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Practical aspects for the coupling of gas analytical methods with thermal-analysis instruments

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Abstract

The coupling of mass spectrometry, Fourier-transform infrared spectroscopy and gas chromatography with thermal-analysis methods is discussed from the practical point of view. The gas-flow conditions in thermobalances, the design of coupling interfaces, and the features of the gas analysers relevant to the coupling are shown. The high sensitivity of the Skimmer coupling as compared to the capillary coupling of mass spectrometers is explained by the perfect gas-flow conditions and elimination of condensation effects. Optimisation of transfer systems and gas cells contribute to a high sensitivity also for the FTIR coupling. The evaporation of zinc and phosphorus from a $ZnGeP_2$ semiconductor is shown by the Skimmer coupling with MS and the HF evolution from a brick clay is measured by coupled FTIR. © 1997 Elsevier Science B.V.

Keywords: Combined gas analysis; Coupled TA-MS; Orifice; Semiconductor; Polymer decomposition; Skimmer coupling

1. Introduction

When combining or coupling different thermal-analysis methods and when using the combined instruments with the aim of detection and analysis of evolved volatiles, a series of basic requirements must be valued and decided by the user, which are:

- selection of the methods to be combined;
- selection of the coupling method and coupling interface;
- gas-flow conditions in the combined instruments;
- detection limits for the evolved gases;
- relevance of response time and resolution of the gas-detection-and-analysis system;
- temperature range and samples to be analysed;
- correlation between the data acquired from different detector systems;
- interpretation of the results; and
- possibility of calibration and quantitative work.

In the work described here, the practical aspects for deciding on these requirements are given preference over the theoretical aspects.

From the large number of gas-analysis methods, available for combination with predominantly thermogravimetry (TG), a choice is made here of the most frequently used methods: mass spectrometry (MS), infrared spectroscopy (IR) and gas chromatography (GC). Other detection systems, based on variations of gas density or thermal conductivity, as well as chemical methods (e.g. titration) and physical methods (e.g. adsorption, desorption, etc.), are not discussed here.

The knowledge of the amount and composition of evolved gases is of greatest interest in thermogravimetry as compared to other methods of thermal analysis, as this is the method by which a sample is

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decomposed for characterisation and for quantification of its decomposition steps, without originally knowing the decomposition products.

For the discussion of the gas-flow conditions in coupled instruments and the distribution of the evolved gases in a purge gas flow, the situation in various commonly used TG systems is analysed. Influences of laminar-, turbulent- and molecular-flow conditions – convection, partial-pressure ratio, diffusion, condensation and background – will be analysed with respect to the question of detectability of evolved gases. The features of the gas analysers, relevant for the coupling, are illustrated together with general rules for the coupling interfaces. Because of the widespread application of hyphenated techniques, only few results will be discussed to show the possibilities of software and interpretation.

2. Gas flow in thermobalances

The conditions for the gas flow in thermobalances and in coupling interfaces influence to a great extent the characteristics of the results in a coupled gas analyser. The main aspects of the flow in the thermobalance, relevant to hyphenated techniques, are:

- volume and geometry of the sample chamber;
- flow rate of the gas;
- flow profile;
- flow direction;
- influence of temperature and temperature gradients;
- convection;
- distribution of evolved gases in the purge gas flow; and
- connection of the coupling interface.

All efforts for coupled gas-analysis methods should aim in a complete detection and analysis of the evolved gases from the sample under test. Loss of gas by condensation at cold spots, low-detection sensitivity because of heavy dilution with the purge gas, low-time-and-temperature resolution because of long transfer times and mixing with the purge gas by diffusion and by uncontrolled flow conditions, and variation in gas composition in the coupling interface should be avoided, if at all possible.

Coupling of gas-analysis methods with thermobalances is nowadays possible for application temperatures up to more than 2000°C and for nearly all vertical and horizontal balance arrangements.

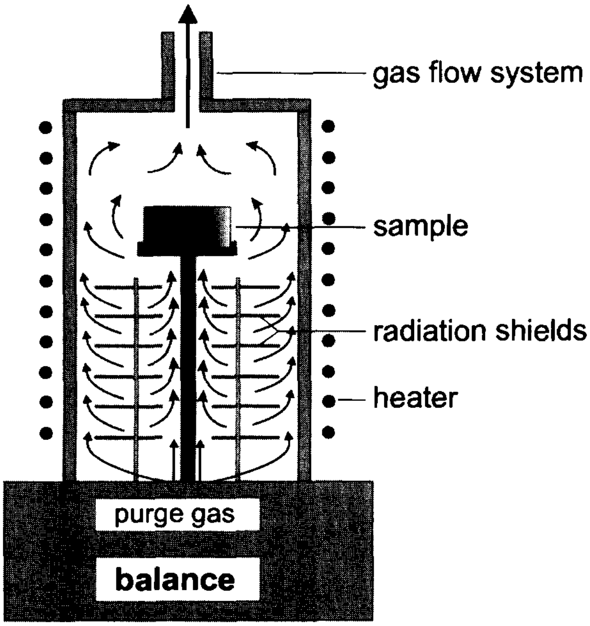


Fig. 1. Vertical, top-loading TG system with upward gas flow.

The experiments with rising temperature induce, in all TG arrangements, a vertical component for the gas flow at hot surfaces, due to the density decrease of the gases with temperature (convection flow). This convection flow can contribute to the purge gas-flow direction when it is parallel to it in vertical, top-loading balances and it can be of disturbing influence when it is opposite to the purge gas-flow direction in vertical, bottom-loading balances or when it is perpendicular to the flow direction in horizontal balances.

2.1. *Gas flow in vertical thermobalances*

The straightforward vertical flow of the purge gas in this balance type has to be protected against an additional uncontrolled convection flow, e.g. by gas baffle plates. Radiation shields in Fig. 1 have the double function of protection of the balance against heat radiation and of hindering the convection flow. The intensive mixing of the gas-flow paths through the radiation shields improves the temperature distribution in the system, as it would be found similar in turbulent flow profiles. The flow rate of the purge gas can be small, as the evolved gases from the sample start also with a vertical flow direction. Especially with a small volume of the sample chamber, a fast gas transfer with small dilution effects can be realised. The connection of the coupling interface is made above the sample crucible (orifice or Skimmer coupling for QMS) or at the end of the gas-flow system of the TG (capillary coupling for QMS and transfer line for FTIR or GC).

The purge gas flow in this balance has to overcome the opposite convection flow and to reverse the flow direction of the evolved sample gases. A higher flow rate is required to achieve a dominant downward flow direction and, therefore, a higher mixing and dilution effect of purge gas and evolved sample gas is encountered (Fig. 2). Gas baffle plates are of no help to achieve a better flow profile, sometimes additional inner flow tubes help to guide the gas in the desired direction. This TG system can be coupled via capillary to QMS and transfer lines to FTIR and GC. The connection is usually made at the end of the gas-flow system of TG. If the entrance of the coupling interface is arranged directly above the sample crucible, some of the disadvantages coming from the gas-flow conditions can be avoided.

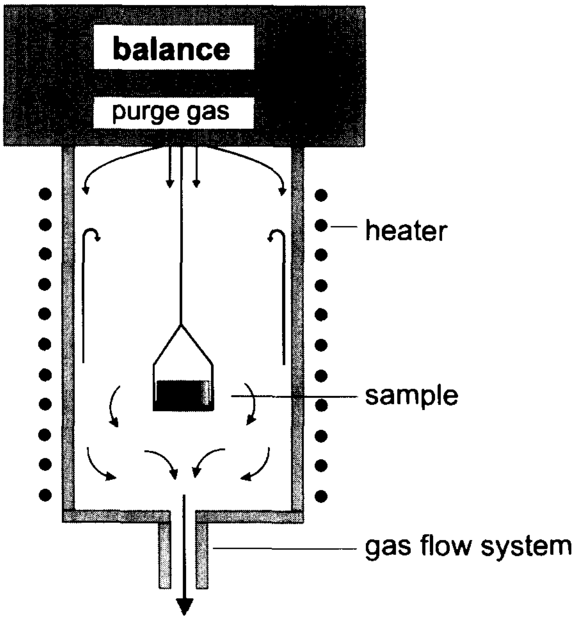


Fig. 2. Vertical, bottom-loading TG with downward gas flow.

2.2. *Gas flow in horizontal thermobalances*

The laminar flow of the purge gas in a horizontal TG can be slightly disturbed by a convection flow, mainly in case of small purge gas-flow rates (Fig. 3). On the other hand, high flow rates can reduce the heat exchange through the laminar flow pattern and lead to significant temperature gradients [1]. These balances can be coupled to QMS by capillaries and to FTIR and GC by transfer lines, which are connected at the end of the gas-flow system of the TG.

