NETZSCH

Proven Excellence.

Multiple Module Calorimeter MMC 274 *Nexus*®

ARC, Scanning and Coin Cell Modules

Analyzing & Testing

Multiple Module Calorimeter

Synergy of Proven Methods

Scientists and engineers generally recognize that more product and process information can be obtained by multiple analytical methods rather than using a single technique. Different signals can be recorded, and superimposed sample effects can often be much better explained. The technique has to be reliable, fast and easy to use in everyday operations.

The NETZSCH Multiple Module Calorimeter MMC 274 *Nexus*® is an instrument which can be operated with different modules for the investigation of energetic materials and batteries (coin cells). It can be used in commercial R&D, universities and research centers and in QC/QA for various industries. The MMC is capable of the following on gram-size samples:

- Measurement of chemical reactions
- Measurement of phase changes
- Analysis of process safety
- Characterization of coin cells

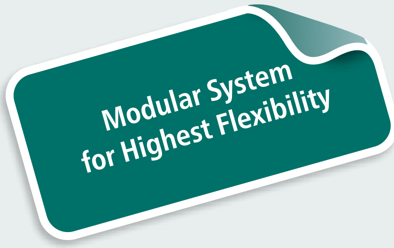
This allows for organic/inorganic multiphase mixtures testing. For these tests, the MMC 274 *Nexus*® can be equipped with three different calorimeter modules: ARC, Scanning and Coin Cell Module.

The MMC 274 Nexus® consists of two parts: the base unit with electronics and the interchangeable calorimeter modules for maximum flexibility.

MMC 274 *Nexus*® base unit with status indicator (left) for three interchangeable measuring modules (middle to right)

Advantages and Key Features of the MMC 274 Nexus®

- Multiple testing modes in one instrument to cover a wide application range:
  - 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
- Wide pressure range
- Various sample containers of different materials and volumes
- *Proteus*® software for complete evaluation of thermoanalytical data in one plot



ARC Module – Process Safety

The amount of energy released by a given chemical reaction has to be known in order to allow for safe and reliable processes. With the ARC (Accelerating Rate Calorimetry) Module, the worst case scenario can be studied at elevated temperatures without any heat loss to the environment.

ARC systems in accordance with ASTM E1981 have been widely used for decades to simulate the behavior of actual large-scale reactors. However, these instruments have a large footprint. In contrast, the MMC 274 *Nexus*® with ARC Module has a space-saving table-top design.

Typical ARC Applications

- Chemical process safety
- Thermal runaway (Heat-Wait-Search)
- Storage and transport studies
- Energetic material testing
- Effect of autocatalysis and inhibitors under exaggerated conditions

Scanning Module – Screening of High Reaction Enthalpies

The Scanning Module is the choice for more sophisticated applications. It can be used to analyze exo- and endothermal reactions with high energies. The module can be used for both solids and liquids.

Typical Scanning Applications

- Sample screening
- Isothermal tests
- Constant temperature ramp tests

Coin Cell Module – Battery Testing

The Coin Cell Module is specially dedicated to coin cell battery studies. Data generated from the MMC test is merged with data generated from the cycler/analyzer, allowing for battery and thermal data to be plotted on the same axis.

Typical Coin Cell Applications

- Characterization of coin cells as a whole to mimic cell performance in the real world
- Amount of heat released or absorbed during chemical changes
- Charging/discharging
- Rate of energy change
- Efficiency

Thermal runaway scenarios can be understood by investigating the runaway reaction. Questions arise which can be answered by means of measurements under adiabatic conditions. For this purpose, the NETZSCH MMC 274 *Nexus*® can be configured with the ARC Module, which can also be equipped with *VariPhi*®.

Process Safety

A chemical reaction is said to be 'runaway' when its own heat production rate is higher than heat losses.

What is the thermal behavior of the material?

What is the thermal hazard potential of the material?

At what temperature does the reaction occur (onset)?

What is the enthalpy of reaction?

What is the Time-to-Maximum Rate (TMR)?

What is the rate of temperature and pressure change?

How does the material behave within a given time frame; e.g., 24 h?

What maximum temperature can be expected under adiabatic conditions?

What is the temperature of no return?

What are the kinetic parameters?

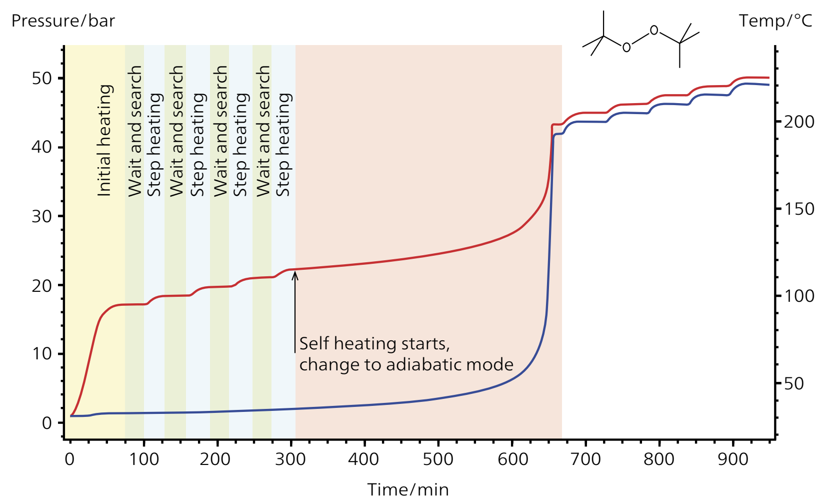
The ARC Module

Heat-Wait-Search Test

During a Heat-Wait-Search (HWS) test, the sample is heated to a defined temperature (HEAT) and the system is allowed to settle at this temperature (WAIT). The system then checks whether any temperature rise has occurred that stems from the sample itself (SEARCH). If no rise is detected, the procedure starts again by heating to a higher temperature.

In cases where a thermally induced exothermal reaction starts and the self-induced temperature increase of the sample exceeds a predefined value (threshold), the system continues to track the temperature change of the sample.

