

# Experimental challenges in differential scanning calorimetry for Hydrogen storage applications

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# Outline

**01** Introduction

**02** Metal Organic Frameworks

**03** Differential Scanning Calorimetry

**04** Standard vs MDSC

**05** Polystyrene

**06** Measurement procedure

**07** Effect of different factors on  $C_p$

**08** Conclusion

# Introduction

Significant increase in greenhouse gas emissions



**Global warming**

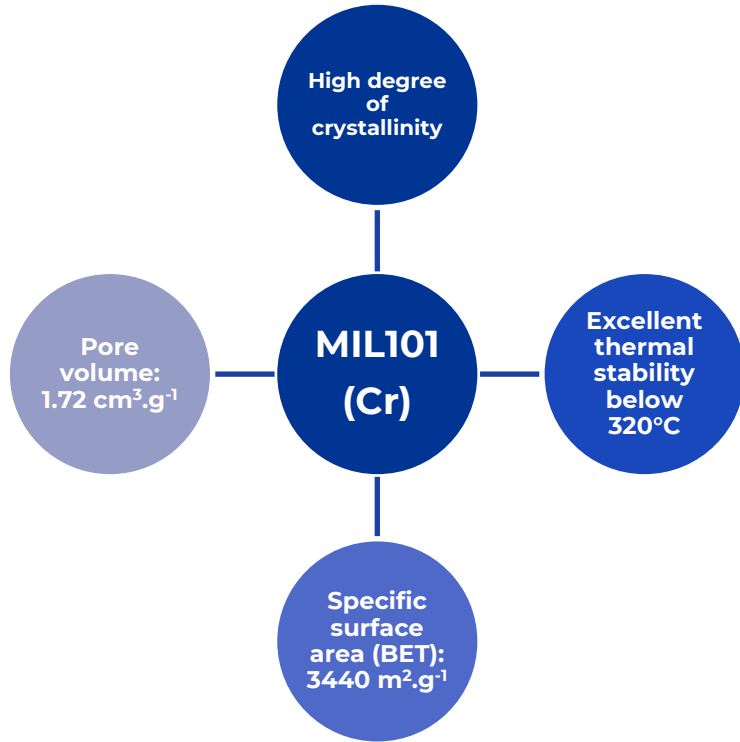
**Solution?**

Fossil fuels → Renewable resources

**HYDROGEN**



# Metal Organic Frameworks



Investigating their thermal properties (thermal conductivity, effusivity, diffusivity, heat capacity)



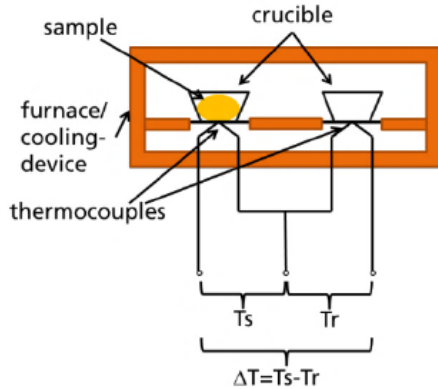
## Heat capacity

The amount of heat to be supplied to an object to produce a unit change in its temperature.

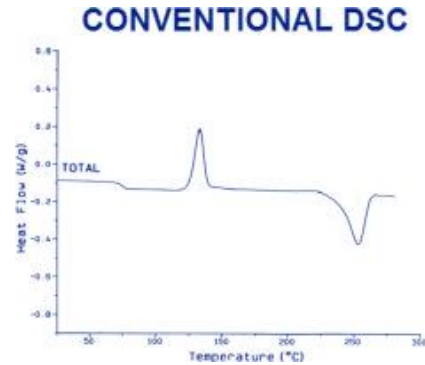
Formula:  $C_p = \left(\frac{\partial H}{\partial T}\right)_p \times \frac{1}{m}$

Unit: J.kg<sup>-1</sup>.K<sup>-1</sup>

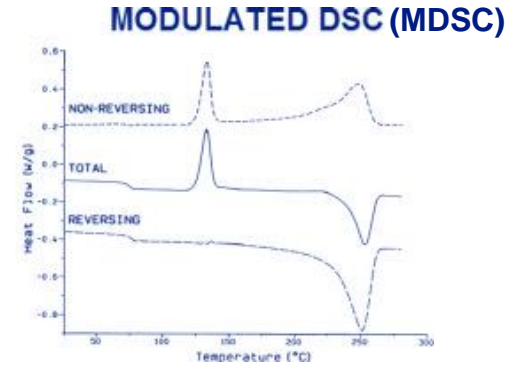
# Differential Scanning Calorimetry (DSC)



Schematic drawing of a DSC cell. [1]



Conventional heat flow signal vs MDSC (total heat flow, reversing heat flow, non-reversing heat flow) as a function of temperature. [2]



