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Quantitative calibration of mass spectrometric signals measured in coupled TA–MS system

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Abstract

The influence of several experimental parameters such as concentration of the analyzed species, temperature, flow rate and properties of the carrier gas, on the sensitivity of the mass spectrometric analysis in a TA–MS system Netzsch STA 409 thermoanalyzer coupled via a heated capillary with a Balzers QMG 420 quadrupole mass spectrometer has been investigated. The determination of the calibration factor, facilitating the quantification of the MS signal, was carried out by means of two methods: decomposition of solids and injection of a known volume of gas into the carrier gas stream. The intensity of the MS signal decreases with increasing carrier gas flow rate, showing a linear dependence, and is not influenced by temperature and amount of analyzed gas. The use of helium as a carrier gas reduces the intensity of the mass spectrometric signal and leads to its broadening. The calibration offers the possibility of quantifying components being present in amounts as small as 0.2–0.5 wt%. © 1997 Elsevier Science B.V.

Keywords: Quantitative calibration of a TA–MS system; Thermal analysis coupled with mass spectrometry

1. Introduction

Generally, the interpretation of thermoanalytical curves does not cause difficulties if the investigated reaction proceeds via one or more well resolved steps and stoichiometry and composition of the reactant, intermediate(s) and product(s) are known. Unfortunately, in practice these requirements are seldom fulfilled. Frequently, the temperature ranges of the various decomposition stages, particularly in multicomponent systems, overlap each other and the exact composition of the evolved gaseous products is unknown. This phenomenon has led to the coupling of thermoanalysis (TA) with other techniques, which allow analysis of the evolved gases, such as gas chromatography (GC), Fourier transformed infra-red spectroscopy (FTIR), and mass spectrometry (MS). Due to the possibility of continuous monitoring of the gas composition, MS is probably the most universal of these techniques for analysing multicomponent systems and reactions with unknown gaseous products. Because of its high potential, the simultaneous TA–MS technique has gained increased application and attention, which is reflected by reviews of several authors: Friedman [1], Dollimore et al. [2], Holdiness [3] and Szekely et al. [4].

The main application of the TA–MS technique is the identification of the gaseous products, which together with the thermal effects (DTA) and mass changes (TG), aids in interpreting the course of the investigated reaction. The qualitative MS analysis is routinely made by comparing the recorded spectrum with references containing key fragments ions and

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their relative intensities for known elements and compounds. A more difficult, but important problem is the quantitative interpretation of mass spectrometric data, which needs the calibration of the system, i.e. the determination of the relationship between the observed intensities of the ion currents and the amount of the analyzed species. Furthermore, for the quantitative interpretation of the kinetic measurements, the relationship between the measured shape of the MS-signal and the experimental conditions, such as kind of carrier gas and its flow rate must be known.

For gases, the common method of calibration of mass spectrometric curves is based on the determination of the relationship between ion current and concentration of the calibrated gas. However, this method is time consuming and requires the application of gaseous mixtures with well-defined composition. An additional difficulty is such that the calibration is usually performed at room temperature, while during thermal decomposition the temperature of the gas phase often changes considerably what can render the results obtained by calibration at low temperature doubtful.

The calibration can be performed by introducing into the TA–MS system a known amount of the calibration gas and determining the relationship between the amount of the gas and the observed integral signal of the MS curve. Specified amounts of the species to be calibrated can be introduced into the mass spectrometer by two principal methods:

1. **by decomposing solids via a well known, stoichiometric reaction**, and
2. **by injection of known amounts of calibration gas into the carrier gas stream flowing with constant rate through the system**.

Method (1) has been used by Wang et al. [5] and Price et al. [6] during decomposition in high vacuum and by Yoshimura et al. [7], Muller–Vonmoos et al. [8] and Dünner et al. [9] under atmospheric pressure, whereas method (2) has only been applied by Bernal et al. [10]. All the described calibrations have been made under arbitrarily chosen conditions only, and systematic investigations of an important experimental conditions such as temperature, kind and flow rate of the carrier gas, and dependence of the calibration factor on the amount of the analyzed species, have not been performed yet.

Here we report a systematic study of the influence of experimental parameters on the course of MS-curves measured in combined TA–MS system. The aim was to improve the opportunities for quantitative interpretation of mass spectrometric data gained by this technique.

2. Experimental

The TA–MS system used consisted of a Netzsch STA 409 thermoanalyzer coupled with a quadrupole mass spectrometer QMG 420 (Balzers). The ionization of the analyzed gas was performed by axial beam ion source (100 eV). The ions separated according to their mass to charge ratio were detected by a Secondary Electron Multiplier (SEM). Thermal analysis was performed under atmospheric pressure, consequently the thermoanalyzer was linked to the mass spectrometer by a two-stage pressure reducing system GES 010 (Balzers). Due to the specific valve design, this system largely eliminates mass dependent separation processes (mass discrimination). Analyzed gases are pumped from the high-pressure side into the valve body through a heated (ca. 200°C) steel capillary with i.d. 0.15 mm. A small amount of the gases in the valve body is able to flow molecularly through the orifice into the measurement vacuum chamber of the mass spectrometer. The collection of the TA and MS data is performed by the Netzsch Acquisition Software running on 16/32-bit H 9000 computer. Two different acquisition modes were applied: Multiple Ion Detection (MID) or Scanning (SCAN). The MID-mode allows the acquisition of up to 16 single mass numbers with a resolution of ±10 000 digits (14 bits plus sign) and a storage of up to 10 000 points/channel/measurement. In the SCAN-mode it is possible to record up to 100 scans with maximum 4096 measuring points/scan with the same resolution as for MID.

