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TWO-GRAM DTA AS A THERMAL COMPATIBILITY TOOL

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A useful alternative to the standard techniques described by the North American Treaty Organization STANAG 4147 for determining thermal compatibilities of an energetic with other materials could be a simple 2-gram scale Differential Thermal Analysis (2gDTA). The 2gDTA system consists of samples introduced into standard size test tubes inserted into a controlled aluminum-heating block. Relatively inexpensive thermocouples are used for both temperature control and data collection. Cost of the entire system is much less than any commercial DSC. Since valuable instrumentation need not be protected, the 2gDTA allows thermal decomposition reactions to proceed to complete runaway, mimicking the true worst-case scenario.

Keywords: *compatibility, DTA, explosive, propellant*

Introduction

The very nature of energetic materials warrants respect to the safe shelf life. For a formulation to be considered successful, it must have an extended period (20–30 years) of predictable functional response while avoiding unintended initiation. Given the extended shelf life, any material in close contact with the energetic has the potential to alter the original anticipated shelf life. Such potential is measured as the material's compatibility with the energetic.

As weapons systems/trains change, consideration must be taken as to the compatibility of the new ingredient with respect to the energetic with which it is in contact. For obvious reasons, such design changes cannot be limited to pure field monitoring but must be accomplished through modeling based on driving reactions over kinetically favorable time frames. Use of thermal methods to project thermal compatibilities of materials over extended time has been readily accepted. These compatibility methodologies exist as NATO STANAG 4147 [1].

For relatively high throughput testing, dynamic heating rate techniques utilizing Differential Scanning Calorimetry (DSC) or Thermogravimetric Analysis (TG) have been developed to determine compatibilities within a few days of study. A few milligrams of each material are heated at 2°C min^{-1} until the material is consumed. The admixture is also run under the same conditions. The first thermal event observed in the admixture is compared to those found in the isolated materials. Although there is a current review of STANAG 4147 that may alter the compatibility criteria [2], the ratified methodologies are summarized here. For DSC, heat flows are considered: if the peak temperature flow is not shifted significantly (<4°C) between the admixture and the more thermally sensitive material, the materials are considered compatible. If the heat flow event occurs greater than 20°C below that of the more thermally sensitive material, then the materials are incompatible [1]. For TG, the magnitude of the first mass loss is considered between the admixture and the expected contributions of the isolated materials. A less than 4% difference between the observed and projected mass losses indicates compatibility, while a greater than 20% difference in the calculation indicates incompatibility [1].

While the DSC/TG methods as described are useful screening, there are drawbacks to these methods. The first concern is that the small quantities of material used in tests may not be representative of the larger samples. Per common guidelines, the most precise DSC data is expected when instrumental response is 0.1–10 mW for the thermal event. Exceeding this response can lead to a thermal runaway at minimum or in the worst case, damaged instrumentation. While the low heating rates specified in 4147 permit larger quantities of energetics to be used than could measured at 10°C min^{-1}, the lack of homogeneity within certain formulations remain a concern. The other concern is that the mechanisms driving the DSC/TG observations are less likely to be the same mechanisms as would be observed via long-term aging.

Isothermal methods such as Vacuum Thermal Stability or Heat Flow Calorimetry can simulate years of propellant aging in weeks by raising temperature from ambient to over 80°C. The samples used are typically 1 g or larger, so homogeneity effects are lessened. The

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mechanisms observed via isothermal testing are also more likely to model long-term aging than in the screening tests. The major drawback to these tests is lower sample efficiency relative to the screening techniques, which increases analysis costs. For VTS to be effective, the energetic must produce gases as part of decomposition, which not all formulations do.

One philosophical drawback to the use of each of these four techniques is that the test performed is to model increased sensitivity of a catastrophic event without the actual observation of that event. The practice is considered necessary to protect valuable instrumentation: no one wants to have to keep replacing expensive cells or furnaces, much less the effort involved in recalibrating the equipment only to run a test or two. The only way to avoid this drawback is to design tests that can go to deflagration or detonation without incurring major costs over the DSC/TG test methods. The simple 2gDTA is proposed here as a way to fulfill these goals.

