BIGGER IS BETTER: PUSHING THE LIMIT OF TG AND TG/FTIR

Abstract

In Thermogravimetry (TG) and TG/FTIR systems, there are many variables that can affect the detection limit of the system. It is demonstrated in this paper that the larger the sample size, the better the detection limit. For TG/FTIR, with a certain kind of TG/FTIR interface, the detection limit is dependent upon the sample holder volume of the TG system. It is proved that, for a sample mixture, the ratio of balance sensitivity to standard sample holder volume should be used to characterize the detection limit of TG, while the standard sample holder volume of the TG system should be used to characterize that of TG/FTIR.

Introduction

Thermogravimetry (TG) has widely been used as a tool to detect material composition. ' When the sample's evolved gases are also of interest, an evolved gas analyzer (EGA) unit will be utilized. Among the options for EGA, Fourier Transform Infra-Red spectroscopy (FTIR) and Mass Spectroscopy (MS) are two techniques often used. Between TG/FTIR and TG/MS, TG/FTIR is the more common combination because of the relatively simple coupling technique involved.

In a TG system, the important measured parameters are weight, temperature and time. Weight is the signal which is the most important of these, and much is made (correctly) of capacity and sensitivity of the balance used in the TG system. In FTIR, besides the accuracy of the wavenumber, another important feature is the signal to noise ratio or sensitivity.

To measure small amounts of a component in a sample, the detection limit will ultimately decide if the measurement can be made. The detection limit is defined as the smallest concentration or percentage of a components which can be detected. Such a definition has been widely used for various analytical instrumentation, and in general, the higher sensitivity, the better the detection limits. However, this term has not been applied to TG or TG/FTIR, because sample size will decide the amount of evolved gases and sample weight loss/gain, and eventually the detection limit for a sample.

It is the purpose of this paper to demonstrate that the detection limit is directly related to the sample size, for both TG and TG/FTIR.

Experimental

Experiments were performed on a Synergy TG-FTIR system. The thermogravimetric analyzer was a Thermo Cahn TG-131 with a capacity of 100 grams and maximum temperature of 1100 °C. The FTIR was a Thermo Mattson RS-2. They were coupled by a Thermo Cahn TG/FTIR interface.

In order to show the effect of sample size on TG and TG/FTIR, two sets of experiments were performed. One set of experiments was performed where 100 % of the interested component was solid. Only the sample sizes were decreased, along with volume. Another set of experiments was performed with liquid samples which had different concentrations. The sample volumes were kept about the same.

Calcium oxalate monohydrate ($CaC_2O_4 \cdot H_2O$, from Aldrich) and calcium carbonate ($CaCO_3$, from Aldrich) were used as the solid samples. The sample sizes ranged from 190 mg to 50 μg. Formaldehyde solution at various concentrations, 0.0 % to 1.15 % (diluted from 37 % formaldehyde solution (from Aldrich)), were used as the liquid samples. 1.0 ± 0.1 mL (about 1.0 gram) of solutions were used for experiments.

Samples were heated under a nitrogen environment. Solid samples were heated from room temperature up to 1000 °C at a heating rate of 10 °C/min. The temperature profile for liquid samples was: an isotherm for 10 minutes at room temperature, a ramp to 200 °C at a heating rate of 5 °C /min, followed by an isotherm for another 15 minutes. The evolved gases passed through a heated gas cell where the FTIR spectra were collected. The FTIR spectra were collected continuously at a resolution of 4 cm^{-1}, and the sampling scan number for each spectrum was 64 (about 11 seconds). The FTIR background was collected at 256 scans, before loading the sample. The transfer lines and the FTIR cell of TG-FTIR interface were heated at 250 °C to prevent evolved gases from condensing.

Results and Discussion

Solid and liquid samples are analyzed for two different purposes, one is about TG, and another is about TG/FTIR. Therefore, the following results and discussion section is divided into two parts, TG and TG/FTIR.

