TGA-IR Analysis Using the OMNIC Mercury TGA Software

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Key Words

Nicolet iS50, OMNIC Series, Mercury TGA, TGA-IR, Deformulation

Abstract

Procedures like failure analysis, process validation and competitive investigations often require that a sample be deformulated to identify components and to understand processing differences. TGA-IR provides tools for just this purpose. This White Paper describes the TGA-IR experiment and then focuses on the infrared data analysis, starting with manual tools and then describing the function of the Thermo Scientific OMNIC Mercury TGA software. This algorithm provides speed, thoroughness and consistency to the analysis while enabling any level of user to extract useful information from TGA-IR data sets.

Introduction

Operators working with materials like rubbers, plastics, resins, pharmaceuticals, adhesives and packaging need to understand differences between competitive products, causes of failures or the origin of odors or potentially toxic off-gassing. Standard analytical procedures are often incapable of distinguishing subtle differences like the presence of low-concentration additives or contaminants. Further, the same components may be present in two different materials, but the process used to make the products – such as the processing temperature – may vary, causing the interactions between components in the material to differ. This can lead to poor performance, such as early material fatigue or complete material failure.

A complete analysis requires these materials to be deformulated – essentially torn apart to expose their underlying nature. Thermal Gravimetric Analysis (TGA) is a common tool for doing this. A temperature ramp is applied to the sample and the breakdown tracked through weight loss as components vaporize. While providing quantitative information through weight loss, this process does not give insights into the chemical identity of the off-gassing materials.

In TGA-IR, the off-gassing materials are directed through a transfer line to a gas cell, where the infrared light interacts with the gases. The spectra can be used to identify the materials. The output of such an experiment is shown in Figure 1, from the analysis of a wood sample. At the top are the temperature ramp and first derivative weight loss information from the TGA and a Gram-Schmidt (GS) profile; the GS profile essentially shows the total change in the IR signal relative to the initial state (similar to a chromatogram). The bottom pane contains the spectrum collected at the time indicated. In most cases, the GS and the derivative weight loss will be similar in shape, although the intensity of the two can differ. The next step involves the extraction of useful information from this data set.
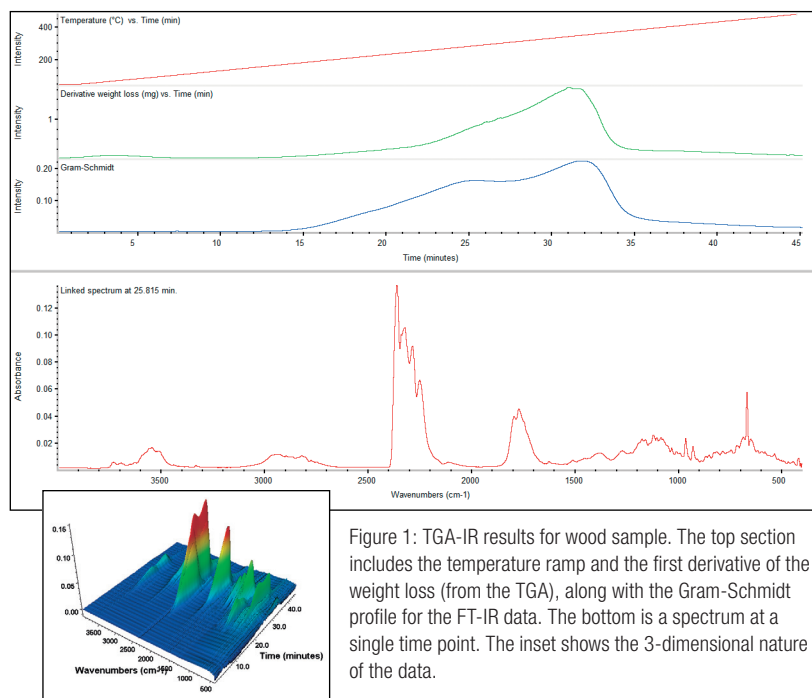

Figure 1: TGA-IR results for wood sample. The top section includes the temperature ramp and the first derivative of the weight loss (from the TGA), along with the Gram-Schmidt profile for the FT-IR data. The bottom is a spectrum at a single time point. The inset shows the 3-dimensional nature of the data.

