

THERMAL ANALYSIS OF POLYMERS BY TIME-OF-FLIGHT MASS SPECTROMETRY

III. ADVANCED AUTOMATIC DATA PROCESSING BASED ON FREQUENCY MODULATED ANALOG TAPE AND HYBRID COMPUTER*

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ABSTRACT

Polymer samples were pyrolyzed at a linear heating rate of $10^{\circ}\text{C min}^{-1}$. Time-of-flight mass spectrometer output was continually recorded on FM analog tape together with time-clock and start-of-scan pulses. Similar data were collected for known calibration samples which were admitted to the mass spectrometer directly following pyrolysis. The data were digitized by use of a hybrid computer system based on a Beckman 2200 Analog Computer and a SDS 930 Digital Computer. The digitized data were then processed by the digital computer to locate mass spectral peaks, to assign mass numbers, and to evaluate signal intensities. Further data processing by digital computer sorted the data into sets according to mass number and provided automatic graph plotting for each ion observed (ion intensity vs. time). The instrumentation is described, computer programs are discussed, and an example of their application to polyquinoxaline is presented.

INTRODUCTION

Evolved gas analysis by mass spectrometry (EGA-MS) has been carried out for about ten years. Earlier work has been discussed in two reviews^{1,2}. Several different automatic data processing systems have been developed to efficiently handle the large quantities of data generated by EGA-MS³⁻⁷. References 3 and 6 described a system which employed a programmed stepped mass selector, an on-line analog-to-digital conversion system, with subsequent data processing by digital computer. References 4 and 5 recorded mass spectrometer output on analog magnetic tape, and used an electronic gate upon tape replay to plot ion intensity vs. time with an x-y plotter for one mass at a time. Reference 7 utilized a modified dedicated GC/MS computer hardware and software system for total data processing.

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The present paper describes a system where the mass spectrometer output is recorded on analog magnetic tape, with subsequent data processing with a hybrid computer.

EXPERIMENTAL

The pyrolysis and mass spectrometer systems that were used for these studies have been described previously^{2,6}. The horizontal quartz tube is heated by a tube furnace about 1 m away from the inlet of the mass spectrometer. The tube and sample holder were baked-out in advance of sample introduction². A Honeywell temperature controller-recorder provided a linear heating rate of $10^{\circ}\text{C min}^{-1}$. Polymer samples weighing approx. 1 mg were pyrolyzed in vacuo from ambient temperature to about 1000°C . All of the pyrolysis gases entered the modified Bendix Model 14-100 time-of-flight mass spectrometer through a cluster of 821 2 mil diameter holes arranged within a 1 inch diameter circle. The plate containing the holes was located just before the 70 V electron beam of the mass spectrometer. The electrometer of the Bendix Analog Output System was replaced with a Kiethley Model 416 High Speed Piccoameter.

The mass spectrometer output, from continuous scans of approx. 20 sec duration, were recorded on two channels (one regular and the other attenuated) of FM analog magnetic tape with a Sangamo Model 3560 Portable Recorder Reproducer at a rate of $3\frac{1}{2}$ ips. The third channel contained the start of scan pulse for each mass spectrometer scan, and the fourth channel recorded a high frequency sinusoidal clock pulse. Test run data were recorded first, followed by calibration data for hydrogen, n-butane and hexachloroethane, usually in that order. The recorder was stopped between sets of data, and a clock pulse free gap of about ten feet was left in order to identify that gap. Three blank scans were usually recorded in advance of each calibration and the calibration gas was admitted just at the start of the fourth scan. About five data scans were recorded for hydrogen, and ten for the others.

DATA PROCESSING

The hybrid computer system used for this work consisted of a Beckman Model 2200 Analog Computer and an SDS Model 930 Digital Computer. The following programs were used.

Digitization

The analog magnetic tape (Tape I) was played through the Beckman Model 2200 Analog Computer, which digitized the information. The frequency of digitization was a function of the clock pulse frequency. The latter was chosen to give just less than 4000 data points per scan. The SDS-930 Digital Computer stored the digitized data and wrote a digital magnetic tape (Tape II). One set of digitized data was written for each scan. (From time-to-time, noise pulses appeared on the start-of-scan channel,

which caused short scan records to result. This error was corrected by the next program.) Digitization was accomplished at $7\frac{1}{2}$ ips. Separate passes were made for test run and calibration data, and for both levels of attenuation. Printouts of the digitized data were obtained for several scans and a printout of scan number vs. counts per scan was recorded for all of the data.

