

## Review

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# Thermal analysis–mass spectrometry coupling and its applications

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## Abstract

The direct coupling systems operating under vacuum and the systems in which the thermobalance works under atmospheric pressure are described in detail. In addition, the characteristics of the most widely used mass spectrometers and computer facilities are also discussed.

To illustrate the potential and limitations of this coupling, some typical cases of qualitative and quantitative applications are considered. These examples demonstrate that the coupling is used extensively for the identification of thermal degradation products, to determine their sequence of release and to resolve thermogravimetric curves. The technique is used only to a limited extent for quantitative analysis and kinetic studies.

## INTRODUCTION

Thermogravimetric analysis (TGA) is a very powerful analytical technique for studying the stability and determining the composition of a variety of materials [1]. The ability of the technique to characterize materials is greatly enhanced if it is combined with other analytical techniques for analysing the off-gases from various weight-loss steps. Numerous methods are used for evolved gas analysis (EGA) [2]. Thermogravimetric (TG) systems have been coupled with gas chromatography (GC) [3], infra-red (IR) or Fourier transformation infra-red spectroscopy [4–7], but most often it is coupled with mass spectrometry (MS). This is due to the high sensitivity and specificity of MS which is typically sufficient for identifying the gases evolved. The use of EGA evolved gas analysis with MS has been discussed in three excellent reviews [8–10].

In thermal analysis studies simultaneous TG–differential thermal analysis (DTA)–MS instruments are often used [11–24] providing a large amount of information on the process under study. In the analysis of a complex decomposition process, such as the thermal degradation of polymers, the MS study of the effluent gases is often preceded by GC separation

(TGA-GC-MS) [24–28] and, in certain cases, a tandem mass spectrometer is coupled with the TG analyser (TGA-MS-MS) [29–31].

In coupling the TG analyser to the mass spectrometer two basic types of system can be distinguished. (1) Direct coupling under vacuum, when the mass spectrometer is included in the high vacuum system of the thermobalance. (2) Systems in which the thermobalance works under atmospheric pressure. This system has significant advantages as in many applications it is desirable to carry out thermal analysis in inert, oxidizing, reducing or self-generated atmospheres.

The problems associated with atmospheric pressure thermal analysis-mass spectrometer coupling lies mainly in the difference of the working pressure of the two instruments. In thermogravimetric experiments gas flow rates of, typically, up to  $100 \text{ cm}^3 \text{ min}^{-1}$  can be expected at ambient pressures. The mass spectrometer operates under high vacuum. Typical operating pressures in the analyser part of the mass spectrometer should be better than  $10^{-5} \text{ Pa}$  (ca.  $10^{-10} \text{ atm}$ ) otherwise the relation between the partial pressure and the ion current will not be linear. The pressure in the ion source in the electron impact (EI) ionization mode should be about  $10^{-3} \text{ Pa}$  and in chemical ionization (CI) mode about  $10^2 \text{ Pa}$ . Even large pumping systems cannot cope with the total effluent from a thermogravimetric analyser. To solve the problem, a wide variety of pressure reducing systems (interfaces) have been developed.

In the latest instruments quadrupole mass spectrometers are used almost exclusively in coupling with TGA. Mass spectrometric data acquisition and processing is done by computers.

The TGA-MS coupled technique is mainly used for qualitative purposes; in some cases quantitative analysis and kinetic studies have also been reported.

#### TGA-MS COUPLING UNDER VACUUM [11,12,16,17,23,32–36]

Locating a quadrupole mass spectrometer directly in the thermoanalyser alleviates practically all the problems of gas transport from the TGA sample holder to the ion source of the mass spectrometer, as well as the pressure reduction necessary for the mass spectrometry. Evolved molecules are immediately ionized without dilution or separation and without collision with other molecules. So this type of coupling is the easiest way of determining permanent gases and non-condensing products with high sensitivity.

However, operating the TG analyser under high vacuum means a considerable restriction. Often it is more desirable to study the thermal behaviour under atmospheric pressure. Materials with vapour pressures of  $10^{-3}$  to  $10^{-5} \text{ Pa}$  may be lost during evacuation. Such materials may include liquids,

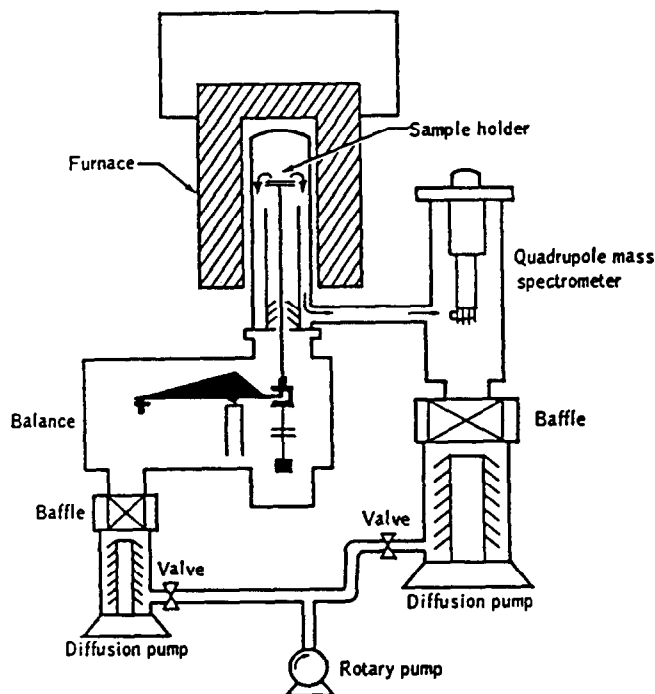


Fig. 1. Schematic diagram of a vacuum thermobalance quadrupole mass spectrometer coupling [11].

absorbed or chemisorbed gases and losses due to the decomposition of metastable compounds (e.g. a number of hydrates).

When constructing coupled systems operating under vacuum, the distance and geometric arrangement of the ion source of the mass spectrometer and the sample crucible are decisive [37]. The distance between the ion source and the sample must be reduced in order to reduce losses of intensity due to contact with the walls. To form an aligned molecular beam the sample crucible can be covered with a perforated lid (similar to a knudsen cell) [17,23]. In a new instrument designed for quantitative gas analysis and kinetic studies [23] two additional orifices located on a slide valve are applied between the sample crucible and the ionization chamber of the mass spectrometer.

For TGA-MS analysis under high vacuum, the amount of sample should not exceed a certain value, determined by the rate of gas evolution during decomposition and by the pumping speed of the vacuum system. In general, a slow heating rate is applied ( $2-6^{\circ}\text{C min}^{-1}$ ) which also results in better resolution of TGA peaks.

A possible arrangement of TGA-MS coupling under vacuum is shown in Fig. 1. The connection is made using a stainless steel interface [11,12,32,33,36] or a T-flange [16], which can usually be heated to avoid

condensation. The pumping system of TGA equipment is modified according to the requirements of MS [11,33] or separate vacuum systems are applied for TGA and MS [23]. In order to reduce the "memory effect" the TGA furnace may be heated to 600–700 °C for at least 2 h and the ion source heated to 340 °C to bake out the system [12].

