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Review Article

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A Review on Differential Thermal Analysis

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Abstract Differential thermal analysis (DTA) is a thermal analysis technique, the term "differential" indicates that the difference in behaviour between the material under study and a supposedly inert reference material is examined. In this way the temperature at which any event either absorbs or releases heat can be found. The record is the thermogram or DTA curve; the temperature difference should be plotted on the ordinate with endothermic reactions downward and temperature or time on the abscissa increasing from left to right. This allows the determination of endothermic and exothermic transitions, e.g. chemical reactions, phase transition temperatures and the study of order-disorder transitions. The results given from the Differential thermal analysis curves depend on the preparation of the sample and on the instrument sensitivity and provide data that have occurred, such as glass transition, crystallization, melting and sublimation. It is a highly sensitive technique to study the thermotropic and chemical properties of a polymeric material.

Keywords Thermal analysis, Analytical Technique, Differential Thermal Analysis, Endothermic and Exothermic Reaction

1. Introduction

Thermal analysis is used to determine thermodynamic properties which are essential for understanding the behaviour of the material under different cooling and heating rates, under inert, oxidation or reduction atmosphere or under different gaseous atmosphere. The thermal analysis embraces a group of techniques in which a physical property of a substance is measured under a controlled temperature program. Differential thermal analysis is basically a modification of the classical procedure of studying phase transformation by the means of time temperature records during uniform heating or cooling of the system. It appears to have been first employed by Le Chatelier in 1887. It did not, however, receive extensive popular attention until after Norton's work which was reported in the Journal of the American Ceramic Society in 1939 [1]. The method of Differential Thermal Analysis, as it is known, become famous as other techniques such as x-ray diffraction, microscopes, etc. as a helpful research and control tool. Its importance is increasing because of the development of equipment refinements and the potential value of the data with the growth of the knowledge of crystal chemistry and thermodynamics of non-metallics.

The adoption of the name for the technique is based on the method of measurement which determines the difference in temperature between the sample and the reference material or furnace by means of a differential thermocouple [2].

Principle

Differential thermal analysis (DTA) is based upon measurement of the difference in temperature between a substance and inert reference material (like glass beads, Al_2O_3, etc.) while the substance and the reference material are subjected to a controlled temperature program. Endothermic or exothermic changes in the sample lead to characteristic deviation in temperature.

DTA is the oldest thermo analytical method. The schematic diagram of DTA apparatus is shown in Figure 1.

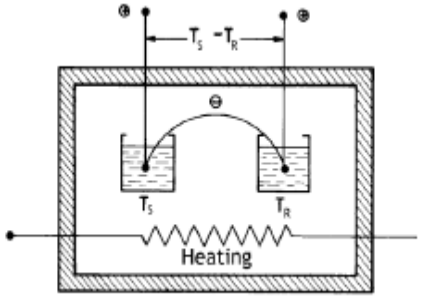

Figure 1: The schematic diagram of DTA

Usually, the temperature process involves heating the sample and reference material in such a way that the temperature of the sample T_S increases linear with time. The difference in temperature ΔT between the sample temperature T_S and reference temperature T_R ($\Delta T = T_S - T_R$) is then monitored and plotted against sample temperature to give a differential thermogram [3].

a) Emissions of heat (exothermic).

b) Absorptions of heat (endothermic) (Figure 1).

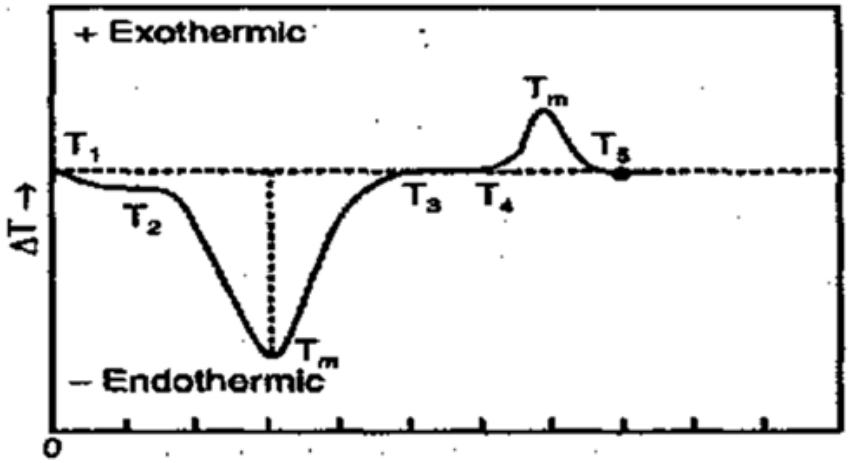

Figure 2: An ideal DTA curve

The DTA curve would parallel to the temperature or time axis till the sample undergoes any physical or chemical changes of state.

