SIMULTANEOUS TG-DTA MASS-SPECTROMETRY TO 1550°

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Newly developed coupling systems are introduced and discussed for the combination of a simultaneous TG-DTA apparatus with a quadrupole mass-spectrometer. In the study of decomposition processes under atmospheric pressure, two-stage pressure reduction systems allow an exact gas analysis by the simultaneous operation of a mass-spectrometer up to 1550°. For measurements under high vacuum, the pressure reduction systems are removed, and by direct viewing between test body and ion source a high sensitivity is achieved. The function of these combined units is demonstrated by means of applications in inorganic and organic chemistry.

Nowadays, for almost all thermoanalytical experiments, an exact control of the sample atmosphere is required. Therefore, many testing arrangements are already provided with the necessary devices for static or dynamic atmospheres at variable pressures. In this way a provision for the frequent use of evolved gas detection (EGD) and analysis (EGA) methods in combined equipment is fulfilled.

Nevertheless, the simultaneous application of thermogravimetry and differential thermal analysis cannot eliminate the interpretation difficulties remaining for almost all thermoanalytical methods in spite of much information. The detection and analysis of gaseous reaction products and the determination of changes in partial pressures in the sample atmosphere can contribute considerably to the interpretation of results obtained.

Mass-spectrometry is the most effective EGA method, because of the good qualitative and sufficient quantitative results achieved on the investigation of gases and vapors. Only the high vacuum necessary for analyzer systems has precluded up to now a frequent coupling with thermoanalyzers.

Experimental

Combination of a mass-spectrometer with a thermoanalyzer is judicious in any case, because with the high apparatus expense that thermal analysis requires, a optimum of information is gained. This is guaranteed in modern apparatus, allowing the simultaneous application of differential thermal analysis and thermogravimetry to one and the same sample.

In simultaneous TG – DTA – DTG equipment coupled with a mass-spectrometer, the following two operating modes, which depend on the pressure relations, have to be distinguished:

1. High vacuum in the thermoanalyzer and the mass-spectrometer.
2. Atmospheric pressure in the thermoanalyzer, high vacuum in the mass-spectrometer.

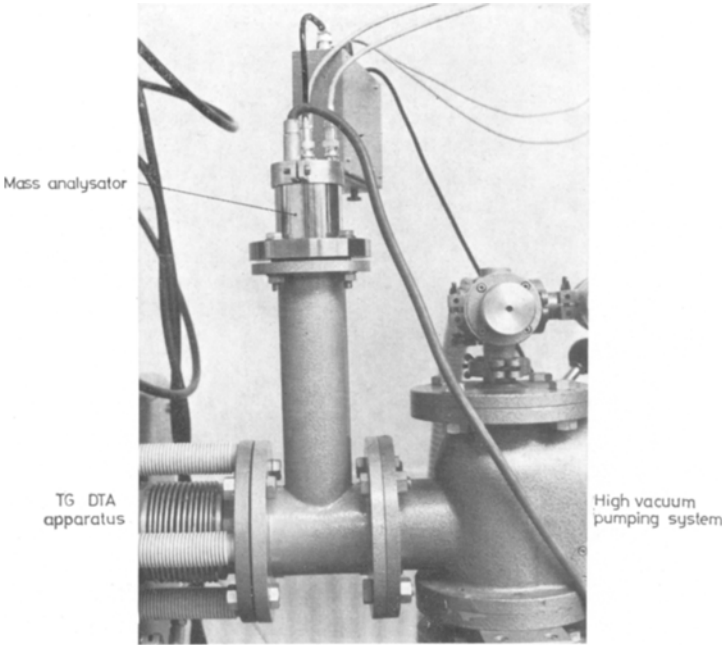

Fig. 1. T-flange linking a thermoanalyzer (TG-DTA) with a quadrupole mass-spectrometer (QMS) for high-vacuum tests

The equipment relating to point 1 shows simple construction. The analyzer of a quadrupole mass-spectrometer is arranged directly in the high vacuum system of the thermoanalytical apparatus; for example, by means of a T-flange between the vacuum kettle and high vacuum pumping system (Fig. 1). The pressure in the whole system may not exceed 10^{-4} mbar, not even during decomposition of the substance, because the mass-spectrometer suffers loss of linearity above this pressure limit, i.e. the proportionality between partial pressure and ion flow, necessary for quantitative measurements, is not given. In many practical problems of thermal analysis a restriction of the high vacuum as "sample atmosphere" cannot be accepted, and therefore the possible applications of such a combined apparatus are limited.

The second operating method needs a complicated interface for pressure reduction, situated between the test space of the thermoanalyzer and the analyzer of the mass-spectrometer.

By means of a commercial combination of units offering adapting possibilities for both kinds of operation, the claims expected from the single components are discussed.

