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Accuracy and precision of heat capacity measurements using a heat flux differential scanning calorimeter☆

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Abstract

The accuracy and precision of a Setaram DSC 121 for the measurement of heat capacities of solids in the continuous mode was tested using sapphire and benzoic acid. The influence of the heating rate, mass of sample, and position of the crucible in the measuring tube on the obtained results is discussed. In the temperature range studied (320–440 K for sapphire and 320–370 K for benzoic acid) the accuracy and precision of the determination, based on the average results of three independent experiments, are better than 1% provided that adequate experimental conditions (large sample masses and low heating rates) and data handling procedures are used.

Keywords: DSC; Heat capacity accuracy; Heat capacity precision; Heat flux calorimetry

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1. Introduction

Differential scanning calorimetry (DSC) is a widely used method for the determination of the heat capacity of substances [1]. In general, the accuracy claimed for C_p measurements by DSC, when compared to well established results obtained by adiabatic calorimetry, varies from ~ 5 to ≤ 1%, depending on the calorimeter type, on the experimental method, and on the data handling procedure used [1, 2].

We have been applying a Setaram DSC 121 heat flux calorimeter for routine determination of the heat capacity of solids above ambient temperature [3]. The influence of the heating rate, mass of sample, and position of the crucible in the

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measuring tube, on the accuracy and precision of the obtained results for sapphire and benzoic acid are discussed in this paper.

2. Experimental

2.1 Materials

Two samples of synthetic sapphire (α-Al_2O_3 pellets, NIST-RM 720) were used in the experiments. One of the samples was treated at 1173 K as recommended by the supplier and the other was used as received. It was found, however, that for a given set of experimental conditions the heat capacities obtained with different samples agreed within the uncertainty of the measurements. Benzoic acid (Baker and Adamson, 99.98%) was dried in a vacuum oven at 378 K for three days and kept in a desiccator prior to use. The melting point of the benzoic acid sample obtained in this work by DSC was 395.3 K. A standard indium sample from Perkin–Elmer (99.999%; $T_{fus} = 429.6$ K and $\Delta_{fus}H = 28.4$ J g^{-1} [4]) was used to check the calibration of the calorimeter.

2.2. Apparatus

The DSC 121 from Setaram is a heat flux calorimeter. The crucible containing the sample and the empty crucible used as the reference (aluminum crucibles were always used in this work) are placed inside sintered alumina tubes. The measuring zone of each tube is enveloped by a thermopile detector. The tubes and the detectors are in the horizontal position inside a thermostatted metal block. The temperature of the metal block can be increased (or decreased) at a programmed rate and the difference between the heat fluxes from the block to the sample, and to the reference (or vice versa), is recorded as a function of temperature or time.

The calibration of the temperature and heat flux scales of our calorimeter was performed by Setaram. The temperature scale was calibrated by measuring the melting temperature of Hg, In, Sn, Pb, Zn, and Al, at different heating rates. The heat flux scale was calibrated by the Joule effect. In the present study the accuracy of these calibrations was checked by measuring the temperature of fusion, T_{fus}, and the enthalpy of fusion of indium. Five experiments at a heating rate of 2 K min^{-1}, with indium samples having masses in the range 10–20 mg, led to $T_{fus} = 429.5 \pm 0.1$ K and $\Delta_{fus}H = 28.1 \pm 0.2$ J g^{-1}, where the uncertainties quoted are twice the standard deviations of the mean. These results are accurate to 0.06 and 1%, respectively, when compared with the recommended values [4]. Further tests at 1, 5, and 10 K min^{-1}, indicated that the accuracy in $\Delta_{fus}H$ is not affected by changes in the heating rate. However, the accuracy of T_{fus} decreases as the heating rate increases.

2.3. Method

The general method for determination of heat capacity by DSC in the continuous mode is well established [1]. Fig. 1 illustrates the procedure used in this work to measure the heat capacity of sapphire and benzoic acid as a function of the temperature. Each C_p vs. T determination requires two consecutive runs. In the blank run

