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Subtracting the water effect from DSC curves by using simultaneous TGA data

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Abstract

In this work, a method to calculate the baseline when weight loss processes take place is presented. Such method combines the information obtained by TGA with the simultaneous heat flow signal obtained in a Simultaneous Thermal Analyzer. Once the water evaporation step is identified, thermal parameters such as specific heat and enthalpy of vaporization can be combined with the instantaneous weight loss to subtract the heat flow corresponding to this component from the DSC baseline. In this paper the model was applied to water evaporation in forest litter samples.

Keywords: Simultaneous DSC TGA; Subtraction

1. Introduction

It has been said that DSC measurements obtained when a change of mass occur in the sample, in general, do not represent useful information [1]. The use of sealed pans may help to avoid this problem, but care must be taken to assure sample hermeticity during the experiment. To assure hermeticity some laboratories routinely perform a TGA experiment with a sample encapsulated in the same way as will be used in DSC. The reversing heat flow signal obtained by modulated DSC is not affected by the evaporation process but, since MDSC does not measure the sample mass during the experiment, it is not possible to refer that heat flow to the actual instantaneous mass of the sample.

An interesting attempt to measure ΔH when mass change takes place has previously been done with TG–DTA [2]. The equation to determine the enthalpy of a reaction from a DSC experiment is

$$\Delta H = \frac{KA}{m}$$

where ΔH is the enthalpy change of reaction, m is the mass of the sample at the beginning of the experiment, K is the calibration coefficient, and A is the area under the peak. Determinations of the mass provide a means by which mass changes can be incorporated into DSC calculations [2]. Nevertheless, the literature does not show any example where the baseline is calculated by subtraction of the effect from a component of the sample that volatilizes. The authors propose that it can be done by combining simultaneous information on mass and heat flow obtained in a Simultaneous Thermal Analyzer. The method was applied to the DSC baseline calculation in the case of samples of forest litter in the range of temperatures where water evaporation takes place. Measurement of thermal properties of these materials is necessary for the fire spreading models used in forest fire fighting.

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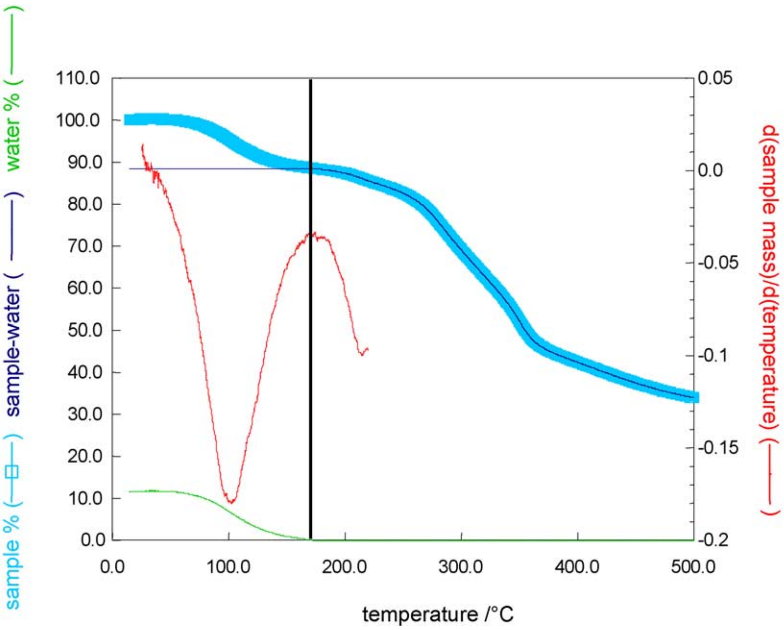

Fig. 1. Black spruce feather moss TGA trace decomposed in two processes. The range of study was limited to the area on the left of the vertical line.

2. Experimental

Samples of different types of forest litter were ground and blended in a planetary mill. Samples of around 8 mg were encapsulated in aluminium crucibles and a pinhole was punched on the top. The samples were analyzed in a simultaneous thermal analyzer Rheometric STA 1500. Each experiment consisted of a heating ramp from 25 to 500 °C at 10 K/min, with argon flow at a rate of 50 ml/min, although the range of data considered in this work was always below 200 °C.

3. Results

Fig. 1 shows the TGA and DTG plots obtained from a forest litter sample.

In wood samples, the first weight loss at around 100 °C is attributed to water evaporation [3]. Assuming that it is what happens in these forest samples, the water content was directly calculated and plotted in Fig. 1, using the DTG peak as end point of water evaporation.