The thermal analysers most often used are the Mettler TA-1 simultaneous TG–DTG–DTA equipment [11,23,32,34], the Netzsch STA 429 simultaneous TG–DTG–DTA equipment [16,33], the Cahn RH vacuum microbalance [36] coupled with the Finnigan equipment [11,36], and Balzers QMG-511 [16,33] quadrupole mass spectrometers with or without a UTI 100 precision mass analyser [12]. Some of these combinations can also be used for gaseous atmospheres [12,16,33].

#### INTERFACES USED FOR ATMOSPHERIC PRESSURE TGA-MS COUPLING

An ideal interface for TGA–MS would possess the following characteristics: (1) no dilution of the sample; (2) no mass discrimination; (3) no loss of highly volatile or non-volatile components; (4) no degradation or reaction of the evolved material; (5) continuous monitoring; and (6) easy adaptation to various instruments. No interface has yet been constructed which meets all these requirements. In general, a compromise between the factors is made taking into account the purpose of the system's use. The requirements for qualitative analysis are not as strict as those for quantitative analysis or kinetic studies.

The interfaces developed for coupling range from those used for batch applications to those used for continuous flow operations. In batch systems a variable amount of gas sample is collected in a suitable container which is then introduced into the mass spectrometer through a batch inlet. In the simplest method of batch sampling the substances evolved during a certain weight-loss step are condensed in a U-shaped liquid nitrogen cooled trap and then introduced into the mass spectrometer by switching a six-port microvalve [38]. The retention of the trap is 95% and this can be improved further by packing the trap with glass wool in order to minimize the carry-over. If a suitable carrier gas (e.g. helium) is used there is no dilution of the evolved gases, so the technique is highly sensitive for determining trace amounts of effluent from TGA. The cold trap + valve combination is applied extensively in coupling with batch methods such as GC or as an interface between TGA and GC in GC–MS systems [7,26,27].

Another interface of this type consists of a T section and a constant volume sampler [9]. The sampler is attached to the ion source of the mass spectrometer through a gas reservoir and a gold leak tube. If part of the gas is vented via the third arm of the T towards the atmosphere, no enrichment is achieved. This interface can also be operated in continuous mode by opening both stopcocks. In the continuous mode, depending on

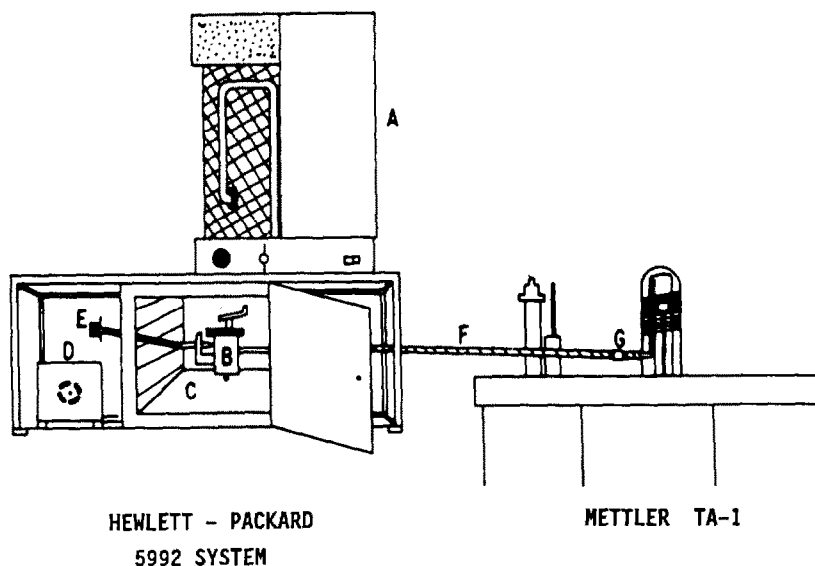


Fig. 2. A schematic drawing of the combined Mettler Thermoanalyser and Hewlett-Packard 5992 quadrupole mass spectrometer. (A) HP-5992 quadrupole mass spectrometer; (B) Varian leak valve; (C) GC oven; (D) fore pump; (E) leak valve fine adjustment control shaft; (F) thermoanalyser-mass spectrometer transfer line; (G) 3/8 in. to 1/4 in. a stainless steel Swagelock union [18].

the interface geometry, the pumping rate and the carrier gas applied, a certain amount of enrichment of the evolved gases occurs which increases sensitivity.

The effluent splitting principle described above is applied in the case of a simple glass-T interface [38].

Different types of valves are also applied for effluent splitting: a metering valve [39,40], a leak valve [13,18], a capillary combined with bellows valve [41], a micrometer valve [29,31], and a metering valve + diaphragm valve combination [7].

The capillary is often used for gas sampling or as the first stage in a two-stage coupling system. The advantage of the capillary is that it is relatively simple and inexpensive. It is, however, prone to blockage, components of the effluent may condense, and absorption, chemical reactions or a certain type of chromatographic separation may also occur. Due to the above-mentioned problems capillary systems often require optimization in terms of their length, diameter and possible heating.

A glass-lined stainless-steel capillary has been used as an interface [42]. At a carrier gas stream flow rate of  $10 \text{ cm}^3 \text{ min}^{-1}$  the resulting source pressure (ca.  $10^{-2} \text{ Pa}$ ) gave less than optimum sensitivity and resolution but, for the desired purpose (fibre and paint analysis), it was sufficient.

A capillary + leak valve combination [13] is shown in Fig. 2, where about 10 mol% of the gas stream leaving the furnace is passed through a stainless

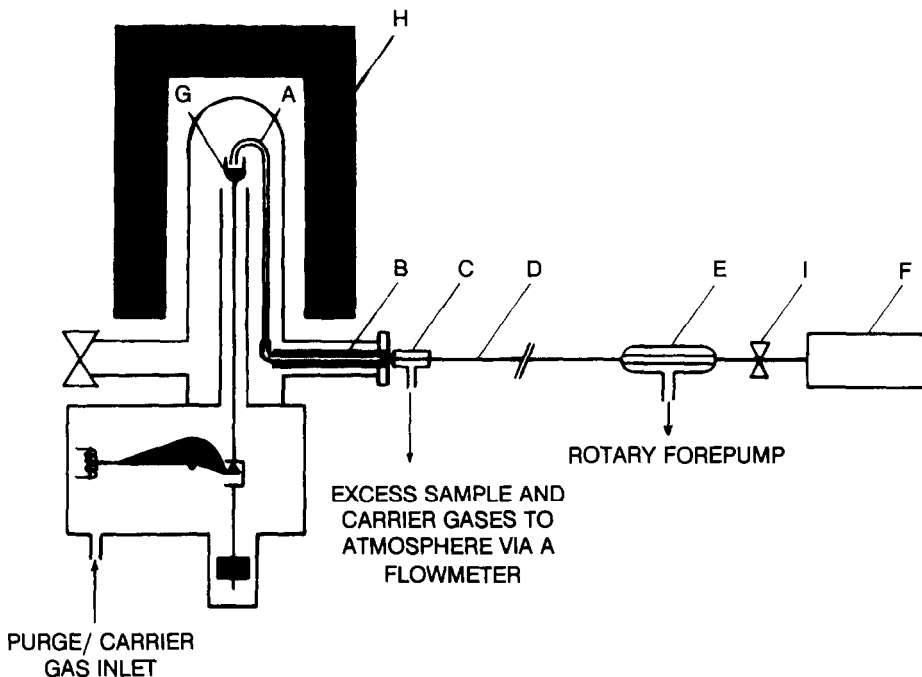


Fig. 3. Schematic diagram of a thermoanalyser-mass spectrometer combination. (A) Silica glass sampling tube; (B) heated silica glass transfer tube; (C) bypass and sampling capillary; (D) PTFE capillary tubing; (E) Watson-Biemann molecular separator; (F) quadrupole gas analyser; (G) sample; (H) furnace; (I) shut-off valve [44].

steel capillary and a variable leak valve (Varian 951-5100). During the experiment, the pressure in the leak valve is 50 Pa. According to the opening of the leak valve 1–2 mol% of the gas enters the high vacuum of the mass spectrometer.