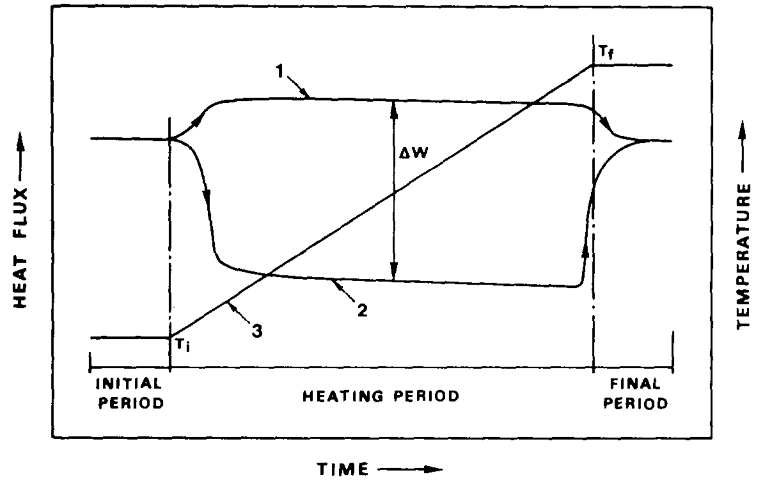


Fig. 1. Heat capacity determination in the continuous mode: (1) blank curve, (2) sample curve, (3) temperature program.

(curve 1) the reference and the sample-measuring tubes contain empty crucibles. The temperature of the metal block is increased, at 2 K min^{-1}, from room temperature to the initial temperature of the experiment, T_i. The data acquisition starts at T_i. After 600 s at this temperature, the block is heated again at a programmed rate (rates from 1 to 10 K min^{-1} were used in this work) and the calorimetric signal deviates from the initial isotherm. The heating period stops at T_f and , subsequently, there is a decay of the calorimetric signal to the baseline during the final 600 s isotherm. In the second experiment (curve 2) the crucible previously contained in the sample-measuring tube, is filled with the sample and the temperature program described above is repeated. The amplitude difference (ΔW) between the blank and the sample heat fluxes at each temperature (Fig. 1) gives the heat capacity of the sample according to the equation:

$$C^{*}_{\mathrm{p,m}}/\mathrm{J\,K^{-1}mol^{-1}} = \frac{M}{m\beta}\Delta W \tag{1}$$

where m and M are the mass and molar mass of the sample, respectively, and β is the heating rate.

Fig. 1 represents an ideal curve. Usually, however, the baselines of the blank and the sample curves are not perfectly superimposed and, in this case, the value of ΔW in Eq. (1) is determined as

$$\Delta W = w_1 + w_2 \tag{2}$$

where w_1 and w_2 are the amplitude differences measured from the blank and sample baselines, respectively, as shown in Fig. 2.

No purge gas was used during the experiments. Unless otherwise stated, the crucibles always contained the maximum amount of sample possible (~ 600 mg for sapphire and ~ 240 mg for benzoic acid powder). The benzoic acid powder samples were pressed into the crucible and were not pre-melted prior to the heat capacity measurement.

