



Simultaneous Mass Spectrometry and Fourier Transform Infrared Spectrometry of Off-Gases from a Thermogravimetric Analyzer

Carleton G. Slough, PhD

TA Instruments, 109 Lukens Drive, New Castle, DE 19720, USA

ABSTRACT

The use of mass spectrometers (MS) and Fourier transform infrared (FTIR) spectrometers in the identification of evolved gas species from thermogravimetric analyzers (TGA) is well known (1-3). Both types can be easily interfaced directly to the outgas port of thermogravimetric instruments. Detection is typically performed on a real time basis with the TGA scans and is mainly used for identification. Both MS and FTIR have their separate advantages in off gas analysis. The former is more sensitive, while the latter is typically more straightforward. This paper describes the simultaneous connection of both a MS and a FTIR to a TGA system.

INTRODUCTION

As stated above, the hyphenated evolved gas analysis techniques of TGA-MS and TGA-FTIR have been well established. Most commercial systems have typically been used in either configuration. Since each has its limitations, the ability to perform TGA-MS-FTIR simultaneously could be beneficial in many instances. For example, the high sensitivity of the MS makes it useful where very little sample is available or where small amounts of a specific chemical are being released. Conversely, the FTIR allows for a more subtle analysis of fragment such as in the presence of side groups in polymers. In this work, a simple heated interface was used to connect, in parallel, a mass spectrometer and a FTIR to a TA Instruments Q5000 IR Thermogravimetric Analyzer. The parallel configuration decreases the likelihood of a dilution in concentration that would result from a series connection as the gases pass from one spectrometer to the other. Data is collected simultaneously on all three instruments and the files from the MS and FTIR instruments can be loaded into and analyzed by Universal Analysis software.

EXPERIMENTAL

The instruments used in these experiments were a TA Instruments Q5000 IR TGA, a Pfeiffer ThermoStar™ mass spectrometer and a ThermoNicolet 6700 FTIR spectrometer. The device connecting all three instruments is a modification of the standard TA Instruments heated interface used to connect the Q5000IR to the Pfeiffer ThermoStar mass spectrometer. This interface is constructed of stainless steel and uses a resistive cartridge heater to heat the interface to approximately 200 °C. It has a 0.6 mm diameter core into which the MS capillary is inserted and fed into the TGA chamber. It also has a 1/8" diameter stainless steel tube extending at a right angle relative to the capillary. Since the MS only needs to sample a small portion of the gas coming from the

TGA, the rest of the off gas exits via this tube, which makes it an excellent point at which to join the FTIR instrument. The simple modification of adding a female 1/8" Swagelok connector and a 1/8" Swagelok elbow permit easy attachment of the FTIR instrument. Figure 1 shows the interface attached to the outgas port of the Q5000IR, while Figure 2 shows both the MS and the FTIR attached to the TGA through this heated interface.

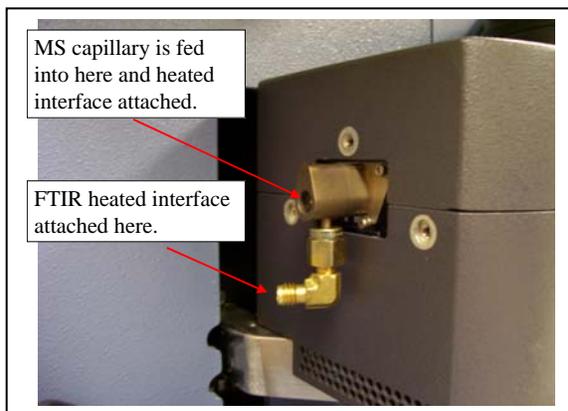


Figure 1. Heated interface attached to TGA



Figure 2. Interface with MS/FTIR attached

Calcium oxalate monohydrate ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$) from Fisher Scientific, polystyrene from Aldrich and Duco® cement were analyzed to test the capabilities of this hyphenated system. The samples were run in platinum pans in the Q5000 IR instrument either isothermally or at a scan rate of 20 °C/min to the final temperature. The MS was run in fast scan mode, which gives a dwell time of 0.2 seconds per mass. The mass range analyzed depended upon the material being investigated. The FTIR was scanned at a rate which collected a spectra every 6 seconds with a resolution of 0.964cm^{-1} . The scan range was from 400 to 4000cm^{-1} .

