

Thermal Techniques Used in the Hazard Evaluation of Pyrotechnics

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ABSTRACT

A hazard assessment provides important information for determination of safe conditions for the manufacture, storage and transportation of pyrotechnics. Sensitivity to thermal stimuli is an important aspect of an overall hazard assessment. This paper describes a number of laboratory techniques that can be used to determine thermal properties of pyrotechnics and other energetic materials. The experimental methods and variable parameters of thermogravimetry (TG), differential scanning calorimetry (DSC), accelerating rate calorimetry (ARC), heat flux calorimetry (HFC) and simultaneous TG/DTA (SDT, for simultaneous differential thermal analysis) are described, along with the information they provide. Experimental examples are provided in each case. All the techniques described are in use at the Canadian Explosives Research Laboratory. No single technique is without its limitations, and a combination of techniques, to provide complementary information, is often the best approach. Many of the methods employed are described in ASTM standards.

Keywords: thermal hazards, differential scanning calorimetry, DSC, thermogravimetry, TG, differential thermal analysis, DTA, accelerating rate calorimetry, ARC, heat flux calorimetry, HFC, simultaneous differential thermal analysis, SDT

Introduction

The production, transportation and storage of pyrotechnic mixtures are fraught with potential hazards. Many of these compositions are sensitive to mechanical and electrostatic stimuli, but

thermal sensitivity is also of concern. The thermal activity, stability and thermal explosion potential of pyrotechnic mixtures must be well known, in order to identify any risk of thermal runaway reactions that could lead to catastrophic events.

A thermal runaway reaction occurs when the rate of heat generated by that reaction exceeds the rate of heat loss. Chemical reactions of pyrotechnics generally produce large amounts of heat and many of them generate a significant quantity of gaseous products. When confined in a closed system, a decomposing pyrotechnic can produce considerable pressures, resulting in vessel rupture and explosion. While most pyrotechnic mixtures deflagrate (burn) when ignited, many can undergo the transition to detonation (supersonic burning), especially when confined. A detonating material presents a severe hazard in many ways, with contributions from fragments, blast waves and heat.

Thermal techniques are often very useful for quality control purposes and can help avoid the malfunction of pyrotechnic devices. Poorly functioning devices can create significant hazards, either directly or indirectly.

Numerous experimental techniques are available to examine the thermal properties of materials, many of which are specifically useful for examining pyrotechnic compositions. An extensive review of the thermal analysis of pyrotechnics was published by Laye and Charsley in 1987.^[1] The purpose of the present paper is not to provide an exhaustive review of thermal analysis as applied to pyrotechnics, but to highlight some of the techniques that can be of use in evaluating the thermal hazard properties of pyrotechnics and other sensitive energetic materials. All of the techniques described are cur-

rently in use at the Canadian Explosives Research Laboratory.

Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) is the most widely used technique in the study of the thermal properties of pyrotechnics. DSC is a technique in which the heat flow in and out of the sample is monitored against temperature or time, while the temperature of the sample, in a specified atmosphere, is either ramped at a constant rate or held isothermal. If the sample undergoes an exothermic reaction, heat will flow out from it; endothermic processes cause heat to flow into the sample. A similar technique, differential thermal analysis (DTA) measures the temperature difference between the sample to be investigated and a reference sample as a function of temperature (or time). If the sample generates heat, its temperature will be above that of the reference and vice versa. Since the two techniques provide largely equivalent information, they can often be used interchangeably. It should be noted, however, that DTA only provides qualitative information on heat flow, so that DSC is the preferred method for quantitative heat flow measurements.

Experimental Parameters

A typical sample size for DSC measurements is of the order of a few mg, but for pyrotechnic compositions a sample size less than 1 mg is recommended, particularly when using sealed sample holders. Small sample size helps to reduce the risk of damaging the apparatus. A larger sample could be used if the temperature were kept well below the expected ignition temperature. Various sample holders, such as aluminum pans (open, hermetically sealed, or having a pin-hole lid^[2]), glass ampoules^[3] and closed metal (non-aluminum) containers,^[4] can be used for various purposes. Also, Teflon-coated pans are often used for compositions that react with aluminum, such as halogen-containing samples.^[2]

If an open or hermetic pan is used for experiments with pyrotechnic compositions, limited quantitative information about the energetics of the decomposition is generally obtained

because of venting of the gas products. However, quantitative data for non-gassy processes, such as phase transitions or thermite reactions, can be obtained.

