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

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Explosives and related matters:
Miscellaneous

Screening procedures for estimating the SADT of 50 kg packages

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I. Introduction

1. The self-accelerating decomposition temperature (SADT), the lowest temperature at which self-accelerating decomposition may occur in a substance in the packaging as offered for transport, is one of the defining characteristics of self-reactive substances and organic peroxides. Among other differentiation criteria, substances should be considered self-reactive if they have an SADT of 75 °C or less for a 50 kg package. The thermal stability should be determined by one of the four SADT test methods of Test Serie H as described in Section 28 of the *Manual of Tests and Criteria*.

2. These tests, however, generally require specialized equipment and significant amounts of substance. These requirements present a barrier for groups with limited experience in the classification of dangerous groups, as well as for situations where only limited amounts of substance are available (e.g., in research and development settings). This barrier might cause substances to be transported incorrectly as not self-reactive, or might cause substances that should not be classified as self-reactive to be unnecessarily over-regulated.

3. Appendix 6 of the *Manual of Tests and Criteria* (MTC) provides screening criteria for several of the hazard classes. Specifically for self-reactive substances, Section A6.5.1 (b) states that classification procedures need not be applied if "the estimated SADT is greater than 75 °C" which offers an exemption from classification as a self-reactive substance without going through the extensive testing for formal classification.

4. Unfortunately, the MTC does not offer any guidance as to which techniques would be appropriate to properly and reliably estimate the SADT beyond a generic reference to "a suitable calorimetric technique."

5. Closing this gap in the MTC by establishing a simple and reliable screening method would greatly benefit the transport of dangerous goods by:

(a) Making classification more efficient and avoiding unnecessary testing while focussing lab resources on substances that realistically could pose a self-reactive hazard; and

(b) Simplifying initial assessment of potential self-reactive substances and thus increasing accessibility to groups with less experience in classification.

6. Differential scanning calorimetry (DSC) is a well recognized calorimetric method for determining the thermal stability of a substance with very small amounts of sample. It is also a standard technique that is more widely available than the specialized methods of Test Series H and is thus a more accessible method, especially for organizations less familiar with transport regulations. DSC-measurements are already used in other classification procedures

(e.g., to assess temperature control for thermally sensitive samples, see Section 20.3.4 of the MTC).

7. From the screening criteria in Appendix 6 of the MTC (see paragraph 3 above), we don't need to accurately determine the SADT to exclude a substance from classification as a self-reactive, but rather show that the estimated SADT is above 75 °C. This paper uses fundamental equations of thermal safety along with reasonable yet conservative assumptions to derive calorimetric criteria for reliably estimating if the SADT of a liquid or solid is greater than 75 °C from an appropriate DSC-measurement.

8. Cefic asks the Sub-Committee to carefully review the intended proposal laid out in this paper. Written comments by the delegations are highly appreciated and should be sent by e-mail to the Cefic representative. Based on the feedback, Cefic will submit a formal proposal for the subsequent summer session.

II. Proposed classification screening rules for a 50 kg package

9. To derive screening rules to estimate the SADT for a 50 kg package for exemption from classification as self-reactive, we first need to consider the conditions that could bring about a critical decomposition of a substance. These conditions generally occur when the heat generated by the decomposition of the substance is greater than the heat loss of the package.

10. The theoretical heat flow for a substance undergoing spontaneous decomposition at 75 °C in a 50 kg package, the temperature and packaging relevant for classification as a self-reactive, can be calculated starting from fundamental equations in thermal and chemical safety. Full details for these calculations and their underlying assumptions can be found in the appendices to this paper and in an upcoming publication.

11. From this heat flow the expected onset temperature for the decomposition in a DSC experiment can be determined. For this calculation a sensitivity of 20 W kg^{-1} for the DSC-measurements was taken as a conservative assumption. Although commercial machines are generally much more sensitive (< 5 W kg^{-1}), the conservative value assumed in this paper not only leads to a higher level of safety in the screening but also accounts for non-systematic errors in the measurement (e.g., visual setting of the start of the exotherm by the operator).

12. For classification purposes, the last revision of the MTC defined default values for the specific heat loss from a 50 kg package for both solids and liquids (see footnote b in Table 28.4). In the following calculations a 50 kg package with these heat loss characteristics was taken as "standard."

13. Following the recommended classification criteria from the MTC and representative activation energies, the following critical heat flow and corresponding DSC-onset temperature can be calculated for **liquids** in a 50 kg container with a given SADT of 75 °C (Table 1).

