

SDT 2960

Simultaneous DSC-TGA

including DTA capabilities



TA Instruments
Thermal Analysis & Rheology
A SUBSIDIARY OF WATERS CORPORATION



Simultaneous DSC-TGA: The Technique

Simultaneous DSC-TGA measures both the heat flows (DSC) and weight changes (TGA) associated with transitions in a material as a function of temperature and time in a controlled atmosphere. Simultaneous measurement of these key material properties not only improves productivity but also simplifies interpretation of results.

The complimentary information obtained allows differentiation between endothermic and exothermic events which have no associated weight loss (e.g. melting and crystallization) and those which involve a weight loss (e.g. degradation). The combined evaluation also assures identical experimental and sampling conditions for both measurements, thereby eliminating those sources of uncertainty.

Simultaneous DSC-TGA covers a wide temperature range from ambient to 1500°C making it a powerful tool for studying a wide variety of materials including polymers, ceramics, metals, and other inorganics.

TA Instruments SDT 2960 Simultaneous DSC-TGA

The SDT 2960 combines two thermal analysis measurements in a single instrument, thus providing easier interpretation of results and improved productivity at an attractive cost. The SDT 2960's exceptional TGA sensitivity, DSC sensitivity, and stable baseline over a wide temperature range result in unmatched versatility for the selection of materials and the prediction of product performance and in-use lifetime.

A unique feature of the TA Instruments SDT 2960 is the ability to calculate normalized DSC data based on the "actual" weight of the sample. DSC data is "normalized" by dividing the heat flow signal by the sample weight. Most instruments simply use the initial sample weight for this calculation. This practice can yield misleading results since the weight of the sample can (and often does) change during the experiment. The SDT 2960 provides the user with the ability to specify how the DSC signals are to be normalized providing more accurate, meaningful, and repeatable results.

Further improvements over competitive instruments include mechanical and electronic automation features that will appeal to novices as well as experienced thermal analysts. Convenient and easy sample handling minimizes the possibility of damaging the balance mechanism or thermocouples. The furnace assembly operates via a motor-driven screw for precise alignment and automatic opening and closing. The balance is based on a proven horizontal design which assures excellent sample/atmosphere interaction while minimizing chimney and sample weight effects. In addition, low volume inside the balance and sample areas permits rapid atmosphere changeover. Furthermore, the overall atmospheric flow dynamics make the SDT 2960 ideal for coupling to a mass spectrometer or FTIR for evolved gas analysis.

TA Instruments proprietary electronics and furnace design assure precise temperature control for stable baselines and optimum DSC performance. Proprietary software corrects for beam growth effects at elevated temperatures even under changing weight conditions. Five-point temperature calibration capability optimizes the accuracy of temperature measurements.

The SDT 2960 is one of many TA Instruments thermal analysis and rheology techniques that complement each other. These modules, along with TA Instruments controllers and software, constitute the most complete, versatile and cost effective systems available for characterizing materials.

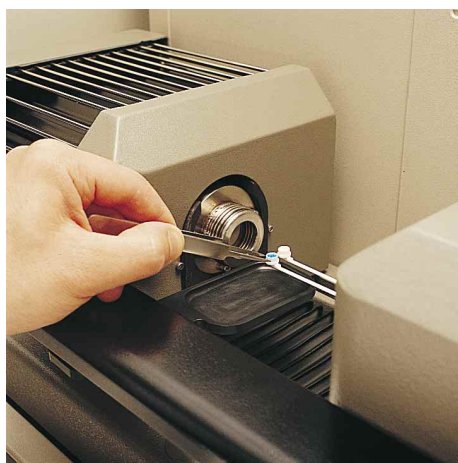


Figure 2
Loading Sample Cups on the Balance Arm

What Simultaneous DSC-TGA Can Tell You

DSC-TGA experiments provide important information that can be used to select materials, predict product performance, and improve quality. The technique is particularly useful for determining:

- Transition temperatures
- Melting points
- Composition of multicomponent systems
- Estimated lifetime of a product
- Heats of fusion and reactions
- Decomposition kinetics of materials
- Oxidative stability of materials
- Atmosphere effects on materials
- Reaction kinetics
- Moisture and volatile content of materials
- Thermal stability of materials
- Boiling points

Uses of DSC-TGA

- Research and Development
- Theoretical research of new materials and processes
- New materials development
- Materials selection
- Formula optimization
- Applications development
- End-use performance prediction
- Competitive product evaluation
- Quality Control/Assurance
- "Fingerprinting"
- Vendor certification
- Incoming/outgoing material consistency
- Process optimization
- Finished product performance
- Troubleshooting

