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ANALYSIS OF CURED CARBON-PHENOLIC DECOMPOSITION PRODUCTS TO INVESTIGATE THE THERMAL DECOMPOSITION OF NOZZLE MATERIALS

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ABSTRACT

This paper describes the development of a mass spectrometer/thermal analyzer/computer (MS/TA/Computer) system capable of providing simultaneous thermogravimetry (TG), differential thermal analysis (DTA), derivative thermogravimetry (DTG) and evolved gas detection and analysis (EGD and EGA) under both atmospheric and high pressure conditions. The combined system has been was used to study the thermal decomposition of the nozzle material that constitutes the "throat" of the solid rocket boosters (SRB).

is described

atomic mass units (amu). All data are presented in real time on a color or monochrome CRT. Multitasking features allow simultaneous data acquisition and processing. The system is also capable of functioning as the front panel of the console unit allowing the operator to set and adjust twenty one (21) parameters of the mass spectrometer from the keyboard of the computer. Other features include keyboard control of all tuning parameters, the ability to monitor up to 28 selected ions simultaneously, top acquisition speeds of up to 1000/amu/sec, subtraction of background gases, scaling, translation and normalization of data. The capability to search a mass spectra data base is an optional feature.

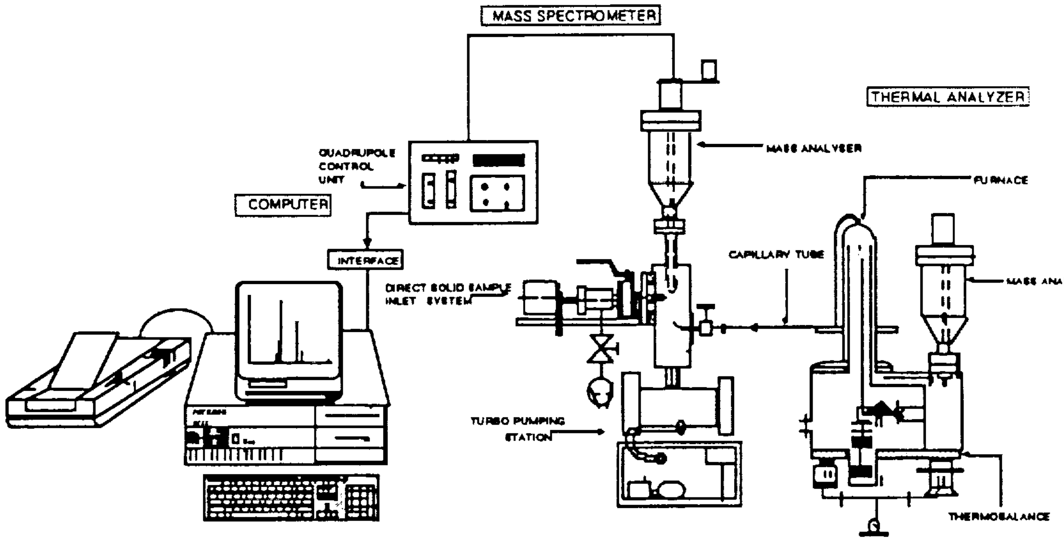


Figure 1. A Schematic Diagram of the Combined MS/TA/Computer System.

Through joint efforts with the Teknivent Corporation, low cost modifications have been made to the software and electronic interface of the Microtrace™ unit so that thermal data may also be obtained from the Mettler TA-2 thermoanalyzer. As a result of these modifications, the combined MS/TA/Computer system is able to acquire, monitor and process (in real time) TG, DTA, DTG, temperature and partial pressure data simultaneously with mass spectral data. By implementing these modifications, the need to re-plot weight loss vs. temperature curves has been eliminated; thermal data among different nozzle material samples may now be compared at the computer; weight loss curves may be superimposed upon mass chromatograms and hard copies of all data generated. Thermal data may also be monitored by the strip chart recorder of the TA-2 unit.

Again, through joint efforts with Teknivent, a second IBM-AT compatible microcomputer has been outfitted with a remote processing unit. Thus, data collected using the dedicated computer may now be transferred to the remote unit and processed. Overall, these modifications have increased production and facilitated data interpretation. The installation of the Teknivent Microtrace™ unit has vastly enhanced the capability of the MS/TA system to acquire and process mass spectrometric data on decomposition gases.

The MS-TA-Computer system has also been modified to allow partial pressure curves to be generated as part of the data provided by the thermal analyzer. This modification becomes significant when thermal decompositions are conducted under vacuum conditions.

ANALYSIS OF CURED CARBON-PHENOLIC DECOMPOSITION PRODUCTS TO INVESTIGATE THE THERMAL DECOMPOSITION OF NOZZLE MATERIALS

Introduction

Since the development of the first themrobalance by Honda in 1915, thermal analysis has become an important instrumental method in understanding the behavior of non-metallic materials. The method is especially important in understanding the properties of polymeric materials. For instance, the procedure has been used in determining the flexibility, impact strength, resistance to wear, oxidative stability, amount of additive, and cure time of polymeric materials. Thermal analysis also plays an important role in solving production and quality control problems and it has become an indispensable tool in thermal studies of strategic materials.

The workers in this laboratory have developed an MS/TA/Computer system which has been used to study the thermal decomposition of the nozzle material that constitutes the "throat" of the solid rocket boosters (1-5). This material consists of a carbon cloth impregnated with a modified phenolic resin in which certain additives have been added. The uncured prepreg material is built up in layers to form the throat of the solid rocket booster and then cured in place. Thermal stability of this cured material is most important in materials evaluation and in component failure analysis.

Prior to beginning this work, several workers had reported the coupling of a mass spectrometer with a thermoanalyzer (6-16). Relying on this information, a Balzers QMG-511 quadrupole mass spectrometer has been successfully coupled with a Mettler thermoanalyzer (TA-2). In addition, the mass spectrometer has been interfaced with a microcomputer. This has resulted in a versatile instrument system whereby mass spectral data on decomposition gases may be rapidly acquired and processed under programmed conditions. Data from the mass filter and other units of the spectrometer may be digitally transferred to the computer whereupon mass spectral data are generated and displayed on the CRT and/or produced as hard copies. The combined system is also capable of providing simultaneous TG, DTA, DTG as well as partial pressure changes when studies are carried out under vacuum conditions.

While commercial thermoanalyzers are capable of providing valuable thermal information, these instruments are usually incapable of providing information on the identity of decomposition products. Obviously, such information represents an important complement to the traditional thermal data and is often useful in expanding our understanding of the thermal behavior of materials.

