

## MASS SPECTROMETRIC THERMAL ANALYSIS: A REVIEW\*

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### INTRODUCTION

Chemical analysis and monitoring of decomposition gases may be used to study the chemistry of degradation processes of solids and to provide a quantitative measure of the rate of decomposition. The latter serves as a measure of thermal stability. In the decomposition of many solids a single gaseous product is evolved, or just a few gases are evolved in well separated stages. For many other substances, especially polymers, a number of different gaseous products are often given off, and in a large number of cases part of the evolution is concurrent. One may expect to gain more or less insight into the chemistry of any given decomposition by matching the ability of the analytical method to differentiate, with the complexity of the gas evolution. Many examples of such methods may be found in several reviews<sup>1-4</sup>. One that has been developed rather recently, but is coming into wider use is mass spectrometric thermal analysis (EGA-MS\*\*).

### THEORY

This article is limited to a discussion of methods where materials are pyrolyzed and where one, several, or all of the ions formed by electron bombardment of the pyrolysis gases are monitored continually with a mass spectrometer. EGA-MS systems are composed of such components as a furnace, a temperature regulator and monitor, a mass spectrometer with associated equipment, and a recorder. An auxiliary vacuum system is a usual component, and is used for such purposes as external vacuum pyrolysis, differential pumping, removal of excess gases from external pyrolysis in carrier gases, and introduction of calibration samples. Perhaps the most straight forward use of the method includes linear programmed heating of the sample in vacuum. The pyrolysis gases are analyzed continually as the mass spectrometer continually scans the ionic mass range of interest. The results are recorded with an oscillograph or a sufficiently fast strip chart recorder. One may then plot ion signal intensity *vs.* time (or temperature) for each ionic mass observed. Ions arising from

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\*\*Evolved gas analysis by mass spectrometry; abbreviation recommended by Committee on Nomenclature of the International Confederation for Thermal Analysis<sup>5</sup>. Abbreviations such as MTA and MSA are used commonly.

the same product would have the same contours in graphs where there are no interfering ions. This fact aids in the qualitative analysis of that component. One may refer to mass spectral listings or to calibration spectra run on one's own instrument in order to choose the most likely product. Since the quantity of each ionic fragment is nearly proportional to the quantity of that product entering the mass spectrometer, any graph without a direct interfering ion may be used for quantitative analysis of that component. Even with interference it is possible to account for the various ionic contributions in some cases.

An alternative method of operation is to monitor a single ionic mass for the duration of pyrolysis and to observe the ion yield as a function of time with an oscillograph or sufficiently fast strip chart recorder. It is possible to plot ion intensity *vs.* temperature directly with an x-y recorder. It is sometimes possible to use a multi-channel system to monitor several ionic masses simultaneously, but this is not practical if the number of products (producing non-interfering spectra) exceeds the number of channels available.

## SYSTEMS

### *Conventional*

Although the instrumental capabilities at that time were somewhat limited, one of the first attempts of this type of analysis was carried out by Zemany<sup>6</sup>. A thin film sample of polystyrene was deposited on quartz and was heated adjacent to the inlet leak of a magnetic mass spectrometer. Temperature was elevated slowly and over many individual steps. Mass spectra were recorded intermittently at each temperature. At first the main spectra were attributed to solvent, unpolymerized monomer, and other impurities. About 1% weight loss was observed during that stage of heating. Evolution of decomposition products started at about 230°C. Heating in small intervals was carried out to 330°C over a period of ten days. The signals due to the main products, styrene, benzene, and toluene, were found to be a function of temperature only, and thus were thought to be proportional to their rates of formation. Plots of log intensity *vs.*  $1/T$  gave good straight lines and activation energies were evaluated from them. Other products were observed in smaller quantities, the most prevalent of which was styrene dimer. The method was successfully extended to polymethylmethacrylate.

With the development of dependable temperature programmers and fast scanning mass spectrometers, it became possible to carry out such studies with much greater efficiency. The first modern use of EGA-MS was reported by Langer and Gohlke<sup>7</sup>. The sample holder shown in Fig. 1 was mounted on the temperature sensor shown in Fig. 2. The entire assembly was coupled with a mounting flange and was inserted into the vacuum chamber of a time-of-flight mass spectrometer, so that the sample holder was surrounded by the furnace and was near the electron beam of the

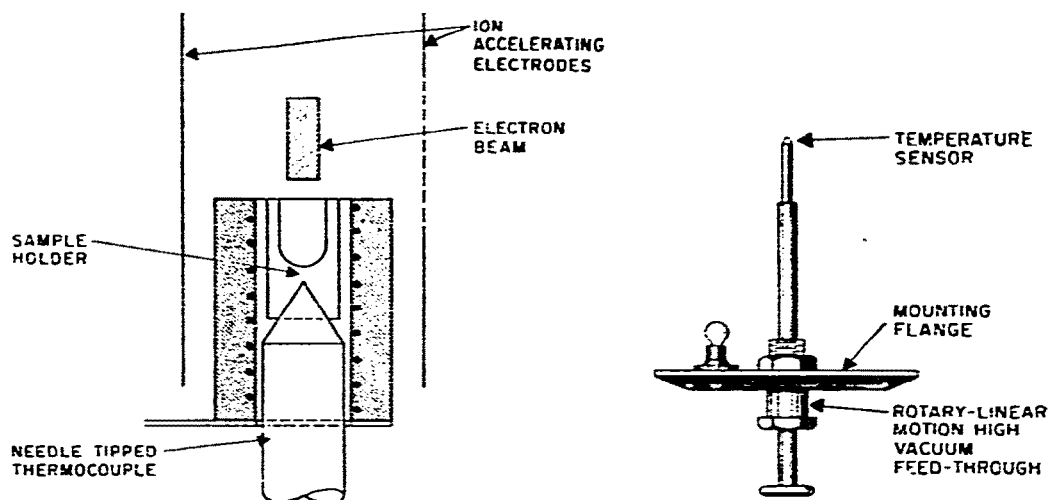


Fig. 1. Schematic of EGA-MS furnace (reprinted by permission from Langer and Gohlke<sup>8</sup>).

Fig. 2. Schematic of EGA-MS furnace mounting flange (reprinted by permission from Langer and Gohlke<sup>8</sup>).

mass spectrometer. In the time-of-flight mass spectrometer, positive ions formed by electron bombardment are accelerated through a comparatively field free flight path by strong negative potential. The ions with the smallest mass-to-charge ratio ( $m/e$ ) arrive at a distant electron multiplier detector earliest, and those with the highest  $m/e$  arrive last. Langer and Gohlke's instrument repeated this event every 500  $\mu\text{sec}$ , *i.e.*, its cycling frequency was 2,000 Hz. One may choose to utilize all the data generated, or more usually, select only a portion of the data. The total data may be observed with an oscilloscope, although it is usual to just see the results of repetitive scans atop each other. Most time-of-flight mass spectrometers are equipped with gated multipliers. The output to a recorder is blanked for all but a very short interval during each cycle of mass spectrometer operation, so that only the signal appearing during that interval is received by the recorder. Thus, one may select and read the signal for only one  $m/e$  value. Several gates allow as many signals as gates to be monitored continually. It is also possible to move the gate between two values of  $m/e$  at a predetermined rate of speed, and to do this repetitively. Use of the gate tends to damp the instrument output, thus reducing the scatter from single ion pulses. Langer and Gohlke recorded total ion current, *i.e.*, the total signal generated by all ions formed during each cycle of operation, as the sample was subjected to a linear rate of temperature rise. When gas evolution started, as shown by elevation of total ion current or by observing the oscilloscope, they switched to recording gated sweeps (in several seconds) or to monitoring a representative ion from a single product. Their results for  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$  are shown in Fig. 3, together with DTA from another instrument. Note evidence of the four stages of dehydration and later  $\text{SO}_3$  evolution. Water was monitored at  $m/e$  18 ( $\text{H}_2\text{O}^+$ ), but a relatively strong signal could also have been observed at  $m/e$  17 ( $\text{OH}^+$ ), and a much weaker one at  $m/e$  16 ( $\text{O}^+$ ). Very weak ones could be observed at  $m/e$  1

( $H^+$ ),  $m/e$  19 ( $HDO^+$ ), and  $m/e$  20 ( $H_2^{18}O^+$ ) with sufficiently sensitive instrumentation. In using an oscillographic recorder, it is rather common to use several channels, each set to different levels of sensitivity, thus increasing the range of the instrument to detect both strong and weak signals. They also studied decomposition of germanium (IV) (ethylenedinitrilo) tetraacetate dihydrate, (ethylenedinitrilo) tetraacetic acid dihydrate dihydrochloride and equimolar mixtures of  $CaSO_4 \cdot 2H_2O$  and  $CuSO_4 \cdot 5H_2O$ .

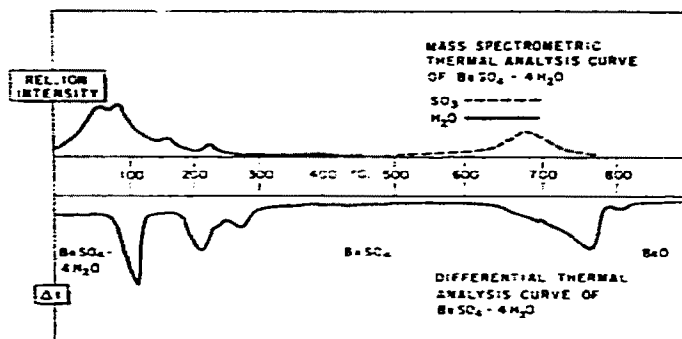


Fig. 3. Comparison of EGA-MS and DTA curves from  $BeSO_4 \cdot 4H_2O$  (reprinted by permission from Langer and Golhke<sup>7</sup>).

Friedman and coworkers originally planned to use EGA-MS to aid in the kinetic analysis of TG data, but found the EGA-MS data to be of such good quality as to render the results of TG virtually useless for complex gas evolution. These workers used remote pyrolysis (about a meter away from the electron beam of the mass spectrometer) by tube furnace, and eventually introduced the capability to pyrolyze the sample after the furnace tube had been baked-out at very high temperatures. This was for the purpose of minimizing the gases added from the system. One such arrangement is shown in Fig. 4. The sample is carried to the crucible, and

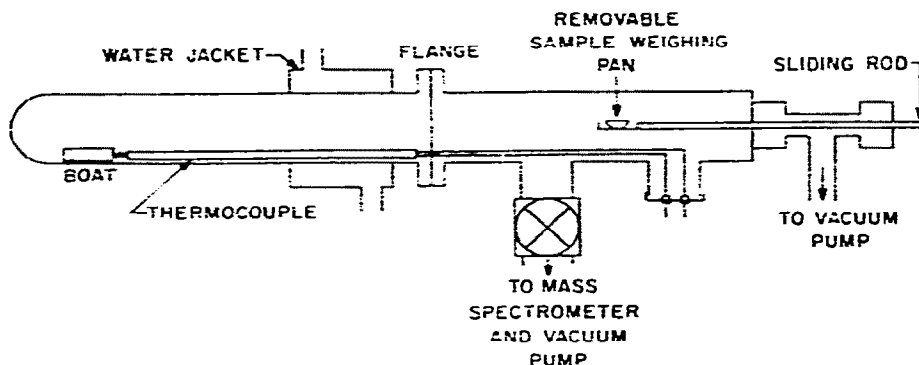


Fig. 4. Schematic of remote EGA-MS pyrolysis tube for bake-out in advance of pyrolysis (reprinted by permission from Friedman, Goldstein, and Griffith<sup>8</sup>).

dumped, after bake-out, through use of a differentially pumped gland. Most of Friedman and coworkers' experiments are described in reports to the Air Force