After the exothermal reaction is finished, the system returns to the HWS operation until either the next exothermal effect is detected or the measurement has completed by means of having reached the maximum temperature (predefined in the software).



HWS test on 20% di-tert-butyl-peroxide (DTBP) in toluene. For the investigation of self-heating behavior, the measurement can include isothermal segments or temperature ramps.

Key Technical Data for the ARC Module	
Temperature range	RT to 500°C
Temperature readability	0.01 K
Heating rate	0 to 5 K/min 0 to 2 K/min with *VariPhi®*
Pressure limit	150 bar
Pressure readability	0.01 bar
Sample Container volume	0.1 to 8.5 ml
Container	Stainless steel, Inconel, Hastelloy, glass inlet
Tracking rate	Up to 50 K/min

The ARC Module – Simulation of the Worst Case Scenario

The best way to understand worst case scenarios is to investigate runaway reactions under adiabatic conditions, which means no heat exchange occurs with the sample's environment.

The ARC Module is able to minimize heat loss from the sample container by maintaining the temperature of the surroundings equal to that of the sample temperature.

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

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.

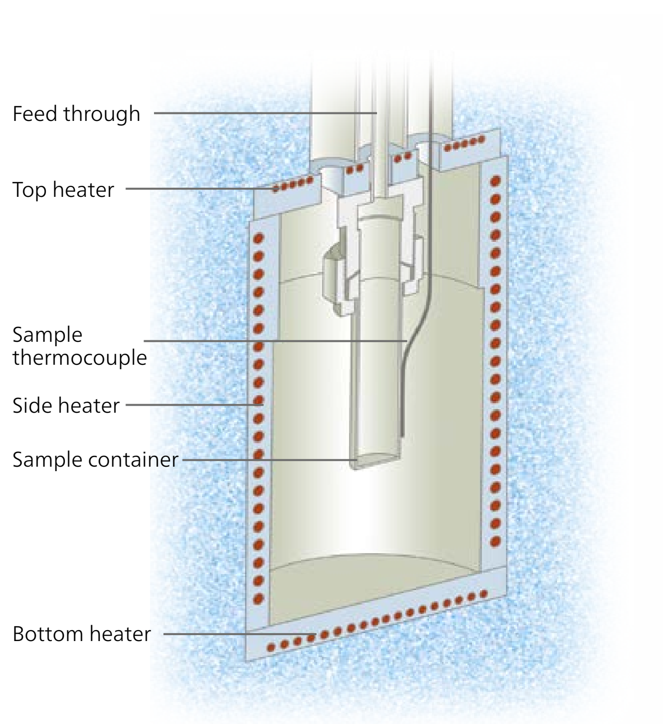
Usually, the sample container has a volume of between 0.1 ml and 8.5 ml.
The tracking rate can be allowed up to 50 K/min. Pressures of up to 150 bar can be detected.

Isothermal Aging

It is possible to investigate the sample behavior at a constant temperature using the Iso-Fixed or Iso-Track Mode.

ARC Module – Key Features

- Heat-Wait-Search tests for thermal runaway reactions
- Pressure measurement
- *VariPhi®* (optionally upgradable, see page 7)
- Solid and liquid samples
- Isothermal aging



ARC Module

ARC Module with VariPhi® – Determination of Reaction Enthalpies

VariPhi® is an additional controlled variable DC heater which is in contact with the sample material (internal heater). It allows for the definition of thermal inertia for a real-world thermal environment by compensating for heat loss from the sample to the container.

Since both the sample and the container are under adiabatic conditions, the heat generated by the sample causes not only an increase in its own temperature but also in that of the container.

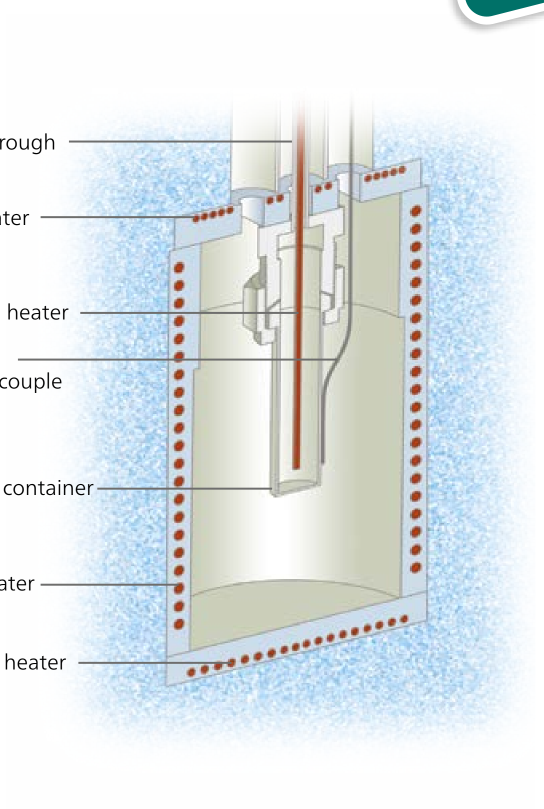
The sample container absorbs some of the energy from its own reaction depending upon its mass and heat capacity.

On a small scale, the thermal mass of the reactor vessel is usually a much larger fraction of the total thermal mass than for large-scale operation. This is taken into account by the sum of the heat capacities of the sample and the container divided by the heat capacity of the sample, which results in what is known as the Φ-factor:

$$\Phi = \frac{T_{ad}}{T_{obs}} = 1 + \frac{m_v \cdot C_{p,v}}{m_s \cdot C_{p,s}}$$

T_{ad} adiabatic
T_{obs} observed
m_v mass of the vessel
m_s mass of the sample
$c_{p,s}$ specific heat capacity of the sample
$c_{p,v}$ specific heat capacity of the vessel

Ideally, the Φ-factor amounts to 1.
In reality, the Φ-factor is always larger than 1.



