

# Isothermal Microcalorimetry: A Versatile Tool for Real-Time Thermodynamic Insights

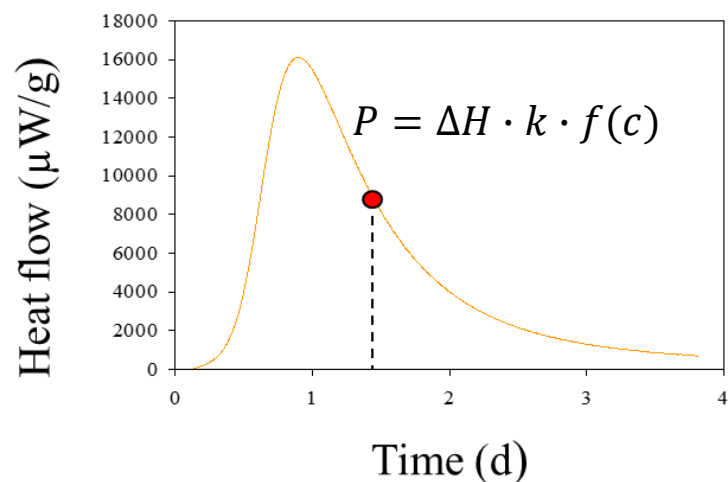
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'Credits shall be given to Authors for any use of this materials !'

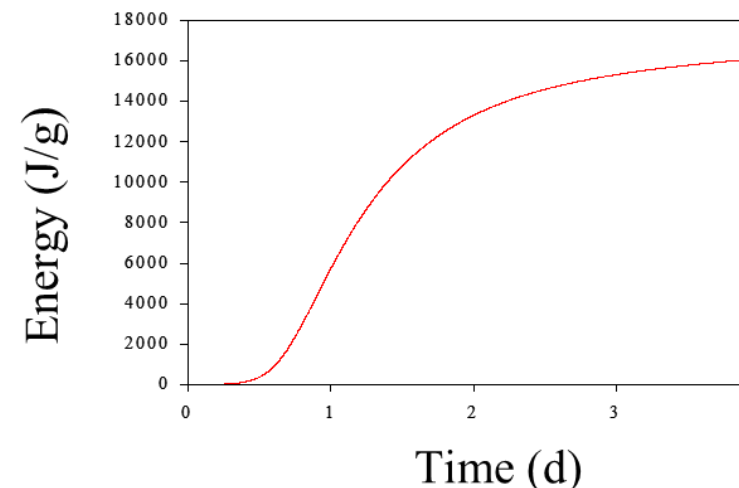
*Virtually all chemical and physical processes result in either heat production or heat consumption.*

- A heat flow calorimeter measures **heat flow**:  $dQ/dt$
- Heat flow is directly related to the **heat production** (or **consumption**) rate in a sample:  $P$
- $P$  and  $dQ/dt$  are measured in  $W = J/s$
- A microcalorimeter is a calorimeter that can measure heat production in the  $\mu W$  range or lower

*The heat production rate is directly related to the rate of reaction*



*Total heat produced is related to the extent of the reaction*



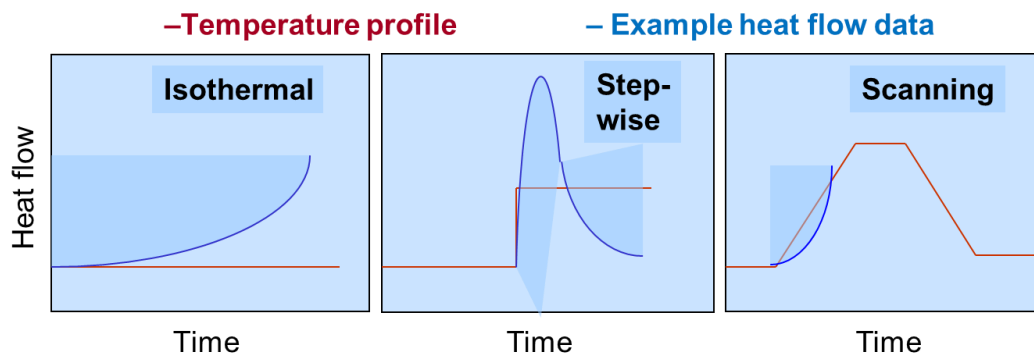
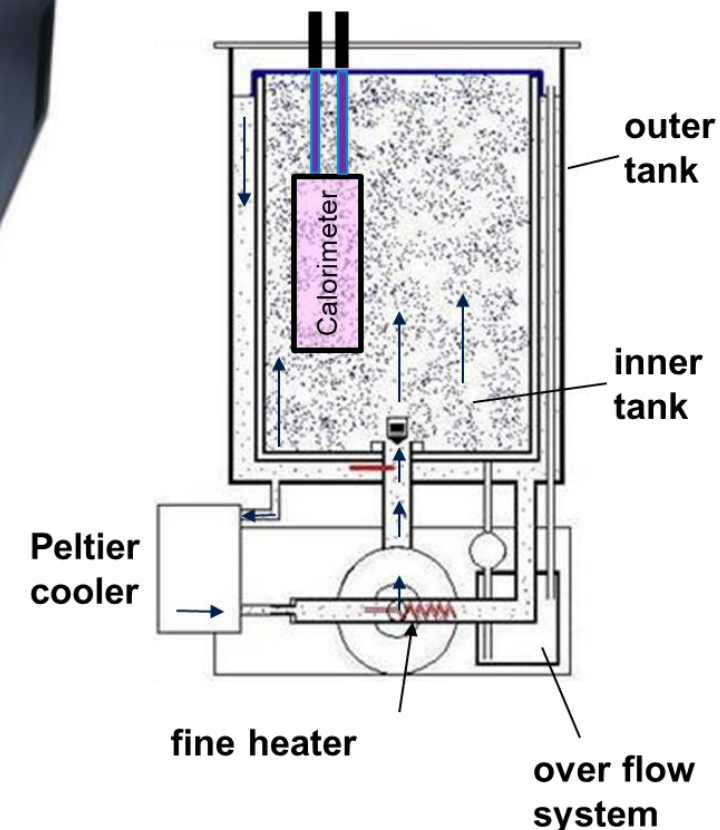
# Isothermal Microcalorimeters

- General Purpose:
  - **Thermal Activity Monitors** (e.g. TAM IV, TAM 48, TAM AIR) are general purpose IMC which can be accessorized to study many different processes such as materials stability and compatibility, cement curing, heats of solution, pharmaceutical stability, and microbiological growth.
- Specialized:
  - An isothermal titration calorimeter (ITC) is an IMC specifically designed to measure the heats of interaction when one liquid is titrated into another. ITC is used to study intermolecular binding, surfactant properties (e.g. micelles), and enzyme kinetics.