Principles of Operation

The schematic of the SDT 2960 Simultaneous DSC-TGA is shown in Figure 3. The system is based on a dual beam horizontal design that supports both DSC and TGA measurements. A bifilar-wound furnace provides uniform controlled heating up to 1500°C. The furnace and furnace tube are a single assembly assuring that the upper temperature limit can be achieved consistently without compromising furnace life. A cooling ring facilitates direct introduction of an air purge into the furnace assembly for rapid automatic cool down between experiments. The entire furnace assembly operates on a motor driven screw to allow automatic opening and closing.

Purge gas enters the unit through the balance assembly and flows horizontally over the sample and reference. A purge gas flow rate of 100 ml/min is typically used, but it can be increased to 1000 ml/min to rapidly purge the balance and sample areas before starting atmosphere sensitive determinations. The backpressure generated by the flowing gas during the experiment prevents the diffusion of gaseous decomposition products into the balance area.

DSC measurements are based on a “heat flux” design. The sample, contained in a pan, and the reference (typically an empty pan) sit on platinum sensors at the end of each balance arm. Differential heat flow to the sample and reference is measured using thermocouples in the balance arms (see Figure 4). Heat flow calibration is based on sapphire heat capacity measurements from 200 to 1500°C. Continuous direct measurement of sample temperature accounts for high transition temperature repeatability and accuracy.

The TGA weight is measured by a taut-band meter movement located at the rear of each balance arm. An optically activated servo loop maintains the balance arm in the horizontal (null) position by regulating

the amount of current flowing through the transducer coil. An infrared LED light source and a pair of photo-sensitive diodes detect movement of the arm. A flag at the end of the balance arm controls the amount of light reaching each photo sensor. As weight is lost or gained, the beam becomes unbalanced, causing unequal light to strike the photo-diodes. A restoring current is generated to eliminate this imbalance and return to