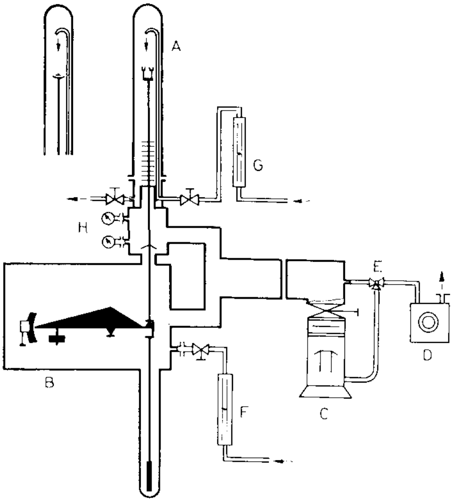

Fig. 2. Vacuum and gas inlet system (Netzsch STA 429). A sample space; B balance space; C oil diffusion pump; D two-step rotation pump; E three-way valve; F inert-gas flow meter; G reaction-gas flow meter; H vacuum measuring tubes

The basic unit comprises a simultaneous Netzsch TG – DTA – DTG apparatus in simple construction. The thermogravimetric device has a readability to 20 μg with compensation, or a maximum of 2 μg when applied as a registering inclination balance, the DTA device possessing measuring ranges to 100 nV/mm. High vacuum or different static or dynamic atmospheres with inert or even aggressive gases can be employed in the apparatus up to sample temperatures of 1550°. Figure 2 gives a view of the vacuum system as well as the possible gas inlets.

The top-pan sample arrangement enables an exact separation of the gas path towards the sample and balance, and facilitates the protection of the mechanic weighing system against thermal radiation of the furnaces in the case of high-temperature tests.

Numerous accessories – for example, magnetic supplement for studying magnetic transitions, plug-in for tests under quasi-isothermal conditions, temperature control according to tape programs, furnace for water-vapor or solvent-vapor atmosphere up to 1000°, interface for data processing with computer – give this apparatus multipurpose applicability.

A quadrupole system has been selected as an analyzer for the investigation of mass distribution in the gas atmosphere. The simple and room-saving construction of a quadrupole mass filter, and the sufficient resolving capacity, even at a rapid mass scan, render the quadrupole mass-spectrometer well suited to be combined with thermoanalyzers. Normally, a mass filter from Balzers of Liechtenstein for the mass range 1 to 511, with variable operating possibilities via a digital electronic control system, is provided. The mode of operation can be described as follows:

1. In the mass range of interest, up to 12 fixed mass units (m/e) can be registered simultaneously with respect to their dependence on the temperature with an optimum selected sensitivity. (Simultaneous and continuous mode of operation with the thermoanalyzer.)
2. A preselectable mass range can be scanned once or repeatedly with scan speeds between 0.1 ms/mass unit and 30 s/mass unit. (Simultaneous and quasi-continuous mode of operation.)

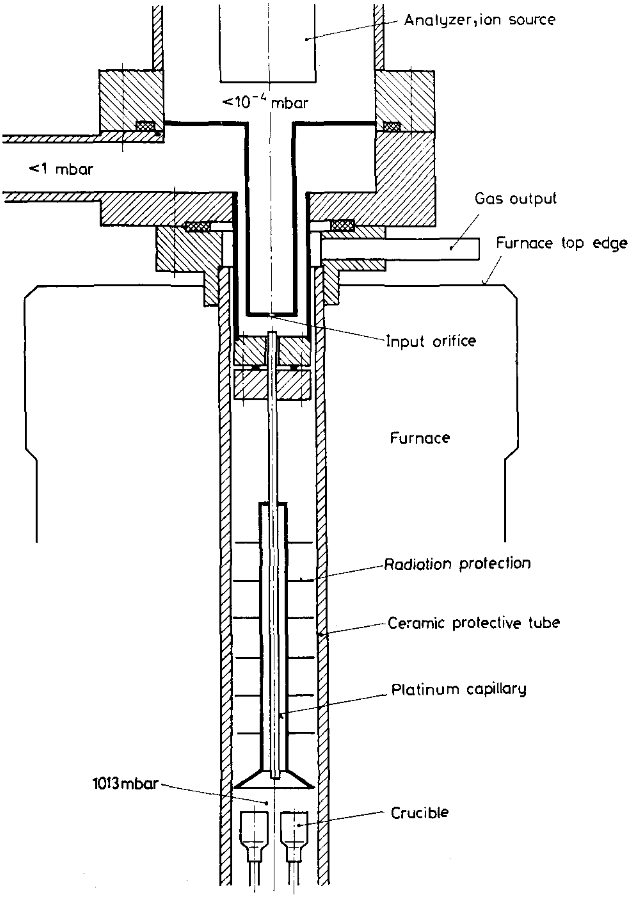

Fig. 3. Gas inlet system with platinum capillary tube. $T_{\max} = 1500°$

3. Total pressure is measured in a preselected mass range with information on the contribution of the most frequent masses to the total pressure (integral spectrum).

