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

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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 (1). The paths for released vapours, i.e. distances between sample, orifices and MS analyser, have been kept as short as possible. The measurements reported demonstrate the greatly increased sensitivity of the new system, particularly necessary when analysing metal vapours.

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 (1). When applying such equipment to the problematic field of longterm storage of radioactive waste, resitrictions in detecting condensable materials became apparent. Therefore, considering the laws of gas dynamics, and the possibilities of molecular beam generation of high-temperature resistant metal, a new gas inlet system consisting of a divergent nozzle and then a skimmer has been constructed and tested 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 a (at least) two-stage pressure reducing system (2). With the coupling system described in (1) a clear increase of the detection sensitivity could be achieved by introduction of a vacuum control of the first suction point, responsible for the viscous flow in. Good results have been achieved for chemistry of complexes (3) and coal analysis (4). However, a clear detection of silver vapour to 1200°C (saturation vapour pressure 0,24 mbar) was not obtainable

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with the ceramic orifice system in the available design, i.e. the beam losses in the orifice system reduced the ion intensity below the detection limit of the mass spectrometer.

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

1) Molecular stream 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 (intermediate free path $>$ diameter of orifice).

To 2) It was possible to construct a furnace which almost fulfilled all the 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.

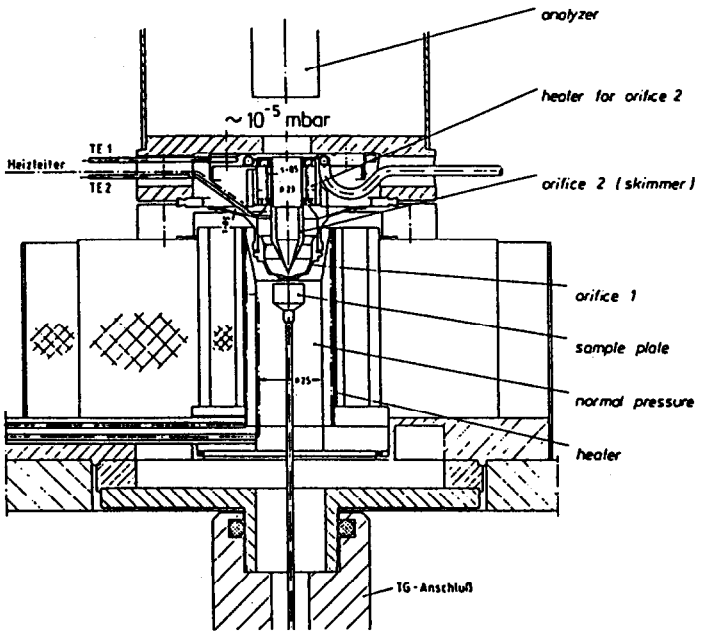
To 3) Orifice arrangement and orifice geometry influence greatly the formation and the intensity of a molecular beam. Therefore, the knowledge of gas dynamics was more considered for the flow conditions at a two-stage orifice system and the shapes of the orifices and their arrangement optimised accordingly.

Criterion for choosing the material were the desired working temperature of 1200°C, the oxygen resistance, chemical resistance and small tendency to enbrittle. 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 space 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 pressure energy to speed energy takes place with adiabatic subsonic stream. Then from the narrow pass the velocity of sound is reached or surpassed. During the following iso-entropic expansion thermal energy is converted to direct kinetic

energy of a laminar stream, the gas cools down. Behind the orifice a bottle-shaped expansion zone is formed and in its field stream 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 (regarding speed). Beam losses are found at the orifices through adsorption, condensation, reflection at/or in the orifices, scattering through residue gas molecules and by distance losses orifice - MS in the molecular field (wall reflections). 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 directly as a well directed molecular beam without high deviation losses with the corresponding skimmer shape and size. Compared to the influence of the skimmer counter effect the beam deviation from the residue gas becomes less important with this arrangement.

To avoid condensation effects in the first orifice by gradual pressure reduction (and with it gas cooling), a divergent nozzle was used. This combination (divergent nozzle + skimmer) resulted in the highest beam intensity after theoretical considerations and practical measurements.



gas sampling system, two stage with orifice and skimmer-nozzle
$T_{max.}$ =1200°C

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 when the orifice closed with lead oxide (lower vapour pressure); using inert gas atmospheres at the sample this oxidation could be avoided and lead vapour be 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 rutheniumnitrosylnitrato-complex as well as of Cs from $CsNO_3$ + glass was measured (5).

CONCLUSION

With the development of an optimised metal orifice system with divergent nozzle and subsequent skimmer it became possible to achieve molecular beams of sufficient intensity for the detection in the mass spectrometer. Condensable vapours with saturation pressure $p > 0{,}1$ mbar could be successfully seen. The orifice system can be used as an alternative to existing orifices of Al_2O_3 in a commercially available high-temperature coupling system between a simultaneous TG-DTA-DTG instrument and a quadrupole mass spectrometer

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