THERMOGRAVIMETRIC ANALYSIS(TGA)

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Thermogravimetric analysis(TGA)

- Thermogravimetric analysis or thermal gravimetric analysis (TGA) is a method of thermal analysis in which the mass of a sample is measured over time as the temperature changes.

- This measurement provides information about physical phenomena, such as phase transitions, absorption and desorption as well as chemical phenomena including chemisorptions, thermal decomposition, and solid-gas reactions (e.g., oxidation or reduction)

Three types of thermogravimetry:

1. **Isothermal or static thermogravimetry**: In this technique the sample weight is recorded as function of time at constant temperature.

2. **Quasistatic thermogravimetry:** In this technique the sample is heated to constant weight at each of series of increasing temperatures.

3. **Dynamic thermogravimetry:** In this technique the sample is heated in an environment whose temperature is changing in a predetermined manner generally at linear rate. This type is generally used.

Principle of TGA:

- In thermo-gravimetric analysis, the sample is heated in a given environment (air, N2, CO2, He, Ar, etc.) at controlled rate. The change in the weight of the substance is recorded as a function of temperature or time.

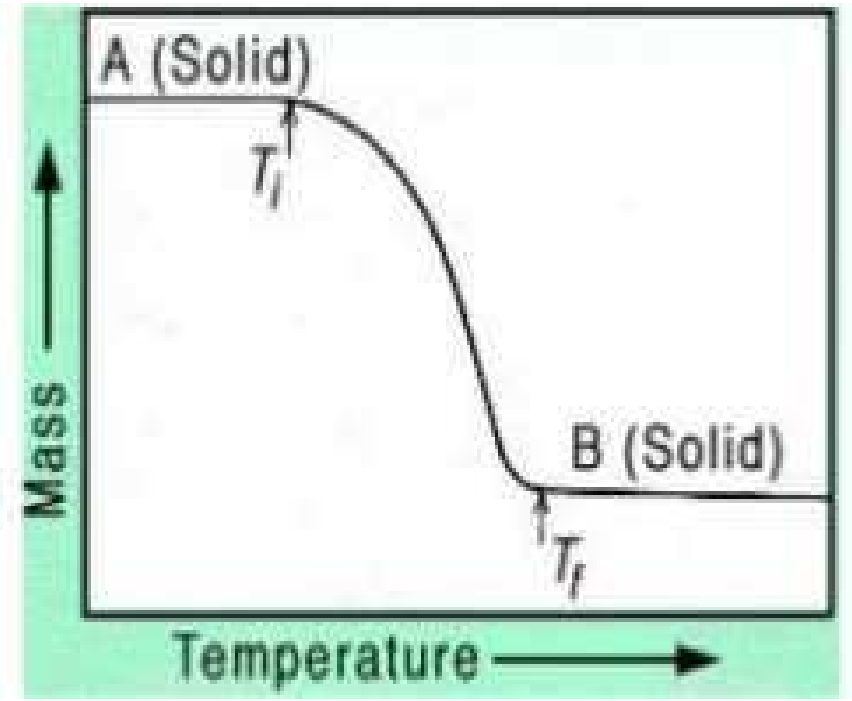
- The temperature is increased at a constant rate for a known initial weight of the substance and the changes in weights are recorded as a function of temperature at different time interval.

- This plot of weight change against temperature is called thermo-gravimetric curve or thermo-gram, this is the basic principle of TGA.

TGA curve:

- The instrument used for themo-gravimetry is a programmed precision balance for rise in temperature known as Thermo-balance.

- Results are displayed by a plot of mass change versus temperature or time and are known as Thermogravimetric curves or TG curves.



TGA curve:

- TG curves are normally plotted with the mass change (D_m) in percentage on the y-axis and temperature (T) or time (t) on the x-axis.

