Unit-8

Instrumental Methods of Analysis : Principle and application of Thermal methods of Analysis. (TGA, DTA, DSC), Basic concepts of spectroscopy, Lambert and Beers law, Absorption and Emission spectroscopy Different spectroscopic Techniques (UV-Visible and IR spectroscopy) elementary discussion on Flame photometry.

Analytical chemistry deals with the qualitative and quantitative methods of analysis of compound or molecule in precise and accurate way.Some analytical methods are

PNMR

ESR

Electron diffraction

X-ray diffraction

Mass spectroscopy

UV-Visible and IR spectroscopy,etc

Thermal methods of Analysis

An instrumental technique is regarded as a thermal analysis method ,if the physical parameters are taken as a function of temperature or time.

Some thermal methods are

TGA

DTA

DSC

Thermogravimetric Analysis

1. Introduction
2. Recording of result
3. Information from TG curve
4. Factors affecting TG Curve
5. Instrumentation
6. Applications

TGA

1 Introduction-It is a technique where weight of the substance ,in an enviroment ,heated or cooled at a controlled rate is recorded as a function of time or temperature.

a)Isothermal or static –Sample weight is recorded as a function of time at constant temperature.

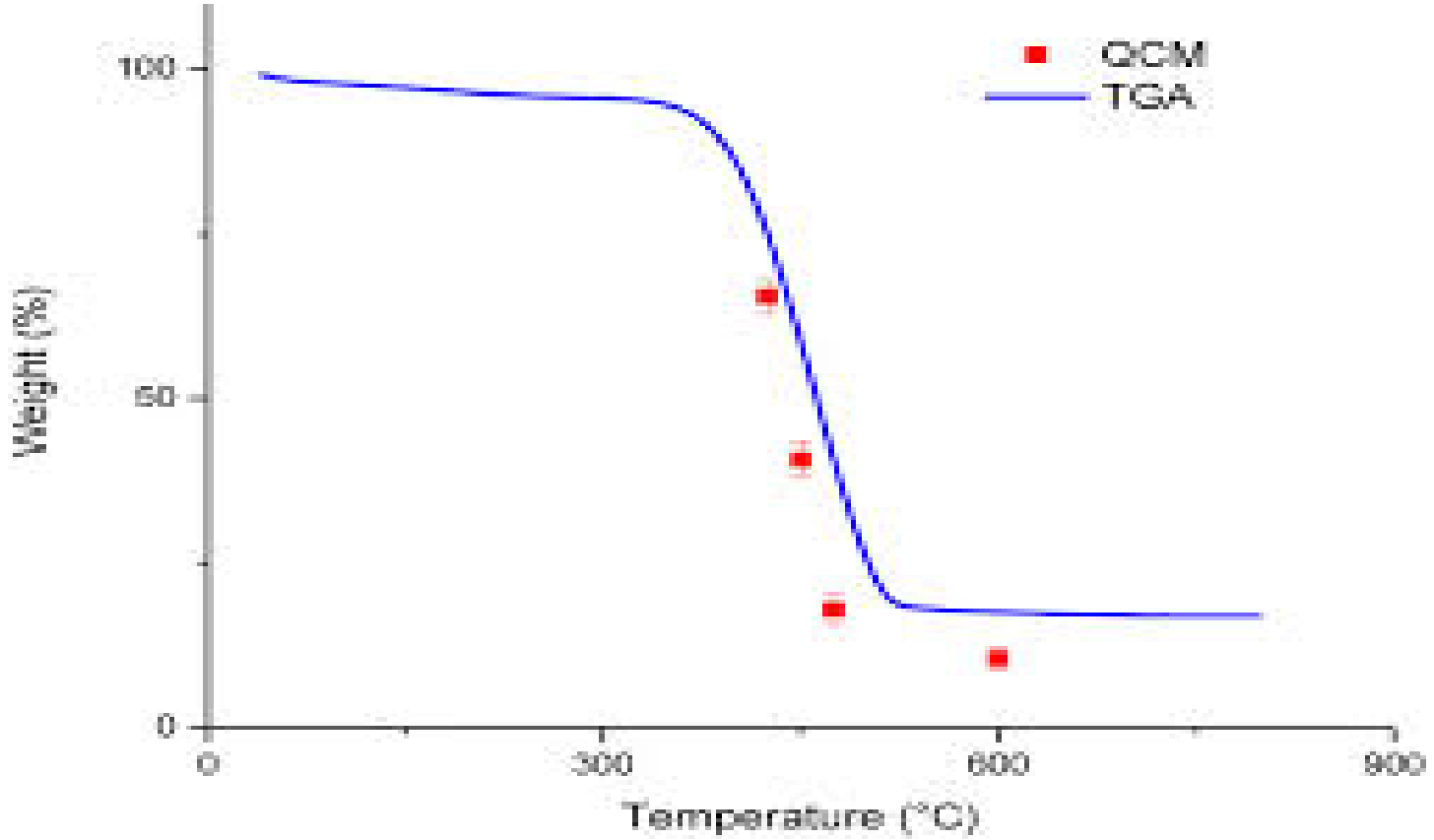
b)Dynamic TGA-Sample is heated in an environment ,whose temperature is changing in a predetermined manner,generally at linear rate.

