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The possibility of manufacturing a single-pan differential thermal analyzer unit

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Abstract

The use of a single-pan differential thermal analyzer (DTA) unit is proposed in this paper based on the experimental results and justified from the theory for DTA units. Such a design would simplify the construction and operation of DTA units. A basic requirement for this kind of design is the accurate measurement of sample temperature. It would also make the design of simultaneous TGA (thermogravimetry analyzer)–DTA units more robust and less likely to mechanical breakage.

Keywords: Coupled technique; DTA; Instrument; TGA

1. Introduction

In the present design of DTA units, two pans are used, one for the sample and the other labeled the reference pan. This may be used empty or filled with a reference material. The temperature difference between the sample and reference pans is recorded as the ΔT signal against the temperature of the sample pan. Clearly, if no reaction or transition occurs in the sample, then the sample pan temperature can be programmed most often under a controlled heating condition. There is a perturbation of this signal when a transition occurs. In equipment using Boersma-type pans [1], a heat flux is present which can be harnessed by calibration

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to produce a quantitative DTA unit which in present nomenclature usage is termed a heat flux differential scanning calorimeter (DSC). However there is an alternative method of making such equipment quantitative, namely power-compensated DSC, in which electrical energy is introduced into either the sample or the reference pan to keep their temperatures identical.

Based on the fact that a projected baseline could in theory be established, then a ΔT signal can be generated as the difference between the perturbed sample pan temperature and such a baseline. Equipment is, however, available commercially which allows experimental testing of such theories. In the present study, such experimental evidence is provided and backed by theoretical justifications.

2. Experimental

A simultaneous TGA and DTA unit (TA SDT 2960) was used throughout this paper. In the design of this equipment, the temperature difference between the two pans is recorded as the DTA signal (ΔT) while the temperature of the sample pan is taken as the sample temperature (T). Fig. 1 shows the schematic arrangement needed to obtain the sample temperature and ΔT. In the unit, two thermocouples are in contact with the sample and reference pans and are located at the end of the balance.

The experimental data for calcium oxalate monohydrate were provided from the TA Instrument company as demonstration data, while other experimental data were detained using a mixture of calcium hydroxide and calcium carbonate (analytical grades from Fisher) at a ratio of approximately 60:40. The reference used in the demonstration data and one of the experiments for the mixture was calcined aluminum oxide (previously heated to 950°C). Other experiments on the mixture were carried out without reference or reference pan. The heating rate used in the

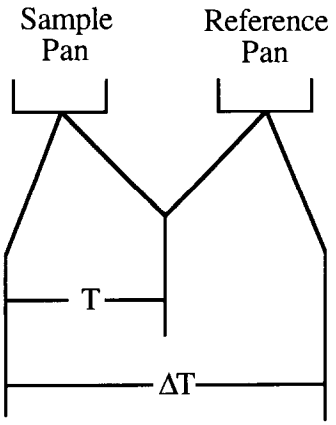

Fig. 1. Schematic DTA system.

demonstration data was 20°C min^{-1} and in the other experiments 10°C min^{-1}, in a flowing nitrogen atmosphere (flow rate, 50 ml min^{-1}). The sample size was 56 ± 1 mg placed in a platinum crucible.

3. Results and discussion

The reason for including the calcium oxalate monohydrate results from a demonstration file is simply to show that the manipulative exercises on the data used here can be carried out on all data obtained from this unit and is not just confined to data processed in our own laboratory. The experimental data for the TGA and DTA curves of calcium oxalate monohydrate and the mixtures are shown in Figs. 2, 3 and 4. The three typical steps for the decomposition of calcium oxalate monohydrate can be easily seen in Fig. 2 (demonstration data supplied by TA Instruments) and the same comment applies to the two steps for the decomposition of calcium hydroxide and calcium carbonate shown in Figs. 3 and 4.

