Thermogravimetric Analysis (TGA) & Differential Scanning Calorimetry (DSC)

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Lab Test Methods Day 2014

Background

Thermogravimetric Analysis (TGA)

- Test method capable of measuring the **mass evolution** of a milligram-scale sample.
- Gas atmosphere is well defined at all times during the experiment.
- The atmospheric temperature is well-defined and follows a pre-defined program.

Data Collected:

Mass of sample with respect to Time/Temperature.

Properties/Parameters Determined from Data:

Heterogeneous Reaction/Thermal Degradation Kinetics, Temperature Range for Pyrolysis

Background

Differential Scanning Calorimetry (DSC)

- Test method capable of measuring the **heat flow rate** to a milligram-scale sample.
- Gas atmosphere is well-defined at all times during the experiment.
- The atmospheric temperature is well-defined and follows a pre-defined program.

Data Collected:

Heat flow to sample with respect to Time/Temperature.

Properties/Parameters Determined from Data:

Heat Capacity, Enthalpy of Melting/Fusion, Enthalpy of Reaction/Thermal Degradation, Glass Transition Temperature.

Governing Principles

Background

Governing Principles

Operational Procedure

Data Analysis

Limitations

Sensitivity Analysis

Tips for Operation

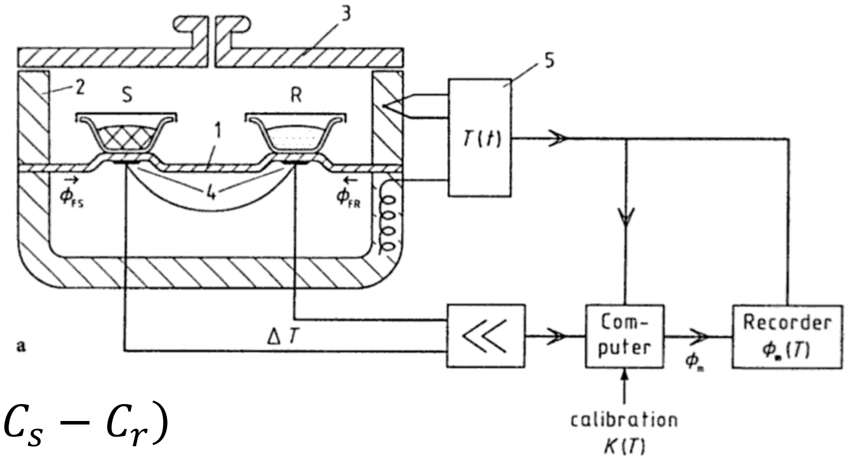
Additional Information

Heat Flux DSC

$$T_h \neq T_{sm} \neq T_s$$

$$R \neq R' \neq 0$$

$$\Delta T = T_{rm} - T_{sm} = R\left(\frac{dT}{dt}\right)(C_s - C_r)$$



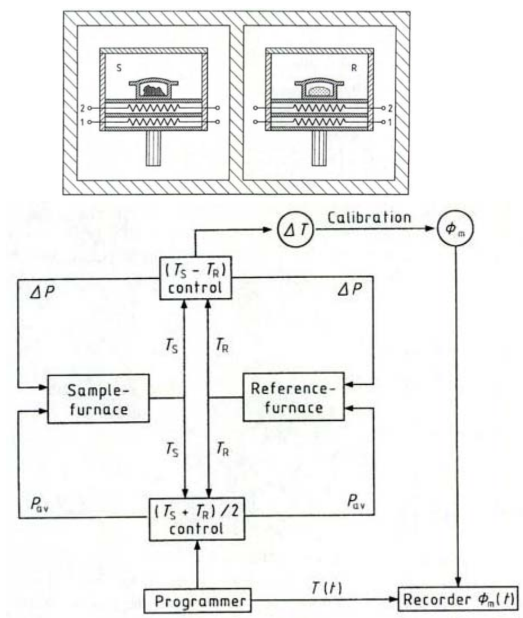
Power Compensation DSC

Power is varied such that:

