Thermogravimetric Analysis (TGA)

Theory and Applications

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TGA: Theory and Applications





•TGA measures weight/mass change (loss or gain) and the rate of weight change as a function of temperature, time and atmosphere.





What TGA Can Tell You

- Thermal Stability of Materials
- Oxidative Stability of Materials
- Composition of Multi-component Systems
- Estimated Lifetime of a Product
- Decomposition Kinetics of Materials
- The Effect of Reactive or Corrosive Atmospheres on Materials
- Moisture and Volatiles Content of Materials
- Residue



Mechanisms of Weight Change in TGA

•Weight Loss:

- Decomposition: The breaking apart of chemical bonds.
- Evaporation: The loss of volatiles with elevated temperature.
- Reduction: Interaction of sample to a reducing atmosphere (hydrogen, ammonia, etc.).
- Desorption.
- •Weight Gain:
 - Oxidation: Interaction of the sample with an oxidizing atmosphere.
 - Absorption.
 - All of these are kinetic processes (i.e. there is a rate at which they occur).



DSC-TGA (SDT): The Technique

- Simultaneous DSC-TGA measures both heat flow and weight changes in a material as a function of temperature or time in a controlled atmosphere from room temperature to 1500°C.
- 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).





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- Moisture and Volatiles Content of Materials
- Residue
- Transition Temperatures
- Heats of Fusion and Reactions
- Melting and Boiling Points
- Heat capacity



Thermal Stability of Polymers





Oxidative Stability (Polypropylene)





TGA of Drug A Monohydrate





TA Instruments TGA/SDT Models





Discovery TGA





SDT 650





TGA Specifications

	TGA 5500	TGA 550/50
Temperature Range	Ambient to 1200°C	Ambient to 1000°C
Hearting Rate Range	0.1 to 500°C/min (Linear) >1600°C/min (Ballistic)	0.1 to 100°C/min (Linear)
Sample Weight Capacity	1000 mg	1000 mg
Dynamic Weighing Range	1000 mg	1000 mg
Baseline Dynamic Drift (50-1000°C)	< 10 µg	<50 µg



SDT Specifications

	SDT 650
Temperature Range	Ambient to 1500°C
Hearting Rate Range	0.1 to 100°C/min (Linear)
Sample Weight Capacity	200 mg
Baseline Dynamic Drift (50-1000°C) (1000°C t0 1500°C)	<50 μg <50 μg



TGA: Schematic Diagram





TGA Balance and Operation



- •Null-balance principle operation
- •Current is applied to the meter movement
- Amount of current applied is proportional to the weight change



TGA Furnace Options: Wire Wound Furnace

- Standard furnace for TGA 55 and 550
- Ambient to 1000 °C
- •Linear controlled heating rates of 0.01 to
- Ballistic heating rates >600 °C/min
- Exchangeable with EGA furnace



Wire Wound (Pt/Rh) Furnace

Flow rate Balance/Sample : 40/60 ml/min



TGA Furnace Options: EGA Furnace

- •Optional for TGA55 and 550
- Ambient to 1000 °C
- Linear controlled heating rates of 0.0
- Quartz liner makes furnace easy to c
- Exchangeable with wire wound furna



EGA Furnace

Flow rate Balance/Sample : 10/90 ml/min



TGA Furnace Options: Infra Red (IR) Furnace

- Quartz halogen lamps as heating source
- Ambient to 1200°C
- Linear controlled heating rates of 0.01 to
- Ballistic heating rates >1500 °C/min
- Integrated electromagnet for Temperatur with Curie point standards
- Evolved Gas Analysis capacity



IR Furnace

Flow rate Balance/Sample : 25/25 ml/min



SDT: Schematic Diagram





TGA Calibration and Verification

•Two types of calibration are needed:

- Weight
- Temperature
- Temperature calibration is affected by:
 - Purge gas and flow rate
 - Thermal conductivity of helium ≠ Thermal conductivity of nitrogen/air/oxygen ≠ Thermal conductivity of argon
 - Pan type
 - Heating rates



General Calibration and Verification Guidelines

Calibration

- Use Calibration Mode
- Calibrate upon installation
- Re-calibrate if does not pass verification or if instrument setup is modified (see previous slide)

Verification

- Determine how often to verify data
- Run a reference material as a sample (in standard mode)
- Compare results vs literature values
- Re-calibrate if results are out of tolerance



Requirements Prior to Calibration

- The TGA pan should be cleaned prior to calibration procedures.
- •The purge gas flow rate should be set (see flow rates according to furnace type). The flow rate should not deviate by more than +/- 5ml/min.
- Use high purity reference materials (>99.99%) for calibration



Mass/Weight Calibration

•Weight calibration can be performed:

- Manual, using an empty pan and calibration weights
- Automatically, using the three weight calibration fixtures (pans) P/N 957341.901 (on Q5000IR, Discovery, and TGA 55XX).
- •The calibration pans may only be used when a platinum reference pan is installed.



