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# Simple methods for calibrating IR in TGA/IR analyses

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## Abstract

This work reports the calibration of the IR signals from TGA effluent gas using decomposition of solids and evaporation of liquids. The IR signal separates the TGA weight losses for quantitation, and allows a successful deconvolution of the TGA data where several compounds are evolving from the TGA at the same time. It is unnecessary to heat the transfer lines and IR cell as long as the effluent has some volatility at ambient temperature. A DSC pinhole pan makes a very effective device for the calibration of low boiling components and produces calibration data equivalent to that achieved by decomposition of solid substrates. The value of the technique is demonstrated by quantitation of overlapping components in the TGA effluent.

*Keywords:* TGA; IR; Calibration; Evolved gas analysis

## 1. Introduction

Thermogravimetric analysis (TGA) has long been used as a means for studying thermally activated processes in a quantitative manner. The addition of mass spectrometry (MS) or the complementary technique of Fourier transform infrared spectroscopy (IR) permits identification of gaseous species [1–16] evolved during thermal processes. Both of these combined techniques (TGA/MS and TGA/IR) have been practiced for some time. In many cases, the quantitative aspects of the combined techniques are taken care of by the thermal analyzer, while the spectroscopic techniques are used primarily for identification purposes. In cases where two or more gaseous species are evolved simultaneously, quantitation of the individual components by spectroscopy offers a significant advantage. Several papers have been published where the IR [16–20] or MS [6,17,21–23,28] was used to quantify the off-gases.

Each of the spectroscopic techniques has its own advantages and disadvantages, and the complementary nature of the two is well known from the general characterization of organic molecules. They are used as detectors for gas chromatography, and more recently, for liquid chromatography. Mass spectrometry is particularly useful for determining the molecular weight of evolved species, for identifying homologs in series, and for identifying homonuclear diatomic molecules. On the other hand, IR is particularly effective at identifying molecular functional groups, complex gas mixtures, isomers, and low molecular weight species (e.g., $H_2O$, CO, $CO_2$, $NH_3$). The low molecular weight species are often decomposition products which are more difficult for MS to distinguish from the ubiquitous “air background”.

Because the TGA is quite well suited for quantitation of single evolved species, this paper will describe the use of TGA for dynamic calibration of an IR used for evolved gas analysis (EGA). The use of gas phase IR has additional advantages in the numerous, well-resolved, rotational bands. As an example, many of the rotational–vibrational bands of $H_2O$ and $NH_3$, appearing in the 1500–1700 $cm^{-1}$ region, are baseline resolved, and have the potential for use in calibration of the IR for those species. In gas phase IR, it is possible to use a different spectral region if bands overlap; e.g., use of the 1653 or 3853 $cm^{-1}$ bands for $H_2O$.

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Historically calibration of the IR signal to quantify evolved solvents, and organics in general, was done using heated transfer lines to a heated IR gas cell. In this work, the use of ambient temperature transfer lines will be discussed.

Quantitation by IR has been used to great advantage in our laboratories to solve a variety of problems, including the following: thermally activated evolution of adsorbed species from used catalysts and adsorbents, determination of residual solvents and decomposition products from polymers, including poly (vinyl alcohol), vinyl acetate copolymers, polyurethanes and epoxies. Examples where the use of reactive gases as our purge gas has allowed unique quantitative analyses are: (a) the measurement of catalyst reduction using 3% $H_2/N_2$ and (b) determination of coke on catalysts using synthetic air.

## 2. Experimental

All thermogravimetric analyzers used in this study were from TA Instruments, Inc., and included models 951 and 2050 (with EGA furnace) TGA and model 2960 Simultaneous DTA/TGA (SDT). Heating rates ranged from 5 to 20 °C/min and the analyzers were purged with nitrogen, air or 3% $H_2/N_2$ at 100 mL/min. The flow rate is controlled using flow orifices and a supply pressure controlled by a two-stage regulator. This results in a very stable flow. TA Instruments Universal Analysis Software was used to analyze the TGA data.