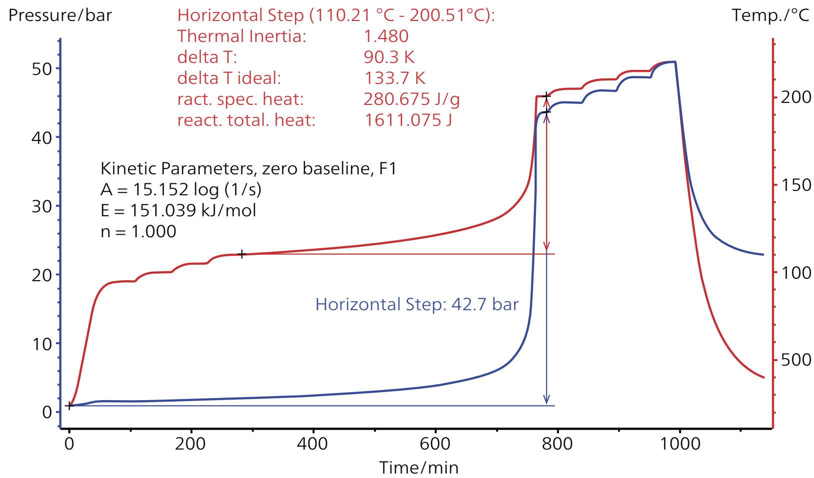
ARC Module with optional *VariPhi®* (internal heater)

Key Features of the ARC Module with *VariPhi®*

In addition to the key features of the ARC Module:

- Compensation for heat loss to the sample container during the test
- Influence of thermal inertia or Φ factor: Scanning and isothermal modes allow for the detection of exo- and endothermic effects
- Scanning mode: Screening to reduce the testing time by 75%
- Fire exposure mode: Simulation of additional heat to the sample

Self-Decomposition Behavior of DTBP in Toluene



Heat-Wait-Search test on 5.74 g of 20% di-tert-butyl-peroxide (DTBP) in toluene in a spherical titanium vessel (mass 10.028 g); exothermal threshold 0.02 K/min, thermal inertia: 1.48

This example shows a test investigating the self-decomposition behavior of DTBP in toluene. At 110°C, heat production from the sample's self-decomposition exceeded the exothermal threshold of 0.02 K/min. Due to this, the HWS mode was changed to an adiabatic mode.

The calorimeter heaters were then tracking the sample temperature. Due to the tracking, the sample temperature and temperature of the surrounding calorimeter were identical and both heat flow and heat loss were avoided. The observed temperature rise of the self-decomposition was evaluated to be 90.3 K. Taking thermal inertia into account, the adiabatic temperature rise was calculated to be 133.7 K.

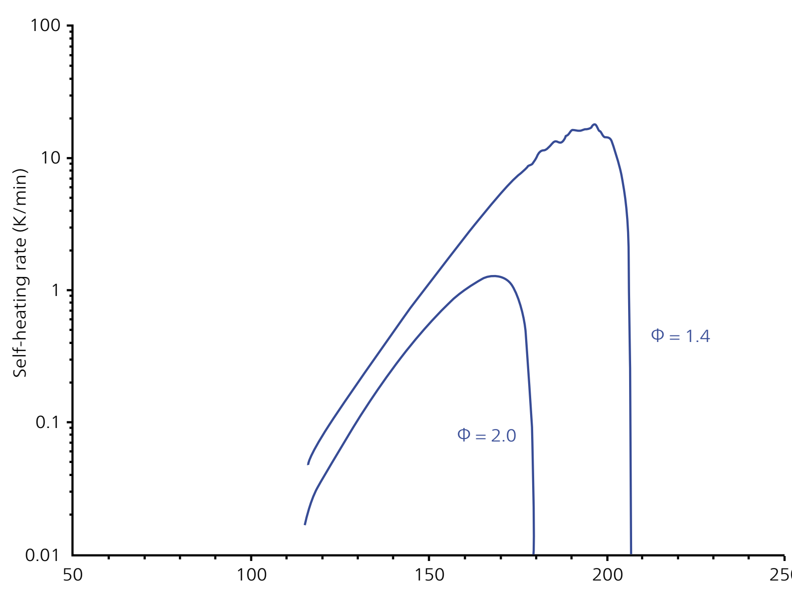
Knowing the specific heat of all of the components allows for determination of the heat of reaction.

The pressure associated with the decomposition reaction was measured to be 42.7 bar. Using a single-step 1st order decomposition mechanism, both the pre-exponential factor and the activation energy can be calculated.

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 Φ-factor close to the value of 1.

This plot shows measurements on 1.25 g of 20% DTBP in toluene with two different Φ-factors. At a Φ-factor of 1.4, the self-heating rate increased by more than one magnitude over what is seen with a Φ-factor of 2.0.



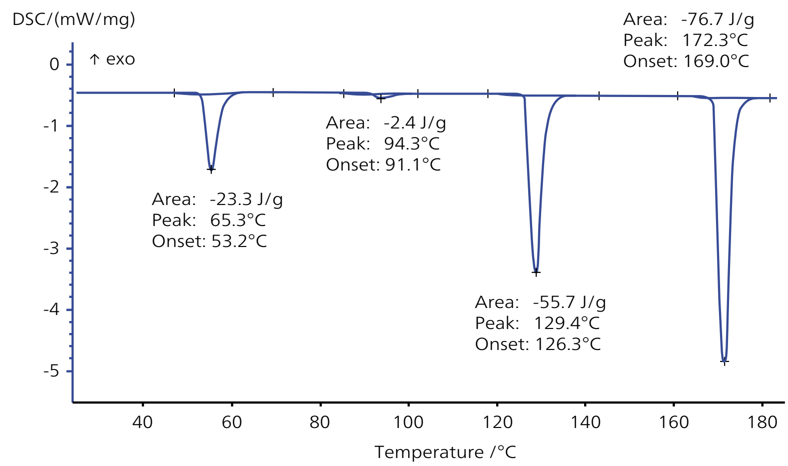
Adjustment of the Φ-factor

MMC with ARC Module in Comparison with Ordinary Differential Scanning Calorimetry (DSC) Tests