RESULTS and DISCUSSION

Figure 3 shows a typical TGA scan of calcium oxalate monohydrate. This is a logical first choice as a demonstration material for this study not only because of the three large, well spaced weight loss transitions in TGA, but also because each transition releases a single, simple gas. Figures 4 and 5 show MS and FTIR data captured simultaneously during the same TGA run in Figure 3. Figure 4 shows a typical Trend scan plotting intensity versus temperature for the different masses, indicating the expected loss of water ($m/e=18$), carbon monoxide ($m/e=28$) and carbon dioxide ($m/e=44$) during the first, second and third weight loss transitions respectively. There is some CO_2 during the second weight loss due to the fact that there is some background oxygen in the system and the released CO reacts with the O_2 to form CO_2 . Additionally, there is some CO detected during the third weight loss because of fragmentation of the CO_2 by the mass spectrometer. The data in Figure 5 represents a Gramm-Schmidt plot, which is essentially a plot of FTIR intensity during the experimental run. Each peak can be analyzed for its characteristic spectra and the insets show the spectra obtained for each which are the well-known ones for H_2O , CO and CO_2 respectively.

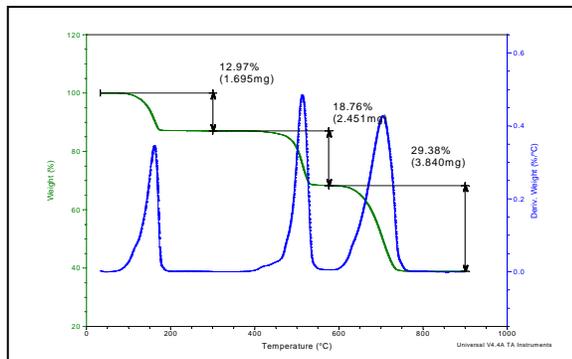


Figure 3. TGA data of calcium oxalate

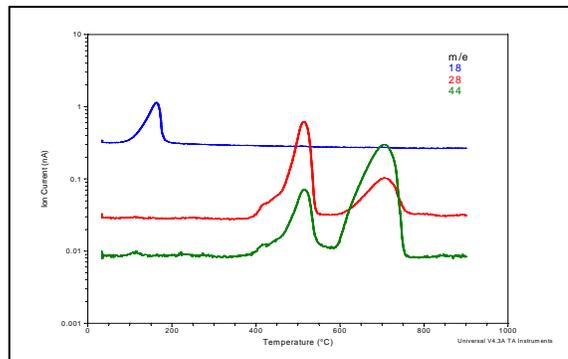


Figure 4. MS trend scan of calcium oxalate

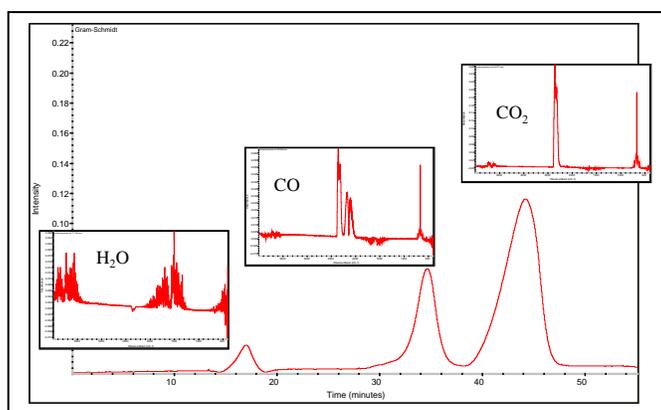


Figure 5. Gram-Schmidt plot with corresponding spectra for calcium oxalate

Figure 6 shows TGA data from an isothermal experiment illustrating the drying of Duco[®] cement. The experiment was run at room temperature for thirty minutes. As expected, during the drying process, the weight of the sample decreases due to the release of solvent. Figure 7 shows a typical mass spectrum captured during the drying process. Also shown is a library spectrum for acetone, a potential solvent evolved during the drying process. Due to the presence of peaks from background air in the system, the

