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PART II

KINETICS AND MECHANISMS OF THERMAL DEGRADATION OF POLYMERS USING TIME-OF-FLIGHT MASS SPECTROMETRY FOR CONTINUOUS GAS ANALYSIS

H. L. Friedman and G. A. Griffith

General Electric Company

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Air Force Materials Laboratory
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Wright-Patterson Air Force Base, Ohio

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KINETICS AND MECHANISMS OF THERMAL DEGRADATION OF POLYMERS USING TIME-OF-FLIGHT MASS SPECTROMETRY FOR CONTINUOUS GAS ANALYSIS

H. L. Friedman and G. A. Griffith

FOREWORD

This report was prepared by the General Electric Company under USAF Contract No. F33615-69-C-1318. The contract was initiated under Project No. 7342, "Fundamental Research on Macromolecular Materials and Lubrication Phenomena", Task No. 734203, "Fundamental Principles Determining the Behavior of Macromolecules", and was followed by USAF Contracts No. F33615-67-C-1372 and F33615-68-C-1107. It was administered under the direction of the Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio, with Dr. Ivan J. Goldfarb, LNP, Project Scientist.

This work was performed in the Space Sciences Laboratory and the Environmental Sciences Laboratory of the Valley Forge Space Technology Center, King of Prussia, Pennsylvania. The following personnel participated in this program: Dr. H. L. Friedman, Principal Investigator; Mr. G. A. Griffith, Technician; and Mr. John R. Mallin, Electronic Engineer.

The authors gratefully acknowledge the help given to them by Dr. G. Liebling. Discussions with and advice from Dr. I. J. Goldfarb was also very helpful.

This report covers work from November 1969 to November 1970. The report was submitted by the author in December 1970.

This technical report has been reviewed and is approved.

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ABSTRACT

Research was continued using mass spectrometric thermal analysis (MTA) to study the thermal degradation of various polymers. Full 200 mass scan runs, limited mass scan runs, and data processing were carried out for a polybenzimidazole, bis benzimidazo benzophenathroline polymer, its ladder polymer, polyquinoxaline and quinoxaline-bis benzimidazo benzophenathroline ladder copolymer. The results were compared with each other and with earlier data.

The concept of an improved data processing system was developed, based on the use of analog magnetic tape. The new system is discussed, together with steps taken to implement it.

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SECTION I

INTRODUCTION

During the past few years, through a continuing research program of the Air Force Materials Laboratory and its contractors, many new classes of thermally stable polymers have been and are being synthesized. The thermal stability of most of these classes of materials has been investigated by thermogravimetry. This method has led to some qualitative relationships between chemical structure and behavior in the thermobalance. Quantitative relationships between these properties are not available.

The previous work related to the present program is described in five reports (refs. 1-6). The first stage attempted quantitative measurements through vacuum microthermogravimetry (refs. 1,2). This was later supplanted by mass spectrometric thermal analysis (MTA) (refs. 1-6). Automatic data collecting and processing instrumentation and methods were then developed to handle the large quantity of data generated in a single MTA experiment (refs. 2-4). A considerable effort was related to assuring reasonable accuracy in the data collected by automatic methods (refs. 3-5). The type of polymers studied in the earlier stages have included polybenzimidazoles (refs. 1-3, 5), aliphatic polyesters (refs. 4-6), aliphatic-aromatic polyesters (ref. 5), aromatic polyesters (ref. 5), aliphatic polyamides (ref. 4), aliphatic-aromatic polyamides (ref. 5), aromatic polyamides (refs. 4, 5), bis benzimidazo benzophenathroline polymer (refs. 4-6), and its ladder polymers (ref. 6). Five papers by Space Science Laboratory authors (refs. 7-11) and four papers by Air Force Materials Laboratory authors (refs. 12-15) are based on the earlier studies.

The first research (refs. 1-3) emphasized the relationship between structure and thermal stability of new high temperature polymers, and also emphasized the development of MTA. The more recent parts (ref. 4-6) stress the systematic application of MTA to explore the kinetics and mechanisms of thermal degradation of polymers in depth.

A brief review of the experimental method is appropriate at this point. Polymer samples weighing approximately 1 mg. are pyrolyzed in vacuum from room temperature to 1000°C at a rate of 10°C/min. The effluent gases are pumped into a time-of-flight mass spectrometer where 200 different pre-selected ionic masses are scanned repetitively approximately every two minutes. Sample temperature, mass number, and ion intensity are recorded on perforated tape for each step in the mass scan. The data are then subjected to various data processing methods. Some experiments have been carried out where data for a single mass peak or a limited number of mass peaks were scanned at a much greater frequency than for the 200 mass scans (ref. 6).

SECTION II

MODIFICATION OF MTA APPARATUS

The apparatus and method of operation were generally the same as described previously (refs. 4-6). Trouble continued to arise from the scanner that switches the three parameters recorded on perforated tape, although a new one was installed quite recently (ref. 6). When it was found that the old one was better than the new one, the old one was reinstalled. It was found that the old problems were remedied by changing the timing sequence so that when the scanner was reset from the last position back to the first one, the operation stopped until the reset was completed. This is the slowest step in the process, and its time varies considerably, but it does not influence the quality of the data.

The need for random selection of a limited number of mass peaks was discussed previously (ref. 6), and this was accomplished through fabrication of a flexible 20 position potentiometer. The new potentiometer was used for MTA of polyquinoxaline - bis benzimidazo benzophenathroline ladder copolymer. Tests on the potentiometer are described in Section IV. E.

Several laboratories have recently had good success in recording time-of-flight mass spectra from the analog scanner on FM analog magnetic tape (refs. 16-18). It seems likely that it would be beneficial to use that approach instead of the present system for several reasons that are listed below.

1. Reduced set-up and experiment time would result in greater efficiency, reduced opportunity for breakdown, and reduced instrument drift during an experiment period. The need to assure mass spectral and gate coincidence would be eliminated, as is presently required for the stepped mass selector, since the analog gate would be swept over the full mass range of interest. This would eliminate: (1) measurement of gate voltages for mass peaks of hexachloroethane; (2) computer least squares polynomial analysis of gate voltage as a function of mass number; (3) alignment of 200 position mass selector potentiometer; (4) spot check of representative hexachloroethane peaks before the start of the run, with associated adjustments; and (5) the need to wait for residual hexachloroethane vapors to be pumped away before the start of the

experiment. Calibration would be carried out after the completion of pyrolysis, and would not necessitate any particular delay because the light gases generated at the end of pyrolysis are pumped away very quickly.

2. No necessity to carry out limited mass scan experiments. Recording and scan speeds may be arranged to be fast enough so that the number of data points collected for each peak far exceed that of the present system. Consecutive temperatures for the same mass peak will be separated by no more than 4°C.

3. Fuller mass coverage will be possible. The present system allows only preselected peaks to be investigated.

4. Elimination of the present complex switching system will increase the dependability of data collecting.

5. It will be possible to make a quick evaluation of data quality directly after the run, instead of waiting for partial data processing. This may be accomplished through high speed replay of data with visual oscilloscope examination.

6. Greater efficiency will also result from the elimination of perforated paper tape, and the various handling steps that are required with the present system.

The present system concept is to record two signal levels, having a ten to one intensity ratio, at a speed of 3-3/4 ips on two tape channels while scanning the mass spectrometer gate with a linear saw-tooth voltage ramp so that a complete mass spectrum is generated every 24 seconds (equivalent to every 4°C at a heating rate of 10°C/min). A high frequency clock signal would be recorded on the third channel, and a start of gate scan signal would be recorded on the fourth channel. Calibration data for hydrogen, n-butane and a perfluorocarbon would be recorded directly following the pyrolysis run. The other signals will be recorded as before, but scan duration will be consistent with the mass range to be covered for each standard.

After the run, the analog tape will be replayed at high speed and will be examined for quality of data by viewing an oscilloscope trace. For example, an expanded picture of mass 18 will be followed throughout both the pyrolysis

and calibration records as triggered by the start-of-scan pulse. Any strong variations in peak display time will indicate a change in ion flight time, a tape speed defect, or a defect in the saw-tooth voltage ramp that drives the gate. This will be observed as x-axis shift or jitter. Any sudden changes in peak amplitude would tend to indicate a drastic change in sensitivity or a leak. In case of questions, one or more other peaks would be examined. If the run was thought to be defective, then no effort would be wasted in further processing of data. The experiment would be carried out again, after the source of the problem is corrected.

The intensity channels of the analog magnetic tape will be converted to a digital magnetic tape, so that two values, one from each channel, will be recorded for each clock pulse. The start and end of each scan will be indicated. Conversion will be accomplished with the SDS Model 910 Computer using as fast a playback speed as possible, and computer programs that have already been developed for that purpose. This tape will contain two digitized values of intensity for each clock pulse, organized into sets for each mass spectrometer scan for both pyrolysis and calibration data.

The digital magnetic tape will then be replayed through the same computer which will be programmed to find peaks, evaluate their intensities, and to determine the pulse count number at the center. The pulse count number will eventually be used to calculate mass number, by comparison with a calibration standard. This tape will then contain sets according to scan number of peak intensity vs. pulse count at peak center for all peaks above a preselected threshhold, for the pyrolysis and calibration data. A printout will be obtained and will be studied. Mass peaks will be identified for the calibration standards, so that mass number will be known as a function of pulse counts. Intensity values will be taken from the higher sensitivity channel, unless overloading occurred, in which case the lower sensitivity values will be used, multiplied by a suitable correction factor. The calibration data will eventually be used to calculate instrument sensitivity for quantitative evaluation.

Pyrolysis and calibration data will then be input to the GE 635 Computer which will be programmed to convert clock pulse counts to mass numbers and pyrolysis time, and to sort the data into sets according to mass number in a time sequence. A value of zero will be assigned for each scan when a peak found in other scans is not detected. A graph plotting tape will be generated at the same time, and a graph of intensity vs. time will be plotted for each mass that is observed. An accompanying graph or table of temperature vs. time will be included, taken directly from the strip chart recorder or from data recorded on perforated paper tape with the present system.

In order to test this concept, data were recorded on magnetic tape for hexachloroethane on one channel, with a start of scan pulse on the second channel and a 1.25 kc clock pulse on the third channel. The mass range 0 to above 205 was swept in more than 20 seconds using a linear saw tooth voltage ramp, thus providing more than 25,000 clock pulses per scan. The data were recorded at 3-3/4 ips and were replayed through an oscilloscope at 60 ips. The spectra were excellent, having Gaussian shaped peaks, and all but the very weakest peaks could be observed visually. A crude attempt was made to tally pulse counts from starts of scan to approximate peak centers, and were found to be quite reproducible. A more rigorous test will have to involve computer data processing, and will be run for the total time that it takes to run MTA and the three calibration gases.

SECTION III

COMPUTER PROGRAM DEVELOPMENT

Two major computer programs, namely (1) the one for sorting the data according to mass number, and (2) that for graph plotting with the Stromberg-Carlson Model 4020 Graph Plotter were successfully rewritten for the General Electric Model 635 Computer. A graph plotting program was also written for the Cal Comp Model 575 Remote Drum Plotter, and was applied to the twenty mass scan runs, as may be seen in Figures 11 - 22.

Programs are being written for the SDS Model 910 Computer to be used for the new data processing system, as described in Section II.

SECTION IV

MTA OF POLYMERS

The MTA experiments described in this section are listed in Table I. Five successful MTA runs were carried out on four different polymers during the period of this report. Data reduction was performed for an earlier experiment (ref. 6) for a fifth polymer. Note that large errors are associated with the measurement of % weight loss, as explained in reference 5.

A. Poly (m-Phenylene) Bibenzimidazole

PBI-M was the starting material for the preparation of PBI-MFD1 and PBI-M2F3, for which MTA results were described in reference 5. PBI-MFD1 was freeze dried and PBI-M2F3 was a portion obtained by fractional precipitation methods.

Representative MTA results for PBI-M are shown in Figures 1 and 2 and products are listed in Table II. The data were excellent, except for a minor problem. The background was extremely clean, as noted by the absence of many systemic peaks observed in earlier experiments (refs. 5, 6). There was a scanner fault which started at m/e-84 at 620.5°C where no signals were recorded for any of the three parameters. This continued until m/e-108 at 639.1°C, where normal functioning resumed. Only the recorded points were used, but it was necessary to perform a linear interpolation for m/e-85 through 107 from the results of earlier and later scans in order to permit computations with the present computer programs, and to save the maximum quantity of information. A brief instrument fault was indicated from m/e-67 through 97 at above 800°C, which may be seen as negative spikes in the results for m/e-78, 92 and 93 in Fig. 2. Fortunately, it did not occur in a critical zone.

B. Bis Benzimidazo Benzophenathroline Polymer

Data processing was completed for the 40 position scan MTA run carried out earlier (ref. 6) for Celanese BBB polymer at m/e-0, 1, 2, 12-18, 22, and 24-52. Selected results are shown in Fig. 3 and products are listed in Table III.