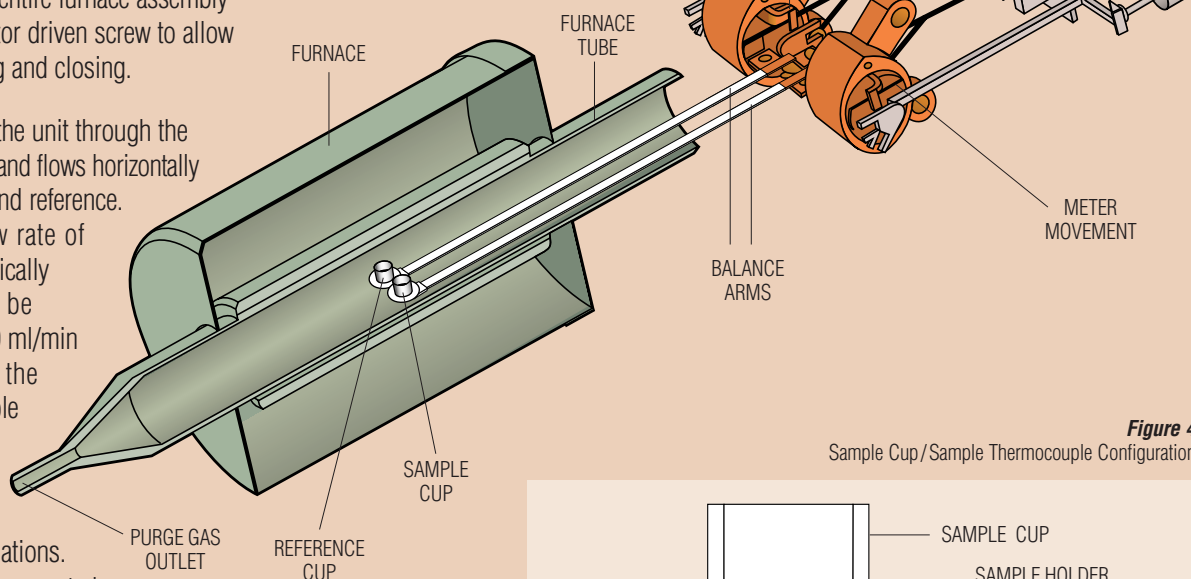


Figure 3
SDT 2960 Schematic

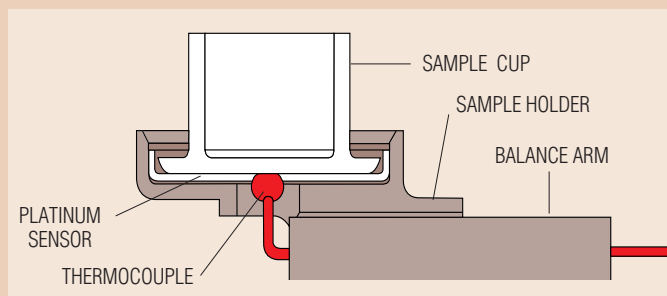


Figure 4
Sample Cup/Sample Thermocouple Configuration

the null position. The amount of restoring current is a direct measure of the weight change. The sample balance monitors actual sample weight, while the reference balance is used to correct the TGA measurement for temperature effects like beam growth via a proprietary algorithm.

Dynamic Normalization™ is a unique feature of the TA Instruments SDT 2960 which provides the ability to calculate normalized DSC data based on the “actual” weight of the sample. DSC data is “normalized” by dividing the heat flow signal by the sample weight. Most instruments simply use the initial sample weight for this calculation.

This practice can yield misleading results since the weight of the sample can (and often does) change during the experiment. The SDT 2960 takes advantage of its continuous weight measurement providing the user with the ability to specify how the DSC signals are to be normalized providing more accurate, meaningful, and repeatable results.

Features and Benefits

The SDT 2960 is designed with the operator in mind. It offers levels of performance and convenience which are not present in other commercial DSC-TGA instruments. Many of the SDT 2960's benefits are inherent in its operation as a component of a Thermal Analyst System. Key features and benefits include:

Wide Temperature Range, permitting evaluation of transition temperatures and weight changes for polymers and organic chemicals, as well as inorganic materials including ceramics, metals, and glasses.

Exceptional Weight Sensitivity, facilitating detection and measurement of very small weight gains or losses (0.1µg), and the use of small quantities of material. Dual beam design and proprietary software correct for beam growth effects at elevated temperatures even under changing weight conditions, assuring high accuracy and precision.

High DSC sensitivity with Dynamic Normalization™, provides the ability to detect weaker transitions, and to “normalize” heat flow calculations using the actual (instantaneous) sample weight providing more accurate, meaningful and repeatable results.

Dynamic Heat Flow Calibration, provides accurate and precise evaluation of heats of reaction over a wide temperature range.

Five-Point Temperature Calibration, for maximum temperature accuracy. The operator can choose from one to five calibration standards. High-purity metals with well-documented melting points are typically used.

Controlled Atmosphere, with horizontal flow of gas across the sample. This flow pattern helps assure good sample/atmosphere interaction while minimizing chimney and sample weight effects, and is ideal for directing the evolved decomposition gases to an FTIR or mass spectrometer for analysis.

Ease of Use Operator-oriented features including:

- Automated temperature calibration
- Automated heat flow calibration
- Automated weight calibration
- Automated taring and recording of sample weight
- Automated collection, storage, and display of data
- Automated furnace opening and closing
- Automated cool-down between experiments

Experimental Flexibility, with the ability to store virtually an unlimited number of methods containing up to 60 segments; each selected from 13 available functions, including control of heating (0.1 to 100°C/min), purge gas, and data handling. Both ceramic and platinum sample cups are available in several sizes to facilitate evaluation of a wide variety of samples.

Rapid Turnaround, with programmable end-of-run conditions including accelerated furnace cooling using a forced air purge.

Compatibility with other thermal/rheology techniques, broadening the range of materials and the types of measurements which can be performed. These other techniques include differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), thermomechanical analysis (TMA), dynamic mechanical analysis (DMA), dielectric analysis (DEA) as well as rheology. These techniques can be run individually, or in multimodule configurations, by the Thermal Analyst controller to provide complete materials characterization.

Data Analysis Software

Universal Analysis

A versatile “general purpose” data analysis program is an integral part of the *Thermal Advantage software™*. This program analyzes files from all the core modules (DSC, DTA, TGA, SDT, TMA, DEA, and DMA) as well as Micro-Thermal Analysis (µTA™) and provides many analysis capabilities including:

DSC/TGA Standard Analysis

- Temperatures of transitions
- Heats of fusion/reaction
- Dynamic Normalization
- Weight loss or gain
- Weight % at temperature
- Weight loss at temperature
- Moisture-free/ash-free calculation
- Residue analysis

Generic Functionality

- Peak integration
- Partial areas
- Onset temperature
- Step transition
- Running area integral plots
- Data point value
- Tabular data report
- Results report
- File export in a variety of formats
- Curve rotation
- File addition and subtraction
- Generic equation calculations
- X and Y linear transformation
- Curve overlay
- Saved analysis
- Saved session

Applications

The versatility of the TA Instruments SDT 2960 as a valuable tool for materials characterization and quality control is illustrated by these representative applications. These examples also illustrate many of the benefits inherent in the SDT 2960 system.

