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A DTA SYSTEM WITH SIMPLE "TRIAC CONTROL" AND ITS APPLICATION IN LABORATORY COURSES AND RESEARCH

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ABSTRACT

In order to make DTA accessible to a larger group of interested people a new simple DTA concept was developed. Without large-scale electronics linear changes of temperature in the range of + 20 to + 1000°C are realized. The system seems to be suitable for both laboratory courses and research. Constructional features, the mode of operation and a selection of different DTA curves are reported.

INTRODUCTION

Linear temperature changes in DTA systems are usually achieved by an electronic attachment. As a rule, this unit raises the price of DTA equipment considerably, so restricting the application of this important and informative method to larger research laboratories. To make DTA accessible to a larger group of interested people, a new concept was developed, which allows good quality DTA measurements in a temperature range of + 20 to + 1000°C without large-scale electronics[1]. The easy operation and low cost of this compact DTA equipment makes it a valuable instrument especially for use in laboratory courses, but also in many research applications.

In the first part of this paper constructional features and the mode of operation will be described. In the second part a selection of various measurements is reported. These may show that the apparatus and method described are not a step back from the century of high technical standards to the "Middle Ages".

CONSTRUCTIONAL FEATURES, MODE OF OPERATION

The main difference to conventional DTA instruments is the use of a system which is "slow" with respect to the transfer of heat from oven to sample and reference. Figure 1 shows a schematic comparison between a conventional DTA system and the "Triac-controlled" system. In a conventional system (I in Fig. 1) control of the current consumption of the DTA furnace is achieved by an electronic unit with a thermocouple as feedback near the heating element. To produce constant temperatures or time-linear temperature changes without undulation, the system must have a low thermal

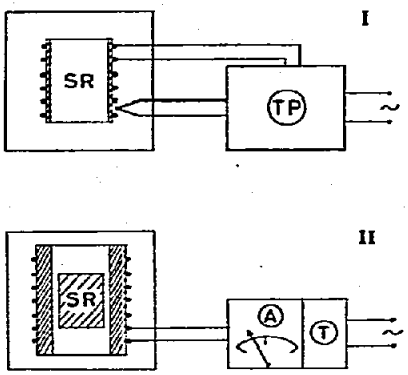


Fig. 1. Schematic comparison between a conventional DTA system (I) and the "Triac-controlled" system (II). S, sample; R, reference; TP, temperature programming attachment; T, Triac-controlled power supply; A, ammeter.

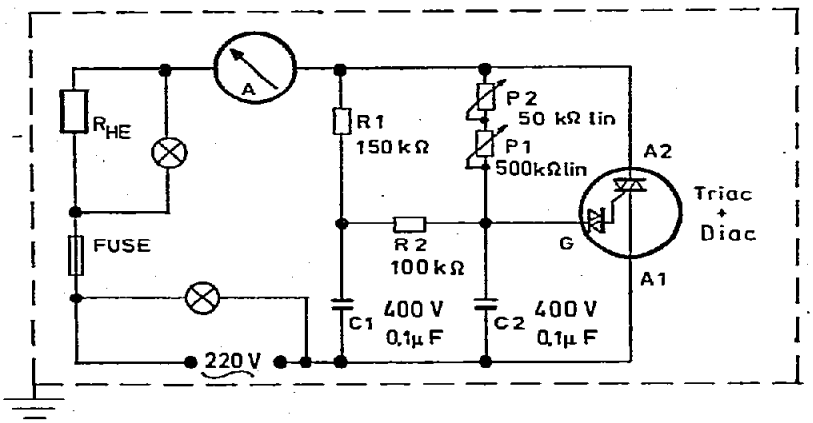


Fig. 2. Circuit of the Triac-controlled power supply. Internal resistance of the heating element (R_{HE}) ~ 25 Ω.

inertness, i.e., transfer from oven to sample (S) and reference (R) must be fast. In other words, the temperature of the furnace is nearly equal to the temperature of the sample and reference at any time of the temperature program.

