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Quantitative calibration of spectroscopic signals in combined TG-FTIR system

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Abstract

In thermoanalytical investigations the determination of the composition of the evolved gases is very important, especially when investigating decomposition processes or gas–solid reactions occurring in multi-component systems. The potential of simultaneous techniques, enabling the qualitative analysis of evolved species, such as TG-MS or TG-FTIR has been further improved by the introduction of the pulse thermal analysis (PulseTA®). This method provides a quantitative calibration by relating the mass spectrometric or FTIR signals to the injected quantity of probe gas.

The influence of several experimental parameters such as concentration of the analyzed species, temperature and flow rate of the carrier gas on FTIR signals has been investigated. The reliability of quantifying FTIR signals was checked by relating them to the amount of evolved gases measured by thermogravimetry. In order to extend the opportunities for quantifying FTIR signals, the possibility of the injection of liquids into the carrier gas stream was studied. The linear dependence between the injected amount of liquids and the integral intensity of spectroscopic signals (peak area) enabled easy quantification of FTIR data. Systematic studies on a new method based on isothermal vaporization of liquids further widen the application range of in situ calibrations.

Keywords: TG-FTIR; Hyphenated techniques; Quantitative evolved gas analysis; Calibration techniques; Pulse thermal analysis combined with Fourier transmission infrared spectroscopy; Thermal analysis

1. Introduction

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), allows interpreting the course of the investigated reactions. The qualitative analysis is routinely done by comparing recorded spectra with key fragment ions and their relative intensities for known elements and compounds (MS) and with reference spectroscopic signals (FTIR). The development of TG-FTIR and TG-MS hyphenated techniques have been reviewed in detail by Materazzi et al. [1–3]. The first application of coupling thermogravimetric and spectroscopic analysis was reported in 1969 by Kiss [4]. He has monitored the content of water and ammonia in evolved gases formed during the decomposition of ammonium paramolybdate and paratungstate and the dehydration of copper sulfate. The water molecules after passing over calcium carbide were transformed into acetylene and the amount of the generated acetylene was measured.

A variety of efforts [5–7] were made in the following years to gain benefits from coupling complementary techniques. Compared to other methods of evolved gas analysis (EGA), FTIR is fast, sensitive and can detect almost all molecules except homonuclear diatomic gases.

In the strive for extending the opportunities of coupled techniques, successful quantification has been achieved recently, applying FTIR [8–10] or MS [8,11–14] spectrometry. Such quantification is especially important when investigating multistage decomposition reactions, or, when two or more gases evolve simultaneously. In such cases, the thermoanalytical 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 conventional method of quantification of FTIR spectra is based on time-consuming calibration, which requires the preparation and measuring of reference mixtures with varying

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concentrations. Therefore, several expensive gas standards and an accurate flow control are required to obtain reliable values of concentrations in the FTIR gas cell. Moreover, due to the influence of several experimental parameters on the intensity of FTIR signal (as e.g. change of the baseline), the calibration has to be frequently repeated. In order to avoid these problems, pulse calibration techniques were investigated by de la Guardia and co-workers [15,16]. They developed a direct and simultaneous application to quantify different fluids, e.g. butyl acetate, toluene and methyl ethyl ketone based on the use of vapor phase FTIR measurements. However, these experiments were only carried out with FTIR spectrometer without coupling it to the thermoanalyzer. First quantification of evolved gases based on the pulse technique combined with TG systems was performed by Maciejewski et al. [12,13]. Quantification of the FTIR signals in the FTIR-TG system was targeted by Eigenmann et al. at the beginning of 2000 [17] by decomposing a known amount of solids with known stoichiometry of the decomposition process and by injection of liquids into the TA-FTIR system. The extension to FTIR-TA coupled technique was achieved by Marsanich et al. [18]. They applied also the gas-pulse calibration using ammonia, carbon monoxide and carbon dioxide. They introduced the vaporization technique for calibration of the FTIR signals by liquids samples using the vaporization technique. The applied procedure enabled indirect quantification of evolved gases. The injections (calibrations) were not carried out in situ that is during the same experimental run in which the decomposition of the investigated samples was studied.

The opportunity of injecting a known amount of a particular gas or liquid into the carrier gas stream provides a quantitative calibration by relating the FTIR signal to the injected quantity of probe species. A linear relation between spectral absorbance at a given wavenumber and low concentration of gaseous compounds is postulated by Lambert–Beer's law: $A_\nu = c \times d \times \varepsilon_\nu$, where A is the integral absorbance over a wavenumber interval ν (cm^{-1}), c the concentration of the absorbing species ($mol\,l^{-1}$), d the optical path length (cm) and ε the integral molar absorption coefficient ($l\,mol^{-1}\,cm^{-1}$). Three different methods of quantifications in coupled TA systems have been applied so far. They are based on calibration by:

A) decomposing solids with well-known stoichiometric reaction e.g. calcium carbonate [12,14], calcium oxalate [12,14,19,20] or sodium bicarbonate [12,19] in TG-MS systems,
B) injection of a known amount of the calibration compound into the carrier gas stream flowing through the thermoanalyzer and evolved gas analysis device (MS [12] or FTIR [17,18]),
C) vaporization of known amounts of liquids in the thermoanalyzer itself [18,21].

In order to extend and validate the opportunities of quantification of evolved gases in TG-FTIR systems, we present the results of in situ calibrations applying different techniques and using gases, liquids and solids. Additionally, the influence of experimental parameters such as the concentration of the analyzed species, temperature and flow rate of carrier gas on the FTIR signals was investigated. Furthermore, the PulseTA® [13] developed in our group was expanded to new applications, involving liquid components. This new technique, in contrast to the known vaporization methods, is based on isothermal or non-isothermal calibration, which allows in situ calibration before the reaction (decomposition) of the target compound has already started.

2. Experimental

Experiments were carried out on a Netzsch TG 209 and 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 [13]. 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 two heated injection ports were installed before and after (on the top of) the thermoanalyzer allowing injections of liquids with a Hamilton syringe CR-700-20. The amount of injected liquid was usually in the range from 1 to 10 μl.

The flow rate was controlled by mass flow controllers, Brook's model 5850E, based on a thermal mass flow sensing technique. A helium (purity 99.999%, PanGas) carrier gas flow rate of $50\,ml\,min^{-1}$ was used. The thermoanalyzer was connected by a heated (ca. 200 °C) transfer-line to a Bruker Vector 22 FTIR spectrometer.

The FTIR apparatus is equipped with a MCT detector and a specifically 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 to $4\,cm^{-1}$ and co-addition of four scans per spectrum was applied. As a consequence spectra were recorded with a temporal resolution of about 6 s, depending on the integration methods. The IR acquired interferograms constantly during the time of the test, and the residence time of the injected species in the gas cell was about 10 s (flow rate: $50\,ml\,min^{-1}$). In this way, the spectra of all gases were averaged, without cutting peaks of the calibration pulses, which would lower the accuracy of the quantification of the evolved species.

2.1. Pulse calibration

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. In order to quantify the FTIR signals, pulses of a known volume were injected before and/or after the decomposition of the investigated sample. For injections of the liquids another home-made device consisting of a T-port tube was applied, which allows quantifying the evolved gases on the same experimental set-up.

The T-port tube heated to ca. 100 °C was closed with a septum on the top, enabling the injections of liquids or dissolved solids with a syringe. Another injection port was installed on the top of the thermoanalyzer, allowing injections of liquids after the thermoanalyzer, therefore, not being in contact with the sample and passing directly to the FTIR cell. This device was especially used for dissolved solids and liquids possessing higher boiling points (>150 °C) in order to avoid condensation on cold spots in the thermoanalyzer. The carrier gas flow was set to 20 ml min^{-1}. The flow rate has to be relatively low, because the residence time in the transfer line is very short, which, in turn, results in a very sharp and narrow FTIR signal compared to the one obtained upon injection before the thermoanalyzer. In that case, the injected gas has to pass through a much larger volume (TA) and FTIR response has a longer tailing due to prominent backmixing phenomena occurring in the TA-chamber.

