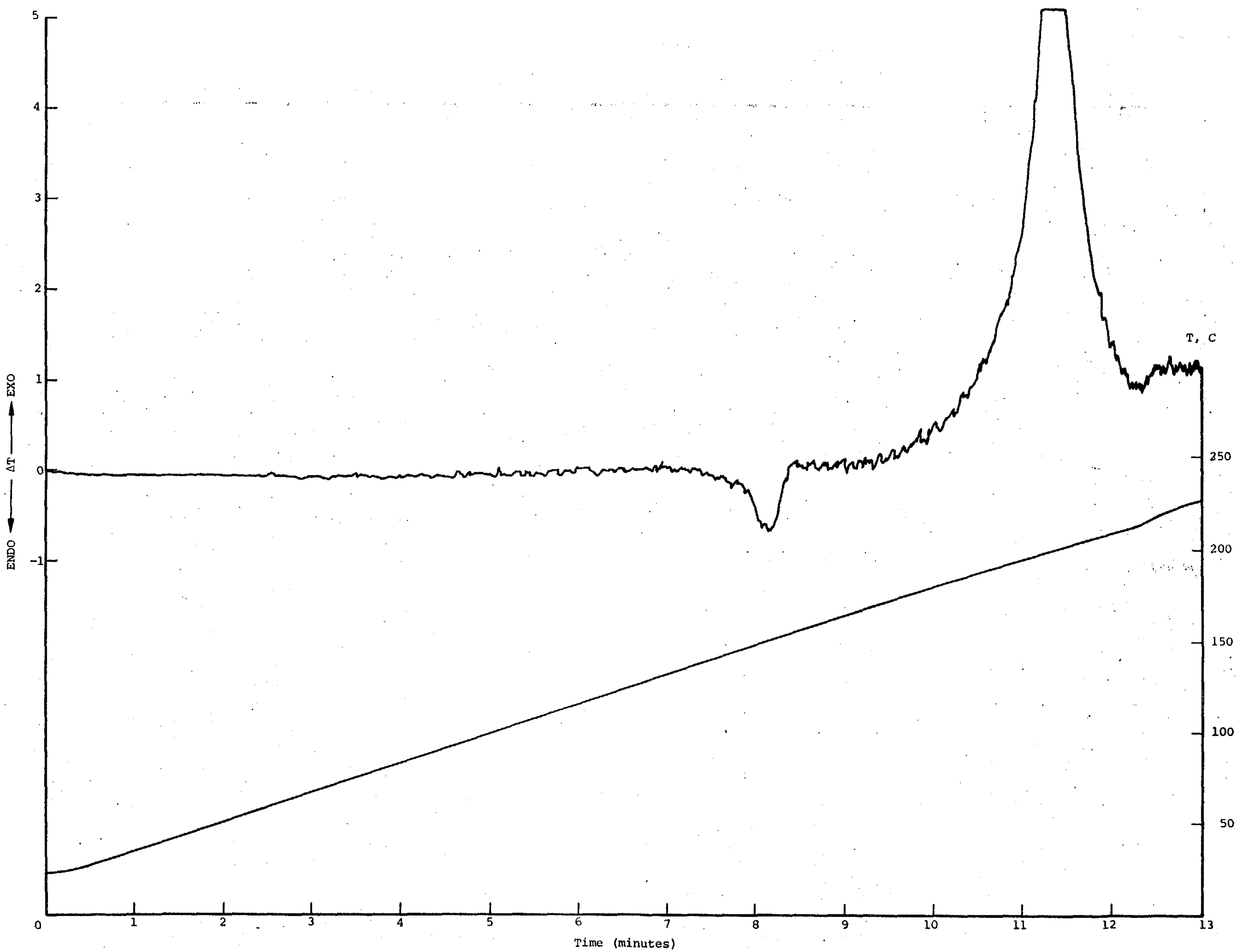


Fig. 16. DTA of Tetryl 10,000 psi of N_2 Heating Rate 10 C/min