In the case of the mixture of $Ca(OH)_2$ and $CaCO_3$ shown in Fig. 3, no reference pan was used, i.e. the experiment represents a run with two thermocouples but no reference pan. This may be compared with a reference pan containing alumina as the reference material (Fig. 4). There is no significant difference between Figs. 3 and 4. The peak analysis results for the two DTA peaks of these figures are listed in Table 1. From the results, it can be seen that there is a very slight temperature shift

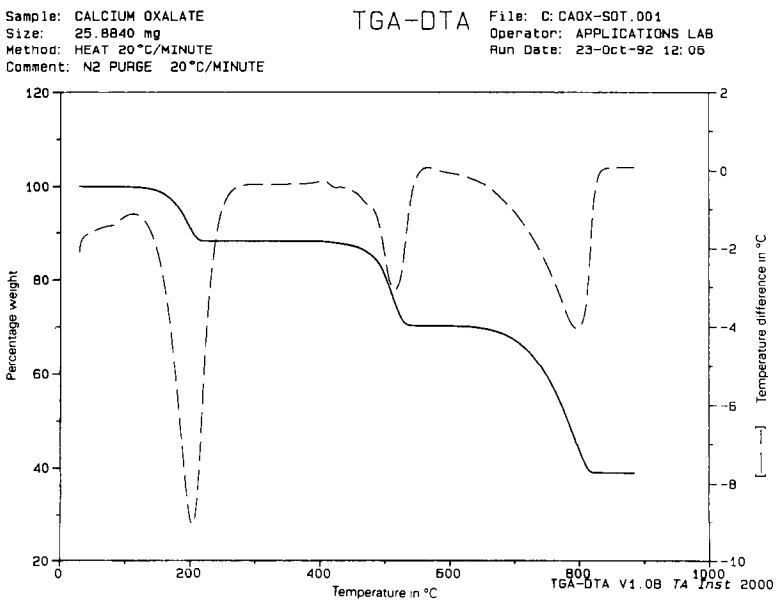

Fig. 2. TG and DTA curves for calcium oxalate monohydrate (data supplied by TA Instruments).

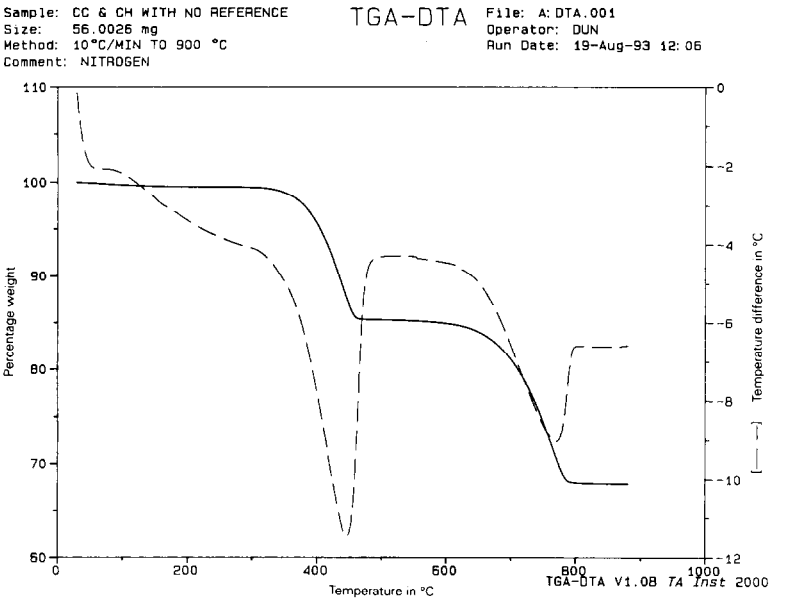

Fig. 3. TG and DTA curves for calcium hydroxide and calcium carbonate mixture without reference pan.