However as soon as the sample has reached a temperature of the change of state, the additional heat flux reaching the sample will not increase the sample temperature at the same rate as that of the reference and the differential signal appears as a peak.

Sharp endothermic peaks give information's of changes in crystallinity or fusion processes while the broad endosperms signify dehydration reactions. Physical changes give rise to endothermic curves whereas chemical reactions give rise to exothermic peaks. The Differential thermal analysis allows the detection of every chemical or physical change whether or not it is accompanied by a change in weight [4].

2. Determination of Characteristic Temperature

The sample temperature T_S is increasing with time in a linear fashion if no change in the sample occurs. The temperature of the reference material T_R shows a similar pattern. When an endothermic process occurs, the sample temperature lags behind that of the reference material (pattern a), with an increasing amount of sample this lagging last even longer. When the transformation is over, the sample temperature rises quickly and become equal with that of the reference material. Therefore plotting the DTA signal as a function of the sample temperature, only a little deviation can be observed in the position of the DTA peak (T and T') when the sample mass is changed (pattern e). Plotting the DTA signal as a function of T_R, a significant error in the peak position is observed (pattern e).

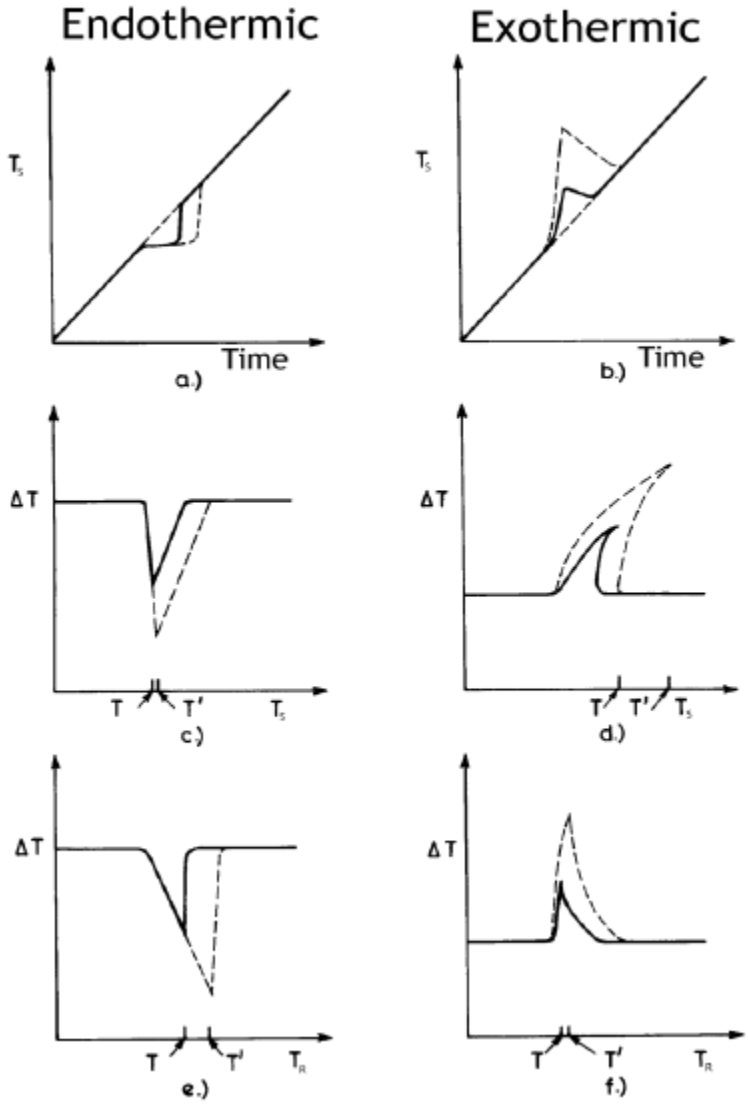

Figure 3: Determination of the temperature characteristic of endothermic and exothermic transformation