A variety of purge gases can be used in DSC measurements, and selection of the type of purge gas may be for a specific purpose in an open system. For example, nitrogen is often used to avoid complication of the analysis by oxidation of the sample. In contrast, air can be used to determine whether there is a component of the sample that is easily oxidised. A pressure cell can be used to conduct measurements above or below atmospheric pressure. This cell can be used to measure vapor pressures^[5] and the effect of pressure and different atmospheres on decomposition.

Generally useful heating rates in DSC measurements range from 2 to 20 °C min⁻¹ although the lower end of the range is more commonly used for energetic compositions, to avoid uncontrolled reaction. Additionally, DSC can be conducted in a constant temperature or isothermal mode.

The instrument used for DSC should be calibrated under the same experimental conditions as those intended for the pyrotechnic composition using ASTM procedures.^[6,7] This calibration must be carried out before conducting DSC measurements, if the results are intended to stand alone, in an absolute sense, and to be published. In contrast with heat flux calorimetry (see below), for which calibration is stable for up to a year, calibration for DSC measurements should be checked before each study.

Information Obtained by DSC

For pyrotechnic compositions or their individual components, DSC is used to measure onset temperatures and energetics of phase transitions,^[8] to estimate purity, to determine heat capacities,^[9] and to measure the enthalpy change (ΔH) and kinetic parameters of the decomposition process.^[10,11] Studies using a series of isothermal temperatures yield kinetic parameters^[12,13] that can be compared with those obtained using a variable heating rate method.^[14]

DSC measurements can also “fingerprint” a component in a pyrotechnic composition (e.g.,

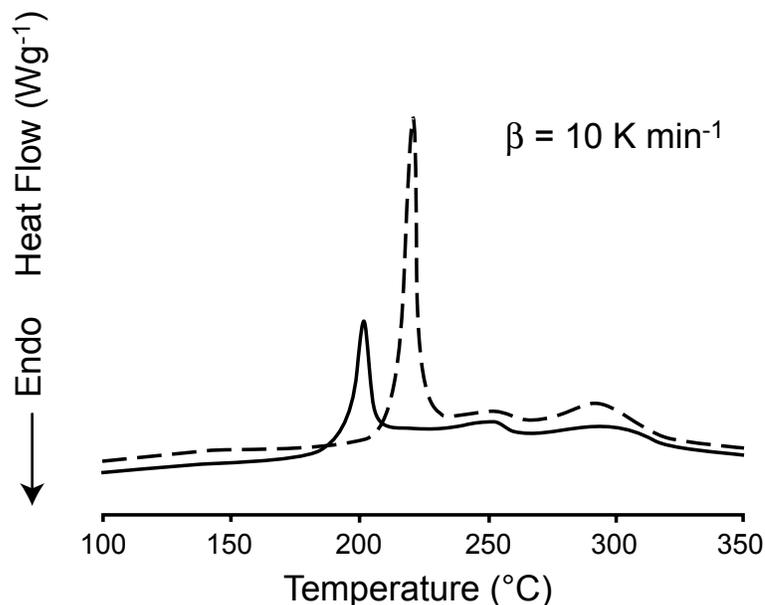


Figure 1. Effect of isothermal aging on the thermal decomposition of the primary explosive KDNBF. Solid line: with aging at 176 °C. Dashed line: without aging. Sample mass 0.2 mg. Nitrogen atmosphere.

Because of the small sample size required by DSC, sampling for heterogeneous pyrotechnic compositions should proceed as follows:

- 1) Select several samples at random from the composition
- 2) Conduct DSC experiments on each of the samples and use the variation in the results to estimate an experimental uncertainty
- 3) Conduct experiments on each pure component of the composition

A careful sampling methodology is necessary, as the material might not be well mixed on the scale of the sample.

The primary advantage of DSC is the rapid turn-around of experimental work, with single experiments lasting approximately one hour, much shorter than the timescales typical of accelerating rate calorimetry (ARC) and heat flux calorimetry (HFC) measurements (see below). DSC is therefore often useful as a preliminary characterization technique before other measurements. However, for pyrotechnic compositions, requiring a careful sampling program as described above, there may not be any signifi-

cant savings in experimental effort. Laboratories that rely solely on DSC for characterization should commit, however, to such a sampling program. It should also be recognized that, because of the small sample sizes involved, DSC does not provide a meaningful indication of safe operating temperatures for full-scale manufacturing processes. Thermal onset temperatures measured by DSC can be substantially (several tens of degrees) higher than those measured by larger-scale experiments such as ARC.

Figure 1 shows DSC traces obtained for the primary explosive potassium dinitrobenzofuroxan (KDNBF), before and after thermal aging below its runaway decomposition temperature.^[15] A strong exothermic decomposition is seen in both traces. However, the onset temperature is substantially lower in the sample that had been previously heated, increasing the thermal hazard.

