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AN AUTOMATED SYSTEM FOR SIMULTANEOUS THERMAL ANALYSIS AND MASS SPECTROMETRY. PART II. COMBINATION WITH GAS CHROMATOGRAPHY/MASS SPECTROMETRY

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ABSTRACT

Our system for simultaneous thermal analysis and mass spectrometry (TA/MS) which consists of a Mettler thermoanalyzer model TA-1 coupled with a Hewlett-Packard 5992 quadrupole mass spectrometer has been extended to include gas chromatography/mass spectrometry (GC/MS) capability. The separation power of GC offers tremendous advantage for analyzing complex gaseous mixtures resulting from thermal analysis. The combination of real-time MS and subsequent GC/MS eliminates artifacts commonly associated with trapping and hence, permits accurate and efficient interpretation of the nature of the volatiles.

INTRODUCTION

Thermal analysis (TA), gas chromatography (GC) and mass spectrometry (MS) are important analytical techniques for materials characterization. When combined together, they provide useful information regarding the thermal behavior of a sample, its thermal stability, and the identities of the volatile products which are liberated during thermal transitions. Since gas chromatography is a batch process, its combination with thermal analysis often involves trapping the off-gases from the thermoanalyzer [1]. Because secondary reactions may occur inside the trap, this approach may not necessarily provide true identification of the volatiles. Direct combination of TA with MS minimizes the risk just mentioned. Various techniques for achieving effective interfacing between a thermoanalyzer and a mass spectrometer have been published [2–13]. But in general, this simultaneous method is disadvantaged in that it is ineffective in analyzing complex gaseous mixtures which may result from parallel or overlapping reactions during thermal analysis.

In this paper, we will describe how we achieved a system which is free from the foregoing shortcomings. We will also illustrate the usefulness of the system with examples.

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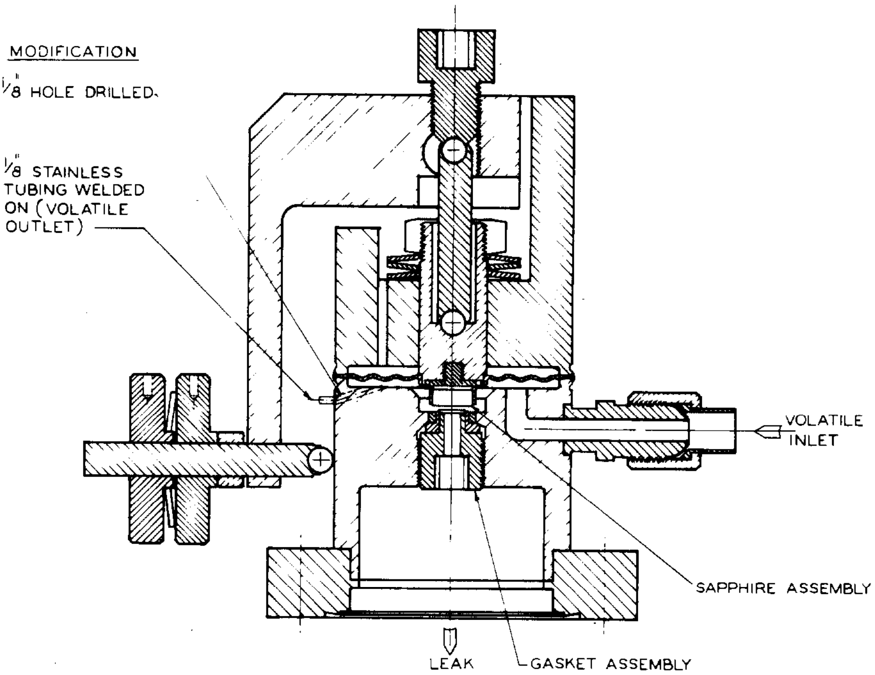


Fig. 1. A schematic drawing of the Varian leak valve showing the modifications.

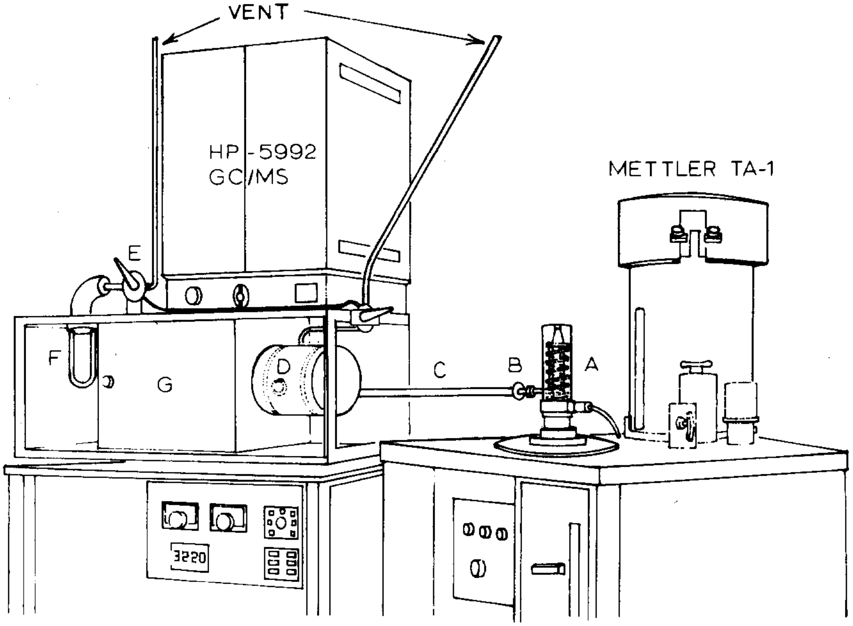


Fig. 2. A schematic drawing of the combined Mettler thermoanalyzer and Hewlett-Packard 5992 quadrupole mass spectrometer. A, Quartz furnace; B, Swagelock union; C, Monel tube for volatile transfer; D, Varian leak valve enclosed by two half-moon insulation blocks; E, six-port Valco valve; F, trap; G, GC oven.

