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Sub-Committee of Experts on the Transport of Dangerous Goods

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OTHER BUSINESS

Proposals of amendments to the *Manual of Tests and Criteria*
Test methods for the determination of the self-accelerating decomposition temperature (SADT)

Transmitted by the International Dangerous Goods and Containers Association (IDGCA)

Introduction

1. There are many problems related to the SADT determination (uncertainties in the definition of this parameter, peculiarities of the test methods recommended in the *Manual of Tests and Criteria*), especially with regard to solid products. This situation requires revision of numerous articles of Section 28 of the *Manual of Tests and Criteria*. Proposals that are contained in this document are based on the detailed comparative analysis of the methods recommended in the *Manual of Tests and Criteria* as presented in the annex to this document.

Proposals

Sub-section 28.2 (Test methods)

2. It can be shown that not all the methods recommended in the *Manual of Tests and Criteria* are equally applicable to liquids and solids (see Section 2 of the annex to this document). Therefore it is proposed to replace current paragraph 28.2.2

"Each of the methods listed is applicable to solids, liquids, pastes and dispersions."

with

"The H1 and H4 methods are applicable to solids, liquids, pastes and dispersions. The H2 and H3 methods are applicable only to low-viscous liquids."

Sub-section 28.3 (Test conditions)

3. It is proposed not to apply the specific heat loss as the criterion of thermal equivalence of packagings of different size and to introduce the cooling tempo as the physically better grounded and reliable criterion (see Introduction and section 2.3.4 of the annex). The main advantages of this criterion are as follows:

(a) It corresponds in full measure to the statement contained in 28.3.5 that reads "the quantity of substance, dimensions of the package, heat transfer in the substance and the heat transfer through the packaging to the environment" should be taken into account;

(b) The analytical expressions have been derived that allow calculation of the cooling tempo for packagings of various geometries if physical properties of a substance and heat transfer from a package surface are known;

(c) If cooling tempo has been measured and the existing analytical expression is applicable to a packaging then the detailed data about internal (heat transfer in the substance) and external heat transfer can be evaluated. These data are necessary for scale-up;

(d) For liquids equality of cooling tempos for packagings of different size is equivalent to the equality of specific heat losses;

(e) For solids cooling tempo has clear physical meaning whereas half-time of cooling is only empirical parameter that is not defined from physical point of view;

(f) Matching the cooling tempos for vessels of different shape and size having different physical properties ensure equivalence of their thermal behavior, therefore the cooling tempo provides reliable basis for scale-up.

4. Following this replacement it is proposed to recommend calibration of a packaging by measuring the cooling tempo instead of half-time of cooling. The additional advantage of this parameter is that the results of its measurement do not depend on the position of a sensor within a package. On the contrary, the results of half-time of cooling measurement are position-sensitive in those cases when heat transfer on different surfaces of a vessel is different (example is a DEWAR flask).

5. The method for determination of the cooling tempo is similar to the method cited in article 28.3.6 (sixth line and further). The existing sentence:

"For scaling, it may be necessary continuously to monitor the temperature of the substance and surroundings and then use linear regression to obtain the coefficients of the equation:

$$\ln\{T - Ta\} = c_0 + c \times t \qquad (1a)$$

where T = substance temperature (^oC);
Ta = ambient temperature (^oC);
C_0 = ln{initial substance temperature – initial ambient temperature};
C = L/Cp (s^{-1});
T = time (s)."

should be replaced with the following sentence:

"To measure the cooling tempo it is necessary to monitor continuously the temperature of the substance and surroundings, then select the linear part of data after a lapse of transient period and use linear regression to obtain the coefficients of the equation:

$$\ln\{T - Ta\} = c_0 + \omega \times t \qquad (1b)$$

where T = substance temperature (^oC);
Ta = ambient temperature (^oC);
C_0 = ln{initial substance temperature – initial ambient temperature};
ω = cooling tempo (s^{-1});
T = time (s)."

As it follows from comparison of equations (1a) and (1b) they are identical for liquids so that the cooling tempo is directly proportional to specific heat loss. Moreover for a vessel containing liquid (well stirred tank) there will not be a noticeable transient period, therefore the cooling data plotted in the axes ln{T-Ta} – time will form the straight line.

6. As the specific heat loss is inapplicable for solids as the criterion it is proposed to remove the second part of Table 28.3 "For solids".

7. It is proposed to include a new 28.3.8 that describes the method for cooling tempos calculation for packagings of different shapes, to read as follows:

"28.3.8 Calculation of cooling tempo for vessels of different shapes

28.3.8 The cooling tempo can be easily calculated for bodies of different shapes if thermal-physical properties of a substance and external heat transfer coefficient are known.

Equation for a sphere:

$$\omega = a[\mu_1(Bi)/r]^2$$

where r = radius for a sphere (m);
Bi = Biot criterion, Bi=Ur/λ;
a = thermal diffusivity (m^2/s); $a = \lambda/c_p/\rho$,
c_p = specific heat (J/kg/K);
ρ = density (kg/m^3);

U = heat transfer coefficient ($W/m^2/k$);

$\mu_1(Bi)$ = the first root of the characteristic equation $tg\mu = -\mu/(Bi-1)$

Values for $\mu_1(Bi)$ can be found in tabular in Table 1

Equation for a barrel:

$$\omega = a[\mu_{1s}^2/(h/2)^2 + \mu_{1c}^2/r^2];\ Bi_s = \frac{U_s h/2}{\lambda};\ Bi_c = \frac{U_c r}{\lambda},$$

where r = radius (m)

h = height (m)

$\mu_{1s}(Bi_s)$ = the first root of the characteristic equation $ctg\mu_s = \mu_s/Bi_s$

$\mu_{1c}(Bi_c)$ = the first root of the characteristic equation $\frac{J_0(\mu_c)}{J_1(\mu_c)} = \mu_c/(Bi_c - 1)$

indices c = side surface of a barrel;

s = end surfaces of a barrel

Values for $\mu_1(Bi)$ can be found in tabular in Table 1

Equation for a parallelepiped (rectangular box):

$$\omega = a\sum_{i=1}^{3}\left(\frac{\mu_{1s}(Bi_{si})}{h_i/2}\right)^2;\ \ Bi_{si} = \frac{U_{si}h_i/2}{\lambda}$$

where h_i = dimensions of a box (m);

$\mu_{1s}(Bi_{si})$ = the first root of the characteristic equation $ctg\mu_s = \mu_s/Bi_{si}$

U_{si}, Bi_{si} = heat transfer coefficient and the corresponding value of Biot criterion on every pair of opposite surfaces of a box

Values for $\mu_1(Bi)$ can be found in tabular in Table 28.4

Table 28.4: First roots of the characteristic equations

Bi	μ_1 (Bi) **for Sphere**	μ_1 (Bi) **for Slab**	μ_1 (Bi) **for Cylinder**
0.02	0.24450	0.141	0.1995
0.04	0.34500	0.1987	0.2814
0.06	0.42170	0.2425	0.3438
0.08	0.48600	0.2791	0.396
0.1	0.54230	0.3111	0.4417
0.2	0.75930	0.4328	0.617
0.4	1.05280	0.5932	0.8516
0.6	1.26140	0.7051	1.0184
0.8	1.43200	0.791	1.149
1	1.57080	0.8603	1.2558
1.5	1.83660	0.9882	1.4569
2	2.02880	1.0769	1.5994
3	2.28890	1.1925	1.7887
4	2.45570	1.2646	1.9081
5	2.57040	1.3138	1.9898
6	2.65370	1.3496	2.049
7	2.71650	1.3766	2.0937
8	2.76540	1.3978	2.1286
9	2.80440	1.4149	2.1566
10	2.83630	1.4289	2.1795
15	2.93200	1.4729	2.2509
20	2.98750	1.4961	2.288
30	3.03700	1.5202	2.3261
50	3.07880	1.54	2.3572
Polynomial approximation of the dependency μ_1(Bi): $\mu_1 = a_0 + \sum_1^4 a_i X^i; \quad X = \sqrt{Bi}$			
a_0	- 0.0736	- 0.0288	- 0.0529
a_1	2.1513	1.2059	1.7423
a_2	0.5748	- 0.3724	- 0.501
a_3	0.0689	0.0518	0.0651
a_4	-0.0031	-0.0027	-0.0031
R^2	0.9997	0.9998	0.9998

The polynomial provides sufficient precision of approximation (correlation coefficients for all the geometries are very close to 1) and can be used for calculations.”

Sub-section 28.4 (Series H test prescription)

28.4.2 "Test H.2: Adiabatic storage test"

8. The procedure of the SADT determination foreseen by the H2 test essentially uses the Semenov theory which is based on the model of a well stirred vessel. Therefore the H2 test can be applied only for low-viscous liquids. Moreover, the SADT estimates obtained by the H2 test will be valid for the single-stage reactions without self-acceleration (such as autocatalytic or chain reactions) (see section 2.2 of Annex 1). Therefore it is proposed to replace the last sentence of paragraph 28.4.2.1.1:

> "The method is appropriate for every type of packaging including IBCs and tanks."
>
> with
>
> "The method is appropriate for every type of packaging including IBCs and tanks containing liquid substances that are decomposed along a single-stage non-self accelerating reaction."