2.2. Pinhole calibration

This method was used to calibrate the FTIR spectra when making calibration with organic liquids or water. Usually 25 mg of the investigated liquid was placed in the crucible closed by the lids with pinholes with different diameters (0.1, 0.5, 1 and 2 mm). The heating and flow rate were 10 K min^{-1} and 50 ml min^{-1}, respectively.

2.3. Differential calibration

Last method allows carrying out the calibration of the FTIR signal and investigation of the decomposition (or desorption) process during one run. The set-up consists of two crucibles: the first contains the liquid used for the calibration and the second one the investigated sample. The quantification is based on the FTIR signal obtained during vaporization of the liquid at low, constant temperature (25–50 °C) or during a non-isothermal run carried out with low heating rate up to a temperature lying significantly below the decomposition temperature of the solid sample. The rate of vaporization can be changed in a very broad range by varying the temperature and the pinhole diameter. The experiments were normally performed applying an isothermal period of about 30 min followed by the decomposition period with a heating rate of 10 K min^{-1}. The sample mass of the calibrated liquid was in the range of 10–25 mg and the mass of decomposed sample was 100–200 mg. In order to avoid overlapping of the calibration and measuring processes, it was important that the liquid reference material used for the calibration had fully evaporated during the isothermal run, before beginning of the decomposition of the solid. The carrier gas flow was set to 25–50 ml min^{-1}.

3. Results and discussion

We have investigated the three methods of calibration of FTIR signals described above. The presented examples describe the application of both, gases and liquids in the calibration procedure.

3.1. Quantification of FTIR signals using gases

The application of PulseTA® for quantitative interpretation of FTIR signals is illustrated by comparing results obtained by means of thermogravimetry and FTIR in a simultaneous PulseTA®-FTIR experiment. 36.15 mg of $NaHCO_3$ was decomposed under helium with a heating rate of 10 K min^{-1}. The decomposition of sodium bicarbonate occurs according Eq. (1):

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2 \quad (1)$$

In order to quantify the FTIR signal of CO_2, two 1 ml pulses of CO_2 were injected before and after the decomposition of $NaHCO_3$ (Fig. 1A).

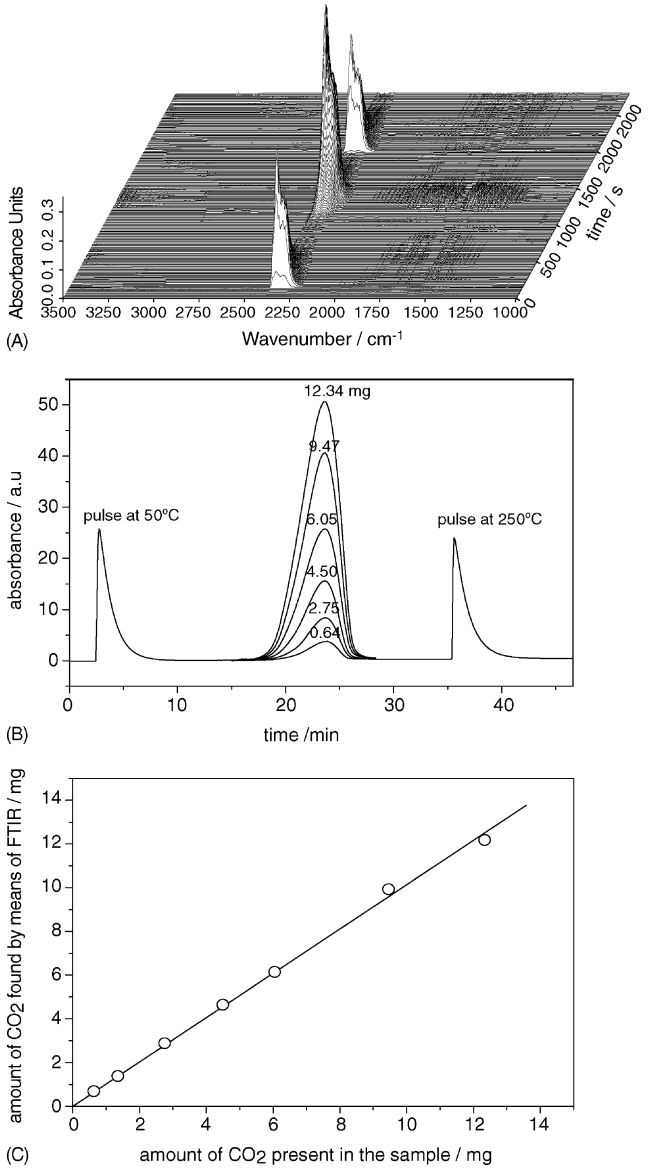

Fig. 1. (A) 3D FTIR-diagram of the calibration (two pulses) and the evolved gases during the decomposition of $NaHCO_3$. (B) Relationship between amount of evolved CO_2 in the sample and intensity of CO_2 traces recorded in TA-FTIR system. (C) Amount of CO_2 found by FTIR as a function of amount of CO_2 present in the sample.

The mean value of the integral intensities of the injected pulses was 1727 a.u., while the integral intensity of the signal of the evolved CO_2 was 9236 a.u. The temperature of the injected gas was 28 °C. The amount of CO_2 formed during the decomposition calculated from these data corresponds to 9.52 mg, which agrees well with the stoichiometric value of 9.47 mg, confirming the accuracy of the quantification method. In order to check the dependence between the intensity of FTIR signals and amount of evolved species, different amounts of $NaHCO_3$ were decomposed. The resulting CO_2 traces are presented in Fig. 1B.

Fig. 1C shows the relation between the amount of evolved CO_2 derived from FTIR signals and the amount of CO_2 present in the sample. The obtained linear dependence between the integral intensities of CO_2 traces (peak areas) and amount of evolved gas has been hold in a wide range: in the presented case from 0.64 to 12.34 mg of evolved CO_2.

The influence of the temperature (in the TA chamber) on the shape and intensity of the FTIR signals was investigated. At each temperature two pulses of CO_2 have been injected into the carrier gas stream; the integral intensity I (Eq. (2)) was independent of the temperature (50 °C: 101/100 a.u. 350 °C: 101/99 a.u. 950 °C: 101/98 a.u.)

$$I = \int_{t_1}^{t_2} \left[\int_{\nu_1}^{\nu_2} A(\nu)\, \mathrm{d}\nu \right] \mathrm{d}t \tag{2}$$

The results confirmed the conclusion by Maciejewski et al. [12] for the TA-MS system that in the range room temperature–1000 °C the shape of the spectra is slightly changing but the integral intensities remain constant. Note that at higher temperature the backmixing and diffusion in the TA are enhanced, which in turn affects the residence time distribution of the calibration gas.

The comparison of the integration of CO_2 and NH_3 signals at different wavenumbers presented in Table 1 clearly illustrates the potential source of errors in the calibration, resulting from application of too strong vibrational signals. For species giving very intensive signals as e.g. CO_2, it is relatively easy to leave the range where linearity of the Lambert–Beer relationship is guaranteed [22]. Best correlation was obtained at 3600 cm^{-1} for CO_2 ($r^2 = 0.9998$), whereas the band at 2350 cm^{-1} gave also good results ($r^2 = 0.9952$). NH_3 measurements showed good correlation at 1630 cm^{-1} ($r^2 = 0.9994$), but at 950 cm^{-1} the linear dependence was slightly poorer ($r^2 = 0.9909$).

