$CuSO_4.5H_2O$ Analysis with a Hyphenated TGA 8000 and Hiden Analytical HPR-20 EGA Mass Spectrometer

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Background

As part of the commissioning of a new hyphenation system, a sample of copper sulphate pentahydrate was analysed using the PerkinElmer TGA 8000 hyphenated with a Hiden HPR-20 EGA mass spectrometer to provide a series of weight losses with simple inorganic gases. For simplicity, a small sample mass of the copper sulphate (~5mg) was used, and a heating rate of 40°C/min as a proving test for the evolved gas hyphenation connection.

Sample Presentation and Analysis

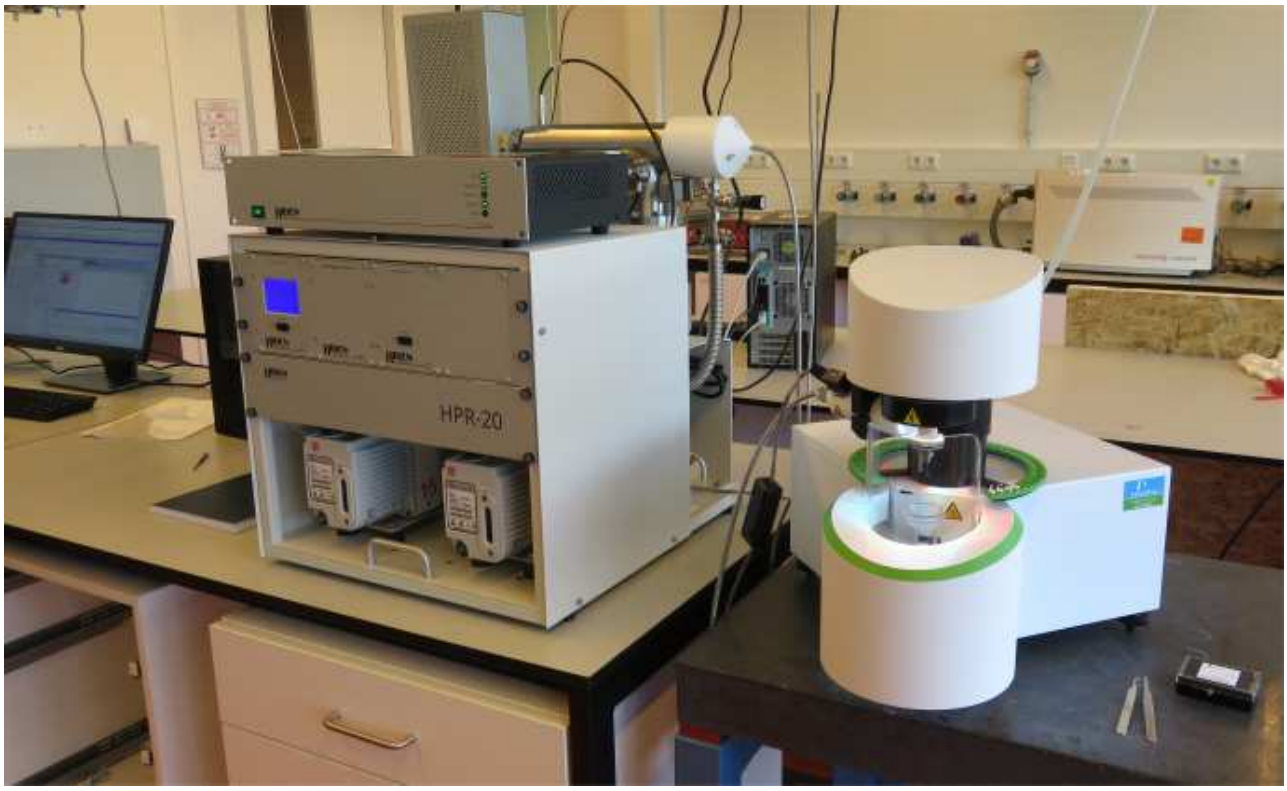
A small sample of around 5.4mg of CuSO4.5H2O was loaded into the TGA ceramic sample pan following gentle grinding in an agate mortar and pestle to produce a fine powder. By reducing the particle size in this way, the gas path length for interactions between the solid phase and the gas phase is minimised, which produces better resolution in both the TGA weight loss curve and the mass spectrometer gas evolution peaks. The sample was distributed evenly across the inside of the TGA ceramic pan to provide a thin layer, which further contributes towards maximising resolution between adjacent weight loss events.