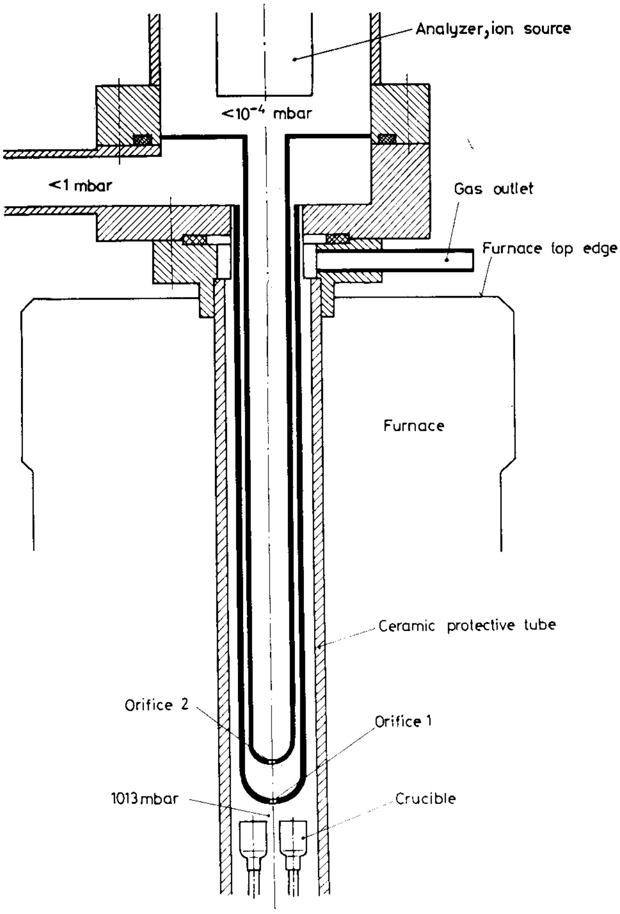

Fig. 4. Gas inlet system with orifices of Al_2O_3. $T_{max} = 1500°$

High vacuum is either realized with a diffusion pump with polyphenyl ether oil as a pumping medium, or by a turbomolecular pump. In this way trace analysis with low background and residual gas or elementary analysis at detection limits of 10^{-16} mbar are established (depending on the analyzer system).

The coupling interface between the thermoanalyzer and the mass-spectrometer fulfills two functions. It operates simultaneously as *gas input system* for the quadrupole mass filter and as *pressure reduction system*, if the pyrolytic decomposition occurs in gas atmospheres. In high-temperature measurements, or in the case of heavy volatile condensable gases and vapors, the usual arrangements resulted in insufficient function.

Two exchangeable orifice systems fulfill the three main functions expected from an interface:

1. unvaried gas composition for reliable qualitative and quantitative interpretation;
2. short response time;
3. no condensation.

The developed systems effect a pressure reduction in two steps with an interposed vacuum of about 1 mbar.

One design in platinum consists of a specially-dimensioned capillary with input funnel above the open sample crucibles, as well as a connected orifice as inlet into the high-vacuum system (Fig. 3).

