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ML-TDR-64-274
Part III

THE RELATIONSHIP BETWEEN STRUCTURE AND THERMAL STABILITY OF NEW HIGH TEMPERATURE POLYMERS

H. L. Friedman, G. A. Griffith and H. W. Goldstein

General Electric Company

TECHNICAL REPORT ML-TDR-64-274, Part III

April 1967

Each transmittal of this document outside the Department of Defense must have prior approval of the Polymer Branch (MANP), Nonmetallic Materials Division, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio 45433.

Air Force Materials Laboratory
Research and Technology Division
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

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NOTICES

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FOREWORD

This report was prepared by the General Electric Company under USAF Contract No. AF 33(657)-11300. This contract was initiated under Project 7340, "Nonmetallic and Composite Materials," Task No. 734004, "New Organic and Inorganic Polymers." The work was administered under the direction of the Air Force Materials Laboratory, Research and Technology Division, with Dr. Ivan J. Goldfarb, Project Engineer.

This work was performed in the Space 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; Dr. H. W. Goldstein, Physical Chemist; Mr. H. J. Galbraith and Mrs. P. P. Brazel, Mathematicians; Mr. G. A. Griffith, Mr. J. E. Brown and Mr. E. J. Brady, Jr., Technicians.

This report covers work accomplished from May 1965 to December 1966. The manuscript was released by the author in January 1967 for publication as an RTD technical report.

The author wishes to express his gratitude to John R. Mallin for help with the design of the automatic data processing system.

This technical report has been reviewed and is approved.

William E. Gibbs

WILLIAM E. GIBBS
Chief, Polymer Branch
Nonmetallic Materials Division
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ABSTRACT

Research aimed at obtaining quantitative relationships between structure and thermal stability of polymers was continued. Mass spectrometric thermal analysis was used to study differences in pyrolysis chemistry of untreated and heat treated poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole, and to study the pyrolysis chemistry of polybenzimidazole. An automatic data collecting system was successfully developed for this research, and was utilized for these measurements. Computer programs were developed for adjusting the data processing system and for automatic graph plotting of the data. Computer programs are being developed for refined data plotting and for final qualitative and quantitative analysis of the results. Several modifications were made in the pyrolysis and sampling vacuum systems.

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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.

In the first part of this program[1,2], an attempt was made to develop a vacuum microthermobalance to provide basic data for the evaluation of kinetic equations, which describe the chemistry of decomposition and serve as the quantitative measure of thermal stability. As research progressed, it was found that several errors influenced the results, and made them very difficult to interpret. Measurements that showed the effects of aerodynamic drag in vacuum thermogravimetry were the basis of a technical paper[3].

Continuous chemical analysis of decomposition gases formed during linear programmed heating of polymer samples was started with a time-of-flight mass spectrometer for identifying chemical reactions as an aid to kinetic analysis of thermogravimetry data. This method, which is now known as mass spectrometric thermal analysis (MTA) proved to produce even more useful data than thermogravimetry, so MTA was emphasized in the later research. As pyrolysis and analysis methods and apparatus were improved, it became evident that such vast quantities of data were generated in a single experiment, that data handling and processing were severe obstacles. Therefore an automatic data collecting system was planned, and parts were obtained, so that automatic qualitative and quantitative analysis of all decomposition gases, for any polymer, could be computed shortly after MTA was completed.

TECHNICAL DESCRIPTION

Apparatus

Automatic Data Collecting System

As a result of research completed during the period of this report, development of the automatic data collecting system has been completed. Schematic diagrams of the entire MTA system and of the automatic data collecting system are shown in Figures 1 and 2, respectively. A timing diagram for the latter is shown in Figure 3. A description of the operation and components of the automatic data collecting system is given below.

The three parameters, sample temperature, gate voltage, and ion signal are recorded continually as the mass selector is automatically programmed through a preselected series of steps, repetitively. The temperature and ion intensity signals originate from the retransmitting slidewire of the temperature recorder and from the analog output of the mass spectrometer, respectively. The gate voltage monitors the mass-to-charge ratio. These were found to be related to each other by the polynomial equation:

$$V = a + bm^{1/2} + cm + dm^{3/2} + em^{2}.$$

This relationship was obtained by least squares computer analysis of calibration data over a wide range of known masses, using several different polynomial forms. Appropriate gate voltages are generated by the mass selector, which consists of a Fluke Model 407DR power supply, a group of 200 Bourns wirewound Trimpots that are connected in series in a styrofoam insulated housing, and a Cunningham Scannex Model 309 Scanner. The power supply is a particularly stable unit, which was found to be necessary after several less steady supplies produced excessive gate voltage drifts. The scanner replaced a less accurate rotary reed switch. The individual potentiometers are adjusted to divide the power supply output into a series of discrete gate voltages. The scanner is a 600 position crossbar switch. Although 200 switches are in use currently, part of these could be eliminated or more potentiometers could be added, as needed. The input scanner is an Electronic Associates Inc. Model 5700 Data Point Scanner, which is a 60 position crossbar switch, but only three positions are used, one for each parameter. The signals are read with an Electronic Associates Inc. Model 6000 Digital Voltmeter. Four digit values are utilized, ranging from 0.000 to 9.999 V. Although the temperature and ion intensity readings fall within this range, the gate voltage signals are too high and are sent through a voltage divider. The signals are retained in the DVM by a hold pulse which is triggered shortly after the value is switched in, and are held in until all four digits have been transferred to paper tape with a Tally Model 420 PR-48-10 Tape Perforator.

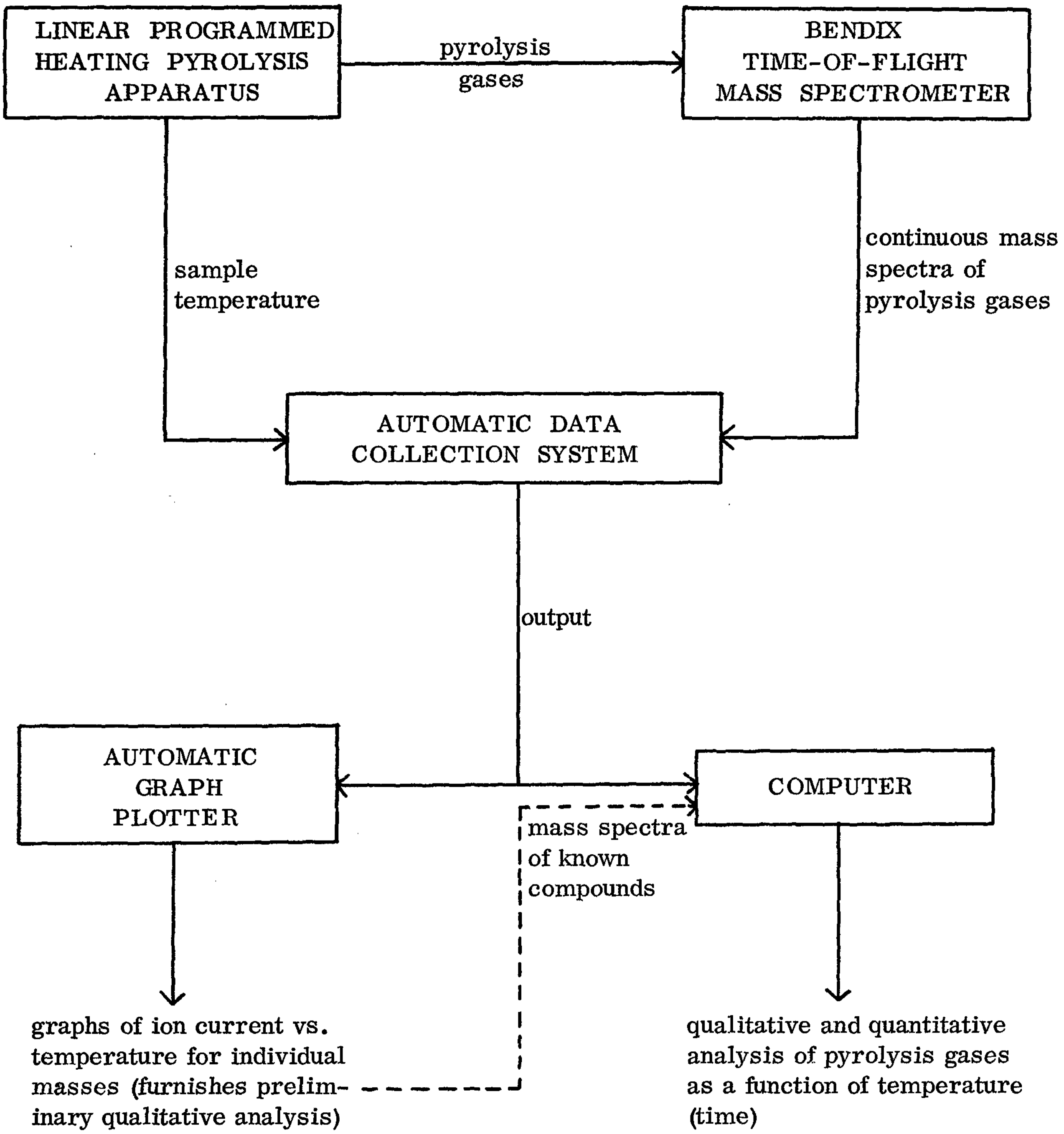

Figure 1. Mass Spectrometric Thermal Analysis System

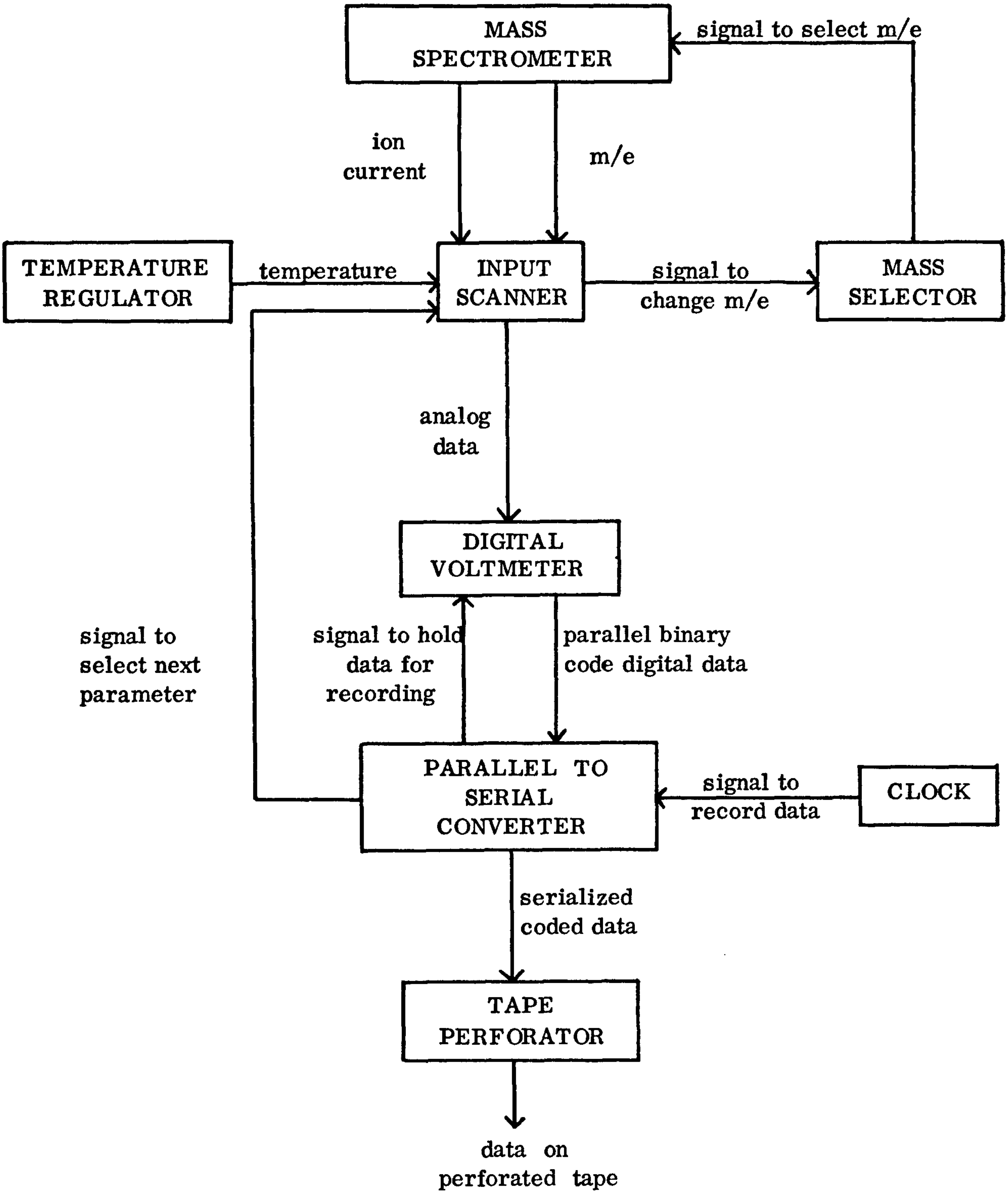

Figure 2. Automatic Data Collecting System

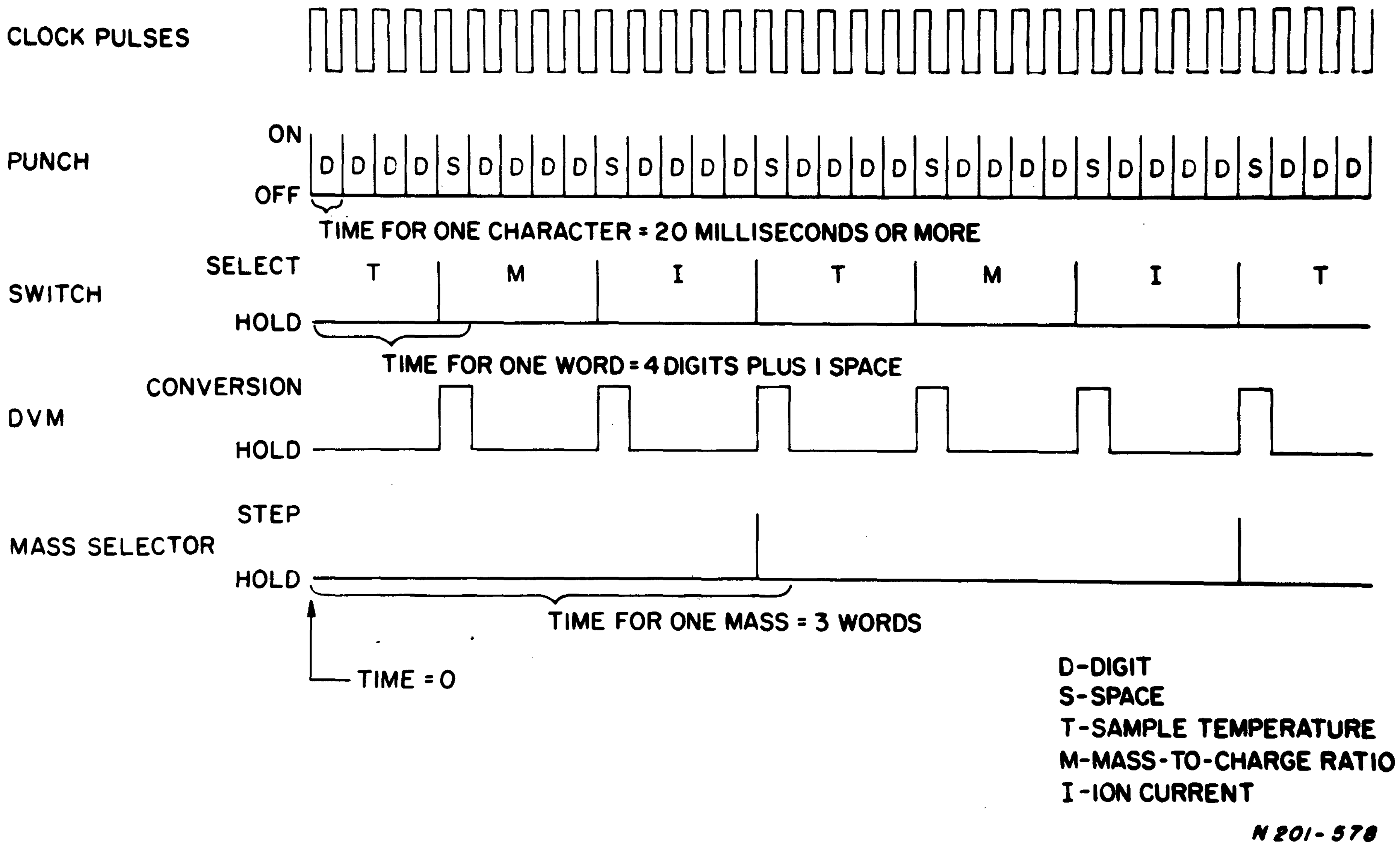

Figure 3. Timing Diagram for Automatic Data Collecting System

A space perforation separates the various values, and the hold is defeated in time for the next parameter to be accepted. An Electronic Associates Inc. Model 5010 Parallel to Serial Converter converts the DVM digital code to tape language. When the three parameters have been recorded, a signal pulse drives the mass selector to the next position. Since four digits and a space are recorded for each signal, fifteen perforations result for each mass setting. Three thousand perforations result for a scan of 200 masses, occupying 25 feet of tape. The maximum recording speed is governed by the perforator, which is rated at up to 60 perforations per second. The perforator has been modified to accept 3000 ft. reels so that its higher speeds may be utilized. The clock is a Tektronix Model 160 Waveform Generator. It governs recording speed by regulating the time between perforations.

In order to adjust the mass selector, gate voltages are measured for a least thirteen different known ionic fragments from hydrogen and hexachloroethane ranging from mass 1 to about 199. The five constants of the polynomial equation are determined by least squares using a General Electric Model 225 Computer. A table of gate voltage vs. mass number is provided by the same computer for all of the desired values. A list of experimental and calculated values of gate voltage appears in Table 1. Experience with the mass selector shows that it holds its adjustment very well over the duration of a run. For example, the gate voltages for m/e-1 ranged from 2.072 to 2.076 V for 67 values during a 100 minute pyrolysis, while the values for m/e-212 varied from 8.425 to 8.431 V. When the values must be adjusted, as is necessary from time-to-time, it is often accomplished by changing the two end potentiometers. Otherwise, small individual changes are made using DVM readings as a guide. Generally, less than 50% of the values are changed during a major readjustment. It is expected that even this situation will improve with the introduction of a more stable mass spectrometer high voltage power supply, as is planned for the near future.

One aspect of data collection which requires some improvement is accuracy of the data recorded by the automatic collection system. Comparison of the data with earlier results that were recorded with an oscillograph showed that while the ion intensity vs. temperature (time) relationships were maintained reasonably well for a single peak, the quantitative relationships between different mass peaks from the same substance were not nearly as accurate as the mass spectrometer could generate. Analysis of the situation showed that this was caused by inability to place the center of the analog gate of the mass spectrometer at the exact center of each mass peak. Oscilloscope measurements showed that while peak duration was about 140 nanoseconds, the effective gate duration that was used was about 35 nanoseconds. Uncertainty in mass selector positioning could contribute errors up to about 10 nanoseconds, and drift could perhaps contribute up to 10 nanoseconds more. Being 20 nanoseconds off center could cause a 25% reduction in signal to occur in the absence of an adjacent peak.

