NETZSCH

Analyzing & Testing

Multiple Mode Calorimetry

Precisely Engineered Solutions on a Common Platform

Leading Thermal Analysis

Multiple Mode Calorimetry – Synergy of Proven Methods

Synergy of Proven Methods

Scientists and engineers generally recognize that the combination of two or more analytical methods can obtain much more product and process information than by using the single technique alone. Different signals can be recorded and superimposed sample effects can often be explained in a much better way. The technique has to be reliable, fast and easy to use in day-to-day business.

The NETZSCH development team has created a totally new calorimeter system which can be used in commercial R&D, universities and research centers and QC/QA of various industries. Like a DSC, the MMC measures chemical reactions, phase changes, and specific heat but on gram-size samples.

This allows for organic/inorganic multi-phase mixtures/slurries testing. Like an ARC, it can run adiabatic tests necessary for process safety. With the new addition of the High Temperature Coin Cell Module, the MMC can do the DSC test on a whole coin cell. The MMC successfully creates the synergy of two well-proven methods, DSC and ARC.

MMC 274 *Nexus*®
Base unit with two additional calorimeter modules

NETZSCH

Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) in accordance with ISO EN DIN 11357 or ASTM E 793 is the most-often used Thermal Analysis method. With DSC, transition temperatures and enthalpy changes in solids and liquids can be determined at controlled temperature conditions: heating, cooling or isothermal. DSC is a rapid analysis; it is often used in the quality control and assurance of polymers, pharmaceuticals, foods, metals and ceramics.
But the use of only small sample quantities (mg) and the missing pressure signal yield incomplete information, especially for inhomogeneous multiphase substances and for measuring chemical processes.

Typical DSC applications

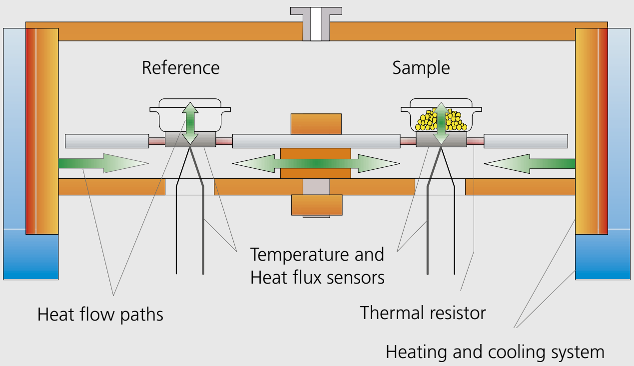
- Glass transition
- Specific heat capacity
- Melting
- Crystallization
- Cross-linking
- Oxidation
- Polymorphism
- Purity
- Degree of crystallinity
- Degree of curing

Accelerating Rate Calorimetry

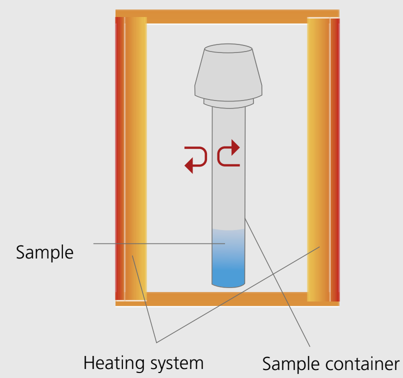
Chemical research and related industries aim to provide safe and reliable processes. The energy release from a chemical reaction has to be known. With Accelerating Rate Calorimetry the worst case scenario, without any heat loss to the environment, can be studied at elevated temperatures. Accelerating Rate Calorimeters (ARC) in accordance with ASTM E 1981 have been widely used for decades to simulate the behavior of actual large scale reactors. However, these instruments require a large footprint and the tests are very time-consuming.

Typical ARC applications

- Chemical process safety
- Battery testing
- Storage and transport studies
- Energetic material testing
- Effect of autocatalysis and inhibitors at exaggerated conditions



DSC principle



ARC principle

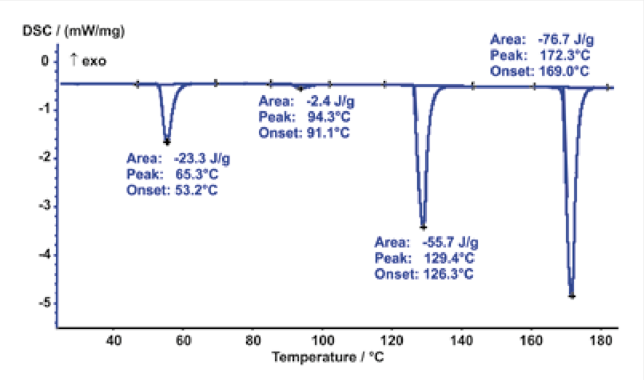
Multiple Mode Calorimeter MMC 274 *Nexus*®

