The principle of thermogravimetric analysis and its applications

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الرئيسية | المحاضرات | السيرة الذاتية | البحوث الرصينة | المحاضرات الفيديوية

الرئيسية

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دكتوراه في الكيمياء حياتية فيزيائية - بريطانيا -

Biochemistry, Biophysics, Nanomaterials, Structural biology

استاذ مساعد في الكيمياء حياتية -

زميل الاكاديمية البريطانية للتعليم العالي -

عضوة (محكّم) في مجلة نانوسكيل- الجمعية الملكية للكيمياء -

عضوة (مراجع) في مجلة نانوبايوتكنولوجي-

عضوة في الجمعية الملكية للكيمياء MRSC-

عضوة في الجمعية الكيميائية الامريكية ACS-

My previous projects :

- The efficiency of nano chitosan to encapsulate bovine serum albumin: A Biophysical study, for controlled therapeutic protein release
- Biophysical basis of nanochitosan grafted sodium alginate, for controlled drug release therapy of hypothyroidism
- Synthesis and characterization of some transition metal complexes with poly dentate ligands of pyrazole, for clinical study to control autism spectrum disorder
- Green synthesis, and characterization of metal oxide nanoparticles and their clinical application on Osteoporosis patients and computational study on S-protein of COVID-19.

My current interest:

- Photo degradation study of glucose and urea in the aqua solutions and serum of diabetic and renal failure patients
- green synthesis of nano metal oxides for clinical applications on diabetic patients with anemia.
- Preparation of protein nanoparticle and its applications
- A clinical study on L-Arginine amino acid as an antiaging factor.

CONTENTS :

- Thermal Analysis
- Applications
- Different thermal analytical methods
- Thermogravimetry
- Types of Thermogravimetry
- Principle
- Description
- Recording of result
- Information obtained from a TG curve
- Advantages of TGA
- Factors affecting a TG curve

APPLICATIONS OF THERMOGRAVIMETRIC ANALYSIS

a) Thermal stability: Similar or related materials can be contrasted at higher temperatures under desired atmospheric conditions. TGA plot helps to explicate decomposition mechanisms,
b) Materials Characterization: TGA plot may be employed for material finger printing in identification as well as quality control,
c) Compositional analysis: By a careful choice of temperature programming and gaseous environment, complex materials/mixtures can be examined by removing or decomposing their constituents. For example: filler concentration in polymers; carbon black in oils; ash and carbon in coals, and the moisture content of many substances,
d) Kinetic studies: Several procedures can help in examining the kinetic features of weight loss or gain through controlling the chemistry or predictive studies,
e) Corrosion studies: T GA can be used to analyze oxidation or other reactions with different reactive gases or vapors,
f) Evaluation of gravimetric precipitates,
g) Evaluation of suitable standards,
h) Testing of purity of samples,
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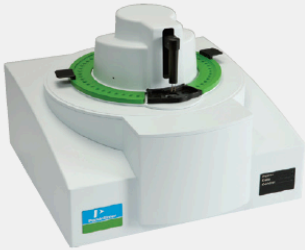
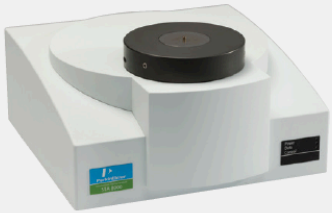
Thermogravimetric analysis
TGA Instrument

TGA 8000



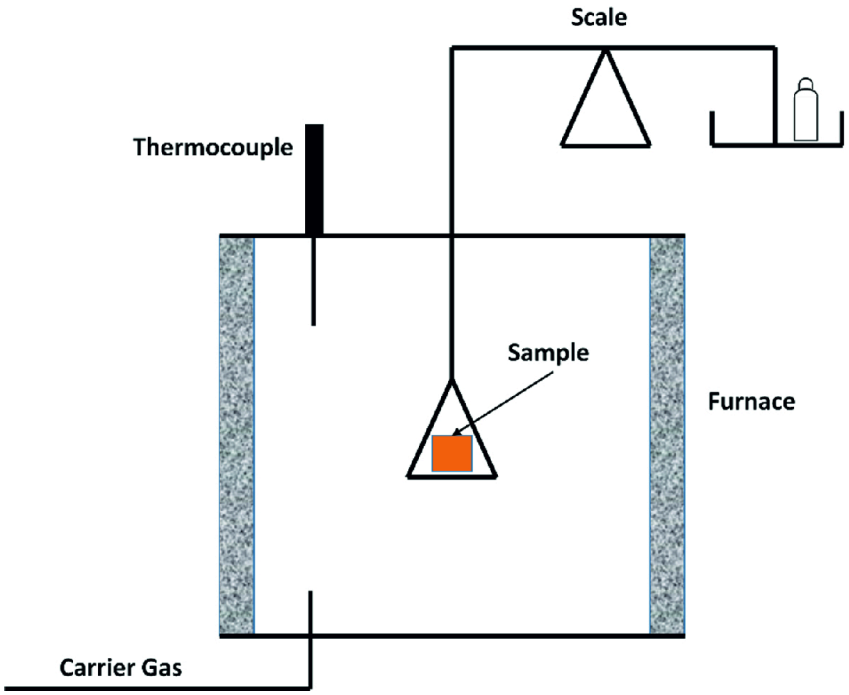
TGA 4000



STA 6000 / STA 8000

The Thermogravimetric Instrument Family

THE MAIN COMPONENTS OF TGA



1. A high precision thermobalence (± 10 μg)
2. Furnace with temperature programming facility.
3. Facility for providing inert atmosphere (like N_2 gas) Or Oxidizing environment
4. A computer which can collect, store and process data – like plotting the graph.

THERMAL ANALYSIS

- **Thermal analysis refers to those techniques in which some physical parameters of the system is determined and/or recorded as a function of temperature or time.**

- **When a material heats, it undergoes several steps of physical and chemical changes. These changes provide us with information to identify the unknown material.**

- **Based on the above definition, various techniques of thermal analysis are summarised in the table 1:**

DIFFERENT THERMAL ANALYTICAL TECHNIQUES

No	name of the technique	abbreviation of the technique	instrument employed	parameter measured	graph
1.	thermogarvimetry	TG	thermobalance	Mass	Mass vs. Temperature or Time
2.	derivative thermogravimetry	DTG	thermobalance	dm/dt	dm/dt vs. Temperature
3.	differential thermal analysis	DTA	DTA Apparatus	ΔT	ΔT vs. Temperature
4.	differential scanning calorimetry	DSC	calorimeter	dH/dt	dH/dt vs. Temperature
5.	thermometric titrimetry	-	calorimeter	Temperature	Temperature vs. Titrant Volume

DIFFERENT THERMAL ANALYTICAL TECHNIQUES

S.No	name of the technique	abbreviation of the technique	instrument employed	parameter measured	graph
6.	dynamic reflectance spectroscopy	DRS	spectro-photometer	reflectance	% Reflectance vs. Temperature
7.	evolved gas detection	EGD	thermal conductivity cell	Thermal conductivity (T.C.)	T.C. vs. Temperature
8.	thermo-mechanical analysis (dialotometry)	TMA	dilatometer	volume or length	Volume or Length vs. Temperature
9.	electrical conductivity	EC	electrometer	Current (I)or Resistance (R)	I or R vs. Temperature
10.	emanation thermal analysis	ETA	ETA Apparatus	radioactivity (E)	E vs. Temperature

THERMAL ANALYTICAL TECHNIQUES

Any analytical instrument technique is considered a thermal analysis method if the physical parameter is measured as a function of temperature (or time). (According to Wendlandt)

- **According to this definition,**
- **PROTON NUCLEAR MAGNETIC RESONANCE,**
- **ELECTRON SPIN RESONANCE,**
- **ELECTRON DIFFRACTION,**
- **X- RAY DIFFRACTION,**
- **MASS SPECTROMETRY,**
- **UV, Visible and IR SPECTROPHOTOMETRY**

are thermal methods.

