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Advanced pulse calibration techniques for the quantitative analysis of TG–FTIR data

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Abstract

Two different pulse calibration techniques to estimate the total quantities of evolved gaseous substances formed in thermogravimetric (TG)–FTIR runs were compared and assessed. A gas-pulse calibration method was based on the use of a specific device able of sending a known quantity of a gaseous compound of interest to the FTIR analyzer. A second calibration method was based on the vaporization in the TG analyzer of liquid solutions of the compound of interest. Data obtained by these techniques were compared to those from conventional concentration-based calibration. The results confirmed the reliability of pulse calibration techniques to obtain quantitative data on evolved gaseous products in TG–FTIR applications. Moreover, both the gas-pulse and the vaporization-based calibration techniques proved to have several advantages with respect to conventional techniques. Among these are the need of a more limited number of standards and no need for online gas dilution systems.

Keywords: TG–FTIR; Hyphenated techniques; Quantitative evolved gas analysis; Calibration techniques; Thermal analysis

1. Introduction

In recent years, an increasing interest has been devoted to the development of hyphenated experimental techniques. The coupling of thermogravimetric (TG) analyzers with FTIR spectrometers for the online monitoring of volatile compounds evolved during the decomposition or gas–solid reactions taking place in the TG furnace is nowadays a widely diffused technique [1–5] and several coupling devices are commercially available. Low-volume gas cells have been specifically developed for these applications.

The main use of TG–FTIR data is the qualitative identification of decomposition or reaction products formed during the TG run [6–10]. However, several authors proposed the use of the TG–FTIR system for quantitative determinations of the compounds evolved in the TG experiments [11–15]. This requires the use of a calibration procedure to obtain quantitative data from FTIR online gas phase measurements. The conventional technique used for quantitative FTIR determinations of gaseous compounds is based on a calibration performed using different gaseous mixtures containing known concentrations of the compound of interest [14,16–18]. However, this technique

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Nomenclature

A	absorbance
c	concentration (mol l^{-1})
D	integral of I with respect to time (cm^{-1} s)
E_m	mean percentage relative error
E_max	maximum percentage relative error
F	volumetric gas flow rate (l s^{-1})
I	integrated absorbance (cm^{-1})
K	experimental correlation factor relating I to concentration (cm^{-1} $\mu\mathrm{mol}^{-1}$l)
K'	experimental correlation factor relating D to n (cm^{-1} $\mu\mathrm{mol}^{-1}$ s)
l	optical path length (cm)
n	total amount of compound evolved (mol)
N_c	measurement noise of concentration values (μmol l^{-1})
N_m	measurement noise of integrated absorbance values (cm^{-1})
r	regression coefficient
s_y	standard deviation (cm^{-1})
t	time (s)
U_pc	mean percentage uncertainty due to measurement noise
Greek letters	
ε	extinction coefficient (cm^{-1} mol^{-1} l)
$\tilde{\nu}$	wavenumber (cm^{-1})
τ_p	peak time (s)
τ_s	sampling interval (s)

has several disadvantages. If calibration standards are used as received, a high number of standards at different concentrations is required. If calibration standards are diluted in the system to obtain different concentrations, errors may be introduced. Moreover, the method directly relates the concentration to the absorbance, while in TG–FTIR experiments the total amount of substance evolved is usually the quantity of interest.

Thus, the use of concentration-based FTIR calibration techniques is time-consuming and costly. Furthermore safety and disposal problems may arise if the compounds of interest are toxic or corrosive substances. To limit these problems, pulse calibration techniques were proposed [19–22], even if up to now the application to TG evolved gas analysis was performed only for TG–MS couplings [23,24]. In these methods, a pulse containing a known quantity of the compound of interest is sent to the FTIR analyzer and the integral of absorbance with respect to time is related to the quantity injected. This was obtained by two methods: (i) by decomposing solids via a well-known stoichiometric reaction [21,22]; (ii) by the injection of a known amount of the calibration compound into the carrier stream flowing towards the FTIR analyzer [19].

However, the first method has several limits: a suitable solid and a suitable reaction should be available and no direct measurement of the amount of the calibration gas sent to the FTIR analyzer is possible. On the other hand, a system able of supplying known quantities of the compound of interest in the gas phase to the FTIR analyzer is required for the application of the second method. Several specific devices were proposed [19,23], but their use still has important limitations, in particular if substances that are liquid at ambient temperature are of interest. Moreover, the reliability of these techniques also in comparison with the conventional calibration methods needs to be further investigated.

The present study was mainly aimed to the comparison and the assessment of pulse calibration techniques for TG–FTIR applications. Two different pulse calibration techniques were considered. A gas-pulse calibration method was based on the use of a specific device able of sending a known quantity of the gaseous compound of interest to the FTIR analyzer. A second method was based on the vaporization in the TG analyzer of liquid solutions of the compound of interest. The results of the two pulse calibration techniques were compared to that of the conventional concentration-based method, to estimate the accuracy and the reliability of the proposed techniques.

2. Experimental

2.1. Materials

Calibration runs were performed using ammonia, carbon monoxide, carbon dioxide and hydrogen bromide.

The following gas chromatographic (GC) standard gaseous mixtures were used for calibration runs: ammonia/nitrogen, 507 and 4000 ppm NH_3; carbon monoxide/nitrogen, 1000 and 1995 ppm CO; carbon dioxide/nitrogen, 2500 ppm CO_2. Standards were supplied by Rivoira (Florence) or by SOL (Milan).

In a limited number of cases, the GC standards were diluted with nitrogen in the experimental apparatus described in the following. The composition of the resulting gas mixture was then checked by GC analysis.

Liquid samples used for vaporization-based calibrations were obtained diluting ammonia/water (0.103 or 0.992 mol l^{-1}) or hydrobromic acid (48 wt.%) standard solutions, all supplied by Aldrich (Milan).

2.2. Techniques

The measurements were carried out using a TG–FTIR equipment composed of a Bruker Equinox 55 spectrometer coupled with a Netzsch STA 409/C thermoanalyzer by means of a transfer line (Fig. 1). The latter is a 800 mm long Teflon tube with an internal diameter of 4 mm, heated at a constant temperature of 230 °C.

FTIR measurements were carried out with a MCT detector in a specifically developed low-volume gas cell (8.7 ml) with a 123 mm path length, heated at a constant temperature of 250 °C. The interferometer and the gas cell compartments were purged with dry air. The spectra were collected at 4 cm^{-1} resolution, co-adding 16 scans per spectrum. This resulted in a temporal resolution of 9.5 s.