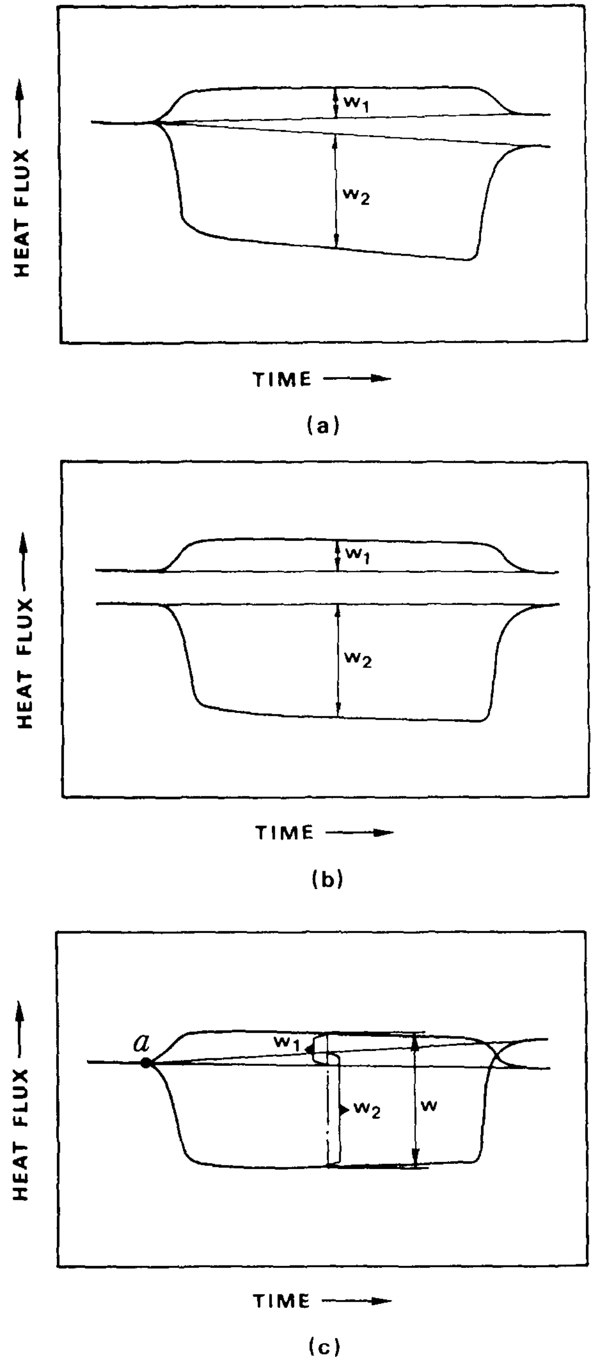


Fig. 2. Examples of heat capacity determination when the baselines of the blank and the sample curves: (a) are not coincident in the final period and do not cross each other. (b) are not coincident in the initial and final periods. (c) are not coincident in the final period and cross each other; the meaning of point *a* is explained in the text.

3. Results and discussion

The accuracy of the heat capacity measurements described in this work for sapphire and benzoic acid was evaluated by computing the deviations of the results obtained from Eqs. (3) and (4), respectively,

$$C^*_{\mathrm{p,m}}\,(\text{sapphire, cr})/\mathrm{J\,K^{-1}mol^{-1}} = AT^{-3} + BT^{-2} + C/T + D + ET + FT^2 + GT^3 + HT^4 \tag{3}$$

$A = -1.3251 \times 10^8$ $\quad E = -0.171503$

$B = 4.54238 \times 10^6$ $\quad F = 1.289719 \times 10^{-4}$

$C = -5.475599 \times 10^4$ $\quad G = -4.60768 \times 10^{-8}$

$D = 2.574076 \times 10^2$ $\quad H = 6.31755 \times 10^{-12}$

$$C^*_{\mathrm{p,m}}(\mathrm{C_7H_6O_2},\ \mathrm{cr})/\mathrm{J\,K^{-1}mol^{-1}} = \mathrm{A} + \mathrm{B}T + CT^2 + \mathrm{D}T^3 \tag{4}$$

$A = -201.95$ $\quad C = -5.717 \times 10^{-3}$

$B = 2.36207$ $\quad D = 5.733 \times 10^{-6}$

where T is the temperature in K. Eq. (3) is given in the NBS Certificate for Standard Reference Material 720. Eq. (4) was derived from a polynomial fit to the heat capacity data for benzoic acid reported in [5], and is valid in the temperature range 320–380 K. In the following we will refer to the molar heat capacities of sapphire and benzoic acid given by Eqs. (3) and (4) as $C^*_{\mathrm{p,m}}$ (3) and $C^*_{\mathrm{p,m}}$ (4), respectively.

3.1. *Evaluation of the software supplied with the calorimeter for the calculation of the heat capacity*

Usually, in our experiments, a curve of the type indicated in Fig. 2c was obtained. In this case, and quite surprisingly, measuring the amplitudes w_1 and w_2 (Eq. (2)) with a ruler from a plot of the curve and computing $C^*_{\mathrm{p,m}}$ from Eq. (1) (method 1), always led to smaller deviations from Eqs. (3) and (4) than using the software supplied by Setaram (method 2). Fig. 3 shows typical examples of the deviations found when the heat capacities of sapphire obtained in this work, $C^*_{\mathrm{p,m}}$ (exp.), by methods 1 or 2 are compared to the standard values, $C^*_{\mathrm{p,m}}$ (3), given by Eq. (3). The fact that, for curves such as that in Fig. 2c, method 2 always leads to smaller heat capacity values than method 1, suggests that the software from Setaram uses $\Delta W = w$ instead of $\Delta W = w_1 + w_2$ (Fig. 2c) in the calculation of $C^*_{\mathrm{p,m}}$. If the software package *Additional operations on the curves* has also been supplied with the calorimeter, it is possible to transform the experimental curve into a curve of the type represented in Fig. 1 using the *Slope correction* option. This option enables a rotation of the baselines of the reference and sample curves to the horizontal. In the case of the curve represented in Fig. 2c, correcting the baselines of the reference and sample curves by a rotation centred on