Improved Interpretation of Thermal Events

Simultaneous DSC-TGA results are often used to improve the interpretation of thermal events by providing both DSC and TGA data simultaneously on the same sample. The DSC analysis identifies exothermic/endothermic transitions while the TGA analysis evaluates weight changes which may be associated with those transitions.

Calcium Oxalate Monohydrate is a standard material often used to verify TGA performance. Like many materials, it behaves very differently when heated in oxidizing versus inert environments. The addition of DSC data illustrates this effect, and proves very helpful in interpreting data for a wide range of materials.

Figure 6 shows Calcium Oxalate Monohydrate data from two SDT experiments, one run in a nitrogen environment, and one run in air. In an inert atmosphere, the sample first loses H_2O , then CO and finally CO_2 . (TGA-Mass Spec data indicates that some of the CO evolved in step two reacts to form CO_2 , specifically, $2CO \rightarrow CO_2 + C$). All three of these weight losses are endothermic reactions as is evidenced in the DSC data. The TGA data from the experiment in air looks very similar to the data from the test in nitrogen. The DSC data, however, is substantially changed. The second weight loss is now accompanied by an exotherm, rather than the endotherm seen in the nitrogen atmosphere. In the oxidizing atmosphere, the CO evolved from the sample, immediately reacts with oxygen in the atmosphere to form CO_2 . This exotherm seen in the DSC data is evidence of this reaction.

Dynamic Normalization

Provides Accurate Transition Heat Flows

DSC data is routinely "normalized" by dividing the heat flow signal by the sample weight. This normalization provides the ability to quantify heats of fusion, reaction, etc in units of energy per unit mass so that samples of different sizes can be easily compared. The sample weight used in this calculation is typically the initial weight of the sample. However, many samples exhibit weight loss prior to the transition of interest, so use of the initial weight could induce substantial error.

Using its unique Dynamic Normalization™ algorithm, the SDT enables the user to specify how the DSC signals are to be normalized. Figure 7 shows DSC data from 3 sequential heats of Sodium Chloride using standard normalization. It would seem that the magnitude of the melting endotherm decreases with each heat. However, the TGA data shown in figure 8 shows that there is a weight loss associated with the volatilization of $NaCl$ that occurs upon melting. The result is that in each sequential heat, there is less sample weight.

The DSC data shown in figure 8 illustrates the benefit of Dynamic Normalization. Here the sample weight for transition normalization was taken as the weight at the beginning of each transition, and indeed all three heats show reproducible heats of fusion.

