Application Brief

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Measuring Crystal Water in Hydrates by Thermogravimetry

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1. Introduction

The mass of crystal water in hydrates can be measured using thermogravimetry. However, the dehydration of crystal water in hydrates often occurs over several steps at close temperatures and standard measurement methods often do not completely isolate these multiple dehydration reactions. However, there are methods to isolate dehydration and breakdowns that occur at similar temperatures. These include ultra-low heating rate measurement, quasi-sealed measurement[1)], and quasi-isothermal thermogravimetry[2)]. In the past, quasi-isothermal thermogravimetry was not widely used as there were no commercially-available instruments that could easily perform measurements using this method.

The TG/DTA220, TG/DTA320 and RTG220 Thermogravimetry/Differential Thermal Analyzers have a controlled rate thermal analysis (CRTA) mode that can be used to automatically raise the temperature for quasi-isothermal thermogravimetry measurements. This mode simplifies quasi-isothermal thermogravimetry and makes it possible to isolate the various reactions that occur at similar temperatures and produce more accurate thermogravimetry.

This brief explains the quasi-isothermal thermogravimetry. As an example of this method, measurement results are presented for the crystal water of calcium sulfate dihydrate (gypsum) and copper sulfate pentahydrate samples. Results of the quasi-sealed method are provided for reference and comparison.

2. Measurements

The measurement samples were calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$) and copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$). All measurement samples were commercially-available and had a purity of more than 99.9%.

For the measurements, a TG/DTA220 Thermogravimetry/Differential Thermal Analyzer was connected to a SSC5200H Disk Station. For the quasi-isothermal thermogravimetry, the temperature control mode was used as the controlled rate thermal analysis mode. Heating rate between heating was a constant rate of 5°C/min. For the quasi-sealed measurements, the measurement sample was placed into an aluminum pan and then a lid with a pin hole was crimped into position and heating rate was 5°C/min. The weight of samples was approximately 10mg. Measurements were performed at a nitrogen flow of 200 ml/min.

3. Quasi-Isothermal Thermogravimetry

In 1972, the Paulik brothers devised an instrument to perform quasi-isothermal thermogravimetry[3]. Unlike previous thermogravimetry, measurements were performed under quasi-equilibrium (quasi-isothermal and quasi-isobaric) conditions. The Paulik brothers named this method Quasi-Isothermal and Quasi-Isobaric Thermogravimetery[4]. Later, a method of performing measurements under only quasi-isothermal conditions was referred to as Quasi-Isothermal Thermogravimetry or simply Quasi-Isothermal Analysis (QIA)[5].

Figure 1 shows the principles of quasi-isothermal thermogravimetry[5]. In these measurements, the heating at a constant rate when there is no weight change. When dehydration or decomposition causes a weight change and the DTG signal (TG differential signal) passes over the upper limit threshold, the temperature temporarily stops rising. At this temperature, an isothermal plateau (quasi-isothermal condition) is maintained and the weight change due to dehydration or decomposition is measured. When the weight change stops in the quasi-isothermal condition and the DTG signal passes below the lower limit threshold, the heating again and continues to rise until the next weight change. By repeating these operations, it is possible to isolate the weight changes that occur at unusually close temperatures.

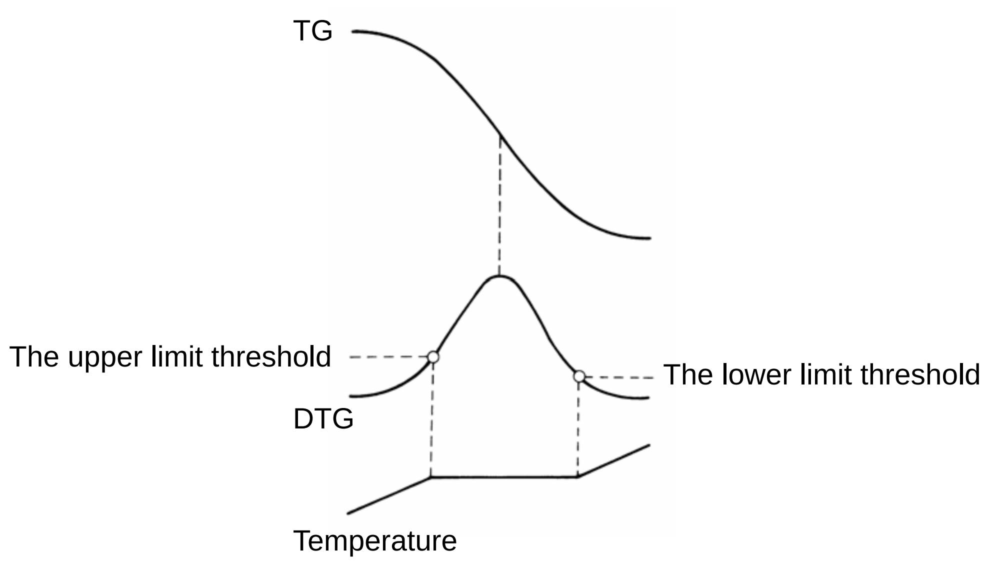

Figure 1 The Principles of Quasi-Isothermal Thermogravimetry[5]

4. Measurement Results

Figure 2 shows the quasi-isothermal measurement results for the calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$). These results show that the crystal water of the calcium sulfate dihydrate dehydrates in the following process.

$$CaSO_4 \cdot 2H_2O \xrightarrow{-3/2H_2O} CaSO_4 \cdot 1/2H_2O \xrightarrow{-1/2H_2O} CaSO_4$$

Formula weight: 172.17 145.15 136.14

In Figure 2, there are two quasi-isothermal conditions in the between of 120°C and 180°C. This indicates that dehydration was isolated and detected at two steps. Furthermore, the rate of weight decrease of each dehydration was almost the same as the theoretical value.