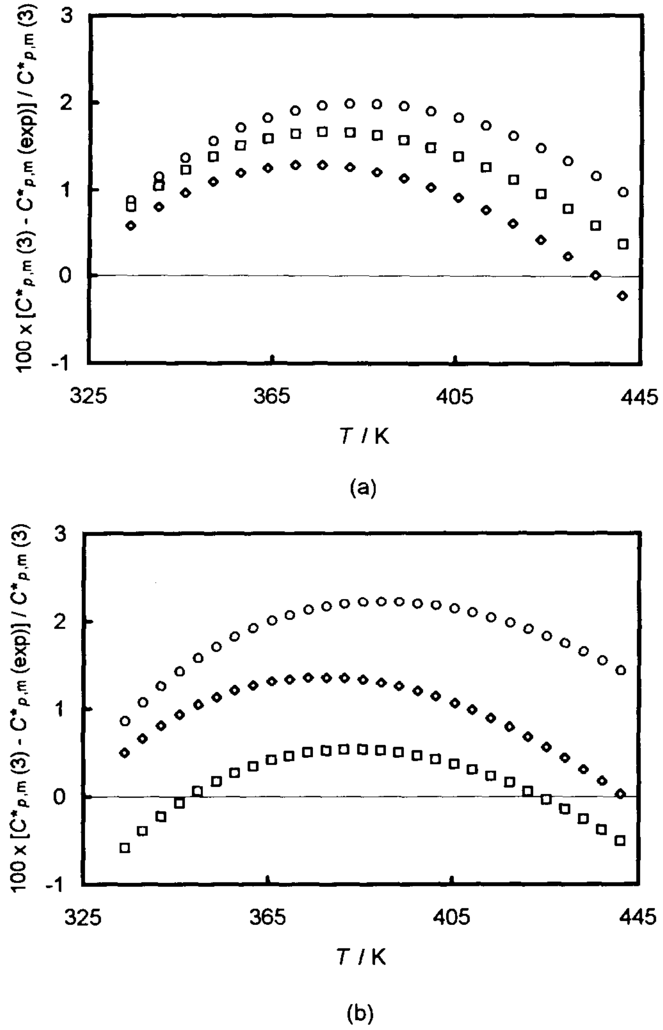
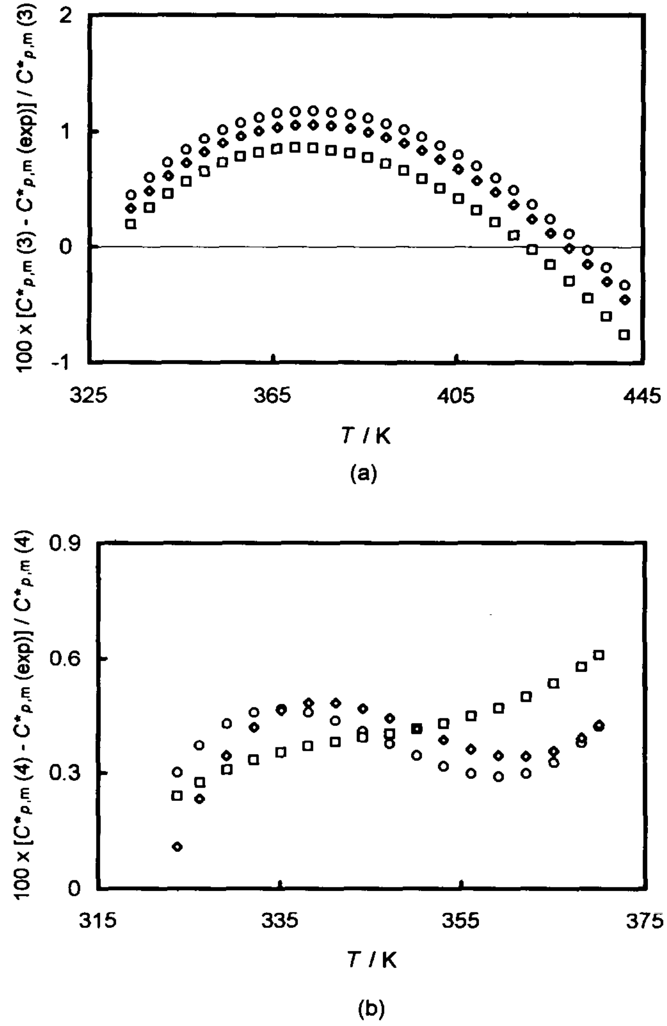


