New proposed methodology for specific heat capacity determination of materials for thermal energy storage (TES) by DSC

Gerard Ferrer[1], Camila Barreneche[1,2], Aran Solé[1], Ingrid Martorell[1,3,*], Luisa F. Cabeza[1,¥]

[1]GREA Innovació Concurrent, Edifici CREA, Universitat de Lleida, Pere de Cabrera s/n 25001, Lleida, Spain
[2]Department of Materials Science & Physical Chemistry, Universitat de Barcelona, Martí i Franqués 1-11, 08028-Barcelona, Spain
[3]Serra Húnter Fellow
*Current address: Department of Computer Science and Industrial Engineering, Universitat de Lleida, Campus de Cappont, Jaume II 69, Lleida, Spain
[¥]Corresponding author: lcabeza@diei.udl.cat

Abstract

This study presents a methodology to determine the specific heat capacity (C_p) of materials for thermal energy storage (TES) by DSC. These materials have great energy storage capacities, and due to that, important heat flow fluctuations can be observed for each temperature differential, taking more time to reach a desired temperature gradient. Three different DSC methods are considered to be applied in the methodology, and are explained and compared in this study in order to select the most proper one for C_p determination. To perform this study, the C_p of three materials commonly used in sensible TES systems, slate, water, and potassium nitrate (KNO_3), is determined. Excellent results with errors lower than 3 % are obtained when using the proposed methodology with the *areas method*. Worse results are obtained with both *dynamic* and *isostep* methods, with errors up to 6 % and 16 % respectively, as a consequence of sensitivity problems during the measurements.

Keywords: specific heat capacity (C_p), differential scanning calorimetry (DSC), thermal energy storage (TES), sensible heat storage.

1. Introduction

The current perspective of lack of fossil energetic resources along with its price and the need to decrease CO_2 emissions [1,2], has lead researchers to focus on developing new energy systems able to take profit of renewable energy and be environmentally friendly and less expensive.

Thermal energy storage (TES) systems are presented as one of the possible solutions to accomplish this demand and have been widely studied and applied in a great variety of engineering fields. Solar energy is a good example case, as it is an abundant and clean energy source, easy accessible. The problem resides on the intermittency of its use, as the hours of maximum energy demand match with the hours of no solar irradiation (night hours). Therefore, and with the aim to fill this existing energy supply gap, TES systems are presented as the solution to store the energy and use it anytime.

One of the most used TES technologies is sensible heat storage, the process by which the heat is accumulated due to the increase of the material temperature without experimenting structural changes, thus, no phase change [3]. Other TES techniques are latent heat storage, which

involves a phase change of the material to store or release the energy, and thermochemical energy, which implies the heat storage of a both sided chemical reaction of a thermochemical material (TCM) [4,5]. A key parameter for the performance of all the TES storage techniques just mentioned is the material selection. A high storage capacity of this material is needed to ensure a good an efficient performance of the system, hence it is important to perfectly know the thermo-physical properties of the material [6–8].

The energy storage capacity in the sensible heat storage depends, according to equation (1), of the specific heat capacity of the material (C_p), the temperature differential (dT) and the sample mass (m).

$$\dot{Q} = \int_{T_i}^{T_f} mC_p(T)dT \quad (1)$$

Therefore, to enhance the energy stored, it is important that the material used in the sensible heat storage system has a high specific heat capacity.

The importance of knowing the specific heat capacity of materials for sensible heat energy storage in TES systems along with the lack of a clear and common methodology in the literature has lead the authors to focus on this issue. Therefore, the most used DSC methods for C_p measurement have been reviewed [9–12] and the three main ones selected to be used in the proposed methodology for C_p measurements of materials for TES systems. The *dynamic method* has traditionally been used to measure PCM latent heat but also for C_p measurements applying high heating rates in the temperature range of study [13]. The *areas method* is specifically based on the C_p value, thus, how much heat flux is needed to heat up a material for temperature increase, and consists of consecutive isothermal stages differing 1 ºC with no heating segments amid [14]. The *isostep method* is an intermediate between these two, as it is a succession of dynamic methods applied to heat up the material just 1 ºC between isothermal segments. This method has been tested in glass transition pharmaceutical studies with good results obtained [15], but it has not been used for TES materials C_p determination, thereby its selection for this study.