The standard TG–FTIR coupling system is shown in Fig. 1c. Beside this conventional set-up, two additional configurations were used to carry out calibration experiments:

- the calibration gas flow was directly sent to the transfer line head, bypassing the TG furnace, as shown in Fig. 1a;
- the gas flow was sent from the gas supply to the transfer line head through a gas injection system described later and shown in Fig. 1b.

The gas injection system used is directly derived from that used in GC to supply known volumes of gas samples [25]. It consists in a rotary sample valve allowing a carrier gas to purge a known-volume loop, previously filled with a calibration gas of known composition. Thus, the system allows a known quantity of gas to be carried to the measurement cell by the carrier gas flow. Volumes of available loops were: 1.15, 3, 12, 50 and 200 ml.

2.3. Procedures used in calibration runs

Three different calibration procedures were applied.

- *Concentration-based calibration (method 1)*: FTIR measurements were carried out using gaseous binary mixtures of the compound of interest in nitrogen. A constant total flow rate of 300 ml min^{-1} (at 25 °C) was fed to the IR measurement cell using the system configuration shown in Fig. 1a. In each run data acquisition was performed for 2 h. This time was more than sufficient to allow the system to reach a steady state condition. Different concentrations of the compound of interest in nitrogen were used. Method 1 was applied in the present study to ammonia, carbon monoxide and carbon dioxide.
- *Gas-pulse calibration (method 2)*: A known quantity of the gaseous compound of interest was sent to the IR measurement cell using the gas injection device and the system configuration shown in Fig. 1b. As discussed above, loops of different volume were used for the experimental runs. A 100% nitrogen carrier gas flow rate of 60 ml min^{-1} (at 25 °C) was used. Experimental runs were performed on ammonia, carbon monoxide and carbon dioxide.
- *Vaporization-based calibration (method 3)*: TG–FTIR measurements were performed vaporizing water solutions of the compound of interest in the TG analyzer (Fig. 1c). At the beginning of each calibration run, a quantity of solution in the range of 15–45 μl was inserted in an alumina crucible using a chromatographic syringe. A pierced lid was positioned on the crucible, to limit evaporation caused by gas phase diffusion at the beginning of the TG run. The initial weight of the sample and the composition of the solution allowed the calculation of the quantity of the compound of interest vaporized in the TG run. The use of solutions of different concentration and of samples of different weight allowed the vaporization of different quantities of the compound of interest, that

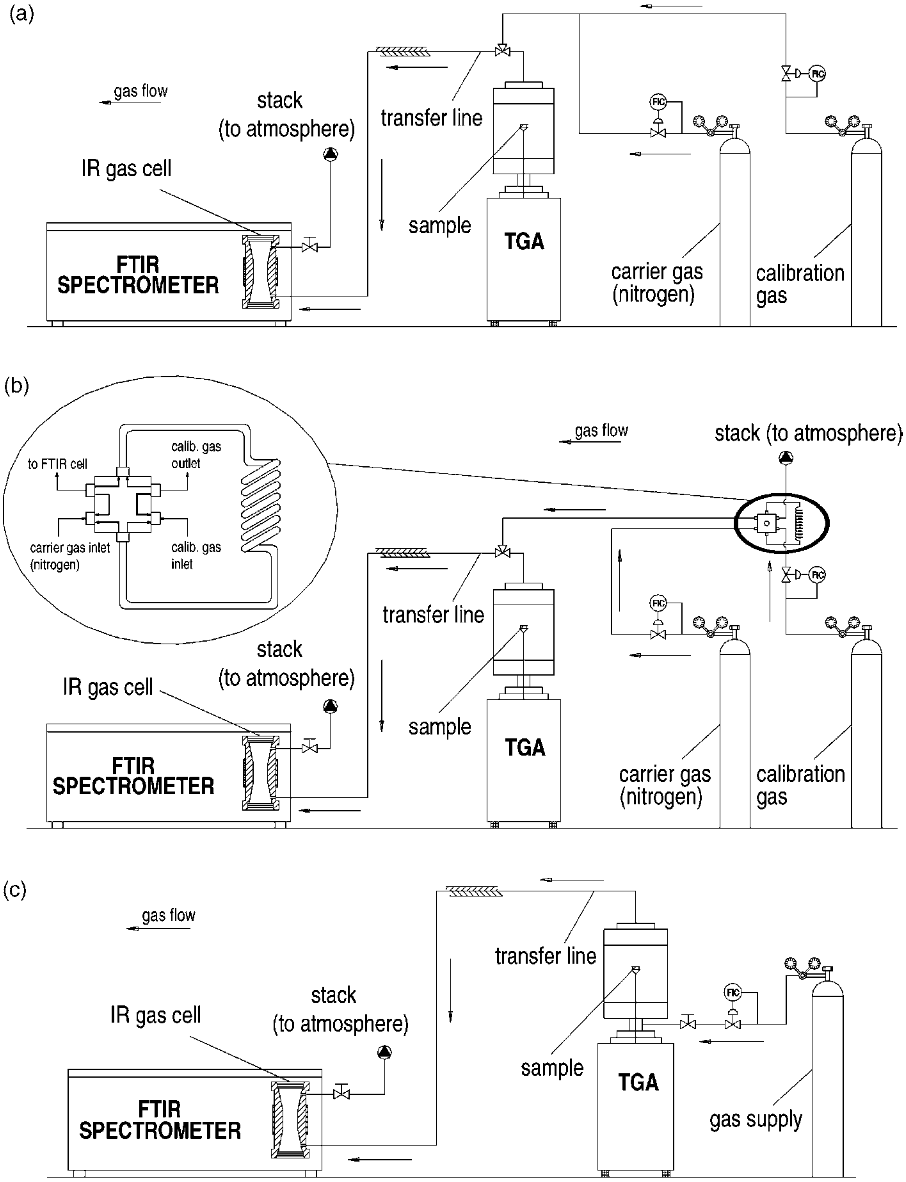

Fig. 1. Configurations of the TG–FTIR coupling used for: (a) concentration-based calibration; (b) gas-pulse calibration; (c) vaporization-based calibration.

were carried to the IR measurement cell by the carrier gas flow. A constant heating rate of 5 °C min^{-1} from 25 to 200 °C was used for experimental runs. The carrier gas was 100% nitrogen, and a gas flow rate of 60 ml min^{-1} was used. Ammonia and hydrobromic acid solutions in water were used for experimental runs.

A first dataset was obtained to calculate the calibration curves by the procedures described in the following. A second dataset was produced by method 2 for carbon dioxide and carbon monoxide and by methods 2 and 3 for ammonia in order to compare and assess the results of the different calibration methods.

