Techniques to Assess the Thermal Hazard Properties of Ammonium Nitrate and Ammonium Nitrate Solutions

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Outline

- Properties of AN and how they Affect Thermal Hazard Assessment
- Experimental Techniques to Assess Thermal Hazards
- Examples of the Effect of Process Conditions on Thermal Stability

- New Canadian Regulations to Control AN
- IGUS

Properties of AN and how they Affect Thermal Hazard Assessment

- Not this simple! $2\ NH_4NO_3 \Rightarrow 2\ N_2 + 4\ H_2O + O_2$
- AN decomposition is complex: many steps, several equilibria, lost gaseous products change chemistry, acid catalysed…
- Initially endothermic, e.g. $Heat + NH_4NO_3 \Leftrightarrow NH_3 + HNO_3$
- Exothermic stages later, e.g. $NH_4NO_3 \Rightarrow N_2O + 2\ H_2O + Heat$
- Experimental conditions affect the results greatly

Experimental Techniques to Assess Thermal Hazards

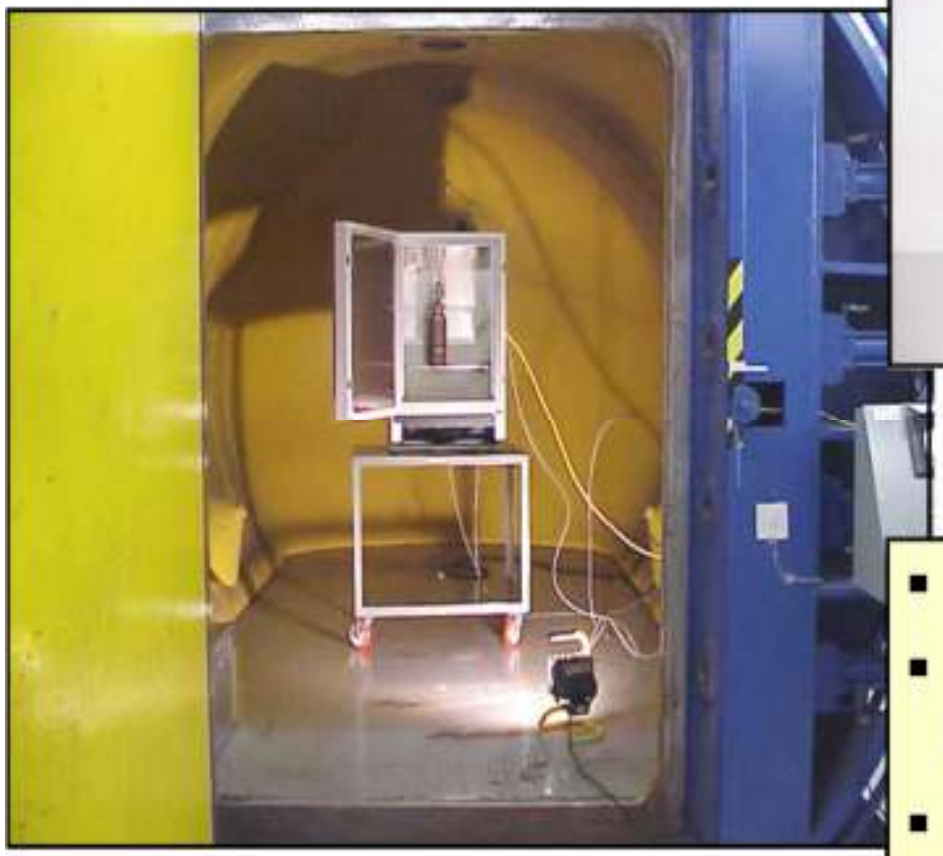
- Common, small-scale (milligram) techniques such as differential scanning calorimetry and differential thermal analysis have their place and are easy to use, but cannot provide meaningful safe operating temperatures for safe operating temperatures for large-scale manufacturing processes involving AN and AN solutions

Experimental Techniques to Assess Thermal Hazards (II)