The aim of the present study is to test the proposed methodology's performance with each DSC method by determining the C_p of three materials, water, slate and potassium nitrate (KNO_3), commonly used in sensible TES systems, compare the results and find out the measurement errors in order to select the best DSC method to determine the C_p of TES materials.

2. Materials

To ensure the performance of the methodology in a representative variety of material phase forms and chemical structures, three different materials widely used in sensible heat storage systems have been chosen to perform this study.

- *Water*. Its thermal properties are well known, and therefore, these values can be used as a reference to see the approach on the measurements each method has. Commercial Bi-distillated water from Panreac has been used to perform the experiments.

- *Slate*. It is a widely used construction material and its performance depends on its specific heat capacity, therefore authors find it an interesting material to be tested. The slate samples used in this study were taken from a quarry in the Catalan Pyrenees.
- *Potassium nitrate*. It is an inorganic salt mainly used as molten salt in concentrated solar power plants (CSP Plants). It has high melting point (320 ºC) and, as all inorganic salts, a complex chemical structure, and that is why it is also found to be useful for this paper's purpose.

It is important to remark that this material selection responds to the need to test the methodology and not to tie it to a concrete material type or a specific TES application. Therefore, materials used in different TES systems and with which authors commonly work have been selected.

3. Methodology

The specific heat capacity has been determined by differential scanning calorimetry (DSC) using a Mettler Toledo 822e DSC. The equipment can operate between -20 ºC and 500 ºC and it is calibrated with zinc and indium, with calibration checks run monthly. The DSC is always turned on 20 minutes prior to the beginning of an experiment in order to homogenize furnace and intracooler temperatures and operates under a constant 200ml/min N_2 flow.

Standard 40 µL aluminium crucibles have been used in this study. To ensure repeatability three samples of 10 mg were prepared for each one of the materials, weighing them with a Mettler Toledo AG135 analytical balance with a precision of 0.01 mg.

The procedure to determine the specific heat capacity of a material consists of three different measurements, all done under the same conditions, thus, using the same DSC method:

- **Blank measurement**. It is necessary to run an experiment with an empty crucible to measure the heat flux that corresponds to the crucible material in order to subtract this signal and consider only the sapphire and material sample ones.

- **Sapphire measurement**. Sapphire is the material used as reference as its specific heat capacity is well known at every temperature and its signal is hugely stable over temperature, data necessary for the material's C_p calculation.

- **Material measurement**. Needed to determine the C_p value of the material under study.

To ensure precision on the measurements, crucibles differing less than 10 µg on their weight must be taken.

The specific heat capacity is calculated with equation (2):

$$\dot{Q} = m \cdot C_p \cdot \beta \tag{2}$$

Where $\dot{Q}$ [mW] is the heat flux measured by the DSC, m [g] is the mass of the sample and β [K/s] is the heating rate of the method used.

The sensitivity of the analysis is tied to the heating rate and the sample mass. To observe the signal fluctuation due to the material specific heat capacity and according to the literature studies found [11,12], high heating rates of about 10–20 K/min are desired, thus, and as equation 2 shows, minor sample masses are needed. Lower heating rates would not conduct to desired results as the material would increase its temperature due to the thermal inertia in DSC, but would not take in the complete heat amount that corresponds to the C_p, thus, lower, incomplete or no fluctuations would be then observed in the DSC curve. Therefore, authors consider the appropriate heating rate selection for C_p studies proven and do not conduct any comparative experiments regarding this issue.

In addition, the maximum deflection on the sapphire DSC signal due to the material C_p is considered to be of about 5 mW [11], therefore the mass and the heating rate need to be adjusted conveniently to accomplish this restriction. Consequently, and as both sapphire and material curves need to be compared, the material mass will also need to be adjusted accordingly; hence, similar sapphire and material masses need to be used. Nevertheless, to prevent stratification, 40 µL volume pans are recommended.

The C_p was measured between 15-16 ºC, 25-26 ºC and 35-36 ºC for all the materials under study. These measurement ranges were selected in order to ensure that water was in liquid state and to be able to take the certain known water 4.18 J/g·ºC C_p value at 25 ºC [16] as a reference to evaluate each method performance.

3.1. DSC measurement methods

The present paper describes three different DSC measurement methods to calculate the C_p of a material: the *dynamic method*, the *isostep method* and the *areas method*.

