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Round Robin Test on the Measurement of the Specific Heat of Solar Salt

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Abstract. Solar salt (SS), a well-known non-eutectic mixture of sodium nitrate (60% w/w) and potassium nitrate (40% w/w), is commonly used either as Thermal Energy Storage (TES) material (double tank technology) or Heat Transfer Fluid (HTF) (solar tower) in modern CSP plants worldwide. The specific heat (c_p , $\text{kJ kg}^{-1} \text{ }^\circ\text{C}^{-1}$) of SS is a very important property in order to support the design of new CSP Plants or develop novel materials based on SS. A high scientific effort has been dedicated to perform a suitable thermophysical characterization of this material. However, there is still a great discrepancy among the c_p values reported by different authors¹. These differences may be due to either experimental errors (random or systematic) or divergences in the starting material (grade of purity, presence of impurities and/or water). In order to avoid the second source of uncertainty (the starting material), a Round Robin Test (RRT) was proposed starting from a common material. In this way, the different methods from each laboratory could be compared. The study should lay the foundations for the establishment of a systematic procedure for the measurement of the specific heat of this kind of materials. Nine institutions, research centers and companies, accepted the proposal and are contributing with their results. The initiative was organized within the Workshop SolarPACES Task III – Material activity.

INTRODUCTION

A precise determination of the c_p of the Solar Salt is essential to fulfil both research and industrial purposes. The investigation of new TES materials, the design of novel industrial TES systems and the improvement of their effectiveness are based on this property. With these aims, the analytical technology is improving day by day to achieve more accurate results and reduce the measurement errors in order to comply with the requirements of industry. Nowadays, the most widespread thermal analysis technique to measure the c_p is the Differential Scanning Calorimetry (DSC).

The sources of uncertainty for the c_p measurement can be classified in two main groups:

- Device precision: the experimental errors from the devices employed in the measurement (balance, DSC or other calorimeter) and their use (human error), they are also divided in random and systematic.
- Starting material: the divergences on the starting material: lack of homogeneity, presence of impurities or moisture.

The experimental errors are not easily minimized. The device supplier (DSC or other) usually reports a certain error for the equipment. However, the final error is the sum of many factors. For example, the calibration of the equipments (balance, DSC) is very important, as well as the skills of the person who will perform the measurements. In most cases, the final error is strongly influenced by the method of measurement. The election of the measurement method should be adapted to the properties of the material. The provider usually recommends the proper method for the application requested by the customer. In this way, there are standards that are commonly accepted for specific materials, but the technology is advancing and these standards should be revised periodically.

In order to avoid the divergences on the starting material, it is strongly recommended to assure that the sample is representative of the starting material. Performing the measurements on different samples from the same starting material may reduce the errors due to the lack of homogeneity. In the case of thermal characterization, it is essential to remove traces of water from the sample prior to measurements. The presence of humidity may induce errors for two reasons: part of the weight introduced in the device for the c_p measurement corresponds to water, and that the c_p of water ($4.18 \text{ kJ kg}^{-1} \text{ }^\circ\text{C}^{-1}$ at 25°C) is much higher than the sample one.

With the aim to compare different techniques of measurement, it is essential to eliminate the uncertainties due to the starting material. In this way, a RRT becomes a powerful tool to compare the methods and devices employed by different laboratories. The same sample is delivered to all the partners involved in the RRT. All the partners do the same conditioning treatment prior to analysis. Therefore, the errors can only be attributed to the equipments and the methods employed by each partner.

AIM

The aim of this work is to perform a RRT for the measurement of the c_p of SS. The different methods of measurement of c_p will be compared for this specific application.

METHOD

Sample Preparation and Conditioning

Sodium nitrate (Labkem, analytical grade) and potassium nitrate (Labkem, analytical grade) were dried at 100°C overnight in an oven (Raypa). A SS batch (120 g) was prepared by mixing 72 ± 0.1 g of sodium nitrate with 48 ± 0.1 g of potassium nitrate. (60:40% w/w). The mixture was homogenized and melted in a furnace (Nabertherm) at 350°C for $\frac{1}{2}$ h. After being cooled, the SS was milled and stored under dry conditions.

Prior to the sample preparation, the SS batch was dried in an oven at 100°C for 1 hour. Nine samples were prepared by weighing enough quantity to perform the measurements (~ 2 g) from the SS batch under argon and dry atmosphere (<0.5 ppm O_2 , <0.5 ppm H_2O) using a glovebox (mod. UNILabplus ECO, Mbraun). Samples were closed inside the glovebox and stored under dry conditions.