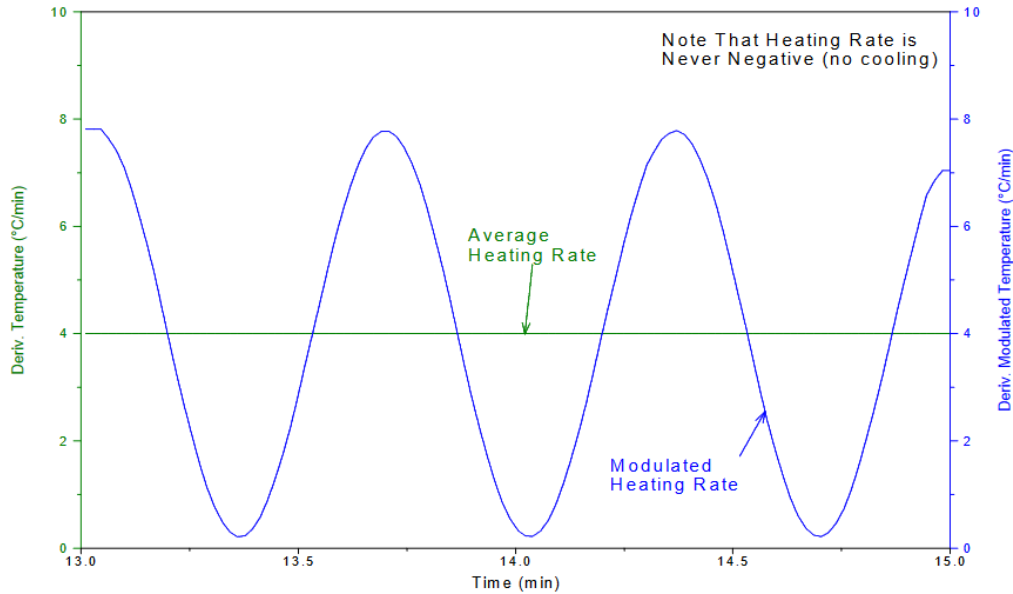
Determination of the heat capacity

LNCS cooling system

Ref: DSC Q1000 (Tzero™ technology  
DSC, TA instruments Inc., USA)

1. S. Gschwander et al. (2015). Standardization of PCM characterization via DSC. In *Proceedings of SHC 2015 International Conference on Solar Heating and Cooling for Buildings and Industry* (pp. 2-4).
2. M. Knopp et al. (2016). Recent advances and potential applications of modulated differential scanning calorimetry (mDSC) in drug development. *European Journal of Pharmaceutical Sciences*, 87, 164-173.

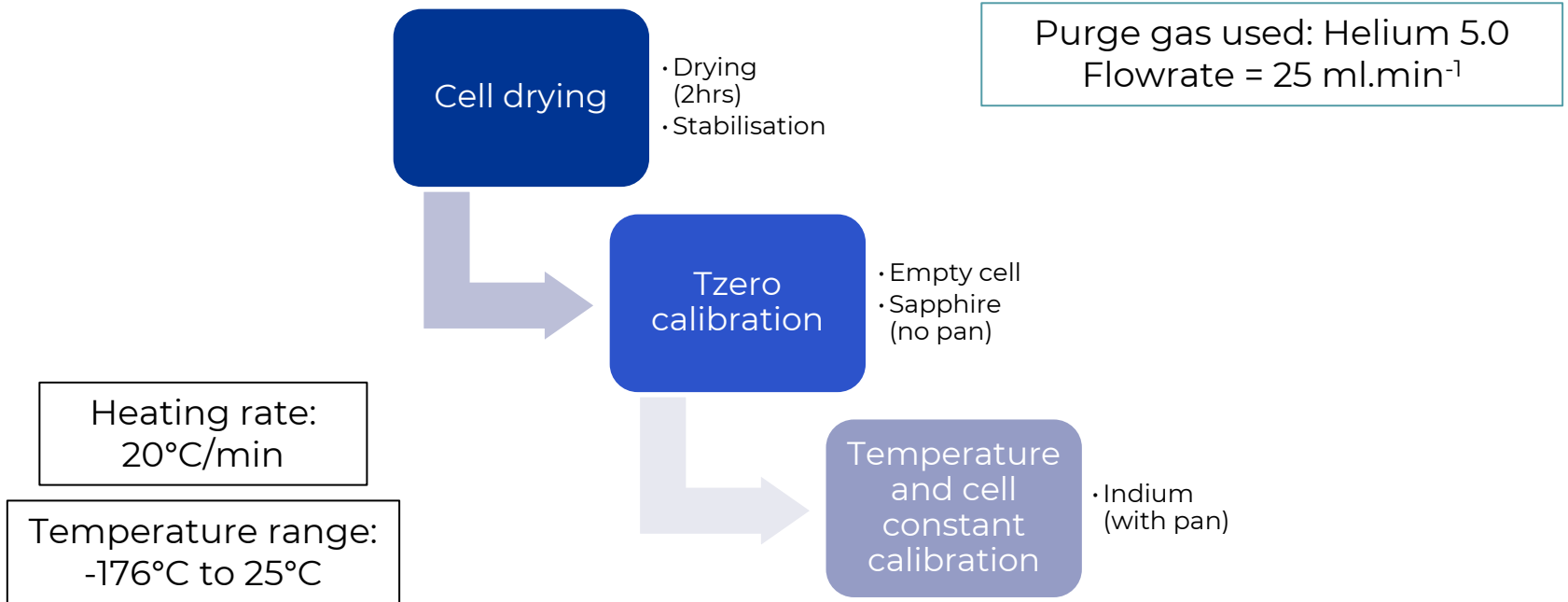
# Modulated DSC



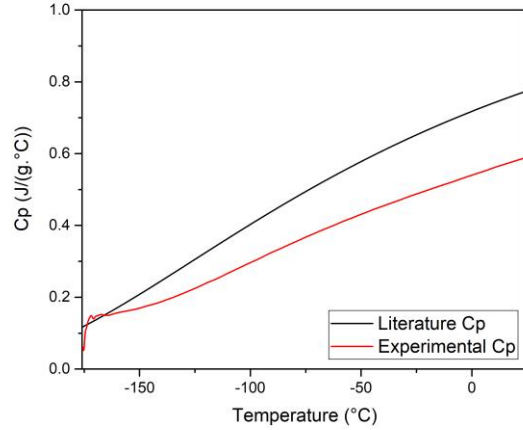
➡ A temperature modulation (TMDSC) is adapted.

➡ Accuracy of  $\pm 5\%$  against  $\pm 10\%$  for the classic DSC method.