TABLE I

SUCCESSFUL MTA EXPERIMENTS

Polymer	Code	Date	Sample Wt. mg	Wt. Loss %	Max. Temp. °C
Celanese bis benzimidazo benzophenathroline polymer	BBB	8/29/69[a]	1.037	21.3	900
bis benzimidazo benzo-phenathroline ladder polymer	BBL-SN2	9/16/69[b]	0.745	30.2	930
poly (m-phenylene) bibenzimidazole	PBI-M	5/8/70	1.722	36.1	910
quinoxaline-bis benzimidazo benzophenathroline ladder copolymer	FF-17EC	5/15/70	1.580	22.9	920
polyquinoxaline	PQ	5/22/70	1.612	30.9	920
quinoxaline-bis benzimidazo benzophenathroline ladder copolymer	FF-17EC	7/19/70[c]	1.399	29.3	885

[a] Scanned from m/e - 0 to 52

[b] Scanned m/e 0, 27, and 28

[c] Scanned 20 selected values of m/e

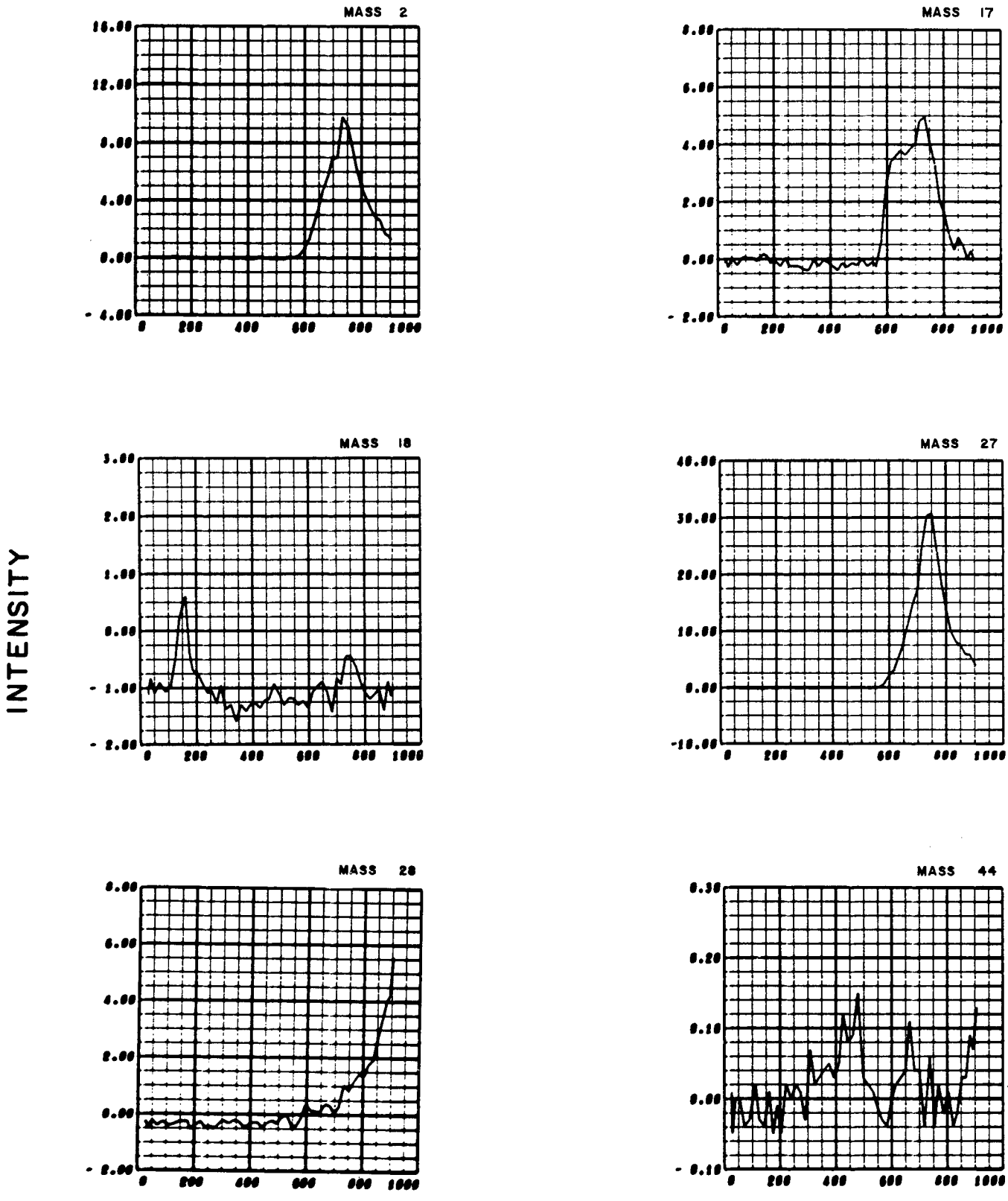

Figure 1. Representative Standardized MTA Results for Poly (m-Phenylene) Bibenzimidazole (PBI-M) (Part 1)

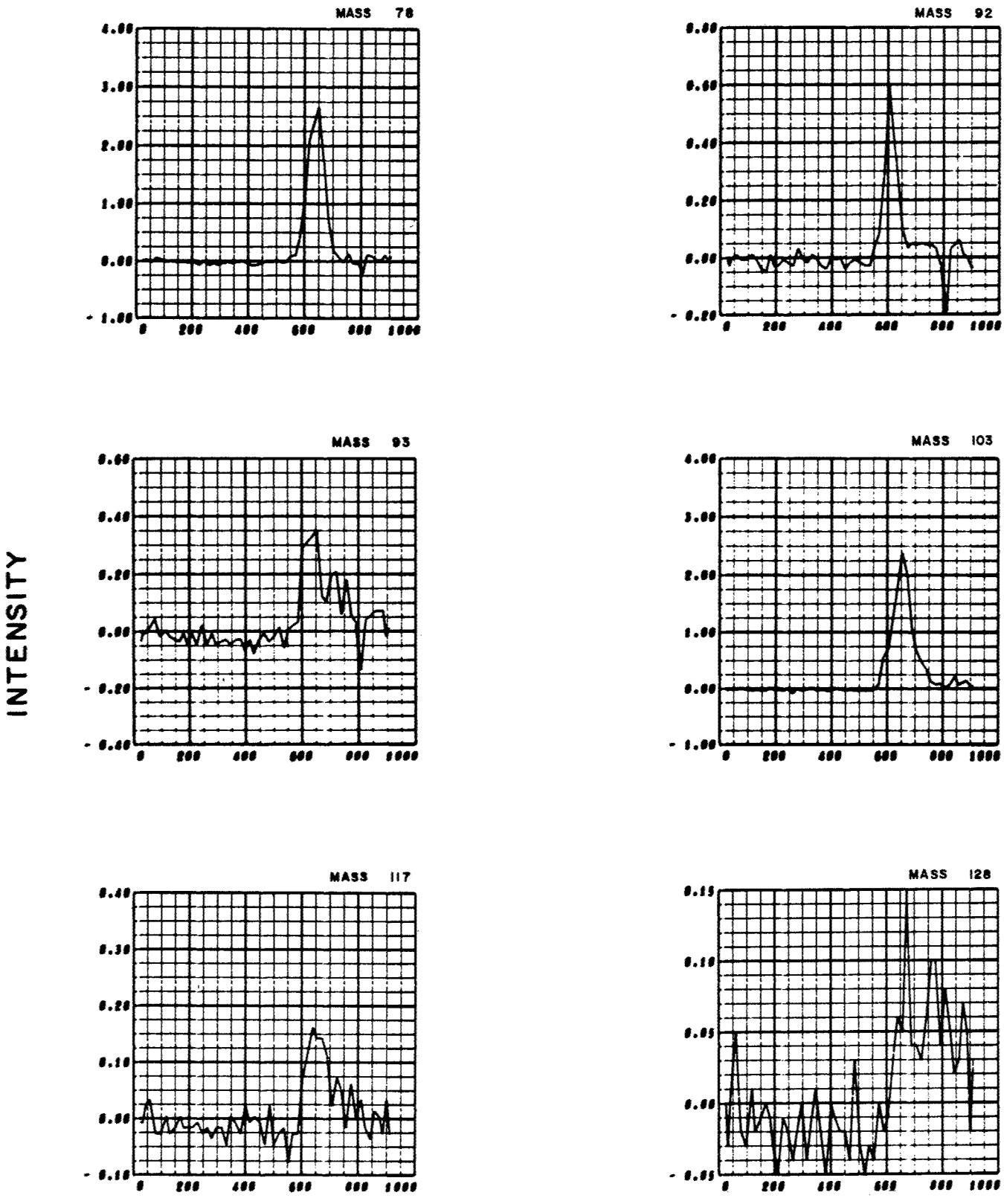

Figure 2. Representative Standardized MTA Results for Poly (m-Phenylene) Bibenzimidazole (PBI-M) (Part 2)

TABLE II

MTA RESULTS FROM POLY (M-PHENYLENE BIBENZIMIDAZOLE) (PBI-M)

Product	Evolution Temperature, °C		
	Start	Peak	Finish
Water	100	155	350
Carbon Dioxide	~200	~480	~580
Toluene	540	600	670
Benzene[a]	540	650	740
Aniline	550	~625	~800
Benzonitrile[a]	550	650	760
Phthalonitrile	~560	~670	900+
Ammonia[a]	560	730	900
Hydrogen[a]	560	740	900+
Hydrogen Cyanide[a]	560	740	900+
Nitrogen[a]	~575	900+	
Cyanoaniline (?)	590	650	820

[a] Present in sizable quantities

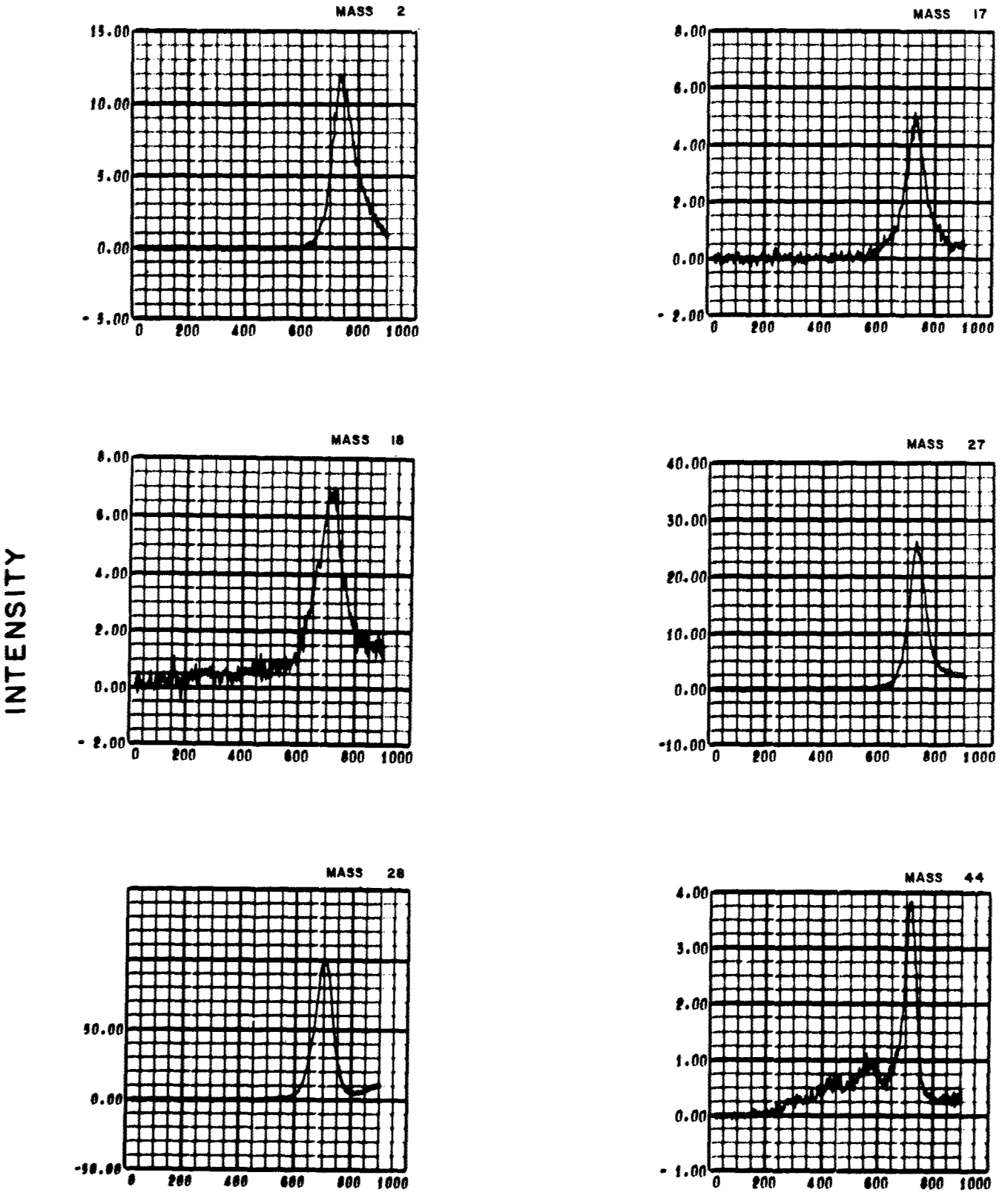

Figure 3. Representative Standardized MTA Results for 40 Mass Scan of Celanese Bis Benzimidazo Benzophenathroline Polymer (BBB)

TABLE III

MTA RESULTS FROM 40 MASS SCAN OF CELANESE BIS BENZIMIDAZO BENZOPHENATHROLINE POLYMER (BBB)

	Evolution Temperature, °C		
Product	Start	Peak	Finish
Carbon Dioxide	200	560	640+
Water[a]	~500	715	~850
Carbon Monoxide[a]	550	705	810+
Ammonia[a]	550	720	~870
Hydrogen Cyanide[a]	590	730	900+
Hydrogen[a]	600	740	900+
Carbon Dioxide[a]	<640	710	800
Nitrogen[a]	<810	900+	

[a]Present in sizable quantities

C. Bis Benzimidazo Benzophenathroline Ladder Polymer

A limited mass scan run was carried out for BBL-SN2 at only m/e-0, 27, and 28 in order to obtain many more data points than are available in a 200 mass scan run. The reduced results are shown in Figures 4 and 5. The automatic data collecting system was operated at a rate of 22.2 sec/scan, so data points were repeated at each mass approximately every 3.7°C. The graphs included only points where the heating rate was 10 ± 1°C/min.