Materials Laboratory<sup>9</sup>. Examples of polymers studied are polybenzimidazoles<sup>9a-c, e</sup>, polyesters<sup>9d, e</sup>, polyamides<sup>9d, e</sup>, and bis benzimidazo benzophenathroline polymer<sup>9d, e</sup>. These studies have shown that it is possible to (1) differentiate between stages of evolution of different products, (2) sometimes differentiate between concurrent evolution of different products, (3) observe evolution of solvents and loosely bound water, and (4) differentiate between products of incomplete condensation and decomposition products. Most of their work has utilized the Model 14-100 Bendix Time-of-Flight Mass Spectrometer which generates mass spectral pulses every 100  $\mu$ sec (10 kHz frequency). Linear programmed heating was regulated and monitored with a proportional control system, where the thermocouple served both as the detector and thermometer. In their earliest experiments<sup>9a</sup>, full scan mass spectra were recorded in about 10 seconds, every minute with an oscillograph. Later, continuous slower scanning was used, at a rate of about a minute per scan. Still later, an automatic data collecting system was introduced, and that will be described later. One example of their results is shown in Fig. 5. Samples of untreated and heat treated

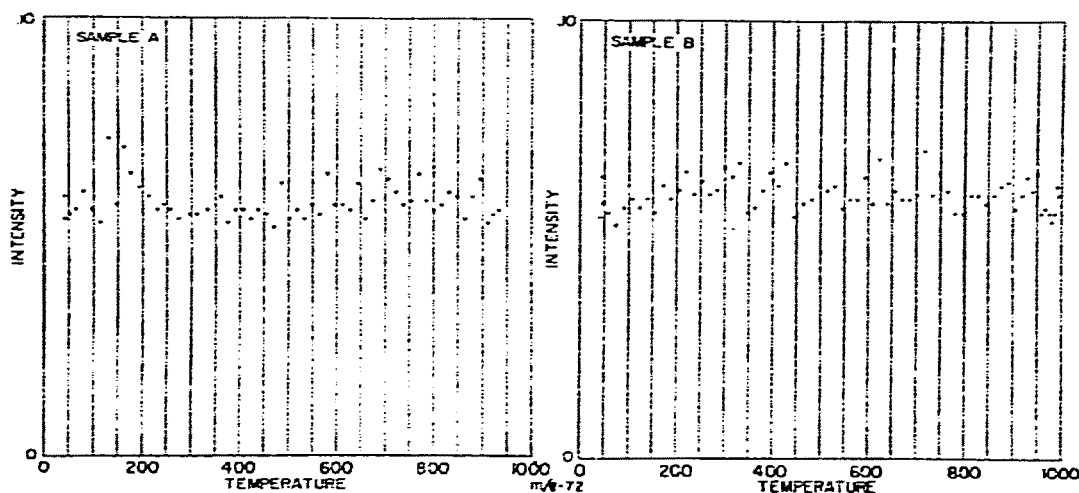


Fig. 5. EGA-MS at  $m/e$  72 of untreated (A) and heat treated (B) samples of poly-2,2'-(*m*-phenylene)-5,5'-bibenzimidazole (reprinted by permission from Friedman, Griffith, and Goldstein<sup>9c</sup>).

poly-2,2'-(*m*-phenylene)-5,5'-bibenzimidazole were subjected to EGA-MS at 10°/min. Ionic spectra at  $m/e$  72 showed that the heat treatment process successfully removed methyl ethyl ketone solvent. In studying aliphatic polyesters and polyamides, Friedman and coworkers<sup>9c-e</sup> found that many products were evolved concurrently in a single stage of reaction. While it was possible to differentiate between some of them, as one would in the more usual practice of mass spectrometry, the advantages of time resolution were lost. The authors felt that gas chromatography would have been a great help in such studies.

Shulman and coworkers used a system similar to that of Friedman and coworkers' earlier system. Their mass spectrometer was the Bendix Model 12-101 Time-of-Flight unit, which included a Knudsen cell cross. Polymer samples were heated

near the electron beam in a fashion similar to that used by Langer and Gohlke<sup>7</sup>, but a Knudsen cell with a pinhole orifice was used<sup>10</sup> instead of Langer and Gohlke's open cup. Spectra were reported for polytetrafluoroethylene, a phenol-formaldehyde polycondensate, and for poly-2,2'-(*m*-phenylene)-5,5'-bibenzimidazole. A kinetic analysis was also applied to early degradation, assuming that the reactant was relatively unchanged during that period and that the rate of formation of the component was proportional to its ion intensity. Later, Shulman and Lochte<sup>11</sup> subjected the phenol-formaldehyde polycondensate to further studies. Fig. 6 shows the results of

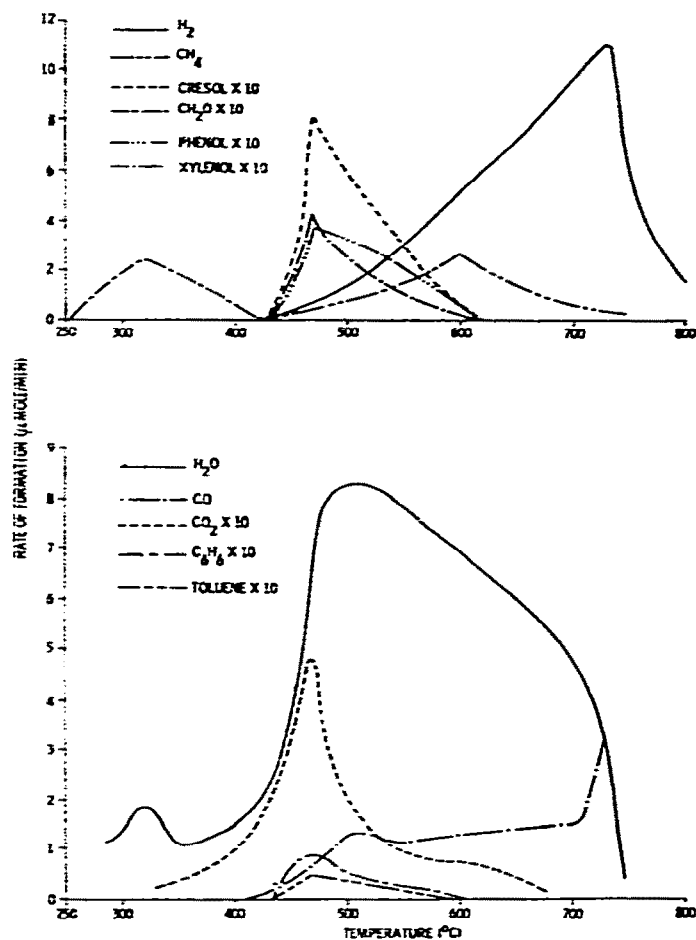


Fig. 6. EGA-MS products from a phenol-formaldehyde polycondensate (reprinted by permission from Shulman and Lochte<sup>11</sup>).

pyrolyzing a 14.9 mg sample at a rate of 29°/min. The ionic masses used for the assignments are listed in Table I. Kinetic evaluations were made as described previously from the plots shown in Fig. 7. Material balances obtained by integrating under the various curves were found to range from 70 to 110% of measured weight loss. These authors carried out isothermal EGA-MS on samples of the same resin. The results of an experiment at 405°C are shown in Fig. 8. Arrhenius plots were made

TABLE I

CHARACTERISTIC MASS NUMBERS FOR EGA-MS OF A PHENOL-FORMALDEHYDE POLYCONDENSATE (REPRINTED BY PERMISSION FROM SHULMAN AND LOCHTE<sup>11</sup>).

Species	Mass no.	Ion	Interfering fragments (source)
H <sub>2</sub>	2	H <sub>2</sub> <sup>+</sup>	None
CH <sub>4</sub>	15	CH <sub>3</sub> <sup>+</sup>	CH <sub>3</sub> <sup>+</sup> (cresol, xyleneol)
H <sub>2</sub> O	18	H <sub>2</sub> O <sup>+</sup>	None
CO	28	CO <sup>+</sup>	CO <sup>+</sup> (CO <sub>2</sub> , phenol, cresol, xyleneol)
CO	12	C <sup>+</sup>	C <sup>+</sup> (CO <sub>2</sub> )
CH <sub>2</sub> O	29	CHO <sup>+</sup>	COH <sup>+</sup> (xyleneol)
CH <sub>2</sub> O	31	CH <sub>2</sub> OH <sup>+</sup>	None
CO <sub>2</sub>	44	CO <sub>2</sub> <sup>+</sup>	None
C <sub>6</sub> H <sub>6</sub>	78	C <sub>6</sub> H <sub>6</sub> <sup>+</sup>	C <sub>6</sub> H <sub>6</sub> <sup>+</sup> (cresol, xyleneol)
Toluene	91	C <sub>7</sub> H <sub>7</sub> <sup>+</sup>	None
Phenol	94	C <sub>6</sub> H <sub>5</sub> OH <sup>+</sup>	None
Cresol	107	C <sub>7</sub> H <sub>7</sub> O <sup>+</sup>	None
Xyleneol	122	C <sub>8</sub> H <sub>10</sub> O <sub>2</sub> <sup>+</sup>	None

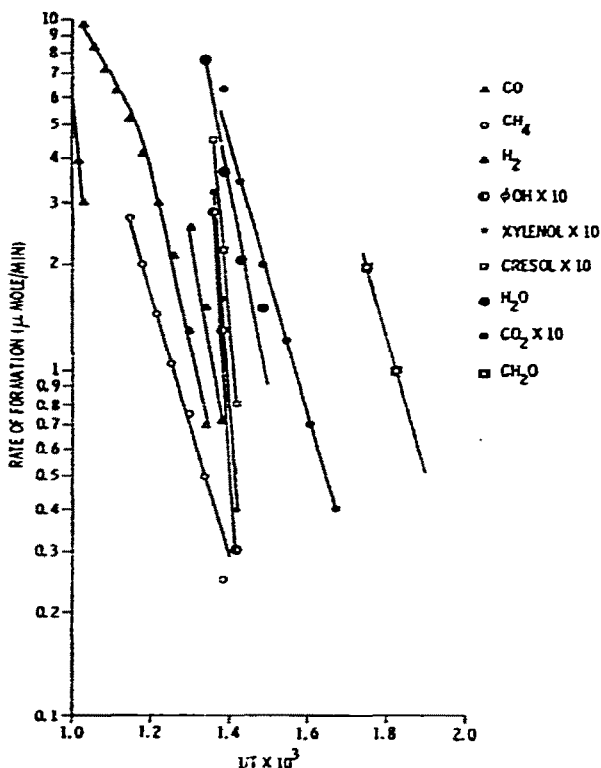


Fig. 7. Temperature dependence of formation rate of EGA-MS products from a phenol-formaldehyde polycondensate (reprinted by permission from Shulman and Lochte<sup>11</sup>).

from results at several temperatures. A similar isothermal kinetic treatment was demonstrated for polytetrafluoroethylene, where their results were in good agreement

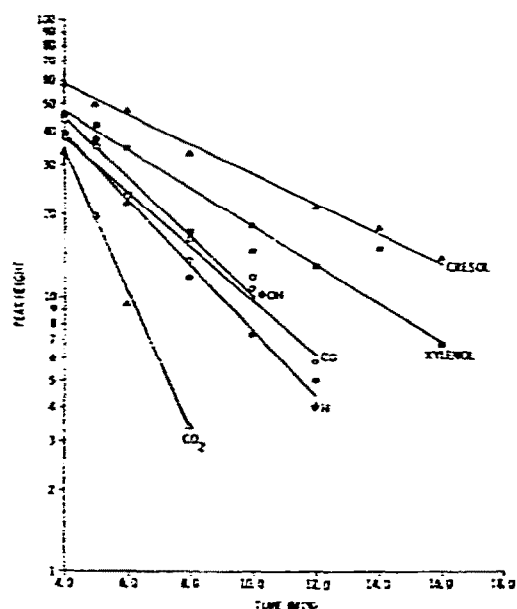


Fig. 8. Isothermal EGA-MS of a phenol-formaldehyde polycondensate at 405°C (reprinted by permission from Shulman and Lochte<sup>11</sup>).

with the literature. Using the results of EGA-MS, infrared spectrophotometry of heated films, pyrolysis-gas chromatography, and elemental analysis of residues from TG, the authors were able to offer a very comprehensive mechanism of thermal degradation of phenol-formaldehyde polycondensates. It is extremely tedious to carry out this type of experiment. First, the recorder output must be read, corrected for background, and plotted on graphs as a function of temperature. Even mass assignments may be tedious, depending on the use of standards, and instrument resolution. The graphs must then be compared to each other, and with reference standards in order to make reasonable qualitative choices. Instrument sensitivity must also be related to daily runs to the calibration standards library in order to put both on the same basis. Only then can quantitative evaluations be made.

