

## **AN AUTOMATED SYSTEM FOR SIMULTANEOUS THERMAL ANALYSIS AND MASS SPECTROMETRY. PART I**

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### **ABSTRACT**

An automated system which permits differential thermal analysis (DTA), thermogravimetry (TG), derivative thermogravimetry (DTG) and mass spectrometry (MS) measurements to be performed simultaneously on a test sample under an inert or oxidative atmosphere has been developed. The system involves interfacing a Mettler thermoanalyzer, model TA-1, with a Hewlett-Packard 5992 quadrupole mass spectrometer.

Data acquisition from the thermoanalyzer and the mass spectrometer is handled by two separate Hewlett-Packard 9825 calculators with the mass spectral data stored on a floppy disk. Computer software has also been developed to permit (1) continuous MS monitoring of volatiles, (2) screening of the acquired MS data, (3) tabulation of mass spectra, (4) subtraction of mass spectra acquired at two different times and (5) thermograms and mass ion profiles plotted together as a function of temperature or time.

### **INTRODUCTION**

Thermal analysis (TA) and mass spectrometry (MS) are two powerful analytical techniques in their own right. The former, through differential thermal analysis (DTA), reveals the energetics of phase transitions or reactions and through thermogravimetry (TG) and derivative thermogravimetry (DTG), provides information on thermal stability such as the percent weight change between two temperature limits. Thermal analysis, however, provides no clues on the identities of the volatiles which result in the observed weight change or endotherm/exotherm. This shortcoming can be readily remedied by combining the technique with mass spectrometry. Numerous methods for coupling a thermoanalyzer with a mass spectrometer for analyses under high vacuum or normal atmosphere have been described in the literature [1–11]. In all cases, these combined systems permitted one or more of the following four operations to be performed: (1) continuous TG/MS measurements, (2) continuous TG and discrete MS monitoring at regular temperature intervals, (3) continuous DTA/TG/DTG/MS measurements with MS limited to a few selected mass-ions (SIM), and (4) continuous DTA/TG/DTG and discrete MS measurements at intervals along the TG curve.

In this paper, we will describe an automated system which enables DTA, TG,

DTG and MS measurements to be performed simultaneously under an inert or oxidative atmosphere. The system is supported by computer programs which, in addition to acquiring data automatically and graphing the results, will greatly facilitate data reduction for the mass spectral analysis.

## EXPERIMENTAL

### *Instrumental*

The system consists of a Mettler thermoanalyzer, model TA-1, coupled with a Hewlett-Packard 5992 quadrupole mass spectrometer. Figure 1 shows a schematic diagram of the combined instrument.

The GC column inside the oven of the HP-5992 system was replaced with a Varian 951-5100 leak valve which could deliver a minimum leak rate of  $1 \times 10^{-9}$  torr  $l \text{ sec}^{-1}$  under normal operation and was bakable to  $450^\circ\text{C}$ . The fine adjustment shaft of the valve was extended to the outside of the GC oven for easy operation. To avoid oxidation and contamination, the copper gasket assembly of the valve was gold plated. The inlet to the valve was a 30 in. long  $3/16$  in. monel tube which served as the primary path for the volatile transfer. The tube was first jacketed by a  $3/8$  in. copper tube for uniform heat distribution before the assembly was wrapped by a heating tape and insulated. At mid length of the transfer line, a small hole was drilled through the copper jacket to accommodate a chromel-alumel thermocouple which was in direct contact with the monel tubing. The transfer line was powered by