28.4.3 "Test H.3: Isothermal storage test"

9. Similarly to the H2 test the procedure of the SADT determination foreseen by the H3 test essentially uses the Semenov theory which is based on the model of a well stirred vessel. Therefore the H3 test can be applied only for low-viscous liquids. Moreover, the SADT estimates obtained by the H2 test will be valid for the single-stage reactions (see section 2.2 of the annex to this document). Therefore it is proposed to replace the penultimate sentence of paragraph 28.4.3.1.1:

> "The method is appropriate for every type of packaging including IBCs and tanks"
>
> with
>
> "The method is appropriate for every type of packaging including IBCs and tanks containing liquid substances that are decomposed along a single-stage non-self accelerating and autocatalytic reactions"

28.4.4 "Test H.4: Heat accumulation storage test"

10. It is stated in 28.4.4.1.1 that "The method is based on the Semenov theory of thermal explosion i.e. the main resistance to heat flow is considered to be at the vessel walls". It means that the H4 test is applicable in full measure for determination of the SADT for liquids. The scale-up procedure described in the *Manual of Tests and Criteria* does not allow correct prediction of the SADT for solids (see section 2.3 of the annex). Therefore it is proposed to emphasize this limitation explicitly by replacing the last sentence of paragraph 28.4.4.1.1:

> "The method can be used for the determination of the SADT of a substance in its packaging, including IBCs and small tanks (up to 2 m^3)."
>
> with

"The method can be used for the determination of the SADT of a liquid substance in its packaging, including IBCs and small tanks (up to 2 m^3).

The method can be used for the determination of the SADT of a solid substance in its packaging having the volume up to 0.03 m^3 provided that special scale-up procedure is applied (see 28.4.4.2.9)"

11. Furthermore it is proposed to add a new 28.4.4.2.9 describing the appropriate scale-up procedures that provide reliable prediction of the SADT for packages containing solids. Pertinent contents of the proposed article can be prepared on the basis of the analysis presented in section 2.3 of the annex to this document.

Specifically three scale-up methods considered in the abovementioned section can be recommended:

(a) new method based on the theory of regular cooling mode;

(b) the Bowes method which represents the advanced version of the Grewer method;

(c) method based on equality of half-cooling times measured for every DEWAR flask and specific package.

General proposals

Unification of the SADT definitions

12. Two different definitions of the SADT are cited in the *Manual of Tests and Criteria*. The first one relates to the US SADT test H1 and the heat accumulation storage test H4:

SADT is the lowest environment (oven) temperature at which overheat in the middle of the specific commercial packaging exceeds 6 °C after a lapse of the period of seven days (168 hours) or less.

The second one corresponds to the adiabatic storage test H2 and isothermal storage test H3:

SADT is the critical ambient temperature rounded to the next higher multiple of 5 °C.

13. The first definition is focused on two essential parameters – maximal permissible overheating and minimal acceptable induction period. The second definition suggests only one parameters – critical temperature of thermal explosion rounded to the next higher multiple of 5 °C. No limits are set on the induction period. This discrepancy may result in obtaining essentially different estimates of the SADT because of the following reasons:

(a) It can be shown that, if the SADT is regarded in terms of the first definition, correlation between the SADT and critical temperature depends on the feature of a reaction. Specifically, if a non-self accelerating reaction proceeds in a substance, the SADT is slightly lower than critical temperature and is reached after the period shorter than 7 days. In case of an autocatalytic reaction the SADT is always higher than critical temperature and this difference may reach 5 - 15 °C (see sections 2.1 and 2.2 of the annex to this document);

(b) Due to the discrepancy between the definition the SADTs determined by using the H1 or H4 test for the substance decomposing along the self-accelerating reaction may significantly differ from each other.

14. Therefore it is proposed to derive a unified definition that would cover all the tests.

Inclusion of new method of the SADT determination

15. All the experimental methods recommended by the *Manual of Tests and Criteria* for the SADT determination have essential limitations, especially when it concerns solid substances. Moreover, there are several practical cases that remain out of the scope of the existing methods. They are:

(a) Determining the SADT for large-tonnage tanks (tank-trucks, tank-wagons), stacks of packages;

(b) Evaluating safety margins at transport of bulk cargoes of self-reactive products (an example is transportation of ammonium nitrate-based fertilizers);

(c) Assessing potential hazards at transportation or storage of self-reactive products for more than 7 days.

16. All these problems can be resolved by applying the kinetics-based simulation method. Modelling of thermal explosion development in solids is complex task from physical-chemical and mathematical standpoint. Nevertheless availability of up-to-date high-performance personal computers in combination with an appropriate software allows this advanced method to be widely applied. By combining the advantages of experimental and simulation methods for the SADT determination one can achieve much more reliable and robust results for much wider spectrum of practical problems (see section 3 of the annex 1 for more details). This method can provide the basis for generalized unified definition of the SADT. Possible formulation is cited in section 3 of the annex.

17. Taking into account all these consideration it is proposed to include the kinetic-based simulation method in the list of methods recommended by the *Manual of Tests and Criteria*.

Safety implications

18. Application of more reliable methods for determination of the SADT will increase safety during transport and storage of self-reactive substances.

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Annex (ENGLISH ONLY)
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Comparative Analysis of the Methods for SADT Determination.

1. Introduction

The self-accelerating decomposition temperature (the SADT) is an important parameter that characterizes thermal hazard under transport conditions of condensed self-reactive substances. The SADT has been introduced into the international practice by the United Nations "*Recommendations on the Transport of Dangerous Goods*, *Manual of Tests and Criteria*" (TDG) [1]. The Globally Harmonized System (GHS) [2] had inherited the SADT as a classification criterion for self-reactive substances. According to TDG the SADT is defined as "the lowest temperature at which self-accelerating decomposition may occur with a substance in the packaging as used in transport". Important feature of the SADT is that it is not an intrinsic property of a substance but "…a measure of the combined effect of the ambient temperature, decomposition kinetics, packaging size and the heat transfer properties of the substance and its packaging" [1].

If the SADT ≤50°C for organic peroxides and ≤55°C for self-reactive substances, the following control and emergency temperatures are set for a packaging (Table 1).

Table 1 : Derivation of control and emergency temperatures

Receptacle	**Group**	**SADT**	**Control t-re**	**Emergency t-re**
Single packagings and IBSs	1	20°C or less	20°C below SADT	10°C below SADT
	2	Over 20°C to 35°C	15°C below SADT	10°C below SADT
	3	Over 35°C	10°C below SADT	5°C below SADT
Portable tanks	4	<50°C	10°C below SADT	5°C below SADT

The Manual recommends four tests for determining the SADT:

1. The United States SADT test (US SADT test) H1;
2. Adiabatic storage test (AST) H2;
3. Isothermal storage test (IST) H3;
4. Heat accumulation storage test (Dewar test) H4.

The H1 test foresees the experimental determination of the SADT for a commercial packaging. The H4 test is also based on experimental determination of the SADT for a small Dewar vessel which is supposed to be representative for a commercial packaging provided that the special scale-up procedure is used.

The H2 and H3 tests are based on the use of adiabatic and isothermal calorimetric technique respectively with the following estimation of the SADT.

The US SADT test is the only method that gives the direct and, hence, the most reliable answer. Nevertheless it is used rather rarely because of its expensiveness. Moreover this test can be applied only for packagings of up to 220 liters so that large tanks or intermediate bulk containers (IBCs) turn out to be out of the scope of this test. The H2-H4 tests are very attractive because they are based on the lab-scale experiments, don't involve such a large amount of reactive product and therefore are less expensive and dangerous. At the same time all these tests have essential limitations that should be taken into account when selecting one or another test. Special attention should be drawn to the fact that there exists an element of uncertainty with regard to the SADT definition.

Detailed analysis of problems related to the SADT determination methods have been presented by Fisher [3], numerous more recent papers are focused on correctness of some particular methods (see, for instance, [4-10]). This paper continues discussion of certain important aspects of the SADT determination methods. The consideration is illustrated by the abstract simulated examples that are capable of conveying the ideas without superfluous details.

2. Overview of the methods for SADT determination

2.1 The United States SADT test H1

The US SADT test H1 (and the Dewar test H4) is based on the following definition of the SADT:

SADT is the lowest environment (oven) temperature at which overheat in the middle of the specific commercial packaging exceeds 6 °C after a lapse of the period of seven days (168 hours) or less (D1)

This period is measured from the time when the packaging center temperature reaches 2 °C below the oven temperature (Fig.1a).

The US SADT test represents the series of full-scale experiments that are carried out with the specific commercial packagings of a product. The packaging is inserted in the test chamber (oven) and is maintained at a constant oven temperature. The temperature in the center of the packaging is monitored. Every experiment of the series is implemented with the new packaging. The step of the oven temperature variation is 5 °C.

The H1 test provides direct experimental determination of the SADT therefore there are not any particular problems concerning the test by itself. Nevertheless the challenge is issued by an element of uncertainty with regard to the SADT definition.

