

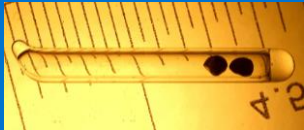


Industrial Examples of Misuse of DSC Crucibles for Thermal Stability Hazard Evaluation

Min Sheng, Ph.D., P.E.

Reactive Chemicals Technical Leader at Corteva AgriScience

DSC Crucibles: High Pressure vs. Al pan

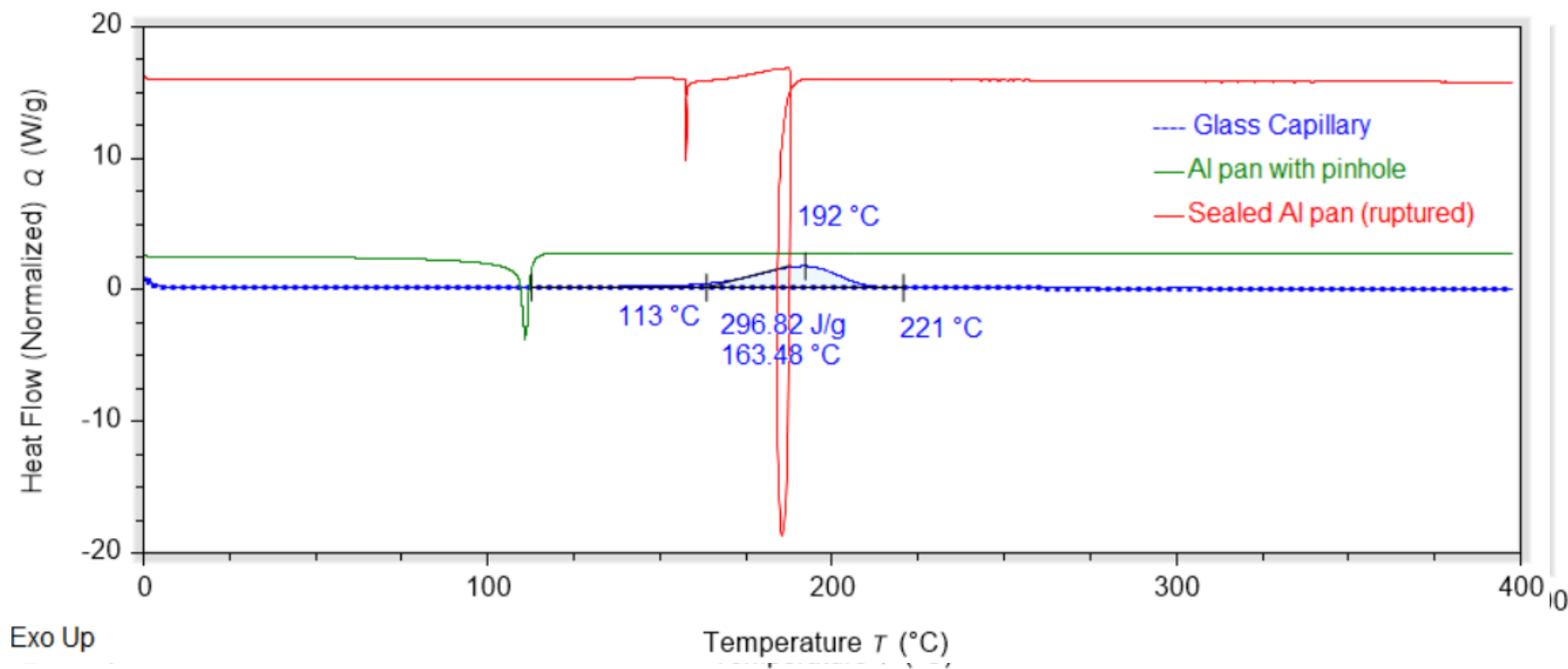
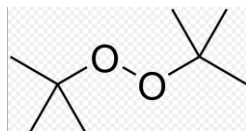
Inert High Pressure (HP) DSC crucible is recommended by ASTM E537 for thermal stability hazard evaluation

Sample container			
container material	HP DSC Crucible: Sealed glass capillary (cap.)	Aluminum pan with pinhole	Sealed Aluminum pan
Rated max pressure	3000 psig		30 psig

1. Aluminum metal reacts with oxidizer, acid, strong base, halogenated organic (R-X) and others
2. Al pan with pinhole:
 - a. Endotherm effect from liquid vaporization: For a sample containing 20% water, endotherm from water vaporization is 451 J/g (water heat of vaporization: 2256.4 J/g)
 - b. After leaked, sample composition changes or even no sample is left
3. Sealed Al Pan:
 - a. Rupture: Most organic solvents have a boiling point < 200°C + Ideal gas law
 - b. Al metal gets weak at high temperature