The thermogravimetric analyzers were interfaced with either of two Fourier transform infrared (IR) spectrometers: Midac and Nicolet Avatar. Resolution was typically set at 4 $cm^{-1}$ with a gain of 1. To generate each spectrum, 32–45 scans were co-added over a minute. These spectra were saved at the rate of one spectrum per minute over the time frame of the experiments. Grams 32 software was used with the Midac IR and Nicolet Omnic software was used with the Nicolet Avatar IR to display the spectra and to manipulate the data.

The purge gas (100 mL/min) exiting the TGA passed through one meter of 1/8″ OD (3.175 mm) PTFE tubing to a 10 cm IR path length gas cell (Industrial Crystal Lab) with KBr windows. The 30 mL cell volume provides three gas turnovers/min of data collection. Initially, it was thought necessary to heat the transfer lines and the IR gas cell to avoid condensation of less volatile components in the cooler zones. However, these studies show that even polar compounds of low vapor pressure at room temperature (e.g., $H_2O$ and dimethyl acetate with vapor pressures of 2.26 and 0.2 kPa, respectively) can be transferred from TGA to IR quantitatively. This practice simplifies the apparatus as a whole.

For calibration using solids, the sample is placed in an open TGA pan (no lid) and the closed furnace is purged to remove $H_2O$ and $CO_2$ which entered the system during the sample loading process. For calibration using organic liquids and water, hermetically sealed aluminum DSC pans were used to contain the materials of interest. In the lids of these pans, 50 μm pinholes were laser-drilled to allow equilibration of the pan contents with the atmosphere in the instrument. These pans and lids have been used for vapor pressure and boiling point measurements by DSC [24–26]. Laser drilled pinhole lids are available from TA Instruments, Inc.

Reagents used in this study were of the highest purity conveniently available in the laboratory. Generally, purities ranged from reagent grade to HPLC grade.

Something to be aware of is the propensity of certain compounds to adsorb onto or react with the KBr windows of the IR gas cell. An example is the analysis of acetic acid where the potassium acid salt of the acid forms on the window. These ill-effects can be minimized between runs by frequently acquiring new background spectra, thus subtracting the spectrum of interfering compounds, or by cleaning or replacing the lines and cell windows.

Even though the IR reference library spectra [27] are obtained at various temperatures (25–290 °C), identification of unknowns by matching against the spectral library is very good.

## 3. Results and discussion

As was described in Section 2, we have chosen to maintain both the transfer line and the IR gas cell at ambient temperature. While this practice permits condensation of less volatile compounds, it does provide the advantages of simplifying the experimental setup by eliminating heat tracing and insulating the transfer lines and gas cell. For most of the materials of interest in our laboratory, vapor pressures at room temperature are high enough to keep the evolved compounds in the gas phase. This is because the sample size is normally limited to milligram quantities and the purge gas flow rate is high (100 mL/min). In our work, the lack of heat tracing may cause broadening or tailing of the IR profiles, but in general, should not affect quantitation from the IR signal, provided the IR data is collected until the profile returns to baseline. High boiling and low volatility compounds are exceptions to this rule-of-thumb and heating of the transfer lines and cell may be necessary.

Calibration of the IR signal has been achieved by several methods historically. One approach is to introduce standard gas mixtures with known concentrations of the materials of interest into the IR cell and measure the equilibrium absorbance of particular IR bands or the integrated areas of these IR bands [18,30,34–36]. Another approach is to inject known amounts of gaseous or liquid materials into the flowing gas stream and measure the change in absorbance or integrated band area over time [29–33].