3.1.1. Dynamic method

It is a temperature controlled method that achieves the thermal equilibrium before and after a controlled heating segment. As Figure 1 shows, it consists of three segments. At first an isotherm stage is set for 10 - 15 minutes to homogenize the material temperature. This stage is followed by the heating segment, where the material is heated at a constant and high heating rate (10-20 K/min) until a final set temperature, where the material undergoes another isothermal stage again for 10 - 15 minutes. The maximum difference between the lower and higher temperatures of the method can be 150 ºC [12].

Measuring both the sapphire and the material, and after subtracting the blank curve of the pan, two DSC signals are obtained as Figure **1** shows. To calculate the C_p of the material, the C_p values of the reference material, sapphire, are needed and can be easily found in the literature. Then, the material specific heat capacity can be calculated with equation 3.

$$C_{pm} = \frac{\dot{Q}_m . C_{ps} \cdot m_s}{m_m \cdot \dot{Q}_s} \tag{3}$$

where $\dot{Q}_m$ [mW] is the material heat flux signal, C_{ps} [J/g·ºC] is the sapphire specific heat capacity, m_s [mg] is the sapphire sample mass, m_m [mg] is the material sample mass and $\dot{Q}_s$ [mW] is the sapphire heat flux signal.

3.1.2. Isostep

Similar to the previous explained dynamic method, the isostep method consists of short dynamic stages along the whole temperature range of the method with isothermal stages before and after each heating segment to stabilize the material temperature. The temperature increase of each heating stage needs to be small, between 1-3 ºC, and the heating rate high for this low temperature change, 1-2 ºC/min [15]. As the temperature increases are low, the isothermal stages do not need to be as long as in the dynamic method, thus, 2-3 minutes might be enough so that the DSC base signal is stable again, ensuring this way the thermal equilibrium of the sample. Again, the maximum temperature range covered is up to 150 ºC, as shown in Figure **1**.

This method uses equation (3) to calculate the C_p of the material along each heating segment.

3.1.3. Areas

The areas method consists of consecutive isothermal segments with no heating stages amid, as shown in Figure 1 along with the DSC signal obtained with this method. Each of the peaks corresponds to every temperature step of the method. The temperature difference between isotherms is of 1 ºC.

Integrating the peak on the DSC curve for both sapphire and material and applying it to equation (3), equations (4) and (5) are obtained:

$$A_s = \frac{\dot{Q}_s}{m_s} = C_{ps} \cdot \beta \tag{4}$$

$$A_m = \frac{\dot{Q}_m}{m_m} = C_{pm} \cdot \beta \tag{5}$$

where A_s [J/g] is the integrated peak area for the sapphire curve, A_m [J/g] is the integrated peak area for the material curve, C_{ps} [J/g·ºC] is the sapphire specific heat capacity, m_s [mg] is the sapphire sample mass, m_m [mg] is the material sample mass and $\dot{Q}_s$ [mW] is the sapphire heat flux signal, $\dot{Q}_m$ [mW] is the material heat flux signal, and β [ºC/s] is the heating rate, the same one for both measurements.

As said in former paragraphs, the sapphire specific heat capacity can be found in the literature, thus, as all the required parameters are known, the specific heat capacity of the material can be calculated using equation (6):

$$C_{pm} = \frac{C_{ps} \cdot A_m}{A_s} \tag{6}$$

All three methods along with its DSC signals are graphically shown in the following Figure 1.

