

## **THE COMPARATIVE SENSITIVITY OF TEST METHODS FOR DETERMINING INITIAL EXOTHERM TEMPERATURES IN THERMAL DECOMPOSITIONS OF SINGLE SUBSTANCES**

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### **Summary**

The temperature at which the initiation of exothermic decomposition is detected during thermal stability testing of single substances depends on several factors. These do not only concern the material properties and the specific decomposition reaction but can include the experimental systems' characteristics and experimental parameters. Four materials, with known thermal behaviour were selected and subjected to standard testing procedures using a number of experimental systems. These systems included both micro-thermal and macro-thermal analytical techniques. An overall comparison of the sensitivity of the different techniques, employing five commercially available instruments and common "in-house" methods in detecting the initial exotherm of the samples under typical test conditions has been obtained.

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### **Introduction**

In a recent study, Barton and Nolan [1] showed that particular areas of the chemical industry, e.g. dyestuffs, pharmaceuticals, resins and organic intermediates, use batch processing and due to economic considerations, reaction kettles tend to be of a general design and useful for a range of unit processes rather than dedicated to the manufacture of a specific product. In such circumstances, it is particularly important to specify safe operating conditions, which means that any thermal hazards should be identified at the development stage of the process.

In particular, the thermal stability of the desired product and any residues are of primary importance, since any problem which results in loss of thermal control in any part of the process could potentially lead to a catastrophic decomposition reaction or thermal runaway. It is therefore a good plant practice to attempt to define a "safe operating temperature" for a particular product (or reaction intermediate), upon which process operating conditions can be based.

The safe operating temperature is affected by a number of factors. The primary consideration is that the processing temperature should not exceed that at which the bulk product becomes thermally unstable. The possible deviations from standard operating procedures, such as loss of cooling during the reaction or delays should also be considered. Often a particular safety margin, of say 30 or 50 K is specified as the acceptable difference between the maximum anticipated process temperature and the minimum detected initial exotherm temperature for the product, which has been previously measured in a laboratory-based test.

In the context of this investigation, the initial temperature for a substance (solid or liquid) is defined as that at which an exothermic reaction is first detected, using a particular test method. The initial temperature recorded for a particular material will depend on a number of experimental parameters, which can include:

(a) *Sample size*: This will affect the extent of heat accumulation within the sample during the test, at a particular temperature.

(b) *Constructional material of sample container*: This must be chosen carefully, since it is possible to catalyse or inhibit the decomposition reaction in the laboratory test apparatus. It may also be desirable to add samples of the industrial reactor's materials of construction and corrosion products to determine the possibility of any catalysis or inhibition due to contamination by these materials.

(c) *Sample heating rate*: This will affect detection sensitivity; since exothermic self-heating of the sample will not be easily detected unless it is significantly large compared to the external heating rate.

(d) *Thermal inertia*: This is a property of the sample container and it may impede the continued self-heating, particularly in small sample masses. It is defined as

$$I = 1 + (M_c C_{vc} / M_s C_{vs})$$

where  $I$  = thermal inertia,  $M$  = mass, and  $C_v$  = specific heat at constant volume. The subscripts  $s$  and  $c$  relate to the sample and container, respectively.

It should be recognised that the specific heat terms may vary due to temperature and the reaction mechanism.

(e) *Endothermic effects*: These can include: (i) evaporation of residual solvent, (ii) gas evolution, and (iii) phase changes. Such effects may lead to different measurements of the sample behaviour in different experimental apparatus (e.g. in open or closed vessels). A number of substances decompose on melting and this may cause problems in identifying initial temperatures — particularly if trace impurities have a large effect on melting point.

### Experimental methods

A number of established thermal stability test methods are considered below. They can be operated to provide additional data to the initial exotherm tem-

perature. It is possible to classify them into micro-thermal and macro-thermal methods.

#### *Micro-thermal methods*

These use very small samples (of typically a few milligrammes) and include established commercial instrumentation such as differential thermal analysis (DTA) and differential scanning calorimetry (DSC). Such equipment is used in many industrial, analytical applications other than for the detection of thermal hazards and therefore is commonly available.

