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Characterizing phase change materials using the T-History method: On the factors influencing the accuracy and precision of the enthalpy-temperature curve

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Abstract

While research on using the latent heat of so called phase change materials (PCMs) for thermal energy storage has gained increasing interest in the last decade, the measurement of its thermal properties are still subject to research. The T-History method has been frequently used by researchers to measure the enthalpy-temperature curve of PCMs but the factors influencing its accuracy and precision have rarely been discussed. This work provides a systematic experimental study of an organic PCM based on different insulated sample holders. It is first shown that the data evaluation method has to be adjusted against noise to improve both accuracy and precision for all experimental setups. The results moreover show that neglecting the insulation thermal mass in the experimental setup leads to systematic errors in the enthalpy results due to oversimplification of the mathematical model. This

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confirms a previous numerical study by the authors. It is recommended that either the mathematical model or the experimental setup are adjusted in future work to decrease this error. Until then it is generally recommended to use sample holders with a high ratio between the thermal mass of the PCM to the insulated sample holder. This is further supported by a measurement uncertainty analysis via Monte Carlo simulations.

Keywords: Phase Change Materials, Thermal Analysis, Calorimetry, T-History

1. Introduction

Utilizing the latent heat of melting and solidification of so called phase change materials (PCMs) has been an active field of research in the last decade, due to the potentially higher energy storage densities compared to sensible storage materials for the same temperature difference [1, 2, 3]. When evaluating a PCM, differential scanning calorimetry (DSC) is typically used to derive the enthalpy versus temperature curve to visualize its phase transition temperature as well as its heat storage potential. However, the small sample sizes in the milligram range used in commercial DSC devices can pose limitations regarding how representable the sample is for the bulk material, especially when measuring heterogeneous materials [3]. Therefore, results from the so called T-History method [4, 5], which utilizes sample sizes in the gram range, have been frequently presented as either an alternative or complementary to DSC measurements [6, 7].

When selecting any measurement method, it is useful to discuss the method with respect to the terms measurement "accuracy" and "precision"

17 [8]. A measurement is considered as accurate, if the derived value of the
18 measurand is close to it's true value. On the other hand, a measurement
19 is considered as precise or repeatable, if the measurand values of repeated
20 measurements do not show a significant spread [8].

21 The ideal method therefore should be both precise and accurate. That is,
22 it should be both repeatable and low of systematic errors resulting from the
23 experimental setup and the mathematical model that converts the measured
24 input quantities to the output quantity. For DSC measurements, a recent
25 round robin test has improved both precision and accuracy after defining a
26 common methodology that can be applied across different DSC devices [9].
27 For the T-History method on the other hand, work is still ongoing to find a
28 suitable experimental setup as well as data evaluation technique [5, 10, 11].
29 Moreover, recent work has started to critically address the underlying method
30 assumptions [12, 13].

31

32 *Discussion of the T-History Method assumptions*

33 The T-History method subjects a PCM sample and a reference mate-
34 rial to step changes of the ambient temperature within the same controlled
35 environment (typically an air climate chamber). The recorded temperature
36 versus time responses of the PCM sample and reference are then compared
37 to calculate the enthalpy change of the PCM sample based on two major
38 assumptions [14]:

- 39 1. It is assumed that the heat flows between the reference material and
40 the ambient \dot{Q}_{ref} , and between the PCM and the ambient \dot{Q}_{PCM} , are

41 equal for the same temperature difference $T - T_{amb} = T_{ref} - T_{amb} =$
 42 $T_{PCM} - T_{amb}$:

$$\dot{Q}_{ref}(T) = \dot{Q}_{PCM}(T) = \frac{1}{R_{th}(T)}(T - T_{amb}) \quad (1)$$

43 2. It is assumed that the measured temperature change over time is repre-
 44 sentative for the whole sample holder via a lumped model formulation
 45 for the sample or reference $k = \{\text{ref}, \text{PCM}\}$ and the sample holder tube:

$$\dot{Q}_k(T) = (m^k \cdot c_p^k(T) + m^{tube,k} \cdot c_p^{tube}(T)) \cdot \left. \frac{dT}{dt} \right|_k \quad (2)$$

46 It is important to note that multi-dimensional heat transfer occurs in
 47 the actual T-History experiment and that it may be practically difficult to
 48 assure one-dimensionality of the heat transfer as well as the uniformity of
 49 the temperature profiles in the PCM. Eq. 1 can therefore only be seen as an
 50 approximation of the effective heat flux from the sample holders to the ambi-
 51 ent. The thermal resistance $R_{th}(T)$ then includes form factors like the overall
 52 heat transfer area of the sample holders. A minimum requirement for the
 53 first assumption is therefore that the sample holders for PCM and reference
 54 are of the same geometrical dimensions. In order to additionally support
 55 this assumption, a number of experimental setups previously reported in the
 56 literature placed an additional insulation layer around the sample holders [5]
 57 making it the dominant component of $R_{th}(T)$.

58

59 Previous works using uninsulated sample holders often applied the Biot
 60 number criteria $Bi < 0.1$ in order to support the second assumption. How-
 61 ever, it is known that thermal gradients still exist during the experiment

62 [15, 16]. The thermal gradients can be reduced by either using sample hold-
63 ers with a small diameter or by decreasing the overall heating or cooling rate
64 in the experiment. For the latter, the ambient temperature step change can
65 be decreased and/or the sample holders insulated.

66

67 Recent numerical studies done by Mazo et al. 2015 [12] on uninsulated
68 sample holders and by the authors [13] on insulated sample holders have
69 started to critically address the validity of the assumptions in Eq. 1 and 2.
70 Both works relied on simplified 1-dimensional heat transfer simulations by
71 studying the effect of parameter variations of the simulated experiment on
72 the enthalpy versus temperature curve. Both works come to the conclusion
73 that systematic errors are present in the enthalpy results, since Eq. 1 and
74 2 can only be seen as approximations for the actual transient effects taking
75 place in both the uninsulated and insulated setup since both approaches have
76 certain limitations.

77 A first deviation in the heat flux is present after the initial ambient tem-
78 perature step change when the thermal diffusivity of sample and reference
79 are not exactly equal [13].

80 When the sample holders are uninsulated, the heat flux of sample and
81 reference to the ambient is moreover determined by the heat convection co-
82 efficient between the sample holder wall and the ambient. The alternative
83 would be to insulate the sample holders and make R_{th} being dominated by
84 heat conduction through the insulation layer.

85 In a recent work by Badenhorst & Cabeza 2017 [10], it was shown that
86 the heat convection coefficient may vary largely in an air climate chamber.

87 Therefore, the assumption of equal thermal resistances may be better sup-
88 ported by using the latter approach, when the experiment is done in these
89 kind of chambers.

90 In [13], however, systematic errors in the range of up to 4% of the con-
91 sidered enthalpy difference due to neglecting transient effects caused by the
92 thermal mass of the insulation material itself were predicted. The error in-
93 creased the more insulation thermal mass was present in the setup. A first
94 methodology was also proposed on how to correct the measurement results.
95 However, it was concluded that this error has to be first experimentally con-
96 firmed and placed within the context of an overall measurement uncertainty
97 analysis of an actual experiment.

98 To the best of the authors knowledge, no attempt has been made so far to
99 perform a systematic experimental study regarding the factors that influence
100 both accuracy and precision of the T-History results. Uncertainties of previ-
101 ous experimental studies are usually not reported and these are only based
102 on a single experimental variant. Moreover, details of the data evaluation
103 procedure are usually not fully disclosed.

104 These kind of studies are however needed to critically assess the validity
105 made in the mathematical model and the experimental setup as well as to
106 confirm the previous numerical work done so far. In this work, the study is
107 based on T-History setups using insulated sample holders. The thermal mass
108 of the insulation is deliberately neglected in Eq. 1 to study experimentally
109 the influence of this assumption in the enthalpy results in analogy to our
110 previous numerical work [13].

111

112 *1.1. Research objectives*

113 The aim of this work is to improve the T-History method with respect
114 to its accuracy and precision. This is done by identifying and discussing the
115 factors for the experimental setup and the data evaluation which influence
116 the accuracy and repeatability of the enthalpy results.

117 For this we present an experimental study based on three different T-
118 History setups by using two sample holder and three insulation types. For
119 each T-History setup, the target of the data evaluation method is to yield
120 repeatable results within repetitive measurement cycles for both cooling and
121 heating. The assumptions of equal heat flux and uniform temperature are
122 moreover critically checked for each setup by using three temperature sen-
123 sors per sample holder and calculating enthalpy curves from each sensor's
124 temperature measurements individually.

125 A first measure for the accuracy within each setup is then given by the
126 difference between cooling and heating cases. Lastly, if the mathematical
127 model is valid, no differences in the results by changing experimental setup
128 parameters and between the different sensors should be present. However,
129 if differences exist, then this is likely due to systematic errors as mentioned
130 above.

131 We show that the data evaluation method has to be adjusted individually
132 for cooling and heating in order not to interpret the raw measurement data
133 erroneously. Their influence on the enthalpy calculations are discussed in
134 detail compared to an idealized case.

135 Furthermore, we perform a study on how estimated input quantity un-
136 certainties (e.g. related to temperature measurements) propagate through

137 the mathematical model and our data evaluation method via Monte Carlo
138 simulations.

139 **2. Material and Methods**

140 *2.1. Experimental Setup*

141 The experiments were conducted using cylindrical sample holders, which
142 are made from conventional copper pipes of 10 and 15 mm diameter and 100
143 mm length (see Fig. 1). Copper is chosen, because it's high thermal conduc-
144 tivity supports the lumped capacity formulation of the sample holder. Addi-
145 tionally, the temperature sensor can be placed directly on the sample holder
146 wall. The sample holders were filled at approximately atmospheric pressure
147 $p \approx 0.1013\text{MPa}$ with the commercially available paraffin based RT28HC (Ru-
148 bitherm) as PCM at $T \approx 40^\circ\text{C}$ and distilled water as reference at $T \approx 20^\circ\text{C}$.
149 We refer to other works in the literature that copper may not be compatible
150 with other types of PCMs due to long term corrosion issues [17, 18]. The
151 sample holders are sealed with conventional copper end caps and glue. The
152 sample holders were insulated with different types of closed cell pipe insula-
153 tions (Armaflex AF) intended for the respective pipe diameter. Due to the
154 geometry of the setup, heat transfer from the sample holder to the ambient
155 is expected to be mostly through the larger cylindrical lateral surface area.
156 The properties of the setups are summarized in Table 1.

157 The temperature of the sample holders was measured by attaching 10
158 kOhm thermistors using aluminum tape on the sample holder wall before
159 placing the insulation around the setup. Three thermistors were placed
160 per sample holder along its axial length and denoted as "top", "center" and



Figure 1: Photo of the sample holders used for Setup A (left) and for Setup B1 and 2 (right)

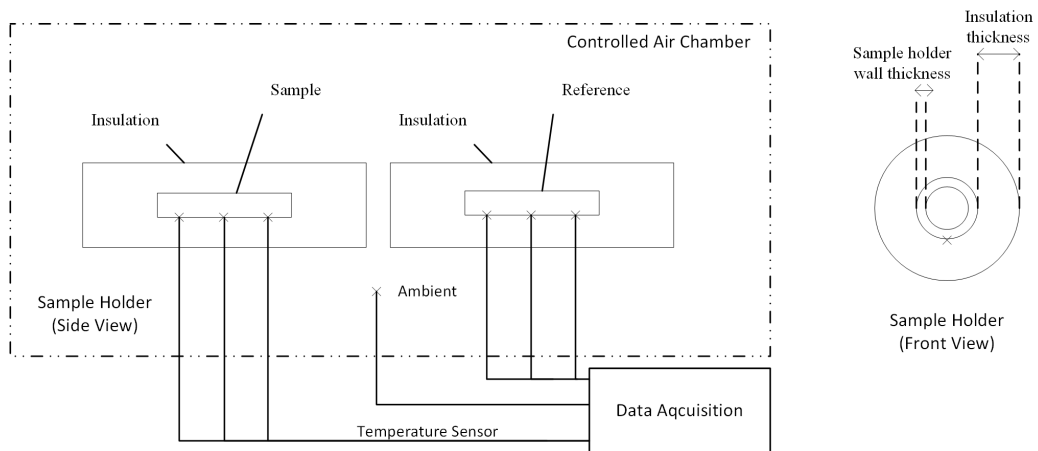


Figure 2: Sketch of the experimental setup. Temperature sensor locations are marked by 'x'.

161 "bottom" sensor location (see Fig. 2 and 3).

