DIRECT FOURIER ANALYSIS IN MODULATED THERMOGRAVIMETRY

Elena Moukhina
NETZSCH-Gerätebau GmbH, Wittelsbacherstraße 42, 95100 Selb, Germany
elena.moukhina@netzsch.com

Modulated temperature is the sum of the underlying linear heating or constant temperature and sinus-shaped temperature oscillations with user-defined amplitude and period. Direct analysis method for the temperature-modulated thermogravimetry is proposed. The method is based on the Fourier analysis and calculates the activation energy signal for the modulated thermogravimetric measurement. The method produces correct results for the noisy measurements where standard calculation method fails.
Analysis method of modulated thermogravimetry, also known as modulated-temperature thermogravimetry, was introduced by R.L. Blaine and B.K. Hahn, [1]. It applies modulated temperature T = Ti + To sin(ωt) to kinetic equation dα/dt =Z·f(α)·exp(-Ea / (R·T)) and finds the activation energy from logarithm of ratio of maximum and minimum reaction rates:

$$Ea = R \cdot \ln((d\alpha 1)/(d\alpha 2)) \cdot (Ti^2 - \cdot To^2) / (2 \cdot To).$$

Main problem in this method that it needs the top curve and bottom curve having the same sign ensuring positive ratio for logarithm calculation. This is not always the case (see Figure). In the current work an alternative way is described, how to find the activation energy from a modulated thermogravimetry, and where the above listed problems are not present. Fourier analysis is applied to DTG signal [2] and activation energy is found directly from the amplitude of the main frequency A_{DTG} and average DTG_{avg} of DTG over period. In linear approach it looks like

$$Ea = (R \cdot Ti^2 A_{DTG}) / (To \cdot DTG_{avg}).$$

In this new method the activation energy Ea is found from the amplitude of the modulated DTG signal. This amplitude can be well-defined from experiment by discrete Fourier analysis even when noise is present. The influence of the noise on the results in current method is much lower than in the known method[1]. The software [3] calculates activation energy of chemical reactions from thermogravimetric measurement according to both methods. The activation energy is shown as the continuous function of time, temperature or reaction conversion over the whole measurement

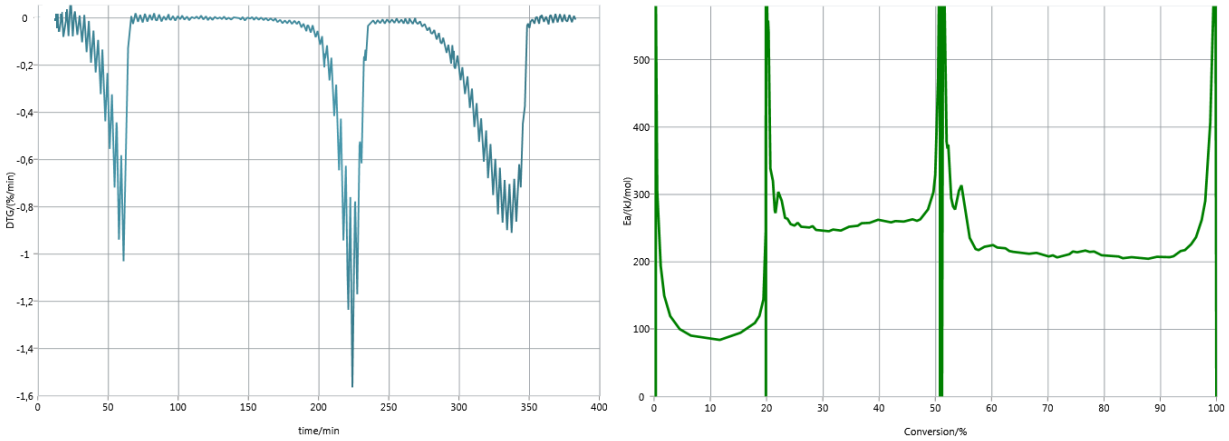

Figure. Measured DTG signal for decomposition of Calcium oxalate monohydrate and activation energy calculated by current method. For initial range, maximal and minimal rates of reaction have different signs, and therefore standard method [1] fails. However, current method of Fourier analysis provides correct activation energy.

[1] R.L. Blaine and B.K. Hahn, *J. Therm. Anal.* **54** (1998) 695-704.
[2] E. Moukhina, *Thermochimica Acta.* **576** (2014) 75-83.
[3] Description for NETZSCH directA. https://ngbdownloads.netzsch.com/directa/