In the case of an exothermic transformation, the sample temperature is temporarily higher than that of the reference material. When the transformation is over, the sample cools back to the temperature of the reference material via dissipating heat to the environment [5]. With increase sample mass, the rise of the sample temperature is even higher (pattern b). Plotting the ΔT signal as a function of the sample temperature T_S, a distorted DTA peak and a big difference in peak temperature T and T' are obtained (pattern d). Thus, for an exothermic reaction, the DTA signal shall be plotted against the temperature of the inert material (pattern f). If in the same sample both endothermic and exothermic processes occur, the ΔT signal shall be plotted together with the sample temperature T_S as a function of

time (Figure 4). In this way, the characteristic peak temperature for the endothermic process (T_1) can be obtained by projecting the DTA peak down to the T curve. In the case of an exothermic transformation, the projection is made to the temperature of the inert material obtained by extrapolation [6].

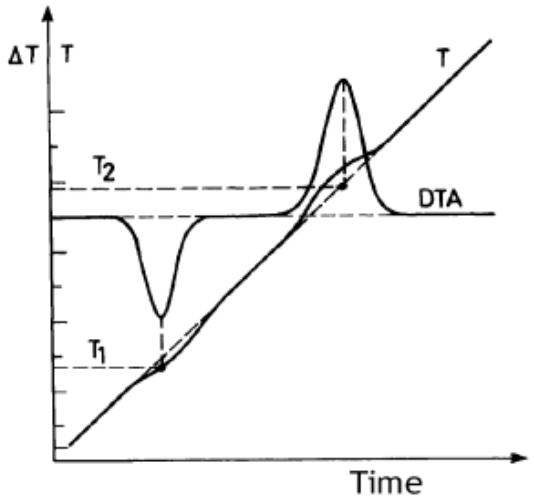

Figure 4: Determination of the characteristic temperature in a sample in which an endothermic and a subsequent exothermic transformation takes place

3. Factors affecting DTA Curve

The DTA curve is affected by a larger number of factors. Majority of these factors are common. However, their special influences on DTA curves will be considered. The various factors affecting the DTA curve are as follows:

3.1 Environmental Factors: The DTA technique is highly sensitive to the gaseous environment around the sample. The reaction of sample with the gaseous atmosphere may also produce extra peaks in the curve. For example

a. Presence of oxygen in the air causes an oxidation reaction which may give rise to an exothermic peak.

b. If we record the DTA of lignite in the dynamic nitrogen atmosphere, it pyrolysis and distils off the volatile matter. However, in the dynamic oxygen atmosphere, the lignite oxidizes, resulting exothermic instead of endothermic peaks.

In DTA studies two types of the gaseous atmosphere are used:

(i) A static gaseous atmosphere.

(ii) A dynamic gaseous atmosphere.

Generally, the peak minimum temperature is shifted to lower temperatures in the dynamic gas technique. However, the shapes of the curve remain similar in the two techniques.

For example: Effect of the introduction of an atmosphere of the evolved gas, on the DTA curve of decomposition of $SrCO_3$. In the DTA curve of this decomposition which is recorded in an oxygen atmosphere, the decomposition peak and the peak due to the rhombic – hexagonal transition of $SrCO_3$ overlap each other. When CO_2 is introduced as a dynamic atmosphere, the transition peak remains at 927 ºC but the decomposition peak ($SrCO_3 = SrO + CO_2$) gets shifted to much higher temperature.

3.2 Instrumental factors:

3.2.1 Sample holder: The material and geometry used in the manufacturing of the sample holder affect the shape, size and resolution of the DTA peaks.

If the sample holder are made from the material of high thermal conductivity (e.g. metals), sharp exothermic peaks but comparatively flat endothermic peaks are obtained. For better resolution, the size of the holders and amount of the sample should be as small as possible.

3.2.2 Furnace Characteristics: The type of winding shows a straight effect on the DTA curve. If the winding used in the furnace is not uniform, the baseline is changed. But in commercial equipment's machine-wound furnaces is used which eliminate this problem.

3.2.3 Differential temperature sensing device: Generally, heats of transitions are much less as compared to the heat of reactions. Therefore, the differential temperatures in the former case are much smaller and their pre-amplification is essential.

