INFLUENCE OF MEASURING CONDITIONS ON THE QUANTIFICATION OF SPECTROSCOPIC SIGNALS IN TA-FTIR-MS SYSTEMS

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Simultaneous thermal analysis (TA) and evolved gas analysis by mass spectrometry (MS) and/or Fourier transform infrared spectroscopy (FTIR) is a powerful hyphenated technique combining direct measurement of mass loss and sensitive spectroscopic analysis. In the present study the influence of several experimental parameters which may affect the quantification of FTIR signals have been studied using a combined TA-FTIR-MS system. Parameters studied include: sample mass (1–400 mg), carrier gas flow rate (25–200 mL min^{-1}), resolution of the FTIR spectrometer (1–32 cm^{-1}), and location of injection of the calibrating gas.

MS analysis, which was not significantly affected by the experimental conditions, was used as a reference for assessing the accuracy of quantification by FTIR. The quantification of the spectroscopic signals was verified by the decomposition ($NaHCO_3$) or dehydration ($CuSO_4 \cdot 5H_2O$) of compounds with well-known stoichiometry.

The systematic study of the parametric sensitivity revealed that spectral resolution and carrier gas flow rate, which affect the acquisition time in the IR-cell, are key parameters that must be adjusted carefully for reliable quantification. The dependence of the reliability of quantification on these parameters is illustrated and conditions leading to proper quantification are discussed. As an example, for a standard spectral resolution of 4 cm^{-1} and a FTIR gas cell volume of 8.7 mL, the carrier gas flow must be lower than 100 mL min^{-1} for warranting accurate results (relative deviation <2%). The concentration range of analyzed species is limited but can be extended by proper selection of the wavenumber regions for molecules giving strong IR signals.

Keywords: *calibration techniques, hyphenated techniques, pulse TA combined with FTIR, quantitative evolved gas analysis, TA-FTIR-MS*

Introduction

A disadvantage of classical thermal analysis (TA) is that gases released from the probe sample during the measurement are normally not analyzed. This shortcoming can be overcome by coupling TA with mass spectrometry (MS) or Fourier-Transform-Infrared (FTIR) spectroscopy. The main advantage of the coupled techniques TA-MS and TA-FTIR is the identification of gaseous products, which together with the thermal effects (DTA) and mass changes (TG) allow a more thorough investigation of the target reaction. The qualitative analysis is routinely performed by comparing recorded spectra with key fragment ions and their relative intensities for known elements and compounds (MS) or with reference spectroscopic signals (FTIR). The development of TA-FTIR and TA-MS hyphenated techniques has been reviewed by Materazzi *et al.* [1–3].

Besides the identification of evolved gases, their quantification by FTIR [4–6] or MS [4, 7–9] spectrometry has been addressed. Quantification is especially important when investigating multistage decomposition reactions, or, when two or more gases evolve simultaneously. In such cases the thermo-analytical methods alone fail for the quantitative description of the investigated process and have to be coupled with MS or FTIR enabling quantitative and qualitative determination of the evolved gases.

The common method of quantification of spectrometric signals is time-consuming and requires the application of gaseous mixtures with well-defined composition. First quantification of evolved gases based on the pulse technique combined with TA systems was reported by Maciejewski *et al.* [8, 10]. The extension to FTIR-TA coupled technique was investigated by Eigenmann *et al.* [11, 12] by decomposing solids with known stoichiometry of the decomposition process and by injection of liquids into the TA-FTIR system. Marsanich *et al.* [13] applied the gas-pulse calibration using ammonia, carbon monoxide and carbon dioxide. They introduced the vaporization technique of liquid samples for calibration of the FTIR signals. Similar procedure was applied also by Slager and Prozonic [14].

Quantification using MS combined with the pulse calibration technique is facilitated by the fact that the linear relationship between the observed intensities of the ion current and the amount of the analyzed species is hold in a wide concentration range. Furthermore the

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MS data acquisition time is generally short and recording evolved gases can be achieved with a high time resolution. In contrast, quantification of evolved gases in TA-FTIR systems is complicated by the fact that the Lambert–Beer's law is often valid only in a small concentration range, and consequently the amount of injected gas by the single-point calibration must closely match that evolved during decomposition. Additionally the data acquisition time in FTIR is only comparable with that applied in MS when choosing poor spectral resolution (e.g. 32 cm^{-1}). The other parameters such as residence time in the IR-cell are also important for achieving high accuracy in data collection.

A closer look on the experimental conditions applied in the various reported TA-FTIR studies indicates that in certain cases the conditions deviate significantly from the optimal settings for quantification of FTIR traces. Some experimental conditions used for TA-FTIR investigations are listed in Table 1 [4, 6, 14–22]. Comparison of acquisition time and residence time describes the precision and completeness of the recorded traces: values of this ratio below or equal one indicate a big likelihood that each molecule could be detected and contributed to the integral intensity of recorded traces. Values above one indicate that most likely some of the target molecules did not contribute to the signal thereby lowering the accuracy of quantification. This is especially important, if pulse calibration is applied, resulting in generally sharp peaks, which can result in the situation that under extreme conditions (high quotient of acquisition time divided per residence time) the pulses are not fully recorded.

Preliminary investigations clearly indicated a significant influence of improper experimental settings on the accuracy of the quantification of IR spectra by the pulse technique. The importance of this aspect for proper application of FTIR in combined TA-FTIR systems has prompted us to study systematically the influence of the experimental conditions on the quantitative interpretation of FTIR traces.

