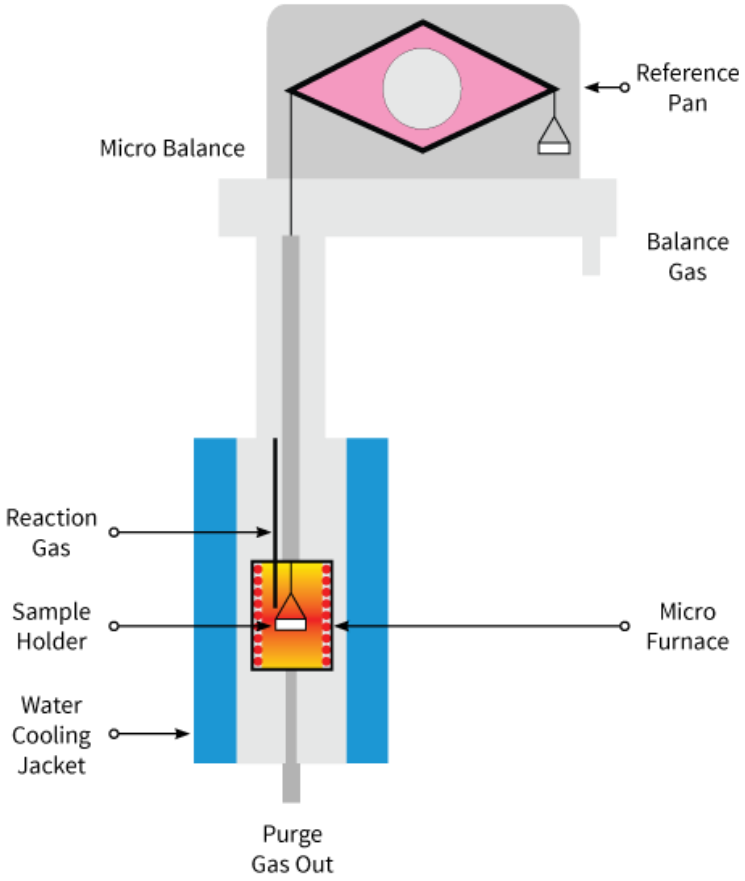
Sveučilište u Zagrebu
Fakultet kemijskog
inženjerstva i tehnologije

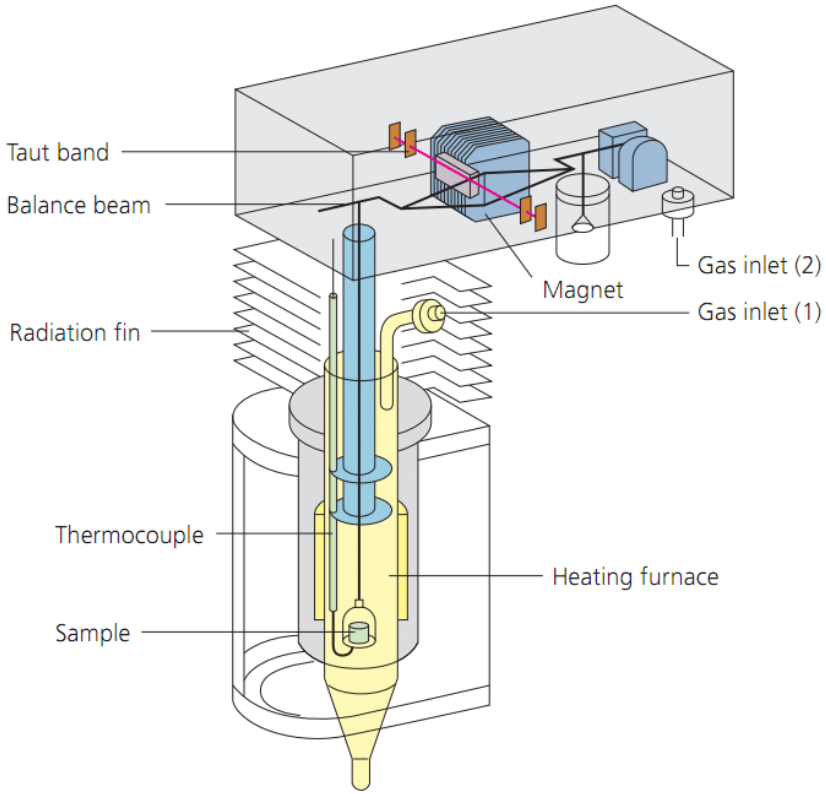
University of Zagreb
Faculty of Chemical Engineering and Technology

Structure and properties of polymer materials

seminars

Zagreb, October 2021


Reference Pan
Micro Balance
Balance Gas
Reaction Gas
Sample Holder
Micro Furnace
Water Cooling Jacket
Purge Gas Out


Taut band
Balance beam
Gas inlet (2)
Magnet
Gas inlet (1)
Radiation fin
Thermocouple
Heating furnace
Sample

THERMOGRAVIMETRIC ANALYSIS (TGA)

Thermogravimetric analysis is a technique which records the weight/mass change (loss or gain) and the rate of mass change as a function of temperature, time and surrounding atmosphere

TGA measures a sample's weight as it is heated in a furnace

Measurements are used primarily to determine the composition of materials and to predict their thermal stability. The technique can characterize materials that exhibit mass loss or gain.

Mechanisms of mass change in TGA

Mass loss:

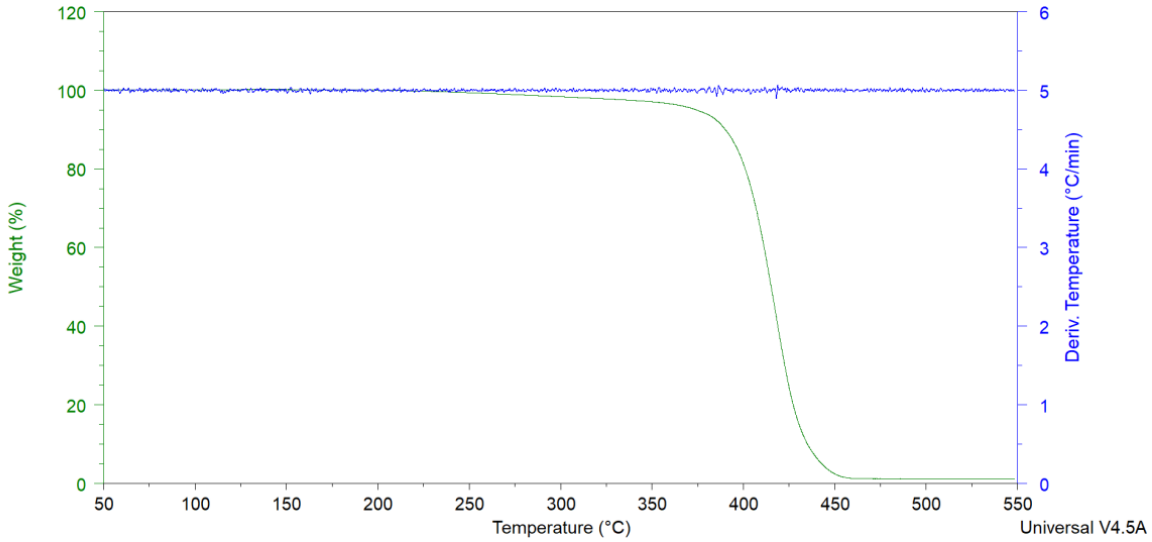
- Decomposition: the rupture (breaking) of chemical bonds
- Evaporation: the loss of volatiles with increasing temperature
- Chemical reduction: interaction of sample with a reducing atmosphere (hydrogen, ammonia, etc.)
- Desorption

Mass gain:

- Oxidation: interaction of sample with an oxidizing atmosphere (air, oxygen)
- Absorption

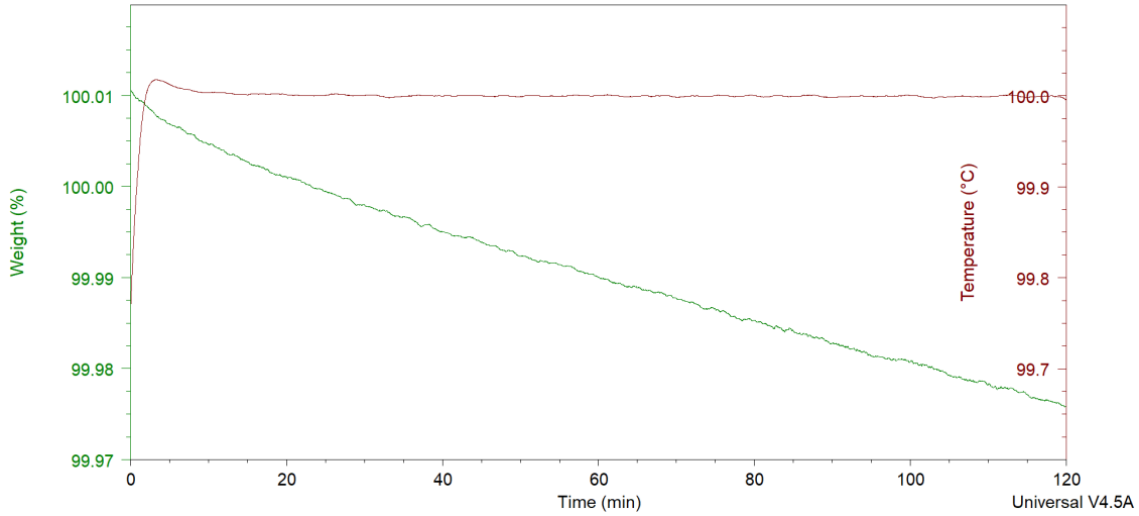
Dynamic TGA

Mass loss is measured while heating a sample in an environment whose temperature is changing in a predetermined manner, generally linearly, e.g. with 5 °C/min, 10 °C/min, …

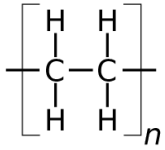


Isothermal TGA

Mass loss is measured at constant temperature as a function of time

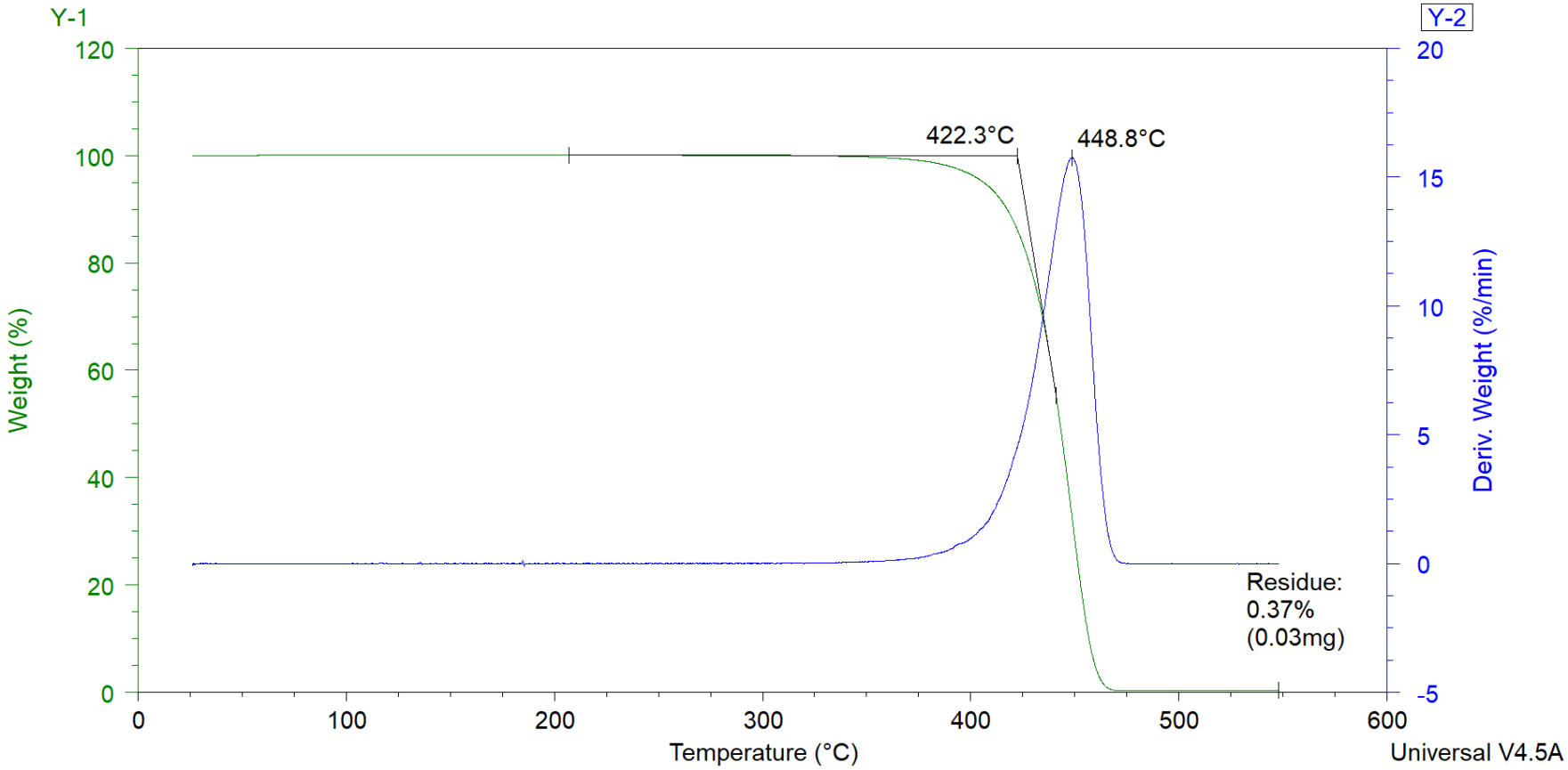


Polyethylene (PE)



Thermogravimetric (TG) curve (mass %)

