

NETZSCH



Differential Scanning Calorimetry – DSC 404 **F1/F3** Pegasus®

Method, Technique, Applications

Differential Scanning Calorimetry

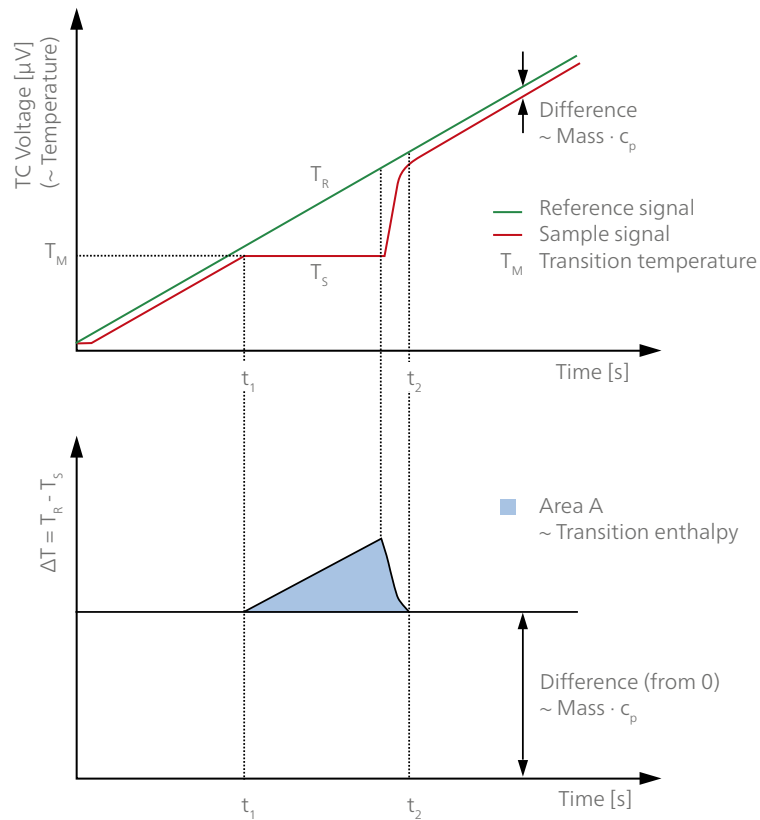
Method

Differential scanning calorimetry (DSC) is one of the most frequently employed thermal analysis methods. It can be used to analyze nearly any energetic effect occurring in a solid or liquid during thermal treatment.

DSC Analysis Possibilities

- Specific heat capacity
- Melting and crystallization behavior
- Solid-solid transitions
- Polymorphism
- Phase transitions/diagrams
- Liquid crystal transitions
- Eutectic purity
- Degree of crystallinity
- Glass transition temperatures
- Cross-linking reactions
- Oxidative stability
- Decomposition onset
- Compatibility
- *Purity Determination*
- *Thermokinetics*





Signal generation in a heat flux DSC

The DSC 404 **F1** and **F3** Pegasus® systems operate according to the heat flux principle. With this method, a sample and a reference are subjected to a controlled temperature program (heating, cooling or isothermal). The actual measured properties are the temperature of the sample and the temperature difference between sample and reference. From the raw data signals, the heat flow difference between sample and reference can be determined.

The DSC 404 **F1/F3** Pegasus® instruments are in line with nearly every respective instrument and application standard, including: ISO 11357, ASTM E793, ASTM D3895, ASTM D3417, ASTM D3418, DIN 51004, DIN 51007.

DSC 404 **F1/F3** Pegasus®

Outstanding Features

DSC 404 **F1/F3** Pegasus®

At NETZSCH, we mastered the challenge of high-temperature DSC measurement years ago. Today, that same drive for perfection allows us to consistently offer the best solutions on the market.



Furnace Variety for the Broadest of Temperature Ranges

Various furnaces including those for special applications extend the application range beyond that of common thermal analyzer systems. Measurements can be performed in the range from -150°C to 2000°C.

Efficient Time Management

The double hoist allows for either the simultaneous connection of two furnaces or one furnace in combination with the automatic sample changer (ASC). The ASC is designed to handle up to 20 samples. Flexibility and high sample throughput allow for efficient time management.



The Right Sensor For Each Application

The instrument's ample flexibility is extended by an impressive assortment of sensors. The great variety of possible furnace/sensor combinations ensures optimal configuration for any application. Easy handling is guaranteed by means of the user-friendly design.

Elimination of Atmospheric Influences – Vacuum-Tight Design

Mass flow controllers provide an ideal control of atmospheres. The vacuum-tight design is prerequisite for the investigation of materials sensitive to oxidation. Enthalpy changes and the specific heat capacity (c_p) can be analyzed at unmatched levels of accuracy.

Various Furnace Systems

The DSC 404 **F1/F3** Pegasus® systems can be equipped with a wide range of different furnaces accommodating different temperature and application ranges between -150°C and 2000°C. Silver and steel furnaces are available for the sub-ambient temperature range. Controlled cooling is guaranteed with the liquid nitrogen cooling device or the Vortex tube. For higher temperature ranges, SiC, Pt, Rh and graphite furnaces are available. The platinum and the rhodium furnaces in combination with dedicated DSC sensors are specifically suited for determination of the specific heat capacity in the higher temperature range.

Double Hoist

The electrically driven double furnace hoist is a standard feature of the DSC 404 **F1/F3** Pegasus® systems. It allows for simultaneous installation of two different furnaces to conduct, for example, low- and high-temperature tests with the same instrument. For an improved sample throughput, it is also possible to connect a single furnace along with the automatic sample changer (ASC) instead.

