APPLICATION NOTE

Hyphenated Technology – TG-IR

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Advanced Data Analysis of Evolved Gases from TG-IR Hyphenation Studies of Polymers

Introduction

The combination of Thermogravimetric Analysis with Infrared Spectroscopy (TG-IR) is the most common type of evolved gas analysis. Thermogravimetric Analysis (TGA) accurately measures the percentage weight loss of a sample as a function of temperature, but does not provide any information regarding the chemical composition of the evolved gases. Additionally, IR alone is not always sufficient for detecting the presence of components at low concentrations. Interfacing a TGA with an FT-IR spectrometer allows identification of the gases evolved, thus a more comprehensive study of the processes which occur in thermal analysis may be conducted.

TG-IR is suited to a variety of applications which require identification of evolved gases upon sample heating. Such applications include residual solvents in pharmaceuticals, as well as polymer and plastic decomposition. Industries working with these materials often require deformulation of samples to identify components and understand processing differences for competitive product investigations, product-failure studies, and quality assurance.[1] This application note describes the development of a spectral library of TG-IR weight losses for polymers as well as the use of library-searching techniques for the identification of polymers and evolved gases from simple and more complex polymer formulations.

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Experimental

The Polymer Standards Kit (Cat#205) supplied by Scientific Polymer Products, Inc. consists of 100 polymer standards covering a wide range of polymer and copolymer types. These polymer standards were used to develop the spectral database consisting of the mean spectra of each weight loss for each of the 100 polymer standards. Thermal decomposition and evolved gas analysis of the polymer samples was performed on a PerkinElmer TG-IR hyphenated system (Figure 1).

Pyris™ Software was used to control the TGA 8000™ and specify the temperature program to be used. Spectrum TimeBase™ was used for time-resolved IR data analysis and The Unscrambler® X by CAMO software was used for multivariate data analysis. The IR background scan was taken after zeroing the ceramic pan in the nitrogen gas flow. Polymer samples (~10 mg) were placed in the pan and analysis performed according to the conditions shown in Table 1.

Figure 1. TGA 8000 coupled to a Frontier FT-IR spectrometer with a TL 8000 transfer line (all from PerkinElmer).

Table 1. Experimental parameters for the TG-IR experiment.

TGA Parameters	
Temperature Program	1. 30 - 600 °C at 20 °C/min 2. Hold for 1 min at 600 °C
Gas Flow (TL 8000)	Nitrogen 25 mL/min
Purge Gas Flow	Nitrogen 30 mL/min
Sample Quantity	10 mg ± 10 %
Transfer Line and Cell Temperature	270 °C
FT-IR Parameters	
Scan Range	4000 - 450 cm^{-1}
Resolution	4 cm^{-1}
Scan Time	4 seconds

Experimental Data and Data Extraction

The polymer samples analyzed are of varying sample complexity:

- Polystyrene, a simple polymer, exhibits a single weight loss
- Polyvinyl chloride, a simple homopolymer, exhibits multiple weight losses
- VC-VA (12 % VA), copolymer, exhibits multiple weight losses

The TGA weight-loss curve and first derivative of the weight-loss curve for the decomposition of polystyrene are shown in Figure 2, illustrating the occurrence of one weight loss step. The peak of the first derivative indicates the point of greatest rate of change on the weight loss curve and is also known as the inflection point. A Gram-Schmidt profile of absorbance versus temperature is also overlaid for the FT-IR data. The peaks in a Gram-Schmidt profile directly correlate with the steps in the TGA weight-loss curve, and effectively show the total change in the IR absorbance relative to the initial state.

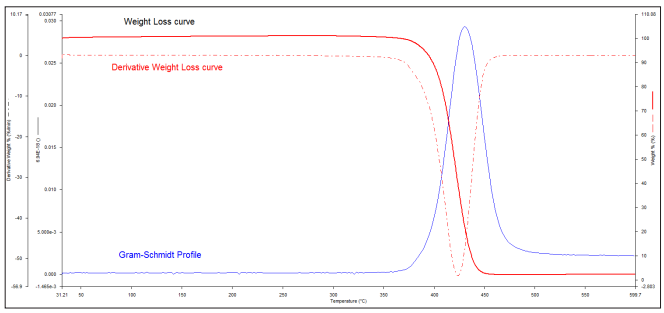


Figure 2. Polystyrene weight-loss curve (solid red), derivative weight-loss curve (dotted red), and Gram-Schmidt profile (blue).