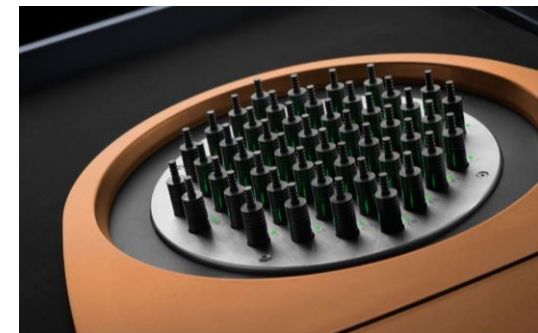
# TAM – Isothermal and Scanning Thermostat

- Temperature range: 4° – 150 °C
  - Isothermal and slow scanning (2 °C/h)
  - Temperature stability: < 0.1 mK/24 h
  - Temperature accuracy: ±0.1°C
  - Temperature precision: < ±0.1 mK
- Outstanding sensitivity and long-term stability (μW-nW)
- Multi functional calorimeters and accessories
  - Different measuring modes: isothermal, step-wise scanning, slow scanning (max ±2 °C/hr)



# TAM IV – A Modular and Flexible Microcalorimeter System

- The microcalorimeter system base is the TAM IV thermostat.
- Functionality and measuring capacity is obtained by adding:
  - Calorimeters
  - Sample handling systems (ampoules)
  - Auxiliary equipment



# TAM IV – Flexibility in Size and Sensitivity

## Sample Size



## Absolute Sensitivity

	Nanocalorimeter	4 mL Multicalorimeter	Microcalorimeter	20 mL Multicalorimeter	Micro XL	Macrocalorimeter	Solution Calorimeter
<b>Short Term Noise</b>	< ± 10 nW	< ± 100 nW	< ± 100 nW	< ± 300 nW	< ± 75 nW	< ± 500 nW	<i>Detectability</i> < ± 10 μ°C
<b>Baseline Drift</b>	< 40 nW/24h	< 200 nW/24h	< 200 nW/24h	< 1 μW/24h	< 1.5 μW/24h	< 6 μW/24h	1-4 mJ
<b>Accuracy</b>	< 2%	< 5%	< 2%	< 5%	< 3%	< 5%	< 0.2% Q < 0.5 J: < ±10 mJ Q < 0.1 J: < ±5 mJ
<b>Precision</b>	± 100 nW	± 200 nW	± 100 nW	± 300 nW	± 1 μW	± 3 μW	Q > 100 J: 0.02%

# TAM IV – Sample Handling Systems

The TAM IV offers a complete array of ampoules in two basic types; closed and open.

Closed, also referred to as static, ampoules contain the specimen in a static fashion: no manipulation of the sample is performed during the measurement.



Disposable glass, glass, SS and Hastelloy

Open ampoules are part of the micro reaction system (MRS) for the direct manipulation or modification of the sample or its surroundings during the experiment.



RH perfusion

Perfusion

Titration

Vacuum/Pressure

Waters™



# Applications

## Isothermal Microcalorimeters

TAM IV



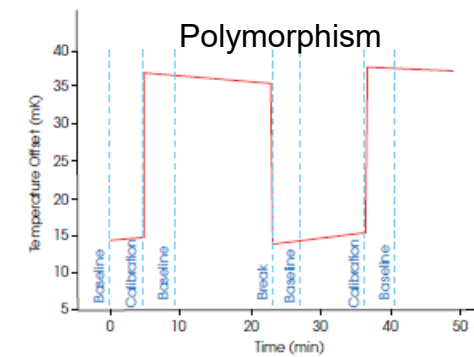
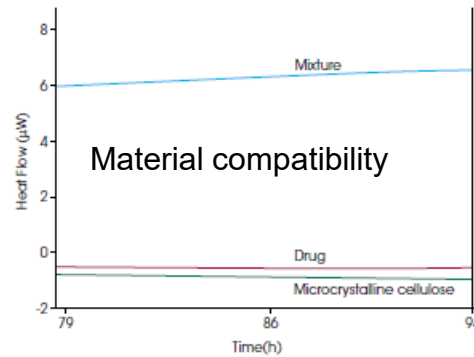
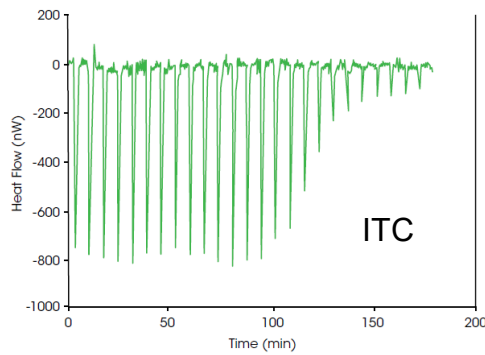
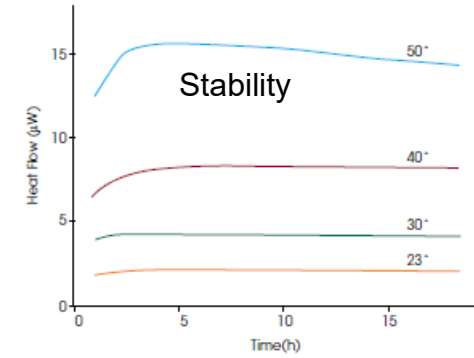
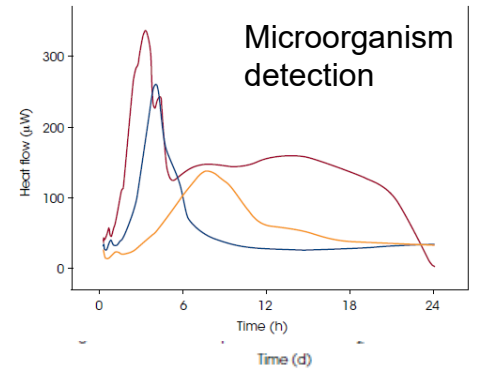
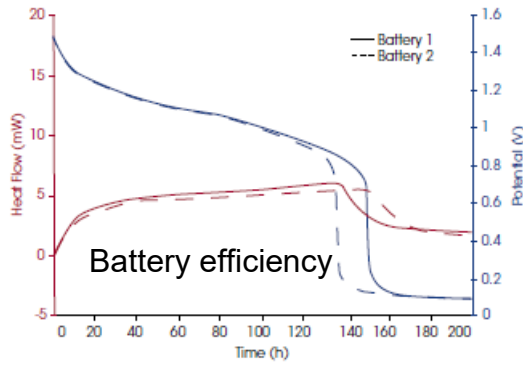
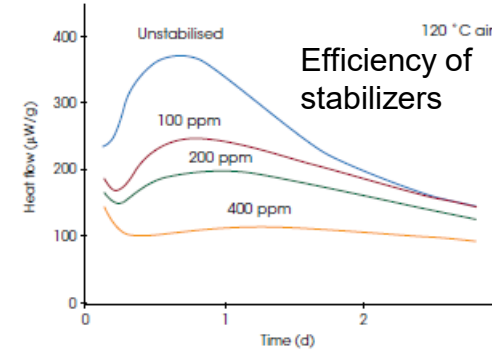
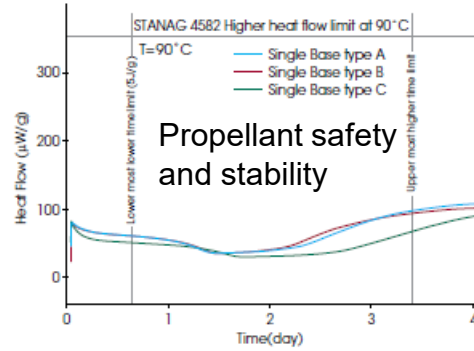
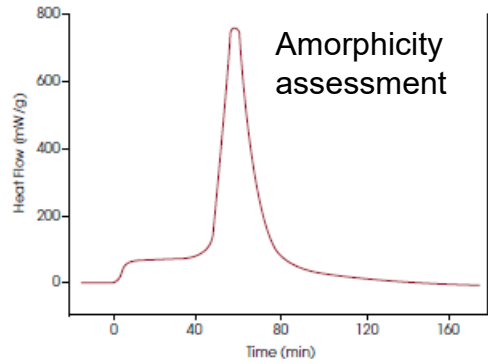
TAM 48