#### *Macro-thermal methods*

These tend to be used specifically for the detection of exothermic behaviour in considerably larger samples, i.e. on the gramme scale. The commercially available instruments include the accelerating rate calorimeter (ARC) and the sensitive detector of exothermic processes (SEDEX). A number of test procedures have also been developed, using widely available and simple equipment by, among others, the Association of the British Pharmaceutical Industry [2] and Cronin [3].

#### *Heating methods*

A further classification of the experimental methods can relate to the methods of heating the sample. The four common methods are: scanning, adiabatic, isoperibolic, and isothermal heating.

##### *Scanning heating*

The sample temperature is increased at a fixed linear rate between previously defined limits. The exothermic behaviour of the sample is detected either by a non-linear sample temperature profile, or by deviation of the sample temperature from that of an inert reference material. In DSC, energy changes are studied rather than simply temperature changes.

##### *Adiabatic heating*

The temperature of the sample container is continuously set to that of the sample, once an exothermic reaction is detected. This procedure enables the progress of the decomposition to be monitored under conditions of heat accumulation, approaching those found in bulk materials. It is claimed that adiabatic operation simulates the reaction mass in industrial plant, in which loss of cooling and agitator failure has occurred, by providing a "worst case" condition.

##### *Isoperibolic heating*

The sample temperature is increased in discrete, pre-defined steps and is allowed to equilibrate before being monitored for exothermic self-heating. This

“heat-wait-search” mode is claimed to increase detection sensitivity by eliminating the continuous experimental “back-ground heating” present in scanning experiments. Once exothermic behaviour has been detected during an isoperibolic experiment, it is either automatically monitored in an adiabatic mode or subsequently by a separate adiabatic experiment.

#### *Isothermal heating*

The sample is maintained at a constant temperature and the surrounding environment at a constant, lower temperature. The variation in heat flux required to maintain this equilibrium may be used to calculate heat of reaction for any process occurring, over a given time period.

### **Equipment**

The operating principles of the different methods and instruments used in this comparative investigation are discussed below.

#### *Differential thermal analysis (DTA)*

As stated earlier, this is a well established thermal method used for a range of analytical applications. A small sample, typically less than 10 mg, of the test material is placed in a metal sample container and an equal mass of a thermally inert reference material, e.g. graphite or alumina for solids and silicone oil for liquids, is placed in an identical reference container. Both are fixed into a miniature support, in close contact with calibrated platinum thermistors. The whole assembly is lowered into a temperature controlled furnace. The furnace temperature is increased in a scanning mode. The differential temperature between sample and reference is recorded as a function of furnace temperature (or time); any exothermic behaviour in the sample is indicated by an increase in sample temperature relative to that of the inert reference.

#### *Differential scanning calorimetry (DSC)*

A sample, usually less than 10 mg, of the test material is placed in a metal container and an equal mass of a thermally inert reference is placed in an identical container. On occasions it has been found advantageous to keep the reference container empty in the study of organic substances, particularly when using very small samples of material in comparison to the mass of the container. In normal operation, the sample and reference are placed in each of two compartments provided in an internally cooled calorimetric block, the whole being isolated from the outside environment by an air-tight lid and protective, insulating cover. Both sample and reference compartments are provided with integral platinum thermopiles and thermistors. The DSC controller maintains a pre-defined linear temperature increase in both compartments. The differential power requirement to achieve this is recorded as a function of sample

temperature (or time). The exothermic behaviour of the sample is indicated by a decrease in the power input required to maintain the desired temperature profile in the sample, compared to that in the reference compartment. The power—time profile may be integrated during a thermal transition (exothermic or endothermic) to yield the heat of reaction and approximate kinetic data.

#### *Accelerating rate calorimetry (ARC) [4,5]*

The (1–10 g) sample is fitted into a specially designed spherical metallic “bomb”. This sphere is fitted with a small bore, elongated neck, which is connected to a pressure transducer and bursting disc via a compression fitting and a capillary tube. The bomb temperature is monitored by an externally connected platinum resistance thermometer.

