

## THE THERMAL SCREENING UNIT (TS<sup>U</sup>) A TOOL FOR REACTIVE CHEMICAL SCREENING

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The thermal screening unit is an instrument specifically designed for the fast and efficient hazard screening of liquids, solids and heterogeneous systems. The unit provides an alternative device to DSC and DTA for use in hazard assessment and provides information regarding reaction “onset temperatures”, rates of temperature rise as well as crucial information regarding the rates and magnitudes of pressure rise in chemical systems. Typical data from the unit is presented together with case studies and a comparison to differential scanning calorimetry (DSC) data.

Keywords: Reaction hazards, Decomposition, Unstable compounds, Hazard screening, Runaway reaction, Exotherm.

### INTRODUCTION

Virtually all large multi-national chemical companies are involved with some form of hazard assessment program. An important element of this is reactive chemical testing, which incorporates the assessment of feeds, intermediates and products for thermal stability so that hazards during storage, manufacture and transportation can be accurately assessed. In recent years, even medium and small companies have had to include such testing in the route from the R&D laboratory to full-scale production. Regardless of the size of corporation, the evaluation procedure will frequently include a “screening step” aimed at separating the innocuous chemical materials from those that are potentially hazardous. Typically thermal hazard screening is performed by either a theoretical and/or an experimental investigation.

Theoretical methods of hazard screening are based on mathematical models that are designed to evaluate the potential energy release on the decomposition of the study material into smaller more stable species. In principal such calculations require only a knowledge of heats of formation for the chemical species involved, however, in practice the calculations become more complex because this essential information is not often available in the literature.<sup>1</sup> By employing these techniques it is sometimes possible to make a first guess or estimate of a compounds hazard potential. However, the limitations of theoretical calculations are widely recognised. These include the limited number of predictable reactions that can be assessed and the difficulty of potential side reactions that may have major influence on the magnitude of a runaway reaction and process safety.

A significant draw back of many theoretical calculations is the limited information that is generated regarding the rates and magnitudes of the pressure rises. This information is pre-requisite if a process is to be safely scaled-up, since it is the build up of pressure that will cause the product to be vented from a reactor or worse still cause damage to an industrial plant. These draw backs in conjunction with the considerable user experience required to perform a theoretical calculation makes this approach rarely sufficient to enable direct process scale-up without further downstream experimentation.

Experimental thermal screening methods on the other hand primarily involve the heating of a few milligrams of sample over a user defined temperature range to examine the presence or absence of thermal activity. Classically, these analyses have been performed by popular techniques such as DSC (differential scanning calorimetry) and DTA (differential thermal analysis). However, although these test methods have found widespread application in many areas of chemical research and development, in the area of hazard screening there are

numerous shortcomings that are not always recognised. Consequently, many chemical systems are scaled-up on the basis of this hazard assessment data even though it is not always appropriate to do so.

To improve the situation slightly some organisations will supplement the data obtained from DSC and DTA<sup>2</sup> with kinetic studies performed in a reaction calorimeter<sup>3</sup>. Reaction calorimetry is a powerful tool for the elucidation of thermodynamic information from the normal (or desired) reaction. It also enables the operator to examine the profile by which heat is liberated from a reaction. However, in situations where the chemistry is unknown such an instrument should be applied with extreme caution, particularly when there is the possibility of unknown side reaction products since these materials could be potentially more hazardous than the proposed reaction under study. Reaction calorimeters also have the disadvantage that they employ sample volumes in the range 50 ml to 1 litre, which is too large, from both a safety and economical viewpoint for sample screening.

## DIFFERENTIAL SCANNING METHODS

### GENERAL FEATURES OF DSC/DTA TESTING

In a typical DSC or DTA experiment a few milligrams of sample (often in a sealed metal pan) and an inert reference material are heated together at a defined rate of typically 10 degree Celsius per minute<sup>2</sup>. The temperature of the sample and the reference are monitored and if the temperature of the sample begins to diverge from that of the reference, evidence of thermal activity is inferred. Using this data it is possible to determine an "onset temperature" for the thermal event and measure the amount of heat released.

Using this information the "onset temperature" can be compared with the materials' proposed operating or storage temperature. If these are similar, it might represent a potential hazard. In a similar manner the information relating to energy release can be used to estimate the likely temperature and pressure rise if the exothermic reaction did occur. It is through this type of comparative analysis that DSC/DTA data can be used to estimate the severity of a possible hazard.

The principle benefit of this type of testing is that it can be conducted in just a few hours, requiring limited operator skill. When low running cost is also taken into account, the widespread use of DSC/DTA methods can be easily understood. However, in practice these aspects should be weighed against the many disadvantages that relate to the possible reliability of the data and the potential problems that can ensue from not screening reactions properly.

### LIMITATIONS OF DIFFERENTIAL SCANNING DATA

The differential thermal instruments described above are employed for a wide range of analytical determinations in addition to hazard screening. In fact most DSC and DTA applications do not relate to hazard assessment at all and the comments made in this paper will not be concerned with these alternative functions.

A design feature that contributes significantly to the ease of use and low running cost of DSC and DTA is the small mass of sample required which is typically in the milligram scale. From a hazard evaluation perspective, this extremely low sample mass can be a serious disadvantage due to the increased uncertainty in experimental reproducibility. Whilst the testing of pure materials presents no problems, taking a representative sample of a mixture on such a small scale can be difficult. For example, in order to evaluate process intermediates

(and sometimes, even products), it is frequently necessary to draw a "live" sample from a reactor. The extraction of such low sample masses that are wholly representative of the system under these conditions can be difficult.