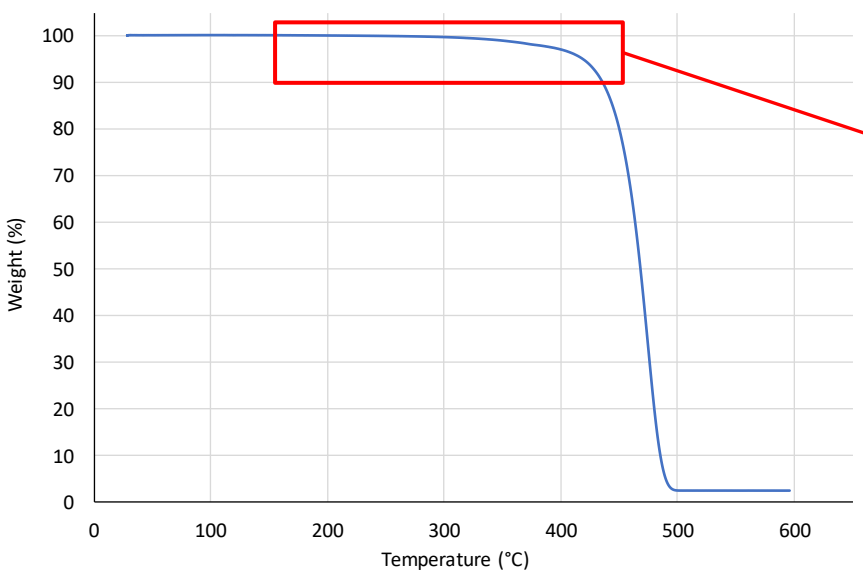
Derivative thermogravimetric (DTG) curve (mass %/min)

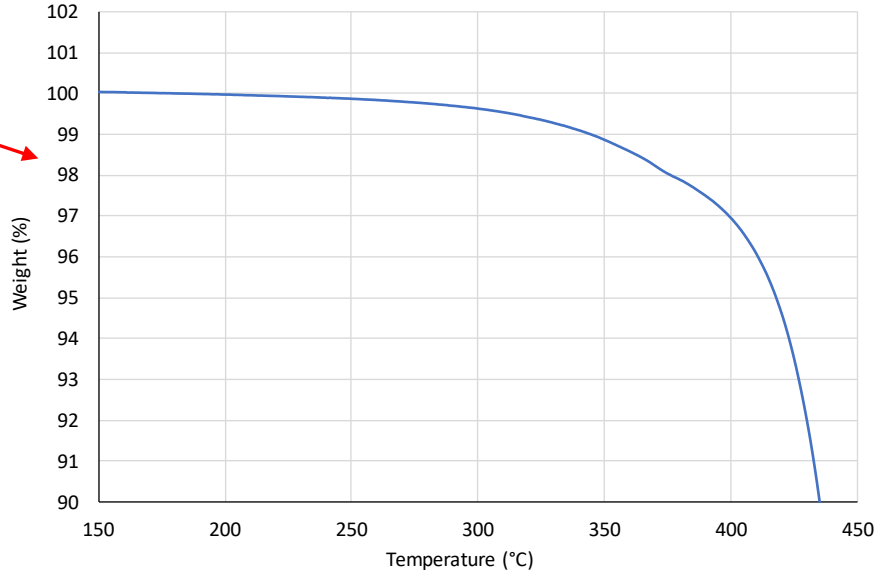


TG curve – start and the end of degradation, residue

DTG curve – temperature at maximum degradation rate

At what temperature does the degradation start?

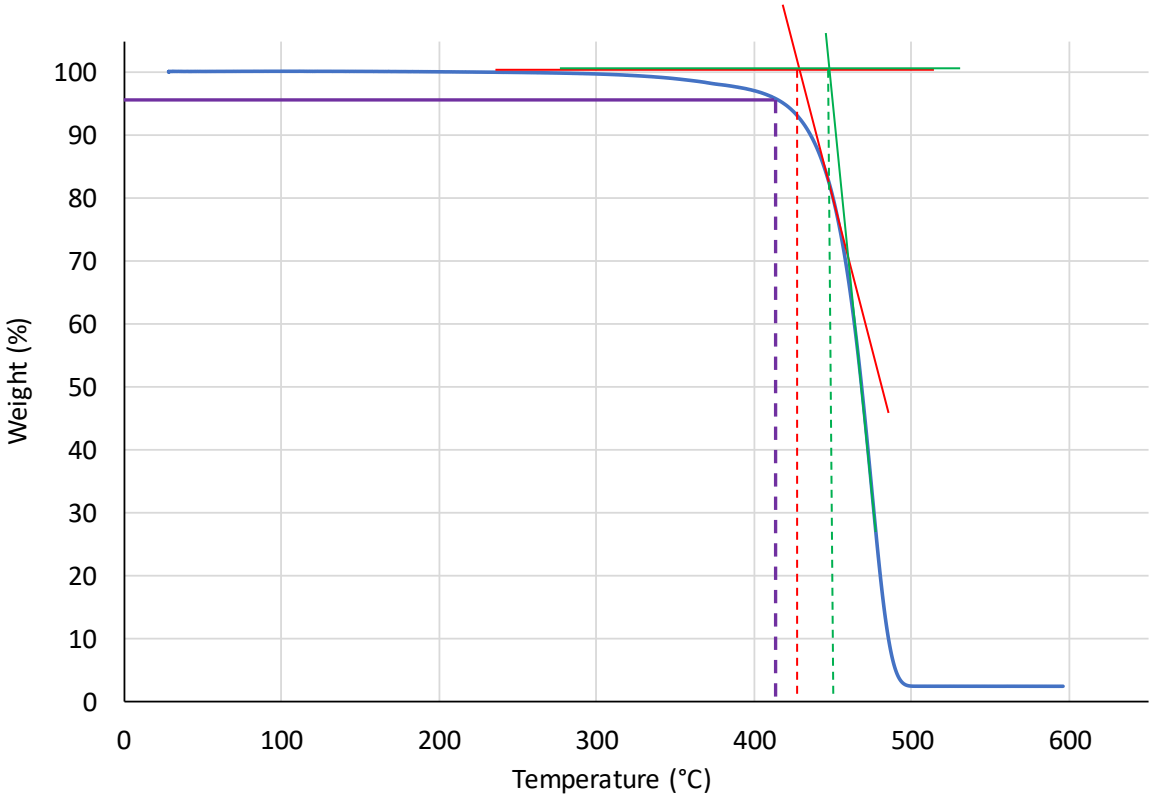




≈ 300 °C

≈ 200 °C

At which temperature does the degradation start?



Tangent method

Person A = 415 °C

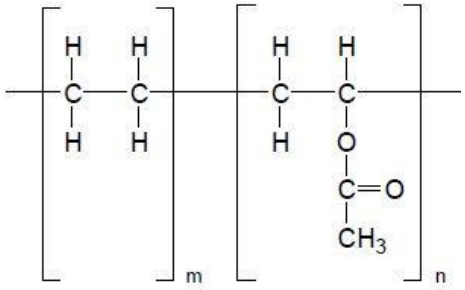
Person B = 425 °C

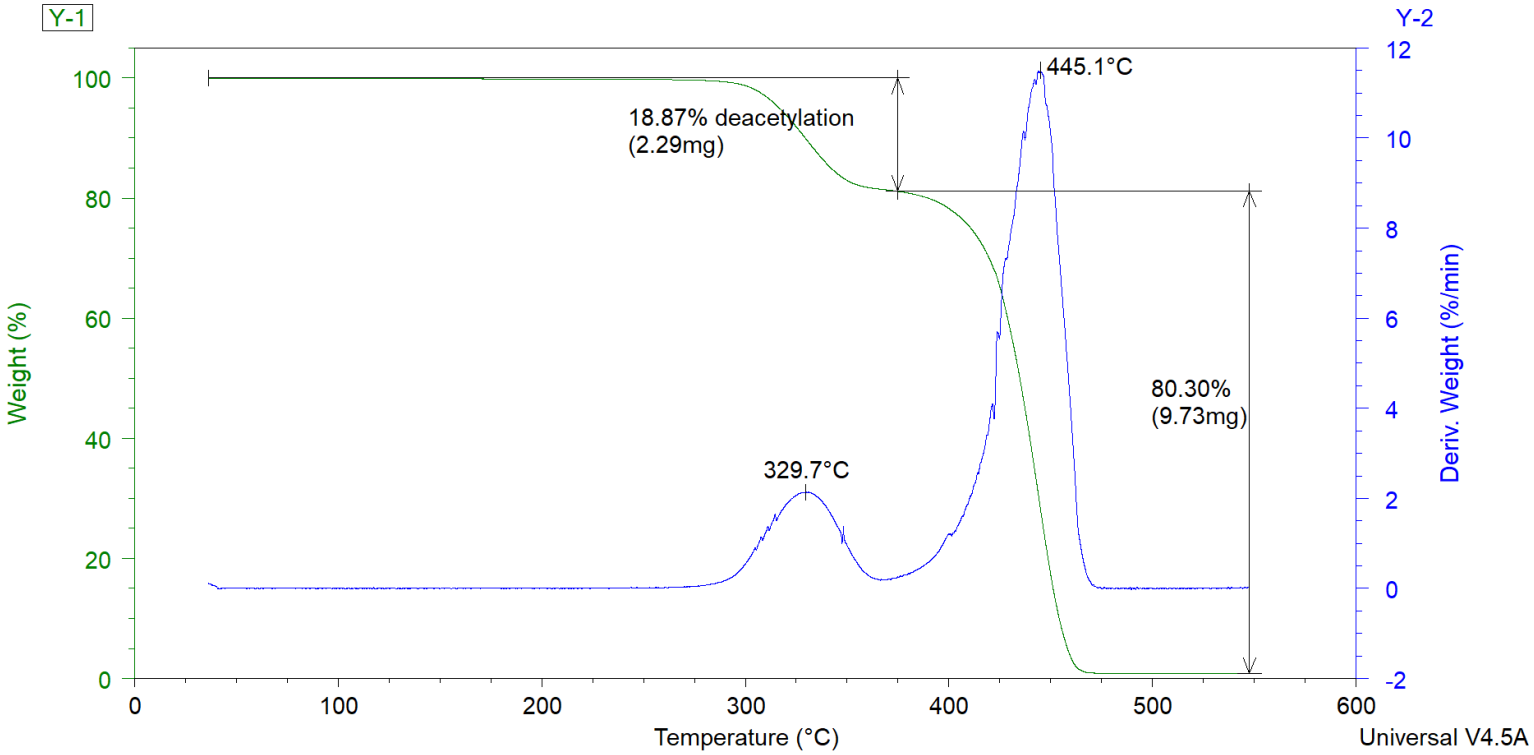
Person C = ?

$T_{95/90}$ method

Person A/B/C/… = 409 °C

Ethylene vinyl acetate (EVA)





% Vinyl acetate = % Acetic acid * (M_w (VAc)/M_w (AA))

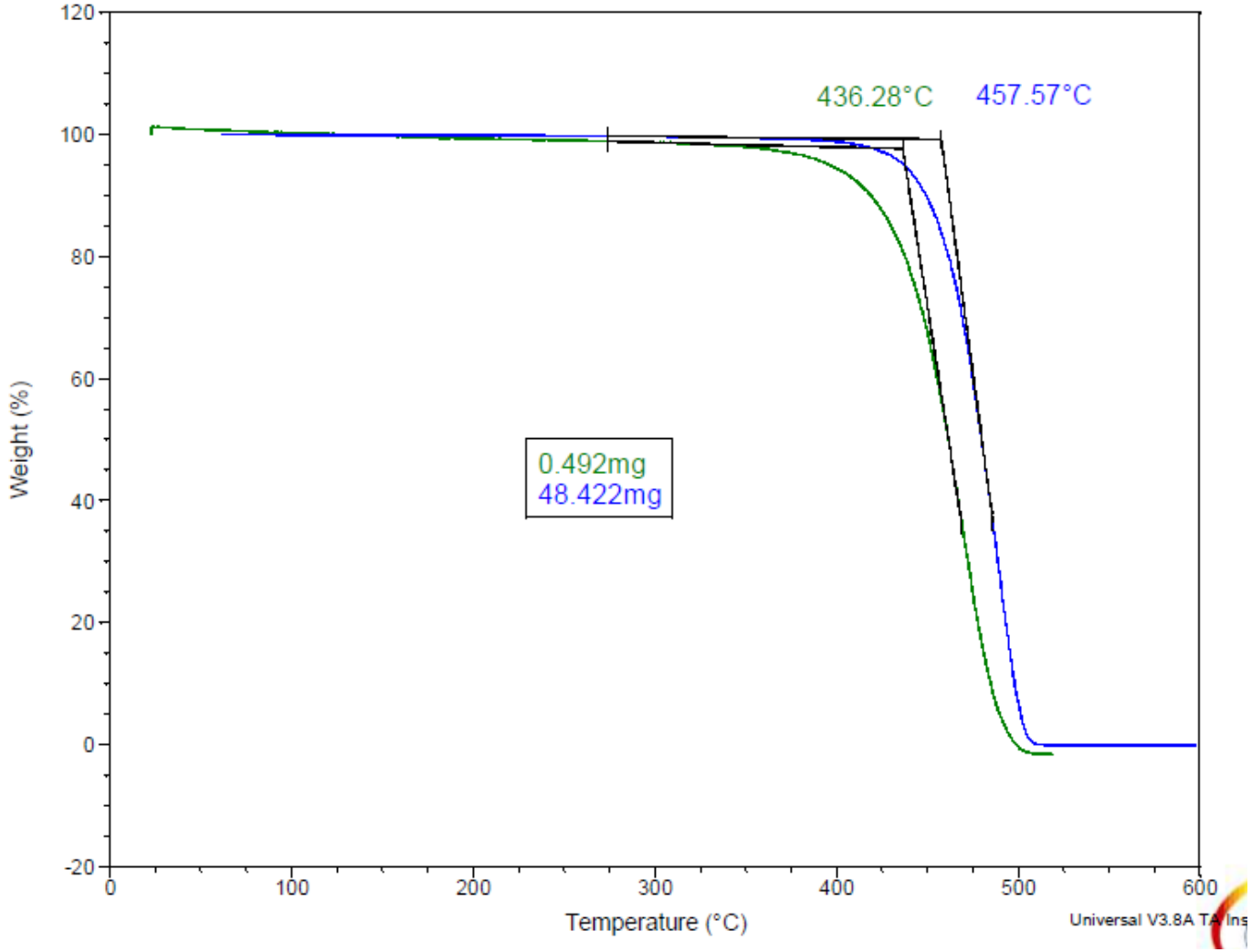
VA% = 18.87 * (86.1/60.1) = 27.0%

TGA curves are not 'fingerprint' curves

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 affect the reaction rate will change the shape / transition temperatures of the curve. These parameters include:

- Heating rate
- Purge gas type
- Sample mass
- Sample volume/form and morphology

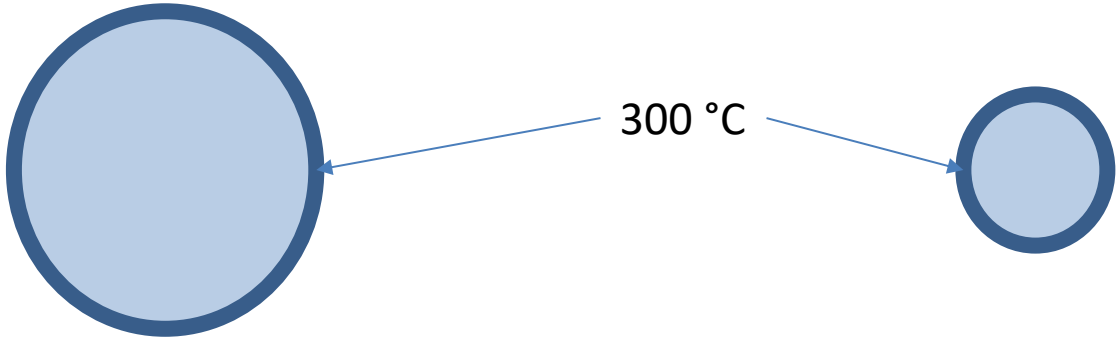
Sample mass effect



Mass Effect

Sample mass 20 mg

Sample mass 10 mg



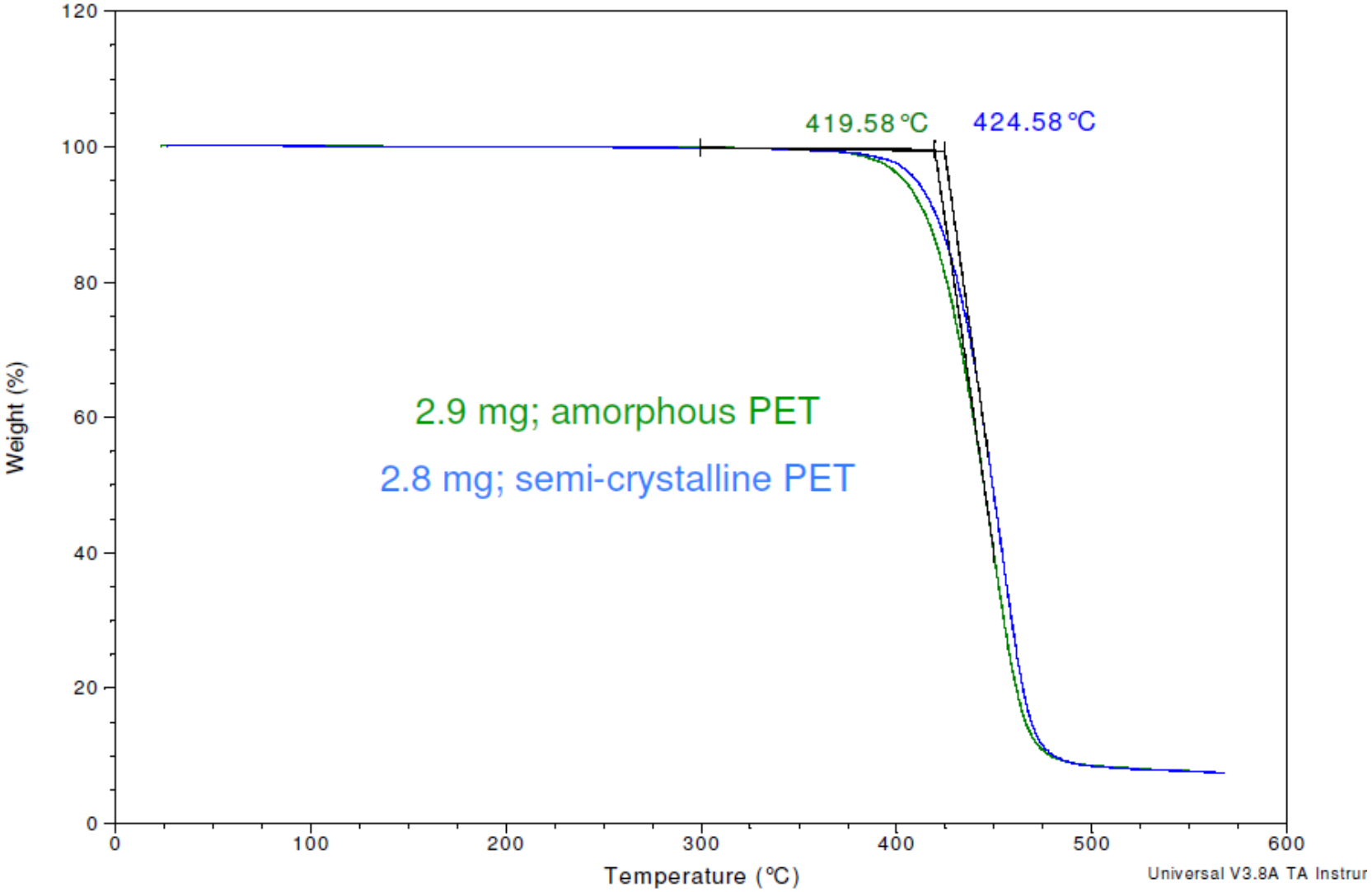
At 300 °C 1 mg of sample's mass is lost

5% mass loss

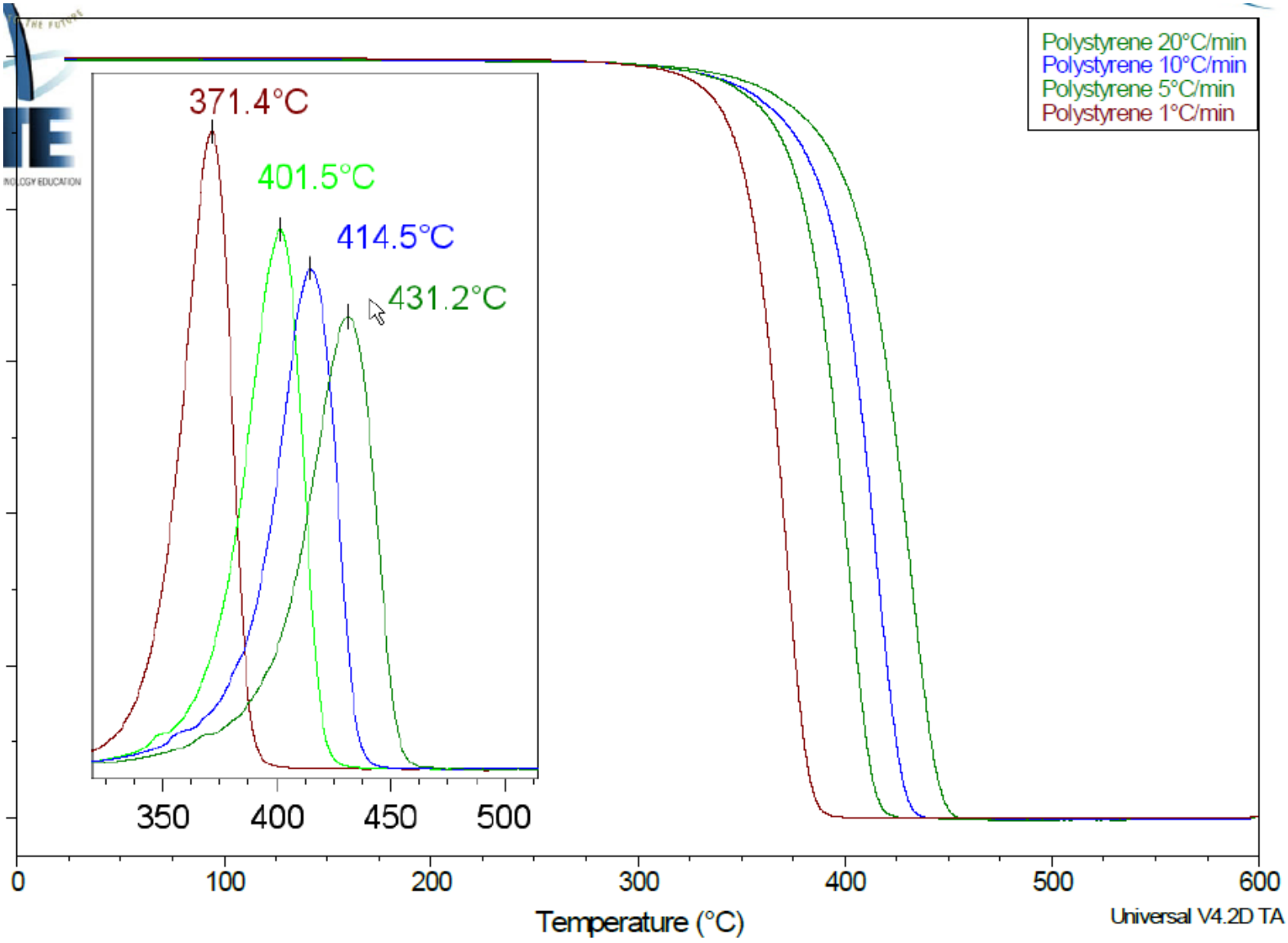
At 300 °C 1 mg of sample's mass is lost

10% mass loss

Sample Morphology Effects



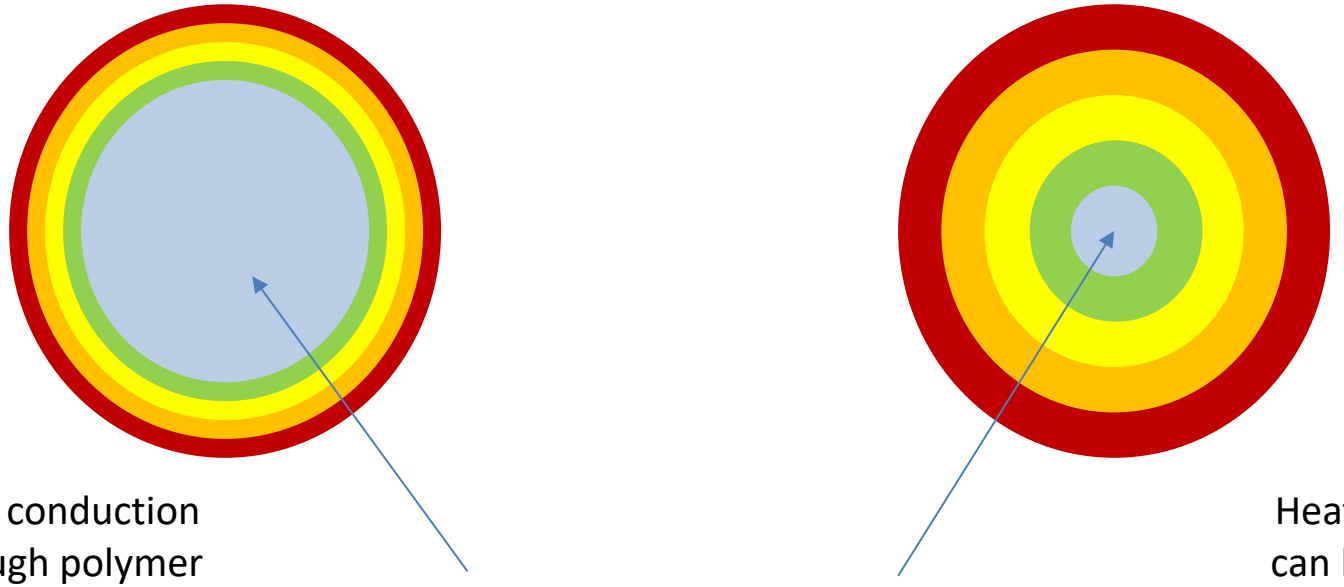
Effect of Heating Rate



Effect of Heating Rate

20 °C/min heating rate

1 °C/min heating rate



Heat conduction through polymer is a bottleneck

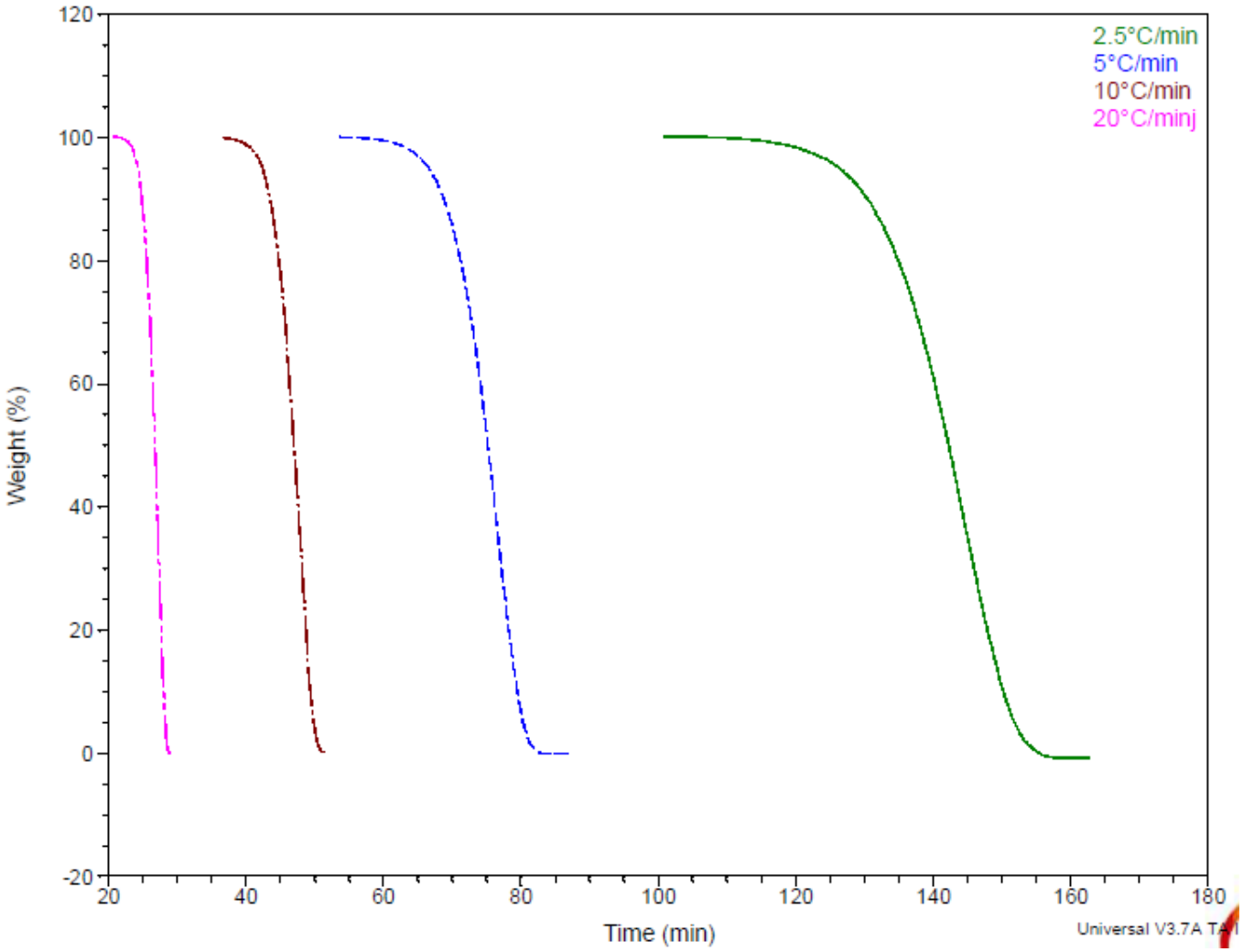
Large temperature gradient

Below degradation temperature

Heat conduction can keep up with increasing temperature

Small temperature gradient

Time to complete degradation at different ramp rate

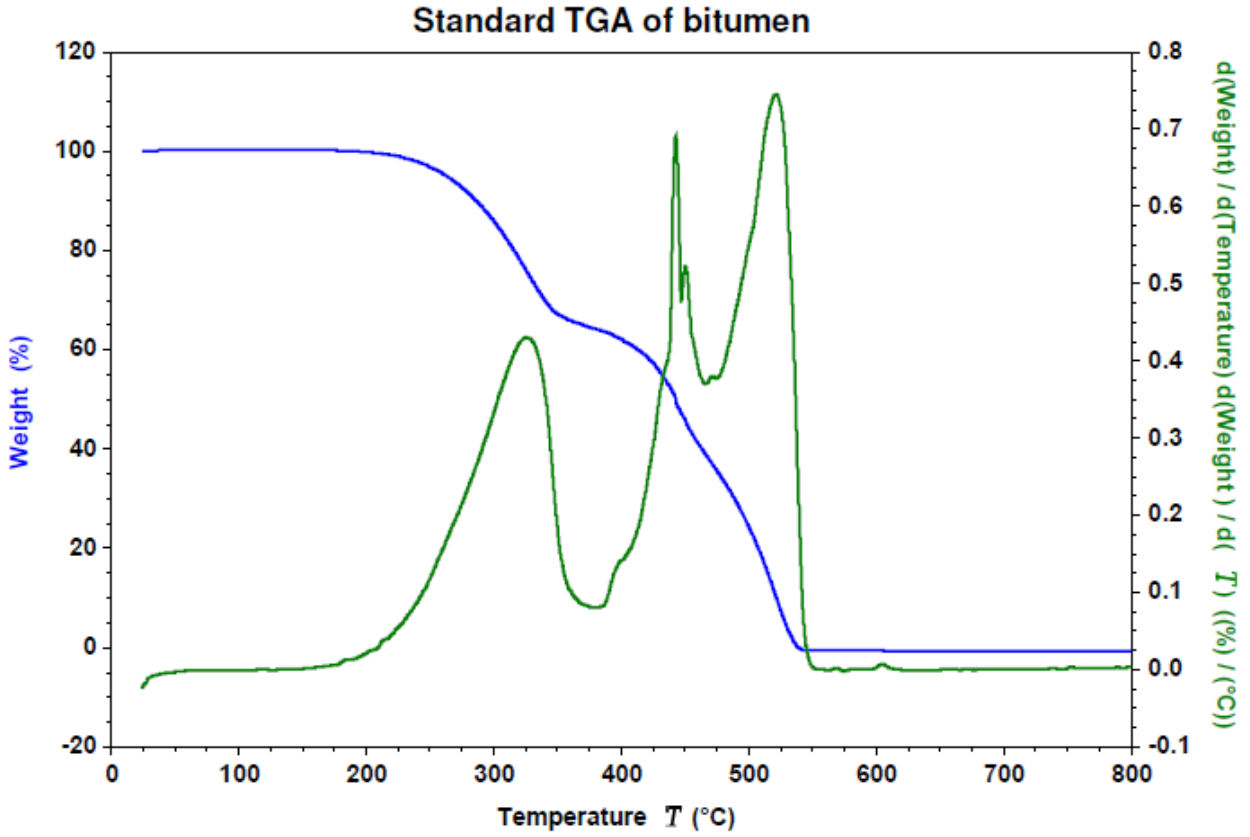


Higher ramp rate = lower resolution!

TGA resolution

When the individual decomposition steps occur at well-separated temperatures, quantitative information for each step can be obtained