Figure 6

Calcium Oxalate Monohydrate
Simultaneous DSC-TGA in Air and in Nitrogen

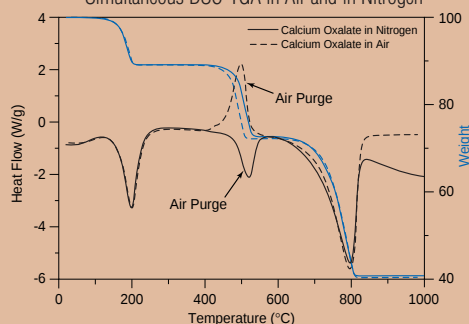


Figure 7

Sodium Chloride - Simultaneous DSC-TGA
without Dynamic Normalization

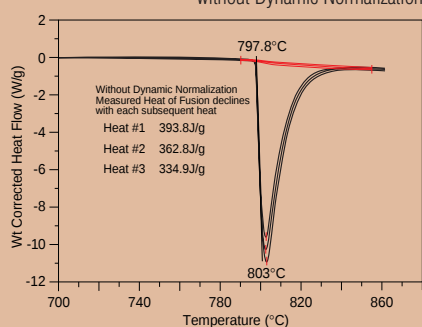


Figure 8

Sodium Chloride - Simultaneous DSC-TGA
with Dynamic Normalization

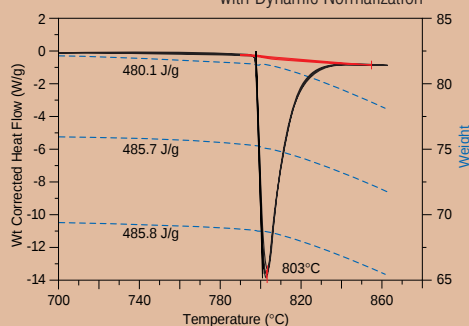
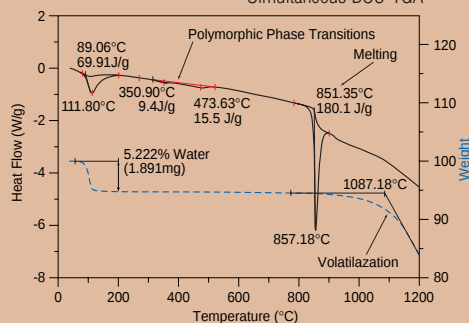


Figure 9

Soda Ash
Simultaneous DSC-TGA



Evaluation of Transitions Over a Wide Temperature Range

Simultaneous DSC-TGA provides evaluation of materials up to 1500°C. This ability to obtain measurements at higher temperatures is most useful for inorganic materials such as cements, clays, ceramics, superconductors, and metals. Figures 9 - 10 show typical examples.

Figure 9 shows DSC-TGA results for soda ash. TGA data shows the loss of water, as well as the onset of the vaporization process at higher temperatures. The excellent DSC sensitivity of the SDT 2960 enables us to see not only the endotherms associated with the water loss, and the large melting transition, but also the subtle endotherms associated with the two polymorphic transitions.

Kaolin, or china clay as it is often called, is an industrial mineral widely used in the paper, ceramics, catalyst, paint, and polymer industries. It is an aluminosilicate material that is used as a filler or coating material to provide enhanced performance including improved brightness and opacity. Figure 10 shows kaolin data from an SDT experiment. The TGA curve shows both the loss of free water just above room temperature, as well as the expulsion of water from the crystal lattice. The TGA derivative curve facilitates selection of analysis limits for these two weight losses, both of which correspond with endotherms in the DSC data. Also seen in the DSC data is a sharp endothermic peak associated with recrystallization.

Temperature and Enthalpy Accuracy and Reproducibility

Key to any DSC measurement is the ability to accurately and reproducibly measure temperatures and enthalpies of transitions. Figure 11 and Table 12 demonstrate the superior DSC performance of the SDT 2960. Figure 11 shows SDT data for multiple runs of zinc, aluminum, sodium chloride, and gold. These four materials cover a wide temperature range and hence are an excellent test of accuracy and reproducibility. Table 12 shows the results from eight runs in tabular format. Enthalpy accuracy and precision (reproducibility) for these four materials are better than 2%.

Excellent Performance Over a Wide Temperature Range

While the SDT 2960 design has been optimized to provide the best possible DSC performance at temperatures above 200°C, good DSC performance can be achieved at lower temperatures. An example of this lower temperature performance (of both DSC & TGA signals) is the analysis of gypsum. One of the uses of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is in the manufacture of portland cement, where 5% gypsum is used to reduce the rate of setting. The gypsum is added to the fused clinker during processing, and the two are milled to obtain uniform mixing and the required particle size. During this milling process, the thermal energy generated may cause partial dehydration of the gypsum to hemihydrate ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$). This adversely affects the rate of setting as well as the long term properties of the cement. The ability to study this two step dehydration is critical to insure optimum end use properties. Figure 13 shows SDT data for gypsum. Both the DSC and TGA curves clearly show both steps in the dehydration process.

Figure 10
Kaolin - Simultaneous DSC-TGA

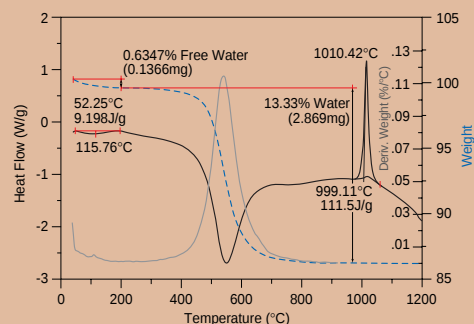


Figure 11
Temperature & Enthalpy Accuracy and Reproducibility - Simultaneous DSC-TGA

