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A Comparison of Reaction Hazard Screening Techniques

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Abstract:

The requirement for a systematic approach to chemical reaction screening is described along with a comparison of results from some commercially available equipment. The limitations of using differential scanning calorimetry (DSC) as a screening tool are discussed and how the implementation of a technique (TS^U) (thermal screening unit [Hazard Evaluation Laboratory Ltd., 50 Moxon Street, Barnet, Hertfordshire, EN5 5TS, UK; Internet: http://www.helgroup.co.uk]) for rapid identification of thermal and pressure hazards has helped to overcome the DSC shortcomings. This TS^U test is described along with some in-house modifications made to the commercially available system to reduce heat losses. Comparative results for 20 thermally unstable compounds, using commercially available equipment, are presented which show how the combination of both temperature and pressure information obtained with the TS^U can help increase levels of safety.

Introduction

A chemical process goes through various stages of evolution. This life cycle of a process begins with its initial concept (discovery), and then the process grows through stages of process development and design. The preferred philosophy to process safety is to eliminate a hazard completely or reduce its magnitude to avoid the need for elaborate safety systems and procedures. This approach builds inherent safety[2] into the process. For this approach to be effective, it is important that the hazard assessment of the process commences at an early stage of development.

However, the effort of assessing each process with the same thoroughness independent of scale or development stage is not feasible in a research-based environment where speed of development is a major factor in commercial success. It therefore becomes necessary to define different levels of hazard assessment using a staged approach that allows us to have combined speed and accuracy and at the same time not to knowingly accept safety risks.

A general staged strategy for reaction hazard assessment is outlined below:

1. **Desk screening** - including literature searches and desk top[3,4] calculations such as oxygen balance[4] and CHETAH[5] calculations.

2. **Screening tests** - used primarily at the laboratory-scale development stage, including amongst others DSC, Carius tube, and DTA techniques.

3. **Characterisation of the desired process** - usually carried out by using isothermal calorimetry[4] to give data on reaction heats, reaction kinetics, thermodynamics, and heat transfer. Equipment includes the commercially available RC-1 (Mettler-Toledo) and SIMULAR[1] calorimeters.

4. **Characterisation of the undesired process or worst case scenario** - usually performed using adiabatic calorimetry to gain reaction runaway data on reactions and individual materials. This also then leads to data for reaction pressure-relief sizing and other protective measures. Commercially available equipment[4] includes accelerating rate calorimeter (ARC), Phi-Tec, VSP, and adiabatic Dewar tests.

This report is primarily concerned with arguably the most important area of reaction hazard assessment, the screening phase. The tests used at this stage tend to use small samples that give rapid results and hence are ideal for use at early stages of compound development. The aim of these tests is to differentiate the innocuous materials from the potentially hazardous ones.

As mentioned above, thermal screening is typically performed in two ways: (1) theoretical evaluation of the potential energy release on the decomposition of the study material into smaller more stable species and (2) thermal scanning, in which a small mass of a sample is heated over a temperature range to seek evidence of exothermic activity.

The limitations of theoretical calculations are widely recognised and include: (i) the limited number of predictable reactions that can be easily assessed, (ii) the difficulty of unpredictable side reactions that cannot be included in the calculation, (iii) the lack of information on the rate of heat release, (iv) the absence of pressure data, and (v) lack of experience required to perform a reliable assessment.

It is commonly accepted that a theoretical assessment alone is rarely sufficient to permit scale-up. Also, with the speed at which information can be obtained with modern instruments it is often easier and more reliable to obtain experimentally measured thermal stability data. However, the limitations of experimental methods are not always recognised as readily.

DSC is probably the most common screening technique[6] in use today and has been in use for many years in a number of different areas of chemistry, not just hazard analysis. It is primarily a thermal analytical tool that has found use in hazard assessment due to its ability to give accurate thermal information on small samples, relatively quickly and easily.

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(1) Hazard Evaluation Laboratory Ltd., 50 Moxon Street, Barnet, Hertfordshire, EN5 5TS, UK; Internet: http://www.helgroup.co.uk.

(2) Rogers, R.; Hallam, S. *Trans. Inst. Chem. Eng.* **1991**, *69*, 149.

