

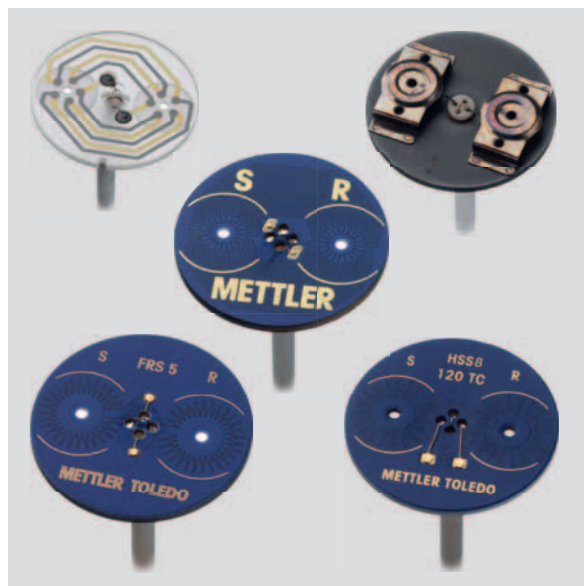
The MultiSTAR[®] DSC Sensor Family Outstanding Resolution and Sensitivity

The sensor is the heart of any DSC measuring cell. Ideally a modern DSC sensor should be very sensitive, have a fast response, a baseline that is absolutely flat, and yet at the same time be rugged and robust. With conventional design techniques this is impossible to attain.

Major breakthrough in DSC measurement technology

The unique MultiSTAR[®] FRS5 and HSS8 sensors however achieve these goals by making use of an ingenious new DSC sensor invention. Their unrivalled performance is based on several major technological advances:

- **Thermal multiplier technique** – amplifies the original signal by using a large number of thermocouples
- **Thick film technology** – makes it possible to construct the sensor in layers with an uppermost ceramic layer for protection
- **Star-shaped arrangement (multiple measurement of T_0)** – eliminates drift and results in flat baselines
- **Multi-layer thermocouple technology** – increases the number of thermocouple layers, which greatly improves the sensitivity (signal-to-noise ratio)



Features and benefits

The METTLER TOLEDO DSC sensors available today combine properties that up until now have been in opposition, namely high sensitivity, excellent resolution, flat baselines and robustness:

- **Extremely high sensitivity** – to detect even the weakest transitions in the μW -range
- **Excellent resolution** – to separate very close-lying effects
- **Unique star-shaped arrangement of thermocouples** – which guarantees flat baselines
- **Outstanding robustness** – the ceramic surface protects the sensor against contamination

The DSC Sensor Development Success Story

When METTLER TOLEDO first entered the DSC market in 1971, the company benefited from its previous experience with research-grade DTA instruments. The first DSC sensor was the result of pioneer research and was based on the thermal multiplier technique. Using thin film technology, 10 gold-nickel thermocouples were vapor-deposited on a glass support.

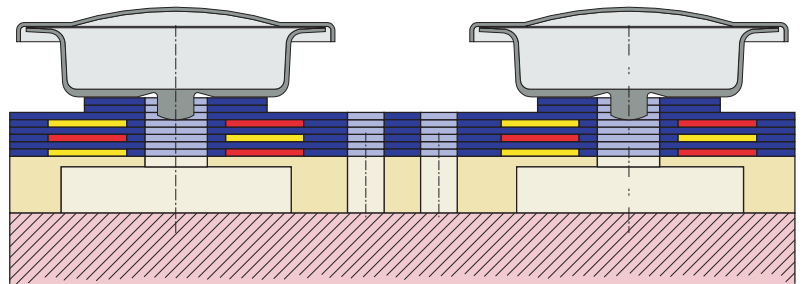
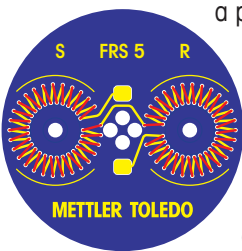
This resulted in a sensor with very good sensitivity characteristics. In 1987, it was joined by a robust chromium-nickel metal sensor, a design that is still used today by some other companies. 1990 witnessed a further important breakthrough with the introduction of a new 14-thermocouple ceramic sensor. Using thick film technology, in

a process consisting of several manufacturing steps, it became possible to successfully deposit the gold-palladium thermocouples and the hard, chemical-ly resistant protective layer.

