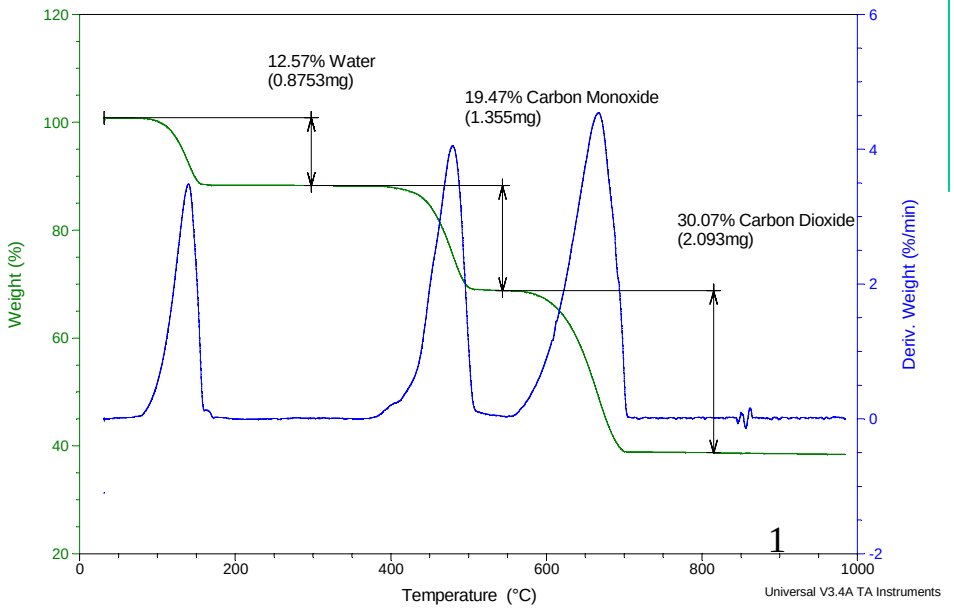
Thermogravimetric Analysis
Theory, Operation, Calibration and Data Interpretation

TA Instruments



Definitions of Thermal Analysis

- **A group of techniques in which a property of the sample is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is programmed.**

Definitions of Thermogravimetry (TGA)

- A technique in which the mass of the sample is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is programmed.
- A technique in which the mass of a sample is measured as the function of the temperature while varying the sample temperature in a specified program. (JIS definition(

Agenda: TGA Theory, Operation and Calibration

- Definitions and review of instrument
- Balance, furnace and heat exchanger review
- Mass and temperature calibration
- Purge gas considerations
- Baseline considerations
- Sample preparation and pan selection
- Method development

TGA: The Technique

- Thermogravimetric Analysis (TGA) measures the amount and rate of change in the weight of a material as a function of temperature or time in a controlled atmosphere.

- Measurements are used primarily to determine the composition of materials and to predict their thermal stability at temperatures up to 1000°C.

- The technique can characterize materials that exhibit weight loss or gain due to decomposition, oxidation, or dehydration.

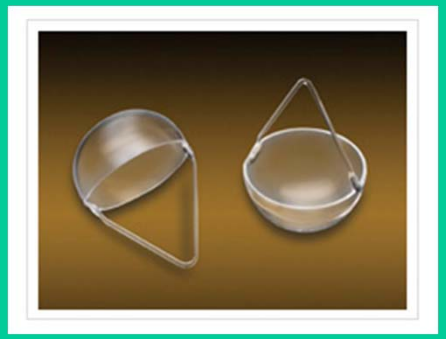
TGA Technique Characteristics

- Quantitative
  - Monitor mass in regards to change in temperature
  - Thermal Stability
  - Decomposition Kinetics
  - Oxidation
  - Loss of water or Solven
  - Weight percent of Ash
- Qualitative
  - Can reveal sample components
  - Characteristics dissociation temperature

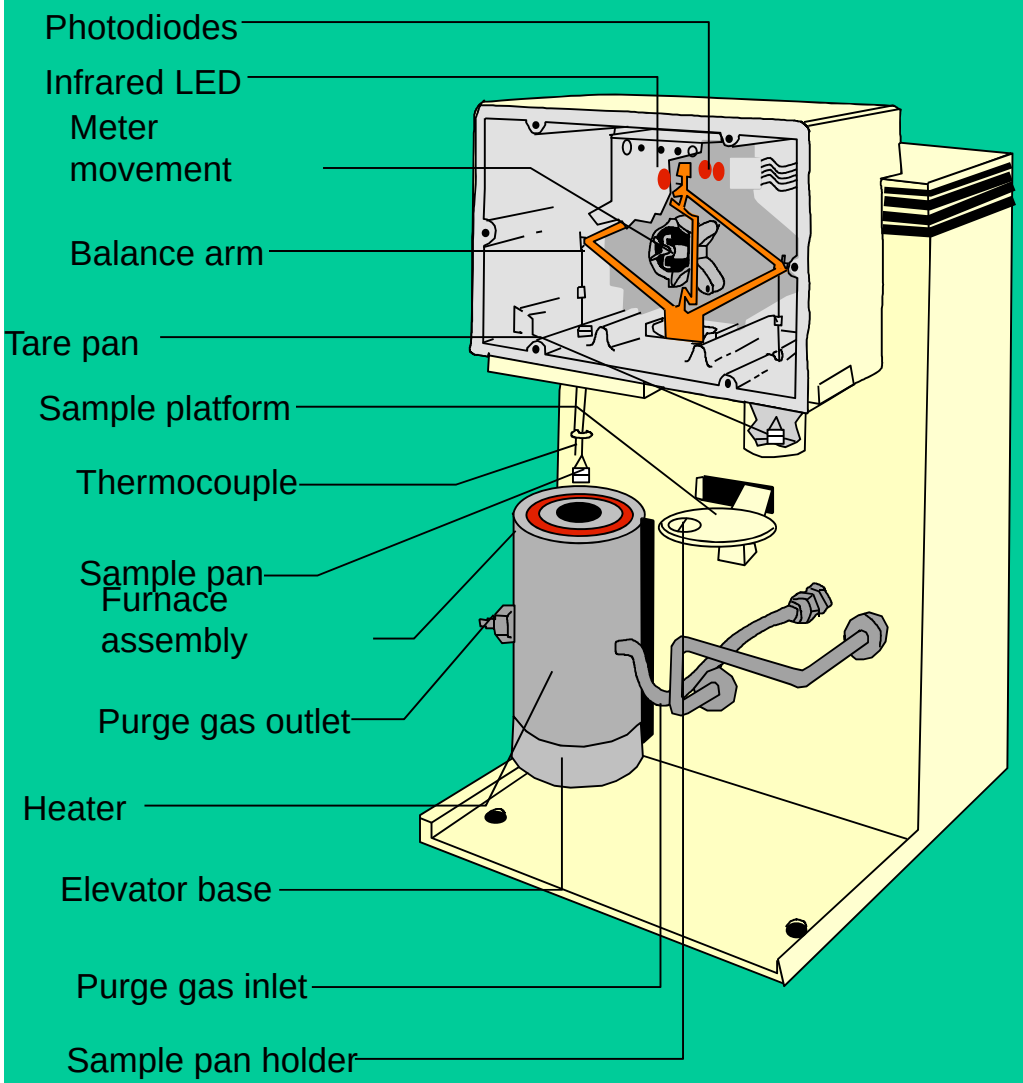
Mechanisms of Weight Change in TGA

- 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).



