

A METHOD FOR CONSTANT-RATE HEATING OF MILLIGRAM-SIZED SAMPLES

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Heating a milligram-sized sample of material at a constant heating rate is usually achieved by controlling the temperature of an electric-resistance furnace with a proportional integral derivative (PID) controller. Here we present a new method for constant-rate heating that is based on a semi-empirical mathematical expression relating sample temperature, heating rate, and electric power supplied to the furnace. This method uses PID control only for second-order corrections of the heating rate. The linearity of the sample temperature *vs.* time curves obtained by applying this method to a simple furnace setup is the same as the linearity of the curves generated by modern commercial thermogravimetric analyzers.

Keywords: constant-rate heating, milligram-sized samples, new method

Introduction

Heating a small (1–10 mg) sample of material at a constant heating rate (typically, 0.1–1.0°C s⁻¹) is a technique that is used widely in thermal analysis and pyrolysis experiments [1, 2]. The constant-rate heating is usually achieved by employing a furnace equipped with a resistive heating element. The temperature of the element is monitored by a thermocouple and controlled by a proportional integral derivative (PID) controller [1, 3]. The controller manipulates electric power supplied to the element in order to keep its temperature as close as possible to the programmed temperature, which is a linear function of time. A separate thermocouple is used to monitor the temperature of a sample, which is usually placed in the middle of the furnace.

Here we present a new method for constant-rate heating that is based on a semi-empirical mathematical expression relating sample temperature, heating rate, and electric power supplied to the furnace. In this method, a single thermocouple is used to monitor the temperature of a sample and control its heating rate. According to the comparative analysis described below, the linearity of the sample temperature *vs.* time curves obtained using this method in combination with a simple furnace setup is the same as the linearity of the curves generated by modern commercial thermogravimetric analyzers.

Experimental

A schematic of the setup used in the heating experiments is shown in Fig. 1. A ceramic tube (1.5 mm thick wall) with a nichrome wire tightly spiraled around the outside served as a furnace. This tube was enclosed in a metal box (approximately 10·10·12 cm). The tube was continuously purged with 80 cm³ min⁻¹ of nitrogen. A small ceramic cup (about 6 mm in diameter and 0.5 mm thick walls) was used as a sample container. The cup was placed on a ceramic post located on the axis of the tube. A type K thermocouple was built into the post. The bead of the thermocouple was in direct contact with the bottom of the sample cup. Direct electric current generated by a programmable power supply (RKW48-7K by KEPCO Inc.) was used to heat the furnace. A PC equipped with a data acquisition board (PCI-6014 by National Instruments Corp.) and LabVIEW software [4] was used to

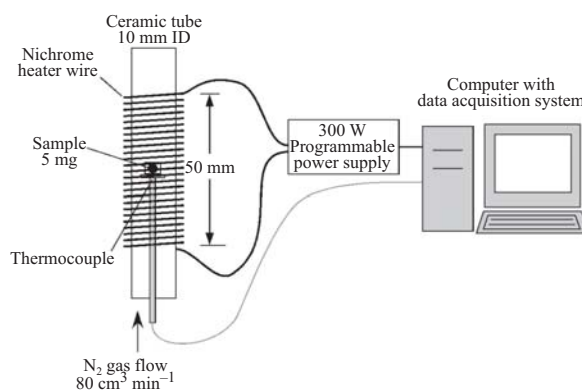


Fig. 1 Experimental setup

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control the power supply output (0–48 V) and read the temperature of the thermocouple.

Heating rate control methodology

Temperature histories obtained by application of constant voltages to the furnace are shown in Fig. 2. The sample container used in these measurements was empty. It is apparent from the shape of the curves that they can be described by an exponential-rise function,

$$T = B - Ae^{-kt} \quad (1)$$

where B , A , and k are adjustable parameters and t is time. The results of the least-square fit of the experimental data with this function are presented in Fig. 2.

Differentiation of Eq. (1) with respect to time and subsequent expression of the result in terms of temperature (using Eq. (1)) yield a linear relation between the temperature and heating rate:

$$\frac{dT}{dt} = kAe^{-kt} = k(B - T) = kB - kT \quad (2)$$

The form of Eq. (2) indicates that the system under consideration is a lumped-heat-capacity system, which is an idealization frequently used to describe