This 14-thermocouple ceramic sensor was very robust, very sensitive and had a fast response.

In 1995, a truly revolutionary new METTLER TOLEDO technical innovation was introduced – the star-shaped arrangement of 56 thermocouples. In this design, heat flow is measured separately on both sides together with a multiple measure-

View of the high-resolution FRS5 sensor. An outer ring of thermocouples measures the sensor temperature around the crucible (multiple measurement of T_0). The inner ring measures the sample temperature numerous times underneath the crucible. This design allows the heat flow on the sample and reference sides to be measured separately and very accurately.

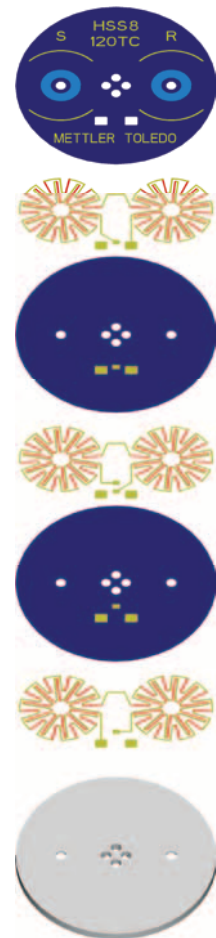


The multi-layer construction of the high-sensitivity HSS7 sensor with thick film technology. The substrate material (yellow) of the sensor lies on top of the silver furnace (pink). The thermocouples (yellow and red) and insulating material (blue) are deposited in layers on the substrate.

ment of T_0 . Possible temperature gradients are thereby automatically compensated, resulting in very flat baselines. The performance of the FRS5 sensor is today still unbeatable, in particular with regard to resolution and sensitivity. The sensor is used as a universal full-range DSC sensor in our instruments.

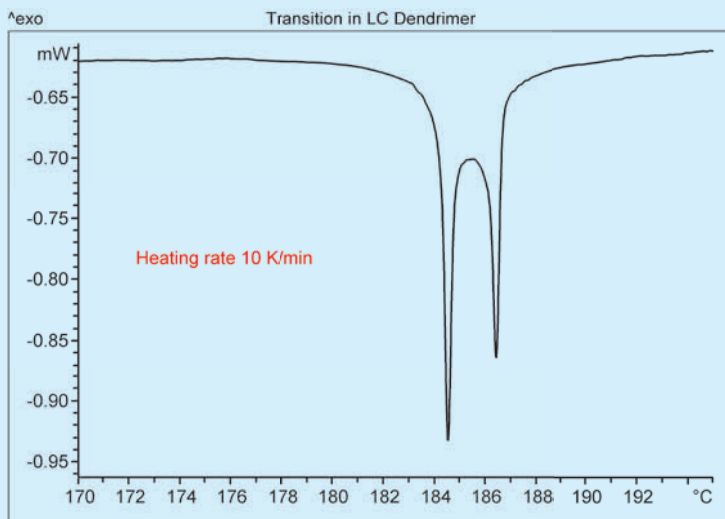
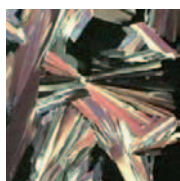
The next step in 2004 was in fact a quantum leap forward in DSC sensor development design. The innovative multi-layer thermocouple technology made it possible to arrange thermocouples on top of one another in several layers. This amplifies the measurement signal still further. It results in very low noise at the sub-microwatt level.

The weakest effects in the μW range can now be measured, something that was previously only possible with microcalorimeters. The HSS8 sensor is the most sensitive DSC sensor on the market that at the same time provides good resolution performance.