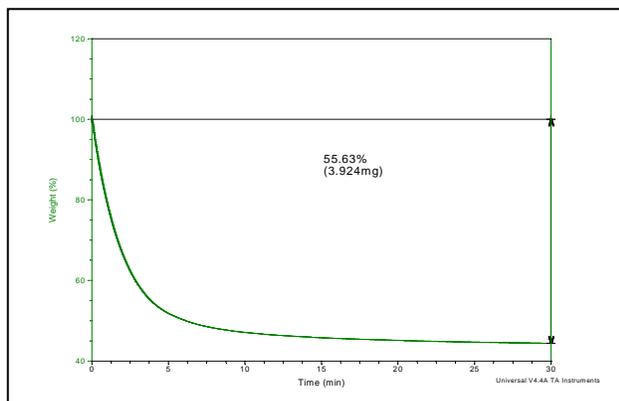


Figure 6. TGA of the drying of Duco cement

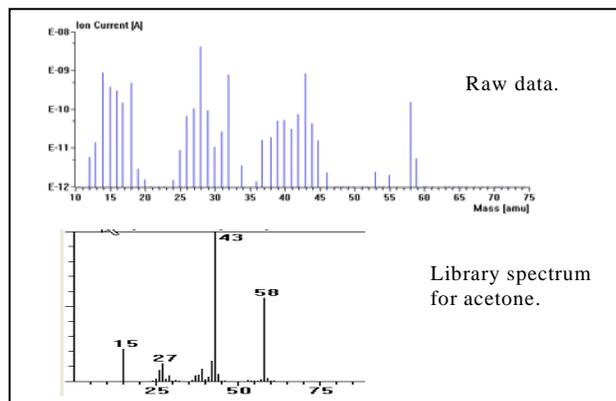


Figure 7. MS raw and acetone library data

the spectrum is more complex to analyze and compare. When the TGA furnace is opened to load the sample, air enters the system and upon closure, is replaced by the purge gas. Typically, a ten-minute isothermal period is programmed into the method to permit stabilization of the background spectra prior to the start of a temperature scanning evolved gas experiment. However, this is not possible with the Duco cement, since gas is evolved immediately upon loading the sample. Also, a MS background subtraction cannot be done since the background initially changes rapidly and a single scan is insufficient. With FTIR, the same sensitivity to an unstable background does not exist. This is partly due to the fact that the background is analyzed over longer time period than in MS and several scans are averaged. Also, the main gases in air, nitrogen and oxygen, are transparent to FTIR. Thus, in FTIR experiments, a background is routinely collected and then subtracted from the subsequent scans, which simplifies spectral interpretation. Figure 8 shows the FTIR spectrum captured during the drying process plus a match from the internal software library for acetone. The match is excellent with only some minor detection of CO₂, proving in this case that FTIR excels MS in analyzing the evolved gas.