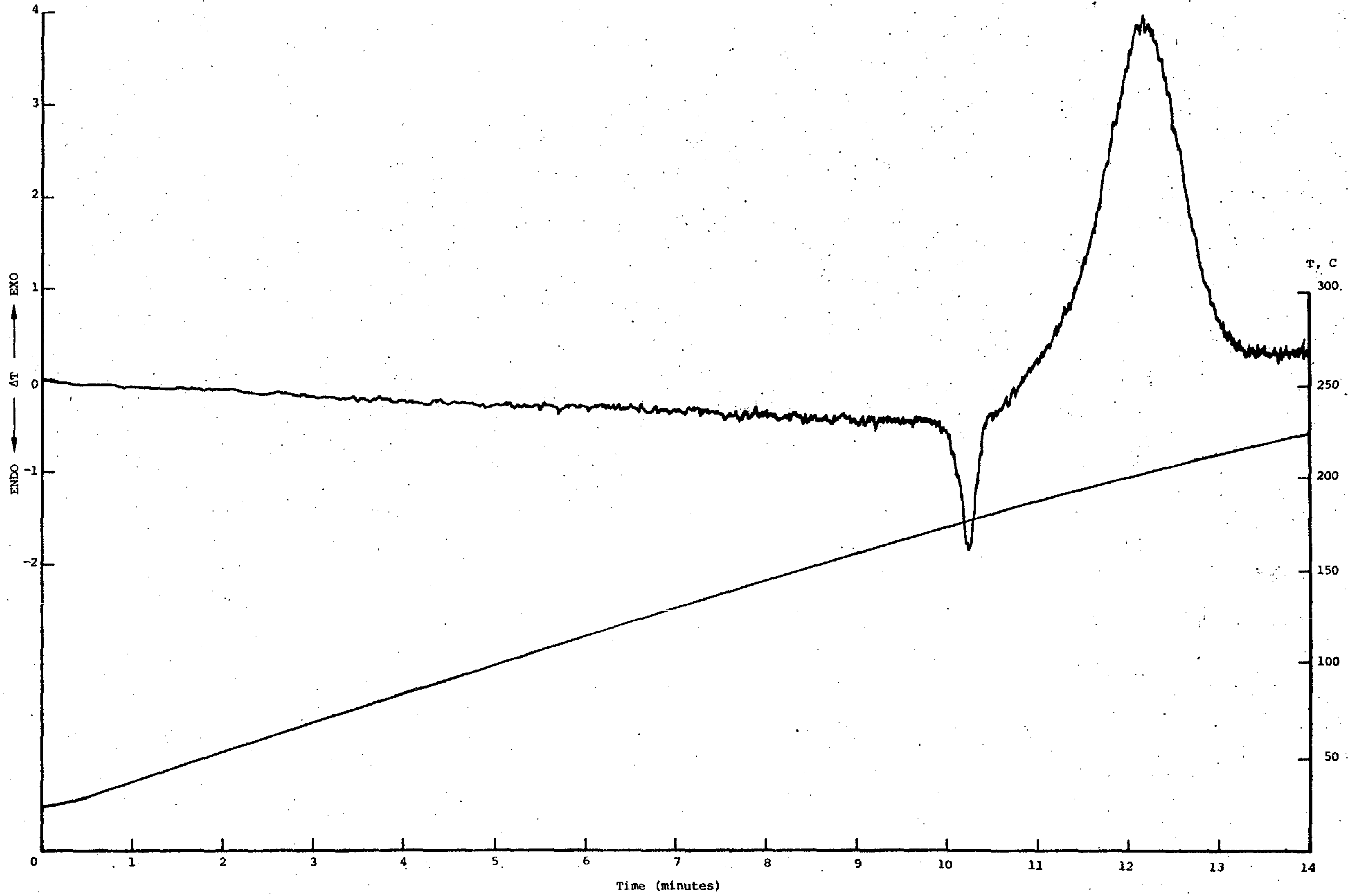


Fig. 17. DTA of Tetryl at 30,000 psi of N Heating Rate 100 C/min