Experimental

Methods

Experiments were carried out on a Netzsch STA 449 analyzer equipped with two pulse devices enabling injection of a certain amount of one or two different gases or gaseous mixtures into the carrier gas stream flowing through the system. The amount of injected gas could be changed from 0.01 to 2.0 mL. Volumes of 0.25, 0.5, 1.0 and 2.0 mL were mainly used.

Additionally the option of bypassing the thermoanalyzer by injecting species after the thermoanalyzer (into the transfer-line) was used, which enabled calibration without contact of the calibrating pulse with the investigated sample. This alternative method results in much sharper signals and therefore calibration is less accurate (vide infra).

The carrier gas flow rate was controlled by mass flow controllers, Brook's model 5850E, based on a thermal mass flow sensing technique. Helium and argon (purity 99.999%, PanGas) were used as carrier gases with flow rates from 12.5 to 200 mL min^{-1}. The thermoanalyzer was connected by a heated (ca. 200°C) transfer-line to a Bruker Vector 22 FTIR spectrometer. Gases leaving the FTIR spectrometer were passed through a heated (ca. 200°C) capillary to a Pfeiffer Omni Star GSD 301 O mass spectrometer.

The FTIR spectrometer is equipped with a MCT detector and an especially developed low-volume gas cell (8.7 mL) with a 123 mm path length and ZnSe windows. To avoid condensation of low volatile compounds the cell was heated to a constant temperature of 200°C. The whole FTIR compartment was continuously purged by nitrogen and additionally molecular sieves were used to minimize the water and carbon dioxide background in the recorded spectra. The resolution of the collected spectra was set between 1 and 32 cm^{-1} and co-addition of 4 scans per spectrum was applied. As a consequence spectra were recorded with a time resolution of about 2–20 s, depending on the integration methods and applied FTIR spectral resolution.

MS measurements were performed directly after the FTIR chamber resulting in similar temporal traces of the evolved species. The few characteristic mass to charge ratios (e.g. for CO_2 and H_2O m/z=44 and 18, respectively) were monitored *vs.* temperature or time in the multiple ion detection mode. Data acquisition time was relatively short, generally about 2 s. Such an acquisition time could only be applied on cost of low resolution i.e. 32 cm^{-1} in the FTIR system.

Materials

$NaHCO_3$ (p.a. Merck) and $CuSO_4 \cdot 5H_2O$ (Fluka AG) were used as reference samples with well-known stoichiometry of the decomposition. In order to check the behavior of the system in a wide range of CO_2 concentrations the sample mass of $NaHCO_3$ was varied between 2 and 420 mg, while the sample mass of $CuSO_4 \cdot 5H_2O$ was 50 mg.

For the gas injections a home-made device was placed before the thermoanalyzer. It contains a rotary sample valve enabling a carrier gas to purge the loop of a given volume, which had been previously filled with the calibration gas of known composition (CO_2, purity 99.990%, PanGas). In order to quantify the FTIR signals, pulses of a known volume were injected generally before the decomposition of the investigated sample. A standard heating rate of 10 K min^{-1} was applied for all decompositions.

Table 1 Comparison of TA-FTIR systems with different measuring conditions

| Apparatus	Reference	Resolution/cm⁻¹	Co-adding/scans	Acq. time/s	Flow rate/mL min⁻¹	Vol. IR cell/mL	Resid. time/s	Quotient Acq. t/Res. t
Bruker IFS 28	Post [15]	4	10	ca. 10	15	8.7	34.8	0.3
Perkin Elmer	Pitkänen [16]	8	4	ca. 4	89	ca. 10	ca. 7	0.6
Digilab FTS 60	Mittleman [4]	8	16	ca. 5	50	6	7.2	0.7
Bruker Equinox	Barontini [17]	4	16	9.5	60	8.7	8.7	1.1
Bruker Equinox	Jackson [18]	4	–	17.5	35	8.7	14.9	1.2
IBM IR 85	Bassilakis [19]	–	–	30	–	555.6	25	1.2
Digilab FTS 7	Cai [6]	8	16	13	10	6	7.2	1.8
Midac and Nicolet Avatar	Slager [14]	4	32–45	60	100	30	18	3.3
Nicolet Magna 750	Perez/Ponze [20]	16	3	ca. 3	50	0.49	0.6	5
Bruker Vector 22	Balabanovic [21]	2	16	75	100	19.7	11.8	6.4
Perkin Elmer	Groenewoud [22]	–	–	ca. 60	95	4.8	3	20

Results and discussion

From preliminary investigations [12] it emerged that the following experimental parameters can affect the accuracy of the quantification of FTIR signals: sample mass, place of the injection of the calibrating gas, carrier gas flow, resolution of the spectrometer and accordingly acquisition time in the IR cell. FTIR data were compared with the simultaneously gained MS data, which allowed significant optimization of the various parameters and led to increase of the accuracy of the FTIR quantification method.

