

## Coupling between FTIR (Bruker IFS 66) and TG (Du Pont TGA 951-2000) <sup>1</sup>

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### Abstract

In our laboratory for the first time a combination between the Bruker IFS 66 FTIR spectrometer and the Du Pont TGA 951-2000 was realized. The interface allows the spectral monitoring of gases evolving from heated samples in the TGA system. The purpose of this paper is to demonstrate the capabilities of the instrumentation and the software.

### INTRODUCTION

Thermogravimetric analysis (TG) has become an indispensable tool for the analysis and characterization of materials. The great variety of additives in many materials and the complexity of the thermal degradative processes require the combination of TG with other techniques in order to obtain an unambiguous identification of the evolved compounds.

Fourier transform infrared spectroscopy (FTIR) is a technique well suited as a means of identification, taking into account the fact that molecules have their own characteristic IR fingerprints. The coupling of TG with FTIR offers the capability of simultaneous characterization of thermal behaviour and identification of the decomposition products.

### EXPERIMENTAL SECTION

#### *Instrumentation*

The thermogravimetric analyzer is a Du Pont TGA 951-2000 and the FTIR instrument is a Bruker IFS 66. The gaseous compounds are analysed

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by transmission FTIR. The outlet of the TG is connected to the FTIR by an interface that consists of: (1) a gas cell (22 ml) with outer (KBr) and inner (ZnSe) windows; the gas cell is heated (200°C) to prevent condensation on the windows; (2) a heatable (200°C) transfer line to connect the cell with the TG; (3) a RS 232 cable for data transfer from the TG controller to the FTIR system.

The detector is a liquid nitrogen cooled MCT (Hg–Cd–Te, 4800–600  $\text{cm}^{-1}$ ) detector. Carrier gases transparent to the IR beam are used.

### Software

The FTIR spectrometer is used at the appropriate speed to acquire two to five complete IR spectra within 1 s at a spectral resolution of 8  $\text{cm}^{-1}$ . From the interferogram a total IR spectrum is calculated in real time. Using the background single beam as reference ( $I_0$ ), the IR transmission spectrum is calculated as usual by ratioing  $I/I_0$ .

The change in transmission during a TG–IR run can be monitored in discrete spectral regions using IR group specific (IR window) spectra. The calculations of the window interferograms involve all the steps of computation typical in FTIR spectroscopy (apodization, Fourier transformation,

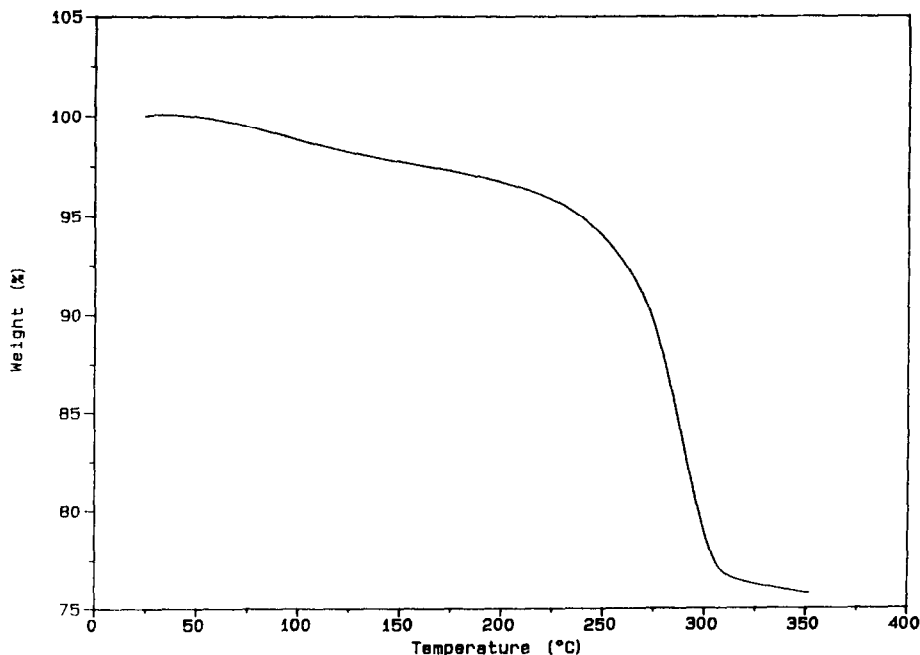


Fig. 1. TG curve obtained for  $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$  at a heating rate of  $20^\circ\text{C min}^{-1}$  in a nitrogen flow of  $50 \text{ ml min}^{-1}$ .

phase correction, referencing to a stored background spectrum, conversion to absorbance and integration of the spectral intensity within the selected frequency windows). The total IR spectrum can be calculated from the algorithms working directly on the interferometric data: a vector projection technique such as the Gram–Schmidt orthogonalization can be used.