Helium, nitrogen, and argon containing less than 20 ppm impurities were used as carrier gases. The inorganic compounds used for the calibration (method (1)) were of the highest commercially available purity. Calibration experiments according to method (2) were performed by injection of the investigated gas into the carrier gas stream. Injections were made by an eight port external volume sample injector (Valco Instruments) equipped with two loops (possible change of the volume from 2 µl to 10 ml). The applied volume of the injected gas was generally in the range 0.25 to 1.0 ml.

The calibration and quantitative TA–MS measurements were carried out under well-defined flow of the carrier gas. The exact flow was achieved by mass flow controllers (Brooks model 5850 E) based on thermal mass flow sensing technique. Flow controllers were calibrated with argon, for other gases intrinsic sensor conversion factors were applied. Because it is generally accepted that by applying conversion factors the mass flow rate of a new gas can only be controlled within ±5%, the flows of helium and nitrogen were additionally calibrated.

The quantification of the MS-signals was made by integrating the area under the respective ion current peaks.

3. Results

Calcium oxalate monohydrate, copper sulphate heptahydrate (calibration of water), sodium bicarbonate (water and carbon dioxide), silver carbonate (carbon dioxide and oxygen), calcium and barium carbonates (carbon dioxide) and palladium oxide (oxygen) were used as references for calibrations carried out by the decomposition of inorganic compounds. These compounds were chosen because their decomposition stoichiometry is well known, they are not hygroscopic, and decomposition steps are distinct and well resolved. Two stages of the decomposition for $CuSO_4 \cdot 5H_2O$ (in the first stage four-, in the second, one water molecule) and Ag_2CO_3 (first stage - CO_2, second stage O_2) or two gases evolved in one stage (H_2O and CO_2 during decomposition of $NaHCO_3$) enabled performing double calibration in one experiment. In order to relate the measured weight losses to the observed mass spectrometric signals, all compounds used for calibration were analyzed by means of TA prior to calibration. The results of the thermogravimetric measurements are listed in Table 1. The courses of the decompositions (thermoanalytical and mass spectrometric curves) of PdO, Ag_2CO_3, $CuSO_4 \cdot 5H_2O$ and $NaHCO_3$ are depicted in Figs. 1–4.

The influence of the following experimental conditions on the quantitative calibration of the MS signals was investigated: flow rate of the carrier gas, amount of the analyzed component, temperature, and kind of the carrier gas.

3.1. *Influence of carrier gas flow rate*

Because only a small part of the gas evolved during measurements is analyzed by MS, the ratio between analyzed and carrier gas can be influenced by fluctuations of the flow rate, since its perturbation will generate an apparent change of the intensity of the MS signal. The steadiness and stability of the carrier gas flow is therefore an important prerequisite for the quantitative interpretation of the MS-curves. Two contracting factors have to be taken into account when setting the flow rate: on one hand, the dilution of the analyzed gas by the inert gas should be as small as

Table 1
Stoichiometric and measured weight losses during thermal decomposition of inorganic solids used for the quantitative calibration of MS signals

Compound	Supplier	Stoichiometric weight loss (wt%)				Measured weight loss (wt%)
		CO_2	O_2	H_2O	total	
Ag_2CO_3	Fluka	15.96	5.80	–	21.76	21.75
$NaHCO_3$	Fluka	26.19	–	10.71	36.90	36.72
$CuSO_4 \cdot 5H_2O$	Fluka	–	–	28.45[a]		28.58[a]
				36.05[b]	36.05	35.96[b]
$CaC_2O_4 \cdot H_2O$	Fluka			12.31		11.06
PdO	Fluka	–	13.07	–	13.07	13.30
$CaCO_3$	Merck	43.96	–	–	43.96	43.20
$BaCO_3$	Fluka	22.30	–	–	22.30	22.62

[A] Four water molecules.
[b] Five water molecules.

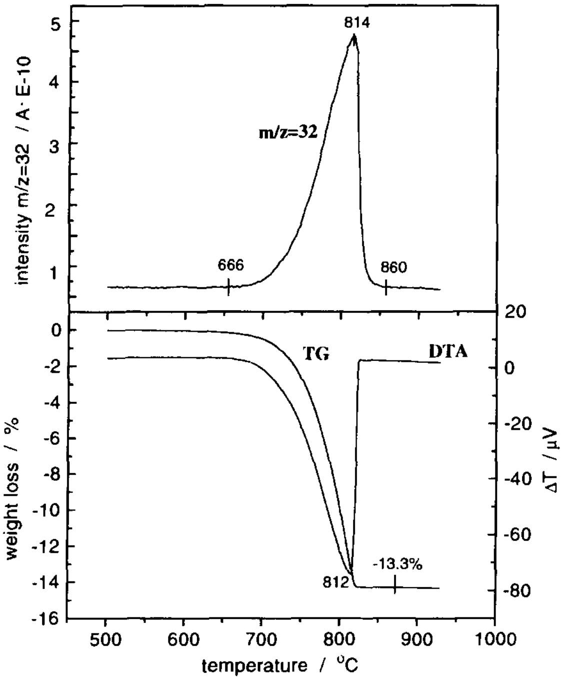

Fig. 1. Decomposition of palladium oxide under argon investigated by TG, DTA and MS (evolution of oxygen monitored by m/z=32).