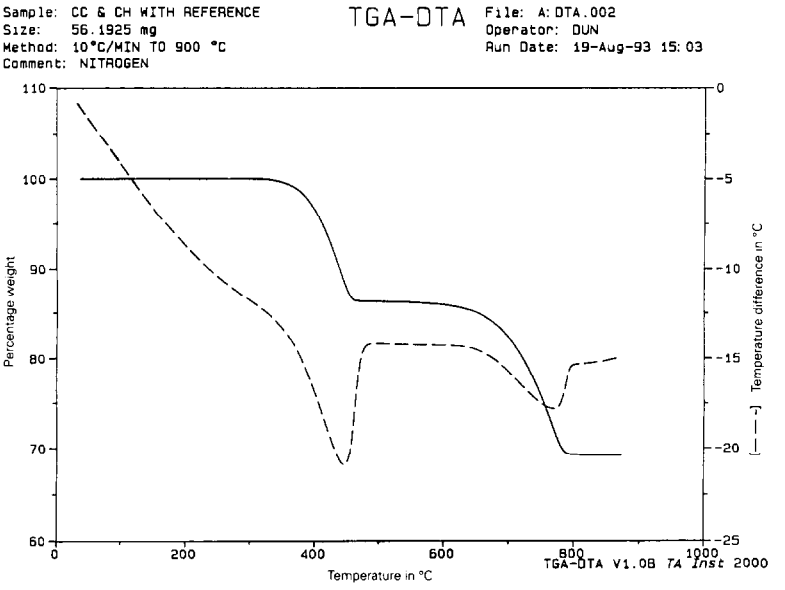

Fig. 4. TG and DTA curves for calcium hydroxide and calcium carbonate mixture with reference pan.

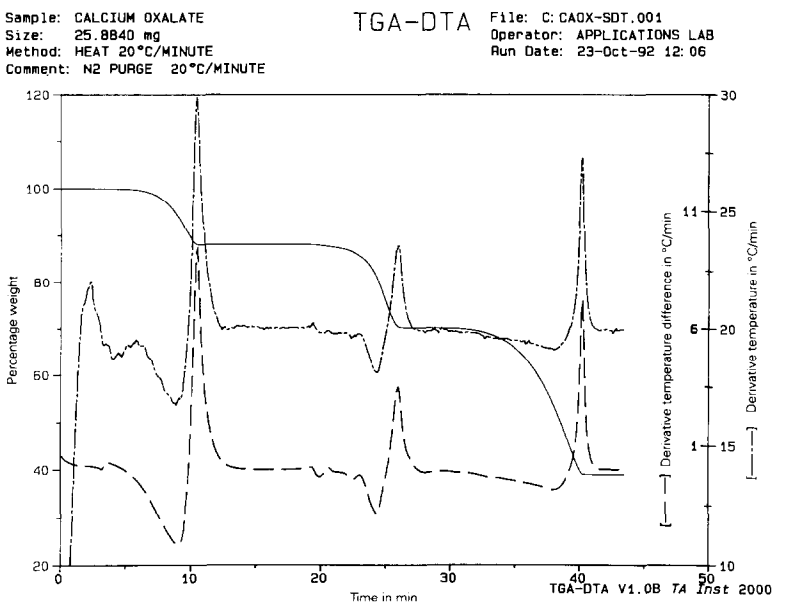

Fig. 5. First derivative plots of both DTA and heating curves against time with their TG curves for calcium oxalate monohydrate (data supplied by TA Instruments).

(<0.3%) in the peak temperatures for both calcium hydroxide and calcium carbonate. Where the peak area is concerned, the results show that there is an increase in the peak area when no reference pan is used. By taking the ratio of the peak areas for calcium hydroxide and calcium carbonate between the two conditions, it is found that the peak areas are increased at the same extent when no reference pan was used which indicates an increase in the signal output. At the same time, the ratio of peak areas between calcium hydroxide and calcium carbonate is unchanged which confirms that the change in the peak area is related to the use of reference material. Therefore there is no point in using a pan containing a reference material or even an empty pan. The data obtained without the use of a reference pan are as good as those from any other technique showing that, on this unit, it is only necessary to operate with a single pan to record the temperature difference signal from the two thermocouples.

It was thought that it would be instructive to determine if a derivative plot based on the plot of the sample temperature against time would produce data which would give the same information as the derivative plot of ΔT against time t. For this purpose the first derivative of the heating curve ($T-t$) was compared with the first derivative of the DTA curve ($\Delta T-t$). Fig. 5 shows plots for the demonstration data on calcium oxalate monohydrate superimposed over the TGA plot. The scales for the first derivative plot of the heating curve have been chosen so that it coincides in magnitude with the first derivative plot of the DTA curve. It can be seen that they coincide very well except for the initial "warm up" period. Figs. 6

Table 1
DTA peak information for calcium hydroxide and calcium carbonate mixtures

	Sample size/mg	Peak temperature/°C		Peak area/(°C min)	
		$Ca(OH)_2$	$CaCO_3$	$Ca(OH)_2$	$CaCO_3$
Without reference	56.0026	446.69	762.44	47.37	25.81
With reference	56.1925	447.08	765.04	39.63	21.59