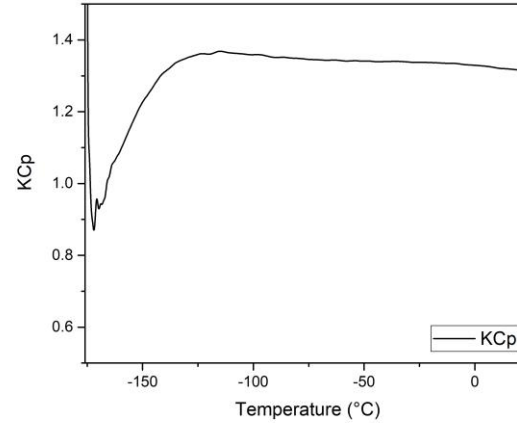
# DSC CALIBRATION



Experimental and literature Cp of sapphire as a function of temperature. Literature values from Ditmars et al. (1982)



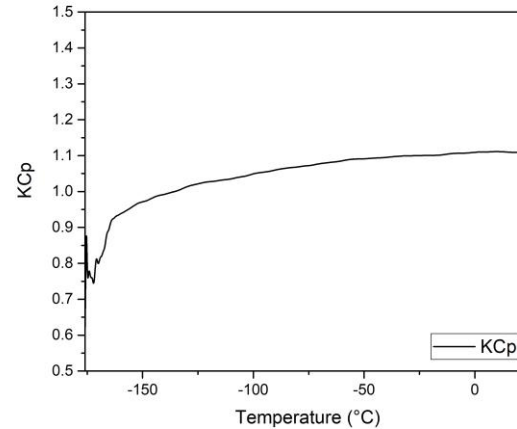
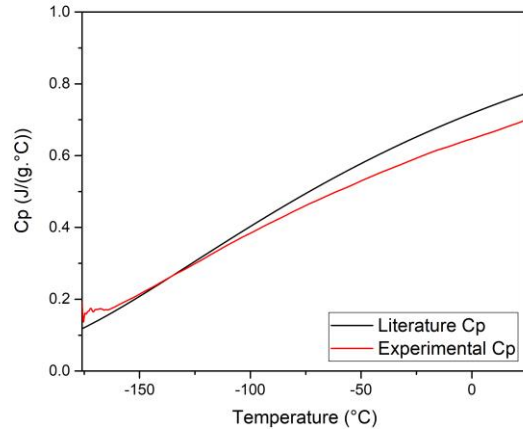
KCp of sapphire as a function of temperature



$$KC_p = \frac{C_p(\text{literature})}{C_p(\text{experimental})}$$

Old calibration procedure

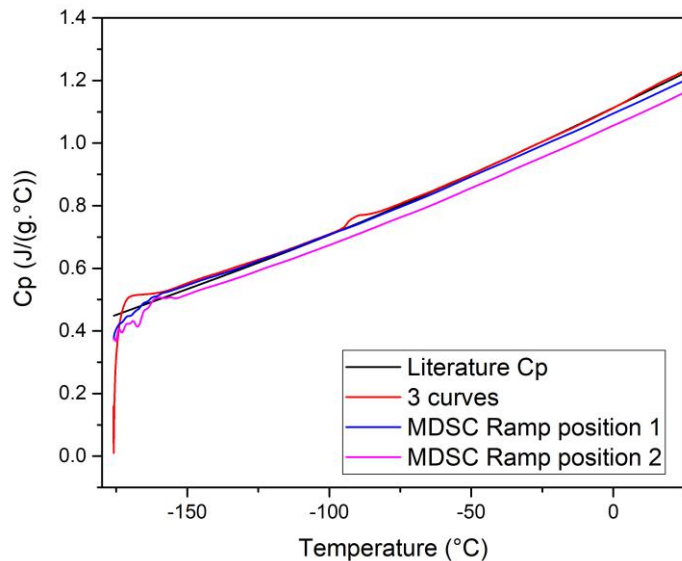
New calibration procedure





# Polystyrene (NIST705a)

$m = 18.69 \text{ mg}$



Literature (Chang and Bestul, 1968) and experimental Cp of Polystyrene NIST®SRM®705a as a function of temperature

## Standard DSC

### 3 curves method

(same reference pan for all tests with the same mass)

- Empty pan vs reference
- Sapphire vs reference
- Sample vs reference

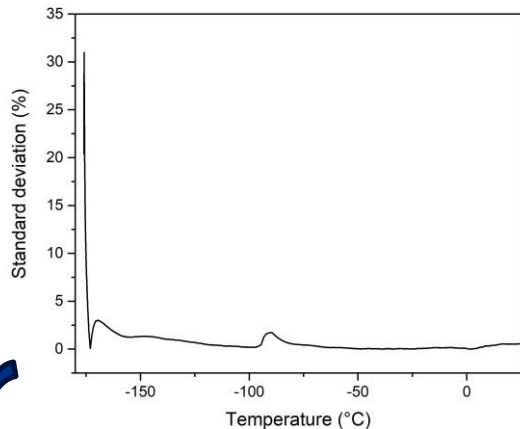
Ramp from  $-176^{\circ}\text{C}$  to  $25^{\circ}\text{C}$   
Heating rate:  $20^{\circ}\text{C}/\text{min}$

## Modulated DSC

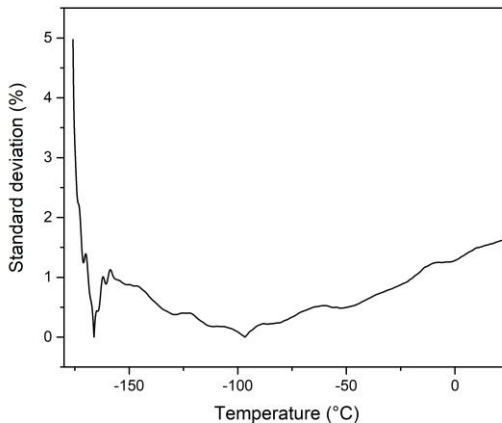
Ramp ➤ Sample vs reference

Ramp from  $-176^{\circ}\text{C}$  to  $25^{\circ}\text{C}$   
Heating rate:  $4^{\circ}\text{C}/\text{min}$