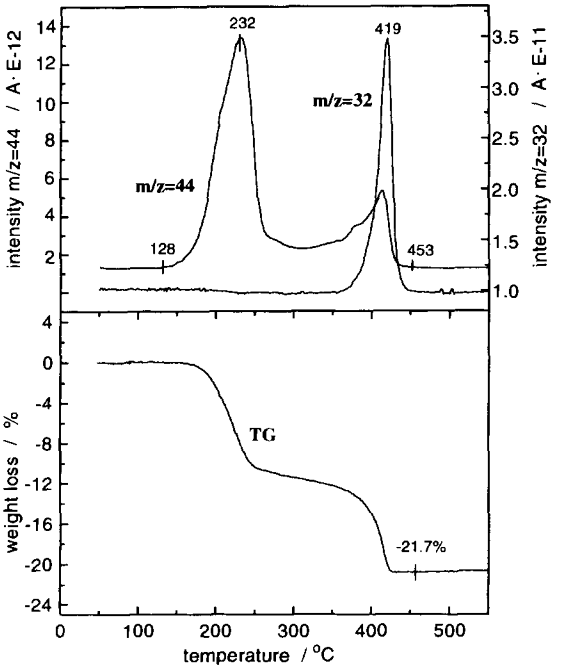

Fig. 2. Decomposition of silver carbonate under argon investigated by TG and MS (evolution of carbon dioxide and oxygen monitored by the curves m/z=44 and 32, respectively).

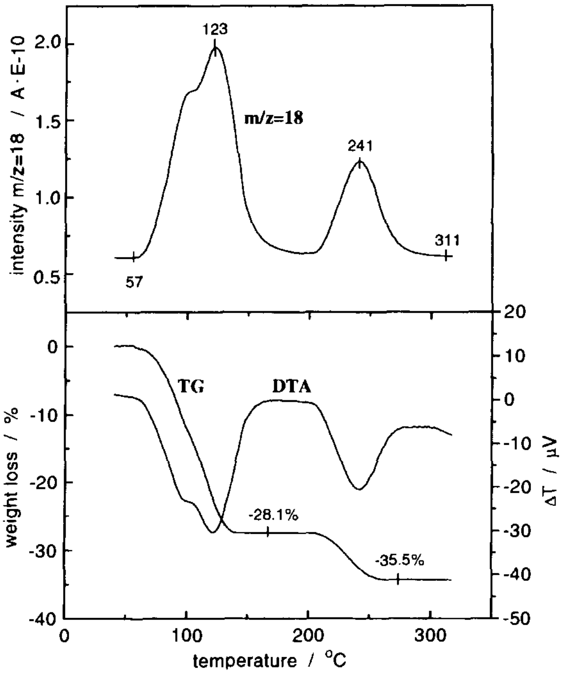

Fig. 3. Two-stage dehydration of copper sulphate pentahydrate under argon investigated by TG, DTA and MS (evolution of the water monitored by the curve m/z=18).

possible in order to increase the sensitivity of the MS-signal, especially when investigating multicomponent systems where the amount of evolved species is in the range of 1–2 wt%. On the other hand, too low flow rates influence the relationship between TA and MS-curves, shifting the latter towards higher temperatures due to the back diffusion phenomena. A quantitative description of this problem has been reported recently [11].

The above considerations are illustrated in Figs. 5 and 6. Fig. 5 depicts the changes of the shape and intensity of the m/z=44 signal formed after injection of 1.0 and 0.25 ml of CO_2 into the carrier gas. The flow rate of He was changed from 20 to 100 ml min^{-1}. Lower flow rates result in an increased holding time of CO_2 in the system, which, in turn, leads to the growth of the MS signal, but also broaden it due to diffusional effects. The relationship between the size of the MS signal and the characteristic time defined as the ratio of the injected volume (1 ml) to the flow rate of carrier gas (ml min^{-1}) is shown in Fig. 6.

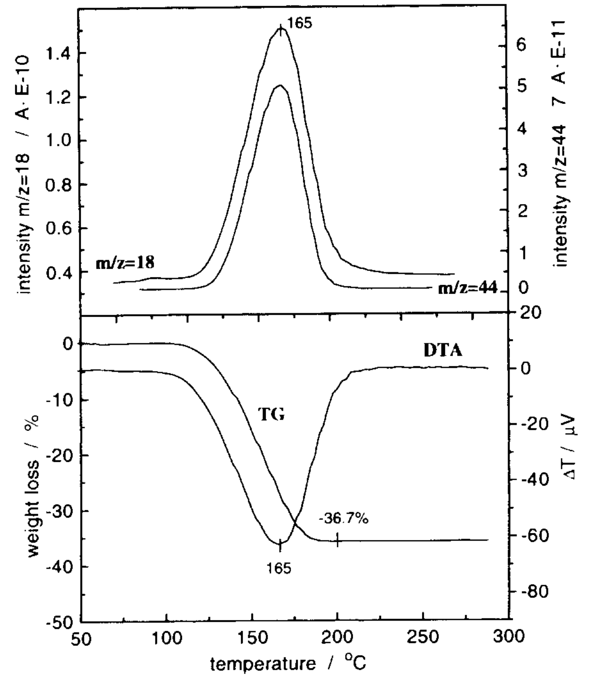

Fig. 4. Decomposition of sodium bicarbonate under argon investigated by TG, DTA and MS (simultaneous evolution of H_2O and CO_2 is monitored by the curves $m/z=18$ and $m/z=44$, respectively).