Table 1

Experimental and Calculated Values of Gate Voltage

m/e	Observed	Gate Voltage Calculated	Difference
1	2.074	2.077	+ 0.003
2	2.281	2.277	- 0.004
12	3.251	3.249	- 0.002
18	3.610	3.612	+ 0.002
24	3.919	3.917	- 0.002
35	4.387	4.389	+ 0.002
37	4.465	4.466	+ 0.001
47	4.823	4.825	+ 0.002
49	4.890	4.892	+ 0.002
59	5.209	5.208	- 0.001
61	5.269	5.268	- 0.001
82	5.849	5.848	- 0.001
84	5.902	5.899	- 0.003
94	6.147	6.147	0.000
96	6.198	6.195	- 0.003
117	6.670	6.673	+ 0.003
119	6.717	6.716	- 0.001
129	6.927	6.927	0.000
164	7.609	7.608	- 0.001
166	7.642	7.645	+ 0.003
199	8.216	8.217	+ 0.001
201	8.252	8.250	- 0.002

Standard Deviation = ± 0.0022 V

In order to eliminate these sources of error, one would ideally like to have a gate that admits the entire peak despite drift and placement errors. A gate duration of 180 nanoseconds would suffice for a 140 nanosecond peak. The maximum gate pulse for the standard system lasts about 95 nanoseconds. A related problem is associated with mass resolution, since defective placement or drift could move the gate to part of an adjacent mass peak, especially in the high mass end of the spectrum where resolution is poorest. The resolution problem is currently being attacked by lengthening the flight tube and modifying source geometry and pulses. Substantial improvements have already resulted in both peak separation and narrowing. Peak duration is down to about 120 nanoseconds, and further improvements are expected. Lengthening of the flight tube has resulted in loss of the m/e-1 ion for the compensation adjustments are not adequate to bring these ions to the multiplier. This is not serious, because these ions are not particularly important for analysis of the data. The strength and/or the position of the compensating magnets will be changed in the future, if necessary.

The gate pulse form may also contribute to errors. The gate pulse is a triangle whose apex reaches to about -150 V. Gating action goes into effect only below about -70 V, and gate duration is varied by changing the apex value. Because of the triangular form, ions that enter near the beginning or end of the gate pulse make less of a relative contribution to the overall signal than those near the center. A variable amplitude and duration square wave pulse generator with a nanosecond rise time range, several of which are available commercially, would be ideal. A recent modification of the gate pulse form has resulted in a partial squaring of the apex of the triangle and in an increase of duration so that it is wider than the peaks. These changes are currently being tested for accuracy.

The integration effect of utilizing the whole peak, rather than just peak height, as in using an oscillograph, should also increase the accuracy, for signal-to-noise ratio is expected to vary with the square root of the number of ions that are counted. This effect has already been indicated by the improved smoothness of results, as obtained by the automatic data collecting system, that will be described below.

Data Processing

Perforated tapes are converted to punched cards with an International Business Machines Model 533 Tape Reader. The cards are sorted according to mass number sequence, and are then used to generate a magnetic plotting tape with an International Business Machines Model 7094 Computer. The plotting tape is converted to a series of graphs of ion intensity vs. temperature for each mass fragment with a Stromberg Carlson Model SC 4020 High Speed Microfilm Recorder (automatic graph plotter).

The programs for this purpose were developed during the period of this report. A new graph plotting program is currently under development. The new program will do several things that the present one will not. (1) It will provide sorting of the data by sequence from the magnetic tape that is made from the punched cards. Preparation of punched cards is nearly automatic, except for entry of numbers that are required for sorting for the present graph plotting routine. (2) Temperatures as furnished from the retransmitting slide wire are different from actual sample temperatures, but have been adjusted so that there is a linear relationship between the two values. The program will correct the temperatures. (3) It is sometimes necessary to adjust scaling factors during a run. The new program will account for these changes so that the final graphs will have a single ordinate scale. (4) Zero signal level background must be maintained above instrument zero because both positive and negative ion intensity signals would result at or too near zero, and some of the data collecting system sequencing pulses would not function with a negative signal. Therefore, it is necessary to relate ion intensity signals to zero signal background level. The zero signal will be indicated on each graph. An instrument peculiarity complicates items (3) and (4). There are two scale adjustments; a decade factor and a doubling factor. The decade adjustment does not influence zero level, but the doubling factor does. The computer program will take these differences into account. (5) The graphs will indicate if a defective ion current has been recorded, as would occur if the operator would fail to attenuate the signal during excessively high evolutions.

The computer program for determination of qualitative and quantitative analysis is being developed. Preliminary qualitative analysis will be obtained by visual examination of the graphs. Calibration standards will be run for all compounds which are possible, and the results of all of these will be compared with the pyrolysis experiment in order to establish the final analysis. The following is a description of the digital computer routine, as presently developed, to analyze the mass spectrometer data. The argument is based on a heating rate of 10°C/min. and a mass scan rate of 200 masses/min., but is perfectly general and can be used for any rates.

The mass spectrometer sample is heated from ambient temperature to 1000°C at an approximately constant rate of 10°C/min. The mass selector reads at a rate of 200 masses/min. with monotone increase of the mass numbers until the largest mass number is encountered; then a new cycle starts, beginning again with the first mass number. Each mass number corresponds to a different sample temperature during a cycle; and to higher sample temperature during the following cycle. Also, the qualitative analysis of the system is a function of the sample temperature. In order to calculate the quantitative composition of the product gases from the mass spectrometer data the signal strengths of all fragments must be compared at the same corresponding sample temperature within a cycle.

The scheme for reducing the mass spectrometer raw data proceeds through the following steps:

(a) For one cycle, the signal strengths of all mass numbers are reduced by interpolation to a common temperature.

(b) The partial pressure of each product gas having a unique signal is calculated. A "unique" signal is a signal deriving from one, and only one, product gas.

(c) The total signal strengths of the product gases with unique signals are subtracted from the original set of signal strengths.

(d) A set of most sensitive signals for the product gases which contain no unique signals is then determined; (one signal for each product gas), and the partial pressures for these product gases are then calculated by a matrix inversion algorithm.

GLOSSARY OF SYMBOLS

Symbol	Description	Dimension
R	Heating Rate	^{o}C/Min.
S	Mass Selector Rate	Fragments/Min.
T	Temperature	^{o}C
θ	Time	Minutes
N	Total Number of Mass Fragments	---
Z	Total Number of Product Gases	---
u	Total Number of Product Gases with Unique Signals	---
h, H	Signal Strength	Arbitrary Divisions
E	Any Product Gas	---
P	The Partial Pressure of any Product Gas	Microns
M, A	A Calibration Quantity	---
I	Relative Intensity	---
B	Base Peak Sensitivity	Divisions/Micron
Φ	n-Butane Sensitivity for a Calibration	Divisions/Micron
Ψ	n-Butane Sensitivity for a Run	Divisions/Micron

The following symbols are indices:

Indicial Symbol	Symbol Type	Range
n	Fragment index	1, 2, --(n - 1), N
m	Fragment index	1, 2, --(m - 1), N
α	Cycle index	
j	Product gas index	1, 2, --(j - 1), Z
i	Product gas index	1, 2, --(i - 1), μ

Two arrays of indices are also needed. They are:

L_i = An array of j type indices

K_i = An array of n type indices

If $j = L_i$ then E_j has a unique signal and

$n = K_i$ when $j = L_i$

For step (a) described above:

$$(1) \quad T^{\alpha}_{m} - T^{\alpha}_{n} = (m-n)\frac{R}{S} \text{ where } m>n$$

$$(2) \quad T^{\alpha+1}_{n} - T^{\alpha}_{m} = \frac{NR}{S}$$

$$(3) \quad T^{\alpha}_{n} < T^{\alpha}_{m} < T^{\alpha+1}_{n}$$

Assuming that the signal strength can be interpolated linearly between T^{α}_{n} and $T^{\alpha+1}_{n}$

$$(4) \quad H_n = H^{\alpha}_{n} + \frac{m-n}{N}\left(H^{\alpha+1}_{n} - H^{\alpha}_{n}\right)$$

In practical application:

$$\frac{\Delta T}{\Delta \alpha} = 10^{o}C$$

$$\frac{\Delta \theta}{\Delta \alpha} = 1 \text{ minute}$$

Thus the assumption that the signal strength can be interpolated linearly is not too radical. Previous experience shows that the assumption is reasonable.

For step (b) described above:

(5) $$\text{let } A_j^n = \frac{I_n B_j}{100\ \Phi_j}$$

When $j = L_i$, $n = K_i$ by definition

(6) $$\gamma_{L_i}^{j}\ P_j = \frac{\gamma_{K_i}^{n}\ H_n}{A_j^n\ \Psi} = P_i$$

Equation (6) reduces to the identity

$0 = 0$ when $j \neq L_i$

When $j = L_i$ equation (6) calculates P_i, the set of u partial pressures for the product gases which contain unique signals, (A_j^n is dimensionless in equations (5) and (6) above.)

γ = the Kronecher delta

For step (c) described above:

(7) $$h_n = H_n - \sum_{i=1}^{i=u} P_i A_j^n\ \Psi$$

In equation (7) h_n is the entire set of adjusted signal strengths.

For step (d) described above:

let $r = (Z - u) = c$

and h_r = the set of r adjusted signals of maximum sensitivity

and $M_c^r = \frac{I_r B_c \Psi}{100\,\Psi_j}$

M_c^r has the dimensions divisions/micron

(8) let $M = \left\| M_c^r \right\|$

Then:

(9) $M \cdot P_c = h_c$

(10) $M^{-1} \cdot h_c = P_c$

Equation (10) now calculates P_c, the set of (Z - u) partial pressures for those product gases with no unique signals and the analysis is now completed.

The fortran coding of the program follows directly from equations (1) thru (10) above. The kernel letter is the name of a variable, an array, or a matrix while the corresponding indices are the subscripts for the array, or matrix.

The input data for the routine is:

(1) A scan of mass spectrometer signals

(2) A record of T and θ for the scan

(3) I_j^n, B_j, ϕ_j, E_j, Z, u, L_i, K_i, R, S, N.

The output data will be a plot of P_j versus temperature.

The matrix to be inverted will first be transformed so that it is nearly normal and orthogonal, then inverted by Gaussian elimination. This matrix will vary in size from about (15 x 15) maximum to (4 x 4) minimum.

Meyer, Olson and Berlint[4] have recently prepared a FORTRAN program to provide quantitative analysis for 20 components with 30 fragments each. Flash photolysis products of gases are studied with a time-of-flight mass spectrometer. The data are recorded with a drum camera and the film is digitized with an x-y film reader. These authors have made their program available to this Laboratory. Final development of the computation program will probably be aided by the existing program, and is expected to commence shortly because of the prospect of obtaining accurate quantitative data with the automatic data collecting system in the very near future.

Experimental

An addition to the existing gas inlet system for the introduction of calibration samples of low volatility has been built. A sample container which can be sealed and attached to the gas inlet system will be evacuated, weighed with a microbalance in a dry box which has been modified for this work, filled with the sample and reweighed. Analog spectra for volatilization of all or part of the sample will be recorded and then the sample will be reweighed. Thus the integrated ion intensity will be obtained as a function of sample weight. During the calibration procedure the fragmentation pattern will also be obtained. All calibration experiments will be compared with samples of n-butane in order to account for any changes in the mass spectrometer sensitivity.

The obtaining of "pure" samples for the quantitative calibration of the decomposition products obtained from the pyrolysis of the four polybenzimidazoles has been initiated. Several compounds have been purified by chromatographic techniques. Others are expected to be available soon. Recrystallization will be used for the less volatile samples.

Evidence of pyrolysis products of silicone stopcock grease appears from time-to-time, indicating that this material may be transferred in handling the various parts of the pyrolysis system. Therefore, the pyrolysis apparatus has been modified in order to eliminate the use of greases. The new pyrolysis vacuum system is shown in Figure 4.

It is customary, now, to pyrolyze only samples that have been passed through a 325 mesh sieve.

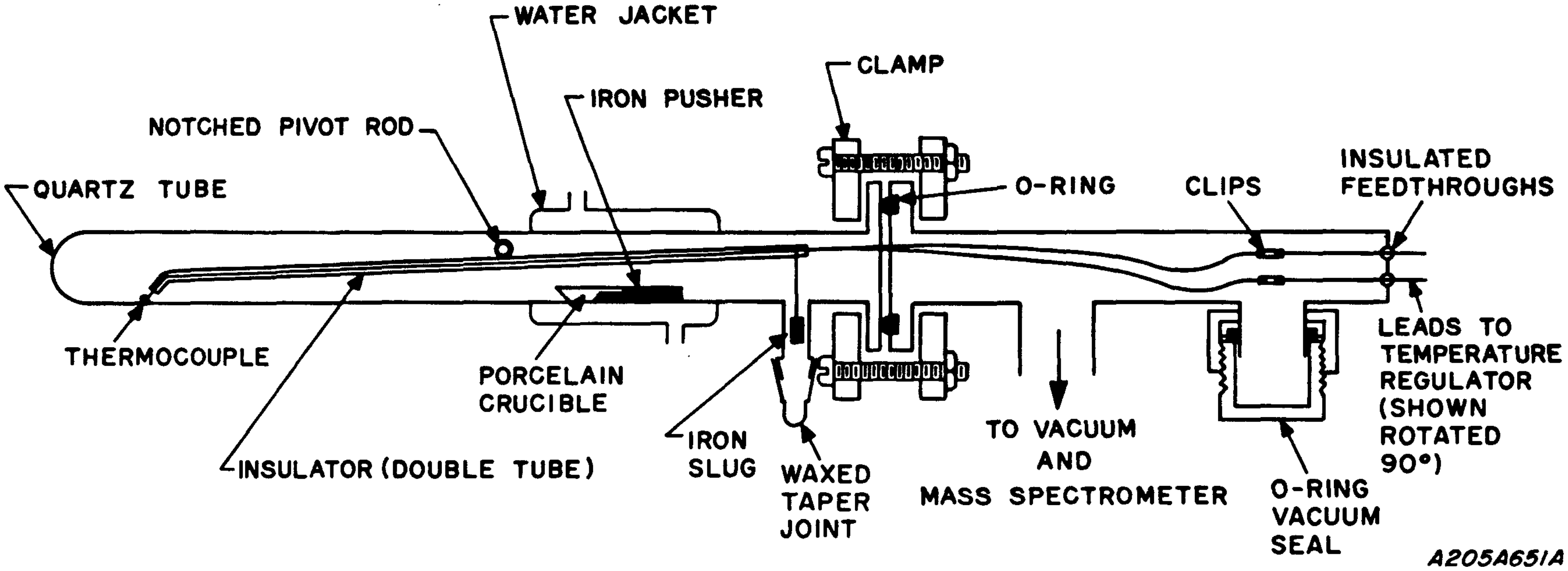

Figure 4. Details of Pyrolysis Vacuum System

RESULTS*

The first results to be described were obtained from manual reading of oscillograph traces. The data were converted to punched cards and were then plotted automatically to test the then newly developed graph plotting program. A 1 mg. sample of poly-2, 6-(m-phenylene)-diimidazobenzene was pyrolyzed at a rate of 10°C/min. Some of these graphs are shown in Figures 6 through 16. Comparison of the graphs with those of reference 1 showed them to be quite similar to the earlier pyrolysis. Curves for hydrogen (Figure 6), ammonia (Figure 7), hydrogen cyanide (Figure 9), nitrogen (Figure 10), benzene (Figure 12), aniline (Figure 13), benzonitrile (Figure 15), m/e-117 (Figure 16), cyanoaniline and/or benzimidazole (m/e-118), and phthalonitriles (m/e-128) were found to have quite similar shapes and appear in about the same temperature region as for the earlier experiment. A few differences were noted, as follows. While the water (Figure 8) evolution for the earlier run was low, it was not possible to separate it from the background in this experiment. Carbon dioxide (Figure 11) was not so different as direct comparison with reference 1 would indicate, for only a partial plot was shown for the earlier experiment. A small later evolution was noted for benzene (Figure 12) in the present work. The very weak signal at m/e-94 (Figure 14) may represent phenol up to about 420°C, but cannot be explained at the higher temperature at this time. Graphs have not been shown for m/e-118 or 128 because manual errors in the punched cards distorted the sizes of their ordinates so that they were useless. The tabulated results were found to be all right. Relative yields, as shown by comparative ion intensities, were consistent with earlier values in almost all cases. Hydrogen appeared to be somewhat high, probably due to a shift in magnetic compensation, while aniline was somewhat weaker. The absence of significant quantities of phenylene diamine was consistent with the low yield in the earlier experiment. The reduced smoothness was probably due to reduction in sample size from 10 to 1 mg. and diminishing the heating rate from 16-2/3 to 10°C/min.

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* It is necessary to provide information for the reader to understand the graphic results. The plots are of ion intensity vs. temperature for single mass peaks. The ordinate is in arbitrary units while the abscissa is in °C. Since the temperatures are as recorded, they must be corrected using the information in Figure 5, except for polybenzimidazole. The corrections for that polymer will be given with the results. The graph plotting program arranges the ordinate scale to start at the integer below its lowest value and to end at the integer above its highest value. This is also true for decimal values, but in that case odd decimal numerals are not printed.

