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# GAS ANALYTICAL METHODS OF THERMAL ANALYSIS IN COMPARISON

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## ABSTRACT

The undisputed advantages of simultaneous detection and analysis of released gases are today frequently utilized in thermoanalytical experiments. Some aspects of the function principles, the coupling systems and the applicability of different gas detectors are discussed. Both, sufficient qualitative and quantitative informations can be expected from the use of mass spectrometry. The coupling techniques between a quadrupole mass filter and a simultaneous high temperature TG-DTA equipment is described as to some theoretical points of view and verified by test results on complex compounds. It has shown, that for universally usable apparatus gas inlet systems with pressure reducing two-stage orifice arrangements as well as direct sample evaporation in high vacuum should be mutually realized.

## INTRODUCTION

Continuously working gas detectors are best adapted to the thermal analysis technique, because thereby a direct correlation of the result of the gas analysis to every reaction temperature is achieved. In commercial EGD or EGA instruments very different properties of the evolved gases are studied to gain characteristic measuring values: thermal conductivity, gas density or molecular weight, reaction in solution, radioactivity, mass and electric charge (table 1).

## METHODS

Thermal conductivity and gas density detectors are marked out by simple construction and can easily be coupled to different thermoanalytical apparatuses. In the thermal conductivity detector the changing resistance of two hot wires is measured whereat gas flow is established over these sensing elements. The evolved gas, taken away by a carrier gas stream, gets direct contact with one hot wire. The sensitivity of the detector depends on the difference in thermal conductivity between carrier gas and evolved gas, further on some adjusting parameters like carrier gas flow rate, heating current, detector temperature, sample weight and heating rate. The peak area is linear correlated with the sample weight and shows the quantitative operation method of the detector.

TABLE 1

Characterization of EGA Methods

| Parameter | Method | | | |
|---|---|---|---|---|
| | thermal conductivity | gas density | emanation (ETA) | Quadrupole mass spectrometry |
| measured value | thermal conductivity | density | $\alpha$-radiation | mass/charge |
| sensing element | hot wire | hot wire | semi-conductor | mass filter |
| coupling interface | simple | simple | simple | simple (high-vacuum) sophisticated (atmos. pressure) |
| carrier gas (non-aggressive) | necessary | necessary | necessary | no (high vac.) necessary (normal pressure) |
| detectable gas | non-corrosive | all | radioactive | all (non-corrosive) |
| gas pressure (at the sample) | atmospheric | atmospheric | atmospheric | high vacuum/ atmospheric |
| sample preparation | no | no | doting or activation | no |
| quantitative operation | yes | yes | yes | yes |
| qualitative operation | restricted | restricted | no | yes |

Based on the very high sensitivity of the thermal conductivity detector and the usability of all non-aggressive gases, many applications, especially in technical routine tests, are possible, e.g. glass formation /1/, degassing of alloyed steels /2/.

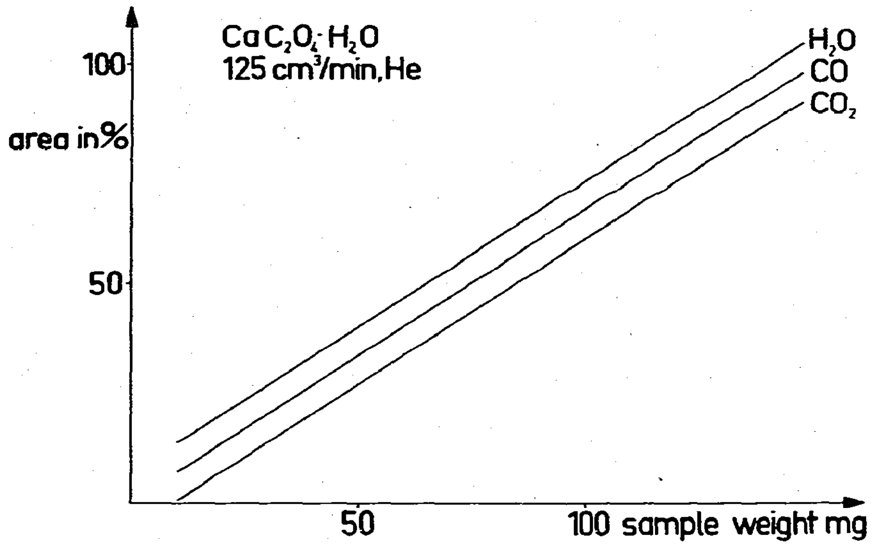

Fig. 1 Thermal conductivity detector quantitative evaluation: linear response for the gases $H_2O$, CO, $CO_2$, for different sample weight of $CaC_2O_4.H_2O$

