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STANDARDIZATION ON STANAG TEST METHODS FOR EASE OF COMPATIBILITY AND THERMAL STUDIES

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STANAG is the NATO abbreviation for Standardization Agreement, which sets up processes, procedures, terms and conditions for common military or technical procedures and equipment between the member countries of the alliance. One of the purposes is to provide common operational and administrative procedures.

STANAG 4147 (Ed. 2) deals with the 'Chemical Compatibility of ammunition components with explosives'. In this paper it will be shown that by standardizing on methodology, information can be exchanged between laboratories and it will still be applicable for their test equipment. The test procedures in this standard are: 1) vacuum stability test (manometer and pressure transducer), 2) heat flow calorimetry, 3) thermogravimetry (dynamic, isothermal, kinetic decomposition), 4) differential scanning calorimetry and 5) chemical analysis.

A case study will show that this methodology can be used in conjunction with 'normal' DSC (in-house) and vacuum stability tests (VST).

Keywords: *DSC, energetic materials, STANAG, TG, VST*

Introduction

The goal of these tests is to establish a method of hazard assessments that could prevent potential hazards at the incipient stage. These methods could adequately reduce loss of life and damage to property during the development stage and even later at the process stage.

Some pitfalls that could occur during developing 'in-house' thermal test methods can be: 1) sample preparation, 2) instrument set-up, 3) sentencing criteria and 4) analyst bias. Probably the most difficult is the sentencing criteria. How far can the peak temperature shift? How much may the baseline drift? Questions like these were asked a lot in our environment. STANAG 4147 addresses sample preparation, instrument set-up and to a certain extent, sentencing criteria. It must also be stated that one should never use only one technique to qualify a material as a compatible partner for an energetic material [1, 2].

Experimental

Materials

The energetic materials (RDX, NQ, PETN and NC) used in this work are production samples from our company (DLSWC) and the possible anti-static samples were supplied by local packaging manufacturers.

Methods

STANAG 4147 TG (dynamic 3A)

TG was performed using a TA Instruments TG 951. The TG was purged with dry nitrogen at 30 mL min^{-1} and a heating rate of 2 K min^{-1} was selected. All samples were run from room temperature till completion of the exotherm. A platinum pan with an aluminium insert was used with a sample mass of approximately 1 mg in a 1:1 mixture of energetic material to anti-static agent for each run [3].

For dynamic TG, the difference between the observed mass loss and the total calculated mass loss of the explosive and the test material in the admixture at a given temperature is noted. The temperature selected is either the 1st derivative TG peak or close to it. If the observed mass loss of the admixture is greater than that of the sum of the individual explosive/test material (total calculated), then this is an indication of incompatibility. The greater the difference between the observed and calculated mass loss, the greater the degree of incompatibility [3].

Example: observed mass loss at 193.05°C
(1st derivative TG peak NC+A129)

Compound A (NC neat) mass loss=32.71%, compound B (A129 neat) mass loss=4.01%.

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The mixture consists of compound A=0.8715 mg, compound B=1.1315 mg.

Therefore the mass% fraction of compound A= 43.5%, compound B=56.5%.

The observed mass loss of this admixture at 193.05°C=20.13%.

Calculated mass loss

Compound A=(observed mass loss A)·(mass fraction A=(0.3271·43.5)=14.23%. Compound B=(observed mass loss B)·(mass fraction B)=(0.0401·56.5)=2.27%.

Total calculated mass loss=16.5% (14.23+2.27).

Sentencing

Observed mass loss>calculated mass loss difference=3.6%.

- <4% mass difference indicates compatible

STANAG dynamic TG results is summarized in Table 1.

'Normal' DSC (in-house)

DSC was performed using a TA Instruments DSC Q10. The DSC was purged with dry nitrogen at 30 mL min^{-1} and a heating rate of 10 K min^{-1} was selected. All samples were run from room temperature till completion of the exotherm. Standard aluminium pans with pierced lids were used. A sample mass of approximately 1 mg was used in a 1:1 mixture of energetic material to antistatic agent for each run.