The Mass Spectrometer/Computer Interface

The mass spectrometer/computer interface has been achieved using the Teknivent Microtrace™ system (Teknivent Corp.). This turnkey system consists of a dual card interface-controller and the software necessary to control, acquire and process data from the QMG-511 quadropole mass spectrometer. The interface card plugs into the BF-511 buffer of the mass spectrometer, while the controller card plugs into an IBM-AT (or one of the compatible systems). The MS/TA Computer system, which is schematically shown in figure 1, is capable of continuous or disjointed spectrum scanning up to 1023

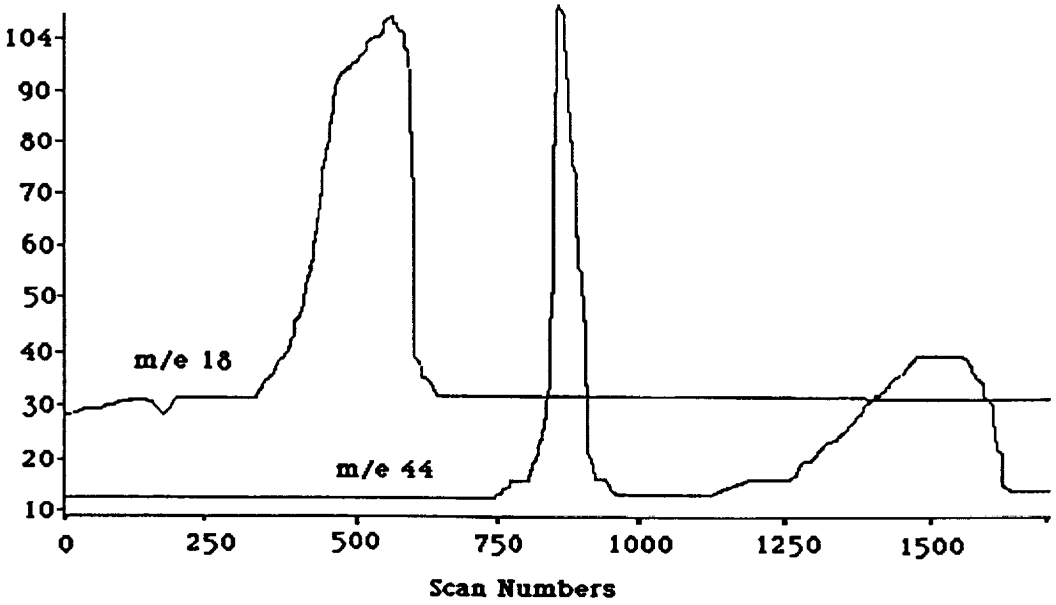


Figure 3. The Overlaid Mass Chromatograms for m/z 18 and 44 from the Thermal Decomposition of $CaC_2O_4 \cdot H_2O$ under Atmospheric Conditions (Note: the CO formed in the Second Decomposition Step Reacts with O_2 in the Air to form CO_2; thus, CO is Not Observed).

Based on the overlaid mass chromatograms shown in figure 3, three gas evolutions were observed as shown below. The first evolution consisted of water, followed by CO (which reacts with O_2 to produce CO_2). The last decomposition produced CO_2.

$$CaC_2O_4 \cdot H_2O \text{ -----------> } CaC_2O_4 + H_2O$$

$$CaC_2O_4 \text{ ----------> } CaCO_3 + CO$$

$$CaCO_3 \text{ -------> } CO_2 + CaO$$

The nature of the gases, their order of evolution, and the temperatures corresponding to each evolution were consistent with repeated values, thus confirming the accuracy and reliability of the system.

The Thermal Decomposition of Nozzle Material (FLX-D) Under Atmospheric Pressure Between 25 - 1000°C

A 106.55 mg powdered sample of nozzle material (called FLX-D) was placed in a 0.45 ml platinum crucible and positioned on the thermocouple crucible holder. The crucible holder is designed so that the "hot junction" of the thermocouple is in direct contact with the bottom of the crucible. The furnace was mounted over the sample and both sample and reference heated between 25 - 1000°C at a linear temperature rate of 8°C/min. The chamber of the mass spectrometer was monitored under computer control for fragment ions between 5-200 mass units. The thermal decomposition was conducted using

Another major enhancement to the MS/TA/Computer system includes the addition of a second mass analyzer which occupies a permanent position in the chamber of the thermobalance (figure 2). Prior to installing this second unit, it was necessary to transfer the mass analyzer from the vacuum chamber of the mass spectrometer to the chamber of the thermobalance when evolved gas studies were desired under high vacuum conditions. This cumbersome procedure often required a retuning of the resonance frequency generator, a procedure which was awkward and time consuming. With the second analyzer in place, evolved gas studies can now be undertaken under both atmospheric and high vacuum conditions at any pressure between with only a transfer of cables.

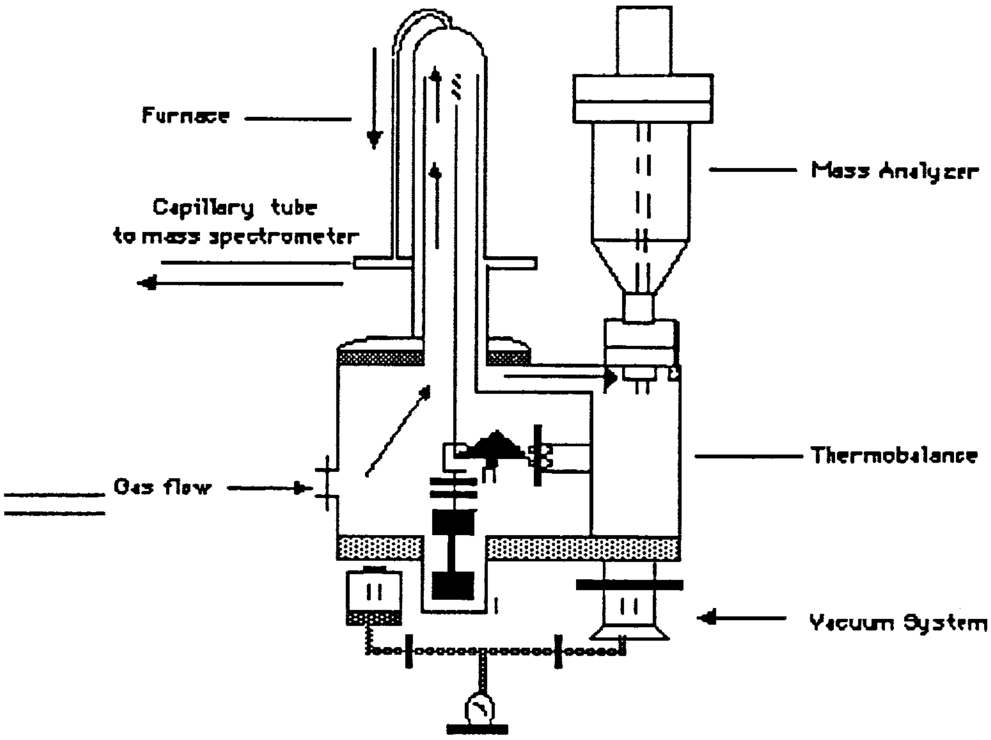


Figure 2. A Schematic Diagram of the Thermobalance of the Mettler Thermoanalyzer Showing the Second Mass Analyzer in the Vacuum Chamber.

Determination of the Accuracy and Reliability of the MS/TA/Computer System

The decomposition of $CaC_2O_4 \cdot H_2O$ has been studied by several workers (17-27) and its thermal decomposition profile is well known. Consequently, it was decided to use this material to determine the reliability and accuracy of the mass spectrometer unit of the combined system. In determining the accuracy and reliability of the unit, a sample of $CaC_2O_4 \cdot H_2O$ was placed in a 0.45 ml platinum crucible, and in a second identical crucible was placed an Al_2O_3 reference standard. Both materials were placed on the DTA sample holder and the sample and reference heated between 25 - 1000°C by the middle range temperature furnace. As the decomposition gases evolved, they were pulled into the chamber of the mass spectrometer through a heated capillary tube (figures 1 and 2). During the entire heating period, evolved gases between amu 1-55 were monitored using the computer/Teknivent system.