We have chosen to use the weight loss of the reference material as measured by the TGA balance and the absorbance at the IR band maximum, measured over time, as our approach. The data for the $H_2O$ calibration shown in Figs. 1 and 2 are from decomposition of solids (calcium oxalate hydrate, ammonium bicarbonate) and from liquid water using a pinhole pan. These data can be used in two ways: (1) The absorbance

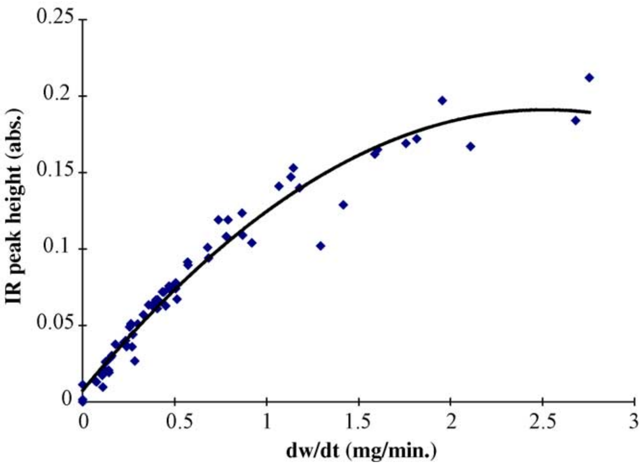

Fig. 1. $H_2O$ calibration curve using the differential of the weight change and the absorbance at the IR band maxima (various calibrants; heating rates from 5 to 20 °C/min). The line is a second order least squares polynomial fit of the data.

of the IR band at the maximum of the absorbance–time plot can be compared directly to the maximum in the differential weight loss of the TGA. Fig. 1 shows the result of this type of approach for water. Only at low concentrations is the calibration curve linear. At the higher levels, the data approaches the saturation vapor pressure for water. The height of the differential weight plot is very sensitive to the heating rate (data not shown). (2) The integrated area of the IR band absorbance–time profile can be compared to the total weight loss seen by the TGA. Fig. 2 shows the results for water using all three calibrants; each has been plotted using a different symbol. While each of the reference samples would produce a slightly different calibration curve, using all the data produces an average calibration curve of sufficient accuracy for our wide range of applications. Using the data analysis method of calculating the area of the IR profile curve was found to be more accurate over a larger dynamic range than other approaches. The signal for the IR band profile is averaged over a much greater number of absorbance readings, most of which are in the linear range of the spectrometer. Data scatter is due to changes in heating rate and sample size and can be improved if the experimental parameters are more focused. We chose to allow a large parameter space to demonstrate that very usable data can be obtained.

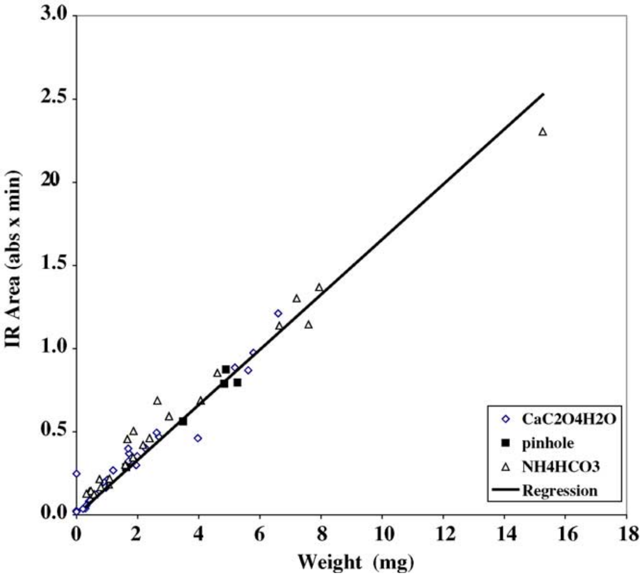

Fig. 2. $H_2O$ calibration curve using the weight loss and total area of the IR profile (various calibrants; heating rates from 5 to 20 °C/min). The line is a linear least squares fit of the data.

Because the IR cell has a volume of 30 mL, some band broadening occurs due to diffusion as the evolved gas from the TGA flows through the IR cell. This is not a problem since the calibration samples and the unknown samples are analyzed under the same conditions making the integrated areas proportional.