Ordering

The last printout from digitization was examined to determine the range of counts per full scan. This varied typically by about 5 in about 3950, except for the short scans (due to noise pulses), as described above. The first complete scan was identified and was assigned scan number one. The ordering program grouped the data in sets according to the determined number of minimum counts per scan, and started with the first complete scan that was recorded. The output from this program was a digital magnetic tape (Tape III) of intensities arranged into sets, one for each mass spectrometer scan. A printout of scan number vs. counts per scan was generated, too. This program was applied to all of the data that were digitized.

Peak finding and intensity evaluation

The ordered data were subjected to a peak finding program based on the work of Savitzky and Golay⁸. This program fitted a parabola to the peak and evaluated the intensity and location of the maximum. (Initially a Gaussian fit was employed, but was found to require an enormous quantity of computer time. The parabolic fit was found to be much faster, and was found to be reasonably accurate with respect to scatter of the data.) The program wrote a digital magnetic tape (Tape IV) of maximum peak intensity vs. central peak clock pulse count for each scan. Each scan commenced more than 100 counts before m/e 1, so the first 100 digits were averaged as the baseline value and the standard deviation was evaluated. The existence of a peak was established only when three consecutive values exceeded the average plus two times the standard deviation. The duration of the strongest peaks was of the order of 10 counts. The program then examined all of the values associated with the data point and found the center and intensity at the center by interpolation. The average baseline intensity was subtracted from the peak intensity. From time-to-time, a noise spike distorted the baseline computation or the evaluation of single peaks. This could usually be determined by visual inspection of the printout from this tape, and provisions were available for editing at a later stage.

Mass fit

The printouts from peak finding and intensity evaluation for the calibration compounds were examined manually to determine the peak center pulse counts as a function of their related mass numbers. These were then subjected to least squares analyses with the SDS-930 Computer, using the equation

$$n_i = n_0 + k_1 (m_i)^{\frac{1}{2}} + k_2 m_i$$

where n = pulse counts, m = ion mass-to-charge ratio, k = constant, subscript "i" represents the i-th mass value and subscript 0 represents the hypothetical mass zero. The mass fit for a typical set is shown in Table 1. There was no problem in achieving accurate mass assignments for the mass range of interest, since the mass spectrometer scans were quite reproducible.

TABLE 1
MASS FIT FOR TYPICAL SET OF CALIBRATION DATA

<i>m/e</i>	<i>Counts at peak center</i>		<i>m/e</i>	<i>Counts at peak center</i>	
	<i>Obs.</i>	<i>Calc.</i> ^a		<i>Obs.</i>	<i>Calc.</i> ^a
2	245	241.4	59	1741	1741.7
12	733	733.1	82	2071	2069.4
16	861	861.5	84	2096	2095.6
17	890	891.0	94	2223	2221.9
18	920	919.6	96	2247	2246.4
27	1146	1147.8	117	2491	2488.9
28	1169	1170.7	119	2513	2510.8
29	1191	1193.1	121	2534	2532.5
35	1320	1320.0	164	2962	2961.8
37	1360	1359.9	166	2981	2980.3
41	1434	1436.4	199	3269	3270.5
43	1472	1473.3	201	3286	3287.3
47	1545	1544.6	203	3303	3304.0
49	1580	1579.0	205	3320	3320.6

^a Least squares equation: $n_1 = -98.412 + 240.44(m_1)^{\frac{1}{2}} - 0.11517m_1$. Standard deviation = 1.40852.

Mass assignment

Pyrolysis data from Tape IV were processed to convert mass peak center counts to mass numbers, using the values generated in Section 4. The output was a digital magnetic tape (Tape V) of mass number vs. intensity in sets according to scan number, and a printout. Both the regular and attenuated data were processed in this way.

Merge

The regular and attenuated data from Tape V were merged into an averaged single regular data set. If a peak was found in only one channel, then that value was used. If the data point intensity exceeded magnetic tape saturation value on the regular channel, then only the data from the attenuated channel was used. If the two values were widely different, then that fact was noted on the printout and the individual values were examined to see if one of them was obviously incorrect. It was sometimes necessary to examine the Section 3 printout to see if the peak center was widely different from the expected value, as occurred if a noise peak appeared on one or on both channels. The output of this program was a digital magnetic tape (Tape VI) of mass number vs. intensity in sets according to scan number, and a printout.