THERMOGRAVIMETRY

It is a technique allows thermal analysis of a substance when subjected to a controlled temperature programmer, where its physical property is measured as a function of temperature or time. It can scan over a wide range of temperature (25 – 1200 ^{o}C)

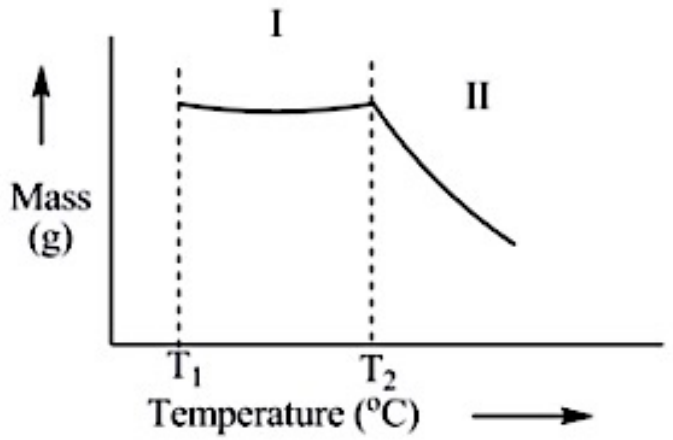
This measurement provides information about physical phenomena, such as thermal decomposition, phase transition, absorption, adsorption, and desorption.

❖The principle of thermogravimetry is based on measuring the changes in the mass of a substance when it is continuously being heated to elevated temperatures.

❖Not all thermal changes/events bring a change in mass of sample i.e. melting, crystallization but some thermal events i.e. desorption, absorption, sublimation, vaporization, oxidation, reduction and decomposition bring a drastic change in the mass of sample. Therefore, it is very important to optimize those conditions/factors on which the change of mass of sample depend throughout the experiment.

تقنية التحليل الحراري لمادة ما عند تعريضها الى ارتفاع مبرمج بدرجة الحرارة ، حيث يتم قياس خصائصها الفيزيائية كدالة لدرجة الحرارة أو الوقت.
مبدأ القياس يعتمد على قياس التغيرات في كتلة المادة عند تعريضها إلى درجات حرارة مرتفعة بشكل منظم.
ليست كل الدرجات الحرارية تؤدي إلى حدوث تغيير في كتلة العينة ، أي الذوبان ، والتبلور ، ولكن بعض الاحداث الحرارية ، مثل الامتصاص ، والامتصاص ، والتسامي ، والتبخر ، والأكسدة ، والاختزال ، والتحلل تؤدي إلى تغيير جذري في كتلة العينة.

The mass vs Temperature plot is called Thermogram.



an idealized thermogram is shown in the figure

Region I: The horizontal indicates the region where there is no mass change. Ie from T1 to T2 the material is thermally stable.

Region II: The graph declines indicating a weight loss (weight loss can be due to dehydration, decomposition, sublimation, desorption, Evaporation etc. [Weight gain during Metal Oxidation, adsorption etc]

Sample Preparation

Usually 10-20 mg of material is desirable in most applications.

For volatile materials 20-100 mg of sample is required. The instruments have a baseline drift of +-0.25% of a 10 mg sample.

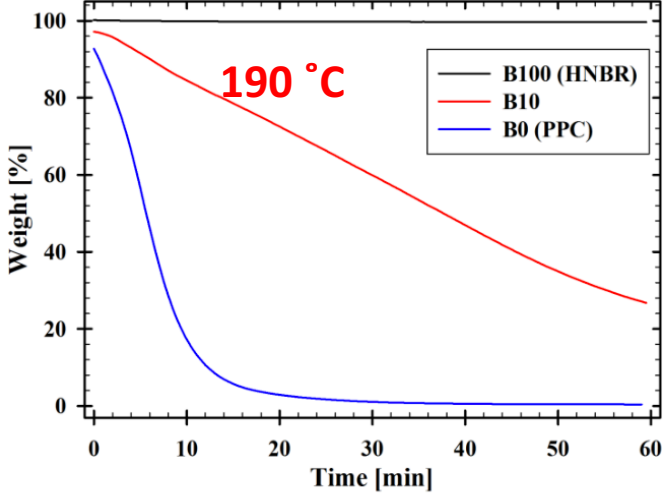
TYPES OF THERMOGRAVIMETRY

There are three types of Thermogravimetry:

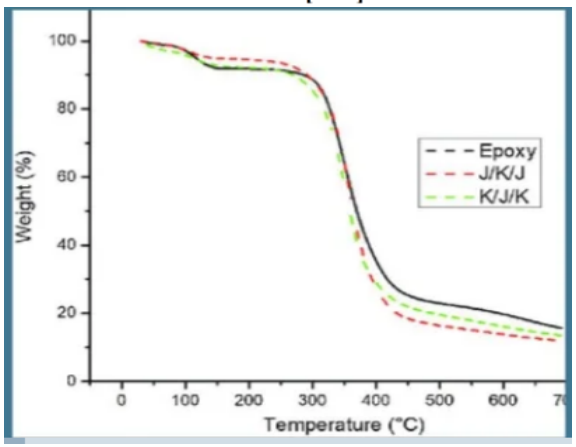
1. **Isothermal / Static Thermogravimetry ثابت حراري/**
2. **Quasistatic Thermogravimetry ثابت شبه**
3. **Dynamic Thermogravimetry متحرك ديناميكي**

Most of the studies are generally carried out with dynamic thermogravimetry. Therefore it is generally referred to as thermogravimetry.

