Calorimetric Principles and TAM III

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Nomenclature

t	time	[sec]
P	Heat production rate or Thermal power	[W = J s^{-1}]
Φ (dq/dt)	Heat flow	[W = J s^{-1}]
Q	heat	[J]
Δ*H*	Enthalpy change	[J mol^{-1}, J g^{-1}]

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Thermal Analysis

”*Thermal analysis* refers to a group of techniques in which a physical property of a substance is measured as a function of temperature whilst the substance is subjected to an imposed temperature alteration”

Examples: DTA, DSC, TGA,
TAM in non-isothermal mode

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Calorimetry

"Calorimetry refers to those measuring techniques that are used for direct determination of rate of heat production, heat, and heat capacity as function of temperature and time"

Examples: DTA, DSC and TAM

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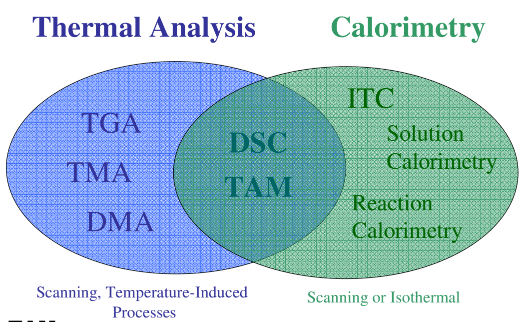
TA vs. Calorimetry



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Calorimetry

- All kinds of processes; Chemical, Physical and Biological
- Non-specific
- Non-destructive
- Not dependent on the physical shape of the sample
- No need for sample preparation
- Direct and continous

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Rate ⇔ Heat production rate

$$\frac{dC}{dt} = k \cdot f(c)$$

$$P = \frac{dC}{dt} \Delta H$$

$$P = \Delta H \cdot k \cdot f(c)$$

Enthalpy → Thermodynamic Information

Reaction rate → Kinetic Information

Concentration → Analytical Information

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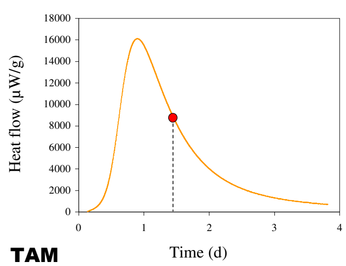
Heatflow vs. Time



Shows how the reaction rate varies with time.

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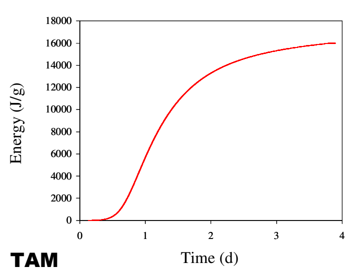
Energy vs.Time



Shows how the extent of reaction varies with time.

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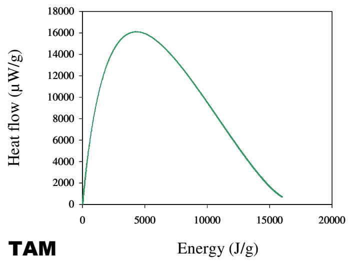
Heatflow vs. Energy



Shows how the reaction rate varies with the extent of reaction

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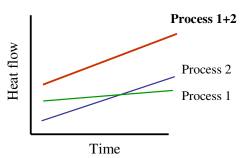
TAM is a non-specific technique

- TAM is sensitive to <u>all</u> physical and chemical processes associated with a heat flow. Thus, the monitored heat flow may contain <u>contributions</u> from several processes.
- Individual contributions may be distinguished by varying the experimental conditions.