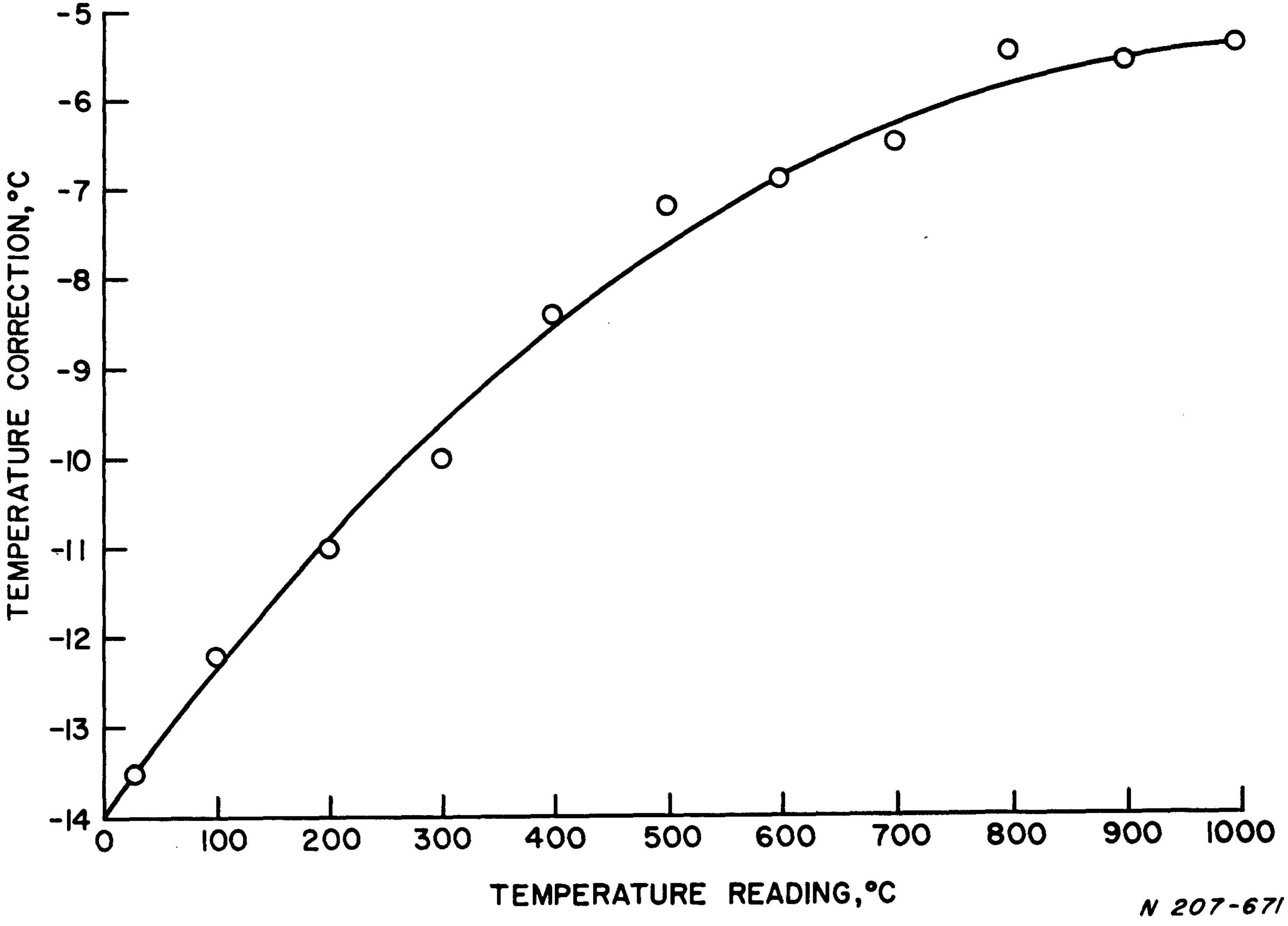

Figure 5. Temperature Correction for Figures 6 - 25

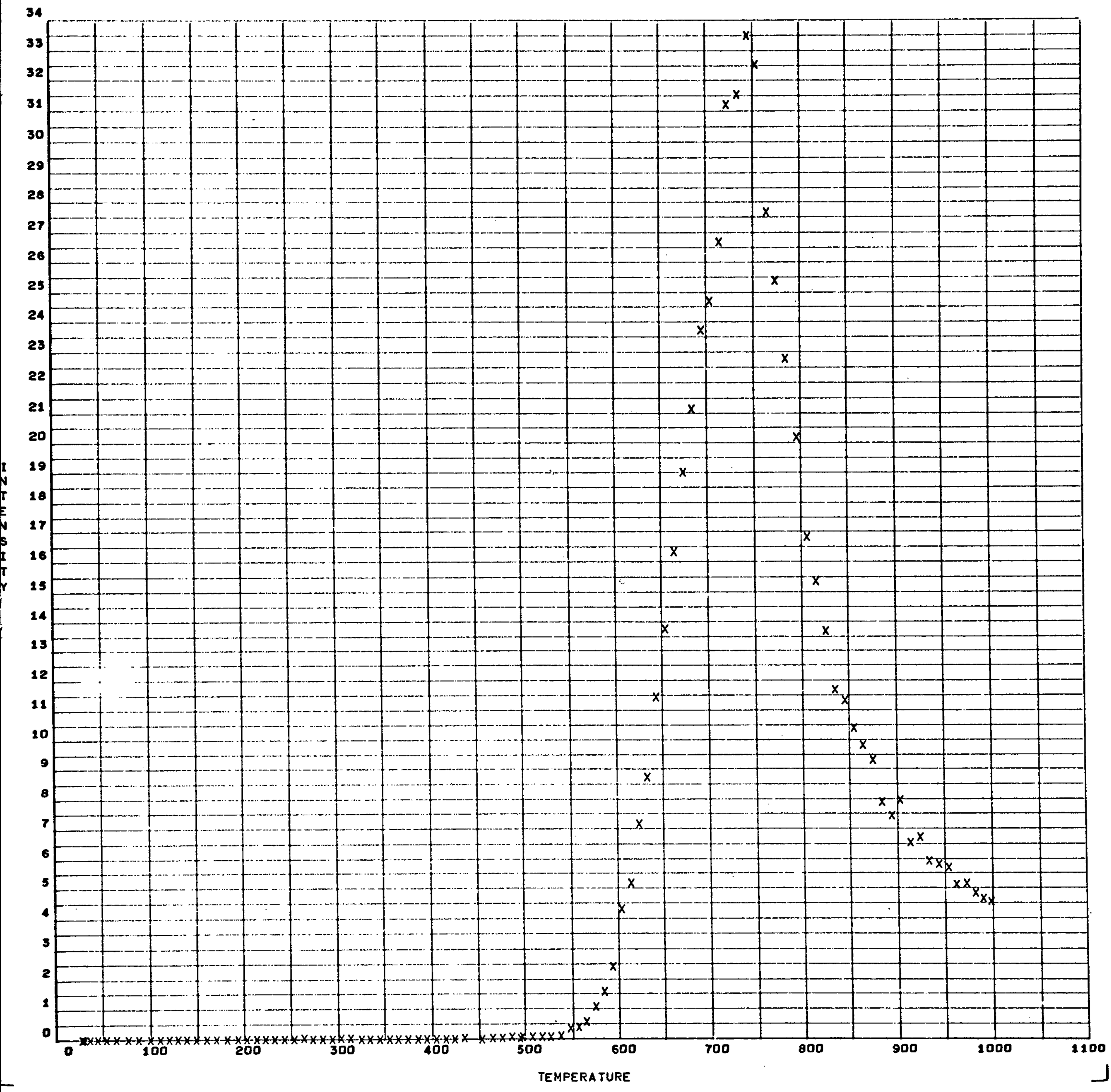

FIGURE 6 - Mass Spectra of Poly-2, 6-(m-phenylene)-diimidazobenzene Pyrolysis Gases, m/e-2

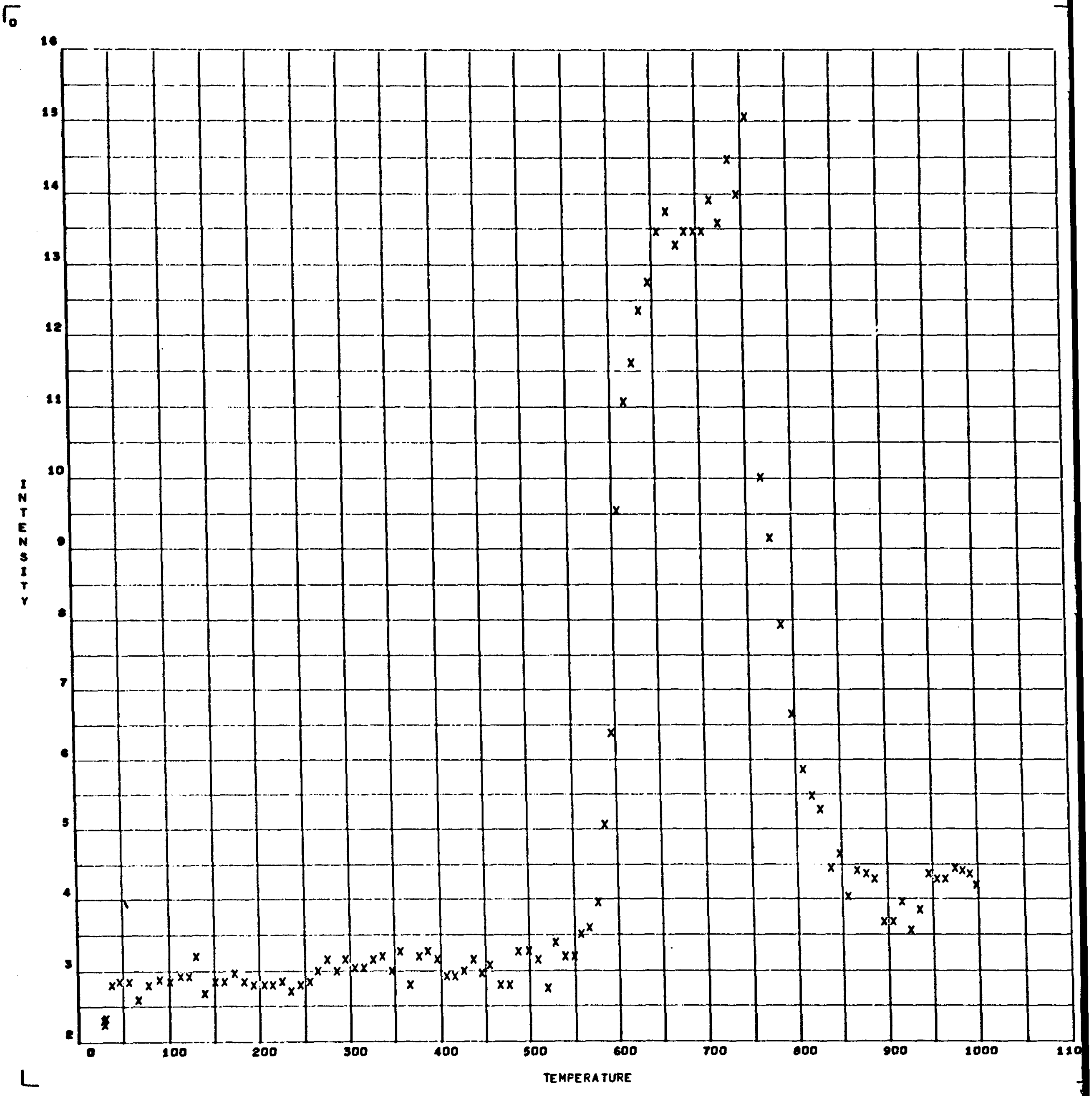

FIGURE 7 - Mass Spectra of Poly-2, 6-(m-phenylene)-diimidazobenzene Pyrolysis Gases, m/e-17

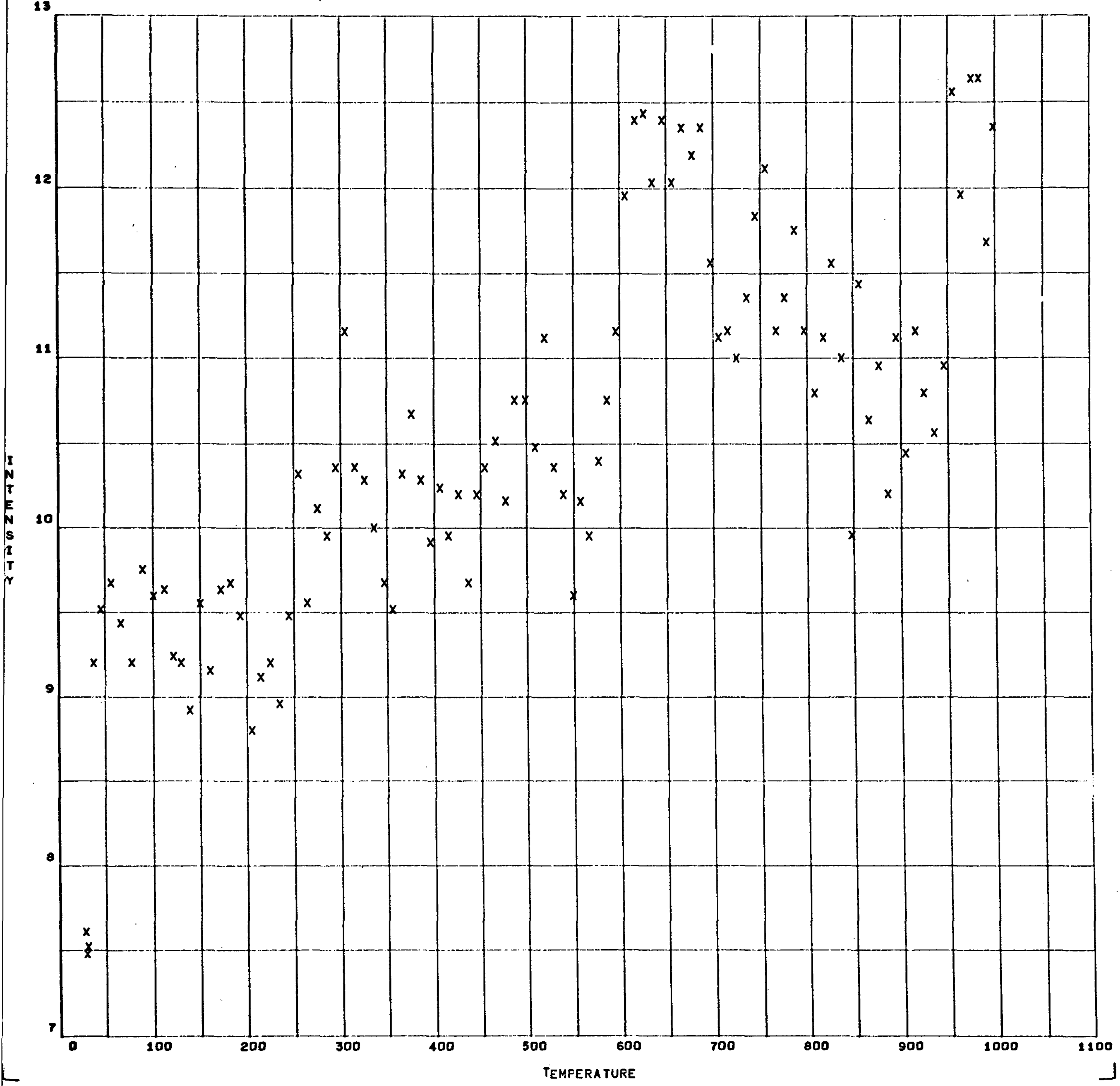

FIGURE 8 - Mass Spectra of Poly-2, 6-(m-phenylene)-diimidazobenzene Pyrolysis Gases, m/e-18

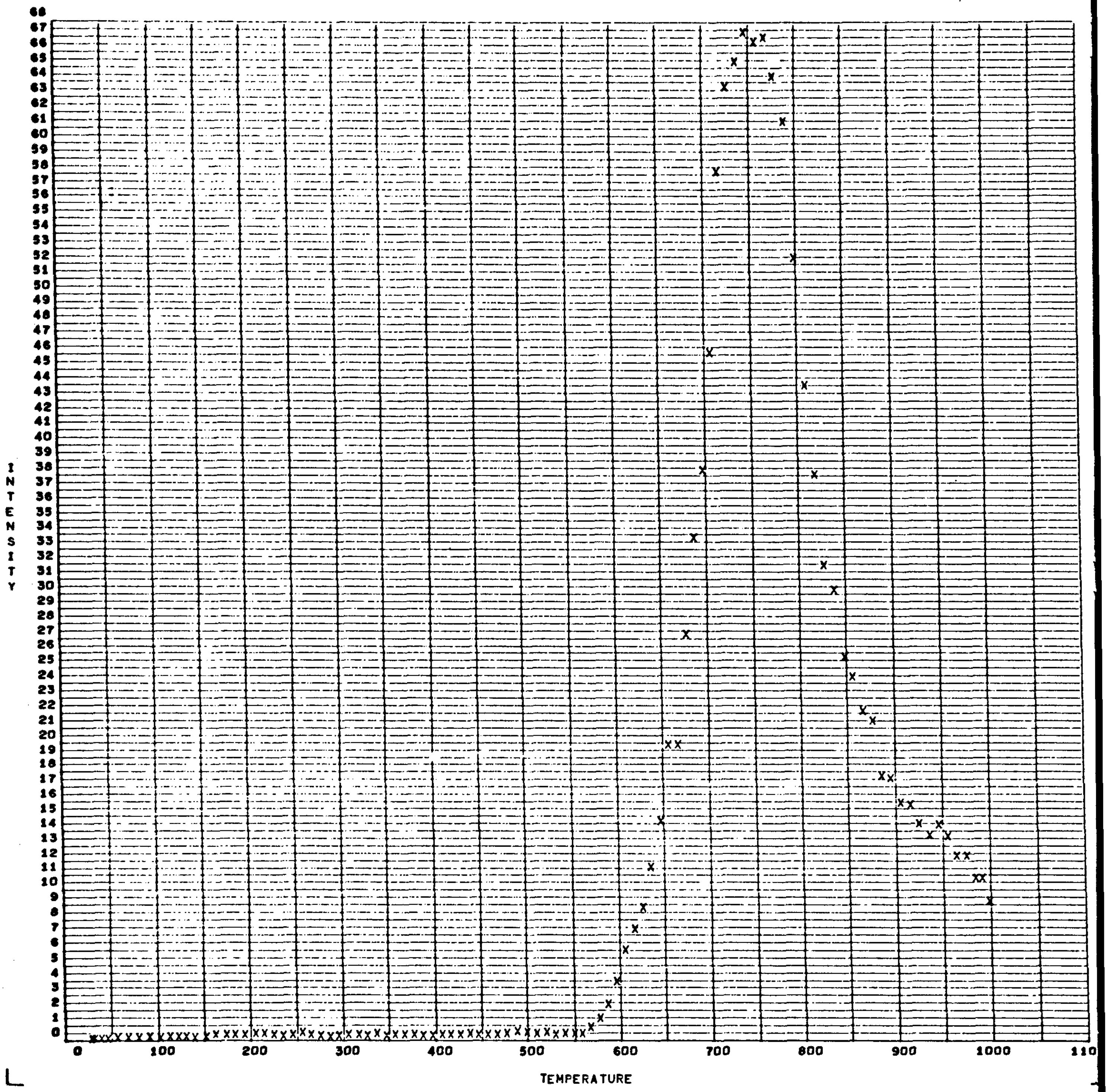

FIGURE 9 - Mass Spectra of Poly-2, 6-(m-phenylene)-diimidazobenzene Pyrolysis Gases, m/e-27

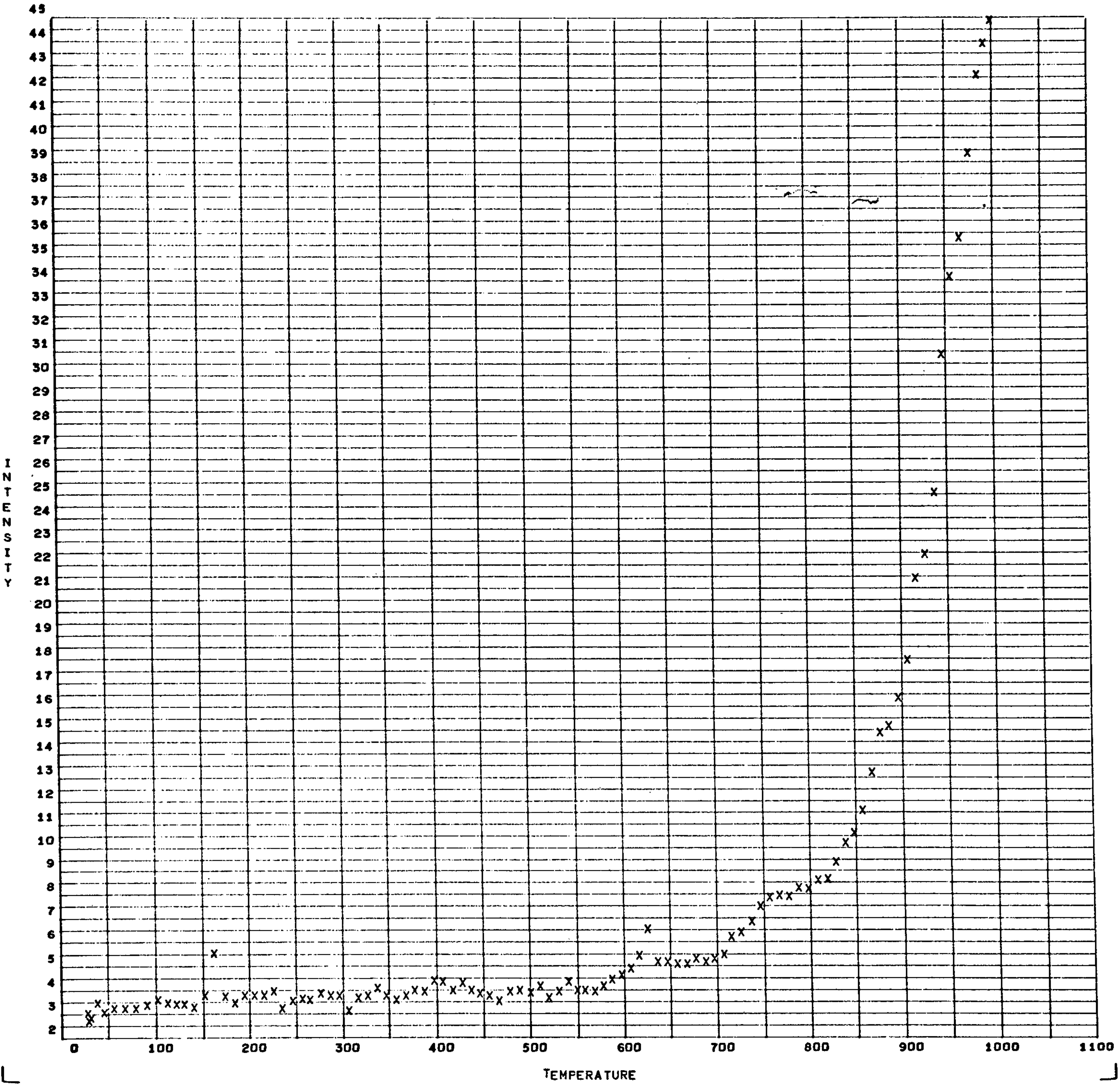

FIGURE 10 - Mass Spectra of Poly-2, 6-(m-phenylene)-diimidazobenzene Pyrolysis Gases, m/e-28