Wide Variety of Furnaces



Interchangeable Furnaces

Furnace type	Temperature range ¹	Cooling system	Atmospheres
Steel	-150°C to 1000°C	Liquid nitrogen/ Vortex	Inert, oxidizing, reducing, vacuum, corrosive
Silver ²	-120°C to 675°C	Liquid nitrogen/ Vortex	Inert, oxidizing, reducing, vacuum, corrosive
Silicon carbide	RT to 1600°C	Air	Inert, oxidizing, reducing, vacuum, corrosive
Platinum ²	RT to 1500°C	Air	Inert, oxidizing, reducing, vacuum
Rhodium ²	RT to 1650°C	Air	Inert, oxidizing, reducing, vacuum
Graphite	RT to 2000°C	Tap or chilled water ³ (or cooling thermostat)	Inert, oxidizing (with protective tube up to 1750°C), reducing

¹ Corresponds to maximum sample temperature range

² Optimally suited for c_p determination

³ Requires connection to cooling water



Various Sensors

The DSC 404 **F1/F3 Pegasus**® instruments are generally used to obtain accurate specific heat (c_p) measurements. However, the systems allow for simple DTA measurements or conventional DSC tests as well. DTA sensors can be used for applications such as routine tests on aggressive sample substances. Various thermocouple types allow optimum sensitivity and time constants in all temperature ranges. The sensors can easily be changed in less than a minute by the operator.

Unique Sensor Adjustment System

For optimizing the baseline, a micrometer adjustment system is integrated into the measurement part. This adjustment system allows placement of the sensor at the optimum central position in the furnace. This guarantees a stable and reproducible baseline without any major adjustment efforts.

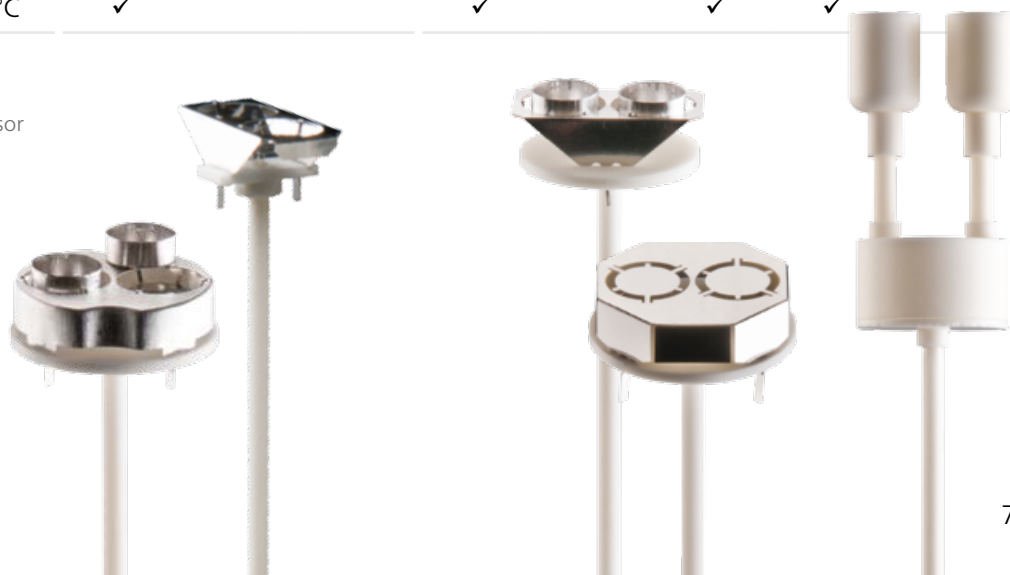
and Sensors for Flexibility

Ensures Best Measurement Conditions

Interchangeable Sensors

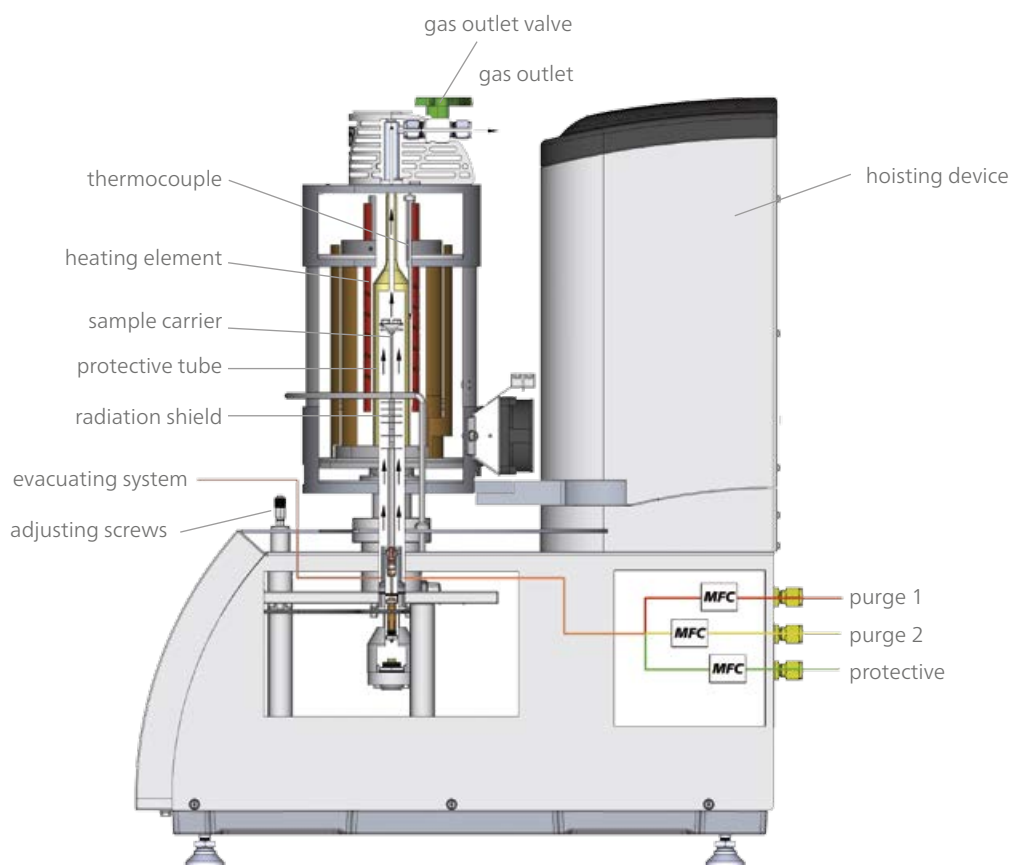
Thermocouple	Temperature range	Sensor types			Atmospheres				
		DTA	DSC	DSC- c_p	Inert	Oxidizing	Reducing ¹	Vacuum	Corrosive
E	150°C to 700°C	✓	✓	✓	✓	✓ ⁴	✓	✓	
K	160°C to 800°C	✓	✓	✓	✓	✓ ⁴	✓	✓	
P	150°C to 1000°C		✓	✓	✓	✓	✓	✓	
S	RT to 1650°C	✓	✓	✓ ²	✓	✓	✓	✓	
S _{Protected}	RT to 1650°C	✓			✓	✓	✓	✓	
B	RT to 1750°C	✓	✓	✓ ³	✓		✓	✓	✓
W/Re	RT to 2000°C	✓			✓		✓	✓	