Ammonium Nitrate (NH_4NO_3)

DSC Investigation

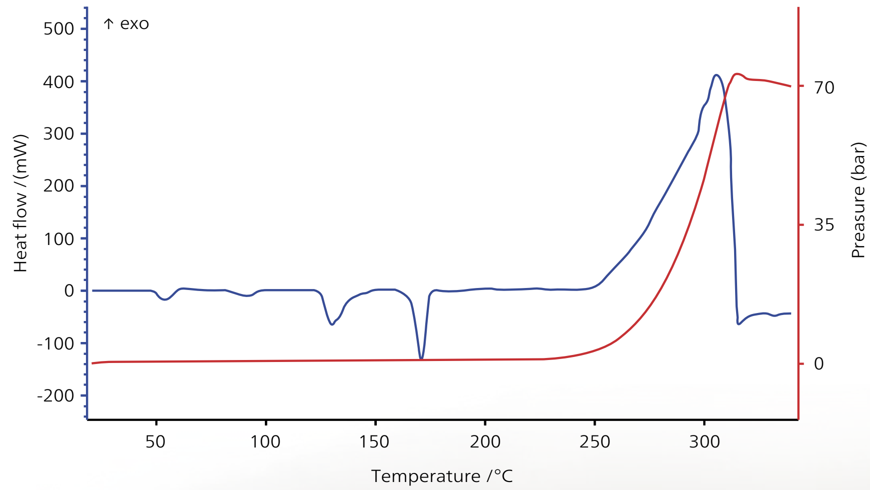
With standard DSC measurements, endo- and exothermal effects are monitored under isothermal or increasing temperature at atmospheric pressure. Usually, the measurement is carried out and evaluated up to the point at which the material melts. The sample is placed in an open crucible or sealed in an aluminum pan with a pierced lid.



DSC 204 ***F1*** *Phoenix*® measurement on NH_4NO_3 up to 200°C. The sample undergoes three endothermal solid-solid phase transitions followed by melting at 169°C (onset). With increasing temperature after melting, the material will thermally decompose.

Typical MMC Measurements with ARC Module

MMC measurements allow for monitoring a sample's behavior into the decomposition. In contrast with DSC tests, these kinds of measurements are performed in sealed vessels. Decomposition occurs as an exothermal reaction. This is also unlike DSC, in which an endothermal reaction is recorded using an open crucible.



ARC Module with *VariPhi*® plot of NH_4NO_3 with heat flow and pressure versus time

Understanding exothermic reactions is essential for safe processing, storage and transport of chemicals and systems.

The Scanning Module

Screening of Solids and Liquids – Even in Isothermal Tests

The Scanning Module has an additional heater which is positioned on the outside of the sample container. This allows for a defined input of power in order to be able to separate endo- and exothermal effects.

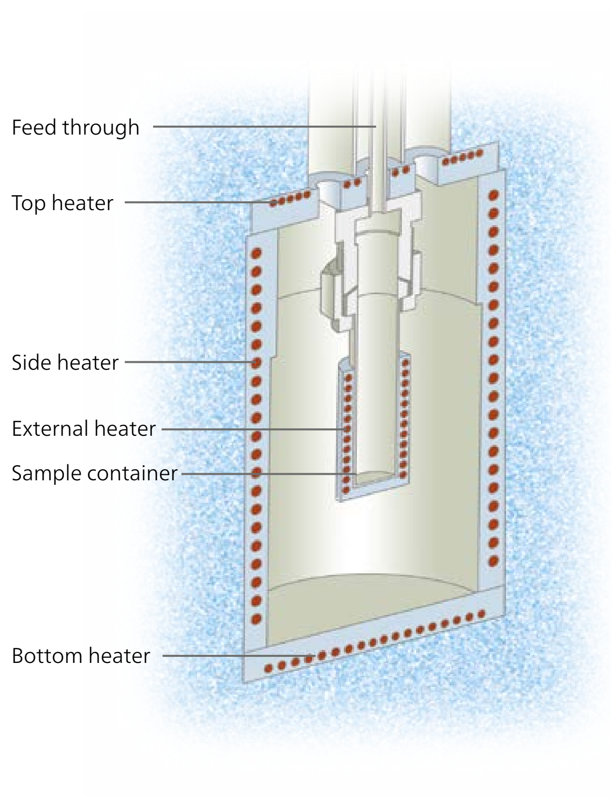
The Scanning Module is useful for running isothermal and constant temperature ramp tests, especially in experiments where reaction energies are higher.

The Scanning Module is especially suitable for small masses of highly energetic samples.

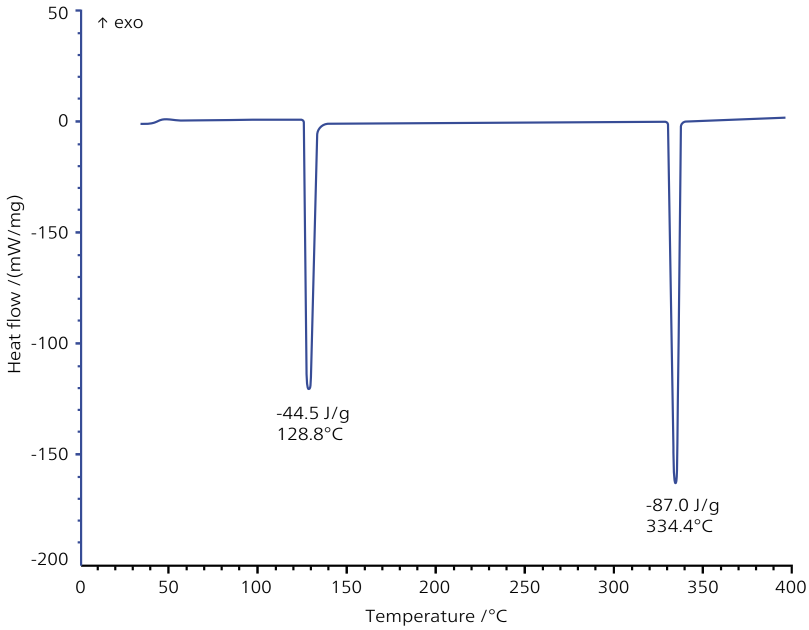
Key Technical Data for the Scanning Module	
Temperature range	RT to 500°C
Temperature readability	0.01 K
Heating rate	0 to 5 K/min
Pressure limit	150 bar
Pressure readability	0.01 bar
Sample container volume	2.6 ml
Container	Stainless steel, Inconel, Hastelloy, glass inlet
Tracking rate	Up to 50 K/min