Modular System

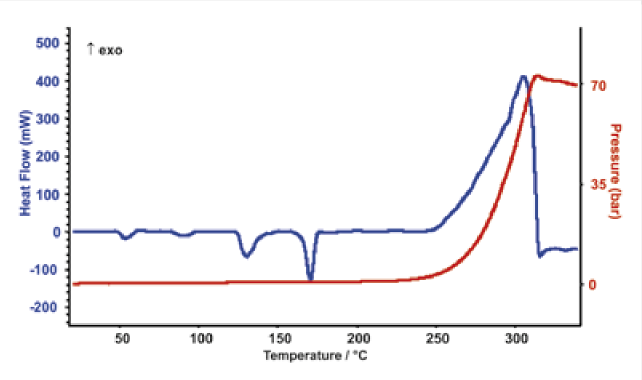
The MMC 274 *Nexus*® consists of two parts: the base unit with electronics and the exchangeable calorimeter module. This guarantees maximum flexibility.

Exchangeable calorimeter modules are available for different applications. ARC modules can be used for standard process safety work. Scanning module and fast *VariPhi*® modules can be employed for more sophisticated measurements. And HT coin cell module can characterize coin cell as a whole.

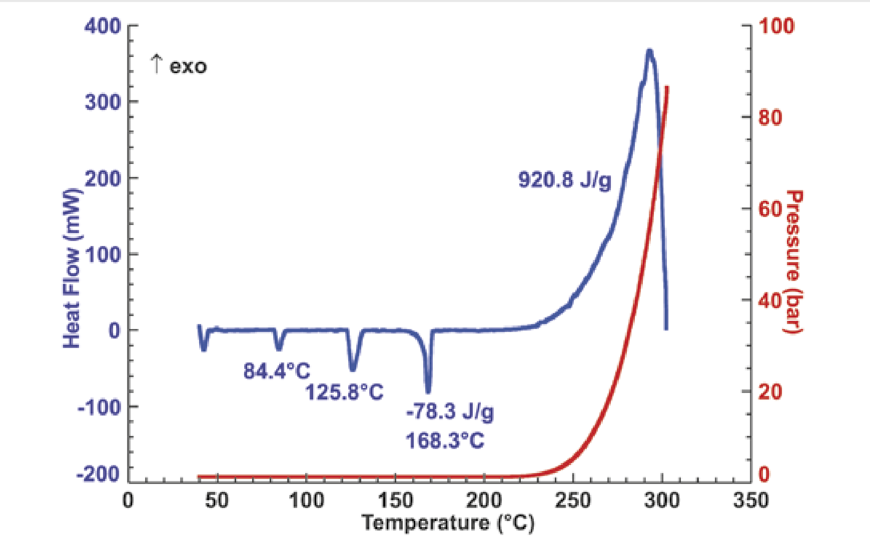
General Technical Specifications of MMC 274 *Nexus*® (module dependent)	
Temperature range	25°C to 500°C
Temperature readability	0.01 K
Heating rate	0 to 2 K/min
Pressure range	0 to 200 bar
Pressure readability	0.01 bar
Sample container volume	0.1 ml to 10 ml
Tracking rate	up to 250 K/min
Sensitivity tracking rate	down to 0.002 K/min (depending on temperature range)
Sensitivity heat flow	down to 10 µW
Options	injection, stirring (max. 350°C), specific containers



DSC plot of NH_4NO_3 with evaluated temperatures and enthalpies



ARC with *VariPhi*® plot of NH_4NO_3 with endothermal effects, heat flow and pressure



Ammonium nitrate undergoes three solid-solid phase transitions followed by a melt around 170°C. Following the melt the compound will energetically decompose. These tests measuring phase changes, decomposition and pressure are crucial for safety studies on such highly energetic materials.

MMC plot of NH_4NO_3 with evaluated effects, heat flow and pressure

Key Features and Advantages of MMC 274 *Nexus*®

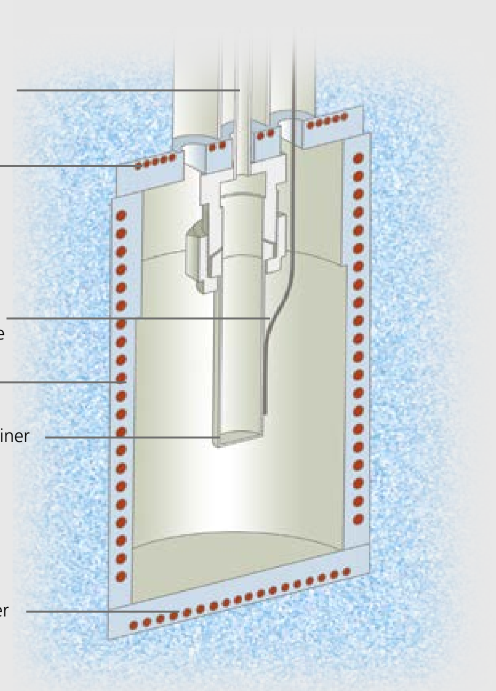
- Multiple testing modes in one instrument for wide application coverage
  - Scanning mode (constant power, constant heating rate)
  - Isothermal mode (including isothermal charging/discharging)
  - Adiabatic mode with Heat-Wait-Search for process safety tests
- Wide temperature range up to 500°C
- Wide pressure range up to 200 bar (20 MPa)
- Various sample containers of different materials and volumes
- *Proteus*® software for the evaluation of onset, peak, area, etc., which may be combined with other thermo-analytical data in one plot
- Exchangeable calorimeter modules in one table-top instrument
  - ARC module for safety testing
  - Scanning module for sample screening
  - Fast *VariPhi*® module for fire exposure tests, specific heat, endothermal effects
  - HT coin cell module for coin cell characterization

