



Weight Loss Determined from Mass Spectrometry Trend Data in a Thermogravimetric/Mass Spectrometer System

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ABSTRACT

The use of mass spectrometry for the identification of evolved gas species in thermogravimetric (TG) experiments is well known. The mass spectrometer (MS) can be attached directly to the outgas port of the thermogravimetric (TGA) instrument. Typically the mass spectrometer is used for identification only. However, there are situations where it would be desirable to obtain more information. For example, when two or more species are evolved during a weight transition, the total weight loss is known from the TGA, but the weights for the individual components are unknown. Using a simple calibration technique, trend data from a mass spectrometer can be used to semi-quantitatively determine the amount of material evolved for low mass-to-charge (m/e) ratio species such as water and carbon dioxide.

INTRODUCTION

It is very common in the field of thermogravimetry to analyze the gases evolved during experiments by techniques such as mass spectrometry or Fourier transform infrared spectrometry (FTIR) (1). Such “hyphenated” techniques are typically used for detection and identification purposes only. However, it is beneficial if further information is derived. For example, when multiple species are released during a single weight loss event in a TGA, only the total weight loss is known. It is useful to know how the weight loss is distributed among the various components. Also, if reactions occur between the evolved gases and the purge gas, information concerning the masses involved is valuable.

If a mass spectrometer is attached to the TGA, then it is possible to analyze the ion current data for a specific m/e species during a weight transition and convert it to a mass for that species. The technique involves first calibrating the TG/MS system by running a sample that evolves only the gas species of interest. For example, if water is the component of interest, then calibration involves collecting TG/MS data from a sample that only gives off water during a weight transition.

EXPERIMENTAL

A TA Instruments Q50 TGA was attached to a Pfeiffer Vacuum ThermoStar mass spectrometer. The Q50 TGA has a quartz-lined furnace that is ideal for evolved gas experiments. Evolved gas components from the TGA are fed via a capillary heated to

200 °C to the mass spectrometer. The input gas is ionized by electron impact. The ions are then sent through a quadrupole mass filter and finally impacted onto a secondary electron multiplier (SEM) that produces an output current proportional to the ion current.

Powder samples of calcium oxalate monohydrate ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$) from Fisher Scientific and 99.97 % pure calcium carbonate (CaCO_3) from Alfa-Aesar were run in 100 μL platinum pans. The pans were cleaned and tared prior to sample loading.

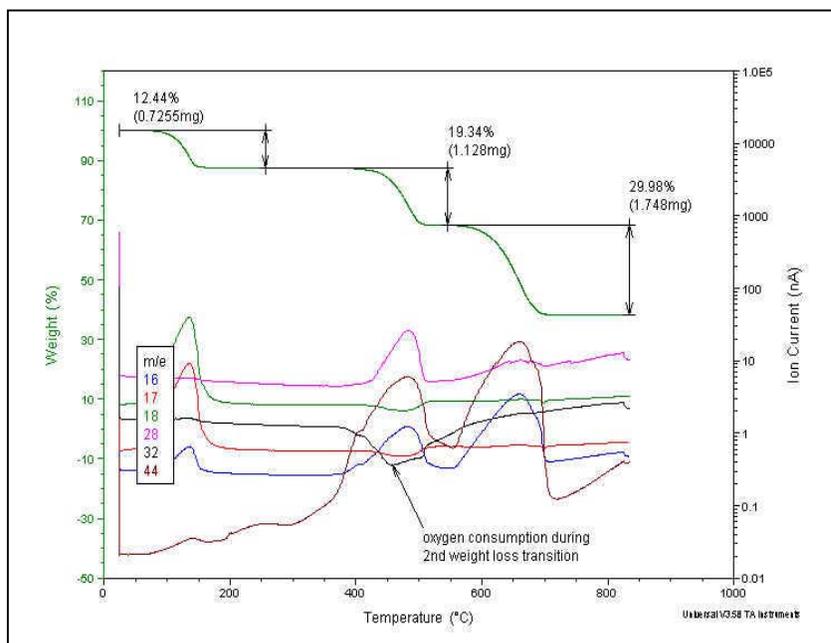


Figure 1 – Simultaneous TGA/MS Thermal Curves of Calcium Oxalate Monohydrate

RESULTS

Figure 1 shows a typical thermogravimetry thermal curve of calcium oxalate monohydrate in a helium atmosphere. As shown, $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ decomposes in an inert atmosphere in three steps (2).