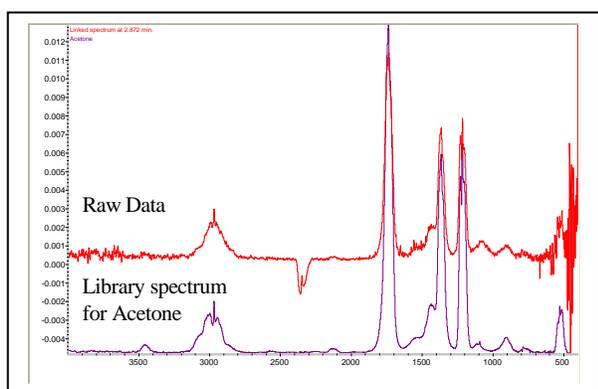


Figure 8. FTIR data compared to acetone library

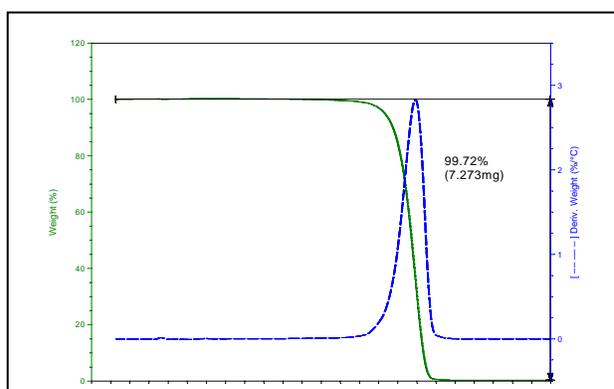


Figure 9. TGA data of polystyrene

The TGA analysis of polystyrene (Figure 9) shows that it decomposes to essentially zero weight percent in a single step, beginning at approximately 350 °C.

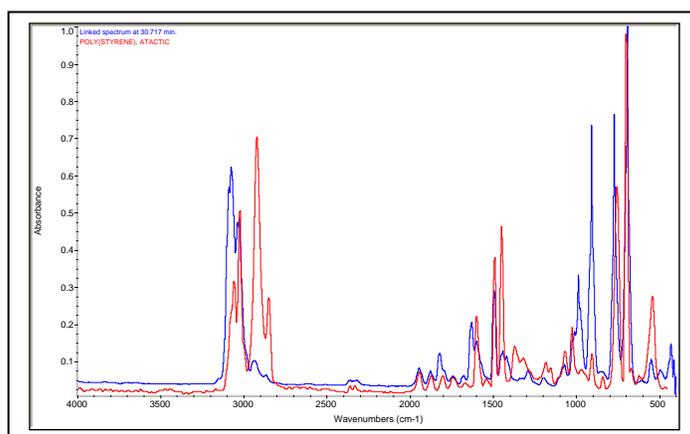


Figure 10. FTIR raw data compared to library atactic polystyrene spectrum

Figure 10 shows an overlay of the FTIR spectrum obtained with that of a library spectrum for atactic polystyrene. The match is good in some areas but poor in others.

Figure 11 shows the mass spectrum data from the sample and the library spectrum for styrene monomer. Here the match is perfect, not only to the peaks detected, but largely to the relative sizes of the peaks. Background air does not pose an issue here because the peaks are higher.