The quite limited amounts of sample used in TG experiments (usually <50 mg), the limited heating rate of TG devices (usually <100 °C min^{-1}) and the presence of a purge gas that dilutes the gaseous compounds evolved from the sample during experimental runs limit the maximum quantities and the maximum concentrations of evolved gases formed in TG–FTIR applications. Thus, concentrations and quantities of calibration compounds were selected to range over the values usually of interest in TG–FTIR applications. Fig. 2 and Table 1 summarize the concentration intervals and the quantity intervals explored during calibration runs.

2.4. Analysis of calibration data

A linear relation between spectral absorbance at a given wavenumber and concentration of a gaseous compound is postulated by the Lambert–Beer law. However, due to the limited resolution of FTIR measurements, the Lambert–Beer relation is generally used in an integral form on a characteristic wavenumber interval:

$$I = \int_{\tilde{\nu}_1}^{\tilde{\nu}_2} A(\tilde{\nu})\,\mathrm{d}\tilde{\nu} = c\int_{\tilde{\nu}_1}^{\tilde{\nu}_2} \varepsilon(\tilde{\nu})l\,\mathrm{d}\tilde{\nu} = Kc \tag{1}$$

where A is the measured absorbance, I the integral value, ε the extinction coefficient of the gaseous compound, l the optical path length used in the measurement, c the concentration and $(\tilde{\nu}_1, \tilde{\nu}_2)$ the wavenumber interval selected for the measurement. The value of K depends on the compound considered, the wavenumber interval, the temperature of the gas, the optical path length and the instrument resolution. Thus, a reliable value of K may be obtained only by a calibration procedure. Moreover, K is also dependent on concentration, unless deviations from the Lambert–Beer law may be neglected [16,26].

Table 1
Results of concentration-based, gas-pulse and vaporization-based calibrations

	NH_3	CO_2	CO	HBr
Concentration-based calibration				
K'	2.91	141.6	8.21	–
E_m (%)	4.0	6.3	5.7	–
E_{max} (%)	7.3	10.3	11.9	–
Gas-pulse calibration				
Minimum quantity (μmol)	0.06	0.12	0.09	–
Maximum quantity (μmol)	32.74	20.45	16.32	–
K'	2.96	136.5	7.86	–
r	0.994	0.993	0.997	–
s_y	3.95	138.3	3.39	–
E_m (%)	4.0	6.3	5.5	
E_{max} (%)	8.8	7.9	8.9	–
U_{pc} (%)	0.07	0.01	0.04	–
Vaporization-based calibration				
Minimum quantity (μmol)	1.02	–	–	5.58
Maximum quantity (μmol)	42.33	–	–	70.25
K'	2.99	–	–	0.14
r	0.993	–	–	0.996
s_y	4.67	–	–	0.28
E_m (%)	3.87	–	–	–
E_{max} (%)	9.87	–	–	–
U_{pc} (%)	0.05	–	–	–

Concentration-based calibration procedures may be directly based on Eq. (1). Selecting single or multiple wavenumber intervals characteristic of the compound of interest, K may be estimated as a function of concentration. This approach was used in the present study to obtain a calibration curve from data produced with method 1. A single wavenumber interval was selected for FTIR quantitative determination of each compound: 942–976 cm^{-1} for ammonia, 2240–2400 cm^{-1} for carbon dioxide, 2143–2236 cm^{-1} for carbon monoxide and 2498–2516 cm^{-1} for hydrogen bromide.

On the other hand, the analysis of data from pulse calibration methods requires the integration of Eq. (1) with respect to time:

$$D = \int_{t_1}^{t_2}\left[\int_{\tilde{\nu}_1}^{\tilde{\nu}_2} A(\tilde{\nu})\,\mathrm{d}\tilde{\nu}\right]\mathrm{d}t = \int_{t_1}^{t_2} Kc\,\mathrm{d}t \tag{2}$$

where the (t_1, t_2) interval is that in which the compound of interest passes through the FTIR sampling cell (e.g. the entire duration of the experimental run). The total amount n of the compound of interest evolved during the (t_1, t_2) interval may be expressed as:

$$n = \int_{t_1}^{t_2} Fc\,\mathrm{d}t \tag{3}$$

where F is the total volumetric gas flow rate at the actual gas temperature in the measurement cell. The