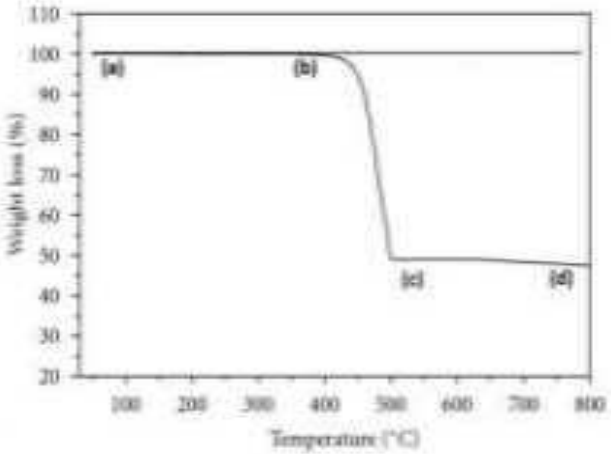
- There are two temperatures in the reaction, Ti(procedural decomposition temp.) and Tf(final temp.) representing the lowest temperature at which the onset of a mass change is seen and the lowest temperature at which the process has been completed respectively.

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

TGA curve of $AgNO_3$:

Example: TGA Curve for AgNO3

- The horizontal portion of the curve indicates that, there is no change in weight (AB & CD) and the portion BC indicates that there is weight change.
- The weight of the substance (AgNO3) remains constant upto a temperature of 473°C indicating that AgNO3 is thermally stable upto a temperature of 473°C.

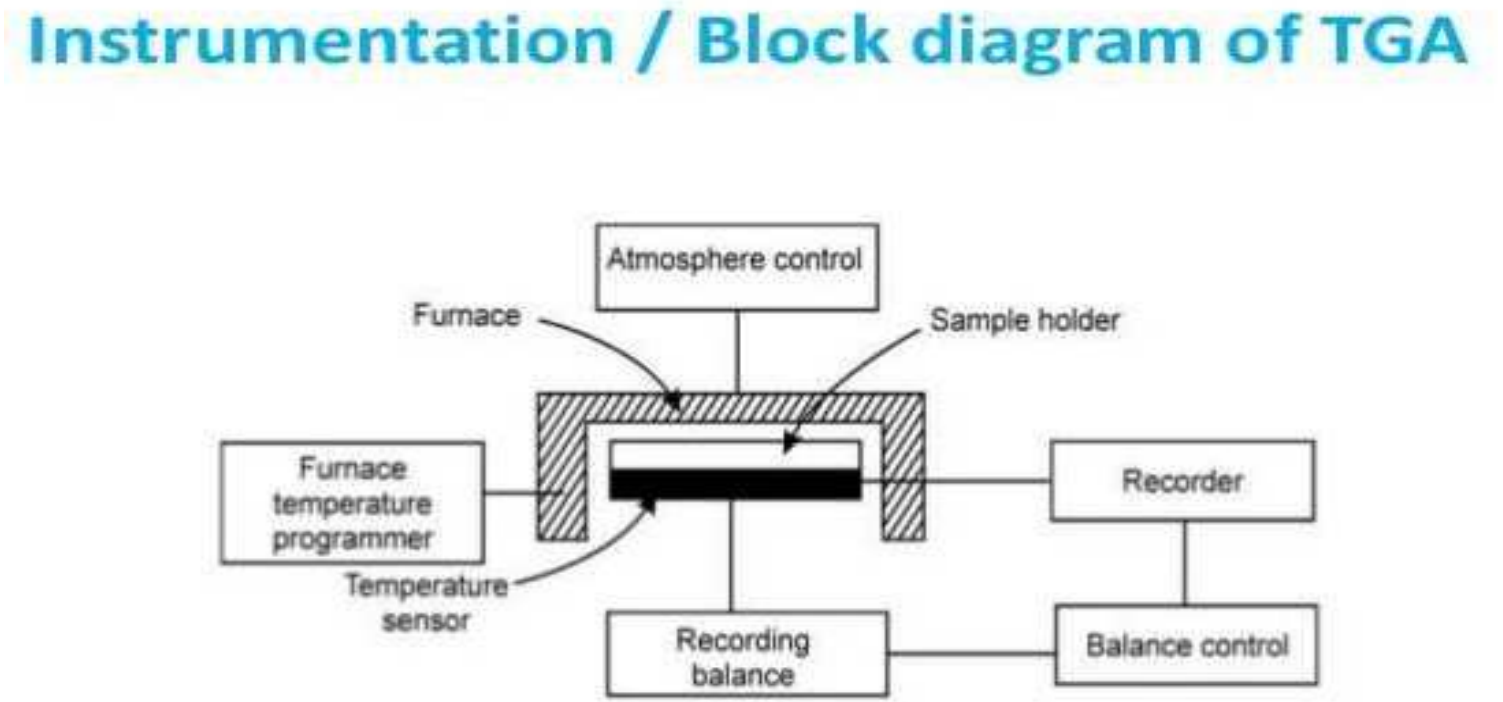


The diagram indicates the TGA curve for $AgNO_3$.