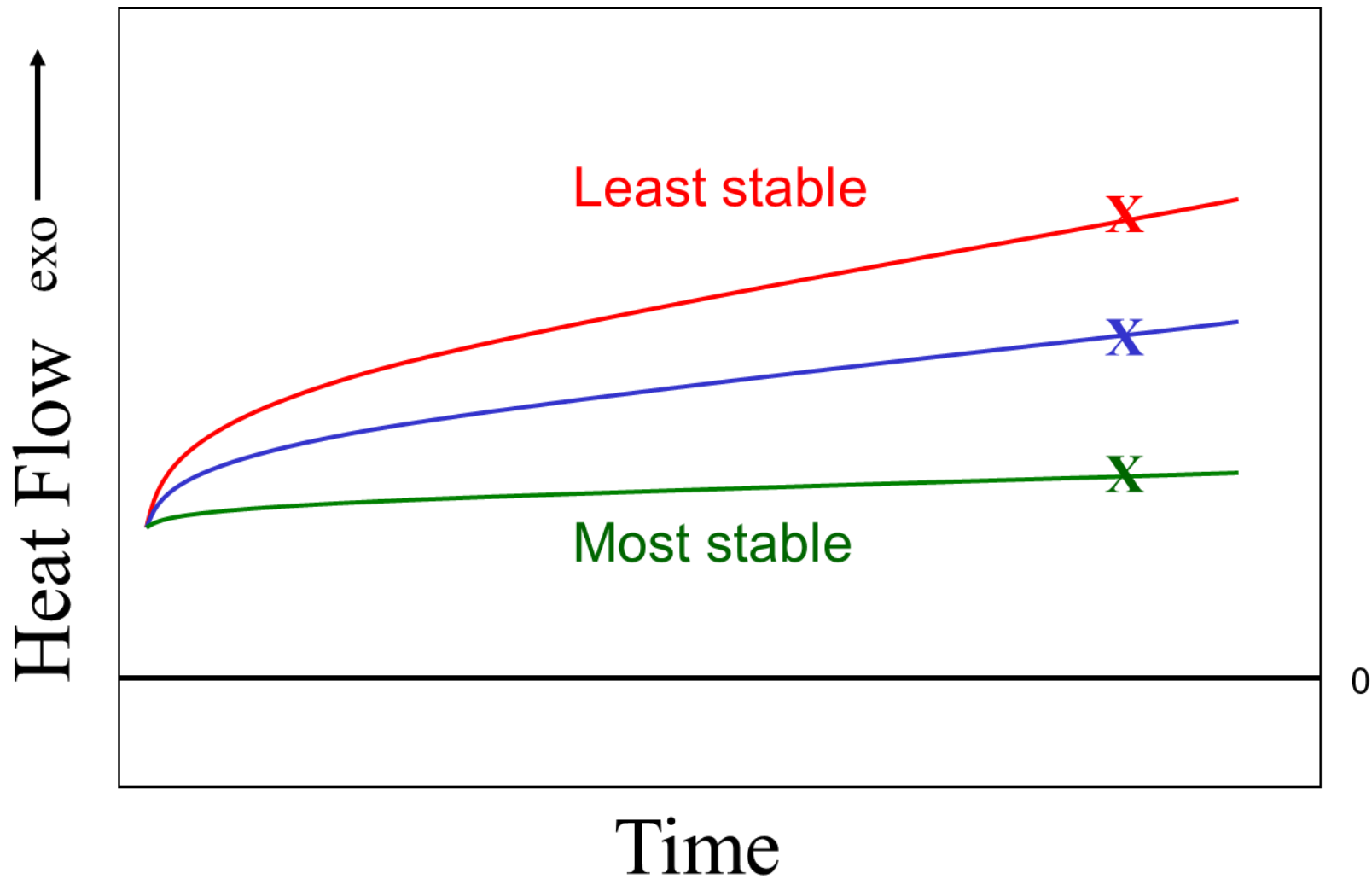


- **Pharmaceutical shelf-life stability:** detect both chemical and physical changes within a sample
- **Material compatibility:** evaluates interactions between constituents in a multi-component sample
- **Heats of crystallization and dissolution:** quantify thermal events to assess stability and solubility dynamics
- **Polymorphism:** determine relative stability of polymorphic pairs
- **Improve battery shelf life and charge density** by measuring parasitic heat during cycling
- **Monitor storage stability** of energetic materials