Scanning Module – Key Features

- Scanning mode via constant heating rate or constant power
- Isothermal mode
- Determination of endothermal and exothermal enthalpies
- Pressure measurement
- For liquids and solids
- Inhomogeneous samples
- Higher sample masses
- Shorter test times than for Heat-Wait-Search tests



Scanning Module with external heater



Measurement on potassium nitrate using the Scanning Module

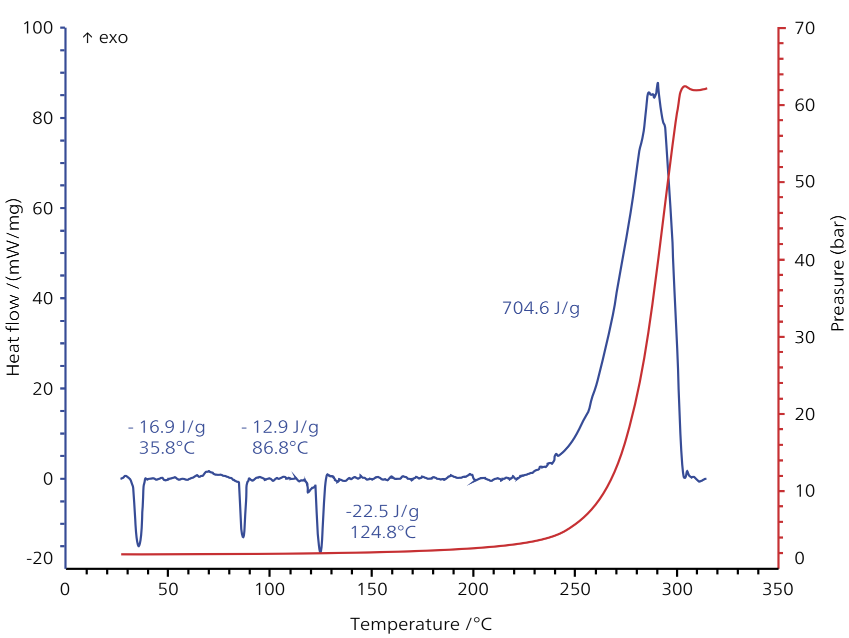
Potassium Nitrate (KNO_3)

Besides sulfur and charcoal, KNO_3 is used for the synthesis of gunpowder. It is also used in food preservation (E252) and as an important potassium- and nitrogen-containing fertilizer.

This 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.

Redox reactions that occur rapidly with the production of gases (e.g., nitrogen) are often explosive.

$$52\ NH_4NO_3(s) + C_{17}H_{36}(l) \longrightarrow 52\ N_2\ (g) + 17\ CO_2\ (g) + 122\ H_2O\ (g)$$



Measurement with Scanning Module on an ANFO sample

NH_4NO_3 Fuel Oil (ANC)

ANC is a mixture of solid ammonium nitrate (NH_4NO_3) and fuel oil. It can be safely used in mining, stone quarrying, and tunnel construction. The basic reaction during detonation is the decomposition of the hydrocarbon and the NH_4NO_3 into CO_2, N_2 and H_2O.

For this test, a mixture of NH_4NO_3 and toluene was used. Prior to 150°C, three endothermal phase transitions were observed. For the large exothermal decomposition, an energy release of 705 J/g was detected starting at approx. 235°C.

Coin Cell Module

Advantages of the Coin Cell Module

- No special sample preparation required
- Analysis of the behavior of a complete coin cell instead of individual components
- Merging of heat generation data with battery data (current, voltage, power)
- Charging and discharching of the coin cell
- Simple interface to a cycler unit

Heat Signature as Key Information for Battery Development & Testing

Specifically, an understanding of the heat generation during charging/discharging cycles is crucial for improving the cell efficiency, performance and lifetime of batteries.

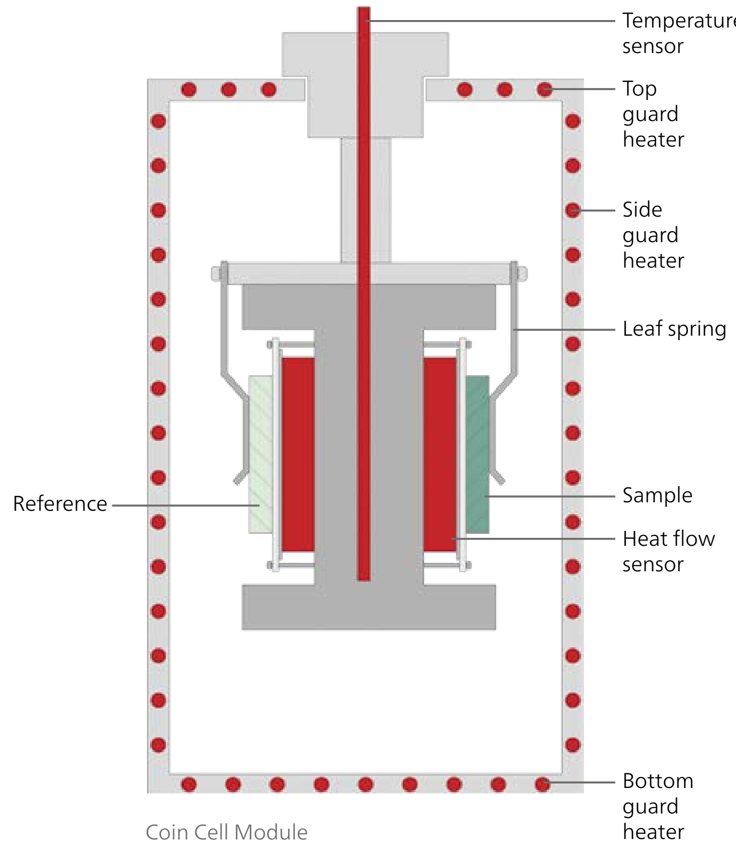
Measuring the heat signature of coin cells during cycling provides insight into the underlying processes and provides a quantitative way of comparing changes in chemistry above and beyond current and voltage measurements.