In order to save the electronic temperature control unit, just the contrary conditions have to be met (II in Fig. 1). The furnace consists of a bifilar (induction-free) winding of a nicrothal heating element, which is fixed on a thick-walled crucible of oxidic material. A ceramic block inside the crucible contains the sample (S) and reference (R). A pre-set constant power output from a Triac-controlled power supply (circuit depicted in Fig. 2) to the heating element induces a change of temperature at the positions of sample and reference inside the DTA cell, which is linear within a broad temperature and time range and without any undulation. Different heating rates are obtained by variation of the pre-set current. A selection of some characteristic changes in temperature vs. time curves obtained with a "Triac-controlled" DTA system is given in Fig. 3.

Figure 4 shows a schematic drawing of the complete table-top DTA. The lower part of the system contains the Triac circuit and the ammeter, the zero-point reference,

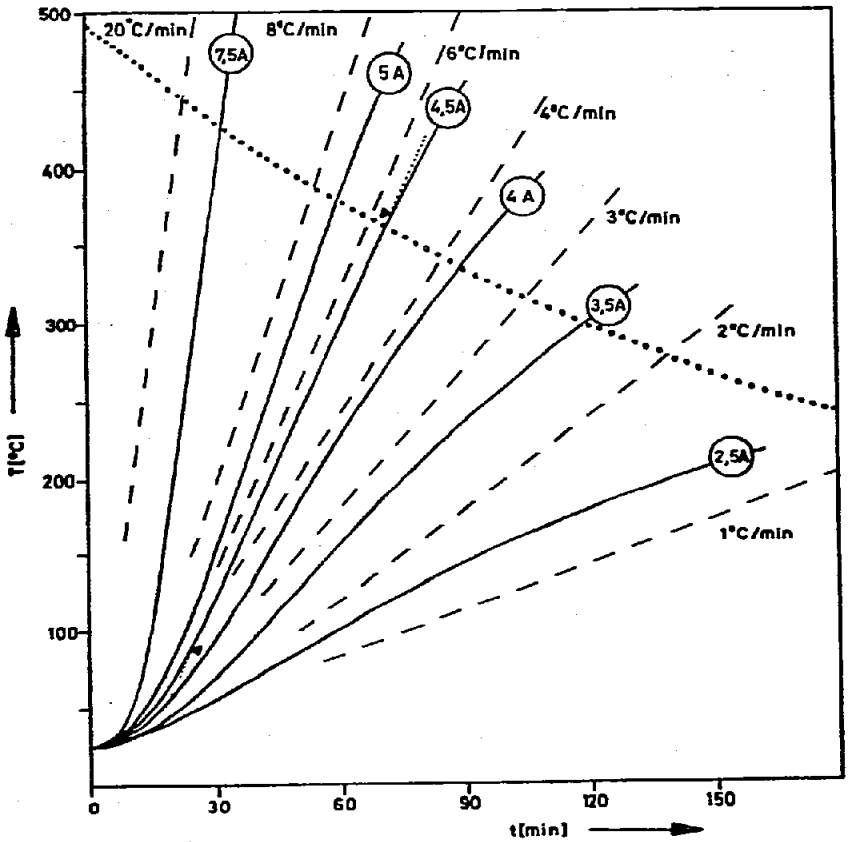
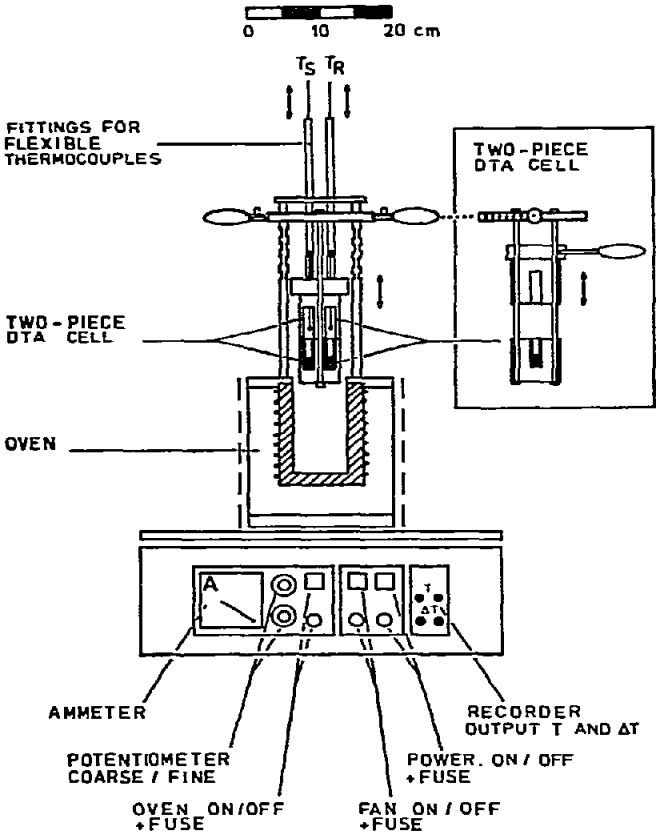


