1 Title

2 Analysis of the influence of thermal gradients inside T-history samples on the method 3 accuracy: theoretical approach

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11 Abstract

12 The present work analyses the effect of radial thermal gradients inside T-history samples on 13 the enthalpy temperature curve measurement. A conduction heat transfer model has been 14 utilized for this purpose. Some expressions have been obtained that relate the main 15 dimensionless numbers of the experiments with the deviations in specific heat capacity, phase 16 change enthalpy and phase change temperature estimations. Although these relations can only 17 be strictly applied to solid materials (e.g. measurements of shape stabilized phase change 18 materials, SSPCM), they can provide some useful and conservative bounds for the deviations 19 of the T-history method. Biot numbers emerge as the most relevant dimensionless parameters 20 in the accuracy of the specific heat capacity and phase change enthalpy estimation whereas 21 this model predicts a negligible influence of the temperature levels used for the experiments 22 or the Stefan number.

23

Keywords: T-history method, Phase Change Material, Enthalpy, Storage Capacity

24 Nomenclature

А	Time integral of T_{∞} -T _{sur} [K·s]	δT_{m}	Error in phase change temperature [°C]
Â	Measured time integral of T_{∞} - T_{sur} [K·s]	θ	Dimensionless temperature
Bi	Biot number	λ	Thermal conductivity $[W/(m \cdot K)]$
С	Thermal capacity [J/K]	ξ	Eigenvalue of cond. heat transfer problem
Ĉ	Measured thermal capacity [J/K]	ρ	Density [kg/m ³]
c_p	Specific heat capacity [J/(kg·K)]	Abbreviations	
e	Thickness of the tube [m]	DSC	Differential Scanning calorimetry
e_q	Relative error in surface temperature	PCM	Phase Change Material
$e_{\overline{T}}$	Error in the sample average temperature	SSPCM	Shape Stabilized Phase Change Material
f	Liquid fraction	Subscripts	
h	Enthalpy $[kJ/(kg \cdot K)]$, heat transfer coefficient $[W/(m^2 \cdot K)]$	0	Initial conditions
$\mathbf{J}_{\mathbf{o}}$	Zeroth order Bessel function	cn	Measured in the centreline of the sample
\mathbf{J}_1	First order Bessel function	e	Relative to the T-history experiment
Lc	Characteristic length [m]	m	Relative to the melting process
m	Mass [kg]	ms	Relative to a measured temperature
R			
	Radius [m], thermal resistance $[K \cdot m^2/W]$	r-c	Combined radiation and convection
r _e	Radius [m], thermal resistance [K·m ² /W] Relation between temperature errors	r-c ref	Combined radiation and convection Relative to the reference sample
r _e Ste	Radius [m], thermal resistance [K·m ² /W] Relation between temperature errors Stefan number	r-c ref s	Combined radiation and convection Relative to the reference sample Relative to a T-history sample
r _e Ste T	Radius [m], thermal resistance [K·m ² /W] Relation between temperature errors Stefan number Temperature [°C]	r-c ref s sur	Combined radiation and convection Relative to the reference sample Relative to a T-history sample Relative to the surface of the tube
r _e Ste T t	Radius [m], thermal resistance [K·m²/W] Relation between temperature errors Stefan number Temperature [°C] Time [s]	r-c ref s sur t	Combined radiation and convection Relative to the reference sample Relative to a T-history sample Relative to the surface of the tube Relative to the tube

 ΔT_m Phase change temperature range [°C]

25 **1. Introduction**

26 The determination of the thermo-physical properties of phase change materials is essential27 both for the correct design of thermal energy storage systems and for their simulation. The

enthalpy versus temperature curve determination (h-T) is therefore crucial. Although the DSC technique is the most commonly used for this determination, the T-history method is currently attracting increasing attention due to its simplicity and its good results [1]. In light of the results of previous experimental works dealing with the evaluation of the accuracy of the T-history method, such as that of Lazaro et al. [2] on the empirical verification of a T-history set up, researchers [2-3] generally agree on the suitability of this methodology for measuring the enthalpy temperature curve in a typical PCM application.