The general definition states that the SADT is "the lowest temperature at which self-accelerating decomposition may occur…" but it doesn't contain any quantitative measure that would allow to judge whether self-acceleration occurred or not. The next definition (D1) gives such a measure (overheat in the center in combination with period after which it is reached) but the physical ground of these figures remains unclear.

The characteristic 6-degrees overheat ΔT_6 may mean a conservative estimate of the critical temperature rise known from the thermal explosion theory (typical value of this parameter is 10 – 20 ^oC). The origin of the 7 day period is unintelligible. One can only guess that the 7-days period has been chosen assuming that longer transportation time is very unlikely; therefore a possibility of an explosion to occur after a lapse of this period is out of interest. Such an assumption is quite arguable because even 10 – 15 days transportation is not at all uncommon, not to mention about accidental delays.

Bearing in mind the abovementioned uncertainties it is important to understand in more detail how the SADT correlates with the critical temperature of thermal explosion T_{CR} which, for a packaging of given size, delimits the explosive and non-explosive domains of reaction proceeding and represents fundamental attribute of an explosion. To answer this question we considered two cases when the simple first-order reaction and the autocatalytic reaction occur in a product (ρ=1000 kg/m^3, c_p=2000 J/kg/K). In both the cases an explosion in the barrel of 0.6 m height and 0.2 m radius (S = 1 m^2, V = 75 l) had been simulated assuming that temperature distribution in the barrel is uniform (model of a well stirred tank, hereafter referred to as the lumped system). This model is suitable for low-viscous liquids. The initial temperature T_0 is 20 ^oC, boundary conditions of the 3-rd kind with heat transfer coefficient U=4.7 W/m^2/K were specified on all the external surfaces of the barrel. Mass of a product was 75 kg.

Case 1. The first order reaction:

$$\frac{dQ}{dt} = Q^{\infty} k_0 e^{-\frac{E}{RT}} (1-\alpha) \ ; \ k_o = 1.19\times10^9 \ s^{-1}; \ E=93.6 \ kJ/mol; \ Q^{\infty}=500 \ J/g \quad (1)$$

The SADT (Fig.1a) equals to 44.5 ^oC (Fig. 1a). The temperature course of the reaction reveals that it proceeds in the non-explosive domain. ΔT_6 is reached after a lapse of ~2.2 days. T_{CR} for the barrel (Fig. 1b) is 46.7 ^oC, the induction period is about 4 days.

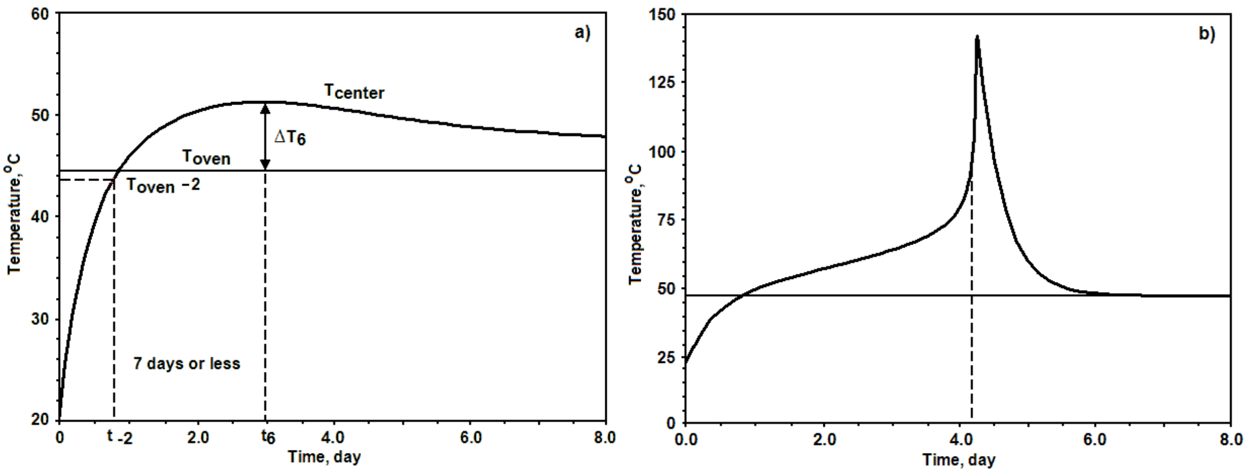


Fig. 1. Determining SADT along the H1 test: the first-order reaction, lumped system.
(a) – the ambient temperature equals SADT (H1 test);
(b) - the ambient temperature equals the critical temperature of thermal explosion .

Case 2. The autocatalytic reaction:

$$\frac{dQ}{dt} = Q^{\infty} k_0 e^{-\frac{E}{RT}} (1-\alpha)(z+\alpha)\text{; } k_o\text{=}4.84\times10^9 \text{ s}^{-1}\text{; E=90 kJ/mol; } Q^{\infty}\text{=500 J/g; z=0.03} \qquad (2)$$

Fig. 2 depicts the results of simulation. In this case the SADT equals to 34.8 °C (Fig. 2a), ΔT_6 is reached after a lapse of 7 days, and the explosion occurs soon after reaching ΔT_6. T_{CR} (Fig. 2b) is 31.2 °C, the induction period is about 18 days. It is obvious that at the SADT determined in accordance with definition (D1) the reaction proceeds in the explosive domain far above the criticality.

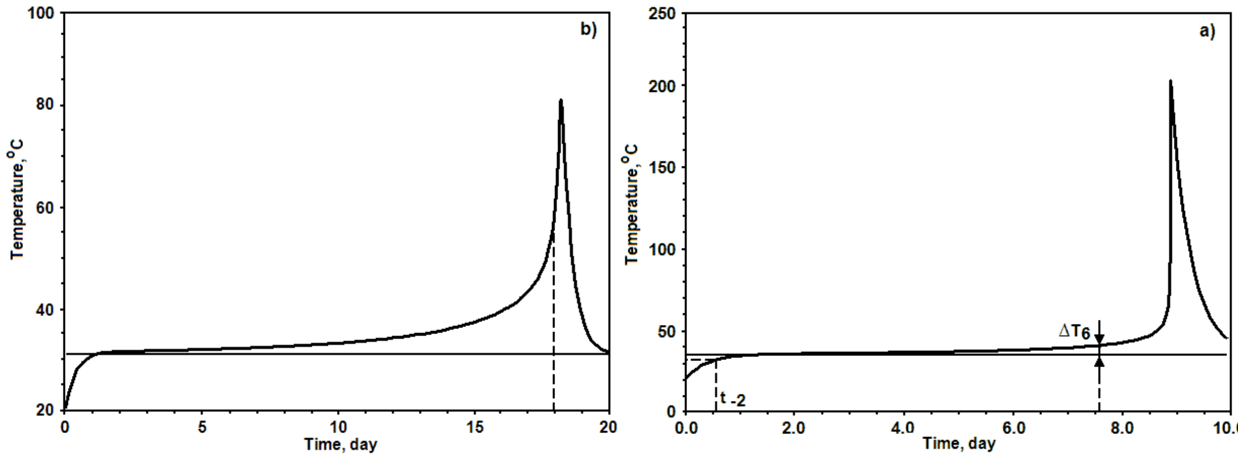


Fig. 2. Determining SADT along the H1 test: the autocatalytic reaction, lumped system.
(a) – the ambient temperature equals SADT (H1 test);
(b) - the ambient temperature equals the critical temperature of thermal explosion .

Let us now determine the SADT for a solid substance when heat transfer in is governed by thermal conductivity (substance properties are the same as indicated above). In this case temperature distribution across the vessel is essential. The H1 test has been simulated for the same barrel by using the complete model with distributed parameters [11] (distributed system).

The results simulated are presented in Table 2 together with the results for the lumped system.

The non-uniformity of a system causes quite big difference in the SADT and T_{CR} for the first-order reaction. Diminution of thermal conductivity results in lowering of the SADT and T_{CR} so that the packaging with a solid product can even pass into the group 2 (Table 1) instead of 3. The SADTs and critical temperatures for the autocatalytic reaction are less sensitive to change of the heat transfer mechanism and variation of thermal conductivity.

Table 2: Comparison of SADT and T_{CR} for lumped and distributed systems

Type of the system	First-order reaction		Autocatalytic reaction	
	SADT, °C	T_{CR}, °C	SADT, °C	T_{CR}, °C
Lumped	44.5	46.7	34.8	31.2
Distributed, (λ=0.6 W/m/K)	38.7	41.6	32.7	27.2
Distributed, (λ=0.1 W/m/K)	28.5	31.4	28	20.9

Specific feature of the autocatalytic reaction explains this fact. Namely, the initial reaction rate is very low; reaction accelerates mostly because of accumulation of the product-catalyst. During the main part of the induction period heat is evolved slowly and its amount is rather small (see [11, 12] for more details). Therefore the system turns out to be closer to uniformity so that for solids with high and moderate thermal conductivity the lumped system model properly predicts the SADT. Note that because of small amount of heat which is accumulated in a substance during the induction period ΔT_6, in contrast to the non-self accelerating reaction, is reached just before the explosion occurs.