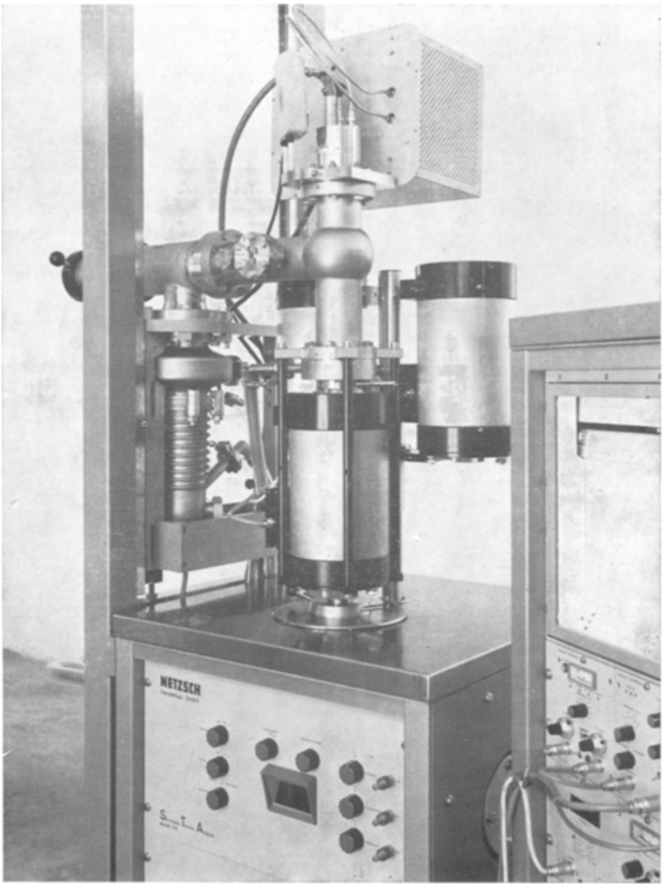

Fig. 5. Simultaneous TG-DTA apparatus (STA) with furnace lift, special furnace, high-vacuum pumping system and quadrupole mass-spectrometer (QMS)

The emitted gas flows through the capillary into the interposed volume and is sucked off by means of a slide-rotary pump. Part of the gas is drawn in a molecular stream through the orifice into the high-vacuum recipient of the quadrupole analyzer. By the installation of an orifice system into the furnace of the thermoanalyzer and supplementary heating of the fixing flange of the capillary, the influence of rising temperature gradients is low and condensation is eliminated.

For problems which are unfavorably influenced by platinum parts due to their catalytic activity, an orifice system has been developed made from high-temperature-resistant oxide ceramic. Two Al_2O_3 tubes, mounted concentrically and bearing anode apertures in the bottoms, are arranged after short distance from one another directly above the sample crucibles, and make up the gas sampling and pressure reduction system (Fig. 4).

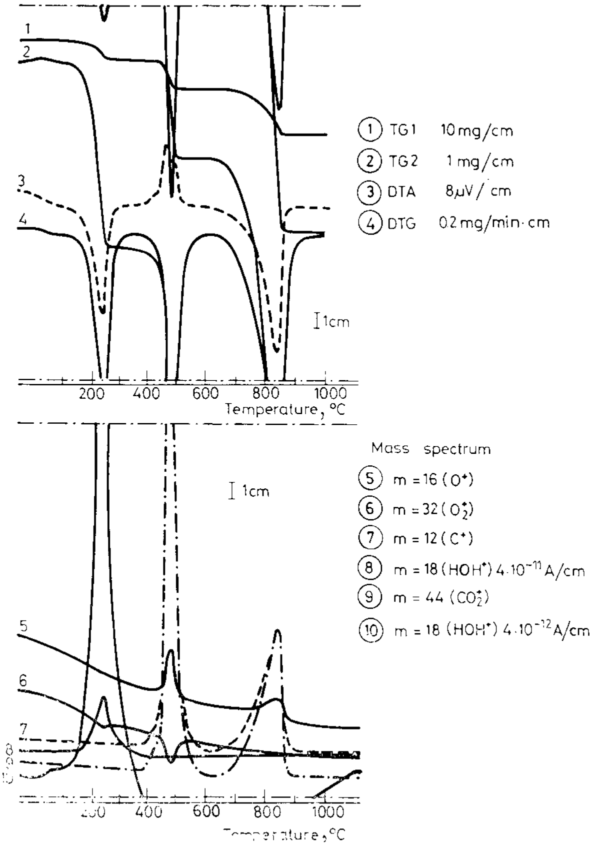

Fig. 6. Decomposition of calcium oxalate monohydrate in air. Sample weight: 100 mg; heating rate: 10 K/min, in static air. Thermal and MS curves taken simultaneously

For decompositions in high vacuum, both mentioned orifice systems can be removed and replaced by an intermediate flange; thus, the ion source of the mass-spectrometer is in direct view of the sample, and a high sensitivity is achieved.

In the case of dynamic gas atmospheres, because of the relatively low gas suction through the orifices (about 10 ml/min), the surplus gas leaves through the overflow tube.

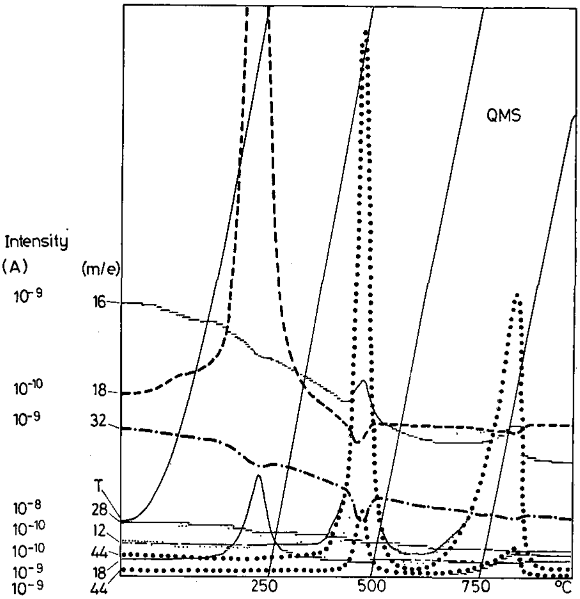

Fig. 7. Course of intensities for selected mass units (*m/e*) during $CaC_2O_4.H_2O$ decomposition in air. Sample weight: 75 mg; heating rate: 5 K/min, in static air