35 The T-history method assumes a uniform temperature distribution inside the samples. In order

36 to ensure this condition, the restriction for the lumped capacitance systems (Bi= $h \cdot L_c/\lambda < 0.1$)

has been used [4]. This restriction is based on the analysis of classical transient heat

38 conduction problems, where the phase change process is not considered. In this restriction,

39 different definitions can be used for the characteristic length: the ratio between volume and

40 heat transfer area or the distance corresponding to the highest temperature gradient. Some

41 researchers [5-7] have used the first expression (Bi= $h \cdot R/(2 \cdot \lambda)$), whereas the second and more 42 conservative one (Bi= $h \cdot R/\lambda$) has been utilized in [8-10].

43 Hong et al. [9] claimed that the classical condition for the Biot number was not sufficient for 44 ensuring a uniform temperature distribution during the phase change process. They measured 45 radial thermal gradients inside a sodium acetate sample (R=8mm) during its cooling process. 46 Temperature differences during its solidification were higher than those corresponding to the 47 sensible heat transfer stages. They found that more accurate calculations were obtained when 48 the temperature of the centreline was used. However, since a qualitative explanation of this 49 fact was not found, they suggested that an analytical investigation of the effect on h-T 50 calculations of these thermal gradients would be interesting. The objective of the present 51 study is to analyse the influence of radial thermal gradients inside the T-history samples on the deviations of the calculated h-T curve. 52

53 **2.** Methodology

54 For this purpose, the thermal gradients inside T-history samples resulting from conduction 55 heat transfer are evaluated. Only radial temperature distribution is considered, since T-history 56 tubes are usually designed with a large ratio between their length and diameter (L/D>10). 57 Hong et al. [9] and Rady et al. [11] have empirically proved that axial thermal gradients are 58 negligible during the experiments. Two approaches have been followed: first, an analytical 59 model allows a prediction of the deviation in heat capacity measurements and, secondly, a 60 numerical model has been used in order to evaluate these effects when the phase change 61 process takes place. Dimensionless analysis has been used with the objective of obtaining 62 general relations between the conditions of the T-history experiments and the deviations in h-63 T curve calculations.

64 **2.1 General assumptions**

65 In this work, only conduction heat transfer is considered and therefore the influence of natural 66 convection during the phase change process or the effect of movement of the solid phase during the melting or solidification process are not taken into account. Additionally, it has 67 68 been assumed that the cylindrical section of the sample holder is completely filled by the 69 PCM and reference material. For these reasons, the results can only strictly be applied to the 70 measurements of Shape Stabilized PCM (SSPCM) where a solid material is used for the 71 reference sample. The use of the T-history method for the evaluation of the h-T curves of 72 these solid PCM composites is very promising. For example, Rady et al. [11] applied this 73 method for the thermal characterization of PCM granules and Palomo and Dauvergne [12] 74 developed an experimental methodology similar to T-history –in terms of sample geometry 75 and thermal excitation- that allowed the complete thermodynamic characterization of SSPCM 76 by means of a mathematical inverse method analysis.

78 Considering the particular phenomena that take place during the phase change process, 79 researchers have used different designs for the sample holders in order to control them with 80 the aim of approaching the ideal case of uniform radial melting or solidification. For 81 instance, horizontal tubes have been used in [2, 13] thus minimizing the axial displacement of 82 the solid phase. Additionally, Hong et al. [8] located a stainless wire in the centre of the 83 sample in order to prevent the ice from floating. With the objective of ensuring that the tubes 84 remain filled during the experiment, a vertical volume expansion buffer was used by Peck et 85 al. [13]. When extrapolating the results of this study to a particular T-history experimental set 86 up, the importance of these effects has to be considered. 87 On the other hand, the influence of natural convection during the melting process can be 88 evaluated using the correlation of Raithby and Hollands [14]. For the thermal gradients 89 calculated in this work or experimentally measured by Hong et al. [9], a relation between the 90 effective and liquid thermal conductivity of near 1.5 can be obtained. Therefore, for a general 91 case, the results from this study can be taken as a conservative estimation of the maximum 92 errors due to the radial thermal gradients inside the T-history tubes. 93 Additionally, with the aim of simplifying the dimensionless analysis of the problem, thermal 94 conductivity and heat capacity of the liquid and solid phases are considered equal and a 95 constant equivalent convective and radiant coefficient is assumed (h_{r-c}) . In this work sub-96 cooling and hysteresis are not taken into account.