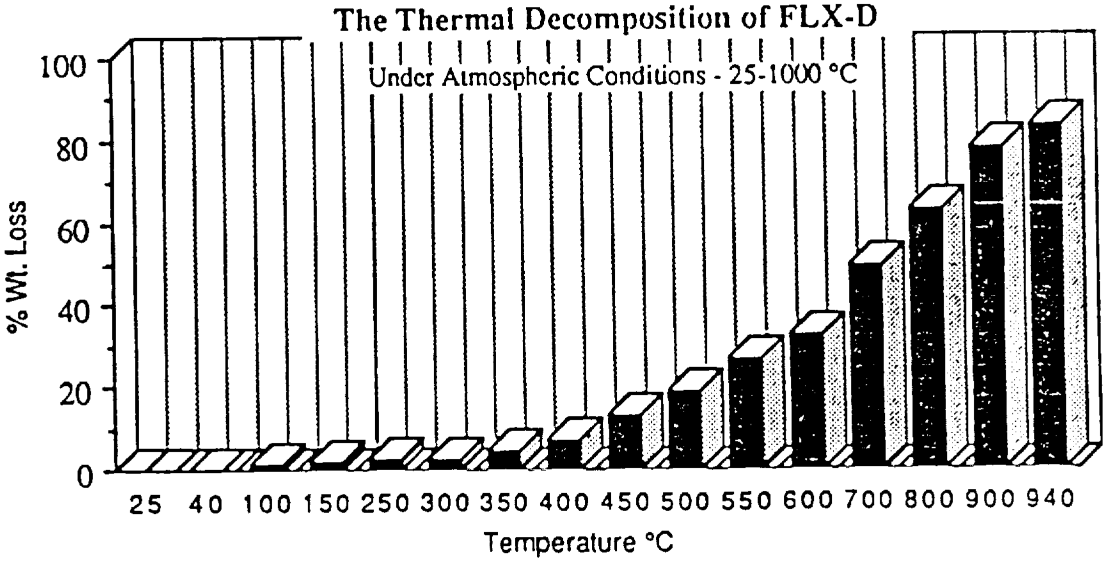


Figure 5. Bar Chart Showing the Thermal Decomposition of FLX-D Under Atmospheric Conditions Between 25 - 1000°C.

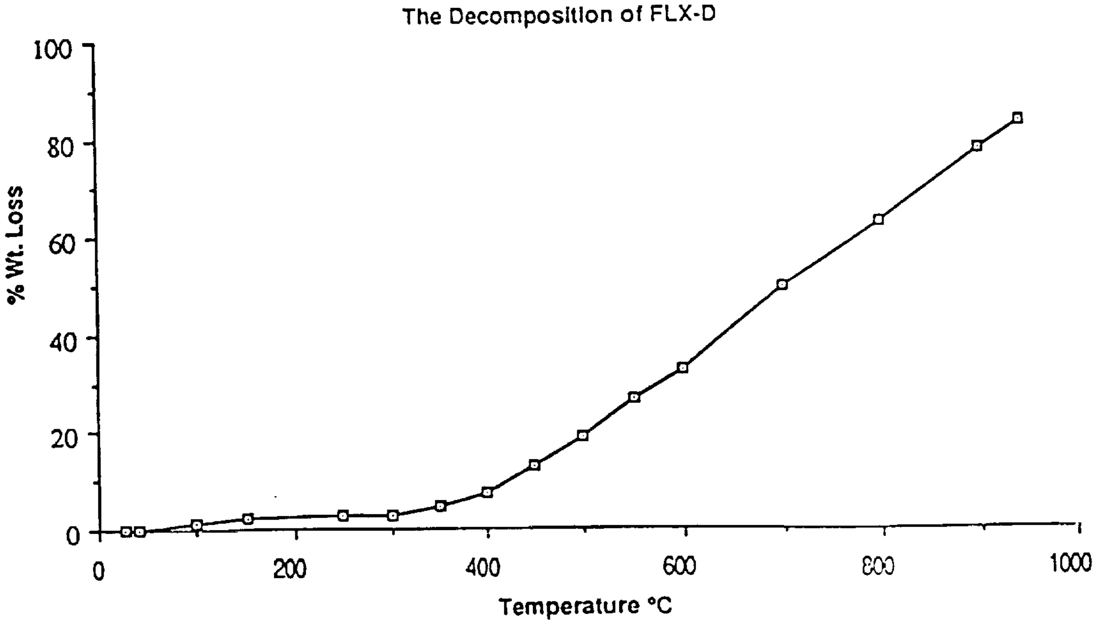


Figure 6. Replotted TG Curve, Showing the Thermal Decomposition of FLX-D Under Atmospheric Conditions Between 25 - 1000°C.

a non-discriminating gas inlet valve (figure 4) and a special dual side arm quartz furnace (figures 1 and 2). The non-discriminating inlet valve is a two stage pressure reduction gas inlet valve that allows the evolved gases to enter the chamber of the mass spectrometer without changing the ratio of the gaseous components or the chamber pressure. One end of a heated (200°C) one meter stainless steel capillary tube (with a diameter of 0.15 nm) was attached to the side-arm of the furnace and the other end to the non-discriminating gas inlet valve. The decomposition gases were swept out of the furnace by a stream of dry air which traveled through the thermobalance up the inner tube and to the side arm of the furnace (figure 2). Once the gases reached the side arm of the furnace, they were pulled through the heated stainless steel tube by a rotary vane pump attached to the non-discriminating valve. From the stainless steel capillary, the gases entered the non-discriminating valve and moved into the vacuum chamber of the mass spectrometer. In the chamber, the gases were ionized by electron impact and the positive ions accelerated into the quadropole filter where they were separated and detected in normal fashion.

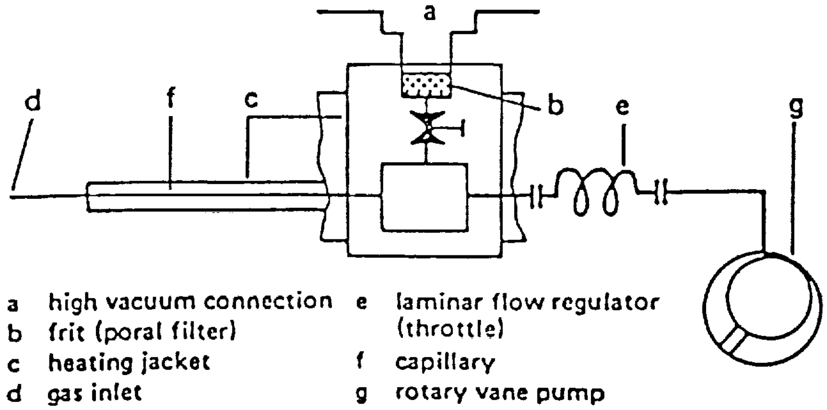


Figure 4. Schematic Diagram of the Non-Discriminating Gas Inlet System (Balzers High Vacuum Systems).