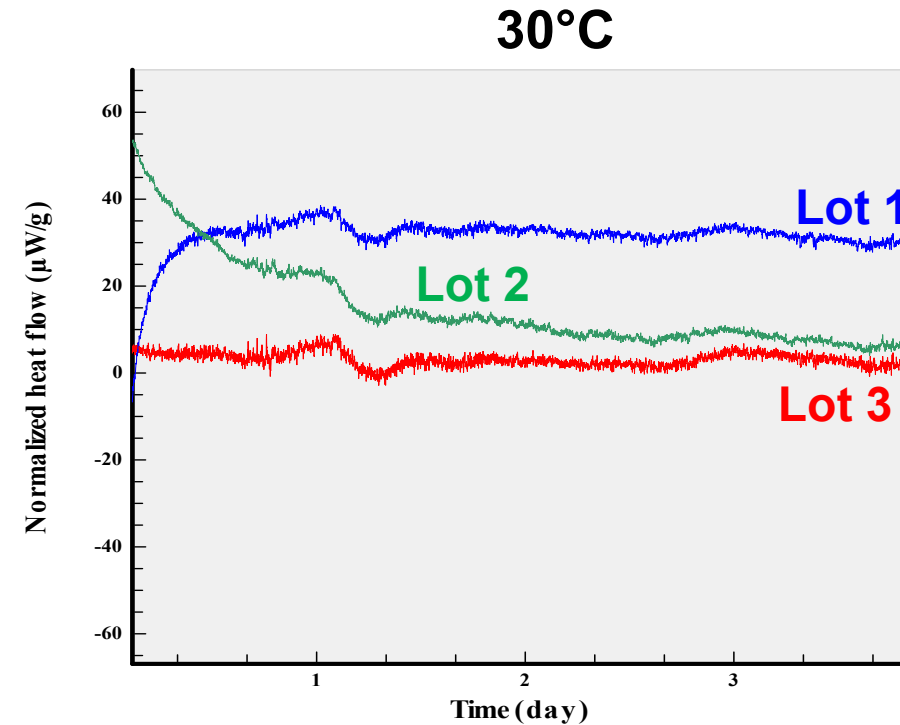
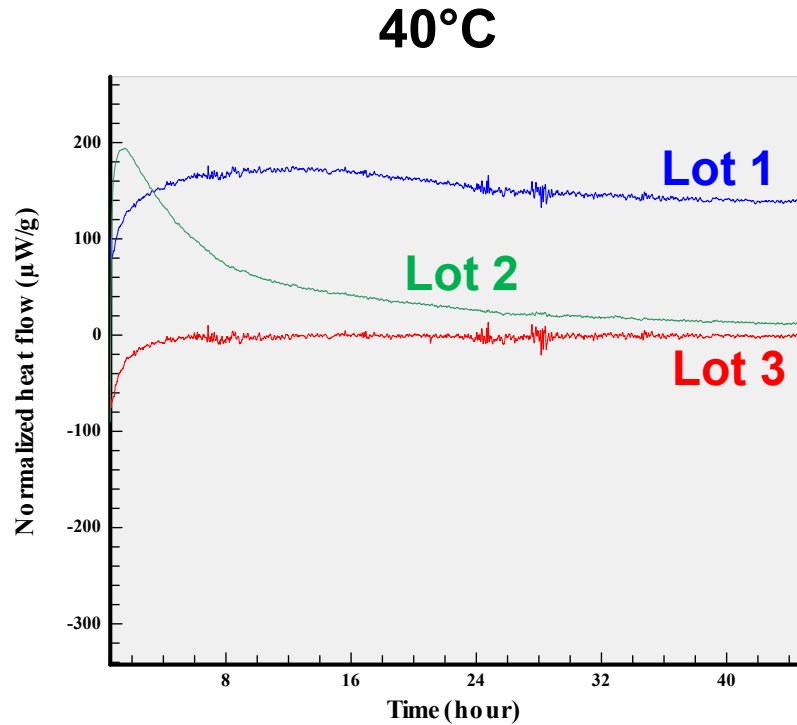
### How it Works

- Weigh a **sample** into a calorimetric **ampoule**
- Lower the ampoule into a **TAM calorimeter** at a predefined **temperature**
- Collect the **heat flow** data as long as required (hours, days or weeks)
- Remove the **sample** and do other analysis on the sample if needed

