Thermochimica Acta, 10 (1974) 227–235

DESIGN FEATURES OF A NEW QUANTITATIVE LOW TEMPERATURE DIFFERENTIAL THERMAL ANALYSIS SYSTEM AND ITS INDUSTRIAL APPLICATION

W. PERRON
Mettler Instrumente AG, CH-8606 Greifensee (Switzerland)
(Received 16 July 1974)

ABSTRACT

Though many of the commercially available DTA instruments are supplied with sub-ambient accessories, none of the cooling systems is considered to be fully satisfactory. The main features where the requirements are not achieved are:

inaccurate temperature measurement;
inability either to quench- or to program-cool a sample at any desired rate (down to 0.1 °C min^{-1});
baseline disturbance due to condensation of atmospheric moisture in the measuring cell;
inconvenient handling of the sample, the instrument and/or the coolant.

The paper discusses design features of a novel cooling system for a modular low temperature DTA equipment (Mettler TA 2000 System). The performance of the new instrument is illustrated by means of some typical low temperature DTA experiments.

INTRODUCTION

The first DTA studies at sub-ambient temperature were performed by Taylor and Klug in 1936 on a home-made instrument. Since that time low temperature DTA has found a wide field of industrial application. It is estimated that the temperature range from −170 to +550 °C covers more than 85% of today's DTA measurements. In the context of this paper the notation "low temperature DTA" means DTA from −170 to +550 °C because it must be allowed that many DTA measurements which are commenced at sub-ambient temperature are extended to around +500 °C where most of the organic materials are decomposed.

A few of the home-made and some of the commercially available DTA instruments are equipped with low temperature accessories. According to Bohon[1] many of the low temperature accessories exhibit serious technical deficiencies and inconveniencies of operation. The main points, where the requirements for industrial low temperature DTA measurements are not achieved, are:

In the temperature measuring system

Inaccurate temperature measurement due to a non-linear response of the thermocouple or a low e.m.f. output per degree. Some special cryogenic thermocouples, e.g. iron–gold/chromel, appear to exhibit disadvantages for use in low temperature DTA equipment since they are limited in temperature range and certainly cannot be used above +100 °C and suffer from calibration drift caused by ageing of the alloys.

In the cooling system

The inability either to quench- or to program-cool and heat a sample in situ at desired rates down to 0.1 °C min^{-1}. This becomes important for many reasons, the principal being the thermal history dependency of so many of the interesting low temperature phenomena in solids.

Disturbance of the DTA baseline due to condensation or vaporization of atmospheric moisture within the measuring cell or due to the application of inadequate heating or cooling power to the DTA cell.

Inconvenient handling of the sample, the instrument or the coolant (e.g., liquid nitrogen).

The above-mentioned technical deficiencies in low temperature DTA instrumentation led to the conviction that the improvement of commercial instrumentation and techniques should expand the field of industrial application impressively.

INSTRUMENTAL

It is the purpose of this paper to present a new instrument in the field of low temperature DTA which claims to eliminate all the typical disadvantages mentioned above. Figure 1 shows the new instrument which is a further development in the Mettler modular thermal analysis system TA 2000. Figure 2 shows a schematic view of the same instrument. The program selector TA30, the power amplifier TA31 and the DTA-amplifier TA20 are common for the −20 to +500 °C DTA system and the new −170 to +550 °C DTA system.

Specifications of the TA 2000 System (DTA −170 to +550 °C)

Temperature

range		−170 to +550 °C
accuracy	−100 to +550 °C	±0.5 °C
	−100 to −170 °C	±1.0 °C
reproducibility		±0.1 °C

Calorimetric information

sensitivity with standard Al crucibles (40 µl)	at +157 °C	$60 \frac{\mu V}{mcal\ sec^{-1}}$