One of the most important pieces of information obtained from thermal scanning devices is the so-called "onset temperature" for exothermic activity. However, it is important to realise that this "onset" threshold is not a fundamental property of a reaction and the measured value depends very much on the instrument sensitivity and the procedure by which the experiment is performed. In Figure 1<sup>4</sup>, the onset temperature determined by DSC is compared with that from an adiabatic instrument (in this case the "accelerating rate calorimeter", ARC) using approximately 5g of sample<sup>5</sup>. This information was reported by the Dow Chemical Company from their historical data bank. It shows that in many cases, the "onset temperature" detected by DSC can be as much as 50 °C higher than that reported from adiabatic instruments. In fact in a substantial number of instances the difference between two methods is as much as 100 °C. (There are several cases where the DSC determined "onset temperature" is lower than that reported by the adiabatic testing, but this can be attributed to the study of non-representative DSC samples).

### DSC Vs. ARC Detection Temperatures

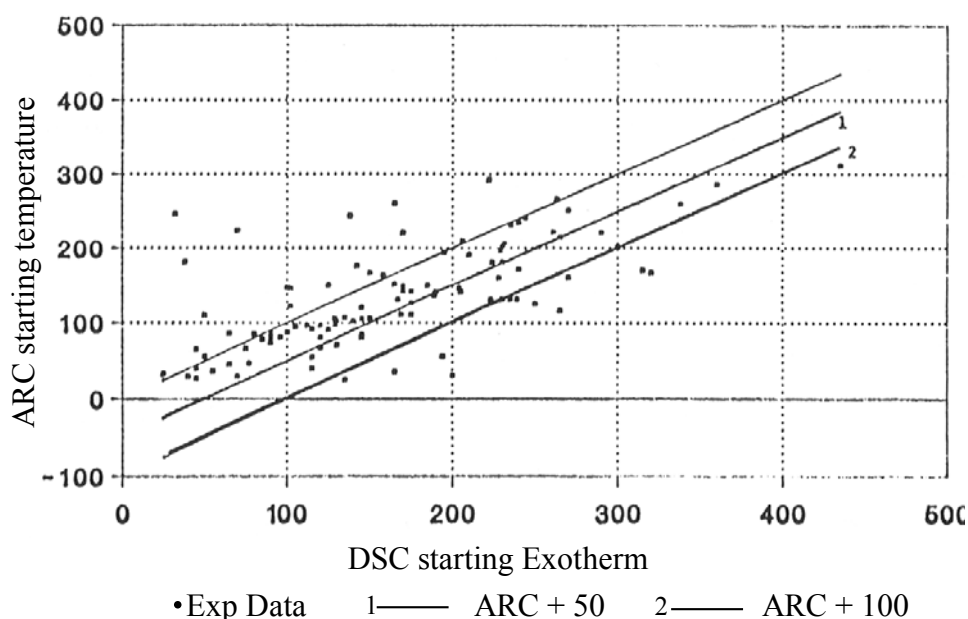


Figure 1: A comparison of "onset temperatures" between DSC and ARC data.

The most significant shortcoming of a DSC or DTA type instrument is that they do not provide any information regarding the pressures generated or the rates of pressure rises measured during a screening a test. The authors are aware that some effort has been made recently to address this problem and produce pressure measuring DSC devices, but so far the data reported has been found to be unclear and noisy and such instruments are limited to only a few psi. However, if the DSC is to be considered as an instrument for accurate hazard assessment and safe process scale-up this information is crucial, since the extent of thermal hazard will be directly represented by the pressure generated during the reaction. It is after all

it is the large pressures generated in runaway reactions that generally cause product venting and in extreme cases catastrophic damage to plant and equipment.

Another important factor that needs to be considered when examining the hazard potential of a material is the aspect of time. It is vital to remember that it is not only the amount of energy released that is important but also the rate at which this energy is released (i.e. the reaction kinetics). Although the aspect of DSC scans do partially reflect the kinetics of the chemical system under study the information that is obtained is very often indirect and can be applied in a qualitative manner. The time scales determined bear almost no relation to the real life incident and unless considerable effort and rigour is put into the kinetic analysis, it is not possible to estimate the rates at which events might occur on the plant.

Taking into account all the above points, it is clear that choice of DSC or DTA, as the primary, or worse still only, method of thermal screening can be misleading and if used without information from additional adiabatic calorimeters could be potentially dangerous.

#### PRACTICAL CASES OF HAZARDS UNDETECTED BY DSC/DTA

There are at least three incidents known to the authors, over the last few years, where major hazardous accidents have resulted, in spite of DSC or DTA data being available. For reasons of confidentiality, it is not possible to give very much detail of these cases but they all resulted in serious accidents.

The first was a fine chemicals plant in New Jersey, USA, where the mixture in a distillation column underwent a violent runaway reaction. This material had been thoroughly tested using a DSC; in this case by the operating chemical company themselves and this had revealed no signs of a potential hazard. The company was experienced in the use of calorimetry and relied on differential scanning techniques for hazard screening followed by reaction calorimetry to check the “desired” reaction. Subsequent to the accident, which caused catastrophic damage to the column plus substantial damage to neighbouring equipment, samples (around 5 to 10g) were tested in an adiabatic calorimeter where the runaway incident was readily reproduced and repeated. This highlights the importance of employing suitable and representable sample sizes when performing hazard assessment.