$$T_{sm} = T_{rm} = T_h$$

$$R = 0$$

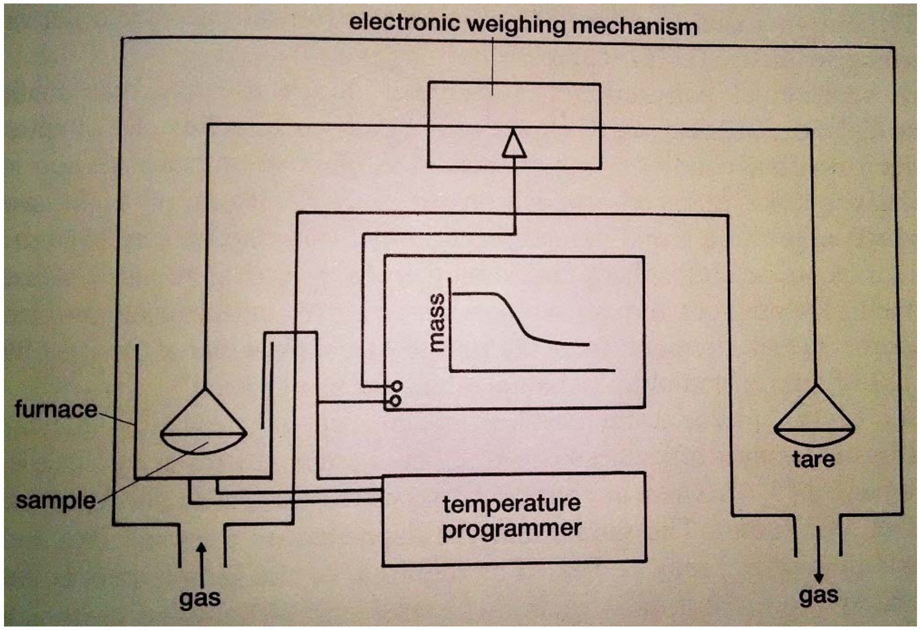
$$\Delta\left(\frac{dq}{dt}\right) = \left(\frac{dT}{dt}\right)(C_s - C_r)$$



Governing Principles

TGA

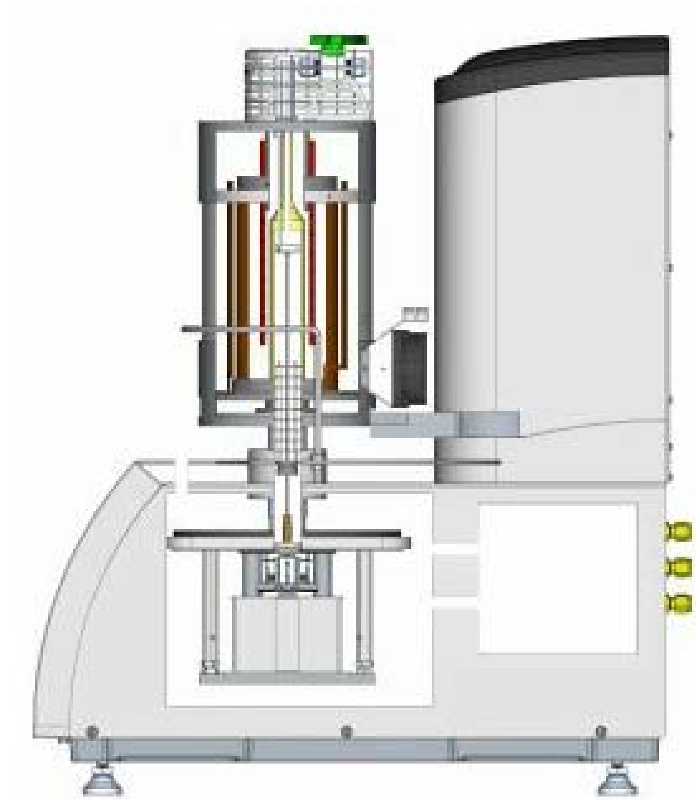
Micro–thermobalance measures any changes in the mass of the sample, whether due to adsorption of oxygen, thermal degradation, oxidation, or other heterogeneous reactions.



Governing Principles

Netzsch Simultaneous Thermal Analyzer (STA)

Incorporates TGA and DSC to measure mass change and heat flow rate simultaneously.