The possibility of the exact quantification of FTIR signals by means of PulseTA® increases significantly the potential of the coupled TA-FTIR method. A further application of PulseTA® for the quantification of evolved gases is illustrated by the results obtained for the decomposition of zinc oxalate dihydrate (Eq. (3)):

$$ZnC_2O_4{\cdot}2H_2O \rightarrow 2H_2O + CO + CO_2 + ZnO \tag{3}$$

To calibrate the FTIR signals, 1 ml pulses of CO and CO_2 were injected before decomposition into the carrier gas stream. The traces of CO and CO_2 pulses were normalized in order to compare the integral intensities of traces of CO and CO_2 formed during decomposition. The resulting curves, presented in Fig. 2, indicate that the amounts of both evolved species are equal. This agrees well with the reaction stoichiometry (Eq. (3)). Note that confirmation of this stoichiometry is difficult when applying conventional mass spectrometry. Due to the fragmentation of CO_2 species the determination of the composition of CO and CO_2 mixture needs very time consuming calibration of the MS signals and accurate determination of the fragmentation pattern of CO_2 molecules in the applied mass spectrometer. The use of tabulated data of CO_2 fragmentation for calibration purposes without their experimental corroboration can lead to uncertain results due to overlapping of current ions of $m/z = 28$ resulting from the presence of CO and fragmentation of CO_2.

The gas-pulse calibration method is a single point in situ calibration, where calibration and investigated reaction are performed in the same experimental run. This enables quantification of the spectroscopic signals without taking into account several parameters such as flow rate and kind of the carrier gas, rate of the FTIR data acquisition or other experimental factors. In order to carry out the quantification in the linear range, where of Lambert–Beer' law is obeyed, the calibration should be made with the smallest possible amounts of injected calibration gases.

Table 1
Pulse calibration: FTIR integral intensity recorded during injections of CO_2 and NH_3

Loops (ml)	CO_2 (1)	CO_2 (2)	R.S.D. (1) (%)	R.S.D. (2) (%)
0.25	0.28	0.26	10.5	3.1
0.50	0.56	0.52	9.3	3.1
1.00	1.03	1.00	3.0	0.4
2.00	1.96	1.99	−1.5	−0.3
Linear correlation r^2			0.9952	0.9998
Loops (ml)	NH_3 (1)	NH_3 (2)	R.S.D. (1) (%)	R.S.D. (2) (%)
0.25	0.27	0.25	9.6	−8.6
0.50	0.54	0.52	7.3	−3.1
1.00	1.10	1.02	9.6	−6.9
2.00	1.94	1.98	−3.0	2.3
Linear correlation r^2			0.9909	0.9994

Slopes of linear regression through 0 were normalized to 1 in order to simplify comparison of the values, gained by different integration methods, for CO_2 (1: 2350 cm^{-1}) and (2: 3600 cm^{-1}), for NH_3 (1: 950 cm^{-1}) and (2: 1630 cm^{-1}).

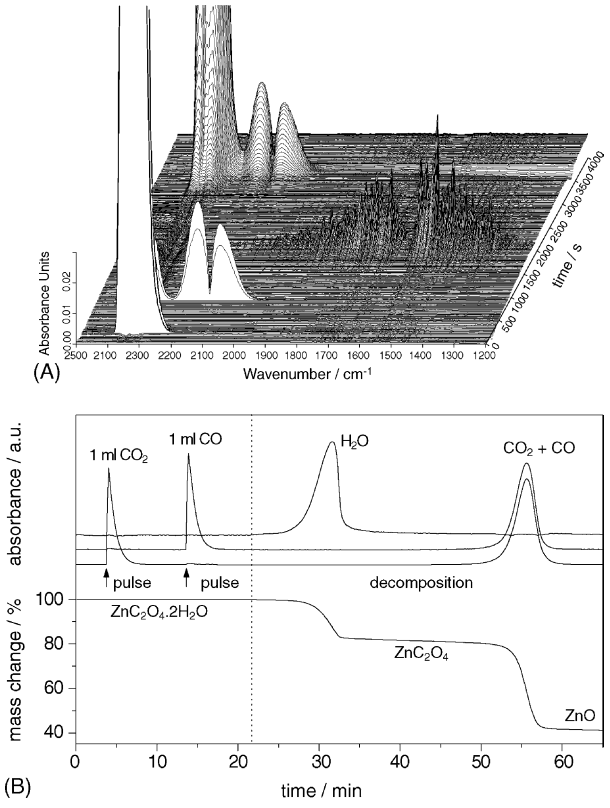

Fig. 2. (A) 3D FTIR-diagram of the calibration (first pulse: CO_2, second pulse: CO) and the evolved gases during the decomposition of $ZnC_2O_4{\cdot}nH_2O$. (B) Normalized CO and CO_2 traces obtained during calibration (injection of 1 ml CO and CO_2) and decomposition of $ZnC_2O_4{\cdot}nH_2O$; TG curve is shown in the lower part of the plot.

Additionally, the amount of the analyzed substance should be chosen in such away that the amount of evolved gases are similar to those used for the calibration, especially if adsorption bands with high intensity are used.

Marsanich et al. [18] also found a linear relationship between FTIR signals and the amount of injected gases with pulse calibration for NH_3, CO_2 and CO (0–35 μmol). In contrast to our strategy, they injected the gases not in the carrier gas flow passing through the TGA system. They applied a separate gas stream that was directly passed to the FTIR cell.

The in situ method described in this chapter was recently applied for the quantification of NO_2, NO and NH_3 during the selective reduction of NO by NH_3 over manganese-cerium mixed oxides [23].

3.2. Quantification of FTIR signals by liquids

For gases the quantification of FTIR signals is possible either by conventional calibration (varying concentrations of target gases) or, as described above, by the injection of a known amount of the calibrating gas into the carrier gas stream. For the quantification of FTIR signals by the liquids, we applied several methods, pulse calibration and two methods based on the evaporation of liquids: pinhole and differential calibrations. These methods were studied applying different organic liquids and water.

3.2.1. Pulse calibration

In order to extend the opportunities of quantifying FTIR signals, the possibility of injection of liquids into the carrier gas stream was studied. The signals resulting from the injection of pulses of ethanol into the carrier gas stream are shown in Fig. 3A. In order to check the dependence between amount of injected liquid and resulting intensity of FTIR signals, the amount of ethanol was changed from 5 to 80 μl. The traces of ethanol obtained by applying different integration modes at the characteristic wavenumbers are shown in Fig. 3B. The averaged integral intensities of the signals as a function of injected volumes are presented in Fig. 3C. The applied integration modes for the characteristic bands for ethanol revealed a linear relationship: best correlations were obtained at 3670 cm^{-1} ($r^2 = 0.9999$) and at 2970 cm^{-1} ($r^2 = 0.9999$), whereas, the linearity obtained with the band at 1055 cm^{-1} was slightly less perfect ($r^2 = 0.9996$).

Other calibrations (injection from 1 to 8 μl) were performed with hexane (b.p. 69 °C), 1-propanol (b.p. 97 °C) and water (b.p. 100 °C). The linear dependence between amount of injected liquid and integral intensity of FTIR signal (peak area) enables the quantification of FTIR data (Fig. 3D).

It is worth mentioning that the injection of various gases or liquids allows also creating own libraries facilitating identification of gaseous products evolving during reaction or desorption.

