Complete Materials Deformulation Using TGA-IR

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Introduction

Key applications in analytical laboratories often involve failure analysis and competitive deformulation. For example, black rubber gaskets from two suppliers stating the same production process behave differently – one seals, the other fails – or two expanded polymer foams exhibit very different mechanical behavior. These situations call for deformulation, and a qualitative and quantitative comparison of the results, to determine the source of the differences.

Thermal Gravimetric Analysis (TGA) is a powerful deformulation tool common in material analysis. Basically, a small amount of sample placed on a pan is inserted into a furnace, with the pan hanging on a sensitive microbalance. A slow temperature ramp is applied with the sample bathed in an inert purge gas. The increasing temperature forces various components of the material into the vapor phase, resulting in weight loss. TGA provides excellent quantitative information about weight losses as a function of temperature, but does not identify the vapors being driven off.

Coupling the TGA to a Fourier Transform infrared (FT-IR) spectrometer adds considerable utility to the method. The vapors released from the material pass through a gas cell inserted in the FT-IR, where the spectrum is obtained. Spectral searching provides the last link – identification of the vapors. The weight loss data from the TGA, the rapid response and high sensitivity of the spectrometer, and spectral searching combine to provide potent analytical insights into the chemistry of the sample.

Traditionally, the one difficulty with the infrared portion of the analysis has been the simultaneous evolution of gases. The TGA does not discriminate between simple and complex gas evolutions, but the instantaneous IR spectra are summations of all the gases being driven off at that time. This complexity normally requires some skill to untangle. The need to use multiple search regions to selectively extract individual components and the generally unfamiliar look of gas phase spectra to many investigators contribute to the potential for missed critical answers. As shown below, this difficulty is largely surmounted with the powerful Thermo Scientific OMNIC™ Specta™ spectroscopy software, which performs multi-component searches at a single click.

We will examine three different scenarios, based on industrial situations with finished products and feedstock supplies. The first involves an epoxy, examining the components of the mixture prior to and during setting. The second situation compares black rubber samples similar to those used in gasket manufacturing. The third study involves two, blown polymer foam materials. This range of experiments illustrates both the power and the flexibility of TGA-IR.

Experimental

An in-sample compartment TGA accessory equipped with a double pass gas cell heated to 220 °C was coupled to the TGA with a heated transfer line. The sampling accessory was inserted into a Thermo Scientific Nicolet™ iZ™10 sampling module coupled to the Nicolet iS™10 FT-IR spectrometer; shown in Figure 1. The FT-IR was driven using OMNIC spectroscopy software and OMNIC Series time-base software. In all cases, data were collected at 4 cm^{-1} resolution with background and Gram-Schmidt (GS) basis vector collection occurring just before data collection. The GS display is, in short, a simple way to visualize the total change in the spectrum from the initial time. Multi-component searching was performed by sending the OMNIC data to OMNIC Specta.

Figure 1

The thermal analysis was performed with a TA Instruments Q5000 TGA with autosampler. Pre-tared platinum pans were used to contain the samples, and the samples were between 10 and 50 mg in size. The same computer was used to control both instruments, and a trigger cable allowed simultaneous initiation of data collection. Various temperature ramps were applied to the materials, as noted below. The TGA data was imported to OMNIC via the Universal Analysis (UA) software (TA Instruments). Similar export of experimental profiles, including the Gram-Schmidt profile, to UA is available.

Results

Epoxy

A single drop of a freshly mixed two-part epoxy (normal 12 hour cure time) was placed in a TGA sample pan. The temperature was ramped from ambient to 500 °C at the rate of 15 °C/min.