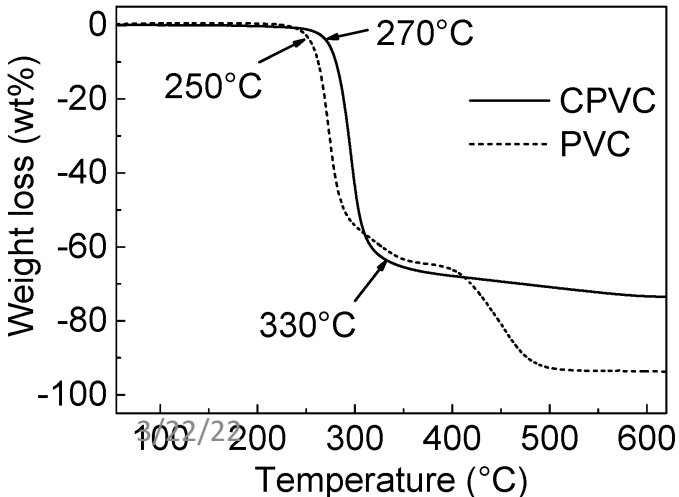
TYPES OF THERMOGRAVIMETRY



1. Isothermal/ Static Thermogravimetry: A sample weight is recorded as a function of time at constant temperature.



2. Quasistatic Thermogravimetric: A sample is heated to constant weight at each of the series of increasing temperature.



3. Dynamic Thermogravimetry: A sample is heated in linear rate of increasing temperature, for example 20 ˚C/ min .

RESULT of TGA

- **The instrument used for themogravimetry is a programmed precision balance for control rising in temperature, known as Thermo balance.**
- **Results are displayed by a plot of mass change% on the y-axis vs temperature (or time) on the x-axis. These results are known as Thermogravimetric curves or TG curves.**
- **A typical TG curve is in the Figure.**

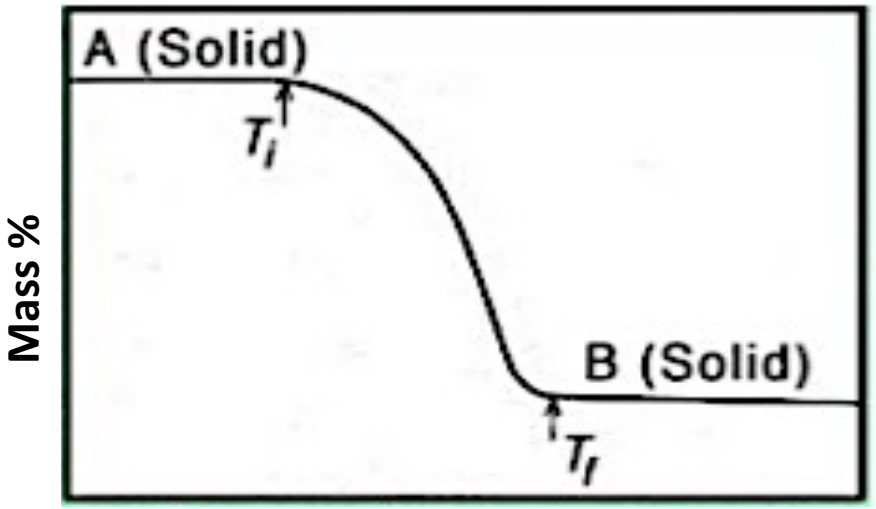
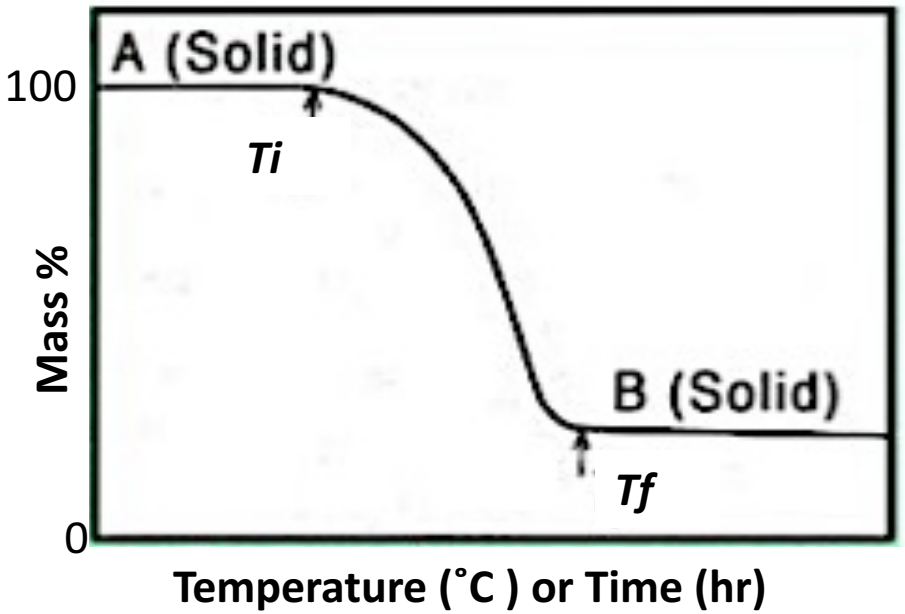


Figure . Characteristics of a single-stage mass-loss curve

RESULT of TGA



There are two temperatures in the reaction,

- **Plateau: T_i (initial temp.) A plateau part= the lowest temperature causes no significant mass change.**
- **Final Temperature T_f (final temp.) = the lowest temperature at which the decomposition process has been completed respectively.**

➢ **Procedural Decomposition Temperature Ti-Tf (The reaction temperature and interval) = depend on the experimental condition; therefore, they do not have any fixed value.**

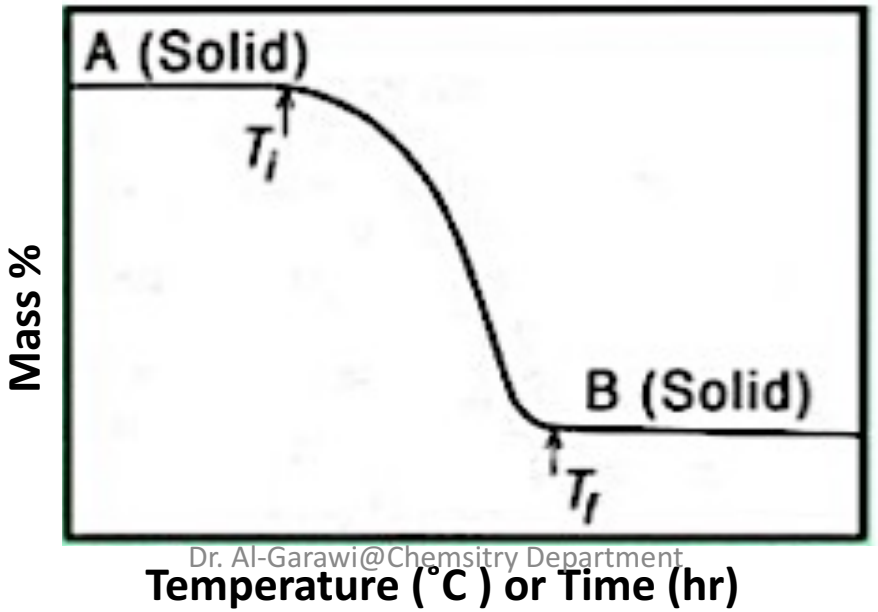
Conclusion of TGA chart

It can be concluded that Thermogravimetry is concerned with the change in weight of a material as its temperature changes.