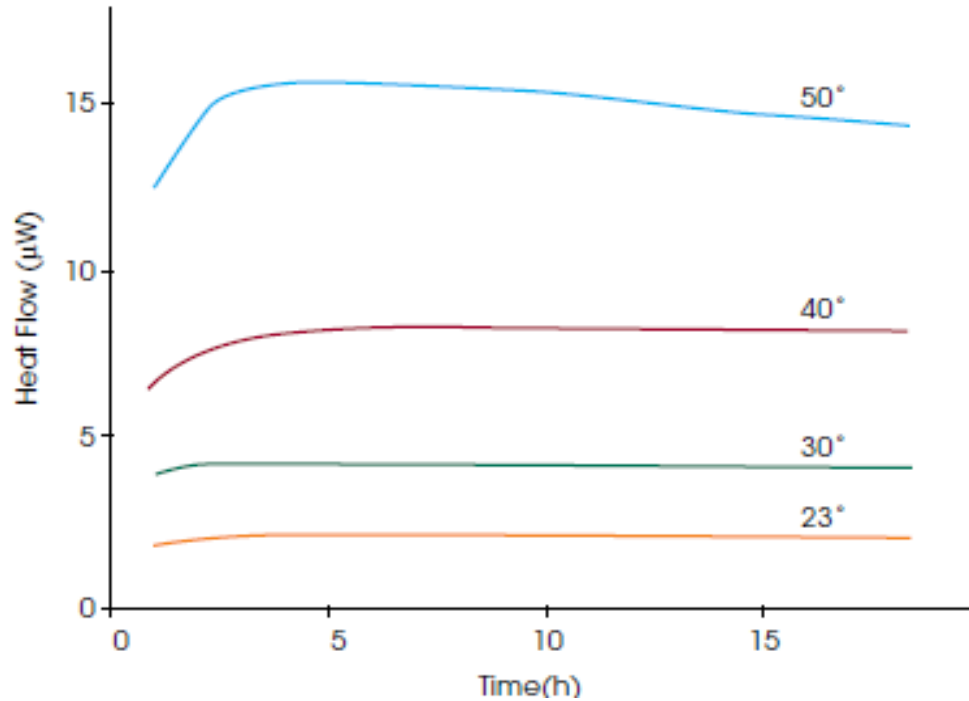




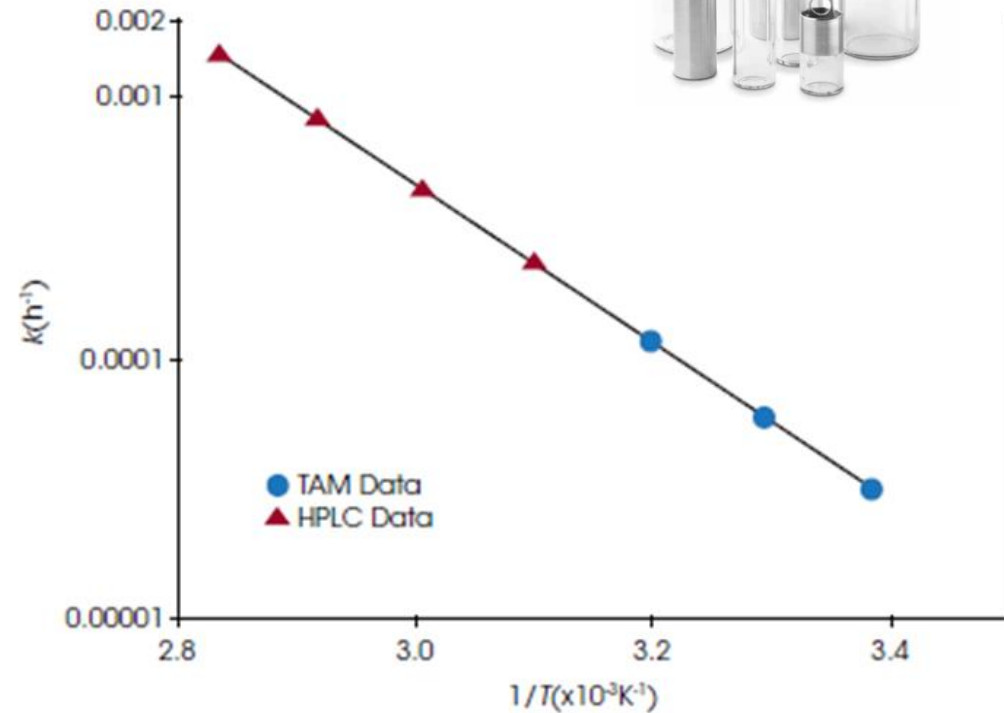
- Three different lots of the same material at two different temperatures.
- To evaluate stability the heat production for samples for each lot was measured over time at two different temperatures.



## Oxidation of Meclofenoxate Hydrochloride Containing dl- $\alpha$ -Tocopherol (TP)



Heat flow for TP degradation at different temperatures



Arrhenius plot of the apparent first order rate constant of TP degradation

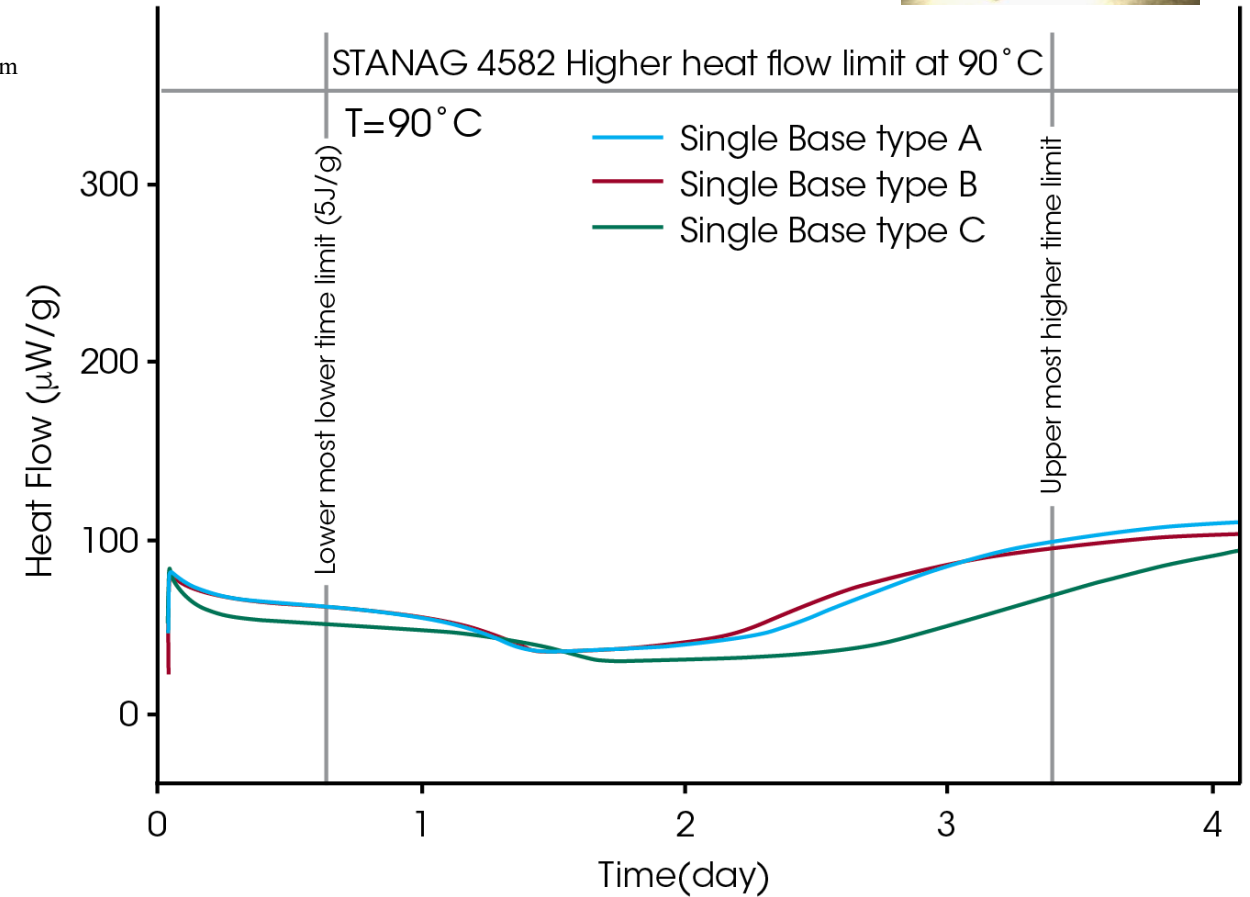
# Propellant Stability – STANAG 4582

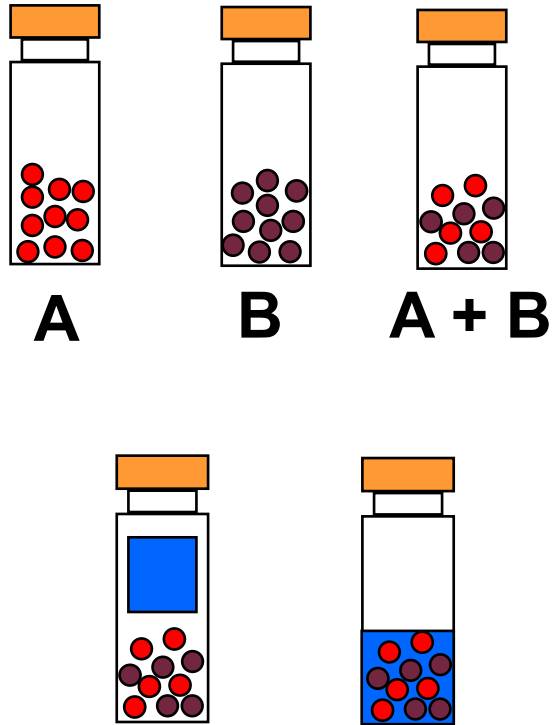


Propellants stored at 25°C will remain chemically stable for a minimum 10 years if the following criterion is met:

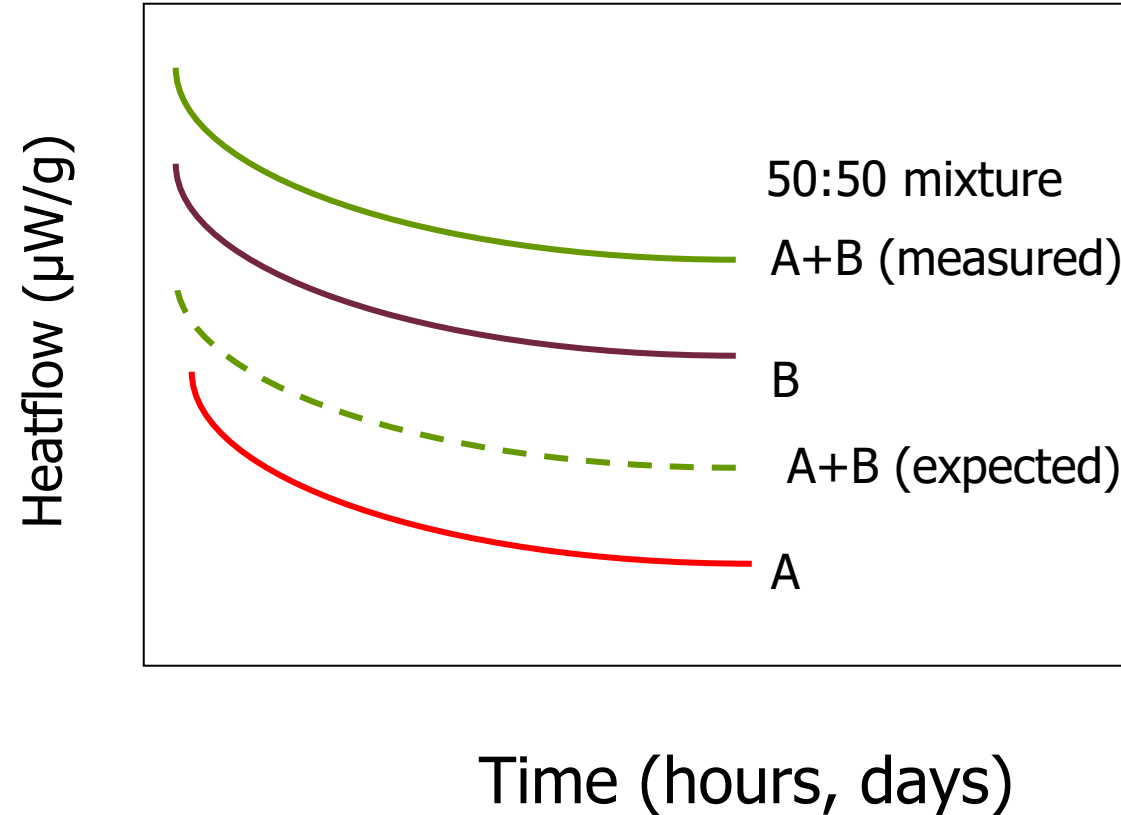
Calculation of test times  $t_m$  and heat flow limits  $P_1$  for different test temperatures  $T_m$

$T_m$ [°C]	$t_m$ [days]	$P_1$ [ $\mu$ W/g]	$T_m$ [°C]	$t_m$ [days]	$P_1$ [ $\mu$ W/g]
60	123	9.8	76	16.9	71.1
61	108	11.1	77	15	80
62	95	12.6	78	13.4	90
63	83.6	14.4	79	11.9	101
64	73.6	16.3	80	10.6	114
65	64.9	18.5	81	9.43	127
66	57.2	21	82	8.41	143
67	50.5	23.8	83	7.5	160
68	44.6	27	84	6.7	179
69	39.4	30.5	85	5.98	201
70	34.8	34.5	86	5.35	225
71	30.8	39	87	4.78	251
72	27.3	44	88	4.28	281
73	24.2	49.7	89	3.83	314
74	21.5	56	90	3.43	350
75	19	63.1			