Figure 2 shows the FT-IR data in OMNIC Series. The upper trace reveals the evolution of the overall IR signal in time (the GS plot), while the lower trace is the IR spectrum present at the time point indicated by the scroll bar in the upper window. The small signals in the GS plot around 11-12 minutes (190–210 °C) result from CO_2 and water bubbles evolving from the sample. The larger peak rising after 15 minutes (about 250 °C) is associated with many features in the infrared.
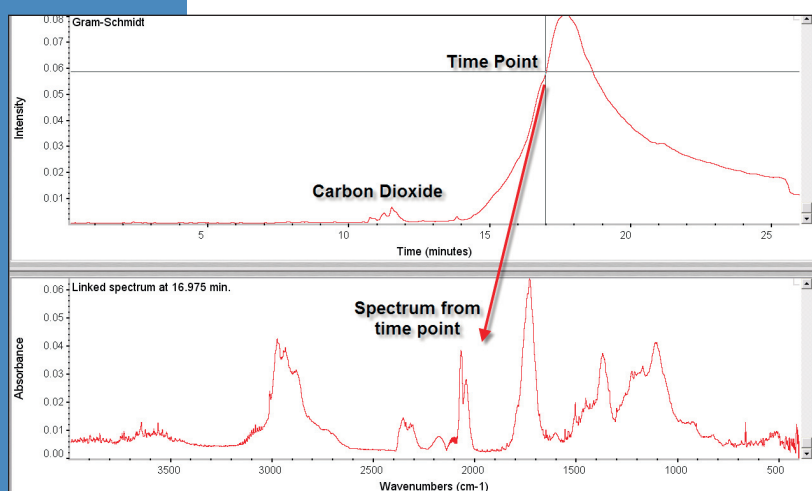
The single spectrum shown in Figure 2 (bottom) demonstrates the multiple gas evolution discussed above. A simple search on this spectrum indeed extracts one of the components, but leaves the user in need of multiple subtraction steps. Unfortunately, gas phase spectra are very sensitive to environmental conditions (temperature, pressure, mixtures), which affect both peak shapes and line intensities, making spectral subtraction based on library spectra a difficult proposition. Figure 3 shows a 3-dimensional view (time-wavenumber-intensity) of the entire file in the OMNIC Series software – the overlapping emissions and complex time behavior are quite apparent.
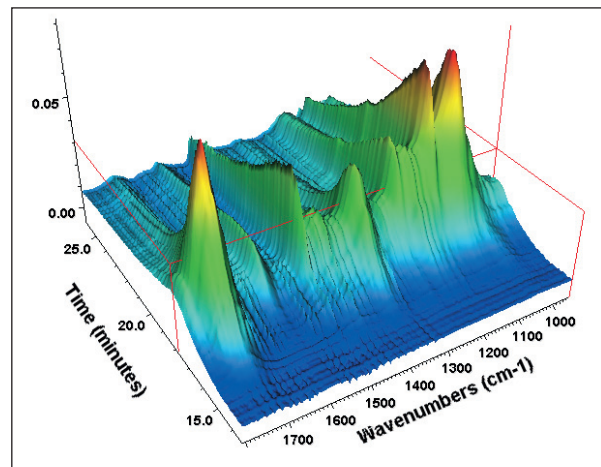

Figure 2

Figure 3

OMNIC Specta permits these complexities to be unraveled. Choosing the HR (High Resolution) Nicolet TGA Vapor Phase library and executing the multi-component search in OMNIC Specta provides the results shown in Figure 4 for multiple time points in the OMNIC Series file. The visual agreement between the original spectrum and the composite is outstanding in all cases, giving the user high confidence in the results. Further, each of these multi-component searches required less than one minute. The slight differences seen in the composite and the original are due to the same factors discussed above regarding spectral subtraction – spectral changes due to environmental variations between the experimental and library collection conditions.