The second case occurred in the Middle East, this time in a reactor vessel. The process had been run for some time on pilot plant scale without any problem. When it was due to be transferred to the commercial scale plant, three thermal evaluations were performed, two on separate DSC devices (run by two different companies) and one on the Mettler RC-1 reaction calorimeter.<sup>6</sup> The DSC tests were performed to determine the likelihood of a thermal runaway and the reaction calorimetry test was used to confirm the heat release during a normal, controlled batch. When the process was transferred to the large scale, a violent runaway reaction occurred totally overwhelming the relief vent on the reactor. This led to an over-pressurisation of the vessel resulting in large quantities of reactants being discharged as the vessel cover was lifted under pressure. Subsequently the hot vapours released ignited and caused further damage.

The incident in the final example was less dramatic but illustrates an important point. It involved a small company that had recently acquired a DSC as its first hazard evaluation tool. The process required the mixing of two liquids at room temperature, followed by heating to 85 °C before the slow addition of the final reactant to make an organic intermediate for the pharmaceutical industry (Figure 2). Tests had been performed with a mixture of the two reagents added at the start and with samples of the three reactants together. No problem was detected in the first test but the second test indicated some exothermic heat release.

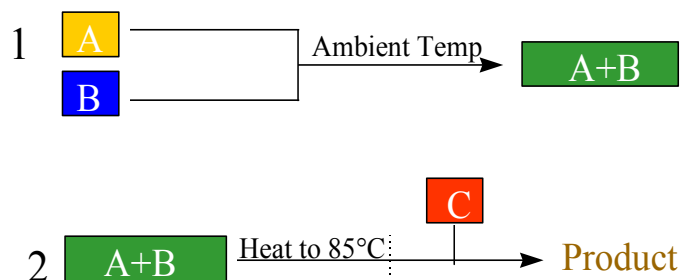


Figure 2: Two preparation of a an organic intermediate

Based on results of the first test, it was decided that the two starting ingredients could be safely pre-mixed in drums ready for charging. However, when this was performed the drums were found to rupture after about 2 hours. Subsequent testing with an adiabatic device (in which pressure data was measured) revealed that while the DSC had correctly reported a lack of exothermic activity, however, it had failed to register the fact that, even at room temperature a considerable amount of gas was being generated albeit at a slow rate. This highlights the necessity for pressure data when scaling up a process.

## THE TS<sup>U</sup> AS A SCREENING TOOL

### ESSENTIAL FEATURES

The TS<sup>U</sup> (Thermal Screening Unit) has been developed as an alternative to DSC as a primary thermal screening method. A schematic diagram and a photograph of the TS<sup>U</sup> are shown below in Figure 3.

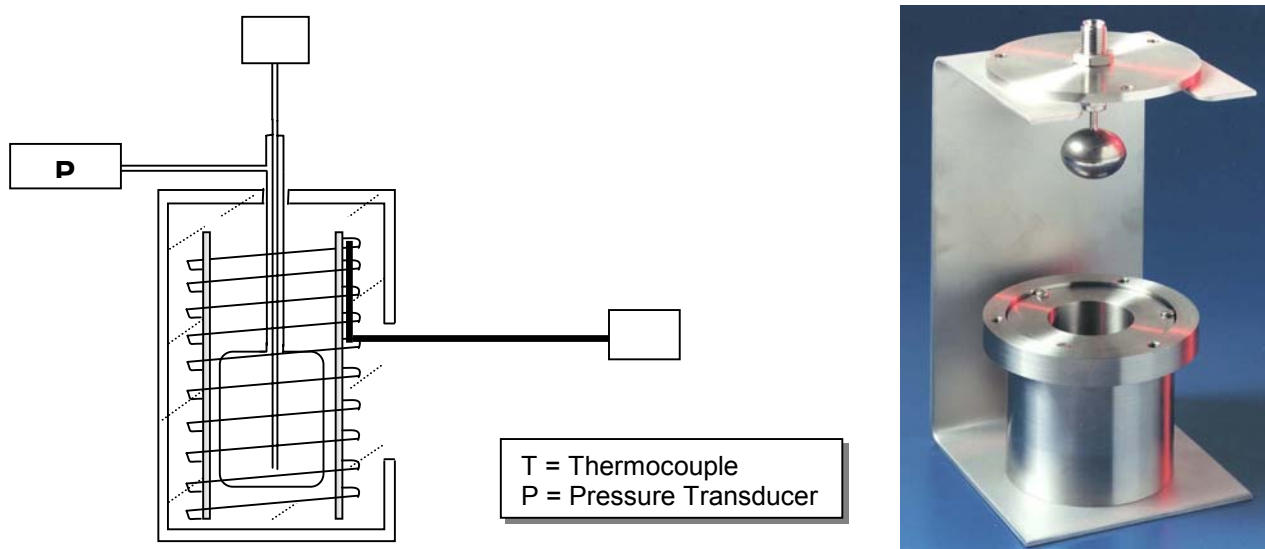


Figure 3: Schematic diagram and photograph of the Thermal Screening Unit (TS<sup>U</sup>).

