

## Multiple Mode Calorimetry

Various Modules in One Calorimeter



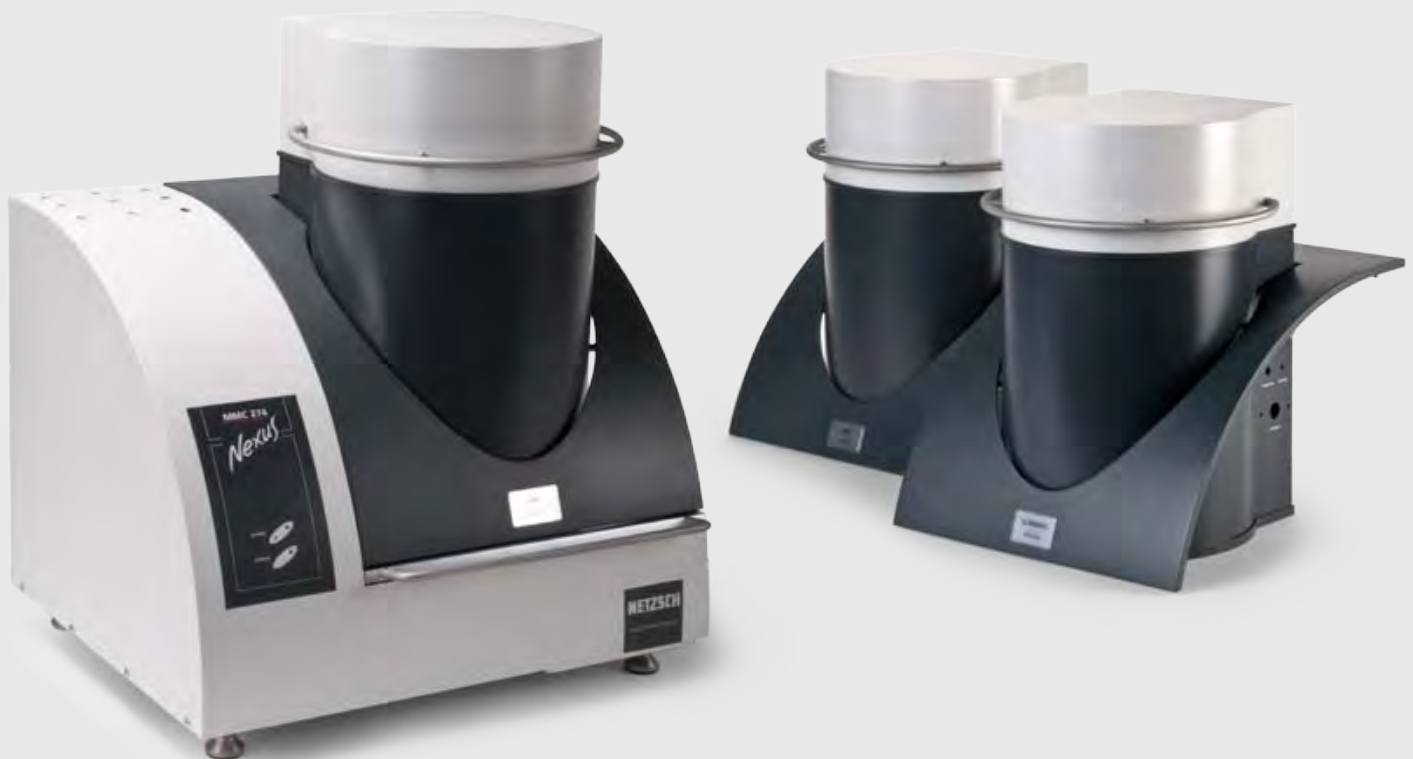
# Multiple Mode Calorimetry – Synergy of Proven Methods

## 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. The MMC successfully creates the synergy of two well-proven methods, DSC and ARC.