The Effect on TG

Figures 1a, 1b and 1c show TG curves for $CaC_2O_4 \cdot H_2O$, $CaCO_3$ and formaldehyde solution, respectively. Calcium oxalate monohydrate weight loss curve, Figure 1a, shows three distinguishable weight loss steps. Figure 1b shows the typical weight loss curve for calcium carbonate. In Figure 1c for the formaldehyde solution, there is only one weight loss step. One can see that it is impossible to separate the weight loss steps for water and formaldehyde due to the high vapor pressure of formaldehyde.
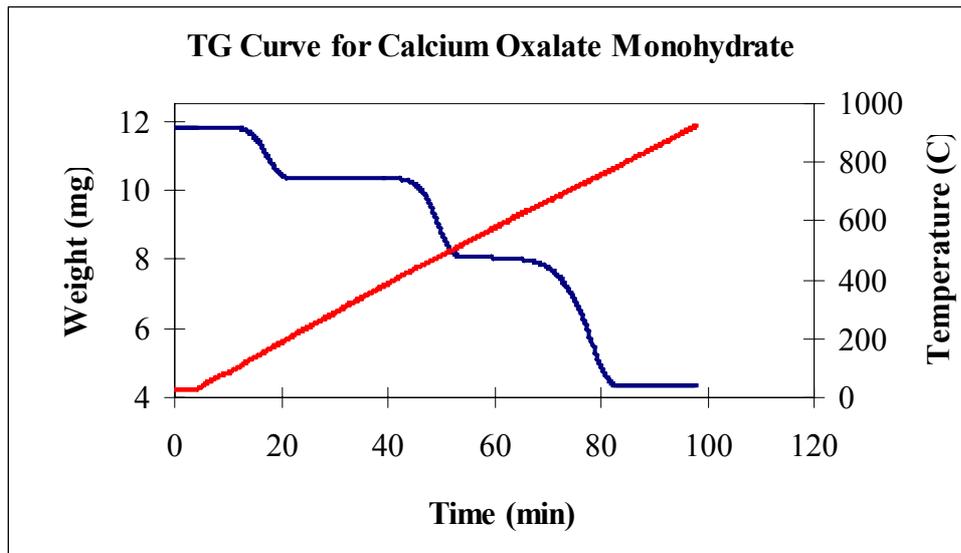
TG Curve for Calcium Oxalate Monohydrate

Figure 1a: Curve of Weight change vs. temperature for Calcium Oxalate Monohydrate

TG Curve for Calcium Carbonate
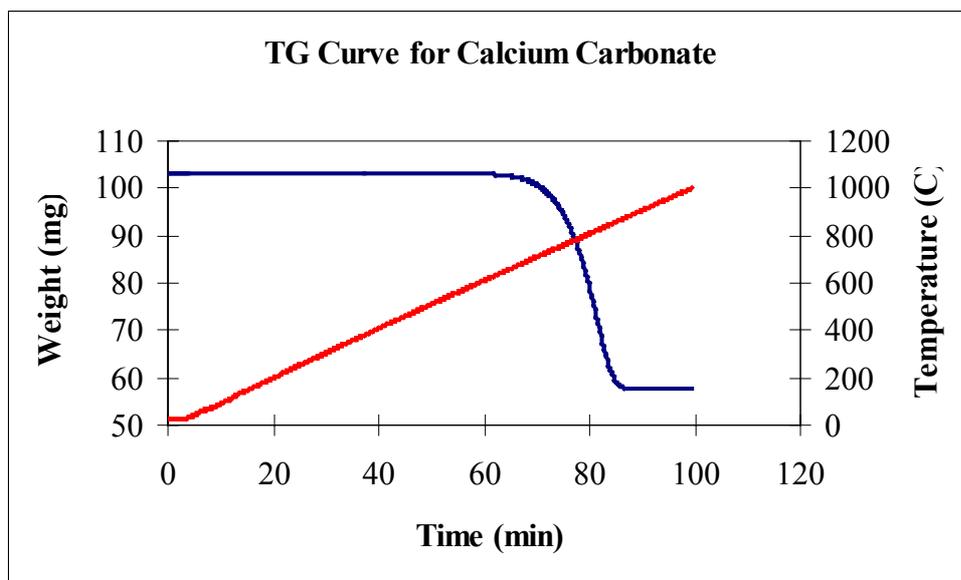
Figure 1b: Curve of Weight change Vs temperature for Calcium Carbonate
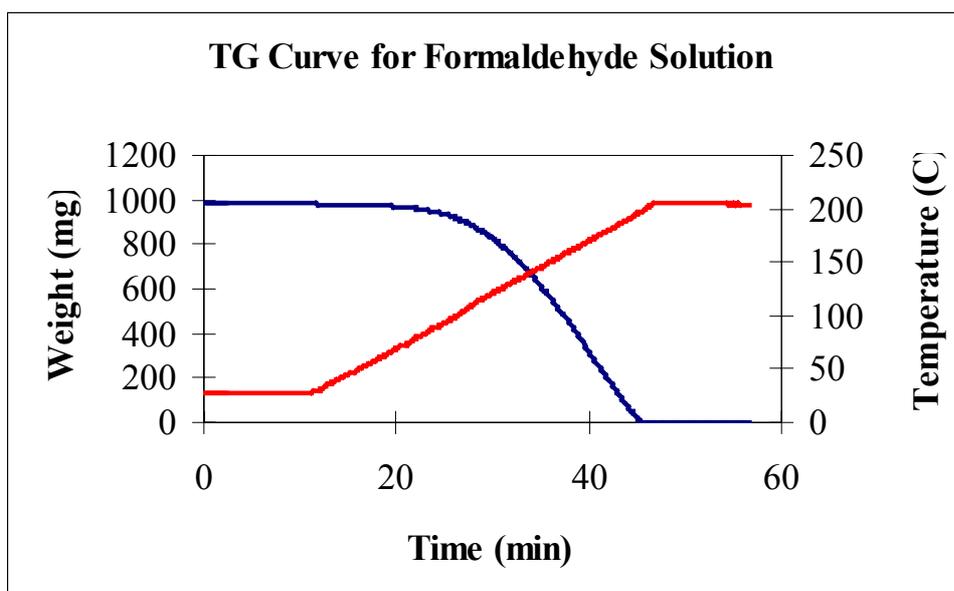
TG Curve for Formaldehyde Solution

