Thermal methods

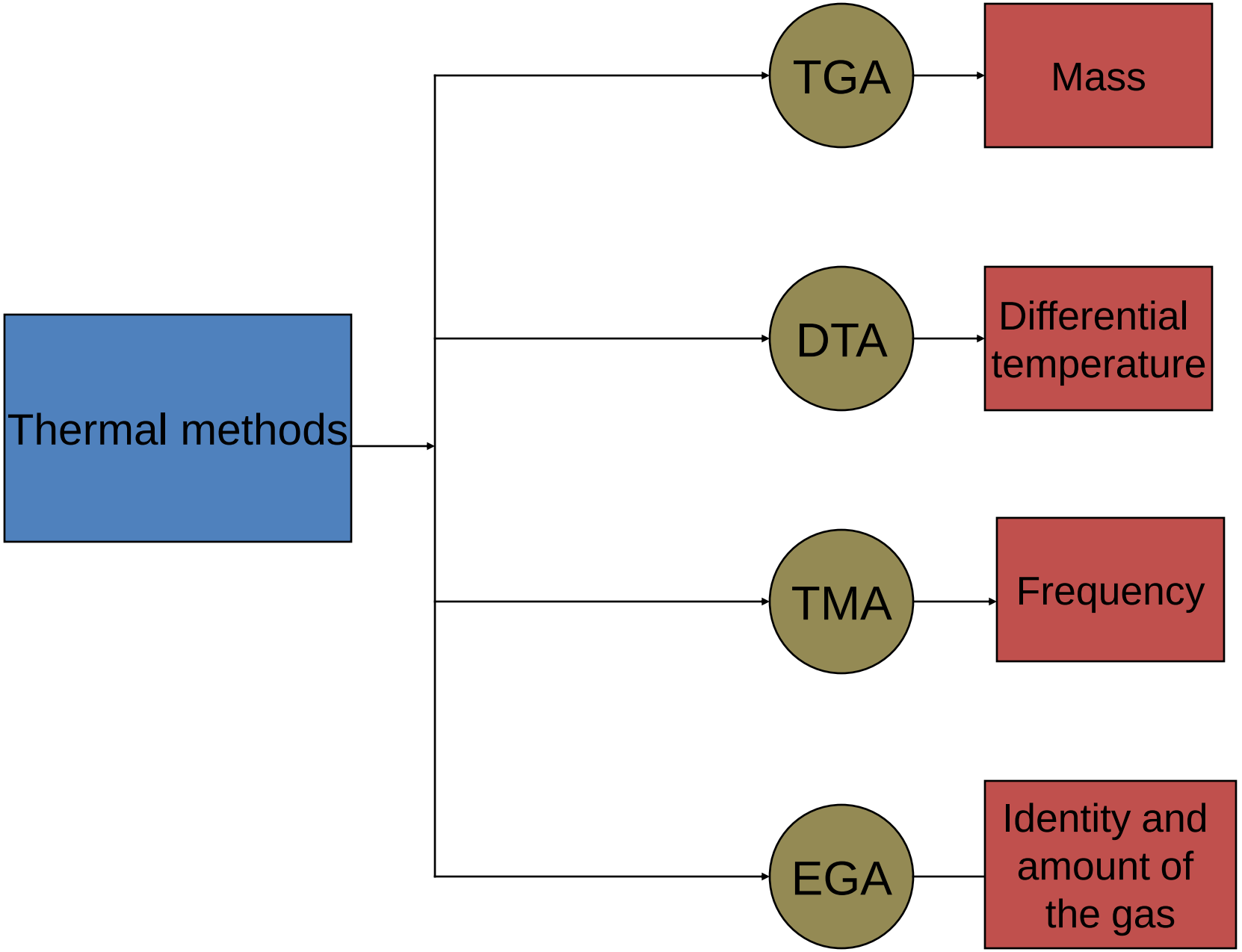
P A Sathe
Ramnarain Ruia College, Mumbai

Thermal methods:

- Thermal analysis is a group of methods in which any physical property of the analyte is measured as a function of temperature when the analyte is subjected to continuous temperature programming.