- 1 Upper temperature limit may deviate from the maximum temperature range of the sensor
- 2 Optimum accuracy to 1500°C
- 3 > 300°C to max. 1200°C
- 4 Up to 500°C



Groundbreaking Technology

A variety of useful accessories for augmenting the application range of the DSC method is available, including evacuation devices, the *AutoVac* for automatic evacuation and refilling of the DSC system, and the *OTS*[®] oxygen trap system.



Atmosphere – Mass Flow Controllers

In the DSC 404 **F3 Pegasus**[®], the purge or reactive gas flow is generally controlled via frits, manual control systems or tailor-made mass flow control systems (MFCs). The DSC 404 **F1 Pegasus**[®] comes standard-equipped with integrated metal-housed mass flow control systems for three different gases. Both MFC systems allow software-controlled gas switching and purge gas rates as well as recording of the flow rates in the software.

Glove Box and Corrosion-Resistant Instrument Versions

Special DSC versions are available for use in a glove box and for measurements in corrosive atmospheres. This great flexibility allows the DSC 404 **F1/F3 Pegasus**[®] systems to be optimized and configured according to your needs – both now and in the future.

Vacuum-Tight Design – Optimum Atmosphere Control

The DSC 404 **F1/F3 Pegasus**[®] instruments stand out as first-rate vacuum-tight high-temperature DSCs. Practically every component was specifically constructed with the requirements of high-vacuum and high-purity gas applications in mind. Various pump systems (from rotary or diaphragm to turbo molecular pumps) are available to evacuate the system down to 10^{-4} mbar. Automatic evacuation is of course possible, as is backfilling with various kinds of purge gases.

OTS[®] Oxygen Trap System

The OTS[®] accessory can be used to drastically reduce the oxygen concentration at the sample to below 1 ppm.



A Diverse Array of Accessories



Selection of DSC crucibles and lids

Reshaping tool for PtRh/ceramic crucible system

A Wide Variety of Crucibles

What sets the DSC 404 **F1/F3 Pegasus**[®] systems apart is not only their flexibility in furnaces and sensors but also the huge variety of available crucibles. For the broad temperature range from -150°C to 2000°C, the crucible materials vary from metals (Al, Ag, Au, etc.) to ceramics (Al₂O₃, MgO, ZrO₂, Y₂O₃, BN, etc.) to graphite. For inhomogeneous samples and those with low density, larger crucibles are available.

Should samples need to be shut off from the influence of the ambient atmosphere, or should gas emissions from the samples need to be contained, aluminum crucibles can be sealed shut, gas-tight, with a handy sealing press.

For measurements under increased pressures of up to 100 bar, reusable stainless steel and titanium autoclave crucibles handle the job.

A PtRh/ceramic crucible system for measurements on metal melts or other reactive test materials is available with a removable liner. Liners are available made of thin-walled Al₂O₃, MgO, and Y₂O₃.

Calibration Materials

For the calibration of temperature, enthalpy and specific heat capacity in both the low- and high-temperature range, multiple sets containing different calibration materials are available for the various crucible materials (including high-pressure autoclaves). The calibration materials are selected and prepared for measurement in accordance with the recommendations of the corresponding ASTM and CEI-IEC standards.



Automatic Sample Changer (ASC)

An automatic sample changer (ASC) can be installed on both the DSC 404 **F1** and **F3 Pegasus**® systems. The sample carousel allows for 20 samples and is removable for easy loading. Each sample can be assigned an individual measurement and evaluation macro. Preprogramming permits measurements to be carried out overnight or on weekends. This significantly enhances the sample throughput, laboratory and instrument efficiency. Optimum crucible placement is guaranteed by design. The ASC with its gripper and carousel allows for the use of nearly any crucible type including specialties such as medium- and high-pressure crucibles.

"Remove Lid" Function of the ASC

For unstable samples – i.e., samples sensitive to oxygen or ambient room conditions while waiting their turn on the crucible magazine to be inserted into the sample compartment – a "remove lid" device can be ordered with the instrument. Closing the crucibles with a lid minimizes the risk that critical samples would evaporate or react with ambient humidity prior to the measurement.