162 Prior to the experiment, the thermistors were calibrated against a ref-
 163 erence thermistor (Fluke 5610-6, traceable expanded $k = 2$ calibration un-

Table 1: Sample holder properties. For setup B1 and B2 the same 15mm sample holder is used but with different insulation types. (Insulation properties are taken from the respective product sheets)

Parameter	Setup A	Setup B1	Setup B2	
Sample holder (outer) diameter	10	15	15	mm
Sample holder length	100	100	100	mm
Insulation type	AF-04-10	AF-04-15	AF-06-15	
Insulation length	150	150	150	mm
Insulation thickness	15.5	17	32	mm
Insulation density	60-80	60-80	60-80	kg m^{-3}
Insulation thermal conductivity (at 0°C)	0.033	0.033	0.033	$\text{W m}^{-1} \text{K}^{-1}$
m^{PCM} (RT28HC, paraffin)	4.2	10.1	10.1	g
m^{ref} (distilled water)	5.4	13.1	13.1	g
$m^{tube,PCM}$	25.2	46.8	46.8	g
$m^{tube,ref}$	25.0	46.9	46.9	g
$R_{th}^{tube} \cdot L$	7.21×10^{-5}	5.92×10^{-5}	5.92×10^{-5}	m K W^{-1}
$R_{th}^{Insulation} \cdot L$	6.61	5.71	8.01	m K W^{-1}

164 certainty of 0.01 °C plus 0.01 °C due to first-year drift) in the center of
165 a massive aluminum block. The calibration was performed by comparing
166 the thermistors against the reference sensor readings as follows: The sensors
167 were inserted in the aluminum block and the block placed inside a climate
168 chamber (TERCHY MHK408-YK). The temperature in the chamber was in-
169 creased from 10 to 55 °C in four step changes with enough time (9 hours) for
170 the block and sensors to reach thermal equilibrium after each step change.
171 In a second iteration, the temperature was decreased from 55 to 10 °C in the

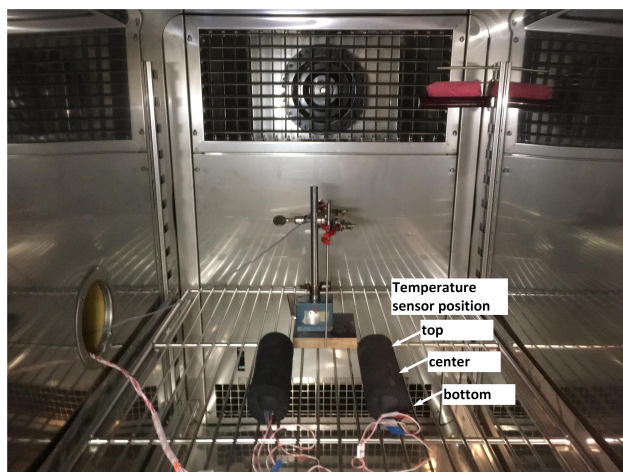


Figure 3: Photo of the experimental setup. All temperature sensors are attached on the underside of the sample holders along its axial length. The "top" sensor is oriented towards the climate chamber fan.

172 same four steps. We estimate that the fitted coefficients of the Steinhart-Hart
173 resistance to temperature equation using readings from the four temperature
174 steps for each thermistor does not exceed a combined standard uncertainty
175 of $u(T) = 0.1$ °C (expanded uncertainty of $U_c(T) = 0.2$ °C, $k = 2$ (95% level
176 of confidence)). The largest uncertainty contribution was due to the radial
177 temperature uniformity in the aluminum block. The reference thermistor
178 itself was used to record the ambient temperature during the experiments.

179 Data logging for both calibration and the T-History experiments were
180 performed using the same data acquisition unit (Keysight 34972A with a
181 16-ch. 34902A multiplexer module).

182 Each setup was placed centrally inside the above mentioned climate cham-
183 ber, with the "top" sensor location pointed towards the fan inside the cli-
184 mate chamber (see Fig. 3). The sample holders were placed horizontally in

Table 2: Climate chamber program for setup A and B

Parameter	Program I	Program II	
$T_{amb}^{min} - T_{amb}^{max}$	18 – 38	13 – 43	°C
$T_{pcm} \pm \Delta T$	28 ± 10	28 ± 15	°C
Duration of one complete heating and cooling cycle	2 · 12	2 · 12	h
Heating and cooling cycles performed	5	5	
Data acquisition interval	5	5	s

185 the climate chamber with the temperature sensors facing downwards. The
 186 sample holders were then subjected to the two different step temperature
 187 programs according to Table 2, representing a higher or lower effective heat-
 188 ing and cooling rate. Before the first measurement, the samples were kept at
 189 the highest program temperature to ensure that the first solidification starts
 190 from a homogenized liquid state. The samples were cycled 5 times to study
 191 the repeatability within a single setup and program. The complete exper-
 192 imental study was done over the course of 5 weeks in the following order:
 193 B2-I → B2-II → B1-I → B1-II → A-I → A-II. Since the thermistors were
 194 not re-attached during the first four experiments, the results for the B type
 195 sample holders are expected to be independent from the goodness of thermal
 196 contact between sensor and sample holder wall. The difference in the results
 197 are then due to the different levels of insulation and heating/cooling rates.

198 In addition, three different enthalpy curves are calculated for a single
 199 cooling or heating case using the PCM and reference temperature readings
 200 from the three sensor locations. This allows an evaluation of the assumption
 201 in Eq. 2, that a single temperature sensor is representative for the whole
 202 sample holder.

203 The temperature measurements obtained from the experiments are shown
204 exemplary in Fig. 4 for Setup A-I and A-II. Measurements for the other
205 setups are reported in the supplementary file to this work. A measure for
206 the uniformity of the climate chamber is given by maximum differences of
207 $0.2 - 0.3^{\circ}\text{C}$ between all sensors at steady state conditions.

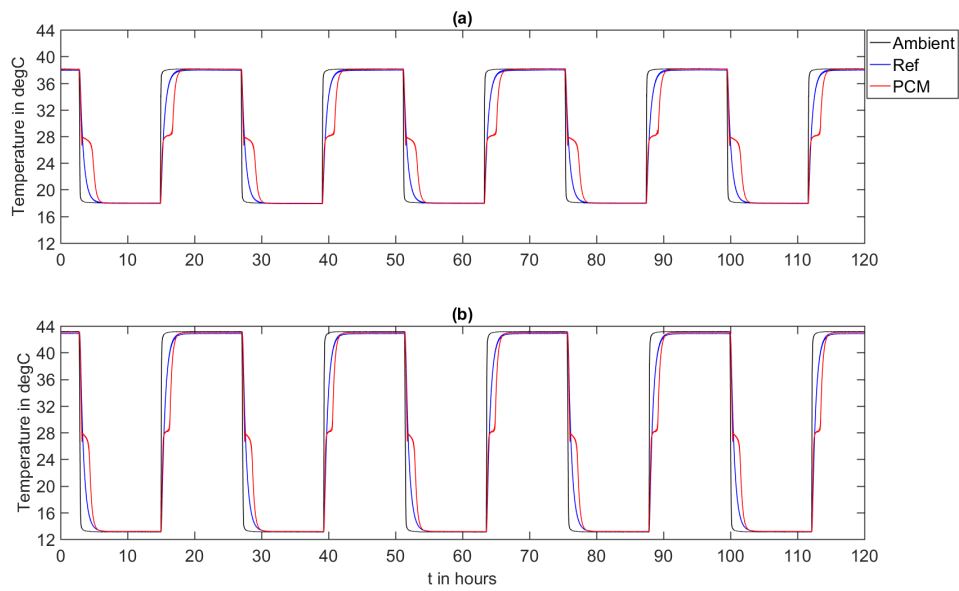


Figure 4: T-History measurements of RT28HC for setup A: (a): A-I, (b): A-II (all three sensor positions for reference and PCM are plotted with the same color, respectively).

208 *2.2. Mathematical model*

209 Enthalpy changes of the PCM can be calculated by combining Eq. 1-2
 210 and solving for the unknown PCM specific heat capacity:

$$c_p^{PCM}(T) = \frac{m^{ref} \cdot c_p^{ref}(T) + m^{tube,ref} \cdot c_p^{tube}(T)}{m^{PCM}} \cdot \frac{\left. \frac{dT}{dt} \right|_{ref}}{\left. \frac{dT}{dt} \right|_{PCM}} - \frac{m^{tube,PCM} \cdot c_p^{tube}(T)}{m^{PCM}} \quad (3)$$

211 For convenience, the terms can be grouped together:

$$212 \quad C_{ref}(T) = \frac{m^{ref} \cdot c_p^{ref}(T) + m^{tube,ref} \cdot c_p^{tube}(T)}{m^{PCM}} \quad \text{and} \quad C_{tube,PCM}(T) = \frac{m^{tube,PCM} \cdot c_p^{tube}(T)}{m^{PCM}}$$

$$c_p^{PCM}(T) = C_{ref}(T) \cdot \frac{\left. \frac{dT}{dt} \right|_{ref}}{\left. \frac{dT}{dt} \right|_{PCM}} - C_{tube,PCM}(T) \quad (4)$$

$$\Delta h^{PCM} = \int_T^{T+\Delta T} c_p^{PCM}(\tau) d\tau \quad (5)$$

213 The mathematical expression $\frac{\left. \frac{dT}{dt} \right|_{ref}}{\left. \frac{dT}{dt} \right|_{PCM}}$ in Eq. 4 represents the essential
 214 idea of the T-History method: The latent heat of a PCM being calculated
 215 by the difference in time it takes for the PCM to undergo the same tempera-
 216 ture change compared to a reference, which does not undergo phase change.
 217 In alternative formulations, this principle has been expressed in the form of
 218 different areas under the temperature versus time curve for the same tem-
 219 perature interval for PCM and reference, respectively [10, 19].

220

221 In the following, the data evaluation method is presented on how the en-
 222 thalpy versus time curve is calculated from the actual measured temperature

223 over time response. We describe necessary simplifications and adjustments
224 in the data evaluation method based on encountered difficulties when using
225 experimental temperature over time data.

226 2.2.1. Ideal case

227 In our previous paper [13], the utilization of Eq. 4 from a simulated
228 T-History experiment was straightforward. Only interpolation between tem-
229 perature and time values was needed in order to express the terms $\frac{dT}{dt}\Big|_{ref}$ and
230 $\frac{dT}{dt}\Big|_{PCM}$ for the same temperature for both PCM and reference. Interpolat-
231 ion was possible because the simulated temperature vs time curve was in a
232 sense ideal. Because no noise, supercooling or other effects were considered,
233 a strictly monotonically increasing or decreasing temperature curve was ob-
234 tained with unique $T = f(t)$ values depending on a cooling or heating case.
235 These ideal cases can be defined by the following conditions:

- 236 • Cooling: Both reference and PCM temperature curves $T = f(t)$ are
237 strictly monotonically decreasing and their time derivatives are $\frac{dT}{dt}\Big|_{PCM} <$
238 0 and $\frac{dT}{dt}\Big|_{ref} < 0$.
- 239 • Heating: Both reference and PCM temperature curves $T = f(t)$ are
240 strictly monotonically increasing and their time derivatives are $\frac{dT}{dt}\Big|_{PCM} >$
241 0 and $\frac{dT}{dt}\Big|_{ref} > 0$.

242 The resulting enthalpy curve was then subjected to two major systematic
243 errors due to the limitations of the mathematical model: (1) by neglecting
244 the temperature gradient inside the PCM sample holder due to the lumped
245 model assumption. This is represented via the well known hysteresis of the

246 enthalpy curve between cooling and heating cases [16]. (2) by neglecting the
 247 insulation thermal mass. This results in differences in transmittive heat flows
 248 at the temperature sensor location, which in turn underestimated the latent
 249 heat released and overestimated the effective heat capacity in the sensible
 250 parts [13]. The underestimation of the latent heat was by far the most dom-
 251 inant error when evaluating the enthalpy difference across the phase change
 252 temperature range. The two errors on the resulting enthalpy curve can be
 253 seen as an assignment of the enthalpy value to the wrong temperature or a
 254 calculation of a wrong enthalpy value itself, respectively. Since the two errors
 255 are systematic, they pose a limit on the achievable accuracy of the T-History
 256 method.

257

258 2.2.2. Non-ideal cases

259 For discrete data, the derivatives $\left. \frac{dT}{dt} \right|_{ref}$ and $\left. \frac{dT}{dt} \right|_{PCM}$ in Eq. 4 can only be
 260 approximated with numerical schemes. In this work we utilize the forward
 261 approximation of the derivative:

$$\frac{dT}{dt}(t) = \frac{T(t + \Delta t) - T(t)}{\Delta t} - O(\Delta t) \approx \frac{T(t + \Delta t) - T(t)}{\Delta t} \quad (6)$$

262 This scheme is first order accurate, since the truncation error $O(\Delta t)$ would
 263 decrease direct proportionally with the chosen step length Δt . In the exper-
 264 iment, the smallest possible step length is given by the data acquisition rate
 265 of 5s.

