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THERMAL PROPERTIES AND CHEMICAL REACTIVITY

L. C. Myers

DEVELOPMENT DIVISION

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Section B

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THERMAL PROPERTIES AND CHEMICAL REACTIVITY

ABSTRACT

A very high boiling impurity was concentrated from a sample of FEFO with a hexane wash. Additional washing of this sample has increased the concentration of this impurity. A mass spectrum was obtained but an identification has not been made.

The results of the analysis of the products from the thermal decomposition of FEFO at 120, 135, and 150 C are discussed. A chromatogram of FEFO heated for 22 hours at 150 C shows a definite increase in low and high boiling impurities.

The evaluation of the condition of the two coupon test assemblies aged at 80 C for 21 and 27 months are discussed. Thermal analysis of the LX-09 from these two coupon tests, a PASS A mechanical test specimen and a control sample are reported.

A PDP-12/30 was interfaced with a Perkin Elmer DSC-1 to measure the heat of fusion of PETN. Some of the problems associated with getting reproducible data are discussed. The heat of fusion for six lots of LX-13 grade PETN are given.

FEFO STUDIES

IMPURITIES

Last quarter mass spectra were reported for five of the low boiling impurities found in a sample of FEFO. Some attempts have been made to identify these impurities but no great effort has gone into this because Pantex's high resolution mass spectrometer will be operational in the near future—probably the first part of next quarter.

Also, last quarter it was reported that the extracted percentage of one of the high boiling impurities in FEFO could be increased by washing a sample of impure FEFO with hexane. This impurity was more soluble in hexane than FEFO or the other impurities. Therefore, a sample was obtained with a larger percentage of impurity. During this quarter some tests were made to determine if another solvent could be used to obtain higher concentration of this impurity.

Ether proved to be the most successful. Figs. 1 and 2 show the chromatograms and the changes in concentration of the impurities resulting from hexane and ether washes. It is estimated that the sample obtained with hexane had about 50% of the very high boiling impurity and the ether wash resulted in a sample with 80% or more.

A rather poor spectrum of the very high boiling impurity was obtained using the direct inlet probe on the TOF mass spectrometer, but as was expected, there was

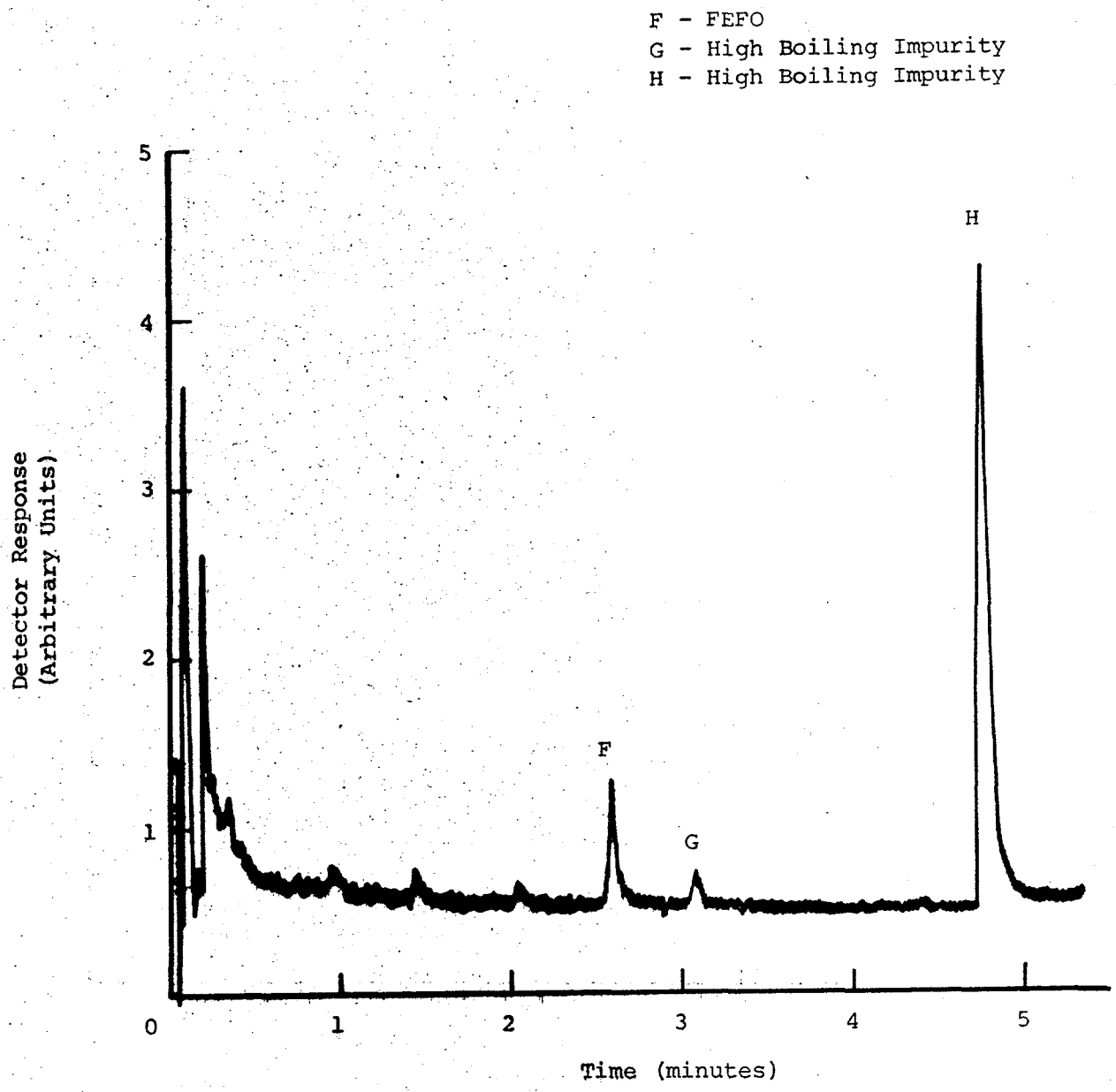

Fig. 1. Chromatogram of High Boiling Impurity Removed on Hexane Wash

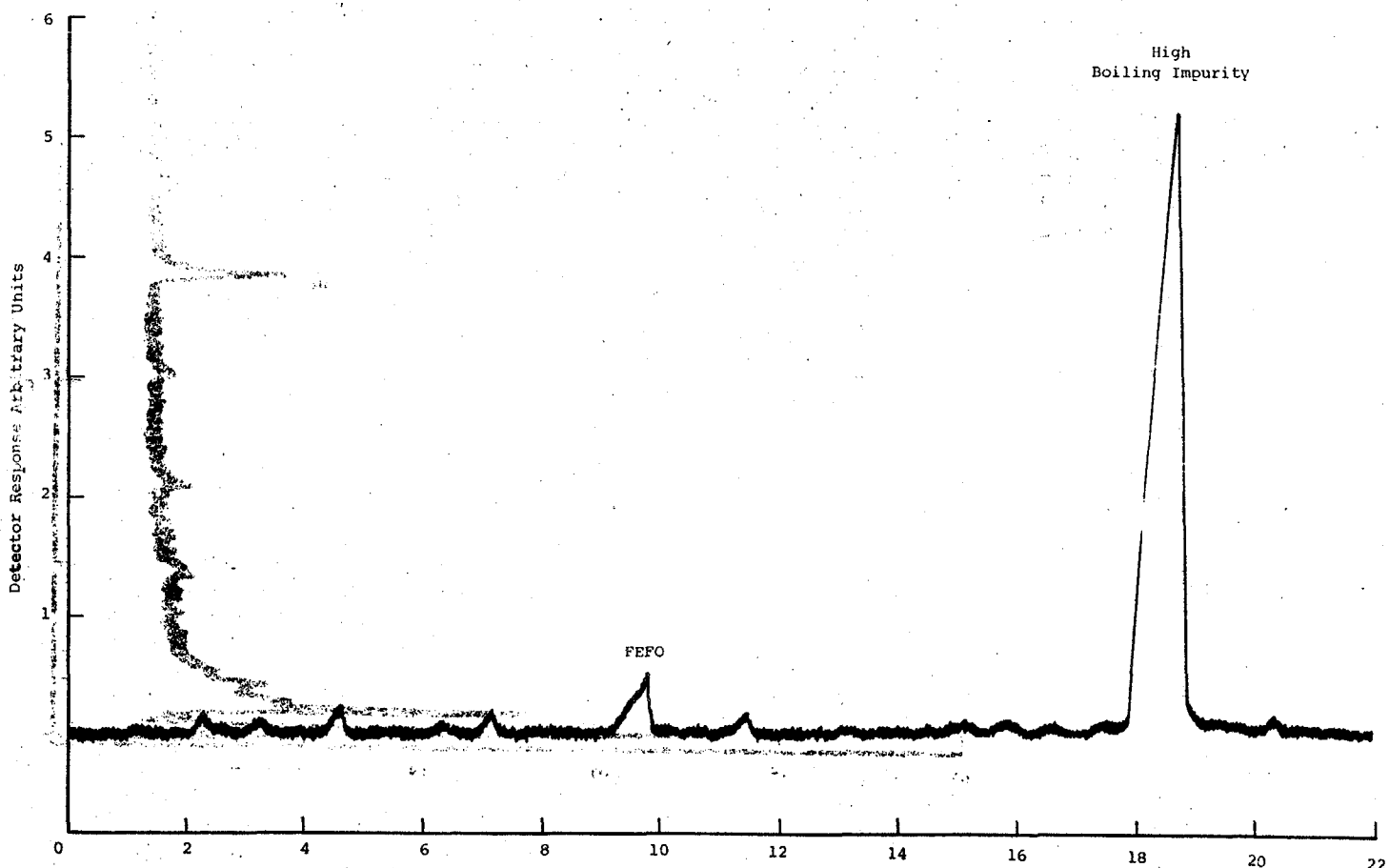

Fig. 2. Chromatogram of the material removed with an ether wash from a FEFO sample

no similar spectra in the mass spectrometer index(*1,2*) so an identification has not been made. Because the high resolution mass spectrometer will be in operation in the near future no great effort has been made to identify this compound from the low resolution mass spectra. It will be run in the high resolution instrument as soon as possible.

THERMAL DECOMPOSITION

A study was initiated this quarter to obtain information about the thermal decomposition of FEFO. The chemical reactivity sample holders were used with glass crucibles and standard size samples (0.250 g). The samples were conditioned at 120, 135 and 150 C for varying periods of time. It was determined that the rate was much too fast at 150 C, and runs at this temperature were discontinued.

Table I gives the analysis of the decomposition gases from FEFO at 120 C and 135 C and Figs. 3 - 7 are graphs of these products as a function of time. There is some scatter in the data but if it is represented by a linear fit then decomposition rates can be determined. A linear relation between the products and time can be expected since the change in the concentration of FEFO at these times and temperatures is essentially zero. From these graphs the decomposition rates were determined and are given in Table II.

More testing will be done at other temperatures to determine if these assumptions (decomposition rates) are true. Tests will also be run in stainless steel crucibles rather than glass to determine what effects this will have on the decomposition products and rates.

