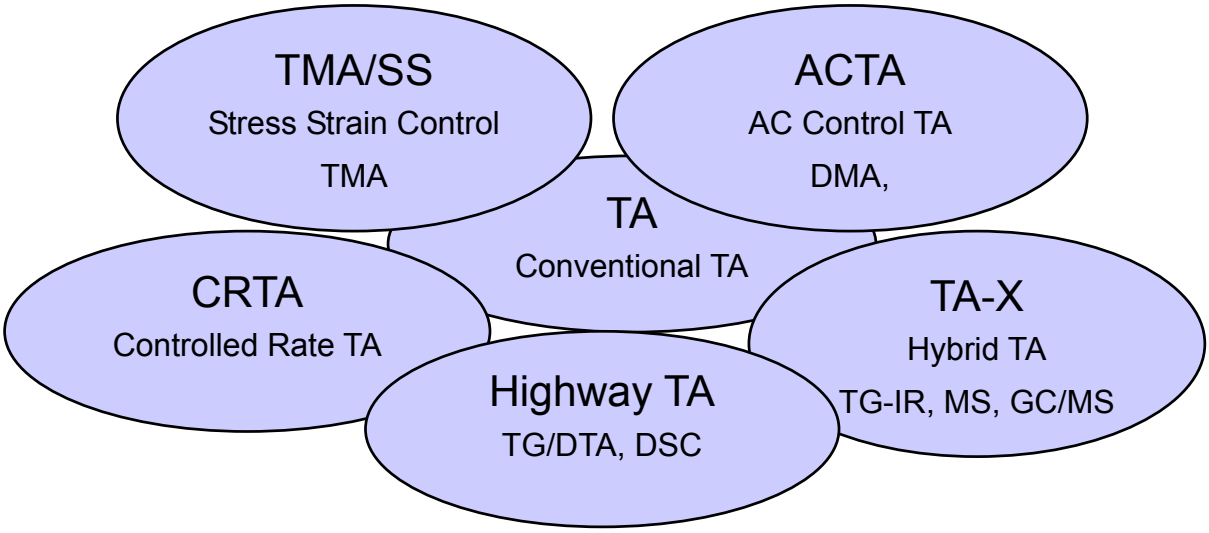
New Thermal Analysis Techniques



In addition to the conventionally used thermal analysis techniques, new thermal analysis techniques have attracted attention in recent years. The below techniques that have especially attracted attention are explained in the following chapters.

1. Controlled Rate Thermal Analysis
2. Highway TA
3. Hybrid Thermal Analysis

1. Controlled Rate Thermal Analysis (CRTA)

- A family of techniques which monitors the temperature-versus-time profile needed to maintain a chosen, fixed rate of change of a property of the sample in a specified atmosphere.
- For example, in controlled-rate experiments, power to the furnace is controlled to ensure a fixed rate of mass loss (or gain).

Controlled Rate Thermal Analysis is abbreviated as CRTA.

The above is the definition for CRTA from “For Better Thermal Analysis and Calorimetry” 3rd Ed. (1991) published by ICTAC.

Although CRTA deviates from the original definition of thermal analysis, it is specially defined as thermal analysis as it is often conducted using thermal analysis devices.

While temperature is programmed and mass is measured in thermal analysis, mass is programmed and temperature is calculated in CRTA.

This relationship is shown in the next page.