The total IR spectrum and between one and four window spectra are obtained simultaneously in real time.

#### TG–FTIR results on $Zn_5(OH)_6(CO_3)_2$

In a first experiment the well known compound  $Zn_5(OH)_6(CO_3)_2$  was chosen for the following reason. Because its degradation, starting from 50°C, takes place in a rather continuous way, TG alone cannot give information about the specific temperatures at which  $CO_2$  and/or  $H_2O$  are released. The on-line coupling with FTIR offers that information.

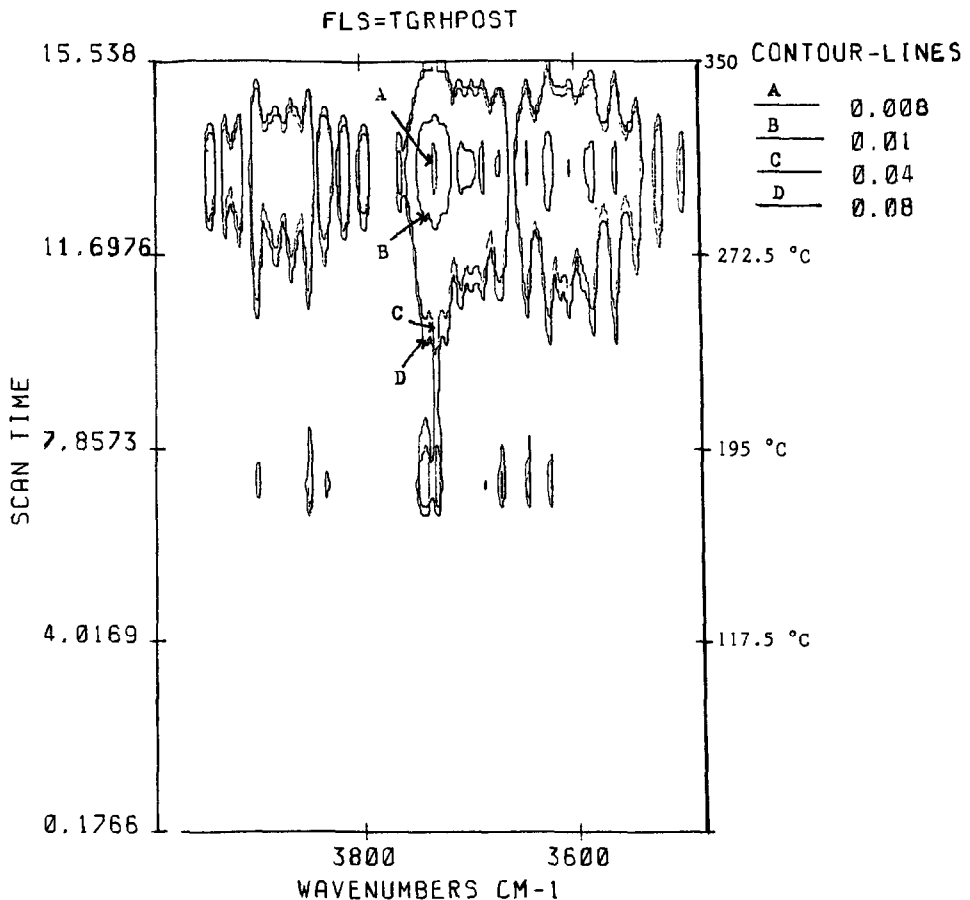


Fig. 2. Contour plots at four intensity levels obtained by TG–FTIR for the evolution of  $H_2O$ .