$$AgNO_3 \rightarrow Ag + NO_2 + O_2$$

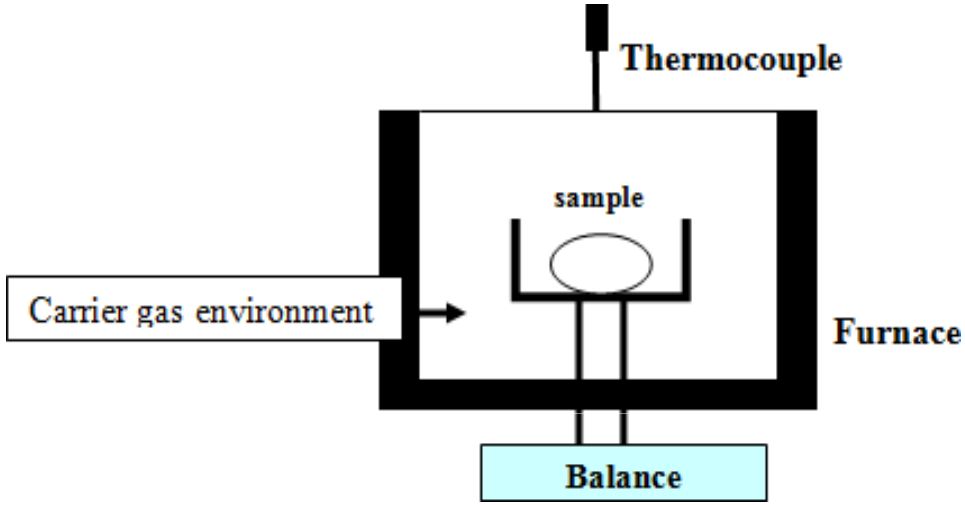
- At this temperature it starts losing its weight and this indicates that the decomposition starts at this temperature. It decomposes to NO2, O2 and Ag. The loss in weight continues upto 608°C leaving metallic silver as the stable residue. Beyond this temperature the weight of the sample remains constant (CD).

Instrumentation of TGA:



Instrumentation of TGA:

- Recording balance
- Sample holder
- Furnace



- Temperature programmer /controller (thermocouple)
- Recorder

Recording balance :

A microbalance is used to record a change in mass of sample/ substance.

An ideal microbalance must possess following features:

- It should accurately and reproducibly record the change in mass of sample in ideal ranges of atmospheric conditions and temperatures.

- It should provide electronic signals to record the change in mass using a recorder.

- The electronic signals should provide rapid response to change in mass.

Recording balance :

- It should be stable at high ranges, mechanically and electrically.

- Its operation should be user friendly.

After the sample has been placed on microbalance, it is left for 10-15min to stabilize. Recorder balances are of to types:

I. Deflection-type instruments and

II. Null-type instruments

Recording balance :