MMC 274 Nexus®  
Base unit with two additional calorimeter modules

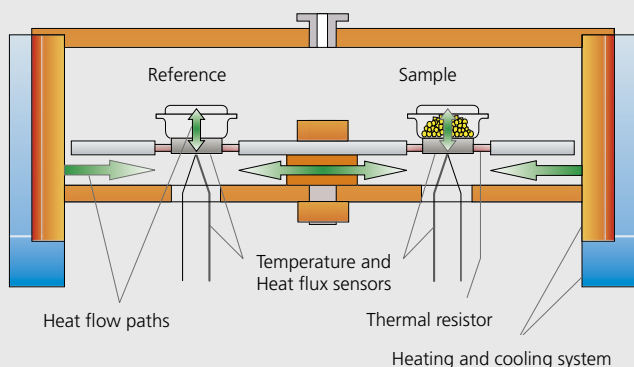
## Differential Scanning Calorimetry

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



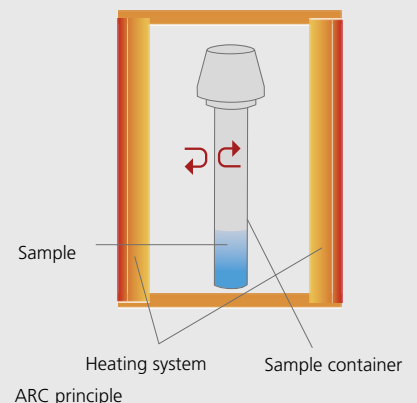
DSC principle

## Adiabatic Reaction 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 Adiabatic Reaction 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



ARC principle

# Multi Module Calorimeter MMC 274 *Nexus*<sup>®</sup>



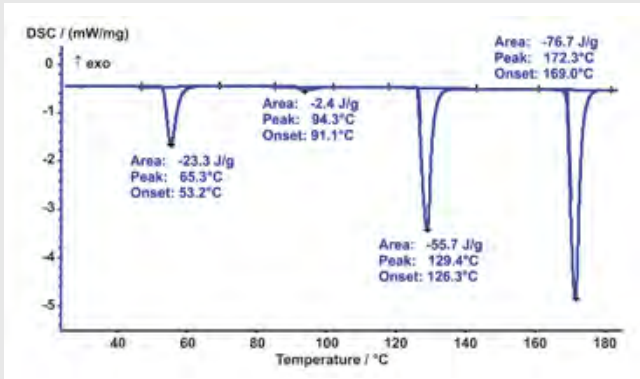
## Modular System

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

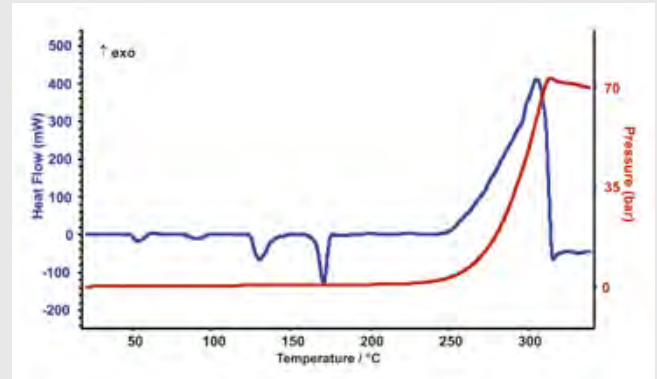
Exchangeable calorimeter modules are available for different applications. ARC modules can be used for standard process safety work. External heater and *VariPhi*<sup>™</sup> modules can be employed for more sophisticated measurements.

### General Technical Specifications of MMC 274 *Nexus*<sup>®</sup>

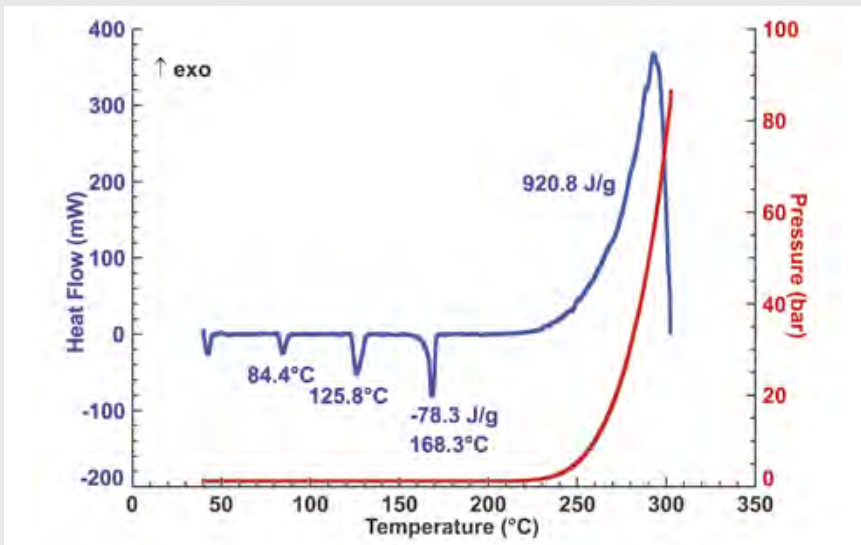
Temperature range	25°C to 500°C
Temperature readability	0.01 K
Heating rate	0 to 2 K/min
Pressure range	0 to 100 bar
Pressure readability	0.01 bar
Sample container volume	0.1 ml to 2.5 ml
Tracking rate – fast module	up to 250 K/min
Tracking rate – standard module	up to 50 K/min
Sensitivity tracking rate	down to 0.002 K/min (depending on temperature range)
Sensitivity heat flow	isothermal: 25 $\mu$ W/g, dynamic: 250 $\mu$ W/g
Options	injection, stirring (max. 350°C), specific containers