1- This loss indicated decomposition or evaporation of the sample.

2- the temperature at which no weight loss takes place indicates stability of the material.

3- These temperature ranges are identification of physical properties of chemical composition of the material.



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TGA of Calcium Oxalate Monohydrat

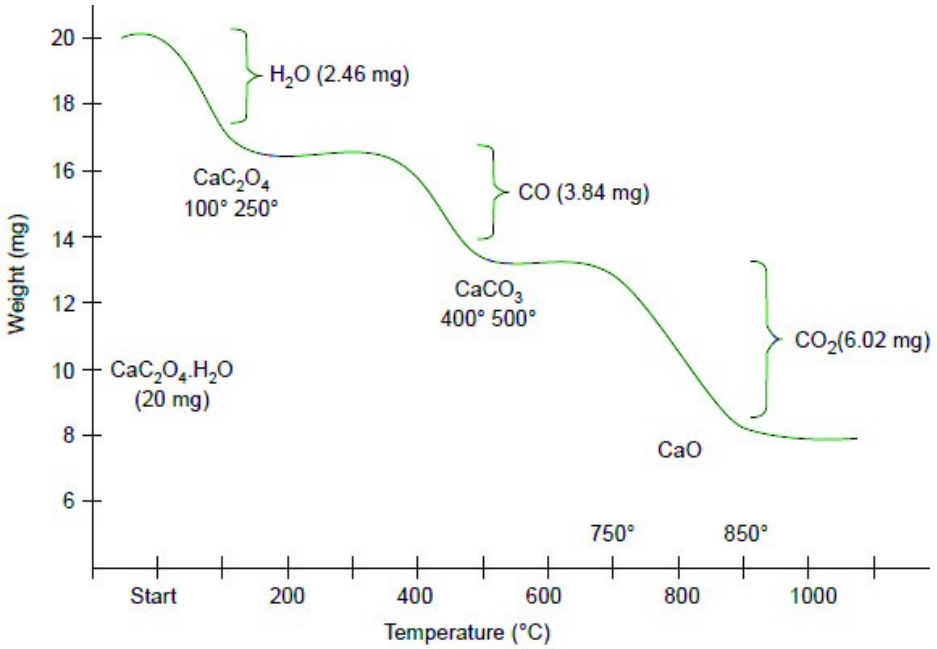


Figure 11.2 : Thermogravimetric Evaluation of Calcium Oxalate

- 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*

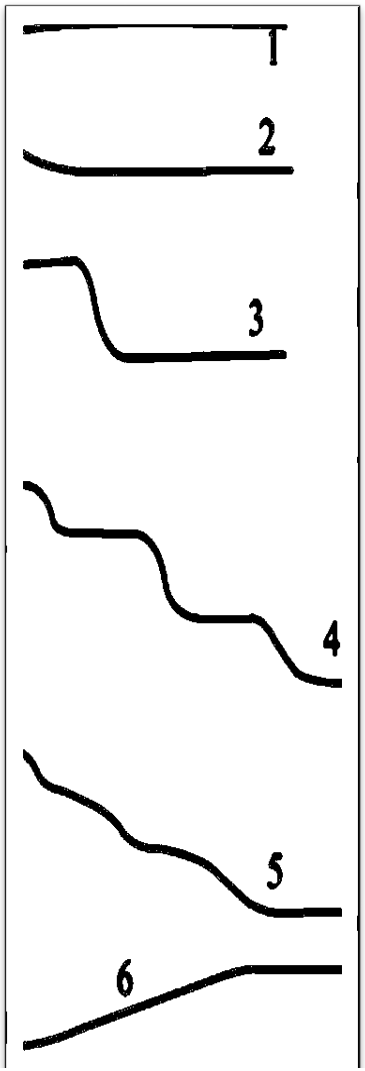
- 3rd Step $CaCO_3\ (s) \longrightarrow CaO\ (s) + CO_2\ (g)$

  Calcium Carbonate — *Calcium Oxide*

The successive plateaus signify the development of anhydrous salt, calcium carbonate and calcium oxide, respectively, and can be given by the above equations.

The thermogravimetric curve signifies that removal of water starts at 100°C and removal of CO at 450°C and CO2 at 600°C.

Types of TGA curves



1) There is no decomposition with removal of volatile products.

(2) Fast initial weight loss. It is characteristic of sample drying (repeat experiment after drying the sample).

(3) Single phase decomposition.

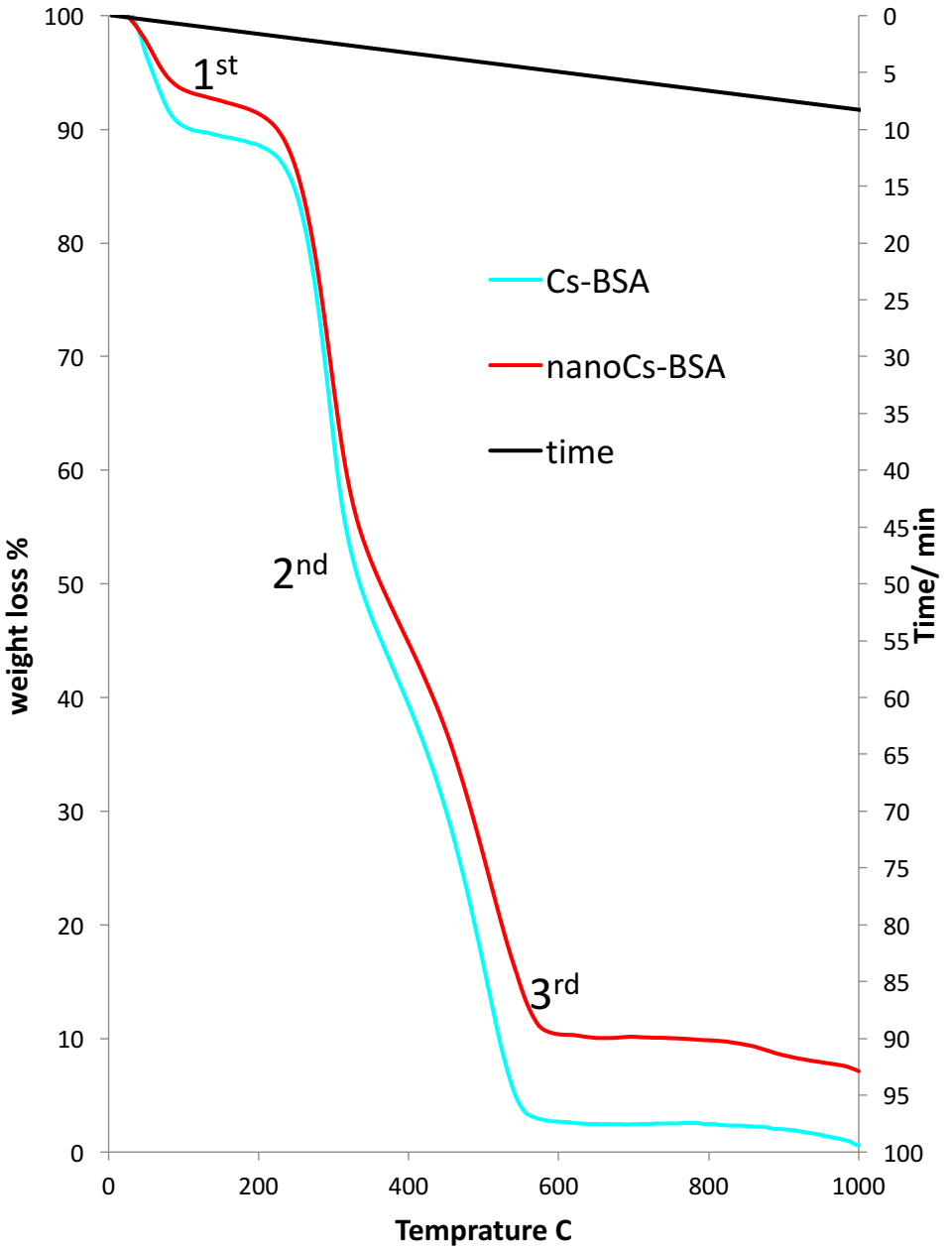
(4) Multi-step decomposition with stable intermediate products.