OMNIC Specta's multi-component search algorithm identifies three unique compounds in an epoxy in less than a minute.
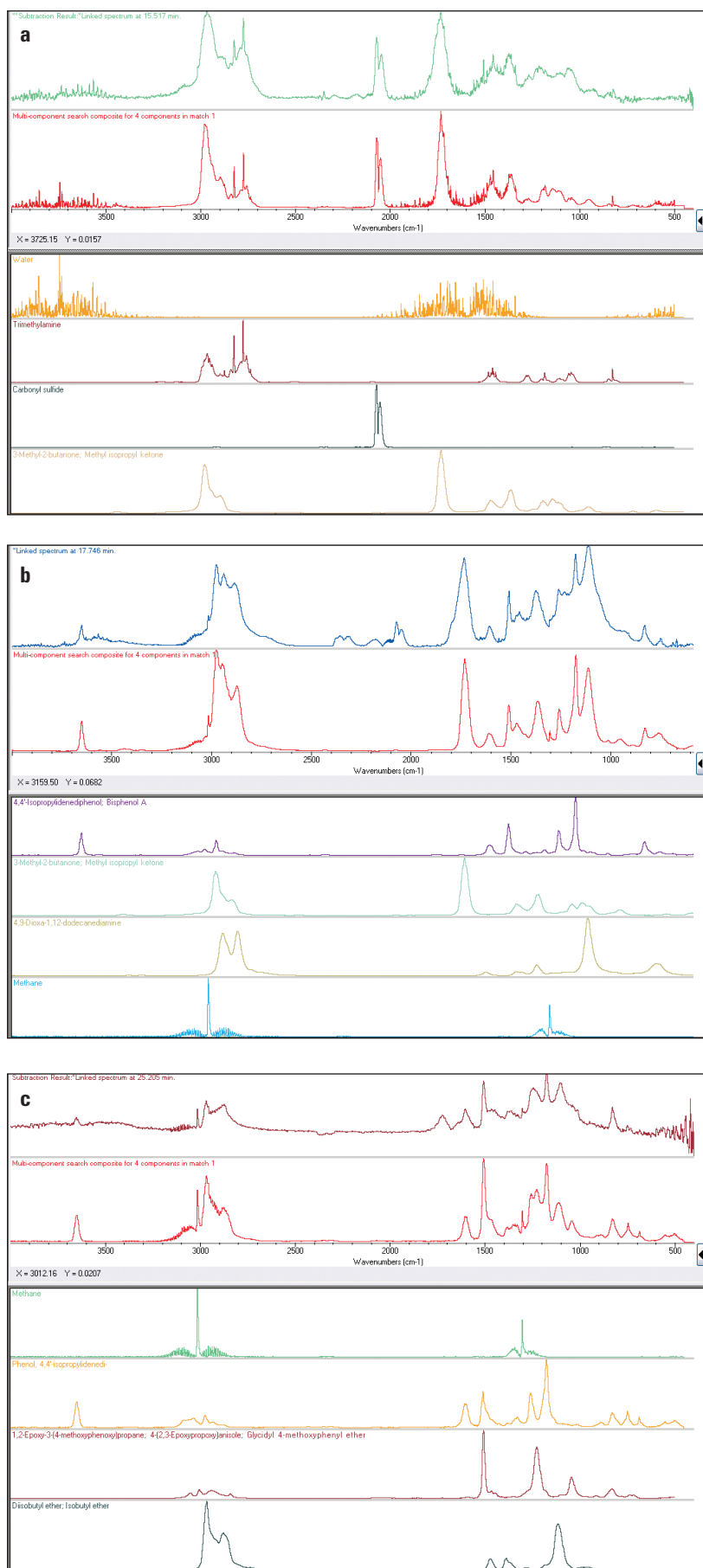
Figure 4

The first gases to emerge are clearly from the unreacted base materials of the epoxy and hardener, including the common epoxy ingredient bisphenol-A. As the temperature rises, ester peaks appear, indicative of the accelerated curing. Late in time, methane evolution along with low levels of bisphenol-A are evident as the epoxy breaks down. Broadening the idea of using a TGA to drive more general reactions, the ability to ramp and hold, or to change the purge gas during a run, gives great flexibility. Indeed, elevated temperature often accelerates reactions, and the purge gas could even be a reactant.

Black Rubber Samples

Pieces of raw rubbers (one light, one dark) used in producing high performance black rubbers were analyzed using a two-step TGA ramp. Figure 5 shows GS profiles for the two rubber samples, along with the derivative weight loss and temperature ramp information imported from the TGA. The GS curves clearly point to differences in the formulations. Below 200 °C, neither material shows major gas evolution, but above 350 °C, strong signals appear. The derivative weight loss and the GS trace are also highly correlated in time, which allows the temperature profile to be coordinated with the IR data confidently.
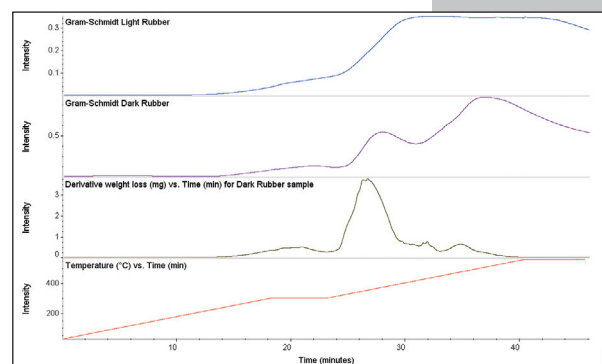