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TAM III - a Modular and Flexible Multichannel Microcalorimetric System

- Easy to use
- Temperature range: 15 – 150 °C
  - Isothermal and slow scanning (2 °C/h)
  - Temperature stability: < 0.1 mK/24 h
- Multi functional calorimeters and accessories
  - Different measuring modes
- High sample throughput
  - Up to 48 individual twin heat flow calorimeters.
- Outstanding sensitivity and long-term stability (μW-nW)
- Network identity – IP address

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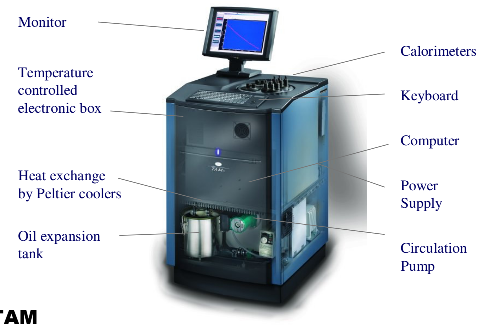
TAM III Thermostat – an Integrated System



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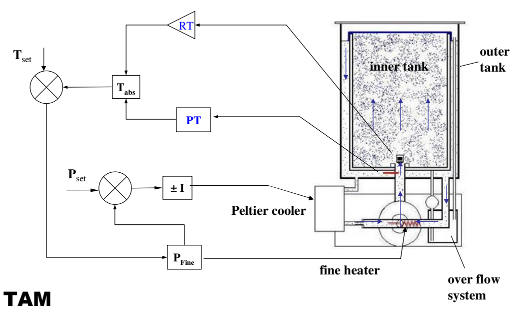
TAM III Thermostat Principle



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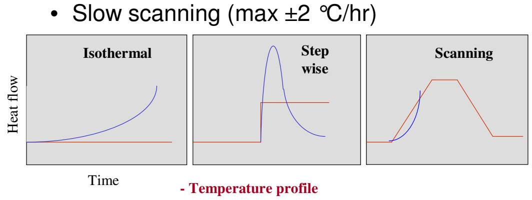
Temperature Modes of TAM III

- Isothermal
- Step-wise scanning
- Slow scanning (max ±2 °C/hr)



- Temperature profile
- Heat flow data

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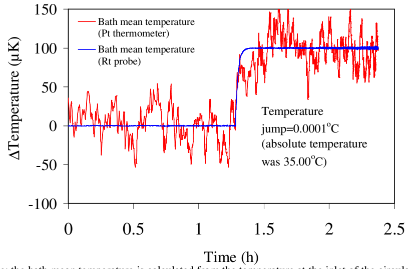
TAM III Thermostat
- a step-wise change in temperature

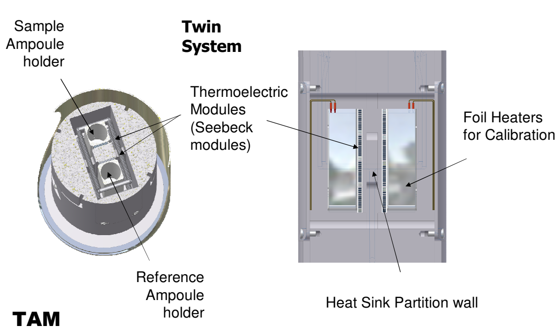


Note: the bath mean temperature is calculated from the temperature at the inlet of the circulating bath. The Pt thermometer shows the estimated bath temperature. The RT probe shows the true fluctuations of the inflowing thermostat liquid.

Nanocalorimeter

- Highest sensitivity twin channel calorimeter
  - < 5 mL
- Reference accessible by user
- Used with 4 mL and 1 mL Micro Reaction System(s)
  - Titration ampoule
  - RH Perfusion ampoule
  - Perfusion ampoule
  - Combinations of ampoules

3201 4-ml Nanocalorimeter



Minicalorimeter

- Reference permanent and below the sample ampoule
- All type of 4 mL ampoules can be used
- Contains all necessary electronics for connecting to TAM III

A minicalorimeter attached to its computer interface

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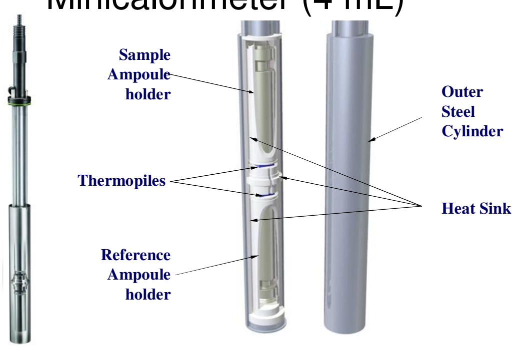
Minicalorimeter (4 mL)