2 . Recording of result

It is a precision balance for linear rise of temperature and known as thermobalance.

Result of thermobalance-Result of thermobalance are represented by plot of weight change v/s temp.or time,which is known as TG curve.

Weight should plotted on Y-axis,and temp.or time on X-axis,increasing from left to right.


QCM
TGA
100
50
0
Weight (%)
0
300
600
900
Temperature (°C)

3 .Information from TG curve

- Horizontal portion shows no weight loss, or thermal stability of the compound.
- Slanting portion shows, the weight lost by heating a sample to a given temperature. By this information inorganic chemist can determine the composition of a compound and reaction involved in this decomposition.

Factors affecting TG Curve

Instrumental factors

Heating rate

1. If the sample is heated with fast heating rate ,the temperature of decomposition will be higher than the obtained at slower heating rate.

Example-Polystyrene 1^{o} C heating rate 375 ^{o}C Decomposition Temp.

While 5 ^{o} C heating rate 394. 5 ^{o} C Decomposition Temp.

2.Heating rate also affect the position of intermediate

Example $NiSO_{4.}\ 7H_2O$ 2.5 ^{o} C /min one break is observed

0-6 ^{o} C /min Four breaks are observed

2. Effect of furnace atmosphere
3. Sample holder

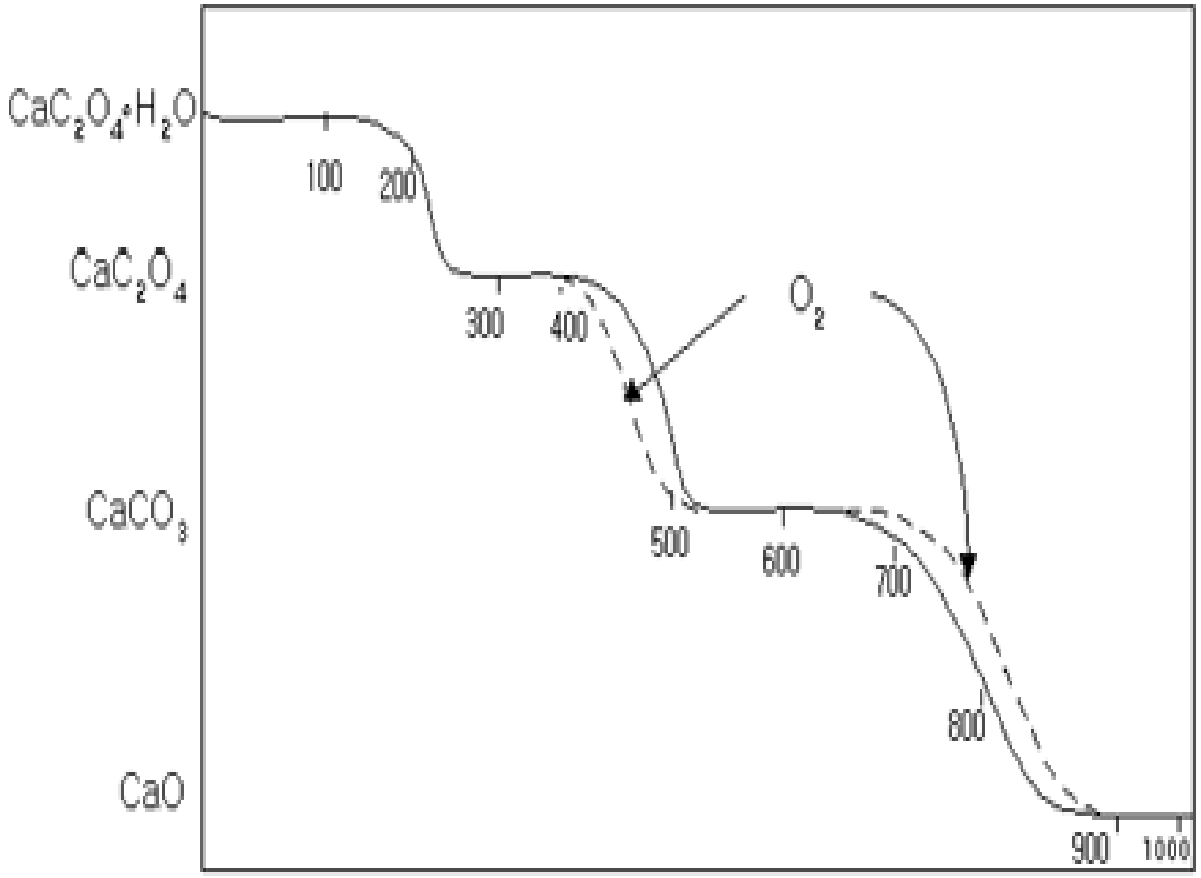
- Characterstics of sample
- Weight of sample