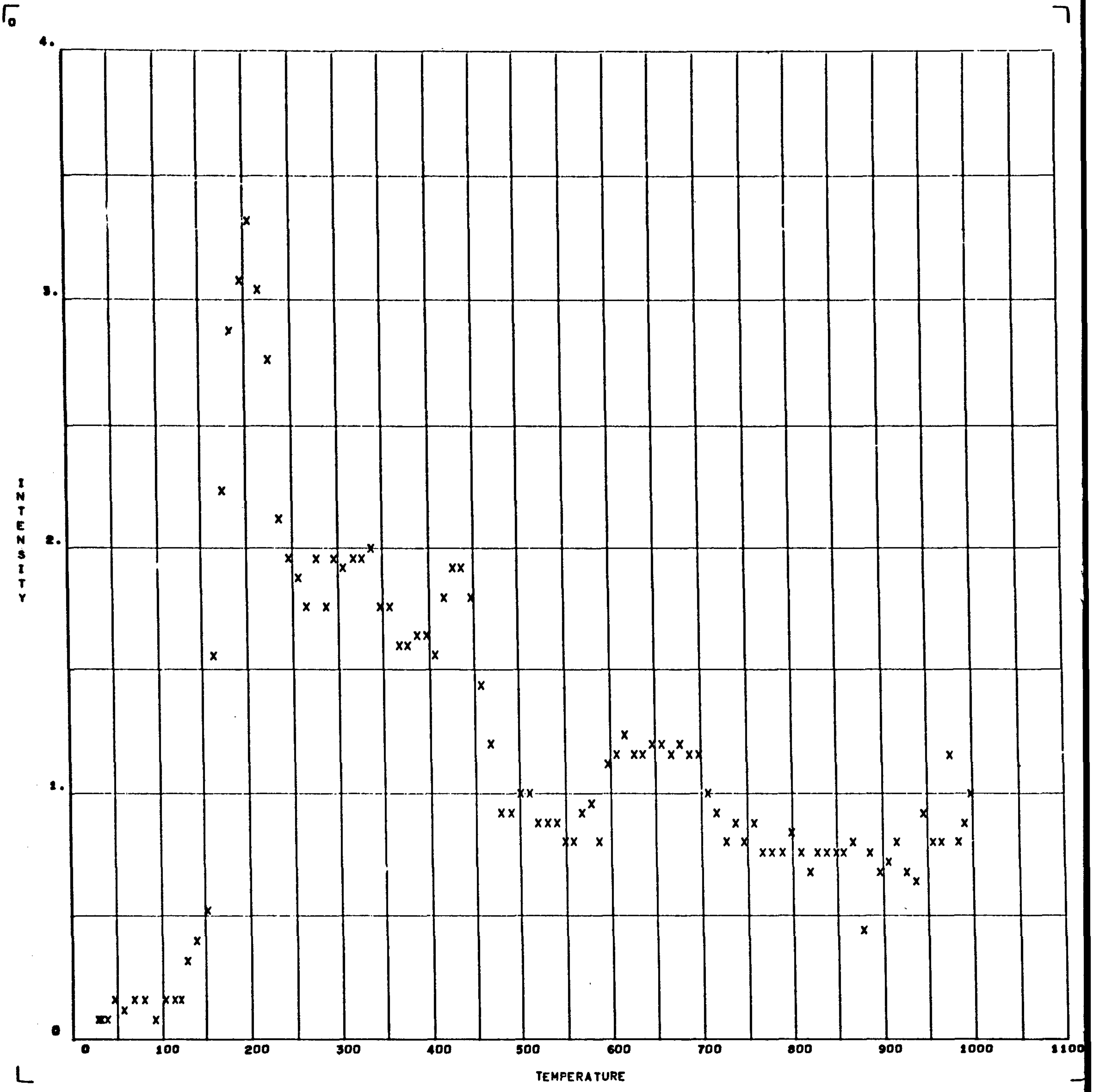

FIGURE 11 - Mass Spectra of Poly-2, 6-(m-phenylene)-diimidazobenzene Pyrolysis Gases, m/e-44

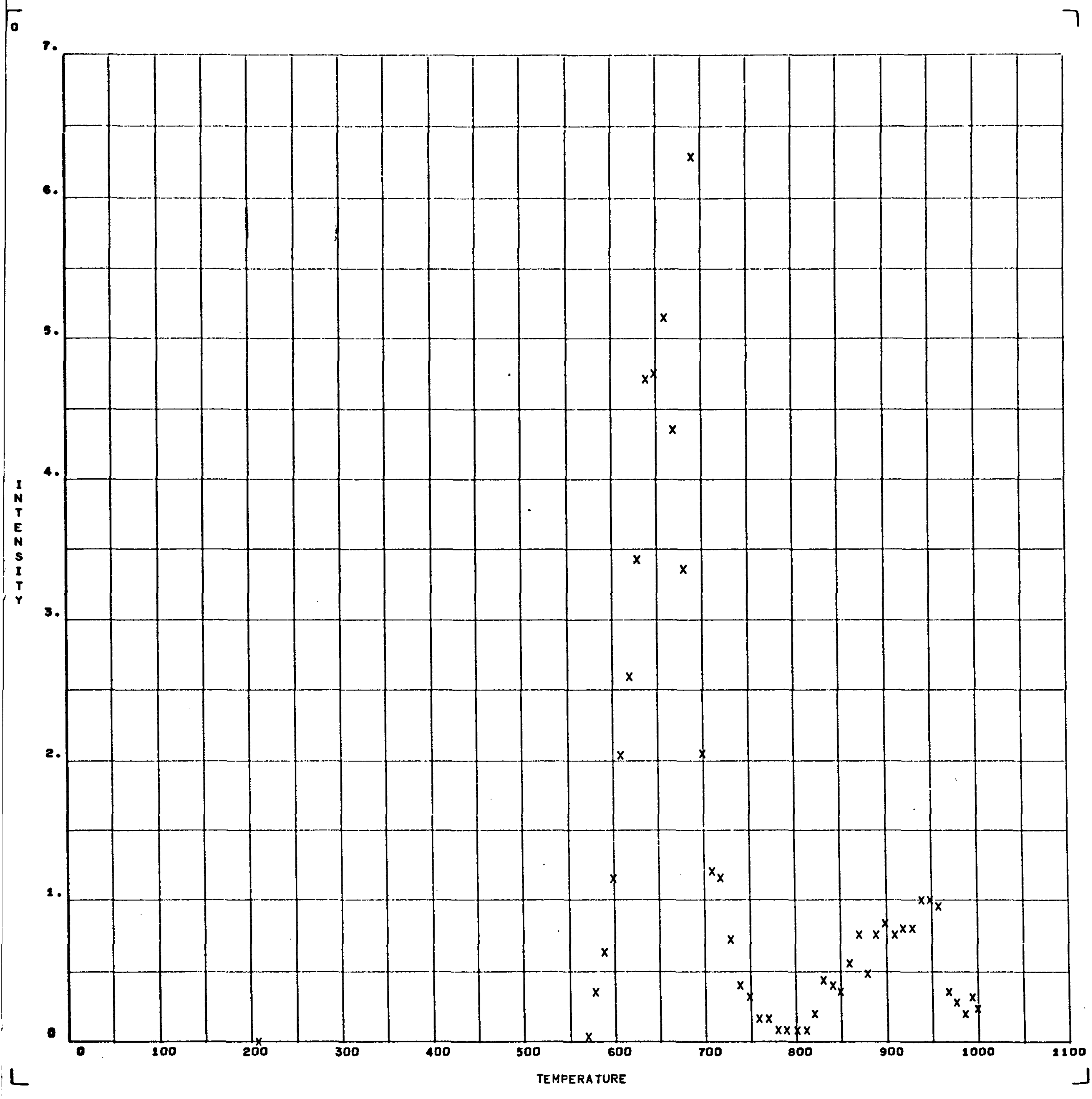

FIGURE 12 - Mass Spectra of Poly-2, 6-(m-phenylene)-diimidazobenzene Pyrolysis Gases, m/e-78

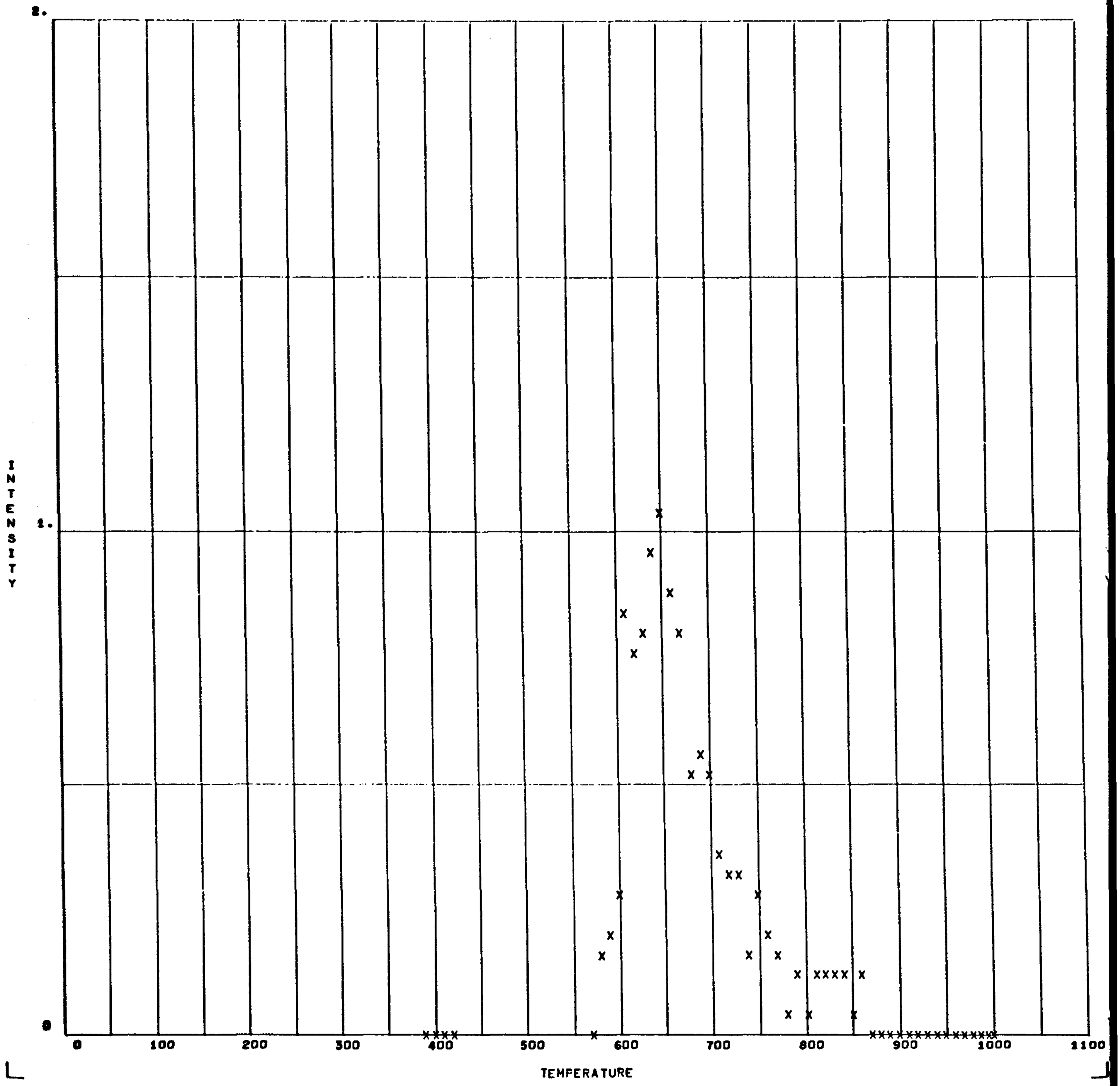

FIGURE 13 - Mass Spectra of Poly-2,6-(m-phenylene)-diimidazobenzene Pyrolysis Gases, m/e-93

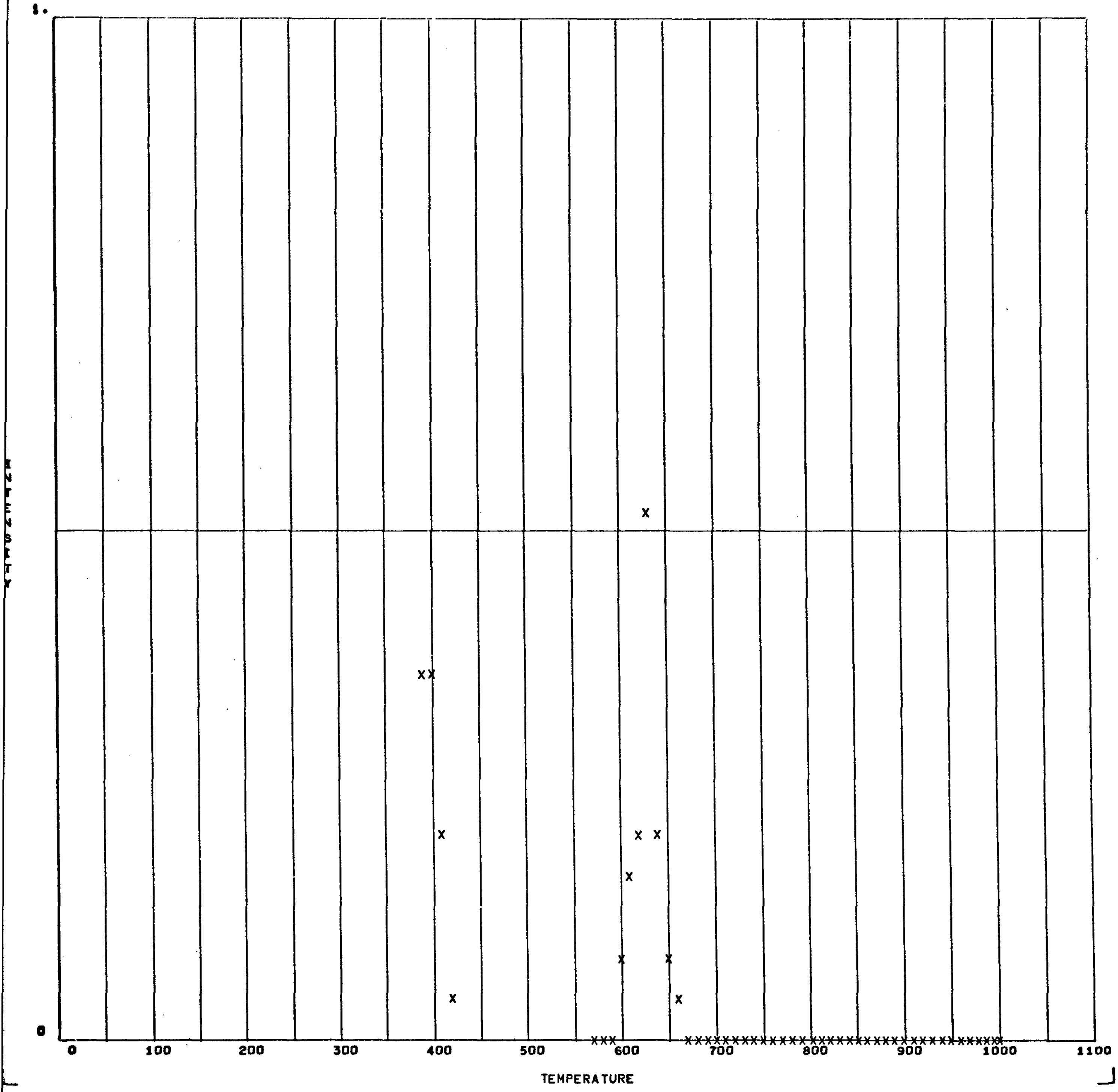

FIGURE 14 - Mass Spectra of Poly-2, 6-(m-phenylene)-diimidazobenzene Pyrolysis Gases, m/e-94

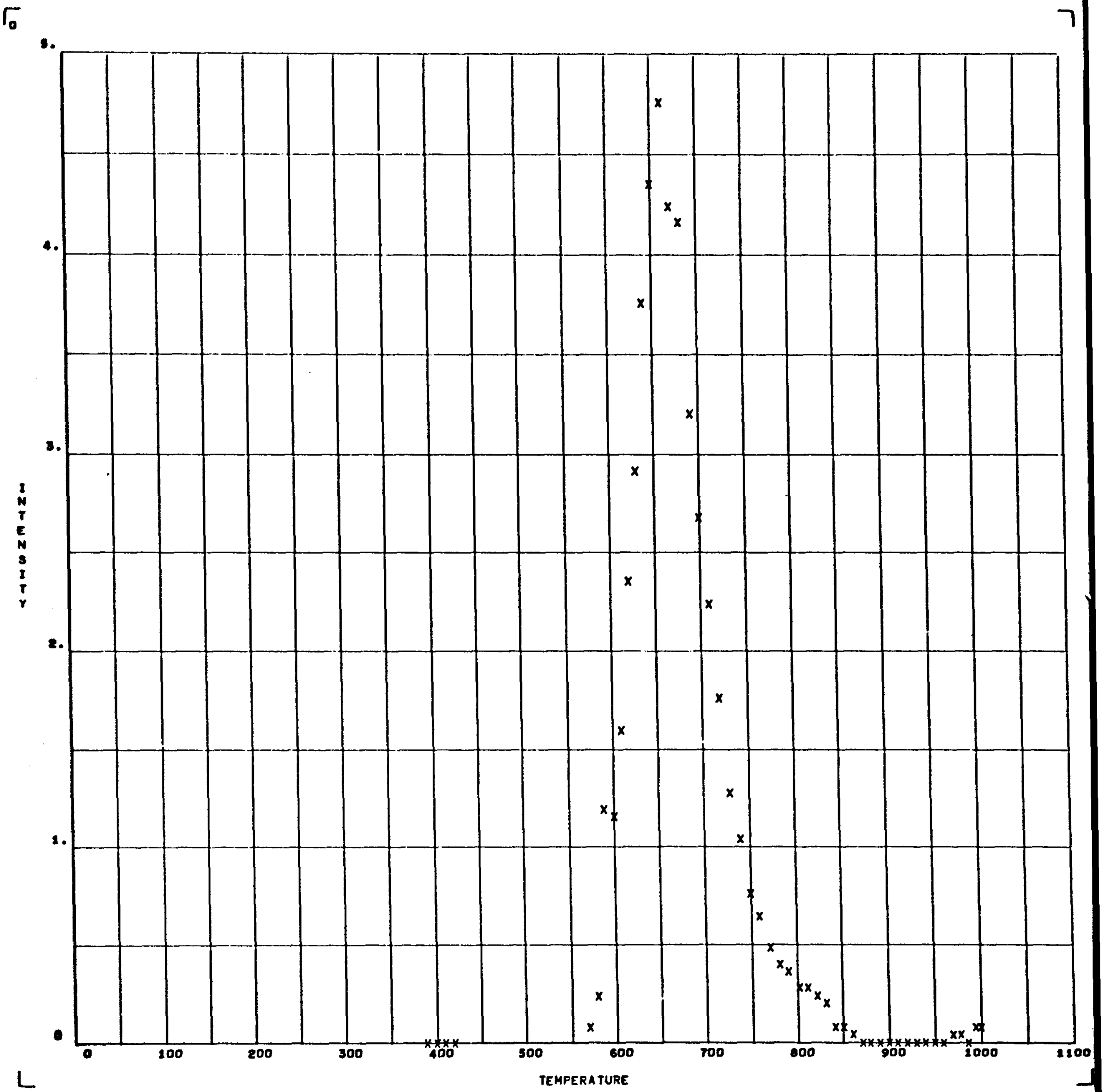

FIGURE 15 - Mass Spectra of Poly-2, 6-(m-phenylene)-diimidazobenzene Pyrolysis Gases, m/e-103