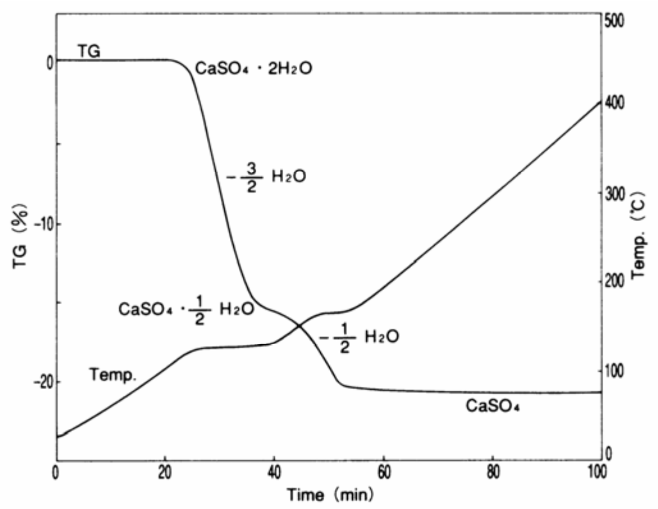

Figure 2 Quasi-Isothermal Measurement Results for the Calcium sulfate dihydrate

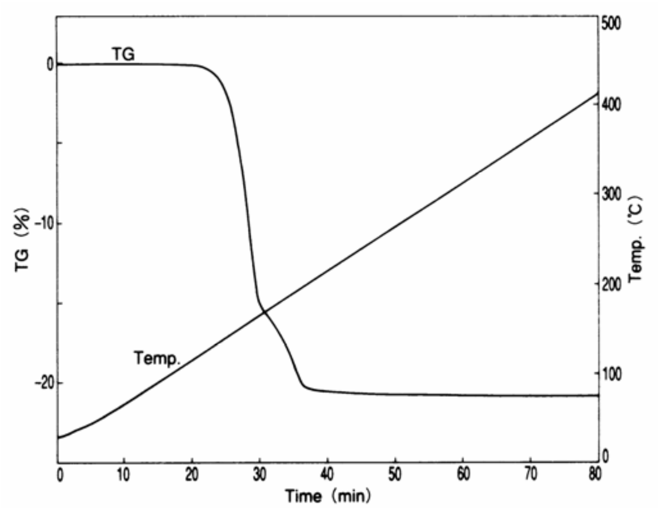

Figure 3 Quasi-Sealed Measurement Results for the Calcium sulfate dihydrate

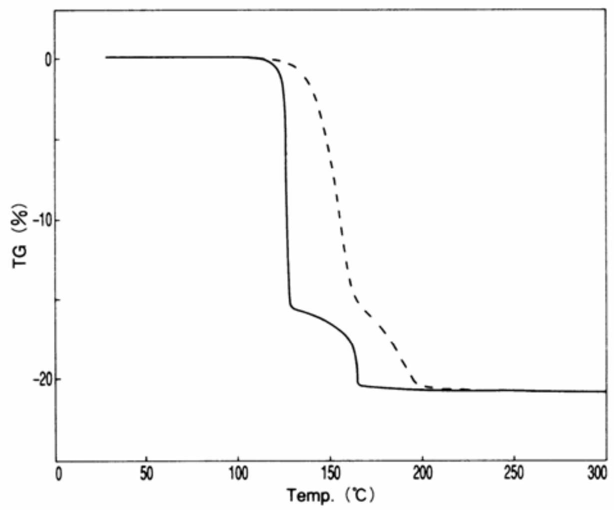

Figure 4 Comparison of Quasi-Isothermal and Quasi-Sealed Method in TG curves for the Calcium sulfate dihydrate

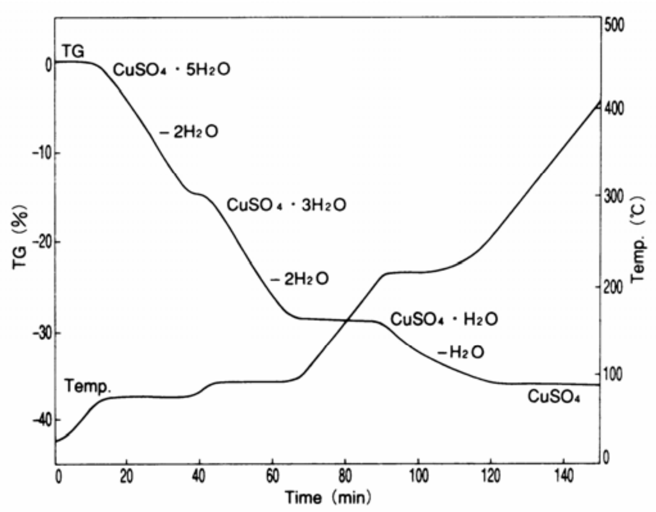

Figure 5 Quasi-Isothermal Measurement Results for the Copper sulfate pentahydrate