TA and CRTA Comparison

	Control Subject	Operation Object	Measurement Object
TA	Δ (Tp, Tr)	Heater Control	P (physical qty)
CRTA	Δ (Pp, Pr)	Heater Control	T (temperature)

Tp: program temperature	Tr: control object temperature
Pp: program physical quantity	Pr: control object quantity

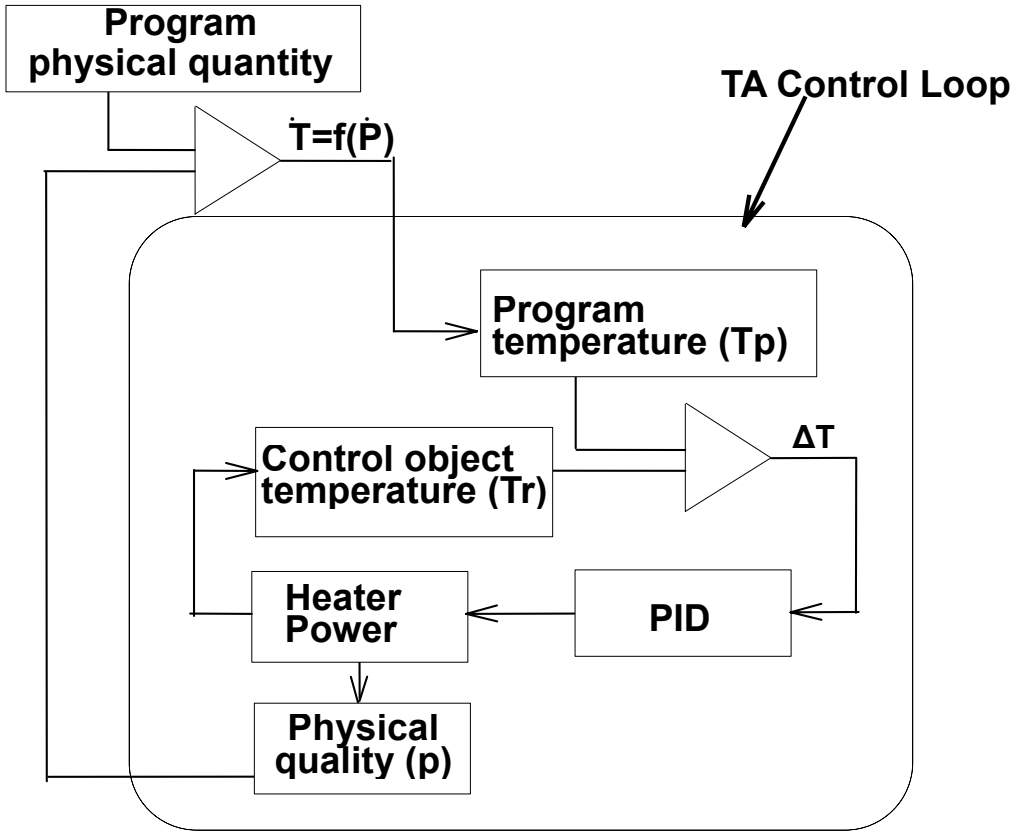
The above shows comparisons of control subject, operation quantity and measurement quantity between CRTA (Controlled Rate Thermal Analysis) and TA (Thermal Analysis).

In TA, electricity to the heater is controlled against the difference between the program temperature and the control subject temperature, and the resulting physical quantity of the sample is measured.

In CRTA on the other hand, electricity to the heater is controlled against the difference between the programmed physical quantity and the control subject physical quantity, and the resulting sample temperature is measured.

In essence, TA and CRTA are two measurement techniques whose control subject and the measurement object are reversed.

Actual CRTA Control



The above diagram shows an actually used CRTA control loop.

In reality, it is difficult to directly control the heater without using the measured temperature from the physical quantity feedback, so a two-fold control loop is used as shown above.

Rate Control Thermal Analysis

- **Quasi-isothermal Analysis (QIA) or Stepwise Isothermal Analysis (SIA)**
  The control technique in which heating is stopped and fixed temperature control is started when the speed of physical quantity change exceeds a set upper value, and heating is restarted when the speed of physical quantity change goes below a set lower value.

- **Reaction Speed Control Analysis**
  The control technique in which the temperature-programming rate is changed so that the speed of physical quantity change keeps at a constant speed.