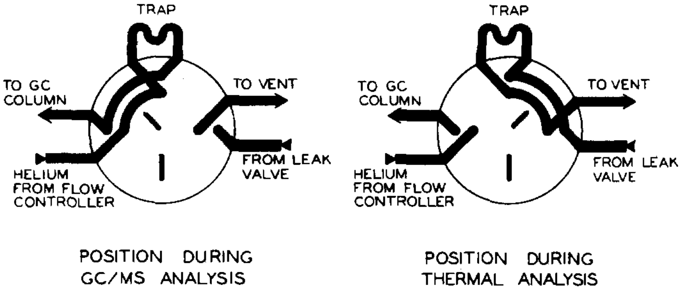


Fig. 3. A cross-section of the six-port Valco valve showing its connections and the flow pattern of the volatiles during thermal and GC/MS analyses.

EXPERIMENTAL

In a previous publication [13], we have described in detail our tandem instrument for simultaneous TA/MS and the computer software we developed for data reduction and presentation. In brief, the instrument involved coupling a Mettler thermoanalyzer model TA-1 with a Hewlett-Packard 5992 quadrupole mass spectrometer via a Varian 951-5100 leak valve housed inside the GC oven of the HP system. To facilitate analyses of a complex volatile mixture resulting from thermal analysis, we have since extended this instrument to include gas chromatography/mass spectrometry (GC/MS)

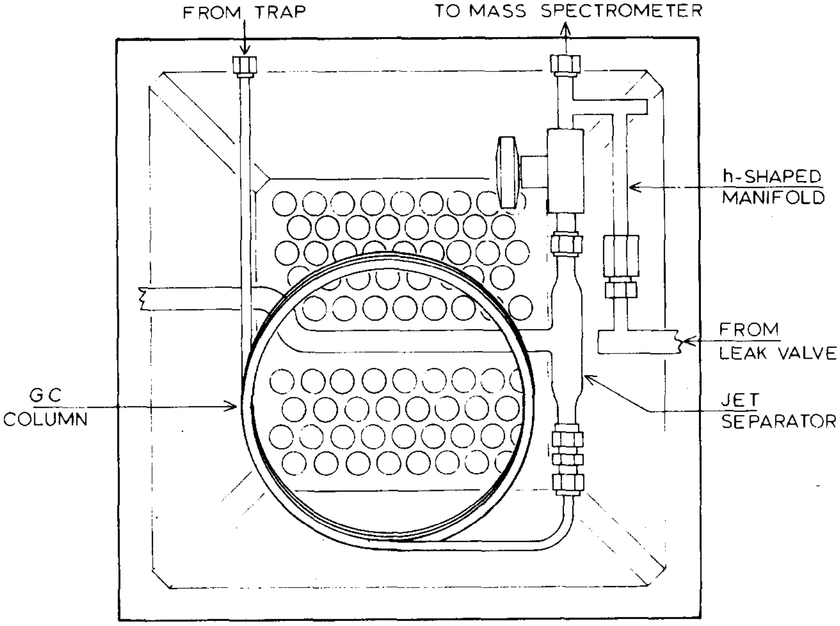


Fig. 4. A schematic drawing showing the h-shaped manifold, jet separator and GC column inside the GC oven.

capability. Some modifications and some new hardware needed for this extension are discussed as follows.

The leak valve, which may be baked to 450°C, was modified by drilling a small hole through the body on the side at a right angle to the inlet (Fig. 1). A length of 1/8 inch stainless-steel tubing was welded to the opening to serve as the outlet to the valve. This modification permits the bulk of the volatile sample from the thermoanalyzer to flow across the valve while a small amount of the volatile sample was leaked through the valve seat and into the mass spectrometer.

Figure 2 shows a schematic drawing of our improved system. In this case, the leak valve was supported from the base of the HP system. A heating tape controlled by a Variac® was wrapped around the leak valve which in turn was enclosed by two half-moon insulation blocks. The fine adjustment shaft of the valve was extended for easy operation. Connected to the outlet of the leak valve was a three-way, high-temperature, zero-volume, stainless-steel valve manufactured by Valco. This valve was used to govern the direction of flow of the volatiles during thermal analysis. In one direction, the volatiles were vented. In the other direction, the volatiles were transported through another 1/8 inch stainless-steel line and were trapped in liquid nitrogen inside a U tube. To facilitate GC/MS analysis, the stainless-steel line and trap were connected to another Valco valve with six ports. The injection port of the HP-5992 system was modified to accommodate a third section of stainless-steel tube (1/8 inch) also connected to the Valco valve. This straight tube was silver soldered to the injection port nut on the outside and passed through a high temperature silicone septum inside. The original helium purge line to the injection port was rerouted from the flow controller so that it terminated at the Valco valve. Figure 3 shows the connections to the six-port Valco valve and the flow pattern of the volatiles during thermal and GC/MS analyses.