The same type of leak valve has been used as an interface in another study [17]. The value had a minimum leak rate of  $10^7 \text{ Pa dm}^{-3} \text{ s}^{-1}$  under normal operating conditions and could be heated up to  $450^\circ \text{C}$ . The value was calibrated using argon or carbon dioxide in helium.

A combined glass capillary + sintered disk leak system, connected via a small chamber with a rotary pump has been described [43]. A 4 mm internal diameter stainless steel tube was used to connect the system to the TGA furnace, because the direct capillary connection was found to be prone to blockage. Under a pressure gradient from atmospheric to 1 Pa the flow through the sinter was found to be ca.  $1.5 \text{ cm}^3 \text{ min}^{-1}$ .

The experience of connecting a capillary to the TGA furnace through a "bypass" tube has been realized in the design of a special sampling system for a Mettler thermoanalyser as shown in Figs. 3 and 4 [44]. A small fraction of the furnace purge gas is drawn through a capillary (H, Fig. 4) and conducted to the pre-vacuum inlet system of the mass spectrometer,

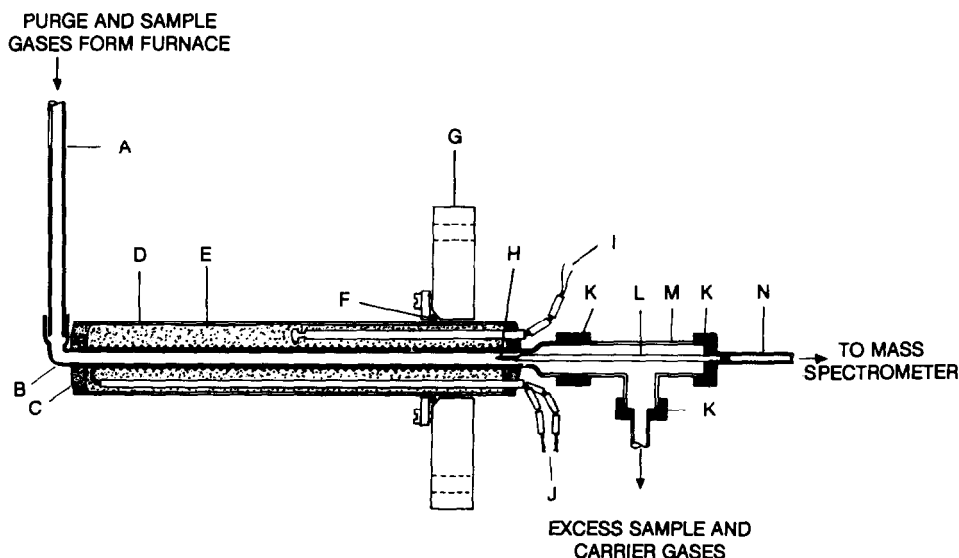


Fig. 4. Details of gas sampling system from Fig. 3. (A) Silica glass sampling tube; (B) silica glass transfer tube; (C) airtight refractory cement plug; (D) silica glass sheath; (E) ceramic fibre insulation; (F) O ring seal; (G) brass flange; (H) glass sampling capillary; (I) thermocouple; (J) heater windings; (K) 'swageloch' unions; (L) stainless-steel sheath; (M) glass T-piece; (N) 1.5 mm PTFE capillary [44].

where a constant pressure of 10 Pa is maintained. A molecular leak gives a further reduction in pressure to  $10^{-4}$  Pa. A unique feature of this system is the position of the sampling tube (A) inside the furnace with its tip in the sample holder. By constraining the furnace purge gas to exit through this tube, rapid and efficient collection of the thermal analysis off-gases is achieved.

The commercially available Stanton Redcroft 1500 integrated TG-DTA-MS system (generally coupled with a VG quadrupole mass spectrometer) has another feature which makes it well suited for EGA: within the furnace there is an aluminium cup which surrounds the measuring head (Fig. 5), [20-22,24]. The cup is of small volume ( $4 \text{ cm}^3$ ) so that dilution of the evolved gases is minimized. The high purge rate, typically  $50 \text{ cm}^3 \text{ min}^{-1}$ , preserves the resolution of closely spaced thermal events. Some  $10 \text{ cm}^3 \text{ min}^{-1}$  of the purge gas + product mixture is drawn into an alumina tube. This is connected by a glass-lined stainless-steel capillary to the second stage of the interface system, which may be either a molecular leak or a jet separator (Fig. 6).

In two-stage pressure reduction systems the first stage in particular is prone to condensation. The selection of the appropriate means of coupling depends on the highest temperature of the TGA test and on the expected condensation temperature of the gases/vapours evolved [33]. Longer capillaries outside the TGA furnace (such as those used in the constructions

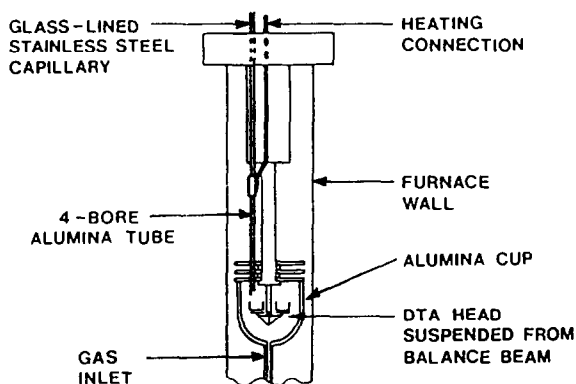


Fig. 5. Gas sampling arrangement of Stanton Redcroft 1500 integrated TG-DTA-MS system [21].

described above) are designed to be heated, but the maximum temperature is usually limited to  $250^{\circ}\text{C}$ . Therefore these capillaries cannot be used if gases with a condensation temperature above ca.  $200^{\circ}\text{C}$  are expected. Shorter capillaries can be integrated into the TGA furnace and heated to ca.  $600^{\circ}\text{C}$  (if a suitable material is selected), so the majority of gases and vapours reach the second pressure stage even when the sample is heated to  $1500^{\circ}\text{C}$ . The diameters of the capillaries and orifices used are determined by the conductances and the capacity of the pumping system, but are usually below 0.2 mm.