Shulman and Lochte carried out similar studies for poly-2,2'-(*m*-phenylene)-5,5'-bibenzimidazole<sup>12</sup>. This was another extremely comprehensive study. Shulman<sup>13</sup> developed an open cell pyrolysis system similar to that of Langer and Gohlke (Figs. 1. and 2), but was to heat it at rates up to 1200°/min. A sketch of that system is shown in Fig. 9. Some results on a silicone polymer were also reported in that reference.

Austin *et al.*<sup>14</sup> recently carried out study of gases desorbed from graphite and from rutile using programmed heating and an Associated Electrical Industries (AEI) Model MS10 Mass Spectrometer, a magnetic instrument. These authors allowed evolved gases from the pyrolysis chamber to expand into a larger volume before sampling with the mass spectrometer. Results of EGA-MS were compared with those from TG.

Conventional systems have been used to study reactions, *e.g.*, Gray *et al.*<sup>15</sup> studied the reaction of diphenyl isophthalate and 2,2',3,3'-tetraaminobiphenyl to form



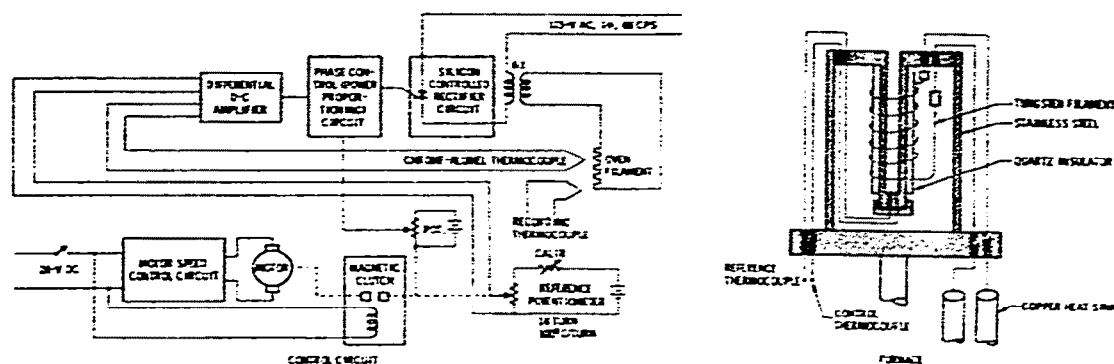


Fig. 9. Schematic of EGA-MS system for heating rates to 1200°/min. Near electron beam of time-of-flight mass spectrometer (reprinted by permission from Shulman<sup>13</sup>).

poly-2,2'-(*m*-phenylene)-5,5'-bibenzimidazole. The evolution of phenol and water as shown in Fig. 10 gave valuable insight on the mechanism of polymerization.

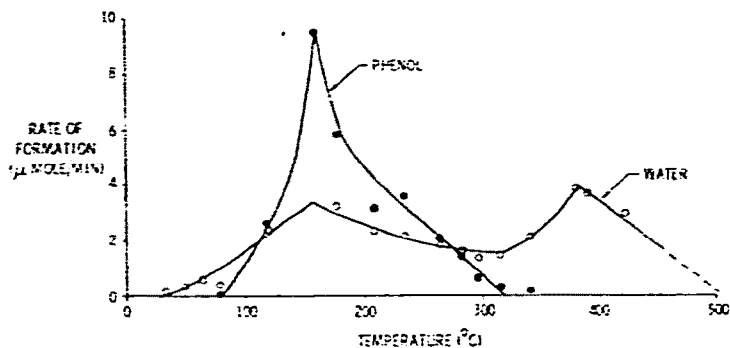


Fig. 10. EGA-MS of reaction products from diphenyl isophthalate-tetraaminobiphenyl mixture (reprinted by permission from Gray, Shulman, and Conley<sup>15</sup>).

Very recently high resolution mass spectrometers have been used in EGA-MS systems<sup>16, 17</sup>. The high resolution mass spectrometer has the advantages of being able to provide the exact atomic composition of the ionic fragment, and to differentiate between two or more molecules of extremely close atomic masses. For example, CO, N<sub>2</sub>, and C<sub>2</sub>H<sub>4</sub> have masses of 27.9949, 28.0061, and 28.0313, respectively. These are readily separated with a high resolution mass spectrometer. Goshgarian<sup>16</sup> used a Consolidated Electrodynamics Corp. (CEC) Model 21-110 double focussing mass spectrometer to study the thermal decomposition of hydroxylamine and methoxyamine perchlorates. Gaulin *et al.*<sup>17</sup> used a similar mass spectrometer, but coupled it with a DTA system. Their work will be described in the following section.

#### Simultaneous measurements including EGA-MS

The earliest simultaneous measurements combining EGA-MS with other thermoanalytical methods were reported by Langer *et al.*<sup>18</sup>, and by Wendlandt and Southern<sup>19</sup>, the former combining it with DTA and the latter with EGA by thermal

conductivity. Later workers added TG and several have combined three methods. Coupling of different systems may give more information than one can obtain from a single measurement, *e.g.*, DTA is sensitive to physical and chemical changes where no weight is lost, in contrast to TG and the various EGA methods.

(I) *EGA + EGA-MS*

Wendlandt and Southern<sup>19</sup> used the Associated Electrical Industries Model MS-10 Mass Spectrometer, a magnetic instrument, for their system, which is shown in Fig. 11. The EGA system comprises a programmable pyrolysis tube followed by a

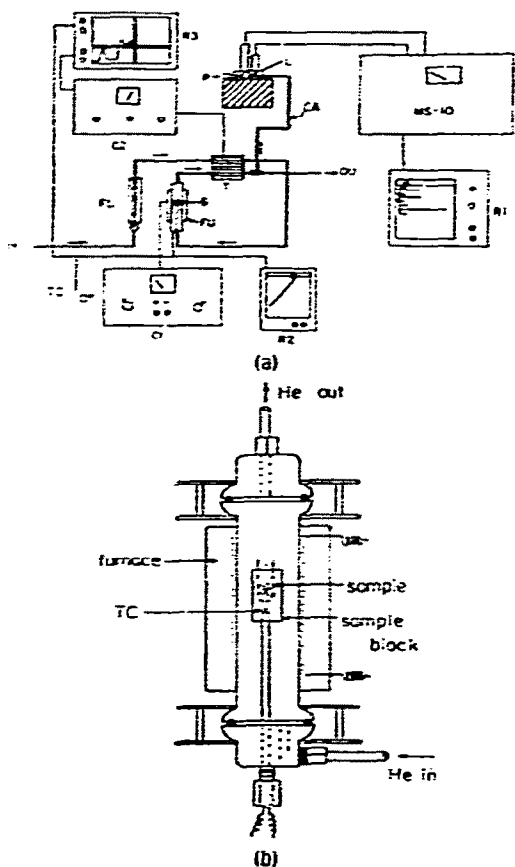


Fig. 11. (a) Schematic diagram of apparatus for simultaneous determination of EGA by thermal conductivity and EGA-MS; (b) schematic of the pyrolysis chamber (reprinted by permission from Wendlandt and Southern<sup>19</sup>).

thermoconductivity cell. Helium or another carrier gas transports the sample through the detector, and then to the mass spectrometer inlet. Only a small portion of the total gases enter the mass spectrometer, as regulated by differential pumping and a capillary tube. The mass spectrometer was able to sweep the mass range of 12 to 45 or 18 to 100 in 3.5 min, slow by T-O-F standards, but fast enough to handle certain situations. Newer versions of this instrument and many other types of mass spectro-

meters provide much faster scanning than in the past, especially those designed to handle gas chromatograph effluents. The EGA and EGA-MS curves for decomposition of  $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$  are shown in Fig. 12. The authors postulated the following mechanism:

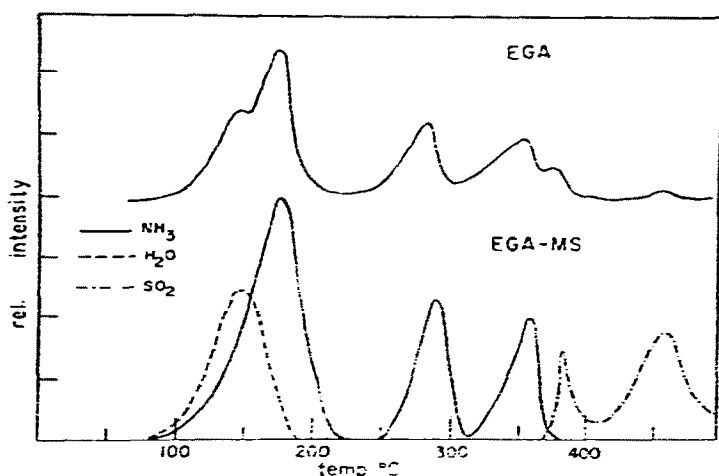
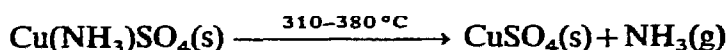
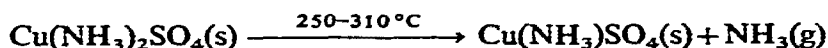
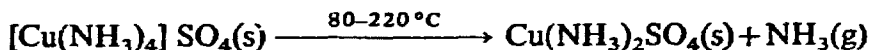
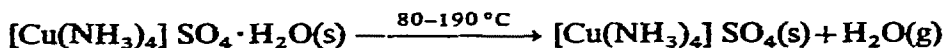


Fig. 12. EGA and EGA-MS curves from  $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$ ; 80-mg sample heated at  $6^\circ/\text{min}$  in helium at flow rate of 50 ml/min (reprinted by permission from Wendlandt and Southern<sup>19</sup>).

All stages of gas evolution showed up by both methods. The superiority of EGA-MS in resolving the different products is obvious.

Gohlke and Langer<sup>20</sup> employed their conventional system<sup>7</sup> to investigate the decomposition of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{Cu}(\text{NH}_3)_4 \text{SO}_4 \cdot \text{H}_2\text{O}$ . From these experiments and mass spectrometry of fuming sulfuric acid, they concluded that the last step of Wendlandt and Southern's mechanism was not justified, and that  $\text{SO}_3$  may be a primary product from decomposition of  $\text{CuSO}_4$ , rather than  $\text{SO}_2$ . They demonstrated that under Wendlandt and Southern's experimental conditions it would be difficult to differentiate between  $\text{SO}_2$  and  $\text{SO}_3$ . Further arguments were presented in Ref. 8. Thus it may be seen that EGA-MS may not necessarily be a panacea for all gas analysis, as confusions may result. Other methods have had to be used to clarify information in several cases.

## (2) DTA + EGA-MS

Langer *et al.*<sup>18</sup> replaced the furnace used by Langer and Gohlke (Figs. 1 and 2) with a modified DuPont DTA cell (Fig. 13), and obtained simultaneous DTA and gas analysis thermograms. The valve shown in Fig. 14 was developed by Langer and Gohlke<sup>20a</sup> and was used to reduce gas pressure entering the mass spectrometer. This system was used to study the thermal decomposition of triphenyltin hydroxide<sup>18</sup> and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . Langer and coworkers<sup>20a, 21</sup> used essentially the same system with

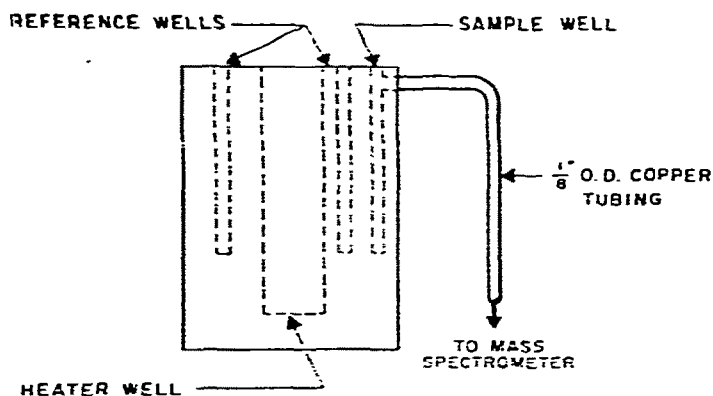


Fig. 13. Modified DuPont DTA cell for simultaneous DTA and EGA-MS (reprinted by permission from Langer, Gohlke, and Smith<sup>18</sup>).