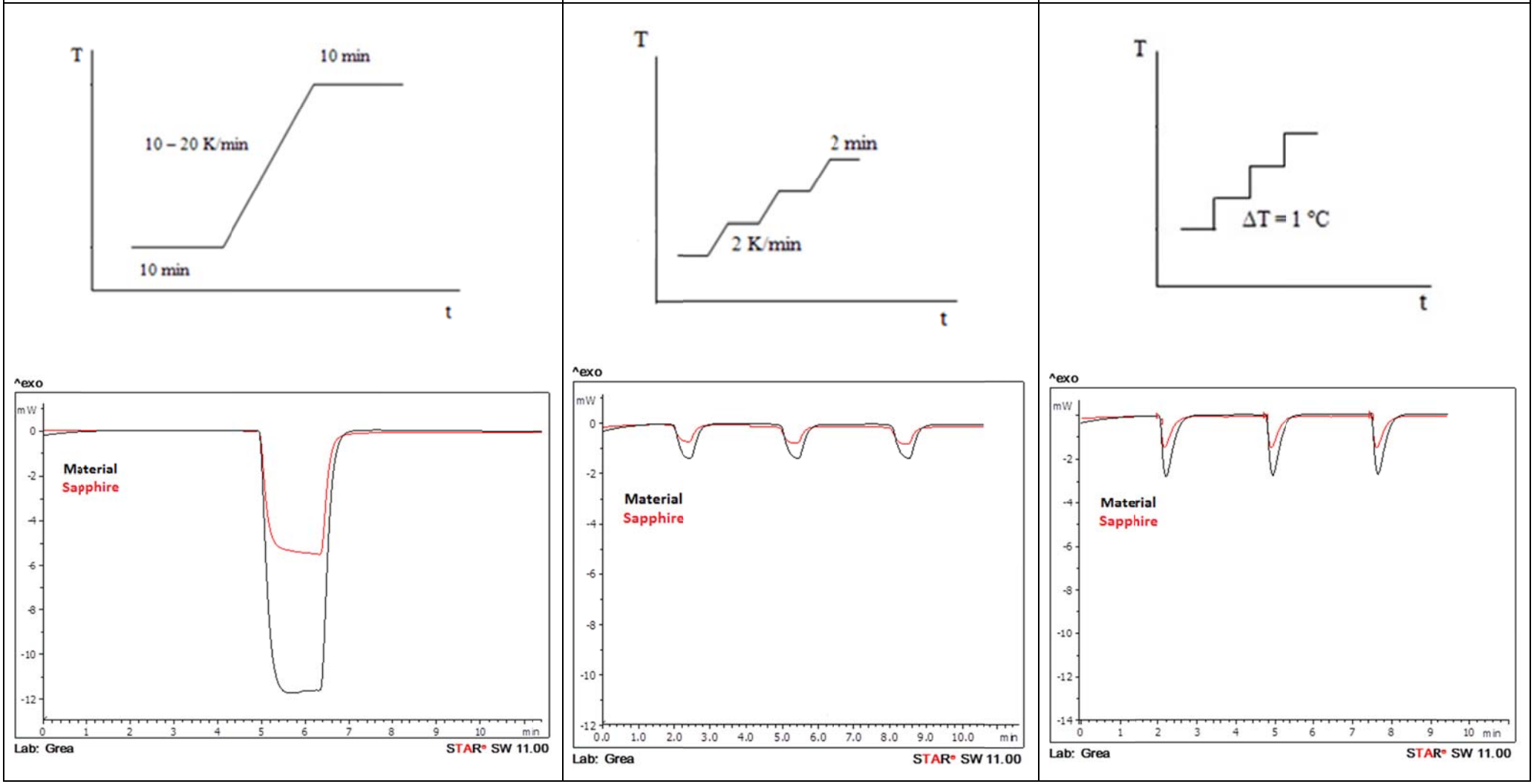
DYNAMIC METHOD	ISOSTEP METHOD	AREAS METHOD
		

Figure 1. Dynamic method, isostep method and areas method along with their DSC signal

4. Results

The methodology explained in former paragraphs has been applied with each one of the DSC methods presented to determine the specific heat capacity of water, slate and KNO_3 in order to compare the results and conclude which is the most suitable method for Cp determination of materials for TES. The measurements were done between 15 ºC and 36 ºC for all the materials.

Literature values [17–20] have been taken as reference in order to evaluate the measurement methods results, and thus, its performance. The errors taken in the consulted literature C_p measurements [21, 22] range between 2-5 %. In this study, results are given with an error of 3 %, including both equipment and calculation errors.

As stated before in the text, three samples of each material were prepared in order to ensure repeatability on the measurements. The main values of the three measurements were calculated and are the ones presented in this result section.