The sample is contained in a pressure tight metal (or glass) test cell, suspended in the middle of an “oven”. The oven consists of a metal cylinder with a heating coil wrapped around the outer surface that is heated at a user-defined rate. On performing a test the user controls the ramp rate(s) of the oven. After an initial delay due to “thermal lagging” effects the sample temperature will be found to follow the oven ramp at the same rate with a slight “offset” (which will depend on the physical characteristics of the test material such as specific heat). When an exothermic or endothermic process is detected the sample temperature will be found to deviate from the background-heating rate identifying the “onset temperature”. The rate of rise in sample temperature ( $dT/dt$ ) and the maximum value reached,  $T_{Max}$  before returning to the background-heating rate reflects important characteristics of the thermal event.

In addition to temperature data, the thermal screening unit is also equipped with a pressure transducer that records changes in sample pressure as the reaction proceeds. This provides the operator with a second method by which sample activity can be identified. This alternative method of sample analysis is particularly useful since it provides a measure of the total pressure generated in the reaction,  $P_{Max}$  and the rate of pressure rise ( $dP/dt$ ). The pressure data also enables very mild exothermic decomposition reactions which result in the production of non-condensable gas to be detected even if the associated temperature rise is too low to be reliably detected.

#### THERMAL SCREENING OF TOLUENE

The application of the thermal screening unit is illustrated below for the screening of toluene, Figure 4.

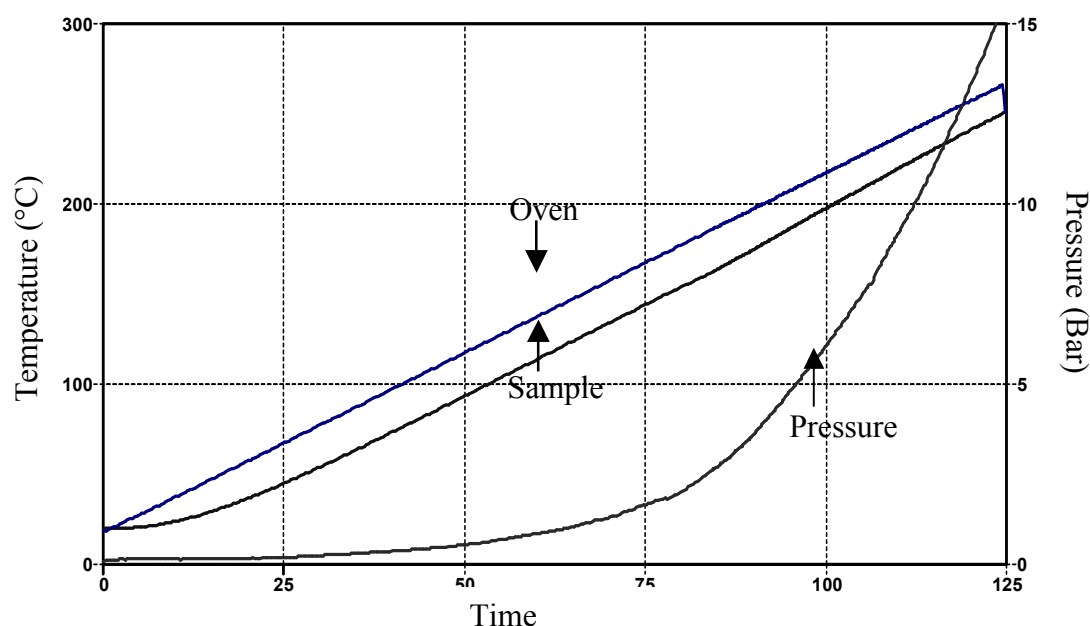


Figure 4: Thermal Screening of HPLC grade toluene (4.8 g) at 2°C/min from ambient temperature to 300 °C.

From Figure 4 it can be observed that after an initial “settling period” the oven and sample temperature ramps are found to run almost parallel to each other, indicating no thermal activity within the solvent. This is exactly what we would expect for an inert material and the trace can essentially be considered as a reference to which other chemical systems can be compared. On examination of the pressure data it is found that the pressure increases with

temperature. This increase in pressure is due to the increasing vapour pressure of toluene with temperature. Upon completion of the test the sample is allowed to return back to ambient temperature and pressure. On cooling the pressure temperature curve is identical to that observed for heating confirming that absence of sample activity.

#### THERMAL SCREENING OF 20% DI-*T*-BUTYL PEROXIDE (DTBP) IN TOLUENE

The thermal screening of 20% DTBP in HPLC grade toluene (4.8g) at 2°C/min is shown below in Figure 4. The reaction consists of the decomposition of an organic peroxide with the formation of ethane gas. This is shown mechanistically in equation (1.1).

