ESTIMATION OF STABILITY TEMPERATURES FROM DIFFERENTIAL THERMAL ANALYSIS AND THERMAL ACTIVITY MONITOR DATA IN COMBINATION

M W Whitmore
AgrEvo Ltd, Chesterford Park, Saffron Walden, Essex CB10 1XL, UK

Many methods for determining stability temperatures exist but most have practical disadvantages arising from scale, cost or time. Data is presented which shows that reasonable estimates of stability temperatures can be obtained by combining differential thermal analysis and thermal activity monitor data. This offers a quick and inexpensive small-scale method which can be useful in overall strategies for determining stability temperatures.

Key Words: differential thermal analysis: differential scanning calorimetry: thermal activity monitor: self-accelerating decomposition temperature.

INTRODUCTION

A knowledge of stability temperatures is necessary for the safe handling of exothermically unstable materials. With respect to transport, the critical parameter defined by the United Nations (UN) is the 7-day self-accelerating decomposition temperature (SADT)(1). Whilst SADT is not universally the most useful measure, SADTs comprise much of the stability temperature data found in the literature and the principle of its estimation is general. It is taken, therefore, as the basis of discussion here.

UN Recommendations(2) describe four methods for SADT: the United States (US) SADT test(3); the isothermal storage test (IST)(4); the adiabatic storage test (AST)(5) and the heat accumulation storage test(6). In addition, adiabatic Dewar tests are available(7,8) and a g-scale adiabatic storage device, the self-ignition tester (SIT), has been described(9) which appears to give reasonable agreement with other methods(10,11).

There is no shortage of methods, therefore, but those mentioned suffer one or more of the following disadvantages: large samples required; lengthy and expensive. Because of these drawbacks they are not ideal for use early in development when material definition and quantities are limited, or when high value materials are being considered. Consequently there is interest in relatively quick and inexpensive small-scale methods for estimating SADT.

One approach is to estimate stability temperatures from the correlation of small-scale exotherm onset temperatures with large-scale stability temperatures.

Differential scanning calorimetry (DSC) and differential thermal analysis (DTA) are probably the techniques most widely used in this way(12) but a number of commercial or in-house g-scale tests are also employed(13,14,15). The usefulness of this approach is limited because, since it relies on generalised extrapolation, wide safety margins are required. With DSC or DTA, for example, the '100 degree rule' is often applied and even this wide margin can be questioned(16).

The use of accelerating rate calorimeter (ARC) data to estimate SADT(17,18) offers better precision because the extrapolation is specific rather than general and is over a narrower temperature range. Even so, it can be argued that the necessary safety margins are wide in relation to the precision required(19).

INTERPOLATIVE ESTIMATION OF STABILITY TEMPERATURES

Generally, interpolation is preferable to extrapolation because the scope for error due to invalidity of the model being used is reduced.

In estimating stability temperatures, the possibility of interpolation is afforded by the thermal activity monitor (TAM). This is a high sensitivity isothermal calorimeter which is described in detail elsewhere (20). Essentially, it consists of measuring vessels enclosed in metal heat sinks which are kept at a highly stable temperature by being immersed in a large volume of water (25ℓ) under thermostatic control. The heat flow from the sample to the heat sinks is monitored by Peltier arrays.

With a sensitivity down to 10^{-4} W kg^{-1}, the TAM is easily capable of measuring heat outputs well below the heat loss factors of commercial packs (typically, 0.05 - 0.10 W kg^{-1} for 25 - 50 kg). Indeed, it can measure directly heat generation rates at the temperatures of interest for large masses of unstable materials(21).

In combination with the ARC, TAM has been used to provide interpolative estimates of SADT(22). Applied to a set of materials exhibiting diverse decomposition behaviours, a single TAM measurement combined with onset data from an ARC run gave estimates of SADT which were in better overall agreement with US SADT results than those obtained by extrapolating ARC data.