*Influence of sample mass and concentration of the target gas*

The application of PulseTA® for quantitative interpretation of FTIR signals is based on the Lambert–Beer's law. Figure 1 shows the pulse calibration using the example of CO_2 where different amounts of the gas were injected into the TA-FTIR-MS system. CO_2 traces were monitored using two characteristic wavenumber regions, namely 2450–2150 cm^{-1} (asymmetric stretch, peak – 2350 cm^{-1}), which is widely applied for identification and quantification purposes, and 3780–3480 cm^{-1} (overtone band, peak – 3600 cm^{-1}), which shows much lower FTIR intensity and interferes with water bands in the same region. The integral intensities I Eq. (1) resulting from calibration pulses are shown in Fig. 2.

$$I = \int_{t_1}^{t_2} \left[\int_{v_1}^{v_2} A(v)\mathrm{d}v \right] \mathrm{d}t \tag{1}$$

The absorbance of the evolved CO_2 was much larger for the traces recorded at 2350 than at 3600 cm^{-1} and this led to a significant deviation from linearity
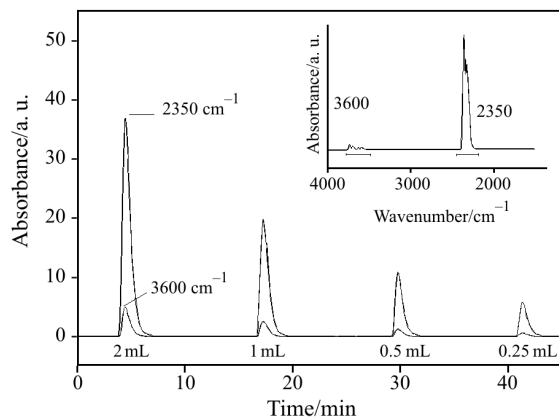

Fig. 1 Pulse calibration: intensity of CO_2 signals recorded in TA-FTIR system at the characteristic wavenumbers 2350 and 3600 cm^{-1}, respectively. Carrier gas: 100 mL min^{-1} He, resolution: 4 cm^{-1}. Inset: IR-spectrum of CO_2. Note that 'absorbancs' on the *y*-axis in Figs 1, 4, 6, 7a, 9, 11 and 12 represent integral absorbance values on specific wavenumber regions
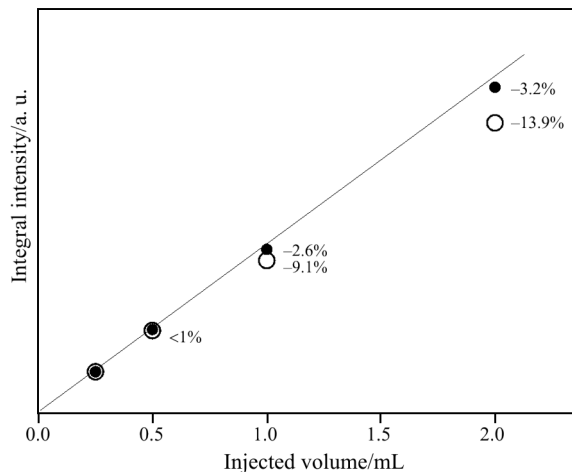
Fig. 2 Relationship between injected volume and integral intensity of evolved CO_2 measured in TA-FTIR system for different IR regions: ● – 3600 and ○ – 2350 cm^{-1}

during injections of higher amounts of CO_2. Integral intensities observed for 2 mL injections deviated by 13.9% from the linear dependence for the traces recorded for 2350 cm^{-1}, whereas for 3600 cm^{-1} only small non-linearity was observed (–3.2%).

Figure 3 shows the relationship between the mass of the decomposed sample (NaHCO$_3$) and the integral intensity of evolved CO_2 as determined using the TA-FTIR system. The traces gained at 2350 cm^{-1} show a linear dependence between integral intensity of the signal and mass up to 50 mg (ca. 13 mg of evolved CO_2). Quantification based on the band at 3600 cm^{-1}, however, could be achieved even up to 400 mg sample (ca. 105 mg CO_2) with a spectral resolution of 4 cm^{-1} and a carrier flow rate of 50 mL min^{-1} He. For sample masses over 100 mg (ca. 26 mg of evolved CO_2) no linear relationship was obtained using the signal at 2350 cm^{-1} biasing quantification.
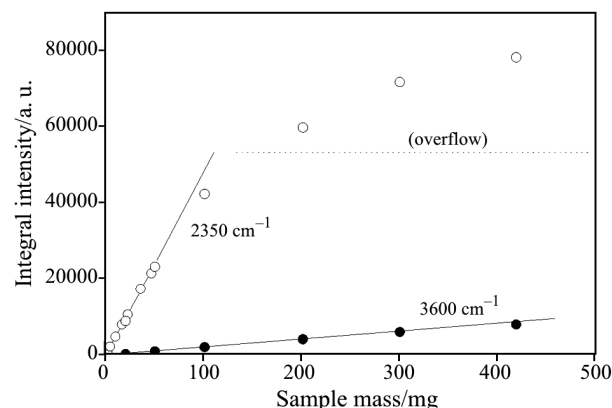

Fig. 3 Relationship between the mass of the investigated sample (NaHCO$_3$) and integral intensity of evolved CO_2 measured in TA-FTIR system: ● – 3600 and ○ – 2350 cm^{-1}. Carrier gas: 50 mL min^{-1} He, resolution: 4 cm^{-1}