(5) Multi-step decomposition with no stable intermediary.

(6) Certain reactions (such as oxidation of metals) with atmosphere may result in increase in mass.

The TGA curve of 2 compounds

- revealed three weight loss stages.
- The first stage (12% of weight loss) due to the loss of water and light volatile compounds.
- The second stage (~50%of weight loss) due to due to thermal decomposition of the polymer.
- The third stage started from 570°C, where no significant loss in the weight, which indicated the pyrolysis of the remaining carbonaceous material resulting in vaporization and elimination of volatile products after 97 min heating up to 1000 °C.



The TGA curve of 2 compounds

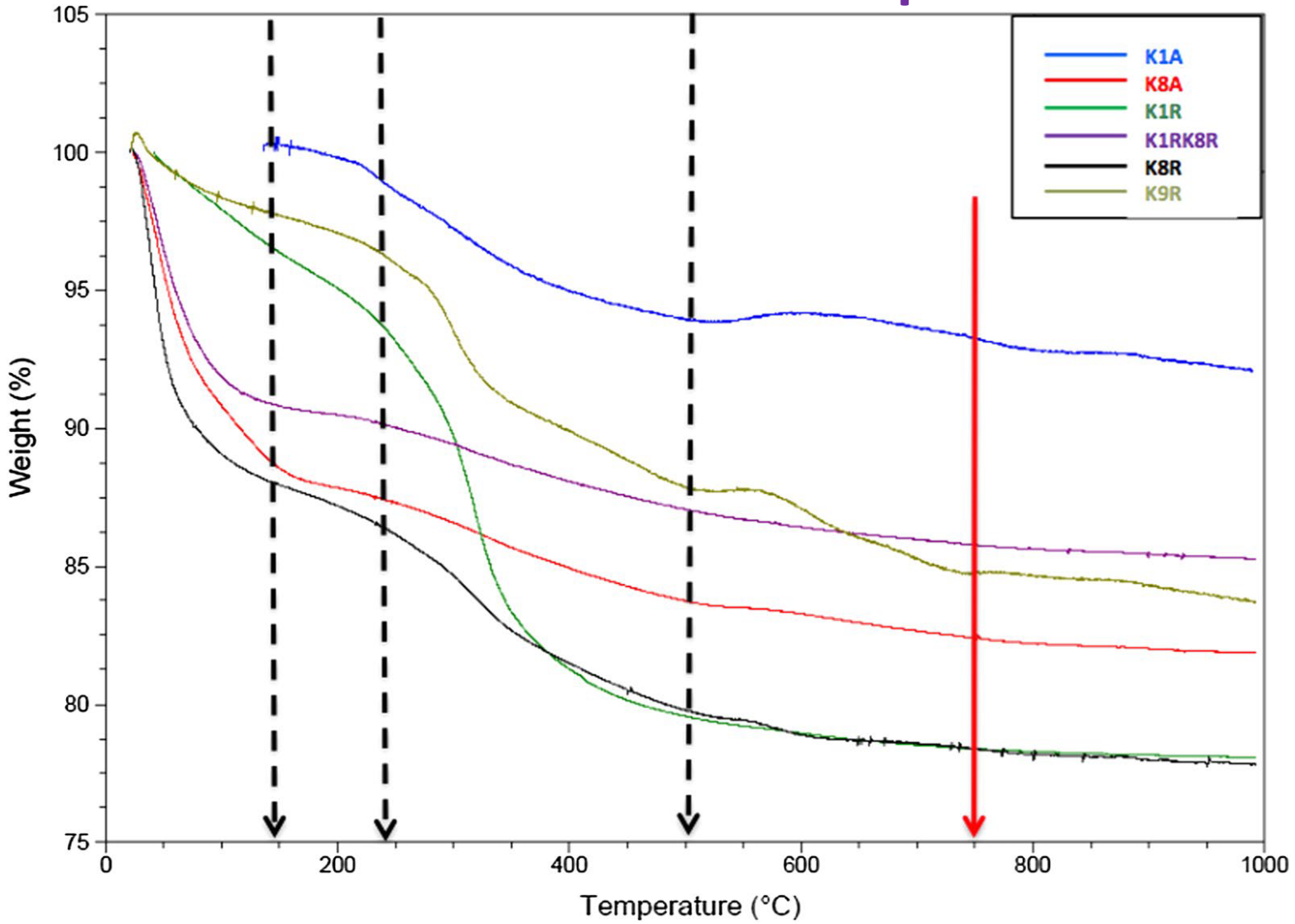
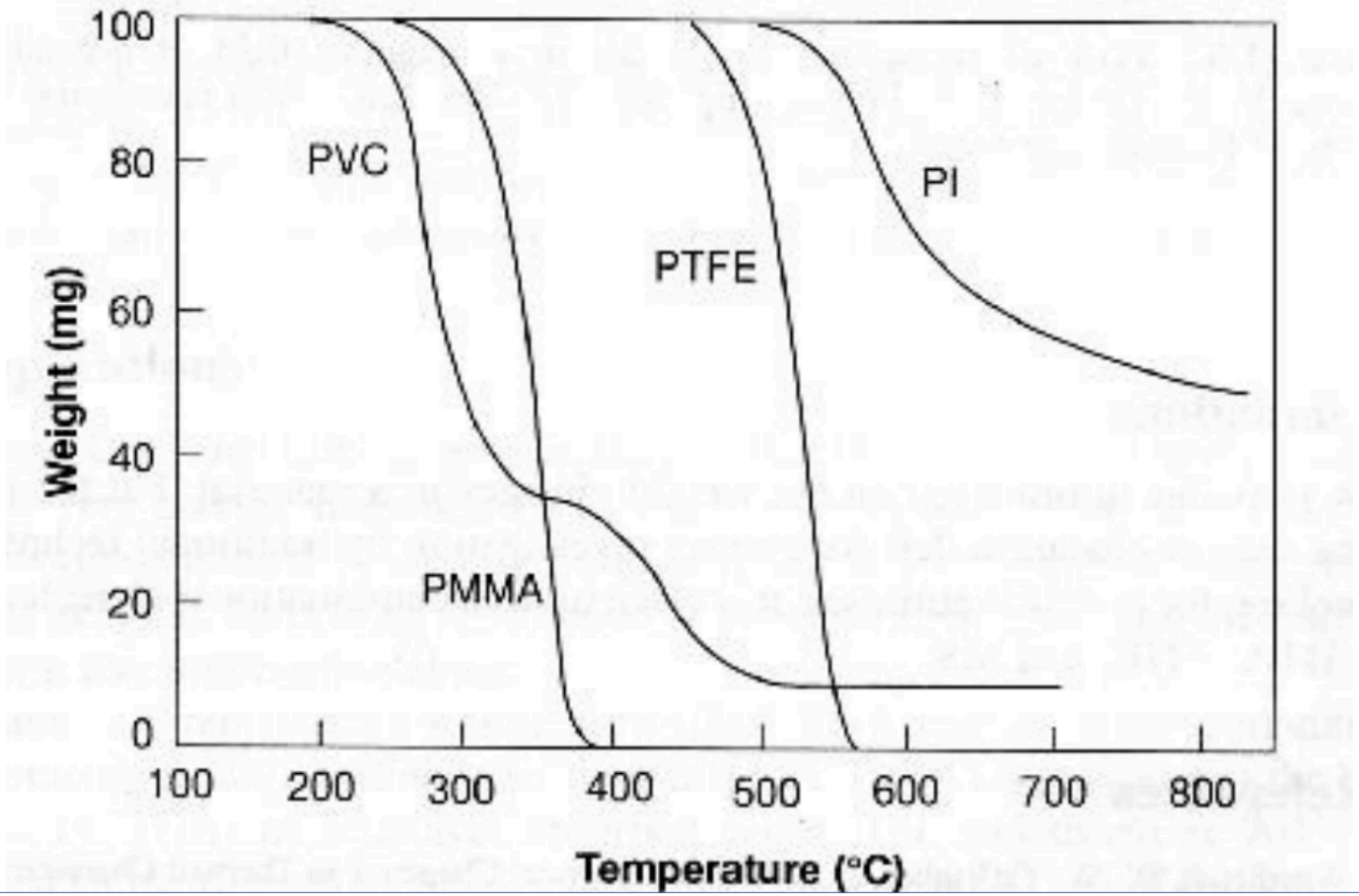