Some preliminary runs were made by gas chromatography on the FEFO after the thermal conditioning discussed above. The samples conditioned for the shorter times showed no noticeable changes in their chromatograms but there were two changes in those conditioned for the longer times. First a small peak appeared on the leading edge of the FEFO peak. This can be seen by comparing the chromatograms (Figs. 8 - 9). Fig. 10 is chromatogram of the same sample but the columns were heated at 4 C/min instead of 10 C/min and this small peak is more pronounced.

Secondly, the chromatograms (Figs. 11 and 12) of the FEFO sample before and after conditioning at 150 C for 22 hours show a definite increase on the amount of impurities, both low and high boilers. Therefore, the impurities are thermal decomposition products.

These data indicate that part of the thermal decomposition products are not volatile. Also, the retention times of the decomposition products appear to correspond to the retention time of the impurities observed in other studies.

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

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

Table I. Analysis of Thermal Decomposition Projects from .250 gm of FEFO

(Gas volumes in microliters corrected to STP)

120 C

Time	N_2	CO	NO	CO_2	N_2O	Total
7 hrs	15.4	.56	2.11	10.6	1.40	30.1
7 hrs	4.97	.894	8.77	6.54	1.21	22.4
22 hrs	22.8	5.72	29.9	21.9	9.34	89.7
22 hrs	40.16	2.88	12.0	20.4	4.08	79.5
22 hrs	18.2	3.54	25.8	21.4	4.93	73.8
46 hrs	29.4	8.05	48.5	31.6	8.54	126.1
46 hrs	28.6	7.01	47.7	38.2	9.43	130.9
70 hrs	56.6	17.4	77.8	*	*	—
70 hrs	44.3	10.4	85.20	46.8	15.3	202.0
94 hrs	53.4	14.9	93.0	70.1	18.2	249.6
94 hrs	64.1	17.0	71.4	56.5	20.8	229.8

135 C

22 hrs	47.4	15.4	105	54.3	16.3	238.4
22 hrs	52.4	18.1	117	61.4	19.8	268.7
46 hrs	118	54.5	236	141	43.0	592.5
46 hrs	119	57.9	235	146	41.3	599.2
70 hrs	203	102	310	239	67.6	921
70 hrs	221	112	351	253	70.3	1007
94 hrs	268	145	463	344	82.0	1302
94 hrs	247	124	357	323	84.2	1135
114 hrs	303	137	428	319	96.4	1283
118 hrs	395	119	193	482	160	1349
118 hrs	321	147	391	336	97.1	1292
166 hrs	452	202	471	559	116	1800
166 hrs	573	272	520	718	184	2267

150 C

22 hrs	211	157	392	269	69.7	1099
22 hrs	233	173	426	288	75.8	1196

This portion of the run was lost due to a power failure.