Process Safety: The ARC Module

Heat-Wait-Search and Pressure Tests

A defined volume of a sample (ml scale) is placed in a tube-shaped or spherical container. The container is surrounded by a sophisticated heating system.

Depending on the operating mode, the surroundings of the sample container are controlled to the same temperature as the sample. If there is no temperature difference between the surrounding heaters and the sample, then all the heat generated by the sample stays inside the sample.



ARC Module

Wide Range of Applications

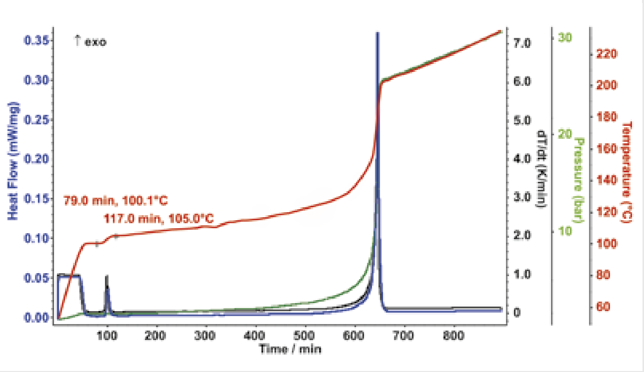
- Chemical Processing Industries
- Storage and Transportation of Chemicals
- Energetic Materials Testing
- Battery Testing
- Physical Properties Measurements

NETZSCH

Applications and Features of the ARC Module

DTBP

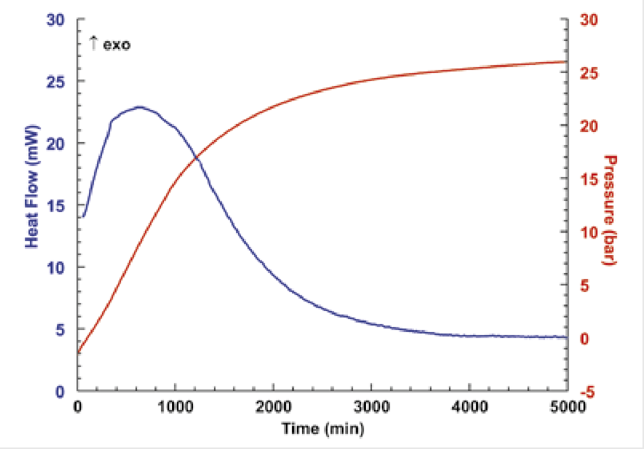
DTBP (Di-tert-butyl peroxide) is the commonly used standard substance to verify ARC operation. The plot shows the thermal runaway reaction of 20% DTBP in toluene, accompanied by the pressure increase after 600 min.



HWS test of 1.25 g 20% DTBP in toluene

3-Methyl-4-Nitrophenol

Nitrophenols were used until the 80s as herbicides, fungicides and insecticides. They can also be found in the soils of explosives manufacturing sites. Today they are suspected to be responsible for forest dieback.
3-methyl-4-nitrophenol isothermally measured shows the autocatalytic decomposition behavior with heat and pressure propagation.