Accepting the assumption that the first step corresponds to water evaporation, the original TGA trace was decomposed

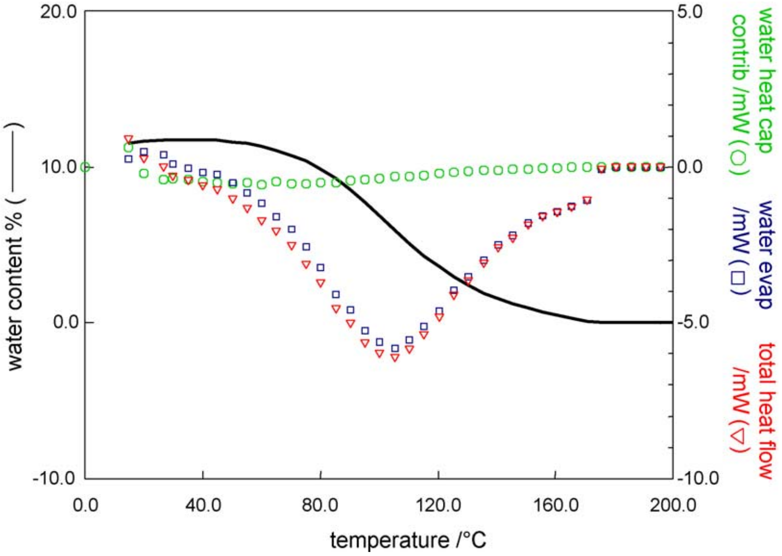

Fig. 2. Calculated evaporation, heat capacity and total contributions along with the instantaneous water content in a black spruce feather moss sample.

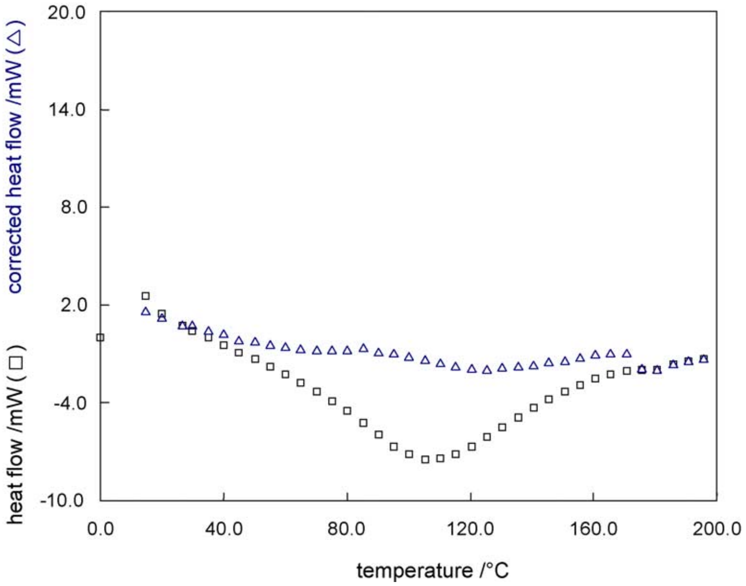

Fig. 3. Measured heat flow and heat flow after water contribution subtraction obtained from a black spruce feather moss sample.

into two traces, one corresponding to water evaporation and the other to the sample with water content subtracted. Since the thermal properties of water are well known, it is possible to subtract its contribution from the heat flow data, as follows:

$$\begin{aligned}&\text{heat flow(water contribution)}\\&\quad=\text{heat flow(water evaporation)}\\&\quad+\text{heat flow(heat capacity of water)}\end{aligned}$$

Since the data were recorded at intervals of 1 s in order to obtain good resolution, all the forthcoming calculations were performed at intervals of 1 s. The heat flow from water evaporation was calculated by multiplying the instantaneous rate of mass loss of water by its evaporation enthalpy value.

The heat capacity heat flow spent in increasing the temperature of the not yet evaporated water was calculated by multiplying the instantaneous mass of water by the water C_p value and the increment of temperature in each 1 s step. An evaporation enthalpy of 2418 J/g and C_p of 4.187 J/g K were assumed.

Fig. 2 shows the calculated evaporation, heat capacity and total contributions along with the instantaneous water content in a sample. It is evident that the heat capacity contribution is almost negligible compared to the evaporation process.

Fig. 3 shows the measured heat flow and the heat flow after water contribution subtraction.

Since the water contribution can be subtracted from the heat flow and mass data, it is possible to calculate the specific heat of the dry sample by comparison with a sapphire experiment under identical conditions. Heat capacity values for sapphire were obtained from [4]. Two replicates of the same sample confirmed the reproducibility of the results. Other samples gave similar results.

4. Discussion

This methodology allows subtracting the evaporation contribution of a volatile component when the thermal properties of the substance that evaporates are known. The heat capacity contribution of the substance that evaporates can also be subtracted, since the actual instantaneous weight of the substance that evaporates can be obtained from the TGA trace. Calculation of specific heat flow of the sample, less the total effect of the substance that evaporates, can be performed by combining the corrected heat flow with the actual mass of the remaining sample.

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