## Solutions for TGA/STA- EGA coupling

### INTRODUCTION

Hyphenated techniques are also known as Evolved Gas Analysis (EGA). They are well established in the field of thermogravimetric analysis (TGA) or simultaneous thermal analysis (STA) with many applications. They have proved particularly interesting for the investigation of gases emitted by the samples enabling their detections, their identifications and in some cases their quantifications.
Hyphenated solutions include MS, FTIR, GCMS and combinations of these.
This technical note describes each of these techniques used in the field of thermal analysis.

### 1/ Coupling with Mass Spectrometers (MS) – TGA/STA-MS

By coupling a TGA or a STA instrument to a MS, the gases evolved by the sample from the crucible are quickly transferred to the ion source of the mass spectrometer thanks to the pressure difference between the TGA furnace (approx. 1 bar) and the MS (approx. 10-7 mbar). The gases are not exposed to a temperature lower than 300 °C during the transfer thanks to the use of a heated transfer line.


***Figure 1: THEMYS ONE thermal analyzer (on the right) coupled with a mass spectrometer (on the left) from Pfeiffer Vacuum.***

After being ionized, the molecules and fragments are then separated according to their mass-to-charge ratio (m/z) thanks to a quadrupole and detected by a SEM or a Faraday detector. The intensity of one or more selected characteristic m/z can be monitored and superimposed to the mass variation signal. Full spectra can also be acquired frequently over the duration of the TGA experiment. Mass spectrometers with amu ranges up to 300 can be employed.

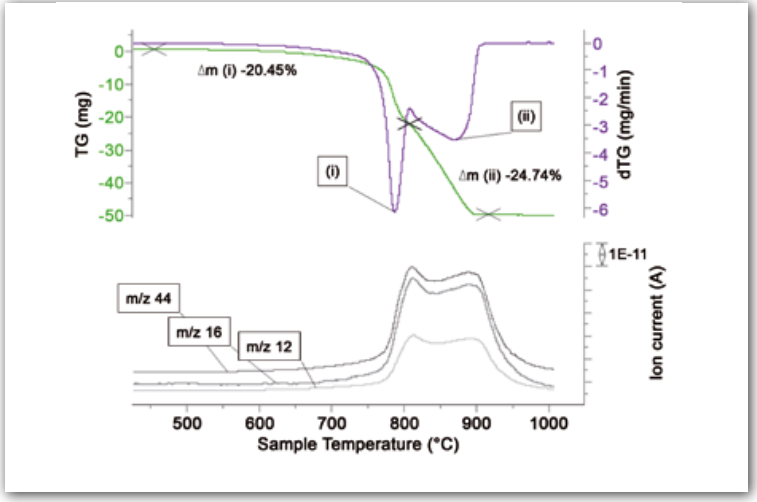



***Figure 2 - Two-steps decarbonatation of a dolomite (CaMg) (CO3)2 sample CO2 evolution is identified thanks to the ion current intensity of m/z 44, 16 and 12 signals***

## 2/ Coupling with Fourier transformed infra-red spectrometers (FT-IR) – TGA/STA-FTIR

During the coupling of a TGA or STA instrument with a FTIR, the whole carrier and evolved gases from the sample flow through a heated transfer line (up to 300 °C) and up to the FTIR gas cell. Inside the gas cell, chemical groups of the gaseous molecules are identified according to their specific absorption of IR light wavelengths.
The Gram-Schmidt signal - i.e. the integral of the whole spectrum or of a chosen chemical function - can be overlaid with the mass variation. Experimental spectra can be compared with ones from reference materials libraries for identification of evolved substances.

