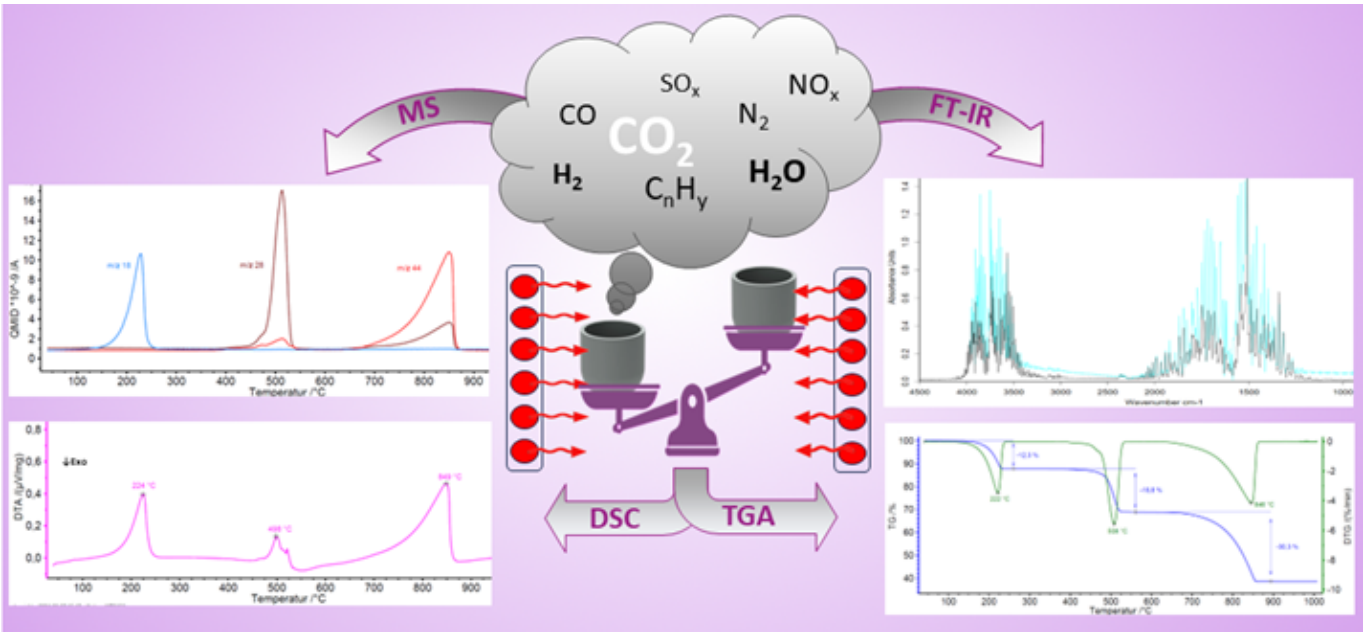
EVONIK
Leading Beyond Chemistry

FOCUS ANALYTICS

NEWSLETTER OF RD&I ANALYTICS AUGUST 2024

Thermal Emission Gas Analysis-
Better identified when coupled: Analysis in 4D



WHETHER FOR MATERIAL DEVELOPMENT OR FOR PROCESS OPTIMIZATION – THERMOGRAVIMETRIC EMISSION GAS ANALYSIS PROVIDES IMPORTANT INSIGHTS AND CONCLUSIONS FOR EFFICIENT MATERIAL AND METHOD DEVELOPMENT.

While spectroscopic or physical methods usually allow only a static examination of materials or substances, the Thermal Emission Gas Analysis (EGA) enables the tracking of the dynamic behavior of a material or substance under the influence of temperature: During a selectable temperature increase, the sample is weighed, and the resulting volatile by-products are simultaneously detected using infrared spectroscopy and mass spectrometry. In this way, the temperature resistance of various materials and substances can be examined and the resulting decomposition products, for example, can be identified. In addition, different atmospheres can be adjusted to simulate the application case and generate important parameters for future processes. The residue obtained from the EGA can then be used for further analyses such as electron microscopy or X-ray analyses.