Some of these processes are reversible, some occur during the initial few cycles, and others take place over a period of weeks, months, or even years. The amount of heat released or absorbed during all these physico-chemical changes and the rate of energy change within the coin cell provide additional pieces of the puzzle and can accelerate the development process.

The Coin Cell Module

The Coin Cell Module is specially designed for coin cell battery studies. The instrument can be connected with a fully featured battery analyzer. Data generated by the MMC test is merged with data generated by the cycler/analyzer, allowing battery and thermal data to be plotted on the same axis.

The user can perform charge/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.



Coin Cell Module

Coin Cell Module – Superior Performance via Quality Engineering

Key Technical Data for the Coin Cell Module	
Temperature range	RT to 300°C
Temperature readability	0.01 K
Heating rate	0 to 5 K/min
Coin cell size	▪ Typically CR2032 ▪ Diameter: 5 to 25 mm ▪ Thickness: 1 to 5 mm
Operation modes	▪ Isothermal ▪ Constant heating rate
Number of sample cell/reference cell	1/1

Innovative and Robust Coin Cell Module for High-Quality Tests

Outstanding Value of the Coin Cell Module

- The only calorimeter specifically designed for coin cell measurements
- Unique differential measuring principle for improved stability and sensitivity; captures even weak heat signals from coin cells
- Characterization of coin cells as a whole to mimic cell performance in the real world
- Easy operation
- Complete characterization of coin cells by the following methods:
  - Isothermal charging/ discharging
  - Scanning tests

Cross section of the Coin Cell Module

Connection to an External Cycler Made Simple

The Coin Cell Module for MMC 274 *Nexus*® is designed to be connected to a battery charger/analyzer through a LEMO connector located on the right side of the instrument's hood.

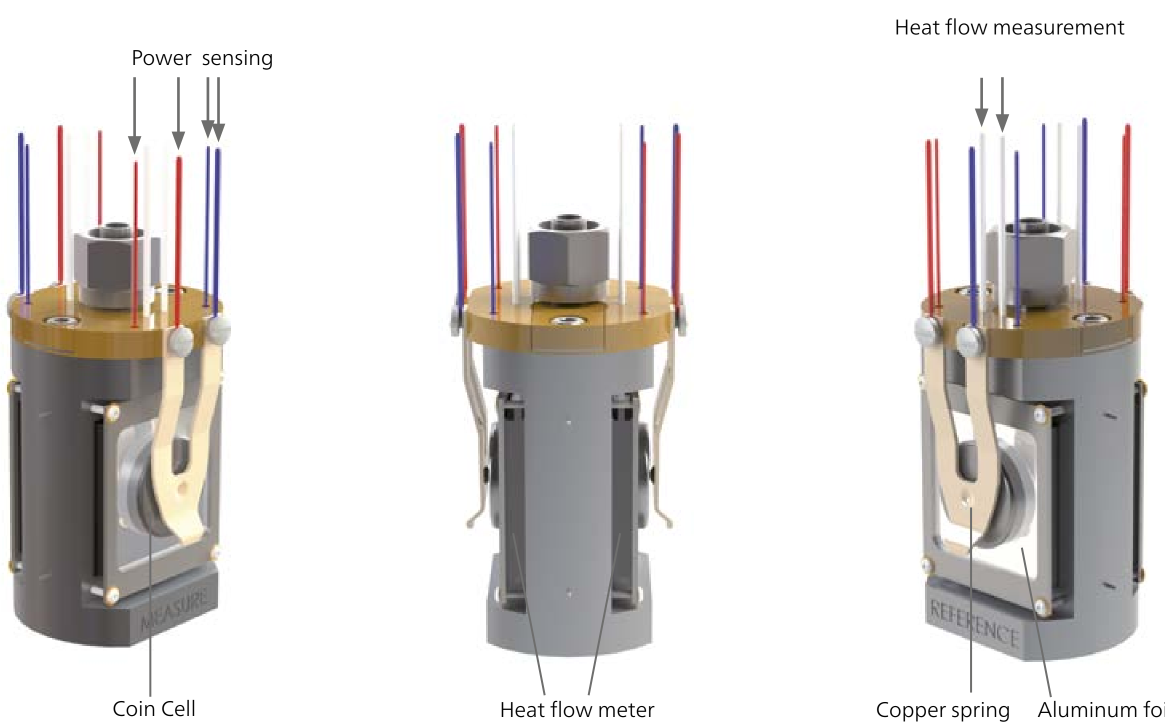
Four wires are used to charge and discharge the coin cell; two are for providing electrical power and two are for measuring the exact voltage at the coin cell. Charging/discharging can be handled on both sides of the sensor, and data coming from the battery charger can easily be imported into the *Proteus*® analysis software for combined analysis.

Coin Cell Sensor

The key component of this module is the sensor. It features an innovative differential measurement design based on thermopiles for improved sensitivity and stability in heat-flow measurements. The calorimetric block is equipped with a Resistance Temperature Device (RTD) in order to precisely monitor and control its temperature using the surrounding furnace.