Two different methods of generating the calibrant in the TGA were used. They are decomposition of a solid standard to produce the component of interest and heating of the desired liquid in a sealed aluminum pan having a laser-drilled pinhole.

### *3.1. Calibration by decomposition of solids*

Calibration of the IR signal for quantitation can be accomplished dynamically in the TGA by decomposition of solid materials that produce a variety of volatile compounds. The major requirement is that the material decomposes in a manner that allows the TGA signal to be directly related to signals seen by the IR. For decomposition of inorganic materials or desorption of gases from adsorbents and catalysts, the number of components of interest is limited: $H_2O$, $NH_3$, CO, $CO_2$, and $SO_2$. These can be generated by decomposition of a variety of compounds: calcium oxalate monohydrate produces $H_2O$, CO and $CO_2$; ammonium bicarbonate and ammonium carbonate both produce $NH_3$, $H_2O$ and $CO_2$; and ammonium forms of zeolites provide $NH_3$ and $H_2O$. In these reference materials, the TGA can be used to quantify the amount of weight lost in sequence or, when more than one component is released simultaneously, the weight loss can be quantified according to the stoichiometry. For hygroscopic samples, care must be taken to separate desorption of adsorbed water from water released during decomposition. Typically this is done by allowing the samples to reach a stable weight in the dry gas stream prior to starting the experiment.

Fig. 3 shows the derivative TGA signal for decomposition of $NH_4HCO_3$ and the IR profiles for $H_2O$, $CO_2$ and $NH_3$ that occur during this decomposition. Since $NH_4HCO_3$ does not decompose in a simple series of steps, the weight of each gas was calculated based on the assumption that it decomposes to $NH_3$ (21.52 wt.%), $H_2O$ (22.78 wt.%) and $CO_2$ (55.70 wt.%). These data are presented as part of Fig. 4. Also included in Fig. 4 are data from calcium oxalate decomposition, carbon combustion and water evolved from a pinhole

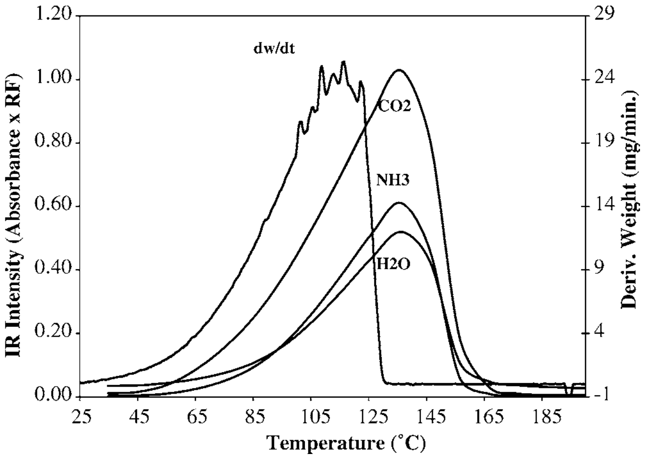

Fig. 3. DTG and IR profiles for $NH_4HCO_3$ decomposition (heating rate: 10 °C/min).

pan. The data points from these different calibrants fall on the same lines, indicating that all of these techniques provide equivalent IR calibration. The data for each component were fit with a second order polynomial. At very high loadings, the data for $NH_3$ and $CO_2$ show curvature, while the $H_2O$ calibration remains linear. The calcium oxalate decomposition sequence has been presented in other papers [17,19,28]. The middle step in the calcium oxalate hydrate decomposition produces both CO and $CO_2$ by disproportionation. Since the first ($H_2O$) and third ($CO_2$) steps do not overlap with any other component, they were used to calibrate $H_2O$ and $CO_2$. By using the $CO_2$ calibration to correct for co-evolved $CO_2$, we have successfully prepared a CO calibration curve.