Under 'normal' DSC it is understood that the thermal analyst (who also does the sentencing) should have a few year's experience in the thermal field as well as in the explosive industry. It is very important to be able to have a 'good eye' for the shapes of thermoanalytical curves.

This in-house test is conducted by a skilled analyst who should be able to distinguish between compatible and incompatible components. Obviously this could lead to biased results.

As seen in Fig. 1 the NC+A163 shows signs of incompatibility. A large peak shift of ~30°C. The NC+A129 also shifted but not as much (~2°C). The endotherms from *rT* to about 110°C are the contribution from the non-explosive components.

As seen in Fig. 2 the NQ+A163 shows signs of incompatibility. A large peak shift of ~18°C. Even the melting endotherm of NQ has disappeared. Both NC+A129 and cond. polym. also shifted but not as much (6–7°C). But the melting endotherms has been affected. The endotherms from *rT* to about 110°C are the contribution from the non-explosive components.

As seen in Fig. 3 the PETN+A163 shows signs of incompatibility. A large peak shift of ~65°C. Even the melting endotherm of PETN is disappearing. PETN +cond. polym. shifted about 31°C. PETN+anti-stat and A129 shifted ~6–8°C. The endotherms from *rT* to about 110°C are the contribution from the non-explosive components.

As seen in Fig. 4 the RDX+A163 shows signs of incompatibility. A large peak shift of ~64°C. Even the melting endotherm of RDX has disappeared. RDX+cond. polym. shifted about 6°C but the baseline shows exothermic activity well before the melting endotherm. RDX+A129 shifted about 12°C and melting endotherm is affected. The endotherms from *rT* to about 110°C are the contribution from the non-explosive components.

Table 1 Summary of STANAG dynamic TG results (%)

	A129	A163	Anti-stat	Conductive polymer
PETN (179.6°C)	obs. mass loss=26.35 calc. mass loss=31.44 obs<calc compatible	obs. mass loss=45.35 calc. mass loss=35.62 obs>calc difference=9.73 degree of incompatibility	obs. mass loss=29.08 calc. mass loss=22.51 obs>calc difference=6.57 degree of incompatibility	obs. mass loss=38.44 calc. mass loss=34.67 obs>calc compatible
nitrocellulose (193.05°C)	obs. mass loss=20.13 calc. mass loss=16.5 obs>calc compatible	obs. mass loss=91.3 calc. mass loss=21.72 obs>calc difference=21.72 not compatible	obs. mass loss=10.18 calc. mass loss=11.57 obs<calc compatible	obs. mass loss=19.88 calc. mass loss=18.05 obs>calc compatible
RDX (212.55°C)	obs. mass loss=42.29 calc. mass loss=30.78 obs>calc difference=11.51 degree of incompatibility	obs. mass loss=74.17 calc. mass loss=50.73 obs>calc not compatible	obs. mass loss=21.07 calc. mass loss=23.23 obs<calc compatible	obs. mass loss=42.27 calc. mass loss=37.08 obs>calc difference=5.19 degree of incompatibility
nitroguanidine (241.06°C)	obs. mass loss=48.09 calc. mass loss=45.95 obs>calc compatible	obs. mass loss=60.79 calc. mass loss=77.06 obs<calc compatible	obs. mass loss=20.44 calc. mass loss=21.28 obs<calc compatible	obs. mass loss=32.53 calc. mass loss=28.98 obs>calc compatible

'grey area' for a degree of incompatibility is rather large (4–20%).