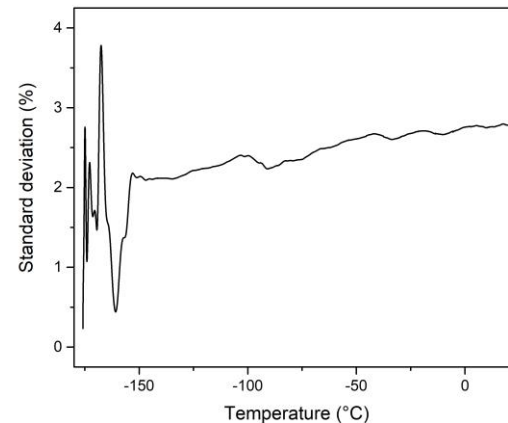
### Standard vs literature



### MDSC vs literature



### Position



**Beginning of the experiment  
→ Standard deviation ~ 30%**

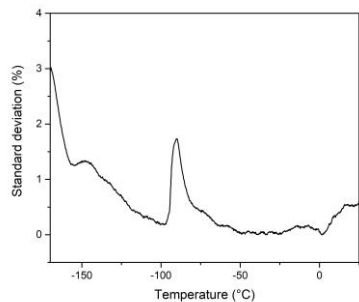
**Beginning of the experiment  
→ Standard deviation ~ 5%**

**Standard deviation < 4%**

**After → Standard deviation < 2%**

$$\text{Standard deviation} = \sqrt{\frac{1}{n-1} \sum_{i=1}^n (x_i - \bar{x})^2}$$

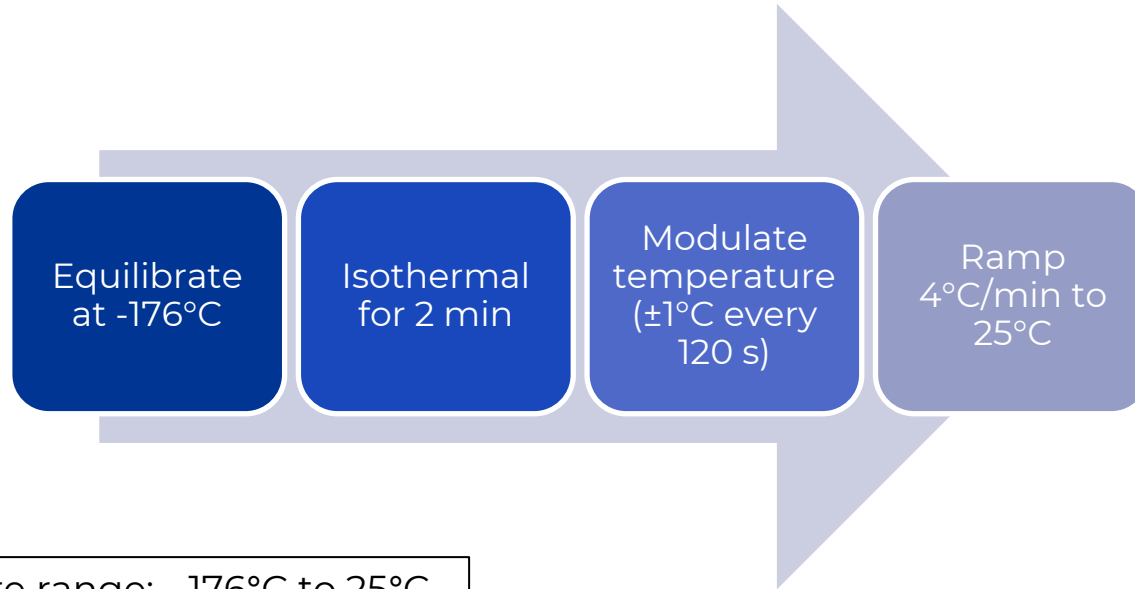
**➡ MDSC gives more accurate results than 3 curves**



**Standard deviation < 3%**

# Measurement procedure

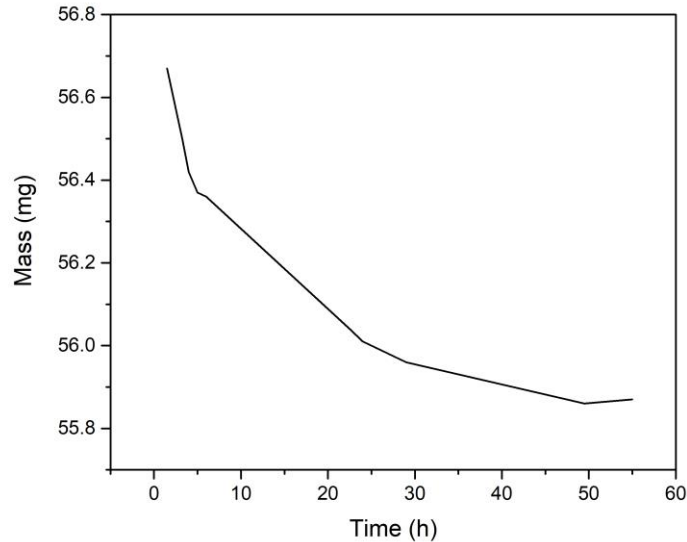
Purge gas used: Helium 5.0 / Flowrate = 25 ml.min<sup>-1</sup>



