UN/SCETDG/39/INF.21

Committee of Experts on the Transport of Dangerous Goods and on the Globally Harmonized System of Classification and Labelling of Chemicals

Sub-Committee of Experts on the Transport of Dangerous Goods **10 June 2011**

Thirty-ninth session
Geneva, 20 June – 24 June 2011
Item 2 (d) of the provisional agenda
Explosives and related matters: DDT Tests and Criteria for flash compositions

Changes to screening test for substances that may have explosive properties

Transmitted by the expert from Japan and by the International Council of Chemical Associations (ICCA)

1. Japan and ICCA jointly proposed to 38th session of TDG Sub-Committee to discuss exclusion of adiabatic calorimetry from the screening procedure described in subsection 20.3.3.3 of the Manual of Tests and Criteria, where both adiabatic calorimetry and differential scanning calorimetry (DSC) are allowed to be used to measure the exothermic decomposition energy for the substances that may have explosive properties (ST/SG/AC.10/C.3/2010/60).

2. This proposal was based on the necessity of improving the reliability of the calorimetric measurements in the screening test and motivated by the experimental findings that there are considerable disagreements between two exothermic decomposition energies of the very same samples; QDSC and Qadia , measured by DSC and adiabatic calorimetry, respectively, and a tendency of Qadia to be lower than QDSC suggesting that the adiabatic calorimetry tends to underestimate the exothermic decomposition energy.

3. This finding is not surprising but can be scientifically explained: Main factors are the heat loss and the response time of the adiabatic equipment (i.e. the method is only near adiabatic): In such cases, the oven temperature is not able to follow the sample temperature which means that the adiabatic conditions are lost. Due to the different approach of the DSC, heat loss and heat capacity are implicitly accounted for in this method.

4. Therefore, limiting the calorimetric method to DSC was expected to be an effective procedure to standardize the calorimetric measurements and improve their reliability.

5. The proposal was accepted and this issue will be discussed at TDG Sub-Committee in the next biennium although there were several counterarguments among the delegates against the exclusion of the adiabatic methods.

6. This issue was discussed with further rationale at the IGUS-EOS meeting (Washington DC, April, 2011) and no counterargument was presented from the participants against limiting the calorimetric method to DSC.

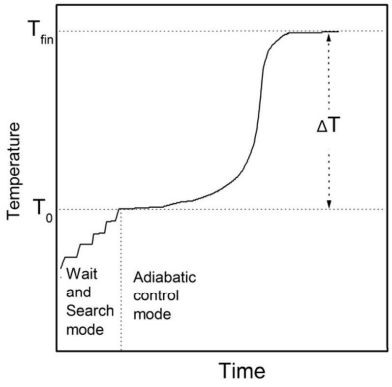
Proposal

7. Sub-Committee is invited to consider effective procedure to optimize the calorimetric measurements in the screening test referring the basis of difficulty of the adiabatic calorimetry in evaluating exothermic decomposition energy as shown in the annex of this document.

Annex

Difficulty of adiabatic calorimetry in accurate evaluation of the exothermic decomposition energy

① Unknown sample heat capacity



The exothermic decomposition energy,

$Q_{adia} = C_s \cdot \Delta T_{adia}$,

$= C_s \cdot \varphi \cdot \Delta T$.

where

ΔT_{adia} : adiabatic temperature rise of sample,

ΔT : measured temperature rise of sample & container,

C_s: assumed sample heat capacity and,

$\varphi = \left(1 + \frac{M_b \cdot C_b}{M_s \cdot C_s}\right)$ thermal inertia,

where

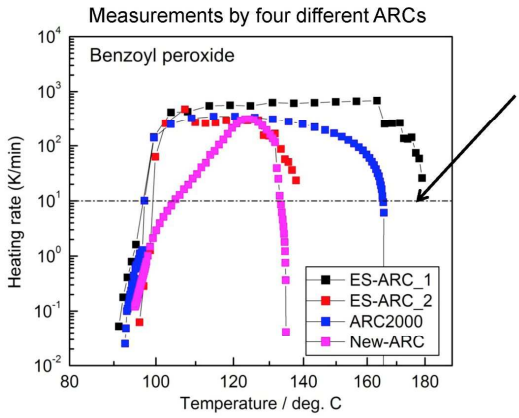
M_b: container mass,

C_b: container heat capacity and

M_s: sample mass.

In adiabatic calorimetry, exothermic decomposition energy has to be calculated using assumed value of sample heat capacity: C_s.

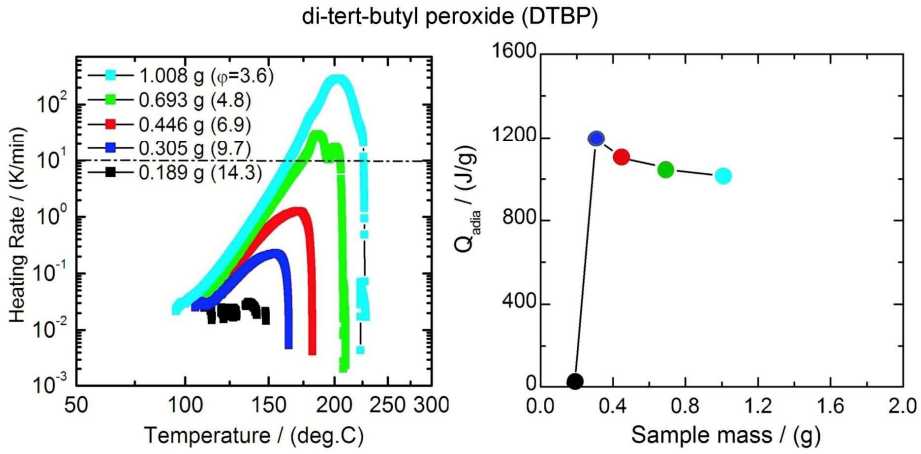
② Limited response speed of adiabatic mode to heating rate



When heating rate exceeds 10 K/min, four typical ARCs can not guarantee the adiabatic condition.

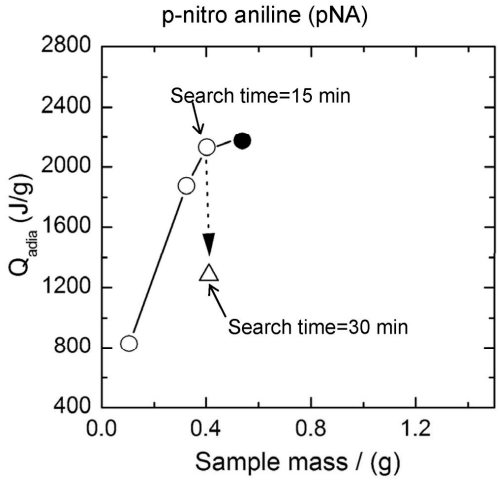
Decreasing the sample mass may reduce the heating rate, but increase the value of the thermal inertia φ that rises the uncertainty in the energy calculation.

③ Effect of sample mass



Decreasing the sample mass may reduce the heating rate, but increase the value of the thermal inertia φ resulting in a significant sample mass dependency.

④ Effects of searching time



Q_{adia} also showes significant search time dependency.