Discussion

Soon after heating, the nozzle material sample underwent a small weight loss which was attributed to either surface or occluded water as indicated by the bar chart in figure 5, the replotted TG curve in figure 6 and the overlaid mass chromatograms in figure 7. The water loss reached its maximum intensity near 375°C. Also, near 375°C, CO_2 was observed and its presence was evident for the remaining of the heating cycle (figure 7). No other evolved gases were observed.

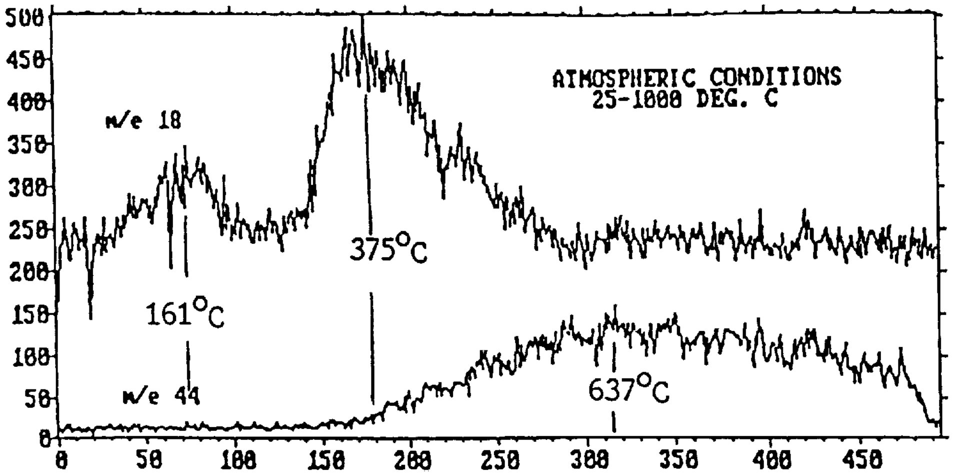


Figure 7. The Overlaid Mass Chromatograms for m/z 18 and 44 from the Thermal Decomposition of the FLX-D Nozzle Material Between 25 - 1000°C Under Atmospheric Conditions.

Evolved Gas Studies Between 35 –300°C Under High Vacuum Conditions.

The study of evolved gases under high vacuum conditions was conducted using the MS/TA/Computer system shown in figure 1; however detection of the decomposition gases was carried out using the mass analyzer which had been installed in the chamber of the thermobalance (figure 2).

Each of the seven nozzle material samples which were the object of this study was reduced to powder form, weighed and placed in a platinum crucible. An Al_2O_3 reference material was placed in an identical crucible and both sample and reference were placed on the DTA thermocouple. Sample size was kept to a specific weight level so as to maintain a pressure at the mass analyzer of no higher than 10^{-4} torr. Beyond this pressure, the proportionality between ion current and sample concentration is no longer valid. The standard middle temperature range furnace was sealed over the sample and reference and both the furnace chamber and chamber containing the mass analyzer were evacuated to approximately 1 - 5 x 10^{-6} torr using a pumping system consisting of both rotary and diffusion pump. Once the approximate vacuum had been reached, the sample and reference were heated between 25 - 1000°C at a linear rate of 5°C/min. Just prior to heating the sample, the mass spectrometer was placed under computer control to receive the mass spectrometric data output. The furnace pressure, temperature, DTA, TG, and DTG were monitored using the strip chart recorder located on the control unit of the thermoanalyzer, while the decomposition gases were monitored at the CRT. Evolved gas studies were carried out under programmed control between 10-200 amu using the Teknivent Microtrace™ system. During data acquisition the total ion current (TIC) curve and ion masses at m/z 18, 28, 32, and 44 were selected for direct monitoring.

Discussion

As indicated by figure 8 and Table 1, all seven samples of nozzle material underwent small weight losses between 25°C and approximately 300°C, under both atmospheric and high vacuum conditions. These initial weight losses were relatively small, ranging between 3.1 and 4.5% of the total weight of the sample (Table 1). Under high vacuum conditions, major decompositions of the nozzle material occurred near 350°C and near 300°C under atmospheric conditions.

Of the seven samples, FLX-D was arbitrarily selected for evolved gas studies between 25 - 300°C. On heating, the sample lost approximately 3.1% of its original weight as shown by the replotted TG curve in Figure 9. This weight loss did not include a 0.02% weight loss which was observed during pump down.

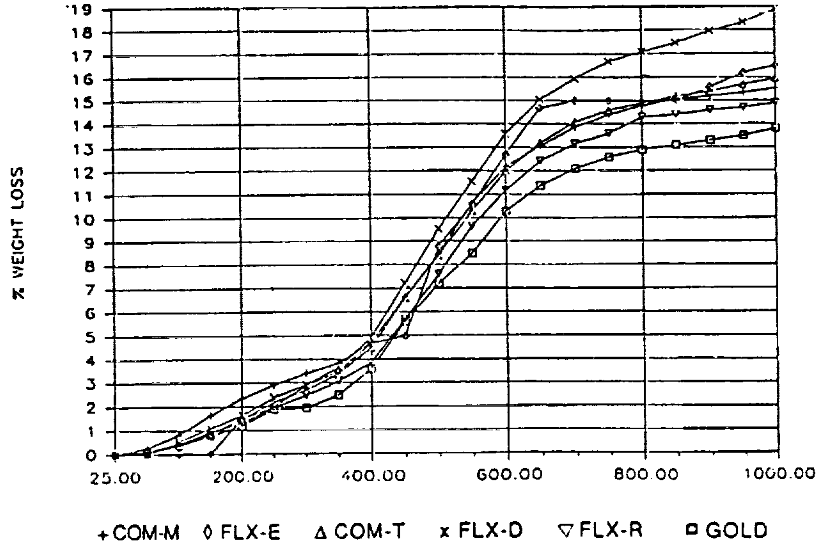


Figure 8. A Series of TG Curves Showing the Small Weight Loss of Different Nozzle Material Samples Between 25 - 1000°C When Thermally Decomposed Under High Vacuum Conditions.

Table 1. Percent Weight Loss of Several Samples of the Nozzle Materials When Thermally Decomposed Between 25°C and 300°C Under High Vacuum Conditions.

Sample	Temperature of First Weight Loss (°C)	% Weight Loss
COM-M	(35-40) - 240	3.9
FLX-R	40-180°C	4.0
FLX-E	(30-40) - 190	4.2
GOLD	35 -200b	4.1
COM-T	(35-40) - 150	3.1
COM-A	30-190	4.5