SAMPLE EXAMINATION

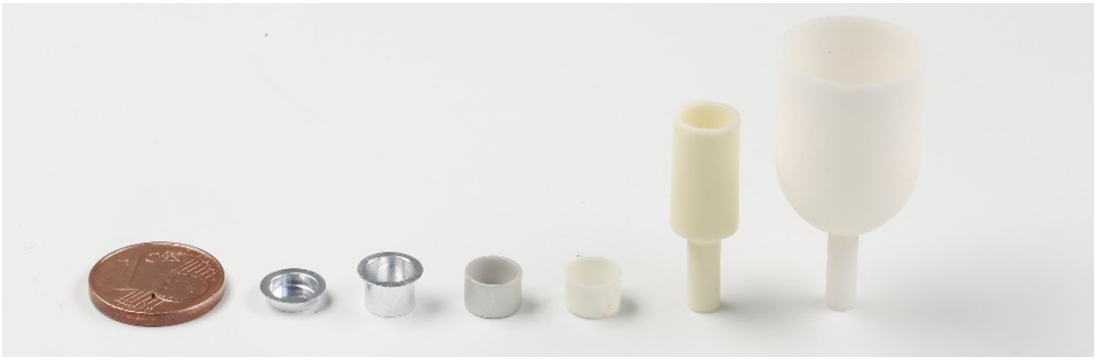
» **Materials: inorganic, organic solids and liquids. For example:** Plastics, coated glasses /ceramics/ catalysts, multi-component systems, coating reagents

» **Sample size:** Up to 4 mm in diameter and 5 mm in height; **sample weight:** 10 mg to 1000 mg

» **Temperature range:** From 40 to 1400 °C; **heating rates:** 5 K/min to 20 K/min

» **Atmospheres:** Inert (He, N_2, CO_2, Ar), reducing (forming gas with 5 % H_2), oxidizing (air, O_2)

» **Detection limits for emissions:** Up to approx. 1 wt.-% in the sample, emission species with a boiling point up to approx. 200 °C



▲ *Source: Electron Microscopy Evonik Analytics Hanau*

Fig. 1: By flowing different gases around the sample and using crucibles of different sizes (adapted to the application and question), a wide variety of tests can be carried out.

SPECIAL FEATURES OF EGA PROCEDURE

» Precise examination of the **thermal behavior** of the material / the substance

» **4-in-1-solution:** Thermo weighing (TGA) with optional heat flux signal (DSC/DTA) and a simultaneous analysis of the emission gases with infrared spectroscopy (IR) and mass spectrometry (MS)

» **Individual setting of temperature levels**

» Behavior of the sample in **different atmospheres** (inert, oxidizing, reducing)

» **Simple** to no sample **preparation**

» **Adsorption experiments** (CO_2, H_2)

» Resulting **residue can be used for further analysis with** other methods

» **Selective presentation of the results** (mass loss, IR spectra, mass spectra, also in 3D)

» **Stabilization tests:** During thermolysis temperature resolved detection and identification of the decompositions products

EXAMINATION OF DECOMPOSITION PROCESSES

» **Investigation of separation processes:** Decarboxylation, loss of crystal water and drying processes

