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GASEOUS PYROLYSIS PRODUCTS IDENTIFIED
BY COMBINED THERMAL AND
MASS SPECTROMETRIC ANALYSES

Keith J. Grossaint

Quality,
SERVICE LABORATORIES,
MASS SPECTROMETRY GROUP

DOW CHEMICAL U.S.A.
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U. S. ENERGY RESEARCH AND
DEVELOPMENT ADMINISTRATION
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SUBJECT DESCRIPTORS

Outgas Analysis
Thermal Analysis
Pyrolysis
Mass Spectrometer
Flame-Retardant Additives
Toxic Vapors
Methacrylic

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GASEOUS PYROLYSIS PRODUCTS IDENTIFIED BY COMBINED THERMAL AND MASS SPECTROMETRIC ANALYSES

Keith J. Grossaint

Abstract. A combined thermal analysis and mass spectrometric analysis (TA-MS) capability developed in the Mass Spectrometry Laboratory at Rocky Flats is described. The technique was adapted for two different instrumental systems to give optimum use of portability and high-resolution capability of the available thermal analysis and mass spectrometer instruments. The TA-MS method was developed for dynamic outgas analyses, resulting in correlations of evolved gases with observed thermal events and postulated decomposition mechanisms. In addition, the method proved especially useful for characterization of flame-retardant additives in Plexiglas transparent window materials and outgas of flammable vapors for a woven-glass laminate structural material.

INTRODUCTION

The development of a combined thermal-mass spectrometric analysis (TA-MS) capability at Rocky Flats was necessary to evaluate materials and compounds used in structures and processes for potential hazards (flammability and toxicity), prior to installation or use. Simultaneous determinations of outgas information and thermal properties were not available until recently, when analyses of the effluent from thermal analysis cells by infrared and mass spectrometric techniques were reported.^{1, 2, 3, 4} The early emphasis was on the identification of volatiles from thermal decomposition of glove-box windows and gloves,

gasket elastomers, plastic bags and containers, and products from the pyrolysis of waste. The thermal investigations required a determination of the order of gaseous evolution, as well as component identity.

The determination of gasses evolved during thermal analysis was desired because the sample could be pyrolyzed at atmospheric pressure in an inert or other controlled atmosphere instead of the *in vacuo* conditions of pyrolysis for normal mass spectrometric analyses. (The latter gave results that were often difficult to correlate with thermal properties obtained by other methods.)

Dynamic analysis was preferred over static trapping of evolved gases to distinguish between the observed thermal events. The temperature dependence of gas evolution was important for characterization of flame-retardant additives and for determining the decomposition mechanism under different (oxidizing, reducing, inert, or vacuum) conditions.

The problems inherent to combining mass spectrometric identification with thermal analysis result from the difficulty of transferring the evolved gases from the thermal analysis cell at high temperature and near one atmosphere pressure to the ion source of the mass spectrometer at 10^{-6} torr pressure. [For SI (metric) use: 1 torr = 133 pascals.] The report describes the technique used to overcome these problems and gives some examples of data obtained by the TA-MS method.

INSTRUMENTATION

DuPont Spectrometer and Thermal Analyzer:

One of the two TA MS systems currently in operation at Rocky Flats employs the DuPont

¹ Fred Zitomer, "Thermogravimetric-Mass Spectrometric Analysis," *Analytical Chemistry* 40:1091. 1968.

² R. S. Gohlke and H. G. Langer, "Thermal Analysis by Mass Spectrometry," *Analytical Chemistry* 37:25A. 1965.

³ W. W. Wendlandt and T. M. Southern, "An Apparatus for Simultaneous Gas Analysis," *Analytical Chemistry* 32:405. 1965.

⁴ C. H. Griffiths and M. S. Walker, "A Combined Differential Thermal Analysis and Spectrophotometric Cell," *Review of Scientific Instruments* 41:1313. 1970.