The *dynamic method* gives a continuous signal along the whole temperature study range, as shown in red in the following Figures 2-4. Three different continuous signals are obtained with the *isostep method*, one for each heating segment, thus, for the 15 – 16 ºC, 25 – 26 ºC and 35 – 36 ºC steps. However, as the measurement temperature range is of just 1 ºC and the material is heated at a really fast rate, the three signals are really steep and no clear tendency can be seen in the results, fact that already shows the low sensitivity this method has for C_p calculation. Nevertheless, and in order to compare the methods, an average value of the most constant parts of these three signals is presented in the graphics. Contrary, the *areas method* provides just three points, one for each temperature increment between the isothermal segments, hence, one at 16 ºC, one at 26 ºC and one at 36 ºC.

The three DSC methods are next compared, first by material, and after a global result analysis and summary are done in order to draw clear conclusions about its performance and select the best method.

4.1. Water

Figure 2 shows the specific heat capacities calculated for water with the three DSC methods. Results show that the *areas method* is the one that gets closer values to the theoretical water specific heat capacity of 4.18 J/g·ºC at 25 ºC [16], with small C_p increases with temperature. The blue line links the C_p obtained by this method at 16 ºC, 26 ºC and 36 ºC in order to easily see their pattern with temperature.

The *dynamic method* results present a wide constant C_p range of around 4 J/g·ºC from 22 ºC until 34 ºC. However, inconsistent values are found first, in an increasing C_p value stage until 20-21 ºC, and at the end of the experiment with a sudden increase of the C_p from 34 ºC to 36 ºC, slightly overcoming the theoretical water value as well as the values obtained by the areas method, and that indicates sensitivity problems in these two measurement parts.

As already said in former paragraphs, the C_p values presented in the graphic for the *isostep method* are the average of the most constant parts of the obtained signal, being the standard deviation for water of ± 0.08 J/g·ºC. The results obtained with this method are the most inconsistent ones, as C_p are almost constant with temperature and of around 3.5 J/g·ºC, differing

a 27% from the theoretical Cp and notably differing from the other methods results as well. By increasing just 1 ºC at a really high heating rate, the sensitivity of the measurement is decreased, which explains the steep and unclear patterns obtained, from which no clear results can be withdrawn.

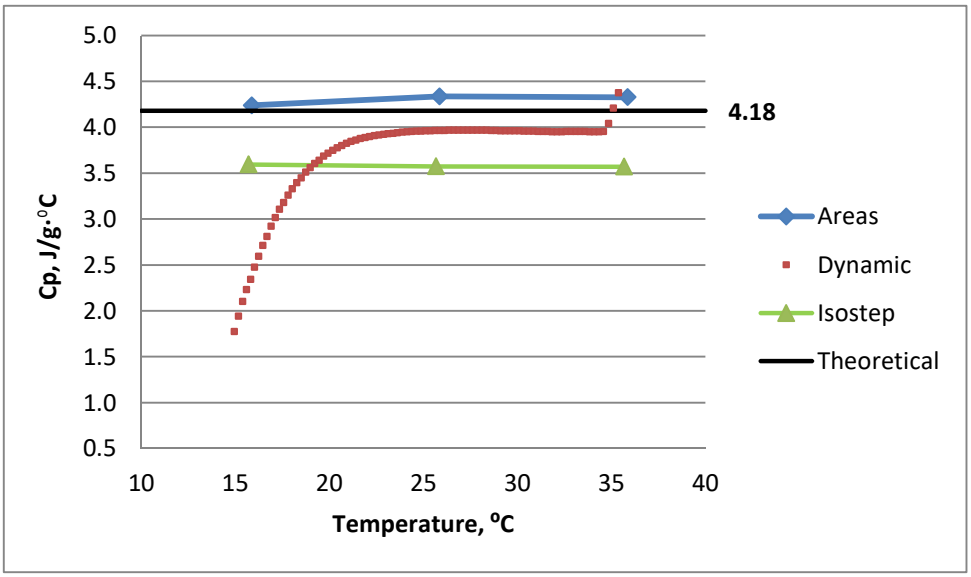


Figure 2. Specific heat capacity measurements for water

The sensitivity problems observed with the *dynamic* and *isostep methods* are explained as a consequence of the high rates applied in both methods to heat the material. Due to the abrupt temperature change on both initial and end points, the DSC temperature sensor cannot react fast enough to read the real temperature, and consequently, the obtained DSC signal presents "noise" at the beginning and at the end of each heating stage, obtaining bad lectures in these points, hence, lowering down the measurement sensitivity. This fact has greater significance in the *isostep method* results due to the higher relation between heating rate and temperature increase.