(3) Craven, A. *Inst. Chem. Eng. Symp. Ser.* **1982**, *102*, 97−111.

(4) Barton, J., Rogers, R., Eds. *Chemical Reaction Hazards*, 2nd ed.; Institution of Chemical Engineers: Rugby, UK, 1997.

(5) Frurip, D. J.; Freedman, E.; Hertel, G. R. *International Symposium on Runaway Reactions*; Boston, 1989; CCPS/Institute of Chemical Engineers: New York, 1989; pp 39−51.

(6) Lambert, P.; Amery, G. *Inst. Chem. Eng. Symp. Ser.* **1988**, *115*, 85−95.

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Typically in these tests a sealed metal pan (containing a few milligrams of sample) and a reference pan are heated together at a defined rate (usually 1−10 K/min). If the temperature of the sample starts to diverge from that of the reference, then thermal activity is observed. The benefits include quick and safe quantification of the thermal event, small sample size, rapid turnaround, and low running costs.

A design feature that contributes significantly to the ease of use of the DSC is the small sample mass required. However, from a hazard evaluation perspective this can also be a serious disadvantage, as lack of sample representation can lead to poor experimental reproducibility.

One of the most important pieces of information obtained from thermal scanning is the so-called “onset” threshold for exothermic activity. The onset temperature measured by DSC has been compared to that from an adiabatic calorimeter, and in many cases the DSC onset is 50 °C or more higher than that reported from the adiabatic test. To get round this problem there is often quoted a “100 °C” [4] rule in the evaluation of chemical hazards. This rule basically states that if the operating temperature of a process is 100 °C higher than the detectable exotherm found in small-scale screening tests, then the process operation will not experience this thermal event. However, on the basis of experience it is known that many factors influence the temperature-dependent rates of heat generation as detected by screening-test methods. These include the physical aspects of the test procedure, such as heating rate, sample size, thermal inertia, sensitivity for the particular type of substance involved, the agitation, and the activation energy. It is therefore important that safety margins from small-scale tests are only used as guides and not for defining a basis of safety.[7]

However, the most important limitation of DSC screening is the lack of pressure data. For accurate and reliable hazard assessment this information is crucial, as it is the pressure effects that cause the most damage to vessels, plant, and people.

Therefore, whilst DSC testing has its place as a preliminary screening tool, it does have some shortcomings which reduce its effectiveness as a hazard assessment tool, especially when used in isolation of other techniques. However, DSC does allow quantification of the thermal events studied and thus can provide information on severity that other screening tests cannot.

Results and Discussion

To fulfill the need for a screening technique to complement our existing DSC test, we worked closely with the manufacturers[1] on the design and development of the TS^U. The TS^U is now commercially available, and a single TS^U unit is schematically shown in Figure 1.

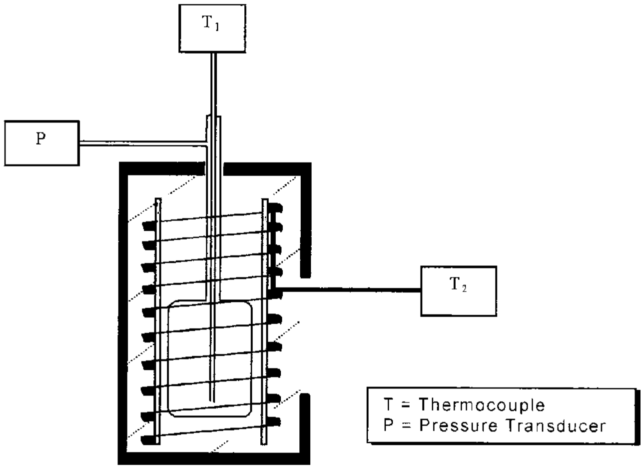

Figure 1.

The sample is contained in a metal or glass test cell which fits into a small oven which is essentially a metal cylinder with a heating coil inside. The oven, and hence the sample, can then be heated at a linear rate with an internal thermocouple measuring the temperature of the sample and thus detecting any thermal activity. The top of the cell is connected by a stainless steel tube into a pressure transducer for simultaneous pressure measurement.