DSC plot of  $\text{NH}_4\text{NO}_3$  with evaluated temperatures and enthalpies



ARC plot of  $\text{NH}_4\text{NO}_3$  with endothermal effects, heat flow and pressure



Ammonium nitrate shows solid-state phase transitions and melting as well as the decomposition behavior. These tests are crucial for safety studies on such highly energetic materials.

MMC plot of  $\text{NH}_4\text{NO}_3$  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
  - Adiabatic mode with Heat-Wait-Search for process safety tests
- Wide temperature range up to 500°C
- Wide pressure range up to 100 bar (10 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 thermoanalytical data in one plot
- Exchangeable calorimeter modules in one table-top instrument
  - ARC module for safety testing
  - External sample heater module for scanning tests as with DSC
  - VariPhi™ module for fire exposure tests, specific heat, endothermal effects

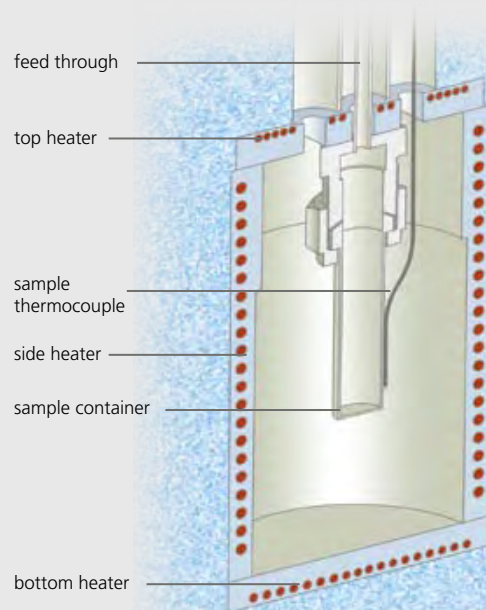
# Process Safety: The ARC Module

## Heat-Wait-Search and Pressure Tests

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

Depending on the operating mode, the surroundings of the tube vessel 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.



Accelerating Rate Calorimeter Module

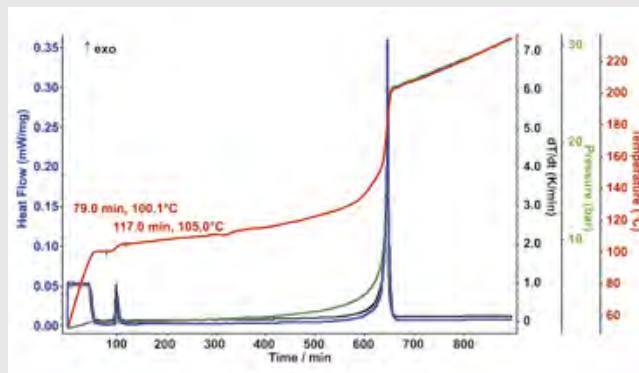
### Wide Range of Applications

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

## Applications and Features with the ARC Module

### DTBP

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

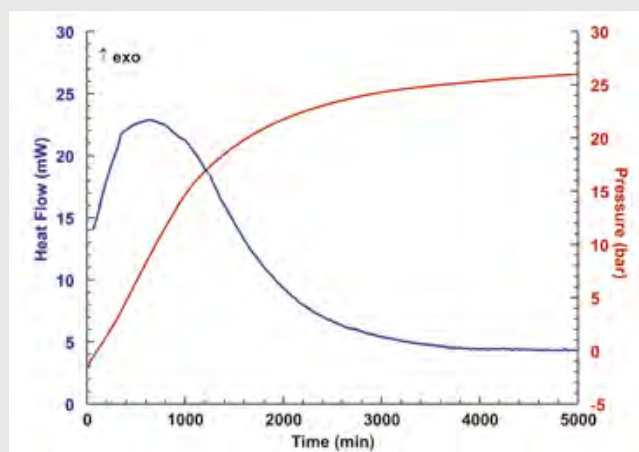


HWS test of 1.25 g  
20% DTBP in toluene

### 3-Methyl-4-Nitrophenol

Nitrophenols were used until the 80s as herbicides, fungicides and insecticides. They can also be found in the soil of explosives manufacturers. 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