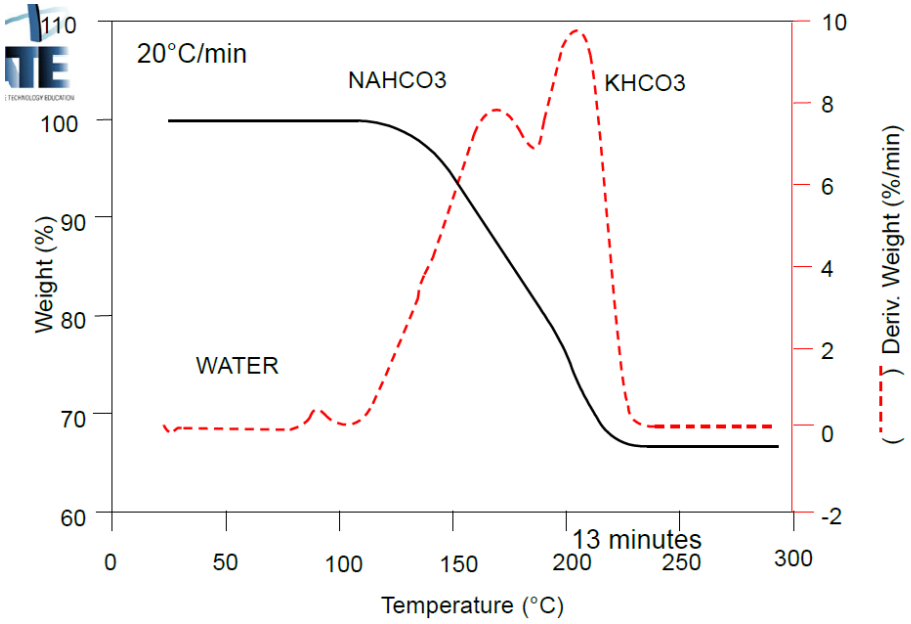
Complex thermal scans with broad weight losses, overlapping weight losses, multiple peaks/shoulders

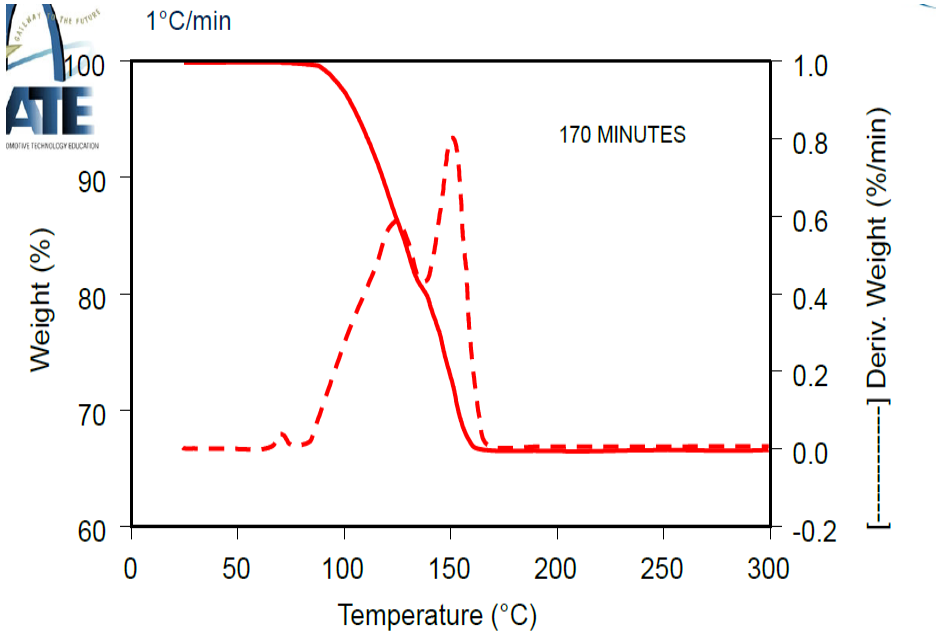


How to enhance resolution?

- Slower heating rate
- Reduced sample size

Lower ramp rate = longer analysis time





High-resolution technique

- In a Hi-Res TGA experiment the heating rate is controlled by the rate of decomposition
- Faster heating rates during periods of no mass loss, and slowing down the heating rate during a mass loss – therefore not sacrificing too much time

Sensitivity:

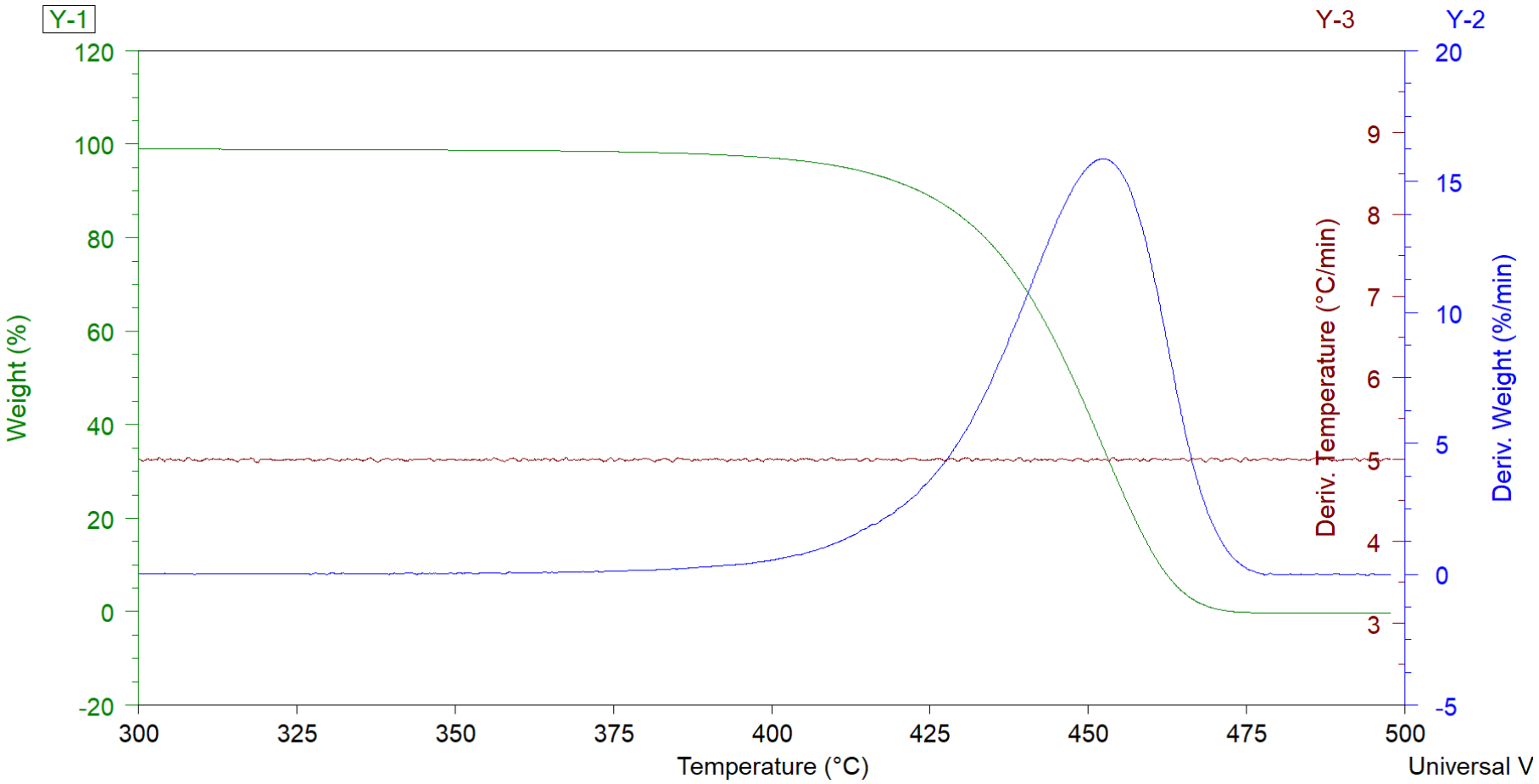
- Controls the response of the Hi-Res system to changes in decomposition rates (Δwt%/min) (SECOND DERIVATIVE)
- Determines the relation between the increase in decomposition rate and the reduction in the heating rate
- Higher sensitivity values make the Hi-Res system more responsive to small changes in the rate of reaction