97

2.2 Dimensionless numbers

Assuming these simplifications, the heat transfer problem of the PCM sample can be
represented by the following equations (1)-(6). An analogous formulation can be applied to
the reference sample.

101
$$\rho_{PCM} \cdot \left(c_{p,PCM} \cdot \frac{\partial T_{PCM}}{\partial t} + h_m \cdot \frac{\partial f}{\partial t} \right) = \frac{\lambda_{PCM}}{r} \cdot \frac{\partial}{\partial r} \left(r \cdot \frac{\partial T_{PCM}}{\partial r} \right) \quad 0 \le r \le R - e \tag{1}$$

102
$$\lambda_{PCM} \cdot \frac{\partial T_{PCM}}{\partial r} \Big|_{r=R-e} = \lambda_t \cdot \frac{\partial T_t}{\partial r} \Big|_{r=R-e}$$
 (2)

103
$$\rho_t \cdot c_{p,t} \cdot \frac{\partial T_t}{\partial t} = \frac{\lambda_t}{r} \cdot \frac{\partial}{\partial r} \left(r \cdot \frac{\partial T_t}{\partial r} \right) \qquad R - e < r \le R$$
(3)

104
$$\lambda_t \cdot \frac{\partial T_t(R,t)}{\partial r} = h_{r-c} \cdot \left(T_{\infty} - T_t(R,t)\right)$$
 (4)

105
$$T_{PCM}(r, t = 0) = T_0 \quad 0 \le r \le R - e$$
 (5)

106
$$T_t(r, t = 0) = T_0$$
 $R - e < r \le R$ (6)

107 According to these conduction heat transfer problems, a set of dimensionless numbers has

108 been defined for the analysis, shown in the following table (table 1). The range of variation

- 109 for each dimensionless number is also presented. These values have been determined
- 110 according to the typical thermal properties and experimental conditions used in the T-history
- 111 method.

112 **Table 1.** Dimensionless numbers used in this study. In brackets values for the base case.

Dimensionless number	Range of variation	Dimensionless number	Range of variation
$Bi_{ref} = \frac{h_{r-c} \cdot R}{\lambda_{ref}}$	[0-0.2] (0.05)	$Ste = \frac{c_{p,PCM} \cdot (T_{\infty} - T_m)}{h_m}$	[0.1-1] (0.3)
$C_{r,ref} = \frac{m_{ref} \cdot c_{p,ref}}{m_{ref} \cdot c_{p,ref} + m_t \cdot c_{p,t}}$	[0.5-0.9] (0.85)	$R_t/R_{r-c} = \frac{\lambda_t}{h_{r-c} \cdot e}$	[0-0.005] (0.003)
$Bi_{PCM} = \frac{h_{r-c} \cdot R}{\lambda_{PCM}}$	[0-0.2] (0.15)	$\theta_m = \frac{\Delta T_m}{T_\infty - T_m}$	[0.02-0.16] (0.08)
$C_{r,PCM} = \frac{m_{PCM} \cdot c_{p,PCM}}{m_{PCM} \cdot c_{p,PCM} + m_t \cdot c_{p,t}}$	[0.5-0.9] (0.7)	$\theta_e = \frac{T_\infty - T_m}{T_\infty - T_0}$	[0.3-0.7] (0.06)

114 **2.3 Analytic model: estimation of deviation in specific heat**

A simplified model is proposed for the analytic estimation of the deviation in the specific heat
capacity calculation. In this model the following additional assumptions are made:

117 -no latent heat is considered;