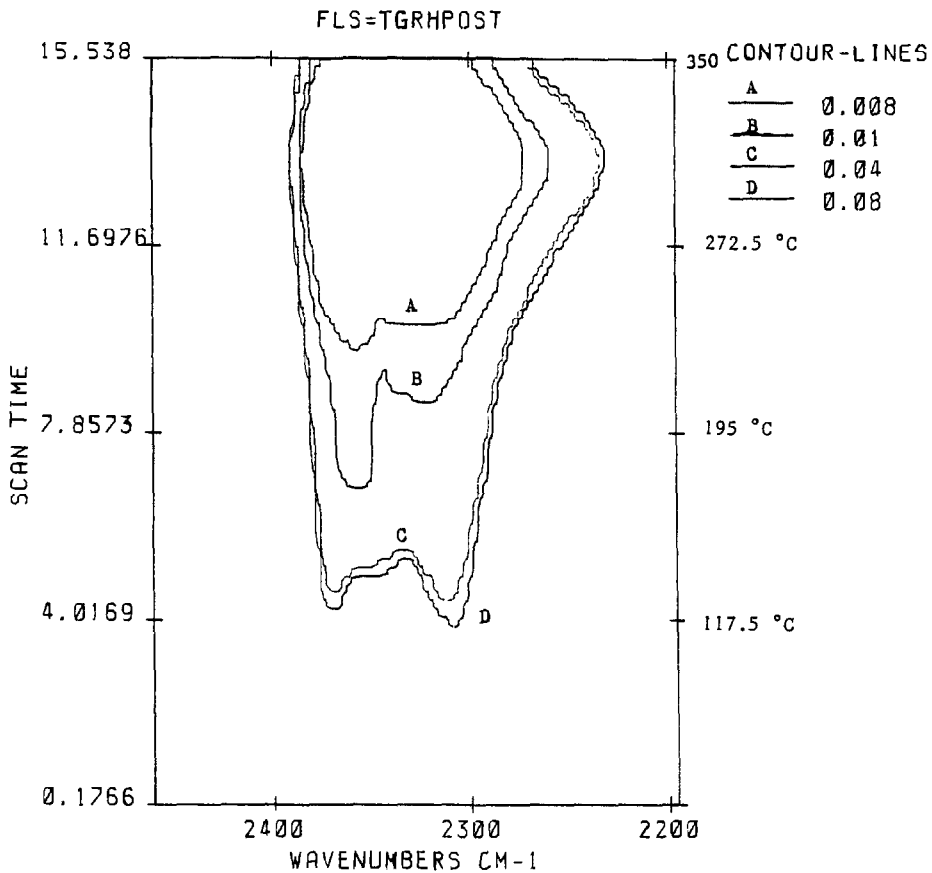


Fig. 3. Contour plots at four intensity levels obtained by TG-FTIR for the evolution of  $\text{CO}_2$ .

Figure 1 shows the TG curve obtained with a heating rate of  $20^\circ\text{C min}^{-1}$  and a  $\text{N}_2$  flow of  $50 \text{ ml min}^{-1}$ . Sample size was ca. 33 mg.

Figures 2 and 3 show some typical contour plots of the TG-FTIR results at four intensity levels. Fourier transform IR spectra of the evolved products ( $\text{H}_2\text{O}$  in Fig. 2 and  $\text{CO}_2$  in Fig. 3) are recorded continuously as a function of time or temperature (y axis) throughout the heating cycle, so that the contour plot gives a qualitative idea of the relative intensities of the different characteristic IR bands as a function of time or temperature.

Figure 4 gives the same information in the so-called Stack plot (a three dimensional plot of the IR spectra as a function of time or temperature): the high degree of resolution and fine structure is typical of gas phase IR spectra as compared with those of liquids or solids.

From the experiments on this sample it is evident that, at lower temperatures, primarily  $\text{CO}_2$  has been thermally evolved. At temperatures higher than  $230^\circ\text{C}$ ,  $\text{H}_2\text{O}$  as well as  $\text{CO}_2$  is evolved.

