THERMOGRAVIMETRIC ANALYSIS (TGA)

1. The technique of thermogravimetric analysis is concerned with an analysis of the sample weight change curve.
2. Thermogravimetric analysis is carried out in an apparatus called Thermobalance.
3. The technique involves change in weight of a sample under examination as the temperature is increased at a predetermined and preferably at a linear rate.
4. Use of an automatic recording thermobalance, a curve of weight change of the sample vs sample temperature can be obtained directly.

TYPES OF THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric analysis is usually of two types.

(1) Dynamic TGA- In this type of analysis. the sample is subjected to conditions of continuous increase in temperature usually linear with time.

(2) Isothermal or Static TGA : In this type of analysis, the sample is maintained at a constant temperature for a period of time during which any changes in weight are noted.

PRINCIPLE of TGA

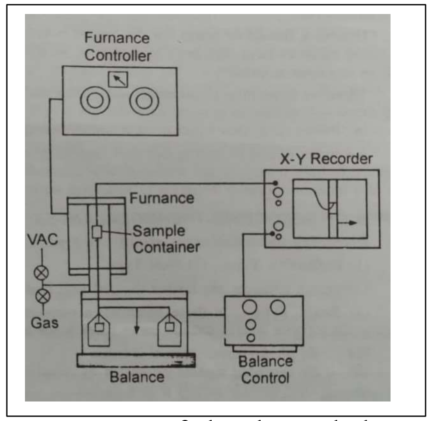
The principle of the technique is as follows

1. A sample is placed in a small pan or crucible within a furnace.
2. The furnace is programmed to heat the sample at a controlled rate (or maintain a constant temperature).
3. A sensitive balance continuously measures the sample's weight as it's heated.
4. The weight changes are recorded and plotted against temperature or time, generating a TGA curve.

INSTRUMENTATION

1. The principles of TGA are based on the fact that the sample be continuously weighed as it is heated to elevated temperatures.
2. The sample in continuously weighed by an instrument, called a thermobalance.
3. Both manual as well as auto-matic recording balances have been built.
4. A modern thermobalance is illustrated schematically in the figure generally consists the following components.

i) Recording balance
ii) Sample holder
iii)Furnace.
iv) Furnace programmer or controller
v) Recording device.



Recording balance: It is the most important component of the thermobalance. Accuracy, reproducibility, sensitivity, capacity, rugged construction and insensitivity to ambient temperature changes are the most important requirements of an analytical recording balance. The balance should have the following important characteristics.

1. It should be able to respond rapidly to changes in weight.
2. The temperature should be recorded to an accuracy of better than ± 1°C.
3. It should be capable of adjusting the range of weight change.
4. It should cover a wide range of temperature even upto 2000°C or more
5. It should have a high degree of electronic and mechanical stability.
6. The recorded temperature should ideally be the sample temperature.
7. The heating rate should be linear and should be reproducible over the complete temperature range of the instrument.
8. It should be simple to operate and has good sensitivity

Sample holder: Generally sample holders are made up of quartz, alumina, stainless steel, platinum, graphite and alloys.

Sample holders are of different sizes and shapes

Shallow pans are used where it is necessary to eliminate diffusion as a rate controlling step.

Deep crucibles are used in large scale calcinations.

Loosely covered crucibles are used in self generated atmospheric studies

Retort cups are used in in boiling point studies.

Furnace : It operates at maximum temperature upto 2000°C. They are constructed to allow easy access to the sample holder and also to cool down rapidly after the completion of a run.

Furnace control: It must be able to provide a suitable smooth input which maintain either a linear heating programme or fixed temperature.

Control is usually carried out via a thermocouple.

Nichrome winding and Pt-Rh windings have been found to permit a temperature of 1000°C and 1450°C respectively.

Higher temperature can also be obtained by using a graphite tube furnace.

The most common method of measuring temperature is via thermocouple.