Spectrum TimeBase software provides a 3D graphical representation, consisting of stacked IR spectra, a feature which provides a snapshot of the entire TG-IR separation. The 3D display demonstrates a "mountain range" representing evolved species. Additionally, a linked 2D graphical representation is provided. Figure 3 shows the combination of 3D and 2D displays of wavenumber, time, and absorbance for the TG-IR analysis of polystyrene.

Spectral library searching using commercial libraries of gases and vapors can be used to identify materials evolved during the TG-IR experiment. For the gas evolved in the decomposition of polystyrene, a Search Score (Figure 4) of 0.949237 is achieved, representing a good match. This approach works well for materials, such as polystyrene, which produce a single pure component upon thermal decomposition. However, the thermal decomposition of many polymers often results in a complex mixture of components being evolved in one decomposition step.

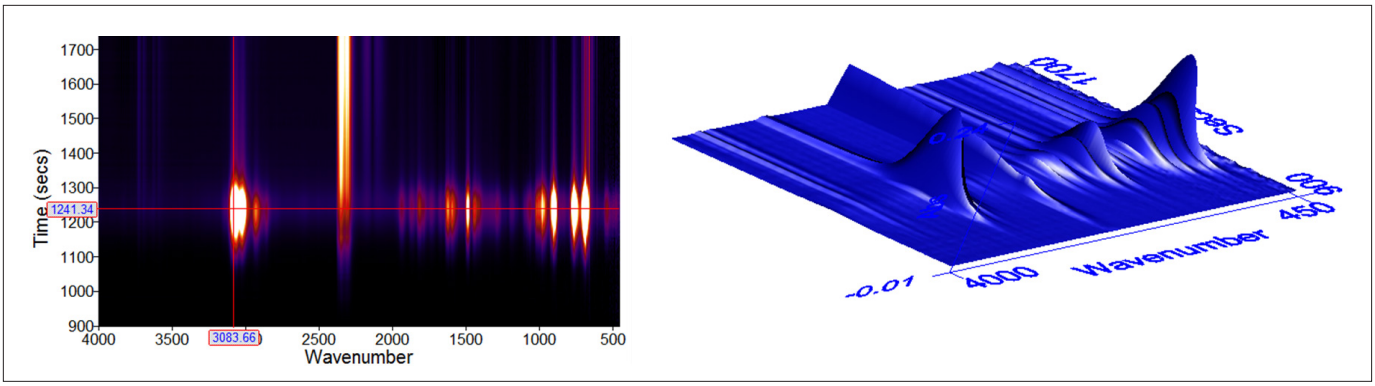
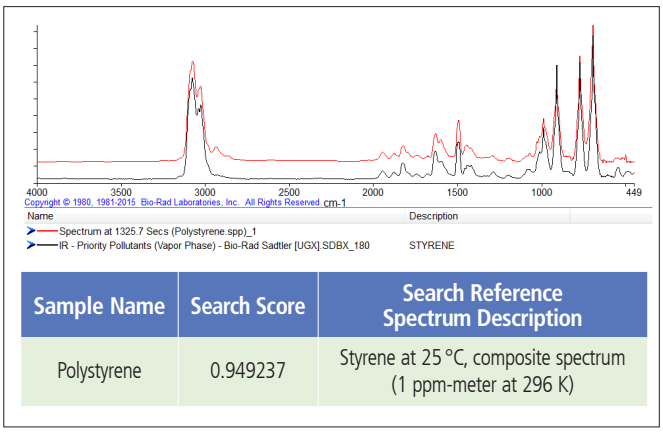


Figure 3. Spectrum TimeBase linked 2D and 3D displays of the time-resolved data for polystyrene.