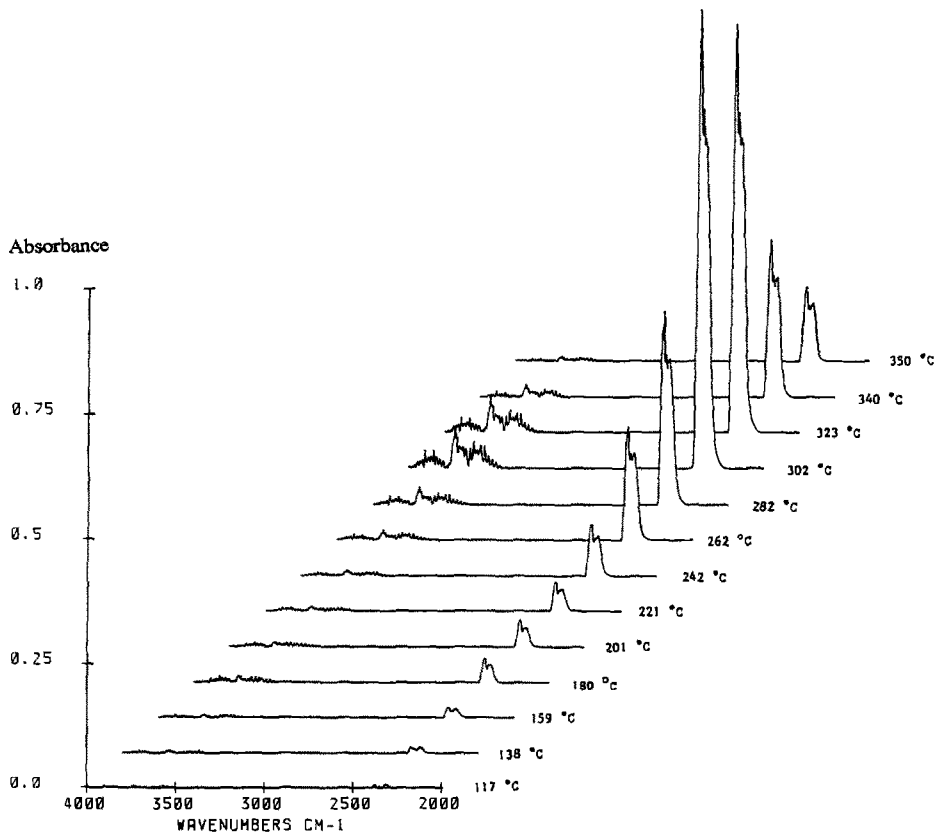


Fig. 4. Stack plot of TG-FTIR results obtained by heating  $Zn_5(OH)_6(CO_3)_2$ .

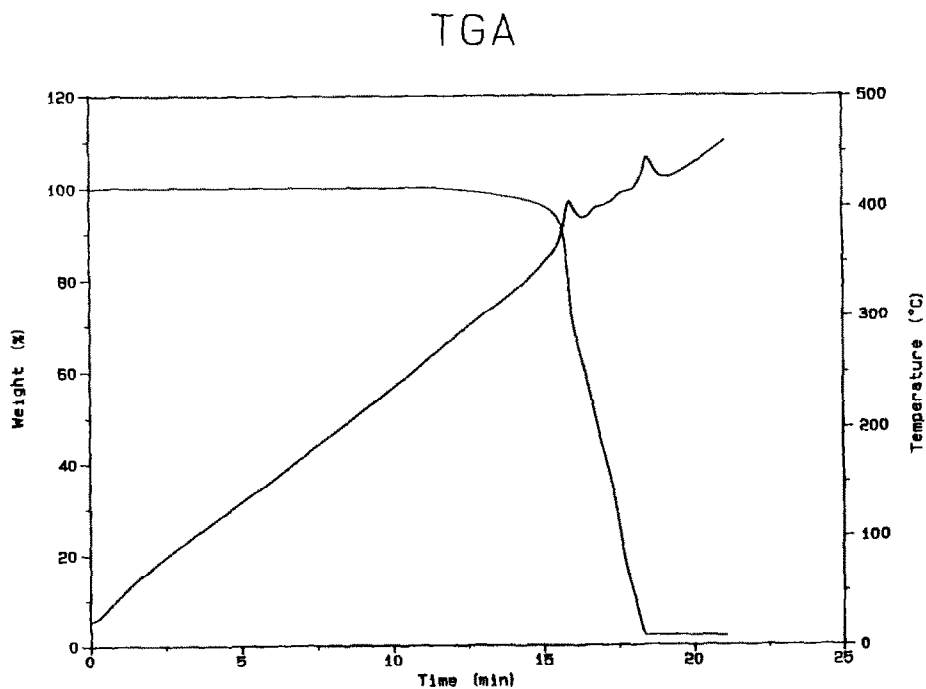


Fig. 5. Weight loss of polyethylene heated in air at  $20^\circ C \text{ min}^{-1}$ ; sample size ca. 16 mg.