The quantification of the FTIR spectra by injecting liquids was extended to binary organic mixtures. Fig. 4A and B shows FTIR spectra of binary mixtures of methanol and methyl formate and their characteristic traces due to integration of the bands at 1030 and 1180 cm^{-1}, respectively. Fig. 4C shows a linear dependence of the intensity of the FTIR signals on the amount of injected liquids (methanol and methyl formate), and finally, Fig. 4D depicts the dependence of the FTIR absorbance ratio on the mass ratio of methanol in the mixture (wt.%). These results corroborate that if the selected characteristic FTIR bands of two or more investigated compounds do not overlap than the quantification of the resulting spectra is also possible in the case of binary mixtures. Of course, as mentioned by Barontini et al. [24], it is necessary to take into account possible factors influencing the composition of the gaseous phase during evaporation of liquids (as e.g. formation of azeotrops). It is in principle possible to obtain the vapor–liquid equilibrium data, but a serious limitation is the poor mixing (natural convection only). Sample stirring is not possible in the commonly used TG-FTIR systems.

As an example of quantification of FTIR spectra by pulse calibration with liquids, we present the determination of the amount of water evolved during the decomposition of sodium bicarbonate and dehydration of copper sulfate pentahydrate.

Fig. 5A shows the water traces recorded during two calibration pulses and decomposition of 106.5 mg $NaHCO_3$ according to reaction (1). The mean value of the integral intensities of the injected pulses was 445 a.u., while the integral intensity of the signal of the evolved H_2O was 515 a.u. The amount of injected water was 10.0 mg (ca. 10 μl). The amount of H_2O formed during the decomposition calculated from these data corresponded to 10.87 wt.%, which agrees well with the stoichiometric value of 10.69 wt.%, confirming the accuracy of the quantification method. The stoichiometry of the decomposition was corrob-

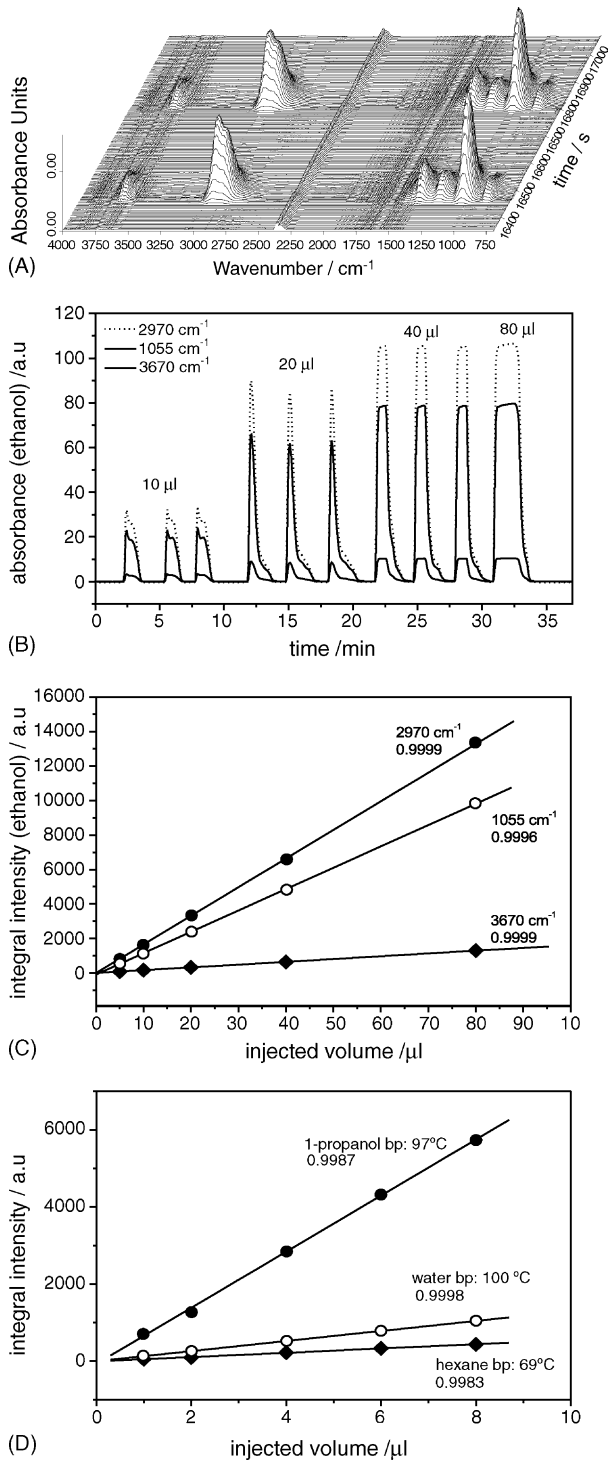

Fig. 3. (A) 3D FTIR-diagram of the calibration of ethanol (one pulse: 5 µl). (B) Ethanol traces due to different integration methods at three characteristic wavelengths for ethanol (1055, 2970 and 3670 cm^{-1}). (C) Linear dependence between the integral intensity of the FTIR signals on the amount of injected ethanol. (D) Linear dependence between the intensity of the FTIR signals on the amount of injected liquids (1-propanol, water and hexane).

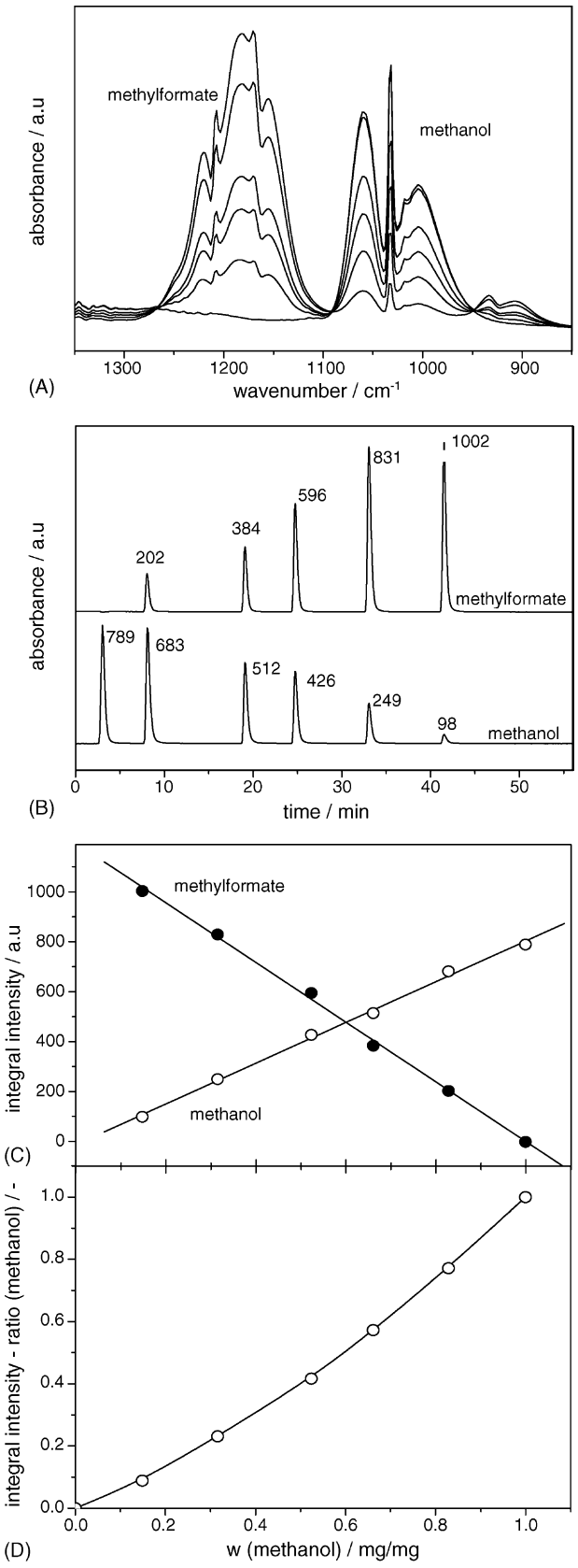

Fig. 4. (A) FTIR spectra of binary liquid mixtures of methanol and methylformate. (B) Methanol and methylformate traces as a function of the mixtures composition. (C) The dependence between the integral intensity of the FTIR signals on the mixture composition. (D) Resulted FTIR absorbance ratio vs. mass ratio (W) of methanol in the binary mixtures.