The Hewlett-Packard GC column was replaced by a custom-made one packed with 3% SP-2100 on 100/120 supelcoport (methyl silicone on diatomaceous earth) from Supelco. One end of the column was connected to the injection port while the other end was connected to a molecular jet separator (MJSS/ST) marketed by American Instrument Services. The jet separator was evacuated through its side branch with a Welch model 1402 vacuum pump. A custom-designed h-shaped manifold fabricated in stainless steel (Fig. 4) was connected at one end to the mass spectrometer and to the jet separator at the other end. The third end of the h was united with the Varian leak valve mentioned previously. The vacuum seal in this case was achieved with a nickel gasket.

During analysis, the leak valve and all the transfer lines to and from it, the GC oven and the GC injection port were maintained at about 220°C to prevent condensation. For the same purpose, the two Valco valves were also heated by their own heater to about 250°C. The temperature of the six-port

Valco valve was regulated by a proportional controller.

A typical experiment began with autotuning the mass spectrometer using perfluorotributylamine. Afterward, the simultaneous TA/MS analysis was performed [13] with the bulk of the liberated volatiles preserved in the trap. At the completion of this real-time run, the GC/MS experiment was carried out by revolatilizing the frozen sample. The software (disk version) provided by Hewlett-Packard was used for data acquisition and reduction during this subsequent analysis. A utility program, "TOTAB", which listed the total ion abundance and the base ion against spectrum number was, however, developed to facilitate the use of the supplied "Subtraction" option. To eliminate the problems due to possible secondary reactions inside the trap (see Introduction), the GC/MS results were checked against the real-time mass spectral data. Only compounds which could be cross-referenced in this fashion were accepted as real and reported. The others were either discarded or treated as suspect.

RESULTS AND DISCUSSION

It is apparent from the foregoing description that our use of a leak valve to achieve the necessary pressure reduction for coupling the Mettler thermo-

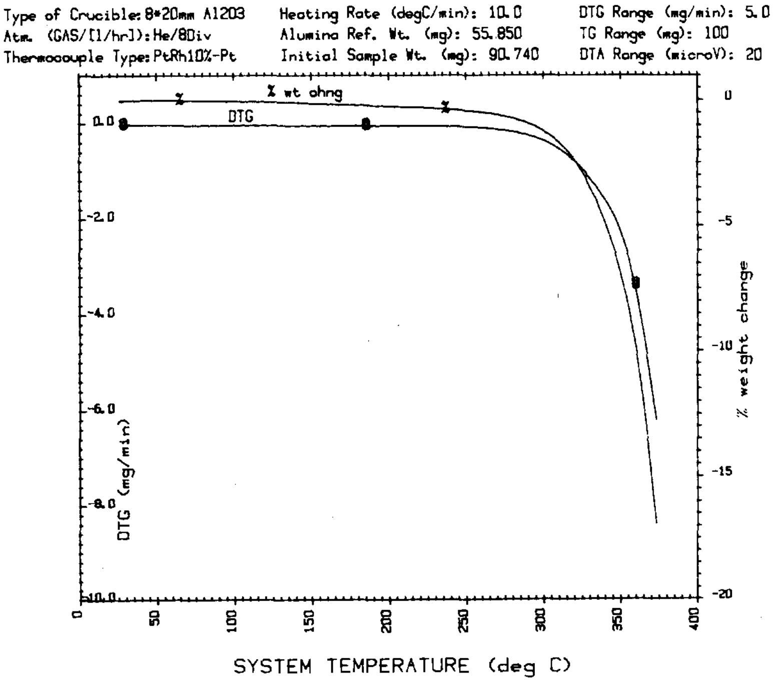


Fig. 5. Thermogravigram of a copolymer of ethyl acrylate/ethyl hexyl acrylate obtained under a helium atmosphere.

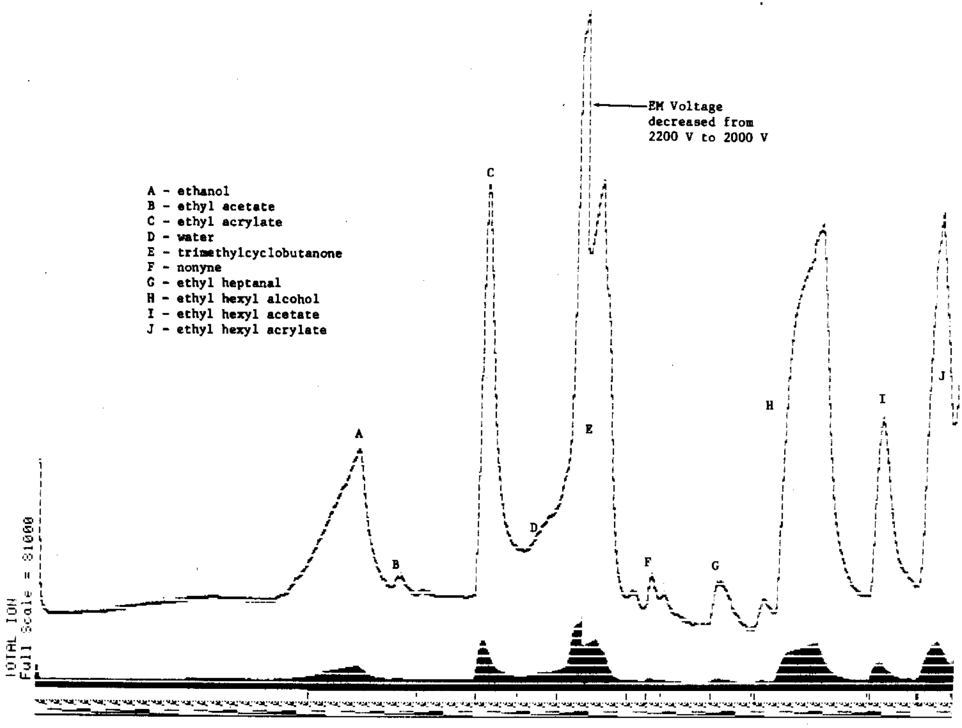


Fig. 6. Gas chromatogram scanned from −50 to ~150°C on the volatiles collected during thermogravimetric analysis of an ethyl acrylate/ethyl hexyl acrylate copolymer.