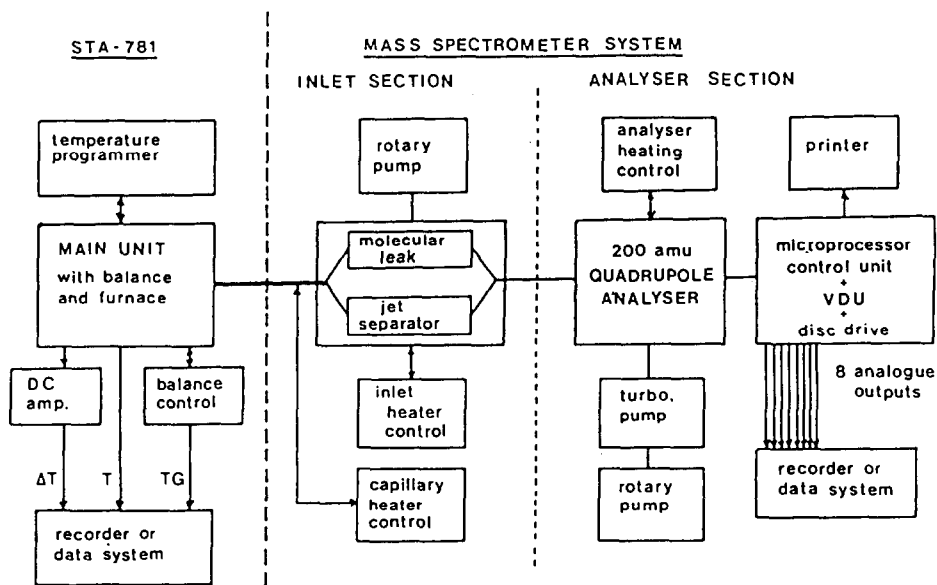


Fig. 6. Block diagram of simultaneous TG-DTA-MS system [21].



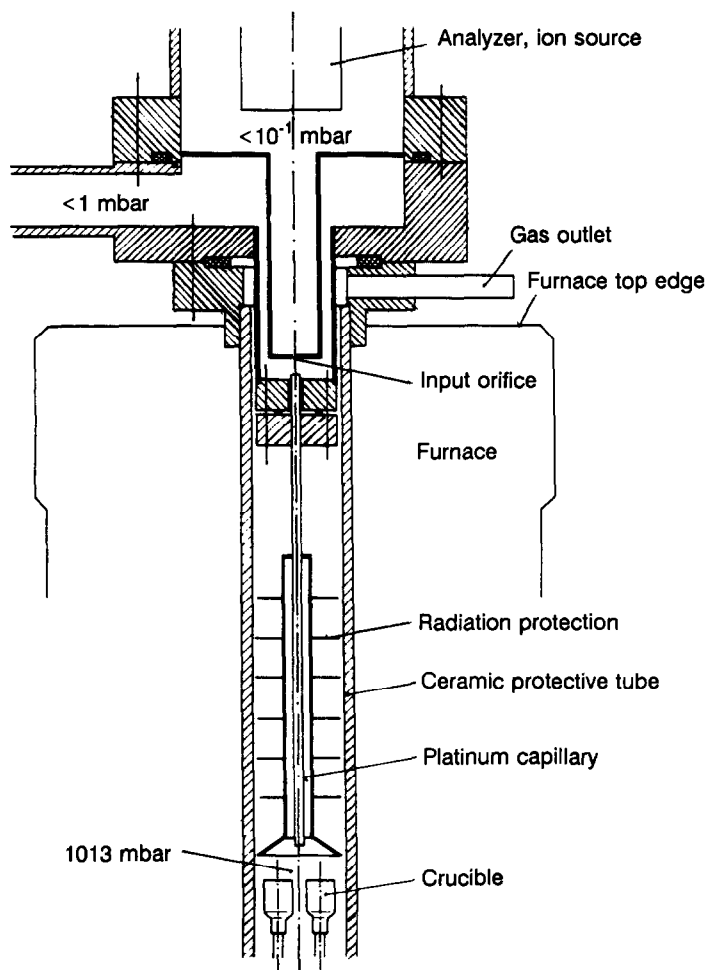


Fig. 7. Gas inlet system with platinum capillary,  $T_{\max} = 1500^{\circ}\text{C}$  [16].

In order to illustrate the principle of operation of such systems, a capillary-orifice combination is shown in Fig. 7 and an orifice-orifice construction is shown in Fig. 8.

The two-stage pressure-reduction system shown in Fig. 7 has been designed for furnace temperatures up to  $1400^{\circ}\text{C}$  [15,16]. The system consists of a platinum capillary and a pinhole orifice in a platinum sheet. The platinum capillary has a gas concentrating cone. Radiation shields serve to prevent excessive heating of flange F1. By heating the flange of the capillary (F2) condensation is eliminated. The gas flow coming from below passes the furnace. Some of the carrier gas containing gases and vapours evolving from the sample passes through the capillary at a pressure of 100 Pa and proceeds through the second orifice.

Platinum parts usually catalyse the decomposition of organic compounds, so an orifice-orifice system has been developed which is made of

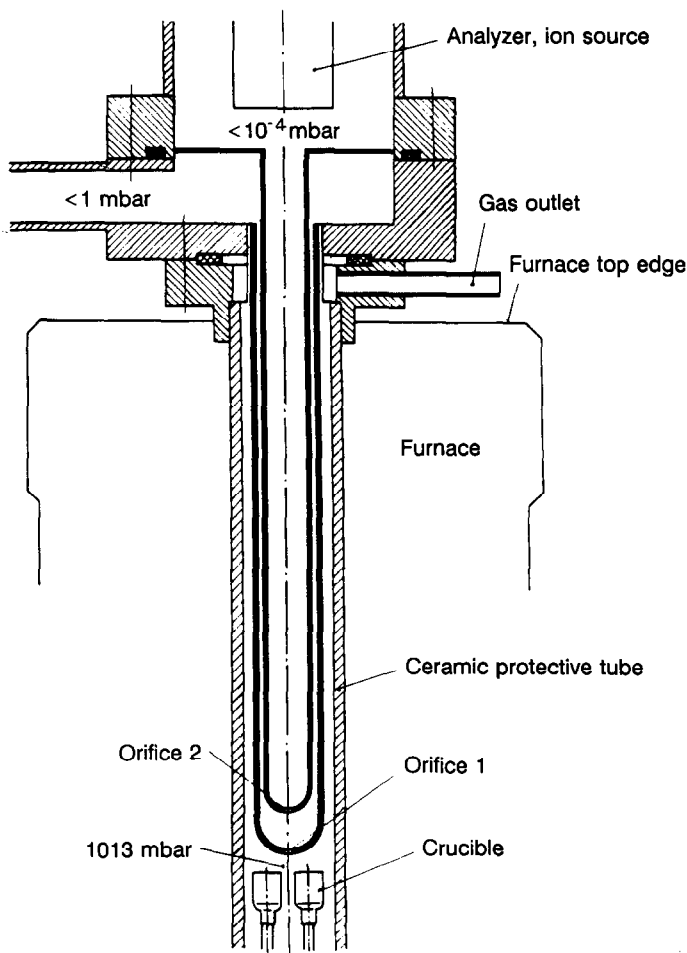


Fig. 8. Gas inlet system with orifices of  $\text{Al}_2\text{O}_3$ ,  $T_{\text{max}} = 1500^\circ \text{C}$  [16].

high temperature resistant oxide ceramics (usually alumina) (Fig. 8). Two concentric alumina tubes with orifices in the bottom are arranged close together directly above the sample crucibles. The mode of operation is the same as that described above. The advantage of this system compared with the platinum capillary-orifice interface (besides eliminating the catalytic effect) is that the gas reaching the mass spectrometer ion source will undergo less wall collisions, and so these walls are easier to clean than are the platinum capillaries. Alumina orifice-orifice systems can be used up to  $1550^\circ \text{C}$ .