Recording device: The weight loss curve can be recorded on a potentiometric strip chart recorder as a function of time. An X-Y recorder is used in which weight loss is recorded as a function of temperature. The choice of recording system, however. depends upon the analyst.

Factors effecting results of TGA

There are two important factors upon which the TGA depends. These are:

(i) Instrumental Factors.

(ii) Sample Characteristics.

(i) Instrumental Factors : Instrumental factors includes Furnace heating rate, recording chart speed, furnace atmosphere, geometry of sample holder, geometry of the furnace, sensitivity of recorder and recording balance and composition of sample container.

For example, the decomposition of polystyrene in an atmosphere of nitrogen. Thus for 10% decomposition of polystyrene, the temperatures are 375°C and 394°C respectively for a heating rate of 1° C and 5° C per minute.

For a reversible reaction, the rate of heating has little or no effect, but it affects the position of intermediate compounds on thermogravimetric curves.

For example, at a heating rate of 2.5°C per minute, the TG curves of nickel sulphate ($NiSO_4$, $7H_2O$) indicate one curve break corresponding to the substance $NiSO_4.1H_2O$, but if nickel sulphate is heated at a heating rate of 0.6°C per minute the TG curve shows various breaks corresponding to $NiSO_4$, $6H_2O$, $NiSO_4$, $4H_2O$, $NiSO_4$, $2H_2O$ and $NiSO_4.1H_2O$.

Furnace atmosphere also influences the TG Curves. For example, decomposition of calcium car bonate takes place at a moch higher temperature if it is carried out in an atmosphere of CO, instead of N_2.

The function of inert gas in the furnace is to remove the gaseous products liberated during thermogravimetric analysis in reactions or to stop the reaction (c) from taking place.

In thermogravimetric analysis, there are three common furnace atmospheres. These are static air (air from air is passed through the furnace), dynamic air (compressed air is allowed to flow through the furnace at a constant and measured rate of flow) and inert atmosphere (where oxygen free nitrogen gas is used as an inert atmosphere in the furnace)

For example, in the decomposition of $CaCO_3$ in CO_2, atmosphere, the geometry of the container has no effect on the TG curve because the gas evolved in the decomposition of $CaCO_3$, is also CO_2, which is also present in the furnace atmosphere.

(ii) Sample Characteristics- The important characteristics of the sample, which affect the TG curve or weight loss curve are the amount of sample, solubility of evolved gases in the sample, sample particle size, heat of decomposition of the reaction, sample packing, nature of the sample and thermal conductivity of the sample.

A deviation from linearity with the rise in temperature takes place especially in fast exothermic reaction, if a large sample is used. Liberation of CO during the decomposition of calcium oxalate to calcium carbonate is an example of this type.

$$CaC_2O_4 \longrightarrow CaCO_3 + CO$$

$$CaCO_3 \longrightarrow CaO + CO_2$$

The presence of intermediate compounds can best be detected by making use of small samples in preference to large ones.

For example, 1800 mg of CuSO4.5H,O, when studied thermogravimetrically. does not indicate the plateau corresponding to CuSO4 $3H_2O$, but a plateau corresponding to this inter mediate compound appears in the TG curve when 0.426 mg of CuSO, SH_2O sample is employed.

The rate of reaction and hence the shape of TG curve is altered by using samples of different particle size. The decomposition takes place much earlier and at comparatively low temperature with samples having particle size of smaller dimension. Decomposition temperature has been found to decrease with a decrease in sample particle size. A decrease in particle size also causes a decrease in temperature at which complete decomposition takes place.

Sample packing in the sample holder also affects the TG curves. A compressed sample decomposes at higher temperature than a loose sample.

Heat of decomposition of the reaction has also been found to affect the TG curves. Heat of decomposition has been found to change the difference between sample temperature and furnace temperature. If the decomposition is exothermic, the sample temperature leads the furnace temperature, but if the decomposition is endothermic, the sample temperature lags behind the furnace temperature.

