

THERMAL AND CHEMICAL CHARACTERIZATION OF NON-METALLIC MATERIALS USING COUPLED THERMOGRAVIMETRIC ANALYSIS AND INFRARED SPECTROSCOPY



Timothy L. Huff
George C. Marshall Space Flight Center

ABSTRACT

Thermogravimetric analysis (TGA) is widely employed in the thermal characterization of non-metallic materials, yielding valuable information on decomposition characteristics of a sample over a wide temperature range. However, a potential wealth of chemical information is lost during the process, with the evolving gases generated during thermal decomposition escaping through the exhaust line. Fourier Transform-Infrared spectroscopy (FT-IR) is a powerful analytical technique for determining many chemical constituents while in any material state, in this application, the gas phase. By linking these two techniques, evolving gases generated during the TGA process are directed into an appropriately equipped infrared spectrometer for chemical speciation. Consequently, both thermal decomposition and chemical characterization of a material may be obtained in a single sample run. In practice, a heated transfer line is employed to connect the two instruments while a purge gas stream directs the evolving gases into the FT-IR. The purge gas can be either high purity air or an inert gas such as nitrogen to allow oxidative and pyrolytic processes to be examined, respectively. The FT-IR data is collected real-time, allowing continuous monitoring of chemical compositional changes over the course of thermal decomposition. Using this coupled technique, an array of diverse materials has been examined, including composites, plastics, rubber, fiberglass epoxy resins, polycarbonates, silicones, lubricants and fluorocarbon materials. The benefit of combining these two methodologies is of particular importance in the aerospace community, where newly developing materials have little available data with which to refer. By providing both thermal and chemical data simultaneously, a more definitive and comprehensive characterization of the material is possible. Additionally, this procedure has been found to be a viable screening technique for certain materials, with the generated data useful in the selection of other appropriate analytical procedures for further material characterization.

INTRODUCTION

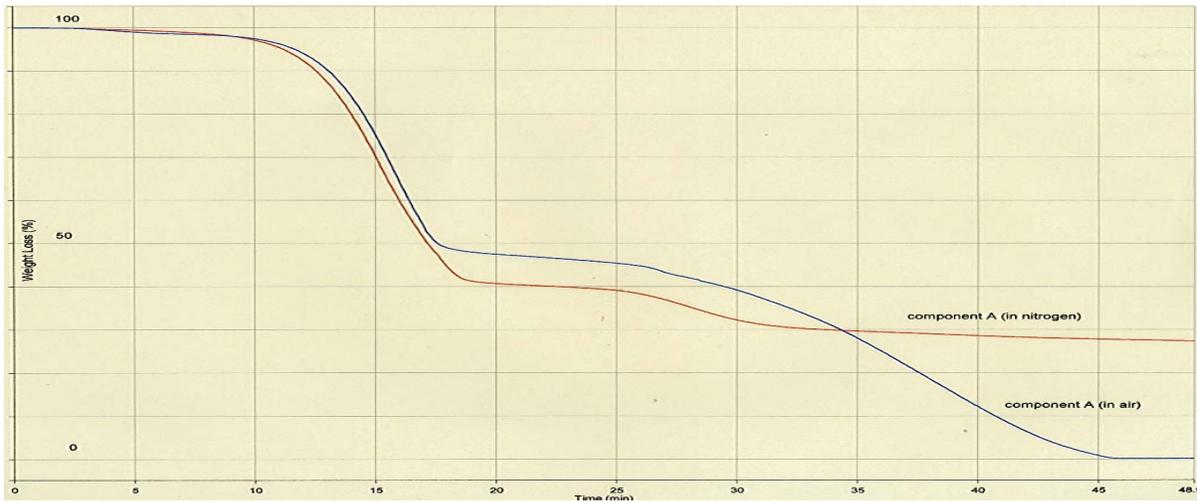
Thermogravimetric (TG) analysis is a well-established procedure for determining non-metallic material properties such as percent moisture content, percent ash content, percent composition, oxidative induction time, and decomposition kinetics. These characteristics are measured as the change in mass of a sample as it is heated, cooled or held at a constant temperature under a controlled atmosphere, that can be oxidative, inert, or a combination of both. In decomposition studies, the obvious objective is to reach temperatures sufficient to decompose the material, and thus is destructive in nature. Conversely, Fourier Transform Infrared (FTIR) techniques are especially useful in the chemical speciation of non-metallic materials simply because they are non-destructive in nature, providing reproducible, quantitative data while preserving the sample for further testing. However, FTIR is also a proven technique for identifying chemical constituents in gas phase as well. Thus these two techniques can be complementary to each other, with the gases generated during material decomposition in the TG available for chemical speciation by FTIR techniques. Specific applications using these combined techniques are presented, with the versatility and limitations further discussed.