Multi-layer thermocouple technology. The thermocouples and insulation material are deposited in alternate layers on the substrate in several manufacturing steps.

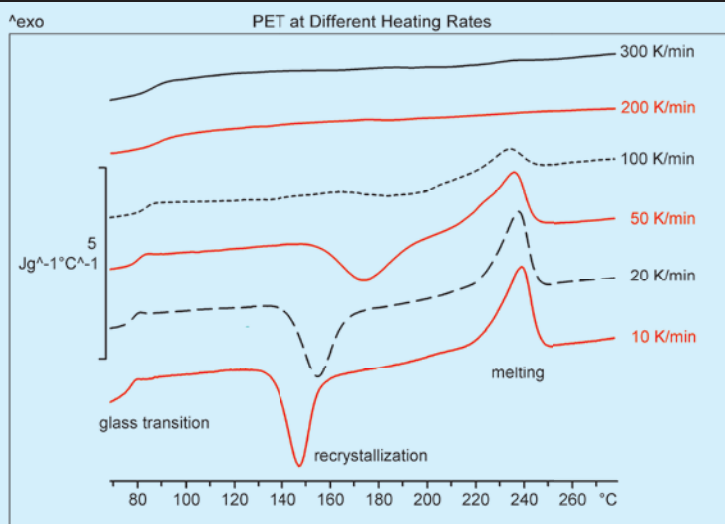
Application Examples



Separation of close-lying transitions (FRS5)

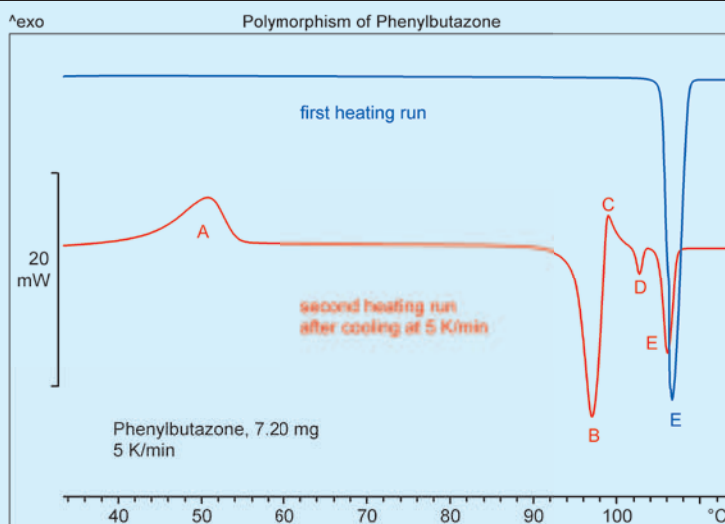
Phase transitions in liquid crystals sometimes lie very close together. The fullerene-containing dendrimer exhibits several liquid crystal transitions and changes from the smectic to the nematic and finally the isotropic state within 12 seconds at a heating rate of 10 K/min.

The endothermic peaks associated with these transitions at 184 °C and 186 °C can be completely separated using the FRS5 sensor. This is the sensor to use when optimum time or temperature resolution is required at high heating rates.



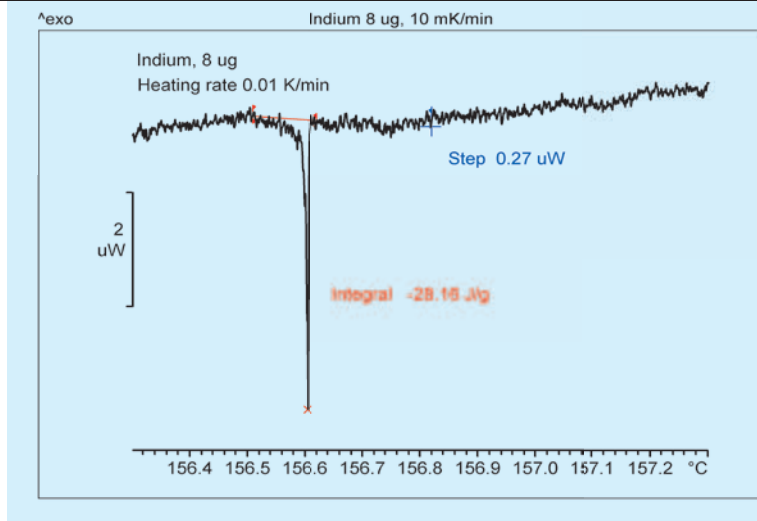
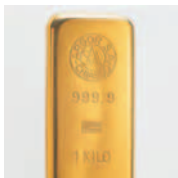
PET at high heating rates (FRS5)