Temperature range: -176°C to 25°C

# Drying test for MIL101Cr

Pan mass = 42.32 mg

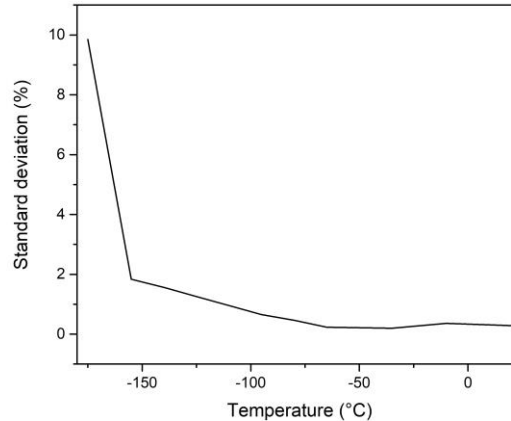
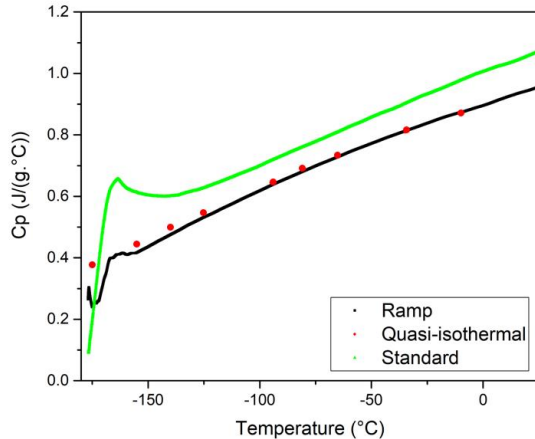


Sample mass:  
14.38 mg → 13.55 mg

- ➡ All samples were dried in an oven at 100°C
- ➡ After 48h, the sample mass becomes stable

# Heat capacity measurements: Standard vs Modulated DSC (ramp/QI)

MIL101Cr  
m = 8.69 mg



**Ubove -160°C  
→ Standard deviation < 2%**

## Ramp

- Sample pan vs ref
- Ramp from -176°C to 25°C
- Duration: 1h

## Quasi-isothermal (QI)

- Sample pan vs ref
- Equilibrate at each temperature
- Duration: 4h

**Aluminum Hermetic sealed pans**

- ➡ Modulated DSC is more accurate than Standard DSC
- ➡ Quasi isothermal and ramp methods give the same results

# Effect of different factors on heat capacity

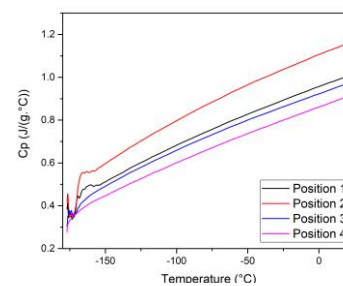
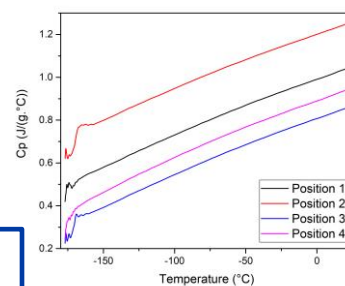
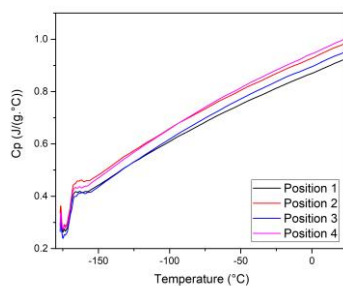
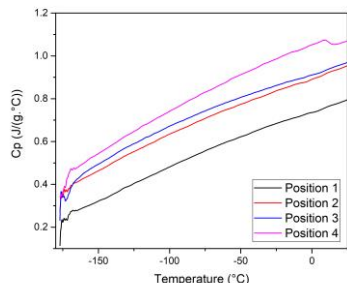
## Hermetic pans

m = 5.34 mg

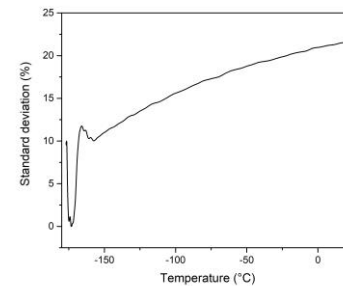
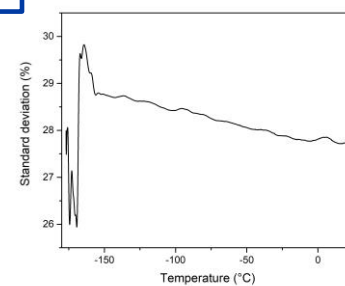
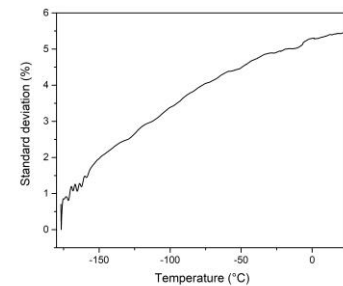
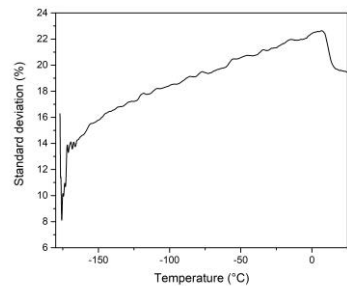
m = 8.69 mg