2.3. *Distribution of the evolved gas in the purge gas flow*

The distribution of the evolved gas in a purge gas flow is depending on the volume ratio, the flow profile and the diffusion coefficients. The volume ratio can be calculated from the amount of gas evolved (weight loss of the sample), the duration of the gas evolution and the purge gas volume-flow-rate, i.e. all parameters are under the influence of the operator. The flow profile is determined by the geometry of the flow paths within the TG and the coupling interface, i.e. by constructional elements. The diffusion effect [2], responsible for the mixing of the evolved gas with the

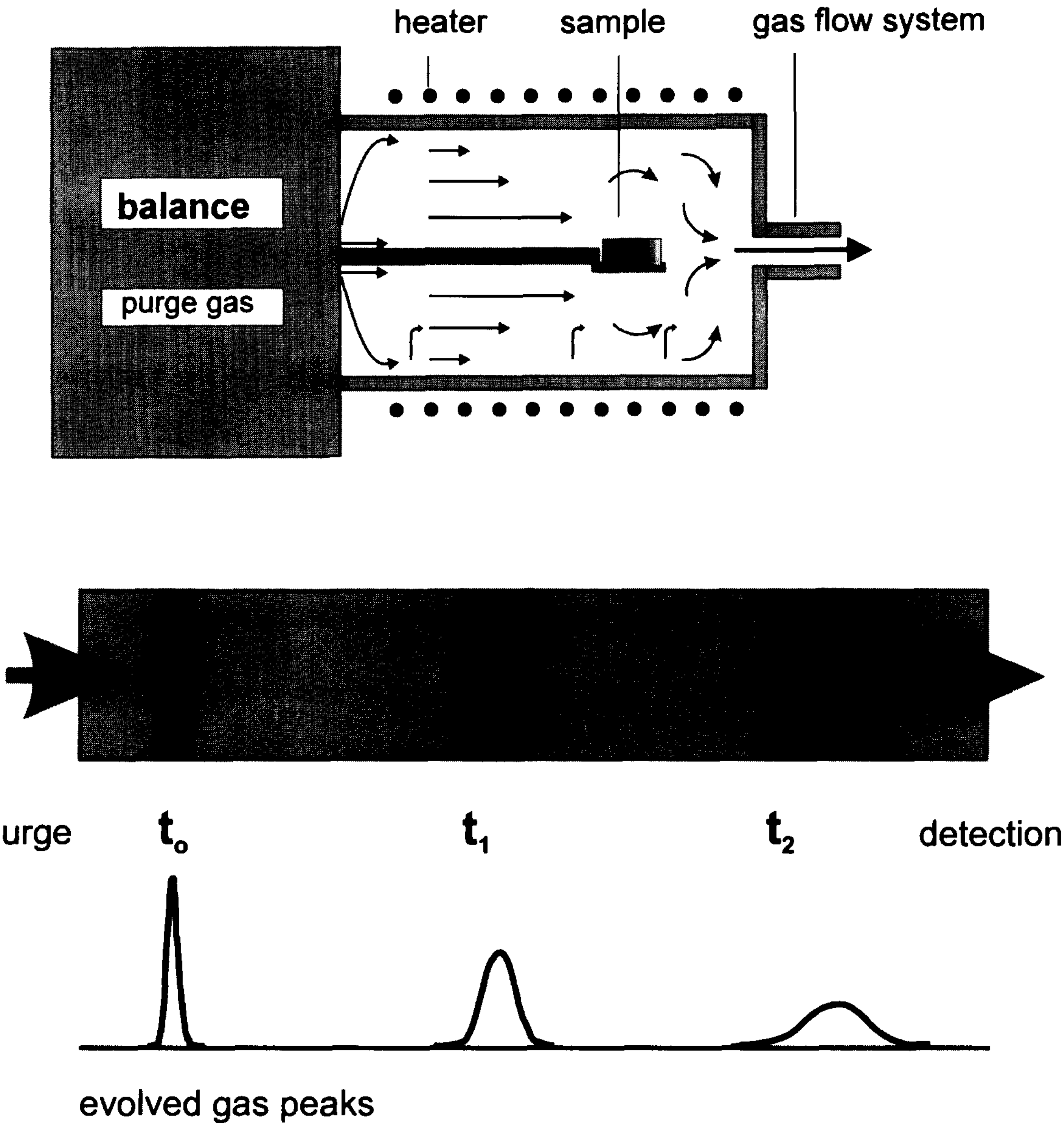


Fig. 4. Broadening of the evolved gas distribution in the purge gas flow with time.

purge gas, is influenced by the kind of gas evolved and the purge gas, and also by the duration of flow in the balance and the transfer system.

The distribution of the evolved gas is illustrated schematically in Fig. 4.

With sampling of the evolved gas near to the sample crucible, one can achieve a narrow initial distribution (t_0) and, with a short transfer time, one can limit the time-dependent broadening effect based on diffusion. Large changes in the cross section of the gas paths in the thermobalance and the transfer system to the gas analyser will also lead to higher mixing effects between evolved and purge gases.

3. Coupling of mass spectrometers

3.1. Characteristics of MS

For coupling mass spectrometers to thermobalances, it is highly desirable to use only small-scale dynamic mass filters as opposed to heavy magnetic instruments. Ion-trap instruments tend to suffer from limited detection of low mass numbers and increased interference between the ions within the mass-separation section. On the other hand, quadrupole mass spectrometers (QMS) meet the requirements for coupling well, i.e. small dimensions, light weight, fast scans and constant resolution in a broad mass range.

The main components of a QMS are:

- ion source;
- quadrupole mass filter; and
- detector.

Although far from ideal, the standard way to produce ions in commercially available QMS systems is by electron-impact ionization.

Commonly used ionization energies in the electron bombardment of the gases being analysed are in the 70–100 eV range, which is very high compared to the ionization potential of atoms or molecules, being in the 5–25 eV range for most materials. The high ionization energy has the advantage of producing a relatively constant ion current; however, a great deal of fragmentation of molecules has to be taken into account in the interpretation of results.

Quadrupole mass filters, which are dynamic mass-separation systems on the basis of the mass-to-charge ratio of the ions, are available for the 1–1024 amu mass range for coupling. The geometry of the quadrupole system varies from simple rods to complex hyperbolic cross sections, and the supply electronics are usually designed for unit resolution, i.e. separation of ions with mass m and $m+1$. Single- and double-charged ions are commonly found in the mass spectra.

One has to recall here that the full function of the quadrupole mass filter is achieved only in a high vacuum of better than 10^{-4} mbar (10^{-2} Pa), where the interference between the residual gas in the system and the gas (ions) to be analysed can no longer disturb the results.

For the detection of the ions after the separation according to their mass-to-charge ratio, Faraday detectors as well as secondary electron multipliers (SEM) are in use. The high amplification of the SEM makes it the preferred detector.

The vacuum for the QMS is nowadays achieved using small turbo molecular pumps, which reduce the effects of oil back-streaming (increased hydrocarbon background level), common with previously used oil-diffusion vacuum pumps. Completely oil-free pumping systems are offered nowadays on the basis of turbo molecular and diaphragm pumps.

The function of the QMS is a continuously or quasi-continuously working partial-pressure monitoring system, i.e. it records the relative changes in the composition of the gases introduced via the gas inlet system. The results can be displayed as spectra of the relative intensity of the individual mass numbers in a selectable mass range (amu range) in the so-called SCAN-mode or as a continuous recording of several fixed mass numbers in the so-called MID-mode (multiple ion detection mode). It has to be pointed out that a low background must be ensured in mass spectrometry by maintaining clean working conditions (pure purge gases) and frequent degassing of the construction parts, e.g. by heating to desorb gases and moisture from the surface.

3.2. MS coupling interfaces

The coupling interface between a thermobalance and a quadrupole mass spectrometer has two main functions (Fig. 5):

- efficient transfer of a representative part of the evolved gases from the thermobalance; and
- pressure reduction, so that the evolved species can enter the QMS and be detected.

3.2.1. Vacuum coupling

Only for TG experiments in high vacuum, which could be vapour-pressure determinations according the Knudsen effusion method [3], is a direct coupling of the QMS, i.e. the integration of the QMS analyser into the vacuum system of the thermobalance, possibly without any coupling interface. Samples with vapour pressures lower than 10^{-4} mbar (10^{-2} Pa)

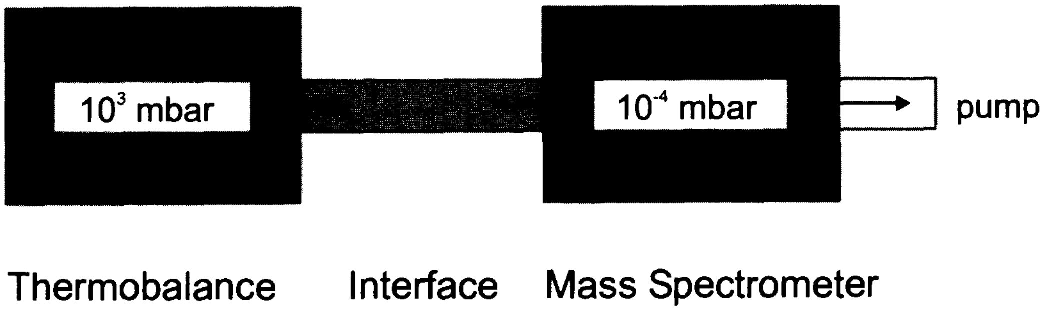


Fig. 5. Combination of thermogravimetry and mass spectrometry by a coupling interface.

and gases with partial pressures below this value can be analysed easily in the direct vacuum coupling. The advantage of high sensitivity of the mass spectrometers can be taken without restriction and this leads to detection limits in the ppb (parts per billion) range. The only disadvantage is the need to disconnect the QMS when loading the samples into the thermobalance and the time-consuming evacuation procedure with each sample measurement.

However, the majority of TG experiments is performed in a gas flow with a system open to the surrounding at atmospheric pressure. The necessary coupling interface is then predominantly a pressure-reduction system, which can be achieved by a single- or a double-step mechanism.

3.2.2. *Single-step coupling system*

The pressure reduction is effected in one step by using a small orifice or a capillary. The flow through this coupling interface is influenced by the large pressure gradient and the gas finally enters the impact area of the ion source under molecular-flow conditions. The flow through the single-step interface depends on the molecular weight of the gas species: in case of a gas mixture, a time-dependent separation is to be expected for the orifice and a fractionation for the capillary. Gradually, lighter molecules are enriched in the QMS, the heavier molecules stay more in the gas mixture. The user has to estimate the importance of this effect for his work as, for slow gas-evolution processes, a precise quantitative gas detection and analysis seems to be restricted.

3.2.3. *Double-step coupling systems*

For the analysis of the continuous gas flow from a thermobalance, the combination of a laminar-flow and a molecular-flow system is the most widely used pressure-reduction interface for the coupling of mass spectrometers [4] (Fig. 6).