These examples clearly demonstrate one intrinsic peculiarity of the SADT defined in accordance with (D1) – for non-self-accelerating reaction the SADT is always below T_{CR} whereas for autocatalytic reaction the SADT can be much higher than T_{CR}. The difference between the SADT and T_{CR} depends on the reaction kinetics, but the tendency remains in force. It can be shown that the same feature is valid for complex multi-stage reactions.

The observations discussed lead to several important conclusions:

1. Mechanism of heat transfer in a substance essentially affects critical temperature irrespective of the type of a reaction. The SATD is sensitive to mechanism of heat transfer; this effect ranges from quite strong for non-self-accelerating reactions to moderate for autocatalytic reactions.
2. The SADT defined in accordance with (D1) is reasonable indicator of criticality for non-autocatalytic reactions (though it can be somewhat conservative).
3. In case of autocatalytic reactions the SADT doesn't give any information about critical conditions but the SADT is essentially higher than critical temperature.

2.2 The Adiabatic and Isothermal Storage tests H2 and H3

The H2 and H3 tests are based on the different definition of the SADT:

SADT is the critical ambient temperature rounded to the next higher multiple of 5 °C (D2)

Both these tests are laboratory-scale experimental methods. The specific rate of heat generation evaluated from the corresponding calorimetric data is plotted on the Semenov diagram (Fig. 3) together with the straight line of the specific heat loss for a commercial packaging.

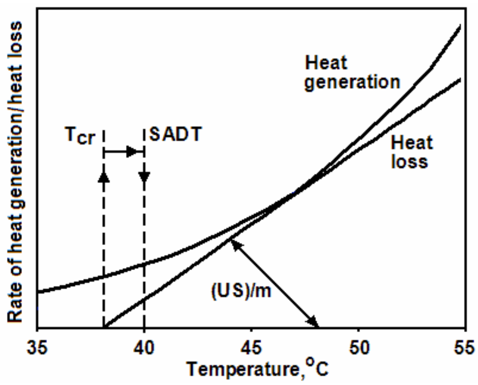


Fig. 3. Determining SADT in accordance with the H2 and H3 tests.

Ambient temperature at which the heat loss line becomes the tangent to the heat generation curve represents critical temperature of thermal explosion.

This principle of the SADT determination implies that the H2 and H3 tests are essentially based on the lumped system model (the Semenov model of thermal explosion is valid only for a lumped system). Therefore the first limitation is that they cannot be applied for characterizing solid products.

The H2 and H3 tests differ from each other in calorimetric technique used for experimental investigation, and in the reaction types that can be assessed.

The H2 test exploits adiabatic calorimetry. The heat generation rate is evaluated from the self-heat rate data taking into account thermal inertia of the adiabatic bomb. The resultant data contain information about reactant consumption and temperature dependency of a reaction.

The H3 test is based on the use of isothermal calorimetry. Therefore series of experiments at different temperatures should be implemented to determine temperature dependency of a reaction rate. Moreover, in accordance with the test procedure the maximal rate of heat generation should be drawn on the Semenov diagram. It results in two important features:

1. In case of non-self acceleration reaction maximal rate occurs at the very beginning of a reaction. Therefore the heat generation rate curve on the Semenov diagram will not take into account the reactant consumption (as if the reaction were of zero-order) and Tcr evaluated from the diagram will be lower than the real critical temperature.
2. In case of autocatalytic reaction Tcr evaluated from the diagram will represent the correct critical temperature. As it was shown by Merzanov [12], author of the quasi-stationary theory of thermal explosion for autocatalytic reactions, the Semenov method can be applied for evaluating Tcr for such reactions provided that the maximal reaction rate is used instead of initial one.

This overview reveals additional limitations of the tests.

1. The H2 test cannot give reliable estimates if a reaction is autocatalytic. Moreover it is unusable for complex reactions because of the limitations of the Semenov theory.

2. The H3 test is capable of proper estimation of T_{CR} for autocatalytic reactions, but will always result in conservative estimates of T_{CR} for non-self acceleration reactions. Applicability of this test in case of complex reaction requires special analysis.

Let us now apply the H2 and H3 tests for determining the SADT for the same two cases from pervious section. The results for the lumped system are presented in Table 3.

Table 3: Comparison of the SADTs calculated in accordance with H1, H2 and H3 tests

Test	First-order reaction		Autocatalytic reaction	
	SADT, °C	T_{CR}, °C	SADT, °C	T_{CR}, °C
H1	44.5	46.7	34.8	31.2
H2	45	44.8	40	37.5
H3	45	43.3	35	30.1

All the tests discussed give nearly the same SADT value for the first-order reaction. As it was predicted the Isothermal test H3 slightly underrates T_{CR}, but it doesn't affect the SADT estimate. In case of the autocatalytic reaction the H2 test results in the noticeably inflated values of the SADT and T_{CR}.

It should be emphasized that in case of the pronounced autocatalysis the difference in definitions of the SADT the tests H1 and H3 are based on (compare (D1) and (D2)) may result in serious inconsistency of the values. For instance, if T_{CR} determined by the H3 test for the autocatalytic reaction were just 0.2 degrees lower, i.e. 29.9 °C, then the SADT would be 30 °C which is by ~5 degrees lower than determined by using the H1 test. Let us cite another example related to the same barrel as discussed earlier, which contains organic peroxide. Its decomposition is highly exothermic (the overall heat effect is ~2000 J/g) and is characterized by strong autocatalysis. The SADT calculated according to the H1 test is 51 °C, T_{CR}=32.5 °C. The H3 test gives precisely the same value of T_{CR} so that the SADT=35 °C. The H1 test suggests that for this peroxide assignment of control temperature is not required (the SADT >50 °C) whereas the H3 test results indicate that the product should be attributed to Group 2 (Table 1)!

2.3 The Heat Accumulation Storage test H4

The H4 test is based on the same SADT definition (D1) as the H1 test and the same procedure is used for determination. The main difference is that the small Dewar vessel (up to 1 liter) filled with the tested substance is used for experiments instead of a commercial packaging. Therefore some scale-up of the results on the full-size packaging is required. This is the key problem of the test.

Several scale-up methods have been proposed and are applied in practice. How to choose any certain method and which one is better? The answer strongly depends on the physical state of a product and size of a packaging under interest.

2.3.1 TDG scale-up procedure

The TDG suggests that the SADT determined by using the H4 test will be representative for a commercial packaging or IBS if the specific heat loss (in W/kg/K) is the same for the Dewar vessel and the packaging:

$$\left(\frac{US}{V}\right)_P = \left(\frac{US}{V}\right)_D, \tag{3}$$

where indices P and D denote packaging and Dewar respectively.

This condition is easily derived from the heat balance equation for the lumped system. The important and very useful practical feature of the scale-up condition (3) (and of the Semenov theory in general) is that it doesn't depend on the specific geometry of a vessel but only on the ratio of the surface of a vessel to its volume.

The TDG also suggests determining specific heat loss by measuring half-cooling time $t_{1/2}$ for a packaging:

$$\frac{US}{V} = \rho c_p \frac{\ln 2}{t_{1/2}} \tag{4}$$

This scaling method is valid only for a well-stirred tank and, strictly speaking, the H4 test can be applied only for low-viscous liquids because in this case the temperature distribution in the Dewar vessel and in a packaging is approximately uniform.

Applicability of the H4 test for determining the SADT for solids, when internal heat transfer is governed by thermal conductivity, is perhaps the most disputable issue related to the SADT (see, for instance, recent publications [6-10]) because of the complexity of the scale-up problem. Therefore we will consider it in more detail.

Just as the scale-up method for liquids is based on the Semenov theory the scale-up for solids must be derived from the Frank-Kamenetskii theory (we deliberately consider only the simplest theories). Unfortunately there are several factors that hamper in direct application of this theory.

1. The theory had been created assuming that temperature on the surface of a solid body is defined (boundary conditions of the first kind). Contrary to it heat losses along the Newtonian law are typical for transportation or storage conditions (boundary conditions of the third kind).
2. This stationary theory doesn't consider development of a process in time whereas the SADT involves time (approximate of explosion induction period) as the essential parameter.
3. The theory gives analytical relations that are mostly applicable to the bodies of the simplest shapes – sphere, infinite cylinder and infinite slab. Many practical shapes such as barrel or box remain above its range.

2.3.2 Scale-up based on similarities between Semenov and Frank-Kamenetskii theories

For the first time the possibility to apply the results of the Semenov theory for approximate analysis of thermal explosion development in solid bodies of simple shapes was demonstrated by Frank-Kamenetskii [13]. Based on the formal similarity of the critical conditions for the lumped and the distributed system

$$\frac{E}{RT_0^2} Qk_0 e^{-E/RT_0} = \frac{1}{e}\frac{US}{V} \qquad\qquad \frac{E}{RT_0^2} Qk_0 e^{-E/RT_0} = \frac{\lambda}{r^2}\delta_{cr} \qquad (5)$$

lumped system distributed system

Frank-Kamenetskii derived that the results of the Semenov theory can be approximately applied to solid bodies of simple shapes if to use the effective value of the heat transfer coefficient:

$$U_0 = \frac{V}{Sr^2}\lambda e \delta_{cr} \qquad (6)$$

where r denotes the characteristic size (radius for a sphere or cylinder, half-thickness of an infinite slab).