118 -the container is considered as a lumped heat capacity system: this simplification can be

119 acceptable if
$$\frac{\lambda_s}{\rho_s \cdot c_{p,s} \cdot (R-e)^2} \ll \frac{\lambda_t}{\rho_c \cdot c_{p,t} \cdot e^2}$$
 and $h_{r-c} \ll \frac{\lambda_t}{e}$

According to these assumptions, the transient conduction heat transfer problem corresponding to each sample can be represented by a single domain formulation (equations (7)-(8)). If this is compared to the classical problem of transient conduction heat transfer in cylinders [4], only one additional term –the heat capacity of the tube- is introduced into the boundary condition equation (equation (8)).

125
$$\rho_s \cdot c_{p,s} \cdot \frac{\partial T_s}{\partial t} = \frac{\lambda_s}{r} \cdot \frac{\partial}{\partial r} \left(r \cdot \frac{\partial T_s}{\partial r} \right) \quad 0 \le r \le R - e \tag{7}$$

$$126 \qquad -\lambda_t \cdot \frac{\partial T_s(R-e,t)}{\partial r} + h_{r-c} \cdot \frac{R}{R-e} \left(T_\infty - T_s(R-e,t) \right) = \frac{m_t \cdot c_{p,t}}{2\pi \cdot (R-e)} \cdot \frac{\partial T_s(R-e,t)}{\partial t}$$
(8)

Similarly to the classical transient heat transfer problems, the solutions can be expressed using
a function series (equation (9)). In the following calculations, the first term approximation
will be used.

130
$$T(r,t) \approx T_{\infty} - (T_{\infty} - T_0) \cdot \sum_{i=1}^{\infty} C_i \cdot J_0\left(\frac{\xi_i \cdot r}{R-e}\right) \cdot e^{-\frac{\xi_i^{-2} \cdot \lambda_s}{\rho \cdot c_{p,s} \cdot (R-e)^2} \cdot t}$$
(9)

131 where ξ_i are the infinite solutions of the transcendental equation (equation (10)).

132
$$2 \cdot \frac{J_1(\xi_i) \cdot \xi_i}{J_0(\xi_i)} + \xi_i^2 \cdot \frac{m_t \cdot c_{p,t}}{m_s \cdot c_{p,s}} = 2 \cdot Bi$$
(10)

For low numbers of the Biot number, Bessel functions can be truncated in order to simplify the solution. Therefore, the transcendental equation (equation (10)) can be approximated by equation (11), expressed in terms of the Biot number and relative heat capacity of the sample (C_r , defined in table 1), for the calculation of the first eigenvalue of the problem (ξ_1).

137
$$\xi_1^2 \approx \frac{2 \cdot Bi}{\left(1 + \frac{m_c \cdot c_{p,c}}{m_s \cdot c_{p,s}}\right)} = 2 \cdot Bi \cdot C_r \tag{11}$$

138 The exact thermal energy balance equation on which the T-history method is based is

equation (12). This equation can be modified in order to consider the measured temperature

- 140 (T_{ms}) (equation (13)) using the relative errors (e_q , $e_{\overline{T}}$) associated to the surface temperature
- 141 and the average sample temperature which are defined in equations (14) and (15). These heat
- 142 balance equations (equations (12) and (13)) are formulated in a differential form. Similar

143 expressions were used by Moreno-Alvarez et al. [15] in their proposed differential analysis

144 method for the temperature evolutions measured by the T-history method.

145
$$C_c \cdot \frac{d\bar{T}_s}{dt} + C_s \cdot \frac{d\bar{T}_t}{dt} = \bar{h} \cdot A \cdot (T_\infty - T_{sur})$$
(12)

146
$$C_c \cdot \frac{dT_{ms}}{dt} \cdot (1 + e_{\bar{T}}) + C_s \cdot \frac{dT_{ms}}{dt} \cdot (1 + e_q) = \bar{h} \cdot A \cdot (T_{\infty} - T_{ms}) \cdot (1 + e_q)$$
(13)

$$147 \qquad e_{\bar{T}} = \frac{T_{ms} - \bar{T}_s}{T_{\infty} - T_{ms}} \tag{14}$$

148
$$e_q = \frac{T_{ms} - T_{sur}}{T_{\infty} - T_{ms}}$$
 (15)

149 For low values of the Biot number, the errors in surface and average temperatures can be

approximated (equations (16) and (17)). Here, it has been considered that the temperature is
measured in the centreline of the cylinder. Similarly, analogous expressions can be obtained if
the temperature is measured at the surface.