Fig. 3. A selection of some characteristic changes of temperature vs. time curves obtained with a "Triac-controlled" DTA system. The parameter given is the current. By pre-selection of, for example, 4.5 A there is a linear heating rate of 6 °C min^{-1} from 90 to 360 °C (arrows). The dotted line shows cooling of the closed DTA system from ~ 500 °C.

a fan, the T_s-(temperature of the sample) and ΔT-(DTA) output. On top of this unit a heat insulator and the DTA furnace are mounted. The upper part of the system consists of two guide rods which allow movement of the ceramic DTA cell in a vertical direction. In its lowest position the DTA cell is completely inserted in the furnace; in its uppermost position the DTA cell is accessible to be filled with sample and reference. Intermediate positions of the DTA cell and additional use of the fan allow various cooling rates from elevated temperatures.

The DTA cell (Fig. 4) consists of two parts: the lower part contains two sleeves of metal inserted in respective bores; on top of the upper part two fittings for flexible thermocouples (Ni/NiCr) reach into the metal sleeves.

To fill the DTA cell with sample and reference, the upper part is lifted and fixed at a special rod. Tubes containing sample and reference (Fig. 5) are inserted into the sleeves of metal in the lower part of the DTA cell and the thermocouples are put into special tube fittings. The two-piece DTA cell is then reassembled and completely inserted into the furnace without running the risk of unintended altering of the positions of the thermocouples. By pre-selection of a constant current a DTA meas-



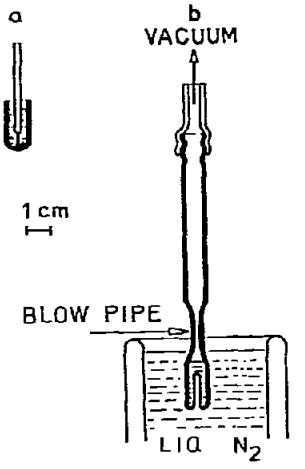


Fig. 4. Schematic drawing of the complete table-top DTA system.

Fig. 5. Sample tubes (quartz glass) with fittings for thermocouples. a, Used for DTA measurements in "open" systems; b, used for DTA measurements in "closed" systems.

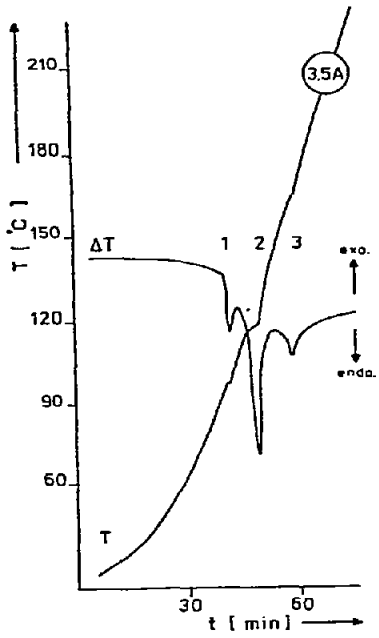
urement can now be started. The signals T_s and ΔT are recorded by an appropriate conventional two-channel recorder.

