ELSEVIER

Thermochimica Acta 324 (1998) 197–201

thermochimica acta

Applications for skimmer coupling systems, combining simultaneous thermal analysers with mass spectrometers

E. Kaisersberger*, E. Post

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

Abstract

The sensitivity of the Skimmer coupling for combining the simultaneous thermal analysis (STA) method TG–DTA/DSC and mass spectrometry (MS) is further improved by a factor of three using an automatic vacuum control device. Especially high mass numbers are detected without the common condensation problems met in capillary couplings, as is shown by application of the skimmer coupling for coal, $CuGaSe_2$-semiconductor material and polystyrene. The basic idea of the novel pulse thermal analysis technique (PTA) is demonstrated. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Skimmer coupling; TG-MS; Coal Analysis; Semiconductor; Polystyrene; Pulse thermal analysis (PTA)

1. Introduction

For the coupling of thermal analysis methods with gas analysis techniques, a series of basic questions has to be answered by the user:

- selection of the analysis techniques for coupling
- coupling interface
- necessary detection limits
- temperature range
- possibility for calibration and quantitative work.

As thermogravimetry is the method by which a sample is decomposed for its characterization and for quantification of the decomposition steps, without normally knowing the decomposition products, a combination with gas detection and gas analysis methods is of greatest interest here. On the other hand, quadrupole mass spectrometers show a lot of advantages amongst gas analysers as they supply very sensitive signals for all kinds of gaseous products [1]. They meet the requirements for coupling with thermogravimetry with small instrument dimensions, light weight and fast scans at constant resolution in a broad mass range.

2. Skimmer coupling

The most widely used interface for coupling TG with MS is a double stage pressure reduction system to extract a representative amount of gas out of the continuous gas flow from the thermobalance, combining laminar flow as the first step and molecular flow into the MS as the second step [2]. The Skimmer coupling systems combine ideal gas flow conditions for complete gas transfer (Fig. 1) with homogeneous heating of first and second pressure reduction steps to prevent condensation.

The very high precision needed for the construction of the divergent nozzle and the Skimmer orifice can now be achieved with heat resistant metals for application temperatures up to 800°C, with alumina up to 1450°C and glass-carbon up to 2000°C.

Coupling systems with variable orifice temperatures, like the Skimmer coupling, show reduced per-

*Corresponding author.

0040-6031/98/$ – see front matter
PII: S0040-6031(98)00536-X

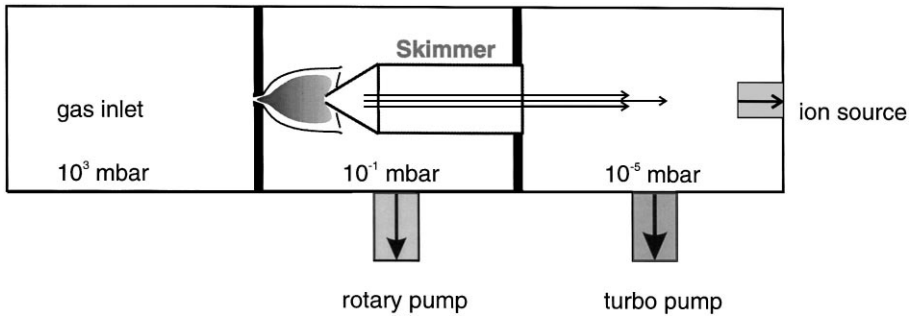

Fig. 1. Gas flow and pressure conditions in a two stage Skimmer coupling system.

meability for the purge gases from the sample with higher temperature because of the increasing viscosity of the gases. An improved automatic pressure regulation system maintains the pressure inside the high vacuum recipient constant at a selectable level and ensures therefore a constant sensitivity of the mass spectrometer at all temperatures. A precise measurement of the high vacuum is the basis for regulating the suction capacity of the pumps. The effect of this pressure control is demonstrated in Fig. 2 by the increase of the peak heights by a factor of three for the detection of CO_2 from the well known sample $CaC_2O_4{\cdot}H_2O$ in argon atmosphere.

3. Results and discussion

One of the concerns for coupled gas analysis systems is the quantification of the results. The recently introduced pulse thermal analysis technique (PTA) is an excellent means for calibration of the specific MS signals and for studying reaction courses in small increments by adding the reactive gas in well-defined pulses to the purge gas flow at the sample [3]. The injection of 500 µl CO_2 to an argon flow of 75 ml/min at a constant temperature of 3.5°C leads to peaks with precisely determinable areas. The calibration factor is nearly 1 µA s/µl CO_2 in argon (Fig. 3). The example shows clearly that the automatic injection of the small amount of gas does not disturb the weight and vacuum curves and it proves the high sensitivity of the PTA technique with the coupled MS. This gas injection can be made at any temperature during an experiment and with a broad selection of gases and injected volumes.