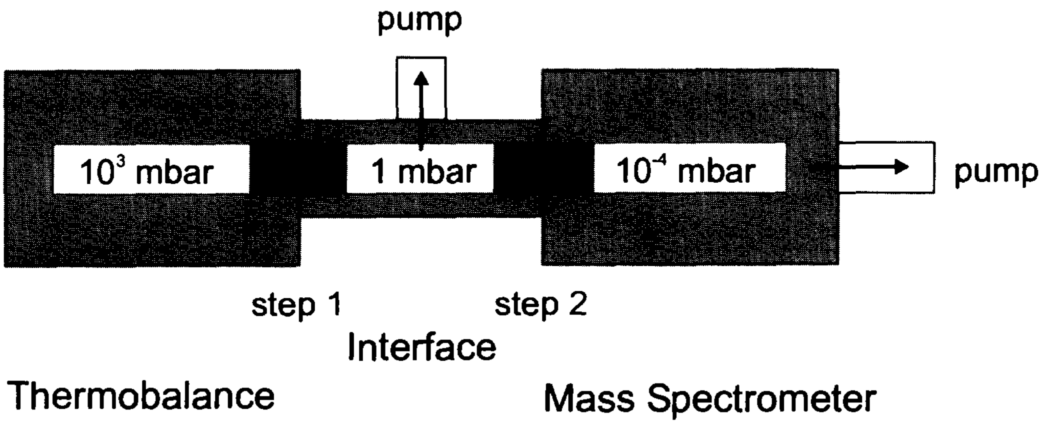


Fig. 6. Double-step coupling interface.

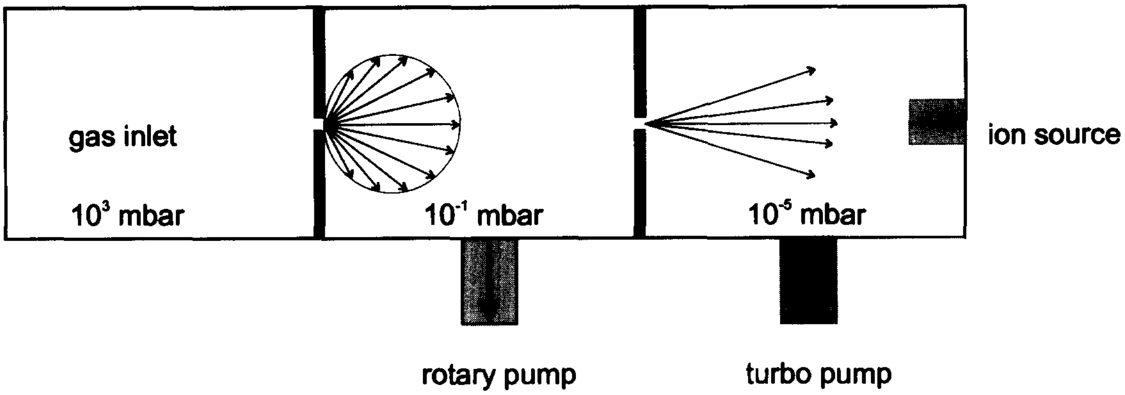


Fig. 7. Gas-flow and pressure conditions in a two-stage MS coupling interface.

Practical solutions for the first pressure reduction steps are:

- capillary, and
- orifice.

The dimensions of a capillary or an orifice have to be adjusted to the capacity of the vacuum-pumping devices to achieve laminar-flow conditions for the gas and a pressure reduction from 10^3 mbar down to the 10^{-1}–1 mbar range in the intermediate vacuum. Practically, this can be realised with orifice diameters in the range of 100 μm in thin foils of metals, ceramics or glass, and with capillaries with internal diameters ~ 150 μm and a length of up to 1 m. The pumping devices used for the intermediate vacuum are usually two-stage rotary pumps with capacities in the 1.5–4.5 $m^3\ h^{-1}$ range, or special stages of a turbo molecular pump. Filters at rotary pumps are recommended to avoid oil back-streaming into the intermediate vacuum.

The temperature change of the gases from the thermobalance causes changes of the gas viscosity, which significantly influences the 'permeability' of the orifice and the capillary under laminar-flow conditions.

The second step of pressure reduction is achieved by orifice or Skimmer systems [5], which reduce the pressure down to 10^{-5} mbar and control the gas flow as a molecular flow into the ion source of the mass spectrometer. The diameters of the orifice or skimmer openings are in the 80–120 μm range, again depending on the capacity of the turbo molecular pump at the QMS.

The geometrical arrangement of the first and second pressure-reduction steps has to ensure an optimum transfer of the gases (Fig. 7).

The distance between this first pressure reduction system and the sample (sample crucible) determines the transfer time (response time) of the coupled MS to the greatest extent. The transfer times in the first and second pressure-reduction steps are normally negligible compared to the time to transport the gas to the first orifice or to the entrance of the capillary. See, for this discussion, the chapter on gas-flow conditions in thermobalances. The transfer time (t) in a capillary can be estimated according to Eq. (1), when taking the flowing gas as a continuum:

$$t = \frac{LA}{Q} \qquad (1)$$

where L is the length of capillary, A the is cross section of the capillary and Q is volume-flow rate of the gas.

In a capillary with a length of 1 m and an inner diameter of 0.15 mm, pumped by a rotary pump with 1.5 $m^3\ h^{-1}$ capacity, the flow rate is 4.5 ml min^{-1}, and the transfer time is 0.24 s at laminar-flow conditions, which is negligible in standard temperature programs for thermal analysis. The higher gas flow through the thermobalance requires a by-pass at the entrance of the capillary or the first orifice for the excess gas flow.

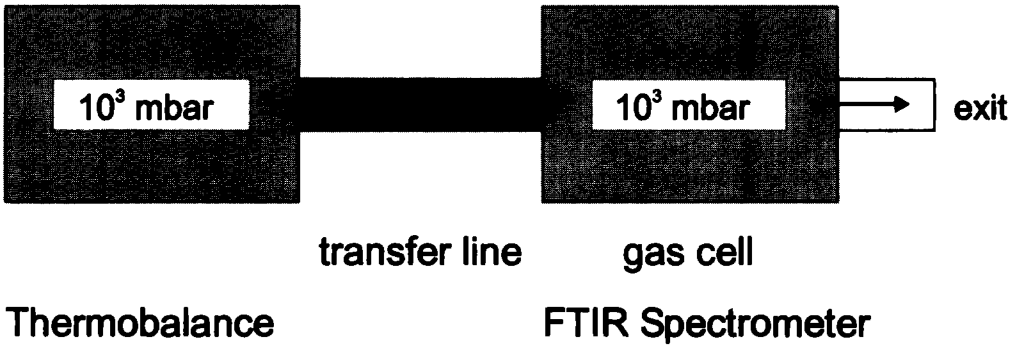


Fig. 8. Coupling of TG and FTIR with a transfer line.

4. Coupling of infrared spectrometers

4.1. Characteristics of IR

Infrared spectrometry is widely introduced for the identification of solid and liquid organic materials. It is based on the interaction of the infrared radiation with molecules having a dipole moment. For coupling with thermogravimetry, the infrared radiation must be brought into an intensive contact with the gas flow including the evolved gases, which is achieved in specially designed gas-measuring cells. Fourier-transform infrared spectrometers (FTIR) provide the high scan speeds which are required for the on-line coupling with thermal analysers for a continuous monitoring of the gas composition. The main components of an FTIR spectrometer for the coupling are:

- IR source;
- Michelson's interferometer;
- laser source as wavelength reference;
- gas-measuring cell; and
- detector.

4.2. Coupling of FTIR spectrometers

Opposite to the coupling of mass spectrometers, the whole gas flow from the thermobalance should pass through the gas cell of the infrared spectrometer, i.e. the transfer line should not change the flow rate and the pressure of the gas. (Fig. 8)

These conditions can be realised with transfer lines having an inner diameter of, e.g. 2 mm. The transfer time for the gas is directly determined by the gas-flow rate chosen for the thermobalance and the length of the transfer line. Normally, it is in the range of few seconds and the flow profile is laminar.

The results of the FTIR spectroscopy are displayed as absorbance or transmittance spectra, i.e. the wavelengths (wavenumbers) of the radiation absorbed by a molecule or functional groups of the molecule are shown as peaks in the range of wavenumbers covered by the instrument, usually 4000–400 cm^{-1} for the middle infrared range. The requirements on the resolution of an FTIR spectrometer depend on the application problems, mostly 4 cm^{-1} is fully sufficient.

5. Coupling of gas chromatographs

5.1. Characteristics of GC

For the chemical analysis of many organic materials, a pre-separation into less complicated components is achieved with gas chromatography. The volatile sample is transported by a carrier gas through the separation system, e.g. a coated capillary or packed column, and due to an interaction between the sample and the stationary phase, the different components of the sample leave the separation system at different times (retention times). The detectors monitor either just the retention times or they additionally analyse the separated components (e.g. GC–MS or GC–FTIR). A continuous analysis of a gas stream from a thermal analyser is therefore not possible by gas chromatography; one has to use a gas-sampling loop for intermittent operation.