Experimental

The 2gDTA begins with an aluminum heating block. In the Naval Surface Warfare Center Indian Head (NSWCIH) system, there are four holes drilled in the block to accommodate 15 mm OD test tubes. A final hole drilled in the block is filled by the thermocouple feeding back to the control unit. The resistive heater control in our case is an Omega CN4401TR controller connected to an Omega Solid state relay SSR240AC45. The default setting for our instrumentation yields a 1°C min^{-1} heating rate to a preset set point temperature. The aluminum-heating block resides in a separate stainless steel box covered with a Lexan splatter guard to capture any test debris on decomposition.

Each sample is typically performed in duplicate. The typical reaction cell begins with a Pyrex 15·125 mm test tube. For compatibility work, samples are cut into fine cubes if necessary to promote contact. After the sample is in the tube, a 1.5–1.8·90 mm glass melting point capillary tube is inserted into the sample. Two pierced Fiberfrax Duraboard plugs are used to hold the capillary in the center of the test tube. The plugs are punched out with a cork borer and drill bit kept for this purpose. After the capillary and first plugs are in place, alumina is used as an inert filler to minimize thermal lag due to air gaps in the sample to be tested. In the space between the plugs, glass wool is used for additional insulation. The test system is completed once an Omega TMQSS-020G-6 thermocouple is completely inserted down the capillary tube. A reference tube of alumina is also prepared.

Once the individual test tubes are in place in the heating block, the thermocouple leads are fed through a hole in the bay to a simple RS-232 port attached to a computer running Labview software. For compatibility tests, NSWCIH collects the reference temperature, the sample temperature, the difference between the two and the time every second during the course of the test as an ASCII file. On completion of the experiment, the data is uploaded into Microsoft Excel where a series of macros convert it into a file readable by the TA Instruments Universal Analysis (UA) software. This last step is performed as a matter of preference as we have not found interpreting the data on the MS Excel charts to our liking.

Heating two grams of energetic in this system has one of three outcomes. The most usual occurrence is that the decomposition of the material expels the thermocouple housing. In this case, a peak temperature is observed in the difference curve prior to rapidly going to negative as the sample thermocouple returns to ambient. A vigorous reaction may dislodge all other thermocouples. The second most common case is thermocouple destruction: the sample thermocouple reading becomes a nonsensically high value for the duration of the test. The third and least likely case is that the energetic exotherms in place and the 2gDTA curve appears similar to the conventional DSC curve. These three cases are depicted as Fig. 1.

To be a useful compatibility determinant, the arbiter must be reproducible. Peak maximum cannot be used, as some systems eject, others are destroyed, while others may remain in place. Similarly, the 1% reacted value cannot be evaluated [2]. One logical determinant would be the leading extrapolated onset of the observed exotherm. A second logical determinant comes from the history of the machine's use: it had been observed for many formulations that when the tangent to Delta Temperature curve was 45°, self-ignition could not be quenched [3]. The decision to import the ASCII data into UA was largely based on the ease with which that program could calculate the first derivative: the tangent line of 45° equates to the

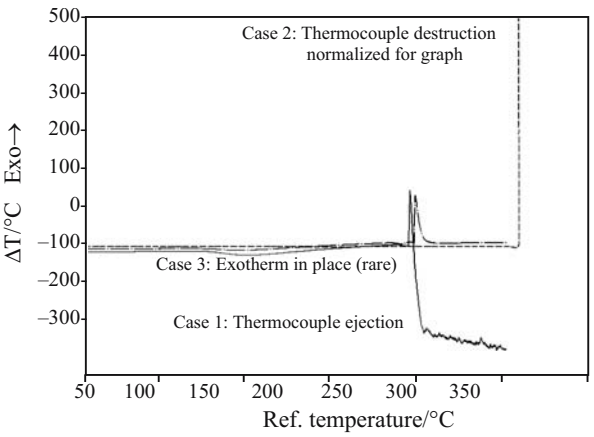

Fig. 1 Types of 2gDTA exotherms observed

instantaneous derivative reaching 1°C/°C for the derivative with respect to temperature.