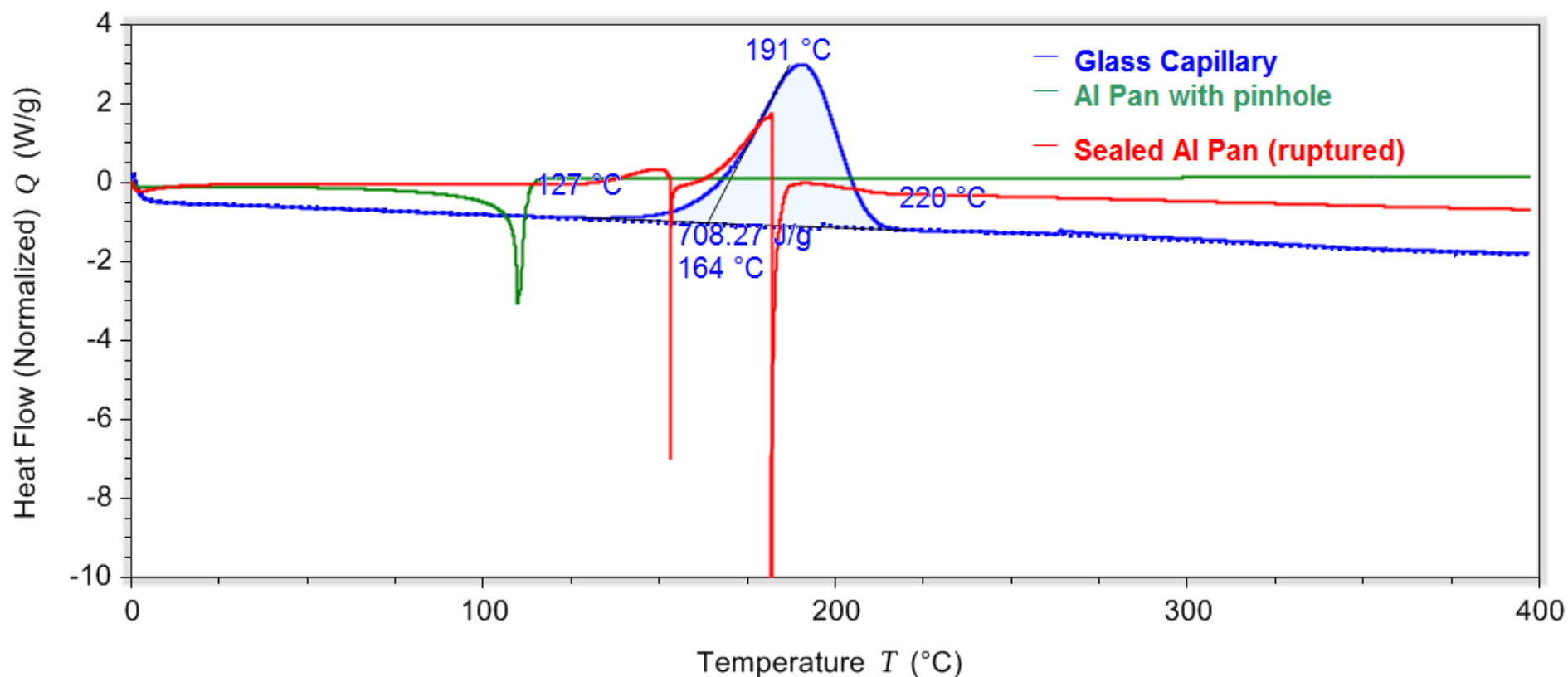
DSC Crucibles: High Pressure vs. Al pan

DSC result of 20% di-tert-butyl-peroxide in toluene with three sample containers



DSC Crucibles: High Pressure vs. Al pan

DSC result of 50% di-tert-butyl-peroxide in toluene with three sample containers



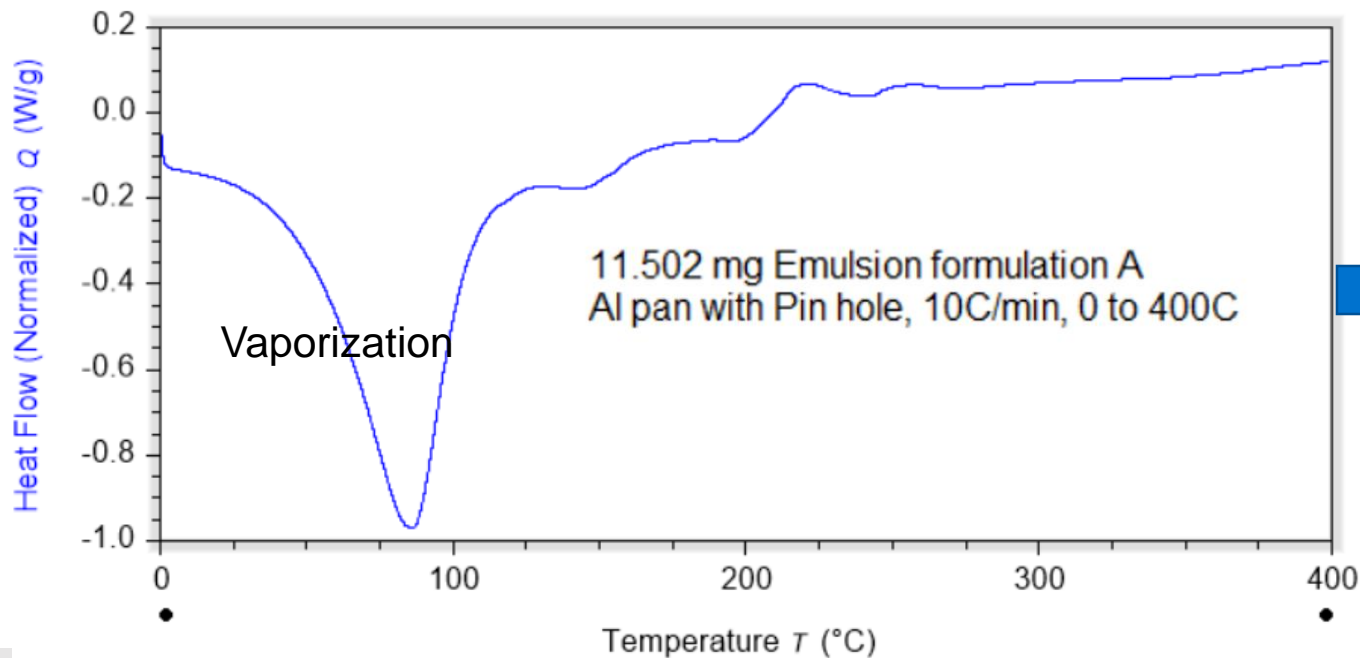
Example A of Misuse of DSC pan: liquid sample