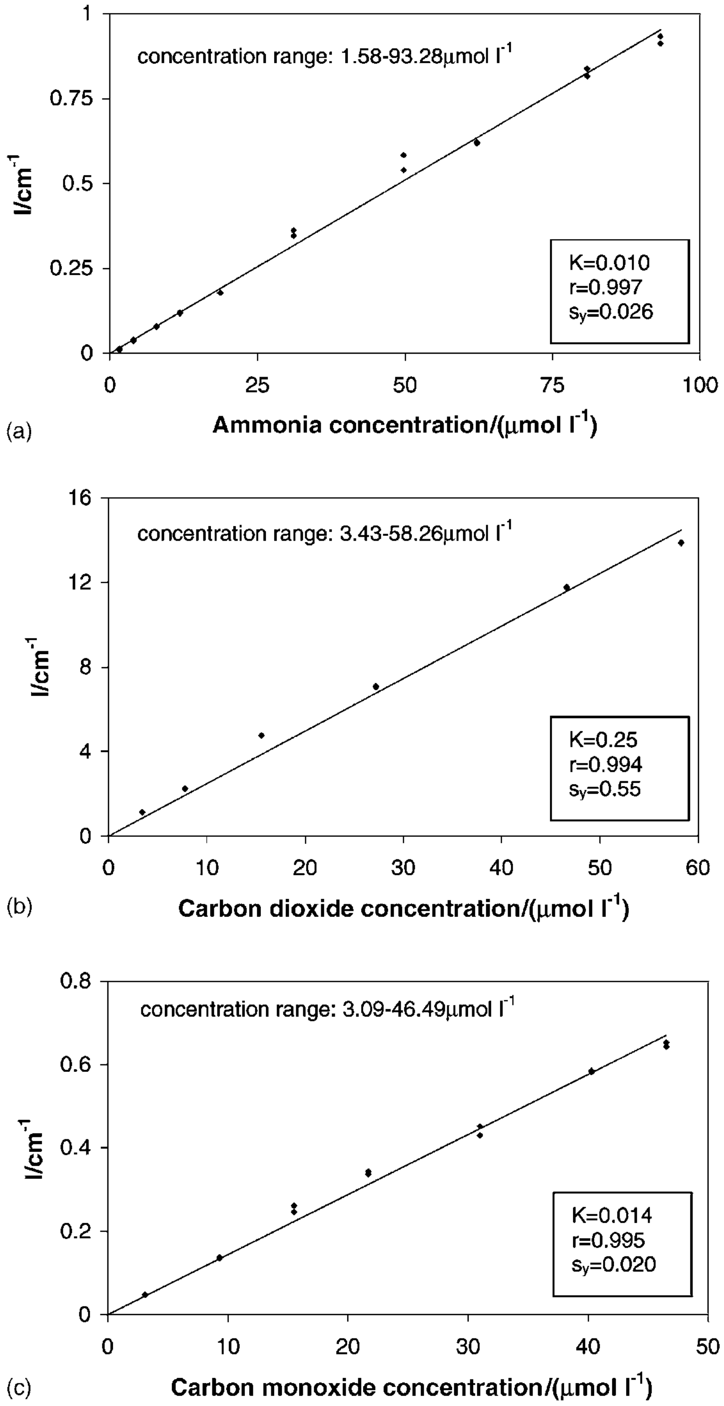

Fig. 2. Concentration-based calibration results for: (a) ammonia; (b) carbon dioxide; (c) carbon monoxide.

value of integral D may be related to n using Eqs. (2) and (3):

$$D = \frac{\int_{t_1}^{t_2} Kc\,\mathrm{d}t}{\int_{t_1}^{t_2} Fc\,\mathrm{d}t} n = K'n \tag{4}$$

where K' is a correlation factor that depends on n and on the operating conditions of the experimental run. K' may be experimentally determined by pulse calibration data. Selecting single or multiple wavenumber intervals, the value of D may be measured in pulse calibration experiments, thus allowing the estimation of K' as a function of n, obtaining a calibration curve that may be used to assess experimental data acquired in the same operating conditions. This approach was applied to analyze data from methods 2 and 3, using for each compound the wavenumber intervals listed above.

It is clear from Eq. (4) that the values of K' are dependent on the flow rate (F) of the gas through the measurement cell. However, this is not an important limitation, since the same gas flow rate may be used in calibration and experimental runs. Moreover, usually a single or a limited interval of flow rate values are of interest in TG–FTIR runs, since in general this parameter is fixed by heat flow or temperature calibrations of the thermal analyzer.

Only if deviations from the Lambert–Beer law are negligible and gas flow rate during calibrations and experiments is constant, K' is a constant that may be easily related to K:

$$D = K'n = \frac{K}{F} n \tag{5}$$

2.5. Uncertainty due to measurement noise

When comparing and assessing the different calibration techniques, uncertainty due to measurement noise should be estimated. Measurement noise for each compound was calculated by “blank” TG–FTIR measurements performed in the same conditions of calibration runs:

$$N_m = \frac{\sum_{i=1}^{z} |I_i - \bar{I}|}{z} \tag{6}$$

where N_m is the mean measurement noise, I_i a measured value of the integrated absorbance and $\bar{I}$ the mean value of I_i over the z measurements selected (usually $\bar{I} = 0$, if background is correctly subtracted). Thus, the mean absolute error caused by noise on concentration values is:

$$N_c = \frac{N_m}{K} \tag{7}$$

Detection limits of the technique were defined in the literature [11] as the concentration values corresponding to $3N_c$ calculated by Eq. (7). A proposed correlation to estimate the mean percentage uncertainty due to measurement noise in pulse calibration methods was the following [11]:

$$U_{pc} = \frac{N_c F (\tau_s \tau_p)^{0.5}}{n} 100 \tag{8}$$

where τ_s is the sampling interval (9.5 s in the experiments performed) and τ_p is the peak time (time interval during which I is above detection limits).

3. Results and discussion

3.1. Concentration-based calibration runs (method 1)

In each calibration run, a gaseous mixture with a constant concentration of the compound of interest was fed to the FTIR measurement cell, as discussed in the experimental section. The value of the integrated absorbance (I) defined in Eq. (1), was calculated using the wavenumber intervals reported above for the compound of interest.

As expected, in each run the integrated absorbance (I) rapidly reached a constant value, depending on the concentration of the compound of interest in the mixture. The asymptotic value of I was reported in Fig. 2 as a function of the concentration for each of the compounds considered. In all cases, a linear dependence of I on the gas concentration was found, as expected when a limited range of concentrations is explored [16,26]. The slopes, the regression coefficients and the standard deviations of the calibration curves obtained are also reported in the Fig. 2. The mean absolute error in concentration values due to measurement noise (N_c) resulted of <0.08 $\mu\mathrm{mol\,l^{-1}}$ for all the compounds considered.

3.2. Gas-pulse calibration runs (method 2)

Method 2 is based on sending a known quantity of the gaseous compound of interest to the FTIR measurement cell. Fig. 3 shows the results of a typical carbon monoxide calibration run performed by method 2, as described in the experimental section. Fig. 3 reports the IR spectra recorded by the system as a function of time. The passage of carbon monoxide through the measurement cell is evidenced by the absorbance values within 2000–2250 cm^{-1}. The absorbance almost immediately reaches a constant value until the gas-pulse entirely passes through the measurement cell, after about 320 s in the case. Fig. 4c shows the integrated absorbance (I) as a function of time, calculated from the data in Fig. 3. The figure clearly evidences the above described trend of absorbance as a function of time. Similar plots were obtained from gas-pulse calibration runs performed with ammonia and carbon dioxide. Typical results for these compounds are shown in Fig. 4a and b, respectively. It is clear from Fig. 4 that all the calibration runs performed show limited deviations of the system from a plug-flow behavior. As expected, deviations are more pronounced in the case of ammonia, due to the higher diffusivity in nitrogen of this compound.

For all the experimental runs, the values of I were integrated with respect to time, obtaining for each run the value of D in Eq. (2). The results obtained for ammonia, carbon dioxide and carbon monoxide are reported in Fig. 5 as a function of the quantity of the compound of interest that was present in the loop at the beginning of the run. The values of D obtained in different runs with the same loop and using the same gas concentration showed a good reproducibility (maximum relative error being <3.5% for NH_3 and <3% for CO and CO_2).

As shown in Fig. 5, a linear dependence of D with respect to n was found for all the three compounds. Thus, for each compound a linear calibration curve could be obtained, relating the value of D to the total quantity of gas that passed through the FTIR measurement cell. The slopes, the regression coefficients and the standard deviations of the calculated curves are reported in Table 1. Table 1 also reports the uncertainty in estimated molar quantity values caused by measurement noise, that resulted of <0.1% for all the compounds considered.