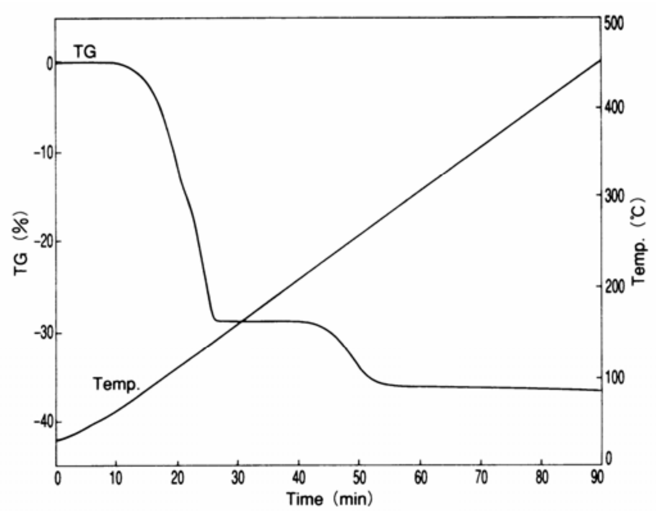

Figure 6 Quasi-Sealed Measurement Results for the Copper sulfate pentahydrate

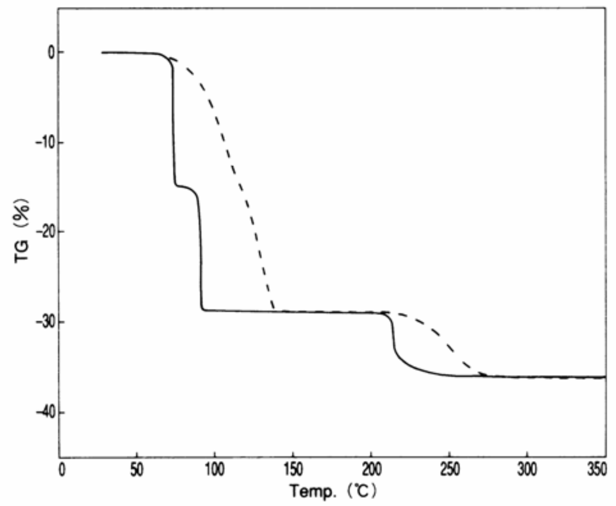

Figure 7 Comparison of Quasi-Isothermal and Quasi-Sealed Method in TG curves for the Copper sulfate pentahydrate

Figure 3 shows the quasi-sealed measurement results for the calcium sulfate dihydrate. Figure 4 compares the TG curves for the quasi-isothermal (Figure 2) and quasi-sealed (Figure 3) measurements. While the quasi-sealed measurement results in Figure 3 confirm the two steps of dehydration, the comparison data in Figure 4 shows that the quasi-isothermal results more clearly isolated the two steps.

Figure 5 shows the quasi-isothermal measurement results for the copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$). These results show that the crystal water of the copper sulfate pentahydrate dehydrates in the following process.

$$CuSO_4 \cdot 5H_2O \xrightarrow{-2H_2O} CuSO_4 \cdot 3H_2O \xrightarrow{-2H_2O} CuSO_4 \cdot H_2O \xrightarrow{-H_2O} CuSO_4$$

Formula weight:	249.69	213.66	177.63	159.61

As with the calcium sulfate dihydrate results, the results in Figure 5 clearly distinguish each step of the multi-step dehydration. Furthermore, the weight decrease rate at each dehydration was almost the same as the theoretical value.

Figure 6 shows the quasi-sealed measurement results for the copper sulfate pentahydrate. Figure 7 compares the TG curves for the quasi-isothermal (Figure 5) and quasi-sealed (Figure 6) measurement results. Both Figures 6 and 7 shows that the quasi-isothermal method more clearly isolates the first and second steps of dehydration process.

5. Summary

In this brief, quasi-isothermal thermogravimetry was used to measure the mass of crystal water in calcium sulfate dihydrate and copper sulfate pentahydrate. The quasi-isothermal thermogravimetry accurately isolated and quantified the multiple steps of the dehydration of crystal water of these hydrates at close temperatures. The controlled rate thermal analysis (CRTA) mode simplifies quasi-isothermal thermogravimetry measurements. These measurements can be applied to various materials, including other inorganic compounds, pharmaceuticals and polymers.

Reference

1) Application Brief, TA No. 22, Hitachi High-Tech Science Corporation (1985)
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4) J.Paulik, F.Paulik, Anal.Chim., 56, 328 (1971)
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