Operational Procedure

Background

Governing Principles

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Additional Information

TGA & DSC

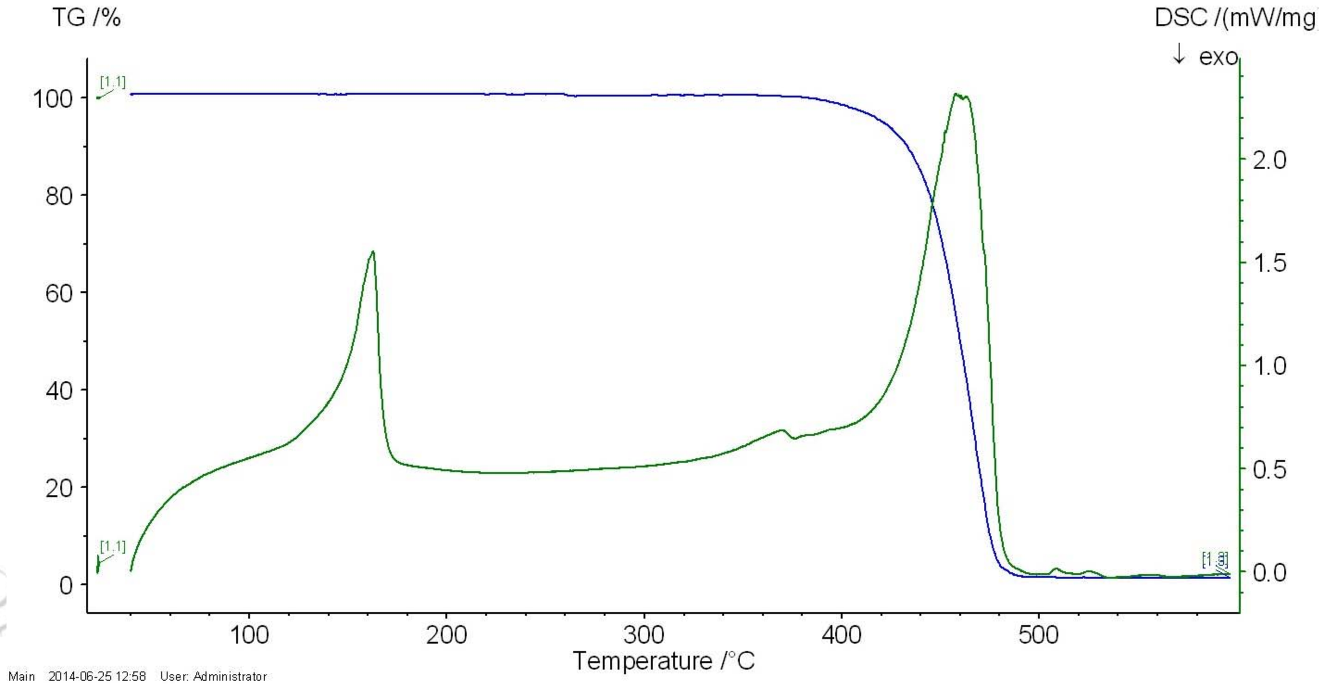
1. Conduct baseline experiment with empty sample crucible along a pre-defined temperature program in a well-defined gas atmosphere.
2. Prepare sample crucible by evenly packing sample material into crucible and measure mass of entire crucible.
3. Conduct experiment with sample along the same temperature program in the same gas atmosphere as in the baseline experiment.
4. Allow furnace to cool and clean the sample crucible used in experiment.