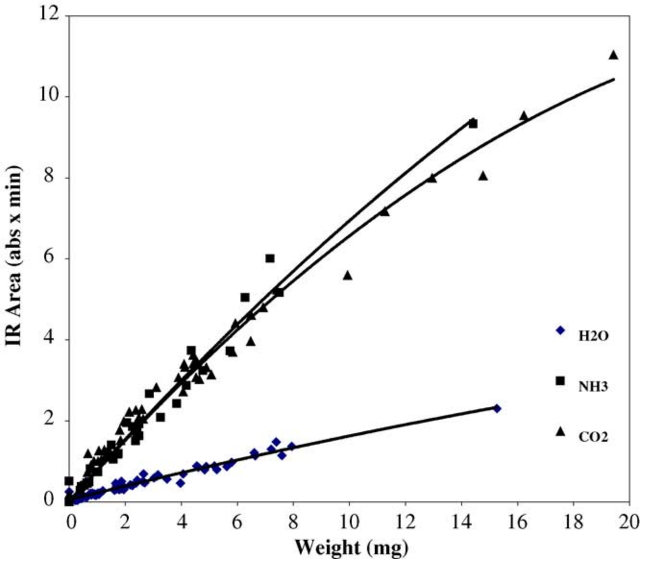

Fig. 4. Calibration curves for $H_2O$, $CO_2$ and $NH_3$ from all of the calibration experiments (various calibrants: heating rates from 5 to 20 °C/min). Lines are a first or second order polynomial least squares fit of the data.

### 3.2. Calibration using evaporation of liquids

In this case, we have constructed calibration curves for materials with boiling points as low as 56 °C (acetone) as seen in Table 1. Since the TGA uses a flowing gas (100 mL/min), volatile materials evaporate from an open pan over a wide temperature range according to their vapor pressures. For highly volatile materials, significant evaporation may occur before the TGA run is actually started, or they may be completely volatilized before the boiling point is reached. Because of these characteristics, it is difficult to obtain an accurate weight of material removed from an open TGA pan, and thus to obtain an accurate calibration constant.

In order to limit the temperature range for volatilization, the volatile calibration standards were analyzed in a DSC pan with a laser-drilled pinhole in the lid. This is similar to a procedure used for determining vapor pressure and boiling points by DSC [24–26]. By using this technique, the compound of interest leaves the pan through the pinhole only by diffusion until its vapor pressure is greater than atmospheric pressure (i.e., at the boiling point) thus improving the accuracy of the weight measurements. This technique also concentrates the material in the TGA purge gas over a relatively narrow temperature range, improving the IR signal to noise ratio.

Fig. 5 shows the derivative TGA (DTG) and IR absorbance curves for solvents with a range of vapor pressures and boiling points. In this figure, the temperatures for the DTG curve are taken directly from the TGA data file, while the temperatures for the IR curve are calculated from the time of the individual spectra and the TGA heating rate. In calculating the temperatures for the IR data, we did not account for the time needed to pass between the TGA and the IR.

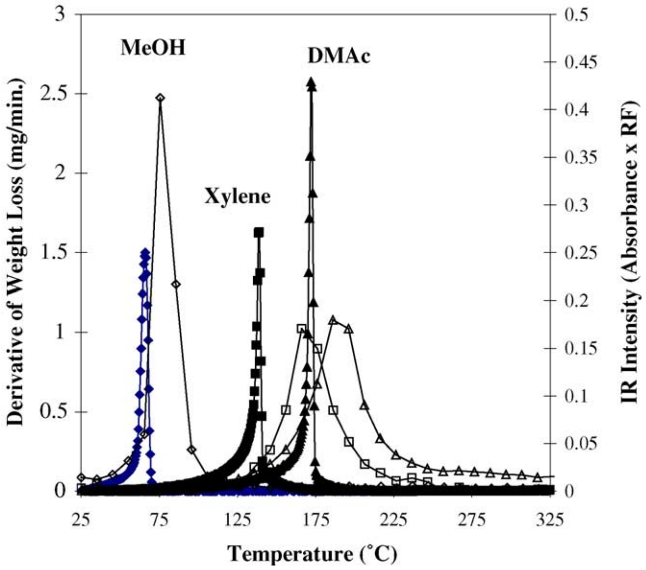

Fig. 5. Pinhole calibrations for methanol, xylene and dimethyl acetamide (TGA: filled symbols, IR: open symbols) using 1 μL sample size (heating rate: 10 °C/min).