In principle, SADT could be estimated interpolatively by combining rate data from a number of tests. For example, in the ARC/TAM method(20), TAM data could be replaced by data from the UN IST. In practice, however, this is not attractive because the IST requires more sample, is probably more expensive and is less readily available. On the other hand, the combination of DTA (or DSC) and TAM data could have economic and practical advantages.

The comparison of DTA onset, ARC onset and TAM data is exemplified in Figures

1 - 3, in which power outputs (P W kg^{-1}) have been plotted in Arrhenius form. Overall the correspondence between the methods is reasonable. In particular, it is not evident that interpolating from DTA points rather than ARC points would introduce a consistent bias into SADT estimates.

ESTIMATION OF SADT FROM DTA AND TAM DATA

DTA measurements

These were performed using a Mettler TA 3000 instrument under self-pressurising conditions (stainless steel pressure crucible or glass ampoule) at a scanning rate of 2 K min^{-1} with a detection threshold of 0.2mW.

TAM measurements

Glass sample containers of 2 cm^3 volume with samples of approximately 1g were employed.

Commonly, TAM traces have the profile illustrated in Figure 4A. Thus, the power output stabilises and there is little doubt as to the value to be taken for calculation. However, this is not invariably the case.

Figure 4B, for example, represents the case where there is a rapid initial reaction in addition to the reaction represented by the subsequent steady power output. Provided the energy associated with the initial reaction is small (a few J g^{-1}), calculation as outlined below is probably still valid. Alternatively, both reactions may be taken into account as previously described(21).

In some cases a continually increasing power output (Figure 4C) is observed. In these instances, the calculation method given below cannot be applied and it is necessary to extend the time period of the measurement and conduct measurements at lower temperatures.

Calculation

1 DTA onset gives power output, P_o, at T_o °C

$P_o = 0.2/m$ W Kg^{-1}
where m = sample mass in g

TAM gives P_1 at T_1

2 Calculate apparent activation energy, E, from

$$E = [R(T_o + 273)(T_1 + 273)/(T_o - T_1)] \ln (P_o/P_1)$$

3 Calculate times to maximum rate at T_o and T_1 according to

$$t = R(T + 273)^2 C/PE$$

where C = specific heat (available from DTA run)

4 Plot ln t against $1/(T + 273)$, interpolate to the time constant, t_{con}, of the package and read-off the temperature of no return, T_{NR}. The following values of t_{con} were used: 25kg 8 hour, 50kg 10 hours; 135kg 16 hours.

5 Calculate SADT

$$SADT = T_{NR} - R(T_{NR} + 273)^2/E$$

Results

SADT estimates were made by the above method for the set of compounds, embracing a range of decomposition behaviour, previously used to examine the use of ARC and TAM data in combination. The results, together with ARC and ARC/TAM estimates of SADT and US SADT test results, are given in Table 1.

DISCUSSION

The method used for calculating SADT, previously employed elsewhere(17,20), is an approximate zero order Seminov-type solution to the problem of heat accumulation. Theoretically, its application to solids can be strongly challenged. However, for masses in the range 10-150kg, in our experience SADTs obtained in this way for solids agree closely with evaluations based on Frank-Kamenetskii critical parameters. Additionally, as time constants are similar for solids and liquids in small commercial packs (17), standardised values can be used and no additional data are required. Therefore, for estimations based on limited kinetic data, such a quick and simple procedure is considered appropriate for small commercial packs.

For other situations, more rigorous evaluation methods, such as those based on Frank-Kamenetskii critical parameters or transient models(21), are available. The Frank-Kamenetskii approach was usefully summarised recently, albeit in this case applied to extrapolated kinetic data(22).

The data of Table 1 show that the DTA/TAM estimates of SADT are in as good agreement with US SADT test results as the ARC/TAM estimates: there is no significant increase in bias or loss of precision associated with the use of DTA as opposed to ARC onset data.

On the basis that at DTA onset the zero order kinetics assumption involved in calculating SADT may be violated and that DTA onsets are rather imprecise, this conclusion could be regarded as surprising. However, it has already been shown (Figures 1-3) that the correspondence of DTA, ARC and TAM data shows no systematic bias between the techniques. Also, as the estimation is interpolative, the uncertainty in the estimated parameter may be less than in the measurement.