Table 1: Critical heat flow and corresponding DSC-onset for liquids with an SADT of 75 °C for a standard 50 kg package

Activation Energy (kJ mol^{-1})	50	100	150	200
$\dot{q}_{SADT}$ (mW kg^{-1})	444	222	148	111
$T_{onset\text{-}DSC}$ (°C)	173	127	111	103

Note: Minimum heat flow and maximum DSC-onset highlighted in red

14. As can be seen from Table 1, the calculated critical heat flow is greater than 100 mW kg^{-1} for all assumed activation energies, and the highest DSC-onset temperature for a substance with an assumed SADT of 75 °C is approximately 175 °C.

15. From these calculations we propose that the estimated SADT for **liquids** in a standard 50 kg package is above 75 °C if:

(a) the DSC-onset is equal to or higher than 175 °C, or

(b) the isothermal heat flow at 75 °C is equal to or less than 100 mW kg^{-1}.

16. Similarly, the following critical heat flows and expected DSC-onset temperature can be derived for **solids** in a standard 50 kg package with a given SADT of 75 °C (Table 2).

Table 2: Critical heat flow and corresponding DSC-onset for solids with an SADT of 75 °C for a standard 50 kg package

Activation Energy (kJ mol^{-1})	50	100	150	200
$\dot{q}_{SADT}$ (mW kg^{-1})	222	111	74	56
T_{DSC} (°C)	198	136	117	107

Note: Minimum heat flow and maximum DSC-onset highlighted in red

17. As can be seen from Table 2, the calculated critical heat flow is greater than 50 mW kg^{-1} for all assumed activation energies, and the highest DSC-onset temperature for a substance with an assumed SADT of 75 °C is approximately 200 °C.

18. From these calculations it is reasonable to assume that the estimated SADT for **solids** in a standard 50 kg package is above 75 °C if:

(a) the DSC-onset is equal to or higher than 200 °C, or

(b) the isothermal heat flow at 75 °C is equal to or less than 50 mW kg^{-1}.

19. Note that for the derivation of these screening rules, no specific characteristics were assumed for the solid or liquid substances other than their physical states. Thus, these calculations apply generally to substances when considered for exemption from classification in a 50 kg package.

20. In a comparison of the predictions from these screening rules with empirical data graciously provided from industry and competent parties for over 300 compounds (both liquids and solids), no case was found where a compound with an SADT less than 75 °C (as measured by any of the recommended methods in Test Series H) had a DSC-onset of greater than 150 °C. The calculated DSC-onsets above are even higher than this result, which supports the validity of our approach and models, and highlights the conservative nature of our assumptions.

21. To date we are not aware of any “false negatives” from these proposed rules (i.e., a substance with a DSC-onset above 175 °C or 200 °C and with an SADT below 75 °C). While a few cases were revealed as “false positives”, where a substance had an SADT above 75 °C for a 50 kg package despite having a DSC-onset below 175 °C or 200 °C, a much larger number of these samples would have been correctly identified as having an SADT greater than 75 °C from their DSC-onset temperature. These observations show both that the proposed guidelines are conservative enough to maintain a high level of safety in transport,

while still allowing for the vast majority of non-critical cases to be properly assessed with a minimal of effort.

22. These screening rules might fail for substances that show strong autocatalytic behaviour during decomposition. Further calorimetric data is needed for such substances to determine if the DSC rules can be applied when attempting to exclude them from classification as self-reactive. Such information could be attempts to detect critical shifts in the onset temperature by comparing:

(a) DSC-measurements of tempered samples in comparison to fresh samples, or

(b) DSC-scans with different scan rates.

The onset temperature or heat flux criteria should always be met for fresh and aged samples representing the anticipated duration of transport.

III. Conclusion

23. The preliminary proposal, presented here for further discussion, offers a simplified and readily accessible method for estimating if the SADT for a 50 kg package is above 75 °C. This simplification closes a gap in the current screening rules given in Appendix 6 of the MTC and provides much needed guidance for the classification of self-reactive substances.

24. Through these rules organizations not familiar with transport regulations will be given the added security of knowing via a simple and readily applied test method if a given substance requires further testing in terms of self-reactivity. Thus, it is clearer when substances need to be further tested or provisionally handled as self-reactive substances.

25. Similarly, application of the screening rules in this proposal would help define when new substances clearly would not fall under the provisions of Division 4.1 Self-reactives, thus simplifying transport of these substances and avoiding unnecessary further testing.

26. In this manner it will increase safety in the transport of dangerous goods and support our green goals.

VI. Preliminary proposal

27. Insert the following text after Section A6.5.1 (b) of the MTC:

“(c) The estimated SADT for a 50 kg package is greater than 75 °C if:

1. The first detected exothermic reaction (onset, detection limit max. 20 W kg^{-1}) in a screening DSC is equal to or above 175 °C for liquids or 200 °C for solids;
2. The measured isothermal maximum heat flow at 75 °C is equal to or less than 100 mW kg^{-1} for liquids or 50 mW kg^{-1} for solids.

