

TGA-IR Analysis of Museum Materials

Francesca Casadio, Conservation Department, The Art Institute of Chicago, Chicago, IL, USA
Michael S. Bradley, Thermo Fisher Scientific, Madison, WI, USA

Key Words

- Corrosives
- FT-IR
- Out-gassing
- Textiles & Paints
- TGA-IR

Introduction

The preservation and presentation of museum objects, such as textiles, paintings, and sculpture, requires careful control of the environment. This includes observing specific limitations for parameters such as temperature, relative humidity, and light exposure, but extends also to accurate control of the materials that are chosen for display. In planning an exhibition, exclusion of corrosive gases from the environment and damage from inappropriate mounting must be balanced with optimal aesthetics. It is an important responsibility of conservators in museums to make sure that the display materials (wood, velvet, adhesives, etc.) do not themselves become a source of corrosive vapors.

Potential corrosives from these types of materials include ammonia, cyano-compounds, and acetic acid. The out-gassed vapors are normally present at extremely low concentrations. However, in the confined area of a display case, and with cumulative exposure over a long period, damage can still occur. A rapid, sensitive, and easy-to-use method of analysis to test materials is needed.

Heating, using a Thermal Gravimetric Analysis (TGA) instrument, can stimulate out-gassing from these materials. The TGA provides weight-loss information, but does not qualitatively identify the vapor being driven off. The Nicolet™ 6700 FT-IR spectrometer is a sensitive, rapid-response gas analyzer, useful at low concentrations and in flow-cell conditions. Thus, the TGA-IR combination is ideally suited for analyzing these materials.

Experimental

The analysis of materials from museum display cases – wood, velvet, and gum arabic (found on paintings) – was carried out via TGA-IR. Between 20 mg – 80 mg of material was used.

A Nicolet 6700 FT-IR spectrometer running the OMNIC™ software with OMNIC Series option was used to collect the infrared spectra. OMNIC Series software allows collection of IR data at regular intervals, paralleling the TGA experiment. The TGA-IR interface fits directly into the Nicolet 6700 sample chamber. The accessory contains a gas cell heated to 230° C to prevent gas condensation. This couples to the TGA-IR interface via a heated transfer line (220° C). The entire system was equilibrated (temperature and purge), for 24 hours. Both a Thermo Scientific TGA and a TA Associates™ TGA were used. The Thermo Scientific TGA software imports the TGA data directly into OMNIC Series software during collection. The TA Associates software requires a single keystroke import of the data after the run is complete. In all runs, the mass-loss, first derivative and temperature ramp data were imported into the OMNIC Series software.

Various temperature ramping profiles were used, generally timed to take about an hour. The final temperature was kept relatively low (200 – 250° C) to prevent major destruction of the samples, while enhancing the out-gassing. Backgrounds of 256 scans and ten basis vectors were collected for calculation of the Gram-Schmidt reconstructions (essentially, changes from background integrated over the entire spectrum)¹ before the TGA run started. The IR spectra during the run were collected using 18 scans at 8 cm⁻¹ resolution, requiring about 10 seconds per spectrum, for the duration of the temperature ramp. As an exception, the gum arabic experiment used 8 scans of 2 cm⁻¹ resolution (also requiring 10 seconds), for comparison. The gas phase spectra were then identified by searches against the TGA Vapor Phase spectral library.

OMNIC Series software permits the “profiling” of the TGA run. The height or area of a single peak or region, or the ratio of two peaks/regions, can be calculated across the entire time profile. This permits the tracking of a particular component, such as ammonia, over the entire time of the TGA run. As the actual data set contains massive amounts of information, this profiling is used to clarify trends and aid in presentation.

Results and Discussion

Vapor phase spectra are generally characterized by a series of sharp peaks caused by rotational transitions.² These cluster into two or three bands, called the P-Q-R bands, representing rotational transitions (changes) of -1, 0 and +1 energy levels, respectively. Not all bands show a Q-branch (such as CO), while ammonia has two.³ The intensities of these bands are strongly affected by the temperature (Boltzmann distribution).² The gas cell in the TGA accessory is stabilized at 230° C, and the spectral library was collected under these conditions, so spectral searching generally results in excellent matches. Furthermore, the extremely high signal-to-noise of the spectra obtained on the Nicolet 6700 spectrometer permits even small signals to be searched and identified.

Figure 1 shows the early time TGA-IR data of a run with high water content, and figure 2 shows a profile from a wood sample. The peaks due to water (first profile) are clearly seen in the initial “drying” stage, as the temperature ramps past 110° C, but are essentially gone by 130° C. The peaks due to cyano-materials and ammonia then become clear. The waterfall plot in figure 3 shows this in a different manner.

The TGA-IR data for velvet showed very interesting, complex spectra. The most interesting component, from the perspective of the end use of the material in a museum, was acetic acid, seen at the higher temperature end of the run in figure 4.

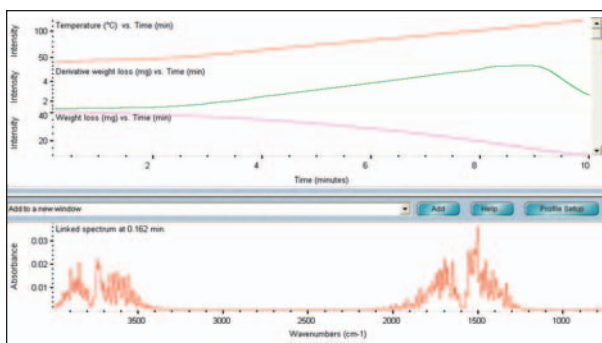


Figure 1: Low temperature, early time, TGA-IR result for a high-moisture content sample.