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Thermogravimetry (TG)

Thermogravimetry (TG) is a technique in which the mass of a sample is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is either ramped at a specified rate or held isothermal. Thermobalances used in TG experiments are highly sensitive, with mass resolution as low as 1 μg .

Experimental Parameters

Sample sizes in TG studies can be up to 50 mg, although with energetic compositions, such as pyrotechnics, the normal sample size is a few mg, to reduce the risk of damaging the equipment. As for DSC, it is important with such a small sample size to take precautions to obtain results that are representative of the bulk sample. Typical heating rates range from 2 to 20 $^{\circ}\text{C min}^{-1}$, with a typical temperature range from ambient to 1000 $^{\circ}\text{C}$. Normally, TG measurements are conducted in an open system with a purge gas flow. The gas environment can be changed either during an experiment or in separate experiments. This feature can be useful in elucidating the oxidation of a component in an oxidizer/fuel system. Isothermal TG can be used to model pyrotechnic storage conditions, to estimate rates of volatilization and/or decomposition and to model the kinetics as in DSC.^[16]

Mass and temperature calibrations are required prior to TG studies. A standard reference material is used for mass calibration and this material is checked against a precalibrated microbalance having a reproducibility of $\pm 1 \mu\text{g}$. The Curie point technique^[17] for temperature calibration makes use of the apparent mass change that occurs when a ferromagnetic sample subjected to a magnetic field exhibits a definite transition temperature at which it becomes paramagnetic.

Information Obtained by TG

Changes in mass of a pyrotechnic composition with temperature or time (at constant temperature) can be determined from TG experi-

ments. This information can help elucidate the nature of the reactions occurring in a pyrotechnic composition and can be used to determine the overall kinetics.^[10] However, before investigating a pyrotechnic mixture, it is extremely helpful to carry out TG experiments on each of the components. Mass changes for the components may result from evaporation, sublimation, interaction with the purge gas, or decomposition. Characteristic thermal behaviour may be attributed to individual components and this property may be used to provide information about the environmental and thermal stability of the components as well as analytical information^[18] for the pyrotechnic composition. Additionally, the kinetic parameters for the processes attributable to each of the components may be determined by a variable heating rate method^[19] or an isothermal study.^[10,15] Compositional analysis of a pyrotechnic composition for volatile and combustible matter and ash can be obtained using another ASTM procedure.^[20]

Figure 2 shows an example of the sort of information that can be obtained by TG. Plotted are TG curves for two anthraquinone dyes used in the manufacture of pyrotechnic smoke compositions. The two dyes are nominally the same and do begin to vaporise at the same temperature. However, one of the dyes has a substantial non-volatile component, as can be seen from the residual mass. Of practical interest is the fact that one of the dyes gave rise to substantial performance problems in the final product. Although this is an example of the use of TG to perform quality control on components of pyrotechnics, there are often hazards associated with the malfunction of pyrotechnics devices.

Simultaneous Techniques

A significant improvement in characterization as well as productivity is achieved by combining DSC or DTA and TG in one apparatus. The union of DTA and TG, a technique known as simultaneous differential thermal analysis (SDT), offers the additional advantage that the temperature calibration in DTA also applies to the TG measurements. However, the experiment can only be done in an open system in a flowing gas environment.