Final formulation product, aqueous capsules emulsion

Preparing for a trial production in 7,000 gallon vessel in a month

Questionable DSC data identified in final process safety review

Redo DSC within a flame sealed glass ampoule



➡ No Thermal Stability Concern

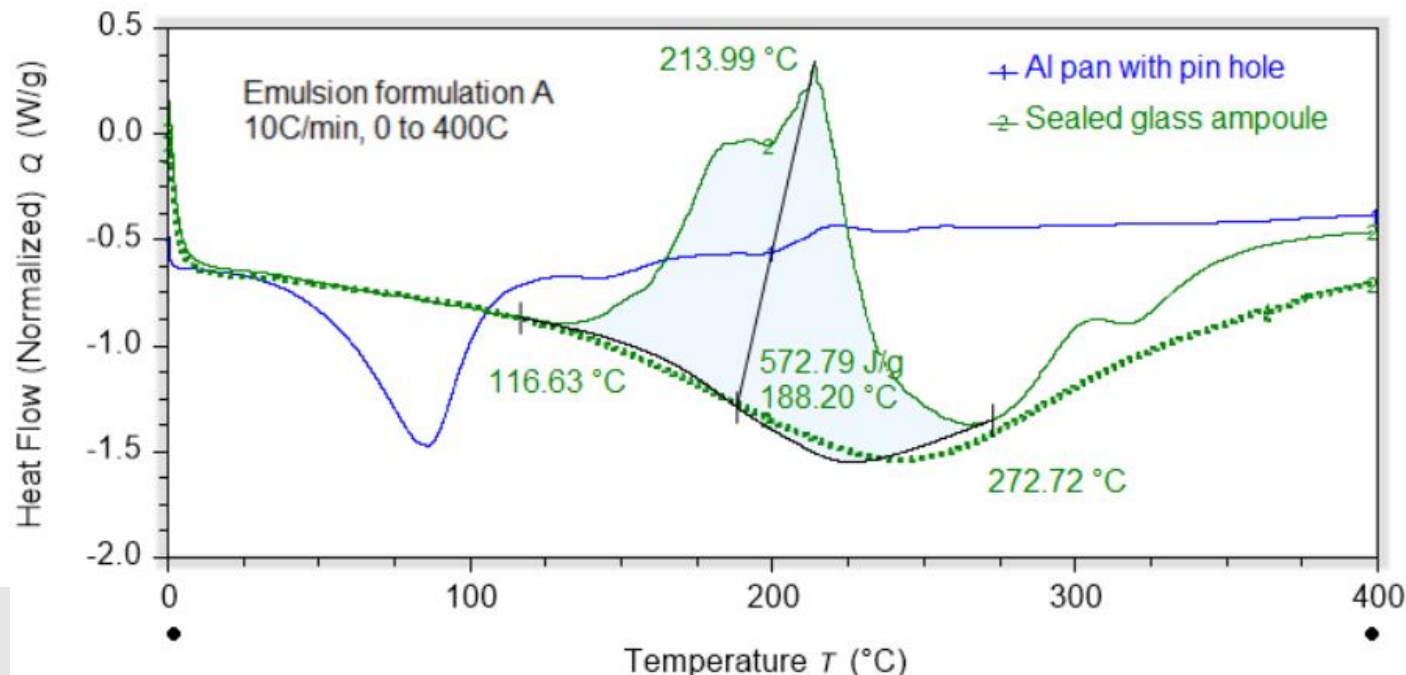
Example A of Misuse of DSC pan: liquid sample