When the coin cell releases or absorbs any heat due to charging/ discharging or internal physical changes, this heat is detected by the sensor. To nullify the effect of external disturbances, the signal coming from the reference heat flow meter is subtracted from the signal detected by the sample heat flow meter, thus yielding a true differential measurement. This technique is much more accurate and sensitive than that of a single-sensor system.

The module carries out efficiency tests for coin cells.



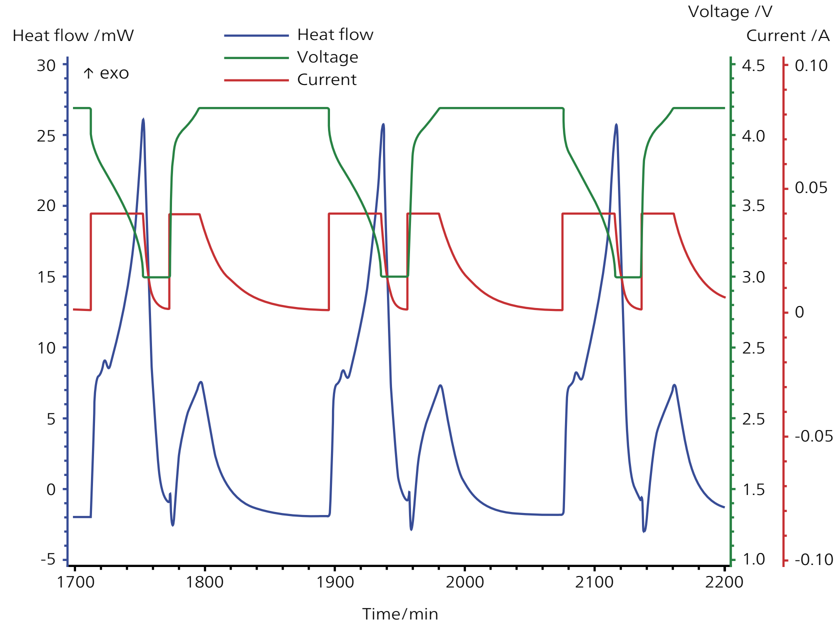
Lithium Coin Cell

Test parameters of the measurement on the Li coin cell:

- 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

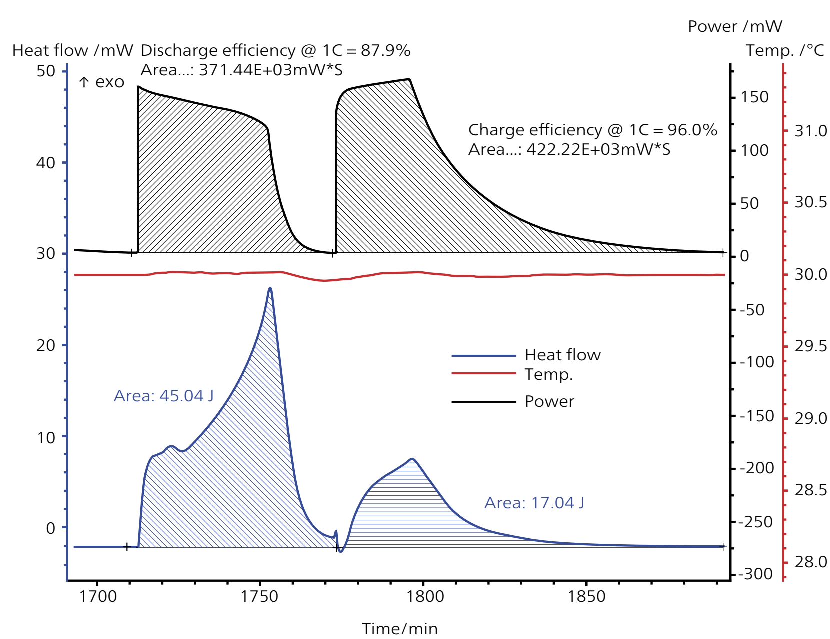
The measurement curves (upper plot) show the exothermal signature of the LiR2023 during three cycles of discharging and charging.

The efficiency is calculated by dividing the electrical energy by the total energy (electrical energy + heat flow) during discharging and charging (lower plot).



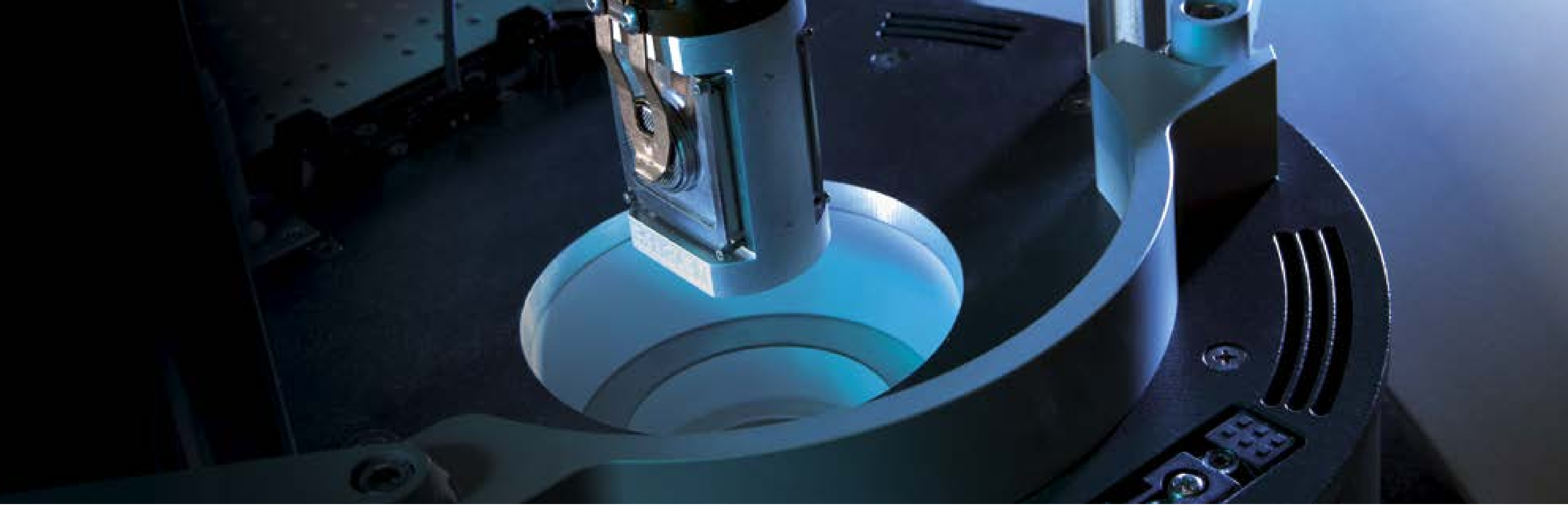
Three isothermal cycles of discharging and charging of an LiR2023 coin cell