» **Effect of different atmospheres** on the reaction

» **Analysis of combustion gas components**

» **Identification of outgassing products**

EXAMPLE 1: DECOMPOSITION OF CALCIUM OXALATE MONOHYDRATE

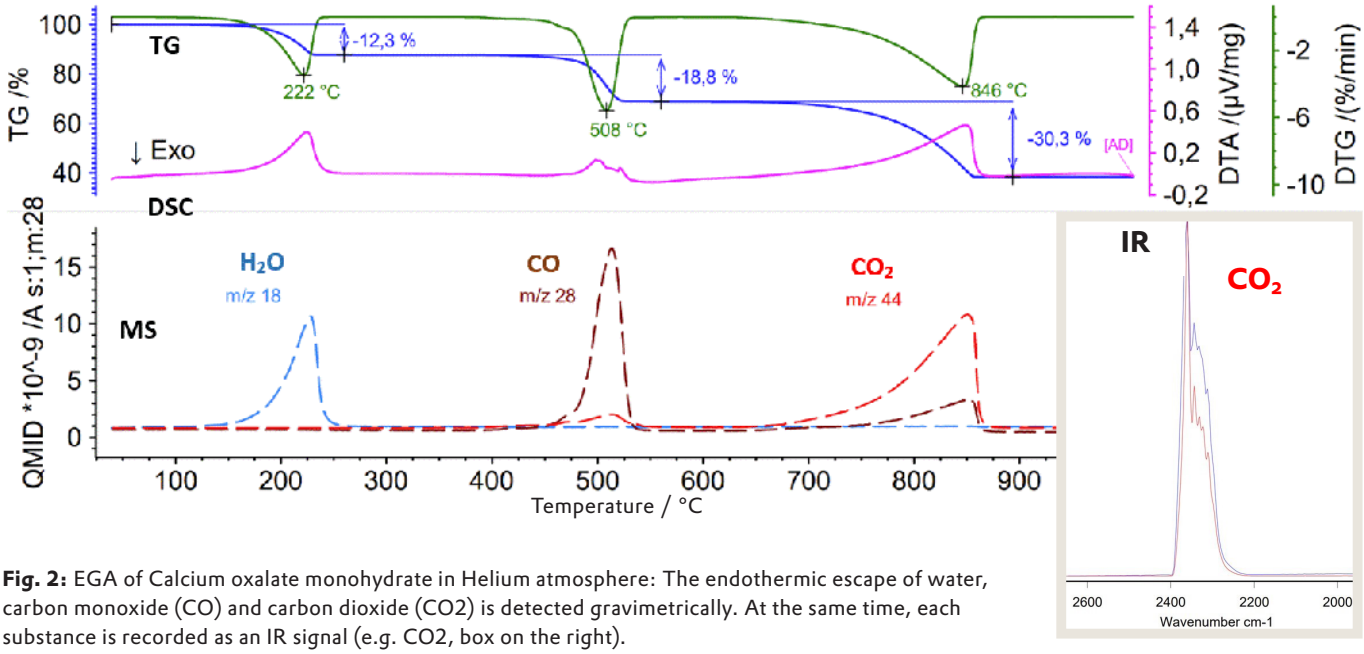


Fig. 2: EGA of Calcium oxalate monohydrate in Helium atmosphere: The endothermic escape of water, carbon monoxide (CO) and carbon dioxide (CO2) is detected gravimetrically. At the same time, each substance is recorded as an IR signal (e.g. CO2, box on the right).

With the help of EGA, it is possible to specifically examine the emissions or the separation of gaseous thermolysis products of a sample. Due to the variably adjustable temperature ramps, effects such as decarboxylation or the loss of crystal water can be accurately recorded and the cleavage products can be detected simultaneously from the gas phase using mass spectrometry and IR spectroscopy: The example of calcium oxalate (Fig. 2) shows that water, carbon monoxide (CO) and carbon dioxide (CO_2) escape stepwise one after another stoichiometrically. This is proved by loss of weight (TG signal in Fig. 2 top, blue), the mass-to-charge ratio mass (m/z signal, CO, brown, and CO_2, red) and an IR spectrum (exemplified on CO_2 with the reference spectrum, Fig. 2, bottom right) of the sample.

Additionally, the DSC signal shows whether the processes are endothermic or exothermic (e.g. crystal rearrangements). As all volatile substances are recorded, it is possible to detect unexpected byproducts and gain valuable insights into the thermal decomposition reaction of the sample.

The substance can be thermally modified with EGA to the desired intermediate stage and then analyzed by further methods (e.g. XRD, XPS, electron microscopy). EGA enables, for example, to precisely monitor drying or rearrangement processes, without decomposing of the material, and to use these findings for the next larger scale.