21-110B high resolution mass spectrometer (DuPont Instruments, E. I. du Pont de Nemours Company, Incorporated, Monrovia Operations, Monrovia, California) and the three modular thermal analysis cells of the DuPont-990 Thermal Analyzer (DuPont Instruments, E. I. du Pont de Nemours Company, Incorporated, Wilmington, Delaware).

The Mass Spectrometer has Mattauch-Herzog double focusing geometry with resolving capability of 5000 under normal operating conditions. Mass scanning is done magnetically at a normal scan rate of 0.2 octaves per second. The best feature of this spectrometer is the high resolution capability which allows identification of ions from different molecules at the same nominal mass, [as the hydrogen cyanide ion (HCN^+) in the presence of C_2H_3^+ ion at mass 27, or acetic acid in the presence of ethanol amine, carbonyl sulfide, or methyl hydrazine fragments at mass 60, etc.], and the collection of ions of high mass [mass per charge (m/e) >1000 easily collected and resolved]. The gas-inlet manifold was modified to permit bypassing the molecular leak with continuous sampling of the effluent from the TA pyrolysis furnace.

The DuPont-990 Thermal Analyzer consists of a control-recording unit with three remote cells:

1. Low temperature Differential Thermal Analysis (DTA) (-120 to 500°C).
2. High temperature (0 to 1200°C) DTA.
3. Thermal Gravimetric Analysis (TGA) (0 to 1200°C).

The three remote modules cannot be operated simultaneously, and this limits the extent of thermal data collected, but the portability of the modules permits placement close to the ion source of the mass spectrometer. The TGA module has a horizontal balance and horizontal sweep of carrier gas while the carrier gas flows vertically over the sample in the DTA cells.

AEI Spectrometer and Mettler Thermal Analyzer:

The second TA-MS system consists of an AEI MS-20 Mass Spectrometer (AEI Scientific Apparatus, Incorporated, Elmhurst, Illinois) coupled to a Mettler Thermoanalyzer 2 TGA-DTA-DTG instrument (Mettler Instrument Corporation, Princeton, New Jersey).

The MS-20 Mass Spectrometer is a portable, 180-degree, single-sector, electrical-scanning instrument. The resolution capability of 240 (at mass 240) permits identification of unit masses in the range 2 to 250 mass units. The lower resolution requires longer scan periods than with the DuPont 21-110B, and sample temperature may rise 10°C during a scan of 200 mass units (at the programmed rate of 10°C per minute). The gas inlet was modified to permit continuous sampling of the TA gaseous effluent.

The Mettler Thermoanalyzer-2 (TA) is a high-sensitivity thermal balance with the capability to perform simultaneous differential thermal and thermogravimetric analysis. The furnace was modified to permit direct dynamic sampling of the carrier gases which flow vertically from below the sample. The Mettler cell must be placed on a fixed, stable bench to maintain the balance stability. Longer distances are necessary between the TA cell and mass spectrometer. The ability to collect high quality TGA and DTA information simultaneously is an important advantage of this system.

Both TA-MS systems employ similar techniques for the transfer of gaseous effluent from the TA cell to ion source of the mass spectrometer (Figure 1). The gases are taken from directly over the sample in a resistance-heated 0.063-inch outside diameter stainless-steel transfer tube. The other end of the transfer tube is projected into a 0.25-inch T-fitting interface to allow differential pumping of the effluent gas. The flow of gas from the TA cell is controlled by a variable leak valve on the differential pumping line. A side stream from this flow is leaked into the ion source via a metering valve to maintain the desired ion-source pressure. The entire interface is heated by temperature-controlled heating tape or resistance

Legend

TGA – Thermal Gravimetric Analysis.
 DTA – Differential Thermal Analysis.
 DTG – Derivative Thermogravimetric Instrument.