D. Polyquinoxaline

Representative graphs for the 200 mass scan run for polyquinoxaline are shown in Figures 6-8. A mass shift occurred above 300°C, which affected the baseline for mercury isotopes. It did not appear to have a serious effect on the results. The problem was traced to dust in the high voltage divider circuitry, which was then cleaned. The results were compared with those of an earlier defective run and were found to be in good agreement, where the earlier data were thought to be valid.

The results are summarized in Table IV. The polymer appears to be contaminated with copious quantities of solvents and other impurities. Dichlorotetrafluoroacetonehydrate, for which no calibration spectrum exists, and m-cresol were reported to have been used during preparation of the polymer (ref. 19). The former was identified from m/e-164 (Fig. 8) (dehydro-chlorination) and m/e-85 (CF_2Cl^+). The presence of other fluorocarbon groups with peaks at ~250°C may indicate that the solvent contained impurities. Benzene evolved as a very broad peak, (see m/e-78, Fig. 8) and may at least in part have been a decomposition product. Hydrogen chloride (see m/e-36, Fig. 7) evolution probably originated from chlorinated solvents such as dichlorotetrafluoroacetonehydrate, its impurities, and chloroform. The latter was used during preparation (ref. 19) but was not observed as a product. The m/e-108 (Fig. 8) intensity was very weak and appeared in such a high temperature range that m-cresol may be a poor assignment.

E. Quinoxaline-Bis Benzimidazo Benzophenathroline Ladder Copolymer

A small fault in mass alignment was observed for the 200 mass scan FF-17EC MTA run, but most of the results were verified in the 20 mass scan experiment. The fault was most serious for the higher masses, but the masses were assigned by comparing the gate voltages with those values in the alignment table. The intensity values are relative, rather than quantitative. Representative results are shown in Figs. 9 and 10, and are listed in Table V. Several stages

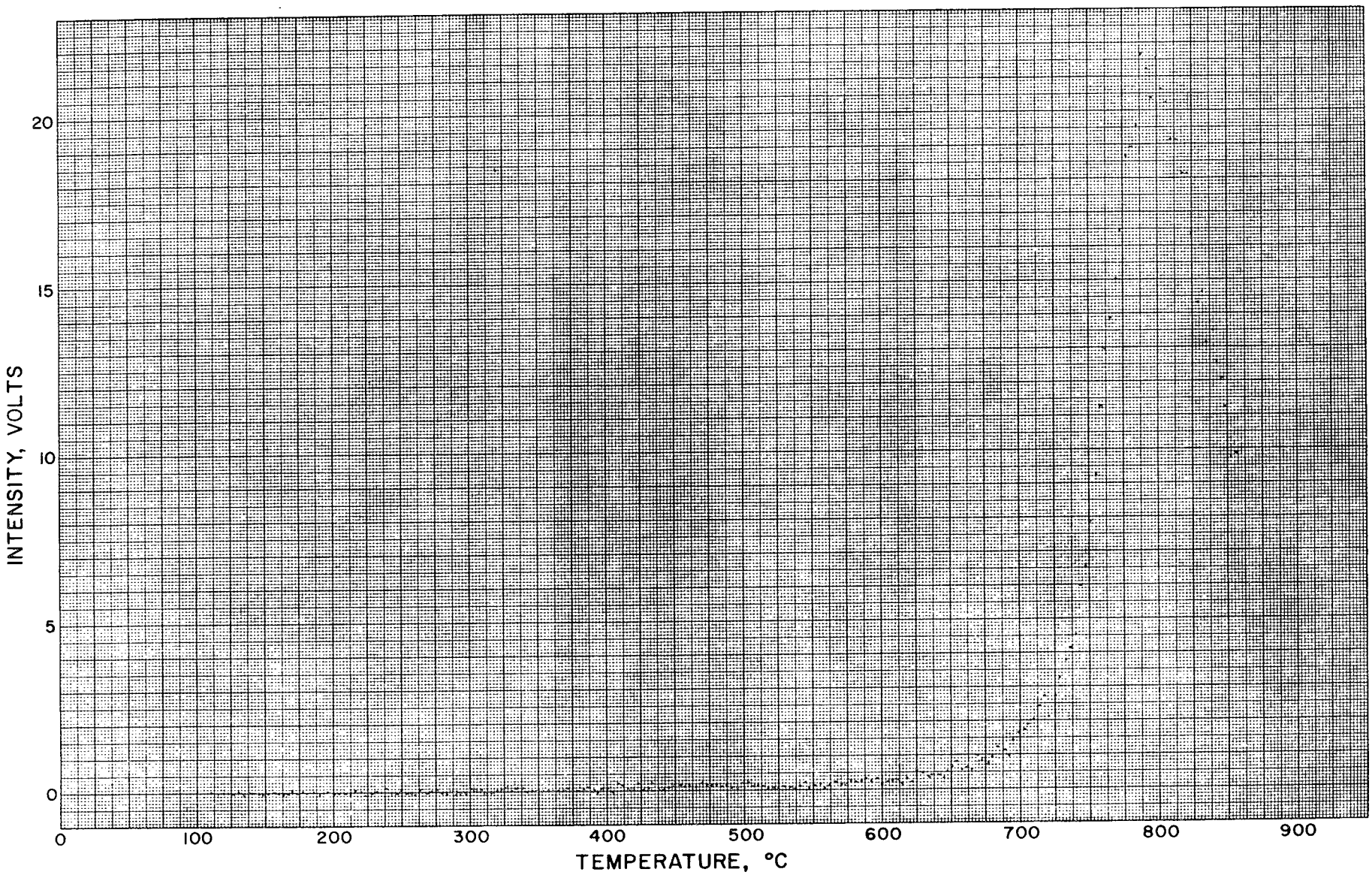

Figure 4. MTA Results for Bis Benzimidazo Benzophenathroline Ladder Polymer (BBL-SN2) at m/e-27

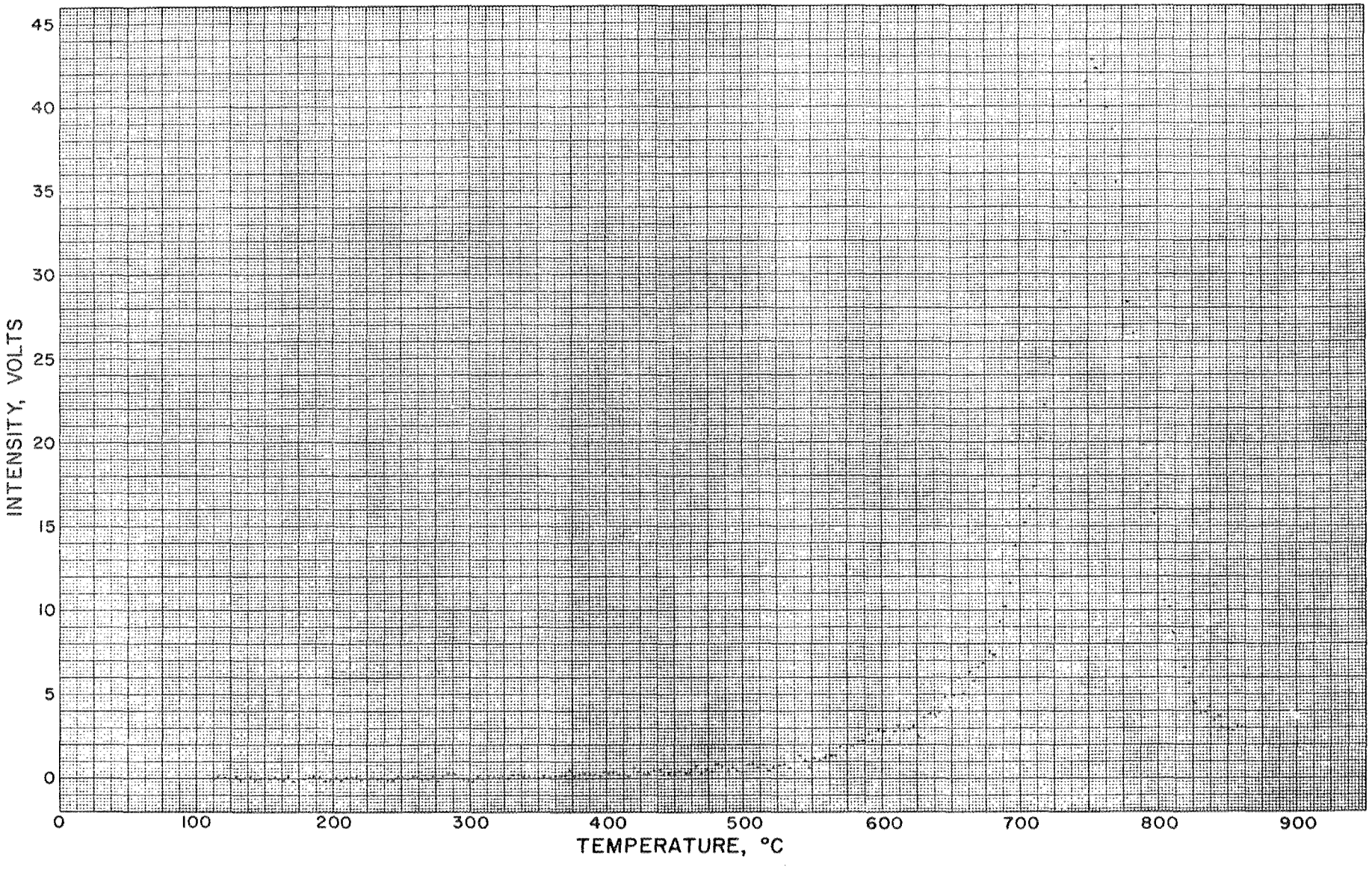

Figure 5. MTA Results for Bis Benzimidazo Benzophenathroline Ladder Polymer (BBL-SN2) at m/e-28

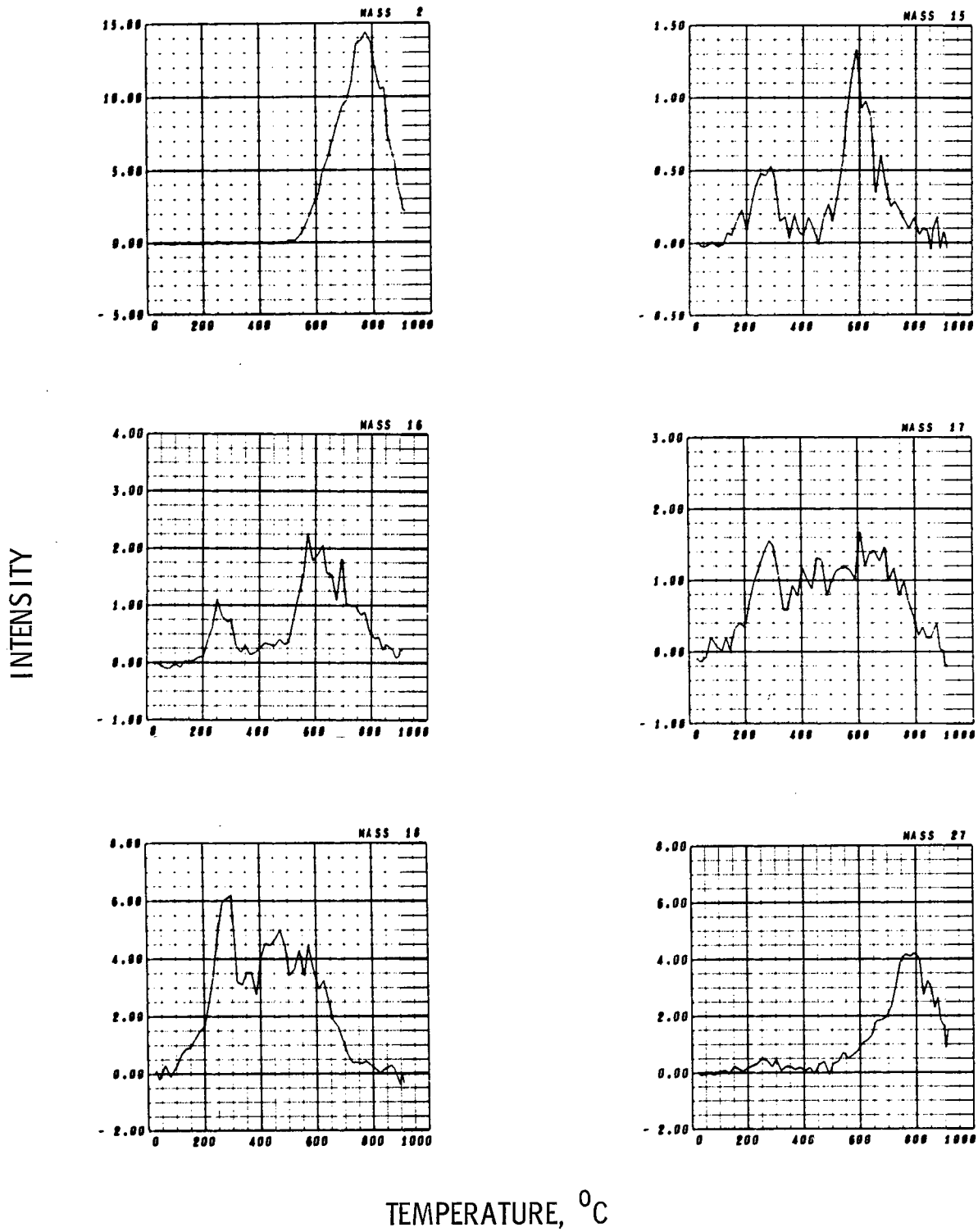

Figure 6. Representative Standardized MTA Results for Polyquinoxaline (Part 1)