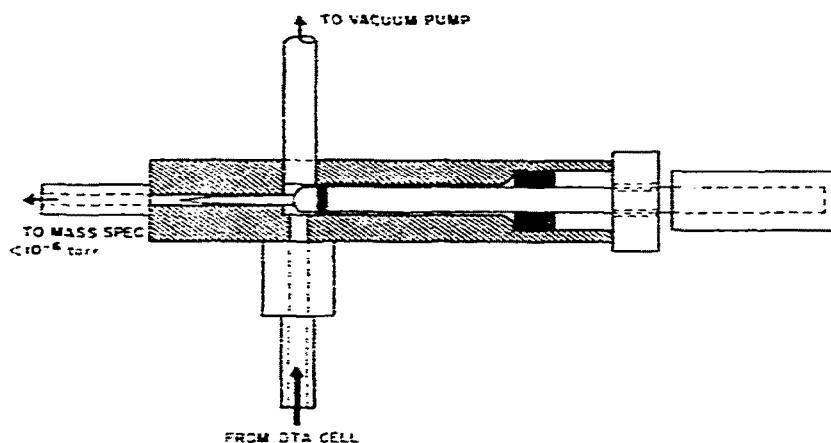
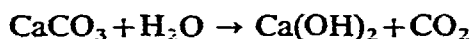


Fig. 14. Sampling valve for simultaneous DTA and EGA-MS system (reprinted by permission from Langer and Gohlke<sup>20a</sup>).

automatic data processing to study decomposition of many compounds and some gas-solid reactions. An example of a gas-solid reaction studied by Langer and Gohlke<sup>20a</sup> is the thermal decomposition of  $\text{CaCO}_3$  in inert and  $\text{H}_2\text{O}$  atmospheres. Their EGA-MS results are shown in Fig. 15. Note that dry  $\text{CaCO}_3$  does not begin to decarboxylate until  $450^\circ\text{C}$ , while decarboxylation starts at about  $200^\circ\text{C}$  in a water atmosphere, as shown by masses 18 and 44, due to the reaction



The data processing system used by Langer and coworkers will be described below. Langer and Brady<sup>22</sup> added an internal DTA cell for high vacuum operation and demonstrated its use for cyclopentadienyl nickel chloride-triphenyl phosphine complex. They also used the earlier system<sup>21</sup> for trivinyltin hydroxide. Redfern *et al.*<sup>23</sup> recently coupled a Stanton Model 671 compact differential thermal analyzer with an AEI Model MS-10 mass spectrometer and applied them to inorganic hydrates and organic materials. Spectra were recorded by scanning accelerating voltage or by monitoring selected peaks.

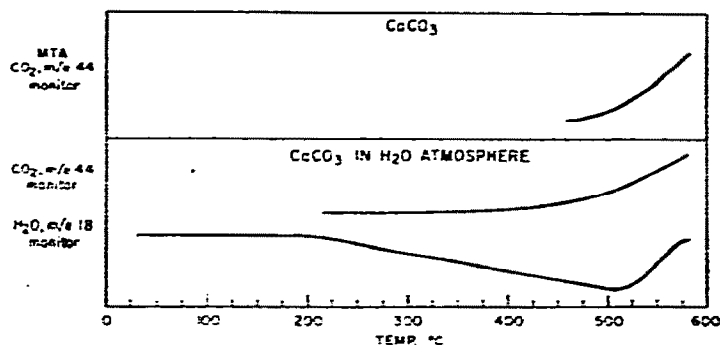


Fig. 15. EGA-MS from  $\text{CaCO}_3$  in inert and  $\text{H}_2\text{O}$  atmospheres (reprinted by permission from Langer and Gohlke<sup>20a</sup>).

Gaulin *et al.*<sup>17</sup> used high vacuum DTA based on the  $1200^\circ\text{C}$  DuPont DTA cell as shown in Fig. 16. The effluent was coupled with a CEC Model 21-110B high resolution mass spectrometer through the molecular beam former shown in Fig. 17. Although the instrument was capable of resolving 1: 39,000 AMU at  $m/e$  142, 1: 3000

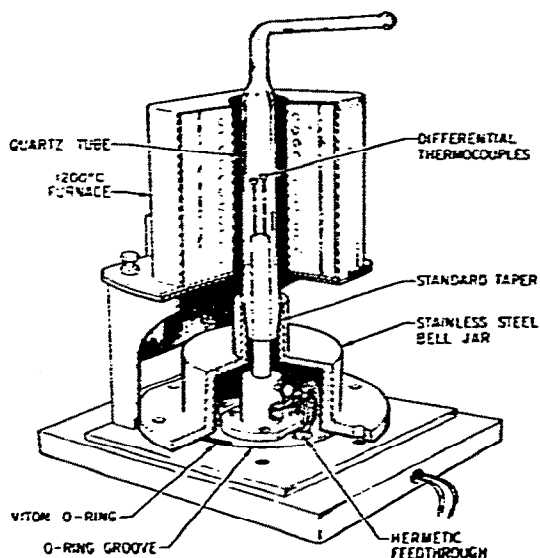


Fig. 16. Modified DuPont DTA cell for high vacuum EGA-MS by high resolution mass spectrometry (reprinted by permission from Gaulin, Wachi, and Johnston<sup>17</sup>).

was sufficient for the reported studies. Two modes of recording were used. The mass range 12–200 AMU could be scanned in 3 min by varying magnetic field (a slow process due to hysteresis), or a single peak could be monitored. These authors studied the thermal decomposition of polystyrene and a polyimide.

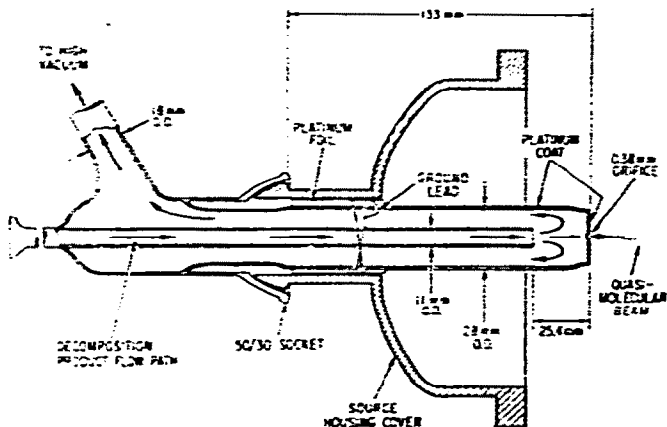


Fig. 17. Quasi-molecular beam former for DTA-high resolution EGA-MS system (reprinted by permission from Gaulin, Wachi, and Johnston<sup>17</sup>).

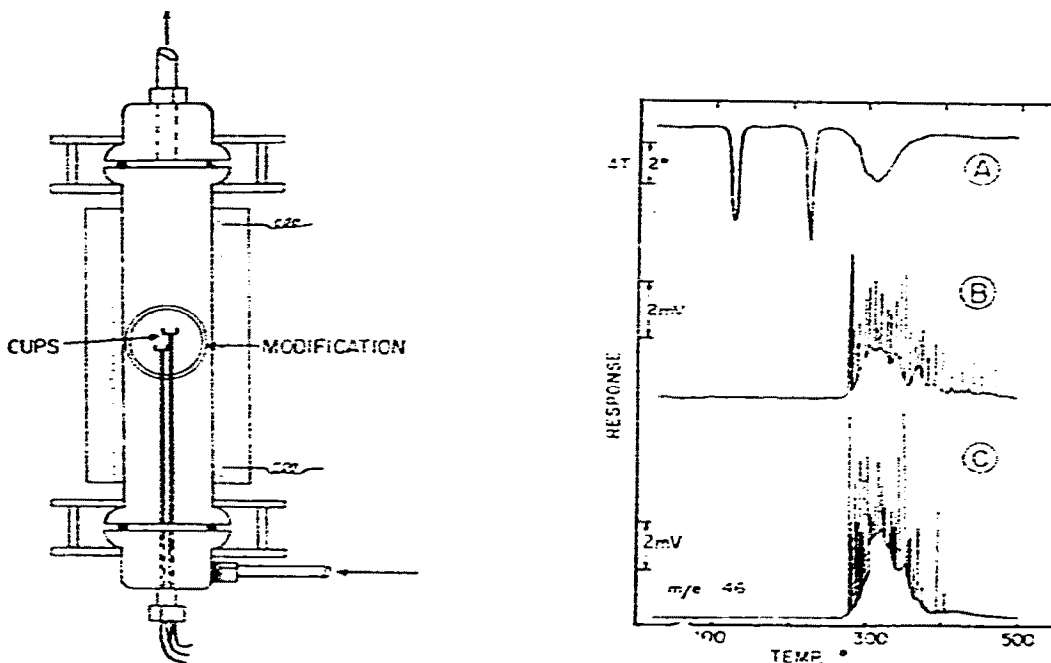
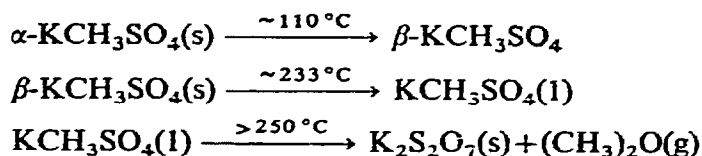


Fig. 18. Pyrolysis chamber for simultaneous EGA, DTA, EGA-MS system (reprinted by permission from Wendlandt, Southern, and Williams<sup>24</sup>).

Fig. 19. Results of (A) DTA; (B) EGA by thermal conductivity; (C) EGA-MS of  $KCH_3SO_4$  in a helium atmosphere (reprinted by permission from Wendlandt, Southern, and Williams<sup>24</sup>).

## (3) DTA + EGA + EGA-MS

Wendlandt *et al.*<sup>24</sup> modified the system of Wendlandt and Southern<sup>19</sup> by incorporating a DTA system for pyrolysis. The pyrolysis chamber is shown in Fig. 18, and results for potassium methyl sulfate are shown in Fig. 19. The results were explained by the following transitions:



Note that all three transitions were detected by DTA, while only the last one was observed by the EGA methods. EGA-MS, however, was able to identify the gaseous product as  $(\text{CH}_3)_2\text{O}$ .

## (4) TG + EGA-MS

The direct combination of a thermobalance and EGA-MS was first reported by Zitomer<sup>25</sup>, who coupled a DuPont Thermobalance with a Bendix Model 12 Time-of-Flight Mass Spectrometer or a CEC Model 21-104 Magnetic Mass Spectrometer. Gaseous atmospheres are used, and a diaphragm valve controls the quantity of gas reaching the mass spectrometer. Background mass spectra are recorded and the thermobalance is activated. Mass spectra are scanned periodically during heating, especially after weight loss is indicated by the thermobalance. The Bendix mass spectrometer is able to sweep  $m/e$  12,300 in approximately 5 sec, while the CEC instrument sweeps an octave in 3-1/3 sec. Sweep activation tends to be somewhat irregular. Zitomer studied thermal decomposition of polymethylene sulfide and maleic hydrazide-methyl vinyl ether copolymer. More recently, Haddon *et al.*<sup>26</sup> reported on the use of the same system with other polymers, including aliphatic polyamides, polybenzimidazoles, and the oxidation of polystyrene.