PRESENTATION

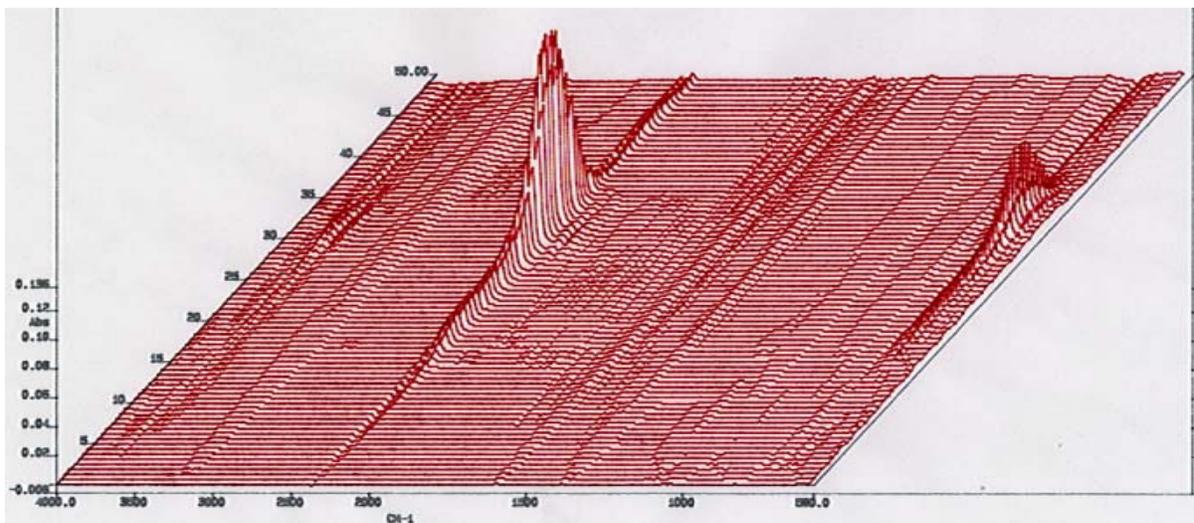
The coupled thermogravimetric analyzer (TGA) and FTIR are shown below. Briefly, evolving gas generated in the thermogravimetric analyzer (right side) during material decomposition is purged through a heated transfer line into a heated gas cell within the FTIR. The carrier gas may be either high purity air or an inert gas such as nitrogen to allow oxidative and pyrolytic processes to be examined, respectively. A liquid nitrogen-cooled detector is employed for identification of chemical groups, owing to specific functional group/wavelength interactions. For example, a non-aromatic carbon-hydrogen (C-H) group interacts in the infrared region at a wavelength range of $3000\text{-}2800\text{ cm}^{-1}$.