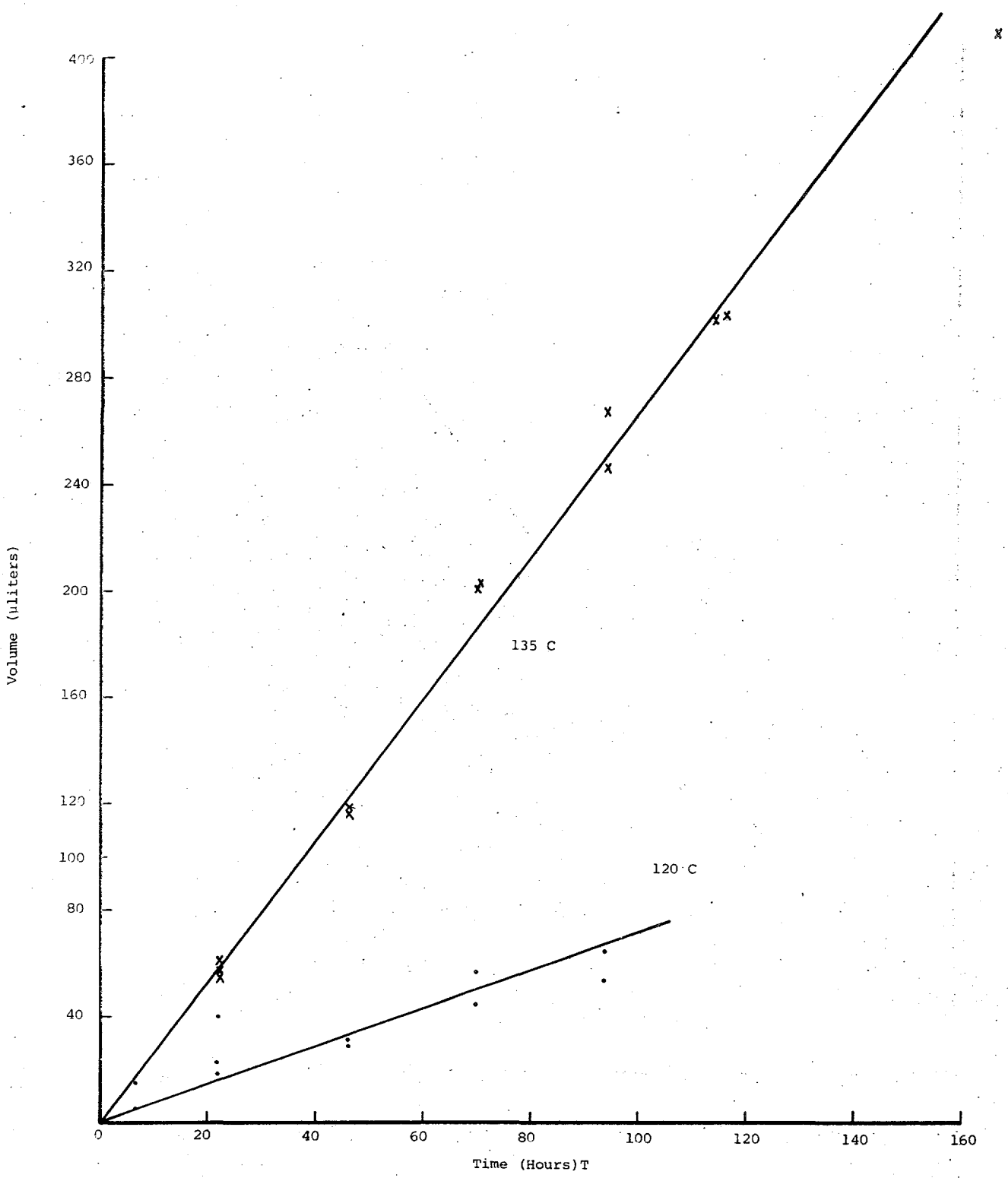

Fig. 3. Microliters of N_2 evolved from 0.250 gm of FEFO at 135 C and 120 C

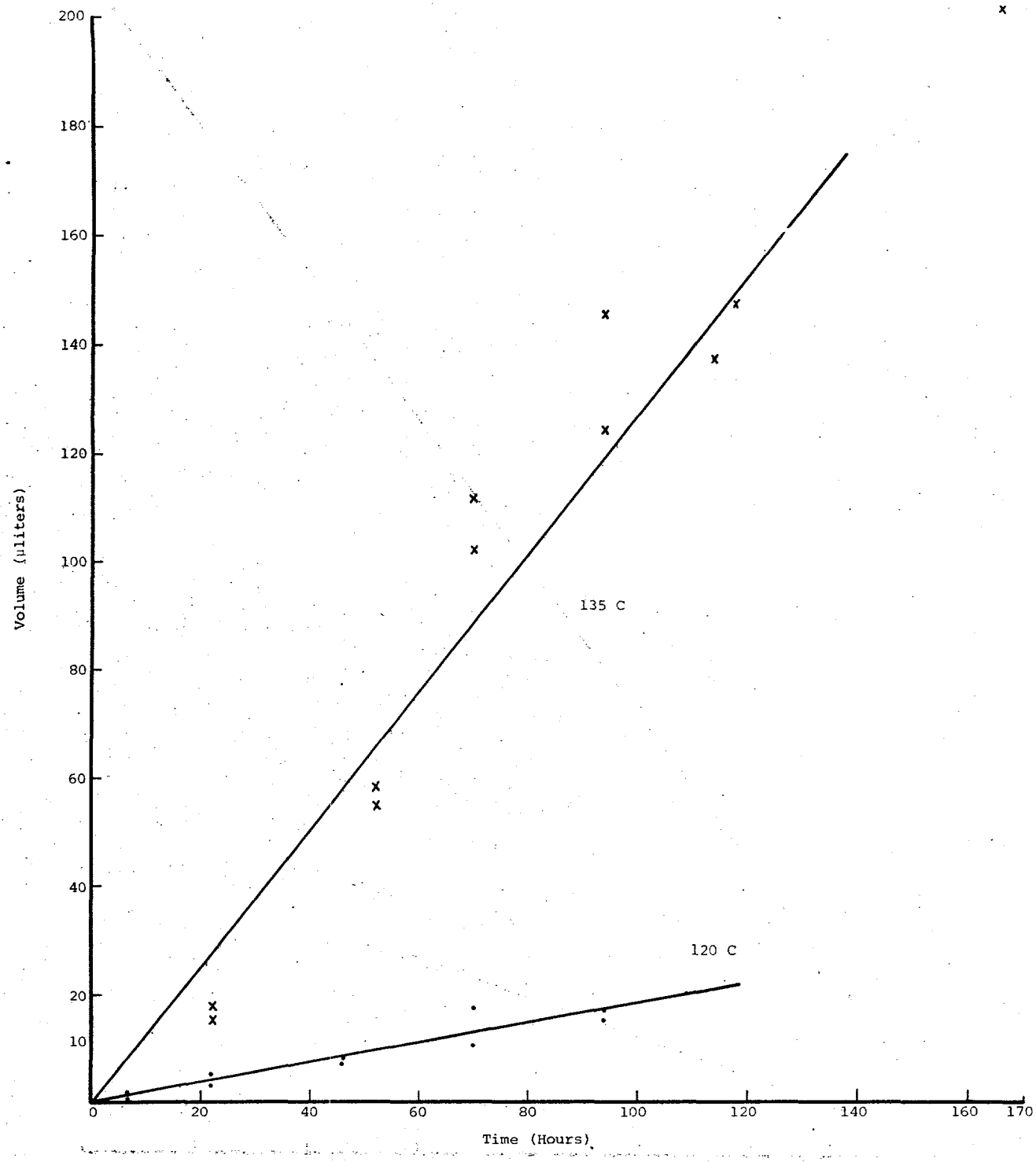

Fig. 4. Microliters of CO evolved from 0.250 gm of FEFO at 135 and 120 C

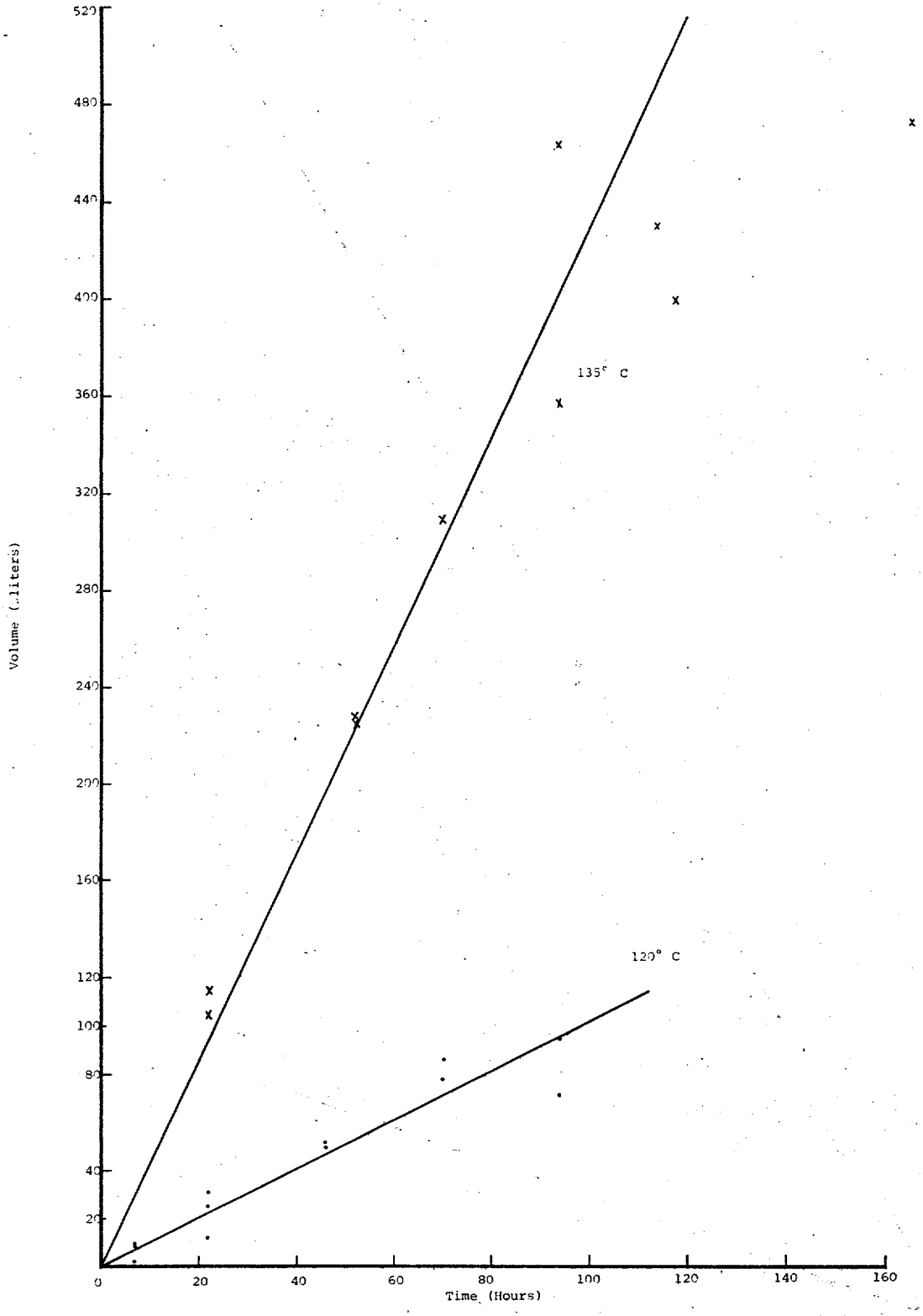

Fig. 5. Microliters of NO evolved from 0.250 gm of FEFO at 135 and 120 C

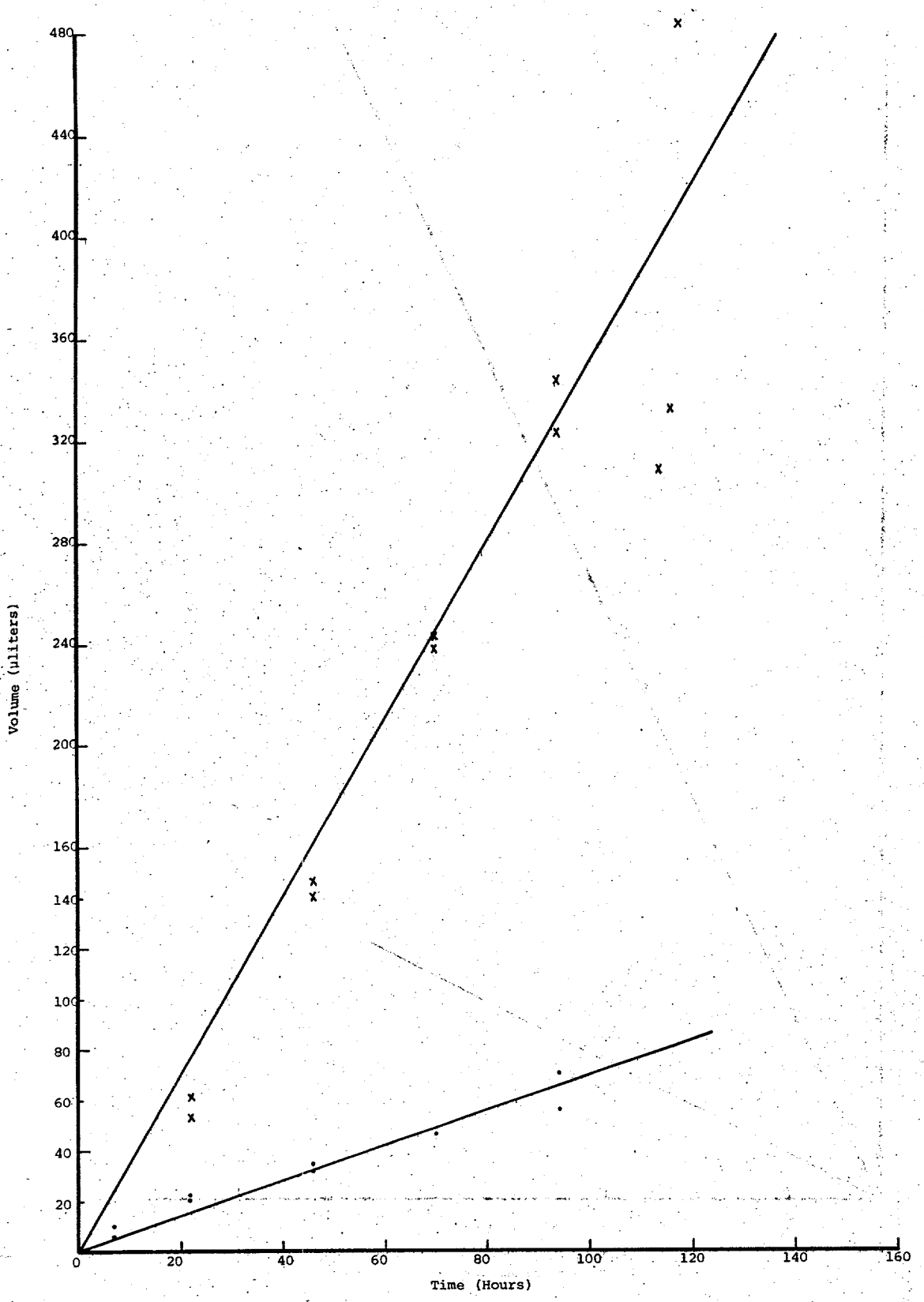

Fig. 6. Microliters of CO_2 evolved from 0.250 gm of FEFO at 135 and 120 C

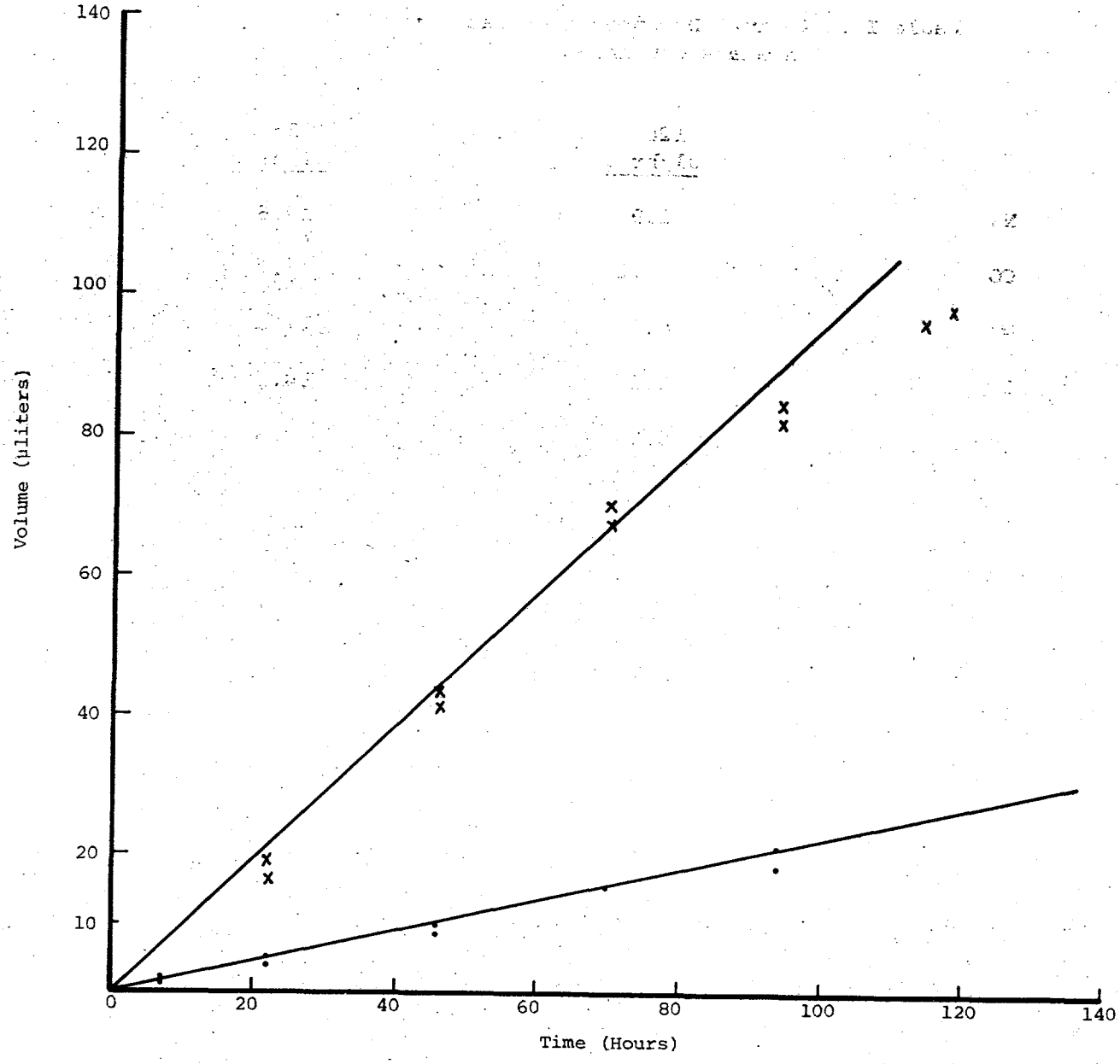

Fig. 7. Microliters of N_2O evolved from 0.250 gm of FEFO at 135 and 120 C