- **Quasi-Isothermal Analysis**

  In 1972, the Paulik brothers conceived a quasi-isothermal, quasi-isobaric thermal mass measurement technique (1), and afterwards, thermal mass measurements conducted only under quasi-isothermal conditions came to be known as Quasi-Isothermal Mass Measurement or Quasi-Isothermal Analysis (QIA).

- **Reaction Speed Control Analysis**

  Reaction Speed Control Analysis was first advocated by Rouquerol in 1989 (2) and was later adopted by ICTAC as a CRTA classification.

  In actual use, the upper and lower values are set the same as defined by QIA method, and the function is set to an appropriate value according to the change in the temperature-programming rate (3)(4).

  As CRTA, it is applied to TG and TMA.

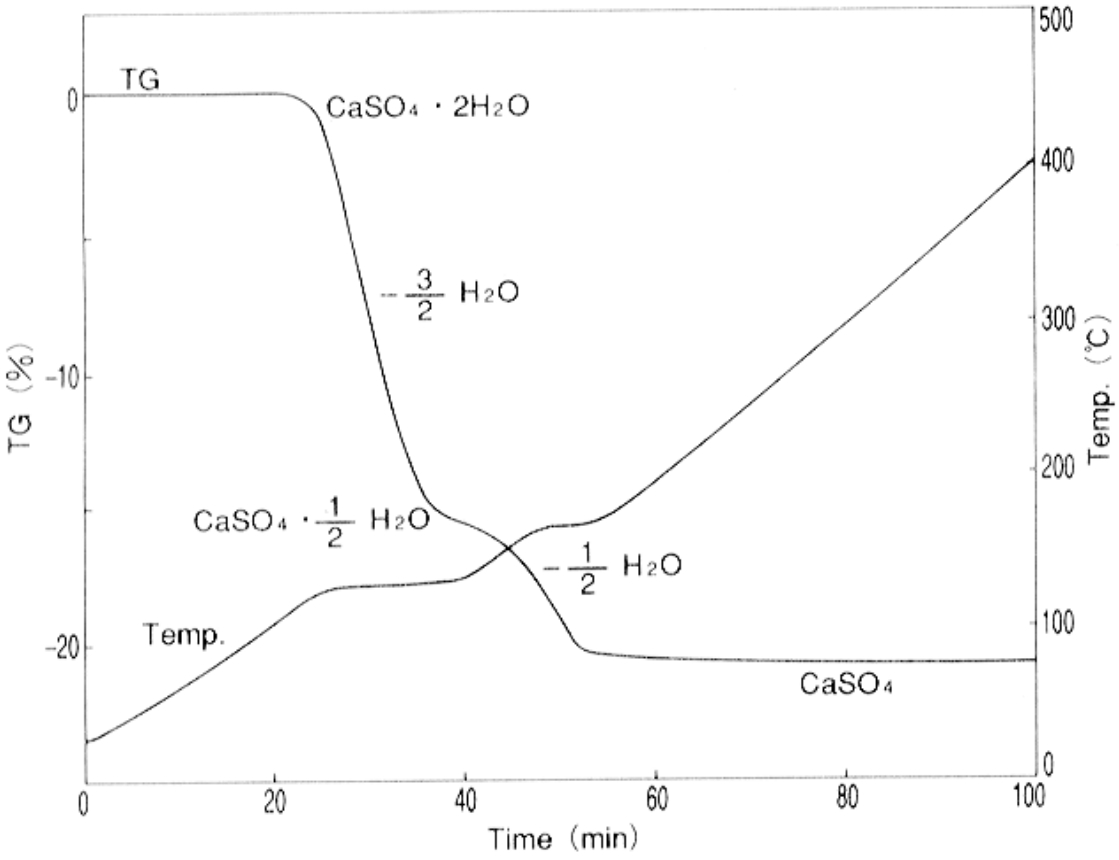
(1) F. Paulik, J. Paulik, Thermochim. Acta, 4, 189 (1972)

(2) J. Rouquerol, Thermochim. Acta, 144, 209 (1989)

(3) Japanese Published Unexamined Patent Application 5-297961

Arii et al., Netsusokutei, 21, 151 (1994)

QIA Measurement Data



The above diagram shows a measurement data of Quasi-Isothermal Analysis (QIA), measuring calcium sulfate dihydrate (dihydrate gypsum) using QIA.