Features of the Q500 TGA



1. Q Series Two Point Mass Adjustment
   - •200mg range
   - •1000mg. range

*No need to do a mass recalibration when switching from regular Pt pans to Pt pans with Al hermetic pans.

*Mass Loss Reference Materials

➢Materials with nominal 2%, 50% and 98% mass loss are available for verification of TGA weight calibration.

2. Curie Point Transition Temperature Calibration
   - •ASTM 1582

*Curie Temperature Reference Materials:

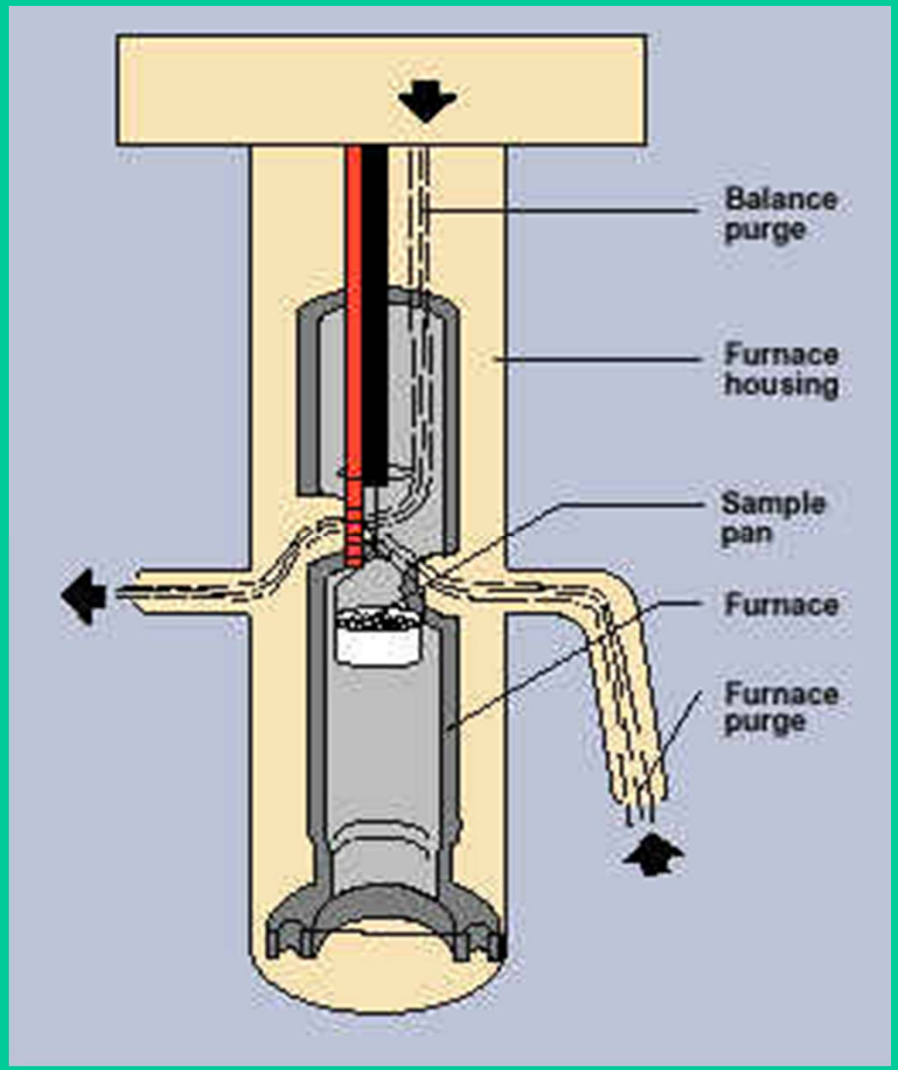
➢TA Instruments is the exclusive worldwide distributor for a set of six certified and traceable Curie temperature materials developed by ICTAC

TGA Furnaces

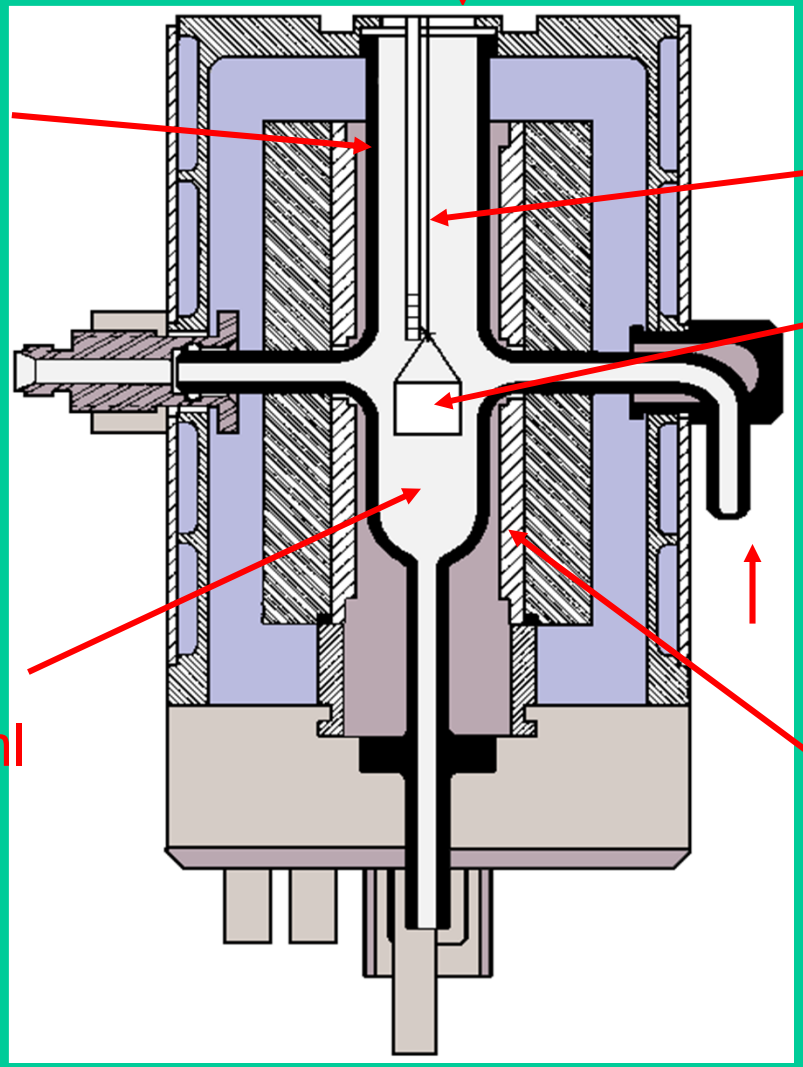
- Standard Furnace
  - Low mass
  - Used for Hi-Res Runs
  - Cools down in <20min