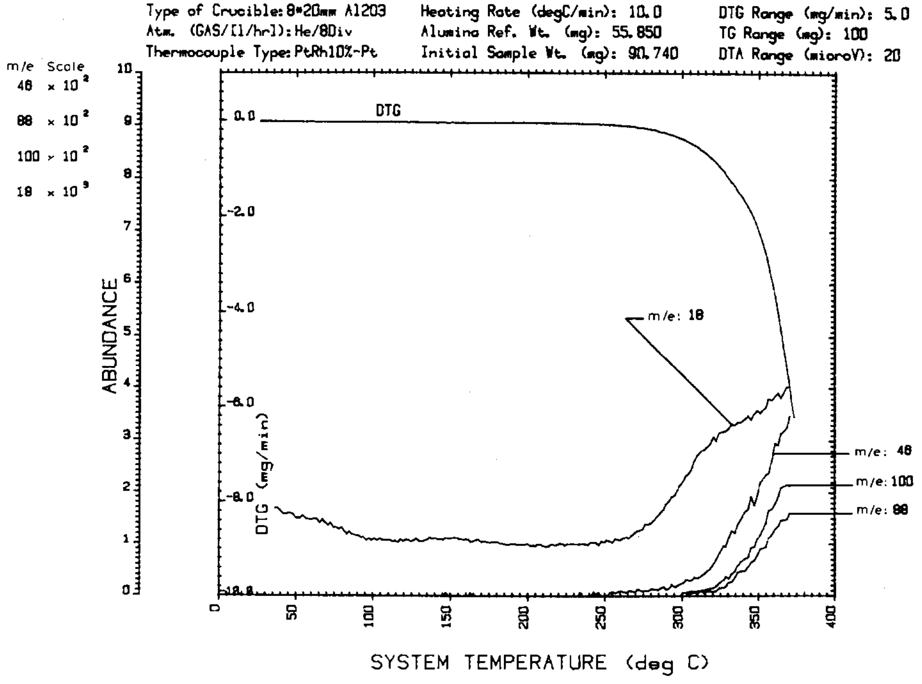


Fig. 7. DTG thermogram and MS profiles of an ethyl acrylate/ethyl hexyl acrylate copolymer showing evolution of ethanol ($m/e = 46$), ethyl acetate ($m/e = 88$), ethyl acrylate ($m/e = 100$) and water ($m/e = 18$).

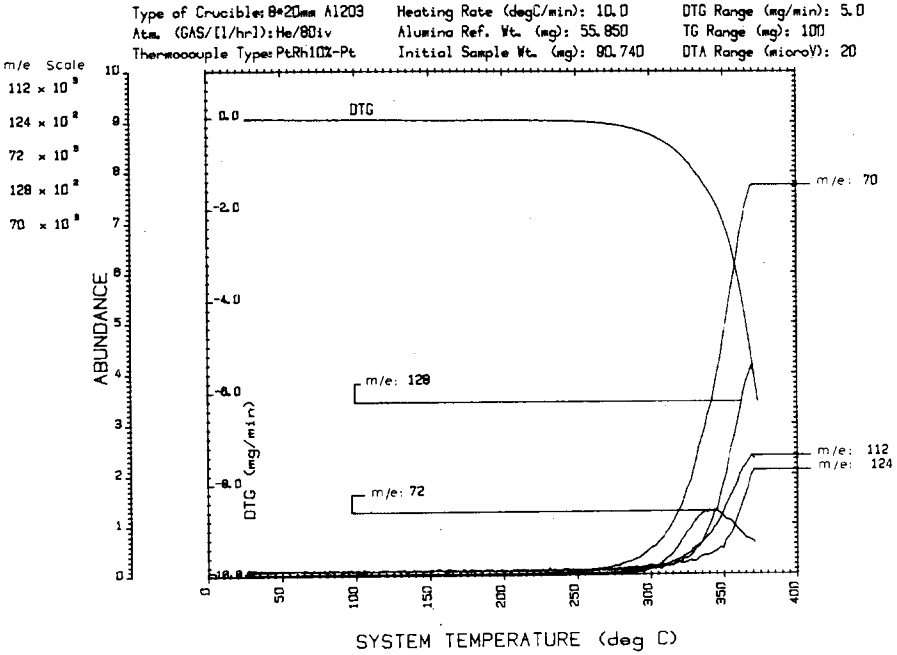


Fig. 8. DTG thermogram and MS profiles of an ethyl acrylate/ethyl hexyl acrylate copolymer showing evolution of trimethylcyclobutanone ($m/e = 112$), nonyne ($m/e = 124$), ethyl heptanal ($m/e = 72$), ethyl hexyl alcohol ($m/e = 128$), ethyl hexyl acetate and ethyl hexyl acrylate ($m/e = 70$).