Polymers often form metastable semi-crystalline structures that recrystallize on heating. At higher heating rates, the amount of recrystallization decreases. This can be demonstrated by measuring samples of amorphous polyethylene terephthalate (PET) at heating rates between 10 and 300 K/min. For comparison purposes the curves are displayed in heat capacity units. The glass transition is observed at about 80 °C. This is followed by recrystallization and finally melting between 220 and 260 °C. The amount of recrystallization decreases noticeably with increasing heating rates. At 200 K/min and 300 K/min the heating rate is so fast that practically no recrystallization occurs during the measurement. The two curves characterize the original amorphous material.



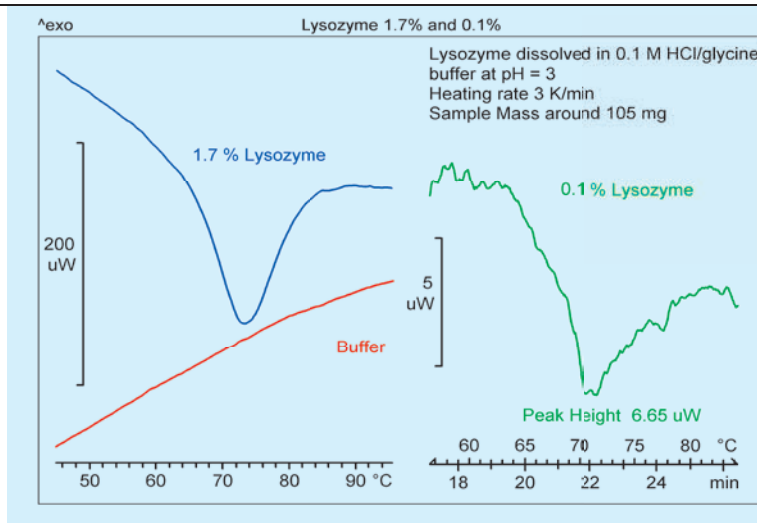
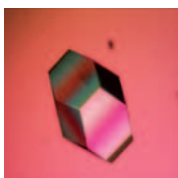
Polymorphism of phenylbutazone (FRS5)

DSC is a simple and rapid method for measuring polymorphic transitions in pharmaceutical substances. Depending on a sample's thermal history, it either melts or exhibits different transitions on heating. For example, phenylbutazone that has been cooled from the melt crystallizes on heating at about 50 °C (A). These crystals melt at about 94.5 °C (B, onset). Crystals that are more stable then form from this melt (C). The two new modifications (D, E) melt above 100 °C (E at about 105.0 °C, onset). Polymorphic transitions often lie very close together. Successful measurement of such transitions requires the use of a fast sensor with a small time constant (FRS5).