A blast shield surrounds a cylindrical calorimetric jacket, in which the bomb is placed. The calorimetric jacket contains an internal sample heater and top, base and side-wall heaters. During an experiment the sample temperature is increased in an isoperibolic mode by the heater until an initial exotherm of a specified magnitude (self-heating of, typically  $0.02^{\circ}\text{C min}^{-1}$ ) is detected by the bomb thermistor. Thereafter, the jacket wall temperature is continuously set to that of the bomb and the decomposition is allowed to run to completion in an adiabatic or “exotherm” mode. The temperature and internal pressure of the bomb are recorded as a function of time. It is possible to estimate the heat of reaction and kinetic parameters for the decomposition by compensating for the thermal inertia of the equipment and assuming perfect adiabatic operation.

Problems of loading the sample can be overcome by using pressure-tight, custom-built bombs made from two hemi-spheres. A stirred bomb has recently been introduced.

#### *Sedex [6,7]*

A (5–30 g) sample is placed in the most appropriate of several possible containers. Typically, a small tube or beaker is used, but other options include a miniature autoclave or small stirred reaction vessel. The chosen container is fixed within a fan assisted oven and the temperatures of the sample and circulating air are monitored by platinum resistance probes fitted through the oven roof. The oven temperature may be controlled in scanning, adiabatic, isoperibolic and isothermal modes. The oven and sample temperatures are recorded as functions of time. The initiation of exothermic activity is indicated by a decrease in the difference between oven and sample temperatures. (Positive in the absence of reaction.) As with some of the other methods, it is possible to estimate heats of reaction and kinetic data for decompositions by using an adiabatic mode and compensating for the thermal inertia of the container.

*Sikarex [8,9]*

This safety calorimeter shares many of the operational control features as the Sedex having been developed by Sandoz AG.

The (5–30 g) sample is placed in a specially manufactured borosilicate glass tube, fitted with a glass vent, the whole being fixed within a steel jacket. The jacket consists of a series of concentric cylinders and its temperature is controlled by heated air, which is rapidly circulated between the cylinder walls. The jacket and sample temperature are continuously monitored using platinum resistance probes. During a scanning experiment, the sample temperature and the temperature difference between the jacket and sample are recorded as a function of time. The data can be processed in a similar manner to that described for the Sedex.

*“In-house” methods*

A number of manufacturing companies have their own “in-house” methods of assessing thermal hazards. Although numerous variations exist, typical examples of the methods employed have been described by the Association of the British Pharmaceutical Industry (ABPI) [2]. While such methods are not claimed to replace the usually more rigorous methods employing the previously described expensive commercial systems, they do provide a useful cost-effective guide to potentially hazardous reactions. In this comparative study, variations on the ABPI open and closed tube tests were used.

*Closed tube*

The (2–10 g) sample is placed in a small bore borosilicate glass tube; fitted with a re-entrant thermocouple pocket. This is then placed within a thick-walled stainless steel tube, which is sealed at either end by removable compression fittings. The outer steel tube is connected via a capillary to a pressure transducer and bursting disc assembly, and is also fitted with an internal (type K) thermocouple which penetrates into the inner glass sample tube. An equal mass of a thermally inert reference material (see DTA above) is placed in an identical container. Both sample and reference are fixed in a temperature programmed oven and are heated in a “scanning” mode. The internal pressure in the sample container and the differential temperature between sample and inert reference material are recorded as a function of the sample temperature or time. The initiation of exothermic behaviour in the sample is indicated by an increase in recorded differential temperature.

*Open tube*

The (2–10 g) sample is placed in a borosilicate glass tube, and an equal amount of a thermally inert reference is placed in an identical tube. Both tubes are suspended within a temperature programmed oven. The open-end of each tube is vented through holes provided in the oven roof. The oven is placed

inside a fume-cupboard. The reference material temperature, the differential temperature between sample and reference are monitored using (chromel—alumel thermocouples (type K)) which are provided with protective glass sheaths. The initiation of exothermic behaviour in the sample is indicated by an increase in the recorded differential temperature when plotted against the sample temperature.