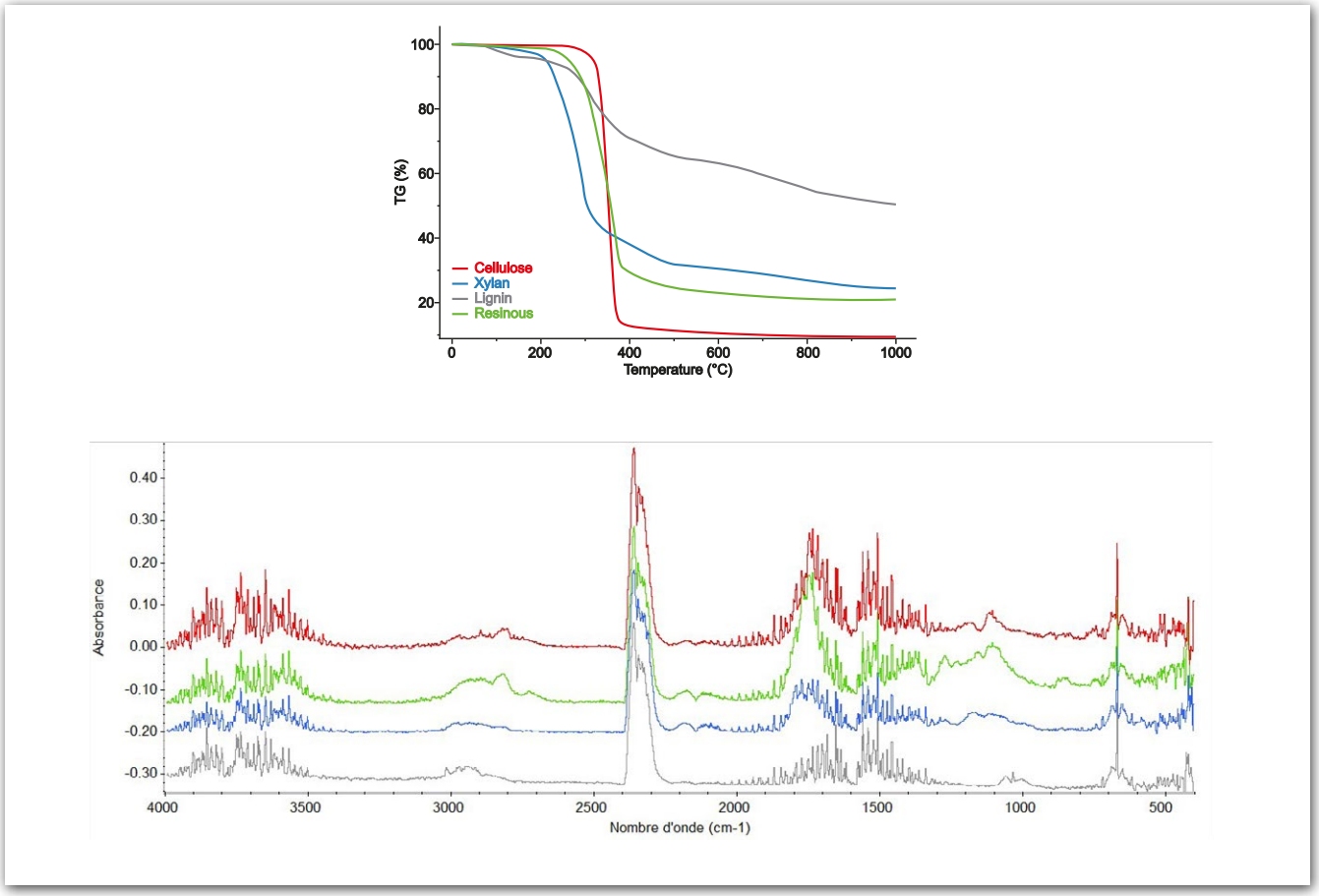



***Figure 3 - Biopolymers and wood samples mass losses (up) and corresponding IR spectra at maximum mass loss rates (down). Vibration bands specific to $CO_2$, $H_2O$, aldehydes and carboxylic acids could be identified from the cellulose sample IR spectrum.***

## 3/ Coupling with combined gas chromatography and mass spectrometry (GC/MS) - TGA/STA-GC/MS

TGA-GC/MS is becoming increasingly popular, as gas chromatography allows the separation of the evolved species before their detections and identifications by the mass spectrometer. This is particularly interesting when analyzing the thermal decomposition of complex organic substances such as biomass or polymeric materials.