Grewer [14] proposed to apply this idea for scaling-up the results of H4 test on the commercial packaging. Specifically he showed that the Dewar test performed for a self-reactive powder in a 500 cm^3 Dewar flask with $U_0 \approx 0.33$ $W/m^2/K$ will be representative for a spherical packaging with r=0.27 m calculated from (6) at $\delta_{cr}=3.32$, which corresponds to the volume of about 80 l (see also [8]).

Unfortunately there are several principal arguments against this scale-up method. As a matter of fact the very similarity between the critical conditions for the lumped and the distributed systems (5) is purely formal and doesn't have solid physical grounds. Nevertheless the concept of an effective heat transfer (6) can be used for rough estimates of explosion development in a solid but only under conditions of the first kind. It is quite evident from the expression (6), which doesn't contain real heat losses but characterizes only internal heat transfer governed by thermal conductivity. For instance, Grewer's results correspond to a packaging with Biot criterion Bi>30 which means that the H4 test from the example cited by Grewer is in fact representative for a packaging well under boundary conditions of the first kind.

The boundary problem of the explosion theory (an explosion under condition of Newtonian heat exchange with environment) had been considered in detail in [15]. Authors proposed more general approximate expression for effective value of the heat transfer coefficient U_{eff} that takes into account both internal heat transfer and external heat exchange U:

$$U_{eff} = \frac{U \bullet U_0}{U + U_0}, \; U_0 = \frac{V}{Sr^2}\lambda e \delta_{cr} \qquad (7)$$

Bowes [16] showed that by substituting this effective coefficient in the condition (3) instead of the real value U one can achieve more reliable scaling-up of the H4 test results. Nevertheless this scale-up method is still applicable only to simple forms and, hence, doesn't allow correct estimation of the SADT for many practical cases. Moreover, it is principally inapplicable if a complex exothermic reaction proceeds in a product (including autocatalytic reactions) because neither Semenov nor Frank-Kamenetskii theory covers such cases.

2.3.3 Scale-up based on equality of half-cooling times – the HCT method

In the case of a solid substance specific heat loss doesn't have definite physical meaning therefore any attempts to estimate this parameter for a Dewar flask on the basis of the calibration of a packaging lead to wrong results. This makes it impossible to use the parameter for scaling-up. Nevertheless it turns out to be possible to approximately scale-up the results of the Dewar test if the same specific heat loss or, which is the same, half-cooling time as for a packaging can be provided for a Dewar flask experimentally. It will be demonstrated later that this method allows obtaining somewhat conservative estimate of the SADT. . Unfortunately in majority of practical cases the equality of half-cooling times cannot be ensured.

2.3.4 Scale-up based on the theory of regular cooling mode

One can propose more universal scale-up method based on providing thermal equivalence of solid bodies of different size and even of different shapes having different physical properties. The theoretical ground of the method is the concept of regular cooling mode introduced by Kondratiev [17].

Let us consider temperature variation in inert solid bodies of simple shapes (sphere, slab, infinite and finite cylinder, parallelepiped) heated in an environment with constant temperature Te (boundary conditions of the third kind). Temperature in any point of a body is represented by the infinite series [18].

$$\frac{T - T_e}{T_0 - T_e} = \sum_{n=1}^{\infty} \prod_{i=1}^{3} A_{n,i} X_{n,i} \exp\left(-\frac{\mu_{n,i}^2}{r_i^2} at\right). \qquad (8)$$

Here $A_{n,i}$ stand for initial thermal amplitudes that depend on initial temperature distribution and body shape, $X_{n,i}$ are geometry-dependent functions, r_i denote characteristic dimensions of a body; $\mu_{n,i}$ are the roots of the characteristic equations, they are complex tabular functions of Bi: $\mu_{n,i} = \mu_{n,i}(Bi_i)$, $Bi_i = Ur_i / \lambda$.

After a lapse of the transient period tr only the first term of the series (8) remains significant and the regular mode of cooling is set in:

$$\frac{T - T_e}{T_0 - T_e} = \prod_{i=1}^{3} A_{1,i} X_{1,i} \exp\left(-\frac{\mu_{1,i}^2}{r_i^2} at\right). \qquad (9)$$

or, in the differential form

$$\frac{\partial(T-T_e)}{\partial\tau}=-\omega(T-T_e)\,,\ \frac{\partial\ln(T-T_e)}{\partial\tau}=-\omega\,;\ \omega=a\sum_{i=1}^{3}\frac{\mu_{1,i}^2}{r_i^2} \qquad (10)$$

where ω is the cooling tempo, $\mu_{1,i}$-the first roots of the corresponding characteristic equations.

The regular cooling (or heating) mode is distinguished by several important features.

1. At the expiration of the transient period the logarithmic rate of temperature variation in any point of a solid body of any shape regardless of the initial temperature distribution becomes identical and constant.
2. The cooling tempo ω depends on heat transfer coefficient (through $\mu_1(\mathrm{Bi})$) and on thermal diffusivity of a substance. Thus ω represents an integral characteristic that gives proper weigh of external heat exchange and internal conductive heat transfer within a solid substance.
3. Matching the cooling tempos for vessels of different shape and size having different physical properties ensures equivalence of their thermal behavior. Specifically, a Dewar flask and a commercial packaging will be equivalent if

$$\omega_D=\omega_P\,. \qquad (11)$$

Strictly speaking this condition of thermal equivalence is valid only for inert systems. For a self-reacting substance only approximate equivalence can be observed provided that heat generation due to an exothermic reaction is small and deviation of a reactive system form the inert one is also small. Usually this requirement is fulfilled during the most part of the induction period especially in the vicinity of criticality. In particular this is the case when the SADT is to be determined because the overheating doesn't exceed 6 °C.

The scale-up method based on regular cooling mode (hereafter referred to as the RCM method) has several essential advantages.

1. The cooling tempo can be easily calculated from (10) for bodies of different shapes if thermal-physical properties of a substance and external heat transfer coefficient are known.

For simple shapes (sphere, infinite cylinder and infinite slab) (10) is reduced to the formula

$$\omega=a[\mu_1(\mathrm{Bi})/r]^2 \qquad (12a)$$

where r is the characteristic dimension (radius for a sphere or cylinder and half-thickness for a slab); the function $\mu_1(\mathrm{Bi})$ in tabular form can be found in [18, 19] (see also Appendix A).

As it follows from (10) cooling tempos for bodies of more complex shapes are calculated on the basis of the superposition principle. Thus, a finite cylinder (barrel) can be interpreted as the intersection of an infinite cylinder and slab, therefore

$$\omega = a[\mu_{1s}^2/(h/2)^2 + \mu_{1c}^2/r^2];\ Bi_s = \frac{U_s h/2}{\lambda};\ Bi_c = \frac{U_c r}{\lambda}, \tag{12b}$$

where indices s and c denote slab and cylinder respectively; μ_{1s} and μ_{1c} represent the first roots of the characteristic equations for infinite slab and infinite cylinder; r is radius of a cylinder, h is its height.

A parallelepiped is the intersection of three infinite slabs, therefore

$$\omega = a\sum_{i=1}^{3}\left(\frac{\mu_{1s}(Bi_{si})}{h_i/2}\right)^2;\ Bi_{si} = \frac{U_{si}h_i/2}{\lambda}, \tag{12c}$$

where h_1, h_2 and h_3 represent dimensions of a parallelepiped.

2. The cooling tempo can be determined experimentally by using an inert solid substance or a reactive substance at temperatures where a reaction is negligibly slow.

Fig. 4 depicts typical cooling curves for spherical vessels of different size with a solid substance (c_p =2000 J/kg/K, ρ=1000 kg/m^3, λ=0.2 W/m/K). Curves 1 and 2 represent cooling of the thermally equivalent vessels of significantly different size, the equality of ω is provided by selecting the appropriate values of heat transfer coefficient (U=10 W/m^2/K for the large vessel as against U=0.456 W/m^2/K for the small one). Curve 3 demonstrates significant increase of ω for a vessel of a medium size with the same specific heat transfer US/V as for the large one (in both the cases US/V = 120 W/m^3/K so that for the medium vessel U=6 W/m^2/K). Note that for the small vessel, which is thermally equivalent to the large vessel US/V = 27.4 W/m^3/K.

Fig. 4 vividly illustrates the complete inapplicability of the concept of the specific heat transfer to solids emphasized by Fierz [6]. In case of a packaging with a solid both internal heat transfer governed by thermal conductivity and external heat losses from the surface are of key importance. Contributions of these mechanisms essentially depend on thermal diffusivity of a substance, heat transfer coefficient, and geometry and dimensions of a package. From this point of view results of packaging calibration cannot be transferred on the same packaging containing any other solid substance with different physical properties. It is in contrast with TDG recommendation to use dicyclohexyl phthalate as a calibration substance.

Furthermore, transient period that precedes the regular mode goes up significantly with increase of a packaging size and can be comparable or even longer than half-cooling time (compare curves 1 and 2 in Fig4).