Table II. Thermal Decomposition Rates for FEFO in Glass Crucibles

	120 C µl/hr g	135 C µl/hr g
N_2	2.9	10.6
CO	0.72	5.0
NO	4.1	17.0
CO_2	2.8	14.1
N_2O	0.90	3.8

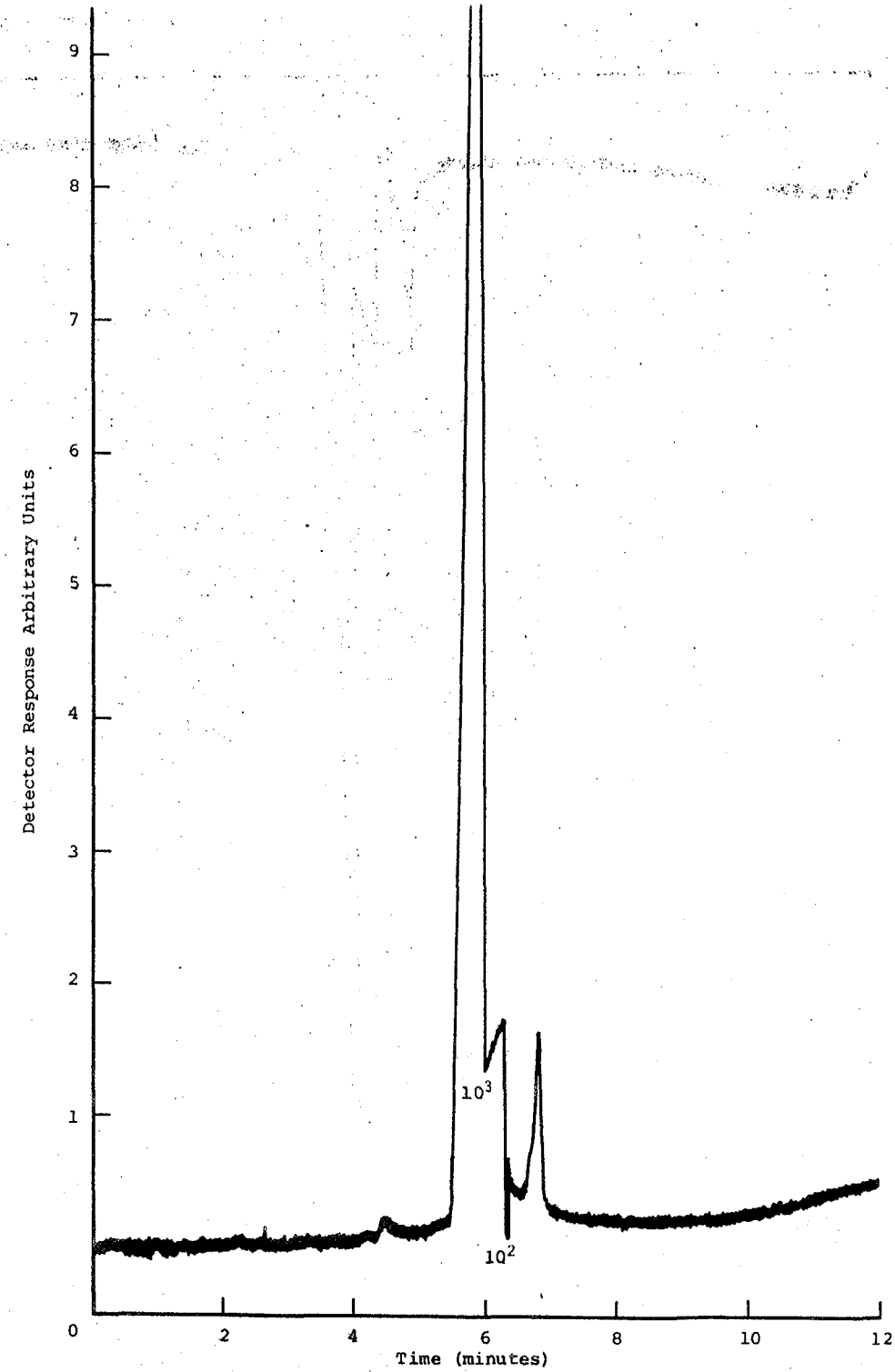

Fig. 8. Chromatogram of Standard Sample of FEFO, Column Heating Rate 10 C/min

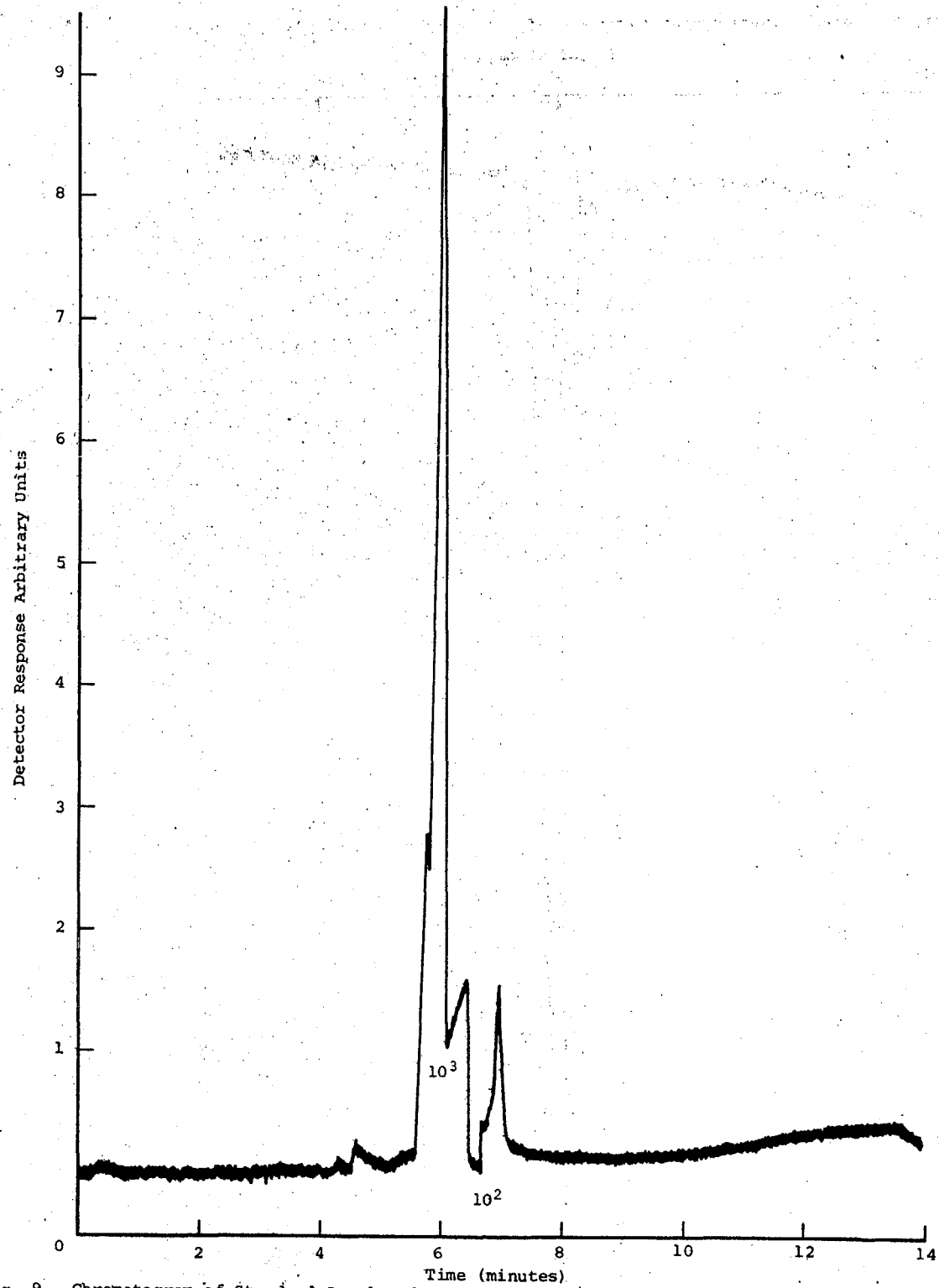

Fig. 9. Chromatogram of Standard Sample of FEFO after 94 Hours at 120 C Column Heating Rate 10 C/min

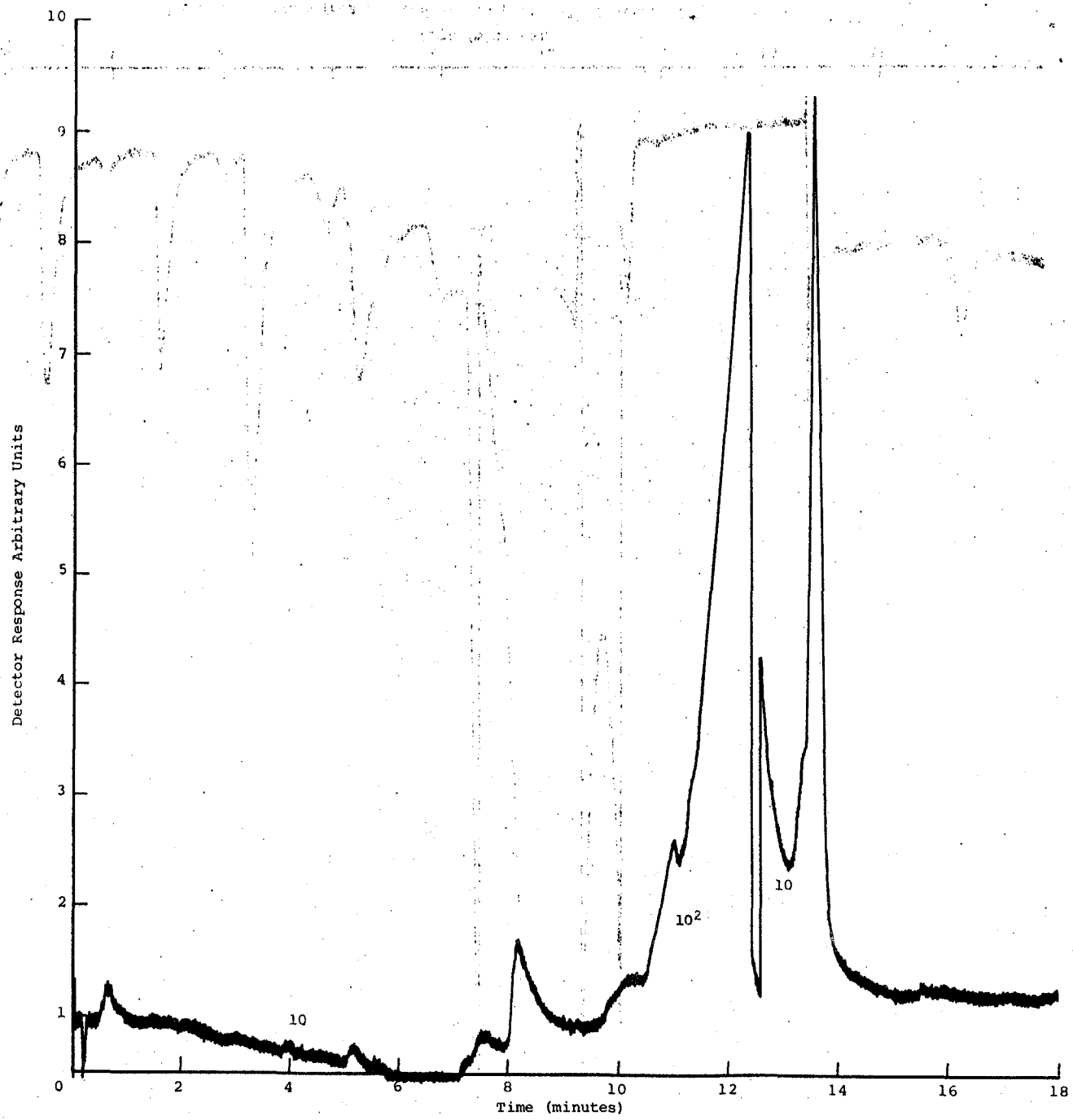

Fig. 10. Chromatogram of Standard Sample of FEFO after 94 Hours at 120 C, Column Heating Rate 4 C/min