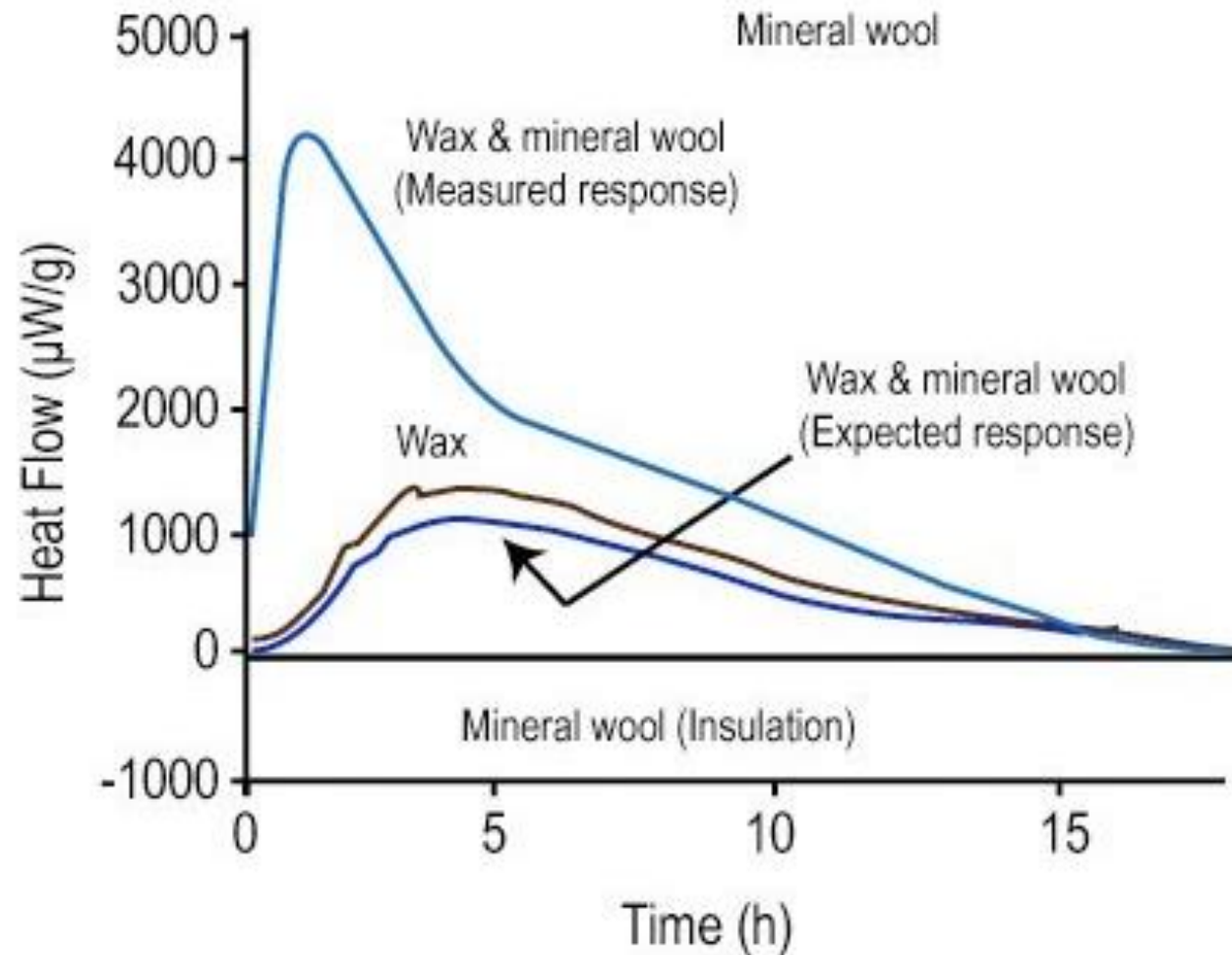


Blank experiments important!



If the heat flow curve of **A+B (measured)** differs from **A+B (expected)**, this is an indication that the materials affect each other or are incompatible.

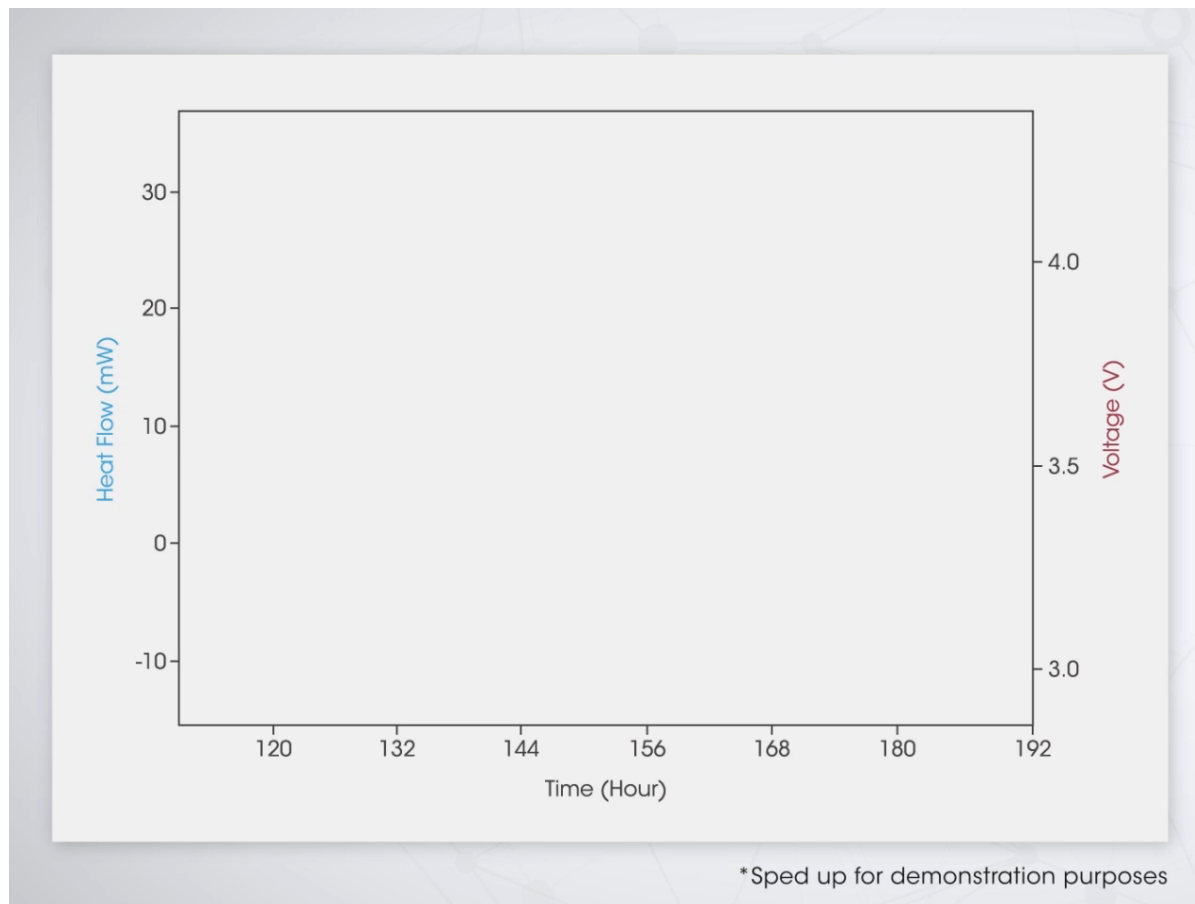
# Compatibility Between Wax and Mineral Wool



Data provided by Svensson, *Bodycote Materials AB*, Sweden (2003)

# Battery Cycler Microcalorimeter Solution (BCMS)

In-operando measurement for simultaneously analyzing the **heat flow** and **electrochemical data** of battery cells in real time to **predict battery life and performance**