4.2. Slate

The results obtained for slate are presented in Figure 3. The specific heat capacity of building materials, irrespective of type, varies within the limits of 0.7 – 0.95 J/g·ºC [18], and results show that the *areas method* is the method that provides C_p close to the theoretical range, 0.95 J/g·ºC at 16 ºC and 1 J/g at both 26 ºC and 36 ºC, equal or a bit above the superior theoretical limit. The values obtained by the *dynamic method* are around 0.62 J/g·ºC, thus, not in the expected theoretical C_p range. Again, three average points are presented for the *isostep method*, with a standard deviation of 0.03 J/g·ºC. The C_p tendency observed is, again, the most inconsistent as its values decrease with temperature. In addition, the values obtained are close to the dynamic ones but not in the expected range found in the literature. Furthermore, and as observed in the water results (Figure 2), sensitivity problems in both *dynamic* and *isostep* methods were noticed, clearly observed on the *dynamic method* curve in the graphic as the discontinuous C_p values at the beginning and at the end of the experiment.

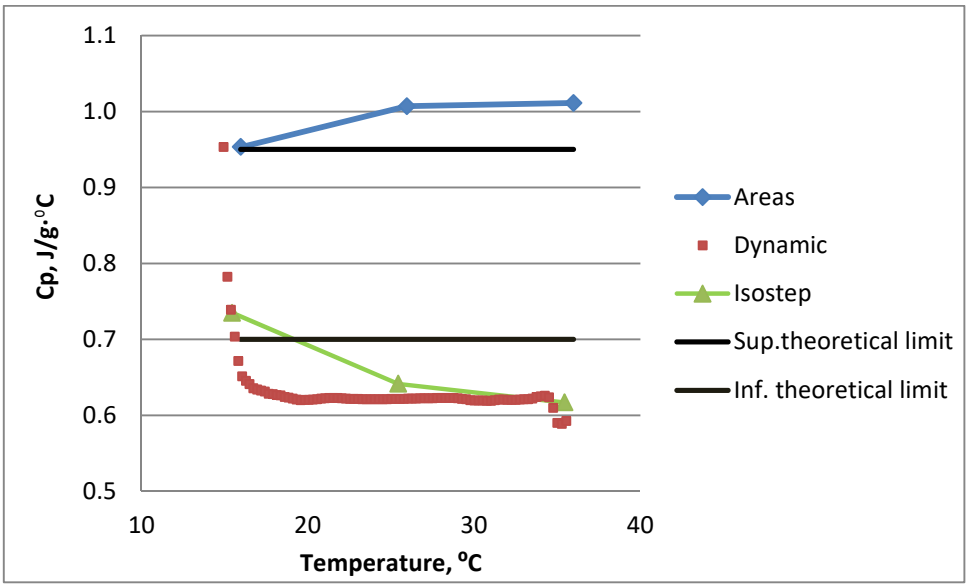


Figure 3. Specific heat capacity measurements for slate

4.3. Potassium nitrate (KNO_3)

Results for potassium nitrate are shown in Figure 4. Similar C_p values of around 0.95 J/g·ºC are obtained for this material with both *areas* and *dynamic* methods, results that match with the literature value of 0.95 J/g·ºC [17]. However and as already seen in water and slate results, the *dynamic method* curve obtained shows the same sensitivity problems as non-constant values at the beginning and at the end of the experiment.

The *isostep method* results are as inconsistent as for water and slate, mainly due to the sensitivity problems this method shows for C_p measurement. The C_p decreases with temperature and has lower values than the ones obtained with the other two methods.