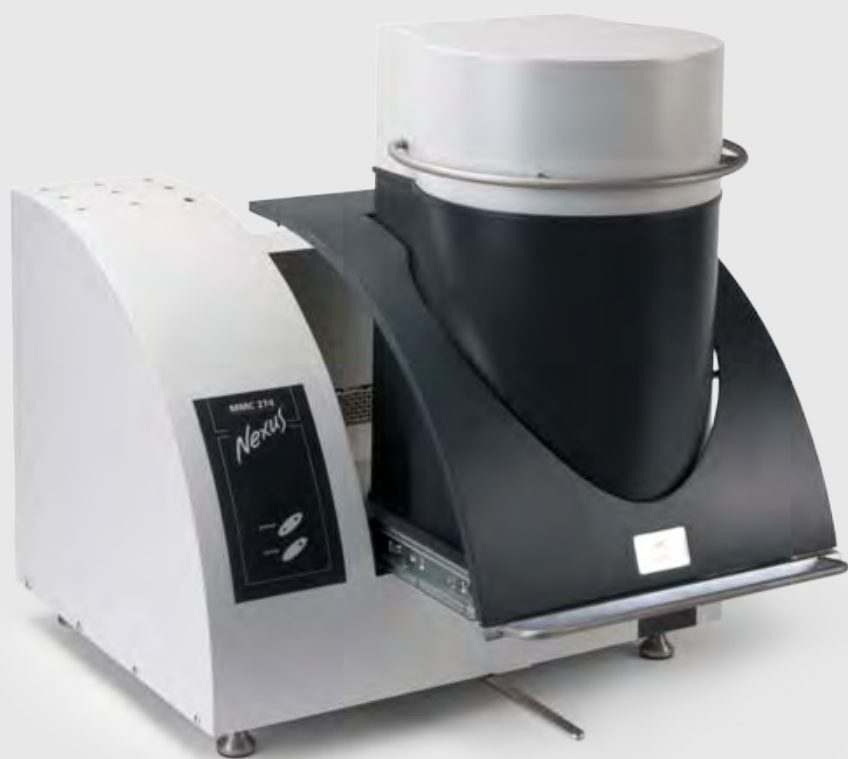
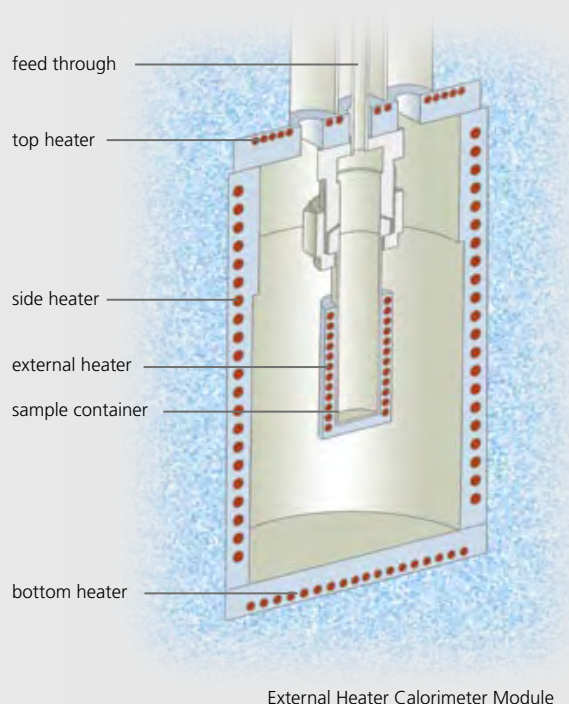
### Key Features of the ARC Module

- Heat-Wait-Search tests for thermal runaway reactions
- Ramp mode for fast screening of unknown samples
- Pressure measurement
- *VariPhi*<sup>™</sup>: 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

# DSC-like Testing: The Module with External Heater

## 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 external heater is useful for running isothermal and constant temperature ramp tests, especially in those experiments where reaction energies are higher.