Influence of the parameters of data-acquisition and carrier gas flow

Figure 4 illustrates the influence of the parameters of data acquisition and other experimental conditions on the shape and intensity of CO_2 traces recorded using the TA-FTIR system after injection of 1 mL CO_2. Figure 4a shows pulses recorded with different spectral resolutions. Generally the injection was made before the thermoanalyzer, but in the case where contact of the injected gas with the investigated sample has to be avoided, the calibrating gas can be injected into the carrier gas by-passing the TA chamber. This procedure leads to much sharper peaks (Fig. 4b) with a huge maximal intensity which may give rise to errors and allows quantification using only the weaker signal at 3600 cm^{-1}. Due to the small distance between injection and detecting sensor the number of recorded data points at the same carrier gas flow (marked in brackets) was much lower than in the case where the injected gas passed through the relatively large volume of the TA chamber resulting in dilution of the injected gas. The influence of the carrier gas flow on the
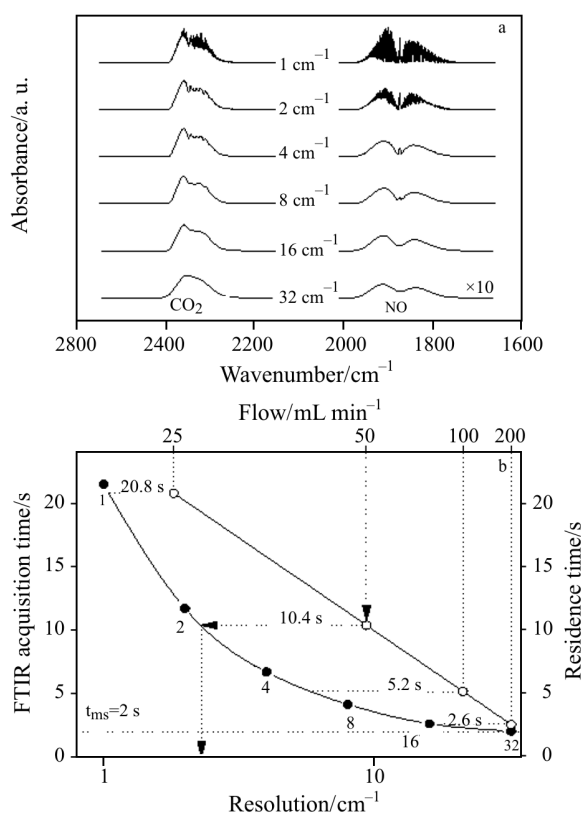
shape and intensity of FTIR signal is presented in Fig. 4c. The number of recorded data points increases with decreasing flow rate leading additionally to lowering of the maximal concentrations in the FTIR cell. The tailing of the signal can be caused not only by lowering the carrier gas flow but also by the application of different carrier gas. The results presented in Fig. 4d show that CO_2 pulses in helium result in broader peaks (larger tailing) than in argon due to higher diffusivity of the investigated gas in helium. Application of helium enables the collection of significantly more data-points which results in better description of the real traces of the evolved gas. On the other hand, larger peak tailing may cause worse description of the real course of the evolved species, overlapping of peaks and errors in quantitative determinations, which will be illustrated later (cf. different carrier flow rate, Fig. 11). Similar dependence was observed by Roduit *et al*. by quantitative calibration of mass spectrometric signals [7]. They found that due to the much higher diffusivity of CO_2 in helium compared to argon, the mixed-flow zone in the TA chamber significantly increases leading to peak
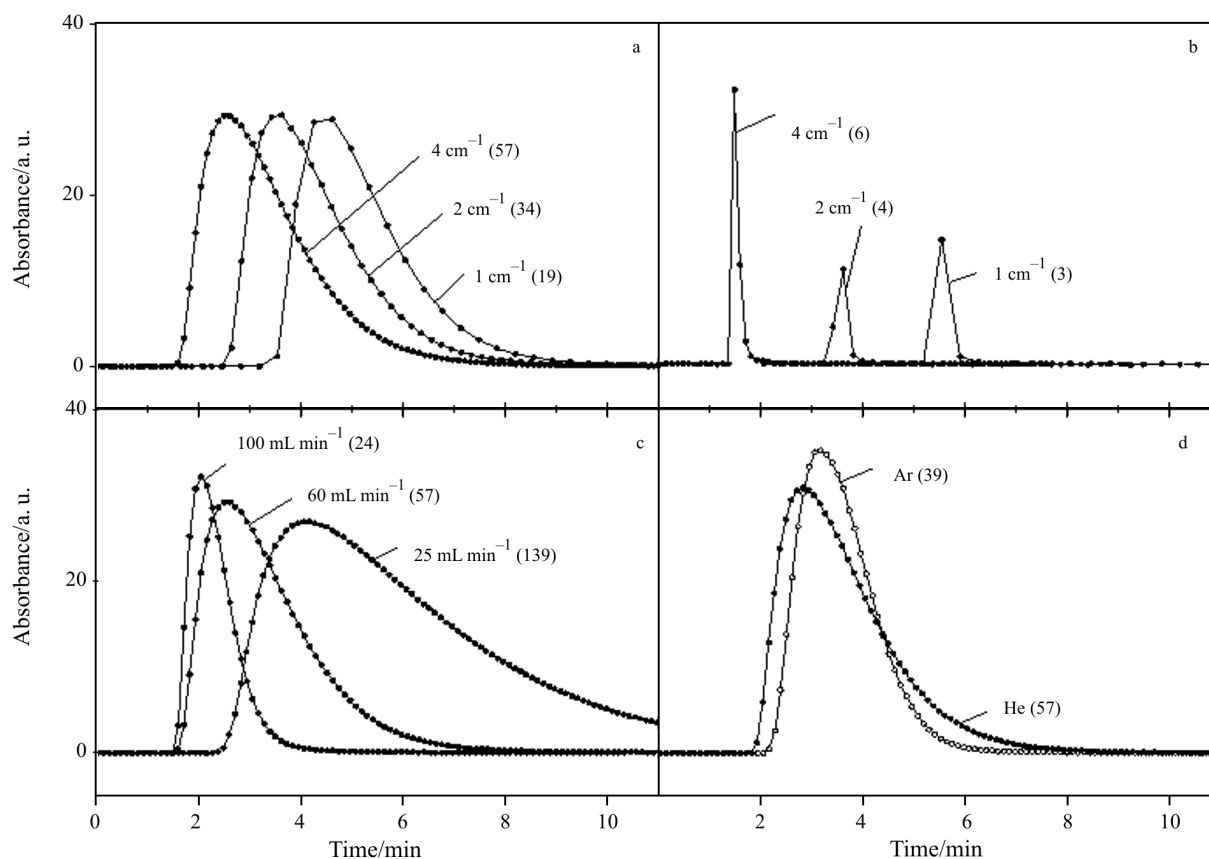
Fig. 4 Influence of the experimental conditions on the shape and intensity of CO_2 traces recorded in TA-FTIR system after injection of 1 mL CO_2. Numbers of recorded data points (>1% of maximal intensity) are given in brackets. a – carrier gas: 50 mL min^{-1} He, injection before TA, (CO_2 traces at 2350 cm^{-1}); b – carrier gas: 50 mL min^{-1} He, injection after TA, (CO_2 traces at 3600 cm^{-1}); c – carrier gas: 100, 50 and 25 mL min^{-1} He, injection before TA, resolution 4 cm^{-1}, (CO_2 traces at 2350 cm^{-1}); d – carrier gas: 50 mL min^{-1} He and Ar, injection before TA, resolution 4 cm^{-1}, (CO_2 traces at 2350 cm^{-1})

