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SIMULTANEOUS THERMAL ANALYSIS – MASS SPECTROMETER SKIMMER COUPLING SYSTEM

W.-D. Emmerich and E. Post

NETZSCH-Gerätebau GmbH, Wittelsbacherstraße 42, D-95100 Selb/Bavaria, Germany

Abstract

A mass spectrometer coupling system for simultaneous TG/DSC/DTA-QMS measurements will be introduced that is capable of operation at temperatures up to 2000°C. The coupling is maintained at a temperature very close to that of the sample, minimizing condensation, and features an extremely short gas flow path. The efficiency of this coupling system will be demonstrated through examples from the area of polymers, ceramics, metallurgy and recycling.

Keywords: ceramics, metals, polymers, recycling, TG/DSC/DTA-QMS

Introduction

The quantitative transfer of condensable gases or vapors from a thermobalance to a quadrupole mass spectrometer requires highly-developed, extremely sophisticated technical solutions. When such evolved products are involved, especially at higher temperatures, the conventional commercial capillary coupling quickly reaches the limit of its detection capability.

A two-stage orifice gas inlet system was developed for a simultaneous TG-DSC/DTA instrument, with consideration given the important laws of gas dynamics [1]. The initial technical realization has been described in reference [2]. A portion of the gases evolved from the sample, which are under atmospheric pressure, are drawn through the first orifice by a vacuum. A pressure reduction occurs at approx. 0.2 mbar. The second orifice (skimmer) is arranged such that a representative sample of the gas is transferred to the QMS in the form of a molecular beam.

Through technical advances and optimization, an STA with QMS skimmer coupling is now available for application up to 2000°C. Since, in addition to consideration of the laws of gas dynamics, the entire skimmer coupling system is located in the hot part of the furnace and is thus practically at sample temperature, the condensation of products evolved from the sample is prevented to the greatest extent possible. A schematic of the Skimmer coupling system is shown in Fig. 1.

Experimental

In order to check the efficiency of the Skimmer coupling system against conventional capillary couplings, comparative TG-MS measurements were carried out on

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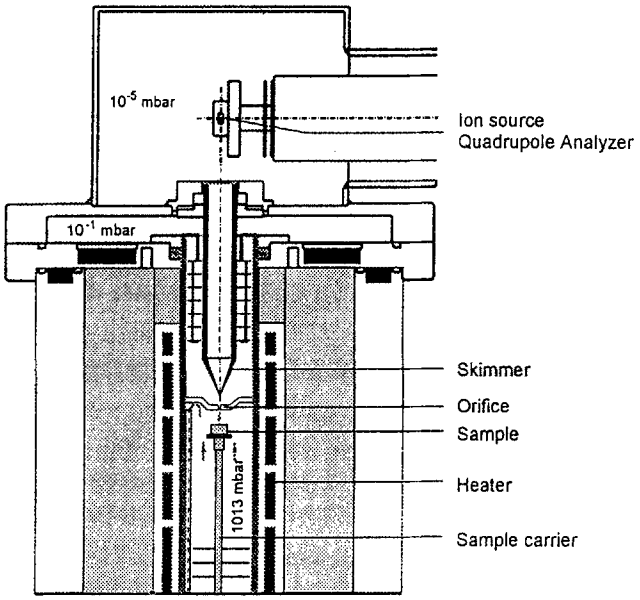

Fig. 1 STA-MS skimmer coupling system (2000°C)