The following temperature program was used for this testing, which was carried out under an argon purge with a total flow rate of 80mL/min (balance purge flow of 50mL/min and sample purge flow of 30mL/min).

1. Isothermal at 30°C for 1 minute
2. Trigger the MS to start collecting data at start of segment
3. Heat from 30°C to 900°C at 40°C/min
4. Isothermal at 900°C for 0.1 minute
5. Trigger MS to stop collecting data at start of segment

In some applications the isothermal segment shown in step 1 can be used to complete purging with argon after loading the sample. For example, if carbon monoxide (CO) was expected as an evolved species, any N2 in the system would interfere with the detection of CO at ppm levels below 1000ppm. In this situation, using argon would solve the detection issue but would require effective purging to remove any nitrogen resulting from the lab air around the sample during loading. This purging could be achieved by allowing perhaps 3-4 minutes at the starting temperature after closing the TGA following sample loading.

Equipment



The following equipment was used

PerkinElmer TGA 8000 with 48 position Autosampler. This unit includes mass-flow control for both the balance purge and the sample purge, with the flow rates to each specified in the test method used in Pyris Software for Windows.

Hiden Analytical HPR-20 EGA quadrupole mass spectrometer with the EGAsoft time based data collection software. The interface between the TGA and the MS is designed to have minimal dead-space, which gives good resolution between events and eliminates tailing between weight loss events. The heated transfer line also eliminates cold spots to prevent condensation of evolved organic fragments passing from the TGA.

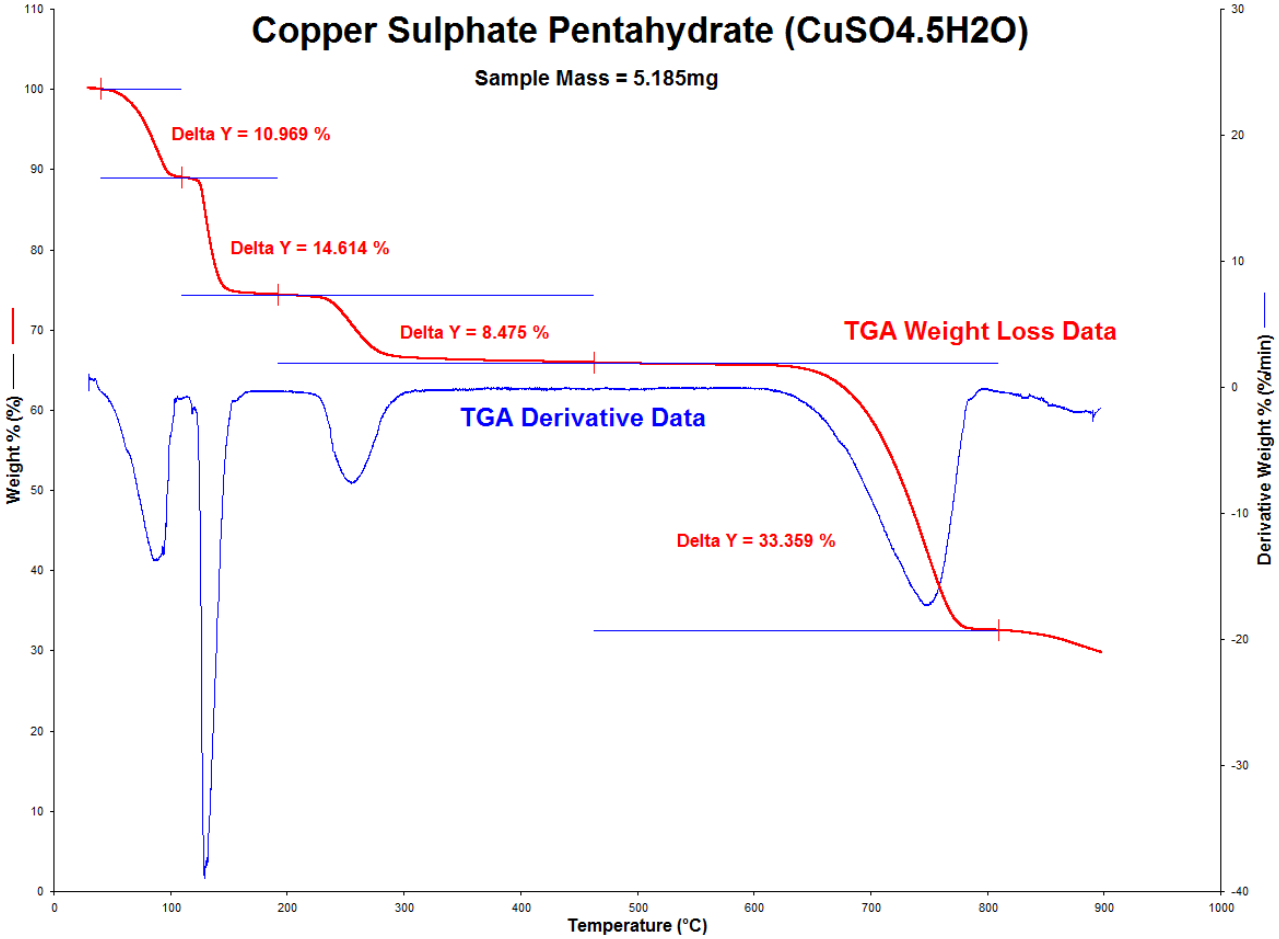
Both systems were controlled from the same PC, which also controlled the trigger box to signal start the mass spectrometer data collection when the TGA data collection started.