Important features of the system are:

(i) Temperatures up to 400 °C can be studied.

(ii) Pressures up to 200 bar can be recorded (depending on the test cell).

(iii) Heating rates of between 0.25 and 5.0 K min^{-1} can be employed.

(iv) Isothermal experiments are possible.

(v) Different materials of construction can be used for the test cells.

(vi) Samples can be solid or liquid.

(vii) Each TS^U cell is independent, allowing multiple units to be controlled individually from the same computer.

(viii) Agitation of the samples is possible.

It must also be stated that many of the features of the TS^U listed above are not unique and the TS^U is similar in many respects to the ICI 10g sealed-tube test[3] (Carius tube) which has been used for many years. However, we feel the TS^U offers the advantages of smaller sample size (5 mL cf. typically 30 mL for the Carius tube), agitation, and multiple units that utilise the minimum of laboratory space.

Initial in-house trials focusing on the heating of common organic solvents found that at high temperatures substantial levels of reflux occurred, with consequent heat losses on the colder metal fittings at the top of the sample vessel. This was worst for sample cells that had a larger (1/4 in.) neck and for lower-boiling solvents.

To minimise this problem the design of our unit was changed by: (1) increasing the distance between the cell lid and the pressure transducer using small-bore ($^1/_{16}$-in.) tubing, (2) filling this line with inert silicone oil, (3) modifying the lid design to allow the use of a re-entrant thermocouple pocket on the test cells (we use glass cells routinely), and (4) insulating the lid.

By following these in-house modifications even low-boiling solvents in the larger-necked cells ($^1/_4$ in.) could be heated to high temperatures without the cooling reflux effect as mentioned above.

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(7) Hofelich, T. C.; Thomas, R. C. *The Use/Misuse of the 100 °C Rule in the Interpretation of Thermal Hazard Tests*; International Symposium on Runaway Reactions; Boston, 1989; CCPS/Institute of Chemical Engineers: New York, 1989; pp 74−85.

Table 1. **Summary of experimental techniques/conditions**

	DSC (Mettler Toledo)	SETARAM C80 (Setaram, France)	TS^{U} [1]	[10]ARC[a] (Columbia Scientific)
typical sample size	10 mg	50 mg	1−2 g	5 g
typical test duration	1 hour	24 h (including cool down time)	3 hours	24 hours
heat rate	5 K/min	0.5 K/min	2 K/min	N/A

[a] The ARC results were taken from a previous comparison of some thermal analytical techniques.[9] Results from the ARC were used in this comparison as the ARC has become the "standard" by which other techniques are generally compared.

Table 2. **Summary of materials tested and decomposition onsets**

		mp (°C)	DSC (°C)	C80 (°C)	ARC (°C)	TS^{U}1 (°C)[a]	TS^{U}2 (°C)[b]	TS^{U}3 (°C)[c]
1	2-amino-4-chloro-5-nitrophenol	225	205	187	166	198	180	200
2	4-methoxyphenylhydrazine hydrochloride	161	135	127	121	130	120	135
3	1,4-diphenyl butadiyne	86	170	142	136	170	230	170
4	methyl carbazate	71	189	110[d]	141	185	125	180
5	4-chloro-2-nitrobenzoic acid	144	265	255	241	279	220	280
6	azo-iso-butyronitrile	107	99	90	56	96	79	96
7	hydroxylamine sulfate	no data	190	137	131	161	131	170
8	4-tolylhydrazine hydrochloride	>200	175	125	156	155	156	160
9	4-nitrophenyl hydrazine	156	160	120	106	138	140	120
10	2,6-dichloro-4-nitroaniline	191	290	250	286	300	260	260
11	4-amino-1,2,4-triazole	85	260	200	190	240	192	240
12	1,1- carbonyldiimidazole	119	170	140	140	200	170	170
13	4-nitroso-diphenylamine	144	142	135	115	138	116	130
14	2,4- dinitroaniline	177	285	278	266	285	280	285
15	5-nitro-1H-indazole	208	300	290	292	300	282	300
16	4-hydrazinobenzoic acid hydrochloride	218	230	210	121	210	190	200
17	1,2,4-triazole-3-thiol	222	276	238	231	290	245	280
18	3-methyl-4-nitrophenol	128	247	188	181	240	193	240
19	di-*tert*-butyl peroxide	bp 109	164	120	116	160	130	150
20	dibenzoyl peroxide	105	99	93	86	94	95	95

[a] TS^{U}1 = °C onset detected from temperature data. [b] TS^{U}2 = °C onset detected from pressure increase. [c] TS^{U}3 = °C onset detected from heat rate/time plots. [d] Onset difficult to quantify due to variable baseline.