- The mass signal generated by a TGA is compared to the mass of a reference material traceable to a national reference laboratory. A linear correlation using two calibration points is used to relate the mass (or weight) signal generated by the TGA and that of the reference material
- This test method calibrates or demonstrates conformity of thermogravimetric apparatus at ambient conditions. Most TGA experiments are carried out under temperature ramp conditions or at isothermal temperatures distant from ambient conditions. This test method does not address the temperature effects on mass calibration
- •On Manual calibration, TA Instruments uses a zero tare, then a 100mg and 1000mg mass standards



Calibration – Weight (Auto)

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Calibration – Weight (Manual)

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Calibration – Weight (Manual)

Simply reload the mass to verify – mass difference of ~ 0.005%





ASTM E 1582 - Calibration of Temperature Scale for TGA

- The standard describes two methods by which the TGA can be calibrated for temperature; by melting point or magnetic transition. The most common approach for a TGA would be the magnetic transition approach
- Curie Point Temperature that temperature where the material loses its magnetic susceptibility - defined as offset point
- Paramagnetic a material that is susceptible to attraction by a magnet
- Temperature Calibration points are determined by comparing the measured melting onset temperature to the literature value
- TA Instruments software allows for up to 5 temperature calibration points

 Generally, these should bracket the temperature range of interest for subsequent samples



TGA: Temperature Calibration

Vertical Balance Configuration



lost at the Curie Transition

Temperature

SDT: Temperature Calibration

Horizontal Balance Configuration





- International Confederation for Thermal Analysis and Calorimetry (ICTAC) developed a set of six certified and traceable Curie temperature reference materials for the calibration of TGA
 - Alumel 153°C
 - Nickel 358C
 - Ni83Co17 555°C
 - Ni63Co37 747°C
 - Ni37Co63 931°C
 - Cobalt 1116.0°C
- The materials permit temperature calibration in about 200 °C intervals over the range of 150 to 1120 °C
- TA Instruments is the exclusive worldwide distributor for these Curie point materials



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Verification – Temperature

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From the 'Results' Pane, Choose both the Alumel and Nickel Runs





Choose 'Calibrations' and 'TGA Temperature'




Calibration – Temperature

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TGA – Temperature Calibration







TGA – Temperature Verification







Calibration – Temperature: Verification





Curie Standards with ICTAC traceability





- Although Calcium Oxalate is not generally accepted as a "Standard Material," it does have practical utility for INTRAlaboratory use
- Carefully control the experimental conditions; i.e. pan type, purge gases/flow rates, heating rate
- Particularly control the amount (~5mg) and the particle size of the sample and how you position it in the pan
- Perform multiple runs, enough to do a statistical analysis
- Analyze the weight changes and peak temperatures and establish the performance of YOU and YOUR instrument
- When performance issues come up, repeat the Calcium Oxalate analysis



Calcium Oxalate Decomposition

1. step $CaC_2O_4 \cdot H_2O(s)$

Calcium Oxalate Monohydrate

Calcium Oxalate

2. step

 $CaC_2O_4(s) \longrightarrow CaCO_3(s) + CO(g)$

Calcium Oxalate

Calcium Carbonate

^{3. step} CaCO₃(s) \longrightarrow CaO(s) + CO₂(g)