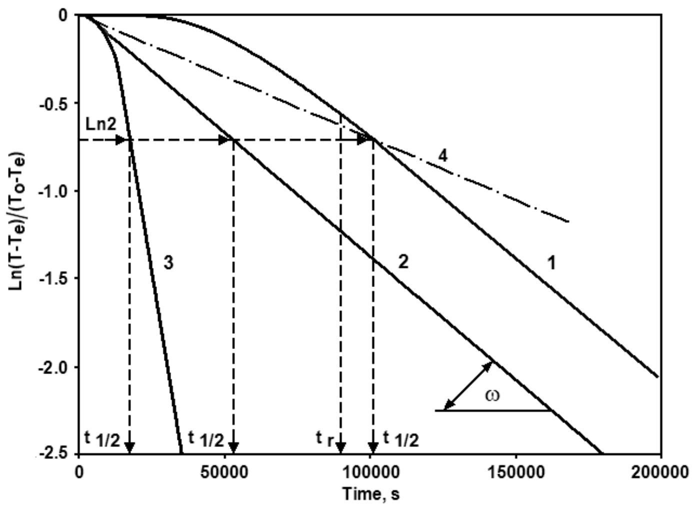


Fig.4 Cooling of spherical vessels
1 – r=25 cm; 2 – r=5 cm; 3 – r=15 cm; 4 – a small vessel has the same $t_{1/2}$ as a large one;
To=80°C, Te=20°C, U_1= U_3=10W/m²/K; U_2=0.456 W/m²/K.

It can lead to some confusing results. Thus, the small vessel would have the same half-cooling time as the large one (curve 4, Fig.4) if U were 0.24 W/m²/K, i.e. U would be almost two times smaller than it is required for thermal equivalence. It demonstrates once more that the half-cooling time cannot be used as a proper indicator of thermal equivalence.

3. The fact that the cooling tempo measured experimentally has well defined physical meaning allows applying various ways of a vessel calibration.

A cooling experiment can be performed by using some inert solid substance with physical properties different form those of a reacting product. Then U is calculated by using one of the formulas (12a)-(12c) with the following calculation of ω for the solid product under interest.

In the same way the results of calibration of a commercial packaging allow calculation of U_D for a Dewar flask that will ensure thermal equivalence and vice versa.

The following examples illustrate these possibilities and will allow several useful conclusions.

<u>Example 1</u>: The cooling tempo $\omega=2.67*10^{-5}$ s^{-1} has been determined (simulated in our case) for the commercial spherical packaging (r=0.25 m) containing a solid product (c_p=1000 J/kg/K, ρ=1000 kg/m³, λ=0.2 W/m/K, a=$2*10^{-7}$ m²/s).

a. In accordance with (12a) $\mu_{1,P} = r_P\sqrt{\omega/a} = 0.25\sqrt{2.67\bullet10^{-5}/2\bullet10^{-7}} = 2.89$.

This value corresponds to $Bi_P=U*r_P/\lambda=12.5$ (Table A1 of Appendix A) hence $U_P = Bi_P*\lambda/r_P =12.5*0.2/0.25 =10$ W/m^2/K for the packaging.

b. Now we can calculate U_D for the spherical Dewar with $r_D=0.05$ m filled with the same substance. The cooling tempo for the Dewar must be the same as for the packaging, therefore $\mu_{1,D} = r_D\sqrt{\omega/a} = 0.05\sqrt{2.67 \bullet 10^{-5} / 2 \bullet 10^{-7}} = 0.578$.

From Table A1 we get $Bi_D=0.113$ so that $U_D = Bi_D*\lambda/rD = 0.113*0.2/0.05=0.452$ W/m^2/K. The SADT determined for the Dewar flask and the packaging are presented in Table 4. It demonstrates also the SADTs determined for the same spherical Dewar flask on the basis of other scale-up methods. The SADT values determined by using the US H1 test (also simulated in our case) are considered here as the references.

Table 4 : The SADTs for thermally equivalent spherical Dewar and packaging

Reaction type	US test H1 (packaging)	Heat accumulation storage test H4, different scale-up methods			
		RCM (ω=const)	$t_{1/2}$=const	Bowes ($U_{eff}S/V$=const)	TDG (US/V=const)
		U_D=0.452*	U_D=0.24*	U_D=0.4*	U_D=2*
N-order	33.6	35.9	30.3	34.5	48.4
Autocatalytic	30.3	31.7	29.8	31.3	36.9

*) in W/m^2/K

Example 2 represents more complex case of a real Dewar flask with round bottom described in [10] (see Fig. 5a) with different heat loses on different surfaces, specifically $U_{top}=3.5$ W/m^2/K whereas $U_{side}=U_{bottom}=0.29$ W/m^2/K. The flask is filled with a solid reactive substance ($\rho=464$ kg/m^3, $\lambda=0.16$ W/m/K, cp=1450 J/kg/K). The inner flask is supposed to be made of stainless steel: wall thickness is 1 mm, $\rho=7000$ kg/m^3, $\lambda=16$ W/m/K, c_p =500 J/kg/K. The effective thermal inertia of the Dewar is 1.37, i.e. the same as indicated in [10].

a. Thermal behavior of this object has been simulated numerically. The pronounced temperature distribution along the symmetry axis appears in the course of cooling. Fig. 5b depicts variation of relative temperature in three different points – near the top (curve 1), in the middle (curve2) and close to the bottom (curve3). After a lapse of the transient period the regular cooling mode is set and the cooling tempo in all the points becomes the same: $\omega=4.97*10^{-5}$ s^{-1}.

b. Now one can calculate the parameters of a barrel (commercial packaging) that will be represented by this Dewar flask. Under the assumption that $h_P=2r_P$ and that heat losses are the same on all the surfaces formula (13b) gives: $\omega = a(\mu_{1s}^2 + \mu_{1c}^2)/r^2$; $Bi_s = Bi_c = U_P * r/\lambda$. The packaging contains the same solid substance so that a= $2.38*10^{-7}$ m^2/s. There are two unknown parameters – radius r_P and the heat transfer coefficient U_P therefore one can estimate U_P for a barrel of given size or calculate the size for the given U_P.

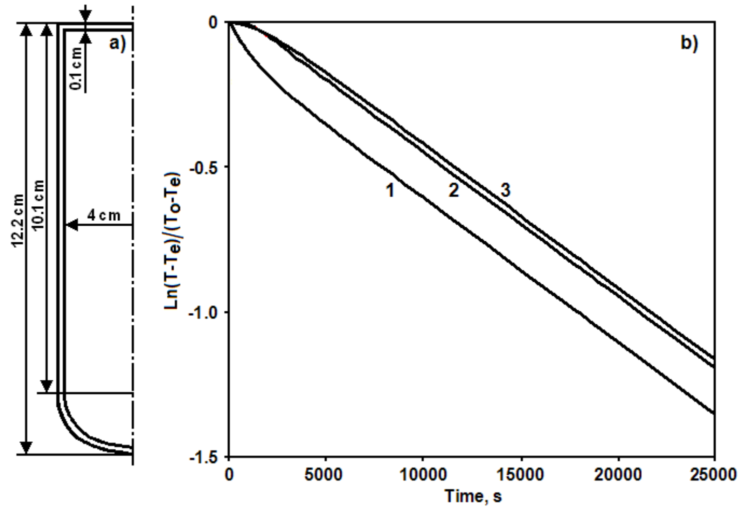


Fig. 5. Cooling of the Dewar flask.
a) – Sketch of the inner flask; b) - Temperature variation in different locations: 1 – 1 cm from the top, 2 – the middle, 3 - 1 cm from the bottom.

1. The barrel size is assigned: r_P = 0.18 m (volume of the barrel is ~36 l). The appropriate values of the first roots should be found in Table A2 and A3 (Appendix A). They must correspond to the same value of Bi and the sum of their squires must be equal to $\omega r^2/a$=6.76. The sought for values correspond to Bi=9.71: μ_{1s} =1.43 and μ_{1c} =2.17 . Finally the required value of Up is 8.6 $W/m^2/K$. It should be emphasized that the correlation between packaging size and intensity of heat exchange is very strong. Thus, for a barrel of radius r_P = 0.2 m (volume is ~50 l) Bi will be more than 100, i.e. the barrel proves to be under the conditions of the first kind.

2. It is known that Up = 3 $W/m^2/K$. In this case determination of the appropriate values of μ_{1s} and μ_{1c} requires several iterations: First, Bi is calculated for some initial guess on r, then values of μ_{1s} and μ_{1c} are evaluated, cooling tempo ω_P is calculated and compared with ω_D. If $\omega_P \neq \omega_D$ the next iteration is implemented with the changed value of r. In our case the resultant values of the first roots are μ_{1s} =1.16, μ_{1c}=1.74, and radius of the barrel is 0.145 m (Bi=2.72).

Table 5 represents the calculated SADTs for the Dewar flask and the equivalent barrels.