- EGA Furnace
  - Higher Mass
  - Used for EGA runs due to quartz liner
  - Cools down in ~40min

Standard Furnace



EGA Furnace Schematic



Calcium Oxalate Decomposition

- 1st Step $CaC_2O_4 \cdot H_2O\,(s) \longrightarrow CaC_2O_4\,(s) + H_2O\,(g)$

  Calcium Oxalate Monohydrate *Calcium Oxalate*

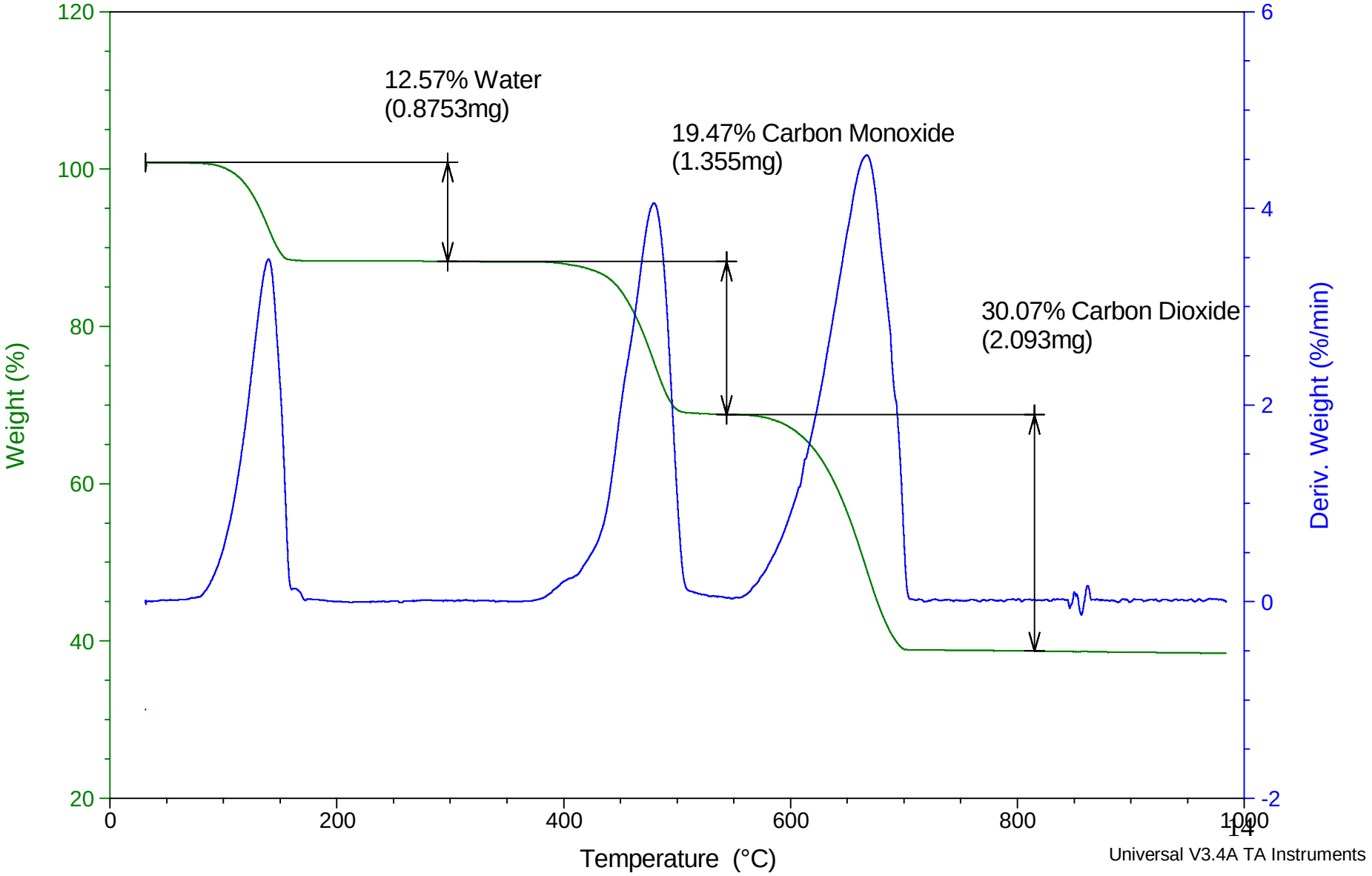
- 2nd Step $CaC_2O_4\,(s) \longrightarrow CaCO_3\,(s) + CO\,(g)$