Will heat to 75°C with low pressure steam for capsule shell formation

Runaway scenarios identified: loss control of steam (135C)

Followed with an ARC test: onset of 110°C and heat of -563J/g

Kinetic modeling based on DSC and ARC data, estimate max heat rate and max pressure rate for reactive relief sizing



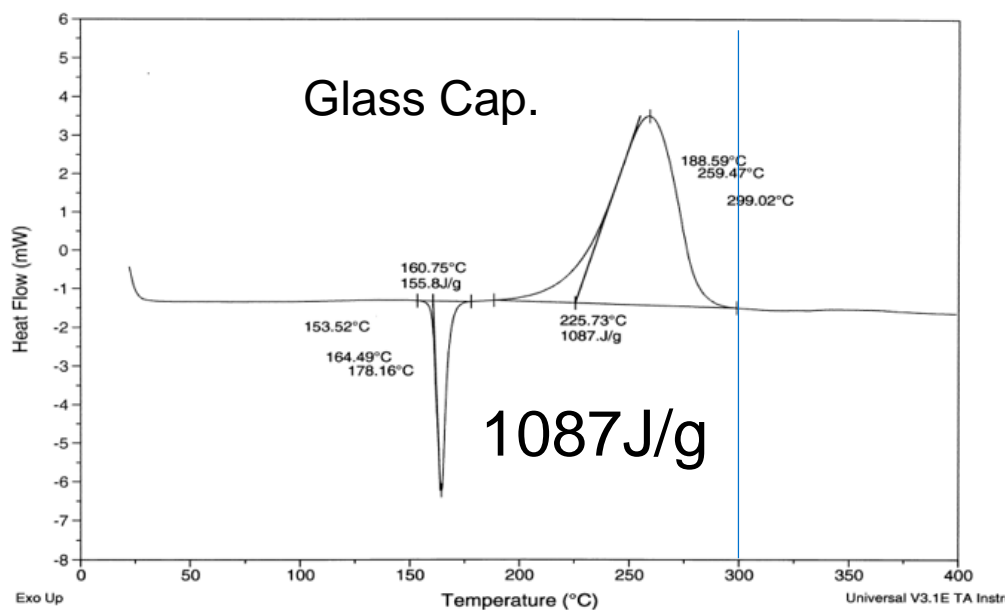
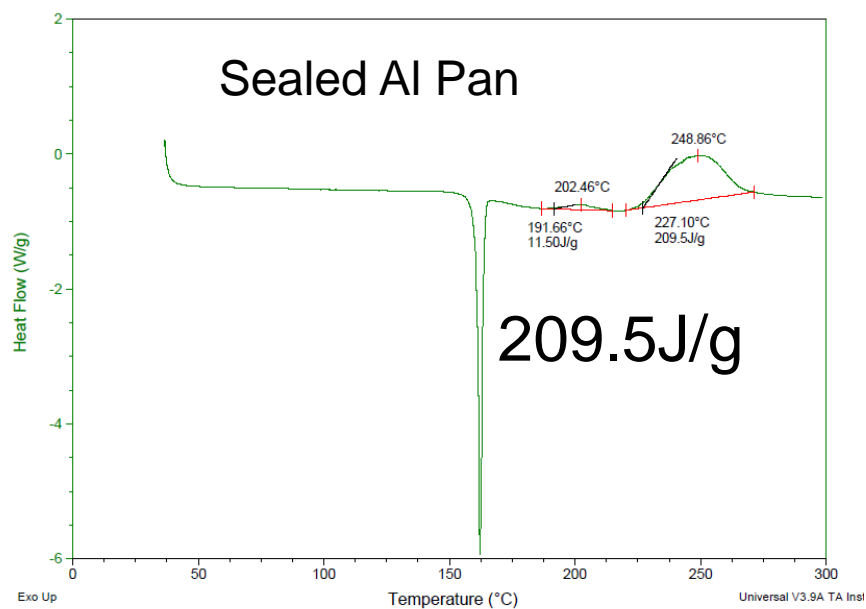
Example B of Misuse of DSC pan: solid sample

Sometime, “rupture” of a sealed pan is not obvious.

Chemical B: Solid, melts at 160°C and boils at 357°C

In a R&D safety review, low thermal runaway risk based on sealed Al pan DSC result.