- To get meaningful results for thermal onset temperatures, one needs to minimize heat losses
- Adiabatic techniques are best – apparatus tracks sample self-heating, so no heat is lost to the outside
- Still have to heat the sample container, so want to limit the 'phi' factor:

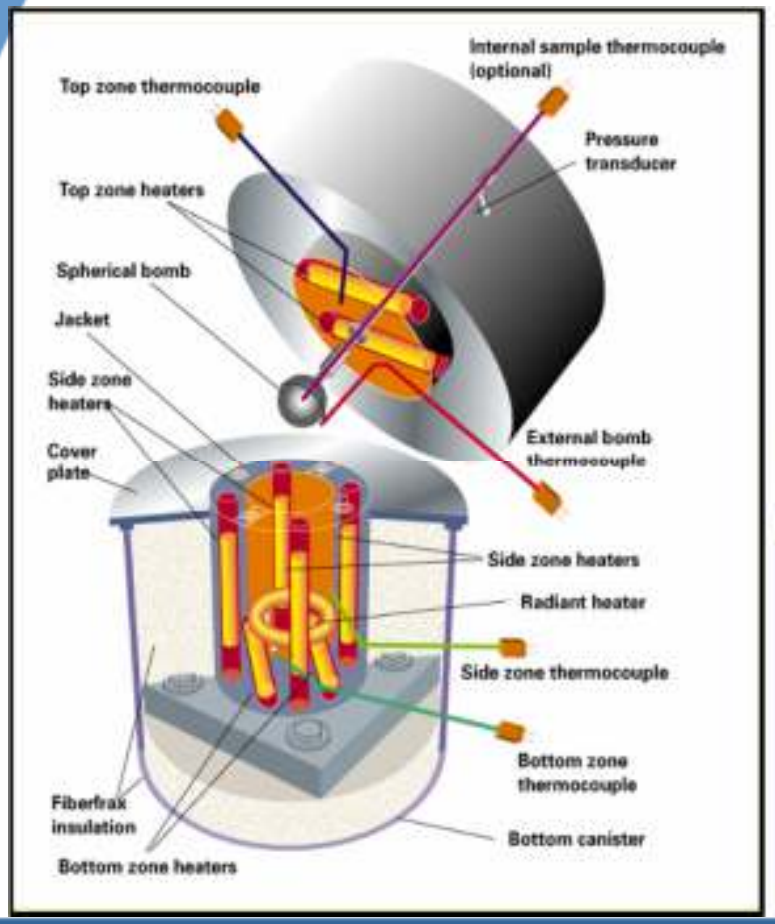
$$\phi = \frac{m_S\, c_S + m_C\, c_C}{m_S\, c_S}$$

Adiabatic Dewar Calorimetry (ADC)



- 100 g samples
- Blast protection
- $\phi = 1.6$

Accelerating Rate Calorimetry (ARC)



