# Thermal Analysis Techniques

Thermal analysis comprises a group of techniques in which a physical property of a substance is measured as a function of temperature, while the substance is subjected to a controlled temperature programme. In differential thermal analysis, the temperature difference that develops between a sample and an inert reference material is measured, when both are subjected to identical heat–treatments. The related technique of differential scanning calorimetry relies on differences in energy required to maintain the sample and reference at an identical temperature.

Length or volume changes that occur on subjecting materials to heat treatment are detected in dilatometry; X–ray or neutron diffraction can also be used to measure dimensional changes.

Both thermogravimetry and evolved–gas analysis are techniques which rely on samples which decompose at elevated temperatures. The former monitors changes in the mass of the specimen on heating, whereas the latter is based on the gases evolved on heating the sample. Electrical conductivity measurements can be related to changes in the defect density of materials or to study phase transitions.

# Differential Thermal Analysis (DTA)

### Introduction

DTA involves heating or cooling a test sample and an inert reference under identical conditions, while recording any temperature difference between the sample and reference. This differential temperature is then plotted against time, or against temperature. Changes in the sample which lead to the absorption or evolution of heat can be detected relative to the inert reference.

Differential temperatures can also arise between two inert samples when their response to the applied heat–treatment is not identical. DTA can therefore be used to study thermal properties and phase changes which do not lead to a change in enthalpy. The baseline of the DTA curve should then exhibit discontinuities at the transition temperatures and the slope of the curve at any point will depend on the microstructural constitution at that temperature.

A DTA curve can be used as a *finger print* for identification purposes, for example, in the study of clays where the structural similarity of different forms renders diffraction experiments difficult to interpret.

The area under a DTA peak can be to the enthalpy change and is not affected by the heat capacity of the sample.

DTA may be defined formally as a technique for recording the difference in temperature between a substance and a reference material against either time or temperature as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate.

## Apparatus

The key features of a differential thermal analysis kit are as follows (Fig. 1):

1. Sample holder comprising thermocouples, sample containers and a ceramic or metallic *block*.
2. Furnace.
3. Temperature programmer.
4. Recording system.

The last three items come in a variety of commercially available forms and are not be discussed in any detail. The essential requirements of the furnace are that it should provide a stable and sufficiently large hot–zone and must be able to respond rapidly to commands from the temperature programmer. A temperature programmer is essential in order to obtain constant heating rates. The recording system must have a low inertia to faithfully reproduce variations in the experimental set–up.

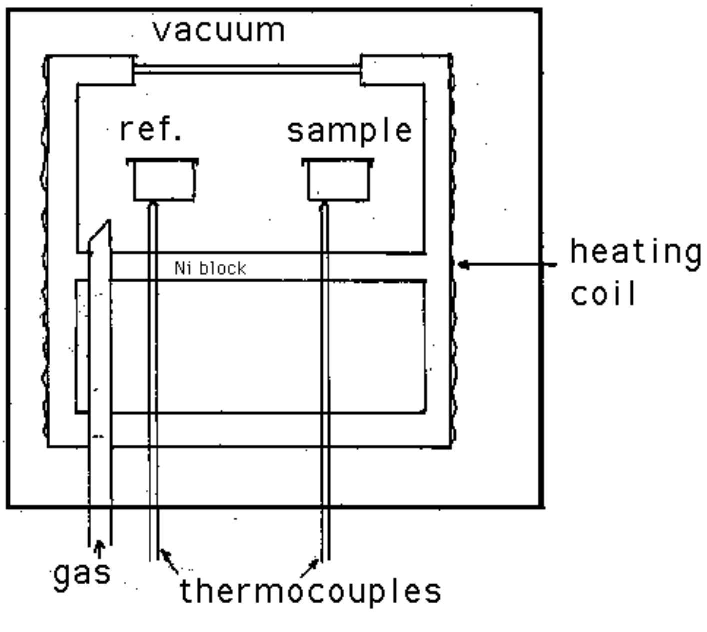

Fig. 1: Schematic illustration of a DTA cell.