The next step was to compare the results obtained from our modified TS^{U} with those obtained with other hazard analysis equipment to ensure the test method gives quality results.[8]

Therefore, 20 organic compounds that are known to decompose exothermically have been tested by using the test methods and equipment as summarised in Table 1. It should be noted that this comparison does have some shortcomings in that we did not employ the same scanning rate for each test but used a heating rate we would typically use in our laboratories and that the ARC results were obtained on different samples (i.e., may not have been of identical quality). It should also be noted that ARC also gives pressure data, but this information was not reported in the literature data source[9] and hence is not available for inclusion in this report. However, despite these concerns the initial comparisons presented below are still of value in highlighting the merits of various techniques when used for hazard-screening purposes.

The compounds used and the results are summarised in Table 2.

Examination of the results obtained for the 20 compounds by the four test methods are presented in Figures 2−5 using the ARC results for direct comparison. The TS^{U} results were analysed for decomposition onset in three ways, on temperature detection, on heat rate versus temperature, and finally when pressure increase was noted. To remove vapour pressure effects from the pressure data, plots of log pressure against $1/T$ (K^{-1}) were produced as deviations from straight line plots to indicate the onset of permanent gas formation.

To summarise the data, DSC results show average onset temperatures 34 K higher than for those of the ARC. This ties in with the generally accepted but conservative "100 °C" rule safety margin described earlier in this paper. However, it should be noted that in one test (sample 16) the DSC onset was 109 K above the ARC onset temperature, highlighting the general issue of using a "100 °C rule" which should really only be used as guide for safety purposes and not a hard and fast rule.[7]

The Setaram C80 generally gives results that are within 20 K of the ARC results and thus offers greater sensitivity than the DSC and TS^{U}. However, the C80 has limited use as a rapid screening tool because the tests (including cooling back to ambient) take around 24 h to run. It should be noted the Setaram can also be configured to record pressure data by using commercially available test cells, but these were not used for this comparative study.

The TS^{U} (thermal) results shows onset temperatures on average 30 K higher than ARC, and the results are comparable with those of DSC (see Table 3). Indications

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(8) Cronin, J.; Nolan, P. *J. Hazard. Mater.* **1987**, *14*, 293−307

(9) Fenlon, W. *Plant/Oper. Prog.* **1984**, *3*, 197.

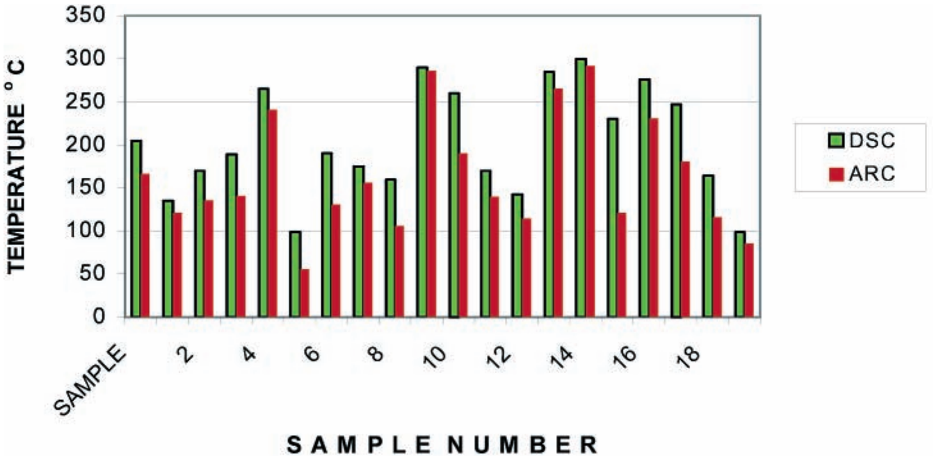

Figure 2. **DSC versus ARC “onset” comparison. ARC lower onset in all samples. ΔT range = 4−109 K. Average ΔT = 34 K.**