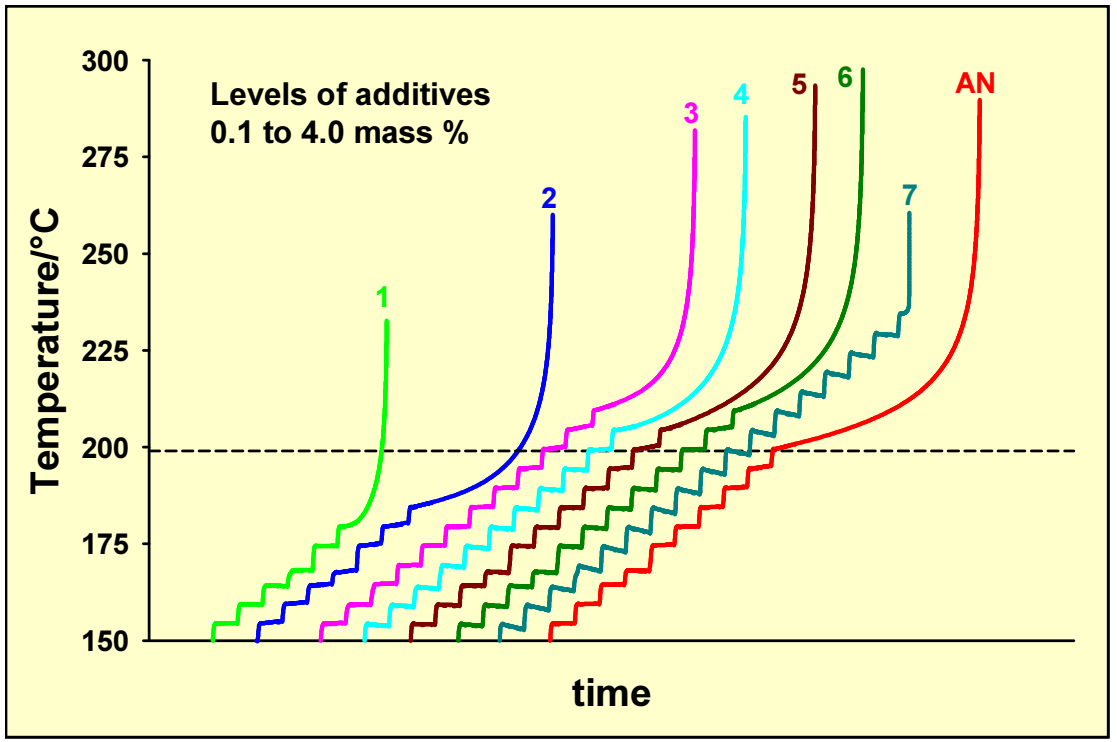
- 1-3 g samples
- Lab Environment
- ϕ = 2.9 (3 g)
- ϕ = 6.4 (1 g)

Examples of the Effect of Process Conditions on Thermal Stability

- Effect of contamination
- Open vs. closed systems
- Effect of time
- Extrapolation to large scales

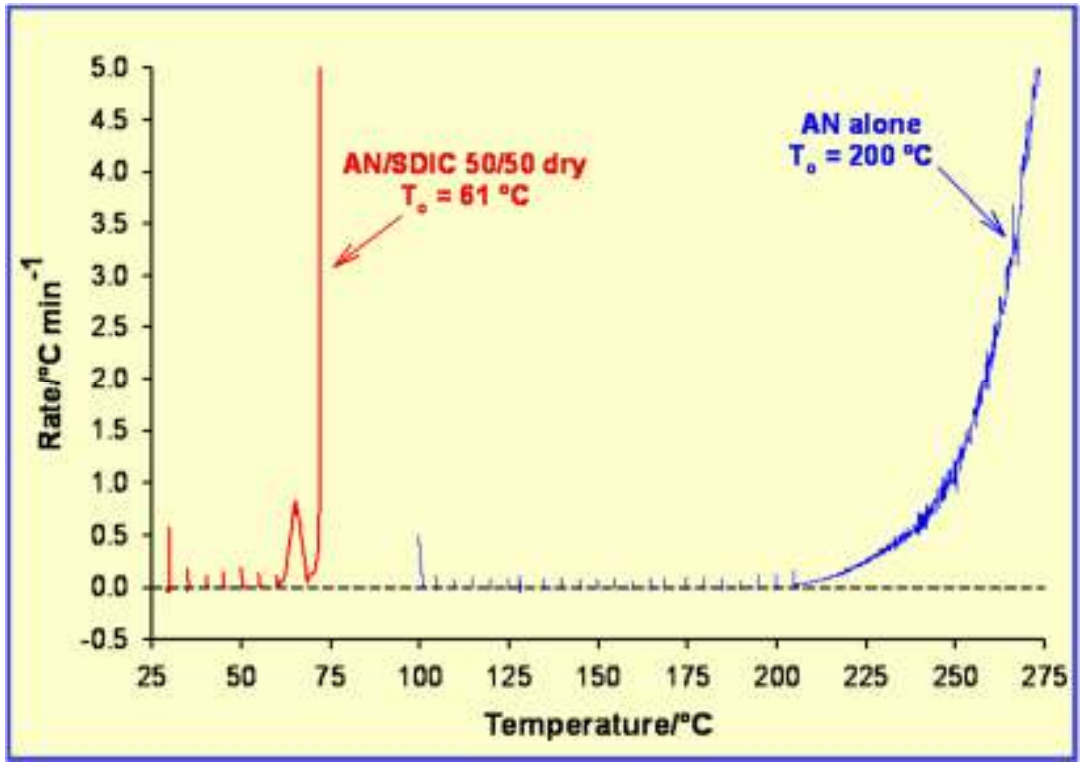
Effect of contamination

- Onset temperature sensitive to presence of additives
- ARC is a great screening tool for incompatibilities
- Additive 1 bad; Additive 7 good