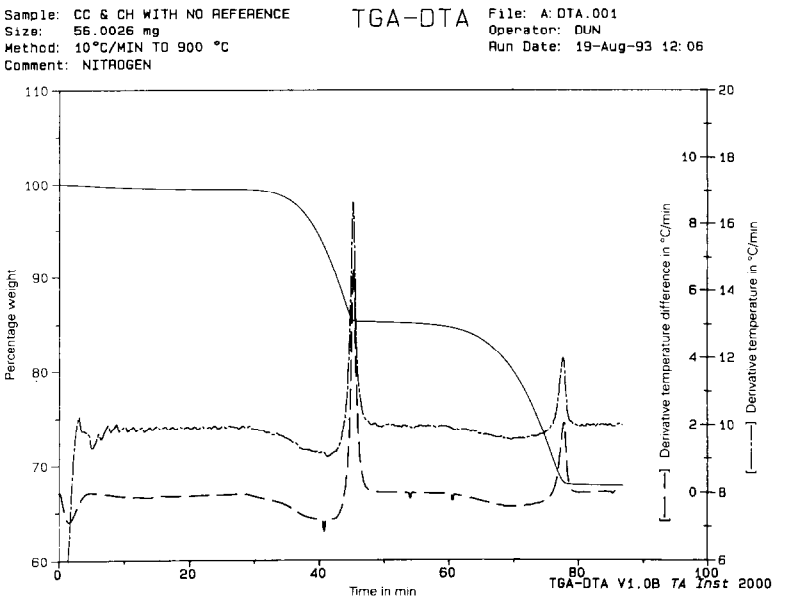

Fig. 6. First derivative plots of both DTA and heating curves against time with their TG curves for calcium hydroxide and calcium carbonate mixture without reference pan.

and 7 show a similar successful comparison for calcium hydroxide and calcium carbonate mixtures for the first derivative plots of the DTA curve and the first derivative of the heating curve, based on the data portrayed in Figs. 3 and 4. This identity of the first derivative plots suggests that DTA plots for the samples shown in Figs. 1–3 should coincide with plots of $\Delta T = T - \beta t$ (where β is the heating rate) obtained from the heating curve. This is demonstrated in Fig. 8 for calcium oxalate monohydrate where the ΔT obtained from the heating curve plot is compared against the conventional DTA signal. This shows an identity between the DTA signal obtained in the usual manner and that obtained from a single sample pan, single thermocouple data. Similar data are shown in Figs. 9, 10 and 11 for the calcium hydroxide and calcium carbonate mixtures. Fig. 10 is a rescaled version of Fig. 9 in order to show the identity more clearly. This proves that it is possible

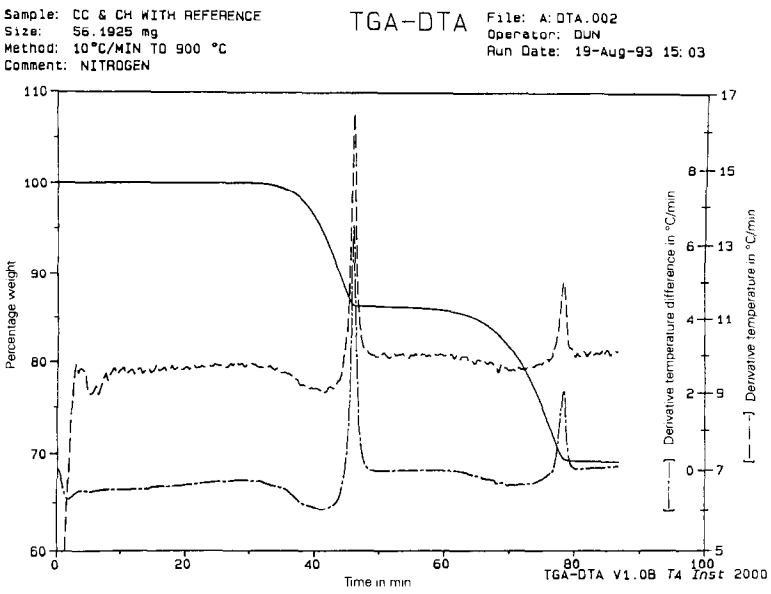

Fig. 7. First derivative plots of both DTA and heating curves against time with their TG curves for calcium hydroxide and calcium carbonate mixture with reference pan.