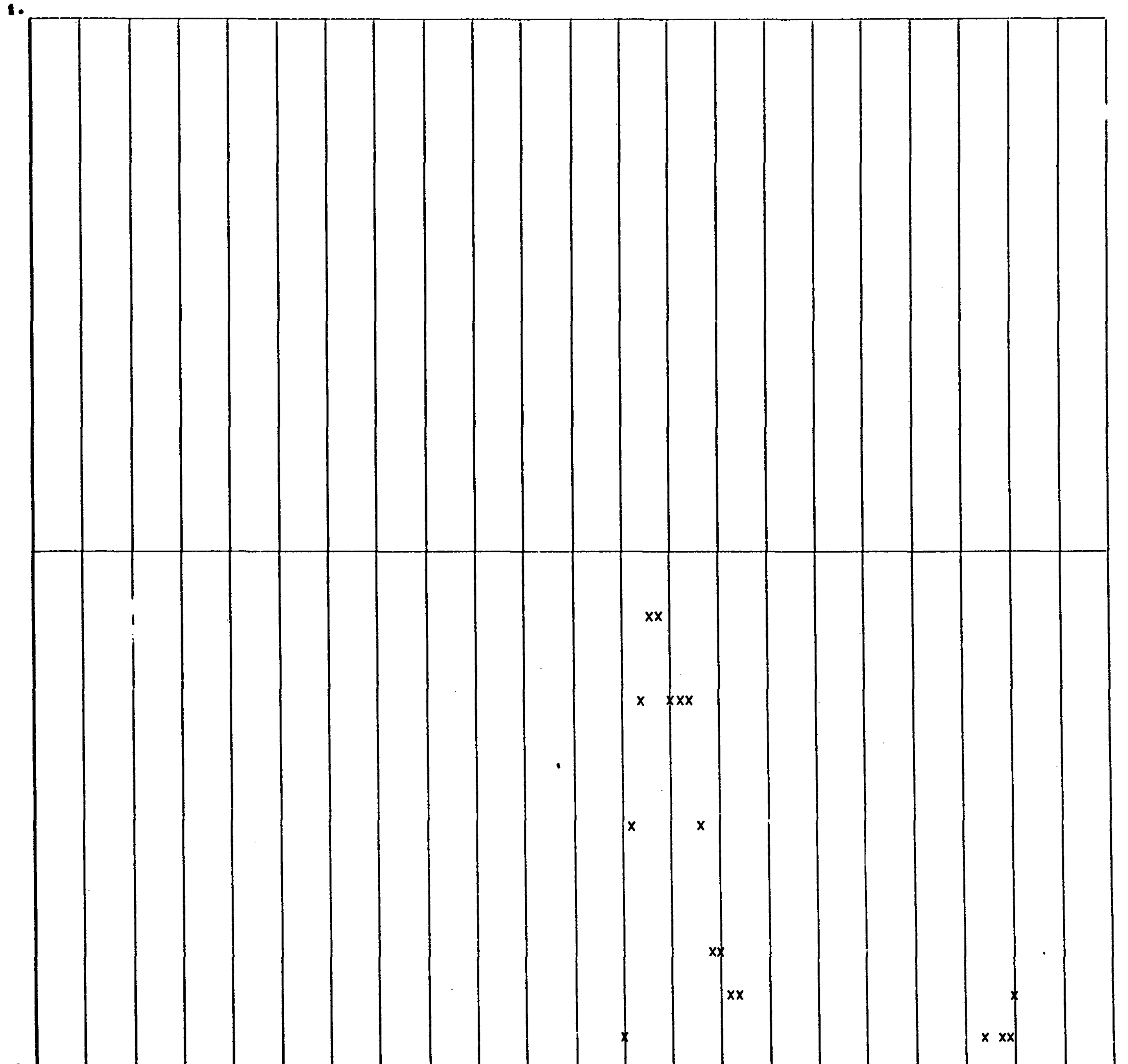

FIGURE 16 - Mass Spectra of Poly-2, 6-(m-phenylene)-diimidazobenzene Pyrolysis Gases, m/e-117

Two samples of poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole were pyrolyzed from room temperature to about 1000°C at a rate of about 10°C/min. The first sample (A) was the raw material precipitated from methyl ethyl ketone (MEK). The second sample (B) was the same as (A), but it was treated by heating in a vacuum thermobalance to 300°C. The thermogram indicated that all of the readily volatilized components were driven off by this temperature. Samples (A) and (B) weighed 1.446 and 0.708 mg., respectively. Nine of the 200 mass spectra that were obtained for each sample are shown in Figures 17 through 25. Zero background level readings for sample (A) ranged from 0.052 to 0.062 and averaged at 0.056. One spurious signal of 0.043 was recorded. The range for sample (B) was 0.052 to 0.065, the average being 0.059. Several tape breaks occurred during the recording of sample (A). The paper reel feed mount has been corrected to prevent this.

Figure 17 shows the yield of hydrogen as H_2^+. Note that yield curves have similar shapes and appear in approximately the same temperature range. Since the quantity of product formed is proportional to the area below the yield curve, about 50% more H_2 was formed in the pyrolysis of sample (A), on an equal initial weight basis. The NH_3^+ from ammonia (Figure 18) appears in about the same temperature range. About four times more ammonia was generated for sample (A). The higher temperature portion of Figure 19 represents CN^+ from HCN, while the 220°C peak for sample (B) was attributed to acrylonitrile. The HCN^+ from HCN (Figure 20) show similar shapes in the lower temperature portion, but small differences in the higher temperature range. Approximately equal yields of HCN were observed. The m/e-28 curves of Figure 21 represent mainly nitrogen as N_2^+. Note that not all of this product has been driven off at 1000°C. The lower temperature portion of Figure 22 shows the parent ion peak from MEK in sample (A). It is not surprising that heat treatment has driven this off for sample (B). Benzene (Figure 23) appears in approximately the same temperature range for both samples. About 50% more was generated for sample (A). Since the raw polymer probably contains some dimethyl acetamide, m/e-87 has been shown in Figure 24 to indicate that no appreciable quantity appeared in either sample. Benzonitrile was observed for both samples at m/e-103 (Figure 25) in about the same temperature region. Yields were approximately equal. Other ions produced significant spectra as well.

Two larger samples, about 5 mg. of sample (A) and 10 mg. of sample (B) were then subjected to MTA. Most of the data were in good agreement with the earlier results. Since the larger samples were used to improve the accuracy for minor products, study of these was emphasized. It should be noted, however, that use of the larger samples produced the expected improvement in smoothness of the data. MEK was observed at about 150°C for each sample, but about 3 times more was observed for sample (A) on an equal weight basis. Acrylonitrile was observed at about 230°C in each case as well. About 2.8 times more was observed for sample (A). Evidence for the appearance of this product was found in earlier MTA results from

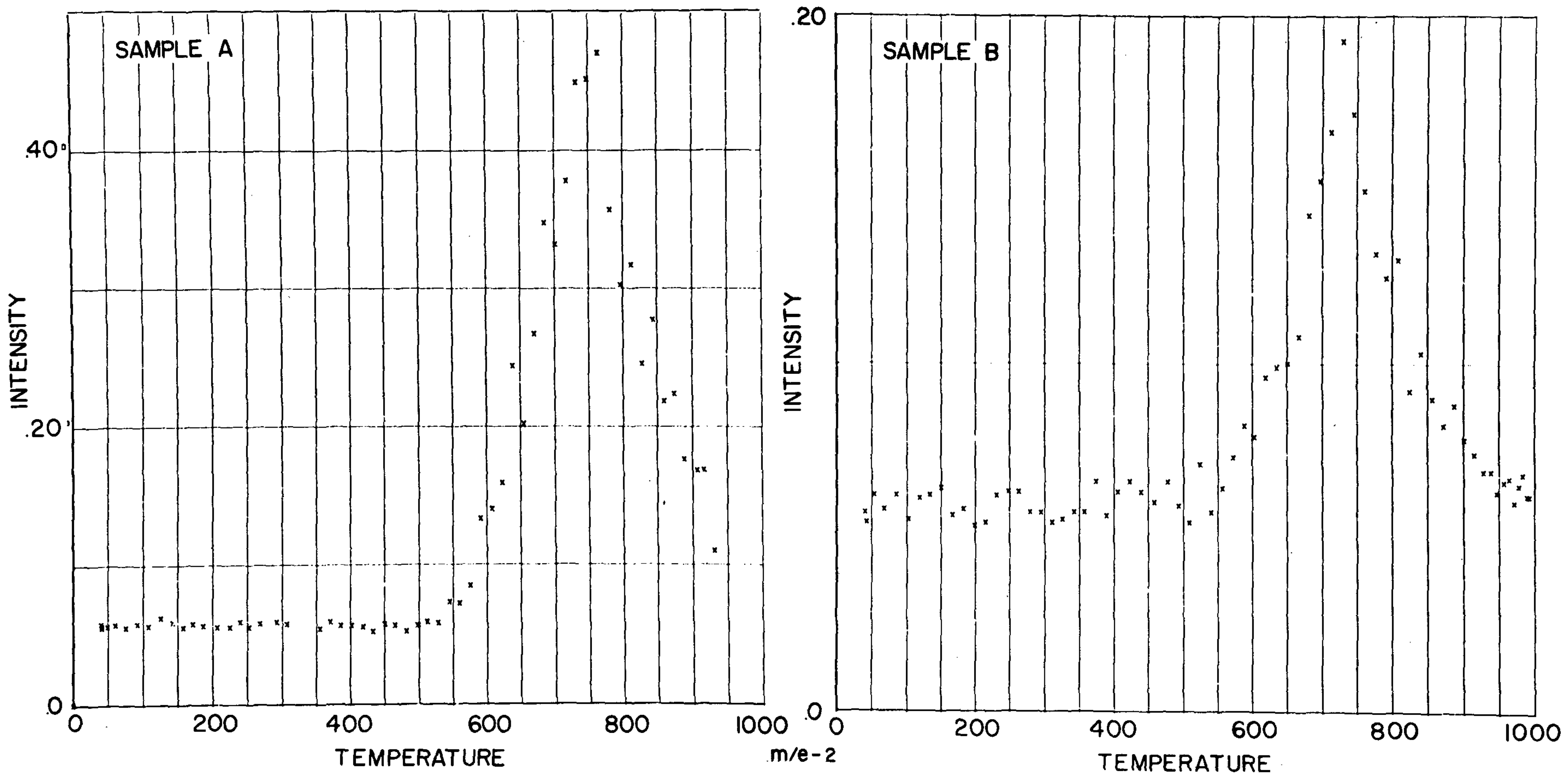

FIGURE 17. Mass Spectra of Untreated (A) and Heat Treated (B) Samples of Poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole Pyrolysis Gases, m/e-2

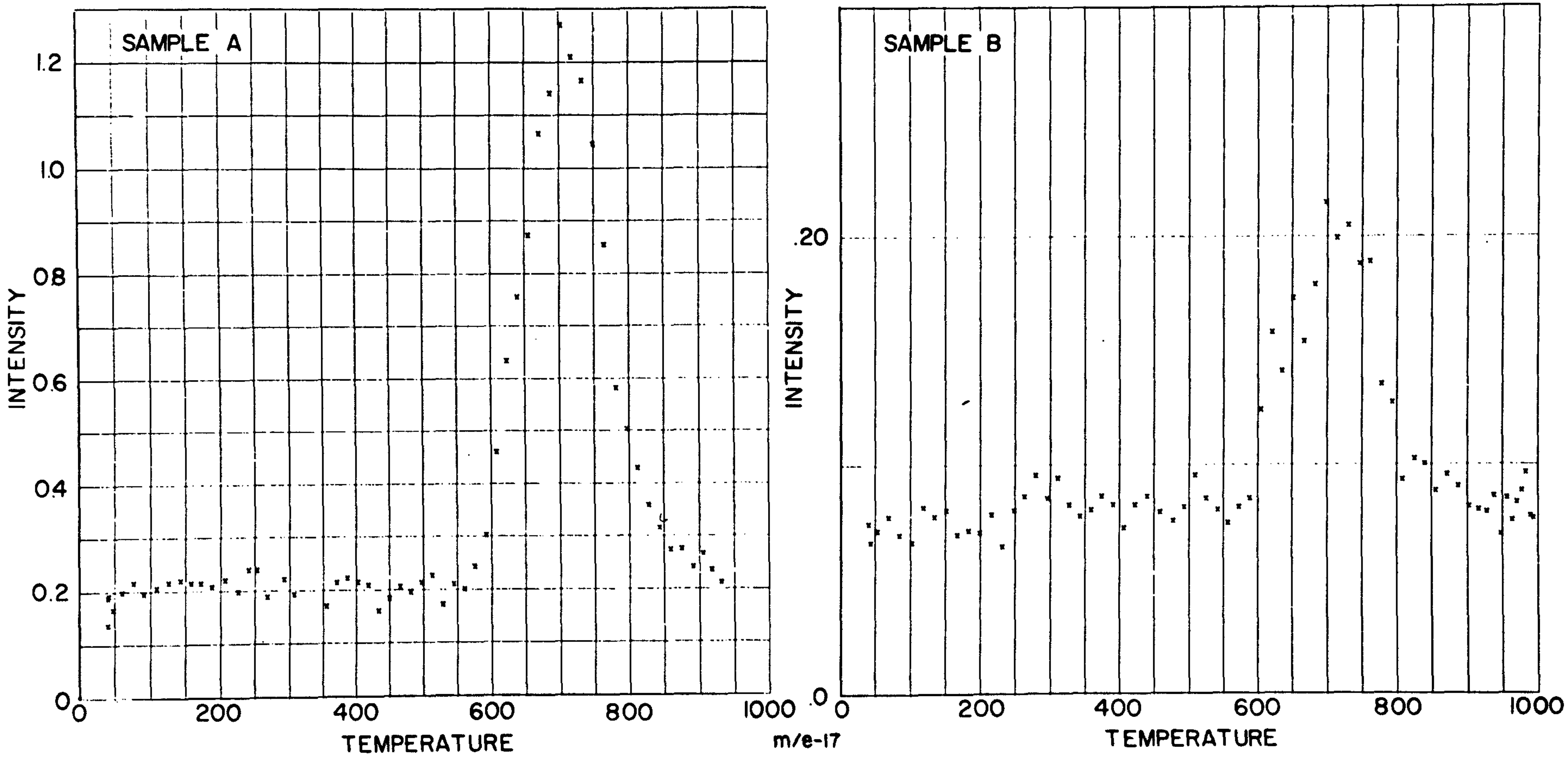

FIGURE 18. Mass Spectra of Untreated (A) and Heat Treated (B) Samples of Poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole Pyrolysis Gases, m/e-17

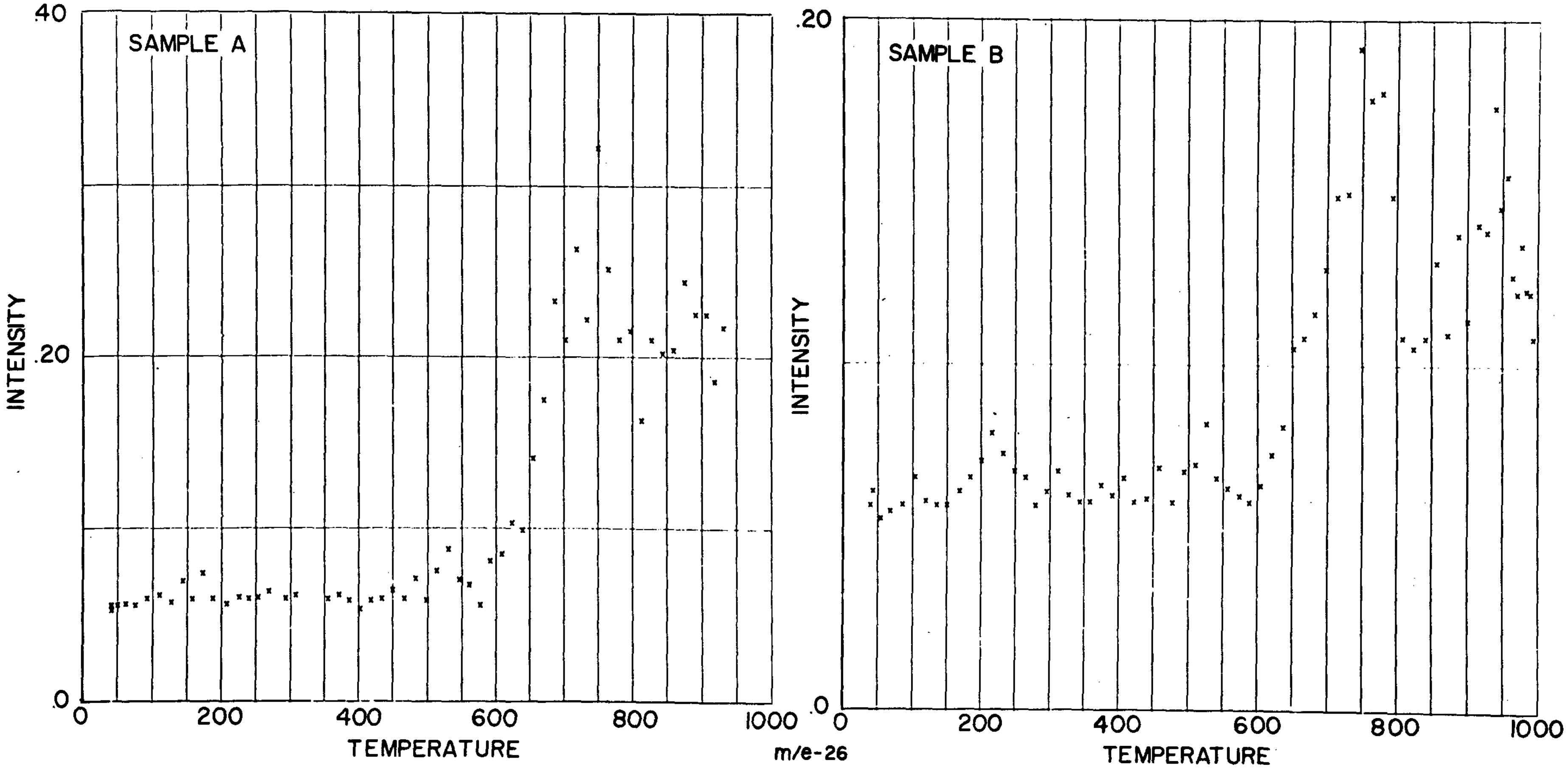

FIGURE 19. Mass Spectra of Untreated (A) and Heat Treated (B) Samples of Poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole Pyrolysis Gases, m/e-26

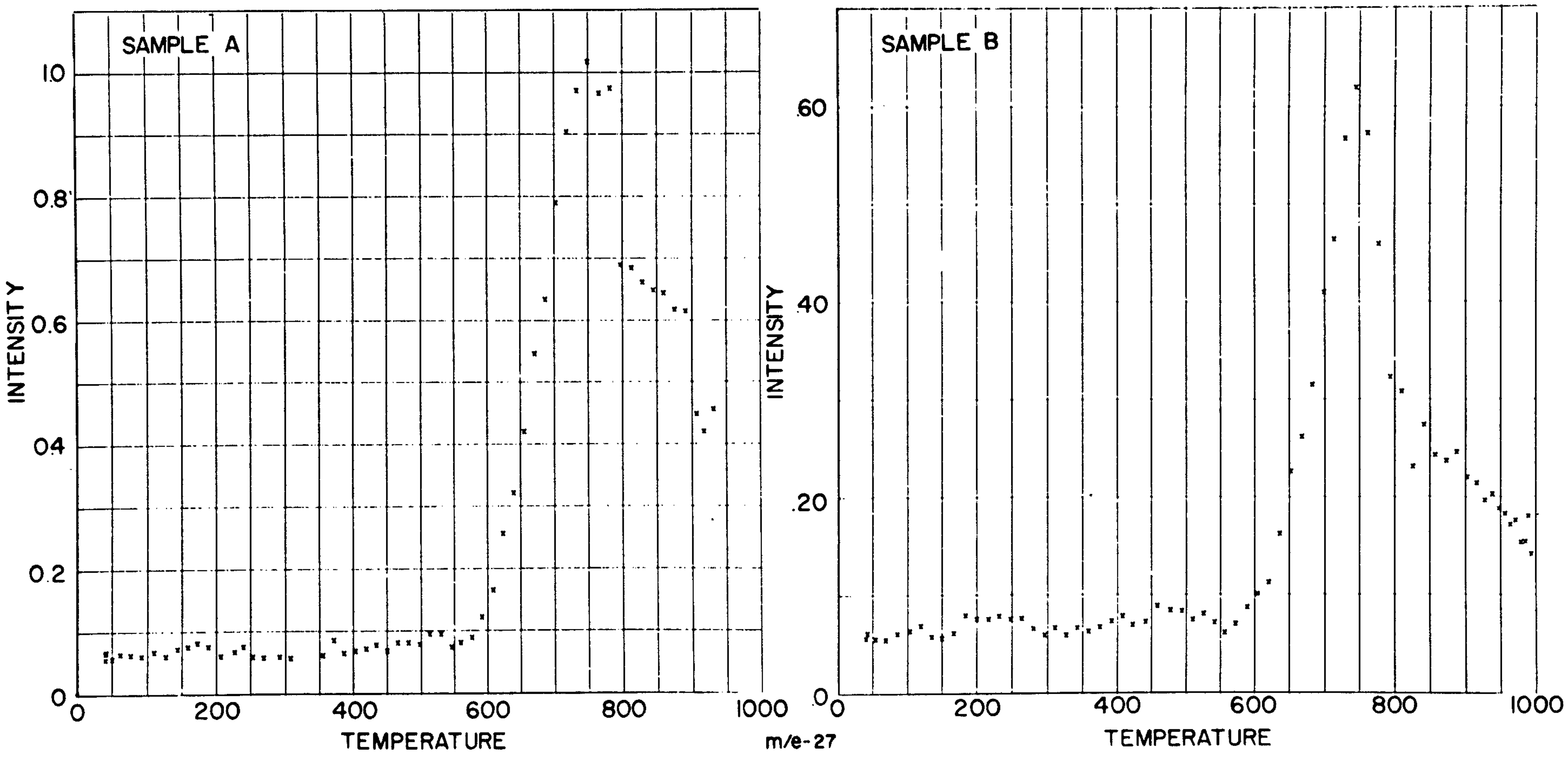

FIGURE 20. Mass Spectra of Untreated (A) and Heat Treated (B) Samples of Poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole Pyrolysis Gases, m/e-27

