Qualification and Energetic Materials Challenges

IMEMTS
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Outline

- Introduction
- MSIAC Workshops – The Repeating Issue
- Materials in Munitions
- Models & Benefits
- Current Testing Requirements
- How to Move Forward

Multiple materials present in munitions

Visualising the bulk engineering materials in property space ($\rho$ vs $\epsilon$)

https://www.grantadesign.com/products/ces/find.htm
Supporting Munitions Safety

Material Properties Data & Modelling

- NIMIC/MSIAC workshops
  - Cook Off
  - Shaped Charge Jet
  - Fragment Impact
  - XDT
  - Sympathetic Reaction
- Gaps highlighted

- Few explosives have all experimentally determined observables\(^1\)
- Why?
  - Improved models
  - Technology provides wider access to capability (Moore’s Law)
  - No data collection (needs don’t match requirements)

## What types of parameters

<table>
<thead>
<tr>
<th>Physical</th>
<th>Chemical</th>
<th>Thermal</th>
<th>Mechanical</th>
</tr>
</thead>
<tbody>
<tr>
<td>State (s, l, g)</td>
<td>Enthalpy of formation (kJ mol(^{-1}))</td>
<td>Thermal conductivity (W g(^{-1}).K(^{-1}))</td>
<td>Tensile strength (MPa)</td>
</tr>
<tr>
<td>Density (g cm(^{-3}))</td>
<td>Enthalpy of combustion (kJ mol(^{-1}))</td>
<td>CTE (μm m(^{-1}))</td>
<td>Compressive strength (MPa)</td>
</tr>
<tr>
<td>Molecular weight (g mol(^{-1}))</td>
<td>Enthalpy of detonation (kJ mol(^{-1}))</td>
<td>Specific heat capacity (J g(^{-1}).K(^{-1}))</td>
<td>Complex modulus</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>Solubility (mg L(^{-1}))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Decomposition temperature (°C)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

## Hazard

<table>
<thead>
<tr>
<th>Shock</th>
<th>Performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Impact (J)</td>
<td>Detonation velocity (km s(^{-1}))</td>
</tr>
<tr>
<td>Friction (N)</td>
<td>Detonation pressure (GPa)</td>
</tr>
<tr>
<td>ESD (J)</td>
<td>Critical diameter (mm)</td>
</tr>
<tr>
<td>Run distance (mm)</td>
<td>Gurney energy (kJ kg(^{-1}))</td>
</tr>
</tbody>
</table>
What are the challenges?

- Multiple materials present within munitions
  - Focus on energetic materials (this presentation)
- Understanding required across all scales
  - Material properties (physical, chemical, mechanical) to system response
- From single molecule to warhead
  - Scale – 10 orders of magnitude (nm to m)
  - Mass – 6 orders of magnitude (mg to kg)

1. Luscher, D. J. et al, Crystals 2017, 7(5), 138
2. Heller, A. Science & Technology Review 2009, 4-10
4. Kopp, C. AGM-84E SLAM, 1988
Current Situation - Munition

- Testing focussed on performance and safety in storage, transport and service
  - STANAG 4123 / UN Hazard Classification
  - AOP-15 / Safety & Suitability for Service
  - STANAG 4439 / Insensitive Munitions

- Criteria for tests can be binary - usually pass/fail
  - Limited number of tests
  - High costs

- Reliance on ‘whole body of evidence’ for assessment
Experiments performed to elucidate response to a hazard
Some tests determine scientific understanding whilst other provide pass/fail
- Friability
- EMTAP 36 (UK Fragment Impact)
All results are compared against existing EM knowledge
Difficult to use information for prediction of munition response
Qualification

- Development cycle – no requirement to fully characterise materials
- Testing focussed on performance and safety
- AOP-7
  - Qualification for inclusion of energetic material in a military munition
- Hazard Classification
  - Assessment for transportation
- Material Safety Data Sheets
  - Some physical and chemical properties

Known Issues
EM down selection based on performance
### Qualification of new EM based on assessment of safety and performance