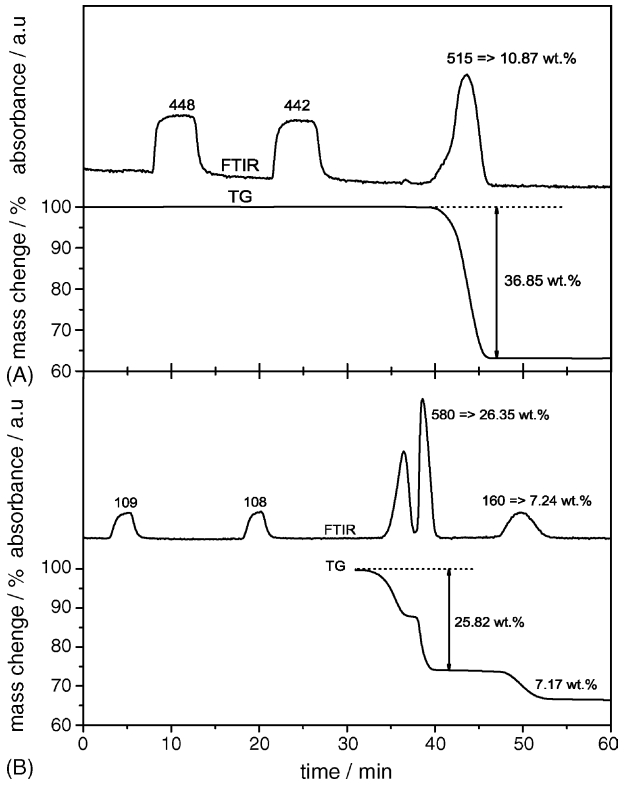

Fig. 5. Pulse calibration: water-traces recorded during decomposition of 106.5 mg $NaHCO_3$ (A) and 48.9 mg $CuSO_4{\cdot}5H_2O$ (B). Heating rate: 10 K min^{-1}, carrier gas: 50 ml min^{-1}, injected water volumes: 10 μl (A), 2.5 μl (B).

orated by the TG analysis: the observed mass loss due to the evolution of CO_2 and H_2O was 36.85 wt.%, while the stoichiometric value amounts to 36.90 wt.%.

Fig. 5B shows the water traces recorded during two calibration pulses and dehydration of 48.9 mg $CuSO_4{\cdot}5H_2O$. At lower temperatures the dehydration of the pentahydrate occurred in two steps: the observed mass loss corresponded to 25.82 wt.% and agreed well with the evolved amount of water found by means of FTIR (26.35 wt.%).

During the further dehydration at about 220 °C (between 48 and 52 min) the residual water molecules evolved (dehydration of monohydrate), as confirmed by experimental and stoichiometric mass losses (7.17 and 7.21 wt.%, respectively). The amount of water determined from the FTIR traces by comparing the integral intensity of the injected 2.41 mg (ca. 2.5 μl) water and the intensity of the decomposition peak was 7.24 wt.% which is in accord with the gravimetric results and the reaction stoichiometry.

3.2.2. Pinhole calibration

During the pinhole calibration the compound is not injected into the carrier gas stream, but placed into the thermoanalyzer and vaporized isothermally or by a linear heating ramp. For liquid mixtures (cf. binary mixtures) it is important to select a characteristic wavenumber interval to avoid overlapping of related absorption bands.

Fig. 6 shows the mass losses and FTIR signals recorded during vaporization of acetone (A), ethanol (B), water (C) and hexanol (D) from the pans with different pinhole sizes. Due to the low boiling points of acetone and ethanol remarkable mass losses were recorded immediately after starting measurement. In this case, especially when working without lid or using larger pinhole sizes, it is difficult to determine an accurate mass loss during evaporation (cf. Fig. 6A) because a certain amount of the substance will evaporate even at room temperature, which in turn, will disallow finding the relationship between the amount of evaporated liquid and intensity of FTIR traces. A lid with a pinhole size of 0.1 mm was necessary to prevent the acetone vaporization at room temperature and obtain the FTIR trace, which started at the baseline and enabled proper integration of the recorded peak. For ethanol a pinhole size of 2.0 mm was enough and for water and hexanol even no lids were necessary to achieve accurate calibration. To avoid uncertainty caused by the mass loss in the beginning of the experiment due to the high evaporation rate (vapor pressure) of some liquids, the amount of the calibrating substance used was higher than 25 mg. During experiment settling and some isothermal part of the temperature ramp the mass loss of the sample was not recorded. The calibration measurements were started exactly when the mass of the calibration liquid, measured by the internal TA balance, was precisely 25.0 mg.

The detailed results of the pinhole calibrations are listed in Table 2, the relative standard deviation (R.S.D.) was smaller than 4% for all four liquids with boiling points ranging from 56 °C (acetone) to 154 °C (hexanol). The vaporization at low temperatures at the beginning of the experiment or even before its start, which can introduce a significant error during the pinhole calibration procedure, was also reported by Slager and Prozonic [21]. They found that for highly volatile compounds e.g. acetone and methanol significant evaporation occurred before the TGA run was actually started.

The carrier gas flow is a crucial factor in the calibration procedure, it affects intensity and shape of the recorded signals. Low flow leads to higher maximum intensity of the observed spectra, but increases the residence time of the evaporated molecules in the TA-FTIR system and leads to more prominent backmixing, resulting in significant tailing of the signals. This phenomenon can cause difficulties in the evaluation of the integral intensities of the recorded signals when the reaction or desorption does not occur in a single stage due to overlapping signals. The influence of the flow on the shape and intensity of spectroscopic signals

Table 2
Pinhole calibration: FTIR integral intensity recorded during vaporization of 25 mg of different liquids (acetone, ethanol, water and hexanol) from pans covered by lids with various pinhole sizes

Sample	0.1 mm	0.5 mm	1 mm	2 mm	No lid	R.S.D. (%)
Acteone	98.7	–	101.1	101.5	98.6	1.52
Ethanol	97.2	–	99.1	102.8	100.9	2.38
Water	102.0	–	–	98.8	99.2	1.78
Hexanol	104.2	102.7	94.8	98.1	100.2	3.73

Peak areas were determined at their characteristic wavenumber and normalized to an average of 100 a.u.

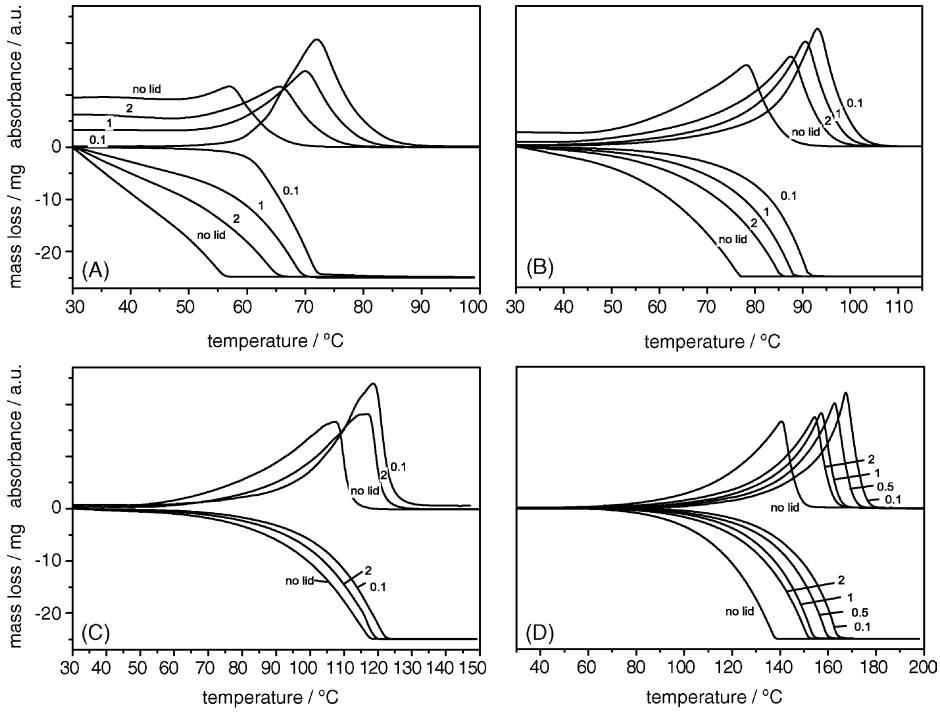

Fig. 6. Pinhole calibration of acetone (A), ethanol (B), water (C) and heaxanol (D), sample mass: 25 mg, heating rate: 10 K min^{-1}, flow rate: 50 ml min^{-1}, pinhole diameters are indicated on the curves.