3.3. Vaporization-based calibration runs (method 3)

Method 3 is based on the same principle of method 2: a known quantity of the compound of interest is sent to the FTIR measurement cell. However, in method 3 the compound of interest is sent to the FTIR cell vaporizing a known quantity of a liquid solution of known composition in the TG analyzer. The use of vaporization-based calibration requires a particular attention in the appropriate selection of the wavenumber intervals used to obtain I (see Eq. (1)), in order to avoid interference caused by the other components of the vaporized solution.

Fig. 4 shows the typical results obtained in the calibration runs performed for ammonia (a) and hydrogen bromide (d). The value of the integrated absorbance (I) was reported with respect to time. The vaporization of the sample takes place in a limited temperature interval, thus generating a pulse of the compound of interest. As soon as this enters the FTIR measurement cell, the value of I grows until a maximum value is achieved, approximately corresponding to the time (and temperature) at which the compound of interest is completely vaporized. From the comparison of ammonia calibration runs in Fig. 4a, it is clear that vaporization-based calibration runs result in a profile of I with respect to time qualitatively similar to that obtained by gas-pulse calibrations. This result was likely to be expected, since both methods are based on the generation of a pulse of the compound of interest through the measurement cell.

As in the case of gas-pulse calibration, the values of I were integrated with respect to time, thus calculating for each run the value of D in Eq. (2). The results obtained for ammonia and hydrogen bromide are reported in Fig. 6 as a function of the quantity of the compound of interest that was vaporized (n). Also in this case, a linear dependence of D with respect to n was found. The slopes, the regression coefficients and the standard deviations of the calculated curves are reported in Table 1. Since the use of exactly the same quantity of liquid sample in different runs was not easy to obtain, a direct check of reproducibility of the values of D could not be performed. The uncertainty in estimated molar quantity values caused by measurement noise was estimated for ammonia and also in this case resulted of <0.1%.

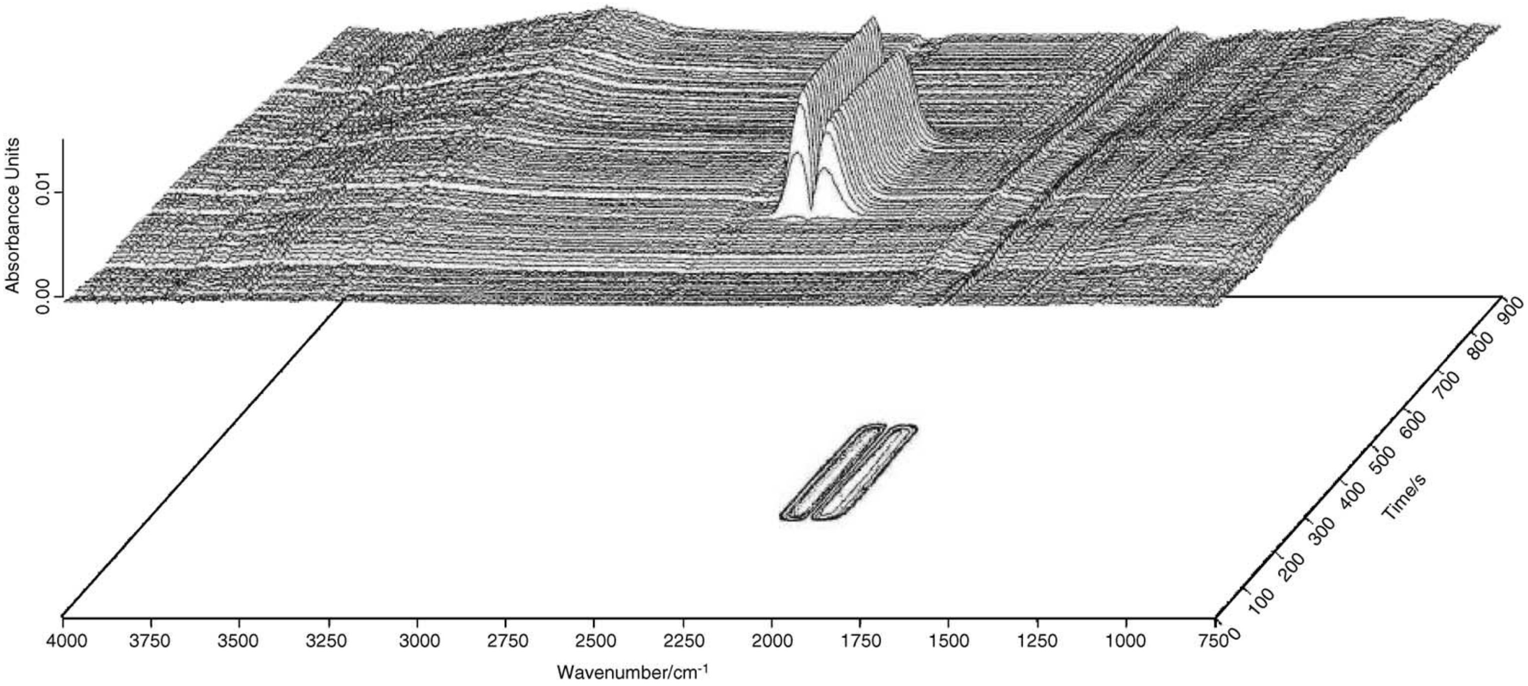

Fig. 3. IR spectra collected during a gas-pulse calibration run with carbon monoxide.