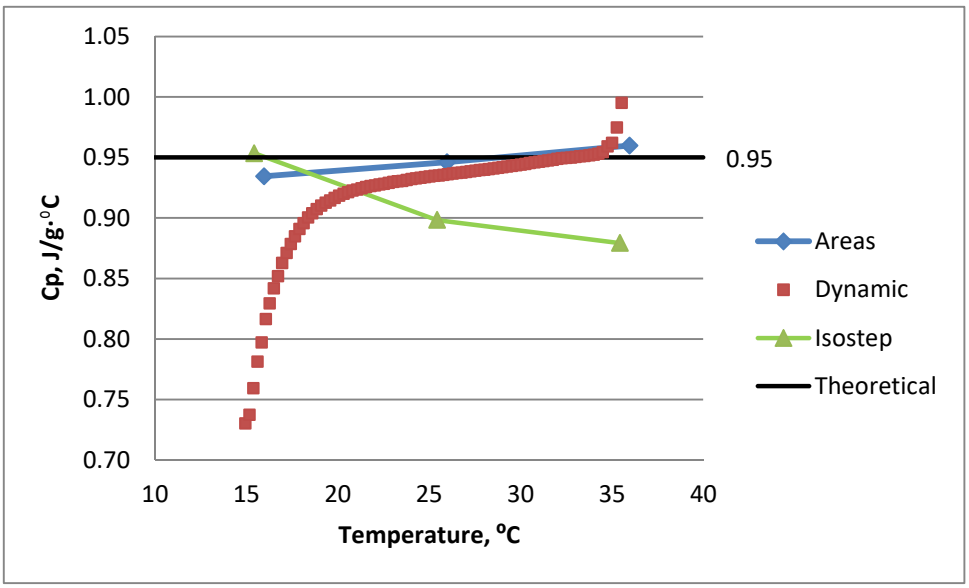


Figure 4. Specific heat capacity measurements for KNO_3

4.4. Results discussion and summary

As explained in former paragraphs, both *dynamic* and *isostep method* measurements are limited by the high heating rates applied, that low down the sensitivity of the analyses and increase the error of the results. It is clear in the results presented that these two methods show two segments in which the C_p has inconsistent values due to equipment response limitations to the method characteristics, making the data acquired at these points despicable. All in all, the dynamic method results are quite approximate to the literature ones once the DSC has stabilized, and better than the results obtained with the isostep method. However, no matter the temperature range considered, an experiment programmed with the dynamic method would always have the limitation of not having reliable data in the whole desired temperature range as after switching the heating rate, the DSC need time for instrument stabilization and consequently, the initial and final low sensitivity data points would always be obtained. Therefore, a wider temperature segment would always be needed in order to calculate the C_p at the desired temperatures. That would be, as an example, programming the experiment between 10 ºC and 40ºC to obtain reliable C_p values between 15 ºC and 35 ºC.

Taking this into account and comparing the three material results analysis, at this point it is clear that the *areas method* is, by far, the best method applied in this study to determine the specific heat capacity of a material. However, for a deeper result analysis, the C_p obtained were compared to the theoretical values found in the literature. The relative errors between the measured values and the literature ones have been calculated with equation (6):

$$relative\ error = \frac{C_{pt} - C_{pc}}{C_{pt}} \cdot 100 \tag{6}$$

where $C_{p\,t}$ is the theoretical C_p and $C_{p\,c}$ is the calculated C_p.

Table 1 shows the relative errors calculated for water and KNO_3. As no specific value for the slate used in this study was found in the literature, this material was not included in this analysis. It is important to point out that the initial and final points of both dynamic and isostep methods were discarded for this analysis due to the sensitivity problems observed, thus only the points that showed a constant and clear pattern are considered in the errors given.

Results show that the *areas method* is, for both water and KNO_3, the method that presents less and lower relative error compared to theoretical values. This relative error comparison also proves the sensitivity differences between methods explained in former paragraphs. For water, the *dynamic method* presents a relative error of 6 %, larger error compared to the 3 % obtained by the areas method. The difference is more important with respect to the isostep method, with a relative error of 16 %. The same tendency but with lower differences is observed in the relative errors obtained for KNO_3. The *areas method* relative error is really low, 0.4 %, the *dynamic method* results present 1.5 % or error and the *isostep method* is again the one that has more error, 4 %.

Table 1. Relative errors of water and KNO_3 with respect to the corresponding theoretical values

Water	**Areas method**	**Dynamic method**	**Isostep method**
Relative error, %	2.78	-6.02	-16.52
Theoretical C_p = **4.18 J/g·ºC**			

KNO_3	**Areas method**	**Dynamic method**	**Isostep method**
Relative error, %	-0.36	-1.55	-4.07
Theoretical C_p = **0.95 J/g·ºC**			

Summarizing, the methodology proposed in this study has been proved useful and good results have been obtained with the *areas method*, which has been found as the best and most proper method to determine the specific heat capacity of a material from the ones tested in this study. Really low relative errors with respect to the theoretical C_p of the materials have been obtained with this method and no sensitivity problems as the ones observed with the *dynamic* and *isostep* methods have been detected. The *dynamic method* achieves quite approximate values, but always worse than the *areas method*, with higher error with respect to the theoretical C_p and with the limitation of the sensitivity problems at the beginning and at the end of each measurement. Furthermore, the *isostep method* has been found as a useless method to be implemented for the C_p calculation of materials for TES systems. Huge sensitivity errors have been found in this method and no clear results can be taken from the measurements.

