APPLICATION NOTE

Hyphenation

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Study of the Decomposition of Calcium Oxalate Monohydrate using a Hyphenated Thermogravimetric Analyser - FT-IR System (TG-IR)

Introduction

Hyphenation is the combination of different instruments to gain analytical insights which would previously not be observed by either instrument on their own. The combination of a Thermogravimetric Analyser (TGA) with an Infrared Spectrometer (TG-IR) is the most common type of evolved gas analysis. TGA accurately measures the percentage weight loss of a sample as a function of temperature, but will not provide any information regarding the chemical composition of the evolved gases. Interfacing a TGA with an FT-IR Spectrometer allows identification of the gases evolved, thus more comprehensive studies of the processes which occur in thermal analysis may be conducted.

TG-IR is suited to a variety of applications which require identification of evolved gases upon sample heating. Such applications include residual solvents in pharmaceuticals, and polymer and plastic decomposition[1]. In this application, the thermal decomposition of calcium oxalate monohydrate ($CaC_2O_4.H_2O$) has been studied.

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Figure 1. PerkinElmer TGA 8000, Frontier FT-IR Spectrometer and TL8000 mass flow controller.

Decomposition of Calcium Oxalate Monohydrates

Calcium oxalate monohydrate ($CaC_2O_4.H_2O$), also known as whewellite, is a main component in kidney stones and is an industrially useful compound used to make oxalic acid and organic oxalates. $CaC_2O_4.H_2O$ is commonly used as a standard to test TGA performance due to its well-known decomposition steps and products[2].

When heated, $CaC_2O_4.H_2O$ decomposes in three well defined steps as shown below with the overall reaction equation. Step 1 involves loss of water of crystallisation to form anhydrous calcium oxalate. Calcium oxalate then thermally decomposes to calcium carbonate in step 2 with the loss of carbon monoxide. The final step involves thermal decomposition of calcium carbonate to calcium oxide with the loss of carbon dioxide[2]. The theoretical stoichiometric percent weight loss of each step, calculated using the molar masses of each compound, is shown in Table 1.

Overall Reaction: $CaC_2O_4.H_2O \rightarrow CaO + H_2O + CO + CO_2$

1) $CaC_2O_4.H_2O \rightarrow CaC_2O_4 + H_2O$

2) $CaC_2O_4 \rightarrow CaCO_3 + CO$

3) $CaCO_3 \rightarrow CaO + CO_2$

Table 1. Theoretical stoichiometric weight loss for each TGA step.

Step	Theoretical stoichiometric weight loss (%)
1	12.3
2	19.2
3	30.1

Experimental

$CaC_2O_4.H_2O$ (Puratronic®, 99.9985 % (metals basis)) was obtained from Alfa Aesar. Thermal decomposition and evolved gas analysis of $CaC_2O_4.H_2O$ was performed on the PerkinElmer TG-IR hyphenated system.

The IR background scan was taken after zeroing the ceramic pan in the nitrogen gas flow. $CaC_2O_4.H_2O$, 6.8170 mg (typically between 5-25 mg), was placed in the pan and analysis performed according to the conditions shown in Table 2. The final hold for five minutes in air at 950 °C was implemented to clean the crucible. The IR spectrometer parameters were set to collect a co-added scan every 20 seconds.

Table 2. Experimental parameters for the TG-IR experiment.

TGA Parameters	
Temperature Program	1. Hold for 1min at 30 °C 2. Heat from 30 °C to 950 °C at 20 °C/min 3. Hold for 5 min at 950 °C
Pan Used	Ceramic
Balance Purge	50 ml/min
Sample Purge	N_2, 30 ml/min for Step 1 to 2 Air, 30 ml/min for Step 3
Sample Quantity	6.8170 mg
Transfer Line	270 °C
FT-IR Parameters	
Scan Range	4000-450 cm^{-1}
Resolution	4 cm^{-1}
Co-added Scans	4

Results and Discussion

The TGA thermogram for the decomposition of $CaC_2O_4.H_2O$ is shown in Figure 2, which illustrates the occurrence of three weight loss steps. After the third step, the weight stabilized at 38%. Using Pyris software, the percent change in weight, onset temperature, and inflection point were calculated as shown in Figure 2. The measured percent weight losses of each step were close to the theoretical stoichiometric values (Table 3). The inflection point is the point at which the greatest rate of change on the weight loss curve occurs. The extrapolated onset temperature is a reproducible calculation for further characterisation of a sample and is the temperature at which the weight loss initiates.

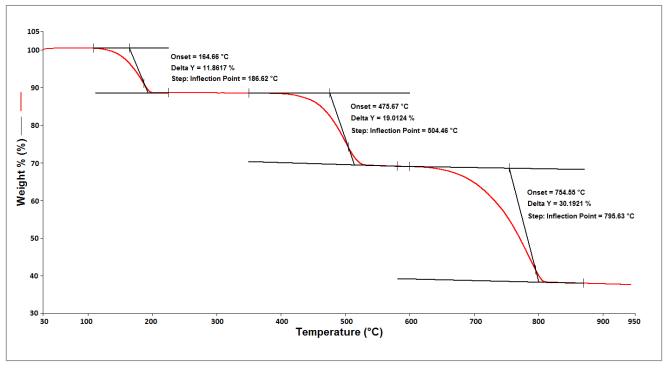

Figure 2. $CaC_2O_4.H_2O$ thermogram.