Data Analysis: Information Overload

The FT-IR data set from the TGA-IR experiment is three dimensional – frequency versus intensity (the spectrum) versus time – which is clearly evident in the 3D View inset to Figure 1. To get an estimate of the size of the data file, consider that a typical TGA experiment ramps at 15 °C/minute from ambient to 900 °C then holds at 900 °C for 2 minutes. This results in a run time of approximately one hour. In parallel, the typical FT-IR experiment collects 4 scans at 4 wavenumber resolution, resulting in one spectrum being collected about every 5 seconds. For a one hour run, this could result in around 720 spectra being acquired. Manual analysis of all these spectra would be overwhelming and highly inefficient.

There are two critical pieces of information desired from the FT-IR data: the identity of the off-gassing materials and the time dependence of the gas evolution (called the profile) for each component. The former identifies what comes off the sample; the latter tracks when the component is released. Most of the time, "what is it?" is the

main target. However, the profile conveys considerable information about how the material was produced. For instance, a shift of 30 °C in the evolution temperature for a component in a carbon black rubber may relate directly to the thermal robustness of that rubber and hence to the lifetime expectation when used in tire manufacture.

There are three complications: First, the quantity of spectra makes a complete manual analysis impractical, so the analyst is forced to select time regions to analyze. Second, the selection of those regions inherently risks missing information, which may or may not be critical to the analysis. Third, and most perplexing, much of the time multiple gases are being evolved simultaneously. This means the resulting spectra are complex, intertwined combinations, not single components.

The need for skilled analysts to perform this task, who can ensure both completeness and correctness of the results, has led to an underutilization of this important tool. The OMNIC™ Mercury TGA software surmounts all three of the complications, giving fast, consistent and thorough results to operators of any skill level. The following discussion begins with simple cases and manual analysis and then shows the tremendous power of the Mercury TGA tool.

Getting Started: Basic TGA-IR Profiles

Calcium oxalate monohydrate is a standard TGA test sample, which shows three relatively sharp TGA weight losses and, in parallel, three peaks in the Gram-Schmidt profile. Figure 2 shows GS and FT-IR data focusing on just the first two emission peaks. Using the cursor tool, a spectrum within the first peak of the GS profile has been selected (note the crosshair in the upper pane). The spectrum is easily identified as being water vapor due to dehydration (note even here these is a small amount of CO_2). The third GS peak is also "pure," showing carbon dioxide evolution. Very few materials emit pure gases; much more common are mixtures such as seen in the second GS peak, shown in the inset (CO and CO_2).
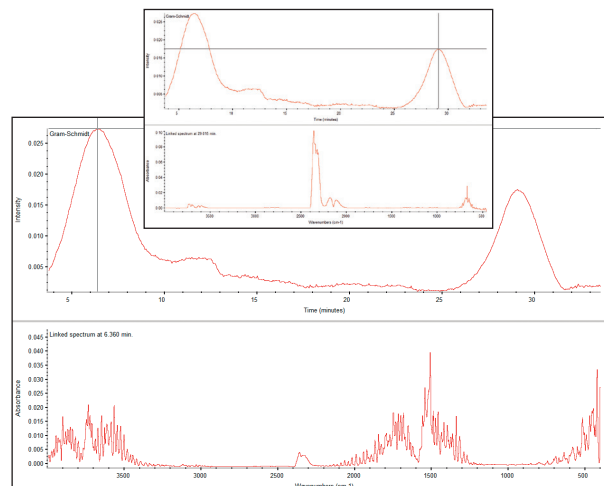

Figure 2: TGA-IR analysis (first two peaks) of Calcium Oxalate Monohydrate. The first peak is water; the second peak (inset) shows both CO and CO_2.