Proteus[®] Software

for the DSC 404 **F1/F3** Pegasus[®]

Software Features

Operating systems Windows[®] operating system

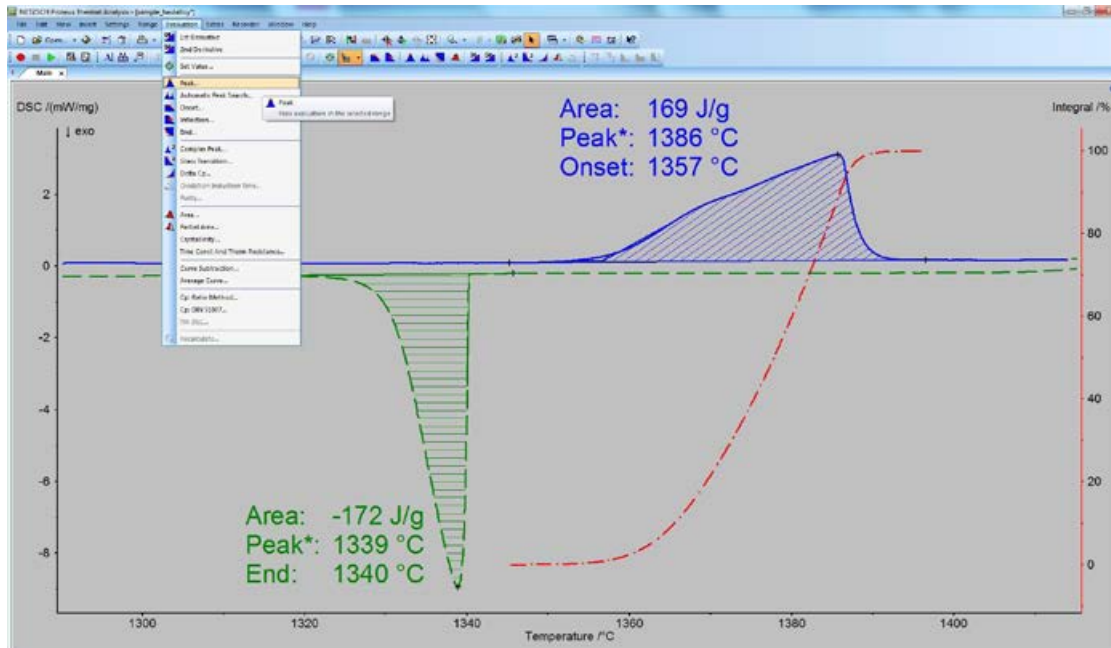
General software features

- Multi-tasking: simultaneous measurement and evaluation
- Multi-moduling: operation of different instruments from one computer
- Comparison and/or evaluation of STA, DSC, TGA, DIL, TMA and DMA measurements in one plot
- Calculation of 1st and 2nd derivative including peak temperatures
- Gas manager control
- Calibration and correction routines for temperature, sensitivity, baseline
- PIP graphical function (picture in picture)
- Context-sensitive help system
- Up to 256 programmable temperature segments
- Snapshot for online evaluation of the measurement in progress
- Changing of upcoming segments during measurement

DSC-specific features

- Comparison analysis of up to 64 curves/temperature segments from the same or different measurements
- Loading of single files and simultaneous loading of multiple files
- Determination of onset, peak, inflection and end temperatures, incl. automatic peak search
- Integration of the $c_p(T)$ curve for determination of the enthalpy of a reaction
- Curve subtraction of baselines and sample runs; subtraction of physically identical curves
- DSC-integral curve
- TM-DSC (only DSC 404 **F1** Pegasus[®])
- Comprehensive glass transition analysis
- Degree of crystallinity
- OIT (Oxidative-Induction Time)
- Connection of segments by spline interpolation: Dynamic segments with the same heating direction and isothermal segments can be analyzed as interrelated and temperature-scaled

Both DSC systems run under the *Proteus*® software on Windows® XP Professional, or on Windows® 7 32-/64-bit Professional, Enterprise or Ultimate. The *Proteus*® software includes everything you need to carry out a measurement and evaluate the resulting data. User-friendly menus combined with automated routines make this very easy to use while still providing sophisticated analysis. The *Proteus*® software is licensed with the instrument and can of course be installed on other computer systems.



Advanced Software (options)

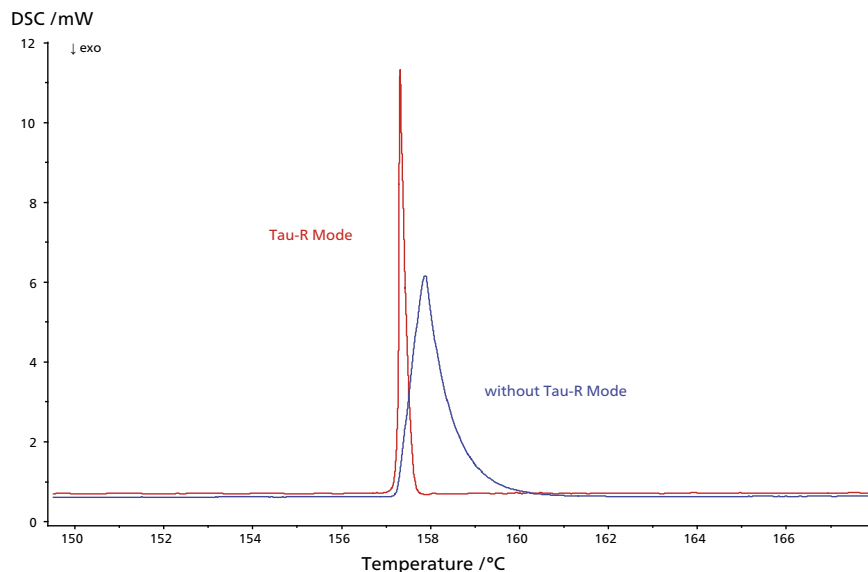
- *Peak Separation* permits accurate separation and evaluation of overlapping transitions
- NETZSCH *Thermokinetics* offers advanced characterization of reactions and kinetic parameters on the basis of multiple-step kinetic analysis on up to 16 curves; also provides predictions of the process
- *Purity Determination* via analysis of the DSC melting peak
- *Specific Heat Capacity Determination*
The DSC method allows for convenient and reliable determination of the specific heat capacity (c_p). Knowledge of c_p supports the improvement and development of many technical and technological processes, as well as that of a broad variety of materials from building materials to turbine plates. This software module is based on standardized methods described in standards such as ASTM E1269, ISO 11357, and DIN 51007. It is included in DSC 404 **F1 Pegasus**®; optional for DSC 404 **F3 Pegasus**®.