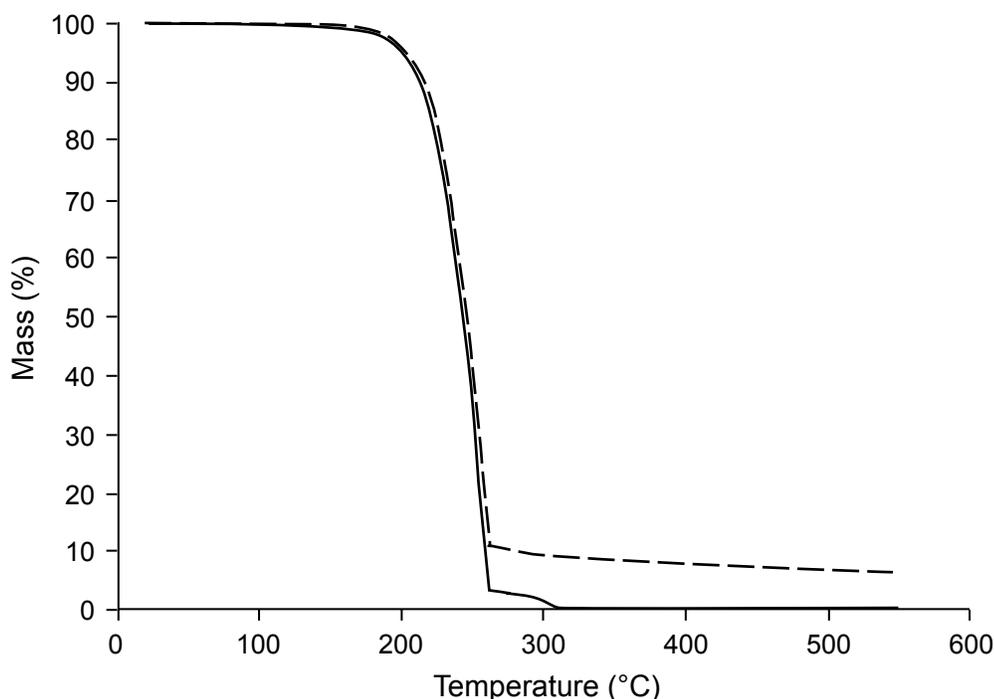


Figure 2. TG curves for two anthraquinone dyes used in the manufacture of smoke compositions. Heating rate $5\text{ }^{\circ}\text{C min}^{-1}$ in nitrogen atmosphere. Sample mass 1.7 mg.

Research Laboratory, both MS and FTIR options are available. Combining these techniques with SDT produces the “hyphenated” technique TG-DTA-FTIR-MS. This powerful combination provides important information about the nature of the potentially hazardous gases produced on decomposition of an energetic material, as well as the associated heat and mass changes.

Figure 3 shows TG-DTA-FTIR results for a sample of Black Powder. The combination of the three techniques is very powerful. A full interpretation of these and other results on Black Powder will be given elsewhere^[21] and only some illustrative points will be mentioned here. For example, the endothermic DTA feature at $130\text{ }^{\circ}\text{C}$ corresponds to a phase change in potassium nitrate; there is no mass loss associated with the phase change, nor is there a concomitant evolution of a gaseous product. In contrast, the final stages of reaction above $350\text{ }^{\circ}\text{C}$ give rise to an exothermic DTA feature, with a corresponding steep mass loss caused by the formation of gaseous products. By FTIR, both the major (carbon dioxide) and minor (e.g., nitrous oxide) products can be identified in the gas phase.

Accelerating Rate Calorimetry

The accelerating rate calorimeter (ARC) is a commercial, automated adiabatic calorimeter described by Townsend^[22,23] and used for assessing the thermal hazard potential of chemicals. An ASTM Standard,^[24] which uses this particular instrument, has been published. Figure 4 provides a cut-away drawing of the calorimeter vessel. An increase in temperature at the bomb thermocouple causes a mismatch with the zone thermocouples resulting in activation of the zone heaters to minimise heat flow out of the sample. This response ensures that heat losses are small and that the system mimics a much larger sample.

Experimental Parameters

Samples sizes of several grams are typical in ARC experiments with non-energetic materials. However, with pyrotechnic mixtures, where uncontrolled runaway and bomb rupture are possible, sample size is usually kept to 1 g or below, to minimize the risk of damage to the equipment. At this scale, the sample size is approximately three orders of magnitude greater