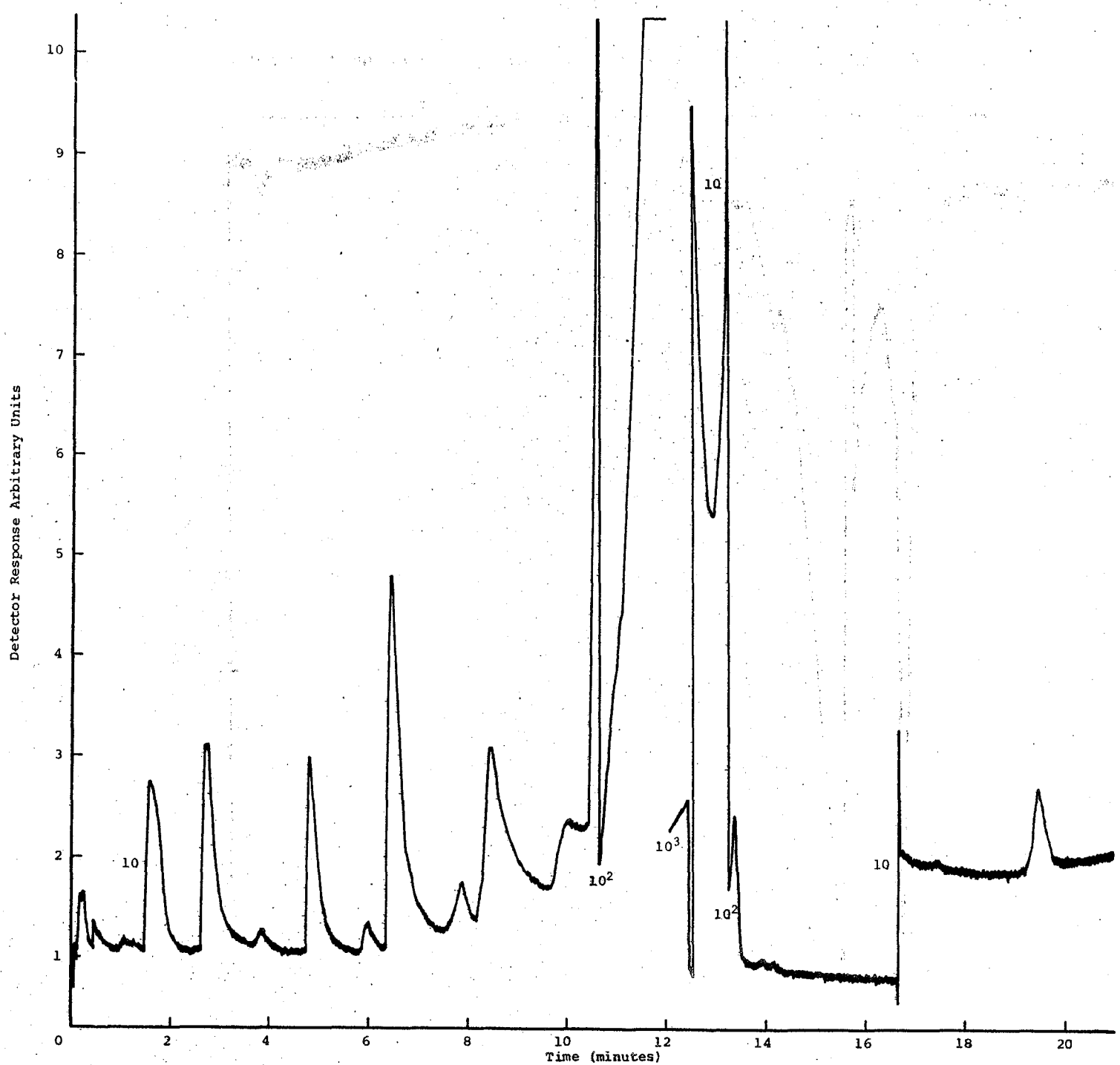

Fig. 11. Chromatogram of Standard Sample of FEFO after 22 hrs. at 150 C

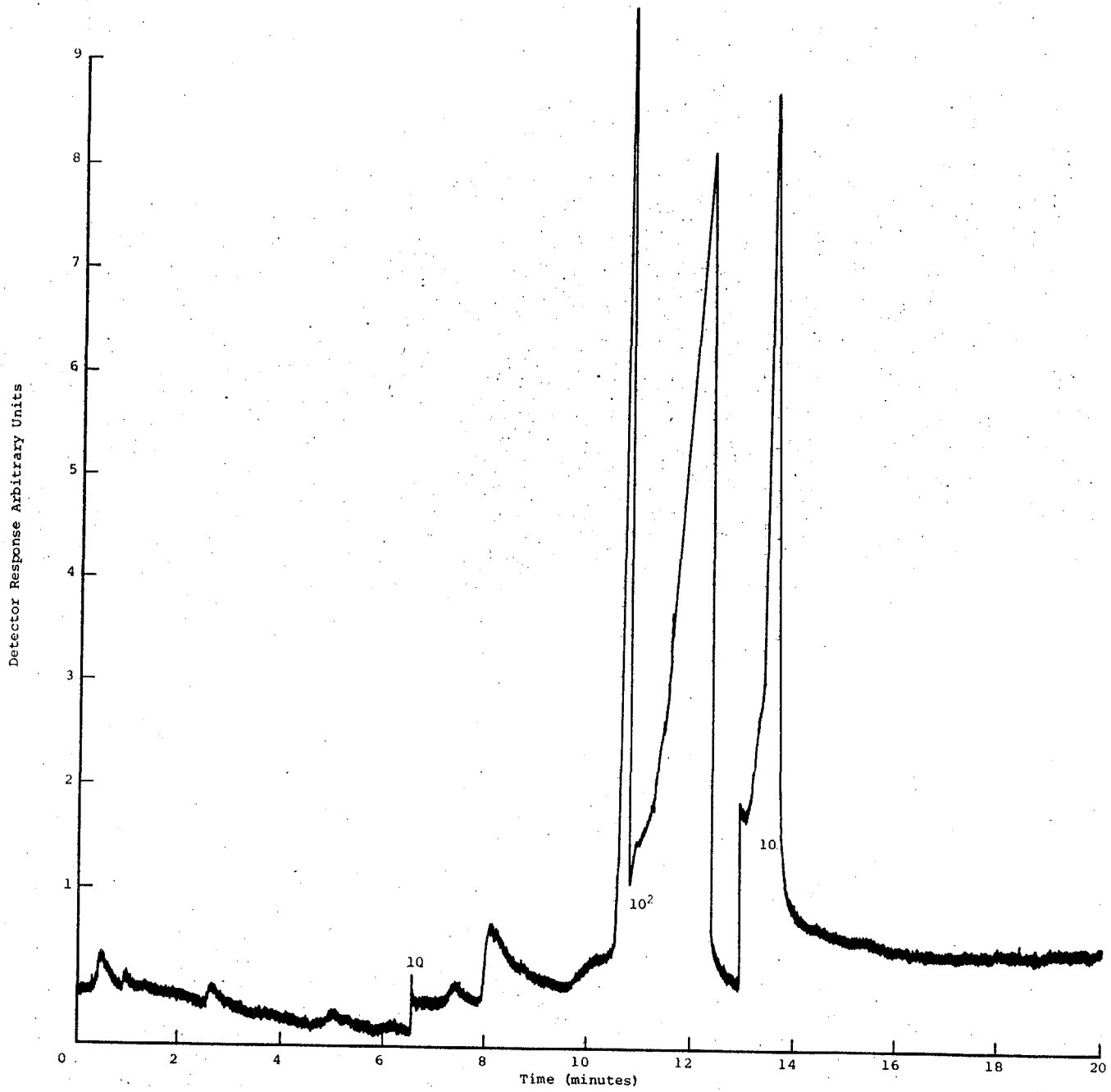

Fig. 12. Chromatogram of Standard Sample of FEFQ

Similar runs will be made on the FEFO test in the stainless steel crucibles.

COUPON TESTS

An analysis was made on two coupon test assemblies and an LX-09 sample for a PASS A mechanical test specimen this quarter. Sample No. 31, a coupon test sample, was conditioned at 80 C for 27 months. The coupon was 1 inch by 6 inches and contained LX-09, Sylgard and Mulberry. The atmosphere was CO_2 with a 50% relative humidity at 80 C. Coupon test sample No. 38 was conditioned at 80 C for 21 months and was the compression type (spring loaded for 30 psi) which used the 1-inch diameter coupon made up of LX-09, Sylgard, boron loaded silastic and Mulberry in a nitrogen atmosphere.

The following observations were made during the disassembly of sample No. 31.

1. *The Sylgard was in very good condition and bonded the parts together.*

2. *The LX-09 seemed weak and broke when it was separated from the metal parts. There was some discoloration (darker) of the LX-09 as shown in Fig. 13.*

3. *The Mulberry was badly oxidized and there was some scaling which stuck to the Sylgard as shown in Fig. 14.*

On the disassembly of coupon test No. 38 the following observations were made:

1. *The Sylgard was in very good condition.*

2. *The boron loaded silastic was fragile and had lost most of its flexibility.*

3. *The LX-09 appeared to be slightly weaker and was a little darker (Fig. 15).*

4. *The Mulberry was oxidized.*

The Development Division requested samples of the LX-09 from the first series of PASS A mechanical test specimens, one from each atmosphere. These samples were to be tested in a number of thermal analysis tests to determine if any changes in the LX-09 could be detected. One sample was received and tested with the coupon test Nos. 31 and 38 and their control sample for comparison.

The DTA thermograms are shown for samples No. 38 and 31, PASS A mechanical test specimen and a control in Figs. 16 - 19. There were no significant differences in the thermograms.

The Henkin time-to-explosion are given in Table III. Times-to-explosion for sample No. 31 are shorter than the control sample, and there is no significant differences between the other two samples and the control.