The evolution of the species emitted by the sample from the TGA furnace must be carefully coordinated with the injections on the GC column. This can be accomplished by using an appropriate automated sampling loop that allows the sampling of the whole gas stream from the TGA instrument and their injection on the GC column.

The whole line including the sampling loop has been designed to be heated up to 350 °C to avoid the condensation of the evolved gases from the sample.

Switching between injections and sampling needs to be done in relation to the progress of the sample decomposition process.

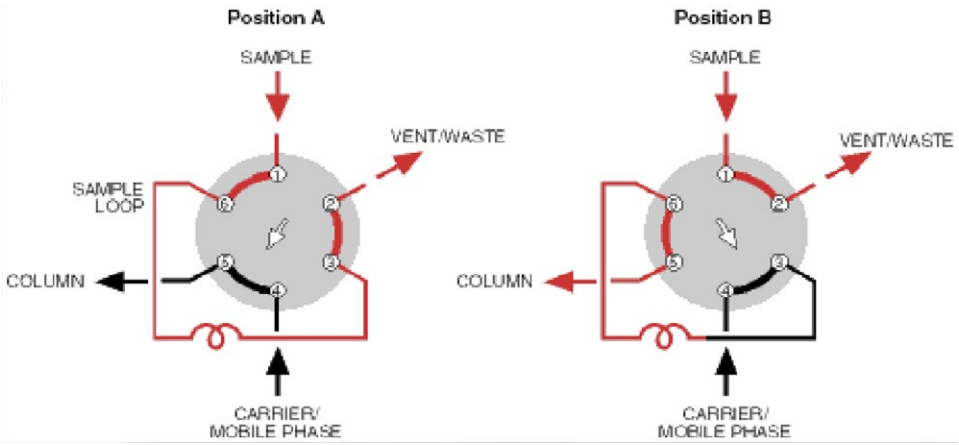



***Figure 4: Sample path diagram during sampling phase (position A) and injection into the Autoinjector (position B).***

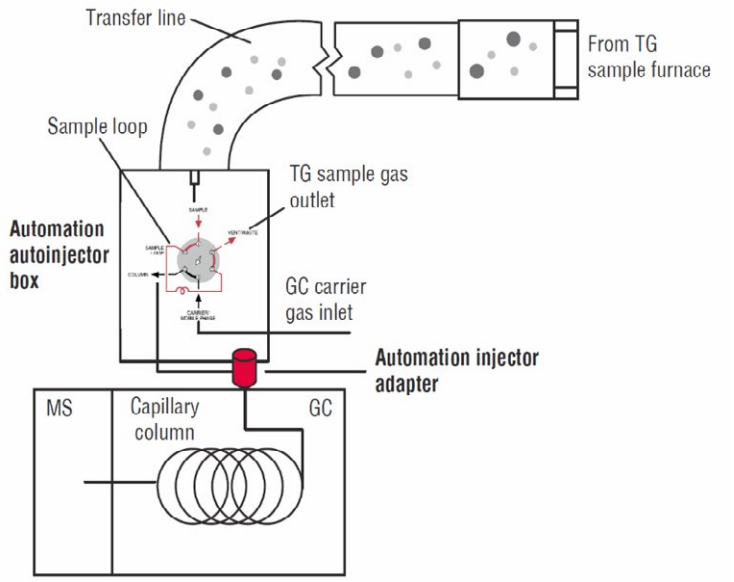



***Figure 5: Diagram of the Autoinjector's connection to the GC/MS.***

Three modes are available with this Autoinjector:

• Discrete sampling mode: it is meant to achieve a good separation of all the components in the gas mixture but restricts the number of injections that can be analyzed during the TGA run.
• Quasi-continuous sampling mode: the separation cycle is faster and so the gas sampling frequency can be significantly increased. Following the kinetics of production of one specific substance evolved during the TGA run is possible in this mode.
• Timed mode: injections at user-defined times or temperatures corresponding to characteristic TGA events (like mass loss rate maxima).