153
$$1 + e_{\bar{T}} = \frac{T_{\infty} - \bar{T}_s}{T_{\infty} - T_{ms}} = 2 \cdot \frac{J_1(\xi_1)}{\xi_1} \approx 1 - \frac{\xi_1^2}{8} = 1 - \frac{Bi}{4} \cdot C_r$$
(16)

154
$$1 + e_q = J_0(\xi_1) \approx 1 - \frac{{\xi_1}^2}{4} = 1 - \frac{Bi}{2} \cdot C_r$$
 (17)

The following equations represent the approximated method for obtaining the heat capacity of the measured material (equation (18)) and the exact formulation –taking into account 1D heat conduction effects- using the previously defined errors ($e_{\bar{T}}$, e_q) (equation (19)).

158
$$\hat{C}_s + C_c = \left(C_{ref} + C_t\right) \cdot \frac{\int (T_{\infty} - T_{ms,s}) \cdot dt}{\int (T_{\infty} - T_{ms,ref}) \cdot dt} = \left(C_{ref} + C_t\right) \cdot \frac{\hat{A}_s}{\hat{A}_{ref}}$$
(18)

159
$$C_s \cdot (1 + e_{\bar{T},s}) + C_t \cdot (1 + e_{q,s}) = \left[C_{ref} \cdot (1 + e_{\bar{T},ref}) + C_t \cdot (1 + e_{q,ref})\right] \cdot \frac{\hat{A}_s}{\hat{A}_{ref}} \cdot \frac{1 + e_{q,s}}{1 + e_{q,ref}}$$
(19)

160 where \hat{C}_s is the measured heat capacity of the sample and \hat{A}_s and \hat{A}_{ref} the time integrated 161 difference between ambient and measured temperature of each material (sample and 162 reference). The following relation (equation (20)) between temperature measurement 163 deviations can be defined in order to obtain a more compact expression. It is important to note

164 that this relation is the same whether the temperature is measured at the surface or in the

165 centreline of the T-history samples.

166
$$r_e = \frac{1+e_{\bar{T}}}{1+e_q} \approx \frac{1-\frac{Bi}{4}\cdot c_r}{1-\frac{Bi}{2}\cdot c_r}$$
 (20)

Dividing equations (18) and (19), an expression for the deviation of specific heat capacity (e_{cp}), defined in equation (21), can be obtained. This relation between equation (18) and (19) (equation (22)), can be thus expressed (equation (23)) in terms of the ratio of temperature measurement errors (r_e), the relative heat capacities of the samples ($C_{r,i}$) and the relative error in heat capacity (e_{cp}).

172
$$e_{c_p} = \frac{\hat{c}_s - c_s}{c_s}$$
 (21)

173
$$\frac{\hat{c}_s + c_t}{c_s \cdot r_{e,s} + c_t} = \frac{c_{ref} + c_t}{c_{ref} \cdot r_{e,ref} + c_t}$$
(22)

174
$$\frac{e_{c_p} \cdot c_{r,s+1}}{c_{r,s} \cdot (r_{e,s-1}) + 1} = \frac{1}{c_{r,ref} \cdot (r_{e,ref} - 1) + 1}$$
(23)

From equation (23), an explicit formulation for the relative deviation in heat capacity can beobtained (equation (24)).