broadening. However, the maximal concentration due to injections of certain amount of CO_2 into the carrier gas is smaller in helium than in argon.

Figure 5 illustrates the relationship between IR-resolution, the acquisition time and the residence time of injected molecules. Figure 5a shows the CO_2 and NO spectra recorded with different spectral resolutions between 1 and 32 cm^{-1}. The application of high spectral resolution (2 cm^{-1}) allows quantification of specific mixtures where the vibrational signals of both gases overlap as e.g. acetylene and hydrogen cyanide. For NO, at higher resolution, even differentiation between isotopes is possible. However, the application of high resolution has a significant drawback in dynamic TA experiments. In order to increase the accuracy of quantification at a given flow rate, the acquisition time has to be decreased, which can only be achieved by lowering the spectral resolution, as shown in Fig. 5b. High resolution, as e.g. 1 cm^{-1}, results in a temporal acquisition of 21.5 s, and low resolution as 32 cm^{-1} in 2.1 s, the latter is comparable to the acquisition time of mass spectrometric signals used for quantification in this study.

The acquisition time has to be strictly correlated with the mean residence time of the evolved gas in the FTIR gas cell. For too long acquisition time it is impossible to quantify properly the analyzed species. The mean residence time in the gas cell estimated by the quotient between the volume of the IR cell compartment and the carrier gas flow through the system, is shown as an upper line in Fig. 5b (carrier gas flow: reciprocal scale). The comparison of both dependences presented in this figure allows choosing a maximal resolution required for a good description of the traces, enabling accurate quantification. For example, when using a carrier flow rate of 50 mL min^{-1} (residence time 10.4 s), the resolution should not be higher than 4 cm^{-1}. For higher resolutions, i.e. 2 or 1 cm^{-1}, data acquisition needs a time larger than 10.4 s (11.7 and 21.5 s, respectively), therefore when using a flow of 50 mL min^{-1} part of the target gas species will not be accounted for, leading to erroneous quantification.

When investigating the influence of the experimental conditions on the integral intensity of FTIR signals one has to apply an independent reference allowing exact comparison of signals obtained in different experiments. In our studies, parallel to the IR technique, we applied mass spectrometry. In all experiments we compared the data obtained by both techniques. As reported in our previous studies [8, 10] the integral intensities of MS signals are almost independent of experimental conditions, as also corroborated in the present study. This observation allowed us to use the MS signal as a reference for interpretation of the intensity of IR signals obtained under different conditions and specify optimal FTIR measurement conditions.

In order to compare the FTIR results obtained by using different experimental set-ups with the MS results, we introduced the ratio *F* as illustrated in Fig. 6. *F* is the normalized ratio between integral intensities
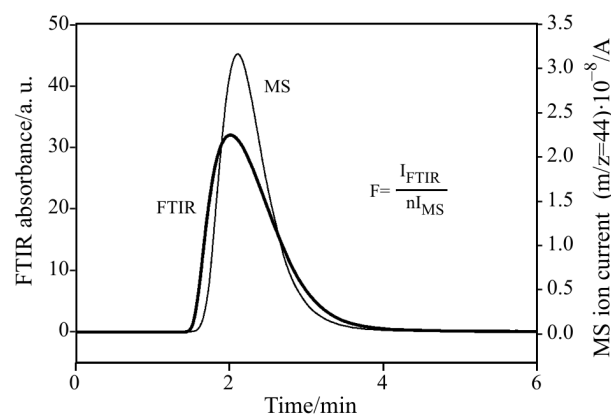