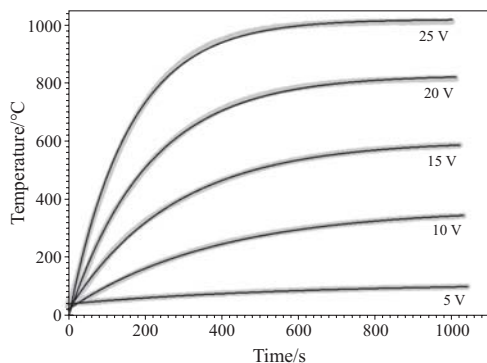


Fig. 2 Constant-voltage temperature histories. Gray dots are experimental data. Black lines are results of the least-square fit with Eq. (1)

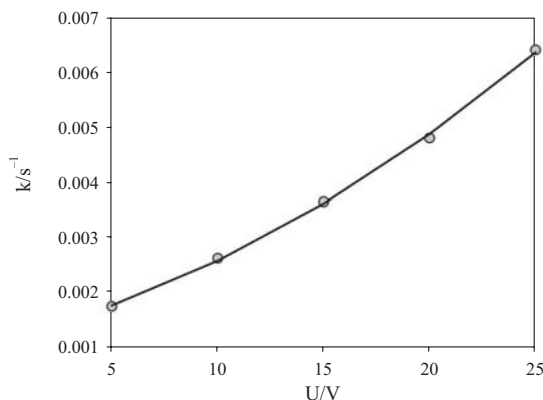
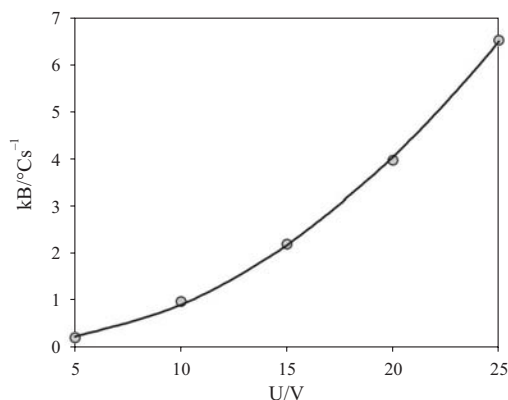


Fig. 3 Dependencies of parameters of Eq. (2) on voltage. Circles are parameter values derived from experimental data. Black lines are the least square fits with Eqs (3) and (4)

transient heat conduction [5]. The kB product and k are two parameters that depend on the voltage applied to the furnace. The values of these parameters (obtained from the fit of the constant-voltage temperature histories) are plotted with respect to the voltage, U , in Fig. 3. As demonstrated by the graphs, these dependencies can be captured by second-order polynomials:

$$kB = b_0 + b_1U + b_2U^2 \quad (3)$$

$$k = k_0 + k_1U + k_2U^2 \quad (4)$$

Substitution of these polynomial expressions into Eq. (2) yields a quadratic equation:

$$(b_2 - k_2T)U^2 + (b_1 - k_1T)U + \left(b_0 - k_0T - \frac{dT}{dt} \right) = 0 \quad (5)$$

The positive root of this equation,

$$U = \frac{-(b_1 - k_1T) + \sqrt{(b_1 - k_1T)^2 - 4(b_2 - k_2T) \left(b_0 - k_0T - \frac{dT}{dt} \right)}}{2(b_2 - k_2T)} \quad (6)$$

is an expression of the voltage in terms of the temperature and heating rate. This expression provides us with a means of calculating the voltage that needs to be applied to the furnace in order to heat a sample, which is currently at temperature T , at the rate dT/dt .

The applicability of expression (6), which is subsequently referred to as the control expression, to heating rate control is based on the assumption that kB and k parameters of Eq. (2) depend only on the voltage applied to the furnace and are insensitive to the rate of change of this voltage with time. It is further assumed that the presence of a sample does not have a significant effect on the heating process. The range of heating rates and temperatures covered by the control expression is, to a large degree, determined by the range of voltages used in the generation of constant-voltage temperature histories.

Table 1 Summary of the results of constant heating-rate experiments (the averages and standard deviations are calculated using the data collected between 90 and 700°C)

Instrument/Method	Set heating rate/ °C s ⁻¹	Average measured heating rate/ °C s ⁻¹	Standard deviation from the set heating rate/°C s ⁻¹
Commercial 1	0.250	0.250	0.006
Commercial 2	0.250	0.247	0.008
Present method	0.250	0.250	0.011
Commercial 1	0.500	0.499	0.016
Commercial 2	0.500	0.495	0.013
Present method	0.500	0.498	0.016
Commercial 1	1.000	1.010	0.050
Commercial 2	1.000	1.000	0.030
Present method	1.000	0.990	0.030
Commercial 1	2.000	2.070	0.190
Commercial 2	2.000	2.020	0.090
Present method	2.000	1.960	0.110

Initial tests indicated that the control expression could be used to keep the heating rate at a constant, preset value over a broad range of temperatures. However, the parameters of the control expression were found to be somewhat unstable. These instabilities were attributed to shifts in the positions of the nichrome wire coils of the heater. The shifts usually occurred during the heating-cooling cycles where a temperature above 600°C was reached. In order to avoid significant deviations (10–30%) of the average heating rate from its set point, the parameters of the control expression had to be reevaluated every 10–20 high temperature heating-cooling cycles. Development of an automated calibration program (implemented using LabVIEW [4]), which essentially followed the parameter determination procedures described above, mitigated the problem.