EXPERT SOFTWARE SOLUTIONS

The *Proteus*[®] modules and expert software solutions offer further advanced processing of the thermoanalytical data for more sophisticated analyses. The advanced software packages *Peak Separation*, *Purity Determination* and *Thermokinetics* are optionally available for both DSC versions. The *Proteus*[®] software extensions *Tau-R*[®] Mode, *BeFlat*[®] and *Specific Heat Capacity Determination* are optionally available for the DSC 404 **F3 Pegasus**[®]. TM-DSC is exclusively available for the DSC 404 **F1 Pegasus**[®].

Tau-R[®] Mode

The DSC curve incorporates not only important information about the sample, but also residual information from the instrument. To correct for this established fact, the *Tau-R*[®] Mode has been developed. This method is based on two essential correction factors: the thermal resistance (R) and the time constant (τ). The determination and creation of a correction file need only be carried out once for identical measurement parameters. The true raw data can then be accessed by just one click of the mouse.

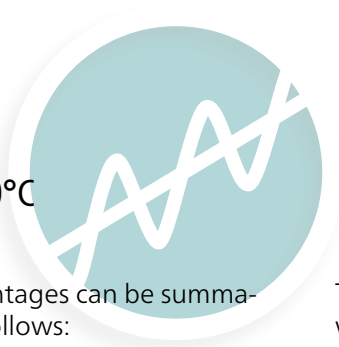


Correction of the thermal resistance and the time constant lead to defined peaks (*Tau-R*[®] Mode)

BeFlat[®]

Perfect thermal symmetry, which is often expected in a differential measurement set-up, is virtually impossible to realize in practice. The unique *BeFlat*[®] software corrects DSC baseline discrepancies attributable to thermal asymmetry by using a multi-dimensional polynomial dependent upon temperature and heating rate. *BeFlat*[®] removes the baseline discrepancies from the DSC signal and yields perfect horizontal DSC baselines with minimal deviations in the μ W range. The true raw data signal can be re-accessed at any time with a simple click of the mouse.





Temperature-Modulated DSC up to 1650°C

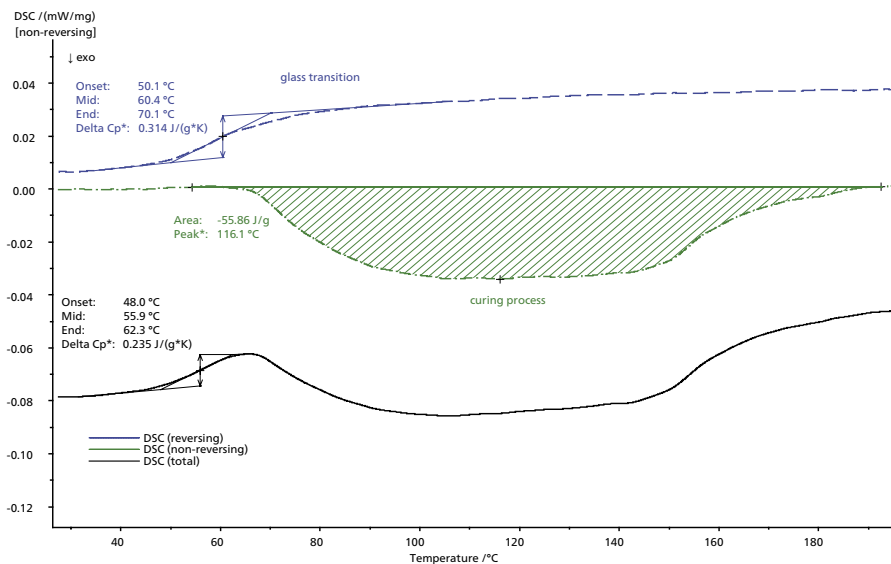
Temperature-modulated DSC (TM-DSC) is a DSC technique whereby a sample is subjected to a superposition of a linear and a periodic temperature program. Temperature-modulated DSC enables the separation of overlapped DSC effects by calculating the reversing and non-reversing signals. Glass transitions can therefore be well separated from, for example, exothermal curing, decomposition, evaporation, relaxation or cold-crystallization processes in a single TM-DSC test.

The DSC 404 **F1 Pegasus**® is the only DSC which allows for TM-DSC tests up to 1650°C. Nearly all available furnaces in combination with different DSC sensors are suited for such tests. It is totally based on a software solution. The NETZSCH TM-DSC solution improves separation of time-dependent events from the total heat flow.

The advantages can be summarized as follows:

- Offline evaluation after the measurement. This means there is no time delay of evaluated data, which is common for online evaluations.
- FRC* method which takes into account the dependence of the calibration coefficient on frequency, thermal resistance between the sample and crucible, and heat capacity of the sample.
- Unique baseline correction algorithm for average, amplitude and phase of the DSC curve.
- Standard DSC calibrations (using melting points according to DIN 51007, for example)
- Unique method of determination of the calibration coefficients for calculation of the reversing heat capacity (c_p standard required).

* Frequency Resistance Capacity

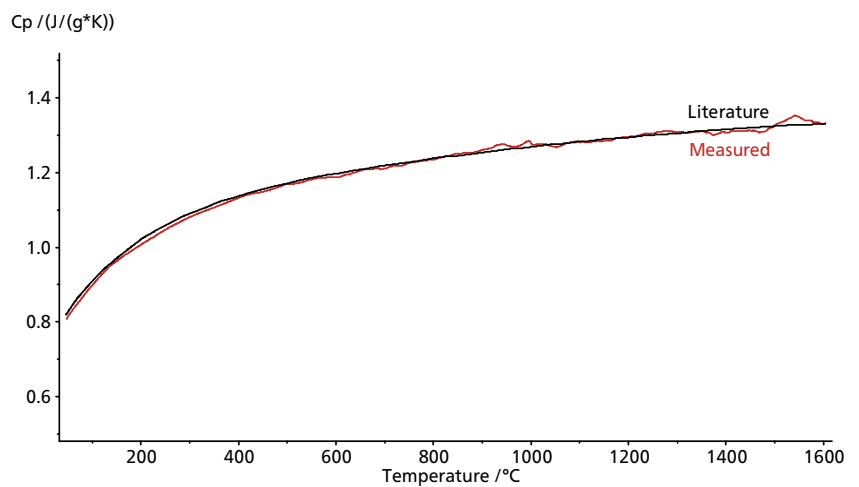


Curing of an unsaturated polyester resin and overlapping of an endothermal glass transition can be separated in a single TM-DSC test.