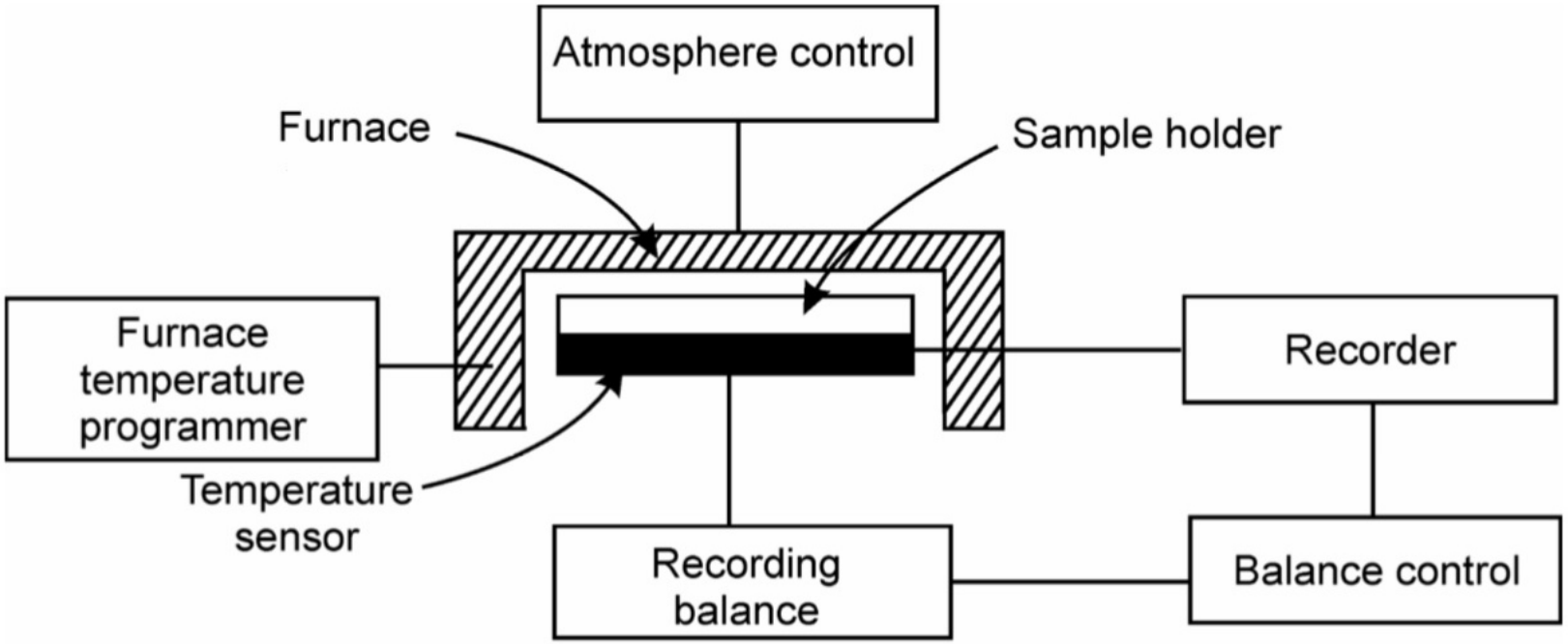
In order to predict the intermediate compounds smaller sample is preferred.

Example $CuSO_4.5H_2O$ 18 mg sample –no intermediate position is observed

While 0-426 mg sample one intermediate position of CuSO4.3H2O is observed.

- Particle size of sample
- Heat of reaction
- Compactness of sample
- Previous history of sample


$CaC_2O_4 \cdot H_2O$
CaC_2O_4
$CaCO_3$
CaO
100
200
300
400
500
600
700
800
900
1000
O_2


Atmosphere control
Furnace
Sample holder
Furnace temperature programmer
Recorder
Temperature sensor
Recording balance
Balance control

Applications

- Automatic thermogravimetric analysis.
- Evaluation of gravimetric precipitate.
- Evaluation of suitable standards.
- Testing of purity of samples.
- Curie point determination.
- In study of organic compounds.
- In study of polymers.
- In study of building material and oxide mixture in glass technology.

Differential Thermal Analysis

Principle: This technique involve the recording of difference in temperature between substance and reference material against time or temperature ,as the two specimens are subjected to identical temperature change in an environment heated or cooled at the controlled rate.

Recording of result: DTA thermo gram consist of record of difference in sample and reference temperature plotted as a function of Time, or sample temperature or reference temperature or furnace temperature.

Information from DTA curve:

1)There are exothermic and endothermic peaks and shape and size of these peaks may furnish good information about the nature of test sample.

2)In most of the cases physical changes give endothermic while chemical changes gives exothermic peaks.

3)Generally sharp endothermic peaks gives good idea about crystallinity and fusion process,while broad endothermic peaks signify deh ydration reaction.

4) The DTA curve would be parallel to the temperature axis till the sample undergoes any physical or chemical change of state.