The only caveat here was that the instantaneous derivative is not calculated based on the digitalized data, but is slightly shifted per the software's smoothing algorithm. For UA, the default smoothing encompasses a 1°C window when the delta temperature is plotted against the reference temperature. Based on the initial data collection rate, the smoothing is then over a 60-second period. The effects of smoothing windows on the 'instantaneous' derivative are depicted in the worst-case (TC destruction) scenario of Fig. 2.

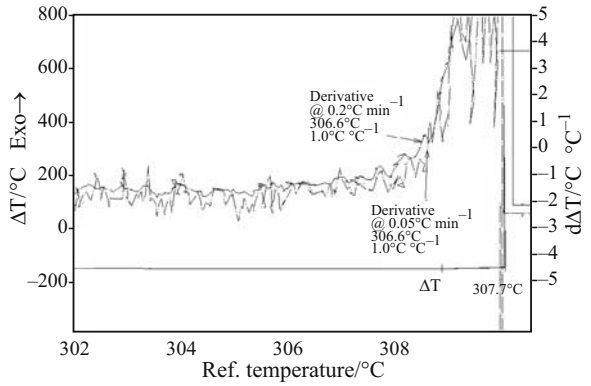

Fig. 2 Effect of smoothing on the derivative delta temperature curve: solid 0.2°C min^{-1} (12 points); dash dot 0.05°C min^{-1} (3 points)

The effect of the smoothing is dramatic in Fig. 2. Only two of the time windows that were considered are plotted here to avoid confusion. The 'instantaneous' tangent temperature is less than the explosive extrapolated onset by more than 1°C in both cases. Derivative curves calculated over broader time windows result in even lower values for this 'instantaneous derivative'. This is due to the jump discontinuity in the delta curve even after the data for the sample temperature has been rescaled from the open circuit value 11762565 to 999. The T-series thermocouples cannot read above 400°C, so the value 999 still allows sense of the result. While the 3-point smoothing is closest to the explosive extrapolated onset temperature, the noise level observed in this data treatment tends to be large. The three-point smoothing is also likely more sensitive than the strip chart measure on which run-away was initially determined [3]. For this reason, the 'instantaneous' derivative for compatibility arbitration will be the 0.2°C –smoothed window.

Results and discussion

The first real case for the 2gDTA as compatibility came from an engineer who wanted to test out compatibilities over an entire weapon system of 11 components. Some of the components had been in previously qualified Navy systems, but new formulations have been investigated. The test request was perfect for the 2gDTA system: the engineer wanted as many components screened together as possible in a short time frame. Conventional DSC/TG testing was not feasible for an 11-component mix. While isothermal testing could have been performed, the associated longer test times were not desirable. The results of testing are depicted as Figs 3 and 4 for one individual tube. As this was one of the first test systems to be compatibility tested via 2gDTA, it was good that the peak temperature, the extrapolated onset temperature, and the first derivative temperature criteria all agree (<4° shifts) that the 11-component system is compatible via the methods used. Similar compatibility testing via 2gDTA has been successfully performed on three other systems, which will not be described here.

The second test case to be discussed is one of known but small incompatibility: RDX (1,3,5-Triazine, hexahydro-1,3,5-trinitro-) with a gas generating fuel. The results of the initial DSC compatibility screening raised processing safety concerns about the integral

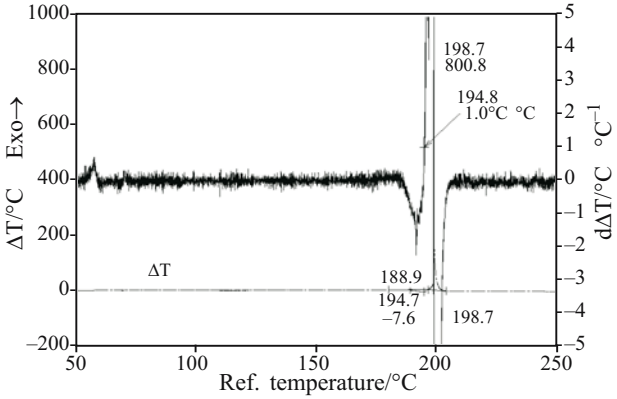

Fig. 3 2gDTA of Energetic 3-component train (no inerts). The three-component train is compatible via the method