Performance and Applications

High c_p Accuracy up to High Temperatures

Presented in the figure is a specific heat capacity test result for a polycrystalline alumina sample between room temperature and 1600°C. Additionally shown are literature values for pure alumina. There are no significant differences between the literature values and the test results. The maximum deviations are in the range of 2%, which demonstrates the outstanding performance of the DSC 404 **F1 Pegasus**®.

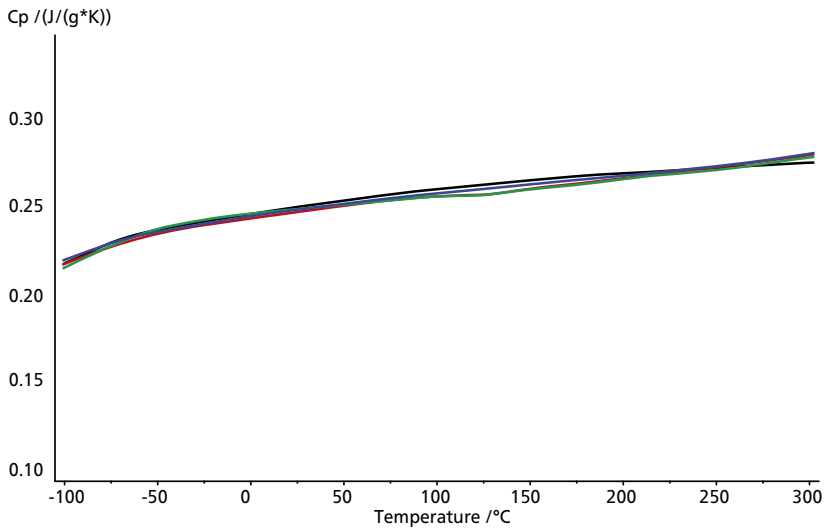


Highly accurate determination of the specific heat capacity across a wide temperature range. For these measurements, the rhodium furnace and the DSC- c_p sensor type S were used.

*Determination of the
Specific Heat Capacity*

Reproducibility ...

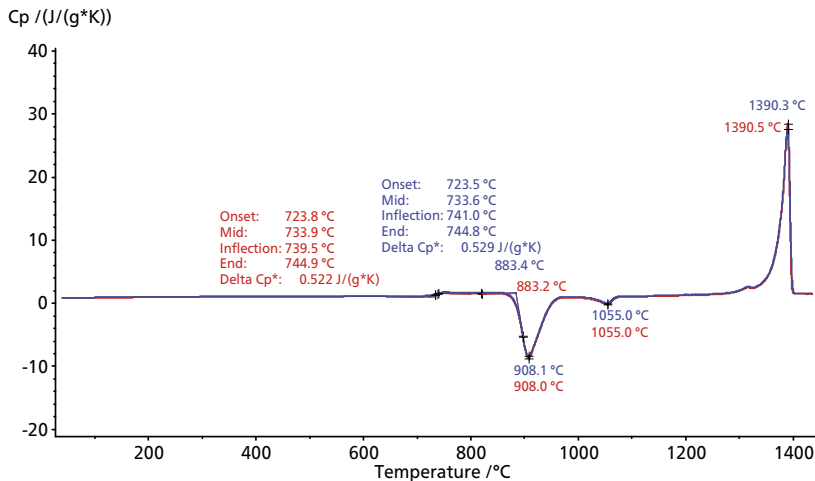
... in the Low-Temperature Range



The specific heat capacity in the sub-ambient temperature range can be determined up to 300 $^{\circ}C$ by means of the steel furnace (-150 $^{\circ}C$ to 1000 $^{\circ}C$) and the DSC- c_p sensor type E.

Here, the specific heat capacity of molybdenum was measured three times between -100 $^{\circ}C$ and 300 $^{\circ}C$ using the low-temperature furnace. The three results (colored lines) are identical to within 2%. Additionally shown are literature values for pure molybdenum (black line). The differences between the measurement results and the literature values are generally less than 2%. This proves the excellent specific heat performance of the system in the low-temperature range.

... in the High-Temperature Range



Excellent reproducibility and the detection of weak phase transitions (glass transition) can be achieved by simply combining the right furnace with the right sensor. These DSC runs were carried out with the Pt furnace and by using DSC- c_p sensor type S.

In this plot, the glass transition of the diopside glass powder occurred at 734 $^{\circ}C$ (midpoint). Crystallization was measured at 883 $^{\circ}C$ (extrapolated onset). Melting took place at 1390 $^{\circ}C$ (main peak temperature). The characteristic temperatures and the corresponding enthalpy changes are in good agreement between the two different samples. The specific heat itself doesn't show relevant differences, which indicates the excellent stability and reproducibility of the DSC system.

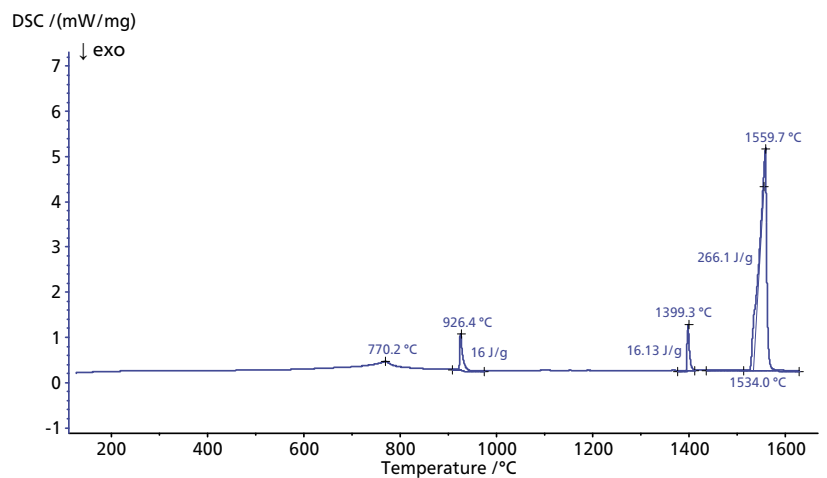
Phase Transitions and Separation of Effects