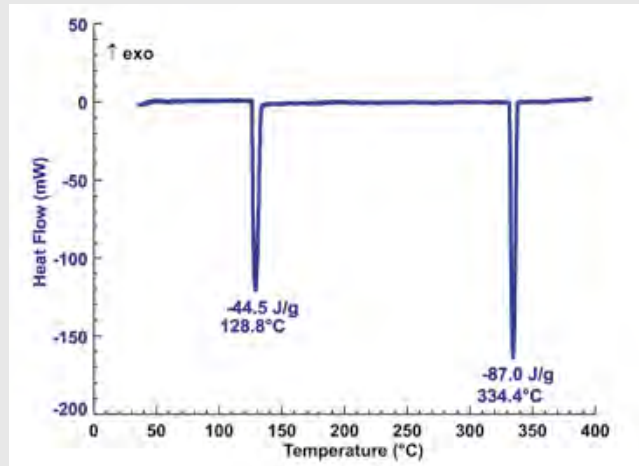


## Applications and Features of the Module with External Heater

### KNO<sub>3</sub>

Potassium nitrate (KNO<sub>3</sub>) is used for the synthesis of gunpowder (sulfur, charcoal and KNO<sub>3</sub>). It is also used in food preservation (E252) and as an important potassium- and nitrogen-containing fertilizer.

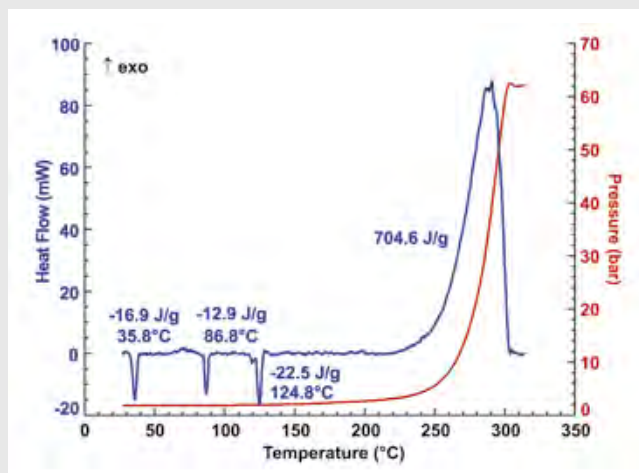
The measurement was carried out in scanning mode with a constant power input of 200 mW. Two endothermic effects at 129°C (peak area of -45 J/g) and at 334°C (-87 J/g) are related to phase transitions.



DSC-like analysis of the phase transitions of 1.9 g KNO<sub>3</sub>

### 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<sub>2</sub>, nitrogen and water. For this test a mixture of NH<sub>4</sub>NO<sub>3</sub> and toluene was used. Three phase transitions (endothermic peaks) up to 150°C and the large exothermic 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 Calorimeter 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

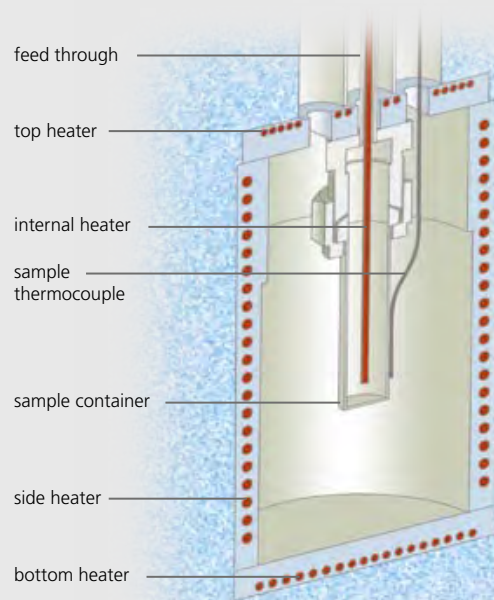
# Unique: The *VariPhi*<sup>TM</sup> Module

## Specific Heat and Low $\Phi$ -Factor

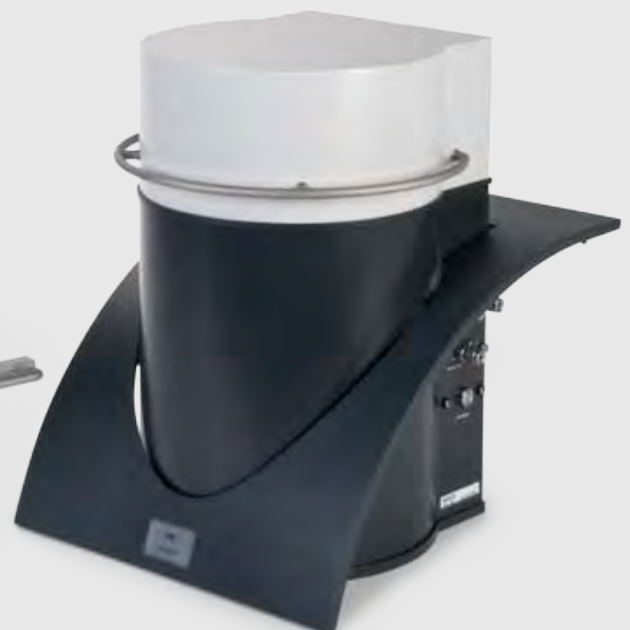
The basis of the *VariPhi*<sup>TM</sup> module is an additional controlled variable DC heater which is in contact with the sample material (internal heater). With this module it is possible to measure specific heat directly. It also allows one to define the thermal inertia for real-world thermal environment 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  $\Phi$ -factor. Ideally this value amounts to 1. In reality the  $\Phi$ -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