Figure 5

Comparing spectra from various time intervals in the two samples shows both similarities and differences. The high carbon-filled (dark colored) rubber releases many of the same gases as the light rubber, but at a much lower temperature. Figure 6 shows spectra from the two samples at different times, and the same basic materials are present in both – but separated in temperature of release. Figure 7, in contrast, shows the 40 minute time points (same temperature point) for both samples. The dark rubber shows CO_2, CO and water while the light rubber is showing the strong release of many components.
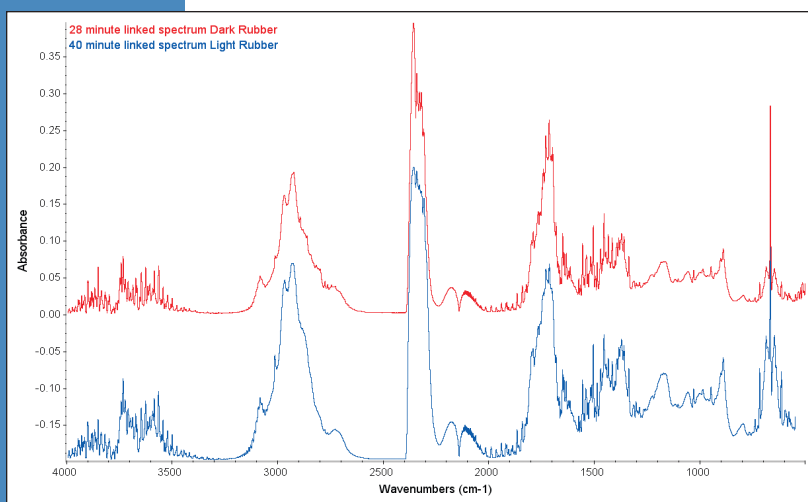
Figure 6
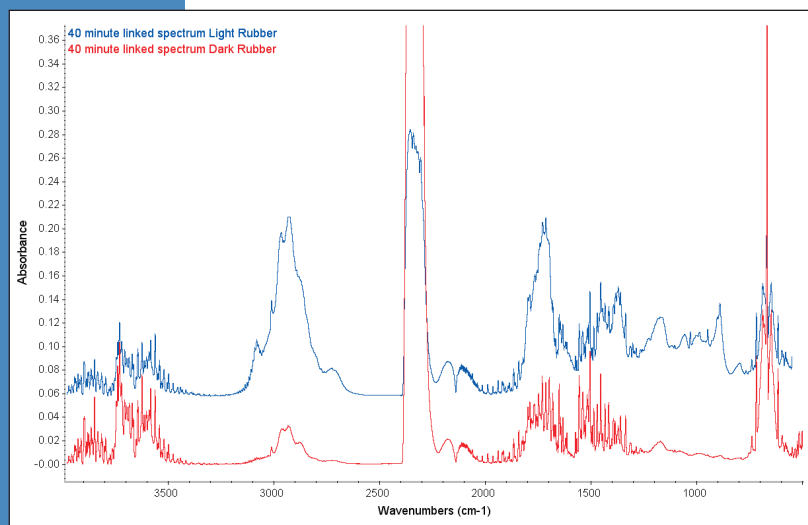
Figure 7

The multiple component gas phase spectra were exported to OMNIC Specta. Preliminary searches over the entire spectrum showed the expected hits – CO, CO_2 and water plus one rubber component. However, we focused the multi-component search algorithm on a narrow range of the spectrum where there were small features. The narrow range, multi-component search result, shown in Figure 8, reveals four materials, included butenes, methanol and methyl-ethyl ketone.
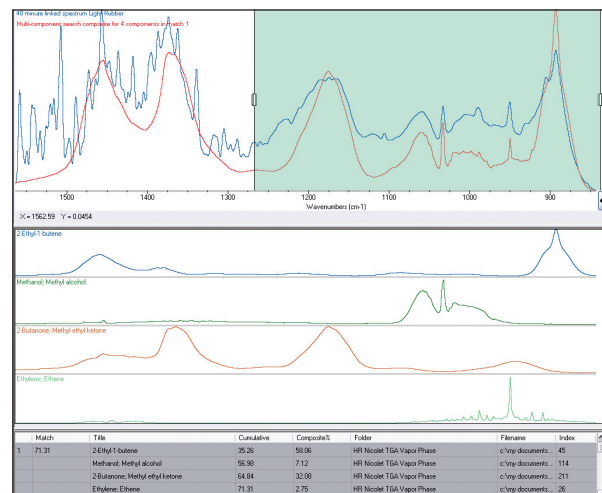