The robustness of interpolation with respect to precision can be illustrated by considering the case of sodium dichloroisocyanurate dihydrate (Figure 5). The error bar for the DTA point represents ± 3 standard deviations (5°C) or ± 15°C.
For a critical power output of 0.135 W kg^{-1}, this variation coupled with that in the TAM points leads to a variation of only ± 7°C in the critical temperature estimate. This treatment is not rigorous but neither is it misleading. Statistically derived confidence intervals are curved, being narrowest at the centroid of the data set(22). As a result, interpolated estimates may be more precise than the measurements upon which they are based.

Additional uncertainty can be caused by bias which in the present context would arise from a change in reaction mechanism. For instance, it has been shown that azodiisobutyronitrile probably starts to melt in the region of the ARC onset temperature(20). Therefore, the data of Figure 2 are probably better represented as two lines, one for the solid and one for the liquid, as shown in Figure 6. Even so, as has already been shown, interpolation results in negligible bias. On the other hand, the potential bias from extrapolation is obvious.

The accuracy required for stability temperature estimates depends upon how close they are to the temperatures a material is likely to experience. Where this gap is wide, the indications of DTA or DSC alone can be sufficient. Frequently, though, additional data is required and in our experience a TAM measurement at this stage can be very helpful. If further refinement is necessary, additional TAM data can be obtained or another technique, such as ARC, employed. In critical cases, resort to large-scale tests may be necessary.

CONCLUSION

The method of estimating stability temperatures described relies on approximations and assumptions which may be challenged but has been tested by application to a set of compounds with differing decomposition behaviours. It produced estimates of SADT which were in reasonable with US SADT test results. It, therefore, affords a realtively quick and inexpensive small-scale means of estimating stability temperatures which can be useful in overall strategies for determining safe handling temperatures for exothermically unstable materials.

ACKNOWLEDGEMENT

Thanks are extended to Dr F Lopez of Schering AG for helpful discussions.

REFERENCES

1 'Recommendations on the Transport of Dangerous Goods', 7th Edn. United Nations, New York, 1991, p.235.

2 'Recommendations on the Transport of Dangerous Goods, Tests and Criteria', 2nd Edn, United Nations, New York, 1990.

3 Ibid, p.189.

4 Ibid, p.200.

5 Ibid, p.194.

6 Ibid, p.205.

7 Grewer, T. and Klais, O., 1988, 'Exotherme Zersetzung', VDI-Verlag, Düsseldorf, p.36.

8 Rogers, R.L. and Wright, T.K., 1986 'EFCE Publication Series No. 50', Pergamon Press, Oxford, p.121.

9 Kotoyori, T. and Maruta, M., 1983, Thermochim. Acta, 67, 35.

10 Yoshida, T., 1987, 'Safety of Reactive Chemicals', Elsevier, Amsterdam, p.200.

11 Kotoyori, T., 1989, J. Loss Prev. Process Ind., 2, 16.

12 Reference 10, p.201 - 2 and 237.

13 Cronin, J.L. and Nolan P.F., 1987, J. Haz. Mater., 14, 293.

14 Cronin, J.L. and Nolan P.F. 1987, *Plant/Operations Prog., 6(2), 89.*

15 Cronin, J.L., 1987, PhD Thesis, South Bank Polytechnic (now South Bank University), London.

16 Hofelich, T.C. and Thomas, R.C., 1989, 'International Symposium on Runaway Reactions, March 1989, Boston Massachussetts', AIChE, New York, p.74.

17 Wilberforce, J.K., 1981, 'The Use of the Accelerating Rate Calorimeter to Determine the SADT of Organic Peroxides', Columbia Scientific Industries, Milton Keynes.

18 Fisher, H.G. and Goetz, D.D., 1991, J. Loss Prev. Process Ind., 4, 305.

19 Whitmore, M.W., 1992, J. Loss Prev. Process Ind., 5(5), 322.

20 Whitmore, M.W. and Wilberforce, J.K., 1993, J. Loss Prev. Process Ind., 6(2), 95.

21 Tharmalingum, S., 1989, 'International Symposium on Runaway Reactions, March 1989, Boston, Massachussetts', AIChE, New York, p.293.