Fig. 5 Influence of selected spectral resolution of FTIR
a – CO_2 and NO spectra recorded with different spectral resolutions. Intensities of NO spectra are scaled up (×10). Concentration of both gases: ca. 1% in He;
b – relationship between acquisition time, spectral resolution and residence time (FTIR chamber) in TA-FTIR system. Number of averaged scans: 4

Fig. 6 Integral intensity I of 1 mL CO_2 injected in He measured by FTIR (thick line) and MS, respectively. *F* is the normalized ratio between integral intensity of FTIR and MS signals. For FTIR signal measured with a resolution of 32 cm^{-1} and the corresponding MS signal, *F* is set to 1

$$F = \frac{I_{FTIR}}{nI_{MS}}$$

of FTIR and MS signals and provides a reasonable criterion for the correctness of the quantitative FTIR analysis. Figure 6 shows the integral intensities of 1 mL CO_2 injected in He recorded by FTIR and MS. For the FTIR signal recorded using a low resolution of 32 cm^{-1} where the largest amount of data points are collected and a corresponding MS signal the factor F is deliberately set to 1. Note that acquisition times in this case were almost the same for both techniques (2.1 s for FTIR and 2 s for MS).

Figure 7a shows the influence of the resolution on the shape of the FTIR signal recorded during injections of 1 mL CO_2 to a carrier gas flow of 100 mL min^{-1}. High resolution (i.e. 1 cm^{-1}) results in smaller integral intensity due to the low number of collected data points, which leads to a decrease of the value of F. In Fig. 7b the observed relationship between ratio F and resolution for different carrier gas flows is shown. Especially for high carrier gas flows high spectral resolutions are not recommended because the resulting data acquisition time (cf. Fig. 5b) differs significantly from the corresponding residence time in the IR compartment, which
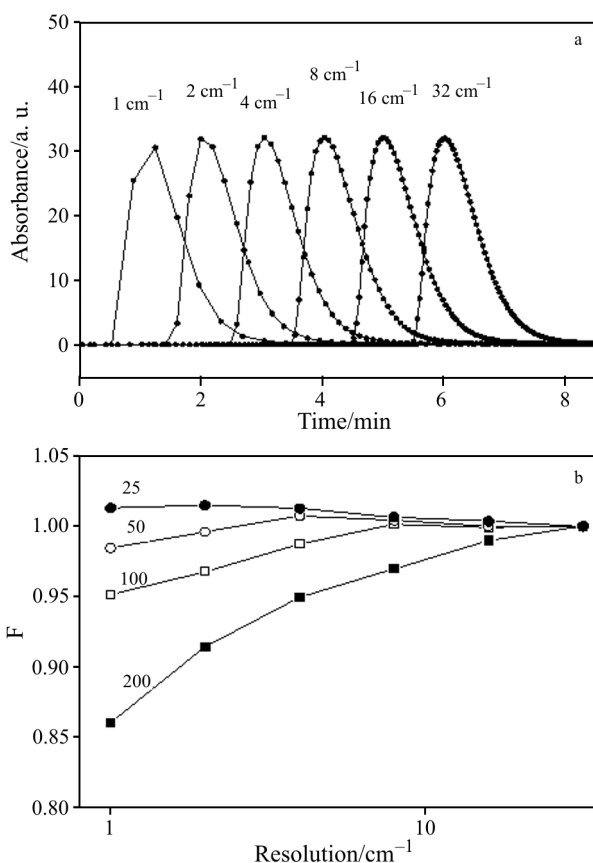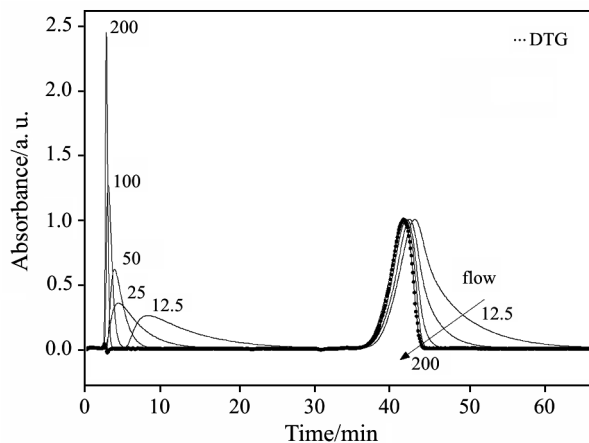
leads to a significant loss of data points. Figure 8 shows the dependence of F on the flow rate and resolution. F decreases not only with increasing the spectral resolution (which decreases the temporal resolution of data acquisition), but also with increasing the flow rate. Proper collection of FTIR data is only achieved when the acquisition time is in the range of the residence time of the gas in IR cell (F is above 0.98). As an example, when using a resolution of 4 cm^{-1} the gas flow should not be higher than 130 mL min^{-1}.
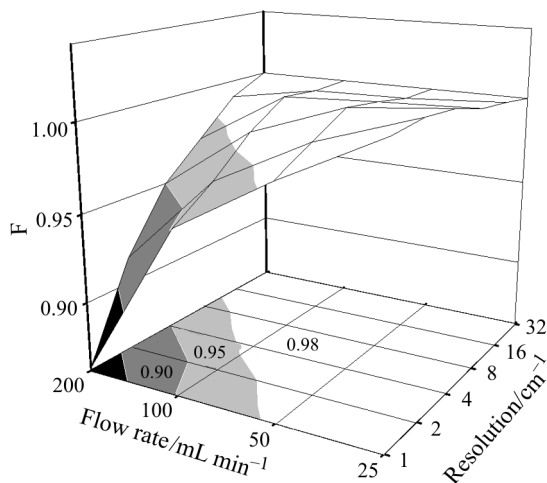