1. $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O} \rightarrow \text{CaC}_2\text{O}_4 + \text{H}_2\text{O}$ (loss of water)
2. $\text{CaC}_2\text{O}_4 \rightarrow \text{CaCO}_3 + \text{CO}$ (loss of carbon monoxide)
3. $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$ (loss of carbon dioxide)

If oxygen is present, a reaction with the CO produced in step 2 occurs:

4. $\text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2 + \text{O}$

Thus, in the presence of low amounts of oxygen, both CO and CO_2 are produced simultaneously during the second weight loss transition. Figure 1 also shows the mass spectral trend data captured for the calcium oxalate run. In a trend scan only certain m/e species are tracked over time by the mass spectrometer. In this example data on m/e species 16, 17, 18, 28, 32 and 44 are collected and plotted. The typical ions associated with these m/e numbers are O, HO, H_2O , CO, O_2 and CO_2 respectively. The data shows that during the second weight loss both CO and CO_2 are detected. This is not unusual, as carbon dioxide will fragment into smaller mass species, including CO, when subjected to electron impact ionization. However, the data also shows that the O_2 level drops during

the second weight loss. This is a definitive indication that reaction 4 is also proceeding. The total weight loss for the second transition from Figure 1 is 1.13 mg. This is all from CO, but it would be interesting to know how much of the CO is converted to CO₂, and how much CO₂ is thus produced. In order to answer this question, the MS system was calibrated to measure weight of evolved CO₂.

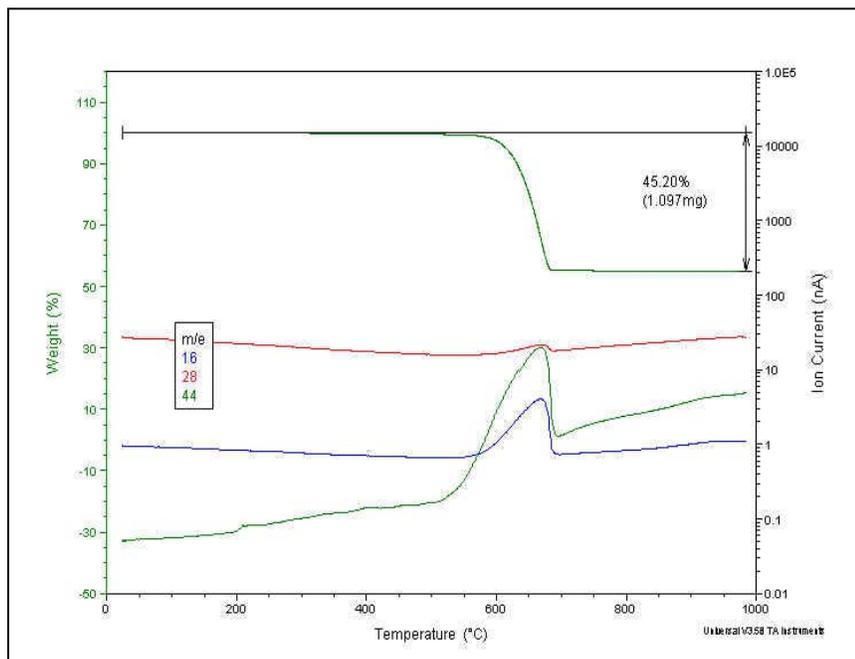


Figure 2 – Simultaneous TGA/MS Thermal Curves of Calcium Carbonate

Calcium carbonate thermally decomposes according to step 3 outlined above. The presence of oxygen at small levels does not influence this reaction (3). Three different masses of calcium carbonate were run in the TG/MS system. Figure 2 shows an overlay of TG and MS trend data from a typical run. One weight loss transition occurs and CO₂ (m/e = 44) is released. In this trend scan, increases in CO (m/e = 28) and O (m/e = 16) are also detected, but these are expected fragments of CO₂. The area under the CO₂ curve can be related to the weight loss detected in the TGA. Figure 3 shows how the area of the CO₂ peak grows with increasing mass of sample. Table 1 lists the relevant measurements from the three runs and Figure 4 plots the area under the CO₂ curve versus weight loss as seen in the TGA. A linear relationship exists between the curve area and the weight loss. Results from a linear fit are also displayed on the graph. The correlation is high and the Y intercept is near 0, as should be the case.