Iron

The specific heat flow rate of iron was here measured between room temperature and 1620°C. The peak at 770°C is due to a change in the magnetic properties of the material (the Curie transition). At peak temperatures of 926°C and 1399°C, two changes in the crystal structure occurred. Most likely due to impurities in the material, these temperatures are slightly shifted from the literature values [1] for pure iron. Melting occurred at 1534°C (extrapolated onset). The heat of fusion was 266 J/g. This is less than a 1.5% deviation from typical literature values for pure iron.

[1] Das Techniker Handbuch, Grundlagen und Anwendungen der Maschinenbau-Technik, 15. Auflage, Herausgeber Alfred Böge, Vieweg Verlag, 1999



Sharp peaks, reliable peak areas and a stable baseline over a broad temperature range are the dominant attributes of results produced by the DSC 404 F3 Pegasus® system equipped with the rhodium furnace.

Temperature-Modulated DSC (TM-DSC) Measurement on a Ceramic Glass

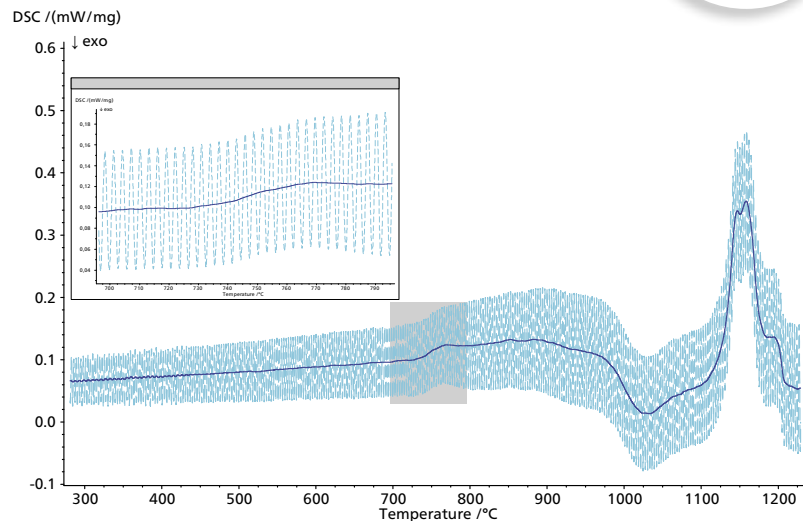


For TM-DSC, the heating rates are varied by overlapping the underlying linear heating rates with a sinusoidal temperature modulation. At the same time, the sample is subjected to a non-linear temperature change which is relatively fast in comparison with the linear rate.

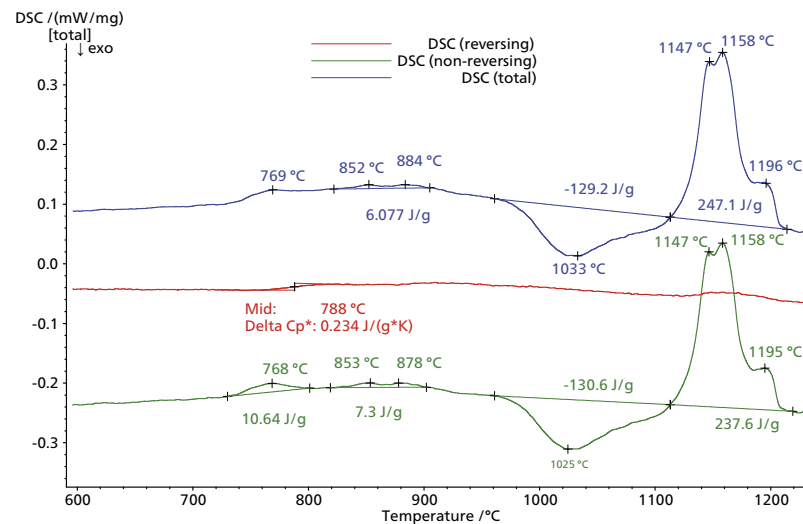
As shown with the example of a ceramic glass, the modulated signal (upper plot, blue curve) is separated in a reversing (lower plot, red curve) and non-reversing (lower plot, green curve) signal. The reversible energetic effect can be seen from the reversing curve. Here, the glass transition was detected at 788°C. The relaxation peak was detected at 769°C in the total signal (lower plot, blue curve) and especially in the non-reversing curve (green). Recrystallization at 1030°C and melting between 1120°C and 1200°C were observed as non-reversing signals.

These results demonstrate that reversible and non-reversible effects – which may overlap in the case of glass transitions and relaxation effects – can be separated by TM-DSC.

The non-reversing signal appears very similar to the total heat flow. It can be used for kinetic studies and evaluation of the relaxation enthalpy and peak temperature.



The simplest evaluation of a typical TM-DSC measurement is the determination of the total heat-flow curve as an average value of the modulated heat-flow differential curve. Modulated signal (light blue curve) and average values (dark blue curve: total heat flow).