  Calcium Oxalate *Calcium Carbonate*

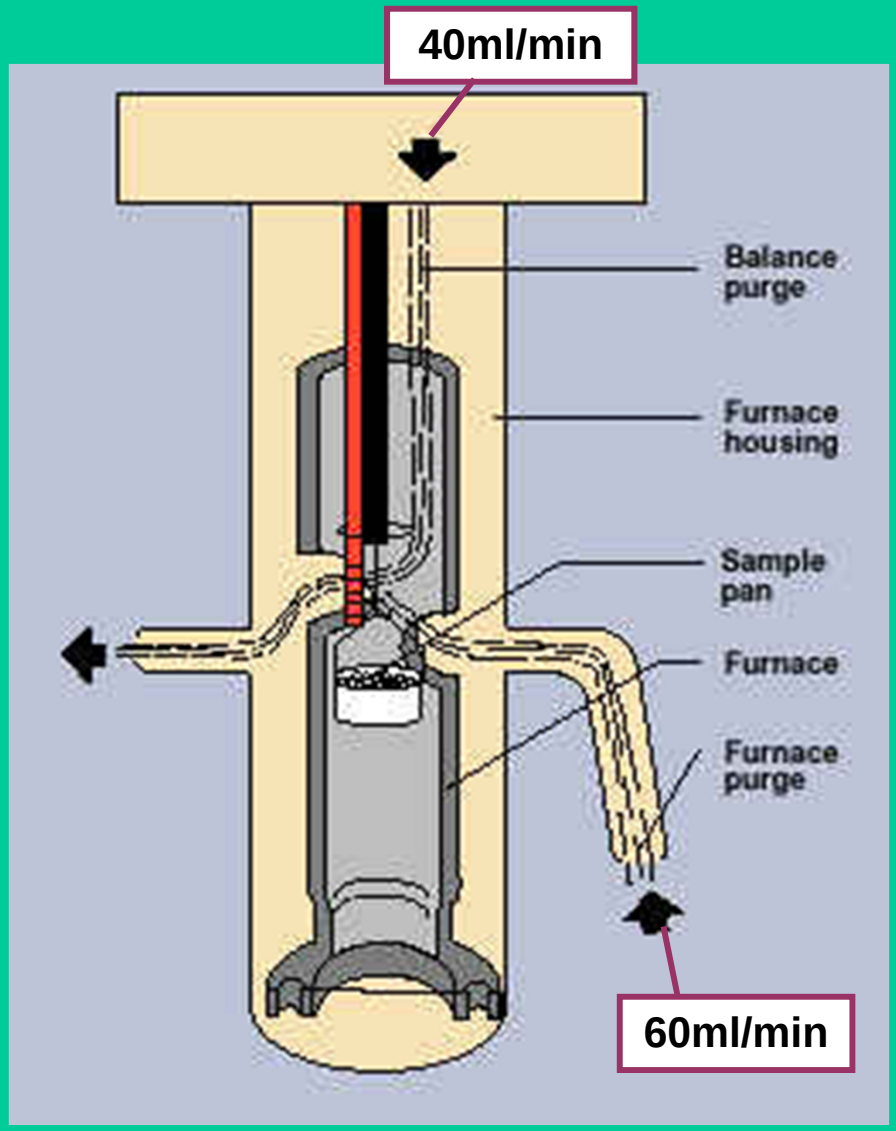
- 3rd Step $CaCO_3\,(s) \longrightarrow CaO\,(s) + CO_2\,(g)$