The user has three options to analyze the data shown in Figure 2 (remember, peaks 1 and 3 of the GS are "pure" while peak 2 is a mixture):

- Classic workflow: Select time points in peaks 1 or 3 and search. Select a time point in 2, search, subtract the top hit, search again or select spectra regions and selectively search.
- Multi-component enhanced workflow: Select time points in peaks 1 or 3 and search. Select a time point in 2 and perform a multi-component search, as discussed in the next session.
- Fully automated workflow: Click on Mercury TGA.

The first process is highly manual and requires a skilled user. The second option removes much of the guesswork from the searching of mixture spectra, but still requires time region selection. The third option, as we will show, provides a complete, thorough analysis for any skill level of user.

Multi-component Analysis at One Time Point

Figure 3 shows a data from a TGA-IR experiment on an epoxy. The spectrum at the bottom appears to be quite complex. However, this is where a major benefit of gas phase spectroscopy comes to the forefront: most gases interact weakly or not at all. This means the mixed gas spectrum is essentially a simple co-addition of the component spectra.
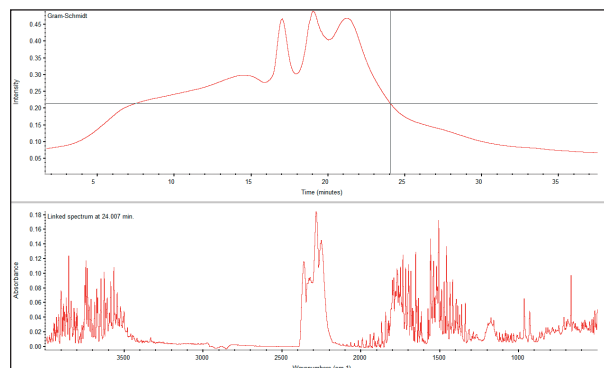

Figure 3: TGA-IR for an epoxy. The spectrum (lower window) shows the typical highly overlapped spectrum for the selected time point.

The Thermo Scientific OMNIC Specta software was designed to enable simple and efficient multi-component searching. For single point TGA gas analysis, OMNIC Specta™ software provides results such as shown in Figure 4. This similarity between the multi-component search result and the original spectrum is striking, even though four components have been found. However, this provides an analysis at only one point or one narrow region.
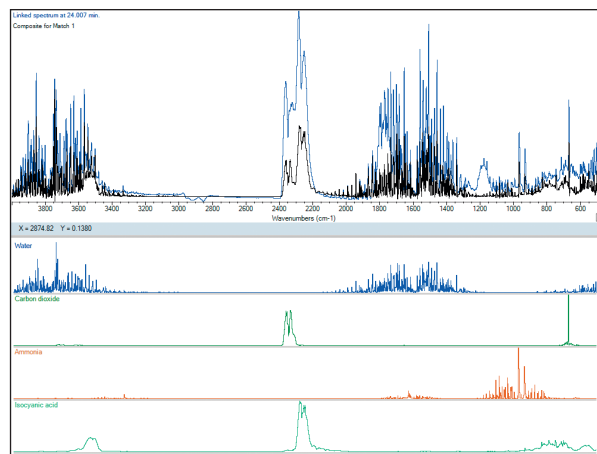

Figure 4: Multi-component search result from the OMNIC Specta software. The algorithm has identified four components and is showing the correlation between the actual spectrum and the synthetic spectrum consisting of the four components in appropriate percentages.

Complete Analysis: Mercury TGA

Ultimately, the process of analyzing narrow time regions – even with OMNIC Specta – leaves the task unfinished. The ultimate requirements for TGA-IR data analysis are as follows:

- Identify most or all of the components in the gases evolved from the TGA
- Use all spectra collected, not just a narrow time region
- Compute the time evolution of all species identified
- Visually ensure the results that are meaningful
- Get consistent answers, regardless of the user
- Compile the results in a complete report

The TGA-IR data from a wood sample, shown in Figure 1, will be used to show the results of the Mercury TGA software.