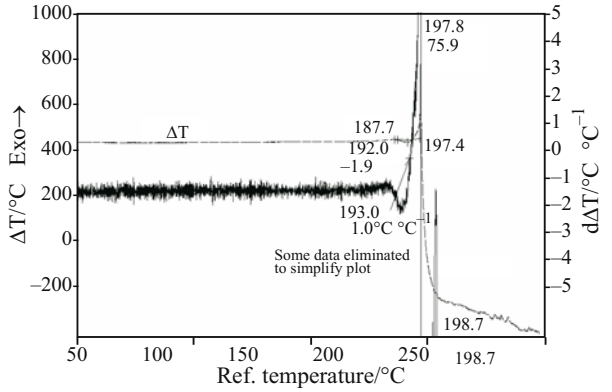

Fig. 4 2gDTA of complete 11-Component Admixture (only one curve for simplicity)

mixing of these two components. While not strictly governed by STANAG 4147, the guidelines are further interpreted by the Navy for formulation process development. To demonstrate the mass effect, the 2gDTA and DSC results at the same 1°C min^{-1} heating rate are compared. For curve simplicity, only one 2gDTA and the DSC curve are shown in the Fig. overlays 5–7.

For RDX, the 2gDTA extrapolated onset is relatively close to the DSC extrapolated decomposition onset as the material melts with decomposition. The fuel shows more thermal mass sensitivity than does RDX, decomposing 13–14°C lower in the 2gDTA (gram-scale) relative to the DSC extrapolated onset (mg scale) at the same heating rate. While the admixture is downshifted by circa 5°C in the 2gDTA extrapolated onset and first derivative values, the magnitude of the shift is less than the DSC result of almost 11°C. The increased mass used in the 2gDTA also increased confidences in the safe processing temperatures. A summary of the findings appears below:

This testing also showed a weakness toward using the first derivative value as the compatibility criterion. In this series, the amount and rapidity of gas generated when the fuel decomposed was sufficient to also dislodge the reference thermocouple from the test block. Therefore, the first derivative result was based on the maximum near the decomposition extrapolated onset if the abscissa never reached one.

The last case to be discussed showed a bias in the test, yet even this has proved useful. One of the standard uses for the 2gDTA has been a time-to-ignition (TTI) or its counterpart, stability at a given temperature.