22 Fischer, H.G. and Goetz, D.D., 1993, J. Loss Prev. Process Ind., 6(3), 183.

23 Caulcutt, R., 1983, 'Statistics in Research and Development', Chapman and Hall, London, p.140.

TABLE 1 COMPARISON OF SADT ESTIMATES WITH US SADT TEST RESULTS

	SADT/°C				Comparison		
Material/ Pack	US	ARC	ARC/ TAM[a]	DTA/ TAM[a]	US- ARC	US- ARC/ TAM	US- DTA/ TAM
1	39	35	38	33	4	1	6
2	64	54	52	60	10	12	4
3	49	45	46	52	4	3	-3
4	57	53	62	56	4	-5	1
5	90	88	83	72	2	7	18
6	115	130	109	111	-15	6	4
7	65	45	58	62	20	7	3
8	50	60	48	50	-10	2	0
9	50	-	48	50	-	2	0
mean difference					2.38	3.89	3.67
standard deviation					10.90	4.81	6.02

a From Reference 20

Key

1 t-Butylperoctoate (100%) 25ℓ
2 Acetylacetone peroxide (SA 3) 25kg
3 Lauryl peroxide 25kg
4 t-Butylperbenzoate 25kg
5 Di-t-butylperoxide 25kg
6 Azodicarbonamide 50kg
7 Sodium dichloroisocyanurate.$2H_{2}0$ 135kg
8 Azodiisobutyronitrile 25kg
9 2,2'-Azobis(2-methylbutyronitrile) 25kg