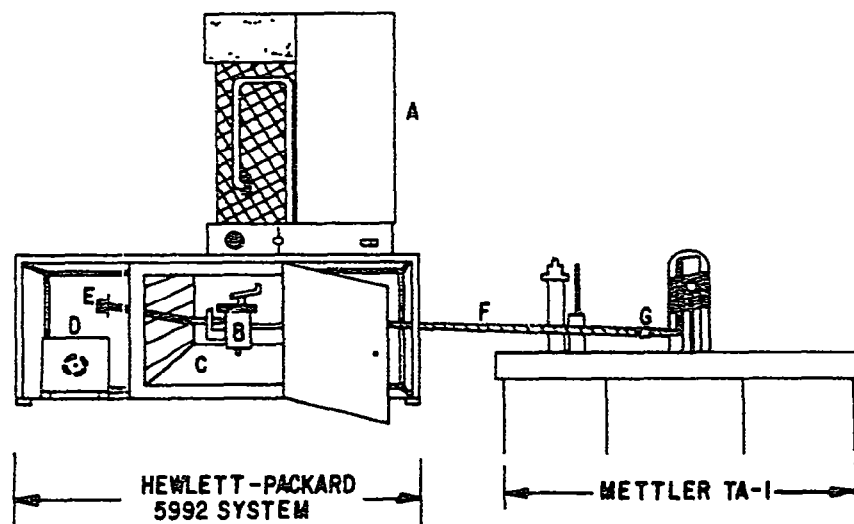


Fig 1. A schematic drawing of the combined Mettler Thermoanalyzer and Hewlett-Packard 5992 quadrupole mass spectrometer A, HP-5992 quadrupole mass spectrometer, B, Varian leak valve; C, GC oven, D, fore pump; E, leak valve fine adjustment control shaft, F, TA/MS transfer line, G,  $3/8$  in to  $1/4$  in s s Swagelock union.

the temperature controller of the HP-5992 system which was originally used to maintain the injection-port temperature.

A special quartz furnace was designed and built for the Mettler thermoanalyzer (Fig. 2). The inner gas tube (25 mm o.d.) was closed at the top but opened on the side to a 4 mm o.d. exit line. This exit tubing was positioned between the bifilar heating coil and the inner gas tube. In order to avoid condensation, the exit tubing was sandwiched between two coils upon leaving the furnace to form the gas outlet. The gas outlet was constructed with a piece of quartz rod  $3/8$  in. in diameter and  $2\frac{3}{4}$  in. in length through which a center bore of  $5/32$  in. had been drilled. The heating coils of the furnace were fitted with a nichrome element  $80\ \Omega$  in resistance. The interface between the furnace and the mass spectral transfer line was accomplished with a  $3/8$  to  $1/4$  in. stainless steel swagelock union which previously had been bored to  $1/4$  in. i.d. During analysis, the furnace outlet and the swagelock union were heated to about  $220^\circ\text{C}$  via a separate heating tape connected to a Variac.

The HP-5992 system was equipped with a thermal printer and dual disk drives and was controlled via a HP-9825 calculator which had a memory size of 63 K. The mass spectrometer had a mass range 10–800 a.m.u. and was autotuned with the Hewlett-Packard supplied program-tape cartridge using perfluorotributylamine as standard. Automatic data acquisition from the Mettler thermoanalyzer was handled by a separate HP-9825S calculator. Details on this system have been reported previously [12]. The data collection program for the mass spectrometer was stored on floppy disk which was placed in the No. 1 disk drive (the "slave" drive). The

