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MODERN METHODS FOR COUPLING QUADRUPOLE MASS SPECTROMETERS WITH THERMOANALYZERS FOR TEMPERATURES UP TO 1500°C*

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ABSTRACT

By coupling a quadrupole mass spectrometer (QMS) with a thermoanalyzer (TA), it is possible to obtain information on the gases evolving during the heating process and this combination has proved to be helpful for the interpretation of thermal processes[1–5]. Necessary conditions for getting full and genuine mass spectrometric information are appropriate devices for sampling and sample transfer, matched to the respective temperature program, atmosphere and condensation temperature and kind of evolving gases.

1. GENERAL CONDITIONS FOR COUPLING A QMS TO A TA

The total pressure within the vacuum chamber with the MS analyzer has to be below $1 \cdot 10^{-4}$ mbar, otherwise the relation between partial pressure and signal will not be linear. For the coupling system, suitable materials have to be chosen to avoid chemical reactions with the gas and these parts must be heated to prevent condensation. The sampling and sample transfer system must not change the composition of the sample, unless some components should be enriched to obtain better detection limit or accuracy. The time constant of the coupling system has to be small enough to guarantee simultaneous signals from MS and TA.

2. DESCRIPTION OF SOME TA/QMS-COMBINATIONS

2.1 *TA in vacuum*

For TA in vacuum the coupling to a QMS is comparatively simple. The QMS analyzer will be attached to the TA vacuum system (Fig. 1)[6]. The pumping unit has to be dimensioned so that the pressure within the measuring chamber remains below $1 \cdot 10^{-4}$ mbar. This implies a small heating rate, normally resulting in better

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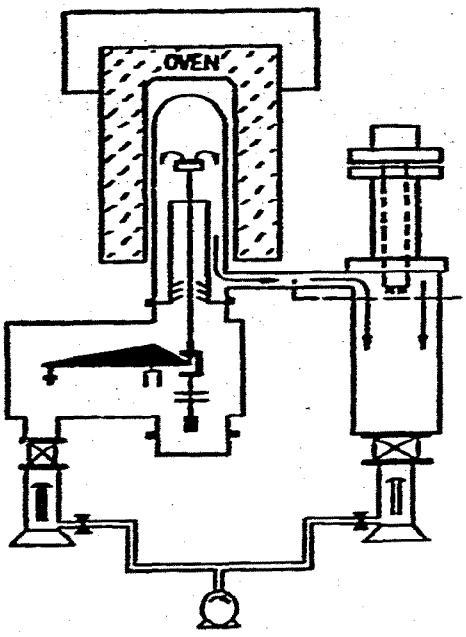

Fig. 1. QMS analyzer attached to TA vacuum system.

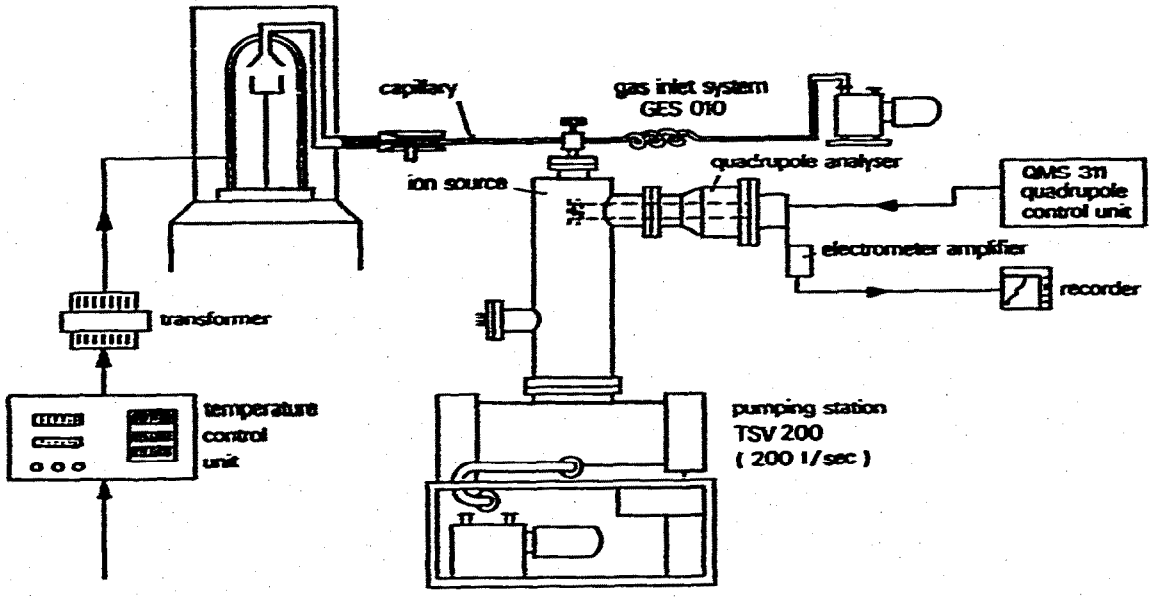

Fig. 2. Principle of TA/MS coupling.