Instrumentation

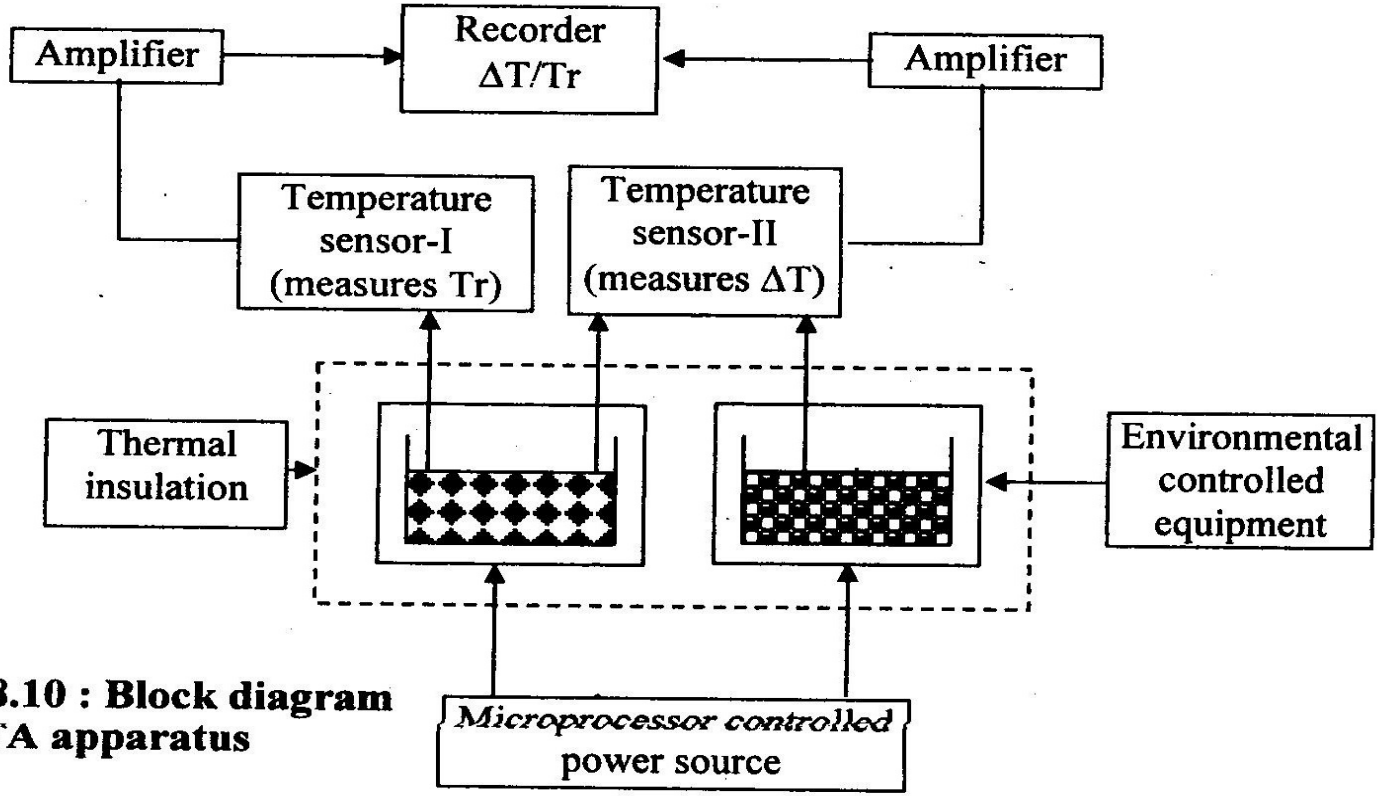


Fig. 8.10 : Block diagram of DTA apparatus

Application

Applications in

1)Physical Chemistry

Generation of phase diagram and study of phase transitions

In determination of heat of reaction.

In specific heat determination.

In determination of thermal diffusitivity.

2)Analytical Chemistry

Identification of substance

Identification of products

Melting point and boiling determination and study of effect of pressure on it.

Quantitative analysis

Quality control

3)Inorganic Chemistry: To study thermal stability of inorganic compounds and complexes

4)Organic Chemistry

Qualitative analysis

For identification and purity determination for oils fats and pharmaceutical substances.