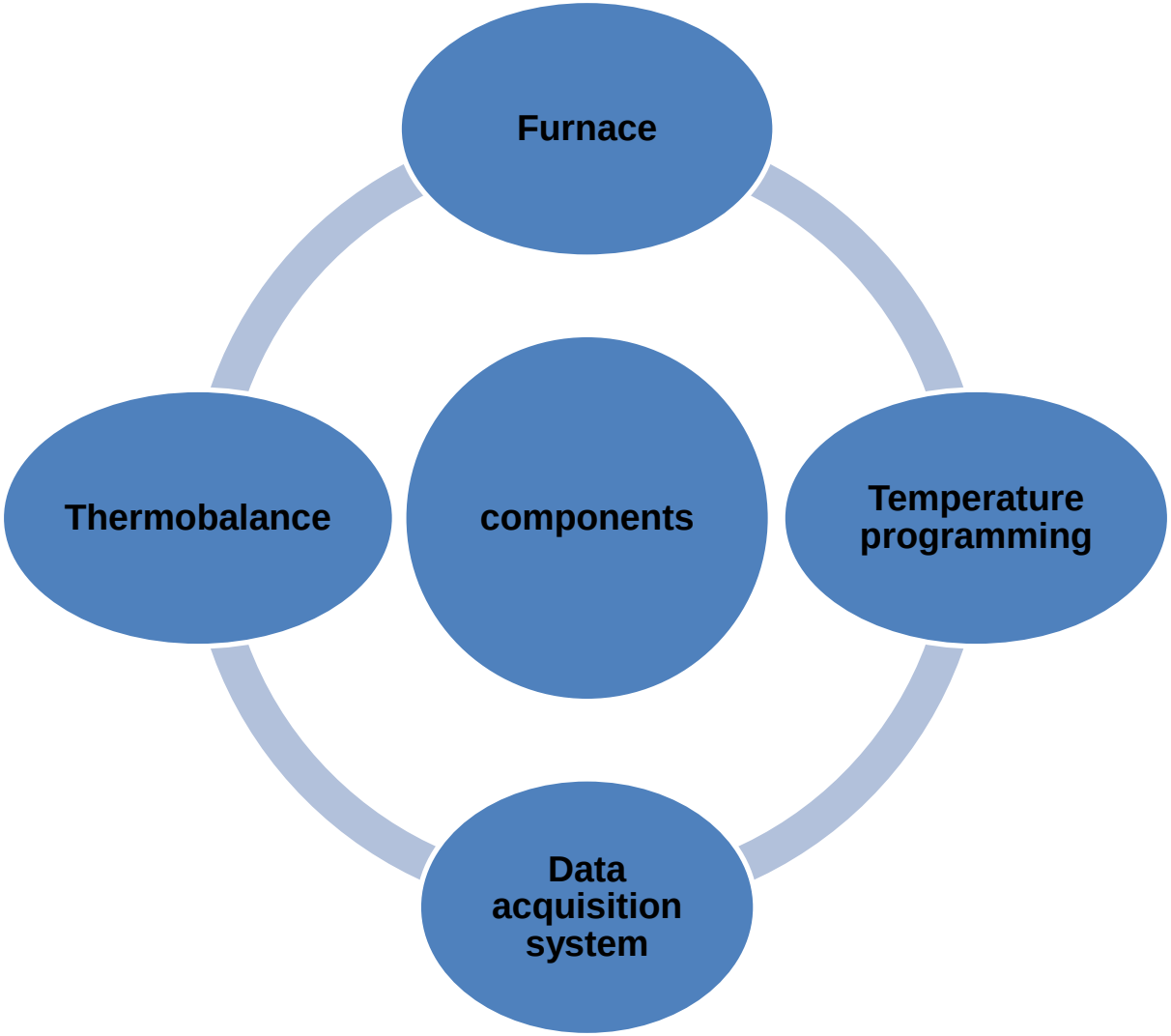
- Methods involve measurement of a single parameter.Technique is a subsequently developed modification of a pre-existing method.

- Applications of the thermal analysis ranging from polymers to earth science.


Thermal methods
TGA
Mass
DTA
Differential temperature
TMA
Frequency
EGA
Identity and amount of the gas

Thermogravimetry:

- It involves continuous measurement of the mass of the analyte as a function of temperature as the analyte is being heated at a programmed rate.
- The resulting plot is known as the thermogram.
- The mass will change if and only if the analyte reacts to produce a gas as a product.
- Otherwise the physical or chemical changes changes or chemical changes that do not involve consumption or liberation of a gas cannot be detectd.