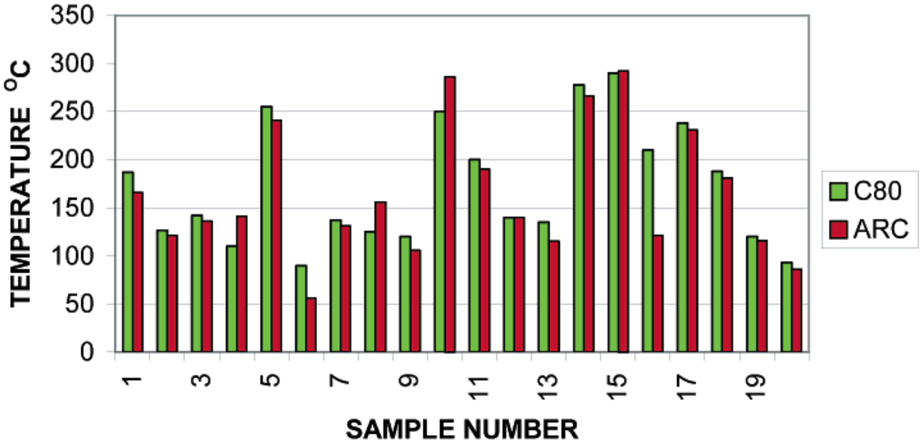

Figure 3. **Setaram C80 versus ARC “onset” comparison. ARC lower onset in 15 samples. C80 lower onsets in four cases. One result the same. Largest ΔT = 89 K. Average ΔT = 18 K.**

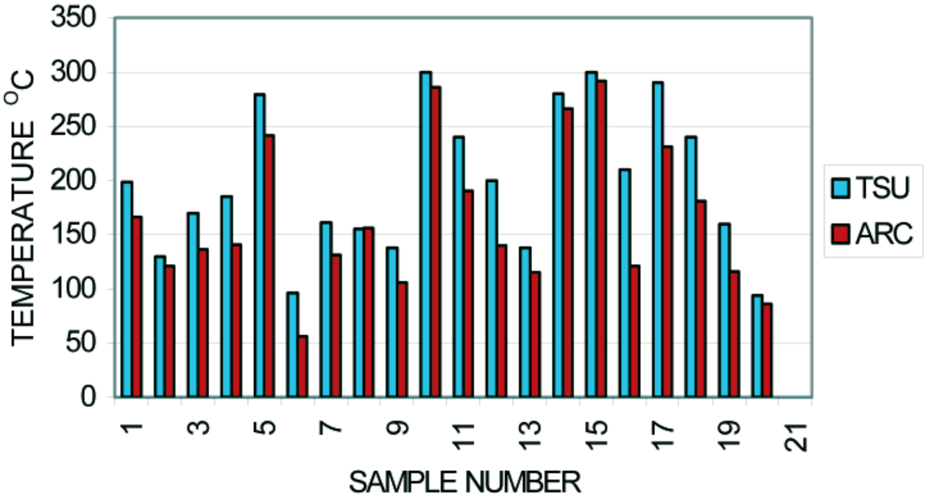

Figure 4. **TS^U (temperature) versus ARC “onset” comparison. ARC lower onset in 19 samples. TS^U (temperature) lower onset in one sample. Largest ΔT = 89 K. Average ΔT = 35 K.**

are that the TS^U is slightly more sensitive, under the conditions employed in this report, than the DSC (average of 5 K lower onsets detected), but this could be improved further if a larger sample was used in the TS^U. In most of the tests run the smallest possible sample size (generally 1−2 g) was employed due to the high energy of the decompositions being studied. Future studies are planned where larger samples of less thermally unstable materials are examined and more comparable heating rates used.