The dialog shown in Figure 5 is used to set up Mercury TGA. The search library is chosen first. Next, an estimate for the number of components present is entered; Mercury TGA provides a tool to estimate this input value. The maximum allowed is eight components. A region selection tool is also present to allow selection of a spectral range to analyze.
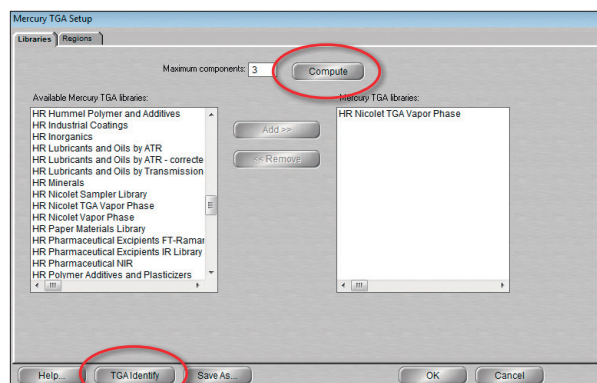

Figure 5: Set up screen for Mercury TGA. All that is required is for the user to select the library and the number of components. Pressing the "Compute" button initiates the estimation routine for number of components.
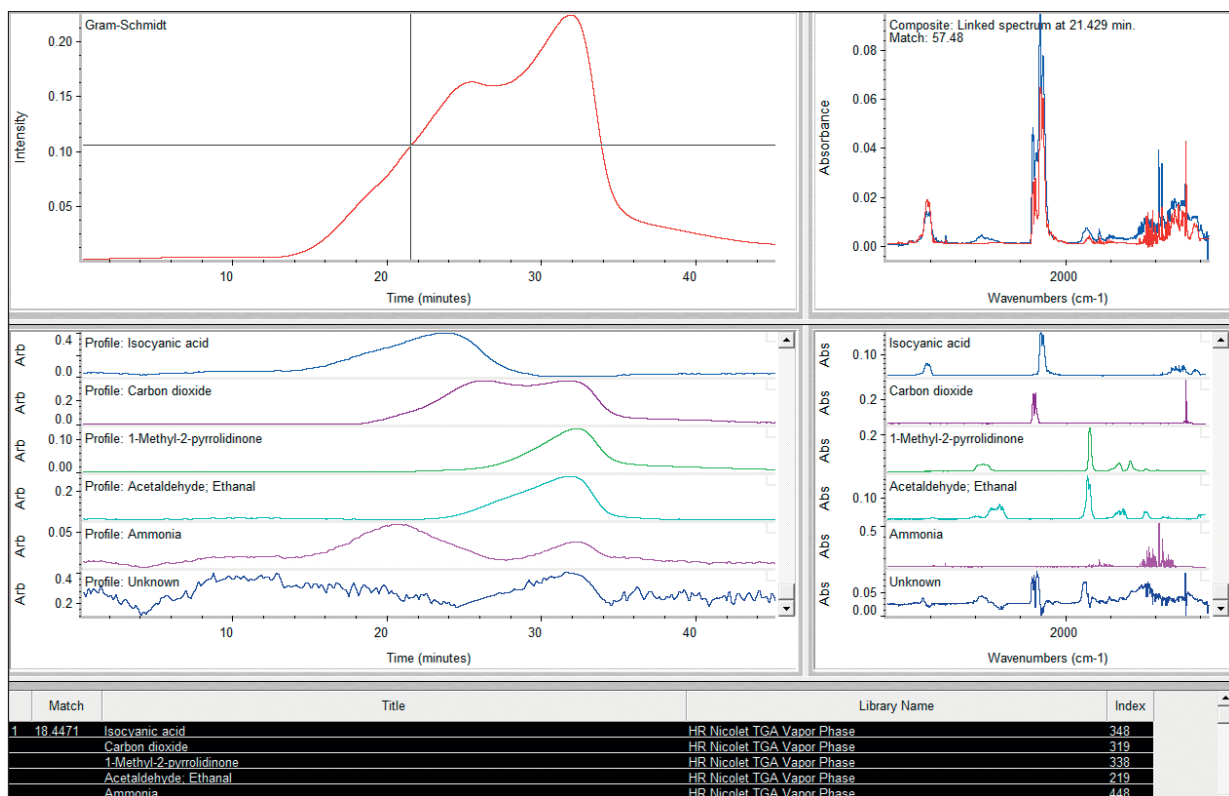
Figure 6: The Mercury TGA result for the wood sample originally shown in Figure 1. See the text for explanation of the various panes of information.

