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APPLICATION NOTE

Evolved Gas Analysis with Thermogravimetric Analysis – Mass Spectroscopy (TGA-MS)

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INTRODUCTION

Materials outgassing and thermal decomposition can lead to performance deterioration, failure, and safety concern. In this regard, Eurofins EAG Lab has established numerous outgassing analytical techniques to meet the industry needs, including TGA-IR, headspace GCMS, Residual Gas Analysis (RGA), and Fractional IGA analysis. While these techniques often overlap in certain capability, each is specialized to provide unique analytical information, depending on sample types (chemistry, geometry, morphology, etc.), applications, temperature range, atmosphere (or vacuum), sensitivity requirement, etc.

TGA with hyphenated technologies such as infrared (IR) and/or mass spectrometry (MS) is specialized in investigating real time outgassing behavior of materials, in the temporal/temperature regime of interest and desired atmosphere, including

- real time, high sensitivity (resolution ~0.1 µg), quantitative analysis of mass loss as the material is heated
- identification of the evolved gas species associated with mass loss, including adsorbed moisture, bound water, residual organic solvents, and volatile decomposition products
- outgassing profile of individual gas species as a function of time and temperature

Previously, we have demonstrated our TGA-IR as a powerful technique in identifying molecular information of evolved gas species, in particular small gas molecules such as hydrocarbons, nitrogen oxides, hydrogen halides, CO, CO^2, H^2O, NH^3, HCN, fluorocarbons, etc. (Heetderks & Wang, 2019). However, TGA-IR is limited to detect infrared-active compounds, and for large molecules, only functional group information can be identified. Outgassing profiles could suffer from broadened temperature/time resolution, due to the time required for evolved species reaching the IR detector after liberated from the TGA analyzer (note in this case the mass transfer efficiency is mainly dictated by the flow gas rate), and a large IR cell volume to be filled which cause mixing of gases evolved from different time/temperature regimes.

TGA-MS addresses the crucial mass transfer issue during evolved gas analysis in several ways to improve real time measurement sensitivity:

- The rapid volumetric mass transfer through a capillary transfer line, driven by the pressure drop from the TGA instrument, which is operated under ambient pressure, to the mass analyzer operated under high vacuum.
- The EGA furnace features horizontal purge stream over the sample, a short path to the exit port and heated EGA adaptor.
- The capillary stainless steel transfer line heated to 300 °C.

These features eliminate dead volume, and condensation and dilution of evolved gas species, and ensure rapid transfer of gas species once evolved from the TGA furnace. The mass analyzer has mass scan range from 1 to 300 amu, enabling analysis from H2 to large volatile molecular species such as octamethylcyclotetrasiloxane. The TRIOS software supports the importation of MS for trend analysis and fine detail analysis. The key features of our TGA-MS are summarized in Table 1.

Table 1. Key TGA-MS instrument specification

Hi-ResTM TGA Instrument		
Model	TA® TGA550 with EGA Furnace	
Temperature control	Range	Ambient – 1000 °C
	Accuracy	± 1 °C
	Precision	± 0.1 °C
Linear Heating Rate	0.1 - 50 °C/min	
Sample Weight Range	1000 mg	
Dynamic Weighing Range	1000 mg	
Weighing Resolution	± 0.01%	
Resolution	0.1 µg	
EGA Furnace Vacuum	50 µTorr	
EGA Furnace Liner	Quartz	
Mass Spectrometer		
Model	MKS CirrusTM 3 Quadrupole Mass Analyzer	
Mass Range	1 – 300 amu	
Mass Resolution	1 amu	
Ionization Source	Electron Ionization	
Filaments	Dual (customer changeable)	
Detectors (Dual)	Faraday and Second electron multiplier	
Sample Pressure	1 atm (nominal)	
Data Collection Modes	Bar graph and Peak Jump	
Inputs	Data collection controlled by TGA trigger	
Mass Transfer from TGA Instrument to Mass Spectrometer		
EGA furnace	Horizontal purge stream	
EGA-Transfer Line Adaptor	Heated	

Evolved Gas Analysis with Thermogravimetric Analysis – Mass Spectroscopy (TGA-MS)

Transfer Line Tube	Capillary stainless steel, 0.22 mm (ID)
Transfer Line Temperature	300 °C (fixed)
Transfer Line Length	1.8 meter, flexible
Software	
Data Analysis	TA® TRIOS software

In the Eurofins EAG Lab, our TGA-MS can analyze sample up to 1 gram, from ambient to 1000 °C, at linear heating rate of 0.1 – 50 °C/min. Evolved gas species are detected in the mass range of 1 to 300 amu. When operated in Hi-Res TGA mode, the heating rate is controlled by the decomposition rate of the sample, which enables separation of broad and overlapping weight losses, and rapid survey over wide temperature range with excellent resolution.