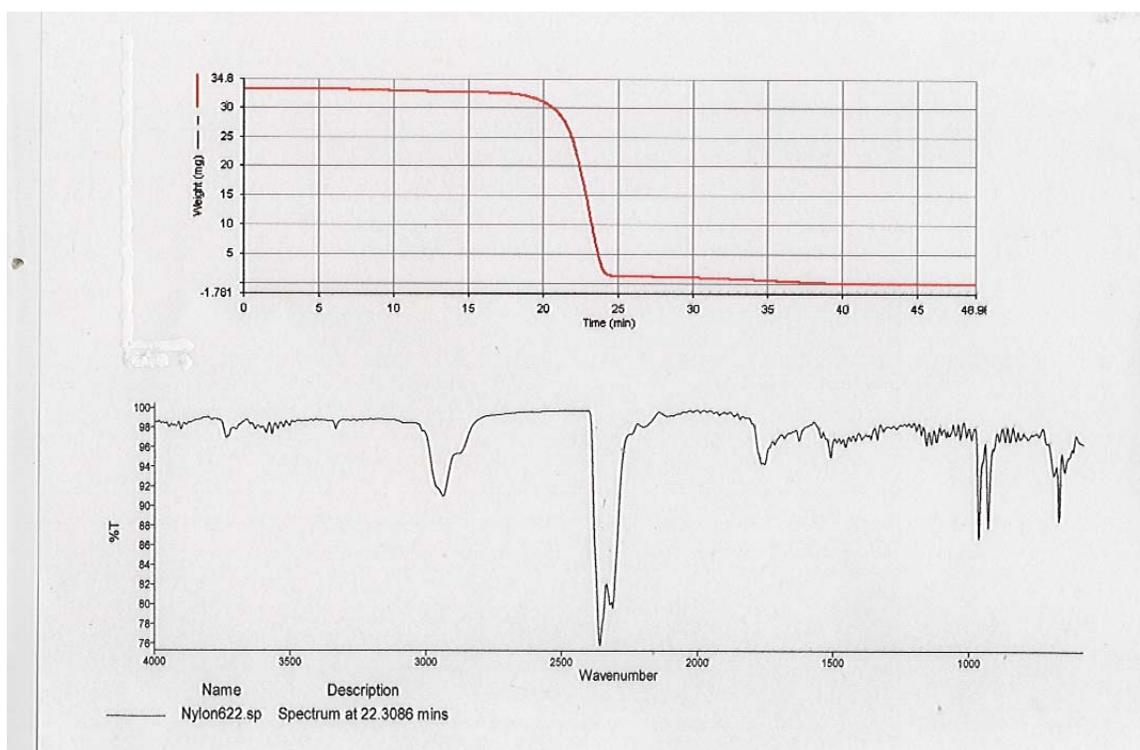
Data generated during the TGA run is presented as a X-Y plot with the ordinate represented as the percent weight of the sample versus run time on the abscissa. This is shown graphically below. The two weight loss curves shown are of the same sample, the difference being the purge gas used for each run. As can be seen, initial decomposition of this sample was similar in both atmospheres, suggesting pyrolytic decomposition. As heating progressed a weight loss was again observed in the sample heated in the oxidative atmosphere, indicating an oxidative process.



During the decomposition process, the evolving gases directed to the FTIR are analyzed real-time for chemical groups. At the end of a run, the data can be presented as a “stacked plot” that presents the spectral data plotted against time throughout the heating cycle for the sample. This allows for the observation of increases and decreases in individual chemical groups (based on peak height and location) as the run progresses. An example of such a plot is presented below.