Figure 5 shows the TGA weight-loss curve and Gram-Schmidt profile for the analysis of polyvinyl chloride. The decomposition is seen to consist of two distinct weight-loss events with the corresponding IR spectra of the gases evolved during the two decomposition steps also shown.

Library searching was performed on each of these decomposition spectra. The chemical species produced during the first decomposition step was determined to be hydrogen chloride, with a Search Score of 0.902654 (Figure 6). However, the library Search spectrum does not account for the peak present in the sample spectrum at around 650 cm^{-1}. In such cases, multicomponent library searching, as implemented in the PerkinElmer Spectrum 10 Multisearch™ software, can be utilized. This software is capable of identifying up to 10 components within a mixture during the library search process. Multisearch was able to identify the presence of two components (Figure 7), namely hydrogen chloride and benzene. The best-fit spectrum accounts for all spectral features and the Multisearch Score for this sample is also an improved match of 0.938259.



Sample Name	Search Score	Search Reference Spectrum Description
Polystyrene	0.949237	Styrene at 25 °C, composite spectrum (1 ppm-meter at 296 K)

Figure 4. Decomposition step spectrum (red) and identified evolved material styrene (black) with Search Score.

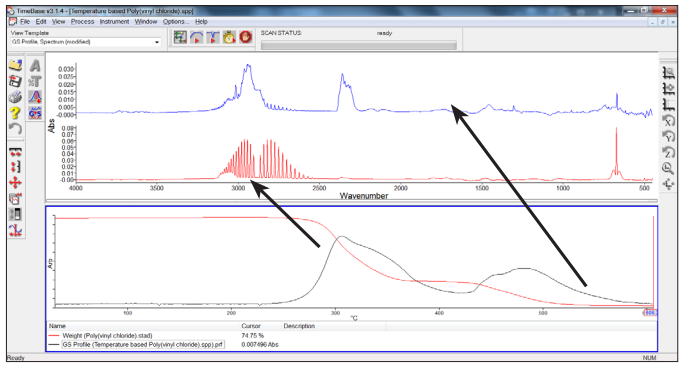
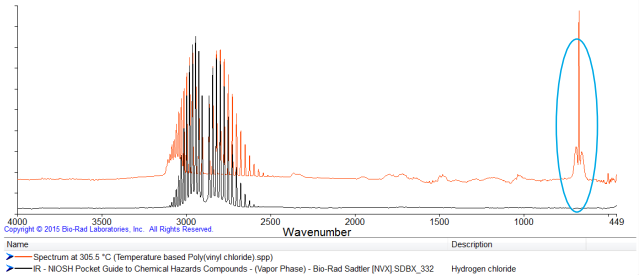
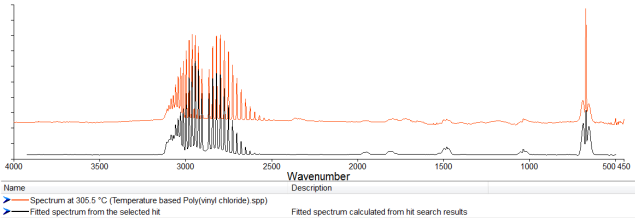


Figure 5. Polyvinyl chloride weight-loss curve (solid red) and Gram-Schmidt profile (black) illustrating two weight losses and their corresponding IR spectra.



Spectra	Score	Description
[VAX].SDBX_8974	0.902654	Hydrogen Chloride

Figure 6. Sample spectrum from the first decomposition step of polyvinyl chloride and overlapped library Search spectrum, with the Search Score.