Table 3. Theoretical stoichiometric weight loss for each TGA step.

Step	Theoretical Stoichiometric Weight Loss (%)	Measured Weight Loss (%)
1	12.3	11.9
2	19.2	19.0
3	30.1	30.2

Evolved gas analysis by FT-IR was carried out to provide confirmation of the identity of gases evolved. The FT-IR generated a Gram-Schmidt profile of absorbance versus temperature, shown in Figure 3 overlaid with the TGA weightloss curve. The peaks in the Gram-Schmidt profile correlate directly with the steps in the TGA weightloss curve.

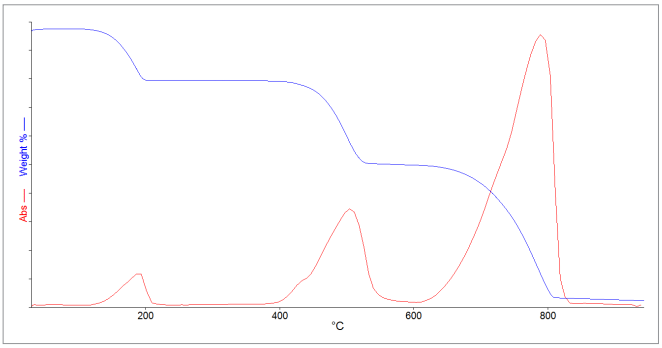

Figure 3. $CaC_2O_4.H_2O$ Weight loss curve (blue) and Gram-Schmidt profile (red).

Figure 4 shows the IR spectra at each of the three weight loss steps. At temperatures ranging 100 - 200 °C, a first weight loss of 11.9% was observed, corresponding to the loss of water of crystallization. The IR spectrum of the evolved gas at 186 °C confirmed the weight loss to be due to water vapour being evolved from the sample.

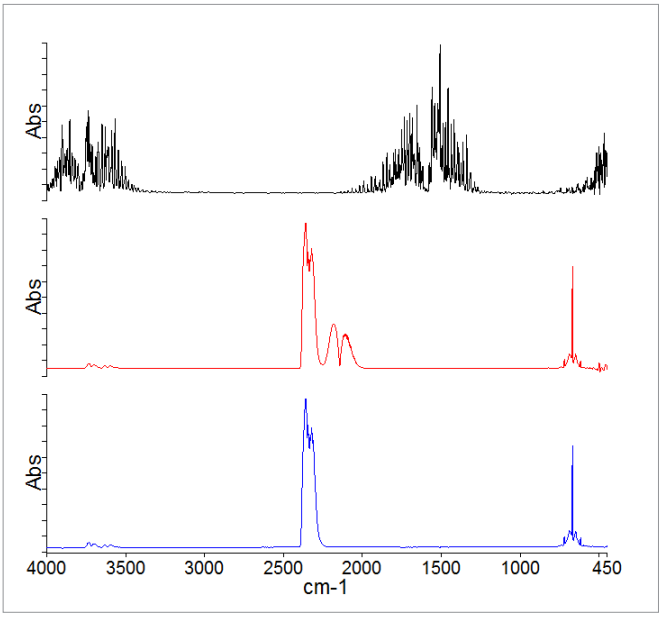

Figure 4. IR spectra from top to bottom; Spectrum at 186 °C, 504 °C and 789 °C.

At temperatures ranging 400 – 530 °C, a second weight loss of 19.1% was observed, corresponding to the decomposition of anhydrous calcium oxalate, with the loss of carbon monoxide. The IR spectrum at 504 °C provided confirmation of evolved CO with the two peaks centered around 2100 cm^{-1}. However, peaks at 667 cm^{-1} and 2350 cm^{-1} indicated that CO_2 was also produced during the second step. Carbon dioxide forms as a result of the disproportionation reaction of CO to CO_2 and carbon (Equation 1).

$$2CO \rightarrow CO_2 + C$$

Equation 1: Disproportionation reaction of CO

The third and final weight loss, at temperatures ranging 600 – 810 °C, was determined to be 30.2%, corresponding to the decomposition of calcium carbonate to calcium oxide with the loss of carbon dioxide. The peaks at 667 cm^{-1} and 2350 cm^{-1} in the IR spectrum at 789 °C provide confirmation of evolved CO_2.

Conclusion

Calcium oxalate monohydrate showed three decomposition steps with obtained weight losses matching the theoretical values. Hyphenating IR analysis to the TGA provided confirmation of the identity of the evolved gases and insights into data which would otherwise not be observed in TGA alone. The PerkinElmer TG-IR system is fully optimised to obtain the highest quality data from the TGA, the FT-IR and the hyphenation of both techniques.

References

1. Nishikida, K., Nishio, E., and Hannah, R. (1995) *"Selected Applications of Modern FT-IR Techniques"*, Kodansha.
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3. Nair, C. and Ninan, K. (1978) *"Thermal decomposition studies: Part X. Thermal decomposition kinetics of calcium oxalate monohydrate — correlations with heating rate and samples mass"*, Elsevier, Volume 23, Issue 1.

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