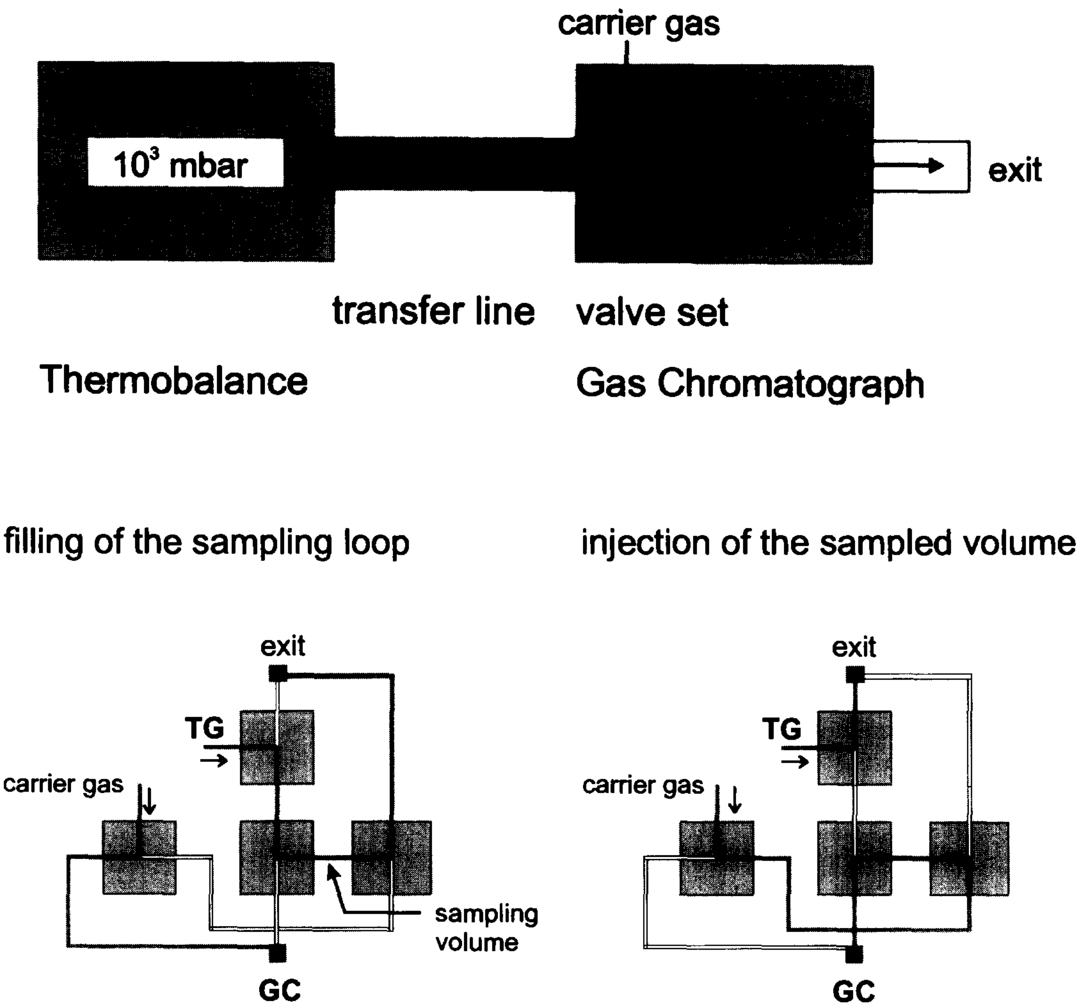


Fig. 10. Example for a of valve-set for the gas inlet at a GC.

5.2. Coupling interface for GC (GC–MS and GC–FTIR)

The connection of the valve-switching set of the GC gas inlet to the thermal analyser is done like that for the FTIR coupling with a heated transfer line. Also, here no flow rate and pressure change is acceptable. (Fig. 9)

Additionally, special care is necessary to prevent any pressure change for the gas flow in the thermal analyser when switching the valves from the sampling position (filling of the well-defined sampling volume) to the injection position (GC measurement). (Fig. 10)

The gas flow from TG with the purge gas and evolved sample gases is used to fill (i.e. purge) the sampling volume, which is, for example, a tube of known length between two valves. When the valves are switched into the measuring (injection) position, the TG purge gas goes to a free exit, whereas the sampled gas is introduced into the GC-separation system by the carrier gas. There is no restriction in selecting a different purge gas for the TG in comparison to the carrier gas for the GC, which is normally at a higher pressure. The complete transfer-and-valve system has to be heated to prevent condensation.

To overcome the problem of the intermittent gas analysis with a GC, one has to adapt the temperature program of the thermoanalytical experiment. This can be a stepwise isothermal heating of the sample to have a precise temperature correlation between the TA results and the gas analysis during the isotherms, or it is a drastic reduction of the heating rate to achieve several GC results during the interesting sample reactions.

6. Description of coupled instruments

6.1. Capillary coupling TG–QMS

A detailed schematic diagram shows the features of a capillary coupling system with gas pick-up just above the sample crucible, heated adapters and connections, heated quartz-glass capillary and heated orifice (Fig. 11). The low dead volume of the small TG sample chamber allows a minimal delay time for the detection of evolved gases, typically below 1 s and the low purge gas-flow rates reduce dilution effects to a minimum. The vacuum-tight construction of the TG and the transfer system allows the work in very clean (and dry) conditions.

The temperature range for the TG 209 is up to 1000°C and the mass range of the QMS is up to 300 amu. The pumping system for the QMS is oil-free for a low-hydrocarbon background in the mass spectra, which makes the coupled instruments specially suitable for the analysis of organic materials and polymers.

For higher temperatures and combination with TG–DTA and TG–DSC, this capillary coupling can be used in a similar manner (Fig. 12).

The larger volume of the sample chamber and the greater distance from the entrance of the capillary lead to transfer times in the order of 10 s. The balance can carry large sample volumes and weights, which allow the study of inhomogeneous sample materials in a temperature range up to 2000°C. The typical flow rate for the purge gas is 50–150 ml min^{-1}, so that the bypass for the excess gas flow (overflow) in front of the capillary becomes very important. On the other hand, one has to calculate with a 'gas dilution' in the range of 2000 : 1 between the thermobalance and the QMS, mainly caused by the pressure-reduction steps. The TG sample holder in Fig. 13 can be replaced with a heat-flux DSC sample holder for simultaneous TG–DSC. It is recommendable to direct the evolved gases upwards by using lids at the sample crucibles with centric holes, ensuring a narrow initial distribution in the purge gas flow.

The simultaneous TG–DSC measurement supplies additional information on the heat of reactions, which

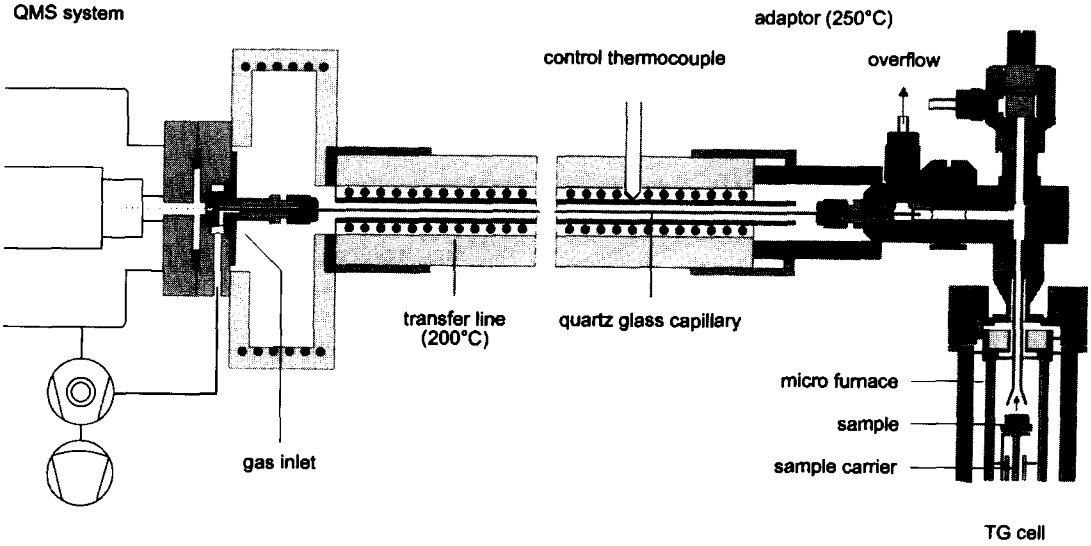


Fig. 11. Capillary coupling of TG 209 (Netzsch) with QMS (ThermoStar, Balzers).

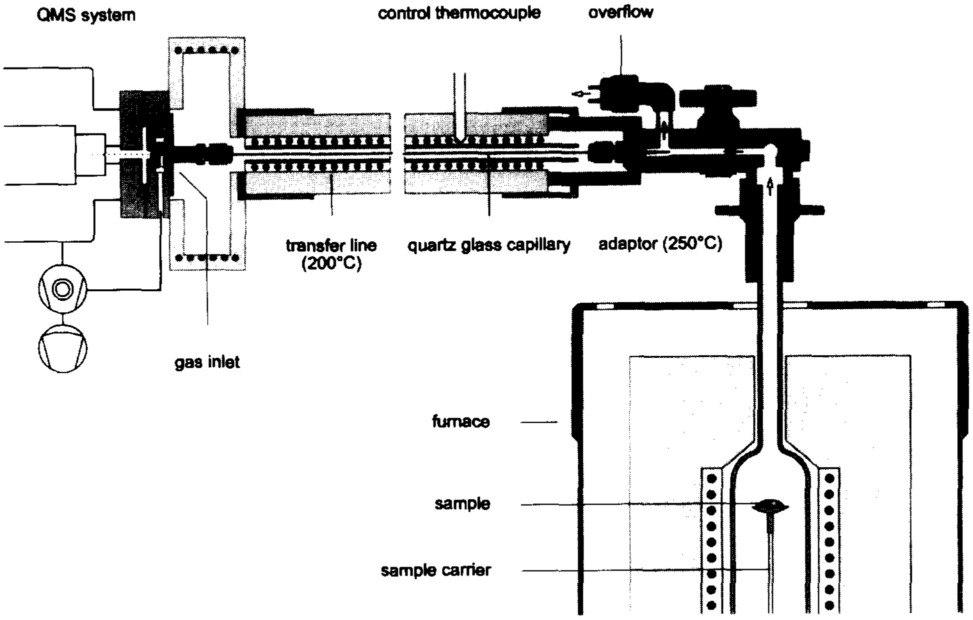


Fig. 12. Capillary coupling of STA 409 (Netzsch) with QMS (ThermoStar, Balzers).

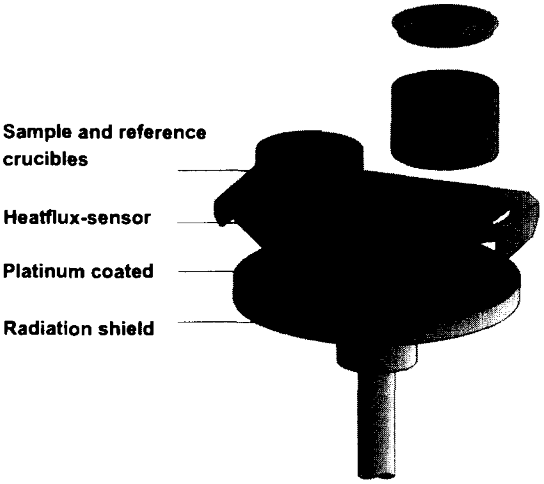


Fig. 13. TG-DSC sample holder.

can be valuable together with the analysis of the evolved gases to characterise the processes and materials under study more completely.