266 Analogous to the forward discretization, temperature intervals can then
 267 be directly defined from adjacent discrete PCM data values:

$$\left. \frac{dT^i}{dt} \right|_{PCM} = \frac{T_{PCM}^{i+1} - T_{PCM}^i}{t_{PCM}^{i+1} - t_{PCM}^i} = \frac{T_{PCM}^{i+1} - T_{PCM}^i}{\Delta t_{PCM}^i} \quad (7)$$

268 In our measurements, the reference temperature curve and its time deriva-
 269 tive fulfill the ideal case conditions for both heating and cooling since the
 270 reference stores or releases only sensible heat (see Fig. 5). Using the PCM
 271 temperature interval it is then possible to interpolate for the reference time
 272 values $t_{ref}^i = f_{interp}^{ref}(T_{PCM}^i)$ and $t_{ref}^{i+1} = f_{interp}^{ref}(T_{PCM}^{i+1})$. A time derivative based
 273 on the PCM temperature interval can then be formulated for the reference:

$$\left. \frac{dT^i}{dt} \right|_{ref} \approx \frac{T_{PCM}^{i+1} - T_{PCM}^i}{t_{ref}^{i+1} - t_{ref}^i} = \frac{T_{PCM}^{i+1} - T_{PCM}^i}{\Delta t_{ref}^i} \quad (8)$$

274 When formulating the ratio of the time derivatives in Eq. 4, the temper-
 275 ature interval is canceled out and only the time differences remain:

$$\frac{\left. \frac{dT^i}{dt} \right|_{ref}}{\left. \frac{dT^i}{dt} \right|_{PCM}} \approx \frac{\Delta t_{PCM}^i}{\Delta t_{ref}^i} = \frac{t_{PCM}^{i+1} - t_{PCM}^i}{t_{ref}^{i+1} - t_{ref}^i} \quad (9)$$

$$c_p^{PCM}(T^i) = C_{ref}(T^i) \cdot \frac{\Delta t_{PCM}^i}{\Delta t_{ref}^i} - C_{tube,PCM}(T^i) \quad (10)$$

276 For the PCM, this is also the case within its sensible temperature range.
 277 However, during phase change, the temperature curve and its time derivative
 278 deviate from the ideal cases for both cooling and heating. This then needs
 279 special attention and adjustments in the data evaluation procedure when
 280 calculating the enthalpy curve from Eq. 10.

281 In the following, we list these deviations separately for cooling and heating
 282 in order to explain the phenomena behind them and discuss their influence
 283 on the accuracy and precision of the enthalpy curve.

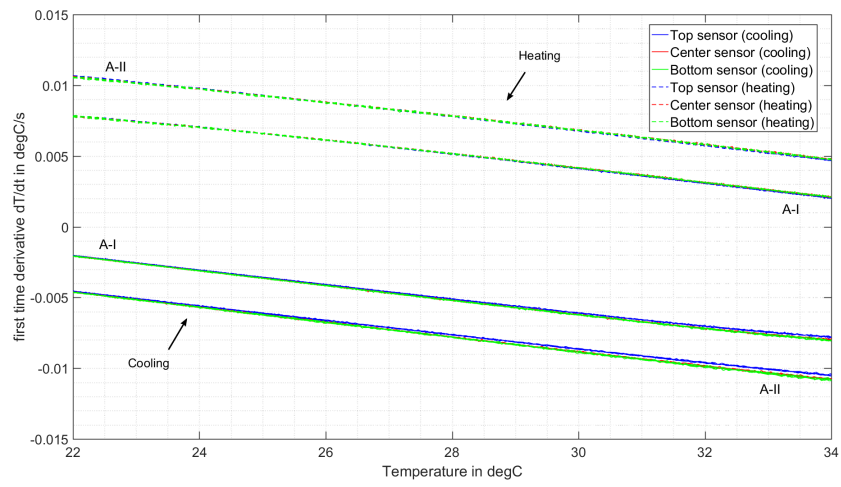


Figure 5: $\left. \frac{dT}{dt} \right|_{ref}$ vs T values for Setup A-I and A-II (sensor data from 5 cycles are plotted with the same color)

284 *Cooling*

285 Fig. 6 shows a typical $\frac{dT}{dt}\Big|_{PCM}$ vs T curve for a cooling case. From the
286 figure, the non-ideal conditions can be summarized as:

- 287 • $\frac{dT}{dt}\Big|_{ref} < 0$, but $\frac{dT}{dt}\Big|_{PCM} > 0$; Due to heat release during recalescence
288 from a supercooled state. In Eq. 4, this leads to negative c_p^{PCM} values.
- 289 • $\frac{dT}{dt}\Big|_{PCM} = 0$; Balance of heat release during recalescence and heat loss
290 to ambient, or due to random noise and a too high data recording rate.
291 In Eq. 4, this leads to $c_p^{PCM} \rightarrow \infty$.

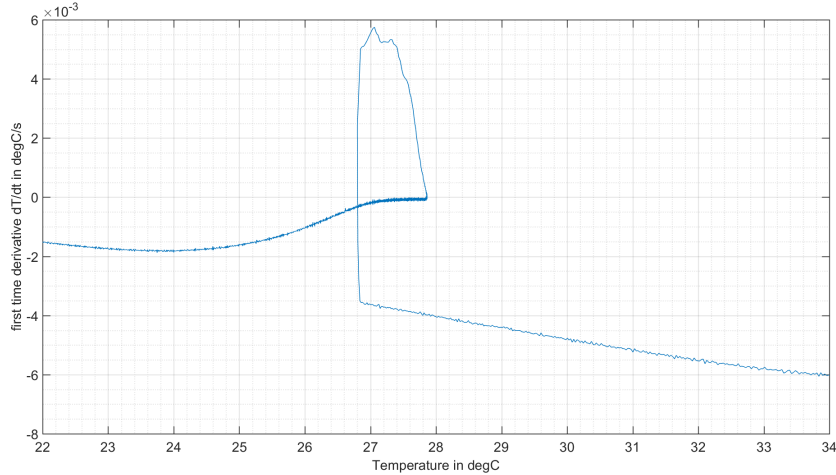


Figure 6: Example of $\frac{dT}{dt}\Big|_{PCM}$ vs T values for Setup B2-I (top sensor, cooling cycle 1)

292 During cooling, the PCM curve has values $\frac{dT}{dt}\Big|_{PCM} > 0$ due to the sudden
293 heat release caused by recalescence (see Fig. 6). That is when the supercooled
294 liquid rapidly solidifies. It is obvious that these derivative values can not be
295 inserted directly into Eq. 4, since they would yield a negative heat capacity
296 $c_p^{PCM}(T) < 0$, which has no physical meaning. What has been proposed

297 in a recent work is to use absolute values for $\left| \frac{dT}{dt} \Big|_{ref} \right|$ [11], which has also
 298 been adopted by our algorithm by setting $\frac{\left| \Delta t_{PCM}^i \right|}{\left| \Delta t_{ref}^i \right|}$ in Eq. 10. However, a
 299 systematic error is likely introduced, since then it is assumed that the heat
 300 flows are equal for a reference cooling case and a PCM heating case.

301 In our experiments, it was moreover observed that using absolute values
 302 for the derivative still leads to negative heat capacity values. This is because
 303 during recalescence $C_{ref}(T) \cdot \left| \frac{dT}{dt} \Big|_{ref} \right| < C_{tube,PCM}(T)$ holds in Eq. 4, since
 304 $\frac{dT}{dt} \Big|_{PCM}$ in the denominator is larger compared to $\frac{dT}{dt} \Big|_{ref}$. For these cases,
 305 we propose to set the negative heat capacity values to $c_p^{PCM} := 0$, which
 306 essentially means that the onset of recalescence is assumed to be adiabatic.

307 This simplification can be justified due to the existing insulation around
 308 the sample holders and if the degree of supercooling is small. In all of our
 309 experiments, the same degree of approx. 1°C supercooling was observed.

310
 311 In the cooling curve, a singularity $\frac{dT}{dt} \Big|_{PCM} = 0$ can moreover occur, e.g.
 312 when the heat release during the final stages of recalescence from supercooling
 313 is in balance with the heat loss to the ambient. It would then not be possible
 314 to evaluate Eq. 4 directly since $c_p^{PCM}(T) \rightarrow \infty$. This problem was already
 315 mentioned previously in [20].

316 A way to circumvent the singularity is to define a minimum allowed eval-
 317 uation step size dT and to compare it with the recorded discrete temper-
 318 ature versus time data within a flexible evaluation window $T_{PCM}^i, T_{PCM}^{i+\Delta i}$.

319 The window size Δi is forced to increase $\Delta i := \Delta i + 1$ when the condition
 320 $\left| T_{PCM}^{i+\Delta i} - T_{PCM}^i \right| \geq dT$ is not fulfilled, following the idea of Stankovic 2014
 321 [21, 22]. If dT is chosen as very small, the evaluation window size will be
 322 $\Delta i = 1$ most of the time, leading to the standard forward difference scheme
 323 using the immediate neighboring discrete data (at $\Delta t = 5$ s data acquisition
 324 rate). However, any singularities $T_{PCM}^i = T_{PCM}^{i+1}$ are circumvented at the
 325 cost that the calculated derivative is then calculated from a larger step size
 326 $t_{PCM}^{i+\Delta i} - t_{PCM}^i$ due to the increased evaluation window $\Delta i > 1$:

$$\left. \frac{dT^i}{dt} \right|_{PCM} = \frac{T_{PCM}^{i+\Delta i} - T_{PCM}^i}{t_{PCM}^{i+\Delta i} - t_{PCM}^i} \quad (11)$$

327 On the other hand, if a large dT is chosen, the T vs t curve is essentially
 328 smoothed out. A trade off therefore has to be found when choosing the eval-
 329 uation step dT .

330

331 Another observed problem is the fixed data acquisition rate and the ther-
 332 mal response time of the temperature sensor itself during recalescence. If
 333 the original data in Fig. 7 were used, then the heat capacity would be over-
 334 estimated due to the apparent low temperature change at the beginning of
 335 recalescence (visible as an apparent plateau in the figure). In reality, the
 336 onset of recalescence likely lies at a lower temperature in between the ap-
 337 parent plateau. In order to make the data evaluation more robust against
 338 these cases, the data point and its adjacent values are skipped. This problem
 339 should be avoided in future experiments by using temperature sensors with
 340 a faster response time and a faster data recording rate.

341

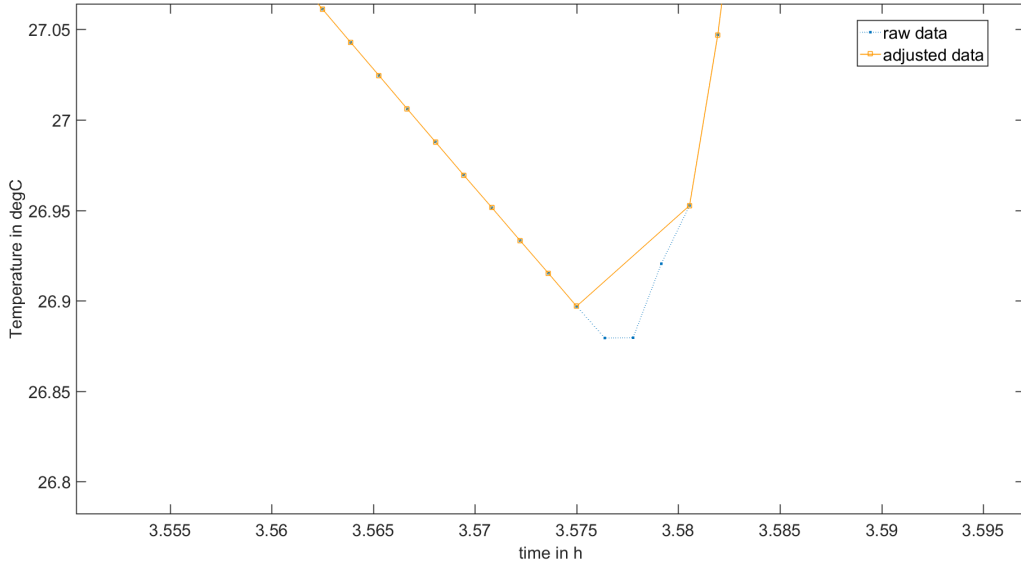


Figure 7: Example of adjustment made for the PCM sample cooling curve to avoid over-estimating the specific heat capacity during recalescence (B2-I, 2nd cooling cycle, bottom sensor)

342 From Figure 4 it can be seen that the PCM apparently solidifies over a
 343 wider temperature range compared to the melting curve. An explanation for
 344 this can be found in an increasing heat transfer resistance between the sensor
 345 location and the solidification front, which progresses from the sensor position
 346 towards the center of the sample holder [3]. Due to this heat conduction
 347 dominated process, little apparent temperature fluctuations are measured
 348 and the time derivative is $\left. \frac{dT}{dt} \right|_{PCM} < 0$ for the remaining cooling part after
 349 recalescence, which makes the treatment of the differentials more straight
 350 forward compared to the heating curve once a suitable value for dT has been
 351 determined. This in turn means that the precision of the cooling curve is
 352 mainly limited by how reproducible the temperature recording of the different

353 sensors is for subsequent cycles. It seems plausible to assume that this can
354 be subject to a certain randomness depending at which location inside the
355 sample holder the PCM starts solidifying and how the solidification front
356 progresses.