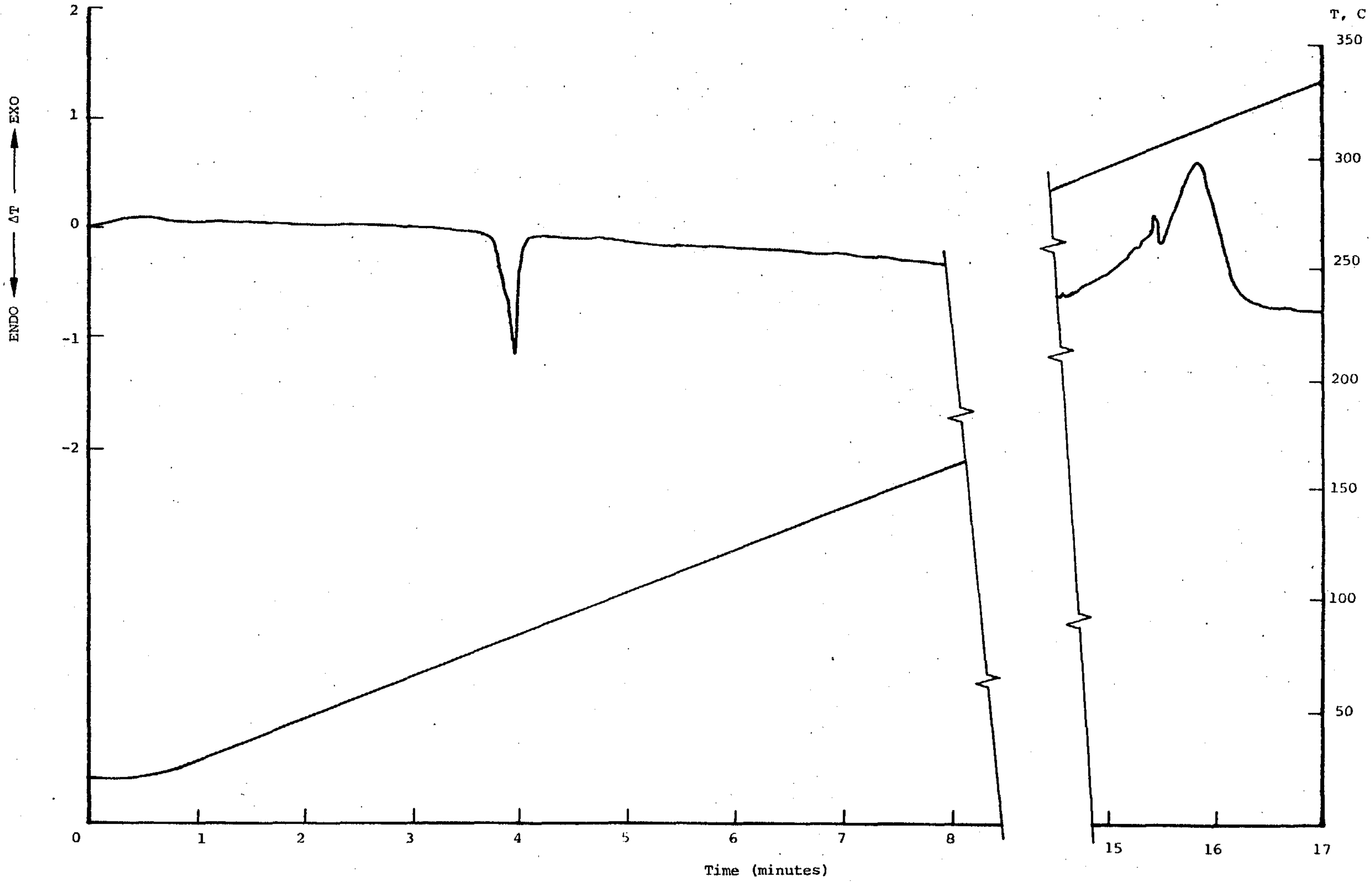


Fig. 18. DTA of TNT at 15 psi of N_2 Heating Rate 100 C/min