Fig. 8 3-D illustration of dependence of F on the flow rate and resolution. The areas in which the F value in the plane 'flow rate *vs*. resolution' lays in the range <0.90, 0.90–0.95, 0.95–0.98 and above 0.98, respectively, are marked

In order to quantify evolved gases in the TA-FTIR system with high spectral resolutions (1 or 2 cm^{-1}) only low flow rates (<50 mL min^{-1}) can be used. The data presented in Table 1 (last column) indicate that in some cases this important parameter has not been taken into account when setting the experimental parameters in TA-FTIR investigations.

A further illustration showing that improper selection of the experimental settings can lead to erroneous quantification of FTIR spectra is presented in Fig. 9, which shows the influence of the carrier gas flow on the shape of FTIR signals recorded during calibration (injection of 1 mL CO_2) and decomposition of 20 mg $NaHCO_3$. The maximal intensities of the decomposition traces are normalized. With increasing flow rate the calibration peaks become sharper and the value of their maximal concentration increases significantly compared to the decomposition traces. On the other hand, lower flow rates (25 or 50 cm^{-1}) show a larger tailing, as clearly emerges from calibrating and decomposition traces. The quantification of the FTIR traces presented in Fig. 9 is shown in Fig. 10. This figure depicts the dependence

Fig. 7 a – Influence of the spectral resolution (and data acquisition time) on the shape of FTIR signal recorded during injections of 1 mL CO_2 at a flow rate of 100 mL min^{-1}; b – relationship between ratio F (FTIR/MS signal) and resolution for different carrier gas flows (indicated in mL min^{-1} on the curves)

Fig. 9 Influence of the carrier gas flow on the shape of FTIR signals measured during calibration (injection of 1 mL CO_2) and decomposition of 20 mg $NaHCO_3$. The intensities of the decomposition traces are normalized. Carrier gas flow rates are indicated on the curves (mL min^{-1})
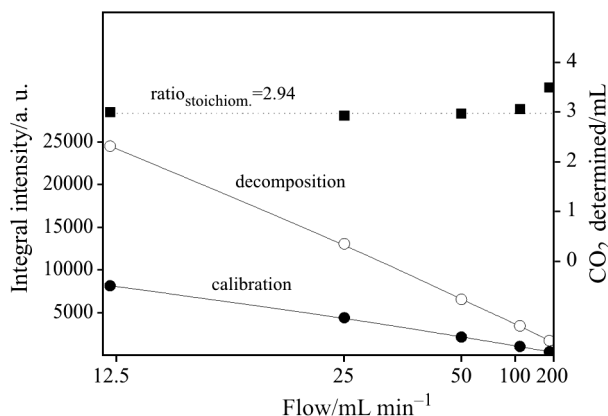
Fig. 10 Dependence of the integral intensities of the calibration and decomposition signals on the carrier gas flow. The amount of evolved CO_2 determined from the comparison of ● – calibration and ○ – decomposition signals is presented in the upper part of the figure. The stoichiometric value for the sample mass 20 mg $NaHCO_3$ and injection of 1 mL CO_2 amounts to 2.94

of the integral intensities of the calibration and decomposition signals on the carrier gas flow. The amount of CO_2 evolved from the sample determined by comparison of integral intensities of calibration and decomposition peaks is shown in the upper part of the plot. The deviation from the stoichiometric amount can easily be seen when increasing the flow rate, which of course influences much more the narrow peaks obtained during calibration than the relatively broad signals resulting from the decomposition.

However, application of low carrier gas flows has, in certain cases, also a disadvantage, e.g. when multistage reactions have to be investigated. Lower flow rate increases the tailing of the signal. This phenomenon is clearly visible in Fig. 9. The lower the

flow rate, the more the real course of the reaction represented by the differential thermogravimetric curve (DTG, dotted line) differs from those represented by spectrometric signals. This aspect is clearly visible also in Fig. 11 depicting the multistage dehydration of copper sulfate pentahydrate. The results illustrate the difficulty in separation of the two consecutive dehydration stages occurring in the range 60–120°C. The water traces recorded using carrier gas flows of 25 and 50 mL min^{-1} cannot be quantified properly due to partial overlap. In contrast, using a carrier gas flow of 100 mL min^{-1} the contribution of these peaks can be determined. Note that better splitting of these two peaks can also be achieved by e.g. decreasing the heating rate, however that lowers the concentration of the detected gas in the system and consequently the accuracy of quantification.