Furnace
Thermobalance
components
Temperature programming
Data acquisition system

Thermogavimetry:

- Thermobalance
  - Null point balance
  - Deviation of the null position detected
  - The balance is restored to the original position

Thermogravimetry:

- Thermobalance
  - Different methods used for the restoration of the original position
  - Optical method
  - Electronic methods

Thermogravimetry:

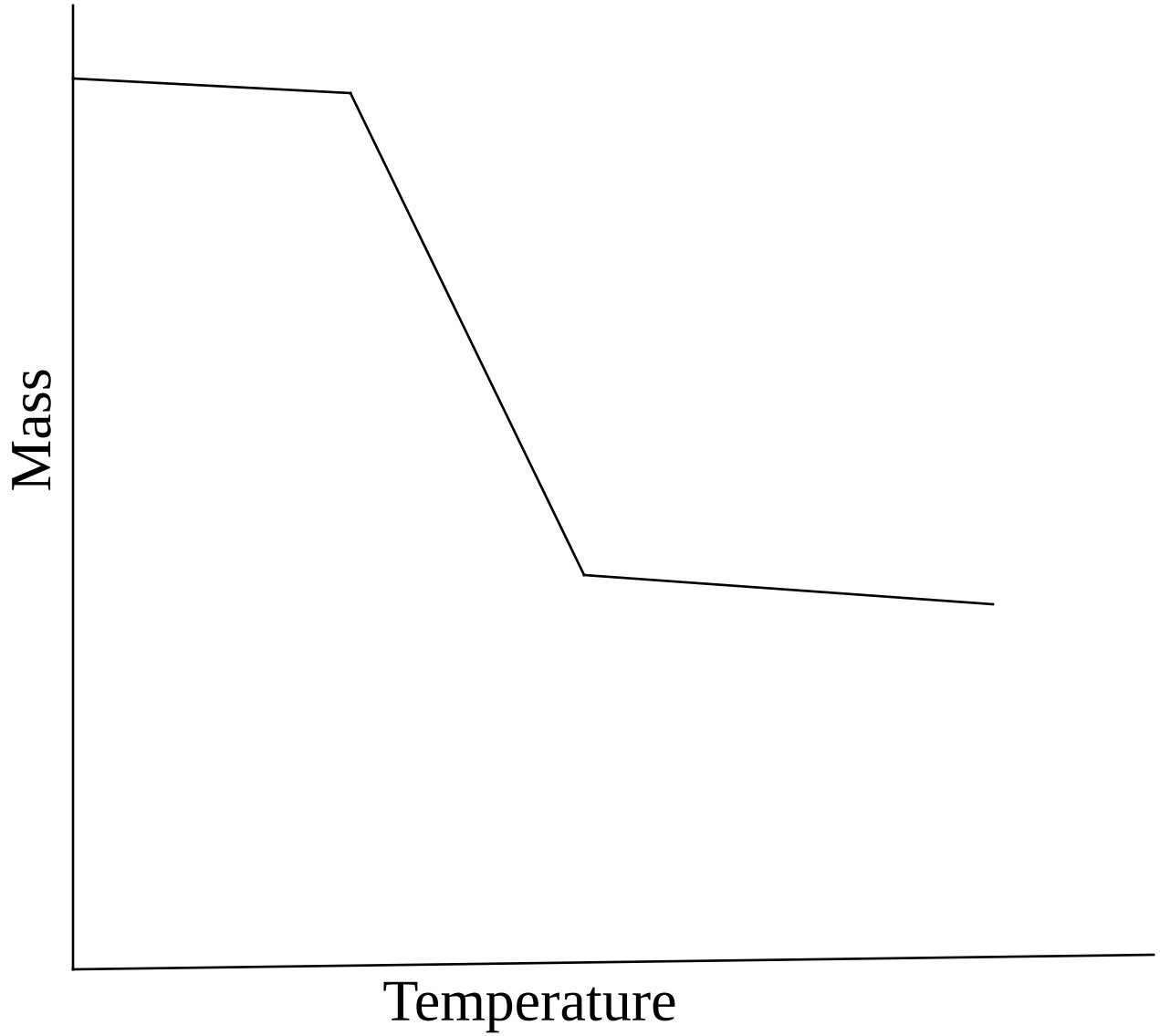
- Thermobalance
  - Circulation of the flow of the gas to remove the liberated gases in the reaction as well as to provide different types of environment to the sample.
  - Small sized samples to minimize the temperature gradients across the sample.