FIGURE 1. Schematic of the Thermal Analyzer and Mass Spectrometric System.
 (a) DuPont System, (b) Mettler System, and (c) Interface and Mass Spectrometer.

heating to about 200 °C to prevent condensation. A short length of capillary tubing may also serve to meter gases into the ion source, but variations in flow cannot be controlled.

The distance between the TA cell and the ion source is somewhat critical because adverse effects such as decomposition and combustion of the sample can take place on the heated stainless steel surface of the transfer tube. When shortening the

transfer tube is not possible, a more fragile (and therefore, less desirable) glass system or silanized metal tubing must be used. Another consideration affecting the length of the transfer tube is the possible *lag time* in the response of the mass spectrometer compared to initiation of the thermal event. This problem is not insurmountable, since an increase in flow through the differential pumping system can readily compensate. The sampling appears to be direct enough to lessen any mixing of effluent inside the thermal furnace,

making the order of evolution unambiguous for all analyses performed to date.

RESULTS AND DISCUSSION

Analysis Procedure:

The state of subdivision of the sample may affect both thermal and mass-spectral results, so care must be taken to standardize this parameter. For materials which were not powders but were brittle, a coarse file was used to provide a relatively equal particle-size distribution. Samples of rigid polymers such as acrylic resins were easily prepared in this manner.

An appropriate amount of sample (usually about 100 milligrams) is loaded onto the thermal analysis sample cup and the mass determined if TGA is to be used. The thermal cell cover is placed over the cell and the stainless-steel transfer tube placed in position through the cell-cover opening. If conditions other than air atmosphere are desired, the cell can be evacuated and flushed several times with the analysis carrier gas. The leads are then attached for resistance heating of the transfer tube with a 6-volt, 35-ampere power supply. The flow rate of gas from the cell is set by adjustment to a standard dynamic pressure on the differential pump after the transfer-tube temperature reaches 200 °C.

The metering valve serves to pass a small portion of the flowing carrier gas into the mass spectrometer. The leak rate through this valve is monitored by both the total ion current and the peak height of the carrier gas in the mass spectrum. The sample decomposition products normally comprise less than one percent of the gas stream, so total ion current is a good approximation of the dynamic leak rate. Relative abundances of sample components are related to constant carrier-gas concentration by normalization. Mass spectra of outgas are collected at room temperature and at selected temperature intervals during thermal analysis. Replicate scans are taken at the upper

temperature limit of the thermal investigation to monitor possible kinetically slow outgas before closing all valves to the mass spectrometer and cycling the system to ambient temperature.

After identification of each outgas component from its characteristic mass spectrum, a plot of component abundance versus sample temperature is made and overlaid on the thermogram. The peak intensity of a major fragment of each component is normally used for the plot. For quantitative analysis, however, this value must be corrected for mass-spectrometer dynamic sensitivity to the gaseous species and the split ratio at the interface. The resultant thermogram shows a direct correlation for maximum outgas of a given component with the inflection point of a TGA weight-loss trace or with the endotherm of a DTA trace.

Flame-Retardant Additives:

The TA-MS technique was successfully applied to a large number of thermal property investigations, including the characterization of flame retardants.⁵ A facile example is the comparison of methyl methacrylate polymer with and without a flame-retardant additive.

Polymethylmethacrylate polymers sold under the trade names Plexiglas-G® and Plexiglas SE-3® (Rohm and Haas Company, Philadelphia, Pennsylvania) were analyzed by TA-MS at one atmosphere of an argon-air mixture. The polymers were also analyzed by high-resolution mass spectrometry at 10⁻⁶ torr vacuum. The thermogravimetric analysis plot for Plexiglas SE-3® exhibited a plateau, indicating a two-step decomposition (Figure 2).

The TA-MS analyses showed outgas of methyl bromide gas corresponding with the first step and

⁵ The information presented here was obtained during an investigation of the physical and thermal characteristics of potential glove-box window materials. It is offered as an illustration of the applications for which TA-MS may be used. For a more complete discussion of the properties of these and other transparent polymer materials, write the author.