  Calcium Carbonate *Calcium Oxide*

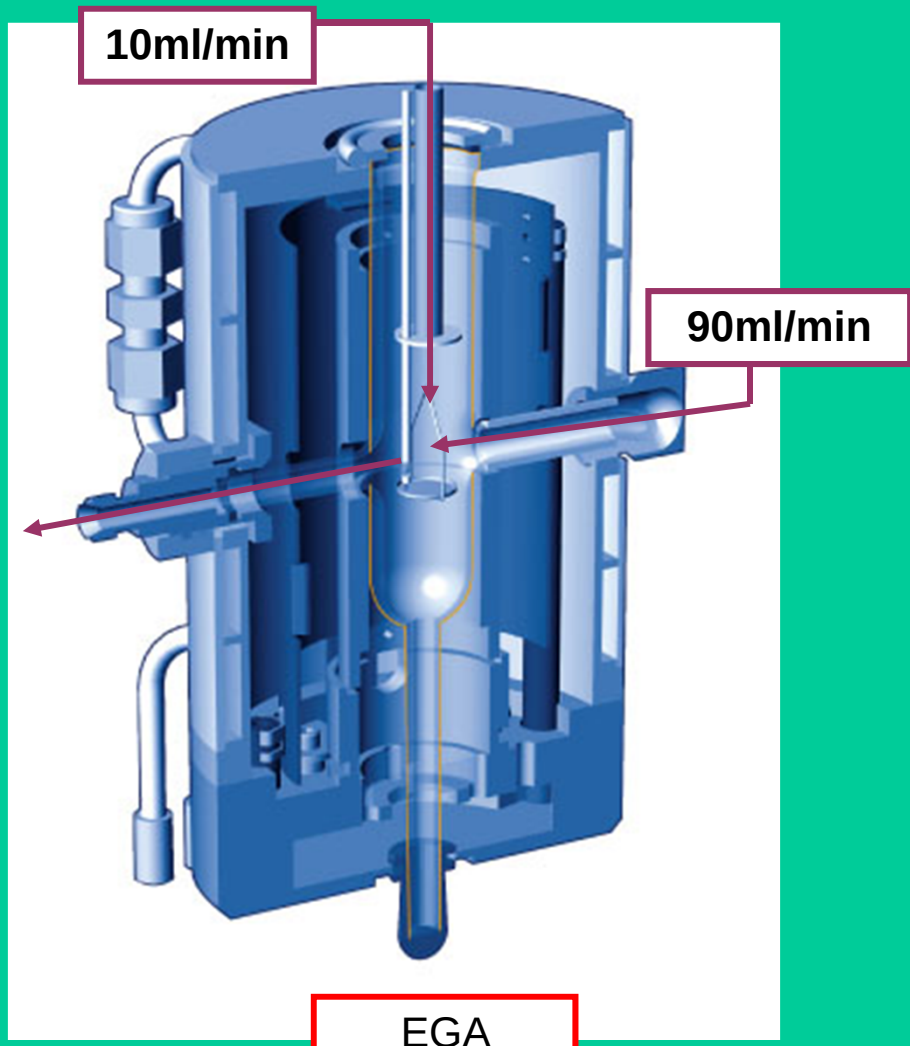
Calcium Oxalate Example



TGA: Purge Gas Flow



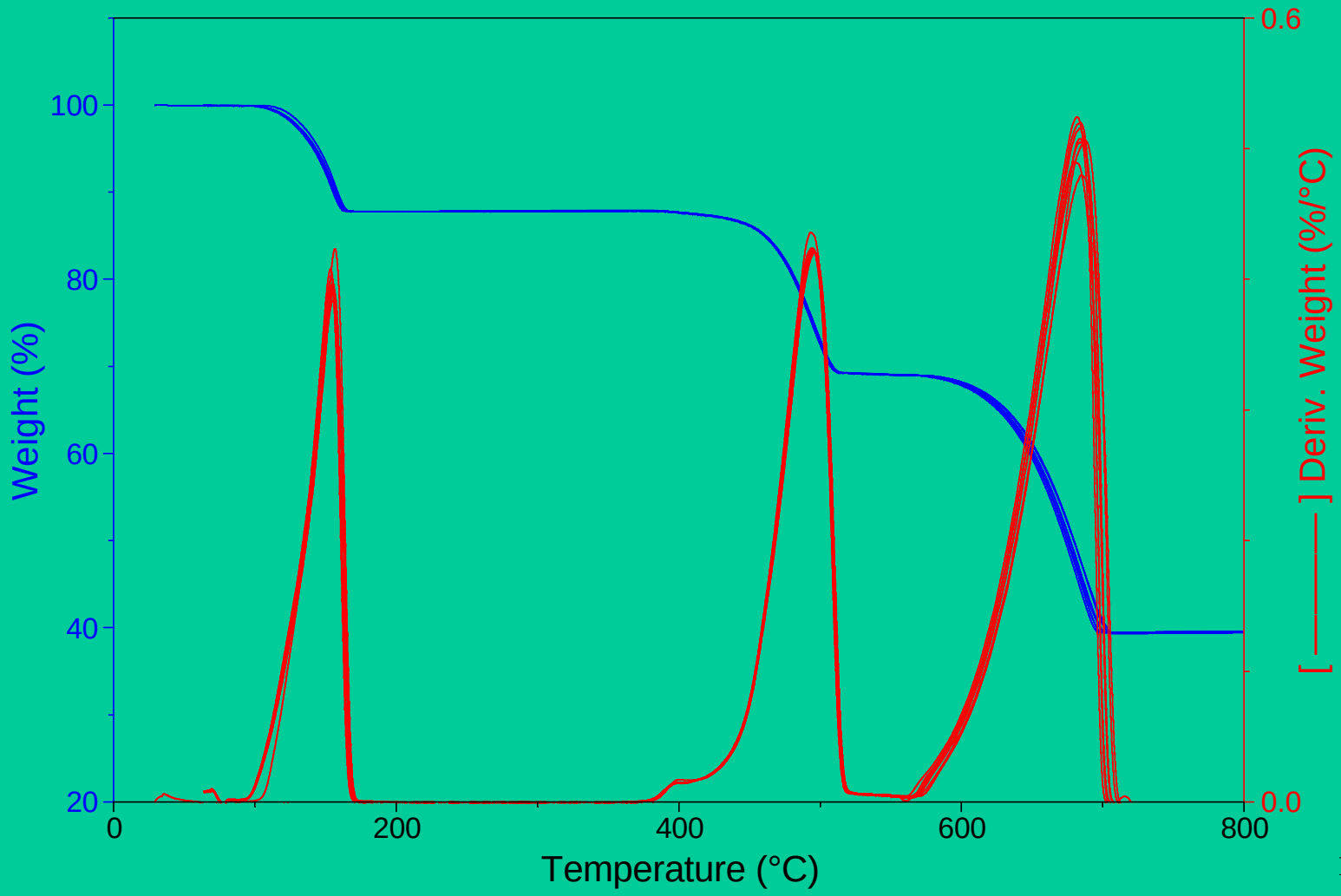
Standard Furnace

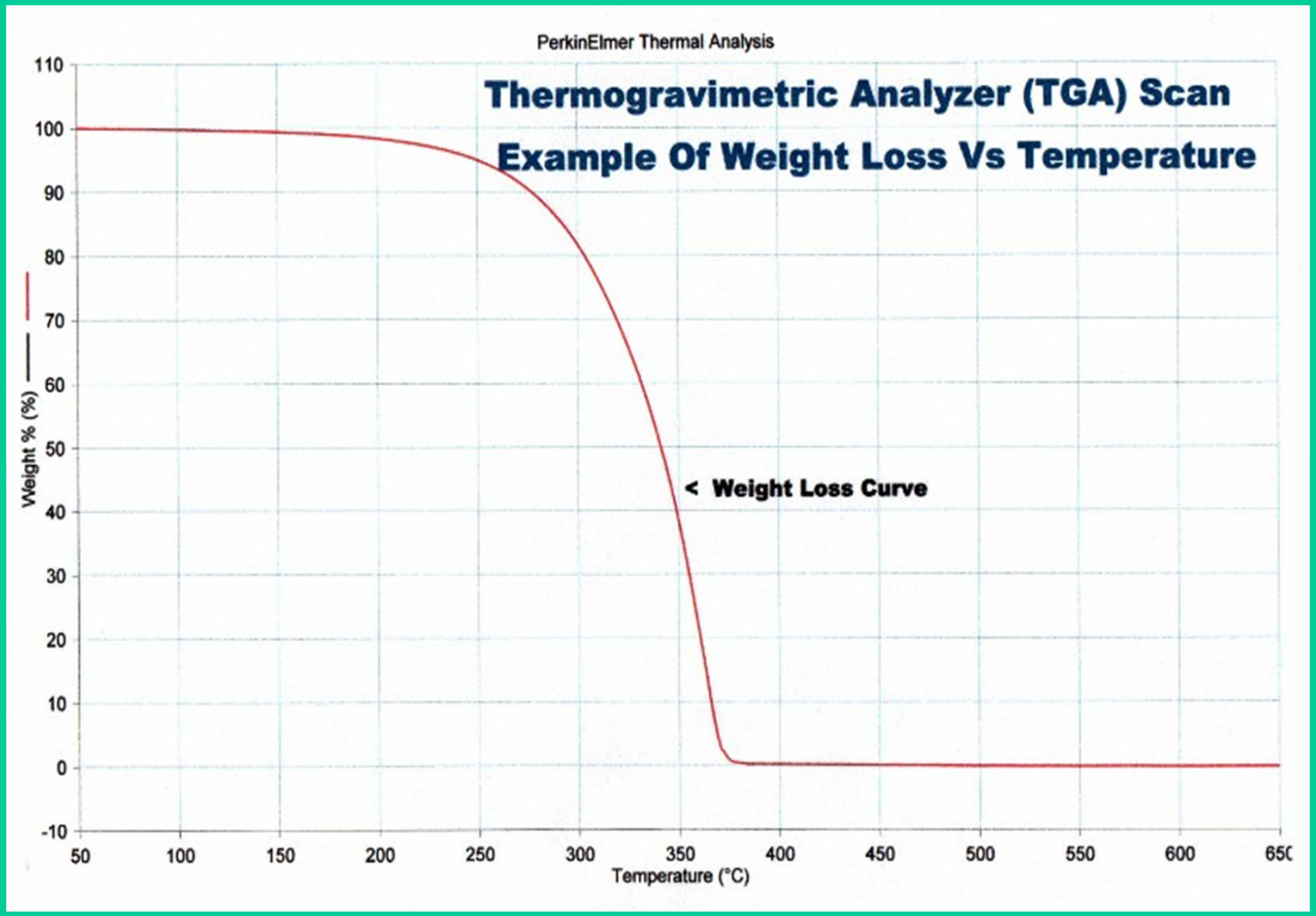


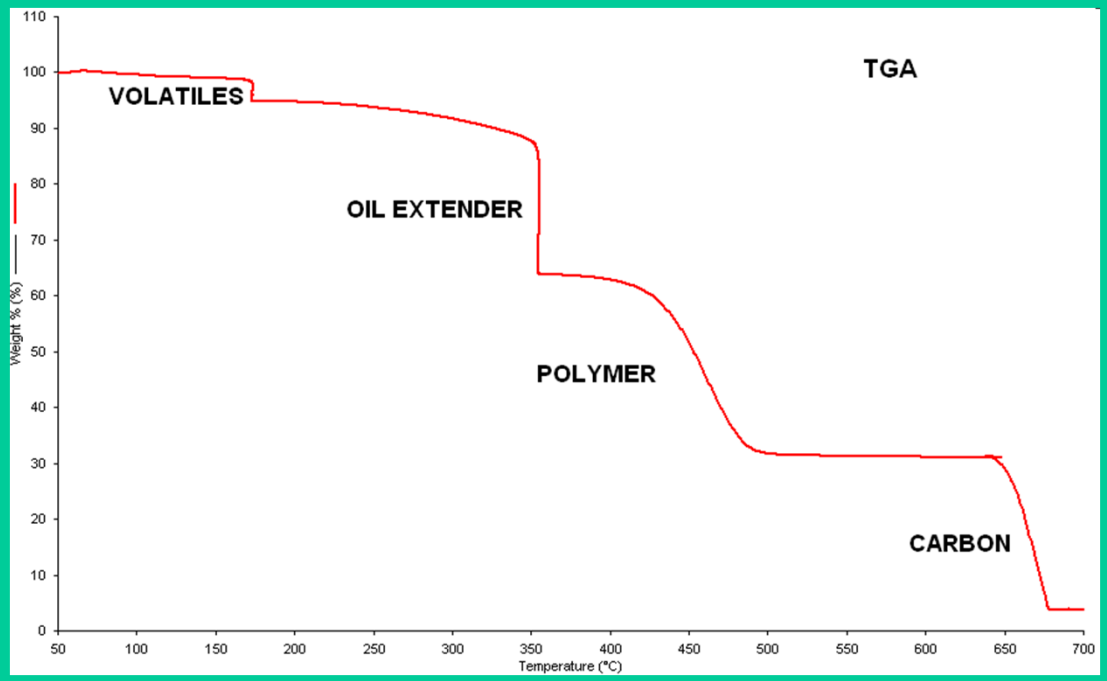
EGA Furnace

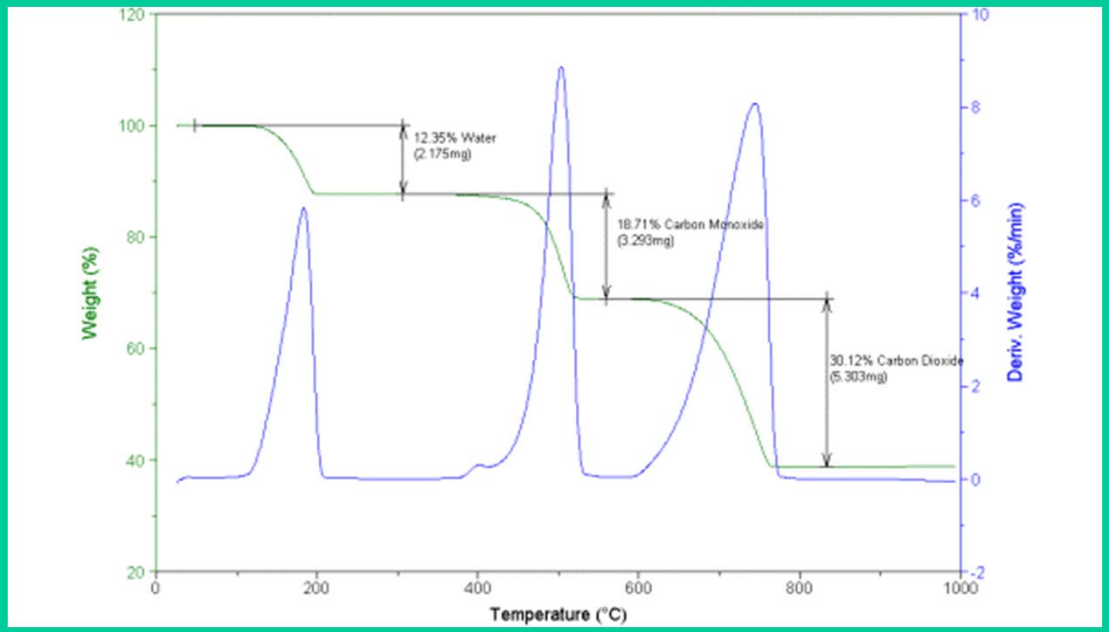
Calcium Oxalate Repeatability

Overlay of 8 runs, same conditions




PerkinElmer Thermal Analysis
Thermogravimetric Analyzer (TGA) Scan
Example Of Weight Loss Vs Temperature
< Weight Loss Curve
Weight % (%)
Temperature (°C)
110
100
90
80
70
60
50
40
30
20
10
0
-10
50
100
150
200
250
300
350
400
450
500
550
600
650


TGA
VOLATILES
OIL EXTENDER
POLYMER
CARBON
Weight % (%)
Temperature (°C)


12.35% Water
(2.175mg)
18.71% Carbon Monoxide
(3.293mg)
30.12% Carbon Dioxide
(5.303mg)
Weight (%)
Deriv. Weight (%/min)
Temperature (°C)

TGA – Thermogravimetric Analysis: Instrumentation

It is a thermo balance consisting of

- **High precision balance**
- **A furnace for achieving high temperatures, e.g.., 1500 ^{o}C**
- **A temperature programmer**
- **Data acquisition system**
- **Auxiliary equipment to provide inert atmosphere**
- **Thermobalance allows for monitoring sample weight as a function of temperature**

- **Weight calibration using calibrated weights**
- **Temperature calibration based on ferromagnetic transition of Curie point standards (e.g., Ni(**
- **Larger sample masses, lower temperature gradients, and higher purge rates minimize undesirable buoyancy effects**