The advantage of gas density detectors is the resistance against corrosion by aggressive reaction products. The evolved gas gets no contact with the sensing elements, which are only in contact with the carrier gas. Guillemin and others /3/ found out, that the sensitivity of a gas density detector can be optimalized at a large ratio between reference gas and measuring gas flow and by using a carrier gas with high density, but low viscosity.

In the linear range of the detector, the quantity of an evolved gas is proportional to the peak area corrected by a factor that depends primarily on the molecular weights of the evolved gas and the carrier gas. The gas density detector is like the thermal conductivity detector sensitive against overcharging of the carrier gas with condensable gases (e.g. $H_2O$), because thereby the correlation with the real reaction temperatures is lost during the continuous temperature increase.

Emanation thermal analysis (ETA) allows the detection of radioactive gases which are released from a natural radioactive or correspondingly activated sample. A detailed description of ETA is given by Balek /4/ in a recently published review, which deals with all aspects of this interesting method.

In a former publication /5/ a high temperature coupling system between a simultaneous TG-DTA apparatus and a quadrupole mass spectrometer with a special gas inlet system was introduced. By means of a two-stage inlet system, the gas released from the sample is led continuously in a short way to the mass spectrometer. The system (fig. 2) works up to a sample temperature of 1500°C.

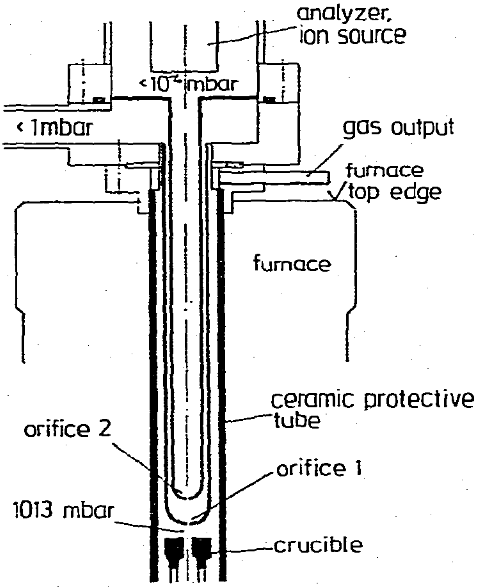

Fig. 2 Gas inlet system with two orifices in $Al_2O_3$

The pressure after the first orifice depends on the viscosity and molecular weight of the flowing gas, the flow through this orifice to the interposed vacuum of about 1 mbar is viscous because of the very small free path length. The flow is therefore pipe flow according to the Hagen-Poiseuille law and independent from the molecular weight of the gas. Because of the pressure conditions on the second orifice molecular streaming with a temporary demixturing of a gas composition depending on the molecular weights is the result. The pressure behind this orifice, i.e. the pressure on the ion source, is directly proportional to the gas pressure in the interposed vacuum. Inspite of the temporary demixturing of a gas composition which is to be expected theoretically by the orifice with molecular streaming, this may remain without effect, because the gas store in front of the orifice is always renewed by means of the viscous flow through the first orifice. So this two-stage gas inlet system fulfills the conditions for quantitative gas analysis.

The decomposition of zinc and nickel-amin-complexes in stationary air atmosphere shows the function of this simultaneous TG-DTA mass spectrometric apparatus.