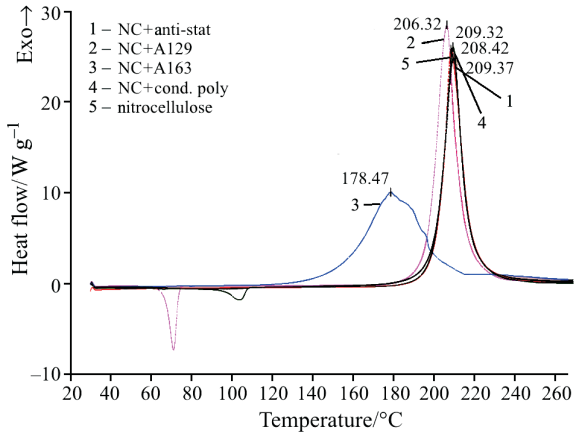

Fig. 1 Curve overlay of 'in-house' DSC, 10°C min^{-1}: NC (nitrocellulose); sentencing would be: A163 – incompatible with NC, A129 – possible incompatibility, further testing adviced, conductive polymer and anti-stat – compatible with NC

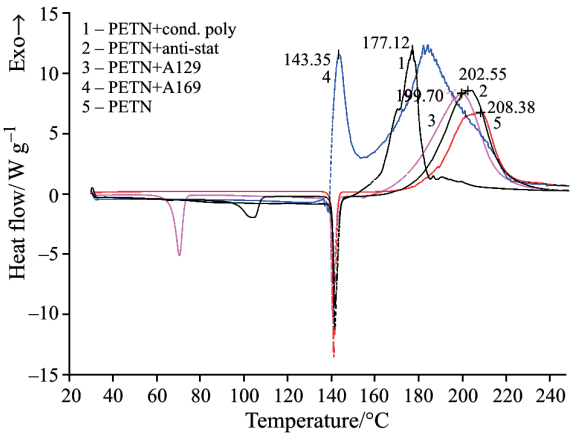

Fig. 3 Curve overlay of 'in-house' DSC, 10°C min^{-1}: PETN (pentaerythritol tetranitrate); sentencing would be: A163 – incompatible with PETN, A129 – possible incompatiblity, further testing advised, conductive polymer – incompatible with PETN, anti-stat – possible incompatibility, further testing advised

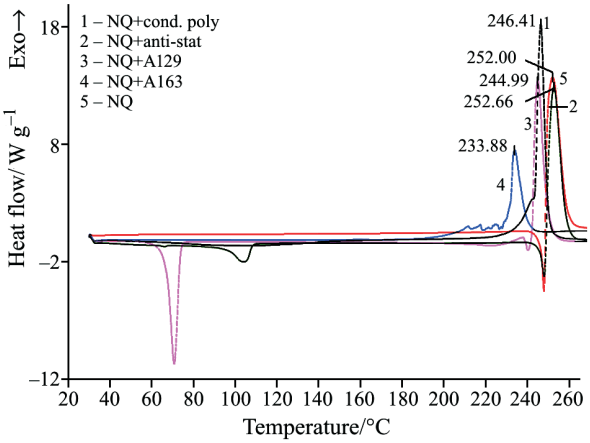

Fig. 2 Curve overlay of 'in-house' DSC, 10°C min^{-1}: NQ (nitroguanidine); sentencing would be: A163, A129 and conductive polymer – incompatible, anti-stat – compatible with NQ

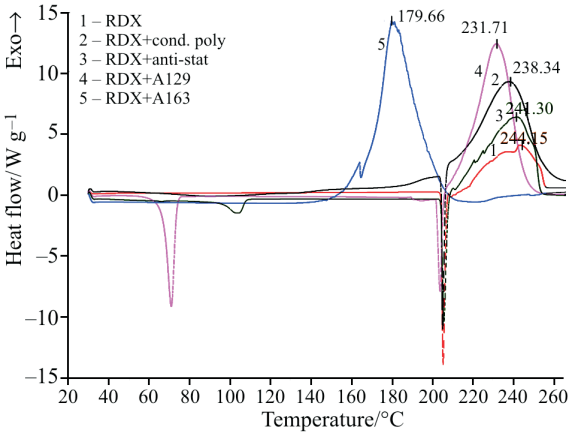

Fig. 4 Curve overlay of 'in-house' DSC, 10°C min^{-1}: RDX (cyclotrimethylenetrinitramine); sentencing would be: A163, A129 and conductive polymer – incompatible, anti-stat – compatible with RDX

Vacuum stability (VST 1A)

The volume of gas evolved, when a mixture of equal parts of an explosive and the material under test is heated at a constant temperature of e.g. 90°C for 91 h (user selectable) in an initial vacuum, is compared with the volumes evolved from the explosive and the test material when heated separately under identical conditions. Compatibility is sentenced by means of the volume of additional gas produced by the contact between the two components in the mixture [3].