Isothermal measurement at 180°C of 3 g 3-methyl-4-nitrophenol

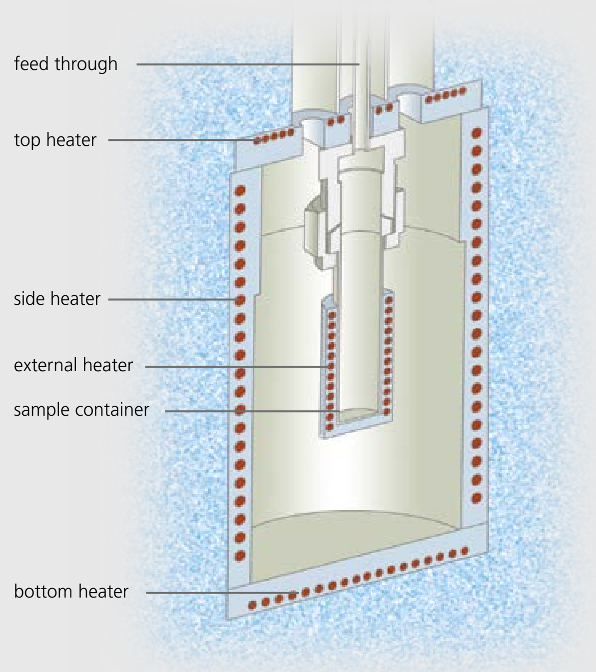
Key Features of the ARC Module

- Heat-Wait-Search tests for thermal runaway reactions
- Ramp mode for fast screening of unknown samples
- Pressure measurement
- Fast *VariPhi*®: scanning and isothermal modes allow the detection of exothermic and endothermic effects (optional)
- Stirring of the sample up to 350°C (optional)
- Injection of liquid samples during the measurement

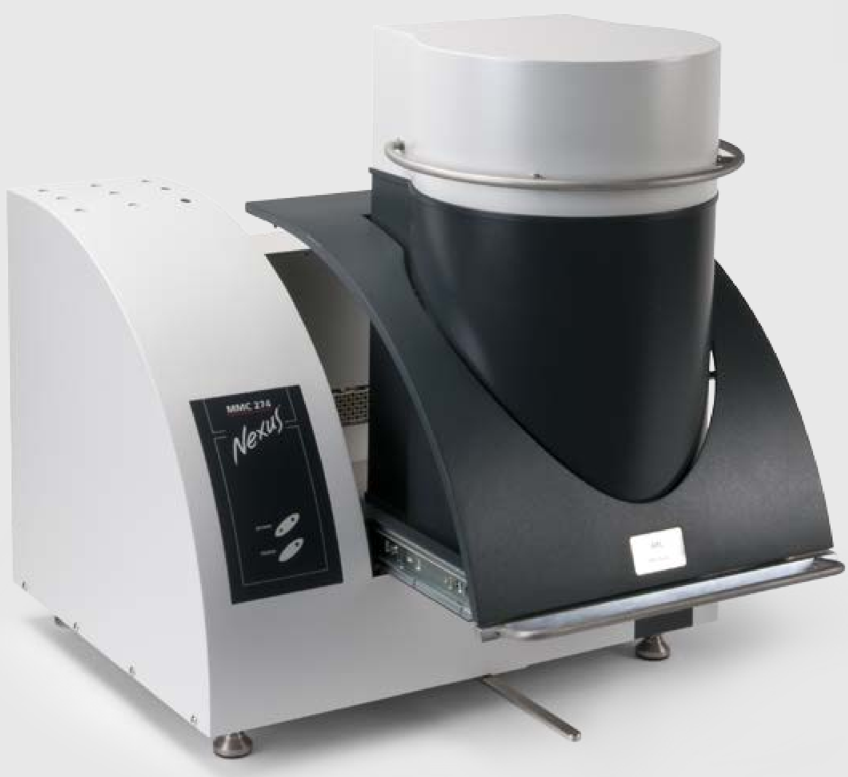
Sample Screening: The Scanning Module

Isothermal and Scanning Tests

Here, an additional heater is placed on the outside of the sample container. This allows for a defined power input and more accurate temperature control of the sample. The scanning module is useful for running isothermal and constant temperature ramp tests, especially in those experiments where reaction energies are higher.