In addition, the areas method describes a thermal experiment that fits completely to what the theoretical C_p defines, that is, the energy required to increase 1 ºC the temperature of 1 g of material.

Finally, Figure 5 displays the specific heat capacity of the materials measured by the *areas method* at the three temperatures, 16 ºC, 26 ºC and 36 º C, with their respective 3% error bar (note that the error for slate and KNO_3 is really small and therefore the bars can be barely seen in the graph).

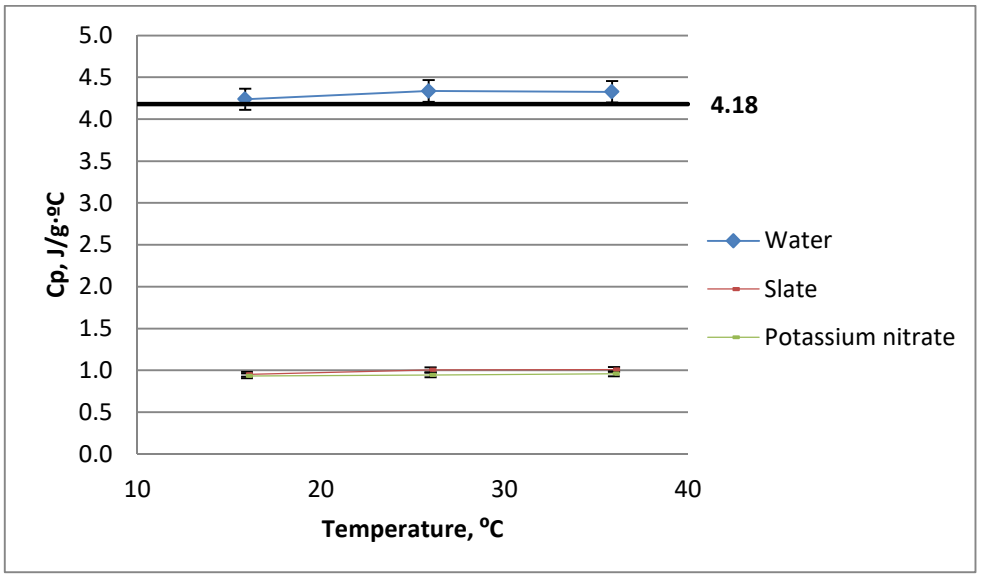


Figure 5. Specific heat capacity of water, slate and KNO_3 measured with the areas method

5. Conclusions

A new methodology for specific heat capacity determination of materials for TES systems by DSC is proposed in this paper. The three most used DSC methods in the literature have been applied in this methodology in order to compare their results and select the best one to be used for C_p determination.

It has clearly been stated in both dynamic and isostep method results that the DSC instrument requires of certain stabilization time after switching the scanning at high rates, obtaining wrong measures during the first 1-2 minutes of experiment. The knowledge of this limitation is important in order to design DSC experiments with larger temperature ranges than the ones in which the Cp wants to be measured due to the negligible data on both extremes. The *isostep method* has been found as a useless method for C_p determination of materials for TES systems as it presents really unclear results due to important sensitivity problems and the C_p obtained show important differences with respect to the theoretical values.

The *dynamic method* has shown better performance and values closer to the literature ones have been obtained. However, sensitivity problems have also been found in this method, mainly during the initial and final points of the measurement, which does not lead to clear values along the whole temperature range in which the C_p wants to be measured.

The *areas method* has been found as the method with best performance of the three tested. It presents really low relative errors (< 3%) with respect to the theoretical C_p of the materials and no sensitivity problems as the *isostep* and *dynamic* methods do. Therefore, it is presented as the proper method to perform C_p measurements of materials for thermal energy storage with the proposed methodology, which, at the same time and due to the great results obtained with this method, has been proved to highly work.

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