has been analyzed quantitatively by some of us for the MS-TA system [11]. In order to study this influence on the calibration by the pinhole method, experiments were carried out with different carrier gas flow rates. The real progress of the evaporation is reflected by the derivative TG curve (DTG) that indicates the rate of the mass change. This progress has been compared to the recorded FTIR spectra, which allowed to investigate the changes of the shape of the recorded spectroscopic signals as a function of the carrier gas flow rate.

Fig. 7 shows the quantification of the FTIR signals using pinhole (2.0 mm) calibration of ethanol when varying the carrier gas flow rate. 25 mg sample of ethanol was heated with 10 K min^{-1}. All DTG and FTIR curves were normalized in order to allow comparison of flow rate influence on the shape of the FTIR signals. The results presented in Fig. 7 clearly indicate that low carrier gas flow leads to increase of the residence time in the TG-FTIR system and results in a long tailing of the recorded FTIR traces due to prominent backmixing. (cf. the comparison of the real rate of the evaporation process represented by DTG curve to the delayed FTIR traces for the flow of 20 ml min^{-1}). However, there exists a linear relationship between FTIR absorbances and the reciprocal values of the flow rate (Fig. 7B). A detailed study of the influence of mass transfer (by convection and diffusion) on the relation between thermoanalytical and mass spectrometric curves was reported by Roduit et al. [11].

Although, the best accordance between DTG and FTIR traces was found for the highest flow rate of 65 ml min^{-1}, in further experiments generally a flow rate of 50 ml min^{-1} was used. This flow rate proved to be a good compromise to achieve high analytical sensitivity and sampling frequency-allowing discrimination of different TG-steps in a narrow temperature window. De la

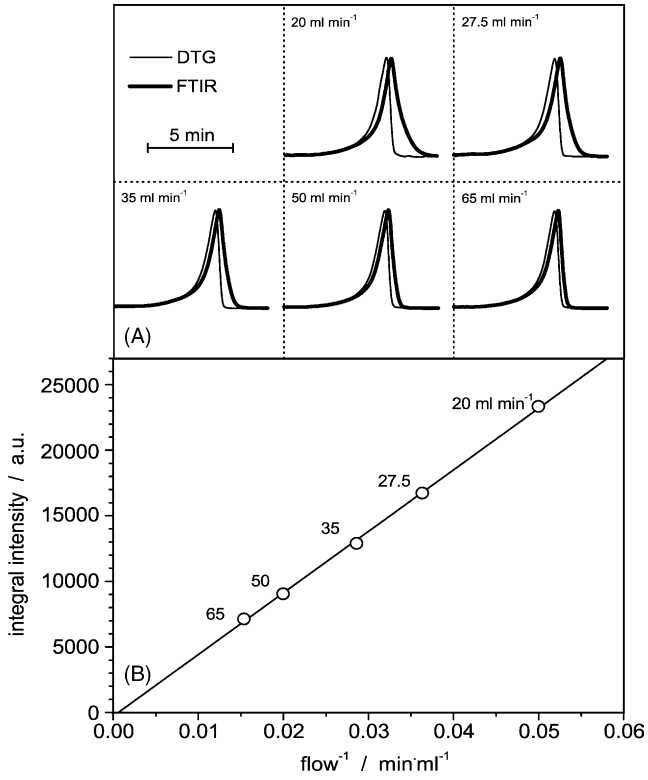

Fig. 7. (A) Pinhole calibration of ethanol with varying carrier flow rate, sample size: 25 mg, heating rate: 10 K min^{-1}, DTG (thin) and FTIR (thick lines). (B) The relationship between the integral intensity and the reciprocal flow defined as the ratio of injected volume (1 ml) to the flow rate of carrier gas (ml min^{-1}), which are marked on the data.

Guardia and co-workers [25] found that the carrier gas flow rate is a critical parameter in vapor phase FTIR spectrometric analysis which affects the analytical sensitivity and the sampling frequency. They selected a nitrogen flow rate of 50 ml min^{-1}, which allows a 20 h^{-1} sampling frequency. Marsanich et al. [18] used a similar flow rate (60 ml min^{-1}) in his studies with the same FTIR gas cell volume (8.7 ml) and FTIR path length (123 mm). Generally, it can be stated that a higher diffusivity of the evolving species in the carrier gas requires a higher minimal carrier gas flow rate to minimize the differences between thermoanalytical (e.g. TG or DTG) and FTIR signals.

The main disadvantage of pinhole-calibration beside uncontrolled mass loss due to evaporation of the sample already during experiment settling (see Fig. 6A) lies in the fact that the calibration and decomposition can not be done in one experimental run. As shown by Slager and Prozonic [21], using this method temperatures up to the boiling point of the calibrating substance are necessary to obtain the dependence between mass loss and integral intensity of the FTIR signal required for the calibration. Application of such high temperatures can, however, affect the process to be investigated, if one wants to follow it in situ. Therefore we developed and applied another method in our laboratory, which will be discussed next.

3.2.3. Differential calibration

The differential calibration is based on the isothermal or non-isothermal vaporization of a liquid compound at different temperatures, with low heating rates and simultaneous monitoring, in differential time periods, corresponding mass losses and intensities of FTIR signals. Fig. 8A shows the principle of this method applied for isothermal calibration with ethanol at temperatures between 30 and 70 °C. The integral absorbances were measured during constant time intervals (5 min) and plotted against the mass loss Δm recorded during the same time intervals by the TG signal. This dependence is presented in Fig. 8B where additionally the same relationship for water collected during the longer time intervals (10 min) is depicted. The very good regression coefficients obtained for ethanol ($r^2 = 0.99998$) and water ($r^2 = 0.9975$) indicate the high accuracy of the applied calibration technique.