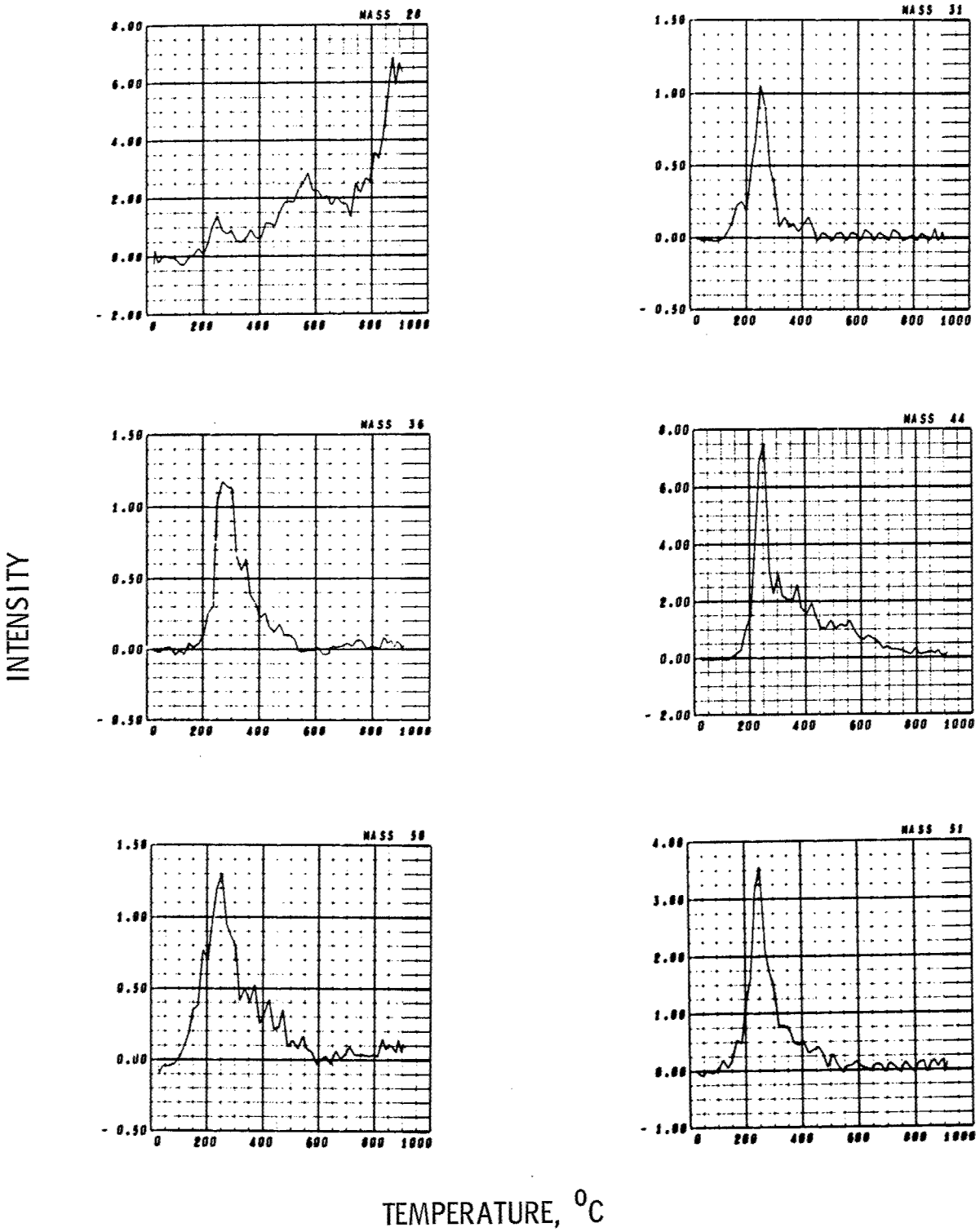

Figure 7. Representative Standardized MTA Results for Polyquinoxaline (Part 2)

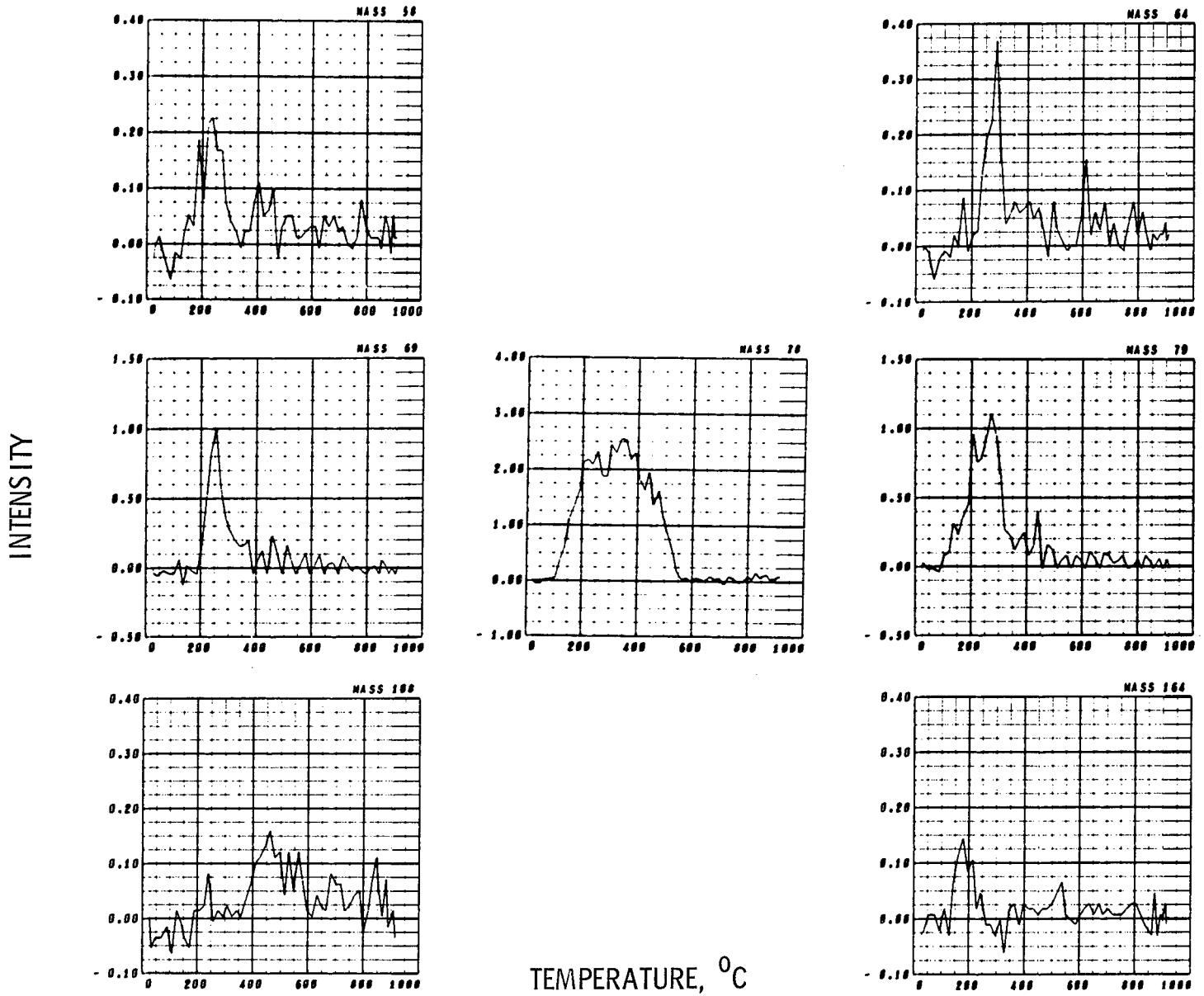

Figure 8. Representative Standardized MTA Results for Polyquinoxaline (Part 3)

TABLE IV

MTA RESULTS FROM POLYQUINOXALINE

Product	Evolution Temperature, °C		
	Start	Peak	Finish
Water[a]	80	285	375+
Pyridene[a]	90	270	~350
Acetone[a]	100	230	350
Benzene[a]	100	350	560
Carbon dioxide[a, b]	125	250	800
Dichlorotetrafluoroacetonehydrate	130	180	300
CF_3[a] (m/e-69)	190	250	390
CF_2H[a] (m/e-51)	~100	250	~ 400
CF_2 (m/e-50)	~100	250	~ 320
CF[a] (m/e-31)	<200	250	450
Hydrogen chloride[a]	140	275	540
Sulfur dioxide	200	290	320
m-Cresol	345	460	610
Water[a]	<375	475	900
Nitrogen[a]	~400	575	725+
Ammonia[a]	~400	~ 700	900
Hydrogen cyanide[a]	~400	775	900+
Methane[a]	~450	590	900
Hydrogen[a]	500	775	900+
Nitrogen[a]	<725	900+	

[a] Present in sizable quantities

[b] Some m/e-44 contribution could be from C_2FH; some m/e-32 may be due to CFH in same temperature range as for other fluorocarbon ions, but difficult to be certain because of high background noise.

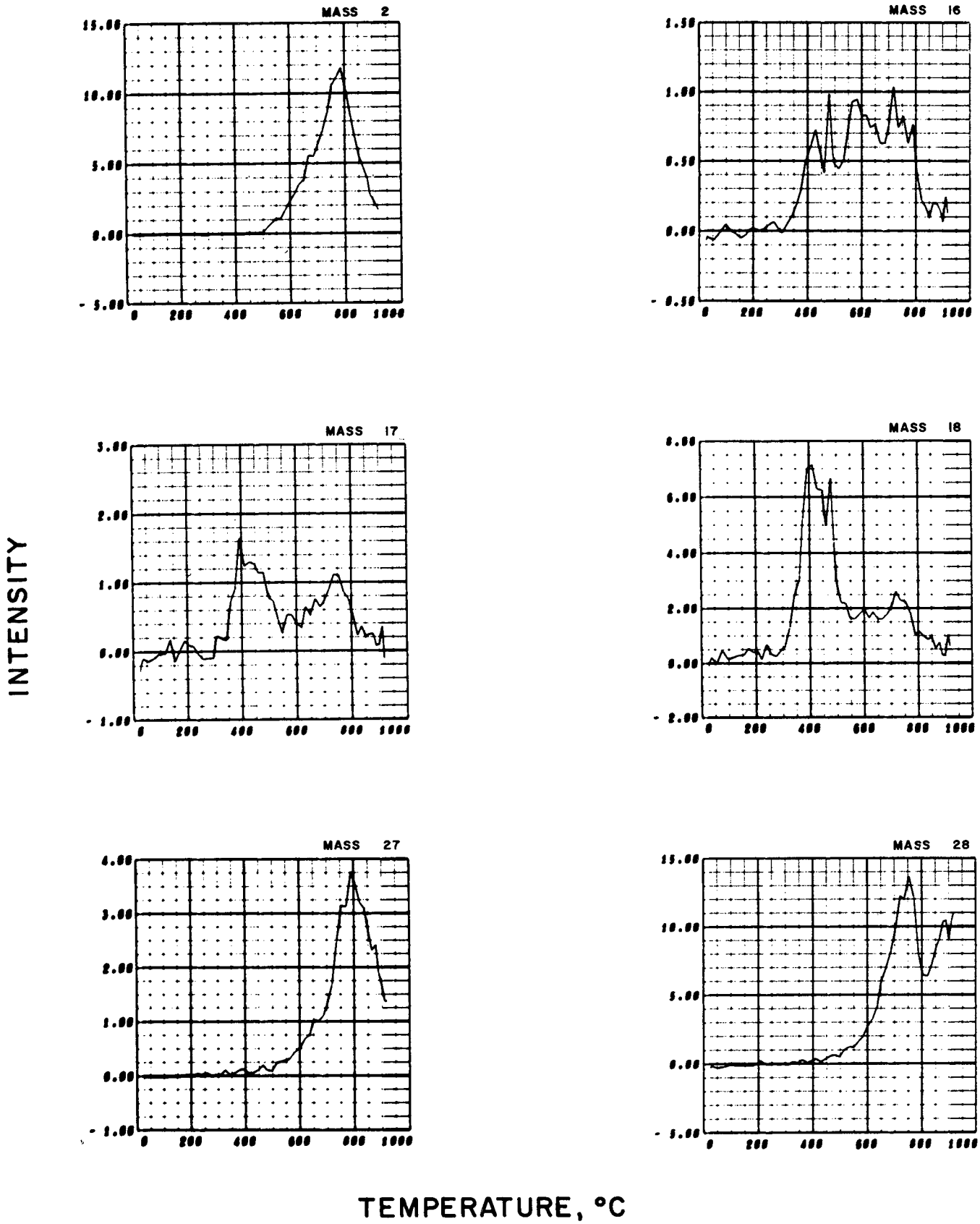

Figure 9. Representative Standardized MTA Results for Quinoxaline-Bis Benzimidazo Benzophenathroline Ladder Copolymer (Part 1). (Mass alignment somewhat defective)