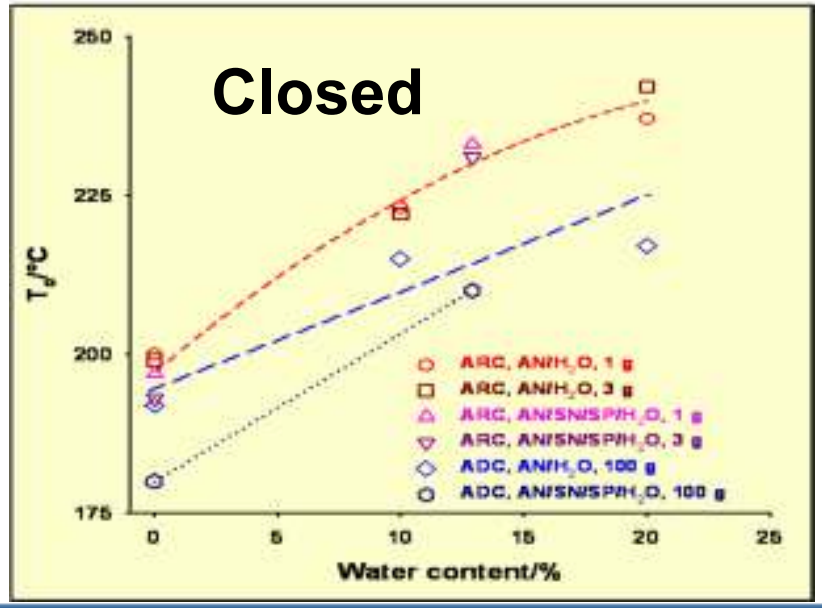
Effect of contamination (II)

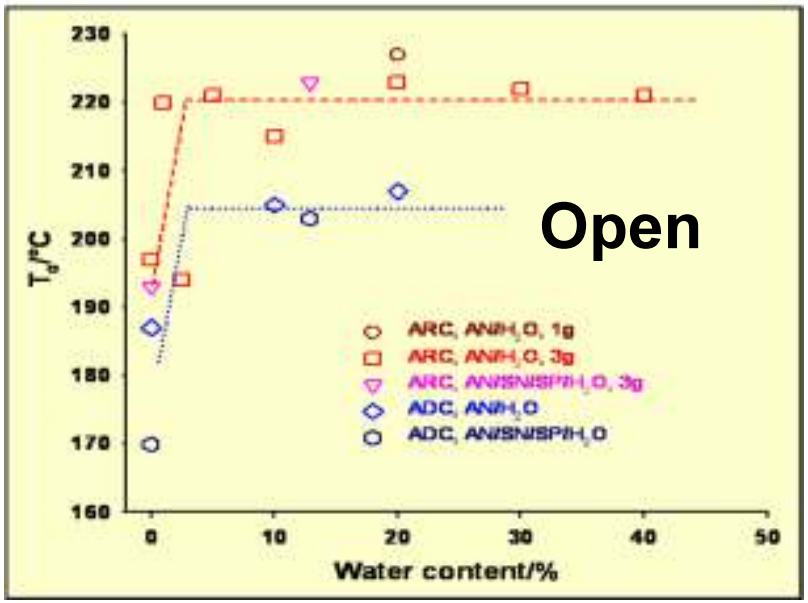
- Drastic effect of sodium dichloroiso-cyanurate (SDIC), a swimming pool chemical, on AN stability