Wilson and Hamaker<sup>27</sup> developed a system based on an ultra-high vacuum, semimicro, automatic recording balance coupled to a Varian Quadrupole Residual Gas Analyzer (mass range 1-250 AMU), as shown in Fig. 20. They used quartz lamp heaters at a rate of  $1^\circ/\text{min}$  to  $435^\circ\text{C}$ . The mass range 5-120 AMU was scanned at a rate of 2 sec/AMU. Studies were made of polymethylmethacrylate, polyoxymethylene, polystyrene, polyvinylchloride, and a mixture of polymethylmethacrylate and polyvinylchloride. Results for polymethylmethacrylate are shown in Fig. 21. There is obviously reasonable agreement between the derivative TG curve and the ion current curve for  $m/e$  41 ( $\text{C}_2\text{H}_5^+$ ), the principal fragment of methylmethacrylate monomer. The formation of pure monomer from thermal degradation of this polymer is well established. Kinetic analysis was carried out using the assumption that the signal at any time is proportional to the rate of formation of the product, and that the remaining area under the curve is proportional to the quantity of reactant remaining at that time. These assumptions were used earlier by several workers, including Friedman<sup>9a</sup> and Shulman and Lochte<sup>27a</sup>. The area under the total curve was assumed to be

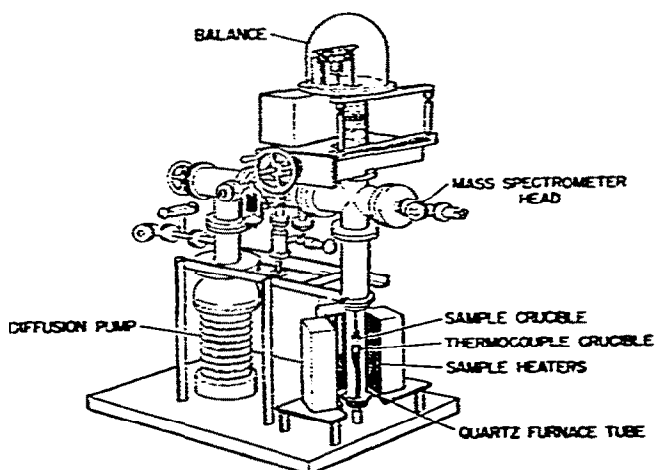


Fig. 20. Apparatus for simultaneous TG and EGA-MS (reprinted by permission from Wilson and Hamaker<sup>27</sup>).

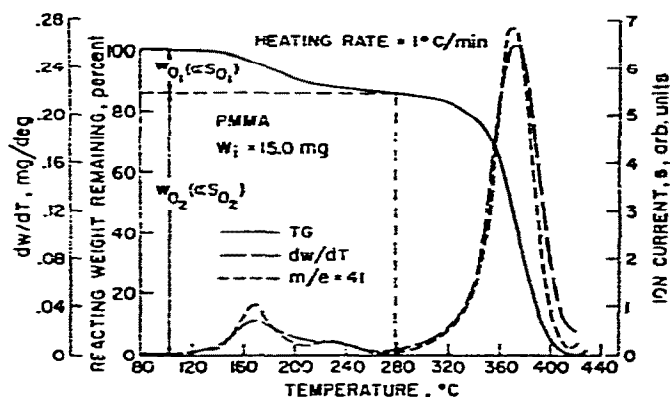


Fig. 21. Results of simultaneous TG and EGA-MS for polymethylmethacrylate (reprinted by permission from Wilson and Hamaker<sup>27</sup>).

proportional to initial quantity of reactant. Activation energies obtained by use of well known methods yielded answers in reasonable agreement with literature values. For a review of applicable kinetic treatments see Ref. 4, which also lists other reviews.

Vaughan<sup>28</sup> also described the combination of a mass spectrometer and a vacuum TG system applied to inorganic and organic reaction systems.

While TG weight losses are not as informative as EGA-MS results, it is important to determine sample weight at the various stages of decomposition, including the start of the experiment and final residue weights. Such weights may be used to check if the qualitative and quantitative analyses obtained from EGA-MS are reasonable, and serve as an aid to kinetic analysis.

##### (5) DTA + TG + EGA-MS

Three papers have recently appeared where the three methods, DTA, TG, and EGA-MS were combined in a single system. Smith and Johnson<sup>29</sup> used the thin pan



sample holder shown in Fig. 22. The holder was attached to a Cahn Model RA Electrobalance enclosed in a bell jar. Temperature signals were obtained from junctions at the center of the balance beam. A Deltatherm system was used for recording DTA and TG signals, and the derivative of either one, and for controlling heating rate.

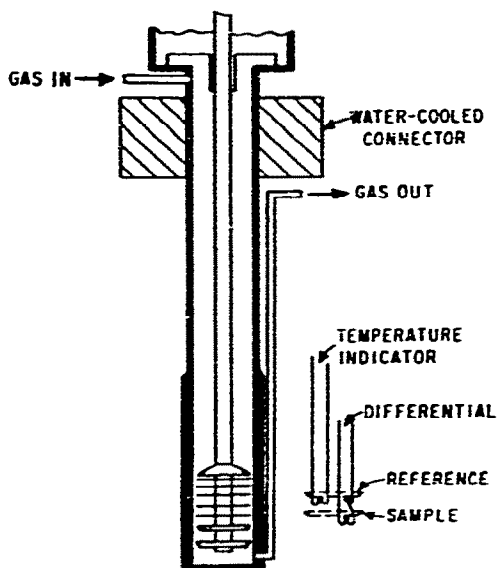


Fig. 22. Sample holder for simultaneous DTA, TG, and EGA-MS (reprinted by permission from Smith and Johnson<sup>29</sup>).

A Cahn Model Mark II Derivative Computer obtained a derivative TG for separate recording. The mass spectrometer was a Quad Model 150 Residual Gas Analyzer. The mass range of 1–150 a.m.u. could be swept from 130 msec to 10 min. It is also possible to monitor single peaks. The carrier gas is maintained at 1 atm pressure, but is reduced by a Granville-Phillips Automatic Pressure Controller before entering the mass spectrometer. The controller regulated by a signal from a Bayard Alpert ionization gauge at the low pressure side to within  $1 \times 10^{-7}$  torr. This system was designed for natural fuels, but was tested with nahcolite and clay.

Wiedemann<sup>30</sup> described a system based on the Mettler Thermoanalyzer and a Balzers Quadrupole Mass Spectrometer. A sketch of the system is shown in Fig. 23. The usual way of operating is in vacuum, but gaseous atmospheres may be used with the usual reduction of pressure to the mass spectrometer. The sketch does not show a DTA sample system at R, but such an accessory is available. The system A, B, C is for admission of calibration gases under operating conditions, and M, N, P is for venting after a test. The mass range of the instrument is 1–100 and 10–400 a.m.u. The scan rate for an oscilloscope is 1 msec/a.m.u. or slower. Single mass peaks may be monitored. In a sense, the ionization gauge, S, acts as a pressure sensor, and adds EGA capability to the other three measurements. Wiedemann studied thermodecomposition of  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  and  $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ . Fig. 24 shows the influence of packing on diffusion of water from 7 mg samples of 150 mesh  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  heated at  $10^\circ/\text{min}$ .

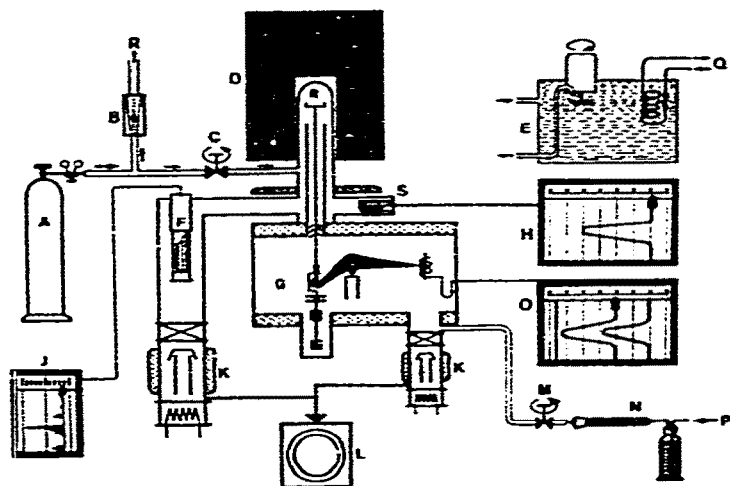


Fig. 23. System for simultaneous DTA (sample holder not shown), TG, and EGA-MS (reprinted by permission from Wiedemann<sup>30</sup>).

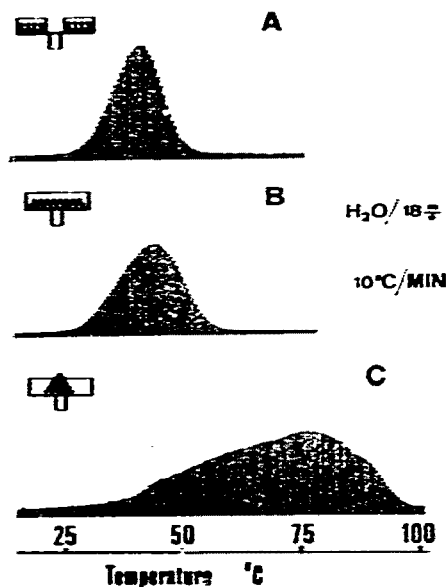


Fig. 24. Influence of sample packing on evolution of  $\text{H}_2\text{O}$  from 7-mg samples of  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  heated at  $10^\circ/\text{min}$  (reprinted by permission from Wiedemann<sup>30</sup>).

Müller-Vonmoos and Bach<sup>31</sup> used the same type of system to study an oil shale containing Dawsonite. A 30-mg sample was pyrolyzed at  $6^\circ/\text{min}$ . The range  $m/e$  1–50 was scanned in 50 sec. Some of the results of this complicated reaction are shown in Fig. 25.

#### Filament heating

Filament heating systems have mainly been used for pyrolysis-gas chromatography studies, but have been applied to EGA-MS in several laboratories. These studies

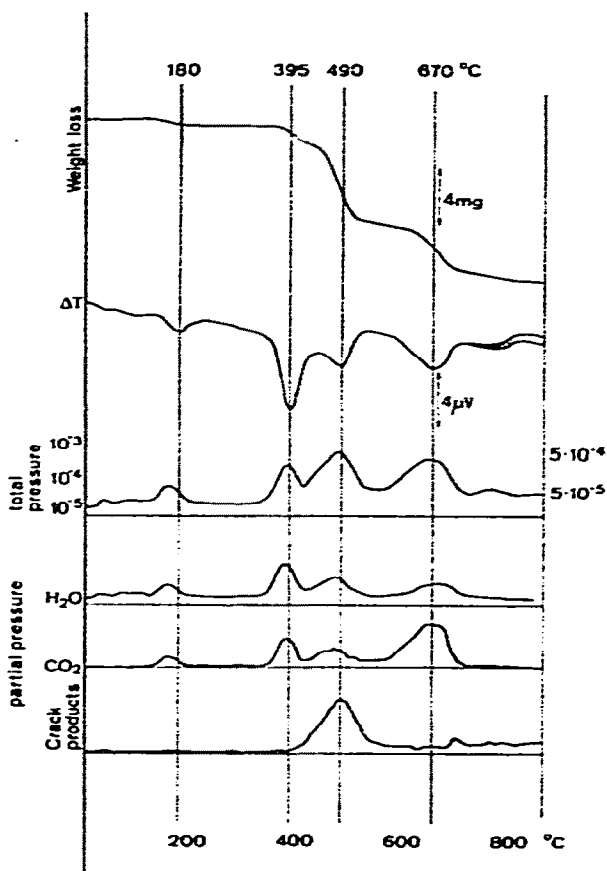


Fig. 25. Results of simultaneous DTA, TG, and EGA-MS of 30-mg sample of extracted shale heated *in vacuo* at 6°/min (reprinted by permission from Müller-Vonmoos and Bach<sup>31</sup>).