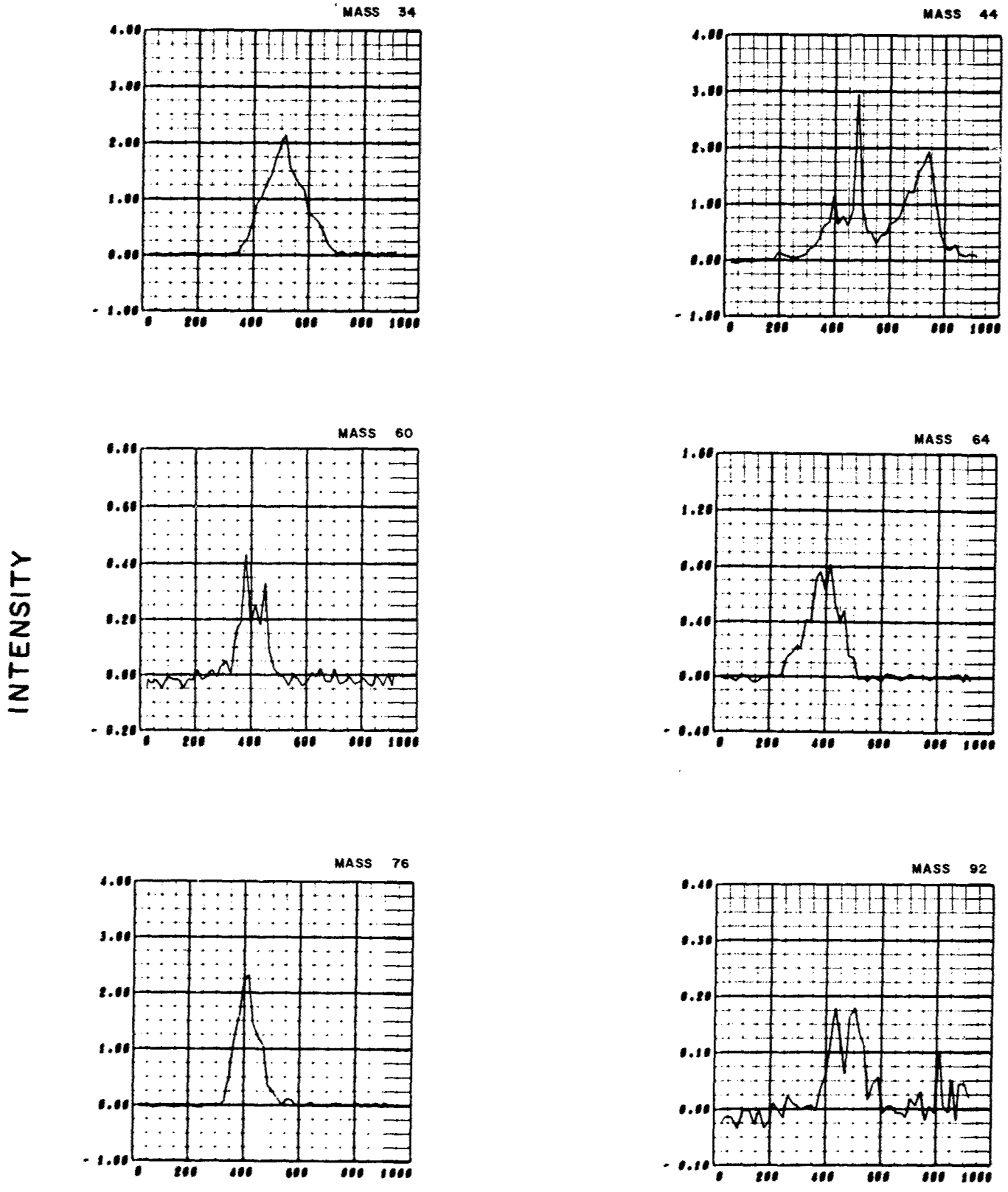

Figure 10. Representative Standardized MTA Results for Quinoxaline-Bis Benzimidazo Benzophenathroline Ladder Copolymer (Part 2). (Mass alignment somewhat defective)

TABLE V

TENTATIVE MTA RESULTS FROM QUINOXALINE-BIS BENZIMIDAZO BENZOPHENATHROLINE LADDER COPOLYMER (FF-17EC) (200 MASS SCAN RUN)

	Evolution Temperature, °C		
Product	Start	Peak	Finish
Carbon Dioxide	180	400	450+
Sulfur Dioxide	230	400	520
Water[a]	275	405	550+
Carbonyl Sulfide	~300	~400	~510
Carbon Disulfide[a]	310	405	600
Carbon Dioxide[a]	<450	485	~550
Water	<460	480	~550
Methane	<460	480	~550
Hydrogen Sulfide[a]	320	510	700
Toluene	~370	~480	~625
Methane	<400	~600	680+
Hydrogen Cyanide[a]	~300	790	910+
Carbon Monoxide[a]	~350	750	910+
Hydrogen[a]	500	790	910+
Carbon Dioxide[a]	<550	740	910+
Ammonia	<550	745	910+
Water	<600	710	~900
Nitrogen	<810	910+	

[a]Present in sizable quantities

of degradation are indicated, as grouped in the table. The presence of such copious quantities of sulfur products indicates contamination of the polymer. The sharp spikes that are evident for m/e-16, 18 and 44 at about 480°C could be due to popping and sudden release of entrained gases.

The following mass peaks were monitored for the 20 mass scan run: 0, 2, 14-18, 27, 28, 34, 44, 48, 59, 60, 63, 64, 75, 76, 78 and 92. Switching operations were very poor during the run, necessitating a considerable amount of manual data processing. Cal Comp plots of the most important results are shown in Figs. 11 through 22. The results are summarized in Table VI. The gases evolved earliest in the 200 mass scan run were missing in the 20 mass scan run. This is thought to be a consequence of very long evacuation preceding the 20 mass scan experiment. Note that the hydrogen cyanide, carbon monoxide and both stages of carbon dioxide evolution seemed to start at very high temperatures, and rather suddenly, compared to the 200 mass scan run. This sometimes indicates a shift in mass spectrometer sensitivity or in the location of the mass spectrum or gate. Since there was no indication of such changes in accompanying spectra, it is thought that evolution of those products was accurately indicated by the graphs. Perhaps the cause is related to the popping observed in the 200 mass scan experiment, and the bulk of those products being trapped in pockets within the polymer particles.

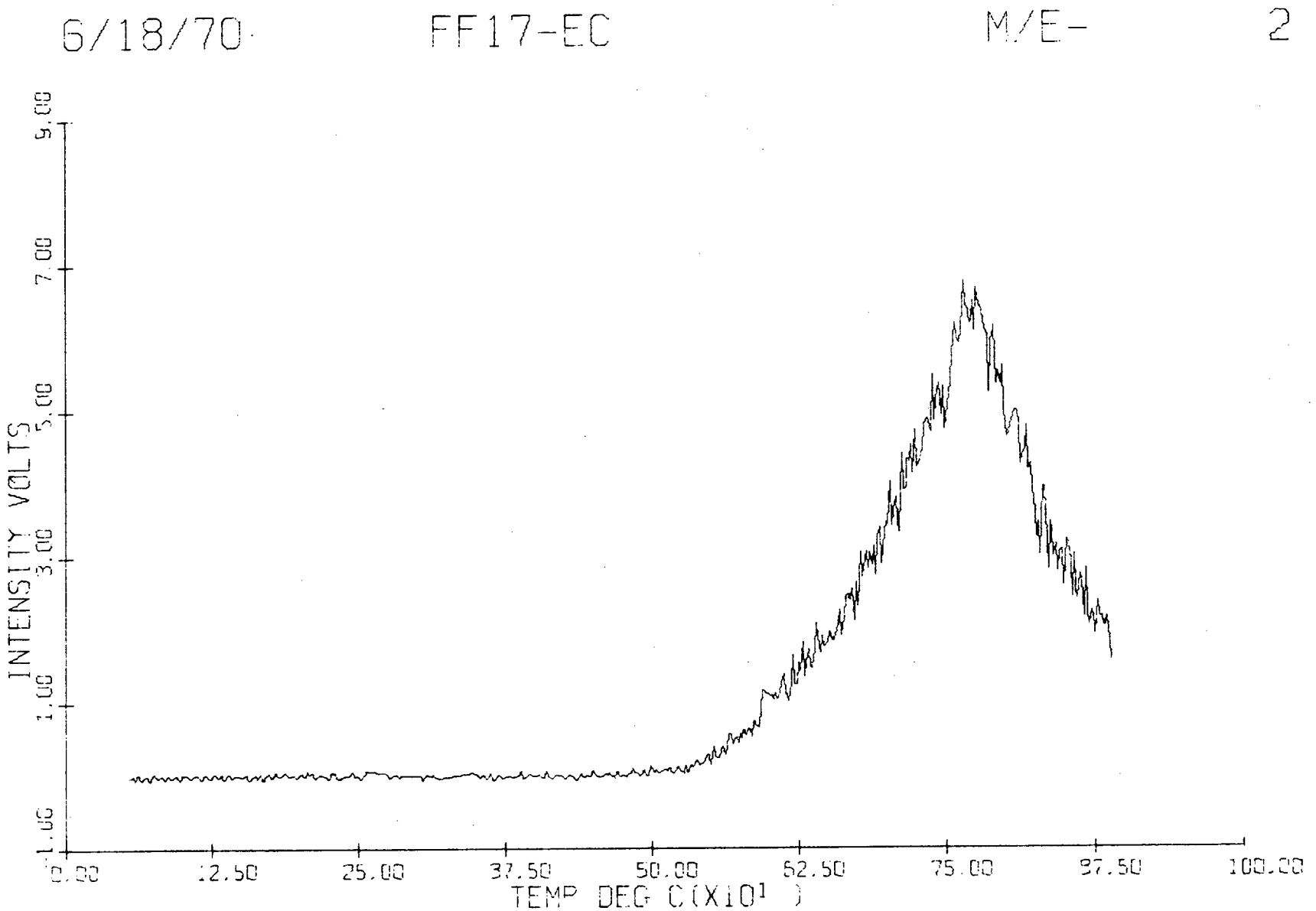

Figure 11. Standardized MTA Results for 20 Mass Scan Pyrolysis of Quinoxaline-Bis Benzimidazo Benzophenathroline Ladder Copolymer, m/e-2

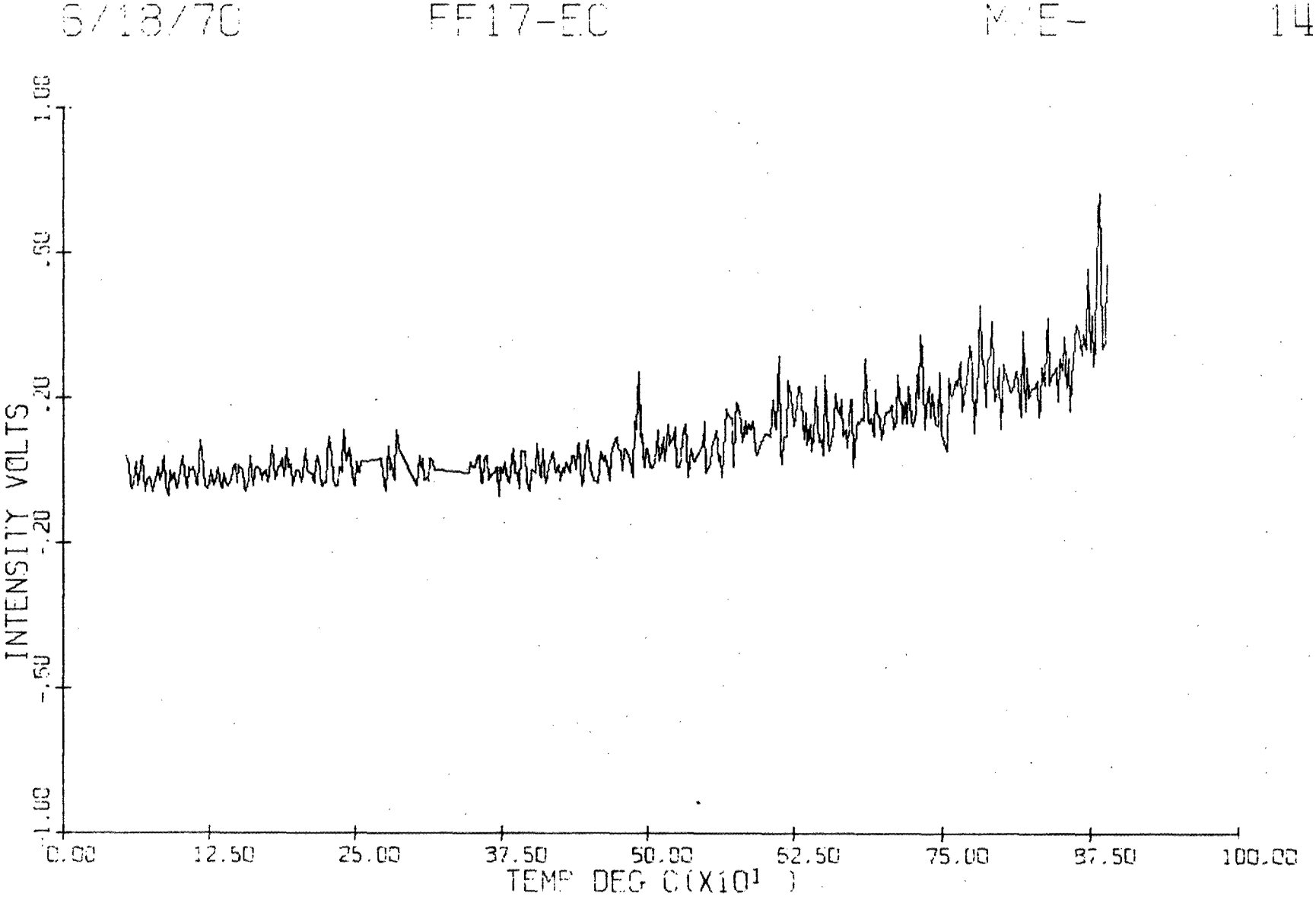

Figure 12. Standardized MTA Results for 20 Mass Scan Pyrolysis of Quinoxaline-Bis Benzimidazo Benzophenathroline Ladder Copolymer, m/e-14