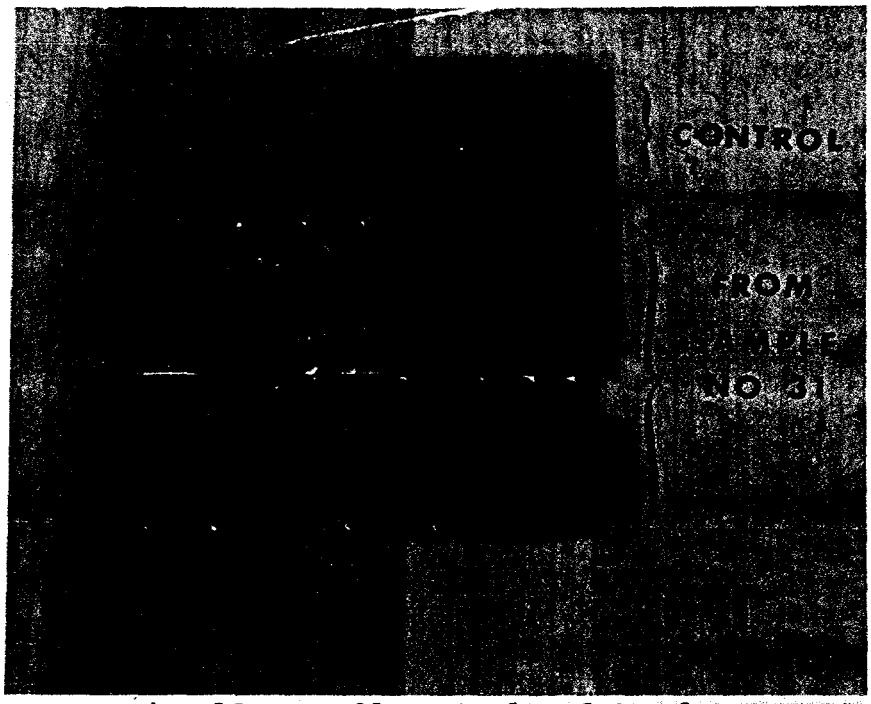

Fig. 13. LX-09 Control and Samples from Coupon Test No. 31

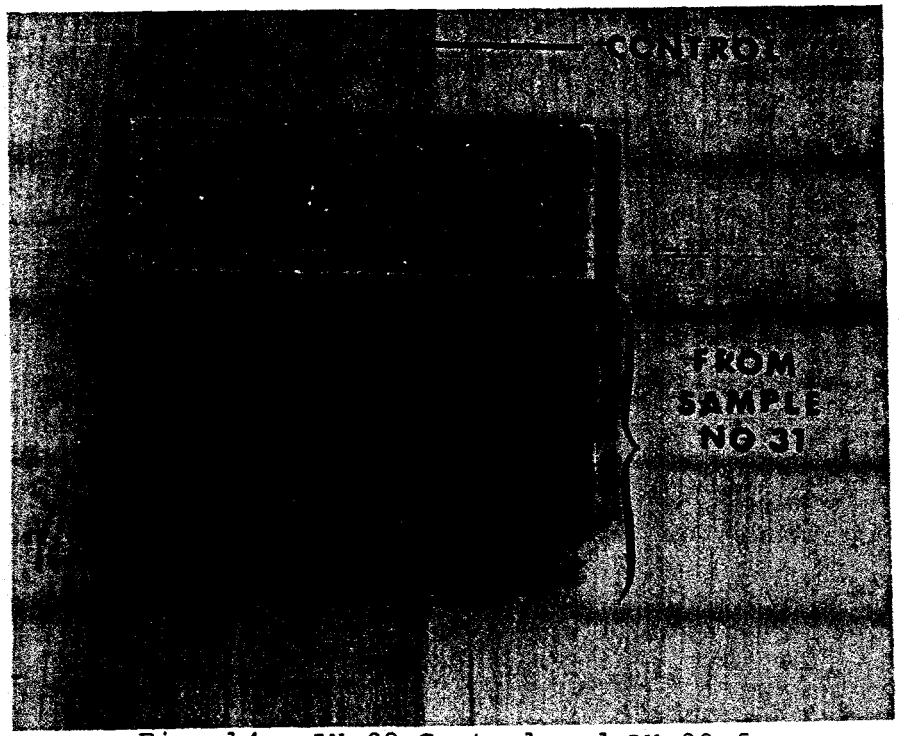

Fig. 14. LX-09 Control and LX-09 from Coupon Test No. 31

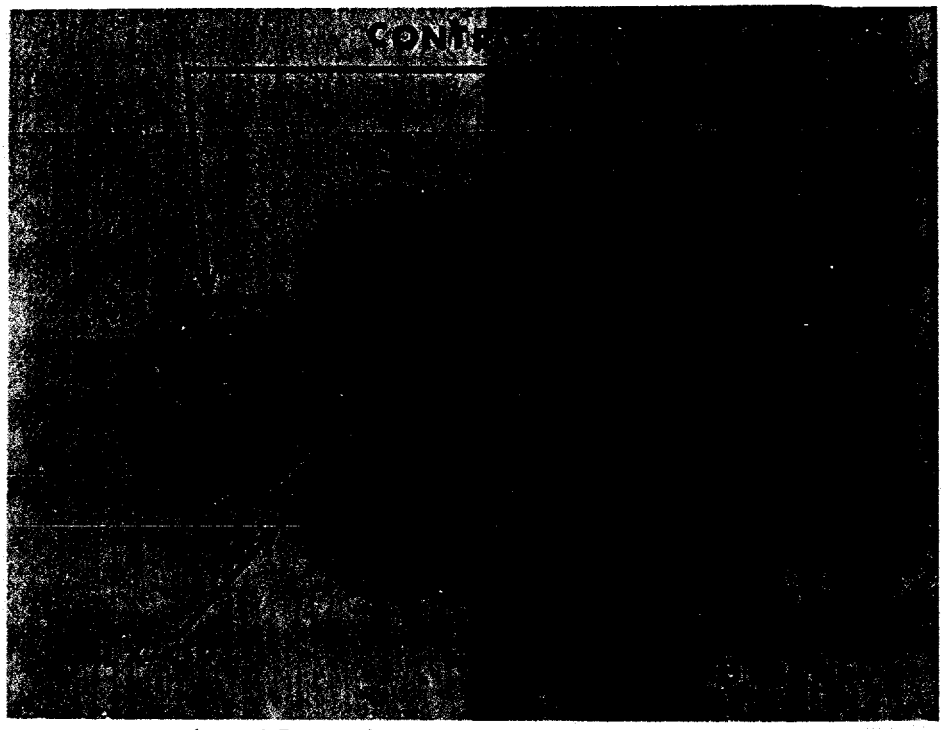

Fig. 15. Time Study Sample No. 38

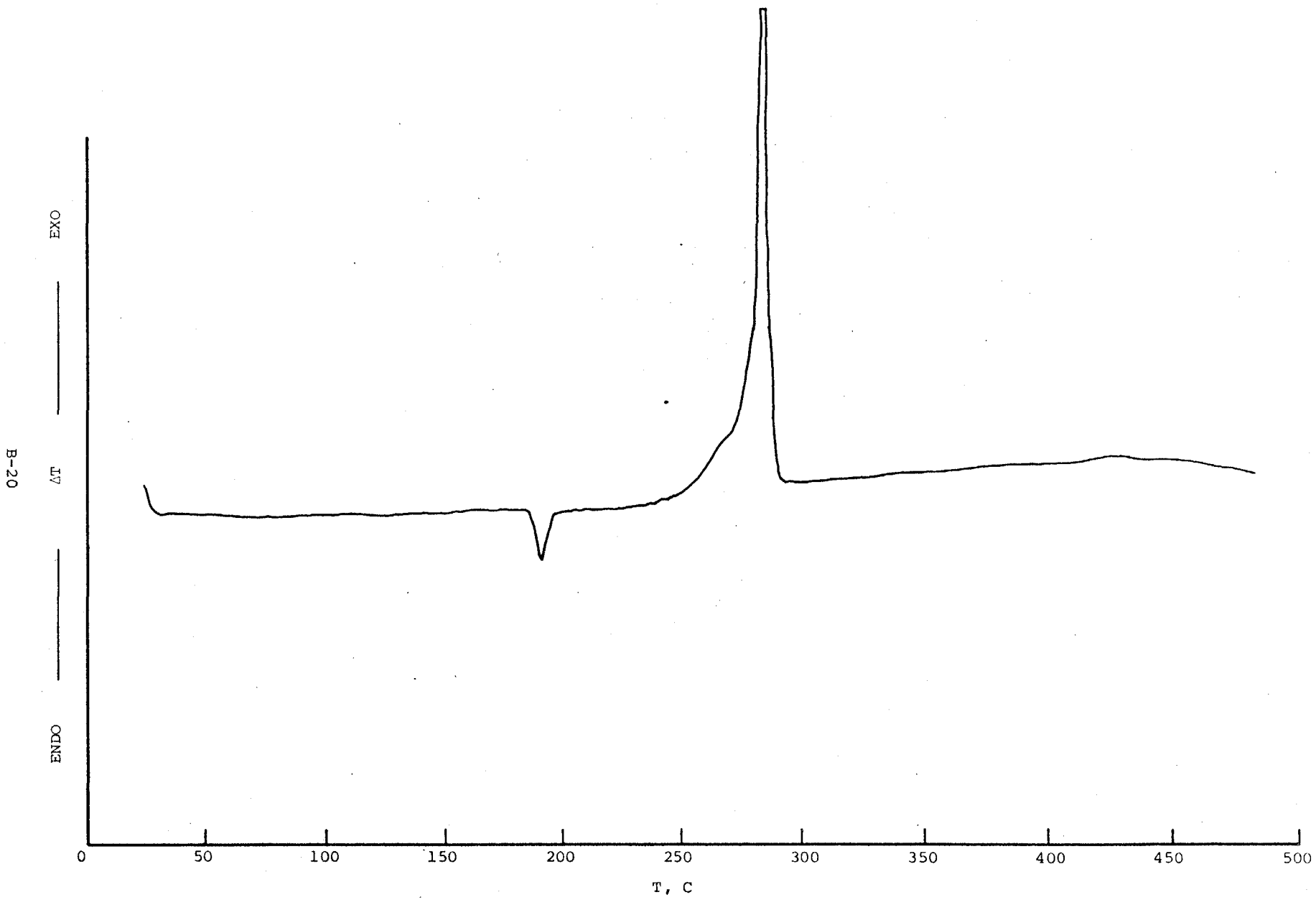

Fig. 16. LX-09, Sample No. 38, 11°/min

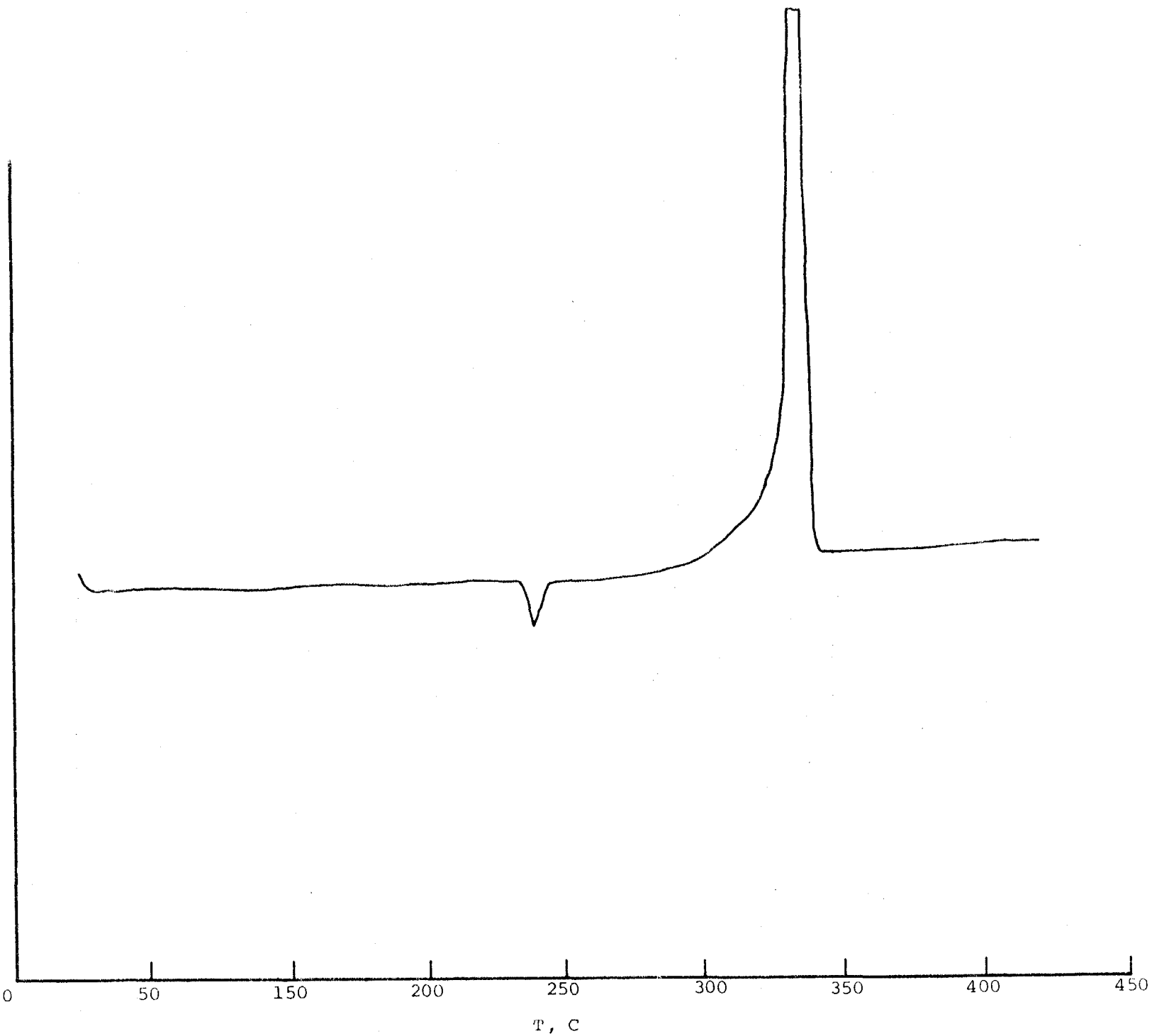

Fig. 17. LX-09, Sample No. 31, 11°/min

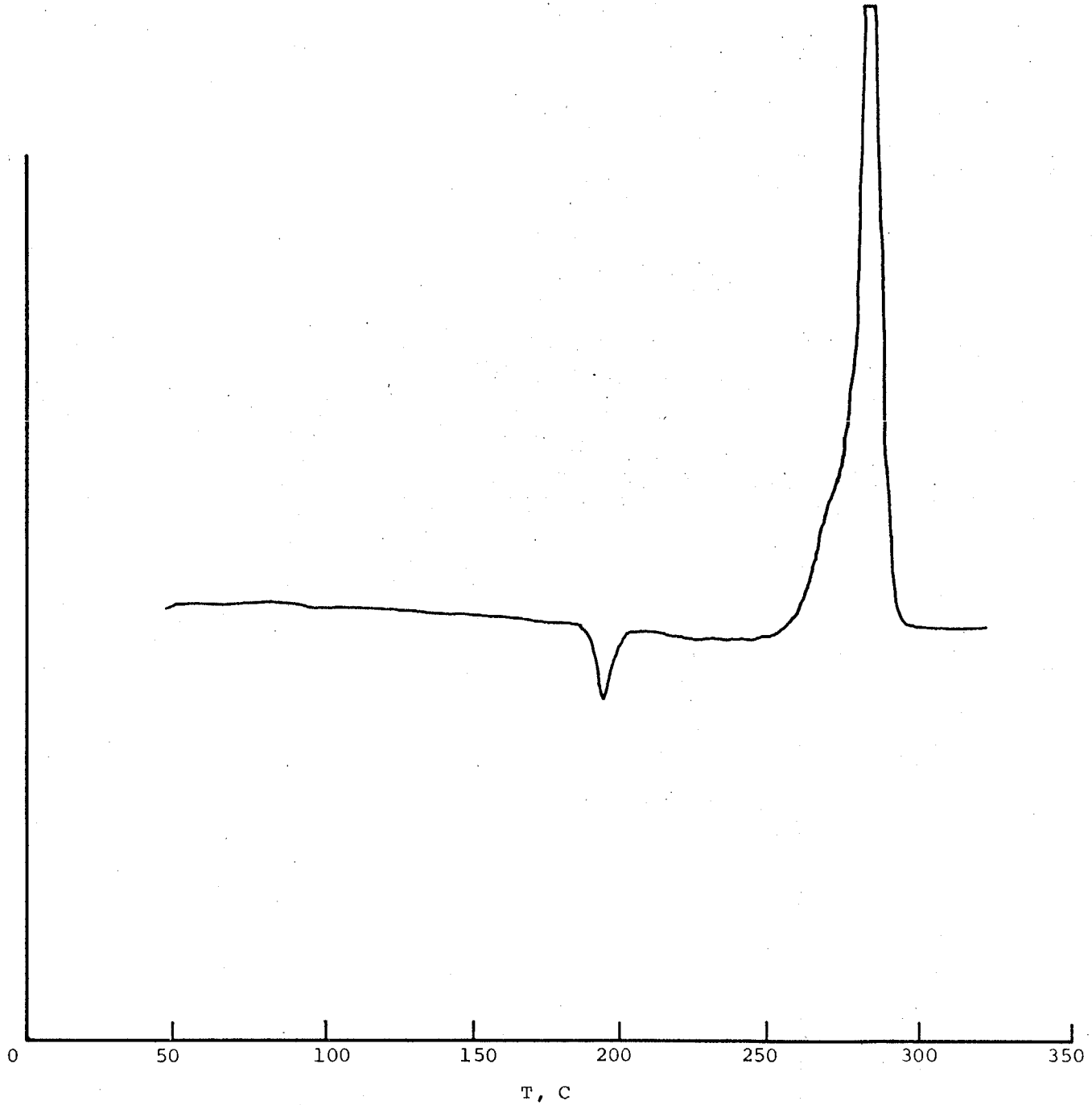

Fig. 18. LX-09, Pass A Sample, 11°/min

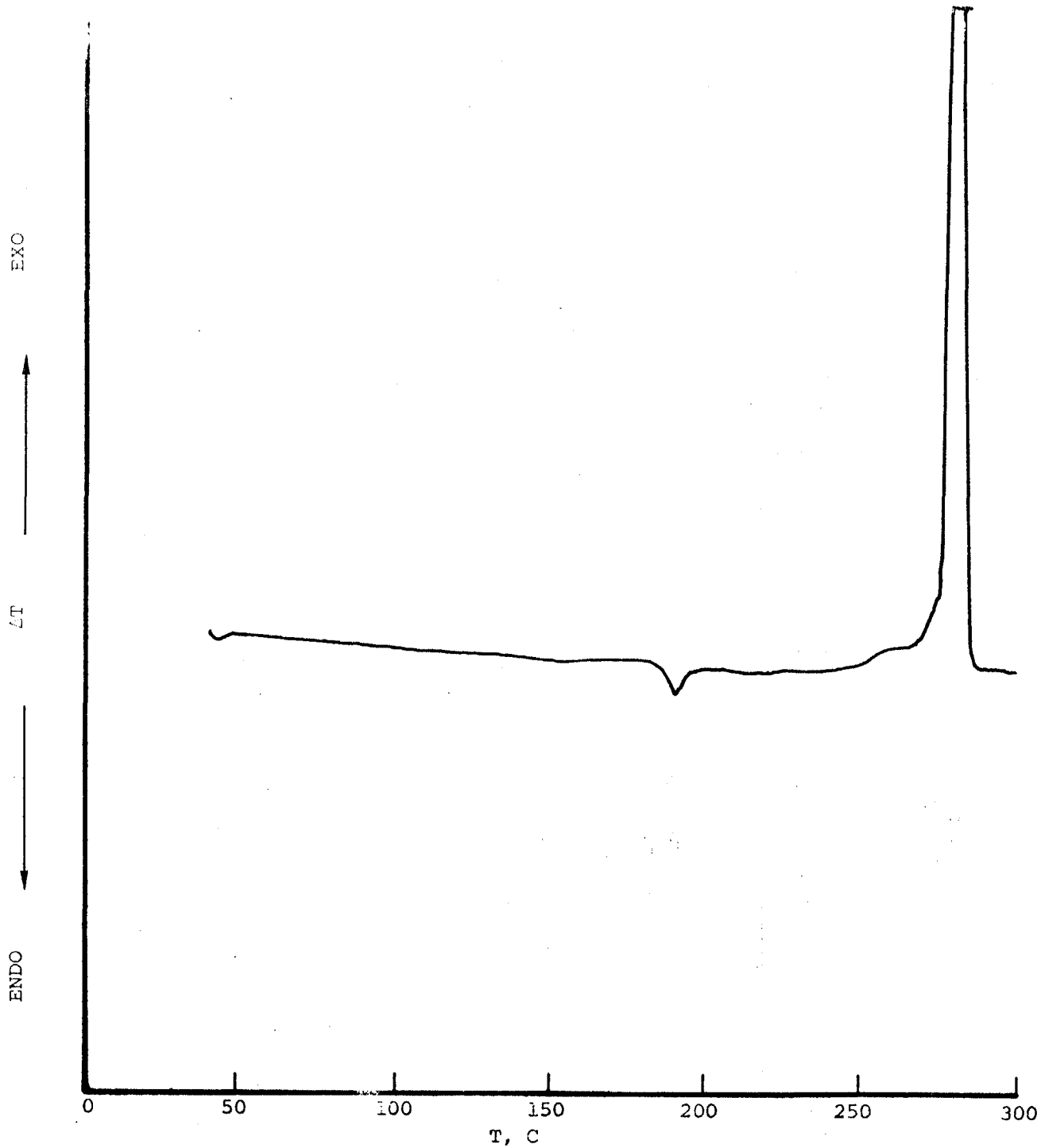

Fig. 19 LX-09 Control 11 C/min

Table III. Henkin Time-to-explosion for Various LX-09 Samples

	Time in Seconds @ 228 C	236	247	258
LX-09 Coupon Sample No. 38	554	265	89	30
	550	246	101	32
	491	271	121	35
	443	238	90	37
	474			
	467			
(Harmonic Mean)	493	254	98.7	33.3
LX-09 Coupon Sample No. 31	455	174	87	27
	477	234	68	28
	327	192	83	35
	330	203	80	33
	345			
	388			
(Harmonic Mean)	378	198	78.8	30.4
LX-09 PASS A	455	174	87	
	566	281	115	29
	562	289	81	32
	595	260	98	33
	467	288	90	33
	505			
	483			
(Harmonic Mean)	525	279	94.4	31.7
LX-09 Control	648	357	122	36
	593	273	96	32
	583	301	106	34
	540	287	112	34
	535			34
	452			30
(Harmonic Mean)	512	301	108	31.2