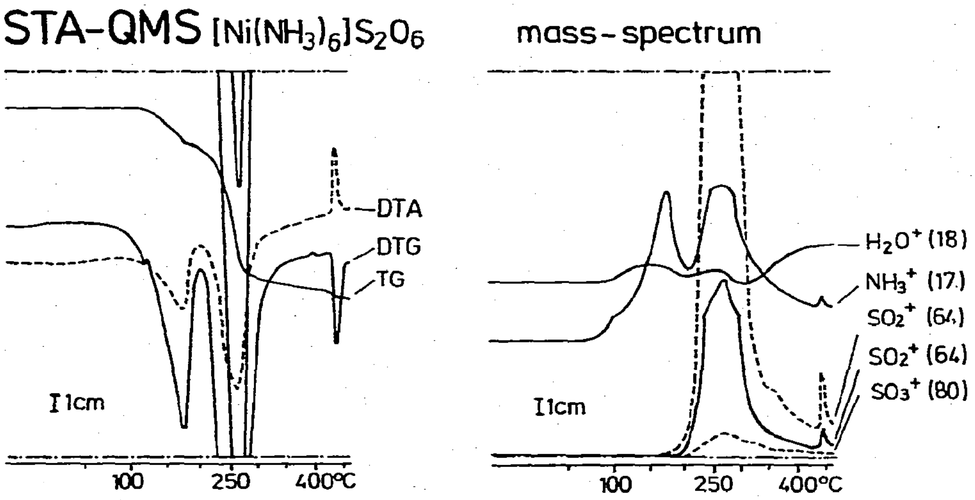
STA-QMS $[Ni(NH_3)_6]S_2O_6$ mass-spectrum

Fig. 3 Nickel-hexamin-dithionate

The decomposition of the Ni complex is according to the reaction scheme

| | | | |
|---|---|---|---|
| 1st step | up to 205°C | 2 mol $NH_3$ | weight loss 10,6 % |
| 2nd step | 205 ... 355°C | 3 mol $NH_3$,<br>1 mol $SO_2$ | weight loss 25,9 % |
| 3rd step | starting at 355°C | release of $NH_3$ | not complete |

Exothermal reaction at 435°C is supposed to be oxidation of $NH_3$ catalysed by the platinum thermocouple wires.

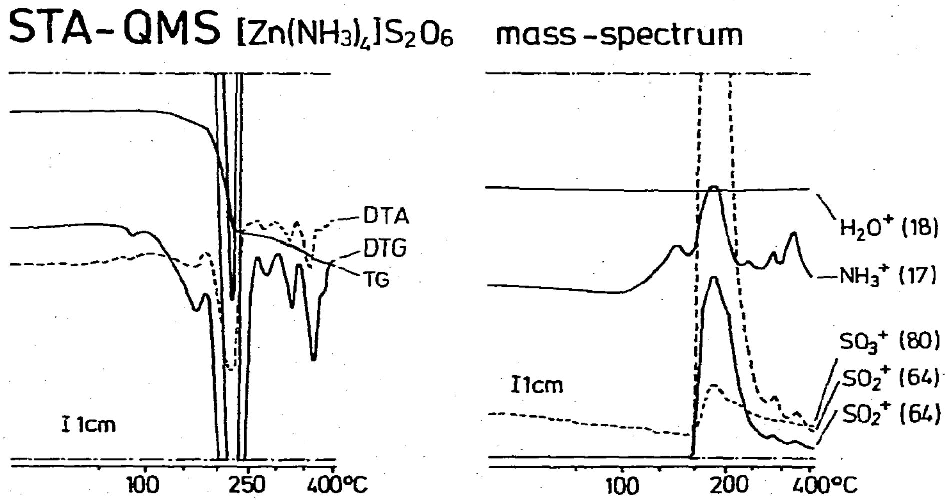
STA-QMS $[Zn(NH_3)_4]S_2O_6$ mass-spectrum

Fig. 4 zinc-tetramin-dithionate

reaction scheme

| | | | |
|---|---|---|---|
| 1st step | to 190°C | 1 mol $NH_3$ | weight loss 5,6 % |
| 2nd step | 190°C ... 245°C | 1 mol $NH_3$<br>1 mol $SO_2$ | weight loss 27,6 % |
| 3rd step | up to 370°C | 1 mol $NH_3$<br>rest not yet identified | 7,6 % |

Further tests to higher temperatures will clear up all decomposition stages of these amin-complexes.

The ionization energy for these experiments was 70 eV in an axial-beam electron impact ion source.

Besides the operation of the instrument with this high-temperature gas inlet system also the possible direct sample introduction in high vacuum has proved in this apparatus. The ion source is in short distance above the vaporizing sample, both open sample crucibles and Knudsen cell arrangements may be used. Results of high vacuum experiments will be published later.

## CONCLUSION

Informations and possible interpretations of thermoanalytical results can be still essentially enlarged by the simultaneous gas detection and analysis methods. Surely, the applications for the different systems are not yet completely exploited, the decision on the detector to be selected depends on the points of view of either more quantitative or more qualitative operation.

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