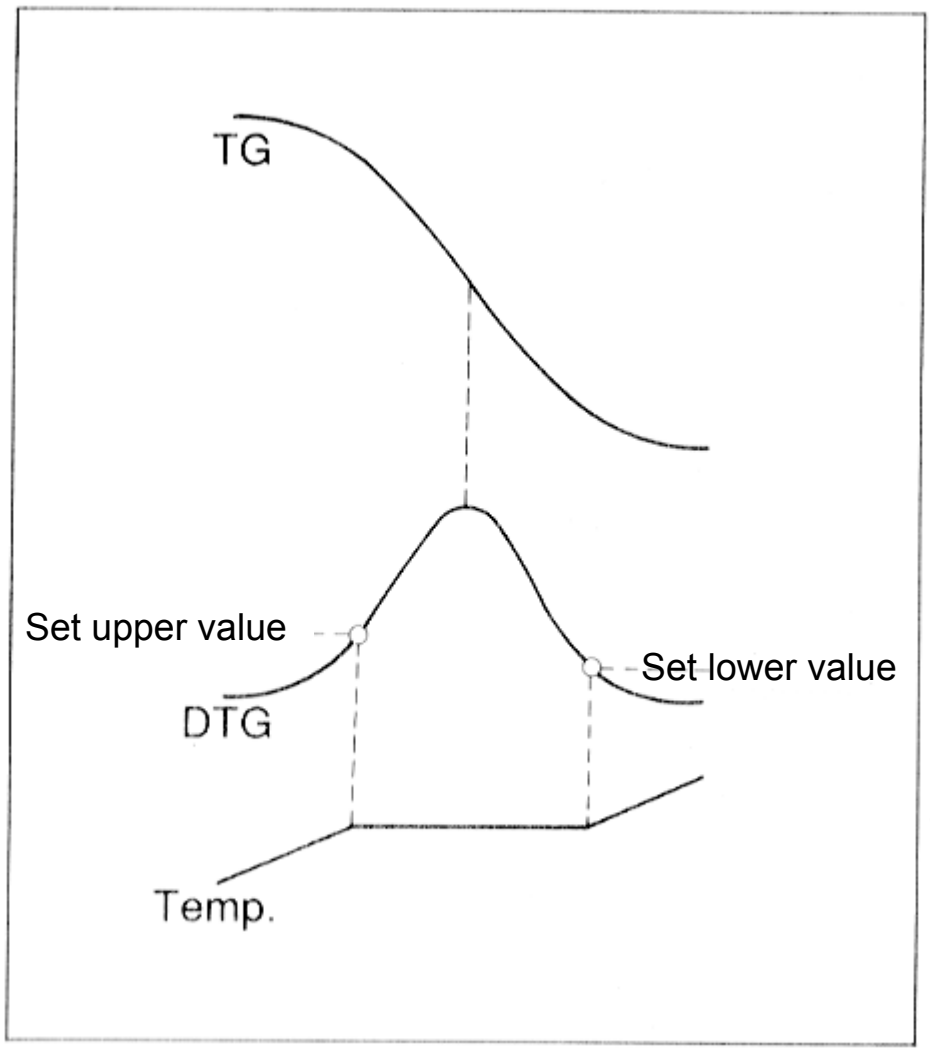
Water evaporate from calcium sulfate dihydrate according to the below steps.

$$\text{-}3/2H_2O \qquad \text{-}1/2H_2O$$

$$CaSO_4\ 2H_2O \Rightarrow CaSO_4\ 1/2H_2O \Rightarrow CaSO_4$$

According to the data, isothermal control occurs at around 120ºC and 180ºC, and H_2O evaporation occurs at each temperature range.