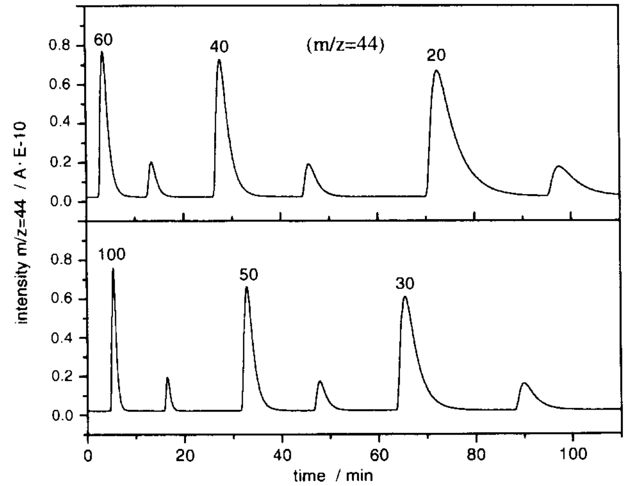

Fig. 5. Change of shape of the mass spectrometric signal ($m/z=44$) resulting from injection of 1 ml (large-) and 0.25 ml (small peak) of CO_2 into the stream of helium as a function of flow rate of the carrier gas (indicated on curves in ml min^{-1}).

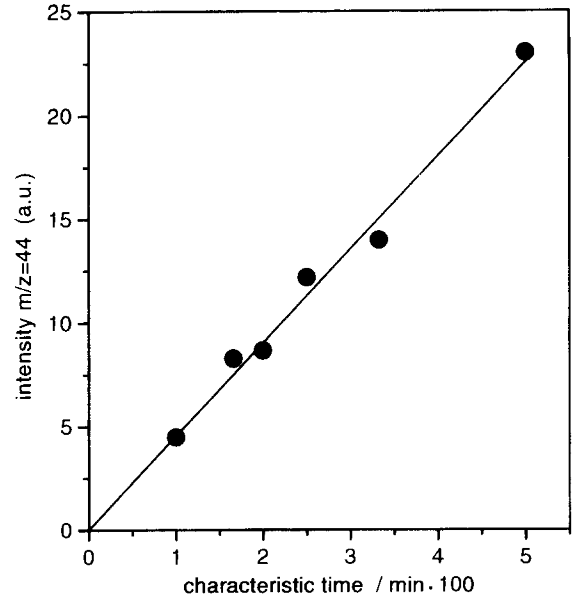

Fig. 6. Relationship between intensity of the mass spectrometric signal ($m/z=44$) resulting from injection of 1 ml of CO_2 and characteristic time (see text for the definition).

These results indicate that a fivefold increase of the carrier gas flow does not influence the linear relationship between flow rate and intensity of the mass spectrometric curve.

3.2. Influence of amount of analyzed species

In order to check whether the change of the amount of the evolved gases during thermoanalytical run alters the MS calibration factor, the mass of the decomposed reactant was increased tenfold . The results of the decomposition of $NaHCO_3$, for samples ranging from 3.99 to 40.69 mg are presented in Fig. 7, as relationship between the intensity of the $m/z=44$ signal and the sample mass. The intensities of the curves $m/z=18$ (water) and $m/z=44$ (carbon dioxide) related to the sample mass are depicted in Fig. 8. The relationships illustrated in Fig. 8 confirm the previous conclusions concerning the influence of a change of the carrier gas flow. Again a tenfold increase of the amount of the analyzed component does not affect the linearity between input (amount of gas) and output (the size of the mass spectrometric response) signals.

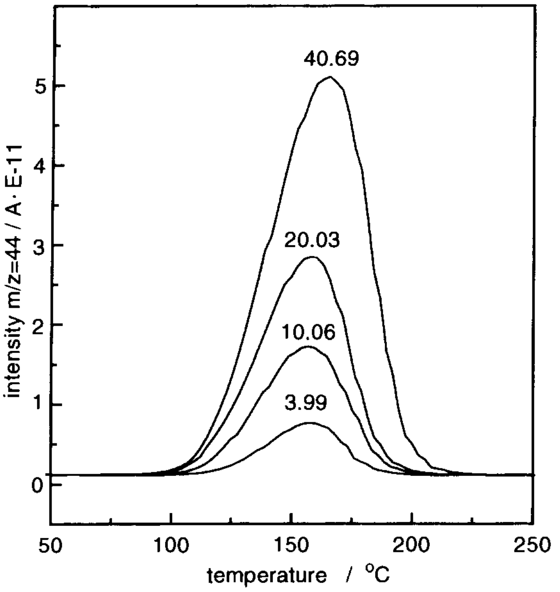

Fig. 7. Intensities of mass spectrometric CO_2 signal (m/z=44) during decomposition of different amounts of $NaHCO_3$ under argon. The mass of the solid samples is indicated on curves in mg.