Treatment of Results

Displaying the imported data on the same graph as the sample data allows a clear correlation of species evolved in relation to the events observed in the TGA. Therefore, after data collection by the MS software, data for each mass species of interest is exported as ASCII text data, which can then be imported directly into the PerkinElmer Pyris TGA software for display alongside the sample data. After importing and display of the mass data with the TGA weight loss profile has been completed, the mass data can be to be saved in native Pyris data file format which can then be readable by Pyris without any further treatment if required for subsequent re-display.

Results

Curve #1 – TGA Data for $CuSO_4.5H_2O$ Decomposition



The overall change in this copper sulphate material can be characterised by the following equation:-

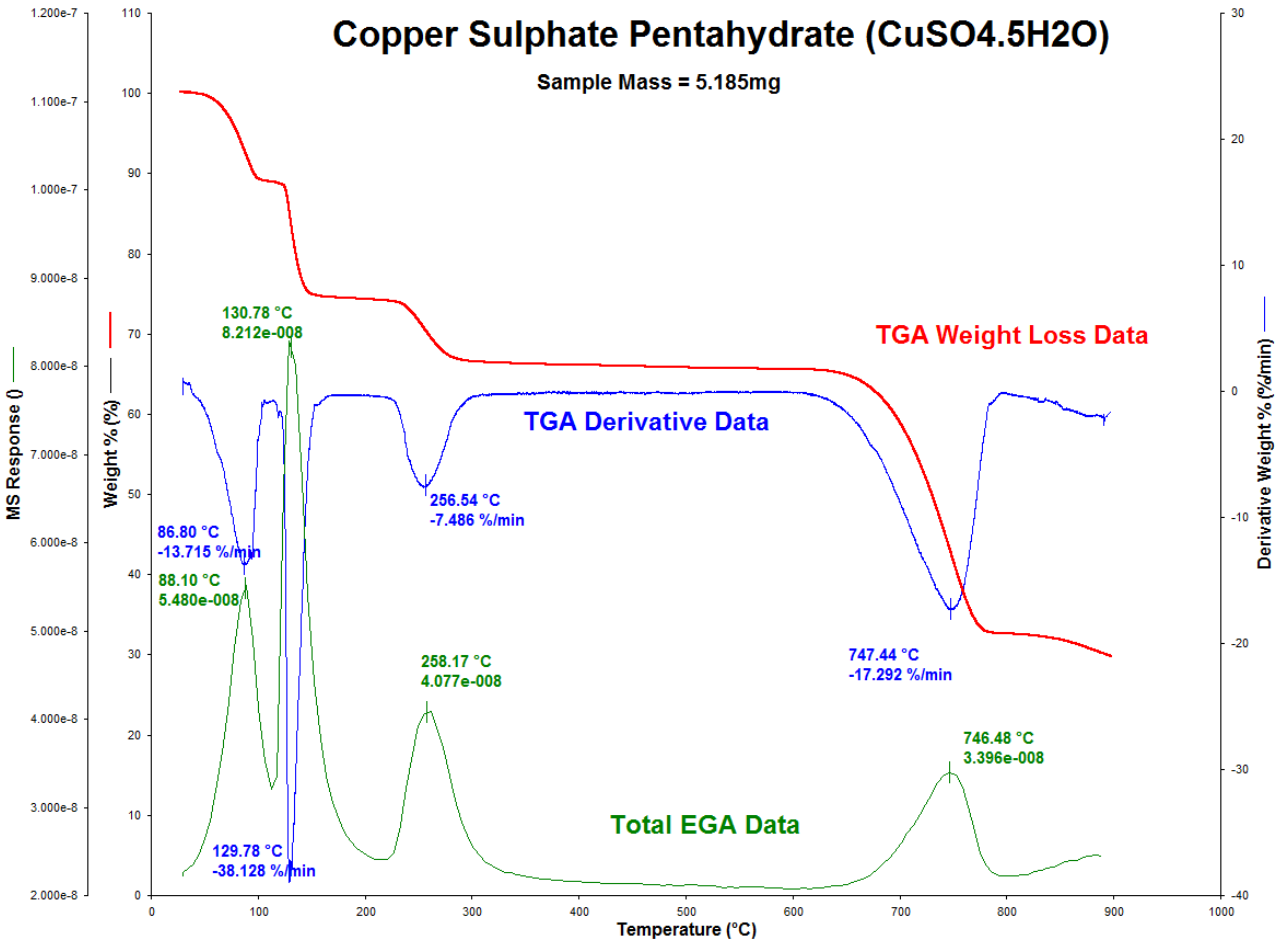
$$2CuSO_4.5H_2O \rightarrow 2CuO + 2SO_2 + O_2 + 10\ H_2O$$

The weight loses are characterised as follows:

50°C to 330°C	Loss of five waters of crystallisation
550°C to 870°C	Loss of SO_2 and O_2

Notice the shape of the first derivative curve which, as is shown below, almost exactly duplicates the shapes of the total evolved gas profile seen at the mass spectrometer. This is an important feature since it demonstrates that all the gases evolved have reached the mass spectrometer, although with the fixed gas evolved species here is less useful.