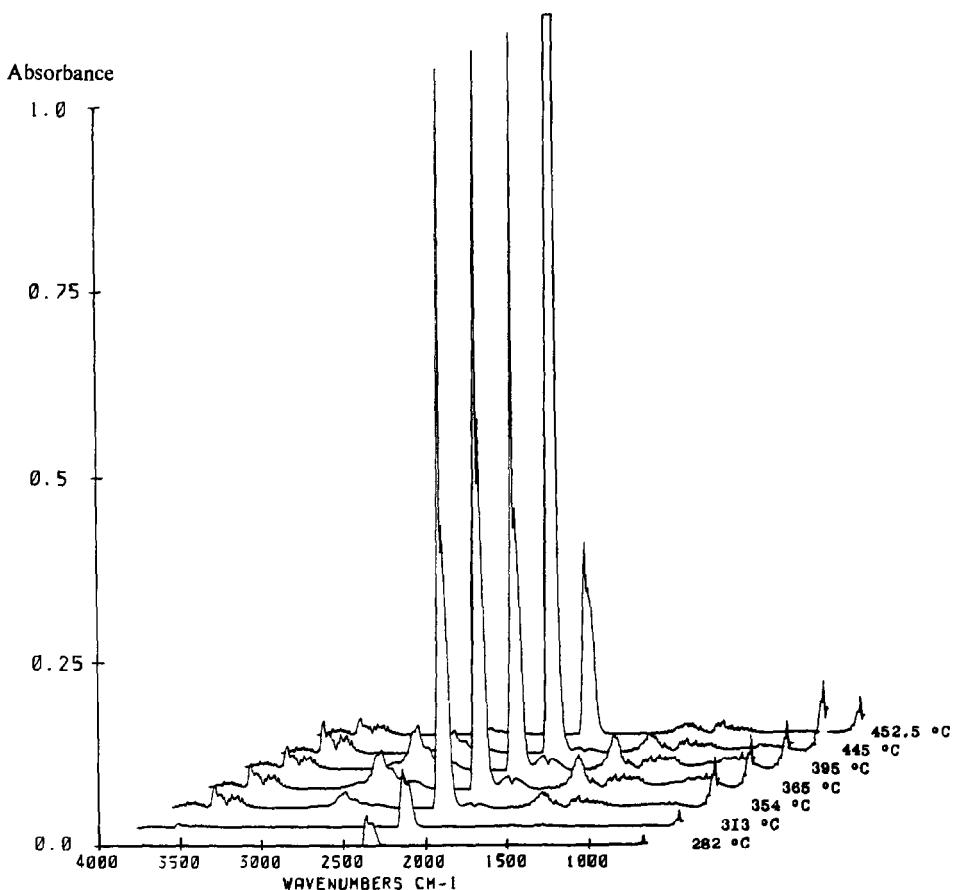


Fig. 6. Results of TG-FTIR of polyethylene showing products released at different temperatures.

### *TG-FTIR results on a polyethylene sample*

Figure 5 shows the percent weight loss of a polyethylene sample as a function of temperature at a heating rate of  $20^{\circ}\text{C min}^{-1}$  in an air flow of  $50 \text{ ml min}^{-1}$ . Oxidative degradation starts at about  $280^{\circ}\text{C}$ . The combustion of the polymer is clearly shown by the weight decrease, but also by the stepwise increase in temperature at the time of combustion.

The Fourier transform IR spectra are plotted at different temperatures in Fig. 6. The assignment of the spectra is:  $\text{H}_2\text{O}$  ( $3600\text{--}3400$  and  $1650\text{--}1600 \text{ cm}^{-1}$ );  $\text{CO}_2$  ( $2360\text{--}2340$  and  $750 \text{ cm}^{-1}$ ) and hydrocarbons (C-H stretching  $3000\text{--}2800 \text{ cm}^{-1}$  and C-C skeletal vibrations  $1500\text{--}1300 \text{ cm}^{-1}$ ). FTIR shows that the oxidative heating of a polymer such as polyethylene involves the release not only of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  but also of hydrocarbons.

## CONCLUSIONS

The on-line combination of TG with FTIR offers important information about gaseous decomposition products as a function of temperature. Use of the appropriate dynamic purge gas allows the simulation of oxidative (in air or oxygen) or pure thermal (in inert atmosphere) degradation processes. Other combinations of thermal analysis with, e.g., MS and GC–MS [1] or with specific detectors [2] also find application in evolved gas analysis. In some experiments multiple sampling is achieved by the introduction of isothermal steps in the temperature programme [3]. This allows the successive collection of material in different solvents or on different adsorbents for the off-line combination of thermal analysis with other techniques [4]. Taking into account the great variety of additives that can be present in many materials, the combination of thermal analysis with other techniques is of great value.

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