Redo DSC within a flame sealed glass capillary, move to high risk



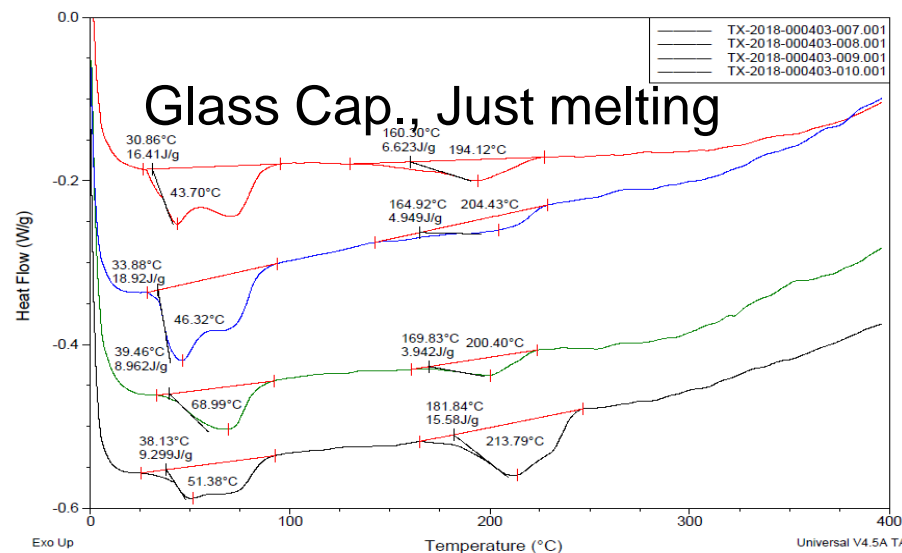
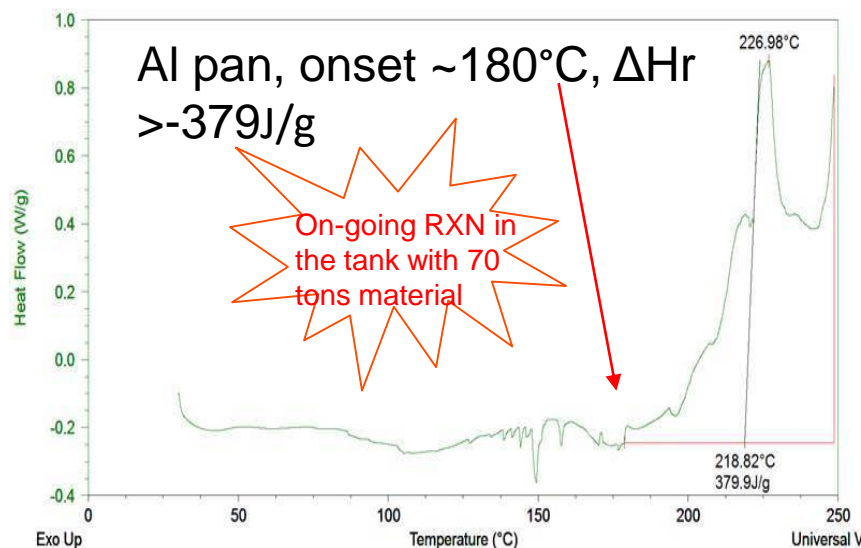
Example C of Misuse of DSC pan: reaction w/. Al

Aluminum metal reacts with a lot of Chemicals: oxidizer, acid, strong base, halogenated organic (R-X)

- Over 70 tons highly chlorinated waste material was stored in a tank at 200°C with an outlet pipeline plugging issue.
- A repeatable exotherm event above ~180° C on DSC within Al pan
- Multiple DSC in Glass capillary confirmed No reaction, but melting

Sample: T502A_010218_3

DSC File: C:\Users\lu395347\Desktop\lvonne\T-502A_010218_3

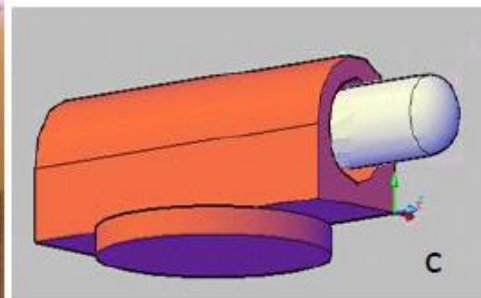
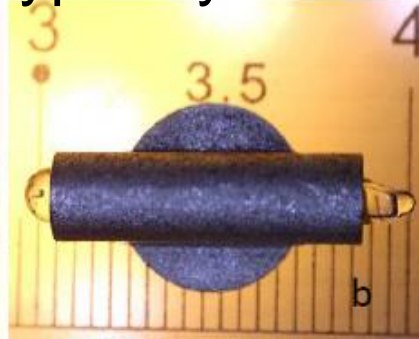
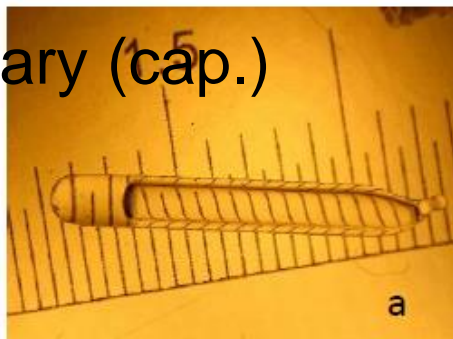


Inert High Pressure DSC crucible

Three such DSC crucibles we typically use:

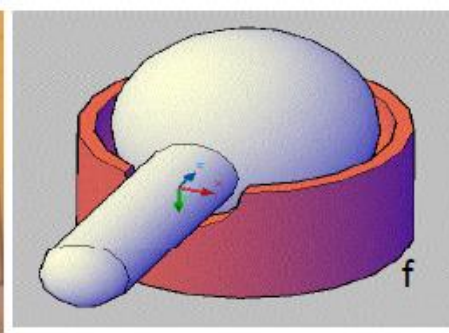
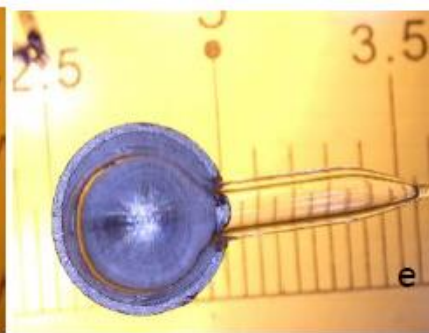
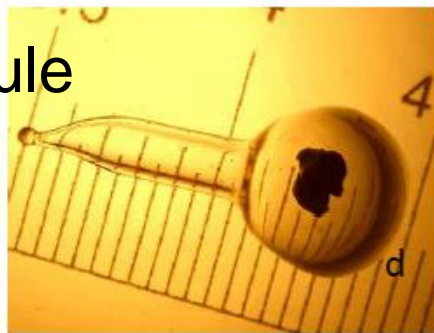
1. Glass capillary (cap.)

~5 μ L, 3000 psi
~1mg sample
\$0.17 per each



2. Glass ampoule (amp.)

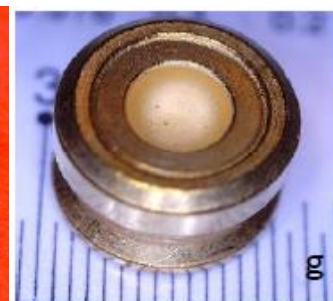
~25 μ L, 1000 psi
~1mg sample
\$5.61 per each



3. Gold-plated HP Pan (GP)

20 μ L, 3000 psi,
~3mg sample
\$33 per each

<https://store.fauske.com/dsc-m20.html>

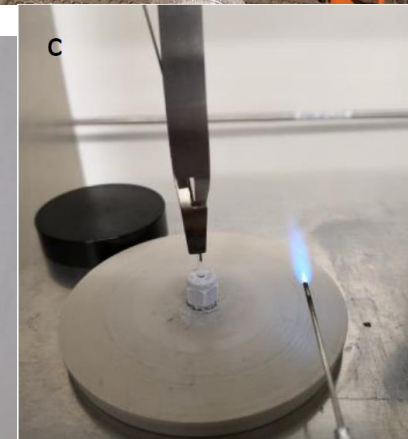
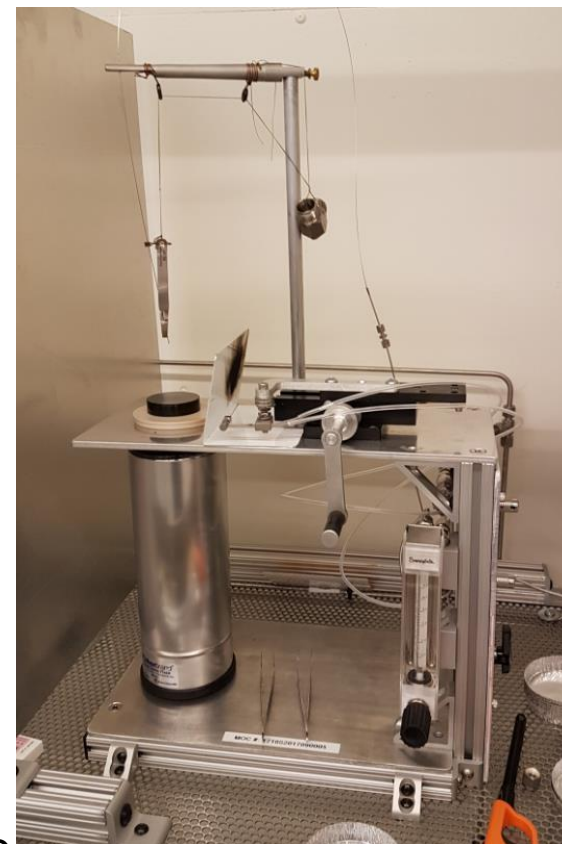


Inert High Pressure DSC crucible

Standard RC DSC method:

- 1, Run Indium check weekly
- 2, Sample pan: glass capillary_N2 or glass ampoule_Air
- 3, Flame (propane + oxygen) sealing with liquid Nitrogen cooling
- 4, always check sealing under microscope
- 5, 0 to 400C, 10C/min
- 6, Rescan the same sample
- 7, Always check the mass loss after DSC run. Sample mass loss greater than 10% will be considered as rupture and the data will be discarded.