177
$$e_{c_p} = \frac{c_{r,s} \cdot (r_{e,s}-1) - c_{r,ref} \cdot (r_{e,ref}-1)}{c_{r,s} \cdot [c_{r,ref} \cdot (r_{e,ref}-1)+1]}$$
(24)

Finally, if the above-mentioned approximation of r_e for low Biot numbers is assumed (equation (20)) and the first terms of the Taylor series (developed from variables $Bi_i \cdot C_{r,i}$) of equation (24) are taken, a simplified expression for the deviation of the heat capacity measurement can be obtained.

182
$$e_{cp,s} \approx \frac{1}{4} \cdot \left(C_{r,s} \cdot Bi_s - \frac{c_{r,ref}^2}{C_{r,s}} Bi_{ref} \right)$$
(25)

It should be noted that this analytical model predicts the same deviation in the heat capacity estimation whether the temperature of the samples is measured in their centreline or on their surface, since the relation r_e is identical for both cases. Using equation (25), a maximum deviation of 6% in the specific heat estimation can be obtained if the Biot number limit (Bi=h·R/(2· λ)=0.1) is considered.

189 **2.4 Numerical model**

A finite difference scheme has been developed for calculating conduction heat transfer inside the samples during the phase change process, where the phase change is formulated using the enthalpy method. The spatial mesh is uniformly distributed and a fully implicit method is used for time discretization. A spatial resolution of 0.2 mm and a time step of 10s have been used. The h-T curve is described in the simulations by an analytical function (equation (26)). Palomo et al. [12] have already used this analytical equation in the numerical study of their experimental methodology.

197
$$h(T) = c_p \cdot (T - T_o) + \frac{1}{2} \cdot h_m \cdot \left[1 + tanh\left(\frac{4 \cdot (T - T_m)}{\Delta T_m}\right)\right]$$
(26)

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2.4.1 Analysis of the errors

199 The results of the numerical model have been integrated following the methodology proposed 200 by Marín et al. [6]. Other researchers have proposed alternative algorithms in order to obtain 201 the enthalpy-temperature curve from experimental data. Kravvaritis et al. [16] proposed what 202 they called the "thermal delay method" which was based on a comparison of the heat balance 203 equations corresponding to both samples during the same time interval. On the other hand, 204 Moreno-Alvarez et al. [15] proposed a differential method considering the instantaneous temperature change rate of each material. It should be noted that under the assumptions of the 205 206 proposed model for the analysis -the constant heat transfer coefficient (h_{r-c})-, the obtained 207 enthalpy temperature curve is the same whichever of these methods is applied. 208 A constant temperature increment has been taken for the integration. This temperature 209 increment (0.1°C) is lower than the melting temperature range and much higher than the 210 numerical precision of the calculated temperatures. The accuracy of the integration method 211 has been verified for all cases by comparing the original analytical enthalpy-temperature 212 curve with the numerical table obtained from the exact formulation (considering real 213 temperatures of each material, equation (12)). The errors attributable to this numerical

integration of the results are lower than 0.001% in the enthalpy estimation and smaller than0.001°C in the phase change temperature measurement.

The resulting h-T curve is compared with the original analytical function. Three main parameters have been identified in this study: c_p , h_m and T_m . In figure 1 a representation of these parameters is shown. Equations (21) and (27) define the relative errors in specific heat and enthalpy that are analysed in the following sections. Since the shape of the calculated h-T can vary from the original one, an average error in melting temperature is calculated with equation (28) and made dimensionless by using equation (29).

$$222 e_{h_m} = \frac{\hat{h}_m - h_m}{h_m} (27)$$

223
$$\delta T_m = \frac{\int_{f=0.1}^{f=0.9} (\hat{T}_{PCM}(f) - T_{PCM}(f)) \cdot df}{0.8}$$
(28)

224
$$e_{\delta T_m} = \frac{\delta T_m}{(T_\infty - T_m)}$$
(29)