***Note**: These screening rules can fail for substances showing strong autocatalytic behavior in the decomposition. For such substances, further information is needed to determine if these simple screening rules apply to the particular substance (e.g., the effect of sample aging on the decomposition). Information concerning potential autocatalytic behaviour may be obtained from further calorimetric measurements (e.g., comparison of DSC-measurements of tempered samples with fresh samples, or DSC-scans with different scan rates). The onset temperature criteria or heat flow criteria should always be met for fresh and aged samples representing the anticipated duration of transport.”*

Appendix 1

Derivation of the proposed screening rules

28. One of the fundamental boundary conditions for a self-accelerating thermal decomposition of a substance is the point where the heat generated by the decomposition is greater than the heat loss to the surroundings. A mathematical way to describe this situation is given by the ratio between the adiabatic induction time (τ_{chem}) and the thermal relaxation time (τ_{relax}) respectively. The critical value for this ratio where the decomposition leads to a thermal runaway varies with the physical state of the substance and the packaging in question. When considering a liquid sample under the Semenov model for heat flow, where the main resistance to heat flow is at the boundary of the package with the surroundings, this value is approximately given by 1/e.

$$\frac{\tau_{relax}}{\tau_{chem}} = C \approx \frac{1}{e}$$

τ_{relax} = Thermal relaxation time (s)
τ_{chem} = Adiabatic induction time (s)
C = Constant
e = Euler's number

29. Conservatively assuming zero-order kinetics for the decomposition reaction, the adiabatic induction time can be calculated from the following equation:

$$\tau_{chem} = \frac{c_p \cdot R \cdot T^2}{E \cdot \dot{q}_T}$$

τ_{chem} = Adiabatic induction time (s)
$\dot{q}_T$ = Specific heat release rate at temperature T (W kg^{-1})
c_p = Heat capacity (J kg^{-1} K^{-1})
E = Activation energy (J mol^{-1})
R = Universal gas constant (8.314 J mol^{-1} K^{-1})
T = Temperature (K)

30. Meanwhile, τ_{relax} for the substance in question can be derived by solving Newton's law of cooling for the half-time of cooling.

$$\tau_{relax} = \frac{t_{1/2}}{\ln(2)}$$

τ_{relax} = Thermal relaxation time (s)
$t_{1/2}$ = Half-time of cooling (s)

31. A relationship between τ_{relax} and the heat loss per unit mass (L) for the packaged substance can then be derived by combining this equation with one defining the heat loss from a package (see paragraph 28.3.5 of the MTC):

$$\tau_{relax} = \frac{c_p}{\mathrm{L}}$$

τ_{relax} = thermal relaxation time (s)
c_p = Heat capacity (J kg^{-1} K^{-1})
L = Heat loss per unit mass (W kg^{-1} K^{-1})

32. Finally, combining the three equations from paragraphs 28, 29, and 31 allows for a derivation of the critical heat flow that leads to a thermal explosion as a function of the characteristic heat losses from the given package.

$$\dot{q}_T = \frac{R \cdot T^2}{E} \cdot L \cdot \frac{1}{e}$$

$\dot{q}_T$ = Specific heat release rate at temperature T (W kg^{-1})
E = Activation energy (J mol^{-1})
R = Universal gas constant (8.314 J mol^{-1} K^{-1})
T = Temperature (K)
L = Heat loss from the packaging (W kg^{-1} K^{-1})
e = Euler's number

33. Solving this equation with representative activation energies (50-200 kJ mol^{-1}) and the standard heat loss for liquids (60 mW kg^{-1} K^{-1}) recommended by the MTC for classification purposes (see paragraph 12 above) gives the critical heat flows at 75 °C presented in Table 1 above.

34. The temperature dependence of heat flow from an exothermic reaction at low levels of conversion (e.g., at the beginning of the decomposition) is given by the following equation.

$$\dot{q}_T = \Delta H_r \cdot k_0 \cdot e^{-\frac{E}{RT}} \cdot C$$

$\dot{q}_T$ = Specific heat release rate at temperature T (W kg^{-1})
ΔH_r = Reaction enthalpy (J kg^{-1})
k_o = Arrhenius pre-exponential factor (s^{-1})
E = Activation energy (J mol^{-1})
R = Universal gas constant (8.314 J mol^{-1} K^{-1})
T = Temperature (K)
C = Constant
e = Euler’s number

35. To derive our screening rules for classification of a substance in a 50 kg package, we need to compare the critical heat flow at two different temperatures, specifically, that at the temperature relevant for classification (75 °C, T_{SADT}), and that at the observed onset temperature in a DSC-experiment (T_{DSC}). The ratio of these two heat flows is given by:

$$\frac{\dot{q}_{SADT}}{\dot{q}_{DSC}} = e^{\frac{E}{R}\left(\frac{1}{T_{DSC}} - \frac{1}{T_{SADT}}\right)}$$

