Development of standards for materials testing and quality control of PCM

H. Mehling [(a)], H.-P. Ebert [(b)], P. Schossig [(c)]
[(a)] ZAE Bayern Division 1, Walther-Meissner-Str. 6,
85748 Garching, Germany
+49 89 329442-22, Mehling@muc.zae-bayern.de
[(b)] ZAE Bayern Division 2, Am Hubland,
97074 Würzburg, Germany
+49 931 70564-34, ebert@zae.uni-wuerzburg.de
[(c)] Fraunhofer Institute für Solar Energy Systems ISE, Heidenhofstr. 2
79110 Freiburg, Germany
+49 761 4588 5130, peter.schossig@ise.fraunhofer.de

ABSTRACT

During recent years, more and more commercial applications of PCM can be seen on the market. For any kind of product development, the relevant material properties have to be known with sufficient accuracy. During the production process, tests have to be done to ensure that the PCM, or the product that contains PCM, has a constant quality.

For PCM, no special standards have been available until now. Even worse, common standards for calorimetry can lead to large errors when applied to PCM. To solve this problem, the “RAL-Gütegemeinschaft PCM e.V.” was founded in 2005 by several companies to have a quality label for PCM that by setting standards assures quality. The ZAE Bayern and the Fraunhofer Institute FhG-ISE were then contracted to develop standards for materials testing and quality control. The focus points were the testing of PCM-materials and PCM-composite materials with respect to the stored heat as a function of temperature, the reproducibility of the phase change and the thermal conductivity. The main problems in materials testing and the resulting guidelines regarding the “stored heat as a function of temperature” are presented here. The quality label was granted in Spring 2006.

1. INTRODUCTION

1.1. Necessity for standards

During recent years, more and more commercial applications of PCM can be seen on the market. For any kind of product development, the relevant material properties have to be known with sufficient accuracy. During the production process, tests have to be done to ensure that the PCM, or the product that contains PCM, has a constant quality. A common standard for the determination and presentation of the relevant data is thus important for

- the people in R&D for system development,
- the producer to ensure product quality,
- the sales man for marketing and data sheets,
- the customer to compare products.

To meet the needs of all these groups there are boundary conditions for quality control. These are sufficient accuracy, however also simplicity to assure easy use and understanding, and last but not least acceptable costs regarding time and money necessary to perform quality control (fig. 1).

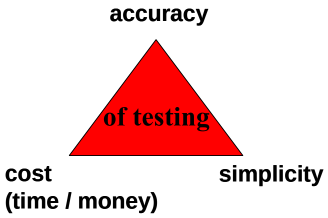


Figure 1. Boundary conditions for quality control.

As PCM are most efficiently used when the temperature change in an application is small, the technical goal for the accuracy of the "stored heat as a function of temperature" was set to ±10% in specific enthalpy h and to ± 0.5°C in temperature T. This accuracy should also be sufficient for current developments in the building sector where temperature changes during application of the PCM are only a few degrees. For PCM, no special standards have been available until now to assure this accuracy.

1.2. State of the art on measurement

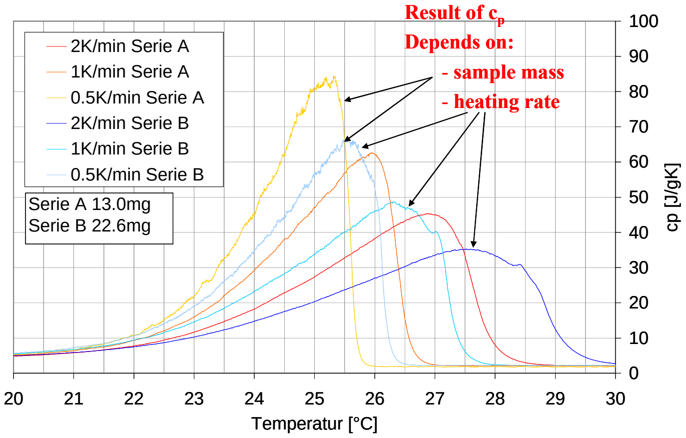


Figure 2. Results for the heat capacity of a PCM determined using a hf-DSC in dynamic mode with varying heating rates and sample mass.

