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Short Communication: Analysis Method

Significant hidden temperature gradients in thermogravimetric tests

Carlos Gracia-Fernández[a], Begoña Álvarez-García[b], Silvia Gómez-Barreiro[b], Jorge López-Beceiro[b], Ramón Artiaga[b,*]

[a] TA Instruments-Waters Cromatografía, Alcobendas, 20108, Madrid, Spain
[b] University of A Coruña, EPS, Avda. Mendizábal s/n, 15403, Ferrol, Spain

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ABSTRACT

In thermal analysis, correct measurement of temperature is usually ensured by means of a calibration procedure. However, in addition to make sure that the right value of temperature is measured, estimation of temperature gradients into the sample is important. That is especially important in thermogravimetric (TG) analysis, where combinations of some of the common sample sizes heating rates could lead to important differences of temperature into the sample. If there is a significant gradient between different parts of the sample, then the temperature of the thermocouple, although correct, does not actually represent the temperature of the whole sample. While the correctness of the temperature is always important, errors in temperature measurement are critical in kinetic studies. Thus, estimations of the temperature gradients that appear into the sample as a result of a given treatment are of highest interest to choose the right operational conditions that minimize that gradient. That is particularly important for kinetic studies. In this work, thermal gradients originated into a sample during a typical TG test are estimated through a simulation study performed on the Comsol ™ software. A typical vertical TG furnace, sample size of about 125 mg, and several heating rates were used. Additionally, samples of different void contents were considered. The results of the simulation show that significant gradients of temperature can be achieved into the sample with experimental conditions like those that are often used. It is also observed that the difference of temperature between the sample and the furnace wall not only depends on the heating rate, which can be easily corrected by calibration at the corresponding heating rate, but also varies with temperature, which makes highly recommended to calibrate in more than one temperature point when broad ranges of temperature are considered.

1. Introduction

Thermogravimetry is a technique that measures the mass of a sample as a function of temperature or time while it is subjected to a controlled temperature program in a controlled atmosphere [1]. The origin and first developments of this technique were thoroughly described by different authors [2–5]. Most of the early thermobalances were constructed by individual investigators [6], such as Nernst and Riesenfeld [7], Brill [8], Truchot [9], Urbain and Boulanger [10] and Honda [11] at the beginning of the twenty-first century. It is also remarkable the work of Duval [12], who developed an automated analytical method based on thermogravimetry. His work provided a strong impetus for this technique [13]. The first commercial thermobalance appeared in 1945 and it was based on the work of Chevenard [14]. The evolution has been fast from the beginning up to now, and the sensibility and precision of the thermobalance were increasing continuously. Nowadays, TG is one of the most common thermal analysis techniques and it is used in many industrial and scientific fields. A clear review of TG and other thermophysical characterization techniques has been provided by K.P. Menard [15].

Temperature calibration is routinely performed in any thermal analysis technique. While there are many works discussing the importance of temperature calibration and several standards indicating the right procedures to calibrate temperature of different instruments [16–26], only a few works paid attention to the possible gradients of temperature originated into the sample while subjected to a typical thermo-analytical temperature program [27,28]. Thermal gradients originated into the sample during a typical thermogravimetric (TG) test are estimated here through a simulation study. For the simulation, a typical vertical TG furnace, samples of different porosity and thermal conductivity, and a few of the most common heating rates were used.

* Corresponding author.
E-mail address: ramon.artiaga@udc.es (R. Artiaga).

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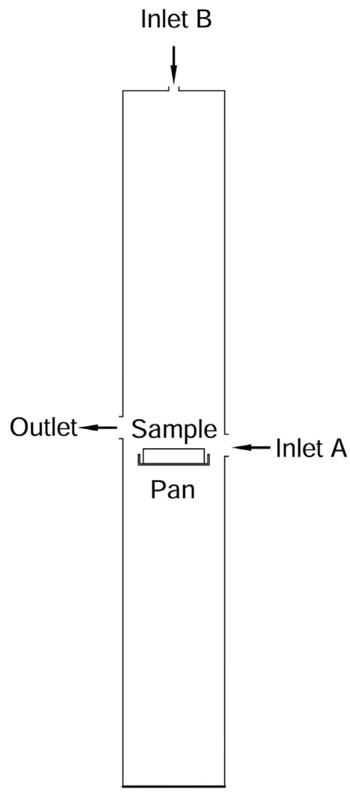

Fig. 1. Layout of the furnace geometry considered for this work.