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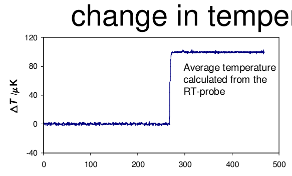
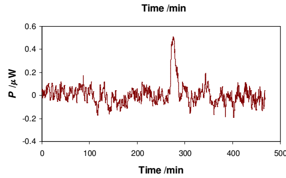
Minicalorimeter - response to a step-wise change in temperature



Temperature jump of 0.0001°C



Corresponding response in heat flow. Signal returns to 0 μW heat flow much faster than nanocalorimeter due to smaller time constant of heat sink.

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Twin System

- Twin Calorimeter (identical)
  - Sample (A-side)
  - Reference (B-side) - should be inert
- TAM measure the difference in heat flow between the sample and the reference:

$$P = P_S - P_R$$

Positive heat flow values ⇔ Exothermic reactions

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Theory

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Summary

- When a reaction proceeds the temperature of the sample will change.
  - ✓ Exothermic reactions => Temp. increases
  - ✓ Endothermic reactions => Temp. decreases
- The change in temperature results in a heat exchange (heat flow) with the surrounding
- The heat flow is related (in many cases directly proportional) to the rate of the reaction

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Definitions

- Rate of heat production
  - The rate of heat produced (exothermic) or absorbed (endothermic) by the sample
- Rate of heat exchange or heat flow
  - The rate of heat flow between the sample and the surrounding

Note: During Steady State or "near steady state" conditions these properties are equal.

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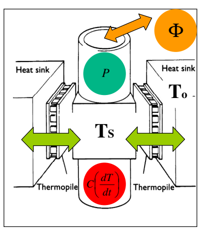
Heat Balance Equation



General Heat Balance Equation

$$P = \Phi + C\left(\frac{dT}{dt}\right)$$

Rate of Heat Production = Heat flow + Rate of Heat Accumulation or depletion

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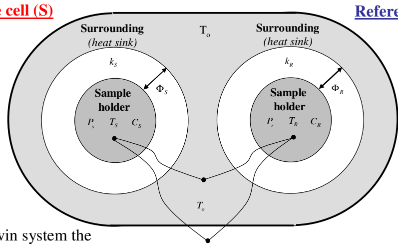
Twin System
(used in TAM)

Sample cell (S) — Reference cell (R)



With a twin system the noise is reduced!

$\Delta T=(T_s-T_o)-(T_R-T_o)=T_s-T_R$

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The Heat Balance Equation
(Twin System)

Sample side

$$P_S = k_S(T_S - T_o) + C_S \frac{dT_S}{dt}$$

Reference side

$$P_R = 0 = k_R(T_R - T_o) + C_R \frac{dT_R}{dt}$$

Subtraction gives

$$P = k_S(T_S - T_o) + C_S \frac{dT_S}{dt} - k_R(T_R - T_o) - C_R \frac{dT_R}{dt}$$

For well designed instruments:

$$k = k_R = k_S \qquad C = C_R = C_S$$

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The Heat Balance Equation
(Twin System)

$$P = k(T_S - T_R) + C\frac{d(T_S - T_R)}{dt}$$

Note: dQs/dt does not depend on the surrounding temperature.
Thus, the stability is improved !!

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Heat Balance Equation
(in Terms of Voltage)

$$P = \Phi + C\frac{dT}{dt}$$

$$\Phi = k(T - T_o) = \frac{k}{g}U \quad \Rightarrow \quad T = \frac{U}{g} + T_o \quad \Rightarrow \quad \frac{dT}{dt} = \frac{1}{g}\frac{dU}{dt}$$

$$P = \frac{k}{g}U + \frac{C}{g}\frac{dU}{dt} = \frac{k}{g}\left(U + \frac{C}{k}\frac{dU}{dt}\right) = \varepsilon\left(U + \tau\frac{dU}{dt}\right)$$

Tian's Equation (used to dynamically correct cal. data)

$$\frac{dQ}{dt} = \varepsilon\left(U + \tau\frac{dU}{dt}\right)$$

g = Seebeck coefficient (V/K)
ε = calibration constant (W/V)
τ = time constant (s)

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Calibration of TAM III

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Purpose of calibration

- To ensure that the displayed heat flow corresponds to the true heat flow caused by the sample;
  - Conversion of measured voltage to heat flow
  - Account for heat losses i.e. heat not passing the detectors
- Calibration of TAM is performed using inbuilt calibration heaters.
- The inbuilt calibration can be validated using external calibration heaters or chemical test reactions.