The problem with the heating rate deviation was solved by using a simple implementation of PID control to correct the heating rate input to the control expression. In the beginning of a heating experiment, the control expression heating rate (dT/dt) was assigned the value of the set heating rate (dT/dt_{set}). Subsequently, each time the measured heating rate ($(T-T_{\text{old}})/t-t_{\text{old}}$) deviated further from the set point, the control expression heating rate was reevaluated as follows:

$$\frac{dT}{dt} = \frac{dT}{dt_{\text{old}}} + \left(\frac{dT}{dt_{\text{set}}} - \frac{T-T_{\text{old}}}{t-t_{\text{old}}} \right) t_{\text{control}} \quad (7)$$

Here, *old* subscripts are used to refer to the values that correspond to the preceding cycle of the control algorithm. The t_{control} parameter is a characteristic time of response to the deviation from the set point. Setting this parameter to 12 s provided an adequate rate of response at the set heating rate of 0.5°C s⁻¹. No further optimization of t_{control} was performed.

Application of the heating-rate correction to the control expression virtually eliminated the need for calibration, which was required only when a new furnace tube or thermocouple post was installed. It should be noted that the need for frequent calibration might also have been eliminated by employing a furnace equipped with a more stable heating element. An obvious advantage of the heating rate correction, however, is that, in addition to handling instabilities of the furnace, it mitigates heating rate perturbations introduced by other sources (nitrogen flow, sample, etc).

Comparison with commercial thermogravimetric analyzers

Samples of poly(methyl methacrylate) were heated at rates of 0.25, 0.50, 1.0 and 2.0°C s⁻¹ from room temperature to 750°C using the present method and two modern thermogravimetric analyzers from leading manufactures. In this paper, the commercial instruments are referred to as Commercial 1 and 2. All furnaces were purged with the same flow of nitrogen –80 cm³ min⁻¹. A platinum pan was used as a sample container in Commercial 1. The sample container used in Commercial 2 was a ceramic cup similar to that used in the present setup. In both commercial instruments, the thermocouples monitoring sample temperatures were positioned under the bottom of a sample container. Poly(methyl methacrylate) samples were in the form of spherically shaped pellets of almost identical mass –5.0±0.1 mg. These pellets decomposed endothermically at about 400°C, which introduced significant perturbations into the heating processes.

Sample temperature and heating rate histories measured in the constant heating-rate experiments are shown in Fig. 4. According to the results summarized in Table 1, the commercial instruments and the pres-