Scanning Calorimeter Module

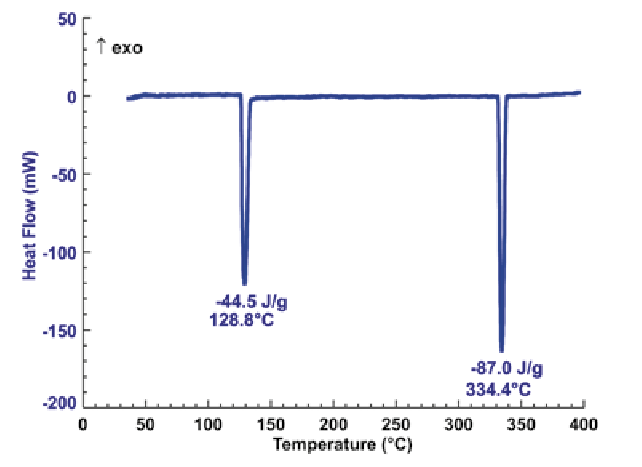


NETZSCH

Applications and Features of the Scanning Module

KNO_3

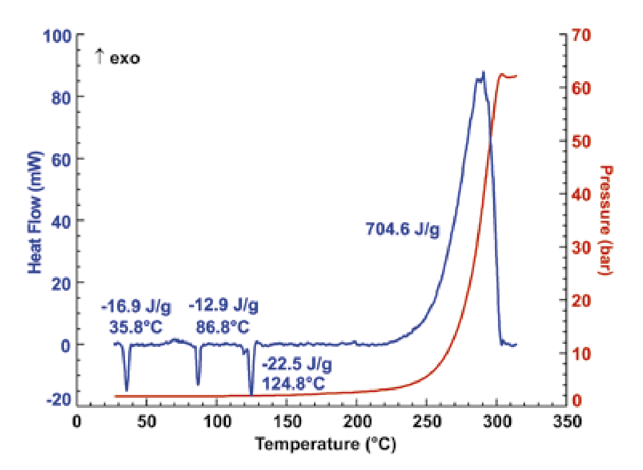
Potassium nitrate (KNO_3) is used for the synthesis of gunpowder (sulfur, charcoal and KNO_3). It is also used in food preservation (E252) and as an important potassium- and nitrogen-containing fertilizer.
The measurement was carried out in scanning mode with a constant power input of 200 mW. Two endothermal effects at 129°C (peak area of -45 J/g) and at 334°C (-87 J/g) are related to phase transitions.



DSC-like analysis of the phase transitions of 1.9 g KNO_3

ANFO

Ammonium nitrate fuel oil (ANFO) is a mixture of solid ammonium nitrate and fuel oil. Easy handling allows it to be used safely in mining, stone quarrying, and tunnel construction. The basic reaction during detonation is the decomposition of the hydrocarbon and the ammonium nitrate into CO_2, nitrogen and water. For this test a mixture of NH_4NO_3 and toluene was used. Three phase transitions (endothermal peaks) up to 150°C and the large exothermal decomposition peak starting at approx. 235°C can be detected.



Constant power measurement (200 mW) of 0.24 g ammonium nitrate and toluene

Sample containers of different materials and volumes

Key Features of the Scanning Module with External Heater

- Scanning mode as with DSC via constant heating rate or constant power
- Isothermal mode as with DSC
- Pressure measurement
- Stirring of the sample up to 350°C (optional)
- Injection of liquid samples during the measurement

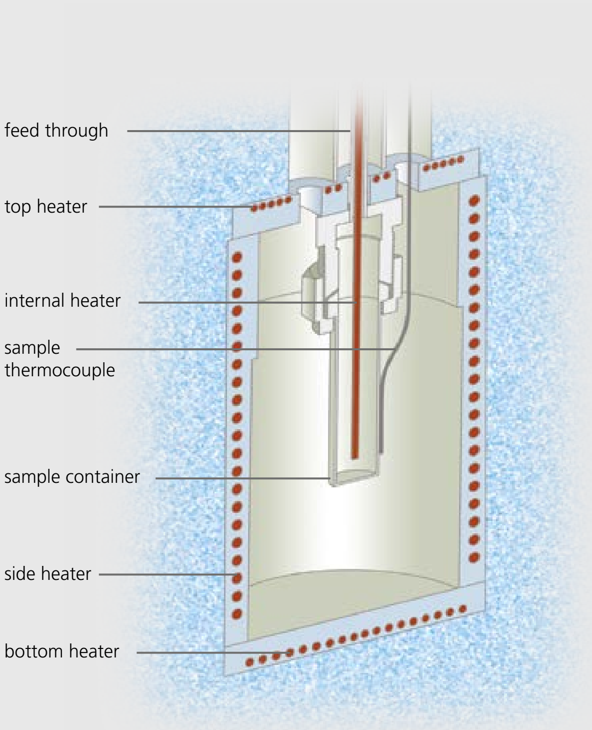
Unique: The Fast *VariPhi*® Module

Specific Heat and Low Φ-Factor

The basis of the fast *VariPhi*® module is an additional controlled variable DC heater which is in contact with the sample material (internal heater). With this module it is possible to measure specific heat directly. It also allows one to define the thermal inertia for real-world thermal environment by compensating for heat loss from the sample to the container. Sample containers absorb some of the energy from the reaction of the sample. The heat absorption of the container depends upon its mass and heat capacity. The sum of the heat capacities of the sample and the container divided by the heat capacity of the sample results in the Φ-factor. Ideally this value amounts to 1. In reality the Φ-factor is always larger than 1.

$$\Phi = 1 + \frac{m_c \times c_{p,c}}{m_s \times c_{p,s}}$$

m_c mass of the container
$c_{p,c}$ specific heat capacity of the container
m_s mass of the sample
$c_{p,s}$ specific heat capacity of the sample



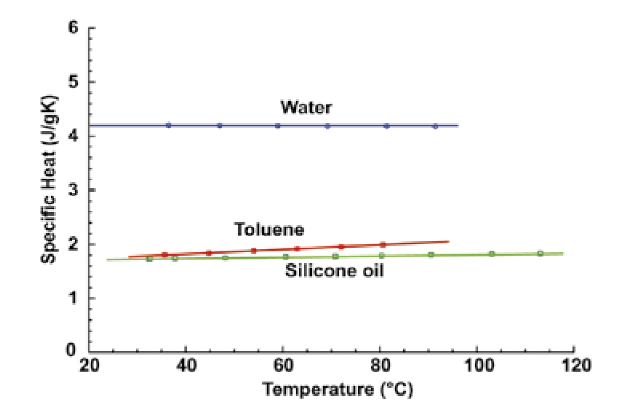
Fast *VariPhi*® Calorimeter Module (Internal Heater)