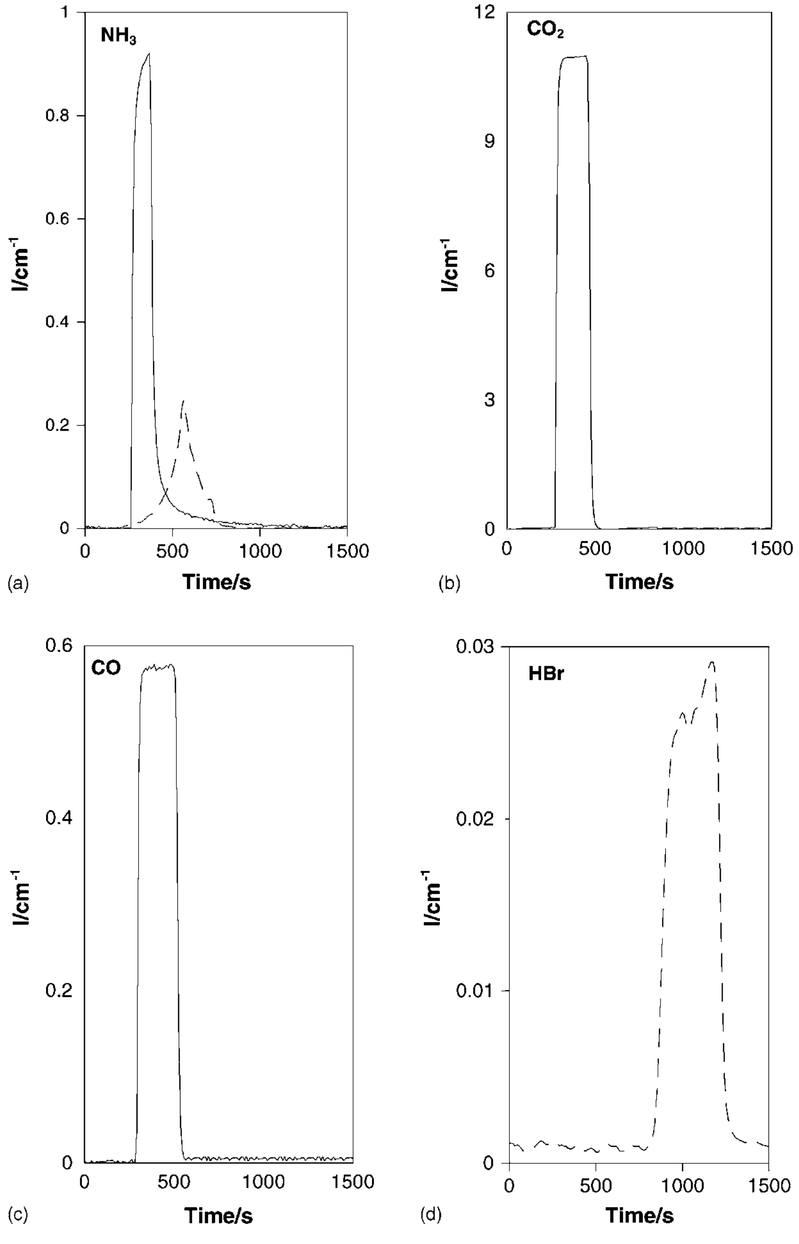

Fig. 4. Integrated absorbance profiles obtained in pulse calibration runs for: (a) ammonia; (b) carbon dioxide; (c) carbon monoxide; (d) hydrogen bromide. Continuous line: gas-pulse calibration run; dashed line: vaporization-based calibration run.

3.4. Comparison of the calibration methods

An example of the application of the different calibration data obtained was performed using the experimental results from the thermal degradation of an electronic board. Fig. 7 shows the results of a TG–FTIR run (heating rate: 10 °C min^{-1}; purge gas: nitrogen 60 ml min^{-1} at 25 °C) on a 50.31 mg sample of an epoxy-resin electronic board support, previously milled under liquid nitrogen. Fig. 7 clearly shows the

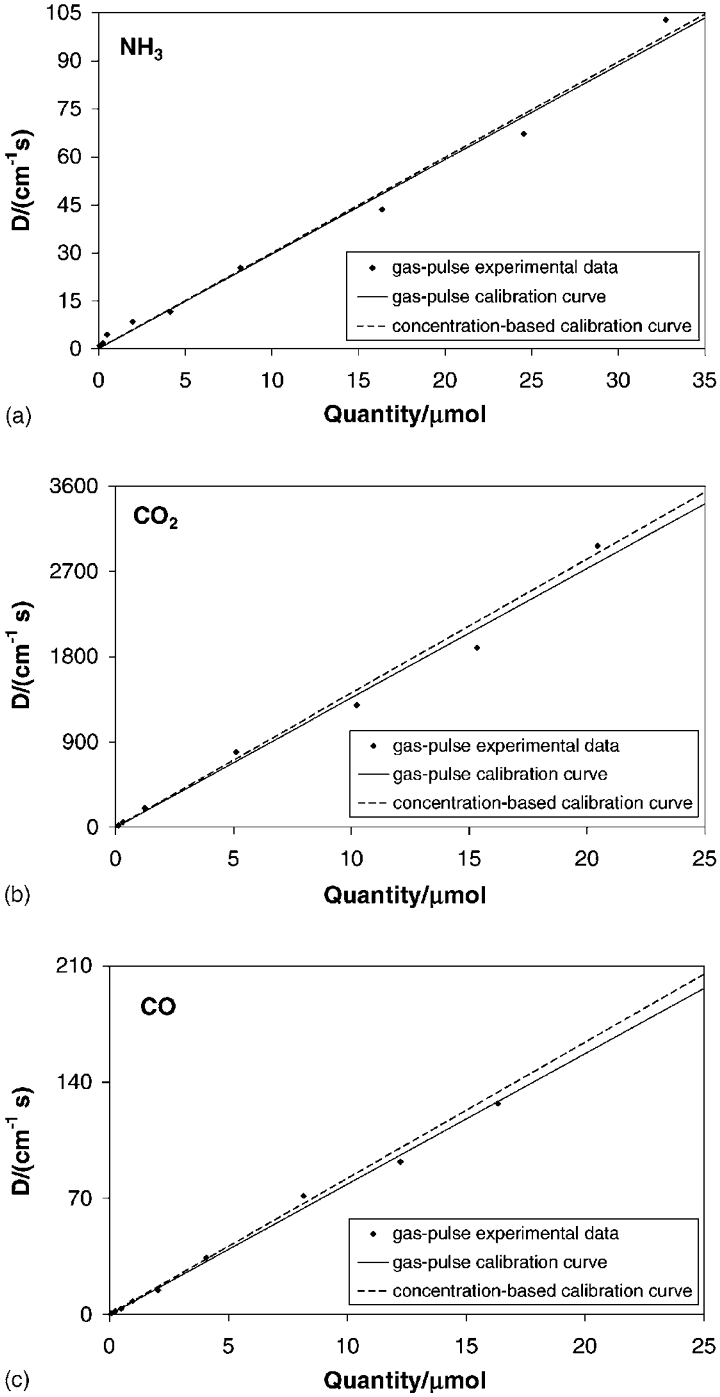

Fig. 5. Gas-pulse calibration results for: (a) ammonia; (b) carbon dioxide; (c) carbon monoxide.