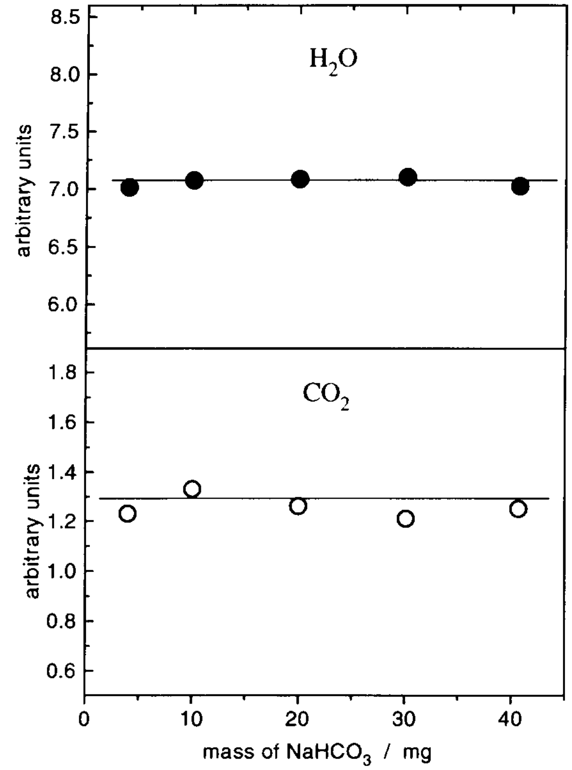

Fig. 8. Relative intensities of the water and CO_2 mass spectrometric signals recorded during decomposition of $NaHCO_3$ under argon as a function of the solid sample mass. Intensities are related to 1 g of $NaHCO_3$.

3.3. *Influence of temperature*

The quantitative calibration of the TA–MS system by means of the decomposition of a solid is carried out at specific temperature and may not be accurate when the investigated reaction occurs at another temperature. The temperature increase during thermoanalytical run changes the mass transfer conditions in the system. Due to the change of density and viscosity of the carrier gas, the flow conditions through the thermoanalytical chamber and the capillary change, and thereby influence the transfer of the molecules to the mass spectrometer. Consequently the influence of temperature on the calibration factor in the temperature range of 25–1000°C was investigated using both calibration methods, i.e. decomposition of solids and injection of gas into the carrier gas stream.

Applying the first method, five compounds evolving CO_2 in different temperature ranges from 125°C ($NaHCO_3$) to 1380°C ($BaCO_3$) were used. The size of the m/z=44 MS-peaks originating from a constant amount (1 g) of evolved CO_2 are shown in Fig. 9 as a function of the temperature at which the rate of CO_2 evolution was maximal (DTG peaks). The calibration factor for carbon dioxide as appearing from this plot, is almost independent of temperature. In order to confirm this conclusion, the calibration by the injection, enabling the calibration at any temperature, was carried out. 1 ml-volume pulses of CO_2 and O_2 were injected into the argon stream flowing with a constant rate of 50 ml min^{-1} in the temperature range of 25–1000°C. The course of the m/z=44 curve as a function of temperature of injection is shown in Fig. 10. In the insets *A* and *B*, low- and high temperature peaks marked A_1, A_2, and B_1, B_2, respectively, are displayed in enlarged scale. The change of the peak shape caused by the temperature increase is apparent, but on the other hand, the areas under the MS signals are only little affected by temperature. At higher temperatures, peaks become more narrow, but their areas remain almost constant, what is apparent in Fig. 11, which depicts the relationship between intensities of MS

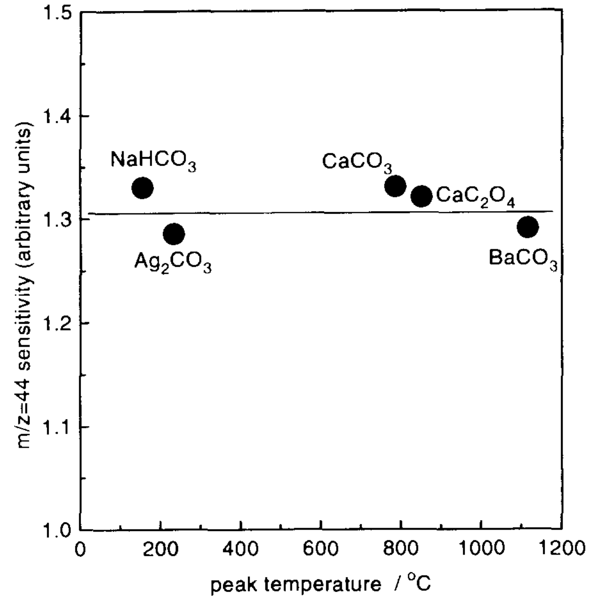

Fig. 9. Relationship between relative intensity of the MS signal (m/z=44) during decomposition of carbonates and the temperature. Intensities are related to 1 g of CO_2.

signals for m/z=32 and 44 and the temperature. The change of the peak shape is caused by the different temperature dependence of convectional and diffusional flow properties of the carrier gas, which give rise to a change of the transport of the target molecules in the carrier gas.

3.4. Influence of carrier gas properties

Three gases: helium, nitrogen, and argon were used in order to investigate the influence of the carrier gas properties on the quantitative calibration of the mass spectrometric curves. The calibration was carried out with hydrogen, oxygen, and carbon dioxide. Due to the differences in the density of these carrier gases (densities at 0°C and 1013 mb for He, N_2 and Ar are: 0.1785, 1.2505, and 1.7839 g l^{-1}, respectively) and diffusion coefficients for the systems: carrier gas-injected gas (listed in Table 2, data for calculation were taken from [12]), it seemed to be meaningful to check, whether a change of these properties will influence the MS-calibration factors. For that purpose the investigated gases were injected into the stream of the respective carriers at room temperature.