Figure 8

In normal infrared spectroscopy, water and CO_2 often originate from the atmosphere, and produce undesired signals in the spectrum, which is why atmospheric corrections and instrument purging are often used. However, in the TGA experiment, both water and CO_2 provide information, as they are generated by the sample during heating. Thus, software corrections should be avoided, while purge, if applied, must be maintained at a constant level.

Normally atmospheric water and carbon dioxide are to be avoided in FT-IR. With TGA they both provide useful information as the sample is heated.

The two rubbers are apparently similar in underlying chemistry. However, the large difference in the temperature of release shows the formulations or treatments applied to the samples cause differences. In a high performance application, it may well be that the lower temperature of evolution causes a failure; at the least, it would indicate a potential target for further analytical investigation.

Blown Polymeric Foam

Decorative or functional covers for many manufactured items are often produced in a "blowing" process. A two (or more) component mixture of a base polymer and a blowing agent are inserted into a mold. The mold is then subjected to heating, which melts the base polymer. At a higher temperature, the blowing agent releases gas, usually with a sharp onset, which quickly expands the material to fill the mold. In the present study, the mechanical properties of two plastics made with the same base polymer, but different blowing agents, were similar. Either would have been useable mechanically, but one of the materials emitted unacceptable levels of noxious vapors.

Pieces of the blown polymers and pellets of the two blowing agents and the base polymer were analyzed by TGA-IR; only a critical subset of this data is shown here. The temperature ramp ended at 200 °C, as the thermal decomposition of the base polymer was not of interest – only the behavior of the residual blowing agents or trapped gases. The entire piece melted around 190 °C, releasing gases caught in the matrix, but there was little or no decomposition of the base polymer at this temperature.

GS profiles for the blowing agents and a cover blown with Agent 2 are shown in Figure 9. Agent 1 shows a single, rapid-onset, gas emission (which is almost explosive in nature). Agent 2 shows two transitions, and blown cover material shows the same transitions. The 3-D plot in Figure 10 for Agent 2 shows only CO_2 in either of the two emissions. In Figure 11, the same region is shown for Agent 1. The onset is rapid and only occurs at one temperature, but the signals show more than one gas is coming off. The OMNIC Specta multi-component search result, shown in Figure 12, reveals that the second peak is isocyanate. A very small shoulder on the low wavenumber side of the isocyanate is due to CO. The OMNIC Series results for the base polymer alone (not shown here) reveal none of these signals, so the problem lies with the choice of blowing agent.
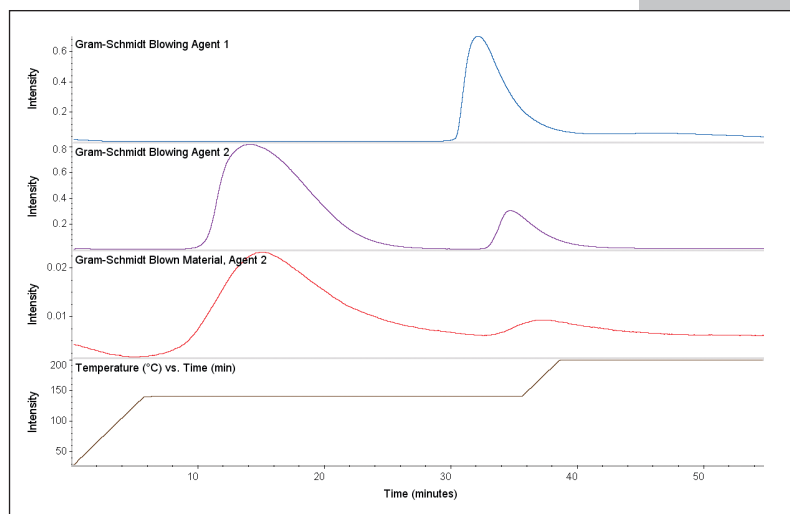
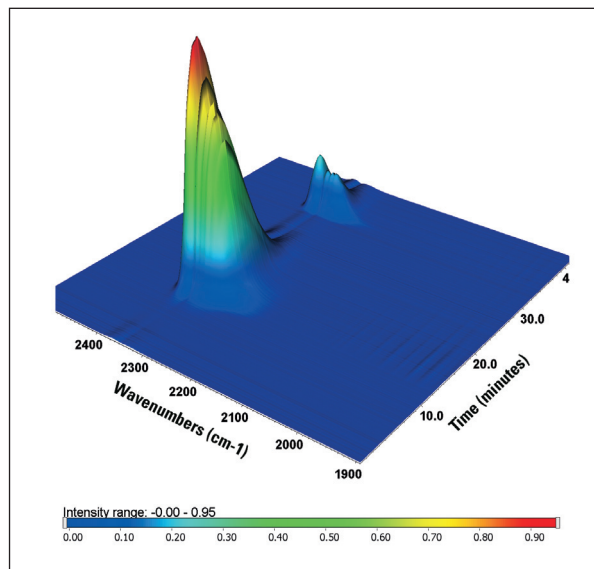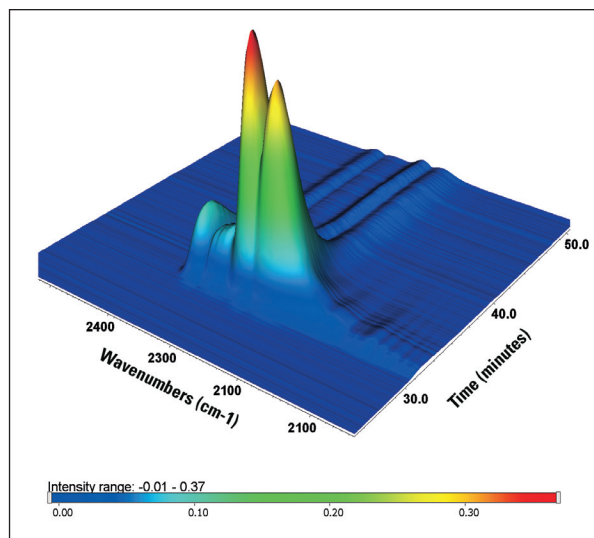*The additional information provided by FT-IR enables the analyst to identify which Agent is proper to use in blown polymeric foam.*