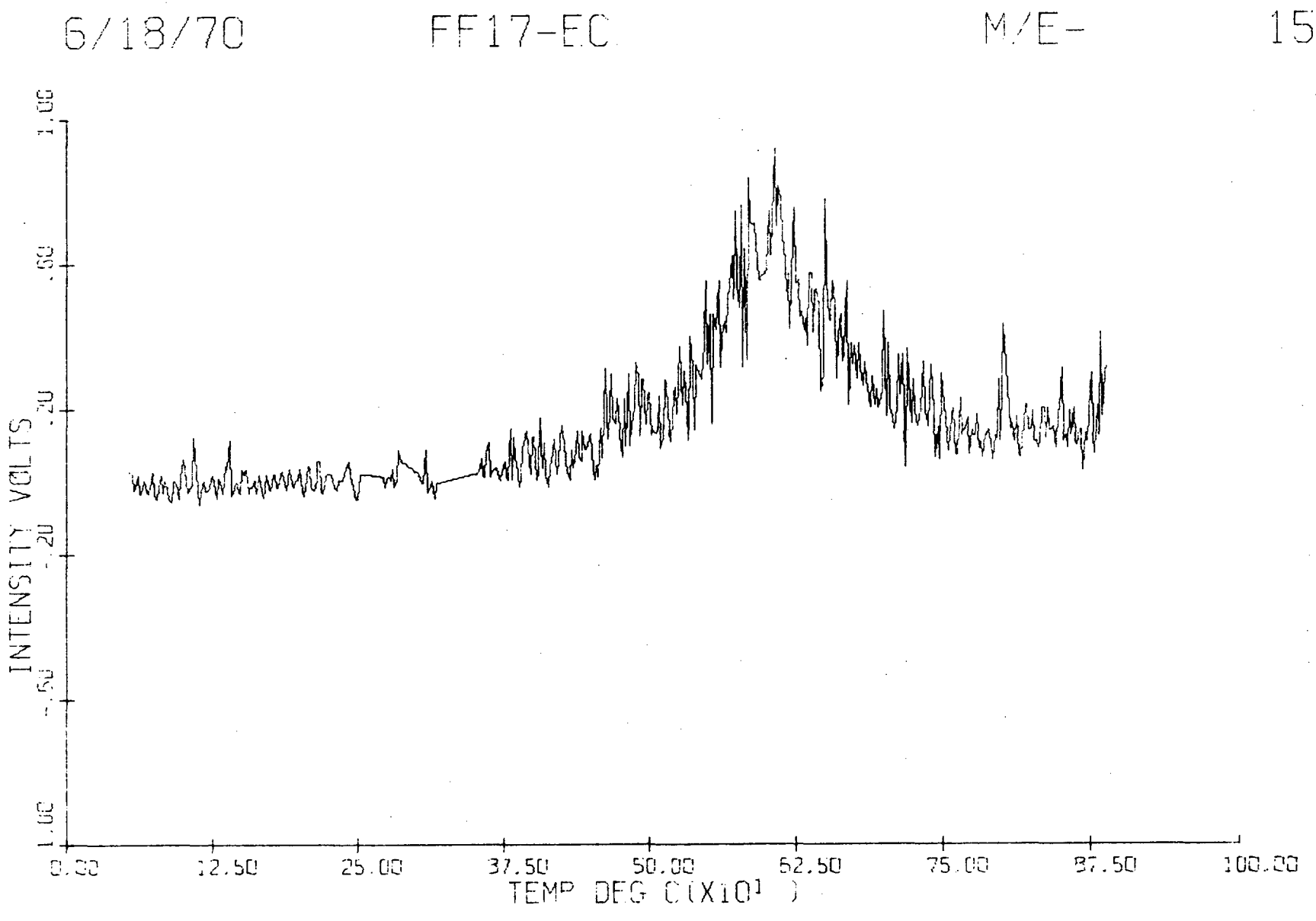

Figure 13. Standardized MTA Results for 20 Mass Scan Pyrolysis of Quinoxaline-Bis Benzimidazo Benzophenathroline Ladder Copolymer, m/e-15

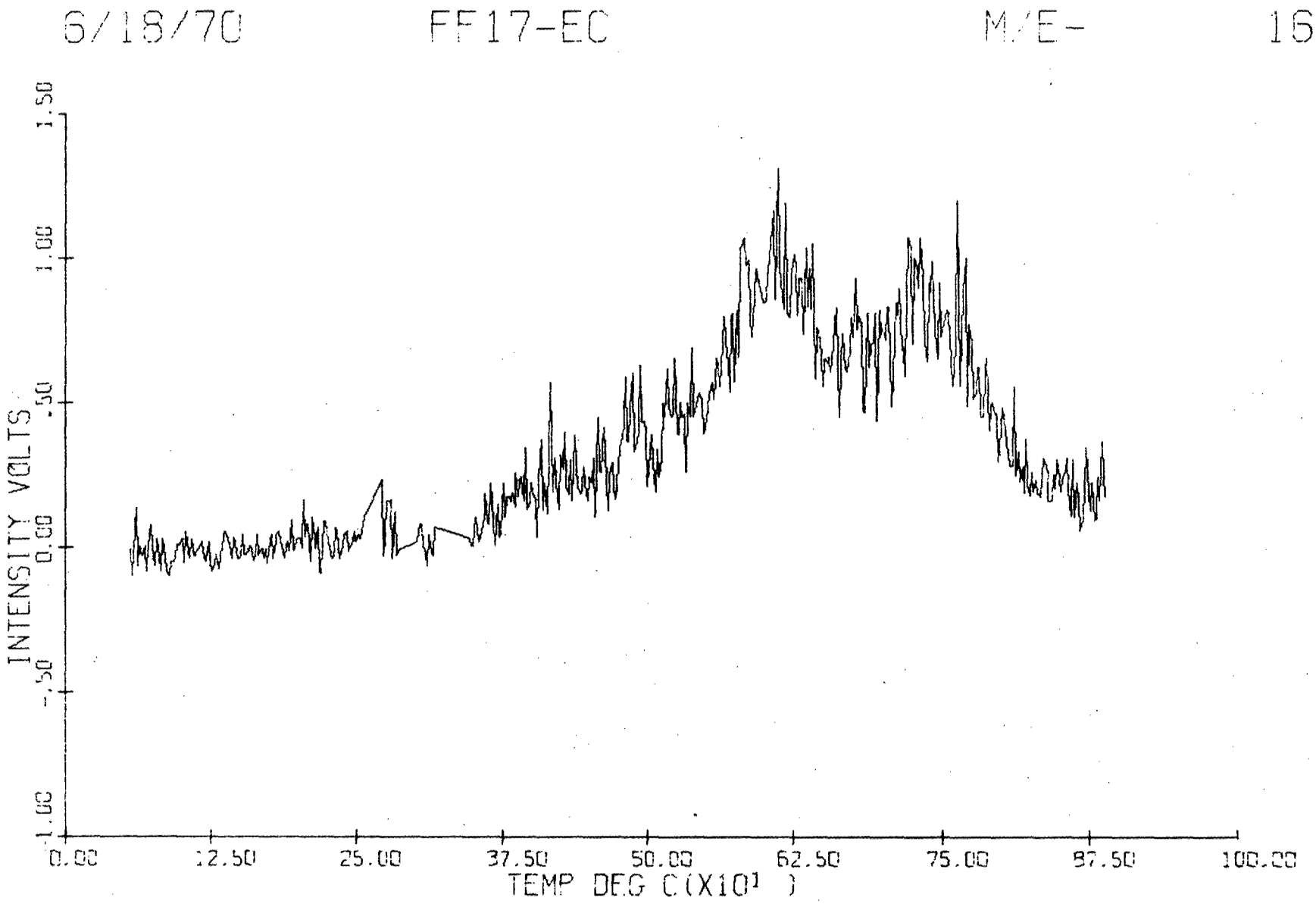

Figure 14. Standardized MTA Results for 20 Mass Scan Pyrolysis of Quinoxaline-Bis Benzimidazo Benzophenathroline Ladder Copolymer, m/e-16

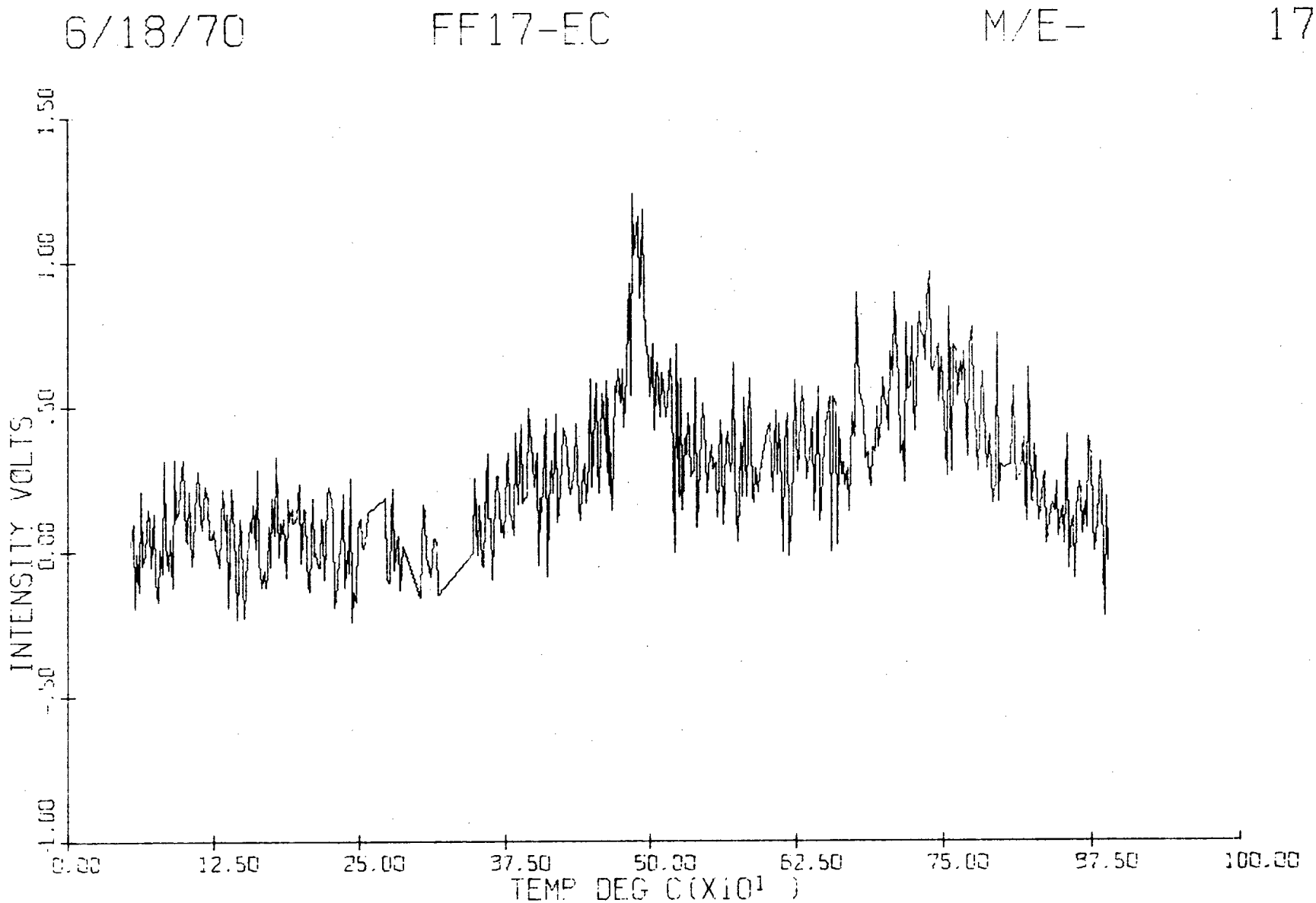

Figure 15. Standardized MTA Results for 20 Mass Scan Pyrolysis of Quinoxaline-Bis Benzimidazo Benzophenathroline Ladder Copolymer, m/e-17