Considerations:
Temperature, Heating Rate, Sample Size

Data Analysis

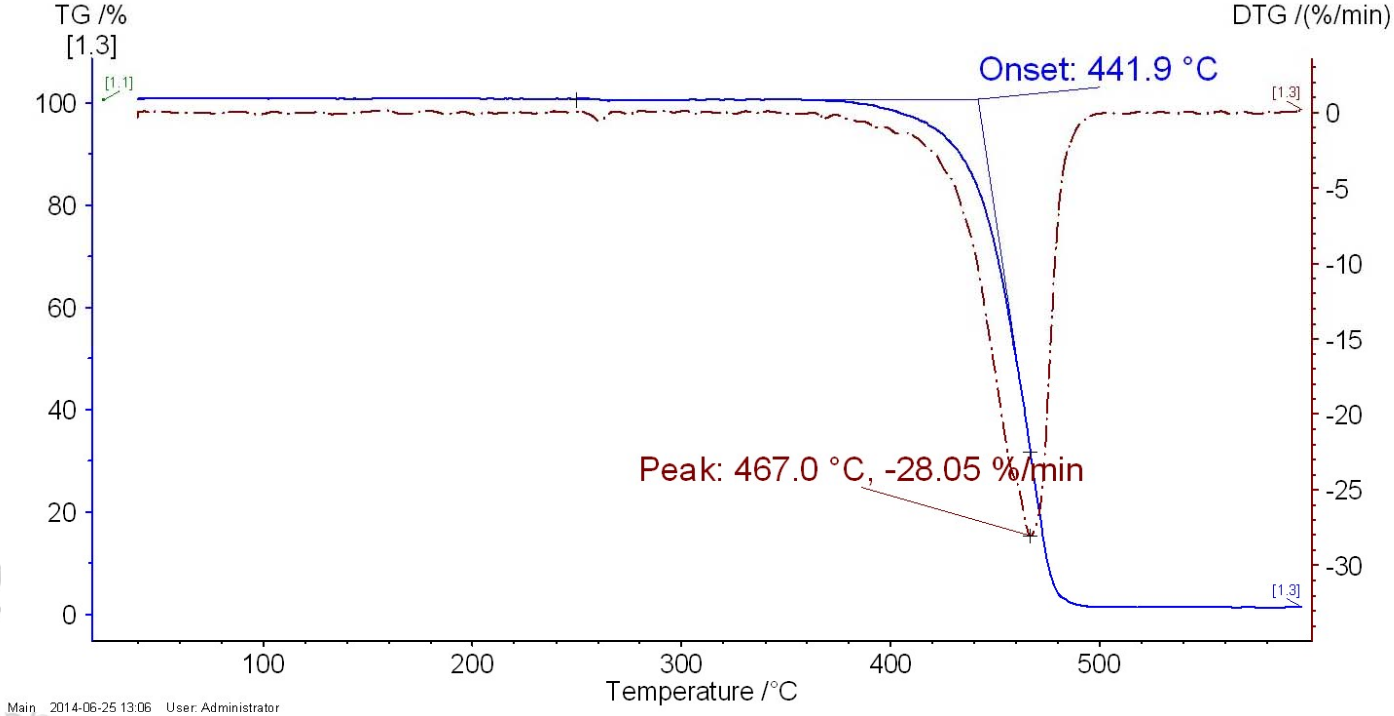
- Background
- Governing Principles
- Operational Procedure
- **Data Analysis**
- Limitations
- Sensitivity Analysis
- Tips for Operation
- Additional Information

TGA/DSC



Data Analysis

TGA



Data Analysis

TGA

A general homogeneous reaction is of the form:

$$A \rightarrow B + C$$

The rate of the reaction is assumed to be the product of a rate constant *k* and a function of the concentration of reactants and products. Where *k* is given by:

$$k = AT^m e^{-E/RT}$$

A similar analysis can be applied to heterogeneous reactions:

$$A(s) \rightarrow B(s) + C(g)$$

Concentration does not hold the same meaning with heterogeneous reactions, and degree of reaction or conversion is used:

$$\alpha = (m_0 - m)/(m_0 - m_f)$$

Data Analysis

TGA

For constant heating rate measurements ($\Phi = \frac{dT}{dt}$):

$$\frac{d\alpha}{dT} = \left(\frac{d\alpha}{dt}\right)\left(\frac{dt}{dT}\right) = \left(\frac{1}{\Phi}\right)\left(\frac{d\alpha}{dt}\right)$$

$$\frac{d\alpha}{dT} = \left(\frac{1}{\Phi}\right)\left(\frac{d\alpha}{dt}\right) = \left(\frac{A}{\Phi}\right)e^{-\frac{E}{RT}}g(\alpha)$$

$$\int_0^{\alpha}\left(\frac{1}{g(\alpha)}\right)d\alpha = \int_{T_0}^{T}\left(\frac{A}{\Phi}\right)e^{-\frac{E}{RT}}dT = f(\alpha)$$

Where:

$$f(\alpha) = kt \qquad g(\alpha) = \frac{1}{k}\frac{d\alpha}{dt}$$

Many methods to determine A, E, and functional form of $f(\alpha)$ or $g(\alpha)$.