(according to standard sensitivity curve)	at +550 °C	$\sim 35 \frac{\mu V}{mcal\ sec^{-1}}$
	at −150 °C	$\sim 30 \frac{\mu V}{mcal\ sec^{-1}}$
precision		±2% ±0.5%
High speed cooling time		
from +550 °C to ambient		6 min
from ambient to −100 °C		3 min
from ambient to −150 °C		5 min
Heating and cooling rates		
Scan speeds selectable		0.1 to 29.9 °C min^{-1}
in steps of		0.1 °C min^{-1}
high speed		100 °C min^{-1}

The cooling system

Many of the disadvantages of known low temperature equipment can be attributed to the inadequate performance and to inconvenience of operation of the cooling system. The cooling system for the TA 2000 system shows a novel principle and consists of the following items (Figs. 1 and 2):

The liquid nitrogen container with a heater, a pressure gauge and a safety valve.
The heat exchanger fitted tightly around the DTA furnace,
A sensor for the temperature of the nitrogen gas at the exit of the heat exchanger.
The control valve.
The coolant controller TA34.

In the liquid nitrogen container a constant pressure of 0.5 atm is built up by means of a control loop which consists of a pressure gauge, a heater immersed in the liquid nitrogen and a controller, which is part of the coolant controller TA34. The cold gas is fed into the heat exchanger fitted over the DTA furnace. At the outlet of the heat exchanger there is a heater which heats the cold nitrogen gas to a temperature above room temperature. This avoids condensation of water in the control valve which regulates the gas flow in the cooling system.

An excellent control of the DTA furnace temperature is achieved by using two separate controllers: A heater controller TA33 and a coolant controller TA34. The set temperature for the coolant controller is electronically derived from the set temperature for the heater controller, which is displayed on the temperature controller. The set temperature for the coolant controller is always a few degrees centigrade below the temperature of the DTA furnace. In order to permanently maintain this temperature difference between the DTA furnace and the heat exchanger the control valve is

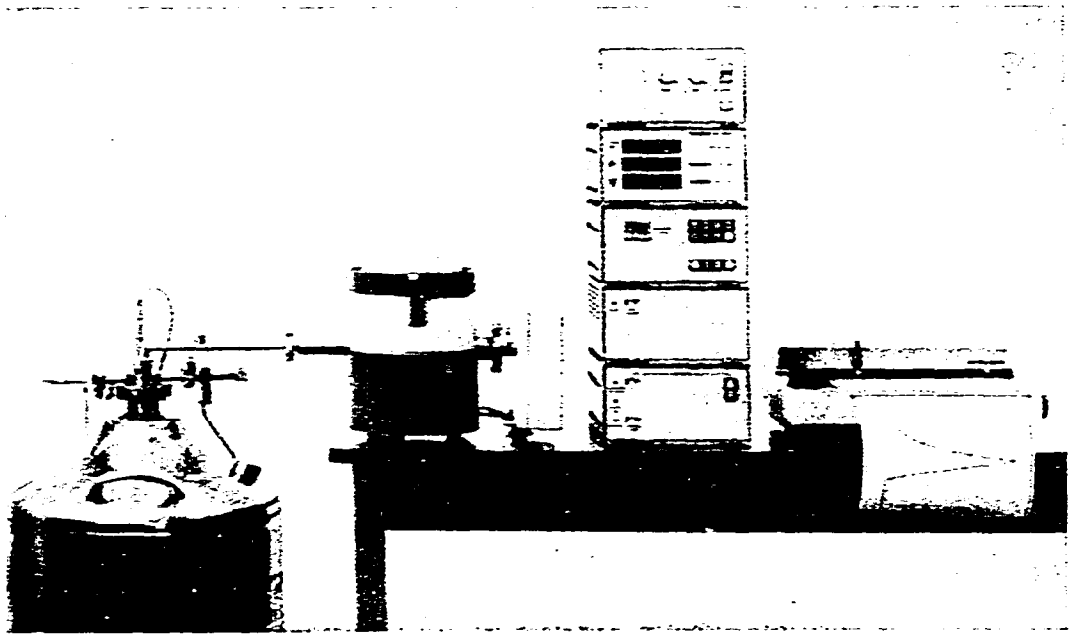

Fig. 1. General view of the Mettler TA 2000 low temperature DTA equipment.