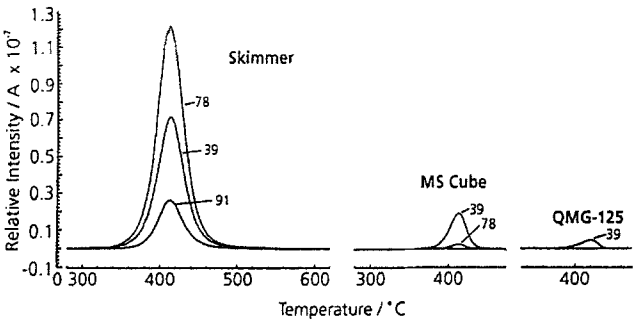

Fig. 2 Intensity comparison between skimmer and capillary systems

polystyrene. For this purpose, the intensities of several selected fragments which occur during pyrolysis were compared. Figure 2 depicts the relative intensities of mass numbers 39, 78 and 91. Normalization of the integrated peak areas demonstrates that the Skimmer coupling system is far more sensitive, especially for higher mass numbers, and thus has a much higher detection sensitivity than conventional capillary coupling systems. For example, the intensity of mass number 91 (tropylium) is approx. 2100 times higher with the Skimmer coupling system than with the capillary coupling (Table 1). An additional example is the detection of the silver isotopes 107 and 109 amu during sublimation (Fig. 3). Since silver does not begin to noticeably evaporate until approx. 1100°C (vapor pressure at 1310°C is 133 Pa [3]), detection with a capillary coupling, which is usually heatable to a maximum of 200°C, is not

Table 1 Comparison of the peak areas for mass numbers 39, 78 and 91 for polystyrene

System	Mass number					
	39		78		91	
	Peak area/ (A–s) g^{-1}	Normalized	Peak area/ (A–s) g^{-1}	Normalized	Peak area/ (A–s) g^{-1}	Normalized
QMS-125 Capillary	$6.9 \cdot 10^{-5}$	1	$3.9 \cdot 10^{-6}$	1	$4.4 \cdot 10^{-7}$	1
MS-Cube Capillary	$4.5 \cdot 10^{-4}$	7	$5.9 \cdot 10^{-5}$	15	$1.1 \cdot 10^{-6}$	2.5
Skimmer	$2.6 \cdot 10^{-3}$	38	$4.4 \cdot 10^{-3}$	1100	$9.5 \cdot 10^{-4}$	2100