Samples were delivered to participants within silica gel in order to protect them from moisture. The samples were dried for 1 hour prior to be measured.

Standard ASTM E1269

The standard ASTM E1269² is the most accepted procedure to measure the c_p of materials. Three different heat flow measurements are required for the specific heat calculation: blank curve (two empty crucibles), sapphire curve (a crucible with a certified sapphire disc in the sample side and an empty reference crucible) and sample curve (a crucible with salt in the sample side and an empty reference crucible).

The specific heat determination requires the use in the temperature program of an isothermal segment, followed by a dynamic segment where the data are collected, and a final isothermal segment because the signal needs to be stabilized (isothermals) before and after the dynamic segment.

MDSC Testing

TA Instruments developed an innovative technique³ to measure the c_p based on the registration of the heat absorbed (or released) by the sample when a modulated heating rate (changing heating rate) is superimposed on top of a linear heating rate. This modulation is defined by the amplitude (A, °C) and the cycle time (s). MDSC can be applied either on dynamic or isotherm methods. The main advantage of this technique is that one single experiment is required to obtain accurate results.

Calorimeter SETARAM

The principle of working of this calorimeter is similar to DSC, but in this case the volume of cell is 12 cm³. The use of higher amounts of sample would hopefully lead to lower errors. This device allows a correct calibration of the measure thanks to its reference cell. It features a high precision Calvet 3D detector with a thermocouple network totally surrounding the reference cell and the sample cell so that heat flux could be measured in every direction. The calorimeter measures the heat flux difference between the sample and a reference material subjected to the same temperature variations under a controlled atmosphere, and thus allows calculating the corresponding c_p of the sample material.

Description of the Methods

The description of the methods used by the partners is shown in Table 1 (dynamic) and Table 2 (isotherm). The partner 1 performed several measurements using different methods, therefore it appears in four rows (2 dynamic and 2 isotherm). Basically, in dynamic methods, the measure of c_p is done during a heating or cooling ramp. Before and after the heating ramp, there is an isotherm step. The parameter ΔT means the interval of temperatures where the heating ramp is applied (between isothermal steps). The range of temperatures (Range T) is the complete range of measurement. In the case of isotherm methods, the measurements are performed as fixed temperatures also indicated. The parameter Est (min) indicates the time for stabilization at the temperature of measurement. The modulate parameters are also specified (amplitude and period) where MDSC was used.

Some other parameters about the crucible: the atmosphere (Atm) inside the crucible (argon or air), the material of the crucible (M), the type (hermetic or non-hermetic), the sample weight and the number of replica for the same starting material are also shown in Table 1 and 2.

TABLE 1. Description of dynamic methods used by different partners to perform the c_p analysis.

P	Device	Method	Parameters						Crucible				
			Ramp °C/min	ΔT °C	MDSC A °C	t s	Range T °C	Flow	Atm	M	Type	Sample Weight mg	N
1	Mettler Toledo (DSC2)	ASTM E1269	20	130	n.a.	n.a.	370-500	N ₂	Air	Al	40 μ l pinhole	10-15	6
1	TA Instruments (Q2000)	MDSC	5	320	0.5	60	80-400	N ₂	Air	Al	T-zero	10-22	3
2	TA Instruments (Q2000)	MDSC	2	390	1	120	50-440	N ₂	Ar	Al	T-zero	25	3
3	Netzsch (DSC 204)	ASTM E1269	10	300	n.a.	n.a.	150-450	N ₂	Air	Pt	no hermetic	22-25	3
4	Mettler Toledo (DSC1)	DIN51007	30/10	50	n.a.	n.a.	50-550	Air	Air	Al	40 μ l pinhole	25	4
5	Mettler Toledo (PDSC132)	ASTM E1269	10	50	n.a.	n.a.	170-420	N ₂	Air	Al	40 μ l pinhole	13	2
6	Mettler Toledo (DSC2)	ASTM E1269	20	50	n.a.	n.a.	175-475	N ₂	Air	Al	40 μ l sealed	20-21	4
7	Mettler Toledo (DSC2)	ASTM E1269	10	425	n.a.	n.a.	25-450	N ₂	Air	Pt	no hermetic	25	3

*P = Partner, Ramp = heating rate, ΔT = gradient of temperatures between isotherm steps. A = amplitude. t = period. Range T = range of measurement temperatures. Flow = flow gas during measurement. Atm = gas inside the crucible. M = material crucible. T-Zero = hermetic Al pan & lid from TA Instruments. N = number of replica

TABLE 2. Description of isotherm methods used by different partners to perform the c_p analysis. All measurements were performed under a constant N₂ flow in the device.