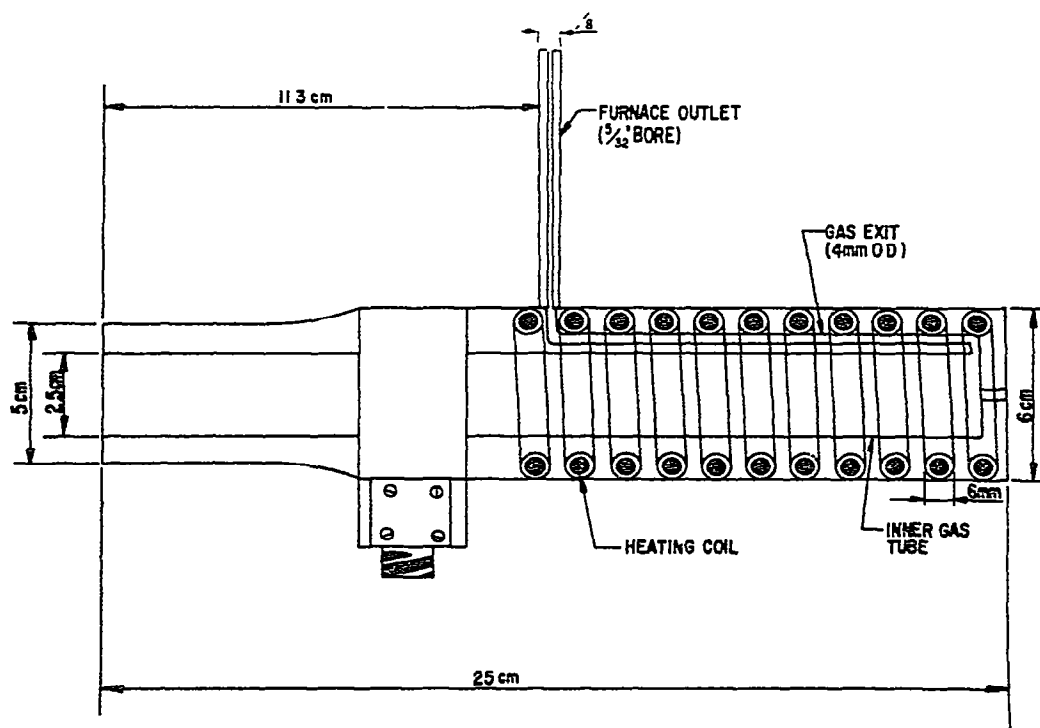


Fig. 2. A schematic drawing of the special quartz furnace designed for simultaneous TA-MS analyses

program we developed took mass scans once every 10 sec, the same data rate as used in the thermal data collection. Real time data were displayed via the thermal printer which traced the profiles of the total ion and any two mass ions chosen by the analyst. The collected mass spectral data within the defined mass range were stored in files, created by the program, on the data disk placed in the master disk drive (drive No. 0). The program would prompt a warning display on the calculator when the current file was filled. The analyst could then either respond with a new file name or the program would store the data in successive continuation files. The two mass ions selected for real time display and their respective abundance scales together with that for the total ion could be changed any time during the data collection process by actuating special keys on the calculator. Function keys were also set up for starting and terminating the data acquisition and printing the instantaneous spectrum collected.

The mass spectrometer was autotuned prior to any analysis. With the autotune parameters entered and with the GC oven and the mass spectral transfer line controlled at 220°C by the mass spectrometer data collection program, the leak valve was calibrated with a gas mixture containing 1000 p.p.m. of argon or carbon dioxide in helium. The gas was connected to the transfer line using 1/4 in. polyethylene tubing. The leak valve was opened gradually through its fine adjustment screw until the abundance value for mass ion 40 (argon) or 44 (CO<sub>2</sub>) was maximum. This maximum was ascertained when further opening of the valve caused the ion abundance to drop due to an excessive pressure effect. With the maximum value noted, the leak valve was closed until the ion abundance was about 50% of the maximum. This value again was noted. The ratio of the latter abundance value to the maximum would then represent the instrument calibration constant, *K*, for the analysis to follow.

### *Data reduction*

The computer software developed for thermal analysis using the Mettler thermo-analyzer [12] had been expanded and modified to permit rapid analysis of the enormous amount of mass spectral data collected. Since the thermal analysis and the mass spectra were acquired through two separate HP-9825 calculators, handshaking between data based on common time was used to express the mass ion information in terms of temperatures.

#### (1) Program "SCREEN"

As the name implies, the function of this program was to examine the acquired mass spectral data stored on the disk. The program correlated the time information between the thermal and the mass data and performed the following tasks, results of which were automatically tabulated on the thermal printer, in sequence.

(a) The program identified those mass ions which traversed through a maximum and which had a sharpness coefficient (second derivative of ion abundance/time) larger than or equal to that entered by the analyst. Information on the temperatures and abundances measured at the peak and at the minimum point just prior to the

peak, their abundance difference, the mass ion, and the determined sharpness coefficient are summarized and listed in the order of increasing temperature.

(b) The program then sorted the results reported in (a) and listed the temperatures and abundance measured at the peak in the order of increasing mass/charge ratios ( $m/e$ ).

(c) The third table the program generated was a listing of the mass ions whose measured abundances were found to increase with temperature whether or not they traversed through a maximum. Again, information on temperatures at which the mass ion abundance is maximum and minimum was provided in increasing order of  $m/e$ . The abundance difference between the maximum and minimum permits a ranking of the mass ions.