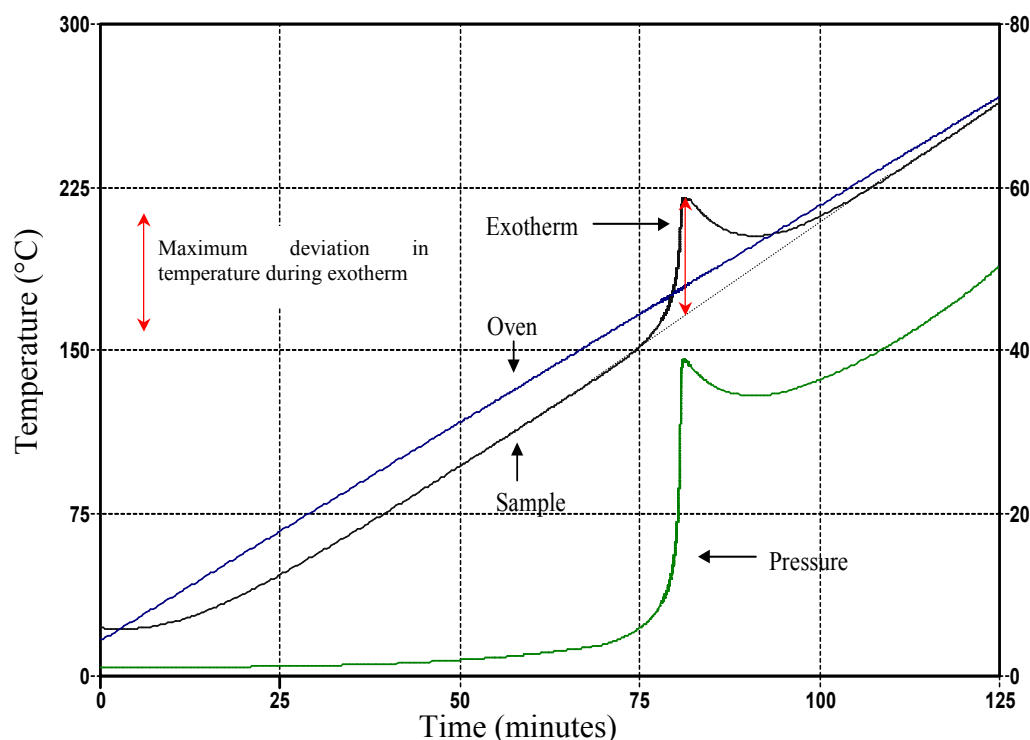
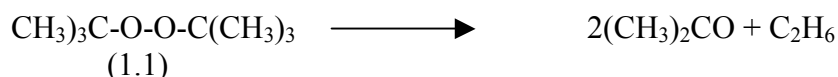


Figure 5: Thermal screening of 20% DTBP in toluene.

From Figure 5, it can be seen that the oven and sample heating traces at the start of the screening are similar to those of just toluene with the establishment of two linear ramps separated by an offset  $\Delta T$  after an initial settling period. However, once the sample temperature has reached approximately 130 °C a clear deviation from linearity in the sample temperature profile can be detected. This marks the “onset” or “start” of thermal activity in the sample. This deviation from linearity continues to increase as the sample undergoes a thermal runaway until eventually the sample temperature reaches a maximum temperature of almost 50 °C higher than the oven. The peaking in the sample temperature profile indicates the end of the thermal decomposition reaction upon which the temperature is found to fall. The fall in sample temperature continues until it re-establishes a new baseline value which is almost identical to that achieved before the exotherm. The re-establishment of a second

baseline after the exotherm is valuable since many decomposition reactions generate by-products that themselves can decompose further at higher temperatures.

In addition to the sample temperature data a wealth of information can be obtained from examination of the associated pressure curve. Similar to the sample temperature response, a clear deviation from the expected vapour pressure curve can be observed in the reaction at approximately 130 °C. In fact it could be argued that the reaction “onset” is clearer in the pressure data than the temperature. Again the shape of the pressure profile provides information on the period over which the reaction occurs. The pressure data also provides additional information about the reaction. On termination of the experiment at 300 °C the sample temperature is found to gradually return to ambient values, but the pressure remains at 14.87 bar. This shows that the decomposition reaction has occurred with the production of non-condensable gas. The knowledge of whether a runaway reaction does or does not proceed with the production of non-condensable gas is significant since it will determine the requirements of the safety system that will be required on scaling up the process. The magnitude of the pressure rise ( $P_{Max}$ ) in the system is also important since it will also have an influence on the pressure rating of reactor to be employed.

It has already been discussed that from analysis of the temperature and time profile the thermal decomposition of 20% DTBP has been found to provide a reaction “onset temperature” of approximately 130 °C. However, it is important to remember that the determination of an onset temperature is purely subjective and will depend upon a number of factors including; the method by which the experiment has been performed, the thermal mass of the test cell relative to the sample and the method by which the data is analysed. This can be demonstrated by plotting the data in a different manner to determine the onset temperature. Figure 6 shows a plot of  $dT/dt$  against temperature for the above decomposition reaction.