Fig.4 TGA analysis of silica-NWs (12 months old) showing the stability up to 1000 °ΔC peptides -NWs. The rate of temperature increases as 20 °ΔC/min, under N2 gas.

Thermal degradation profile of common polymers



Inert atmosphere: Depolymerization or Carbonization

Air Atmosphere: Oxygen in air active ingredient in degradation

ADVANTAGES OF TGA

1. Thermal Stability of Materials: Explain decomposition mechanism, fingerprint materials for identification & quality control

2. Oxidative Stability of Materials: Oxidation of metals in air, Oxidative decomposition of organic substances in air/O2, Thermal decomposition in inert atmosphere

3. Composition of Multi-component Systems: Behaviors sufficiently different on the temperature scale can be identified and reaction mechanism formulated

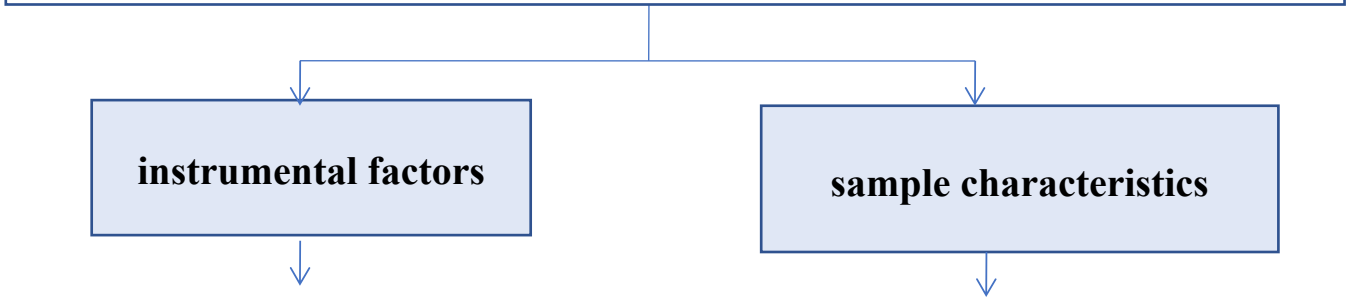
4. Estimated Lifetime of a Product: Related to thermal stability

5. Decomposition Kinetics of Materials: Rate of reaction, Activation Energy

6. The Effect of Reactive or Corrosive Atmospheres on Materials: Oxidation & Corrosion Studies

7. Moisture and Volatiles Content of Materials: Loss of moisture, drying, desorption

FACTORS AFFECTING THERMOGRAVIMETRIC CURVE



1. heating rate
2. effect of furnace atmosphere
3. sample holder

1. weight of the sample
2. sample particle size
3. compactness of the sample
4. Method of preparation