(d) The fourth table tabulated by the program consisted of a listing of mass ions which were not detected by the mass spectrometer.

(e) This last tabulation reported on those mass ions which were detected by the mass spectrometer but whose peaks, if any, had sharpness coefficients less than that specified by the analyst.

#### (2) Program "Spctr"

This program was developed so that mass spectra acquired at any time during the analysis could be listed for examination. Mass ions and their abundances were tabulated on the thermal printer. An option was provided for saving the spectrum on magnetic tape cartridge.

#### (3) Program "Spesub"

This program was normally used subsequent to "Spctr". With the mass spectra saved on tape, this program permitted subtraction of spectra collected at any two different times.

#### (4) Program "Plots"

This was an expanded disk version of that previously developed for graphing thermal analysis results [12]. A plotting program was added so that mass ion profiles could be traced in the same format as the thermograms. Options were provided for 11 in.  $\times$  14 in. or 8 in.  $\times$  11 in. size plots to be made on an HP-9872 four-colour plotter, with or without symbols, as a function of temperature or time. The mass ions were graphed against a fixed abundance scale (0-10) with their identifications and scale multiplication factors color-coded on the left side of the plot. The program also permitted each mass ion profile to be labeled. The plotter pen would automatically reset itself to the maximum of the peak before the label was added. In addition, capability for data smoothing using 0, 5, 7, 9, 11 or 13 data points was also included.

## RESULTS AND DISCUSSION

The major difficulty in simultaneous thermal analysis/mass spectrometry is data analysis of the acquired mass spectral information. Because of the large volume of spectra involved, manual manipulation is often impractical if not impossible. Our data reduction programs are aimed towards meeting this goal. Programs "SCREEN",

“Spctr” and “Spesub” greatly reduce the man power required for the task and summarize the results in formats which permit interpretation to be carried out effectively. Demonstrated in Fig. 3 are the first two tables generated by “SCREEN” on a set of data acquired for a sample of calcium oxalate monohydrate. The results obviously suggest that volatiles such as water ( $m/e=18, 17$ ), carbon monoxide ( $m/e=28$ ) and carbon dioxide ( $m/e=44, 28, 16$  and  $12$ ) are liberated as the sample is heated to high temperatures. The same results are plotted together with DTA, TG, DTG thermograms in Fig. 4. The remarkable match in line shape between the DTG and the mass ion peaks suggests insignificant dead-volume effect during volatile transfer. In each case, the DTG minimum and the mass ion maximum are seen to occur at the same temperature.

The benefit of having DTA simultaneously performed during the analysis is apparent in Fig. 5 which shows the decomposition of another sample of calcium oxalate monohydrate under a 20% oxygen in helium atmosphere. The DTA shows detectable exothermic activity starting at about 385°C. This activity which otherwise will reach a maximum is seen to be intercepted at about 450°C by an endotherm which reaches a minimum at the same temperature (482°C) as that for the DTG. The MS profile for  $m/e=44$  shows that carbon dioxide starts to increase also at about 385°C. Carbon monoxide liberation is apparent from the  $m/e=28$  profile and is first detected at a higher temperature. Although these two ions reach their maximum at the same temperature as the minima for the DTA and DTG, their

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Table 1. List of all peaks found, with Temp from 25.0 to 850.0  
If abundance at a peak is below 20 it will not be counted.  
Peaks will not be counted when sharpness is less than 18.00

Temp	m/e	Peak abundance	previous Temp	previous abundance	Peak height	Peak sharpness
202.6	18	3033	25.2	34	2499	86.1
204.6	17	887	63.4	12	375	37.5
496.7	28	10424	343.6	1289	9135	215.8
500.7	44	1075	25.4	12	1063	24.7
786.0	44	10118	573.0	47	10071	44.6
790.1	28	2162	557.5	1225	404	24.9
792.0	16	384	358.1	0	384	13.2
	16	611	576.7	44	587	23.9

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Table 2. Abundance peaks, sorted by mass.  
Temp is printed only for the first 346 ions encountered,  
and only the first 4 peaks, plus the last, for those ions.

m/e	Temp	abundance	Temp	abundance	Temp	abundance	Temp	abundance
12	732.0	384						
16	732.0	611						
17	204.6	887						
18	202.6	3033						
28	496.7	10424	790.1	2162				
44	500.7	1075	786.0	10118				

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Fig 3. Computer output (first two tables) generated by program “SCREEN” on a set of data collected for calcium oxalate monohydrate.