generally utilize very fast heating, thus requiring some special components. Friedman *et al.*<sup>32</sup> electrically heated polymeric samples that are deposited in a groove that is machined in a graphite rod of 0.030 in (diameter), in the apparatus shown in Fig. 26. The electrodes are spring-loaded and water-cooled. The assembly is attached to a modified Bendix Model 12-101 Time-of-Flight Mass Spectrometer so that the groove is in line with a slit that leads to the electron beam, in a fashion similar to the Knudsen cell arrangement of Shulman<sup>10</sup>. Differential pumping is used to reduce gas pressure. Sample temperature is measured with a thermocouple in contact with the sample. Temperature signals are recorded with an oscillograph together with scanned mass spectra. The electrometer of the Bendix Analog Output unit is replaced with a high speed recording picoammeter. Typical scan rates are  $m/e$  1–200 in 0.2 sec. An example of an oscillograph scan is shown in Fig. 27. Very stable D.C. power supplies are used for heating. Experiments are carried out in two ways. One is partly controlled rapid linear heating rate studies, where rates up to about 1000°/sec have been achieved. The other is isothermal heating, where sample temperature is elevated to a constant value as rapidly as possible; usually a few seconds. Some of the results of pyrolyzing

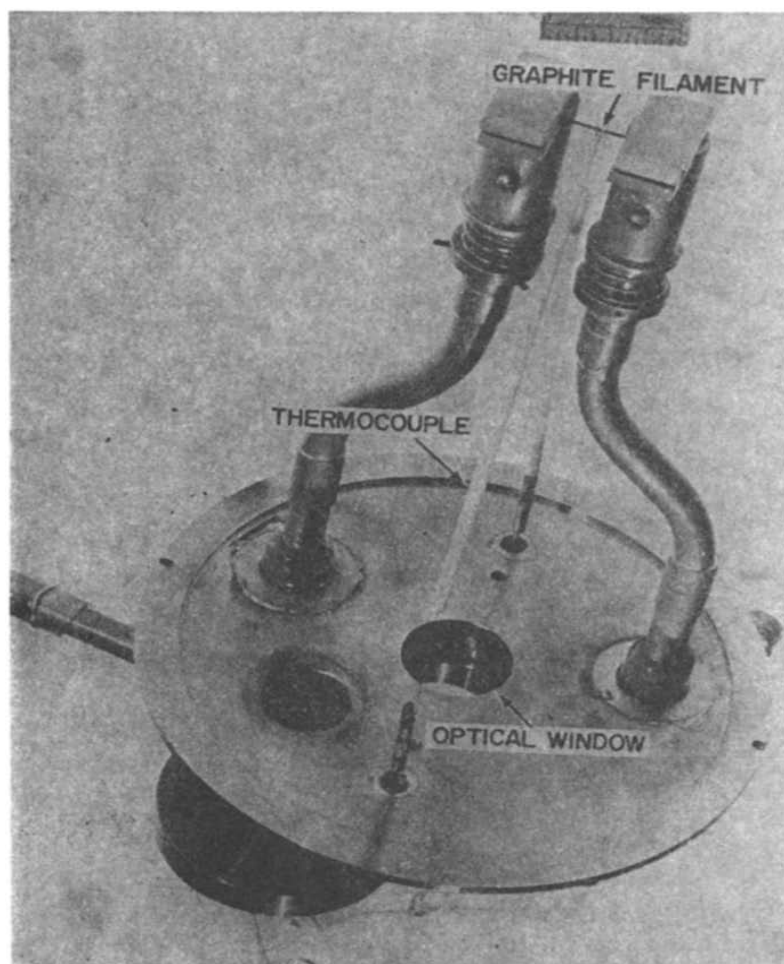


Fig. 26. Filament heater assembly for EGA-MS<sup>33a</sup>.

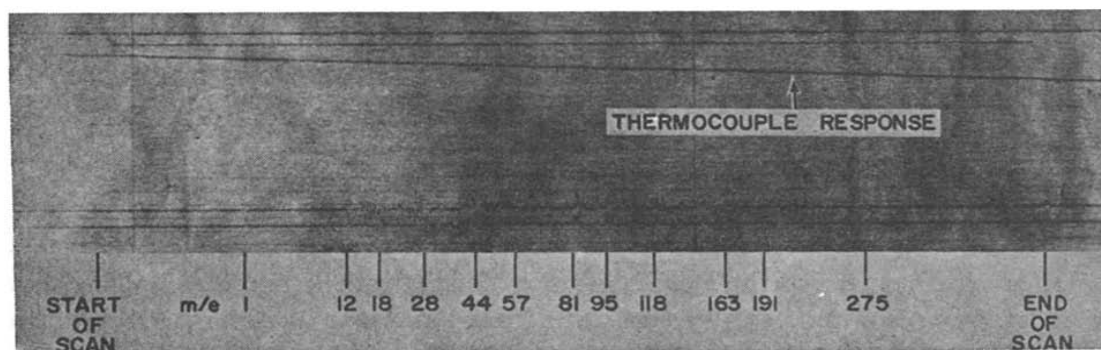


Fig. 27. Representative oscillograph scan for filament heater EGA-MS polymer pyrolysis<sup>33a</sup>.

a phenol-formaldehyde sample at a rate of 930°/sec are shown in Figs. 28 and 29. The products were much the same as observed for this polymer by other methods.

Goldstein has used this method to study a polyimide, poly-2,2'-(*m*-phenylene)-5,5'-bibenzimidazole, and polymethyl siloxanes<sup>33a</sup> and several other polymers<sup>33b</sup>. In the latter study, filament heating was compared with Knudsen cell pyrolysis of similar polymers. The results showed that polymer heterogeneity could be as serious as changes in heating method for the polymers tested, and could make results difficult to interpret.

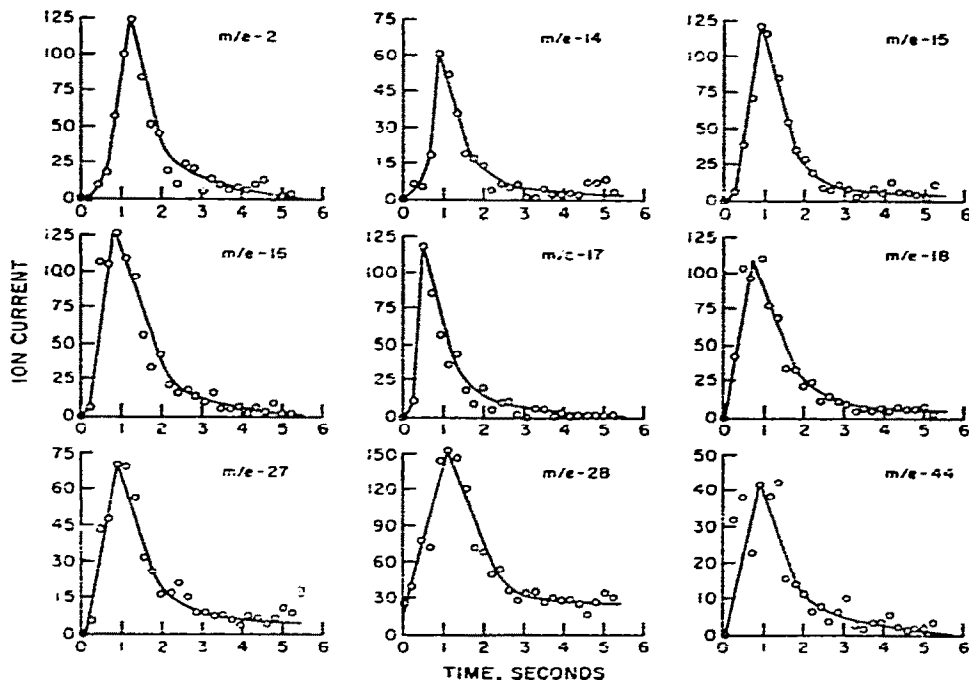


Fig. 28. Representative EGA-MS results from filament heating of phenol-formaldehyde at 930°/sec. Part 1<sup>32</sup>).

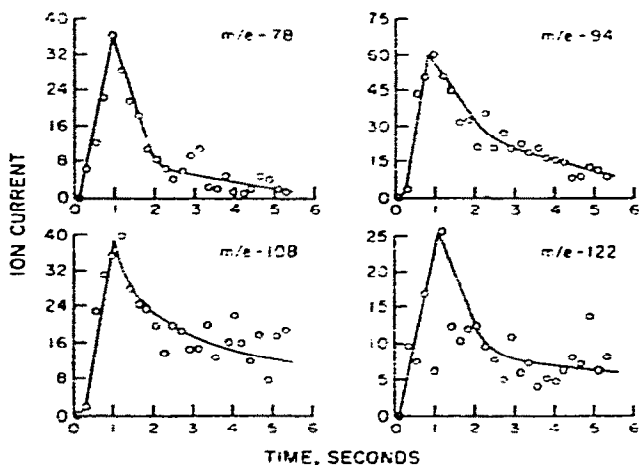


Fig. 29. Representative EGA-MS results from filament heating of phenol-formaldehyde at 930°/sec. Part 2<sup>32</sup>).

A very recent filament heating study of solid rocket propellants was carried out by Stapleton<sup>34</sup>. The system uses a Bendix Time-of-Flight Mass Spectrometer equipped with a Bendix Filament Heater System. Samples weighing 5–20  $\mu\text{g}$  are coated on a resistive platinum ribbon which is located 2 mm from the ionizing electron beam. Battery and capacitor discharges are used for slow and fast heating rates, respectively. The ribbon forms one arm of a Wheatstone bridge for the purpose of measuring filament temperature. For slow heating rates, the mass spectra are displayed on an oscilloscope face and are recorded cinematographically at a rate of 200 frames/sec. For fast heating rates, the mass spectra are recorded photographically utilizing z-axis modulation of the oscilloscope delay. The z-axis modulation method was developed by Lincoln<sup>35</sup>. An example is shown for flash pyrolysis of glycolaldehyde in Fig. 30. Mass number is displayed as the  $x$ -value, and the  $y$ -value is time. The

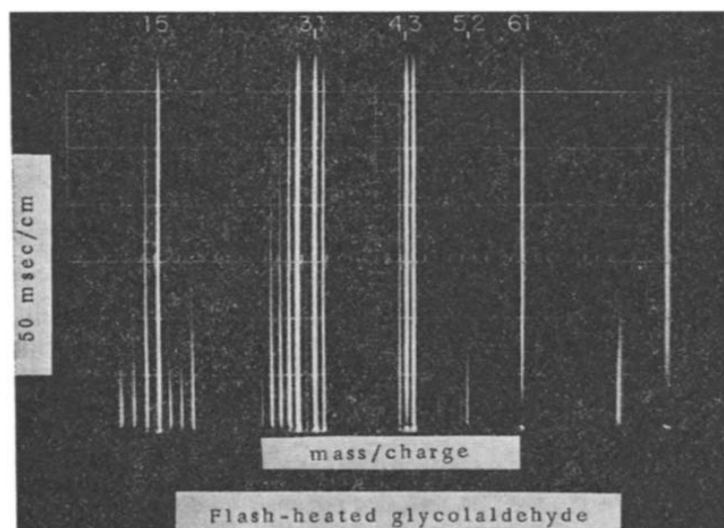


Fig. 30. Time-resolved raster oscilloscope display of mass spectra from flash-heated glycolaldehyde (reprinted by permission from Lincoln<sup>35</sup>).

$x$ -axis represents the time of the flash. The flash triggers a series of sweeps, each being above the preceding one. Whenever an ionic pulse occurs, a spot on the oscilloscope face. The greater the ionic signal, the brighter the spot, as regulated by z-axis modulation. Thus one obtains a series of vertical lines of varying brightness, and appearing at various times. Semi-quantitative evaluation may be obtained with a densitometer.

A number of mass spectrometric studies have been carried out in connection with flash lamp discharges and laser heating, but these will not be discussed here. They are reviewed in Ref. 4.

#### *Automatic data processing*

If mass spectral peaks appear for many ionic masses, and if one scans many times, a formidable number of data points are generated. In addition, one needs to relate the points to time and temperature, and to account for background and

instrument sensitivity. Lastly, one would desire to compare the spectra with a library of calibration compounds to accomplish a complete time-resolved qualitative and quantitative analysis. It would be delightful to be able to carry out all of these operations automatically, but this has not yet been accomplished. Two groups, however, have made some progress in these areas for time-of-flight mass spectrometers, as will be described below.