Pressing "TGA Identify" then starts the analysis. The speed of the calculation depends upon the number of data points, number of components, the library selection (bigger or multiple library selections means longer analysis time) and the speed of the computer. The 5-component analysis shown in Figure 6 involved processing 450 spectra in the Series file using the 460 spectra in the High Resolution Nicolet TGA Vapor Phase library. The process took less than 20 seconds.

The upper left corner of the display shows the GS Profile. Below that are the calculated time profiles for each of the gases determined to have evolved. Note how the gases evolve at different times during the deformulation, with a complex pattern of overlapping profiles. To the right of the profiles are the spectra of the identified gases from the library. The table at the bottom provides text information about the search results.

The last profile and spectrum, labeled "Unknown", show what is essentially a residual of the analysis – the spectral components of the overall run for which the algorithm has not yet accounted. In this case, the Unknown profile is mostly noise, indicating that the majority of the spectral features are assigned.

The upper right window is critical to the user experience. This shows the composite spectrum (in red) created from the library spectra of the identified species compared to the collected spectrum (in blue) at a particular time point. Note this does not include the "Unknown" component, so it represents the analytical results only.

Scrolling the bar in the Gram-Schmidt pane (upper left) allows the user to compare each spectrum in the Series file to the calculated composite at that time – essentially playing back the synthetic and actual Series files simultaneously. This display is critical to determining if the algorithm has identified all of the critical components in the file – more will be said of this below.

As can be seen, with this set of result panes, Mercury TGA has fulfilled the requirements outlined above. The number of components selected and the choice of spectral library are the only variables. The Thermo Scientific Nicolet Vapor Phase Library containing over 8,500 spectra, serves as an excellent basis for analysis. User libraries based on proprietary or product-specific materials can also be constructed and searched simultaneously with the commercial library.

Choosing the Number of Components

Mercury TGA has three inputs – the OMNIC Series data file, the choice of libraries and selection for the number of components. Several high quality vapor phase libraries are available and the user can create libraries specific to their application. Mercury TGA assists with the selection of number of components in two ways. The first, mentioned above, involves an approximation tool used during setup. This performs a quick overview of the data set and estimates the number of factors needed to describe the data. Typically, this algorithm is "conservative," underestimating the actual number. However, it provides a starting point for the analysis.
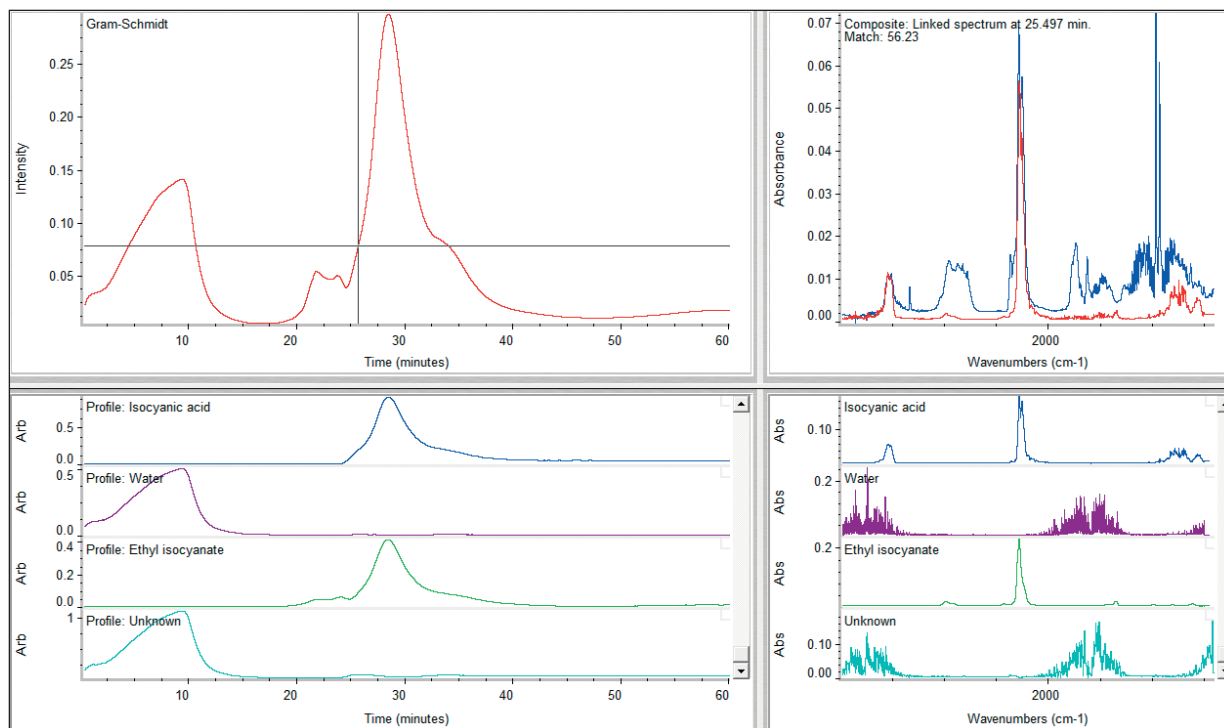
Figure 7: TGA-IR results for a polymer resin analyzed by Mercury TGA using only three components. The comparison in the upper right pane of the synthetic (red) and actual (blue) spectrum shows that several components have been missed.