The vacuum stability (80°C for 90 h) is shown in Tables 2 and 3.

Summary of sentencing criteria

Sentencing criteria – TG (dynamic 3A) [3]

- <4% mass difference indicates compatible
- >4 and <20% mass difference indicates a degree of incompatibility
- >20% mass difference indicates incompatible

Sentencing criteria – 'normal DSC' (in-house)

- exotherm peak maximum shift
- exotherm peak shape (narrower, temperature hook)
- exotherm peak onset shift/slope
- baseline shift/drift

Table 2 Summary of VST results

	A129	A163	Anti-stat	Conductive polymer
PETN	–0.29 cm^3	liquid	–0.36 cm^3	+5.46 cm^3
nitrocellulose	not done	liquid	+0.05 cm^3	+1.26 cm^3
RDX	–0.16 cm^3	liquid	+0.28 cm^3	–1.28 cm^3
nitroguanidine	+0.39 cm^3	liquid	+0.41 cm^3	+1.07 cm^3

Table 3 Summary of TG, DSC and VST results

	A129		A163		
	DSC	TG	VST	DSC	TG
PETN	possible incompatibility	compatible	compatible	not compatible	possible incompatibility
NC	possible incompatibility	compatible	not done	not compatible	not compatible
RDX	not compatible	possible incompatibility	compatible	not compatible	not compatible
NQ	not compatible	compatible	compatible	not compatible	compatible

	Anti-stat			Conductive polymer		
	DSC	TG	VST	DSC	TG	VST
PETN	possible incompatibility	possible incompatibility	compatible	not compatible	compatible	not compatible
NC	compatible	compatible	compatible	compatible	compatible	compatible
RDX	compatible	compatible	compatible	not compatible	possible incompatibility	compatible
NQ	compatible	compatible	compatible	not compatible	compatible	compatible

Sentencing criteria – vacuum stability 1A [3]

If gas generation approaches 5 cm^3 a re-test is done to confirm incompatibility. An additional confirmation test should also be done using a test based on another principle.

DLSWC criteria

insignificant	$x<1.0$
very slight	$1.0\leq x<2.0$
slight	$2.0\leq x<3.0$
moderate	$3.0\leq x<5.0$
excessive	$x\geq 5.0$

Related STANAG procedures

- STANAG 4117 – Stability test procedures and requirements for propellants stabilized with diphenyl amine, ethyl centralite or a mixture of both.
- STANAG 4491 – Thermal sensitiveness and explosiveness tests.
- STANAG 4515 – Thermal characterization by TG, DSC or DTA.
- STANAG 4525 – Physical/mechanical properties, Thermomechanical analysis for determining the coefficient of linear thermal expansion (TMA).
- STANAG 4550 – Procedures for dynamic mechanical analysis (DMA) and determination of glass transition temperature.
- STANAG 4556 – Vacuum stability test.
- STANAG 4582 – Nitrocellulose based propellants, stability test procedures and requirements using heat flow calorimetry.

Conclusions

Although most laboratories that test energetic materials have some or all of the above-mentioned capabilities it is highly possible that the method and/or sentencing criteria would differ from laboratory to laboratory. Even in one laboratory contradictory sentencing is found between different test methods. It is therefore very important to use more than one test method (preferably based on different principles) before sentencing is done [1, 2].

The next logical step would be to standardize. These STANAG agreements are all work in progress and are continuously reviewed. Pitfalls of certain methods cannot be overlooked but it proves still to

be an effective tool for compatibility testing. With global trading opening up with respect to energetic materials and related products, standardisation of methodologies should be encouraged. With this approach history data could be built up for future reference purposes. This should by no means be seen as a replacement for current practices, but rather as complimentary data when doing assessments.

References

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