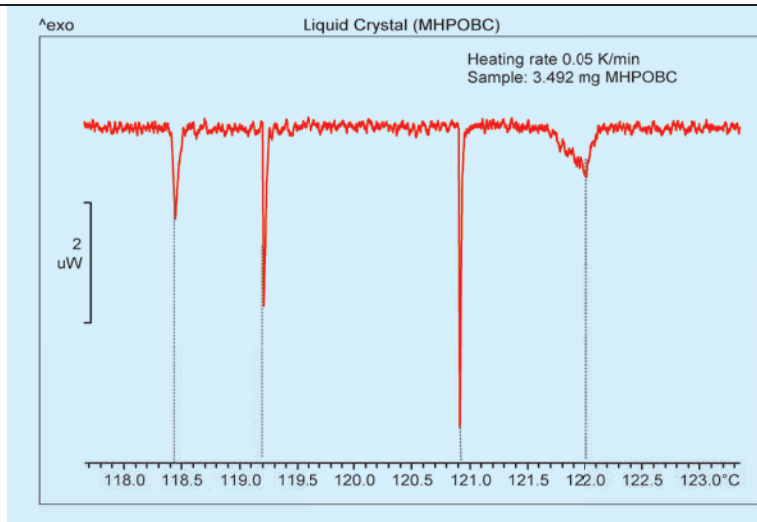
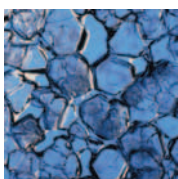
Melting of indium (HSS8)

The melting peak of indium is a thermal event frequently used to characterize DSC sensors. To demonstrate the excellent sensitivity of the HSS8 sensor, an extremely small sample of indium (8 μg) was measured at an exceptionally low heating rate (0.01 K/min). The sharp melting peak and the very low noise level are immediately apparent in the DSC curve. The indium peak has a height of 5.08 μW with a width at half height of 0.0038 K. The largest peak-to-peak noise is less than 0.3 μW ; the RMS noise is 0.06 μW .



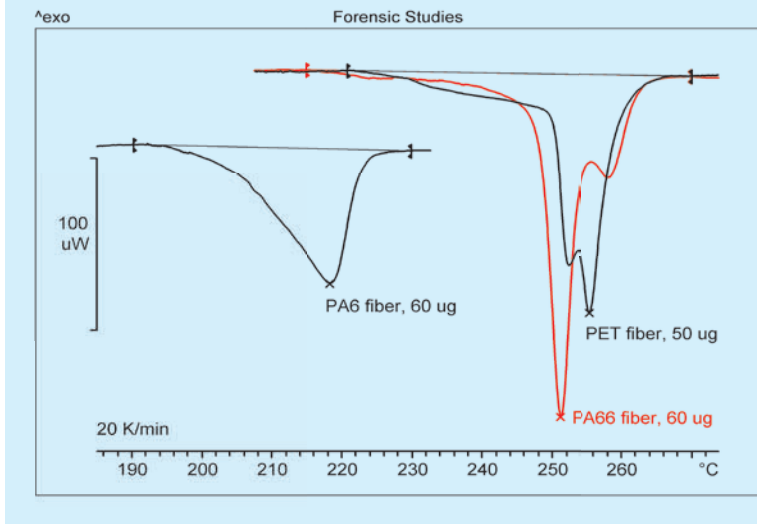
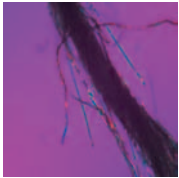
Unfolding of dissolved lysozyme (HSS8)

Biopolymers in dilute solution have traditionally been studied in microcalorimeters. Such studies are now possible with a DSC 1 equipped with the new high sensitivity HSS8 sensor. The example shows the unfolding of lysozyme dissolved in a buffer solution (pH 3). The endothermic peak (7.8 μW) can still be clearly measured even at the very low concentration of 0.1%. The curves for the lysozyme samples were corrected by subtracting the curve of the buffer solution.



Liquid-liquid transitions of MHPOBC (HSS8)