Figure 1c: Curve of Weight change Vs. temperature for formaldehyde solution

When the sample size for solid samples was decreased, smaller amounts of weight loss were observed. In this case, the sensitivity of the balance used in the TG system is very important. Therefore, the least amount of sample which can be measured is dependent upon the sensitivity of the balance.

In the above discussion, samples with 100 % of the interested component were used. However, most experiments involve samples containing a mixture of components. For samples of this type, the sample holder volume should also be considered.

In order to demonstrate the importance of sample holder volume and balance sensitivity, calcium carbonate, which has a density of 2.7 g/mL and will loose 44 % of its weight as CO_2, is used as an example. Assuming the balance sensitivity is 10 μg and without considering the noise, the smallest amount of 100 % calcium carbonate which can be detected based upon the weight loss signal of CO_2 is 23 μg (10 μg/44%) or 0.0084 μL (23 μg/2.7 g/mL). If a sample mixture contains 0.0001 % (1 ppm) of calcium carbonate, in order to obtain the percentage of calcium carbonate in a sample of this kind, 22.727 grams (10 μg/(44% * 0.0001% * 1000000)) or 8.4 mL (22.727 grams/2.7 g/mL) of the mixture must be used. This will work fine, if the sample holder is BIG enough AND the balance capacity is large enough. Therefore, for TG systems, the capacity and sensitivity of the balance, as well as the sample holder volume are important parameters. Because the sample's density is often not high enough to reach the balance's capacity, the more important parameter becomes the volume of sample holder.

From the above discussion, it is proposed that the detection limit of TG systems should be evaluated by the ratio of the balance sensitivity to standard sample holder volume.

The Effect on TG/FTIR

When evolved gases were analyzed by FTIR continuously, it is possible to qualify and quantify the evolved gases. Figures 2a, 2b, and 2c show TG curves with corresponding time-evolved IR traces for carbon dioxide and formaldehyde. The frequency windows used to construct time-evolved FTIR traces were from 2200.00 to 2500.00 cm^{-1} for carbon dioxide, and from 2650.00 to 2856 cm^{-1} for formaldehyde. The net absorbance at frequency of 2361.02 cm^{-1} (CO_2) and 2802.75 cm^{-1} (formaldehyde) were used to construct the time-evolved FTIR traces. It can be seen that the gases evolved from samples were given off during the sample decomposition processes. For $CaC_2O_4 \cdot H_2O$, CO should be monitored during the second weight loss step, however, beside CO, CO_2 was also observed. This was due to the small amount of oxygen present in the reaction gas, which reacted with carbon monoxide and formed carbon dioxide.
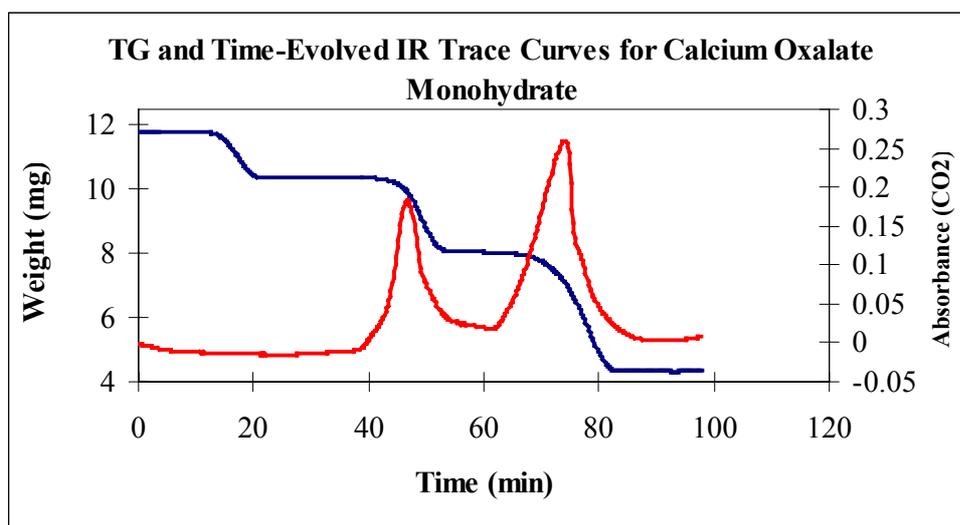