Open vs. closed systems

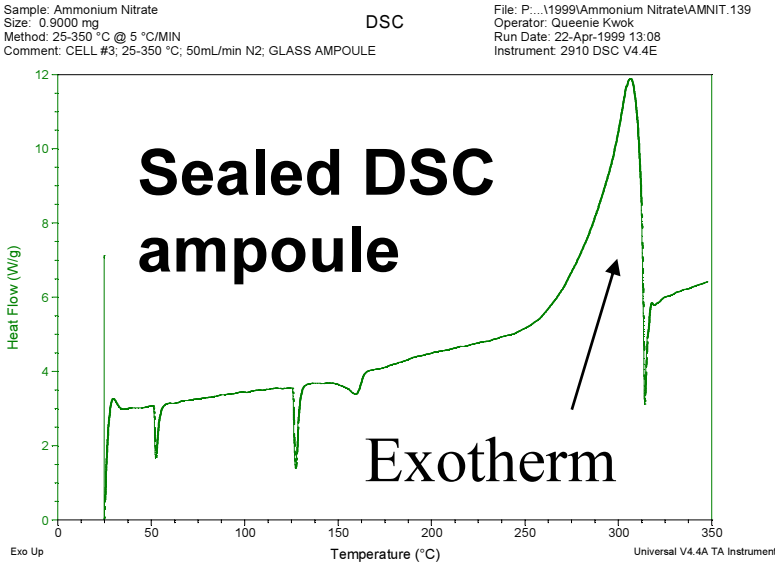
- Oxidizer solutions: AN/SN/SP
- Closed: onset temperature increases with water content
- Open: onset temperature steady above a few % water

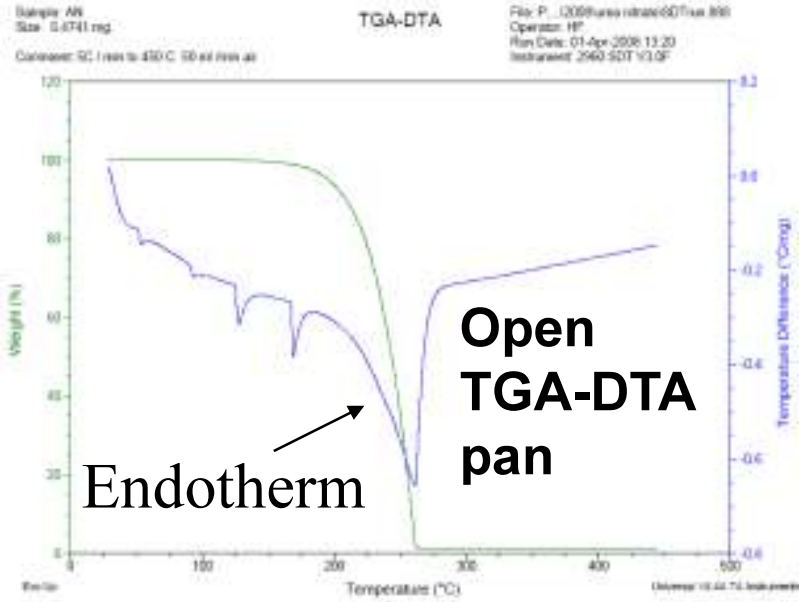




Open vs. closed systems (II)