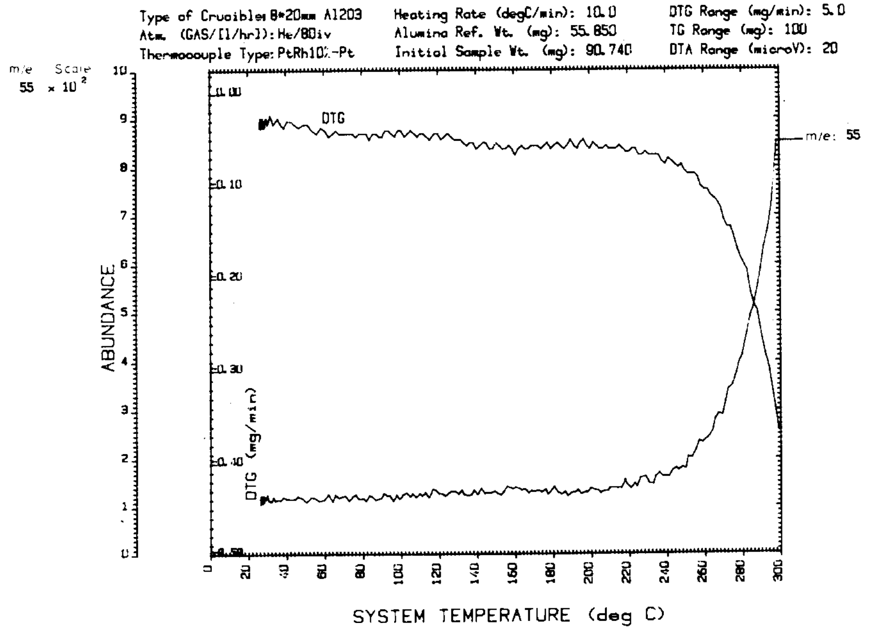


Fig. 9. An expanded plot on the evolution of ethyl acrylate and ethyl hexyl acrylate monomers from an ethyl acrylate/ethyl hexyl acrylate copolymer.

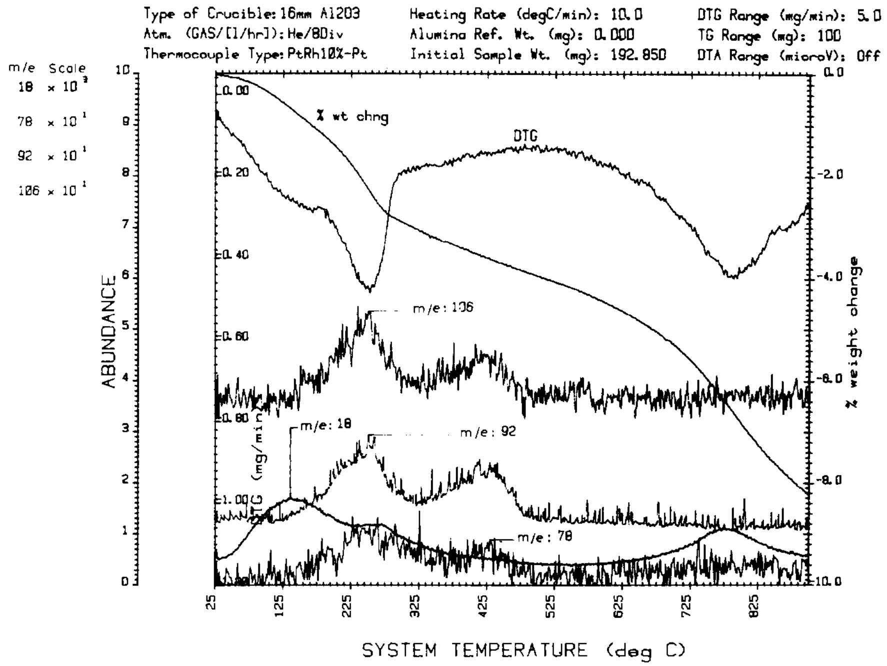


Fig. 10. TG and DTG thermograms and MS profiles of a petroleum coke sample showing evolution of water, benzene, toluene and ethyl benzene.