- Agreed minimum data set
- Whether the EM characteristics change during the lifecycle
- Information on the chemical and physical properties *shall* be provided
- Compliance with National H&S requirements *shall* be provided
  - MSDS
  - EHDS

### Shall

- Can be interpreted as not mandated

### Chemical, Physical and Mechanical Properties:
- **Stability & Thermal Characterization**, Variation of Properties with Age, **Compatibility**, Density, Melting Point, Thermal Characterisation, Glass Transition Point and **Mechanical/Rheological Properties**

### Hazard Assessment

- **Ignition Temperature**, Explosive Response when Ignited (Confined and Unconfined), Electrostatic Discharge, Impact, Friction, and Shock

### Performance Assessment:

- Detonation Velocity and **Critical Diameter**

### Those indicted in bold are mandatory qualification data or properties
## Qualification Program

<table>
<thead>
<tr>
<th>Category</th>
<th>Test Performed</th>
<th>Criteria</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Stability Characterisation</strong></td>
<td>Vacuum Thermal Stability</td>
<td>&lt; 2 cm³ gas</td>
</tr>
<tr>
<td></td>
<td>Thermal Stability</td>
<td>No change</td>
</tr>
<tr>
<td><strong>Thermal Characterisation</strong></td>
<td>Thermo gravimetric analysis</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Self Heating (onset)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Compatibility</td>
<td>&lt; 2 cm³ gas</td>
</tr>
<tr>
<td><strong>Ignition Temperature</strong></td>
<td>Woods Metal Bath</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Henkin Time to Explosion</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Critical Temperature</td>
<td>&gt; 82 °C</td>
</tr>
<tr>
<td></td>
<td>1-L Cook Off</td>
<td></td>
</tr>
<tr>
<td><strong>Explosive Response</strong></td>
<td>Variable Confinement (SCO)</td>
<td>Deflagration or less</td>
</tr>
<tr>
<td></td>
<td>Variable Confinement (FCO)</td>
<td>Deflagration or less</td>
</tr>
<tr>
<td></td>
<td>Small Scale Burn</td>
<td>Less than explosion</td>
</tr>
<tr>
<td><strong>Sensitivity Tests</strong></td>
<td>ESD</td>
<td>No reaction at 0.25 J</td>
</tr>
<tr>
<td></td>
<td>Impact</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Friction</td>
<td>&gt; 96 N</td>
</tr>
<tr>
<td></td>
<td>Shock Sensitivity</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cap Test</td>
<td></td>
</tr>
<tr>
<td><strong>Chemical, Physical, Mechanical</strong></td>
<td>CTE</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Density</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Growth</td>
<td>1 %</td>
</tr>
<tr>
<td></td>
<td>Exudation</td>
<td>0.1 %</td>
</tr>
<tr>
<td></td>
<td>Young’s Modulus</td>
<td></td>
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<tr>
<td></td>
<td>Compressive Strength</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Strain @ Max Stress</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cube Cracking</td>
<td>No fissures</td>
</tr>
<tr>
<td><strong>Variation with Age</strong></td>
<td>Ageing protocol</td>
<td></td>
</tr>
<tr>
<td><strong>Toxicity Evaluation</strong></td>
<td>MSDS</td>
<td></td>
</tr>
<tr>
<td><strong>Performance Properties</strong></td>
<td>Detonation Velocity</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dent Depth</td>
<td></td>
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<tr>
<td></td>
<td>Explosivity of Dust</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Critical Diameter</td>
<td></td>
</tr>
</tbody>
</table>

- **US Example**
  - IMX-104 qualification
  - Zunino et al (IMEMTS 2012)

- **Greater testing requirements than AOP-7 minimum**

- **Tests**
  - Included chemical & physical parameters

- **Gaps**
  - Not reported
  - C_p
  - Wedge
Global Harmonised System
- EU requirement CLP (EU1272/2008)
- Information gathered by manufacturer for Material Safety Data Sheet (MSDS)
- 16 sections including Hazards, Transport and....

