Thermochimica Acta, 85 (1985) 275—278
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

NEW TA-MS COUPLING SYSTEM WITH INCREASED SENSITIVITY FOR LOW VOLATILE MATERIALS

E. Kaisersberger and W.D. Emmerich
Netzsch-Gerätebau GmbH, P.O.Box 1460, D-8672 Selb (F.R.Germany)

ABSTRACT

The quantitative transfer of condensable gases and vapours from a thermal analysis instrument to a quadrupole mass spectrometer presents technical and physical problems, particularly at high temperatures. This paper describes a new orifice system for coupling a simultaneous TG-DTA unit with a quadrupole mass spectrometer, able to measure quantitatively the vapour pressures of iodine, selenium, tellurium, lead, silver, etc. up to 1200°C. In designing the new two-stage orifice system the laws for gas flow dynamics were considered. A new high temperature furnace guarantees both small temperature gradients within the system and optimal flow conditions.

INTRODUCTION

Using commercially available units TG-DTA-MS, gases and vapours can be transferred to a coupled mass spectrometer via sophisticated ceramic, metallic or vitreous orifice systems at sample temperatures of up to 1500°C (ref.1). When applying such equipment to the problematic field of longterm storage of radioactive waste restrictions in detecting condensable materials became apparent. Therefore, considering the laws of gas dynamics, and the possibilities of molecular beam generation a new gas inlet system consisting of a divergent nozzle and a skimmer has been constructed and tested up to 1200°C.

EXPERIMENTAL

A gas inlet system from atmospheric pressure in the sample space of a thermal analyser into the high vacuum of a mass spectrometer without change in the composition of the gas mixture is only possible with an (at least) two-stage pressure reducing system (ref.2). With the coupling system described in (ref.1) good results have been achieved for chemistry of complexes (ref.3) and coal analysis (ref.4). However, a clear detection of silver vapour to 1200°C (saturation vapour pressure 0,24 mbar) was not obtainable with the ceramic orifice system in the available design.

Following points were considered for the development of an orifice system which is suitable for the detection of condensable materials:

0040-6031/85/$03.30

1) Molecular flow into high vacuum
2) Heating of the orifices to prevent condensation
3) Variable orifice geometry to optimise gas dynamics of the orifice system.

To 1) An enlargement of the suction cross sections gave an interim pressure of 0,2 mbar before the 2nd orifice, which is for the given orifice diameter of 0,1 mm sufficient for molecular flow through the 2nd orifice (mean free path > diameter of orifice).

To 2) It was possible to construct a furnace which almost fulfilled all requirements, considering orifice dimensions and the needs of thermal analysis. Due to the metal components and the large volume of the vacuum flange connections temperature gradients cannot be totally avoided, particularly in the high temperature range to 1200°C.

To 3) Orifice arrangement and orifice geometry influence greatly the formation and the intensity of a molecular beam. In developing the shapes of the orifices, and optimizing their arrangement the laws of gas dynamics were applied to the flow conditions at the two-stage orifice system.

Criterium for choosing the material were the desired working temperature 1200°C, the oxygen resistance, chemical resistance and small tendency to embrittle. Austenitic steel 1.4841 (25,20 CrNi) was chosen as, in addition, it has good workability.

When theoretically considering the flow conditions at a two stage orifice system the following picture results: From the sample chamber the vapour expands from the initial pressure $p_0 \approx 1000$ mbar through the first orifice opening to the pressure in intermediate vacuum p_1 = 0,2 mbar. Up to the smallest flow cross section in the orifice a conversion of potential energy to kinetic energy takes place forming an adiabatic subsonic stream. Then from the narrow pass the speed of sound is reached or passed. During iso-entropic expansion which follows thermal energy is converted to directed kinetic energy of the laminar flow, the gas cools. Behind the orifice a bottle-shaped expansion zone is formed and in this area sample flow characteristics change irregularly. A second orifice should be arranged outside the expansion zone so that the molecular gas flow into the high vacuum shows the same composition as in the sample chamber. The molecular beam after the second orifice normally occurs with a cosine distribution. Beam losses are found at the orifices through adsorption, condensation, reflection at or in the orifices, scattering through residual gas molecules and by distance related losses from orifice to MS. If a beam skimmer is placed in the expansion zone after the first orifice, a highly increased beam intensity can be achieved. The gas stream which is already pre-directed in the expansion zone is transferred into the high vacuum as a well directed molecular beam with low deviation losses when the skimmer shape and size are ideal. Compared to the

influence of the skimmer's scattering effect the beam deviation from the residual gas becomes less important with this arrangement.