FIGURE 1 COMPARISON OF DTA (○), ARC (+) AND TAM (●) DATA

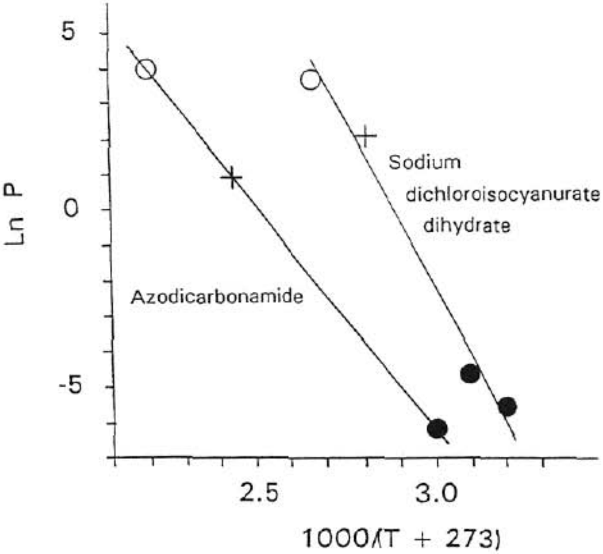

FIGURE 2 COMPARISON OF DTA (○), ARC (+) AND TAM (●) DATA

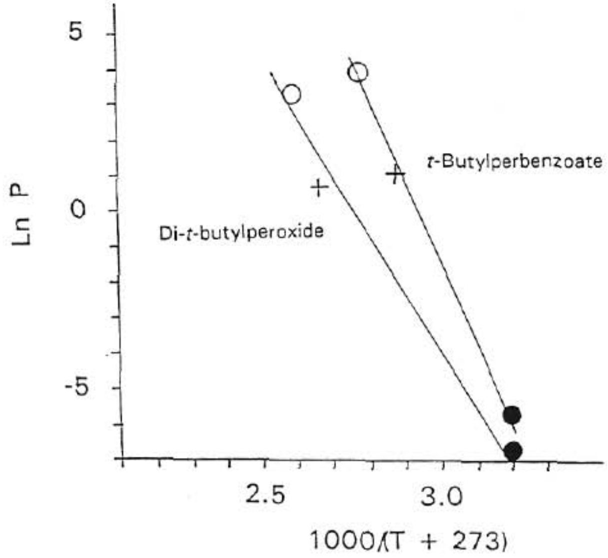

FIGURE 3 COMPARISON OF DTA (○), ARC (+) AND TAM (●) DATA

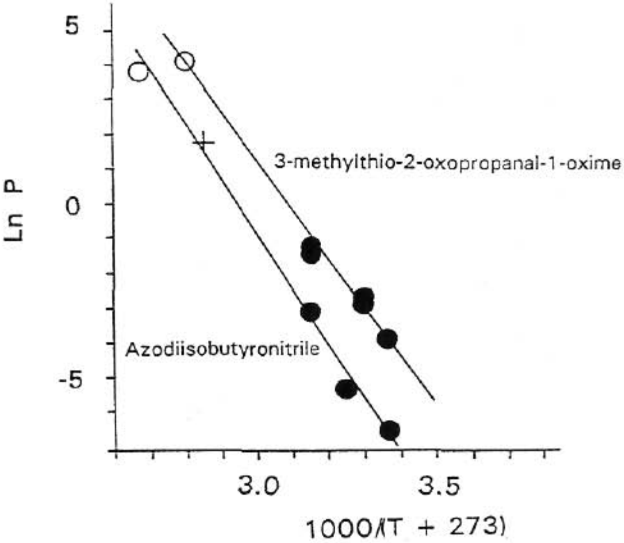

FIGURE 4 TAM TRACES

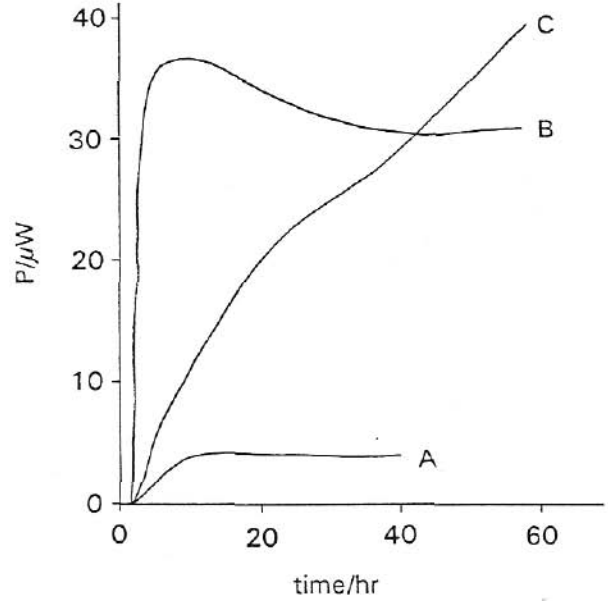

FIGURE 5 PRECISION OF INTERPOLATED ESTIMATES

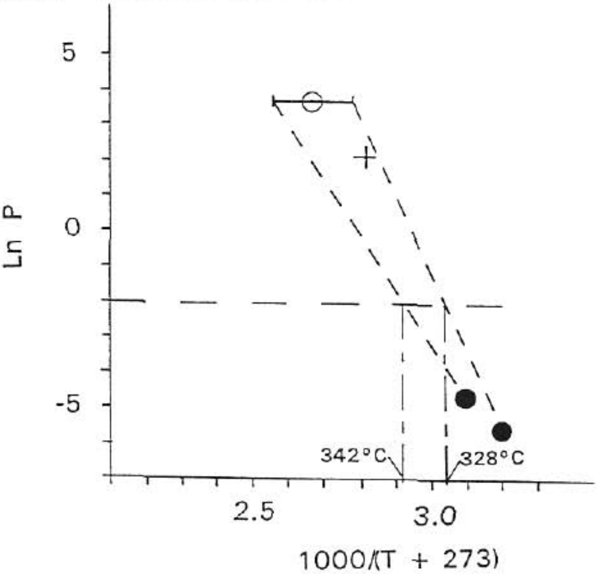

FIGURE 6 BIAS OF EXTRAPOLATED ESTIMATES