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Calibration of TAM III

- The calorimeters of TAM III has been calibrated at Thermometric at 4 different temperatures so as to diminish the influence of temperature on the users calibration results.
- When the user makes a calibration, the results is compared with that obtained from the "factory calibration" and deviation is calculated.
- The deviation is represented by a unit-less calibration constant (called the gain constant in TAM Assistant) and should be close to unity (normally 0.95-1.06).

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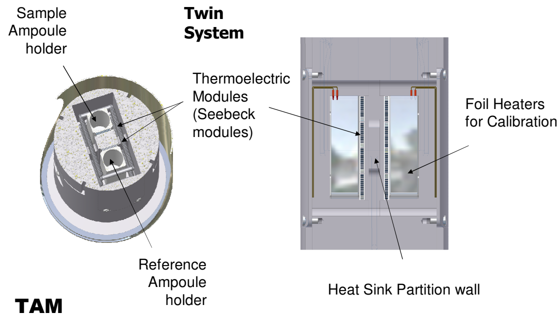
3201 Nanocalorimeter



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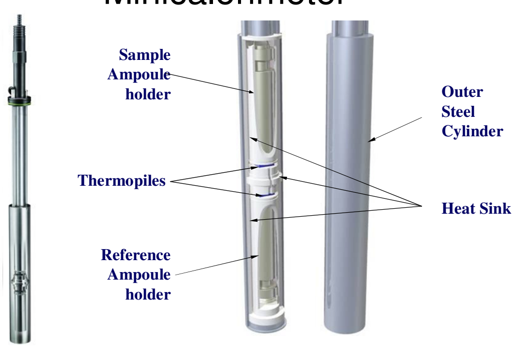
Minicalorimeter



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A new calibration should be performed whenever;

- TAM has been switched off
- Measuring temperature has been changed
- Whenever a new ampoule type is going to be used
- Routinely at regular intervals due to ageing of the semi-conductor thermopiles (e.g. ones every third month)

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Two types of calibrations

- Heat flow calibration – for 'slow' processes
- Dynamic calibration - for 'fast' processes

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Calibration Conditions

- **Ampoule experiments**
  – empty ampoule lifters (or empty ampoules) should be in position in both sample and reference side

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Heat flow Calibration

-General procedure

- Ensure that the baseline is stable
- Apply settings: steady state calibration (2-3h) or pulse and integration (20 min) and power to the calibration heaters (Calorimeter device / settings ..).
- Start the calibration in TAM Assistant (Calorimeter device / control tab / perform calibration)

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Thermal inertia ⇔ Time delay

- Due to the thermal inertia of a calorimetric unit the true response in heat flow by a sample will differ somewhat from the heat flow monitored by the heat detectors)
- For fast processes, i.e. response time < 10-15min dynamic calibration should be used to give true process rates

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Dynamic correction

For reactions where the slope of the heat flow time curve (ϕ) is changing rapidly a dynamic correction can be applied to obtain the true response of the sample (P) using the following formula (*Tian's equation*) ;

$$P = \phi + \tau \frac{\mathrm{d}\phi}{\mathrm{d}t}$$

τ = a time constant obtained from dynamic calibration

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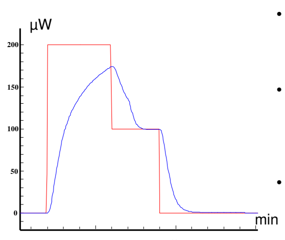
Dynamic Calibration



- Dynamic calibration refer to calibration under non-steady state conditions, i.e. during a curvature
- A known electrical calibration power is applied in two steps and the dynamic of the curvature is analysed in terms of time constants.
- A dynamic calibration should always be performed if the response time of a process is less than 15 min since the shape during that part will be affected