Fig. 3. Influence of the method of calculation on the accuracy of the heat capacity of sapphire measured at a heating rate of 2 K min^{-1} (see text). (□) method 1; (○) method 2, (◇) method 3. (a) Results obtained for a curve of the type represented in Fig. 2c. (b) Results obtained for a curve of the type represented in Fig. 2b.

point *a* leads to a curve of the type represented in Fig. 1 and ΔW becomes equal to $w_1 + w_2$. As shown in Fig. 3a, applying the heat capacity program to the corrected curve (method 3) leads to considerable improvement of the deviation $100 \times [C^*_{\mathrm{p,m}}(3) - C^*_{\mathrm{p,m}}(\mathrm{exp.})]/C^*_{\mathrm{p,m}}(3)$ relative to method 2. In this case, method 3 also gives better results than method 1. If, however, the experimental curve is similar to the one shown in Fig. 2b (i.e. the baselines of the blank and the sample runs are not coincident in the initial and final periods) it is impossible to obtain a Fig. 1-type curve using the slope correction program. In this case $\Delta W \neq w_1 + w_2$ and method 3 may give less accurate results than method 1 (Fig. 3b). In this work methods 1 or 3 were always used to obtain $C^*_{p,m}$(exp.).

3.2. Influence of the position of the crucible

The crucible (sample or reference) is introduced horizontally inside the alumina tube and pushed to the measuring zone using a steel rod. The rod is marked so that the



(a)

(b)

Fig. 4. Influence of the variation in the position of the crucible inside the measuring tube on the accuracy of the heat capacity of (a) sapphire and (b) benzoic acid. Heating rate: 2 K min^{-1}. (○) First set of experiments; (□) second set of experiments; (◇) third set of experiments (see text).

crucible can always be placed approximately in the same position. In order to test the influence of small variations in the position of the crucible containing the sample in the measurement of the heat capacity, the following sets of experiments were performed. A mark was made in the crucible so that, if desired, its orientation inside the measuring tube could be approximately controlled. In the first set of experiments, after the blank run, the crucible was filled with the sample, re-introduced in the measuring tube with the same orientation, and three consecutive runs were made without removing it from the measuring tube. The second set of experiments also consisted of a blank run and

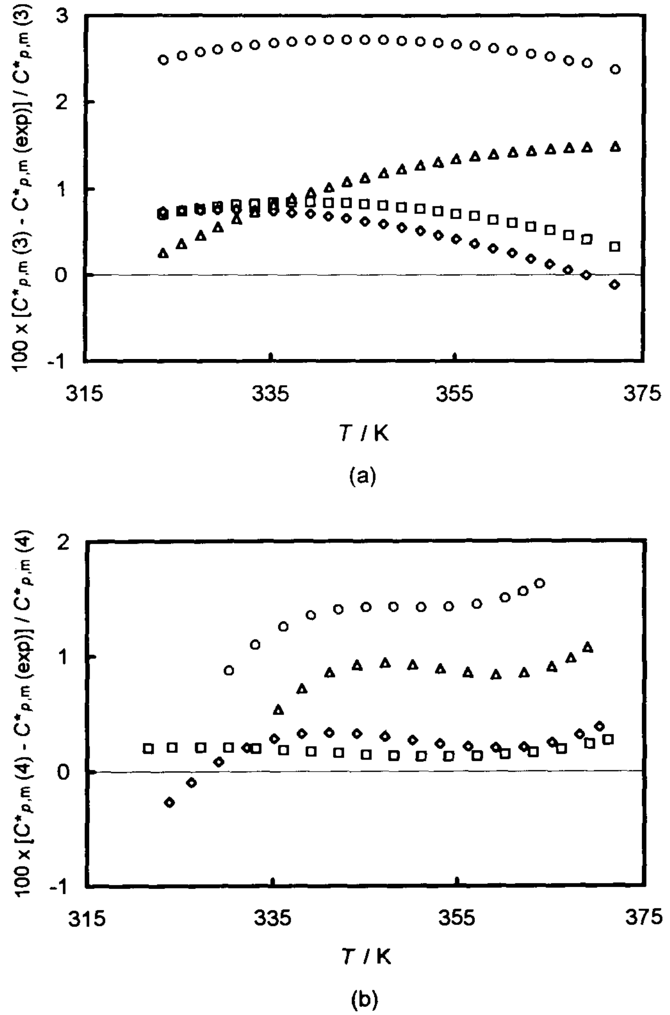


Fig. 5. Influence of the heating rate on the accuracy of the heat capacity of (a) sapphire and (b) benzoic acid. (□) 1 K min^{-1}; (◇) 2 K min^{-1}; (Δ) 5 K min^{-1}; (○) 10 K min^{-1}.