Calcium Carbonate

Calcium Oxide



 $CaC_{2}O_{4}(s) + H_{2}O(g)$

Calcium Oxalate Repeatability

Overlay of 8 runs, same conditions





Calcium Oxalate Repeatability

	Transition 1		Transition 2		Transition 3	
	Wt Change	Peak Temp	Wt Change	Peak Temp	Wt Change	Peak Temp
Run #	%	°C	%	°C	%	°C
1	12.13	156.68	18.78	493.37	29.62	684.33
2	12.22	153.60	18.75	494.17	29.56	680.43
3	12.20	155.40	18.76	495.6	29.63	684.11
4	12.21	155.58	18.77	495.98	29.69	688.11
5	12.21	154.05	18.75	494.72	29.54	684.28
6	12.20	154.91	18.73	495.62	29.58	684.83
7	12.21	155.09	18.77	494.71	29.61	683.92
8	12.20	153.52	18.77	493.84	29.57	681.85
Ave	12.20	154.85	18.76	494.75	29.60	683.98
Std Dev	0.028	1.08	0.016	0.93	0.048	2.24
Theoretical	12.3		19.2		30.1	
Accuracy	0.8%		2.3%		1.7%	
Precision	0.2%		0.1%		0.2%	



SDT Calibration and Verification

- Calibrate upon initial installation
- Re-calibrate anytime the beam set, experimental heating rate, or purge gas is changed
- •Types of calibration available:
 - Weight Calibration: (TGA weight signal)
 - DTA Signal Setup: Analyzing the Delta T signal data
 - Temperature (Melting point or curie point standards as in TGA. Commonly use melting point standards)
 - DSC Heat Flow
 - MDSC Reversing Heat Capacity (SDT 650)



SDT Calibration and Verification

• DTA signal:

Not required when using the SDT as a DSC-TGA

- This run usually utilizes the same baseline run obtained for TGA Weight Calibration
- Heat flow and cell constant:
 - Based on analyzing the heat capacity curve for sapphire over the range 200 to 1500°C. Three experimental runs are required: two runs to generate the heat flow curve and another run to refine that calibration through cell constant calibration using a known metal standard (zinc, for example)

• MDSC Reversing heat capacity:

A heat capacity calibration curve is generated by running a sapphire sample over a desired temperature range using appropriate modulated conditions. The collected Reversing Heat Capacity curve is calibrated against the true value of the heat capacity of sapphire over the experimental temperature range



Instrumental Considerations



Instrument Hardware and Gas Selection Considerations

- Gas Delivery Module and Mass Flow Controllers
 - The gas 1 port purges both sample and balance areas
 - Gas 1 should be an inert gas (N2, He, Ar)
 - The gas 2 port is used when a different purge gas is required, or gas switching is used
 - Typically this is air or O2
 - Gas type is assigned to Mass Flow Controller in the Instrument section of the control software and chosen before on the setup page.

Gases Typically used on TGA/SDT

- Nitrogen inert, inexpensive and readily available
- Helium inert, commonly used on TGA-MS
- •Argon inert
- Air/Oxygen used when studying oxidative stability of materials, can sometimes improve resolution of weight loss events





- For use with TGA 550,TGA 5500 and SDT 650
- Allows blending two gases as main sample purge for a test. Nitrogen, helium, argon, oxygen, air, carbon dioxide, carbon monoxide, and forming gas (a blend of 4% hydrogen with 96% nitrogen) may be blended



Four gases can be used in a test





Blending Gas Delivery Module

Balance and sample purge flow will depend on the instrument:



Back panel of the Blending GDM.

TGA 550	40	60	
TGA 5500	25	25	Balance/Sample
SDT 650	100	100	



Test for Oxygen Contamination of N2 Purge Gas





Effect of Oxygen on Copper Oxalate





Test for Oxygen Contamination of N2 Purge Gas





Effect of Oxygen on Copper Oxalate



Copper Oxalate – Large Mass





Baseline Performance Verification

- A good way to quantify how well the TGA is working
- Especially important for measuring small weight losses associated with volatilization or small amounts of residue
- Run clean, empty, tared pan, over temperature range of interest, at desired heating rate
- Plot weight in µg vs. temperature
- Dynamic drift should be less than 10 µg for the Discovery TGA 5500, and Discovery TGA and less than 50 µg on the Discovery TGA 550/55 & Q Series TGA's when using platinum pans and 20°C/min heating rate

TGA: Factors Influencing Baseline

- Stability of table
- Hang down wire / beam condition
- Hang down tube condition
- Leveling of TGA
- Cleanliness of the furnace
- Purge gas flow rates





Empty Platinum Pan Baseline Scan @ 20°C/min



Effect of Purge Gas Flowrate on Baseline





Effect of Purge Gas Flowrate on Baseline





Balance Sensitivity- 120 µg Calcium Oxalate





Sample: 27µg Sodium Tartrate





TGA: High Sensitivity Volatiles Analysis





TGA: Sample Preparation

- Sample mass
 - 10-20mg for most applications
 - 50-100mg for measuring volatiles or residues
- If a TGA has a baseline drift of +/-25mg then this is 0.25% of a 10mg sample