Table 5 : The SADTs for thermally equivalent Dewar and barrels

	SADT, °C	
Vessel	First-order reaction	Autocatalytic reaction
Shelled Dewar, r=0.04 m	47	36.5
Barrel, r=0.18 m (U=8.6 $W/m^2/K$)	42	34.4
Barrel, r=0.145 m (U=3 $W/m^2/K$)	42.7	34.7

As in the previous cases the resultant SADTs for the autocatalytic reaction are close enough to each other and no significant sensitivity to the approximate nature of the scale-up method is observed. Results for N-order reaction are more sensitive so that difference between the SADTs for the Dewar and the barrels reaches about 5 °C.

2.3.5 Comparative analysis of Scale-up methods

General discussion of capabilities and limitations of four different scale-up methods have been presented in previous sections. The results presented in Table 4 allow implementation of comparative analysis of these methods.

We could see that three different scale-up methods resulted in obtaining comparable estimates.

The **RCM scale-up method** ensures reasonable correspondence between the SADTs determined though the H4 test gives somewhat overstated values. In case of an autocatalytic reaction the results are less sensitive to the approximate nature of scaling. Limitation of method is that cooling tempo cannot be calculated analytically for such complex objects as the real Dewar (complex geometry or different and asymmetrical heat losses on different surfaces). In these cases the RCM method allows only one-way scale-up– from a Dewar to a packaging, therefore the cooling tempo for a Dewar should be determined experimentally. The use of numerical simulation allows applying the RCM method in full measure to complex systems.

Estimates provided by the **Bowes method** are in good accord with results of the RCM method. Nevertheless the Bowes method has several serious limitations. Two of them have been mentioned already – inapplicability in case of complex geometry or reaction mechanism. Another limitation is that it cannot be applied if heat losses are asymmetrical. Moreover, detailed knowledge about thermal properties of a system is required, in particular heat transfer coefficient should be known for a packaging or a Dewar. As it was mentioned, this parameter can be reliably evaluated only from cooling tempo after its determination, i.e. Bowes method should be applied in combination with the RCM –based calibration.

Scale-up based on **equality of half-cooling times** also allows obtaining reasonable estimates but on a conservative side. The origin of this conservatism has been discussed earlier (see Fig.4). Important note is that this scale-up method will give such results only provided that half-cooling times were determined by direct measurement for every specific substance, Dewar and packaging. Important problem is that, because this method is purely empirical when it concerns solids, it is impossible to predict how variation of geometry, physical properties and features of a reaction can affect reliability of the results.

Finally, the **TDG method** demonstrates total inadequacy.

Summarizing all these facts one can conclude that the RCM method, having better justified physical basis, has better prospects, especially in combination with methods of mathematical simulation.

Important practical observation is that in all the cases irrespective of the scale-up method applied it appeared that the ~400 ml Dewar flask, depending on its geometry and geometry of a package, can be reasonably representative for a packaging with the volume of about 30 - 40 l. Determination of the SADT for solid-containing packages of larger volume by using the H4 test is impossible.

The last note of this section concerns the reason why the results of the SATD determination for many organic peroxides by using the H4 and H1 tests are in good agreement (see statement in [8- 10]). We believe that the main reason is in autocatalytic decomposition mechanism which is typical for organic peroxides. We could see that in this case due to specific feature of self-accelerating reactions different methods for the SADT determination give very comparable results. It is also very likely that more correct half-cooling time scale-up method has been used, i.e . $t_{1/2}$ was measured for the Dewar and a packaging.

3. Applying the kinetics-based simulation for SADT determination

Overview of the tests recommended by the TDG for determining the SADT reveal numerous problems that can be met while applying one or another method.

The H1 test is very time and cost consuming and cannot be used for big packages or tanks.

The H2 an H3 tests are rather flexible and cost-effective but they are principally inapplicable for solid products. In addition they are based on different definition of the SATD, which can lead to getting the results that are incomparable with the results of other methods.

The H4 test is also time consuming and is fraught with various problems when it concerns investigation of solid substances. Moreover this test cannot predict properly the SADTs for big packages or tanks.

There are several practical problems that are totally out of the scope of the TDG recommendations, namely:

- Determining the SADT for large-tonnage tanks (tank-trucks, tank-wagons), stacks of packages;
- Evaluating safety margins at transport of bulk cargos of self-reactive products (an

example is transportation of ammonium nitrate-based fertilizers);

- Assessing potential hazards at transportation or storage of self-reactive products for more than 7 days.

In all these cases experimental methods for the SADT determination are either inapplicable at all or are very troublesome or problematic. Only one method is capable of responding to this challenge. This is the kinetics-based simulation approach which can be very beneficial addition to the tests.. It comprises three main steps:

- implementing necessary series of calorimetric experiments;
- creating the mathematical model of a reaction on the basis of experimental data;
- incorporating the kinetic model into the model of a process and achieving the practical target by using mathematical (numerical) simulation.

The detailed discussion of the approach is out of the scope of this paper; it can be found in [20]. Here we will mention only that it can help in resolving various problems. Let us mention only two of them.

(1) The SADT can be determined (calculated) for a package, vessel of any size having various shapes.

(2) We could see that there are two different definitions of the SADT that may lead to inconsistent estimates. We also discussed the fact that the very concept of SADT contains some vagueness. As simulation allows calculation of any parameter or quantity with regard to thermal explosion development one can propose more precise unified definition of the SADT:

> **SADT is the lowest environment (oven) temperature at which thermal explosion occurs in the specific commercial packaging after a lapse of the presetted transportation time, otherwise SADT is the critical ambient temperature rounded to the next lower multiple of 5 ^{o}C.**

We deliberately avoided mentioning any fixed transportation time in the definition. It may be the same 7 days as in the TDG definition or any other value depending on the specific scenario.

The definition envisages two cases we met when analyzing the impact of a reaction mechanism on the SADT:

- For those cases when SADT is higher than critical temperature (autocatalytic reactions) the definition requires that induction period must exceed transportation time.
- It may happen that the induction period is less than transportation time even at critical temperature (this is the case for N-order reactions). Then the SADT is taken as critical ambient temperature rounded to the next lower multiple of 5 ^{o}C. In such a way the system is being located in the non-explosive domain thus ensuring safety at transportation.

Material presented in previous sections clearly demonstrates efficiency and usefulness of the kinetics-based simulation method for analysis of various scenarios – all the illustrative results were simulated. Let us present one more example.

This example demonstrates how the simulation method helps in solving the problem when neither of experimental methods is applicable. It concerns determination of the SADT for the stack of boxes. In accordance with TDG the SADT should be determined for a commercial package subject to transport. However it is usual practice to transport packaged goods in stacks rather than to carry every single packaging separately. Doubtless the SADT for a stack will differ form those for a single package. It is also obvious that this parameter cannot be estimated by either of the experimental tests.

Let us compare the shelled box of 20x20x20 cm size containing 7.5 kg of reactive solid product and the stack of 27 (3x3x3) boxes. The product decomposes along the single-stage first order reaction with E=110 kJ/mol, $k_o=1.96*10^{11}$ s^{-1}, Q^{∞}=500 J/g.

The container wall thickness is 2 mm. We will consider two cases – metallic container (λ=16 W/m/K) and container made of polymer (λ=0.2 W/m/K). In both these cases thermal conductivity of a product was the same: λ=0.15 W/m/K.

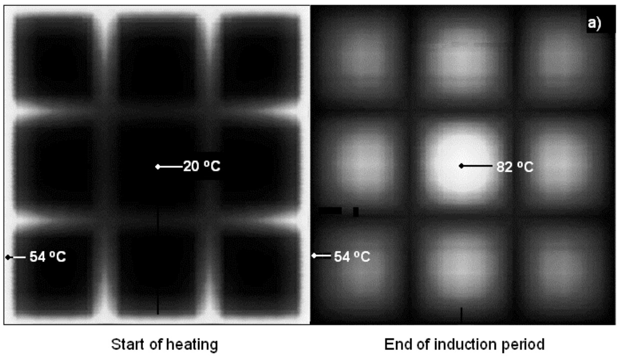
Table 6 : SADT and critical temperature for a box and for a stack of boxes.

Container	Single box		Stack of boxes	
	SADT, °C	T_{CR} , °C	SADT, °C	T_{CR} , °C
Metallic	57	61	48	54
Polymer	55	57	39	42

The simulated results (Table 6) demonstrate that the SADT for the single box is much higher than those for the stack and even exceeds its critical temperature so that the use of this SATD for the stack will be absolutely unsafe. Thus, for boxes with polymer containers, the induction period of the stack explosion at ambient temperature 55 °C is 4.5 days, i.e. smaller than the permissible 7 days.

The remarkable detail of the results obtained is that significant difference between the SATDs and critical temperatures for the stacked-up boxes with metallic and polymer containers is observed whereas single boxes with different container materials behave similarly. Analysis of the temperature fields in the stacks (Fig.6) gives the detailed explanation.

If containers are of metal the walls, though thin enough, serve as very efficient heat conducting elements. At the heating stage they facilitate external heat to penetrate into a stack (Fig. 6a, left drawing) thus accelerating the heating. On the contrary, when reaction heat release becomes significant metallic walls help to withdraw heat from a stack outwards (Fig. 6a, right drawing), which leads to elevation of the SADT and critical temperature.



