Simultaneous Thermal Analysis of the Decomposition of Calcium Oxalate

Simultaneous thermal analysis (STA) performs thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) simultaneously on a sample. STA allows for precise correlation of changes in mass with changes in energy and vice versa. It provides not only results one can get from separate TGA or DSC analysis, but also better correlation between the two kinds of analyses because they are run under the exactly same conditions.

STA is invaluable in certain applications, such as differentiating between phase transformation and decomposition, or recognizing pyrolysis, oxidation and combustion reactions. The technique can also be used to determine reaction kinetics, physical transitions, residual mass or curing and evaporation rates. STA has applications in characterizing pharmaceutical materials, cements, minerals, resins, etc. Any material that undergoes changes in mass or internal energy when subjected to a controlled heating program can be analyzed using STA.

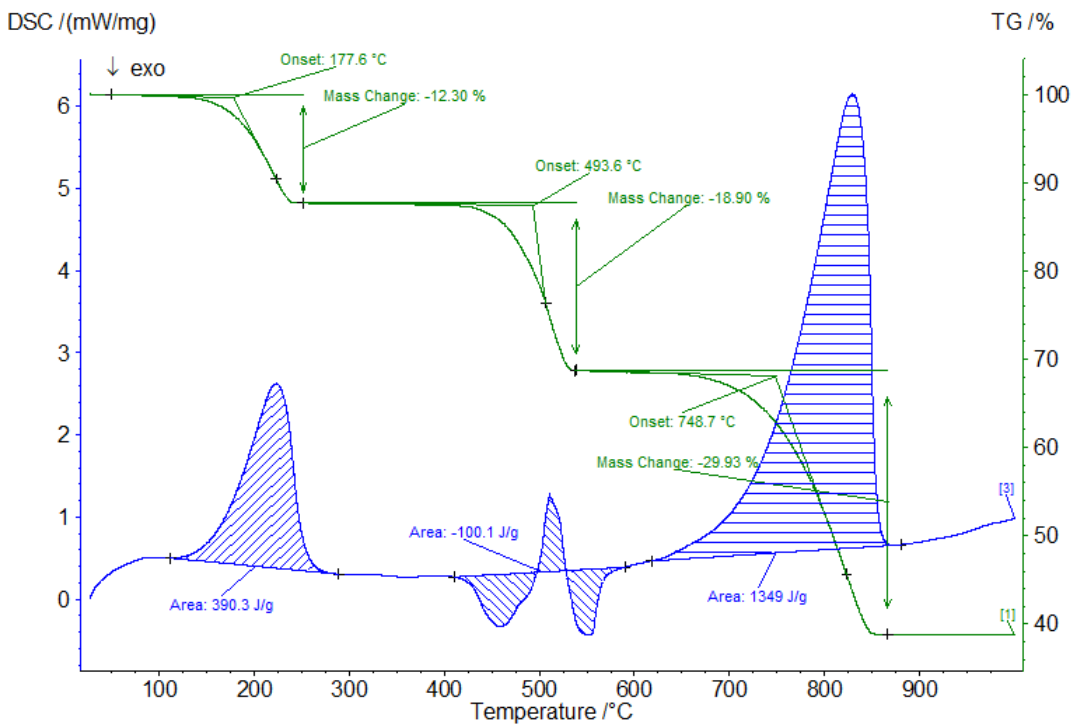

Figure 1. STA Data for the Decomposition of Calcium Oxalate Monohydrate.

Calcium Oxalate Monohydrate, CaC2O4•H2O, is a useful industrial compound used to make organic oxalates, and glazes. Understanding Calcium Oxalate's thermal behavior when applied as part of a glaze is crucial to determining kiln temperature. If the kiln is not hot enough, the calcium oxalate won't decompose properly. If it is overheated, the glaze's viscosity will lower to the point that it runs off the surface of the pottery it was applied to. Thermal decomposition data for $CaC_2O_4 \cdot H_2O$ was obtained using a Netzsch STA 449 F3 Jupiter Simultaneous TGA-DSC (Germany). Table 1 summarizes the three decomposition reactions that occurred during the test.

Table 1 Thermal Decomposition Reactions of Calcium Oxalate Monohydrate

Step	Reaction	Enthalpy (J/g)	Theoretical Mass Loss	Measured Mass Loss	% Error
1	$CaC_2O_4 \cdot H2O \rightarrow CaC_2O_4 + H_2O$	390.3	12.33%	12.30%	-0.24%
2	$CaC_2O_4 \rightarrow CaCO_3 + CO$	-100.1	19.17%	18.90%	-1.41%
3	$CaCO_3 \rightarrow CaO + CO_2$	1349	30.12%	29.93%	-0.63%

The DSC data shows that the first and third reactions are purely endothermic, as would be expected from a simple decomposition reaction. However, the second reaction step shows evidence of two overlapping reactions, one endothermic and the other exothermic. This can be explained by the Boudouard reaction, the equilibrium redox reaction of carbon monoxide into carbon dioxide and carbon. At elevated temperatures that are less than 700^{o}C, carbon monoxide will react to form carbon and carbon dioxide, which is an exothermic reaction.

The measured mass losses during steps 1 to 3 closely match the predicted mass losses, which verify the theoretical predictions of the thermal decomposition for the calcium oxalate monohydrate. It is interesting to note the slight difference in the mass loss between theoretical calculation and actual measurement for decomposition in step 2. This can be explained by the Boudouard reaction depositing carbon residue on the sample, resulting in a mass loss that is significantly lower than expected.

If this experiment had been performed using only DSC or TGA, there would not have been enough information to analyze and fully understand the reactions occurring.