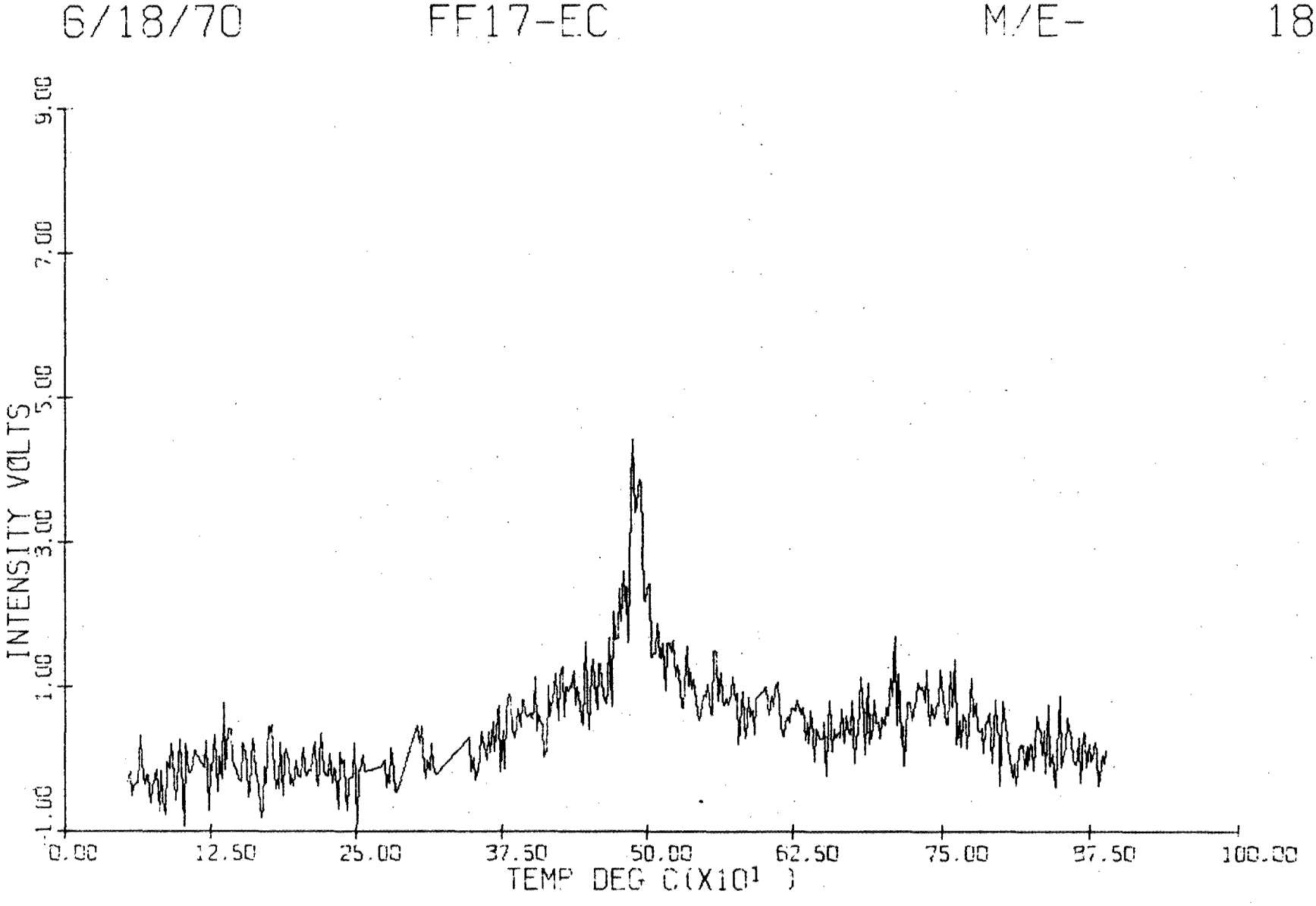

Figure 16. Standardized MTA Results for 20 Mass Scan Pyrolysis of Quinoxaline-Bis Benzimidazo Benzophenathroline Ladder Copolymer, m/e-18

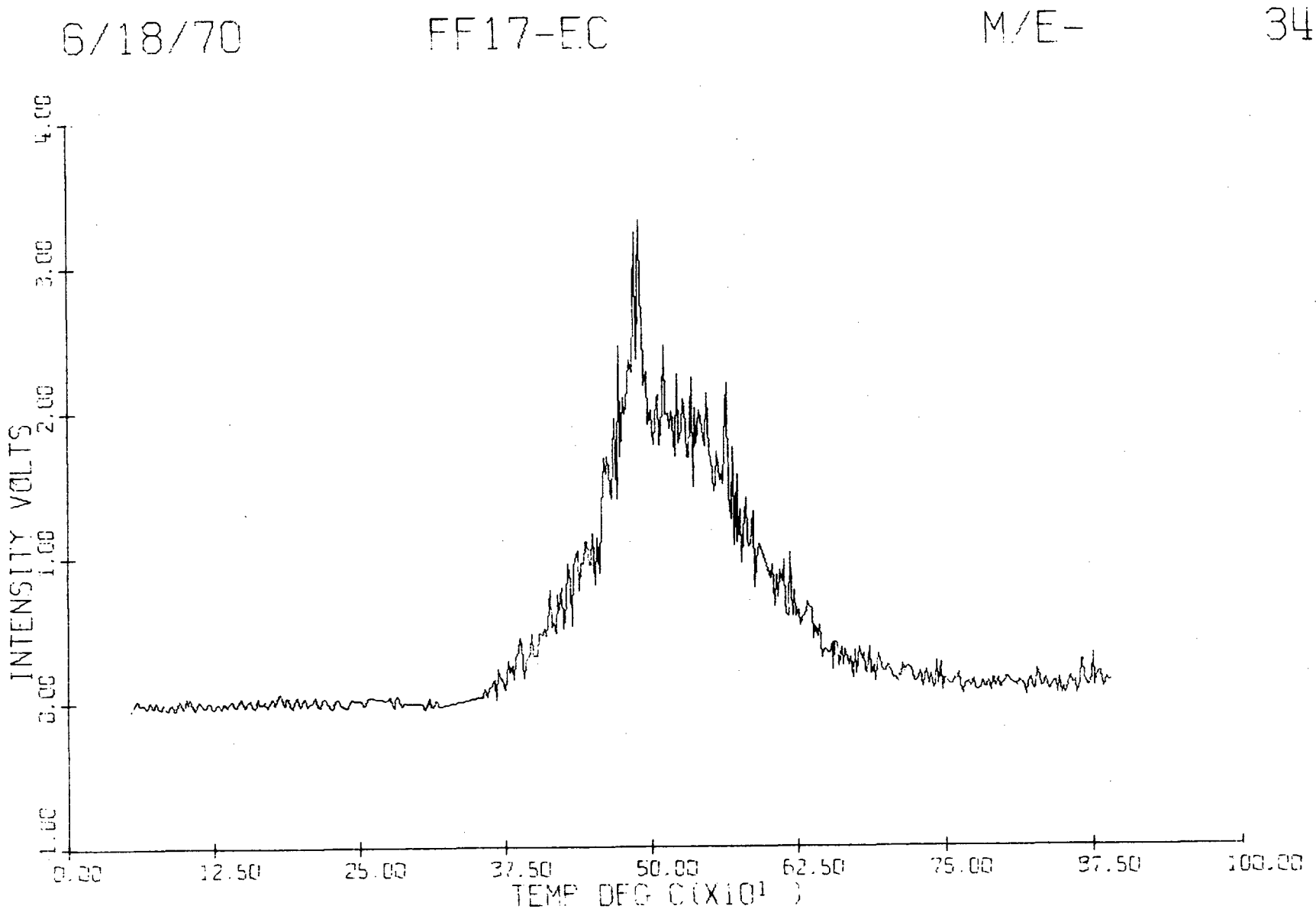

Figure 19. Standardized MTA Results for 20 Mass Scan Pyrolysis of Quinoxaline-Bis Benzimidazo Benzophenathroline Ladder Copolymer, m/e-34

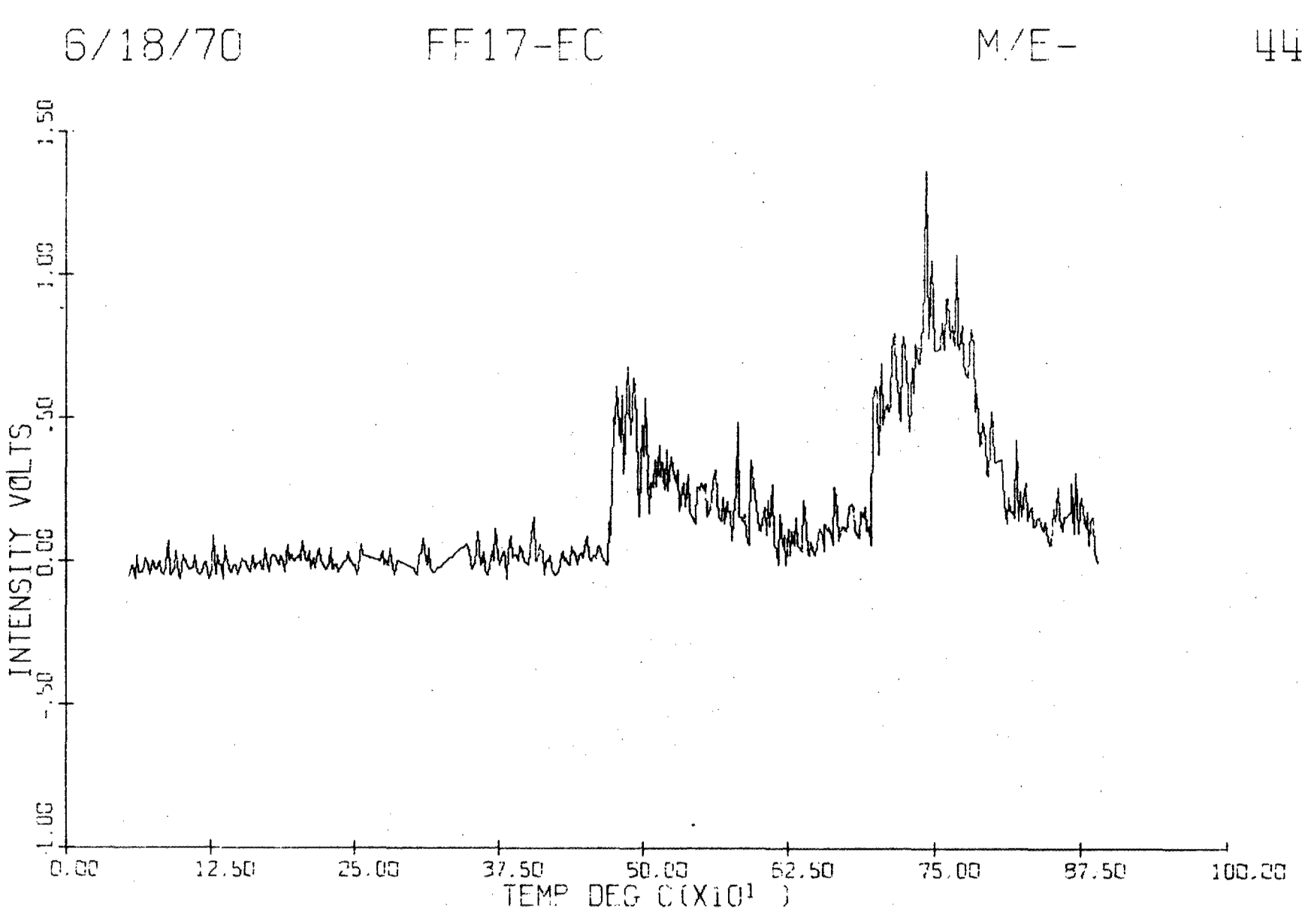

Figure 20. Standardized MTA Results for 20 Mass Scan Pyrolysis of Quinoxaline-Bis Benzimidazo Benzophenathroline Ladder Copolymer, m/e-44