Fig. 2 shows results for the heat capacity of a PCM determined using a hf-DSC in dynamic mode with varying heating rates and sample mass. It can be observed that heating rate and sample mass strongly influence the resulting heat capacity data and that an accuracy of ± 0.5°C is not reached at all. Existing standards in calorimetry which were designed for other materials than PCM often recommend even higher heating rates, thus making the results even worse. These standards can therefore not be used for PCM. Looking at fig. 2, one would spontaneously suggest reducing the sample mass and heating rate, but we will explain later that this is not a solution that can be applied in all cases.

1.3. State of the art on data tabulation

A common "solution" for the above problem is to tabulate the enthalpy change over a larger temperature range and the peak onset as melting temperature. But this approach is not accurate at all, it just hides the problem.

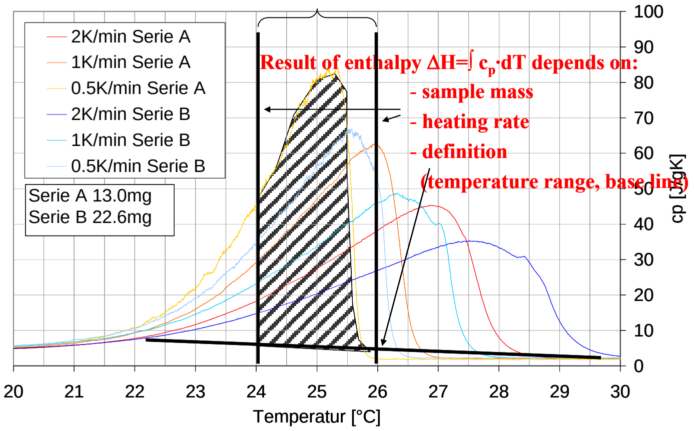


Figure 3. Uncertainties in the determination of the enthalpy change by integration of the peak area in a fixed temperature intervall from heat capacity data.

Fig. 3 shows uncertainties in the determination of the enthalpy change from heat capacity data. First, it is known that many materials have a melting range much broader than 0.5°C and not a melting temperature. If the melting enthalpy is attributed to a single temperature as usually tabulated (Lane 1983, Zalba et el, 2003), the data do not reflect the reality with the necessary accuracy at all. For the enthalpy change it also becomes clear that even if the temperature interval is given, what is often not done, the result still depends on heating rate and sample mass. And actually, what is the enthalpy change? Is it the "enthalpy or latent heat of the phase change" which is determined from the peak area above a base line which represents the sensible heat of the material; or is it the "enthalpy change during phase change"? For example for a paraffin with a heat capacity of 2J/gK and a peak width of 10K, the area under the baseline is 20J/g which can be about 10% of the enthalpy change.

To solve this problem, that is to find out how to measure and tabulate data, the "RAL-Gütegemeinschaft PCM e.V." (http://www.ral.de/gz/de/php/gz_details.php?GZ_ID=197) was founded in 2005 by several companies as the first quality label for PCM. The ZAE Bayern and the Fraunhofer Institute FhG-ISE were then contracted by the companies to develop standards for materials testing and quality control. The focus points were the testing of PCM-materials and PCM-composite materials with respect to the stored heat as a function of temperature, the reproducibility of the phase change and the thermal conductivity. For the "stored heat as a function of temperature", which is discussed in this paper, the tasks were:

- to perform a survey of common measurement techniques,
- to perform an intercomparison test, to find out which measurement techniques can be used for which materials and what the measurement errors are that have to be expected,
- to give recommendations for a standard.

This paper summarizes the main problems in materials testing that were found and the resulting guidelines regarding the "stored heat as a function of temperature".