The method of preparation of the sample may sometimes affect the shape of the TG curve. For example, magnesium hydroxide is naturally occurring and can also be prepared by precipitation method, It has been found that $Mg(OH)_2$ obtained by both these sources have different temperatures of decomposition when studied thermogravimetrically. This study indicates that source of the method of formation of the sample should be ascertained before going for thermogravimetric analysis.

Applications of TGA

Calcium oxalate monohydrate ($CaC_2O_4.H_2O$). It undergoes 3 specific weight losses that are separated by enough temperature to easily identify each of the 3 decomposition products, as shown by the chemical reactions below:

$$CaC_2O_4.H_2O\ (s)$$

$$\Delta \rightarrow CaC_2O_4\ (s) + H_2O\ (g)\ (1)$$

$$\Delta \rightarrow CaCO_3\ (s) + CO\ (g)\ (2)$$

$$\Delta \rightarrow CaO\ s + CO_2\ (g)\ (3)$$

Each of these reactions has a decomposition byproduct of water, carbon monoxide and carbon dioxide, respectively. Figure 1 displays the TGA data of the calcium oxalate sample. Each of the 3 plateaus in the graph represent the point at which the decomposition process is complete. The water (1) has been removed at approximately 200 °C. Each of the 3 decompositions has a corresponding weight loss associated as shown in Table 1. Based on stoichiometry, a theoretical weight % loss can be calculated for each of the 3 different reactions. Table 1 compares the theoretical values to that of the measured values and a very good agreement is shown.

Reaction	Theorhetical Stociometric Weight Loss (%)	Measured Weight Loss (%)
1	12.3	12.34
2	19.2	18.70
3	30.1	30.09

Table 1. Theoretical vs Measured Weight Loss (%) for Calcium Oxalate in TGA

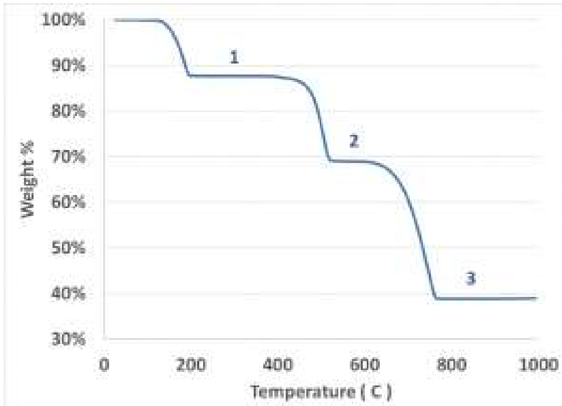


Figure 1. TGA Data for Calcium Oxalate.

Another common method to display TGA data is shown in Figure 2 which overlays the 1st derivative of the Weight % curve. The peaks of the derivative curve represent the point of largest rate of change in the Weight % curve and are also the inflection points. Each of the 3 decompositions of the Calcium Oxalate has a corresponding inflection point as shown in figure 2. Displaying the data in this manner makes it easier to decipher the temperature of greatest mass loss in the sample.

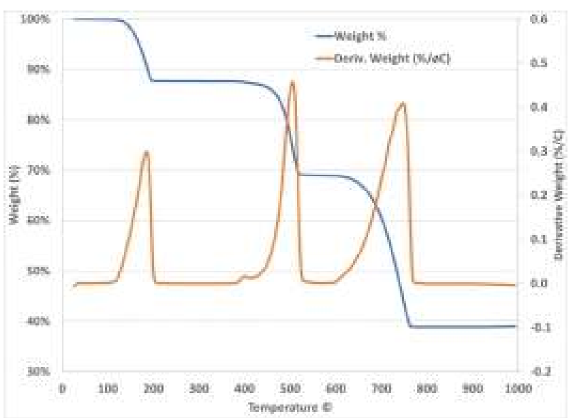


Figure 2. TGA data of Weight Loss % and Derivative Weight Loss for Calcium Oxalate.