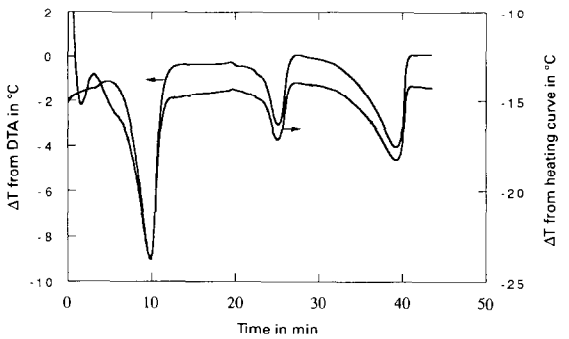

Fig. 8. ΔT plots from both DTA and heating curves for calcium oxalate monohydrate.

to obtain DTA curves using only one thermocouple under different heating conditions.

From the above discussion, it can be seen that the DTA signal can be obtained by treating the heating curve of the sample, thus eliminating the need for a reference pan and a second thermocouple. It is believed that this is the first time that a single pan, single thermocouple DTA plot has been obtained using commercial instrumentation. It is however in accord with the theory of DTA where ΔT is simply the difference between the temperature baseline and the sample temperature.

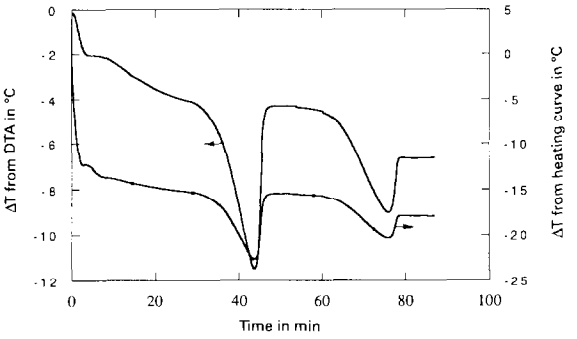

Fig. 9. ΔT plots from both DTA and heating curves for the mixture without reference.

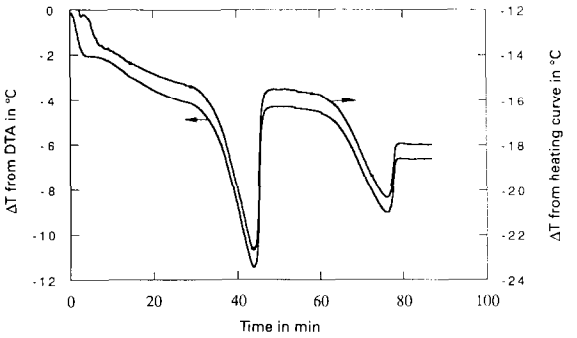

Fig. 10. Rescaled plot of Fig. 9.

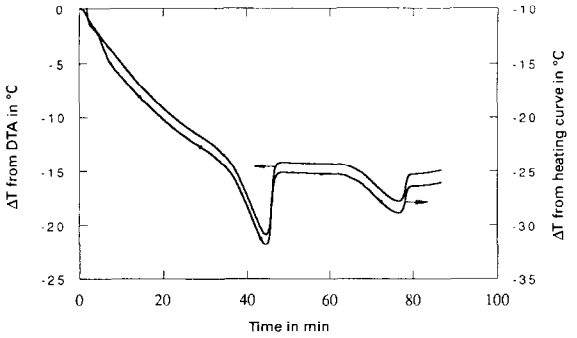

Fig. 11. ΔT plots from both DTA and heating curves for the mixture with reference.

4. Conclusions

It is shown that the simultaneous TGA and DTA unit (Thermal Analyzer SDT 2960) can provide, through the existing programs and without modification, all that is necessary to obtain DTA curves employing only a single sample pan and the data

from the sample thermocouple. The accuracy of measuring the sample temperature in such experiments is very important and the "warm up" period is still a problem. However the concept of a single pan, single thermocouple design can be realized, as demonstrated here, with existing equipment. Further improvement on calculating the temperature difference signal is possible. In the use of simultaneous TGA–DTA equipment, this concept should allow a great simplification in the design of the equipment resulting in more robust equipment.

Reference

[1] S.L. Boersma, J. Am. Ceram. Soc., 38 (1955) 281–284.