Sort

The edited data in Tape VI were sorted into sets according to mass number, in scan number sequence. A value of zero intensity was assigned for each scan where no peak for each particular mass number was observed. If no peak appeared between two values at that mass, then linear interpolation was performed, and the average value was assigned. This was done, because the threshold value is always above zero. Sorting was carried out for each mass number up to a selected maximum value, in sets of five. This number was chosen because of the memory capacity of the computer system. It required a rewind of Tape VI, and a complete replay for each set of five masses. If no mass peak was observed in any scan, then that set was discarded and was not recorded on the digital magnetic tape output. Thus, the output from this program (Tape VII) was the mass number followed by a series of intensities (one value for each scan), for every mass that was observed. A printout was generated.

Plot

The printout from Section 7 was examined to select the mass numbers for graphs to be plotted. Those containing only single values, or a few weak values that were separated by large time intervals, were eliminated. The plot program permitted writing a title, the mass number, and labelling and dimensioning of the axes. The ordinate scale was a function of maximum peak intensity, and was one of several chosen to give a convenient value to each vertical subdivision. A time was computed for each data point in the following way. n_i was computed for the first scan from the mass number and from the constants that were determined in the mass fit section. The time of the first peak was n_i/f , where f = clock pulse frequency in pulses min^{-1} . The time for each subsequent peak was evaluated by adding the total time for each scan, as obtained from dividing the total counts per scan by f . The above resulted in the final digital magnetic tape (Tape VIII). The graphs were plotted by the hybrid computer system with an Electronics Associates Inc. Model 1110 x-y plotter. Representative examples are shown below.

RESULTS

The data processing system was applied with success to five polymers, but only the results for one, a polyquinoxaline which was carefully cleaned of solvents, will be described here. Only two defective experiments were carried out, in which (1) the furnace coils burned out, and (2) the mass spectrometer became defective. The former was observed in the temperature record, while the latter was disclosed during the first magnetic tape playback of data through an oscilloscope. The results shown in Figs. 1-7 were obtained from a 1.538 mg sample heated to 970°C, during which period the sample weight loss was 20.9%. The original graphs were not dark enough for photo reduction, so only tracings are included here. All points of zero intensity before and after gas evolution have been eliminated from the tracings. Note the abrupt increase of intensity above zero, which is due to threshold considerations in peak finding. This

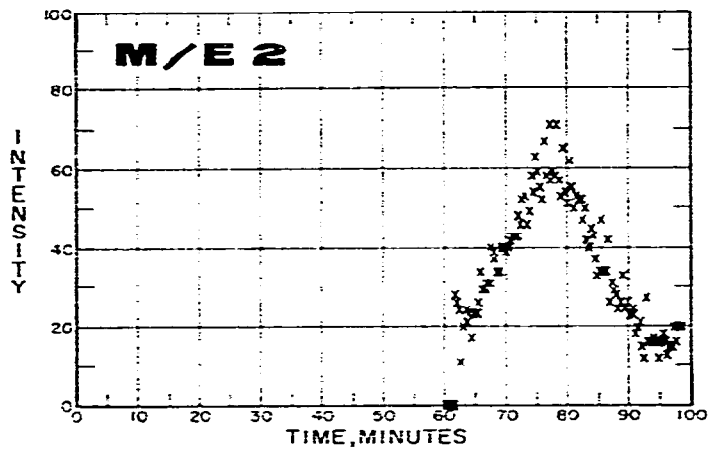


Fig. 1. EGA-MS results for polyquinoxaline at m/e 2.

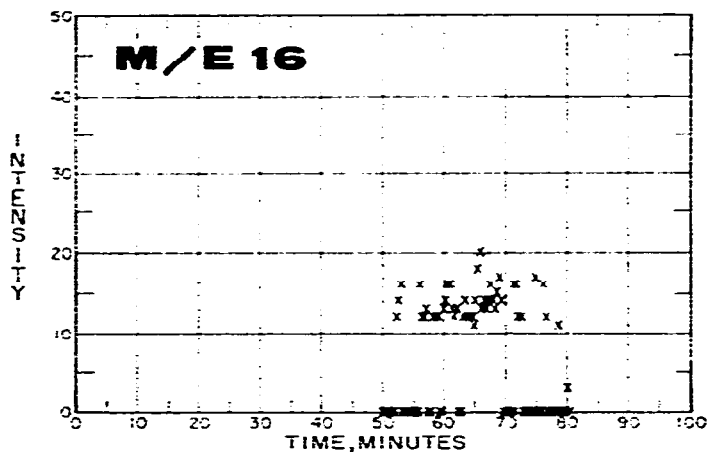


Fig. 2. EGA-MS results for polyquinoxaline at m/e 16.