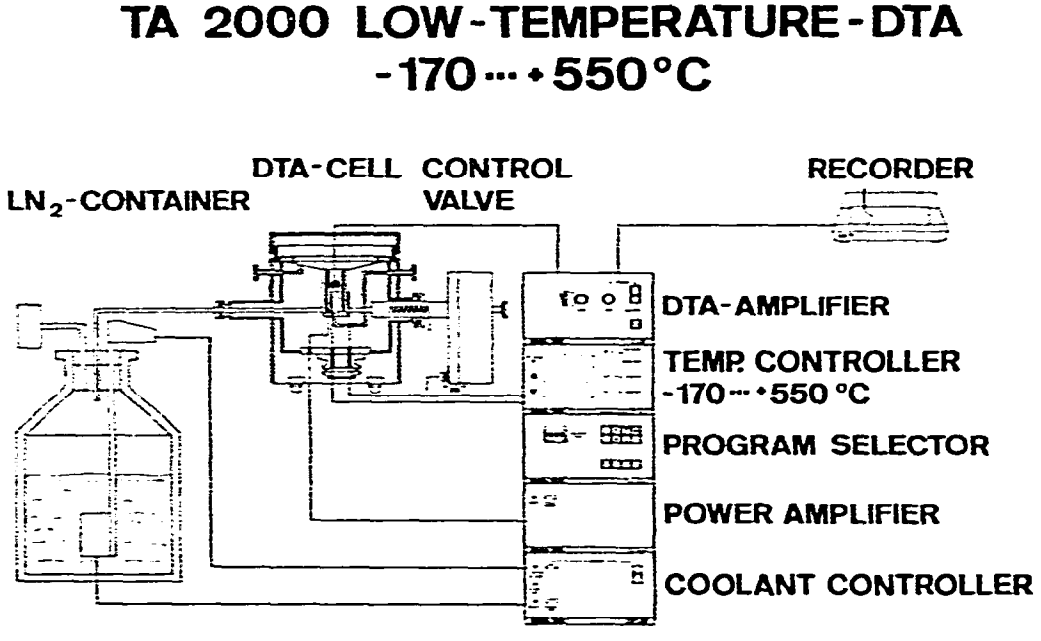

Fig. 2. Schematic view of the low temperature DTA instrument.

activated accordingly by the coolant controller. This cooling system is very fast and allows program- or quench-cooling (and heating) over the entire temperature range at a wide variety of selectable scan speeds.

This cooling system operates automatically and does not need any attendance. The capacity of the container is adequate to the liquid nitrogen demand of a few days of normal operation. The cooling system has built in several safety precautions: All pressure and temperature levels are controlled electronically and the system is switched off automatically if one of the levels is exceeded. Two additional level controls are installed in the liquid nitrogen container: One for the indication of the liquid nitrogen level being low and a second at a still lower level which automatically switches off the heater power whereby the further vaporization of liquid nitrogen is stopped.

The temperature measuring system

As Redfern and Treherne[2] have pointed out many of the commonly used temperature sensors show serious disadvantages for the use from liquid nitrogen temperature to +550 °C. For the temperature measurement in the low temperature DTA furnace platinum resistance sensors are successfully used down to −170 °C. This results in an unprecedented temperature accuracy of ±0.5 °C from +550 °C down to −100 °C and of ±1 °C from −100 °C down to −170 °C.

The ΔT sensor is a special glass disk supporting the thin film evaporated gold/nickel thermopile and the sample and reference cups. Gold/nickel thermocouples have shown not to suffer from calibration drift by ageing.

EXPERIMENTAL

It is the purpose of this paper to demonstrate the ease and convenience of operation of a novel cooling system but since this cannot end in itself also the positive consequence on the quality of quantitative DTA-measurements shall be illustrated in the following.