Resolution:

- Adjusts the heating rate based on the sample decomposition rate (wt%/min) (FIRST DERIVATIVE)
- As the decomposition rate increases, the heating rate is further decreased (and *vice versa*)
- Higher resolution number (absolute value) results in a greater reduction in heating rate at smaller values of wt%/min

Classic ramp vs. high-resolution technique

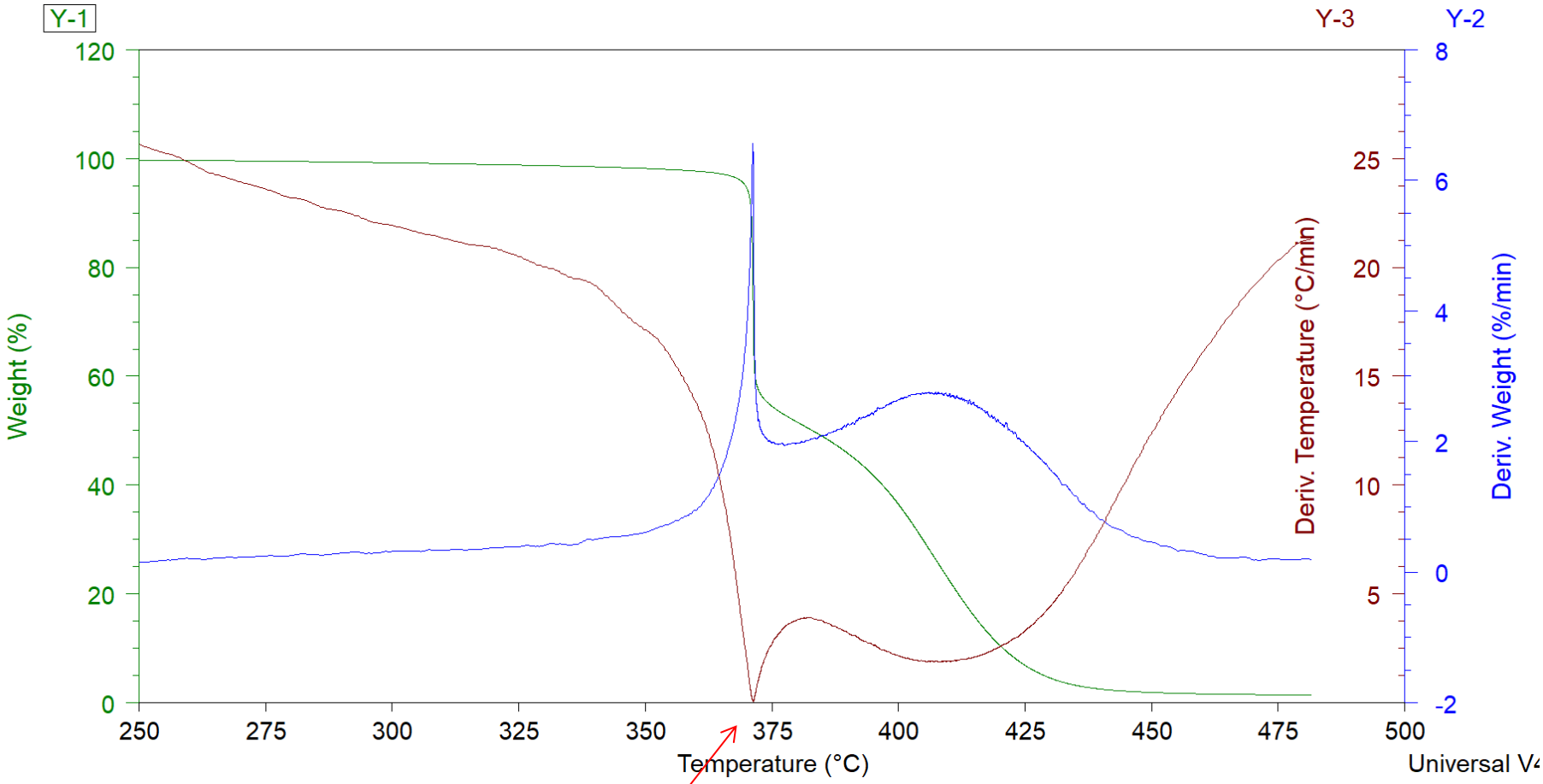
Classic ramp, 5 °C/min



Experiment time = 95 min

Classic ramp vs. High-resolution technique

High-resolution

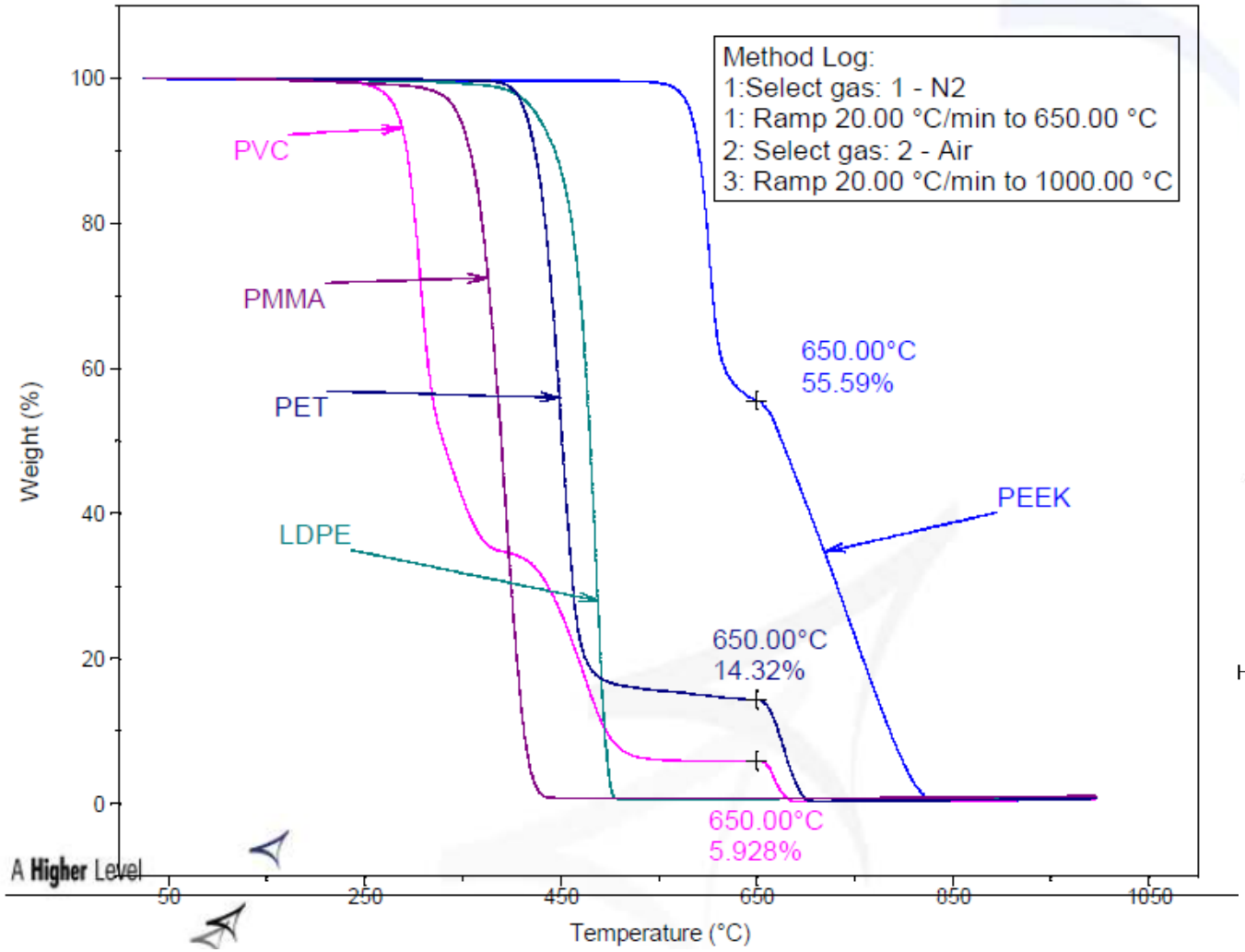


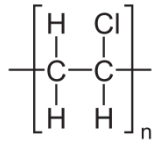
Experiment time = 50 min

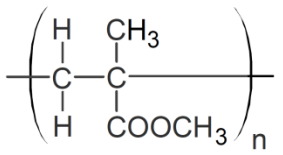
Classic method (1 °C/min) = 475 min

Typical TGA applications

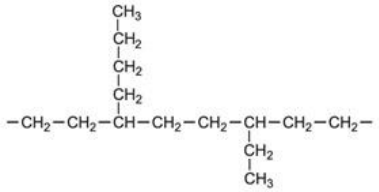
- Thermal Stability
- Compositional analysis