The correlation of the integral intensity of the FTIR signal with the exact amount of evaporated liquid measured by thermobalance in arbitrarily chosen periods of time allowed the extension of the method for the simultaneous calibration and measurement of evolved species in one experimental set-up. Depending on the flow rate, the time lag between the beginning of the reaction (observed on DTG curve) and the appearance of the FTIR signals was in the range of 4.3 s (for flow of 65 ml min^{-1}) to 14.1 s (flow of 20 ml min^{-1}). Data collection occurred during a few minutes after steady state of the mass loss and FTIR signals had been reached. The 5.6 s delay (flow: 50 ml min^{-1}) between the real course of the reaction (DTG curve) and that of measured FTIR signals did not influence the calibration results. At low flows the back mixing became prominent leading to some tailing of the FTIR traces, but the calibration was not significantly affected by this phenomenon. The target sample and the calibration sample are placed in two

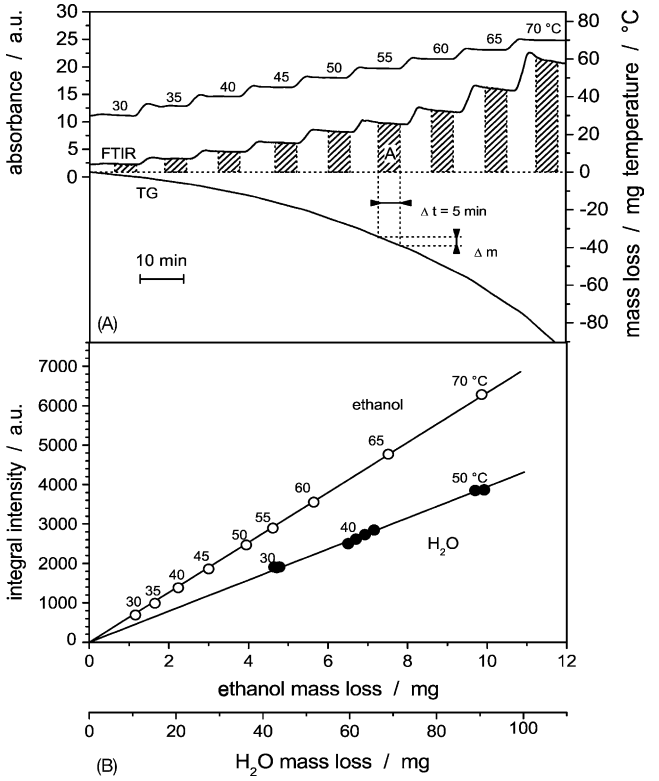

Fig. 8. (A) Differential calibration of ethanol at various temperatures. Interval time: 5 min, flow rate: 50 ml min^{-1}. (B) Linear dependence between the integral of absorbance over a specified time (5 min ethanol and 10 min water) on the amount of evolved liquids during the same time interval. Corresponding temperatures are indicated on the temperature curve. Crucible diameter was 7.5 mm for ethanol and 17.0 mm for water calibration.

separate pans, which are weighed continuously as during conventional thermogravimetric runs. The first calibration period is performed in the isothermal mode at relatively low temperature. During this period the relationship between the intensity of the FTIR signal and the amount of evaporated liquid can be determined in a few differential time periods which increases the accuracy of the calibration. After total evaporation of the calibration liquid, which is indicated by the end of the mass loss on the TG curve, the second experimental stage is started, during which the temperature in the system is raised according to the chosen temperature ramp.

This in situ calibration is shown in Fig. 9, which depicts the quantification by FTIR of the evolved water formed during dehydration of sodium bicarbonate and copper sulfate pentahydrate. Fig. 9A shows the water trace recorded during calibration and decomposition of 200 mg $NaHCO_3$ according to reaction (1). The integral of the FTIR absorbance over the interval of 10 min was 2039 a.u., while the integral intensity of the signal of the evolved H_2O was 5045 a.u. The amount of evolved water during the calibrating stage was 8.90 mg. The amount of H_2O formed during the decomposition calculated from these data corresponds to 10.98 wt.%, which agrees well with the stoichiometric value of 10.69 wt.%, corroborating the very good accuracy of the differential quantification method.

Fig. 9B shows water traces recorded during differential calibration and decomposition of 200 mg $CuSO_4 \cdot 5H_2O$. At the first

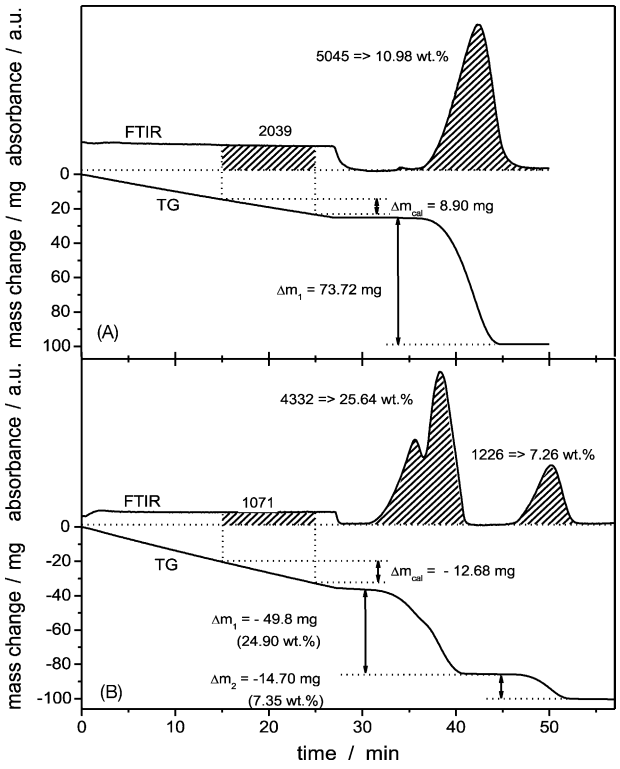

Fig. 9. Differential calibration: water-traces recorded during decomposition of 200 mg $NaHCO_3$ (A) and 200 mg $CuSO_4{\cdot}5H_2O$ (B). Heating rate: 10 K min^{-1}, carrier gas: 25 ml min^{-1} (A), 50 ml min^{-1} (B). The mass of water used for the calibration at 50 °C was ca. 25 mg (A) and 35 mg (B). Interval time: 10 min. Crucible diameter: 7.5 mm.

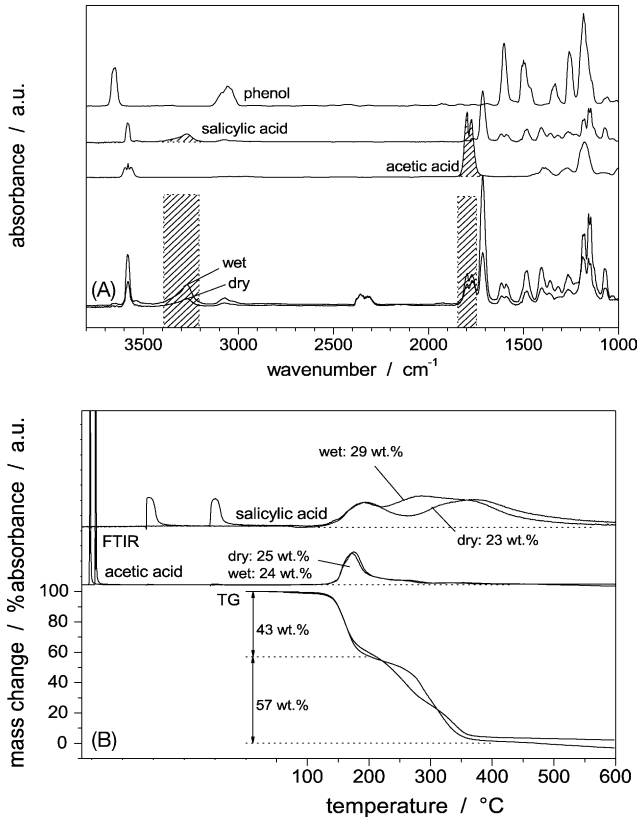

Fig. 10. (A) Extracted spectra recorded during decomposition of aspirin at approximately 260 °C under wet (thick line) and dry conditions. The window of the characteristic wavelength is marked and used for further time-resolved traces. (B) Acetic acid and salicylic acid traces recorded during decomposition of 21.5 mg aspirin under wet and dry conditions and calibration pulses injected before decomposition: Injections were done after the TA, immediately before the FTIR-transfer-line.

step of decomposition the observed mass loss corresponded to 24.90 wt.% and agreed well with the evolved amount of water found by FTIR (25.64 wt.%).