A standard low temperature DTA experiment is carried out as follows:

The sample is enclosed in a gas-tight aluminium crucible which has a volume of 40 µl. The crucible is placed on the DTA measuring head at any temperature above the dew-point. The DTA cell is then closed. The DTA cell is permanently flushed with dry purging gas which enters the DTA cell at exactly the furnace temperature and therefore does not influence the DTA measurement. Then the DTA cell is quench- or program-cooled to the lower starting temperature of the experiment. The experiment is started by pushing one of the different program push-buttons. As mentioned before the cooling system does not need any attendance.

The accuracy of all DTA measurements is limited by the baseline quality. An excellent baseline typical for the TA 2000 low temperature DTA cell is shown in Fig. 3.

In the following a few typical industrial applications for low temperature DTA are given with the corresponding DTA traces.

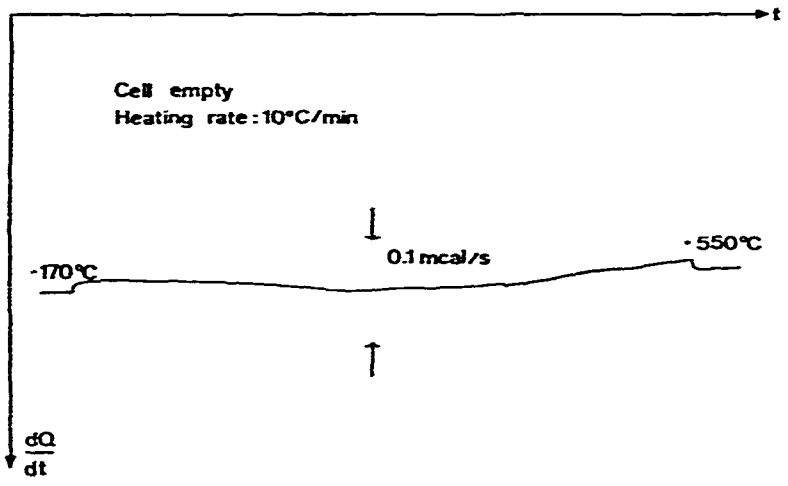

Fig. 3. Typical baseline −170 to +550 °C.

The application of low temperature DTA to the polymer field is one of the successes of this technique. One of the main interests of the polymer chemist is in the assignment of a temperature to the glass transition. The DTA trace of natural rubber in the temperature region of the glass transition is shown in Fig. 4. Low temperature DTA has been used extensively in the study of oils and fats. The effect of different

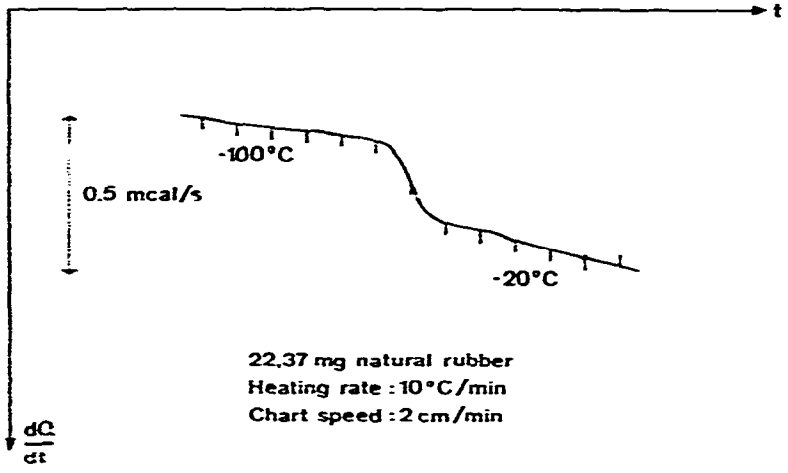

Fig. 4. Glass transition of natural rubber.

rates of cooling on the melting phenomena and polymorphism of fats are studied. It is of interest to note that some authors recommend that the cooling DTA curve be used for the identification of fats because it is essentially simpler than the melting curve since polymorphic effects do not seem to occur. Figure 5 represents the "fingerprint" of a vegetable oil which can be used for its identification.