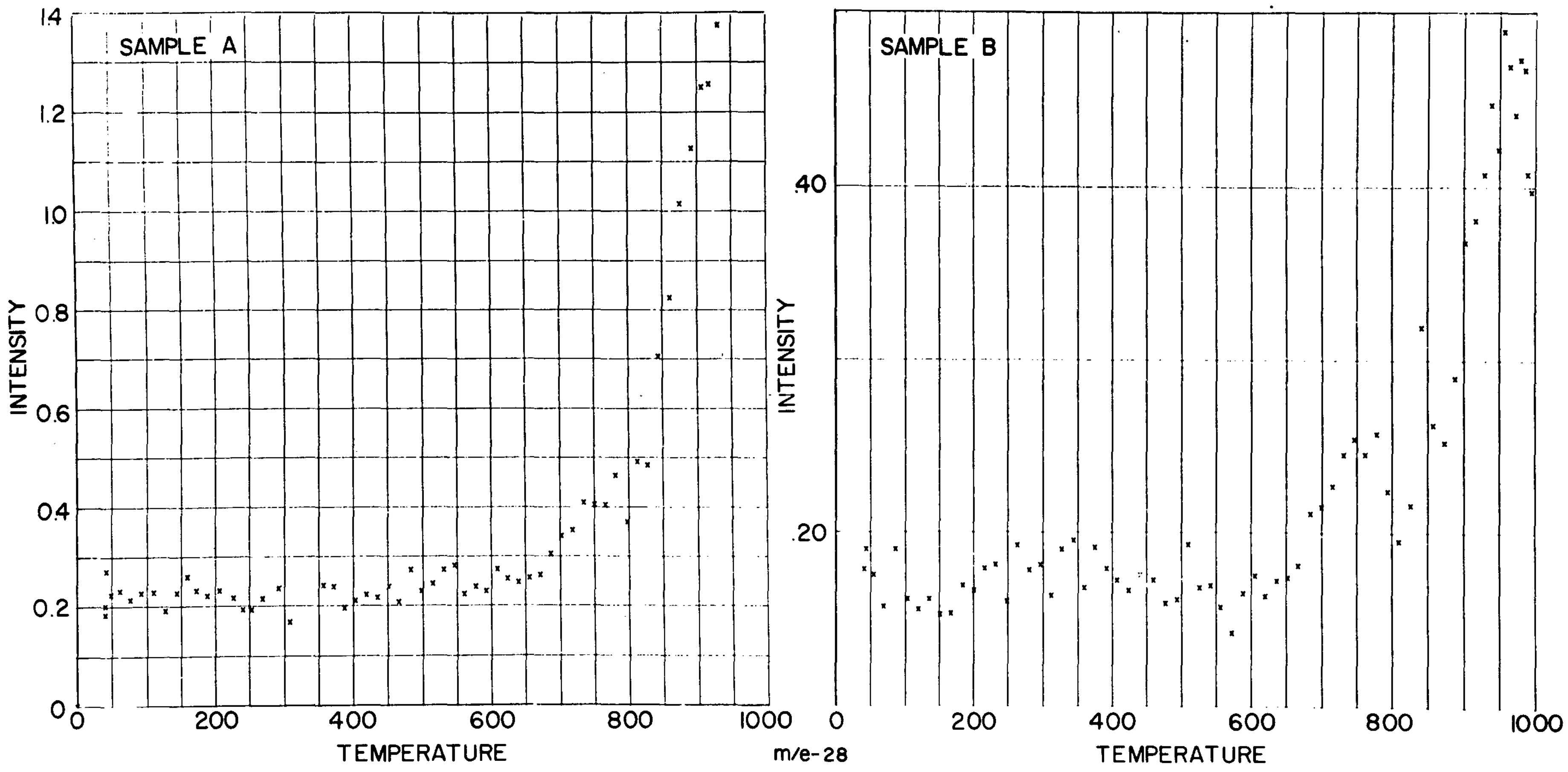

FIGURE 21. Mass Spectra of Untreated (A) and Heat Treated (B) Samples of Poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole Pyrolysis Gases, m/e-28

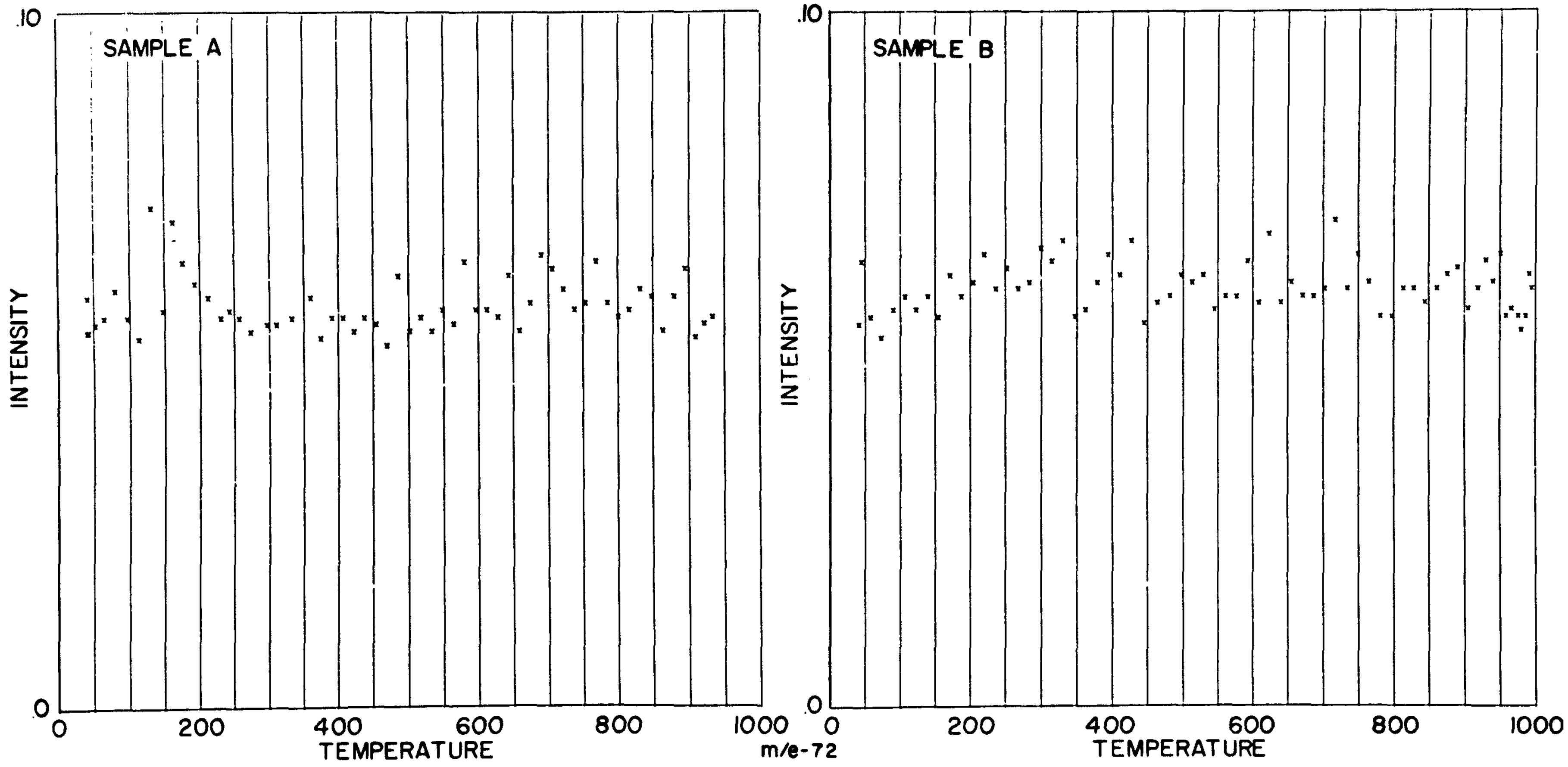

FIGURE 22. Mass Spectra of Untreated (A) and Heat Treated (B) Samples of Poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole Pyrolysis Gases, m/e-72

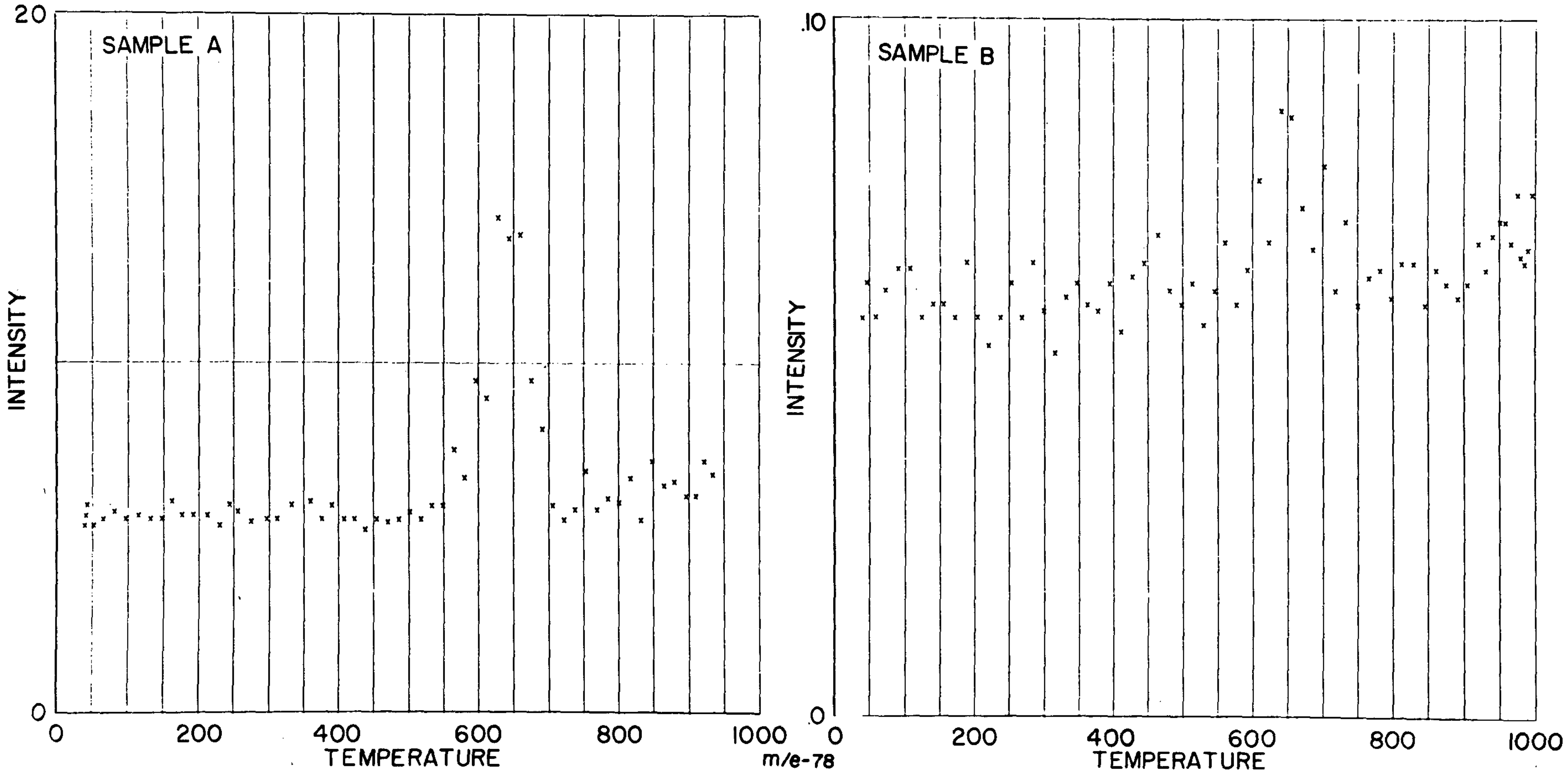

FIGURE 23. Mass Spectra of Untreated (A) and Heat Treated (B) Samples of Poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole Pyrolysis Gases, m/e-78

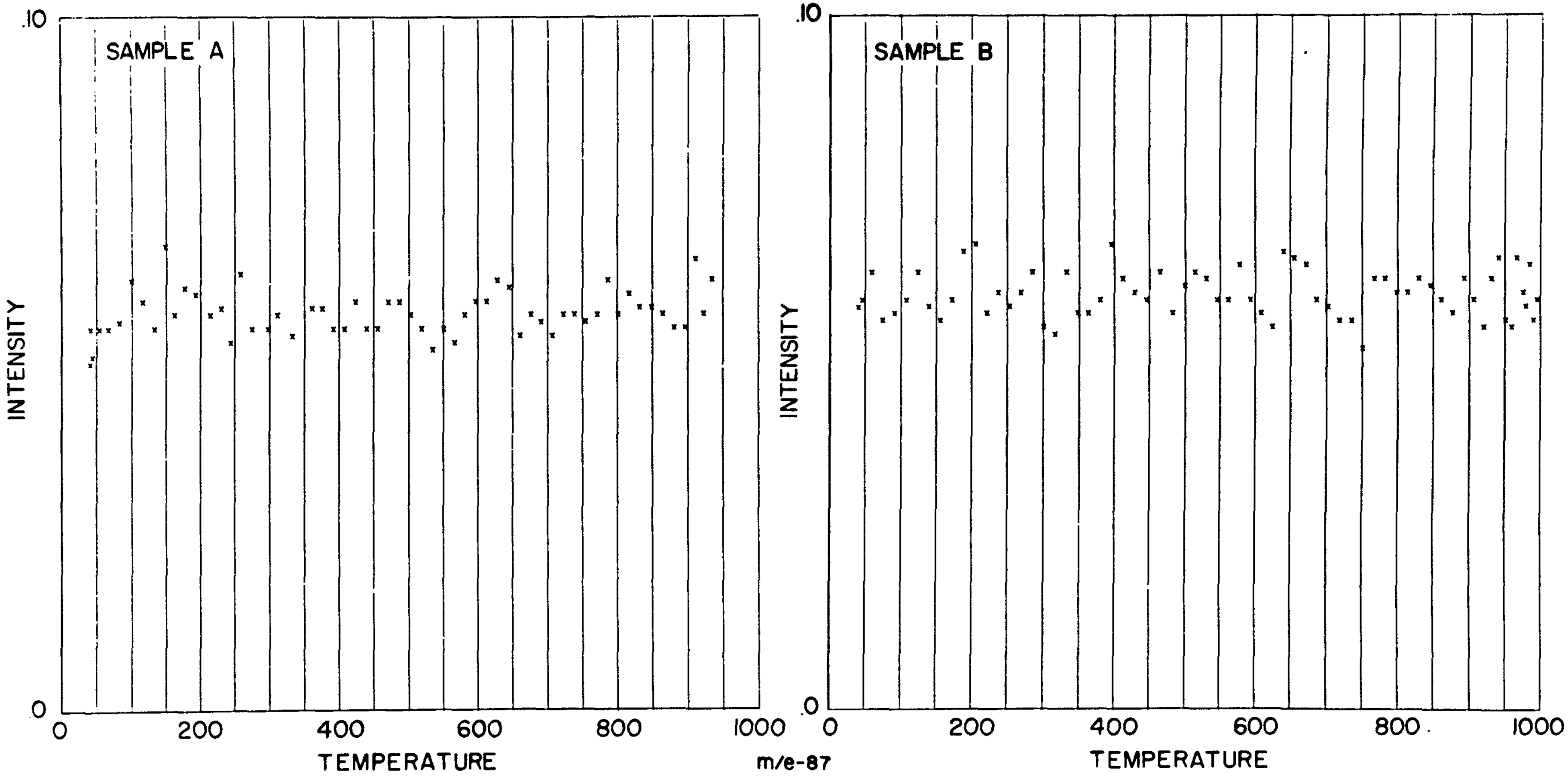

FIGURE 24. Mass Spectra of Untreated (A) and Heat Treated (B) Samples of Poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole Pyrolysis Gases, m/e-87

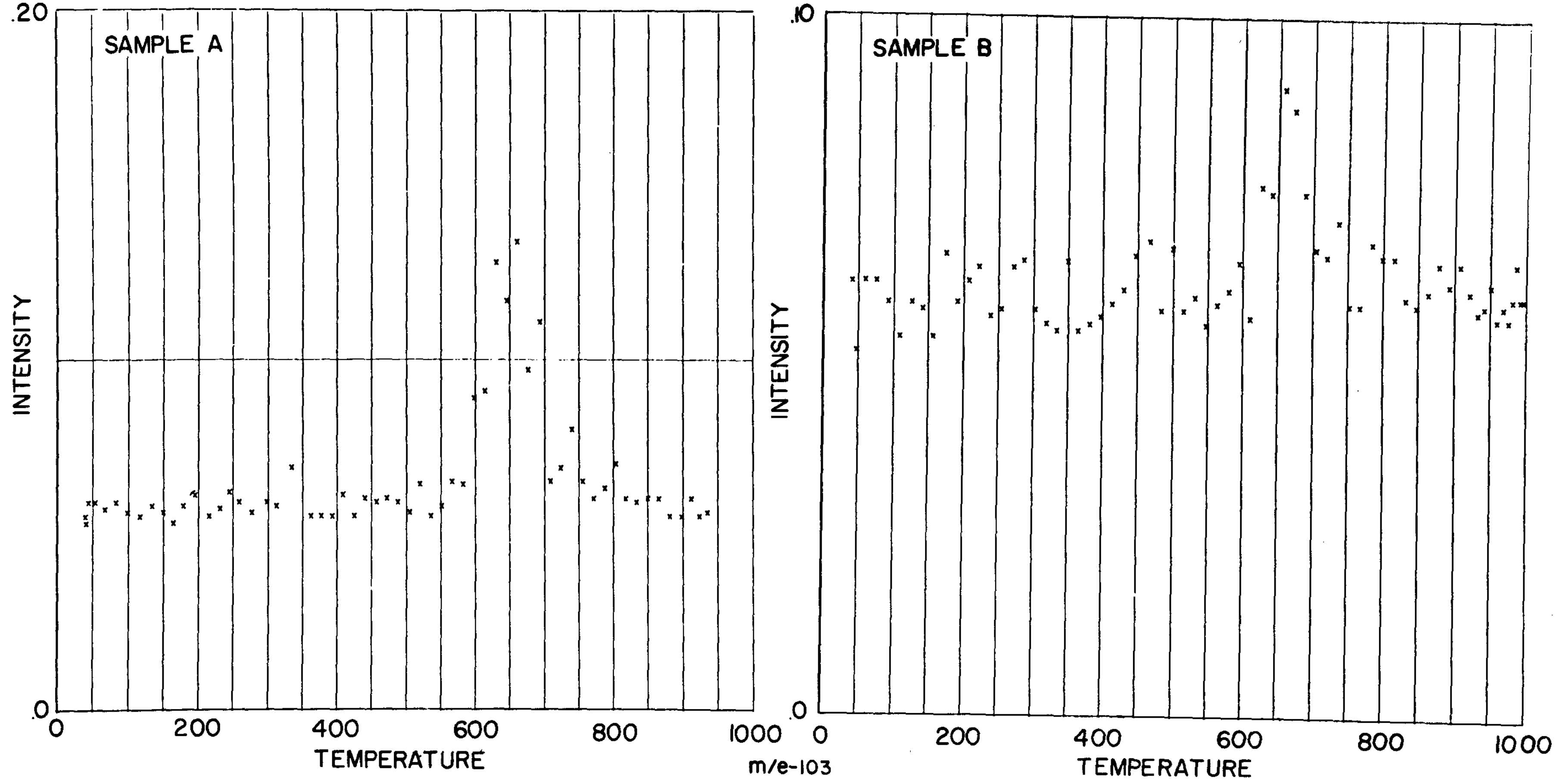

FIGURE 25. Mass Spectra of Untreated (A) and Heat Treated (B) Samples of Poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole Pyrolysis Gases, m/e-103

polymers of this family. It is thought to be caused mainly by degradation which occurs during preparation, although some of it could have formed during heat treatment in the present case. Some water evolution occurred between 150 and 400°C, perhaps due to incomplete polymerization, however, no phenol was observed. Some other spectra were evident in the 100 to 400°C region for sample (B), but the products were not identified.