FIGURE 2. Thermal Analyzer and Mass Spectrometric Plot for Plexiglas SE-3: (a) Thermal Gravimetric Analysis trace indicating two-step decomposition, and (b) Temperature dependence of the outgas intensity for methyl bromide and methyl methacrylate.

methyl methacrylate monomer corresponding with the second step of decomposition. The high-resolution mass spectrometric analysis identified the flame-retardant additive in SE-3 as tris-(dibromopropyl) phosphate. The different volatilization products of the phosphate ester resulted from the different conditions of pyrolysis for the TA-MS and mass spectral high-vacuum outgas. The TA-MS analyses indicated that the halogenated phosphate ester decomposed to volatile methyl bromide at a lower temperature than the decomposition point of the methacrylate polymer. After evolution of the major portion of methyl bromide was complete, outgas (and weight loss) of the

polymer paralleled closely the curve obtained for Plexiglas-G®. The latter contained no additives and out-gassed only methyl methacrylate monomer (Figure 3). The phosphate group apparently did not volatilize, but remained in the residue of the Plexiglas SE-3®.

Subsequent tests in the study indicated the effectiveness of the flame retardant was dependent on the rate-of-rise in polymer temperature. This had been inferred from the observation of relative decomposition temperatures of the flame-retardant additive and polymer. That is, at low rates of temperature increase, the retardant was significantly

FIGURE 3. Thermal Analyzer and Mass Spectrometric Plot for Plexiglas-G: (a) Thermal Gravimetric Analysis trace indicating continuous outgas after decomposition begins, and (b) Temperature dependence of outgas intensity for methyl methacrylate.

depleted before evolution of the methyl methacrylate monomer became large enough to give flammable air-monomer concentrations. Some dependence on the rate of air flow over the polymer surface was also noted.

Note that the temperature of maximum outgas for the methacrylate monomer was different for the two polymers. Temperature of maximum outgas is a function of the initial sample weight as well as heating rate, particle size, and other factors. The possibility for the flame retardant contributing to a delayed outgas of methacrylate in the case of SE-3 was not investigated.

Flammability and Toxic Vapors:

The temperature outgas stability and flammable vapor outgas were determined by TA-MS for a commercially available glass-fiber laminate. The material was a continuous-filament woven glass fabric impregnated with an organic resin. Thermogravimetric analysis with a heating rate of 10 °C per minute gave the plot shown in Figure 4. Carbon dioxide from combustion of glycidol appears at the same nominal mass as the C_2H_4O glycidol fragment ($m/e = 44$) used for the plot. The plot was made using the sum of intensity for both components. For a 96.7-milligram sample

FIGURE 4. Thermal Analyzer and Mass Spectrometric Plot for Epoxy-Impregnated Woven Glass-Fiber Fabric: (a) Thermal Gravimetric Analysis trace indicating rapid weight loss from 250 to 450 °C, and slow weight loss above 450 °C, and (b) Temperature dependence of outgas intensity for glycidol and phenol from decomposition of the epoxy resin.

prepared with a coarse file, no weight loss was observed until the sample temperature reached 250 °C. As noted by the TGA curve, 28.5 percent of the sample weight was lost between 250 and 450 °C. An additional 5 percent weight loss experienced from 450 to 700 °C was almost completely due to outgas of another component, phenol. The glycidol and phenol outgas indicated thermal decomposition of the bisphenol A-glycidol epoxy resin used to laminate the glass-fiber fabric. The implication for mechanical failure of the laminate above 250 °C was noted,

as well as the potential for flame propagation by combustion of flammable glycidol. A sample of the powdered material was found to have a measured flash point of 270 °C (Cleveland open-cup method). The flash points for most materials studied by TA-MS have generally occurred within 10 to 20 °C of the temperatures determined for outgas of flammable decomposition products. The identification of a decomposition product such as phenol, which contributed to a weight loss, made possible the determination of toxic hazards of the material.