The second tool involves visual review of the results combined with an "Add One" button. This allows the user to add another component (up to eight may be chosen) and restart the algorithm. The main driver for adding one is the composite versus actual screen in the upper right. This is best shown in an example.

Figure 7 shows the Mercury TGA result for a polymer resin. The analysis was started with three components (which was chosen by the estimation tool), so four hits appear (three plus the unknown). Scrolling across the profile revealed a poor agreement of the composite with the actual data, as seen in the upper right box. Figure 8 shows the effect of pressing the "Add One" button repeatedly until six components were selected. The comparison is very good (only the profiles and identities are shown here for clarity). Isocyanic acid/ethyl isocyanate are very similar and have the same profile, so it is likely this is one component, not two. Since the library spectra and the actual data may be collected under different conditions, some intensity variations in the composite versus actual are to be expected, but the peaks should all be accounted for, as in this case. Since iteration took less than a minute, this visually driven process of refinement is not onerous or complex.
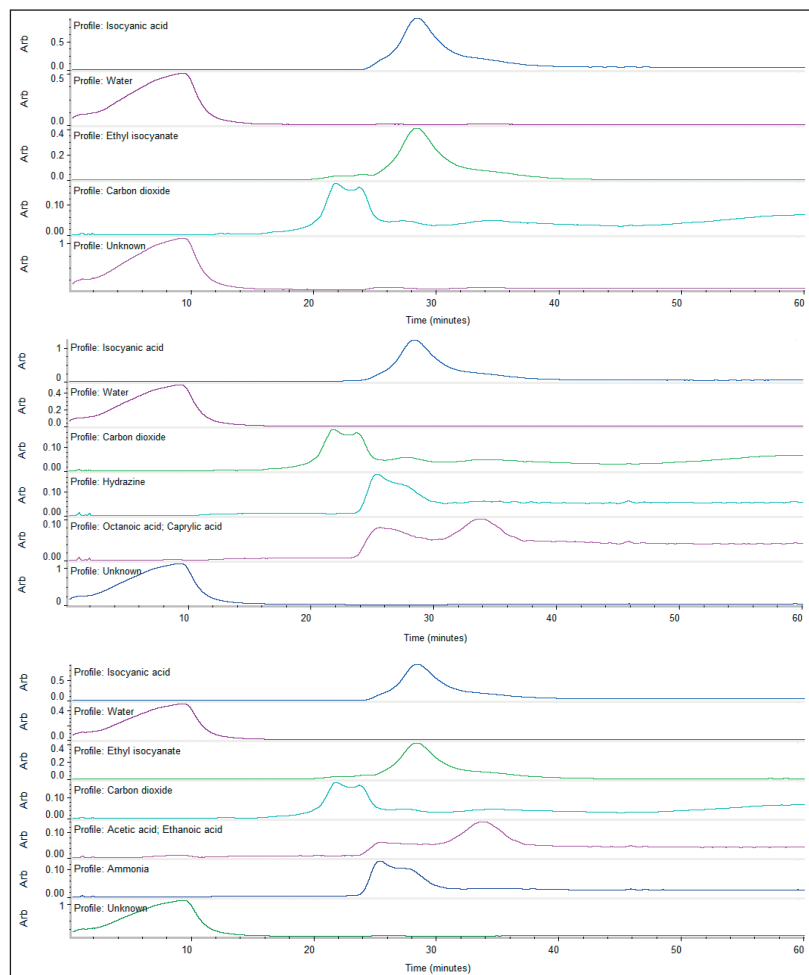