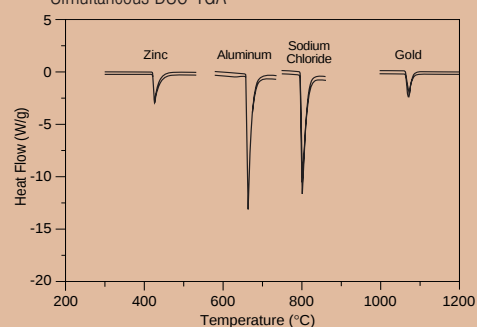
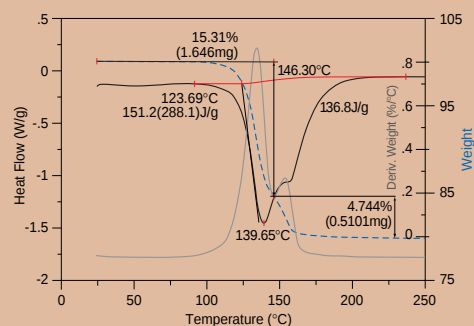


Figure 12
Temperature & Enthalpy Accuracy and Reproducibility - Simultaneous DSC-TGA

Run #	Zinc	Aluminum	NaCl	Gold
1	108.9 J/g	400.0 J/g	474.2 J/g	63.8 J/g
2	110.7	395.1	475.4	61.9
3	110.2	393.7	471.5	64.7
4	109.2	394.6	472.1	63.6
5	110.6	395.0	470.3	64.7
6	109.7	386.8	472.9	63.2
7	108.5	396.0	478.2	64.6
8	107.3	389.7	475.7	64.1
Average	109.4 J/g	393.9 J/g	473.8 J/g	63.8 J/g
Std Dev	1.2	4.0	2.6	1.0
Known Value	108.7 J/g	400.1 J/g	480.0 J/g	63.7 J/g
Accuracy	0.6%	1.6%	1.3%	0.2%
Precision	1.1%	1.0%	0.5%	1.5%

Figure 13
Gypsum - Simultaneous DSC-TGA



Specifications

<i>Temperature Range:</i>	Ambient to 1500°C**
<i>Sample Capacity (max):</i>	200 mg (350 mg including sample holder system)
<i>Balance Sensitivity:</i>	0.1 µg
<i>Calorimetric Accuracy:</i>	± 2% (based on metal standards)
<i>Calorimetric Precision:</i>	± 2% (based on metal standards)
<i>Heating Rate:</i>	0.1 to 100°C/min in 0.01°C/min increments (ambient to 1000°C) 0.1 to 25°C/min in 0.01°C/min increments (ambient to 1500°C)
<i>Purge Gas Rate:</i>	up to 1 liter/minute
<i>Purge Gases:</i>	Nitrogen, air, oxygen, argon, helium. 50 millitorr vacuum.
<i>Sample Pans:</i>	Platinum: 40 µl, 110 µl; Alumina: 40 µl, 90 µl*
<i>Temperature Calibration:</i>	1 to 5 points, based on metal standards
<i>Furnace Cooling:</i>	Forced air; 1500 to 50°C in less than 30 minutes
<i>Thermocouples:</i>	Platinum/Platinum-Rhodium (Type R)
<i>Data Collection Rate:</i>	0.5 to 1000 sec/point

*90 µl alumina pans recommended for DSC studies

**DSC performance optimized for 200-1500°C

DTA-TGA Capabilities

The SDT 2960 can easily be configured to provide DTA data for comparison with historical records. The high ΔT sensitivity (0.001°C) allows detection of small endothermic and exothermic transitions. Results are expressed either in °C or in µV.

TA Instruments Commitment

The SDT 2960 Simultaneous DSC-TGA is designed and engineered to assure easy, reliable, trouble-free operation. It is supported by a full range of services, including an applications laboratory, publications, training courses, seminars, applications CD's, internet website, and a telephone Hotline for customer consultation. Highly qualified service personnel specializing in thermal analyzer/rheometer maintenance and service are available throughout the world. All of these items reflect TA Instruments commitment to providing innovative thermal analysis & rheology products and related services that deliver the maximum value for your investment.

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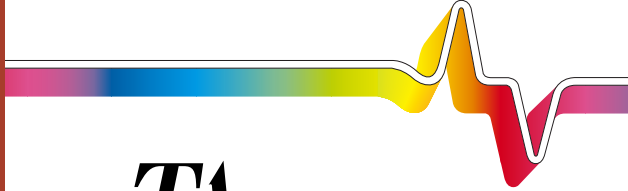
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