three consecutive experiments with the sample, but in this case the crucible was removed from the measuring tube and re-introduced with the same orientation between each run. In the third set the crucible was removed from the measuring tube and its orientation was deliberately changed between runs. Fig. 4a shows the average deviations from Eq. (3) obtained in each set of experiments for sapphire (note that in this case $C^*_{p,m}$ (exp.) represents the average of the three heat capacity values obtained at each temperature in a complete set of experiments). The corresponding values for benzoic acid are represented in Fig. 4b.

For sapphire, the averages of the standard deviations obtained for $C^*_{p,m}$ (exp.) in the temperature range of the experiments (which measures the precision of the method) are 0.66, 0.74, and 1.02 J K^{-1} mol^{-1}, for sets 1, 2, and 3, respectively. The corresponding values for benzoic acid are: 0.38 (set 1), 0.47 (set 2), and 0.29 (set 3) J K^{-1}mol^{-1}.

It can be concluded from these results that, although the precision of the measurements decreases, in general, when the position of the crucible is not controlled, the accuracy is not significantly affected if the average results of at least three experiments are considered.

3.3. *Influence of the heating rate*

Fig. 5 shows the deviations of the experimental results for sapphire and benzoic acid from Eqs. (3) and (4), respectively, for different heating rates. Three runs were made at each heating rate, and the values of $C^*_{p,m}$ (exp.) used in the calculation of the deviations in Fig. 5 correspond to the average of the results obtained at each temperature in the three different experiments. For sapphire, the averages of the standard deviations obtained for $C^*_{p,m}$(exp.) in the temperature range of the experiments are: 0.44 (1 K min^{-1}), 0.25 (2 K min^{-1}), 0.32 (5 K min^{-1}), and 2.65 (10 K min^{-1}) J K^{-1} mol^{-1}.

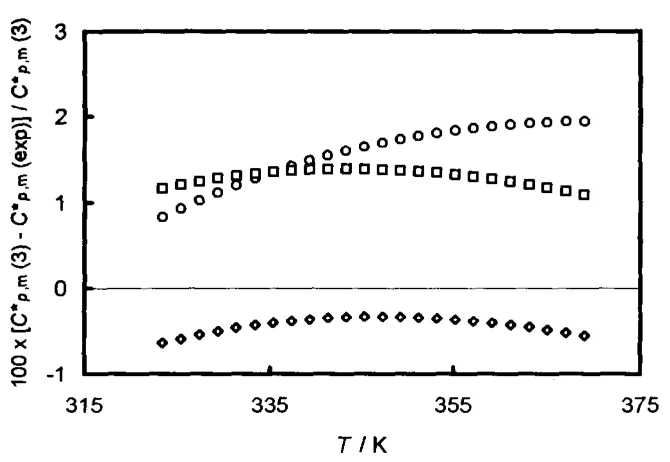


Fig. 6. Influence of the mass of sample on the accuracy of the heat capacity of sapphire. Heating rate: 2 K min^{-1}. (○) m = 102.0 mg; (□) m = 300.0 mg; (◇) m = 604.8 mg.

The corresponding values for benzoic acid are: 0.46 (1 K min^{-1}), 0.42 (2 K min^{-1}), 0.12 (5 K min^{-1}), and 0.21 (10 K min^{-1}) J K^{-1} mol^{-1}.

Fig. 5 shows that for heating rates larger than 2 K min^{-1} the accuracy of the results obtained decreases considerably with the increase in the heating rate. On the other hand, the standard deviations quoted above indicate that the precision of the results is not significantly different except for a heating rate of 10 K min^{-1}.

3.4. *Influence of the mass of sample*

The influence of the mass of sample used in the measurement of the heat capacity was studied for sapphire only. Three independent runs were made for each mass. Fig. 6 shows that the accuracy of the results decreases as the mass of sample used decreases. The averages of the standard deviations obtained for $C^{*}_{p,m}$(exp.) in the temperature range of the experiments are: 0.17 (604.8 mg), 0.37 (300.0 mg), and 1.73 (102.2 mg) J K^{-1} mol^{-1}, indicating that the precision of the measurement also decreases as the mass of sample decreases.

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