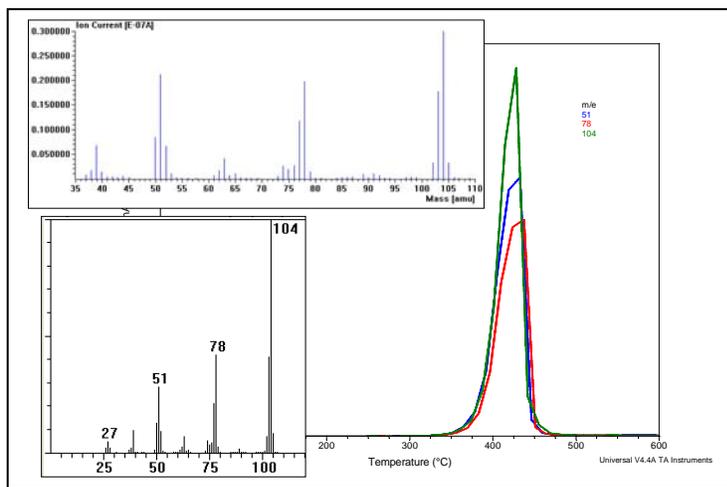


Figure 11. MS data compared to styrene monomer library spectrum

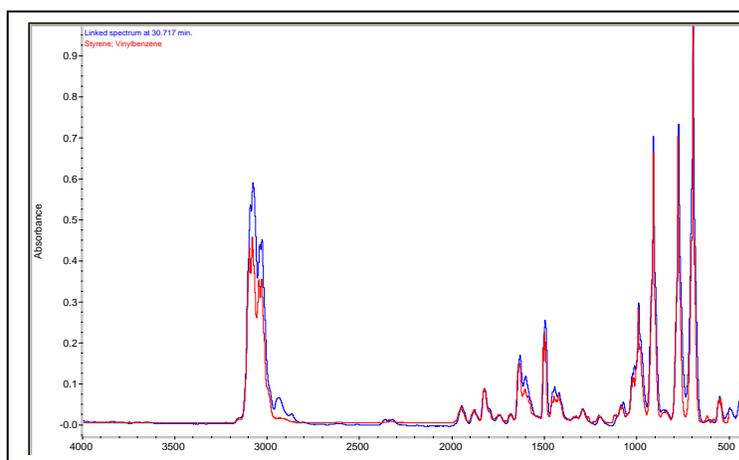


Figure 12. FTIR raw data from PS compared to Styrene monomer library spectrum

Figure 12 now matches the FTIR data to a styrene monomer spectra. Here the match is also very good. However, a closer look indicates the FTIR spectra shows something the MS spectra cannot. Observing the relative sizes of some of the peaks, it can be seen that the match is not perfect. The reason can be found by reviewing the spectra for the polystyrene. We can see for instance, between 2800 to 3000 cm^{-1} , that peak structure has been added that is similar to what is present in pure polystyrene. Thus, the FTIR spectra indicate, that while the vast majority of fragments coming from the TGA are just styrene monomer, there are also some larger oligomer fragments. In this case, the MS and the FTIR work well together to give a complete picture of the decomposition of polystyrene.

As with any combined system, there are advantages and disadvantages to the setup. In combined TGA / MS / FTIR experiments, the main challenge is to optimize the sample mass. In most cases, FTIR requires a typical size TGA sample, 10mg or more, to get good signal strength. Conversely, MS has excellent sensitivity and so requires a smaller sample for best results. In fact, running large samples often increase the likelihood of the capillary becoming blocked. A minor difficulty is positioning the MS and FTIR instruments next to the TGA. The entire combination takes up significant bench space. A distinct advantage is found in the fact that the MS needs very little gas, while the FTIR needs a relatively large amount. Thus, the two pieces of equipment work well together in this respect.

CONCLUSIONS

A simple modification of the Q5000 IR TG/MS heated interface has been shown to allow the additional coupling of a FTIR spectrometer. The resultant simultaneous analysis of off-gasses from the TGA by the MS and FTIR has been shown to be a very powerful technique. For the most part, these two spectrometers are complementary when attached simultaneously to a TGA instrument.

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NOTES

1. Thermostar is a trademark of Pfeiffer Vacuum.
2. Duco is a registered trademark of the Devcon Corporation.

KEY WORDS

TGA, FTIR, MS, Gas analysis, Combined techniques

TA INSTRUMENTS

United States

109 Lukens Drive, New Castle, DE 19720 • Phone: 1-302-427-4000 • E-mail: info@tainstruments.com

Canada

Phone: 1-905-309-5387 • E-mail: shunt@tainstruments.com.

Mexico

Phone: 52-55-5200-1860 • E-mail: mdominguez@tainstruments.com

Spain

Phone: 34-93-600-9300 • E-mail: spain@tainstruments.com

United Kingdom

Phone: 44-1-293-658-900 • E-mail: uk@tainstruments.com

Belgium/Luxembourg

Phone: 32-2-706-0080 • E-mail: belgium@tainstruments.com

Netherlands

Phone: 31-76-508-7270 • E-mail: netherlands@tainstruments.com

Germany

Phone: 49-6196-400-7060 • E-mail: germany@tainstruments.com

France

Phone: 33-1-304-89460 • E-mail: france@tainstruments.com

Italy

Phone: 39-02-2742-11 • E-mail: italia@tainstruments.com

Sweden/Norway

Phone: 46-8-555-11-521 • E-mail: sweden@tainstruments.com

Japan

Phone: 813-5479-8418 • E-mail: j-marketing@tainstruments.com

Australia

Phone: 613-9553-0813 • E-mail: sshamis@tainstruments.com

India

Phone: 91-80-2839-8963 • E-mail: india@tainstrument.com

China

Phone: 8610-8586-8899 • E-mail: info@tainstruments.com.cn

Taiwan

Phone: 886-2-2563-8880 • E-mail: skuo@tainstruments.com

Korea

Phone: 82.2.3415.1500 • E-mail: dhreece@tainstruments.com

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