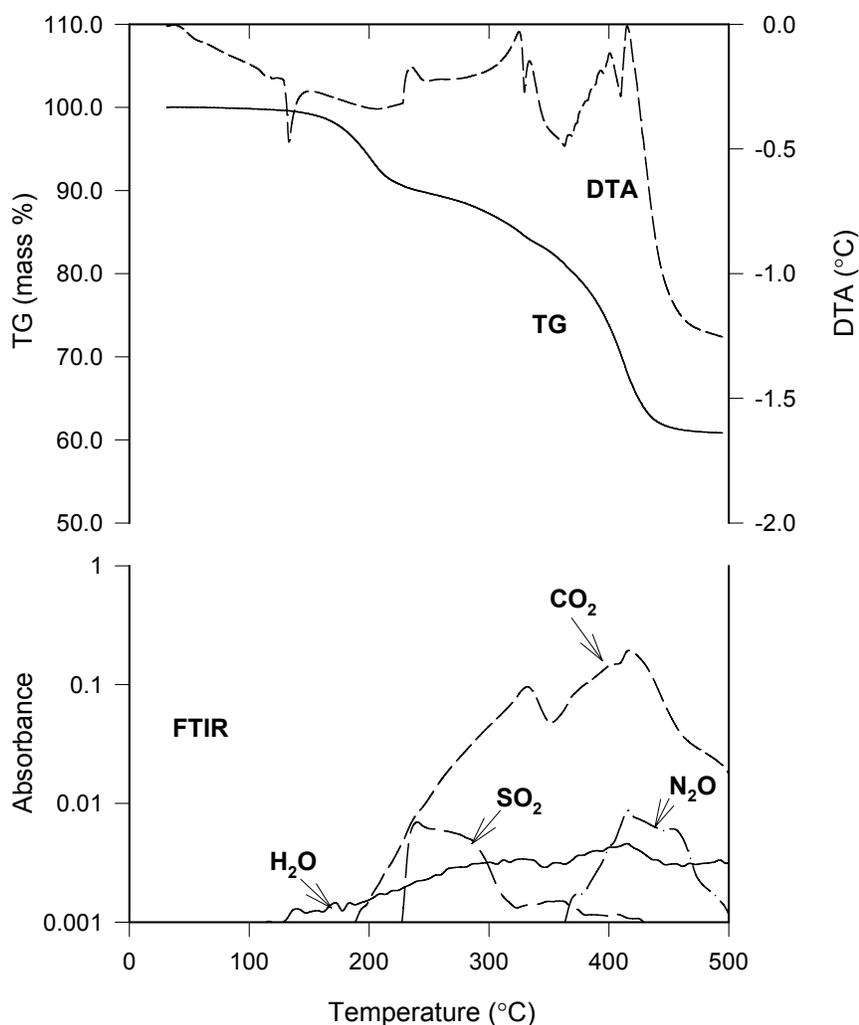


Figure 3. TG-DTA-FTIR traces for 5FA Black Powder in air. Heating rate $5\text{ }^{\circ}\text{C min}^{-1}$. Sample mass 5 mg.

sible, sample size is usually kept to 1 g or below, to minimize the risk of damage to the equipment. At this scale, the sample size is approximately three orders of magnitude greater than in DSC and TG experiments. A single sample, collected at random throughout the sample, will normally be quite representative of the bulk material.

In the standard ARC procedure of “heat-wait-search”, the temperature of the calorimeter is raised by user-selected steps (usually $5\text{ }^{\circ}\text{C}$). The calorimeter is then maintained under adiabatic conditions until thermal transients have dissipated and while a “search” is made for an exotherm. The onset of an exotherm is the tem-

perature at which the self-heating rate (R) exceeds a threshold value (generally $0.02\text{ }^{\circ}\text{C min}^{-1}$). If no self-heating is observed, the temperature is incremented again and the process repeated. In the instrument commonly used for ARC measurements, adiabatic conditions can be maintained provided $R < 10\text{ }^{\circ}\text{C min}^{-1}$. ARC experiments can also be conducted in a quasi-isothermal mode, from which induction times may be obtained under a variety of conditions. The options of using an open or closed system and inert or reactive atmospheres are also available in ARC studies. In a closed system, a transducer (see Figure 4) continuously monitors the pressure. Spherical sample bombs (about 10 cm^3)