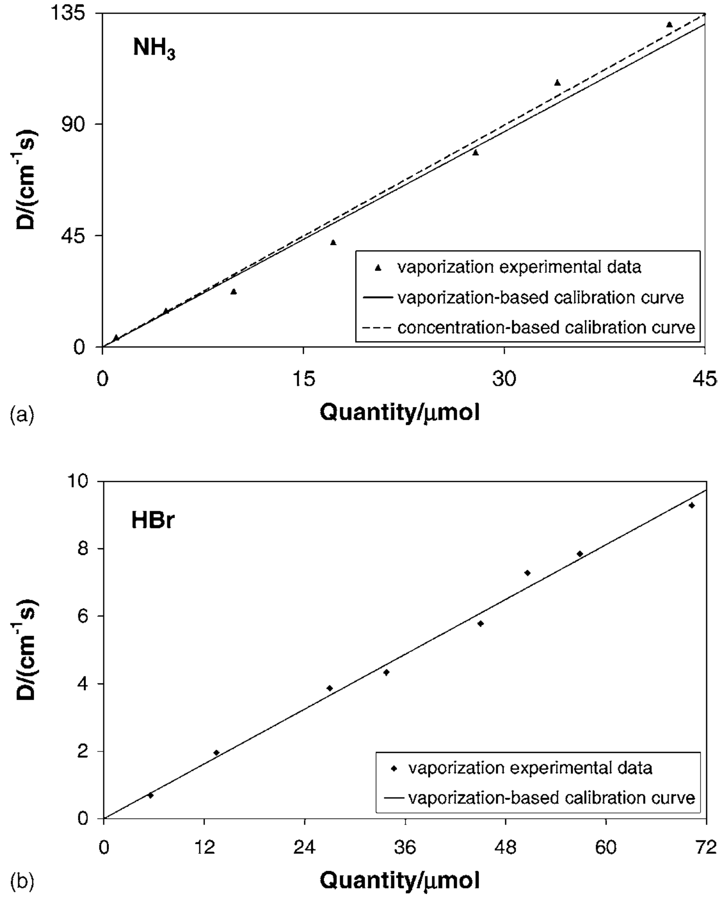

Fig. 6. Vaporization-based calibration results for: (a) ammonia; (b) hydrogen bromide.

formation of ammonia, carbon dioxide, carbon monoxide and hydrogen bromide in the thermal decomposition of the board. Table 2 reports the total quantities of these compounds estimated using the three calibration techniques. Table 2 shows that the results obtained by the different calibration methods well agree. Furthermore, data on hydrogen bromide were found to be in accordance with the results obtained by conventional titration techniques in larger scale experiments [27].

The three methods used for the quantitative calibration of FTIR measurements are not equivalent. In

Table 2
Quantitative determinations of ammonia, carbon dioxide, carbon monoxide and hydrogen bromide formed in a TG–FTIR decomposition run of an electronic board

	Calibration results		
	Concentration- based	Vaporization-based	Gas-pulse
g NH_3/100 g sample	0.05	0.05	0.05
g CO_2/100 g sample	0.68	–	0.71
g CO/100 g sample	0.03	–	0.03
g HBr/100 g sample	–	3.75	–

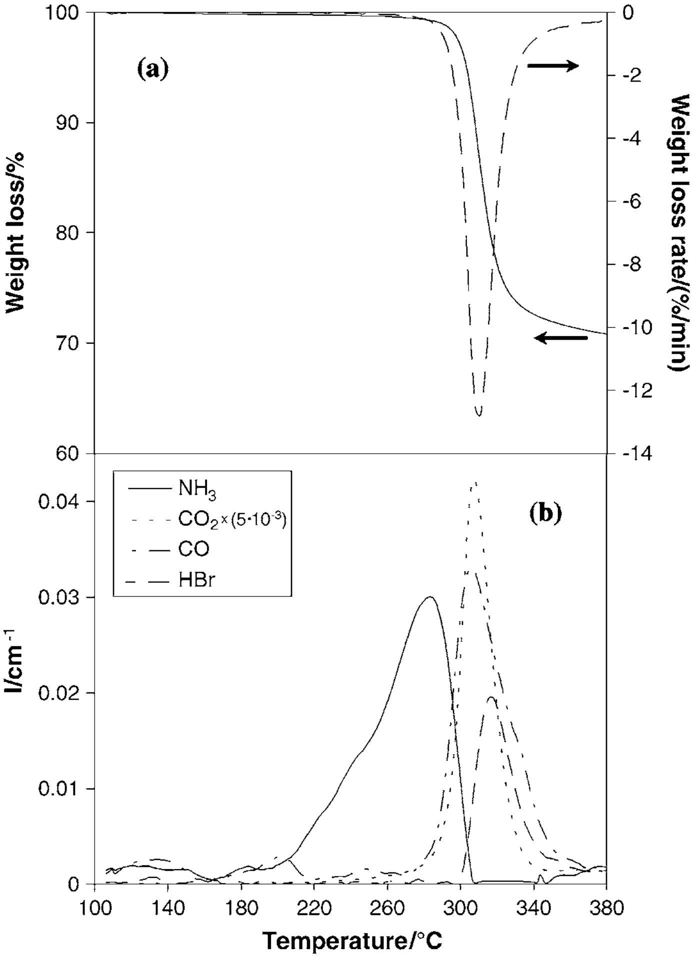

Fig. 7. Results of a TG–FTIR run performed on an electronic board sample (10 °C min^{-1}, 100% nitrogen, 60 ml min^{-1}): (a) weight loss and weight loss rate; (b) integrated absorbance profiles of selected gaseous compounds produced.

particular, only the first method allows the determination of the concentration of the compound of interest in the gas that flows through the FTIR measurement cell. Methods 2 and 3 may only be used to estimate the total quantity of the compound of interest that passes through the measurement cell over a time interval of interest. Moreover, the correlation factors obtained by the application of methods 2 and 3 are dependent on the total carrier gas flow rate (F), used in the calibration runs.

The linearity of all the calibration curves suggests that limited deviations from the Lambert–Beer relation are present in the concentration intervals explored in experimental runs. Thus, a direct comparison of the different calibration curves was possible, using the relation between K and K' shown by Eq. (5). The values of K' calculated for a 60 ml min^{-1} carrier gas flow rate from calibration data are reported in Table 1. As shown in Table 1 and in Figs. 5 and 6, limited differences are present in the calibration curves obtained by the different methods.