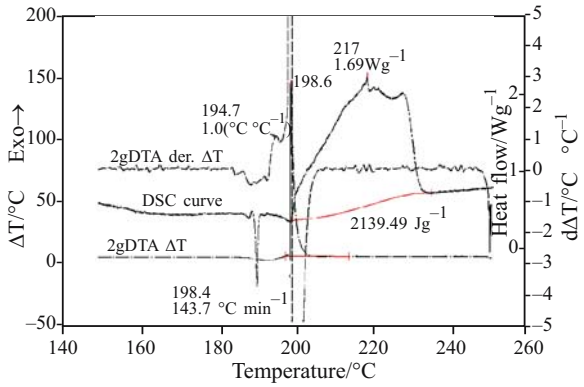

Fig. 5 Comparative 2gDTA and DSC decompositions: RDX

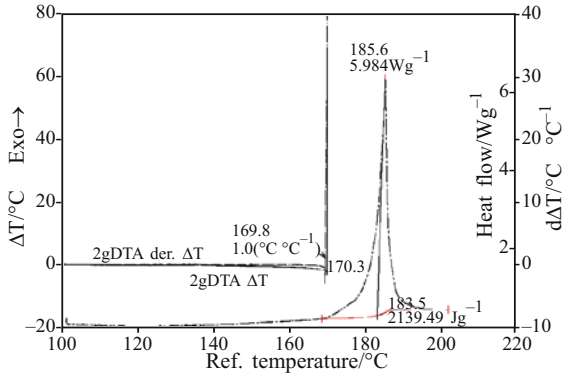

Fig. 6 Comparative 2gDTA and DSC decompositions: Gas Generating Fuel

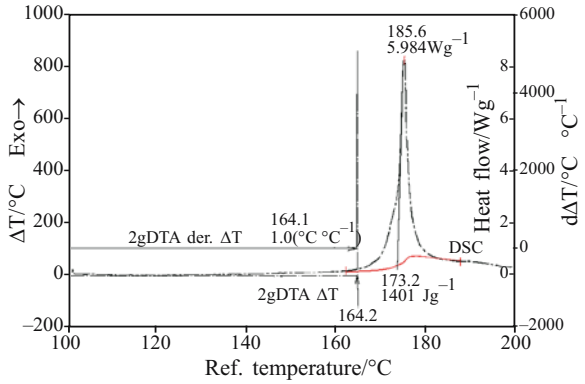

Fig. 7 Comparative 2gDTA and DSC decompositions: Gas Generating Fuel/RDX Admixture

This test originsaly utilized alumina as a thermal fill to ensure good contact. However, after several stability tests of a formulation containing liquid nitrate esters (NE) as plasticizers, it was noted that small trickles of yellow/orange diffused from the propellants into the alumina. The NE plasticizer apparently carried stabilizer with it on diffusion at the test temperatures. The question then became: could adding alumina to the test tube eventually cause an interaction not normally found? To test the scenario, a liquid NE fuel was examined with and without alumina. Figure 8 shows that indeed the alumina does appear to have a degree of inter-reaction with this liquid NE fuel. Since that time, use of alumina in the 2gDTA stability or TTI testing has been eliminated if the material is known to contain NE plasticizers.

Table 1 Comparison of 1°C min^{-1} DSC and DTA results

Sample	DSC peak temperature/°C	DTA extrapolated onset temperature/°C	DTA 1st derivative temperature/°C
RDX	217.9	199.3±0.9 (2 tests)	195.4±0.7 (2 tests)
Fuel	185.6	168.9±0.5 (4 tests)	168.8±0.8 (4 tests)
Admixture	174.7	163.7±2.6 (4 tests)	163.7±0.7 (3 tests)

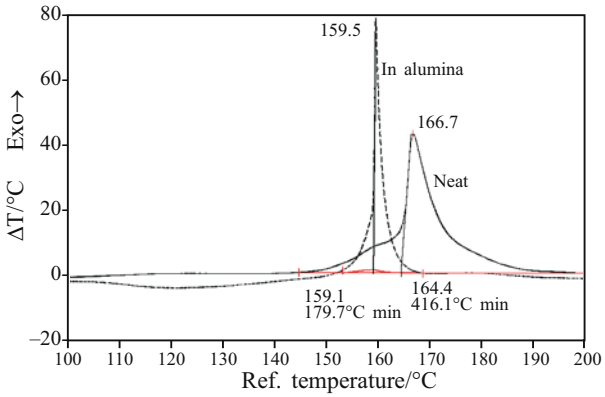

Fig. 8 Replicate 2gDTA of Liquid NE Fuel decompositions: dotted line in alumina, solid neat

Conclusions

The 2gDTA described here shows promise as a candidate for thermal compatibility testing. While admittedly more testing is necessary before the methodology becomes mature, the relatively low cost of the system makes it attractive to all NATO partners. The 2gDTA results tend to mimic DSC screening, though the increased mass component requires a new criterion. The simplest compatibility criterion for the 2gDTA is the extrapolated onset of thermal runaway (explosion).

References

1 NATO STANAG 4147, Ed. 2.
2 NATO STANAG 4147, Ed. 3 CNG Draft 9.
3 Ray Bazil, personal communication.

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