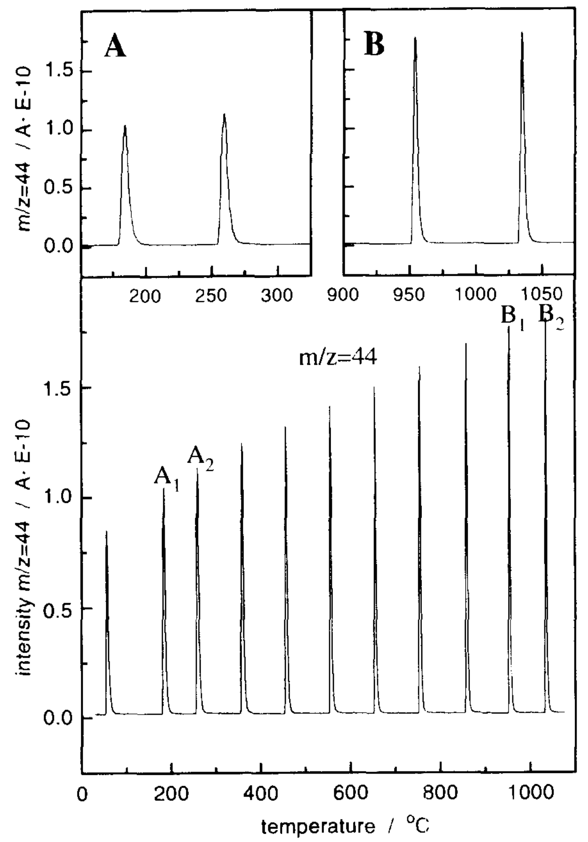

Fig. 10. Change of shape and the intensity of m/z=44 signal resulting from injection of 1 ml CO_2 into argon stream during heating with 4 K min^{-1}. In the insets A and B, the enlargement of the two low- (A_1, A_2), and two high-temperature (B_1,B_2) peaks are presented.

The intrinsic properties of the carrier gas, influencing the rate of diffusion in the system, distinctly alter the shape of the MS signal. The results showing the m/z=44 peak formed due to the injection of 1 ml of CO_2 into the stream of He and Ar are presented in Fig. 12. Higher diffusivity of CO_2 in He than in Ar leads to the faster detection of the CO_2 by the mass spectrometer, under constant flow of 50 ml min^{-1} of both carriers, CO_2 injected is detected after 0.58 min in He and after 1.00 min in Ar, respectively. Also note the difference in the position of the peak maxima of m/z=44 curves for both carriers- the maximum in He appeared faster. On the other hand, due to the higher back-diffusion of CO_2 in He, the mass spectrometric CO_2 signal showed a larger tailing compared to that in argon.

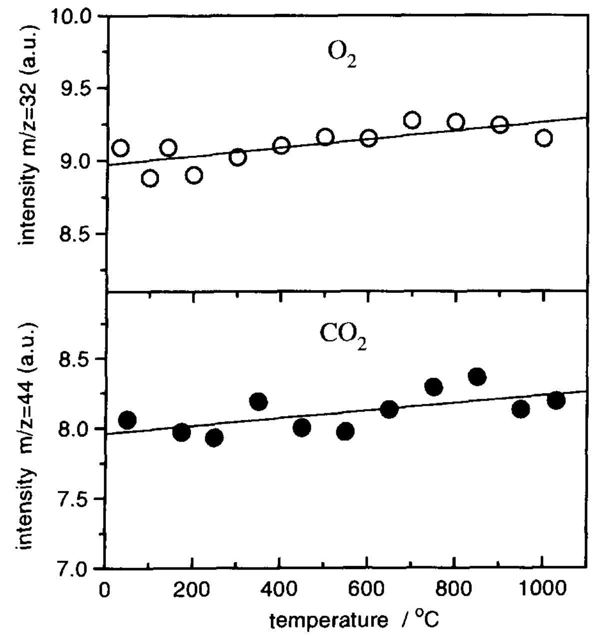

Fig. 11. Relationship between intensities of the MS signals, m/ z=32 and 44, and temperature. The 1 ml pulses of oxygen and carbon dioxide were injected into the argon stream during heating with 4 K min^{-1}.

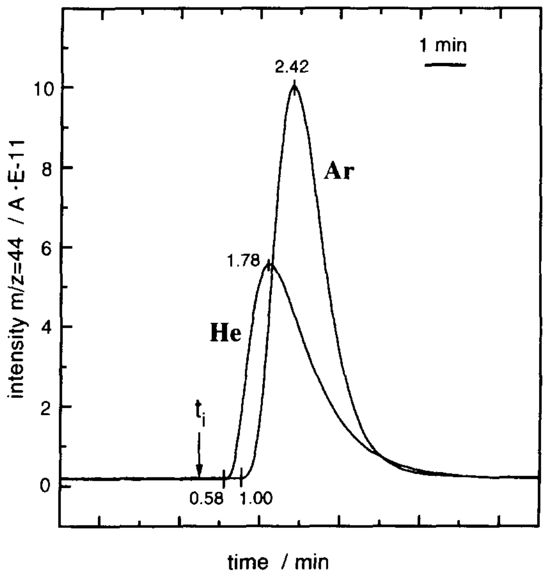

Fig. 12. Comparison of m/z=44 signals produced by injection of 1 ml of CO_2 into the streams of argon and helium (flow rate 50 ml min^{-1}). The moment of injection is labelled on the curves as t_i, the numbers describing the beginning and maximum of the signal are expressed in minutes.