If the wires used in temperature sensing devices are much thick, more distortion of the peak heights and the peak temperatures may take place. However, if thinner wires are used, lesser distortion in peak height and peak temperatures may take place.

3.2.4 Thermal regime: The heating rate has a great influence on the DTA curves. If a substance heated at a higher rate, the temperature of decomposition will be higher than that obtained at a slower rate of heating. Generally, heating rates of 10 to 20 ºC per minute are employed. In some cases, even higher heating rates are preferred.

3.2.5 Temperature Programmer controller: Temperature-programmer controller has an important role on the DTA curve, because a constant heating rate is required in DTA. For measuring small differential temperature, one should maintain the highest accuracy, control and precision in temperature measurement.

3.2.6 Recorder: DTA curve is greatly influenced by the type, chart-speed and pen-response of a recorder. As the differential signal lies in the range of several tens to hundreds of microvolts, one should be very careful while selecting the recorder span and is some cases it becomes essential to pre-amplify the signal [7].

3.3 Sample Characteristics

3.3.1 Physical: In quantitative DTA, one makes the assumption that heat capacity remains constant with the progress of the reaction. But this is changing with the progress of the reaction. In order to maintain the heat capacity nearly constant, the usual practice is to mix a small quantity of the sample with an excess amount of an inert material.

The packing density affects the overall thermal conductivity of the sample and hence the heat flow. But it is not possible to get reproducible packing densities and it is never constant.

The effect of particle size is related to the effects of packing density and overall thermal conductivity of the sample. In general, following inferences are drawn from the variation in the size of the particle:

1. Particle size alters the peak area: Decreased with increasing particle size.
2. Particle size also influences the peak temperatures: With an increase in particle size, the peak temperature is shifted to higher values.
3. Particle size also influences the completion temperature: Generally, with decreasing particle size the completion temperature also decreases.

The weight of the sample also influences the peak intensity and temperatures. Both these increase with increasing weight. But it is important to remember that with smaller amounts of the sample the resolution is greatly increased.

In order to maintain the heat capacity nearly constant during heating, the sample is generally mixed with diluents. Generally, diluent affects the temperature, area and even resolution of the DTA peaks.

3.3.2 Chemical: The chemical reactivity of the sample, sample holder material, thermocouple material, the surrounding gaseous environment and added diluents greatly affect the DTA peaks. Therefore, one should make every effort to select these materials as inert chemically as possible with the sample [8].

4. Instrumentation

A large no of different types of instruments are available for DTA studies. However, a typical DTA apparatus is shown in Figure 5. The various component of DTA apparatus are as follows:

(i) **Furnace:** This is a device for heating the sample.

(ii) **Sample holder:** This is used to contain the sample as well as the reference material.

(iii) **Differential temperature detector**: The function of this detector is to measure differential temperature.

(iv) **Furnace temperature programmer:** The main function of this is to increase the temperature of the furnace at a steady rate.

(v) **Recorder:** This is to record the DTA curve.

(vi) **Control equipment:** Used to maintain a suitable atmosphere in the furnace & sample holder [9].

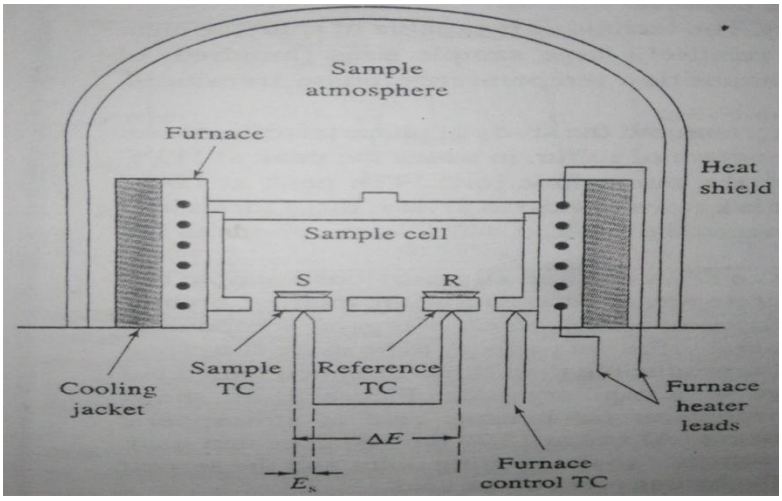

Figure 5: A schematic diagram of a typical DTA apparatus

4.1 Sample holder:

(a) Material: Generally, materials are selected on the basis of low cost, ease of fabrication, inert towards the product and material in the temperature range.