2. BASIC DEFINITIONS

The heat stored in a sample in an interval of 1°C (or 1K) at constant pressure is given by the heat capacity C_p. $C_p(T)$ gives the stored heat as a function of temperature. For solid-liquid phase changes this is equal to the heat stored at constant volume $C_{v,}$ that is

$$C_p(T) = C_v(T) = \frac{\partial H}{\partial T} = \frac{\partial Q}{\partial T} \tag{1}$$

Mass or volume specific values are given as c_p and c_v and are the typical output of a measurement using a calorimeter. By integration the heat stored in a given temperature range is found as

$$\Delta Q = \Delta H = \int_{T_1}^{T_2} C_p(T) \cdot dT \tag{2}$$

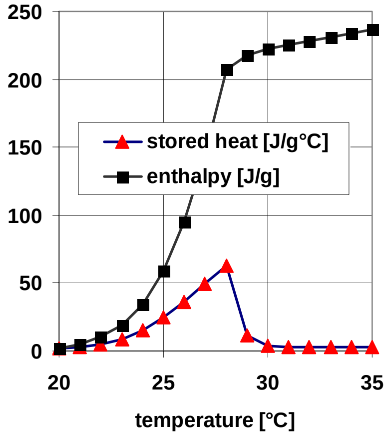


Figure 4. Stored heat (heat capacity) and enthalpy.

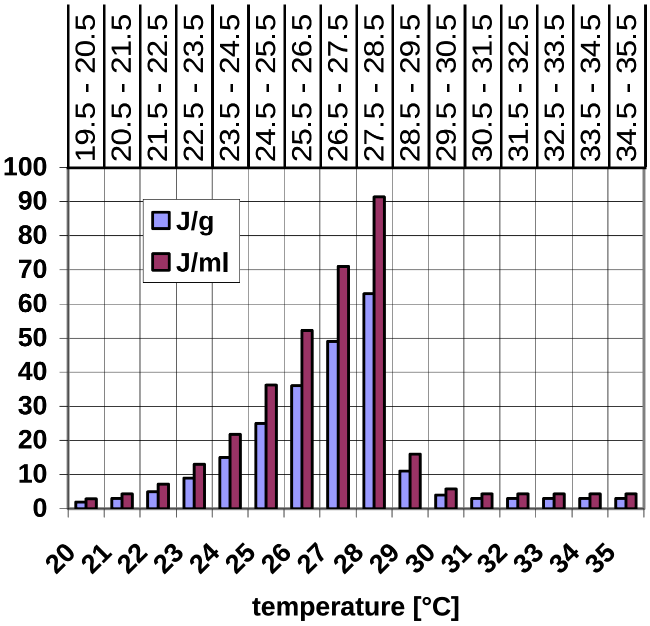
3. STANDARD HOW TO PRESENT DATA

Based on the ambiguities in the different ways that data were tabulated in the past (see 1.2 and 1.3) and taking into account that the data have to be accurate and at the same time easy to understand also for non scientists, the following standard for data presentation was defined.

The stored heat as a function of temperature has to be declared for the case of heating and for cooling, as in most cases differences are observed. It has to be tabulated in given temperature intervals. This has to be done with respect to

- mass in J/g
- volume in J/ml

This way of representing data is easy to understand eg. for marketing purposes. Further on it does not lead to any uncertainties regarding baseline or melting point definition. The values needed can be directly read from the table. An example is shown in fig. 5.



Temperature interval [°C]	stored heat [J/g]	stored heat [J/ml]
19.5 - 20.5	2	2.90
20.5 - 21.5	3	4.35
21.5 - 22.5	5	7.25
22.5 - 23.5	9	13.05
23.5 - 24.5	15	21.75
24.5 - 25.5	25	36,25
25.5 - 26.5	36	52,2
26.5 - 27.5	49	71,05
27.5 - 28.5	63	91,35
28.5 - 29.5	11	15,95
29.5 - 30.5	4	5,8
30.5 - 31.5	3	4,35
31.5 - 32.5	3	4,35
32.5 - 33.5	3	4,35
33.5 - 34.5	3	4,35
34.5 - 35.5	3	4,35
min. density [g/ml]	1.45	

Figure 5. Example how to present data of the stored heat as a function of temperature. These data originate from a heating experiment; the same has to be done for the cooling experiment.