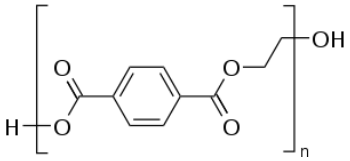


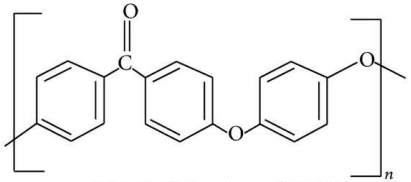




Polymethyl methacrylate: PMMA

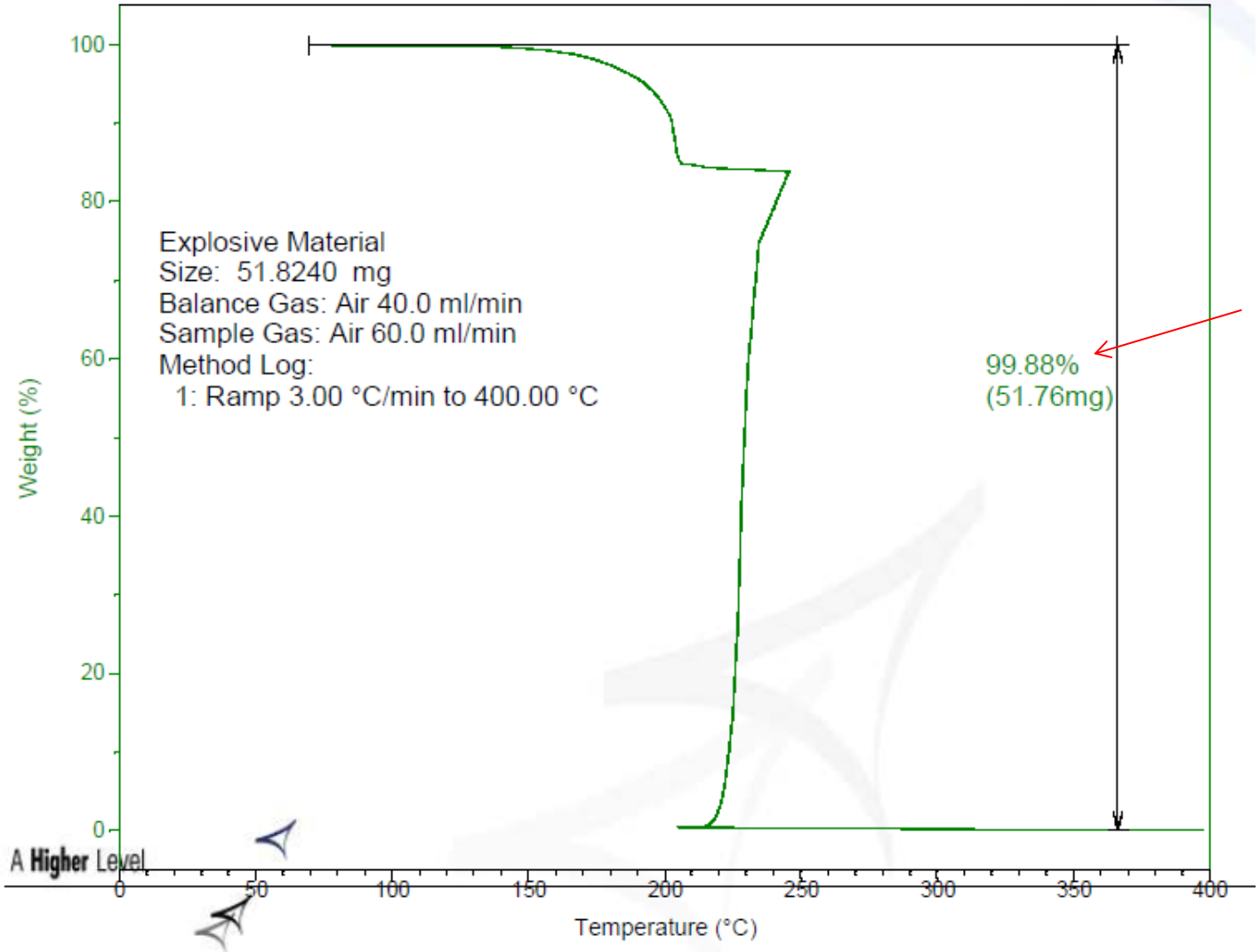






Chemical structure of PEEK

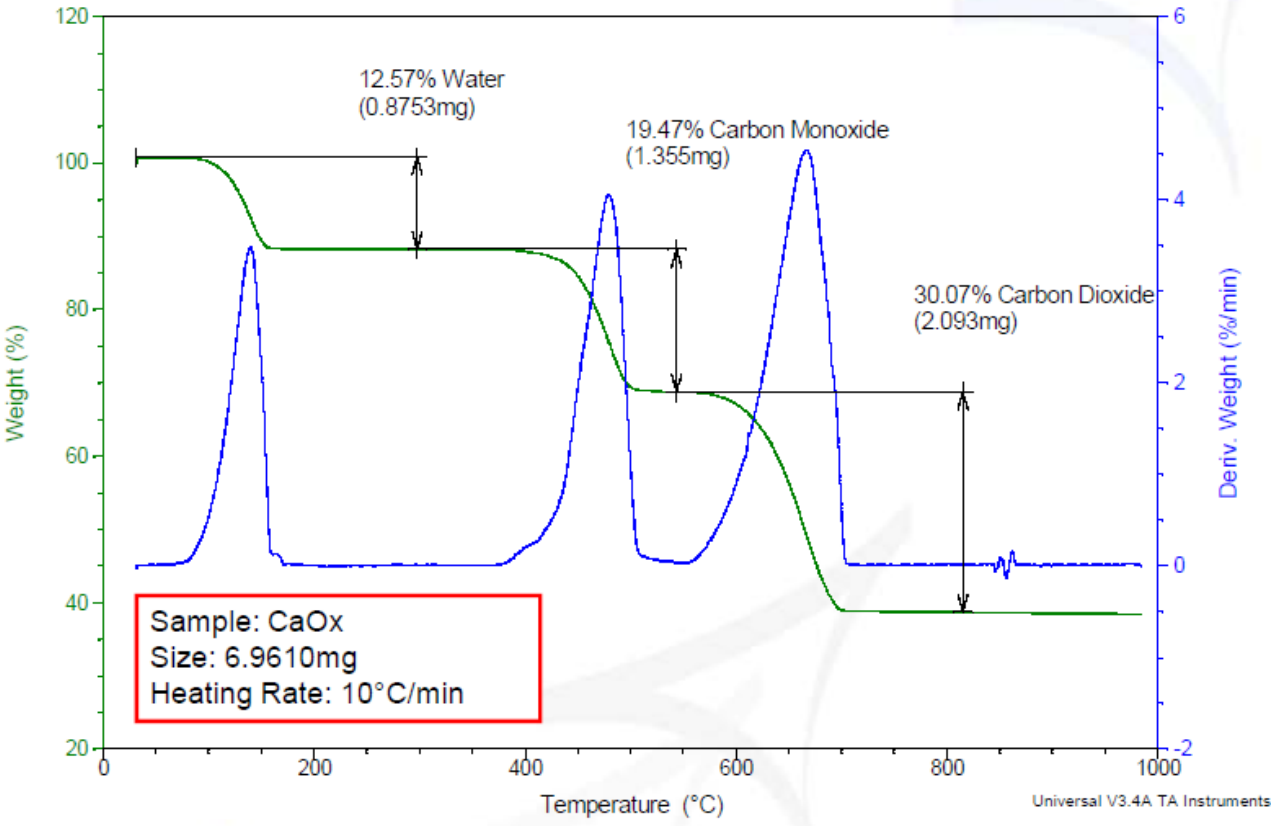
Thermal stability of an explosive material



All gas products

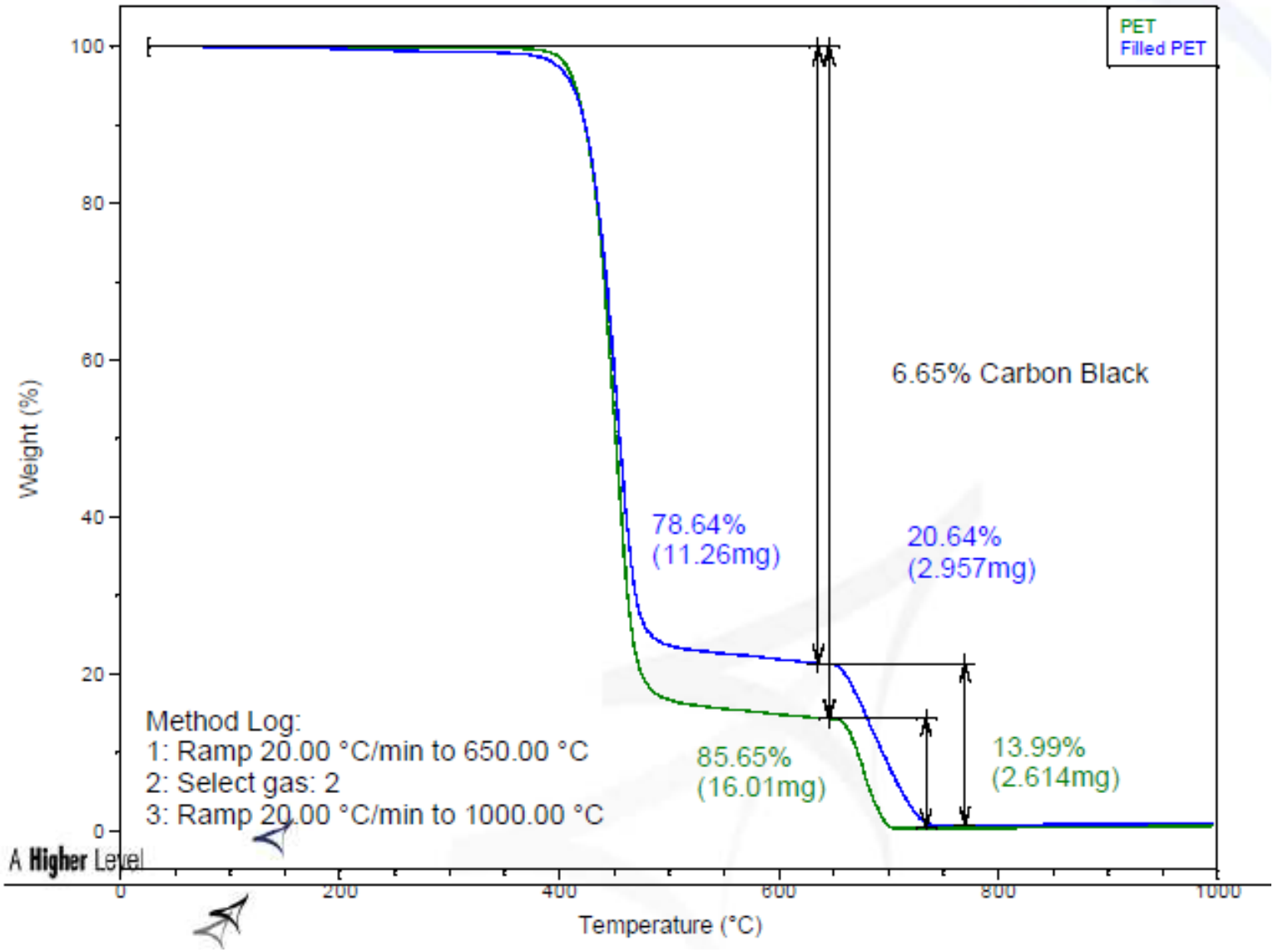
Compositional analysis

Evolved gas analysis ?

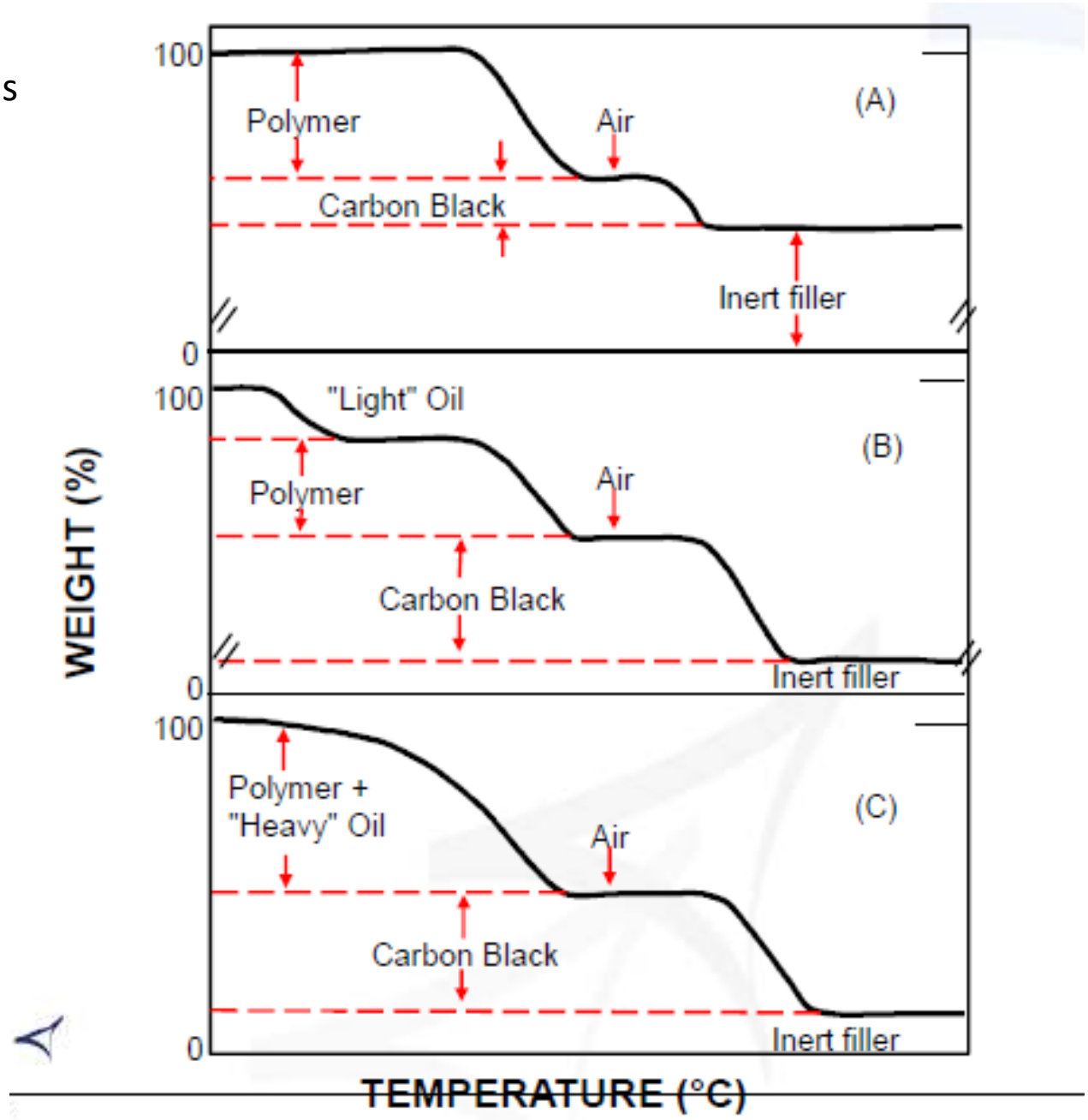


- 1st step $CaC_2O_4 \bullet H_2O\ (s) \rightarrow CaC_2O_4\ (s) + H_2O\ (g)$
- 2nd step $CaC_2O_4\ (s) \rightarrow CaCO_3\ (s) + CO\ (g)$
- 3rd step $CaCO_3\ (s) \rightarrow CaO(s) + CO_2\ (g)$