TAM Assistant Software  
*Control Interface & Analysis*

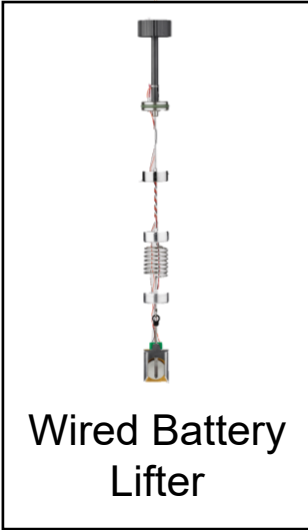
Software Integration



Isothermal Calorimetry



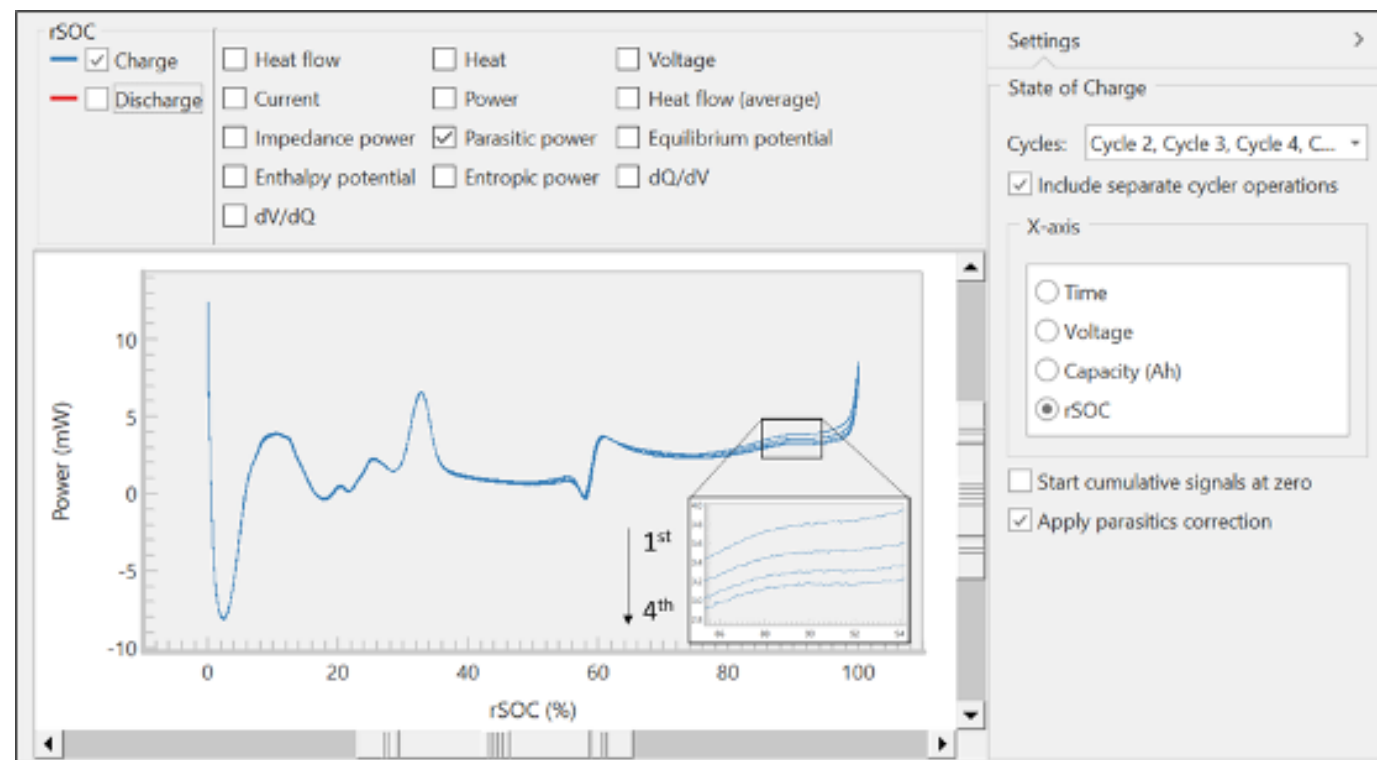
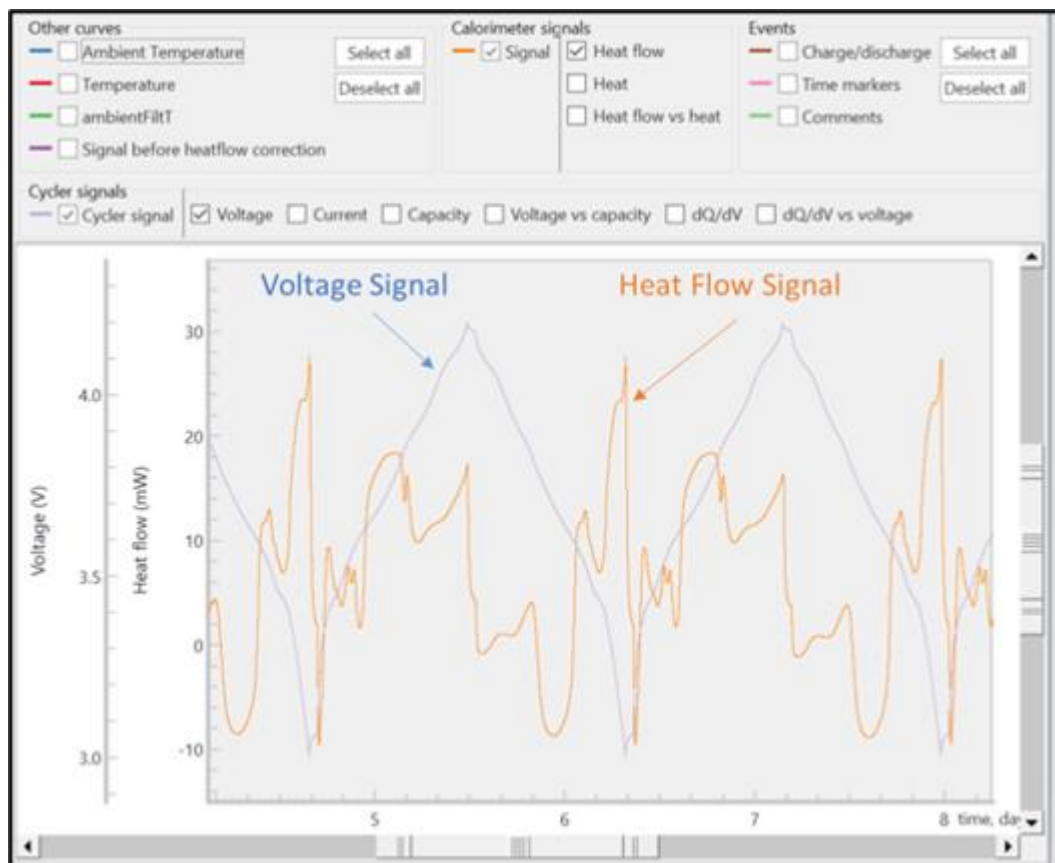
Electrochemistry



Wired Battery Lifter

Physical Interface

# Parasitic Heats – Screen Batteries Early to Prevent Failure Later



## Benefits of Using Isothermal Microcalorimetry

- Highly sensitive – no need for accelerated conditions
- Can detect both chemical and physical changes.
- Non-specific
- Non-destructive and real-time data

# Thank You



The World Leader in Thermal Analysis, Rheology, and  
Microcalorimetry