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Dynamic Correction function in TAM Assistant

- The TAM Assistant software contains functions for considering the effects of the thermal inertia, *i.e.* it calculates a property close to the true thermal power.
- TAM Assistant uses *two* time constants rather than one to get a better precision in the correction (*cf.* Taylor expansion). In this case the fitting parameters has no relevant physical interpretation

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Effect of Dynamic calibration

- **Heat flow data** will not reflect the true response of the sample for reactions with response times less than 10 min.
- **Dynamically corrected data** represents the true data of the sample and has been calculated from Heat flow data using the information about time constants obtained from Dynamic calibration.

$$P = \phi + (\tau_1 + \tau_2)\frac{d\phi}{dt} + \tau_1 \cdot \tau_2 \frac{d^2\phi}{dt^2}$$

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Heat flow and "corrected" data

- If only a static calibration has been performed only heat flow data, ϕ, (data monitored by the heat detector) can be displayed
- If a dynamic calibration has been performed dynamically corrected data (data representing the true response of the sample) can be displayed

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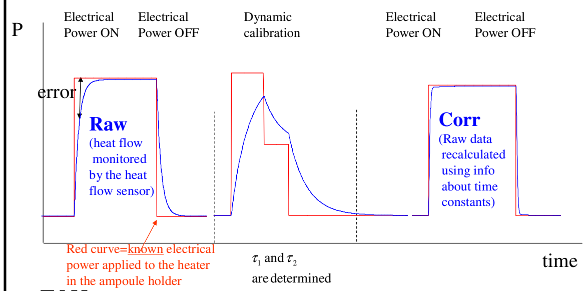
Heat flow and corrected data



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Dynamic Calibration

-General procedure

- Set measuring principle to "Dynamic correction" (Calorimeter device / control / measuring mode.
- Introduce the ampoule with sample (or a sample "mimic").
- Wait until the calorimetric signal is stable.
- Start the calibration: there are two options i) time-constant calibration and ii) full dynamic calibration (Calorimeter device / control / perform calibration ..)
- After 20-30 minutes the dynamic calibration is completed and the calibration heater is turned off automatically

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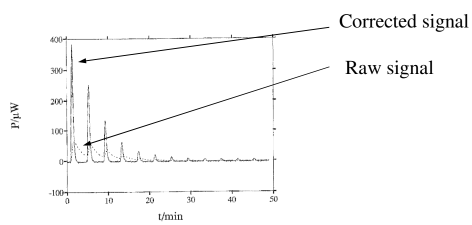
Dynamic calibration



$$dQ/dt = \varepsilon \cdot (V + (\tau_1+\tau_2) \cdot dV/dt + \tau_1 \cdot \tau_2 \cdot d^2V/dt^2)$$

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General Performance Test

- General Performance Test
  - A test to evaluate the performance of a calorimetric system, i.e. thermostat with a calorimetric unit.
- Calculated parameters (for A- and B-side)
  - Time constants and difference between A- and B side.
  - Drift, Fluctuation and Error over 24 hours
  - Short term noise
- Method: GPT experimental wizard
- Evaluation: GPT analysis
- Results: The analysis function gives a Yes or No answer as to whether the calorimeters are within specifications

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Sample preparation and experimental considerations

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Designing an experiment

- Choice of sample handling system
- Handling of ampoules
- Sample considerations
- What to use as reference

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Sample Handling Systems

- Closed or sealed (static) Ampoules
- Open ampoules - Micro Reaction System
- Micro Solution Ampoule

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Static Ampoules

- Disposable Glass Ampoules
- Heat seal ampoules
- Stainless Steel Ampoules with Threaded Cap
- Stainless Steel Ampoules with Circlip Cap
- Glass Ampoules with Circlip Caps

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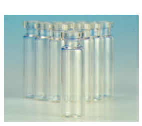
Disposable Glass Ampoules

- Preconditioning of ampoules
  - Ampoules and lids should be stored for 24 hours at the operating temperature of TAM
  - Volatiles and moisture will be desorbed
- Always consider the risk for interaction between the sample and the ampoule
  - Steel ⇔ peroxides, HCl
  - Basic solvents ⇔ glass