The modification of the above system for the detection of condensable vapours has been described [45-47]. In conventional ceramic orifice systems beam losses reduce the intensity significantly. By optimizing the orifice arrangement and geometry a special metal orifice system has been developed which has a divergent nozzle and a subsequent skimmer. Using

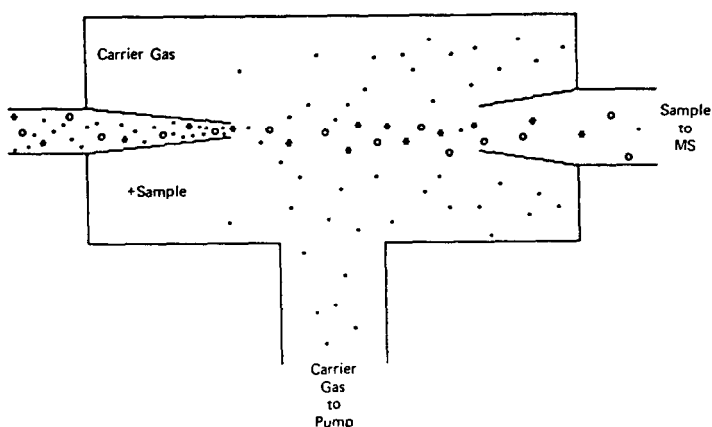


Fig. 9. Principle of the jet separator [2].

this interface vapours having a saturation vapour pressure greater than 100 Pa can be successfully detected.

Both of the interfaces described above are claimed to be quantitative and to provide a gas throughput of constant composition because the pressure of gases sampled is such that viscous, laminar flow is ensured prior to entry into the mass spectrometer analyser.

The interface systems described are commercially available for the Netzsch STA 429 TGA–DTA equipment + Balzers QMG-511 quadrupole mass spectrometer coupling.

## JET SEPARATORS

The jet separator was originally used in GC–MS coupling [48–53]. The principle of the separator is shown schematically in Fig. 9. The mixture of the sample and a light carrier gas leaves the first nozzle at high velocity in the form of an expanding jet. After leaving the nozzle the molecules of low molecular weight expand rapidly and are pumped away, while the sample molecules of relatively higher molecular weight are mostly collected by the skimmer nozzle and subsequently enter the mass spectrometer [8,54]. As a consequence of the separation process described above, the use of a light carrier gas (hydrogen or helium) in the thermal analyser increases the separation efficiency and thus increases the sensitivity. The separation efficiency decreases as the difference between the molecular weight of the sample and the carrier gas decreases and as the amount of injected sample gas increases [14].

A jet separator usually transfers ca. 50% of the sample to the mass spectrometer ion source. Adjustable separator jets are constructed from quartz in order to minimize adsorption and catalytic effects. These components can also be heated.

Commercially available jet separator systems for GC-MS are generally expensive. A simple jet separator, which can be produced by a glass blower, has been described in ref. 43. A single stage jet separator has been used as an interface [51,55].

If the normal flow through the thermobalance exceeds the capability of the jet separator, it may be combined with valves [28,43,52], another jet separator [14] or a capillary with bypass [20-22,24].

## MASS SPECTROMETERS

The first TGA-MS instruments often used time-of-flight mass spectrometers [41,56]. In current systems, however, quadrupole mass spectrometers are usually used because of their simple and space-saving construction, good resolution in fast mass scans and constant resolution over the whole mass range.

Two types of ion source can be used in quadrupole mass spectrometers. In the axial beam ion source the electron beam and ion extraction are in the axial direction. This source is of simple construction and ensures high sensitivity. In the cross-beam ion source the particle beam, the electron beam and ion extraction are located at right angles. This arrangement reduces source contamination and can be applied to the analysis of corrosive gases by using a cooling flap collector [16,33].

At present the Balzers QMG-511 mass spectrometer seems to be most frequently used. This may be due to the fact that a commercially available TGA-MS system is also based on this spectrometer [16]. In some cases magnetic instruments have also been used in TGA-MS coupling [14,42,43,55].

The most common ionization mode used in mass spectrometers is electron impact. Using this ionization mode, both molecular and fragment ions are observed. However, although it provides important structural information, extensive fragmentation makes the identification of individual components difficult, especially when several compounds are evolved together (as, for example, in polymer degradation).

The next most often used ionization mode which is well suited to coupling with atmospheric pressure thermogravimetry, is chemical ionization [39]. In this case ionization occurs by ion-molecule reactions between the ionized reagent gas and the sample. The amount of energy exchanged in these reactions tends to be low, and thus the amount of fragmentation of the sample molecules is greatly reduced. As mentioned above, chemical ionization allows higher pressures in the source, so the use of complicated interface systems can be avoided. The gas used to purge the thermobalance can be used as the reagent gas. Chemical ionization can be used for the molecular mass determination of the components of a complex mixture,

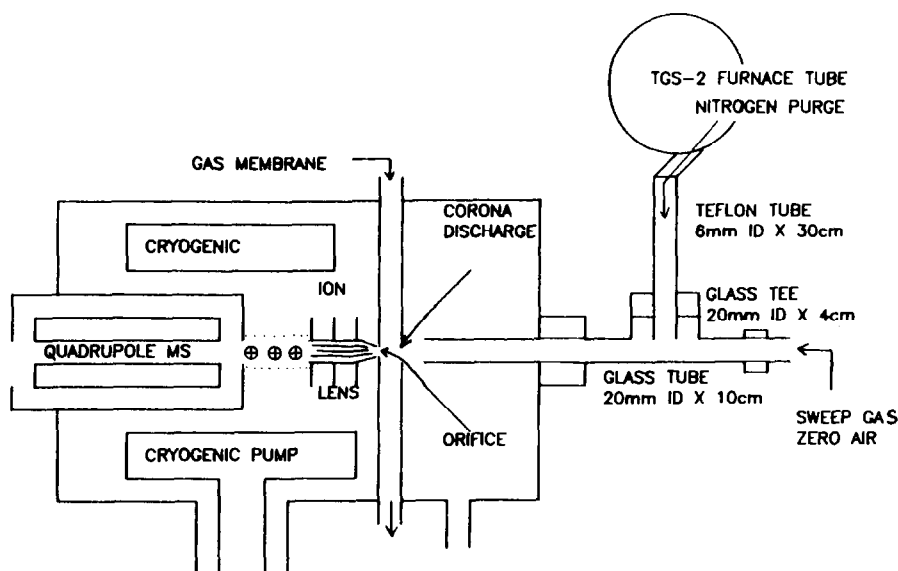


Fig. 10. Schematic diagram of Sciex TAGA 3000 atmospheric pressure ionization mass spectrometer and the coupling with TGS-2 [57].

quantitative studies and trace analysis, but gives limited structural information.