P	Device	Method	Parameters					Crucible				
			Est min	Meas. min	MDSC A °C	t s	Temperatures °C	Atm	M	Type	Sample Weight mg	N
1	TA Instruments Q2000	MDSC	0	20	0.5	60	400/350/300	Air	Al	T-zero	10-22	3
1	TA Instruments Q2000	MDSC	2	15	0.5	60	400/350	Air	Al	T-zero	15-25	4
8	TA Instruments Q1000	MDSC	20	10	0.6	110	400/300/200	Ar	Al	T-zero	26-27	3

*P = Partner. Est. = stabilization time. Meas = measurement time. A = amplitude. t = period. Temp = measurement temperatures. Atm = atmosphere inside the crucible. T-Zero = hermetic Al pan & lid from TA Instruments. M = material. N = number of replica.

Specific Heat Result Analysis

The c_p results provided by the partners were statistically treated according to the following procedure⁴. The mean, the Standard Deviation (SD) and the Relative Standard Error (RSE) were calculated for each set of data, considering a Student's t-distribution with a 95% confidence interval. These parameters were obtained according to the Equations 1-3.

$$SD = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n-1}} \quad (1)$$

where SD is the standard deviation, x_i is one of the individual measurements, \bar{x} is the mean value of the sample and n is the number of replicas.

$$CI = \bar{x} \pm \Delta x = \bar{x} \pm t_{\alpha/2} \cdot \frac{SD}{\sqrt{n}} \quad (2)$$

where CI is the confidence interval, \bar{x} is the mean value of the sample, Δx is the amplitude of the interval, $t_{\alpha/2}$ is the percentile of the Student's t distribution with a significance level of α and n-1 degrees of freedom, SD is the standard deviation and n is the number of replicas.

$$RSE = \frac{\Delta x}{\bar{x}} \cdot 100 \quad (3)$$

where RSE is the Relative Standard Error, Δx is the amplitude of the interval and \bar{x} is the mean value of the sample. The RSE should not be confounded with the Relative Error (RE) that is calculated as the Absolute Error (AE) divided by the average of a finite number of samples:

$$RE = \frac{x_i - \bar{x}}{\bar{x}} \cdot 100 \quad (4)$$

The RE gives an idea of the dispersion of each individual measurement with respect to the average among them.

RESULTS

The results reported by all the partners are shown in Fig. 1. As it can be seen in the graphic, some c_p values are highly deviated from the average (inside red lines). The measurements resulted from the calorimeter SETARAM C80 were anomalous, and highly dispersed. Therefore, they are not presented. Further research should be done to achieve more confident results with this technique. A statistical analysis will be done.