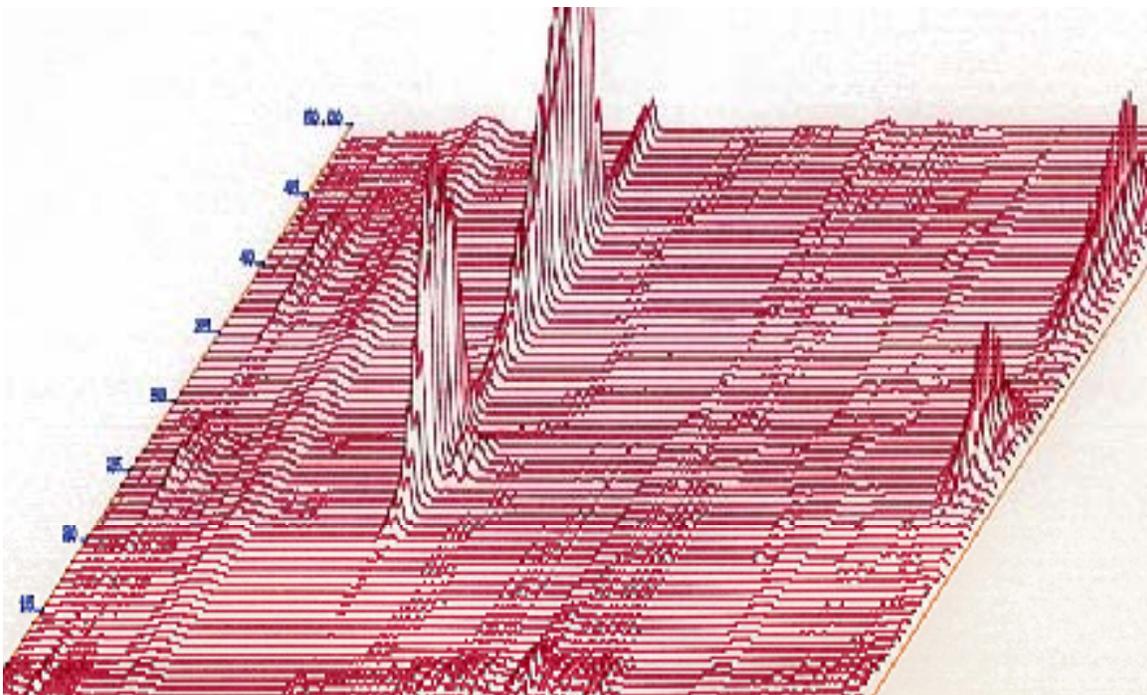
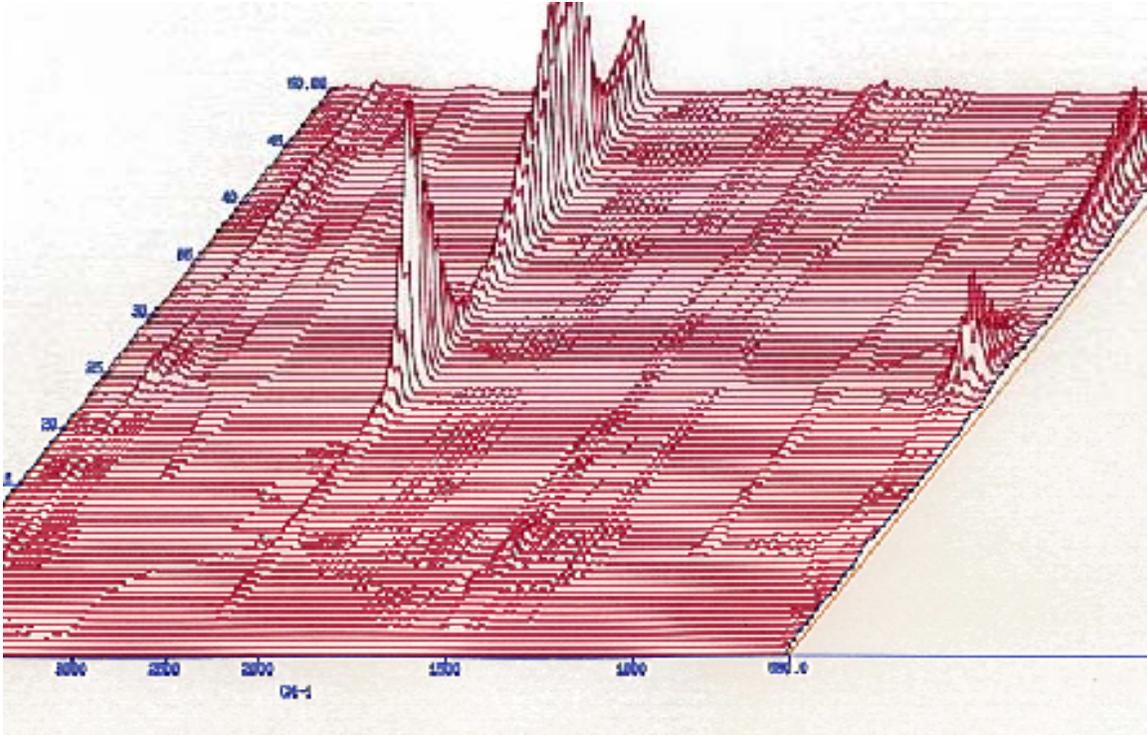