A SELECTION OF DTA CURVES OBTAINED WITH THE "TRIAC-CONTROLLED" DTA SYSTEM

The use of completely prepared and re-usable samples with well-known reproducible thermal effects proves to be very favourable in laboratory courses with demonstrative DTA experiments. Four respective examples (DTA of S, Se, Te and Tl) are given below, all samples being sealed in DTA tubes of quartz glass.

Figure 6 shows the DTA curve of sulphur. There are three endothermic peaks: at 96 °C the transformation α-S $\rightarrow$ β-S takes place and is followed by melting of β-S at 119 °C. The third effect at $\sim$ 160 °C represents the transformation in the melt from fluid to viscous.

In Fig. 7 the DTA curve of vitreous selenium is given. The first endothermic peak at $\sim$ 48 °C corresponds to softening of vitreous selenium. At temperatures $>$ 100 °C, and depending on the heating rate, exothermic transformation to trigonal selenium takes place, and at 223 °C melting of trigonal selenium is observed.



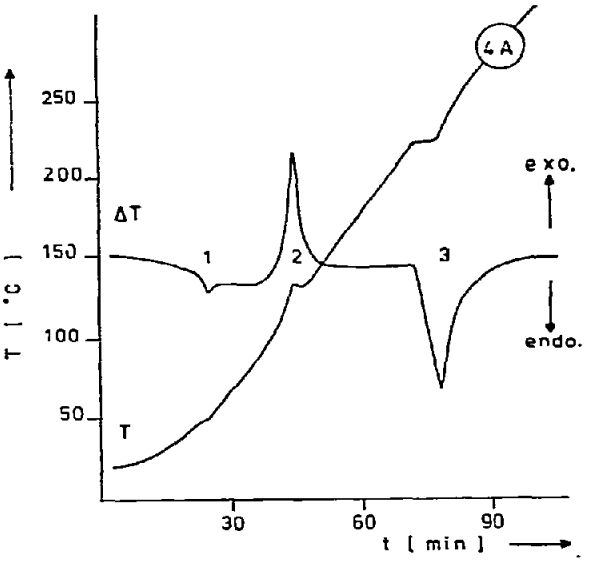


Fig. 6. DTA of sulphur. Closed tubes; weight-in, 1.20 g S; reference material, Te; ΔT-sensitivity, 1 mV; thermocouples, Ni/NiCr.

Fig. 7. DTA of selenium. Closed tubes; weight-in, 2.66 g Se; reference material, Te; ΔT-sensitivity, 1 mV; thermocouples, Ni/NiCr.

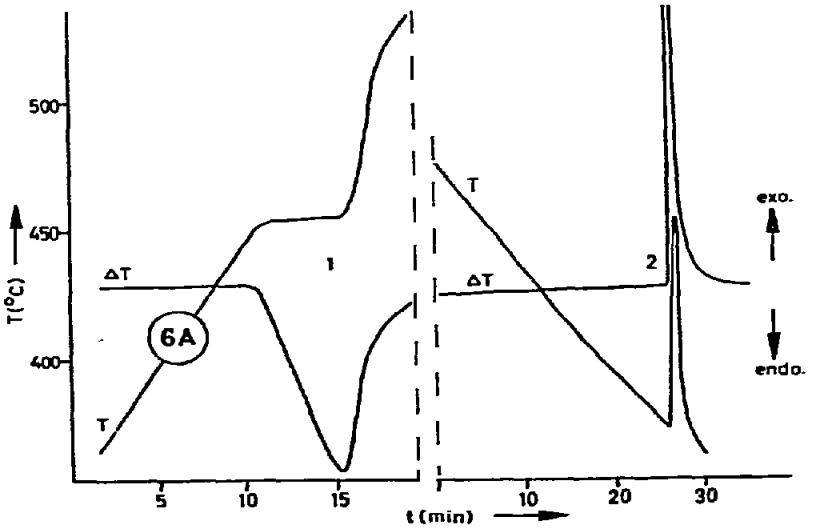
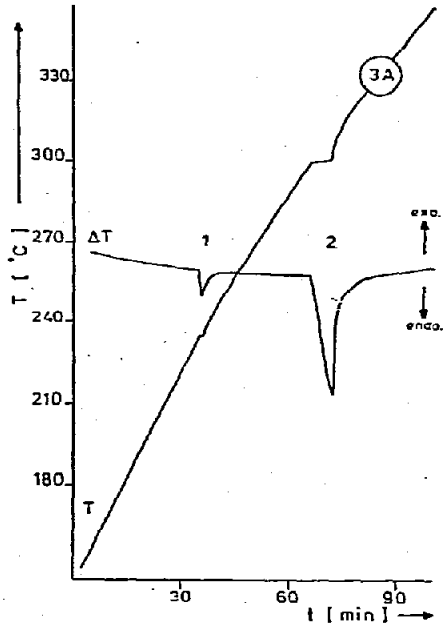