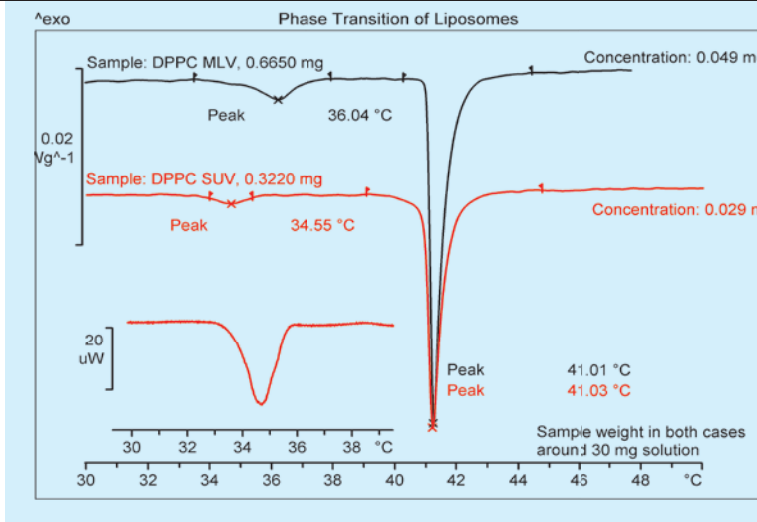
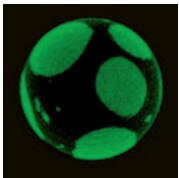
The DSC curve shows liquid-liquid transitions in a liquid crystal (MHPOBC). The sample was heated very slowly (0.05 K/min). MHPOBC is known to exhibit different smectic phases with transition temperatures at 118.4 $^{\circ}\text{C}$, 119.2 $^{\circ}\text{C}$, 120.9 $^{\circ}\text{C}$ and 122.0 $^{\circ}\text{C}$. The transition peaks are extremely sharp and occur within a fraction of a degree. The data demonstrates the excellent temperature resolution and sensitivity that can be achieved with the HSS8 sensor.



Forensic studies (HSS8)

Forensic investigations necessitate the use of highly sensitive analytical instruments because usually only very small amounts of sample are available. In such work, the thermal behavior of forensic material is compared with that of relevant reference samples.

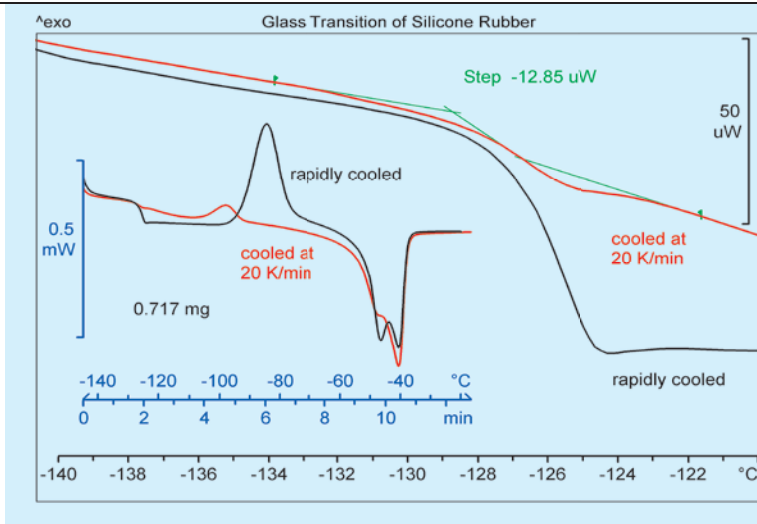
The example shows how a DSC 1 equipped with the high sensitivity HSS8 sensor can unequivocally identify extremely small samples (typically 50 μg) of different plastic materials (PA6, PA66 and PE) on the basis of melting peak temperatures.



Phase transitions of liposomes (HSS8)

Liposomes are important as carriers for moisture in cosmetic applications or as drug delivery systems.

The diagram shows the phase transitions of multi-lamella vesicle (MLV) DPPC and single unit vesicle (SUV) DPPC. The first peak corresponds to the transition from the LB (gel phase, tilted) to the P β ' (rippled phase). This transition depends mainly on the lipid polar head (the hydrophilic part of the molecule, at the surface of the lipid bilayer or liposome). The second peak is the main transition to the liquid crystalline phase (L α). The SUVs can clearly be distinguished from the MLVs by the peak temperature of the first transition (around 35 °C). The high sensitivity of the HSS8 DSC sensor allows this to be detected even if the concentration of the sample solution is very low.