sample characteristics

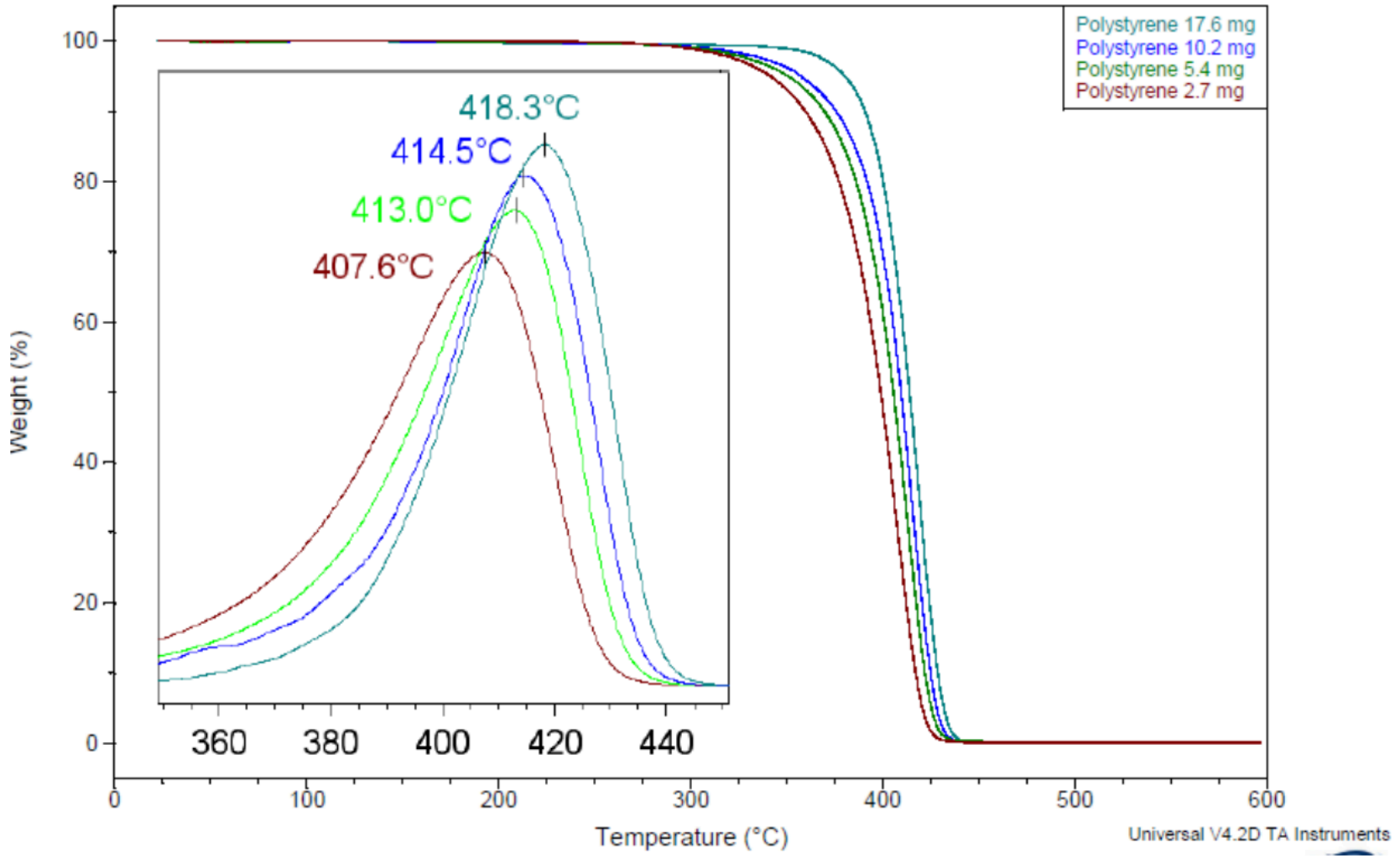
1. **Weight of the sample**: If a large sample is used, there occurs a deviation from linearity as the temperature rises, especially for an exothermic reaction. Eg.: evolution of CO during decomposition of calcium oxalate to $CaCO_3$.

2. **Sample particle size**: If the particle size is small dimension, the decomposition takes place earlier, while with greater particle size, the decomposition proceeds only at higher temperatures.

3. **Compactness of the sample:** A compressed sample will decompose at higher temperatures than a loose sample.

4. **Method of preparation of the sample**: Method of formation of the sample affect the decomposition of the materials. Eg.: TG studies showed that $Mg(OH)_2$ prepared by precipitation method has a different temperature of decomposition from that of the naturally occurring material.