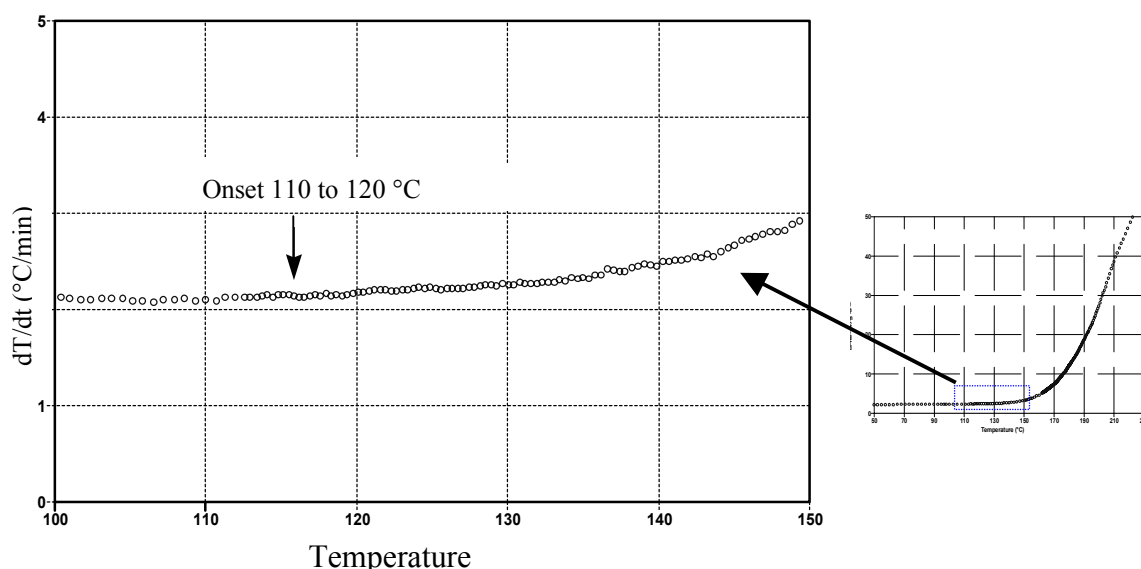


Figure 6:  $dT/dt$  versus temperature data for the thermal screening of 20% DTBP in toluene.

In plotting  $dT/dt$  against temperature it can be seen that the observable onset temperature for this reaction can now be determined to be in the region of 110 to 120 °C, almost 20°C lower than previously identified from the temperature-time profile and similar to data,



reported for larger adiabatic calorimeters. This highlights the importance of careful data analysis during the interpretation of screening data to determine onset temperatures. Also from the plot of  $dT/dt$  against temperature it is also easy to determine the rates of temperature rise at different temperatures and to provide an unambiguous measure of the rate of the reaction runaway.

To examine the reproducibility of the thermal screening unit data for this reaction the experiment was repeated eight times and various parameters recorded. These included the maximum rates of temperature and pressure rise and the maximum deviation from the sample baseline during the exotherm to determine the exotherm temperature rise (the baseline was assumed to follow a linear ramp at the specified heating rate of the sample, as shown in Figure 5). A summary of these experiments is given below in Table 1.

Table 1: Experiments on the thermal screening of 20% DTBP in toluene to establish reproducibility.

Experiment Number	1	2	3	4	5	6	7	8
Onset temp (°C)	120	115	115	122	132	120	117	110
Maximum temperature of exotherm (°C)	227	229	229	220	225	231	229	231
Maximum deviation from sample temperature ramp (°C)	68	68	69	53	62	71	68	68
Maximum $dT/dt$ (°C/min)	61	58	52	41	45	59	56	56
Maximum $dP/dt$ (bar/min)	94	119	110	101	-	99.01	-	148

Examination of the maximum deviation of the sample temperature from its baseline value during the exotherm provides an average temperature rise of  $65.9\text{ °C} \pm 3.76$  (at 95% confidence) indicating that the magnitude of the temperature rise is reproducible. Measurement of the sample temperature rise therefore provides a suitable method by which the extent of a reaction runaway can be compared. To investigate this hypothesis further the reaction was performed with a 10 % solution of DTBP from which an average temperature rise of  $21.86\text{ °C} \pm 3.17$  (at 95% confidence) was observed. This is exactly what would be expected for a lower peroxide charge and re-enforces the qualitative value of using peak heights as a measure of exothermic activity. These trends in reproducibility are also mirrored in the data recorded for  $dT/dt$  max,  $dP/dt$  max and the maximum observed temperature of the exotherm, suggesting that for similar reacting systems the magnitudes of these quantities provide suitable markers by which reaction runaway potential can be compared.

The width of the exotherm peak is also found to be important diagnostically since the width of the peak will provide some idea of the time period over which the reaction occurs. For the nitrocellulose dye systems that are discussed below we find that the exotherm peaks are extremely narrow revealing that the rate of heat release are much higher and occur over a very short time period.

## THERMAL SCREENING RESULTS FROM RECENT STUDIES.

### THERMAL SCREENING OF A SERIES OF NITROCELLULOSE DYES

It is well known that nitrocellulose compounds will catalytically decompose in their dry state to give CO, CO<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub> and NO. Nitrocellulose pigment dispersions contain up to 50% nitrocellulose, which makes them particularly difficult to handle during manufacturing and processing. These materials have therefore been the focus of both DSC and adiabatic calorimeter studies making them an ideal test series by which the performance of the thermal screening unit can be compared.

A series of nitrocellulose dyes (0.5 g) were heated from ambient temperature to 280 °C at a rate of 2 °C/min to assess their thermal stability. A typical trace for the thermal screening of a yellow nitrocellulose dye is shown below in Figure 7.