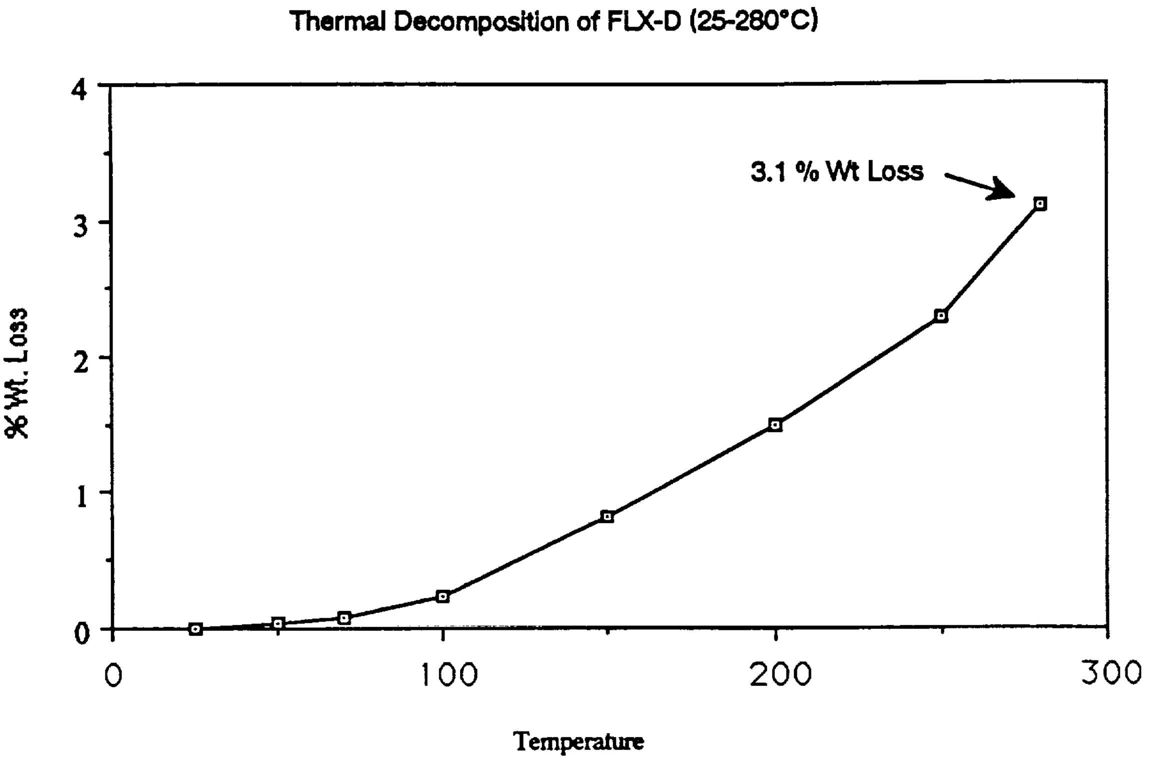


Figure 9. The Replotted TG Curve for the Thermal Decomposition of FLX-D Under High Vacuum Conditions Between 25 - 1000°C.

An Analysis of the Evolved Gases Resulting From the Decomposition of FLX-D Nozzle Material Between 25 - 300°C Under High Vacuum Conditions

The Total Ion Current -FLX-D

The total ion current (figure 10) was uneventful, revealing a slight but continuous increase in total ion abundance between the 25 - 300°C heating cycle.

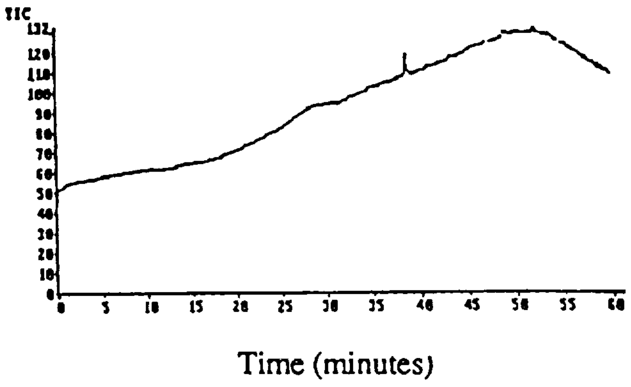


Figure 10. The Total Ion Current for the Thermal Decomposition of FLX-D Nozzle Material Between 25 - 300°C Under High Vacuum Conditions.

Mass 18

Based on a comparison of figures 11-14, the chromatogram corresponding to mass 18 revealed the largest overall increase in ion abundance, suggesting that the major weight loss of the FLX-D nozzle material during the 25 - 300°C heating cycle was due to water. The abundance of the m/z 18 ion over the heating range was sufficiently high that it partially influenced the overall shape of the TIC curve (compare figures 10 and 11). The suggestion that water constitutes the major weight loss of the FLX-D sample between 25 - 300°C was also supported by an analysis of the mass spectral histograms.

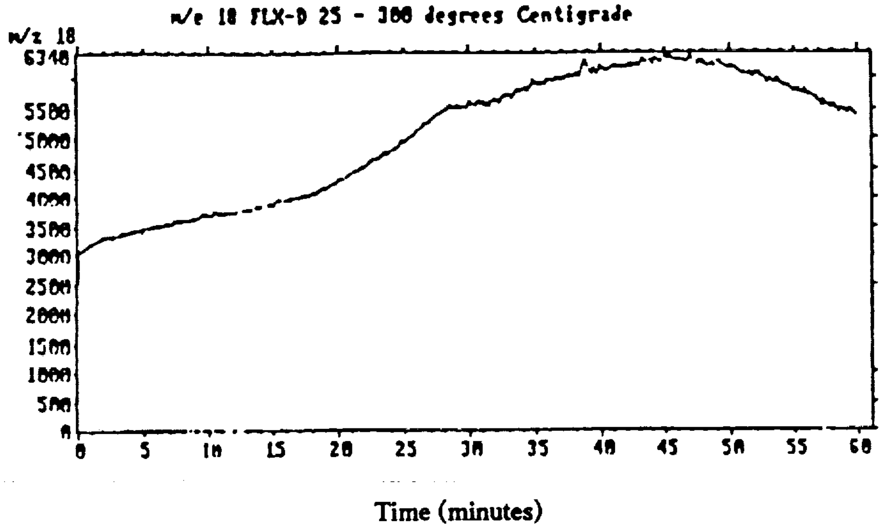


Figure 11. The Mass Chromatogram of m/z 18 (H_2O^+) Obtained from the Thermal Decomposition of the FLX-D Nozzle Material Between 25 - 300°C Under High Vacuum Conditions.

Mass 28

The m/z 28 mass chromatogram (figure 12) revealed only a slight increase in overall abundance between 25 - 300°C. However, near 150°C, the abundance of the ion began to increase and reached a maximum near the 300°C temperature limit. Based on separate studies which are not reported here, the mass 28 ion appears to have resulted, at least in part, from the fragmentation of isopropyl alcohol (5). This contention is based on observations that the m/z 28 ion and certain other fragments were common to both the evolved gases of the FLX-D sample and to the mass spectrum of isopropyl alcohol. These fragment ions appeared at m/z 27, 29, 31, 41, 42, 43, 44 and 45 (base peak in the mass spectrum of isopropyl alcohol). In addition, the shapes of the mass chromatograms corresponding to these ions revealed a distinct commonalty, suggesting that they probably resulted from the fragmentation of a common parent ion which may very well have been isopropyl alcohol. Still, the relative abundance of the mass 28 fragment (as indicated by the counts on the vertical y-axis) suggests that more than one mass 28 fragment may be implicated. Structural possibilities for the m/z 28 ion include CO^+, $H_2C = CH_2$, and N_2^+.