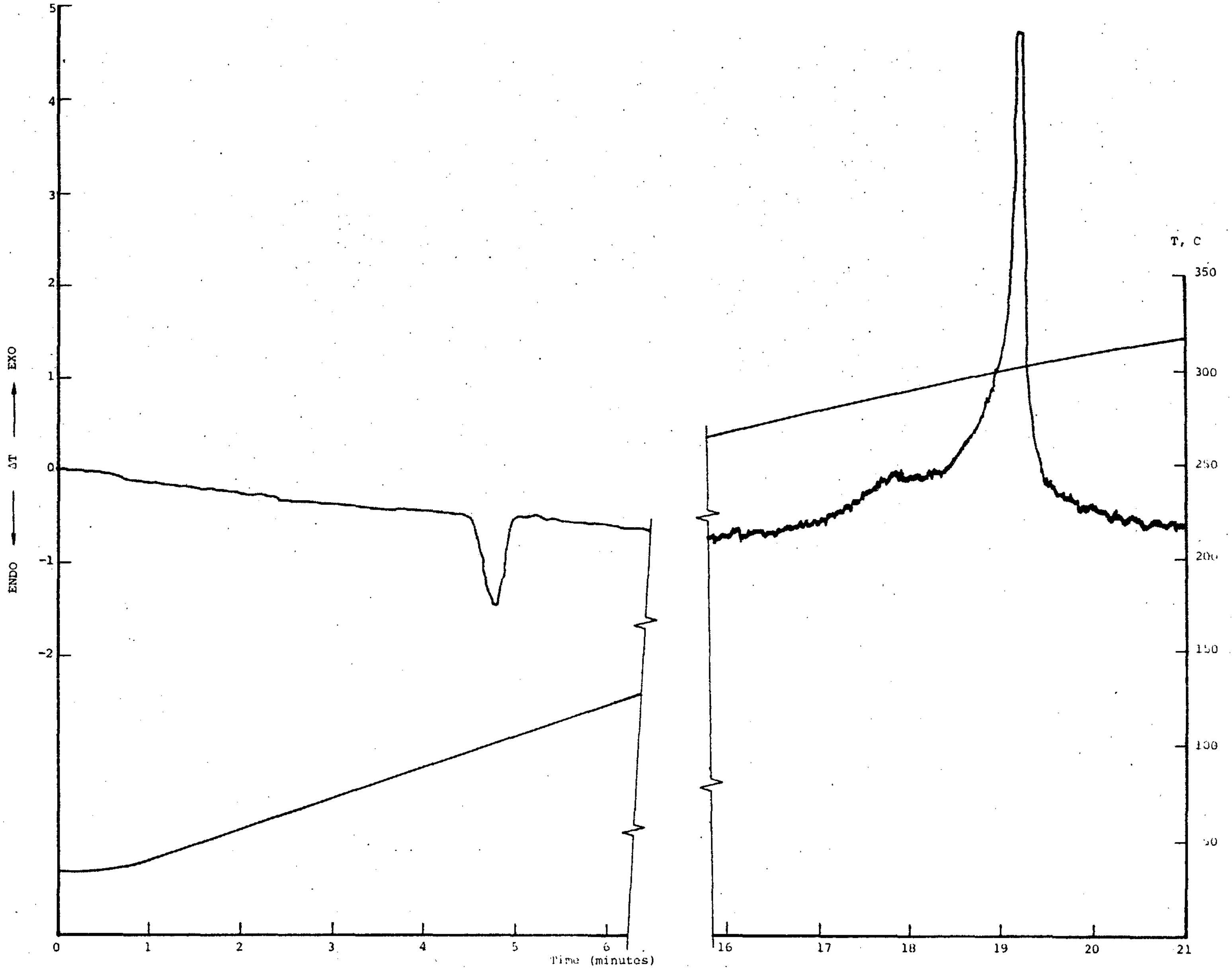


Fig. 19. DTA of TNT at 10,000 psi of N_2 Heating Rate 100 C/min