Principles of QIA

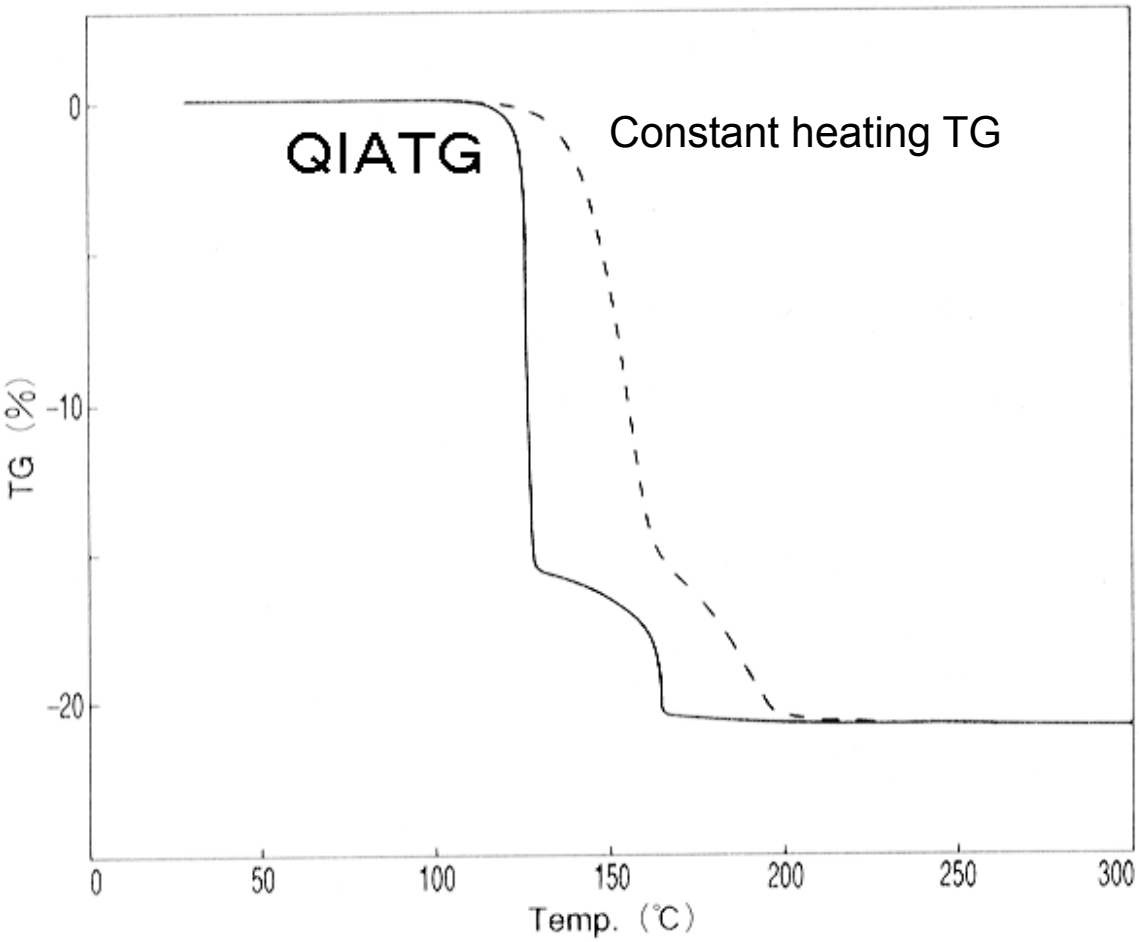


The above shows the measurement principles of QIA.

Upper and lower limits are set on the differential signal (DTG signal) of the TG curve. When heating is started and mass reduction begins and the DTG signal crosses the upper value, temperature programming is switched to isothermal control and the mass reduction speed is lowered.