PET w/ Carbon Black Filler



Filled Polymer Analysis

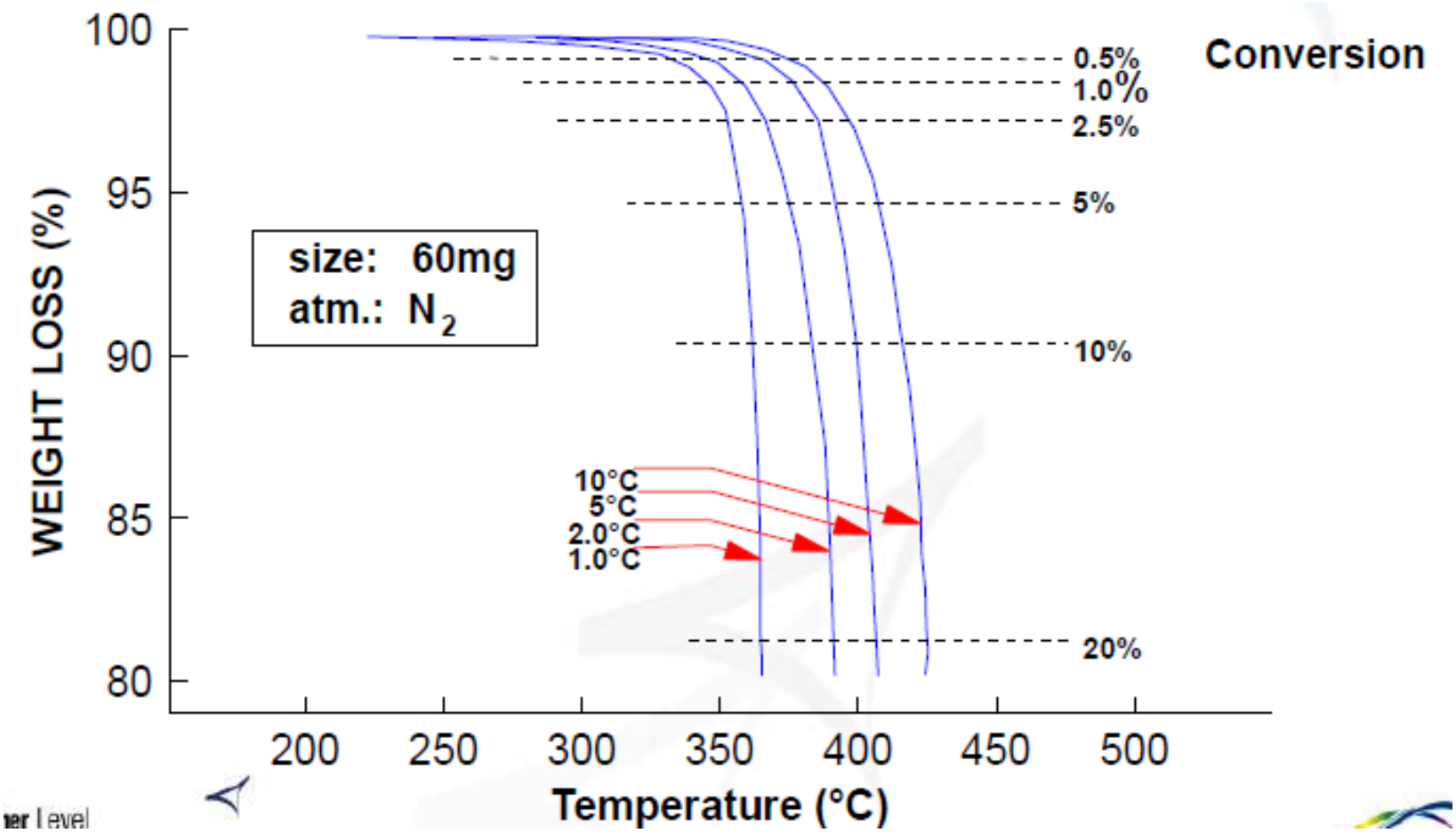


TGA decomposition kinetics

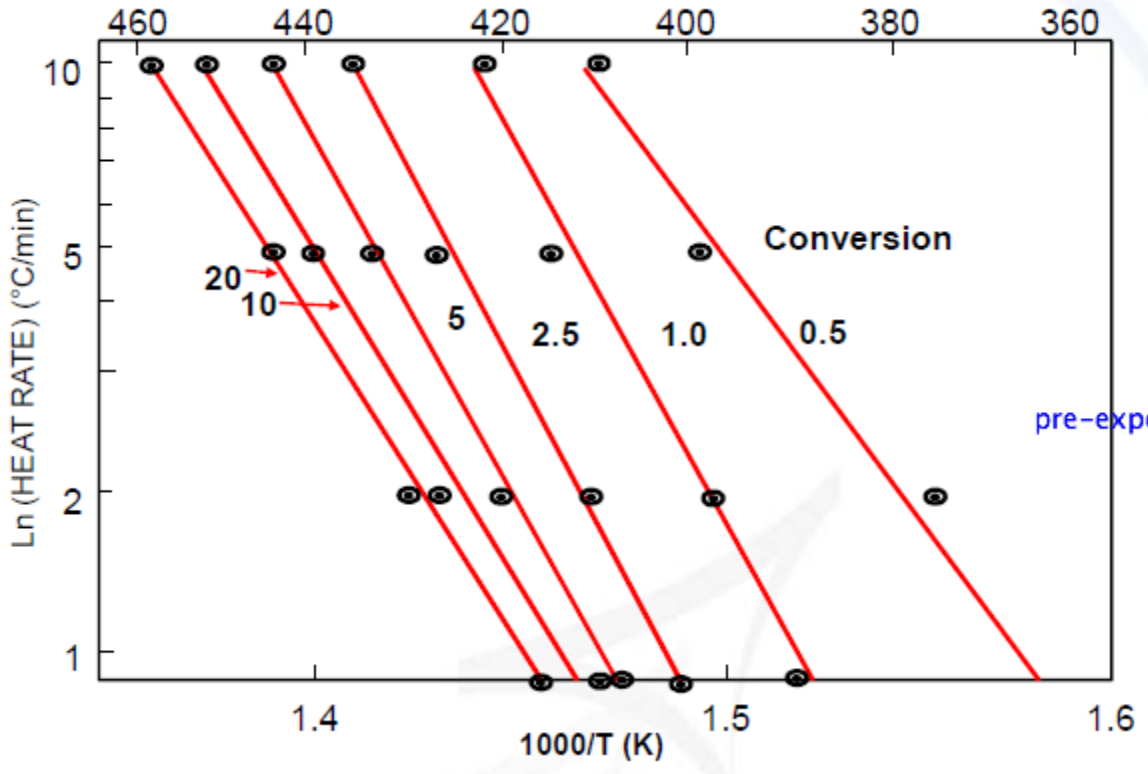
- Requires at least 3 TGA runs at different heating rates
- Typically kinetic analysis is concerned with obtaining parameters such as activation energy (E_a), reaction order (n)
- Ultimate benefit is obtaining predictive curves: "lifetime plots"

- The rate at which a kinetic process proceeds depends not only on the temperature of the specimen, but also on the time it has spent at that temperature

TGA Kinetics – wire insulation thermal stability



TGA Kinetics – heating rate *vs.* temperature



Zeroth order kinetics

$$A \rightarrow \text{Products}$$

The differential rate law for the reaction is

$$-\frac{d[A]}{dt} = k[A]^0 = k$$

$$\therefore d[A] = -k\,dt$$

Arrhenius equation

$$k = A\,e^{-\frac{E_a}{RT}}$$

E_a: activation energy

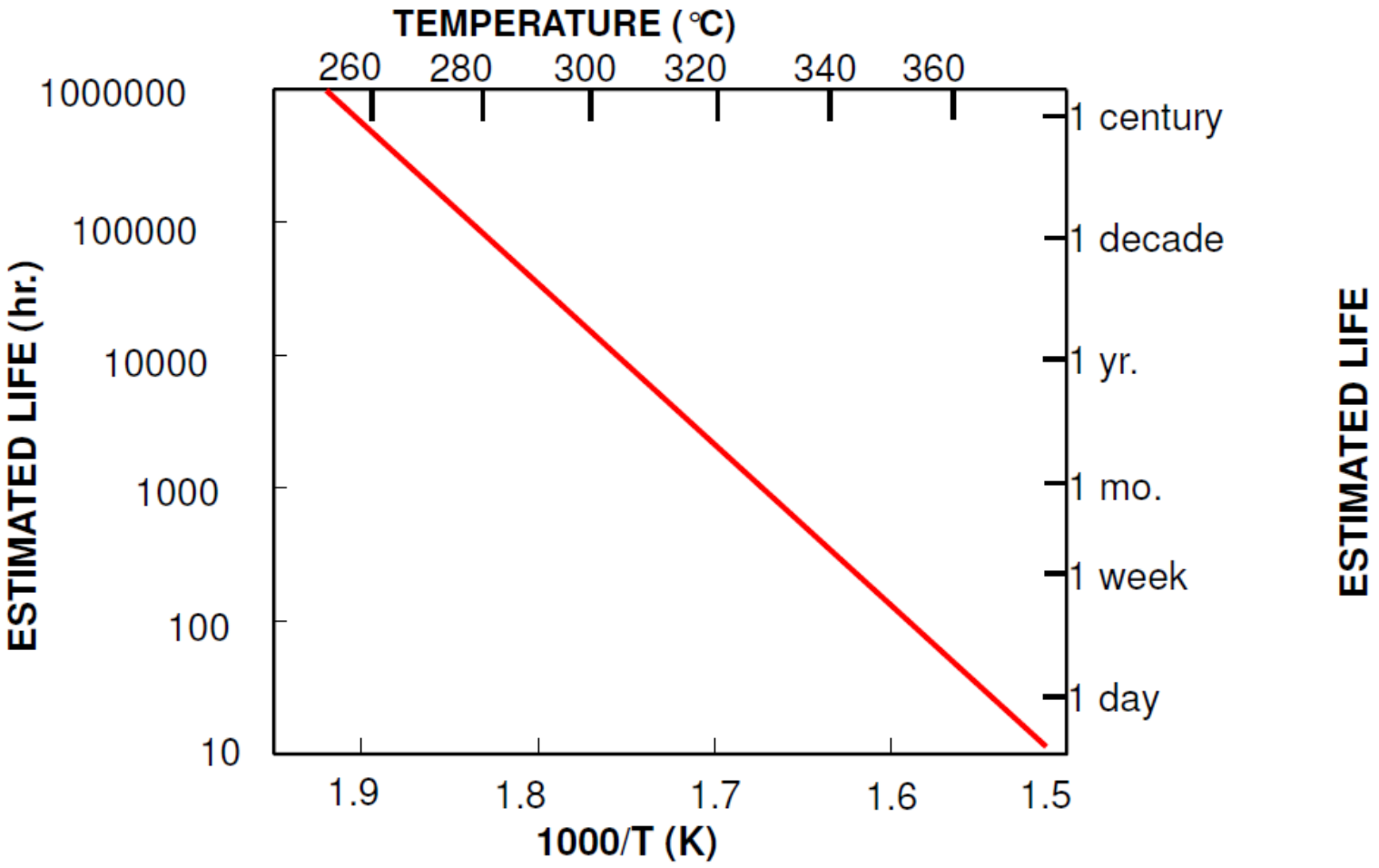
A: pre-exponential factor

RT: average kinetic energy

Ozawa–Flynn–Wall
Tang Wanjun
Coats–Redfern methods
(details elsewhere)

activation energy (E_a) ∝ slope (slope = $-E_a/R$)

TGA kinetics – estimated lifetime



Evolved Gas Analysis (EGA)

- 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

TGA – FTIR

Advantages:

- On-line measurement
- Hydrocarbons are easy to identify

Disadvantages:

- No detection of inert gases (no dipole moment)
- Detection of inorganic gases is limited

TGA – mass spectrometry

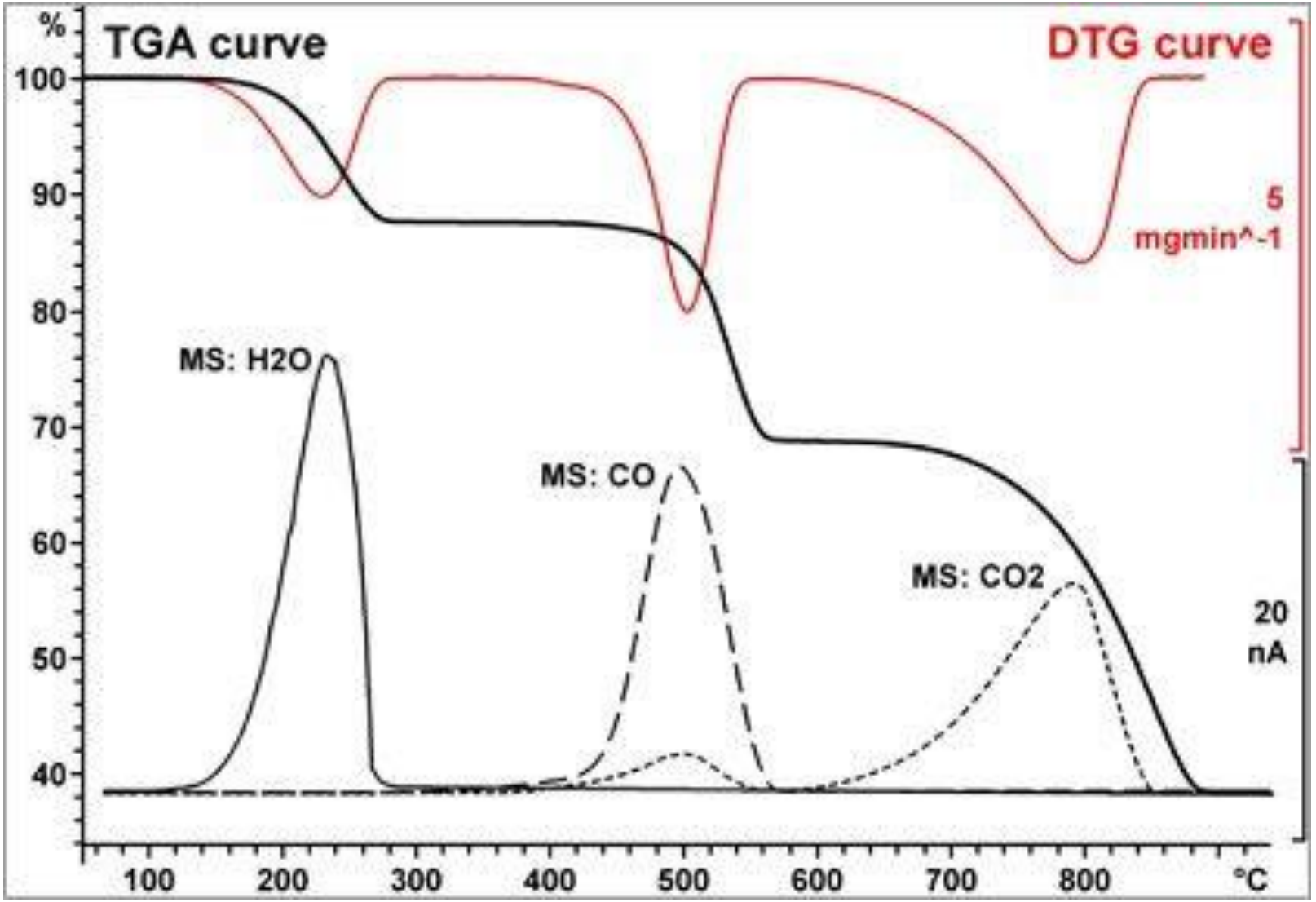
Advantages:

- Higher sensitivity and wider dynamic range than FTIR (1 ppm *vs.* 10 ppm).
- Suitable for non-IR absorbing gases