Table 2
Molecular diffusion coefficients at 20°C($\mathrm{cm}^2\ \mathrm{sec}^{-1}$) for respective gas systems calculated using data taken from [12]

	H_2	O_2	CO_2
He	1.606	0.742	0.595
N_2	0.745	0.204	0.154
Ar	0.777	0.195	0.143

Table 3
Mass spectrometric sensitivity expressed as area of m/z=44 signal (arb. units) resulting from injection of 1 ml of calibration gas (H_2, O_2 and CO_2) into the carrier gas stream gas (He, N_2 and Ar)

Carrier gas	Injected gas		
	H_2	O_2	CO_2
Helium	74.5	9.4	7.9
Nitrogen	99.5	12.3	11.0
Argon	105.6	11.9	11.7

The comparison of the calibration factors, i.e. the ratios of the peak areas related to the amount of injected gas, leads to the conclusion that when Ar and N_2 are used as carrier gases, the sensitivities of the mass spectrometric curves are very similar. The data summarized in Table 3 indicate that the calibration factors for H_2, O_2 and CO_2 in nitrogen and argon differ by ±5%. Much larger differences were found when helium was used as a carrier gas: the ratios of the calibration factors for O_2, H_2 and CO_2 in argon to those in helium were 1.3, 1.4, and 1.5, respectively. This indicates that mass spectrometric signals obtained with helium as a carrier gas are less intensive compared to those resulting under nitrogen or argon.

3.5. Comparison of calibration methods

The investigations show that both calibration methods, i.e. the decomposition of solids and injection of the target gas, can be used for the determination of the calibration factor. In order to check the accuracy of the calibration, the amount of CO_2 evolved by decomposition of calcium carbonate was determined applying both methods. The m/z=44 signal obtained during

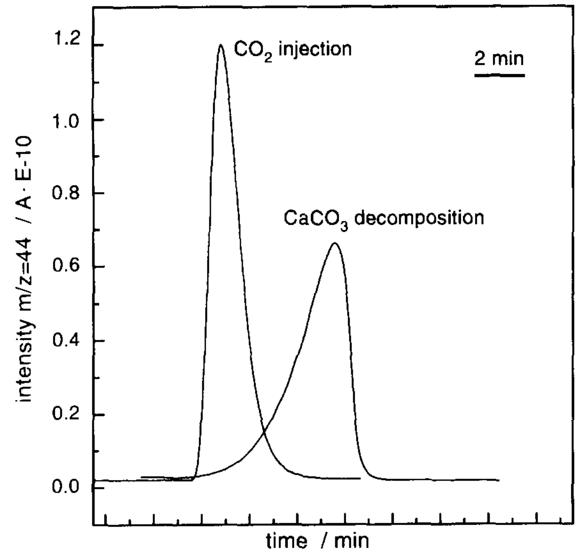

Fig. 13. The comparison of the shape and intensities of the m/z=44 signals produced by the injection of CO_2 and decomposition of $CaCO_3$ in the stream of the argon (flow rate 50 ml min^{-1}). In both cases the volume of CO_2 was 1 ml.

the decomposition of 4.49 mg of $CaCO_3$ under argon (theoretical evolution of 1.0 ml of CO_2) was quantified by applying the calibration made by injection of a 1.0 ml pulse of CO_2 into the argon stream at constant temperature of 745°C (temperature of peak maximum during decomposition). Both MS curves are compared in Fig. 13. Using the pulse method for calibration, the amount of CO_2 found in $CaCO_3$ from the mass spectrometric curve was 1.95 mg. Thermogravimetric analysis combined with mass spectrometry gave 1.97 mg corroborating that the error of the carbon dioxide determination from MS data was smaller than 1%.

4. Discussion

The results of this study indicate that by using a well designed TA–MS system one obtains reproducible mass spectrometric data, which can be used for a quantitative evaluation of the investigated process. The following practical conclusions can be drawn from the experiments carried out:

1. The application of helium as a carrier gas should be restricted to those cases, where due to the presence of an intensive signal of m/z=28 (nitrogen, traces of nitrogen in argon) it is impossible to detect or determine the presence of carbon monoxide species (m/z=28). Helium is the least suitable from the commonly used carrier gases due to its very high diffusivity giving rise to changes of the shape of the MS signal and decrease in its intensity. Nitrogen and argon have very similar properties concerning their application as a carrier gas in TA–MS systems.
2. The investigated TA–MS system shows linearity between the amount of the analyzed species and the corresponding mass spectrometric signals even when the sample mass is increased by a factor of ten. Some uncertainties caused by the nonproportionality between input (amount of the evolved species) and output (MS curve) signals have their origin in the specific course of the reaction (e.g. very fast increase of the decomposition rate due to the strong exothermicity). Depending on the experimental settings (sampling time), a part of the MS data can be lost with rapid exothermic reactions, which, in turn, decreases the detected amount of the analyzed species.
3. Possessing a well-designed and properly heated coupling system between the thermoanalyzer and mass spectrometer, it is possible to determine water quantitatively, despite the common problems with its condensation. The data presented in Fig. 8 show very similar dependence of the MS-signal on the sample mass for water as for CO_2, which does not condense under the conditions given.
4. The sensitivity of the mass spectrometric curves does not depend on the temperature in the range investigated. This important conclusions enables quantitative evaluations of MS-curves obtained at any temperature using a single-point calibration.
5. The relative intensity of the MS signal (i.e. related to the unit of carrier gas flow rate) is constant in a wide range of flow changes. An n-fold decrease of the flow rate results in an n-fold increase of the peak area of mass spectrometric curve (see Figs. 5 and 6). This conclusion demonstrates how essential the stability of the flow rate is in TA–MS systems during quantitative measurements. A decrease of the flow rate is advantageous for the qualitative recognition of very small signals, but leads to a distinct broadening and shifting of the signal to

higher temperatures during experiments carried out under non-isothermal conditions.