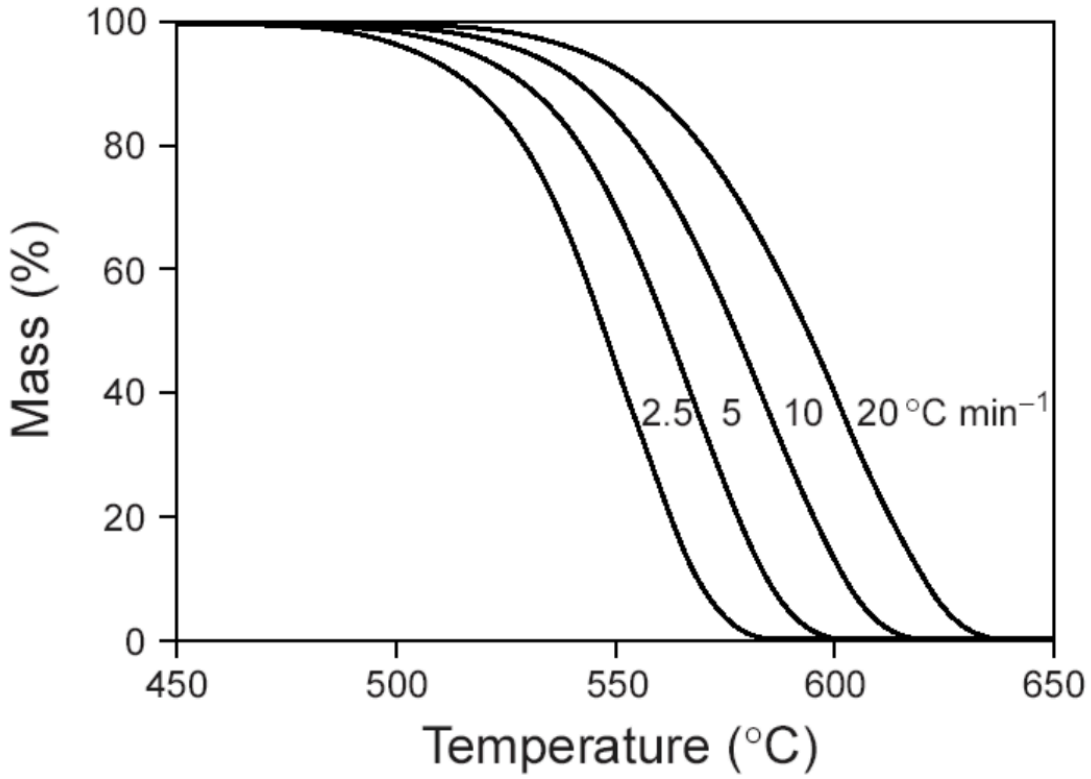
Effect of Sample Weight



instrumental factors

Effect of heating rate

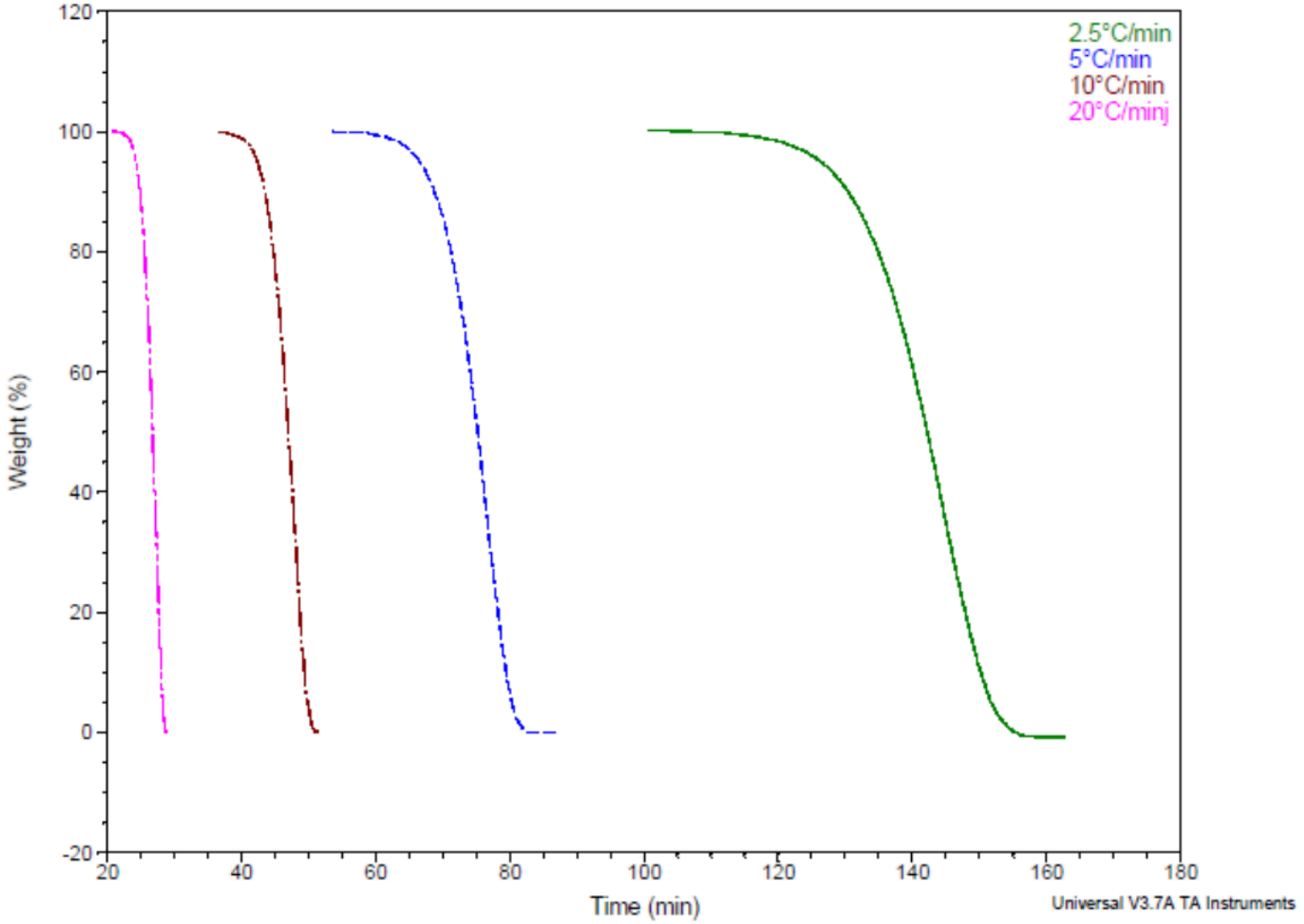
10 mg samples of PTFE, heated at 2.5, 5, 10 and 20 °C/min



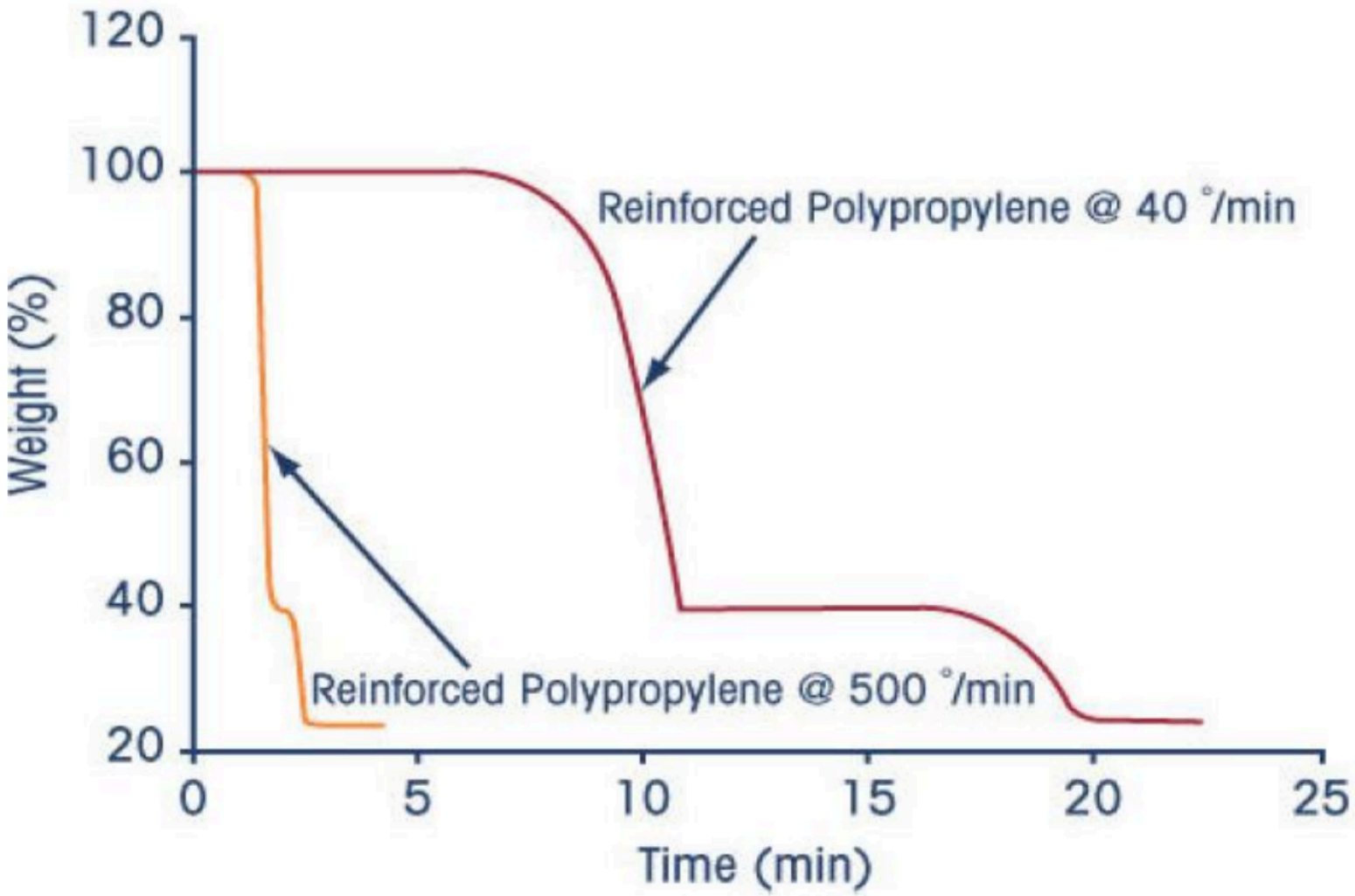
Slow heating ⟷ approach thermal equilibrium

Fast heating ⟷ generates thermal lag

Time to complete degradation



Influence of heating rate on resolution



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- ***Thermal Analysis Dr. S. Anandhan, Asst. Professor, Dept. of Met. And Mat. Engg., NITK***
- ***www.Google.com/image***