Figure 8: Same data as in Figure 7, with the number of components being set to 4 (top), 5 (middle) and 6 (bottom). See text for details.

TGA-IR, Mercury TGA and Kinetics

The first step in a TGA-IR analysis is to ensure good quality data. While many options exist, typical collection parameters (with the DLaTGS detector) are 4 cm^{-1} resolution, 0.4747 mirror velocity and co-adding 4 scans for each spectrum in a purged system. Most spectral libraries search well against 4 cm^{-1} data. These conditions give about a 5 second data collection time and good signal-to-noise. Faster collection is rarely needed as the gas evolution in the TGA during a slow temperature ramp does not rapidly change. As water and carbon dioxide are very common in TGA-IR, a purge is highly recommended.

During the analysis, the actual versus composite spectra in the upper right of the Mercury TGA output provides visual confirmation of the results. This is far more exacting than the numerical metric: poor metrics can result even when the analysis is correct, due to the complexity of the analysis and the huge number of spectra being modeled. Further, inclusion of user libraries containing TGA-IR spectra from proprietary materials can substantially improve the results.

A very exciting extension of the Mercury TGA algorithm involves the analysis of data from kinetics experiments. In kinetics, the Series file is an overlapped set of spectra from starting reagents, intermediates and products, plus solvents. Mathematically, this is exactly the same situation as the TGA-IR file. The profiles from analysis of a reaction (materials were proprietary so only profiles are shown) are shown in Figure 9 – the evidence of reactants disappearing and product forming is clear, even to the level of a bound and released agent.
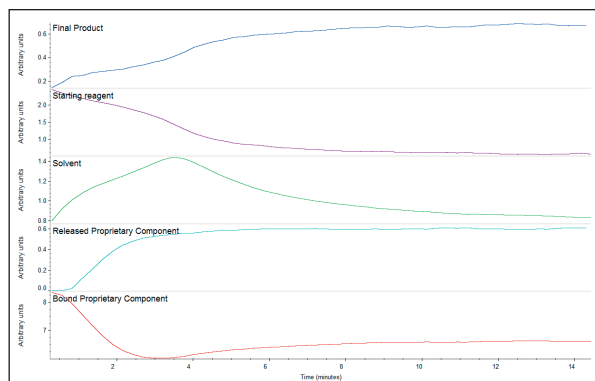
Figure 9: Profiles showing evolution of reactants and products during a kinetics experiment, as extracted by the Mercury TGA algorithm.

Conclusion

TGA-IR is a very powerful analytical procedure for deformulation of rubbers, plastics and many types of compounded materials. The traditional roadblocks have been the large number of spectra generated and the over-lapped gas phase evolutions, leading to the need for some skill in the analysis. The OMNIC Mercury TGA algorithm completely overcomes the barriers, making TGA-IR a tool which can be used at any level of expertise. Further, complex, interwoven data sets like those in TGA-IR or kinetics previously required manual selections and analysis of single spectra (or co-added spectra) one-by-one, an inefficient and time consuming process. Mercury TGA software analyzes hundreds of spectra against large libraries, providing the multicomponent information efficiently, often in less than one minute. Now users at any skill level and working in any market can apply TGA-IR to their deformulation problems, confidently and consistently.

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