When the mass reduction is almost finished in the isothermal state and goes below the lower value, heating restarts.

Comparison between QIATG and Constant Heating TG

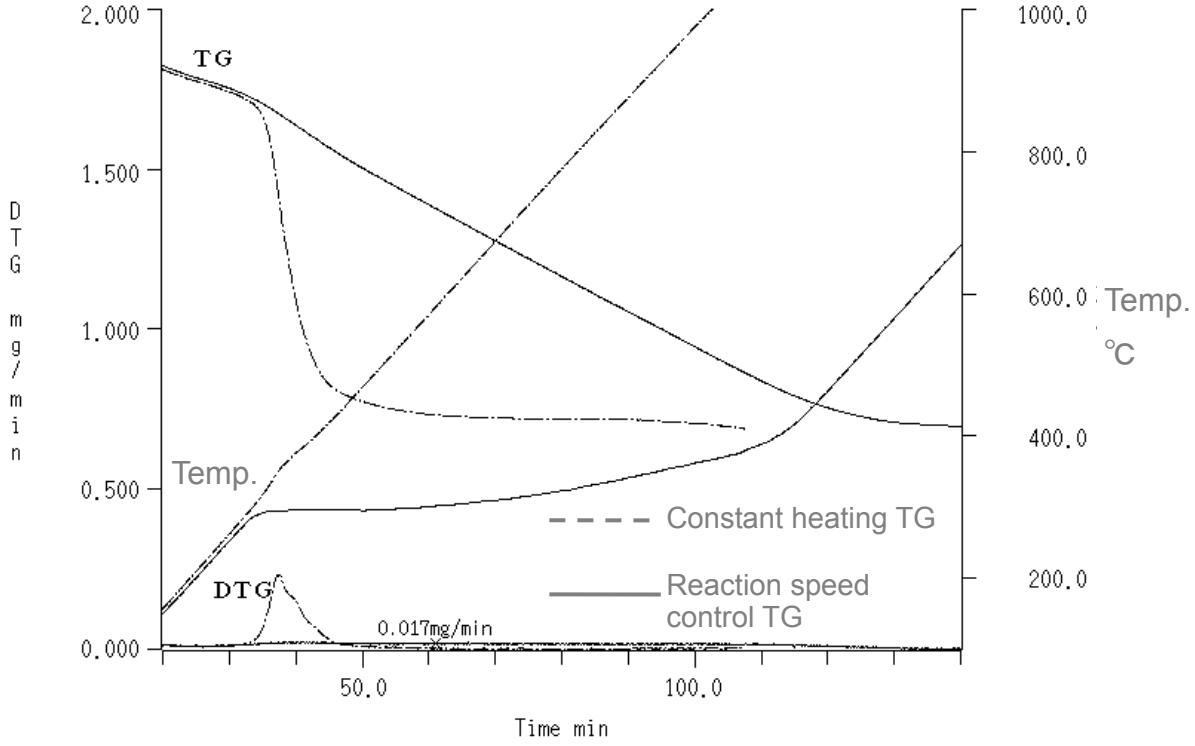


The above shows a data comparison between QIATG and constant heating TG. Taking the data from the previous page, the temperature axis is represented on the horizontal axis, and was compared to constant heating TG.

Two-step TG loss is seen in constant heating TG as well, but because temperature rise is stopped during water separation in QIATG, partial scale contraction occurs and the visual resolution improves.

As demonstrated above, QIATG is an effective technique for samples with known TG behavior.

Measurement Data of Reaction Speed Control TG



The above shows a measurement example of reaction speed control TG.