357 The accuracy in turn should be mainly limited by systematic errors in
358 the mathematical model given by the discussed problems during supercool-
359 ing, neglecting the insulation thermal mass and by assuming that a single
360 temperature sensor is representative for the whole sample holder.

361

362 *Heating*

363 Fig. 8 shows a typical $\frac{dT}{dt}\Big|_{PCM}$ vs T curve for a heating case. From the
364 figure, the non-ideal conditions can be summarized as:

- 365 • $\frac{dT}{dt}\Big|_{ref} > 0$, but $\frac{dT}{dt}\Big|_{PCM} \leq 0$ in the form of pronounced "noise" due to
366 natural convection, especially towards the end of melting

367 In contrast to the cooling curve, all temperature sensors recorded strong
368 temperature fluctuations over the entire melting duration (which we define as
369 apparent "noise" subsequently) in the PCM sample holder. Since we observed
370 that these fluctuations are especially pronounced during the later stages of
371 melting, it is likely that natural convection is occurring within the sample
372 holder. The noise can then be explained by the notion that the initially
373 formed liquid phase at the sample holder wall is heating up faster, while
374 the remaining solid phase stays at the phase change temperature. When
375 more liquid phase forms and heats up at the sample holder wall, the solid
376 phase becomes smaller and is increasingly subjected to the convective flows

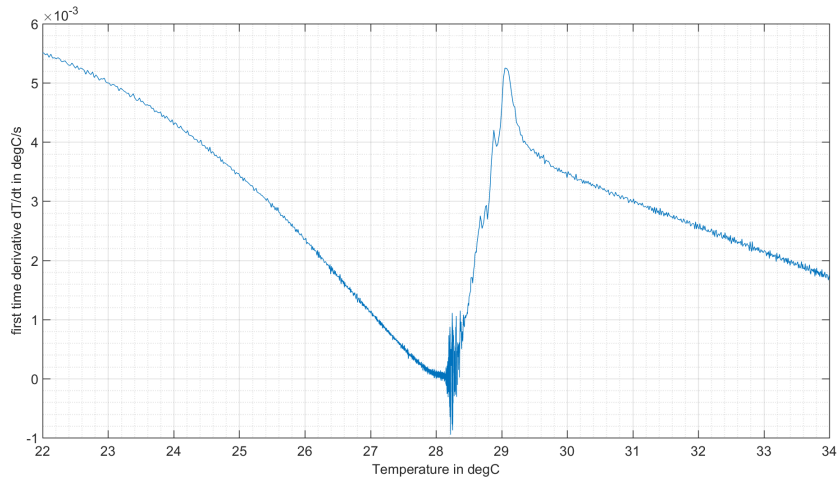


Figure 8: Example of $\left. \frac{dT}{dt} \right|_{PCM}$ vs T values for Setup B2-I (top sensor, heating cycle 1)

377 occurring in the liquid phase. It is likely that this is more pronounced with
 378 increasing differences in densities between the solid and liquid phase.

379 Any movement between solid and liquid phases of different temperatures
 380 at the temperature sensor location cause the sensor to record these fluctua-
 381 tions as apparent noise due to the high thermal conductivity of the copper
 382 sample holder and our high data sampling rate.

383 The fact that melting of the PCM is observed to be faster than solidifica-
 384 tion in our experiments, despite the similar temperature difference between
 385 ambient and phase change temperature, also supports that natural convec-
 386 tion is present, since it is known to reduce the melting time. If only conduc-
 387 tive heat transfer would be present during melting, a shorter solidification
 388 time compared to melting would be expected since the thermal conductivity
 389 is known to be significantly larger in the solid phase for paraffins such as
 390 n-octadecane [23], which RT28HC is likely based on.

391 Because natural convection has already been discussed even for small DSC
392 sample sizes [24], it is likely that the phenomenon is even more pronounced
393 in the larger T-History samples.

394 The apparent noisy temperature data has a direct influence on the time
395 derivative of the PCM melting curve $\left. \frac{dT}{dt} \right|_{PCM}$, which changes between positive
396 $\left. \frac{dT}{dt} \right|_{PCM} > 0$ and negative values $\left. \frac{dT}{dt} \right|_{PCM} < 0$ during melting. Due to the
397 randomness, there are also cases where singularities $\left. \frac{dT}{dt} \right|_{PCM} = 0$ can be
398 present in the time derivative leading to the same problem as discussed above
399 for cooling.

400 When the temperature versus time curve is noisy, it contributes to both
401 under and overestimations of the PCM specific heat capacity. Apparent rapid
402 temperature changes are e.g. interpreted as "reduced" heat capacity and
403 enthalpy changes by the mathematical model. On the other hand, random
404 noise may also artificially lower the calculated value of $\left. \frac{dT}{dt} \right|_{PCM}$ leading to
405 an overestimation of the heat capacity and enthalpy change (similar to the
406 previous example of Fig. 7 for cooling cases).

407 Moreover, since noise is amplified when differentiating, the value of $\left. \frac{dT}{dt} \right|_{PCM}$
408 itself becomes distorted (see Fig. 8) and the noisy derivative values can not
409 be simply inserted into Eq. 4.

410

411 In any of our experimental setups, the existence of natural convection in
412 the form of noise has therefore a pronounced influence on both accuracy and
413 precision of the method when the enthalpy is calculated from the heating
414 case. The evaluation of $\left. \frac{dT}{dt} \right|_{PCM}$ then turns into a signal conditioning prob-
415 lem, where a derivative has to be reconstructed from noisy data. In signal

416 processing, it is well known that differentiation of noisy data is not a trivial
 417 problem [25, 26]. A compromise has to be therefore made when formulating
 418 the data evaluation method.

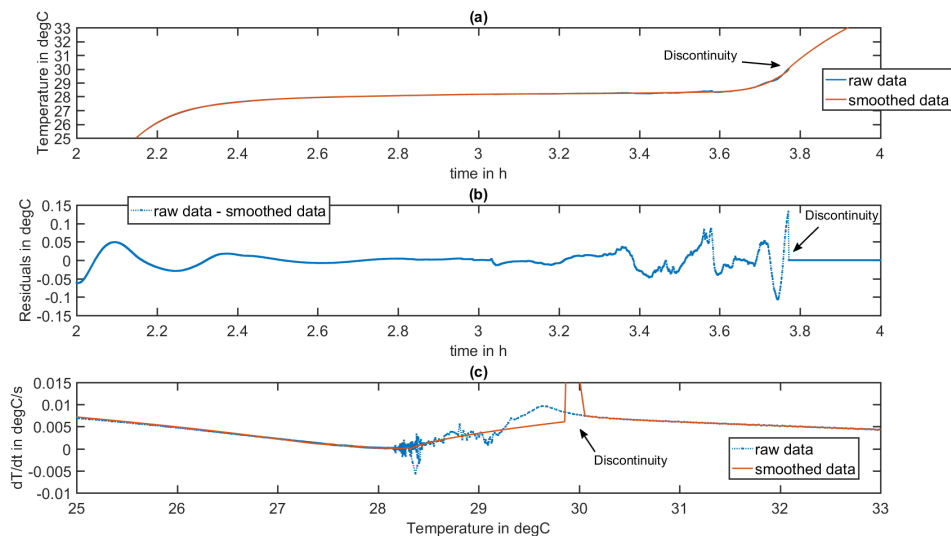


Figure 9: Example of smoothing the PCM sample heating curve (A-I, 1st heating cycle, top sensor) using the SLM toolbox: (a): T vs. t , (b): Residuals = $T_{raw} - T_{smooth}$ vs. t , (c): $\left. \frac{dT}{dt} \right|_{PCM}$ vs. T (The discontinuity at $T = 30^\circ\text{C}$ is because smoothing is only performed until $T < 30^\circ\text{C}$ and then the original data is used.)

419 One approach is to smoothen the original T versus t curve itself. This
 420 should be done with care, since smoothing manipulates the original data
 421 and a bias trough the user is introduced. There is also the risk that intrinsic
 422 behavior of the PCM is overwritten. Moreover, signal smoothing can be done
 423 in a variety of ways [26].

424 In this work, we propose to perform smoothing based on the previously
 425 formulated conditions of an ideal heating curve. The noisy temperature over

426 time data is then smoothened out by fitting a strictly monotonous increasing
 427 spline for all heating curves in this work. For this, the MATLAB based
 428 Shape Language Modeling (SLM) toolbox by D’Errico [27] is utilized. Once
 429 the spline has been applied, no further adjustments are necessary since the
 430 derivative of the smoothed curve is $\left. \frac{dT}{dt} \right|_{PCM} > 0$ for the entire range (e.g. see
 431 Fig. 9). In order not to over-smooth the sensible regions, the spline is applied
 432 only until $T < 30^\circ\text{C}$. For $T > 30^\circ\text{C}$, the original data is used. This causes
 433 a discontinuity in the derivative $\left. \frac{dT}{dt} \right|_{PCM}$ and an underestimation of the heat
 434 capacity in the transition between smoothed and original data. Since this is
 435 only over a small temperature difference of two data points and within the
 436 sensible region, the error in the overall enthalpy curve is negligible.

437 It will be seen later via the resulting enthalpy curves that smoothing the
 438 data significantly improves the precision and overall accuracy since random
 439 high frequency noise is smoothed out and the overall time derivative for
 440 $\left. \frac{dT}{dt} \right|_{PCM}$ can be approximated in a consistent way. However, it comes at
 441 the cost that the systematic error introduced by smoothing the data itself is
 442 unknown.

443 2.2.3. Algorithm

444 The above discussed details for cooling and heating cases are then imple-
 445 mented into a data evaluation algorithm in MATLAB v2016b. The algorithm
 446 is summarized as pseudo code in Fig. 10. The temperature dependent heat
 447 capacities for water and copper are given by functional expressions of the
 448 temperature formulated in [28] and [29], respectively. However, in the actual
 449 T-History experiment the exact pressure p and $u(p)$ is unknown inside the
 450 PCM and reference sample holder. Using temperature dependent isobaric

451 specific heat capacities formulated near atmospheric pressure can therefore
452 only be seen as an estimate, which introduces additional systematic errors.

453 Fig. 11 shows the evaluation temperature intervals for three different dT
454 values for a cooling case. As mentioned above, if a very small dT is chosen,
455 essentially the original raw data points are used to calculate the enthalpy.
456 When forming the derivative as shown in Fig. 12, it can be seen that the
457 derivative of the raw data points are noisy especially in the region where
458 the temperature versus time curve has its plateau. Similar to heating, it is
459 likely that the enthalpy curve is being distorted as well when it is calculated
460 from the original noisy derivative. It can be seen that choosing a larger dT
461 essentially smooths out the differential and yields a more plausible enthalpy
462 curve in Fig. 13, while using the noisy derivatives appears to yield an over-
463 estimation of the enthalpy curve. Since there was only little difference in the
464 enthalpy curve between $dT = 0.01^\circ\text{C}$ and $dT = 0.001^\circ\text{C}$, the latter is chosen,
465 since this step length approximated the temperature versus time curve better
466 as seen in Fig. 11.