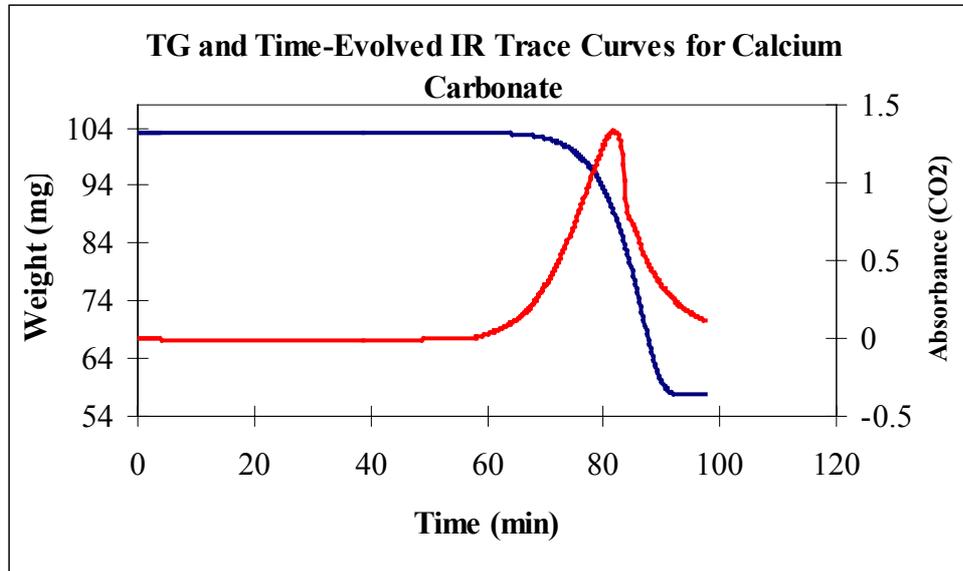*Figure 2a: TG and IR curves for Calcium Oxalate Monohydrate*

TG and Time-Evolved IR Trace Curves for Calcium Carbonate

Figure 2b: TG and IR curves for Calcium Carbonate

1.0 % Formaldehyde Solution
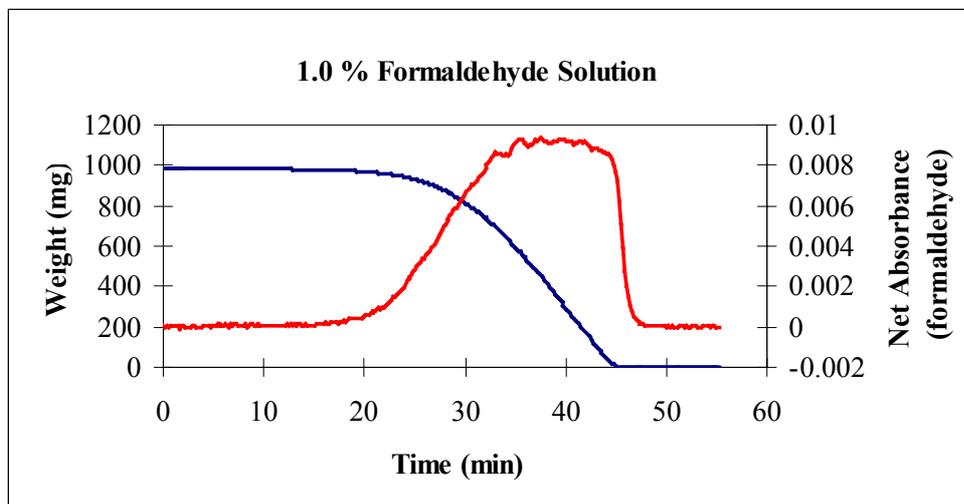
Figure 2c: TG and IR curves for Formaldehyde Solution