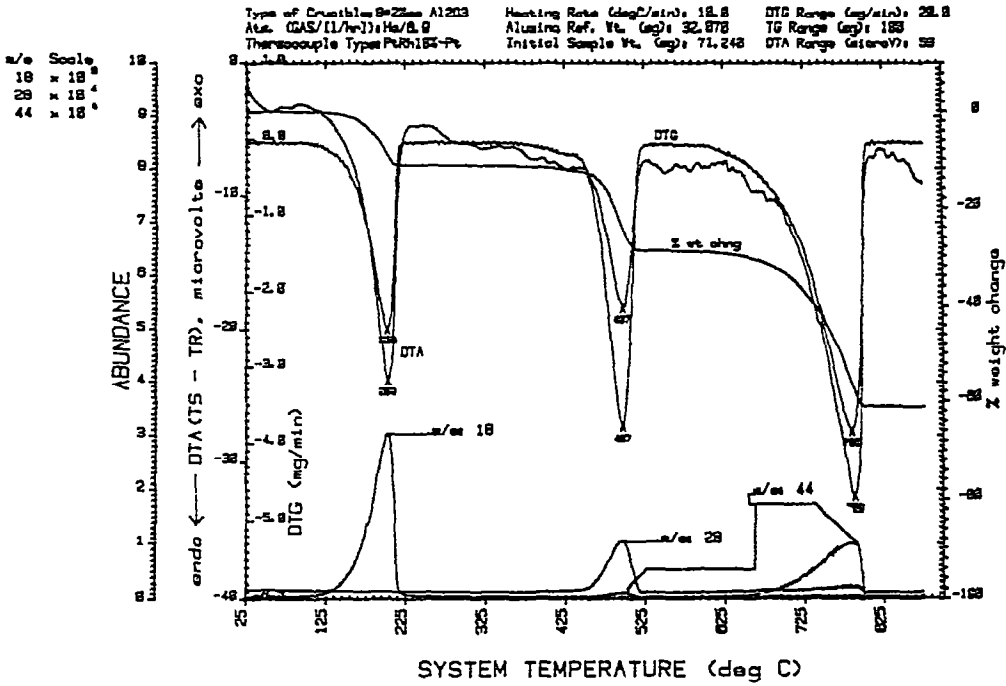


Fig 4 DTA, TG and DTG thermograms plotted together with MS profiles for calcium oxalate monohydrate studied under a helium atmosphere