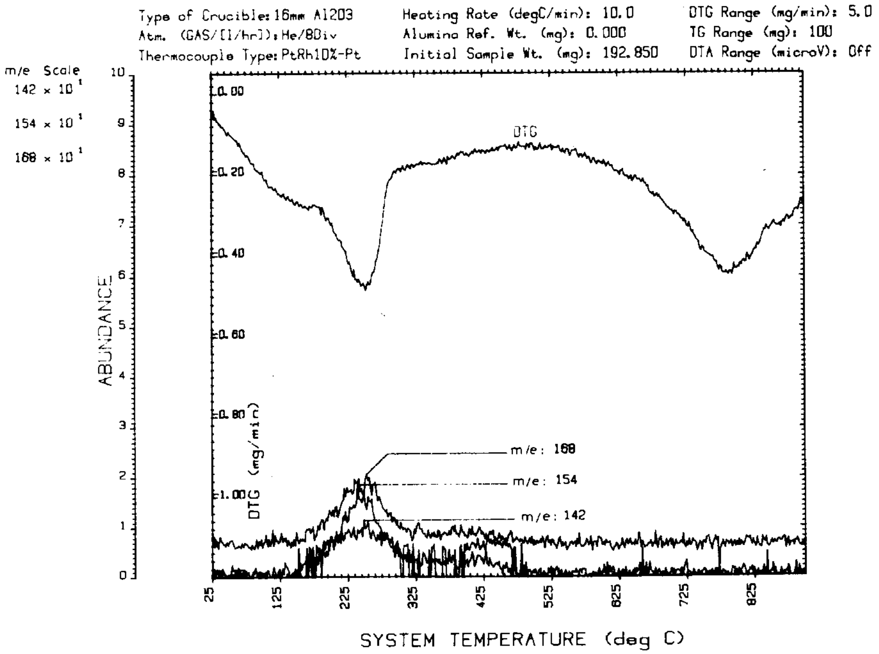


Fig. 11 DTG thermogram and MS profiles of a petroleum coke sample showing evolution of methyl naphthalene, biphenyl and methyl biphenyl.

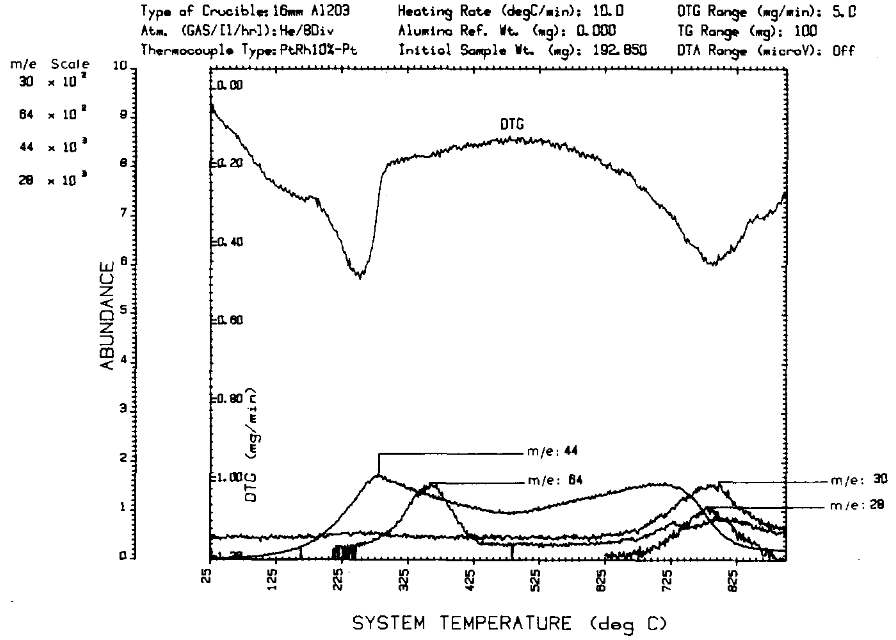


Fig. 12. DTG and MS profiles of a petroleum coke sample showing evolution of nitric oxide, sulfur dioxide, carbon dioxide and carbon monoxide.

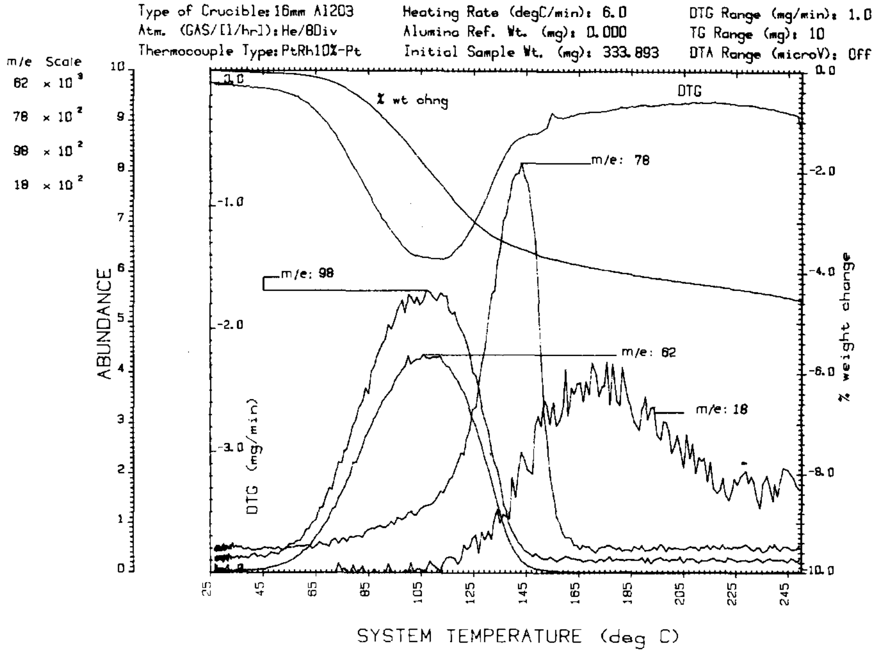


Fig. 13. TG, DTG and MS profiles of an ethylene maleic anhydride copolymer showing evolution of chloroethylene, benzene, ethylene dichloride and water.