Calculation of efficiency



The same data was used to calculate the cell efficiency during discharging and charging

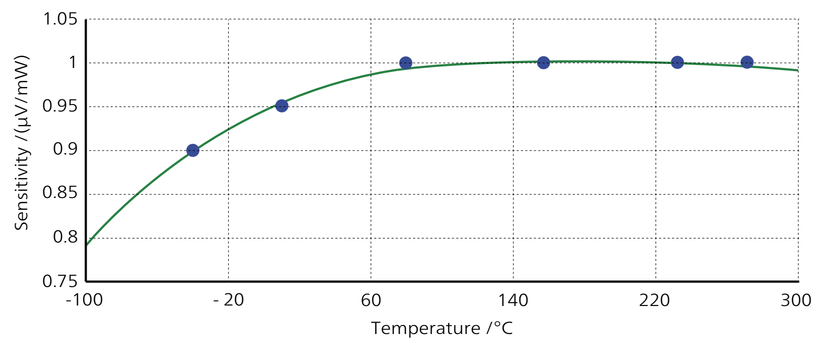
Empty coin cell cases for the Coin Cell Module



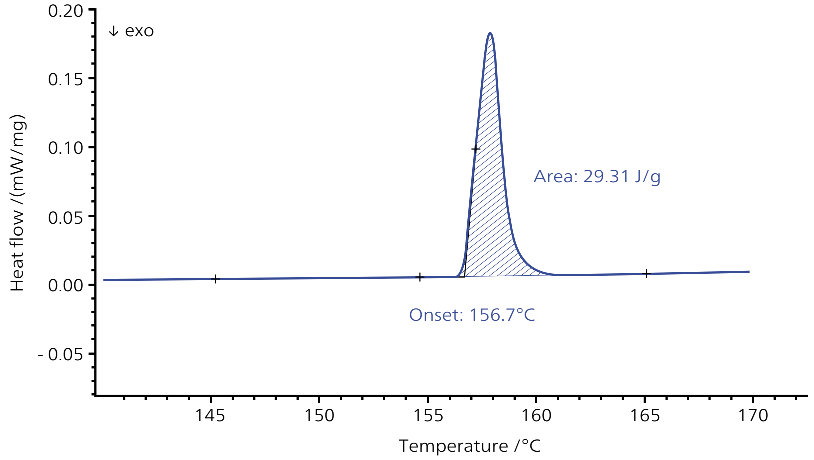
Calibration of the Coin Cell Module

Temperature and Enthalpy Calibration Over the Entire Temperature Range

For calibration of the Coin Cell Module, NETZSCH offers a calibration set containing four reference materials. The lower plot shows a measurement on indium. The peak area and onset temperature for the melting effect are in good correlation with literature data. Enthalpy and temperature calibration is achieved through evaluation of all measurement files for the reference materials – a calibration polynomial is created by the software.



Enthalpy calibration polynomial



Calibration run on indium between 140°C and 170°C


NETZSCH Thermokinetics
Curing of Epoxy Resin
Heat flow rate/(W/g)
20.4 K/min
10.1 K/min
5.0 K/min
Temperature/°C

Expertise in Service

Our Expertise – Service

All over the world, the name NETZSCH stands for comprehensive support and expert, reliable service, before and after sale. Our qualified personnel from the technical service and application departments are always available for consultation.

In special training programs tailored for you and your employees, you will learn to tap the full potential of your instrument.

To maintain and protect your investment, you will be accompanied by our experienced service team over the entire life span of your instrument.

Summary of Our Services

- Installation and commissioning
- Hotline service
- Preventive maintenance
- On-site repairs with emergency service for NETZSCH components
- Moving / exchange service
- Technical information service
- Spare parts assistance

Our Expertise – Applications Laboratories

The NETZSCH Thermal Analysis Applications Laboratories are a proficient partner for thermal analysis issues. Our involvement in your projects begins with painstaking sample preparation and continues through meticulous examination and interpretation of the measurement results. Our measuring methods are state-of-the-art.

Customers of our laboratory services stem from a wide range of large companies in industries such as chemical, automotive, electronics, air/space travel, racing, and polymer and ceramics.

Commercial Testing

Within the realm of thermal analysis and thermophysical properties, we offer you a comprehensive line of the most diverse thermal analysis techniques for the characterization of materials (solids, powders and liquids). Measurements can be carried out on samples of the most varied of geometries and configurations.

Consult with the experts in our applications laboratories to choose the best-suited measuring method for your specific needs.

You will be working with scientists (physicists, chemists, materials scientists) possessing consolidated knowledge about the most varied of methods and materials spectra.

The NETZSCH Group is an owner-managed, international technology company with headquarters in Germany. The Business Units Analyzing & Testing, Grinding & Dispersing and Pumps & Systems represent customized solutions at the highest level. More than 3,700 employees in 36 countries and a worldwide sales and service network ensure customer proximity and competent service.

Our performance standards are high. We promise our customers Proven Excellence – exceptional performance in everything we do, proven time and again since 1873.

When it comes to Thermal Analysis, Calorimetry (adiabatic & reaction), the determination of Thermophysical Properties, Rheology and Fire Testing, 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.

Proven Excellence.

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