TGA-MS can analyze a broad range of samples, from simple inorganic compounds to formulated drug products, from synthetic polymers to biomass materials, as demonstrated in Figures 1 and 2. The results are typically plotted by overlaying MS data of identified species over the corresponding TGA profiles.

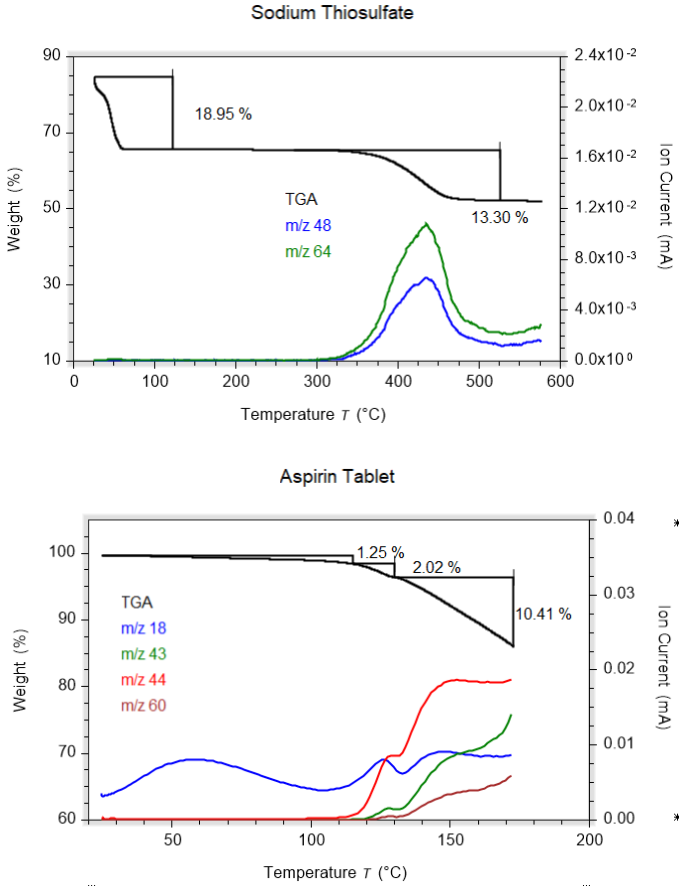

Figure 1: (a) TGA-MS of sodium thiosulfate, demonstrating the quantitative determination of moisture content and temporal /temperature profile of decomposition product SO^2; and (b) TGA – MS of formulated aspirin revealing three H^2O outgassing events from ambient to 100 °C, 100 °C – 130 °C and above 130 °C, corresponding to physiosorbed (note: moisture can be accurately determined in this case), chemically bound and/or thermal decomposition nature, respectively. Other clearly observed temporal/temperature outgassing profiles include the decomposition products CO^2 and CH^3COOH. Operating conditions: TGA heating rate 10 °C/min, purge gas flow 100 mL/min nitrogen, and mass data collection in Bar Graph mode, sample size 2 and 15 mg, respectively.