NETZSCH

Applications and Features of the Fast *VariPhi*® Module

Reliable Specific Heat

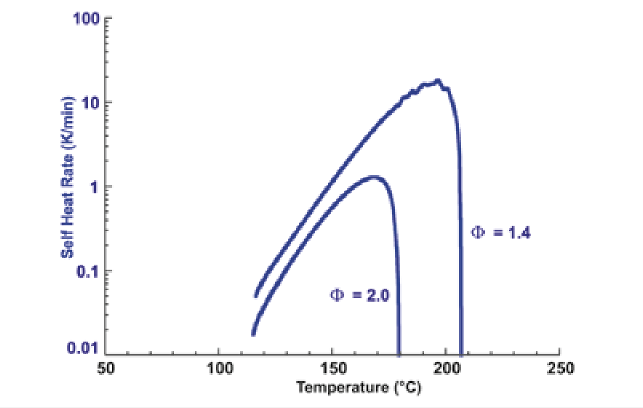
An advantage of the *VariPhi*® heater is the ability to easily determine c_p values of liquid and solid materials. Measured here are three liquids over a temperature range from room temperature to 90°C and 115°C.



Specific heat of water, toluene and silicone oil

Compensated Φ-Factor

The mass of the container can be completely compensated for when *VariPhi*® is used. This allows for either an adjusted Φ-factor – similar to the real reaction vessel of a plant – or for an ideal Phi factor close to the value of 1.



1.25 g 20% DTBP in toluene with varying Φ-factor

Key Features of the Fast *VariPhi*® Module

- Heat-Wait-Search tests for thermal runaway reactions
- Isothermal calorimetry for studying storage conditions/auto-catalytic reactions (iso-aging tests)
- Compensation for heat loss to the sample container during the test
- Thermal inertia or Phi (Φ) factor can be defined
- Specific heat can be measured as a function of time or temperature
- Endothermic transitions can be analyzed
- Scanning mode: reduction of the test time by 75% without loss of sensitivity
- Fire exposure mode: simulation of additional heat to the sample
- Stirring of the sample up to 350°C (optional)
- Injection of liquid samples during the measurement (optional)

Additional Information

www.netzsch.com/n13103

Coin Cell Characterization: The High Temperature Coin Cell Module

MMC 274 *Nexus*® and different modules

A New Module for MMC 274 *Nexus*®

The HT Coin Cell Module is a new calorimeter module for the MMC 274 *Nexus*® specially dedicated to coin cell battery studies. The instrument can be coupled with a fully featured battery analyzer. Data generated from the MMC test is merged seamlessly with the data generated from the cycler/ analyzer allowing for generation of battery and thermal data to be plotted on the same axis. The user can perform discharge tests to evaluate battery condition, cycle batteries to improve performance and gain insight into overall battery condition in an isothermal or temperature scanning mode.

Outstanding Value

- The only dedicated calorimeter for coin cell measurements up to 300°C
- Uses unique differential measuring principal for improved stability and sensitivity to capture even weak heat signals from coin cells
- Characterize coin cells as a whole to mimic cell performance in real world
- Easy to use and runs both isothermal charging/discharging method and scanning method for complete characterization of coin cells