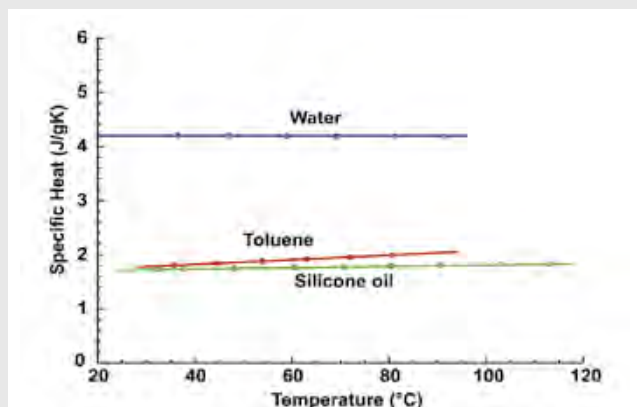
*VariPhi*<sup>TM</sup> Calorimeter Module (Internal Heater)



## Applications and Features of the *VariPhi*<sup>TM</sup> Module

### Reliable Specific Heat

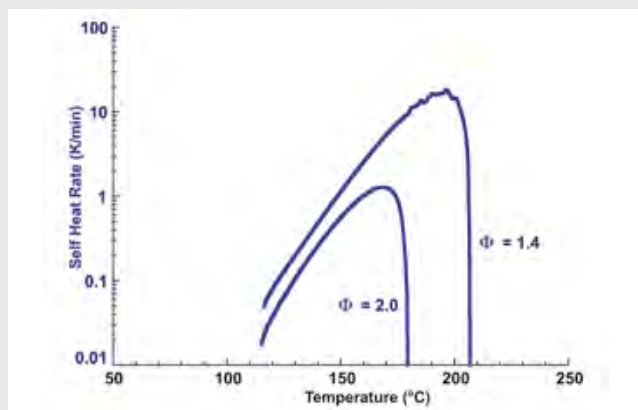
An advantage of the *VariPhi*<sup>TM</sup> heater is the ability to easily determine  $c_p$  values of liquid and solid materials. Measured here are three liquids over a temperature range from room temperature to 90°C and 115°C.



Specific heat of water, toluene and silicone oil

### Compensated $\Phi$ -Factor

The mass of the container can be completely compensated for when *VariPhi*<sup>TM</sup> is used. This allows for either an adjusted  $\Phi$ -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  $\Phi$ -factor

### Key Features of the Unique *VariPhi*<sup>TM</sup> 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 ( $\Phi$ ) 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

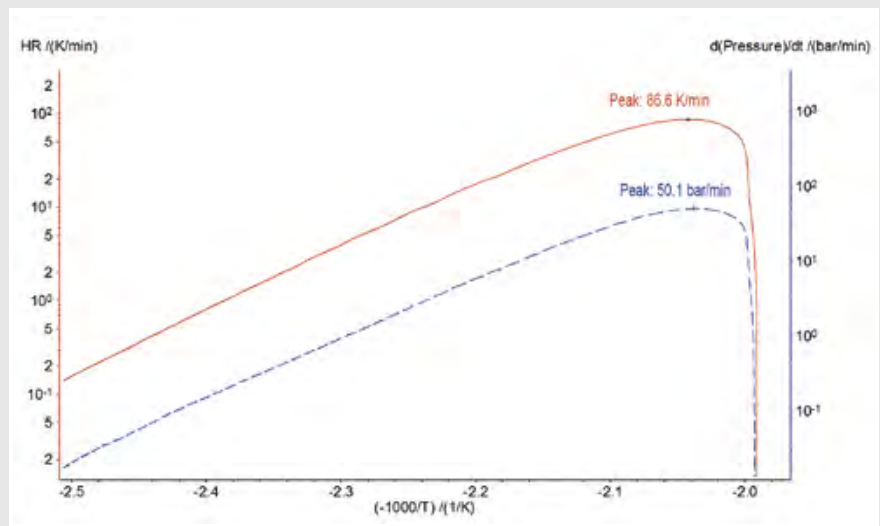
visit [www.mmc274.info](http://www.mmc274.info)