TGA – Thermogravimetric Analysis: Requirements of a TG Balance

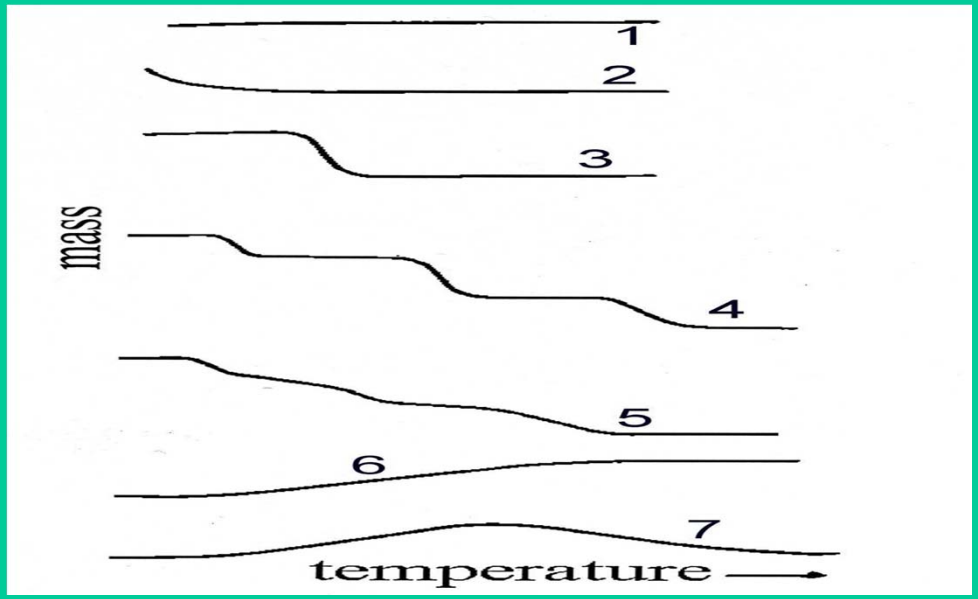
1. A thermo balance should provide accurate weight of the sample as a function of temperature. (capacity upto 1g, typical sample in mg). Its reproducibility should be very high and also highly sensitive.

2. It should operate over a wide temperature range, say from RT to 1000-1500 oC.

3. The design of thermo balance should be such that sample container is always located within a uniform hot zone inside the furnace.
4. The sample container should be such that it does not react with the sample at any given temperature

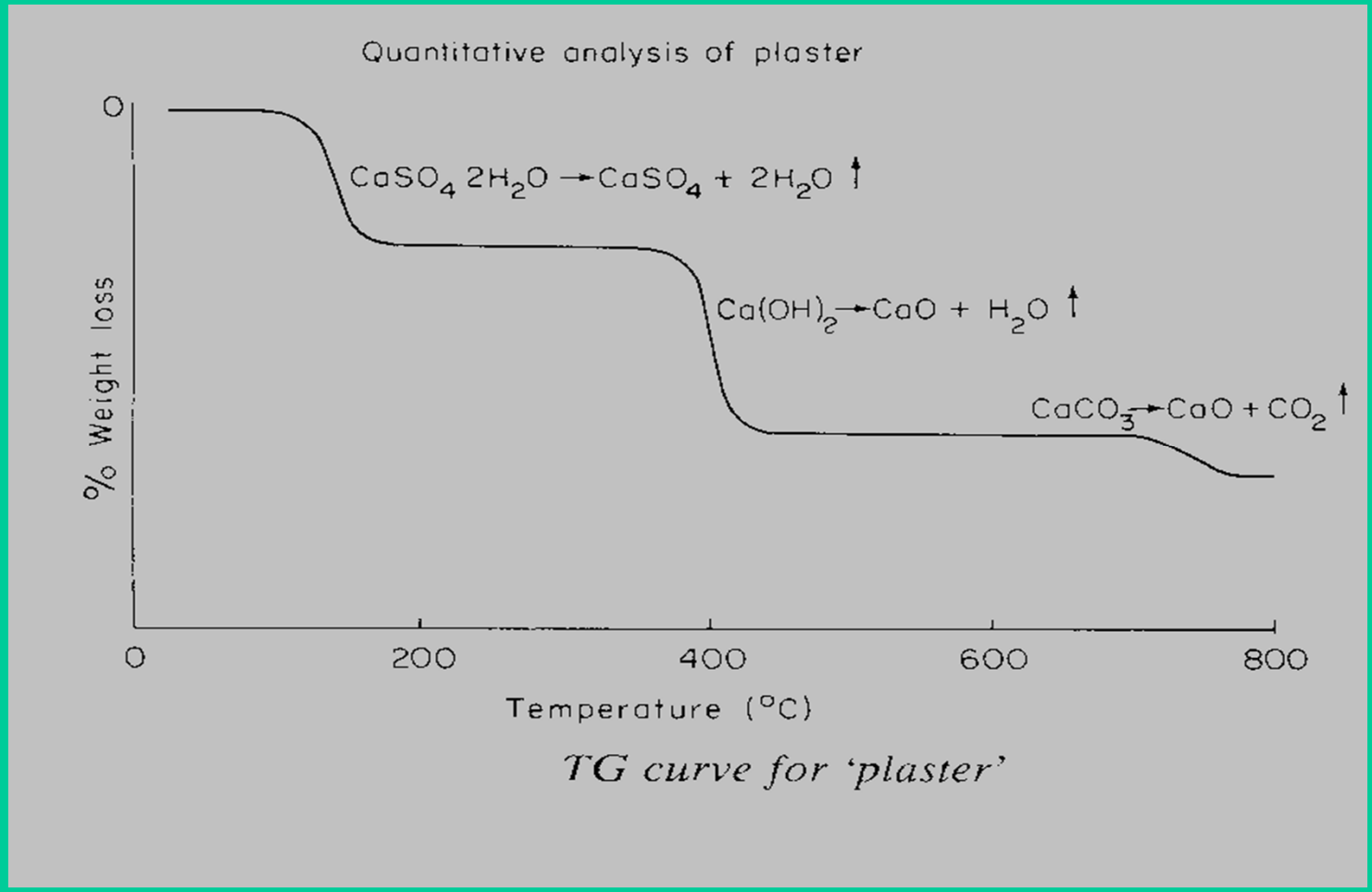
5. It will be advantageous if thermo balance can be coupled to a GC or IR or to MS.

Types of TG Curves



1. no change
2. desorption/drying (rerun(
3. single stage decomposition
4. multi-stage decomposition
5. as 4, but no intermediates or heating rate too fast
6. atmospheric reaction
7. as 6, but product decomposes at higher temperature

Plaster contains gypsum ($CaSO_4 2H_2O$), lime $Ca(OH)_2$ and chalk $CaCO_3$.



TG curve for 'plaster'

YCa, Sr and Ba are precipitated as monohydrated oxalates.