The volume specific values (fig. 5 right) have to be calculated from the mass specific values by multiplication with the smallest density in the temperature range of application (fig. 5 right).

Furtheron, the degree of subcooling for the selected temperature range of application has to be declared. How this has to be done will be presented in a future publication.

4. SPECIAL PROBLEMS IN CALORIMETRY FOR PCM

The most important things to consider to develop a standard for measurements, can be found from various standards regarding calorimetry (DIN 53765, EN ISO 11357-1, ASTM E 793) and from literature on calorimetry and thermal properties measurement in general (Speyer 1994).

Regarding the sample the following things are important:

- Representative sample size: to assure sample homogeneity, subcooling might depend on sample size
- Sample preparation

The calibration of the measurement system (Cammenga et al. 1993, Gmelin et al. 1995, Hemminger et al. 1989, Höhne et al. 1990, Sarge et al. 1994, Sarge et al. 2000, Schubnell, 2000) has to be done for:

- Correct measurement of the temperature by the sensor
- Correct measurement of heat flow

Regarding the measurement parameters:

- Thermodynamic equilibrium in the sample
  - sample is isothermal (Androscha, 2001, Sneker et a. 1997)
  - sample is in reaction equilibrium (problem with subcooling)

The requirement of having a thermodynamic equilibrium in the sample during a measurement is crucial to get well defined data on the one hand and to compare different measurements using different methods. On the other hand, to determine the enthalpy as a function of temperature, the interesting temperature range has to be scanned with a certain temperature resolution. The scanning of the temperature range is a time consuming task and there is a natural tendency to do it as fast as possible. However, if it is done too fast, (heating / cooling rates of 10 to 20K/min are often recommended in standards for other materials than PCM) the sample will not be in thermodynamic equilibrium and the measured enthalpy will be attributed to a different temperature depending on the scanning speed. Thermodynamic equilibrium in this respect means two things: thermal equilibrium (the sample is isothermal) and reaction equilibrium.

With regard to thermal equilibrium, the mass and actually the geometry of the sample influence the result. To change the enthalpy during scanning, heat must be supplied to or extracted from the sample. The heat transfer within the sample leads to a temperature profile within the sample because otherwise heat would not flow. The measured enthalpy change is thus resulting from all temperatures in this temperature profile but at the end only attributed to one single temperature measured somewhere in the sample or close to the sample. Due to the low thermal conductivity and high melting enthalpy of PCM it is much more complicated to remain close to thermal equilibrium than with non PCM materials. The problem can be minimized by scanning as slow as possible and having small samples. Small samples however might not be representative for an inhomogeneous PCM and slow scanning rates might lead to a low signal to noise ratio. That means one has to find a balance between all the requirements.

The reaction equilibrium also becomes important especially when subcooling or diffusion effects in incongruent melting PCM become significant. Subcooling can thereby also be dependend on the sample mass if selfnucleation dominates, thus becoming an increasing problem with small sample masses.

5. INTERCOMPARISONTEST

5.1. Scope and range of the test

The important things to consider as discussed above are at this point only qualitatively known. To determine quantitatively when e.g. a heating rate is too large, one has to perform tests with different measurement systems, measurement parameters and different PCM. For that purpose an intercomparison test at different institutes was performed (table 1).

Table 1. Measurement systems and institutes

system	type	measurement	institute
hf-DSC	Phönix 204, Netzsch	dynamic steps	ZAE Bayern, Div. 1, Germany
m-DSC	TA Instruments	modulated (Wunderlich et al. 1994)	ZAE Bayern, Div. 2, Germany
DSC	Calvet, Setaram	dynamic	FhG-ISE, Germany
T-History	self developed (Zhang et al. 1999, Lázaro et al.)		ZAE Bayern, Div. 1, Germany

Here we present results from two different commercial PCM. The first is paraffin RT27 from Rubitherm, where no subcooling is expected and reaction equilibrium is expected to be fulfilled under all measurement conditions. The second is the salt hydrate TH29 provided by Dörken where little subcooling is expected.