DETERMINATION OF PROCESS PARAMETERS

» **Monitoring of material changes** e.g. from softening to foaming to thermolysis

» **Determination of material properties:** Dehydration, oxidation, melting and boiling points, determination of softening and decomposition temperatures

» **Investigation series** using different heating rates up to a desired maximum temperatur

EXAMPLE 2: EXPANSION PROCESS OF A FLAME-RETARDANT POLYIMIDE POLYMER

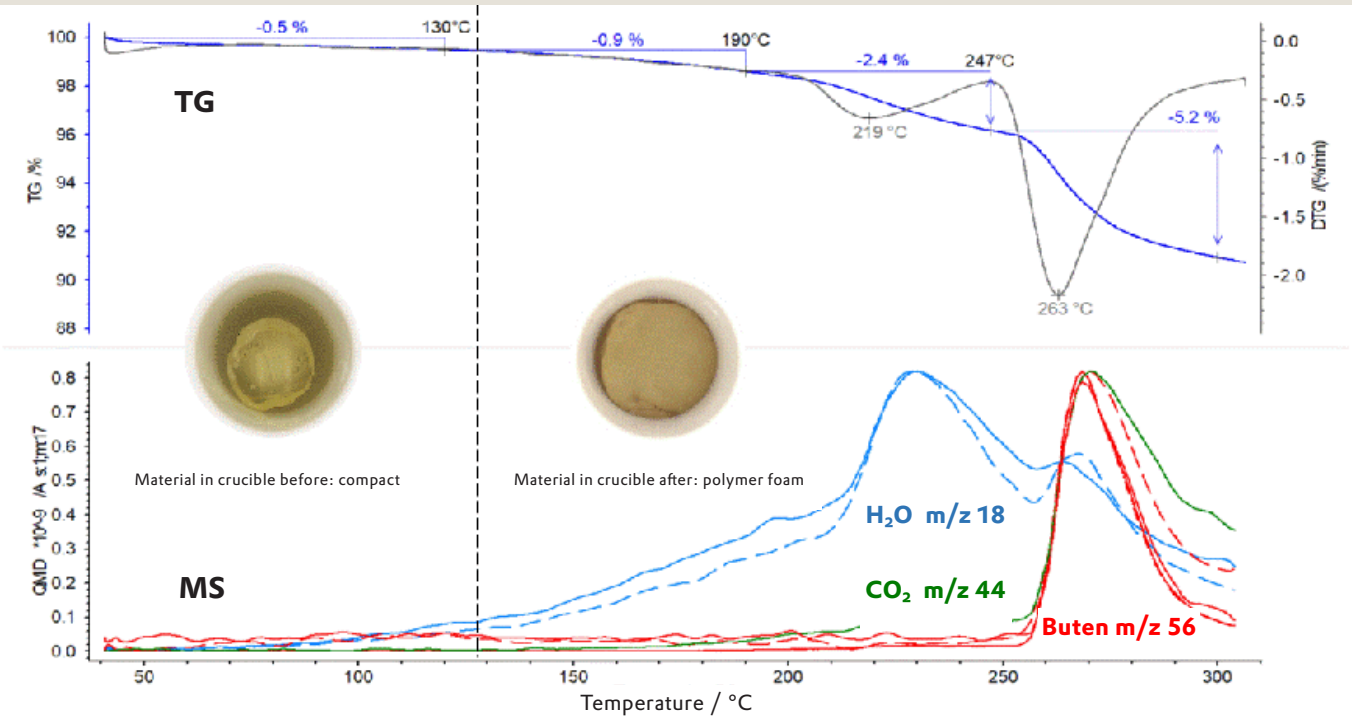


Fig. 3: EGA of a foamable polyimide polymer in a N2 atmosphere: The yet compact material (crucible on the left) is transparent. Above approx. 200 °C, the material gradually foams up and becomes opaque (crucible on the right). Emerging water, CO2 and butene are detected as MS Peaks.