Cross section of HT Coin Cell Module

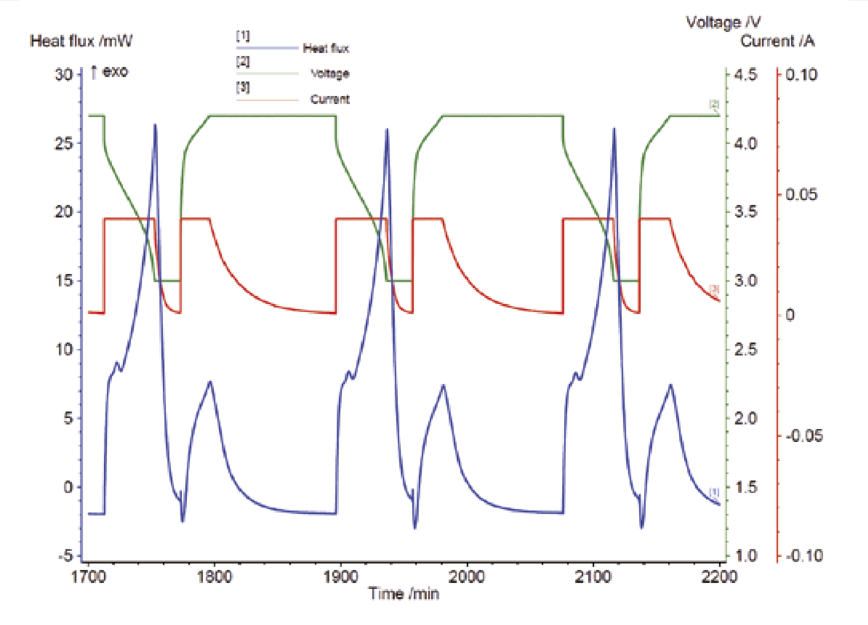
NETZSCH

Applications and Features with the High Temperature Coin Cell Module

Isothermal charging/discharging experiment

- Type of sample: Coin Cell LiR2032
- Isothermal mode with temperature set at 40°C
- Charging/Discharging cycle Constant current Constant voltage (CC-CV) – 40 mA from 4.2 V to 3.0 V

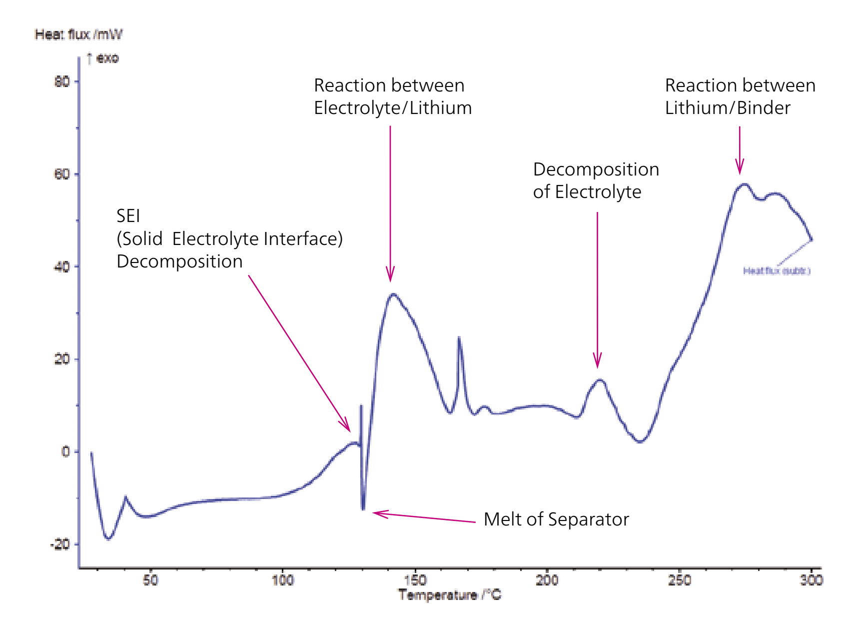
The data shows that charging is characterized by a short endotherm followed by a small exothermic reaction while discharging is characterized by a long exothermic reaction. Cycles are reliably repeatable.



Isothermal charging/discharging of LiR2032 coin cell

DSC Scanning experiment

Scanning data of a commercial coin cell LiR2032 from room temperature to 300°C at 1°C/min, showing multiple reactions during coin cell disintegration. It is evident that the exothermic SEI decomposition is followed by the melting of the separator at approximately 130°C (sharp endothermic event). This endotherm occurs nearly simultaneously with the bulk decomposition and reaction of the electrolyte, anode and cathode.



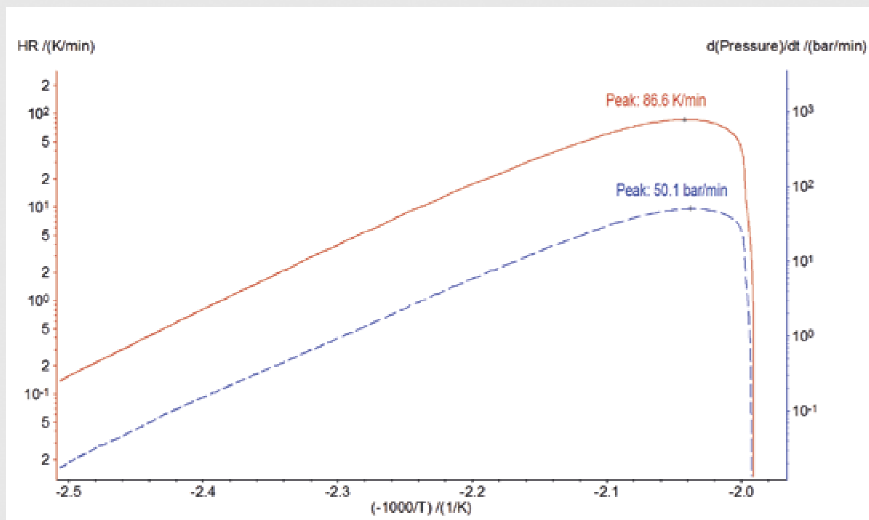
DSC measurement of a fully charged LiR2032 cion cell