# Intelligent Software Solutions

## Software Solutions for Your Applications

### NETZSCH *Proteus*® Software

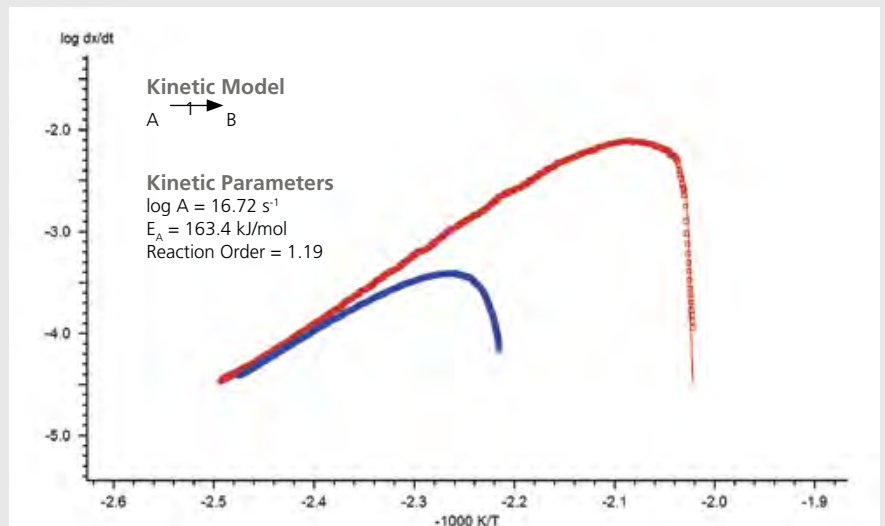
- Evaluation of characteristic temperatures and enthalpies
- ARC-specific presentation with heat generation rates or pressure development as examples



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

## Thermokinetics

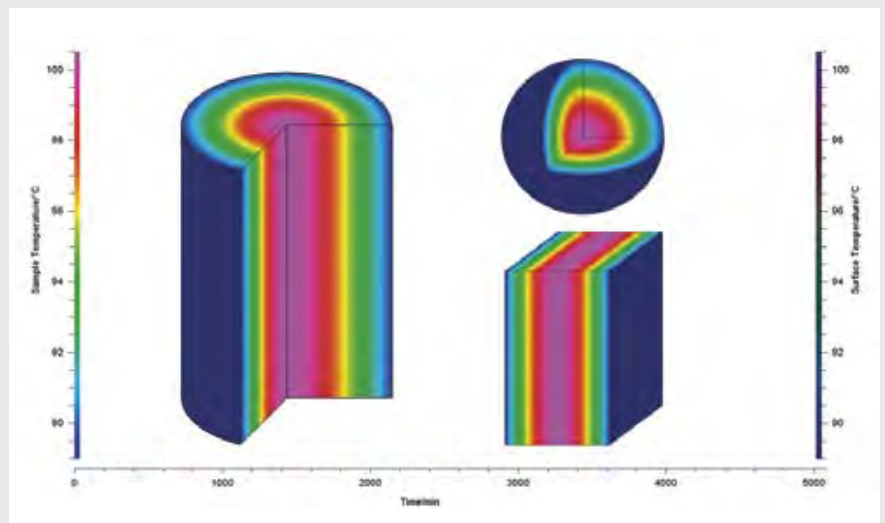
- Comprehensive kinetic analysis of multiple reaction steps
- Prediction of temperature and pressure changes for user-defined measurement and storage conditions



Comparison of measured data (symbols) and formal kinetic model (solid lines) for a single step reaction of 1<sup>st</sup> order, decomposition of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>)