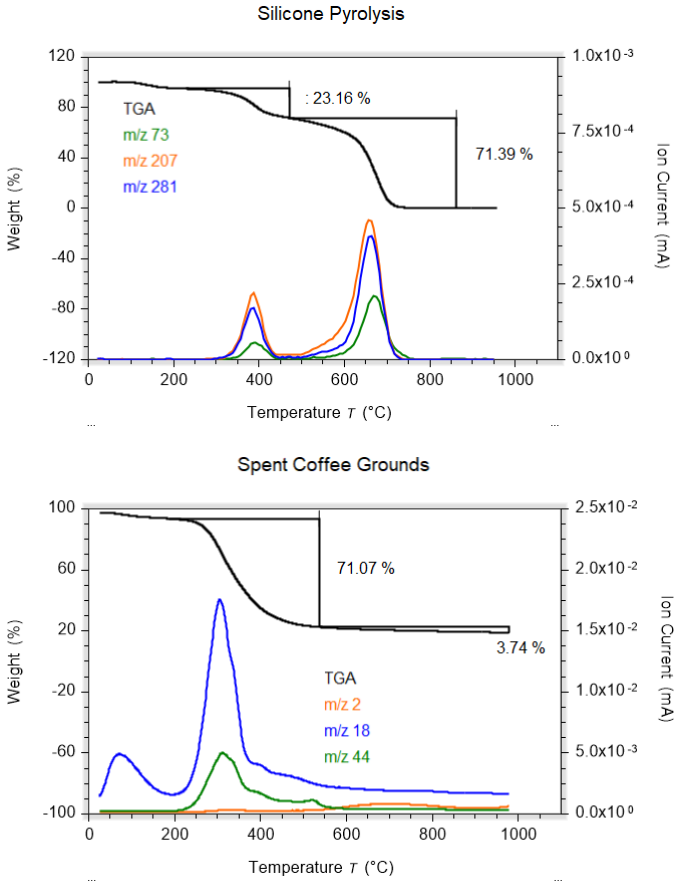

Figure 2: (a) TGA-MS analysis of degree of curing in synthetic silicone. Residual monomer content was determined, including hexamethylcyclotrisiloxane (D3) and octamethylcyclotetrasiloxane (D4) monomers which were evolved between 300 °C and 450 °C. Additional D3 and D4 were also detected from 600 °C to 700 °C, as a result of siloxane decomposition. (b) TGA-MS study of pyrolysis/carbonization behavior of biomass materials - spent coffee grounds. H^2O adsorbed and formed from thermal decomposition were detected at below 200 °C, and from 200°C to 400 °C, respectively. Note H^2 evolution was detected after major decomposition and carbonization was completed at around 600 °C. Operating conditions: TGA heating rate 20 and 10 °C/min, purge gas flow 100 mL/min nitrogen, and mass data collection in Bar Graph mode, sample size 2 mg.

Evolved Gas Analysis with Thermogravimetric Analysis – Mass Spectroscopy (TGA-MS)

TGA-MS is also a very powerful tool for reaction kinetic studies, such as curing of adhesives and thermosetting resins that are of industry importance, hydrolytic stability of materials under high temperature steam, poisoning of petroleum catalysts, debinding of green parts, additive manufacturing of polymer-derived ceramics, etc. Figure 3 demonstrates the application of TGA-MS in the curing kinetic study of a silicone adhesive.

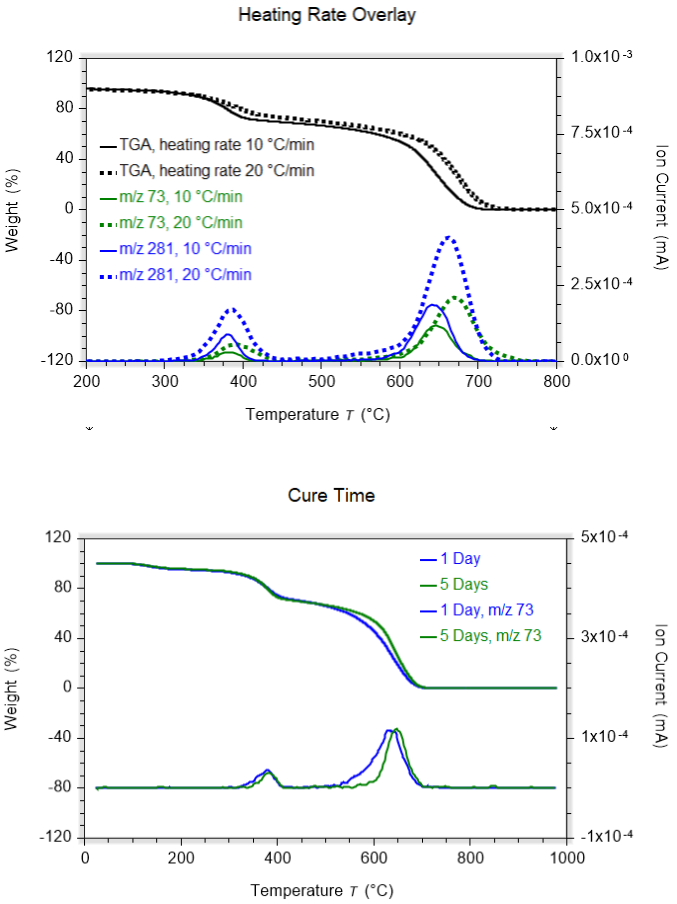

Figure 3: TGA-MS investigation of decomposition kinetics of silicone. (a) TGA-MS scan of cured siloxane at different heating rates 10 °C/min and 20 °C/min. As expected, the two analyses show similar overall mass loss and fragments, and a faster heating rate (dotted line) shifts the decomposition to a slightly higher temperature range. Notice MS signal intensity can be improved by running at a higher heating rate, due to evolving of gas species in a shorter time window; (b) TGA-MS comparison of degree of curing for siloxanes cured for 1 day and 5 days. The curing was monitored with mass fragment m/z 73, i.e., $(CH^3)^2SiO$-+, from evolved gas species. The results indicate that curing is not completed within one day and that 5-day curing improves the thermal stability of the siloxane.

SUMMARY

In summary, TGA-MS is a standard technique for evolved gas analysis, along with TGA-IR. In Eurofins EAG Lab, we combine the strength of TGA-MS and TGA-IR, to provide real time evolved gas analysis for a variety of materials and processes of industry relevance, from ambient to 1000 °C.

REFERENCES

Heetderks, T., & Wang, X. (2019). Thermogravimetric Analysis – Fourier Transfer Infrared Spectroscopy (TGA–FTIR) Services. Retrieved from EAG.com: https://www.eag.com/resources/appnotes/thermogravimetric-analysis-fourier-transfer-infrared-spectroscopy-tga-ftir-services/