6. The described methods of calibration facilitate a quantitative interpretation of mass spectrometric curves with an accuracy of a few percent. However, there are some specific advantages and restrictions inherent to both methods:

(a) *Calibration by decomposition of solids*: It does not require any changes or additional reconstruction of the commercial thermoanalytical system, the accuracy of the dosing of the analyzed species into the system is very high, it is possible to calibrate and to determine quantitatively the water. Disadvantages are: the method is time consuming, does not offer the simple possibility of investigating the influence of temperature on the calibration procedure, and can be applied only for the species evolved during decomposition of solids.

(b) *Calibration by injection*: It is very fast, easy for reproducibility determinations, can be performed at any temperature in both operation modes (iso- or non-isothermally), it can be used with any gas (except water due to the condensation problems), the shape of the MS response depends only on the mass transfer in the investigated TA–MS system and is independent of the chemical reaction. Restrictions are: the amount of injected gas can not be changed arbitrarily and is determined by the volume of the injection loops, the method requires some reconstructions of the gas supply system.

Both the calibration methods described were used in our laboratory many times for the quantitative interpretation of the mass spectrometric results. They were applied for the determination of:

- the composition of PdO/ZrO_2 catalysts prepared by the oxidation of amorphous glassy metals [13,14]
- the copper content in a copper/alumina catalyst [15]
- the organic residues in sol–gel derived catalysts such as zirconia and mixed titania–silica- [15], palladium–titania- [16] and vanadia–titania aerogels [17]
- the amount of the active phase in supported CrO_x/TiO_2 catalysts [18,19]
- the amount of carbonates and deposited carbon in potassium-promoted iron oxides after catalytic reaction [20]
- the amount of the carbon incorporated into the palladium lattice during CO disproportionation [21,22]

Very often, the amount of the analyzed components was in the range of 1 wt%, as e.g. during determination of oxygen evolved in the thermal decomposition of CrO_x/TiO_2, or even below, as in the case of analysing the organic residue content in aerogels or iron oxide catalysts. Elemental microanalysis – compare e.g. [16,17,20] – confirmed the high accuracy of the quantitative MS measurements based on the calibration procedure described in this paper.

5. Conclusions

The investigation of the influence of several experimental parameters on the course of mass spectrometric signals indicate that in the system Netzsch STA-409 thermoanalyser quadrupole mass spectrometer Balzers QMG 420, it is possible to perform quantitative interpretation of the MS data. Two method of calibration, decomposition of the inorganic solids and injection of the target gas, confirmed that the relative calibration factor in the system does not depend on the flow rate of the carrier gas, the amount of the analyzed species and temperature. The application of helium as a carrier gas is not recommended due to the reduction of the intensity of the MS signal and its diffusional broadening. If proper care is taken in the experimental design, the combination of TA and MS offers a powerful tool for the quantitative analysis of solids and gas-solid reactions.

References

[1] H.L. Friedman, Thermochim. Acta, 1 (1970) 199.
[2] D. Dollimore, G.A. Gamlen and T.J. Taylor, Thermochim. Acta, 75 (1984) 59.
[3] M.R. Holdiness, Thermochim. Acta, 75 (1984) 361.
[4] G. Szekely, M. Nebuloni and L.F. Zerilli, Thermochim. Acta, 196 (1992) 511.
[5] J. Wang and B. McEnaney, Thermochim. Acta, 190 (1991) 143.

[6] D. Price, D. Dollimore, N.S. Fatemi and R. Whitehead, Thermochim. Acta, 42 (1980) 323.

[7] M. Yoshimura and E. Tajma, in H. Chihara (Ed.), Thermal Analysis, Vol. 1, Heyden, London (1978) p. 71.

[8] M. Muller-Vonmoos, G. Kahr and A. Rub, Thermochim. Acta, 20 (1977) 387.

[9] W. Dünner and H. Eppler, in I. Buzsas (Ed.), Thermal Analysis, Vol. 3, Akademiai Kiado, Budapest, Hungary (1975) p. 1049.

[10] S. Bernal, R. Garcia and J.M. Rodriguez-Izquierdo, Thermochim. Acta, 70 (1983) 249.

[11] B. Roduit, J. Baldyga, M. Maciejewski and A. Baiker, Thermochim. Acta, 295 (1997) 59.

[12] J.R. Welty, C.E. Wicks and R.E. Wilson, Fundamentals of Momentum, Heat and Mass Transfer, 3rd edn., Wiley, London (1984) p. 487.

[13] A. Baiker, M. Maciejewski and S. Tagliaferri, Ber. Bunsenges. Phys. Chem., 97 (1993) 286.

[14] P. Marti, M. Maciejewski and A. Baiker, J. Catal., 139 (1993) 494.

[15] M. Maciejewski and A. Baiker, J. Therm. Anal., 295 (1997) in print, and references cited herein.

[16] M. Schneider, M. Wildberger, M. Maciejewski, D.G. Duff, T. Mallat and A. Baiker, J. Catal., 148 (1994) 625.

[17] M. Schneider, M. Maciejewski, S. Tschudin, A. Wokaun and A. Baiker, J. Catal., 149 (1994) 326.

[18] M. Maciejewski, K. Kohler, H. Schneider and A. Baiker, J. Solid State Chem., 118 (1995) 13.

[19] K. Kohler, M. Maciejewski, H. Schneider and A. Baiker, J. Catal., 157 (1995) 301.

[20] A. Knell, D. Monti, M. Maciejewski and A. Baiker, Appl. Cat., A 124 (1995) 367.

[21] M. Maciejewski and A. Baiker, J. Phys. Chem., 98 (1994) 285.

[22] M. Maciejewski and A. Baiker, Pure and Appl. Chem., 67 (1995) 1879.