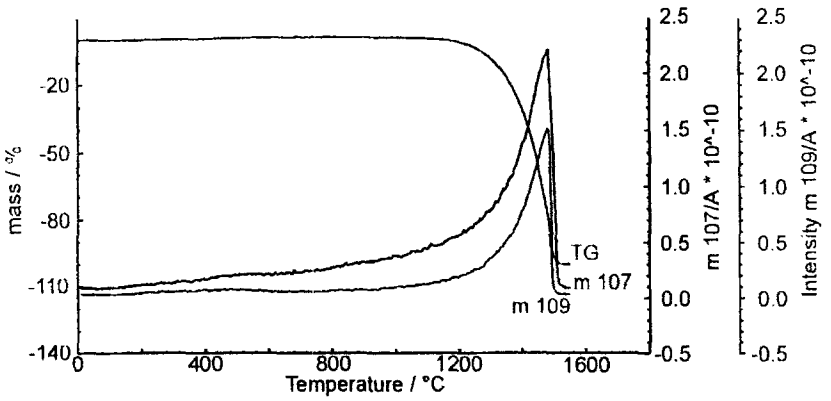

Fig. 3 Ag isotopes measured with the skimmer coupling system

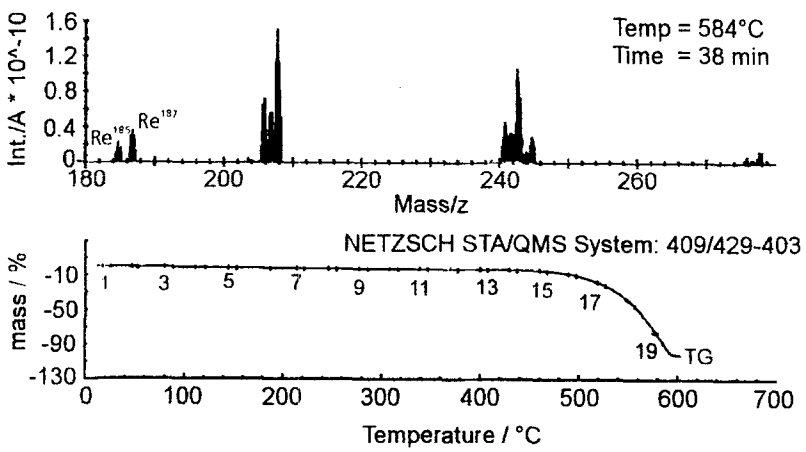

Fig. 4 TG-QMS measurement of $PbCl_2$

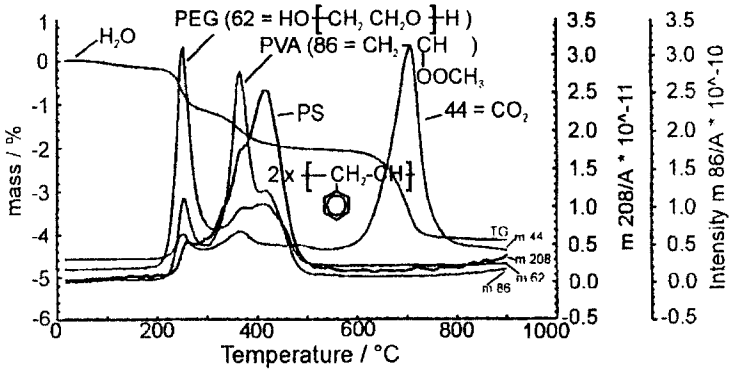

Fig. 5 Binder burnout of a grinding/bead ceramic

possible due to condensation. An STA-MS measurement on $PbCl_2$ shows that higher mass numbers are of course detectable as well (Fig. 4). The upper part of the plot shows a scan (no. 19) during the evaporation of the $PbCl_2$. The mass numbers for Pb (206, 207, 208), PbCl (241, 242, 243, 244, 245) and $PbCl_2$ (276, 277, 278) and the mass numbers of their isotopes (and combinations) were found.

The range of applications for these methods is so varied, that only a few possibilities can be mentioned here. A classic example is the burn-out of binders in ceramics. The TG curve and selected mass numbers for an oxide ceramic with added binders and plasticizers are plotted with respect to temperature in Fig. 5. Surface water emerges between room temperature and approx. 150°C. At approx. 200°C (1st TG step), the decomposition of polyethyleneglycol (PEG) begins. This is followed by the decomposition of the polyvinylacetate (PVA). The polystyrene (PS) decomposes at approx. 400°C and decomposition of the carbonate component begins at approx. 600°C.

For molding purposes in powder metallurgy, waxy binders are often added to the metal powders, which are then expelled when the parts are sintered. Figure 6 is a