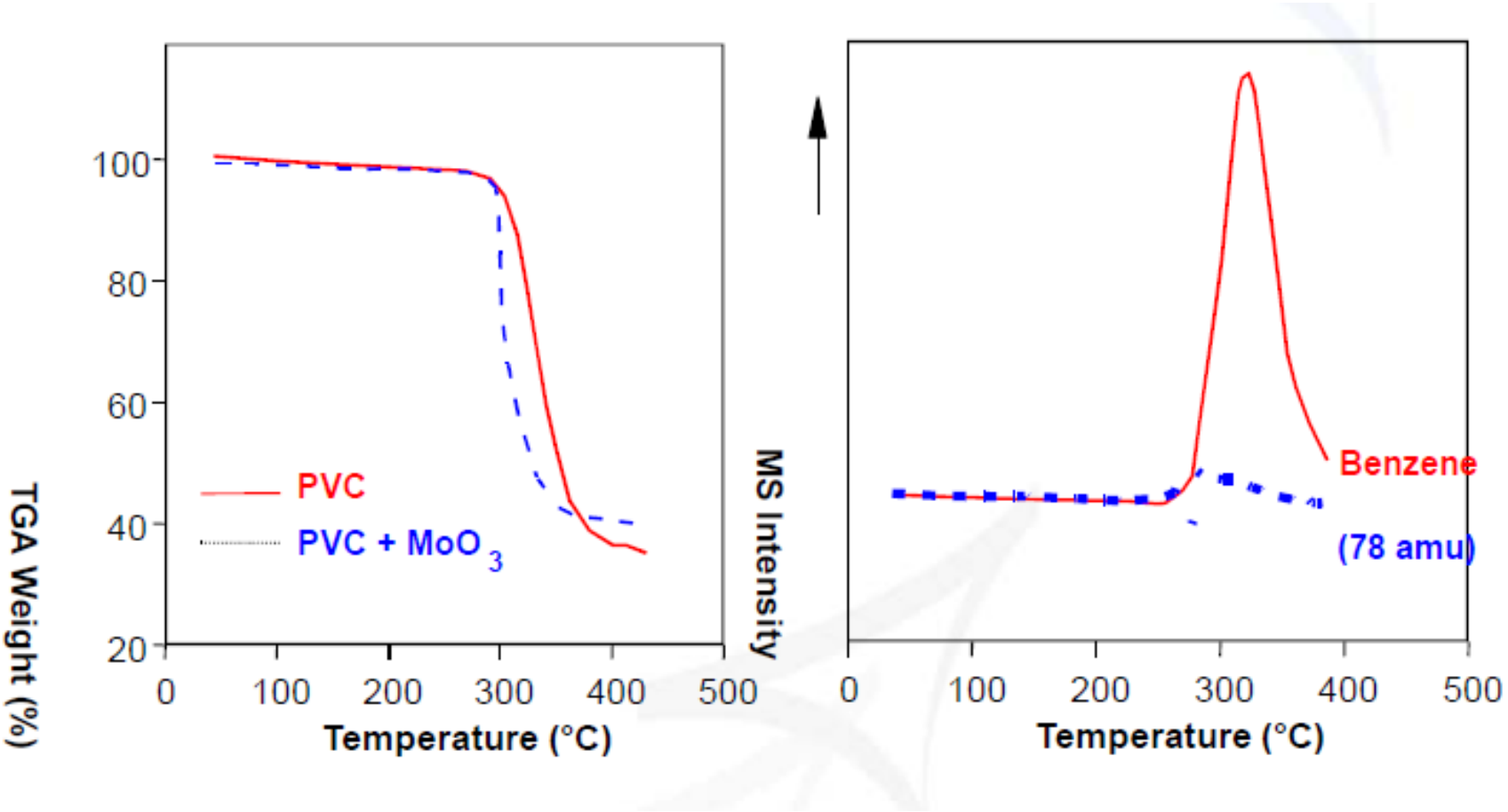
Disadvantages:

- Cannot distinguish between isomers (*e.g.* N_2 and CO)
- Problem with detecting small molecules

TGA – MS Calcium Oxalate



Smoke generation in flame retarded polymers (PVC)



Benzene is a component of smoke

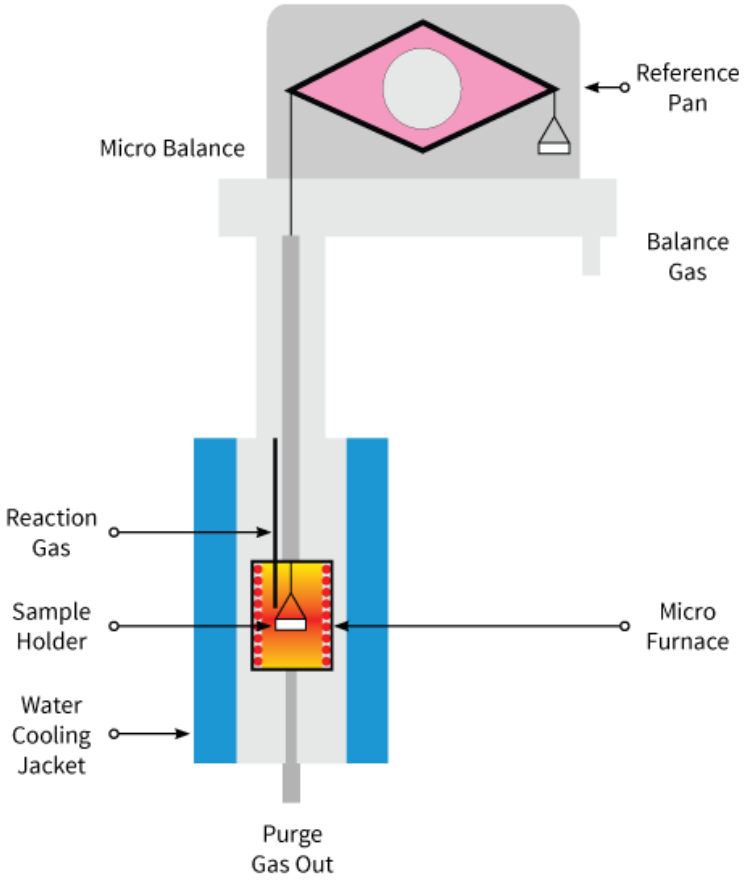
In a sample containing flame retardant, benzene content in smoke is much reduced

A TGA consists of three major parts:

Microgram balance

Thermocouple

Furnace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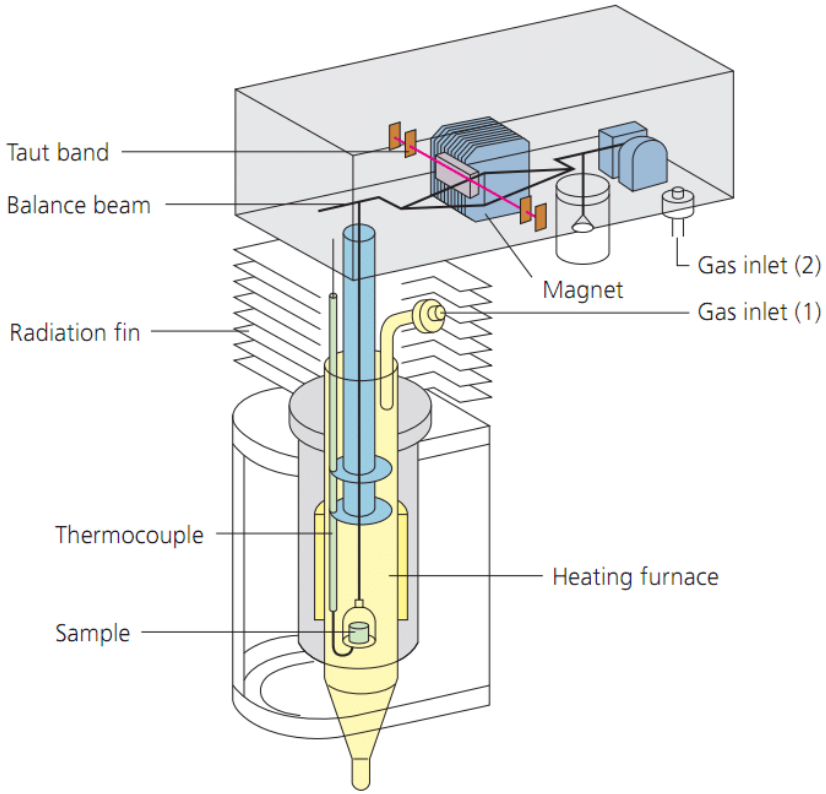
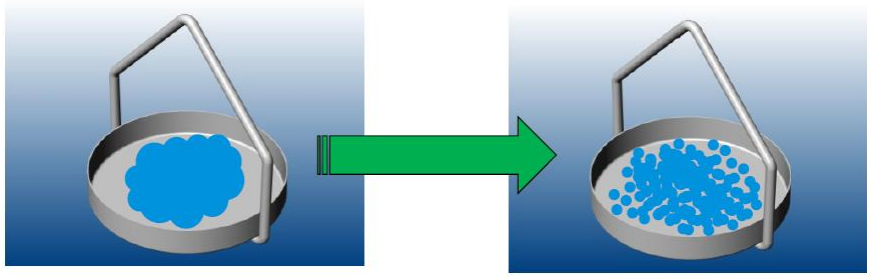
Purge Gas Out


Taut band
Balance beam
Gas inlet (2)
Magnet
Gas inlet (1)
Radiation fin
Thermocouple
Heating furnace
Sample

Sample Preparation

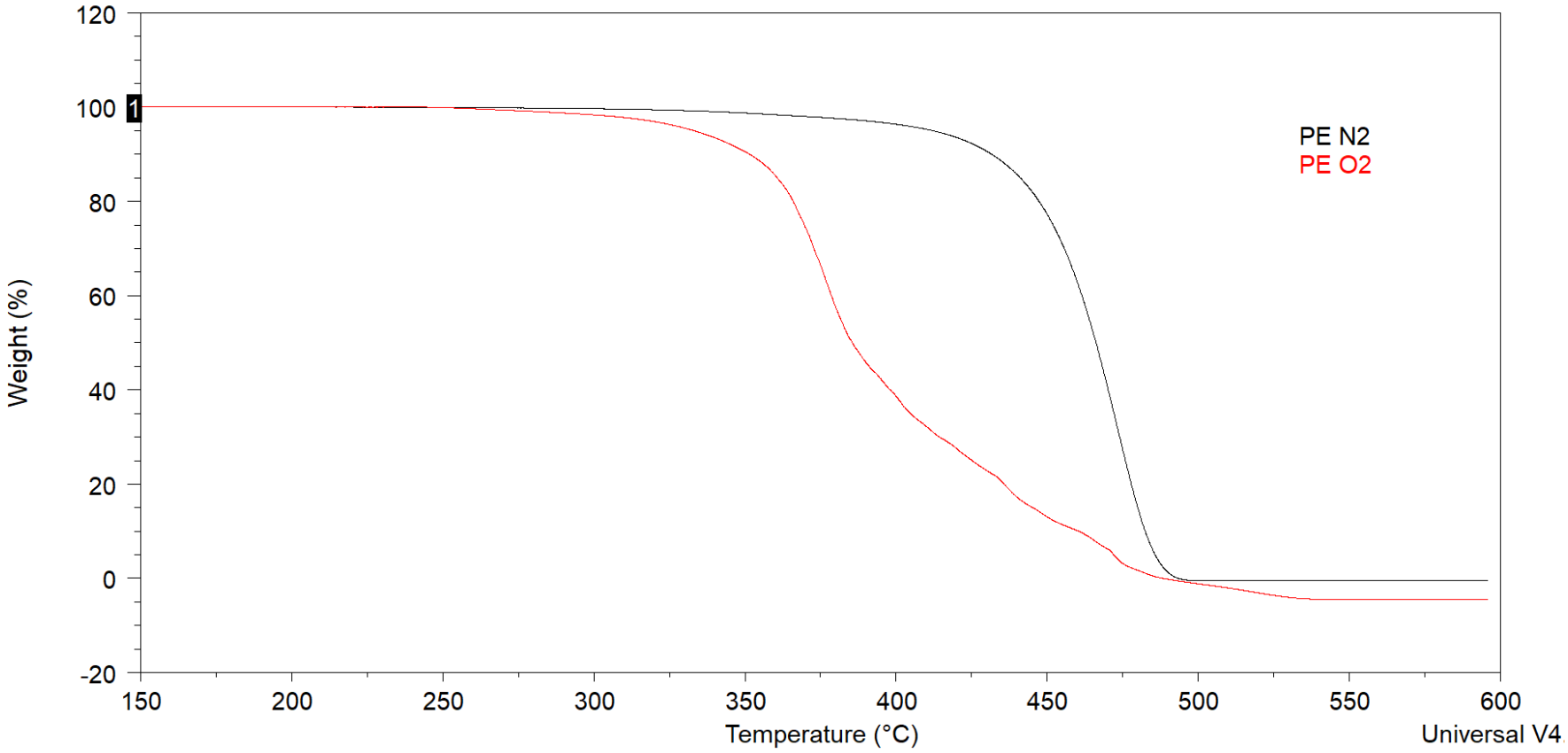
- Sample preparation has a significant effect in obtaining good data
- Maximizing the surface area of the sample in a TGA pan improves resolution and reproducibility of weight loss temperatures.



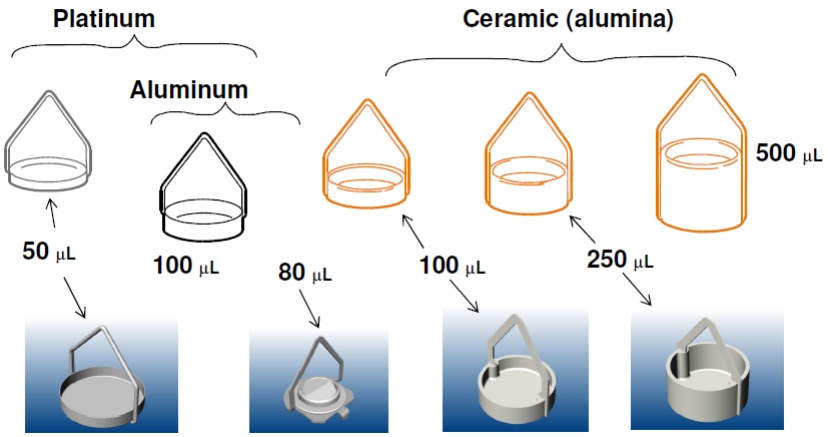
- The sample weight affects the accuracy of weight loss measurements
- Typically 5 – 20 mg of sample is preferred in most applications
- For high-volatiles samples 50 – 100 mg of sample is considered adequate
- Most TGA instruments have a baseline drift of ±0.025 mg which is ±0.25% of a 10 mg sample

Experimental conditions – purge gas

- Nitrogen is the most common gas used to purge samples in TGA due to its inert nature
- Helium provides the best baseline
- Air is used for thermo-oxidative degradation



TGA: Sample pans – types/sizes



- Platinum (useful for most materials)
  - easy to clean
  - nonporous
  - can form alloys with most metals
- Alumina (ceramics)
  - corrosives/inorganics
  - large samples
- Aluminum (designed for one-time use)
  - low-cost, disposable
  - low temperature limit (<= 600°C)