### **Materials used for comparative purposes**

In order to allow an objective comparison, four substances were selected to demonstrate different types of thermal behaviour prior to decomposition. Ideally, substances would have been chosen to illustrate the direct decomposition of liquid and solid, phase change followed by decomposition and autocatalytic decomposition. It is stressed that the individual substances were representative of many available from the UK chemical industry, and of commercial grade.

The selected materials are as follows:

(a) *Tertiary butyl peroxybenzoate*: This is a liquid organic peroxide, which is used as a free radical initiator in polymerisation reactions. It undergoes violent thermal decomposition below its normal boiling point.

(b) *3-Nitrobenzenesulphonic acid*: This is an organic intermediate and the sample investigated was a crude, unrefined residue from a sulphonation kettle. It undergoes a long endothermic process including evaporation of residual liquid and melting of crystalline solid, prior to undergoing exothermic decomposition in the liquid phase.

(c) *2-Bromo-2-nitropropan-1,3-diol*: This is a crystalline solid and undergoes two well defined endothermic transitions; desorption of associated water is followed by melting. Exothermic instability is detected immediately on completion of the latter phase change.

(d) *Azodicarbonamide*: This is a solid material, which is used as a blowing agent in the manufacture of polymer foams. The decomposition is accompanied by the evolution of large volumes of gas and would appear to be autocatalytic.

The investigation was not intended to give an overall hazard assessment of the above substances but to provide a variation of properties to assess the performance of the various detection methods and instrumentation.

### **Experimental results**

The results obtained in the thermal stability tests for the above substances are shown in Tables 1–4. Each table provides the relevant details of the experimental procedure and instrument manufacturers.

TABLE 1

Test results for tertiary butyl peroxybenzoate

Test method	Experimental condition	Sample mass	Initial exotherm detected	Instrument/Comments
DTA	10°C min <sup>-1</sup>	8.15 mg	125°C 398 K	Stanton—Redcroft STA 781 open platinum capsule
DSC	10°C min <sup>-1</sup>	3.42 mg	122°C 395 K	Perkin—Elmer DSC 2 using sealed stainless steel pan
	5°C min <sup>-1</sup>	4.40 mg	101°C 374 K	Perkin—Elmer DSC 4 with data station using sealed stainless steel pan
	1°C min <sup>-1</sup>	6.48 mg	93°C 366 K	Perkin—Elmer DSC 4 with data station using sealed stainless steel pan
ARC	Start: 50°C Heat step: 10°C Wait: 15 min I: 2.21	3.57 g	81.8°C 354.8 K	Columbia Scientific Instruments ARC “Light” Hastelloy bomb
Sedex	0.5°C min <sup>-1</sup> “scanning” experiment	5.80 g	84°C 357 K	Systag TSC 510/511 open tube
	0.5°C min <sup>-1</sup> “scanning” experiment	2.00 g	88°C 361 K	Systag TSC 510/511 mini-autoclave
Sikarex	0.125°C min <sup>-1</sup>	5.00 g	72°C 345 K	Systag Sikarex 3
ABPI	Closed 0.5°C min <sup>-1</sup>	2.00 g	84°C 357 K	
	Open 4°C min <sup>-1</sup>	2.00 g	100°C 373 K	



TABLE 2

Test results for 3-nitrobenzenesulphonic acid

Test method	Experimental condition	Sample mass	Initial exotherm detected	Instrument/Comments
DTA	10°C min <sup>-1</sup>	11.08 mg	146.3°C 419.3 K	Stanton—Redcroft STA 781 open platinum capsule
DSC	10°C min <sup>-1</sup>	7.25 mg	147°C 420 K	Perkin—Elmer DSC 2 using sealed stainless steel pan
	5°C min <sup>-1</sup>	2.49 mg	88°C 361 K	Perkin—Elmer DSC 4 with data station using sealed stainless steel pan
	5°C min <sup>-1</sup>	11.64 mg	165°C 438 K	Perkin—Elmer DSC 4 with data station using gold plated sealed steel pan
	1°C min <sup>-1</sup>	9.18 mg	150°C 423 K	Perkin—Elmer DSC 4 with data station sealed steel pan
ARC	Start: 50°C Heat step: 10°C Wait: 15 min  <i>I</i> : 2.71	3.59 g	82.3°C 355.3 K	Columbia Scientific Instruments ARC "Light" Hastelloy bomb
Sedex	0.5°C min <sup>-1</sup> "Scanning" experiment	30 g	164°C 437 K	Systag TSC 510/511 Open beaker
	0.5°C min <sup>-1</sup> "scanning" experiment	5.11 g	130°C 403 K	Systag TSC 510/511 mini-autoclave
Sikarex	0.125°C min <sup>-1</sup>	5.00 g	150°C 423 K	Systag Sikarex 3
ABPI	Closed 0.5°C min <sup>-1</sup>	2.00 g	145°C 418 K	
	Open 4°C min <sup>-1</sup>	2.00 g	163°C 436 K	