The two ionization techniques mentioned above impose some limitations on TGA-MS analysis. Both are vulnerable to the presence of oxygen, since the ion source filament may oxidize rapidly and burn out [31,43]. This problem has been overcome by constructing atmospheric pressure chemical ionization mass spectrometers (APCI-MS); these were originally used for environmental analysis. In such systems no heated filament is used and ionization takes place in a current regulated corona discharge. The problem of pressure reduction from atmospheric to vacuum is resolved inside the mass spectrometer, and thus coupling with a TG analyser is quite simple [57,58]. A schematic diagram of a Sciex TAGA 3000 APCI-MS is shown in Fig. 10.

In the case of complex mixtures, the easy identification of the components by using their molecular ions (limited fragmentation by chemical ionization) and then obtaining more precise structural information on selected ions can be made using tandem mass spectrometry (MS-MS), e.g. an atmospheric pressure ionization triple quadrupole mass spectrometer (APCI-MS-MS) [29-31]. The construction of a Sciex TAGA-6000 instrument is shown in Fig. 11.

In MS-MS the molecular ions arising from the first quadrupole can be analysed structurally. Thus ions with a particular mass-to-charge ( $m/z$ ) ratio are selected by the first quadrupole ( $Q_1$ ) and collided with a neutral target gas such as argon in the second quadrupole ( $Q_2$ ) (a process referred

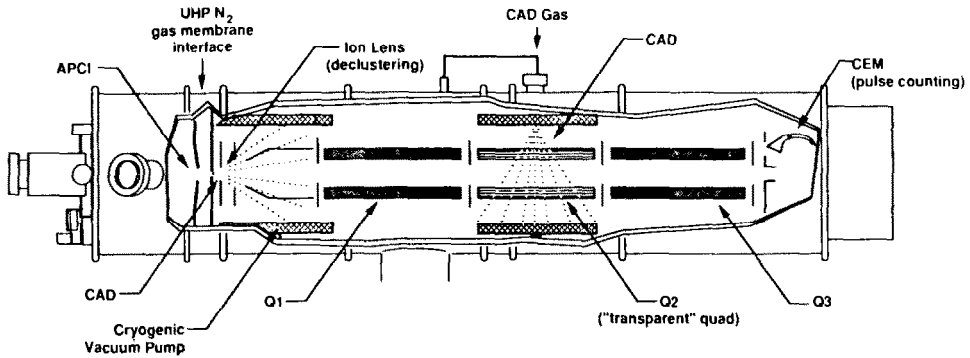


Fig. 11. Schematic diagram of Sciex TAGA 6000 triple quadrupole MS-MS system [31].

to as collisionally activated decomposition (CAD)) to produce daughter ions that are indicative of the precursor ion's structure. Scanning the third quadrupole generates daughter ion spectra that serve as chemical fingerprints used to identify these ions and, therefore, the corresponding neutral molecules entering the ion source. This process is particularly useful in distinguishing isobaric ions which may co-evolve during complex pyrolysis reactions.

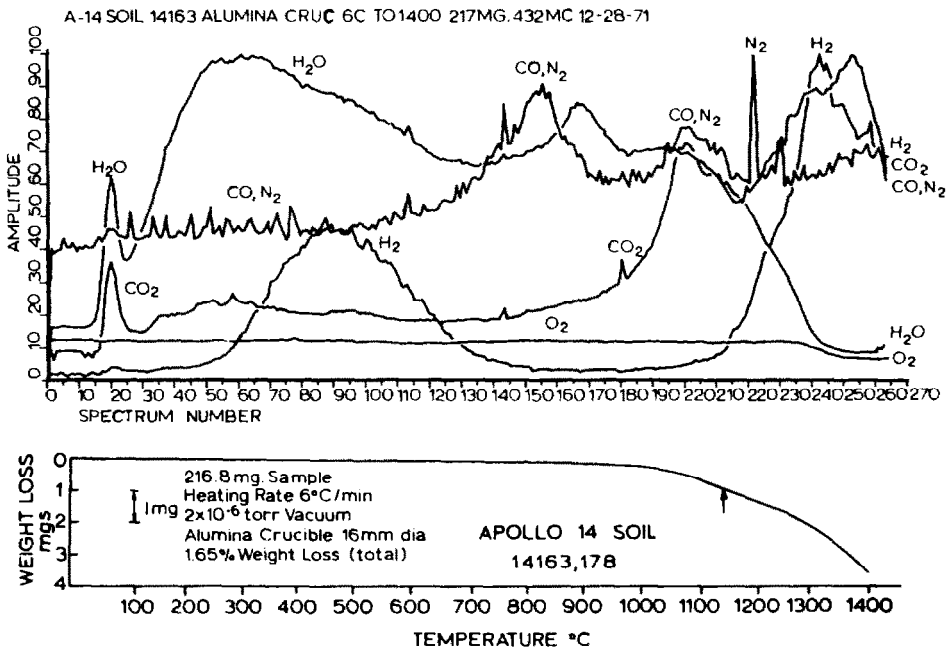


Fig. 12. Weight loss curve and gas release profile for Apollo 14 soil. The arrow on the weight loss curve around 1140 °C indicates the initial melting of the sample [34].

## SYSTEM CONTROL, DATA ACQUISITION AND PROCESSING

The data-acquisition and processing system must: (1) acquire and store relevant data points; (2) relate the points to time and temperature; (3) account for background and instrument sensitivity; (4) accomplish automatic mass calibration; and (5) compare the obtained mass spectra with a library of mass spectra of known compounds.

The early automatic data-collection systems [53,59,60] have changed along with the hardware facilities. A modern data-collection system consists of a computer with peripherals and interfaces connecting both the TGANalyser and the mass spectrometer to the computer. Often however the TGANalyser and the mass spectrometer are controlled separately by two computers.

The interface between the computer and mass spectrometer consists of a digital to analogue (DA) converter, an integrator + analogue to digital (AD) converter, and a timing generator. The DA converter converts the data typed by the operator to analogue control signals. The integrator + AD converter integrates the output signal from the mass spectrometer (ion current) over a specified period of time and converts it into digital form. The timing generator serves to generate the sampling times and automatically adjusts the integration time as a function of the signal strength.

In these applications small desk-top computers (PDP-8, PDP 11, HP 2116C and HP 9825) are used [18,34,55,61,62].

The software allows two possible modes of operation [21,24,34,57]: (1) the scanning mode, and (2) the peak-select mode. In the scanning mode several mass spectra can be recorded during a weightloss process. This mode is generally used for the identification of unknown products.

In the peak-select mode several mass spectral peaks can be monitored continuously as a function of time. This increases sensitivity and time resolution and reveals finer detail than the scanning mode.

The computer software developed by System Industries is described in ref. 34. This software package includes executive programs, diagnostic routines for checking the performance of the interface, and utility and maintenance programs. An additional element to the general software functions is provided by a program [28] which correlates the time information of the thermal and mass spectral data acquired by two separate computers.