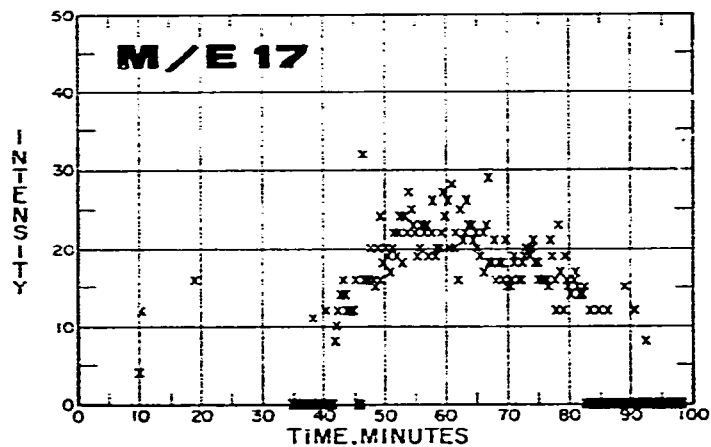


Fig. 3. EGA-MS results for polyquinoxaline at m/e 17.

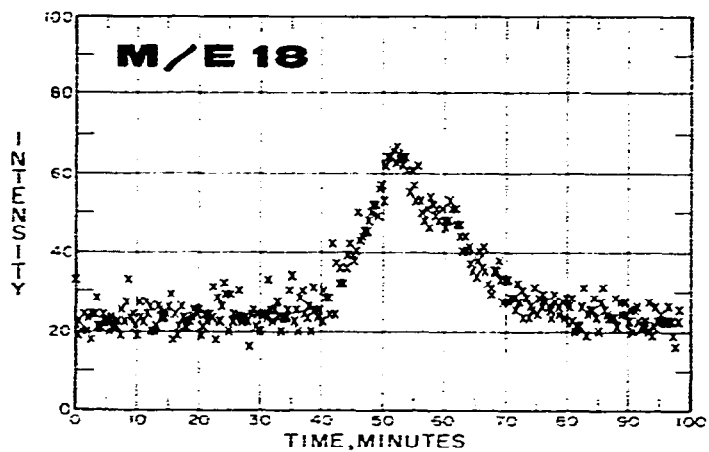


Fig. 4. EGA-MS results for polyquinoxaline at m/e 18.

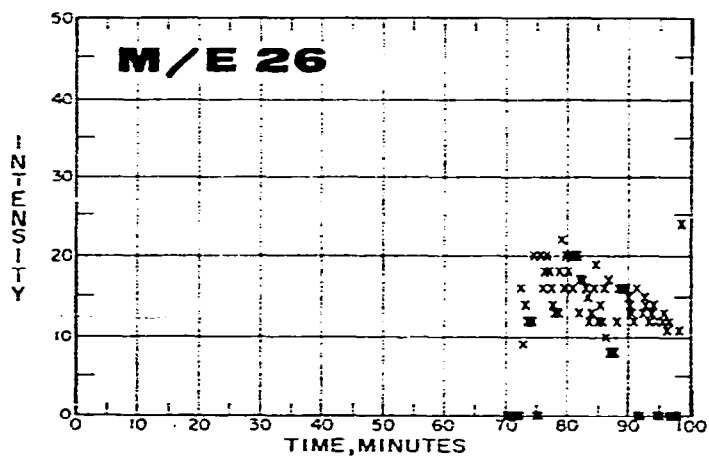


Fig. 5. EGA-MS results for polyquinoxaline at m/e 26.

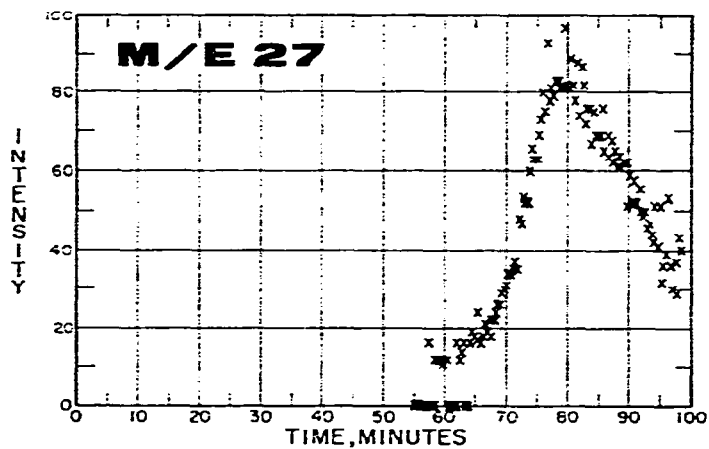


Fig. 6. EGA-MS results for polyquinoxaline at m/e 27.