Friedman and coworkers<sup>9b-e, 32, 36-39</sup> have developed an on-line analog-to-digital converter for recording EGA-MS data on perforated paper tape. Other components of their systems were described in the section on conventional systems. The system is based on a very stable programmed power supply that steps the gate to preselected discrete ionic mass peak locations. Mass peak locations have also been rendered stable and adjustable by appropriate instrumental modifications. In actual operation, analog gate voltages (time delay following ionization) are determined for about 20 peak centers from  $m/e$  1 to about 203 for hydrogen and hexachloroethane, as monitored by a digital voltmeter. These are then analyzed by a least squares shared-time computer program using a polynomial equation that includes 5 constants. If all of the calculated points are within values equivalent to 10 nanosec of the observed time delay, the fit is accepted and a print-out is obtained for all analog gate voltages

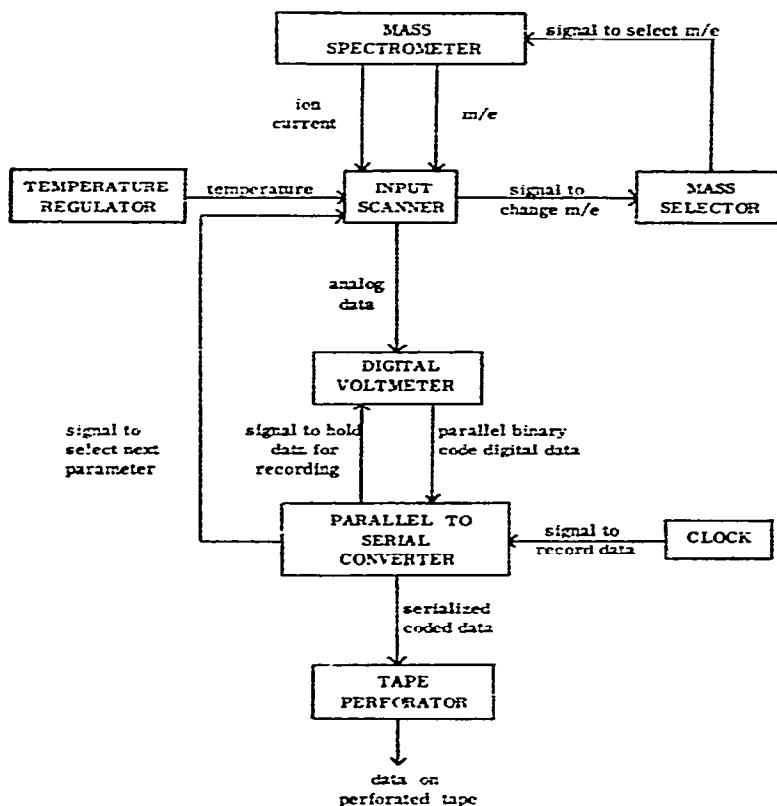


Fig. 31. Schematic of automatic data collecting system for EGA-MS (reprinted by permission from Friedman, Griffith, and Goldstein<sup>38</sup>).

as a function of mass number, by interpolation and extrapolation. Mass peaks get closer as the mass increases. Separation at  $m/e$  100 is about 130 nanosec. Peaks tend to range in duration from about 30 to 80 nanosec, depending on composition and signal intensity. Square wave gate pulses last for about 110 nanosec. The set of computed gate voltage values has been found to hold for many months, with minor adjustments, but first it is necessary to establish each discrete value on a very stable potentiometer, as monitored by the digital voltmeter. The three parameters, sample temperature, gate voltage, and ion intensity are recorded for each data point. They are selected, in turn, by a crossbar switch. The temperature originates from the thermocouple in the sample, and is generated from a retransmitting slidewire. The gate voltage originates in the programmed power supply, and ion intensity comes from the mass spectrometer. The system is synchronized by a pulse generator that acts as a clock. The digital voltmeter acts as the analog-to-digital converter. The serializer converts the data from binary code to paper tape code. The system currently scans 200 discrete masses in about 2 min, but is able to work more rapidly when everything is in best order. At a heating rate of  $10^\circ/\text{min}$ , it returns to each mass peak every  $20^\circ\text{C}$ . The mass range can be limited to give better time resolution. A flow chart of the automatic data-collecting system is shown in Fig. 31. The perforated paper tapes generated during a run are then cut appropriately for conversion to

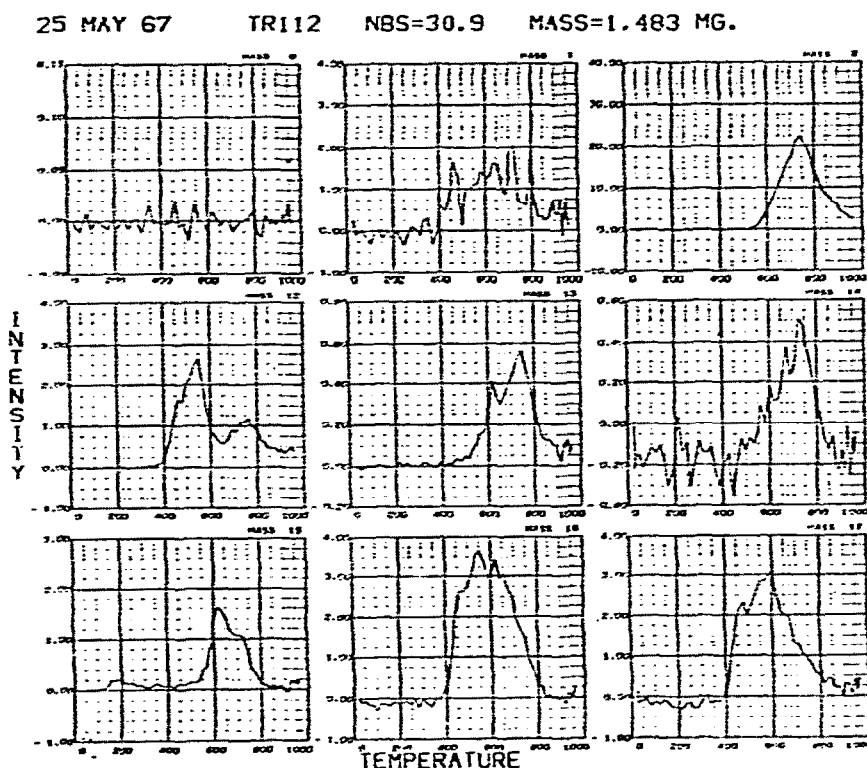


Fig. 32. Typical graphic output from automatic data processing of EGA-MS. Some results from pyrolysis of 1.483-mg sample of aromatic polyamide at  $10^\circ/\text{min}$  (reprinted by permission from Friedman, Griffith, and Goldstein<sup>38</sup>).



digital magnetic tape by a small computer equipped with an optical reader. A large computer sorts the data by mass number and then prepares a magnetic tape for the Stromberg-Carlson Model 4020 Automatic Graph Plotter. The plotted data are corrected for background, instrument sensitivity, editorial corrections, and are normalized to 1 mg initial sample weight. A typical graph plot for an aromatic polyamide is shown in Fig. 32. Eighteen products were observed for this polymer, as listed in Table II. A quantitative analysis computer program is in a partial state of development.

TABLE II

TENTATIVE QUALITATIVE ANALYSIS OF EGA-MS PRODUCTS FROM AN AROMATIC POLYAMIDE (REPRINTED BY PERMISSION FROM FRIEDMAN, GRIFFITH, AND GOLDSTEIN<sup>35</sup>).

Product	Mol. wt	Temperature, °C		
		Start	Peak	Finish
Dimethyl acetamide	87	50	190	500
Carbon dioxide <sup>a</sup>	44	340	460-510	650
Water <sup>a</sup>	18	350	460-550	800
Unidentified	120-122	400	~600	950
Phenylenediamines	108	400	575	950
Aniline <sup>a</sup>	93	400	575	950
Benzene <sup>a</sup>	78	400	580	725
Benzonitrile <sup>a</sup>	103	440	575	800
Phenyl isocyanate	119	450	540	650
Carbon monoxide <sup>a</sup>	28	~450	550	650
Cyanoanilines	118	470	~580	800
Acetylene	26	475	550	800
Dicyanobenzenes	128	490	650	960+
Diphenyl	154	500	650	960+
Ammonia <sup>a</sup>	17	~500	~600	900
Hydrogen cyanide <sup>a</sup>	27	490	750	950+
Hydrogen <sup>a</sup>	2	510	740	950+
Methane	16	<580	615	>650

<sup>a</sup>Present in sizeable quantities.

Friedman and coworkers<sup>32, 38</sup> have carried some pyrolytic studies on washed and lyophilized bacteria samples with the system described above. Although only limited work has been done, it is possible to discuss certain aspects of extension of EGA-MS to this application. In working with about six different specimens, few qualitative differences have been observed, *i.e.*, they produce very much the same products in the same temperature range. It is difficult to achieve reproducible results, probably because it is hard to eliminate nutrients completely. A further problem associated with reproducibility is that some products arise and decay so rapidly that more points are required for accurate evaluation, than may be handled by the present data processing system, as it is used. In only one case, *Sarcinea lutea* 272, a yellow pigmented bacterium, have distinctly characteristic peaks appeared. The results at *m/e* 44 (carbon dioxide) for this bacterium, *Escherichia coli* 1485 and *Serratia mar-*

*escens* 80K are shown in Fig. 33. *S. marcescens* would normally be red, but its pigment was washed out during preparation. Thus it appears that EGA-MS may be expected to have some success in differentiating between certain bacteria, but that sample preparation may well present some great difficulties.

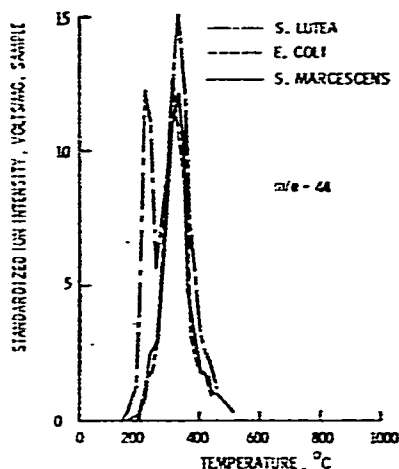


Fig. 33. EGA-MS results for three bacteria at  $m/e$  44. Samples of  $\sim 1$  mg. Heated at  $10^\circ/\text{min}$  (reprinted by permission from Friedman, Griffith, and Goldstein<sup>38</sup>).

Langer and coworkers<sup>20a,21,22,40</sup> have developed an automatic data processing system for their DTA + EGA-MS system described earlier. A sketch of this system is shown in Fig. 34. The mass spectrometer signal from the electron multiplier is fed into a sampling oscilloscope equipped with a display scanner which is swept by

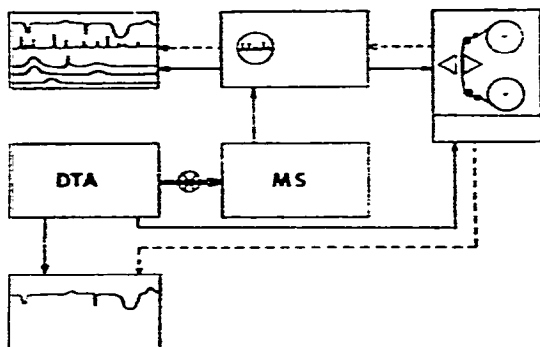


Fig. 34. Schematic of automatic data processing system for simultaneous DTA and EGA-MS (reprinted by permission from Langer and Brady<sup>22</sup>).

a wave form generator. These act as an external gate. The scanned mass range and rate of scan (3-10 scans/sec) are adjusted for the needs of the experiment, and the gated data are recorded on a multichannel magnetic analog tape recorder, together with the DTA signal and a timing pulse. The signal from the tape can be played back in many ways, but the most interesting is to feed it back into the oscilloscope with the gate adjusted to operate only for the time of appearance of a single ionic mass. This can be repeated a number of times for different masses, and a series of ion yield

curves may be recorded as a function of time (proportional to temperature) on a single X-ray recorder tracing. Some of their results for  $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$  are shown in Fig. 35. These should be compared to the results obtained by Wendlandt and

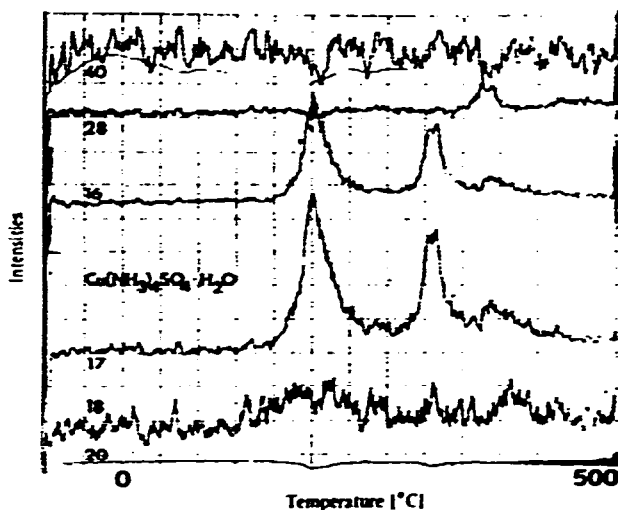


Fig. 35. Selected EGA-MS results from automatic data processing of  $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$  pyrolysis as obtained by use of simultaneous DTA and EGA-MS (reprinted by permission from Langer and Brady<sup>22</sup>).