Intelligent Software Solutions

Software Solutions for Your Applications

NETZSCH *Proteus*® Software

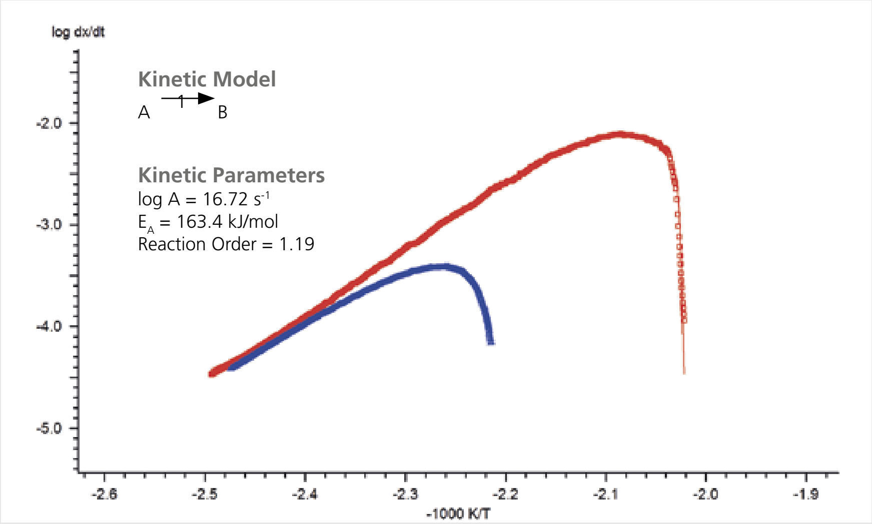
- Evaluation of characteristic temperatures and enthalpies
- ARC-specific presentation with heat generation rates or pressure development as examples



Self-heating rate and pressure increase rate for a solution of 20%-DTBP in toluene

Thermokinetics

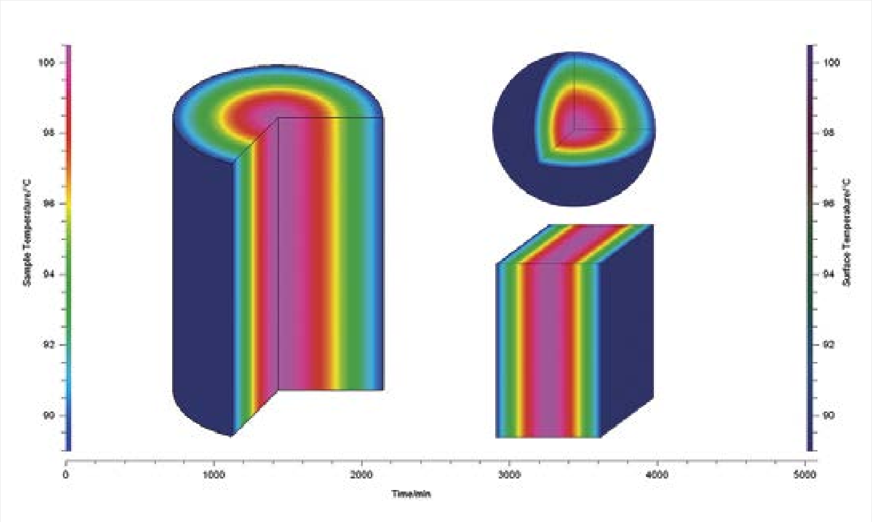
- Comprehensive kinetic analysis of multiple reaction steps
- Prediction of temperature and pressure changes for user-defined measurement and storage conditions



Comparison of measured data (symbols) and formal kinetic model (solid lines) for a single step reaction of 1st order, decomposition of hydrogen peroxide (H_2O_2)

Thermal Simulation

- Simulation of the temperature distribution in large reactor vessels of different geometries
- Knowledge of consequences for better process safety



Heat distribution for various container geometries (2200 min)

The NETZSCH Group is a mid-sized, family-owned German company engaging in the manufacture of machinery and instrumentation with worldwide production, sales, and service branches.

The three Business Units – Analyzing & Testing, Grinding & Dispersing and Pumps & Systems – provide tailored solutions for highest-level needs. Over 3,000 employees at 163 sales and production centers in 28 countries across the globe guarantee that expert service is never far from our customers.

When it comes to Thermal Analysis, Calorimetry (adiabatic & reaction) and the determination of Thermophysical Properties, NETZSCH has it covered. Our 50 years of applications experience, broad state-of-the-art product line and comprehensive service offerings ensure that our solutions will not only meet your every requirement but also exceed your every expectation.

www.netzsch.com/n13103

NETZSCH-Gerätebau GmbH
Wittelsbacherstraße 42
95100 Selb
Germany
Tel.: +49 9287 881-0
Fax: +49 9287 881 505
at@netzsch.com

www.netzsch.com

NGB · MMC 274 *Nexus*® · EN · 700 · 0414 · LH · Technical specifications are subject to change.