TABLE 3

Test results for 2-bromo-2-nitropropan-1,3-diol

Test method	Experimental condition	Sample mass	Initial exotherm detected	Instrument/Comments
DTA	10°C min <sup>-1</sup>	9.61 mg	193.6°C 466.6 K	Stanton—Redcroft STA 781 open platinum capsule
DSC	10°C min <sup>-1</sup>	0.71 mg	212°C 485 K 185°C	Perkin—Elmer DSC 2 using sealed stainless steel pan
	5°C min <sup>-1</sup>	3.29 mg	458 K	Perkin—Elmer DSC 4 with data station using sealed stainless steel pan
	1°C min <sup>-1</sup>	3.56 mg	171°C 444 K	Perkin—Elmer DSC 4 with data station using sealed stainless steel pan
ARC	Start: 50°C		141.1°C	Columbia Scientific Instruments ARC
	Heat step: 10°C Wait: 15 min <i>I</i> : 3.97	3.68 g	414.1 K	“Light” Hastelloy bomb
Sedex	0.5°C min <sup>-1</sup> “Scanning” experiment	5.00 g	133°C 406.1 K	Systag TSC 510/511 open tube
	0.5°C min <sup>-1</sup> “Scanning” experiment	2.00 g	131.5°C 404.5 K	Systag TSC 510/511 mini-autoclave
Sikarex	0.125°C min <sup>-1</sup>	5.00 g	135°C 408 K	Systag Sikarex 3
ABPI	Closed 0.5°C min <sup>-1</sup>	2.00 g	143°C 416 K	
	Open 4°C min <sup>-1</sup>	2.00 g	143°C 416 K	

TABLE 4

Test results for azodicarbonamide

Test method	Experimental condition	Sample mass	Initial exotherm detected	Instrument/Comments
DTA	10°C min <sup>-1</sup>	9.72 mg	213.5°C 486.5 K	Stanton—Redcroft STA 781 open platinum capsule
DSC	10°C min <sup>-1</sup>	0.70 mg	207°C 480 K 180°C	Perkin—Elmer DSC 2 using sealed stainless steel pan
	5°C min <sup>-1</sup>	2.88 mg	453 K	Perkin—Elmer DSC 4 with data station using sealed stainless steel pan
ARC	Start: 50°C Heat step: 10°C Wait: 15 min I: 4.54	3.02 g	131.9°C 404.9 K	Columbia Scientific Instruments ARC "Light" Hastelloy bomb
Sedex	0.5°C min <sup>-1</sup> "Scanning" experiment	5.00 g	133°C 406 K	Systag TSC 510/511 open tube
			105°C	Systag TSC 510/511
	0.5°C min <sup>-1</sup> "Scanning" experiment	2.00 g	378 K	mini-autoclave
Sikarex	0.125°C min <sup>-1</sup>	5.00 g	135°C 408 K	Systag Sikarex 3
ABPI	Closed 0.5°C min <sup>-1</sup>	2.00 g	132°C 405 K	
	Open 4°C min <sup>-1</sup>		2.00 g	

## Discussion

In the chemical industry, it is necessary for exothermic reactions to be quantified in terms of initial temperature, induction time, magnitude and rate of heat release. These data are determined from a range of small scale tests and together with plant operating experience allow manufacturers to specify safe

operating conditions using arbitrary safety margins. Problems do occur, in relation to the accuracy of the laboratory tests and the application of these results to predict the behaviour of bulk materials, i.e., to compensate for the effects of scale.

