62. Thermal Analysis

"Thermal Analysis" is a generic term for a variety of techniques to measure the physical properties of a substance as a function of temperature and/or time.

Among the physical properties, phase transitions such as solid/liquid phase transition (melting, freezing) and crystal polymorphism or thermal behavior such as heat evolution or absorption accompanying thermal degradation or chemical reaction can be detected by the techniques of differential thermal analysis (DTA) or differential scanning calorimetry (DSC). DTA is a method for detecting the thermal behavior of a specimen in terms of the temperature change, while DSC employs the heat quantity (enthalpy) change. There is also a method, thermogravimetry (TG), in which the mass change of a specimen caused by dehydration, adsorption, elimination or oxidation etc., is detected as a function of temperature and/or time.

Among the above three different methods, TG can be used as an alternative method for "Loss on Drying" or "Water Determination". However, it must be confirmed beforehand that no volatile component except for water is included in the test specimen when TG is used as an alternative method for "Water Determination".

Method 1 Differential Thermal Analysis (DTA) or Differential Scanning Calorimetry (DSC)

Apparatus Apparatus for DTA or DSC is usually composed of a heating furnace, a temperature-controller, a detector, a device for controlling the atmosphere, and an indicator/recorder.

Differential Thermal Analysis (DTA) In a DTA apparatus, a sample specimen and an inert reference material placed in the heating furnace are heated or cooled at a constant rate, and the temperature difference evolved between the sample and reference material is detected continuously by a device such as a thermocouple and recorded as a function of time and/or temperature. As an inert reference material, α-Alumina for thermal analysis is usually adopted.

Differential Scanning Calorimetry (DSC) Two kinds of DSC apparatus, based upon different principles are available as shown below.

1. Input compensation-type differential scanning calorimetry (Input compensation DSC)

A sample specimen and the reference material in twin furnaces are programmed to be heated or cooled at a constant rate, and the temperature difference between the sample and the reference, which is detected by a device such as a platinum resistance thermometer, is kept at null by controlling the heating unit with a compensation feed-back circuit. The instrument is designed to measure and record continuously the balance of thermal energy applied to each furnace as a function of temperature and/or time.

2. Heat flux-type differential scanning calorimetry (Heat flux DSC)

A sample specimen and the reference material in twin furnaces are programmed to be heated or cooled at a constant rate, and the temperature difference between the sample and the reference is detected as a difference of heat flux and recorded as a function of temperature and/or time. In heat flux DSC, thermal conductors are adopted so that the heat flux between the sample and the heat reservoir is proportional to the temperature difference between them.

In usual DSC analysis, α-Alumina is used as a reference material, both in Input compensation DSC and in Heat flux DSC. But in some cases, an empty sample container can also be used without any reference material.

Procedure A sample specimen and the reference material are put in sample pans, and the furnace is heated or cooled under a controlled temperature program. As the temperature changes, the temperature difference (DTA) or heat quantity change (DSC) that develops between the specimen and the reference is detected and recorded continuously. Apparatus equipped with a data-processor is operated according to the instruction manual provided with the instrument.

A preliminary experiment is needed to determine the appropriate temperature range of measurement, within which a predicted physical change such as melting or polymorphic phase transition will occur, and to confirm that unpredicted thermal changes are not induced in a specimen in that temperature range. In this preliminary test, a wide temperature range (room temperature-the temperature at which degradation begins) can be scanned at a rapid heating rate (10-20°C/min). Thereafter, tests by DSC or DTA should be performed at a low heating rate, usually 2°C/min, in the chosen temperature range. However, when a clear heat change cannot be observed, such as in a case of glass-transition, the heating rate may be changed to a higher or a lower rate, as appropriate for the kind of physical change being observed. By analyzing the measured DTA-curve or DSC-curve, a quantity of heat change and/or a specific temperature (ignition, peak or end temperature) that accompanies a physical change, such as melting or polymorphic phase transition, can be obtained.

Calibration of the apparatus

1. Temperature calibration for DTA and DSC

Temperature calibration for DTA and/or DSC apparatus can be performed by using reference substances having an intrinsic thermal property, such as melting point of pure
metals or organic substances, or phase transition point of crystalline inorganic salts or oxides. Melting points of Indium for thermal analysis and/or Tin for thermal analysis are usually employed for calibration.