Additionally, weight loss data can be incorporated into the spectral data, with specific “slices” in the plot generated that correlate individual point-in-time spectra with observed weight changes. In the example below, a spectrum collected during a weight loss event occurring approximately 22 minutes into the run is shown. By observing the peak locations on the X-axis, information on the types of chemical groups evolving at that time can be attained. In this example, the observed peaks indicate the presence of nitrogen-hydrogen groups, non-aromatic carbon-hydrogen groups, carbon dioxide, carbon monoxide and carbonyl (C=O) groups.

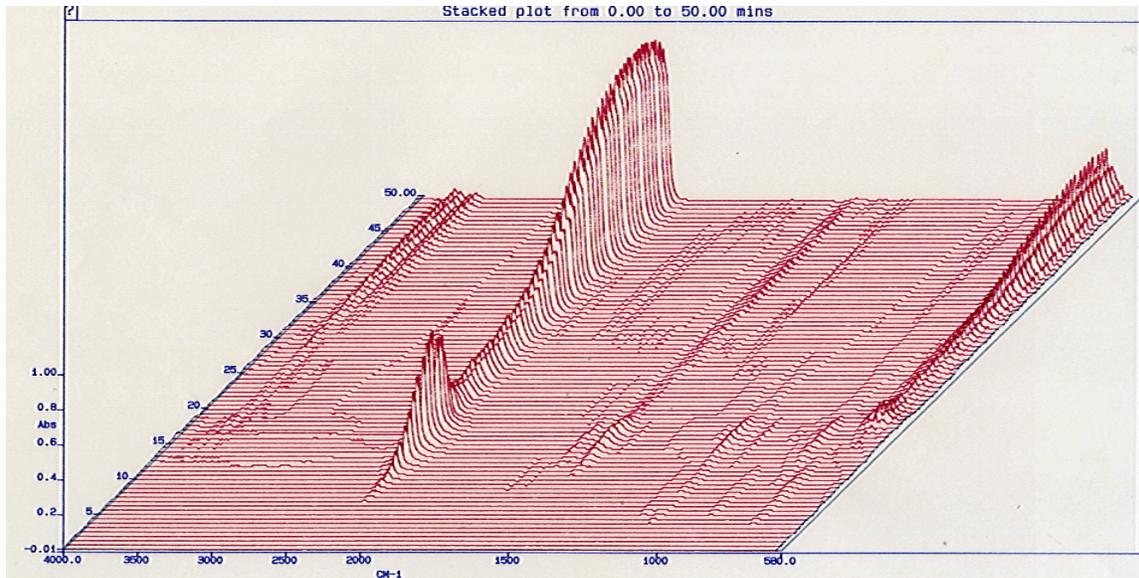


Interpretation of the spectra is usually qualitative with only the presence or absence of specific functional groups noted. However, semi-quantitative estimates of functional group concentrations can be made from spectral peak height and area information. From the example above, a strong peak is observed at approximately 2400 cm^{-1} . This region corresponds to the presence of carbon dioxide and is often observed in runs conducted in an oxidizing environment. This is commonly due to sample charring, with the resulting carbon being oxidized further to carbon dioxide. The reactive nature of this environment can also result in loss of functional group information if the group is susceptible to oxidative effects. In the first of two stacked plots below, the sample was run in an oxidative atmosphere with the expected prominent carbon dioxide peak at 2400 cm^{-1} observed. Sample charring is indicated by the recurrence of carbon dioxide in the latter stages of the run. The second plot, run in an inert atmosphere, shows small additional peaks at wavelengths just below that of carbon dioxide during the initial decomposition