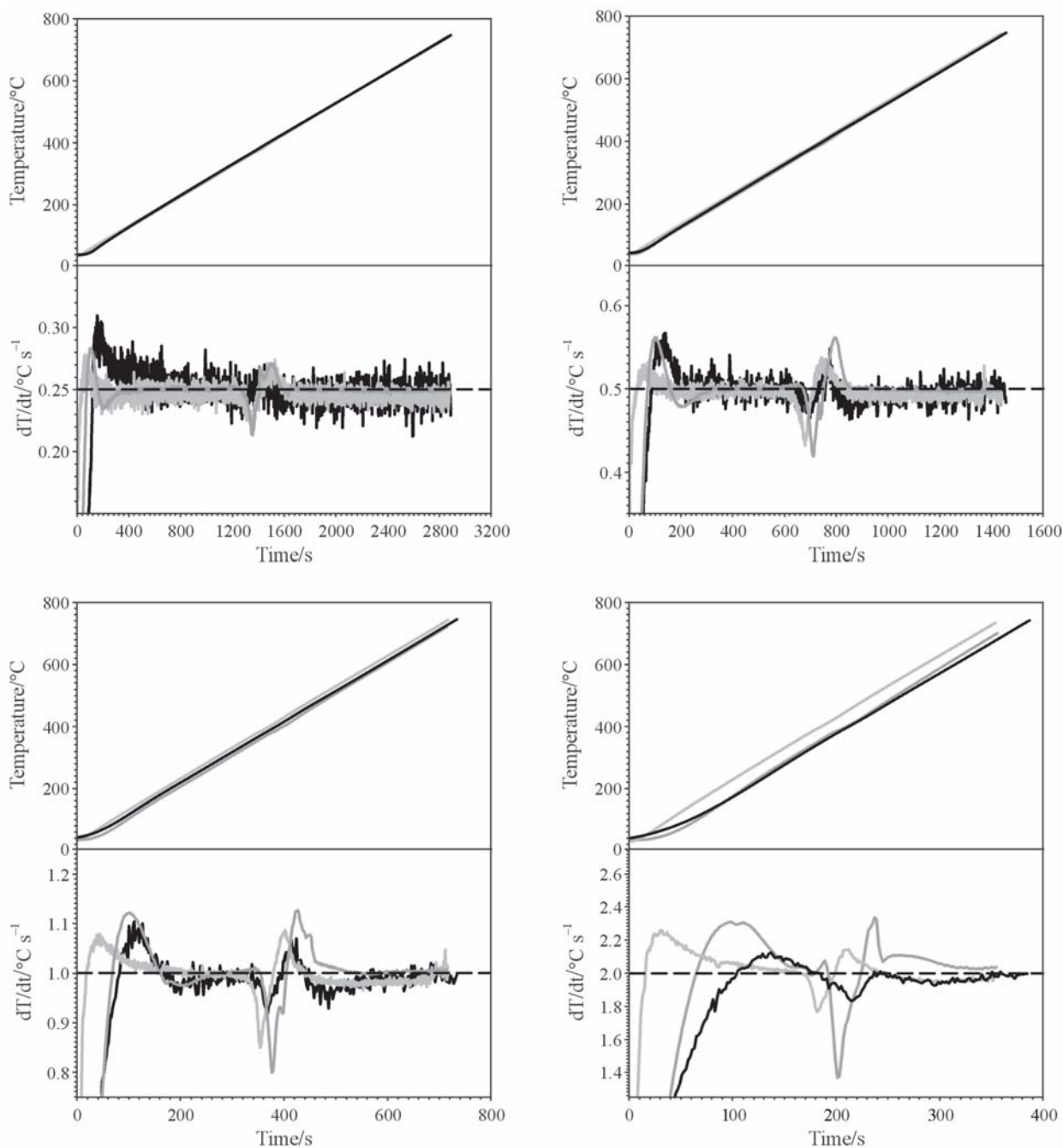


Fig. 4 Sample temperature and heating rate histories measured in constant heating-rate experiments. The heating rate was set at 0.25, 0.50, 1.0 and 2.0 °C s⁻¹. Each pair of graphs shows results obtained for one set point, which is depicted by a dashed line. Dark gray and light gray solid lines are data obtained using Commercial 1 and 2 instrument, respectively. Black solid lines are results of the present method

ent method perform equally well. The temperature signals of the commercial instruments are notably less noisy (the noise manifests itself as a scatter in the measured heating rate), which is probably a consequence of the use of noise suppression filters and/or better screening in their temperature-reading circuits. A somewhat slower rate of the initial rise to the set heating rate displayed by the present method is a re-

sult of a larger size and mass (and therefore higher thermal inertia) of the furnace.

Conclusions

The present method is a promising alternative to the traditional approach to maintaining a constant heating rate. Application of this method to a simple furnace

setup has resulted in the level of heating rate stability that matches the heating rate stability of modern thermogravimetric analyzers. This method is currently employed in the new version of the pyrolysis-combustion flow calorimeter – an instrument that measures heat of combustion, heat release capacity, and ignition temperature of materials using milligram-sized samples [6, 7].

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References

- 1 M. E. Brown (ed.), Handbook of Thermal Analysis and Calorimetry, Elsevier, Amsterdam 1998, Vol. 1.
- 2 T. Hatakeyama and F. X. Quinn, Thermal Analysis. Fundamentals and Applications to Polymer Science, John Wiley and Sons, Chichester, England 1999.
- 3 R. P. Hunter, Automated Process Control Systems. Concepts and Hardware, Prentice-Hall, Englewood Cliffs, NJ 1978.
- 4 LabVIEW Professional Development System 7.0 for Windows, National Instruments Corporation.
- 5 J. P. Holman, Heat Transfer, 9th Edition, McGraw-Hill, Boston, MA 2002, pp. 133–135.
- 6 R. E. Lyon and R. N. Walters, J. Anal. Appl. Pyrol., 71 (2004) 27.
- 7 R. E. Lyon, R. N. Walters and S. I. Stoliarov, J. ASTM Inter., 2006, Vol. 3.

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