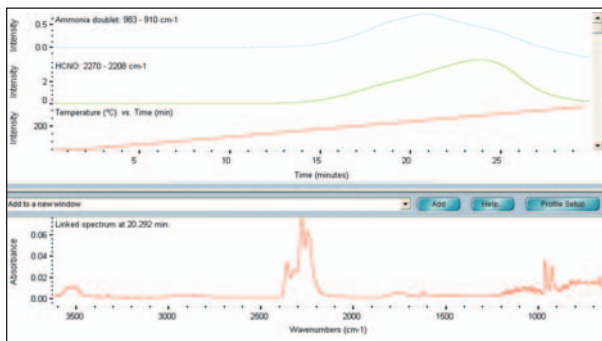


Figure 2: Moderate temperature TGA-IR result for wood. The tall quartet between 2000 and 2500 cm^{-1} is due to carbon dioxide (higher frequency doublet) and HCNO (lower frequency doublet); ammonia is evidenced by the doublet around 950 cm^{-1} . The profiles at the top show the time evolution of each of these signals.

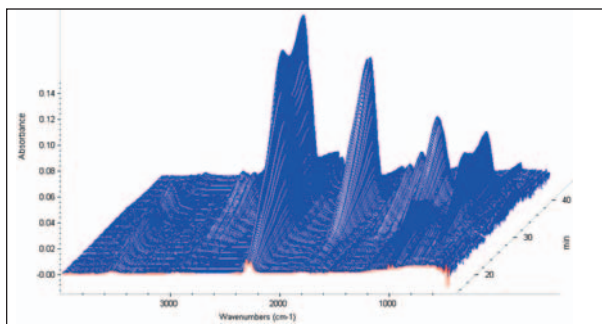


Figure 3: A waterfall plot presentation of the spectra from the same sample as in figure 2. The rise and fall of various components is visible.

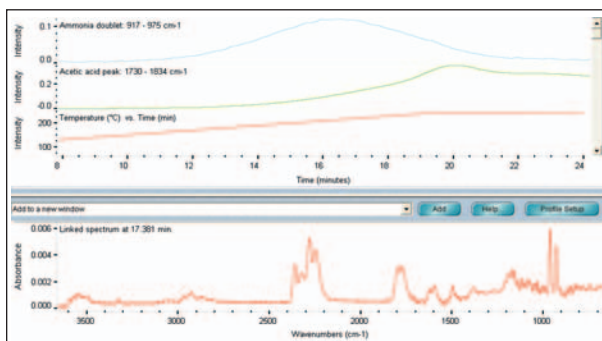


Figure 4: TGA-IR results for velvet, showing the strong evolution of acetic acid and ammonia, profiled in the upper window.

The high-resolution (2 cm^{-1}) run on Gum Arabic is shown in figure 5. Comparing this with the other runs shows that 8 cm^{-1} resolution was satisfactory for component identification. However, the extremely tight P and R branch structure of CO is clear at this resolution, rather than run-together as at lower resolution. These spectra are actually collected at higher resolution than the library, so a de-resolution routine is (automatically) applied during searching. The high signal-to-noise shows the ability of the Nicolet 6700 spectrometer to achieve excellent results without extensive signal averaging even at high resolution.

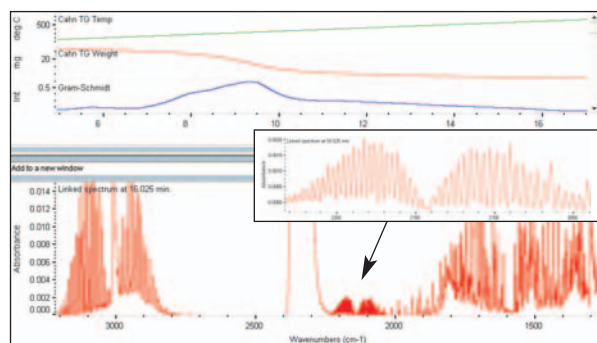


Figure 5: An x-axis and y-axis zoom on the high resolution IR spectra from gum Arabic. The extremely high signal-to-noise of the system is evidenced by the excellent resolution of various P-Q-R branch structures. The inset shows a zoom on the small signals around 2140 cm^{-1} .

Conclusions

The presence of potentially corrosive out-gassing products, such as ammonia and acetic acid, reinforces the need to thoroughly test materials before they are considered suitable for museum exhibition display cases. It is vital to exclude the possibility that the materials used to construct a display may have long-term, detrimental effects on the artifacts.

The Nicolet 6700 FT-IR spectrometer and TGA-IR interface combination is shown to be an effective tool for discerning the potential detrimental nature of some display materials so as to rule out their use for exhibition of invaluable artworks. The short time required – less than two hours total per run (with furnace cool down time) – means TGA-IR should find applicability in predicting and diagnosing problems. The ease of use through the OMNIC software platform, the high quality of the data, and the profiling and searching analysis steps enhance this capability.

References

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