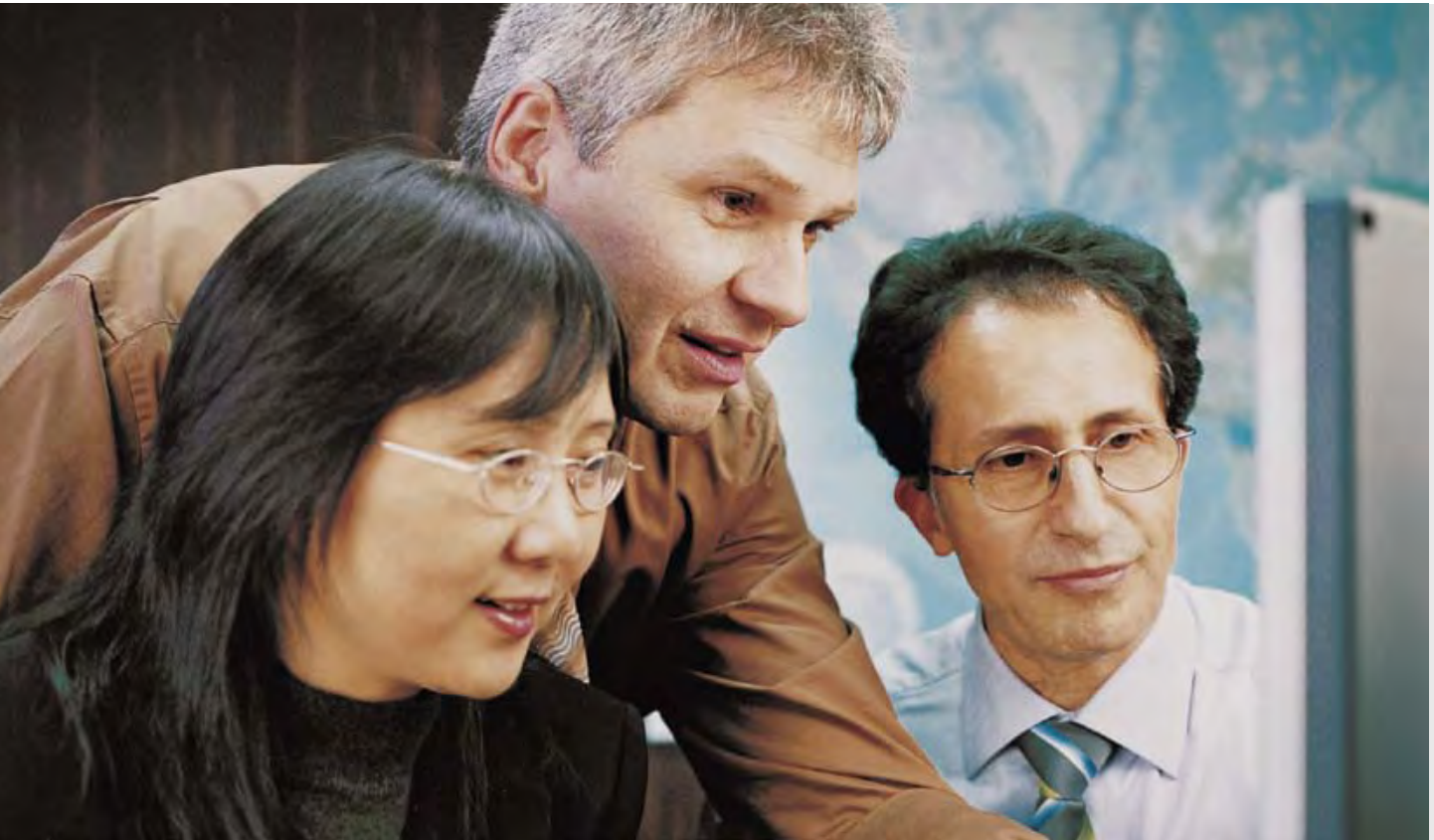
## Thermal Simulation

- 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)

## 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
- Calibration service
- IQ /OQ/PQ
- 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 nearly any thermal analysis issue. Our involvement in your projects begins with proper sample preparation and continues through meticulous examination and interpretation of the measurement results. Our diverse methods and over 30 different state-of-the-art measuring stations will provide ready-made solutions for all your thermal needs.

Within the realm of thermal analysis and the measurement of thermophysical properties, we offer you a comprehensive line of the most diverse analysis techniques for materials characterization (solids, powders and liquids).

Measurements can be carried out on samples of the most varied of geometries and configurations. You will receive high-precision measurement results and valuable interpretations from us in the shortest possible time. This will enable you to precisely characterize new materials and components before actual deployment, minimize risks of failure, and gain decisive advantages over your competitors.

For production problems, we can work with you to analyze concerns and develop solutions. The minimal investment in our testing and services will reward you with reduced down time and reject rates, helping you optimize your processes across the board.



The NETZSCH Group is an owner-managed, internationally operating technology company headquartered in Germany.

The three Business Units – Analyzing & Testing, Grinding & Dispersing and Pumps & Systems – provide tailored solutions for highest-level needs. Over 2,300 employees at 130 sales and production centers in 23 countries across the globe guarantee that expert service is never far from our customers.

## Leading Thermal Analysis

When it comes to Thermal Analysis, Adiabatic Reaction Calorimetry 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.

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