Watch video >>

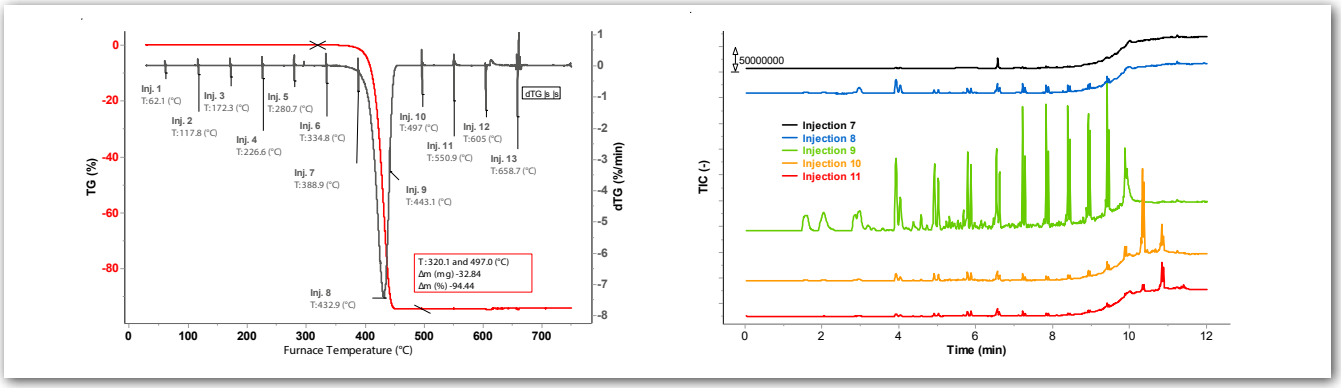



***Figure 6 - Mass loss during the pyrolysis of an ethylene and 1-octene copolymer (left) and chromatogram corresponding to injections 7-11 (right). The complex mixture of alkanes and alkenes is separated. Substances like hexadecene (i) and hexadecane (ii) are only detected from injection 10 (497 °C).***

*Figure 7: THEMYS thermal analyzer (on the right) coupled with a GCMS (on the left) from ThermoFisher.*

## 4. Coupling techniques features & benefits

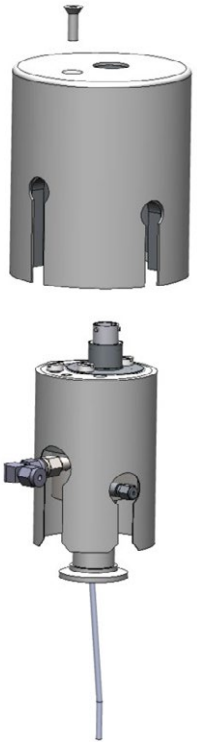
| Technique | Features | Benefits | TGA or STA Models | Temperature range |
|---|---|---|---|---|
| TGA-MS or STA-MS | Best limit of detection Fast transfer time | Applicable to small mass variations, easy to setup, detection of heavy molecules (with Supersonic System) | CALVET PRO THEMYS ONE / ONE+ THEMYS THEMYS LV | -120 °C up to 2400 °C |
| TGA-FTIR or STA-FTIR | Signals specific to chemical functions | Applicable to the detection of families of substances in complex gas blends evolved from decomposition of organic samples | CALVET PRO THEMYS ONE / ONE+ THEMYS | -120 °C up to 2400 °C |
| TGA-GC/MS or STA-GC/MS | Best gaseous molecules separation and identification | Applicable to the identification of substances in complex gas blends evolved from decomposition of organic samples | CALVET PRO* THEMYS ONE / ONE+ THEMYS THEMYS LV* | RT to 2400 °C |