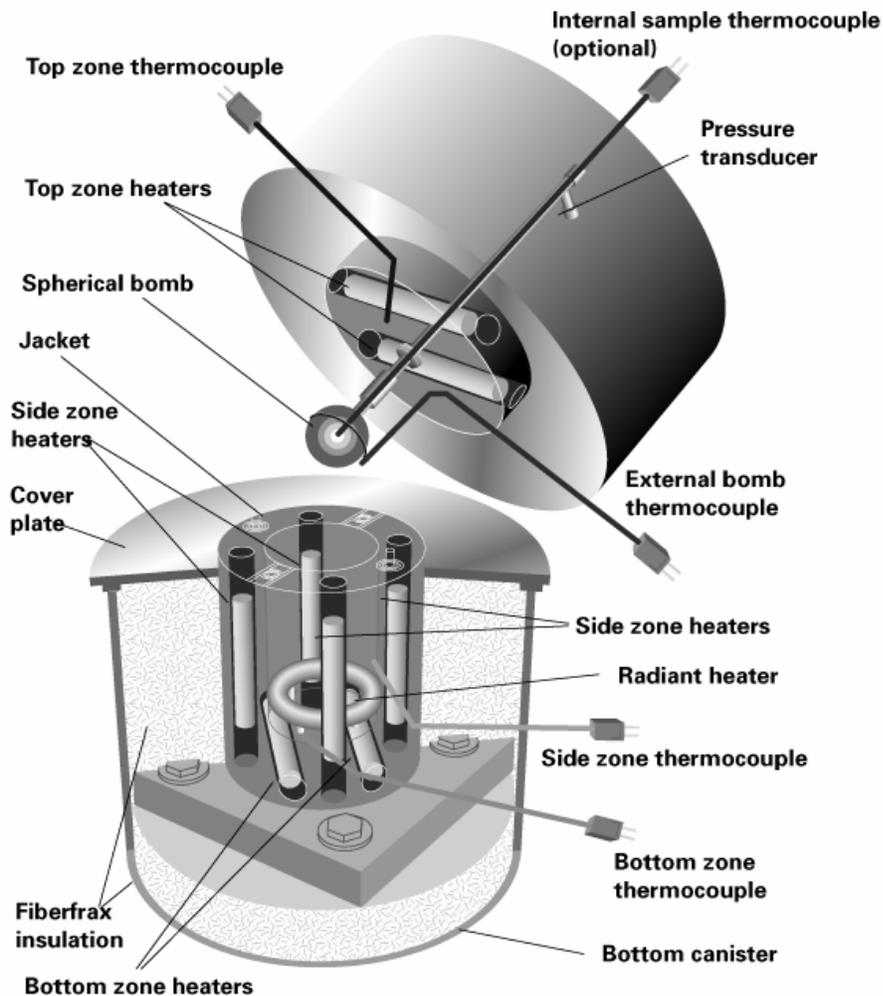


Figure 4. Cutaway diagram of the accelerating rate calorimeter. ARC® is the registered trademark of Arthur D. Little, Inc. Used with permission. All rights reserved.

are available in titanium, stainless steel, glass and Hastelloy. Cylindrical ones are available in Hastelloy. Bomb selection and sample size depend on the purpose of the experiment and the type of sample.

Information Obtained by ARC

ARC is primarily used to derive information about exothermic events, although data for endothermic processes, such as phase transitions, can sometimes be obtained indirectly. Time, temperature and pressure data for a pyrotechnic composition prior to and during decomposition are obtained from a heat-step-wait-search experiment.

The information most commonly obtained from ARC experiments is the onset temperature for exothermic reaction. This value can be used to set limits on operating, storage and transport temperatures. Because ARC measurements are conducted adiabatically (i.e., no heat losses), the results can effectively simulate real bulk behaviour of an energetic material. However, because the heat generated by the sample is used to heat both the sample and the bomb, the effective rate of self-heating is reduced. The threshold temperature at which self-heating is observed can thus be slightly below that of a large bulk sample and may depend somewhat on sample size.

In addition to onset temperatures, ARC can provide information on the kinetics of decomposition, based on how quickly the self-heating takes place once detected. Overall, energetics can be obtained from the total temperature rise in the system due to self-heating, but DSC can usually obtain more precise values. Post-run residual mass and pressure measurements provide useful information about the volatile, non-condensable products of decomposition. It is also possible to collect gas samples for further analysis.

An ARC experiment takes at least one and more usually two or more days for completion, considerably longer than a single DSC experiment. However, owing to the large sample mass, it is not usually necessary to carry out experiments on several samples.

Results of an ARC experiment on 5FA Black Powder are shown in Figure 5. After a series of heat-wait-search steps, the onset temperature ($R > 0.02 \text{ } ^\circ\text{C min}^{-1}$) is reached.

Heat Flux Calorimetry (HFC)

Precision heat flux calorimetry (HFC) can be undertaken using a Tian-Calvet instrument,

as described in the literature.^[25] This instrument, as depicted in Figure 6, consists of a massive aluminium block, with two identical cylindrical cavities located symmetrically about the centre; a thermopile surrounds each cavity. The design results in a sensitivity to heat flow that is significantly higher than for ARC and DSC measurements.

Experimental Parameters

HFC experiments are conducted in the same manner as for DSC (i.e., in a scanning mode or isothermally). However, the maximum heating rate is $2 \text{ } ^\circ\text{C min}^{-1}$, so that HFC measurements usually require a relatively longer period of time. Additionally, the instrumental design imposes a narrow temperature range (ambient to $300 \text{ } ^\circ\text{C}$), which is somewhat limited in comparison with that available from DSC (ambient to $600 \text{ } ^\circ\text{C}$), and ARC (ambient to $400 \text{ } ^\circ\text{C}$). Because energetic materials often decompose at temperatures well below $300 \text{ } ^\circ\text{C}$, the temperature range of HFC may not be limiting. Further, the onset of decomposition may be shifted to lower temperature by reducing the heating rate, albeit at the expense of prolonging the experiment.