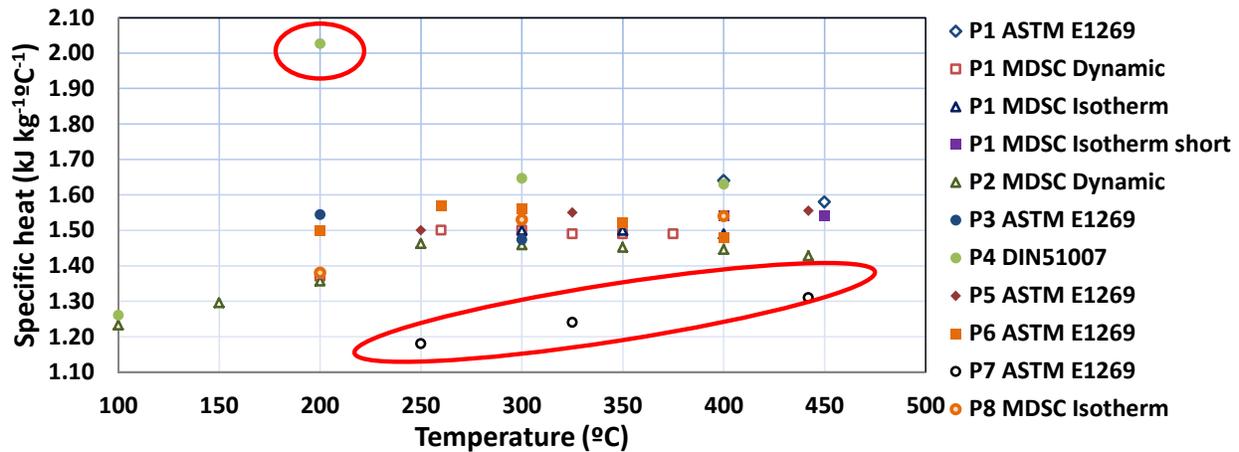


FIGURE 1. Results reported by the partners of the RRT on the measurement of c_p of SS.

In order to compare the accuracy of the results, three temperatures were selected (200 °C, 300 °C and 400 °C), Fig. 2 and Fig. 3 show the SD and the RSE (%) calculated by the expressions (1) and (3) from the measurements reported by each partner. Partner 5 only provided two measurements (from two crucibles), the RSE is very high and no representative for this small number of samples. For this reason, it was omitted. The SD of Partner 5 is in the order of magnitude of the other partners.

The SDs are lower than $0.1 \text{ kJ kg}^{-1} \text{ }^\circ\text{C}^{-1}$ for all the partners except Partner 7, and in the order of $0.05 \text{ kJ kg}^{-1} \text{ }^\circ\text{C}^{-1}$ in most cases. Regarding to RSE (%), it was lower than 10% for all the partners except Partner 7. This limit of RSE (10%) can be considered too high. However, due to the low amount of measurements (in the order of 3-4 for most of the partners), it can be considered acceptable.

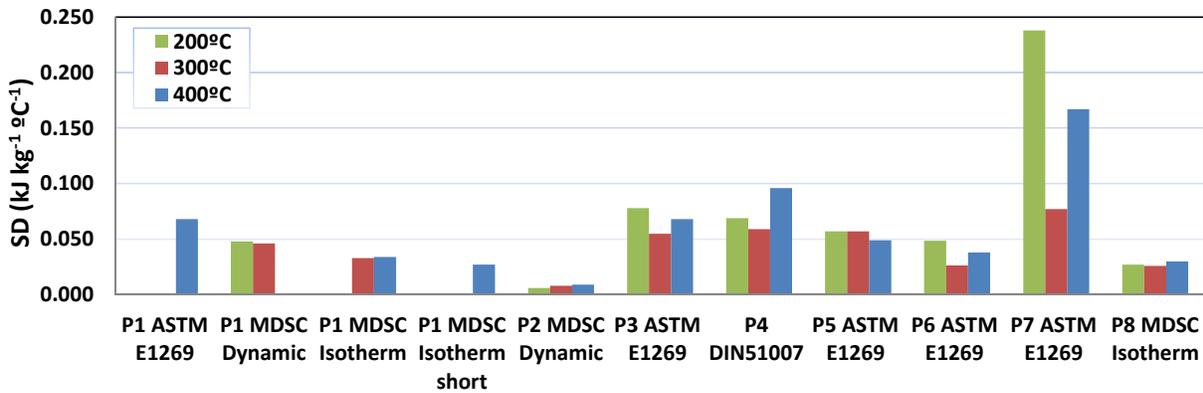


FIGURE 2. SD ($\text{kJ kg}^{-1} \text{ }^\circ\text{C}^{-1}$) calculated from the results reported by each partner according to equation (1).