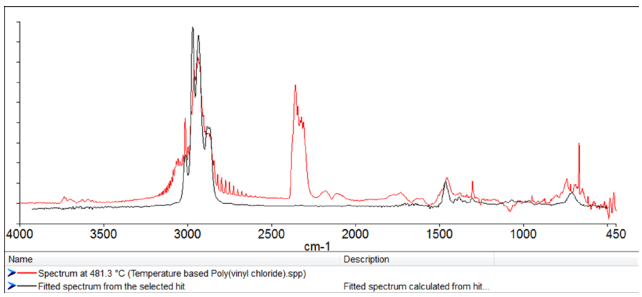
Spectra	Level (%)	Score	Description
[VAX].SDBX_8974	67.5352	0.938259	Hydrogen Chloride
[VAX].SDBX_1090	32.4648		Benzene

Figure 7. Sample spectrum from the first decomposition step of polyvinyl chloride and overlapped Multisearch best-fit spectrum, with the Multisearch results.

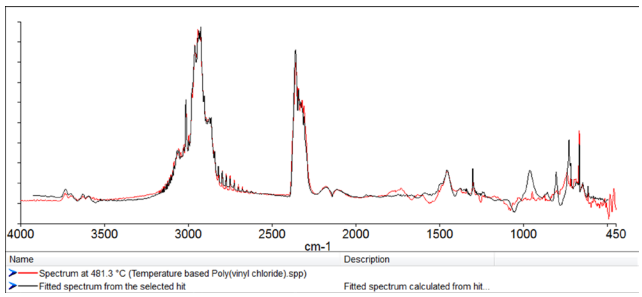
In the second decomposition step of polyvinyl chloride, Search identified the component evolved as cis-3-Nonene, with a poor Search Score of 0.302556. However, Multisearch detected the presence of eight components with a much improved Multisearch score of 0.82218, demonstrating that Multisearch is an extremely useful tool when complex mixtures need to be analyzed. Figure 8 illustrates the best-fit spectra for Search and Multisearch, overlayed with the sample spectra.

Knowledge of the decomposition products can give invaluable information about both the original material type and the decomposition processes involved.

Further useful information can be derived from the developed spectral database consisting of the mean spectra of each weight loss for each of the 100 polymer standards. An unknown spectrum collected during the run, or the mean spectrum of any weight-loss event, can be searched against this database, thereby matching the unknown material against polymers that generate similar decomposition products. A spectrum collected from a further run was searched against the database and generated the search result shown in Figure 9. The weight loss clearly matches the mean 1st weight loss from the PVC standard.



Spectra	Score	Description
[VAX].SDBX_8070	0.302556	3-NONENE, CIS-,



Spectra	Score	Description
[VAX].SDBX_6987	0.82218	2-HEPTENE, TRANS-,
[VAX].SDBX_3283		ISOBUTYLAMINE, HYDROCHLORIDE
[VAX].ELX_2911		CARBON DIOXIDE
[VAX].SDBX_2117		PHENANTHRENE
[VAX].ELX_2903		METHANE
[VAX].SDBX_8974		HYDROGEN CHLORIDE
[GSX].SDBX_132		CARBON MONOXIDE
[ELX].SDBX_1771		1-BUTANOL, 2-AMINO-,

Figure 8. Search best-fit spectrum (left) and Multisearch best-fit spectrum (right), overlayed with the sample spectrum, for the components evolved in the second decomposition step of polyvinyl chloride.

Search Hit List

	Search Score	Search Reference Spectrum Description
1	0.994007	Poly(vinyl chloride) mean 1st weightloss.sp
2	0.988601	Vinylidene chloride-vinyl chloride copolymer mean
3	0.987219	VC-VA-vinyl alcohol terpolymer mean 1st weightloss.sp
4	0.982854	Poly(vinyl chloride) mean

Figure 9. Search results from decomposition spectrum obtained in the PVC analysis.

Principal Components Analysis of TG-IR Data

Principal Components Analysis (PCA), a type of multivariate data analysis, is an alternative method for identifying components from the thermal decomposition of a polymer by TG-IR. This method involves generating a PCA model containing all the spectra from a TG-IR run of a standard polymer. Each model accounts for the major sources of spectral variance observed during the decomposition of the standard polymer sample. An example is shown in Figure 10 using KnowItAll® software from Bio-Rad Laboratories, where four models are shown for four different standard Nylon materials. The PCA analysis is able to differentiate the different Nylon types as well as being able to detect when the material is a nanocomposite.