m = 12.14 mg

m = 16.63 mg



Position changing



Standard deviation < 24%

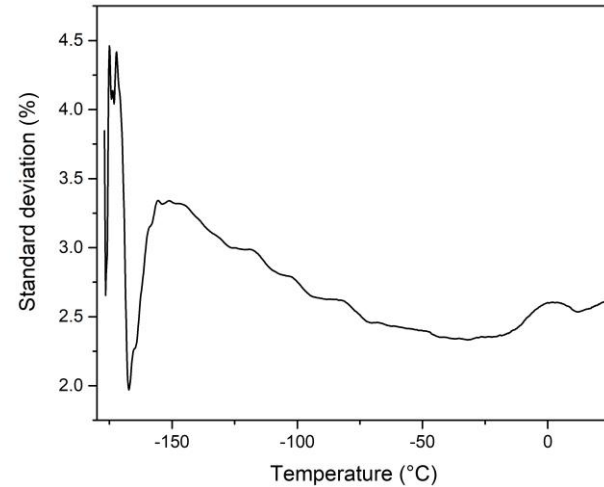
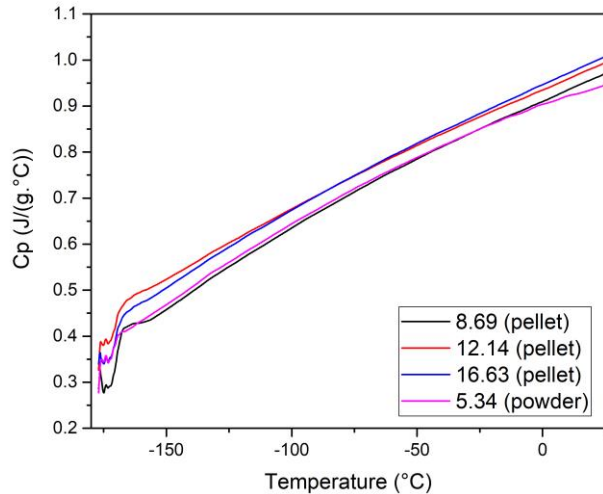
Standard deviation < 5.5%

Standard deviation < 30%

Standard deviation < 23%

# Effect of different factors on heat capacity

## Hermetic pans



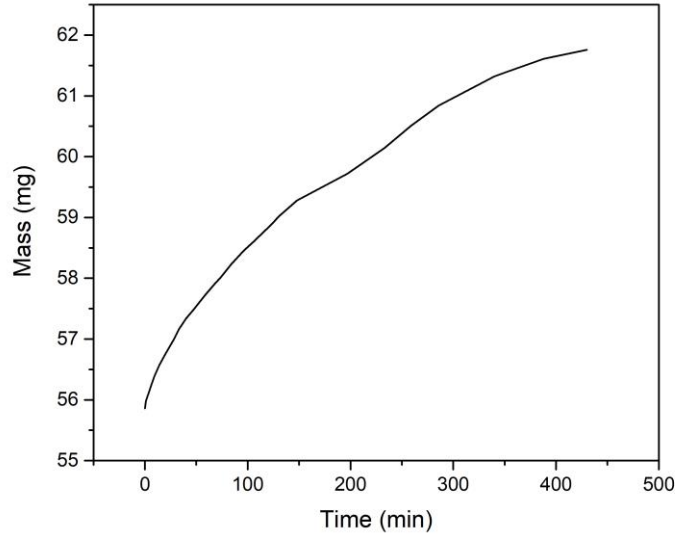
**Standard deviation < 4.5%**

Compaction rate has no influence on  $C_p$  results

After calculating the average  $C_p$  of each mass  
→ Same results with minor deviation

# Humidity test for MIL101Cr

Pan mass = 42.32 mg



Sample mass:  
13.55 mg → 19.48 mg

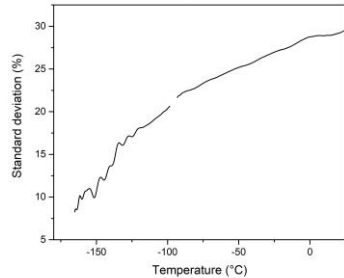
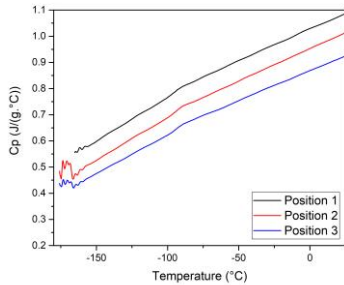
➡ MIL101Cr powders gain humidity in a matter of seconds



# Effect of different factors on heat capacity

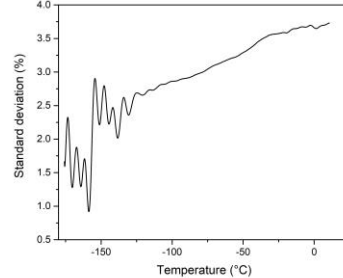
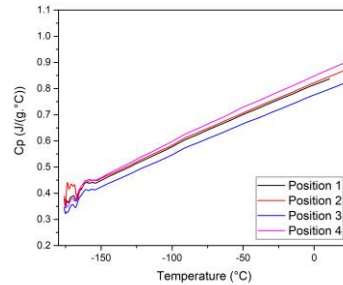
## Lid with pinhole pans

$m = 6.29 \text{ mg}$

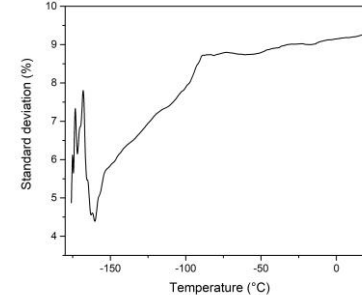
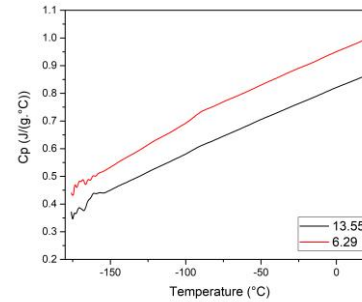