The present study has examined the comparative sensitivity of a number of established methods in determining the initial exotherm temperature. It is stressed that the instruments used have, in general, the capacity to measure other necessary properties in a total thermal hazard assessment.

The important parameters identified in the introduction can be considered in detail.

#### *Sample size*

In general, the macro-thermal methods (ARC, Sedex, Sikarex, ABPI) are more suitable for thermal hazards evaluation than micro-thermal methods. The former methods record lower initial temperatures for exothermic reactions due to heat accumulation effects. The properties of a bulk material, including thermodynamic and kinetic parameters, can be estimated using macro-thermal methods more accurately, primarily because in micro-thermal techniques the thermal mass of the sample holder is extremely large compared to that of the sample. The use of milligramme size samples does not allow for thorough investigation of heterogeneous materials or reaction mixtures. However, micro-thermal methods may be already available for other than hazard evaluation work and they can provide a very useful preliminary indication of potential hazards.

#### *Constructional material of sample container*

In general, it is necessary to know the effects of the industrial plant constructional materials and/or packaging materials on the thermal behaviour of substances. In laboratory tests it is often preferable that a chemically inert (glass, ceramic or noble metal) sample holder should be employed initially. When a closed system is required, this would normally form an insert or lining for a steel pressure vessel. For example, gold plated sealed stainless steel pans may be used in thermal hazard evaluations employing differential scanning calorimetry. However, data from laboratory tests using non-inert sample containers, particularly those employing the same constructional materials as the intended industrial scale plant have considerable relevance. The results for the 3-nitrobenzenesulphonic acid (Table 2) indicate an early exothermic reaction in both stainless steel DSC capsules and the Hastelloy ARC bomb. In larger scale tests, such as those given in the U.N. Transport of Dangerous Goods Tests and Criteria manual, a proportionate amount of packaging material is added specifically to determine the properties of the substance in the presence of its normal packaging material.

The specific heat term varies with temperature, and for the sample may vary

TABLE 5

Modes of heating in tests

	DTA	DSC	ARC	Sedex	Sikarex	ABPI
Scanning	✓	✓ (energy changes)		✓	✓	✓
Adiabatic	—	—	✓	✓	✓	(in other ABPI tests)
Isoperibolic	(✓)	(✓)	✓	✓	✓	(✓)
Isothermal	✓	✓	—	✓	✓	✓

( ) = possible mode.

significantly during the course of the decomposition reaction. As expected the results indicate that the macro-thermal methods (ARC, Sedex, Sikarex, ABPI), where the thermal mass of the sample is significantly large compared to that of the container, are the most sensitive for initial exotherm detection.

#### *Endothermic effects*

The effects of evaporation and gas evolution can be suppressed by the use of closed vessels; however, this generally involves an increase in thermal inertia when compared to the equivalent open system. If a material undergoes a phase change prior to decomposition, then this must be identified, otherwise problems can occur in the evaluation of subsequent thermal behaviour. The decomposition of azodicarbonamide would appear to occur at a lower temperature in a closed vessel, probably due to early catalysis of the reaction by accumulation of a gaseous product.

#### *Sample heating mode and rate*

The methods of sample heating are summarised in Table 5.

For all methods, the lowering of the scanning or isoperibolic heating rate can be expected to result in lower recorded initial exotherm temperatures. This is shown most clearly in the DSC experiments, in which 3 different scanning rates were employed.

#### *Thermal inertia*

The thermal inertia of the sample container is an important consideration in the detection of the initial decomposition temperature and in the subsequent monitoring of the decomposition and interpretation of data and derivation of results.

Specific observations with regard to the substances employed in the investigation are:

(a) *3-Nitrobenzenesulphonic acid*: The Accelerating Rate Calorimeter detected an initial exotherm at 82.3°C, this temperature coincides with the

end of an endotherm detected by Sedex and Sikarex. The DSC results also suggest possible catalysed exothermic reaction with the steel container.