Chemical & Physical Properties
- Section 9
- No consistency in reported information
  - From 0/20 to 18/20
- Data usually only gathered at one temperature and/or pressure
  - 25°C (not consistent)
  - 133.3 hPa (also not consistent)

So how can we measure the parameters?
- Understand munition response to key abnormal threats include
  - Thermal
  - Shock
  - Impact

- Discrete data sets available
  - Relates to specific tests

- Therefore we use
  - Models to test our understanding…but
  - Do we have the right information

Development of a scaling hierarchy for cook off hazards
Atwood, A. et al. (2010), IMEMTS, Munich
Models

- Greater reliance on modelling for
  - Simulation
  - Safety assessment
  - Ultimate aim → Prediction

- Development of computational tools for simulating abnormal thermal events (e.g.)
  - Critical Temperature\(^1\)
  - ALE3D\(^2\)
    - LLNL
  - Eularian & Lagrangian\(^3\)
    - University of Utah
  - Multiple codes
    - SNL

- Thermal Hazards
- Time to ignition
  - Thermal & physical parameters
  - Chemistry
  - Confinement - complex

1. Rogers, R. N. Thermochimica Acta, (1975), 11, 131-139
Benefits of Modelling

- Assess interdependence of, and sensitivity to changes in, variables
  - Size
  - Volume
  - Materials
  - External conditions
- Test mechanistic understanding
- Increases confidence in observed behaviour
- Provides insight into reaction that can not always be observed experimentally
  - Time to reaction
  - Location of reaction
  - Reaction growth
  - But cannot reliably predict reaction violence
Modelling Requirements

- Requirement to populate model(s) with experimental data as 
  \([f_n(T)]\) and \([f_n(P)]\)
  - Coefficient of Thermal Expansion\(^1\)
  - Specific Heat Capacity
    - Solid phase\(^1\)
    - Gaseous phase\(^2\)
  - Shear Modulus\(^1\)
  - Bulk Modulus\(^1\)
  - Reaction kinetics, detonation\(^1\)
  - Condensed Phase Activation Energy\(^2\)

- Good models need
  - Well defined experiments
  - Information on the boundary conditions
  - An iterative development cycle supported by progressive experimental design and testing programme

- Discussion
  - Mismatch in requirement to obtain data

Methods for Obtaining Parameters

Chemical & Physical Properties
- MSDS
  - Density, vapour pressure (if recorded)
- AOP-7
  - Onset of decomposition; Ageing includes mechanical properties

Parameters still required
- Function of temperature (e.g. -60 to 120°C – material dependent)
- Determine other factors from these selected parameters e.g. critical temperature, enthalpy of formation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vapour pressure (P&lt;sub&gt;vap&lt;/sub&gt;) hPa</td>
<td>ASTM E 1782, Differential Scanning Calorimetry or Differential Thermal Analysis</td>
</tr>
<tr>
<td>Heat Capacity (C&lt;sub&gt;p&lt;/sub&gt;) J g&lt;sup&gt;-1&lt;/sup&gt;°C&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>ASTM E 1269, Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>Thermal Conductivity (λ) W cm&lt;sup&gt;-1&lt;/sup&gt;°C&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>ASTM E 1225, Longitudinal Heat Flow Meter Apparatus</td>
</tr>
<tr>
<td>Coefficient of Thermal Expansion (CTE) µm m&lt;sup&gt;-1&lt;/sup&gt;°C&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>ASTM E 831, D696, Thermochemical analysis, Thermochemical analysis, Thermal Mechanical Analyser (TMA)</td>
</tr>
<tr>
<td>Activation Energy (E&lt;sub&gt;a&lt;/sub&gt;) kJ mol&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>ASTM E 1614, Thermogravimetry, Using Ozawa/Flynn/Wall Method</td>
</tr>
<tr>
<td>Physical Density (ρ) g cm&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>ASTM D 792, Displacement, Pycnometry</td>
</tr>
<tr>
<td>Enthalpy of Combustion (ΔH&lt;sub&gt;c&lt;/sub&gt;) kJ mol&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>ASTM D 4809, liquid hydrocarbon fuels, Bomb Calorimetry</td>
</tr>
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Methods for Obtaining Parameters