Standard deviation < 30%

$m = 13.55 \text{ mg}$



Standard deviation < 4%



Standard deviation < 10%

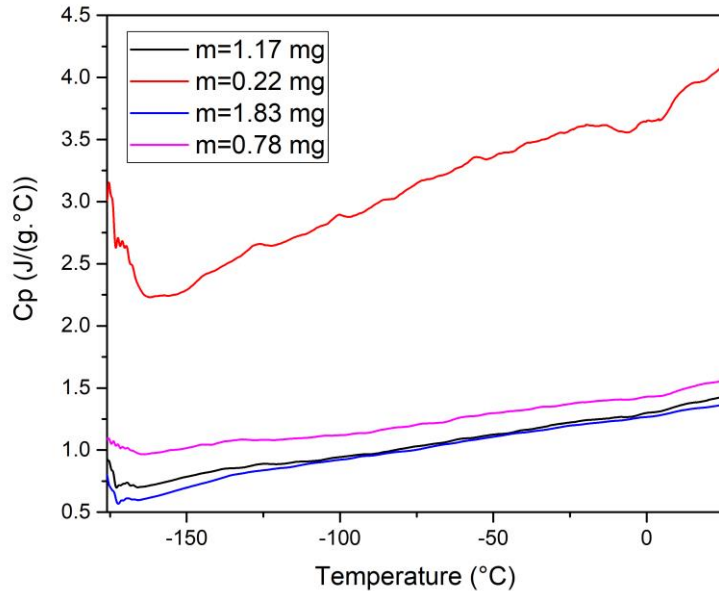
Pans with pinhole have a better stability at the beginning of the experiment

Higher dispersion for lower mass

With a sufficient mass quantity inside the pan  
→ Heat capacity results are more stable

# Effect of different factors on heat capacity

## Reduced Graphene Oxide



Heat capacity of reduced Graphene Oxide as a function of temperature

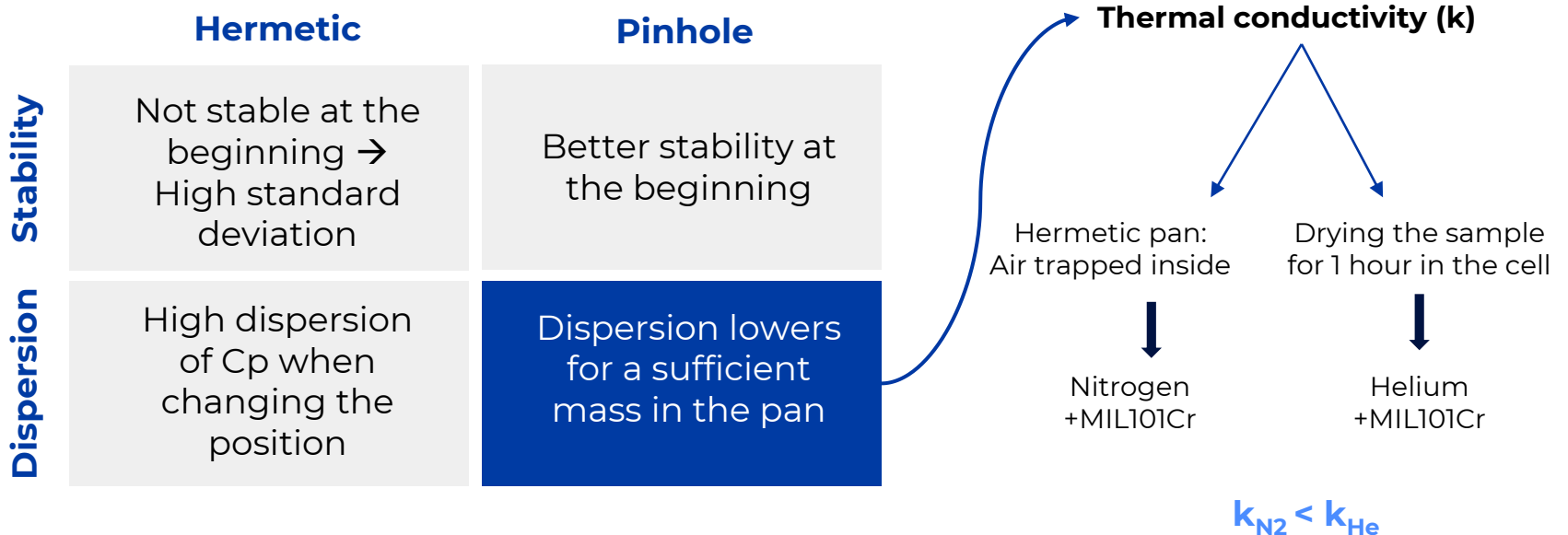
**A sufficient quantity inside the pan is needed to stabilize  $C_p$  results**