separation of the TA peaks. The connecting tubes between TA and chamber and the chamber itself have to be heated to prevent condensation of vapours of interest as well as to avoid incorrect measurement by re-evaporation of condensated components.

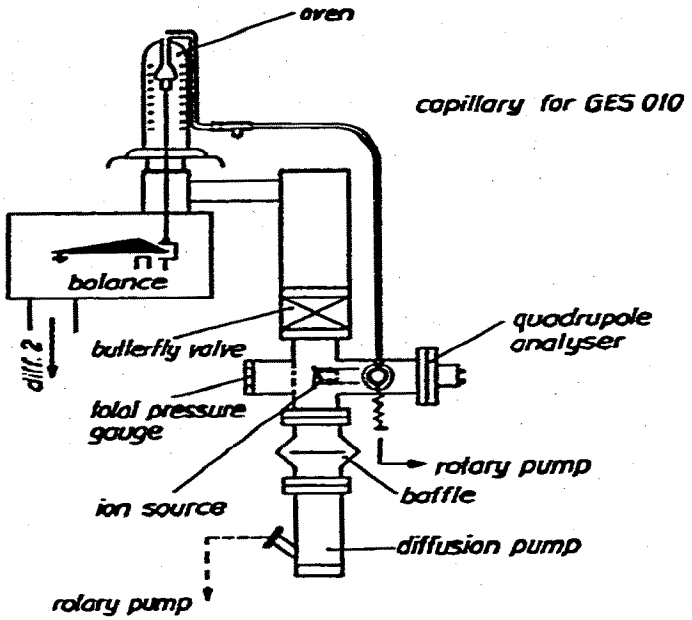

Fig. 3. Experimental set-up of TA/MS coupling.

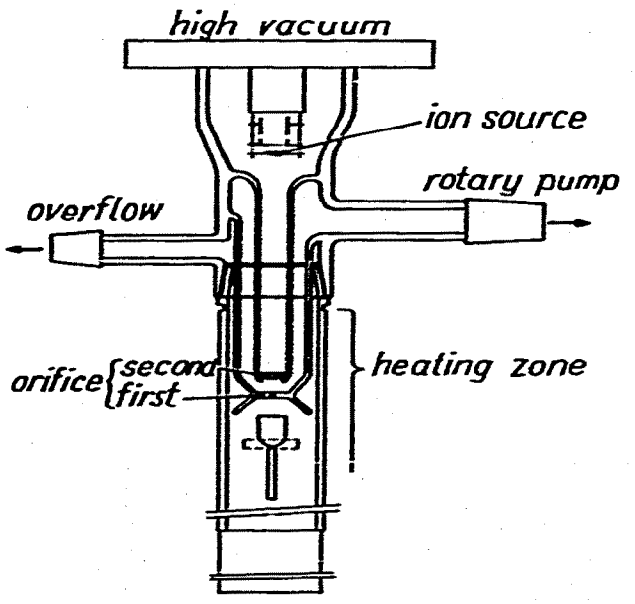

Fig. 4. Quartzglas inlet system.

2.2 *MS-coupling for TA up to 1000°C in gas atmospheres*

Figure 2 shows the principle of such a unit[1]. The gas, in which the sample is thermally treated, flows through the balance into the furnace and leaves it together with evolving gases and vapours through the heated quartz tube at the top. The gas sample for MS analysis is taken within this tube by the capillary of the two-stage dynamic gas inlet system. To prevent condensation of water vapour the capillary,

inlet system and vacuum chamber are heated to about 150°C. The time constant of this system is about 1 sec, which is small compared with signal changing speed normally observed in TA. TA- and MS-signals can be considered to be simultaneous.

By combining the two coupling systems described above, one gets a MS coupling for TA in vacuum and in gas atmosphere, suitable for vapours with not too high condensation temperatures (Fig. 3).