Due to the diverse detection channels of EGA, complex material manufacturing processes, can be examined in an uncomplicated and efficient way. The knowledge gained from the examinations fosters the development: The controlled foaming of polymers often is a technical challenge, which is why testing in small-scale provides important parameters for future formulation and process development. A sample amount of less than one gram is sufficient for a meaningful analysis.

The EGA example of an expandable polyimide polymer shows the different stages that need to be considered in the process: initially, the still-compact precursor is transparent (crucible in Fig. 3, left). Above approx. 130 °C, the material gradually foams up and becomes opaque: water, CO_2 and butene evolve simultaneously and serve as a blowing agent until, at approx. 300 °C, the thermolysis of the now foamed material sets in.

While increasing the temperature of the sample, typical signals in the mass spectrum (MS, Fig. 3, bottom) show an increasing escape of water (blue) and CO_2 (green) as well as the elimination of butene (red).

At the same time, an FT-IR signal is detected for each stage of mass loss (TG signal, Fig. 3 top), which confirms the identity of the substances.

The temperature range for the subsequent process control can thus be determined very easily.

INVESTIGATION OF SAFETY(-RELATED) ISSUES

» **Investigation of hazardous substances forming during thermolysis (concerning e.g. disposal, recycling)**

» **Screening for emissions of hazardous substances (for REACH, prohibition lists...)**