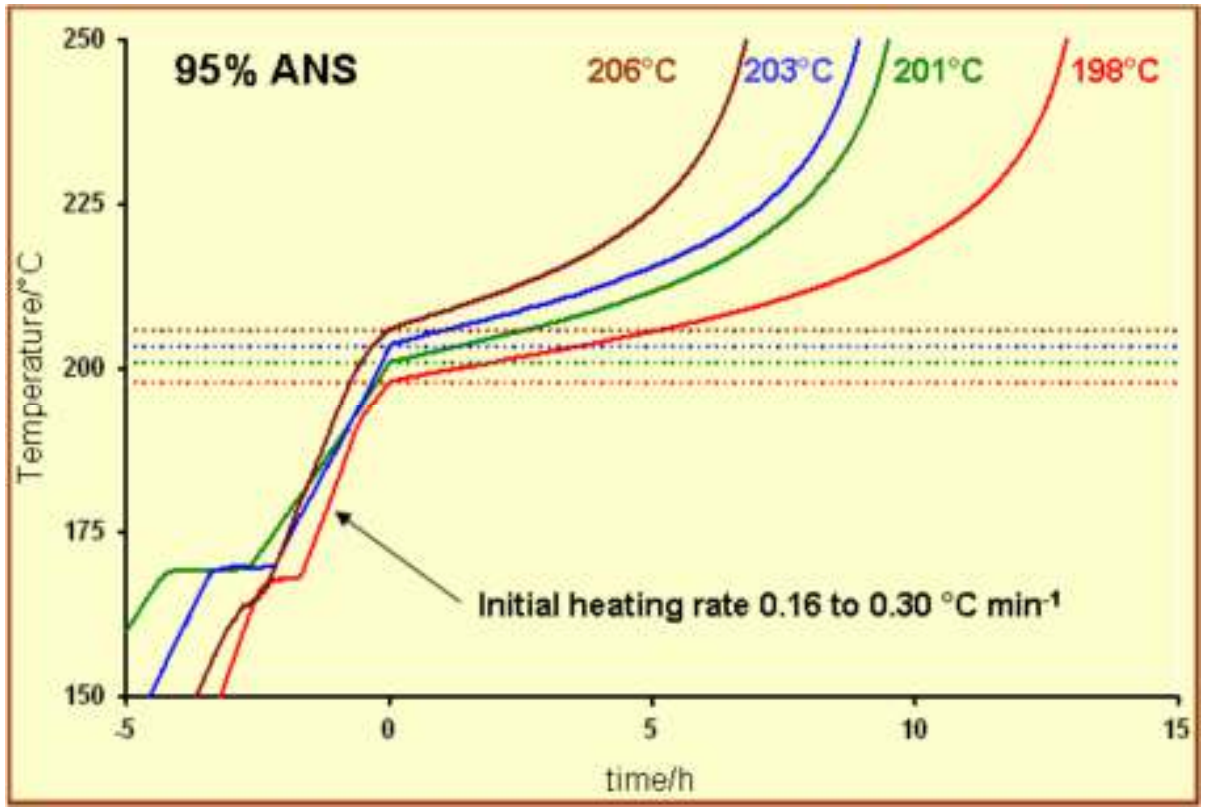
- AN displays strong exotherm when tightly sealed
- At small scales in an open system, AN does not self-heat