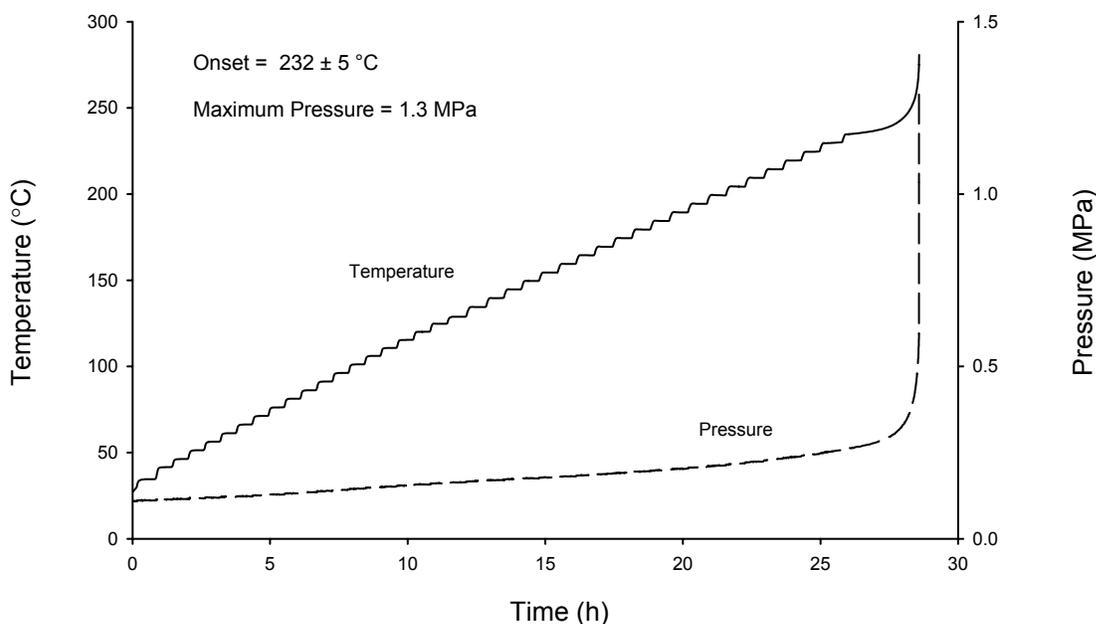


Figure 5. Temperature and pressure traces for ARC experiment on 0.5 g of Black Powder in air.

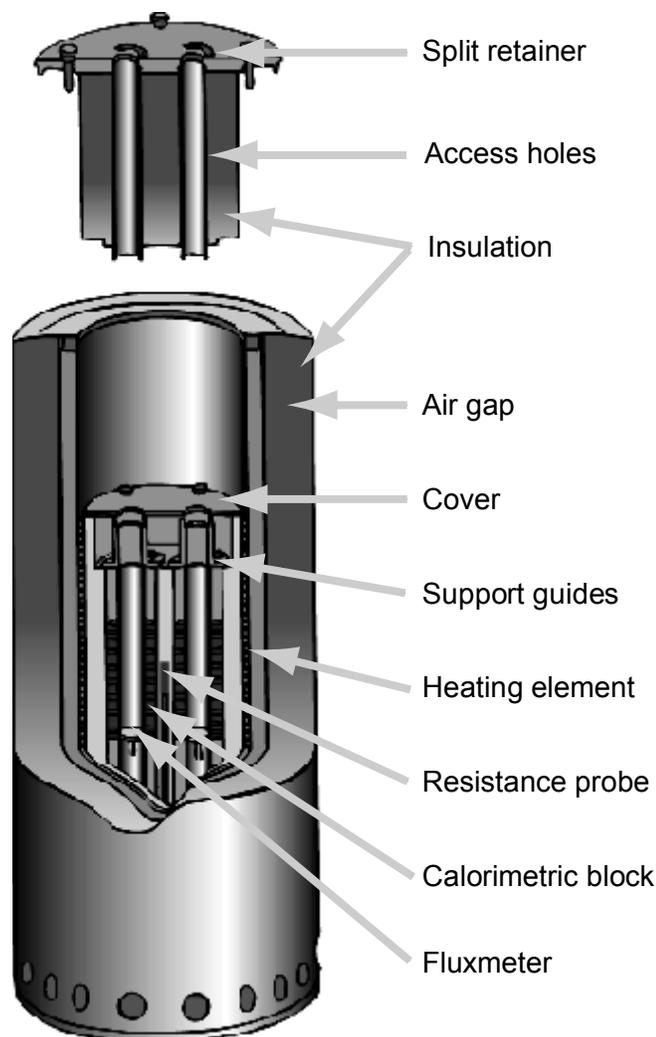


Figure 6. Cutaway diagram of heat flux calorimeter.

Samples sizes used in HFC experiments on energetic materials are on the order of 100 mg, a significant advantage over both DSC and TG where about 1 mg of an energetic material is commonly used. Sampling is not nearly as critical an issue, so that results for heterogeneous compositions are quite reproducible.