Thermogravimetry:

- Furnace
  - Temperature of about 1600^0 c
  - Small hot zone
  - Reproducibility of temperature
  - Design of the balance will decide the position of the furnace.

Thermogravimetry:

- Furnace
  - Temperature measurement with thermocouple
  - Thermocouple should be as close to the sample as possible.
  - Sensitive thermometers are also used.


Mass
Temperature

Thermogravimetry:

- Effect of the environment on the thermogravimetric curve
  - Solid samples are used hence the prehistory must be known
  - X-ray data is used for the same purpose
  - Nature of the surface and the sites available for adsorption

Thermogravimetry:

- The gas flowing on the sample
  - Its nature
  - Its interaction with the material
  - Reactant or the product
  - Ability to change the reaction taking palce.

Thermogravimetry:

- Nature of the sample container
- Geometry i.e. size and shape of the container
- The mass of the sample
- Spreading of the sample in the container

Thermogravimetry:

- The heating rate decides the exact shape of the TG curve.
- For the same sample the change in the rate of heating will produce a change in the slope of the TG curve.
- Derivative TGA could be of better use in the determination of the exact decomposition temperature.

Applications of Thermogravimetry:

- Qualitative
  - Determination of the temperature of decomposition possible if and only if the mass changes in the process.
  - Stability range for the sample.
  - Identification of the type of the reaction taking place.
  - identification of the product of the reaction from the decomposition temperature

Applications of Thermogravimetry:

- Quantitative
  - Based on the original mass of the sample and the loss in mass and the temperature at which the loss in mass has occurred.
  - Evaluation of the percentage composition of the sample.

Differential Thermal Analysis:

- Both DTA and DSC measure the energy changes occurring in the system.
- The word differential indicate that the measurements are carried out for reference and the sample.
- The difference in the two techniques is in the signal that is received.

Differential Thermal Analysis:

- The sample and the reference material are heated at the same rate
- The difference in the temperature of the sample and the reference is recorded.
- The temperature will change if the sample undergoes a change.

Differential Thermal Analysis:

- If the sample undergoes a physical or a chemical change the process will involve absorption or evolution of heat
- Accordingly, the heat will accumulate at the sample or will be taken from the sample.
- Thus the temperature of the sample will differ from that of the reference.

Differential Thermal Analysis:

- The plot obtained is of difference in temperature of the sample and the reference ΔT vs. the temperature of the reference.

- Temperature programming is used.

Differential Thermal Analysis

- Reference material should be inert and should not undergo decomposition in the temperature range in which heating is carried out.

- Alpha alumina is often used as the reference material.

Differential Thermal Analysis:

- Two thermocouples are placed in direct contact with the reference and the sample.
- The third thermocouple records the temperature of the furnace
- The temperature difference is small and hence needs magnification by a factorof about 1000

Differential Thermal Analysis:

- The area under the curve is proportional to the amount of energy transferred in or out of the sample.

- In each and every case it may not be proportional to the actual amount of energy flowing in and out of the system.

Differential Thermal Analysis:

- Integration of the area under the curve will be required for calculation of the energy flow.

- The temperature difference of about 0.2^0C is the resolution that can be achieved.

Differential Thermal Analysis:

- Any change physical or chemical will involve energy change i.e. the energy flow in and out of the system.
- Any energy flow will lead to change in the temperature of the sample.
- Therefore, the method is more sensitive than all other thermal methods.

Differential Scanning Calorimetry:

- The instrumentation involved in the two cases is identical.
- The method of recording the signal is different.
- In DTA the difference in temperature is recorded as a function of time or temperature.
- In the case of DSC the signal is modified and recorded.

Differential Scanning Calorimetry:

- The two temperatures are equalized by supplyung energy to the system.
- The amount of energy supplied to the system is measured.
- It should correspond to amount of energy utilized by the sample.
- Thus the area under the curve represents the amount of energy supplied to the system i.e. the amount of energy used by the system.