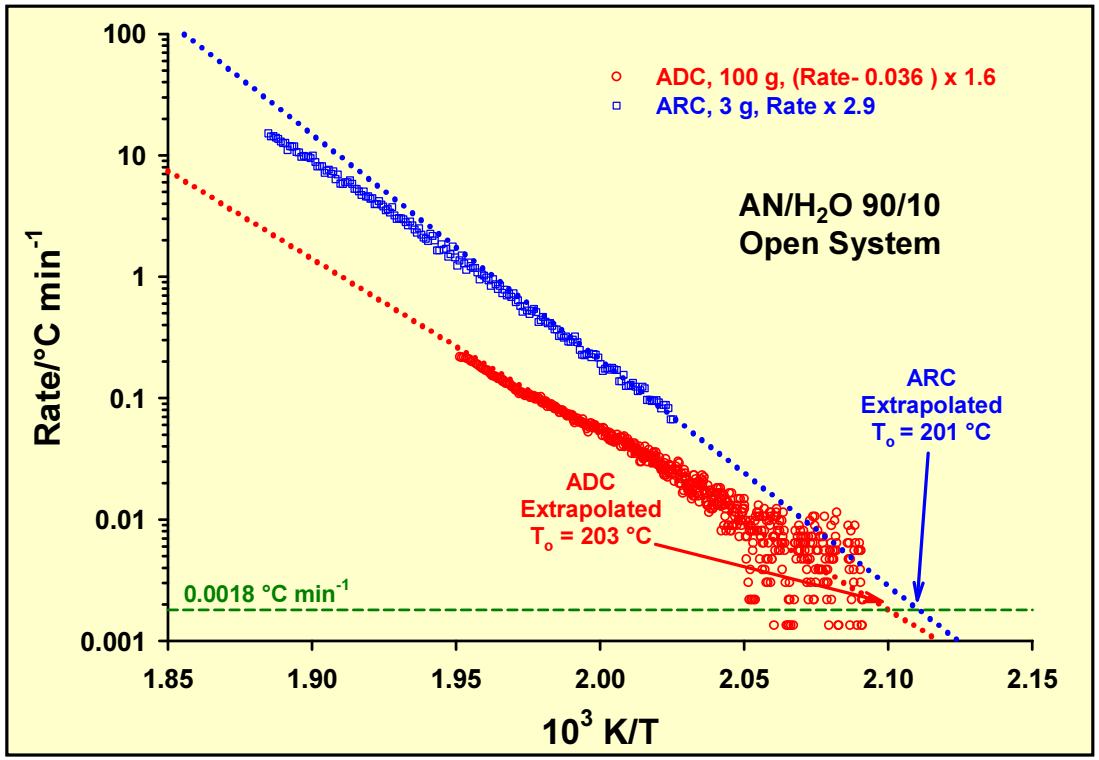
Effect of time

- Time is always a factor
- Time to runaway decreases with increasing temperature



Extrapolation to large scales

- Arrhenius plot of self-heating rate against temperature
- Multiply by phi factor
- Extrapolate to critical self-heating rate
  - 0.0018 °C min^{-1}

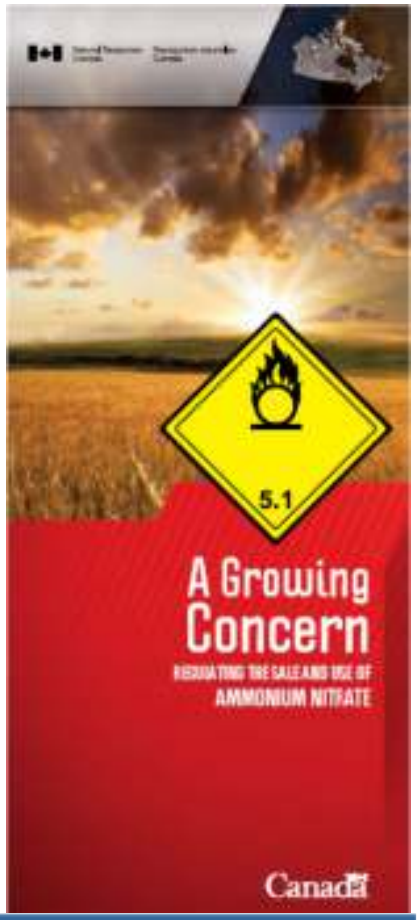


Conclusions

- Difficult to obtain quantitative results on AN with small-scale techniques such as DSC
- We like to use ARC: lab-based, realistic onset temperatures, representative sample, vented or not
- Physical chemistry of AN is complex and experimental conditions need to be carefully controlled to get realistic results

New Canadian Regulations to Control AN

- Effective June 1, 2008
- Applies to solids >80% AN
- Regulations for sellers of AN
  - enroll with NRCan to ensure you are on the list of authorized sellers;
  - secure your AN supply and related documentation;
  - provide educational notices to both your end users and your transporters; and
  - provide annual inventory reports.



New Canadian Regulations to Control AN

- Requirements for users of AN
  - provide proper ID to your supplier and explain how you intend to use the AN
  - should take security measures to prevent the theft of AN
  - report immediately to local police any signs of theft, attempted theft, tampering or loss
  - strictly prohibited from reselling any amount of AN
- For more info: http://www.nrcan.gc.ca/mms/explosif
- NB: Eight other explosive precursor chemicals also controlled to a lesser extent

IGUS

- International Group of experts on the explosion risks of Unstable Substances
- The aim of IGUS is to exchange information on the behaviour of unstable substances. Two sub-groups: Explosives Propellants and Pyrotechnics (EPP), Energetic and Oxidizing Substances (EOS)
- Next EPP meeting Newcastle, Australia, Oct 2008
- Industry participation welcome!
- http://www.oecdigus.org/index.html

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Thank you for your attention