Figure 9

Figure 10

Figure 11

Both blowing agents work very well so far as the mechanical properties of the final material are concerned. However, the additional gases evolved permitted the manufacturer to prefer Agent 2. Note that the weight loss profiles alone would be insufficient to discriminate between the two materials. The additional information provided by the infrared analysis provides the needed differentiation.
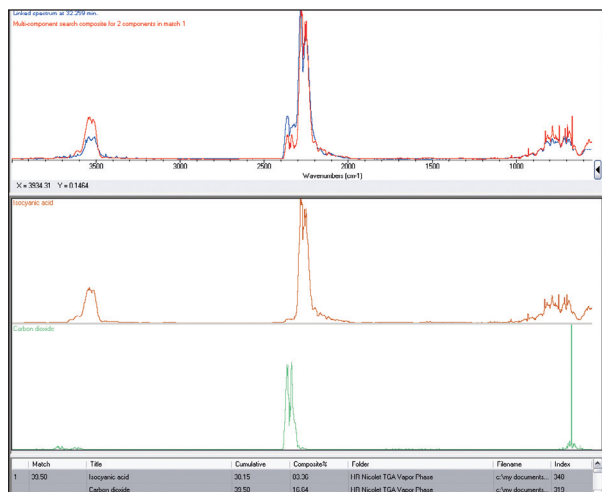

Figure 12

Conclusions

TGA-IR is a general purpose, powerful technique for the deformulation of materials in many industries, including plastics, resins, rubbers, coatings and pharmaceuticals. The melding of the two techniques more than doubles the analytical power for these applications. With the addition of OMNIC Specta multi-component searching, the identification of the overlapped vapor emissions no longer requires spectral interpretation skills, greatly reducing the time per analysis for experienced and inexperienced users alike. Consistency in the analysis is also assured.

OMNIC Specta is shown to greatly improve an analyst's to interpret overlapped gas phase spectra.

The key conclusion from the examples shown here is that TGA-IR coupled with OMNIC Specta provides actionable results. In essence, the operations personnel can make process modification decisions based on a solid foundation.

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