2.3 *Coupling system with condensation temperature considerably higher than 100°C*

For these reactions a two-stage pressure reduction system of quartz has successfully been used[1], consisting of two orifices which are situated within the furnace and near the sample (Fig. 4). The two orifices are at about the same temperature as the sample, which prevents contamination and clogging of the pinholes.

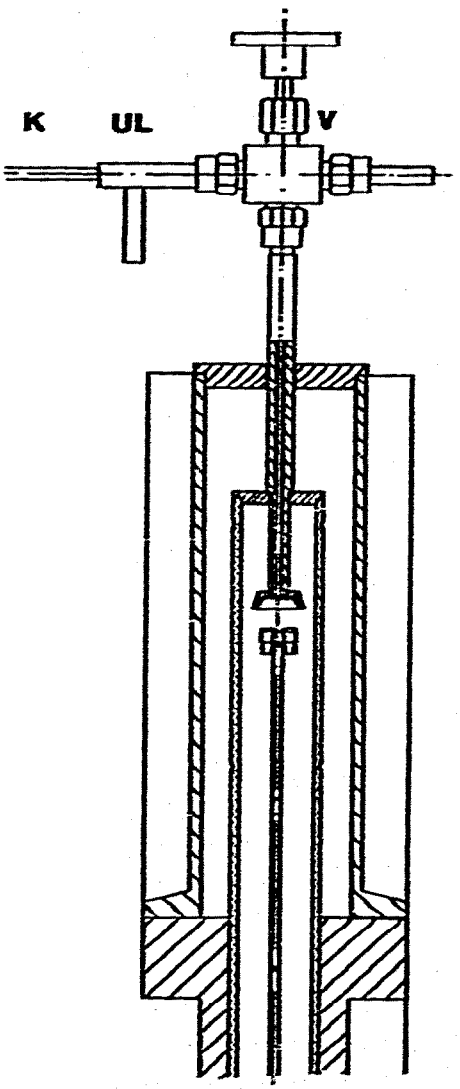

Fig. 5. Alumina furnace for TA at temperatures higher than 1000°C.

The gas flow comes from below, passes the sample holder and most of the gas leaves the furnace through the overflow. Some of the carrier gas with the gases and vapours evolving from the sample reaches the intermediate vacuum through the first orifice and the high vacuum through the second orifice. The intermediate vacuum is kept at about 1 mbar by a rotary pump.

This system allows temperatures up to 800°C. The pressure in the high vacuum chamber will decrease with increasing temperature according to the temperature dependence of gas viscosity. For qualitative measurements the partial pressures have to be related to the total pressure.