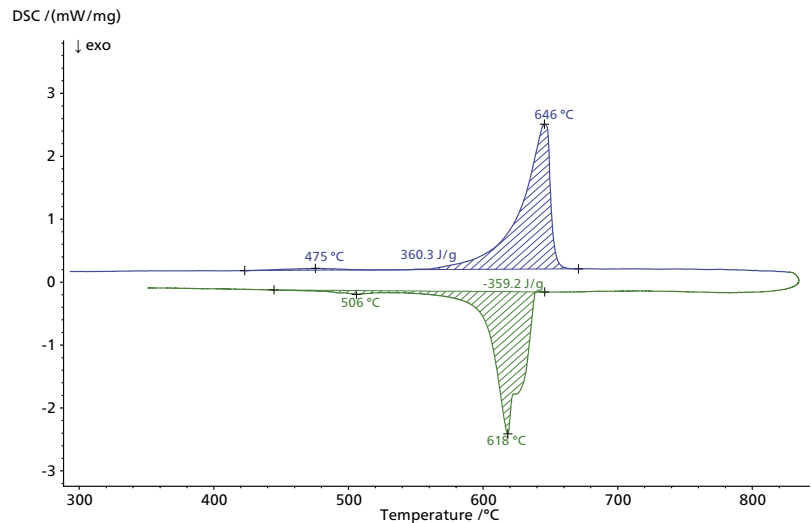


This TM-DSC measurement was carried out in a synthetic air atmosphere at a heating rate of 3 K/min and amplitude of 0.5 K/min for a period of 60 s. High-platinum crucibles with pierced lid were used. The sample mass amounted to 45 mg.

Melting and Crystallization

AlCuMg

The DSC 404 **F1/F3 Pegasus**® systems are able to perform controlled cooling runs. Here, the heating (blue curve) and cooling (green curve) runs on an AlCuMg alloy are presented. Melting occurs at 646°C (peak). Up to 800°C, no further thermal effects can be observed. Subsequent cooling leads to crystallization of the alloy. After a minor super-cooling effect, crystallization reaches its maximum at 618°C. The melting and crystallization enthalpies are nearly identical. However, the shoulder in the crystallization peak already indicates crystallization of more than one structure.



Pt crucibles with an Al_2O_3 liner were used in order to prevent chemical reactions between the melt and the crucible material during a DSC measurement. Oxidation was avoided by using an argon atmosphere.



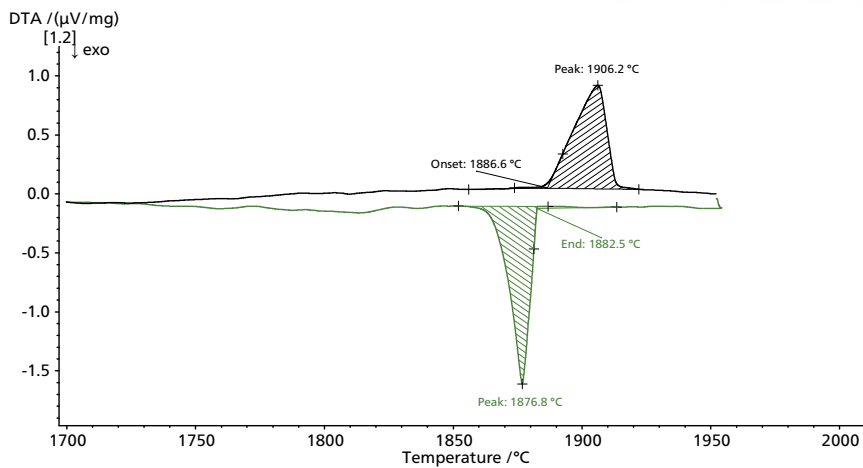
23	vanadium	50.94
0.489 J/(g·K)	V	1902 °C
30.7 W/(m·K)		422.0 J/g
8.3 ·10 ⁻⁶ /K		3409 °C
[Ar]3d ³ 4s ²		6.11 g/cm ³
		6.75 eV

NETZSCH

Thermal Properties of the Elements

NETZSCH is a leading provider of thermal analysis solutions. For more information, visit www.netzsch.com/ThA.

Vanadium in ZrO₂ Crucible



DTA measurement on vanadium in crucibles made of zirconium oxide (ZrO₂); heating rate 20 K/min, cooling 75 K/min in a helium atmosphere.

Use of the appropriate DTA sensor (type W/Re) along with the graphite furnace allows for determination of the melting and crystallization temperature to 2000°C. This example shows the heating (black curve) and cooling (green curve) runs on a vanadium sample (99.7%). The DTA crucibles made of ZrO₂ are suitable for use in the highest temperature range. Melting occurs at an extrapolated onset temperature of 1887°C. During cooling, the sample recrystallizes with only a small supercooling effect at 1877°C (peak).

	DSC 404 F1 Pegasus®	DSC 404 F3 Pegasus®
Temperature range	-150°C to 2000°C	-150°C to 2000°C
Furnaces	Standard and special furnaces	Standard and special furnaces
Heating/cooling rate	0.001 K/min to 50 K/min (depending on furnace type)	0.001 K/min to 50 K/min (depending on furnace type)
Furnace hoist	Motorized double hoist for two furnaces or one furnace combined with the ASC	Motorized double hoist for two furnaces or one furnace combined with the ASC
Sensor types	DTA, DSC, DSC-c _p (quick and safe interchange)	DTA, DSC, DSC-c _p (quick and safe interchange)
c _p measuring range ¹	Up to 5 J/(g*K)	Up to 5 J/(g*K)
c _p determination ¹	Yes	Optional
TM-DSC	Yes	No
BeFlat® (DSC)	Yes	Optional
Tau-R® Mode	Yes	Optional
Purity Determination	Optional	Optional
Gas atmospheres	Inert, oxidizing, reducing	Inert, oxidizing, reducing
Vacuum-tightness	10 ⁻⁴ mbar (10 ⁻² Pa)	10 ⁻⁴ mbar (10 ⁻² Pa)
Gas control	3 integrated mass flow controllers (MFCs)	3 integrated frits (optionally 3 mass flow controllers (MFCs))
Automatic sample changer (ASC)	20 samples, removable carousel (optional)	20 samples, removable carousel (optional)
Automatic evacuation	Software-controlled	Optional
Coupling to evolved gas analyzers	FT-IR, MS, FT-IR-MS, GC-MS, GC-MS-FT-IR	FT-IR, MS, FT-IR-MS, GC-MS, GC-MS-FT-IR
PulseTA®	Optional	Optional

¹ c_p, specific heat capacity

Key Technical Data



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
- 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.