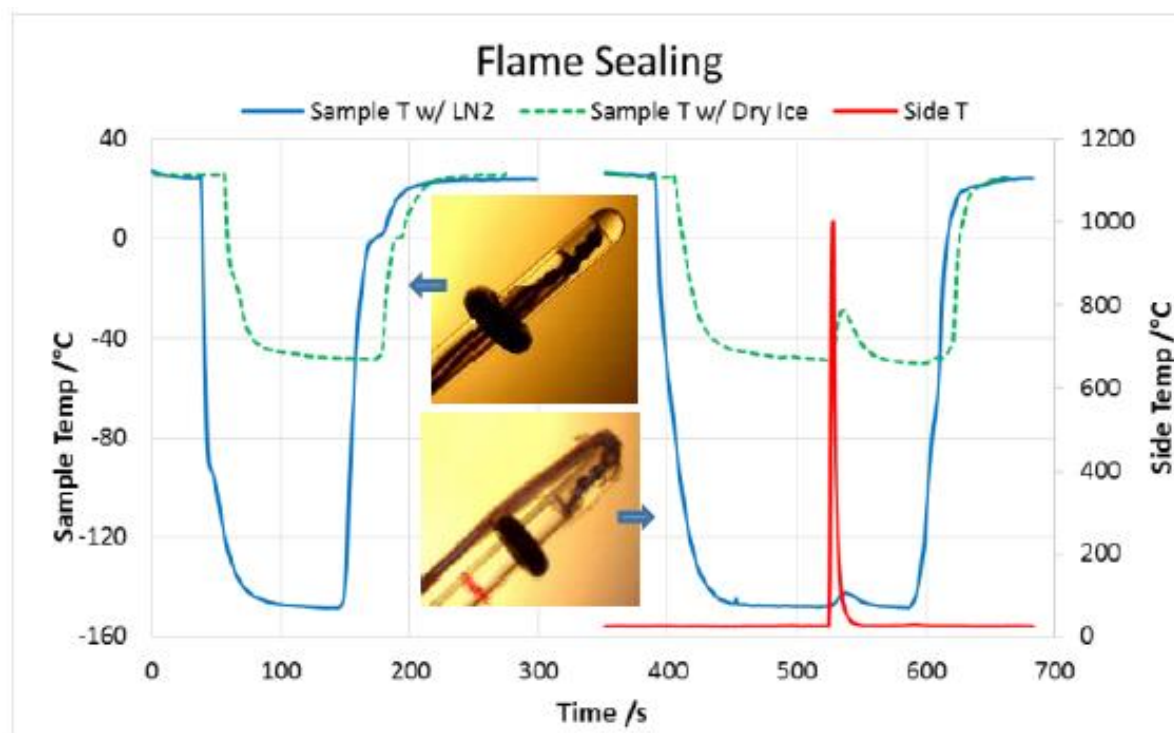
Min Sheng, et. al., Practical Use of Differential Scanning Calorimetry (DSC) for Thermal Stability Hazard Evaluation, Org. Process Res. Dev., 2019, 23, 2200-2209