226 227

Figure 1. Graphical representation of the analysed parameters

228

3. Results

3.1 Parametric analysis

230 A first parametric analysis has been made in order to identify the dimensionless variables that 231 influence the errors defined in the previous section. In this analysis each dimensionless 232 variable has been independently modified within the range shown in Table 1 –while the rest 233 of the variables remain at the fixed values shown in the same table. The influence of each 234 independent dimensionless variable on the deviations is plotted in figures 2 and 3. The 235 influences that are considered relevant in this study are highlighted with a continuous line. 236 This analysis shows Bi and Cr as the most relevant numbers for the calculation of ecp and ehm. 237 Considering the error in the phase change temperature estimation ($e_{\delta Tm}$), the most influential 238 variables are Bi_{PCM} and the dimensionless temperature θ_m . As predicted by the previously 239 defined analytical model, the estimation of the heat capacity is the same whether the 240 temperature is measured at the surface of the tube or in the centreline.



Figure 2. Parametric analysis of the errors.





Figure 3. Parametric analysis of the errors in phase change temperature measurement.



255

3.2 Interaction between dimensionless variables

Secondly, the interaction of the influential dimensionless variables identified in the previous 246 247 parametric analysis has been investigated. First of all, the influence of different combinations 248 of Bi_{PCM}, Bi_{ref}, C_{r,PCM} and C_{r,ref} on the estimation of c_p and h_m has been analysed. In the case of 249 the estimation of the phase change enthalpy when the temperature is measured at the surface, 250 the influence of R_t/R_{r-c} has also been analysed. The correlations obtained from this analysis 251 are plotted in figure 4. They show a good fit to the calculated deviations. Furthermore, the 252 correlation for the error in the specific heat capacity estimation is the same as the expression 253 predicted by the analytical approach.



Figure 4. Correlations obtained from the study.



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Figure 5. Influence on the phase change temperature of Biot number and θ_m 258 As can be seen in figure 5, a more complex relation has been found between the Biot number 259 260 of the PCM sample and the dimensionless temperature θ_m with the error in the phase change 261 temperature measurement. If a melting T-history experiment is considered, the phase change 262 temperature is always overestimated when the temperature is measured at the surface whereas 263 the opposite effect is observed if the temperature of the centreline is used. For low values of 264 θ_m (corresponding to materials with a narrower phase change temperature range), the error is 265 reduced if the centreline temperature is taken and increased if the surface temperature is 266 considered. Some useful simplified relations can be extracted from this analysis in order to 267 provide some bounds for these errors (equations (30)-(31)).

268
$$-0.22 \cdot Bi_{PCM} \le \frac{(T_{\infty} - T_m) \cdot \delta T_{m,c}}{|T_{\infty} - T_m|^2} \le 0$$
(30)

269
$$0.22 \cdot Bi_{PCM} \le \frac{(T_{\infty} - T_m) \cdot \delta T_{m,c}}{|T_{\infty} - T_m|^2} \le 0.35 \cdot Bi_{PCM}$$
(31)

270

3.3 Analysis of the correlations obtained over a sample of the whole space of

271

dimensionless numbers

The expressions obtained for the error estimations are based on a correlation over a sample space where only the "active" dimensionless numbers are varied. However, in this analysis the influence of some dimensionless numbers may have remained concealed. Therefore, the 275 correlations have been tested and verified within a more representative sample of the input 276 variable space (defined in table 1). Since the number of input variables is high, a Montecarlo 277 based sampling method has been used for this purpose. A sample of 100 cases has been 278 obtained using Latin Hypercube (LH) Sampling [17], where each dimensionless number has 279 been considered as a uniformly distributed random variable over the intervals defined in table 280 1. The previously obtained relations for the errors are compared to the results corresponding 281 to the Montecarlo sample. As can be seen in figure 6, these relations fit these numerical 282 results: the maximum root-mean-square deviation (RMSD) is 0.12% and the worst coefficient 283 of determination is 0.992.



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6 4. Conclusions

The effect of radial conduction heat transfer inside T-history samples on the deviations produced in the h-T curve evaluation has been analysed. In this study, the measurement of temperature in the centreline of the sample and at its surface has been taken into account. The errors have been quantified and some useful relations have been obtained between the dimensionless numbers that define the experiments and the errors produced in heat capacity,phase change enthalpy and temperature (table 2).