2.4 *MS-Coupling to TA for temperatures higher than 1000°C*

For TA at temperatures higher than 1000°C, furnaces of alumina are normally

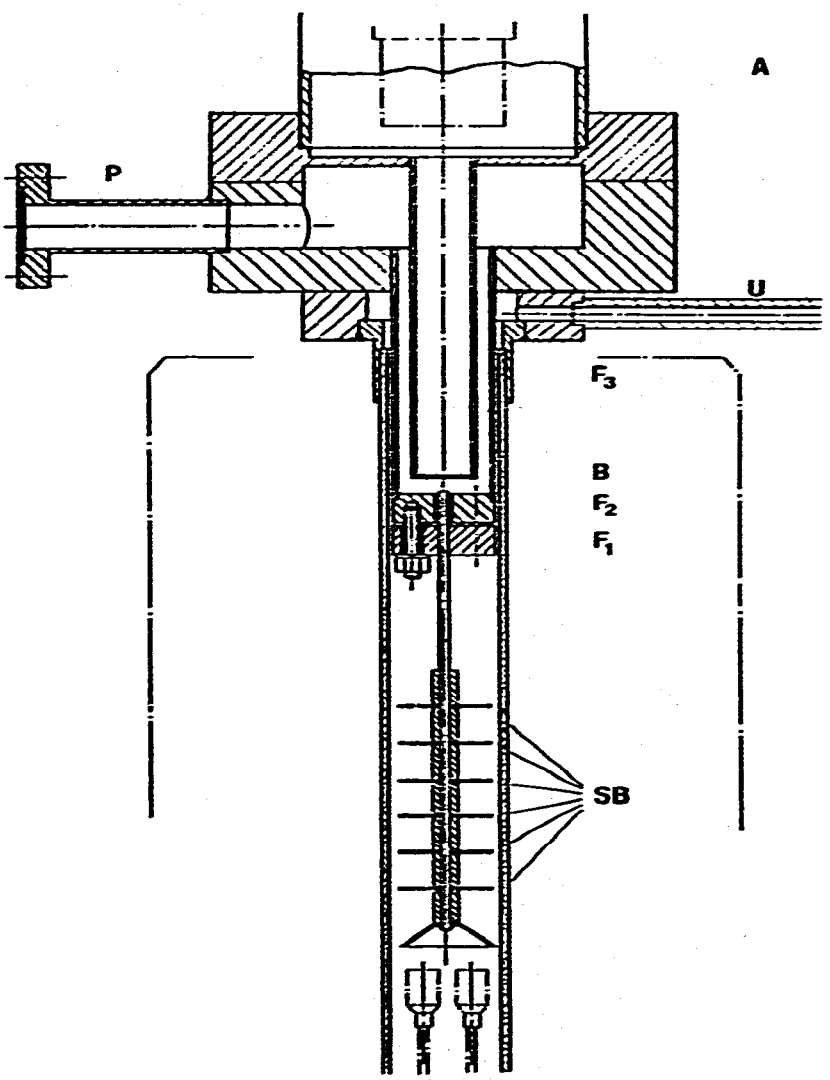

Fig. 6. System for furnace temperatures to 1400°C.

used. If no gases with condensation temperatures considerably higher than 100°C are expected, coupling to the MS can be done by a two-stage inlet system with capillary as in Fig. 2. Such an alumina furnace is shown in Fig. 5. Valve V allows to close the outlet for evacuation prior to changing the gas for Ta. Attached to the valve is the overflow UL, where the gas sample is taken by the capillary K. Outlet of the TA, valve and overflow have to be heated to about 150°C.

If gases evolve with a condensation temperature considerably higher than 100°C, the sample transfer unit has to be kept at an appropriate temperature. The system according to Fig. 6 has been designed for furnace temperatures up to 1400°C. The two-stage pressure reduction consists of a platinum capillary and a pinhole orifice B in a platinum sheet. The platinum capillary is vacuum brazed to flange F 1, has a gas concentrating cone at the lower end and some radiation shields SB to prevent excessive heating of flange F1. To avoid condensation within the capillary near the flange at low furnace temperatures, flange F2 is fitted with an additional heating. The intermediate vacuum between capillary and orifice B is kept at about 1 mbar by a rotary pump. For TA in vacuum, the capillary and orifice can be removed.

The next step in TA/MS-coupling for high temperature furnaces is an entire alumina system, with two orifices B_1 and B_2 for two-stage pressure reduction, as

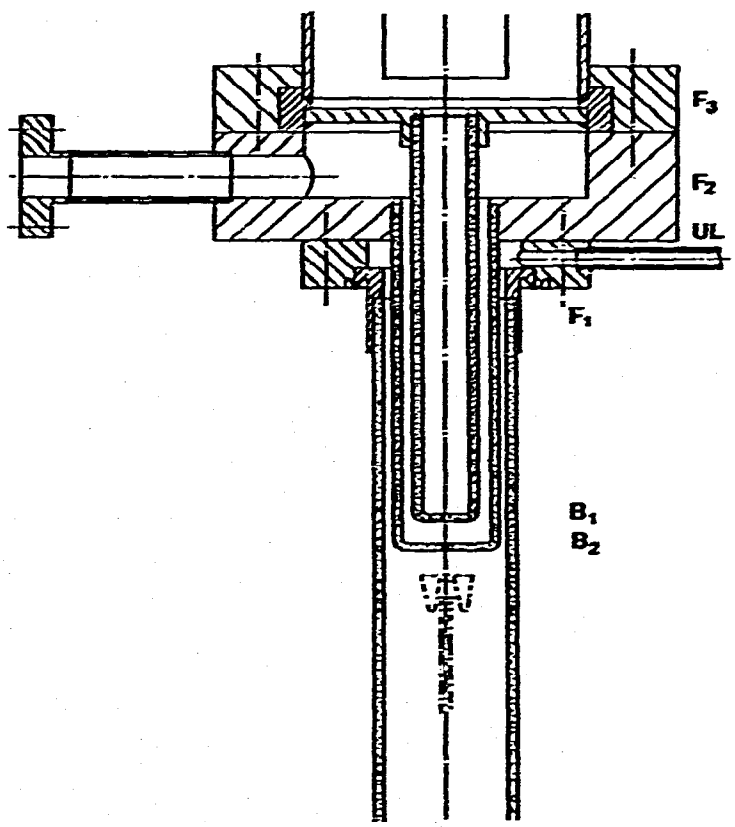

Fig. 7. Alumina system with two orifices B_1 and B_2 for two-stage pressure reduction.

shown in Fig. 7. The orifices are within the hot zone of the furnace and have approximately the same temperature as the sample, avoiding condensation at the orifices and clogging of the pin holes. The two pin holes are drilled into the bottom of the two alumina tubes, which are vacuum-brazed to flanges F2 and F3. The alumina tube of the furnace is sealed to flange F1, which is fitted with the overflow UL. For TA in vacuum the two flanges with the orifices can be removed and substituted by a dummy flange.