- **In the first step,**

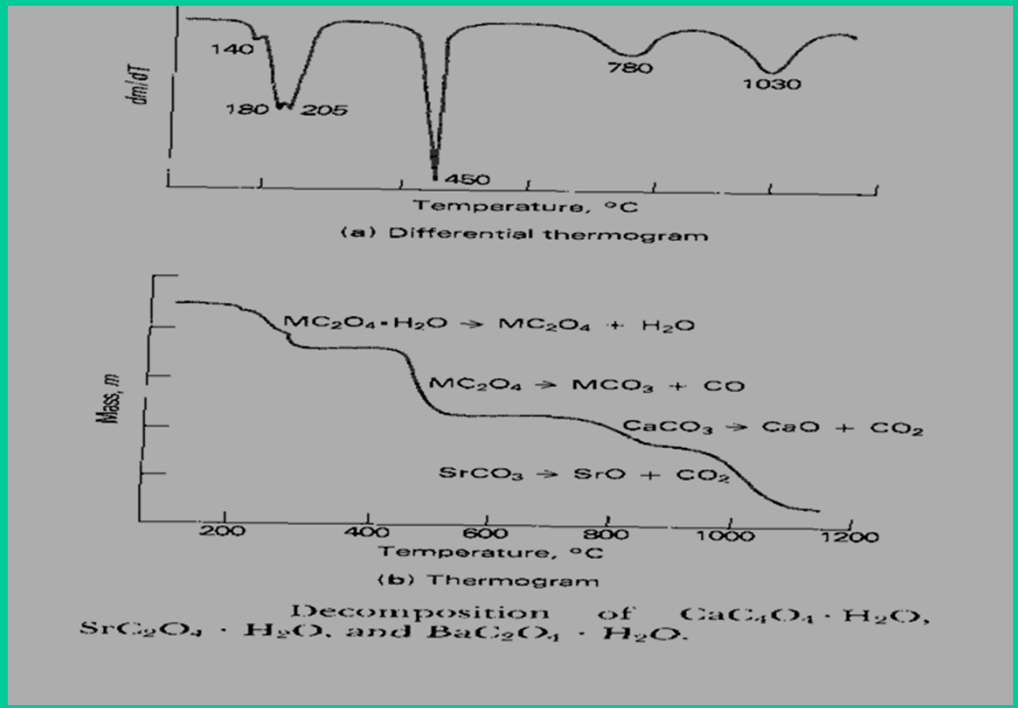
H_2O is removed from all the three oxalates

- **In 2nd step,**

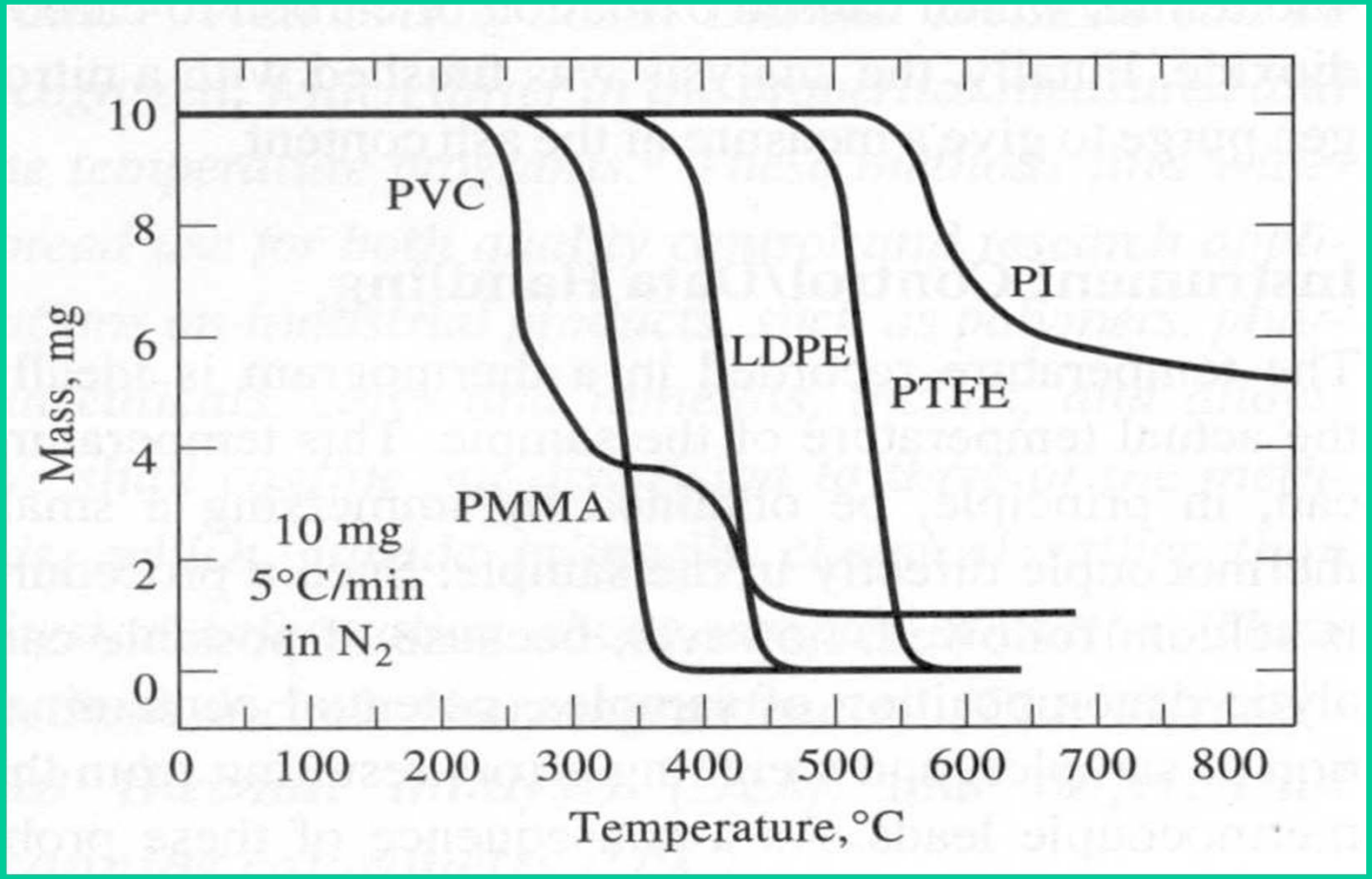
carbonates are formed by losing CO

- **In 3rd step,**

stable oxides are formed by losing CO_2



Decomposition of $CaC_2O_4 \cdot H_2O$, $SrC_2O_4 \cdot H_2O$, and $BaC_2O_4 \cdot H_2O$.


Mass, mg
10
8
6
4
2
0
PVC
PMMA
LDPE
PTFE
PI
10 mg
5°C/min
in N_2
0
100
200
300
400
500
600
700
800
Temperature,°C

- **<u>High flow purge rates</u> ? Not recommended, specially for vertical TGA balances due to more turbulence: (**
- **Better controlled atmosphere (inert) specially at higher temperatures**
- **Typical purge gas flow rate for small furnace:**

60 ml/min for a vertical TGA , but can be increased up to 500 ml/min (even 1000 ml/min

(in case of horizontal models, to rapidly purge the furnace without the use of vacuum.