6.2. Skimmer coupling STA–QMS

The Skimmer coupling is the most advanced way of combining a thermobalance or simultaneous TG–DTA and TG–DSC instrument with a quadrupole mass spectrometer from the perfection of the gas-flow conditions in the coupled system.

The Skimmer is arranged behind an orifice (first pressure-reduction step) in such a way that a parallel-oriented molecular beam is achieved during the second pressure-reduction step (Fig. 14). The first orifice is constructed as a divergent nozzle, through which the gas reaches supersonic speeds and forms a barrel-shaped compression zone behind it. The Skimmer cuts out a narrow beam, if the pressure is low enough for molecular-flow conditions, i.e. the mean free path of the gas molecules is larger than the diameter of the Skimmer opening [6]. (Fig. 15)

The short distance between sample and first orifice, the integration of the orifice and Skimmer into the furnace which heats the sample, and the short distance in the molecular-flow region from the Skimmer to the ion source result in a drastic increase in detection sensitivity of the Skimmer coupling in comparison to capillary or double-orifice couplings for mass spectrometers.

This high sensitivity becomes especially evident at high mass numbers, where the gain in sensitivity reaches a factor of 2000 compared to a capillary coupling, as could be shown with the decomposition

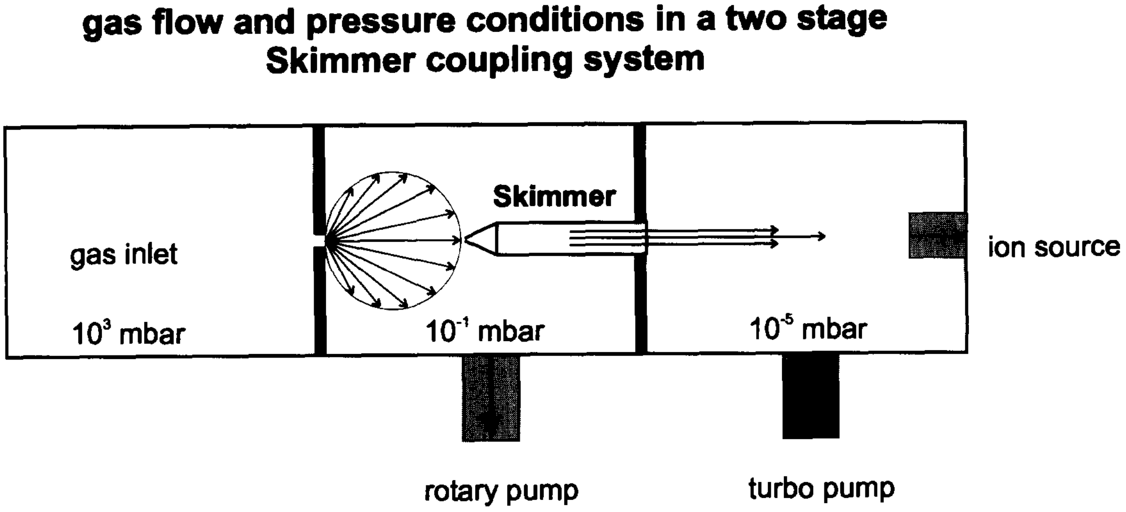


Fig. 14. Skimmer coupling system.

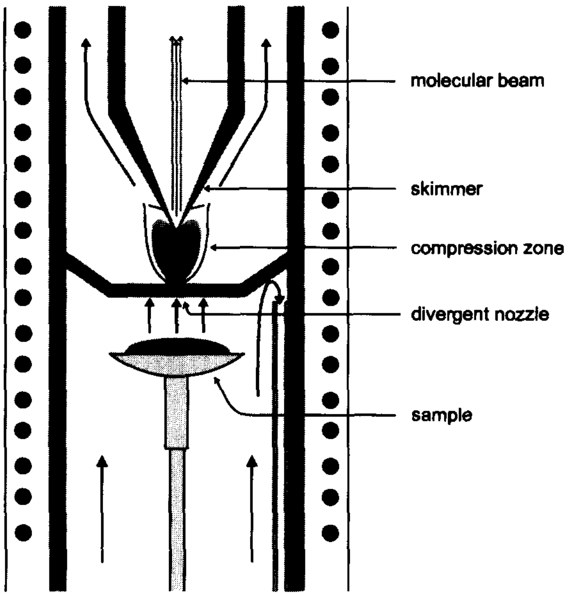


Fig. 15. Skimmer coupling system, detailed.

of polystyrene [7]. The perfect gas-flow conditions and the homogeneous temperature distribution at the Skimmer coupling allow the detection of materials with low vapour pressures and condensable vapours, like metals. High mass numbers up to 512 amu or even 1024 amu are detectable as well with the Skimmer coupling, due to the low interferences along the gas-flow path.

A very high precision is needed in the construction of the divergent nozzle and the Skimmer. This can be realised with special steel for application temperatures up to 800°C, with alumina up to 1500°C and with glass carbon up to 2000°C, and applying modern production technologies (e.g. laser-drilling) (Fig. 16). The Skimmer coupling originated from experience with double-orifice couplings up to 1500°C, made out of alumina tubes with laser-drilled holes [8].

QMS-coupling systems with variable orifice temperatures, like the Skimmer coupling, require a pressure regulation system, as the flow through the orifices changes with temperature because of the temperature-dependent changes in the viscosity of the gases [9]. With a corresponding automatic pressure regulation, the sensitivity of the coupling is constantly higher than that without a pressure control (see Fig. 17).

6.3. Coupling TG–FTIR using a transfer line

The interface for the coupling of FTIR to a thermobalance or an STA instrument has to transfer the complete gas flow into the gas cell of the spectrometer, without pressure changes and without losses by condensation. With a heated transfer line, e.g. made up of a PTFE those with inner diameter 2 mm, one can fulfil these conditions with the advantage of flexibility of the transfer line.(Fig. 18)

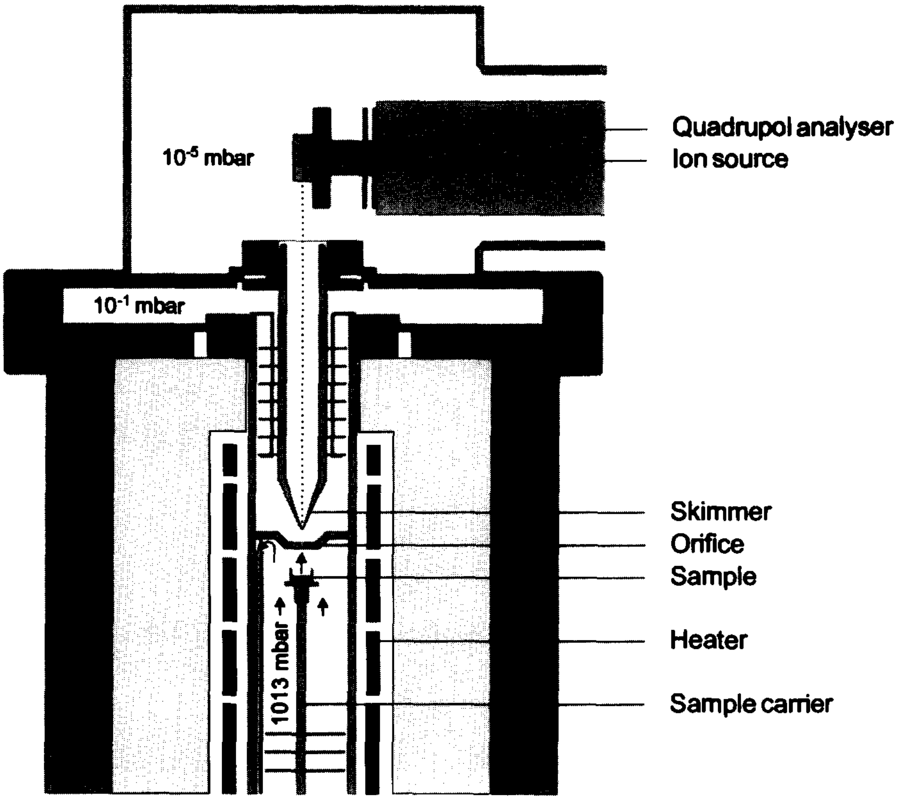
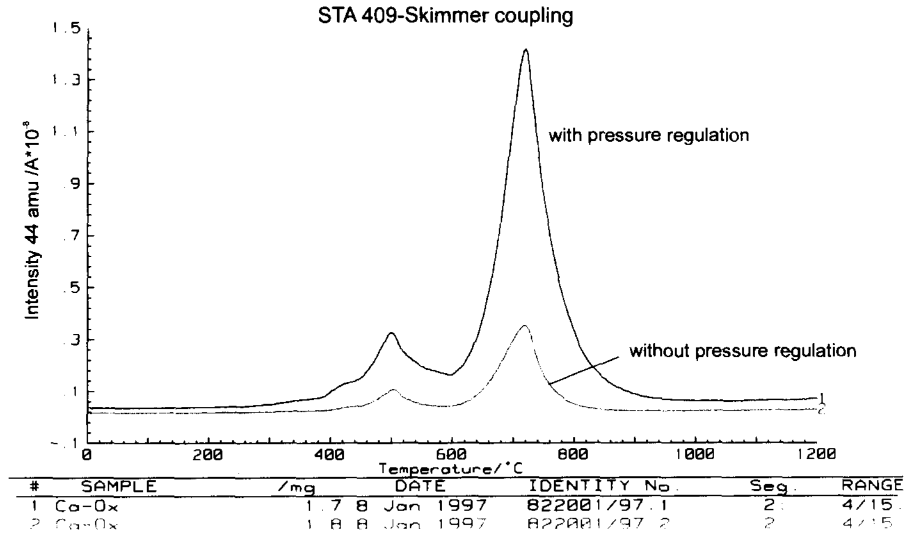


Fig. 16. Skimmer coupling STA 409 (Netzsch) with QMS (QMG 421, Balzers).