The analyzer of the quadrupole mass-spectrometer consists of an ion source, mass filter and ion detector. Ionization is effected by electron impact, the electron beam being raised by easily interchangeable cathodes. In the case of ionization energies of about 5 to 100 eV (axial-beam ion source, standard 70 eV) or 5 to 100 eV (cross-beam ion source) ions arise which have charges of +1 or more. During ionization, molecules can suffer fragmentation processes.

In order to achieve optimum measuring conditions, two types of ion sources can be used:

Axial-beam ion source: Electron beam and ion extraction in the axial direction ensure high sensitivity in a simple construction.

Cross-beam ion source: Particle beam, electron beam, and ion extraction are related vertically. This arrangement effects a reduced contamination, and with the use of a cooling flap as collector it can also be applied for the analysis of corrosive gases.

The mechanical construction of the combined unit is characterized by a simple arrangement. Good accessibility for the single components, easy handling during the experiments and high stability of the consequent plug-in system are characteristic features.

A special furnace with coupling interface, mass-spectrometer and a high-vacuum pumping system are mounted on a so-called furnace lift on the simultaneous TG–DTA–DTG apparatus (Fig. 5).

For loading the thermobalance, the whole furnace-mass-spectrometer arrangement is moved upwards. The vacuum connections need not be loosened for working under atmospheric pressure, and the thermal centering of the measuring arrangement is retained.

For recording the large amount of information obtained with this unit combination, two multi-channel compensation point printers are used. The 6-channel printer having a printing sequence of 1 s, which is normally supplied with the simultaneous apparatus, records T, TG1, TG2, DTA, DTG, (P); a 12-channel printer, with a printing sequence of 1 s too, registers the T, P and MS intensity curves.

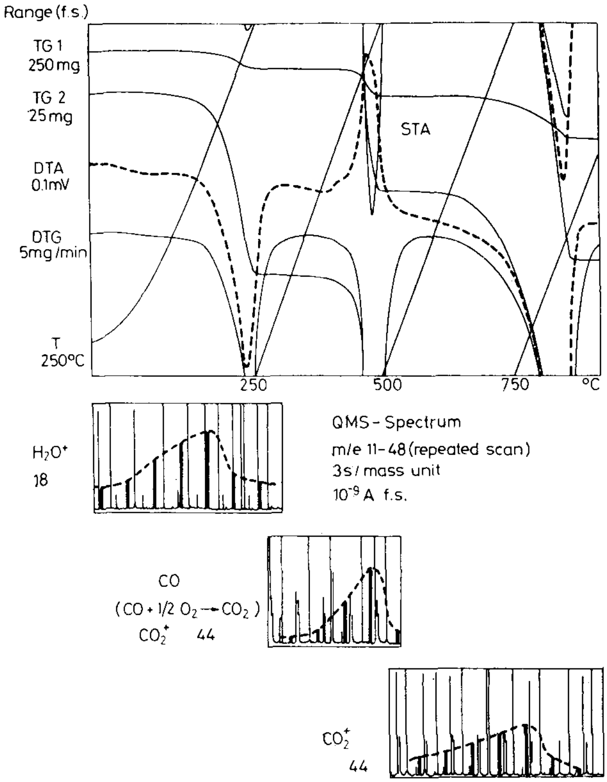

Fig. 8. Quasi-continuous operation of the mass-spectrometer during $CaC_2O_4.H_2O$ decomposition in air. Sample weight: 100 mg; heating rate: 10 K/min, in air

The autocontrol unit in the quadrupole programmer allows the storage of 12 programs with all parameters adjusted on the front panel, so that the intensities for a maximum of 12 masses are registered simultaneously.

With the point printer used alternatively as an one-line recorder, mass ranges at scan speeds from 1 to 30 s/mass unit are scanned fully evaluably. During the recording with an oscillograph, the other scan speeds from 100 μs to 0.3 s/mass unit are used.

Results and discussion

Since introduction of this new coupling technique between a thermoanalyzer and a quadrupole mass-spectrometer for the first time at the end of 1975, numerous problems with the existing equipment have been studied. Some results may demonstrate the capacity of these coupled simultaneous units.