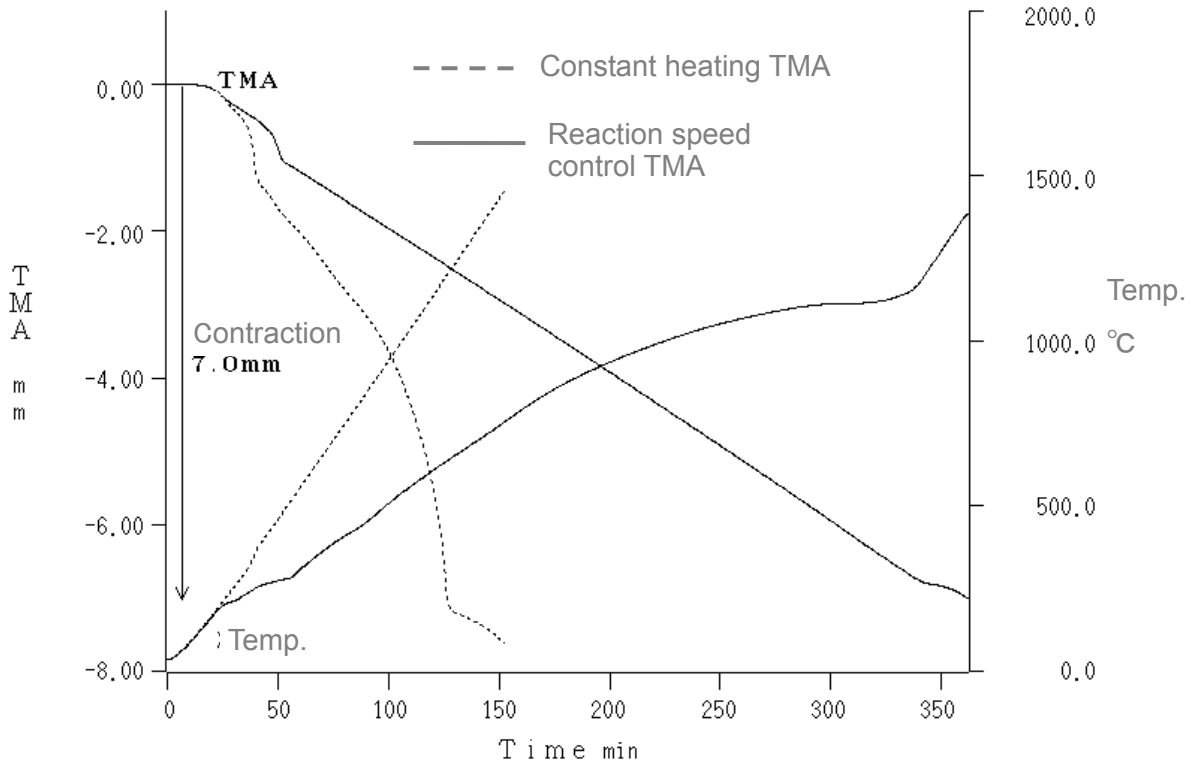
The dashed lines show the standard fixed temperature-programming TG data and the solid lines represent reaction speed control TG data.

Inconstant heating TG data, rapid mass reduction starts at around 300ºC and ends at around 400ºC.

In reaction speed control TG data, it is controlled so that TG loss speed (proportional to reaction speed) remains almost constant, and temperature profile is recorded.

From this data, potential uses include simulation of a furnace's temperature profile for controlling gas production amount from plastic combustion.

Measurement Data of Reaction Speed Control TMA



The above shows a data of reaction speed control TMA.

A molding of aluminum compound ($NH_4AlO(OH)HCO_3$), a material for high grade alumina, is measured with constant heating TMA and reaction speed control TMA.

During the combustion process, ceramic contraction occurs accompanied by the decomposition of the included binder and gas production from inside the ceramic, but there are accuracy problems such as cracks because the gas production is too fast.

In constant heating TMA data, rapid contraction can be seen at temperature regions of 200ºC to 300 ºC and at above 900ºC.

But in reaction speed control TMA, contraction speed is controlled at almost constant and the temperature profile is recorded. This temperature profile can be used in temperature condition simulation of the ceramic