3.1. Coal

As a rule, during the pyrolysis of coal, a large number of aliphatic and cyclic fragments is evolved,

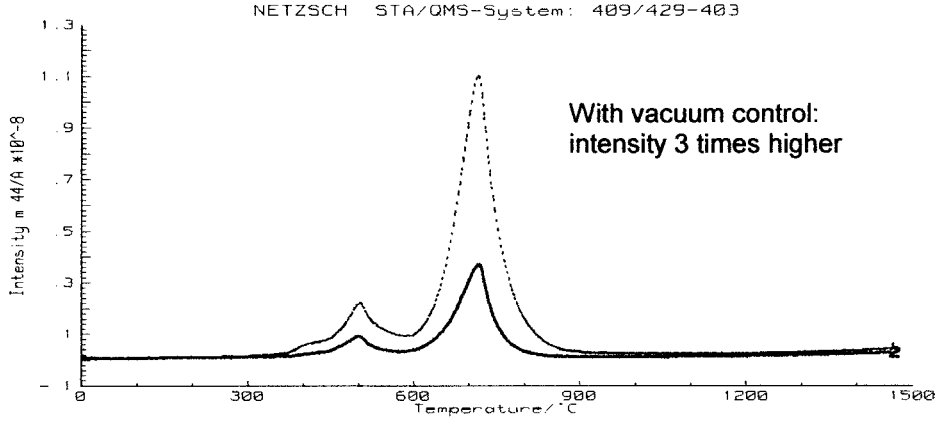

Fig. 2. Effect of pressure regulation in the Skimmer coupling system, sample $CaC_2O_4{\cdot}H_2O$ 1.8 mg, argon flow 75 ml/min, 15 K/min.

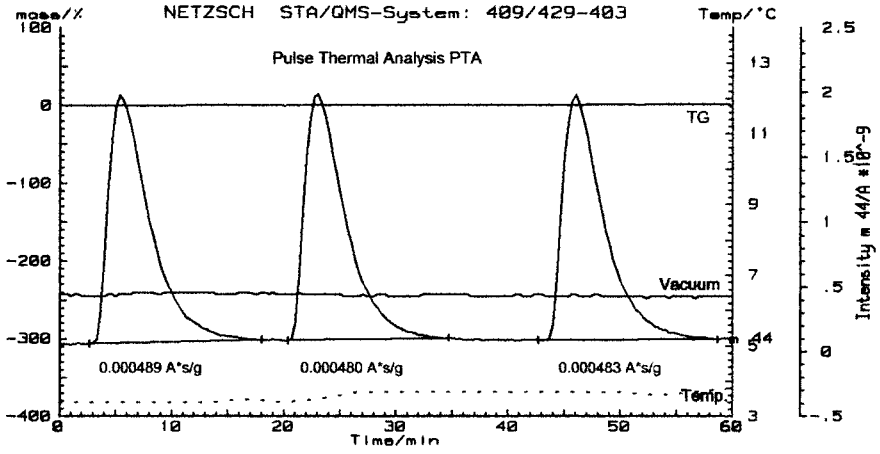

Fig. 3. Pulse thermal analysis (PTA): injection of 500 μl CO_2 into an argon flow of 75 ml/min.

which, in addition, can show a greater or lesser degree of S, N and O in the compounds, depending on the origin or formation of the coal. Fig. 4 is a three-dimensional plot for the TG changes together with a segment of the fragments found during the pyrolysis of a coal-resin compound (mass number range 80–140 amu).

The greater sensitivity of the skimmer coupling system as compared to the capillary coupling can be clearly shown with this substance. With the skimmer coupling, a higher intensity for all mass numbers is achieved on the one hand and, on the other hand, it is possible to detect even relatively large fragments, as condensation is practically eliminated. Fig. 5 shows a comparison of the fragment spectra obtained with the skimmer and capillary couplings during the pyrolysis of the above-mentioned coal at ca. 430°C. The sample weights and measurement parameters were, of course, identical.