#	SAMPLE	/mg	DATE	IDENTITY No.	Seg.	RANGE
1	Ca-Ox	1.7	8 Jan 1997	822001/97.1	2	4/15
2	Ca-Ox	1.8	8 Jan 1997	822001/97.2	2	4/15

Fig. 17. Effect of pressure regulation in a high-temperature QMS coupling system: sample $CaC_2O_4{\cdot}H_2O$ 1.7 and 1.8 mg, argon flow 75 ml/min, and 15 K/min

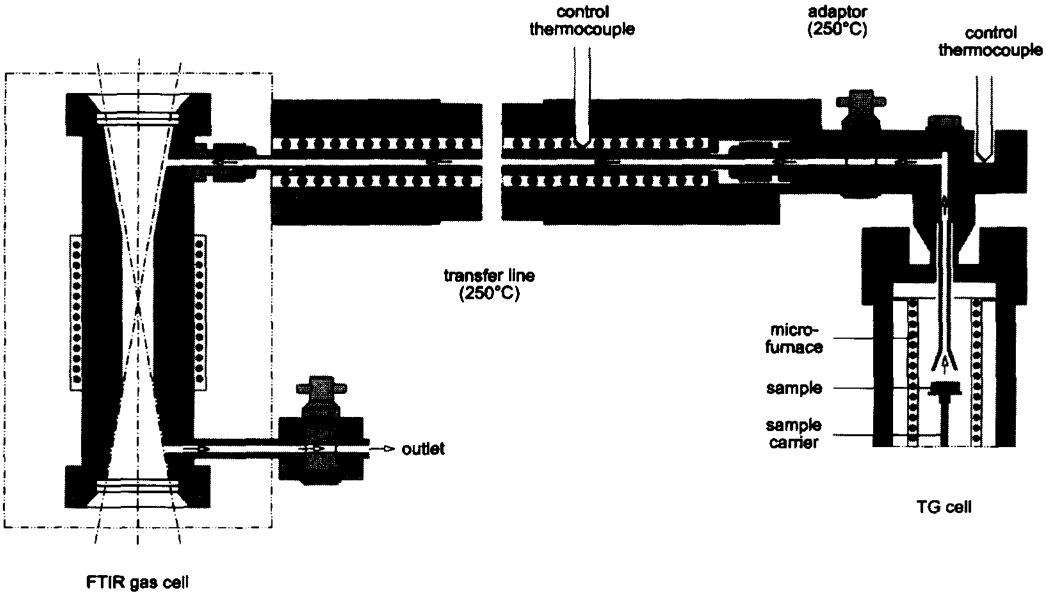


Fig. 18. TG 209 (Netzsch) with transfer line for FTIR (Vector 22, Bruker).

The vacuum-tight connection of thermobalance and gas cell allows an immediate gas change after evacuation of the whole system and, therefore, short equilibration times before start of the combined instruments. The small purge volume of the balance, the transfer line and the gas cell reduce dilution effects as one can work with low gas-flow rates. The special design of the heated gas cell with a long light path ensures high sensitivity and, on the other side, a good light transmission also in case of fumes coming from decomposing samples. The loading of samples into the thermobalance is simple by opening the furnace lid, and there is no need to disconnect the transfer line.

7. Application of coupled instruments

In the discussion on the presentation of results from coupled instruments, there is always one of the main concerns – the integration of the different information from the separate methods in one graphic. Indeed, there is the importance of a precise temperature and time correlation of the results, especially when working independently with different software for measurement and evaluation. Different levels of software integration will be discussed in the following, with the presentation of application results.

7.1. Application of TG–MS

Fully integrated handling of data from a thermal analyser and a quadrupole mass spectrometer, coupled by the Skimmer coupling system, is shown in Fig. 19. For the development of semiconductors, a good knowledge of their thermal behaviour is necessary to optimise the production technology. Zinc-germanium-diphosphide shows a weight loss of 56% in the 660–820°C temperature range, which can be attributed to evaporation of zinc and phosphorus from the compound. With the integrated software, one can display the weight-loss curve together with the position of the repeated scans made in the selected mass range (lower section of Fig. 19), and at the same time, one can display an individual scan with exact time and temperature information and background subtraction (upper section of Fig. 19). In the 50–210 amu mass range, the dominant peaks are 62 (P_2) and 124 (P_4) in scan No. 35 at 776°C.

To analyse the temperature-dependent changes in selected mass numbers, there is one solution to follow

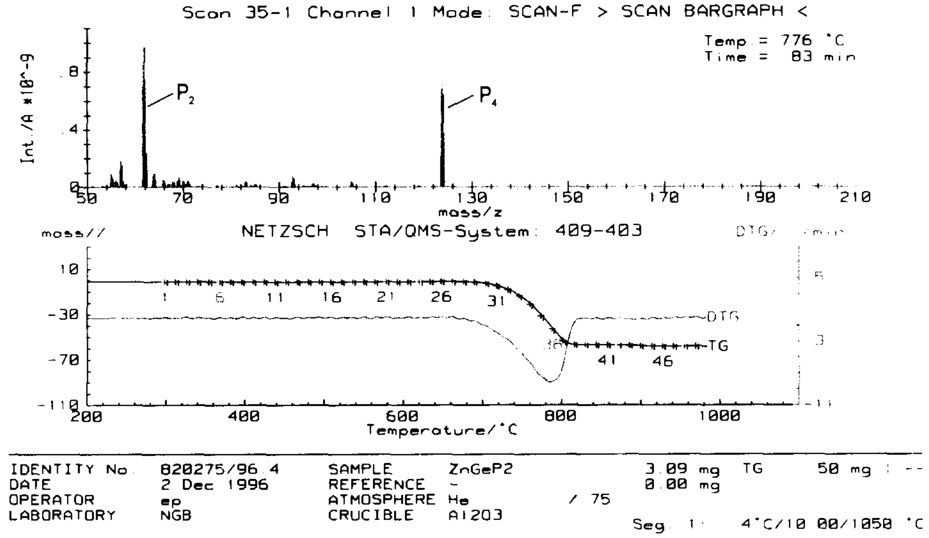


Fig. 19. Simultaneous plot of TG with scan positions, DTG (bottom), and a selected scan (top).

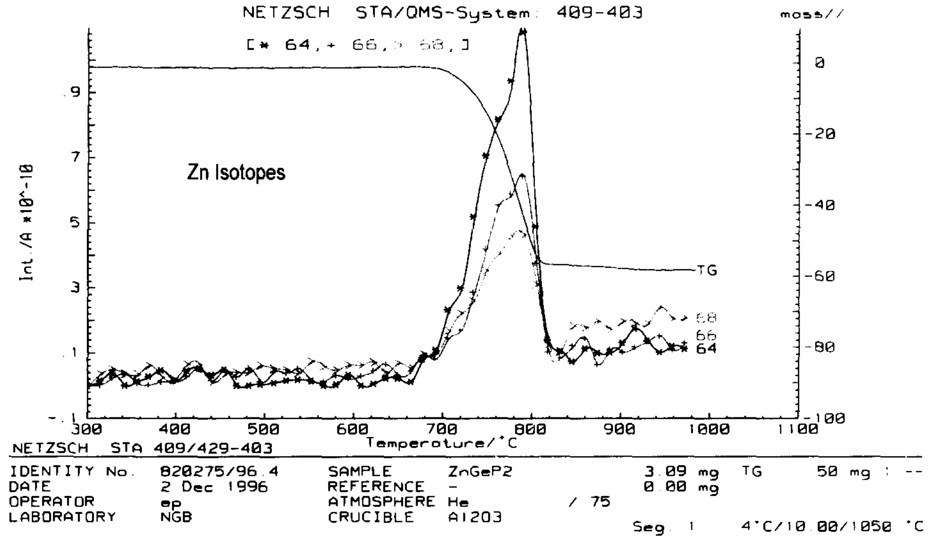


Fig. 20. Quasi-continuous curve for the evaporation of zinc from the $ZnGeP_2$ semiconductor, reconstructed from the repeated scans.

the peaks in the repeated scans and display the changes against the temperature axis as a quasi-continuous curve (Fig. 20). The second common way is to adjust the QMS to several interesting mass numbers and to follow the changes continuously only for these mass numbers (multiple ion-detection mode).

The evaporation of zinc with the natural isotope distribution shows a different peak profile compared to the evaporation of phosphorus in the same temperature range, and the detected intensities are ten times lower.

A very clear picture for all evolved gases were detected and the temperature range of a gas evolution is found by a three dimensional display of the TG and MS curves. The following example for the pyrolysis of poly-methylmethacrylate (PMMA) illustrates this, and one can easily see that, with the start of the

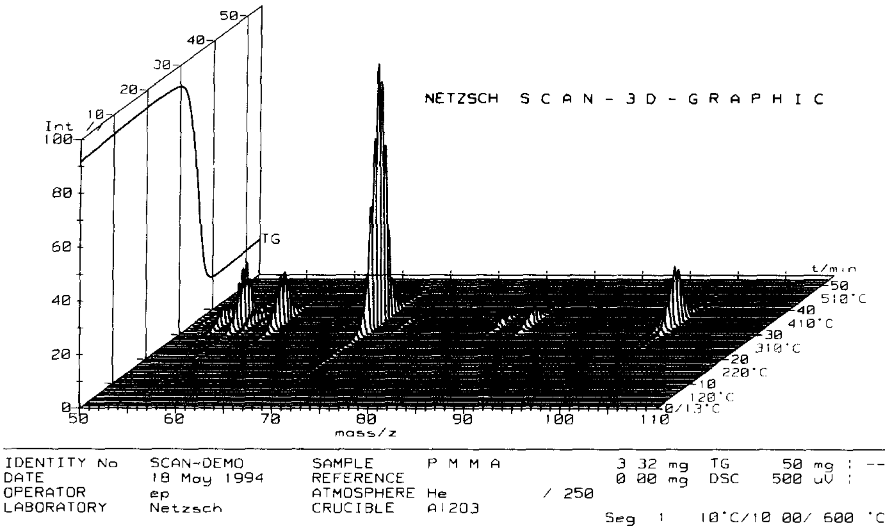


Fig. 21. Pyrolysis of PMMA with detection of the methylmethacrylate monomer (100 amu).

decomposition of this material (30 min, 310°C), the mass number 100 amu for the methylmethacrylate monomer is also detected.(Fig. 21)

The software integration allows further a qualitative comparison of the shape of the DTG curve with the integration over all detected mass numbers (total-ion curve). This comparison can help to estimate that the selected mass range for the measurement was sufficient to describe all weight-loss effects by corresponding MS signals (DTG and total-ion curve show parallel course), and it can be used to see insufficient mass range, retention and condensation effects (non-parallel course of DTG and total-ion curve). (Fig. 22)

This comparison shows that the coupled mass spectrometer (Skimmer coupling) detected all volatiles during the plasticizer and the rubber decomposition of this butyl rubber.