2. Heat-quantity calibration for DSC

   For accurate estimation of a quantity of heat change (enthalpic change) of a sample specimen, caused by a certain physical change accompanying a temperature change, it is necessary to calibrate the apparatus by using appropriate reference substances. As indicated in the section of Temperature calibration, heat-quantity calibration for DSC apparatus can be performed by using appropriate reference substances having a known definite enthalpic change caused by such physical changes as melting of pure metals and/or organic substances, or phase transition of crystalline inorganic salts. Melting points of Indium for thermal analysis and/or Tin for thermal analysis are usually employed for calibration.

Notes on operating conditions

   When DTA or DSC measurements are made, the following items must be recorded: sample size, discrimination of open- or closed-type sample container, heating or cooling rate, measuring temperature range, and kind and flow rate of atmospheric gas.

Method 2 Thermogravimetry (TG)

Apparatus

   The construction of a TG apparatus is fundamentally similar to that of DTA or DSC apparatus. However, the detector for TG is a balance, called a thermobalance, which can be classified to hanging-, Roberval's-, and horizontal-type balances. The TG apparatus is designed to detect small mass changes of a specimen, placed at a fixed position on a thermobalance, caused by temperature change of the furnace under a controlled temperature program. Mass change with time and/or temperature is recorded continuously.

Procedure

   A specimen is put in a sample container, which is placed at a fixed position of the thermobalance, then the heating furnace is run under a controlled temperature program. During this temperature change of the furnace, the mass change of a specimen with time and/or temperature is recorded continuously. Apparatus equipped with a data-processor is operated according to the instruction manual provided with the instrument.

   When TG is used as an alternative method for "Loss on Drying" or "Water Determination", the measurement starts at room temperature and ends at a temperature above which no further mass change due to drying and/or vaporization of water can be observed. The standard heating rate is usually 5°C/min, and a linear heating program is recommended. However heating conditions (rate and time span) can be changed as necessary, depending on the kind of specimen and the extent of the measuring temperature range. Further, in TG measurement, dry air or dry nitrogen is usually passed through the heating furnace to ensure rapid elimination of evolved water or other volatile components and to avoid the occurrence of any chemical reaction, such as oxidation. By analyzing the TG curve plotted against time and/or temperature, absolute mass change and/or relative mass change with respect to the initial quantity(%) is obtained.

   When the mass change caused by oxidation or degrad-ation of a specimen is measured, a specific temperature range has to be determined beforehand so that stable baselines can be obtained before and after a targeted chemical reaction. Subsequent operating procedures are the same as described above.

Calibration of the apparatus

1. Temperature calibration

   The Curie temperature of a ferromagnetic substance such as pure Nickel can be used for temperature calibration for TG, based on the occurrence of an apparent mass change at the Curie point. In the case of a TG apparatus capable of simultaneously conducting DSC and DTA, the same reference substances as those for DTA and DSC can be adopted.

2. Scale calibration and confirmation

   The scale calibration for TG must be done by using reference masses for chemical balances and/or semimicrobalances in the appropriate range. This is called a primary scale calibration, and is performed under ordinary temperature and pressure when the apparatus is set up initially and periodically, thereafter.

   In usual measurement by TG, scale calibration or confirmation is done by using Calcium Oxalate Monohydrate Reference Standard to take account of such effects as buoyancy and convection due to atmospheric gas flow in the real measurement state. This is called secondary scale calibration, and is performed under the standard operation conditions stated below by using the above-mentioned Reference Standard, with a certified water content. When the difference of water content between the measured value and the certified one for the Reference Standard is less than 0.3%, normal operation of the apparatus is confirmed. However, when the difference is more than 0.3%, scale calibration for TG must be done, based on the certified water content of the Reference Standard.

   The standard operation conditions are as follows,

   Amount of Calcium Oxalate Monohydrate Reference Standard: 0.01 g

   Heating rate: 5°C/min
   Temperature range: room temperature—250°C
   Atmospheric gas: dried Nitrogen or dried Air
   Flow rate of atmospheric gas,
   hanging- or Roberval’s-type balance: 40 mL/min
   horizontal-type balance: 100 mL/min

Notes on operating conditions

   In TG measurement, the following operation conditions must be recorded: sample size, heating rate, temperature range, kind and flow rate of atmospheric gas, etc.

63. Thin-layer Chromatography

Thin-layer Chromatography is a method to separate each ingredient by developing a mixture in a mobile phase, using a thin-layer made of a suitable stationary phase, and is applied for identification, purity test, etc. of substances.

Preparation of thin-layer plate

   Generally, proceed by the following method.

   A smooth and uniformly thick glass plate having a size of 50 mm × 200 mm or 200 mm × 200 mm is used for preparing a thin-layer plate. Using a suitable apparatus, apply a