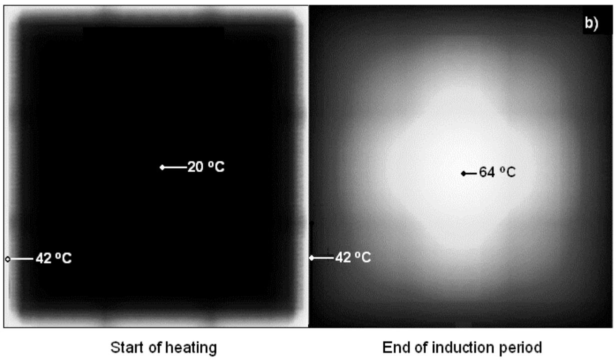


Fig. 6. Temperature distribution in the stack cross-section .
a) stack of boxes with metallic containers;
b) stack of boxes with polymer containers

The polymer has about the same thermal conductivity as the reactant therefore the stack behaves almost as a monolithic box of the reactant of the same size as the stack so that both the SADT and critical temperature are much lower than for the single small box (Fig. 6b).

In spite of great capabilities of numerical simulation there are some serious difficulties that impede the wide use of this method. First of all, mathematical complexity of the approach renders it impossible to apply simulation without powerful computers and appropriate software. Moreover, detailed enough knowledge about reaction kinetics is required.

As far as software is concerned, there are several well-known commercial codes of general designation that can be used for thermal explosion simulation. Let us mention as the examples the CFX (ANSYS Inc.) and FLUENT (FLUENT Inc.) software. However, these universal codes are expensive, difficult for use and often are not efficient enough for solving specific problems. Therefore, development of problem-oriented software (an example is AKTS-TA-Software, Switzerland) is a challenging decision.

The Thermal Safety Software (TSS) series developed by Cheminform Ltd. (CISP), Russia is another example of the specialized software. This series comprises the ThermEx and ConvEx program packages designed for comprehensive simulation of thermal explosions in solids and liquids, set of programs for reaction kinetics evaluation, and some other applications. Therefore TSS supports all the stages of an investigation aimed at assessment of safety at transport of self-reactive products. Specifically, all the results presented in the paper were obtained by using the Fork program for simulation of well stirred tanks and the ThermEx package - for simulation of processes in solids (distributed systems) and automatic SADT determination in compliance with the US SADT test.

Conclusions

1. The principal limitation of the adiabatic and isothermal storage tests H2 and H3 is that they are unfit for determination of the SADT for solid products. Furthermore, the H2 test is fraught with obtaining erroneous and, more important, unsafe estimates of the SADT if an autocatalytic reaction proceeds in a product. Therefore it shouldn’t be applied in such cases.

2. The H2 and H3 tests are based on different definition of the SADT as against the H1 and H4 tests. This difference can result in obtaining inconsistent estimates of the SADT for the same package. To avoid such kind of misleading it is highly desirable to use one definition for any of methods intended for the SADT assessment. As long as no new universal definition is proposed one can recommend to apply the definition based on permissible overheat (the H1 and H4 tests) which ensures reasonable estimates both for non-self accelerating and autocatalytic reactions.

3. The heat accumulation storage (Dewar) H4 test can be considered as restrictedly applicable for determining the SADT for solid products provided that the adequate scale-up method has been selected. In particular, the 400 ml Dewar flask can be representative for packages of up to approximately 30 liters. It was shown that the half-cooling time method can give reasonable results if this time interval is measured directly both for the flask and for a packaging. The Bowes method can be applied for simple determinations (simple geometry and kinetics).

4. The RCM method proposed in the paper represents the advanced, more universal approach to scaling though it requires use of mathematical simulation in complex cases. It was also demonstrated that this method provides the most correct determination of thermal physical properties of a vessel. Nevertheless it should be emphasized that all the scale-up methods are approximate ones and don't guaranty real thermal equivalence of reactive systems of different sizes and geometries.

5. Kinetics-based simulation approach is the general method for SADT determination. In some cases (complex geometry, complex reactions, SADT for stack of packages or bulked cargos, etc.) numerical simulation is the only way to get answers. Therefore it can be proposed as very useful and promising additional method.

All the demonstrated results have been obtained by using the software developed by Cheminform St.-Petersburg, Ltd. Specifically the Fork program was used for simulation of lumped systems and the ThermEx package - for simulation of processes in solids (distributed systems) and automatic SADT determination in compliance with the US SADT test.

Nomenclature

E- activation energy, kJ/mol

k_o – preexponential factor, s^{-1}

α - degree of conversion

Q^{∞} – heat effect of a reaction, J/kg

dQ/dt – specific rate of heat generation due to a reaction, W/kg

z - autocatalytic constant

R - universal gas constant, R= 8.31 J/mol/K

T – temperature, K

T_o – initial temperature of a product, K

T_e – ambient temperature, K

T_{CR} – critical temperature of thermal explosion, K

c_p – specific heat of a product, J/kg/K

ρ – product density, kg/m^3

λ – thermal conductivity coefficient, W/m/K

a – thermal diffusivity, $a = \lambda/c_p/\rho$, m^2/s

μ_i – roots of the characteristic equation

ω - cooling tempo, s^{-1}

U – heat transfer coefficient, $W/m^2/K$

S – surface of heat exchange, m^2

V – volume of a vessel or a package, m^3

h – height of a barrel, m

r – radius of a barrel, m

m_p – mass of a product, kg

ΔT_6 – the characteristic 6-degree overheat in the middle of a package, ΔT_6 =6 °C

T_{CR} – critical temperature of thermal explosion, K

(US)/m –specific heat loss, W/kg/K

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Appendix A – first roots of the characteristic equations

Bi	μ_1		
	Sphere (A1) $tg\mu = -\mu/(Bi-1)$	**Slab (A2)** $ctg\mu = \mu/Bi$	**Cylinder (A3)** $J_0(\mu)/J_1(\mu) = \mu/(Bi-1)$
0.02	0.24450	0.141	0.1995
0.04	0.34500	0.1987	0.2814
0.06	0.42170	0.2425	0.3438
0.08	0.48600	0.2791	0.396
0.1	0.54230	0.3111	0.4417
0.2	0.75930	0.4328	0.617
0.4	1.05280	0.5932	0.8516
0.6	1.26140	0.7051	1.0184
0.8	1.43200	0.791	1.149
1	1.57080	0.8603	1.2558
1.5	1.83660	0.9882	1.4569
2	2.02880	1.0769	1.5994
3	2.28890	1.1925	1.7887
4	2.45570	1.2646	1.9081
5	2.57040	1.3138	1.9898
6	2.65370	1.3496	2.049
7	2.71650	1.3766	2.0937
8	2.76540	1.3978	2.1286
9	2.80440	1.4149	2.1566
10	2.83630	1.4289	2.1795
15	2.93200	1.4729	2.2509
20	2.98750	1.4961	2.288
30	3.03700	1.5202	2.3261
50	3.07880	1.54	2.3572
Polynomial approximation of the dependency μ_1(Bi): $\mu_1 = a_0 + \sum_1^4 a_i X^i; \quad X = \sqrt{Bi}$ (13)			
a_0	- 0.0736	- 0.0288	- 0.0529
a_1	2.1513	1.2059	1.7423
a_2	0.5748	- 0.3724	- 0.501
a_3	0.0689	0.0518	0.0651
a_4	-0.0031	-0.0027	-0.0031
R^2	0.9997	0.9998	0.9998

The polynomial (13) provides sufficient precision of approximation (correlation coefficients for all the geometries are very close to 1) and can simplify calculations required when using the RCM method. Fig. 7 illustrates dependency of $\mu 1$(Bi) and quality of polynomial approximation.

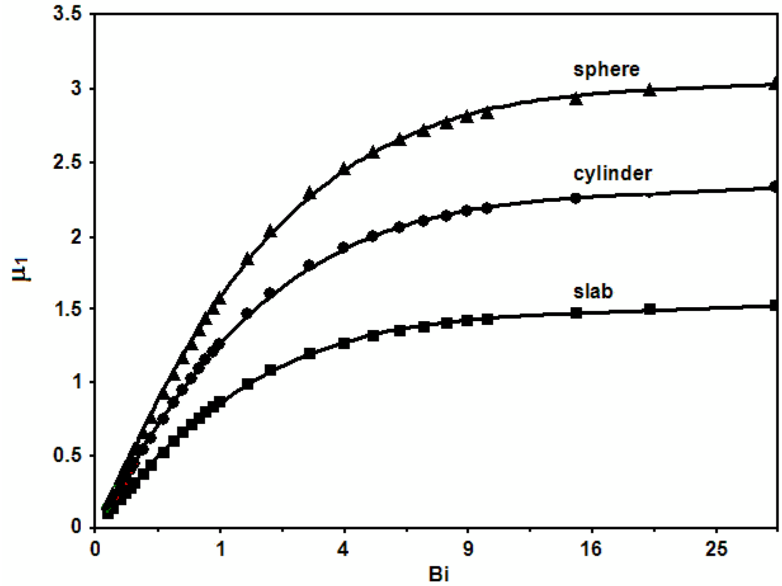

Fig. 7. Dependency of the first roots on Bi .
■ ■ ■, ● ● ●, ▲▲▲ - tabular values; __ - polynomial approximation

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