Table 1
Solvent response factors (RF)

| Solvent | Primary frequency ($cm^{-1}$) | Response factor (abs. × min/mg) | Secondary frequency ($cm^{-1}$) | Response factor (abs. × min/mg) |
|---|---|---|---|---|
| Xylene | 3031 | 21.4 | 767 | 24.8 |
| Methanol | 1032 | 3.8 | 2966 | 9.3 |
| 2-Butanol | 991 | 30.8 | 2973 | 5.9 |
| Tetrahydrofuran | 1084 | 9.5 | 2981 | 4.6 |
| Hexane | 2959 | 4.7 | 1465 | 37.1 |
| Acetone | 1739 | 4.8 | | |
| *N*-Methylpyrrolidinone | 1734 | 2.6 | 1294 | 11.4 |
| Ethyl acetate | 1770 | 3.8 | 1244 | 2.6 |
| Aniline | 1621 | 9.2 | 3045 | 25.0 |
| Cyclohexylamine | 2933 | 3.6 | 799 | 13.0 |
| Dimethylformamide | 1714 | 1.7 | 2939 | 11.8 |
| Dimethylacetamide | 1693 | 3.0 | 2935 | 14.0 |
| Cyclohexanone | 1733 | 5.0 | 2944 | 5.9 |
| Acetic acid | 1795 | 3.7 | 1182 | 21.4 |
| Crotonaldehyde | 1724 | 3.2 | 2731 | 26.6 |
| Benzophenone | 1657 | 16.4 | 704 | 16.9 |
| Acetonitrile | 1422 | 37.5 | 2969 | 149 |
| Butylamine | 2939 | 5.3 | 777 | 7.6 |
| Acrylonitrile | 971 | 46.4 | 679 | 65.8 |
| Ethanol | 1066 | 7.0 | 2989 | 8.7 |

For methanol, a relatively volatile solvent (vapor pressure: 12.9 kPa at 20 °C) there is a delay of about 1 min between the peaks of the DTG and IR curves. This delay is primarily due to the time required for transfer of the solvent from the TGA to the IR gas cell, and to the fact that IR spectra are registered at 1 min intervals. Quantitation is still accurate because the IR acquires interferograms constantly during the time of the test, and the residence time of the plug of purge gas in the gas cell is about 20 s. In this way, the spectra of all gases are averaged, without overlap of spectra due to reading the same plug of gas more than once. The latter effect had been observed by Mittleman [17].

As the vapor pressure decreases, the delay between the DTG and IR peaks becomes greater, and the tail on the IR peak becomes longer. This effect is seen for xylene (vapor pressure: 0.93 kPa at 20 °C) in Fig. 5, where the time delay for the DTG and IR peaks is greater than that observed for methanol, and the IR signal is broadened considerably compared to the DTG curve. This band broadening is due to the sluggish movement of less-volatile material through the transfer line, where partial condensation of the material is followed by further volatilization and travel through the transfer line. Even though the shapes of the DTG and IR curves are different, the areas are consistent enough for accurate calibration of weight versus area. As might be expected, the time delay and broadening are lessened when the sample size for the calibration standard is decreased. Use of a slower TGA heating rate also improves the match between the TGA and IR signals. The effect of sample size can be seen by comparing the DTG and IR curves for xylene in Figs. 5 and 6 (1 and 5 μL, respectively).