Table IV. Chemical Reactivity Test

0.250 mg Samples of LX-09 Conditioned at 120 C for 22 Hours

	Gas Evolved on µliters at STP					
	N_2	CO	NO	CO_2	N_2O	Total
LX-09	24.5	1.28	23.6	13.7	8.94	72.0
from #38	18.2	1.61	24.5	15.3	11.0	70.6
LX-09	19.5	3.14	32.0	24.7	16.0	95.3
from #31	18.1	2.90	31.6	21.6	16.1	90.3
LX-09	6.20	.73	9.38	7.73	4.94	29.0
PASS A	9.39	.60	6.91	9.35	5.18	31.4
Control	6.55	.60	13.9	8.8	4.34	31.1
LX-09	5.39	.40	11.6	5.4	3.4	26.2

Table IV gives the chemical reactivity test data for a control sample of LX-09 and samples from the coupon tests and the first PASS A mechanical testing specimen. LX-09 chemical reactivity data from sample Nos. 31 and 38 show increases in all the decomposition gases and the PASS A mechanical test sample are approximately the same as the control sample.

HEAT OF FUSION OF PETN

The initial work on measuring the heat of fusion of PETN with a Perkin Elmer DSC-1, a Datex DIR-1 system for data acquisition, and a Wang 700 with a paper tape reader for data reduction indicated that measurements could be made with a repeatability of approximately 1%. However, the Datex System is limited in the data collection rates and it is normally used as the integration for the chemical reactivity test. This caused some scheduling problems. The Wang 700 calculator was not always available when it was needed which increased the scheduling problems.

A PDP-12/30 Laboratory Data Processor (Digital Equipment Corp.) was purchased for Pantex's Thermal Analysis Laboratory for data acquistion and some data reduction. Since the PDP-12 would be more versatile than the Datex System, the DSC-1 was interfaced with the PDP-12.

The PDP-12/30 has two analog to digital converters, one is 10 bits (9 bits plus a sign bit) with a resolution of 1/512 or 0.2%. The other is 15 bits (14 bits plus a sign bit) with a resolution of 1/16384 or 0.006%. Since previous work indicated that a resolution of 0.2% would be adequate and there were existing programs to collect data with the 10 bit A to D but none for the 15 bit A to D, it was decided that the 10 bit A to D would be used until a program could be written for the 15 bit A to D.

Since the DSC-1 has a maximum output of ± 5 millivolts and the PDP-12's analog to digital converters were ± 1 volt some type of interface was needed. Currently a Hewlett Packard Model 7100B recorder with a retransmitting potentiometer and a Harrison Laboratory, Inc., Model 865B power Supply (for constant voltage supply) is being used. The constant voltage supply is connected to the retransmitting potentiometer and the A to D converter is connected to the potentiometer. To obtain maximum resolution the recorder is set for 5 millivolts full scale and 1 volt across the retransmitting potentiometer.

The Catacal program supplied with the PDP-12 will accept analog data from an instrument and then display this data on the PDP-12 oscilloscope. This program has a number of data handling commands which are applicable to the reduction of the DSC-1 data. The sequences used in collection and reduction of the DSC-1 data are as follows:

First, a data collection rate was determined. Since Catacal will collect up to 2048 points, a data collection rate of 2000 point in 120 sec was chosen. From these 2000 points, 1000 can be selected which contain the endotherm. The indium and PETN melting endotherms are defined by 450 and 650 points, respectively. PETN has more points because its endotherm is broader.

After the 1000 data points are selected, a scaling command is used to make the peak full scale on the oscilloscope, i.e., set the baseline on zero and multiply each point by an appropriate factor to make the peak full scale. This factor is printed out and is used when different runs are compared. For convenience, a y-invert command can be used to invert the peak.

A command is then given to display two cursors (Points) on the oscilloscope. These cursors can be located at any point on the oscilloscope using four controls located on the PDP-12. The cursors are located at the beginning and end of the peak.

The integration command integrates the data between the two cursors using them as a baseline. The area is printed out on a teletype.

By using this procedure, the data in Table V was obtained for nine lots of PETN. Table VI gives the results of the calibration runs on indium.

The PETN data shows that a 4 mg sample has a larger standard deviation than most of the 8 mg samples. The 4 mg samples are run on the 16 millical/sec range and the 8 mg sample must be run on the 32 millical/sec range.

The indium calibration runs on the 16 millical/sec range has a standard deviation smaller than the samples run on the 32 millical/sec range, just the opposite from the PETN runs. The calibration factor obtained on the 16 millical/sec range is not in agreement with the factor for the 32 range. There is an error of approximately 1%.

The data is not conclusive yet but there is an indication that the heat of fusion of a given lot of PETN decreases very slightly with each run or until the sample holder is heated (to $\sim$ 500 C) or cleaned. The first two runs on Lot 10-71-492-01 followed runs made on another lot of PETN. Before the last two runs were made the sample holder was heated to 500 C and there was a change of 34.68 and 34.94 to 35.72 and 35.18 cal/gm. Tests will be run to determine if a contaminated sample holder is the cause of some of the variations.

The Mettler microbalance which was used to weigh the PETN samples developed some problems and had to be repaired. After repairing the balance, the indium data shows that the same results are obtained if a sample is weighed on Mettler 5-place balance, a Mettler microbalance, or is supplied by Perkin Elmer.

Most of the DSC-1 thermograms of PETN show an offset near the peak of the melting endotherm. This has also been observed on DTA thermograms. When this was first observed on DTA thermograms it was assumed to be the movement of the sample around the thermocouple as it melted. However, this type of change would not be expected to affect the DSC-1 thermograms. At this time no explanation is offered for this.

Table V. PETN Heat of Fusion

Lot #	mg	Cal/g
10-71-406-01	5.184	33.76
	4.503	34.09
	4.234	33.43
	3.952	34.77
	Mean	34.01
	σ	0.57 or 1.7%
10-71-482-01	4.00	36.42
	4.30	35.61
	4.76	34.34
	3.87	35.23
	3.99	33.70
	5.40	34.02
	Mean	34.89
	σ	1.04 or 3.0%
10-71-498-01	9.80	35.98
	9.37	34.56
	10.24	35.01
	9.07	34.60
	Mean	35.04
	σ	0.66 or 1.9%
10-71-295-01	4.68	34.39
	5.28	32.96
	4.16	35.01
	4.36	35.58
	Mean	34.49
	σ	1.1 or 3.3%
10-71-484-01	9.65	35.35
	8.73	35.28
	9.88	35.70
	9.64	35.74
	9.92	35.77
	Mean	35.57
	σ	0.23 or 0.66%
10-71-506-01	8.11	35.39
	8.92	35.66
	9.02	35.13
	9.65	35.16
	9.09	34.88
	Mean	35.24
	σ	0.29 or 0.84%
10-71-269-01	4.94	34.95
	4.95	34.69
	4.92	34.70
	5.02	34.26
	Mean	34.65
	σ	0.28 or 0.83%
10-71-497-01	10.13	35.58
	10.39	35.79
	10.21	35.46
	10.04	36.13
	10.24	35.91
	Mean	35.77
	σ	0.27 or 0.74%
10-71-492-01	9.67	34.68
	8.74	34.94
	9.27	35.72
	9.79	35.18
	Mean	35.13
	σ	0.44 or 1.3%

Table VI. Indium Calibration Runs

Day	Sample Wt (mg)	Range Setting 16 Counts/Calorie
1	15.395	492
1	15.515	493
2	6.75	493*
2	13.35	491**
2	13.81	493
3	15.515	490
3	10.226	494
24	15.395	490
27	15.395	491
27	10.226	489
	Mean	491.6
	σ	1.6 or 0.3%
		Setting 32
28	21.424	243.1 = 486
28	21.424	241.6 = 483
28	21.424	241.9 = 484
29	21.424	243.6 = 484
30	21.424	245.9 = 492
30	15.395	244.5 = 489
31	21.424	243.9 = 488
	Mean	243.5
	σ	1.49 or 0.6%

**Standard - Weighed and Supplied by Perkin Elmer.*

***Weighed on 5-place Mettler balance, others were weighed on 6-place Mettler balance.*

FUTURE WORK; COMMENTS; CONCLUSIONS

An identification has not been made as to what some of the impurities in FEFO are. This part of the project is being delayed until Pantex's high resolution mass spectrometer is in operation (should be operational in January 1972).

Thermal decomposition studies were made on FEFO at 120, 135 and 150 C. Analysis of the gaseous decomposition products were obtained and some preliminary gas chromatograms analysis of the sample after heating show that there is an increase in the amount of low and high boiling impurities. From the analyses of the decomposition gases the thermal decomposition rates were determined. Additional testing will be done next quarter using both glass and stainless steel crucibles to hold the FEFO.

Two coupon test samples were disassembled this quarter and a series of thermal analysis test were run on the LX-09. Sample No. 31 and 38 were conditioned at 80C for 27 and 21 months, respectively.

The Sylgard in both assemblies was in good condition. Sample No. 38 contained a sample of a boron loaded silastic which had lost most of its flexibility.

A sample of LX-09 from a PASS A mechanical test specimen was analyzed with the coupon test samples and their control for comparison. The DTA and Henkins time-to-explosion data show no significant differences with one exception, the time-to-explosion for sample No. 31 was a little shorter.

The chemical reactivity test shows that samples No. 31 and 38 envolved more decomposition gases than the control sample. The Pass A and control samples evolve approximately the same amount of gas.

The DSC-1 was interfaced with a PDP-12 (Digital Equipment Corp) to give more versatility in data acquisition and to simplify data reduction. The indium calibration runs on the 16 and 32 millical/sec range had a standard deviation of 0.3% and 0.6%, respectively. The heat of fusion for PETN using 4 mg samples had a standard deviation about twice that of 8 mg samples. There is an indication that the heat of fusion numbers become smaller with each additional run or until the sample holder is heated or cleaned. Additional test will be made to improve the repeatability of the heat of fusion measurements.