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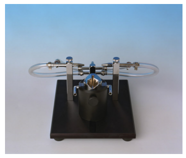
Heat seal ampoules

- Completely sealed
- Heat seal ampoules of glass
- Special ampoule lifters

Note: precautions should be taken to protect the sample towards the heat during the sealing procedure



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Threaded Cap Ampoules

- Stainless steel
  - resistance towards corrosion
  - should not be used for solvent with pH < 4
- Hastelloy
  - Improved resistance towards corrosion and acids
  - excellent for use with organic solvents
- The cap is sealed with a disposable Teflon disc (inert) and o-ring
- Stable for most applications
- Stands pressures up to at least 2 bar

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Circlip Cap Ampoules

- Stainless steel
  - resistance towards corrosion
  - should not be used for solvent with pH < 4
- Hastelloy
  - Improved resistance towards corrosion and acids
  - excellent for use with organic solvents
- Glass
- O-sealing made in Nitril, EPDM, Viton or Kalrez (most inert)
- Stands 8 bar pressure (precautions must be made)

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Sealing procedure of Disposable Glass Ampoules

- Crimping tool
  - Used to seal the cap on the glass ampoule
- Adjustment tool
  - Adjust the dimension of the caps when in position
- Centring tool
  - Used to make a mark for the lifter eyelet
- Caps
  - Contains Al, Butyl rubber and a Teflon gasket
- May introduce initial disturbances !

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Disturbances associated with Disposable Glass Ampoules

- These ampoules may be associated with a disturbance in the 1-5 µW-range during the first 10 hours due to;
  - the sealing procedure introducing stress and subsequent relaxation phenomena
  - sorption/desorption phenomena
- Can be minimised by
  - pre-storing the ampoules and lids at the operating temperature for 24 hours
  - Preparing the sample and the reference ampoule at the same time (use a new reference for each measurement)

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Equilibrium

- Thermal equilibrium
  - Within 60 min after loading
- Physical equilibrium
  - Depends on the sample and the pre-history
  - Might depend on the ampoule itself
- Chemical equilibrium
  - Slow/fast reactions

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Pre-history of the sample

- The sample should be stored under controlled conditions for at least 24 hours before a measurement
  - relative humidity
  - temperature
  - atmosphere (e.g. nitrogen, air, oxygen)
- The time to reach physical equilibrium must be considered

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Sample geometry

- Powder (small particle size)
  - Chemical processes will occur homogeneously in the sample
- Bulk samples (large particle size)
  - May show a heterogeneous response
    - diffusion limited oxidation
    - pressure build-up by volatiles formed

The influence of geometry can be studied using different particle size with the same amount of sample. If the specific heat flow (µW/g) is the same for two different sizes, this effect is not important. Otherwise it must be considered.

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Sample amount

- The response in heat flow may be dependent on the amount of samples (different bed volumes) in the ampoule
  - If the specific heat flow (µW/g) is the same for different amounts of samples this effect is not important. Otherwise it must be considered.

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Kinetic evaluation

- Be sure the response in heat flow reflects the kinetics of the process of interest
- In many case the first 5-10 hours should be excluded because of a non physical equilibrium (other process contributes to the monitored heat flow)

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Choice of Reference Materials

- A reference material is used to balance the heat capacity of the sample and the reference ampoule.
- With a good balance in heat capacity the short-term noise will be reduced. However, if the system is not well-balanced the average heat flow values is not affected.
- A proper balancing of the ampoules is needed when the response in heat flow is low, e.g. during titration experiments.
- Example of reference materials: sand, glass pearls, water

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The Heat Balance Equation
(Twin System)

$$P = k(T_S - T_R) + C\frac{d(T_S - T_R)}{dt}$$

For well designed instruments:

$$k = k_R = k_S$$

$$C = C_R = C_S$$

$$\tau = \frac{C}{k}$$

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Balancing sample and reference

- Calculate from heat capacity
- Calculate from time contants
  - – Measure τ of an empty ampoule
  - – Measure τ of ampoule with different amount of e.g. water

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