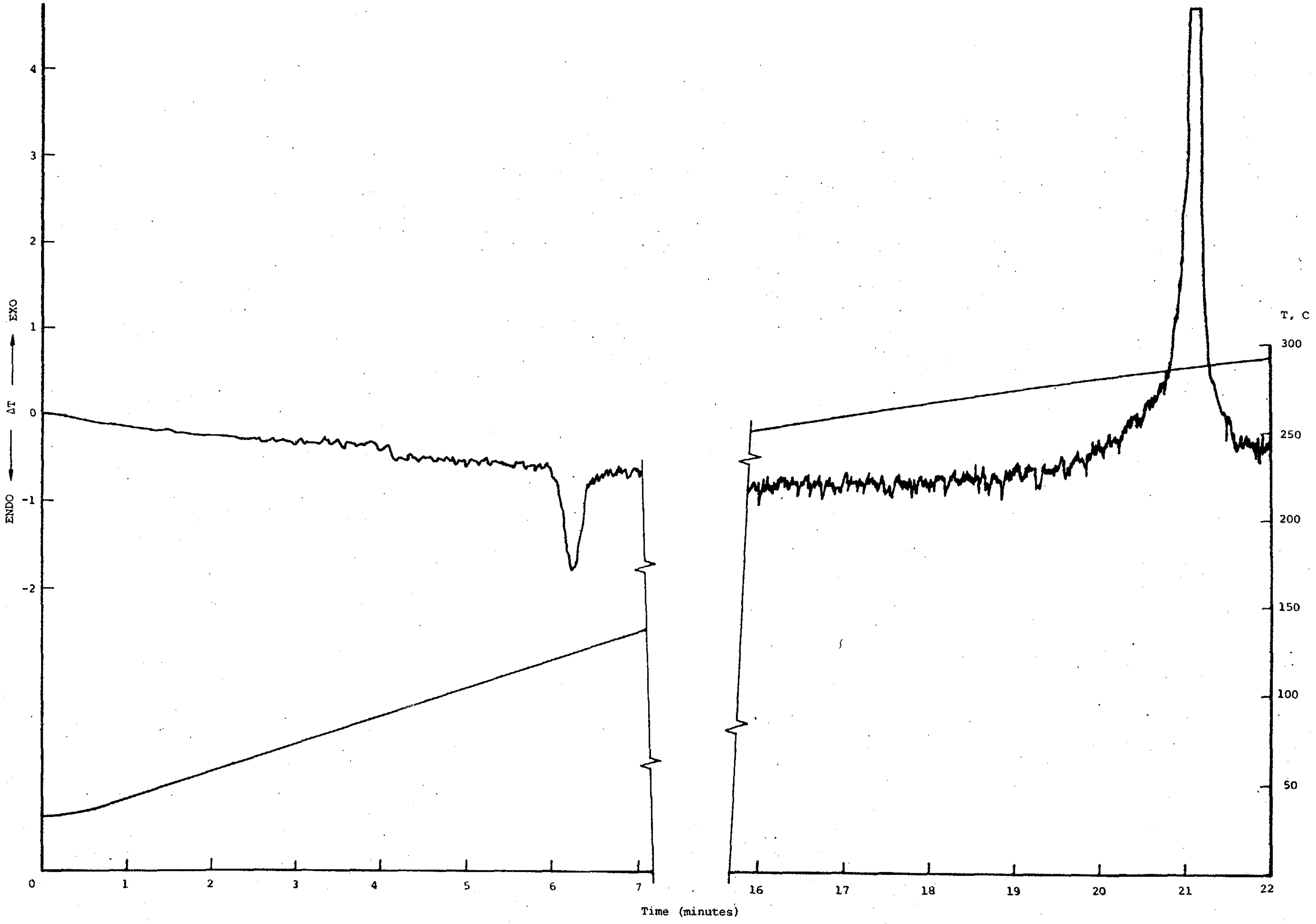


Fig. 20. DTA of TNT at 30,000 psi of N_2 Heating Rate 10°C/min