1. The decomposition of calcium oxalate monohydrate to CaO in air is effected in three steps. The mass-spectrum (a continuous recording of six mass numbers)

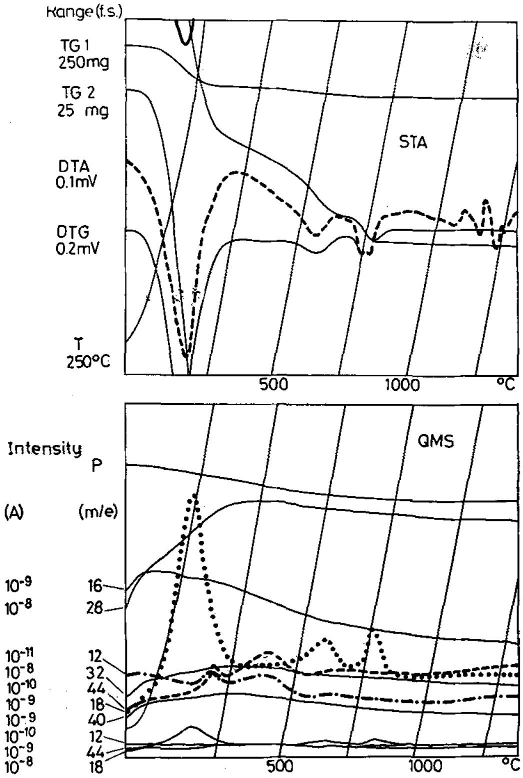

Fig. 9. Simultaneous TG-DTA-DTG-EGA analysis of montmorillonite. Sample weight: 150 mg; heating rate: 10 K/min, in air

shows the effects for H_2O, CO_2, O and O_2. As known, the three steps correspond with increasing temperature to H_2O, CO and CO_2 emission from the sample, and CO is oxidized to CO_2 in air (DTA exothermic). Atomic oxygen as well as carbon are fragments of the released gases CO and CO_2. This diagram was registered with the coupling system platinum capillary and following anode aperture (Fig. 6).

2. Figure 7 shows the course of intensities of six different mass numbers for the decomposition of calcium oxalate monohydrate in air. This plotting was obtained by means of the ceramic double orifice system, and demonstrates the equivalence of the information with the above-mentioned result.

3. Figure 8: Cutouts from the mass-spectrum of the gas phase during the decomposition of calcium oxalate monohydrate. In quasi-continuous operation the mass range 11 to 48 (m/e) was scanned repeatedly with a scan speed of 3 s/mass unit. The changes of intensities at m/e = 18 (H_2O^+) and at 44 (CO_2^+) (two steps) can be clearly seen. No further changes can be noticed in the selected mass range.

4. Figure 9: The water emission from clay minerals influences their applicability and technological treatment in ceramics. The identification of the gases in a mont-

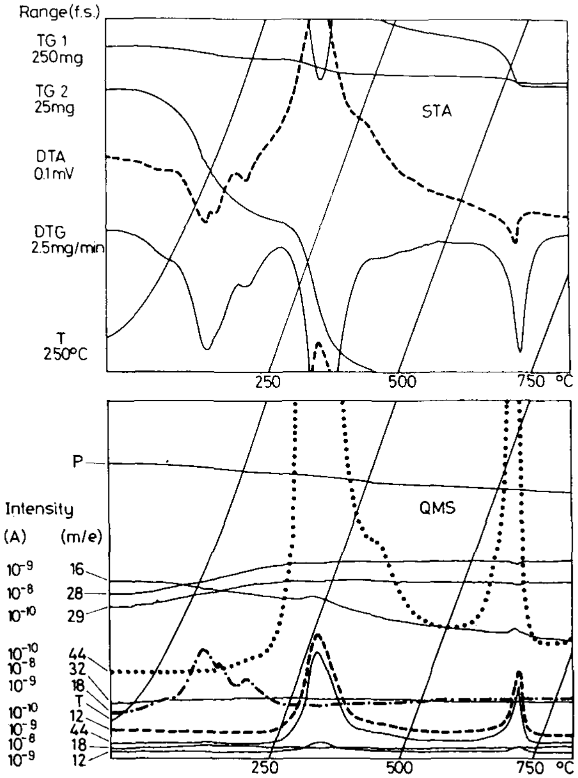

Fig. 10. Decomposition of barium titanyl oxalate tetrahydrate. Sample weight: 50 mg; heating rate: 10 K/min, in air

morillonite decomposition succeeds in the described arrangement, also during the detection of the condensable water.