The advantage of this system compared with the platinum capillary system is that the gas reaching the mass spectrometer ion source will have undergone less wall collisions and that it is much easier to clean the ceramic tubes than the platinum capillary.

3. REDUCTION OF ION SOURCE CONTAMINATION BY CONDENSATION AT CRYO SURFACES

All systems described above are normally fitted with an axially arranged MS-analyzer opposite the particle beam. If there are substances with a high condensation temperature, this may cause heavy contamination of the MS ion source and analyzer.

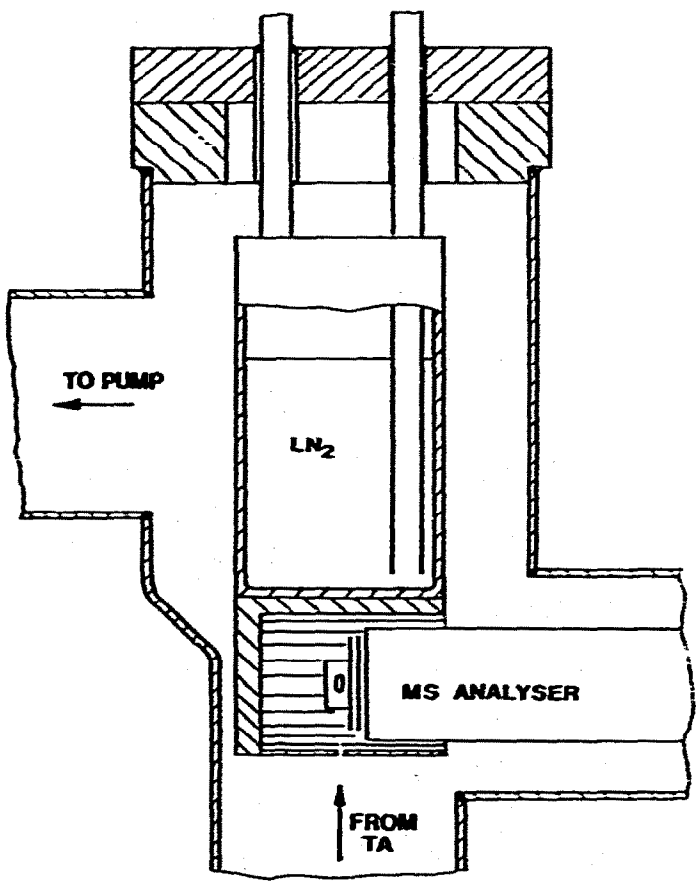

Fig. 8. System to reduce ion source contamination by condensation.

For such applications an arrangement according to Fig. 8 has to be used. The analyzer, fitted with cross beam ion source, is arranged perpendicularly to the TA axis and the ion source is surrounded by cryo surfaces, the temperature of which has to be matched to the process. The vapour stream, coming from the pressure-reducing orifice is adjusted by further cooled orifices so that the beam traverses the sensitive region of the ion source without collision with parts of the ion source or the analyzer. Behind the ion source the particle beam is trapped on cryo surfaces. The contribution of condensable substances outside the collimated beam can be kept so low that contamination of the MS-analyzer can be avoided almost completely.

4. FACILITIES OF MODERN QUADRUPOLE MASS SPECTROMETERS

The mass scan of modern QMS is so fast that it is possible to obtain mass spectra over the entire mass range at any point of the temperature scale compared with the heating rate of some degrees per minute normally used in TA and the comparatively slow change in TA signals. When using a programming and demultiplexing unit and a multi-channel recorder, multiple ion monitoring is possible, i.e., the intensity of different gases as a function of time can be recorded. The latest generation of QMS with a digitized control unit is extremely versatile. It allows very flexible programming and coupling to a computer by relatively simple interfaces and the mass spectrometer can completely be controlled by the computer. Acquisition and processing of data by a computer allows handling of much more data, saves times and results in higher accuracy.

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