TGA particle size matters, NaCl decrepitation





TGA: Sample Preparation

- Use brass tweezers to eliminate static effects
- Tare a clean sample pan before every run
- Distribute sample evenly over bottom of pan
- Liquid samples use hermetic pan with a pin-hole lid





TGA: Sample Pan Selection

- Platinum (useful for most materials)
 - Easy to clean
 - Nonporous
 - Can alloy with most metals
- Alumina (Ceramic)
 - Corrosives/Inorganics
 - Large samples
 - Porous, can be easily contaminated
- Aluminum (TGA) (designed for one-time use)
 - Lower cost, disposable
 - Lower temperature limit (<=600°C)





SDT: Sample Pans - Types/Sizes

- Platinum:
 - 40 mL
 - 110 mL

- Alumina:
 - 40 mL
 - 90 mL





Sealed Aluminum Pans





Sealed Aluminum Pans and Punching




TGA: Sample Pan Cleaning

- All sample pans are reusable (except Aluminum)
- If using platinum or alumina pans, a flame torch can be used to burn off organic residue. (do not flame Aluminum pans)
- Scrape off remaining ash (DSC fiberglass brush)
- Swab out with an organic solvent such as acetone or alcohol. Let it dry out before using it





- Avoid areas near heater or air conditioner ducts
- Avoid tables with drawers or those near a door
- For optimum results, use a marble table



Evolved Gas Analysis

Identification of Decomposition Products Using TGA/FTIR and TGA/Mass Spec



Why Use Evolved Gas Analysis?

- TGA measures weight changes (quantitative)
- Difficult to separate, identify, and quantify individual degradation products (offgases)
- Direct coupling to identification techniques (Mass Spec, FTIR) reduces this problem

TGA-EGA: Typical Applications

- Polymers (composition, hazard evaluation, identification)
- Natural Products (contamination in soil, raw material selection {coal, clays})
- Catalysts (product/by-product analysis, conversion efficiency)
- Inorganics (reaction elucidation, stoichiometry, pyrotechnics)
- Pharmaceuticals (stability, residual solvent, formulation)



Why Use Evolved Gas Analysis?

- •TGA measures weight changes (quantitative)
- Difficult to separate, identify, and quantify individual degradation products (off-gases)
- Direct coupling to identification techniques (Mass Spec, FTIR) reduces this problem



Requires a heated transfer line so that the off-gases remain in the vapor state as they are transferred from the TGA to the off-gas analysis equipment.





Caused by

- •Formulation Process
- •Molecular Structure
- •Contaminates



Investigate Chemical Composition

Multi-Component Systems
Hydrate/Solvate Systems
Decomposition Products
Volatiles





Understand & Predict

- •Composition
- •Decomposition Pathways
- •Undesirable Residual Components
- •Reaction Products



Hyphenation

- TA partners with and sells the Pfeiffer ThermoStar Quadrupole Mass Spectrometer.
- TA recommends ThermoNicolet as the preferred vendor for FTIR spectrometers, but if the transfer line can attach to our TGA, we will hyphenate with others.
- TA has worked closely with Red Shift (Italy) and Agilent in providing a GC/MS solution.
- Possible to hyphenate more than one instrument to the TGA output.





Which Technique is Best?

- •TGA decompose sample in the furnace
- Off gases (Often times mixture of gases) send to secondary detection
- •Type of detection
 - MS further broke down into ions and detects ion fragments in m/z cannot identify ion fragments with the same m/z, such as m/z 28 N₂ or CO
 - FTIR detects energy absorption in different wavenumbers Cannot detect molecules without change of dipole moments, such as N₂ or O₂
- Mixture of gas
 - GC/MS chromatographic separation ensures that a mass spectrum of a pure compound is obtained



Continuous versus Non-continuous Spectra Collection

Continuous:

Multiple spectra obtained over time during expt.

- MS
- FTIR

Non-Continuous:

One spectrum obtained at only one time during expt.

GCMS
 Inject gas into GC and required time for separation





Types of Hyphenation: Mass Spectrometry





TGA-Mass Spectroscopy

Advantages:

- Continuous method
- •Higher sensitivity than IR Spectroscopy.
- Measures non-IR absorbing gases.
- •Rapid response (gases drawn into capillary).