In contrast to the standard how to present the data, the presentation of the intercomparison test data was done in a different way. The integration of c_p to get h leaves the “0”-point free to choose. The consequence is, that an h(T)-plot allows an easy visual check of the accuracy of h and its temperature dependence at the same time. This is not possible in a c_p-plot; the eye can see a shift in temperature, but not check the result of the integration at the same time. As the "0"-point we have chosen a point in the liquid phase, somewhat after the melting is completed. The reason is that in contrast to the solid state the heat capacity in the liquid state is usually not changing very much with temperature and thus an uncertainty in the temperature dependence will not strongly interfere with an error in the enthalpy change over a larger temperature range.

5.2. Results of the intercomparison test on a paraffin with little or no subcooling

Fig. 6 shows the results of the measurements on paraffin RT27 where all enthalpies have been normalized to 0J/g at 30°C. The upper two graphs show measurements performed at the FhG-ISE with a Calvet DSC using different sample mass and heating / cooling rate. It can be observed, that with smaller heating / cooling rates, enthalpy curves from heating and cooling come closer to each other as thermodynamical equilibrium in the sample during a measurement is approached with smaller heating / cooling rates. The difference at the lowest heating and cooling rates between the h(T) curves is less than 0.5°C total or ±0.25°C. This proves that RT27 has negligible subcooling.