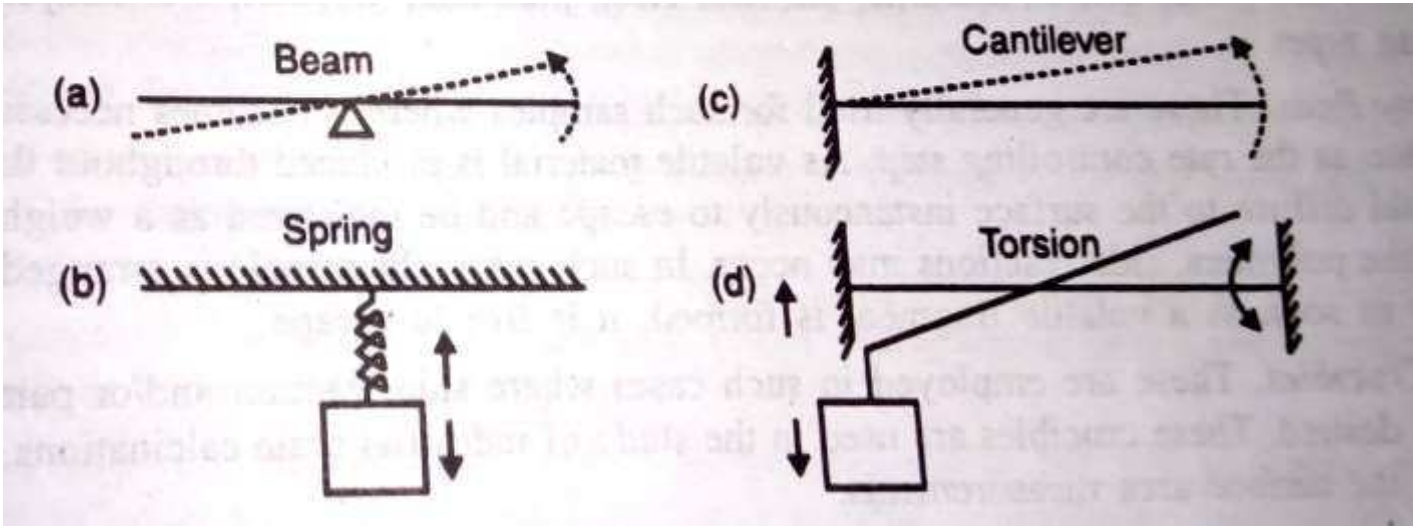
I. Deflection balances :they are following types-

i. Beam type

ii. Helical type

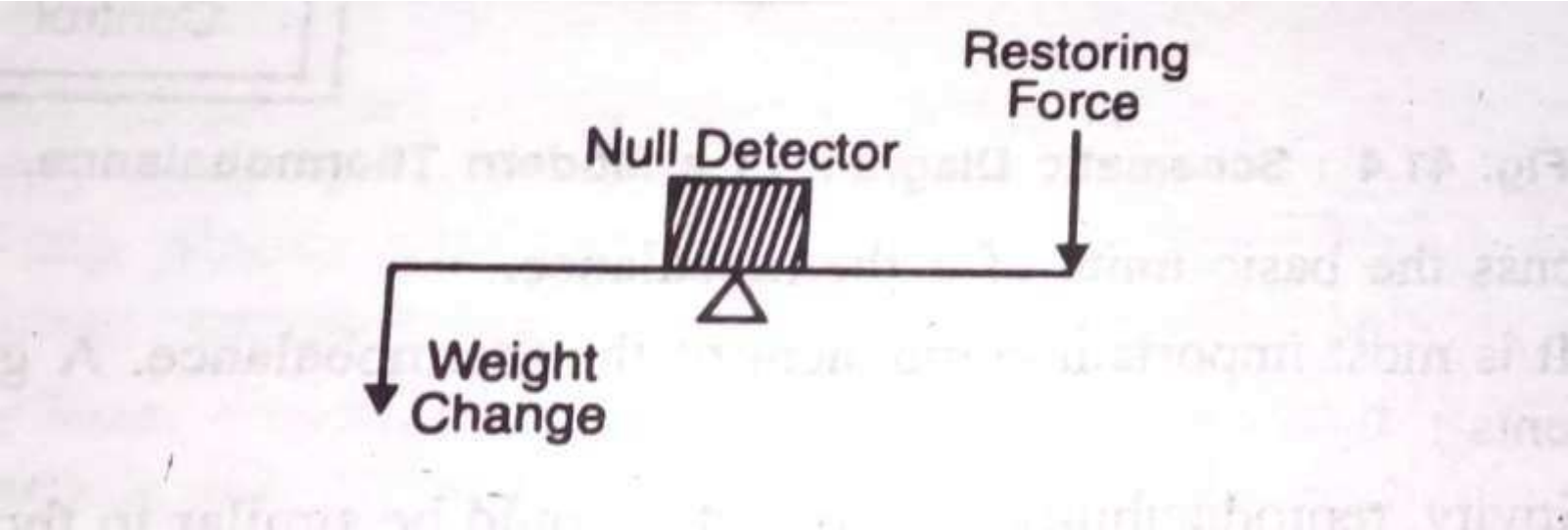
iii. Cantilevered beam

iv. Torsion wire



Recording balance :

- **II.Null point balances**: It consist of a sensor which detects the deviation from the null point and restores the balance to its null points by means of restoring force.