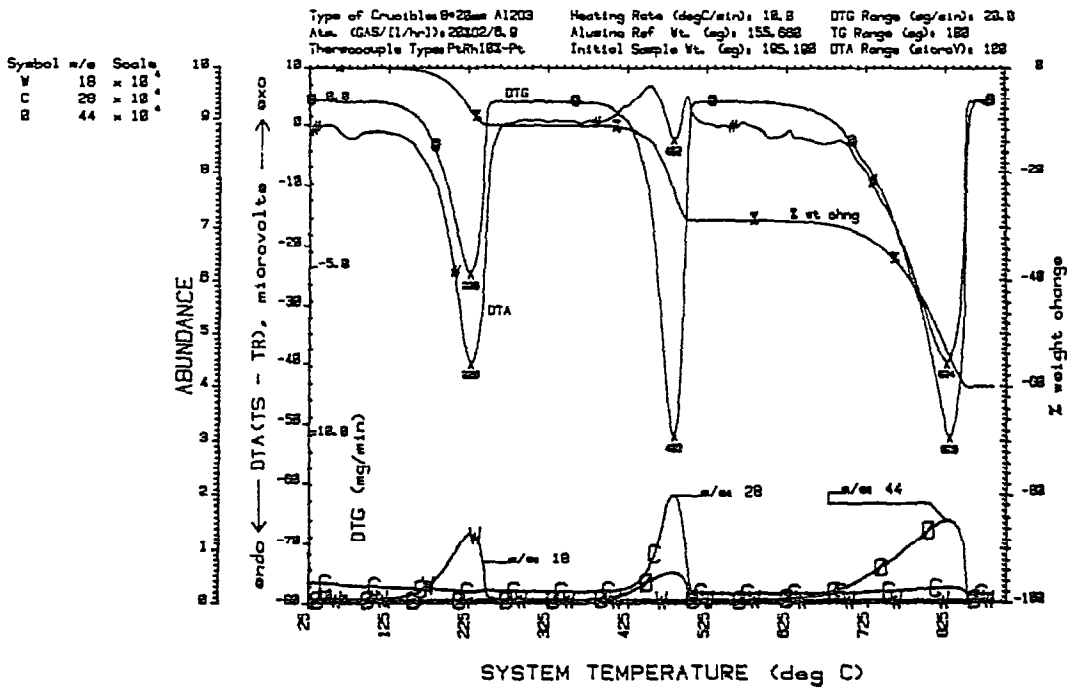


Fig. 5 DTA, TG, DTG and MS profiles for calcium oxalate monohydrate analyzed under a 20% oxygen in helium atmosphere

shapes are quite different;  $m/e = 44$  is much broader than  $m/e = 28$ . The above suggests that the single weight loss observed in this temperature region is still due to decarboxylation of the oxalate to carbonate. Oxidation of the liberated carbon monoxide to dioxide is only partially completed. The exothermic activity seen on the DTA is a direct result of the oxidative process, while the endotherm is attributed to a faster rate of carbon monoxide liberation which remains unoxidized. The relative abundance ratio measured at the peak also shows a higher concentration of carbon dioxide in this case than the one shown in Fig. 4 where the study was performed under a helium atmosphere and the small amount of  $\text{CO}_2$  present was due to oxidation from the residual quantity of oxygen still present in the system.

Many polymers will undergo thermal depolymerization at elevated temperatures. In the cases of polystyrene and polybutadiene, 42% styrene and 14% butadiene monomers have been reported when the polymers were degraded under vacuum [13]. Figure 6 shows the results obtained on a styrene/butadiene diblock copolymer (Shell Co.) under a helium atmosphere. The complex nature of the degradation (240–510°C) is apparent from the DTG curve. The two shoulders ahead of the peak at 456°C indicate the presence of overlapping reactions. The inclusion of DTA in the combined technique is again advantageous in this case. DTA shows that the first shoulder on the DTG peak is due to a strong exothermic reaction while the remainder are endothermic. A glass transition due to polystyrene is also revealed at 100°C. The simultaneous MS analysis confirms the existence of butadiene ( $m/e = 54$ ), and styrene ( $m/e = 104$ ) due to polymer unzipping. Thermal depolymeriza-