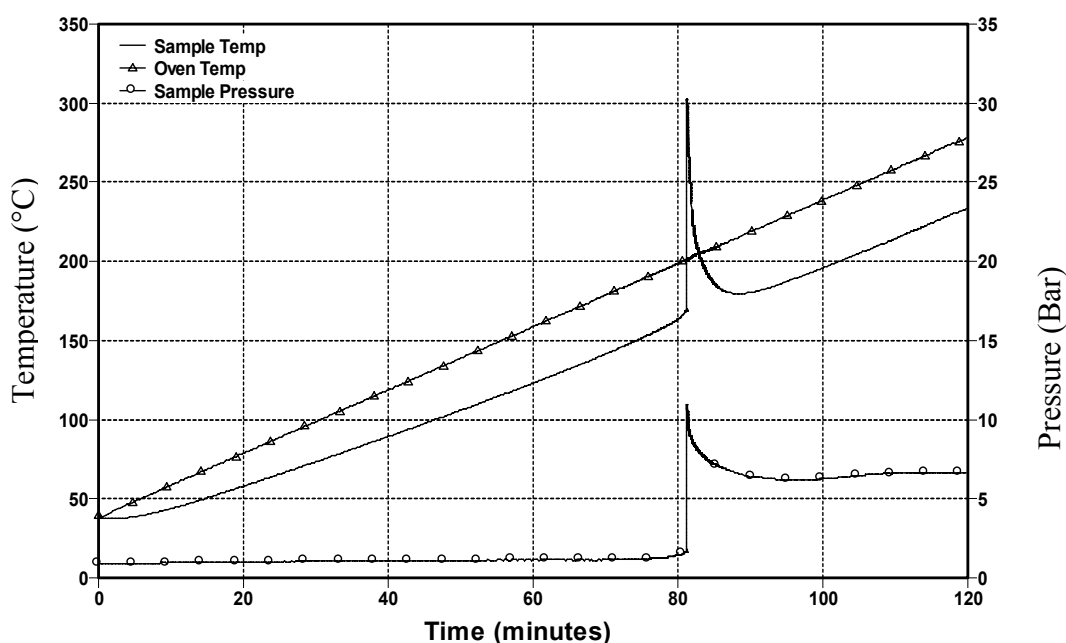


Figure 7: Thermal screening of a nitrocellulose dye at 2 °C/min from ambient to 280 °C.

From Figure 7 it can be clearly seen that the rate of decomposition of nitrocellulose is much greater than that observed previously for the screening of DTBP ( $dT/dt_{Max} = 269.5$  °C/min and  $dP/dt_{Max} = 550$  bar/min compared to 53.5°C/min and 111.8 bar/min for DTBP). This difference in thermal activity is also evident from the width of the sample temperature profile which is significantly narrower than that observed for DTBP, showing that the width of the sample temperature deviation provides evidence of the rate of energy release.

The results obtained during the screening of a series of nitrocellulose dyes are shown below in table 2. From these results the violet pigment can be identified as having the lowest thermal stability with an onset temperature (as determined from a  $dT/dt$  against temperature graph) of 127.4 °C and a deflagration temperature of 161 °C. (“Deflagration” is used here to describe the point at which the temperature and pressure begin to rise sharply).

Table 2: Thermal screening of a series of nitrocellulose dyes.

Pigment	Onset Temp (°C)	T <sub>Max</sub> (°C)	dT/dt <sub>Max</sub> (°C/min)	dP/dt <sub>Max</sub> (Bar/min)	T <sub>deflagration</sub> (°C)	ARC data T <sub>deflagration</sub> (°C)
Violet	127.4	338.8	318.4	497	157	149
Yellow	139.5	302.5	269.5	550	165	160
Red	149.3	392.8	422.8	630	170	-

Table 2 also shows data for analysis of the same dyes using an accelerating rate calorimeter (ARC) in which the experiment is performed in an adiabatic environment (heat step temperature of 10 °C and a slope sensitivity of 0.02 °C/min). Again the same trend in thermal stability is detected and similar onset and deflagration temperatures recorded. Unfortunately, due to the high pressures that were generated in these experiments it was not possible to analyse these samples by DSC to make a direct comparison. However, other workers have reported an alternative temperature scan DSC procedure in which the onset temperature measured for these dyes were found to give the same trend in thermal stability (no deflagration temperatures recorded).

#### DETECTION OF ENDOTHERMIC ACTIVITY

In addition to the detection of exothermic processes the thermal screening unit can also be used to detect endothermic reactions. A demonstration of this capability is shown in the thermal screening of 4 g of hydroquinone at 2 °C/min from ambient to 300 °C, shown below in Figure 8.