As the vapor pressure decreases further, both the time delay and broadening of the IR signal are worsened. This effect is exaggerated with increasing sample size. This can be seen by comparing the DTG and IR curves for dimethyl acetamide (vapor pressure: 0.2 kPa at 20 °C) in Figs. 5 and 6. With the 5 μL sample in Fig. 6, the apparent delay between the DTG and IR signals is about 85 °C, and the IR signal broadens to the point where it does not return to baseline by 325 °C. Even with these severe effects, moderately high boiling solvents can be calibrated using the TGA/IR system without heating the transfer line or the IR gas cell, provided the amount of solvent to be detected is kept below its saturation vapor pressure. This can be accomplished by minimizing the amount of sample used on the TGA pan.

The effects of low vapor pressure on the calibration curve can also be seen in the plot of the IR profile area versus sample weight, as in Fig. 7. Even with band broadening, the

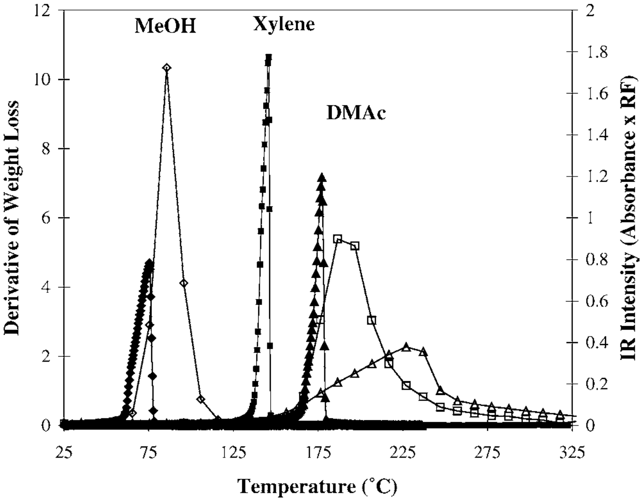

Fig. 6. Pinhole calibrations for methanol, xylene and dimethyl acetamide (TGA: filled symbols, IR: open symbols) using 5 μL sample size (heating rate: 10 °C/min).

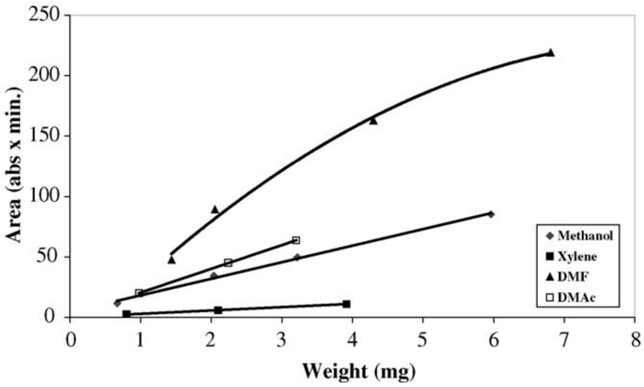

Fig. 7. Typical calibration plots for methanol, xylene, dimethyl formamide and dimethyl acetamide (heating rate: 10 °C/min). Lines are a first or second order polynomial least squares fit of the data.

area/weight curves are linear up to sample weights of 6 mg for methanol, and 3 mg for xylene and DMAc. For DMF, however, the effects are more pronounced, and linearity of the calibration is not maintained. The IR profile for DMF (data not shown) was similar to that of DMAc (5 μL) therefore integration of the peak must be continued over a longer time span to ensure that all the area is included. It is obvious in the curvature of the DMF data that some of the IR area is not being detected as the sample weight increased. Linear calibration curves for high boiling solvents, without the use of a heated transfer line, are accurate only over limited ranges of sample weights. The range over which the material of interest can be quantified must be determined experimentally.

Since these calibrations with low boiling solvents were obtained with the pinhole pan technique, evolution of the material from the pan occurs over a short time interval. This has the beneficial effect of increasing the IR signal, but there is noticeable band broadening in the IR signal due to diffusion effects. With actual samples (e.g., polymers with residual solvent), there is a natural broadening of the DTG signal due to the desorption process, thus lowering the instantaneous rate of solvent evolution, and increasing the probability that the IR signal will be in the linear range of the calibration curve.