During the decomposition starting at about 220 °C (45 min), the water corresponding to the monohydrate evolved: the observed mass loss agrees well with the stoichiometric value (7.35 wt.% versus 7.21 wt.%, respectively). The amount of water determined from FTIR traces based on calibration data was 7.26 wt.% (mass loss due to release of 12.68 mg of water results in FTIR signal with an integral intensity 1071 a.u).

3.3. Quantification of the FTIR signals using solids

Some of the methods described above for the calibration of FTIR signals could also be applied with solid calibration materials. In this case, before injection into the TG-FTIR system the calibration substance must be dissolved in a solvent that possesses different characteristic FTIR bands than the calibration substance.

Fig. 10A shows the spectra recorded during decomposition of acetylsalicylic acid (ASA or aspirin) at 260 °C under dry and wet conditions, and the spectra of the main products from IR-library: acetic acid, salicylic acid (SA) and phenol. The bands used for the quantification were 1800 cm^{-1} (acetic acid) and 3300 cm^{-1} (SA).

Fig. 10B depicts the acetic acid and SA traces recorded during decomposition of 21.5 mg aspirin under dry and wet (saturation of the carrier gas by purging through water at 30 °C) conditions. For the calibration a solution of 10 mg SA dissolved in 100 ml ethanol was used. Two microliters of acetic acid and 2 μl of the SA/ethanol mixture were injected after the thermoanalyzer in order to avoid the crystallization of SA in the TA chamber. Gravimetric traces (TG) show clearly a two-step-decomposition of aspirin under dry conditions (43 and 57 wt.% for the first and second step, respectively), whereas during the reaction under wet conditions the decomposition steps are not so well resolved. Acetic acid is evolved mainly in a first step, at higher temperature (ca. 260 °C) the main decomposition product is SA and at about 360 °C additionally the evolution of phenol is observed. The amount of evolved SA found by means of FTIR under wet conditions (29 wt.%) was slightly higher than under dry conditions (23 wt.%). However, the amounts of the acetic acid were almost the same (24 and 25 wt.%) for both conditions. Asakura Robeiro et al. [26] reported also a mass loss in two consecutive steps, between 120 and 400 °C. The first step up to 260 °C occurred with a loss of 42.8% followed by 57.2% in the second step, which agrees with our results. They attributed the first mass loss to the evolution of acetic acid and evaporation of ASA and SA. They identified the evaporation process by means of chromatography but were not able to quantify it.

To characterize the influence of the gas flow on the FTIR spectra of the SA in the same TG-FTIR system, salicylic acid was heated under nitrogen with different flow rates and pressures by Jackson and Rager [27], who found considerable peak broadening because of the high boiling point of salicylic acid. With higher flow rate the IR responses would be narrower, but in TGA system high carrier flow rates can generate instability problems of the balance. The fact, that we injected the SA directly on the top of the thermoanalyzer just before the heated transferline (200 °C) to the FTIR spectrometer and kept the flow rate high (50 ml min^{-1}), leads to accurate quantification and avoids condensation of SA on possible cold spots in the system. This procedure slightly lowers the accuracy of the data acquisition due to the sharpness of the peaks caused by the high flow rate and the short distance between injection position and IR cell (cf. acetic acid peaks in Fig. 10B), but condensation or resublimation of SA would result in much larger error than some peak cutting in the calibration segment.

3.4. Comparison of the calibration methods

Table 3 compares the results of the quantification of the FTIR spectra using two in situ methods, pulse calibration (PC) and differential calibration (DC). The comparison is based on the amounts of water evolved during decomposition of sodium bicarbonate and copper sulfate pentahydrate. Both compounds decompose with well-known stoichiometry and the thermogravimetric curves recorded simultaneously allow comparing the accuracy of the applied procedures used for the quantification of the spectroscopic signals.

The relative standard deviation (R.S.D.) is calculated based on TG and FTIR results, except the decomposition of sodium bicarbonate, where TG results are not taken into account because CO_2 and water evolved simultaneously, i.e. in the same temperature range. Here the R.S.D. is related to the expected stoichiometric value only. All deviations between gravimetric and spectroscopic results are lower than 3%, which corroborates the good accuracy of the applied methods. The fact that both these methods could be applied in situ, in one experimental run, underlines their potential. They offer a much less time-consuming calibration procedure than generally applied. The opportunity of injecting the fluid before or after the thermoanalyzer widens the application range of the hyphenated TG-FTIR technique. Fluids, injected before the TA, can react with the sample (allowing e.g. the investigation of adsorption or gas–solid reactions), whereas injection after the TA allows simple quantitative analysis of the evolved species.

Table 3
Comparison between gravimetric and spectroscopic results of water evolution obtained by pulse calibration (PC) or differential calibration (DC) during the decomposition of sodium bicarbonate and copper sulfate pentahydrate

Samples	Step	Method	Stoichiometric	TG	FTIR	R.S.D. (%)
$NaHCO_3$	1	PC	10.69	–	10.87	1.68[a]
$NaHCO_3$	1	DC	10.69	–	10.98	2.71[a]
$CuSO_4{\cdot}5H_2O$	1	PC	28.84	25.82	26.35	2.05
$CuSO_4{\cdot}5H_2O$	1	DC	28.84	24.90	25.64	2.97
$CuSO_4{\cdot}5H_2O$	2	PC	7.21	7.17	7.24	0.98
$CuSO_4{\cdot}5H_2O$	2	DC	7.21	7.35	7.26	1.22

The relative standard deviation (R.S.D.) is calculated based on TG and FTIR results.
[a] R.S.D. is related to the stoichiometric expected value.

The pinhole calibration method significantly extends the scope of liquid calibration. The results presented in this study confirmed its applicability for quantification of volatile compounds. The use of different diameters of the pinhole and different temperature ramps during calibration provides the opportunity of calibrating FTIR signals with liquids having very different evaporation rate (vapor pressure) at room temperature. Slager and Prozonic [21] achieved calibrations for methanol, xylene, dimethyl formamide and dimethyl acetamid with this method using a constant flow rate, however changing experimental parameters (e.g. flow rate) limits this application. We showed that the amount found by means of FTIR absorbance is proportional to the reciprocal of the flow rate.

Another serious limitation of the pinhole method is its application with substances possessing very low boiling point as e.g. acetone. Part of the calibration agent evaporates already during sample handling and experiment settling, rendering the relation between the amount of evaporated liquid and the FTIR integral signal inaccurate.

The differential method, described in this paper, further extents the opportunities of liquid calibrations by the vaporization methods described by Slager and Marsanich et al. [18,21]. Especially high volatile materials (e.g. acetone, ethanol) can be applied without any limitations for quantification with this method. For the calibration, the experimental data from only a certain, arbitrarily chosen differential time interval are taken, omitting the ill-defined start of the experiment, where already significant mass losses may occur before the TG-FTIR data are collected.

4. Conclusions

The methods of quantification of FTIR signals based on the pulse and differential techniques, described in this work, allow in situ applications and easy and less time-consuming calibration procedure which can be used in different studies, such as the quantification of adsorption phenomena [28], gas–solid reactions [22] and decomposition of solids. The main advantages of the pulse and differential calibration methods compared to the commonly used quantification of the FTIR spectra are: simplicity, accuracy and very good reproducibility. The fact that both the calibration and experiment can be performed in a single run significantly decreases the influence of artefacts and minimizes experimental errors (e.g. shift of the base-line in FTIR cell, influence of changes in the carrier gas flow, etc.), which can bias the quantification based on FTIR spectra. The described calibration methods widen the application range of the TG-FTIR technique, which is a very sensitive and reliable tool for characterizing reactions involving solids and gases such as complex decomposition reactions. The extension of the quantification by applying liquid and solid–liquid solutions opens up further opportunities in

the area of quantification of spectroscopic signals in coupled TG-FTIR/MS systems.

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