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Governing Principles

Operational Procedure

Data Analysis

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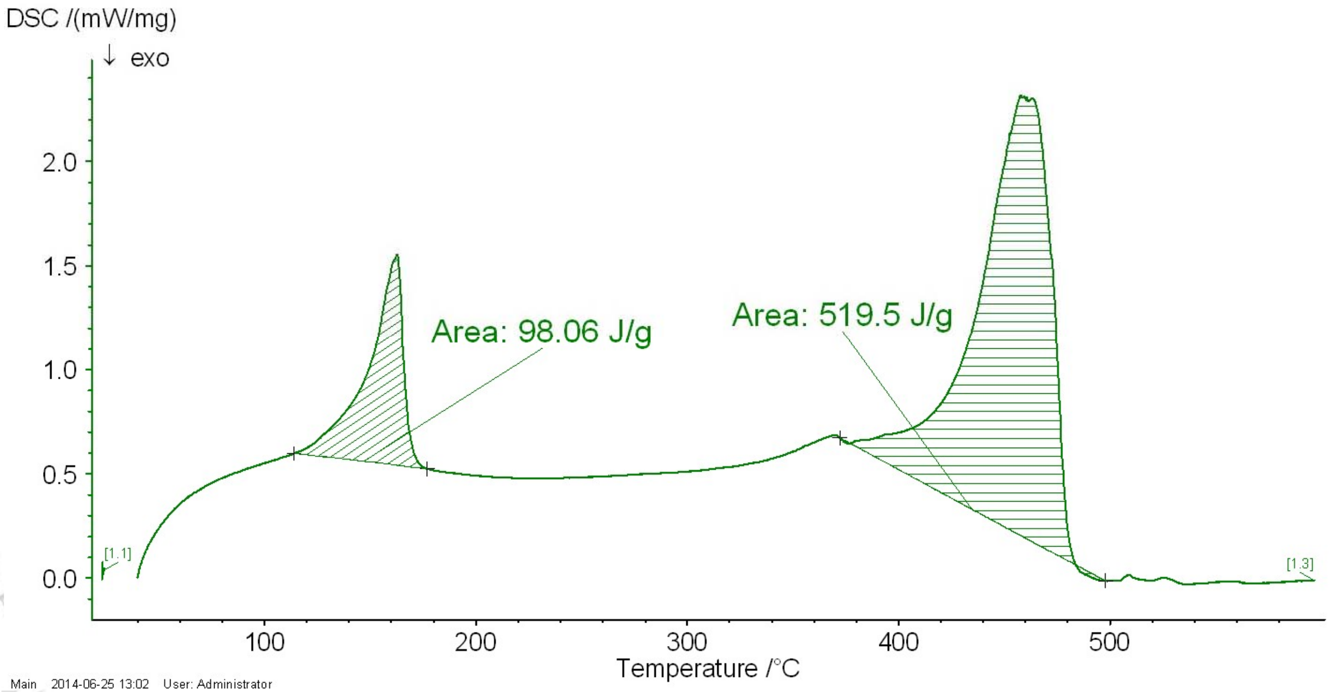

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Background

Governing Principles

Operational Procedure

Data Analysis

Limitations

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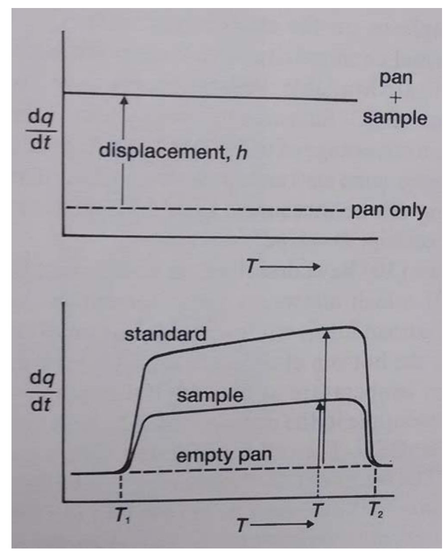
DSC