This quantity depends on the material

# Effect of different factors on heat capacity

## Pans used



# Conclusion

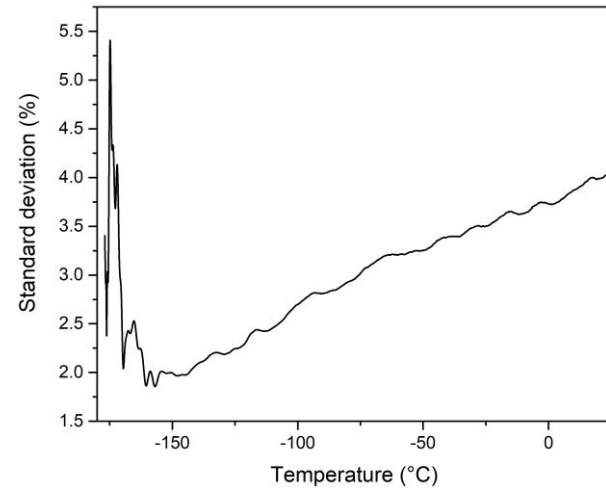
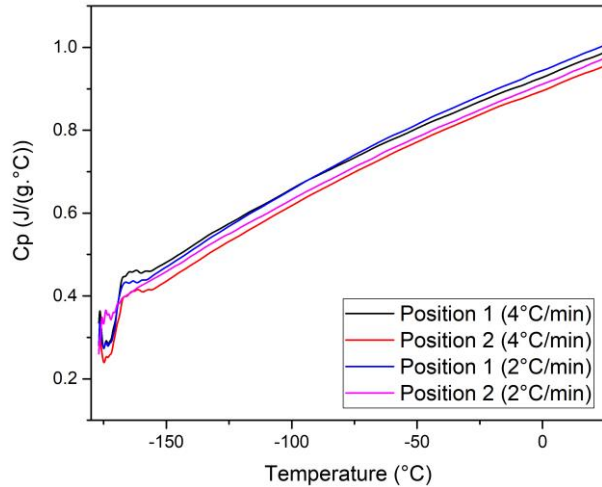
- A DSC Q1000 with a Tzero technology was used to determine heat capacity of MIL101Cr at low temperatures.
- The new calibration procedure enhanced the accuracy of the results.
- Modulated DSC gives better results than standard DSC specifically at the beginning of the experiment.
- Heat capacity is affected by the pan positioning with both hermetic and pinhole pans, however for pinhole pans the dispersion decreases after a sufficient mass inside the pan.
- Pan positioning could be related to the thermal conductivity of the material and gas surrounding it.

**THANK YOU FOR YOUR ATTENTION**

# Effect of different factors on heat capacity

## Heating rate

MIL101Cr  
m = 8.69 mg



Both heating rates give Cp results with good sensitivity

Standard deviation < 5.5%

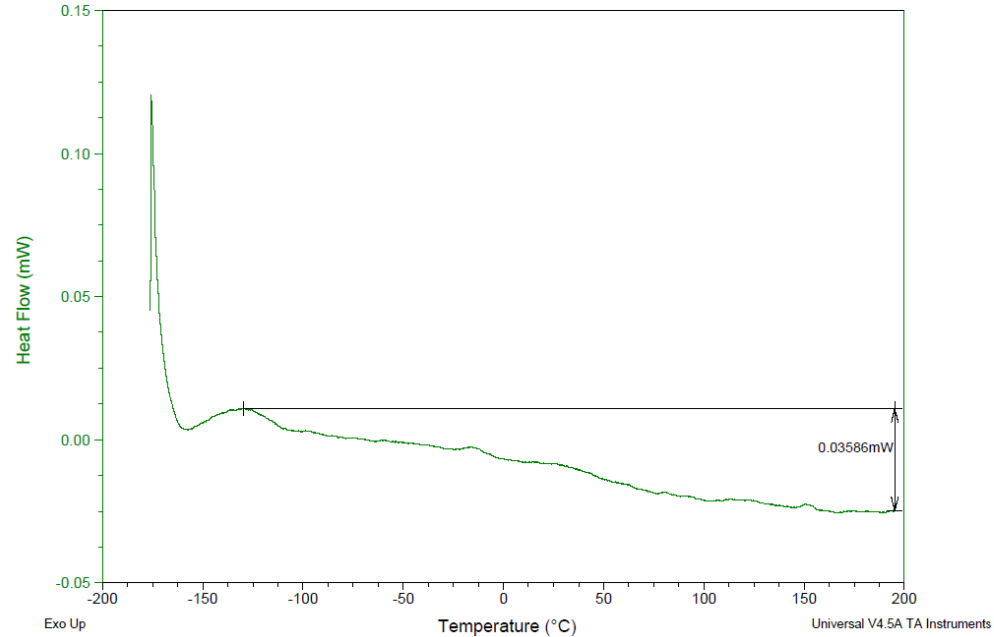
# Baseline

Sample: none  
Size: 0.0000 mg

DSC

File: ligne de base.001

Run Date: 17-Apr-2024 09:28  
Instrument: DSC Q2000 V24.11 Build 124

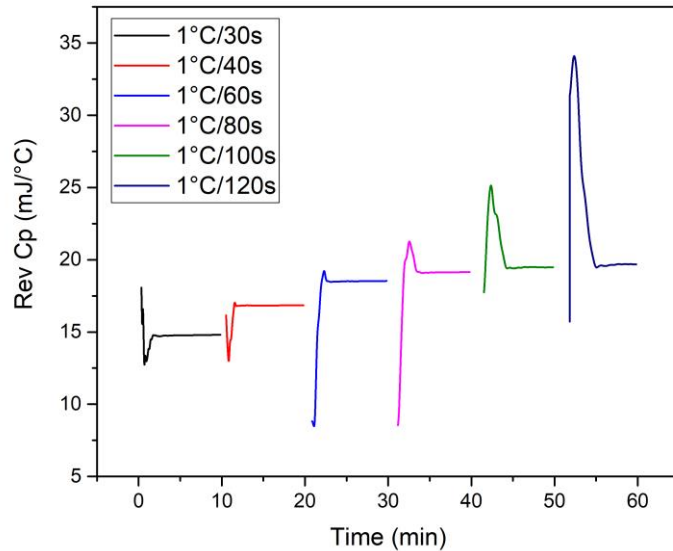


**Heat flow deviation should be less than 100  $\mu$ W**

**In our case  $\Rightarrow$  Heat flow deviation = 35.86  $\mu$ W**

# Temperature Modulation

Polystyrene  
m=18.69 mg



- Experiment was performed at 25°C
- Fixed temperature modulation amplitude of  $\pm 1^\circ\text{C}$
- Temperature modulation period was increased in ten minutes steps

From 30 to 60s → Rev Cp ↑ by 20%

From 60 to 100s → Rev Cp ↑ by 5%

From 100 to 120s → Rev Cp ↑ by 10%

**AFCAT**