3.2. $CuGaSe_2$ ternary semiconductor

For electronic applications (fast semiconductors, solar cells, radiation detectors, electro-optical components), research continues on the development of new types of materials, which could replace or surpass the properties of the known and best-researched semiconductor material, silicon, in certain niche areas. A very

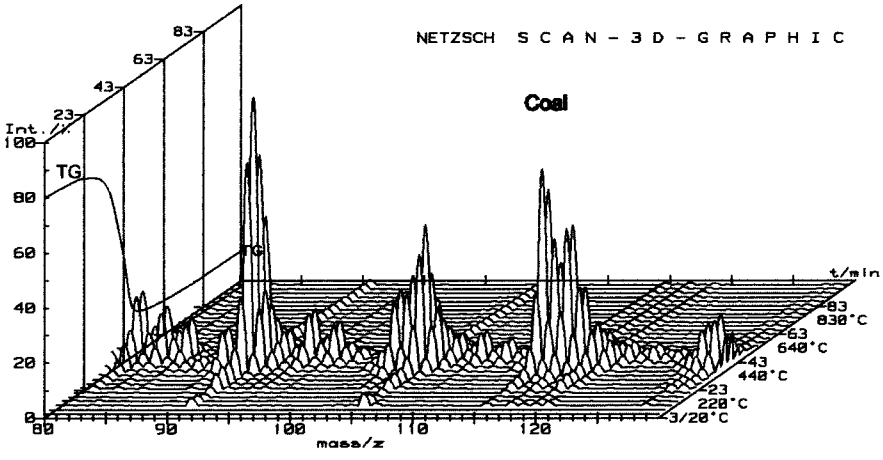

Fig. 4. STA–QMS skimmer coupling measurement of a coal sample, 6.64 mg, helium 75 ml/min, 10 K/min.

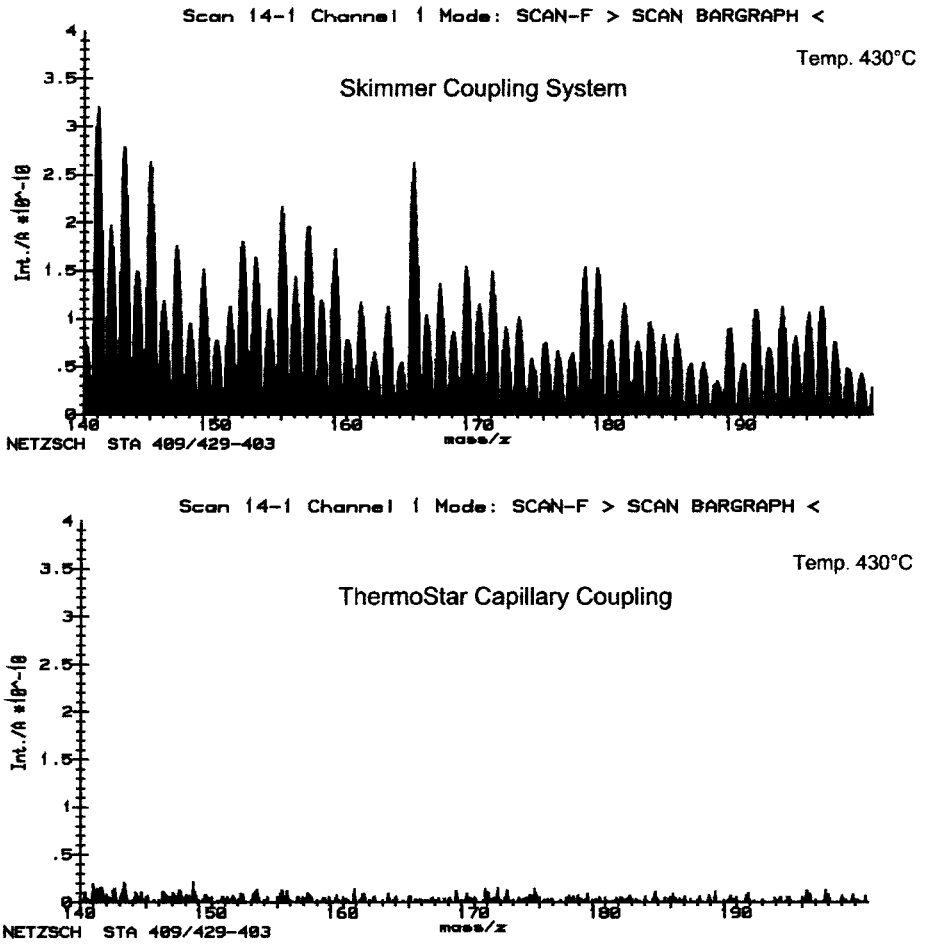

Fig. 5. Comparison of skimmer and capillary coupling results during TG step of coal, 6.64 mg, helium 75 ml/min, 10 K/min.

promising group of materials [4] crystallizes in the chalcopyrite structure, which can be derived from the diamond structure of the silicon. $CuGaSe_2$ belongs to this group and, due to the energy gap and the high absorption factor, it is of interest for terrestrial solar radiation for thin-layer solar cells, etc. Because this deals with a compound semiconductor, not only the doping and mono-crystallinity, or the size and phase interfaces of the crystal domains, play a role; the stoichiometry of the compound is an additional parameter. In the example depicted in Fig. 6, prior to the actual thermal decomposition of $CuGaSe_2$ at $\approx$1000°C, an additional weight-loss step is found ($\approx$300°C), during which both selenium, as Se_3 rings (230–245 amu), and I_2 (254 amu) vaporize. Iodine I_2 appears to have been present as an impurity in the initial components or served as a 'mineralizer' in the synthesis of the $CuGaSe_2$.