293 According to the results of the analysed heat transfer model, the deviation of heat capacity 294 and phase change enthalpy does not depend on the Stefan number and temperature levels of 295 the experiment (related to θ_m and θ_e). The difference between the Biot numbers corresponding 296 to the PCM and the reference substance is the most important contribution to the deviation of 297 the heat capacity estimation, whereas the Biot number of the PCM sample is the most relevant 298 dimensionless variable in the phase change enthalpy evaluation if the temperature is measured 299 in the centreline. Considering the heat capacity estimation, the same results are obtained 300 whether the temperature is measured in the centreline or at the surface of the sample. A lower 301 error in phase change enthalpy is obtained if the temperature is measured at the surface. 302 Furthermore, this error does not depend on the PCM thermo-physical properties. However, 303 this temperature measure produces a higher deviation in the phase change temperature 304 estimation, especially when testing pure substances or materials with a narrow phase change 305 temperature range.

306 As previously mentioned, the results of this study can only be strictly applied to T-history 307 experiments with SSPCM where a solid material is used as the reference sample. In these 308 cases, the relations obtained can be utilized to size the samples, to determine the favourable 309 experimental conditions and to calibrate or correct the results. Calibration of the T-history is 310 an interesting method for improving the accuracy of the measurements. For instance, 311 Rathgeber et al. [18] applied a calibration to the heat capacity and phase change enthalpy 312 measured values based on the characterization of reference materials that produced an 313 improved agreement with DSC results.

314

Table 2. Correlations and bounds for T-history deviations owing to radial conduction

Correlation	Bounds for T _m deviations	
$e_{c_p} = 0.25 \cdot C_{r,PCM} \cdot Bi_{PCM} - 0.25 \cdot \frac{C_{r,ref}^2}{C_{r,PCM}} \cdot Bi_{ref}$		
$e_{h_{m,cn}} = 0.5 \cdot Bi_{PCM} - 0.25 \cdot C^2_{r,ref} \cdot Bi_{ref}$	$-0.22 \cdot Bi_{PCM} \le \frac{(T_{\infty} - T_m) \cdot \delta T_{m,Cn}}{ T_{\infty} - T_m ^2} \le 0$	
$e_{h_{m,sur}} = -0.25 \cdot C^2_{r,ref} \cdot Bi_{ref} - 0.6 \cdot \frac{R_t}{R_{r-c}}$	$0.22 \cdot Bi_{PCM} \le \frac{(T_{\infty} - T_m) \cdot \delta T_{m,sur}}{ T_{\infty} - T_m ^2} \le 0.35 \cdot Bi_{PCM}$	

316

317 The extrapolation of these results to a general case of T-history measurement has to be done 318 carefully: the similarity of each particular case to the main assumptions of the analysed model 319 has to be revised (free convection and solid PCM movement inside the sample being 320 neglected, having a fully filled section). However, considering free convection effects, the 321 analysed heat conduction model overestimates thermal gradients inside the samples. Since it 322 produces a conservative estimation of the deviations, the relations obtained can be used in 323 order to establish some bounds for these errors. For example, if the temperature is measured 324 inside the sample the following relations (equations (32)-(34)) can be applied. These can be 325 useful to complete the classical restriction for the Biot number since they relate some 326 parameters associated with the experimental conditions to the accuracy of the method. 327 Considering these relations, the more restrictive Biot conduction (Bi= $h \cdot R/\lambda < 0.1$) is 328 recommended in order to ensure that the deviations in heat capacity and phase change 329 enthalpy measurements are lower that 5%. 330 (32) $e_{c_n} \leq 0.25 \cdot C_{r,PCM} \cdot Bi_{PCM}$

331
$$e_{h_{m,c}} \le 0.5 \cdot Bi_{PCM}$$
 (33)

$$332 \quad -0.22 \cdot |T_{\infty} - T_m| \cdot Bi_{PCM} \le \delta T_{m,c} \cdot \frac{(T_{\infty} - T_m)}{|T_{\infty} - T_m|} \le 0$$

$$(34)$$

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