A study aimed at optimizing the performance of a Perkin Elmer TGS-2 thermoanalyser + Balzers QMG-511 mass spectrometer + PDP 11 micro-computer system according to the special requirements of solid fuel and complex organic material analysis led to the elaboration of new computer software [61]. Besides the usual data, pressures and gas flow rates are also monitored in order to be able to analyse the system's performance and to locate occasional malfunctions. The software allows rapid digital filtering of

mass spectrometric data, rapid processing of the peaks, and rapid acquisition of time-averaged weight and temperature data.

#### APPLICATIONS OF TGA-MS

A major part of the application of TGA-MS is the qualitative analysis of evolved gases for the determination of their sequence of release and for mechanistic studies. In a few cases TGA-MS is used for quantitative analysis and kinetic studies. From the numerous applications that have been described a few special cases have been chosen to illustrate the advantages and limitations of TGA-MS.

##### *Differentiating between two compounds with identical thermogravimetric behaviour*

The mass spectra of evolved gases can be used to differentiate between two compounds, whose thermogravimetric behaviour is identical. For example, the identification of natural and modified guar gums (polysaccharide structures) has been described [57]. Thermal degradation products from TGA were identified using atmospheric pressure ionization MS. In this application the mass spectra obtained were further processed by subtracting the mass spectrum of the thermal decomposition product of a standard compound from those of the modified compounds. The differences can be used for screening in the identification of commercially used guar gums.

##### *Evolved gases showing no weight loss on the thermobalance*

The high sensitivity of the mass spectrometer can indicate the presence of evolved gases even when, because of its limited sensitivity, the thermobalance shows no weight loss. The use of MS in such situations is extremely useful, especially when the sample quantity is limited. For example, the results of a TGA-MS analysis of an Apollo 14 lunar soil sample are shown in Fig. 12 [34]. The sample was investigated under vacuum and the total weight loss up to 1400 °C was only 1.65%. During the analysis five selected masses were followed as a function of temperature, and the release of H<sub>2</sub>O, CO<sub>2</sub>, CO and N<sub>2</sub>, H<sub>2</sub> and O<sub>2</sub> was recorded. This was explained on the basis of previous investigations on meteorite and lunar samples.

The high sensitivity of the MS has also been used in identifying polymer additives and trace solvents and in impurity analysis. The lowest possible concentration detected depends on the interface used. Using a combination of a capillary and a leak valve the identification of additives at concentrations as low as 20 ppm has been reported [18].



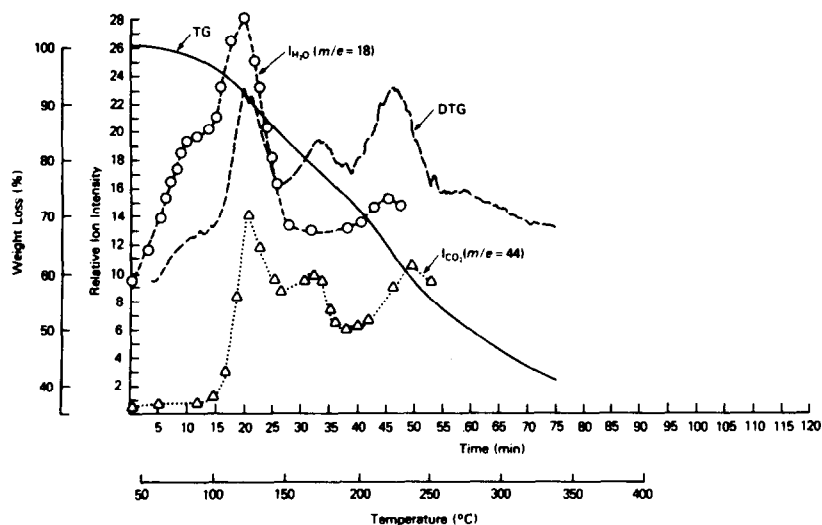


Fig. 13. TG, DTG and mass spectral ion intensities ( $I$ ) for water ( $m/z = 18$ ) and carbon dioxide ( $m/z = 44$ ) vs. time and temperature for freeze-dried Giant Ragweed Allergenic Extract [51].

The detection level of MS for different gases is important in the toxicological evaluation of the thermal degradation products of polymers [41]. Applications include the construction of aircraft interiors, where in catastrophic conditions short-term exposure to such compounds can occur. The minimum detection level of a time-of-flight system with a capillary + bellows valve interface was found to be in the range 3–120 ppm.

#### *The resolution of the TGA curves of coevolving compounds*

TGA–MS plots obtained using a helium stream from freeze-dried biological products are shown in Fig. 13 [51]. The transition due to residual moisture cannot be easily distinguished from the TGA data. The ion intensities of  $\text{H}_2\text{O}$  ( $m/z = 18$ ) and  $\text{CO}_2$  ( $m/z = 44$ ) were monitored as a function of temperature and superimposed on the thermogram. In this way it was possible to identify the weight loss due to the residual moisture and this was easy to distinguish from the water of decomposition whose evolution coincides with the evolution of  $\text{CO}_2$ . The interface used (jet separator) was sensitive enough to distinguish these gases from the background level. The applicability of the technique has been demonstrated for the analysis of freeze-dried biological products (with usually less than 5% residual moisture content) where the amount of sample is limited and not available in the amounts necessary for moisture testing by the coulometric Karl–Fischer methodology (approximately 15 mg/test) or gravimetric analysis (200 mg/test).

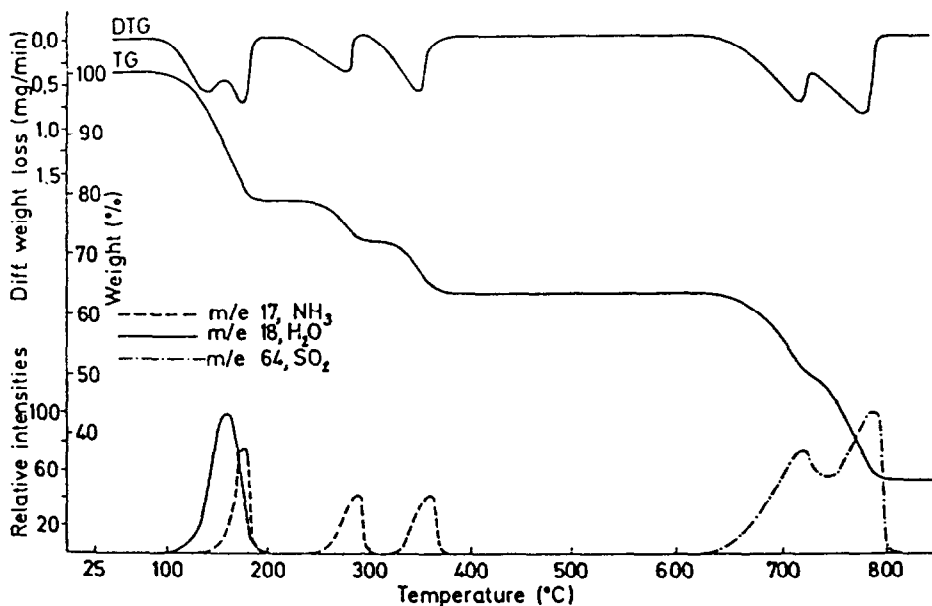


Fig. 14. TG, DTG curves and MS profile of copper tetrammine sulphate hydrate (reagent gas, argon) [39].