$\dot{q}$ = Heat flow (W kg^{-1})
E = Activation energy (J mol^{-1})
R = Universal gas constant (8.314 J mol^{-1} K^{-1})
T = Temperature (K)
e = Euler’s number

36. Solving this equation then for T_{DSC} leads to:

$$T_{DSC} = \frac{1}{\frac{R}{E} \cdot \ln\left(\frac{\dot{q}_{SADT}}{\dot{q}_{DSC}}\right) + \frac{1}{T_{SADT}}}$$

$\dot{q}$ = Heat flow (W kg^{-1})
E = Activation energy (J mol^{-1})
R = Universal gas constant (8.314 J mol^{-1} K^{-1})
T = Temperature (K)

37. To obtain the DSC-onset temperatures in Table 1, this equation was solved using:

(a) The representative activation energies (50-200 kJ mol^{-1}) and corresponding critical heat flows calculated in paragraph 33.

(b) Taking 75 °C (348 K) as the T_{SADT} relevant for classification of a 50 kg package.

(c) Assuming 20 W kg^{-1} for $\dot{q}_{DSC}$ (see paragraph 11 above).

38. Similar treatment of solids with the Frank-Kamenetzkii model (with Thomas correction), which assumes that the principal barrier for heat transfer lies within the substance itself, gave the results from Table 2. More information can be obtained by contacting the Cefic delegate.

Appendix B

Sensitivity tests for the derived screening rules

39. The proposed DSC rules for both liquids and solids were subjected to sensitivity analyses.

40. Taking the assumed values for heat losses for liquids (60 mW kg^{-1} K^{-1}), activation energy (100 kJ mol^{-1}) and the DSC-detection limit (20 W kg^{-1}), a DSC-onset temperature of ca. 130 °C can be calculated as a starting reference point for this analysis (black dash line). Systematically varying one of these three variables while holding the other two constant then leads to the following sensitivity plot for the screening rules for liquids (Figure 1).

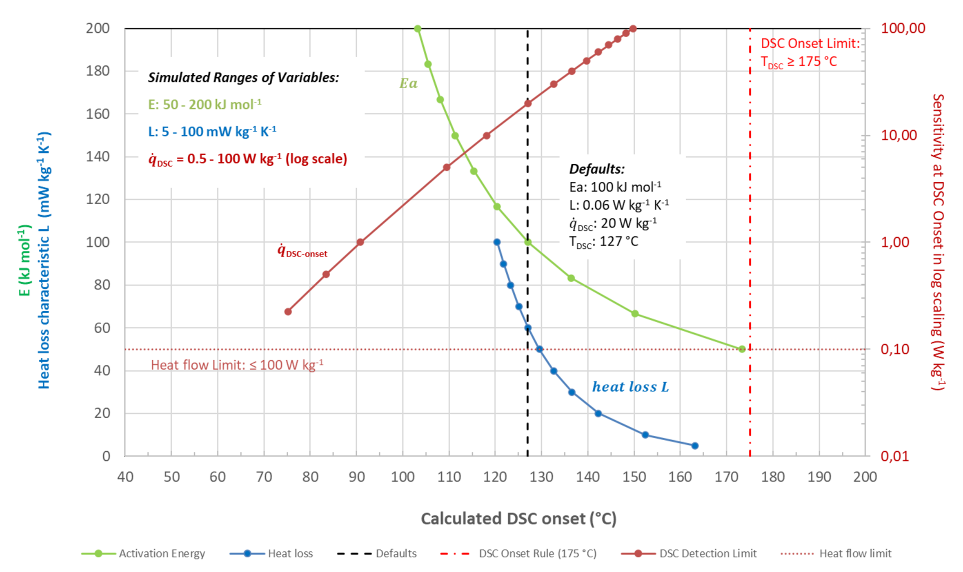

Figure 1: Sensitivity plot for the screening rules for liquids

41. The sensitivity test showed that the screening rules liquids are sufficiently conservative versus variation in DSC-detection limit, and that the 175 °C limit would only be breached at unrealistically poor levels of detection (>> 100 W kg^{-1}). On the other hand, very low activation energies (< 50 kJ/mol) or heat loss values (< 50 mW kg^{-1} K^{-1}) could lead to false negatives using these screening rules.

42. While such low activation energies are not to be expected for substances presented for transportation, the sensitivity to lower heat losses show that while these screening rules are appropriate for exemption from classification purposes, they should not be applied when assessing self-reactive properties in other situations or settings (e.g., larger package sizes).

43. Similar results were obtained when this sensitivity analysis was performed for the screening rules for solids.

44. These sensitivity analyses support the use of the proposed DSC-screening rules for excluding liquid or solid substances from classification as self-reactive according to the guidelines for classification described in Section 28 and Appendix 6 of the MTC.