In order to test the accuracy of the different calibration methods, a second dataset, different from that used for the calculation of calibration curves, was produced for ammonia (by gas-pulse and vaporization runs) and for carbon dioxide and monoxide (by gas-pulse runs). Fig. 8 shows the calculated total quantity of ammonia versus the actual ammonia content of the

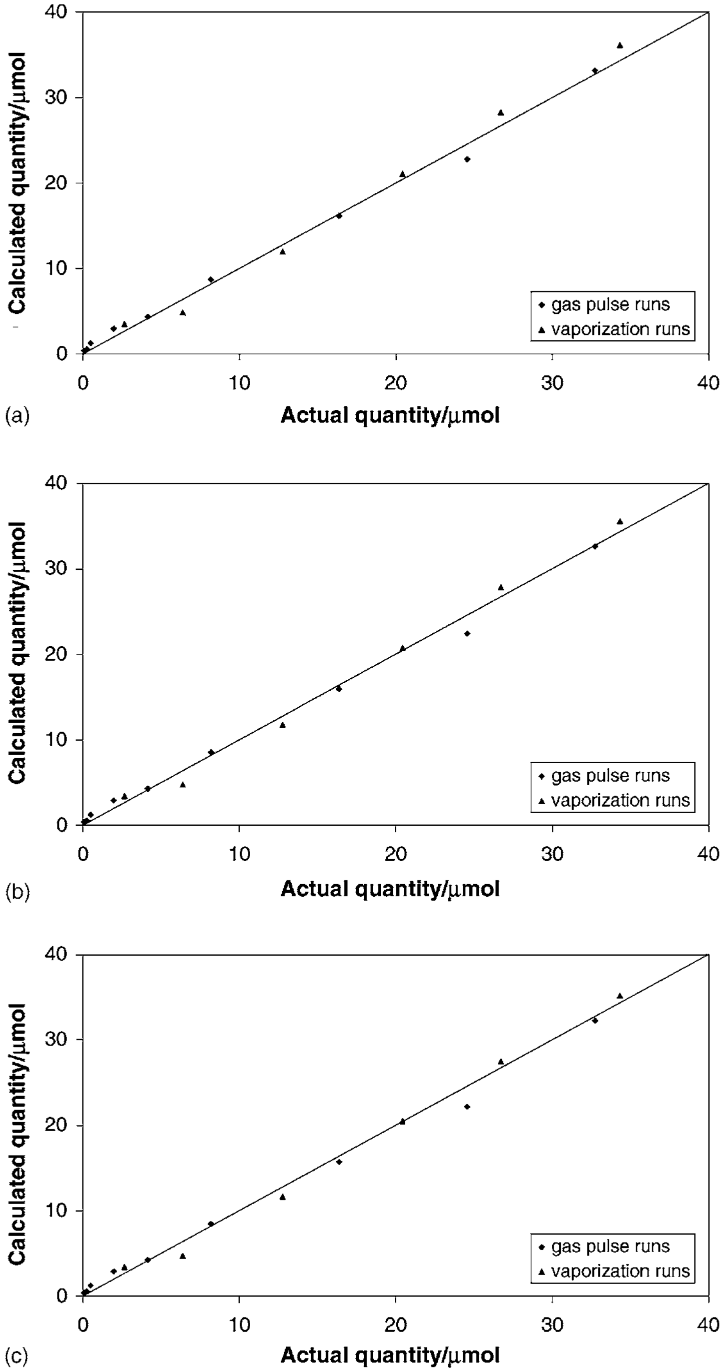

Fig. 8. Comparison of actual and calculated quantities of ammonia from: (a) concentration-based calibration; (b) gas-pulse calibration; (c) vaporization-based calibration.

pulse in experimental runs. Table 1 reports the mean and the maximum relative error of the quantities calculated by the application of calibration curves versus the actual quantities used in experimental runs. Fig. 8 and Table 1 show that the mean relative error always resulted <5% and that comparable values were found for the three different calibrations methods. Similar results were found for carbon dioxide and monoxide, as shown in Table 1.

The limited differences present in the calibration curves and in the relative errors estimated for the different methods confirm that the accuracy of the three calibration methods is comparable in the TG–FTIR applications considered. Therefore, if only the global amount of a compound is of interest, gas-pulse or vaporization-based calibration methods may constitute reliable alternatives to the conventional concentration-based calibration method.

Moreover, concentration-based calibration has important disadvantages with respect to both gas-pulse and vaporization-based calibration. Several expensive gas standards at different concentrations or an accurate flow control and measurement system is required to obtain reliable values of concentration in the FTIR gas cell. Storage and manipulation of standards may cause serious hazards in the case of toxic and/or corrosive gases, such as hydrogen chloride, hydrogen bromide or carbon monoxide. Furthermore, important limitations are present in the case of condensable compounds (i.e. compounds that are liquid at ambient temperature but that are released in the gas phase at high temperature during TG runs) since calibration standards are only available with concentrations lower than those corresponding to the vapor pressure of the compound at ambient temperature.

The gas-pulse calibration method proved to be a valuable alternative to concentration-based calibration in the case of compounds that are in the gas phase at ambient temperature and pressure. The calibration may be performed using different volume loops and a single standard gas mixture. Calibration data may be used directly to evaluate the quantity of gas evolved in TG–FTIR runs. All these factors result in a straightforward and less time-consuming calibration procedure.

However, when it may be used, the vaporization-based method seems the more attractive calibration method. Liquid solutions may be easily manipulated using conventional laboratory equipment and different concentrations of the compound of interest may be easily obtained. Very little amounts of the compound of interest (down to 1 μmol) may be easily used in the calibration runs, reducing the concentration of the solution but not the total amount of sample used in the experimental run. This avoids the need of complex low-volume liquid vaporizers, proposed for the direct quantitative calibration of liquid substances in TG–FTIR systems [23,24]. Vaporization is performed directly in the TG apparatus, without the need of external devices.

The main limitation of the vaporization-based technique is that it can be used only if a reasonably low volatility liquid solution of the compound of interest is available at ambient temperature. Furthermore, the contribution of the compound of interest should be clearly separable from that of the solvent. Nevertheless, liquid solutions with these properties can be obtained for a wide range of compounds and in particular for some hazardous gaseous compounds as hydrogen chloride, hydrogen bromide and ammonia.

4. Conclusions

Two pulse calibration techniques were assessed to estimate the total amounts of evolved gaseous compounds formed in TG–FTIR runs. Calibration data obtained by these methods were compared to those obtained by conventional concentration-based calibration. Negligible differences resulted in the absolute quantities estimated by the three techniques and no relevant differences were found in the order of magnitude of experimental error in the range of concentrations and of quantities explored. An example of application of the calibration techniques confirmed the validity of the results, also by comparison with quantitative data obtained using different analytical techniques. Thus, these results confirm the reliability of pulse calibration techniques to obtain quantitative FTIR data in TG–FTIR applications.

Both the gas-pulse and the vaporization-based pulse techniques proved to have several advantages with respect to conventional concentration-based techniques. Among these are the need of a more limited number of standards and no need for online gas dilution systems, that may induce errors in concentration values. Moreover, the use of a more limited number of standards or of liquid solutions significantly reduces safety and disposal problems that may arise if toxic or corrosive substances are used in calibration runs, such as hydrogen bromide, ammonia or carbon monoxide.

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