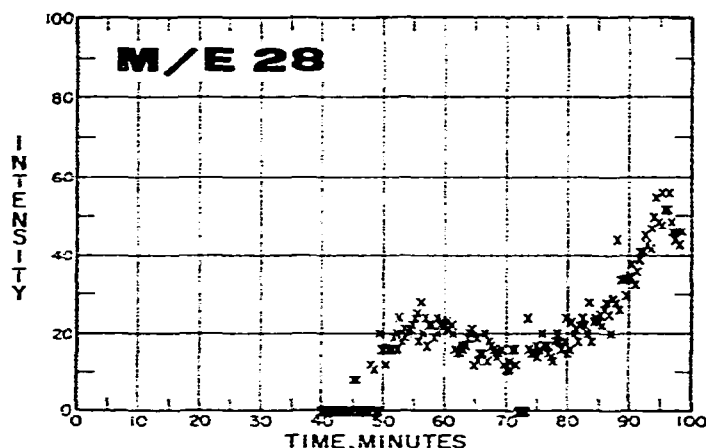


Fig. 7. EGA-MS results for polyquinoxaline at m/e 28.

effect is reduced, considerably, when the mass spectrometer is operated at higher sensitivity, or if larger samples are used. The water background in the mass spectrometer may be seen in Fig. 4. Nitrogen background did not exceed the threshold level (Fig. 7) for this experiment. For reference purposes, the n-butane sensitivity was 122.0 divisions μ^{-1} at m/e 43. The units for the ordinate are divisions. The results are summarized in Table 2.

TABLE 2
EGA-MS RESULTS FROM POLYQUINOXALINE

Product	Evolution temperature ($^{\circ}\text{C}$)		
	Start	Peak	Finish
Water ^a	390	520	800
Carbon monoxide ^a	<450	560	700+
Ammonia	<400	600	870+
Hydrogen cyanide ^a	<575	790	970+
Methane	500	Broad	800
Hydrogen ^a	<610	780	970+
Nitrogen ^a	<700	950+	

^a Present in sizable quantities.

CONCLUSIONS

The data processing system described in this paper functioned very satisfactorily in that: (1) where runs were carried out for the same sample with the earlier system, the results were quite similar; (2) far fewer wasted MTA runs were carried out; and (3) formal data processing was never started for poor data.

In order to choose the type of data processing system, it is necessary to evaluate the operating characteristics of the mass spectrometer (especially its stability and

reproducibility of scanning), other instruments available for the system, and computer facilities that are available and their capabilities. If a dedicated computer is available, and especially if a GC/MS hardware and software system is on hand, it would be best to employ those capabilities, if at all possible.

The following list of benefits is based on comparing our two data processing systems, i.e., the older one which comprised a programmed stepped mass selector with an on-line analog-to-digital conversion system, with the one described in this paper. It is written from the point-of-view of the new system.

(1) The lengthy set-up procedure was eliminated. A further benefit was that the degree of instrument drift and probability of instrument failure were both reduced.

(2) Precise coincidence of mass peak and mass spectrometer gate positions did not have to be assured to obtain accuracy.

(3) Faster scanning was permitted, resulting in more data points per run.

(4) Oscilloscope replay of raw data permitted accurate decision of whether or not to process data.

(5) A comprehensive permanent record resulted which could be subjected to alternate forms of data processing.

(6) Once scan range was selected, all data included in that range were recorded.

(7) Use of narrower gate provided improved mass resolution.

(8) Use of two data channels increased range of intensities handled. (Benefit partly offset by disproportionate differences in noise level.)

While relating mass number to time (through clock pulse count) was suitable for the present work, the authors feel that for the higher masses, and for ramp generators (driver for scanning) with poorer reproducibility than the one used for this work, it would be beneficial to use the method of Grayson and Conrads⁹ for mass evaluation. Their method correlates mass with gate driving voltage instead of with time (as in using clock pulse count). By using a scale expander, they were able to determine mass to higher accuracies, despite poor scanning reproducibility with a time-of-flight mass spectrometer.

It would be beneficial to combine the various computer programs, and to thus reduce computer operating time. Further benefits could be gained from writing the combined programs for a computer with larger memory capacity and with faster speed of operation. Several sophistications could be put into the programs, based on operations that must now be carried out manually.

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