Calibration response factors (essentially the slopes of the calibration curves) for a variety of solvents are reported in Table 1. Vapor pressures of these compounds range from 12.8 kPa for methanol to 0.065 kPa for aniline. These response factors are calculated as the averages of three or more experiments using different sample sizes. While these values are only valid for our particular setup (100 mL/min, 10 cm cell path, 10 °C/min heating rate, and the specific instruments used to collect the data), they are presented as an indication of the relative responses of various compounds.

### *3.3. Example*

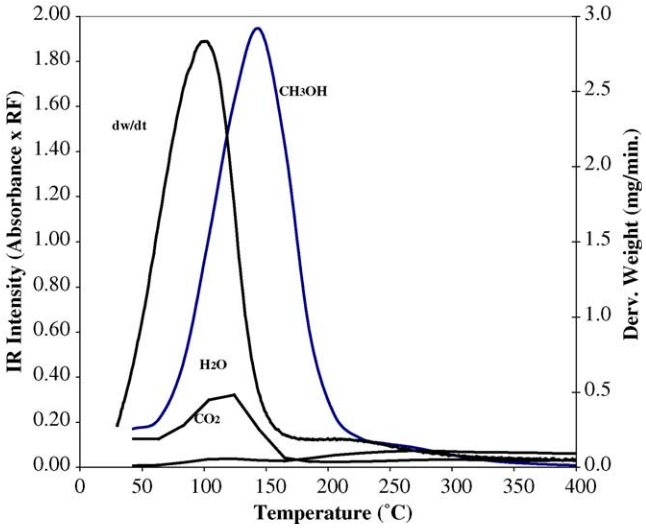

Fig. 8. DTG and IR profiles for carbon adsorbent (heating rate: 20 °C/min).

Activated carbon is often used as an adsorption bed in the gas feed line for chemical processes. In this case, the problem was to identify and quantify the components adsorbed on the bed. The IR successfully identified water, methanol and carbon dioxide, which desorbed simultaneously. Fig. 8 shows the differential weight loss and IR desorption profiles for the TGA/IR experiment. The TGA shows a weight loss of 12.36%. The IR calibration curves created by integrating the area under the IR profile were used to quantify the amounts of water (1.33%), methanol (10.33%) and carbon dioxide (0.69%). The sum for these components (12.35%) agrees well with the weight loss seen by TGA. Typical material balances between the IR quantitation and the TGA weight losses have been less than 1% in our laboratory.

## 4. Conclusions

Calibration of the IR signal from a coupled TGA/IR experiment can be achieved using both solids decomposition and liquids volatization. For the solids, it is necessary to have a weight loss that has only one decomposition product, or a weight loss which can be deconvoluted by knowing the chemistry or stoichiometry of the decomposition process. For liquids, the use of a pinhole DSC pan is a successful means of delaying volatilization until the boiling point of the volatile material is reached. In this study, data for water from solid decomposition and the pinhole DSC pans are not significantly different, indicating that the calibration procedures are equivalent.

As long as one is not interested in very high boiling materials or materials with very low vapor pressure at room temperature, it is not necessary to heat the transfer lines to the IR or the IR cell itself. Use of this technique greatly enhances the ease of system setup. In spite of tailing that occurs, very useful calibration curves can be achieved.

Calibration using organic materials was done in order to quantify the residual solvent in polymer formulations, the amount of material appearing as a decomposition product and the amount of material adsorbed on an adsorbent. In many cases, as seen in the carbon adsorbent example, solvent volatilization occurs at the same temperature as does evaporation of residual or adsorbed moisture. This makes quantitation of the solvent impossible by TGA alone, and demonstrates the utility for coupling TGA with IR. Another example is found in the thermal decomposition of ammonium chabazite [37].

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