467 For heating, the fitted spline over the noisy T versus t data intrinsically
468 yields a smooth derivative and the enthalpy results are therefore more robust
469 from a chosen dT value (see Fig. 14).

```

let  $i := 1, \Delta i := 1;$ 
let  $T_{PCM}^i, T_{PCM}^{i+\Delta i} \in [T_{min}, T_{max}]^{eval};$ 
if "Heating Case" then
  | perform SLM smoothing;
else
  | skip recalescence values;
end
repeat
  if  $|T_{PCM}^{i+\Delta i} - T_{PCM}^i| \geq dT$  then
     $\Delta t_{PCM}^i = t_{PCM}^{i+\Delta i} - t_{PCM}^i;$ 
     $\Delta t_{ref}^i = f_{interp}^{ref}(T_{PCM}^{i+\Delta i}) - f_{interp}^{ref}(T_{PCM}^i);$ 
     $c_p^{PCM}(T^i) = C_{ref}(T^i) \cdot \frac{|\Delta t_{PCM}^i|}{|\Delta t_{ref}^i|} - C_{tube,PCM}(T^i);$ 

    if  $c_p^{PCM}(T^i) < 0$  then
      | let  $c_p^{PCM}(T^i) := 0;$ 
    end
     $\Delta h^{PCM}(T^i) = \int_{T^i}^{T^{i+\Delta i}} c_p^{PCM}(\tau) d\tau;$ 
    let  $i := i + \Delta i;$ 
    let  $\Delta i := 1;$ 
  else
    | let  $\Delta i := \Delta i + 1;$ 
  end
until  $T_{PCM}^i, T_{PCM}^{i+\Delta i} \notin [T_{min}, T_{max}]^{eval};$ 

```

Figure 10: Pseudo code to calculate enthalpy values from discrete data using a flexible

temperature window size and absolute $\frac{|\Delta t_{PCM}|}{|\Delta t_{ref}|}$ values.

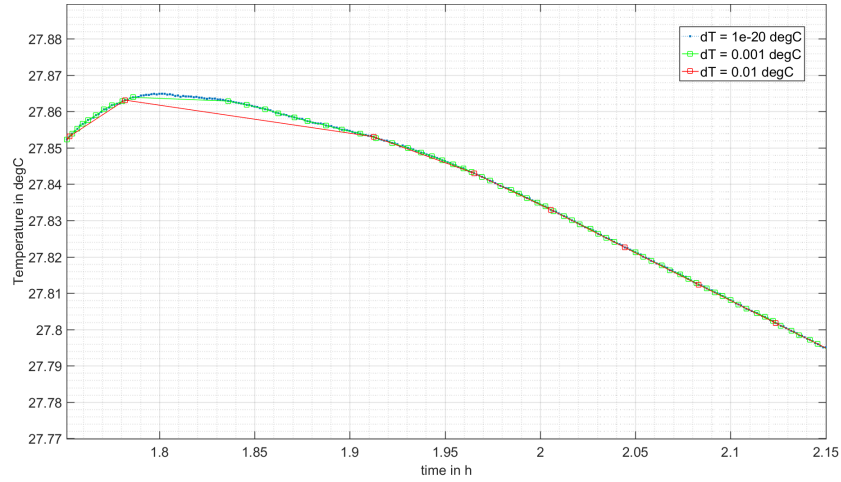


Figure 11: Example of T_{PCM} vs t values using different minimum evaluation step sizes dT for Setup B2-I (top sensor, cooling cycle 1)

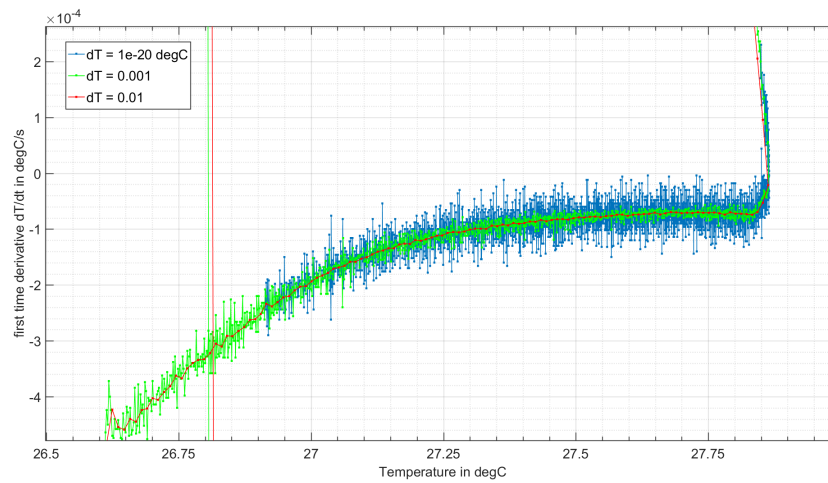


Figure 12: Example of $\left. \frac{dT}{dt} \right|_{PCM}$ vs T values using different minimum evaluation step sizes dT for Setup B2-I (top sensor, cooling cycle 1)

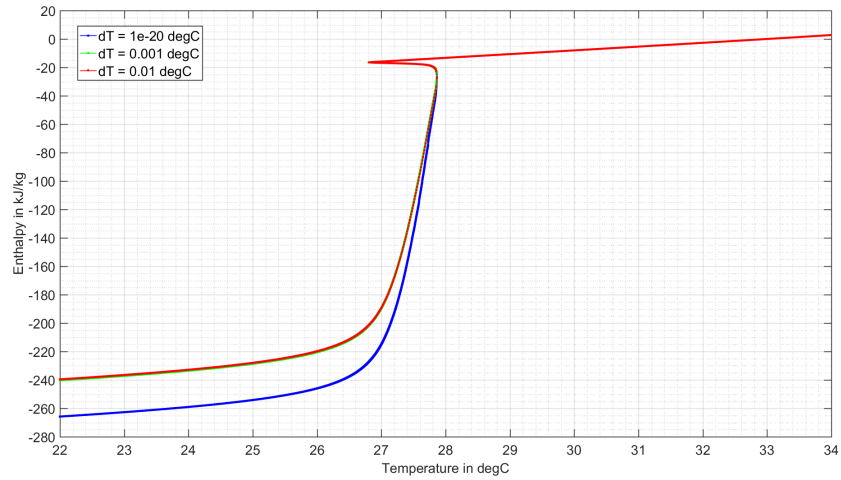


Figure 13: Example of h vs T values using different minimum evaluation step sizes dT for Setup B2-I (top sensor, cooling cycle 1, normalization of h values at 33°C)

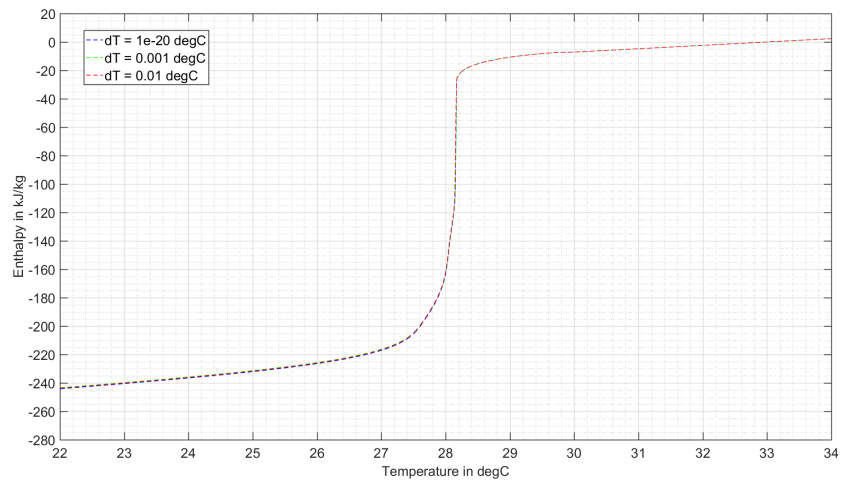


Figure 14: Example of h vs T values using different minimum evaluation step sizes dT for Setup B2-I (top sensor, heating cycle 1, normalization of h values at 33°C)

470 3. Results & Discussion

471 3.1. Enthalpy curves

472 For each experimental setup, the data evaluation algorithm from Fig.
473 10 is applied for the evaluation window of $[22^{\circ}\text{C}, 34^{\circ}\text{C}]^{eval}$ and a chosen
474 minimum temperature step interval of $dT = 0.001^{\circ}\text{C}$. Examples for enthalpy
475 curves for each sensor location and heating and cooling cycle are shown for the
476 climate chamber program I in Fig. 17-19. The mean enthalpy difference over
477 the temperature interval of $33 - 23^{\circ}\text{C}$ (with a combined standard uncertainty
478 of $u(T) = 0.1\text{K}$ for the temperature sensors) and the standard deviation
479 over the five repeated heating and cooling cycles are shown in Fig. 15-
480 16. In total, 30 enthalpy curves are calculated for each experimental setup.
481 However, systematic deviations appear to be present when comparing the
482 results among the different setups.

483 Setup A yields a systematically smaller enthalpy value compared to setup
484 B1 and B2. This is likely due to the smaller sample size with the same level of
485 insulation compared to B1 and B2. This is in agreement with the prediction
486 of our previous simulation study that the larger the present thermal mass of
487 the insulation is with respect to the sample size, the larger the systematic
488 underestimation of the enthalpy [13]. However, the enthalpy shift of setup B2
489 with respect to B1 on average appears to be not significant when compared
490 to the limits of repeatability within repetitive cycles. Since it was shown
491 that systematic errors are observable, it can be concluded that the transient
492 heat transfer effects due to the insulation thermal mass should not have been
493 neglected in this experimental setup.

494 The precision of the enthalpy value for each sensor location over the five

495 cycles is acceptable since the largest standard deviation in any setup was
496 found to be $\leq 1.25 \text{ kJ kg}^{-1}$. This is mainly due the performed smoothing of
497 the heating curve and by choosing dT carefully for the cooling curve. It is
498 likely that the good repeatability is a direct result of insulating the sample
499 holders, which dominates the heat transfer in the experiments.

500 Moreover, the enthalpy values between cooling and heating cases appear
501 to be consistent within $< 5 \text{ kJ kg}^{-1}$.

502 It can be seen that the top sensor located towards the fan generally es-
503 timates a lower enthalpy value compared to the center and bottom sensor
504 locations. Since this is valid for all setups, it is likely that the cause for this
505 is the climate chamber fan itself causing the top part of the PCM sample to
506 cool down or heat up faster compared to the top part of the reference.

507 Concerning the hysteresis between cooling and heating cases, it can be
508 concluded that in general the larger temperature step change of program II
509 leads to a larger hysteresis, compared to program I, regardless of the setup.
510 A complete figure of the enthalpy plots can be found in the supplementary
511 file for this paper. This observation is in analogy with DSC measurements,
512 that the overall lower heating or cooling rate leads to smaller temperature
513 gradients inside the sample [9, 16]. It can also be seen that setup A yields a
514 smaller hysteresis compared to setup B1, due to the smaller diameter of the
515 sample holders in A. However, the hysteresis can be also decreased with a
516 thicker layer of insulation in setup B2. Moreover, the enthalpy shift to lower
517 values is then not as pronounced as in setup A. Therefore, setup B2-I appears
518 to be a good trade off between a desired low hysteresis ($\Delta T_{melting-solid.} \leq 1^\circ\text{C}$)
519 and a low error by neglecting the insulation thermal mass.

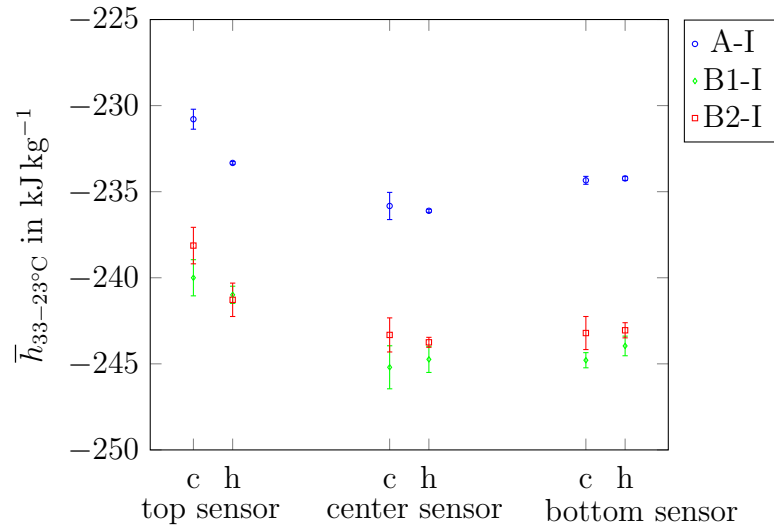


Figure 15: Mean enthalpy results and standard deviation for Setup A-I, B1-I and B2-I over five cycles for each sensor location (c: cooling, h: heating).