Fig. 8. DTA of tellurium. Closed tubes; weight-in, 3.30 g Te; reference material, Sb; ΔT-sensitivity, 1 mV; thermocouples, Ni/NiCr.

Figure 8 shows the DTA curve of tellurium during heating and cooling. At 453 °C melting of tellurium is recorded and solidification of tellurium during cooling is observed with large supercooling.

Figure 9 contains the DTA curve of thallium during heating. At 235°C a solid state transformation α-Tl (hexagonal) → β-Tl (cubic) is recorded. The high



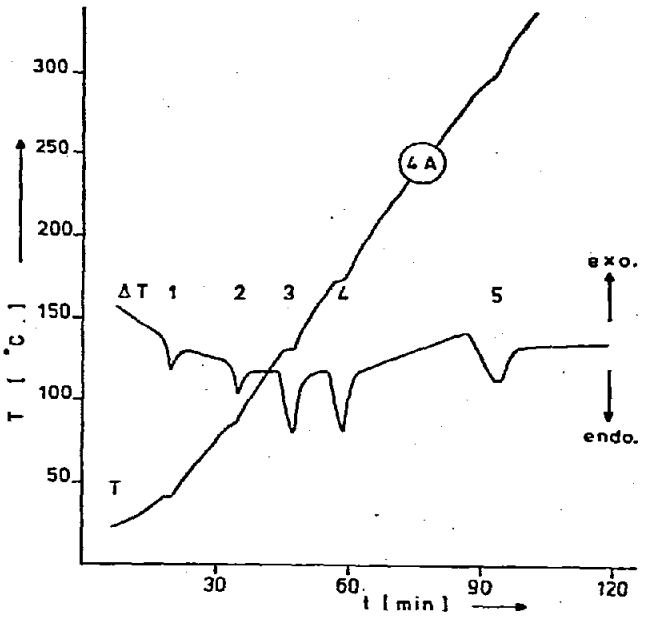
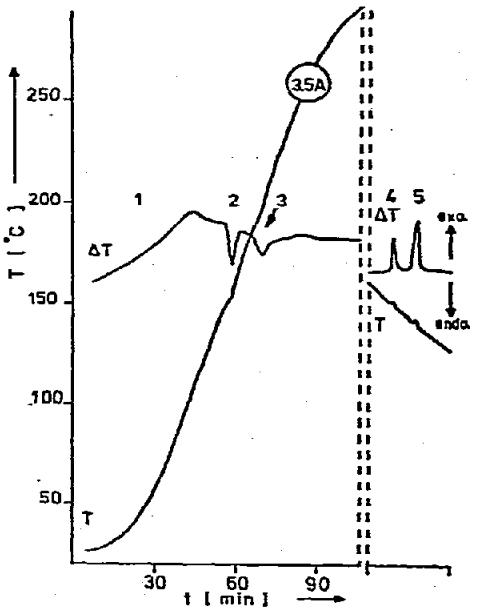


Fig. 9. DTA of thallium. Closed tubes; weight-in, 6,4 g Tl; reference material, Sb; ΔT-sensitivity, 1 mV; thermocouples, Ni/NiCr.