Both metallic, as well as non-metallic materials are employed for fabrication of sample holder. Metallic materials generally include nickel, stainless steel (up to 1000^0C), platinum and its alloy and it gives rise to sharp exotherms and flat endotherms. Non-metallic materials generally include glass, vitreous silica or sintered alumina and it gives rise to sharp endotherms and flat exotherms.

(b) Geometry: the ideal geometry around the thermocouple junctions is spherical. But this poses great problems in the fabrication. Therefore, a cylindrical geometry is used.

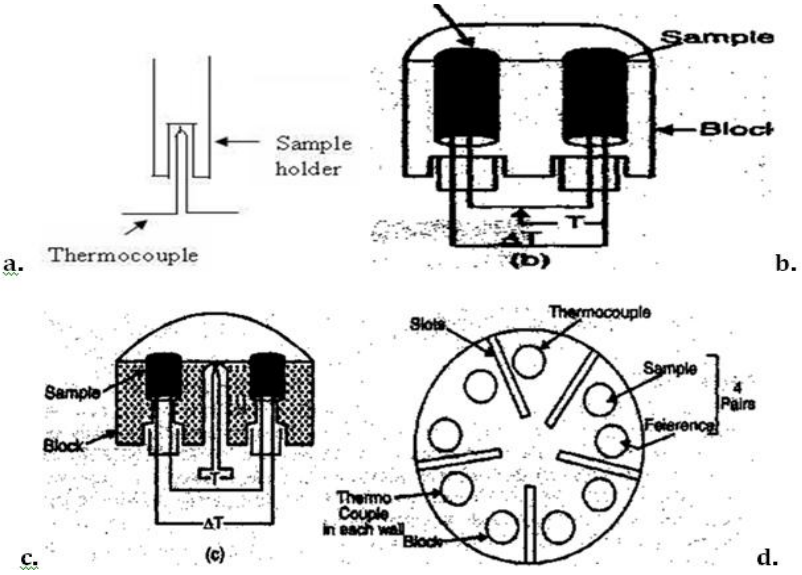

Figure 6: Geometry

4.2 Furnace:

In DTA apparatus, a tubular furnace is preferred, which is constructed with an appropriate material (wire or ribbon) wound on a refractory tube.

The power required to operate the furnace at the maximum temperature can be calculated by the relation between the power demand P in watts, furnace dimensions and the temperature for cylindrical tubular furnace. The relation is as follows:

$$P = 2.729\ Km\ (T1-T2)\ l/\ \log d2/d1$$

Where,

P = Power

L = Length

Km = Thermal conductivity coefficient

d1 = Diameter of heater coil round on the ceramic

d2 = Diameter of furnace cell

T1 & T2 = temperature of heating element & surface temperature of the furnace shell

Table 1: Commonly used material

Material	Maximum Elemental Temperature ^{0}C
1. Nichrome V, Chromel C	1200
2. Kanthal A, Kanthal A-1	1400
3. Silicon carbide	1700
4. Platinum-rhodium alloy	1800
5. Tungsten	2900

4.3 Temperature controller and Recorder:

4.3.1 Temperature control:

The three basic elements are required to control temperature is

(a) Sensor
(b) control element
(c) heater

The rate of heat-input required to match heat loss from the system is govern control element.

A proportional control method is used in DTA; the heat input to the system is progressively reduced as the temperature approaches the desired value.

4.3.2 Temperature programmer:

Thermal apparatus requires a time-dependent temperature cycling of the furnace, In order to produce the desired rate of heating or cooling and to maintain a constant temperature at any desired value, this can be achieved by employing a temperature programmer which transmit a certain time-based instruction to the control unit.

4.3.3 Recorder:

The signals from the sensors arerecorded in which the signal trace is produced on paper or film by ink, heating style, electric writing or optical beam.

The mode of analog recording is two types:

(a) Deflection type: In this type of recorder, the recording pen is moved directlyby the input signal.
(b) Null type: In this type of recorder, the input signal is compared withthe reference or standard signal and difference is amplified and used toadjust the reference signal until it matches the input signal.