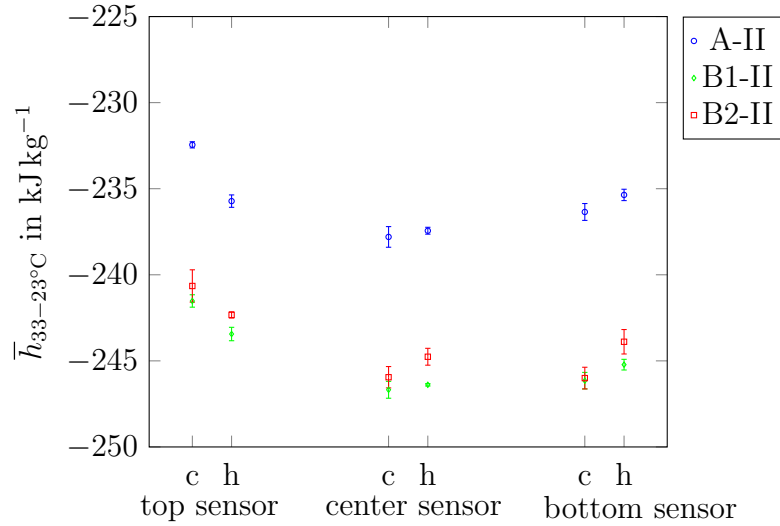


Figure 16: Mean enthalpy values and standard deviation for Setup A-II, B1-II and B2-II over five cycles for each sensor location (c: cooling, h: heating).

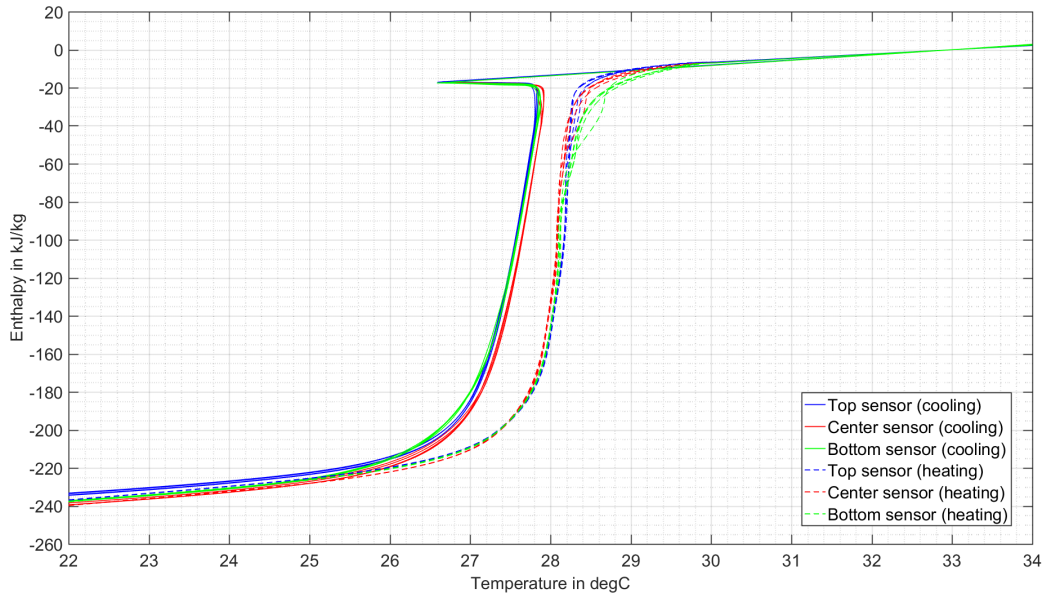


Figure 17: h versus T curve for setup A-I using $dT = 0.001^\circ\text{C}$ (all five cycles are plotted with the same color depending on the sensor position, normalization of h values at 33°C)

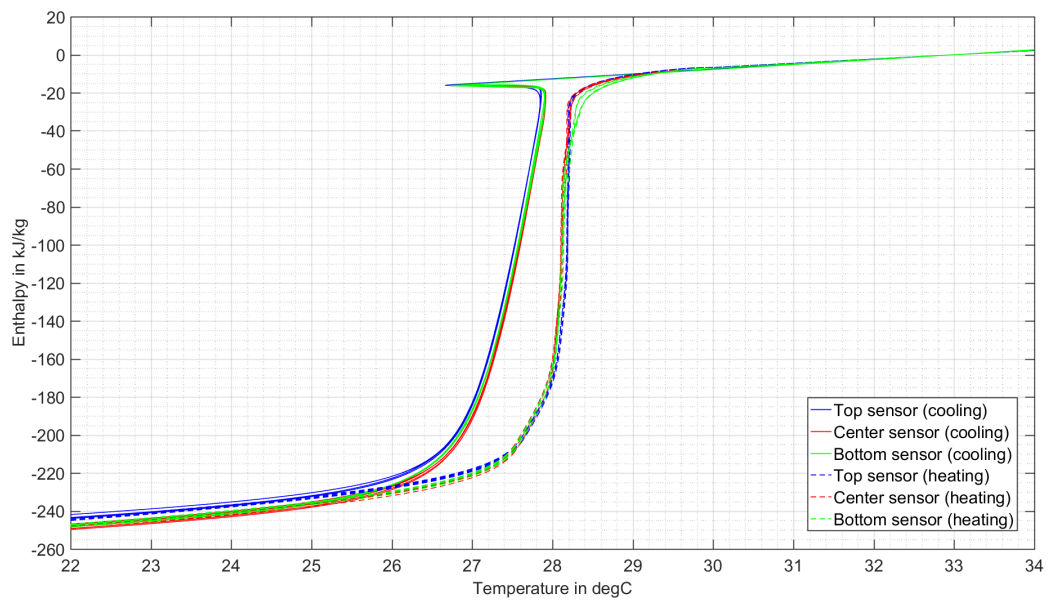


Figure 18: h versus T curve for setup B1-I using $dT = 0.001^\circ\text{C}$ (all five cycles are plotted with the same color depending on the sensor position, normalization of h values at 33°C)

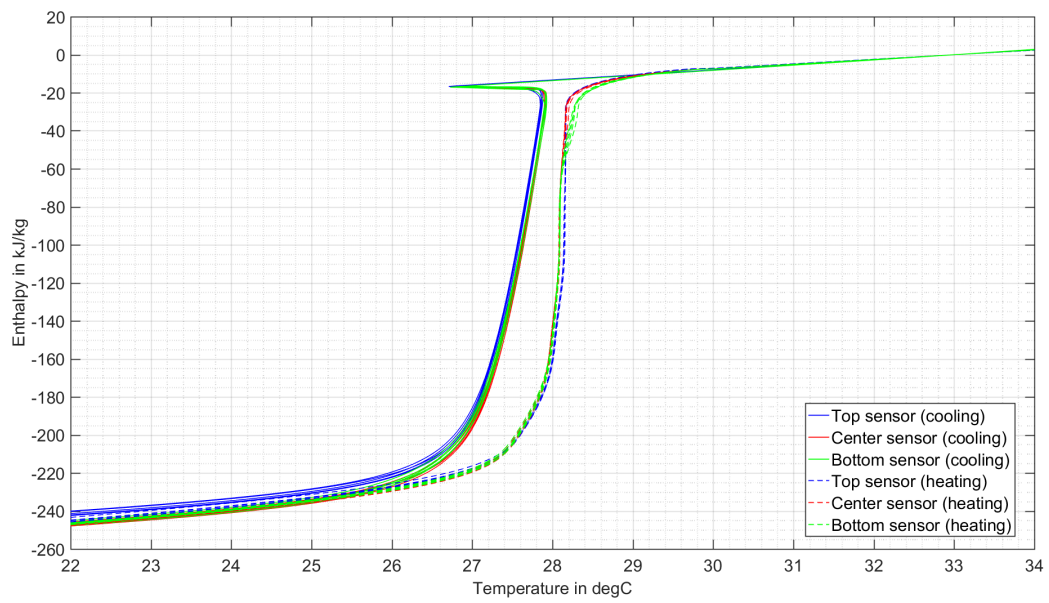


Figure 19: h versus T curve for setup B2-I using $dT = 0.001^\circ\text{C}$ (all five cycles are plotted with the same color depending on the sensor position, normalization of h values at 33°C)

521 It can be seen that the enthalpy value is in good agreement with the man-
 522 ufacturers data sheet shown in Fig. 20 ($h_{33-23^{\circ}\text{C}} \approx -237$ to $-243.5 \text{ kJ kg}^{-1}$)
 523 obtained using a so called three-layer calorimeter. The measurement princi-
 524 ple resembles the T-History method [30, 31]. However, no further details on
 525 experimental parameters and data evaluation method are given.

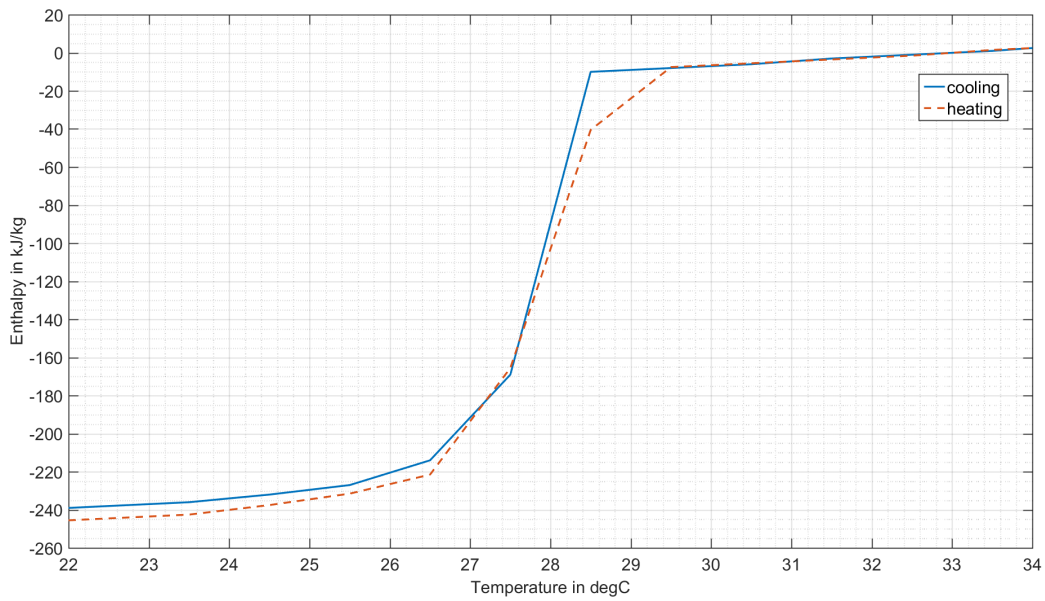


Figure 20: h versus T curve plotted from the manufacturer's data sheet [32] (normalization of h values at 33°C). (Cooling: $h_{33-23^{\circ}\text{C}} = -237 \text{ kJ kg}^{-1}$, Heating: $h_{33-23^{\circ}\text{C}} = -243.5 \text{ kJ kg}^{-1}$)

526 *3.2. Solid and liquid specific heat capacities*

527 The mathematical model of the T-History method also allows an evalu-
 528 ation of the liquid and solid specific heat capacity of the PCM. From Eq. 1
 529 and 2 an expression for c_p^{PCM} can be derived in the liquid and solid regions:

$$(m^{PCM} \cdot c_p^{PCM}(T) + m^{tube,PCM} \cdot c_p^{tube}(T)) \cdot \left. \frac{dT}{dt} \right|_{PCM} = \frac{1}{R_{th}(T)} (T_{PCM} - T_{amb}) \quad (12)$$

$$\left. \frac{dT}{dt} \right|_{PCM} = \frac{1}{R_{th}(T) \cdot (m^{PCM} \cdot c_p^{PCM}(T) + m^{tube,PCM} \cdot c_p^{tube}(T))} (T_{PCM} - T_{amb}) \quad (13)$$

530 When Eq. 13 is evaluated over a small temperature difference in the
 531 sensible regions, the temperature dependence of the terms may be neglected.
 532 Then it may be assumed that a linear relationship between $\left. \frac{dT}{dt} \right|_{PCM}$ and
 533 T_{PCM} should hold:

$$\left. \frac{dT}{dt} \right|_{PCM} \approx K \cdot (T_{PCM} - T_{amb}) \quad (14)$$