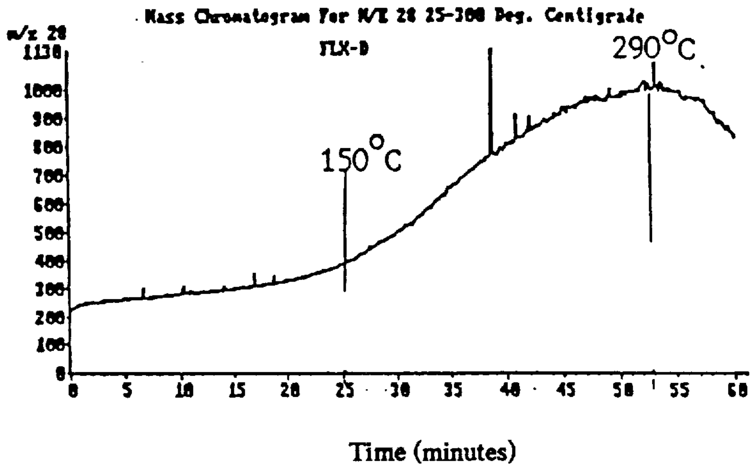


Figure 12. The Mass Chromatogram for m/z 28 Obtained from the Thermal Decomposition of the FLX-D Nozzle Material Between 25 - 300°C Under High Vacuum Conditions.

Mass 32

The mass 32 chromatogram (which is believed to be O_2^+) is shown in figure 13. Among the ions shown by the chromatograms in figures 11-14, this ion revealed the lowest increase in overall abundance over the 25 - 300°C heating range, suggesting the production of only a relatively small amount of O_2.

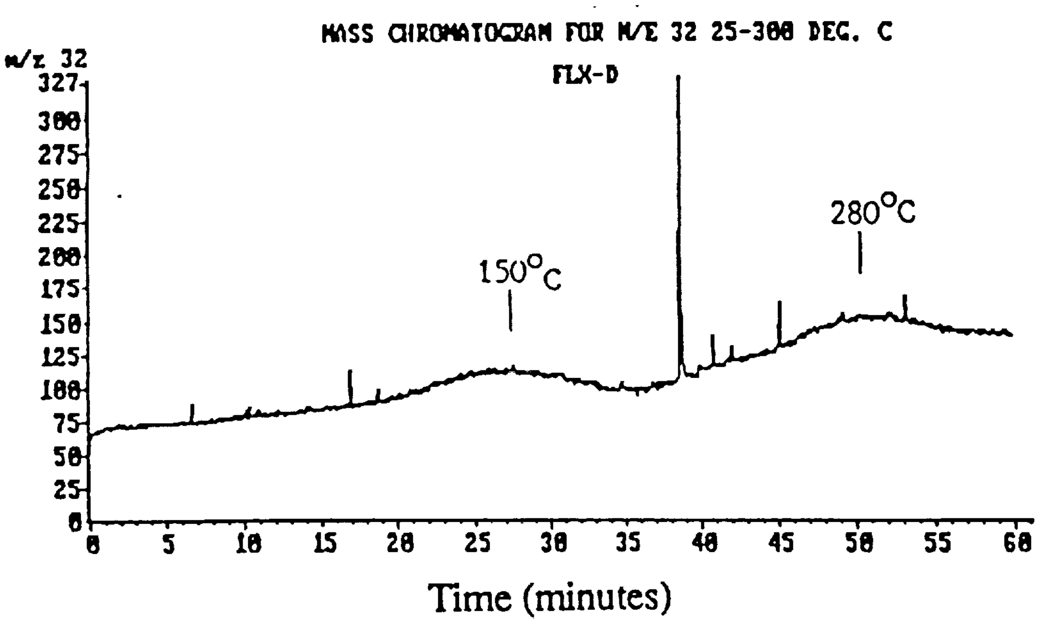
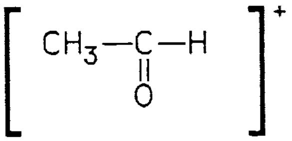


Figure 13. The Mass Chromatogram for m/z 32 (O_2^+) Obtained from the Thermal Decomposition of the FLX-D Nozzle Material Between 25 - 300°C Under High Vacuum Conditions.

Mass 44

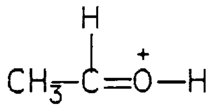
The chromatogram represented by mass 44 (figure 14) was almost devoid of ion activity until about 125°C. Between 125 and 170°C, a relatively sharp increase in abundance was observed. Near 170°C, the overall abundance of the ion decreased just slightly, followed by a relatively sharp increase which continued for the duration of the heating period. The presence of the mass 44 ion is consistent with the fragmentation of isopropyl alcohol and may represent, at least in part, the following "isopropyl" fragment or some modification thereof.



$$\left[\mathrm{CH_3{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}H}\right]^+$$

m/z 44

Fragment ions detected at m/z 15 (CH_3^+) and m/z 45 (shown below) also offer support to the argument that isopropyl alcohol is implicated in the thermal decomposition of the nozzle material. It should also be mentioned that the most abundant fragment ion in the mass spectrum of isopropyl alcohol is m/z 45.



$$\mathrm{CH_3{-}\overset{\overset{\displaystyle H}{|}}{C}{=}\overset{+}{O}{-}H}$$

m/z 45

As mentioned, other ions corresponding to the fragmentation of isopropyl alcohol were observed in the decomposition gases of FLX-D. These ions were located at m/z 19, 27, 29, 30, 38, 42, 43. A conclusive identification of the structure of the m/z 44 fragment must await a study of the nozzle material using TG/FTIR.

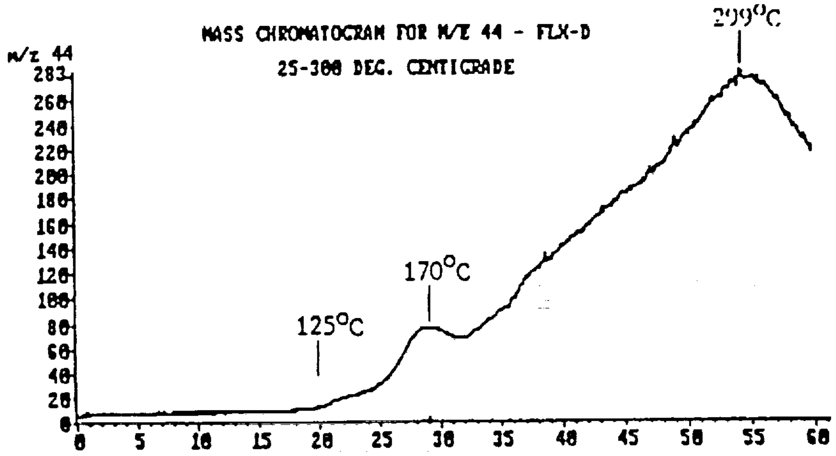


Figure 14. The Mass Chromatogram of m/z 44 Obtained from the Thermal Decomposition of the FLX-D Nozzle Material Between 25 - 300°C Under High Vacuum Conditions.

An Analysis of the Evolved Gases Resulting From the Decomposition of FLX-D Nozzle Material Between 300 - 1000°C Under High Vacuum Conditions

After obtaining evolved gas data on the FLX-D sample between 25 - 300°C, the same sample was heated between 300 - 1000°C (without cooling) and evolved gas data acquired and processed under computer control as previously described. The sample was scanned 1488 times between a mass range of 10-3000 amu at a rate of 5,478 seconds per scan, making a total heating time of approximately 140 minutes. During data acquisition, the TIC curve (Figure 15) and mass chromatograms corresponding to masses 18, 28, 32 and 44 were again monitored (figures 16-19).