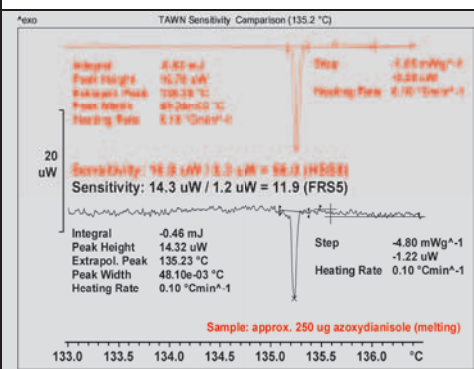
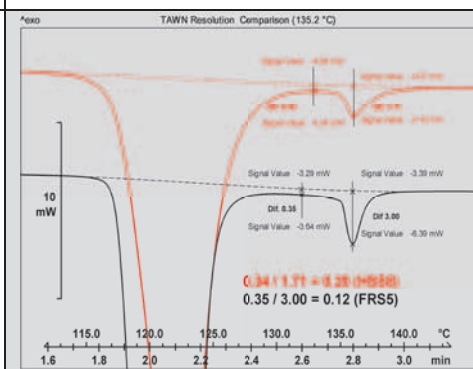
Glass transition of silicone rubber (HSS8)

If silicone rubber is rapidly cooled (by inserting the sample at -145 °C), there is no time for crystallites to form and the material is in a glassy or amorphous state.

The heating curve measured afterward exhibits a well-defined glass transition followed by cold crystallization. When an identical sample is cooled more slowly (e.g. at 20 K/min), it undergoes partial crystallization. The height of the glass transition step decreases accordingly. Under these conditions, it may then be difficult to detect the glass transition, especially with small samples (here 717 μg). In such cases, a high sensitivity sensor that can measure very small heat flows (here about 13 μW) has to be used.

Specifications MultiSTAR® Sensor Family

	FRS5 (Full-range sensor)	HSS8 (High-sensitivity sensor)
Temperature range	-150 °C to +700 °C	-150 °C to +700 °C
Thermal multiplier	56 thermocouples (AuAuPd)	120 thermocouples (AuAuPd)
Multi-layer thermo-couple technology	Thermocouples are arranged in one layer.	Thermocouples are arranged in three layers.
Star-shaped design	2 star-shaped arrangements of thermocouples measure the net heat flow on the sample and reference sides separately thanks to a double multiple measurement of T_0 .	12 star-shaped arrangements of thermocouples measure the net heat flow on the sample and reference sides separately thanks to a double multiple measurement of T_0 .
Substrate material	Ceramic	Ceramic
Resulting properties	<ul style="list-style-type: none"> extremely high resolution high sensitivity robust flat baselines 	<ul style="list-style-type: none"> high resolution extremely high sensitivity robust flat baselines
Applications	A universal DSC sensor for all general applications in the polymer, pharmaceutical, chemical and food industries.	For the measurement of weak effects. This is often of great importance with active pharmaceutical substances, foodstuffs, polymers or biotechnological and medical products. Alternatively with small quantities such as are often encountered in pharmaceutical, medical and forensic studies.
Recommended for	<ul style="list-style-type: none"> high heating rates polymorphism of pharmaceutical substances electronics (liquid crystals) 	<ul style="list-style-type: none"> low-energy transitions (melting, solid-solid) Tg with small ΔC_p (high degree of crystallization) small sample quantities (forensic, pharmaceutical) dilute solutions (foodstuffs, biotechnology) low heating rates
TAWN (sensitivity)	11.9	56.0
TAWN (resolution)	0.12	0.2
Signal time constant	1.8 s	3.1 s



Mettler-Toledo AG, Analytical
 CH-8603 Schwerzenbach, Switzerland
 Tel. +41 44 806 77 11
 Fax +41 44 806 72 60

Subject to technical changes
 © 09/2010 Mettler-Toledo AG
 Printed in Switzerland, 51724386B
 Marketing MatChar / MarCom Analytical

www.mt.com

For more information