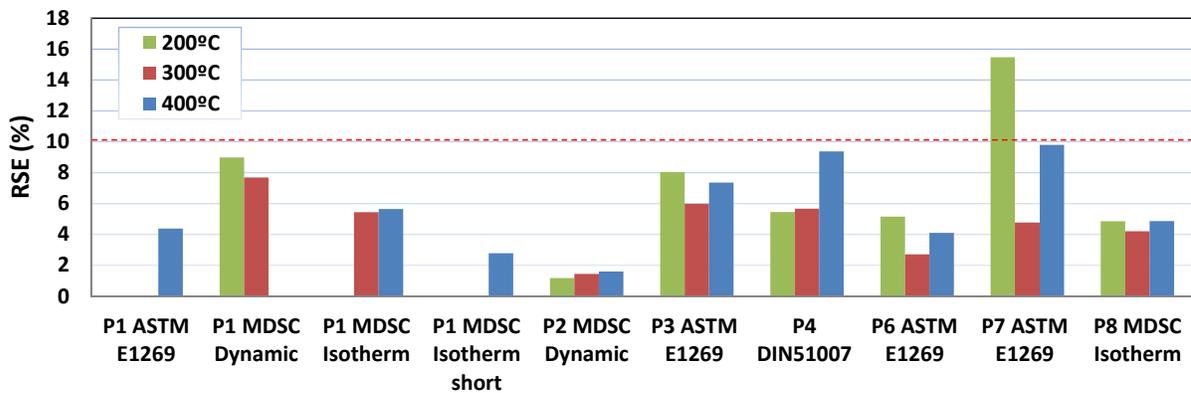


FIGURE 3. RSE (%) calculated from the results reported by each partner according to equation (3).

Table 3 shows the average of the c_p measurements at the three selected temperatures (200, 300 and 400 °C) performed by all the partners. The average values shown in this table are graphically represented in Fig. 1. Taking into account the measurements from all the partners, the SD and RSE are too high. This fact reveals a high dispersion between the results. The relative error (RE) of the measurement of each partner was calculated according to equation (4). REs from Partners 4 and 7 were higher than the rest (36.75% and 20.38% at 200°C). Particularly, the c_p measurements of Partner 7 are more dispersed between them than the other partners' ones (Fig. 2 and Fig. 3). The origin of these deviations is not well known, but these results have been not considered for further statistical analysis. The revised results are shown in Table 4.

It can be concluded that the average values for the c_p of SS, according to the partners results, are $1.442 \text{ kJ kg}^{-1} \text{ }^\circ\text{C}^{-1}$ (200 °C), $1.510 \text{ kJ kg}^{-1} \text{ }^\circ\text{C}^{-1}$ (300 °C) and $1.521 \text{ kJ kg}^{-1} \text{ }^\circ\text{C}^{-1}$ (400 °C). Table 4 shows an acceptable RSE, lower than 6% for the three temperatures. The c_p results are represented graphically in Figure 4, all the c_p measurements

are within the interval between 1.20 and 1.65 $\text{kJ kg}^{-1} \text{ }^\circ\text{C}^{-1}$. After the revision of results (Table 4), there are no REs higher than 10%, and most of them are lower than 5%.

TABLE 3. Average values of c_p ($\text{kJ kg}^{-1} \text{ }^\circ\text{C}^{-1}$) measurements performed by the partners.

	c_p ($\text{kJ/kg}^{-1} \text{ }^\circ\text{C}^{-1}$)			RE (%)		
	200°C	300°C	400°C	200°C	300°C	400°C
Partner 1 ASTM E1269			1.640			8.53
Partner 1 MDSC Dynamic	1.370	1.500		7.57	0.30	
Partner 1 MDSC Isotherm		1.500	1.490		0.30	1.40
Partner 1 MDSC Isotherm short program			1.540			1.91
Partner 2 MDSC Dynamic	1.357	1.459	1.446	8.45	2.44	4.31
Partner 3 ASTM E1269	1.544	1.474	1.480	4.17	1.44	2.06
Partner 4 DIN51007	2.027	1.647	1.630	36.75	10.13	7.87
Partner 5 ASTM E1269	1.500	1.550	1.555	1.20	3.64	2.91
Partner 6 ASTM E1269	1.500	1.560	1.480	1.20	4.31	2.06
Partner 7 ASTM E1269	1.180	1.240	1.310	20.39	17.09	13.31
Partner 8 MDSC Isotherm	1.380	1.530	1.540	6.90	2.30	1.91
Media	1.482	1.496	1.511			
SD	0.248	0.111	0.095			
RSE (%)	14.00	5.70	4.50			

TABLE 4. Average values of c_p ($\text{kJ kg}^{-1} \text{ }^\circ\text{C}^{-1}$) measurements, removing Partner 4 and 7.