Disadvantage:

- Cannot distinguish between molecules with similar molecular weights. (e.g. N₂ and CO)
- Sometime is difficult for data interoperation



Pfeiffer ThermoStarQuadrupole Mass Spectrometer

- Benchtop, unit resolution quadrupole mass spec designed and optimized for evolved gas analysis (EGA)
- Quadrupole detection system includes...
 - a closed ion source
 - a quadrupole mass filter assembly
 - 1-300 amu range
 - dual detector system (Faraday and microchannel plate)



EGA Furnace

IR Furnace



TGA MS: Polyphenylene Oxide (PPO)





TGA-MS: Polyphenylene Oxide (PPO)





TGA-MS: Polyphenylene Oxide (PPO)













FTIR (Fourier Transform Infrared Spectroscopy):

Advantages:

- Continuous method
- Easy Spectral Subtraction
- Library searches are straightforward / deconvolution possible

Disadvantages:

- No detection of gases lacking a dipole moment
- Need to input the time for FTIR data collection



TGA-FTIR: Analysis of Polyphenylene Oxide





TGA-FTIR: Analysis of Polyphenylene Oxide





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EGA Example – TGA/FTIR

- The gases produced during thermal breakdown of the sample flow through a heated transfer line into a gas cell where infrared radiation passes through.
- The total infrared absorption and frequency as a function of time is stored in an array as the Gram Schmidt file which is opened with the instrument software (Gram Schmidt Reconstruction).
- The Gram Schmidt reconstruction will typically resemble the derivative with respect to temperature of the weight loss curve in the TGA experiment.
- Individual FTIR spectra are displayed by selecting points on the x-axis of the Gram Schmidt reconstruction which has units of intensity as a function of time.
- Typically spectra can be searched using vendor supplied spectral data bases and reliable identifications of species can be made.



TGA-FTIR: Analysis of Polyphenylene Oxide





- Libraries give the best <u>single</u> spectra match to the data presented.
- If multiple components are being emitted during a single weight loss event, the spectra will be superimposed upon each other possibly leading to difficulties.
- •The existence of searchable libraries does not relieve the analytical chemist from critically analyzing the search results.
- ThermoNicolet FTIR software can attempt to deconvolute a spectrum to a maximum of four components. Demonstration can be found in this TA Instrument webinar: <u>https://www.tainstruments.com/evolved-gas-analysis-tgaftir/</u>



















- •Compounds that have weak intermolecular force (IMFs) with the column coating (low boiling points), spend little time in the stationary phase, exit the column early, and have shorter retention times.
- •Compounds that have strong IMF's with the column coating (high boiling points), have longer retention times.



Abundance	1			2.520	4.446
700000	1.858				
600000-		Heptane	Octane	Nonane	Decane
500000-		(C7H16)	(C8H18)	(C9H20)	(C10H22)
400000-					
300000-					
200000-	Lowest b.p.				Highest b.p.
100000-					
Time>	1.50	2.00 2.5	3.00	3.50 4.00	4.50 5.00



Advantages:

- Chemical Separation
- Easy library searching

Disadvantages:

- •Typically time consuming not a continuous measurement
- Require Redshift interface

Anatomy of a GC/MS Run: Polyphenylene Oxide





TGA-GC/MS: Analysis of Polyphenylene Oxide

After gas injection, the GC/MS Oven is ramped from 50 to 250°C at 10°C/min





GC/MS Library Search; Largest Peak





Evolve Gas Analysis – TGA Hyphenation

REDshift





General Considerations

Experimental Effects



- •Because most events that occur in a TGA are kinetic in nature (meaning they are dependent on absolute temperature and time spent at that temperature), any experimental parameter that can effect the reaction rate will change the shape / transition temperatures of the curve.
- These things include:
 - Sample Mass
 - Heating Rate
 - Purge gas
 - Sample volume/form and morphology



Larger sample mass increases the observed decomposition temperature





Higher heating rates increase the observed decomposition temperature





Sample Morphology Effects – PET




High-Heating Rate TGA Analysis



High-Heating Rate TGA Analysis





What if I need help?

TA Tech Tips

http://www.youtube.com/tatechtips

Email the TA Instruments Hotline

<u>thermalsupport@waters.com</u>

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