534 However from Fig. 21 and 22 it can be seen that a linear relationship in
 535 the sensible parts does not hold for the PCM or reference in the solid region
 536 for a heating case and in the liquid region for a cooling case, which mark
 537 the beginning of the experiment. This is likely because the mathematical
 538 model does not account for the initial heat flux with the present insulation
 539 directly after the step change of T_{amb} . This phenomenon was shown in the
 540 previous simulation study [13]. Therefore, $c_{p,s}^{PCM}$ and $c_{p,l}^{PCM}$ are evaluated
 541 as mean value from the $dT = 0.001^\circ\text{C}$ steps within the marked tempera-
 542 ture interval close to T_{amb} . $c_{p,s}^{PCM}$ is calculated from the cooling curve within

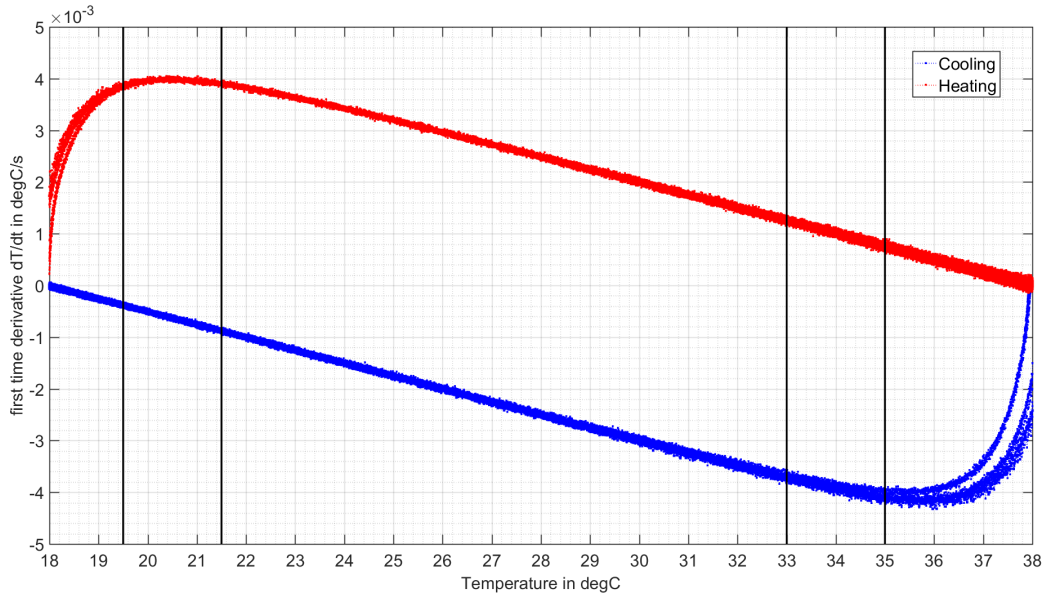


Figure 21: $\left. \frac{dT}{dt} \right|_{ref}$ versus T curve for setup B2-I (all sensor positions and cycles are plotted with the same color depending on heating or cooling)

543 $[19.5^{\circ}\text{C}, 21.5^{\circ}\text{C}]^{eval}$ and $c_{p,l}^{PCM}$ from the heating curve within $[33^{\circ}\text{C}, 35^{\circ}\text{C}]^{eval}$.

544

545 The results in Fig. 23-24 indicate that both liquid and solid heat capaci-
 546 ties are overestimated compared to the specified $2 \text{ kJ kg}^{-1} \text{ K}^{-1}$ for solid and
 547 liquid c_p^{PCM} by the manufacturer (no information about the corresponding
 548 temperature range and its uncertainty is given) [32]. This is because the
 549 assumption of equal heat flux is likely only valid if the thermal diffusivity of
 550 both sample and reference are identical [13]. If not, also the heat capacities
 551 in the sensible region need to be systematically corrected when the insulation
 552 thermal mass is neglected as shown in our previous work [13].

553 On a positive note, the standard deviations for repeated cycles are very
 554 low (2.5×10^{-3} to $28.9 \times 10^{-3} \text{ kJ kg}^{-1} \text{ K}^{-1}$), showing a very good precision

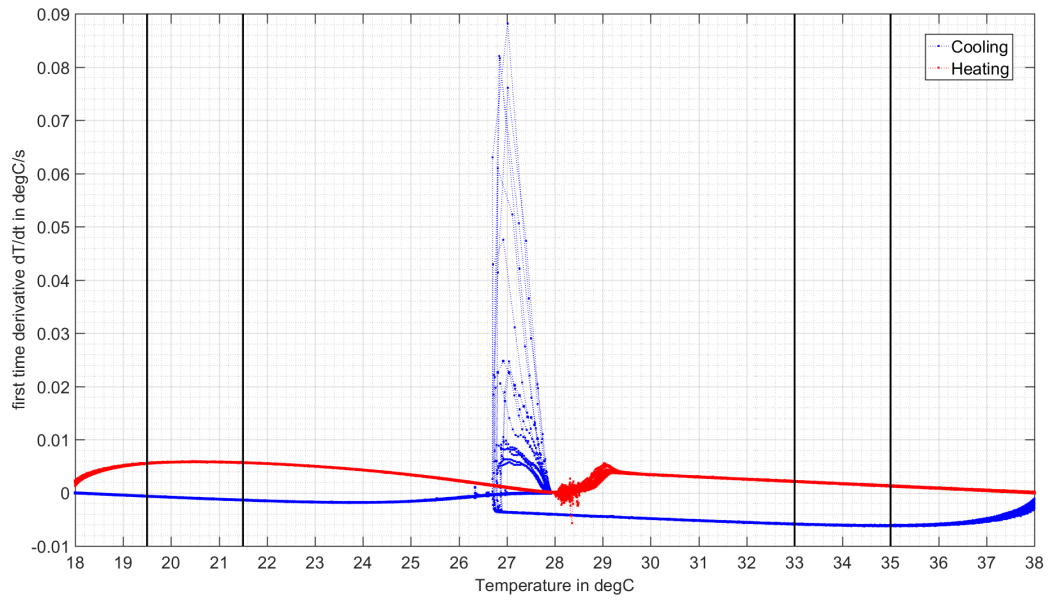


Figure 22: $\left. \frac{dT}{dt} \right|_{PCM}$ versus T curve for setup B2-I (all sensor positions and cycles are plotted with the same color depending on heating or cooling)

555 of the method. The exact values are given in the supplementary file.

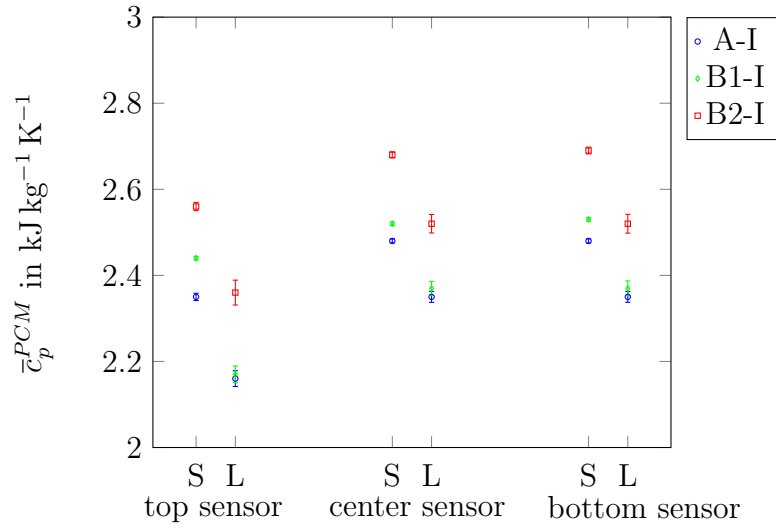


Figure 23: Mean specific heat capacity and standard deviation for Setup A-I, B1-I and B2-I over five cycles for each sensor location (S: solid phase, L: liquid phase).

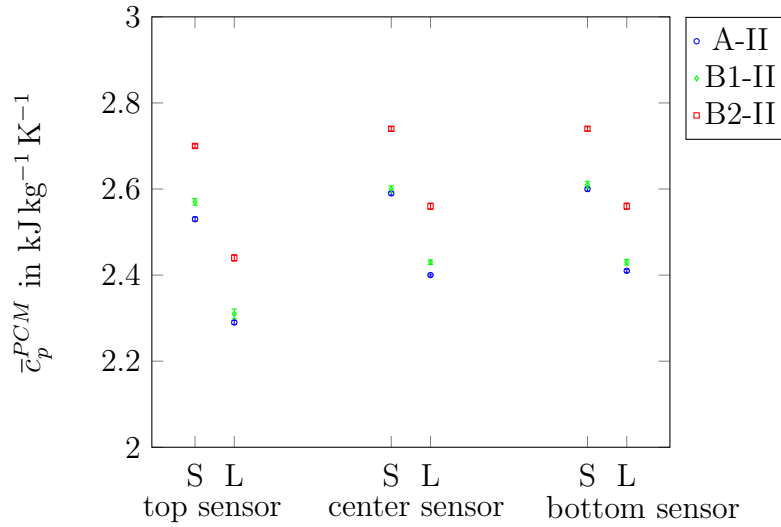


Figure 24: Mean specific heat capacity and standard deviation for Setup A-II, B1-II and B2-II over five cycles for each sensor location (S: solid phase, L: liquid phase).

556 *3.3. Estimation of propagation of input quantity probability density functions*
557 *(PDF's)*

558 In addition to the enthalpy results, we evaluate how the uncertainty of
559 the enthalpy values are related to uncertainties in the other input parame-
560 ters (such as temperature, mass and specific heat capacity) in Eq. 3. Since
561 the mathematical model is non-linear and the data evaluation method ap-
562 plies further adjustments to the raw data, a measurement uncertainty anal-
563 ysis is not straightforward. For such cases, the Joint Committee for Guides
564 in Metrology (JCGM) recommends to apply Monte Carlo simulations [33].
565 This method allows the estimation of propagation of uncertainties of the in-
566 put quantities X_i to the output quantity Y , for any functional relationship
567 between them:

$$Y = f(X_1, X_2, \dots, X_N) \quad (15)$$

568 For T-History, input quantities are the parameters given in Eq. 3 (see
569 Fig. 25 as illustration). The output quantity is the enthalpy value for a given
570 temperature obtained by the functional relationship of the above discussed
571 data evaluation algorithm in Fig. 10.

572 In this part we utilize the Monte Carlo methodology described in the
573 Guide to the Expression of Uncertainty in Measurement (GUM), to estimate
574 how the probability density functions (PDF's) of the input quantities in Eq.
575 3 propagate through the enthalpy calculation algorithm. We assume that all
576 input quantities follow their distribution assigned in Table 3. Considering
577 the experimental temperature range, Arblaster 2015 [29] specifies the copper
578 specific heat capacity for two temperature regions and their respective stan-

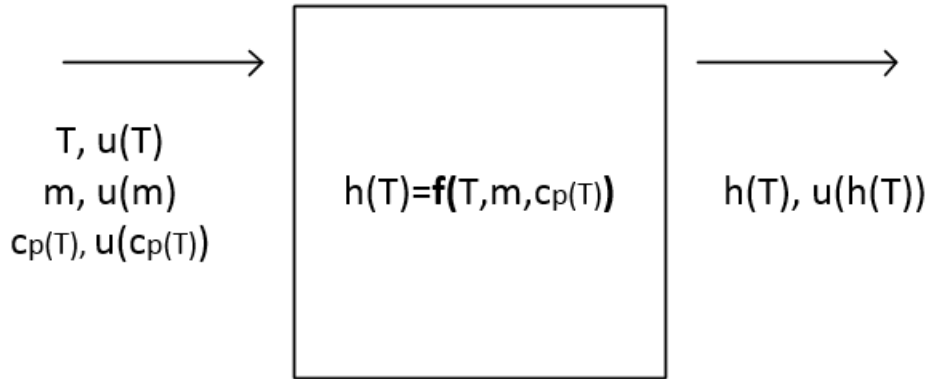


Figure 25: Illustration of the propagation of PDF's according to GUM [33]

579 dard deviations. As simplification and conservative estimate, we assign the
 580 highest relative standard deviation (0.1%) to both regions.

581

582 For this study, in every Monte Carlo trial, a value for each input quantity
 583 is drawn from its assigned distribution using MATLAB's Marsenne Twister
 584 random number generator. We assume that the complete temperature data
 585 for each cooling or heating case to be shifted by a single value drawn from
 586 the temperature PDF, given by the calibration standard uncertainty.