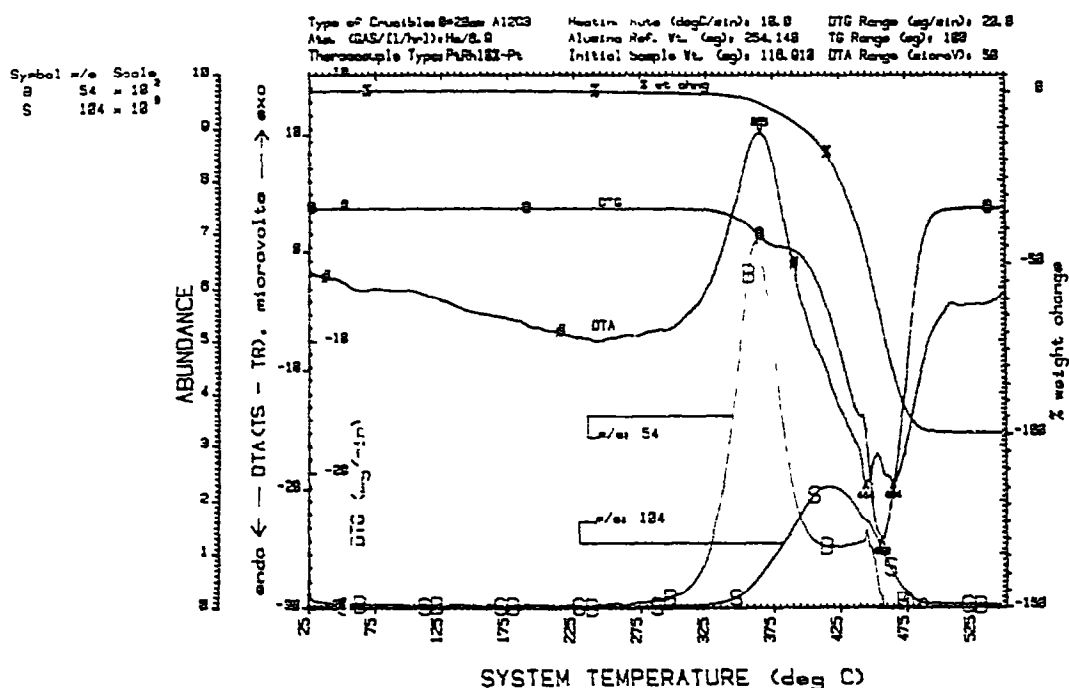


Fig. 6 Thermograms and MS profiles showing the presence of butadiene and styrene monomers during thermal depolymerization of styrene/butadiene diblock copolymer



tion of the butadiene block is seen to be exothermic in nature.

The combined technique is also found to be useful in identifying additives. The sensitivity of our system is shown by the results in Fig. 7, where a sample of Elvax<sup>®</sup> 220 was examined under helium. Elvax<sup>®</sup> 220 by DuPont is an ethylene/vinyl acetate (28%) copolymer containing about 750 p.p.m. of butylated hydroxytoluene (BHT) as antioxidant. The exothermic weight loss at about 275°C, as indicated by the simultaneous MS analysis, is due to the decomposition of vinyl acetate to acetic acid ( $m/e = 43, 45$  and  $60$ ) [14] and the liberation of the BHT antioxidant ( $m/e = 205, 220$  and  $206$ ). The loss of the antioxidant is seen to precede the degradation. The noisy nature of the MS profiles is related to the intermittent nature of the weight loss which is also evident in the DTG curve.

We have been able to identify additives at concentrations of about 20 p.p.m. using our system. In addition, our instrument also permits volatiles to be determined quantitatively from their respective mass peak areas. In Fig. 8, the effective peak areas of mass ions, 18, 28 and 44 for water, carbon monoxide and carbon dioxide measured from five different sample weights of calcium oxalate monohydrate are plotted against their amount of loss determined by thermogravimetry (Fig. 4). The linear relationship in each case is apparent. Here, the effective area is the integrated peak area corrected for changes in conditions of the mass spectrometer and the leak valve. It is obtained according to