The Total Ion Current

As expected, the total ion current (figure 15) obtained for the 300 - 1000°C run was totally different from what was observed for the 25 - 300°C run (compare figures 10 and 15). In addition, the maximum number of counts were larger for the 300 - 1000°C run, suggesting, as expected, that decomposition at the higher temperature range was more pronounced. For the 300 - 1000°C run the TIC curve (figure 15) revealed two levels of high ion abundance near 450 and 590°C. Beyond 590°C, there was a decrease in ion abundance, reaching a minimum near 850°C. Between 850 - 1000°C, the ion current was almost level.

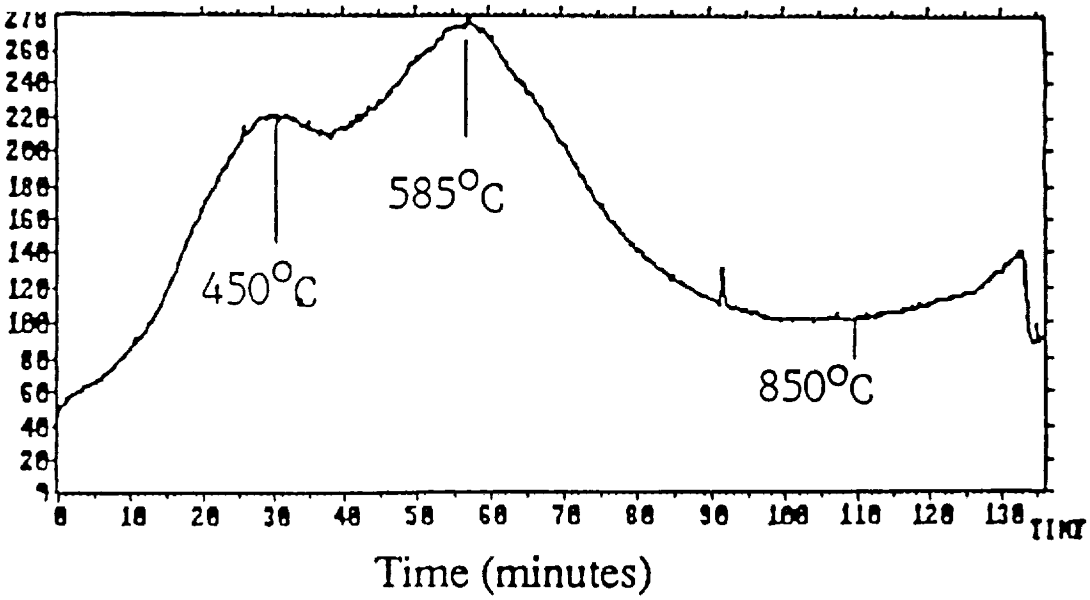


Figure 15. The Total Ion Current (TIC) for the Thermal Decomposition of FLX-D Under High Vacuum Conditions Between 300 - 1000°C.

Mass 18

The mass 18 fragment which is believed to be due to H_2O^+ was so abundant during the decomposition that it caused the mass chromatogram to go off scale near 450°C and reappear near 650°C (Figure 16). Based on the mass 18 chromatogram, it appears that water is also the major decomposition product between 300 - 1000°C, just as it was for the 25 - 300°C study. Thus, water appears to be the major overall decomposition product.

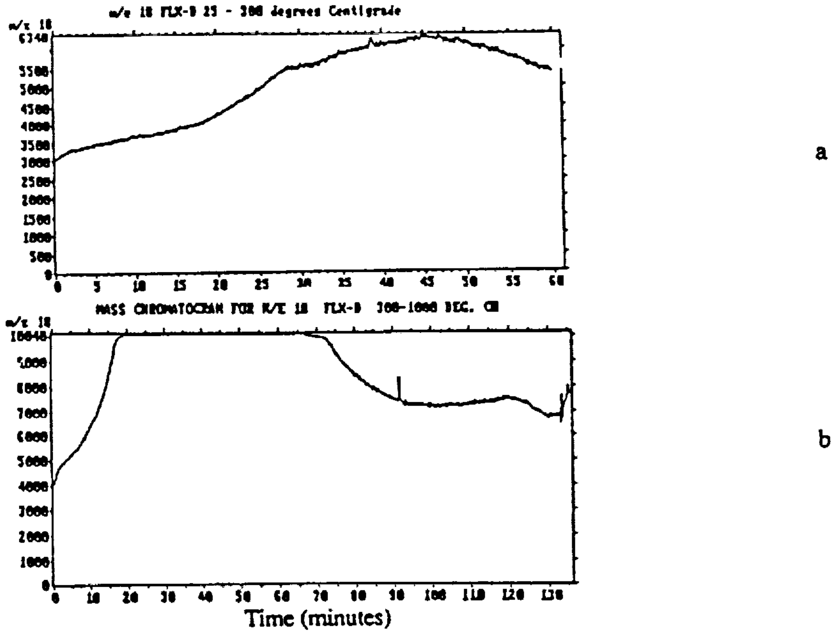


Figure 16. The m/z 18 Mass Chromatogram for the Thermal Decomposition of the FLX-D Nozzle Material Between (a) 25 - 300°C and (b) 300 - 1000°C Under High Vacuum Conditions.

It is believed that an amine curing agent is involved in the fabrication of the nozzle material, thus the mass 18 fragment may also include fragments attributed to NH_4^+

Again, the mass 28 chromatogram (figure 17) is believed to be related, at least in part, to the fragmentation of isopropyl alcohol. Structural possibilities include N_2^+, and $CH_2 = CH_2^+$ with CO^+ and/or $CH_2 = CH_2^+$, probably resulting from the decomposition of isopropyl alcohol. The abundance of this ion peaked near 595°C, followed by a fairly sharp drop.

Again, the overall abundance of the mass 32 ion (figure 18) was much smaller than for m/z 18, 28 or 44, reaching a maximum between 435 to 575°C

The mass 44 chromatogram (figure 19) revealed a number of peaks and valleys indicating changes in the relative abundance of the ion during the 300 - 1000°C heating cycle. The increase in abundance continued beyond the 300°C temperature limit of the first study, reaching a maximum near 435°C.

Other Fragment Ions Observed for the Thermal Decomposition of FLX-D Between 300 - 1000°C Under High Vacuum Conditions

Recognizing the versatility of the Teknivent Microtrace™ data collecting system, it was decided to recall from the acquired data, the mass chromatograms of all major fragments observed between the 10-300 amu limits. This resulted in a total of 114 fragment ions of varying relative abundances. Efforts to identify a number of these fragments have been reported elsewhere (5). Because of space limitations, discussion is prohibited in this paper.