Supporting Munitions Safety

- Chemical & Physical Properties
  - MSDS
    - Density, vapour pressure (if recorded)
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<td>$P_{vap}$ hPa</td>
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<tr>
<td>Heat Capacity</td>
<td>$C_p$ J g^{-1} °C^{-1}</td>
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<tr>
<td>Thermal Conductivity</td>
<td>$\lambda$ W cm^{-1} °C^{-1}</td>
</tr>
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<td>Coefficient of Thermal Expansion</td>
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<tr>
<td>Activation Energy</td>
<td>$E_a$ kJ mol^{-1}</td>
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<table>
<thead>
<tr>
<th>Physical</th>
<th></th>
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<tr>
<td>Density</td>
<td>$\rho$ g cm^{-3}</td>
</tr>
<tr>
<td>Enthalpy of Combustion</td>
<td>$\Delta H_c$ kJ mol^{-1}</td>
</tr>
</tbody>
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Methods for Obtaining Parameters

<table>
<thead>
<tr>
<th>Notes</th>
<th>Thermal Units</th>
<th>Equipment</th>
<th>Methods</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Vapour pressure</td>
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<td>Differential Scanning Calorimetry or Differential Thermal Analysis</td>
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<td></td>
<td>Heat Capacity</td>
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<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td></td>
<td>Coefficient of Thermal Expansion</td>
<td>ASTM E831, D696</td>
<td>Thermochemical analysis Thermal Mechanical Analyser (TMA) ASTM E2716</td>
</tr>
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<td></td>
<td>Activation Energy</td>
<td>ASTM E1614</td>
<td>Thermogravimetry Using Ozawa/Flynn/Wall Method ASTM E698</td>
</tr>
<tr>
<td></td>
<td>Physical Density</td>
<td>ASTM D792</td>
<td>Displacement ASTM D1217, Pycnometry</td>
</tr>
<tr>
<td></td>
<td>Enthalpy of Combustion</td>
<td>ASTM D4809</td>
<td>liquid hydrocarbon fuels Bomb Calorimetry</td>
</tr>
</tbody>
</table>
## Methods for Obtaining Parameters

### Chemical & Physical Properties
- **MSDS**
  - Density, vapour pressure (if recorded)
- **AOP-7**
  - Onset of decomposition; Ageing includes mechanical properties

### Parameters still required
- Function of temperature (e.g. -60 to 120°C – material & model dependent)
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<tr>
<th>Thermal</th>
<th>Units</th>
<th>Existing Methods Notes</th>
<th>Equipment</th>
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**Notes**:
Data
- Capability exists to better characterise materials
- Request for chemical, physical and mechanical information is usually much later in the qualification process (type qualification)
- Propose at an earlier stage in development (pre-AOP-7)

Modelling
- Modelling is being used throughout munition development
  - Design
  - Safety assessment
  - Prediction
- Access to codes and models across most MSIAC nations
- Capability to run simulations is now faster and cheaper

Benefits
- Reduced time in development
- Greater insight into internal behaviour
- Improved assessment of time to reaction
- Well-posed models enable easier design modifications
- Increased confidence in assessed response level
- Helps assess programme risk

Stakeholders
Manufacturers
Design Authorities
Safety Authorities
Modellers
Experimentalist
How is MSIAC helping?

- Enabling exchange of information
  - Workshops
- Generating guidance on models and methodology
  - L-195 (Babcock & van der Voort)
  - L-213 (Babcock)
- Data reviews
  - L-198 (Andrews)
- Repository for data
  - Energetic Materials Compendium (EMC)
- Developing models
  - TEMPER
- Promoting discussion
Acknowledgements

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MSIAC Team: Dr Ernie Baker, Christelle Collet, Martin Pope, Dr Michael Sharp, Martijn van der Voort