In preparation for HFC measurements, the instrument is calibrated for sensitivity using standard reference material (SRM) sapphire. Temperature calibration is similar to that used for DSC. HFC calibrations are valid for about a year, in contrast with DSC and ARC where more frequent calibrations are usually required. Verification of the calibration is conducted by means of an HFC experiment on another SRM, such as benzoic acid.

HFC measurements may be carried out in open or closed systems. In a closed system the cells may be connected to a manifold.^[25] In this system, the pressure is measured simultaneously or, alternatively, the effect of pressure and/or atmosphere on thermal behaviour may be investigated. The manifold in use in our laboratory is designed to work at pressures up to 68 MPa (10,000 psi).

When using a manifold, the free volume is significant (i.e., $>12 \text{ cm}^3$). To reduce the free volume, the energetic material may be enclosed in a sealed glass ampoule, the volume of which is about 0.7 cm^3 . In using this technique, there is a loss of sensitivity as a result of the reduced thermal conductivity of glass, and no pressure results accompany the heat flow information.

Information Obtained by HFC

HFC is used to obtain the same information normally derived from DSC measurements but with significantly enhanced precision. Onset temperatures measured by HFC are lower than measured by DSC and comparable to those obtained by ARC, owing to the greater sensitivity and lower heating rates. HFC is capable of detecting weakly exothermic events not generally observed in ARC, because of the enhanced sensitivity of HFC equipment.

Figure 7 shows the results of a HFC experiment on a Black Powder sample. Of note are the strong exotherm above 230 °C, the endothermic potassium nitrate phase change at 130 °C and the two weak endotherms due to sulfur phase changes in the region of 120 °C (inset). Onset temperatures measured by HFC are close to those found by ARC, but there are substantial differences between the HFC and DTA (see Figure 3) profiles, owing to the very different sample sizes, atmospheres and degrees of confinement in the two experiments. This example demonstrates clearly the benefits of using several techniques to assess the thermal hazard properties of pyrotechnics. In particular, small-scale experiments can give very misleading results.

Conclusions

There are a number of thermal techniques that can be used to provide hazard information on pyrotechnic mixtures. Each of the techniques provides useful information, but none provide a complete picture. A powerful approach is to use a number of different, but complementary techniques to address the same problem. For example, DSC will provide the enthalpy change for an exothermic decomposition, allowing an assessment to be made of the heat that could be generated by a runaway reaction. Although onset temperatures can be measured by DSC, ARC would provide a much better estimate of the temperature at which thermal runaway will occur. Through pressure measurements, ARC can also be used to estimate the volume of gaseous products generated and the rate at which pressure is built up. Further useful information can be obtained by TG, which can be used to detect mass loss corresponding to the early formation of gaseous products. Coupling TG to MS or FTIR instruments can provide information on the nature of the gaseous products and their toxicity. By using complementary thermal techniques in this way, it is possible to make a very informed assessment of the thermal hazard of a particular pyrotechnic mixture.

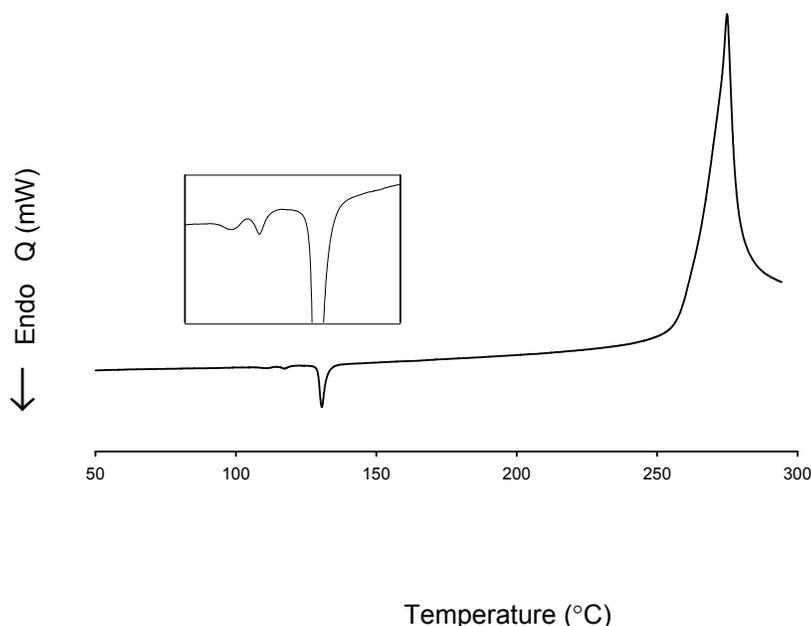


Figure 7. Heat flux calorimetry results for 5FA Black Powder in an argon atmosphere. Sample size 100 mg. Heating rate 0.3 °C min^{-1}

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