	c_p ($\text{kJ kg}^{-1} \text{ }^\circ\text{C}^{-1}$)			RE (%)		
	200°C	300°C	400°C	200°C	300°C	400°C
Partner 1 ASTM E1269			1.640			7.80
Partner 1 MDSC Dynamic	1.370	1.500		4.98	0.69	
Partner 1 MDSC Isotherm		1.500	1.490		0.69	2.06
Partner 1 MDSC Isotherm short program			1.540			1.22
Partner 2 MDSC Dynamic	1.357	1.459	1.446	5.88	3.40	4.95
Partner 3 ASTM E1269	1.544	1.474	1.480	7.09	2.41	2.72
Partner 5 ASTM E1269	1.500	1.550	1.555	4.03	2.62	2.21
Partner 6 ASTM E1269	1.500	1.560	1.480	4.03	3.28	2.72
Partner 8 MDSC Isotherm	1.380	1.530	1.540	4.29	1.30	1.22
Media	1.442	1.510	1.521			
SD	0.082	0.038	0.061			
RSE (%)	5.95	2.32	3.35			

There is some discrepancy on the c_p values at 200 °C resulted from methods based on ASTM E1269 standard with respect to those derived from MDSC methods as shown in Fig. 4. The MDSC methods produce lower results at this temperature than those produced by ASTM E1269-based methods, independently of the temperature program used (dynamic or isotherm). At 200 °C, the dispersion between the MDSC results is extremely low. The reason of this is not clear, maybe the lower conductivity of the salt in the solid state has an effect on the c_p measurement, or maybe there is an endothermic process like a change on crystallinity at this temperature, or the proximity of the melting point (220°C). Even, it is not well-known which of the measured values is more accurate.

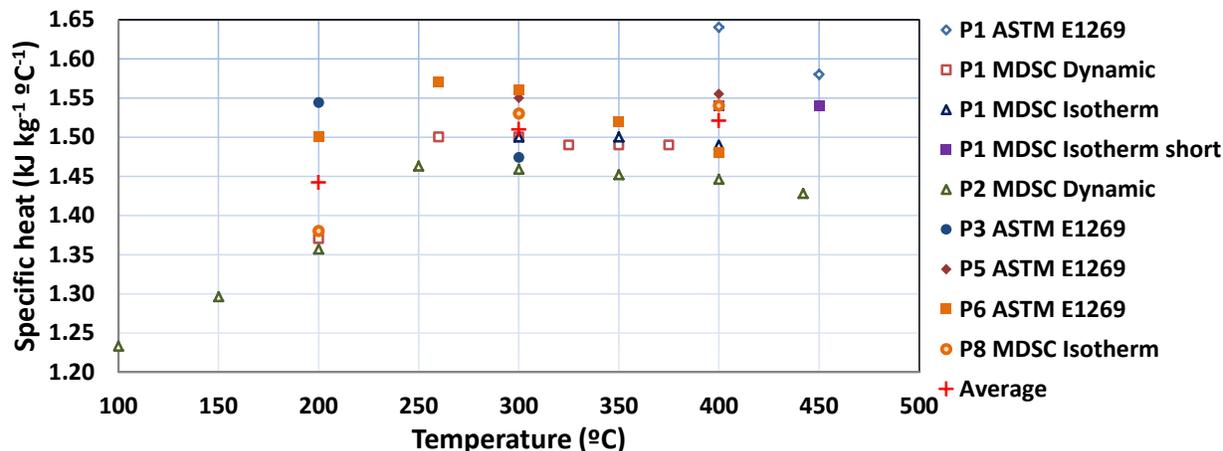


FIGURE 4. Results reported by the partners 1, 2, 3, 5, 6 and 8 on the measurement of c_p of SS.

In the liquid state, no conclusions can be deduced about the goodness of the methods used. The deviations are very low for almost all partners. Only Partner 1, using an ASTM E1269-based method gave higher c_p values at 400°C (1.64 kJ kg⁻¹ °C⁻¹) than the others. However, the measurements performed by Partner 1 following the ASTM E1269 standard are very dispersed (SD > 0.05 kJ kg⁻¹ °C⁻¹).

CONCLUSIONS

A RRT on the measurement of the c_p of SS was done involving 9 Partners. Eight of them used DSC devices. One of the partners used a calorimeter SETARAM C80. Each partner performed the c_p test according to their own criteria and routine. The usual standard ASTM E1269 employed to the c_p determination in a wide diversity of materials was shown to be adequate for the Solar Salt in terms of low results scattering. In addition the MDSC method developed by the DSC supplier TA Instruments, also demonstrated its suitability.

The next step on this research work will be the selection of the best measurement method with the standard ASTM E1269 and MDSC. All the partners will perform the tests under the same conditions to determine the c_p of the Solar Salt with a high level of accuracy.

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