By plotting heat rate versus temperature[11] it is sometimes possible to detect lower onset temperatures than that from the normal temperature/time plot. Carrying out this analysis (Table 2) shows that in eight cases this would lower the original onset quoted for the TS^U. However in only two cases

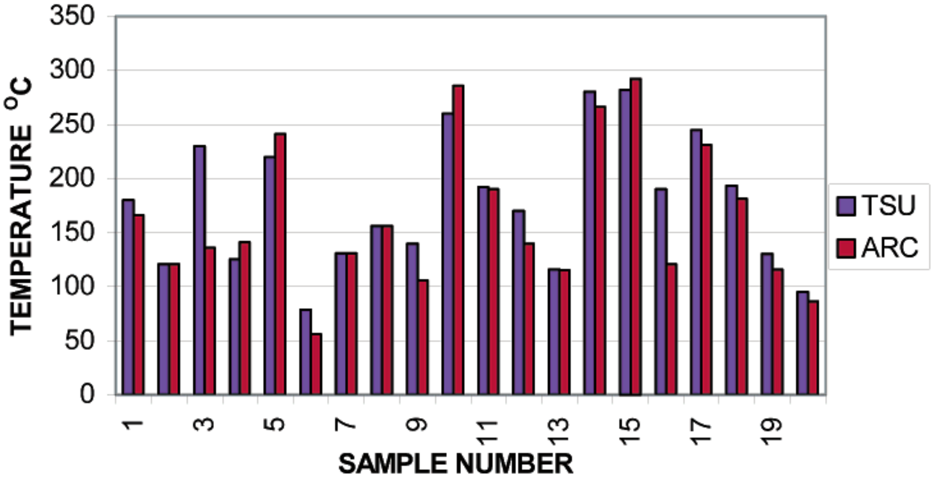

Figure 5. **TS^U (pressure detection) versus ARC (temperature) “onset” comparison. ARC lower onset in 13 samples. TS^U lower in five cases. Two results the same. Largest $\Delta T = 20$ K. Average $\Delta T = 3$ K.**

Table 3. **TS^U/DSC onset comparison**

TS^U exotherm onset versus DSC onset	TS^U pressure onset versus DSC onset
TS^U 14 lower	TS^U 18 lower
two equal	one equal
TS^U four higher	TS^U one higher
TS^U average ≈ 5 K lower	TS^U average ≈ 30 K lower

would it lower it below the detected pressure onset point. This type of analysis is easy to do with the commercial TS^U software, and hence we would recommend looking at both normal temperature/time plots and derived heat rate/temperature plots in order to get the most accurate value for onset detection from a single experiment.

TS^U pressure data shows onset results much closer to the ARC data than to the thermal TS^U data. Comparison of TS^U and DSC results are shown in Table 3, and comparing TS^U pressure onset with DSC thermal onset shows that pressure detects significantly lower onsets in many cases. In only one case (sample 3) is the TS^U (pressure) onset higher than the DSC onset, indicating that this sample does not undergo much gas evolution during the early stages of decomposition.

Conclusions

The TS^U has been incorporated into our process safety work programme, and with slight modifications to the original design it provides fast and reliable onset data for both temperature and pressure effects.

The TS^U has advantages as a screening tool because it gives pressure data which in many cases is a more sensitive method for detection of the onset of decomposition than temperature data. The use of DSC as the sole tool for thermal hazard screening can be dangerous[12] as this pressure information cannot be obtained. However, it must be remembered DSC can give quantitative values for thermal events and hence valuable information about severity.

This report concludes that the TS^U is a valuable tool to be added to a chemical hazard assessment laboratory on these bases (1) fast turn-around time, (2) production of both temperature and pressure data, (3) availability of agitation, and 4) the use of small but representative amounts of material. In our laboratories this technique is in routine use as a supplement to DSC (DSC is still the test of choice when only very small amounts of material are available) and has already highlighted a number of cases where DSC data alone could be misleading. However, it should always be remembered that the most reliable results are obtained when a variety of techniques/analysis methods are used, as different test methods have different strengths and weaknesses. This report, although highlighting the importance of a pressure screening test, must therefore stress that reliance on any one screening technique should be avoided.

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