Sample holder :

- The sample to be studied is placed in sample holder or crucible. It is attached to the weighing arm of microbalance.

- There are different varieties of crucibles used. Some differ in shape and size while some differ in materials used.

- They are made up from platinum, aluminum, quartz or alumina and some other materials like graphite, stainless steel, glass etc

Sample holder:

Crucibles:

Crucibles should have temperature at least 100K greater than temperature range of experiment and must transfer heat uniformly to sample. Therefore the shape, thermal conductivity and thermal mass of crucibles are important which depends on the weight and nature of sample and temperature range.

There are different types of crucibles. They are:

1. Shallow pans(used for volatile substances)
2. Deep crucibles (Industrial scale calcination)
3. Loosely covered crucibles (self generated atm. Studies)
4. Retort cups (Boiling point studies)

Types of crucibles:

A) Shallow Pans

B) Deep Crucible

C) Loosely covered crucibles

D)Retort Cups

Fig. Different Types of Sample Holders

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Furnace

- The furnace should be designed in such way that it produces a linear heating range.

- It should have a hot zone which can hold sample and crucible and its temperature corresponds to the temperature of furnace.

- There are different combinations of microbalance and furnace available. The furnace heating coil should be wound in such a way that there is no magnetic interaction between coil and sample or there can cause apparent mass change

Temperature programmer/controller:

- Temperature measurement is done in no. of ways thermocouple is the most common technique.

- The position of the temperature measuring device relative to the sample is very important.

- The major types are:

a . The thermocouple is placed near the sample container and it has no contact with the sample container. This isn't a good arrangement where low-pressure are employed.

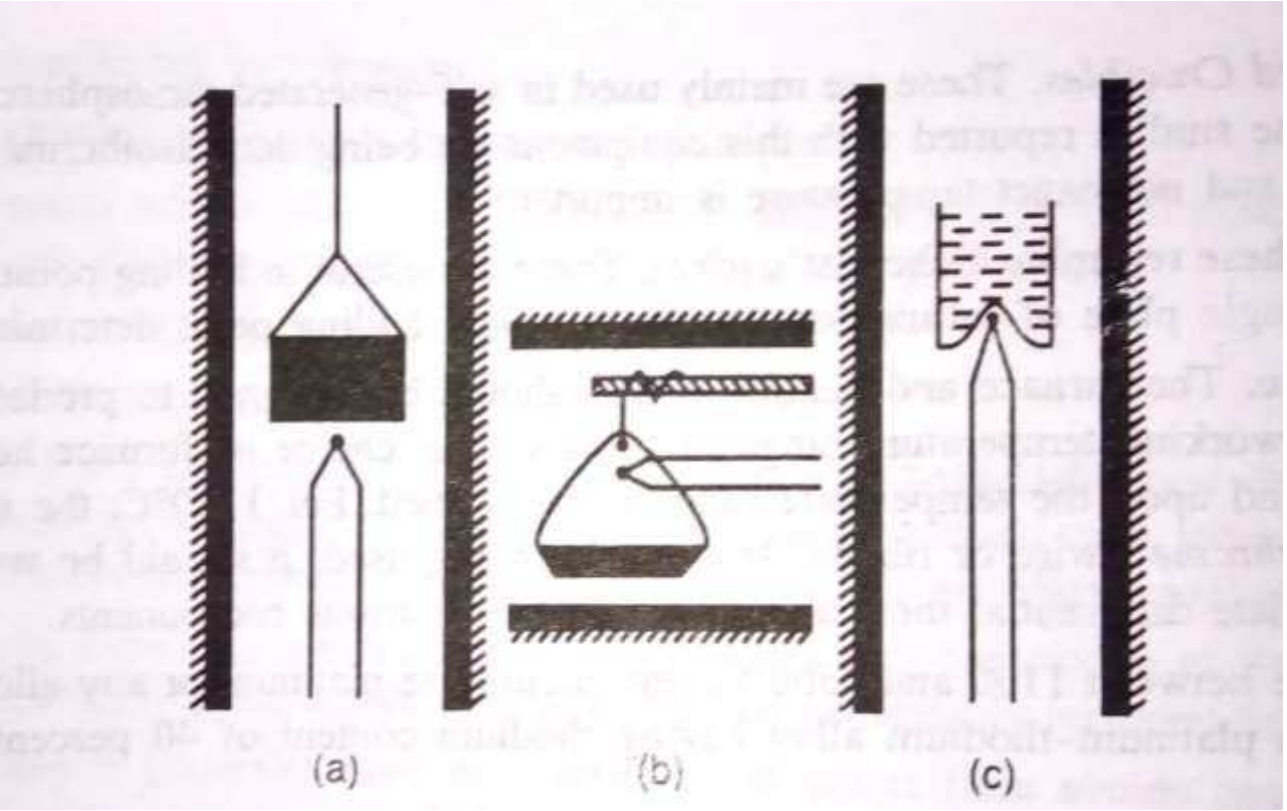
Temperature programmer/controller:

b. The sample is kept inside the sample holder but not in contact with it. This arrangement is better than that of (a) because it responds to small temperature changes.

c . The thermocouple is placed either in contact with sample or with the sample container. This is the best arrangement of sample temperature detection.

Temperature programmer/controller:

Thermocouple in a thermo-balance:



Recorder:

The recording systems are mainly of 2types

1. Time-base potentiometric strip chart recorder.
2. X-Y recorder.

- ✓ In some instruments, light beam galvanometer, photographic paper recorders or one recorder with two or more pens are also used.
- ✓ In the X-Y recorder, we get curves having plot of weights directly against temperatures.
- ✓ However, the percentage mass change against temperature or time would be more useful.

Factors affecting TGA:

Factors affecting the TG curve The factors which may affect the TG curves are classified into two main groups.:

(1) Instrumental factors:

(a) Furnace heating rate

(b) Furnace atmosphere

(2) Sample characteristics includes :

(a) Weight of the sample

(b) Sample particle size

Factors affecting TGA:

1.Instrumental factors :

a. Furnace Heating rate: The temperature at which the compound (or sample) decompose depends upon the heating rate. When the heating rate is high, the decomposition temperature is also high. A heating rate of 3.5°C per minute is usually recommended for reliable and reproducible TGA.

b. Furnace atmosphere: The atmosphere inside the furnace surrounding the sample has a profound effect on the decomposition temperature of the sample. A pure N_2 gas from a cylinder passed through the furnace which provides an inert atmosphere.

Factors affecting TGA:

2.Sample characteristics:

(a) Weight of the sample: A small weight of the sample is recommended using a small weight eliminates the existence of temperature gradient throughout the sample.

(b) Particle size of the sample: The particle size of the sample should be small and uniform. The use of large particle or crystal may result in apparent, very rapid weight loss during heating.

Other factors affecting TGA curve:

- Sample holder
- Heat of reaction
- Compactness of sample
- Previous history of the sample

Advantages of TGA:

- A relatively small set of data is to be treated.
- Continuous recording of weight loss as a function of temperature ensures Equal weightage to examination over the whole range of study.
- As a single sample is analyzed over the whole range of temperature, the variation in the value of the kinetic parameters, if any, will be indicated.

Limitations of TGA:

- The Chemical or physical changes which are not accompanied by the change in mass on heating are not indicated in thermo-gravimetric analysis.

- During TGA, Pure fusion reaction, crystalline transition, glass transition, crystallization and solid state reaction with no volatile product would not be indicated because they provide no change in mass of the specimen.

Applications of TGA:

- From TGA, we can determine the purity and thermal stability of both primary and secondary standard.

- Determination of the composition of complex mixture and decomposition of complex OR composition of complex systems.
- For studying the sublimation behavior of various substances.

- TGA is used to study the kinetics of the reaction rate constant.

Applications of TGA:

- Used in the study of catalyst: The change in the chemical states of the catalyst may be studied by TGA techniques. (Zn-ZnCrO4) Zinc-Zinc chromate is used as the catalyst in the synthesis of methanol.

- Analysis of the dosage form.

- Oxidative stability of materials.

- Estimated lifetime of a product.

Applications of TGA:

- TGA is often used to measure residual solvents and moisture, but can also be used to determine solubility of pharmaceutical materials in solvents.

- The effect of reactive or corrosive atmosphere on materials.

- Moisture and volatiles contents on materials.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