EXAMPLE 3: EMISSIONS FROM FLUORINE-CONTAINING COATINGS AND IMPREGNATIONS

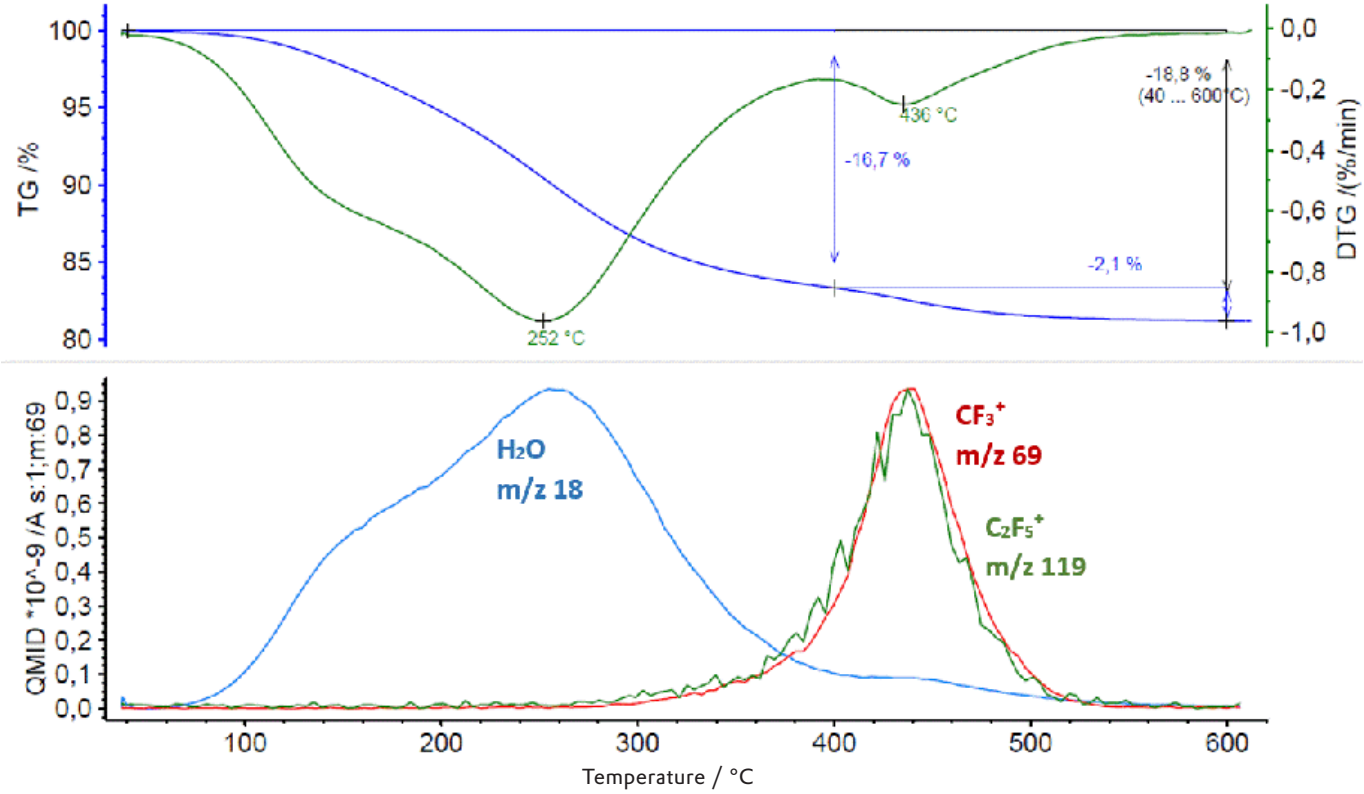


Fig.4: EGA of a non-stick coated molecular sieve (zeolite) in air: First, the water stored in the material is released. Above approx. 200 °C, fluorine-containing emission products such as CF_3^+ und $C_2F_5^+$, so-called ionic PFAs, escape due to the pyrolysis of the non-stick coating.

Particularly, when it comes to safety-related topics EGA is a quick method of obtaining reliable information: In the context of the PFAs issue, non-stick and dirt-repellent coatings and impregnating agents containing fluorine are suspected of releasing PFAs (per- and polyfluoroalkyl substances).

With the help of EGA, it is possible to simulate what happens when a glass treated with a non-stick coating is exposed to elevated temperatures. For this purpose, a commercially available, aqueous fluorine-containing non-stick solution was applied to zeolite beads (molecular sieve) and, after drying at 23 °C, analyzed by EGA. The thermogram shows first the release of stored water, then the gradual separation of fluorine-containing components, the decomposition products of the solution ingredients: The ions with a mass-to-charge ratio (m/Q) of 69 and 119 are characteristic fragment ions that are formed during the thermolysis of PFAS.

The ion with m/Q 69 corresponds to a trifluoromethyl ion (CF_3+), a common and stable fragment of PFAs, Ion C_2F_5+ at m/Q 119 is another characteristic fragment of the non-stick coating used.

The results show that fluorine-containing compounds or PFAs do indeed gradually evolve at temperatures above 200 °C, and this must be considered in the glass recycling process, but that no PFAs are emitted in the environment, if the substances and materials are handled at low temperatures that usually occur during regular use.

DO YOU HAVE ANY QUESTIONS?

We are glad to advise you on the most suitable methods for your questions and coordinate all the necessary steps, from the arriving of the sample to its examination and the final analytical report.

Our devices as well as the evaluation metods follow the current state of the art.

We stay in personal contact with you and support you in evaluating the results, if you like.

Get in touch with us!

We are happy to create a customized concept or offer.

CONTACT

Uwe Schneider
Phone: +49 6181 59 3009
uwe.us.schneider evonik.com

Evonik Operations GmbH
RD&I Analytics
Kirschenallee
64293 Darmstadt

IMPRESSUM

Evonik Operations GmbH
RD&I Analytics

Darmstadt
Kirschenallee
64293 Darmstadt

Essen
Goldschmidtstraße 100
45127 Essen

Hanau
Rodenbacher Chaussee 4
63457 Hanau

Marl
Paul-Baumann-Straße 1
45772 Marl

Evonik (SEA) Pte Ltd.
21 Biopolis Road Nucleos T
Tower A (South)
Level 1M Unikt #01-35
Singapore 138567, Singapore

Evonik (SHA) IM Co., Ltd.
68 Chundong Road,
Xinzhuang Industry Park
Shanghai 201108, China

Evonik Corporation
7001 Hamilton Blvd.
18087 Trexlertown-Allentown, PA
United States

Responsible Person: Dr. Matthias Janik
Figures: Evonik
Information Status: August 2024