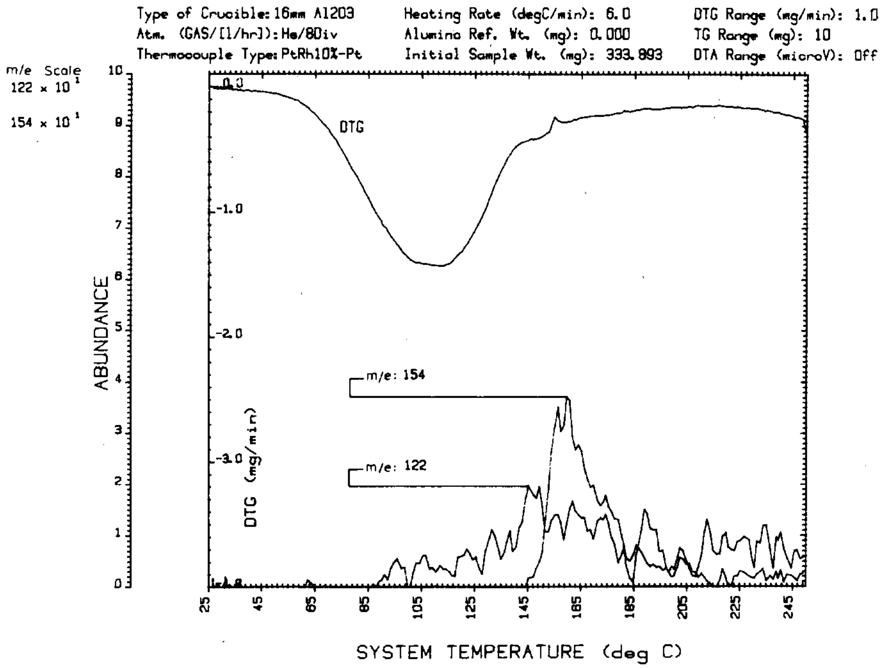
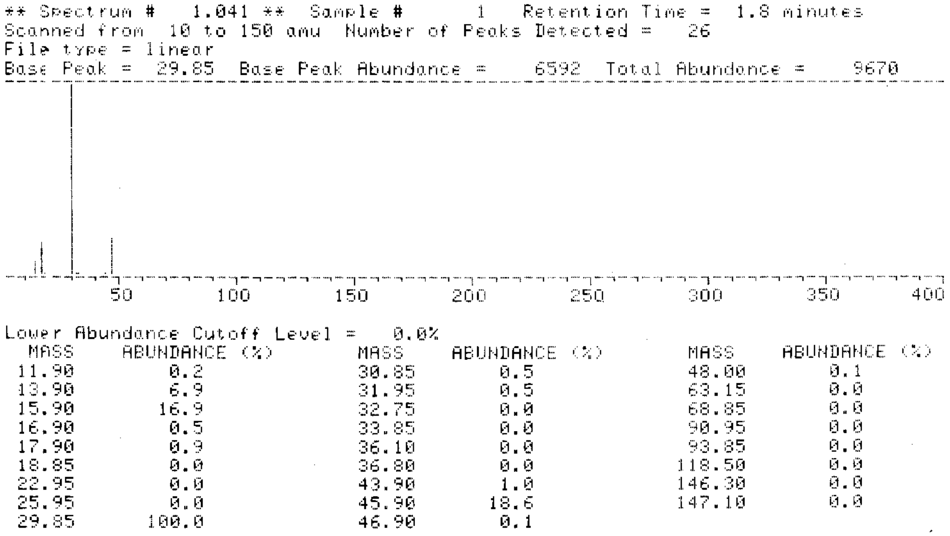


Fig. 14. DTG and MS profiles of an ethylene maleic anhydride copolymer showing evolution of benzoic acid and biphenyl.



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Scanned from  10 to 150 amu  Number of Peaks Detected =   26
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Base Peak =  29.85  Base Peak Abundance =    6592  Total Abundance =    9670
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Lower Abundance Cutoff Level =   0.0%
  MASS     ABUNDANCE (%)          MASS    ABUNDANCE (%)          MASS    ABUNDANCE (%)
 11.90          0.2               30.85        0.5               48.00        0.1
 13.90          6.9               31.95        0.5               63.15        0.0
 15.90         16.9               32.75        0.0               68.85        0.0
 16.90          0.5               33.85        0.0               90.95        0.0
 17.90          0.9               36.10        0.0               93.85        0.0
 18.85          0.0               36.80        0.0              118.50        0.0
 22.95          0.0               43.90        1.0              146.30        0.0
 25.95          0.0               45.90       18.6              147.10        0.0
 29.85        100.0               46.90        0.1
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Fig. 15. The mass spectrum of a GC peak separated from the volatiles collected from an acid-treated carbon showing the presence of NO_2.

analyzer directly with the HP-5992 mass spectrometer has at least two advantages over the other interfacing methods: (1) a capillary is not necessary and (2) easy modification is possible to permit the bulk of the liberated volatile to be preserved for subsequent GC/MS analyses. The first advantage means that our system is practically freed from being clogged. In fact, under non-discriminatory use, a period of six to eight months elapsed before the leak valve needed maintenance. This long service permits a more cost-effective analytical support function to be accomplished. Besides having the same cost-effective benefit (no separate experiments need to be performed), the second advantage also offers the necessary separation power for analyzing complex volatile mixtures during thermal analysis. The GC column used is general in nature and provides good separation for non-polar as well as polar compounds. Furthermore, the jet separator in conjunction with the GC column also provides enrichment. The fact that the GC/MS experiment is supportive in nature, i.e. we can eliminate artifacts associated with trapping by cross-referencing with the real-time mass spectral data, greatly enhances the efficiency and accuracy in determining the identities of the evolved volatiles.