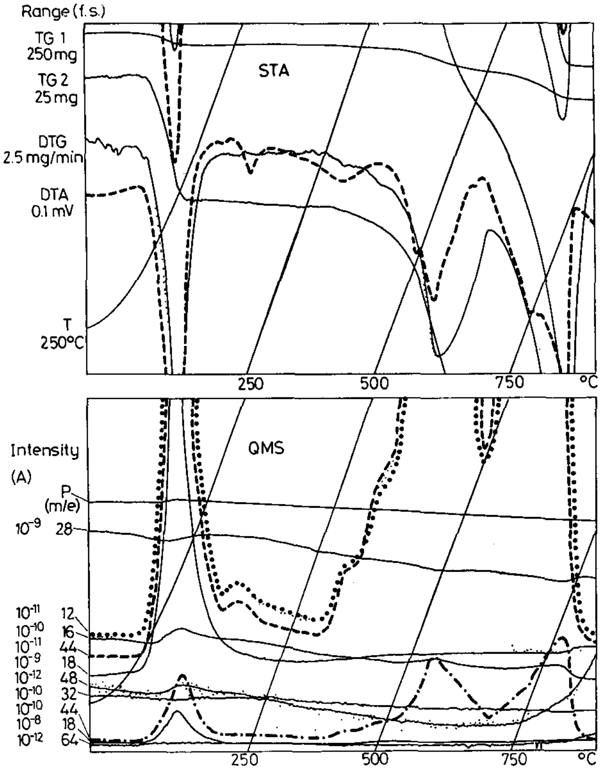

Fig. 11. Melting of a glass batch with simultaneous gas study. Sample weight: 200 mg; heating rate: 10 K/min, in air

Up to 330° the first step of H_2O generation is shown, which is superimposed by CO_2 emission at 200–290° and 300–630°. Further, the second step of water emission at 400–730° and the third one at 790–940° is clearly registered. An exothermic crystallization is superimposed on H_2O emission at 850° (DTA). The agreement of the results of the TG, DTG, DTA and MS intensity curves is good.

5. Figure 10 shows another oxalate decomposition. Barium titanyl oxalate tetrahydrate shows in air the emission of:

4 molecules of H_2O in the range 40–280°;
CO or CO_2 in the range 240–590°;
CO_2 in the range 600–770°;
C^+ and O^+ are fragments of CO or CO_2, respectively.

The possibility of changing the atmosphere above the sample (for example, non-oxidizing), allows an exact distinction between CO and CO_2 emission. Such tests will be continued.

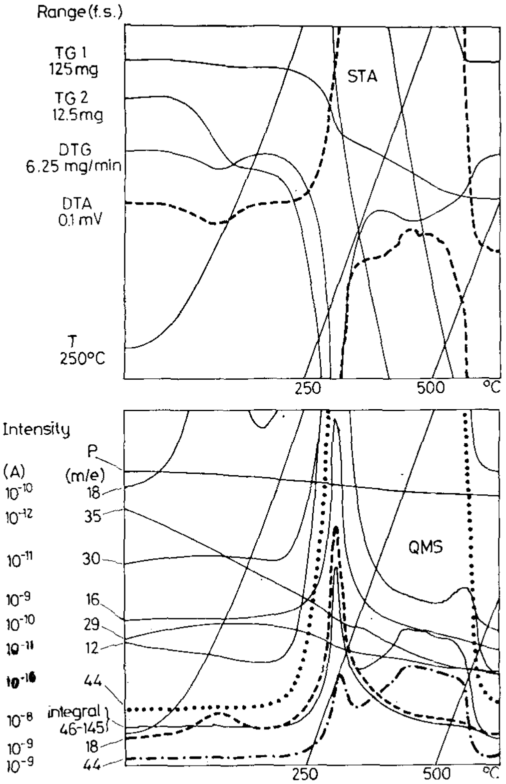

Fig. 12. Combustion of pine wood in air. Sample weight: 50 mg; heating rate: 10 K/min

6. Figure 11: For the production of glass, the knowledge of gas emission from raw materials is of great importance in the attainment of good-quality products. The sintering of glass ingredients gives interesting insights into the complicated system of gas emission from solids, melts and vaporizing components.

Composition of glass ingredients:

sand	60.5 %
soda (Na_2CO_3)	16.2 %
dolomite	18.9 %
Na_2SO_4	4.1 %
C	0.2 %

Reactions:

Temperature	Nature of gas
a. 70–180°	water CO_2 (or CO) SO_2 C SO
b. 210°	CO_2
c. 250°	(Solid transition of Na_2SO_4, DTA endothermal)
d. ex 450°	CO_2 emission increasing in steps
573°	(Overlapped $\alpha-\beta$ transition of quartz, DTA endothermal)