Fig. 10. DTA of NH_4NO_3. Open tubes; weight-in, 0.94 g NH_4NO_3; reference material, Al_2O_3; ΔT-sensitivity, 1 mV; thermocouples, Ni/NiCr.



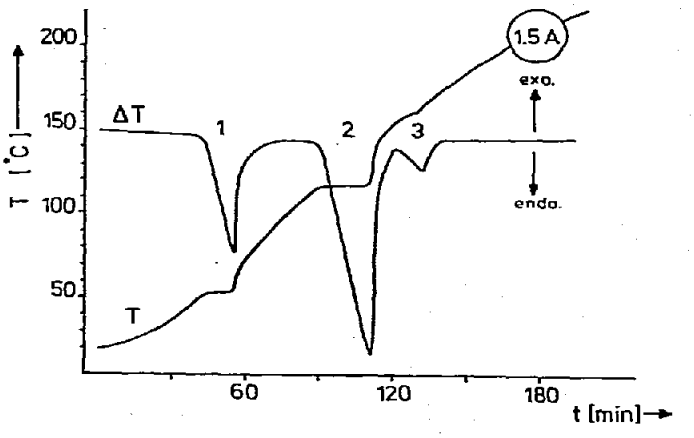


Fig. 11. DTA of the reaction $3\ SnI_2 + 2\ TeI_4 \rightarrow 2\ TeI + 3\ SnI_4$. Closed tubes; weight-in, mixture of 1.65 g SnI_2 and 1.92 g TeI_4; reference material, Te; ΔT-sensitivity, 1 mV; thermocouples, Ni/NiCr.

Fig. 12. DTA of $Na_2PHO_3 \cdot 5H_2O$. Open tubes; weight-in, 1.05 g $Na_2PHO_3 \cdot 5H_2O$; reference material, Al_2O_3; ΔT-sensitivity, 1 mV; thermocouples, Ni/NiCr.

temperature modification melts at 303 °C and solidifies during cooling without supercooling. The reversible phase transformation to α-Tl is slightly supercooled.

Another example suitable for an illustrative DTA experiment — in this case in an "open system" — is the DTA curve of NH_4NO_3, which is given in Fig. 10. There are three endothermic phase transformations in the solid state at ~ 42, 85 and 127 °C, which belong to the transformations, orthorhombic I → orthorhombic II → tetragonal → cubic. The cubic phase melts at 170 °C and at temperatures ≥ 283 °C decomposition of the melt takes place.

The last two examples of DTA measurements with the "Triac-controlled" system belong to different fields of our recent research work in inorganic and structural chemistry.

Figure 11 shows the DTA curve of the reaction

$$3\ SnI_2 + 2\ TeI_4 \rightarrow 3\ SnI_4 + 2\ TeI$$

which is part of a systematic study of ternary systems Sn–Te–X (X = Cl, Br, I)[2]. The exothermic reaction takes place in the solid state and is finished at about 100 °C. Melting of the reaction products is observed at 144 °C (SnI_4) and 183 °C (TeI). In the course of cooling from the melt slightly supercooled solidification of SnI_4 and TeI is recorded. The products were identified by their X-ray patterns.

Figure 12 gives the DTA curve of $Na_2PHO_3 \cdot 5H_2O$[3]. There are three endothermic peaks: incongruent melting of $Na_2PHO_3 \cdot 5H_2O$ at 53 °C, evaporation of water, and formation of a new intermediate phase $Na_2PHO_3 \cdot 0.5H_2O$ at 114 °C. Dehydration of the new hemihydrate is observed at temperatures > 150 °C. These results are confirmed by TG measurements. The phases are identified and characterized by their X-ray patterns.

CONCLUSIONS

Besides the main fact, that real good quality DTA measurements can be made with this simple "Triac-controlled" DTA equipment, it should be noted that there is no undesirable "black-box" effect, that the operation is very easy and that it is nearly impossible to destroy the apparatus (even the thermocouples). Because of the low cost of the system simultaneous use of several DTA units appears possible. These facts make the "Triac-controlled" DTA equipment a valuable instrument for use in laboratory courses[4] as well as in the field of research work.

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