Differential scanning calorimetry(DSC)

Principle:In this technique the heat energy is supplied at the varying rate to the sample or reference so as to keep their temperature equal and this heat energy is recorded as a function of temperature or time when both substance and reference material are heated or cooled at a predetermined rate.(approx.10degree celcius per minute)alternatively

It is a thermal method where energy necessary to establish zero temperature difference between substance and reference material is recorded as a function of time or temp., when both are heated or cooled at a predetermined rate.

DSC Thermogram

1)The heat supplied to sample is given a “positive sign” while reference material is given a

“negetive sign”

2)The DSC curve is a record of transition temperature on x-axis and dH/dt on y-axis.

3)The DSC thermogram is similar to DTA curve only difference that dH/dt instead of ΔT(of DTA)

)The area under DSC peak is directly be related to enthalpy change occuring.

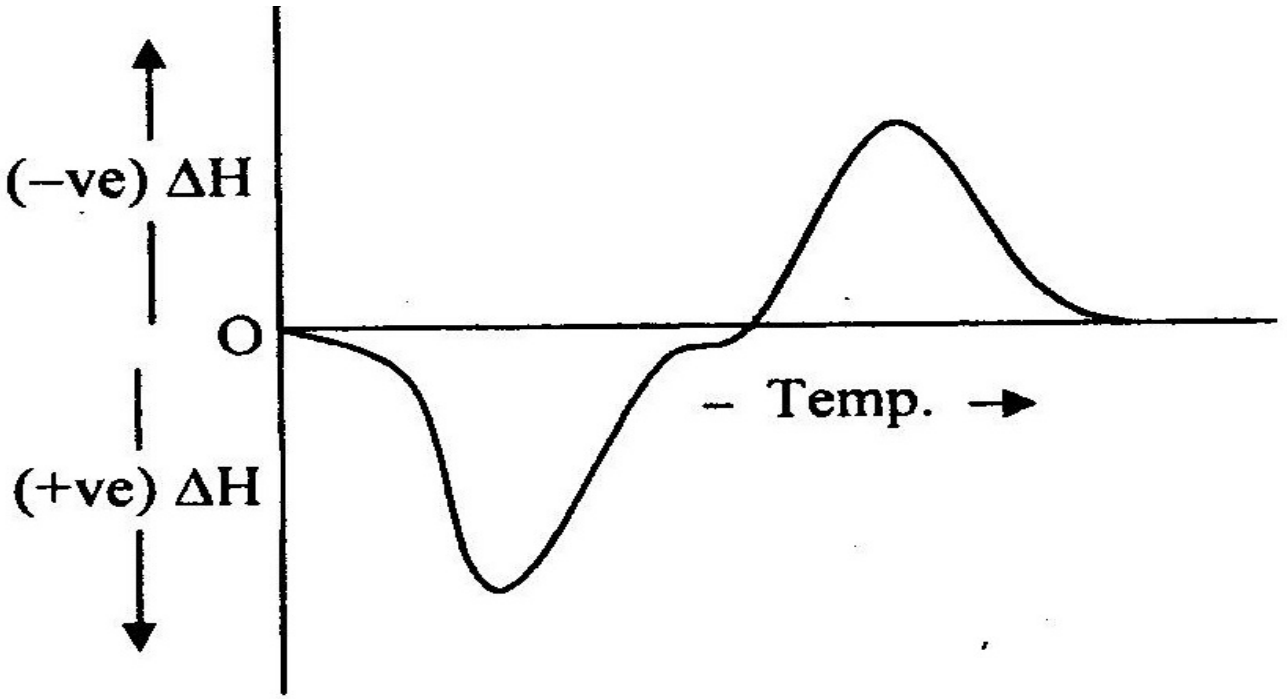


Fig. 8.11. DSC Curve

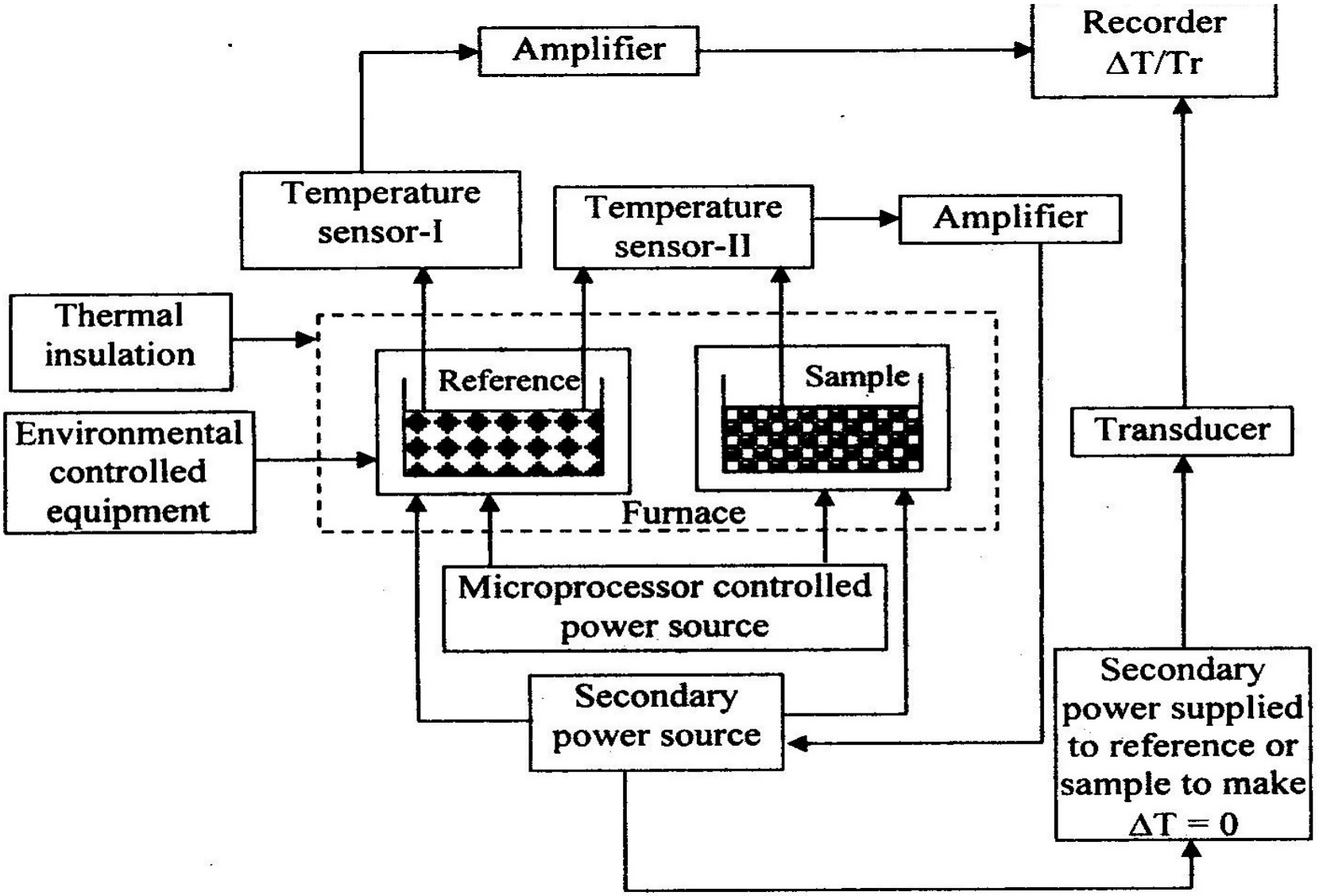


Fig. 8.12 : Block diagram of the DSC apparatus

Applications of DSC

1) Determination of enthalpy of transition.
2) Determination of percentage crystallinity of polymeric material.
3) Determination of purity of drug samples .