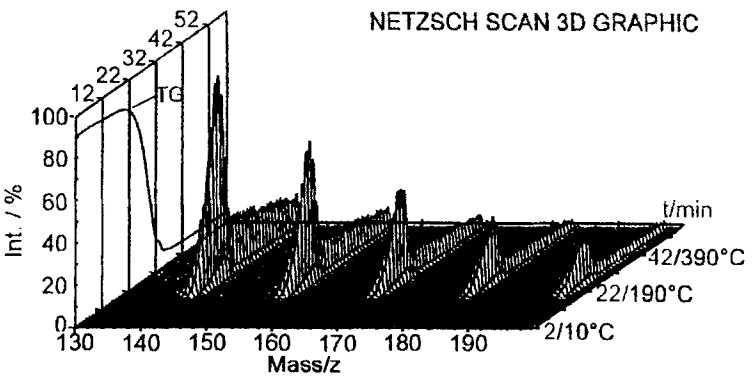

Fig. 6 Three-dimensional plot of the dewaxing process for a Co sintered metal

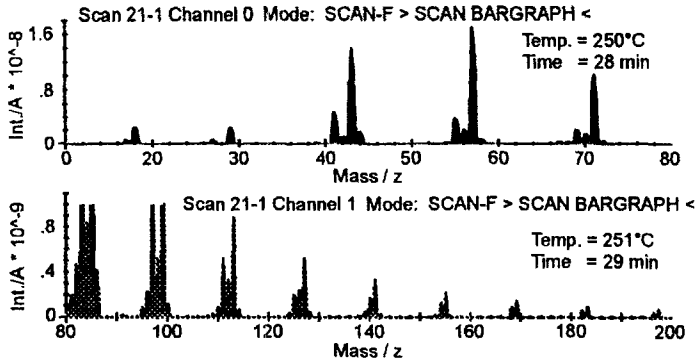

Fig. 7 Mass numbers occurring during the dewaxing of a Co sintered metal

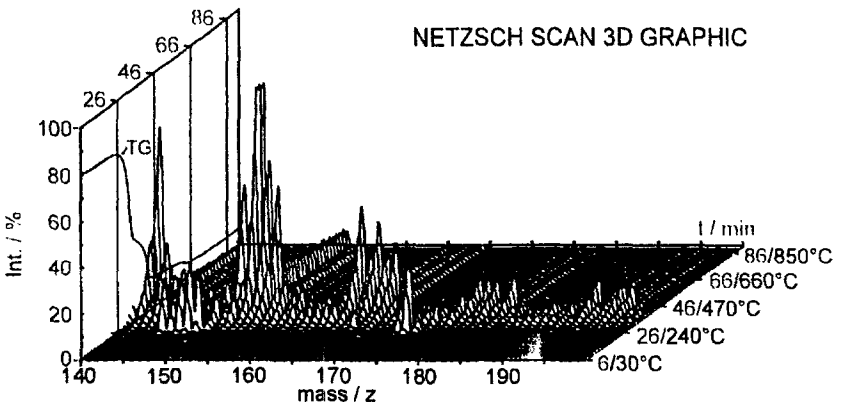

Fig. 8 TG-MS results for an aluminum sandwich foil

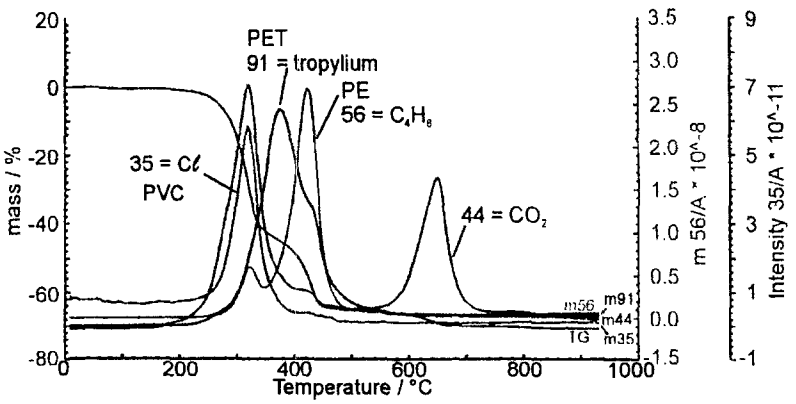

Fig. 9 Decomposition steps of an aluminum sandwich foil

three-dimensional representation of the dewaxing process for a Co powder. The paraffin evaporates as typical aliphatic fragments (fragment spacing $m/e = 14 = CH_2$, Fig. 7).

An important area of application for STA-MS analysis is the simulation of thermal recycling processes. For example, there is an interest in recovering the aluminum components of composite materials. Depending on the application, the foils are coated with several different plastic materials, which must be removed. Through TG-MS measurements, a determination can be made as to when pyrolysis and/or combustion of the plastics occurs and which gaseous products result (toxic, hazardous to the environment). Figure 8 is a three-dimensional representation of a TG-MS measurement on an aluminum sandwich foil in a helium atmosphere to 1000°C. The TG curve shows three mass-loss steps. During these pyrolysis steps, numerous fragments are detected. In order to identify when which plastic components decompose, selected individual mass numbers were plotted with respect to temperature and the TG curve (Fig. 9). In the first TG step, the decomposition of the PVC begins, during which the Cl is separated. At the beginning of the second TG step, the PET component pyrolyzes. During this process, tropylium, among other things, is formed through transposition processes. The PE component of the sample decomposes at approx. 400°C. Finally, CO_2 is detected at approx. 600°C, which indicates carbonate components.

Conclusions

With the Skimmer-QMS Coupling system for the STA 409 now capable of operation to 2000°C, TG/DSC/DTA and mass spectrometer data can be recorded simultaneously in the temperature range from room temperature to 2000°C. This provides yet another interesting tool for the investigation of thermal processes in materials.

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