4.4 Thermocouple:

In DTA temperature sensor are thermocouples. Selecting the thermocouple as the temperature sensor following points are considered

a. Temperature interval.
b. Thermoelectric coefficient.
c. Chemical compatibility with the sample.
d. Chemical gaseous environment.
e. Availability and cost.

It is made of Chromel P and Alumel wires are used to measure and control the temp upto 1100^0C in air. Above 1100^0C should use thermocouple made from pure platinum and platinum-rhodiumalloy wires [10].

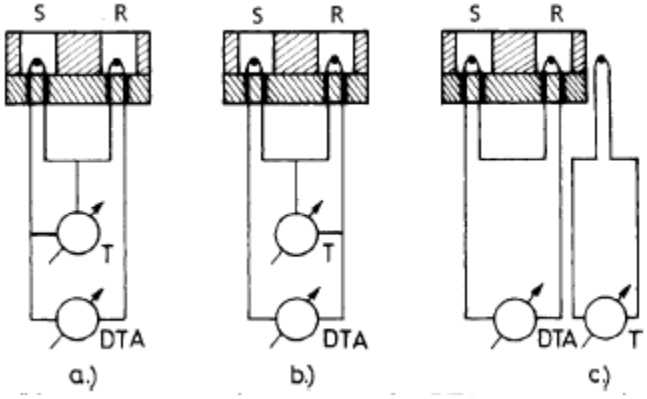

Figure 7: possible ways to measure the temperature in DTA apparatus. a) in the sample, b) in the inert material, c) inside the furnace

5. Application of DTA

DTA has an unlimited number of applications. DTA has been employed by geologists, ceramists, metallurgists for many years. It is a rapid analytical tool for determination of clays and other minerals, physical transformations like melting, freezing, volatilization, change in crystallinity, and specific heat, adsorption and desorption as well as chemical change.

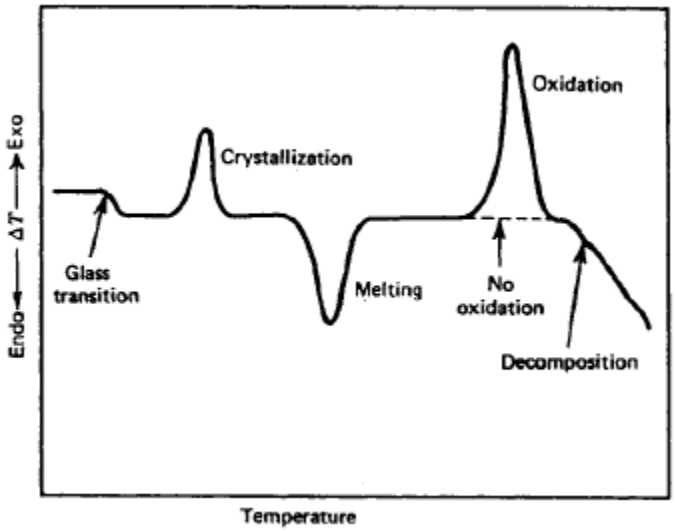

Figure 8: A generalized DTA curve for organic polymer

5.1 In Physical Chemistry:

(a) Heat of reaction: Borchardt and Daniels worked on the derivation of expression relating area under a DTA peak to the heat of reaction and they concluded that the peak area 'A' in DTA is always a linear function of the heat of reaction $\Delta H=KA/N_O$.

(b) Specific heat: David employed DTA to determine the specific heat of substances like naphthalene. The samples donot undergo any thermal effect other than the normal change in specific heat. CP was determined by using the following formula: $C_P=KK'(b-a)/dm_s dT$

(c) Thermal diffusivity: The thermal diffusivities can be determined by DTA, by measuring the temperature difference ΔT between the centre and surface of the sample, heated at a uniform rate. The thermal diffusivity, D was determined by using me following relation: $D=\beta r2/\delta\ \Delta T_S$

Where r is the radius of the spherical sample cavity and β is the heating state[11].

5.2 In Analytical chemistry:

(a) Identification of substances: We know that the DTA curve for two substances is not identical. Therefore, these serve as fingerprints for various substances.

(b) Identification of products: The specific DTA curves helps in identifying the products when a substance reacts with another substance.

(c) Melting points: It can be easily identified by DTA. So, this method is used directly to check the purity of the compound.

5.3 Quantitative analysis:

The area of the peak is directly proportional to the total heat of the reaction. Therefore, the quantitative analysis is possible with the help of the standard curve of peak area vs. weight.