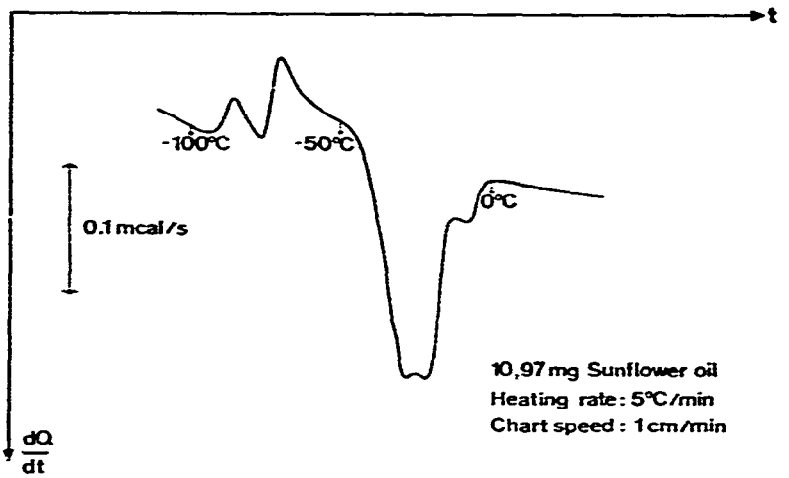

Fig. 5. DTA "fingerprint" of sunflower oil.

By using a high quality low temperature DTA instrument purity determination of organic solvents eliminates some of the uncertainties met with in gas chromatography. Figures 6 and 7 represent the melting curves of a pure and an impure sample of n-hexane. A well-introduced method[3,4] determines the purity of organic substances by a computer-aided analysis of the shape of the melting curves.

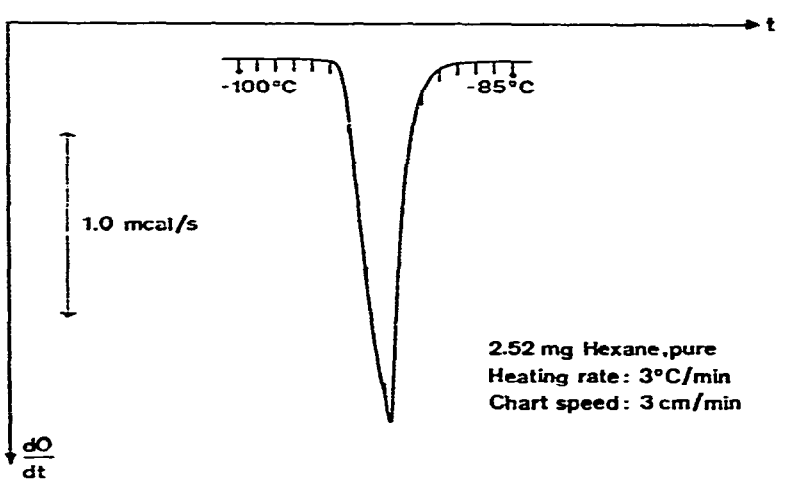

Fig. 6. DTA trace of a sample of pure n-hexane.

Low temperature DTA has found wide application in the investigation of organic and inorganic materials. Three classes can be distinguished, namely: second-order transitions; specific heat measurements; and phase studies on mainly binary mixtures. Figure 8 shows two solid–solid transitions of cyclopentane at −152.5 and

−135.0°C as well as the melting endotherm at −96.0°C. The somewhat low melting temperature indicates an impure substance. Figure 9 finally shows the second-order transition of KH_2PO_4 with a maximum conversion-rate at −153.4°C.