Inert High Pressure DSC crucible

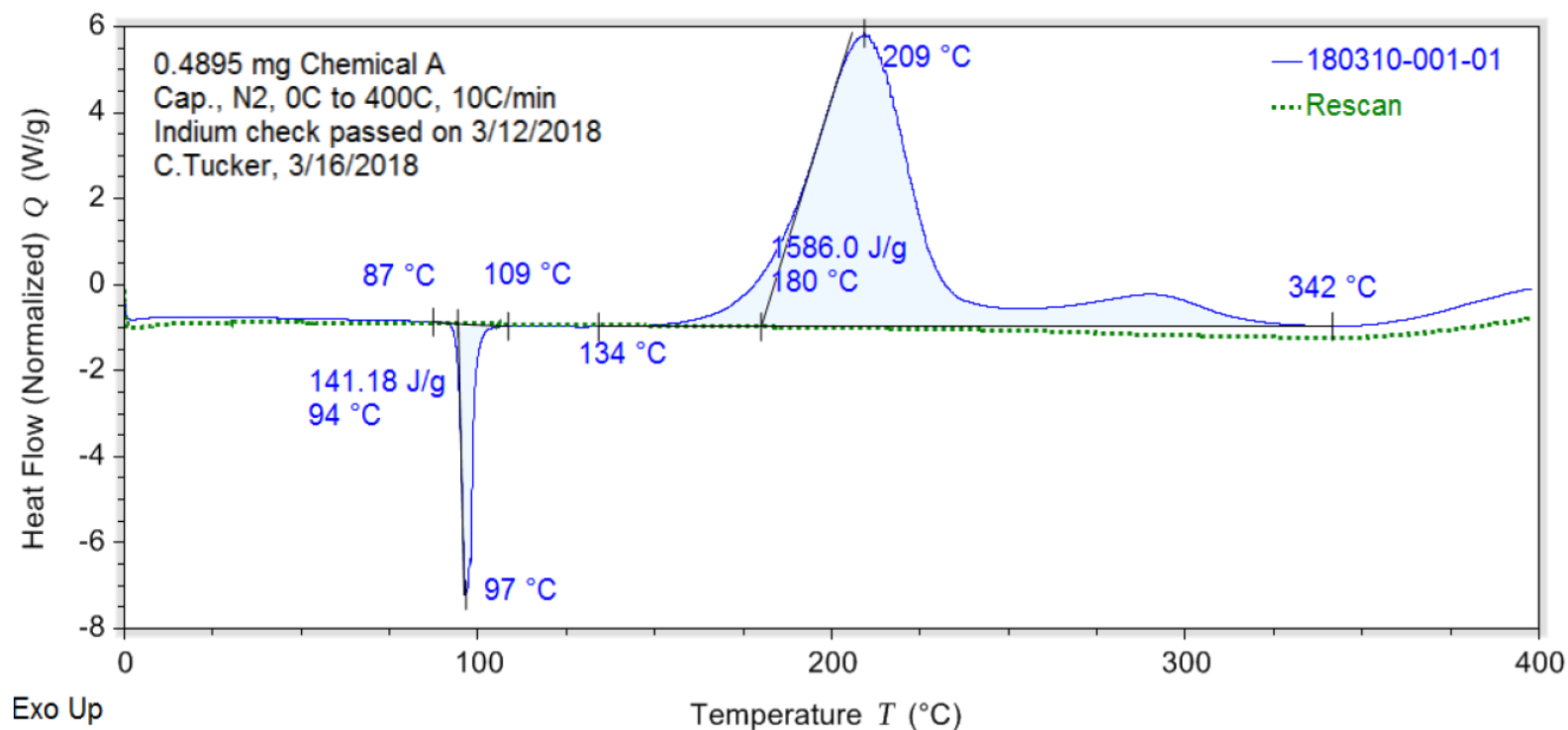
Overheat sample concern during flame sealing:

- Sample Temp increases from -147°C to -141°C during flame sealing for Liq. Nitrogen, -49°C to -29°C for dry ice/acetone
- Prevent liquid Oxygen formation (-183°C)



Inert High Pressure DSC crucible

Typical result of Standard RC DSC



First scan gives thermal activities, while the rescan serves as a reference for the baseline

Inert High Pressure DSC crucible

How to select?

Glass capillary (\$0.17) as Default for inert headspace (N₂);

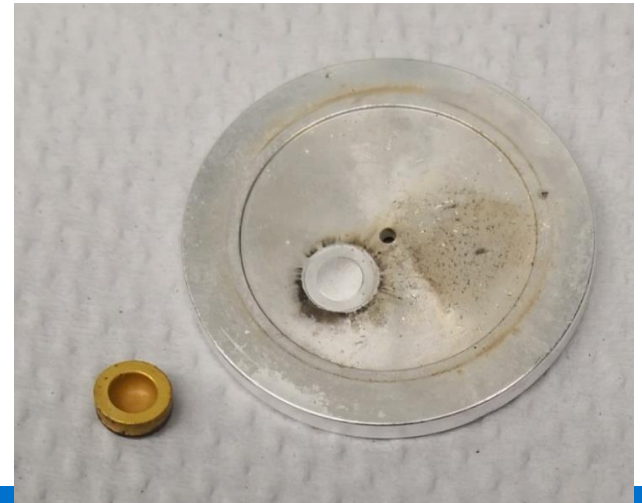
Glass ampoule (\$5.61) for Air headspace (oxidation reaction);

Cases to use GP (\$33): A. two parts needed to be combined; B. glass reactive chemicals. (A Risk: rupture can cause more damage to DSC)

Sample Description	Test	Endo or Exo	Detecte d onset, °C	Peak °C	End °C	Heat J/g	
10% NaOH	DSC in Cap_N2	Exo	75	180	220	-144	
50% NaOH	DSC in Amp_Air	Exo	125	200	268	-569	Additional endo above 295°C
50% KOH	DSC in Cap_N2	Exo	138	221	287	-406	Additional endo above 314°C
50% NaOH	DSC in GP_Air	No Exo					Endo above 251°C
50% KOH	DSC in GP_Air	No Exo					Endo above 301°C

Inert High Pressure DSC crucible

- Ruptures can potentially damage the Instrument, so Do NOT overload tested sample
- More damage from a rupture of metal GP than a glass pan



Conclusion: DSC data quality matters! DSC crucibles matter!!

ACKNOWLEDGMENTS to Reactive Chemicals Group in The Dow Chemical Company (our heritage company) for sharing of testing methodologies and historical data

More information can be found in our DSC paper: Practical Use of Differential Scanning Calorimetry (DSC) for Thermal Stability Hazard Evaluation

Questions?

- We are hiring an additional Reactive Chemicals SME
- Please submit your research to [ACS Chemical Health & Safety](#) (new ACS journal)