Following model generation of standard materials, unknown samples are subsequently analyzed and predicted against these models. Any part of the spectrum not accounted for by the model, known as the residual, can indicate extra components present in the sample (additives or copolymers for example). A library search conducted against the residual spectrum can be used to identify the additional components.

PCA was applied to the data from the TG-IR analysis of the VC-VA (12 % VA) copolymer, which exhibited multiple weight losses (Figure 11). Figure 12 shows an unknown spectrum taken during the TG-IR run, the calculated fit spectrum of the unknown against the PCA model, and the residual spectrum. The residual was identified as acetic acid by performing a library search.

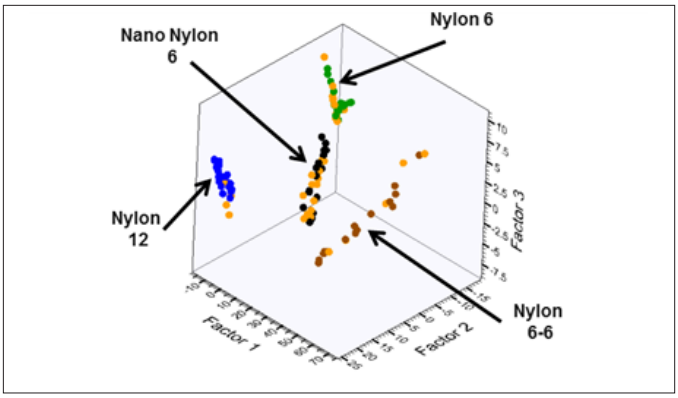


Figure 10. PCA models of various Nylon materials.

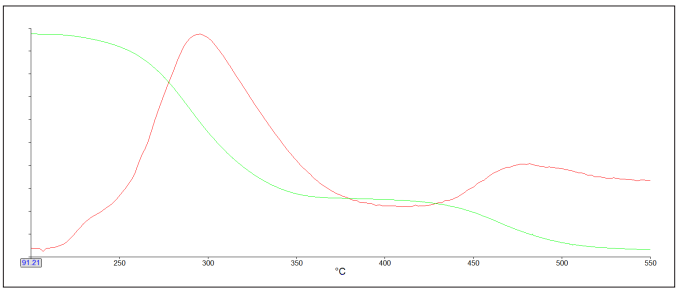


Figure 11. VC-VA (12 % VA) weight-loss curve (green) and Gram-Schmidt profile (red).

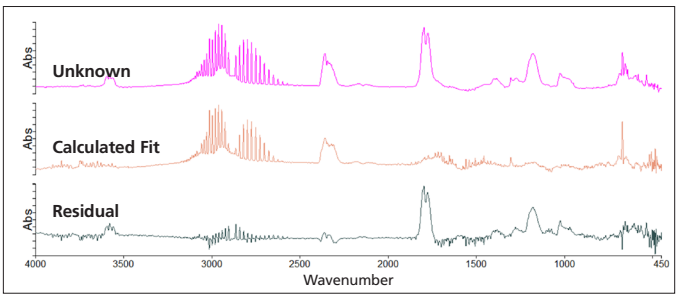


Figure 12. Unknown, calculated fit, and residual spectra for the analysis of VC-VA (12 % VA).

Multivariate Curve Resolution (MCR) to Resolve Components

Multivariate Curve Resolution with an Alternating Least Squares algorithm (MCR-ALS) is another alternative and useful method for resolving components in complex mixtures. MCR-ALS mathematically decomposes data into the contributions due to the individual components present in a mixture. It is typically used to resolve time-evolving data, such as TG-IR data, by generating component-spectra and time profiles by performing Evolving Factor Analysis (EFA) on the dataset.[2,3]

In PCA, the principal components are chosen such that the major sources of spectral variance are captured, resulting in the potential for multiple sources of variation to be modelled by a single factor. For these reasons, the principal components resulting from PCA cannot definitively be assigned to model sources of chemical or spectral significance. Alternatively, the method of data decomposition using MCR allows for the factors to be assigned chemical and physical significance and can be used to approximate mixture component-spectra and time profiles.[4]

The MCR-ALS algorithm in the Unscrambler software was used for the TG-IR analysis of the VC-VA (12 % VA) copolymer. Figure 13 shows the calculated components profile, illustrating the change in concentration of each component throughout the run, and the calculated components spectra. A library search may then be performed to identify each of the pure component spectra.