A sample of polybenzimidazole ($\eta = 4$ in H_2SO_4) weighing 1.25 mg. was subjected to MTA. Some of the results are shown in Figures 26-32. Temperature corrections, which are different for these graphs than for the earlier ones, are shown in Figure 33. Examination of the graphs showed several similarities and differences compared to earlier polymers, which contained m- and p-phenylene groups. Evolution of hydrogen (Figure 26), ammonia (the higher temperature portion of Figure 27), hydrogen cyanide (Figure 29), and nitrogen (Figure 30) were similar to the earlier polymers. Water evolution (Figure 28) started at room temperature and continued to about 400°C. Maximum evolution occurred at about 200°C. Hydrogen sulfide and sulfur dioxide were observed at about 500°C. Carbon dioxide was evolved at about 400°C. One or more high molecular weight cycloparaffins were observed between 150 and 600°C with a very broad maximum at about 350°C. The evolution at m/e-70 (Figure 31) was typical. The source of these materials was probably a solvent. Indications of molecular sizes up to cyclododecane were observed. The aromatic products which were observed for the other polymers were present in very small quantities, if at all, in the usual range of 600 to 700°C. Traces of benzene, aniline and benzonitrile (Figure 32) were present.

Comparisons with Other MTA Research

Shulman and Lochte[5] recently studied the composition of gases that were formed when several samples of poly-2, 2'-(m-phenylene)-5, 5'-bibenzimidazole were heated linearly in a Knudsen cell inlet of a Bendix Time-of-Flight Mass Spectrometer. While polymer preparation was presumably similar in both cases, their Polymer A was post cured under pressure to 400°C, while Polymer C was cured as a powder to 400°C under 1 atm. of nitrogen, cast to a 0.6 mil thick film from a solution in dimethyl sulfoxide, air dried in a forced draft oven for 1-2 hours at 150°C, then aged in air at 300°C for 58 hours. While there were a number of similarities in the results of both types of experiments, there were many more differences. Evolution of only H_2O, H_2, HCN, and CH_4 was observed for Polymer C. While H_2 and HCN were evolved in approximately the same temperature range and peaked at about the same temperature as in the present research, CH_4, which was a minor product, was not observed in the present work. Many products including ammonia, benzene, aniline, benzonitrile, phenylene diamine, aminobenzonitrile, and phthalonitrile appeared only