5.4 Quality control:

The quality control of a large number of substances like cement, glass, soil, catalysts, textiles, explosives, resins, drugs etc. is done by DTA, The purity, polymorphism, stability of the drug substance can be easily evaluated using thermal analysis. The characterization of limestone used in the production of Portland cement has been done by DTA. Through the quantitative analysis of the DTA curve, the amount of magnesium carbonate in cement can be controlled [12].

5.5 Inorganic chemistry:

DTA technique has been used to study the thermal stability of a large number of inorganic compound and complexes. DTA technique also helps indistinguishing between reversible phase changes and irreversible decompositions. DTA techniques have been used to study oxalates, hydrates, metal amine complexes, carbonates and oxides.

5.6 Organic chemistry:

In organic chemistry, DTA investigations help in identification, purity determination and quantitative analysis including the evaluation of kinetic parameters of polymers, explosives, pharmaceuticals, oils, fats and other organic chemicals [13].

5.7 In mineralogy:

Differential thermal analysis can be applied as either a single or a combined method for three purposes in mineralogical studies:

(a) For the qualitative identification of minerals and the semi-quantitative determination of the components of rocks and soils,

(b) For the characterization of crystal-physical and crystal-chemical properties, including the study of kinetics and the determination of thermodynamic data, phase and reaction equilibria,

(c) For special petrogenetic investigations concerning the interrelation of mineralogical properties with the formation, decomposition or recrystallization of minerals [14].

6. Recent Advancement in TGA

Nowadays most of the manufacturers no longer make true DTA systems but rather have incorporated this technology into thermo gravimetric analysis (TGA) systems, which provide both mass loss and thermal information. With today's advancements in software, even these instruments are being replaced by true TGA-DSC instruments that can provide the temperature and heat flow of the sample, simultaneously with mass loss.

Reference

[1]. Norton, F.H. (1939). Critical Study of the Differential Method for the Identification of the Clay Mineral. *Journal of the American Ceramic Society*, 22(5): 63.

[2]. Joseph, A. and Maurice, F.W. (1953). Differential thermal analysis method and technique. *University of California*, 5(18):1-15.

[3]. Skoog, D.A., Holler, F.J., and Crouch, S.R. (2009). *Instrumental analysis*. Cengage Learning India Pvt. Ltd, 3rd Ed., 980-82.

[4]. Yang, J. and Roy, C. (1999). Using DTA to quantitatively determine enthalpy change over a wide temperature range by the mass difference baseline method. *Thermochimica Acta*, 33(3): 131–140.

[5]. Grega, K., Jozef, M. and Primoz, M. (2010). Differential thermal analysis (DTA) and Differential Scanning Calorimetry (DSC) as a method of material investigation. *RMZ – Materials and Geoenvironment*, 57(1): 127–142.

[6]. Horvath, E. Kristof, J., Frost, R.L., Redey, A., Vagvolgyi,V., and Cseh, T. (2003). Journal of Thermal Analysis and Calorimetry. *Springer*, 110(3): 707.

[7]. Riarjorie, J.V. (1949). Differential Thermal Analysis. *Anal. Chem*, 21(6): 683–688.

[8]. Nirav, S. (2017). Thermal Methods of Analysis. *Mod Appl Pharm Pharmacol*. 1(2). MAPP.000509.

[9]. Muller, R.H. (1963). Differential Thermal Analysis. *Anal. Chem*, 35(4): 103A–105A.

[10]. Kamboj, P.C. (2015). Pharmaceutical analysis-II. *Vallabh publications* 1st Ed, 451-55.

[11]. Borchardt, H.J. and Farrington, D. (1957). The Application of Differential Thermal Analysis to the Study of Reaction Kinetics. *Journal of the American Chemical Society*, 79 (1): 41–46.

[12]. Monajjemzadeh, F. and Ghaderi, F. (2015) Thermal Analysis Methods in Pharmaceutical Quality Control. *Journal of Molecular Pharmaceutics & Organic Process Research*, 3(1); 121.

[13]. Chatwal GR, Anand SK. (2007). *Thermal methods: Instrumental method of chemical analysis*. Himalaya Publishing House 5th Ed. 2.719-2.738.

[14]. Werner, S. K. (1982). Application of differential thermal analysis in mineralogy. *J. Thermal Anal.* 23(1):15-44.