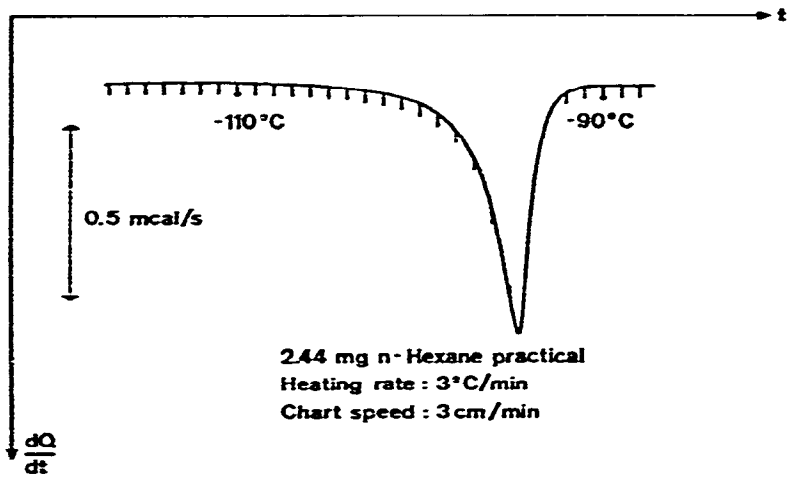

Fig. 7. DTA curve of impure n-hexane.

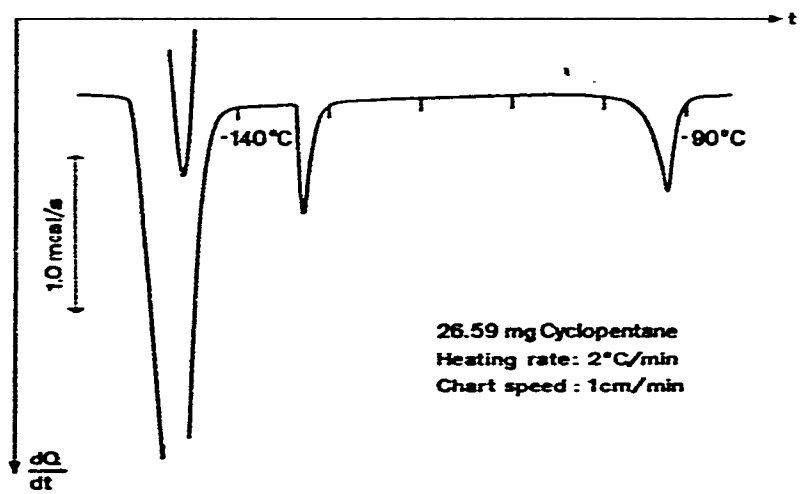

Fig. 8. DTA curve of impure cyclopentane (solid–solid transitions at −152.5 and −135.0°C; melting endotherm at −96°C).

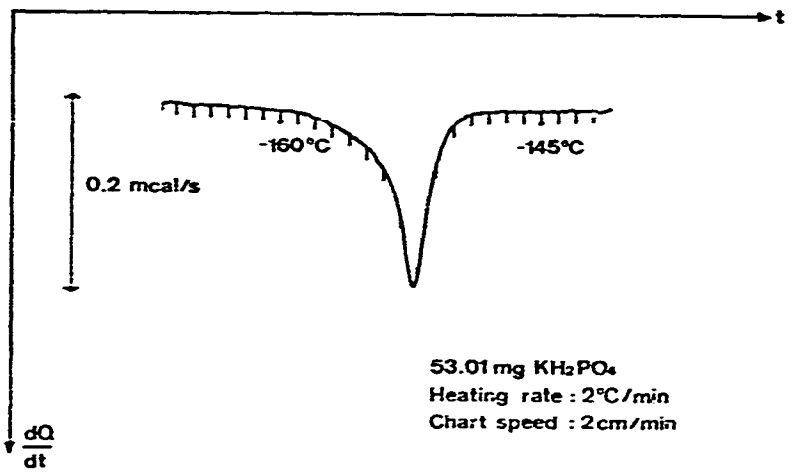

Fig. 9. Second-order transition of KH_2PO_4.

REFERENCES

1 R. L. Bohon, *Proc. Toronto Symp. Therm. Anal. 3rd*, 33 (1969).
2 J. P. Redfern and B. L. Treherne, *Thermal Analysis*, Vol. 1, *Proc. Int. Conf. Therm. Anal., 3rd.* 55 (1971).
3 Mettler Information TA 2000, No. 1, 1973.
4 Mettler Information TA 2000, No. 3, 1974.