3.3. Polystyrene

In the recycling of polymers thermal treatment is an important step for getting back pure materials for further use. The pyrolysis of polystyrene in a simultaneous TG–DSC equipment leads to single, double and triple monomer units, as detected by the MS-skimmer coupling. The corresponding mass numbers 104, 208, and 312 amu are clearly shown from the beginning of the decomposition in inert gas (Fig. 7). The DSC shows an endothermal peak for the decomposition reaction, proving also that there is no residual oxygen in the vacuum-tight STA instrument.

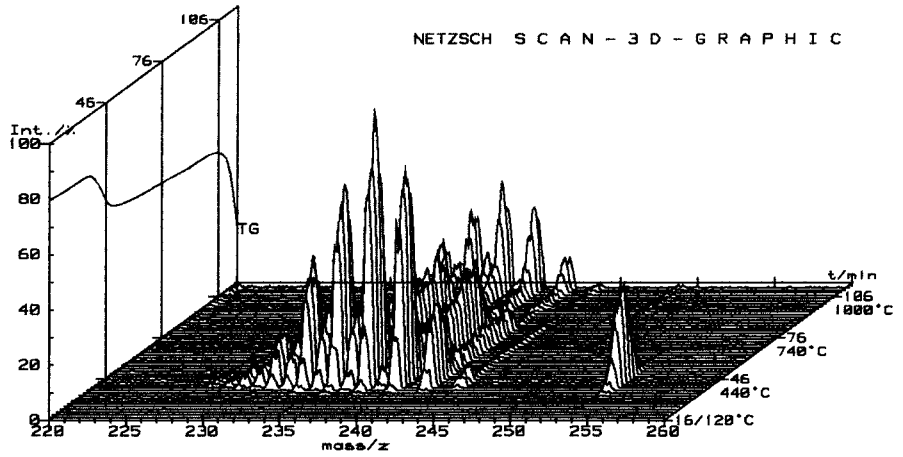

Fig. 6. Evolution of Se_3 isotopes and I_2 from a $CuGaSe_2$ semiconductor material, 333.08 mg, helium 75 ml/min, 10 K/min.

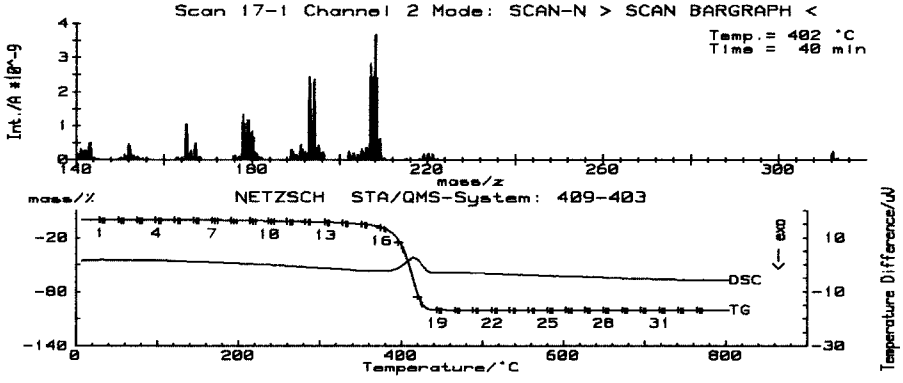

Fig. 7. Decomposition of polystyrene, 7.77 mg, helium 75 ml/min, 10 K/min.

4. Summary

The high sensitivity of the Skimmer coupling system could be further improved by a new automatic vacuum control device. The special advantages of this MS-coupling system are shown by applications on complex materials, where detection of high mass numbers is of importance for the characterization of materials, their origin and formation, and the synthesis or the behavior during recycling.

References

[1] K.G.H. Raemaekers, J.C.J. Bart, Applications of simultaneous thermogravimetry-mass spectrometry in polymer analysis, Thermochim. Acta 295 (1997) 1–58.
[2] H. Kienitz (Ed.), Massenspektrometrie, Verlag Chemie, Weinheim/Bergstrasse (1968).
[3] M. Maciejewski et al., Novel pulse thermal analysis method and its potential for investigating gas–solid reactions, Thermochim. Acta, 295 (1997) 167–182.
[4] J.L. Shay, J.H. Wernick, 1975. Ternary Semiconductors: Growth, Electronic Properties and Applications, Pergamon Press, Oxford.