Working with separate software packages for thermal analysis and mass spectrometry, at least a correlation with the time and temperature of the experiment should be achieved. This can be done by displaying the temperature/time curve together with the MS results in the multiple ion-detection mode. (Fig. 23)

7.2. *Application of TG–FTIR*

Infrared spectroscopy is especially well-introduced for the analysis of organic materials. It found therefore broad application in polymers and organic chemistry, but mainly for solids. In the coupling with thermal analysis, it often allows an easy interpretation of the gas spectra and identification of the evolved gases via their functional groups. The normally available library spectra are of great help for the interpretation of overlapping effects, which are usually found in combination with thermal analysis. Also, for inorganic materials, one can profit from the coupling of FTIR. In environmental research, one big concern is the environmental compatibility of production processes, and even very traditional processes like the firing of ceramics and building materials became of actual importance because of possible impact on the environment by evolved gases. Although FTIR, in general, does not have the same sensitivity like MS for the detection of gases in low concentration, it could be applied successfully for the detection of evolved gases during firing of a brick clay (Table 1).

The heating of the brick clay in flowing air shows a complex weight-loss behaviour up to 1000°C with three main DTG peaks.

Discrepancies in the qualitative comparison of the DTG curve with the integration over all absorbance peaks in FTIR, the so-called Gram Schmidt reconstruction, indicate that the FTIR does not detect all changes with gas evolution (nonpolar molecules) and it shows different sensitivities for various gases

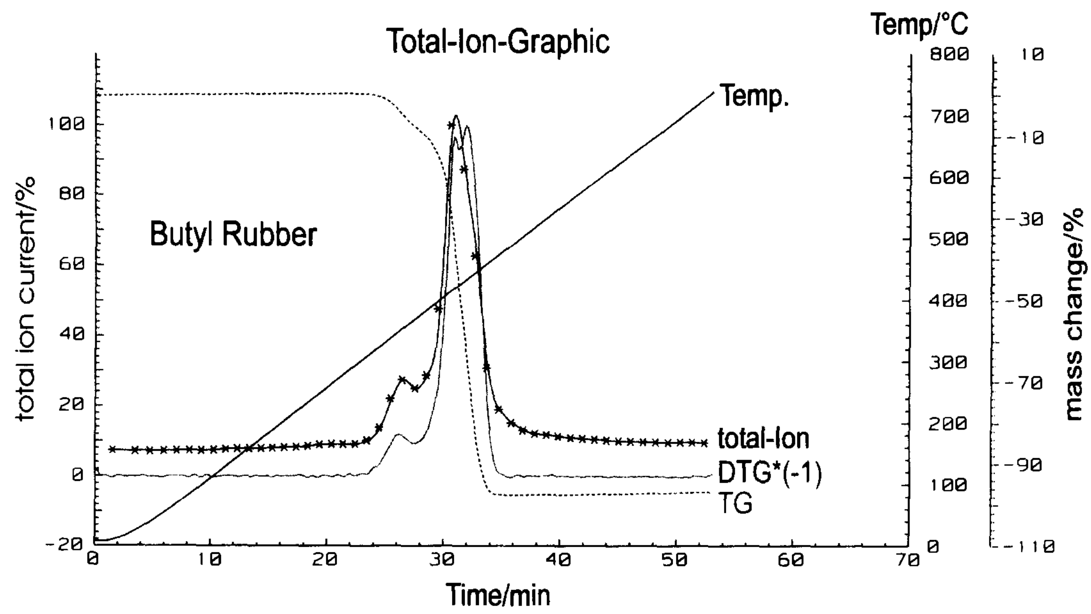


Fig. 22. Comparison of DTG course and integration over all detected mass numbers (total ion curve) for the pyrolysis of a technical butyl rubber mixture.

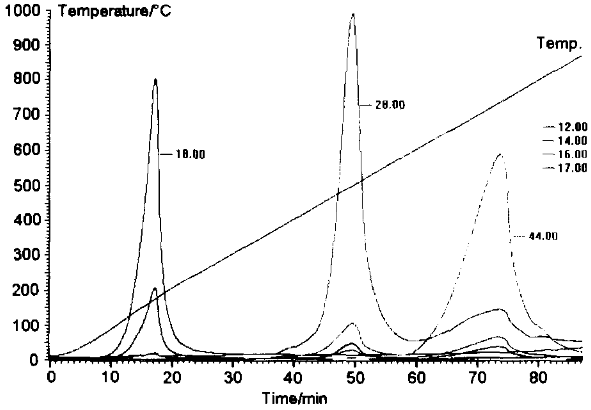


Fig. 23. Embedding of the temperature curve in MS results ($CaC_2O_4{\cdot}H_2O$) when working with separate TA and MS software.

Table 1
Mineral composition of the tested brick clay

Mineral	Mass percentage
Kaolinite	5
Mica	10–15
Illite+montmorillonite	5–10
Chlorite	20–25
Feldspar	5–10
Quartz	32
Dolomite	1
Haematite	5

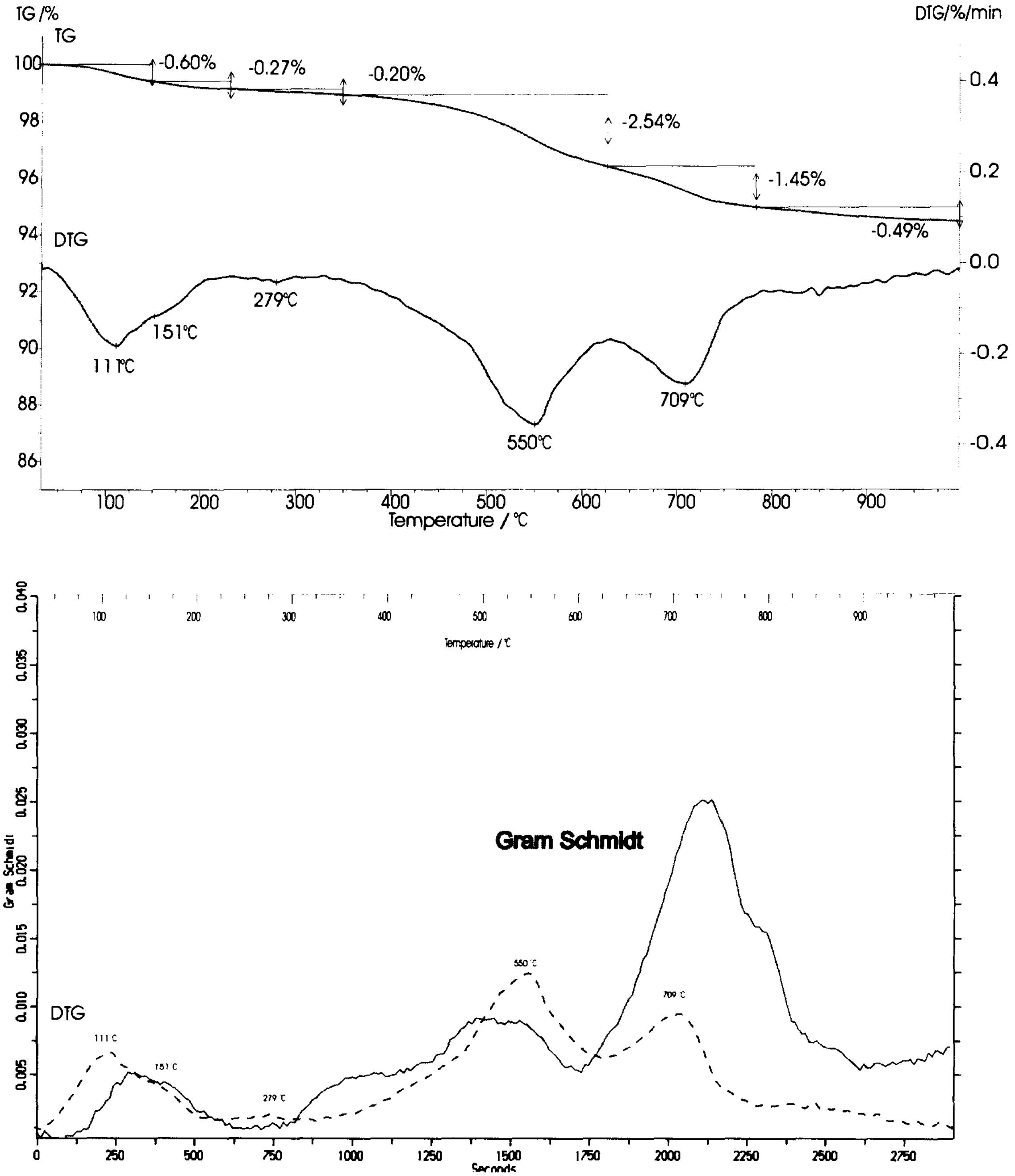


Fig. 24. Firing of a brick clay in combined TG-FTIR, 94.51 mg, air, 20 K min^{-1}, comparison of DTG and Gram Schmidt reconstruction.