Table 1 – Replicate Determinations of CaCO₃ MTGA/MS Calibration

Initial Weight	Weight Loss	Weight Loss	CO ₂ Peak Area
0.437 mg	0.204 mg	46.7 %	0.939 μA s
2.43 mg	1.10 mg	45.2 %	5.327 μA s
12.3 mg	5.42 mg	44.2 %	28.24 μA s

This working curve can now be used to estimate the amount of CO₂ formed during the second transition in the calcium oxalate data. Integration of the CO₂ peak from the data in Figure 2 gives an area of 39.6 nA min. Evaluating this data using the linear equation obtained in Figure 4 gives a calculated amount of 0.46 mg of CO₂ formed. Multiplying this by the ratio of the molecular weight of CO to the molecular weight of CO₂ gives a value of 0.29 mg of CO converted.

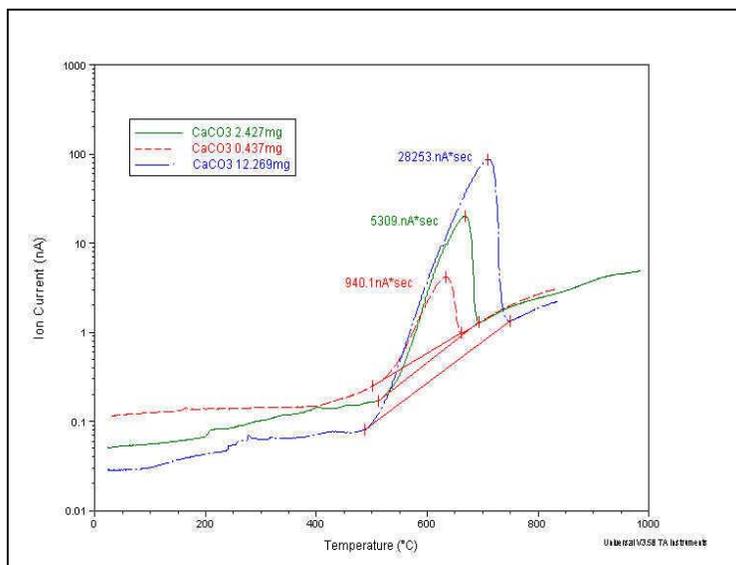


Figure 3 – Increase in CO₂ Mass Spectral Data with Initial Mass of Calcium Carbonate

It is difficult to measure the accuracy of the technique. An alternate measure by a separate technique should be employed. However, as an approximate check of the accuracy of the method, the peak area of the CO₂ can be converted to a weight for the third weight loss event in calcium oxalate. Here only CO₂ is being released. The calculation gives a value of 1.36 mg as compared to a value of 1.74 mg by the TGA. These values are within 22 % of each other.

DISCUSSION

The calibration technique also works for other gases. Figure 5 shows the resultant plot for water. The first weight loss in calcium oxalate, which only releases water, was used to produce this curve. Again, three different masses of calcium oxalate were run and the results graphed. As with the graph for CO₂, the data is highly linear with a Y intercept near 0. Accuracy checks of this calibration were performed using cupric sulfate (hydrate), which loses water in two well-separated transitions. Calculations gave results that were within 15 % and 20 % of the TGA measurements of these two weight losses respectively

To ensure that the best accuracy is obtained the several points concerning experimental procedure should be observed. The calibration must be done in the same purge gas as the sample being run. Changing purge gases could potentially shift baseline levels of the gases of interest. The calibration is sensitive to the baseline level and if the baseline is not the same during the experimental run as during the calibration run the

results will be in error. The error is roughly proportional to the ratio of the baseline levels.