$$A' = A \times \frac{K_i}{K}$$

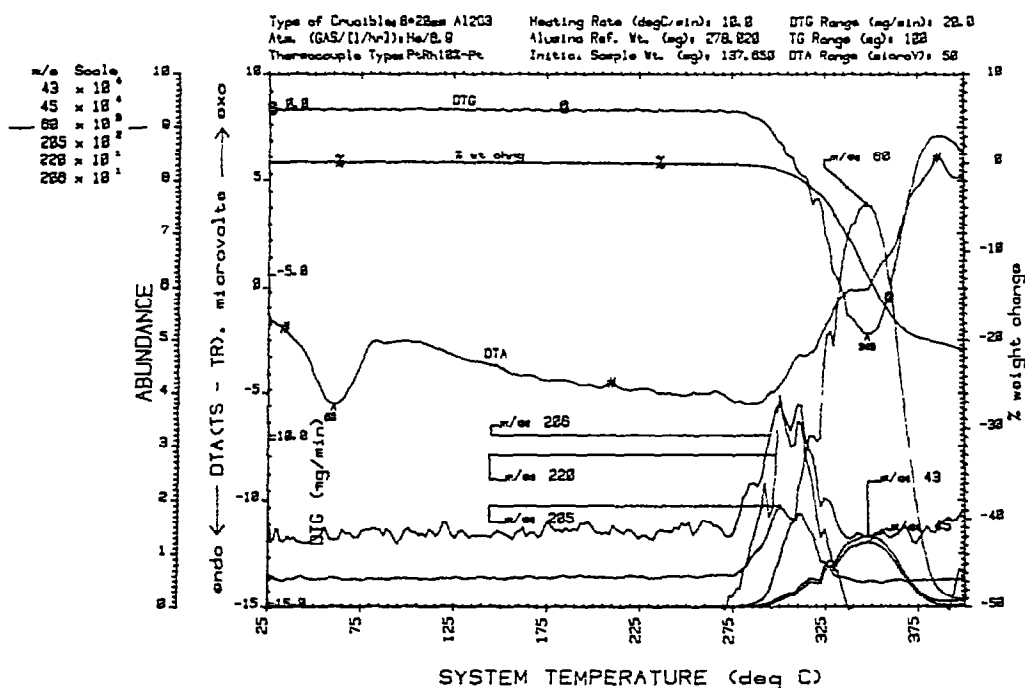


Fig. 7. TA-MS analyses of Elvax<sup>®</sup> 220 (ethylene/vinyl acetate copolymer) showing the release of BHT antioxidant prior to vinyl acetate decomposition

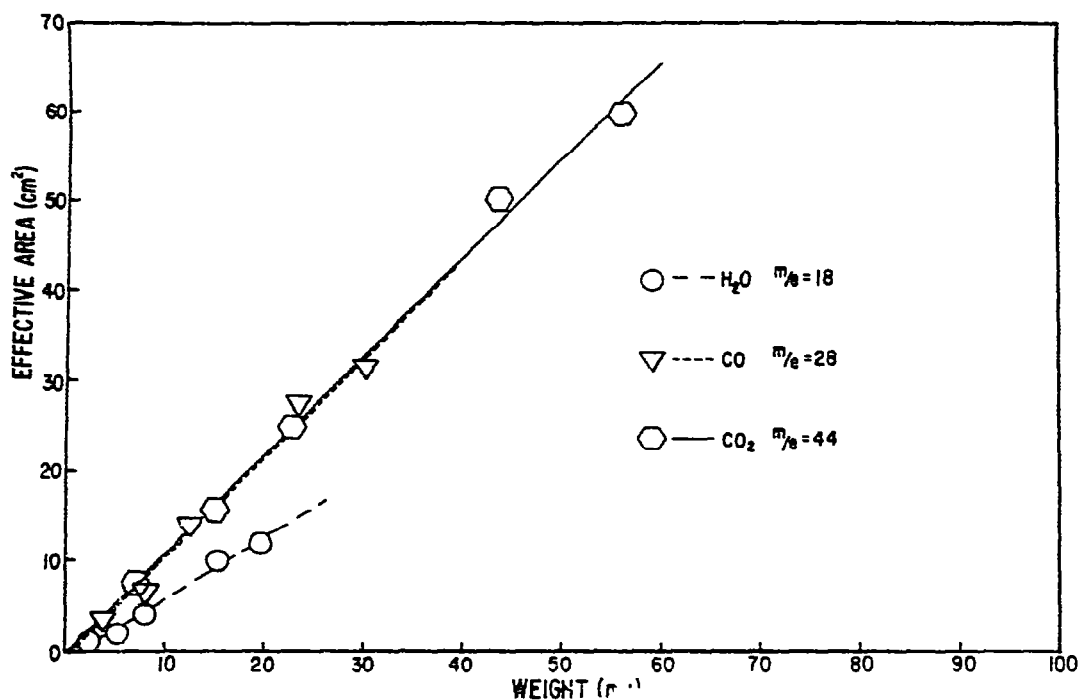


Fig 8 A plot of the effective mass peak area vs amount loss for water, carbon monoxide and carbon dioxide from calcium oxalate monohydrate

where  $A'$  and  $A$  are the effective and integrated peak areas and  $K$  and  $K_1$  are the instrument calibration constant (see Experimental) for the sample run and the one against which all other results are normalized, respectively.

#### ACKNOWLEDGEMENT

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