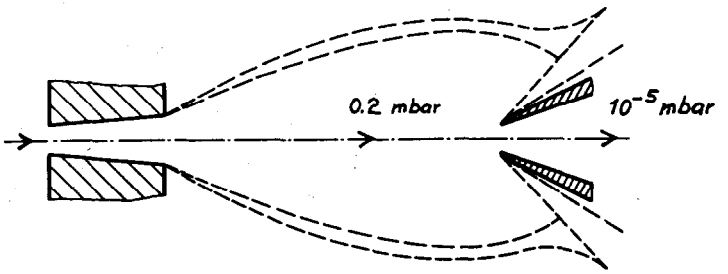

Fig. 1. Gas inlet system for MS consisting of divergent nozzle and skimmer.

To avoid condensation effects in the first orifice where the pressure and therefore the temperature of gas gradually reduce, a divergent nozzle was used. This combination of divergent nozzle and skimmer resulted in the highest beam intensity after both theoretical considerations and experiments.

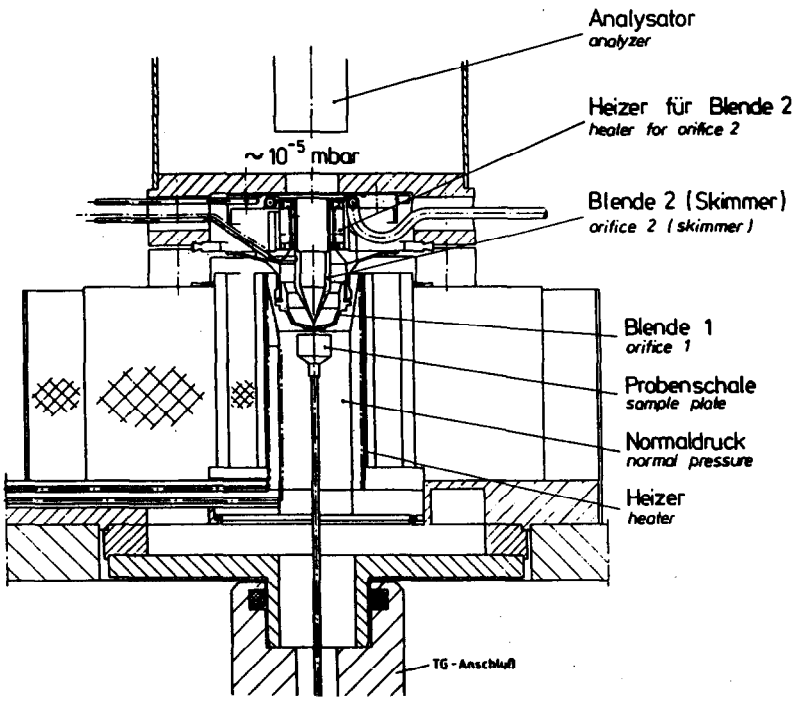

Fig. 2. General viev of orifice system and heater for TG-MS coupling.

RESULTS

Measurements of vapour pressure were carried out on iodine, selenium, tellurium, lead and silver between ambient temperature and 1235°C. Problems arose only with lead where the orifice closed with lead oxide (lower vapour pressure); using inert gas atmosphere at the sample this oxidation could be avoided and lead vapour detected to 1200°C.

Among the radioactive fission products ruthenium and caesium seem to be the most volatile materials. With the above arrangement the evaporation of RuO_4 from a rutheniumnitrosylnitrato-complex as well as Caesium from $CsNO_3$ + glass was measured (ref.5).

CONCLUSION

With this new development of an optimized metal orifice system with divergent nozzle and subsequent skimmer it is now possible to achieve molecular beams of sufficient intensity to be detected in a mass spectrometer. Condensable vapours with saturation pressure $p > 0{,}1$ mbar can be successfully seen. The orifice system can be used as an alternative to existing orifices of Al_2O_3 as in commercially available high-temperature coupling systems between simultaneous TG-DTA -DTG instruments and quadrupole mass spectrometers.

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ACKNOWLEDGEMENT

We gratefully acknowledge the experimental work of Dr. H.J. Jagdfeld, Jülich which is described in detail in his doctoral thesis.