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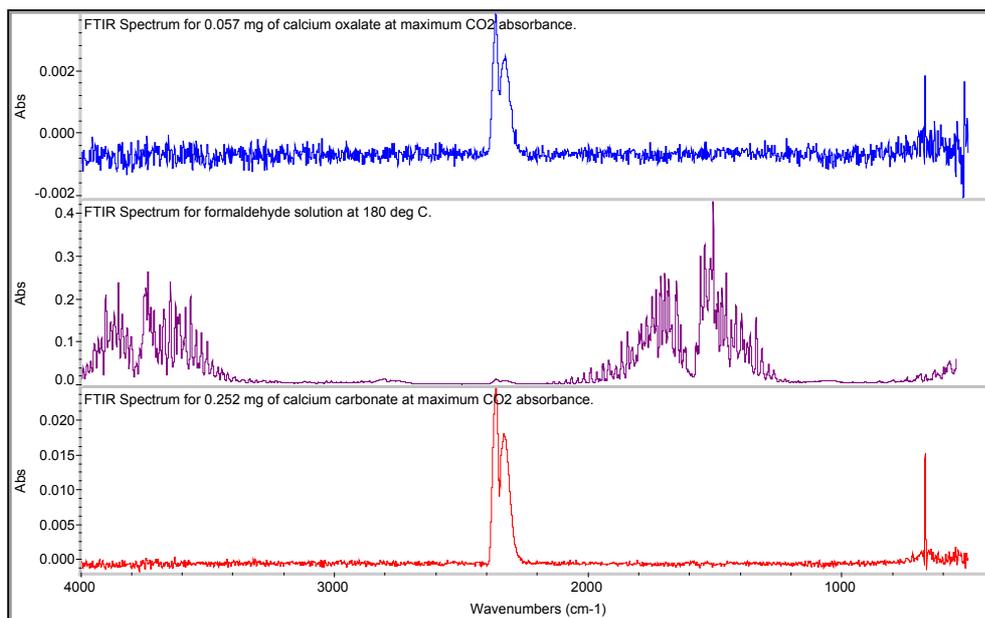
Figure 3: FTIR spectra for the experiments

Figure 3 shows FTIR spectra collected during the experiments for $CaC_2O_4 \cdot H_2O$ (57 µg), $CaCO_3$ (0.252 mg), and formaldehyde solution (1.0 %) samples, respectively. Figure 3 represent the characteristic FTIR spectra at maximum absorbance of CO_2 and formaldehyde. It can be seen that CO_2 and formaldehyde peaks are well above the noise level. This means that with even smaller amounts of the interested component, evolved CO_2 and formaldehyde gases can still be detected.

However, there are many factors that will affect the detection limit for TG/FTIR. The most important of them is the type of interface used for coupling the TG and FTIR. The conventional interface technique is total flow coupling, in which all gases vented from TG flow through the FTIR gas cell. Under this type of coupling, evolved gases from the sample are diluted by the reaction and purge gases, which will result in a lower signal output. A more recent design is the Thermo Synergy coupling, in which a Sniffer tube is used to withdraw gases right above the sample. In this case, the evolved gases, and maybe a small amount of reaction and purge gases, are analyzed by the FTIR. This has resulted in a greater signal output and was presented in a previous paper. With both TG/FTIR coupling systems, there are other factors which will affect the detection limit. These include the length of the gas cell, the flow rate of gas through the cell, the flow rate of the reaction gas, the resolution of the FTIR used for collecting the spectra, the time used to collect each spectrum, etc. Each of these plays an important role in deciding the detection limit of TG/FTIR and needs to be optimized. Even under optimized conditions, the detection limit is still dependent upon the amount (or concentration) of the interested gases evolved from the sample.

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The more of the gases evolved from the sample, the better the detection limit. In other words, the bigger the sample size, the better the chance to detect the evolved gases.

Therefore, the detection limit of TG/FTIR is dependent upon the standard sample holder volume of the TG system.

Conclusions

For TG, the experimental results proved that the larger the sample size, the better the detection limit. For TG/FTIR, there are many other variables that can affect the detection limit. With one type of TG/FTIR interface, the detection limit is dependent upon the sample holder volume of the TG system. It is proved that, for a sample mixture, the ratio of balance sensitivity to standard sample holder volume should be used to characterize the detection limit of TG, while the standard sample holder volume of TG system should be used to characterize the detection limit of TG/FTIR.

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