Thermal events in the sample manifest as deviations from the baseline, most likely as exothermic or endothermic peaks.

$$\dot{q} = \Delta h_r - c_p \frac{dT}{dt}$$

Specific heat capacity is determined by comparing the heat flow rate curves yielded from the sample and a standard reference:

$$\text{displacement} = B\Phi C_p$$



Limitations

TGA

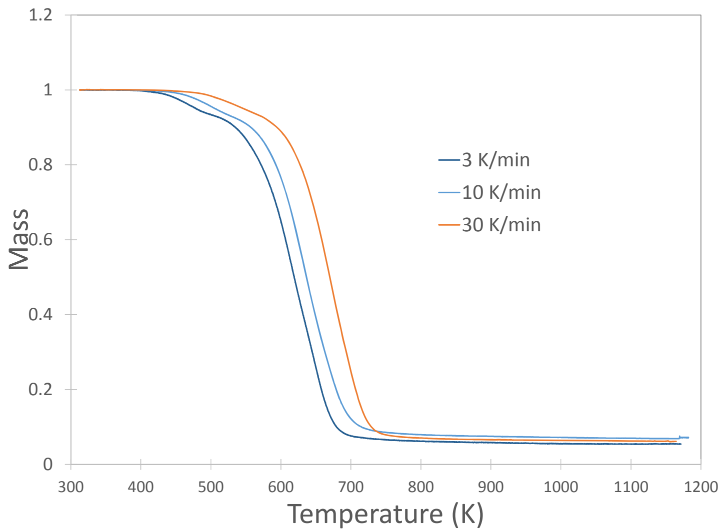
- Only provides meaningful data when a change in mass occurs.
- Some liquids can be measured, but this is generally very difficult to do.
- Very small samples are used, so non–homogeneous materials generally cannot be tested

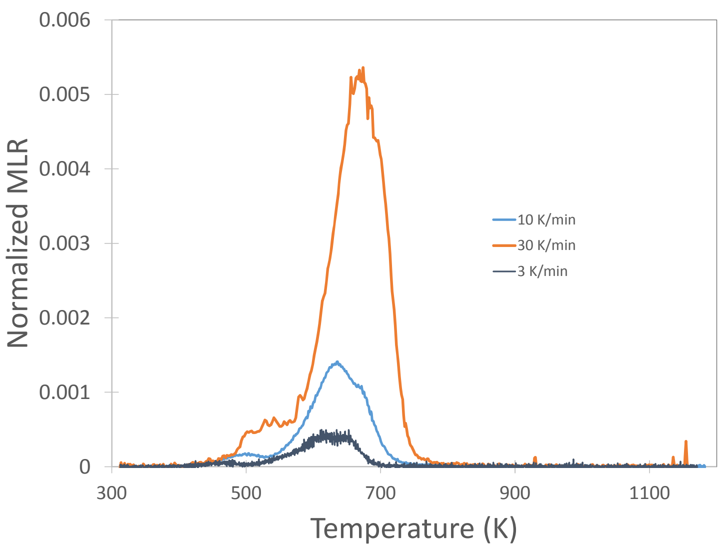
DSC

- Very sensitive to any change in the sample or crucible.
- Requires very good thermal contact with bottom of sample crucible
- Very sensitive to heating rate

Sensitivity Analysis

TGA and DSC are both sensitive to the **heating rate** and **sample masses** and either can result in shifts in the temperature.





Tips for Operation

- Make sure sample and reference crucibles are perfectly clean prior to tests.
- For heat capacity determination make sure that orientation of sample and reference crucibles are consistent between all replicant tests.
- Make sure the crucible material will not react or interfere with the sample material and vice versa.
- Always build in an isothermal period prior to linear heating to allow the sample to reach equilibrium with the furnace conditions.

Additional Information

Brown, Michael E. 1988. *Introduction to Thermal Analysis: Techniques and Applications*. New York, NY: Chapman and Hall

Hohne, Gunther, Hemminger, Wolfgang F., Flammersheim, H.J. 2003. *Differential Scanning Calorimetry* 2 ed. New York, NY: Springer

Thank you!
Questions?