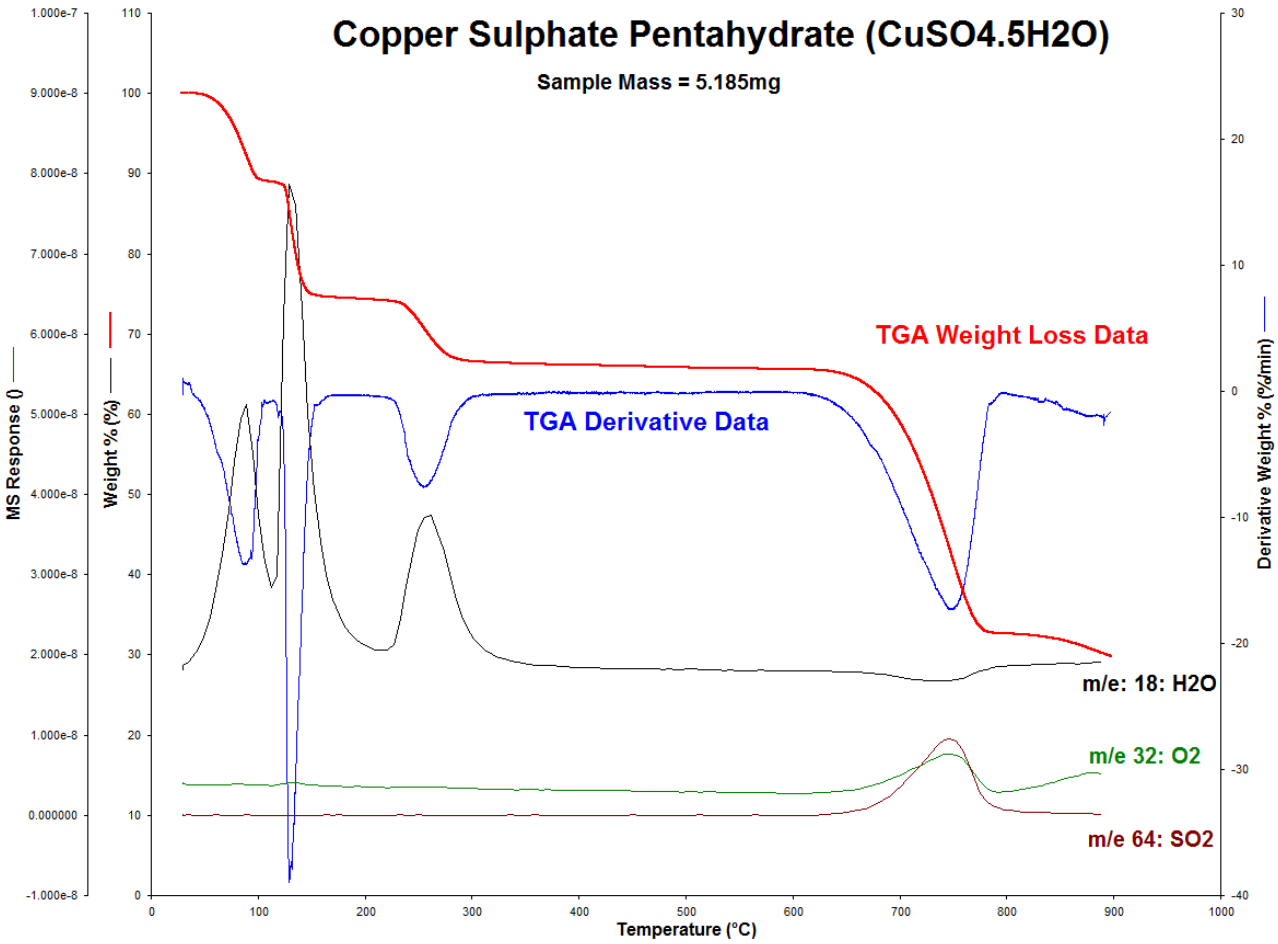
Curve #2 – TGA Data With Total Evolved Gas Species



As can be seen in the plot above, the shape of the total evolved species curve follows very closely with the TGA first derivative curve. The actual size of the individual EGA peaks will depend on the response of the MS to each of the evolved species, but nevertheless, much can be learned from the shapes of curves, including whether there has been any loss in the gas transfer process between the TGA and MS.

There is a small delay – perhaps 1°C - 2°C – between the peaks on the TGA derivative and the MS peaks, although some of the difference is as a result of the frequency with which the data from the MS is collected with respect to the heating rate. In this example, data was collected at approximately 8.5 second intervals, which is equivalent to about 5.7°C between each data point at 40°C/min.

Curve #3 – TGA Data With Individual Evolved Gas Species



This display shows the individual ion species detected by the mass spectrometer alongside the TGA weight and TGA derivative weight loss curves. For a simple inorganic decomposition, these species are relatively straightforward to predict from the empirical equation. This display also demonstrates the ease with which the decomposition fragments from the empirical equation can be confirmed.