(b) *2-Bromo-2-nitropropan-1,3-diol*: This substance is unstable above its melting point, 403 K (130°C) and enters an exothermic transition immediately after melting is complete. The initial temperatures recorded by ARC, Sedex and ABPI methods reflect the point of inflection in the melting endotherm.

## Conclusions

A number of techniques and associated instrumentation exist for investigations into the thermal stability of single substances. The instrumentation is either specially designed for the assessment of thermal hazards or can be applicable to a range of analytical requirements. For any thermal stability assessment of substances in the form of reactants, intermediates and products in processing vessels or in storage, it is necessary to have knowledge of the initial exotherm temperature, induction time, magnitude and rate of heat release. The present study has concentrated on the measurement of the initial exotherm temperature. The following points have been found:

(1) When an initial exotherm temperature for a substance is quoted, it is necessary to supply information on the type of test equipment and the experimental conditions employed.

(2) Factors, which can affect the experimentally determined value of the initial exotherm temperature include sample size, material and construction of test enclosure, mode and rate of sample heating and the nature of the sample itself. It is necessary to consider the sensitivity of the results to the above factors. Ideally, large well mixed samples should be heated slowly in inert containers or in containers made of materials with similar specific heat losses to that of the industrial plant.

(3) It is difficult to take bulk effects into consideration using techniques employing very small samples; however, even techniques not specifically designed for thermal hazard assessment will give some indication of thermal instability problems of the substance if the experimental conditions are chosen with care.

(4) The "in-house" techniques give good cost-effective guidance to thermal behaviour and provide a useful stage prior to using the available safety calorimeters, which are capable of providing a more comprehensive range of kinetic and thermodynamic data.

(5) It is important to appreciate the significance of the data, which is being processed in automatically controlled thermal hazards instrumentation. An experienced operator is required to interpret results even for the most sophisticated instrumentation currently available.

(6) Problems can exist in calculating the thermal inertia term due to inac-

curacies caused by changes in the specific heat due to temperature and reaction, particularly in the later stages of decomposition. Ideally, residues and evolved decomposition products should be analysed.

(7) The initial exotherm temperature is only one consideration in specifying safe plant conditions for the production and handling of substances. The rate of decomposition and degree of self-heating at slightly lower temperatures should be assessed together with the induction period for the decomposition.

(8) An overall definition of safe operating conditions in respect of full-scale operation should concern plant temperatures, hold-up times, construction materials, possible deviations from operating procedures, contaminations and the storage and packaging of final products.

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### References

- 1 J.A. Barton and P.F. Nolan, Runaway reactions in batch reactors, In: *The Protection of Exothermic Reactors and Pressurised Storage Vessels*, IChemE Symp. Ser., 85 (April 1984) 13-21.
- 2 Association of the British Pharmaceutical Industry, *Guidance Notes on Chemical Reaction Hazard Analysis*, 1982.
- 3 J.L. Cronin, Ph.D. Thesis CNAAs (South Bank), *A practical strategy for thermal hazards analysis in batch chemical systems*, January 1987.
- 4 D.I. Townsend and J.C. Tou, Thermal hazard evaluation by an accelerating rate calorimeter, *Thermochim. Acta*, 37 (1980) 1-30.
- 5 D.W. Smith, M.C. Taylor, R. Young and T. Stephens, Accelerating rate calorimetry, *Amer. Lab.*, 12 (1980) 51-54.
- 6 J. Hakl, Sedex — Sensitive detector for exothermic processes, In: *Runaway Reactions, Unstable Products and Combustible Powders*, IChemE Symp. Ser., 68 (March 1981) 3/L 1-11.
- 7 J. Hakl, Advanced Sedex (sensitive detector of exothermic processes), *Thermochim. Acta*, 80 (1984) 209-219.
- 8 L. Hub, Two calorimetric methods for investigating dangerous reactions, In: *Chemical Process Hazards VI*, IChemE Symp. Ser., 49 (April 1977) 41-48.
- 9 L. Hub, Adiabatic calorimetry and Sikarex technique, In: *Runaway Reactions, Unstable Products and Combustible Powders*, IChemE Symp. Ser., 68 (March 1981) 3/K 1-11.