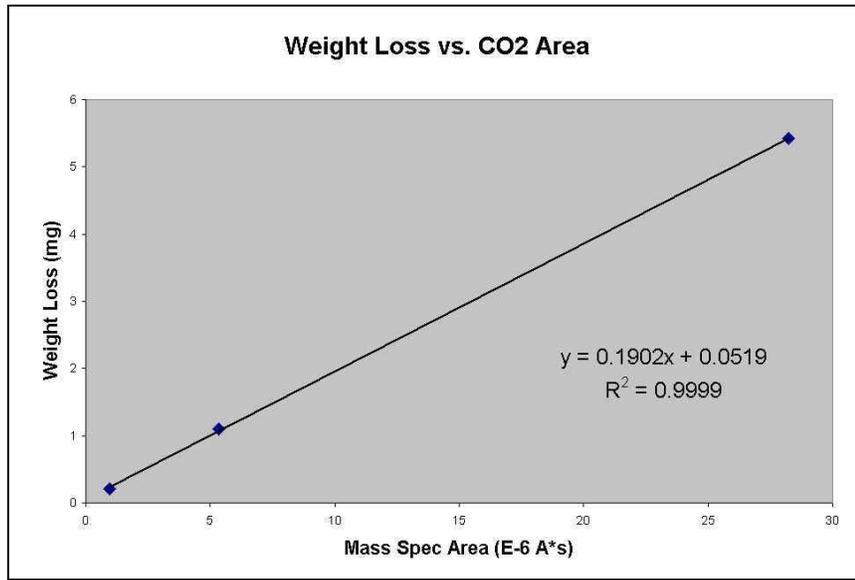


Figure 4 – Correlation of TGA Weight Loss with Mass Spectral Peak Area of CO₂

As a calibration material, powders are the best choice. Preliminary data show that use of chunk samples can produce a highly non-linear relation between peak area and weight loss.

Finally, the assumption is made that a gas fragments in the mass spectrometer always in the same proportions. For example, CO₂ will fragment into CO and O (and other fragments) always in the same proportions. Statistically, for large numbers of molecules, this assumption should be valid. Comparing the ratio of CO₂ to O for the three calibration runs can test this assumption. The ratio was the same in all three runs.

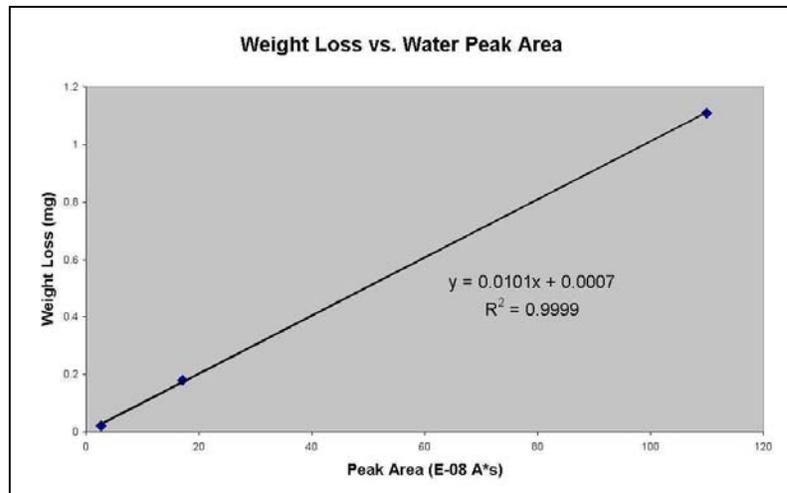


Figure 5 – Correlation of TGA Weight Loss with Mass Spectral Peak Area for Water

CONCLUSIONS

A simple calibration technique for converting areas under mass spectral data curves to weights of the detected species has been discussed. Results for low m/e species such as H₂O and CO₂ were presented with accuracies within 25% obtained. While better accuracy is desirable, baseline shifts in the mass spectral data that occur during the collection probably make it difficult. The technique may be extended to higher m/e ratios.

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KEYWORDS

Compositional analysis, decomposition, inorganics, mass spectrometry, thermogravimetry

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