### *The importance of selecting the correct ionization mode in MS*

TG-DTG-MS profiles recorded during the thermal decomposition of copper tetrammine sulphate hydrate are shown in Fig. 14 [39]. Chemical ionization with argon as the reagent gas was used. Under such conditions the detection of the NH<sub>3</sub> molecular ion ( $m/z = 17$ ) is not disturbed by the OH fragment of water.

However a peak due to Ar<sub>2</sub><sup>+</sup> occurs at  $m/z = 80$  which coincides with the molecular ion peak of SO<sub>3</sub>. It can be seen from Fig. 14 that, despite the low resolution of the quadrupole filter, the evolution of ammonia and water can be clearly distinguished. In the first weight-loss step the water of crystallization and two molecules of ammonia are volatilized. The other two NH<sub>3</sub> molecules are released in the second and third decomposition steps which begin at 240 and 326 °C, respectively. The remaining copper sulphate remains stable until 626 °C, above which it decomposes in a two-step process.

As SO<sub>3</sub> cannot be detected because of interference with Ar<sub>2</sub><sup>+</sup> another experiment was done using a nitrogen atmosphere in order to decide whether SO<sub>2</sub> and SO<sub>3</sub> are primary decomposition products. The registered curve shows the simultaneous evolution of SO<sub>2</sub> and SO<sub>3</sub>, which corresponds to the thermodynamic data.

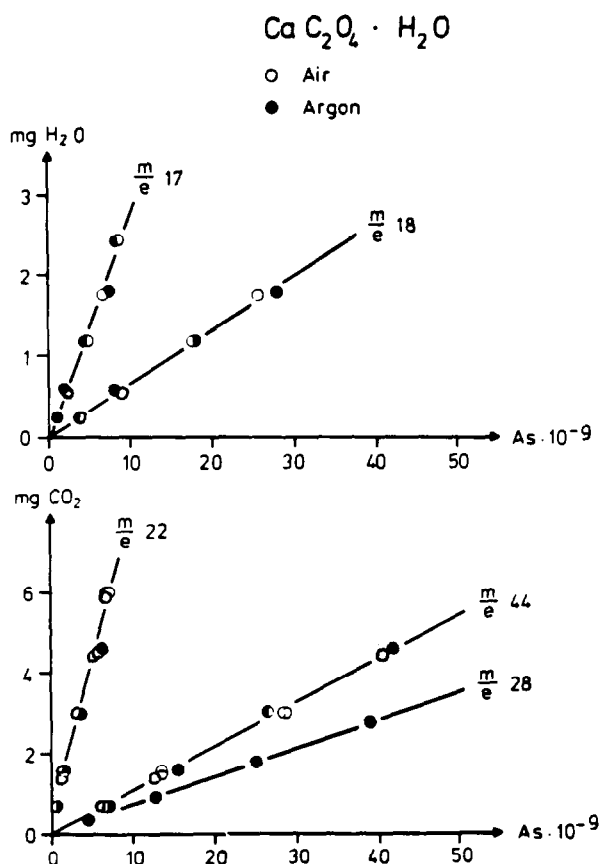


Fig. 15. Calibration curves determined for H<sub>2</sub>O, CO and CO<sub>2</sub> [13].

### *The use of TGA-MS for quantitative analysis*

TGA usually provides quantitative information on the total weight loss at a certain temperature, while MS identifies the off-gases and determines their relative proportion. To relate the amount of a specific component in the off-gas to the original sample requires the determination of the absolute weight of the component on the basis of MS data. This can be done by constructing a calibration curve where the integrated peak area of a selected mass peak is plotted against the weight losses found in samples of known composition.

For example, the calibration for H<sub>2</sub>, CO and CO<sub>2</sub> has been determined using known amounts of CaC<sub>2</sub>O<sub>4</sub> · H<sub>2</sub>O (Fig. 15) [13]. The equations for the straight lines were elucidated using linear regression. It was found that the relationship between the peak area of the ion current of selected masses and the weight of the evolved H<sub>2</sub>, CO and CO<sub>2</sub> is only linear up to an ion current of  $0.9 \times 10^{-10}$  A. The calibration curves were applied to the

quantitative determination of  $H_2$  and  $CO_2$  evolved simultaneously from  $NaHCO_3$  and very good agreement with the theoretical value was found. This technique has also been used to investigate a sample of Opalinuston. A similar study involved the quantitative analysis of an ethyl/vinyl acetate copolymer [63].

Another method of quantitative analysis [23] has been used in simultaneous thermogravimetry and modulated molecular beam mass spectrometry studies and involves an extensive mathematical treatment of data. A set of equations is solved in order to determine the coefficients relating the selected ion mass signals to the amounts of the components in the reaction cell. Using this method, quantitative analysis can be carried out without having to determine the mass spectrometer sensitivity for all gas species.

### *The use of TGA-MS in kinetic studies*

The use of TGA-MS in kinetic studies is based on the assumption that at any time the mass spectral ion current is proportional to the rate of formation of the product, whilst the area under the whole MS ion current curve is assumed to be proportional to the initial quantity of the reactant. A further assumption is that the flow of the evolved gases from the sample to the ionization region of the mass spectrometer is instantaneous and so the gases are not fractionated prior to analysis. By applying the above assumptions kinetic parameters such as reaction order and activation energy can be determined.

For example, the kinetics of polytetrafluoroethylene (PTFE) and polytetrafluoroethylene/hexafluoropropylene copolymer (FEP) have been studied in various atmospheres [52]. The results give important information on the mechanism of the thermal degradation of these compounds.

### CONCLUSIONS

In selecting or designing a coupled TGA-MS system it is important to take into consideration exactly what type of information is required. Unfortunately, all the available TGA-MS interfaces have some drawbacks and may not be suitable for all types of study.

The coupling of a thermobalance operating under vacuum with a mass spectrometer is relatively easy, but this may limit the applicability of the thermal analysis. From the point of view of applications, working at ambient pressures and under various (oxidizing, reducing, inert, etc.) atmospheres may be advantageous. Thus it may be necessary to use an atmospheric pressure ionization mass spectrometer or a complicated interface system between the thermogravimetric analyser and the mass spectrometer. The interface, however, may compromise the overall performance of the TGA-MS system.

Besides the generally used interfaces special ones have been designed for some applications. For example, it may be particularly important to have uniform and representative sampling of the evolved gases or to enrich minor components. High temperature TGA-MS coupling requires special design and materials, and in some cases modification of the thermal analyser furnace is also necessary.

In MS single quadrupole instruments are usually used which are adequate for most applications. Depending on the application electron impact, chemical ionization or atmospheric pressure ionization may be selected. Only in special cases will it be necessary to use a high resolution magnetic instrument or a tandem mass spectrometer.

The coupled TGA-MS method is used extensively for the identification of thermal degradation products, to determine their sequence of release, and to resolve thermogravimetric curves. The technique has only limited use in quantitative analysis and kinetic studies.

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