The usefulness of the TA/MS–GC/MS combination is illustrated by the results we obtained on a copolymer of ethyl acrylate/ethyl hexyl acrylate. Figure 5 shows its thermogravigram obtained under a helium atmosphere at

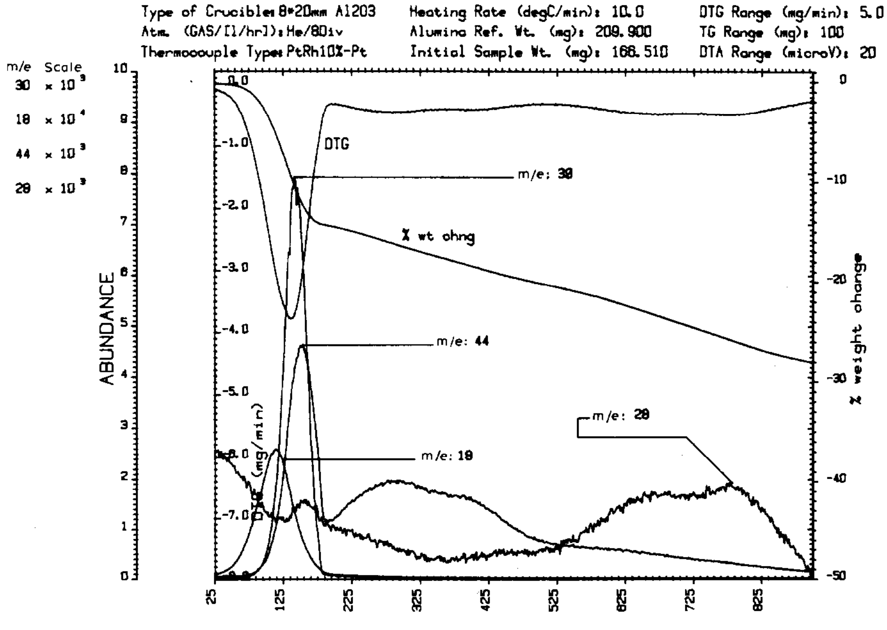

Fig. 16. TG, DTG and MS profiles of an acid-treated carbon showing evolution of nitric oxide, water, carbon dioxide and carbon monoxide.

10°C min^{-1}. It is seen that heavy weight loss due to decomposition is experienced by the sample above 275°C. Although the weight loss is continuous, the decomposition yields quite a spectrum of products. The gas chromatogram of the trapped volatiles, scanned from −50°C to 150°C, is reproduced in Fig. 6. The GC peaks are well-separated to permit identification by MS. The GC/MS analysis indicates that ethanol, ethyl acetate, ethyl acrylate, water, ethyl hexyl acetate, ethyl hexyl alcohol, and possibly also, trimethylcyclobutanone, nonyne and ethyl heptanal are evolved. The evolution profiles of these compounds are illustrated in Figs. 7 and 8. The ethyl acrylate and ethyl hexyl acrylate monomers which are due to depolymerization, are further plotted in terms of their base ion ($m/e = 55$) in Fig. 9. We see that this copolymer can be conditioned up to 210°C without degradation.

With the aid of the subsequent GC/MS analysis, we were also able to identify most of the volatiles coming off a petroleum coke sample as it was heated to 900°C under a helium atmosphere at 10°C min^{-1}. In Fig. 10, we notice from the percent weight change and DTG curves that the sample undergoes two major weight losses: (a) between 25 and ~ 500°C, and (b) from ~ 500 to 900°C. The shape of the DTG curve further indicates that these weight losses are from overlapping reactions. The volatile products separated by GC and identified by MS include water ($m/e = 18$), benzene ($m/e = 78$), toluene ($m/e = 92$) and ethyl benzene ($m/e = 106$) as shown in Fig. 10, and methyl naphthalene ($m/e = 142$), biphenyl ($m/e = 154$) and methyl biphenyl ($m/e = 168$) as shown in Fig. 11. In addition, the sample also appears to liberate nitric oxide ($m/e = 30$), sulfur dioxide ($m/e = 64$), carbon dioxide ($m/e = 44$) and carbon monoxide ($m/e = 28$) as illustrated in Fig. 12.

In a similar manner, the combination technique permitted us to characterize a sample of ethylene/maleic anhydride copolymer when it was heated to 250°C. The 4.5% weight loss (Fig. 13) is indicated by DTG to be probably the result of several processes. This is confirmed by the simultaneous MS and the subsequent GC/MS analyses. Some of the volatile products detected are chloroethylene ($m/e = 62$), benzene ($m/e = 78$), ethylene dichloride ($m/e = 98$) and water ($m/e = 18$), as demonstrated in Fig. 13, and benzoic acid ($m/e = 122$) and biphenyl ($m/e = 154$) as shown in Fig. 14.

It has been mentioned that by cross-referencing the GC/MS results to the real-time MS data, artifacts associated with trapping can be eliminated. Figure 15 shows the mass spectrum of a GC peak separated from the volatiles collected from an acid-treated carbon sample. The spectrum indicates the presence of nitrogen dioxide (NO_2). However, when cross-referenced with the real-time results, a contradiction was noticed as the latter suggested nitric oxide (NO) was liberated. In this case, it is obvious that the GC/MS result is fictitious since NO_2 can be formed easily from NO by oxidation. The evolution profiles of NO ($m/e = 30$) and other compounds such as water ($m/e = 18$), carbon dioxide ($m/e = 44$) and carbon monoxide ($m/e = 28$) are plotted together with the percent weight change and DTG curves in Fig. 16.

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