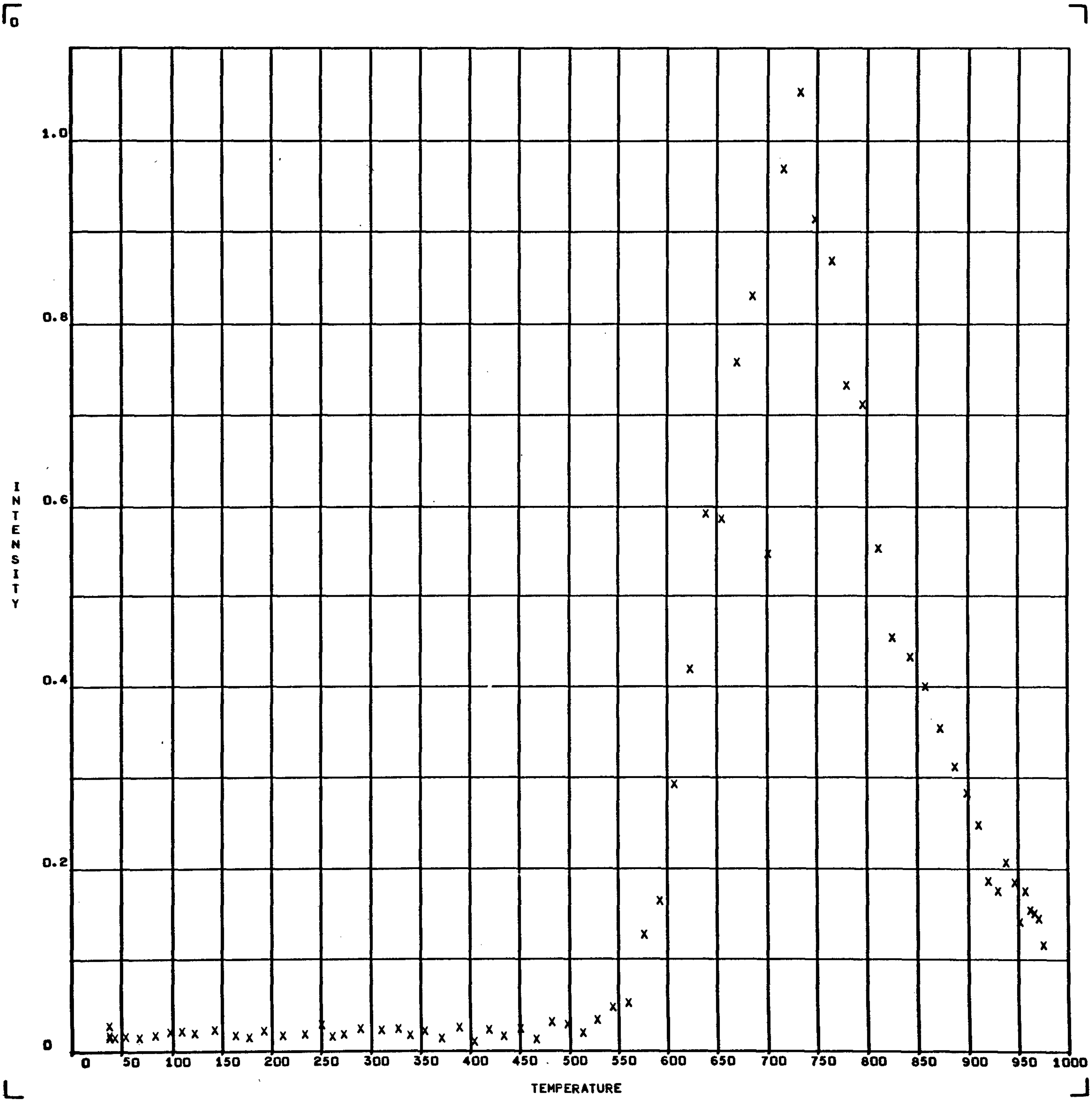

Figure 26 - Mass Spectra of Polybenzimidazole Pyrolysis Gases, m/e-2

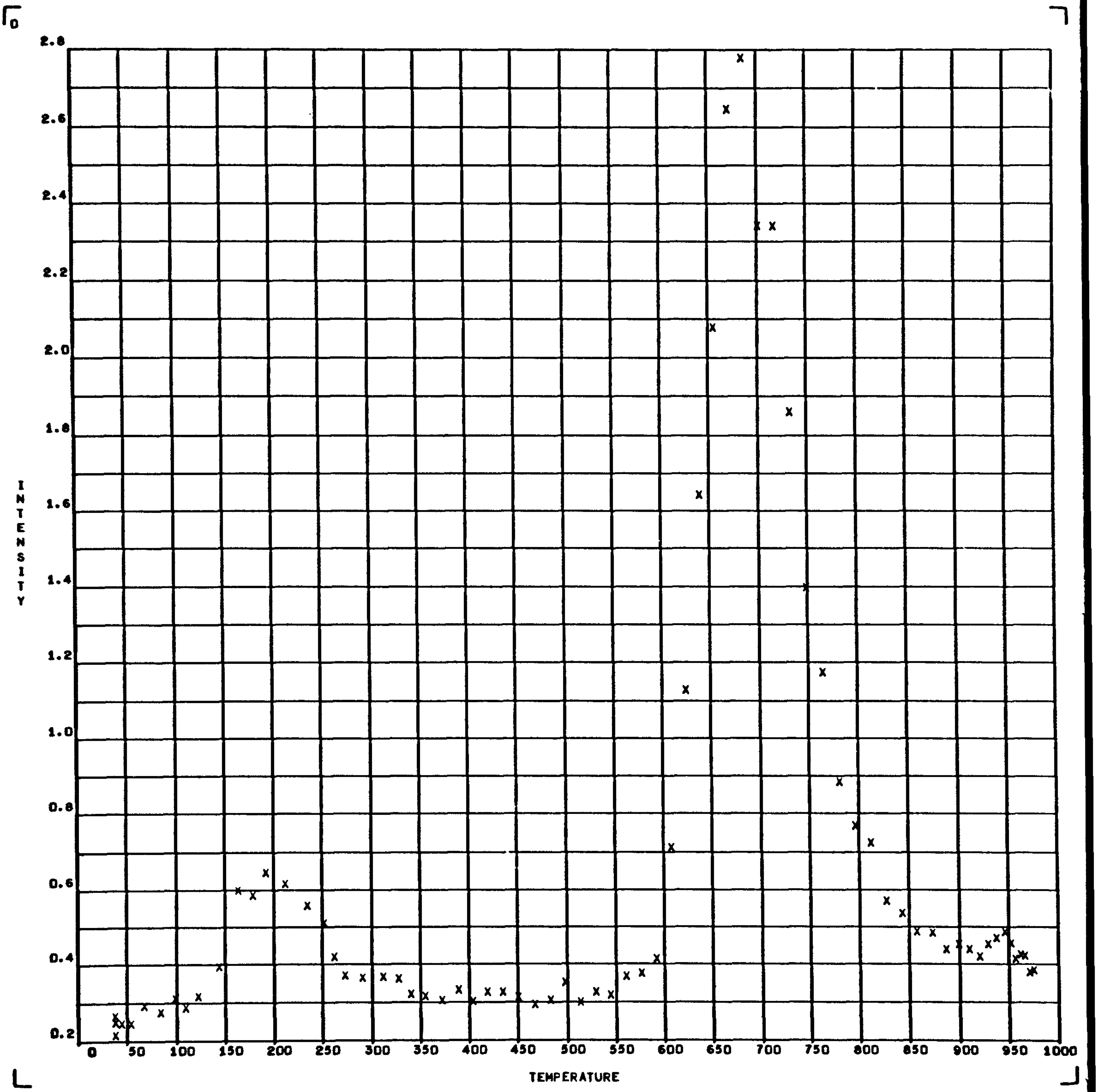

Figure 27 - Mass Spectra of Polybenzimidazole Pyrolysis Gases, m/e-17

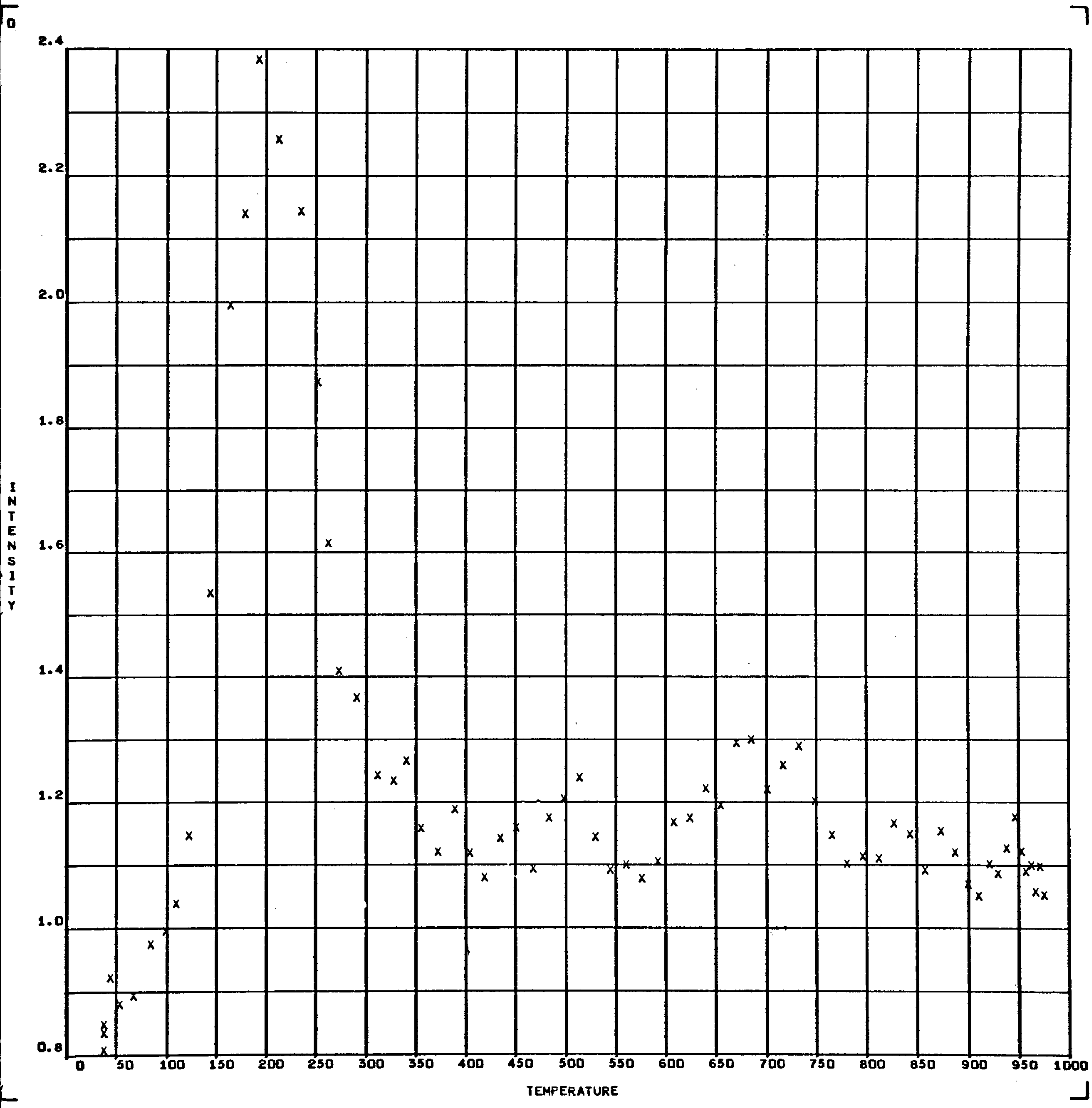

Figure 28 - Mass Spectra of Polybenzimidazole Pyrolysis Gases, m/e-18

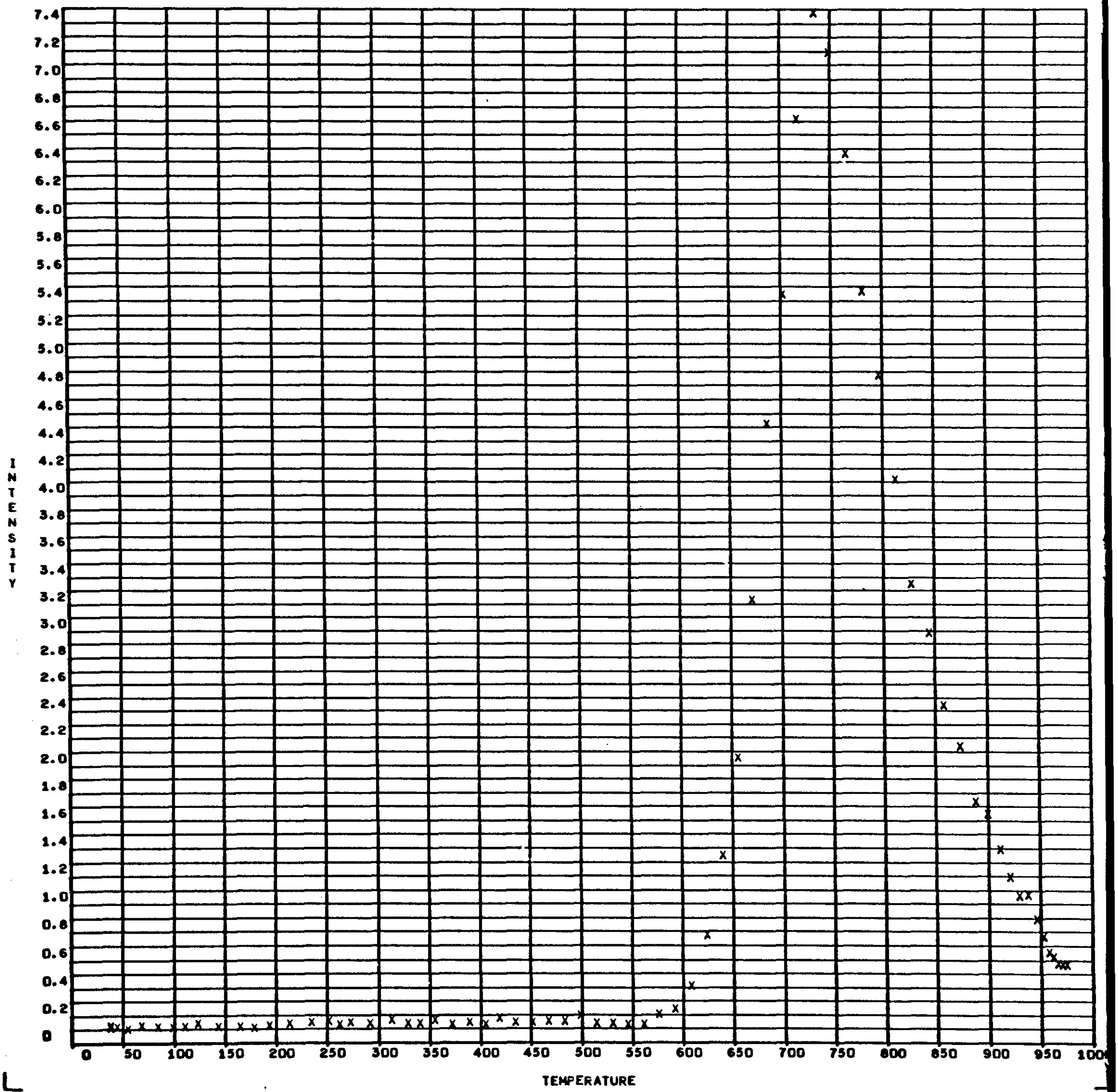

Figure 29 - Mass Spectra of Polybenzimidazole Pyrolysis Gases, m/e-27

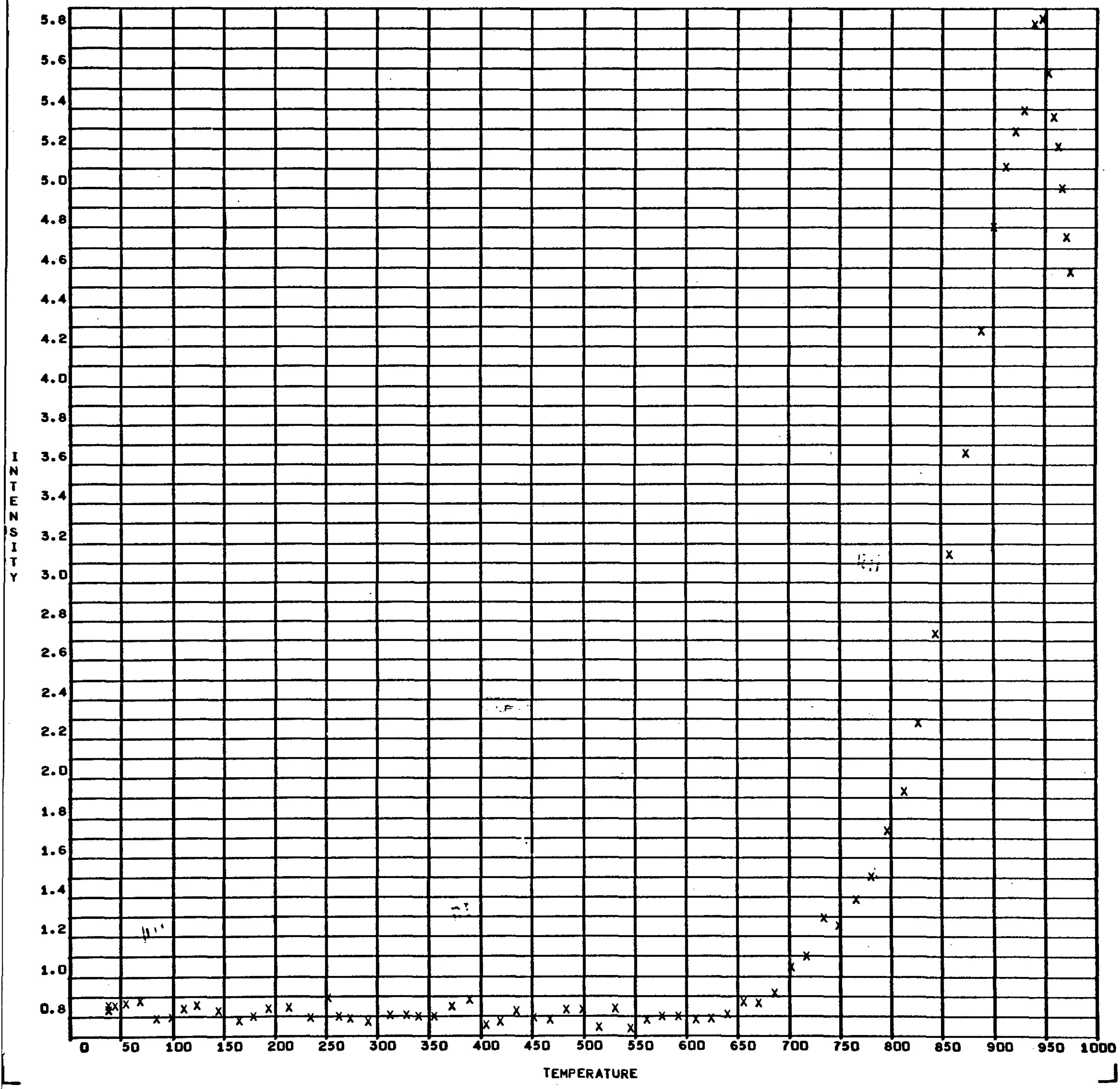

Figure 30 - Mass Spectra of Polybenzimidazole Pyrolysis Gases, m/e-28

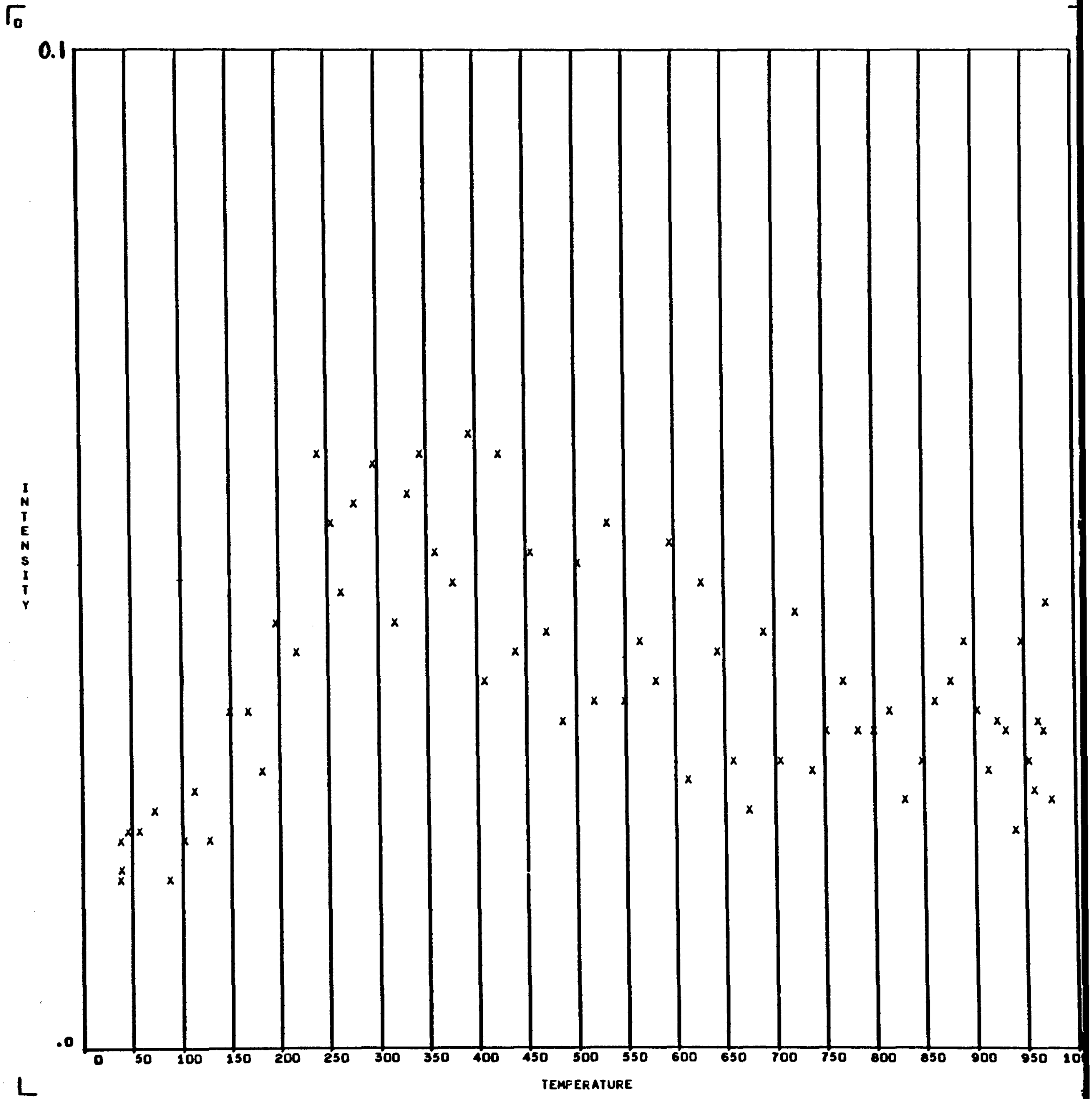

Figure 31 - Mass Spectra of Polybenzimidazole Pyrolysis Gases, m/e-70

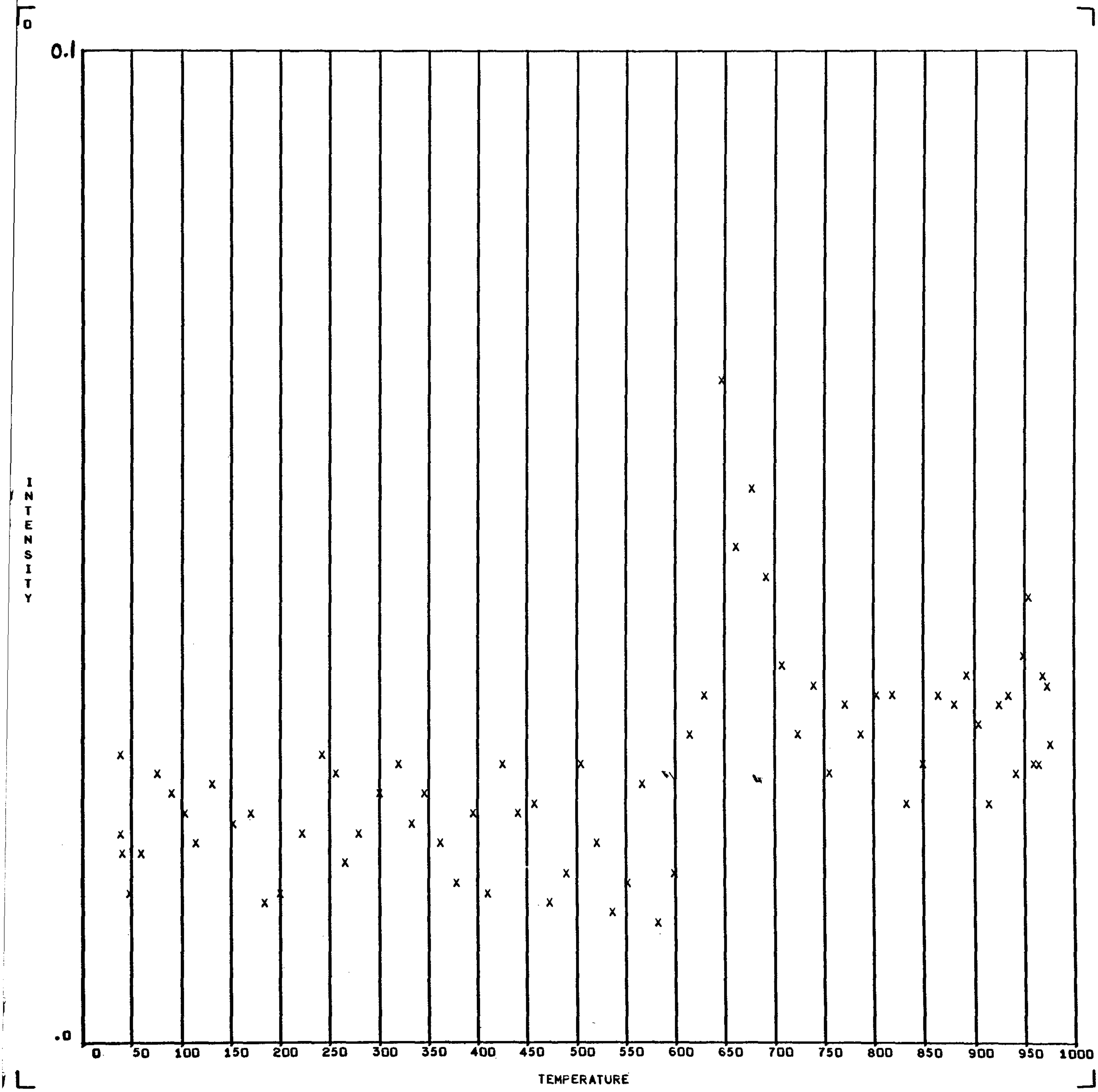

Figure 32 - Mass Spectra of Polybenzimidazole Pyrolysis Gases, m/e-103

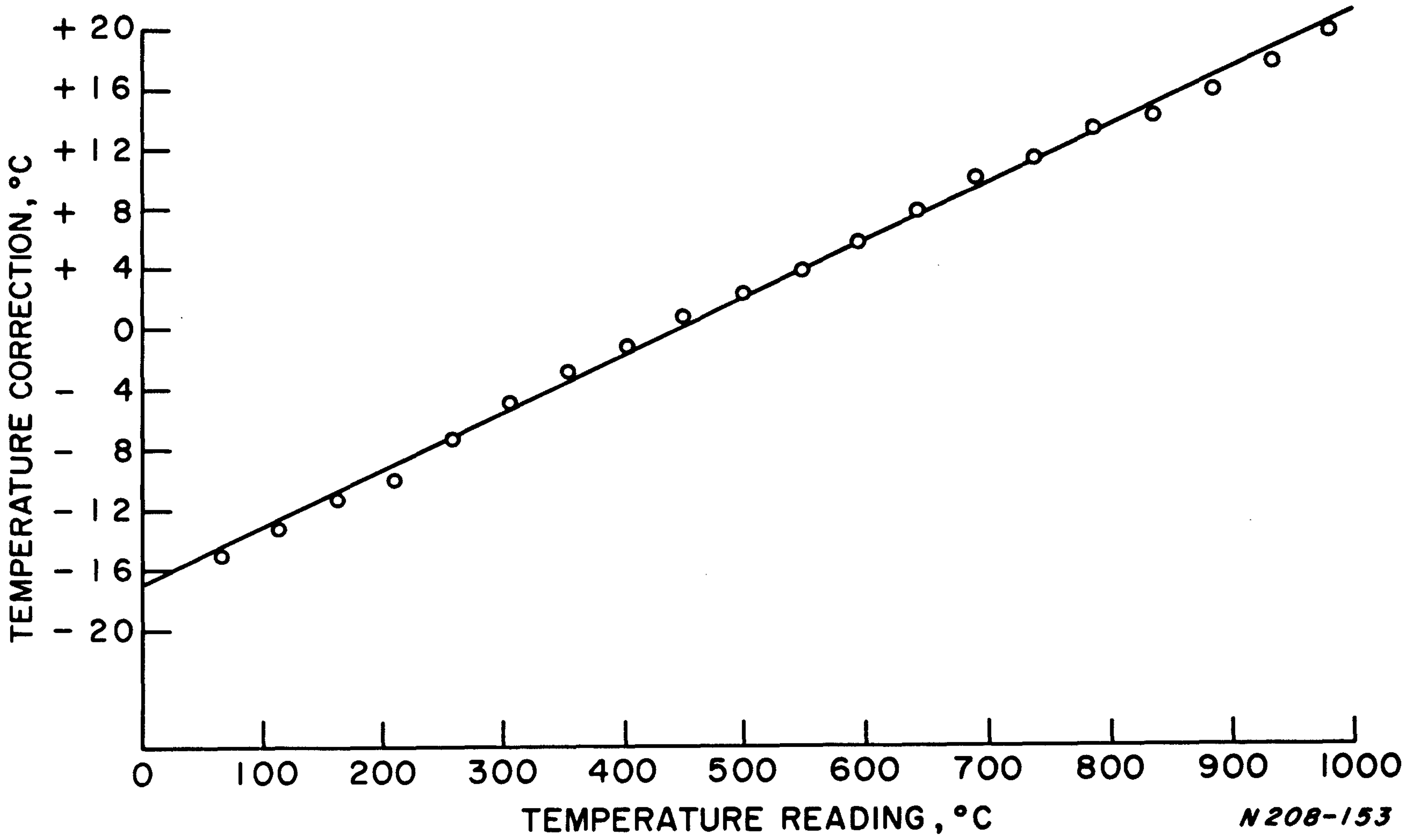

Figure 33. Temperature Correction for Figures 26 - 32

in the Space Sciences Laboratory pyrolysis. The pyrolysis products of Polymer A were still different. The main products, HCN, H_2 and NH_3 were in reasonable agreement. While water evolution produced a rather sharp peak at about 410°C in the present work, two broad peaks at about 520° and 630°C were observed by Shulman and Lochte. They also observed significant evolution of CO and CH_4, which did not appear in the present research, and failed to observe the heavier products than CO_2, except for the condensation product phenol. Their results when compared with the present research show that differences in sample preparation and pyrolysis apparatus may have profound effects on the composition of pyrolysis products. The use of a closed system permits the interaction of primary decomposition products at comparatively high pressures with a resultant reduction in molecular size. The effects of curing the sample in the presence of air are observed in the presence of increased quantities of H_2O and CO. Catalytic decomposition may be induced in the solid or gas phase by the metal of which the Knudsen cell is fabricated. Some of the heavier molecules that are observed in the present research could occur because of secondary reactions of primary products after they leave the sample, however, heavier molecules are generally observed in vacuum pyrolysis of polymers.

Gray and Shulman[6] heated an equimolar mixture of diphenyl isophthalate and 3, 3', 4, 4'-tetra-aminobiphenyl in the same apparatus as in reference 5 and observed that phenol was evolved in advance of later water. This was in agreement with Wrasidlo and Levine[7] and with observations during the pyrolysis of poly-2, 2'-(m-phenylene)-5, 5'-bibenzimidazole as described in reference 1.

CONCLUSIONS

Mass spectrometric thermal analysis, coupled with the automatic data collecting system that was developed for the purpose of efficient acquisition and further processing of the data, have proven to be useful tools for studying the chemistry of thermal decomposition of polymers. The collecting system is functioning fully as planned. The one problem is that the data that have been acquired contain errors of approximately 25%. Current and planned improvements, that are being tested, are expected to reduce this to a level which will be suitable for reasonably accurate qualitative and quantitative analysis. Qualitative form of curves of ion intensity vs. temperature are in good agreement with earlier ones that were obtained from manual reading of oscillograph traces. Data handling methods have been developed. A computer program was prepared for determing the individual settings for the 200 potentiometers that comprise the mass selector. Another computer program was developed for automatic graph plotting of the data obtained from the automatic data collecting system. An improved data plotting program is currently being developed, as well as a program which will yield qualitative and quantitative analysis when the pyrolysis mass spectra are compared to spectra of known calibration standards.

Several apparatus modifications have been made, including changes in the introduction system for solids associated with a new approach for calibration of solids with limited volatility. A drybox has been modified in connection with calibration, as well. Several pure calibration standards have been received. Others are expected soon. The pyrolysis vacuum system has been altered to eliminate the need for greased joints.

Pyrolysis of an untreated and a heat treated sample of poly-2, 2'-(m-phenylene) -5, 5'-bibenzimidazole showed that volatiles such as methyl ethyl ketone and acrylonitrile were largely eliminated during vacuum heating to 300°C. The former was a solvent, while the latter was thought to be caused mainly by degradation which occurred during preparation, although some of it could have formed during heat treatment. That changes in chemical structure of the polymer occurred was indicated by sizeable differences in the yields of most of the decomposition products.

The results of MTA pyrolysis of polybenzimidazole indicated that the aromatic products that come from phenylene-benzimidazole copolymers tend to be derived from the phenylene groups, while hydrogen, ammonia, hydrogen cyanide, and nitrogen result mainly from the benzimidazole structure. Very small differences, if any, in the temperatures of onset of evolution of major products, and in the shapes of the ion intensity vs. temperature curves, indicated that the phenylene groups did not change the stability of the basic polybenzimidazole structure. Of course, the significance of this argument would depend on how the polymers were used.

A paper entitled "Thermal Analysis of Polymers with a Time-of-Flight Mass Spectrometer" by Henry L. Friedman, George A. Griffith and Harold W. Goldstein was presented at the Symposium on Thermal Analysis of Polymers of the Second Western Regional Meeting of the American Chemical Society, San Francisco, California, October 17, 1966.

RECOMMENDATIONS FOR FUTURE WORK

Carry out pyrolysis experiments for various polybenzimidazoles, and perform necessary calibration experiments. Prepare high purity knowns for products where sufficiently pure commercial samples are not available.

Complete programs to provide qualitative and quantitative analyses of products from data collected by automatic data processing system. Apply programs to results of polybenzimidazole pyrolyses.

Carry out kinetic analysis for selected products, especially those that form during early decomposition.

Extend studies to other polybenzimidazole structures, as indicated, and to other polymer families.

Examine the 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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2. ibid, ML-TDR-64-274 Part II, October 1965.

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5. G. P. Shulman and H. W. Lochte, presented at the Atlantic City Meeting of the Amer. Chem. Soc. Div. of Polymer Chem., Polymer Preprints, Vol. 6, No. 2, 773, September 1965.

6. D. N. Gray and G. P. Shulman, ibid, 778.

7. W. Wrasidlo and H. H. Levine, J. Polymer Sci. A2, 4795 (1964).

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13. ABSTRACT

Research aimed at obtaining quantitative relationships between structure and thermal stability of polymers was continued. Mass spectrometric thermal analysis was used to study differences in pyrolysis chemistry of untreated and heat treated poly-2, 2'-(m-phenylene)-5, 5'-bibenzimidazole, and to study the pyrolysis chemistry of polybenzimidazole. An automatic data collecting system was successfully developed for this research, and was utilized for these measurements. Computer programs were developed for adjusting the data processing system and for automatic graph plotting of the data. Computer programs are being developed for refined data plotting and for final qualitative and quantitative analysis of the results. Several modifications were made in the pyrolysis and sampling vacuum systems.

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