The sample holder assembly consists of a thermocouple each for the sample and reference, surrounded by a block to ensure an even heat distribution. The sample is contained in a small crucible designed with an indentation on the base to ensure a snug fit over the thermocouple bead. The crucible may be made of materials such as *Pyrex*, silica, nickel or platinum, depending on the temperature and nature of the tests involved. The thermocouples should not be placed in direct contact with the sample to avoid contamination and degradation, although sensitivity may be compromised.

Metallic blocks are less prone to base–line drift when compared with ceramics which contain porosity. On the other hand, their high thermal conductivity leads to smaller DTA peaks.

The sample assembly is isolated against electrical interference from the furnace wiring with an earthed sheath, often made of platinum–coated ceramic material. The sheath can also be used to contain the sample region within a controlled atmosphere or a vacuum.

During experiments at temperatures in the range –200 to 500 °C, problems are encountered in transferring heat uniformly away from the specimen. These may be mitigated by using thermocouples in the form of flat discs to ensure optimum thermal contact with the now flat–bottomed sample container, made of aluminium or platinum foil. To ensure reproducibility, it is then necessary to ensure that the thermocouple and container are consistently located with respect to each other.

## Experimental Factors

Care is necessary in selecting the experimental parameters. For example, the effects of specimen environment, composition, size and surface–to–volume ratio all affect powder decomposition reactions, whereas these particular variables may not affect solid–state phase changes. Experiments are frequently performed on powders so the resulting data may not be representative of bulk samples, where transformations may be controlled by the build up of strain energy. The packing state of any powder sample becomes important in decomposition reactions and can lead to large variations between apparently identical samples.

In some circumstances, the rate of heat evolution may be high enough to saturate the response capability of the measuring system; it is better then to dilute the test sample with inert material.

For the measurement of phase transformation temperatures, it is advisable to ensure that the peak temperature does not vary with sample size.

The shape of a DTA peak does depend on sample weight and the heating rate used. Lowering the heating rate is roughly equivalent to reducing the sample weight; both lead to sharper peaks with improved resolution, although this is only useful if the signal to noise ratio is not compromised. The influence of heating rate on the peak shape and disposition can be used to advantage in the study of decomposition reactions, but for kinetic analysis it is important to minimise thermal gradients by reducing specimen size or heating rate.

## Interpretation and Presentation of Data

A simple DTA curve may consist of linear portions displaced from the abscissa because the heat capacities and thermal conductivities of the test and reference samples are not identical, and of peaks corresponding to the evolution or absorption of heat following physical or chemical changes in the test sample.

There are difficulties with the measurement of transition temperatures using DTA curves. The onset of the DTA peak in principle gives the start–temperature, but there may be temperature lags depending on the location of the thermocouple with respect to the reference and test samples or the DTA block. It is wise to calibrate the apparatus with materials of precisely known melting points. The peak area ($A$), which is related to enthalpy changes in the test sample, is that enclosed between the peak and the interpolated baseline. When the differential thermocouples are in thermal, but not in physical contact with the test and reference materials, it can be shown that $A$ is given by

$$A = \frac{mq}{gK}$$

where $m$ is the sample mass, $q$ is the enthalpy change per unit mass, $g$ is a measured shape factor and $K$ is the thermal conductivity of sample. With porous, compacted or heaped samples, the gas filling the pores can alter the thermal conductivity of the atmosphere surrounding the DTA container and lead to large errors in the peak area. The situation is made worse when gases are evolved from the sample, making the thermal conductivity of the DTA–cell environment different from that used in calibration experiments.

The DTA apparatus is calibrated for enthalpy by measuring peak areas on standard samples over specified temperature ranges. The calibration should be based upon at least two different samples, conducting both heating and cooling experiments.

It is possible to measure the heat capacity $C_P$ at constant pressure using DTA:

$$C_P = K' \frac{T_2 - T_1}{mH}$$

where $T_1$ and $T_2$ are the differential temperatures generated when the apparatus is first run without any sample at all and then with the test sample in position. $H$ is the heating rate and the constant $K'$ is determined by calibration against standard substances.