587 As a compromise between reliability of the generated random numbers
 588 and the computation time, the Monte Carlo simulation is performed 100,000
 589 times and the results are shown as box plots in Fig. 26 - 27. The number of
 590 trials was determined as enough for this study, since the difference in results
 591 using lower trials were below the chosen number of significant digits (1kJ/kg)
 592 for the enthalpy value $h_{33-23^{\circ}\text{C}}$. The study was performed for setup A-I, B1-I

Table 3: Assignment of PDF's to input quantities of Eq. 3

Input Quantity	Assigned PDF	PDF Parameter	Source
T	normal	$u(T) = 0.1^\circ\text{C}$	Combined standard uncertainty from calibration.
$m^{ref}, m^{PCM}, m^{tube,ref}, m^{tube,PCM}$	rect.	Lower and upper limits: $m \pm 0.1\text{g}$	Estimated from scale specification.
$c_p^{ref}(T)$	normal	$u_r(c_p^{ref}) = 0.05\%$	relative standard uncertainty for pure liquid water at $p = 0.1\text{MPa}$ and $253.15\text{K} \leq T \leq 383.15\text{K}$ from [28] ^a
$c_p^{tube}(T)$	normal	$u_r(c_p^{tube}) = 0.1\%$	relative standard uncertainty for pure solid copper at $300\text{K} \leq T \leq 1357.77\text{K}$ from [29] ^a

^a Since in the T-History experiment p and $u(p)$ is unknown inside the PCM and reference sample holder the actual uncertainties for the isobaric specific heat capacities may be higher than in this table.

593 and B2-I using the first cooling and heating cycle of the center sensor.

594

595 The whiskers for setup A-I extend to about $\pm 20 \text{ kJ kg}^{-1}$ from the median,
596 while they extend to only $\pm 12 \text{ kJ kg}^{-1}$ for setup B1-I and B2-I. This is likely
597 because of the smaller ratio of PCM sample- to insulation- and sample holder
598 tube thermal mass in setup A compared to setup B, while the absolute input
599 quantity uncertainties is unchanged in the Monte Carlo study. Moreover,
600 the spread of the enthalpy results are larger compared to the deviations be-
601 tween the different sensor positions or the standard deviation within repeated
602 cycles. To decrease the uncertainty of the enthalpy results, a future focus
603 should therefore be to decrease the uncertainty of the input quantities.

604 Therefore, it is recommended that future T-History experiments should
605 be done with as accurate mass and temperature measurements as possible.

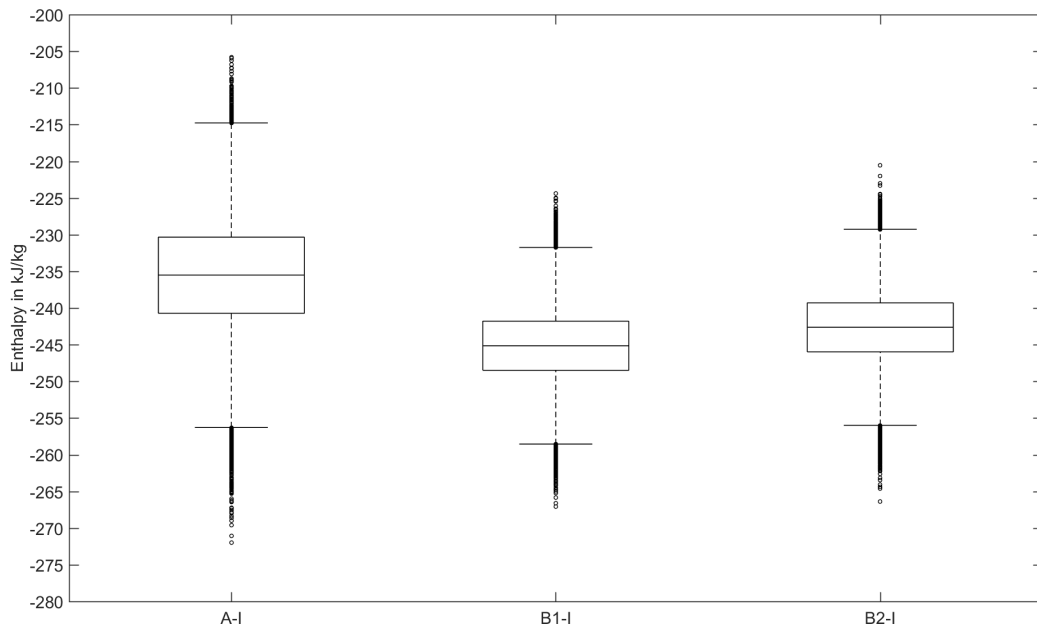


Figure 26: Box plots of $h_{33-23^{\circ}\text{C}}$ values from Monte Carlo simulations for setup A-I, B1-I and B2-I using $dT = 0.001^{\circ}\text{C}$ (center sensor position, cooling cycle 1). Whiskers are extended to 1.5 times the interquartile range (IQR) [34]

606 Regarding the sample holder, it is moreover recommended to increase the
 607 ratio of PCM sample thermal mass to insulation and sample holder tube
 608 thermal masses, in order to dampen the uncertainty on the enthalpy output
 609 quantity depending on the same input quantity uncertainties.

610 4. Conclusions & Future work

611 In this work the T-History method has been studied by performing re-
 612 peated measurements using different experimental setups.

613 When deriving enthalpy values from the mathematical model using the
 614 ratio of first time derivatives from the PCM and reference temperature read-

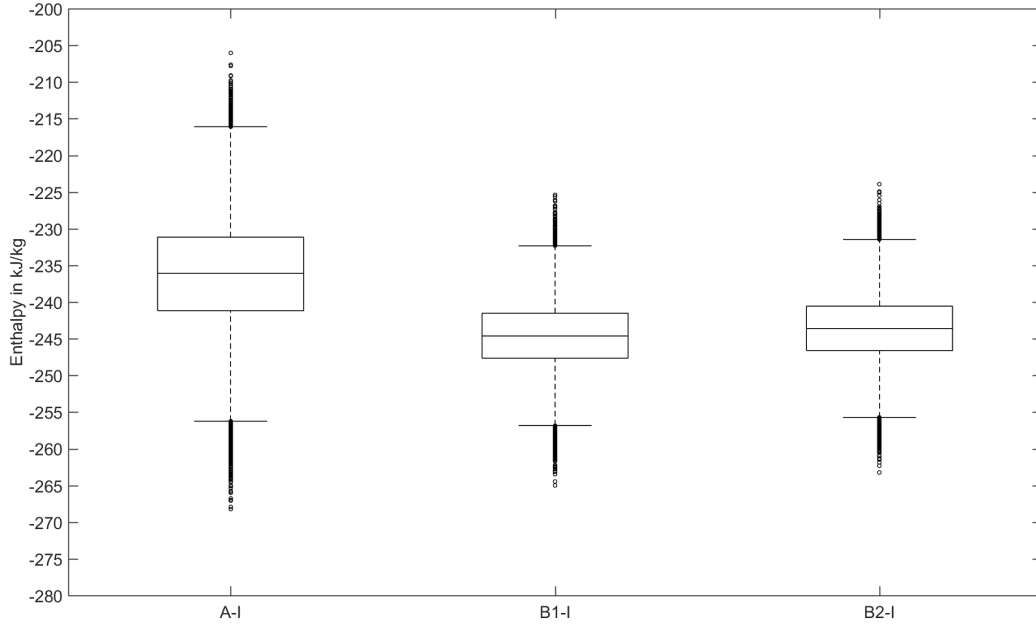


Figure 27: Box plots of $h_{33-23^{\circ}\text{C}}$ values from Monte Carlo simulations for setup A-I, B1-I and B2-I using $dT = 0.001^{\circ}\text{C}$ (center sensor position, heating cycle 1). Whiskers are extended to 1.5 times the interquartile range (IQR) [34]

615 ings, special care has to be taken that noisy data are not interpreted as
 616 apparent small or large specific heat capacities. This is especially true, since
 617 noise is enhanced when differentiating. It was shown that several adjust-
 618 ments in the data evaluation method were necessary in order to obtain a
 619 good enough precision for repetitive measurements within all experimental
 620 setups. A consistent data evaluation method is therefore a minimum require-
 621 ment for discussing other systematic errors present.

622 However, the data evaluation methodology itself likely introduces to a
 623 certain degree systematic errors, such as the proposed smoothing procedure.
 624 It is also expected that the applied method is more valid for PCM's with a

625 small degree of supercooling.

626

627 Nevertheless, the experimental setup used in this study retained its sim-
628 plicity, while being able to achieve repeatable results for the apparent en-
629 thalpy curves of melting and solidification.

630 It was shown that in order to approximate the phase change temperature
631 between the apparent melting and solidification curves, the thermal gradi-
632 ents inside the PCM sample should be decreased. This can be done by either
633 decreasing the sample holder diameter or by increasing the degree of insu-
634 lation leading to smaller overall heating or cooling rates in the experiment.
635 With the current assumptions, one has to be aware that the systematic error
636 due to neglecting the transient heat transfer effects in the insulation is then
637 increased as a trade-off to a lower hysteresis.

638 Three experimental variants were used to show that the influence of the
639 thermal mass of the insulation material on the enthalpy values appears to
640 be significant on top of the other considered phenomena. The systematic
641 shift to lower enthalpy values with a larger insulation thermal mass ratio
642 (with respect to the PCM sample thermal mass) therefore supports the pre-
643 diction made by our previous work [13]. Among the setups used in this
644 work, setup B2-I yielded a good trade-off between a low hysteresis and the
645 error of neglecting the insulation thermal mass compared to the other al-
646 ternatives. However, it is still clear that future setups, which use insulated
647 sample holders and at the same time Eq. 1 as a mathematical basis, have
648 to either decrease the thermal mass of the insulation or subsequently correct
649 the results. An alternative would be to start from a new mathematical basis,

650 which intrinsically accounts for the insulation.

651

652 Monte Carlo simulations for T-History experiments have been moreover
653 introduced as one way to estimate how the different input quantity uncertain-
654 ties propagate through the data evaluation algorithm resulting in a spread
655 of the enthalpy values representing the uncertainty of the results. From this
656 study it can be recommended that the experimental setup should provide a
657 high PCM thermal mass with respect to the sample holder tube. This means
658 that the uncertainty propagation of input quantities are dampened with re-
659 spect to the PCM results in the mathematical model. This also means that
660 setup B2-I is preferable compared to the smaller sample holder diameter of
661 setup A. In future work, this technique should be developed further to incor-
662 porate possible correlations of the input quantity uncertainties. Moreover,
663 the robustness of the method should be tested using a higher number of
664 Monte Carlo trials. For a more rigorous analysis, such as the calculation of
665 confidence intervals, the adaptive Monte Carlo method given by [33, 35] may
666 be implemented in future work. The method can also be used to study the
667 influence of each uncertainty by itself, such as the temperature sensor ac-
668 curacy, to determine which input quantity uncertainty should be decreased
669 primarily.

670 Finally, we believe that Monte Carlo simulations can also be used by other
671 researchers on their own T-History variants leading to an overall improvement
672 of the method by providing more insight to their measurement setups and
673 data evaluation method. These simulations can also be used in future work,
674 when applying correction or calibration factors to minimize all systematic

675 errors in the final results. Then the uncertainty related to these factors itself
676 could be propagated.

677 It is necessary for future work to compare the limits of accuracy and
678 precision of the insulated experimental setup in this work with the predicted
679 errors on the enthalpy results by Mazo et al. 2015 [12] and Badenhorst &
680 Cabeza 2017 [10] using uninsulated sample holder setups.

681 In general, more work is needed to quantify and reduce the systematic
682 errors stemming from the experimental setup and the current assumptions of
683 the T-History method. This also includes using expressions for the isobaric
684 specific heat capacity c_p^{ref} and c_p^{tube} from the literature to calculate the en-
685 thalpy of the PCM, while the actual pressure inside the sample holder over
686 the course of the experiment is unknown. The latter likely depends also on
687 the thermal expansion of the reference material and PCM over the tempera-
688 ture range of the experiment. In order to validate the results from T-History
689 setups, future work should focus on performing round robin tests on a PCM
690 with well documented properties, such as a pure substance.

691

692 The experimental raw data of this work is provided by the authors as
693 additional supplementary material to the article.

694

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703 **Nomenclature**

704 \dot{Q} Heat flux (W)

705 σ_i Standard deviation of quantity i

706 c_p Specific heat capacity ($\text{J kg}^{-1} \text{K}^{-1}$)

707 h Specific enthalpy (J kg^{-1})

708 m Mass (kg)

709 R_{th} Thermal resistance (K W^{-1})

710 T Temperature ($^{\circ}\text{C}$)

711 t Time (s)

712 $u(i)$ Standard uncertainty of quantity i

713 $U_c(i)$ Combined expanded uncertainty of quantity i

714 $u_r(i)$ Relative standard uncertainty of quantity i

715 amb Ambient

716 PCM Phase change material

717 ref Reference material

718 $tube$ Sample holder tube

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