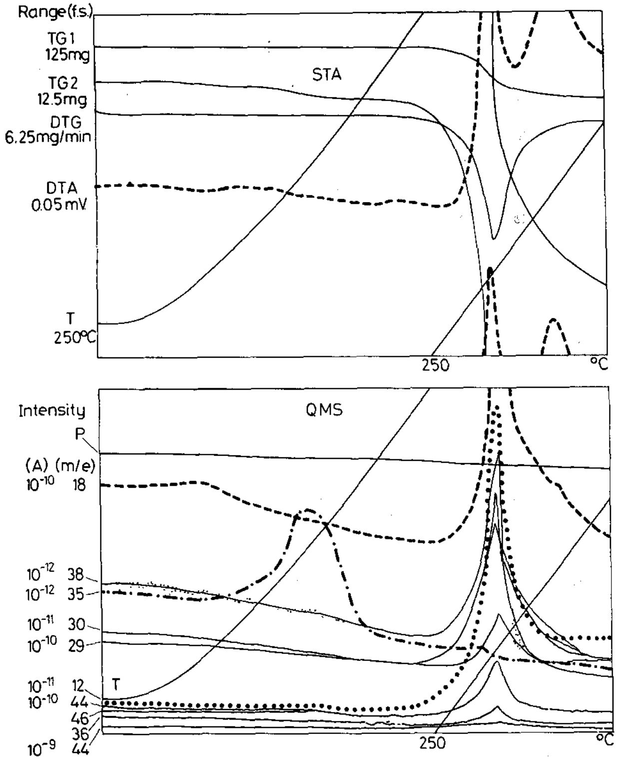

Fig. 13. Decomposition of PVC foam in air. Sample weight: 30 mg; heating rate: 5 K/min

7. Figure 12: The combustion of pine wood in air is correlated with the following gas formation:

40–160°	H_2O
220–350°	Exothermic DTA reaction (ignition) H_2O, CO_2, C and gases in the mass range 46–145 (integral spectrum)
250–590°	Uniform combustion CO_2, C and a little H_2O as well as gases in the mass range 46–145

8. Figure 13: Hard foam made from PVC has to fulfill expectations on temperature-resistance during its application as an insulating material. On heating in air at 70–180°, a gas component with $m/e = 35$ is registered. After the melting range 110–220°, there is a rapid decomposition (DTA) at about 270°. The intensity curves of the mass-spectrometer show another gas emission at 240° (H_2O, Cl, HCl, CO_2).

Conclusion

All the discussed results were obtained under stationary atmospheric conditions. The application of inert gases with flow rates of about 250 cm^3/min which do not influence the weighing, can contribute to interpretation of the decomposition course: for example, of oxalates and other organic compounds (distinction between CO and CO_2 formation).

The application of this combined apparatus seems to be of great interest in combustion and environmental research, in reactor and waste disposal problems, as well as for metal and solid studies.

The requirements expected from a gas inlet system to the mass-spectrometer can be considered as fulfilled, based on the experimental results obtained to date.

Résumé — On présente des systèmes de couplage récemment développés pour relier un appareil simultané de TG—ATD à un spectromètre de masse quadrupole. En étudiant la décomposition sous pression atmosphérique, les systèmes réducteurs de pression à deux étages permettent une analyse des gaz exacte, en opérant simultanément avec un spectromètre de masse jusqu'à 1550°. Afin d'effectuer des mesures sous haut vide, on met hors circuit les systèmes réducteurs de pression et parvient à une haute sensibilité par examen direct entre le corps à examiner et la source d'ions. On montre le fonctionnement de ces unités combinées par des exemples d'application en chimie inorganique et organique.

ZUSAMMENFASSUNG — Für die Kombination einer simultanen TG-DTA-Anlage mit einem Quadrupol-Massenspektrometer werden neuentwickelte Kopplungssysteme vorgestellt. Beim Studium von Zersetzungsvorgängen unter Atmosphärendruck erlauben die zweistufigen Druckreduziersysteme eine exakte Gasanalyse durch die gleichzeitige Betriebsmöglichkeit eines Massenspektrometers bis 1550°. Für Messungen im Hochvakuum werden die Druckreduziersysteme entfernt und durch die direkte Sichtverbindung zwischen Probe und Ionenquelle wird eine hohe Nachweisempfindlichkeit erzielt. Die Funktion der Gerätekombination wird mit Anwendungsbeispielen aus der anorganischen und organischen Chemie demonstriert.

Резюме — Введен и обсужден новый разработанный метод, включающий одновременно ТГ—ДТА аппаратуру и квадрупольный масс-спектрометр. Изучая процессы разложения при атмосферном давления, двухстадийная система дросселирования позволила провести точный анализ газа при одновременной работе масс-спектрометра до 1550°. При высоковакуумных измерениях система дросселирования удалялась и с помощью прямого обзора между исследуемой пробой и ионным источником, достигнута высокая чувствительность. Действие этой комбинированной системы показано на примере применения ее в неорганической и органической химии.