An example indicating how the procedure of the quantification of FTIR spectra by pulse calibration with gases can be influenced by different experimental parameter settings is given in Fig. 12, which presents the CO_2 traces recorded during calibration pulses and decomposition of $NaHCO_3$ according to the following reaction (Eq. (2)):

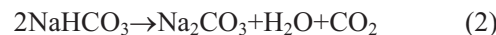$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2 \qquad (2)$$

Table 2 compares the results of the quantification of the FTIR and MS recorded traces shown in Fig. 12 using pulse calibration with significantly different experimental parameteres. The comparison is based on the calculated amounts of CO_2 evolved during decomposition of sodium bicarbonate related to the stoichiometric value. Experiment A (○) shows the error that had been introduced when unsuitable parameters were used, i.e. higher flow rate than 100 mL min^{-1} for a high spectral resolution of 1–4 cm^{-1} (cf. Fig. 8): the sharp pulse ob-
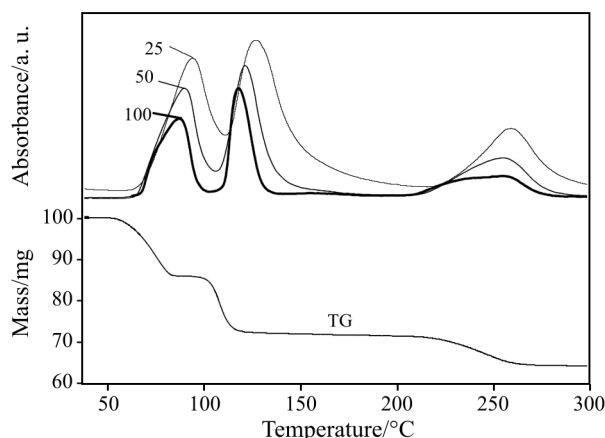

Fig. 11 Water traces during dehydration of 50 mg $CuSO_4 \cdot 5H_2O$ measured at different carrier gas flows. Heating rate: 10 K min^{-1}, carrier gas: He, flow rates are indicated on the curves (mL min^{-1}). Corresponding TG traces are shown in the lower part

Table 2 Results of the pulse calibration technique with different experimental set-ups A and B reported in Fig. 12. CO_2 amounts (%) quantified by MS and FTIR related to stoichiometric value are given

Set-up	MS/%	FTIR/%	F^1/–
A (○)	102.9	134.7	0.76
B (●)	99.2	99.8	0.99

[1]F – normalized ratio between integral intensity of FTIR and MS calibration signal (decomposition peaks were normalized)
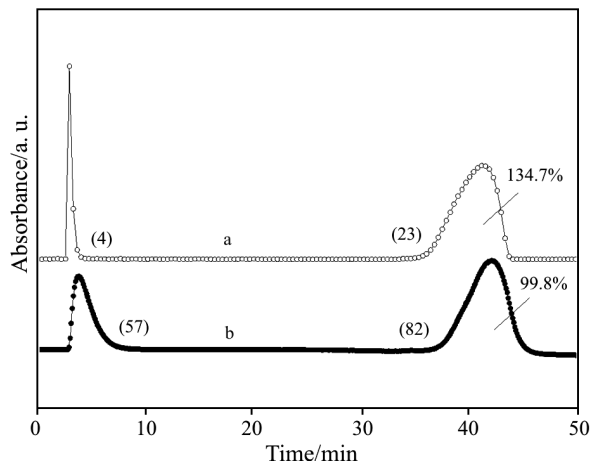
Fig. 12 Example of quantification of FTIR traces by pulse technique during decomposition of 20 mg $NaHCO_3$. Numbers of recorded data points (>1% of maximal intensity) are given in brackets. a – ○ carrier gas: 200 mL min^{-1} Ar, resolution 1 cm^{-1}, (pulse: 4 points). Calculated amount of CO_2 in the sample amounted to 134.7% of the stoichiometric value. b – ● carrier gas: 50 mL min^{-1} He, resolution 4 cm^{-1}, (pulse: 57 points). 99.8% of CO_2 was determined

served using high spectral resolution (1 cm^{-1}) and high carrier gas flow rate (200 mL min^{-1} Ar) led to a large error in the FTIR quantification. Due to the low temporal resolution (collection of only 4 points during injection) and the high maximal intensity significantly lower values of the integral intensities of the calibration pulse were found resulting in overestimation of the amount of CO_2 originating from the decomposition reaction.

Experiment B (●) was performed under optimized conditions as regards quantification: a flow rate of 50 mL min^{-1} was chosen and spectral resolution was set to 4 cm^{-1}, which provided 57 data points during the calibration pulse and led to a more accurate determination of the evolved CO_2 trace. MS and FTIR results obtained using proper experimental conditions (B) corroborated that high accuracy of the quantification of spectral signals can be achieved with both TA-MS and TA-FTIR.

We have shown the importance of choosing adequate experimental conditions, in order to quantify evolved gases by the pulse technique. Several parameters such as carrier flow rate, injection location, amount of injected gas and data acquisition time resulting from the spectral resolution have to be taken into account when setting the experimental conditions optimal for calibration of FTIR signals. We hope that the present study helps the practioner to improve the quantification of evolved components in combined TA-FTIR investigations.

Conclusions

Quantification of evolved gases during thermal analysis by the pulse technique using MS or FTIR spectroscopy requires careful optimization of the experimental settings. Quantification based on FTIR is strongly affected by the chosen experimental parameters, whereas MS analysis is only little affected. The most important factors to be considered in gas quantification by means of TA-FTIR are: the choice of the spectral resolution and carrier gas flow rate. High spectral resolution leads to poor time resolution. Low carrier gas flow rate leads to poor separation of the reaction steps during multistage decompositions, as shown for the dehydration of $CuSO_4 \cdot 5H_2O$. The application of a TA-FTIR-MS system with properly chosen experimental conditions allows an easy and less time-consuming in situ calibration procedure which can be used in different studies, such as the quantification of adsorption phenomena [23], gas-solid reactions [24] and decomposition of solids [12].

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