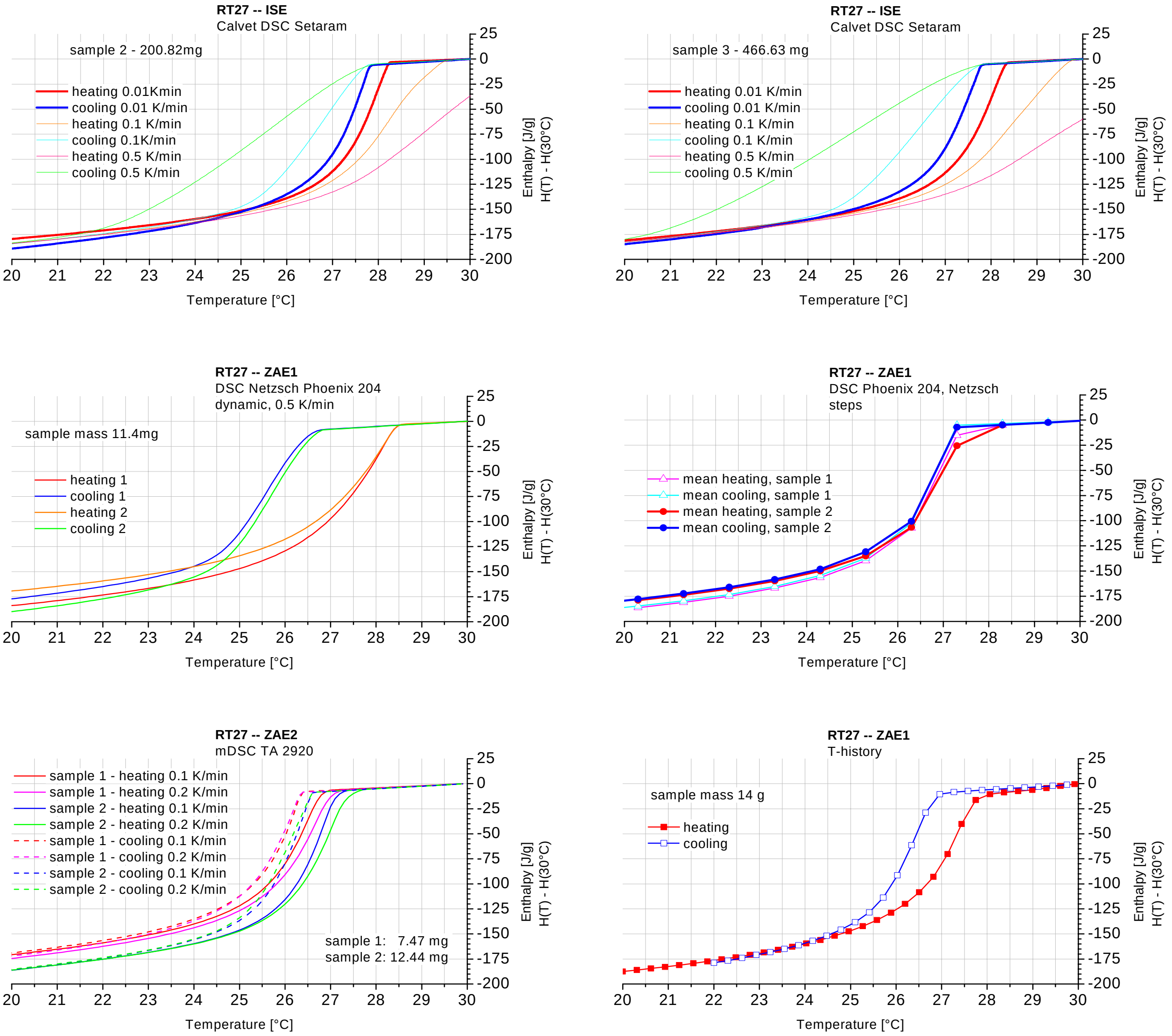


Figure 6. Result of the intercomparison test on paraffin RT27.

The two graphs in the middle are data from the ZAE Bayern Div. 1 using a hf-DSC from Netzsch. The data on the left are from dynamic measurements with the lowest possible heating / cooling rate. They show good agreement regarding the enthalpy difference, but it is obvious that thermal equilibrium has not been reached. The right graph shows data from the same instrument, but with a stepwise heating and cooling where steps were 1°C high. Here thermal equilibrium is reached perfectly; heating and cooling results show no significant difference at all. The temperature accuracy of the data is equivalent to the step height.

The bottom graphs show data using a temperature modulated DSC at the ZAE Div. 2 and a self developed T-history measurement setup at the ZAE Div. 1. Data from the modulated DSC also show little difference between heating and cooling. The systematic difference between the samples could be due to an uncertainty in the determination of the sample mass.

The data on the right show results using a T-history setup which was recently improved. The difference between the h(T) curves for heating and cooling is less than ±0.5°C, even though the sample mass is by far the largest of all the systems, more than 30 times the mass in the Calvet DSC and more than 1000 times compared to the other DSCs.

Regarding the enthalpy difference all results agree within less than ±10%. Regarding the dependence on the temperature, except for the DSC measurements at the ZAE Div. 1 which did not get close enough to thermal equilibrium, all other data show good agreement. The end of melting / onset of crystallization lie within a range of about 1°C.

5.3. Results of the intercomparison test on a salt hydrate with significant subcooling

Fig. 7 shows the results of the measurements on salthydrate TH29 where all enthalpies have been normalized to 0J/g at 35°C. The upper left graph shows a set of data from T-history measurements performed at the ZAE Division 1. Measurements were done on two different samples and varying start and end temperature in the T-history measurement. The graph at the right shows measurements performed at the FhG-ISE with a Calvet DSC using different heating / cooling rate. For the smallest heating and cooling rate, where thermal equilibrium is approached, the h(T) curves agree very well within about 0.5°C with the results from the T-history measurements. The enthalpy difference is also less than 10%.