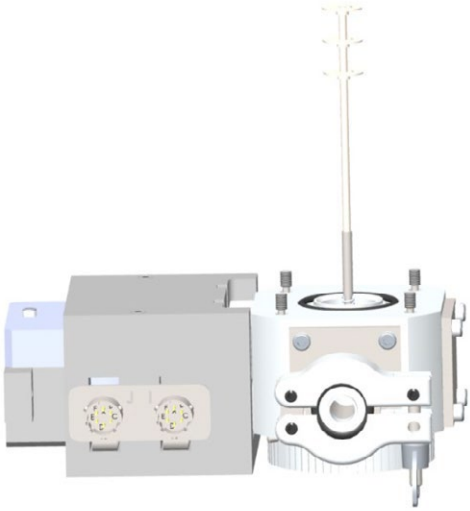
*on request
Multiple coupling like TG-GC/MS-FTIR or TG-MS-FTIR are also available for several TGA and STA instruments.

## 5. Application area of TGA/STA-EGA coupling

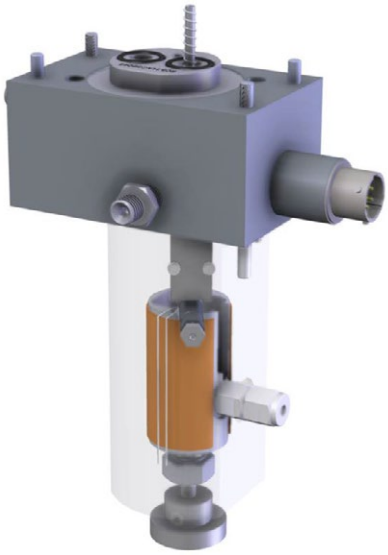
| TYPICAL APPLICATION AREA | MATERIALS |
|---|---|
| Gasification, pyrolysis, combustion | Coal, biomass and wastes |
| Adsorption, desorption, calcination | Catalysts, sorbents, minerals |
| Dehydration, dehydroxylation, decarbonatation | Cements, minerals, ceramics, pharmaceuticals |
| Thermal stability, compositional analysis | Pharmaceuticals, polymers, cements, minerals, ceramics |
| Oxidation | Metals, alloys |
| Residual solvents | Pharmaceuticals |
| Polycondensation, curing | Polymers |

## 6. Coupling parts

| Coupling part for THEMYS ONE / ONE+ | |
|---|---|
|  | |
| **Interface for coupling THEMYS ONE / ONE+ with** | FTIR, MS, GC-MS (single coupling) |
| | MS+FTIR, MS+GC-MS (multiple coupling) |
| **Heated up to** | 300°C |
| **Data acquisition synchronization** | Available as an option |

| Coupling part for THEMYS | |
|---|---|
|  | |
| **Interface for coupling THEMYS with** | FTIR,M S, GC-MS (single coupling) |
| | MS+FTIR, FTIR+GC-MS (multiple coupling) |
| **Heated up to** | 300°C |
| **Data acquisition synchronization** | Available as an option |

| Coupling part for THEMYS LV | |
|---|---|
|  | |
| **Interface for coupling THEMYS LV with** | MS |
| **Heated up to** | 200°C |
| **Data acquisition synchronization** | Available as an option |

| Coupling part for CALVET PRO | |
|---|---|
|  | |
| **Interface for coupling CALVET PRO with** | FTIR, MS, GC-MS (single coupling) |
| | MS+FTIR, FTIR+GC-MS (multiple coupling) |
| **Heated up to** | 200°C or 300°C |
| **Data acquisition synchronization** | Available as an option |