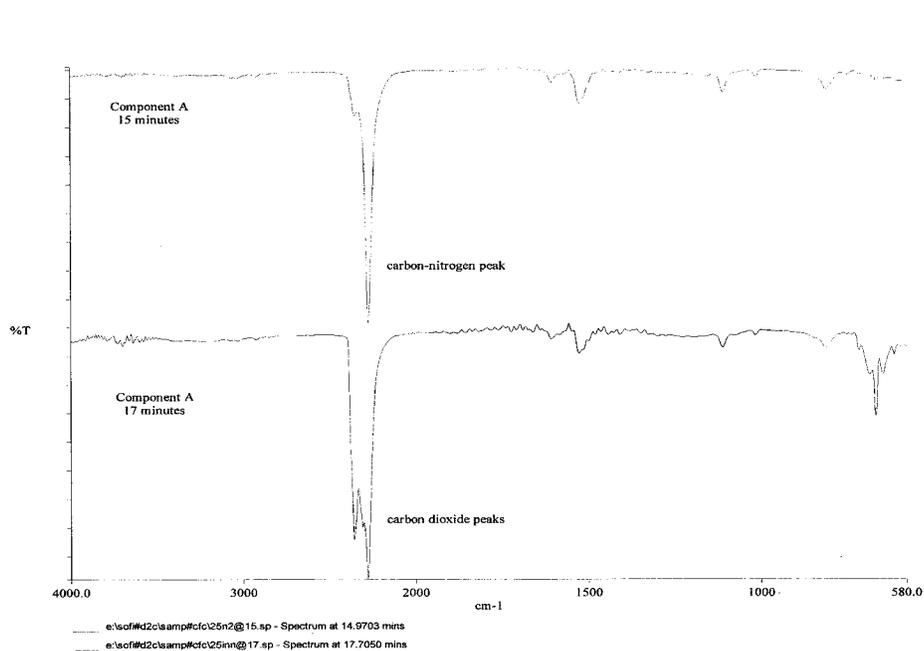
step. These peaks are indicative of carbon monoxide, which are not seen in the oxidative environment due to rapid oxidation to carbon dioxide solely.



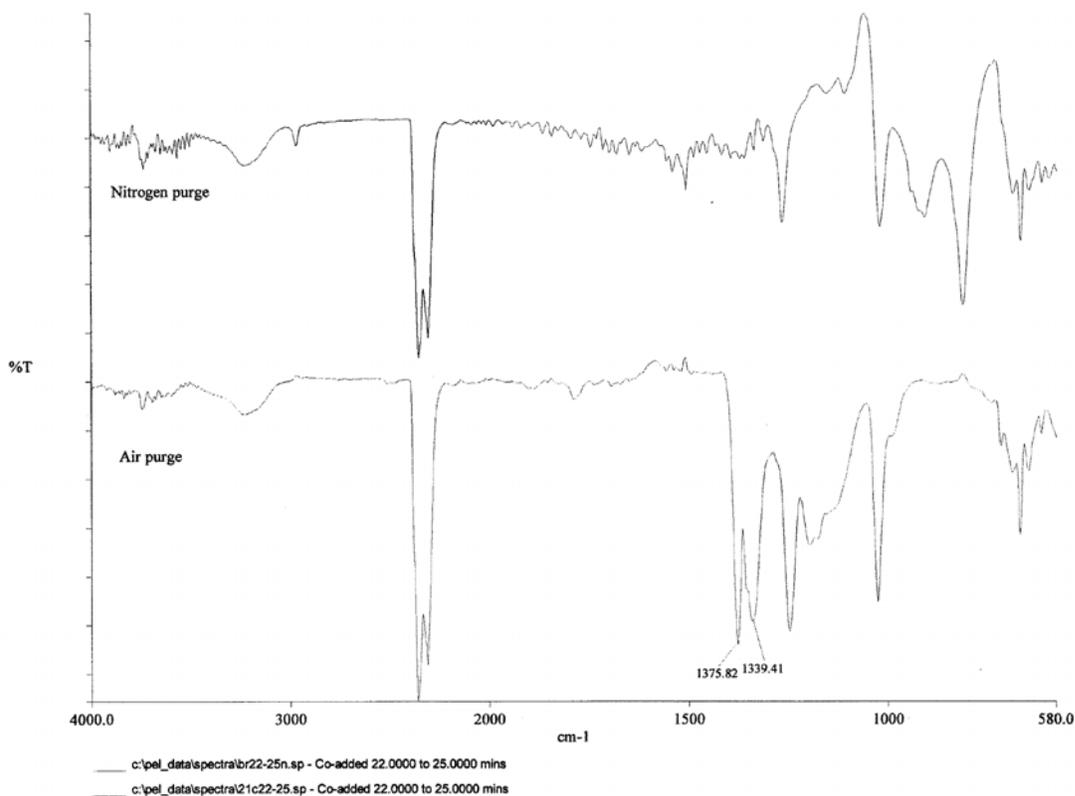
In some instances, the presence of carbon dioxide can also have a masking effect on other functional groups that locate closely to the carbon dioxide peak. Examination of the stacked plot below indicated that sample decomposition was largely associated with the release of carbon dioxide, again seen by the characteristic peak at 2400 cm^{-1} .