Southern<sup>19</sup>, as shown in Fig. 12, and discussed in the section on EGA + EGA-MS. Langer and Brady<sup>22</sup> agreed that 1 mole of  $\text{H}_2\text{O}$  was evolved first, followed almost concurrently by 2 moles of  $\text{NH}_3$ . They also agreed that 1 mole of  $\text{NH}_3$  was given off in the next reaction stage. They felt that a complicated redox reaction occurred in the next stage, with formation of  $\text{SO}_2$ ,  $\text{N}_2$ , and  $\text{H}_2\text{O}$ .  $\text{Cu}_2\text{O}$  was thought to be the residue. This was quite a drastic difference from the conclusions of the earlier workers. The signals at  $m/e$  20 and 40 are for argon carrier gas. Note the small negative signals at  $m/e$  20 concurrent with evolution of major products. This was attributed to electron depletion, and would influence quantitative evaluation of results. No important ions from  $\text{SO}_2$  were shown in Fig. 33.

It is possible to accomplish much more in data processing than has already been done. It seems reasonable to expect that it would be beneficial to combine EGA-MS with a small computer for much greater accuracy and efficiency. While the data processing systems described above were for time-of-flight mass spectrometers, it seems that the concepts could well apply for other mass spectrometers. Stepped scanning would probably work better for quadrupole or monopole mass spectrometers than for most time-of-flight or magnetic units, because the polar mass spectrometers achieve linear mass separation. The latter two types tend to have parabolic separation, with resolution falling at the higher masses.

## CONCLUSIONS

Mass spectrometric thermal analysis has been applied to a number of problems

with great success. Its current popularity is attested to by the fact that eight papers using such methods were presented at both the Second International Conference on Thermal Analysis (August 1968), and the 17th Annual Conference on Mass Spectrometry and Allied Topics (May 1969). It has been possible to determine gaseous product evolution at various stages of decomposition for polymeric, inorganic, organic, metallo-organic, and natural products. Evaluation of the results, comparing them with results from other measurements, and kinetic analysis have allowed improved understanding of mechanisms of thermal degradation. Simultaneous measurements, which incorporate various combinations of evolved gas analysis, differential thermal analysis, and thermogravimetry have also been very helpful. The method has been useful for detecting impurities, differentiating between vaporization of solvents and decomposition products, in observing condensation products in polymerization reactions, and in observing products of other reactions such as solid-gas reactions and desorption studies. Various types of heating have been used, as well as many types of mass spectrometers, and methods of recording.

In selecting or designing a system, it is important to keep in mind what information is desired. In choosing the mass spectrometer it is important to consider mass range, resolution, sensitivity, scanning rate, and structure of the inlet system. If gaseous atmospheres are important, or if excessive quantities of gas are generated, then one must have a way to remove the excess and yet obtain a representative sample. If a transient product is important, then heating should occur close to the electron beam of the mass spectrometer. Otherwise, remote heating may suffice. Close heating is probably better than remote heating for kinetic studies. The recording system is dependent on the speed of data acquisition. Automatic data processing systems should be considered for acquisition and evaluation of large quantities of data.

It is often valuable to examine the various ionic spectra in order to make qualitative identification using fragmentation patterns from calibration compounds. It is also possible to obtain exact qualitative information using high resolution mass spectrometers. Once qualitative analysis is established, it could be useful to simplify (or even eliminate) fragmentation. Various methods are possible, such as photoionization, chemical ionization, field ionization, or the use of low energy electrons. Smith and Johnson<sup>29</sup> mentioned the last method, in connection with their studies.

#### REFERENCES

- 1 W. W. WENDLANDT, *Thermal Methods of Analysis*, Interscience, N. Y., 1964.
- 2 P. D. GARN, *Thermoanalytical Methods of Investigation*, Academic Press, N. Y., 1965.
- 3 W. LODDING (Ed.), *Gas Effluent Analysis*, Marcel Dekker, N. Y., 1967.
- 4 H. L. FRIEDMAN, in I. M. KOLTHOFF, P. J. ELVING, AND F. H. STROSS (Eds.), *Treatise on Analytical Chemistry*, Interscience, N. Y., Part III, Chap. 26, to be published.
- 5 P. C. MACKENZIE, in R. F. SCHWENKER, JR., AND P. D. GARN (Eds.), *Thermal Analysis*, Academic Press, N. Y., 1969, Vol. 1 or 2, Appendix 2.
- 6 P. D. ZEMANY, *Nature*, 171 (1953) 391.
- 7 H. G. LANGER AND R. S. GOHLKE, *Anal. Chem.*, 35 (1963) 1301.
- 8 H. G. LANGER AND R. S. GOHLKE, in Ref. 3, Chap. 3.
- 9 (a) H. L. FRIEDMAN, *The Relationship between Structure and Thermal Stability of New High*

- Temperature Polymers*, ML-TDR-64-274, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio, August 1964; (b) Part II, October 1965; (c) H. L. FRIEDMAN, G. A. GRIFFITH, AND H. W. GOLDSTEIN, Part III, April 1967; (d) H. L. FRIEDMAN, H. W. GOLDSTEIN, AND G. A. GRIFFITH, *Kinetics and Mechanisms of Thermal Degradation of Polymers Using Time-of-Flight Mass Spectrometry for Continuous Gas Analysis*, AFML-TR-68-111, May 1968; (e) Part II, May 1969.
- 10 G. P. SHULMAN, *Polymer Letters*, 3 (1965) 911.
  - 11 G. P. SHULMAN AND H. W. LOCHTE, *J. Appl. Polymer Sci.*, 10 (1966) 619.
  - 12 G. P. SHULMAN AND H. W. LOCHTE, *J. Macromol. Sci. (Chem.)*, A1 (1967) 413.
  - 13 G. P. SHULMAN, *ibid.*, (1967) 107.
  - 14 F. AUSTIN, J. DOLLIMORE, AND B. HARRISON, in R. F. SCHWENKER, JR., AND P. D. GARN (Eds.), *Thermal Analysis*, Vol 1, Academic Press, New York, 1969, p. 311.
  - 15 D. N. GRAY, G. P. SHULMAN, AND R. T. CONLEY, *J. Macromol. Sci. (Chem.)*, A1 (1967) 395.
  - 16 B. B. GOSHGARIAN, presented at the 17th Ann. Conf. on Mass Spectrometry and Allied Topics, Dallas, Texas, May 1969.
  - 17 C. A. GAULIN, F. WACHI, AND T. H. JOHNSTON, in R. F. SCHWENKER, JR., AND P. D. GARN (Eds.), *Thermal Analysis*, Vol. 2, Academic Press, New York, 1969, p. 1453.
  - 18 H. G. LANGER, R. S. GOHLKE, AND D. H. SMITH, *Anal. Chem.*, 37 (1965) 433.
  - 19 W. W. WENDLANDT AND T. M. SOUTHERN, *Anal. Chim. Acta*, 32 (1965) 405.
  - 20 R. S. GOHLKE AND H. G. LANGER, *ibid.*, 36 (1966) 530.
  - 20 (a) H. G. LANGER AND R. S. GOHLKE, *Fortschr. Chem. Forsch.*, 6 (1966) 515, through Ref. 8 and *Chem. Abstr.*, 67 (1967) 26464n.
  - 21 H. G. LANGER AND F. J. KARLE, presented at the 15th Ann. Conf. on Mass Spectrometry and Allied Topics, Denver, Colo., May 1967.
  - 22 H. G. LANGER AND T. P. BRADY, in R. F. SCHWENKER, JR., AND P. D. GARN (Eds.), *Thermal Analysis*, Vol. 1, Academic Press, New York, 1969, 295.
  - 23 J. P. REDFERN, B. L. TREHERNE, M. L. ASPIMAL, AND W. A. WOLSTENHOLME, presented at the 17th Ann. Conf. on Mass Spectrometry and Allied Topics, Dallas, Texas, May 1969.
  - 24 W. W. WENDLANDT, T. M. SOUTHERN, AND J. R. WILLIAMS, *Anal. Chim. Acta*, 35 (1966) 254.
  - 25 F. ZITOMER, *Anal. Chem.*, 40 (1968) 1091.
  - 26 W. F. HADDON, A. H. DIEDUARDO, AND F. ZITOMER, presented at the 17th Ann. Conf. on Mass Spectrometry and Allied Topics, Dallas, Texas, May 1969.
  - 27 D. E. WILSON AND F. M. HAMAKER, in R. F. SCHWENKER, JR., AND P. D. GARN (Eds.), *Thermal Analysis*, Vol. 1, Academic Press, N. Y., 1969, p. 517.
  - 27 (a) G. P. SHULMAN AND H. W. LOCHTE, *J. Macromol. Sci. (Chem.)*, A2 (1968) 411.
  - 28 H. P. VAUGHAN, presented at the 17th Ann. Conf. on Mass Spectrometry and Allied Topics, Dallas, Texas, May 1969.
  - 29 J. W. SMITH AND D. R. JOHNSON, in R. F. SCHWENKER, JR., AND P. D. GARN (Eds.), *Thermal Analysis*, Vol. 2, Academic Press, New York, 1969, p. 1251.
  - 30 H. G. WIEDEMANN, *ibid.*, Vol. 1, p. 229.
  - 31 M. MÜLLER-VONMOOS AND R. BACH, *ibid.*, Vol. 2, p. 1229.
  - 32 H. L. FRIEDMAN, H. W. GOLDSTEIN, AND G. A. GRIFFITH, presented at the 15th Ann. Conf. on Mass Spectrometry and Allied Topics, Denver, Colo., May 1967.
  - 33 (a) H. W. GOLDSTEIN, *Mass Spectrometric Analysis of the Pyrolysis Products of Polymeric Materials*, Rept. No. UCRL-13332, Lawrence Radiation Laboratory, Livermore, Calif., July 17, 1967; (b) *Mass Spectrometric Thermal Analysis of Polymers*, Rept. No. UCRL-13398, Aug. 20, 1968.
  - 34 W. G. STAPLETON, presented at the 17th Ann. Conf. on Mass Spectrometry and Allied Topics, Dallas, Texas, May 1969.
  - 35 K. A. LINCOLN, *Rev. Sci. Instr.*, 35 (1964) 1688.
  - 36 H. L. FRIEDMAN AND G. A. GRIFFITH, in J. P. REDFERN (Ed.), *Thermal Analysis 1965*, Macmillan, London, 1965, p. 22.
  - 37 H. L. FRIEDMAN, *J. Macromol. Sci.*, A1 (1967) 57.
  - 38 H. L. FRIEDMAN, G. A. GRIFFITH, AND H. W. GOLDSTEIN, in R. F. SCHWENKER, JR., AND P. D. GARN (Eds.), *Thermal Analysis*, Vol. 1, Academic Press, New York, 1969, p. 405.
  - 39 H. L. FRIEDMAN, presented at the 17th Ann. Conf. on Mass Spectrometry and Allied Topics, Dallas, Texas, May 1969.
  - 40 H. G. LANGER, *ibid.*