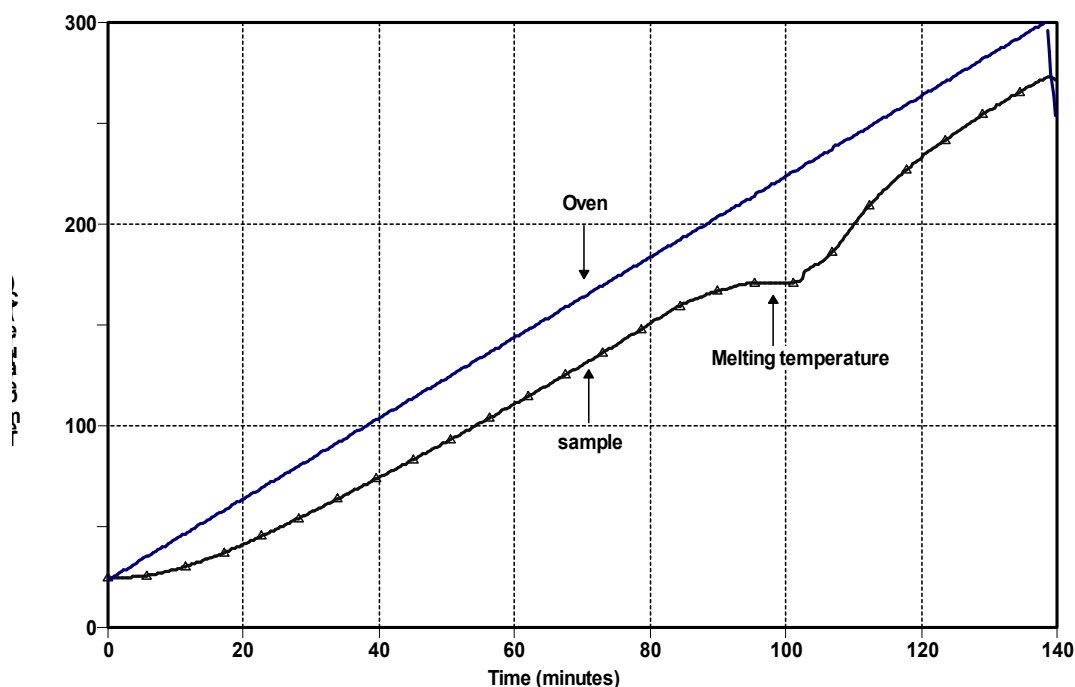


Figure 8: Thermal screening of hydroquinone from ambient to 300 °C at 2 °C/min.

In a similar manner to the screening of liquids, on performing a thermal analysis of a solid sample two linear ramps are generated separated by an offset  $\Delta T$ . Generally, for solid materials it is found that the offset between the two temperature profiles is slightly greater than that obtained for liquid samples and this can be attributed solely to the differences in heat transfer properties between the two types of materials.

On the detection of endothermic activity the sample temperature trace is observed to peak downwards, similar to what would be expected in a DSC type instrument. Again, the depth of this peak and the aspect of the peak provide a wealth of information regarding the magnitude of the endothermic process and the rate at which it occurs. In the example presented here for the screening of hydroquinone a levelling-off in the sample temperature occurs in the range 171 to 173 °C. This corresponds to the solid-liquid phase transition of the sample and continues for several minutes until the entire sample has melted. This is in excellent agreement to other techniques that report a melting point for hydroquinone in the region 171 to 173 °C.

Again on completion of the sample melting the sample profile re-establishes the initial baseline that was achieved before the thermal activity, enabling secondary thermal events to be identified within the sample. An interesting example of an endothermic process followed by an exotherm is in the thermal screening of L-Ascorbic acid (vitamin C) in which the sample melting at 192-193 °C is immediately preceded by a violent exothermic runaway due to the decarboxylation and decomposition of the sample producing pressures in excess of 200 bar.

#### COMPARISON OF THE TS<sup>U</sup> WITH ADIABATIC CALORIMETERS

Adiabatic calorimeters such as the ARC<sup>5</sup> or PHI-TEC II<sup>7</sup> are traditionally considered as the most reliable tool for exotherm detection and for generating quantitative kinetic and thermodynamic data with regards reaction severity. In a typical experiment adiabatic conditions are achieved by taking a sample cell similar to that used in the thermal screening unit and placing it between a set of “guard heaters” that precisely match the sample temperature. Tests are then performed by heating the chemical in temperature steps, (typically 10 to 15 °C) holding the sample for a defined period of time and monitoring the sample for evidence of self-heating. If an exotherm is indeed detected then the guard heaters will follow and thus maintain an adiabatic environment during the reaction runaway.

The thermal screening unit possess many of the desirable characteristics of an adiabatic calorimeter. The system contains a thermocouple within the test cell to enable direct sample temperature measurement and the test cell itself is pressure resistant to over 200 bar and has a thickness of 0.65 mm. The screening unit also uses more representative sample sizes than either DSC or DTA again similar to that employed in an adiabatic system. The thermal screening unit, however, is considerably smaller than an adiabatic system and also much simpler to set-up and operate, often enabling many runs to be performed in a single working day or night. When this is coupled with the ability to operate multiple screening units (up to four) from a single computer interface and the scales of economy involved between the two units it makes the screening unit more suited to rapid screening of multiple compounds.

Clearly the thermal screening unit has not been designed to act in competition with ARC or PHI-TEC II type instruments but instead helps to fill the gap in the market for a device that is wholly concerned with routine, fast and multiple hazard screening.

## CONCLUSIONS

Although DSC and DTA techniques have been applied with great success to many areas of chemical testing and process development their application to thermal hazard screening has in recent years caused much cause for concern. This is particularly true in the modern chemical manufacturing industry where the pressures on process scale-up and development organisations are continually increasing but the development-cycle time scales are under a constant squeeze. This has resulted in the increasing tendency for quick, single test procedures possibly in combination with reaction calorimetry for thermal stability assessment, which without careful interpretation and experience cannot provide a sufficient guarantee that hazardous processes will not slip through the net.

The thermal screening unit has been developed as tool to address some of these problems associated with modern hazard screening and provide an alternative instrument to DSC and DTA. Importantly the unit employs representative sample sizes in the range 0.5 to 5g. These sample sizes not only provide more realistic information for scale up but also enable a whole range of processes to be examined including heterogeneous systems, air sensitive materials, starting materials and intermediates. The unit also importantly provides pressure information, which enables the study of product storage and provides information on expected reactor pressures if a process were to undergo a runaway reaction. By examining information such as  $dT/dt_{Max}$  and  $dP/dt_{Max}$  it is also possible to start to gain information on the rates of energy release from a systems. This latter information is beneficial for the design of vent lines and reactor relief systems and will reduce the number of samples that will have to be examined by an adiabatic calorimeter.

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