Closer examination of the spectra on a scan-by-scan basis actually revealed the presence of a carbon-nitrogen peak co-locating within the carbon dioxide region. The peak was short-lived and could have been easily overlooked.



There are instances, however, when an oxidizing environment may actually provide more information than can be obtained in an inert purge atmosphere, as was observed in a sample containing disulfide groups. Diatomic groups such as these are largely infrared inactive and thus not readily identifiable by standard FTIR means. Analysis of this sample is shown below with runs in both nitrogen and air presented. In the inert nitrogen atmosphere multiple functional groups are observed, none of which are identified as disulfides. When run in air, however, the evolving disulfides reacted with the oxidizing atmosphere, producing sulfoxide groups. These groups are infrared active, producing strong spectral peaks at 1375 and 1339 cm^{-1} . By inference, the presence of sulfoxide peaks indicated decomposition of the disulfide groups.



The example cited above represents a selective application of the TGA-FTIR, where specific information was required. This procedure has also been found useful in some instances as a screening tool, with the information obtained beneficial in the selection of other thermal test procedures. For example, a material exhibiting a low decomposition temperature would suggest a low melting point as well. If this information is required for a sample, Differential Scanning Calorimetry (DSC) may be an appropriate technique since the instrument can operate at subambient temperatures. Conversely, Differential

Thermal Analysis (DTA) may be preferred for materials exhibiting higher decomposition temperatures as this instrument has a higher operating temperature range. Examination of the spectral plot may determine if the decomposition event is due to breakdown of chemical constituents or sample charring, which may also influence the analysis chosen. Analysis of the spectral data will also provide some qualitative data regarding the organic and inorganic nature of the material, which can be useful in the selection of appropriate quantitative chemical procedures.

CONCLUSIONS

The use of thermogravimetric analysis in tandem with Fourier transform infrared spectroscopy allows for the determination of gaseous decomposition products evolved from nonmetallic materials during heating. Thus, not only are the thermal properties of a material examined, but also specific chemical species evolved during decomposition are identified. This can be accomplished in air or inert gas atmosphere, allowing either oxidative or pyrolytic processes to be studied. Spectra collected during an oxidative run are usually characterized by a predominant carbon dioxide peak due to oxidation of some evolving carbon constituents with the air or sample charring. An inert atmosphere generally provides more functional group information, as the evolving species do not react with the atmosphere. The spectral data is largely qualitative, although some semi-quantitative estimates can be made based on spectral intensity. Aside from its use as an analytical tool, this procedure has application as a screening technique in some instances; with the generated data useful in the selection of other appropriate procedures for further material characterization.