2. Furnace geometry and operating conditions

For the simulation, a typical vertical TG furnace geometry was considered. Fig. 1 shows a layout of the furnace where the locations of the gas inlet and outlet holes and of the sample holder can be observed. The sample holder consists of a typical open platinum pan. For simplicity, the hang-down system was not included in the simulation. The inner walls of the furnace are supposed to be made of alumina. In order to realistically reproduce the actual operating conditions, a purge of nitrogen is applied through the A and B inlets at 80 and 20 mL/min, respectively. While entering through two different holes, all gas goes out through one single outlet. All the simulated experiments consist of linear heating ramps. It is assumed that the temperature at the inner wall surface is always uniform. The heating ramp is directly applied on the furnace wall. This is an ideal situation since, in real instruments, the temperature is not completely uniform at the furnace wall surface and the wall surface is normally heated from a resistance embedded in the furnace material. Four heating rates, 5, 10 and 20 °C/min, were used for the different cases as it will be described below. These heating rates are very common in thermogravimetry.

In order to evaluate how some features of the sample may affect the temperature distribution into the sample, two different types of samples were considered:

A-type: this sample is defined as a cylindrical slice of 2.00 mm height and 4.16 mm radius, made of a hypothetical material with thermal conductivity and specific heat capacity values similar to those of a commercial polyamide 66 at 20 °C. For simplicity, it is supposed that the material keeps these features in all the range of temperature considered in the tests. Of course, many polymers would melt and degrade in that range, but including possible transformations of the samples would imply a very high complexity and it would be very difficult to generalize the results to any kind o material. Thus, the values used for simulation were 1140 kg/m^3, which results in a sample mass of 124 mg, thermal conductivity of 0.43 W/(m. K), and specific heat capacity of 1670 J/(kg. K). In order to see the effect of voids in the temperature distribution into the sample, four levels of porosity were considered: 0, 8, 16, and 25%.

B-type: In order to evaluate the effect of thermal conductivity four samples with no porosity but with different thermal conductivities were considered: 0.42, 0.21, 0.084, and 0.042 W/(m. K). In all cases the density was 2650 g/m^3 and heat capacity 758 kg/J/K.

3. Fundamentals of the simulation

The thermal gradients originated into the sample during a typical TG test are estimated through a simulation study performed by means of the Comsol software [29]. In order to perform the simulation, the three-dimensional geometry described above is reduced, for computation, to a two-dimensional geometry. That simplification should not significantly affect the results since the system, including furnace, platform and sample, is cylindrically symmetric except for the entry and exit holes. These three holes were conveniently located on the same plane so that a two-dimensional simulation can take into account the gas flow effect.

On the other hand, the Navier-Stokes equations are coupled with the heat transfer model, being the pressure and the velocity field the solution of the Navier-Stokes equations, while the temperature is solved through the heat transfer model. The buoyancy exerted by the fluid, which depends on temperature and density, is introduced in the Navier-Stokes equations for compressible fluids. Simultaneously, the heat equation accounts for convective heat transfer. The Laminar Flow and the Heat Transfer in Fluids interfaces are coupled through the "Temperature Coupling" and "Flow Coupling" features of the software.

The governing equations in the Laminar Flow and the Heat Transfer in Fluids interfaces are:

- The Navier-Stokes equations

$$\rho\left(\frac{\partial u}{\partial t} + u\cdot\nabla u\right) = -\nabla p + \nabla\cdot\left(\mu(\nabla u + (\nabla u)^T) - \frac{2}{3}\mu(\nabla\cdot u)I\right) + F$$

where u is the fluid velocity, p is the fluid pressure, ρ is the fluid density and μ is the fluid dynamic viscosity. The left-hand side term corresponds to the inertial forces, the first term of right-hand side represents the pressure forces, the second term the viscous forces and the third term the external forces applied to the fluid.

This equation is always solved together with the continuity equation:

$$\frac{\partial\rho}{\partial t} + \nabla\cdot(\rho u) = 0$$

Solving these equations, for a particular set of boundary conditions, allows to predict the fluid velocity and its pressure for a given geometry.

- Heat equation

$$q = h_f(T_w - T_f)$$

where q is the heat flux, h_f is the heat transfer coefficient of the fluid, T_f is the local fluid temperature and T_w is the wall temperature.

The Reynolds number (Re) allows to predict laminar or turbulent patterns for different fluid flow situations. For flow in a cylindrical pipe, the Reynolds number can be defined as:

$$Re = \frac{\rho v_s D}{\mu}$$

where ρ is the fluid density, v_s is the average velocity of the fluid, μ is the fluid dynamic viscosity and D is the hydraulic diameter of the pipe.

According to the Reynolds number prediction, considering the furnace and sample geometry and the gas flow rate, the flow will be always of the laminar type.