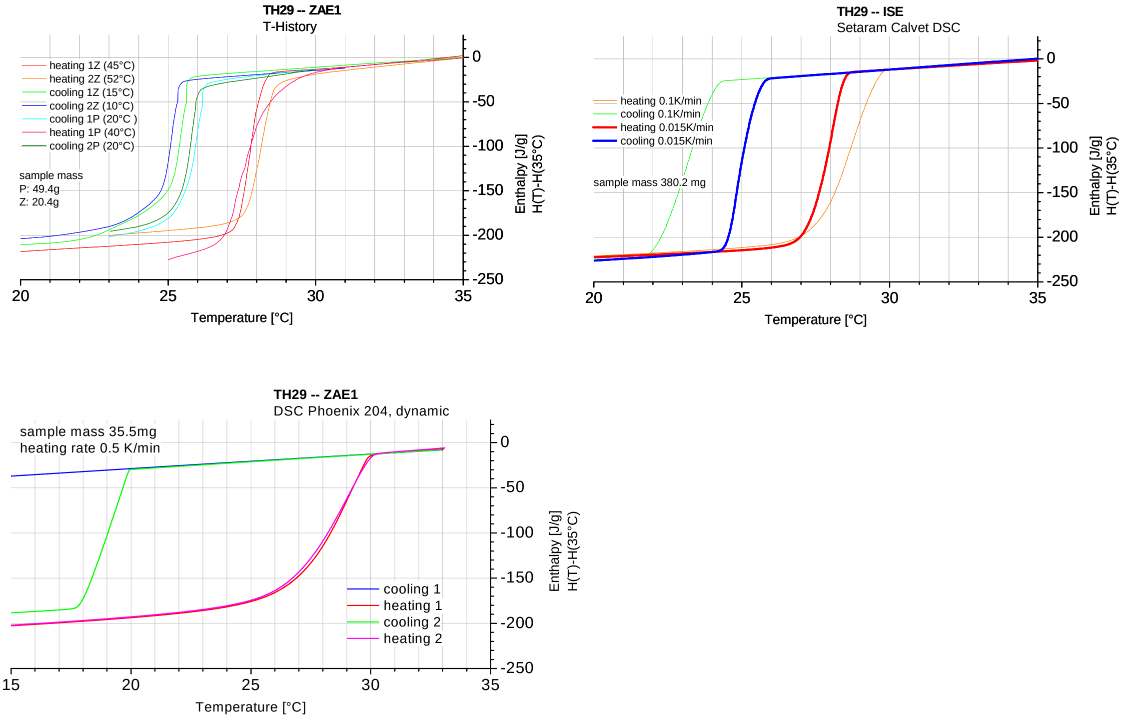


Figure 7. Results of the intercomparison test on salthydrate TH29.

The graph at the bottom of fig. 6 shows measurements performed with an hf-DSC where the sample mass is quite small. It is seen that on cooling the sample strongly subcools, with a strong variation between different experiments. The cooling curve is thus not representative for the performance of this PCM in an application where a bigger mass of the PCM is used.

6. STANDARD HOW TO MEASURE

Based on the results from the intercomparison test the following conclusions have been made. The stored heat can be determined using one of the following methods:

- hf-DSC dynamic mode with constant heating or cooling rate,
- hf-DSC quasi stationary measurement with stepwise heating
- m-DSC,
- T-History-method,
- CALVET-calorimeter,
- Multylayer-calorimeter-method (not described here).

During the realization of a measurement, the guidelines of the Gütegemeinschaft PCM e.V., specifically regarding

- Number of samples and measurements
- Method to ensure the thermal equilibrium within the sample with sufficient accuracy

have to be followed. These will later be available on the website mentioned above.

7. CONCLUSION

The data and their discussion in this paper show that PCM cannot be measured accurate enough simply by using standards that have been developed for other materials. The necessity of being close to thermodynamic equilibrium within the sample during a measurement is especially critical for PCM. Due to their low thermal conductivity and large melting enthalpy common heating and cooling rates recommended for other classes of materials lead to errors in the stored heat as a function of temperature that cannot be tolerated for most PCM applications. The results of the intercomparison test show however, that using standard calorimetric methods sufficient accuracy usually can be attained if the heating and cooling rates are chosen small enough.

Further on, a standard how to present the data has been described. This standard eliminates the ambiguities that arise from only giving melting point and latent heat data, as was done in the past.

NOMENCLATURE

C	heat capacity	(J/°C) or (J/K)	Subscripts	
c	specific heat capacity	(J/g°C) or (J/gK)	p	const. pressure
H	Enthalpy	(J)	v	const. volume
h	specific enthalpy	(J/g)		
DSC	Differential Scanning Calorimetry			
m-DSC	temperature modulated DSC			
hf-*DSC*	heat flux DSC			
T-history method	Temperature-history method			

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