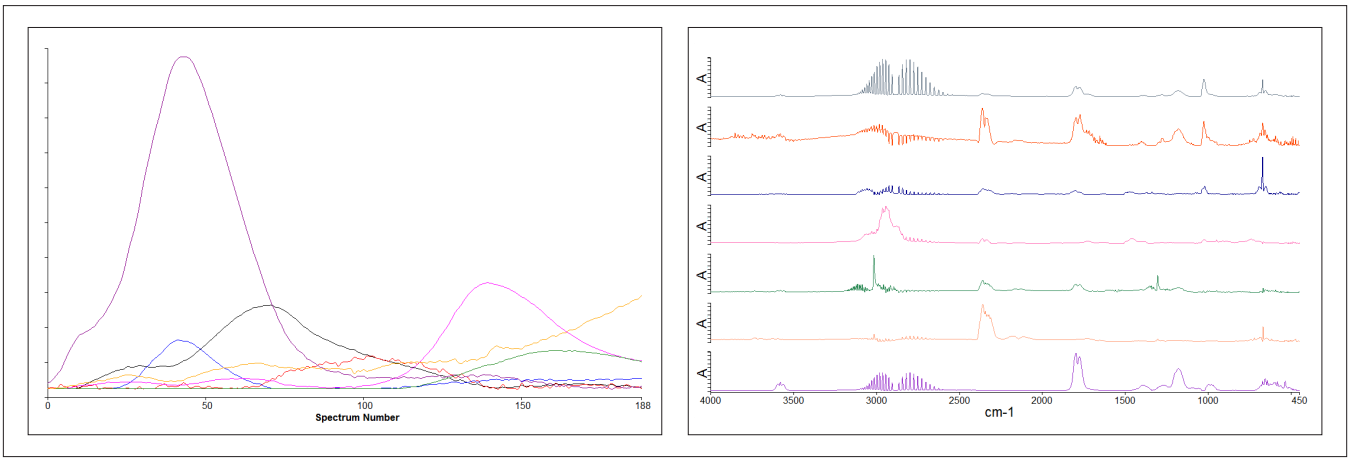


Figure 13. Calculated components profile (left) and calculated components spectra (right) for the TG-IR analysis of VC-VA (12 % VA).

Conclusions

TG-IR combined with spectral library searching provides a powerful analytical technique for deformulation of polymer samples and identification of evolved gases. Interfacing a TGA with an FT-IR spectrometer combines the advantages of both techniques, allowing more comprehensive material characterization. This method can be used for investigation of gas species present during decomposition, thermal decomposition mechanisms, and also detection of residual volatile components. The PerkinElmer TG-IR system with the TL 8000 transfer line is easy to use and its design features guarantee the highest quality and most reliable results.

PerkinElmer's Search and Multisearch features in Spectrum 10 software allow quick identification of components in simple and more complex polymer samples respectively, with the ability to search against large spectral libraries. Alternatively, more advanced forms of data analysis can be used for the identification of components in more complex mixtures, including PCA and also MCR-ALS, to allow time profiling of the pure components.

References

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2. http://www.camo.com/resources/multivariate-curve-resolution.html Date Accessed: September 2017.
3. J. Mendieta. Multivariate Curve Resolution: A Possible Tool in the Detection of Intermediate Structures in Protein Folding, Biophysical Journal, 1998, 74, 2876-2888.
4. K. Awa, T. Okumua, H. Shinazawa, M. Otsuka, Y. Ozaki. Self-modeling curve resolution (SMCR) analysis of near-infrared (NIR) imaging data of pharmaceutical tablets, Analytica Chimica Acta, 2008, 619, 81-86.

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