(Fig. 24). The agreement in the main DTG peaks is acceptable.

Looking at single scans at the second and the third DTG peaks, the FTIR detects the evolution of HCl, CO_2, SO_2, and HF (Fig. 25). The latter is not easy to detect with mass spectrometry because of the overlapping with isotopes of water and fragments from species with higher mass number.

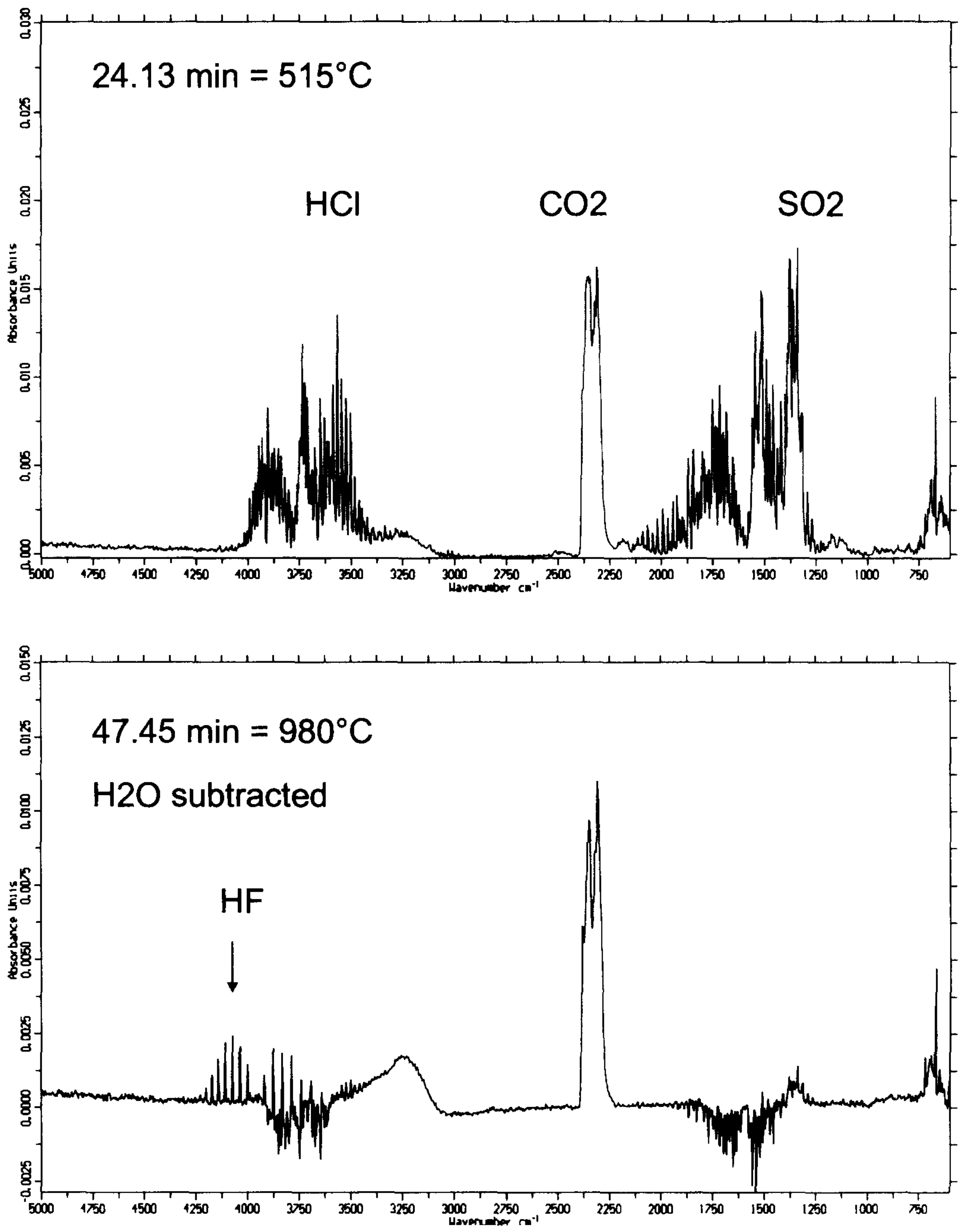


Fig. 25. FTIR absorbance spectra during firing of a brick clay: identification of evolved gases at 515 and 980°C.

The changes in the absorbance peaks for a selected wavenumber range, e.g. for the HF evolution, can be plotted against temperature and then demonstrates clearly the start of the gas evolution and the duration for a certain temperature range (Fig. 25). For HF, significant evolution starts at 800°C and increases up to the end of the temperature program at 1000°C.(Fig. 26)

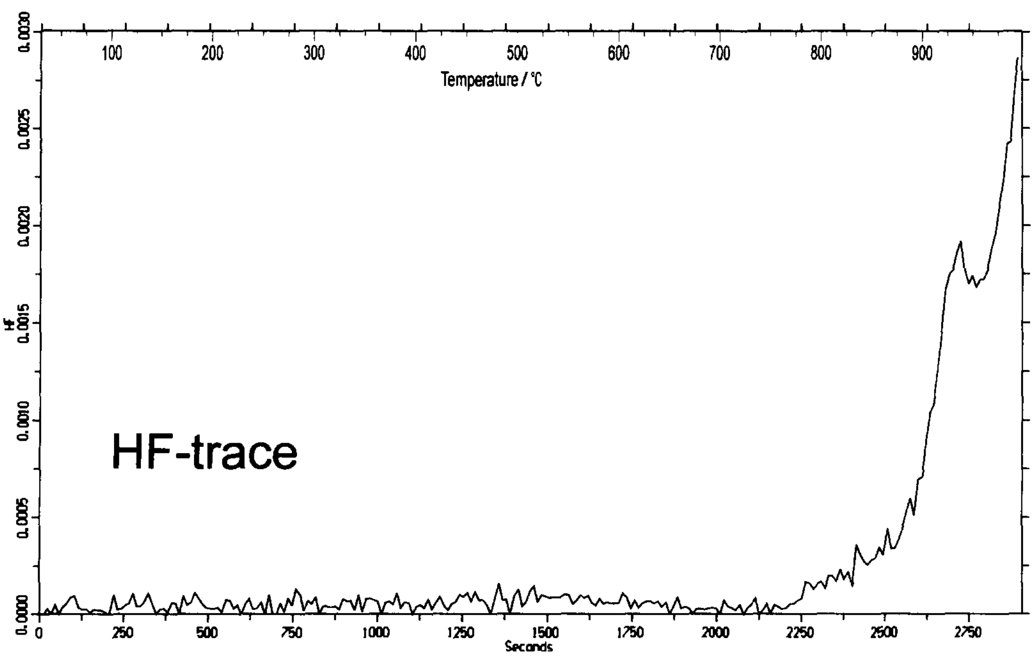


Fig. 26. Evolution of HF during firing of a brick clay in air.

In comparison to a chemical determination of the HF evolution, the FTIR combined with a thermobalance is the much faster method, and it allows a routine analysis of all raw materials to reduce the production of harmful gases and to improve the firing curve to achieve a lower concentration of environmentally problematic residues in the exhaust gases.

7.3. Comparison of QMS and FTIR for evolved gas analysis in combination with thermal analysis

Both mass spectrometry and infrared spectroscopy are very successfully applied, together with thermobalances and simultaneous TG–DTA and TG–DSC instruments. Looking at the capillary coupling for the MS, this is equally simple like the connection of the FTIR by a transfer line. The Skimmer coupling, however, requires higher instrumental efforts with the result of higher sensitivity compared to the capillary coupling by several orders of magnitude.

The effect of electron-impact ionization in a QMS contributes to the fragmentation of molecules much more than the effect of irradiation by the infrared source (see Table 2). The fragmentation into key fragments is, on the other hand, an additional help in the interpretation of mass spectra.

The tools for the interpretation of spectra are relatively useful with FTIR, although the number of gas spectra in libraries is still small compared to the sample spectra for solids and liquids. For QMS, the usefulness of libraries is very limited, as besides the fragmentation during ionization, there is a further contribution to

Table 2
Levels of ionization resp. irradiation energies in QMS and FTIR

Mass spectrometry		Infrared spectroscopy		
Structure/effect	Ionization energy, eV	Wave number, cm^{-1}	Wave length, μm	Energy, eV
Atoms	5–25	500	20	0.062
Molecules	8–15	4000	2.5	0.496
Electron-impact ionization	70–100			

the intensity of mainly lower mass numbers because of thermal dissociation and decomposition in the gas phase. For the detection of trace amounts of volatiles, QMS shows, in general, the higher sensitivity with detection limits in the ppb range.

8. Summary

The coupling of gas analytical methods with thermal analysis is well-introduced for analytical purposes in research, materials development and quality assurance. The basic features of coupling systems were described and a few application results discussed. Mass spectrometry coupling up to 2000°C can be achieved simply not only by connecting a capillary at the end of the gas-flow system of a thermobalance, but also in a much more sensitive way with the Skimmer coupling, integrated into the furnace of the thermal analyser. FTIR coupling is made by the connection of the gas cell with shortest possible heated transfer lines to the gas-flow system of the thermobalance. The precise correlation between the results from different analyser systems with respect to temperature and time is easy in case of full software integration; however, simple means are possible also with separate software packages. The interpretation of results still requires special experience with the gas analytical methods. As the shape of gas evolution curves is strongly dependent on the transfer conditions and diffusion effects, one should be careful with kinetic interpretation of the results from the gas analysers. The coupling of gas chromatography is still not so common because of the intermittent function of the analysis. The pre-separation function by time of a separation system in GC is, to a small and similar extent, also given by thermogravimetry, as the gases are 'temperature separated' before the analysis.

The quantitative work with MS couplings is treated in a very clear way in recent papers of M. Maciejewski [10], also introducing a new experimental technology, the Pulse Thermal Analysis (PTA).

The existence of well-developed commercial-coupling systems will contribute to a broader distribution of hyphenated techniques in the future.

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