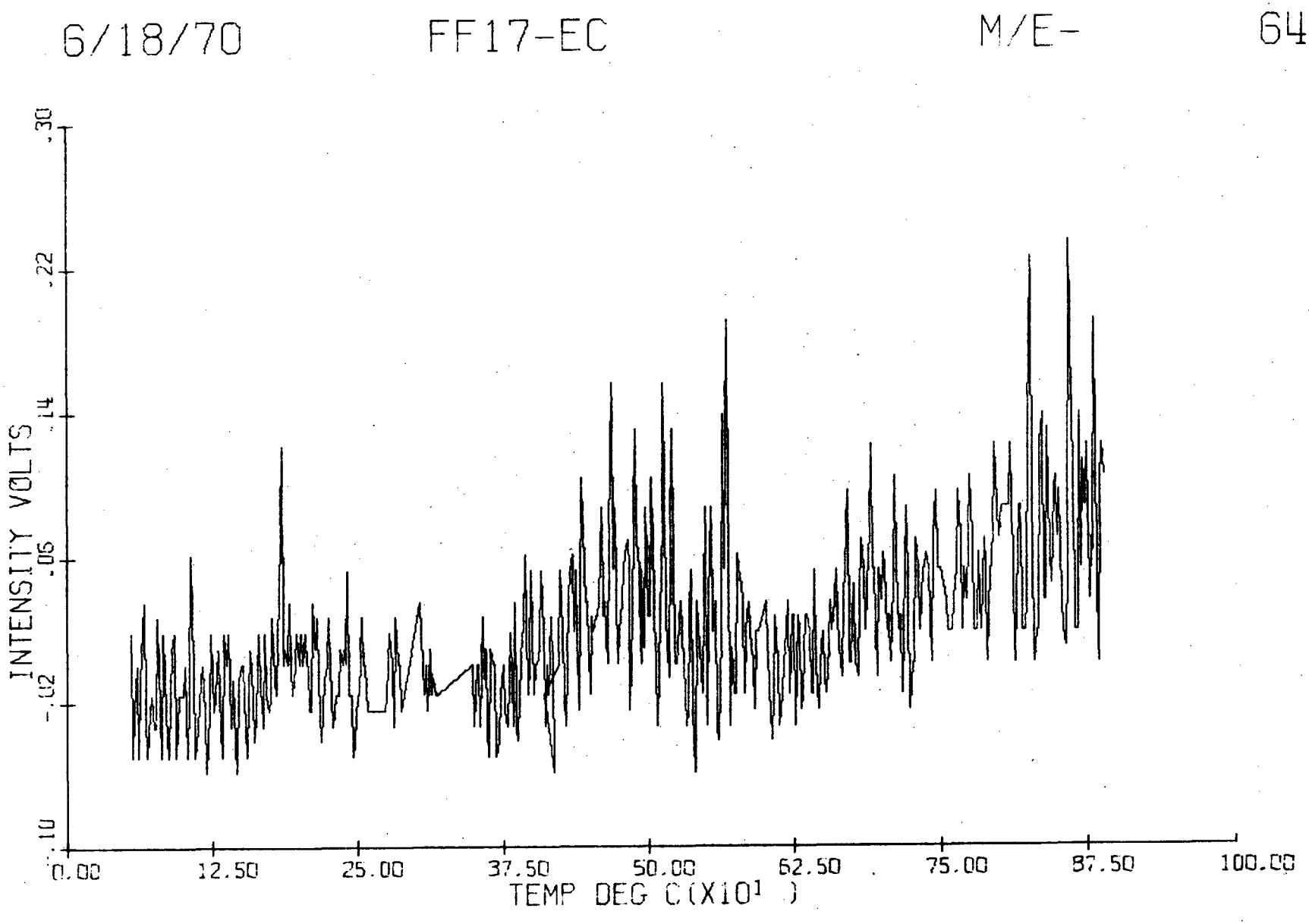

Figure 21. Standardized MTA Results for 20 Mass Scan Pyrolysis of Quinoxaline-Bis Benzimidazo Benzophenathroline Ladder Copolymer, m/e-64

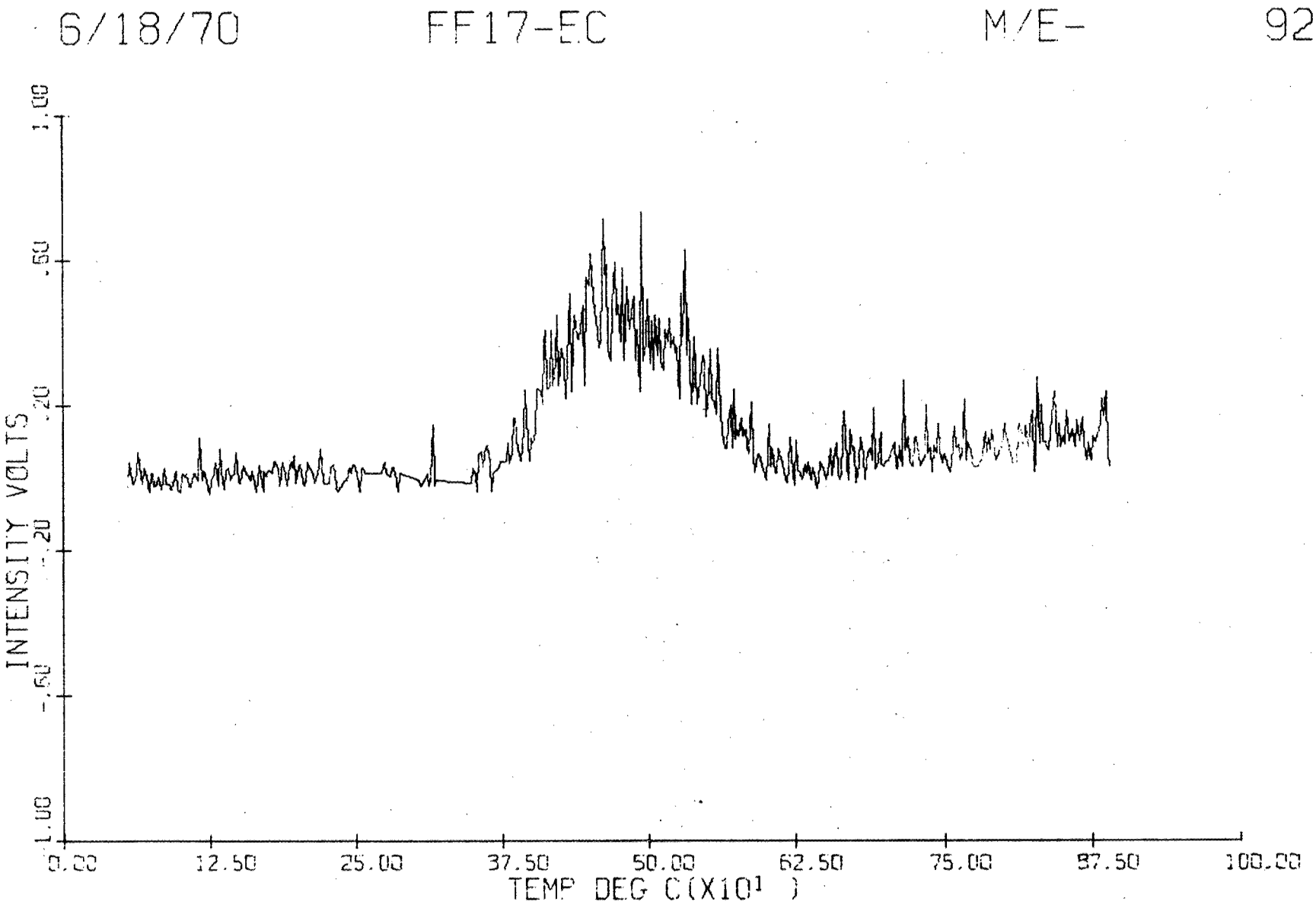

Figure 22. Standardized MTA Results for 20 Mass Scan Pyrolysis of Quinoxaline-Bis Benzimidazo Benzophenathroline Ladder Copolymer, m/e-92

TABLE VI

MTA RESULTS FROM QUINOXALINE-BIS BENZIMIDAZO BENZOPHENATHROLINE LADDER COPOLYMER (FF-17EC) (20 MASS SCAN RUN)

Product	Evolution Temperature, °C		
	Start	Peak	Finish
Sulfur Dioxide	312	476	538
Water[a]	318	488	651+
Hydrogen Sulfide[a]	326	485	763
Toluene	363	463	625
Carbon Dioxide	465[b]	479	641
Methane	428	596	771
Hydrogen[a]	445	770	887+
Water	< 651	731	810
Ammonia	< 625	734	859
Hydrogen Cyanide[a]	694[b]	769	888+
Carbon Monoxide[a]	694[b]	750	839+
Carbon Dioxide[a]	694[b]	739	849
Nitrogen[a]	487.5	887+	

[a]Present in sizable quantities

[b]Very sharp rise of product

SECTION V

DISCUSSION

A. Poly (m-Phenylene) Bibenzimidazole

MTA results for PBI-M were compared to those for PBI-MFD1 and PBI-M2F3, as shown in Figs. 18 to 20 and Tables XII and XIII of reference 5.

The PBI-M results were similar to those for PBI-MFD1, the freeze dried polymer, in most respects, especially for major decomposition products. The treatment process for PBI-M2F3 appeared to render it somewhat more stable than the other polymers, as shown by the somewhat higher temperatures for onset and peak evolution of several major products. The products that peaked at lower temperatures, such as benzene and benzonitrile were relatively more important compared to later peaking products, such as hydrogen and hydrogen cyanide. This is in agreement with thermogravimetric observations of Goldfarb (ref. 19).

B. Bis Benzimidazo Benzophenathroline Polymer

The results for Celanese BBB were compared with those for Monsanto BBB (Fig. 21 and Table XIV of ref. 5) and were found to be similar in most respects. The lower CO_2 and higher HCN yields for the Celanese polymer were described in ref. 6 and were discussed there. The quality of data with more frequent sampling were thought to be excellent.

C. Bis Benzimidazo Benzophenathroline Ladder Polymer

The MTA results for BBL-SN2 were quite consistent with the earlier 200 mass scan run (Fig. 5 of ref. 6), although the previous data were spoiled, in part, by overloading at the peaks for both of these masses. Mass-27 evolution appeared to commence at about 500°C, and peaked at about 795°C. The peak temperature was in good agreement with the earlier run, but the onset temperature was determined much more accurately in the present one, as explained in ref. 6. Mass-28 evolution commenced at about 380°C, peaked at about 755°C and reached a minimum near 850°C. All values were in good agreement with the earlier run. The peak intensity ratio of 28/27 was about 2. It was not possible to make an accurate evaluation for the earlier run because of overloading, but 1.5 is a reasonable estimate. These values were somewhat lower

than for the Celanese BBB polymer, but may actually indicate the degree of oxidation of polymers, as discussed in ref. 6. The temperature of onset of carbon monoxide evolution was much the same for the two polymers, but peak temperatures were 35 to 50°C higher for BBL-SN2.

D. Polyquinoxaline

The data for this polymer are somewhat difficult to interpret because of the evolution of solvent vapors. If most of the m/e-44 peak is due to C_2FH^+, as its shape suggests, then the low yield of CO and CO_2 is similar to that observed for polybenzimidazoles, and is consistent with the absence of oxygen in the structure of the polymer. Very small quantities of the more important decomposition products were observed, suggesting that the polymer has great thermal stability. In comparing the results to BBL-SN2, in this work and in ref. 6, it is clear that far less volatilization occurs for polyquinoxaline, although the onset of decomposition appears to occur at a lower temperature than for BBL.

E. Quinoxaline-Bis Benzimidazo Benzophenathroline Ladder Copolymer

MTA results from FF-17EC were compared with those from the homopolymers in Figures 6-8 of this report and Figures 4 and 5 of ref. 6. To a large extent, the results were a combination of those from both polymers. Carbon dioxide evolution was most like the end-capped BBL polymer, BBL-SN2-EC. Carbon monoxide formation was much like from BBL, but weaker. Nitrogen evolution was similar for all three polymers. Hydrogen cyanide evolution was similar to that from polyquinoxaline, and far weaker than from BBL. It was difficult to compare water. Ammonia evolution was similar to that from polyquinoxaline, and weaker than from BBL. Methane release was similar to polyquinoxaline, and was not observed for BBL. Hydrogen formation peaked at about the same temperature for all three polymers, but the start of evolution was similar to that for polyquinoxaline. Hydrogen evolution started for BBL at higher temperatures.

The absence of early contaminants in the 20 mass scan experiment, compared to the 200 mass scan experiment is quite interesting when one considers that carbon disulfide was observed in the latter case up to about 600°C. This is not a new observation, since volatile materials were observed at temperatures well above their boiling points, as early as in ref. 1. If one wants to study solvents or other volatile contaminants, it is necessary to control storage and the evacuation process very carefully. If decomposition studies in the absence of these materials is thought to be important, then long evacuation is indicated. Perhaps samples should be stored in a continually evacuated chamber long in advance of pyrolysis.

SECTION VI

CONCLUSIONS

A number of conclusions about the various polymers subjected to MTA in this and earlier studies are included in Sections IV and V and will not be repeated here.

The new data processing system is expected to increase the efficiency of operation and the quality of data to a significant extent, as described in Section II. We may therefore expect even more copious quantities of more accurate data from future experiments.

SECTION VII

RECOMMENDATIONS FOR FUTURE WORK

Complete development of analog tape data processing system and related computer programs.

Run MTA pyrolysis of new polymer samples as they are received.

Continue to carry out calibration runs and data processing for samples of products expected from preliminary analysis of completed runs.

Carry out approximate quantitative analysis, based on most reasonable comparison of MTA traces and calibration data.

Carry out kinetic analysis for selected products, and relate to decomposition mechanisms when possible.

Examine resulting information and compare with existing knowledge to determine quantitative relationships on the overall influence of chemical structure on thermal stability which will cover wide varieties of new high temperature polymers.

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13. ABSTRACT

Research was continued using mass spectrometric thermal analysis (MTA) to study the thermal degradation of various polymers. Full 200 mass scan runs, limited mass scan runs, and data processing were carried out for a polybenzimidazole, bis benzimidazo benzophenathroline polymer, its ladder polymer, polyquinoxaline and quinoxaline-bis benzimidazo benzophenathroline ladder copolymer. The results were compared with each other and with earlier data.

The concept of an improved data processing system was developed, based on the use of analog magnetic tape. The new system is discussed, together with steps taken to implement it.

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Bis Benzimidazo Benzophenathroline Ladder Polymer						
Polyquinoxaline						
Quinoxaline - Bis Benzimidazo Benzophenathroline Ladder Copolymer						
Evolved Gas Analysis						
Mass Spectrometry						