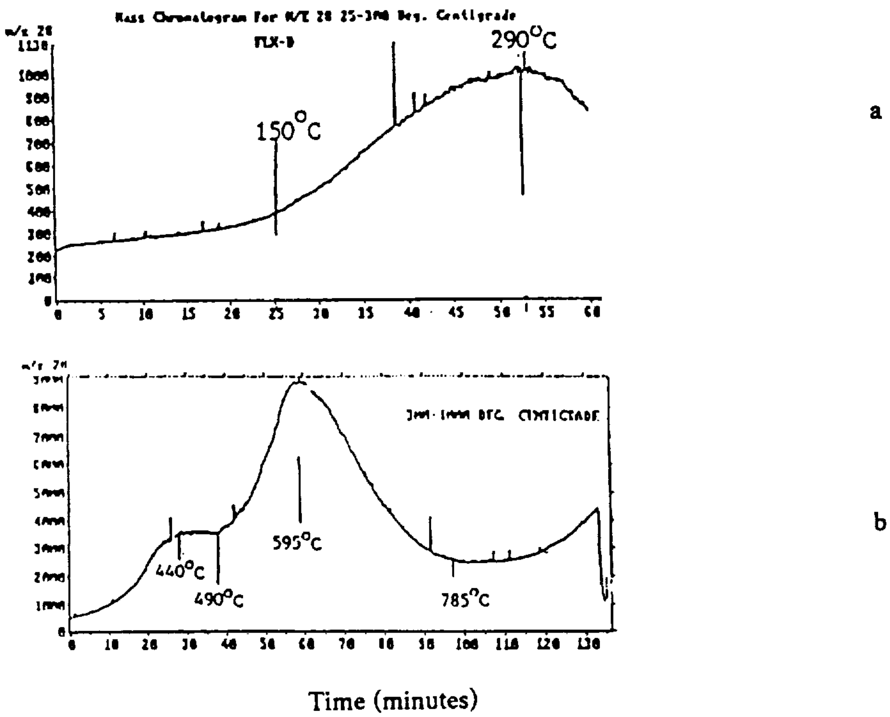


Figure 17. The m/z 28 Mass Chromatogram for the Thermal Decomposition of FLX-D Under High Vacuum Conditions Between (a) 25 - 300°C and (b) 300 - 1000°C.

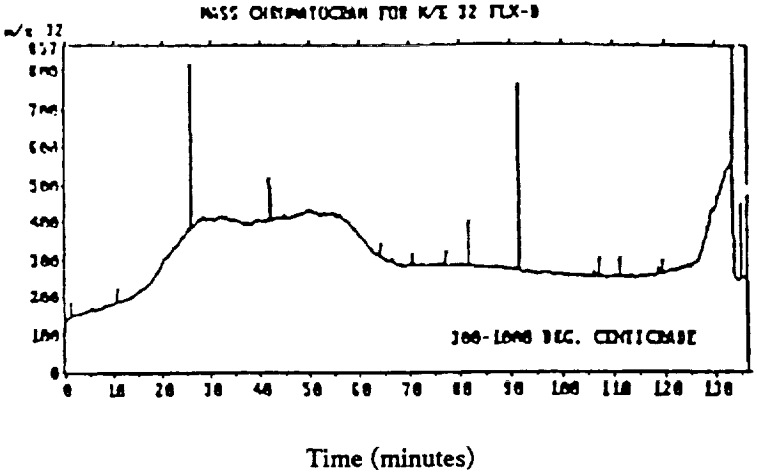


Figure 18. The m/z 32 Mass Chromatogram for the Thermal Decomposition of FLX-D Under High Vacuum Conditions Between 300 - 1000°C.

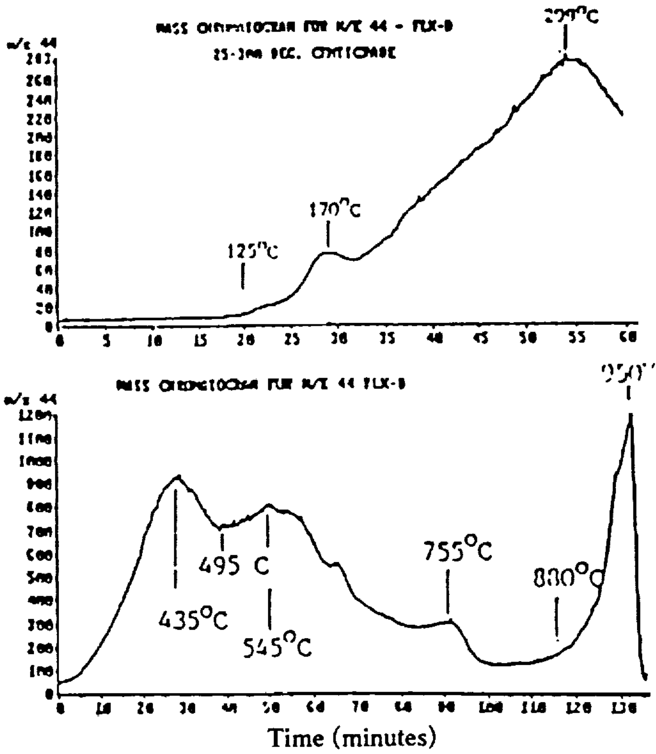


Figure 19. The m/z 44 Mass Chromatogram for the Thermal Decomposition of FLX-D Under High Vacuum Conditions Between (a) 25 - 300°C and (b) 300 - 1000°C.

Conclusions

The MS/TA/Computer system as presently configured has been shown to be a useful and reliable instrument for understanding the thermal decomposition of the nozzle material of the solid rocket booster as well as other non-metallic materials. However, as with any instrument system there are certain inherent limitations, most of which relate to the inability of the present system to make distinctions among different structures of identical masses. The problem becomes even more acute as efforts are made to make structural assignment to fragments of high molecular masses. FTIR/TG data would provide functional group analysis and would aid in the resolution of these structural problems.

The ideal system for studying evolved gas would be a combined TG/MS/FTIR system which has not yet been developed (28). A rough schematic of such a system is shown in figure 20.

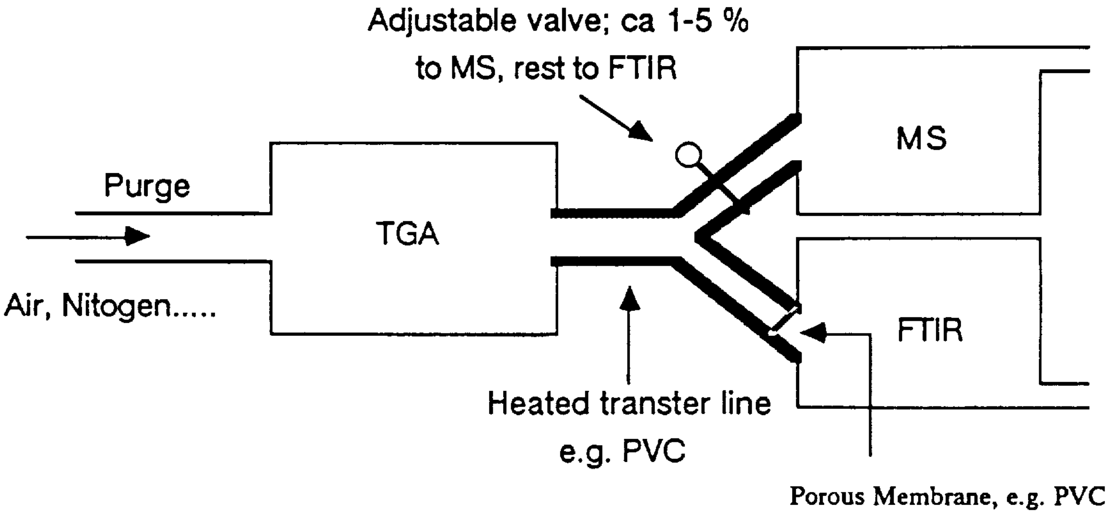


Figure 20. Rough Schematic of a Potential TG/MS/FTIR System (re-drawn from ref. 28).

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